## Electronic Structure and Magneto-Optical Properties of Solids

By Victor Antonov, Bruce Harmon and Alexander Yaresko



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by

Victor Antonov

Institute of Metal Physics, Kiev, Ukraine

#### Bruce Harmon

Ames Laboratory, Iowa State University, Iowa, U.S.A.

and

Alexander Yaresko Max-Planck Institute for the Chemical Physics of Solids, Dresden, Germany

#### KLUWER ACADEMIC PUBLISHERS NEW YORK, BOSTON, DORDRECHT, LONDON, MOSCOW

eBook ISBN: 1-4020-1906-8 Print ISBN: 1-4020-1905-X

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Print ©2004 Kluwer Academic Publishers Dordrecht

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### Preface

In 1845 Faraday discovered [1] that the polarization vector of linearly polarized light is rotated upon transmission through a sample that is exposed to a magnetic field parallel to the propagation direction of the light. About 30 years later, Kerr [2] observed that when linearly polarized light is reflected from a magnetic solid, its polarization plane also becomes rotated over a small angle with respect to that of the incident light. This discovery has become known as the magneto-optical (MO) Kerr effect. Since then, many other magnetooptical effects, as for example the Zeeman, Voigt and Cotton-Mouton effects [3], have been discovered. These effects all have in common that they are due to a different interaction of left- and right-hand circularly polarized light with a magnetic solid. The Kerr effect has now been known for more than a century, but it was only in recent times that it became the subject of intensive investigation. The reason for this recent development is twofold: first, the Kerr effect is relevant for modern data storage technology, because it can be used to 'read' suitably stored magnetic information in an optical manner [4, 5] and second, the Kerr effect has rapidly developed into an appealing spectroscopic tool in materials research. The technological research on the Kerr effect was initially motivated by the search for good magneto-optical materials that could be used as information storage media. In the course of this research, the Kerr spectra of many ferromagnetic materials were investigated. An overview of the experimental and theoretical data collected on the Kerr effect can be found in the review articles by Buschow [6], Reim and Schoenes [7], Schoenes [8], Ebert [9], Antonov et al. [10, 11], and Oppeneer [12].

The quantum mechanical understanding of the Kerr effect began as early as 1932 when Hulme [13] proposed that the Kerr effect could be attributed to spin-orbit (SO) coupling (see, also Kittel[14]). The symmetry between leftand right-hand circularly polarized light is broken due to the SO coupling in a magnetic solid. This leads to different refractive indices for the two kinds of circularly polarized light, so that incident linearly polarized light is reflected with elliptical polarization, and the major elliptical axis is rotated by the so called Kerr angle from the original axis of linear polarization. The first systematic study of the frequency dependent Kerr and Faraday effects was developed by Argyres [15] and later Cooper presented a more general theory using some simplifying assumptions [16]. The very powerful linear response techniques of Kubo [17] gave general formulas for the conductivity tensor which are being widely used now. A general theory for the frequency dependent conductivity of ferromagnetic (FM) metals over a wide range of frequencies and temperatures was developed in 1968 by Kondorsky and Vediaev [18].

The first *ab initio* calculation of MO properties was made by Callaway with co-workers in the middle of the 1970s [19, 20]. They calculated the absorption parts of the conductivity tensor elements  $\sigma_{xx}$  and  $\sigma_{xy}$  for pure Fe and Ni and obtained rather good agreement with experiment. The main problem afterward was the evaluation of the complicated formulas involving MO matrix elements using electronic states of the real FM system. With the tremendous increases in computational power and the concomitant progress in electronic structure methods the calculation of such matrix elements became possible, if not routine. Subsequently many earlier, simplified calculations have been shown to be inadequate, and only calculations from 'first-principles' have provided, on the whole, a satisfactory description of the experimental results. The existing difficulties stem either from problems using the local spin density approximation (LSDA) to describe the electronic structure of FM materials containing highly correlated electrons, or simply from the difficulty of dealing with very complex crystal structures.

In recent years, it has been shown that polarized x rays can be used to determine the magnetic structure of magnetically ordered materials by x-ray scattering and magnetic x-ray dichroism. Now-days the investigation of magnetooptical effects in the soft x-ray range has gained great importance as a tool for the investigation of magnetic materials [21]. Magnetic x-ray scattering was first observed in antiferromagnetic NiO, where the magnetic superlattice reflections are decoupled from the structural Bragg peaks [22]. The advantage over neutron diffraction is that the contributions from orbital and spin momentum are separable because they have a different dependence upon the Bragg angle [23]. Also in ferromagnets and ferrimagnets, where the charge and magnetic Bragg peaks coincide, the magnetic structure can be determined because the interference term between the imaginary part of the charge structure factor and the magnetic structure factor gives a large enhancement of the scattering cross section at the absorption edge [24].

In 1975 the theoretical work of Erskine and Stern showed that the x-ray absorption could be used to determine the x-ray magnetic circular dichroism (XMCD) in transition metals when left- and right–circularly polarized x-ray beams are used [25]. In 1985 Thole *et al.* [26] predicted a strong magnetic

dichroism in the  $M_{4.5}$  x-ray absorption spectra of magnetic rare-earth materials, for which they calculated the temperature and polarization dependence. A vear later this MXD effect was confirmed experimentally by van der Laan et al. [27] at the Tb  $M_{4,5}$ -absorption edge of terbium iron garnet. The next year Schütz et al. [28] performed measurements using x-ray transitions at the K edge of iron with circularly polarized x-rays, where the asymmetry in absorption was found to be of the order of  $10^{-4}$ . This was shortly followed by the observation of magnetic EXAFS [29]. A theoretical description for the XMCD at the Fe K-absorption edge was given by Ebert et al. [30] using a spin-polarized version of relativistic multiple scattering theory. In 1990 Chen et al. [31] observed a large magnetic dichroism at the  $L_{2,3}$  edge of nickel metal. Also cobalt and iron showed huge effects, which rapidly brought forward the study of magnetic 3d transition metals, which are of technological interest. Full multiplet calculations for 3d transition metal  $L_{2,3}$  edges by Thole and van der Laan [32] were confirmed by several measurements on transition metal oxides. First considered as a rather exotic technique, MXD has now developed as an important measurement technique for local magnetic moments. Whereas optical and MO spectra are often swamped by too many transitions between occupied and empty valence states, x-ray excitations have the advantage that the core state has a purely local wave function, which offers site, symmetry, and element specificity. XMCD enables a quantitative determination of spin and orbital magnetic moments [33], element-specific imaging of magnetic domains [34] or polarization analysis [35]. Recent progress in devices for circularly polarized synchrotron radiation have now made it possible to explore the polarization dependence of magnetic materials on a routine basis. Results of corresponding theoretical investigations published before 1996 can be found in Ebert review paper [9].

The aim of this book is to review of recent achievements in the theoretical investigations of the electronic structure, optical, MO, and XMCD properties of compounds and multilayered structures.

Chapter 1 of this book is of an introductory character and presents the theoretical foundations of the band theory of solids such as the density functional theory (DFT) for ground state properties of solids.

We also present the most frequently used in band structure calculations local density approximation (LDA) and some modifications to the LDA (section 1.2), such as gradient correction, self-interection correction, LDA+U method and orbital polarization correction. Section 1.3 devoted to the methods of calculating the elementary excitations in crystals. Section 1.4 describes different magneto-optical effects and linear response theory.

Chapter 2 describes the MO properties for a number of 3d materials. Section 2.1 is devoted to the MO properties of elemental ferromagnetic metals (Fe, Co, and Ni) and paramagnetic metals in external magnetic fields (Pd and Pt). Also

presented are important 3d compounds such as XPt<sub>3</sub> (X=V, Cr, Mn, Fe, and Co), Heusler alloys, chromium spinel chalcogenides, MnB and strongly correlated magnetite Fe<sub>3</sub>O<sub>4</sub>. Section 2.2 describes the recent achievements in both the experimental and theoretical investigations of the electronic structure, optical and MO properties of transition metal multilayered structures (MLS). The most important from the scientific and the technological point of view materials are Co/Pt, Co/Pd, Co/Cu, and Fe/Au MLS. In these MLS, the nonmagnetic sites (Pt, Pd, Cu and Au) exhibit induced magnetic moments due to the hybridization with the transition metal spin-polarized 3d states. The polarization is strong at Pt and Pd sites and weak at noble metal sites due to completely occupied d bands in the later case. Also of interest is how the spin-orbit interaction of the nonmagnetic metal (increasing along the series of Cu, Pd, Pt, and Au) influences the MO response of the MLS. For applications a very important question is how the imperfection at the interface affects the physical properties of layered structures including the MO properties.

Chapter 3 of the book presents the MO properties of f band ferromagnetic materials. Sections 3.1 devoted to the MO properties of 4f compounds: Tm, Nd, Sm, Ce, and La monochalcogenides, some important Yb compounds, SmB<sub>6</sub> and Nd<sub>3</sub>S<sub>4</sub>. In Section 3.2 we consider the electronic structure and MO properties of the following uranium compounds: UFe<sub>2</sub>, U<sub>3</sub>X<sub>4</sub> (X=P, As, Sb, Bi, Se, and Te), UCu<sub>2</sub>P<sub>2</sub>, UCuP<sub>2</sub>, UCuAs<sub>2</sub>, UAsSe, URhAl, UGa<sub>2</sub>, and UPd<sub>3</sub>. Within the total group of alloys and compounds, we discuss their MO spectra in relationship to: the spin-orbit coupling strength, the magnitude of the local magnetic moment, the degree of hybridization in the bonding, the half-metallic character, or, equivalently, the Fermi level filling of the bandstructure, the intraband plasma frequency, and the influence of the crystal structure.

In chapter 4 results of recent theoretical investigations on the MXCD in various representative transition metal 4f and 5f systems are presented. All these investigations deal exclusively with the circular dichroism in x-ray absorption assuming a polar geometry. Section 4.1 presents the XMCD spectra of pure transition metals, some ferromagnetic transition-metal alloys consisting of a ferromagnetic 3d element and Pt atom as well as Fe<sub>3</sub>O<sub>4</sub> compound and Mn-, Co-, or Ni-substituted magnetite. Section 4.1 briefly considers the XMCD spectra in  $Gd_5(Si_2Ge_2)$ , a promising candidate material for near room temperature magnetic refrigeration. Section 4.3 contains the theoretically calculated electronic structure and XMCD spectra at M4.5 edges for some prominent uranium compounds, such as, UPt<sub>3</sub>, URu<sub>2</sub>Si<sub>2</sub>, UPd<sub>2</sub>Al<sub>3</sub>, UNi<sub>2</sub>Al<sub>3</sub>, UBe<sub>13</sub>, UFe<sub>2</sub>, UPd<sub>3</sub>, UXAl (X=Co, Rh, and Pt), and UX (X=S, Se, and Te). The first five compounds belong to the family of heavy-fermion superconductors, UFe2 is widely believed to be an example of compound with completely itinerant 5felectrons, while UPd<sub>3</sub> is the only known compound with completely localized 5f electrons.

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Appendix A provides a description of the linear muffin-tin method (LMTO) of band theory including it's relativistic and spin-polarized relativistic versions based on the Dirac equation for a spin-dependent potential. Appendix B provides a description of the optical matrix elements in the relativistic LMTO formalism.

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#### Acknowledgments

The authors are greatly indebted to Dr. A. Perlov from Münich University and Prof. Dr. S. Uba and Prof. Dr. L. Uba from the Institute of Experimental Physics of Bialystok University, a long-standing collaboration with whom strongly contributed to creating the point of view on the contemporary problems in the magneto-optics that is presented in this book. V.N. Antonov and A.N. Yaresko would like to thank Prof. Dr. P. Fulde for his interest in this work and for hospitality received during their stay at the Max-Planck-Institute in Dresden. We are also gratefull to Prof. Dr. P. Fulde and Prof. Dr. H. Eschrig for helpful discussions on novel problems of strongly correlated systems.

This work was partly carried out at the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-82. This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. V.N. Antonov greatfully acknowledges the hospitality during his stay at Ames Laboratory. This page intentionally left blank

#### Chapter 1

## THEORETICAL FRAMEWORK

Determination of the electronic structure of solids is a many-body problem that requires the Schrödinger equation to be solved for an enormous number of nuclei and electrons. Even if we managed to solve the equation and find the complete wave function of a crystal, we face, the not less complicated problem of determining how this function should be applied to the calculation of physically observable values. While the exact solution of the many-body problem is impossible, it is also quite unnecessary. To theoretically describe the quantities of physical interest, it is required to know only the energy spectrum and several correlation functions (electron density, pair correlation function, etc.) which depend on a few variables.

Since only lower excitation branches of the crystal energy spectrum are important for our discussion, we can introduce the concept of quasiparticles as the elementary excitations of the system. Therefore, our problem reduces to defining the dispersion curves of the quasiparticles and analyzing their interactions. Two types of quasiparticles are of interest: fermions (electrons) and bosons (phonons and magnons).

The problem thus formulated is still rather complicated and needs further simplification. The first is to note that the masses of ions M, forming the lattice, considerably exceed the electron mass. This great difference in masses gives rise to a large difference in their velocities and allows the following assumption: any concentration of nuclei (even a non-equilibrium one) may reasonably be associated with a quasi-equilibrium configuration of electrons which adiabatically follow the motion of the nuclei. Hence, we may consider the electrons to be in a field of essentially frozen nuclei. This is the Born–Oppenheimer approximation, and it justifies the separation of the equation of motion for the electrons between electrons and phonons have little effect on the

electron energy and the shape of the Fermi surface, there exist many other properties which require that the electron–phonon interaction be accounted for even in the first approximation. These properties include, transport and the phenomenon of superconductivity.

In this book, we shall use the adiabatic approximation and consider only the electron subsystem. The reader interested in the electron–phonon interaction in crystals may refer to Ref. [36].

We also use the approximation of an ideal lattice, meaning that the ions constituting the lattice are arranged in a rigorously periodic order. Hence, the problems related to electron states in real crystals with impurities, disorder, and surfaces are not considered.

In these approximations, the non-relativistic Hamiltonian of a many-electron system in a crystal is

$$H = -\sum_{i} \nabla_{i}^{2} + \sum_{i} V(\mathbf{r}_{i}) + \sum_{i,j}' \frac{2}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} , \qquad (1.1)$$

where the first term is the sum of the kinetic energies of the individual electrons, the second defines the interaction of each of these electrons with the potential generated by the nuclei, and the final term contains the repulsive Coulomb interaction energy between pairs of electrons.

Two important properties of our electron subsystem should be pointed out. First, the range of electron density of all metals is such that the mean volume for one electron, proportional to  $r_e = [3/4\pi\rho]^{1/3}$ , is in the range 1 - 6. It can be shown that this value is approximately the ratio of the potential energy of particles to their mean kinetic energy. Thus, the conduction electrons in metals are not an electron gas but rather a quantum Fermi liquid.

Second, the electrons in a metal are screened at a radius smaller than the lattice constant. After the papers by Bohm and Pines [37, 38], Hubbard [39], Gell–Mann, Brueckner [40] were published, it became clear that the long–range portion of the Coulomb interaction is responsible mainly for collective motion such as plasma oscillations. Their excitation energies are well above the ground state of the system. As a result, the correlated motion of electrons due to their Coulomb interactions is important at small distances (in some cases as small as 1 Å), but at larger distances an average or mean field interaction is a good approximation.

The first of these properties does not allow us to introduce small parameters. Hence, we can not use standard perturbation theory. This makes theoretical analysis of an electron subsystem in metals difficult and renders certain approximations poorly controllable. Thus, the comparison of theoretical estimations with experimental data is of prime importance and a long tradition.

The second property of the subsystem permits us to introduce the concept of weakly interacting quasiparticles, thus, to use Landau's idea [41] that weak excitations of any macroscopic many-fermion system exhibit single-particle like behavior. Obviously, for various systems, the energy range where long-lived weakly interacting particles exist will be different. In many metals this range is rather significant, reaching  $\sim 5 - 10 \text{ eV}$ . This has enabled an analysis of the electronic properties of metals based on single-particle concepts.

In calculating band structures, the crucial problem is choosing the crystal potential. Within the Hartree-Fock approximation the potential must be determined self-consistently. However, the exchange interaction leads to a nonlocal potential, which makes the calculations difficult. To avoid the difficulty Slater [42] (1934) proposed to use a simple expression, which is valid in the case of a free-electron gas when the electron density  $\rho$  is uniform. Slater suggested that the same expression for the local potential can also be used in the case of the non-uniform density  $\rho(\mathbf{r})$ . Subsequently (1965), Slater [42] introduced a dimensionless parameter  $\alpha$  multiplying the local potential, which is determined by requiring the total energy of the atom calculated with the local potential be the same as that obtained within the Hartree-Fock approximation. This method is known as the  $X_{\alpha}$ -method. It was widely used for several decades. It was about this time that a rigorous account of the electronic correlation became possible in the framework of the density functional theory. It was proved by Hohenberg and Kohn [43] (1964) that ground state properties of a many-electron system are determined by a functional depending only on the density distribution. Kohn and Sham [44, 45] (1965, 1966) then showed that the one-particle wave functions that determine the density  $\rho(\mathbf{r})$  are solutions of a Schrödinger like equation, the potential being the sum of the Coulomb potential of the electron interacting with the nuclei, the electronic charge density, and an effective local exchange-correlation potential,  $V_{xc}$ . It has turned out that in many cases of practical importance the exchange-correlation potential can be derived approximately from the energy of the accurately known electronelectron interaction in the homogeneous interacting electron gas (leading to the so called local density approximation, LDA).

The density functional formalism along with the local density approximation has been enormously successful in numerous applications, however it must be modified or improved upon when dealing with excited state properties and with strongly correlated electron systems, two of the major themes of this book. Therefore after briefly describing the DFT–LDA formalism in section 1.1, we describe in section 1.2 several modifications to the formalism which are concerned with improving the treatment of correlated electron systems. In section 1.3 several approaches dealing with excited state properties are presented.

The approaches presented in sections 1.2 and 1.3 are not general, final solutions. Indeed the topics of excitations in crystals and correlated electron systems continue to be highly active research areas. Both topics come together in the study of magnets–optical properties.

#### **1.1 Density Functional Theory (DFT)**

The motion of electrons in condensed media is highly correlated. At first glance, this leads to the conclusion that it is impossible to describe such a system in an approximation of essentially independent particles. However, we can use a model system (electron gas) of interacting particles, where the total energy E and the electron density  $\rho(\mathbf{r})$  approximate similar functions of the real system, and the effects of interactions among electrons are then described by an effective field. This is the essence of practical approaches until utilizing density functional theory (DFT).

#### 1.1.1 Formalism

The DFT is based on the Hohenberg and Kohn theorem [43] whereby all properties of the ground state of an interacting electron gas may be described by introducing certain functionals of the electron density  $\rho(\mathbf{r})$ . The standard Hamiltonian of the system is replaced by [44]

$$E[\rho] = \int d\mathbf{r}\rho(\mathbf{r})v_{\text{ext}}(\mathbf{r}) + \int \int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[\rho] \quad , \qquad (1.2)$$

where  $v_{\text{ext}}(\mathbf{r})$  is the external field incorporating the field of the nuclei; the functional  $G[\rho]$  includes the kinetic and exchange–correlation energy of the interacting electrons. The total energy of the system is given by the extremum of the functional  $\delta E[\rho]_{\rho=\rho_0(\mathbf{r})} = 0$ , where  $\rho_0$  is the distribution of the ground state electron charge. Thus, to determine the total energy E of the system we need not know the wave function of all the electrons, it suffices to determine a certain functional  $E[\rho]$  and to obtain its minimum. Note that  $G[\rho]$  is universal and does not depend on any external fields.

This concept was further developed by Sham and Kohn [45] who suggested a form for  $G[\rho]$ 

$$G[\rho] = T[\rho] + E_{\rm xc}[\rho]$$
 . (1.3)

Here  $T[\rho]$  is the kinetic energy of the system of noninteracting electrons with density  $\rho(\mathbf{r})$ ; the functional  $E_{\rm xc}[\rho]$  contains the many-electron effects of the exchange and the correlation.

Let us write the electron density as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2 \quad , \tag{1.4}$$

where N is the number of electrons. In the new variables  $\varphi_i$  (subject to the usual normalization conditions),

$$\left[-\nabla^2 - \sum_{I} \frac{2Z_I}{|\mathbf{r} - \mathbf{R}_I|} + \int 2\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\rm xc}(\mathbf{r})\right]\varphi_i = \varepsilon_i\varphi_i \quad .$$
(1.5)

Here,  $\mathbf{R}_I$  is the position of the nucleus I of charge  $Z_I$ ;  $\varepsilon_i$  are the Lagrange factors forming the energy spectrum of single-particle states. The exchange-correlation potential  $V_{\rm xc}$  is a functional derivative

$$V_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[\rho]}{\delta \rho(\mathbf{r})} \quad . \tag{1.6}$$

From (1.5) we can find the electron density  $\rho(\mathbf{r})$  and the total energy of the ground state of the system.

Although the DFT is rigorously applicable only for the ground state, and the exchange–correlation energy functional at present is only known approximately, the importance of this theory to practical applications can hardly be overestimated. It reduces the many–electron problem to an essentially singleparticle problem with the effective local potential

$$V(\mathbf{r}) = -\sum_{I} \frac{2Z_{I}}{|\mathbf{r} - \mathbf{R}_{I}|} + \int 2\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\rm xc}(\mathbf{r}) \quad .$$
(1.7)

Obviously, (1.5) should be solved self-consistently, since  $V(\mathbf{r})$  depends on the orbitals  $\varphi_i(r)$  that we are seeking.

Equations (1.2–5) are exact in so far as they define exactly the electron density and the total energy when an exact value of the functional  $E_{\rm xc}[\rho]$  is given. Thus, the central issue in applying DFT is the way in which the functional  $E_{\rm xc}[\rho]$  is defined. It is convenient to introduce more general properties for the charge density correlation determining  $E_{\rm xc}$ . The exact expression of  $E_{\rm xc}[\rho]$ for an inhomogeneous electron gas may be written as a Coulomb interaction between the electron with its surrounding exchange–correlation hole and the charge density  $\rho_{\rm xc}(\mathbf{r}, \mathbf{r'} - \mathbf{r})$  [46, 47]:

$$E_{\rm xc}[\rho] = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \frac{\rho_{\rm xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad . \tag{1.8}$$

In (1.8),  $\rho_{\rm xc}$  is defined as

$$\rho_{\rm xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = \rho(\mathbf{r}') \int_0^2 d\lambda [g(\mathbf{r}, \mathbf{r}'; \lambda) - 1] \quad , \tag{1.9}$$

where  $g(\mathbf{r}, \mathbf{r}'; \lambda)$  is the pair correlation function;  $\lambda$  is the coupling constant.

The  $E_{\rm xc}[\rho]$  is independent of the actual shape of the exchange–correlation hole. Making the substitution  $\mathbf{R} = \mathbf{r} - \mathbf{r}'$  is can be shown that [48]

$$E_{\rm xc}[\rho] = 4\pi \int d\mathbf{r} \rho(\mathbf{r}) \int \mathbf{R} d\mathbf{R} \,\overline{\rho}_{\rm xc}(\mathbf{r}, \mathbf{R}) \tag{1.10}$$

and depends only on the spherical average of  $\overline{\rho}_{\rm xc}$ ,

$$\overline{\rho}_{\rm xc}(r,R) = \frac{1}{4\pi} \int d\Omega \rho_{\rm xc}(\mathbf{r},\mathbf{R}) \quad . \tag{1.11}$$

This means that the Coulomb energy depends only on the distance, not on the direction. Moreover, the hole charge density satisfies the sum rule [48]

$$4\pi \int R^2 dR \,\overline{\rho}_{\rm xc}(r,R) = -2 \quad . \tag{1.12}$$

This implies that the exchange–correlation hole corresponds to a net charge around the electron of one.

#### 1.1.2 Local Density Approximation

In band calculations, usually certain approximations for the exchange–correlation potential  $V_{\rm xc}(\mathbf{r})$  are used. The simplest and most frequently used is the local density approximation (LDA), where  $\rho_{\rm xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$  has a form similar to that for a homogeneous electron gas, but with the density at every point of the space replaced by the local value of the charge density,  $\rho(\mathbf{r})$  for the actual system:

$$\rho_{\rm xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = \rho(\mathbf{r}) \int_0^2 d\lambda [g_0(|\mathbf{r} - \mathbf{r}'|, \lambda, \rho(\mathbf{r})) - 1] \quad , \tag{1.13}$$

where  $g_0(|\mathbf{r} - \mathbf{r}'|, \lambda, \rho(\mathbf{r}))$  is the pair correlation function of a homogeneous electron system. This approximation satisfies the sum rule (1.12), which is one of its basic advantages. Substituting (1.13) into (1.8) we obtain the local density approximation [44]:

$$E_{\rm xc}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\rm xc}(\rho) d\mathbf{r} \quad . \tag{1.14}$$

Here,  $\varepsilon_{\rm xc}$  is the contribution of exchange and correlation to the total energy (per electron) of a homogeneous interacting electron gas with the density  $\rho(\mathbf{r})$ . This approximation corresponds to surrounding every electron by an exchange–correlation hole and must, as expected, be quite good when  $\rho(\mathbf{r})$  varies slowly. Calculations of  $\varepsilon_{\rm xc}$  by several techniques led to results which differed from one another by a few percent [49]. Therefore, we may consider the quantity  $\varepsilon_{\rm xc}(\rho)$  to be reasonably well. An analytical expression for  $\varepsilon_{\rm xc}(\rho)$  was given by Hedin and Lundqvist [50]. In the local density approximation, the effective potential (1.7) is

$$V(\mathbf{r}) = -\sum_{I} \frac{2Z_{I}}{|\mathbf{r} - \mathbf{R}_{I}|} + \int 2\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{\rm xc}(\mathbf{r}) \quad , \qquad (1.15)$$

where  $\mu_{xc}(\mathbf{r})$  is the exchange–correlation part of the chemical potential of a homogeneous interacting electron gas with the local density  $\rho(\mathbf{r})$ ,

$$\mu_{\rm xc}(\mathbf{r}) = \frac{d\rho\varepsilon_{\rm xc}(\rho)}{d\rho} \quad . \tag{1.16}$$

For spin–polarized systems, the local spin density approximation [45, 51] is used

$$E_{\rm xc}[\rho^+,\rho^-] = \int \rho(\mathbf{r})\varepsilon_{\rm xc}(\rho^+(\mathbf{r}),\rho^-(\mathbf{r}))d\mathbf{r} \quad . \tag{1.17}$$

Here,  $\varepsilon_{\rm xc}(\rho^+, \rho^-)$  is the exchange–correlation energy per electron of a homogeneous system with the densities  $\rho^+(\mathbf{r})$  and  $\rho^-(\mathbf{r})$  for spins up and down, respectively.

Note that the local density approximation and local spin density approximation contain no fitting parameters. Furthermore, since the DFT has no small parameter, a purely theoretical analysis of the accuracy of different approximations is almost impossible. Thus, the application of any approximation to the exchange–correlation potential in the real systems is most frequently validated by an agreement between the calculated and experimental data.

There are two different types of problems in quantum-mechanical manyparticle systems: macroscopic many-particle systems and atomic systems or clusters of several atoms. Macroscopic systems contain  $N \approx 10^{23}$  particles and effects occurring on a  $N^{-1}$  or  $N^{-1/3}$  scale are negligibly small. Atoms and clusters of N 10 to 100 do not allow neglect of properties that scale with  $N^{-1}$  and  $N^{-1/3}$ . In addition, a strong change in electron density is observed on the boundary of a free atom or a cluster, while the electron density in metals on the atom periphery is a slowly varying function of the distance.

For finite systems (atoms and clusters), the error in the total energy calculated by the local density approximation is usually 5 to 8%. Even for a simple system such as a hydrogen atom, the total energy is calculated to 0.976 Ry instead of 1.0 Ry [52]. Therefore, the case of finite many-particle systems requires some other approach.

Because metals are macroscopic many-particle systems, the application of the local density approximation yields sufficiently good results for the ground state energy and electron density.

The DFT includes the exchange and correlation effects in a more natural way in comparison with Hartree-Fock-Slater method. Here, the exchange– correlation potential  $V_{\rm xc}$  may be represented as

$$V_{\rm xc}(\mathbf{r}) = \beta(r_{\rm e})V_{\rm GKS}(\mathbf{r}) \quad , \tag{1.18}$$

where  $V_{\text{GKS}}$  is the Gaspar–Kohn–Sham potential, and  $r_{\text{e}}$  is given by

$$r_{\rm e}(r) = \left[\frac{3}{4\pi}\rho(r)\right]^{1/3}$$
 . (1.19)

This parameter corresponds, in order of magnitude, to the ratio of the potential energy of particles to their average kinetic energy.

In (1.18), the exchange effects are included in  $V_{\text{GKS}}$ , while all correlation effects are contained in the factor  $\beta(r_{\text{e}})$  that depends on the electron density.

Wigner [53] suggested that the correlation energy for intermediate electron densities could be obtained by interpolating between the limiting values of high and low densities of an electron gas:

$$\varepsilon_{\rm c} = -0.88/r_{\rm e} + 7.8$$
 . (1.20)

With such  $\varepsilon_c$ , we obtain

$$\beta_{\rm W}(r_{\rm e}) = 1 + [0.9604r_{\rm e}(r_{\rm e} + 5.85)/(r_{\rm e} + 7.8)^2]$$
 . (1.21)

Hedin and Lundqvist [50] used the results given in [54] to estimate  $\varepsilon_{\rm c}$  and obtained

$$\beta_{\rm HL}(r_{\rm e}) = 1 + 0.0316 r_{\rm e} \ln(1 + 24.3/r_{\rm e})$$
 (1.22)

More accurate parametrization formulas for  $\varepsilon_c$  were derived [55–57] by combining random phase approximation (RPA) results with the fit to the Green's-function Monte-Carlo results of Ceperly and Alder [58].

#### 1.2 Modifications of local density approximation

Many calculations in the past decade have demonstrated that the local-spindensity approximation (LSDA) gives a good description of ground-state properties of solids. The LSDA has become the *de facto* tool of first-principles calculations in solid-state physics, and has contributed significantly to the understanding of material properties at the microscopic level. However, there are some systematic errors which have been observed when using the LSDA, such as the overestimation of cohesive energies for almost all elemental solids, and the related underestimation of lattice parameters in many cases. The LSDA also fails to correctly describe the properties of highly correlated systems, such as Mott insulators and certain *f*-band materials. Even for some "simple" cases the LSDA has been found wanting, for example the LSDA incorrectly predicts that for Fe the fcc structure has a lower total energy than the bcc structure.

The early work of Hohenberg, Kohn, and Sham introduced the local-density approximation, but it also pointed out the need for modifications in systems where the density is not homogeneous. One modification suggested by Hohenberg and Kohn [43] was the approximation

$$E_{xc} = E_{xc}^{LDA} - \frac{1}{4} \int d\mathbf{r} \int d\mathbf{r}' K_{xc} \left[ \mathbf{r} - \mathbf{r}', \rho \left[ \frac{\mathbf{r} + \mathbf{r}'}{2} \right] \right] \left[ \rho(\mathbf{r}) - \rho(\mathbf{r}') \right]^2, \quad (1.23)$$

where the kernel  $K_{xc}$  is related to the dielectric function of a homogeneous medium. This approximation is exact in the limit of weak density variations

$$\rho(\mathbf{r}) = \rho_0 + \Delta \rho(\mathbf{r}), \qquad (1.24)$$

where  $\Delta \rho(\mathbf{r}) \ll \rho_0$ , but the results for real systems are not encouraging. For free atoms the energy is infinite, indicating that the sum rule (1.14) is not satisfied.

There are several alternative methods to improve the LSD approximation described below. These include the approximations based on an exact equation for  $E_{xc}$ , the gradient correction, the self-interaction correction, the LDA+U method, and orbital polarization corrections.

#### **1.2.1** Approximations based on an exact equation for $E_{xc}$

The equation for the exchange-correlation energy (1.10) shows that the differences between the exact and the approximate exchange holes are largely due to the non-spherical components of the hole. Since these do not contribute to  $E_{xc}$ , total energies and total energy differences can be remarkably good, even in systems where the density distribution is far from uniform. In the LDA we assume that the exchange-correlation hole  $\rho_{xc}(\mathbf{r}, \mathbf{r} - \mathbf{r}')$  depends only on the charge density at the electron. It would be more appropriate to assume [59, 60] that  $\rho_{xc}$  depends on a suitable average  $\overline{\rho(\mathbf{r})}$ ,

$$\rho_{xc}(\mathbf{r},\mathbf{r}'-\mathbf{r}) = \overline{\rho(\mathbf{r})} \int d\lambda \{g_h[\mathbf{r}-\mathbf{r}',\lambda,\overline{\rho}(\mathbf{r})]-1\}.$$
 (1.25)

It is possible to choose the weight function that determines  $\overline{\rho(\mathbf{r})}$  so that the functional reduces to the exact result in the limit of almost constant density. Approximation (1.25) satisfies the sum rule (1.11). Somewhat different prescriptions for the weight function have been proposed in [59, 60]. The approximation gives improved results for total energies of atoms.

An alternative approximation is obtained if we keep the proper prefactor  $\rho(\mathbf{r}')$  in Eq. 1.9, leading to the so-called weighted density (WD) approximation:

$$\rho_{xc}(\mathbf{r}', \mathbf{r} - \mathbf{r}') = \rho(\mathbf{r}')G[|\mathbf{r} - \mathbf{r}'|, \overline{\rho(\mathbf{r})}], \qquad (1.26)$$

where  $\rho(\mathbf{r})$  is chosen to satisfy the sum rule (1.12) [60–62]. Different forms have been proposed for  $G(\mathbf{r}, \rho)$ . Gunnarsson and Jones [48] propose an analytical form of  $G(\mathbf{r}, \rho)$ . They assume that

$$G(\mathbf{r}, \rho) = C(\rho) \{ 1 - exp[-\lambda(\rho) / |\mathbf{r}|^5] \},$$
(1.27)

where C and  $\lambda$  are parameters to be determined. The functional G behaves as  $|\mathbf{r}|^{-5}$  for large distances, which is needed to obtain an image potential. For a homogeneous system with density  $\rho$ , we require that the model functional should both fulfill the sum rule for  $\tilde{\rho}(\mathbf{r}) = \rho$  and give the exact exchange-correlation energy. This leads to two equations:

$$\rho \int d\mathbf{r} G(|\mathbf{r}|, \rho) = -2, \qquad (1.28)$$

$$\int d\mathbf{r} \frac{1}{|\mathbf{r}|} G(|\mathbf{r}|, \rho) = \varepsilon_{xc}(\rho), \qquad (1.29)$$

which are sufficient to determine the two parameters  $C(\rho)$  and  $\lambda(\rho)$ .

This functional is exact in several limiting cases: (1) for a homogeneous system; (2) for one-electron systems, such as the hydrogen atom, where it gives an exact cancellation of the electron self-interactions; (3) for an atom, where it gives the correct behavior of the exchange-correlation energy density far from the nucleus,  $\varepsilon_{xc} = -\frac{1}{r}$ ; (4) for far outside the surface, where it gives the image potential  $\varepsilon_{xc}(z) = -\frac{1}{2z}$ . The LSDA gives qualitatively incorrect answers for cases (3) and (4), and the cancellation in case (2) is only approximate. Since (2) is satisfied, this approximation provides a "self-interaction correction" in the sense that we shall discuss below. Barstel et al. [63] and Przybylski and Barstel [64, 65] have used variations of the WD approximation in studies of Rh, Cu, and V. For Rh they found that the WD approximation correctly shifts unoccupied bands upward. For Cu they obtained an improved description of the *d*-band and Fermi surface, while for V the error in the LSDA for the Fermi surface was substantially over corrected. For semiconductors it was found that there is either only little (Si, [66]) or no (GaAs, [67]) improvement over the LSDA for the band gap.

#### **1.2.2** Gradient correction

An early attempt to improve the LSDA was the gradient expansion approximation (GEA) [43, 44]. Calculations for atoms [68, 69] and a jellium surface [70] showed, however, that the GEA does not improve the LSDA if the ab initio coefficients of the gradient correction [68, 71, 72] are used. The errors in the GEA were studied by Langreth and Perdew [70, 46] and later by Perdew and co-workers [73-75]. It was shown that the second order expansions of the exchange and correlation holes in gradients of the density are fairly realistic close to the electron, but not far away. In the original work of Langreth and co-workers [70, 76] a generalized gradient approximation (GGA) was constructed via cutoff of the spurious small-wave-vector contribution to the Fourier transform of the second order density gradient expansion for the exchange-correlation hole around an electron. Later Perdew and coworkers argued that the gradient expansions can be made more realistic via real-space cutoffs chosen to enforce exact properties respected by zero-order or LSD terms but violated by the second-order expansions: The exchange hole is never positive, and integrates to -1, while the correlation hole integrates to zero.

Numerous GGA schemes were developed by Langreth and Mehl [77], Hu and Langreth (LMH) [76], Becke [78], Engel and Vosko [79], and Perdew and co-workers (PW) [80–83], the three most successful and popular ones are those

by Becke (B88) [78], Perdew and Wang (PW91) [82], and Perdew, Burke, and Ernzerhof (PBE) [83].

In GGA the exchange-correlation functional of the electron spin densities  $\rho_{\uparrow}$  and  $\rho_{\downarrow}$  takes the form

$$E_{xc}^{\text{GGA}}[\rho_{\uparrow},\rho_{\downarrow}] = \int d^3r f(\rho_{\uparrow},\rho_{\downarrow},\nabla\rho_{\uparrow},\nabla\rho_{\downarrow}). \qquad (1.30)$$

Because of the spin scaling relation the exchange part of the GGA functional can be written as

$$E_x\left[\rho_{\uparrow},\rho_{\downarrow}\right] = \frac{1}{2}E_x\left[2\rho_{\uparrow}\right] + \frac{1}{2}E_x\left[2\rho_{\downarrow}\right] , \qquad (1.31)$$

$$E_{xc} = \int d^3 r \ \rho \varepsilon_x^{\text{unif}}(\rho) F_x(s) \,, \tag{1.32}$$

were  $\varepsilon_x^{\text{unif}}(\rho) = -3k_F/4\pi$  is the exchange energy of the uniform electron gas,  $k_F = (3\pi^2\rho)^{1/3}$  is the local Fermi wave vector, and  $s = |\nabla\rho|/2k_F\rho$  is a reduced density gradient. The enhancement factor  $F_x(s)$  is given by

$$F_x^{\text{PBE}}(s) = 1 + \kappa - \kappa / (1 + \mu s^2 / \kappa),$$
 (1.33)

where  $\mu$ =0.21951 and  $\kappa$ =0.804.

The PBE correlation energy

$$E_c^{\text{PBE}} = \int d^3 r \,\rho \{\varepsilon_c(r_s,\zeta) + H^{\text{PBE}}(r_s,\zeta,t)\}\,,\tag{1.34}$$

where  $r_s = (3/4\pi\rho)^{1/3}$ ,  $\zeta = (\rho_{\uparrow} - \rho_{\downarrow})/\rho$ ,  $t = |\nabla\rho|/2k_s\phi\rho$ ,  $\phi = \frac{1}{2}[(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]$ ,  $k_s = (4k_F/\pi)^{1/2}$ ,

$$H^{\text{PBE}} = \gamma \phi^3 \ln \left\{ 1 + \frac{\beta}{\gamma} t^2 \left[ \frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right\}, \qquad (1.35)$$

$$A = \frac{\beta}{\gamma} \left[ \exp\{-\varepsilon_c^{\text{unif}} / \gamma \phi^3\} - 1 \right]^{-1}, \qquad (1.36)$$

and  $\gamma$ =0.031091,  $\beta$ =0.066725. The reduced gradients s and t measure how fast  $\rho(\mathbf{r})$  is varying on the scales of the local Fermi wavelength  $2\pi/k_F$  and the local Thomas-Fermi screening  $1/k_s$ , respectively.

The GGA functionals were tested in several cases, and were found to give improved results for the ground-state properties. For atoms it was found that both total energies and removal energies are improved in the LMH functional compared with the LSDA [77, 76]. The PW functional gives a further improvement in the total energy of atoms [80, 81]. The binding energies of the first row diatomic molecules are also improved by both functionals [84, 85].

In a study of the band structure of V and Cu, Norman and Koelling [86] found that the LMH potential gave an improvement in the Fermi surface for V but not for Cu. The cohesive energy, the lattice parameters, and the bulk modulus of third-row elements have been calculated using the LMH, PW, and the gradient expansion functionals in [87]. The PW functional was found to give somewhat better results than the LMH functional and both were found to typically remove half the errors in the LSD approximation, while the GEA gives worse results than local-density approximation. For Fe GGA functionals correctly predict a ferromagnetic bcc ground state, while the LSDA and the gradient expansion predict a nonmagnetic fcc ground state [88–90]. Also, the GGA corrects LSDA underestimation of the lattice constants of Li and Na.

Large number of test calculations showed that GGA functionals yield great improvement over LSD in the description of finite systems: they improve the total energies of atoms and the cohesive energy, equilibrium distance, and vibrational frequency of molecules [90, 91], but have mixed history of successes and failures for solids [92–95, 91, 96, 97]. This may be because the exchangecorrelation hole can have a diffuse tail in a solid, but not in an atom or small molecule, where the density itself is well localized. The general trend is that the GGA underestimates the bulk modulus and zone center transverse optical phonon frequency [93, 96], corrects the binding energy [98, 96], and corrects or overcorrects, especially for semiconductor systems, the lattice constant [93– 95, 91] compared to LDA. The GGA does not solve the problems encountered in the transition-metal monoxides FeO, CoO, and NiO [89]. The magnetic moments and band structures obtained with the GGA for the oxides are essentially the same incorrect ones as obtained with the LSDA.

Recently, a number of attempts have been made to extend the GGA by including higher order terms, in particular the Laplacian of the electron density, into the expansion of the exchange-correlation hole [99, 100]. However, no extensive tests of the quality of these new potentials with application to solids have yet been made.

#### **1.2.3** Self-interaction correction

In the density formalism each electron interacts with itself via the Coulomb electrostatic energy. This nonphysical interaction would be canceled exactly by a contribution from the exchange-correlation energy in the exact formalism. In the LSD approximation this cancellation is imperfect, but often numerically rather good. The incorrect treatment of the self-interaction in approximate functionals has led a number of people to consider self-interaction corrected (SIC) functionals [101]. Such a correction was studied in the context of the Thomas-Fermi approximation [102], the Hartree approximation [103], the Hartree-Slater approximation [104], and the LSD approximation [105, 106,

56]. Within the LSD approximation the SIC functional takes the form [101]

$$E_{xc}^{SIC}[\rho] = E_{xc}^{LSD}[\rho] - \sum_{i}^{occ} \left[ \int d^3r d^3r' \frac{\rho_i(\mathbf{r}) \ \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r \ \rho_i(\mathbf{r}) \ \varepsilon_{xc}(\rho_i(\mathbf{r}, 0)) \right]$$
(1.37)

where  $\rho_i(\mathbf{r})$  is the charge density corresponding to the solution *i* of the SIC - LSD equation and  $\varepsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow})$  is the exchange-correlation (*xc*) energy of a homogeneous system with the spin densities  $\rho_{\uparrow}$  and  $\rho_{\downarrow}$ . The second term subtracts the nonphysical Coulomb interaction of an electron with itself as well as the corresponding LSD *xc* energy. The corresponding *xc* potential for orbital *i* with spin  $\sigma$  is [101]

$$V_{xc,i,\sigma}^{SIC}(\mathbf{r}) = V_{xc,\sigma}^{LSD}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r})) - \int d^{3}r' \frac{\rho_{i}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - V_{xc,\uparrow}^{LSD}(\rho_{i}(\mathbf{r}),0) \quad (1.38)$$

where  $V_{xc,\sigma}^{LSD}(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r}))$  is the LSD *xc* potential. An important property of the SIC potential is its orbital dependence. This leads to a state-dependent potential, and the solutions are therefore not automatically orthogonal. It is therefore necessary to introduce Lagrange parameters to enforce the orthogonality

$$\left[-\nabla^2 + V(\mathbf{r}) + V_{i\sigma}^{SIC}(\mathbf{r})\right]\phi_{i\sigma} = \varepsilon_{i\sigma}\phi_{i\sigma} + \sum_{i\neq j}^{occ}\lambda_{ij}^{\sigma}\phi_{j\sigma}$$
(1.39)

where  $V(\mathbf{r})$  is the effective potential entering in a normal LSD calculation and  $\lambda_{ij}^{\sigma}$  are Lagrange parameters.

The SIC removes unphysical self-interaction for occupied electron states and decreases occupied orbital energies. Calculations for atoms have been performed by several authors [105, 106, 56, 107–111]. The errors in the total exchange and correlation energies are much less than those obtained with the LSD approximation. Perdew and Zunger [56] also showed that the highest occupied orbital energies of isolated atoms are in better agreement with experimental ionization energies.

The application of the LSDA-SIC to solids has severe problems since the LSDA-SIC energy functional is not invariant under the unitary transformation of the occupied orbitals and one can construct many solutions in the LSDA-SIC. If we choose Bloch orbitals, the orbital charge densities vanish in the infinite volume limit. Thus the SIC energy is exactly zero for such orbitals. This does not mean that the SIC is inapplicable for solids since we can take atomic orbitals or construct localized Wannier orbitals that have finite SIC energies. In many calculations for solids, the SIC was adapted to localized

orbitals, which are selected under some physical assumption. These methods have partly succeeded in providing improved electronic structures for wide-gap insulators [112, 113]. The band gap was found to be substantially better than in the LSD approximation. For LiCl the band gap is 10.6 (SIC), 6.0 (LSDA), and 9.4-9.9 eV (*exp*); for Ar it is 13.5 (SIC), 7.9 ( $X_{\alpha}$ ,  $\alpha = 2/3$ ), and 14.2 eV (*exp*) [112, 113]. In these systems the great improvement of the gap is related to an improvement of the eigenvalues for the corresponding free atoms.

A longstanding problem in the DF formalism is the description of localization, for instance, in a Mott insulator or in the  $\alpha - \gamma$  transition in Ce. The insulating, antiferromagnetic transition-metal (TM) oxides have been studied intensively for several decades, because of the controversial nature of their band gap. The LSD approximation ascribes certain aspects of the loss of the 3d contribution to cohesion [114], but the band gaps are much too small or zero and the magnetic moments are in some cases also too small [115].

Recently, Svane and Gunnarsson [116] and Szotek et al. [117] performed self-consistent calculations for the TM mono-oxides (VO, CrO, MnO, FeO, CoO, NiO, and CuO) within the LSDA-SIC and obtained energy gaps and magnetic moments, which are in good agreement with experiment. They did not impose any physical assumption and chose the solutions from a comparison of the total energies. The selected solutions are composed from localized orbitals for transition metal d bands and extended Bloch orbitals for oxygen p bands. In other words, the SIC is effective only for the transition metal d orbitals and the oxygen p orbitals are not affected directly by the SIC. The electronic structures of TM mono-oxides have also been calculated by the LSDA-SIC [118]. The authors carefully examine the criterion to choose orbitals and try both solutions with localized and extended oxygen p orbitals. The solutions are expressed as linear combinations of muffin-tin orbitals (LMTO). It is shown that the total energies of these solutions are strongly unaffected by the choices of exchange-correlation energy functionals. Alternatively, if the solutions are chosen so that all orbitals are localized as Wannier functions, the energy gaps are overestimated by 1.5-3 eV. However in these solutions, the relative positions of occupied transition-metal d bands and oxygen p bands are consistent with the analysis of photoemission spectroscopy by the cluster configurationinteraction (CI) theory [119, 120].

The tendency to form an anti-ferromagnetic moment in the LSD approximation is severely underestimated in some cases. One example is the onedimensional Hubbard model, for which the exact solution is known [121]. The band gap, the total energy, the local moment, and the momentum distribution are described substantially better by the SIC approximation than by the LSD one [122]. Another example is provided by the high- $T_c$  superconductors, where the Stoner parameter I is at least a factor 2-3 too small when using the LSD approximation [123]. Svane and Gunnarsson [124] performed calculations for a simple model of La<sub>2</sub>CuO<sub>4</sub> which includes the important  $x^2 - y^2$  orbital of Cu and the 2p orbitals of oxygen, pointing towards the Cu atoms. It was found that the tendency to antiferromagnetism is greatly enhanced in SIC, compared with the LSD approximation, and that the experimental moment may even be overestimated by SIC. Recently the electronic structure of La<sub>2</sub>CuO<sub>4</sub> in the LSD-SIC approximation has been calculated [125]. The correct antiferromagnetic and semiconducting ground state is reproduced in this approximation. Good quantitative agreement with experiment is found for the Cu magnetic moment as well as for the energy gap and other electron excitation energies.

#### 1.2.4 LDA+U method

A crucial difference between the LDA and the exact density functional is that in the latter the potential must jump discontinuously as the number of electrons N increases through integer values [126] and in the former the potential is a continuous function of N. The absence of the potential jump, which appears in the exact density functional, is the reason for the LDA failure in describing the band gap of Mott insulators such as transition metal and rare-earth compounds. Gunnarsson and Schonhammer [127] showed that the discontinuity in the one-electron potential can give a large contribution to the band gap. The second important fact is that while LDA orbital energies, which are derivatives of the total energy E with respect to orbital occupation numbers  $n_i$  $(\varepsilon_i = \partial E / \partial n_i)$ , are often in rather poor agreement with experiment, the LDA total energy is usually quite good. A good example is a hydrogen atom where the LDA orbital energy is -0.54 Ry (instead of -1.0 Ry) but the total energy (-0.976 Ry) is quite close to -1.0 Ry [122]. Brandow [128] realized that parameters of the nonmagnetic LDA band structure in combination with on-site interactions among 3d electrons taken in a renormalized Hartree-Fock form provide a very realistic electronic picture for various Mott-Hubbard phenomena. Similar observations led to the formulation of the so-called LDA+U method [129, 130] in which an orbital-dependent correction, that approximately accounts for strong electronic correlations in localized d or f shells, is added to the LDA potential. Similar to the Anderson impurity model [131], the main idea of the LDA+U method is to separate electrons into two subsystems – localized d or f electrons for which the strong Coulomb repulsion U should be taken into account via a Hubbard-like term  $\frac{1}{2}U\sum_{i\neq j}n_in_j$  in a model Hamiltonian and delocalized conduction electrons which can be described by using an orbital-independent one-electron potential.

Hubbard [132, 133] was one of the first to point out the importance, in the solid state, of Coulomb correlations which occur inside atoms. The many-body crystal wave function has to reduce to many-body atomic wave functions as lattice spacing is increased. This limiting behavior is missed in the LDA/DFT.

The spectrum of excitations for the shell of an *d*-electron system is a set of many-body levels describing processes of removing and adding electrons. In the simplified case, when every *d* electron has roughly the same kinetic energy  $\varepsilon_d$  and Coulomb repulsion energy *U*, the total energy of the shell with *n* electrons is given by  $E_n = \varepsilon_d n + Un(n-1)/2$  and the excitation spectrum is given by  $\varepsilon_n = E_{n+1} - E_n = \varepsilon_d + Un$ .

Let us consider d ion as an open system with a fluctuating number of d electrons. The correct formula for the Coulomb energy of d-d interactions as a function of the number of d electrons N given by the LDA should be E = UN(N - 1)/2 [130]. If we subtract this expression from the LDA total energy functional and add a Hubbard-like term (neglecting for a while exchange and non-sphericity) we will have the following functional:

$$E = E^{\text{LDA}} - UN(N-1)/2 + \frac{1}{2}U\sum_{i\neq j}n_in_j.$$
 (1.40)

The orbital energies  $\varepsilon_i$  are derivatives of (1.40):

$$\varepsilon_i = \frac{\partial E}{\partial n_i} = \varepsilon^{\text{LDA}} + U(\frac{1}{2} - n_i).$$
 (1.41)

This simple formula gives the shift of the LDA orbital energy -U/2 for occupied orbitals  $(n_i = 1)$  and +U/2 for unoccupied orbitals  $(n_i = 0)$ . A similar formula is found for the orbital dependent potential  $V_i(\mathbf{r}) = \delta E/\delta n_i(\mathbf{r})$  where variation is taken not on the total charge density  $\rho(\mathbf{r})$  but on the charge density of a particular *i*-th orbital  $n_i(\mathbf{r})$ :

$$V_i(\mathbf{r}) = V^{\text{LDA}}(\mathbf{r}) + U(\frac{1}{2} - n_i).$$
 (1.42)

Expression (1.42) restores the discontinuous behavior of the one-electron potential of the exact density-functional theory.

The functional (1.40) neglects exchange and non-sphericity of the Coulomb interaction. In the most general rotationally invariant form the LDA+U functional is defined as [134, 135]

$$E^{\text{LDA}+U}[\rho(\mathbf{r}), \hat{n}] = E^{\text{L(S)DA}}[\rho(\mathbf{r})] + E^{U}(\hat{n}) - E^{\text{dc}}(\hat{n}), \qquad (1.43)$$

where  $E^{L(S)DA}[\rho(\mathbf{r})]$  is the LSDA (or LDA as in Ref. [130]) functional of the total electron spin densities,  $E^{U}(\hat{n})$  is the electron–electron interaction energy of the localized electrons, and  $E^{dc}(\hat{n})$  is the so-called "double counting" term which cancels approximately the part of an electron-electron energy which is already included in  $E^{LDA}$ . The last two terms are functions of the occupation matrix  $\hat{n}$  defined using the local orbitals  $\{\phi_{lm\sigma}\}$ .

The matrix  $\hat{n} = ||n_{\sigma m,\sigma'm'}||$  generally consists of both spin-diagonal and spin-non-diagonal terms. The latter can appear due to the spin-orbit interaction

or a non-collinear magnetic order. Then, the second term in Eq. (1.43) can be written as [134, 136, 135]:

$$E^{U} = \frac{1}{2} \sum_{\sigma, \sigma', \{m\}} (n_{\sigma m_{1}, \sigma m_{2}} U_{m_{1}m_{2}m_{3}m_{4}} n_{\sigma' m_{3}, \sigma' m_{4}} - n_{\sigma m_{1}, \sigma' m_{2}} U_{m_{1}m_{4}m_{3}m_{2}} n_{\sigma' m_{3}, \sigma m_{4}}), \qquad (1.44)$$

where  $U_{m_1m_2m_3m_4}$  are the matrix elements of the on-site Coulomb interaction which are given by

$$U_{m_1m_2m_3m_4} = \sum_{k=0}^{2l} a_{m_1m_2m_3m_4}^k F^k , \qquad (1.45)$$

with  $F^k$  being screened Slater integrals for a given l and

$$a_{m_1m_2m_3m_4}^k = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle lm_1 | Y_{kq} | lm_2 \rangle \langle lm_3 | Y_{kq}^* | lm_4 \rangle .$$
(1.46)

The  $\langle lm_1|Y_{kq}|lm_2\rangle$  angular integrals of a product of three spherical harmonics  $Y_{lm}$  can be expressed in terms of Clebsch-Gordan coefficients and Eq. (1.46) becomes

$$a_{m_1m_2m_3m_4}^k = \delta_{m_1-m_2+m_3,m_4} (C_{k0,l0}^{l0})^2 C_{km_1-m_2,lm_2}^{lm_1} C_{km_1-m_2,lm_3}^{lm_4}.$$
(1.47)

The matrix elements  $U_{mmm'm'}$  and  $U_{mm'm'm}$  which enter those terms in the sum in Eq. (1.44) which contain a product of the diagonal elements of the occupation matrix can be identified as pair Coulomb and exchange integrals

$$U_{mmm'm'} = U_{mm'},$$
  
$$U_{mm'm'm} = J_{mm'}.$$

The averaging of the matrices  $U_{mm'}$  and  $U_{mm'} - J_{mm'}$  over all possible pairs of m, m' defines the averaged Coulomb U and exchange J integrals which enter the expression for  $E^{dc}$ . Using the properties of Clebsch-Gordan coefficients one can show that

$$U = \frac{1}{(2l+1)^2} \sum_{mm'} U_{mm'} = F^0, \qquad (1.48)$$
$$U - J = \frac{1}{2l(2l+1)} \sum_{mm'} (U_{mm'} - J_{mm'})$$
$$= F^0 - \frac{1}{2l} \sum_{k=2}^{2l} (C_{n0,l0}^{l0})^2 F^k, \qquad (1.49)$$

where the primed sum is over  $m' \neq m$ . Equations (1.48) and (1.49) allow us to establish the following relation between the average exchange integral J and Slater integrals:

$$J = \frac{1}{2l} \sum_{k=2}^{2l} (C_{n0,l0}^{l0})^2 F^k , \qquad (1.50)$$

or explicitly

$$J = \frac{1}{14}(F^2 + F^4) \quad \text{for} \quad l = 2, \qquad (1.51)$$

$$J = \frac{1}{6435} (286F^2 + 195F^4 + 250F^6) \quad \text{for} \quad l = 3.$$
 (1.52)

The meaning of U has been carefully discussed by Herring [137]. In, e.g., a 3d electron system with n 3d electrons per atom, U is defined as the energy cost for the reaction

$$2(d^n) \to d^{n+1} + d^{n-1}, \tag{1.53}$$

i.e., the energy cost for moving a 3d electron between two atoms which both initially had n 3d electrons. It should be emphasized that U is a renormalized quantity which contains the effects of screening by fast 4s and 4p electrons. The number of these delocalized electrons on an atom with n+1 3d electrons decreases whereas their number on an atom with n-1 3d electrons increases. The screening reduces the energy cost for the reaction given by Eq. (1.53). It is worth noting that because of the screening the value of U in L(S)DA+Ucalculations is significantly smaller then the bare U used in the Hubbard model [132, 133].

In principle, the screened Coulomb U and exchange J integrals can be determined from supercell LSDA calculations using Slater's transition state technique [138] or from constrained LSDA calculations [139–141]. Then, the LDA+U method becomes parameter free. However, in some cases, as for instance for bcc iron [138], the value of U obtained from such calculations appears to be overestimated. Alternatively, the value of U estimated from PES and BIS experiments can be used. Because of the difficulties with unambiguous determination of U it can be considered as a parameter of the model. Then its value can be adjusted so to achieve the best agreement of the results of LDA+U calculations with PES or optical spectra. While the use of an adjustable parameter is generally considered an anathema among first principles practitioners, the LDA+U approach does offer a plausible and practical method to approximately treat strongly correlated orbitals in solids. It has been fond that many properties evaluated with the LDA+U method are not sensitive to small variations of the value of U around some optimal value. Indeed, the optimal value of U determined empirically is ofter very close to the value obtained from supercell or constrained density functional calculations.

#### THEORETICAL FRAMEWORK

In order to calculate the matrix elements  $U_{m_1m_2m_3m_4}$  defined by Eq. (1.45) one needs to know not only  $F^0$ , which can be identified with U, but also higher order Slater's integrals  $F^2$ ,  $F^4$  for d as well as  $F^6$  for f electrons. Once the screened exchange integral J has been determined from constrained LSDA calculation the knowledge of the ratio  $F^4/F^2$  (and  $F^6/F^4$  for f electrons) is sufficient for calculation of the Slater integrals using the relation (1.50). De Groot *et al.* [142] tabulated  $F^2$  and  $F^4$  for all 3d ions. The ratio  $F^4/F^2$  for all ions is between 0.62 and 0.63. By substituting these values into Eq. (1.51) one obtains *screened*  $F^2$  and  $F^4$ . Alternatively, one can calculate *unscreened*  $F^n$ using their definition

$$F^{n} = \int_{0}^{\infty} r^{2} dr \int_{0}^{\infty} (r')^{2} dr' \phi_{l}^{2}(r) \phi_{l}^{2}(r') \frac{r_{<}^{n}}{r_{>}^{n+1}}, \qquad (1.54)$$

where  $\phi_l(r)$  is the radial wave function of the localized elections and  $r_{<}(r_{>})$  is the smaller (larger) of r and r'. Then,  $F^n$  can be renormalized keeping their ratios fixed so as to satisfy the relation (1.50). It is worth mentioning, that in solids the higher order Slater's integrals are screened mostly due to an angular rearrangement of delocalized electrons whereas the screening of  $F^0 = U$  involves a radial charge redistribution and a charge transfer from neighboring sites. Because of this,  $F^0$  is screened much more effectively than other  $F^n$ . In 3*d* metals oxides, for example, *U* is reduced from the bare value of about 20 eV to 6-8 eV [129].

The third term in Eq. (1.43) is necessary in order to avoid the double counting of the Coulomb and exchange interactions which are included both in the L(S)DA energy functional and in  $E^U$ . Following the arguments of Czyżyk and Sawatzky [143] one can define

$$E^{\rm dc} = \frac{1}{2}UN(N-1) - \frac{1}{2}J\sum_{\sigma}N_{\sigma}(N_{\sigma}-1), \qquad (1.55)$$

where  $N_{\sigma}$  is the number of localized electrons with the spin  $\sigma$  given by a partial trace of the occupation matrix  $N_{\sigma} = \sum_{m} n_{\sigma m, \sigma m}$ ,  $N = N_{\uparrow} + N_{\downarrow}$ , and U and J are averaged on-site Coulomb and exchange integrals, respectively. The expressions (1.55) for  $E^{dc}$  and (1.44) for  $E^{U}$  substituted together with  $E^{\text{LSDA}}[\rho]$  into the functional (1.43) define the total energy functional of the LSDA+U method. In this approach, the exchange splitting of majority and minority spin states is governed mainly by the LSDA part of the effective one electron potential, whereas the  $E^{U} - E^{dc}$  part is responsible for the Coulomb repulsion between the localized electrons and non spherical corrections to the exchange interaction.
Anisimov *et al.* [130] introduced the LDA+U method in which the double counting term in the form

$$E^{\rm dc} = \frac{1}{2}UN(N-1) - \frac{1}{4}JN(N-2)$$
(1.56)

is used in conjunction with the LDA total energy functional  $E^{\text{LDA}}[\rho]$ . In contrast to the LSDA+U approach, in the LDA+U the exchange splitting of the localized shell is provided by the  $E^U - E^{\text{dc}}$  part of the functional (1.43). Most of the results presented in this book were obtained using the LSDA+U version of the LDA+U method. However, since both versions of the L(S)DA+U approach give similar results if the value of the average exchange integral J is determined from constrained LSDA calculations, we use the more common "LDA+U" abbreviation in what follows.

After the total energy functional has been defined, the effective Kohn-Sham equations of the L(S)DA+U method can be obtained by minimizing (1.43) with respect to the wave function  $\Psi_i^*(\mathbf{r})$ :

$$\frac{\delta E}{\delta \Psi_i^*(\mathbf{r})} - \frac{\delta \sum \varepsilon_j f_j \langle \Psi_j | \Psi_j \rangle}{\delta \Psi_i^*(\mathbf{r})} = 0, \qquad (1.57)$$

where  $\varepsilon_j$  are Lagrange multipliers,  $f_j$  is the occupation of the state, and the electron density is given by

$$\rho(\mathbf{r}) = \sum_{i} f_i |\Psi_i(\mathbf{r})|^2 \,. \tag{1.58}$$

The minimization leads to the set of equations

$$[-\nabla^2 + V^{\text{LDA}}(\mathbf{r})]\Psi_i(\mathbf{r}) + \sum_{\sigma_1 m_1, \sigma_2 m_2} V_{\sigma_1 m_1, \sigma_2 m_2} \frac{\delta n_{\sigma_1 m_1, \sigma_2 m_2}}{\delta \Psi_i^*} = \varepsilon_i \Psi_i(\mathbf{r}),$$
(1.59)

where the orbital dependent potential  $V_{\sigma_1 m_1, \sigma_2 m_2}$  is given by the derivative of  $E^U - E^{dc}$  with respect to the elements of the occupation matrix

$$V_{\sigma_{1}m_{1},\sigma_{2}m_{2}} = \delta_{\sigma_{1}\sigma_{2}} \sum_{\sigma m_{3}m_{4}} U_{m_{1}m_{2}m_{3}m_{4}} n_{\sigma m_{3},\sigma m_{4}} - \sum_{m_{3}m_{4}} U_{m_{1}m_{4}m_{3}m_{2}} n_{\sigma_{2}m_{3},\sigma_{1}m_{4}}$$
(1.60)  
$$- \delta_{\sigma_{1}\sigma_{2}} [U(N - \frac{1}{2}) + J(N_{\sigma_{1}} - \frac{1}{2})].$$

The variation  $\delta n_{\sigma_1 m_1, \sigma_2 m_2} / \delta \Psi_i^*$  defines the projection of the wave function  $\Psi_i$  onto the  $Y_{lm}\chi_{\sigma}$  subspace. Its explicit form depends on the choice of the basis functions of a particular band structure method. The corresponding expressions for the LMTO method will be given in the Appendix A whereas the expressions for the LAPW method can be found in Ref. [144].

As the output from self-consistent LDA+U calculations one obtains the band structure, renormalized due to the correlation effects, and the occupation matrix  $\hat{n}$  of the localized electrons. In order to simplify the analysis of the LDA+U results it is helpful to make a transformation to a new set of local orbitals

$$|li\rangle = \sum_{\sigma m} |lm\sigma\rangle d_{\sigma m,i}, \qquad (1.61)$$

where the matrix  $d_{\sigma m,i}$  diagonalizes the occupation matrix, i.e.

$$\sum_{\sigma\sigma'mm'} d^*_{\sigma m,i} n_{\sigma m,\sigma'm'} d_{\sigma'm',j} = \delta_{ij} n_i \,. \tag{1.62}$$

In this representation the occupation matrix is diagonal and the eigenvalues  $n_i$  have the meaning of orbital occupation numbers for the  $|li\rangle$  local orbitals. Then, the energy of the Coulomb interaction  $E^U[\hat{n}]$  can be written as

$$E^{U} = \frac{1}{2} \sum_{i,j}^{\prime} (U_{ij} - J_{ij}) n_i n_j, \qquad (1.63)$$

where  $U_{ij}$  and  $J_{ij}$  are Coulomb and exchange matrix elements calculated between the new local orbitals  $|li\rangle$ .

The functions  $|li\rangle$  are the partners of the irreducible representations of the local symmetry subgroup of an atomic site with correlated electrons. If the local symmetry is sufficiently high, so that all the irreducible representations are inequivalent, the transformation matrix does not depend on the occupation of the local orbitals and can be constructed using group theoretical techniques. For example, if the spin-orbit coupling is neglected for a 3d ion in a cubic environment  $|li\rangle$  are the well known  $e_g$  and  $t_{2g}$  orbitals.

On the other hand, in the relativistic "atomic" limit, when both the crystalfield splitting of the localized states and their hybridization with delocalized bands are much smaller than the spin-orbit splitting, the occupation matrix is diagonal in the  $|jm_j\rangle$  representation where  $j = l \pm 1/2$  and  $m_j$  are the total angular momentum of a localized electron and its projection, respectively. Then, the index *i* is a short-cut for  $j, m_j$  pairs and the elements of  $d_{\sigma m,i}$  are given by the corresponding Clebsch-Gordan coefficients  $C_{lm,\frac{1}{2}\sigma}^{jm_j}$ .

As one can see from Eq. (1.45) the matrix elements  $U_{m_1m_2m_3m_4}$  contain both  $F^0 = U$ , which provides the splitting of the localized states into "lower and upper Hubbard subbands", and the terms proportional to  $F^n$  with n > 0, which are responsible for angular correlations within the localized shell. In the case when U is effectively screened and  $U^{\text{eff}} = U - J$  becomes small, the latter terms give the dominant contribution to  $U_{m_1m_2m_3m_4}$ . Looking ahead and comparing Eq. (1.45) to Eqs. (1.72)–(1.74), that define the so-called orbital polarization corrections to LSDA described in section 1.2.5, one can notice that the LDA+U method includes the OP corrections between the localized electrons but without making the assumption that the occupation matrix is diagonal in spin indices. Thus, the OP corrections can be considered as the limiting case of the more general LDA+U approach [134]. In the following we will refer to calculations performed using the LDA+U method with  $U^{\text{eff}} = 0$  as LDA+U(OP) calculations.

The most important property of the LDA+U functional is the discontinuity of the potential and the maximum occupied orbital energy as the number of electrons increases through an integer value, the absence of which is the main deficiency of the local-density approximation compared with the exact density functional [126] as far as band gaps are concerned.

It should be mentioned that whereas the SIC equations are derived within the framework of homogeneous-electron-gas theory and the method is therefore a logical extension of LDA, this is obviously not the case for the LDA+Umethod. The latter method has the same deficiencies as the mean-field (Hartree-Fock) method. The orbital-dependent one-electron potential in Eq. (1.60) is in the form of a projection operator. This means that the LDA+U method is essentially dependent on the choice of the set of the localized orbitals in this operator. That is a consequence of the basic Anderson-model-like ideology [131] of the LDA+U approach. That is, the separation of the total variational space into a localized d- (f-) orbital subspace, with the Coulomb interaction between them treated with a Hubbard-type term in the Hamiltonian, and the subspace of all other states for which the local density approximation for the Coulomb interaction is regarded as sufficient. The imprecision of the choice of the localized orbitals is not as crucial as might be expected. The d(f) orbitals for which Coulomb correlation effects are important are indeed well localized in space and retain their atomic character in a solid. The experience of using the LDA+U approximation in various electronic structure calculation schemes shows that the results are not sensitive to the particular form of the localized orbitals.

The LDA+U method was proved to be a very efficient and reliable tool in calculating the electronic structure of systems where the Coulomb interaction is strong enough to cause localization of the electrons. It works not only for nearly core-like 4f orbitals of rare-earth ions, where the separation of the electronic states in the subspaces of the slow localized orbitals and fast itinerant ones is valid, but also for such systems as transition metal oxides, where 3d orbitals hybridize quite strongly with oxygen 2p orbitals [129]. In spite of the fact that the LDA+U method is a mean-field approximation which is in general insufficient for the description of the metal-insulator transition and strongly correlated metals, in some cases, such as the metal-insulator transition in FeSi and LaCoO<sub>3</sub>, LDA+U calculations gave valuable information by providing insight into the nature of these transitions [145].

Using the LDA+U method it was found [129] that all late-3d-transitionmetal monoxides, as well as the parent compounds of the high- $T_c$  compounds, are large-gap magnetic insulators of the charge-transfer type. Further, the method correctly predicts that LiNiO<sub>2</sub> is a low-spin ferromagnet and NiS a local-moment *p*-type metal. The method was also successfully applied to the calculation of the photoemission (X-ray photoemission spectroscopy) and bremsstrahlung isochromatic spectra of NiO [130]. The advantage of the LDA+Umethod is the ability to treat simultaneously delocalized conduction band electrons and localized electrons in the same computational scheme. For such a method it is important to be sure that the relative energy positions of these two types of bands are reproduced correctly. The example of Gd gives us confidence in this [146]. Gd is usually presented as an example where the LSDA gives the correct electronic structure due to the spin-polarization splitting of the occupied and unoccupied 4f bands (in all other rare-earth metals LSDA gives an unphysical 4f peak at the Fermi energy). In the LSDA, the energy separation between 4f bands is not only strongly underestimated (the exchange splitting is only 5 eV instead of the experimental value of 12 eV) but also the unoccupied 4 f band is very close to the Fermi energy thus strongly influencing the Fermi surface and magnetic ground-state properties (in the LSDA calculation the antiferromagnetic state is lower in total energy than the ferromagnetic one in contradiction to the experiment). The application of LDA+U method to Gd gives good agreement between calculated and experimental spectra not only for the separation between 4f bands but also for the position of the 4fpeaks relative to the Fermi energy [146].

## **1.2.5** Orbital polarization correction

Many magnetic metals possess a considerable orbital magnetic moment in addition to the spin magnetic moment. In LSDA the exchange correlation potential does only depend on the spin density and an induced spin moment wold correspond to the gain in exchange energy implies by Hund's first rule for atoms. To obtain an orbital moment the spin-orbit interaction must be included in the Hamiltonian. However the so calculated orbital moment is found to be too small to account for the experimentally observed orbital moments. This is already noticeable for the ferromagnetic transition metals where the orbital moments are very small, but the effect is much more drastic in actinide intermetallic ferromagnets. What is lacking in LSDA is clearly that there is nothing in the theory (by its construction) which would account for Hund's second rule (maximize the orbital moment). In order to correct for this several different orbital splitting theories have been developed [147–151].

The problem is not simple because the appropriate density functional must be nonlocal. The authors of [149] suggest the following approximate method which yields an energy function – and thus eigenvalue shift – rather than

the more accurate but unknown functional and corresponding potential. The ground state of the atomic configuration can be obtained from a vector model [152, 153] involving interaction of type  $\mathbf{s}_i \mathbf{s}_j$  and  $\mathbf{l}_i \mathbf{l}_j$  ( $\mathbf{s}_i$  and  $\mathbf{l}_i$  are the spin and angular momenta for the *i*-th electron in the atomic configuration, respectively). By replacing the interaction energy of the form  $-\sum \mathbf{s}_i \mathbf{s}_j$  with the mean-field approximation  $-(\sum_i s_i^z)(\sum_j s_j^z)$ , one obtains an energy  $-\frac{1}{4}IM_s^z$  ( $M_s = 2s_z$  is spin magnetization and I – Stoner exchange parameter) which is the Stoner expression for the spin-polarization energy [154, 155]. Hence the Stoner energy is a function of the spin and the spin-up and -down bands are split rigidly. For the orbital polarization we follow an analogous route [149]. We replace  $-\frac{1}{2}\sum \mathbf{l}_i \mathbf{l}_j$ , which occurs in the energy of the ground state of an atom as a function of occupation number, with  $-\frac{1}{2}(\sum_i l_i^z)(\sum_j l_j^z)$  and obtain a, so-called, orbital polarization energy

$$E_{op} = -\frac{1}{2}RL_z^2,$$
 (1.64)

where  $L_z$  is the total angular momentum, R is the appropriate Racah parameter, either  $E^3$  (*f*-states) or B (*d*-states). From this energy an associated shift of one-electron eigenvalue is obtained

$$\delta \varepsilon_{m_e} = \frac{\partial E_{op}}{\partial n_{m_e}} = -RL_z m_e. \tag{1.65}$$

Thus, in an open f shell atom, the spin-up or spin-down f manifolds are split into seven equidistant levels when the total orbitals moment is nonzero.  $E^3$  now plays role analogous to the Stoner parameter I.

The possibility of orbital polarization given by the energy correction in Eq. (1.64) has been used for some applications and has to some extent been successful in the sense that a better description of the orbital part of the total magnetic moment is obtained if this splitting is included in the self-consistent band structure calculation. This theory was used to describe the localization-delocalization transition in Ce, Pr, and Nd [149]. Application to Fe, Co, and Ni, transition. metal monoxides and various compounds has also improved agreement between theory and experiment [156–159].

Another scheme suggested by Severin *et al* [150, 151]. The scheme based upon a generalization of Slater's expression for the spin polarization energy of an open atomic shell [160].

In Hartree-Fock theory the exchange energy is written

$$E_{xc} = \frac{1}{2} \sum_{lm,l'm'} \langle lm, l'm' \mid g \mid l'm', lm \rangle n_{lm} n_{l'm'} \delta_{s_l m, s_{l'} m'}, \qquad (1.66)$$

where g is the Coulomb interaction, lm labels the orbitals and in an extended system,  $n_{lm}$  – which are local occupation numbers – are in general nonintegral. This expression is evaluated in terms of Slater integrals through a multipole expansion of the Coulomb interaction. The term lm = l'm' is included in the sum but for integral occupation numbers the first term in the expansion, containing  $F^0$ , exactly cancels the spherical part of the direct Coulomb interaction [160, 161]. Slater therefore removed this contribution but evaluated higher multipole contributions to the exchange interaction using nonintegral orbital occupation numbers. The spin polarization part of Eq. (1.66) is [150]

$$E_{sp}^{s} = -\frac{1}{4} \sum_{l,l'} V_{ll'} m_l m_{l'}, \qquad (1.67)$$

where  $m_l$  is the *l*-th partial spin moment, the exchange integrals  $V_{ll'}$  are given in terms of radial Slater exchange integrals  $G_{ll'}^k$  by

$$V_{ll'} = \sum_{k} \binom{ll'k}{000} G_{ll'}^k, \qquad (1.68)$$

where (...) is a Wigner 3*j* symbol, and  $G_{ll'} = F_{ll}$  when l = l'. When l = l' = 0Eqs. (1.67) and (1.68) reduce to  $E_{sp}^s = -\frac{1}{4}F^0m^2$  and  $F^0 = J_{HFA} = U$ . More generally, but with  $F^0 \gg F^k$  for k > 0 the 3*j* symbol  $\binom{llk}{000} = 1/\sqrt{2l+1}$  and  $J_{HFA} = U/(2l+1)$ , where U is the full Coulomb integral.

We should remind here that LSDA moment formation is driven by the spin polarization energy,  $E_{sp}^{LSDA}$ . In a much used, and often quite good approximation [162]

$$E_{sp}^{s} = -\frac{1}{4} \sum_{l,l'} J_{ll'} m_l m_{l'}, \qquad (1.69)$$

where  $J_{ll'}$  are the LSDA exchange interactions between shells l and l'.

We wish to separate in (1.67) the contributions which would correspond to Hund's first and second rules, since the former is well accounted for in LSDA. This is achieved by writing  $m_{lm} = \overline{m_l} + \delta m_{lm}$ . where  $\overline{m_l} = \frac{1}{2l+1} \sum_m m_{lm}$ is the average spin moment for a shell whereas  $\delta m_{lm}$  represents the deviation of the moments from the average and thus represents the energy gain due to orbital polarization. Since the average moment does not depend on *m* this part of the sum is easily evaluated and the spin polarization energy becomes

$$E_{sp}^{s} = -\frac{1}{4} \sum_{l,l'} V_{ll'} m_{l} m_{l'} - \frac{1}{4} \sum_{lm,l'm'} V_{lm,l'm'} \delta m_{lm} \delta m_{l'm'}, \qquad (1.70)$$

where

$$V_{lm,l'm'} = \sum_{k} [C(lm; l'm')]^2 G_{ll'}^k, \qquad (1.71)$$

C(lm; l'm') is a Gaunt coefficient.

It is known from atomic calculations that Slater integrals are too large due to neglect of screening effects. In atomic theory it is customary to scale them down. Since LSDA works so well and due to the formally equivalence between  $V_{ll'}$  and the exchange integrals obtained in LSDA,  $J_{ll'}$ , it can be proposed the scaling procedure  $V_{ll'} \rightarrow J_{ll'}$ , whence

$$E_{sp} = -\frac{1}{4} \sum_{l,l'} J_{ll'} m_l m_{l'} - \frac{1}{4} \sum_{lm,l'm'} \overline{V}_{lm,l'm'} \delta m_{lm} \delta m_{l'm'}, \qquad (1.72)$$

where

$$\overline{V}_{lm,l'm'} = d_{lm,l'm'} J_{ll'}, \tag{1.73}$$

and

$$d_{lm,l'm'} = \frac{\sum_{k} [C(lm,l'm')]^2 G_{ll'}^k}{\sum_{k} {\binom{ll'k}{000} \cdot G_{ll'}^k}}$$
(1.74)

The spin polarization energy obtained from Eq. (1.72) depends upon the occupation of the individual orbitals, and the energies of the orbitals are shifted by amounts given by

$$\delta \varepsilon_{lm}^{\pm} = \mp \frac{1}{2} \sum_{l'} J_{ll'}(m_{l'} + \sum_{m'} d_{lm,l'm'} \delta m_{l'm'}).$$
(1.75)

Equation (1.75) reduces to LSDA when  $\delta m_{l'm'} = 0$ , so the second term describes the orbital splitting.

The latter approximation produces an improvement, bringing both total magnetic moment and individual contributions to the magnetic moment into better agreement with experiment for US [150].

## **1.3** Excitations in crystals

The Landau theory of the Fermi liquid is very useful in studying the collective excitations and other physical properties of many–fermion systems [163]. We review the salient features relevant for the topics of this book.

# 1.3.1 Landau Theory of the Fermi Liquid

The Landau theory was initially developed for <sup>3</sup>He, an isotropic quantum Fermi liquid. However, the conduction electrons in metals may also be considered to be such a system since their degeneracy temperature is  $\sim 10^4 - 10^5$  K.

According to Landau, the energy spectrum of a Fermi liquid is similar to that of an ideal Fermi gas. This is valid for small deviations of the distribution function  $n(\mathbf{k}) = 1/\exp[(\varepsilon_{\mathbf{k}} - \mu)/T] + 1$  from its equilibrium distribution  $n_0(\mathbf{k})$ :  $\delta n(\mathbf{k}) = n(\mathbf{k}) - n_0(\mathbf{k})$ . The theory proceeds from the assumption that the classification of energy levels remains unchanged in a gradual increase of interaction between particles, i.e., in a transition from a gas to a liquid. Here, the gas particles are represented as elementary excitations behaving as quasi-particles of energies  $\varepsilon$  and momentum  $\mathbf{k}$ . The concept of an elementary excitation arises from the quantum-mechanical description of the collective motion of particles and, in this case it may be identified with a real particle in a self-consistent field of surrounding particles.

The defining characteristics of the Fermi liquid are the quasiparticle dispersion law  $\varepsilon = \varepsilon(\mathbf{k})$  defined as a variational derivative of the total energy E of a system with respect to the distribution function

$$\frac{\delta E}{\delta n(\mathbf{k})} = \varepsilon(\mathbf{k}) \quad , \tag{1.76}$$

and the correlation function  $f(\mathbf{k}, \mathbf{k}')$  giving the quasiparticle energy variation  $\varepsilon(\mathbf{k})$  through the variation of the particle distribution over the k space:

$$\frac{\delta\varepsilon(\mathbf{k})}{\delta n(\mathbf{k}')} = \frac{\delta^2 E}{\delta n(\mathbf{k})\delta n(\mathbf{k}')} = f(\mathbf{k}, \mathbf{k}') \quad . \tag{1.77}$$

When the interaction between quasiparticles is taken into account, the excitation energy of the system can be written

$$W = \sum_{\mathbf{k}} \varepsilon(\mathbf{k}) \delta n(\mathbf{k}) + \frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} f(\mathbf{k}, \mathbf{k}') \delta n(\mathbf{k}) \delta n(\mathbf{k}') \quad .$$
(1.78)

The Landau theory was originally developed for quasiparticles with short range interactions, and may seem inappropriate for describing the conduction electrons in metals which are subject to long–range Coulomb forces. Silin showed [164], however, that the screening of electrons in metals reduce the effective range of this force. The moving electron, which repels its neighboring electrons, can also be seen as an electron surrounded by an exchange– correlation hole of positive charge. With these considerations, it is not surprising that the Landau theory has provided a successful theoretical framework for metals.

The Landau theory is also valid for a periodic potential. The elementary excitations are still defined as quasi-particles with energy  $\varepsilon(\mathbf{k})$  and interaction  $f(\mathbf{k}, \mathbf{k}')$ . However, due to the anisotropy of the lattice,  $\varepsilon(\mathbf{k})$  depends on the direction of  $\mathbf{k}$ , and  $f(\mathbf{k}, \mathbf{k}')$  depends on both  $\mathbf{k}$  and  $\mathbf{k}'$  directions. Although Landau's function  $f(\mathbf{k}, \mathbf{k}')$  is unknown for most metals, it is not essential since this function is often not incorporated within the formulas that relate experimentally measured quantities to values derived from the electron dispersion law.

However, the Landau function can not be completely ignored since  $f(\mathbf{k}, \mathbf{k}')$  is directly included in high frequency, nonlinear and other properties of metals.

The Landau theory provides a framework to describe various collective motions of liquids, i.e., primary acoustic, zero acoustic, plasmons, spin waves, etc., and offers a simple means to interpret different results of the many-body theory. In our case, the most important feature of the Landau theory is that the excitation spectrum of any macroscopic many-fermion system has a general character. Weak excitations of such a system are of a one-particle type (with the quasiparticles representing the particles). The interaction between quasiparticles is of importance only when the number of quasiparticles is small. Thus, at sufficiently low temperatures the interaction between quasiparticles may be ignored and these particles can be considered to be in an ideal gas state.

The Quasiparticle Description in Density Functional Theory. The DFT, rigorously speaking, is applicable only to the description of properties of the ground state, for example, the total energy and the electron density distribution. To calculate the system excitation energy, we need to modify this theory by introducing the occupation numbers,  $n_i$  for each of the states and determine the electron density [165, 166]

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} n_i |\varphi_i(\mathbf{r})|^2 \quad , \tag{1.79}$$

and the functional

$$\widetilde{T} \equiv \sum_{i=1}^{N} n_i t_i \quad , \tag{1.80}$$

where

$$t_i = \int \varphi_i^* (-\nabla^2) \varphi_i d\mathbf{r} = \varepsilon_i - \int \varphi_i^* (V_{\rm C} + V_{\rm xc}) \varphi_i d\mathbf{r} \quad ; \tag{1.81}$$

 $V_{\rm C}(\mathbf{r}) \equiv \delta U / \delta \rho(\mathbf{r})$  is the Coulomb potential;  $V_{\rm xc}$  is the exchange–correlation potential. Then, for the given set of  $n_i$ , the self–consistent solution of the (1.5,1.79) will give the energy of the system

$$\widetilde{E} \equiv \widetilde{T} + U[\rho] + E_{\rm xc}[\rho] \quad , \tag{1.82}$$

where the Coulomb  $U[\rho]$  and exchange–correlation energies depend on the occupation numbers.

In general,  $\tilde{E}$  is not the total energy of the system, since  $T[\rho] \neq \tilde{T}$  for a random set of occupation numbers  $n_i$ . Only when the  $n_i$  are in a Fermi–Dirac distribution (at zero temperature), (1.79) is equivalent to (1.4) and  $\tilde{E}$  is the total energy of the system E. This is because the infinitesimal transfer of a

charge from the region of occupied states to above the Fermi level results in an increase in  $\tilde{E}$ , since the region of free states is always above the occupied levels. Only when all the lower states are occupied  $\tilde{E}$  is at minimum and equals to the total energy of the system E.

Let us differentiate  $\widetilde{E}$  over the occupation numbers

$$\frac{\partial \widetilde{E}}{\partial n_i} = t_i + \sum_j n_j \frac{\partial t_j}{\partial n_i} + \int (V_{\rm C} + V_{\rm xc}) \left( |\varphi_i|^2 + \sum_j n_j \frac{\partial |\varphi_i|^2}{\partial n_i} \right) d\mathbf{r} .$$
(1.83)

Now, using (1.81) we obtain

$$\frac{\partial \widetilde{E}}{\partial n_i} = \varepsilon_i + \sum_j n_j \left[ \int \frac{\partial \varphi_j^*}{\partial n_i} (-\nabla^2 + V_{\rm C} + V_{\rm xc}) \varphi_j d\mathbf{r} + \text{c.c.} \right] \quad , \qquad (1.84)$$

where c.c. is the complex conjugate of the preceding expression in parentheses. From (1.5), the last component in (1.84) becomes

$$\sum_{j} n_{j} \varepsilon_{j} \frac{\partial}{\partial n_{i}} \int |\varphi_{j}|^{2} d\mathbf{r} = 0 \quad .$$
(1.85)

Thus, we obtain finally [165, 166]

$$\varepsilon_i = \frac{\partial \tilde{E}}{\partial n_i} ,$$
(1.86)

which is true only if the energy of the system  $\tilde{E}$  is a continuous function of the occupation numbers and can be differentiated with respect to them. This is the difference between the DFT and the Hartree–Fock methods where the  $n_i$  are either zero or one since every single-determinant wave function is either unoccupied or filled with one electron only.

Let us consider the relationship of the one-particle energy spectrum to the system excitation spectrum. Let the occupation numbers  $n_i$  change by a value  $\eta_i$  due to some excitation of the system. We introduce the intermediate occupation numbers  $n'_i = n_i + \lambda \eta_i$  ( $0 \le \lambda \le 1$ ). The energy of this intermediate state is  $\tilde{E}(\lambda)$ . The excited system energy W [166] is then

$$W = E_{N+1} - E_N = \int_0^1 \frac{\partial \widetilde{E}}{\partial \lambda} d\lambda =$$
  
=  $\sum_i \eta_i \int_0^1 \frac{\partial \widetilde{E}}{\partial n'_i(\lambda)} d\lambda = \sum_i \eta_i \int_0^1 \varepsilon_i(\lambda) d\lambda$  (1.87)

This formula can be written in a more instructive form. By expanding  $\varepsilon_i(\lambda)$  into a series in  $\lambda$  and allowing for the dependence of these values on the occupation numbers  $n_i$ , we obtain [166]

$$W = \sum_{i} \eta_i \varepsilon_i(0) + \frac{1}{2} \sum_{ij} f_{ij} \eta_i \eta_j + \cdots$$
 (1.88)

The values

$$f_{ij} = \frac{\partial \varepsilon_i}{\partial n_j} = \frac{\partial \varepsilon_j}{\partial n_i} \equiv \frac{\partial^2 \tilde{E}}{\partial n_i \partial n_j}$$
(1.89)

can be related to the effective two-particle interaction of quasiparticles existing in the states i and j. The next terms of the expansion will be related to the three-particle, four-particle interaction and so on.

The relationship between  $\varepsilon_i$  and the system excitation energies becomes complicated because real excitations involve discrete electrons. Therefore, the excitation energy is not given by the first derivative of the total energy but by the complete Taylor series (1.88). Slater [42] showed numerical examples of the convergence of this expansion.

Note that (1.88) is identical to the expression postulated by Landau (1.78) for a Fermi liquid, and the function  $f_{ij}$  is the analog of the Landau function  $f(\mathbf{k}, \mathbf{k}')$ .

For a one-particle excitation from state i to j

$$W = \int_0^1 [\varepsilon_j(\lambda) - \varepsilon_i(\lambda)] d\lambda \simeq \varepsilon_j(0.5) - \varepsilon_i(0.5) \quad . \tag{1.90}$$

In this formula, the integral is calculated with a linear approximation for the integrand. The result is equivalent to the transition state method developed by Slater by another way [42] and used by him for the calculation of excited states in the  $\chi_{\alpha}$  approximation.

In conclusion we should mention that Landau theory is applicable to Fermi systems with weak interactions between quasi-particles. The theory fails to describe systems with strong correlations such as occur for excitation within highly localized orbitals. For such systems the most suitable mathematical method is the Green's functions approach initially developed in quantum field theory.

# **1.3.2** Green's Functions of Electrons in Metals and Elementary Excitations

By definition, the Green's function for a macroscopic system is [41]

$$\widetilde{G}(x,x') = -i\langle T\widehat{\Psi}(x)\widehat{\Psi}^+(x')\rangle \quad (1.91)$$

where x is a combination of the time t and the position r;  $\langle ... \rangle$  denotes averaging over the ground state of a system; T is the chronological product, that is, operators following it should be located from the right to the left in order of increasing time t, t';  $\hat{\Psi}$  are the Heisenberg operators. For convenience, we omit in (1.91), the dependence on spin.

The Green's function in the  $\mathbf{r}, E$  representation, i.e., the Fourier image with respect to (t - t'),  $\tilde{G}(\mathbf{r}, \mathbf{r}'; E)$ , is the solution of the Dyson equation [41]

$$(\nabla^2 + E)\widetilde{G}(\mathbf{r}, \mathbf{r}'; E) - \int d\mathbf{r}'' \Sigma(\mathbf{r}, \mathbf{r}''; E) \widetilde{G}(\mathbf{r}'', \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}') \quad . \quad (1.92)$$

Here,  $\Sigma(\mathbf{r}, \mathbf{r}'; E)$  is the mass or self-energy operator that describes the exchange and correlation effects. This non-Hermitian operator is nonlocal and depends on energy. It is an effective potential that allows for the interaction with all other particles of the system. Obviously, the mass operator in a crystal possesses the translational symmetry of the lattice

$$\Sigma(\mathbf{r} + \mathbf{a}, \mathbf{r}' + \mathbf{a}; E) = \Sigma(\mathbf{r}, \mathbf{r}'; E) \quad , \tag{1.93}$$

where a is a lattice vector of the crystal.

Close to the  $\tilde{G}$ -function pole, the r.h.s. of (1.92) may be omitted so that we get a homogeneous integrodifferential equation with the eigenvalues defining the excitation energy spectrum of a system [41, 45]

$$-\nabla^2 \Phi_{\mathbf{k}}(\mathbf{r}, E) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E) \Phi_{\mathbf{k}}(\mathbf{r}', E) = \varepsilon_{\mathbf{k}} \Phi_{\mathbf{k}}(\mathbf{r}, E) \quad . \tag{1.94}$$

Here, the functions  $\Phi_{\mathbf{k}}(\mathbf{r}, E)$  are similar to the Bloch wave functions of an electron in a periodic field. For metals, (1.94) replaces the usual Schrödinger equation. However, in contrast to the latter, the energy eigenvalues in (1.94) are in the general case, complex, because the mass operator  $\Sigma(\mathbf{r}, \mathbf{r}'; E)$  is complex.

From (1.92,1.94), we obtain for the Green's function

$$\widetilde{G}(\mathbf{r}, \mathbf{r}'; E) = \sum_{\mathbf{k}} \frac{\Phi_{\mathbf{k}}(\mathbf{r}, E)\Phi_{\mathbf{k}}^{+}(\mathbf{r}', E)}{E - \varepsilon_{\mathbf{k}}(E) + \mathrm{i}0\mathrm{sign}E} \quad .$$
(1.95)

The quantity  $\varepsilon_{\mathbf{k}}(E)$  is the change in the system energy when a particle is added to it. If we attribute this change to one quasiparticle,  $\varepsilon_{\mathbf{k}}(E)$  may be defined as in (1.76) as the energy of the quasiparticle, in strict conformity with Landau's theory. For states close to the Fermi energy [in (1.95) the energy is referenced to the Fermi level,  $\mu$ ], the function  $\tilde{G}(\mathbf{r}, \mathbf{r}'; E)$  has a pole at  $E = \varepsilon_{\mathbf{k}}(E)$ . Thus, the Green's function poles determine the spectrum of elementary excitations in a multi–fermion system. In general, the energy of a quasiparticle is complex due to interaction with the other quasiparticles. This is manifested as a shift of the Green's function pole into the complex region, expressed by the term i0 in the denominator (1.95). The complex nature of energy levels, according to general rules of quantum mechanics [167], causes the life time  $\tau$  of an excited state to be finite ( $\tau \sim 1/|\text{Im}\varepsilon|$ ). The quantity  $\text{Im}\varepsilon$  defines the width of an energy level. Generally speaking, the description of a multi-fermion system in terms of quasiparticles as the elementary excitations of a system is an approximation whose accuracy decreases with an increase in  $|\varepsilon - \mu|$ . However, one should not take this literally. Since energy is a dimensional quantity, to decide on the suitability of the concept of quasiparticles for a given case it is required that the lifetime of an excited state be compared with the characteristic relaxation times of the system.

In a small vicinity about the Fermi level,  $\operatorname{Im} \varepsilon_{\mathbf{k}}(E) \to 0$  like  $\operatorname{Im} \Sigma \to 0$ . In this case,  $\operatorname{Re} \varepsilon_{\mathbf{k}}(E)$  is obtained as a solution of (1.94) with real  $\Sigma(\mathbf{r}, \mathbf{r}'; E)$  and  $\varepsilon_{\mathbf{k}}(E)$ .

Since the self-energy  $\Sigma(\mathbf{r}, \mathbf{r}'; E)$  is defined by the ground state of the system, according to the Hohenberg–Kohn theorem, it is also a function of the electron density. Proceeding from this, Sham and Kohn suggested using the following form for  $\Sigma(\mathbf{r}, \mathbf{r}'; E)$  [45]:

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) = V_{\mathrm{C}}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + \Sigma_0(\mathbf{r} - \mathbf{r}'; E - V_{\mathrm{C}}(\mathbf{r}_0); \rho(\mathbf{r}_0)) \quad , \quad (1.96)$$

where  $\Sigma_0$  is the energy of an electron gas with zero Coulomb potential and electron density  $\rho$ ;  $V_{\rm C}(\mathbf{r}_0)$  is the electrostatic Hartree potential at the point  $\mathbf{r}_0 = (\mathbf{r} + \mathbf{r}')/2$ . Moreover, in (1.96) we have separated the local part from the self-energy  $\Sigma$  in the form of a Hartree (Coulomb) potential. This operation enables us to isolate the short-range interactions into  $\Sigma_0$ .

If, now we use the following approximation for the eigenfunction  $\Phi_{\mathbf{k}}$ 

$$\Phi_{\mathbf{k}}(\mathbf{r}, E) = A(\mathbf{k}) \exp[\mathrm{i}\mathbf{p}(\mathbf{r})\mathbf{r}]$$
(1.97)

and ignore the dependence of A and the electron momentum on  $\mathbf{r}$ , then, as shown in [50], (1.94), which defines the quasiparticle energy, will be reduced to an equation of the form of (1.5)

$$[-\nabla^2 + V_{\rm C}(\mathbf{r}) + \Sigma_{\rm xc}(\rho(\mathbf{r}), E)]\Phi_{\mathbf{k}}(\mathbf{r}, E) = \varepsilon_{\mathbf{k}}\Phi_{\mathbf{k}}(\mathbf{r}, E) \quad . \tag{1.98}$$

With  $E = \mu$ ,  $\Sigma_{\rm xc}(\rho(\mathbf{r}), \mu) \equiv \mu_{\rm xc}(\rho(\mathbf{r}))$ , we come to the main DFT equation that holds in the local density approximation. In both (1.98) and (1.15), the exchange–correlation potential  $\mu_{\rm xc}$  is the same.

The authors of [50] have tabulated  $\Sigma_{\rm xc}$  relative to E for different  $r_{\rm e}$ . It has been shown that, within a band,  $\Sigma_{\rm xc}$  varies insignificantly (~ 5%) with E. Therefore, for not very high excitation energies, a simple approximation can be used

$$\Sigma_{\rm xc}(\rho(\mathbf{r}), E) \simeq \mu_{\rm xc}$$
 (1.99)

This result corresponds to the neglect of interaction between quasi-particles, that is, to the case when the Landau function  $f(\mathbf{k}, \mathbf{k}') = 0$ .

#### THEORETICAL FRAMEWORK

Thus, with some caveats, one may conclude that band calculations based on the DFT theory, which adequately allows for the exchange and correlation effects, enable us to calculate the energy of elementary excitations in many– electron systems. We do not claim that the argument leading to (1.99) is rigorous, since the theory does not incorporate a small parameter.

The applicability of the one-particle approach requires that the energy bands be broad. In an atomic or local orbital basis this means there should be a strong overlap of the wave function centered at different points and also, the Coulomb interaction energy between electrons in local orbitals should be much less than the band width of a given atom. This will depend on the particular parameters of the system being considered. The approximation (1.99) will be poor in the case of low electron density in the conduction band of semiconductors, where exciton, polaron and other effects are important, and in crystals with narrow bands, e.g., the *f*-band in rare–earth elements. In the latter case, in addition to strong Coulomb correlations, the velocity of an electron in the band state, determined by the derivative of the energy with respect to  $|\mathbf{k}|$ , is so small that the nuclei have enough time to shift and, hence, to stabilize the excitation. Therefore, the electron-phonon interaction becomes important. When a oneparticle approach is suitable (wide energy bands), the velocity of the electron is so high that it can travel a considerable distance during the period required for the nuclei to go out of equilibrium and, hence, the electron-phonon interaction may be neglected.

## **1.3.3** The GW approximation

While we have provided some justifications for using a straight forward LSDA band structure approach to evaluate excitation energies, a number of materials with interesting magnetic properties involve strongly correlated electronic states, and other approximate approaches have been developed to go beyond the LSDA. As described in the section above, the Green's function approach offers a rigorous formulation to evaluate the excitation energies for quasi-particles. Application of Green's function techniques to the electron correlation problem has been extensively reviewed by Hedin and Lundqvist [168]. Within the context of the one-particle Green's function, quasiparticles are associated with the peaks in the spectral function. If the peak is sufficiently sharp, a well-defined quasiparticle energy can be obtained. For the general case of an inhomogeneous system, the quasiparticle energies and wave functions are obtained by solving the Dyson equation (1.94). For the quasiparticle problem, the central issue is an adequate approximation for the self-energy operator,  $\Sigma(\mathbf{r},\mathbf{r}';E)$ . A working method for solving this problem is the so-called GW approximation [169], where the self-energy is calculated to lowest order in the

screened interaction W:

$$\Sigma(\mathbf{r},\mathbf{r}';E) = \frac{i}{2\pi} \int_{-\infty}^{\infty} dE' \tilde{G}(\mathbf{r},\mathbf{r}';E+E') W(\mathbf{r},\mathbf{r}';E').$$
(1.100)

The dressed Green's function  $\tilde{G}$  is given in terms of quasiparticle wave functions and energies, and W is the screened Coulomb interaction given by

$$W(\mathbf{r},\mathbf{r}';E) = \frac{1}{\Omega} \int d^3 r'' \varepsilon^{-1}(\mathbf{r},\mathbf{r}'';E) V(\mathbf{r}''-\mathbf{r}'), \qquad (1.101)$$

where V is a bare Coulomb potential and  $\varepsilon^{-1}$  is an inverse dielectric matrix

$$\varepsilon^{-1}(\mathbf{r},\mathbf{r}';E) = \delta(\mathbf{r}-\mathbf{r}') + \int d^3r'' V(\mathbf{r}'-\mathbf{r}'')P(\mathbf{r}'',r';E) \qquad (1.102)$$

where P is the full response function. We then have

$$W(\mathbf{r}, r'; E) = V(\mathbf{r} - \mathbf{r}') + W_c(\mathbf{r}, \mathbf{r}'; E)$$
(1.103)

where

$$W_c(\mathbf{r}, \mathbf{r}'; E) = \int d^3 r_1 d^3 r_2 V(\mathbf{r}' - \mathbf{r}_1) P(\mathbf{r}_1, \mathbf{r}_2; E) V(\mathbf{r}_2 - \mathbf{r}'). \quad (1.104)$$

The self-energy can now be evaluated using a zeroth-order Green function which gives:

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) = \Sigma_x(\mathbf{r}, \mathbf{r}') + \Sigma_c(\mathbf{r}, \mathbf{r}'; E)$$
(1.105)

where  $\Sigma_x$  is the bare exchange potential

$$\Sigma_x(\mathbf{r}, \mathbf{r}') = -\sum_{kn}^{occ} \psi_{kn}(\mathbf{r}) \psi_{kn}^*(\mathbf{r}') V(\mathbf{r} - \mathbf{r}')$$
(1.106)

and  $\Sigma_c$  is the correlated part of the self-energy given by

$$\Sigma_{c}(\mathbf{r}, \mathbf{r}'; E) = \sum_{kn}^{occ} \psi_{kn}(\mathbf{r}) \psi_{kn}^{*}(\mathbf{r}') W_{c}^{-}(\mathbf{r}, \mathbf{r}'; E - E_{kn})) + \sum_{kn}^{occ} \psi_{kn}(\mathbf{r}) \psi_{kn}^{*}(\mathbf{r}') W_{c}^{+}(\mathbf{r}, \mathbf{r}'; E - E_{kn}))$$
(1.107)

where

$$W_c^{\pm}(\mathbf{r}, \mathbf{r}'; E) = \frac{i}{2\pi} \int_{-\infty}^{\infty} dE' \frac{W_c(\mathbf{r}, \mathbf{r}'; E')}{E + E' \pm i\delta}.$$
 (1.108)

The self-energy in the GWA has the same form as that in the Hartree-Fock approximation except that it depends on the energy and contains a term which

depends on unoccupied states as a consequence of correlation effects. Thus the GWA can be interpreted as a generalization of the Hartree-Fock approximation with a potential which contains dynamical screening of the Coulomb potential.

The detailed description of the GW approximation within the framework of the pseudopotential method can be found in [170]. The GWA has been successful in treating the quasiparticle systems such as free-electron like metals and semiconductors [171–178]. However the plane wave expansion is impractical for the description of the systems with strong correlations such as Mott insulators and d- and f-band materials. For such systems a method for calculating the self-energy in the GW approximation has been proposed in [179]. The method based on the LMTO-TB representation for wave functions, was applied for strongly correlated systems like NiO. It was found that GWA gives a rather good description of the size of the band gap and that it also improves the description of the O p-band compared with the LDA.

The GWA has been applied with success to real systems ranging from simple metals to transition metals but application to more complex systems have not been feasible up to now due to the large computational demands. Another problem in using the GW approximation is that in its practical realization a response function, needed to calculate the screened interaction, is computed with the help of the energy bands and wave functions obtained in the LDA calculation [145]. While such a procedure is justified for systems where correlation effects are small (such as semiconductors), for strongly correlated systems one may need a better starting Hamiltonian than the LDA. This, for example, can be achieved by improving the LDA Hamiltonian using the calculated self-energy in a self-consistent procedure [179].

Although the GWA is the simplest approximation to the self-energy, derived from the many-body perturbation theory, but the computational effort required for even simple systems is already quite large.

It can be shown that the GWA and LDA+U theories may be related to a Hartree-Fock theory with a frequency- and orbital-dependent screened Coulomb interaction and, at least for localized states, such as d or f orbitals of transition metal or rare-earth metal ions, the LDA+U theory may be regarded as an approximation to the GWA [145].

# **1.3.4** Dynamical Mean-Field Theory (DMFT)

A general formulation of the quantum many-body problem is the Green's function method as formulated early by Luttinger and Ward [180] and Baym and Kadanoff [181]. In this method one sets up fully self-consistent equations for the one-particle Green's function using a functional, i.e., an effective action for the Green's function, which has a well defined diagrammatic interpretation in terms of skeleton graphs. However, when considering a realistic band struc-

ture, this method becomes fairly intractable beyond the lowest order or GWapproximation [168] and is inadequate for strongly correlated systems. The first step towards a better description of strongly correlated electron systems was the introduction of the LDA+U method [129], which combines LDA with basically static, i.e., Hartree-Fock-like, mean-field approximation for a multiband Anderson lattice model and hence it does not contain true many-body physics. LDA+U proved to be a very useful tool in the study of long-range ordered, insulating states of transition metals and rare-earth compounds, but not for calculating strongly correlated metals or systems in the vicinity of a Mott-Hubbard metal-insulator transition. Missing in both LDA and LDA+U is the quasiparticle physics, which even at a rather large Coulomb interaction U(or at  $U = \infty$  with a non-integer number of interacting electrons per site) still gives a metallic behavior determined by quasiparticles with a larger effective mass than the LDA electrons. This mass enhancement ranges from a moderate increase in many transition metal oxides to the high effective masses observed in 4f-based heavy fermion compounds. LDA and also LDA+U fail to account for this kind of physics and the associated Kondo-like energy scale gained in comparison with the Mott insulator.

During last decade a new many-body approach was developed which is especially well-suited for the investigation of strongly correlated metals - dynamical mean-field theory (DMFT) [182–186]. It becomes exact in the infinite dimension limit [182] and preserves the dynamics of local interactions; hence it represents a *dynamic* mean-field approximation. In this non-perturbative approach, the Anderson lattice problem of a lattice of ions with a strongly correlated subshell which hybridizes with conduction electrons is mapped onto an effective Anderson impurity model with a frequency-dependent hybridization function,  $\Delta(\omega)$ , which has to be determined self-consistently [187, 188].

LDA+DMFT [189–191] allows one to perform *ab initio* calculations of real materials with strongly correlated electrons. Similar to the LDA+U approach, LDA+DMFT supplements LDA with local Coulomb correlations by adding to the LDA Hamiltonian the local Coulomb matrix approximated by the matrix elements of Coulomb repulsion  $U_{mm'}^{\sigma\sigma'}$  and of Hund's rule coupling  $J_{mm'}$  between the localized electrons, which are specified by  $i = i_d$  and  $l = l_d$ :

$$\hat{H} = \hat{H}_{\text{LDA}} + \frac{1}{2} \sum_{i=i_d, l=l_d} \sum_{m\sigma, m'\sigma'} U_{mm'}^{\sigma\sigma'} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'}$$
$$- \frac{1}{2} \sum_{i=i_d, l=l_d} \sum_{m\sigma, m'} J_{mm'} \hat{c}^{\dagger}_{ilm\sigma} \hat{c}^{\dagger}_{ilm'\bar{\sigma}} \hat{c}_{ilm'\sigma} \hat{c}_{ilm\bar{\sigma}}$$
$$- \sum_{i=i_d, l=l_d} \sum_{m\sigma} \Delta \epsilon_d \hat{n}_{ilm\sigma}.$$
(1.109)

Here, the prime on the sum indicates the sum over non-repeating indices, and  $\bar{\sigma} = -\sigma$  The last term of the Hamiltonian (1.109) produces a shift of the one-particle potential of the interacting orbitals. It is necessary to avoid the double counting of the Coulomb interaction and has the same origin as  $E^{dc}$  in the LDA+U approach. Using the band structure results calculated within LDA as the input, the missing electronic correlations are treated by dynamical mean-field theory.

A central quantity of the DMFT is the k-integrated Dyson equation connecting the self energy  $\Sigma$  and one-electron on-site Green function G at frequency  $\omega$ 

$$G_{lm,l'm'}(\omega) = \frac{1}{V_{BZ}} \int d\mathbf{k} \left( \left[ \omega \mathbf{1} + \mu \mathbf{1} - H^0_{\text{LDA}}(\mathbf{k}) - \Sigma(\omega) \right]^{-1} \right)_{lm,l'm'},$$
(1.110)

where 1 is the unit matrix,  $\mu$  the chemical potential,  $H_{\text{LDA}}^0(\mathbf{k})$  is the effective one-electron Hamiltonian with the matrix elements

$$(H_{\rm LDA}^{0}(\mathbf{k}))_{lm,l'm'} = (H_{\rm LDA}(\mathbf{k}))_{lm,l'm'} - \delta_{lm,l'm'} \delta_{l,l_d} \Delta \epsilon_d \hat{n}_d , \qquad (1.111)$$

 $\Sigma(\omega)$  denotes the self-energy matrix which is non-zero only between the interacting orbitals,  $[...]^{-1}$  implies the inversion of the matrix with elements n(lm), n'(l'm'), and the integration extends over the Brillouin zone with volume  $V_{BZ}$ . The most important approximation of the DMFT is that the one-particle self-energy due to the local Coulomb interaction is purely local [184, 185].

The DMFT single-site problem depends on the Weiss field

$$\mathcal{G}(\omega)^{-1} = G(\omega)^{-1} + \Sigma(\omega)$$

and is equivalent to an Anderson impurity model [192] if its hybridization  $\Delta(\omega)$  satisfies  $\mathcal{G}(\omega)^{-1} = \omega - \int d\omega' \Delta(\omega')/(\omega - \omega')$ . The local one-particle Green function at a Matsubara frequency  $i\omega_{\nu} = i(2\nu + 1)\pi/\beta$  ( $\beta$  = inverse temperature), orbital index m and spin  $\sigma$  is given by the following integral over Grassmann variables  $\psi$  and  $\psi^*$  [189]:

$$G(\omega)^{\sigma}_{\nu m} = -\frac{1}{\mathcal{Z}} \int \mathcal{D}[\psi] \mathcal{D}[\psi^*] \psi^{\sigma}_{\nu m} \psi^{\sigma*}_{\nu m} e^{\mathcal{A}[\psi,\psi^*,\mathcal{G}^{-1}]}.$$
 (1.112)

Here,  $\mathcal{Z}$  is the partition function and the single site action  $\mathcal{A}$  has the form:

$$\mathcal{A}[\psi,\psi^{*},\mathcal{G}^{-1}] = \sum_{\nu,\sigma,m} \psi^{\sigma*}_{\nu m}(\mathcal{G}^{\sigma}_{\nu m})\psi^{\sigma}_{\nu m} -\frac{1}{2} \sum_{m\sigma,m\sigma'} U^{\sigma\sigma'}_{mm'} \int_{0}^{\beta} d\tau \psi^{\sigma*}_{m}(\tau)\psi^{\sigma}_{m}(\tau)\psi^{\sigma'*}_{m'}(\tau)\psi^{\sigma'}_{m'}(\tau) +\frac{1}{2} \sum_{m\sigma,m} J_{mm'} \int_{0}^{\beta} d\tau \psi^{\sigma*}_{m}(\tau)\psi^{\bar{\sigma}}_{m}(\tau)\psi^{\bar{\sigma}*}_{m'}(\tau)\psi^{\sigma}_{m'}(\tau) .$$
(1.113)

The single-site problem (1.112) has to be solved self-consistently together with the k-integrated Dyson equation (1.110) to obtain the DMFT solution of a given problem.

To solve the effective impurity problem one can either use approximative techniques such as iterated perturbation theory (IPT) [184, 193] and the noncrossing approximation (NCA) [194–196], or employ numerical techniques like quantum Monte-Carlo (QMC) simulations [197], exact diagonalization (ED) [185, 198] and numerical renormalization group (NRG) [199]. In principle, QMC, ED and NRG are exact methods, but they require an extrapolation: discretization of the imaginary time  $\Delta_{\tau} \rightarrow 0$  (QMC), the number of lattice sites of the respective impurity model  $n_s \rightarrow \infty$  (ED), and the parameter for logarithmic discretization of the conducting band  $\Lambda \rightarrow 1$  (NRG), respectively [189]. Both IPT and NCA are approximative methods to solve the effective single-impurity problem in the LDA+DMFT scheme. They have the advantage of being numerically inexpensive, but their reliability, especially in the case of multi-band schemes with particle densities of half-filling, is in principle uncertain [189].

In general, the DMFT solution will result in a change of the occupation of the different bands involved. This changes the electron density  $\rho(\mathbf{r})$  and thus, results in a new LDA Hamiltonian  $H_{\text{LDA}}^0$  since it depends on  $\rho(\mathbf{r})$ . At the same time also the Coulomb interaction U changes and needs to be determined by new constrained LDA calculation. This brings one a second selfconsistent loop, the loop over the charge density similar to the one in DFT. Incorporating such an external loop into the algorithm allows one to compute from the first principle the electronic structure of strongly correlated systems [188]. The quantitative difference between non-self-consistent and selfconsistent LDA+DMFT depends on the change of the number of electrons in the different bands after the DMFT calculation, which of course depends on the problem at hand.

The LDA+DMFT approach gains several advantages by using the manybody, instead of the density-functional, description of solids. First, LDA+DMFT is designed to reproduce both ground-state properties and excitation spectra. A main shortcoming of DFT is thus overcome. Second, the method gives direct access to finite temperatures via the use of a temperature Green's function. Thus, in principle, phase transition temperatures, both magnetic and crystallographic, should be accessible. Last but not least, the method works naturally in the local-moment paramagnetic regime - when on a short timescale, magnetic moments exist on atoms, but on long timescales, there is no net moment on the average [187, 188].

The LDA+DMFT includes the correct quasiparticle physics and the corresponding energetics but, at the same time, reproduces the LDA and LDA+U results in the limits where these methods are valid. For weakly correlated sys-

tems the LDA+DMFT approach gives the same results as LDA if the local Coulomb interaction U is small. On the other hand, LDA+DMFT agrees with the LDA+U results for symmetry-broken Mott insulators at large Coulomb interaction U. In addition, LDA+DMFT also describes correlated metals occurring either at somewhat smaller Coulomb interactions U or when Mott insulators are doped. Thus, LDA+DMFT provides the correct physics for all Coulomb interactions and dopings, whereas LDA yields an uncorrelated metal even if the material at hand is a strongly-correlated metal or a Mott insulator. Similarly, LDA+U yields an insulator for the *ab-initio*-calculated U-values of 3d transition metal oxides, even for materials which should be metallic. Of all extensions of LDA only LDA+DMFT approach is presently able to describe the physics of *strongly correlated* paramagnetic metals with well-developed upper and lower Hubbard bands and a narrow quasiparticle peak at the Fermi level. This characteristic three-peak structure is a signature of the importance of many-body effects [185, 200].

The LDA+DMFT method has been applied with success to real systems ranging from transition metals to actinides and metal insulator transition (MIT) compounds. The phase diagram and effects of localization-delocalization in  $\alpha$ and  $\delta$ -plutonium were investigated using the self-consistent LDA+DMFT approach [187, 188]. The spectral properties of  $La_{1-x}Sr_xTiO_3$ , a doped Mott insulator with strong Coulomb correlations, were investigated via LDA+DMFT(X) approximation where X=IPT [186], NCA [201], and QMC [202]. The same strategy was formulated by Lichtenstein and Katsnelson [203] as one of their LDA++ approaches. They applied LDA+DMFT(IPT) [204], and were the first to use LDA+DMFT(QMC) [205], to investigate the spectral properties of iron. Recently, also V<sub>2</sub>O<sub>3</sub> [206], Ca<sub>2-x</sub>Sr<sub>x</sub>RuO<sub>4</sub> [207], LiV<sub>2</sub>O<sub>4</sub> [208], Ni [209], and Ce [210], have been studied by the LDA+DMFT approach.

## **1.4 Magneto-optical effects**

Magneto-optical effects refer to various changes in the polarization state of light upon interaction with materials possessing a net magnetic moment, including rotation of the plane of linearly polarized light (Faraday, Kerr rotation), and the complementary differential absorption of left and right circularly polarized light (circular dichroism). In the near visible spectral range these effects result from excitation of electrons in the conduction band. Near X-ray absorption edges, or resonances, magneto-optical effects can be enhanced by transitions from well-defined atomic core levels to transition symmetry selected valence states. Using straightforward symmetry considerations it can be shown that all MO phenomena are caused by the symmetry reduction, in comparison to the paramagnetic state, caused by magnetic ordering [211]. Concerning optical properties this symmetry reduction only has consequences when SO coupling is considered in addition. To calculate MO properties one therefore has to account for magnetism and SO coupling at the same time when dealing with the electronic structure of the material considered.

## **1.4.1** Classical optics

**Maxwell's equations.** The interaction of the electromagnetic radiation with a magnetic medium is described classically by Maxwell's equations (in GSM or Gaussian units) [212]:

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0, \qquad (1.114)$$

$$\nabla \cdot \mathbf{B} = 0, \tag{1.115}$$

$$\nabla \times \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \frac{4\pi}{c} \mathbf{J},$$
 (1.116)

$$\nabla \cdot \mathbf{D} = 4\pi\rho, \tag{1.117}$$

here **D** is the electric displacement, a quantity that takes into account effects on the electric field **E** caused by polarization **P** of the medium. **B** is the magnetic induction, and **H** the macroscopic magnetic field.  $\rho$  and **J** are macroscopic charge and current densities.

The differential equations (1.114) and (1.115) are satisfied by a vector potential  $\mathbf{A}$  and a scalar potential  $\Phi$  with

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{1.118}$$

and

$$\mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = -\nabla \Phi. \tag{1.119}$$

Substituting the above expressions into Ampere's law (1.116) and employing the general vector identity

$$\nabla \times (\nabla \times \mathbf{A}) = \nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$$
(1.120)

gives the following equation for the vector potential A [213]:

$$\nabla^{2}\mathbf{A} - \frac{1}{c^{2}}\frac{\partial^{2}\mathbf{A}}{\partial t^{2}} = -\frac{4\pi}{c}\mathbf{J} + \frac{1}{c}\nabla\frac{\partial\Phi}{\partial t} + \nabla(\nabla\cdot\mathbf{A}); \qquad (1.121)$$

a characteristic wave equation combining the second time derivative and the second spatial derivative. We also can find a corresponding relationship between the charge density and the potentials. Substituting Eq. (1.119) into Coulomb's law (1.117) yields

$$\nabla \cdot \mathbf{E} = 4\pi\rho = -\nabla^2 \Phi - \frac{1}{c} \frac{\partial}{\partial t} (\nabla \cdot \mathbf{A}).$$
(1.122)

Using the Coulomb gauge

$$\nabla \cdot \mathbf{A} = 0, \tag{1.123}$$

the last term in this equation vanishes yielding Poisson's equation

$$\nabla^2 \Phi = -4\pi\rho, \tag{1.124}$$

A similar relation for the vector potential can be obtained from Eq. (1.116) and using the definition for the vector potential [213]

$$\nabla^2 \mathbf{A} = -\frac{4\pi}{c} \mathbf{J},\tag{1.125}$$

connecting only A to the current density J.

The Maxwell equations are supplemented by so-called material equations which introduce specific properties of the material such as the electrical conductivity  $\hat{\sigma}$ , the dielectric permitivity or dielectric constant  $\hat{\varepsilon}$ , and magnetic permeability  $\hat{\mu}$ 

$$\mathbf{D} = \hat{\varepsilon} \cdot \mathbf{E} = \mathbf{E} + 4\pi \mathbf{P}, \tag{1.126}$$

$$\mathbf{B} = \hat{\mu} \cdot \mathbf{H} = \mathbf{H} + 4\pi \mathbf{M},\tag{1.127}$$

$$\mathbf{J} = \hat{\boldsymbol{\sigma}} \cdot \mathbf{E},\tag{1.128}$$

where M is the magnetization. In above equations we adopted for vacuum permitivity  $\varepsilon_0=1$  and vacuum permeability  $\mu_0=1$ .

The dielectric constant  $\hat{\varepsilon}$  and optical conductivity are complex quantities

$$\hat{\varepsilon} = \varepsilon_1 + i \frac{4\pi\sigma_1}{\omega} = \varepsilon_1 + i\varepsilon_2, \qquad (1.129)$$

$$\hat{\sigma} = \sigma_1 + i\sigma_2. \tag{1.130}$$

The complex dielectric constant and optical conductivity relate to each other through [213]

$$\hat{\varepsilon} = 1 + \frac{4\pi i}{\omega}\hat{\sigma} \tag{1.131}$$

A number of restrictions apply. For example, the dielectric constant  $\hat{\varepsilon}$  is in general not constant but a function of both spatial and time variables. It may not just be a number but a function or linear operator which connects the displacement field  $\mathbf{D}(\mathbf{r}, t)$  with the electric field  $\mathbf{E}(\mathbf{r}', t')$  existing at all other positions  $\mathbf{r}'$  and time t'

$$\mathbf{D}(\mathbf{r},t) = \int \int_{-\infty}^{t} \hat{\varepsilon}(\mathbf{r},\mathbf{r}',t') \mathbf{E}(\mathbf{r}',t') dt' d\mathbf{r}'.$$
 (1.132)

In the general case of anisotropic materials the material quantities  $\hat{\sigma}$ ,  $\hat{\varepsilon}$ , and  $\hat{\mu}$  are symmetric tensors, which, after transformation to principal axes, have three components each. For high electric and magnetic fields, the material parameters  $\hat{\sigma}$ ,  $\hat{\varepsilon}$ , and  $\hat{\mu}$  may even depend on the field strength, in such cases higher order terms of a Taylor expansion of the parameters have to be taken into account to describe the non-linear effects [214–216]. The dielectric properties can also depend on external magnetic fields, and of course the polarization can change due to an applied magnetic field (Faraday effect, Kerr effect see below).

**Wave equations in the medium.** The equation governing the propagation of electromagnetic waves can also be derived directly from Maxwell's equations. The result is the classical foundation upon which optical properties of solids can be discussed. It is still adequate for many optical effects in which the wave nature of light is the significant attribute.

We consider an infinite medium to avoid boundary and edge effects. Furthermore we assume the absence of free charges ( $\rho_{ext} = 0$ ) and external currents ( $\mathbf{J}_{ext} = 0$ ). We use a sinusoidal periodic and spatial dependence for the electric and magnetic waves. Thus

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 \exp[i(\mathbf{qr} - \omega t)] \tag{1.133}$$

and

$$\mathbf{H}(\mathbf{r},t) = \mathbf{H}_0 \exp[i(\mathbf{qr} - \omega t - \phi)]$$
(1.134)

describe the electric and magnetic fields with wavevector  $\mathbf{q}$  and frequency  $\omega$ . We have included a phase factor  $\phi$  to indicate that the electric and magnetic fields may be shifted in phase with respect to each other. Using the vector identity (1.120) and with Maxwell's equations (1.114) and (1.117), we can separate the magnetic and electric components to obtain

$$\frac{1}{c}\frac{\partial}{\partial t}(\nabla \times \mathbf{B}) = \nabla^2 \mathbf{E} - \nabla \Big(\frac{4\pi\rho_{ext}}{\varepsilon_1}\Big).$$
(1.135)

By substituting the three material equations (1.126) - (1.128) into Ampere's law (1.116) we arrive at  $\nabla \times \mathbf{B} = (\varepsilon_1 \mu_1 / c) (\partial \mathbf{E} / \partial t) + (4\pi \mu_1 \sigma_1 / c) \mathbf{E}$ . Combining this with Eq. (1.135) eventually leads to the wave equation for the electric

field

$$\nabla^{2}\mathbf{E} - \frac{\varepsilon_{1}\mu_{1}}{c^{2}}\frac{\partial^{2}\mathbf{E}}{\partial t^{2}} - \frac{4\pi\mu_{1}\sigma_{1}}{c^{2}}\frac{\partial\mathbf{E}}{\partial t} = 0.$$
(1.136)

Similarly we can obtain the expression

$$\nabla^{2}\mathbf{H} - \frac{\varepsilon_{1}\mu_{1}}{c^{2}}\frac{\partial^{2}\mathbf{H}}{\partial t^{2}} - \frac{4\pi\mu_{1}\sigma_{1}}{c^{2}}\frac{\partial\mathbf{H}}{\partial t} = 0, \qquad (1.137)$$

describing the propagation of the magnetic field.

In the case of a medium with negligible electric losses ( $\sigma_1 = 0$ ), Eqs. (1.136,1.137) are reduced to the equations

$$\nabla^2 \mathbf{E} - \frac{\varepsilon_1 \mu_1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = 0.$$
(1.138)

$$\nabla^2 \mathbf{H} - \frac{\varepsilon_1 \mu_1}{c^2} \frac{\partial^2 \mathbf{H}}{\partial t^2} = 0.$$
(1.139)

There are no variations of the magnitude of **E** and **H** inside the material, however, the velocity of propagation has changed by  $(\varepsilon_1 \mu_1)^{1/2}$  compared to when it is in a vacuum.

Solutions to wave equations (1.136) and (1.137) for several types of dielectric tensors have been discussed in the literature [217–219].

**Optical constants.** The material parameters such as the dielectric constant  $\varepsilon_1$ , the conductivity  $\sigma_1$ , and the permeability  $\mu_1$  denote the charge of the fields and current when matter is present. Due to convenience and historical reasons, optical constants such as the real refractive index n and the extinction coefficient k are used for the propagation and dissipation of electromagnetic waves in the medium. To describe the optical properties of the medium, we define the complex refractive index as a new response function

$$\hat{N} = n + ik = \left[\varepsilon_1 \mu_1 + i \frac{4\pi \mu_1 \sigma_1}{\omega}\right]^{1/2} = \left[\hat{\varepsilon} \mu_1\right]^{1/2}, \quad (1.140)$$

the value of the complex wavevector  $\mathbf{q} = \hat{q}\mathbf{n}_q$ , where  $\mathbf{n}_q = \mathbf{q}/q$  is the unit vector along the  $\mathbf{q}$  direction, becomes

$$\hat{q} = \frac{\omega}{c}\hat{N} = \frac{n\omega}{c} + i\frac{k\omega}{c},\qquad(1.141)$$

where the real refractive index n and the extinction coefficient (or attenuation index) k are completely determined by the conductivity  $\sigma_1$ , the permeability  $\mu_1$ , and the dielectric constant  $\varepsilon_1$  [213]

$$\hat{n}^2 = \frac{\mu_1}{2} \left\{ \left[ \varepsilon_1^2 + \left( \frac{4\pi\sigma_1}{\omega} \right)^2 \right]^{1/2} + \varepsilon_1 \right\}$$
(1.142)

$$\hat{k}^{2} = \frac{\mu_{1}}{2} \Big\{ \Big[ \varepsilon_{1}^{2} + \Big( \frac{4\pi\sigma_{1}}{\omega} \Big)^{2} \Big]^{1/2} - \varepsilon_{1} \Big\}.$$
(1.143)

These two important relations contain all the information on the propagation of the electromagnetic wave in the material. The optical constants describe wave propagation and cannot be used to describe the dc properties of the materials. For  $\omega = 0$  only  $\varepsilon_1$ ,  $\sigma_1$ , and  $\mu_1$  are defined. The dielectric constant, permeability and conductivity are given in terms of n and k:

$$n^2 - k^2 = \varepsilon_1 \mu_1 \tag{1.144}$$

$$2nk = \frac{4\pi\mu_1\sigma_1}{\omega},\tag{1.145}$$

and Eq. (1.140) can be written as

$$\hat{N}^2 = \mu_1 \Big[ \varepsilon_1 + i \frac{4\pi\sigma_1}{\omega} \Big] = \mu_1 \hat{\varepsilon} \simeq \frac{4\pi i \mu_1 \hat{\sigma}}{\omega}$$
(1.146)

where the approximation assumes  $|\varepsilon_1| \gg 1$ . If  $\hat{N}$  is split into an absolute value  $|\hat{N}| = (n^2 + k^2)^{1/2}$  and a phase  $\phi$  according to  $\hat{N} = |\hat{N}| \exp(i\phi)$ , then the phase difference  $\phi$  between the magnetic dielectric field vectors introduced in Eqs. (1.133) and (1.134) is given by

$$\tan \phi = k/n. \tag{1.147}$$

In a perfect insulator or free space, for example, the electric and magnetic fields are in phase and  $\phi = 0$  since k = 0. In contrast, in a typical metal at low frequencies  $\sigma_1 \gg |\sigma_2|$ , leads to  $n \simeq k$  and hence  $\phi = 45^{\circ}$ .

The optical reflectivity  $R(\omega)$  in the special configuration of normal incidence can be expressed as

$$R(\omega) = \left|\frac{1-\hat{N}}{1+\hat{N}}\right|^2 = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2}.$$
(1.148)

For a dielectric material without losses  $(k \rightarrow 0)$ , the reflectivity is solely determined by the refractive index:

$$R = \left(\frac{1-n}{1+n}\right)^2,\tag{1.149}$$

and it can approach unity if n is large. The optical reflectivity can also be expressed in terms of the complex conductivity  $\hat{\sigma} = \sigma_1 + i\sigma_2$  as [213]

$$R = \frac{1 + \frac{4\pi}{\omega} (\sigma_1^2 + \sigma_2^2)^{1/2} - (\frac{8\pi}{\omega})^{1/2} \left[ (\sigma_1^2 + \sigma_2^2)^{1/2} + \sigma_2 \right]^{1/2}}{1 + \frac{4\pi}{\omega} (\sigma_1^2 + \sigma_2^2)^{1/2} + (\frac{8\pi}{\omega})^{1/2} \left[ (\sigma_1^2 + \sigma_2^2)^{1/2} + \sigma_2 \right]^{1/2}}.$$
 (1.150)

If  $\sigma_1 \gg |\sigma_2|$ , the reflectivity  $R \to 1$ .

The energy loss function  $L(\omega)$  of the fast electrons moving in the medium is

$$L(\omega) = \operatorname{Im}[-1/\varepsilon(\omega)] = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}.$$
 (1.151)

This function is the basic parameter measured by the electron loss spectroscopy.

Kramers-Kronig relations and sum rules. The various material parameters and optical constants introduced in the previous section describe the response of the medium to applied electromagnetic radiation within the framework of linear response theory; the frequency dependence of the response is called dispersion. The complex dielectric constant  $\hat{\varepsilon}$  and the complex conductivity  $\hat{\sigma}$ can be regarded as the prime response functions to the applied electric field. The change of the electromagnetic wave in the material can be discussed in terms of the complex refractive index  $\hat{N}$ . For the optical parameters, such as the amplitude of the electromagnetic wave which is transmitted through an interface or which is reflected off a boundary of two materials, the second component is the phase shift  $\phi$  which is experienced by the electromagnetic fields. The change in amplitude and phase can be obtained from the appropriate complex response functions describing the system. General considerations, involving causality, can be used to derive important relations between the real and imaginary parts of the complex response functions. They were first given by Kramers [220-222] and Kronig [223, 224]. These relations are of great practical importance: they allow for the evaluation of the components of the complex dielectric constant or conductivity when only one optical parameter such as the reflected or absorbed power is measured. With  $R(\omega)$  obtained over a broad frequency range, the dispersion relations can be utilized to evaluate  $\phi(\omega)$  There are two restrictions of practical importance: the data have to cover a wide spectral range and the sample must be transparent. If just the transmitted power through a sample of finite thickness is measured, the Kramers-Kronig analysis does not allow the determination of both components without knowing the reflected portions. These dispersion relations can also be used to derive what are called sum rules.

A linear response to an external perturbation can be written as

$$\hat{X}(\mathbf{r},t) = \int \int_{-\infty}^{\infty} \hat{G}(\mathbf{r},\mathbf{r}',t,t') \hat{f}(\mathbf{r}',t') d\mathbf{r}', dt'.$$
(1.152)

This describes the response  $\hat{X}$  of the system at time t and position **r** to an external stimulus  $\hat{f}$  at times t' and locations **r**'. The function  $\hat{G}(\mathbf{r}, \mathbf{r}', t, t')$  is called the response function, and may be the conductivity, the dielectric constant, the susceptibility, or any other optical constant, such as the refractive index. Neglecting the spatial dependence of the external perturbation and restricting

ourselves to the local approximation  $\hat{G}(\mathbf{r}, \mathbf{r}', t, t') = \delta\{\mathbf{r} - \mathbf{r}'\}\hat{G}(t - t')$  we can show [213] that

$$\hat{G}(\omega) = \frac{1}{i\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\hat{G}(\omega')}{\omega' - \omega} d\omega'$$
(1.153)

where  $\hat{G}(\omega) = \int \hat{G}(t - t') \exp\{i\omega(t - t')\}dt$  is Fourier transformation of the response function;  $\mathcal{P}$  denotes the principle value. In the usual way, the complex response function  $\hat{G}(\omega)$  can be written in terms of the real and imaginary parts as  $\hat{G}(\omega) = \hat{G}_1(\omega) + i\hat{G}_2(\omega)$ , leading to the following dispersion relations between the real and imaginary parts of the response function [213]:

$$G_1(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{G_2(\omega')}{\omega' - \omega} d\omega'$$
(1.154)

$$G_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{G_1(\omega')}{\omega' - \omega} d\omega'; \qquad (1.155)$$

i.e.  $G_1$  and  $G_2$  are Hilbert transforms to each other. Using these general relations we can derive various expressions connecting the real and imaginary parts of different optical parameters and response functions.

The dispersion relations which connect the real and imaginary parts of the complex conductivity are given by:

$$\sigma_1(\omega) = \frac{2}{\pi} \mathcal{P} \int_o^\infty \frac{\omega' \sigma_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$
(1.156)

$$\sigma_2(\omega) = -\frac{2}{\pi} \mathcal{P} \int_o^\infty \frac{\sigma_1(\omega')}{\omega'^2 - \omega^2} d\omega'$$
(1.157)

The Kramers-Kronig relations for the two components of the complex dielectric function are:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \mathcal{P} \int_o^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$
(1.158)

$$\varepsilon_2(\omega) = -\frac{2}{\pi\omega} \mathcal{P} \int_o^\infty \frac{\omega^{'2} [\varepsilon_1(\omega^{'}) - 1]}{\omega^{'2} - \omega^2} d\omega^{'}$$
(1.159)

The corresponding relations for the refractive index  $\hat{N} = n(\omega) + ik(\omega)$  are:

$$n(\omega) = 1 + \frac{2}{\pi} \mathcal{P} \int_{o}^{\infty} \frac{\omega' k(\omega')}{\omega'^2 - \omega^2} d\omega'$$
(1.160)

$$k(\omega) = -\frac{2}{\pi\omega} \mathcal{P} \int_{o}^{\infty} \frac{\omega^{'2} [n(\omega^{'}) - 1]}{\omega^{'2} - \omega^{2}} d\omega^{'}$$
(1.161)

The Kramers-Kronig relations are non-local in frequency: the real (imaginary) component of the response at a certain frequency  $\omega$  is related to the behavior of the imaginary (real) part over the entire frequency range, although the influence of the contributions diminishes as  $(\omega'^2 - \omega^2)^{-1}$  for larger and larger frequency differences. This global behavior leads to certain difficulties when these relations are used to analyze experimental results which cover only a finite range of frequencies.

We can combine the Kramers-Kronig relations with physical arguments about the behavior of the real and imaginary parts of the response functions to establish a set of so-called sum rules for various optical parameters. The most important sum rules are [213]:

$$\lim_{\omega \gg \omega_0 > 1/\tau} \varepsilon_1(\omega) = 1 - \frac{4\pi N e^2}{m\omega^2} = 1 - \frac{\omega_p^2}{\omega^2},$$
 (1.162)

here N is the electron density in the metal; e and m are the electronic charge and mass,  $\omega_0$  is the characteristic frequency of the mode in solid, at which the rearrangement of the electronic charge occurs,  $1/\tau$  is a phenomenological damping constant,  $\omega_p$  is the plasma frequency defined as

$$\omega_p = \left(\frac{4\pi N e^2}{m}\right). \tag{1.163}$$

0

From Eq. (1.162)we can see that for high frequencies  $\omega \gg \omega_0$  and  $\omega > \omega_p$ , the real part of the dielectric constant  $\varepsilon_1$  always approaches unity from below.

The sum rules for the imaginary part of the dielectric constant can be written:

$$\int_0^\infty \omega \varepsilon_2(\omega) d\omega = \frac{\pi}{2} \omega_p, \qquad (1.164)$$

which in terms of the optical conductivity  $\sigma_1(\omega) = (\omega/4\pi)\varepsilon_2(\omega)$  can be written as

$$\int_0^\infty \omega \sigma_1(\omega) d\omega = \frac{\omega_p^2}{8} = \frac{\pi N e^2}{2m}.$$
 (1.165)

Therefore the spectral weight  $\omega_p^2/8$  defined as the area under the conductivity spectrum  $\int_0^\infty \sigma_1(\omega) d\omega$  is proportional to the ratio of the electronic density to the mass of the electrons.

The sum rule for the energy loss function  $L(\omega)$  (1.151) is

$$\int_0^\infty \omega \operatorname{Im} \left\{ \frac{1}{\hat{\varepsilon}(\omega)} \right\} d\omega = -\frac{\pi}{2} \omega_p^2.$$
(1.166)

We can also establish sum rules for other optical parameters. For example the sum rule for the components of the complex refractive index,  $n(\omega)$  and  $k(\omega)$ , are [213]

$$\int_0^\infty \omega n(\omega) k(\omega) d\omega = \frac{\pi}{2} \omega_p^2, \qquad (1.167)$$

$$\int_0^\infty \omega k(\omega) d\omega = \frac{\pi}{4} \omega_p^2, \qquad (1.168)$$

$$\int_0^\infty [n(\omega) - 1] d\omega = 0. \tag{1.169}$$

These formulations of the sum rules do not express any new physics but may be particularly useful in certain cases.

## 1.4.2 MO effects

Magneto-optics deals with phenomena arising as a result of interaction between light and matter when the latter is subject to a magnetic field. In the case of magnetically ordered matter (ferromagnets, ferrimagnets, etc) magneto-optical effects may appear in the absence of an external magnetic field as well. The presence of a magnetic field changes the dispersion curves of the absorption coefficient and leads to the appearance or variation of optical anisotropy. A great number of magneto-optical phenomena are the direct or indirect outcome of the splitting of energy levels in an external or spontaneous magnetic field. This splitting is the Zeeman effect. Essentially, all magneto-optical effects are consequences of the Zeeman effect.

Optical anisotropy of an magnetized medium manifests itself also in the reflection of light from its surface. Phenomenon arising here are generally refereed to as the magneto-optical Kerr effect. It refers to the influence of the magnetization of the medium on reflected light.

### **MO Kerr effect**

The magneto-optical Kerr effect was discovered by Scottish physicist John Kerr in 1888. He observed that when plane-polarized light is reflected at normal incidence from the polished pole of an electromagnet, it becomes elliptically polarized with the major axis of the ellipse rotated with respect to the plane of polarization of the incident beam [2].

In MO spectroscopy one commonly distinguishes for the incident linearly polarized light between s- and p-polarized light, in which the electric field vector is either normal (s) or parallel (p) to the plane of incident. The MO quantities consequently depend on whether s- or p-polarized incident light is used [217, 225].

Depending on the orientation of the magnetization vector relative to the reflective surface and the plane of incidence of the light beam, three types of the magneto-optical effects in reflection are distinguished: polar, longitudinal (meridional), and transverse (equatorial) effects (Fig. 1.1). The magnetization vector M is oriented perpendicularly to the reflective surface and parallel to the plane of incidence in the polar effect (Fig. 1.1(a)). The geometry of the longitudinal Kerr effect is shown in Fig. 1.1(b). The influence of magnetization in both of these effects is reduced to a rotation of the plane of polarization and the appearance of ellipticity of the reflected linearly polarized light. The transverse (equatorial) Kerr effect (Fig. 1.1(c)) is observed when the magnetization vector is oriented perpendicularly to the plane of incidence of the light, and it is reveled in the change of intensity and phase of the linearly polarized light reflected by the magnetized medium. It can be shown [6] that for large values of the dielectric constant  $\hat{\varepsilon}$  the polar effect (P-MOKE) is proportional to  $\hat{\varepsilon}^{-3/2}$ . while the longitudinal (L-MOKE) and equatorial (E-MOKE) Kerr effects are proportional to  $\hat{\varepsilon}^{-2}$  under the same circumstances. Therefore, the polar Kerr effect configuration is to be preferable if large rotation values are desired. The polar Kerr effect is of great importance for optical data storage, since it is the basis for reading information from magneto-optical disks.



*Figure 1.1.* The three types of geometries of the Kerr effect: (a) the polar Kerr effect, (b) the longitudinal Kerr effect, (c) the transversal, or equatorial Kerr effect.

**Polar Kerr effect.** For the polar Kerr magnetization geometry and a crystal of tetragonal symmetry, where both the fourfold axis and the magnetization **M** are perpendicular to the sample surface and the *z*-axis is chosen to be parallel to them, the dielectric tensor is composed of the diagonal  $\varepsilon_{xx}$  and  $\varepsilon_{zz}$ , and the off-diagonal  $\varepsilon_{xy}$  component in the form

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & 0\\ -\varepsilon_{xy} & \varepsilon_{xx} & 0\\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}.$$
 (1.170)

The various elements  $\hat{\varepsilon}_{\alpha\beta}$  are composed of real and imaginary parts as follows:  $\varepsilon_{\alpha\beta} = \varepsilon_{\alpha\beta}^{(1)} + i\varepsilon_{\alpha\beta}^{(2)}$ , where  $\alpha, \beta \equiv x, y, z, \varepsilon_{xx} = (n + ik)^2$ , and n and k are refractive index and extinction coefficient, respectively. The optical conductivity tensor  $\hat{\sigma}_{\alpha\beta} = \sigma_{\alpha\beta}^{(1)} + i\sigma_{\alpha\beta}^{(2)}$  is related to the dielectric tensor  $\varepsilon_{\alpha\beta}$  through the equation

$$\hat{\varepsilon}_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + \frac{4\pi i}{\omega} \hat{\sigma}_{\alpha\beta}(\omega).$$
(1.171)

A complete description of MO effects in this formalism is given by the four nonzero elements of the dielectric tensor or, equivalently, by the complex refractive index  $\hat{N}(\omega)$ 

$$\hat{N}(\omega) \equiv \sqrt{\hat{\varepsilon}(\omega)} = n(\omega) + ik(\omega)$$
 (1.172)

for several normal modes corresponding to the propagation of pure polarization states along specific directions in the sample. The solution of Maxwell's equations yields these normal modes [225]. One of these modes is for circular components of opposite ( $\pm$ ) helicity with wave vector  $\mathbf{q} \parallel \mathbf{M}$  having indexes

$$\hat{N}_{\pm} = n_{\pm} + ik_{\pm} = \sqrt{\varepsilon_{xx} \pm i\varepsilon_{xy}}$$
(1.173)

The two other cases are for linear polarization with  $\mathbf{q} \perp \mathbf{M}$  [226]. One has electric vector  $\mathbf{E} \parallel \mathbf{M}$  and index  $\hat{N}_{\parallel} = n_{\parallel} + ik_{\parallel} = \sqrt{\varepsilon_{zz}}$ . The other has  $\mathbf{E} \perp \mathbf{M}$  and  $\hat{N}_{\perp} = n_{\perp} + ik_{\perp} = \sqrt{(\varepsilon_{xx}^2 + \varepsilon_{xy}^2)/\varepsilon_{xx}}$ .

At normal light incidence the relation between the polar complex Kerr angle (Fig. 1.2) and the dielectric tensor components is given by [7]

$$\frac{1+\tan\eta}{1-\tan\eta}e^{2i\theta} = \frac{1+N_+}{1-\hat{N}_+} \frac{1-N_-}{1+\hat{N}_-}$$
(1.174)

with  $\hat{N}_{\pm} = (\varepsilon_{xx} \pm i\varepsilon_{xy})^{1/2}$ , the complex indices of refraction,  $\theta$  and  $\eta$  are the polar Kerr rotation and the ellipticity, respectively. From Eq. (1.174) it can be seen that the maximal observable rotation  $\theta$  is  $\pm 90^{\circ}$  and maximal achievable Kerr ellipticity  $\eta$  is  $\pm 45^{\circ}$ .

The Kerr rotation and ellipticity are for most materials less than 1°. The above exact expression can be approximated for small  $\theta$  and  $\eta$  and  $|\varepsilon_{xy}| \ll |\varepsilon_{xx}|$ , by the expression [8]

$$\theta + i\eta \approx \frac{-\varepsilon_{xy}}{(\varepsilon_{xx} - 1)\sqrt{\varepsilon_{xx}}},$$
(1.175)



Figure 1.2. The polar Kerr effect.

**Longitudinal Kerr effect.** For the longitudinal Kerr magnetization geometry, where the magnetization lies in the sample plane and the y-axis is chosen to be parallel to both the direction of the magnetization and the plane of incidence, the dielectric tensor takes the form

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & 0 & \varepsilon_{xz} \\ 0 & \varepsilon_{xx} & 0 \\ -\varepsilon_{xz} & 0 & \varepsilon_{zz} \end{pmatrix}.$$
 (1.176)

The formula for the longitudinal complex Kerr angle as it has been derived from general formulas for the Kerr effect with arbitrary dielectric tensor [227] is given by

$$\theta_{s,p}^{L} + i\eta_{s,p}^{L} = -\frac{2\varepsilon_{xz}\sin\varphi\cos\varphi\sqrt{\varepsilon_{xx}}}{D}, \qquad (1.177)$$

with

$$D = \left(\sqrt{\varepsilon_{xx}(\varepsilon_{zz} - \sin^2 \varphi)} + \sqrt{\varepsilon_{zz}(\varepsilon_{xx} - \sin^2 \varphi)}\right) \times \left(\sqrt{\varepsilon_{xx} - \sin^2 \varphi} \pm \cos \varphi\right) \left(\sqrt{\varepsilon_{xx} \varepsilon_{zz}} \cos \varphi \mp \sqrt{\varepsilon_{zz} - \sin^2 \varphi}\right)$$

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where  $\varphi$  is the angle of light incidence, and the upper and lower signs correspond to the p and s light polarization, parallel and perpendicular to the plane of incidence, respectively.

In the case when the assumption  $\varepsilon_{zz} \approx \varepsilon_{xx}$  is justified the formula (1.177) simplifies to [228]

$$\theta_{s,p}^{L} + i\eta_{s,p}^{L} = -\frac{\varepsilon_{xz}\sin\varphi(\sqrt{\varepsilon_{xx} - \sin^{2}\varphi \pm \sin\varphi\tan\varphi})}{(\varepsilon_{xx} - 1)(\varepsilon_{xx} - \tan^{2}\varphi)\sqrt{\varepsilon_{xx} - \sin^{2}\varphi}}.$$
 (1.178)

**Transversal MO Kerr effect.** The transversal MO Kerr effect measures not the Kerr angle or ellipticity but a modulated intensity difference of the reflected light. In T-MOKE the magnetization can be chosen along the x-axis and the wave vector is then in the y-z plane (Fig. 1.1). There is a MO effect only for the *p*-polarized wave [225, 229], therefore T-MOKE can be measured without a polarizer. The in-plane magnetization, which for T-MOKE is perpendicular to the plane of incidence, can have two orientations, namely, in the  $\pm$  x-direction. The normalized total reflectivity difference  $\delta_K$  for the two magnetization directions is equal to

$$\delta_K = \operatorname{Re}\left[\frac{2\varepsilon_0\varepsilon_{\rm xz}\sin 2\varphi}{\varepsilon_{\rm xx}^2\cos^2\varphi - \varepsilon_0\varepsilon_{\rm xx} + \varepsilon_0^2\sin^2\varphi}\right].$$
 (1.179)

T-MOKE is much less frequently used in spectroscopic studies in comparison with polar and longitudinal MO Kerr effects, although, T-MOKE can be useful in analyzing surface magnetic structures (see i.e. Ref. [230, 231]). The T-MOKE is odd in the magnetization. Therefore it is widely employed in magnetic investigations, particularly for observation of magnetic domains at the surface of a magnetized sample. Also, this effect allows design of transversely magnetized mirrors, as non-reciprocal optical devices. Investigations of the T-MOKE spectrum of various materials have been reported [232–236].

**Faraday effect.** In 1845 Michael Faraday discovered that when a block of glass is subjected to a magnetic field, it becomes optically active. When plane-polarized light passes through glass in a direction parallel to the applied field, the plane of polarization is rotated [1]. From a phenomenological point of view, the Faraday effect is explained by the fact that the refractive indexes,  $n_+$  and  $n_-$  for the left-hand and right-hand circularly polarized light in the case of an originally inactive substance, become different when the latter is placed in a magnetic field. Linearly polarized light with a given plane of polarization can be represented as a superposition of the right-hand and the left-hand circularly polarized waves with a definite phase difference. As a consequence

of the difference between  $n_+$  and  $n_-$ , the right-hand and the left-hand circularly polarized waves propagate with different velocities,  $c/n_+$  and  $c/n_-$ . The plane of polarization of the linearly polarized light therefore rotates through the angle [237]

$$\theta_F = \frac{\omega}{2c}(n_+ - n_+)L \tag{1.180}$$

where  $\omega$  is the angular frequency c is the velocity of light, and L is the path length of an optical beam in the medium.

The Faraday rotation  $\theta_F$  and ellipticity  $\eta_F$  are commonly defined by adopting the same conventions as adopted for the polar Kerr rotation and ellipticity. In the polar geometry the expression for the Faraday effect for small angels is

$$\theta_F + i\eta_F \approx \frac{i\varepsilon_{xy}}{\varepsilon_{xx}^{1/2}} \frac{\omega L}{2c} = \frac{\sigma_{xy}}{(1 + \frac{4\pi i}{\omega}\sigma_{xx})^{1/2}} \left(\frac{2\pi L}{c}\right).$$
(1.181)

Both the Faraday and Kerr effects are evidently caused by the non-zero offdiagonal conductivity  $\sigma_{xy}$ .

In the longitudinal geometry the approximate expression for the Faraday effect is

$$\theta_F + i\eta_F \approx \frac{i\varepsilon_{xy}}{\varepsilon_{xx}^{1/2}} \frac{\omega L}{2c} \tan\phi_l,$$
(1.182)

where  $\phi_l$  is the angle of the refraction.

The Faraday effect has mostly been used to investigate MO properties of transparent semiconductors. Kooy and Enz [238] utilized the Faraday effect to image domain structures in transparent ferromagnets. A survey of the experimental data accumulated until 1960 has been given by Jaggi *et al.* [239], while Schoenes has reviewed data collected from 1960 until 1992 [8].

**Non-linear MO effects.** In centro-symmetric media, an electric field contribution to the second-order optical polarizability is forbidden by symmetry. At a surface or at the boundaries between centro-symmetric media, the inversion symmetry is broken, resulting in the high surface sensitive second-harmonic-generation (SHG) effect [240]. The magnetization of a material does not usually break the inversion symmetry, but it can modify the form of the non-linear susceptibility for surface SHG. Pan *et al.* [241] and Hübner and Bennemann [242] have shown theoretically that a magnetic effect should be detected via SHG. The non-linear magneto-optics (magnetism-induced SHG) is of general interest, and becomes an important tool in the investigation of fundamental problems of magnetic films, multilayers, and surfaces.

The field of non-linear optics was first broached experimentally in the 1960s, but it was not until the 1980s that physicists became really interested in nonlinear MO phenomena [237]. Non-linear optical susceptibilities of magnetic origin possess quite different transformation properties under space and time symmetry operations to non-linear susceptibilities of electric origin. A magnetisminduced mechanism for non-linear MO effects was suggested in Ref.s [240, 243–246]. In this case the non-local electrical polarization vector contains terms depending on the magnetization, and vanishes if the magnetization (or staggered magnetization in antiferromagnets) vanishes. The first experimental evidence for the non-linear surface Kerr effect was given by Reif et al. [247] and Spiering et al. [248]. Vollmer et al. [249] directly compared linear MOKE measurements with non-linear Kerr effect measurements on Co films grown epitaxially on Cu(001). Magneto-induced SHG measurements were carried out in the transverse geometry. It was shown that the transverse non-linear Kerr effect is considerably stronger than the linear T-MOKE. The most interesting materials as regards observing magnetism-induced non-linear MO effects are the so-called magneto-electrical materials (Cr<sub>2</sub>O<sub>3</sub>, BiFeO<sub>3</sub>, etc) whose magnetic structures are odd in space. Agaltsov et al. [250] observed a strong magnetism-induced increase of the SHG in BiFeO<sub>3</sub> below the point of transition into the antiferromagnetic state, Feibig et al. [251] explored in depth the non-linear MO effects in the magneto-electric Cr<sub>2</sub>O<sub>3</sub>. The optical SHG in thin films of magnetic garnets using reflected and transmitted light was investigated in Ref.s [252-254].

Non-linear MO effects and, in particular the second-harmonic-generation effect are becoming increasingly important, because they are non-destructive, and can be remotely sensed *in situ* with high spatial and temporal resolution at any interface accessible to light.

The Kramers-Kronig relations and sum rules. The Kramers-Kronig expressions for the polar Kerr effect have been derived by Schnatterly [255] and Smith [256]. Exact Kramers-Kronig expressions for the polar Kerr rotation  $\theta_K$  and Kerr ellipticity  $\eta_K$  are

$$2\theta_K(\omega) = -\frac{2}{\pi} \mathcal{P} \int_o^\infty \frac{\omega'}{\omega'^2 - \omega^2} \ln \left| \frac{1 - \tan \eta_K(\omega')}{1 + \tan \eta_K(\omega')} \right| d\omega', \qquad (1.183)$$

$$\ln\left|\frac{1-\tan\eta_{K}(\omega)}{1+\tan\eta_{K}(\omega)}\right| = \frac{2}{\pi}\mathcal{P}\int_{o}^{\infty}\frac{\omega}{\omega'^{2}-\omega^{2}}2\theta_{K}(\omega')d\omega'.$$
 (1.184)

For small  $\theta_K$  and  $\eta_K$  the approximate Kramers-Kronig relations become

$$\theta_K(\omega) \approx \frac{2}{\pi} \mathcal{P} \int_o^\infty \frac{\omega'}{\omega'^2 - \omega^2} \eta_K(\omega') d\omega', \qquad (1.185)$$

$$\eta_{K}(\omega) \approx -\frac{2}{\pi} \mathcal{P} \int_{o}^{\infty} \frac{\omega}{\omega'^{2} - \omega^{2}} \theta_{K}(\omega') d\omega'.$$
(1.186)

#### THEORETICAL FRAMEWORK

Combining the Kramers-Kronig relations with physical arguments about the behavior of the real and imaginary parts of the response functions one can establish a set of sum rules. There are sum rules derived for the Faraday effect and the polar Kerr effect [257]. From Eq.s (1.183), (1.184) one obtains

$$\frac{2}{\pi} \mathcal{P} \int_{o}^{\infty} \frac{1}{\omega} \ln \left| \frac{1 - \tan \eta_{K}(\omega)}{1 + \tan \eta_{K}(\omega)} \right| d\omega = 0.$$
(1.187)

An identical expression is found for  $\theta_F$ . For the Faraday rotation one can in addition derive [257]

$$\int_{o}^{\infty} \theta_F(\omega) d\omega = 0.$$
 (1.188)

For products of components of the diagonal conductivity Vilani and Zimmerman [258, 259] derived

$$\int_{0}^{\infty} \omega \sigma_{\alpha\alpha}^{(1)}(\omega) \sigma_{\alpha\alpha}^{(2)}(\omega) d\omega = \frac{1}{\pi} \left(\frac{\omega_p^2}{8}\right)^2.$$
(1.189)

In the special case  $\omega = 0$ , the Kramers-Kronig equation (1.156) yields the sum rule expression

$$\sigma_{\alpha\beta}^{(1)}(0) = \frac{2}{\pi} \mathcal{P} \int_{o}^{\infty} \frac{\sigma_{\alpha\beta}^{(2)}(\omega')}{\omega'} d\omega'.$$
(1.190)

The Hall conductivity  $\sigma_{xy}^{(1)}(0)$  and DC diagonal conductivity  $\sigma_{xx}^{(1)}(0)$  can thus be obtained from an integral of the absorptive part over all excitation energies, which is a useful test of a measured absorptive spectrum.

Most of above sum rule expressions are rarely used in the analysis of MO spectra; however, they do hold potential for performing the interpolation of, e.g., Kerr ellipticity or Faraday effect spectrum to either zero or high frequencies, which are the parts of the spectrum that can not easily be measured.

**Symmetry properties.** The symmetry properties of the many-body linear response expression for the optical conductivity analyzed by Kubo [17]:

$$\sigma_{\alpha\beta}^*(\omega) = \sigma_{\alpha\beta}(-\omega), \qquad (1.191)$$

which implies

$$\operatorname{Re}[\sigma_{\alpha\beta}(\omega)] = \operatorname{Re}[\sigma_{\alpha\beta}(-\omega)], \qquad (1.192)$$

$$\operatorname{Im}[\sigma_{\alpha\beta}(\omega)] = -\operatorname{Im}[\sigma_{\alpha\beta}(-\omega)], \qquad (1.193)$$

as a consequence  $\text{Im}[\sigma_{\alpha\beta}(0)] = 0$ , and  $\text{Re}[\sigma_{\alpha\beta}(0)]$ =constant.
It also can be shown [260] that

$$\sigma_{\alpha\beta}(\omega, \mathbf{B}) = \sigma_{\beta\alpha}(\omega, -\mathbf{B}), \qquad (1.194)$$

which follows from time reversal accomplished by a reversion of the magnetic field. For the off-diagonal conductivity this leads - with the crystal symmetry property  $\sigma_{xy}(\omega) = -\sigma_{xy}(\omega)$  - to

$$\sigma_{xy}(\omega, -\mathbf{B}_z) = -\sigma_{xy}(\omega, \mathbf{B}_z) \tag{1.195}$$

These symmetry properties are valid also in the finite lifetime approximation.

#### MO effects in the X-ray region

In recent years the investigation of magneto-optical effects in the soft x-ray range has gained great importance as a tool for the investigation of magnetic materials [21]. There are at least two alternative formalisms for describing resonant soft X-ray MO properties. One uses the classical dielectric tensor [9]. Another uses the resonant atomic scattering factor including charge and magnetic contributions [24, 261]. The equivalence of these two description (within the dipole approximation) is demonstrated in Ref. [226].

Magnetic circular dichroism is first order in M (or  $\varepsilon_{xy}$ ) and is given by  $k_+ - k_-$  or  $n_+ - n_-$ , respectively, the later representing the magneto-optical rotation (MOR) of the plane of polarization (Faraday effect). Magnetic linear dichroism (MLD)  $n_{\perp} - n_{\parallel}$  (also known as the Voigt effect) is quadratic in M. The Voigt effect is present in both ferromagnets and antiferromagnets, while the first order MO effects in the forward scattering beam are absent with the net magnetization in antiferromagnets.

The alternative consideration of the MO effects is based on the atomic scattering factor  $f(\omega, q)$ , which provides a microscopic description of the interaction of X-ray photons with magnetic ions. For forward scattering (q = 0) $f(\omega) = Z + f'(\omega) + if''(\omega)$ , where Z is the atomic number.  $f'(\omega)$  and  $f''(\omega)$ are the anomalous dispersion corrections related to each other by the Kramers-Kronig transformation. The general equivalence of these two formalisms can be seen by noting the one-to-one correspondence of terms describing the same polarization dependence for the same normal modes [226]. For a multicomponent sample they relate to n and k through:

$$n(\omega) = \frac{2\pi c^2 r_e}{\omega^2} \sum_i Z_i f'_i(\omega) N_i$$
(1.196)

$$k(\omega) = \frac{2\pi c^2 r_e}{\omega^2} \sum_i f_i''(\omega) N_i, \qquad (1.197)$$

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where the sum is over atomic spheres, each having number density  $N_i$ , and  $r_e$  is the classical electron radius. The X-ray absorption coefficient  $\mu^{\lambda}(\omega)$  of polarization  $\lambda$  may be written in terms of the imaginary part of  $f_{\lambda}(\omega)$  as

$$\mu^{\lambda}(\omega) = \frac{4\pi r_e c}{\Omega \omega} f_{\lambda}''(\omega), \qquad (1.198)$$

where  $\Omega$  is the atomic volume. X-ray MCD which is the difference in X-ray absorption for right- and left-circularly polarized photons  $(\mu^+ - \mu^-)$  can be presented by  $(f''_+ - f''_-)$ . Faraday rotation  $\theta_F(\omega)$  of linear polarization measures MCD in the real part  $f'_{\lambda}$  of the resonant magnetic X-ray-scattering amplitude, i.e. [15],

$$\theta_F(\omega) = \frac{\omega l}{2c} \operatorname{Re}[\mathbf{n}_+ - \mathbf{n}_-] = \frac{\pi \mathrm{lr}_e}{\Omega \omega} (\mathbf{f}'_-(\omega) - \mathbf{f}'_+(\omega)).$$
(1.199)

Finally, the scattering X-ray intensity from an elemental magnet at the Bragg reflection measured in the resonant magnetic X-ray-scattering experiments is just the squared modulus of the total scattering amplitude, which is a linear combination of  $(f'_{\pm} + if''_{\pm}, f'_{\pm} + if''_{\pm})$  with the coefficients fully determined by the experimental geometry [262]. Multiple scattering theory is usually used to calculate the resonant magnetic X-ray scattering amplitude (f' + if'') [9, 262, 263].

We should mention that the general equivalence of the dielectric tensor and scattering factor descriptions holds only when considering dipole transitions contributing to the atomic scattering factor  $f(\omega)$ . Higher-order multipole terms have different polarization dependence [24].

Using straightforward symmetry considerations it can be shown that all magneto-optical phenomena (XMCD, MO Kerr and Faraday effects) are caused by the symmetry reduction caused by magnetic ordering [211]. This symmetry reduction only has consequences when SO coupling is considered in addition. To calculate the XMCD properties one has to account for magnetism and SO coupling at the same time when dealing with the electronic structure of a material. The theoretical description of magnetic dichroism can be cast into four categories. On the one hand, there are one-particle (ground-state) and manybody (excited-state) theories; on the other hand, there are theories for single atoms and those which take into account the solid state. To name a few from each category, for atomic one-particle theories we refer to Refs. [264] and [265], for atomic many-particle multiplet theory to Refs. [266–269], for solid many-particle theories to Ref. [270], and for solid one-particle theories (photoelectron diffraction) to Refs. [271–274]. A multiple-scattering approach to XMCD, a solid-state one-particle theory, has been proposed by Ebert et al. [275–277] and Tamura et al. [278].

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Within the one-particle approximation, the absorption coefficient  $\mu$  for incident X-ray of polarization  $\lambda$  and photon energy  $\hbar\omega$  can be determined as the probability of electron transition from an initial core state (with wave function  $\psi_j$  and energy  $E_j$ ) to a final unoccupied state (with wave function  $\psi_{n\mathbf{k}}$  and energy  $E_{n\mathbf{k}}$ )

$$\mu_j^{\lambda}(\omega) = \sum_{n\mathbf{k}} |\langle \Psi_{n\mathbf{k}} | \mathcal{J}_{\lambda} | \Psi_j \rangle|^2 \delta(E_{n\mathbf{k}} - E_j - \hbar\omega) \theta(E_{n\mathbf{k}} - E_F) \,. \tag{1.200}$$

The  $\mathcal{J}_{\lambda}$  is the dipole electron-photon interaction operator  $\mathcal{J}_{\lambda} = -e\alpha \mathbf{a}_{\lambda}$ , where  $\mathbf{a}_{\lambda}$  is the  $\lambda$  polarization unit vector of the photon potential vector  $[a_{\pm} = 1/\sqrt{2}(1, \pm i, 0), a_z = (0, 0, 1)]$ . (Here +/- denotes, respectively, left and right circular photon polarizations with respect to the magnetization direction in the solid).

While XMCD is calculated using equation (1.200), the main features can be understood already from a simplified expression for paramagnetic solids. With restriction to electric dipole transitions, keeping the integration only inside the atomic spheres (due to the highly localized core sates) and averaging with respect to polarization of the light, one obtains the following expression for the absorption coefficient of the core level with (l, j) quantum numbers [279]:

$$\mu_{lj}^{0}(\omega) = \sum_{l',j'} \frac{2j+1}{4} \Big( \frac{\delta_{l',l+1} \delta_{j',j+1}}{j+1} + \frac{\delta_{l',l-1} \delta_{j',j-1}}{j} + \frac{\delta_{l',l+1} \delta_{j',j}}{j(j+1)(2j+1)} \Big) N_{l',j'}(E) C_{l,j}^{l',j'}(E)$$
(1.201)

where  $N_{l^{'},j^{'}}(E)$  is the partial density of empty states and the  $C_{l,j}^{l^{'},j^{'}}(E)$  radial matrix elements

$$C_{l,j}^{l',j'}(E) = \omega c^2 | \int_{0}^{R_{as}} dr^2 [(\kappa' - \kappa + 1)g_{c\kappa}(r)f_{\kappa'}(r) + (\kappa' - \kappa - 1)f_{c\kappa}(r)g_{\kappa}(r)]|^2$$
(1.202)

with  $g_{c\kappa}(r)$   $(f_{c\kappa}(r))$  and  $g_{\kappa}(r)$   $(f_{\kappa}(r))$  big (small) radial wave functions of the core and valence states respectively;  $\kappa$  is the relativistic quantum number.

It is well known that the dipole transition matrix element in (1.201) may be transformed into equivalent forms, and corresponding expressions for the radial matrix elements in the **r**- and  $\nabla V(\mathbf{r})$ -forms can be found in Ref. [279]. Eq. (1.201) allows only transitions with  $\Delta l = \pm 1, \Delta j = 0, \pm 1$  (dipole selection rules) which means that the absorption coefficient can be interpreted as a direct measure for the sum of (l, j)-resolved DOS curves weighed by the square of the corresponding radial matrix element (which usually is a smooth function of energy). This simple interpretation is valid for the spin-polarized case [9].

In order to simplify the comparison of the theoretically calculated x-ray isotropic absorption spectra to the experimental ones one should take into account the background intensity which affects the high energy part of the spectra. The shape of x-ray absorption caused by the transitions from inner levels to the continuum of unoccupied levels was first discussed by Richtmyer *et al.* in early thirties [280]. The absorption coefficient in assumption of equally distributed empty continuum levels is

$$\mu(\omega) = \frac{C\Gamma_c}{2\pi} \int_{E_{cf_0}}^{\infty} \frac{dE_{cf}}{(\Gamma_c/2)^2 + (\hbar\omega - E_{cf})^2},$$
(1.203)

where  $E_{cf} = E_c - E_f$ ,  $E_c$  and  $\Gamma_c$  are the energy and the width of a core level,  $E_f$  is the energy of empty continuum level,  $E_{f_0}$  is the energy of the lowest continuum level, and C is a normalization constant which is usually considred as an adjustable parameter.

**Sum rules.** Concurrent with the x-ray magnetic circular dichroism experimental developments, some important magneto-optical sum rules have been derived in recent years. Thole and van der Laan [281] developed a sum rule relating the integrated signals over the spin-orbit split core edges of the unpolarized XAS to the expectation value of the ground state spin-orbit operator. Later Thole *et al.* [282] and Carra *et al.* [283] derived sum rules to relate the integrated signals over the spin-orbit split core edges of the circular dichroism to ground state orbital and spin magnetic moments by using an ion model for atoms. In the case of solids the corresponding XMCD sum rules were proposed by Ankudinov and Rehr [284] and Guo [285]. Sum rules for X-ray magnetic scattering were derived by Luo *et al* [286].

For the  $L_{2,3}$  edges the  $l_z$  sum rule can be written as

$$\langle l_z \rangle = -n_h \frac{4 \int_{L_3+L_2} d\omega(\mu_+ - \mu_-)}{3 \int_{L_3+L_2} d\omega(\mu_+ + \mu_-)}$$
(1.204)

where  $n_h$  is the number of holes in the *d* band  $n_h = 10 - n_d$ ,  $\langle l_z \rangle$  is the average of the magnetic quantum number of the orbital angular momentum. The integration is taken over the whole 2p absorption region. The  $s_z$  sum rule is written as

$$\langle s_z \rangle + \frac{7}{2} \langle t_z \rangle = - n_h \frac{6 \int_{L_3} d\omega (\mu_+ - \mu_-) - 4 \int_{L_2} d\omega (\mu_+ - \mu_-)}{\int_{L_3 + L_2} d\omega (\mu_+ + \mu_-)}$$
(1.205)

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where  $t_z$  is the z component of the magnetic dipole operator  $\mathbf{t} = \mathbf{s} - 3\mathbf{r}(\mathbf{r} \cdot \mathbf{s})/|\mathbf{r}|^2$  which accounts for the asphericity of the spin moment. It was shown that this term is negligible for cubic systems [9, 277]. The integration  $\int_{L_3} (\int_{L_2})$  is taken only over the  $2p_{3/2}$  ( $2p_{1/2}$ ) absorption region. In these equations, we have replaced the linear polarized spectra,  $\mu_0$ , by  $[\mu_+(\omega) + \mu_-(\omega)]/2$ .

Because of the significant implications of the sum rules, numerous experimental and theoretical studies aimed at investigating their validity for itinerant magnetic systems have been reported, but with widely different conclusions. The claimed adequacy of the sum rules varies from very good (within 5% agreement) to very poor (up to 50% discrepancy) [33, 282, 283, 287– 289]. This lack of a consensus may have several origins. For example, on the theoretical side, it has been demonstrated by circularly polarized 2p resonant photoemission measurements of Ni that both the band structure effects and electron-electron correlations are needed to satisfactorily account for the observed MCD spectra [290]. However, it is extremely difficult to include both of them in a single theoretical framework. Besides, the XAS as well as XMCD spectra can be strongly affected (especially for the early transition metals) by the interaction of the excited electron with the created core hole [291].

On the experimental side, the indirect x-ray absorption techniques, i.e., the total electron and fluorescence yield methods, are known to suffer from saturation and self-absorption effects that are very difficult to correct for. The total electron yield method can be sensitive to the varying applied magnetic field, changing the electron detecting efficiency, or, equivalently, the sample photocurrent. The fluorescence yield method is insensitive to the applied field, but the yield is intrinsically not proportional to the absorption cross section, because the radiative to non-radiative relative core-hole decay probability depends strongly on the symmetry and spin polarization of the XAS final states [33].

To derive the sum rules a great number of assumptions had to be made [9]. For  $L_{2,3}$ , they are: (1) ignore the exchange splitting for the core levels; (2) replace the interaction operator  $\boldsymbol{\alpha} \cdot \mathbf{a}_{\lambda}$  in Eq. (1.200) by  $\nabla \cdot \mathbf{a}_{\lambda}$ ; (3) ignore the asphericity of the core states; (4) ignore  $p \rightarrow s$  transitions; (5) ignore the difference of  $d_{3/2}$  and  $d_{5/2}$  radial wave functions; (6) ignore the inter-atomic hybridization, which means ignoring the energy dependence of the radial matrix elements. The three last points are the most important. The problem of ignoring of the  $p \rightarrow s$  transitions was considered by Wu and Freeman [289] in the case of pure Fe, Co, Ni and their surfaces. They demonstrate that the application of the spin sum rule results in an error up to 52% for the Ni(001) surface. On the other hand, the orbital sum rule is affected much less.

### **1.4.3** Linear-response theory

In previous sections the response of the medium to electromagnetic waves was described in a phenomenological manner in terms of the frequency dependent complex dielectric constant and conductivity. It is important to relate these parameters to the changes in the electronic states of solids, brought about by the electromagnetic fields or by external potentials. One of the ways to fulfill such a task is to use the celebrated Kubo formula in which the conductivity is given in terms of current-current correlation functions. The expression is general and has been useful in formulating a variety of transport and spectral properties in condensed matter.

**Kubo formalism.** In the presence of a vector and scalar potential, the Hamiltonian of N-electron system in a solid is in general given by [213]

$$\mathcal{H} = \frac{1}{2m} \sum_{i=1}^{N} \left( \mathbf{p}_{i} + \frac{e}{c} \mathbf{A}(\mathbf{r}_{i}) \right)^{2} + \sum_{i=1,j=1}^{N,M} V_{j}(\mathbf{r}_{i} - \mathbf{R}_{j}) + \frac{1}{2} \sum_{i=1,i'=1}^{N,N} \frac{e^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{i'}|} - \sum_{i=1}^{N} e \Phi(\mathbf{r}_{i}), \qquad (1.206)$$

here -e is the electronic charge and m is the electron mass. The first term refers to the coupling between the electromagnetic waves (described by the external vector potential **A**) and the electrons with momenta  $\mathbf{p}_i$  and location  $\mathbf{r}_i$ . The second term defines the interaction between the ions and the electrons; this interaction is given by the potential  $V_j$ . In a crystalline solid  $V_j(\mathbf{r}_i - \mathbf{R}_j)$ is a periodic function, and with M ionic sites and N electrons the band filling is N/M. The third term describes the electron-electron interaction ( $i \neq i'$ ); we assume that only the Coulomb repulsion is important; we used the Born-Oppenheimer adiabatic approximation and, hence, neglected the interaction among electrons and phonons. We also neglected the spin dependent interactions between electrons. The last term in the Hamiltonian describes an external scalar potential  $\Phi$  as produced by an external charge.

In general one may split the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int}, \tag{1.207}$$

with the first term describing the unperturbed Hamiltonian in the absence of a vector and a scalar potential:

$$\mathcal{H}_{0} = \frac{1}{2m} \sum_{i=1}^{N} \mathbf{p}_{i}^{2} + \sum_{i=1,j=1}^{N,M} V_{j}(\mathbf{r}_{i} - \mathbf{R}_{j}) + \frac{1}{2} \sum_{i=1,i'=1}^{N,N} \frac{e^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{i'}|}.$$
 (1.208)

The second term in Eq. (1.207) accounts for the interaction of the system with the electromagnetic radiation and with the electrostatic potential. This

interaction with the electromagnetic field is given by

$$\mathcal{H}_{int} = \frac{e}{2mc} \sum_{i=1}^{N} [\mathbf{p}_i \cdot \mathbf{A}(\mathbf{r}_i) + \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i] - \sum_{i=1}^{N} e\Phi(\mathbf{r}_i).$$
(1.209)

Here we have neglected second order terms (e.g. terms proportional to  $A^2$ ).

The operator of the electrical current density is defined as [213]

$$\mathbf{J}(\mathbf{r}) = -\frac{e}{2} \sum_{i=1}^{N} [\mathbf{v}_i \delta\{\mathbf{r} - \mathbf{r}_i\} + \delta\{\mathbf{r} - \mathbf{r}_i\} \mathbf{v}_i], \qquad (1.210)$$

where  $\mathbf{v}_i$  is the velocity of the *i*th particle at position  $\mathbf{r}_i$  (we have implicitly assumed the usual commutation rules). The velocity operator of an electron in the presence of an electromagnetic field in the nonrelativistic limit is given by  $\mathbf{v} = \mathbf{p}/m + e\mathbf{A}/mc$ ; consequently the current density has two terms,

$$\mathbf{J}(\mathbf{r}) = -\frac{e}{2m} \sum_{i=1}^{N} [\mathbf{p}_i \delta\{\mathbf{r} - \mathbf{r}_i\} + \delta\{\mathbf{r} - \mathbf{r}_i\}\mathbf{p}_i] - \frac{e^2}{mc} \sum_{i=1}^{N} \mathbf{A}(\mathbf{r}_i) \delta\{\mathbf{r} - \mathbf{r}_i\}.$$
(1.211)

The second term follows from the fact that  $\mathbf{A}(\mathbf{r}_i)$  commutes with  $\delta\{\mathbf{r} - \mathbf{r}_i\}$ . The first term is called the paramagnetic and the second the diamagnetic current. Since  $\mathbf{p} = -i\hbar\nabla$  we obtain

$$\mathbf{p} \cdot \mathbf{A} - \mathbf{A} \cdot \mathbf{p} = -i\hbar \nabla \cdot \mathbf{A}. \tag{1.212}$$

Using the definition (1.210) of electric current density, the interaction term Eq. (1.209) for transverse field ( $\Phi = 0$ ) can be written as [213]

$$\mathcal{H}_{int} = -\frac{1}{c} \int \mathbf{J}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r}.$$
 (1.213)

We have replaced the summation over the individual positions *i* by an integral, and we have assumed that the current is a continuous function of the position **r**. Note, that the diamagnetic current term leads to a term in the interaction Hamiltonian which is second order in **A**, thus it is not included if we restrict ourselves to interactions proportional to **A**. We define the spatial Fourier transformations of the current density operator  $\mathbf{J}(\mathbf{q})$  and the vector potential  $\mathbf{A}(\mathbf{q})$  as

$$\mathbf{J}(\mathbf{q}) = \frac{1}{\Omega} \int \mathbf{J}(\mathbf{r}) \exp\{-i\mathbf{q} \cdot \mathbf{r}\} d\mathbf{r}$$
  
=  $-\frac{e}{2} \frac{1}{\Omega} \sum_{i=1}^{N} [\mathbf{v}_{i} \exp\{-i\mathbf{q} \cdot \mathbf{r}\} + \exp\{-i\mathbf{q} \cdot \mathbf{r}\} \mathbf{v}_{i}], \quad (1.214)$ 

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and

$$\mathbf{A}(\mathbf{q}) = \frac{1}{\Omega} \int \mathbf{A}(\mathbf{r}) \exp\{-i\mathbf{q} \cdot \mathbf{r}\} d\mathbf{r}.$$
 (1.215)

Here  $\Omega$  denotes the volume element in which the integration is carried out. With these definitions the **q** dependent interaction term in first order perturbation becomes

$$\mathcal{H}_{int} = -\frac{1}{c} \mathbf{J}(\mathbf{q}) \cdot \mathbf{A}(\mathbf{q}).$$
(1.216)

We assume that the incident electromagnetic wave with wave vector  $\mathbf{q}$  and frequency  $\omega$  results in the scattering of an electron from one state to another with higher energy. According to Fermi's golden rule the number of transitions per unit time and per unit volume from the initial state  $|n\rangle$  to a final state  $|n'\rangle$  is

$$W_{nn'} = \frac{2\pi}{\hbar^2} |\langle n' | \mathcal{H}_{int} | n \rangle|^2 \delta\{\omega - \omega_{nn'}\}.$$
 (1.217)

Here  $\hbar\omega_n$  and  $\hbar\omega_{n'}$  correspond to the energy of the initial and final states of the electron system respectively;  $\omega_{nn'} = \omega_{n'} - \omega_n$ .

The transition rate is obtained by substituting Eq. (1.216), into Eq. (1.217), making the summation over all occupied initial and empty final states and using the identity  $\delta(\omega) = 1/2\pi \int \exp\{-i\omega t\} dt$  to obtain the transfer rate per unit volume:

$$W = \sum_{nn'} \frac{1}{\hbar^2 c^2} \int dt \exp\{-i\omega t\} \langle n' | \mathbf{J}(\mathbf{q}) | n \rangle$$
$$\times \langle n | \exp\{i\omega_{s'} t\} \mathbf{J}^*(\mathbf{q}) \exp\{-i\omega_s t\} | n' \rangle | \mathbf{A}(\mathbf{q}) |^2. \quad (1.218)$$

In the Heisenberg representation  $\exp\{-i\omega_s t\}|n\rangle = \exp\{-i\mathcal{H}_0 t/\hbar|n\rangle$ , and then the time dependence is written as

$$\begin{aligned} \mathbf{J}^{*}(\mathbf{q},t) &= \exp\{i\mathcal{H}_{0}t/\hbar\}\mathbf{J}^{*}(\mathbf{q})\exp\{-i\mathcal{H}_{0}t/\hbar\} \\ &= \exp\{i\omega_{s'}t\}\mathbf{J}^{*}(\mathbf{q})\exp\{-i\omega_{s}t\}\,, \end{aligned}$$

and the absorbed energy per unit time and per unit volume then becomes

$$P = \hbar\omega W = |\mathbf{A}(\mathbf{q})|^2 \sum_{n} \frac{\omega}{\hbar c^2} \int dt \langle n | \mathbf{J}(\mathbf{q}, 0) \mathbf{J}^*(\mathbf{q}, t) | n \rangle \exp\{-i\omega t\},$$
(1.219)

where we have replaced n' by n in order to simplify the notation.

Taking into account that the vector potential is given by  $\mathbf{E} = i\omega \mathbf{A}/c$  and that  $P = \sigma_1 \mathbf{E}^2$ , we finally obtain the expression for the conductivity per unit

volume given by the current-current correlation function over the state  $|n\rangle$  of our system in question [213]

$$\sigma_1(\mathbf{q},\omega) = \sum_n \frac{1}{\hbar\omega} \int dt \langle n | \mathbf{J}(\mathbf{q},0) \mathbf{J}^*(\mathbf{q},t) | n \rangle \exp\{-i\omega t\}, \quad (1.220)$$

i.e. the Kubo formula for the q and  $\omega$  dependent conductivity.

Applying the Fermi statistic and dropping the q dependence since we are only interested in the q = 0 limit (direct interband transitions) we arrive at the so called Kubo-Greenwood linear-response expression [17, 19, 20]:

$$\sigma_{\alpha\beta}^{(1)}(\omega) = \frac{\pi e^2}{m^2 \omega} \sum_{\mathbf{k}} \sum_{nn'} \frac{f(\epsilon_{n\mathbf{k}}) - f(\epsilon_{n'\mathbf{k}})}{\omega_{nn'}(\mathbf{k})} \frac{M_{n'n}^{\alpha}(\mathbf{k})M_{nn'}^{\beta}(\mathbf{k})}{\omega - \omega_{nn'}(\mathbf{k}) + i\gamma}, \quad (1.221)$$

where  $f(\epsilon_{n\mathbf{k}})$  is the Fermi function,  $\hbar\omega_{nn'}(\mathbf{k}) \equiv \epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}$  is the energy difference of the Kohn-Sham energies  $\epsilon_{n\mathbf{k}}$ , and  $\gamma$  is the lifetime parameter, which is included to describe the finite lifetime of excited Bloch electron states. The  $M^{\alpha}_{nn'}$  are the dipole optical transition matrix elements. In the relativistic case the  $\mathbf{J} = -ec\alpha$ , with  $\alpha$  being the Dirac operator, therefore

$$M_{nn'}(\mathbf{k}) = \langle \Psi_n^{\mathbf{k}} | c\alpha | \Psi_{n'}^{\mathbf{k}} \rangle \tag{1.222}$$

with  $\Psi_n^{\mathbf{k}}$  being the four-component Bloch electron wave functions.

**Drude-Sommerfeld theory.** Eq. (1.221) for the conductivity contains a double sum over all energy bands, which naturally separates into the so-called interband contribution, i.e.,  $n \neq n'$ , and the intraband contribution, n = n'.

$$\sigma_{\alpha\beta}(\omega) = \sigma_{\alpha\beta}^{inter}(\omega) + \sigma_{\alpha\beta}^{intra}(\omega) \quad , \tag{1.223}$$

For the diagonal tensor components, both terms are important and should be considered simultaneously. The intraband contribution to the diagonal components of  $\sigma$  is usually described by the phenomenological Drude-Sommerfeld model [292, 293]. In this model a metal is regarded as a classical gas of electrons executing diffusive motion. The central assumption of the model is the existence of an average relaxation time  $\tau_D$  which governs the relaxation of the system to equilibrium, i.e. the state with zero average momentum  $\langle \mathbf{p} \rangle = 0$ , after an external field **E** is removed. The rate equation is

$$\frac{d\langle \mathbf{p} \rangle}{dt} = -\frac{\langle \mathbf{p} \rangle}{\tau_D}.$$
(1.224)

In the presence of an external electric field **E**, the equation of motion becomes

$$\frac{d}{dt}\langle \mathbf{p} \rangle = -\frac{\langle \mathbf{p} \rangle}{\tau_D} - e\mathbf{E}.$$
(1.225)

The current density is given by  $\mathbf{J} = -Ne\mathbf{p}/m$ , with N the density of charge curriers; m is the carrier mass, and -e is the electronic charge. For dc fields, the condition  $d\langle \mathbf{p} \rangle/dt = 0$  leads to a dc conductivity

$$\sigma_{\rm dc} = \frac{\mathbf{J}}{\mathbf{E}} = \frac{Ne^2 \tau_D}{m}.$$
 (1.226)

Upon the application of an ac field of the form  $\mathbf{E}(t) = \mathbf{E}_0 \exp\{-i\omega t\}$ , the solution of the equation of motion

$$m\frac{d^2\mathbf{r}}{dt^2} + \frac{m}{\tau_D}\frac{d\mathbf{r}}{dt} = -e\mathbf{E}(t)$$
(1.227)

gives a complex, frequency dependent conductivity [213]

$$\hat{\sigma}(\omega) = \frac{Ne^2\tau_D}{m} \frac{1}{1 - i\omega\tau_D} = \sigma_1(\omega) + i\sigma_2(\omega) = \frac{\omega_p^2}{4\pi} \frac{1}{1/\tau_D - i\omega}.$$
 (1.228)

The plasma frequency  $\omega_p$  is given by Eq. (1.163) and can be presented as follows

$$\omega_p^2 \equiv \frac{4\pi e^2}{m^2 \Omega} \sum_{n\mathbf{k}} \delta(\epsilon_{n\mathbf{k}} - E_F) |M_{nn}|^2 , \qquad (1.229)$$

where  $E_F$  is the Fermi energy and  $\Omega$  is the atomic volume. The intraband relaxation time parameter  $\gamma_D = 1/\tau_D$  may be different from the interband relaxation time parameter  $\gamma$  in Eq. (1.221). The latter can be frequency dependent, and, because excited states always have a finite lifetime, will be non-zero, whereas  $\gamma_D$  will approach zero for very pure materials.

The components of the optical conductivity are

$$\sigma_1(\omega) = \frac{\omega_p^2 \tau_D}{4\pi} \frac{1}{1 + \omega^2 \tau_D^2}$$
(1.230)

and

$$\sigma_2(\omega) = \frac{\omega_p^2 \tau_D}{4\pi} \frac{\omega \tau_D}{1 + \omega^2 \tau_D^2}.$$
(1.231)

The dc limit of the conductivity is

$$\sigma_1(\omega=0) = \sigma_{\rm dc} = \frac{1}{4\pi}\omega_p^2 \tau_D. \tag{1.232}$$

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Within the framework of the Drude model the complex conductivity and consequently all the various optical parameters are fully characterized by two parameters: the plasma frequency  $\omega_p$  and the relaxation rate  $\gamma_D = 1/\tau_D$ ; in general  $\gamma_D \ll \omega_p$ .

Using the general relation (1.131), the frequency dependence of the dielectric constant is

$$\hat{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\omega/\tau_D}$$
(1.233)

with the real and imaginary parts

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \tau_D^{-2}}$$
(1.234)

and

$$\varepsilon_2(\omega) = \frac{1}{\omega\tau_D} \frac{\omega_p^2}{\omega^2 + \tau_D^{-2}}.$$
(1.235)

The Drude picture is fundamentally different for electrons obeying quantum statistics, and the consequences of this have been developed by Sommerfeld [293]. Within the framework of this model, the concept of the Fermi surface plays a central role. In the absence of an electric field, the Fermi surface is centered around zero momentum, and  $\langle \mathbf{p} \rangle = \hbar \langle \mathbf{k} \rangle = 0$ . The Fermi surface is displaced in the presence of an applied field  $\mathbf{E}$ , with magnitude of the displacement given by  $-eE\tau/\hbar$ . The equation of motion for the average momentum is the same as given above. Again with  $\langle \mathbf{J} \rangle = -Ne\hbar \langle \mathbf{k} \rangle/m$  and wavevector  $\mathbf{k} = \mathbf{p}/\hbar$ , expression (1.228) is recovered. However, the scattering processes which establish the equilibrium in the presence of the electric field involve only electrons near to the Fermi surface, states deep within the Fermi sea are not influenced by the electric field. The difference has important consequences for the temperature dependences, and also for non-linear response to large electric fields, a subject beyond the scope of this book.

The intraband contribution to the off-diagonal optical conductivity is very small and usually neglected in the case of magnetically ordered materials. For nonmagnetic metals (which have zero spontaneous exchange splitting), the spin polarization induced by an external magnetic field available in the experiment is small and the contributions of intra- and interband transitions to the off-diagonal optical conductivity tensor component can become comparable. Therefore, in such cases the intraband term should be taken into account on the same footing as the interband one.

The intraband contributions to the off-diagonal  $\sigma_{xy}^D(\omega)$  part of the optical conductivity tensor is equal to [7, 8]

$$\sigma_{xy}^D(\omega) = \frac{\omega_p^2}{4\pi} \frac{\omega_c}{(\gamma_D - i\omega)^2 + \omega_c^2} \quad , \tag{1.236}$$

with  $\omega_c$  being the cyclotron frequency

$$\omega_c = eH/m^*c \quad , \tag{1.237}$$

where H is the applied magnetic field, e is the electron charge,  $m^* = m(1 + \lambda)$  is the effective mass of the carrier, renormalized in solids by the electronphonon interaction constant  $\lambda$ , and  $\omega_p$  is the plasma frequency.

To apply the formula (1.236), suitable values of the parameters are needed. As a first approximation, zero-frequency values taken from dc-transport measurements can be used. The  $\sigma_{xy}^D(\omega)$  conductivity for  $\omega = 0$  is

$$\sigma_{xy}^D(0) = -\frac{\varrho_H}{\varrho^2} \quad , \tag{1.238}$$

where  $\rho$  and  $\rho_H$  are dc and Hall resistivity, respectively [7, 8].

The following formulas for  $\sigma_{xu}^D(0)$  can be obtained for  $\gamma_D \gg \omega_c$ 

$$\sigma_{xy}^D(0) = \frac{\omega_p^2}{4\pi} \frac{\omega_c}{\gamma_D^2} . \qquad (1.239)$$

Therefore  $\gamma_D$  can be expressed as

$$\gamma_D = \frac{\varrho}{|\varrho_H|} \omega_c \quad . \tag{1.240}$$

#### **1.4.4** Optical matrix elements

The electron-photon interaction operator can be presented in standard form

$$\mathcal{J}_{\mathbf{q}\lambda}(\mathbf{r}) = -\frac{1}{c} \mathbf{J} \cdot \mathbf{A}_{\mathbf{q}\lambda}(\mathbf{r}) = -\frac{1}{c} \mathbf{J} \cdot \hat{a}_{\lambda} A e^{i\mathbf{q}\mathbf{r}}$$
(1.241)

where  $\mathbf{A}_{\mathbf{q}\lambda}(\mathbf{r})$  is a vector potential of the photon field treated here in a classical way, **J** is the electron current density operator:

$$\mathbf{J} = -ec\alpha. \tag{1.242}$$

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The polarization vector  $\hat{a}_{\lambda}$  in equation (1.241) is real for linearly polarized light with, for example,  $\lambda = x, y$  or z. For q pointing along the z-axis the complex polarization vector

$$\hat{a}_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\ \pm i\\ 0 \end{pmatrix}. \tag{1.243}$$

represents left (right) circularly polarized light or equivalently light with positive (negative) helicity.

In the optical frequency regime it is generally argued that the amplitude of the vector potential varies only slowly on a microscopic scale. This means that expanding the vector potential factor in equation (1.241) according to

$$e^{i\mathbf{q}\mathbf{r}} = 1 + i\mathbf{q}\mathbf{r} - \frac{1}{2}(\mathbf{q}\mathbf{r})^2 + \dots$$
 (1.244)

The materials of which the MO spectra are investigated consist of unit cells with a lattice parameter of  $a \simeq 2\text{-}10$  Å. Visible light, however, has a wave length of about 600-800 nm. Since  $q = 2\pi/\lambda$ , one can make the approximation  $q \rightarrow 0$  and retain the first term in Eq. (1.244). This amounts to accounting only for the electric dipole interaction.

Investigating magneto-optical phenomena on the basis of a spin-polarized relativistic description of the electronic structure (see Appendix A) together with a corresponding expression for the electron-photon interaction according to equation (1.241), one has to deal with matrix elements of the form

$$M_{nn'}^{\mathbf{q}\lambda}(\mathbf{k}) = \langle \Psi_{n'}^{\mathbf{k}} | \mathcal{J}_{\mathbf{q}\lambda} | \Psi_{n}^{\mathbf{k}} \rangle.$$
(1.245)

where  $\Psi_n$  and  $\Psi_{n'}$  are the crystal wave functions for initial and final states respectively.

The detailed evaluation of the matrix elements (1.245) in the fully relativistic Dirac representation in the framework of the RLMTO method presents in Appendix B.

**Selection rules.** In (B.28) the Clebsh-Gordan coefficients  $C_{1\mu'-\mu,l'\mu'-m_s}^{l\mu-m_s}$  lead to the familiar angular momentum and parity selection rules

$$\Delta l = \pm 1 \tag{1.246}$$

$$\Delta j = 0, \pm 1.$$
 (1.247)

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with the selection rules for the magnetic quantum number  $m_j$  ( $m_j$  is restricted to  $-j, \ldots + j$ )

$$\Delta m_j = \begin{cases} +1 & \text{for } \lambda = + \\ -1 & \text{for } \lambda = - \\ 0 & \text{for } \lambda = z \\ \pm 1 & \text{for } \lambda = x, y \end{cases}$$
(1.248)

we have total selection rules in the MO spectroscopy.

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## Chapter 2

# MAGNETO-OPTICAL PROPERTIES OF *d* FERROMAGNETIC MATERIALS

Among the compounds containing magnetic transition elements, four large classes have attracted special attention for their MO properties. These comprise spinels, garnets, orthoferrites, and Heusler alloys. In recent years, certain other transition-metal alloys containing ferromagnetic 3d element have drawn attention because of their good magneto-optical (MO) properties (see, e.g., Ref. [294–296]). Especially multilayers of Co with Pt or Pd are intensively studied for their potential application as optical storage materials in MO storage devices [297–299]. In addition, it was recently discovered that the compound MnPt<sub>3</sub> exhibits a very large MO Kerr rotation, of about  $-1.2^{\circ}$  at 1 eV photon energy [300, 301]. This discovery suggests that a large group of transition-metal-platinum alloys is exceptionally interesting to MO research, and also offers encouragement that large Kerr effects might still be found in materials which were previously not considered for their MO properties.

With the aim of presenting a systematic investigation of the trends in transition metals and alloys, we present the theoretically calculated and experimentally measured MO Kerr spectra of ferromagnetic Fe, Co, Ni, paramagnetic Pt, Pd, CoPt and CoPd alloys, XPt<sub>3</sub> compounds (with X=V, Cr, Mn, Fe, and Co), Heusler alloys (PtMnSb, PdMnSb and NiMnSb), MnBi, chromium spinel chalcogenides CuCr<sub>2</sub>X<sub>4</sub> (X=S, Se, Te) and the strongly correlated Fe<sub>3</sub>O<sub>4</sub> compound as well as Mg<sup>2+</sup>-, or Al<sup>3+</sup>-substituted magnetite.

## 2.1 Transition metals and compounds

## 2.1.1 Ferromagnetic metals Fe, Co, Ni

We start this section discussing the simple systems Fe, Co and Ni. The MO Kerr spectra of the 3d transition metals were among the earliest measured [302–309, 297, 310–318] and calculated [9, 319–331]. Erskine and Stern [302]

studied the off-diagonal optical conductivity of all three metals using ellipsometric techniques and the longitudinal Kerr geometry. Later these measurements for Ni were extended beyond the quartz limit energy range by Erskine [303]. Krinchik and Artemiev [304, 305] measured magneto-optical spectra of all three metals, both in the polar and equatorial Kerr geometries. Weller *et al.* [312] investigated the orientation dependence of the polar Kerr effect in both fcc and hcp Co. The polar Kerr effect for Ni at low temperature was investigated experimentally by Di and Uchiyama [313]. Interestingly, the low temperature spectrum differs substantially from room temperature data. The common feature of all of the dependencies is the existence of the negative peak of the Kerr rotation near 1.2-1.6 eV for all the 3d transition metals.

The calculated polar Kerr spectra of cubic Fe, Co, and Ni have been published by several authors. Oppeneer et al. [320, 321] calculated the MOKE of cubic Fe, Co, and Ni using the LMTO method and Kubo formalism. Guo and Ebert [322, 323] calculated the orientation dependence of the MOKE in fcc Co, using the spin-polarized, relativistic LMTO method in the ASA, without combined corrections. Antonov et al. [324] investigated the Kerr spectra of bcc Fe, fcc and hcp Co and fcc Ni using the fully relativistic spin-polarized LMTO method including the combined corrections both in the Hamiltonian and the optical matrix elements. Gasche, Brooks and Johansson [325] investigated the effect of orbital polarization on the MOKE spectra of the ferromagnetic 3d transition metals. Mainkar et al. [326] calculated the polar and equatorial Kerr effect using a linear combination Gaussian orbital (LCGO) method. The full-potential linear augmented Slater orbital (FLASO) method was used by Maclaren and Huang [327] to calculate the polar Kerr effect in Fe and Co. The full potential LAPW method was used to calculate the MOKE in Fe, Co, and Ni in Ref.s [328, 329]. The authors investigate the influence of the input parameters and the orbital polarization term [328] and also the influence of tetragonal distortion [329] on the MO spectra of 3d ferromagnetic metals.

#### Iron

Iron crystallizes both in the bcc structure ( $\alpha$ -Fe) and in the fcc structure ( $\gamma$ -Fe). At low temperature  $\gamma$ -Fe is unstable, therefore most experimental investigations of iron's optical and magneto-optical properties are made for the bcc  $\alpha$  phase.

Fig. 2.1 presents the experimentally measured [308, 332] and theoretically calculated [324] MOKE spectra of  $\alpha$ -Fe. At 1 eV the experimentally measured Kerr rotation has its minimum of about  $-0.6^{\circ}$  and a second, smaller minimum of about  $-0.3^{\circ}$  occurs at 4.5 eV. Katayama *et al.* [308] measured, in a wide energy range (up to 10 eV), the polar Kerr spectrum of bcc Fe film, which were covered with a 20 Å thick layer of gold. They discovered the positive peak of the Fe Kerr rotation between 6 and 8 eV. A third feature is a small



*Figure 2.1.* Comparison between the theoretically calculated [324] and experimental (triangles from Ref. [332], squares from Ref. [308]) polar Kerr rotation and ellipticity spectra of bcc Fe.

negative Kerr rotation of  $-0.1^{\circ}$  at 9 eV. As can be seen from Fig. 2.1 LSDA energy band theory reproduces the experimental Kerr spectra rather well. We should mention that the theoretical spectrum is shifted towards higher energy in the 7 to 10 eV energy range. In addition theory gives a smaller value of Kerr rotation in the 6 to 8 eV interval and a substantially larger negative peak at 9 eV (magnitude of about  $-0.45^{\circ}$ ) in comparison with the experimental spectrum (Fig. 2.1). The calculations by Oppeneer *et al.* [320, 321], who used the ASW method, give a negative Kerr rotation of about  $-0.55^{\circ}$ . Miyazawa and Oguchi [330], using the FLAPW method, calculated a smaller peak reaching to  $-0.35^{\circ}$ . The difference with regards of the LMTO [324] and ASW [320, 321] spherical potential calculations was attributed by Miyazawa and Oguchi [330] to effects of the full-potential.

#### Cobalt

Cobalt crystallizes in the hcp crystal structure at low temperature, which at about 700 K undergoes a martensitic transition to fcc Co. However, it was found that thin films of fcc Co are extremely stable on various substrates, such as Cu (110) [333].

MOKE spectra of hcp Co have been obtained by several authors with a rather good correspondence with one another [304, 305, 307, 309, 297, 310, 312, 315]. Since hcp Co is uniaxial, the MO spectrum should depend on the magnetization orientation with respect to the crystallographic axis. Weller *et al* [312] measured the Kerr anisotropy of both fcc and hcp Co. It was shown that the Kerr anisotropy of fcc Co is negligible, but the anisotropy in hcp Co is well pronounced. The experimental Kerr spectra for two magnetization orientations,  $\mathbf{M}||(0001)$  and  $\mathbf{M}||(11\overline{2}0)$ , as obtained by Weller *et al* [312] are shown in Fig. 2.2. The majority of the calculated MOKE spectra of hcp Co is in over-



*Figure 2.2.* Comparison between the theoretically calculated [324] (full line corresponds  $\mathbf{M} \parallel c$ , dotted line  $\mathbf{M} \perp c$ ) and experimental (circles from Ref. [315], triangles from Ref. [312]) polar Kerr rotation and ellipticity spectra of hcp Co.

all reasonable agreement with one another [9, 320–325, 327–329, 331]. In Fig. 2.2, therefore, only the *ab initio* results of Antonov *et al.* [324] are shown. The observed Kerr anisotropy is the largest in both the rotation and ellipticity at 2 to 3 eV (Fig. 2.2). The calculation qualitatively reproduces the MO anisotropy. With regard to the experimental Kerr anisotropy, it should be noted that the two Kerr spectra of hcp Co were not measured on the same crystal, as ought to be done. Compared to the experimental Kerr rotation and ellipticity spectra, but the theoretical spectra are found to be much narrower in comparison with the experiment (Fig. 2.2). Both the minima of the Kerr rotation spectrum are shifted towards higher energy in the theoretical spectrum. This can be corroborated with the *d*-band width, which is predicted too wide by the LSDA [334].

MO spectra of fcc Co have been investigated in Ref.s [312, 315–317]. It was found that the Kerr effect for fcc Co is larger than that of hcp Co. Fig. 2.3 presents the experimentally measured [312] and theoretically calculated [324] MOKE spectra of fcc Co. Theory reproduces the experimentally measured MOKE spectra quite well.

#### Nickel

Fig. 2.4 presets the experimentally measured [316, 307] and theoretically calculated [324] MOKE spectra of fcc Ni. The most prominent difference between theory and the experiment is the width of the spectra and the position of the second minimum of the Kerr rotation spectrum which in experiment is around 3.3 eV but in the calculated spectrum is at 4.3 eV [324]. This indicates



*Figure 2.3.* Comparison between the theoretically calculated [324] and experimental (triangles from Ref. [315], squares from Ref. [312]) polar Kerr rotation and ellipticity spectra of fcc Co.

that the LSDA 3d energy bands for Ni are somewhat wider relative to values that would give ideal agreement.

The deficiency of the LSDA band structure for Ni is well known [12]. As it was deduced from photoemission experiments [335], the lowest bands at X and L symmetry points lie deep below  $E_F$  for the experimental lattice constant. Room-temperature ARPES led to the conclusion that both the measured *d*band width of Ni and exchange splitting are smaller than those predicted by LSDA calculations [334]. The LSDA *d*-band width at the L-point is broader by about 1 eV. The calculated LSDA exchange splitting of the L<sub>3</sub> bands is about 0.67 eV [52], but the PES measurements yield only 0.31±0.07 eV [335].

It is quite likely that many body effects (so called self-energy terms) for the excited state properties will give rise to narrower 3d energy bands in Ni and hence to better agreement between theory and experiment.

## 2.1.2 Paramagnetic metals Pd and Pt

The electronic structure of Pt and Pd metals was extensively studied both experimentally [336–341, 279, 342, 343] and theoretically [344–359] as far back as 15-30 years ago. It is not possible to mention all the publications on this subject in a short introduction. From the very good agreement between various theoretical band structure calculations and a great variety of the experimental measurements, it can be concluded that the electronic structures of Pt and Pd are known in detail.

The shapes of the Fermi surfaces of Pt and Pd are found to be remarkably similar. Each metal has a closed electron surface centered around  $\Gamma$ , a small volume closed-hole surface centered around X and a large-volume open-hole surface (the "jungle gym") also centered around the X point [336–338, 345–



*Figure 2.4.* Comparison between the theoretically calculated [324] and experimental (triangles from Ref. [316], squares from Ref. [307]) polar Kerr rotation and ellipticity spectra of fcc Ni. The experimental spectra are measured at room temperature.

348]. As it can be expected from the band structures, many of the electronic properties of Pt and Pd are also very similar although possible differences can arise from the stronger influence of relativistic effects for Pt metal. The unique properties of Pt and Pd stimulated a large number of investigations including: the de Haas-van Alphen effect [336–338], electrical resistivity [349, 350], lattice dynamics and thermodynamical properties [351, 352], optical properties [344, 339–341, 357], point-contact spectra [358, 359], soft x-ray emission [279], and photoemission spectra [342, 343], electron-phonon interaction [353], the gyromagnetic factor of conduction electrons [354–356] and so on. The magneto-optical properties of Pd and Pt metal have been investigated experimentally and theoretically in Refs [360, 361].

The polar MOKE spectra of paramagnetic Pd and Pt films were measured in the external magnetic field of 1.5 T aligned normally to the film plane over the photon energy range  $0.74 \le \hbar \omega \le 5.6$  eV. Thick (~2000 Å) polycrystalline fcc Pd and Pt films were prepared using a dc sputtering deposition system. The polar Kerr effect induced in Pd and Pt by the magnetic field of 1.5 T is very small (below  $2 \cdot 10^{-3}$  deg) and was detected in a sensitive Kerr spectrometer setup [360, 361] by means of the polarization modulation technique using a piezobirefringent modulator. Besides the high sensitivity reaching  $10^{-5} \cdot 10^{-4}$ deg (depending on the photon energy and corresponding photon shot noise), this method has the advantage that the Kerr rotation and Kerr ellipticity can be determined simultaneously. The resulting complex Kerr rotation values were determined as a half of the difference of the signals measured with the magnetic field of 1.5 T switched alternately between the positive and negative value. Acquisition time was long enough to obtain sufficiently large signal-to-noise



*Figure 2.5.* Comparison between the experimental polar Kerr rotation (a) and ellipticity (b) spectra of fcc Pd metal film measured in the applied field of 1.5 T and the spectra calculated by the SPR LMTO method [360].

ratio. The precise calibration procedure of the Kerr rotation and ellipticity was performed before the measurements. The measurements were repeated a number of times on different samples and the resulting spectra were obtained by averaging over all the measurements. The optical properties were measured directly on the same samples by conventional spectroscopic ellipsometry using the rotating analyzer method over the same spectral range as for the MOKE spectra.

#### Pd

Pd is a nearly ferromagnetic metal with the largest paramagnetic susceptibility among the non-magnetic transition metals and is easily spin-polarized by a small external magnetic perturbation. Due to the high density of electronic states (DOS) at the Fermi level, the bulk fcc Pd metal is near the threshold of becoming ferromagnetic and calculations predict a paramagnetic-ferromagnetic phase transition upon the lattice expanding by 6% [362, 363]. The unique properties of Pd stimulated a large number of experimental and theoretical investigations (see, e.g., Ref.s [364–367, 358] and references therein).

Averaged and smoothed experimental MOKE spectra of the Pd metal film (circles), with the variances indicated by dotted lines, are compared to the corresponding calculated spectra (solid line) in Fig. 2.5. The characteristic feature of the measured Pd Kerr rotation spectrum is a positive peak in the ir spectral range at  $\sim$ 1.2 eV and a negative two-peak structure in the uv range. The Kerr rotation and ellipticity in the ir and uv spectral range are of comparable magnitude and do not overcome the value of  $\sim$ 10<sup>-3</sup> deg in the field of 1.5 T



Figure 2.6. Energy bands structure of fcc Pd in the external magnetic field of 240 T [360].

used. The Kerr rotation zero-crossing at 2 eV corresponds to the peak in the ellipticity spectrum. As can be seen in Fig. 2.5, the agreement between the experimental and the calculated polar Kerr rotation spectra is very good, both in the shape and the amplitude. The calculated Pd spectrum reproduces all the experimentally observed spectral features, although the theoretical curves are slightly shifted to higher energies. For the Kerr ellipticity, the quantitative discrepancy between theory and experiment is somewhat larger, however the shape of the spectra is reproduced well by the calculations. The value of the magnetic moment of  $9.6 \times 10^{-4} \mu_B$  on the Pd atom obtained from the calculations agrees with the value of  $\sim 1.0 \times 10^{-3} \mu_B$  per atom as was estimated from the paramagnetic susceptibility data of Pd at 300K [368].

The calculated band structure of fcc Pd is shown in Fig. 2.6. In the absence of a magnetic field, due to the time-reversal symmetry, all bands of Pd are at least twofold degenerate. The magnetic field lifts the degeneracy, but it is convenient to keep the numeration of the bands by pairs, adding a subscript as necessary to distinguish individual bands. Thus, in the following discussion, "transition  $5\rightarrow 6$ " means the sum over the four possible transitions between the two pairs of bands,  $5_{1,2}$  and  $6_{1,2}$ . In Fig. 2.6, the energy bands of fcc Pd, calculated for the induced moment of  $0.2\mu_B$ , are shown. We choose to plot the bands for strongly magnetized Pd because the splitting of the bands due to the induced magnetization can be clearly seen in this case.

The appropriate discussion of electronic interband transitions underlying the MO effects studied requires the analysis of the spectral dependence of the optical conductivity tensor elements.

As the absorptive parts of  $\sigma$  are additive quantities composed of interband transitions, to better understand the microscopic origin of the magneto-optical activity of Pd, the decomposition of the calculated absorptive part of the off-diagonal optical conductivity,  $\sigma_{xy}^{(2)}$ , into the contributions from separate inter-



*Figure 2.7.* Contributions of different interband transitions to the  $\omega \sigma_{xy}^{(2)}$  spectrum of fcc Pd in the applied magnetic field of 1.5 T [360].



*Figure 2.8.* Contributions of the individual transitions between the 5-th and 6-th pairs of bands to the  $\sigma_{xy}^{(2)}$  (a) and  $\sigma_{xx}^{(1)}$  (b) spectra of fcc Pd in an applied magnetic field of 1.5 T [360].

band transitions, was performed [360]. The results of the analysis are presented in Fig. 2.7. As one can see from the figure, for photon energies up to 8 eV the  $\omega \sigma_{xy}^{(2)}$  spectrum of Pd (solid line) is formed almost entirely by the transitions between 3, 4, 5 and 5, 6 energy bands (full circles). Looking at the bandstructure (Fig. 2.6) one can see that the initial states for these transitions, bands  $3_{1,2}, 4_{1,2}$ , and  $5_{1,2}$ , are rather narrow bands predominantly of d-character, while the final states  $6_{1,2}$  are wide free-electron-like s-p bands. It should be pointed out that the dominant contribution, which determines the characteristic shape of the  $\omega \sigma_{xy}^{(2)}$  spectrum with the negative peak at 1 eV and the two broad positive features within the range of 2–4 eV and at ~7 eV, comes from the 5  $\rightarrow$  6 transitions. Moreover, it has been verified that the negative peak is formed by the transitions from the initial states within the energy range of ~0.5 eV below the Fermi level. Thus, the zero-crossing of the  $\omega \sigma_{xy}^{(2)}$  curve, observed at  $\hbar \omega \approx 2$  eV, cannot be related to the maximum of the photoemission spectra observed at ~ -2 eV [369], as it was suggested in Ref. [370].

It is interesting to consider how the transitions between the individual bands (e.g.,  $5_1 \rightarrow 6_1$  and so on) sum up to form the curves shown in Fig. 2.7. As an example, in the following discussion a detailed analysis of the transitions between  $5 \rightarrow 6$  energy bands will be performed. In Fig. 2.8, the contributions to the absorptive parts of the conductivity tensor,  $\sigma_{xx}^{(1)}$  and  $\sigma_{xy}^{(2)}$ , from the four possible transitions ( $5_1 \rightarrow 6_1$ ,  $5_2 \rightarrow 6_2$ ,  $5_1 \rightarrow 6_2$  and  $5_2 \rightarrow 6_1$ ) between the 5-th and 6-th pairs of the bands are shown, together with their sums denoted as  $5 \rightarrow 6$ . Because the splitting of the bands is very small, the joint densities of states for the transitions are similar, and all the difference in the transitions' intensities is due to the corresponding matrix elements. This deserves analysis.

Let us first consider the spin-flip transitions. As the spin-orbit coupling in Pd is relatively weak, the matrix elements of  $5_1 \rightarrow 6_2$  and  $5_2 \rightarrow 6_1$  transitions are significantly smaller than those of the remaining pair. In the limit of zero spin-orbit coupling strength, the band indexes 1 and 2 enumerate different projections of the electron spin, which is a good quantum number in this case, and the spin-flip  $5_1 \rightarrow 6_2$  and  $5_2 \rightarrow 6_1$  transitions are forbidden.

Considering the spin-up and spin-down transitions, it is worth pointing out that the amplitudes of the  $\omega \sigma_{xy,5_1 \to 6_1}^{(2)}(\omega)$  and  $\omega \sigma_{xy,5_2 \to 6_2}^{(2)}(\omega)$  spectra are only four times smaller than the amplitudes of the corresponding  $\sigma_{xx}^{(1)}(\omega)$  spectra. However, as these spectra are of close shape and magnitude but of opposite sign, their sum,  $\sigma_{xy,5\to6}^{(2)}(\omega)$ , shown by solid line in Fig. 2.8, is more than two orders of magnitude smaller with the magnetic field of 1.5 T. In other words, these transitions are responsible for the absorption of circularly left- and rightpolarized light, respectively. In the absence of the magnetic field, bands  $5_{1,2}$ and  $6_{1,2}$  are degenerate, and the  $\omega \sigma_{xy,5_1 \to 6_1}^{(2)}(\omega)$  and  $\omega \sigma_{xy,5_2 \to 6_2}^{(2)}(\omega)$  spectra cancel exactly leading to zero MOKE. Due to the lifting of degeneracy caused by the magnetization,  $\omega \sigma_{xy,5_1 \to 6_1}^{(2)}(\omega)$  and  $-\omega \sigma_{xy,5_2 \to 6_2}^{(2)}(\omega)$  are no longer equal and the resulting contribution of the transition  $5 \rightarrow 6$  to  $\sigma_{xy}^{(2)}(\omega)$  is given by a small-value difference of the two large quantities. It can be shown that sufficiently far from the transition threshold the difference is proportional to the shift in the energy positions of the constituent curves, i.e., to the average splitting  $\Delta E$  of the 5-th band. The splitting of the free-electron-like 6-th band is much smaller and can be neglected.



*Figure 2.9.* The dependence of  $\omega \sigma_{xy,5_1 \to 6_1}^{(2)}$  and  $\omega \sigma_{xy,5_2 \to 6_2}^{(2)}$  components (a) and their sum, normalized vs the induced moment (see text),  $\omega \sigma_{xy,5 \to 6}^{(2)}$ , (b) on the value of the magnetic filed applied to fcc Pd [360].

To model the MOKE spectra of strongly magnetized Pd, we performed the calculations gradually increasing the external field up to as large value as 480 T. Such a strong magnetic field can not, of course, be obtained experimentally, but it is necessary to induce the magnetic moment of  $0.24\mu_B$  on the Pd atoms, which is close to the value observed in Pd-rich  $Fe_xPd_{1-x}$  and  $Co_x Pd_{1-x}$  alloys. In agreement with the previous calculations [371], a nonlinear dependence of the induced Pd moment on the applied magnetic field is observed for the external fields larger than 100 T. However, the proportionality between the magnetization and the amplitude of the MOKE spectra holds in the whole tested range of the external magnetic fields. To illustrate this, we plot, in Fig. 2.9, the  $\omega \sigma_{xy,5_1 \to 6_1}^{(2)}(\omega)$  and  $\omega \sigma_{xy,5_2 \to 6_2}^{(2)}(\omega)$  components and their sum,  $\sigma_{xy,5\to6}^{(2)}(\omega)$ , for the selected values of the external field. The resulting  $\sigma_{xy,5\to6}^{(2)}(\omega)$  spectra (Fig. 2.9(b)) have been normalized via scaling down by a factor equal to the ratio of the calculated magnetic moment and the moment obtained at the field of 1.5 T. Whereas the differences between the  $\omega \sigma^{(2)}_{xy,5_1 \rightarrow 6_1}(\omega)$ and  $-\omega \sigma^{(2)}_{xy,5_2 \to 6_2}(\omega)$  components increase significantly with the magnitude of the magnetic field (Fig. 2.9(a)), the resulting normalized  $\sigma^{(2)}_{xy,5\to6}(\omega)$  spectra are very close to each other above  ${\sim}3$  eV. The differences of the  $\sigma^{(2)}_{xy,5\to6}(\omega)$ curves in the energy range between  $\sim 0.5$  eV and  $\sim 3$  eV are caused by the transitions from those parts of the Brillouin zone in which the initial states are located within the value of  $\Delta E$  near the Fermi energy, e.g., around the L symmetry point (see Fig. 2.6). As only one of the two split bands is occupied in this



*Figure 2.10.* Experimental (open circles) and theoretical (dashed and dotted lines) MOKE spectra of Pd-rich alloys with 3*d* transition metals. The calculated MOKE spectra of fcc Pd in the external field of 480 T, which induces the magnetic moment of  $0.24\mu_B$ , are plotted by solid lines [360].

case, the contribution of these transitions to  $\sigma_{xy}^{(2)}$  is proportional to  $\sigma_{xy,5_1\to 6_1}^{(2)}$ itself, instead of to the sum of  $\omega \sigma_{xy,5_1\to 6_1}^{(2)}(\omega)$  and  $\omega \sigma_{xy,5_2\to 6_2}^{(2)}(\omega)$ . Similar scaling of  $\sigma_{xy}^{(2)}$  with the magnetic moment was found, also, for the other interband transitions. The reason for the scaling is that, as was already mentioned, the magnitude of the  $\sigma_{xy}^{(2)}$  spectra is proportional to the splitting  $\Delta E$  of the bands which are degenerate in the absence of the external field. The splitting, in turn, is proportional to the induced magnetic moment, as long as  $\Delta E$  is much smaller than the width of *d*-band, which is fulfilled in the case of Pd.

**Magneto-optical properties of Palladium in dilute alloys.** In Ref. [370], the MOKE spectra of  $Fe_{0.06}Pd_{0.94}$  alloy were considered in discussion of the MO properties of spin-polarized Pd. It is interesting to investigate to what extent the MOKE spectra of Pd-rich alloys with 3*d* transition metals are governed

by the MO activity of Pd. For this study, we used the available MOKE spectra of Pd-rich Fe-Pd and Co-Pd alloys. The  $Fe_{0.06}Pd_{0.94}$  spectra [370] and our results for the Co<sub>0,13</sub>Pd<sub>0,87</sub> alloy film [372] are shown in Fig. 2.10. As can be seen, the overall shape of the Fe<sub>0.06</sub>Pd<sub>0.94</sub> Kerr rotation spectrum is similar to the  $Co_{0.13}Pd_{0.87}$  one, nevertheless the fine features are different. The uv peak in the spectrum of the  $Fe_{0.06}Pd_{0.94}$  alloy is sharper and shifted in energy position as compared to the spectrum of the  $Co_{0.13}Pd_{0.87}$  alloy. Also, slightly larger positive rotation is observed for  $Fe_{0.06}Pd_{0.94}$  in the ir range. Comparing the spectra of the alloys to the MOKE spectra of paramagnetic Pd (see Fig. 2.5) one can note that the overall shape of the spectra is strikingly similar. The largest difference is observed for the ratio of ir and uv peak amplitudes; the ratio for Pd is about two times larger than that for the alloys. Notwithstanding the fact that the amplitude of the Pd spectra is about 200 times smaller than that of the alloys, the positions of the uv peak differ only slightly. This leads one to the conclusion that the MOKE spectra of the Pd-rich alloys with magnetic 3dmetals are mainly determined by the MO properties of the spin-polarized Pd. However, the contribution coming from the 3d atoms is substantial, especially in the ir spectral range, in which the polar Kerr rotation in both Fe and Co metals is negative.

The conclusion that 3d transition atoms give only relatively small contribution to the MO spectra of Pd-rich alloys is, also, supported by the results of ab initio calculations. The MOKE spectra calculated for the model alloys Co<sub>1</sub>Pd<sub>15</sub>, Fe<sub>1</sub>Pd<sub>15</sub>, Co<sub>1</sub>Pd<sub>7</sub>, and Fe<sub>1</sub>Pd<sub>7</sub>, and for fcc Pd in the external field of 480 T, are compared to the experimental ones in Fig. 2.10. For all the allovs, the cubic supercells have been constructed with lattice constant equal to that of fcc Pd. The magnetic moment of  $0.24\mu_B$ , induced on the Pd atom by the field of 480 T, is close to the average Pd moment calculated for Fe<sub>1</sub>Pd<sub>15</sub>  $(0.22\mu_B/\text{atom})$  and Co<sub>1</sub>Pd<sub>15</sub>  $(0.25\mu_B/\text{atom})$  alloys. As can be seen from Fig. 2.10, the theoretical MOKE spectra are in good agreement with the experimental spectra of the alloys of correspondingly close composition. The only exception is the Kerr ellipticity spectrum of the Fe<sub>0.06</sub>Pd<sub>0.94</sub> alloy, which, being of similar shape, is, however, shifted upward with respect to the calculated one. The calculated MOKE spectra of  $Fe_1Pd_{15}$  and  $Co_1Pd_{15}$  alloys and strongly magnetized Pd metal are very close to each other (see Figs. 2.10 (a) and 2.10 (b)) and, as could be inferred in advance, differences between the spectra become more pronounced with an increase of the 3d metal content. However, strictly speaking, the subtle modification of the calculated MOKE spectra due to the presence of 3d atoms are still observed even for the diluted Fe<sub>1</sub>Pd<sub>15</sub> and Co<sub>1</sub>Pd<sub>15</sub> alloys. It can be concluded that the MO spectra of Pd based alloys in the limit of small concentration of the magnetic 3d atoms can be considered only as a first approximation to the magneto-optical response of spin polarized palladium. When the amount of the magnetic 3d atoms increases, the contribution to the alloys' spectra, coming from the 3d atoms and the effects of the hybridization of the Pd 4d with the 3d states of transition metals, results in appreciable differences between the Pd and alloys' spectra. The same considerations concerning the importance of the 3d-4d hybridization effects are applicable to the case of the MO spectra of Pt-rich alloys, having in mind that the spin-orbit coupling in Pd is three times weaker than in Pt.

#### Pt

Averaged experimental MOKE spectra of a paramagnetic Pt metal film measured in a magnetic field of 1.5 T (circles) are compared to the corresponding theoretically calculated spectra (dashed lines) in Fig. 2.11. The Kerr rotation and ellipticity in the ir and uv spectral ranges are of comparable magnitude and do not exceed the value of  $\sim 2 \cdot 10^{-3}$  deg in the field of 1.5 T. The characteristic features of the measured Pt Kerr rotation spectrum are a broad maximum in the ir spectral range at  $\sim 1.5$  eV and a prominent minimum in the uv range at 3.8 eV. The essential points of the experimental Kerr ellipticity spectrum are the zero-crossings at 1.5 eV and around 3.5 eV (that correspond to the peaks position in the Kerr rotation), with a broad positive structure between them and a negative shoulder at the energy of  $\sim 4 \text{ eV}$ . A narrow negative peak is observed in the Kerr rotation at  $\sim 0.8$  eV near the edge of the energy interval in which the measurements were performed that coincides with the Kerr ellipticity zerocrossing at the same energy. We should mention that while the sensitivity of the experimental procedure used in the present work is generally within 0.01-0.1 mdeg range (depending on the photon energy and corresponding photon shot noise), the variances (indicated in Fig. 2.11 by the dotted lines) increase significantly (up to  $\pm 0.2$  mdeg) at the high energy edge of the measured energy interval.

The agreement between the experimental and calculated polar Kerr rotation spectrum in the vis-uv spectral range is good. The theoretical calculations reproduce the main peak at 3.8 eV and even the smooth shoulder visible in the experimental Kerr rotation spectrum at  $\sim$ 3 eV. For the Kerr ellipticity, the quantitative discrepancy between theory and experiment is somewhat larger, but the overall shape of the spectrum is reproduced well by the calculations. However, the low energy part of the spectra below 1.5 eV exhibit considerable discrepancies. While the theoretical Kerr rotation forms a positive maximum around 1 eV and then goes smoothly to zero as the photon energy decreases, the experimental curve remains negative in the whole energy range and shows a sharp narrow minimum at  $\sim$ 0.8 eV. The same type of disagreement is seen also between the theoretical and experimental Kerr ellipticity spectra for, which again, below 1.5 eV the theoretical curve goes to zero whereas the experimental one forms the negative minimum and then increases abruptly towards the positive values after zero-crossing at 0.8 eV. It should be pointed out that the



*Figure 2.11.* Comparison between the experimental polar Kerr rotation and ellipticity spectra (circles), with error bars indicated by dotted lines, of fcc Pt metal film measured in the applied field of 1.5 T and the spectra calculated by the SPR LMTO method without intraband transitions (dashed lines) and with the intraband transitions included with  $\gamma_D$  =0.34 eV (full lines) [361].

above-discussed experimental spectra were compared to the theoretical spectra calculated neglecting the intraband contribution to the off-diagonal part of the optical conductivity. The importance of this contribution and its effect on the MOKE spectra of Pt will be discussed below.

The interpretation of the MOKE spectra in terms of electronic transitions is a nontrivial task because the complex Kerr rotation is a rather complicated function of both the diagonal and off-diagonal components of the optical conductivity tensor (Eq. 1.175). The off-diagonal part of the conductivity tensor of Pt obtained from the experimental MOKE spectra and the complex index of refraction (n and k) determined from the ellipsometry measurements are presented in Fig. 2.12. As it is seen from the comparison of Fig. 2.12 and Fig. 2.11 there is a close resemblance between the complex Kerr rotation spectra and the off-diagonal optical conductivity tensor components  $\omega \sigma_{xy}^{(1)}$  and  $\omega \sigma_{xy}^{(2)}$ . This can be explained by the fact that in the considered energy range the optical constants n and k are essentially featureless functions of the photon energy and all the peculiarities of the Pt MOKE spectra are determined by the corresponding features of the  $\sigma_{xy}$  spectra (the measured n and k spectra agree well with those in Ref. [339–341]). In the energy region above  $\sim 2 \text{ eV}$  (see Fig. 2.12) the experimental  $\omega \sigma_{xy}^{(2)}(\omega)$  spectrum agrees well with the calculated one, both in shape and amplitude. In particular, the energy position and the magnitude of the peak at 3.8 eV are very well reproduced. On the other hand, the low energy part of the spectrum below 2 eV exhibits considerable discrepan-



*Figure 2.12.* Comparison between the experimental off-diagonal optical conductivity  $\omega \sigma_{xy}$  spectra (circles), with error bars indicated by dotted lines, of fcc Pt metal film measured in the applied field of 1.5 T and the spectra calculated by the SPR LMTO method without intraband transitions (dashed lines) and with the intraband transitions included with  $\gamma_D$  =0.34 eV (full lines) [361].

cies. The same type of disagreement as in the case of Kerr ellipticity spectra is also seen between the theoretical and experimental spectra of  $\omega \sigma_{xy}^{(1)}(\omega)$ , where below 1.5 eV the theoretical curve goes gradually to zero, whereas the experimental one crosses the zero level and tends to change abruptly towards positive values. One of the possible reasons for the observed large discrepancy in the energy dependence of the  $\omega \sigma_{xy}(\omega)$  in the ir energy range is the contribution from the intraband transitions to the off-diagonal conductivity which has not been included into the calculations of the theoretical spectra.

The intraband contribution to the off-diagonal optical conductivity is very small and usually neglected in the case of magnetically ordered materials. For nonmagnetic metals (which have zero spontaneous exchange splitting), the spin polarization induced by an external magnetic field available in the experiment is small and the contributions of intra- and interband transitions to the off-diagonal optical conductivity tensor component can become comparable. Therefore, the intraband term should be taken into account on the same footing as the interband one. To study the influence of the intraband contribution on the MO properties of Pt, the phenomenological Drude-like model has been adopted in Ref [361]. To use the Drude model in the form of Eqs. (1.228) and (1.236) we need three parameters: the plasma frequency  $\omega_p$ , the cyclotron frequency  $\omega_c$ , and the damping constant  $\gamma_D$ . The first two parameters,  $\omega_p=7.32$  eV and  $\omega_c=1.02\cdot10^{-4}$  eV, were calculated using the Eq. (1.229) and (1.237), respectively. To estimate the renormalized effective electron mass

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 $m^*$  we used the constant of the electron-phonon interaction  $\lambda$ =0.7 calculated in the rigid MT-approximation in Ref. [353]. The inverse intraband Drude relaxation time  $\gamma_D$  can be estimated from the dc and Hall resistivity data using expression (1.240). Such an estimation using the values of  $\rho = 10.8 \times 10^{-6}$ [ $\Omega$ .cm] and  $\rho_H = 3.3 \times 10^{-9}$  [ $\Omega$ .cm] (at 300 K in the magnetic field of 1.5 T) taken from Ref. [373] gives  $\gamma_D$ =0.34 eV.

Adding the intraband contribution term to the off-diagonal conductivity with the value of the relaxation time parameter  $\gamma_D=0.34$  leads to the substantial improvement of the agreement between theoretical and experimental spectra, especially in the ir energy range (solid lines in Figs. 2.11 and 2.12). We should point out that the contribution of the intraband transitions  $\sigma_{xy}^{D(2)}(\omega)$  to the absorptive part of the off-diagonal optical conductivity is proportional to  $1/\omega^3$ for  $\omega \gg \gamma_D$  and is important only in the ir energy range. As a consequence, this contribution determines the low frequency behavior of the Kerr rotation spectrum, whereas in the vis-uv range its effect is relatively small. At the same time,  $\sigma_{xy}^{(1)}(\omega)$  and the Kerr ellipticity are affected by the off-diagonal Drude term in the whole energy interval studied (Figs. 2.11 and 2.12) as  $\sigma_{xy}^{D(1)}(\omega)$ decreases only as  $1/\omega^2$  at high frequencies. In conclusion, it can be stated that the energy dependence of the off-diagonal optical conductivity as well as the MOKE spectra of Pt are greatly affected by the contribution coming from the intraband optical transitions.

Although both the spectral shape and the magnitude of the experimental optical conductivity spectra are well reproduced by the LSDA calculations (Fig. 2.12), the position of the calculated prominent peak at 0.8 eV in  $\sigma_{xy}^{(2)}(\omega)$  and corresponding structures in  $\sigma_{xy}^{(1)}(\omega)$  are shifted to smaller energies as compared to the experimental spectra. One of the possible reasons is that due to the non-exact treatment of the electron exchange and correlations, the LSDA overestimates the *d* bandwidths for transition metals of the end of the series.

Analysis of the magneto-optical transitions in Pt. To elucidate the microscopic origin of the MO properties of Pt metal in terms of electronic transitions, we first consider in detail its electronic structure. The electronic structure underlying the optical transitions responsible for the MOKE spectra of Pd metal was studied in Ref. [360]. To understand the cause of the observed differences in the resulting MOKE response of both metals, in the following discussion a direct comparison between the results for Pt and Pd will be performed. The calculated band structure of fcc Pt and Pd is shown in Fig. 2.13. In the absence of a magnetic field, due to the time-reversal symmetry, all bands of Pt and Pd are at least twofold degenerate. The external magnetic field lifts the degeneracy. As in the previous analysis for Pd, to distinguish individual bands it will be convenient to keep the numeration of the bands by pairs, adding a subscript



Figure 2.13. Energy-band structure of fcc Pt (full lines) and Pd (dotted lines) [361].

if necessary. Thus, for example, the "transition  $n \rightarrow m$ " means the sum over the four possible interband transitions between the initial pairs of bands,  $n_{1,2}$  and final pairs of bands  $m_{1,2}$ .

Although the energy band structures of Pt and Pd (Fig. 2.13) are very similar, there are some distinctive differences in bandwidths and the energy positions of the bands (especially in X and L symmetry points near the Fermi level). These are mainly due to different spin-orbit splitting, slightly different lattice constants, and the difference in the spatial extent of 4d and 5d valence wave functions of Pd and Pt metals.

The small differences in the band positions lead to significant differences in the MO properties of these two sister metals. Although the spin-orbit interaction in Pt is three times larger than in Pd, the absolute value of Kerr rotation in Pt is only two times larger in comparison with Pd. It is due to a notable difference in their paramagnetic susceptibility. The magnetic moments induced by the external magnetic field of 1.5 T is equal to  $0.29 \cdot 10^{-3} \mu_B$  and  $0.96 \cdot 10^{-3} \mu_B$  in Pt and Pd, respectively, as was estimated from paramagnetic susceptibility data (the values agree well with those obtained from the calculations).

To identify the electronic interband transitions responsible for the MO effects, the analysis of the spectral dependence of the optical conductivity tensor should be performed. The absorptive part of the diagonal optical conductivity



*Figure 2.14.* Contributions of different interband transitions to the diagonal  $\sigma_{xx}^{(1)}$  and offdiagonal  $\sigma_{xy}^{(2)}$  spectra (solid lines) of fcc Pt in the magnetic field of 1.5 T: 3  $\rightarrow$  5 (long-dashed lines), 5  $\rightarrow$  6 (short-dashed), 4  $\rightarrow$  6 (dashed-dotted), and 4  $\rightarrow$  5 (dotted lines) [361].

tensor element,  $\sigma_{xx}^{(1)}$ , and of the off-diagonal part,  $\sigma_{xy}^{(2)}$ , are directly connected via Eq. (1.221) to the microscopic interband optical transitions.

As the absorptive parts of the optical conductivity are additive quantities, to explain the microscopic origin of the MOKE activity of Pt in terms of individual electronic transitions, the decomposition of the calculated  $\sigma_{xx}^{(1)}$  and  $\sigma_{xy}^{(2)}$  spectra into the contributions arising from separate interband transitions was performed [361]. (The intraband contributions were neglected for simplicity). As one can see in Fig. 2.14, for photon energies up to 6 eV, the  $\sigma_{xx}^{(1)}$  of Pt is formed almost entirely by the transitions from bands 3, 4, 5 to bands 5, 6. Looking at the band-structure (Fig. 2.13) one can see that the initial states for these transitions, bands  $3_{1,2}$ ,  $4_{1,2}$ , and  $5_{1,2}$ , are rather narrow bands predominantly of *d*-character, while the final states  $6_{1,2}$  are wide free-electron-like *s-p* bands. The characteristic intensive peak in  $\sigma_{xx}^{(1)}$  around 1 eV for Pt is mainly determined by the  $5 \rightarrow 6$  and the  $4 \rightarrow 5$  transitions. The  $4 \rightarrow 6$ ,  $3 \rightarrow 6$  and  $3 \rightarrow 5$  transitions beginning above 1 eV exhibit no pronounced structure in the 1 to 6 eV energy interval.

The characteristic features of  $\sigma_{xy}^{(2)}$  of Pt are a negative peak at 1 eV, positive structures in the range 2-3 eV, an intensive maximum at 3.8 eV and a weaker positive peak at 5.5 eV. As can be seen in Fig. 2.14, all the  $\sigma_{xy}^{(2)}$  features, except for the prominent peak at 3.8 eV, are mainly determined by the 5  $\rightarrow$  6 and 4  $\rightarrow$  5 transitions. The sharp peak at 3.8 eV, which can be considered as the "finger print" of Pt MO response (see Fig. 2.12), is completely determined by

the  $3 \rightarrow 5$  transitions overlapped, in the energy range, with an almost constant contribution arising from the  $5 \rightarrow 6$  transitions. It should be pointed out that the main features in the resulting  $\sigma_{xx}^{(1)}$  and  $\sigma_{xy}^{(2)}$  energy dependence of Pt are formed by different sets of interband transitions. The  $\sigma_{xx}^{(1)}$  spectrum features are mainly determined by the  $5 \rightarrow 6$  transitions with smaller contribution from the  $4 \rightarrow 5$  transitions, whereas in the formation of  $\sigma_{xy}^{(2)}$  spectra the  $3 \rightarrow 5$  transitions play an additionally important role.

To see how the interband transitions between the individual bands are located in the reciprocal space in both Pt and Pd, the **k**-space decomposition of the interband transitions into transitions occurring in the vicinity of the high symmetry points of the Brillouin zone (BZ) was performed [361]. For this purpose all transitions between the bands n and m in a cubic volume surrounding a given point with a cube edge equal to 0.125 of the  $\Gamma$ -X distance (it contains approximately 1.5% of a whole BZ volume) have been summed. Although the results depend on the volume of the cube, one can associate the transitions essentially with these points and their immediate neighborhood.

Figs. 2.15 and 2.16 illustrate the results of the decomposition. As can be seen from Fig. 2.15, the main peak position of Pt arising from  $4 \rightarrow 5$  transitions in  $\sigma_{xx}^{(1)}$  at 1 eV is determined by the transitions near the X symmetry point. It should be pointed out that the spin-orbit interaction in solids splits some energy band states, e.g.,  $\Gamma'_{25} \rightarrow \Gamma_8^+ + \Gamma_7^+$ ,  $X_5 \rightarrow X_6^+ + X_7^+$ , and so on. In the central symmetry field model such a splitting is described by the spin-orbit parameter  $\zeta_{nl}$ . This parameter is energy dependent in solids, and in cubic symmetry crystals can be estimated by the splitting of the top of the *d* energy band  $\zeta_{nl}(E) \simeq E(X_7^+) - E(X_6^+)$  [374]. So, the energy position of the main peak of the  $4 \rightarrow 5$  optical transitions, which mainly occurs in the vicinity of the X point, gives direct information on the spin-orbit parameter  $\zeta_{nl}(E)$  in Pt and Pd metals (Fig. 2.15).

The final state for the  $4 \rightarrow 5$  and  $3 \rightarrow 5$  transitions is the same and, as a result, the transitions are located inside the same parts of **k** space. The overall structure of both the  $4 \rightarrow 5$  and  $3 \rightarrow 5 \sigma_{xx}^{(1)}$  spectra is formed mainly by the transitions at the XUW edge plane of the BZ near X, U and W for both metals. Due to the larger spin-orbit splitting, the corresponding features of the  $3 \rightarrow 5$  and  $4 \rightarrow 5$  transitions in Pt are shifted towards higher energy as compared to Pd. For both transitions there is also a contribution arising from the midpoint of the U-L line (the transition is very important for  $\sigma_{xy}^{(1)}$  spectra, see Fig. 2.16). The  $3 \rightarrow 5$  transitions result in sharp peaks at 2.5 and 3.8 eV in Pd and Pt, respectively. The same part of the **k** space is responsible for small peaks at 2 and 2.8 eV in  $\sigma_{xx}^{(1)}$  for  $4 \rightarrow 5$  transitions in Pd and Pt, respectively.

The  $4 \rightarrow 6$  transitions for both metals are located in the same parts of the BZ, mainly near the L point in the  $\Gamma$ -U-L plane and near X. However, the



*Figure 2.15.* Decomposition of the  $\sigma_{xx}^{(1)} n \to m$  interband transitions in Pt and Pd into transitions localized around different symmetry points in the BZ [361].

energy positions of the transitions are significantly different in both metals. The maxima of  $4 \rightarrow 6$  transitions in Pd occur near L and X at 1.2 eV and 4 eV, respectively, but both corresponding maxima in Pt occur at the same energy, 2 eV. Such a large difference is explained by significantly different energy positions of the 4 and 6 bands of Pd and Pt at the X and L points (Fig. 2.13) relative to the Fermi level.


*Figure 2.16.* Decomposition of the  $\sigma_{xy}^{(2)} n \to m$  interband transitions in Pt and Pd into transitions localized around different symmetry points in the BZ for a magnetic field of 1.5 T [361].

The most intense  $5 \rightarrow 6$  transitions in both metals arise from the same parts of BZ located near the L point along L-  $\Gamma$  and near the X point along the X- $\Gamma$  direction. In the energy range from  $\sim 2$  to 6 eV, the  $5 \rightarrow 6$  transitions are located around the midpoint of the U-L line in both metals. For all the  $5 \rightarrow 6$ transitions the initial states are located within the energy range of 0.5 eV below the Fermi level. The optical conductivity in Pt is larger than in Pd. This, we believe, can be explained by the significantly larger spatial extent of the Pt 5d as compared to the Pd 4d wave functions which results in larger optical interband matrix elements in Pt in comparison with Pd.

Fig. 2.16 shows the results of the **k**-space decomposition for the  $5 \rightarrow 6$ and  $3 \rightarrow 5$  transitions, responsible for the main features of the  $\sigma_{xy}^{(2)}$  spectra of Pt. It should be pointed out that the magneto-optical transitions underlying the  $\sigma_{xy}^{(2)}$  spectra of Pt and Pd are located in the same regions of **k** space as the corresponding  $\sigma_{xx}^{(1)}$  optical transitions discussed above. The  $5 \rightarrow 6$  transitions in the energy range 1.5-5 eV for Pt and 2-6 eV for Pd, occurring mainly at the midpoint of the U-L line in the  $\Gamma$ -U-L plane, have more or less the same shape in both metals. On the other hand, a qualitative difference between  $\sigma_{xy,5\rightarrow 6}^{(2)}$ Pt and Pd is observed in the low energy region. As was mentioned before, the theoretical analysis shows that the  $5 \rightarrow 6$  low-energy transitions, both in Pd and Pt, occur near the L point along the L- $\Gamma$  and L-U directions, and near the X point along the X- $\Gamma$  direction. Due to the differences of the 5th and 6th bands going from Pd to Pt, the  $5 \rightarrow 6$  transitions around the L point results in an intense negative two peaks structure (at 0.4 and 1.0 eV) in Pd, whereas in Pt the corresponding structure forms a small positive peak at 0.5 eV and a negative one at 0.6 eV. The transitions which determine the characteristic shape of  $\sigma_{xy}^{(2)}$  of Pt with the prominent peak at 3.8 eV (as discussed above, see Figs. 2.12 and 2.14) arise mainly from the  $3 \rightarrow 5$  transitions which are located near the U and W points and at the midpoint of the U-L line. For both metals, the low energy part of the  $3 \rightarrow 5$  MO transition is mainly determined by transitions at X. In conclusion, the individual interband  $n \rightarrow m$  transitions arising from the same k points characterize essentially the same spectral shape in both metals. On the other hand, differences in the band structure of Pd and Pt due to spin-orbit coupling strength and the spatial extent of 4d and 5d wave functions result in different energy positions and intensities of the individual transitions that sum up to quite different overall optical and MO spectra in Pt and Pd.

To study the nature of the transitions responsible for the MO spectra features of Pt, we consider the structure of the selected interband transitions,  $5 \rightarrow 6$  and  $3 \rightarrow 5$ , by considering their component transitions. In Fig. 2.17, the contributions to  $\sigma_{xx}^{(1)}$  and  $\sigma_{xy}^{(2)}$  of Pt arising from the four possible transitions between the pair of band states are shown, together with their sums. For the magnetic field used in the MOKE measurements, induced splitting of the bands is very small as compared to the bandwidths. In consequence, the joint densities of states for the transitions are similar, and the difference in the transitions intensities is due to the corresponding matrix elements.

It should be recalled that, in the limit of zero spin-orbit coupling strength, the band indexes 1 and 2 enumerate different projections of the electron spin, which is a good quantum number in this case, and the spin-flip  $n_1 \rightarrow m_2$  and  $n_2 \rightarrow m_1$  transitions are forbidden. The matrix elements of the spin-flip transitions depend on relative magnitudes of the spin-orbit splitting and crystal-field splitting and differ in different parts of the Brillouin zone.

As seen in Fig. 2.17, the spin flip transitions have the largest intensities mainly in the ir spectral range. As was shown above, in this energy region  $3 \rightarrow 5$  transitions take place near X and  $5 \rightarrow 6$  transitions near L in the  $\Gamma$ -L direction. For the spin-orbit coupling switched off, the 4 and 5 bands become degenerate along  $\Gamma$ -X and the 5 and 6 bands along the  $\Gamma$ -L direction. After



*Figure 2.17.* Contributions of the individual transitions between the 5th and 6th pairs of the bands as well as between the 3rd and 5th ones to the  $\sigma_{xx}^{(1)}$  and  $\sigma_{xy}^{(2)}$  spectra of fcc Pt in the magnetic field of 1.5 T [361].

switching on the SO interaction, the resulting band splitting is accompanied by a strong intermixing of the spin-up and spin-down states. On the other hand, the states in an arbitrary **k** point in the BZ, which are already split by the crystal field, do not undergo further splitting [375]. As a result, enhanced spin-flip transitions occur mainly in the high symmetry regions of **k** space.

Although for  $\sigma_{xy}^{(2)}(\omega)$  the spin-flip transitions  $5_1 \rightarrow 6_2$  and  $5_2 \rightarrow 6_1$  are of one order of magnitude smaller as compared to the direct spin-up and spindown  $5_1 \rightarrow 6_1$  and  $5_2 \rightarrow 6_2$  transitions, the corresponding  $3 \rightarrow 5$  transitions (spin-flip and direct ones) are of the same order of magnitude. As it is seen in



*Figure 2.18.* The dependence of  $\sigma_{xy,3_1 \to 5_1}^{(2)}$  and  $\sigma_{xy,3_2 \to 5_2}^{(2)}$  components (a) and their sum, normalized vs the induced moment (see text),  $\omega \sigma_{xy,3 \to 5}^{(2)}$ , (b) on the value of the magnetic field in fcc Pt [361].

Fig. 2.17, the amplitudes of the  $3 \rightarrow 5$  component transitions are much smaller than the corresponding  $5 \rightarrow 6$  transitions.

In the absence of the magnetic field, the bands are degenerate, and all the component spectra cancel exactly leading to zero  $\sigma_{xy}^{(2)}$  and MOKE. Due to the lifting of degeneracy caused by the magnetization, the component spectra are no longer equal and the resulting contribution of the  $n\,\rightarrow\,m$  transition to  $\sigma_{xy}^{(2)}(\omega)$  is given by a small-value difference of the two large quantities. Although the amplitudes of the individual transitions  $(n_1 \rightarrow m_2, n_2 \rightarrow m_1, n_2 \rightarrow m_1)$  $n_1 \rightarrow m_1$  and  $n_2 \rightarrow m_2$ ) responsible for the left and right polarized light are different for each  $n \rightarrow m$  interband transition (Fig. 2.17(b) and (e)), they sum to resulting spectra of the same order of magnitude, but from three to four orders smaller than the components ones (at the magnetic field of 1.5 T, see solid lines in Fig. 2.17(e) and (f)). As it will be shown later, when the magnetic field splitting  $\Delta E$  of the bands is much smaller than the width of the *d*-band, which is fulfilled in the case of Pt, the resulting  $\sigma_{xy,n\to m}^{(2)}$  spectra magnitude is proportional to the average band splitting. For both  $3 \rightarrow 5$  and  $5 \rightarrow 6$ transitions, the contribution of the spin-flip transitions themselves (shown by dotted lines in Fig. 2.17(c),(f))) to the total  $\sigma_{xy}^{(2)}(\omega)$  remains relatively large for transitions occurring at high symmetry points.

To study the dependence of the  $\sigma_{xy}^{(2)}$  on the magnetic field, we performed the calculations increasing gradually the field value. It is known that in a wide range of magnetic field the nonlinear dependence of the induced magnetic moment on the field magnitude exists. It was verified that linear scaling in Pt up to the field of about 300 T holds, whereas in Pd the range of linearity is three times smaller [360] (this is because the magnetic susceptibility of Pt is about three times smaller as compared to Pd). In the ranges of the magnetic field indicated, the linearity between the  $\sigma_{xy}^{(2)}$  amplitude and the value of the external magnetic field is preserved.

In Fig. 2.18(a) the influence of the magnetic field on the  $\sigma_{xy,3\to 5}^{(2)}$  spectra is illustrated for the selected values of the external magnetic field. As it can be seen, the calculated spectra for  $\sigma_{xy,3_1\to 5_1}^{(2)}$  and  $-\sigma_{xy,3_2\to 5_2}^{(2)}$  components change considerably when the magnetic field value increases, but the resulting spectra (Fig. 2.18(b)) are very close to each other. The resulting  $\sigma_{xy,3\to 5}^{(2)}$  spectra have been normalized via a scaling down by a factor equal to the ratio of calculated magnetic moment to the moment obtained at the field of 1.5 T.

The dependences of the component  $\sigma_{xy,n_2 \to m_2}^{(2)}$  and  $\sigma_{xy,n_1 \to m_1}^{(2)}$  spectra and their sum on the magnitude of the external magnetic field in different energy regions are determined by the nature of the transition. For the transitions, for which both the initial and final states do not cross the Fermi level, induced band splitting results in a shift of the  $\sigma_{xy,n_2 \to m_2}^{(2)}$  spectra relative to  $\sigma_{xy,n_1 \to m_1}^{(2)}$  ones, and the resulting  $\sigma_{xy}^{(2)} \sim (\frac{\partial \sigma_{xy,n_1 \to m_1}^{(2)}}{\partial E})$  H.

On the other hand, when the band crossing the Fermi level at given **k** of reciprocal space, induced band splitting  $\Delta E$  leads to changes of occupation. The spin-up states become occupied and spin down unoccupied within a volume of  $\Delta \mathbf{k}$  of BZ proportional to the splitting  $\Delta E$ . For the transitions to (or from) such states, only transitions to the spin down (or from the spin up) states are allowed, and strong linear dependence of the amplitude of the component transitions on  $\Delta E$  arises. The contribution of these transitions to  $\sigma_{xy}^{(2)}$  spectra is proportional to the  $\sigma_{xy,n_n \to m_n}^{(2)}$  itself, and, as it can be easily shown, is of the form  $\Delta \sigma_{xy}^{(2)} \sim (\frac{\sigma_{xy,n_n \to m_n}^{(2)}}{\nabla_{\mathbf{k}} E(\mathbf{k})})$  H. It can be seen that for a band crossing the Fermi level horizontally, the  $\Delta \sigma_{xy}^{(2)}$  can add very substantial contribution to the component as well as the resulting spectra. This is just the origin for significant intensity of  $3 \to 5$  transitions at 3.8 eV and its behavior in the magnetic field.

It was verified that the resulting  $\sigma_{xy}^{(2)}$  spectrum magnitude scales with the induced magnetic moment and with the magnetic field as far as the proportionality between the band splitting and magnetic field holds.

**Magneto-optical properties of Pt in diluted magnetic alloys.** To illustrate that the peak at ~3.8 eV in the Kerr rotation spectrum of paramagnetic Pt is closely related to the peak observed at the same energy in magnetic Pt-3d metal systems we present as an example in Fig. 2.19(a) the absorptive part of the  $\omega \sigma_{xy}(\omega)$  spectrum for the diluted Co<sub>0.07</sub>Pt<sub>0.93</sub> alloy. The spectrum was de-



*Figure 2.19.* Comparison between the experimental absorptive part of the off-diagonal optical conductivity  $\omega \sigma_{xy}$  spectra of the Co<sub>0.07</sub>Pt<sub>0.93</sub> diluted alloy (panel (a), circles, in arbitrary units) and the spectra calculated for the model Co<sub>1</sub>Pt<sub>15</sub> alloy (a) and fcc Pt in the magnetic field of 440 T (b) (solid lines). In the panels (a) and (b) dotted and dashed lines show the calculated contributions to spectra of Co<sub>1</sub>Pt<sub>15</sub> and fcc Pt coming from the transitions from shallow  $(-1.8 < E^{(i)} \le 0 \text{ eV}, \text{ dotted lines})$  and deep  $(-3.9 < E^{(i)} \le -3.1 \text{ eV}, \text{ dashed lines})$  initial states, respectively [361].

rived from the complex Kerr rotation spectra and ellipsometric data measured for a sputter deposited disordered fcc  $Co_{0.07}Pt_{0.93}$  alloy film. Comparing the spectrum to the spectrum of paramagnetic Pt (Fig. 2.12) one can note that their overall shapes are strikingly similar. Marked differences between the  $\omega \sigma_{xy}(\omega)$ spectrum of fcc Pt and the  $Co_{0.07}Pt_{0.93}$  alloy observed in the ir range arise in part due to negligible contribution of the intraband transitions in the magnetic alloy. However, the position and shape of the prominent peak in the uv range at 3.8 eV in both systems are the same. This leads to the conclusion that the MOKE response of Pt-rich alloys with the magnetic 3d metals in the uv range is mainly determined by MO properties of spin polarized Pt, which is supported by the results of model calculations.

Fig. 2.19(a) shows the calculated  $\omega \sigma_{xy}(\omega)$  spectrum of ordered Co<sub>1</sub>Pt<sub>15</sub> alloy (*Im3m* space group symmetry) with the composition closest to the experimentally studied one. Although the experimental spectrum is less structured as compared to the theoretical one owing to the broadening effects caused by the disordered structure of the sample, the spectral dependence of the theoretical optical conductivity agrees very well with the experiment (presented in arbitrary units in Fig. 2.19(a) to simplify shape comparison).

The theoretical spectrum of  $Co_1Pt_{15}$  alloy is to be compared with the  $\omega \sigma_{xy}(\omega)$  spectrum of paramagnetic Pt (solid line in Fig. 2.19(b)) calculated for the external magnetic field of 440 T that is enough to induce the Pt magnetic moment of 0.085  $\mu_B$  close to the average Pt moment calculated for the

ferromagnetic  $Co_1Pt_{15}$  alloy. The comparison of the theoretical spectra reveals again their close similarity in the energy range 3-5 eV.

Here we restrict ourselves to performing the decomposition of both the alloy and Pt spectrum into the contributions from the interband transitions coming from the initial states lying in different energy ranges below the Fermi level to all final states. The dotted and dashed lines in Fig. 2.19 show the contribution to the  $\omega \sigma_{xy}(\omega)$  spectra of Co<sub>1</sub>Pt<sub>15</sub> and strongly magnetized fcc Pt coming from the transitions from shallow  $(-1.8 < E^{(i)} < 0 \text{ eV})$  and deep  $(-3.9 < E^{(i)} < -3.1 \text{ eV})$  initial states, respectively. It should be noted that these two groups of transitions determine practically the whole resulting spectra of both Pt and the alloy. In Pt, the optical transitions from shallow and deep states are clearly identified as the transitions mainly from 5th to 6th and from 3rd to 5th bands, respectively (see Fig. 2.14). Although in the  $Co_1Pt_{15}$ alloy the electronic bands structure (not shown) changes due to hybridization with Co 3d states, the spectral shapes of the contribution from both groups of transitions in the Co<sub>1</sub>Pt<sub>15</sub> are closely related to those of fcc Pt (Fig. 2.19(a) and (b)). However, the modification of the part of the spectrum formed by the transitions from the shallow states in the ir energy range due to the presence of 3d atoms is clearly seen for the  $Co_1Pt_{15}$  alloy. It can be supposed that the differences between the spectra formed by the shallow states will become more pronounced with an increase of the 3d metal content. On the other hand, focusing our attention on the main spectral feature of the  $\omega \sigma_{xy}(\omega)$  spectrum of Co-Pt compounds (i.e., the peak at 3.8 eV) we can state that the contribution of the transitions with the initial states lying in the range ( $-3.9 < E^{(i)} < -3.1$ eV) for Co<sub>1</sub>Pt<sub>15</sub> alloy and Pt are basically the same. Moreover, it was verified that the final states for these transitions are located in the narrow energy range up to 0.3 eV above the Fermi level. Similar results for both groups of transitions are responsible for the  $\omega \sigma_{xy}(\omega)$  spectrum in Fe<sub>1</sub>Pt<sub>15</sub>.

The main features of the  $\omega \sigma_{xy}(\omega)$  spectra in strongly diluted transition metal (TM)-Pt magnetic alloys and their close resemblance to the spectrum of Pt metal in external magnetic field can be understood if we consider the hybridization effects of the Pt 5d and TM 3d states. In TM-Pt alloys with small TM content there is a large number of Pt atoms which have only a few TM nearest neighbors and the electronic states well below the Fermi level are formed mainly by Pt 5d states. These states, which are the initial states for the interband transitions forming the peak at 3.8 eV in the MO spectra, are modified only weakly by the hybridization with TM 3d states but nevertheless acquire a large exchange splitting. On the other hand, TM 3d states contribute more strongly to the states in the vicinity of the Fermi level and their contribution manifests itself in the changes of the MO spectra in the ir range. In conclusion, it can be stated that although the microscopic mechanisms of Pt spin polariza-

tion in the Pt-rich magnetic alloys and Pt metal differ, the spectral dependence of the MO response in the uv range of both the systems is basically the same.

We can conclude that the individual interband  $n \rightarrow n'$  transitions in Pt and Pd metals are localized essentially around the same k points of the BZ and have very similar contributions. The individual behavior of the resulting optical and MO response of the Pt,Pd metals comes from the difference in their spin-orbit coupling strength and the spatial extent of 4d and 5d wave functions that result in different energy positions and intensities of the individual transitions that sum up to quite different overall optical and MO spectra. Comparative analysis of the off-diagonal optical conductivities in Pt and Pd clearly demonstrates that the MO spectroscopy is a very sensitive method to investigate minor differences in the electronic structure of solids. In the Pt (Pd) rich magnetic alloys the characteristic for the systems strong enhancement of the MOKE spectra in the uv range can be considered as coming mainly from the spin-polarization and the resulting spectral dependence of the underlying optical transitions depends only weakly on the source (alloying or external field) of Pt (Pd) magnetization.

## 2.1.3 CoPt alloys

Since its commercial appearance in 1989, magneto-optical recording has been established as a removable and erasable date storage system with a high recording density. Among many different materials Co-Pt compounds have received significant attention as a high-density MO recording medium, owing to their large perpendicular magnetic anisotropy, high remanence, capability of stable and smoothly bordered magnetic domain formation and high read out efficiency, characterized by the material parameters R (reflectivity) and  $\theta_K$ (Kerr rotation). The Co-Pt alloy phase diagram reveals a continuous series of solid solution with ferromagnetic order over nearly the whole range of concentrations [376] with three well established ordered phases: CoPt known as the tetragonal  $L1_0$  structure and CoPt<sub>3</sub> (Co<sub>3</sub>Pt) with the cubic  $L1_2$  structure. Many experimental and theoretical studies have been done especially for the ordered alloys [377, 378, 296, 379-381, 331, 382-384] and it is established that the large magneto-optical Kerr effect (MOKE) of the Co-Pt systems is caused by an interplay between the exchange splitting of Co and the spin-orbit (SO) coupling of Pt in the hybridized bands [379].

### Microscopic origin of magneto-optical properties of CoPt alloys

The characteristic feature of the experimental Kerr rotation spectra of Co–Pt compounds is a pronounced peak in the uv range at around 4 eV. Such a peak is observed also in Fe-Pt alloys and in multilayered structures of Pt with Co, Fe and Ni (see, e.g., Refs. [385–387, 299, 388], and references therein). In the previous section is was shown that pure paramagnetic Pt metal in an external

magnetic field also exhibits the same feature in the uv spectral range, and the peak in the Kerr rotation spectrum of paramagnetic Pt is closely related to that observed at the same energy in ferromagnetic strongly diluted  $Co_{0.07}Pt_{0.93}$  alloy [361]. In both cases the MO response is mainly due to the spin polarization of Pt atoms notwithstanding that the source of the spin polarization (and underlying microscopic mechanisms) are different in both cases. In principle, a close relationship between peaks in pure Pt and strongly diluted Co-Pt alloys can be expected, but it is not so obvious for alloys with Co concentrations up to 50 %. The experimental and theoretical investigation of the compositional dependence of the MOKE enhancement in the uv-range characteristic for Co-Pt alloys presented in Ref. [315].

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The optical and MO spectra for the series of  $\text{Co}_x \text{Pt}_{1-x}$  alloy films with Co content increasing from 3.5% up to 48% have been measured [315]. All the alloys were found to be ferromagnetic at the measured temperature of 290 K except for those with small Co concentrations ( $x \le 0.06$ ) which were found to be paramagnetic. In Fig. 2.20(a) the MO spectra of Pt metal [361] and  $\text{Co}_x \text{Pt}_{1-x}$  alloys with  $x \le 0.06$  measured in the external magnetic field of 1.5 T at 290 K are presented. As it can be seen,  $\theta_k$  magnitude is very small and increases from 1.5 mdeg in Pt up to 8 mdeg in  $\text{Co}_{0.06} \text{Pt}_{0.94}$  alloy. The increase of the  $\theta_k$  magnitude with the Co content is explained by the fact that the field induced MOKE is related to the paramagnetic susceptibility and depends linearly on the induced magnetization.

In Fig. 2.20(b),(c) the evolution of the  $\theta_k$  spectra of those  $Co_x Pt_{1-x}$  alloys that exhibit magnetic ordering at the measured temperature 290 K is presented. The spectra display two well-known features. There is a prominent broad negative peak in uv region and a smaller one in the ir range. The characteristic peak around 4 eV in the  $\theta_k$  spectrum is presented for all Co<sub>x</sub>Pt<sub>1-x</sub> alloys studied and its amplitude increases from 0.017 up to 0.61 deg when the Co amount changes from x=0.07 to x=0.48. At the same time, the amplitude of the fcc Co  $\theta_k$  spectra in the uv energy range included for comparison in Fig. 2.20(c) approaches the value of 0.43 deg and changes its sign at 5.1 eV. As one proceeds from Pt to the  $Co_{0.48}Pt_{0.52}$  alloy, relatively strong changes of the  $\theta_k$ spectra in the ir spectral range are observed and an emerging peak correlates with the peak at 1.5 eV in the Co spectrum. The observed strong decrease in  $\theta_k$  magnitude of the alloys with the decrease of Co content is due to a drop in magnetization and reflects the Curie temperature reduction. It is interesting to note, that both ferromagnetic Co and paramagnetic Pt metals exhibit a  $\theta_k$ peak at 3.8 eV. However, from the observed compositional dependence of the  $\theta_k$  spectra the conclusion can be drawn that the pronounced  $\theta_k$  peak at 4 eV in Co-Pt alloys is mostly correlated with corresponding peak in pure Pt metal. The detailed analysis of the band structure and identification of the states un-

Alloy	<i>Structure</i> type	Lattice constants		$M_S$		$M_L$	
		a	c/a	Co	Pt	Co	Pt
Pt	A1	7.776	1	_	0.160	_	0.028
Co <sub>1</sub> Pt <sub>31</sub>	_	7.827	1	1.967	0.051	-0.044	0.001
Co <sub>1</sub> Pt <sub>15</sub>	_	7.810	1	1.950	0.085	0.014	0.015
Co <sub>1</sub> Pt <sub>7</sub>	_	7.776	1	1.941	0.156	0.031	0.033
$Co_1Pt_7$	_	3.888	2	1.917	0.168	0.022	0.030
$\mathrm{Co_1Pt_7}$	-	7.776	0.5	1.939	0.173	0.036	0.032
$Co_2Pt_{10}$	_	3.876	3	1.862	0.201	0.045	0.040
Co <sub>1</sub> Pt <sub>3</sub>	$L1_2$	7.706	1	1.736	0.238	0.047	0.050
$Co_1Pt_3$	$D0_{22}$	3.853	2	1.758	0.216	0.019	0.040
$\mathrm{Co}_1\mathrm{Pt}_3$	$D0_{23}$	3.853	4	1.777	0.232	0.042	0.048
$Co_1Pt_1$	_	3.725	2	1.604	0.296	0.052	0.056

*Table 2.1.* Characterization of the model crystal structures of the Co-Pt alloys assumed in the LMTO calculations [315]. For all structures, alloy composition, type of the structure, unit cell edges, and calculated spin and orbital magnetic moments of Co and Pt (in  $\mu_B$ ) are listed.

derlying the optical transitions responsible for the peak can help us to verify the conclusion.

To describe the compositional dependence of the MO properties of the alloys studied, the supercell calculation approach was used [315]. The bandstructure and MO spectra were calculated for a number of model ordered structures ( $Co_1Pt_{31}$ ,  $Co_1Pt_{15}$ ,  $Co_1Pt_7$ ,  $Co_2Pt_{10}$ ,  $Co_1Pt_3$ ,  $Co_3Pt_5$ , and  $Co_1Pt_1$ ) of different composition. The sequence corresponds to a variation of the Co content in the range of 3–50%. The crystal structure types, corresponding space groups, and lattice constants of the alloys are presented in Table 2.1. For  $Co_1Pt_7$  and  $Co_1Pt_3$  alloys, cubic and tetragonal lattices with the unit cells with different c/a ratios were studied. For other alloys cubic ( $Co_1Pt_{31}$  and  $Co_1Pt_{15}$ ) and tetragonal ( $Co_2Pt_{10}$  and  $Co_1Pt_1$ ) unit cells were used. The unit cells of the alloys consist of a few vertically and/or horizontally arranged adjacent fcc unit cells, with Co and Pt atoms distributed over nonequivalent atomic positions according to the specific alloy composition. As an example, the unit cells used for cubic  $Co_1Pt_7$  and  $Co_1Pt_3$ , and tetragonal  $Co_1Pt_1$  structures are shown in Fig. 2.21.

A proper discussion of the electronic transitions underlying the MO spectra requires the analysis of the conductivity tensor of the medium. The off-



*Figure 2.20.* The polar Kerr rotation measured for  $Co_x Pt_{1-x}$  alloys of different compositions (indicated in the keys) [315].



*Figure 2.21.* Unit cells used for (a)  $Co_1Pt_7$  (*Fm*-3*m*), (b)  $Co_1Pt_3$  (*Fm*-3*m*), and (c)  $Co_1Pt_1$  (*P*-42*c*) alloys [315].

diagonal components of the optical conductivity tensor  $\omega \sigma_{xy}^{(2)}$  were evaluated from the measured complex polar Kerr spectra (polar Kerr rotation and ellipticity) and the complex index of refraction (*n* and *k*). In Fig. 2.22(a) the absorptive part of the off-diagonal component of optical conductivity  $\omega \sigma_{xy}^{(2)}$  evaluated from experimental data, and in Fig. 2.22(b) the spectra calculated for the selected group of Co–Pt alloys with the composition closest to the experimental one are presented. Because the frequency dependence of the optical constants of the alloys is essentially featureless, a close correlation between the Kerr rotation and  $\omega \sigma_{xy}^{(2)}$  spectra is observed. The experimental  $\omega \sigma_{xy}^{(2)}$  spectra have been scaled by the factors (indicated in Fig. 2.22(a)) equal to the ratio of their magnetizations at low temperature and at 290 K to take into account the decrease of the Curie temperature of  $Co_x Pt_{1-x}$  alloys with the decrease of Co content. At a first glance, both the theoretical and the experimental spectra exhibit a very im-



*Figure 2.22.* Comparison of the absorptive part of the off-diagonal component  $\omega \sigma_{xy}^{(2)}$  of the optical conductivity tensor, determined from the ellipsometric and the complex polar Kerr angle measurements for  $\text{Co}_x \text{Pt}_{1-x}$  alloys (x=0.035, 0.07, 0.123, 0.14, 0.22, and 0.48) (a) with the spectra calculated for the model  $\text{Co}_1 \text{Pt}_{31}$ ,  $\text{Co}_1 \text{Pt}_{15}$ ,  $\text{Co}_1 \text{Pt}_{7}$ ,  $\text{Co}_2 \text{Pt}_{10}$ ,  $\text{Co}_1 \text{Pt}_3$ , and  $\text{Co}_1 \text{Pt}_1$  alloys (b) (the corresponding alloy compositions are given in the key). In the panel (b) triangles and dashed and dash-dotted lines denote the spectra of  $D0_{22}$ ,  $D0_{23}$  and  $L1_2$  structures, respectively. The spectra marked with filled circles are to scale, all other spectra are shifted by a constant offset of 1 and  $3 \times 10^{29} s^{-2}$  towards each other in the panel (a) and (b), respectively [315].

pressive similarity in the evolution of their spectral features with the change of Co content. However, the experimental peaks are more broad which is due to the existence of a variety of local environments in the disordered phase. Weak but systematic changes in the energy position of the spectral peculiarities can be seen in Fig. 2.22. There is a slight increase in the energy position of the uv-peak with the increase of Co content in the experimental  $\omega \sigma_{xy}^{(2)}$  spectra, and even a more pronounced increase in the corresponding theoretical ones. In the ir part of the experimental spectra, the shoulder near 1 eV observed already for Co<sub>0.07</sub>Pt<sub>0.93</sub> becomes more prominent with the increase of Co content and transforms into a distinct peak at 1.5 eV in the  $Co_{0.52}Pt_{0.48}$  alloy. The same tendency in the evolution of the ir spectral features is observed for the calculated spectra. The  $\omega \sigma_{xy}^{(2)}$  spectrum magnitude increases systematically with the increase of Co concentration and exhibits saturation for the Co<sub>1</sub>Pt<sub>1</sub> alloy. The relative amplitudes of the low- and high-energy peaks of the experimental spectra agree well with the theoretical ones in the whole range of investigated Co concentrations. However, the calculated magnitude of the  $\omega \sigma_{xy}^{(2)}$  spectra of

the  $\text{Co}_x \text{Pt}_{1-x}$  alloys are larger. The discrepancies can arise due to: i) chemical disorder and the presence of defects in the disordered samples studied (it is known that the MOKE enhances in an ordered phase due to modification of Pt-Co coordination in the ordered versus disordered phase [377, 378, 381]) and ii) high sensitivity of the optical properties on the sample surface quality (the  $\sigma_{xx}$  spectra evaluated from the measured n and k functions are about 50% smaller as compared to the corresponding calculated spectra which leads to the underestimation of the magnitude of the  $\omega \sigma_{xy}^{(2)}$  spectra evaluated from experimental data).

It is important to point out that for the alloy of a given composition the fine details of the  $\omega \sigma_{xy}^{(2)}$  spectrum are sensitive to its actual crystal structure. This is illustrated in Fig. 2.22(b) for the alloys of the same nominal composition  $\text{Co}_{0.25}\text{Pt}_{0.75}$  having different symmetries and local environments of Co and Pt sites. The spectra were calculated for cubic  $L1_2$  and tetragonal  $D0_{22}$  and  $D0_{23}$  crystal structures. As it can be seen, the change of an atomic arrangement and accompanying changes of the local symmetry of atomic sites results in the shift of the uv-peak energy position as well as in changes of the relative magnitude of ir- and uv- maxima of the  $\omega \sigma_{xy}^{(2)}$  spectra. Modeling of the chemical disorder by averaging over different configurations would lead to the uv peak broadening and to less pronounced  $\omega \sigma_{xy}^{(2)}$  spectral features and, consequently, to better agreement with the experimental spectra.

We should mention that the paramagnetic  $Co_{0.035}Pt_{0.965}$  and  $Co_{0.049}Pt_{0.951}$ alloys exhibit a maximum at ~1.5 eV in  $\theta_k$  spectra (corresponding to a minimum in  $\omega \sigma_{xy}^{(2)}$ ), which is not observed in the theoretical spectra. The same frequency dependence in the ir range is observed for Pt metal. The explanation of this behavior is given in Ref. [361] as coming from the intraband contribution to the *off-diagonal* part of the optical conductivity which has not been included in the calculated spectra of Co-Pt alloys. As it was shown in Ref. [361] the intraband contribution to  $\sigma_{xy}$  is very small and can usually be neglected in the case of magnetically ordered materials. However, for the metals that have zero spontaneous exchange splitting the spin polarization induced by an external magnetic field available in the experiment is small and the contributions of intra- and interband transitions to the off-diagonal component of the optical conductivity tensor can become comparable.

#### Correlation between the electronic structure and the magneto-optical pro-

**perties.** The well-known characteristic feature of the electronic structure of Co-Pt alloys is the strong hybridization of Co 3d and Pt 5d states, the latter being much more delocalized. Fig. 2.23 shows the calculated spin- and site-projected densities of the electronic states for Co and Pt sites in Co<sub>1</sub>Pt<sub>7</sub>, Co<sub>1</sub>Pt<sub>3</sub>, and Co<sub>1</sub>Pt<sub>1</sub> alloys. The DOS for fcc Pt calculated in a magnetic field



*Figure 2.23.* Spin-projected densities of Pt (full line) and Co (dotted line) d states (in electrons/atom eV) calculated for fcc Pt in a magnetic field of 920 T, Co<sub>1</sub>Pt<sub>7</sub>, Co<sub>1</sub>Pt<sub>3</sub>, and Co<sub>1</sub>Pt<sub>1</sub> alloys. The vertical dashed lines indicate the energy windows for initial and final states  $\Delta E_i$  and  $\Delta E_f$  (see text) and the vertical solid line marks the Fermi level [315].

of 920 T is considered here and henceforth as a reference system (this value of magnetic field is needed to induce the Pt magnetic moment of  $0.16\mu_B$  close to the average Pt moment calculated for the ferromagnetic Co<sub>1</sub>Pt<sub>7</sub> alloy). As it is seen, the electronic structure depends strongly on the alloy composition. This is the result of the strong dependence of hybridization details between Co 3d and Pt 5d states on the number of nearest Pt(Co) neighbors for each Co(Pt) atom. Pt lends its strong spin-orbit coupling to the system while inside Co atomic spheres the effect of the spin-orbit coupling is much weaker than the effect of the exchange field. The electronic states at the bottom of the valence band are formed mainly by Pt states. The high density of both Pt 5d and Co 3d states in the energy range from -3.5 to 1.0 eV suggests a high degree of hybridization between them. However, as compared to the spin-up states the spin-down ones are hybridized to a far lesser extent. On the other hand, in the vicinity of the Fermi energy  $(E_F)$  stronger hybridization occurs for the spin-down states. With the increase of Co content in  $Co_x Pt_{1-x}$  alloys the hybridization of Pt states with the exchange split Co states increases. This leads to the increase of the difference in occupation of Pt majority and minority spin states and, as a consequence, of the magnetic moment induced on Pt site which approaches the value of  $0.3\mu_B$  for the alloy of equiatomic composition. In contrast, the magnetic moment of the Co atoms decreases. The compositional dependence of the average value of the Co and Pt spin magnetic moments is presented in Table 2.1. It has been verified that, as opposed to the magnetic moments, the spin-orbit coupling strength on Pt sites is much less sensitive to the alloy composition and changes only within 2.5% for Pt 5d states which agrees with the observation reported in Ref. [383]. Thus, although the SO interaction plays a crucial role in the formation of the MO response, [389] one can conclude that the dependence of the MO spectra of the  $Co_x Pt_{1-x}$  alloys on the Co content is hardly related to the changes of the Pt SO coupling strength but rather to the change of the hybridization and to increased Pt exchange splitting.

**Decomposition of the**  $\omega \sigma_{xy}(\omega)$  **spectra.** To examine and identify the energy position of the initial and final states responsible for main spectral features in  $\operatorname{Co}_x \operatorname{Pt}_{1-x}$  alloys and their relation with those of Pt metal, the analysis of the transitions arising between different narrow energy ranges has been performed. The calculated  $\omega \sigma_{xy}(\omega)$  spectra were decomposed into the contributions coming from the initial states lying in different energy ranges below the Fermi level to all final states, as well as into the contributions coming from all initial states lying in different energy intervals above  $E_F$  [315].

In Fig. 2.24(a-d) the contributions to the  $\omega \sigma_{xy}(\omega)$  spectra of the Co<sub>1</sub>Pt<sub>7</sub>, Co1Pt3, and Co1Pt1 alloys and to the spectrum of strongly magnetized Pt coming from the initial states located within well defined energy windows are shown. The dashed lines in Fig. 2.24(a-d) denote the contribution coming from a 0.8 eV wide energy interval of the initial states just below  $E_F$  to all possible final states. For all the compounds these transitions give almost constant off-diagonal optical conductivity in the 2 to 6 eV photon energy range. The solid lines in Fig. 2.24(a-d) show the contribution coming from the occupied states situated within an energy interval  $\Delta E_i$  between -4.2 and -3.4 eV in Pt which extends down to -4.8 eV in Co<sub>1</sub>Pt<sub>1</sub> (see Fig. 2.23). In Fig. 2.24(e-h) the results of the analysis of transitions coming from all possible initial states to different final states are presented. It was found that a relatively narrow energy window  $\Delta E_f$  lying just above  $E_F$  and equal to 0.3, 0.6, 0.8, and 1.0 eV for Pt, Co<sub>1</sub>Pt<sub>7</sub>, Co<sub>1</sub>Pt<sub>3</sub>, Co<sub>1</sub>Pt<sub>1</sub>, respectively, can be specified. The transitions to the final states within  $\Delta E_f$  are responsible for the main spectral features of  $\omega \sigma_{xy}(\omega)$ , i.e., the peaks in ir and uv regions. The transitions to the final states

lying above  $\Delta E_f$  give both for Pt and for  $\text{Co}_x \text{Pt}_{1-x}$  alloys merely a more or less constant contribution in the 1 to 6 eV photon energy range.

It should be noted that for all the alloys studied an additional peak arises for  $\hbar\omega=1$  to 2 eV in the  $\omega\sigma_{xy}(\omega)$  spectra whose amplitude increases with increasing Co content. It was found that this ir peak comes from the transitions between initial states located in the energy range from -1.9 to -0.8 eV to the states within the  $\Delta E_f$  window just above  $E_F$ . The energy windows coincide well with those responsible for ir peak of pure fcc Co. However, it was found that the  $\omega\sigma_{xy}(\omega)$  spectrum of Co cannot be described by the same kind of contributions as in the alloys studied.

From the analysis of the decomposed spectra for all the examined  $\text{Co}_x \text{Pt}_{1-x}$  alloys as well as for Pt metal, the  $\omega \sigma_{xy}(\omega)$  spectra above 2 eV can be represented with good accuracy as a sum of two contributions:

a) The pronounced peak at 4 eV in the  $\omega \sigma_{xy}(\omega)$  spectra is almost exclusively determined by the interband transitions from the deep lying occupied states within the relatively narrow energy interval  $\Delta E_i$  equal to 0.8, 1.0, 1.1, and 1.4 eV for Pt, Co<sub>1</sub>Pt<sub>7</sub>, Co<sub>1</sub>Pt<sub>3</sub>, and Co<sub>1</sub>Pt<sub>1</sub>, respectively, to the unoccupied states spanning the energy interval  $\Delta E_f$ . These energy intervals responsible for the MO peak at 4 eV are indicated by vertical dashed lines in Fig. 2.23.

b) The weakly energy dependent in the 2 to 6 eV photon energy range arises from transitions between the occupied states lying in the energy window -0.8eV to  $E_F$  and the unoccupied states located above  $\Delta E_f$ .

Broadly speaking, the overall spectral shape of both contributions discussed above look similar and remains close to that observed in Pt, but their magnitude changes considerably with Co content. This observation can be explained on the basis of the simple consideration that the increase of the Co-Pt alloys spectra magnitude with the increase of Co content is mainly due to the increase of Pt exchange splitting from direct hybridization between Pt orbitals and spin polarized Co orbitals. As was shown in Ref. [361], the MO spectra amplitude of Pt metal scales in a wide range with induced magnetic moment. This is definitely seen in Fig. 2.24(a-b), where the same magnetic moment on Pt sites in Co<sub>1</sub>Pt<sub>7</sub> alloy and Pt metal in an external magnetic field results in a comparable amplitude of the contributions to the  $\omega \sigma_{xy}(\omega)$  spectra. We found that this conclusion qualitatively holds also in the case of Co<sub>1</sub>Pt<sub>3</sub> and Co<sub>1</sub>Pt<sub>1</sub> alloys. The origin of the behavior can be understood, because in spite of the low magnetic moment of  $0.16 \div 0.3 \mu_B$  on Pt as compared to  $1.9 \div 1.6 \mu_B$  on Co, there is a large spin-orbit coupling increasing the amplitude of the  $\omega \sigma_{xy}(\omega)$  spectra of Pt in the uv range which is 3-4 times larger as compared to that of fcc Co.

The above explanation can be considered as giving only a rough, qualitative estimate of the  $\omega \sigma_{xy}(\omega)$  spectra. The distinctions between the shapes of the spectra in different spectral regions arise with the changes of alloy composition [Fig. 2.24(a-d)]. In particular, the peak at 4 eV has almost symmetric shape in



*Figure 2.24.* Calculated  $\omega \sigma_{xy}^{(2)}$  spectra (solid lines with circles) of fcc Pt in the magnetic field of 920 T (a), Co<sub>1</sub>Pt<sub>7</sub> (b), Co<sub>1</sub>Pt<sub>3</sub> (c) and Co<sub>1</sub>Pt<sub>1</sub> (d) alloys. Solid and dashed lines show the contributions from the initial states localized within the indicated intervals (in eV) below the Fermi energy to all final states (left panels) and from all initial to those final states that are localized within the indicated intervals (right panels). Other lines denote the transitions between the groups of initial and final bands. Their numbers are given in parentheses in the key [315].

Pt but rather asymmetric one in the alloys. The distinctions in the fine structure of the spectra come from the fact that the  $\omega \sigma_{xy}(\omega)$  spectra of  $\text{Co}_x \text{Pt}_{1-x}$  alloys can not be represented by simple superpositions of Co and Pt contributions, but



*Figure 2.25.* Density of the expectation value of  $\hat{l}_z$  for Pt (full line) and Co (dotted line) states for orbital quantum numbers l=1 (left panels) and l=2 (right panels) in fcc Pt in a magnetic field of 920 T, Co<sub>1</sub>Pt<sub>7</sub>, and Co<sub>1</sub>Pt<sub>3</sub> alloys (in electrons/atom eV). The vertical dashed lines indicate the energy windows for initial and final states  $\Delta E_i$  and  $\Delta E_f$  (see text) and vertical solid line marks the Fermi level [315].

depend on details of the band structure which are influenced by various factors such as the alloy composition, the lattice symmetry, and the local environment of Co and Pt atoms. These details can be only investigated by analysis of the evolution of the band structure of the alloys with the change of Co content. **Correlation between the band structure and the MO peak at 4 eV.** It is well known that the optical and MO spectra reflect information on both the initial and final states simultaneously (joint density of states). Besides, they are strongly influenced by the optical transition matrix elements, which in the case of the MO spectra depend on the spin and orbital polarization of the initial and final states.

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To illustrate the influence of the spin-orbit interaction on the initial and final states involved in the transitions let us introduce a site-dependent function  $dm_{tl}(E)$  given by [390]

$$dm_{tl}(E) = \sum_{n\mathbf{k}} \langle \Psi_{tl}^{n\mathbf{k}} | \hat{l}_z | \Psi_{tl}^{n\mathbf{k}} \rangle \delta(E - E_{n\mathbf{k}}), \qquad (2.1)$$

where  $\hat{l}_z$  is z-projection of the angular momentum operator,  $E_{n\mathbf{k}}$  and  $\Psi_{tl}^{n\mathbf{k}}$  are the energy of the *n*-th band and the part of the corresponding LMTO wave function formed by the states with the angular momentum l inside the atomic sphere centered at the site t, respectively. In analogy to the l-projected density of states,  $dm_{tl}(E)$  can be considered as the site- and l-projected density of the expectation value of  $\hat{l}_z$ . This quantity has purely relativistic origins and when the SO interaction is equal to zero  $dm_{tl}(E) \equiv 0$ . As van Vleck [391] showed for a free ion, the absence of orbital degeneracy is a sufficient condition for the quenching of the orbital moment, which means that the first-order contribution should vanish:  $\langle \Psi_{\mathbf{k}} | \hat{l}_z | \Psi_{\mathbf{k}} \rangle = 0$ . Thus,  $dm_{tl}(E)$  can be considered as a measure of the SO interaction of the electronic states.

Furthermore, just as the number of states is defined as the integral of DOS, we can define the integral of  $dm_{tl}(E)$ 

$$m_{tl}(E) = \int_{E_b}^{E} dm_{tl}(E) dE$$
, (2.2)

where  $E_b$  is the bottom of the valence band. Then, the orbital moment  $M_l$  at the site t is given by:

$$M_l \equiv m_{tl}(E_F) \tag{2.3}$$

(here and henceforth we will drop the index t for simplicity).

One can expect that the electronic states for which the magnitude of the  $dm_{tl}(E)$  function is large should give strong contribution to the MO spectra. Due to the dipole selection rules only the electronic states with an appropriate symmetry contribute to the spectra. In our case the most important are the interband transitions between d and p states. Fig. 2.25(a-f) presents the Co and Pt site-projected  $dm_l(E)$  functions for l=1 and l=2 orbital quantum numbers calculated for Co<sub>1</sub>Pt<sub>7</sub> and Co<sub>1</sub>Pt<sub>3</sub> (fcc Pt is also included for comparison). Let us concentrate our attention on the electronic states which give the largest contribution to the prominent 4 eV peak in the off-diagonal optical conductivity

indicated by vertical dashed lines in Figs. 2.25 and 2.23. As has been shown the peak at 4 eV is determined by the transitions to the final states in the window  $\Delta E_f$  just above the Fermi level which are predominantly of Pt and Co d character. With the increase of Co content the magnitude of both Co and Pt  $dm_{l-2}(E)$  increases appreciably in this range. The initial states for these transitions lie in the narrow energy interval  $\Delta E_i$  below -3.4 eV and, due to the dipole selection rules, are mainly of p character. Remarkably, the  $dm_l(E)$  for Pt p states reaches its maximal magnitude exactly in the same energy range. Going from fcc Pt to the Co<sub>1</sub>Pt<sub>3</sub> alloy one can note that the structure of the peak becomes more complex but its position remains approximately the same. The change of the  $dm_l(E)$  shape in this energy range reflects to some extent the change of the Pt d-Co d hybridization. An indication for this is the appearance of the peak in the  $dm_l(E)$  of Co d states at the border of the energy window  $\Delta E_i$ . The qualitative analysis discussed above can serve as a tool for determination of the initial and final states most probable for the MO active interband transitions.

To find direct correlation between the  $\omega \sigma_{xy}^{(2)}$  spectra of Co-Pt alloys and the corresponding band structure, in the following discussion we focus our attention particularly on the origin of the pronounced peak at 4 eV by identifying the initial and final states involved and their k-space localization. It is obvious that the interpretation of the MO spectra of complex compounds in terms of electronic transitions is quite a complicated problem. The initial and final states involved in optical transitions of Co-Pt systems are hybridized states and their wave functions are delocalized. Moreover, in the formation of the optical as well as magneto-optical spectra of the medium, the matrix elements of the interband transitions and selection rules are also of great importance. In principle, to compare directly band structures of different alloys with that of fcc Pt metal, we should use crystal structures with the same symmetry group and the same number of atoms per unit cell and, therefore, the same type of the Brillouin zone. To this end, the face centered cubic lattice of Co<sub>1</sub>Pt<sub>7</sub> alloy of Fm-3m space group was chosen as a basic lattice. The primitive rhombohedral cell in this case contains 8 atoms and the cubic unit cell containing 32 atoms is shown in Fig. 2.21 (a). In such a representation, the corresponding cubic unit cell of fcc Pt has a doubled dimensions and contain 8 standard fcc A1 unit cells, and that of the  $Co_1Pt_3$  alloy (Fig. 2.21 (b)) – 8 standard  $L1_2$  unit cells of Cu<sub>3</sub>Au type structure.

Fig. 2.26 shows the calculated band structures of Pt,  $Co_1Pt_7$ , and  $Co_1Pt_3$  alloys along symmetry lines of the Brillouin zone. To illustrate the evolution of the band structure with the increase of Co content, in Fig. 2.26 we selected (the same for each case) two group of bands (initial – from 29 to 48, and final – from 77 to 86) by denoting them by thick solid lines (we will see further that optical transitions among those groups of bands are responsible for the MO peak in



*Figure 2.26.* Fully relativistic spin-polarized band structure of fcc Pt in a magnetic field of 920 T and  $Co_1Pt_7$  and  $Co_1Pt_3$  alloys. Solid thick lines at the left panels are a blowup of the groups comprising the most MO active initial and final bands. Solid thick lines at the right panels indicate the most MO active bands in the *L*–*U* symmetry direction of the Brillouin zone, with the band numbers indicated at the right-hand side [315].

the uv at  $\sim 4 \text{ eV}$ ). From Fig. 2.26, the conclusion can be drawn that upon increasing of Co content the band splitting increases, and there is a strong shift of the occupied energy band positions to higher energy as a result of the Co(3d) -Pt(5d) hybridization. Looking at the band structure, it is definitely seen in Fig. 2.26 that, as one proceeds from pure paramagnetic Pt to  $Co_1Pt_7$  and  $Co_1Pt_3$ alloys, the hybridization of the electronic states increases. This is clearly seen, for example, in the right panels of Fig. 2.26 from the  $E(\mathbf{k})$  dependence of the 85,86 bands. In Pt, these energy bands almost do not hybridize with low-lying bands having rather large  $\nabla_{\mathbf{k}} E(\mathbf{k})$  around the U symmetry point. They simply cross the 83,84 bands without any repulsion. In Co<sub>1</sub>Pt<sub>7</sub> and Co<sub>1</sub>Pt<sub>3</sub> alloys, the Co electronic states hybridize with the Pt states. As a result of the band repulsion, these states spread over the energy scale up to  $\sim 0.5$  eV, whereas  $\nabla_{\mathbf{k}} E(\mathbf{k})$ becomes almost equal to zero at the U point in the  $Co_1Pt_3$  alloy. Similar effects of energy levels repulsion with accompanying mixing - hybridization of states after quantum-mechanical crossing of level can be seen in Fig. 2.26 in the whole Brillouin zone. Due to Pt(5d)-Co(3d) hybridization, the  $E(\mathbf{k})$  slopes of the initial and final states become more similar around selected symmetry points, which leads to both an increase of the joint density of states and oscillator strengths of the optical transitions. Another important effect that strongly affects the MO spectra in  $Co_x Pt_{1-x}$  alloys with increasing concentration of Co is a reduction of the Fermi energy due to the fact that Co has less valence electrons in comparison with Pt. The de-occupation of the energy bands by electrons due to decrease of the Fermi level involves additional final states for interband transitions which also increases the intensity of the spectra.

To identify which kind of interband transitions and parts of the Brillouin zone are responsible for the prominent peak at 4 eV, the k-space decomposition of the interband transitions into transitions occurring in the vicinity of the high symmetry points of the Brillouin zone was performed. This was accomplished via the theoretical analysis of about 8000-10000 individual interband transitions in high symmetry points and lines of the BZ. For this aim, all transitions between the bands n and m in a cubic volume surrounding a given point with a cube edge equal to 1/6 of the  $\Gamma$ -X distance (each one contains approximately 4.5% of the whole BZ volume) was summed. Although the results depend on the volume of the cube, one can identify the transitions essentially with these points and their nearest neighborhood. The detailed analysis of the contributions shows that in both Pt and Co–Pt alloys the  $\sigma_{xy}^{(2)}$  spectra are determined by the transitions at the BZ edge along the  $\Gamma$ -L, L-U, and U-W symmetry directions. It was found that the most intensive transitions responsible for the MO peak at 4 eV come from the states located along the L-U symmetry direction. The initial and final bands for these transitions are marked by solid thick lines in the right panels of Fig. 2.26. Moreover, in the alloys the peak observed in the ir range is formed by the transitions between the hybridized states in the  $\Gamma$ -*L*-*U* symmetry plane.

It was determined that the transitions from bands (35–48), (33–44) and (29– 40) in Pt, Co<sub>1</sub>Pt<sub>7</sub>, and Co<sub>1</sub>Pt<sub>3</sub>, respectively, to the same specified group of empty bands (77–86) are responsible for the pronounced peak at 4 eV in MO spectra. The intensity of these transitions [marked by dotted lines in Fig. 2.24(a-c)] almost coincides with the intensity of the peak derived from the  $\Delta E_i$  and  $\Delta E_f$  energy windows. It should be pointed out that when the Co content increases, the alloys' *d*-band width systematically decreases (see Figs. 2.23 and 2.26) and the deep lying initial bands shift to higher energy, giving, a more significant contribution to the peak at 4 eV.

It was verified that the intensities of interband transitions from the analyzed initial states to individual final bands increase with Co content. In particular, the transitions to the (85,86) final bands contribute only about 2 % to the total intensity of the pronounced peak in pure Pt, but their contributions increase to about 10 and 25 % in Co1Pt7 and Co1Pt3 alloys, respectively. The high increase of the intensity of the transitions to unoccupied (85-86) bands is a good illustration of the role of the hybridization. The Pt(5d)-Co(3d) hybridization effects that determine the details of the band structure of the alloys are responsible also for the increase of the intensity of the second contribution (i.e., transitions from the window just below  $E_F$  to all final states) with the increase of Co content. To study the influence of the spin-orbit and the exchange splitting on the band structure of Co-Pt alloys, a test calculation through the manipulation of the magnitude of the interaction on a particular site was performed [315]. It was found that the deep lying initial states undergo the largest changes with a change of the spin-orbit coupling strength, whereas the empty bands are more sensitive to the influence of the exchange splitting arising as a result of hybridization between Pt and Co wave functions.

Although the details of the band structure change dramatically upon increase of Co content, it should be noted that the structure of the peak at 4 eV changes only weakly and remains close to that of Pt metal. To understand the close resemblance between the peak at 4 eV in paramagnetic Pt and in Co–Pt alloys, the role of the final states involved in the transitions was examined [315]. In both cases the final states responsible for the peak at 4 eV are located within a very narrow energy range in the vicinity of  $E_F$  and within the same part of **k**-space. It was found that the increase of the band splitting by the external magnetic field in Pt or due to the direct hybridization (between Pt orbitals and spin polarized Co orbitals) in the alloys results mainly in changes of the occupation of the bands at the Fermi level (i.e., the density of empty spin-down states increases). Thus, the evolution of the  $\omega \sigma_{xy}^{(2)}$  spectra of Co–Pt alloys with the composition in the range studied can be qualitatively considered as due to the similar mechanism as in the case of the induced spin polarization in pure

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Pt in external magnetic field, notwithstanding that the character of the final as well as the initial states are changing.

In conclusion, the individual interband  $n \rightarrow m$  transitions arising in the vicinity of the same **k** points characterize essentially the same MO spectral shape in Pt and Co–Pt alloys. Although the fine details of the MO spectra of the Co<sub>x</sub>Pt<sub>1-x</sub> alloys for x up to 0.5 depend on the details of the spin polarized band structure, the characteristic enhancement of the spectra in the uv range can be considered as coming mainly from the spin-polarized Pt. On the other hand, the differences in the band structure of Pt and Co–Pt alloys due to the different position of the Fermi level and different degree of Co 3d – Pt 5d hybridization result in different shapes and intensities of the individual transitions that sum up to basically similar, but different in details, MO spectra of Pt and Co–Pt alloys.

# Influence of the crystal structure and chemical order on the magneto-optical properties of equiatomic CoPt.

From the point of view of basic research as well as applications, it is important to understand the correlations between the MO properties and the crystal structure and chemical order parameters. In Ref. [392] the results of quantitative modeling of the structure-dependent electronic effects on the magnetic and MO properties of an equiatomic CoPt alloy with  $L1_0$ ,  $L1_1$  and randomly disordered structures in *ab initio* calculations were reported. A strong dependence of the Kerr spectra on crystal structure as well as a very strong sensitivity of the spectra on the degree of chemical ordering was observed.

In the calculations [392], the  $L1_0$  type structure corresponding to tetragonally distorted fcc crystal and the  $L1_1$  structure corresponding to fcc lattice compressed along [111] were used as models of ordered CoPt. Both structures are layered, i.e., monolayers of Co are separated by monolayers of Pt along the [001] direction in the  $L1_0$  and along [111] in the  $L1_1$  structure as is shown in Fig. 2.27(a) and (b), respectively. However, real samples have always some remaining imperfection, and the experimentally derived chemical long-range order (LRO) parameter is usually less than unity [296, 385]. For the equiatomic systems the LRO parameter can be defined as  $S=1 - 2x_{\rm Pt}$ , where  $x_{\rm Pt}$  is the fraction of Pt atoms in the Co-rich layer. To model the layer intermixing a supercell approach was used [392]. As an example, in Fig. 2.27(c) and (d) supercells of the partially ordered  $L1_0$  and  $L1_1$  structures with S=7/9 and 7/8, respectively, are shown.

Fig. 2.28(a,b) shows the polar Kerr rotation ( $\theta_K$ ) spectra for perfect  $L1_1$ and  $L1_0$  structures of the CoPt alloy calculated with the magnetization aligned along the *c*-axis. As can be seen, with the difference in lattice symmetry a large difference between the  $\theta_K$  spectra for the  $L1_1$  and  $L1_0$  crystal phases arises. The evolution of the  $\theta_K$  spectra with the decrease of LRO is shown in Fig.



*Figure 2.27.* Unit cells used for equiatomic CoPt alloy: (a)  $L1_0$ ; (b)  $L1_1$ ; (c)  $c(3/\sqrt{2} \times 3/\sqrt{2})$  supercell of  $L1_0$  type with S=7/8; (d)  $c(2\sqrt{2} \times 2\sqrt{2})$  supercell of  $L1_1$  type with S=7/9 [392].



*Figure 2.28.* Dependence of the Kerr rotation spectra of CoPt on the type of structure and the chemical order. (a)  $L1_1$  structures: experiment (Ref. [380]) (circles); theory: 1 - ordered  $L1_1$ , curves 2,3,4, and 5 – S=7/8, 5/8, 2/8, and 1/8, respectively; (b)  $L1_0$ : experiment (Ref. [377, 378]) (circles); theory: 1 - ordered  $L1_0$ , curve 2 - S=7/9, curve 3 - S=1/2. (c) random fcc structures: experimental data (circles for Co<sub>48</sub>Pt<sub>52</sub> (Ref. [315]) and triangles for Co<sub>47</sub>Pt<sub>53</sub> (Ref. [393])); theory: Co<sub>50</sub>Pt<sub>50</sub> (solid line), Co<sub>47</sub>Pt<sub>53</sub> (dotted line) [392].



*Figure 2.29.* Energy dependence of the magneto-optical anisotropy of CoPt alloy for  $L1_1$  (a) and  $L1_0$  (b) structures [392].

2.28(a,b) for both structures. For the  $L1_1$  structure, a dramatic change of the  $\theta_K$  spectrum with LRO change is observed. The main effect is the large change of the band-shape, particularly in the uv range as compared to the spectrum of the perfect structure. The magnitude of  $\theta_K$  at ~4 eV varies by one order from  $-0.1^o$  for S=1 (curve 1 in Fig. 2.28(a)) to  $-0.9^o$  for S=1/8 (curve 5). As of magnitude, the shape of the experimental  $\theta_K$  spectrum (Ref. [380]) shown in Fig. 2.28(a) is in relatively close agreement with the theoretical spectrum for S between 5/8 and 7/8. One can speculate that sample imperfection (inhomogeneity, mixing with other phases, etc.) would lead to a spread in the S value within the sample, leading to the peaks averaging and broadening. The small amplitude of the experimental spectra can be due, in part, to the well known fact that the optical and magneto-optical spectra tend to depend strongly on the sample surface quality.

In Fig. 2.28(b), calculated and experimental  $\theta_K$  spectra (measured on a  $\text{Co}_{52}\text{Pt}_{48}$  sample, where 90% of the sample volume was ordered [377, 378]) in the  $L1_0$  structure are shown. As compared to the  $L1_1$  structure, the changes of the  $\theta_K$  magnitude upon the decrease of LRO from the perfectly ordered  $L1_0$  (curve 1) to the partially disordered structure (S=7/9 and S=1/2, curves 2 and 3) are less pronounced, and the main effect is a change of the fine structure of the spectrum. While the uv peak for the ideal  $L1_0$  structure is very narrow and shifted to higher energy, for S=7/9 the peak is very close to the experiment.

For completeness, the experimental and calculated spectra for chemically disordered fcc ( $S \sim 0$ ) CoPt are shown in Fig. 2.28(c). The experimental  $\theta_K$  spectrum of Co<sub>48</sub>Pt<sub>52</sub> alloy film prepared by dc sputtering and the spectrum for e-beam evaporated disordered Co<sub>47</sub>Pt<sub>53</sub> film (Ref. [393]) are presented. The two experimental results are in a good agreement. To model the random disor-

der an approach combining LMTO calculations with Monte Carlo simulation was applied [392]. The calculations were performed for a large supercell with randomly generated distribution of Co and Pt atoms over the lattice sites.

It should be stressed that the theoretical spectra shown in Fig. 2.28 have been obtained for the same nominal composition of  $Co_{50}Pt_{50}$ , but different lattice symmetry, long range, and short range order, i.e., different local environments of Co and Pt sites. We can conclude that, when the degree of chemical order decreases the overall shapes of  $\theta_K$  spectra tend to be similar, independent of the crystal lattice type.

Two main structure-dependent effects on the Kerr spectra should be pointed out. They are i) the large change in  $\theta_K$  as the structure changes from the  $L1_1$ type to the  $L1_0$  type and ii) the extremely strong dependence of  $\theta_K$  values for the  $L1_1$  structure on LRO. In particular, for the perfect  $L1_1$  structure, the  $\theta_K$  is unexpectedly quenched at 4 eV, whereas an enhancement of  $\theta_K$  at this energy is expected as is the case of  $L1_0$  and disordered structures.

To describe quantitatively the local atomic arrangement we introduce parameters characterizing the in-plane and out-of-plane coordination [392]. The first neighbor coordination  $N^{\parallel}$ , that describes the number of Co(Pt) atoms surrounded by Pt(Co) in each alternate atomic plane lying perpendicular to the *c* axis, and the corresponding out of plane coordination  $N^{\perp}$  were evaluated. The values of  $N^{\parallel}$  and  $\Delta N = N^{\perp} - N^{\parallel}$  are presented in Table 2.2. It was verified that magnitude of  $\theta_K$  in uv-range for the  $L1_1$  structure scales well with the in-plane Pt-Co coordination number  $N^{\parallel}$  (Fig. 2.28(a)). This observation indicates that for a given structure the MO spectra should depend on the relative orientation of magnetization and the crystallographic axes.

It should be noted that the  $\theta_K$  spectra in Fig. 2.28(a,b) for both  $L1_1$  and  $L1_0$  structures were calculated for magnetization direction aligned along the *c*-axis. This means that for the perfectly ordered crystals the magnetization is oriented perpendicularly to the alternating atomic planes consisting of Pt and Co atoms only, with a threefold rotational symmetry for  $L1_1$  and a fourfold symmetry for the  $L1_0$  structure respectively.

To investigate the orientation effects, calculations for two orientations of magnetization:  $\mathbf{M} \parallel c$  and  $\mathbf{M} \perp c$  were carried out. For the CoPt systems studied, the MO anisotropy was defined as the difference of  $\theta_K$  for different magnetization directions,  $\Delta \theta_K = \theta_K^{\parallel} \cdot \theta_K^{\perp}$ . The calculated  $\Delta \theta_K$  curves are presented in Fig. 2.29 (a,b). As it can be seen,  $\Delta \theta_K$  for  $L1_1$  is much higher than for the  $L1_0$  structure, with the  $\Delta \theta_K$  magnitude in the uv range being comparable with  $\theta_K$  itself. The magnitude of the  $\Delta \theta_K$  decreases systematically with the decrease of S parameter and vanishes for  $S \leq 0.25$ , whereas for the  $L1_0$  structure the changes of  $\Delta \theta_K$  energy dependence are more complex.

It should be noted that the structures studied are uiniaxial crystals and they can exhibit an optical anisotropy. However, the calculated optical anisotropy does not overcome 10 % in all the energy range studied, and, as it was verified, the anisotropy of the Kerr rotation comes basically from the anisotropy of the off-diagonal part of the optical conductivity tensor.

As can be seen from Figs. 2.28 and 2.29, the most prominent difference between the MO spectra calculated with the magnetization oriented  $\mathbf{M} \parallel c$ and  $\mathbf{M} \perp c$  are for the perfect  $L1_1$  structure. When the magnetization direction changes from parallel to perpendicular to the *c* axis, the corresponding symmetry of the crystal with respect to the quantization axis lowers from  $D_{3d}$  to  $C_{2h}$  point symmetry, and the numbers of Co-Pt bonds perpendicular to the actual magnetization direction changes from N=0 to N=6 respectively. The above crystal-structure related parameters are responsible for the small  $\theta_K$  magnitude around 4 eV when  $\mathbf{M} \parallel c$ , and the large magnitude of  $\theta_K$  when  $\mathbf{M} \perp c$ . One can speculate that the effect of "reducing" the MO transitions at 4 eV in  $L1_1$  structure is associated with the symmetry related selection rules for the optical transition when the magnetization direction is perpendicular to the close-packed atomic planes.

Modification of the magneto-optical spectra with the decrease of the long range order parameter can be related with the change in the local arrangement of Co and Pt sites. That is the change of spatial orientation of the Co-Pt bonds directions and the lowering of local site symmetry with respect to the magnetization direction.

To relate the magneto-optical anisotropy with the electronic structure and the anisotropy of the magnetic properties of the systems studied, the calculated spin  $M_S$  and orbital  $M_L$  magnetic moments as well as the difference in the total energy,  $\Delta E$ , are summarized in Table 2.2. The total energy calculations show that the energy of MCA,  $\Delta E$ , is equal to 1.34 meV for the  $L1_1$  and 1.06 meV for the  $L1_0$  ordered structures, respectively, and in both cases the easy magnetization axis is parallel to the c axis. The  $\Delta E$  value decreases with the decrease of LRO.

One can see from Table 2.2 that Co and Pt orbital moments are strongly dependent on the magnetization direction (as opposed to  $M_S$  for which the differences are negligible). The difference  $\Delta M_L = M_L^{\parallel} - M_L^{\perp}$  provides information on the  $M_L$  orientation dependence. The values of  $\Delta M_L$  on Co and Pt sites for  $L1_1$  structures are similar but differ in sign. At the same time, the  $\Delta M_L$  value on the Pt site for the  $L1_0$  structure is considerably reduced as compared to that on the Co site. For both crystal structures, the  $\Delta M_L$  decreases with a decrease of the S parameter, while no anisotropy effect has been observed for the randomly disordered phase. Since the orbital magnetic moment and the MO effects are both caused by SO coupling, so, as it can be seen (Table 2.2 and Fig. 2.29), both the orbital moment anisotropy and the magneto-optical anisotropy are correlated.

*Table 2.2.* Calculated spin  $M_S$  and orbital  $M_L$  magnetic moments (in  $\mu_B$ ) of Co and Pt in CoPt structures [392]. S is the LRO parameter;  $\Delta E = E^{\perp} - E^{\parallel}$  is the MCA energy (in meV per formula unit);  $\Delta M_L = \mathbf{M}_L^{\parallel} - \mathbf{M}_L^{\perp}$ ;  $\parallel$ ,  $\perp$  denote orientation of magnetization with respect to the *c* axis.  $\Delta N = N^{\perp} - N^{\parallel}$  where  $N^{\parallel}$ ,  $N^{\perp}$  are in-plane and out-of-plane Pt-Co coordination numbers.

	S	$N^{\parallel}$	$\Delta N$	$\Delta E$	site	$\mathrm{M}_S^{\parallel}$	$\mathbf{M}_L^{\parallel}$	$\Delta M_L$
L1 <sub>1</sub>	1	0	6	1.34	Со	1.779	0.096	0.030
					Pt	0.234	0.027	-0.026
	7/8	0.75	4.5	1.12	Co	1.769	0.089	0.022
					Pt	0.239	0.031	-0.021
	5/8	2.25	1.5	0.33	Co	1.756	0.078	0.007
					Pt	0.238	0.039	-0.007
	2/8	3.0	0	0.00	Co	1.753	0.071	0.000
					Pt	0.285	0.055	0.000
	1/8	3.75	0	0.00	Co	1.699	0.056	0.000
					Pt	0.310	0.065	0.000
<i>L</i> 1 <sub>0</sub>	1	0	8	1.06	Co	1.723	0.102	0.038
					Pt	0.339	0.059	-0.017
	7/9	0.89	5.33	0.86	Co	1.715	0.089	0.026
					Pt	0.310	0.053	-0.013
	1/2	2.0	3.0	0.17	Co	1.706	0.083	0.016
					Pt	0.283	0.051	-0.005
fcc	${\sim}0$	$\sim 3$	$\sim 0$	$\sim 0.00$	Co	1.743	0.066	0.000
					Pt	0.291	0.059	0.000

The correlation between the  $\Delta M_L$  and  $\Delta \theta_k$  and the structural parameters is evident. Also for the systems studied, it was found that a strong correlation exists between the magnitude of  $\Delta \theta_K$ ,  $\Delta M_L$ , and the structural anisotropy characterized by  $\Delta N$ . When  $\Delta N$  vanishes, the anisotropies tend to zero. Moreover, the  $\Delta \theta_K$  magnitudes in the uv range are related to the  $\Delta M_L$  on Pt sites, thus, in principle,  $\Delta M_L$  can be accessible from  $\Delta \theta_K$  measurements.

To elucidate the origin of the  $\Delta \theta_K$ , the dependence of magneto-optical anisotropy on the optical matrix elements, exchange splitting and SO interaction was examined [392]. The results clearly demonstrate that the main effect of magneto-optical anisotropy comes from changes of orbital character of the wave function due to a rotation of the magnetization axis. Besides, the SO coupling of Pt is mainly responsible for the large MO anisotropy observed in the equiatomic CoPt alloys studied. Although both anisotropies have a common origin, and appear simultaneously in the Co–Pt compounds studied, the relationship between the orbital moment anisotropy and MO anisotropy is very complicated. This is because the  $\Delta M_L$  is the integral property of the occupied states, whereas accompanying magneto-optical anisotropy is an energy dependent quantity and is due to the spin and orbital polarization of occupied initial and empty final states between which electronic excitations arise.

Summarizing the above discussion it can be concluded that, although the large SO interaction (lent by Pt to the CoPt system) plays a crucial role in the formation of the MO spectra of CoPt compounds, it is not a sufficient condition for a large Kerr effect enhancement at around 4 eV. The observed change in the orientation dependence of MO spectra with the crystal structure and chemical order can not be directly related to a change of the Pt SO coupling strength. It is rather due to the difference in the orbital character of Pt *d* states which arises as a result of hybridization details specific for the  $L1_1$  and  $L1_0$  structures and which is manifested in the orbital moment anisotropy on the Pt site (Table 2.2).

# 2.1.4 XPt<sub>3</sub> compounds (X=V, Cr, Mn, Fe and Co)

3d transition metals and Pt form binary alloys in a wide range of concentration ratios having various magnetic properties. At stoichiometric compositions the alloys usually order. When the transition metal (represented by X) is one of the elements among V through Ni, ordered XPt has the CuAuI-type (or  $L1_0$ ) structure and XPt<sub>3</sub> and X<sub>3</sub>Pt have the Cu<sub>3</sub>Au-type (or  $L2_1$ ) structure. [394, 395] Among the Cu<sub>3</sub>Au-type ordered alloys with X= V to Ni, ferromagnetism is found for MnPt<sub>3</sub>, [396] Fe<sub>3</sub>Pt, [397] CoPt<sub>3</sub>, [398] and Ni<sub>3</sub>Pt, [399] while FePt<sub>3</sub> exhibits antiferromagnetism with a (1/2,1/2,0) magnetic ordering vector. For VPt<sub>3</sub> and CrPt<sub>3</sub>, it is widely believed that the magnetic moments on Pt sites align in an anti-parallel direction to those on the 3*d* transition metal sites, forming a ferrimagnetic ordering.

The calculated polar Kerr spectra of VPt<sub>3</sub>, CrPt<sub>3</sub>, and MnPt<sub>3</sub> is shown in Fig. 2.30, and those of FePt<sub>3</sub> and CoPt<sub>3</sub> in Fig. 2.31 [400]. All Kerr spectra given in Figs. 2.30 and 2.31 pertain to the (001) magnetization direction, and are due to the interband optical conductivity tensor only, i.e., no intraband contributions to the conductivity are considered. A Lorentzian broadening with a half width at half maximum of 0.4 eV, taking account of the effects of finite lifetimes and of the experimental resolution, has been applied to all optical conductivity spectra.

In Fig. 2.30, the recently measured Kerr spectra of  $MnPt_3$  are also shown [300]. As one can see from Figs. 2.30 and 2.31, the Kerr spectra of  $VPt_3$ ,  $CrPt_3$ , and  $MnPt_3$  are very similar, as are those of FePt\_3 and CoPt\_3. This is the reason why we show the spectra in this combination together. The theoretical Kerr rotations of  $VPt_3$ ,  $CrPt_3$ , and  $MnPt_3$  have their minimum at the same photon energy of 0.8 eV, followed by a zero crossing at 2 eV. This similarity is partially observed in the Kerr ellipticity too. The Kerr rotations of FePt\_3 and CoPt\_3, however, are distinctly different, as they have no zero crossing, and



*Figure 2.30.* Calculated polar Kerr rotation ( $\theta_{\rm K}$ ) and Kerr ellipticity ( $\varepsilon_{\rm K}$ ) spectra of VPt<sub>3</sub>, CrPt<sub>3</sub>, and MnPt<sub>3</sub> in the AuCu<sub>3</sub> crystal phase with (001) magnetization orientation [400]. The theoretical spectra are all calculated with a relaxation-time broadening of 0.4 eV, and result from the interband optical conductivity only. The experimental data shown are those of MnPt<sub>3</sub> (Ref. [300]).



Figure 2.31. As Fig. 2.30, but for the theoretical polar Kerr spectra of FePt<sub>3</sub> and CoPt<sub>3</sub> [400].

exhibit two minima, one smaller minimum at 1.3 eV, and a larger one at 4.7 eV. Noticeable further is the large value for the Kerr rotations that are predicted by density-functional theory for these compounds.

The largest Kerr rotation is found for MnPt<sub>3</sub>, which reaches a value of  $-1.5^{\circ}$ at 0.8 eV. But also the Kerr rotation of the as yet unmeasured CrPt<sub>3</sub> alloy is surprisingly large, having a peak value of  $-0.9^{\circ}$  at 0.8 eV, larger than that of the transition metals Fe and Co. Further the Kerr rotations predicted for FePt<sub>3</sub> and CoPt<sub>3</sub> have peak values of  $-1.0^{\circ}$  to  $-1.1^{\circ}$  at 4.7 eV, and are also substantial. With respect to the magnitudes of the Kerr rotations displayed in Figs. 2.30 and 2.31, there are three points to be mentioned. In the first place, the precise peak magnitude depends on the applied broadening parameter. A larger broadening than 0.4 eV would generally lead to slightly smaller, but broader spectral peaks. Secondly, the neglect of an intraband contribution to the optical conductivity can play a role for VPt<sub>3</sub>, CrPt<sub>3</sub> and MnPt<sub>3</sub>. An intraband or free-electron contribution to the optical conductivity can be of importance for the Kerr rotation spectrum at small photon energies. As the main Kerr rotation peak of the compounds in Fig. 2.30 occurs at a small energy, the size of this peak will become reduced when a large intraband contribution is present. For CoPt<sub>3</sub> and FePt<sub>3</sub>, the intraband contribution is less important, because these compounds already have a relatively small Kerr rotation at low energies (see Fig. 2.31). Thirdly, it should be noted that the *ab initio* Kerr spectra are essentially calculated for zero temperature. If the Kerr spectra are measured at room temperature, where the magnetization is smaller, then the over-all size of the measured Kerr rotation will be smaller too.

In Fig. 2.30 the recently measured Kerr spectra of ordered  $MnPt_3$  are also shown [300, 301]. These spectra were measured from an annealed thin film of  $MnPt_3$  on a quartz substrate, but from the substrate side, i.e., through quartz [300]. This implies that these can be enhanced over the Kerr spectra measured in air by a factor of about one and a half. Within the limitations concerning the size of the Kerr rotation mentioned above, and the possible influence of the quartz substrate on the Kerr spectra, it can as yet only be concluded that the shape of the theoretical and experimental Kerr rotation and ellipticity spectra are in good agreement.

Density-functional theory predicts a large Kerr effect in the XPt<sub>3</sub> alloys. Noticeably, the Kerr rotations predicted are much larger than those calculated for, e.g., Fe, Co, or Ni. An important issue is therefore to identify the origin of the large Kerr effect in these compounds. To this end, we examine the dependence of the MO spectra on the exchange splitting, the SO interaction, and the optical transition matrix elements. Since the Kerr effect in each of these compounds is of the same origin, we do this only for one compound, CrPt<sub>3</sub>. The exchange splitting and the SO coupling are studied by scaling the corresponding terms in the Hamiltonian artificially with a constant prefactor. This is done in a non-self-consistent way, i.e., after self-consistency has been achieved, only one iteration is performed with the modified Hamiltonian (a self-consistent calculation would lead to a different band structure). From the



*Figure 2.32.* Study of the influence of the exchange splitting (**M**), spin-orbit (SO) coupling, and optical transition matrix elements (ME) on the Kerr rotation of  $CrPt_3$  [400]. The upper panel shows the effect of multiplying the spin-polarized part of the Dirac Hamiltonian with a constant factor on the Cr site or on the Pt site. The middle panel shows the effect of multiplying the SO-coupling part of the Hamiltonian on Cr or on Pt with a constant prefactor (see text). The lower panel depicts the effect of setting the matrix elements on Cr or on Pt to zero.

resulting band structure the optical spectra are then computed. These modifications can in addition be made within each atomic sphere, so that we can investigate the separate effects of these quantities on Cr and on Pt.

The outcomes of these model calculations for the Kerr rotation of  $CrPt_3$  are shown in Fig. 2.32. In the upper panel, the importance of the exchange splitting is illustrated. When the exchange splitting on Pt is set to zero, the Kerr rotation remains as it is. But when we do the same for the exchange splitting on Cr, the Kerr rotation totally vanishes. This implies that the exchange splitting due to Cr is crucial for the sizable Kerr rotation, but that of Pt is unim-



*Figure 2.33.* Influence of the exclusion of various optical matrix elements on the Pt site on the real part of the diagonal optical conductivity ( $\text{Re}[\sigma_{xx}]$ ), the imaginary part of the off-diagonal optical conductivity ( $\text{Im}[\sigma_{xy}]$ ), and Kerr rotation [400]. The notation ME<sub>Pt</sub>(p-d)=0 means that on the Pt site the p–d interband transitions and the d–p interband transitions are excluded from the optical matrix element.

portant. Furthermore, an enhancement of the exchange splitting on Cr by a factor of two (dashed line) leads to a much larger peak in the Kerr rotation. The middle panel of Fig. 2.32 shows the dependence on the SO coupling. If we set the SO coupling on Cr to zero, the Kerr rotation essentially doesn't change (dotted line). On the other hand, when the SO coupling on Pt is zero, the Kerr rotation almost disappears (dashed line). Thus, the SO coupling of Pt is equally responsible for the large Kerr rotation as is the exchange splitting of Cr. An intermediate scaling of the SO coupling of Pt by a factor of 0.5 leads to an approximately half as large Kerr angle, thereby illustrating the almost linear dependence of the Kerr effect on the SO interaction of Pt in these

compounds. Finally, the lower panel in Fig. 2.32, displays the importance of the site-dependent matrix elements. Within an atomic sphere about one of the atomic positions, the optical transition matrix elements, are set to zero. If this is done for the matrix elements on Cr, the Kerr rotation doesn't change much. But if the matrix elements on Pt vanish, a large impact on the Kerr rotation is found (dashed curve). This indicates that the matrix elements on the Pt site are more important for bringing about the large Kerr peak at 1 eV, than those of Cr. Making the matrix elements zero gives only an impression of which site the main contribution comes from. To obtain information about the bands that are responsible for the Kerr peak, it is instructive to exclude a particular transition matrix element. Due to the selection rules for optical transitions, these transitions can only take place between band states with an angular momentum difference of  $\pm 1$ . By excluding for instance the p-d transition matrix element we can investigate the contribution of these type of transitions. However, as the transition matrix must be Hermitian, we have to exclude also the conjugated transition, i.e., both p-d and d-p transitions. The results of an investigation of the importance of the various transitions on Pt are shown in Fig. 2.33, for the real part of the diagonal optical conductivity,  $Re[\sigma_{xx}]$ , the imaginary part of the off-diagonal conductivity,  $Im[\sigma_{xy}]$ , and the Kerr rotation. The upper and middle panel of Fig. 2.33 show that both  $\operatorname{Re}[\sigma_{xx}]$  and  $\operatorname{Im}[\sigma_{xy}]$  are strongly reduced when the p-d and d-p interband transitions are excluded, more than when the d-f and f-d transitions are excluded. Especially the off-diagonal conductivity almost disappears in the energy region around 1 eV if the p-d and d-p transitions on the Pt sites are excluded. Because this peak in the off-diagonal conductivity at 1 eV is responsible for the peak in the Kerr rotation spectrum, this shows that the d-p and p-d transition matrix elements on Pt account for most of the Kerr effect in this frequency region. The other transitions, s-p and d-f, also have a minor influence, but excluding these still gives approximately the same Kerr rotation (see Fig. 2.33, lower panel). Thus, the d states of Pt, being subject to the strong SO interaction on the Pt site, contribute most to the optical transitions that lead to a large Kerr angle.

From these investigations the following picture of the Kerr effect in these compounds emerges: Pt is the magneto-optically active element, and creates the large Kerr rotation through its large SO interaction. The important magneto-optical transitions are the p–d and d–p transitions on Pt. The 3d elements are magneto-optically not very active. Their role is to supply, through their exchange splitting, hybridized spin-split energy bands. This understanding suggests the following recipe for finding a material having a sizeable Kerr rotation: such a material should contain elements with a large SO coupling, for instance Pt, Bi, or an actinide. Also it should contain an element having a sufficiently large magnetic moment, but this element need not have a strong SO interaction, like for instance Mn. Also should there be a substantial hybridization

between states of these two kinds of constituents. Elements having a large, but local atomic moment, like some of the 4f-elements, are in the latter respect not suited, if the moment is due to unhybridized, localized 4f-states.

The behavior of the magnitude of the peak in the Kerr rotation spectra with respect to the 3d element, as shown in Figs.2.30 and 2.31, and also the dependence of the magnitude of the Kerr effect on the magnetization, can furthermore be understood on the basis of the model calculations. The increase of the peak in the Kerr angle at about 1 eV when going from VPt<sub>3</sub> to MnPt<sub>3</sub> (see Fig. 2.30) is caused by the corresponding increase of the exchange splitting. This is most clearly demonstrated by the scaling of the peak in the Kerr rotation of CrPt<sub>3</sub> with respect to the scaling of the exchange splitting (Fig. 2.32, upper panel). Also it can be understood from this behavior that a reduction of the magnetization at room temperature leads to a reduction of the Kerr rotation. This dependence on the magnetization also explains why the Kerr rotation of FePt<sub>3</sub> is larger than that of CoPt<sub>3</sub>.

A few finals points are worth making with respect to these systems. Our results indicate that the total density of states cannot be used to derive information about the shape or magnitude of the Kerr spectra thereof. Also the dependence of the Kerr spectra in XPt<sub>3</sub> compounds on the crystallographic direction of the magnetization is found to be very small. This finding is consistent with the high degree of isotropy of the AuCu<sub>3</sub> crystal structure. The agreement between the *ab initio* calculated Kerr spectra and the experimental spectra for MnPt<sub>3</sub>, Ref. [300, 301] is very reasonable. Further measurements on these compounds are desirable and needed, in order to obtain a complete picture of the correspondence between experimental and first-principles Kerr spectra.

## 2.1.5 Heusler Alloys

The Heusler alloys NiMnSb, PdMnSb, and PtMnSb have been the subject of intensive experimental and theoretical investigations since the early 1980's [294, 307, 401, 402].

The interest in these compounds arose first from the experimental discovery of an extremely large magneto-optical Kerr rotation of  $-1.27^{\circ}$  in PtMnSb at room temperature [294]. This value was for many years the record Kerr rotation observed in a transition metal compound at room temperature and was therefore called a "giant" Kerr effect. Almost simultaneously with the experimental discovery, the theoretical finding of the so-called "half-metallic" nature of PtMnSb was reported [402]. Half-metallicity means that according to (semirelativistic) band structure theory the material is metallic for majority, but insulating for minority spin electrons [402]. Such a gap for one spin type naturally may give rise to unusual magnetotransport and optical properties. Also the isoelectronic Heusler alloy NiMnSb was predicted to be half-


*Figure 2.34.* Spin-projected, partial densities of state calculated for PtMnSb [403]. Majority spin densities are given by the full curves, minority spin densities by the dotted curves. The half-metallic behavior can be seen from the band gap at the Fermi level, which is present for minority spin, but not for majority spin.

metallic, whereas the isoelectronic compound PdMnSb was predicted not to be half-metallic [402]. On the other hand, the MO Kerr rotations in both NiMnSb and PdMnSb were experimentally found to be much smaller than that of PtMnSb, which resulted in a puzzling combination of features. Experimental efforts were undertaken to verify the proposed half-metallic character of NiMnSb and PtMnSb [404–407], which was subsequently established in the case of NiMnSb [404, 407]. Very recently, also experimental evidence in favor of half-metallicity in PtMnSb was reported [408].

On the theoretical side, several model explanations of the MO spectra of the compounds were proposed [409–411]. One of these was based on a possible loss of the half-metallic character due to spin-orbit (SO) coupling, which was suggested to lead to a symmetry breaking between the different *m*-states of the Sb *p*-bands in the vicinity of the Fermi energy  $E_F$  [409]. Another explanation was based on differences of the semirelativistic effects in NiMnSb and PtMnSb [411], and another one on enhancement of the MO Kerr spectra near the plasma resonance [410]. While the proposed models contain interesting physical mechanisms in themselves, one of the remaining major stumbling blocks was to explain the measured differences in the MO spectra of the isoelectronic NiMnSb, PdMnSb, and PtMnSb.

Only owing to the development of *ab initio* calculations of the MO spectra the detailed quantitative comparison between experiment and first-principles spectra became feasible. The Heusler compounds are, of course, most attractive materials for *ab initio* calculations of their MO spectra on account of the mentioned unusual features.

A detailed investigation of the MO Kerr spectra of NiMnSb, PdMnSb, and PtMnSb was reported in Ref. [403]. Fig. 2.34 shows the spin projected, fully relativistic partial densities of states of PtMnSb. As can be recognized from Fig. 2.34, the partial densities of states for minority spin have evidently a gap at the Fermi level.

A similar behavior was found for NiMnSb, but not for PdMnSb. For all three Heusler compounds in Fig. 2.35 we show the calculated relativistic energy bands and total densities of states (DOS). In the case of PdMnSb, three spin-orbit split energy bands are just above the Fermi level at the  $\Gamma$ -point, therefore half-metallic behavior is not supported for PdMnSb by band structure theory. In the case of NiMnSb and PtMnSb, these important bands are just below  $E_F$ , rendering the half-metallicity in these compounds. The band structure results [403] are in agreement with recent experiments on NiMnSb and PtMnSb, in which half-metallic behavior to a degree of nearly 100% was observed [404, 407, 408].

After having verified the half-metallic band structure property we turn to the MO spectra. In Fig. 2.36 we show the calculated [403] and experimental [294, 401] MO Kerr spectra of the three isoelectronic Heusler compounds. There exists rather good agreement between the experimental Kerr spectra and the *ab initio* calculated ones. Overall, the experimental features are reasonably well reproduced, except for the magnitude of the Kerr rotation of PdMnSb, for which theory predicts larger values than are experimentally observed. The first and important conclusion, which we draw from the correspondence between experimental and calculated Kerr spectra, is: the anomalous behavior of the MO Kerr spectra in these compounds is well described by normal band structure theory.

To investigate the origin of the Kerr spectra, we consider the separate contributions of both the numerator of Eq. (1.175), i.e.  $\sigma_{xy}(\omega)$ , and the denominator,  $D(\omega) \equiv \sigma_{xx}(1 + \frac{4\pi i}{\omega}\sigma_{xx})^{1/2}$ . In Fig. 2.37(a) we show how the separate contributions of numerator and denominator bring about the Kerr angle of NiMnSb. The imaginary part of the inverse denominator (times the photon frequency),  $Im[\omega D]^{-1}$ , displays a typical resonance structure at about 1 eV. The imaginary part of  $\omega \sigma_{xy}$ , i.e.  $\omega \sigma_{xy}^{(2)}$ , displays a double peak structure. The double peak structure of the Kerr rotation results roughly from the product of  $Im[\omega D]^{-1}$  and



*Figure 2.35.* Relativistic, spin polarized energy band structures and total densities of states (DOS) of NiMnSb, PdMnSb, and PtMnSb [403].

 $\omega \sigma_{xy}^{(2)}$ : The first peak in the Kerr rotation at 1.5 eV is predominantly caused by a minimum of the denominator, whereas the second peak in the Kerr rotation at 4 eV is due to a maximum in the off-diagonal conductivity,  $\omega \sigma_{xy}^{(2)}$ . The nature of the peak in Im $[\omega D]^{-1}$  can be understand from the top panel in Fig. 2.37(a), where the complex diagonal dielectric function is shown: its real part,  $\varepsilon_{xx}^{(1)}$ , becomes small at about 1 eV, and its imaginary part,  $\varepsilon_{xx}^{(2)}$ , has a shallow mini-



*Figure 2.36.* Calculated [403] and experimental [294, 401] Kerr rotation ( $\theta_K$ ) and Kerr ellipticity ( $\varepsilon_K$ ) spectra of the Heusler compounds NiMnSb, PdMnSb, and PtMnSb.

mum at 1 eV. The second peak in the Kerr rotation, stems from the maximum in  $\omega \sigma_{xy}^{(2)}$ , which in turn is known to be due to the interplay of SO coupling and spin polarization. Thus, the two similar looking peaks in the Kerr rotation arise from quite a different origin.

In a similar way, we consider the spectra for the compound PdMnSb in more detail, in Fig. 2.37(b). In this compound  $\omega \sigma_{xy}^{(2)}$  is larger than that of NiMnSb in the energy range 1–4 eV. This is simply due to the larger SO interaction on Pd as compared to that on Ni. The inverse denominator Im $[\omega D]^{-1}$ , however, does not exhibit such a strong resonance as it does for NiMnSb. The latter is related to the particular shape of the  $\varepsilon_{xx}^{(1)}$  and  $\varepsilon_{xx}^{(2)}$  spectra. The Kerr rotation



*Figure 2.37.* Decomposition of the Kerr rotation spectrum of NiMnSb (a) and PdMnSb (b) in separate contributions [403]. Top panel: calculated real and imaginary part of the diagonal dielectric function,  $\varepsilon_{xx}^{(1)}$ , respectively  $\varepsilon_{xx}^{(2)}$ . Third panel from the top: The imaginary part of  $[\omega D]^{-1}$  which results from  $\varepsilon_{xx}^{(1)}$  and  $\varepsilon_{xx}^{(2)}$ . Bottom panel: The Kerr rotation which results as a combination of  $\text{Im}[\omega D]^{-1}$  and  $\omega \sigma_{xy}^{(2)}$  (second panel from the top). The experimental Kerr angle spectrum is after van Engen *et al.* [294]

in effect displays the same shape as  $\omega \sigma_{xy}^{(2)}$ , being enhanced at 1–2 eV by the contribution from the denominator.

In Fig. 2.38(a) we show the spectral quantities for PtMnSb. The inverse denominator  $\text{Im}[\omega D]^{-1}$  again displays for PtMnSb a strong resonance at 1 eV, which is even larger than that for NiMnSb. In addition, the off-diagonal conductivity  $\omega \sigma_{xy}^{(2)}$  is for PtMnSb larger than that of PdMnSb, in accordance with the larger SO coupling on Pt. The resulting Kerr rotation has a "giant" peak of  $-1.2^{\circ}$  up to  $-2.0^{\circ}$  depending on the applied lifetime parameter (see Fig. 2.38(a)). These values are in good agreement with the available experimental



*Figure 2.38.* (a): as Fig. 2.37, but for PtMnSb [403]. The experimental data are after Ikekame *et al.* [412] The data for annealed PtMnSb are denoted by ( $\triangle$ ), and those for non-annealed, polished PtMnSb by ( $\circ$ ). The calculated Kerr rotation spectrum is shown for two interband lifetime parameters,  $\gamma = 0.05$  Ry and  $\gamma = 0.02$  Ry. (b): model investigation of the influence of the half-metallic character of PtMnSb on the optical and MO spectra [403]. A non-half-metallic band structure has been modeled in two ways: by artificially shifting  $E_F$  in PtMnSb down, and by increasing the calculated plasma frequency  $\omega_p = 4.45$  eV to 6.40 eV.

Kerr peak values for PtMnSb, which range from about  $-1^{\circ}$  to  $-2^{\circ}$  depending on sample preparation and surface quality [294, 413–420, 412]. Careful investigations of the consequences of sample preparation have been performed by Takanashi *et al.* [416] and Sato *et al.* [420, 412]. These investigations showed that annealing of the PtMnSb sample raises the Kerr angle to a maximum value of  $-2^{\circ}$ , whereas the non-annealed sample's Kerr angle is only  $-1.2^{\circ}$ . The offdiagonal conductivity  $\omega \sigma_{xy}^{(2)}$  was found to be rather insensitive to annealing (see Fig. 2.38(a)) [420, 412]. The main impact of annealing thus evidently occurs in the denominator. The reason for the calculated resonance in the inverse denominator lies again in the frequency dependence of the diagonal dielectric function, which is shown in the top panel of Fig. 2.38(a). The calculated  $\varepsilon_{xx}$  compares reasonably well with the experimental one [412], except for the important frequency of the first zero of  $\varepsilon_{xx}^{(1)}$  which is shifted by about 0.5 eV. This difference leads to a shifted position in the resonance peak of  $\text{Im}[\omega D]^{-1}$ , which in turn results in a shifted main Kerr rotation peak of just the same amount. The position of the maximum in  $\text{Im}[\omega D]^{-1}$  thus predominantly determines the position of the main Kerr rotation peak. We mention in addition that the second maximum in the calculated  $\omega \sigma_{xy}^{(2)}$  at 4.4 eV (see Fig. 2.38(a)) is also present in the experimental spectrum, but at a higher energy of 5.2 eV [412],

The origin of the giant Kerr angle in PtMnSb as compared to the Kerr angles in NiMnSb and PdMnSb can completely be understood from the calculations. In these three compounds, first, the off-diagonal conductivities  $\sigma_{xy}(\omega)$ are quite different, which is a direct result of the different relativistic electronic structure. Although both NiMnSb and PtMnSb are both half-metallic, their  $\omega \sigma_{xy}^{(2)}$  spectra are distinctly different, while on the other hand the  $\omega \sigma_{xy}^{(2)}$ of PdMnSb and PtMnSb have a similar structure, but not a similar magnitude (see Figs. 2.37(a), 2.37(b), 2.38(a)). In the second place, there is the influence of the denominators as exemplified in  $\text{Im}[\omega D]^{-1}$ . These are similar in shape and magnitude for NiMnSb and PtMnSb, but the magnitude of  $Im[\omega D]^{-1}$  in PdMnSb is about a factor of two smaller. We find that this difference relates to the half-metallic nature of both NiMnSb and PtMnSb, which is not present for PdMnSb. From Fig. 2.35 it can be seen that for the half-metallic compounds there are three lesser bands at  $E_F$ . One consequence is that the intraband contribution to  $\sigma_{xx}$  will be smaller (see Eq. (1.229)). In Fig. 2.38(b) we show the impact of the half-metallic character of the band structure on the Kerr rotation of PtMnSb. The calculated plasma frequency in PtMnSb is small,  $\hbar\omega_p = 4.45 \,\mathrm{eV}.$ 

Experimentally a somewhat bigger plasma frequency of  $(6.1 \pm 0.4) \text{ eV}$  was found for PtMnSb, and a smaller  $\hbar \omega_p = (4.9 \pm 0.2) \text{ eV}$  for NiMnSb [421]. One should, however, not forget that the sample purity can affect the plasma frequency through the position of  $E_F$ . To investigate the influence of the half-metallicity, we can artificially shift the Fermi energy down, and calculate the spectra for this position of  $E_F$ , or we can leave  $E_F$  as it is, and model a non-half-metallic band structure by adopting a larger  $\omega_p$ . Both ways to mimic non-half-metallicity have a drastic impact on the resulting Kerr rotation, which becomes reduced by a factor 2! As can be seen from the top panel in Fig. 2.38(b), in the absence of half-metallicity the shape of  $\varepsilon_{xx}^{(1)}$  changes and resembles closely that of PdMnSb (see Fig. 2.37(b)). This is especially so for the model where  $E_F$  is shifted, since this leads to the smaller Im $[\omega D]^{-1}$  and also to a reduction of  $\omega \sigma_{xy}^{(2)}$  at photon energies below 2 eV. The later is due to the exclusion of optical transitions from the SO split bands just below  $E_F$ . The consequence of both models for non-half-metallic behavior is that the maximum in  $\text{Im}[\omega\text{D}]^{-1}$  becomes about two times smaller. The Kerr angles derived in these models resemble now that of PdMnSb in shape, but are bigger, because  $\omega \sigma_{xy}^{(2)}$  is larger than that of PdMnSb. We mention with respect to the influence of the denominator on the Kerr rotation in PtMnSb, that experiments in which the stoichiometry and crystalline sample quality were varied also concluded that the denominator contributed appreciably to the giant Kerr rotation [416, 418–420, 412].

In conclusion, the Kerr spectra of NiMnSb, PdMnSb, and PtMnSb can be fully understood from detailed consideration of their electronic structure. The puzzling abnormalities in the Kerr spectra of these compounds arise from an interplay of compound related differences in the SO interaction, in the halfmetallic character, and also in relative positions of energy bands.

#### 2.1.6 MnBi

Although the MO Kerr effect in MnBi was measured some twenty years ago, only very recently a thorough investigation of the spectral dependency of the Kerr effect under variation of the Mn–Bi composition [422] has been conducted.

The experimental Kerr spectra obtained at 85 K as well as the calculated ones are shown in Fig. 2.39. First-principles theory predicts a very large Kerr rotation in MnBi of about  $-1.75^{\circ}$  at 1.8 eV [423], which is even larger than the measured peak value of  $-1.6^{\circ}$  [422]. Experiment also shows a second maximum in the Kerr angle at 3.4 eV, where theory only indicates a smaller shoulder. A tentative explanation of this difference might be the sample composition, which is in experiment  $Mn_{1,22}Bi$  [422, 424]. There is thus an excess of Mn in the sample. To examine the changes caused by the excess of Mn, a test calculation for a hypothetical Mn<sub>2</sub>Bi compound in the Heusler C<sub>1b</sub> structure (i.e., MnMnBi) was made, where each Mn atom is tetragonally surrounded by Bi [423]. In the (111) direction this compound has a trigonal symmetry, like the (0001) NiAs phase. The calculated Kerr spectra of Mn<sub>2</sub>Bi are also shown in Fig. 2.39 (dotted curve). In its Kerr rotation there is a peak at about 4.3 eV and a smaller one at 2 eV, which is at the same position as the main peak of MnBi. As Mn<sub>2</sub>Bi in this structure is only a hypothetical compound, an educated guess was used for the lattice constant. The position of the peak at about 4 eV is rather sensitive to the lattice constant value. Thus, if the stoichiometry shifts from MnBi to  $Mn_2Bi$  there appears to be a tendency to reduce the first peak at 1.8 eV and to enhance the peak at about 3.5 eV. This corresponds exactly to what is seen in the experimental Kerr spectrum for the  $Mn_{1,22}Bi$ 



*Figure 2.39.* Calculated and experimental Kerr spectra of Mn–Bi compounds [423]. The Kerr rotation is denoted by  $\theta_{\rm K}$ , and the Kerr ellipticity by  $\varepsilon_{\rm K}$ . The theoretical spectra are calculated for MnBi in the NiAs structure, for two lifetime broadening, and for hypothetical Mn<sub>2</sub>Bi in the Heusler C<sub>1b</sub> structure. The experimental Kerr spectra were measured at 85 K on a Mn<sub>1.22</sub>Bi film [422].

composition. Other recent experiments on MnBi samples with an almost 2:1 Mn–Bi ratio confirm the trend of an increased Kerr rotation above 3 eV [425].

A further feature of the experimental Kerr rotation is that it exhibits a sign reversal at 0.9 eV. This sign reversal is actually also given by theory, but only for a smaller broadening parameter. This is consistent with the observation that experimentally it disappears in the room-temperature Kerr rotation [422, 426, 427]. Lastly, we mention that there appears to be a substantial intraband contribution to the conductivity present in the sample. In the calculations shown in Fig. 2.39 the intraband conductivity was accounted for by adding a Drude-type conductivity to the calculated interband conductivity. For this Drude conductivity the calculated plasma frequency and an estimated Drude broadening parameter (which are  $\omega_p = 0.26$  Ry and  $\gamma_D = 0.02$  Ry for MnBi) were used. But, as adding a Drude conductivity shifts especially the Kerr ellipticity below 3 eV upwards, we would judge that in the sample there is likely a larger intraband contribution to the conductivity. This can be due to some disorder and the Mn–Bi stoichiometry.

The Kerr spectra depends on the MO conductivity spectra in an entangled way, so that it is difficult to assign features in the Kerr spectra to particular



*Figure 2.40.* Calculated absorptive parts of the optical conductivity,  $\sigma_{xx}^{(1)}$  and  $\sigma_{xy}^{(2)}$ , for MnBi and Mn<sub>2</sub>Bi [423].

band transitions. The absorptive parts of the optical conductivity,  $\sigma_{xx}^{(1)}$  and  $\sigma_{xy}^{(2)}$ , however, relate directly to the interband optical transitions, and provide therefore more physical insight.

These absorptive parts of the conductivity tensor are shown for MnBi and Mn<sub>2</sub>Bi in Fig. 2.40. The main peak in the Kerr rotation of MnBi is due to the maximum in  $\sigma_{xy}^{(2)}(\omega)$  at 2 eV. Several kinds of dipolar optical transitions contribute to the broad structure in  $\sigma_{xx}^{(1)}$ . The main contributions originate from p-d and d-p transitions. The peak in  $\sigma_{xy}^{(2)}$  is, however, mainly due to transitions from Bi *p*-like states.

From these investigations the following picture of the Kerr effect in MnBi emerges: manganese has the required big magnetic moment of  $3.71 \,\mu_{\rm B}$ , while Bi has a small induced moment of  $-0.10 \,\mu_{\rm B}$ . In an applied field the small moment on Bi shifts to Mn (with sign reversed), so that then the total calculated moment compares well with the moment obtained from the saturation magnetization of  $(3.84\pm0.03) \,\mu_{\rm B}$  [428]. Thus, in the interplay of exchange splitting and spin-orbit coupling leading to the record Kerr effect, Mn brings in the exchange splitting and Bi the spin-orbit coupling. The degree of hybridization between Mn and Bi, furthermore, can be recognized from the partial densities of states (not shown). There is a strong hybridization between the Bi and Mn *p*-type states as well as Bi and Mn *d*-type states. The magneto-optically active transitions take place mainly on Bi, from occupied *p*- to unoccupied *d*-states.

We can conclude that the first-principles electronic structure calculations give a satisfactory description of the giant Kerr rotation in MnBi. The difference between the experimental and *ab initio* Kerr rotation at 3.4 eV is anticipated to be related to the stoichiometry of the sample.

### 2.1.7 Chromium spinel chalcogenides

Spinels have the general formula  $M_A^{2+}(M_B^{3+})_2X_4$ , where  $M_A^{2+}$  and  $M_B^{3+}$  are di- and trivalent cations, respectively ( $M_A=Mg$ , Mn, Fe, Co, Ni, Cu, Zn, Cd;  $M_B$ =Cr, Co), and X stands for a chalcogen O, S, Se or Te. Among the transition metal spinels the copper-chromium spinels  $CuCr_2X_4$  (X=S, Se, Te) play a special role. While many other chromium spinels and particularly most oxides are insulators which order antiferromagnetically, CuCr<sub>2</sub>S<sub>4</sub>, CuCr<sub>2</sub>Se<sub>4</sub>, and CuCr<sub>2</sub>Te<sub>4</sub> are metallic and order ferromagnetically with Curie temperatures well above room temperature, e.g.  $CuCr_2S_4(T_c=377 \text{ K})$ ,  $CuCr_2Se_4(T_c=430 \text{ K})$ K), and CuCr<sub>2</sub>Te<sub>4</sub> ( $T_c$ =360 K) [429]. These compounds were first synthesized by Hahn et al. [430] in 1956 while their magnetic properties have been reported by Lotgering in 1964 [431]. The metallic character and the magnetic moment of approximately 5  $\mu_B$  per formula unit, i.e. for two Cr atoms [429], have promoted interest in consideration of these compounds as promising materials for MO devices. The magneto-optical polar Kerr effect measurements on CuCr<sub>2</sub>Se<sub>4</sub> single crystals between 0.55 and 5.0 eV show [432] that the Kerr ellipticity  $\epsilon_K$  reaches  $-1.19^\circ$  at 0.96 eV. The figure of merit  $R^{1/2}(\theta_K^2 + \epsilon_K^2)^{1/2}$ , where R is the optical reflectivity has a maximum value of  $0.84^{\circ}$  at 0.88 eV which is as high as in PtMnSb ( $0.83^{\circ}$  at 1.57 eV). Although CuCr<sub>2</sub>Se<sub>4</sub> doesn't contain any atom with strong spin-orbit coupling (like Pt in PtMnSb), it exhibits almost the same MO properties as PtMnSb.

The fully relativistic spin-polarized energy band structure of ferromagnetic  $CuCr_2Se_4$  is rather complicated [433]. It may, however, be understood from the total and partial density of states (DOS) presented in Fig. 2.41. The occupied part of the band structure can be subdivided into two regions separated by an



*Figure 2.41.* Fully relativistic, spin-polarized total (in states/(unit cell eV)) and partial (in states/(atom eV)) density of states calculated for  $CuCr_2Se_4$ .

energy gap of about 6 eV. The bands in the lowest region have mostly a Se s character with some amount of Cu and Cr sp character mixed in. The highest region can be characterized as a bonding combination of Cu and Cr d and Se p states. This complex is separated from the anti-bonding states by a pseudo–gap around the Fermi level. The antibonding states are created mostly by the Cr d states. Another pseudo–gap arises above the Cr d band at about 4 eV above the Fermi energy.

Table 2.3 presents the experimental and calculated spin and orbital magnetic moments (in  $\mu_B$ ) of CuCr<sub>2</sub>X<sub>4</sub>. The orbital magnetic moment is rather small for all three atoms due to small SO coupling. The calculated magnetic moment of the Cr 3*d* electrons is 2.824  $\mu_B$  and agrees well with the experimental value obtained by Colominas [435] using polarized neutron diffraction measurements (2.81±0.11  $\mu_B$ ). Theoretical net magnetization per formula unit CuCr<sub>2</sub>Se<sub>4</sub> is equal to 5.282  $\mu_B$ .

The main trend in the electronic structure of the sequence of  $CuCr_2X_4$  compounds (X= S, Se, Te) results from the characteristic trend in the chalcogenide p wave functions and from the systematic change of the lattice parameters.

Compound	atom	$M_{total}$ [436]	$M_s$	$M_l$	$M_{total}$	Exper.
	Cu	-0.32	-0.078	-0.011	-0.089	$-0.07 \pm 0.02$
$CuCr_2S_4$	Cr	3.25	2.679	-0.027	2.652	$2.64{\pm}0.04$
	S	-0.27	-0.098	-0.001	-0.099	$-0.05 \pm 0.11$
CuCr <sub>2</sub> Se <sub>4</sub>	Cu	-0.26	-0.073	-0.009	-0.082	0.01±0.13
	Cr	3.54	2.833	-0.009	2.824	$2.81 {\pm} 0.11$
	Se	-0.36	-0.137	-0.005	-0.142	$-0.25 \pm 0.14$
CuCr <sub>2</sub> Te <sub>4</sub>	Cu	-0.19	-0.096	-0.006	-0.102	$0.05 {\pm} 0.14$
	Cr	3.74	3.166	0.021	3.187	$3.11 \pm 0.16$
	Te	-0.48	-0.202	-0.011	-0.213	$-0.25 \pm 0.14$

*Table 2.3.* The experimental and calculated spin and orbital magnetic moments (in  $\mu_B$ ) of CuCr<sub>2</sub>X<sub>4</sub>. The experimental data for CuCr<sub>2</sub>S<sub>4</sub> are from Ref. [434], and for CuCr<sub>2</sub>Se<sub>4</sub> and CuCr<sub>2</sub>Te<sub>4</sub> from Ref. [435].

The counteraction of screening by inner atomic shells and of relativistic effects leads to the characteristic trend in the position of the atomic p state and hence of the center of gravity of the chalcogenide p band, monotonically increasing from S to Te.

On the other hand, the centers of gravity for Cu and Cr d bands monotonically decreases from CuCr<sub>2</sub>S<sub>4</sub> to CuCr<sub>2</sub>Te<sub>4</sub>. The SO splitting of Cu d center of gravity is equal 0.29 eV. For Cr d states this value is smaller and equal to 0.09 eV for all three compounds. But SO splitting for chalcogenide p states shows one order of magnitude increase from S (0.11 eV) to Te (1.24 eV). The p bandwidth is monotonically increasing from S to Te due to the increasing extension of the atomic wave function, although the lattice constant increases too. The increasing of the lattice constant from S to Te leads to the monotonic increase of the spin polarization of the Cr 3d electrons (see Table 2.3).

After the consideration of the band structure property we turn to the MO spectra. In Fig. 2.42 we show the calculated and experimental [432] MO Kerr spectra of the three isoelectronic  $CuCr_2X_4$  compounds. There exists rather good agreement between the experimental Kerr spectra and the *ab initio* calculated one for  $CuCr_2Se_4$ . Overall, the experimental features are reasonably well reproduced, except for the magnitude of the second Kerr rotation peak of  $CuCr_2Se_4$ , for which theory predicts smaller values than are experimentally observed. There is also a small energy shift of about 0.1 eV in the position of the main Kerr rotation and ellipticity peaks in  $CuCr_2Se_4$ . We can conclude, therefore, that the anomalous behavior of the MO Kerr spectra in  $CuCr_2Se_4$  is well described by band structure theory.



*Figure 2.42.* Calculated and experimental Kerr rotation ( $\theta_K$ ) and Kerr ellipticity ( $\varepsilon_K$ ) spectra of the CuCr<sub>2</sub>X<sub>4</sub> compounds. The experimental data are those of [432].

# 2.1.8 Fe<sub>3</sub>O<sub>4</sub> and Mg<sup>2+</sup>-, or Al<sup>3+</sup>-substituted magnetite

The metal-insulation transition (MIT) has fascinated theorists and experimentalists for many years. This transition is associated with Sir N. Mott who laid down the foundations for physical understanding of this phenomenon [437–440]. One of the most famous MIT compounds is magnetite,  $Fe_3O_4$ , which exhibits the so-called Verwey metal-insulation transition [441].

Historically, magnetite, discovered before 1500 B.C., is the first known magnet and is extensively used for industrial applications, notably in magnetic recording. Most of the properties of magnetite have been thoroughly studied and are well documented [442, 443]. However, the electronic structure of  $Fe_3O_4$  as well as that of many other MIT compounds is still a subject of debate [444–448].

 $Fe_3O_4$  is a strongly correlated 3d compound which is ferrimagnetically ordered below a high transition temperature (~850 K). The valence of various atoms is described by the formal chemical formula,  $Fe_{\Lambda}^{3+}[Fe^{2+}Fe^{3+}]_{B}(O^{2-})_{4}$ . The tetrahedral lattice sites (A sites) in the inverse spinel structure are occupied by  $Fe^{3+}$  ions, whereas the octahedral lattice sites (B sites) are occupied alternately by equal numbers of Fe<sup>2+</sup> and Fe<sup>3+</sup>. At  $T_V$ =120 K Fe<sub>3</sub>O<sub>4</sub> undergoes a first-order phase transition (Verwey transition) [441]. This is a particular MIT that has been studied for quite some time [449]. The Verwey transition is characterized by an abrupt increase in the electrical conductivity by two orders of magnitude on heating through  $T_V$  [450–452]. Verwey and co-workers [441, 453] were the first to point out that this transition is associated with an electron localization-delocalization transition. The Fe<sup>2+</sup> ion can be regarded as an "extra" electron plus an  $Fe^{3+}$  ion. When all B sites are equivalent, the "extra" electron is moving between  $Fe_B^{3+}$  ions and the system is a mixed valent metal, with average Fe<sub>B</sub>-valence, Z=2.5. The Verwey phase transition below  $T_V$  is accompanied by long range charge ordering (LRCO) of Fe<sup>3+</sup> and  $Fe^{2+}$  ions on B1 and B2 sites of the B sublattice. Indeed, studies by electron and neutron diffraction and nuclear magnetic resonance [454-456] show that below  $T_V$  the B1 and B2 sites are structurally distinguishable with the crystal structure slightly distorted because of the charge ordering. Just how these charges arrange themselves has been the subject of debate [449] since Verwey first proposed that, below  $T_V$ , all Fe<sup>3+</sup><sub>B</sub> and Fe<sup>2+</sup><sub>B</sub> sit on different chains [441].

The electronic structure of  $Fe_3O_4$  has been investigated experimentally by means of soft X-ray spectroscopy [457–459], Seebeck-effect measurements [460, 461], photoelectron spectroscopy [462–469], optical [470, 471] and MO spectroscopies [472–479] and by magnetic dichroism [480, 481]. The optical data [471] indicate a gap of 0.14 eV between occupied and empty electronic states and also show a strong temperature dependence of the optical conductivity in the energy region of 0 to 1 eV.

The interpretation of the optical and MO spectra of  $Fe_3O_4$  is very difficult due to the existence of three kinds of iron atoms, i.e.  $Fe_B^{2+}$ ,  $Fe_B^{3+}$  and  $Fe_A^{3+}$ . The substitution for one of the types of iron ions by non-magnetic ions provides a possibility for distinguishing transitions from various sites. There are several such experimental studies in the literature. Simsa and co-workers reported the polar Kerr rotation and ellipticity of Fe<sub>3</sub>O<sub>4</sub> as well as the influence of a systematic substitution of Fe<sup>2+</sup> by Mn<sup>2+</sup> in the 0.5–3.0 eV energy range [474, 475]. Zhang and co-workers reported the polar Kerr spectra and the offdiagonal element of the dielectric tensor of Fe<sub>3</sub>O<sub>4</sub> between 0.5 and 4.3 eV. They also reported spectra of Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub> and MgFe<sub>2</sub>O<sub>4</sub> between 0.5 and 5.0 eV [472]. Finally, recent investigation of the optical and MO spectra of Fe<sub>3</sub>O<sub>4</sub> and Al<sup>3+</sup> and Mg<sup>2+</sup> substitution has been carried out in Ref. [473].

Energy band structure calculations for  $Fe_3O_4$  in the high temperature cubic phase have been presented first in Ref. [482] using the self-consistent spinpolarized augmented plane wave method with the local spin-density approximation. The calculations show that  $Fe_3O_4$  is a half-metallic ferrimagnet. The Fermi level crosses only the minority spin energy bands consisting of  $t_{2g}$  orbitals on the Fe(B) sublattice. There is an energy gap for the majority spin bands at the Fermi level. A similar energy band structure of  $Fe_3O_4$  was obtained in the Ref. [483] using the LMTO method. The energy band structure for charge ordering in the low temperature phase of  $Fe_3O_4$  has been calculated in Ref.s [484, 485] using the LMTO method in the LSDA+U approximation.

Details concerning the mechanism of the Verwey transition and the type of LRCO, are still unclear. Many elaborate theories for the Verwey transition have been proposed. Anderson [486] pointed out the essential role of short-range charge ordering (SRCO) in the thermodynamics of the transition. The observed entropy change in the transition  $[(\sim 0.3 \text{ to } 0.35)R/B\text{-site mole}]$  is decisively smaller than the  $R \ln 2=0.69R$  expected in a complete order-disorder transition. Anderson interpreted the Verwey transition as a loss of the LRCO of the "extra" electrons on the *B* sublattice at temperatures above  $T_V$  while the short-range charge order is maintained across the transition. Using a Hartree-Fock analysis, Cullen and Callen [487–489] showed that an ordering transition could occur in Fe<sub>3</sub>O<sub>4</sub> as a function of the ratio V/B, where *B* is the band-width of the "extra" electrons in the absence of disorder. The transition in this case is of second order, while experimentally a first-order transition is observed. The conduction mechanisms in Fe<sub>3</sub>O<sub>4</sub> have been reviewed by Mott [490–492] (see also Ref.s [449, 493]).

A basic problem concerning magnetite is that both the localization of the valence states and the mixing of the oxygen p states and iron d states are considerable. A detailed theoretical study of the electronic structure, optical and MO properties of Fe<sub>3</sub>O<sub>4</sub> in the low temperature phase was presented in Ref. [485]. It was found that the optical and MO spectra are rather insensitive to the precise value of  $U_{eff}$ . The LSDA+U band structure calculations with  $U_{eff}$  varying from 4 to 6 eV provide the optical and MO spectra in reasonable agreement with the experimental data. On the other hand, the value of the energy gap strongly depends on the value of  $U_{eff}$ . We set the  $U_{eff}$  to 4.0 and 4.5 eV for Fe<sup>2+</sup> and Fe<sup>3+</sup> ions, respectively. These values give a band gap of 0.19 eV.



Figure 2.43. Crystal structure of Fe<sub>3</sub>O<sub>4</sub>.

Fe<sub>3</sub>O<sub>4</sub> crystallizes in the face-centered cubic (FCC) inverse spinel structure (Fig. 2.43) with two formula units (14 atoms) per primitive cell. The space group is  $Fd\overline{3}m$  (No. 227). The oxygen atoms form a close-packed facecentered-cubic structure with the iron atoms occupying the interstitial positions. There are two types of interstitial sites both occupied by the iron atoms. One site is called the A or 8a site, tetrahedrally coordinated by four  $O^{2-}$  ions composing a diamond lattice. The interstices of these coordination tetrahedra are too small for larger  $Fe^{2+}$  ions and this site is occupied only by  $Fe^{3+}$  ions. Another cation site is called the B or 16d site, and is coordinated by six  $O^{2-}$ ions forming slightly distorted octahedra, which line up along the  $\langle 110 \rangle$  axes of the cubic lattice sharing edges. The point symmetry of the B site is D3d. This site forms exactly one half of a face centered cubic lattice. The lattice of the B site can be considered as a diamond lattice of cation tetrahedra, sharing corners with each other. All the tetrahedra on the same (e.g. xy) plane are isolated. In the following, we refer to b1 axes or b1 chains and b2 axes or b2 chains. The b1 direction is  $[1\overline{1}0]$ , b2 is [110] and the c axis is [001]. All the Fe octahedral or B sites lie on either b1 or b2 chains. We also should mentioned that the distances  $Fe_A-O_1$  and  $Fe_B-O_2$  are different and equal to 1.876 and 2.066 Å respectively.

In the disordered high temperature phase the *B* sites are occupied by equal numbers of  $Fe^{2+}$  and  $Fe^{3+}$  ions randomly distributed between *B*1 and *B*2 sites. Below  $T_V$  the system undergoes a first-order transition accompanied by long range charge ordering of  $Fe^{3+}$  and  $Fe^{2+}$  ions on the *B* sites. Verwey from the very beginning proposed a rather simple charge separation: *b*1 chains occupied only by  $Fe^{2+}$  ions and *b*2 chains by  $Fe^{3+}$  ions (or vice versa) [441]. Since that time the type of charge ordering has been the subject of debate [449]. As an example, in Mizoguchi's model [494, 495] ions run in pairs of  $Fe^{2+}$  fol-



Figure 2.44. LSDA partial DOS of Fe<sub>3</sub>O<sub>4</sub> [485].

lowed by Fe<sup>3+</sup> along each b chain. Another charge ordering considers three Fe<sup>2+</sup> alternating with one Fe<sup>3+</sup> on one half of the chains, and a sequence of three Fe<sup>3+</sup> alternating with one Fe<sup>2+</sup> on the other half and so on [449]. Despite the wealth of effort devoted to investigating the low-temperature phase of magnetite, there is still no completely satisfactory description of the ordering of the Fe atoms on the octahedral or B sites in this spinel structure. In addition some experimental measurements show that below the Verwey transition temperature there is a small change in the crystal structure which becomes monoclinic accompanied by a doubling of the unit cell along the a, b and c axes [496, 497].

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Figure 2.44 shows the partial density of states obtained from the LSDA calculation. The occupied part of the valence band can be subdivided into several regions separated by energy gaps. The oxygen 2s bands, which are not shown in the figure, appear between -20.0 and -19.7 eV for both spins with the exchange splitting of about 0.2 eV. The next group of bands in the energy region -7.4 to -3.4 eV is formed mostly by oxygen 2p states. The Fe d energy bands are located above and below  $E_F$  at about -4.0 to 3.0 eV. As indicated from Fig. 2.44, the exchange splitting between the spin-up and -down d electrons on the Fe atom is about 3.5 eV. In addition to the exchange splitting, the five d levels of the Fe atom are split due to the crystal field. At the A site ( $T_d$  point symmetry) in the spinel structure the crystal field causes the d orbitals to split into a doublet e  $(3z^2-1 \text{ and } x^2 - y^2)$  and a triplet  $t_2$ (xy, yz, and xz). The octahedral component of the crystal field at the B site is strong enough that the  $t_{2q}$  (xy, yz, and xz) and  $e_q$  (3z<sup>2</sup>-1 and x<sup>2</sup> - y<sup>2</sup>) orbitals form two separate nonoverlapping bands. At the B site the crystal field is trigonal (D3d), as a result the  $t_{2q}$  orbitals split into a singlet  $a_{1q}$  and a doublet  $e'_{q}$ . However, the  $a_{1g} - e'_{q}$  splitting of the  $t_{2g}$  band is negligible in comparison with its width in LSDA calculations, therefore in the following we will denote the states formed by  $a_{1g}$  and  $e'_g$  orbitals as  $t_{2g}$  states. Accordingly, we present in Fig. 2.44 the DOS of " $t_{2g}$ " orbitals as a sum of the  $a_{1g}$  and  $e'_g$ ones. The crystal-field splitting  $\Delta_{CF}$  is approximately 2 eV for the Fe<sub>B</sub> atom and 1 eV for the Fe<sub>A</sub> atom. This difference may be attributed to the large covalent mixing of the Fe<sub>B</sub> orbitals with its six nearest neighbors of the same kind. The spin-polarized calculations show that  $Fe_3O_4$  in the high temperature phase is a half-metallic ferrimagnet. The Fermi level crosses only the majority spin energy bands, consisting of spin-up  $t_{2q}$  orbitals on the Fe<sub>B</sub> sublattice (Fig. 2.44). There is an energy gap for the minority spin bands at the Fermi level. Spin-orbit splitting of the d energy band at  $\Gamma$  is about 0.02 eV and much smaller than the crystal-field splitting.

In Fe<sub>3</sub>O<sub>4</sub> the magnetic moments within the A and the B sublattices are ferromagnetically aligned while the two sublattices are antiferromagnetic with respect to each other. This magnetic structure was first proposed by Néel [499] to explain the magnetization data and was later confirmed by neutron scattering measurements [500]. The calculated spin and orbital magnetic moments on various atoms are given in Table 2.4 and compared with experimental data [498]. Measurements indicated that the magnetic moment of an iron atom on the A site is much smaller than the 5.0  $\mu_B$  of a pure Fe<sup>3+</sup> ion [498]. This is an indication of strong hybridization between the 3d orbitals of Fe<sub>A</sub>. The orbital magnetic moment is rather small for all the atoms due to small spinorbit coupling (see Table 2.4). (in  $\mu_B$ ) of Fe<sub>3</sub>O<sub>4</sub>. The experimental data are from Ref. [498].

atom	Ref. [483]	$M_s$	$M_l$	$M_{total}$	Exper.
Fe(A)	3.46	3.496	0.025	3.521	3.82
Fe(B)	-3.57	-3.658	-0.043	-3.701	-
0	-0.10	-0.052	0.0	-0.052	-
E <sub>sphere</sub>	0.01	0.007	0.0	0.007	-
Total	-3.99	-3.965	-0.061	-4.026	-4.1

Table 2.4. The experimental and LSDA calculated [485] spin and orbital magnetic moments

Spin down LSDA+U 4 2 Fe<sub>A</sub> t<sub>2</sub> Fe<sub>A</sub> e Energy (eV) 0 Fe<sub>B1</sub> e<sub>g</sub> -2 Fe<sub>B2</sub> e<sub>g</sub> O + Fe<sub>B1</sub> -4 -6 -8 Fe<sub>B2</sub> t<sub>2g</sub>,e<sub>g</sub> WΚ Г WU X Г х L 10 20 0 Spin up Fe<sub>B1</sub> e<sub>q</sub> 4 Fe<sub>B1</sub> e 2 Fe<sub>B2</sub> e<sub>g</sub> Fe<sub>B2</sub> t<sub>2g</sub> Fe<sub>B1</sub> ā<sub>1g</sub> Energy (eV) 0 -2 O + Fe<sub>A</sub> -4 -6 Fe<sub>A</sub> e,t<sub>2</sub> -8 WΚ Г L WU X 10 20 Г х 0

*Figure 2.45.* LSDA+*U* energy band structure and total DOS (in states/(unit cell eV)) of  $Fe_3O_4$  [485].

The application of LSDA calculations to  $Fe_3O_4$  is problematic, because of the correlated nature of *d* electrons in this compound. The intersite Coulomb correlation is well described by the LSDA. However, the on-site Coulomb interaction, which is a driving force for Mott-Hubbard localization, is not well

treated within LSDA. As a result, LSDA gives only a metallic solution without charge ordering. The LSDA+U calculations [485] started from a  $d^5$   $(t_{2\uparrow}^3 e_{\uparrow}^2)$ configuration for  $\mathrm{Fe}_\mathrm{A}^{3+}$  ions on the tetrahedral site of the sublattice A and  $d^6$  $(t_{2g\downarrow}^3 e_{g\downarrow}^2 a_{1g\uparrow}^1)$  and  $d^5 (t_{2g\downarrow}^3 e_{g\downarrow}^2)$  for Fe<sup>2+</sup><sub>B</sub> and Fe<sup>3+</sup><sub>B</sub> ions on octahedral site of the sublattices  $B_1$  and  $B_2$ , respectively.  $U_{eff}$  was applied to all the d states and the occupation numbers were obtained as a result of the self-consistent relaxation. Figures 2.45 and 2.46 show the energy band structure along the symmetry lines and the total and partial density of states obtained from the LSDA+U calculation. In contrast to LSDA, where the stable solution is a metal with a uniform distribution of the  $t_{2q\uparrow}$  electrons on the B octahedral sites, the LSDA+U gives a charge-ordered insulator with a direct energy gap value of 0.19 eV at the  $\Gamma$ point. The experimental optical measurements [471] gave a gap of 0.14 eV at T=10 K. The energy gap occurs between the  $\operatorname{Fe}_{\mathrm{B}}^{2+}a_{1g\uparrow}$  (the top of valence band) and  $\operatorname{Fe}_{\mathrm{B}}^{3+} t_{2g\uparrow}$  (bottom of empty conduction band) states (Fig. 2.46). Actually, the LSDA+U band structure calculations support the key assumption that Cullen and Callen have made earlier [487–489] in proposing the one-band model Hamiltonian, where it was assumed that the "extra" electron moves in the  $a_{1g}$  band split off below the rest of the *d* bands of other symmetries. Two electrons at the Fe<sup>2+</sup><sub>B</sub>  $a_{1g}$  orbitals situated in the close vicinity of the Fermi level are mostly localized. Other electrons at the B1 site are well hybridized with oxygen *p*-electrons (Fig. 2.46). We should mention that the screening of the Coulomb interaction in Fe<sub>3</sub>O<sub>4</sub> is very effective and the system is close to the metallic state. Even a small change in the ratio  $(Fe^{2+}/Fe^{3+})_{oct}$  (which can be modeled by changing of the occupation numbers of the  $a_{1q}$  orbital at the  $B_1$  and  $B_2$  sites in the framework of the "virtual crystal approximation") leads to the closing of the energy gap and a suppression of the metal-insulating transition [485].

The LSDA+U calculations also improved the agreement between the theoretically calculated and experimental value of the magnetic moment on the A site in comparison with LSDA calculations (see Tables 2.4 and 2.5). Although the neutron diffraction found that magnetic super-structure scattering in the low temperature phase of Fe<sub>3</sub>O<sub>4</sub> is too weak to be accounted for by an ordering of Fe<sup>2+</sup> and Fe<sup>3+</sup> on the B sites, the experimental study did show larger covalency for the Fe<sup>3+</sup> ions on tetrahedral A sites than those on octahedral B sites [454]. In agreement with such an experimental observation the LSDA+U calculated magnetic moments of Fe<sup>3+</sup> atoms are equal to 3.845 and -4.002  $\mu_{\rm B}$  for A and B sites respectively. This can be explained the by different nearest-neighbor distances Fe<sub>A</sub>-O<sub>1</sub> and Fe<sub>B</sub>-O<sub>2</sub>.

After the consideration of the above band structure properties we turn to the optical and MO spectra. In Fig. 2.47 experimental [470] optical reflectivity and the diagonal part of the dielectric function  $\varepsilon_{xx}$  of Fe<sub>3</sub>O<sub>4</sub> are compared to the theoretical ones calculated within the LSDA and LSDA+U approaches. Better



Figure 2.46. LSDA+U partial DOS of Fe<sub>3</sub>O<sub>4</sub> [485].

agreement between the theory and the experiment was found when we used the LSDA+U approximation. As was mentioned above, the LSDA theory produces the metallic solution and, therefore, gives a wrong asymptotic behavior for the optical reflectivity and the dispersive part of the dielectric function  $\varepsilon_{1xx}$ as  $\omega \to 0$ . In Fig. 2.48 we show the calculated and experimental [470, 471] absorptive part of the diagonal optical conductivity spectra  $\sigma_{1xx}$  in a wide energy range. The characteristic features of the LSDA calculation of  $\sigma_{1xx}$  is an

atom	$M_s$	$M_l$	$M_{total}$	Exper.
Fe <sup>3+</sup> <sub>A</sub>	3.845	0.018	3.863	3.82
$Fe_{B}^{2+}$	-3.541	-0.024	-3.565	-
$Fe_{B}^{\overline{3}+}$	-4.002	-0.024	-4.026	-
$O_1$	-0.091	-0.001	-0.092	-
$O_2$	-0.010	0.001	-0.009	-
Esphere	0.003	0.0	0.003	-
Total	-3.796	-0.003	-3.826	-4.1

*Table 2.5.* The LSDA+U calculated spin and orbital magnetic moments (in  $\mu_B$ ) of Fe<sub>3</sub>O<sub>4</sub> [485].



*Figure 2.47.* Optical reflectivity and diagonal parts of the dielectric function  $\varepsilon_{xx}$  of Fe<sub>3</sub>O<sub>4</sub> calculated in the LSDA and LSDA+*U* approximation compared with experimental data [470] (open circles).

erroneous peak at 1.9 eV which is absent in the experimental measurement. The absence of this peak in the experiment indicates that the LSDA calculations produce incorrect energy band positions. Accounting for the Coulomb repulsion  $U_{eff}$  strongly influences not only the electronic structure but also the calculated optical spectra of Fe<sub>3</sub>O<sub>4</sub>. The LSDA+U calculations give reasonably good agreement between the theoretical and the experimental optical spectra of Fe<sub>3</sub>O<sub>4</sub> (see Fig.s 2.47 and 2.48). The calculated optical conductivity spectrum (Fig. 2.48) can be sorted into the following groups of interband transitions: (1) the interband transitions between the Fe 3*d* bands below 2.5 eV, (2) the transitions from O 2*p* to Fe 3*d* bands in the region of 2.5 to 9 eV, and (3) Fe 3*d*  $\rightarrow$  4*p* and O 2*p*  $\rightarrow$  Fe 4*s* interband transitions above 9 eV. To avoid misunderstanding, we should mention that here and in the following when talking about  $d \rightarrow d$  transitions we mean that the energy bands involved in the transitions.



*Figure 2.48.* The absorptive part of the diagonal optical conductivity of  $Fe_3O_4$  calculated in LSDA (dashed line) and LSDA+U (solid line) approximations [485] compared with experimental data Ref. [471] (solid squares) and Ref. [470] (open circles).



*Figure 2.49.* Calculated Kerr rotation and Kerr ellipticity spectra of  $Fe_3O_4$  [485] compared with experimental data (circles) [476].

sitions have predominantly d character, however, the contribution of p or f states to these bands is sufficient to provide a significant transition probability through optical dipole matrix elements.

Let us consider now the magneto-optical properties of Fe<sub>3</sub>O<sub>4</sub>. In Fig. 2.49 we show the experimentally measured [476] Kerr rotation  $\theta_K(\omega)$  and Kerr ellipticity  $\epsilon_K(\omega)$  MO spectra of Fe<sub>3</sub>O<sub>4</sub>, as well as the off-diagonal parts of the dielectric function calculated with the LSDA and LSDA+U approximations [485]. This picture clearly demonstrates that the better description is achieved with the LSDA+U approach.

We mention that although the O  $2p \rightarrow \text{Fe} 3d$  interband transitions, which start already from about 2.5 eV, play an important role in the formation of the optical spectra of Fe<sub>3</sub>O<sub>4</sub>, the Kerr spectra are mostly determined by transitions between energy bands which have predominantly Fe 3d character. The reason for this is that the spin-orbit and exchange splitting of O 2p states is much smaller in comparison with the Fe 3d ones. The minimum in the Kerr rotation spectrum at 0.9 eV is due to the Fe<sup>2+</sup><sub>B</sub>  $(a_{1g\uparrow}) \rightarrow \text{Fe}^{3+}_{B}(t_{2g\uparrow})$  interband transitions. The second maximum at about 2 eV is associated with the Fe<sup>2+</sup><sub>B</sub>  $(a_{1g\uparrow}) \rightarrow \text{Fe}^{3+}_{B}(e_{g\uparrow})$  interband transitions. The minimum in the Kerr rotation spectrum between 3 and 4 eV can be associated with the Fe<sup>3+</sup><sub>B</sub>  $(e_{g\downarrow}) \rightarrow \text{Fe}^{3+}_{A}$ 

We should note that all the experimental measurements of the Kerr spectra of  $Fe_3O_4$  [472–477] have been performed at room temperature. The LSDA+U calculations, in comparison with the LSDA ones, describe better the electronic structure, optical and MO properties not only in the low temperature semiconducting phase but also in the high temperature metallic phase of  $Fe_3O_4$ . This leads to a conclusion that Fe d electrons remain "correlated" above  $T_{\rm v}$ . The main effect of heating through  $T_{\rm v}$  is a disappearance of the long range charge order on the B sublattice. This leads to the rearrangement of the electronic states in a small vicinity of the Fermi level and to the closing of the energy gap. However, high energy Hubbard bands, whose energy position is mainly determined by on-site exchange and correlation interactions, remain almost unaffected ( $U_{\rm eff} \sim 4$  to 5 eV is much larger than  $T_{\rm v} \sim 0.01$  eV). This picture is supported by recent optical measurements [471], which show a strong temperature dependence of the optical properties of Fe<sub>3</sub>O<sub>4</sub> only in the range from 0 to 1 eV. The absolute value of the measured prominent peak in the optical absorption for photon energies around 0.6 eV determined by the  $\operatorname{Fe}_{\mathrm{B}}^{2+}(a_{1a\uparrow}) \to \operatorname{Fe}_{\mathrm{B}}^{3+}(t_{2a\uparrow})$  interband transitions gradually decreases by about 30% when changing the temperature from 10 K to 490 K. However, the other parts of the spectrum change very little. Other evidence can be found from the temperature dependent magnetic circular dichroism (MCD) measurements of Fe<sub>3</sub>O<sub>4</sub> [481]. MCD spectra in core level absorption are element specific and site selective, thus providing valuable information on the energy position of empty states in a wide energy interval. It was found that the M<sub>2.3</sub> MCD spectra of  $Fe_3O_4$  reflecting the Fe 3d unoccupied states are almost identical at 50 K and 300 K.

### Mg<sup>2+</sup> and Al<sup>3+</sup> substituted Fe<sub>3</sub>O<sub>4</sub>.

Nonmagnetic Al<sup>3+</sup> ions can substitute Fe<sup>3+</sup> ions both at the *A* and *B* sites. However, Mössbauer studies of relatively broad compositional range for the spinel system Fe<sub>3-x</sub>Al<sub>x</sub>O<sub>4</sub> indicate that Al up to x=1.2 shows a strong preference for octahedral *B* sites [501–503]. The optical and MO spectra of Al<sup>3+</sup> substituted magnetite  $\operatorname{Fe}_{A}^{3+}[\operatorname{Fe}^{2+}\operatorname{Fe}_{1-x}^{3+}\operatorname{Al}_{x}^{3+}]_{B}O_{4}^{2-}$  have been presented in Ref. [473] for x = 0.02, 0.2 and 0.4.

The optical and MO spectra of  $Mg^{2+}$  substituted magnetite have been measured in Ref. [472]. Unfortunately it was not possible to prepare the samples with substituted  $Mg^{2+}$  ions only at octahedral *B* sites.  $Mg^{2+}$  ions occupy both the octahedral *B* and tetrahedral *A* sites. The cation distribution formula for substituted magnesium is  $[Mg_x^{2+}Fe_{1-x}^{3+}]_A[Mg_{1-x}^{2+}Fe_{1+x}^{3+}]_BO_4^{2-}$  with x=0.1, 0.13, and 0.24 [472]. The optical measurements clearly show that Mg substituted magnetite is a semiconductor with a substantially larger gap in comparison with pure magnetite [472].  $Fe_A^{3+}[Mg^{2+}Fe^{3+}]_BO_4^{2-}$  is already a charge ordered compound with  $Mg^{2+}$  and  $Fe^{3+}$  ions occupying *B*1 and *B*2 sites respectively. The infrared reflectivity measurements on Mg substituted magnetite at 10 K performed in Ref. [472] show that the spectrum is nearly identical to the room-temperature data.

The electronic structure, optical and MO properties of both the magnesium and aluminum substituted magnetite have been calculated in Ref. [485] using the LSDA and LSDA+U approximations. The local symmetry in substituted magnetite is reduced to  $C_{2v}$  and  $C_{2h}$  at the A and B sites, respectively. The crystal field causes the d orbitals to split into five singlets at each site:  $a'_1$ ,  $a''_1$ ,  $b_1$ ,  $a_2$ , and  $b_2$  at the A site and  $a_{g1}$ ,  $a_{g2}$ ,  $a_{g3}$ ,  $b_{g1}$ , and  $b_{g2}$  at the B site. The tetrahedral component of the crystal field at the A site is strong enough that the  $a''_1$ ,  $a_2$  ( $3z^2$ -1 and  $x^2 - y^2$ ) and  $a'_1$ ,  $b_1$ , and  $b_2$  (the linear combination of the xy, yz, and xz) orbitals form two separate nonoverlapping bands. However, the  $a''_1 - a_2$  and  $a'_1 - b_1 - b_2$  splitting is negligible in comparison with their widths, therefore we present in Fig.s 2.50 and 2.53 DOS of e orbitals as a sum of the  $a''_1$ and  $a_2$  orbitals and  $t_2$  as a sum of the  $a'_1$ , the $b_1$ , and  $b_2$  (former  $e_g$ ) and  $a_{g1}$ ,  $a_{q2}$  and  $b_{q1}$  (former  $t_{2q}$  orbitals).

Figure 2.50 shows the LSDA+U partial density of states of magnesium substituted magnetite  $\operatorname{Fe}_{A}^{3+}[\operatorname{Mg}^{2+}\operatorname{Fe}^{3+}]_{B}O_{4}^{2-}$ . The energy band structure is very similar to the band structure of pure magnetite (compare Fig.s 2.50 with 2.46), except that there are no  $\operatorname{Fe}_{B}^{2+}$  states in the magnesium substituted magnetite. Because the occupied  $\operatorname{Fe}_{B}^{2+} a_{1g\uparrow}$  and  $e'_{g\downarrow}$  states of  $\operatorname{Fe}_{3}O_{4}$ , situated in the vicinity of the Fermi level, just drop out in the  $\operatorname{Mg}_{B}^{2+}$  substituted magnetite the Fermi level in the latter compound is placed at the top of the oxygen 2p bands.

Although the LSDA calculations are able to predict the correct insulating ground state of  $Mg_B^{2+}$  substituted magnetite, they significantly underestimate the energy gap and give a wrong energy position for the *d* states. As a consequence, the LSDA calculations give unsatisfactory agreement between calculated and experimental optical spectra in the 0 to 3 eV energy interval (Fig. 2.51). The LSDA+*U* calculations produce a larger energy gap, shift the energy



*Figure 2.50.* LSDA+U partial DOS of Mg<sup>2+</sup><sub>B</sub> substituted magnetite [485].

bands from the vicinity of the Fermi level and, as a result, give a substantial improvement over the LSDA results (Fig. 2.51). As we mentioned above, below 2.5 eV the optical spectra of pure magnetite are determined only by interband transitions between Fe 3*d* bands. It is not the case for  $Mg_B^{2+}$  substituted magnetite. It was found that for the substituted compound strongly hybridized Mg 3p and O 2p states situated just under the Fermi level (Fig. 2.50) determine the optical spectra. In particular, the prominent peaks of the optical conductivity

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*Figure 2.51.* Optical reflectivity and diagonal parts of the dielectric function  $\varepsilon_{xx}$  of Mg<sub>B</sub><sup>2+</sup> substituted magnetite calculated within LSDA (dashed line) and LSDA+U (solid line) approximations [485] compared with experimental data [470] (circles).

and  $\varepsilon_{xx}$  at 3.5 eV are determined by the O  $(2p_{\downarrow}) \rightarrow \text{Fe}_{A}^{3+}(e_{\downarrow}, t_{\downarrow})$  and O  $(2p_{\uparrow}) \rightarrow \text{Fe}_{B}^{3+}(e_{g\uparrow}, t_{2g\uparrow})$  interband transitions.

After consideration of the band structure and optical properties we turn to the magneto-optical spectra. Compared to pure magnetite the MO spectra of  $Mg_B^{2+}$  substituted magnetite show a decrease of the negative Kerr rotation near 0.9 eV by a factor of approximately ten [472]. Also the rest of the spectra differ markedly from those of pure magnetite. The best agreement between theory and experiment for the MO spectra was found to be when we used the LSDA+U approximation. In Fig. 2.52 we show the experimentally measured [472] Kerr rotation spectrum of  $Mg_B^{2+}$  substituted magnetite, as well as off-diagonal parts of the dielectric function calculated with the LSDA and LSDA+U approximations. The Fe<sub>B</sub><sup>2+</sup>  $a_{1g\uparrow}$  states, responsible for the prominent minimum in Kerr rotation spectrum around 0.9 eV in pure magnetite, do not exist any more. Therefore, this fine structure disappears in the MO spectrum of  $Mg_B^{2+}$  substituted magnetite.

The experimental features of the Kerr rotation and off-diagonal optical conductivity spectra are reasonably well reproduced by the LSDA+U calculations. However, the theory predicts larger Kerr rotation in the 1.5 to 3.5 eV energy interval. One of the possible reasons of such disagreement might be the following. The theoretical calculations in Ref. [485] were performed for the ideally substituted magnetite  $Fe_A^{3+}[Mg^{2+}Fe^{3+}]_BO_4$ . On the other hand, the experimentally measured magnesium magnetite had the nominal composition  $[Mg_{0.1}^{2+}Fe_{0.9}^{3+}]_A[Mg_{0.9}^{2+}Fe_{1.0}^{3+}]_BO_4$ . In Fe<sub>3</sub>O<sub>4</sub> the magnetic moments within the *A* and *B* sublattices are ferromagnetically aligned while the two sublattices are antiferromagnetic with respect to each other, therefore the Kerr rotation spectrum is composed by the signals coming from the *A* and *B* sublattices with



*Figure 2.52.* The off-diagonal parts of the dielectric function  $\varepsilon_{xy}$  and the Kerr rotation spectrum for Mg<sub>B</sub><sup>2+</sup> substituted magnetite calculated within LSDA (dashed line) and LSDA+*U* (solid line) approximations [485] compared with experimental data [472] (circles) for [Mg<sub>0.2</sub><sup>2+</sup>Fe<sub>0.3</sub><sup>3+</sup>]<sub>A</sub>[Mg<sub>0.2</sub><sup>2+</sup>Fe<sub>1.0</sub><sup>3+</sup>]<sub>B</sub>O<sub>3.95</sub><sup>2-</sup>.

opposite signs. Even a small deviation from the ideally substituted magnetite can greatly affect the compensation effect between the A and B sublattices in the Kerr rotation spectrum.

The LSDA+U band structure of  $Al_B^{3+}$  substituted Fe<sub>3</sub>O<sub>4</sub> is also very similar to the band structure of pure magnetite (compare Figures 2.53 and 2.46), except that in the aluminum substituted magnetite there are no Fe<sub>B</sub><sup>3+</sup> energy bands. They are simply dropped out in the Al<sub>B</sub><sup>3+</sup> substituted magnetite with very little change in the position and widths of the rest of the energy bands.

In Fig. 2.54 we show the experimentally measured [473] Kerr rotation  $\theta_K(\omega)$ spectrum as well as the off-diagonal parts of the dielectric function of aluminum substituted magnetite with the nominal composition  $Fe_A^{3+}[Fe^{2+}Fe_{0.6}^{3+}Al_{0.4}^{3+}]_BO_4$  in comparison with the LSDA+U calculated spectra for the ideally substituted  $Fe_A^{3+}[Fe^{2+}Al^{3+}]_BO_4$  compound. As the prominent minimum at 0.9 eV in the Kerr rotation spectrum of Fe<sub>3</sub>O<sub>4</sub> is completely determined by the interband transitions between d states of  $Fe_B^{2+}$  and  $Fe_B^{3+}$  ions it should be suppressed if either initial (Fe<sup>2+</sup><sub>B</sub> d) or final (Fe<sup>3+</sup><sub>B</sub> d) bands for these transitions disappear from the band structure upon substitution. The first case is realized in Mg substituted magnetite (see Fig. 2.52). In Al substituted magnetite, on the other hand,  $Fe_B^{3+}$  ions are replaced by  $Al^{3+}$ . There are no  $Fe_B^{3+}$  derived d bands above the Fermi level and, as a result, the calculated Kerr rotation remains positive below 2 eV. In contrast to the calculations, the measurements of the Kerr rotation spectra have been performed for a partially substituted compound in which only 40 % of  $Fe_B^{3+}$  ions were replaced by Al. Therefore, the minimum at about 1.0 eV derived from the transitions to  $Fe_{P}^{3+}$ states is still present in the experimental spectrum (Fig. 2.54), however its mag-



*Figure 2.53.* LSDA+U partial DOS of Al<sub>B</sub><sup>3+</sup> substituted magnetite [485].

nitude is smaller than in pure magnetite. Experimental measurements of the Kerr rotation spectrum of completely substituted  $AlFe_2O_4$  are highly desired.

Finally, we would like to point out that while the LSDA+U approach does a better job than the LSDA in the treatment of correlation effects, it is still unclear how well it performs in evaluating the subtle energies and interactions affecting the charge ordered ground state and the higher temperature short-range ordered states. The band structure calculations regarded the Fe<sub>3</sub>O<sub>4</sub> compound



*Figure 2.54.* Calculated off-diagonal parts of the dielectric function  $\varepsilon_{xy}$  and the Kerr rotation spectrum for Al<sup>3+</sup> substituted magnetite (full line) [485] compared with experimental data (circles) for Fe<sub>A</sub><sup>3+</sup>[Fe<sup>2+</sup>Fe<sub>1-x</sub><sup>3+</sup>Al<sub>x</sub><sup>3+</sup>]<sub>B</sub>O<sub>4</sub><sup>2-</sup> (*x*= 0.4) compound; [473] dashed line shows theoretically calculated Kerr rotation spectrum of Fe<sub>3</sub>O<sub>4</sub>.

as an ideal system with perfect charge ordering with b1 chains occupied only by  $Fe^{2+}$  ions and b2 chains by  $Fe^{3+}$  ions (the Verwey type of ordering [441]). The real situation is much more complicated. As shown in Ref. [462] above  $T_V$  magnetite becomes metallic, but with a very small value of the density of states at the Fermi level, which becomes larger with increasing temperature. Another temperature-dependent photoemission measurement [469] shows that on heating through the transition temperature  $T_V$  the single particle gap is not eliminated immediately, but gradually reduces with the increasing of temperature above the Verwey transition. This can be an indication of the existence of a short-range charge order or many different short-range charge ordered states with frustrated geometries above  $T_V$ , as proposed by Anderson [486]. Such states are gradually lost on increasing the temperature. We also note that the charge order below  $T_V$  is more complicated than the simple Verwey pattern, and that the phase transition is accompanied by a structural transformation from cubic spinel to monoclinic structure [496, 497]. Magnetite is likely to remain scientifically interesting for many more years as befits its remarkable history.

## 2.2 Magneto-optical properties of magnetic multilayers.

In recent years, artificial layered structures composed of magnetic transition metals separated by nonmagnetic metals have intensively been studied due to the fundamental research interest in these systems and also because of their potential for applications. Oscillatory interlayer exchange coupling [504], giant magnetoresistance [505] and induced magnetic polarization effects in non-

magnetic layers (see, e.g. Ref. [506] and references therein) have become important topics involving layered magnetic structures.

In particular, Co/Pt and Co/Pd multilayered structures (MLS) have attracted attention because these systems exhibit simultaneously a large magneto-optical Kerr rotation [507, 387] and perpendicular anisotropy [508] which makes these materials applicable for a new generation of storage devices [299].

This section is a review of recent achievements in both experimental and theoretical investigations of the electronic structure, optical and MO properties of transition metal multilayered structures. We consider the important scientific and technological Co/Pt, Co/Pd, Co/Cu, and Fe/Au. In these MLS, the nonmagnetic sites (Pt, Pd, Cu and Au) exhibit an induced magnetic moment due to the hybridization with the transition metal spin-polarized 3d states. The polarization is strong at Pt and Pd sites and weak at noble metal sites due to completely occupied d bands in the later case. Also of interest is how the spin-orbit interaction of the nonmagnetic metal (increasing along the series of Cu, Pd, Pt, and Au) influences the MO response of the MLS. From the application point of view a very important question is how the imperfection at the interface affects the physical properties of layered structures including the MO properties.

### 2.2.1 Magneto-optical properties of Co/Pd systems

#### Co/Pd multilayers

A detailed experimental and theoretical study of the electronic structure and MO properties of Co/Pd MLS using MOKE spectroscopy and first-principles band-structure calculations has been presented in Ref. [509]. The Co/Pd multilayers under consideration were prepared on water-cooled glass substrates using the dc magnetically enhanced face-to-face sputtering system described in Ref. [510]. The chemical compositions of the films were determined by x-ray fluorescence analysis from the peak intensities of the characteristic fluorescence radiation. Structural studies were performed by conventional x-ray diffractometry. Formation of multilayer structures was confirmed by low angle x-ray diffraction and the modulation period was deduced from the position of the Bragg peaks. The periods determined from the x-ray measurements agree with those evaluated from the fluorescence analysis. The films were found to be of fcc (111)-textured structure.

**Experimental results.** The polar Kerr rotation  $(\theta_K)$  and ellipticity  $(\eta_K)$  spectra of the Co/Pd MLS measured under saturation conditions, are shown in Figures 2.55(I). For comparison, spectra of a 2000 Å thick fcc Co film, multiplied by a factor of 0.7, are also plotted in Figure 2.55(I). It can be seen that the MLS Kerr spectra never exceed in magnitude those of the fcc Co over the whole spectral range. The prominent features of the  $\theta_K$ -spectra are a broad

negative peak at ~3 eV and a shoulder at ~4.3 eV followed by a  $\theta_K$ -slope varying as a function of the Co layer thickness. The  $\theta_K$ -peak, centered at 1.5 eV, characteristic of fcc-Co, is strongly reduced with decreasing MLS Co sublayer thickness, and the prominent minima at ~3 eV in  $\theta_K$  and at ~5 eV in  $\eta_K$  diminish in amplitude. With decrease of the amount of Co present, the shift of the zero-crossing of  $\eta_K$  up to ~3 eV is accompanied by the formation of an overlapping positive two-peak structure. Similar spectral features of the Co/Pd MLS, although within smaller spectral ranges and for other sublayer thicknesses, were observed in references [387, 511], and [512]. Inspection of the  $\theta_K$ - and  $\eta_K$ -spectra of the MLS leads one to the conclusion that there is a MO contribution independent of, or weakly dependent on, the cobalt sublayer thickness. These effects that are independent of the Co content may arise from Pd spin polarization induced by the proximity of Co layers and/or from the polarization caused by roughness and limited alloying at the Co-Pd interface.

To study the mechanism responsible for the MOKE in the Co/Pd MLS and to enable us to discuss the magneto-optical response of the films in terms of separate contributions of the Co and Pd sublattices, the data should be, in principle, analyzed using the off-diagonal optical conductivity tensor components  $\sigma_{xy}$ , which are directly related to the magneto-optical transitions between the spin-polarized electronic states. From the measured  $\theta_K$ - and  $\eta_K$ -data, and the diagonal  $\sigma_{xx}$ -tensor component, the off-diagonal  $\sigma_{xy}$ -component can be evaluated according to equation (1.175). The values of  $\sigma_{xx}$  for the fcc Co and Pd films and the Co/Pd MLS under consideration were obtained by an ellipsometric method for the range 0.8–5.5 eV. It was found that the  $\sigma_{xx}$ -spectra of the multilayers are close to each other and do not exhibit fine structure, except a small broad peak at about 4–5 eV.

For all of the Co/Pd MLS studied, it was found that the denominator in equation (1.175) evaluated from the optical data is a monotonous and structureless function over the whole energy range and depends weakly on the film composition. Consequently, all of the peaks in the polar Kerr rotation and ellipticity spectra originate from the corresponding features of the absorptive and dispersive parts of  $\sigma_{xy}(\omega)$ , respectively. The energy dependence of the denominator in equation (1.175) only changes the relative amplitudes of the uv and ir peaks of the spectra, without producing any additional spectral features. It can be concluded that in the Co/Pd MLS the MOKE is governed by the off-diagonal part of the optical conductivity tensor.

**Multilayers with perfect interfaces.** In an attempt to reproduce and to explain the experimental MOKE spectra, band-structure calculations of the MO properties of some model MLS were performed. As the influence of the structure of the Co-Pd interface on the MOKE spectra is the subject of this study, in the first step an idealized model with a sharp interface was adopted in the



*Figure 2.55.* (I): Experimental polar Kerr rotation and ellipticity spectra of Co/Pd MLS and fcc Co film. The Co and Pd sublayer thicknesses are given in the keys in units of Å. (II): Calculated polar Kerr rotation and ellipticity spectra for the model nCo/mPd MLS with sharp interfaces (*n* and *m* are the numbers of Co and Pd atomic planes, respectively). For comparison, spectra of fcc Co (calculated with the same value of S<sub>WS</sub> as the MLS), multiplied by a factor of 0.7, are also shown [509].

calculations. The numbers n of Co and m of Pd atomic planes in the model nCo/mPd MLS were chosen as close as possible to the experimentally measured ones. For all the MLS, an abc stacking sequence of closely packed Co and Pd planes was assumed. In reference [513] it was shown that for Co sublayers that are not very thick (less than 30 Å, with the Pd sublayer thickness being 12 Å), the in-plane lattice spacing in Co/Pd MLS is almost independent of the Co sublayer thickness and only ~2% less than the lattice spacing in fcc Pd. Therefore the lattice constant a=2.694 Å of the hexagonal lattice was chosen. The interplane spacings in the Co and Pd sublayers and at the interface were chosen to be equal, and correspond to the ideal c/a ratio ( $c/a = q\sqrt{2/3}$ , where q = n + m is the number of close-packed atomic planes). The sphere radii of Co and Pd were both taken as equal to the average S<sub>WS</sub>-value of 1.49 Å.

*Table 2.6.* Calculated Co and Pd spin magnetic moments ( $\mu_B$ /atom) in the Co/Pd MLS. The number after chemical symbol denotes the number of corresponding atomic planes starting from the Co-Pd interface. For fcc Co with S<sub>WS</sub> set at the same value as for the MLS, the value of  $1.72\mu_B$ /atom was obtained.

MLS	Co2	Col	Pd1	Pd2	Pd3
1Co/8Pd		1.94	0.26	0.12	0.04
2Co/7Pd		1.84	0.23	0.10	0.03
4Co/8Pd	1.72	1.83	0.23	0.11	0.04
6Co/9Pd	1.72	1.83	0.23	0.12	0.04
9Co/9Pd	1.72	1.83	0.23	0.12	0.04

The distributions of the spin magnetic moments in the Co and Pd atomic spheres derived from the band-structure calculations are given in Table 2.6. For all the MLS studied, the dependence of the magnetic moments on the distance from the interface is the same. The Co magnetic moment is enhanced at the interface and is already approaching the bulk value of  $1.72\mu_B$ /atom in the second plane. The same value of the Co moment  $(1.72\mu_B/\text{atom})$  was obtained from the calculations for fcc Co with the lattice constant expanded so that the value of S<sub>WS</sub> was equal to that for the MLS. The value of the magnetic moment induced in Pd rapidly decreases with the distance from the interface. In the MLS with a Pd sublayer consisting of more than six Pd atomic planes, the magnetic moments induced in the middle of the Pd sublayer are smaller than  $0.015\mu_B$ /atom and not shown in Table 2.6. The rapid decrease of the Pd magnetic moment with the increase of the distance from the interface can be easily understood if one recalls that the moment is mainly due to Co 3d-Pd 4d hybridization. A Pd atom, even in only the second atomic plane from the interface has no Co atoms even amongst its second-nearest neighbors, and interacts with the exchange-split Co 3d states only indirectly.

The calculated MOKE spectra of the Co/Pd MLS are shown in Figure 2.55(II). For the sake of comparison, spectra of fcc Co (calculated with the same value of  $S_{\rm WS}$  as the MLS), multiplied by a factor of 0.7, are also shown. From the comparison with the experimental spectra, it is seen that in the uv range the shoulder at ~5 eV, which is a characteristic feature of the experimentally measured polar Kerr rotation spectra of the MLS, manifests itself only in the spectra of the 1Co/8Pd MLS and, to a lesser extent, those of the 2Co/7Pd MLS. For the MLS with larger numbers of Co atomic planes, the magnitude of the Kerr rotation spectra in the uv range increases with the increase of the Co sublayer thickness, whereas the shape of the spectra changes only slightly. As can be seen from Figure 2.55(II), the features of the Kerr

ellipticity spectra, corresponding to the peaks at 1.0 and 4.3 eV in the fcc Co spectrum, become more pronounced as the number of atomic planes of Co increases.

Such a dependence of the calculated MOKE spectra of the MLS on the Co sublayer thickness is explicable. As the magnetic moment induced in the Pd atoms located far from the interface is very small, one can expect these atoms to give only a small contribution to the off-diagonal optical conductivity. Consequently, if the model with a sharp interface is adopted, the MO properties of the MLS are determined by the Co sublayer and one, or perhaps two, adjacent Pd atomic planes. Also, from the calculated DOS curves and Co magnetic moments it follows that only the electronic states in the two Co atomic planes nearest to the interface are modified strongly by the hybridization with the Pd states. Hence, as the Co sublayer thickness increases, the MOKE spectra of the MLS should become closer to that of pure Co. This is exactly what can be seen in Figure 2.55(II). As the number of Co atomic planes increases, the relative contribution of the interfacial layer to the spectra becomes smaller and a shoulder appears at 1.5 eV in the spectra which is evidently related to the corresponding peak in the fcc Co spectrum.

A comparison with the experimental spectra of the MLS (Figure 2.55(I)) shows that the calculations reproduce only moderately well the main peculiarities of the MOKE spectra of the MLS and tendencies in the modification of the MLS, spectra with the variation of the Co sublayer thickness are not in satisfactory quantitative agreement.

The calculated spectra are of smaller magnitude; the decrease of the magnitude for the MLS with a small number of Co atomic planes is larger than in the experiment. The feature at 1.5 eV in the calculated spectra of the MLS with a thin Co sublayer disappears totally and the magnitude of the spectra goes almost to zero in this energy range. The loss of the amplitude at this energy, although observed experimentally, is not so drastic. Also, the calculations predict a rapid decrease of the Kerr rotation amplitude for the shoulder at 5 eV with respect to that of the main minimum as the number of Co atomic planes increases, while the shoulder is observable in the experimental spectra.

It is worth recalling that the spectra of fcc Co shown in Figure 2.55(II) were calculated with the enlarged lattice constant used for the model MLS and, consequently, they should not be compared directly to the experimental Co spectra (see Figure 2.55(I)). The position of the uv minimum in the polar Kerr rotation spectrum of Co, calculated using the experimental fcc Co lattice constant (i.e., for S<sub>WS</sub>=1.395 Å), is shifted to higher energies by  $\sim 1 \text{ eV}$  (see reference [514]). Thus, the shift of  $\sim 0.7 \text{ eV}$  in the energy position of the uv minimum observed in the experimental MLS spectra with respect to that for the fcc Co film is reproduced–although it is overestimated– by the calculations.
There are several possible sources of these discrepancies. First of all, the peaks in the polar Kerr rotation spectra calculated for either fcc or hcp Co are shifted to higher energies with respect to the measured ones and the magnitude of the minimum at 1.5 eV is too small. This discrepancy is apparently due to a failure of the LDA-based calculations to predict correctly the MOKE spectra of the ferromagnetic 3d metals that has recently been extensively discussed in the literature [320, 514, 321]. A plausible cause for this lies in the approximate description of the exchange and correlation of rather localized 3d electrons. If the calculated magnitude of the ir peak of fcc Co were larger, it would bring the theoretical MOKE spectra of the MLS into closer agreement with the experimental ones for the energy range below 2 eV. In the uv range, however, a shift of the Co Kerr rotation peak to lower energies would hardly improve the agreement between the theory and experiment at all.

The shift of the calculated peak positions may also be caused by the difference between the experimental interatomic distances and those used in the calculations. Determination of the in-plane and interplane distances in an individual sublayer of the MLS or overlayered structures is an onerous task and the experimental data available for Co/Pd MLS differ significantly [34-36]. To estimate the sizes of the possible effects of the interplane relaxation, test calculations using the unmodified in-plane interatomic distance but a smaller c/aratio were performed for Co (with a hexagonal supercell) and 4Co/5Pd MLS. It was found that the theoretical MOKE spectra are rather insensitive to the interplane distance. A decrease of the c/a ratio by 5% results in a small increase in amplitude of the polar Kerr rotation spectra, but the peak positions remain unchanged. Thus, though a contraction of interplane distances in the Co sublayer was derived from structural investigations [515, 516], it is unlikely to be responsible for the discrepancies between the theoretical and experimental MOKE spectra of the Co/Pd MLS. An in-plane relaxation in a thick Co sublayer might affect the calculated MOKE spectra strongly, but performing such a calculation is beyond the capability of our facilities. Moreover, there is no experimental evidence that relaxation really occurs in the MLS studied.

The idea of enhanced spin-polarization in the Pd planes adjacent to the Co was also considered. For some of the MLS studied, test calculations were performed in which an additional exchange splitting was introduced for one or two of the Pd atomic layers nearest to the interface. As a result of the additional spin polarization of the Pd atoms, the intensity of the calculated polar Kerr rotation spectra in the uv range increases. However, the strong positive rotation at low photon energies is in disagreement with the experiment in this energy range.

We believe it is likely that the main cause of the differences between the theory and experiment lies in the choice of a model with a sharp interface as a basis for the calculations. An intermixing at the interface, even within just one or two atomic layers, can appreciably change the shape and magnitude of the MOKE spectra of the MLS, especially those with small Co sublayer thicknesses. The next part of this section is devoted to a quantitative study of this problem.

Multilavers with imperfect interfaces. From the discussion above, it follows that interfacial intermixing should be taken into account if one is to describe the MO properties of real Co/Pd MLS systems. A first improvement that takes us closer to describing 'real systems' is that of considering an ordered compound at the interface. To examine the consequences of interface intermixing for Co/Pd MLS MOKE spectra and their relation to the chemical nature of the interface, a model of multilayer supercells with alloyed interfaces was considered. The study was performed with the use of the previously-described formalism of *ab initio* band-structure calculations. As the LMTO method requires a crystal lattice with specified translational and point symmetry, special model supercells of the multilayered structures with alloyed interfaces and fcc (111) texture were constructed. In the [111] direction, for all model MLS an abc stacking sequence of closely packed atomic Co and Pd planes was assumed. As an interface between the neighboring Co and Pd layers, one or two Co-Pd mixed atomic planes were introduced. To satisfy the requirement of overall  $D_{3d}^3$  lattice symmetry of the supercells and to minimize their volume, the unit cell was doubled in the basal plane. As a consequence, interfacial planes in these supercells can consist of mixed atomic planes composed of an ordered Co-Pd compound with 1:3 and 3:1 stoichiometry and threefold rotational symmetry. Three types of multilayered structure with different interfacial atomic planes were considered. The nCo/A/mPd- and nCo/B/mPd-type structures contain Pd-rich Co<sub>1</sub>Pd<sub>3</sub> (A) and Co-rich Co<sub>3</sub>Pd<sub>1</sub> (B) ordered interfacial planar alloys, respectively. The structure nCo/C/mPd with C=Co<sub>3</sub>Pd<sub>1</sub>/Co<sub>1</sub>Pd<sub>3</sub> has a two-layer interfacial ordered alloy composed of consecutive B- and A-type planes.

To understand the relationship between the interfacial structures and the MOKE spectra, a systematic study was performed for Co/Pd MLS with a period of six atomic layers. Calculations for larger supercells are extremely time consuming and were performed only for some selected cases. It was found that the calculations performed are sufficiently representative and illustrate the main trends in the modification of the MO spectra with interface imperfection. In all of the calculations, the same lattice constant as for the ideal model MLS was assumed.

The calculated polar Kerr rotation spectra for the Co/Pd MLS, where the Co and Pd layers are separated by three types of interface alloy layer (A, B, and C), are shown in Figures 2.56(a)- 2.56(c). For comparison, the spectrum of fcc Co calculated with the same value of S<sub>WS</sub> and the spectra of ideal 1Co/5Pd,



*Figure 2.56.* Calculated polar Kerr rotation spectra for the model nCo/X/mPd multilayered structures with imperfect interfaces. n and m are the numbers of Co and Pd atomic planes, respectively. X=A, B, C denotes the interfacial planar ordered alloys Co<sub>1</sub>Pd<sub>3</sub>, Co<sub>3</sub>Pd<sub>1</sub>, and Co<sub>3</sub>Pd<sub>1</sub>/Co<sub>1</sub>Pd<sub>3</sub>, respectively. For a comparison, the corresponding MLS spectra for the ideal model nCo/mPd and the spectrum of fcc Co with the same value of S<sub>WS</sub> as for the MLS are also shown. [509]

2Co/4Pd and 3Co/3Pd MLS are also included. The spectra calculated for the supercell structures in which the Pd layers are separated by alloy layers only are presented in Figure 2.56(a). The supercells 0Co/A/4Pd and 0Co/B/4Pd consist of a two-atomic-layer thickness of alloy, of either  $Co_1Pd_3$  or  $Co_3Pd_1$  composition, separated by a four-atomic-layer thickness of Pd spacer. The su-

percell  $0C_0/C/2Pd$  consists of repeated sequences of four alloy atomic planes,  $C_0_1Pd_3/C_{0_3}Pd_1/C_{0_3}Pd_1/C_0_1Pd_3$ , separated by two Pd atomic planes. These structures can be regarded as limiting cases, where Co atoms are present in alloy planes only.

As is seen from Figure 2.56(a), in the uv range the main features of the 0Co/A/4Pd spectrum are very similar in shape to those of the 1Co/5Pd MLS with the sharp interface. It is interesting that the amplitude of the 0Co/A/4Pd spectrum is about 70% higher than the amplitude of the 1Co/5Pd spectrum, despite the higher Co content in the latter. However, in the energy range below  $\sim$ 2 eV, a positive rotation is observed for the 0Co/A/4Pd MLS. It should be noted that the overall shape of the OCo/A/4Pd Kerr rotation spectrum is very close to that calculated for homogeneous diluted Co-Pd alloys [517]. Thus, the conclusions are that the Kerr rotation spectrum of the 0Co/A/4Pd structure is determined to a great extent by the MO properties of spin-polarized Pd. The spectrum of 0Co/B/4Pd, in which the interface region is formed by the Co-rich alloy, differs significantly from both the 0Co/A/4Pd and the 1Co/5Pd spectra. The two-peak uv structure transforms into a broad minimum centered at 4.2 eV and in the ir region the rotation becomes negative. The structure with a C-type interfacial layer is particularly interesting, as it can be obtained from the ideal 2Co/4Pd multilayer structure simply by interchanging the positions of every fourth Co and Pd atom in the neighboring interfacial Co and Pd layers. As a result, Co-rich Co<sub>3</sub>Pd<sub>1</sub> and Pd-rich Co<sub>1</sub>Pd<sub>3</sub> planar alloy layers appear around the border. The composition of the 0Co/C/2Pd MLS corresponds to that of 2Co/4Pd; however, it should be pointed out that the change of the interface microstructure leads to very large changes in the shape and magnitude of the MO spectra, as can be seen from the comparison of the OCo/C/2Pd and 2Co/4Pd Kerr rotation spectra in Figures 2.56(a) and 2.56(b), respectively.

The Kerr rotation spectra are modified appreciably upon addition of one (see Figure 2.56(b)) or two (see Figure 2.56(c)) Co atomic planes to an MLS with an imperfect interface. In the supercells, the Co and Pd planes are separated by A-, B-, and C-type interfacial layers. The essential points as regards the modification of the spectra can be summarized as follows:

(i) The amplitude of the spectra increases as the amount of Co increases. In the ir spectral range, the characteristic features of the Co spectrum become more pronounced.

(ii) For the supercells containing one planar alloy of  $Co_1Pd_3$  composition treated as an interface region, the change of the relative amplitudes of the characteristic peaks in the uv region upon addition of two Co atomic planes is clearly visible.

(iii) For the supercells containing as an interface region a single  $Co_3Pd_1$  atomic plane or two  $Co_3Pd_1/Co_1Pd_3$  atomic planes, the main effect of increas-

ing the number of Co atomic planes is a shift of the uv peak position to lower energy. This effect is accompanied by a narrowing of the band width.

(iv) The amplitudes of the spectra in the energy range above 4 eV are up to 100% higher than those of the ideal 2Co/4Pd and 3Co/3Pd MLS.

From the band-structure calculation results it follows that the Co and Pd electronic states in the alloy interface layers are strongly modified by the hybridization. As the volume in which the hybridization occurs is significantly larger in a MLS with an imperfect interface, the contribution of these hybridized states to the MO spectra increases compared to that for a MLS with an ideal interface. Hence, the similarity between the nCo/A/mPd MLS spectra and the spectra of Pd-rich CoPd alloys [517] becomes closer, especially for the MLS with a small Co sublayer thickness. Another effect of interfacial alloy formation is stronger (compared to that for the ideal MLS) spin polarization of the whole Pd spacer. The averaged magnetic moment per Pd atom calculated for the different structures approaches values up to 80% larger than those for the ideal MLS models. One can expect that as a result of the increased magnetic moment induced on the Pd atoms, they will make larger contributions to the MO spectra. This can be clearly seen in the energy range below 2 eV, where the Kerr rotation spectra are very sensitive to the Pd contribution. As was established earlier [517, 370], the interband magneto-optical transitions in spin-polarized Pd give a positive Kerr rotation in the ir energy range, whereas the transitions between the electronic states with a large degree of admixture of Co 3d states result in a negative contribution to the Kerr rotation in this range, even when the Co states are considerably modified by the hybridization with Pd states. As a result of the two compensating contributions, the amplitude of the Kerr rotation spectra of the MLS is suppressed in the ir energy range and the rotation becomes positive in the case of 0Co/A/4Pd MLS (see Figure 2.56(a)). As the number of Co atomic planes increases, their relative contribution to the MOKE spectra becomes higher and the Kerr rotation in the ir range becomes negative, which brings the spectra closer to the fcc Co spectrum, as can be seen in Figure 2.56. A peak appearing at 1.5 eV in the MLS spectra is evidently related to the corresponding peak in the fcc Co spectrum.

As it is seen in Figure 2.56(a), in the uv spectral range the contribution to the MLS spectra coming from the interface alloy region and strongly polarized Pd atomic planes is also large enough, contrary to the case for the ideal model of the MLS, and controls the spectral shape in that energy range. The observed overall increase of the rotation amplitude along the sequence 0Co/A/4Pd, 0Co/B/4Pd and 0Co/C/2Pd is related to an increase of the relative Co content in the structures, which changes from 8% in 0Co/A/4Pd up to 33% in 0Co/C/2Pd. If one or two Co atomic planes are included in the structures, the relative contribution of Co to the total Kerr spectra increases. Hence, the



*Figure 2.57.* Comparison of the measured and calculated polar Kerr rotation (a) and ellipticity (b) spectra of the as-deposited 3.5 Å Co/18.3 Å Pd MLS film and the model  $2\text{Co}/(\text{Co}_1\text{Pd}_3)/5\text{Pd}$  as well as the ideal 2Co/7Pd MLS model. The spectra of the film annealed at 800 K and calculated for the model of fcc disordered  $\text{Co}_{0.25}\text{Pd}_{0.75}$  alloy are included [509].

shape of the spectra becomes closer to that of the fcc Co spectra and the enhancement of the Kerr rotation peak amplitude in the uv range can be seen in Figures 2.56(b) and 2.56(c). It is worth pointing out, however, that the MOKE spectra are not simple superpositions of the contributions arising from the constituent sublayers.

It was found that of all the MLS considered, the models in which the interface alloy layer is a Pd-rich alloy reproduce better the main spectral features of the experimentally studied Co/Pd MLS and the tendencies in the modification of the spectra as the thickness of the Co sublayer increases. In Figure 2.57, the MOKE spectra calculated for the ideal 2Co/7Pd MLS and the 2Co/(Co<sub>1</sub>Pd<sub>3</sub>)/5Pd model structure are directly compared to the experimental spectra of the 3.5 Å Co /18.3 Å Pd MLS with the sublayer thicknesses closest to the model structure. It is clearly seen that, if the interfacial alloying is taken into account, the characteristic shape of the measured spectrum with the shoulder in the uv range is reproduced well by the calculations. Also, the amplitude of the calculated Kerr rotation is close to the experimentally studied one, as opposed to the ideal model 2Co/7Pd MLS with the same period for which the amplitude is 50% smaller. The enhancement of the calculated amplitude and better agreement with the experiment can be observed also for the Kerr ellipticity spectra.

To study the effect of total interlayer intermixing on the MOKE spectra and as a final test of the assumed interface model, the 3.5 Å Co /18.3 Å Pd MLS film was annealed under high vacuum at 800 K for 5 h. At such high temperatures the diffusion processes are very intensive and the whole layered structure is uniformly homogenized, becoming a disordered fcc alloy film of effective composition Co<sub>0.2</sub>Pd<sub>0.8</sub>, as was confirmed by structural study. The huge changes of the MOKE spectra after annealing can be seen from Figure 2.57. The Kerr rotation and ellipticity spectra amplitudes increase significantly and the spectral shapes become close to those observed for Co-Pd alloys of comparable composition [517]. The calculated MOKE spectra of disordered Co<sub>0.25</sub>Pd<sub>0.75</sub> alloy taken from reference [517] are also included in Figure 2.57 for comparison. As it can be seen, the agreement of the calculated and measured Kerr rotation and ellipticity spectra of the alloyed structure is excellent (the systematic shifts of the spectra on the energy scale are of common nature for LDA-based calculations. Thus, on the basis of the results obtained for the Co/Pd MLS, the following conclusions have been reached:

(i) the MLS studied have relatively sharp interfaces the 'chemical thickness' the order of one atomic layer; and

(ii) they can be well described by a model MLS structure with an ordered Pd-rich interfacial alloy.

In the real Co/Pd MLS, the interface microstructure may be more complicated and probably only partial chemical ordering occurs. As was inferred from the x-ray diffraction data, the Co/Pd MLS studied have a well-defined layered structure. Nevertheless, some intermixing at the interface during the samples' deposition process is very probable. This effect leads, in turn, to higher induced spin polarization in a larger volume of Pd and makes the whole volume magneto-optically active. The results obtained allow us to explain the origin of the observed MOKE spectra of the MLS and to understand why the thickness of the so-called 'magnetic interface' can be larger than that of the 'crystallographic' one, as was recently reported for other Pd-based multilayered systems [518]. The conclusions are also consistent with the results derived from the phenomenological multi-reflection approach, not presented here, which indicates the Pd spin polarization to extend through a depth of the order of four Pd atomic layers. In conclusion it should be pointed out that in the Co-Pd systems the MOKE is governed by the off-diagonal part of the optical conductivity tensor. It was found that the *ab initio* calculations were performed for model Co/Pd MLS with sharp interfaces reproduced the main peculiarities of the experimental Co/Pd MOKE spectra only moderately well. It is shown that the main peculiarities and the tendencies in the modification of the MLS spectra with the variation of the Co sublayer thickness are adequately reproduced when alloying, even limited to one atomic plane, is taken into account. The MOKE spectra calculated for the model structures with ordered  $Co_1Pd_3$  interfacial planes, reproduce the measured spectra best. The results obtained demonstrate that interface microstructure plays a crucial role in the formation of the MOKE spectra of the Co/Pd layered structures.

#### $Co_x Pd_{1-x}$ alloys

In the real MLS systems the chemical and structural disorder often occurs at the interface. These effects can be examined using model disordered alloys.

The description of the magneto-optical properties of a disordered system on a microscopic level and understanding the effect of chemical order and crystal symmetry on these properties are of great importance. The most powerful approach to calculate the electronic structure of randomly disordered solids is the Coherent Potential Approximation (CPA) in connection with the Korringa-Korr-Rostoker method of band structure calculation (KKR-CPA) [519]. Within this formalism a quantitative description of such phenomena as magnetoresistance [520] and X-ray dichroism [521] was obtained. In both cases the central quantity to be calculated is the optical conductivity tensor [9]. Unfortunately, the techniques to deal with that quantity for finite frequencies in the optical regime of light have not yet been developed. For that reason the theoretical investigations of the optical and magneto-optical properties of disordered  $Co_x Pd_{1-x}$  alloys in Ref. [517] has been made using the supercell approximation. To test the theoretical approach, the MOKE spectra for a set of  $Co_x Pd_{1-x}$ polycrystalline alloy films for x=0.13, 0.22, 0.31 and 0.44 have been also measured.

To investigate the influence of composition and local environment on the MO properties of disordered alloys, *ab initio* band-structure calculations for *ordered* Co–Pd alloys (Co<sub>1</sub>Pd<sub>15</sub>, Co<sub>1</sub>Pd<sub>11</sub>, Co<sub>1</sub>Pd<sub>7</sub>, Co<sub>2</sub>Pd<sub>10</sub>, Co<sub>4</sub>Pd<sub>12</sub>, Co<sub>3</sub>Pd<sub>9</sub>, Co<sub>2</sub>Pd<sub>6</sub>, Co<sub>1</sub>Pd<sub>3</sub> and Co<sub>1</sub>Pd<sub>1</sub>) have been performed. This sequence corresponds to a variation of the Co content in the range of 6–50%. For Co<sub>1</sub>Pd<sub>1</sub> and Co<sub>1</sub>Pd<sub>3</sub> alloys the AuCu ( $L1_0$ ) and AuCu<sub>3</sub> ( $L1_2$ ) structures were assumed, respectively. Supercells for all other alloys, except for Co<sub>1</sub>Pd<sub>11</sub>, consist of two or more adjacent fcc unit cells with Co and Pd atoms distributed over nonequivalent atomic positions according to the specific alloy composition.

For the  $Co_1Pd_7$  and  $Co_1Pd_{15}$  alloys both cubic and tetragonal supercells were constructed, whereas for the  $Co_1Pd_{11}$  alloy a hexagonal unit cell was used. The lattice constant for all the alloys has been chosen to correspond to the experimental data [522].

As was mentioned above, the magneto-optical effects are determined by the dielectric tensor components  $\varepsilon_{\alpha\beta}$ . This tensor can be represented as a sum  $\varepsilon_{\alpha\beta} = \varepsilon^s_{\alpha\beta} + \varepsilon^a_{\alpha\beta}$  of two parts which are symmetric (optical) and antisymmetric (magneto-optical) with respect to the magnetization direction. That is, the relations  $\varepsilon^s_{\alpha\beta}(\mathbf{M}) = \varepsilon^s_{\alpha\beta}(-\mathbf{M})$  and  $\varepsilon^a_{\alpha\beta}(\mathbf{M}) = -\varepsilon^a_{\alpha\beta}(-\mathbf{M})$  hold, where **M** denotes the magnetization vector. The antisymmetric part  $\varepsilon^a_{\alpha\beta}$  can be expressed as  $\varepsilon^a_{\alpha\beta} = ie_{\alpha\beta\gamma}g_{\gamma}$ , where  $e_{\alpha\beta\gamma}$  is the antisymmetric pseudo-tensor and  $g_{\gamma}$  is a component of the gyration vector **g** [218].

For most materials the relation  $|\mathbf{g}| \ll det ||\varepsilon_{\alpha\beta}^s||$  holds and expressions for all non-reciprocal magneto-optical effects, measured usually as a difference quantity with respect to a reversal of the magnetization, can be decomposed into the product of the complex number  $\mathbf{g}\hat{\mathbf{g}}$  and some function depending on the optical part of the dielectric tensor  $\varepsilon_{\alpha\beta}^s$  as well as the light propagation and magnetization directions (see, e.g. Ref. [227]).

It should be noted that it is possible for the optical part of the dielectric tensor may play a crucial role in the MO spectra formation, for example in CeSb [523], or may exhibit a noticeable anisotropy [524], however, this is not the case for the Co-Pd compounds investigated here. It was found that in the energy range  $0.5 < h\nu < 6$  eV the calculated components  $\varepsilon_{\alpha\beta}^s$  are smooth and exhibit only a very weak dependence on both the chemical ordering and the alloy composition. Moreover, for the uniaxial model structures the optical anisotropy defined as  $\delta_A = (\varepsilon_{\perp} - \varepsilon_{\parallel})/\epsilon$  does not exceed 5%. Here we denoted  $\epsilon = (2\varepsilon_{\perp}^s + \varepsilon_{\parallel}^s)/3$ , where  $\varepsilon_{\perp}^s$  and  $\varepsilon_{\parallel}^s$  stand for the main optical dielectric tensor components corresponding to the light polarization perpendicular and parallel to the n-fold symmetry axis (c) of the crystal. Thus, all features of the MO spectra of the Co-Pd compounds are determined by the  $g(\omega)$  function.

As mentioned above, our calculations involved both cubic and uniaxial models. For a crystal with cubic symmetry the dependence of g on the magnetization direction  $\hat{\mathbf{M}}$  is negligible [525], whereas for uniaxial crystals it can be appreciable. Uspenskii *et al.* [526] have shown that, up to the second order in spin-orbit coupling strength, this dependence can be expressed in terms of the gyration vectors  $g_{\parallel}$  and  $g_{\perp}$  calculated for the cases of  $\hat{\mathbf{M}} \parallel c$  and  $\hat{\mathbf{M}} \perp c$ , respectively:

$$\mathbf{g} = \hat{\mathbf{M}}(g_{\parallel}\cos^2\theta + g_{\perp}\sin^2\theta) + \hat{\mathbf{n}}(g_{\parallel} - g_{\perp})\sin\theta\cos\theta, \qquad (2.4)$$

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*Figure 2.58.* Orientation dependence of the Im  $\omega^2 g(\omega)$  spectra for Co<sub>1</sub>Pd<sub>1</sub>, Co<sub>2</sub>Pd<sub>6</sub> and Co<sub>1</sub>Pd<sub>15</sub>. All spectra were convoluted with a Lorentzian of width 0.5 eV [517].

where  $\hat{\mathbf{n}}$  stands for the unit vector, orthogonal to  $\hat{\mathbf{M}}$  and lying in the same plane as  $\hat{\mathbf{M}}$  and  $\mathbf{c}$ , and  $\theta$  is the angle between the magnetization vector  $\mathbf{M}$  and n-fold symmetry axis c.

Fig. 2.58 presents the calculated Im  $\omega^2 g_{\parallel}(\omega)$  and Im  $\omega^2 g_{\perp}(\omega)$  spectra for a selected set of uniaxial crystals. One can see that for the Co<sub>1</sub>Pd<sub>1</sub> and Co<sub>2</sub>Pd<sub>6</sub> the orientation dependence of the gyration vector is rather strong and exhibits itself in changes of the relative magnitude and energy location of both ir and uv maxima. The feature at 2.5 eV in the  $g_{\parallel}(\omega)$  spectra disappears completely for  $\mathbf{M} \perp c$ . For the more diluted tetragonal Co<sub>1</sub>Pd<sub>7</sub> alloy the orientation dependence of the  $g(\omega)$  spectra was found to be relatively weak and it practically disappears for Co<sub>1</sub>Pd<sub>15</sub> (see Fig. 2.58). The same tendencies were found also for the Re  $\omega^2 g(\omega)$  spectra.

To take into account the effects of random orientation of microcrystals in the alloys studied, we have to average Eq. 2.4 over different relative orientations of the crystal axes and magnetization direction which gives:

$$g^{av}(\omega) = (2g_{\perp}(\omega) + g_{\parallel}(\omega))/3.$$
(2.5)



*Figure 2.59.* Effect of the chemical order on the calculated  $\omega^2 g(\omega)$  spectra of the Co<sub>0.25</sub>Pd<sub>0.75</sub> alloy [517].

The main effect of the averaging (see Fig. 2.58) on the  $Co_1Pd_1$  spectrum is a change of the band-shape in the uv range as compared to the spectrum calculated with the magnetization directed along the *c* axis. The position of the main uv maximum shifts to lower energy and in  $Co_2Pd_6$  the band becomes broader. In both alloys the structure at ~1.5 eV becomes less pronounced.

To study the dependence of the MO spectra on chemical ordering, let us consider the results for alloys with 1:3 stoichiometry. The calculations for the cubic  $L1_2$  phase together with those for the tetragonal  $D0_{22}$ ,  $D0_{23}$ ,  $Co_3Pd_9$  and second kind of  $Co_4Pd_{12}$  supercells have been performed. Tetragonal supercells  $Co_3Pd_9$  and  $Co_4Pd_{12}$  consisting of one and two more central planes, respectively, as compared to the  $D0_{22}$  structure, were used. All the alloys have the same nominal composition of  $Co_{0.25}Pd_{0.75}$ , but differ in symmetry and local environment of Co and Pd sites. While all these structures have identical first neighbor coordination (each Co has 12Pd neighbors and each Pd has 8Pd+4Co neighbors), there are differences in the second atomic shell. For the  $L1_2$ ,  $D0_{22}$  and  $D0_{23}$  cells each Co has 6Co, 4Co+2Pd and 5Co+1Pd second neighbors with local site symmetry  $O_h$ ,  $D_{4h}$  and  $C_{4v}$ , respectively. The atomic coordination around Pd in the second shell consists of 6Pd for  $L1_2$  structure,

while there are two inequivalent Pd sites for  $D0_{22}$  (with 6Pd and 2Co+4Pd) and for  $D0_{23}$  (with 6Pd and 1Co+5Pd). These three structures will be taken as basic because the other structures studied, like Co<sub>3</sub>Pd<sub>9</sub> and Co<sub>4</sub>Pd<sub>12</sub>, are composed of various numbers of the above described inequivalent Co and Pd sites.

In Fig. 2.59 the spectra of the imaginary (a) and real (b) parts of  $\omega^2 g(\omega)$  are shown. For Co<sub>2</sub>Pd<sub>6</sub> (DO<sub>22</sub>) and Co<sub>4</sub>Pd<sub>12</sub> (DO<sub>23</sub>) alloys  $\omega^2 g^{av}(\omega)$  is presented. As a result of the change of the atomic arrangement and accompanied lowering of the local site symmetry along the sequence  $L1_2 - D0_{22} - D0_{23}$ , the spectra become less structured and the peaks broaden, as can be seen, for example, comparing the Re  $\omega^2 g(\omega)$  spectra in the spectral range up to 3 eV. This effect apparently arises from the fact that the lowering of the local symmetry of atomic sites generally leads to the appearance of an increasing number of nonequivalent interband transitions, with their contributions, the MO spectra spread out over wider energy range. It was found that the resulting  $\omega^2 g^{av}(\omega)$ spectra calculated for Co<sub>3</sub>Pd<sub>9</sub> and Co<sub>4</sub>Pd<sub>12</sub> alloys can be well reproduced by averaging the basic  $L1_2$ ,  $D0_{22}$  and  $D0_{23}$  spectra, weighted by the corresponding numbers of the equivalent sites in these structures.

To estimate the  $\omega^2 g^{av}(\omega)$  spectrum of disordered Co<sub>0.25</sub>Pd<sub>0.75</sub> alloy it is necessary to assume a procedure of averaging the spectra over possible atomic arrangements. Here the simplest assumption was made that the basic cells appear with equal probabilities and the contribution of each cell to the spectrum is proportional to its' number of atomic sites. On this base the averaged spectrum was obtained as the weighted average of the  $L1_2$ ,  $D0_{22}$  and  $D0_{23}$  spectra with the weights of 1, 2 and 4, respectively. As a result of the configuration averaging, the spectrum becomes less structured and is closest to the spectrum of the  $D0_{23}$  structure (see Fig. 2.59). It can be concluded that for the alloys studied the local atomic arrangement and sites symmetry controls the MO properties.

To discuss the composition dependence of MO properties of the alloys under consideration, we focus here on the polar Kerr rotation spectra, because they are the quantities measured directly in the experiment. If the optical anisotropy  $\delta_A$  is small, the complex Kerr rotation angle, neglecting the second-order quantities ( $\delta_A^2$ ,  $\delta_A g$  and  $g^2$ ), has the form:

$$\phi_K = \vartheta_K + i\eta_K = g/(\sqrt{\epsilon}(1-\epsilon)). \tag{2.6}$$

Eq. 2.6 is linear with respect to g and this allows us to use for the uniaxial systems  $g^{av}$  instead of g. To take into account finite life-time effects the calculated spectra were convoluted with a Lorentzian of width 1.0 eV. Calculated polar Kerr rotation and ellipticity spectra of the Co-Pd alloys of different composition are shown, together with experimentally measured ones, in Fig. 2.60. To take into account the decrease of Curie temperature for diluted alloys, all



*Figure 2.60.* Comparison of the calculated and experimental polar Kerr rotation (a) and ellipticity (b) spectra for the different composition of the Co-Pd alloys [517].

experimental spectra have been scaled with the factor  $M_{4.2}/M_{300}$ , where  $M_{4.2}$ and  $M_{300}$  are magnetization at 4.2 K and 300 K, respectively. Both experimental and theoretical data exhibit the same features. As the Co content diminishes, the magnitude of the rotation angle in the energy range 2.5–4.5 eV decreases. The shoulder at ~1.5 eV, clearly seen in the  $\vartheta_K$  spectrum of Co<sub>1</sub>Pd<sub>1</sub> alloy, disappears completely in diluted alloys and the Kerr rotation changes sign below  $\sim 2 \text{ eV}$ . In the uv range, the peak centered at 4 eV in Co<sub>1</sub>Pd<sub>1</sub> transforms into the broad two-peak structure. Also, a shift of the Kerr ellipticity zero-crossing to higher energy with decrease of Co content is observed, as well as a diminishing of the amplitude at  $\sim 5 \text{ eV}$ . However, the calculated peak positions of both Kerr rotation and ellipticity are slightly shifted to higher energies with respect to the experimental ones. This discrepancy is apparently due to a drawback of the LDA-based calculations which was lately extensively discussed in the literature [514].

It is interesting to note that the calculated MOKE spectra of  $Co_2Pd_{10}$ ,  $Co_1Pd_7$ ,  $Co_1Pd_{11}$  and also  $Co_1Pd_{15}$  alloys are close to each other, although the Co content in the alloys decreases from 16.5% to as low value as 6%. From this one can conclude that the MOKE spectra of diluted Co-Pd alloys are determined to a great extent by the MO properties of spin-polarized Pd. This is in line with the relatively large average Pd magnetic moment obtained from the calculations (e.g.  $0.24\mu_B/atom$  for  $Co_1Pd_{15}$ ) which depends weakly on Co content in the Co-Pd alloys.

It should be noted that the theoretical spectra shown in Fig. 2.60, except for the spectrum of  $Co_{0.25}Pd_{0.75}$ , have been obtained for one specific atomic arrangement. The theoretical spectrum for  $Co_{0.25}Pd_{0.75}$ , obtained as the weighted average of the spectra for  $L1_2$ ,  $D0_{22}$  and  $D0_{23}$  structures according to the procedure described above, is presented in Fig. 2.60. As a result of the averaging over different atomic configurations, the MOKE spectrum of  $Co_{0.25}Pd_{0.75}$  becomes less structured and the minimum in the polar Kerr rotation spectrum, centered at about 4.5 eV in the ordered  $Co_1Pd_3 - L1_2$ , transforms into broad structure as is observed in the measured spectrum of the disordered  $Co_{0.22}Pd_{0.78}$  alloy film.

It can be concluded that the MOKE calculations in which the effects of the random orientation of microcrystals and/or chemical disorder are taken into account reproduce well the experimental spectra of the Co-Pd disordered alloys and the dependence of the spectra on the composition. The optical part of the dielectric tensor of these compounds depends very weakly on both the alloy composition and chemical ordering and does not show noticeable anisotropy for the uniaxial crystals. Moreover, its frequency dependence is structureless and all features in magneto-optical spectra are determined by the gyrotropic part of the dielectric tensor, which exhibits a considerable orientation anisotropy increasing with the Co content.

No	$N_{layers}$	$t_{Co}$ Å	$t_{Pt}$ Å
1	50	4.6	13.6
2	47	5.8	15.2
3	43	6.9	12.5
4	40	9.0	14.4
5	33	18.9	14.3

*Table 2.7.* The parameters of the Co/Pt MLS studied. No is the sample number,  $N_{layers}$  is the number of bilayers,  $t_{Co}$  ( $t_{Pt}$ ) are measured thicknesses of the Co (Pt) sublayer [514].

# 2.2.2 Magneto-optical properties of Co/Pt multilayers

### **Experimental results**

A detailed experimental study of the MO properties of Co/Pt MLS using MOKE spectroscopy has been done in the Ref. [514] for the series of sputter deposited MLS listed in Table 2.7.

The measured polar Kerr rotation and ellipticity spectra of the Co/Pt MLS studied are shown in Fig. 2.61. All samples measured possess well defined MOKE hysteresis curves with saturation characteristics, and all  $\theta_K$  and  $\eta_K$  spectra were measured under saturation conditions. The Kerr rotation spectra display two well known features. There is a prominent broad negative peak in the uv region and a smaller one in the ir part. The ir peak, centered at 1.5 eV is most prominent for a pure Co thick film [527] and for MLS its amplitude continuously diminishes with decreasing MLS Co sublayer thickness. The uv peak slightly varies in energy position from 4.1 eV to 3.9 eV with increasing Co sublayer thickness. The uv peak amplitude overcomes that of a pure Co film centered at 3.7 eV and its amplitude relatively weakly depends on the composition of the MLS studied.

The characteristic feature in the Kerr ellipticity spectra is the shift of the zero crossing from 1.5 eV in pure Co film to 3.7 eV in MLS with decreasing Co sublayer thickness and the formation of a positive peak around 3 eV. The prominent minimum of the Kerr ellipticity centered at 4.9 eV observed in Co film presumably shifts its position to the photon energy region  $\hbar \omega > 5.5$  eV, inaccessible in the experiment considered.

The optical properties of the MLS, in the form of spectral dependencies of the diagonal component of the effective optical conductivity tensor  $\sigma_{xx}$ , are shown for the real  $\sigma_{xx}^{(1)}$  and imaginary part  $\sigma_{xx}^{(2)}$  in Fig. 2.62(a) and Fig. 2.62(b), respectively. For clarity, in the picture the spectra of only three samples are shown and the other MLS spectra are located in between them. As seen from the results, generally there are little differences in the absorptive part of the



*Figure 2.61.* Experimental polar Kerr rotation (a) and ellipticity (b) spectra of Co/Pt MLS and fcc Co film. Sublayer thicknesses marked in the pattern are given as  $t_{Co}$ Å/ $t_{Pt}$ Å[514].

optical conductivity  $\sigma_{xx}^{(1)}$  for all MLS studied. The magnitudes of the spectra scale roughly with the thickness of Co sublayers. The corresponding spectra of thick Co and Pt films prepared by the same technique are shown for comparison. It can be observed that the  $\sigma_{xx}^{(1)}(\omega)$  curves for the MLS are not located between the Co and Pt one in the energy range 2 - 5.5 eV. Several reasons can be considered for this difference. A common problem in metal optics is a great sensitivity of the optical constants on the state of the sample surface [528]. Another cause can be the fact that the optical properties of thick metal films are slightly different from the ones for MLS constituent sublayers [529]. In other words, for individual layer thicknesses of a few atomic monolayers the effective dielectric constants of the medium differ from the dielectric constants of bulk or thick film material. Besides, the response of an ultrathin medium to an electromagnetic wave is substantially influenced by the electronic interaction with adjacent layers.



*Figure 2.62.* The absorptive (a) and dispersive (b) parts of the diagonal components of the conductivity tensor for Co/Pt MLS and Co and Pt films, determined from ellipsometric measurements [514].

The spectra of the dispersive part of the optical conductivity tensor  $\sigma_{xx}^{(2)}$  are also weakly dependent on the MLS composition and are located in between the spectra for thick Co and Pt films.

To separate the contribution to the MOKE coming from the diagonal and off-diagonal conductivity tensor components the function  $\Phi = 4\pi (\omega^2 (\varepsilon_{xx} - 1)\sqrt{\varepsilon_{xx}})^{-1}$  has been evaluated from the optical measurements. The real part of the function  $\Phi^{(1)}$  is shown in Fig. 2.63(a). It has been found that for the compounds under consideration, the product of  $\Phi^{(1)}$  and  $\omega \sigma_{xy}^{(2)}$  gives the main contribution (> 80%) into the polar Kerr rotation spectra. It should be noted that this function is nearly flat over the investigated spectral region for all MLS studied and weakly dependent on their composition. In contrast, the shape and the amplitude of the  $\Phi^{(1)}$  spectrum change significantly in the case of the Co film. As a consequence, the absorptive part of the off-diagonal component of the conductivity tensor,  $\omega \sigma_{xy}^{(2)}$ , presented in Fig. 2.63(b) for the MLS studied



*Figure 2.63.* The contribution to the Kerr rotation spectra from the diagonal part of the conductivity tensor (see text) (a), and (b) the absorptive part of the off diagonal component  $\omega \sigma_{xy}^{(2)}$ , determined from the ellipsometric and the complex polar Kerr angle measurements for Co/Pt MLS and Co film [514].

is in the overall form unexpectedly similar to the polar Kerr rotation, whereas for the case of pure Co the shape of the polar Kerr rotation and  $\omega \sigma_{xy}^{(2)}$  differ significantly. Inspection of these curves shows that the presence of Pt leads to the strong enhancement of the  $\omega \sigma_{xy}^{(2)}$  in the uv range. The enhancement of the polar Kerr rotation measured is much smaller due to the corresponding increase of the diagonal part of  $\sigma$  (see Fig 2.63.a).

Thus, it can be concluded that the peak observed in the ir part of the Co/Pt MLS polar Kerr rotation spectra can be related mainly to the MO activity of Co. On the other hand, the peak observed in the uv region is for pure Co connected rather with the peculiarities in the diagonal part of the conductivity tensor, while for Co/Pt multilayers it is governed by the off-diagonal component of  $\sigma$  and originate from Co-Pt interaction at the MLS interface.

The multilayer MOKE spectra measured are qualitatively similar to the spectra which have been published for Co/Pt MLS prepared by different techniques and for random fcc Co–Pt alloys' [507, 387, 299, 393, 530, 531] and all exhibit similar MOKE enhancement in the uv region.

### Theoretical results and discussions

In order to reproduce the electronic structure of the interlayer interface the band structure calculations of some model ordered Co–Pt alloys and MLS with various layer thicknesses have been performed in Ref. [514]. An *abcabc* stacking sequence of closely packed planes corresponding to the fcc-(111)-texture for all the MLS structures was assumed except for 1Co/1Pt for which the *ababab* stacking has also been studied. No attempt has been made to optimize the interlayer spacing, which was taken corresponding to ideal the c/a ratio. Ordered CoPt<sub>3</sub> and Co<sub>3</sub>Pt alloys were calculated in the Cu<sub>3</sub>Au crystal structure, while for the CoPt alloy the AuCu structure was used. For all the compounds the mean volume per atom was chosen to be equal to the average of the atomic volumes of pure fcc Pt and hcp Co with the experimental lattice constants. The radii of Co and Pt atomic spheres were chosen to be equal to 1.46 Å.

The characteristic feature of the electronic structure of Co-Pt multilayers and alloys is the strong hybridization of Co 3d and Pt 5d states, the later being much more delocalized. Fig. 2.64 shows the spin- and site-projected densities of electronic states (DOS) for Co and Pt sites in 2Co/1Pt, 1Co/1Pt, and 1Co/2Pt multilayers. The valence band width in the MLS is mainly governed by Pt dd hybridization in the close-packed planes consisting of Pt atoms and varies moderately with an increase of the Pt sublayer thickness. Strong spin-orbit interaction in the Pt atomic sphere results in splitting of  $d_{3/2}$  and  $d_{5/2}$  states with the energy difference between their centers being  $\sim 1.5$  eV. Inside the Co atomic sphere the effect of the spin-orbit coupling is much weaker than the effect of the effective magnetic field. The centers of both Pt  $d_{3/2}$  and  $d_{5/2}$ states lie at lower energies than the centers of the corresponding Co states. As a result of the Co d – Pt d hybridization, the electronic states at the bottom of the valence band are formed mainly by Pt states while the states in the vicinity of the Fermi level  $(E_F)$  have predominantly Co d character with an admixture of Pt d states. The hybridization with the exchange split Co d states leads to a strong polarization of Pt d states near  $E_F$ . The resulting difference in occupation numbers for Pt states with the opposite spin projections gives rise to the appearance of a comparatively large spin magnetic moment at the Pt site.

In the case of the 4Co/2Pt, 2Co/4Pt, and 1Co/5Pt MLS the DOS curves for Co and Pt sites at the interface are similar to the curves shown in Fig. 2.64. The DOS projected to a site in the interior of the sublayer is close to that of the corresponding bulk metal.



*Figure 2.64.* Spin- and site-projected densities of *d*-states (in units of states/(atom×spin×eV)) for Co and Pt in 1Co/1Pt, 2Co/1Pt, and 1Co/2Pt multilayers. Full and dotted lines correspond to majority and minority spin states, respectively, dashed line marks the Fermi energy [514].

Calculated spin- and site-projected DOS curves for ordered Co<sub>3</sub>Pt, CoPt, and CoPt<sub>3</sub> alloys are shown in Fig. 2.65. As compared to the Co/Pt MLS, the electronic structure of the alloys depends more on the alloy composition. Variation in relative positions of Co and Pt *d* bands affects the Co d – Pt dhybridization. The valence band width is larger in the Pt-rich alloys due to an increase of the number of Pt nearest neighbors surrounding the Pt site.

Calculated spin  $m_s$  and orbital  $m_l$  magnetic moments of the Co–Pt multilayers and alloys are summarized in Table 2.8. Both spin and orbital moments at the Co site in the MLS are bigger than in bulk hcp Co with the experimental lattice constant. Nevertheless, from the comparison with the values of  $m_s$ and  $m_l$  calculated for either hcp or fcc Co with the lattice constant used for the MLS it follows that the moments' enhancement is mainly due to the lattice expansion. In contrast to the case of the MLS, Co and Pt magnetic moments in the Co–Pt alloys decrease with an increase of Pt content.

When studying the MO properties of the complex Co–Pt compounds it is natural to consider as a reference point the properties of pure Co [324, 532, 322]. The calculated energy dependence of the polar Kerr rotation angle of fcc



*Figure 2.65.* Spin- and site-projected densities of *d*-states (states/(atom×spin×eV)) for Co and Pt in Co<sub>3</sub>Pt, CoPt, and CoPt<sub>3</sub> alloys. Full and dotted lines correspond to majority and minority spin states, respectively [514].

Co with the lattice constant a = 3.539 Å corresponding to the experimental value for hcp Co is shown in Fig. 2.66 (dashed line). A comparison with the experimental data [507, 312] shows that the calculations reproduce correctly the overall shape of the spectra but the uv peak is shifted by about 1 eV to higher energies. The discrepancy is similar to that observed in the theoretical Kerr rotation spectra of Ni [320, 321] and is apparently due to a failure of LSDA to describe correctly the width and the spin splitting of d bands in ferromagnetic 3d metals. A better agreement with the experiments is obtained for the Kerr rotation calculated with a larger lattice constant a = 3.734 Å which is equal to the value chosen for all model MLS studied (see solid line in Fig. 2.66). The increase of the lattice constant results in a narrowing of the d band and, consequently, in an energy scaling of the calculated spectrum. The same tendency have been observed not only for pure Co but also for the Co–Pt alloys and multilayers.

Although the lattice expansion removes the shift of the peaks the calculated amplitude of the peak at 2 eV remains smaller than the experimental one. To elucidate the reason for the discrepancy in amplitudes the dependence of the

	$m_s \ (\mu_B/\text{atom})$		$m_l \ (\mu_B/\text{atom})$	
System	Со	Pt	Со	Pt
hcp Co ( $a = 2.507$ Å)	1.559		0.079	
hcp Co	1.716		0.130	
fcc Co	1.731		0.115	
2Co/1Pt	1.776	0.183	0.098	0.019
1Co/1Pt	1.752	0.255	0.089	0.028
1Co/2Pt	1.880	0.207	0.099	0.022
4Co/2Pt	1.810	0.192	0.103	0.018
	(1.738)		(0.104)	
2Co/4Pt	1.765	0.154	0.095	0.016
		(0.049)		(0.001)
1Co/5Pt	1.869	0.175	0.090	0.018
		(0.058)		(0.006)
Co <sub>3</sub> Pt	1.735	0.339	0.087	0.083
CoPt	1.681	0.321	0.090	0.048
CoPt <sub>3</sub>	1.607	0.199	0.027	0.035

Table 2.8. Calculated spin  $m_s$  and orbital  $m_l$  magnetic moments of the Co–Pt multilayers and alloys. Values in parentheses correspond to the atoms in the layer below the interface. Magnetic moments of hcp Co with the experimental lattice constant a = 2.507 Å is also given [514].



*Figure 2.66.* Experimental and theoretical polar Kerr rotation spectra of Co [514]. The theoretical Kerr rotation spectra of fcc Co calculated using the experimental lattice constant and with the plasma frequency in the Drude term taken from the calculations (dashed curve), with  $\hbar\omega_p = 5 \text{ eV}$  (dotted curve), and calculated using the same lattice constant as for the Co/Pt MLS (solid curve). Experimental spectra are shown by circles (present work), squares (Ref. [312]), and triangles (Ref. [507]).

MOKE spectra on the intraband part of the conductivity tensor was examined [514]. It has been found that in the case of pure Co the Kerr rotation is rather sensitive to the values of  $\gamma$  and  $\omega_p^2$  for energies up to 5 eV. Variation of the values changes the amplitude and the position of the uv peak as well as of the peak at 2 eV. The sensitive effect of the Drude term on the uv peak is due to interband contribution to the  $\sigma_{xx}$  being small in this energy range. Thus, though the absolute values of the intraband conductivity are small, its relative contribution is significant. The calculated plasma frequency of hcp Co with the experimental lattice constant was found to be 7.2 eV and the experimental value for the hcp Co single crystal is  $\sim$ 5 eV [524]. Such a discrepancy is consistent with the previous observation [533] that the calculated values of  $\omega_p$  are, as a rule, 20-50% higher than the experimental values. The polar Kerr rotation calculated with  $\hbar\omega_p = 5 \text{ eV}$  is shown by the dotted line in Fig. 2.66. The use of the smaller value of  $\omega_p$  leads to better agreement with the experiment. Nevertheless, one can not manage to achieve close agreement with the experiment in the ir range varying the Drude constants in reasonably wide limits. It has been found that for the Co-Pt multilayers and alloys the dependence of MOKE on the intraband contribution is much weaker, and in the following we use calculated values of  $\omega_p$  to evaluate the intraband conductivity.

Theoretical results for the absorptive part of the conductivity tensor  $\sigma_{xx}^{(1)}$  for fcc Co, Pt, and some model Co–Pt multilayers and alloys are shown in Fig. 2.67(I). For energies higher than 1.5 eV  $\sigma_{xx}^{(1)}$  of the MLS and the alloys have a similar energy dependence and fall within the range between  $\sigma_{xx}^{(1)}$  curves of bulk Co and Pt; the conductivity of Co rich MLS being closer to  $\sigma_{xx}^{(1)}$  of Co.

The calculated dependence of  $\sigma_{xx}^{(1)}$  on Co content correlates well with the data obtained from the ellipsometric measurements of Co/Pt multilayers with different Co layer thickness. Although the calculations give  $\sigma_{xx}^{(1)}$  of a higher amplitude than the experimental data, the theoretical results reproduce the changes of  $\sigma_{xx}^{(1)}$  with the variation of the Co sublayer thickness. Of all the MLS considered, only  $\sigma_{xx}^{(1)}$  of 4Co/2Pt has a subtle feature at ~5 eV corresponding to bulk Co. The fact that the  $\sigma_{xx}$  curves of the Co–Pt compounds of different composition and of different chemical ordering have similar shapes with no pronounced features suggests that, unlike the case of bulk Co, the two-peaks structure of the polar Kerr rotation spectra of Co/Pt MLS comes from the energy dependence of the off-diagonal part of the conductivity tensor.

The results of the calculations of the absorptive part of  $\omega \sigma_{xy}$  of Co–Pt MLS and alloys are shown in Fig. 2.67(II). The calculated  $\omega \sigma_{xy}^{(2)}$  of pure fcc Co is shown by the solid curve in all figures for a reference sake. All the compounds can be divided into three distinct groups according to differences between their  $\omega \sigma_{xy}^{(2)}$  and that of pure Co. The first group consists of 2Co/1Pt, 1Co/1Pt, and



*Figure 2.67.* Theoretical  $\sigma_{xx}^{(1)}$  (I) and  $\omega \sigma_{xy}^{(2)}$  (II) spectra of the Co–Pt multilayers ((a) and (b)), and alloys (c) [514].

1Co/2Pt multilayers [Fig. 2.67(IIa)], which have no more than two consecutive planes of equivalent atoms. For these MLS the energy dependence of  $\omega \sigma_{xy}^{(2)}$ varies strongly with MLS composition, with the absolute values of  $\omega \sigma_{xy}^{(2)}$  being significantly larger compared to Co. In the case of 2Co/1Pt and 1Co/1Pt the curves have the similar shape, but  $\omega \sigma_{xy}^{(2)}$  of the later is ~1.5 times greater. The position of the peak at ~1.5 eV is not altered compared to Co, while the feature at ~3.5 eV is shifted to lower energies by 1 eV and an additional peak appears around 5.5 eV. There are two maxima in  $\omega \sigma_{xy}^{(2)}$  of 1Co/2Pt, which lies at approximately the same energies as in Co, but their intensities are 2 times higher.

The situation is quite different in the case of multilayers with greater sublayer thickness [Fig. 2.67(IIb)]. Some increase in  $\omega \sigma_{xy}^{(2)}$  is observed only for 4Co/2Pt MLS, with the shape of the curve being similar to that of Co. The  $\omega \sigma_{xy}^{(2)}$  of 2Co/4Pt and 1Co/5Pt lies very close to each other and are reduced compared to  $\omega \sigma_{xy}^{(2)}$  of Co in the energy range of 2.5–4.5 eV. It should be noted that the two last MLS have Co and Pt sublayer thicknesses which are close to those of experimentally studied films.

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Our results for 2Co/1Pt and 2Co/4Pt multilayers are somewhat different from those given in Ref. [323]. The discrepancy is partially due to slightly different values of structural parameters. Nevertheless, calculations performed with the same parameters as in Ref. [323] show that the difference between the two calculations disappears only when the combined corrections to the LMTO Hamiltonian and overlap matrices are not included. This is not surprising, because even with the current density matrix elements computed accurately, the neglect of the combined corrections terms affect the calculated conductivity tensor via changes in band energies.

The calculated  $\omega \sigma_{xy}^{(2)}$  for model alloys are shown in Fig. 2.67(IIc). The common feature of all the spectra is a strong enhancement of  $\omega \sigma_{xy}^{(2)}$  in the energy range 4–6 eV. Of the three curves,  $\omega \sigma_{xy}^{(2)}$  for CoPt<sub>3</sub> is of a different shape with two distinct maxima at ~1.5 eV and 5 eV, the amplitude of the later being more than three times greater than the feature in the spectrum of Co at ~4.5 eV.

It has been shown [525, 321] that in pure 3d metals the off-diagonal conductivity is proportional to the strength of the spin-orbit coupling. In transition metal compounds, however, the dependence of the MO properties on the spinorbit coupling and effective magnetization of constituent atoms is far more complicated [403]. To understand this better it was performed model calculations with the spin-orbit coupling set to zero on either Co or Pt site. It has been found that "switching off" the spin-orbit coupling inside the Co atomic sphere affects only slightly the off-diagonal part of the conductivity tensor, while neglecting the spin-orbit interaction in the Pt sphere results in a strong decrease of  $\omega \sigma_{xy}^{(2)}$ . These results are in qualitative agreement with those obtained by the authors of Ref. [534], who also observed a strong dependence of  $\omega \sigma_{xy}^{(2)}$  on the value of the spin-orbit coupling on the Pt site. Also investigated was the effect of setting optical matrix elements to zero on selected sites, and the effects of setting the exchange effective field to zero on Co or Pt sites. When the exchange effective field on the Co sphere are set to zero, the off-diagonal part of the conductivity decreases drastically. At the same time, "switching off" the effective magnetic field on the Pt site produces a negligible effect on the  $\omega \sigma_{xy}^{(2)}$ spectra. Thus, a strong spin-orbit coupling on only one of the inequivalent atomic sites and a large value of the effective magnetization on another one can be sufficient for alloys to manifest strong MO activity.

In addition, it has been found that the dominant contribution to the  $\omega \sigma_{xy}^{(2)}$  spectra in the energy range of interest (1–6 eV) comes from transitions to unoccupied states lying in a rather narrow energy interval of ~1 eV just above the  $E_F$ . At the same time, these transitions give relatively small contribution to the diagonal part of the optical conductivity. As has been mentioned above, the electronic states in the vicinity of the  $E_F$  are formed by strongly hybridized Co d and Pt d states.

It is worth while to note, that in the case of transition-metals compounds, wave functions of initial and final states involved in optical transition are delocalized. Consequently, it is difficult, if possible at all, to separate contributions of any intra- or interatomic transitions to MO spectra. The assumption that the enhanced MO effects in Co–Pt compounds are due to Co d – Pt d hybridization allows us to explain the relatively small (as compared to Co–Pt alloys) magnitude of calculated  $\omega \sigma_{xy}^{(2)}$  in 2Co/4Pt and 1Co/5Pt multilayers. In these MLS there are Pt layers consisting of atoms which have Co atoms among neither the first nor the second nearest neighbors and the contribution of these layers to  $\omega \sigma_{xy}^{(2)}$  is small. However, switching off the spin-orbit interaction for these atoms leads to a rather strong variation of the spectrum. Neglecting the spin-orbit coupling for Pt atoms at the Co–Pt interface leads to relatively pronounced changes, but the magnitude of  $\omega \sigma_{xy}^{(2)}$  remains considerably higher than the magnitude of  $\omega \sigma_{xy}^{(2)}$  calculated with the spin-orbit interaction of all Pt atoms set to zero.

Calculated polar Kerr rotation spectra are shown in Fig. 2.68. From a comparison with the experimental MOKE spectra of Co/Pt MLS shown in Fig. 2.61 it can be seen that the calculated spectra of MLS do not satisfactory reproduce the experimental data. The magnitude of the calculated MOKE spectra of 2Co/4Pt and 1Co/5Pt MLS [Fig. 2.68(a)] in the energy range of 3–5 eV is significantly smaller than that of pure Co while an enhancement of the rotation angle of MLS vs. pure Co is observed in the experiment. The enhancement is indeed found for Co/Pt MLS with smaller sublayer thickness [Fig. 2.68(b)] but in contrast to the experimental data the peak is shifted to lower energy with respect to its position in Co. Surprisingly, better agreement with the experimentally observed MOKE spectra is observed in the case of Co–Pt alloys [Fig. 2.68(c)]. The calculated spectra reproduce fairly well both the increase of magnitude and the shift of the uv peak to higher energies.

The discrepancy between the experimental Kerr rotation spectra of Co/Pt MLS obtained in the present work and the calculated spectra of the model Co/Pt multilayers may be due to inadequacy of the adopted structure model of the MLS with the sharp interlayer interface. The observed energy dependence of the MOKE spectra of the MLS and their variation with the Co sublayer



*Figure 2.68.* Theoretical polar Kerr rotation spectra of the Co–Pt multilayers ((a) and (b)), and alloys (c) [514].

thickness may be explained by the reasonable assumption that a Co–Pt alloy is formed at the interface.

It is interesting to compare the results of our calculations with the recently published polar Kerr rotation spectra of an artificial  $Co_3Pt$  alloy film [296]. X-ray diffraction data shows that after annealing at 650K the alloy consists of alternating sequence of closely packed Co and CoPt planes with hcp-like kind of stacking. Due to the existence of the well defined order along the crystallo-graphic *c* direction the structure of the alloy is rather close to that of the model 1Co/1Pt multilayer. Nevertheless, because of different compositions of the two compounds, the direct comparison of the experimental and calculated MOKE spectra should be made with care. Calculated MOKE spectra of 1Co/1Pt multilayers with *ababab* and *abcabc* layer sequences are shown in Fig. 2.69 together



*Figure 2.69.* Theoretical polar Kerr rotation spectra of 1Co/1Pt multilayers with *ababab* (solid line) and *abcabc* (dashed line) stacking. Calculated spectrum of the Co<sub>3</sub>Pt alloy is shown by the dotted line. Experimental spectra for the ordered hexagonal Co<sub>3</sub>Pt phase (squares) and chemically disordered fcc phase (triangles) are taken from Ref. [296] [514].

with the experimental spectra. Except in the ir range, the calculated spectra are similar, with slightly different amplitudes. Both theoretical spectra have a negative peak at  $\sim$ 3 eV which is clearly seen in the experimental curve. A 5 eV feature in the experimental spectrum is also reproduced by the calculations but corresponding peaks are slightly shifted to higher energies. The shift may be caused by the difference of experimental and theoretical lattice constants. After annealing at 950K the Co<sub>3</sub>Pt alloy film has been shown to consist of a chemically disordered fcc phase. The modification of atomic arrangement and chemical short range order causes significant changes of the observed MOKE spectra. The 3 eV peak disappears while the amplitude of the spectra in the uv range increases and the 5 eV feature transforms into a peak. Similar changes are readily seen when comparing the calculated MOKE spectra of 1Co/1Pt multilayers with the calculated spectrum of the Co<sub>3</sub>Pt alloy.

In conclusion, it should be pointed out that the Kerr rotation of Co/Pt MLS is governed mainly by the off-diagonal part of the conductivity tensor. The infrared part of the spectrum originates from the MO activity of Co layers and is scaled by the Co content. On the other hand, the peak in the uv region is due to the hybridization of strongly spin-polarized Co *d*-states with spin-orbit split Pt *d*-states and its magnitude weakly depends on the MLS composition. It has been demonstrated that the chemical and structural ordering is accompanied by substantial electronic structure changes and result in a drastic MOKE spectra modification.

It should be noted that the *ab initio* description of the MOKE spectra for model Co/Pt multilayers performed under the assumption of a sharp, ideal interface is not sufficiently adequate for the detailed explanation of the experimentally observed ones. Simultaneously, in the case of model Co–Pt alloys the calculations properly reflect the main features of the spectra observed experimentally. Thus, it can be concluded that in the real multilayer structures the limited interdiffusion region at the interface and its structure and chemical composition play a main role in the formation of the MO spectra of the Co/Pt MLS.

### Interface alloying effects on magneto-optical spectra in Co/Pt multilayers

To examine the consequences of interface intermixing for Co/Pt MLS MOKE spectra and their relation to the chemical nature of the interface, special model supercells of the multilayered structures with alloyed interfaces and fcc (111) texture were constructed in Ref. [535]. The same lattice constant and space group as for the idealized model were used in the calculations. As an interface between the neighboring Co and Pt layers, one or two Co-Pt mixed atomic planes were introduced. Three types of multilayered structures were considered: in the form of single-layer Pt-rich Co<sub>1</sub>Pt<sub>3</sub> and Co-rich Co<sub>3</sub>Pt<sub>1</sub> ordered interfacial planar alloys and also in the form of double alloy layer Co<sub>3</sub>Pt<sub>1</sub>/Co<sub>1</sub>Pt<sub>3</sub> composed of consecutive single layers of different composition. The calculated spectra for Co/Pt MLS structures where Co and Pt atomic planes are separated by single interfacial alloy layer of different compositions are shown in Fig. 2.70. As can be seen, the presence of the interfacial alloy plane does not change appreciably the spectra in the ir range, while significant enhancement of the Kerr rotation amplitude in the uv spectral range is clearly seen.

The enhancement of the Kerr rotation in the uv range brings the spectra to better agreement with the experiment. However, the magnitudes of the calculated spectra are still significantly smaller than those of the experimental ones. In the "real Co/Pt systems" the intermixing is probably extended to more than one atomic plane with composition changing gradually. In Fig. 2.71 the results of the calculations for the Co/Pt MLS model structure composed of double interfacial  $Co_3Pt_1/Co_1Pt_3$  alloy atomic planes are presented. From Fig. 2.70 and 2.71 it can be seen that in the ir region the spectra amplitudes depend weakly on the interfacial layer thickness and composition, whereas in the uv range the amplitudes increase by about 50%, as compared to the spectra with single interfacial alloy layer. Alloying at the Co/Pt MLS interfaces leads to the increasing of the volume in which the strong 3d-5d hybridization occurs and, consequently, the contribution of these hybridized states to the MO spectra increases compared to the ideal MLS models. Another effect of interfacial alloy formation is stronger spin polarization of the whole Pt spacer. The aver-



*Figure 2.70.* Calculated polar Kerr rotation (a) and ellipticity (b) spectra for the model of Co/Pt multilayers with sharp interfaces (lines) and with single-layer interfacial alloys (symbols) [535].

aged magnetic moment per Pt atom calculated for the structures with alloyed interface increases up to 90% compared to that calculated for the ideal MLS model. It was found that the contribution to the MLS spectra coming from the interface alloy region and polarized Pt atomic planes controls the shape and magnitude of the spectra in the uv energy range.

In conclusion, the results obtained clearly illustrate the crucial role that interface structure can play on the magneto-optical spectra of the Co/Pt multilayers. The main peculiarities and the tendencies in the modification of the MLS spectra with the variation of the Co sublayer thickness are adequately reproduced when considering the effects of alloying limited to two atomic planes. Good agreement between the calculated and measured MOKE spectra agrees strongly for the validity of the adopted model and approach.

## 2.2.3 Magneto-optical properties of Co/Cu multilayers

In the pioneering study of Katayama *et al.* [536] it was shown that the Kerr rotation in Fe/Cu bilayers can be enhanced at the absorption edge energy of Cu. Since then, several investigations of MOKE spectra of Fe,Co/noble metal bilayers and multilayers have been performed [537–541]. The observed features of the MOKE spectra were interpreted as mainly related to the plasma edge in the noble metal and also to magneto-optically active transitions in the



*Figure 2.71.* Calculated polar Kerr rotation (a) and ellipticity (b) spectra for the model of Co/Pt multilayers with a double-layer interfacial alloy [535].

noble metal as a consequence of the spin polarization of the noble metal by the proximity of magnetic layers at the interface.

In Ref. [542] the complex MOKE spectra and optical properties - refractive index n and extinction coefficient k — have been measured in a wide spectral range for a set of the Co/Cu MLS structures. For the study the following sets of Co/Cu MLS were prepared: 14.9ÅCo/10.1ÅCu, 15.2ÅCo/15.2ÅCu, 15.1ÅCo/21.7ÅCu, and 22.3ÅCo/23.7ÅCu, all with the same number of repetitions of the Co/Cu bilayer being equal to 40. The MLS have been deposited by the face to face dc sputtering system described in [510]. All samples were deposited on a water cooled glass substrate. The argon pressure during the deposition was about 60 mPa and the deposition rate about 0.5 Å/s. The chemical composition of the films was determined by x-ray fluorescence analysis with an EDX system from the peak intensities of the characteristic fluorescence radiation. The crystal structure was examined by low and high angle x-ray diffraction (XRD) using Co-K( $\alpha$ ) radiation. The layered structure was confirmed by low angle XRD. The modulation period was deduced from the position of the Bragg peaks. From the high-angle XRD the pronounced (111) texture was inferred.

In Figure 2.72(I) the measured polar Kerr rotation  $\theta_K$  and ellipticity  $\eta_K$  spectra of the Co/Cu MLS studied are shown. The measured spectra of  $\theta_K$  and  $\eta_K$  of thick (~2000Å) fcc Co film are included for comparison.



*Figure 2.72.* Experimental polar Kerr rotation and ellipticity (I) and the conductivity tensor (II) of Co/Cu MLS and thick fcc Co film. Co and Cu sublayer thicknesses are given in the legend in units of Å[542].

The essential points of the experimental MOKE results can be summarized as follows:

i) The  $\theta_K$  spectra of the Co/Cu MLS exhibit a two peak structure and are strongly reduced compared to pure Co thick film.

ii) The broad negative  $\theta_K$  peak appearing in the uv energy region has an amplitude which is approximately proportional to the MLS Co content. The energy position of this peak remains the same as for the Co thick film.

iii) The  $\theta_K$  spectra in Co/Cu MLS exhibit a peak at  $\hbar\omega \sim 2.1$  eV not observed in pure Co film. The amplitude and width of this peak is directly connected with the Cu sublayer thickness. For the MLS with the thinnest Cu sublayer the peak transforms into a broad shallow minimum located between  $\sim 1.5$  eV and  $\sim 2.1$  eV, the former energy corresponding to the  $\theta_K$  peak position of the Co thick film.

iv) As the amount of Co in the MLS decreases the spectra generally scale down, while there is an increase in the prominence of the  $\theta_K$  peak located at  $\sim 2.1$  eV.

v) At the energies above  $\sim 2.1 \text{ eV}$  the Kerr ellipticity spectra are very similar. The uv peak position shifts to lower energy compared to the Co thick film and its amplitude scales with the amount of Co. In the energy range 0.8–2.1 eV a strong dependence of the spectra on the MLS composition is seen.

The measured optical properties of the MLS as well as of thick fcc Co and Cu films, prepared by the same technique, are shown in the form of spectral dependencies of the absorptive  $(\sigma_{xx}^{(1)})$  and dispersive  $(\sigma_{xx}^{(2)})$  parts of the diagonal component of the optical conductivity tensor in Figure 2.72(II). The well known prominent feature at the energy ~2.1 eV in the Cu optical conductivity tensor, where there is the superposition of the Drude-like intraband transitions and the interband transitions edge, is clearly observed.

As can be seen from Figure 2.72(II), the  $\sigma_{xx}^{(1)}$  spectra for the MLS studied are located in between the spectra of pure Co and Cu films. These spectra have two features, a shoulder at the energy of ~2.1 eV and a broad maximum at about 5 eV. The feature at ~2.1 eV is related to the Cu plasma edge resonance absorption and its prominence increases with the Cu content. For all Co/Cu MLS studied the  $\sigma_{xx}^{(1)}$  spectra have similar shape and their magnitude in the ir range scales with the amount of Co. This can easily be understood taking into account weak absorption of Cu metal in this energy region.

To separate the contribution to the MOKE coming from the diagonal and off-diagonal components of the optical conductivity tensor the function  $\Phi(\omega)$ 

$$\Phi(\omega) = \Phi^{(1)}(\omega) + i\Phi^{(2)}(\omega) = \frac{1}{\omega\sigma_{xx}\sqrt{1 + i(4\pi/\omega)\sigma_{xx}}}$$
(2.7)

has been evaluated from the optical measurements. It has been found that for the compounds under consideration the imaginary part of the function multiplied by  $\omega \sigma_{xy}^{(2)}$  gives the main contribution into the polar Kerr rotation spectra. For the Co/Cu the MLS  $\Phi^{(2)}(\omega)$  function exhibits a two peak structure (see Figure 2.73(a)), a sharp peak at the same energy ~2.1 eV as in the Kerr rotation spectra and a broader one at the energy around 4.5 eV. Thus, it can be clearly seen that the diagonal part of the optical conductivity tensor significantly influence the shape of the MOKE spectra.

In Figure 2.73(b) the  $\omega \sigma_{xy}^{(2)}$  spectra of the Co/Cu MLS are shown. The shape of the curves for all MLS is qualitatively similar to the shape of the  $\omega \sigma_{xy}^{(2)}$  determined for the Co thick film. Inspection of the curves shows that the magnitude of the  $\omega \sigma_{xy}^{(2)}$  spectra in the uv spectral region scales with the amount of Co. This is, however, not true for the ir spectral region and, in particular, the position of the low energy peak shifts from that for the fcc Co film and depends



*Figure 2.73.* The contribution to the Kerr rotation spectra from the diagonal part of the conductivity tensor (see text) (a) and the  $\omega \sigma_{xy}^{(2)}$  of Co/Cu MLS and the thick fcc Co film determined from the ellipsometric and the MOKE measurements (b) [542]. (The  $\omega \sigma_{xy}^{(2)}$  of Co is multiplied by a factor of 0.5)

on the MLS composition. The changes can be explained by a modification of the electronic states involved in the optical transitions due to existence of the Co/Cu interface.

It can be concluded that the ir peak observed in the polar Kerr rotation spectra is mainly determined by the corresponding feature in the diagonal part of the conductivity tensor. The position of the  $\theta_K$  peak observed in the uv spectral region coincides with the position of the peak in  $\omega \sigma_{xy}^{(2)}$  spectra but its shape is to a great extent affected by the spectral form of the  $\sigma_{xx}$ , just as in the case of pure Co.

To clarify the microscopic origin of the magneto-optical properties of the Co/Cu multilayers, self-consistent local-spin-density calculations of the elec-



*Figure 2.74.* Calculated  $\sigma_{xx}^{(1)}$ ,  $\omega \sigma_{xy}^{(2)}$  and polar Kerr rotation and ellipticity spectra of model Co/Cu multilayers [542].

tronic structure were performed for some model Co/Cu structures by means of the spin-polarized fully relativistic (SPR) LMTO method.

Since the experimentally investigated MLS have pronounced fcc-(111)- texture, in the *ab initio* calculations a number of nCo/mCu model have been constructed with periodicity along [111] direction and consisting of closely packed n Co and m Cu planes with an *abc* stacking sequence. All the structures possess  $D_{3d}^3$  symmetry. The lattice constant (a=3.574 Å) has been chosen as an average of those of fcc Co and Cu metals. No attempt has been made to optimize the interlayer spacing, which was taken to be constant corresponding to the ideal c/a ratio.

The density of Co and Cu d-states of the interior atoms are similar to those of the bulk metals. At the same time, the Co and Cu states at the interfacial sites are strongly hybridized. It is interesting to note, that Cu states at the interface are considerably spin-polarized due to the hybridization with Co states. It has been found that the resulting Cu sp and d spin magnetic moments are of opposite sign and almost compensate each other.

To show the main trends in the formation of the optical and magneto-optical spectra of the Co/Cu MLS, the conductivity tensor of 2Co/4Cu, 3Co/3Cu,

6Co/6Cu, and 4Co/2Cu model multilayers was calculated. The calculated  $\sigma_{xx}^{(1)}$ spectra are shown in Figure 2.74. All the spectra, except for that of Cu, were broadened with a Lorentzian of width 1.2 eV to simulate the finite electron lifetime effects. For the Cu spectrum a Lorentzian of width 0.4 eV was used. To take into account the intraband contribution, the phenomenological Drude term was also added to the diagonal components of  $\sigma$ . In accordance with the experimental data the curves lie very close to each other at the energies higher than  $\sim 4$  eV. In the visible and ir spectral regions a noticeable increase of the absorption with an enlargement of Co content can be seen. An interesting feature of these spectra is the minimum, at the energy  $\hbar\omega \sim 1.5$  eV, which corresponds to a minimum of interband absorption in pure Cu. From the comparison of  $\sigma_{xx}^{(1)}$  for 3Co/3Cu and 6Co/6Cu it can be seen that this peculiarity is enhanced as the number of adjacent Cu layers increases. An analysis of the partial density of states shows that such a behavior of  $\sigma_{xx}^{(1)}$  can be explained by the energy location of Co and Cu d-states. A dominant interband contribution to the  $\sigma_{xx}^{(1)}$  spectra at photon energies lower than  $\sim 4 \text{ eV}$  comes from transitions with Co and Cu d-states involved. As in pure Cu metal, the Cu d-states in the MLS are located  $\sim 1.5$  eV below the Fermi level and, consequently, give no contribution to the  $\sigma_{xx}^{(1)}$  at lower photon energies. In contrast, optical transitions to/from the Co d-states are possible at arbitrary energy because minority spin Co d-states are only partially filled. As a result of a superposition of the absorption in Co and Cu sublayers, the  $\sigma_{xx}^{(1)}$  spectra magnitude of the Co/Cu MLS increases with the Co content for  $\hbar\omega \leq 4$  eV. The peak in  $\sigma_{xx}(\omega)$  at  $\hbar\omega \sim 5.5$  eV is mainly due to transitions from the s-states at the bottom of the valence band to the *p*-states above the Fermi level.

Calculated  $\omega \sigma_{xy}^{(2)}$  spectra are shown in Figure 2.74. The magnitude of the spectra of the Co/Cu MLS is smaller than that of pure fcc Co, also shown in Figure 2.74, and approximately scales with the Co content. As compared to the  $\omega \sigma_{xy}^{(2)}$  curve of Co, the spectra of the MLS have less pronounced structure. The peak, centered at ~ 2 eV in the Co spectrum, for the model multilayers studied is observed most distinctly for 6Co/6Cu structure where the Co sublayer is sufficiently thick. It is remarkable that all the spectra cross zero at the same energy of about 5 eV. Considering the  $\omega \sigma_{xy}^{(2)}$  spectra leads one to a conclusion that the dominant contribution is provided by optical transitions with Co electronic states involved. The states are modified by the hybridization with Cu states at the interface, the hybridization effects being of greater importance for the MLS with smaller Co sublayer thickness.

Magneto-optical effects originate from a complicated interplay of the spinorbit coupling and exchange splitting. As can be inferred from perturbation theory (see, e.g. [15], and [525]), the  $\sigma_{xy}^{(2)}$  spectrum can be expanded as a sum


*Figure 2.75.* The influence of the Co and Cu spin-orbit coupling strength on the theoretical  $\omega \sigma_{xy}^{(2)}$  spectrum of the 2Co/4Cu multilayer. The whole spectrum is shown by solid line. Dashed and dotted lines denote the spectra calculated with nonzero spin-orbit coupling strength at Co and Cu sites, respectively [542].

of contributions proportional to the spin-orbit coupling strength  $\xi_{tl}$  of the electronic states with an angular momentum l at a site t. From the results of test calculations with  $\xi_{tl} = 0$  for all  $l \neq 2$  it has been found that the MO properties of the Co/Cu multilayers are governed mainly by the spin-orbit coupling of *d*-electrons. This was established with calculations using only a nonzero value of  $\xi_{tl}$  for either Co d or Cu d states. The results of the calculations for the 2Co/4Cu multilayer are shown in Figure 2.75. It can be seen that the Cu contribution is, in general, significantly smaller than the contribution from the Co sites. There are two inequivalent Cu atoms in the 2Co/4Cu multilayer, one of them being located at the Co/Cu interface and the another one in the interior of the Cu slab. From the test calculations with  $\xi_{tl}$  set to zero for the interfacial Cu sites it has been found that the contribution from the interior Cu sites into the  $\sigma_{xy}^{(2)}$  spectrum is negligible. The spin-obit coupling strengths for Co and Cu d-states are, however, of the same order of magnitude. The relatively small effect of the Cu sites on the off-diagonal conductivity component can be explained by the fact that the exchange splitting at the Cu sites is much smaller than at the Co ones. Calculations assuming zero exchange splitting at all Cu sites were performed and yielded the results that the effect of the "switchingoff", the exchange splitting on the  $\omega \sigma_{xy}^{(2)}$  of Co/Cu MLS, is negligible. The results demonstrate the dominant role of the Co contribution in MO properties of the Co/Cu MLS.



*Figure 2.76.* Calculated  $\omega \sigma_{xy}^{(2)}$  spectra of 2Co/4Cu multilayers with *abc* and *ab* stacking sequences. In the insert the corresponding  $\sigma_{xx}^{(1)}$  spectra are shown [542].

To investigate a dependence of the  $\sigma_{\alpha\beta}$  on local environment calculations for 2Co/4Cu MLS were performed with *abc* and *ab* closely packed planes stacking sequences. In both MLS the number of Co and Cu atoms among both the first and the second nearest neighbors around each site is the same, but the local symmetry is different. The calculated  $\omega \sigma_{xy}^{(2)}$  spectra are shown in Figure 2.76. Although the overall shape of the curves is similar, the fine structure is rather different. There are, also, differences in the corresponding  $\sigma_{xx}^{(1)}$  curves shown in the insert in Figure 2.76. The calculations also indicated that the joint density of states calculated for the MLS with different kinds of stacking sequences are almost identical. Taking into account that the joint density of states is determined only by the band structure of a compound, one can conclude that the details of the short range order affect the optical and MO spectra of the Co/Cu MLS mainly via the transition matrix elements.

Calculated polar Kerr rotation and ellipticity spectra for the Co/Cu MLS are shown in Figure 2.74. The spectra reproduce well the dependence of the magnitude of the uv peak on the Co content observed experimentally for the Co/Cu MLS studied. However, the calculated spectra are more structured. A well defined peak at  $\sim 2 \text{ eV}$  in the polar Kerr rotation, which is a characteristic feature of all the measured spectra, is present distinctly in the theoretical spectrum of the 6Co/6Cu multilayer. A possible explanation is that due to smaller Co and



*Figure 2.77.* The comparison of the polar Kerr rotation (a) and ellipticity (b) spectra measured for Co/Cu MLS films with the spectra calculated for the model nCo/mCu multipliers (the sublayer thicknesses are expressed in the key for the experimental films in Å and for the calculated structures in atomic layers (AL)) [542].

Cu sublayer thicknesses in the calculated model MLS as compared to the experimentally studied samples, the transitions to/from electronic states modified by the hybridization at the Co/Cu interfaces give relatively large contributions to the MO spectra.

According to the experimental data, the low energy peak in the  $\omega \sigma_{xy}^{(2)}$  spectra of the Co film as well as of the Co/Cu MLS is located below 2 eV. The feature in the  $\sigma_{xx}^{(1)}$ , which is related to the Cu plasma edge and manifests itself as a sharp peak in the Kerr rotation spectra, is centered at 2.1 eV. On the other hand, the calculations predict the peak in the  $\omega \sigma_{xy}^{(2)}$  of Co and the edge of interband transitions in Cu to be at similar energy position of approximately  $\sim 2$  eV. The discrepancy may be due to the fact that the LSDA approximation is only moderately successful in the description of the energy band structure and MO properties of ferromagnetic 3*d*-metals, especially Ni and Co [514, 320, 321].

Ab initio calculations of the polar Kerr rotation and ellipticity spectra were performed for 6Co/3Cu, 6Co/6Cu, and 6Co/9Cu multilayers assuming model multilayer structures with ideal interfaces. The calculated spectra are compared with the experimental ones in Figure 2.77. Despite the idealized multilayer structures, good agreement between the theory and experiment is observed. Besides the overall similarity in the shape of the measured and calculated spectra, the calculations reproduce well the main trends in amplitudes of the spectra in different energy regions.

In conclusion, from both the experimental and theoretical studies it follows that despite of the spin polarization of Cu d states due to the hybridization with the Co states at the MLS interface, the dominant contribution to the off-diagonal part of the optical conductivity tensor of the Co/Cu MLS predominantly comes from the interband transitions with Co electronic states involved. The feature observed at  $\hbar \omega \sim 2.1$  eV in the optical conductivity tensor component  $\sigma_{xx}^{(1)}$  spectra is related to the edge of interband transitions from Cu *d*-states in the Cu sublayers and is responsible for the peak at 2.1 eV in the polar Kerr rotation spectra of the MLS studied. There are some discrepancies between the experimental and theoretical results mainly in the description of the Co-related peaks of the optical and MO spectra of the Co/Cu MLS. Nevertheless, the *ab initio* calculations reproduce the main features of the spectra and provide explanation of their microscopic origin.

## 2.2.4 Magneto-optical anisotropy in Fe<sub>n</sub>/Au<sub>n</sub> superlattices

Many important physical properties of magnetically ordered compounds depend on the relative orientation of the magnetization and the crystallographic axes as the spin subsystem is coupled to the lattice by the spin-orbit (SO) interaction. The magnetocrystalline anisotropy (MCA), which is the energy that determines the magnetization direction along a certain crystallographic axis, is a ground state property of a crystal. The magneto-optical anisotropy (MOA), defined as the dependence of the off-diagonal part of the optical conductivity tensor on the magnetization direction, arises as a result of electronic excitations and is due to the spin and orbital polarizations of initial and final states.

Although the MCA has been widely studied both experimentally [543] and theoretically [544–547] in a large number of materials, the investigations of the MOA are still restricted to a few cases only. Theoretical calculations were performed for Co, FePt, CoPt [548], CoPd [517], and CrO<sub>2</sub> [526]. Experimentally, however, the orientation dependence of the magneto-optical (MO) Kerr effect was observed in only one magnetic system, hcp Co. In the equatorial Kerr effect Ganshina *et al.* [549], and in the longitudinal Kerr effect (LKE) configuration Osgood *et al.* [550] studied the Kerr effect magnitude dependence on the orientation of the magnetization with respect to the c-axis, both lying in the basal plane of the hcp Co sample. For the polar Kerr effect (PKE) configuration with magnetization perpendicular to the sample plane, Weller *et al.* [312] observed an orientation dependence of the PKE by using two epitaxial hcp Co films with different, (0001) and (11 $\overline{20}$ ), basal planes.

An extended experimental and theoretical study of the observed large magneto-optical anisotropy (MOA) was presented in Ref. [390] for a series of Fe<sub>n</sub>/Au<sub>n</sub> superlattices prepared by molecular beam epitaxy with n=1,2,3 of Fe and Au atomic planes of (001) orientation. The (Fe<sub>1</sub>/Au<sub>1</sub>)×20, (Fe<sub>2</sub>/Au<sub>2</sub>)×10 and (Fe<sub>3</sub>/Au<sub>3</sub>)×7 MLS were grown by the MBE in UHV conditions (base pressure during preparation below  $5 \times 10^{-10}$  mbar) on a 30 nm (001)Au buffer layer (preceded by a 4 nm Fe(001) seed layer), deposited on a MgO(001) cleaved substrates in a multi-stage process [551]. The whole structure was finally covered by a 5 nm Au cap-layer. The Fe and Au monolayers were deposited alternately at 340 K at the rate of about 0.2 nm/min, as controlled by a quartz microbalance with an accuracy of  $\pm 5\%$ . Very uniform growth conditions were preserved for subsequent layers, resulting in a high epitaxial quality of the superlattices. For the growth mode and the resulting structure of the Fe/Au MLS an important role is played by the self-surfactant effect, which was observed when single Fe films were grown on the reconstructed (001)Au surface [551, 552]. During the Fe growth, Au surface segregation occurs by an atomic place exchange that leads to the formation of one Au monolayer on top of the growing Fe film. This process, particularly important for the growth of the Fe<sub>1</sub>/Au<sub>1</sub> monoatomic superlattices, is responsible for a deviation from a perfect layer structure as was observed by Takanashi et al. [553] by XRD measurements. The conversion electron Mössbauer spectroscopy (CEMS) analysis [554] clearly reveals that the  $L1_0$  phase, characterized by the tetragonal distortion that is reflected in a large contribution of the quadrupole interaction to the hyperfine pattern, is present in the  $(Fe_1/Au_1) \times 20$  MLS. However, the amount of the  $L1_0$  phase is only ~30% of that expected for the perfect layer growth. The vertical mass transport accompanying the MLS growth leads to Fe aggregation, so that the resulting structure may be regarded as a mixture of a monolayer and double-layer (and to a less extent also tri-layer) MLS. Nevertheless, it is enough to induce a strong perpendicular anisotropy, which forces the magnetization to the normal direction. The  $L1_0$  phase disappears abruptly when the MLS modulation period is increased. For the  $(Fe_2/Au_2) \times 10$  MLS, only traces of the component attributed to the tetragonally distorted phase can be found in the CEMS spectrum. The CEMS spectrum for the  $(Fe_3/Au_3) \times 7$ sample resembles the one measured for a single Fe tri-layer film sandwiched between Au [554].

### Experimental results and data analysis

Most MO studies of the MLS employ polar magnetization geometry, PKE, and normal light incidence. The PKE configurations alone cannot be used, however, to study the MO orientation effects in a very rich family of magnetic layered structures. The reason is that the main structural anisotropy axis is the axis perpendicular to the film surface and no other basal planes exist. The only possibility is to use the polar and longitudinal (or equatorial) Kerr effect geometries simultaneously. This approach is more complicated as additional data on the optical constants are required to extract the basic quantities – the optical conductivity tensor components – underlying the MO spectra.

In Fig. 2.78 the complete set of experimentally obtained ellipsometric and magneto-optical spectra in both the polar and longitudinal magnetization geometry for the Au(5nm)/(Fe<sub>1</sub>/Au<sub>1</sub>) $\times$ 20/Au(30nm)/Fe(4nm)/MgO(001) sample is presented. As it is seen in Fig. 2.78(a), the spectral dependence of the effective refractive index n and the extinction coefficient k of the sample exhibits overall shape close to that of Au metal with the well known feature at the photon energy of 2.5 eV, where there is the superposition of the Drudelike intraband transitions and the interband transition edge. Such dependence can easily be understood by taking into account that the predominant parts of the sample are the Au overlayer and underlayer. The effective magnetooptical PKE rotation  $\theta^{PK}$  and ellipticity  $\eta^{PK}$  spectra of the sample are shown in Fig. 2.78(b). The essential points of the experimental  $\theta^{PK}$  spectrum are the prominent negative peak centered at around 2.5 eV (i.e., in the Au plasma edge spectral region), and a hump clearly visible near 3.2 eV. The  $\theta^{PK}$  changes sign above 4 eV and a positive peak at 4.7 eV is formed. The  $\theta^{PK}$  enhancement at the plasma edge of Au (around 2.5 eV) is well explained by the classical optic multilayer model, and is not related to the modification of the electronic structure of the intrinsic magnetic Fe<sub>1</sub>/Au<sub>1</sub> multilayer. The corresponding  $n^{PK}$ spectrum changes the sign at the energy of the plasma edge of Au and in the uv spectral region exhibits a two peak structure with a negative peak at 3.8 eV and a positive one at 5.5 eV. The PKE spectra measured for the  $Fe_2/Au_2$  and  $Fe_3/Au_3$  superlattices (not shown) exhibit similar behavior like  $Fe_1/Au_1$ , with the peaks structure in the uv spectral range shifted to higher energy. The main features and trends in PKE spectra of Fe<sub>n</sub>/Au<sub>n</sub> superlattices modulated by integer atomic layers of the Fe and Au are in agreement with those reported in Refs. [555] and [556]. Similar characteristic structure in the PKE spectra in the uv spectral range (more distinct than in the multilayers) was observed in ultrathin Fe layers sandwiched by Au layers and assigned to optical transitions involving quantum-well states [557, 558].

The corresponding complex LKE spectra measured in the longitudinal Kerr magnetization geometry at the angle of light incidence 75 deg are shown in Fig. 2.78(c) and Fig. 2.78(d) for s and p light polarizations, respectively. The measured  $\theta^{LK}$  and  $\eta^{LK}$  one order in magnitude smaller than for the PKE. In the LKE spectra, the plasma edge of Au overlayer and underlayer of the sample manifests itself as a peak or shoulder near 2.6 eV. As is seen in Fig. 2.78(c) and (d), in the spectral region above 2.5 eV the  $\theta^{LK}$  spectra are dominated by the peak at 3.2 and minimum around 5.0 eV for s and the peak at 4.1 eV for p polarization, respectively. The corresponding  $\eta^{LK}$  spectra features are the peak centered at 4.1 for s and the peaks at 3.4 eV and 5.1 eV for p polarizations and the optical functions n and k determined from the LKE data. They also agree well with those measured directly by the elipsometric



*Figure 2.78.* Experimental results for  $Fe_1/Au_1$  MLS: refractive index and extinction coefficient (a), polar Kerr rotation and ellipticity (b), longitudinal Kerr rotation and ellipticity for *s* (c) and *p* (d) light polarizations. In the panels, refractive index and rotation are depicted as circles, and extinction coefficient and ellipticity as triangles [390].

method. It should be pointed out that one can not expect direct correspondence between the spectra shape and energy peak positions measured in polar and longitudinal geometry because the LKE spectra are strongly dependent on the angle of light incidence (particularly for p polarization, when the angle of incidence approaches its principal value, equal to about 75 deg for the structures studied). Therefore, the direct comparison of the PKE and LKE spectra is not appropriate and comparison should be made by evaluation of the optical conductivity tensor components from the measured spectra. It is well known that the absorptive part of the tensor only, but not the Kerr rotation itself, is directly connected with the optical transitions between electronic states, their strengths and energy positions. Therefore, in the following, we will consider the energy dependence of the conductivity tensor components underlying the MO effects for the superlattices studied.

The effective optical conductivity tensor components, diagonal  $\sigma_{xx}^{eff}$  and off-diagonal  $\omega \sigma_{xy}^{eff}$ ,  $\omega \sigma_{xz}^{eff}$  were determined with the use of Eq. 1.171 from the measured optical and MO spectra according to Eq. 1.175 for the PKE and Eq. 1.178 for the LKE. The Fe<sub>n</sub>/Au<sub>n</sub> superlattices studied are two-dimensional

structures and can exhibit optical anisotropy (i.e., the  $\sigma_{xx}$  and  $\sigma_{zz}$  tensor components can differ). Consequently, Eq. 1.177 for an optically anisotropic medium should be used instead of Eq. 1.178 to determine the off-diagonal tensor component. Unfortunately, in the case of thin *metallic* films or MLS, direct ellipsometric measurements allow only the determination of the  $\sigma_{xx}^{eff}$  tensor component. As it will be shown in the next section, the errors caused by using equation (1.178) for an optically isotropic medium to extract  $\sigma_{xz}^{eff}$  from LKE data are of little importance for the Fe<sub>n</sub>/Au<sub>n</sub> MLS.

The results for the effective complex  $\sigma_{xx}^{eff}$ ,  $\omega \sigma_{xy}^{eff}$ , and  $\omega \sigma_{xz}^{eff}$  optical conductivity spectra of the Au(5nm)/Fe<sub>1</sub>/Au<sub>1</sub>×20/Au(30nm)/Fe(4nm)/MgO(001) sample are presented in Fig. 2.79(a) and (b), respectively. In Fig. 2.79(a) the  $\sigma_{xx}$  spectra of 100 nm thick fcc Au film deposited on GaAs(001) as well as the buffer sample Au(30nm)/Fe(4nm)/MgO(001) used as the substrate to grow the  $Fe_n/Au_n$  superlattices are also included. As can be seen from Fig. 2.79(a) there is a significant difference between the effective  $\sigma_{xx}^{eff}$  spectra for the whole structure and the buffer sample as compared to that of the Au film in the spectral range below 2.5 eV. The rapid changes of the optical constants at the energy 2.5 eV caused by the onset of Au interband transitions are clearly visible for all the samples. The characteristic features of the absorptive part of the  $\omega \sigma_{ru}^{eff}$  spectrum (Fig. 2.79(b), solid lines with circles) of the whole structure are two broad peaks of comparable amplitude centered around 1.6 and 3.3 eV and a negative minimum at 4.7 eV. The dispersive part of the  $\omega \sigma_{xy}^{eff}$  is dominated by a negative peak at 3.9 eV and a positive one at 5.3 eV. The complex  $\omega \sigma_{xz}^{eff}(\omega)$  functions (Fig. 2.79(b), solid lines with triangles) evaluated independently from the LKE data measured for s and p light polarization are the same. As compared to the energy dependence of  $\omega \sigma_{xy}^{eff}(\omega)$ , significant differences between the spectra shape and magnitude are clearly visible. The ir peak position in the absorptive part of  $\omega \sigma_{xz}^{eff}$  shifts to lower energy and the spectrum amplitude is much smaller.

The conductivity tensor components spectra discussed above represent the effective tensor components of the whole complex sample composed of the specific magnetic  $Fe_n/Au_n$  structure and the Au cap layer and underlayer film. To compare the theoretical *ab initio* calculations with the experiment and to discuss the origin of the magneto-optical and MOA effects of the magnetic superlattices, the tensor components for the intrinsic magnetic  $Fe_n/Au_n$  structure alone should be extracted from the experimental data. For this aim, the phenomenological matrix formalism based on the Maxwell theory was adopted, providing computer modeling of the MO response for a given structure (known as multi-reflection calculations) [559]. The procedure assumes that the dielectric tensors of the constituent layers of the structure and their thicknesses are known. In our calculation, the thicknesses of the constituent layers determined from the technological data were used. To avoid possible uncer-



*Figure 2.79.* Experimental absorptive (left panels) and dispersive (right panels) parts of the optical conductivity for the Fe<sub>1</sub>/Au<sub>1</sub> sample. In the panels (a) the effective diagonal tensor components of the whole sample (solid lines with circles), the buffer sample (dashed lines), thick Au film (dotted lines), and the extracted (see text) component of the intrinsic Fe<sub>1</sub>/Au<sub>1</sub> structure (circles) are shown. In the panels (b) the off-diagonal effective tensor components derived from the polar (solid lines with circles) and longitudinal (solid lines with triangles) Kerr effect are shown. In the panels (c) are the extracted off-diagonal tensor components of the intrinsic magnetic Fe<sub>1</sub>/Au<sub>1</sub> structure derived from PKE (circles) and LKE (triangles) [390].

tainties and obtain the most precise results, the optical and magneto-optical response of the buffer underlying the Fe<sub>n</sub>/Au<sub>n</sub> structure, composed of the Au(30nm)/Fe(4nm)/MgO(001), was directly measured with the use of the control sample and further used in the multi-reflection calculations. Finally, a two-layer system composed of the non-magnetic Au cover layer and a magnetic (Fe<sub>n</sub>/Au<sub>n</sub>)×N superlattice on the Au(30nm)/Fe(4nm)/MgO(100) buffer substrate was considered. In the procedure, the contribution of a single layer of given thickness is determined through its characteristic matrix, composed of the medium boundary and the medium propagation matrices [559]. The overall

structure of the film is treated as a single layer with the parameters expressed in terms of those of individual sublayers.

The unknown tensor components of the intrinsic  $(Fe_1/Au_1) \times N$  MLS structure were extracted by solving numerically multi-reflection equations. The results for the Fe<sub>1</sub>/Au<sub>1</sub> structure are shown in Fig. 2.79(a) for  $\sigma_{xx}$  (circles) and in Fig. 2.79(c) for  $\omega \sigma_{xy}$  (circles) and  $\omega \sigma_{xz}$  (triangles). The spectra represent the results after eliminating the MO contribution from the complex underlayer and Au overlayer. In the following discussion, the off-diagonal component  $\omega \sigma_{xy}$  for the magnetization M parallel to the (001) direction will be denoted as  $\omega \sigma_{\text{off}}^{\parallel}$ , whereas for the  $\omega \sigma_{xz}$  with the magnetization **M** perpendicular to the (001) direction we will use the notation  $\omega \sigma_{\text{off}}^{\perp}$ . As compared to the effective tensor components, the feature related to the plasma edge of Au at 2.5 eV disappears for the  $\omega \sigma_{\text{off}}^{\parallel}$  and  $\omega \sigma_{\text{off}}^{\perp}$  spectra. The overall structure of the extracted off-diagonal tensor components of the magnetic superlattice alone is similar to that of the effective ones and the most significant changes in the spectra appear in the ir spectral range. The most important conclusion is that both the effective and the extracted off-diagonal tensor components of the magnetic superlattice exhibit large orientational anisotropy with respect to the magnetization direction.

# Comparison of the experimental and theoretical spectra in $Fe_n/Au_n$ MLS

The band structure calculations in Ref. [390] considered the  $Fe_1/Au_1$  MLS system with one by one stacking of (001) planes whose structure can be regarded as  $L1_0$  type (Fig. 2.80(a)). The lattice parameters used were chosen as follows. The in-plane atomic spacing was taken as an average between Au and Fe bulk values (a = 4.066 Å). The out-of-plane lattice spacing for the Fe<sub>1</sub>/Au<sub>1</sub> MLS was taken from the recent work of Sato et al. [556] as 1.915 Å which is a slightly lower value as compared to the previously published one [553, 560] and used in our previous calculation [561]. The structures  $Fe_2/Au_2$ and Fe<sub>3</sub>/Au<sub>3</sub> are presented in Figs. 2.80(b) and 2.80(c). There is no experimental knowledge about the three interlayer spacings, Au-Au, Au-Fe, and Fe-Fe, in these structures. The Au-Au spacing was taken to be the same as in fcc Au, 2.04 Å. For the Au-Fe spacing, value of 1.74 Å can be derived from the rigid sphere model as a mean between a fcc Au (2.04 Å) and bcc Fe (1.43 Å) bulk values. Similar values for the Au-Fe interlayer spacings have been obtained by total energy minimization using LMTO *ab-initio* calculations. Using the experimentally determined superlattice periods in Fe<sub>2</sub>/Au<sub>2</sub> and Fe<sub>3</sub>/Au<sub>3</sub> MLS structures published in Ref. [556] as constraints, a one-parameter minimization was performed. As a result, the values of 1.76 Å and 1.74 Å for Au-Fe,



*Figure 2.80.* The unit cells used for  $Fe_1/Au_1$  ( $L1_0$ ) (a),  $Fe_2/Au_2$  (b), and  $Fe_3/Au_3$  MLS (c). Black spheres are Fe atoms and shadowed ones are Au atoms [390].

and corresponding values of 1.69 and 1.58 Å for Fe-Fe interlayer spacing in the  $Fe_2/Au_2$  and  $Fe_3/Au_3$  MLS, respectively, were obtained.

For the quantitative analysis of the magneto-optical anisotropy it is convenient to present the anisotropy as the difference between the off-diagonal conductivity tensor components  $\omega \sigma_{\text{off}}^{\parallel} - \omega \sigma_{\text{off}}^{\perp}$ , where the factor  $\omega$  provides the compatibility with the  $\omega \sigma$  spectra themselves. In Fig. 2.81 the  $\omega \sigma_{\text{off}}^{\parallel}$  and  $\omega \sigma_{\text{off}}^{\perp}$  spectra of the MLS of the nominal Fe<sub>1</sub>/Au<sub>1</sub> structure, extracted from the experimental PKE and LKE data as described in the previous section, and the MOA are compared to the corresponding spectra calculated for the ideal Fe<sub>1</sub>/Au<sub>1</sub>  $L1_0$  structure.

Overall, both the spectral shape and the magnitude of the experimental optical conductivity spectra are qualitatively reproduced by the LSDA calculations. However, the position of the calculated prominent peaks in absorptive part of  $\omega \sigma_{\text{off}}^{\parallel}$  at 3.8 eV and 5.2 eV is shifted toward smaller energies as compared to the experiment. Also, the theoretical calculations predict larger MOA in comparison with the experimental one in the nominal Fe<sub>1</sub>/Au<sub>1</sub> structure. One of the possible reasons for the discrepancy is that due to the non–exact treatment of the electron exchange and correlations. It is known that the LSDA underestimates the binding energy of *d* states and the threshold of interband transitions in noble metals compared to photoemission and optical measurements [562, 563].

It seems quite likely that the use of a more appropriate approximation for the exchange and correlation may give rise to a shift of the quasiparticle energy



*Figure 2.81.* Absorptive (left panels ) and dispersive (right panels) parts of the off-diagonal conductivity tensor of  $Fe_1/Au_1$  MLS: (a) experimental results, (b) LSDA calculated spectra for  $Fe_1/Au_1$  MLS, and (c) the MO anisotropy spectra (symbols represent experimental data, solid lines LSDA, and dashed lines LDA+*U* theory) [390].

bands originating from Au 5d states and, as a result, agreement between the theory and the experiment might be improved. In Ref. [390] the LDA+U method has been adopted as a step beyond the LSDA in the treatment of the electronic correlations. The LDA+U method can be considered as a rough approximation to both the self-interaction correction and to the self-energy of a system with strongly interacting electrons. Moreover, it has been found that the application of the LDA+U method to pure noble metals improves the calculated energy position of the threshold of the interband optical transitions and provides a better approach for describing their MO spectra [564]. In the case of the Fe<sub>1</sub>/Au<sub>1</sub> MLS  $U_{eff}$ =2.5 eV was applied to Au 5d states [390]. This value of  $U_{eff}$ , considered as a parameter of the model, was found to give the best agreement between the calculated and experimental optical conductivity for fcc Au. The use of the LDA+U approximation for Fe<sub>1</sub>/Au<sub>1</sub> MLS does improve slightly the calculated energy position of the peaks of the off-diagonal



*Figure 2.82.* Absorptive (left panels) and dispersive (right panels) part of the MOA measured for the Fe<sub>1</sub>/Au<sub>1</sub> MLS (circles) compared with LSDA calculated spectra: (a) MOA modeled with effective optical conductivity:  $\omega \sigma_{\text{off}} = x \cdot \omega \sigma_{\text{off}}^{1/1} + (1-x) \cdot \omega \sigma_{\text{off}}^{2/2}$  for *x*=0.3 (solid lines) and calculated for a supercell containing 1/1 and 2/2 substructures (see Fig. 2.83) (dashed lines); (b) MOA calculated for the perfect Fe<sub>1</sub>/Au<sub>1</sub> structure (solid lines) and for the structure with substitutional disorder (see Fig. 2.84) (dotted lines) [390].



*Figure 2.83.* Unit cell (doubled along z direction) of the Fe/Au structure composed of the 1/1 and 2/2 substructures (black spheres are Fe atoms and gray ones are Au atoms) [390].

optical conductivity for both orientations of the magnetization (not shown), there is no improvement, however, in the shape of the spectra. Comparing the MOA calculated within LSDA and LDA+U methods (See Fig. 2.81(c)) to the experimental spectrum one can conclude that the LDA+U approximation does not improve the description of the MOA in the nominal Fe<sub>1</sub>/Au<sub>1</sub> structure.



*Figure 2.84.* Doubled  $c(3/\sqrt{2} \times 3/\sqrt{2})$  unit cell used for modeling of alloying effects in the Fe/Au MLS (black spheres are Fe atoms and gray ones are Au atoms) [390].

Another, and maybe even more important source of the discrepancies is that the studied sample is not an ideal monoatomic Fe<sub>1</sub>/Au<sub>1</sub> MLS of  $L1_0$  structure but rather a mixture of mono- and double-layer structures. Having this in mind the effective optical conductivity of the structure was modeled by a weighted average of the conductivities calculated for the Fe<sub>1</sub>/Au<sub>1</sub> and Fe<sub>2</sub>/Au<sub>2</sub> MLS:  $\omega \sigma_{\text{off}} = x \cdot \omega \sigma_{\text{off}}^{1/1} + (1 - x) \cdot \omega \sigma_{\text{off}}^{2/2}$ . The best agreement between theory and experiment, both in the MOA (Fig. 2.82(a)) and the shape of the off-diagonal optical conductivity (not shown), was achieved with x = 0.3. This value agrees well with the results of the CEMS analysis [554].

In a more advanced approach, the interface roughness was studied by calculating the MO properties of the mixture of mono- and double layers, distributed over the whole structure. The composed Fe/Au structure was modeled using a large supercell containing the side-by-side placed  $Fe_1/Au_1$  and  $Fe_2/Au_2$  component structures spread over 3 and 7 lattice constants (see Fig. 2.83). This ratio of the areas was chosen according to the simple procedure described above, in which the resulting spectra were expressed as the sum of individual  $Fe_1/Au_1$ and Fe<sub>2</sub>/Au<sub>2</sub> contributions. The results of the *ab initio* calculations for the composed structure are shown in Fig. 2.82(a), from which an even better overall agreement between the theory and experiment both in the shape and the amplitude of the MOA spectra is observed. Rather than just considering welldefined mono-and double-layers, a series of models were examined to evaluate the effect of substitutional disorder on the MO spectra and MOA. Although the solubility of Au in bulk bcc Fe at temperatures up to 400 K is negligible [565], enhanced solubility of Au within an Fe layer up to 3% was observed for 70 Å thick Fe film on Au(001) [566]. Even up to one order greater substitutional disorder was reported for the Fe/Au (001) structures in the monolayer regime by Blum et al. [552]. The incorporation of Au atoms in the Fe layers can be considered as an explanation (as discussed in Ref. [552]) for the larger Fe-Au interlayer spacing observed experimentally in the Fe<sub>1</sub>/Au<sub>1</sub> structure, as compared to the spacings derived under assumption of rigid atomic spheres of bulk Fe and Au metals. This effect would also lead to the increasing of the effective Fe-Fe and Fe-Au interlayer spacing in Fe<sub>n</sub>/Au<sub>n</sub> MLS. A picture of the



*Figure 2.85.* Absorptive (left panels) and dispersive (right panels) parts of the off-diagonal conductivity tensor of  $Fe_2/Au_2$  MLS: (a) experimental results, (b) LSDA calculated spectra. In the panels (c) the MOA spectra are shown (symbols represent experimental data, solid lines LSDA calculations for perfect  $Fe_2/Au_2$  MLS, and dashed lines calculations for the structure with substitutional disorder) [390].

model structure used in the calculations is presented in Fig. 2.84. The structure is composed of the alternating atomic planes of Fe and Au in which one per nine atoms is interchanged between layers (the interlayer spacing of 1.915 Å was taken). It was found that moderate substitutional disorder leads mainly to the scaling of the calculated  $\sigma_{off}^{\parallel}$  and MOA spectra amplitude, without significant changes of the spectra shape. In Fig. 2.82 (b) the MOA spectra calculated for the model structure (see Fig. 2.84) indicate that there is an approximately twofold reduction of the MOA magnitude when the level of the substitution is 11%.

Figs. 2.85 and 2.86 show the experimentally obtained  $\omega \sigma_{\text{off}}^{\parallel}$  and  $\omega \sigma_{\text{off}}^{\perp}$  spectra in the MLS of nominal Fe<sub>2</sub>/Au<sub>2</sub> and Fe<sub>3</sub>/Au<sub>3</sub> structures for two orientations of magnetization:  $\mathbf{M} \parallel (001)$  and  $\mathbf{M} \perp (001)$ , together with the MOA, in comparison with the corresponding spectra calculated for the ideal Fe<sub>2</sub>/Au<sub>2</sub> and

 $Fe_3/Au_3$  structures. For  $Fe_2/Au_2$  MLS, the overall shape of the theoretical spectra corresponds well to the experimental ones (Fig. 2.85(b)), and a better agreement in MOA as compared to the previously discussed case of the ideal  $Fe_1/Au_1$  (see Fig. 2.81) is observed (Fig. 2.85(c)). The reason is that the ideal  $Fe_2/Au_2$  MLS is a better approximation of the real experimental situation than was in the case of the ideal structure for the Fe<sub>1</sub>/Au<sub>1</sub> MLS [554]. However, in the high-energy part of the spectra, above 4 eV, the  $\omega \sigma_{\text{off}}^{\parallel}$  and  $\omega \sigma_{\text{off}}^{\perp}$  and MOA amplitudes remain considerably higher than the ones obtained experimentally. To examine the origin of such a discrepancy, was the influence of the substitutional disorder on the MOA was modeled. In Fig. 2.85(c) the MOA spectra calculated for a Fe<sub>2</sub>/Au<sub>2</sub> MLS model structure are shown. The model structure used in this case is similar to that considered for the case of  $Fe_1/Au_1$ MLS (Fig. 2.84) with the same substitutional disorder level and is composed of double numbers of the Fe-rich and Au-rich atomic layers with the experimental modulation period of 7.25 Å. It was found that the MOA magnitude for the  $Fe_2/Au_2$  MLS in the high-energy part of the theoretical spectra is markedly reduced and is most closest to the experimental ones when the effect of the limited substitutional disorder at the level of 10% is taken into account.

The experimental and theoretical results for the Fe<sub>3</sub>/Au<sub>3</sub> structure are presented in Fig. 2.86. The overall agreement between the calculated and observed  $\omega \sigma_{\text{off}}^{\parallel}$  and  $\omega \sigma_{\text{off}}^{\perp}$  spectra for the Fe<sub>3</sub>/Au<sub>3</sub> structure is less satisfactory than for the Fe<sub>2</sub>/Au<sub>2</sub> MLS. One of the possible reasons is that the real structure of the Fe<sub>3</sub>/Au<sub>3</sub> superlattice is far from the ideal model considered. Nevertheless, both the theoretical and the experimental MOA spectra are of comparable magnitudes. The modeling of the interface roughness effects and alloying for the Fe<sub>3</sub>/Au<sub>3</sub> structure from first principles (much more complicated than for the simpler structures) has not yet been performed.

Some conclusions can be drawn from the modeling performed: (i) The magnitude of the off-diagonal optical conductivity and MOA spectra is very sensitive to the actual structure at the interfaces, and thus the MO spectroscopy can provide useful independent information about the Fe/Au MLS structures, complementary to that derived from CEMS measurements. (ii) In the modeling of the roughness effect, even using the areas of the component structures as small as a few atomic spacing leads to the results qualitatively close to these obtained from a simple additive formula for the superposition of the spectra. (iii) The magnitude of the MOA decreases with the increase of the number of Fe and Au atomic layers of the superlattices. (iv) Limited substitutional disorder does not suppress the MOA effect in Fe<sub>n</sub>/Au<sub>n</sub> MLS.

As mentioned above,  $Fe_n/Au_n$  MLS can exhibit optical anisotropy, but the  $\sigma_{zz}$  component of the optical conductivity tensor is unavailable directly in the experiment. On the other hand, both the  $\sigma_{xx}$  and  $\sigma_{zz}$  can be easily obtained from the calculations and allow us to verify numerically the correctness of



*Figure 2.86.* Absorptive (left panels ) and dispersive (right panels) parts of the off-diagonal conductivity tensor of  $Fe_3/Au_3$  MLS; (a) experimental results, (b) LSDA calculated spectra. In the panels (c) the MOA spectra are shown (symbols represent experimental data, solid lines LSDA theory for perfect  $Fe_3/Au_3$  MLS) [390].

using the Eq. (1.178) instead of (1.177) to determine  $\omega \sigma_{\text{off}}^{\perp}$  from the experimental data. The absorptive parts of the diagonal components of the conductivity tensor calculated for ideal Fe<sub>1</sub>/Au<sub>1</sub> and Fe<sub>2</sub>/Au<sub>2</sub> structures are shown in Figs. 2.87(a) and (c). The largest difference between  $\sigma_{xx}$  and  $\sigma_{zz}$  spectra is observed for the Fe<sub>1</sub>/Au<sub>1</sub> MLS below the photon energy of about 3.5 eV. For the Fe<sub>2</sub>/Au<sub>2</sub> and also Fe<sub>3</sub>/Au<sub>3</sub> MLS (not shown in the figure) the calculated optical anisotropy is significantly smaller. The theoretical conductivity tensor components were used to calculate the complex longitudinal Kerr angle according to the exact Eq. (1.177). Then, the approximate  $\omega \sigma_{\text{off}}^{\perp}$  was derived from the calculated LKE angle using the Eq. (1.178) for an isotropic medium. The off-diagonal conductivity spectra recalculated in this way are compared to  $\omega \sigma_{\text{off}}^{\perp}$  obtained directly from the *ab initio* calculations in Fig. 2.87(b) and (d). A marked difference between the "exact" and "approximate"  $\omega \sigma_{\text{off}}^{\perp}$  values is observed in the ir range for the Fe<sub>1</sub>/Au<sub>1</sub> MLS only. It diminishes to a



*Figure 2.87.* LSDA calculated absorptive parts of the diagonal  $\sigma_{xx}$  and  $\sigma_{zz}$  (panels a and c) and off-diagonal  $\omega\sigma_{\text{off}}^{\parallel}$  and  $\omega\sigma_{\text{off}}^{\perp}$  (panels b and d) components of the optical conductivity tensor for Fe<sub>1</sub>/Au<sub>1</sub> (left panels) and Fe<sub>2</sub>/Au<sub>2</sub> MLS (right panels). The *ab initio* calculated  $\omega\sigma_{\text{off}}^{\perp}$  spectra are represented by dotted lines and the corrected ones by dashed lines (see text) [390].

negligible value above this energy region and can be completely neglected in the whole energy range for the  $Fe_2/Au_2$  and  $Fe_3/Au_3$  structures. The possible errors caused by using Eq. (1.178) instead of (1.177) are then small and do not affect the conclusion that the large MOA is related to the anisotropy of the off-diagonal conductivity tensor components.

### Microscopic origin of the magneto-optical and orbital moment anisotropy in $Fe_n/Au_n$ MLS

To understand better the microscopic origin of the MOA let us consider in detail the electronic structure of the Fe<sub>1</sub>/Au<sub>1</sub>  $L1_0$  MLS. Spin-projected densities of Fe and Au *d* states are shown in Fig. 2.88 and the calculated spin and orbital magnetic moments are summarized in Table I. Within the Au(Fe) monolayer, each atom is surrounded by four other Au(Fe) atoms at a separation corresponding to the nearest-neighbor spacing in bulk Au(Fe). Due to the smaller number of the nearest neighbors of the same type both Fe and Au *d* states are much narrower than in the corresponding bulk metals. As a result



*Figure 2.88.* LSDA spin-projected fully-relativistic partial DOS (in states/(atom eV spin)) of the  $L1_0$  ordered Fe<sub>1</sub>/Au<sub>1</sub> MLS [390].

the majority spin Fe d states are fully occupied which leads to a significant enhancement of the Fe spin magnetic moment (2.87  $\mu_B$ ) compared to the value of 2.2  $\mu_B$  for bulk Fe. This enhanced magnetization has been observed [560] but the experimental value of  $2.75\pm0.25 \ \mu_B$  is somewhat smaller than the calculated one. Such a difference is however within experimental uncertainty and might also be affected by the deviation of the sample structure from the ideal  $L1_0$ .

The energy bands in Fe<sub>1</sub>/Au<sub>1</sub> MLS calculated for different magnetization directions are shown in Fig. 2.89. This comparison is useful as it helps to identify the states, which are sensitive to the change of the magnetization direction and, consequently, can potentially give a contribution to MOA, MCA and the anisotropy of the orbital moment. In Fe<sub>1</sub>/Au<sub>1</sub> MLS, for example, such states are the electronic states at about -4.0, -2.8, and -1.4 eV in the vicinity of the  $\Gamma$  point and those with energies -5.2, -1.5, and 0.5to1.8 eV located around the *M* symmetry point as well as along the  $\Gamma - X - M - \Gamma$  directions.

Comparing the values of the magnetic moments calculated for different magnetization directions one can see from Table I that Fe spin moments are almost independent of the magnetization direction. At the same time the anisotropy of Fe orbital moment, which is determined mainly by Fe *d* states, is quite large and is of the same order of magnitude as experimentally observed in Co/Au MLS [567]. This behavior could be expected in the presence of the SO interaction the anisotropy of the orbital moment is of the order of  $\xi/\Delta$ ,



*Figure 2.89.* LSDA energy band structure of the  $L1_0$  ordered Fe<sub>1</sub>/Au<sub>1</sub> MLS for two orientations of magnetization:  $\mathbf{M} \parallel (001)$  (solid lines), and  $\mathbf{M} \perp (001)$  (dotted lines) [390].

atom	state	<b>M</b>    [001]		$\mathbf{M} \perp [001]$	
		$M_S$	$M_L$	$M_S$	$M_L$
	s	0.0097	0.0000	0.0098	0.0000
	p	-0.0033	-0.0006	-0.0030	0.0005
Fe	$\overline{d}$	2.8593	0.0920	2.8612	0.0587
	f	0.0019	-0.0008	0.0019	-0.0010
	total	2.8676	0.0906	2.8698	0.0582
Au	8	-0.0346	0.0000	-0.0345	0.0000
	p	-0.0567	0.0035	-0.0566	0.0058
	d	0.1085	0.0293	0.1098	0.0300
	f	0.0100	-0.0014	0.0100	-0.0016
	total	0.0272	0.0315	0.0287	0.0342

*Table 2.9.* Calculated spin  $M_S$  and orbital  $M_L$  magnetic moments (in  $\mu_B$ ) of Fe<sub>1</sub>/Au<sub>1</sub> versus magnetization direction [390].

where  $\xi$  is the SO coupling strength and  $\Delta$  is the crystal field splitting, while the anisotropy of the spin moment is proportional to  $(\xi/\Delta)^2$  [568]. As Au *d* states are fully occupied the spin and orbital moments at Au site are small and depend weakly on the magnetization direction.



*Figure 2.90.* The  $dm_l(E)$  and  $m_l(E)$  for two orientations of magnetization together with  $\Delta m_l(E)$  for the  $L1_0$  ordered Fe<sub>1</sub>/Au<sub>1</sub> MLS (see text) [390].

To understand better the anisotropic behavior of Fe and Au orbital magnetic moments let us introduce the site-dependent functions  $dm_l(E)$  and  $m_l(E)$  given by Eq.s 2.1 and 2.2.

Both  $dm_l(E)$  and  $m_l(E)$  are defined in the local coordinate system chosen in such a way that z axis is directed along the magnetization and, consequently, they depend on the relative orientation of the magnetization with respect to the crystallographic axes. In the case of Fe<sub>n</sub>/Au<sub>n</sub> MLS we will use the notation  $m_l^{\parallel}(E)$  and  $m_l^{\perp}(E)$  for  $m_l(E)$  calculated with  $\mathbf{M} \parallel (001)$  and  $\mathbf{M} \perp (001)$ , respectively. The difference of these two functions

$$\Delta m_l(E) = m_l^{\parallel}(E) - m_l^{\perp}(E)$$
(2.8)

220

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*Figure 2.91.* The *d*-orbital projected  $dm_l(E)$  on Fe sites for two orientations of magnetization, and the d-partial density of states (in states/(atom eV spin)) for the  $L1_0$  ordered Fe<sub>1</sub>/Au<sub>1</sub> MLS [390].

can provide useful information on the orientation dependence of the orbital moment. Fig. 2.90 shows the functions  $dm_l(E)$ ,  $m_l(E)$ , and  $\Delta m_l(E)$  calculated for Fe and Au sites in Fe<sub>1</sub>/Au<sub>1</sub> MLS. Here and in the rest of the chapter we will only consider the contribution coming from d orbitals to the  $m_l$  related functions. All the three functions show strong energy dependence. The variations of the functions at Au and Fe sites are comparable, but the Au d orbital moment,  $m_l(E_F)$ , is significantly smaller as Au d-states are almost fully occupied (see Fig. 2.88). The anisotropy of the Au orbital moment  $\Delta m_l(E)$  vanishes at  $E_F$ . At about -1.2 eV Fe  $d_{\uparrow}$  states are already occupied while  $d_{\downarrow}$  are still almost empty (Fig. 2.88) and, as a result, both  $m_l(E)$  and  $\Delta m_l(E)$  are zero at this energy. At the Fermi energy, however, there is a strong anisotropy of Fe d orbital moment.

To understand better such a behavior let us analyze the orbital character of partial density of Fe d states in the vicinity of the Fermi level (Fig. 2.91). It is worth noting that the only nonzero matrix elements of the  $\hat{l}_z$  operator calculated between real harmonics with l = 2 are  $|\langle d_{x^2-y^2} | \hat{l}_z | d_{xy} \rangle| = 2$  and  $|\langle d_{xz}|\hat{l}_z|d_{yz}\rangle|=1$ . Hence, the largest contribution to  $m_l(E)$  can be expected from the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals. Also, it should be pointed out that, in contrast to the case of transition metal films considered in Ref. [546] in which the on-site SO interaction is the only source for the unquenching of the orbital moment, in a compound consisting of 3d metal atoms with a large magnetization and a relatively weak SO coupling and 5d atoms for which the SO coupling is strong, the unquenching of the 3d orbital moment can be caused, to a great extent, by the 3d-5d hybridization. In the particular case of Fe<sub>1</sub>/Au<sub>1</sub> MLS there is a peak at -0.5 eV in the density of Fe  $d_{x^2-u^2}$  states (Fig. 2.91) which hybridize rather strongly with Au d states. The density of  $d_{xy}$  states is constant in this energy interval and, as a consequence, the  $dm_l(E)$  has a maximum at this energy for  $\mathbf{M} \parallel (001)$ . The states, which form the peak of DOS just above the Fermi level, are predominantly of  $d_{3z^2-r^2}$  character and they do not contribute to  $dm_l(E)$ . When the magnetization direction changes from M  $\parallel$  (001) to  $\mathbf{M} \perp (001)$  the local coordinate system in which  $dm_l(E)$  is calculated should also be changed accordingly. In the new coordinate system the  $d_{3z^2-r^2}$  orbital transforms into a linear combination of the  $d_{3z^2-r^2}$  and  $d_{x^2-y^2}$  orbitals and a sharp peak of  $dm_{L}^{\perp}(E)$  appears above the Fermi level, which follows the shape of the corresponding peak of the density of  $d_{3z^2-r^2}$  states. At the same time, the  $d_{x^2-y^2}$  orbital, which plays the crucial role in the formation of the peak of  $dm_l^{\parallel}(E)$  at -0.5 eV, transforms into  $\frac{\sqrt{3}}{2}d_{3z^2-r^2} + \frac{1}{2}d_{x^2-y^2}$  and, as a result of the reduced contribution of the  $d_{x^2-y^2}$  orbital to the wave function,  $dm_l^{\perp}(E)$ is suppressed below the Fermi level. These simple considerations allow us to explain the strong dependence of the Fe orbital moment on the magnetization direction in the Fe<sub>1</sub>/Au<sub>1</sub> MLS.

The calculated spin and orbital magnetic moments for Fe<sub>2</sub>/Au<sub>2</sub> MLS are given in Table II. As compared to the results for Fe<sub>1</sub>/Au<sub>1</sub> MLS, the change in the local environment and the increase of the number of Fe nearest-neighbors around Fe sites result in broadening of d bands and decrease of the calculated Fe spin magnetic moment to 2.79  $\mu_B$ . In contrast to the Fe<sub>1</sub>/Au<sub>1</sub> MLS where we observed the strong anisotropy of the Fe d orbital moment, the Fe<sub>2</sub>/Au<sub>2</sub> MLS reveals very small anisotropy in the orbital magnetic moment (Table 2.10). In Fig. 2.92 the functions  $dm_l(E)$ ,  $m_l(E)$ , and  $\Delta m_l(E)$  calculated for

atom	state	<b>M</b>    [001]		$\mathbf{M} \perp [001]$	
		$M_S$	$M_L$	$M_S$	$M_L$
Fe	s	-0.0045	0.0000	-0.0044	0.0000
	p	-0.0192	0.0001	-0.0191	-0.0005
	d	2.8056	0.0835	2.8064	0.0934
	f	0.0084	-0.0013	0.0084	-0.0015
	total	2.7902	0.0824	2.7912	0.0914
Au	8	-0.0260	0.0000	-0.0259	0.0000
	p	-0.0200	0.0026	-0.0200	0.0036
	d	0.0778	0.0155	0.0770	0.0182
	f	0.0059	-0.0009	0.0059	-0.0012
	total	0.0377	0.0172	0.0370	0.0206

*Table 2.10.* Calculated spin  $M_S$  and orbital  $M_L$  magnetic moments (in  $\mu_B$ ) for Fe<sub>2</sub>/Au<sub>2</sub> versus magnetization direction [390].

Fe and Au sites in Fe<sub>2</sub>/Au<sub>2</sub> MLS are shown. Although all the three functions show strong energy dependence as in the case Fe<sub>1</sub>/Au<sub>1</sub>, however, at the Fermi energy negligible anisotropy of the Fe *d* orbital moment was observed. The explanation can be found in Fig. 2.93. In the case of Fe<sub>2</sub>/Au<sub>2</sub> MLS there are also two peaks in the partial density of Fe *d* states below and above the Fermi level but in contrast to Fe<sub>1</sub>/Au<sub>1</sub> MLS they have the same  $d_{x^2-y^2}$  character (Fig. 2.93) with a strong admixture of  $d_{3z^2-r^2}$ . Moreover, the partial weights of  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$  states at the Fermi level are such that  $m_l(E_F)$  changes only slightly upon the changing of the magnetization direction from  $\mathbf{M} \parallel (001)$ to  $\mathbf{M} \perp (001)$  and the anisotropy of the Fe orbital moment  $\Delta m_l(E_F)$  is very small (see insert in Fig. 2.92).

The dependence of the MOA on the SO coupling and hybridization strengths is very complicated (see, e.g., Ref. [389]) and does not allow us to introduce a simple model consideration as in the case of the MCA anisotropy [545, 546]. While the anisotropic band splitting can be directly related to the MCA, the situation with MOA is more complex as the eigenvalues and wave functions of both the initial and final states enter the expression for the matrix elements. Therefore, the only way to obtain a realistic description of the MOA is to perform numerical calculations. The optical conductivity can be expressed as a sum of additive contributions coming from interband transitions with the initial and/or final states lying in different non-overlapping energy intervals. In the case of Fe<sub>1</sub>/Au<sub>1</sub>, the Fe  $d_{\uparrow}$  and Fe  $d_{\downarrow}$  states are well separated in energy, but overlapped with the Au d states in a wide energy interval (see Fig. 2.88). An even less distinct separation in the energy position of the initial Fe and Au



*Figure 2.92.* The  $dm_l(E)$  and  $m_l(E)$  functions for the two orientations of magnetization, together with  $\Delta m_l(E)$  for Fe<sub>2</sub>/Au<sub>2</sub> MLS [390].

*d* states is observed in the case of Fe<sub>2</sub>/Au<sub>2</sub> MLS. It seems to be more informative to examine the dependence of the MOA on the site-dependent optical transition matrix elements. The calculations have been performed in the way as described in Ref. [400], where, within an atomic sphere about either one of the atomic positions, the optical transition matrix elements were set to zero. In this way, the optical conductivity spectra and MOA can be analyzed in terms of the contributions arising from the transitions on the particular sites. The decomposition of the MOA into the contributions from interband transitions on the Fe and Au sites in Fe<sub>1</sub>/Au<sub>1</sub> MLS is shown in Fig. 2.94(a). As it can



*Figure 2.93.* The  $dm_l(E)$  on Fe sites for the two orientations of magnetization and the dpartial density of states (in states/(atom eV spin)) for Fe<sub>2</sub>/Au<sub>2</sub> MLS [390].

be seen, the MO anisotropy spectrum magnitude is determined by both the Au and Fe sites, depending on the spectral region. Only in the 0 to ~1 eV energy interval the MOA can be connected exclusively with transitions on the Fe site. The interband transitions on the Au site are mainly responsible for the MOA spectra in the ~1 to ~5 eV energy interval. The transitions occur between the Au  $d_{\downarrow}$  states located at energies  $E \leq -1$  eV below the Fermi level and the hybridized states of p and f characters lying in the energy range up to 2 eV above the Fermi level. The enhanced density of these final states arises due to the strong hybridization with Fe  $d_{\downarrow}$  states in the energy interval. In particular, the



*Figure 2.94.* Decomposition of the calculated MOA spectra (solid lines) into the contributions coming from all interband transitions on Fe (dashed lines) and Au (dotted lines) sites in Fe<sub>1</sub>/Au<sub>1</sub> (a) and Fe<sub>2</sub>/Au<sub>2</sub> (b) MLS [390].

peak at 3.7 eV in MOA spectra is completely determined by these transitions. The peak at 5.3 eV is equally due to both the Fe and Au related transitions. The results of the analysis for Fe<sub>2</sub>/Au<sub>2</sub> MLS is shown in Fig. 2.94(b). As in the case of Fe<sub>1</sub>/Au<sub>1</sub> MLS, the transitions from both Fe and Au sites determine the resulting MOA spectra in the Fe<sub>2</sub>/Au<sub>2</sub> MLS; however, the main contribution arises from transitions on the Au site over the whole spectral range. We have verified that the prominent peak in the Fe<sub>2</sub>/Au<sub>2</sub> MOA spectra at 5.5 eV is mostly determined by Au *d* related transitions to the final states extending up to ~4 eV above the Fermi level.

Two major effects lead to the appearance of the MOA when the magnetization direction is changed: (i) the change of the band energies (Fig. 2.89) and (ii) the change of the orbital character of the wave functions. To determine which of the effects dominates we performed two model calculations. In the first one, the spectra were obtained using the as calculated band energies while the corresponding momentum matrix elements at every **k**-point were averaged over the magnetization directions. The calculated MOA is zero in this case, whereas the MOA obtained from the second calculation, in which - vice versa - the averaged band energies and as calculated matrix elements were used, is in a very good agreement with the results of the *ab initio* calculation. This clearly demonstrates that the main effect of MOA comes from the change of the orbital character of the wave functions due to the magnetization axis rotation. This is exactly the origin also the anisotropy of the orbital moment, as



*Figure 2.95.* Calculated absorptive off-diagonal part of the optical conductivity (a,b) and MO anisotropy (c) in the  $Fe_1/Au_1$  MLS (solid lines) together with the results of the calculations for the SO coupling set to zero on the Au site (dashed lines) and the Fe site (dotted lines) [390].

discussed before. Although the common origin of both anisotropies is the spinorbit interaction, the relationship between the orbital moment anisotropy and the MOA is indirect. While the orbital moment anisotropy is determined by the integral property of the occupied states, the magneto-optical anisotropy is related to the energy dependent quantity being the convolution of all the initial occupied and final unoccupied states within the given energy difference (Eq. 1.221).

The dependence of the MOA on the exchange splitting and the SO interaction was examined in the way describes in Ref. [514] and [400]. It was found that the SO coupling of Au is equally responsible for the large MOA as the exchange splitting of Fe. If we set the SO coupling on Fe to zero, the off-diagonal optical conductivity is changed in the whole energy interval by a negative shift for both magnetization directions (Fig. 2.95(a) and (b)). So, the contribution of the SO coupling on Fe site to the conductivity is significant but almost isotropic. As a result, the MO anisotropy practically does not depend on the SO coupling strength on the Fe site (Fig. 2.95(c)). On the other hand, putting the SO coupling on Au site to zero affects strongly the off–diagonal optical conductivities leading to a strong suppression of the MOA. As in the case of Fe<sub>1</sub>/Au<sub>1</sub> MLS, setting the SO coupling on Fe to zero in the Fe<sub>2</sub>/Au<sub>2</sub> MLS changes the MO anisotropy to a lesser extent than the off–diagonal optical conductivity (not shown). However, putting the SO coupling on Au site to zero affects strongly both the off–diagonal optical conductivity and the MOA. Thus, the SO coupling of Au is mainly responsible for the large MO anisotropy in Fe/Au MLS.

# Chapter 3

# MAGNETO-OPTICAL PROPERTIES OF *f* FERROMAGNETIC MATERIALS

# 3.1 Lantanide compounds

Determination of the energy band structure of solids is a many-body problem. Band theory, a mean-field theory to treat this problem, in the framework of the local spin density approximation (LSDA), has been successful for many kinds of materials, and has become the *de facto* tool of first-principle calculations in solid state physics. It has contributed significantly to the understanding of material properties at the microscopic level. However, there are some systematic errors which have been observed when using the LSDA. In particular, the LSDA fails to describe the electronic structure and properties of f electron systems in which the interaction among the electrons are strong. A wide variety of physical properties arise from the correlations among f electrons: metalinsulator transitions, valence fluctuations in the Kondo effect, heavy fermion behavior, superconductivity, and so on. These are now called strongly correlated electron systems and many new concepts to address these phenomena have been constructed. However, the understanding of these systems is not complete.

Over last decade the MO properties of rare earth compounds have attracted large interest [7], which increased after the discovery of the maximal observable rotation of 90° in CeSb by Pittini *et al.* [569] The majority of MO investigations deal with compounds and alloys of the light rare earth ions Ce<sup>3+</sup> and Nd<sup>3+</sup>, the half filled shell ion Eu<sup>2+</sup>, and the heavy rare earths Tm<sup>2+</sup> and Yb<sup>3+</sup> [7]. As with most lanthanides, cerium and neodymium form face centered cubic (fcc) rock-salt type binary chalcogenides with the VIA elements of the periodic table of the elements (S, Se, Te) and fcc pnictides with the VA elements (N, P, As. Sb, Bi). With the exception of the nitrides, all cerium and neodymium chalcogenides and pnictides order antiferromagnetically in zero

magnetic field. CeN has no order down to 1.5 K, while NdN orders ferromagnetically [7].

### 3.1.1 Ce monochalcogenides and monopnictides

In recent years cerium monopnictides (CeAs, CeSb, and CeBi) and monochalcogenides (CeS, CeSe, and CeTe) attract a great attention partly due to the discovery of the three largest ever measured Kerr rotation angles of 90°,  $-22.08^{\circ}$  and  $-9.2^{\circ}$  for cleaved single crystals of CeSb, CeS, and CeBi, respectively [570]. Cerium monopnictides and monochalcogenides crystallize in simple rock-salt structure and each  $Ce^{3+}$  ion caries a single 4f electron. Furthermore, the cerium monochalcogenides are metals with approximately one conduction 5d electron per formula units, as was confirmed from Hall effect measurements [571], while cerium monopnictides are well compensated semimetals with a low concentration of conduction 5d electrons and valence holes in the p band [572]. The temperature dependence of the electrical resistivity of the cerium monochalcogenides exhibit Kondo behavior [573], indicating non-negligible d - f mixing. Furthermore, the Ce monochalcogenides order magnetically at low temperature in the antiferromagnetic fcc type-II structure [574]. The ordered magnetic moments are rather small and equal to 0.31, 0.45, and 0.66  $\mu_B$  for SeS, CeSe, and CeTe, respectively. The Ce monopnictides have magnetic moments of 0.57, 2.06, and 2.10  $\mu_b$  for CeAs, CeSb, and CeBi, respectively.

### CeS, CeSe, and CeTe

The optical and polar Kerr spectra of Ce monochalcogenides were measured by Reim *et al.* [575] and Pittini *et al.* [576, 577]. All three Ce chalcogenides exhibit sharply peaked Kerr rotations and ellipticities at the energies of their plasma minima. The largest Kerr rotation was observed for CeS, for which  $-22.08^{\circ}$  was reported by Pittini *et al.* [577]. Smaller peak rotations up to  $-6^{\circ}$ were observed for CeSe and CeTe.

Theoretical investigations of the optical and MO of some of the Ce monochalcogenides were carried out by Lim *et al.* [578], Cooper *et al.* [579], Yaresko *et al.* [523], Price *et al.* [580], and Antonov *et al.* [581].

Figure 3.1 shows the energy band structure of CeS for three independent fully relativistic spin-polarized band structure calculations treated the 4f electrons as: (1) itinerant electrons using the local spin-density approximation; (2) fully localized, putting them in the core; and (3) partly localized using the LSDA+U approximation. The energy band structure of CeS with the 4f electrons in the core can be subdivided into three regions separated by energy gaps. The bands in the lowest region around -13 to -14.5 eV (not shown in Fig. 3.1) have mostly S *s* character with some amount of Ce *sp* character mixed in. The next six energy bands are S *p* bands separated from the *s* bands by indirect



*Figure 3.1.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for CeS [581] treating the 4f states as: (1) fully localized (4f in core); (2) itinerant (LSDA); and (3) partly localized (LSDA+U).

energy gap. The highest region can be characterized as Ce spin-split 5d bands. The sharp peaks in the DOS at the Fermi energy and at around 2 eV above are due to  $4f_{5/2}$  and  $4f_{7/2}$  states respectively (see Fig. 3.1). There is a single 4f energy band crossing the Fermi level.

The LSDA+U band structure calculations [581] started from a  $4f^1$  configuration for the Ce<sup>3+</sup> ion with one on-site 4f energy shifted downward by  $U_{eff}/2$ and 13 levels shifted upwards by this amount. The energies of occupied and unoccupied f levels are separated by approximately  $U_{eff}$ . However, the 4fstates are not completely localized, but may hybridize, and together with all other states their energy positions relax to self consistency. The LSDA+U energy bands and total DOS of CeS [581] for  $U_{eff}$ =6 eV are shown in Fig. 3.1.



*Figure 3.2.* Calculated absorptive diagonal part of the optical conductivity  $\sigma_{1xx}$  (in  $10^{14}$  s<sup>-1</sup>), the optical reflectivity R and energy-loss function of CeS [581] compared with experimental data [577]

For  $Ce^{3+}$  ions one 4f band are fully occupied and situated between S p and Ce 5d states but the other thirteen 4f bands are well above the Fermi level hybridizing with Ce 5d states.

Figure 3.2 shows the calculated imaginary part of the energy-loss function  $\text{Im}[-1/\varepsilon(\omega)]$ , absorptive diagonal part of the optical conductivity  $\sigma_{1xx}$  and the optical reflectivity compared with experimental data [577]. The calculated spectra have been convoluted with a Lorentzian whose width is 0.2 eV to approximate a lifetime broadening.

The predominant structure of CeS as well as CeSe and CeTe reflectivity spectra is the edge near 3 eV [577]. This sudden drop is characteristic for metallic rare-earth chalcogenides and is due to a plasma oscillation interfering with interband excitations. This plasma resonance causes the golden color for all metallic rare-earth sulfides. The energy of the conduction electron plasma resonance in the presence of the interband excitations is given by  $\varepsilon_{1xx}(\omega)=0$ . In the particular case of CeS this condition is fulfilled at  $\hbar\omega$ =2.9 eV for the LSDA+U calculations and the maximum peak of the energy-loss spectrum in Fig. 3.2 is shifted only very little from this energy as a result of damping. The correct energy position of the plasma edge in CeS can be obtained only by taking into account  $5d \rightarrow 4f$  interband transitions. The calculations treating 4 f electrons as a core electrons place the zero crossing energy of  $\varepsilon_{1xx}(\omega)$ at higher energies (at 3.2 eV) in comparison with the LSDA+U calculations hence give a wrong energy position for the major minimum in the optical reflectivity spectrum (Fig. 3.2). On the other hand, the calculations with the 4felectrons in core produce more sharp conduction electron plasma resonance than the LSDA+U calculations (Fig. 3.2). As a result, the former calculations give better agreement with the experiment in the absolute value of the minimum of the reflectivity spectrum.



*Figure 3.3.* Calculated and experimental Kerr rotation ( $\theta_K$ ) and Kerr ellipticity ( $\varepsilon_K$ ) spectra (in degrees) of the CeS with the 4*f* electrons treated as: itinerant electrons (LSDA) and partly localized (LSDA+U) [581]. The experimental data are those of Ref. [577].

The best agreement between theory and the experiment for the optical reflectivity was found to be when we used the LSDA+U approximation (Fig. 3.2). The Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure and the optical spectra of CeS. Due to removing the 4f states from the Fermi level, the diagonal part of the optical conductivity  $\sigma_{1xx}$  in the energy interval of 0 to 3.5 eV has only small infrared peak (see Fig. 3.2). This peak originates from interband transitions between eigenvalue surfaces that are quasiparallel around the  $\Gamma$  symmetry point. These quasiparallel bands are visible along  $\Gamma$ -L and  $\Gamma$ -K symmetry directions (see Fig. 3.1). The very broad double peak structure observed between 4 and 10 eV is due to transitions from bands with predominantly S 3p character to unoccupied Ce  $5d(t_{2g})$  and  $5d(t_{2g})$  bands, respectively.

The calculation of the optical conductivity where the 4f's are treated as band states reproduces two additional structures in the 0.0 to 3.5 eV energy interval, namely, the peaks at 0.9 and 2.0 eV (Fig. 3.2). Both the peaks involve the  $5d \rightarrow 4f$  interband transitions. The second peak is responsible for the deep minimum in the optical reflectivity at 1.8 eV which is not observed in the experiment [577] (Fig. 3.2).

After consideration of the bandstructure and optical properties we turn to the magneto-optical spectra. The polar magneto-optical Kerr effect was measured on CeS, CeSe, and CeTe in Ref. [577]. All three spectra are quantitatively very similar. They are dominated by a sharp and large negative Kerr rotation peak of  $-22.08^{\circ}$ ,  $-5.51^{\circ}$ , and  $-3.32^{\circ}$  detected at photon energies of 3.04, 2.60,

and 1.99 eV for CeS, CeSe, and CeTe, respectively with a remarkably small width of 0.1 eV [577]. These Kerr rotation peaks are significant, in particular if one consider the small magnetic moment achieved in the sample at the condition of the experiment. Particularly meaningful is the Kerr rotation peak of  $-22.08^{\circ}$  observed in CeS [577] with a magnetic moment of only 0.31  $\mu_B$ /Ce. This extraordinary peak corresponds to the highest ever observed specific Kerr rotation of  $71.23^{\circ}/\mu_{B}$  and to the second largest ever measured Kerr rotation after the record of 90° recently detected on CeSb [569]. In Fig. 3.3 we show the experimental [577]  $\theta_K(\omega)$  and  $\epsilon_K(\omega)$  MO Kerr spectra of CeS, as well as the spectra calculated with LSDA and LSDA+U approximations. This picture clearly demonstrates that the better description is unambiguously given by the LSDA+U approach. The LSDA spectra have an extra peaks at 0 to 1 eV which is caused by extra structure present in the interband dielectric tensor. Responsible are interband transitions involving the hybridized 4f states, which in the LSDA approach exhibit a maximum resonance near  $E_F$ . In the LSDA+U approach, the 4f state energies are shifted due to the on-site Coulomb interaction  $U_{eff}$ . As a result, the transitions involving the 4f states do not take place at small photon energies any more, and the structures at 0 to 1 eV disappears from Kerr spectra. The calculations in which the 4f electrons are treated as quasicore (not shown) are able to reproduce a very similar structure as the LSDA+Ucalculations, but, due to the lack of corresponding  $5d \rightarrow 4f$  interband transitions, the off-diagonal part of the optical conductivity  $\sigma_{2xy}$  is nearly zero, so that a very small Kerr rotation is obtained. Although the LSDA+U calculations made much better work in the comparison with LSDA one they still produce the less sharp plasma resonance and hence give smaller rotation angle of  $-13^{\circ}$ than experimentally observed -22.08°.

In Fig. 3.4 we show the experimental [577] and LSDA+U results for Kerr spectra of CeSe and CeTe. The results of the LSDA approach are not shown here, but we mention that these do by far not reproduce the experimental data as good as LSDA+U approaches [523]. The main peak in the Kerr rotation spectra in Fig. 3.4 is not found to be due to optical transitions stemming directly from the nearly localized 4f<sup>1</sup>-level. Instead, these peaks are due to a plasma minimum in the denominator  $D(\omega) \equiv \sigma_{xx}(1 + \frac{4\pi i}{\omega}\sigma_{xx})^{1/2}$  and non-zero  $\sigma_{xy}$ .

#### CeSb and CeBi

The optical and MO properties of CeSb were investigated by Schoenes and Reim [582] and Reim *et al.* [583], whereas its optical conductivity to 20 eV was measured by Kwon *et al.* [584]. Reim *et al.* [583] observed the onset of a large Kerr rotation, that reached  $-14^{\circ}$  at 0.5 eV, but that energy was the lower end of the spectral range they could measure. Pittini *et al.* [569] extended the low-energy limit to 0.23 eV. Pittini *et al.* [569] observed a record Kerr rotation which increased to reach  $-90^{\circ}$  at 0.46 eV, and then jumped to  $+90^{\circ}$  at the same



*Figure 3.4.* Theoretical and experimental [570] Kerr angle ( $\theta_{\rm K}$ ) and Kerr ellipticity ( $\varepsilon_{\rm K}$ ) spectrum of CeSe and CeTe. The theoretical spectrum (solid curve) was calculated using the LSDA+U approach with  $U = 6 \,\text{eV}$ .

energy, and decreased with increasing photon energy. Note that the reflectivity of CeSb at the maximum of Kerr rotation was found to be 28% [569]. 90° is the absolute maximum value that can be measured. It is two orders of magnitude larger than the values that are commonly measured for transition-metal compounds, and about one order of magnitude larger than values maximally achieved for other lanthanide and actinide compounds [7]. Later on Salghetti-Drioli et al. [585] prepared well-characterized single crystals of CeSb, but could not reproduce the record Kerr rotation on these crystals. Instead only a peak of  $-17^{\circ}$  at 0.46 eV was observed. They re-measure the CeSb specimen on which record Kerr rotation was found, and obtained for this sample the  $90^{\circ}$ rotation. Salghetti-Drioli et al. polished the surface of the sample on which Pittini had measured the record rotation, in order to exclude surface oxidation effects, but after the surface treatment only a small Kerr rotation could be measured from the sample [585]. Salghetti-Drioli et al. suggest that the observed 90° Kerr rotation might not be the intrinsic rotation of CeSb, but could be caused by a surface oxide layer.

The discovery of 90° Kerr rotation in CeSb attracts a great interest from theoretisists. Several groups tried to produce the Kerr rotation spectrum from the first principles or analyze theoretically the possibility of attaining a 90° Kerr rotation. Using the exact equation for the polar Kerr rotation Uspensii *et*


*Figure 3.5.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for CeSb in the LSDA and LSDA+U ( $U_{eff}$ =6 eV) approximations [523].

*al.* [586] pointed out that a 90° rotation can occur only when the absorptive parts of the diagonal and off-diagonal permitivities are zero. The absolute maximum value of Kerr rotation can be achieve at energy with zero reflectivity and it also attainable for the reflectivity of the order of 30-50% and hence the observation of 90° rotation in principle be possible in CeSb with its 28% reflectivity at 0.46 eV. Pustogowa *et al.* [587] also examined the possibility of a 90° rotation using the modeled MO conductivity and reflectivity with a singular oscillator strength and the SO coupling as a parameter. She was able to obtain a 90° rotation for various values of the SO parameter.

To investigate the nature of a record polar Kerr rotation in CeSb several first principle calculations of the diagonal and off-diagonal optical conductivity and polar Kerr effect of CeSb were carried out in Ref.s [578, 588, 579, 523, 580, 589].

The energy band structure of CeSb in the LSDA and LSDA+U approaches presented in Fig. 3.5 from Ref. [523, 589]. The LSDA calculations place the 4f DOS at and just above the Fermi level. The Coulomb repulsion  $U_{eff}$ strongly influences the electronic structure of CeSb. For Ce<sup>3+</sup> ions thirteen unoccupied 4f states are situated at 2 to 4 eV above the Fermi level hybridizing with Ce 5d states. A single occupied 4f state is located at -3.2 eV in good agreement with photoemission measurements which detected the 4f<sup>1</sup>



*Figure 3.6.* (a) experimental [577] Kerr rotation (in degrees) of CeSb in comparison with LSDA+*U* calculations [523]; (b) the LSDA theoretical spectrum [589] and experiment [585].

level slightly deeper than -3 eV [590–592]. The LSDA+U calculations also improve the magnetic moments producing spin and orbital magnetic moment equal to -1.012 and 2.960  $\mu_B$ , which yield a total moment of 1.948  $\mu_B$ . The experimental value obtained for the antiferromagnetic ground state is equal to  $2.10 \pm 0.04 \mu_B$  [593, 594]. The LSDA strongly underestimates the magnetic moments producing spin, orbital and total magnetic moments equal to -0.897, 1.511, and 0.614, respectively [589].

Lichtenestein *et al.* [588] and Yaresko *et al.* [523] show that LSDA+U calculations also give a substantial improvement over LSDA result in diagonal and off-diagonal optical conductivity of CeSb.

The complex polar Kerr spectra of CeSb were evaluated by Yaresko *et al.* [523] and Antonov *et al.* [589]. The maximal Kerr angle calculated with the LSDA approach was relatively large, about  $-12^{\circ}$  to  $-22^{\circ}$  depending of value of life-time broadening. The LSDA+U approach produces a relatively larger polar Kerr angle. The results for the Kerr spectra of CeSb from Ref. [523] are shown in left panel of Fig. 3.6. A giant Kerr rotation of  $60^{\circ}$  which is less than the observed value of  $90^{\circ}$ . Pittini et al. [569] observed that the maximum Kerr rotation depends on the magnetization and that therefore the intrinsic quantum state plays an important role. In addition, the record Kerr effect occurs close to a plasma minimum. Both observations agree with what was found in the calculations (Fig. 3.6). The denominator  $D(\omega) \equiv \sigma_{xx}(1 + \frac{4\pi i}{\omega}\sigma_{xx})^{1/2}$  nearly vanishes due to the particular frequency dependence of  $\sigma_{xx}$ . A small denominator is in itself not sufficient for obtaining a large Kerr rotation. Also  $\sigma_{xy}$ , which relates to the magnetic polarization, is important. The 4f<sup>1</sup> level in CeSb is a completely spin and orbitally polarized state, which has a large magnetic

moment of about  $2\mu_B$ . The 4f<sup>1</sup> level is, however, located 3.2 eV beneath  $E_F$ , and therefore it cannot contribute directly to the peak rotation. It was found that the  $4f^1$  level plays nevertheless a crucial role, because, due to hybridization of valence states with the anisotropically polarized  $4f^1$  state, the valence bands become anisotropically polarized. This anisotropic polarization leads to an asymmetrical coupling of the left- and right-hand circularly polarized light at small photon energies. The asymmetrical light coupling leads in turn to a relatively large  $\sigma_{xy}$ , which causes the huge Kerr rotation. To emphasize the importance of the anisotropic hybridization, it was performed also quasicore calculations for the 4f<sup>1</sup>-level [523]. One was obtained a very similar  $\sigma_{xx}$ , but due to the lack of anisotropic 4f-hybridization,  $\sigma_{xy}$  becomes nearly zero. Consequently, only a very small Kerr rotation is obtained in quasi-core calculations (not shown). We should note that the large angle of  $-60^{\circ}$  represents the maximal Kerr rotation that could be achieved in the LSDA+U calculations. In tis case no lifetime broadening was including and the plasma frequency was slightly changed. The first principles LSDA+U calculations give smaller, but still substantial Kerr angle of  $-45^{\circ}$  [523]. We also should mentioned that the theoretical Kerr spectrum is more narrow and shifts toward smaller energies in comparison with the experiment.

The right panel of Fig. 3.6 shows the results for the Kerr spectra of CeSb calculated in LSDA approximation [589] in comparison with latest experimental data obtained by Salghetti-Drioli *et al.* [585] on well-characterized single crystals of CeSb. The theoretical spectrum is convoluted on lifetime effect using the parameter of 0.1 eV. Surprisingly LSDA theory produces the experimental spectrum rather good in the shape, position and amplitude. The MO properties of CeSb need further theoretical consideration.

The MO Kerr spectrum of CeBi has also a considerable interest. In most compounds the magnitude of the Kerr effect is proportional to the spin-orbit (SO) coupling interaction. The MO Kerr effect in MnBi is, for example, larger than that in MnSb, because the SO coupling on Bi is larger than that on Sb. One could thus expect that the Kerr angle in CeBi should be as large as, or even larger than, that of CeSb. However, this is not found to be the case[577].

In Fig. 3.7 we show the experimental [577] and theoretical Kerr spectrum of CeBi [595]. The measured maximal Kerr rotation amounts only to  $-9^{\circ}$ . The LSDA+U approach (with U=6 eV) explains the measured MO Kerr spectrum of CeBi fairly well. There is a small energy difference of 0.1 eV in the position of the rotation maximum, and the calculated Kerr ellipticity deviates above 0.5 eV from the experimental curve.

The fact that the Kerr rotation of CeBi is far less that of CeSb is fully reproduced by the calculations [523, 595], but it is not consistent with our experience that the Kerr effect is proportional to the magnitude of SO coupling. The imaginary part of  $\sigma_{xy}$  is for CeBi as large as that of CeSb, but if we compare



*Figure 3.7.* Theoretical [595] and experimental [577] Kerr angle ( $\theta_{\rm K}$ ) and Kerr ellipticity ( $\varepsilon_{\rm K}$ ) spectrum of CeBi. The theoretical spectrum (solid curve) was calculated using the LSDA+U approach with U= 6 eV.

the  $\sigma_{xx}$  of CeBi to that of CeSb, then we find that the denominator does not become as small for CeBi. The resulting Kerr angle of CeBi is therefore not as large as that of CeSb.

# 3.1.2 NdX (X=S, Se, and Te) and $Nd_3S_4$

## NdS

The theoretical study of the electronic structure, optical and magneto-optical spectra of NdX (X=S, Se and Te) as well as  $Nd_3S_4$  has been done in Ref. [596].

Figure 3.8 shows the energy band structure of NdS. The energy band structure of NdS with the 4f electrons in the core can be subdivided into three regions separated by energy gaps. The bands in the lowest region around -14 eV (not shown in Fig. 3.8) have mostly S s character with some amount of Nd sp character mixed in. The next six energy bands are S p bands separated from the s bands by an energy gap of about 6.5 eV. The highest region can be characterized as Nd spin-split 5d bands. There is a strong hybridization between S p and Nd d states. The sharp peaks in the DOS at the Fermi energy and at around 2 eV above are due to  $4f_{5/2}$  and  $4f_{7/2}$  states respectively (see Fig. 3.8). There are three 4f energy bands crossing the Fermi level.

The LSDA+U energy bands and total DOS of NdS [596] for  $U_{eff}$ =7 eV are shown in Fig. 3.8. For Nd<sup>3+</sup> ions three 4f bands are fully occupied and



*Figure 3.8.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for NdS [596] treating the 4f states as: (1) fully localized (4f in core); (2) itinerant (LSDA); and (3) partly localized (LSDA+U).

hybridize with S p states but the other eleven 4f bands are well above the Fermi level and are separated from them by the correlation energy  $U_{eff}$ .

Figure 3.9 shows the calculated absorptive diagonal part of the optical conductivity  $\sigma_{1xx}$  and the optical reflectivity compared with experimental data [597]. There is a small peak at 0.2 eV and a large broad structure centered around 8 eV for the calculations treating 4*f* electrons as a core states. The first peak originates from interband transitions between eigenvalue surfaces that are quasiparallel around the  $\Gamma$  symmetry point. These quasiparallel bands are visible along  $\Gamma$  -L and  $\Gamma$ -K symmetry directions (see Fig. 3.8). The very broad structure centered around 8 eV is due to transitions from bands with predom-



*Figure 3.9.* Calculated absorptive diagonal part of the optical conductivity  $\sigma_{1xx}$  (in 10<sup>14</sup> s<sup>-1</sup>) and the optical reflectivity *R* of NdS [596] compared with experimental data [597]

inantly S 3p character to unoccupied bands which have predominantly Nd 5d character.

The calculation of the optical conductivity where the 4f's are treated as band states reproduces two additional structures in the 0.0 to 3.1 eV energy interval, namely, the peaks at 0.06 and 1.55 eV (Fig. 3.9). Both the peaks involve the 4f electrons in the interband transitions. The second peak is responsible for the deep minimum in the optical reflectivity at 1.3 eV which is not observed in the experiment [597].

The best agreement between theory and the experiment for the optical reflectivity was found to be when we used the LSDA+U approximation (Fig. 3.9). The Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure and the optical spectra of NdS. Due to removing the 4f states from the Fermi level, the diagonal part of the optical conductivity  $\sigma_{1xx}$  in the energy interval of 0 to 3.1 eV has only two small peaks (see Fig. 3.9). The first peak has the same nature as a corresponding peak in the calculations with the 4f electrons in the core. The second peak at around 1.4 eV consists of Nd 5d  $\rightarrow$  4f transitions originating from interband transitions around the  $\Gamma$  symmetry point and along  $\Gamma$ -L and  $\Gamma$ -K symmetry directions (see Fig. 3.8).

In Fig. 3.10 we show the experimental [597]  $\theta_K(\omega)$  and  $\epsilon_K(\omega)$  MO Kerr spectra of NdS, as well as the spectra calculated with LSDA, LSDA+U and with the 4f electrons in the core. This picture clearly demonstrates that the better description is unambiguosly given by the LSDA+U approach. The most prominent discrepancy in the LSDA spectra is the extra peak below 1 eV which is caused by extra structure present in the interband dielectric tensor. Responsible are interband transitions involving the hybridized 4f states, which in the LSDA approach exhibit a maximum resonance near  $E_F$ . In the LSDA+U approach, the 4f state energies are shifted due to the on-site Coulomb interaction



*Figure 3.10.* Calculated and experimental Kerr rotation ( $\theta_K$ ) and Kerr ellipticity ( $\varepsilon_K$ ) spectra (in deg.) of the NdS [596] with the 4*f* electrons treated as: itinerant electrons (LSDA), fully localized (4*f* in the core) and partly localized (LSDA+*U*). The experimental data are those of Ref. [597].

 $U_{eff}$ . As a result, the transitions involving the 4f states do not take place at small photon energies any more, and the erroneous peak structure around 1 eV disappears from Kerr spectra. The calculations in which the 4f electrons are treated as quasi-core are able to reproduce a very similar structure as the LSDA+U calculations, but, due to the lack of corresponding  $5d \rightarrow 4f$  interband transitions, the off-diagonal part of the optical conductivity  $\sigma_{2xy}$  is nearly zero, so that a very small Kerr rotation is obtained.

The situation is clearly seen in Fig. 3.11 where we show the separate contributions of both the numerator, i.e.,  $\sigma_{xy}(\omega)$  and the denominator,  $D(\omega) \equiv \sigma_{xx}(1 + \frac{4\pi i}{\omega}\sigma_{xx})^{1/2}$ , which factor together to give the Kerr angle of NdS.

Due to wrong position of the 4f bands in the LSDA calculations the imaginary part of the inverse denominator (times the photon frequency),  $\text{Im}[\omega D]^{-1}$ , displays a double resonance structure at about 1.0 and 2.4 eV which leads to a disagreement with the experimental Kerr spectra. The LSDA+U calculations as well as the calculations which treated the 4f electrons as core states produce a single resonance maximum of the denominator at about 3 eV. This resonance is even larger in the former calculations, but the imaginary part of  $\omega \sigma_{xy}$ , i.e.  $\omega \sigma_{2xy}$ , displays a very small value at 3 eV. Therefore the peak in the Kerr ro-



*Figure 3.11.* Decomposition of the Kerr rotation spectrum of NdS in separate contributions [596]. Top panel: calculated real and imaginary part of the diagonal dielectric function,  $\varepsilon_{xx}^{(1)}$ , and  $\varepsilon_{xx}^{(2)}$ . Third panel from the top: The imaginary part of  $[\omega D]^{-1}$  which results from  $\varepsilon_{xx}^{(1)}$  and  $\varepsilon_{xx}^{(2)}$ . Bottom panel: The Kerr rotation (in deg.) which results as a product of  $\text{Im}[\omega D]^{-1}$  and  $\omega \sigma_{xy}^{(2)}$  (second panel from the top in  $10^{20} \text{ s}^{-2}$ ). The experimental Kerr angle spectrum is from Ref. [597]

tation at 3.1 eV results as a combination of a deep resonance structure of the denominator and interband Nd  $5d \rightarrow 4f$  transitions contributing into  $\sigma_{2xy}$ .

## NdSe and NdTe

The LSDA+U energy band structure and total DOS of NdSe and NdTe [596] are shown in Fig. 3.12. The main trend in the electronic structure of the sequence of NdX compounds (X= S, Se, Te) results from the characteristic trend in the chalcogenide p wave functions and from the systematic change of the lattice parameters. The counteraction of screening by inner atomic shells and of relativistic effects leads to the characteristic trend in the position of the atomic



*Figure 3.12.* Self-consistent LSDA+U energy band structure and total DOS (in states/(unit cell eV)) of NdSe and NdTe ( $U_{eff}$ =7 eV) [596].

p state and hence of the center of gravity of the chalcogenide p band monotonically increasing from S to Te. On the other hand, the center of gravity for the Nd f bands is monotonically decreasing from NdS to NdTe. The SO splitting at the center of gravity is equal to 0.45 and 0.19 eV for Nd f and drespectively for all three compounds, but SO splitting for chalcogenide p states shows one order of magnitude increase from S (0.09 eV) to Te (0.96 eV). The 6p bandwidth is monotonically increasing from 3.4 eV in NdS to 4.3 eV in NdTe due to the increasing extension of the atomic wave function. With the increasing chalcogenide p band widths the indirect energy gap between the top of the chalcogenide p and the bottom of the Nd 5d bands decreased in NdSe and closed in NdTe (see Fig. 3.12).

Although the SO interaction increases from S to Te, the MO Kerr spectrum is decreasing from NdS to NdTe. The explanation of this phenomena is follow. In NdS the energy position of the resonance structure of the inverse denominator (times the photon frequency)  $\text{Im}[\omega D]^{-1}$  coincides exactly with the maximum in  $\omega \sigma_{2xy}$ . However if one moves from NdS to NdTe through the series, the real diagonal part of complex dielectric function  $\varepsilon_{1xx}$  crosses the energy axis at 2.91, 2.67, and 2.19 eV in NdS, NdSe, and NdTe respectively and, hence, the position of the resonance structure of the inverse denominator shifts to smaller energies. As a consequence, in NdSe and, in particularly, NdTe the

well pronounced resonance structure coming from the inverse denominator is situated to the energy region with a small  $\omega \sigma_{2xy}$  value.

# Nd<sub>3</sub>S<sub>4</sub>

Among the many neodymium-sulphur compounds (NdS, Nd<sub>2</sub>S<sub>3</sub>, Nd<sub>2</sub>S<sub>4</sub>, Nd<sub>4</sub>S<sub>7</sub>, NdS<sub>2</sub>) only Nd<sub>3</sub>S<sub>4</sub> orders ferromagnetically [598] at 47 K. The La<sub>3</sub>S<sub>4</sub> is isostructural but diamagnetic and serves as a reference material. Near normal incidence reflectivity was experimentally determined for Nd<sub>3</sub>S<sub>4</sub> and La<sub>3</sub>S<sub>4</sub> from 0.03 to 12 eV in Ref. [599]. Other optical functions have been derived from the reflectivity data using a Kramers-Kronig transformation. The polar Kerr rotation and ellipticity was also measured [599]. It was found that the optical spectra of Nd<sub>3</sub>S<sub>4</sub> and La<sub>3</sub>S<sub>4</sub> are very similar, which means due to the author's opinion [599] there is no identification of transitions related to the occupied 4*f* state in the Nd<sub>3</sub>S<sub>4</sub> compound.

The LSDA and LSDA+U energy band structure and total DOS of Nd<sub>3</sub>S<sub>4</sub> is shown in Fig. 3.13 [596]. The LSDA energy band structure of Nd<sub>3</sub>S<sub>4</sub> can be subdivided into several regions separated by energy gaps. The bands in the lowest region at -13 eV (not shown in Fig. 3.13) have a mostly S s character with some amount of Nd s character mixed in. The next group of bands is formed by S p states with some admixture of Nd p and d states. The large narrow peak situated at the Fermi energy is formed by 4f bands of Nd. Unoccupied 5d bands of Nd are separated from  $4f_{5/2}$  bands by an energy gap. Thus, applied to Nd<sub>3</sub>S<sub>4</sub> the LSDA places f states just at the Fermi energy.

The main difference between LSDA NdS and Nd<sub>3</sub>S<sub>4</sub> energy band structures is in relative position of the Nd 4*f* and 5*d* states. Nd 4*f* energy bands lay inside of wide Nd 5*d* bands in NdS and strongly hybridize with them. But in the case of the Nd<sub>3</sub>S<sub>4</sub> 4*f*<sub>5/2</sub> bands are situated below the Nd 5*d* bands and separated from them by an energy gap. 4*f* energy bands in La<sub>3</sub>S<sub>4</sub> are empty and situated well above the Fermi energy. In the LSDA+*U* band structure calculations of Nd<sub>3</sub>S<sub>4</sub> ( $U_{eff}$ = 7 eV) the Nd 5*d* band became partly occupied, hence the LSDA+*U* electronic structure of Nd<sub>3</sub>S<sub>4</sub> is similar to the LSDA La<sub>3</sub>S<sub>4</sub> one (not shown) in vicinity of the Fermi energy.

In Fig. 3.14 we show the experimental [599] diagonal parts of complex dielectric function and optical conductivity together with calculated spectra within LSDA, LSDA+U and the 4f electrons as core electrons approximations as well as the LSDA calculation for La<sub>3</sub>S<sub>4</sub>. Calculated plasma frequencies  $\omega_p$  are equal to 1.89 and 0.31 eV in NdS and Nd<sub>3</sub>S<sub>4</sub> respectively. As a consequence a deep minimum in the optical reflectivity in Nd<sub>3</sub>S<sub>4</sub> shifts towards smaller energies in comparison to the NdS compound (see Fig.s 3.9 and 3.14). Above 6 eV the calculated optical reflectivity of Nd<sub>3</sub>S<sub>4</sub> is higher than the experimental one possibly due to non-perfect sample polishing or oxidation of the surface. As a result, the calculated imaginary part of complex dielectric



*Figure 3.13.* LSDA and LSDA+U energy band structure and total DOS (in states/(unit cell eV)) calculated for Nd<sub>3</sub>S<sub>4</sub> [596].

function  $\varepsilon_{2xx}$  is higher then the experimental one above 6 eV. Except for this, there is good agreement between experiment and theory for all the three approximations. Moreover, the optical properties of La<sub>3</sub>S<sub>4</sub> are very similar to those of Nd<sub>3</sub>S<sub>4</sub>, in a good correspondence to experiment measurements [599].

Although the optical spectra of Nd<sub>3</sub>S<sub>4</sub> are not sensitive to the position of the 4*f* bands, it is not the case for the magneto-optics. In Fig. 3.15 we show the experimental [599] and theoretically calculated  $\theta_K(\omega)$  and  $\epsilon_K(\omega)$  MO Kerr spectra of Nd<sub>3</sub>S<sub>4</sub>. In the case of Nd<sub>3</sub>S<sub>4</sub>, as well as NdS, the better description is given by the LSDA+*U* approach. The calculation with fully localized, core like 4*f* electrons gives completely inappropriate results and is not discussed further. The most prominent discrepancy in the LSDA spectra is the extra peak about 2 eV which is caused by extra structures present in the interband dielectric tensor. Responsible are  $4f \rightarrow 5d$  interband transitions involving the occupied 4*f* states, which in the LSDA approach are situated at E<sub>F</sub>. In the LSDA+*U* approach, the 4*f* → 5*d* transitions do not take place at such photon energies any more, and the erroneous peak structure around 2 eV disappears from the Kerr spectra. The LSDA calculation also is not able to produce the right value of the main peak in the Kerr rotation at about 0.9 eV. This peak



*Figure 3.14.* Theoretically calculated optical spectra of  $Nd_3S_4$  and  $La_3S_4$  and the experimental spectra for  $Nd_3S_4$  from Ref. [599].

results from a combination of a deep resonance structure of the inverse denominator  $\text{Im}[\omega D]^{-1}$  and interband transitions between occupied Nd 5d states near the Fermi energy and unoccupied Nd  $4f_{5/2}$  states contributing into  $\sigma_{2xy}$ . Although the LSDA calculations display a resonance structure in the inverse denominator and this resonance is even larger in the LSDA calculations, the



*Figure 3.15.* Calculated and experimental Kerr rotation ( $\theta_K$ ) and Kerr ellipticity ( $\varepsilon_K$ ) spectra (in deg.) of Nd<sub>3</sub>S<sub>4</sub> with the 4*f* electrons treated as: itinerant electrons (LSDA), fully localized (4*f* in the core) and partially localized (LSDA+*U* approach). The experimental data are those of Ref. [599].

imaginary part of  $\omega \sigma_{xy}$ , i.e.  $\omega \sigma_{2xy}$  displays a very small value at 0.9 eV due to wrong position of the LSDA 4*f* bands.

## 3.1.3 Tm monochalcogenides

The Tm monochalcogenides TmS, TmSe and TmTe constitute a well known family of strongly correlated electron systems. They form a very interesting group of materials in which many characteristic phenomena are expressed. In the series of the Tm monochalcogenides one has the interesting possibility to go from integer trivalent metallic TmS to integral divalent semiconducting TmTe through intermediate valence TmSe [600-602]. The unique feature of thulium compounds compared with intermediate valence materials containing cerium, samarium or europium is that both ground-state configurations of thulium have a non-zero magnetic moment. TmS exhibits antiferromagnetic order which is an almost type II sinusoidally modulated structure below  $T_N$ =6.2 K [603]. It has been classified as a Kondo lattice compound due to a metallic resistivity which increases Kondo-like down to about 15 K [604-607]. TmSe has attracted interest because of the valence fluctuation between  $4f^{12}$ and  $4f^{13}$  configurations, Kondo effects, antiferromagnetic order, and a possible metal-insulator transition. This compound has the peculiarity that two magnetic valence states  $Tm^{2+}$  and  $Tm^{3+}$  are involved in the valence fluctuation.

Evidence comes from photoemission experiments [601, 608–611, 600, 612], and also from measurements related to magnetic properties, resistivity and specific heat [613–617]. However, the situation is so complicated that there is no overall consistent explanation of the physical properties of this compound. The resistivity of TmSe shows a Kondo-like logarithmic temperature dependence at high temperatures followed by a sharp increase at  $T_N$ =3.5 K, which is thought to be a transition into an insulating state [616, 618, 619]. This anomaly in the vicinity of  $T_N$  shows a very complicated response to external magnetic fields and to pressure [615, 620].

TmTe is a magnetic semiconductor with a localized 13th f level between a filled Te-5p valence band and an empty Tm-5d conduction band [601]. The lattice constant and the Curie constant show that the Tm ions are divalent at ambient pressure [600]. TmTe is interesting in its own right, especially since it was recently reported [621] to undergo a phase transition at  $T_Q$ =1.7 K, far above the magnetic-ordering temperature ( $T_N \sim 0.2$ -0.4 K depending on the specimen). This transition was ascribed to the onset of long-range ordering among the Tm quadrupolar moments, but the exact mechanism is still controversial [622].

## TmS

**Band structure.** The theoretical study of the electronic structure, optical and magneto-optical spectra of TmX (X=S, Se and Te) have been done in Ref. [623]. It was performed three independent fully relativistic spin-polarized band structure calculations. The 4f electrons have been considered as: (1) itinerant electrons using the local spin-density approximation; (2) fully localized, putting them in the core; and (3) partly localized using the LSDA+U approximation. An important difference with respect to treating the 4f electrons as core electrons is that in the LSDA+U calculation all optical transitions from the 4f states are taken into account.

Figure 3.16 shows the energy band structure of TmS for all three approximations. The energy band structure of TmS with the 4*f* electrons in the core can be subdivided into three regions separated by energy gaps. The bands in the lowest region around -15 eV have mostly S *s* character with some amount of Tm *sp* character mixed in. The next six energy bands are S *p* bands separated from the *s* bands by an energy gap of about 6.5 eV. The width of the S *p* band is about 3.7 eV. The spin splitting of the S *p* bands is very small (about 0.06 eV at the X symmetry point (Fig. 3.16)). The highest region can be characterized as Tm spin-split *d* bands. It is important that the top of the S *p* bands is at -3.5eV below the Fermi level since it means that all the interband transitions in the energy interval of 0.0 to 3.5 eV take part within the Tm *d* bands (see below). The sharp peaks in the DOS calculating in the LSDA at the Fermi energy and near 2 eV below are due to  $4f_{7/2}$  and  $4f_{5/2}$  states respectively (Fig. 3.16).



*Figure 3.16.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for TmS [623] treating the 4f states as: (1) fully localized (4f in core); (2) itinerant (LSDA); and (3) partly localized (LSDA+U).

The LSDA+U band structure calculations [623] have been started from a  $4f^{12}$  configuration for the Tm<sup>3+</sup> ion with twelve on-site 4f energies shifted downward by  $U_{eff}/2$  and two levels shifted upwards by this amount. The energies of occupied and unoccupied f levels are separated by approximately  $U_{eff}$ . We emphasize, however, that the 4f states are not completely localized, but may hybridize, and together with all other states their energy positions relax to self consistency.

The LSDA+U energy bands and total density of states (DOS) of TmS for  $U_{eff}$ =6 eV are shown in Fig. 3.16. The Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure of TmS. For Tm<sup>3+</sup> ions twelve 4f bands



*Figure 3.17.* Comparison the calculated 4f DOS in LSDA and LSDA+U approximations [623] with the experimental UPS spectra from Ref. [612]. The (c) panel shows the LSDA+U 4f DOS taking into account the multiplet structure of the  $4f^{11}$  final state (see explanations in the text).

are fully occupied and hybridize with S p states. The 14th f hole level is completely unoccupied and well above the Fermi level. A hole 13th f level is pinned at the Fermi level. Although it was used a starting configuration with zero occupation of 14th f and 13th f levels, in the process of self-consistent relaxation initially empty 13th f level become partly occupied due to pinning at the Fermi level with occupation number equal to 0.12 (valence 2.88+) in good agreement with the experimental estimations (2.91+) by off-resonance UPS [612]. A fundamental aspect of this observation is that the pinning of the 13th f state at  $E_F$  to be a robust property of the TmS compound: it happens irrespective of the precise value of  $U_{eff}$ .

Photoemission experiments, both x-ray (XPS) and ultraviolet (UPS), have been of central importance for understanding mixed-valence materials (see the review of the early work by Campagna *et al.* [608]). In rare-earth photoemission, when the photon ejects an electron from the  $4f^n$  shell it leaves behind a  $4f^{n-1}$  configuration, hence the kinetic energy distribution curve of the emitted electron measures the spectra of the final-state hole. The final state  $4f^{n-1}$  has a characteristic multiplet splitting which serves as a fingerprint, and these are accurately resolved and calculable in rare-earth photoemission. By identification of the final-state hole the initial state can be inferred.

The partial 4f DOS of the occupied part of the TmS calculated in LSDA and LSDA+U approximations is compared with UPS measurements [610] in Fig. 3.17. The calculated 4f DOS has been broadened to account for lifetime effects and for the experimental resolution. The Tm 4p states essentially do not contribute to XPS and UPS because of the low ionization cross section compared with that of the Tm 4f states [624]. Hence, the measurements only indicate the f excitation energies of trivalent and divalent Tm, relative to the Fermi level. The LSDA calculations places the 4f energy band right at the Fermi level (Fig. 3.16) producing in the 4f DOS a double peak between 0 and -3 eV (Fig. 3.17). In the LSDA+U calculations twelve fully occupied 4f



*Figure 3.18.* Comparison of the calculated partial 4f (N<sub>f</sub>(E)) and 5d (N<sub>d</sub>(E)) DOS in the LSDA and LSDA+U approximations [623] with the experimental BIS spectrum of TmS from Ref. [625].

bands are situated between -4 and -8 eV in the DOS and a partly filled 13th 4f band produces a small peak at around -0.5 eV binding energy (Fig. 3.17).

The LSDA+U DOS cannot, of course, fully account for the multiplet splitting. Therefore we present at right panel in Fig. 3.17 the LSDA+U 4f DOS taking into account the multiplet structure of the  $4f^{11}$  final state. The multiplet structure consists of 15 terms nine of which are the most intensive ( ${}^{4}I_{15/2}$ , <sup>4</sup>I<sub>13/2</sub>, <sup>4</sup>F, <sup>2</sup>H, <sup>4</sup>G, <sup>2</sup>K, <sup>4</sup>D, <sup>2</sup>L, and <sup>2</sup>F) [608]. The relative intensities for the multiplet peaks were obtained on the basis of Cox calculations [626] who used the fractional parentage method [627]. In this method the Hund's rule ground state is assumed for n 4f electrons and then the coefficients of fractional parentage (Racah's) for the n-1 configurations are calculated. The intensities for the various configurations (multiplets) are just the square of the coefficients of fractional parentage. In the right panel in Fig. 3.17 UPS spectrum is modeled by a weighted sum of nine LSDA+U 4f DOS curves. The centroid of the DOS has been aligned with each term of the atomic final state multiplet and summed up the spectra scaling them according to the relative intensities of the multiplets. The agreement between theory and the UPS measurements is very good. It is clear that the structures between -4.5 and -16eV binding energy should be assigned to the final-state multiplet structure derived from twelve fully occupied 4f bands (Tm<sup>3+</sup>) and the structures between 0.0 and -4.5 eV are associated with the final-state multiplet structure of the partly occupied 13th f level.

From the good agreement between theory and UPS measurements we may conclude that the LSDA+U calculations give an accurate position for the oc-

cupied 4f bands. The principle question is the energy position of the empty 4f states, which is usually answered by BIS measurements. Fig. 3.18 shows the experimental BIS spectrum of TmS [625] compared with the calculated energy distribution for the unoccupied partial Tm 4f (N<sub>f</sub>(E)) and 5d (N<sub>d</sub>(E)) density of states in the LSDA and LSDA+U approximations. The experimental spectrum consists of two maxima at about 0.9 eV and 4 eV above the Fermi level. The first narrow peak was identified as having f character, whereas the second broad peak was associated with 5d-6s states [625]. The LSDA places the empty 4f states right at the Fermi level which contradicts the experimental data (Fig. 3.18). The LSDA+U calculations place the maximum of the 14th f hole level well above the Fermi level around 0.7 eV. The 13th f hole level is partly occupied with its maximum DOS situated 0.025 eV above the Fermi level (Fig. 3.16). Due to a rather large experimental resolution of the BIS spectra ( $\sim 1 \text{ eV}$ ) [625] one experimentally observes essentially only a single BIS 4 f peak instead of two. Although, a shoulder can be discerned split off from the main peak [625]. The LSDA+U calculations gives the correct position both the 4f and 5d states (Fig. 3.18) within the experimental resolution.

**Optical spectra.** More precise information on the band positions may be obtained from optical and MO measurements. Although such measurements have much better resolution (the experimental resolution in optics is always in the meV range) in comparison with XPS and BIS, they produce complex functions containing information of both the initial and final states simultaneously (joint density of states) and are strongly influenced by the optical transition matrix elements. Besides, the MO spectra strongly depend of the spin and orbital polarization of initial and final states [7].

Figure 3.19 shows the calculated real and imaginary parts of the dielectric function,  $\varepsilon_{1xx}(\omega)$  and  $\varepsilon_{2xx}(\omega)$ , the optical reflectivity and imaginary part of the energy-loss function Im $[-1/\varepsilon(\omega)]$  compared with experimental data [628]. On the basis of the results of the LSDA+U band structure calculation, the observed optical reflectivity spectrum (Fig. 3.19) can be sorted into the respective interband transition groups: (1) metallic high reflectivity below  $\sim 1 \text{ eV}$ , (2) a steep edge between  $\sim 1$  and  $\sim 2.5 \text{ eV}$ , and (3) above the minimum at  $\sim 2.7 \text{ eV}$  some less pronounced structures with a broad maximum of R between 5 and 7 eV mostly caused by  $3p \rightarrow 5d$  interband transitions.

The predominant structure of the TmS as well as TmSe reflectivity spectra is the edge at 2 eV. This sudden drop is characteristic for metallic rare-earth chalcogenides and is due to a plasma oscillation interfering with interband excitations [628]. This plasma resonance causes the golden color of TmS crystals as it does for all metallic rare-earth sulfides. The energy of the conduction electron plasma resonance in the presence of the interband excitations is given by  $\varepsilon_{1xx}(\omega)=0$ . In the particular case of TmS this condition is fulfilled at  $\hbar\omega=2.15$ 



*Figure 3.19.* Calculated real and imaginary part of the diagonal dielectric function,  $\varepsilon_{1xx}$ ,  $\varepsilon_{2xx}$ , energy-loss function and the optical reflectivity R of TmS [623] treating 4f states in core (dashed line) and by the LSDA+U approximation (solid line) compared with experimental data (solid circles) [628].

eV and the maximum peak of the energy-loss spectrum in Fig. 3.19 is shifted only very little from this energy (by -0.05 eV) as a result of damping. The correct energy position of the plasma edge in TmS can be obtained only by taking into account  $5d \rightarrow 4f$  interband transitions. The calculations treating 4f electrons as a core electrons place the zero crossing energy of  $\varepsilon_{1xx}(\omega)$  at higher energies in comparison with the LSDA+U calculations and as a result give a wrong energy position for the plasma resonance (Fig. 3.19).

To search for possible optical  $5d \rightarrow 4f$  interband transitions the reflectivity of a TmS single crystal has been measured between 2 meV and 12 eV at room temperature and at 6 K (Ref. [625]). One should mentioned that the observation of an optical  $5d \rightarrow 4f$  transitions is quite rare, especially when the metal has a large carrier concentration as in the case of TmS with about one carrier per formula unit. The large amount of carriers effectively screen the optical transition as most of the light intensity gets reflected by the plasmons. The chances to observe the optical  $5d \rightarrow 4f$  transitions in a metal become only realistic when the energy of the optical transitions is very small since the intensity of the transition scales with  $\omega^{-2}$  [625]. Such a situation occurres in TmS where the partly occupied 13th f hole level is very close to the Fermi level with its maximum DOS situated 25 meV above the Fermi level (Fig. 3.16). Reflectivity measurements of TmS single crystals in the mid-infrared region reveal two lines near 53 and 90 meV [625]. The authors interpreted these features as optical transitions from the partly filled 5d conduction states near the Fermi level into the empty crystal field split 13th band f states (acoustic and optical phonon modes are situated at 13 and 37 meV respectively according to Raman scattering measurements [625]). Another less pronounced feature was observed in the reflectivity spectrum measured at 6 K around 0.9 eV. The insert of the Fig. 3.19 shows the unbroadened theoretically calculated optical



*Figure 3.20.* Calculated off-diagonal parts of the dielectric function  $\varepsilon_{xy}$  (in  $10^{29}$  s<sup>-2</sup>), Kerr rotation and Kerr ellipticity spectra (in degree) for TmS [623] treating the 4*f* states as a core electrons, LSDA and LSDA+*U* approximations compared with experimental data (circles) [629].

reflectivity in the 0 to 1 eV energy interval with two well pronounced minima at 0.11 and 0.9 eV. These features reflect the interband transitions from occupied 5d states to empty 13th f and 14th f hole levels situated at 0.025 and 0.7 eV respectively (Fig. 3.16). In real optical experiments such transitions are obscured by broadening from intraband Drude-like transitions, life-time effects and to a lesser extent the experimental distortion.



*Figure 3.21.* Calculated Kerr rotation and Kerr ellipticity spectra (in degree) for TmS in the LSDA+U approximation, and real and the imaginary parts of the function  $[\omega D(\omega)]^{-1}$  [623] compared with experimental data [629].

Fig. 3.20 shows the experimental [629]  $\theta_K(\omega)$  and  $\epsilon_K(\omega)$  MO **MO** spectra. Kerr spectra of TmS, as well as the spectra calculated with LSDA, LSDA+Uand with the 4f electrons in the core [623]. This picture clearly demonstrates that the better description is unambiguously given by the LSDA+U approach. The most prominent discrepancy in the LSDA spectra is the extra peaks between 0 and 2 eV caused by interband transitions involving the hybridized 4fstates, which in the LSDA approach exhibit a maximum resonance near  $E_F$ . In the LSDA+U approach, the occupied 4f state energies are shifted downward due to the on-site Coulomb interaction  $U_{eff}$ . As a result, the transitions involving the occupied 4f states do not take place at small photon energies, and the erroneous peak structures around 0 to 2 eV disappears from the Kerr spectra. The calculations in which the 4f electrons are treated as quasi-core are able to reproduce structure similar to the LSDA+U calculations, but, in wrong the positions. Besides, due to the lack of corresponding  $5d \rightarrow 4f$  interband transitions, the off-diagonal part of the optical conductivity  $\sigma_{2xy}$  is nearly zero, so that a very small Kerr rotation is obtained.

Off-diagonal optical conductivity of TmS shows very large values at low energies with a marked extremum in  $\sigma_{2xy}(\omega)$  near 0.5 eV and it is almost constant in the 2 to 4 eV energy interval (Fig. 3.20). As a result the shape of the Kerr ellipticity and Kerr rotation spectra in this compound are completely determined by a shape of the function  $[\omega D(\omega)]^{-1}$ .

The situation is clearly seen in Fig. 3.21 where we show the theoretically calculated Kerr rotation and ellipticity of TmS using the LSDA+U approximation [623] and the frequency dependence of real and imaginary parts of the

function  $[\omega D(\omega)]^{-1}$  multiplied by a constant to normalize the spectra. Obviously the shape of the Kerr spectra in TmS results mostly from the resonance structure of the function  $[\omega D(\omega)]^{-1}$ . Actually the first principles band structure calculations [623] confirm the idea already drawn by Feil and Haas in Ref. [410] on the basis of model calculations that the sharp Kerr effect in some magnetic metallic rare-earth compounds including TmS and TmSe is not due to the electronic interband transitions, but rather to the influence of a plasma resonance.

## TmSe

The simplest argument that TmS is trivalent, TmSe intermediate valent and TmTe divalent under normal conditions comes from comparing the lattice constants of rare-earth sulfides, selenides and tellurides as done by Bucher et al. [600]. The lanthanide contraction is the cause for the general trend in the curves and the standard divalent Sm, Eu and Yb ions with their larger ionic radius are the obvious deviations. TmTe lies on the divalent curve, TmS on the trivalent one and TmSe is intermediate and by linear interpolation between a hypothetical divalent and trivalent TmSe one obtains a valence of  $Tm^{2.75+}$ . Further evidence that TmSe is intermediate valence comes from x-ray and ultraviolet photoemission spectroscopy measurements [608, 612]. The photoemission study of TmSe [612] gives the mean valence value equal to 2.79 and 2.68 from study of the total yield spectra and off-resonance photoemission respectively, although the mean valence of the same sample obtained from magnetic susceptibility measurement is 2.53. We should mentioned that the total yield spectra reflect more bulk information than photoemission spectra and the values obtained from transport properties or magnetic susceptibility are mostly bulk and not surface sensitive [612].

The ground state of an intermediate valence compound is a quantum mechanical mixture of both the  $4f^n$  and the  $4f^{n-1}5d$  configuration on each rare earth ion. Such compounds need theoretical consideration beyond the mean field one-particle LSDA+U approximation due to possible configuration interaction between different 4f valence states. Although such interaction should be less in Tm compounds in comparison, for example, with mixed-valent Ce compounds due to contraction of the 4f wave function, it can lead to a spontaneous inter-configuration fluctuations (ICF), introduced first by Hirst [630]. As briefly discussed by Varma [631], at T=0, fluctuations could be either static or dynamic. In the static case the system is spatially "inhomogeneous" in the sense that at inequivalent sites different valence states are present. Examples among the rare earth compound are Eu<sub>3</sub>S<sub>4</sub> or Eu<sub>3</sub>O<sub>4</sub> [608]. Such static charge "fluctuations" have been known for a long time in the 3d-series; Fe<sub>3</sub>O<sub>4</sub>, magnetite, being a typical example (see Ref. [485] and references therein). In the dynamic case the system shows fast local fluctuations which give an intrinsic



*Figure 3.22.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for TmSe in ferromagnetic (FM) and antiferromagnetic (AFM) ordering [623].

width to the *f*-levels. At any given site 4*f* charge fluctuations between the two configurations occur on a time scale  $\tau_{ICF}$ , the so called *inconfiguration fluctuation time*. The system on time average is "homogeneous", i.e. all sites are equivalent. TmSe is known to be a homogeneous mixed-valence compound [608]. Experiments such as lattice constant and isomer shift measurements which probe the sample on a time scale much longer than  $\tau_{ICF}$  will see only one intermediate configuration, but experiments such as XPS or UPS measurements which takes place in a time much shorter than  $\tau_{ICF}$  (up to  $10^6-10^7$  times shorter [609]) will see the instantaneous picture of a mixture of the ions in the two valence states.

**Band structure.** The LSDA+U energy bands and total density of states of TmSe for  $U_{eff}$ =6 eV are shown in Fig. 3.22 both for the ferromagnetic and anti-ferromagnetic ordering for the Tm<sup>3+</sup> ions. The band structure calculations [623] gave for the fcc type-II antiferromagnetic phase lower total energy in comparison with fcc type-I phase. We have verified, however, that neither the Tm magnetic moment nor spectral properties depend strongly on the type of antiferromagnetic order. For example the difference in the magnetic mo-



*Figure 3.23.* Expanded view of the DOS of TmSe (solid line), TmS (dotted line), and TmSe with the lattice constant of TmS (dashed line) calculated in the LSDA+U approximation for ferromagnetic (FM) and anti-ferromagnetic (AFM) ordering [623].

ments is about 0.01  $\mu_B$  [623]. Therefore, we present only the results for the fcc type-II antiferromagnetic phase of TmSe. The electronic structure of TmSe for the Tm<sup>3+</sup> ions is very similar to the TmS one with twelve 4*f* bands fully occupied and hybridized with chalcogenide *p* states. The 14th *f* hole level is completely unoccupied and well above the Fermi level. A hole 13th *f* level is partly occupied and pinned at the Fermi level. The occupation number of the 13th *f* level is equal to 0.27 (valence 2.73+) in good agreement with estimations from the lattice constants (2.75+) as done by Bucher et al. [600] and from UPS measurements (2.79+ and 2.68+ from total yield and photoemission spectra respectively). [612]

Fig. 3.23 shows the expanded view of the total DOS of TmSe and TmS both in the ferromagnetic (FM) and anti-ferromagnetic (AFM) states [623]. An important feature of the FM electronic structure is a high DOS at the Fermi energy  $E_F$  in both TmS and TmSe. A large DOS at  $E_F$  signals an instability with respect to metamagnetic phase transitions. Indeed, total energy calculations show that the ground state for TmSe as well as for TmS is an anti-ferromagnetic ordering in agreement with experiment [603, 616]. Through the FM – AFM phase transition a pseudo gap at the Fermi level is opened in both TmS and TmSe (Fig. 3.23). The opening of such a pseudo gap may explain the increasing of the electrical resistivity below Néel temperature [616, 618, 619], as well as an enormous negative magnetoresistivity associated with the metamagnetic transition to the high-field aligned state and decreasing of the Hall coefficient in an external magnetic field [620].

The pinning of a partly occupied 13th f level is different in TmS and TmSe. In contrast to TmS, the Fermi level crosses the 13th f hole level in the vicinity of its DOS maximum in TmSe, both in the FM and the AFM states. The maximum DOS of the 13th f hole level is situated above the Fermi level, as close as 4 meV ( $\sim$  45 K) in the AFM ground state of TmSe. The energy position of the 13th f level is in a good agreement with low temperature far infrared optical measurements by Marabelli and Wachter [632]. According to their measurements the first interband transition appears at about 3 meV. We should mention here that when we speak about partial occupation of the 13th fhole level in TmS we mean that such an occupation is due to the hybridization effect between 5d and 4f energy states. The peak position of the 13th f hole level DOS in TmS is relatively far away from the Fermi level. A different situation occurs in TmSe where the Fermi level crosses the shoulder of the 13th f hole level DOS (see Fig. 3.23), hence the 13th f level is really pinned at the Fermi level. It is a typical situation for mixed-valent crystals.

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The Tm monohalcogenides offer the unique opportunity to follow the evolution of intermediate valence as a function of composition. The driving force is the change of lattice constant upon exchanging the anion. In order to separate the influence of the lattice constant from the influence of the ionic potential of the chalcogenide component on the electronic structure of TmX (X=S and Se), we present in Fig. 3.23 also the DOS of TmSe evaluated with the lattice constant of TmS [623]. The partial occupation of the 13th hole f level in this case is similar to the situation for TmS, although the energy positions of the maxima is not the same as in actual TmS. The mean valency of TmSe with the lattice constant of TmS is equal to 2.90+, very close to valency in actual TmS (2.88+). It can be considered as qualitative theoretical support of the conclusion derived in Ref. [622], that the application of pressure enhances the Tm<sup>3+</sup> state relative to Tm<sup>2+</sup> state in the TmSe.

In Fig. 3.24 the partial 4*f* DOS of the occupied part of the TmSe band structure is compared with XPS measurements [608] for two single crystals with different lattice constants. An off-stoichiometric violet TmSe single crystal, with lattice constant a=5.640 Å, contains almost entirely Tm<sup>3+</sup> ions [608]. The theory calculations using a starting configuration with zero occupation of 14th *f* and 13th *f* levels (Tm<sup>3+</sup> configuration) well describe this experimental XPS spectrum.

The XPS spectrum of TmSe with a=5.689 Å, has a sizable divalent signal between 0 and -3 eV binding energy. The middle panel of Fig. 3.24 shows the theoretically calculated 4f DOS of the Tm<sup>2+</sup>Se taking into account the multiplet structure of the  $4f^{12}$  final state. The right panel shows the experimental XPS spectrum for a=5.689 Å, in comparison with the sum of Tm<sup>3+</sup> and Tm<sup>2+</sup> 4f DOSs in the proportion of fifty-fifty. These results suggest that the valency of the sample with a=5.689 Å, is close to 2.5 as comes from the analysis of



*Figure 3.24.* The calculated  $\text{Tm}^{3+}$  (a),  $\text{Tm}^{2+}$  (b) and  $\text{Tm}^{3+}+\text{Tm}^{2+}$  4*f* (c) DOS of TmSe in LSDA+*U* approximations [623], taking into account the multiplet structure of the 4*f*<sup>12</sup> and 4*f*<sup>11</sup> final states. Comparison is made with the experimental XPS spectra from Ref. [608] measured for *a*=5.640 Å(a) and *a*=5.689 Å(b,c) lattice constants.

the DOSs. Of course it is difficult to make quantitative conclusions about the possible Tm 4 f configuration in TmSe from comparison of theoretically calculated 4 f DOS with XPS or UPS spectra. From such a comparison we can only derive an energy position of final-state multiplet structures from Tm<sup>3+</sup> and  $Tm^{2+}$  ions. The XPS and UPS spectra are strongly affected by the transition matrix elements which have been omitted in the consideration for simplicity. Besides, the relative intensities of  $Tm^{3+}$  and  $Tm^{2+}$  ion final-state multiplet structures depend on the excitation photon energy. This was shown in Ref. [612] where the intensity ratio between the trivalent and divalent components in Tm monochalcogenides changes significantly depending on resonance or off-resonance conditions. Finally, UPS and XPS spectroscopies are strongly surface sensitive methods. The escape depth of a photoelectron with kinetic energy of a kilovolt is about 15 Å. For the softer radiation typical for the UPS measurements (< 100 eV) the escape depth is only about 4 Å [607], hence only the surface layers are probed. A recent advance in our understanding of mixed-valent photoemeission comes from the recognition that surface spectra can be markedly different from that of the bulk. In particular the valence at the surface can be very different [607].

In the optical reflectivity measurements the depth of penetration is given by the inverse absorption coefficient and typically amounts to  $10^2$  to  $10^3$  Å. This means that the optical, as well as MO measurements are not so surface sensitive.

**Optical spectra.** Figure 3.25 shows the calculated diagonal part of the optical conductivity  $\sigma_{1xx}$  and the optical reflectivity of TmSe treating the 4*f* states as: (1) fully localized (4*f* in core); (2) itinerant (LSDA); and (3) partly localized (LSDA+*U*) in comparison with experimental data [628]. The calcu-



*Figure 3.25.* Calculated diagonal part of the optical conductivity  $\sigma_{1xx}$  and the optical reflectivity R of TmSe [623] treating the 4f states as: (1) fully localized (4f in core) (dashed line); (2) itinerant (LSDA) (dotted line); and (3) partly localized (LSDA+U) (solid line) compared with the experimental data [628] (open squares).

lations treating 4f electrons as core electrons place the zero crossing energy of  $\varepsilon_{1xx}(\omega)$  at higher energies in comparison with the LSDA+U calculations and as a result give a wrong energy position for the plasma resonance which determines a deep minimum in the optical reflectivity (Fig. 3.25). Due to the wrong position of 4f energy bands in the LSDA calculations this approximation is not able to produce the correct optical reflectivity in the infrared spectral region. Figure 3.25 clearly demonstrates that the better description of the optical reflectivity spectrum is given by the LSDA+U approach. The  $5d \rightarrow 4f$ interband transitions play an essential role in the fast decrease of the optical reflectivity in 0 to 0.5 eV energy interval.

**MO spectra.** Fig. 3.26 shows the experimental [582]  $\theta_K(\omega)$  and  $\epsilon_K(\omega)$ MO Kerr spectra of TmSe, as well as the spectra calculated with LSDA and LSDA+U [623]. The better description is unambiguously given by the LSDA+U approach. The most prominent discrepancy in the LSDA Kerr spectra is the extra peak at 0.5 eV which is caused by extra structure present in the dielectric tensor. Responsible are interband transitions involving the hybridized 4*f* states, which in the LSDA approach exhibit a maximum resonance near  $E_F$ . In the LSDA+U approach, the occupied 4*f* state energies are shifted downward due to the on-site Coulomb interaction  $U_{eff}$ . As a result, the transitions involving the occupied 4*f* states do not take place at small photon energies, and the erroneous peak structure around 0.5 eV disappears from Kerr spectra.



*Figure 3.26.* Calculated Kerr rotation and Kerr ellipticity spectra (in degrees) for TmSe in the LSDA (dashed line) and LSDA+*U* (full line) approximations [623] compared with experimental data (open squares) [582].

#### TmTe

Fig. 3.27 shows the energy band structure and total density of states of TmTe calculated in LSDA and LSDA+U approximations. Although TmTe is known as a magnetic semiconductor, LSDA calculations gave a metallic solution.

In contrast to LSDA, the LSDA+U calculations predicts a correct ground state of TmTe, namely, a magnetic semiconductor with direct energy gap of 0.86 eV at the  $\Gamma$  symmetry point and an indirect gap of 0.58 eV between the top of Tm 4f valence band at the  $\Gamma$  point and the bottom of Tm 5d conduction band at the X symmetry point. Theory produces a somewhat larger energy gap in comparison with the optical measurements of 0.35 eV [601]. Thirteen completely occupied Tm 4f energy bands located between 0.0 and -2.2 eV are hybridized with Te 5p states. The empty 14th f energy level is situated around  $\sim 5.8$  eV above the Fermi level hybridized with Tm 5d states (Fig. 3.27). In other words theory predicts the Tm atom in TmTe to be in divalent state.

There is no experimental measurements of the MO spectra for TmTe. The measurements have been performed only for the  $TmSe_{0.32}Te_{0.68}$  system [7].

The alloy system  $\text{TmSe}_{1-x}\text{Te}_x$  is one of the most important alloy systems in the field of intermediate valence since it keeps the important cation untouched while exhibiting intermediate-valent metals, intermediate-valent semiconductors, semiconductor-metal transitions, ferro- and antiferromagnets and a new ground state of condense matter, the excitonic insulator [602]. The study of the physical properties of the  $\text{TmSe}_{1-x}\text{Te}_x$  system offers an interesting possibility to go from integer divalent semiconducting TmTe(x=1) to intermediate



*Figure 3.27.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for TmTe [623].

valent metallic TmSe (x=0). The substitution of Te by smaller Se ions causes a reduction of the lattice constant. The reduction of the lattice spacing for the Tm ions due to the substitution is often termed *chemical pressure*. The system TmSe<sub>1-x</sub>Te<sub>x</sub> shows a *compositionally induced* semiconductor-metal transition [633]. For x > 0.4 the compounds are semiconducting and for x < 0.18 metallic. Both phases are separated by a miscibility gap. The substitution of Te by Se reduces the energy gap resulting in a decrease of the electrical resistivity and an increase of the electron concentration by about three orders of magnitude [633].

There are two major effects occurring in the process of substitution: reduction of the lattice constant and increasing of Tm valency. There is also a clear deviation from the Vegard-law (linearity between lattice constant and valence) line for divalent Tm with increasing substitution of Se ions. As for x in the range of 0 to 0.18 the Tm valency is within the 2.9 to 2.8 interval, and for  $0.4 \le x \le 1.0$  the valency is in the interval of 2.3 to 2.0.

The experimental measurements of MO spectra for  $TmSe_{0.32}Te_{0.68}$  have been presented in Ref. [7]. This particular compound has a lattice constant equal to 6.21 Åand a Tm valency of about 2.08+ [633]. The compound is a mixture of  $Tm^{2+}$  and  $Tm^{3+}$  ions. Fig. 3.28 shows the theoretically calculated Kerr rotation and Kerr ellipticity spectra of TmSe and TmTe compounds with



*Figure 3.28.* The experimental (open squares) Kerr rotation and Kerr ellipticity spectra (in degree) for  $TmSe_{0.32}Te_{0.68}$  [7] in comparison with LSDA+U calculated spectra for TmSe and TmTe with a proportion of 32 and 68 % respectively [623].

the intensity of the spectra scaled in the proportion of 0.32 and 0.68 respectively to make comparison with the experimental  $\text{TmSe}_{0.32}\text{Te}_{0.68}$  spectra. We used the lattice constant of 6.21 Å for both the TmSe and TmTe compounds. It can be seen from Fig. 3.28 that the deep negative minimum at 0.7 eV and positive peak at 1.2 eV in the Kerr rotation spectrum of  $\text{TmSe}_{0.32}\text{Te}_{0.68}$  are mostly determined by the divalent Tm ions and the rest of the fine structure of the Kerr spectrum is derived from interband transitions involved the Tm<sup>3+</sup> ions.

# 3.1.4 Sm monochalcogenides

The Sm monochalcogenides offer the interesting possibility to study the transition from semiconductor to the mixed valence (MV) state as a function of pressure. First, it is of great importance to characterize the semiconducting state.

The energy band structure of SmS presented in Figure 3.29 with the 4f electrons in the core can be subdivided into three regions separated by energy gaps. The bands in the lowest region around -11 eV have mostly S s character with some amount of Sm sp character mixed in. The next six energy bands are S p bands separated from the s bands by an energy gap of about 7 eV. The width of the S p band is about 3.2 eV. The unoccupied electronic states can be characterized as Sm 5d bands. The sharp peaks in the DOS calculated in the LSDA just below and above the Fermi energy are due to  $4f_{5/2}$  and  $4f_{7/2}$  states respectively (Fig. 3.29).



*Figure 3.29.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for SmS [634] treating the 4f states as: (1) fully localized (4f in core); (2) itinerant (LSDA); and (3) partly localized (LSDA+U).

The LSDA+U band structure calculations [634] have been started from a  $4f^6$  configuration for the Sm<sup>2+</sup> ion with six on-site 4f levels shifted downward by  $U_{eff}/2$  and eight levels shifted upwards by this amount. The energies of occupied  $4f_{5/2}$  and unoccupied  $4f_{7/2}$  levels are separated by approximately  $U_{eff}$ . The LSDA+U energy bands and total density of states of SmS for  $U_{eff}$ =6 eV are shown in Fig. 3.29. The Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure of SmS. For Sm<sup>2+</sup> ions six  $4f_{5/2}$  bands are fully occupied and situated in the gap between S p and Sm 5d states while the  $4f_{7/2}$  hole levels are completely unoccupied and well above the Fermi level hybridized with Sm 5d states which results in a non-magnetic ground state with the Sm ion in the divalent state. The theoretically calculated energy gap  $\Delta E$ =0.18 eV which is formed between Sm  $4f_{5/2}$  and Sm 5d states is in good



*Figure 3.30.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for SmSe and SmTe in LSDA+U approximation [634].



*Figure 3.31.* Comparison the calculated 4f DOS in LSDA and LSDA+U approximations [634] with the experimental XPS spectra from Ref. [635] taking into account the multiplet structure of the  $4f^5$  final state (see explanations in the text).

agreement with the experimentally estimated 0.15 eV derived from the activation energy [602].

The LSDA+U energy bands and total density of states of SmSe and SmTe for  $U_{eff}$ =6 eV are shown in Fig. 3.30. Their electronic structures are very similar to the SmS one with six Sm  $4f_{5/2}$  bands fully occupied and the  $4f_{7/2}$  hole bands completely unoccupied and well above the Fermi level hybridized with Sm 5d states. Theory gives energy gaps between Sm  $4f_{5/2}$  and 5d bands equal to 0.47, and 0.67 eV in SmSe, and SmTe, respectively. The corresponding experimental values are equal to 0.45 and 0.65 eV [602].



*Figure 3.32.* Calculated optical reflectivity R, real and imaginary parts of the diagonal dielectric function,  $\varepsilon_{1xx}$ ,  $\varepsilon_{2xx}$  of SmS [634] treating 4f states as (1) fully localized (4f in core) (dotted line), (2) itinerant (dashed line) and (3) partly localized (LSDA+U approximation) (solid line) compared with experimental data (open circles) [636].

Photoemission experiments, both x-ray (XPS) and ultraviolet (UPS), have been of central importance for understanding mixed-valence materials (see the review of the early work by Campagna et al. [608]). The partial 4f DOS of the occupied part of the SmS calculated in LSDA and LSDA+U approximations is compared with XPS measurements [635] in Fig. 3.31. The calculated 4fDOS has been broadened to account for lifetime effects and for experimental resolution. The Sm 4p states essentially do not contribute to the XPS spectra because of the low ionization cross section compared with that of the Sm 4fstates [624]. Hence, the measurements only indicate the f excitation energies relative to the Fermi level. The theoretically calculated 4f DOS cannot, of course, fully account for the multiplet splitting. Therefore Fig. 3.31 presents the 4f DOS's taking into account the multiplet structure of the  $4f^5$  final state. This multiplet structure consists of 3 terms <sup>6</sup>H, <sup>6</sup>F, and <sup>6</sup>P [635]. In Fig. 3.31 the XPS spectrum is modeled by a weighted sum of three 4f DOS curves. We aligned the centroid of the calculated occupied 4f DOS peak with the centroid of the atomic final state multiplet. Although, LSDA calculations produce almost the same picture as LSDA+U calculations in the case of SmS, for SmSe and SmTe the LSDA calculations place the  $4f_{5/2}$  energy bands too close to the Fermi level which leads to disagreement with measured XPS spectra (Fig. 3.31).

From the good agreement between theory and XPS measurements we may conclude that the LSDA+U calculations give an accurate position for the occupied 4f bands. The principal question is the energy position of the empty 4f states, which is usually answered by optical or BIS measurements.

In Fig. 3.32 we show the experimental [636] real and imaginary parts of the dielectric function,  $\varepsilon_{1xx}(\omega)$  and  $\varepsilon_{2xx}(\omega)$ , the optical reflectivity and optical conductivity  $\sigma_{1xx}(\omega)$  spectra, as well as the spectra calculated with LSDA,



*Figure 3.33.* Calculated optical reflectivity R, real and imaginary part of the diagonal dielectric function,  $\varepsilon_{1xx}$ ,  $\varepsilon_{2xx}$  of SmSe treating 4f states as (1) itinerant (dashed line) and (2) partly localized (LSDA+U approximation) (solid line) [634] compared with experimental data (open circles). [636]

LSDA+U and with the 4f electrons in the core. This picture clearly demonstrates that the better description is unambiguously given by the LSDA+U approach. As was mentioned above, the LSDA theory produces a metallic solution and, therefore, gives the wrong asymptotic behavior for the optical reflectivity and the dispersive part of the dielectric function  $\varepsilon_{1xx}$  as  $\omega \to 0$ . The most prominent discrepancy in the LSDA spectra is the extra peaks between 0 and 1.5 eV in the  $\varepsilon_{1xx}(\omega)$ ,  $\varepsilon_{2xx}(\omega)$  and optical conductivity  $\sigma_{1xx}(\omega)$  caused by interband transitions involving the occupied  $4f_{5/2}$  and unoccupied  $4f_{7/2}$  hybridized states. In the LSDA+U approach, the empty  $4f_{7/2}$  state energies are shifted upward due to the on-site Coulomb interaction  $U_{eff}$ . As a result, the transitions involving the unoccupied  $4f_{7/2}$  states do not take place at small photon energies, and the erroneous peak structures around 0 to 1.5 eV disappear from the optical spectra.

The calculations in which the 4f electrons are treated as quasi-core are able to reproduce correct asymptotic behavior for the optical reflectivity and the dispersive part of the dielectric function  $\varepsilon_{1xx}$  as  $\omega \to 0$  similar to the LSDA+Ucalculations, but, it fails in producing a peak at around 0.6 eV in the absorptive part of the dielectric function  $\varepsilon_{2xx}$  and optical conductivity spectra. This peak is mostly determined by the  $4f \to 5d$  interband transitions.

The LSDA+U theory also gives good agreement between calculated and measured optical spectra in the cases of SmSe (Fig. 3.33) and SmTe (not shown).

#### High pressure golden phase of SmS

The history of the Sm monochalcogenides as MV materials started at the beginning of the 1970's when Jayaraman *et al.* [637] and then Bucher *et al.* [638] discovered a pressure-induced semiconductor-metal transition and sug-



*Figure 3.34.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for SmS with the LSDA+*U* approximation for divalent and trivalent Sm atoms [634].

gested that the metallic state would be mixed valent. It was a surprise that SmS showed this transition occurring at the incredibly low pressure of 6.5 kbar. Starting the pressure above the phase transition and decreasing, a large hysteresis is observed and the MV state snaps back to a semiconductor state at 1.5 kbar. For SmSe and SmTe the pressure-induced valence transition is continuous and is completed at higher pressures, about 45 and 60 kbar, respectively [602].

By increasing external pressure and hence, decreasing the lattice constant, the widths of Sm 5d and 4f bands are increased. In addition, the crystal-field splitting of the 5d states  $e_g - t_{2g}$  in SmS is also increased. At a given pressure the 5d band overlaps with the  $4f_{5/2}$  states and the energy gap becomes zero (Fig. 3.34). It happens at a lattice constant around 5.70 Å [602]. Starting from the overlap of 4f and 5d states, 4f electrons will spill into the 5d band leaving a  $4f^5$  state behind. The ionic radius of Sm<sup>3+</sup> is about 15% less than the radius of Sm<sup>2+</sup>, so that simultaneously with more electrons in the 5d conduction band the lattice will shrink, thus further increasing the crystal-field splitting of the 5d states, resulting in an avalanche effect and a first-order valence transition. However, the valence transition does not go all the way to trivalency, but stops where the gain in electronic energy is compensated by an increase in lattice strain energy [602].

The LSDA+U energy bands and total density of states of SmS for Sm<sup>3+</sup> are shown in Fig. 3.34. There are five  $4f_{5/2}$  bands fully occupied and hybridized with the bottom of the S p states. The  $4f_{7/2}$  unoccupied states are well above the Fermi level. The initially empty 6th  $4f_{5/2}$  hole level became partly occupied and pinned at the Fermi level in the process of self-consistent relaxation with occupation number equal to 0.25 (valence 2.75+). It is a typical situation for mixed-valent crystals. We should mention here that partial occupation of the 6th  $4f_{5/2}$  hole level in SmS is due to the hybridization effect between 5d and 4f energy band states.

We can use two different representations in the construction of the LSDA+U method, namely,  $(j, m_j)$  and  $(l, m_l)$  representations. Most of rare earths and their compounds have a rather large 4f spin magnetic moment, therefore it is natural to use the  $(l, m_l)$  representation in the calculations of their electronic structure. In this case one chooses the projection of the orbital momentum onto the spin direction  $m_l$  for the occupied states. The SmS black phase as well as SmSe and SmTe have a non-magnetic ground state, therefore it was used in that case the  $(j, m_j)$  representation [634]. For fully occupied  $4f_{5/2}$  states the z projections of the total moment were equal to  $m_j = -5/2, -3/2, -1/2, 1/2, 3/2, \text{ and } 5/2$ .

The situation is not clear for golden SmS. It was used both of the representations for the calculation of the electronic structure of the golden high pressure phase of SmS. Fig. 3.34 presents the energy band structure of golden SmS in the  $(j, m_i)$  representation with  $m_i = -1/2$  for the hole state. Due to the existence of a hole in the  $4f_{5/2}$  shell the LSDA+U gives a so called low magnetic moment ground state with total magnetic moment equal to 0.240  $\mu_B$  (spin and orbital moments have opposite directions with values equal to -0.305 and 0.545  $\mu_B$ , respectively). The  $(l, m_l)$  representation gives a high spin magnetic moment ground state in SmS with total magnetic moment equal to 4.636  $\mu_B$ at each Sm<sup>3+</sup> site (spin and orbital moments have opposite directions with values equal to 5.501 and  $-0.865 \mu_B$ , respectively). We should mention however, that although our LSDA+U band structure calculations give always a nonzero samarium magnetic moment, in golden SmS all the efforts to find a magnetic superstructure in high pressure SmS using neutron experiments have remained unsuccessful. However, one cannot exclude either a weak magnetic component below the limit of the experimental sensitivity (samples for high pressure measurements are very tiny) or an incommensurate structure giving peaks at positions not searched in the neutron experiments. The evaluation of the magnetic ground state of golden SmS from first principles requires further investigation.

The pinning of a partly occupied 6th 4f level strongly depends on the lattice constant. The increasing of the valency with decreasing of the lattice constant which was found in our band structure calculations can be considered as qual-


*Figure 3.35.* Expanded view of the total DOS (in states/(unit cell eV)) of the high pressure golden phase of SmS in the LSDA+U approximation for low spin solution and a=5.826 Å [634].

itative theoretical support of the conclusion derived from various experimental measurements, [602] that the application of pressure enhances the Sm<sup>3+</sup> state relative to Sm<sup>2+</sup> state in SmS. The theoretically calculated samarium valency was found to be equal to 2.55+ and 2.86+ for high and low spin solutions respectively. The experimentally estimated one is about 2.6+ from spectroscopic methods and susceptibility measurements [639–641] and about 2.8+ from the Vegards-low analysis of lattice constant measurements [641].

Some experimental results indicate that the golden phase of SmS could be a narrow-gap semiconductor. Evidence for a gap comes from the activation behavior of the electrical resistivity and point contact measurements [602]. The estimations from the point-contact spectra shows a possible gap of about 6.4 meV [602]. On the other hand some experiments indicate that there may not be a gap but rather a pseudo gap, and the hybridization does not occur over whole Brillouin zone. Although the temperature dependence of the resistivity in the golden phase of SmS is semiconductor-like, the resistivity is increased only one order of magnitude with cooling from room temperature to several K's, whereas e.g. in  $SmB_6$  it is 5 orders of magnitude [602]. Direct optical measurements of mechanically polished (high pressure golden phase) SmS by Travaglini and Wachter [642] shows that, in contrast to SmB<sub>6</sub>, the reflectivity does not tend to a constant value for  $\omega \rightarrow 0$  but it seems to rise toward 100% as for a metal. Besides, there is a linear with  $T \gamma$  term in the specific heat presumably due to conduction electrons [643]. The LSDA+U band structure calculations of golden SmS [634] produce a pseudo gap at the Fermi level with a peak just above and a shoulder below the Fermi level with predominantly of f character. (Fig. 3.35). We should mention that when the density of states at  $E_F$  is small compared to the giant density of states of the f peaks, the resistivity may nevertheless appear activated over a certain temperature range as

experimentally observed, but for the lowest temperatures metallic conductivity should persist [642].

In conclusion we would like to point out that while the LSDA+U approach does a very good job in the treatment of correlation effects in SmS, SmSe, and SmTe at normal pressure, it is still unclear how well it performs in describing the mixed valence state in golden SmS in the pressure range from 6 to 20 kbar. On one hand, it was found the pinning of a partly occupied 6th 4f level at the Fermi level, which is the typical situation for mixed valence systems. On the other hand, LSDA+U calculations always produce a nonzero magnetic moment in the high pressure phase of SmS, although all attempts to find any sign of magnetic ordering in this system gave no positive results for the last 30 years. It is more likely that our LSDA+U calculations describe well the situation in the metallic phase of SmS at pressure  $P \ge 20$  kbar with trivalent samarium ions (see Fig. 3.35).

We should mention that the experimental situation in golden SmS differs from that in  $SmB_6$  in the sense that in the later system a new generation of samples of much better quality became available during recent years, and more reliable data about transport properties and infrared spectroscopy were obtained. In SmS we still use old experimental data and it is difficult to ascertain the full validity of measured gaps or pseudo gaps as well as other properties based on the experiments of the early 70s. The physical nature of the mixed valence state in golden SmS requires further investigation theoretically as well as experimentally.

# **3.1.5** $SmB_6$ and $YbB_{12}$

SmB<sub>6</sub> and YbB<sub>12</sub> are classical mixed valence (MV) narrow gap semiconductors. This class of materials is characterized by their electronic properties, which at high temperatures are associated with a set of independent localized (f) moments interacting with a sea of conduction electrons, while at low temperature the electronic properties resemble those of a narrow gap semiconductor. SmB<sub>6</sub> is the first compound in which the phenomena of MV was detected directly by x-ray absorption [644]. Despite more than 35 years of experimental and theoretical effort, many fundamental aspects of the microscopic description of the MV ground state and the nature of valence fluctuations is still under discussion [602, 645, 646]. The main problem is the origin of the MV ground state, which seems intimately connected with the gap formation. One question is whether Kondo insulating materials actually are true insulators at low temperatures or whether an intrinsic small conduction-electron carrier concentration is present [647]. Infrared absorption [648, 649], inelastic neutron scattering [650-653], optical conductivity [654], electron tunneling [655], and electrical transport [656-658] measurements all detect a small electronic gap  $\Delta$ =3–20 meV. However, the low-temperature transport properties of SmB<sub>6</sub> are

manifestly metallic, having a large but finite resistivity below  $\sim 4$  K [656–658]. There is considerable controversy whether these in-gap states are intrinsic and present in pristine SmB<sub>6</sub> [650–653, 659, 660], or extrinsic and dictated entirely by sample quality [656–658, 661, 662]. The size of the energy gap determined by different methods, varies considerably. For example, the value of the gap in SmB<sub>6</sub> is equal to 2.7 meV by tunneling spectroscopy [655], 5 meV from the temperature dependence of the electrical resistivity [656–658], and 16 meV by point-contact spectroscopy [663]. Direct measurements of the low-temperature dynamical conductivity and dielectric permitivity of single crystalline SmB<sub>6</sub> give evidence for a 19 meV energy gap and an additional narrow donor-type band lying only 3 meV below the bottom of the upper conduction band [664].

The average valence of Sm in the hexaboride was established to be 2.56 at room temperature, and to vary slightly with temperature by measurements of x-ray absorption [644, 665], lattice constant [666], x-ray photoemission [608] and Mössbauer isomer shift [667].

YbB<sub>12</sub> is thought to be the only known Kondo insulator among Yb compounds with a valence instability. It's physical properties observed near room temperature (metallic conductivity, localized magnetic moments) dramatically change when T decreases. At approximately 75 K, the paramagnetic susceptibility goes through a maximum, then decreases rapidly at lower temperatures [668–671]. A steep increase in the electrical resistivity is observed in the same temperature range [668–670]. This, together with the Schottky anomaly in the low-temperature electronic specific heat [669, 671] provides strong support to the opening of a gap in the electronic excitation spectrum [672]. Recent direct optical reflectivity measurements on single crystals of YbB<sub>12</sub> also show the opening of an energy gap upon cooling below 70K [673]. The gap development is coincident with a rapid decrease in the magnetic susceptibility, which shows that the gap opening has significant influence on magnetic properties of YbB<sub>12</sub>. The energy of the gap, determined by different methods, also varied considerably. Tunneling measurements indicate an energy gap of 200-300 meV [674], the transport gap is much smaller  $\Delta \sim 10$  meV [668–670], photoemission measurements reveal gaps of two energy scales [675]. A narrow gap  $\sim 10$  meV and a larger pseudo gap of  $\sim 100$  meV. Optical measurements give an energy gap of  $\sim 25$  meV at 20K [673]. It is not yet clear whether the insulating ground state in YbB12 should be ascribed to a "hybridization gap" as predicted in MV models, or reflects the formation of a Kondo singlet on each  $Yb^{3+}$  ion. More generally, the influence of the degree of valence mixing on the formation of the Kondo insulator state is not well documented. The Yb valency estimated from the Curie constant below room temperature yielded values of about 2.75–2.8 for polycrystals [668, 669], and 2.95 for a single crystal [670]. From the photoemission measurements [676], the valence was estimated to be  $v=2.86\pm0.06$ . X-ray photoelectron spectroscopy (XPS) measurements [677]

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yielded v=2.9, whereas the Yb  $L_3$  edge x-ray absorption spectrum measured in Ref. [668] was simply denoted "trivalent". Recent x-ray absorption and inelastic neutron scattering experiments [672] indicate that the Yb valence is close to 3+. On the other hand, the analysis of the magnetic susceptibility together with the Knight shift of YbB<sub>12</sub>, provided by Wachter [602], shows that the susceptibility is zero for  $T \rightarrow 0$ , in the absence of defects. This might be caused by a nonmagnetic ground state such as Yb<sup>2+</sup> 4f<sup>14</sup> or by a Kondo singlet.

The energy band structures of  $SmB_6$  and  $YbB_{12}$  have been calculated by Yanase and Harima [678] in the local spin density approximation and in Ref. [679] using the LSDA+U approximation.

#### SmB<sub>6</sub>

The compound  $SmB_6$  has the  $CaB_6$  type crystal structure with space group Pn3m (No 221) and lattice constant equal to 4.1333 Å. The structure of samarium hexaboride may be viewed as a CsCl-type lattice with the cesium replaced by samarium and the chlorine by a  $B_6$  octahedron. Figure 3.36 shows the energy band structure of  $SmB_6$  calculated within the LSDA and the LSDA+U approximations [679]. The energy band structure of  $SmB_6$  with the LSDA approximation can be subdivided into three regions separated by energy gaps. The bands in the lowest region around -14 to -16 eV (not shown) have mostly B 2s character with some amount of Sm sp character mixed in. The next group of energy bands are B 2p bands separated from the 2s bands by an energy gap of about 3 eV. The width of the B 2p band is about 8.8 eV. The Sm 5d bands are partly occupied. They are also separated from B 2p states by the energy gap of around 0.7 eV. The sharp peaks in the DOS calculated in the LSDA just below and above the Fermi energy are due to  $4f_{5/2}$  and  $4f_{7/2}$  states respectively (Fig. 3.36). They cross the Sm 5d bands and hybridize with them. There is a small direct energy gap at the Fermi level of around 23 meV.

The LSDA+U energy bands and total density of states (DOS) of SmB<sub>6</sub> for  $U_{eff}$ =7 eV are shown in Fig. 3.36. The Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure of SmB<sub>6</sub>. For Sm<sup>3+</sup> ions five  $4f_{5/2}$  bands are fully occupied and hybridized with the B 2p states. The  $4f_{7/2}$  unoccupied states are above the Fermi level at around 1 eV. A single  $4f_{5/2}$  level is fully unoccupied and situated at about 0.34 eV above the Fermi level.

The LSDA+U band structure calculations [679] have been started from a  $4f^6$  configuration for the Sm<sup>2+</sup> ion with six on-site 4f energies shifted downward by  $U_{eff}/2$  and eight levels shifted upwards by this amount. The energies of occupied  $4f_{5/2}$  and unoccupied  $4f_{7/2}$  levels are separated by approximately  $U_{eff}$  (Fig. 3.36). For Sm<sup>2+</sup> ions eight  $4f_{7/2}$  hole levels are completely unoccupied and well above the Fermi level and hybridized with Sm 5d states. The  $4f_{5/2}$  bands are situated in close vicinity of the Fermi level. They cross the



*Figure 3.36.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for  $SmB_6$  with LSDA and LSDA+U approximations [679].

bottom of Sm 5d band. Fig. 3.37 shows an expanded view of the LSDA+U energy band structure and total DOS for SmB<sub>6</sub> with Sm<sup>2+</sup> ions. There is a hybridization gap at the Fermi level  $\Delta E=27$  meV. Although the LSDA+U calculations [679] used a starting configuration with fully occupied  $4f_{5/2}$  bands, in the process of self-consistent relaxation one of the  $4f_{5/2}$  doubly degenerate bands becomes partly unoccupied and situated above the Fermi level around the X symmetry point (Fig. 3.37) due to Sm 5d - 4f hybridization. There is a small peak in the DOS above the Fermi level at around 0.03 eV with predominantly 4f character. This peak contains 0.02 4f holes. In other words, the LSDA+U calculations produce a semiconducting ground state in SmB<sub>6</sub> with noninteger Sm valency equal to 2.02+.

The XPS spectra for  $\text{SmB}_6$  indicate multiplet structure which can be identified with both  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  configurations being present. Fig. 3.38 shows



*Figure 3.37.* Expanded view of the energy band structure and total DOS (in states/(unit cell eV)) of SmB<sub>6</sub> for Sm<sup>2+</sup> ions calculated in LSDA+U approximations [679].



*Figure 3.38.* Comparison of the calculated 4f DOS of SmB<sub>6</sub> using LSDA+U approximation [679] with the experimental XPS spectra from Ref. [608] taking into account the multiplet structure of the  $4f^5$  and  $4f^4$  final states (see explanations in the text).

the SmB<sub>6</sub> XPS spectrum [608] in comparison with the occupied part of the partial LSDA+U 4f DOS calculated with a multiplet structure of the final states taken into account in the same way as for SmS in previous section. We show in Fig. 3.38 the final state multiplet structure presented in Ref. [608]. Sm<sup>2+</sup> (4 $f^5$  final state) has the multiplets <sup>6</sup>H, <sup>6</sup>F, and <sup>6</sup>P. Sm<sup>3+</sup> (4 $f^4$  final state) has the multiplets <sup>5</sup>I, <sup>5</sup>F, <sup>5</sup>G, and <sup>5</sup>D [608]. It is clear that the structures between 0.0 and -5.5 eV binding energy should be assigned to the final-state multiplet structure derived from six fully occupied 4f bands (Sm<sup>2+</sup>) and the structures between -5.5 and -13 eV are associated with the final state multiplet structure of the Sm<sup>3+</sup> ions. The agreement with the positions of the multiplet peaks indicates that the LSDA+U is giving reasonably correct average positions for the occupied 4f states.

Let us turn now to the optical properties of  $SmB_6$ . Experimental investigation of the reflectivity spectra of  $SmB_6$  was performed by Kierzek-Pecold [680] in a narrow energy range from 1 to 5.6 eV. After that, Travaglini and Wachter measured the reflectivity spectrum of  $SmB_6$  in the energy range from



*Figure 3.39.* Calculated diagonal part of the optical conductivity  $\sigma_{1xx}(\omega)$  of SmB<sub>6</sub> in the LSDA+U approximation [679] compared with the experimental measurements at 13K (open circles) [649].

1 meV to 12 eV at 300K and 4K for investigation of the energy-gap [654]. Kimura with coworkers measured the optical spectra of all single crystal rareearth hexaborides  $RB_6$  (R=La, Ce, Pr, Nd, Sm, Eu, Gd, Th, Dy, Ho, Yb, and Y) in the energy region from 1 meV to 40 eV at 300K and 13K [681, 682, 649, 683].

Fig. 3.39 shows with a logarithmic scale the calculated optical conductivity spectra of SmB<sub>6</sub> compared with experimental data measured at 13K [649]. Calculations were performed for both the divalent and trivalent phases of SmB<sub>6</sub>. The experimentally measured optical conductivity spectrum has two strong peaks at 0.12 and 0.5 eV and a steep rise at 3 eV (Fig. 3.39). As might be expected the experimental optical conductivity spectrum contains key features of both the divalent and trivalent theoretically calculated spectra. However, the three major peaks have different origins in the divalent and trivalent phases. A steep increase of optical conductivity starting at around 3 eV is mostly determined by B  $2p \rightarrow \text{Sm } 5d$  interband transitions around the X symmetry point in the divalent samarium compound. The same feature in the trivalent phase can be described as a combination of the B  $2p \rightarrow \text{Sm } 5d$  and  $\text{Sm } 5d \rightarrow \text{Sm } 4f$ interband transitions. These transitions also occur mostly around the X symmetry point (Fig. 3.36). The low energy peak at 0.12 eV in the divalent phase can be explained as interband transitions between occupied Sm d - f mixed states and unoccupied Sm 5d states near the X symmetry point. The same structure in the trivalent Sm phase is due to interband transitions among of hybridized Sm 5d bands along  $\Gamma$ -X,  $\Gamma$ -M, X-M, and X-R symmetry directions. This peak is shifted at around 0.1 eV toward smaller energies in comparison with the experimental measurements. The peak at 0.5 eV in the divalent phase

arises from interband transitions between occupied Sm d - f mixed states and unoccupied Sm 5d states near the X symmetry point and  $\Gamma$ -X and X–M symmetry directions. The same structure in the trivalent samarium phase is due to interband transitions between occupied Sm 5d states and the empty 6th 4f hole band along  $\Gamma$ -X,  $\Gamma$ -M, and X–M symmetry directions.

As we mentioned above, the XPS measurements cannot distinguish between an inhomogeneously mixed or a homogeneously mixed compound, i.e. whether Sm<sup>2+</sup> and Sm<sup>3+</sup> ions are integer valent and statically mixed or the charge between them just fluctuates slower then the time resolution of XPS. The experimental optical conductivity spectrum also can be considered as a mixture of both the divalent and trivalent spectra. From other experiments, SmB<sub>6</sub> is known to be a homogeneous mixed-valence semiconductor compound with a small energy gap [602]. Mössbauer isomer shift vs. temperature measurements for SmB<sub>6</sub> by Cohen et al. clearly show that above 700K and down to 4.2K the degree of valence mixing is a constant of around 2.56 [667]. The LSDA+U band structure calculations [679] produce a metallic state with trivalent samarium ions if we start the self-consistent procedure from Sm<sup>3+</sup>. On the other hand, if we used as starting configuration with fully occupied  $4f_{5/2}$ levels (Sm<sup>2+</sup>) we able to produce a correct semiconductor ground state for  $SmB_6$  with a small hybridization energy gap, and a theoretically calculated valency 2.02+. A comprehensive theory for the MV state is needed to provide a quantitative measure of the mixing between the two configurational states. The LSDA+U calculations are only able to provide specific details for the individual configurational states.

### YbB<sub>12</sub>

The compound YbB<sub>12</sub> has the UB<sub>12</sub> type crystal structure with space group Fm3m (No 225) and lattice constant equal to 7.464 Å. The crystal structure of YbB<sub>12</sub> can be understood as fcc NaCl type with the sodium replaced by ytterbium and the chlorine by a 12 B atoms.

Figure 3.40 shows the energy band structure of YbB<sub>12</sub> for all three approximations. The energy band structure of YbB<sub>12</sub> with 4f electrons in core can be subdivided into three regions. The bands in the lowest region around -15.5 to -10 eV have mostly B 2s character with some amount of Yb sp character mixed in. The next group of the energy bands are B 2p bands separated from the 2s bands by a small energy gap of about 0.4 eV. The width of the B 2p band is about 8 eV. The Yb 5d bands are partly occupied and cross the Fermi energy. They slightly overlap with B 2p states. The sharp peaks in the DOS calculated in the LSDA just below the Fermi energy are due to Yb  $4f_{5/2}$  and  $4f_{7/2}$  states (Fig. 3.40). They cross Yb 5d bands and hybridize with them. There is a small direct energy gap of about 65 meV at the Fermi level.



*Figure 3.40.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for YbB<sub>12</sub> with LSDA and LSDA+U approximations [679].

The LSDA+U energy bands and total density of states of YbB<sub>12</sub> for  $U_{eff}$ =8 eV are shown in Fig. 3.40. The self-consistent calculations start from the  $4f^{14}$  configuration for the Yb<sup>2+</sup> ion, where all 14 on-site 4f energies are shifted downwards by  $U_{eff}/2$ , and from the  $4f^{13}$  configuration for the Yb<sup>3+</sup> ion with 13 on-site 4f energies are shifted downwards by  $U_{eff}/2$ , and energies are shifted downwards by  $U_{eff}/2$  and one level shifted

upwards by this amount. The energies of occupied and unoccupied Yb<sup>3+</sup> f bands are separated by approximately  $U_{eff}$ .

For divalent Yb ions all 14 4f bands are fully occupied and situated closely below the bottom of Yb d band. They are split due to spin-orbit coupling by  $\Delta \varepsilon_{so}$ =1.4 eV. There is a small hybridization gap at the Fermi level. In other words, the calculations indicate a nonmagnetic semiconducting ground state in YbB<sub>12</sub> for Yb atoms in the divalent state. The theoretically calculated energy gap  $\Delta E$ =65 meV is formed between Yb 4f<sub>7/2</sub> and Yb 5d states. The experimentally estimated energy gap is about 10 meV from the activation energy [668–670], 25 meV from optical measurements [673] and 200-300 meV from tunneling experiments [674].

For the trivalent Yb ion, thirteen 4f electron bands are well below the Fermi energy and hybridized with the B 2p states (Fig. 3.40). The 14th 4f unoccupied hole level is above the Fermi level at around 1.5 eV. We should mention that such an electronic structure is appropriate for the development of the Kondo scenario.

The partial 4*f* DOS of the occupied part of YbB<sub>12</sub> calculated in the LSDA+*U* approximation [679] is compared with ultraviolet photoelectron spectra (UPS) [675] in Fig. 3.41. The double peak structure at 0.1 and 1.5 eV binding energy reflects the spin-orbit doublet of the Yb<sup>2+</sup> density of states. The corresponding spin-orbit doublet for the Yb<sup>3+</sup> DOS is situated at -6.0 and -7.6 eV (Fig. 3.41(a)).

Theoretically calculated 4f DOS cannot, of course, fully account for the multiplet splitting. Therefore we present in Fig. 3.41(b) the 4f DOS's taking into account the multiplet structure [684] in the same way as for SmB<sub>6</sub>. Yb<sup>2+</sup> has the configuration  $4f^{14}$ . The n - 1 state  $4f^{13}$  has one hole in 4f shell and cannot reproduce the experimentally measured four peak structure in the XPS. One would expect only the spin orbit doublet, and the 4 peak structure is almost certainly due to surface effects.

After consideration of the band structure and UPS spectra of YbB<sub>12</sub> we turn to the optical spectra. Recently optical reflectivity experiments have been conducted by Okamura *et al.* on single crystals of YbB<sub>12</sub> [673]. They found that upon cooling below 70K, a strong suppression of the optical conductivity  $\sigma(\omega)$  was seen in the far-infrared region, reflecting the opening of an energy gap of ~25 meV. A narrow, asymmetric peak was observed at ~40 meV in  $\sigma(\omega)$ , which was attributed to optical transitions between the Yb 4*f*-derived states across the gap [673]. They also measured the optical spectra of single crystalline LuB<sub>12</sub> as a reference material.

Fig. 3.42 shows with a logarithmic scale the calculated optical reflectivity  $R(\omega)$  and diagonal part of optical conductivity  $\sigma_{1xx}(\omega)$  spectra of LuB<sub>12</sub> compared with the experimental data [673]. To incorporate the intraband contribution to the optical conductivity tensor it was used the phenomenological



*Figure 3.41.* (a) The calculated 4f DOS of YbB<sub>12</sub> for Yb<sup>2+</sup> and Yb<sup>3+</sup> configurations [679] in comparison with the experimental UPS spectra from Ref. [675]; (b) the calculated 4f DOS of YbB<sub>12</sub> taking into account the multiplet structure of the  $4f^{13}$  and  $4f^{12}$  final states (see explanation in the text) in comparison with the experimental UPS spectra from Ref. [675].

Drude model [389] with intraband Drude relaxation time  $\gamma_D = 0.3$  eV. A sharp onset is seen in the LuB<sub>12</sub> reflectivity spectrum  $R(\omega)$  near 1.6 eV, which can be identified as the plasma edge  $(\omega_p)$  due to a metallic response of free carriers. The peak structures above  $\omega_p$  are due to interband transitions between electronic states far apart from  $E_F$ . Figure 3.42 clearly shows the important role of intraband transitions in formation of the optical conductivity spectrum in LuB<sub>12</sub>.

Fig. 3.43 shows the calculated optical reflectivity spectra of YbB<sub>12</sub> [679] compared with experimental data measured at 290K [673]. Calculations were performed for both the divalent and trivalent phases of YbB<sub>12</sub>. The intraband optical transitions in Drude form with inverse intraband Drude relaxation time  $\gamma_D = 0.1$  eV have been also included.

The optical reflectivity spectrum of YbB<sub>12</sub> measured at 290K has a metallic character, very similar to LuB<sub>12</sub>  $R(\omega)$  with the same plasma edge at 1.6 eV. The two spectra are almost identical for the energy interval above  $\omega_p$ . Below  $\omega_p$ , in contrast, the spectra are strictly different for the two compounds. In LuB<sub>12</sub>,  $R(\omega)$  is nearly flat and  $\sigma(\omega)$  shows a sharp rise, which is typical of a good metal, while in YbB<sub>12</sub> there is a broad dip in  $R(\omega)$  giving rise to a prominent peak at 0.25 eV in  $\sigma(\omega)$ . As can be seen from Fig. 3.43 a broad dip in  $R(\omega)$  comes from YbB<sub>12</sub> with divalent Yb ions. The LSDA+U calculations produce the reflectivity spectrum in YbB<sub>12</sub> with trivalent ytterbium ions very similar to the LuB<sub>12</sub> spectrum. The experimentally measured optical reflectivity spectrum of YbB<sub>12</sub> can be considered as a mixture of two spectra coming



*Figure 3.42.* Calculated optical reflectivity  $R(\omega)$  and diagonal part of the optical conductivity  $\sigma_{1xx}(\omega)$ , of LuB<sub>12</sub> in the LSDA approximation [679]: dashed line without and solid line with Drude term compared with the experimental data (open circles) [673]. Above ~1 eV the dashed and solid lines coincide.



*Figure 3.43.* The experimental optical reflectivity spectrum  $R(\omega)$  of YbB<sub>12</sub> (open circles) measured at 290K (Ref. [673]) in comparison with theoretical calculations in the LSDA+U approximation [679]: dotted line for Yb<sup>3+</sup>, dashed line for Yb<sup>2+</sup> ions, and solid line for R=  $0.2*R^{2+} + 0.8*R^{3+}$ .

from di- and trivalent ytterbium ions. Good agreement between theory and experiment can be reached if one uses the sum of the optical reflectivity spectrum consisting of 20% ytterbium divalent and 80% ytterbium trivalent spectra (Fig. 3.43).

The experimental investigations of the temperature dependence of the optical spectra of  $YbB_{12}$  presented in Ref. [673] show that as the temperature is



*Figure 3.44.* Calculated diagonal part of the optical conductivity  $\sigma_{1xx}$ , of YbB<sub>12</sub> in the LSDA+U approximation [679] for Yb<sup>2+</sup> ion (full line) and Yb<sup>3+</sup> ion (dashed line) compared with the experimental data (open circles) [673].

lowered from 290K to 78K, there is no drastic change in the optical conductivity spectrum. The IR peak becomes slightly enhanced and blue-shifted. At 78K the spectra are still metallic. However, at 20K the spectral weight below ~40 meV in  $\sigma(\omega)$  is strongly depleted and the spectrum becomes typical of a semiconductor with an energy gap of around 25 meV. The reflectivity spectrum at 20K is also typical of a semiconductor having the asymptotic value at  $\omega \rightarrow 0$  of 0.83. The gap development coincides with the rapid decrease of the magnetic susceptibility in exactly the same temperature range [673].

Fig. 3.44 shows the calculated diagonal part of optical conductivity  $\sigma_{1xx}(\omega)$ spectra of  $YbB_{12}$  compared with experimental data [673]. Calculations were performed for both the divalent and trivalent phases of YbB<sub>12</sub>. The experimentally measured optical conductivity spectrum in the 0 to 0.6 eV energy interval has two peaks at 0.05 and 0.25 eV (Fig. 3.44). The experimental optical conductivity spectrum of YbB12 contains key features of both the divalent and trivalent theoretically calculated spectra. The low energy peak at 0.05 eV in the optical conductivity spectrum originates from trivalent phase and can be explained as interband transitions between occupied and unoccupied Sm 5dstates along  $\Gamma$ -X and X-W symmetry directions (Fig. 3.40). The prominent peak in  $\sigma_{1xx}(\omega)$  spectrum at around 0.4 eV (the corresponding experimental peak situated at 0.25 eV) is mostly derived from the interband transitions between occupied Yb 4 f bands and empty Yb 5d bands of divalent phase in the vicinity of the W symmetry point as well as along the X-W symmetry direction (Fig. 3.40). The theoretically calculated  $\sigma_{1xx}(\omega)$  spectrum in divalent phase is shifted toward higher energies due to the larger theoretically calculated energy gap (65 meV) in comparison with the experimental one (25 meV).



*Figure 3.45.* Calculated off-diagonal part of the optical conductivity  $\omega \sigma_{2xy}$  (in  $10^{20} \text{ s}^{-2}$ ), imaginary part of  $[\omega D]^{-1}$  and complex polar Kerr effect (in degrees) of YbB<sub>12</sub> in the LSDA+U approximation for Yb<sup>2+</sup> ion.

After consideration of the bandstructure and optical properties we turn to the magneto-optical spectra. The  $YbB_{12}$  with Yb ions in divalent state has a nonmagnetic ground state with Kerr rotation and eliptisity equal to zero. On the other hand, the compound with  $Yb^{3+}$  ions has spin and orbital magnetic moments equal to 1.042 and 3.048  $\mu_B$ , respectively [679]. Figure 3.45 shows a complex polar Kerr effect of  $YbB_{12}$  in the LSDA+U approximation with  $Yb^{3+}$  ions. Theory predicts rather large Kerr rotation spectrum up to  $13^{\circ}$ . To analyse the nature of Kerr rotation we present in Fig. 3.45 the imaginary part of the energy-loss function  $\text{Im}[-1/\varepsilon(\omega)]$  as well as the separate contributions to the Kerr rotation spectrum from both the numerator, i.e.,  $\sigma_{xy}(\omega)$  and the denominator,  $D(\omega) \equiv \sigma_{xx}(1 + \frac{4\pi i}{\omega}\sigma_{xx})^{1/2}$ , which factor together to give the Kerr angle of  $YbB_{12}$ . As we mentioned above, the predominant structure of the YbB<sub>12</sub> reflectivity spectra is the edge at 1.5 eV. This sudden drop is due to a plasma oscillation interfering with interband excitations. The existence of a very narrow and strong plasmon peak at 1.5 eV (see the left panel of Fig. 3.45) leads to strong resonance structure in the inverce denominator  $\text{Im}[\omega D]^{-1}$  (Fig. 3.45) at the same energy. On the other hand, the value of the off-diagonal optical conductivity  $\sigma_{2xu}(\omega)$  is rather samll at this particular energy. Therefore the large Kerr rotation at 1,5 eV results mostly due to a deep resonance structure of the denominator.

In conclusion we would like to point out that the LSDA+U method which combines LSDA with a basically static, i.e., Hartree-Fock-like, mean-field approximation for a multi-band Anderson lattice model does not contain true many-body physics. However, this method can be considered as the first step towards a better description of strongly correlated electron systems. The LSDA+U method gave a correct insulating ground state solution for Sm monochalcogenides at ambient pressure. This method provides the correct energy positions of 4f energy bands and gives a reasonable description of the optical properties in SmX (X=S, Se, Te), SmB<sub>6</sub> and YbB<sub>12</sub>. However, the paramagnetic phase of high pressure SmS golden phase as well as the formation of the MV state in SmB<sub>6</sub> and YbB<sub>12</sub> clearly requires a treatment that goes beyond a static mean-field approximation and includes dynamical effects, *e.g.*, the frequency dependence of the self-energy.

# **3.1.6** Yb compounds

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### YbMCu<sub>4</sub> (M=Cu, Ag, Au, Pd, and In)

The YbMCu<sub>4</sub> (M=Cu, Ag, Au, Pd and In) compounds crystallize in the cubic AuBe<sub>5</sub>-type (C15b) structure and preserve the Yb ion in its trivalent state with total angular momentum J=7/2 [685, 686]. These systems have been investigated extensively because of their rich variety of phenomena at low temperature. In particular, YbAgCu<sub>4</sub> is known to show a typical dense Kondo behaviour [686, 687], in which localized moments of  $Yb^{3+}$  (4 $f^{13}$ ) at high temperatures are gradually screened through the hybridization with the conduction electrons, resulting in the enhanced Pauli paramagnetic state down to very low temperatures. A moderately large electronic specific heat coefficient has also been reported as  $\gamma = 245 \text{ mJ/mol K}^2$  [688]. Recently prepared by a high-pressure technique YbCu<sub>5</sub> phase with C15b structure also shows Kondolattice formation [689] with an even larger electronic specific heat coefficient  $\gamma = 550 \text{ mJ/mol K}^2$ . Furthermore, the temperature dependence of magnetic susceptibility [686] and magnetic part of specific heat [687] in these systems are well described by the Bethe-ansatz solution of the Coglin-Schrieffer model [690]. No any magnetic ordering was found in both compounds down to 2.0 K [689, 691]. On the other hand, the Kondo effect is not dominant in YbAuCu<sub>4</sub> and YbPdCu<sub>4</sub>, and long range magnetic ordering is observed at 0.6 and 0.8 K, respectively [686, 692]. Finally, YbInCu<sub>4</sub> has attracted much attention because it is the only known stoichiometric compound that undergoes a first-order isostructural valence transition at ambient pressure [685, 693-697]. At high temperature Yb appears to be essentially trivalent, displaying Curie-Waiss susceptibility with a paramagnetic moment near free ion value of 4.5  $\mu_B$ . At the first-order valence transition at  $T_v = 42$  K the Yb valence is reduced to approximately 2.8+ (as estimated by x-ray-absorption and lattice constant measurements [693–695, 698]), with a consequent increase in lattice volume of 0.5% and a reduction in magnetic susceptibility and spin-disorder scattering [696]. High-resolution neutron powder-diffraction studies confirm that the first-order transition is an isostructural one, with YbInCu<sub>4</sub> retaining its C15b structure at all temperatures [699, 700]. Such an "isomorphic" valence transition is fundamentally similar to the  $\alpha \rightarrow \gamma$  transition in cerium [701], which rises the question whether both transitions have a common origin.

Energy band structure for YbInCu<sub>4</sub> together with LuInCu<sub>4</sub> have been presented in Ref. [702] using the self-consistent augmented plane wave method with the local spin density approximation. In LuInCu<sub>4</sub>, the calculations show that this compound is a compensated semimetal with small carrier density. LSDA produces for YbInCu<sub>4</sub> the energy band structure with fully occupied 4f bands located in the vicinity of the Fermi level. In other words, LSDA gives a divalent state for Yb ion in the contradiction to the experimental data, according to which at high temperature Yb appears to be essentially trivalent and after the phase transition at  $T_v = 42$  K the Yb valence is reduced to approximately 2.8+ [693-695, 698]. The calculations of the electronic structure of YbMCu<sub>4</sub> (M=Ag, Au, Pd) in Ref.s [703, 704] in LSDA using full-potential linearised APW method also produce the band structure with 4 f states situated below the Fermi level at  $\sim 0.5$  eV. Direct measurements of the electronic structure of YbMCu<sub>4</sub> (M=Ag, Au, Pd) compounds using x-ray photoemission and bremsstrahlung isochromat spectroscopies suggested that the valence of Yb in this compounds is close to 3+ with occupied 4f states situated between -12to -5 eV and unoccupied hole state just above and close to the Fermi level [705]. The application of LSDA calculations to the YbXCu<sub>4</sub> is inappropriate. because of the correlated nature of 4f electrons in these compounds. LSDA gave wrong energy position for 4 f energy bands and predicted divalent ground state for Yb ion in these compounds in contrast to the experimental data.

A detailed experimental and theoretical study of the electronic structure and optical properties of YbMCu<sub>4</sub> (M=Cu, Ag, Au, Pd, and In) compounds and LuInCu<sub>4</sub> as reference material has been done in Ref. [706]. The energy band structure of the compounds calculated within the *ab initio* approach which takes strong correlations into account. This is achieved by applying a local spin-density approximation to the density functional theory supplemented by a Hubbard U term (LSDA+U).

 $RMCu_4$  (R=Yb, Lu; M=Cu, Ag, Au, Pd, In) compounds are isostructural to MgSnCu<sub>4</sub>, which has a face-centred cubic (fcc) lattice with six atoms per unit cell. The space group is F43m (No. 216) with R at the 4c positions, M at the 4a positions, and Cu at the 16e positions.

The LSDA fully relativistic spin-polarized energy band structure and total density of states (DOS) of LuInCu<sub>4</sub>, are shown in Fig. 3.46. These results well agree with previous band-structure calculations by Takegahara and Kasuya [702]. The calculated energy band structure shows that LuInCu<sub>4</sub> is a compensated semimetal with small carrier density in agreement with electrical resistivity and Hall effect measurements [707]. The bands in the lowest region of the occupied part of the band structure of LuInCu<sub>4</sub> between -9.5 and -7 eV have mostly In *s* character with some amount of Cu and Lu *sp* character mixed in. The highest region can be characterized as a bonding combination of Cu *d* and In *p* states. Cu *d* bands are completely occupied and situated below



*Figure 3.46.* LSDA self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of LuInCu<sub>4</sub> [706].



*Figure 3.47.* Comparison between the experimental (dots) and calculated optical reflectivity  $R(\omega)$ , real part  $\varepsilon_1(\omega)$  and imaginary part  $\varepsilon_2(\omega)$  of the dielectric function of LuInCu<sub>4</sub> calculated within LSDA (solid line) [706].

the Fermi level at -4 to -1.5 eV. Lu *d* states are almost empty and situated above the Fermi level.

In Fig. 3.47 we compare the calculated complex dielectric function  $\varepsilon(\omega)$  and the reflectivity  $R(\omega)$  with experiment. As can be seen, theory in LSDA and experiment agree very well. Above 3 eV theory gives a slightly larger reflectivity in comparison with experimental measurements. One of the possible reasons for this is a non-ideal sample surface, its roughness could reduce the optical reflectivity above 3 eV.

The LSDA total DOS of YbInCu<sub>4</sub> is shown in Fig. 3.48. The energy band structure of YbInCu<sub>4</sub> is very similar to the LuInCu<sub>4</sub> one. The bands in the lowest region have mostly In *s* character with some amount of Cu and Yb *s* character mixed in. Cu *d* bans are completely occupied and situated below the Fermi level between -4 and -1.5 eV. The large narrow peak close to the Fermi energy is formed by Yb 4*f* states. Unoccupied 5*d* bands of Yb are separated from the 4*f* states by a quasigap, a characteristic and important feature of the



Figure 3.48. LSDA total DOS of YbInCu<sub>4</sub> in states/(unit cell eV) [706]



*Figure 3.49.* LSDA+U self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of YbInCu<sub>4</sub> [706] ( $U_{eff}$ =6 eV).

YbInCu<sub>4</sub> compound. The position of the LSDA 4f states close to the Fermi energy is, on the other hand, in contradiction to the findings of XPS and BIS experiments [705].

The spin-polarized fully relativistic LMTO LSDA+U band structure calculations has been started from the  $4f^{13}$  configuration for Yb<sup>3+</sup> ion with 13 on-site 4f energies shifted downwards by  $U_{eff}/2$  and one level shifted upwards by this amount. From total energy calculations it was found that the Yb<sup>3+</sup> ground state corresponds to the projection of the orbital momentum onto the spin direction equal to  $m_l$ =+3 in accordance with all three Hund's rules. The energies of occupied and unoccupied Yb<sup>3+</sup> f bands are separated by approximately  $U_{eff}$ .

The LSDA+U energy bands and total density of states of YbInCu<sub>4</sub> for  $U_{eff}$ =6 eV are shown in Fig. 3.49. For the trivalent Yb ion, thirteen 4f electron bands are well below the Fermi level in the energy range between -6 and

-8 eV. They are split due to spin-orbit coupling  $\Delta \epsilon_{so}$ =1.2 eV and separated from a 4f hole state by the correlation energy  $U_{eff}$ . The unoccupied 14th f hole level, which, through the Coulomb interaction is initially placed above  $E_F$ , is pulled on  $E_F$  during the process of self-consistent relaxation. A fundamental aspect of this observation is that the pinning of the 14th f level at  $E_F$ to be a genetic property of YbInCu<sub>4</sub> compound: It happens irrespective of the precise value of  $U_{eff}$ . The insensitiveness of this feature of the  $U_{eff}$  value, furthermore, can be understood as reflecting the large bandwidth of the In pband with a low DOS and existing of a quasigap just above the Fermi level. The 4f hole level should become partially occupied to achieve the required number of electrons within the Fermi sphere. Due to a small phase space for hybridization and small Yb 4f – In p orbital overlap, the DOS peak of the hole band is as narrow as 0.02 eV. It is now clear why the usual Kondo lattice scenario is inappropriate for this compound. For a Kondo resonance to develop both the occupied and empty 4f-states must be sufficiently far away from the Fermi level. Quite opposite to this situation the (almost) empty level is pinned to the Fermi energy. Since the upper 4f level is only partly occupied, YbInCu<sub>4</sub> is calculated to be an intermediate valent compound in agreement with the experimental data [685, 693-697].

After the consideration of the above band structure properties we turn to the optical spectra. In Fig. 3.50 we show the LSDA and LSDA+U calculated and experimental optical spectra of YbInCu<sub>4</sub>. The best agreement between theory and the experiment was found to be when we used the LSDA+U approximation. The most prominent discrepancy in the LSDA spectra is the shifting of the prominent peak in the optical conductivity and imaginary part of dielectric function  $\varepsilon_2(\omega)$  towards larger photon energies. This peak situated at ~ 1.2 eV in the experimentally measured optical spectra is mostly due to In  $p \rightarrow$ Yb d interband transitions. These transitions take part between occupied and empty energy bands along L-W, X-W, and  $\Gamma$ -K symmetry directions and also in some inner parts of the Brillouin zone. Although 4f states do not participate to the optical interband transitions in the energy interval from 0 to 5 eV (due to a large binding energy of occupied 4f states and extremal narrowness of partly occupied the 14th f hole level, they affect the optical spectra indirectly through changing of the ionicity of the Yb ion. LSDA produces the energy band structure of YbInCu<sub>4</sub> with fully occupied 4f bands for divalent Yb ions (Fig. 3.48). The Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure of YbInCu<sub>4</sub>. Thirteen 4f occupied energy bands are well below the Fermi energy and the 14th f hole level is partly occupied and pinned at the Fermi level. Therefore the ionicity of the Yb ion in the LSDA+U calculations is close to 3+. On the other hand, the 4f-electron density is closer to the nucleus than that of the 4s-, p- and d-electrons. Hence, the increasing of the Yb ionicity (decreasing the number of 4f electrons in the close vicinity of



*Figure 3.50.* Comparison between the experimental (dots) optical conductivity  $\sigma(\omega)$  (in 10<sup>14</sup> s<sup>-1</sup>), reflectivity R, real part  $\varepsilon_1(\omega)$  and imaginary part  $\varepsilon_2(\omega)$  of the dielectric function of YbInCu<sub>4</sub> calculated within LSDA and LSDA+U approximations (solid line) [706].

the nuclear) in the LSDA+U calculations leads to narrowing of Yb d energy bands due to decreasing of nucleus screening. Therefore empty Yb d states in the LSDA+U calculations shift downwards decreasing the In  $p \rightarrow$  Yb d interband energies and the prominent peak shifts to smaller energies in remarkable agreement with the experimental measurements (Fig. 3.50).

The measurements of the optical spectra of YbInCu<sub>4</sub> in Ref. [708, 709] show that its optical response abruptly changes at the phase transition temperature (Fig. 3.51), whereas no distortion of the crystal structure occurs. The major effect of such a phenomenon is also due to the changing of the Yb ionicity. As estimated by x-ray-absorption and lattice constant measurements [693–695, 698] at the first-order valence transition at  $T_v = 42$  K the Yb valence is reduced to approximately 2.8. In order to investigate the influence of the valence reduction of Yb ion the self-consistent LSDA+U calculations of the energy band structure and optical spectra of YbInCu<sub>4</sub> have been performed using starting configuration of unoccupied 14th f hole level equal to 0.9 and 0.8 [706]. Such a "virtual crystal approximation" [710] leads to the energy band structure with wider Yb d energy bands due to increasing of the nuclear screening by 4f electrons. The optical spectra, therefore, are shifted towards higher photon energies with good agreement with the experimental measurements (Fig. 3.51).



*Figure 3.51.* Comparison between the experimental optical spectra of YbInCu<sub>4</sub> measured below (10 K) and above (50 K) phase transition and calculated spectra for different occupation numbers of the hole 4f state in the LSDA+U approximation [706].

The LSDA+U calculations show that the decreasing of Yb ionicity is accompanied by essential decreasing of the density of states at the Fermi level, which is equal to 17.0, 11.5, and 10.8 states/(unit cell eV) for Yb<sup>3+</sup>, Yb<sup>2.9+</sup>, and Yb<sup>2.8+</sup> respectively. This aspect reflects the fact that the ground state of YbInCu<sub>4</sub> has the Yb valence less than 3+. We should mention here that for



*Figure 3.52.* LSDA+U self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of YbAgCu<sub>4</sub> [706] ( $U_{eff}$ =6 eV).



*Figure 3.53.* LSDA+U self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of YbCu<sub>5</sub> [706] ( $U_{eff}$ =6 eV).

the Yb<sup>3+</sup> configuration we mean the starting configuration with zero occupation of 14th *f* level. In the process of self-consistent relaxation initially empty hole 14th *f* level become partly occupied due to pinning at the Fermi level with occupation number equal to 0.14 (valence v=2.86). Using the Yb<sup>2.9+</sup> configuration as initial configuration it was achieved after the self-consistent calculations an occupation number equal to 0.24. These results are in a good agreement with x-ray absorption measurements at the Yb  $L_{III}$  edge which gave  $v(L_{III})=2.9$  and 2.8 above and below  $T_v$ , respectively [693–695].

The total DOS at the Fermi level, resulting essentially from the 4*f* hole states, yields for  $U_{eff}$ =6 eV band structure contribution to the Sommerfeld constant of  $\gamma = \pi^2 k_B^2 N_A N(\epsilon_F)/3 = 40, 27$ , and 25.4 mJ mol<sup>-1</sup> K<sup>-2</sup> for Yb<sup>3+</sup>, Yb<sup>2.9+</sup>, and Yb<sup>2.8+</sup> respectively in good agreement with specific heat measurements [693–695]. These measurements gave  $\gamma = 22.3$  mJ mol<sup>-1</sup> K<sup>-2</sup> at low temperatures below the phase transition. The specific heat is also abruptly increased at the phase transition temperature  $T_v$ = 42 K [693–695].

As an example, we show the LSDA+U energy bands of YbAgCu<sub>4</sub> and YbCu<sub>5</sub> for  $U_{eff}$ =6 eV in Fig.s 3.52 and 3.53. The energy band structure of YbAgCu<sub>4</sub> as well as YbCu<sub>5</sub> compound is similar to YbInCu<sub>4</sub> one (Fig. 3.49). For the trivalent Yb ion, thirteen 4f electron bands are well below the Fermi level in the energy range between -4.5 and -7 eV slightly shifted upwards in comparison with YbInCu<sub>4</sub>. They are split due to spin-orbit coupling  $\Delta \epsilon_{so}$ =1.5 eV and separated from the 4f hole state by the correlation energy  $U_{eff}$ . The position of occupied 4f bands in YbAgCu<sub>4</sub> is in good agreement with x-ray photoemission measurements. According to the XPS measurements the multiplet structure of the  $4f^{12}$  final states on Yb<sup>3+</sup> sites is situated between -5and -12 eV [705]. The most significant difference between the electronic structures of YbAgCu<sub>4</sub> and YbInCu<sub>4</sub> compounds is in the position of the 14th f hole level. In the case of YbInCu<sub>4</sub> upper 4f level is partly occupied and pinned at the Fermi level due to the existence of a quasigap in the density of states just above the Fermi level (Fig. 3.49). In the YbAgCu<sub>4</sub> occupied 4 f states shifted upward, a similar guasigap situated at 1.5 eV above the Fermi energy (Fig. 3.52), therefore a hole level in  $YbAgCu_4$  is completely empty and situated sufficiently far from the Fermi level. Such a situation is appropriate for the developing of the Kondo lattice scenario in this compound. The hole level has a similar position in YbCu<sub>5</sub>, YbPdCu<sub>4</sub> and YbAuCu<sub>4</sub> compounds. YbCu<sub>5</sub> is really a typical dense Kondo system with an electronic specific heat coefficient  $\gamma = 550 \text{ mJ/mol K}^2$  (Ref. [689]), although, the Kondo effect is not dominant in YbAuCu<sub>4</sub> and YbPdCu<sub>4</sub>, where a long range magnetic ordering is observed at 0.6 and 0.8 K, respectively [686]. The different ground states observed in YbMCu<sub>4</sub> (M=Cu, Ag, Au, and Pd) compounds result from the competition between three interactions: the crystal field interaction, the magnetic intersite Ruderman-Kittel-Kasuya-Yosida interaction, and the intrasite Kondo effect. The evaluation of ground states of the compounds from first principles requires further investigation.

In Fig.s 3.54, 3.55 and 3.56 we show the LSDA+U calculated and experimentally measured optical spectra of YbAgCu<sub>4</sub>, YbPdCu<sub>4</sub> and YbAuCu<sub>4</sub>. The agreement between the theory and the experiment is quite good.

### Yb<sub>4</sub>As<sub>3</sub> and related compounds

The rare-earth pnictides Yb<sub>4</sub>X<sub>3</sub> (X=P, As, Sb, Bi) exhibit unusual physical properties [711–718]. The high-temperature phases of these compounds have the cubic anti-Th<sub>3</sub>P<sub>4</sub> structure with space group I4 $\bar{3}$ d. The Yb-ions occupy the P-sites with Wyckoff positions 12a,  $\bar{4}$ ..., *x*=0.069, and the X-ions occupy the Th-sites with special Wyckoff positions 16c, .3., fixed by symmetry [719]. All Yb-atoms are aligned on four families of chains oriented along the four diagonals of the cubic unit cell [720]. All four ytterbium pnictides have anomalously large lattice constants (*a*=8.56, 8.788, 9.322, and 9.573 Å for X=P, As, Sb, and



*Figure 3.54.* Comparison between the experimental (dots) and LSDA+U calculated (solid line) optical spectra of YbAgCu<sub>4</sub> [706].



*Figure 3.55.* Comparison between the experimental (dots) and LSDA+U calculated (solid line) optical spectra of YbPdCu<sub>4</sub> [706].



*Figure 3.56.* Comparison between the experimental (dots) and LSDA+U calculated (solid line) optical spectra of YbAuCu<sub>4</sub> [706].

Bi, respectively) [711, 712]. Because the pnictide ion is trivalent, three of the four Yb ions have a filled 4f shell (valency 2+) while one ion is in a  $4f^{13}$  (valency 3+) configuration. When all Yb sites are equivalent, the hole in the 4f shell is moving between different Yb ions and the system is a mixed valent

metal. Its average Yb-valence Z = 2.25 is rather close to the observed one  $(Z_{exp} = 2.20)$ , obtained from Mössbauer experiments [713].

The most interesting material is Yb<sub>4</sub>As<sub>3</sub>. At about  $T_s$ =300 K it undergoes a weak first-order phase transition with a trigonal distortion. This transformation was clearly established by susceptibility measurements [711], Mössbauer spectra [713], polarised neutron diffraction [721], and elastic constant measurements [722]. At the structural transformation, the crystal shrinks in a volume-conserving way along one of the four Yb-chain directions ( $\langle 111 \rangle$ , say). The resulting trigonal unit cell with the trigonal angle  $\alpha$ =90.8° has the short chain along its main diagonal. The centered triginal space group is now R3c with two inequivalent Yb sites at Wyckoff positions 2a, 3., and two further inequivalent Yb sites at Wyckoff positions 6b, 1, as well as two inequivalent As sites at Wyckoff positions 6b, 1. The distortion is accompanied by charge ordering with  $Yb^{3+}$  ions occupying the short chains [718]. So the 4f electronic state of Yb<sub>4</sub>As<sub>3</sub> changes from a valence fluctuating state in the cubic phase to a charge-ordered state  $Yb^{3+}Yb_{3}^{2+}As_{3}^{3-}$  in the trigonal phase, although the charge ordering is not complete [713, 721]. The  $Yb^{2+}$  ions have a closed 4fshell with no spin magnetic moment. The Yb<sup>3+</sup> ions have the  $4f^{13}$  configuration with spin magnetic moment equal to one. Inelastic neutron scattering experiments on Yb<sub>4</sub>As<sub>3</sub> revealed the existence of low-energy excitations that are characteristic of a one-dimensional anti-ferromagnetic coupling at low temperatures [721].

Below 100 K, Yb<sub>4</sub>As<sub>3</sub> exhibits heavy fermion behaviour: the resistivity shows a  $T^2$  behaviour ascribed to electron-electron interaction involving the heavy quasi-particle band, the Sommerfeld coefficient  $\gamma$  of the electronic specific heat  $C_{el}$  has a relatively high value of about 200 mJ mol<sup>-1</sup> K<sup>-2</sup>, and the extrapolated magnetic susceptibility at 0 K has a rather large value  $\chi(0) \simeq$  $3 \times 10^{-2}$  emu/mol (Ref. [711]). The Sommerfeld-Wilson ratio is found to be of the order of unity, indicating Fermi-liquid behaviour. Below 2 K and for moderate applied magnetic fields (> 2 T), the "high field" magnetic susceptibility of Yb<sub>4</sub>As<sub>3</sub> drops considerably as compared to the low field value [723]. There is also a rapid decrease observed in the specific heat at an applied field of about 1 T [714], both observations indicating the destruction of the heavy electron behaviour.

The Hall coefficient  $R_H$  of Yb<sub>4</sub>As<sub>3</sub>, extrapolated to T = 0, is equal to  $7 \times 10^{18}$  cm<sup>-3</sup> (see Ref. [711]). It would correspond to a carrier concentration of about 0.001 per formula unit if only one type of carriers was present.

The pressure effects on transport properties of Yb<sub>4</sub>As<sub>3</sub> were investigated by Okunuki *et al.* [724] and by Mori *et al.* [725]. A clear increase of the carrier concentration is observed with increasing pressure which leads to a rapid decrease of the resistivity  $\rho$ . The maximum in the temperature dependence of both,  $\rho$  and  $R_H$  also decreases with pressure. However, the inverse Hall mobility, i.e., the resistivity divided by the Hall coefficient, is found to increase with increasing temperature without any anomaly in the low temperature phase even under high pressure. This demonstrates that the mobility is not affected by pressure.

The effect of doping on physical properties of Yb<sub>4</sub>As<sub>3</sub> has been investigated by means of substitution of As with P [726, 712] or with Sb [727]. According to the temperature dependence of the Hall constant and of the resistivity, the Yb<sub>4</sub>(P<sub>x</sub>As<sub>1-x</sub>)<sub>3</sub> system becomes semiconducting for higher concentration of phosphorus. However, the specific heat and magnetic susceptibility are almost the same as those of pure Yb<sub>4</sub>As<sub>3</sub>. The temperature dependences of the magnetic susceptibility and the specific heat of pure Yb<sub>4</sub>P<sub>3</sub> exhibit almost the same behaviour as those of Yb<sub>4</sub>As<sub>3</sub> below the charge ordering temperature  $T_s$ , but above  $T_s$  the susceptibility is about two times larger, indicating an increase of the fraction of Yb<sup>3+</sup> ions in the high temperature phase. The  $\gamma$ -value is also large, about 250 mJ mol<sup>-1</sup> K<sup>-2</sup>, and the behaviour of Yb<sub>4</sub>P<sub>3</sub> in an external magnetic field is very similar to that of Yb<sub>4</sub>As<sub>3</sub>.

The temperature dependence of the Hall coefficient and the electrical resistivity in the Yb<sub>4</sub>(As<sub>1-x</sub>Sb<sub>x</sub>)<sub>3</sub> system shows [727] that with increasing concentration of Sb the number of carriers increases. From x = 0 to x = 0.12, the heavy fermion behaviour is little affected by the increase of the carrier concentration. In Yb<sub>4</sub>(As<sub>0.71</sub>Sb<sub>0.29</sub>), however, no clear evidence of charge ordering is observed any more, and in pure Yb<sub>4</sub>Sb<sub>3</sub> there is no evidence of the ordered state, and a proper  $\gamma$  value of about 40 mJ mol<sup>-1</sup> K<sup>-2</sup> corresponding to the valence fluctuation state is observed.

It was also revealed that  $Yb_4As_3$  shows a strong sample dependence of the transport properties [728, 729].

Summarizing all the experimental data, we can conclude that there is a strong dependence of the transport properties of  $Yb_4As_3$  on doping, pressure and sample preparation but the specific heat and magnetic susceptibility do not change very much. This observation suggests that  $Yb_4As_3$  is not an ordinary heavy fermion system. The latter are usually interpreted within the context of a Kondo lattice model: The heavy quasiparticle bands are thought to originate from Kondo resonance states at the Fermi level which evolve into coherent band states below a characteristic temperature. However this mechanism leads to a similar behaviour of the specific heat coefficient  $\gamma$  and the carrier number as functions of doping. As explained above the opposite behaviour is observed which is a strong argument against the Kondo scenario in this class of compounds.

The electronic structure of  $Yb_4As_3$  has been investigated experimentally by means of photoemission [730], x-ray bremsstrahlung isochromat spectroscopy (BIS) [731], optical properties [732–734]. The optical measurements [732, 733] show a strong temperature dependence of the optical reflectivity in the

far infra-red energy region below 10 meV. The plasma frequency  $\omega_p$  derived from optical measurements [734] is very small. It varies from 0.08 eV for 10 K to 0.14 eV for 70 K indicating again an extremely small carrier number. Photo-electron spectroscopy in the x-ray and ultraviolet ranges (XPS and UPS) provide information on the energy position of Yb<sup>2+</sup> and Yb<sup>3+</sup> 4*f* states in charge ordered Yb<sub>4</sub>As<sub>3</sub>. Structures in UPS and XPS spectra with binding energy between 0 and 4 eV were identified [730] to be the spin-orbit doublet of the 4*f*<sup>13</sup> final states and the structures between 6 and 13 eV to be the multiplet structures of the 4*f*<sup>12</sup> final states. The low temperature photoemission also does not show any evidence for Kondo resonance states close to the Fermi level, confirming the exclusion of the Kondo scenario for Yb<sub>4</sub>As<sub>3</sub>.

Energy band structure calculations for anti-Th<sub>3</sub>P<sub>4</sub> type rare-earth pnictides were performed for La<sub>4</sub>Sb<sub>3</sub> and La<sub>4</sub>Bi<sub>3</sub> [735], and later on for Yb<sub>4</sub>As<sub>3</sub> [736]. The calculations of Ref. [736] were done by means of the self-consistent augmented plane wave method on the basis of the local density approximation and for the cubic  $I4\bar{3}d$  crystal structure. The calculations were able to reproduce the main features of BIS, originating from the Yb 5d states, but failed to reproduce the correct position of the f-band due to the strongly correlated nature of the 4f electrons in Yb<sub>4</sub>As<sub>3</sub>. The calculations obtain the 4f bands at the Fermi level. From the band structure results for the cubic phase it was conjectured that Yb<sub>4</sub>As<sub>3</sub> should be an insulator in the charge-ordered phase. A non-spin-polarized LDA band structure calculations of Yb<sub>4</sub>As<sub>3</sub> and LuYb<sub>3</sub>As<sub>3</sub> in both, the cubic and trigonal crystal structures were reported [678]. The calculations were carried out using the linearized APW method with scalar relativistic effects being included for all electrons, and the spin-orbit interaction was included for valence electrons by a second variational procedure. It was found for a hypothetical LuYb<sub>3</sub>As<sub>3</sub> system that the top of the As p band and the bottom of the Lu d band cross the Fermi energy  $E_F$ . The 4f states are fully occupied due to the 3+ valency of the Lu ion, and are positioned close to  $E_F$ . The cyclotron mass of the largest hole Fermi surface was calculated to be 0.7  $m_0$ .

Two approaches have been proposed to explain the properties of  $Yb_4As_3$ . One is based on a one-electron picture and was applied by Ochiai *et al.* [711] in form of a four-band model and by Kasuya [737] in form of a two-band model. A characteristic feature of this approach is a hole band of As 4p states and an Yb 4f-band with a high density of states near the Fermi level. The second approach treats the 4f electrons as being strongly correlated [738–740]. Charge ordering of the Yb<sup>3+</sup> ions and the associated structural phase transition are a consequence of reducing the sum of the Coulomb repulsion and exchange to a minimum and are described by a band Jahn-Teller effect of correlated electrons. The observed heavy-fermion behaviour is ascribed to spin-like excitations in the Yb<sup>3+</sup> chains.



Figure 3.57. LSDA total DOS of Yb<sub>4</sub>As<sub>3</sub> [741] (in states per cell and eV).

This two approaches have been combined in Ref. [741] by studying the electronic structure and the physical properties of  $Yb_4As_3$  in the trigonal low temperature R3c phase within an *ab initio* band-structure approach which takes strong correlations into account. This aws achieved by applying a local spin density approximation to the density functional theory supplemented by a Hubbard *U* term (LSDA+*U*). The electronic structure of the related compounds Yb<sub>4</sub>X<sub>3</sub> (X=P, Sb, Bi, and P<sub>0.5</sub>As<sub>0.5</sub>) was also considered.

The LSDA total DOS of  $Yb_4As_3$  is shown in Fig. 3.57. These results agree well with previous band structure calculations by Takegahara and Kaneta [736] and by Harima [678]. The occupied part of the valence band can be subdivided into three regions separated by energy gaps. The bands in the lowest region have mostly As *s* character with some amount of Yb *s* character mixed in. The next group of bands is formed by As *p* states with little admixture of Yb *p* and *d* states. The large narrow peak close to the Fermi energy is formed by Yb 4*f* states. Unoccupied 5*d* bands of Yb are separated from the 4*f* states by an energy gap, a characteristic and important feature of the ytterbium pnictides. The position of the LSDA 4*f* states close to the Fermi energy is, on the other hand, in contradiction to the findings of XPS and UPS experiments [730].

The SPR LMTO LSDA+U band structure calculations in Ref. [741] were started from the  $4f^{14}$  configuration for three Yb<sup>2+</sup> ions, where all 14 on-site 4fenergies are shifted downwards by  $U_{eff}^{(2+)}/2$ , and from the  $4f^{13}$  configuration for one Yb<sup>3+</sup> ion with 13 on-site 4f energies shifted downwards by  $U_{eff}^{(3+)}/2$ and one level shifted upwards by this amount. From total energy calculations we found that the Yb<sup>3+</sup> ground state corresponds to the projection of the orbital momentum onto the spin direction equal to  $m_l$ =+3 in accordance with all three Hund's rules. The energies of occupied and unoccupied Yb<sup>3+</sup> f bands are



*Figure 3.58.* Self-consistent LSDA+U energy band structure and total DOS (per unit cell and eV) of Yb<sub>4</sub>As<sub>3</sub> [741].  $(U_{eff}^{(2+)} = 5.3 \text{ eV}, U_{eff}^{(3+)} = 8.8 \text{ eV})$ 

separated by approximately  $U_{eff}^{(3+)}$ . We emphasize, however, that the 4f states are not treated as completely localized. They may hybridize, and together with all other states their energy positions relax to self-consistency.

Usually the Hubbard-like  $U_{eff}$  is estimated by comparing the theoretically calculated energy positions of f bands with XPS and UPS measurements. In our particular case we have two types of Yb ions with different occupation numbers of their 4f shell. Obviously, the effective repulsion of 4f electrons  $U_{eff}$  depends on the number of holes in the 4f shell or the ionicity of the Yb ion [742], and it should increase with increasing ionicity. From photoemission measurements  $U_{eff}$  is found to be in the range of 5–7 eV for different Yb compounds [742]. It can also be calculated from atomic Dirac-Hartree-Fock (DHF) calculations [742], from Green-function impurity calculations [139] and from band structure calculations in super-cell approximation [138]. The DHF calculation gives  $U_{eff} \approx 5.3$  eV and our calculated value of  $U_{eff}$  is rongly depends on theoretical approximations and we prefer to treat the value of  $U_{eff}$  as a parameter and try to specify it from comparison of the calculated physical properties of Yb<sub>4</sub>As<sub>3</sub> with experiments.

The LSDA+U energy bands of AF Yb<sub>4</sub>As<sub>3</sub> for  $U_{eff}^{(2+)}$ =5.3 eV and  $U_{eff}^{(3+)}$ =8.8 eV are shown in Fig. 3.58. For three divalent Yb ions the 4f bands are fully occupied and hybridize with As p states in the energy range between -0.5 and -2.5 eV. They are split due to spin-orbit coupling by  $\Delta \epsilon_{so}$ =1.40 eV. For the trivalent Yb ion, thirteen 4f electron bands per ion are well below the Fermi level and separated from a 4f hole state by the correlation energy  $U_{eff}^{(3+)}$ . One 4f hole band per Yb<sup>3+</sup> ion, doubly degenerate due to AF ordering, appears

closely below the top of the As p band. Since the As p band is separated from the Yb 5d band by an ordinary band gap, the Fermi level must be pinned at the bottom of the 4f hole band. This feature in combination with the small mass of the As p electrons close to the top of the p band appears to be a clue feature for the physics of the ytterbium pnictides. Due to the very small phase space for hybridization and the very small Yb 4f – As p orbital overlap, the DOS peak of the hole band is as narrow as 0.007 eV right above the Fermi level. It is now clear why the usual Kondo lattice scenario is inappropriate for these pnictide compounds. For a Kondo resonance to develop both the occupied and empty 4f-states must be sufficiently far away from the Fermi level. Quite opposite to this situation the (almost) empty level is pinned slightly above the Fermi energy. But due to the very small phase space for hybridization around the  $\Gamma$ -point one still has an almost stable moment of the nearly integer occupation of the f-shell.

Since the 4f binding energy of the Yb<sup>2+</sup> ions is larger than 0.5 eV and hence larger than the Yb 4f – As p orbital hybridization energy both in experiment and in the calculated band structure, the 4f shell of the Yb<sup>2+</sup> ions has been treated as a core shell in the following detailed numerical analysis. It has been checked that this simplification does not affect the issue. Therefore we are left with a charge balance between Yb 4f states of the Yb<sup>3+</sup> ions and pnictide p states only. Any charge transfer between these states causes a change in the Hartree potential which is governed by the *bare Coulomb integral U<sub>f</sub>* of the 4f state being as large as 30 eV. Thus, an artificial shift via tuning  $U_{eff}^{(3+)}$  of the hole f level by 3 eV, say, (corresponding to a change of  $U_{eff}^{(3+)}$  itself by 6 eV) will completely be compensated by a charge transfer as small as 0.1 electron charge. For this reason the 4f hole level, to which the Fermi level is pinned, is itself very rigidly pinned close to the top of the pnictide p band.

In Fig. 3.59 the band structure in the vicinity of the Fermi level is shown for  $U_{eff}^{(3+)}$ =9.6 eV. It corresponds to a ground state with a hole pocket around the  $\Gamma$ -point (k=0) holding 0.0058 As p holes per formula unit. For chosen values  $U_{eff}^{(3+)}$ =5.3, 7.0, 9.6, and 9.8 eV the obtained hole numbers are 0.0717, 0.0225, 0.0058, and 0.0005, respectively. Only for  $U_{eff}^{(3+)} \ge 10$  eV the As pband would be filled and the Fermi level would lie in a gap between this band and the f hole state. This *generic* feature is obtained independent of whether the filled f shell of the Yb<sup>2+</sup> ions is treated as core or as valence, whether AF of ferromagnetic order is assumed on the Yb<sup>3+</sup> chains, or whether spin-orbit coupling is taken into account or not, all the involved energies being small compared to the unscreened  $U_f$ . Fig. 3.60 shows the obtained partial DOS close to the Fermi level for a number of cases.

The carrier density in  $Yb_4As_3$  at low temperature is extremely low, for which the following findings give evidence: (1) a large value of the resistivity



*Figure 3.59.* Self-consistent LSDA+U energy band structure of Yb<sub>4</sub>As<sub>3</sub> along the high-symmetry directions and for energies close to the Fermi level [741]. (Here,  $U_{eff}^{(3+)}$ =9.6 eV, and the f shell of the Yb<sup>2+</sup> ions is treated as a core shell.)

up to 10 m $\Omega$  [711], (2) a very low plasma frequency obtained from optical reflectivity [734], (3) a large value of the Hall coefficient [711] which corresponds to about 0.001 holes per Yb<sup>3+</sup> ion, assuming the single carrier model. Yb<sub>4</sub>As<sub>3</sub> is a compensated semimetal, so the number of As *p* holes exactly equals the number of excess Yb 4*f* electrons in the partially filled 4*f* hole level. However, the mobility of heavy 4*f* electrons is assumed to be negligible in comparison with the mobility of As *p* electrons [711]. So the transport properties of Yb<sub>4</sub>As<sub>3</sub> are mostly determined by the number of As *p* holes.

In the analysis of Ref. [741], a carrier number of 0.001 per formula unit would result from a  $U_{eff}^{(3+)}$  value between 9.6 and 9.8 eV which would not be in contradiction to photoemission.

The small mass at the top of the pnictide *p*-band results in a very low *p*-DOS of 0.015 states per eV, atom and spin, at the *f* hole level for  $U_{eff}^{(3+)}=9.6$  eV. That means that there are very few *p*-band states to broaden the *f* level by hybridization. The width of the hole state equals to about 0.007 eV (80 K) and decreases with increasing  $U_{eff}^{(3+)}$ . The total DOS at the Fermi level, resulting essentially from the 4*f* hole states, yields for  $U_{eff}^{(3+)}=9.6$  eV a large band structure contribution to the Sommerfeld constant of  $\gamma = \pi^2 k_B^2 N_A N(\epsilon_F)/3 = 40$  mJ mol<sup>-1</sup> K<sup>-2</sup>. The calculated  $\gamma$  is substantial, yet it corresponds only to the experimental value in a sufficiently strong magnetic field which suppresses magnetic moment fluctuations [714]. Since Yb<sub>4</sub>P<sub>3</sub>, although a semiconductor, has an even larger value of the Sommerfeld constant than Yb<sub>4</sub>As<sub>3</sub>, a large



*Figure 3.60.* Yb 4*f* partial DOS and As 4*p* partial DOS of Yb<sub>4</sub>As<sub>3</sub> on an expanded energy scale around the Fermi level (dashed vertical line) for various values of  $U_{eff}^{(3+)}$ . The left ordinate scale is for the *f* DOS and the right one for the *p* DOS [741].

part of  $\gamma$  must be due to fluctuations of the magnetic moments in charge ordered  $\langle 111 \rangle$  chains. Beyond LSDA+U, further many-body interactions need to be invoked to account for the full Sommerfeld constant of the specific heat [738, 743].

In Fig. 3.61 we compare the calculated complex dielectric function  $\varepsilon(\omega)$  and the reflectivity  $R(\omega)$  for  $U_{eff}^{(3+)}=7.0$  and 9.6 eV with experiment. As can be seen, theory and experiment agree fairly well for  $U_{eff}^{(3+)}=9.6$  eV. For  $U_{eff}^{(3+)}=7.0$  eV there is an additional As p band crossing the Fermi level near the  $\Gamma$  point.  $U_{eff}^{(3+)}=9.6$  eV yields a very small carrier concentration, hence a small value of the plasma frequency and low intensity of interband transitions to unoccupied As p states in good agreement with the Hall coefficient and optical measurements.



*Figure 3.61.* Comparison between the experimental [732] (dots) and calculated [741] optical reflectivity R, the real part  $\varepsilon_1(\omega)$  and the imaginary part  $\varepsilon_2(\omega)$  of the dielectric function of Yb<sub>4</sub>As<sub>3</sub> calculated with two different values of  $U_{eff}^{(3+)}$ : 7.0 eV (dashed line) and 9.6 eV (solid line).

We mention that with increasing photon energy beyond the range presented in Fig. 3.61, the measured optical reflectivity decreases rapidly from a value of 0.2 at 0.3 eV to 0.05 at 8 eV (Ref. [732]). The calculated reflectivity, however, has a rather flat behaviour at a value of about 0.3 up to 12 eV. To clarify this disagreement between theory and experiment, ellipsometric measurements of the optical properties of Yb<sub>4</sub>As<sub>3</sub> are highly desired.

Fig. 3.62 shows the energy band structure and total density of states near the Fermi level for Yb<sub>4</sub>P<sub>3</sub>, Yb<sub>4</sub>Sb<sub>3</sub>, and Yb<sub>4</sub>Bi<sub>3</sub> calculated in the trigonal R3c AF crystal structure in the LSDA+U approximation with  $U_{eff}^{(3+)}$ =9.6 eV. We should mention that only Yb<sub>4</sub>P<sub>3</sub>, and Yb<sub>4</sub>As<sub>3</sub> reveal the charge ordering cubic-to-trigonal structural transformation. The other two compounds remain in the

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*Figure 3.62.* Self-consistent LSDA+ $U(U_{eff}^{(3+)}=9.6 \text{ eV})$  energy band structure of Yb<sub>4</sub>Bi<sub>3</sub>, Yb<sub>4</sub>Sb<sub>3</sub> (hypothetical R3c symmetry), Yb<sub>4</sub>(P<sub>0.5</sub>As<sub>0.5</sub>)<sub>3</sub>, and Yb<sub>4</sub>P<sub>3</sub> [741].

cubic structure down to lowest temperatures with the  $Yb^{3+}$  ions being randomly distributed among the four chains.

The main trend in the electronic structure of the sequence of  $Yb_4X_3$  compounds (X = P, As, Sb, or Bi) results from the characteristic trend in the pnictide *p* wave functions and from the systematic change of the lattice parameters.

Compound	$E_c$	$\Delta E_{np}$
Yb <sub>4</sub> P <sub>3</sub>	-2.01	4.00
Yb <sub>4</sub> As <sub>3</sub>	-1.79	4.20
$Yb_4Sb_3$	-2.18	4.45
$Yb_4Bi_3$	-2.28	4.65

*Table 3.1.* The centers of gravity  $E_c$  relative to the Fermi energy and widths (in eV) of pnictogen np bands  $\Delta E_{np}$  in Yb<sub>4</sub>X<sub>3</sub> compounds.

The counteraction of screening by inner atomic shells and of relativistic effects leads to the characteristic trend in the position of the atomic p state and hence of the centre of gravity of the pnictide p band, first increasing from P to As and then monotonically decreasing to Bi. The p bandwidth is monotonically increasing from P to Bi due to the increasing extension of the atomic wave function, although the lattice constant increases too (see Table 3.1). Therefore, if one moves from  $Yb_4Bi_3$  to  $Yb_4P_3$  through the series, the unoccupied 4flevel moves from below towards the top of the pnictide p band and beyond, implying a reduction of metalicity and finally a transition to semiconducting behaviour, which is experimentally found in Yb<sub>4</sub>(As<sub>1-x</sub>P<sub>x</sub>)<sub>3</sub> for  $x \ge 0.4$  (Ref. [712]). Fig. 3.62 shows the energy band structure of the series, including also,  $Yb_4(As_{0.5}P_{0.5})_3$ . In this compound, treated as ordered, two AF ordered  $Yb^{3+}$ ions are no longer chemically equivalent and the system becomes ferrimagnetic. This leeds to a splitting of the 4f hole bands. These bands are already well above the top of the valence band, in agreement with the experimental data [712].

Experimentally, Yb<sub>4</sub>Sb<sub>3</sub> and Yb<sub>4</sub>Bi<sub>3</sub> show the typical valence fluctuating behaviour [711]. Their energy band structures calculated for hypothetical trigonal R3c symmetry differ significantly from that of Yb<sub>4</sub>As<sub>3</sub>. With the increasing pnictide p band widths, already in Yb<sub>4</sub>Sb<sub>3</sub> the indirect gap between the top of the Sb 5p valence band and the bottom of the Yb 5d conduction band is closed (Fig. 3.62). In Yb<sub>4</sub>Bi<sub>3</sub> the direct gap has also disappeared due to further broadening of the Bi 6p conduction band. However, there is still no overlap between the partly filled narrow Yb 4f band and the Yb 5d conduction band in both compounds.

In conclusion, the LSDA+U approach to band structure calculations of Yb<sub>4</sub>As<sub>3</sub> [741] with a U value adjusted to experiment but close to theoretical estimates produce a band gap between the As p band and the Yb 5d band in Yb<sub>4</sub>As<sub>3</sub>. As a consequence, a very narrow marginally occupied Yb<sup>3+</sup> 4f hole band is pinned close to the top of the As p valence band via the charge balance between Yb and As which is governed by the large (~30 eV) bare Coulomb

integral of the Yb 4*f* state. The same charge balance pins the Fermi level close to the bottom of this 4*f* hole band which has a width of 0.007 eV (80 K). It leads to an extremely low carrier density in Yb<sub>4</sub>As<sub>3</sub>.

So for Yb<sub>4</sub>As<sub>3</sub>, the LSDA+U band structure calculations provide a twoband model of the electronic structure: (1) a wide, nearly fully occupied As 4p valence band and (2) a very narrow, marginally occupied Yb 4f band, very weakly hybridized with the As 4p band in a small k space region near the  $\Gamma$ point of the BZ (Fig. 3.59).

Pressure, doping etc. may slightly change the relative position of these two bands and hence strongly affected the low carrier density and the transport properties. But the 4f shell of the Yb<sup>3+</sup> ions is little influenced as long as the charge order is maintained.

The LSDA+U band structure calculations [741] treated the Yb<sub>4</sub>X<sub>3</sub> compounds as ideal systems with perfect charge and AF order. The real situation is much more complicated. Yb<sub>4</sub>As<sub>3</sub> shows no magnetic ordering down to a very low temperature of 0.2 K [713]. However, experimental evidence for existence of short range AF correlations was found [721]. An external magnetic field strongly affects the magnetic excitations suppressing the heavy-fermion properties of Yb<sub>4</sub>As<sub>3</sub> [714]. Going from Yb<sub>4</sub>As<sub>3</sub> to Yb<sub>4</sub>P<sub>3</sub>, the number of Yb<sup>3+</sup> ions increases, the degree of charge and AF ordering also increases and despite of the decrease of the number of free carriers (Yb<sub>4</sub>P<sub>3</sub> is a semiconductor) the heavy-fermion properties are more pronounced which is reflected in the increasing value of the Sommerfeld constant  $\gamma$  from about 200 mJ mol<sup>-1</sup> K<sup>-2</sup> in Yb<sub>4</sub>As<sub>3</sub> to 250 mJ mol<sup>-1</sup> K<sup>-2</sup> in Yb<sub>4</sub>P<sub>3</sub>. Going to heavier pnictogen ions, metalicity increases and the tendency to moment and charge order is lost, a typical mixed valence behaviour is found instead.

The semimetal Yb<sub>4</sub>As<sub>3</sub> cannot be described by Landau's Fermi liquid theory. This becomes obvious by realizing that the predicted effective mass of the *f*-like sheet of the Fermi surface differs by approximately a factor of 5 from the effective mass required in order to explain the  $\gamma$  coefficient in the specific heat. This is not surprising as the huge  $\gamma$  value is due to spin excitations in the Heisenberg chains and therefore unrelated to the quasiparticle excitations near the Fermi surface. A large  $\gamma$  value is experimentally found even when the system is nonmetallic, i.e., in the absence of any Fermi surface like in  $Yb_4(As_{1-x}P_x)_3$ . It depends on the characteristic energy for the fluctuations of magnetic moments in the charge ordered  $\langle 111 \rangle f^{13}$  chains which is given by the superexchange of  $f^{13}$  moments along chains via pnictide orbitals. Note that only the effective moments of the lowest crystal field doublets are relevant here. Therefore, if the complete Fermi surface and the effective masses of Yb<sub>4</sub>As<sub>3</sub> could be measured, one would find that they do not explain the specific heat in contradiction with Landau's Fermi liquid theory. Therefore, this concept requires a generalization. One of the strong points of Landau's theory is
that it is a phenomenological approach, which does not require a microscopic model for a given material. It is within that spirit that a generalization is suggested by postulating in addition to the charged fermions (electrons or holes) a liquid of neutral fermions with a density of states  $N^*(0)$ . This density of states is fitted to the  $\gamma$  value of the specific heat. The underlying physical picture is, of course, that the magnon-like spin excitations in the chains, although of bosonic character, can be transformed into charge neutral fermionic excitations giving rise to the large  $\gamma$  value. But, as pointed out above, we are dealing with a phenomenological theory, and therefore no microscopic justification of the postulate is required. A liquid of neutral fermions for the description of a metallic system was suggested before by Kagan et al. [744] in connection with Kondo lattices. In the present case, the neutral fermions do not contribute to electric transport, but, e.g., to the thermal conductivity. They contribute also to the compressibility and to the spin succeptibility. The observed  $\rho(T) = AT^2$ behaviour at low temperature [711] with A=0.75  $\mu\Omega$  cm/K<sup>2</sup> has to be interpreted as resulting from the scattering of the charged quasiparticles off the neutral fermions.

# 3.1.7 La monochalcogenides

The trivalent lanthanum monochalcogenides LaS, LaSe, and LaTe possess metallic character having a carrier density in the range of  $1.5-2\times10^{22}$  cm<sup>-3</sup> [745]. The magnetic susceptibility measurements indicate paramagnetism in these compounds [746]. The paramagnetic susceptibility  $\chi_p$  of conduction electrons has been found to increase from LaS to LaTe suggesting that the the density of states at the Fermi energy  $N(E_F)$  should also increase from LaS to LaTe. The measured electronic specific heat coefficient  $\gamma$  also shows the same trend [600]. The Debye temperature  $\theta_D$  of these compounds is found to decrease from LaS to LaTe [600]. Lanthanum monochalcogenides are found to be superconductors having transition temperatures in the range of 0.8–1.5 K [600]. The superconducting transition temperature  $T_c$  increases from sulphide to telluride. A few experimental studies like point contact spectroscopy [747], x-ray absorption [748], and the phonon spectra measurements [749] for LaS are also available in the literature.

The optical and MO spectra of LaS, LaSe, and LaTe were investigated in relationship to those of the Ce monochalcogenides by Pittini *et al.* [750], Pittini and Wachter *et al.* [751], and Salghetti-Drioli *et al.* [752]. La monochalcogenides are Pauli paramagnets, therefore a non-zero Kerr effect may be obtained only in an external magnetic field. In all three La monochalcogenides a sharp peak in the Kerr rotation was observed, occurring at 3.05, 2.63, and 2.2 eV for LaS, LaSe, and LaTe, respectively. The narrowness of these peaks increases from LaS to LaSe and to LaTe, while the absolute values of the Kerr rotation are 0.99, 2.54, and  $1.52^{\circ}$ , respectively [752]. At higher energies a

second broader structure between 4 and 5 eV was observed. This feature is well developed only in LaTe [752]. It was first suggested [750], that the sharp feature in the Kerr rotation is the direct magneto-optical manifestation of an electronic transitions involving empty 4f states. Such a claim was based on the fact that its sign was opposite to the one encountered when measuring the Cecounterpart series [750]. Moreover, the additional line found at about 3 eV was considered as a proof that both  $4f^1$  spin-orbit states can be optically populated in contrast to the CeX series, where only the  $4f^1$  ground state contributes to the transition [750, 577]. However, Salghetti-Drioli et al. [752] clearly showed that this is not the case. They found that their spectra present some relevant and essential changes with respect to the previous investigation on LaSe [750]. Even though the peak in the Kerr rotation of LaSe at 2.63 eV is equally sharp in both measurements, the sign is opposite, being negative in the new spectra [752] and positive in Ref. [750]. This is due to an incorrect calibration of the spectrometer and particularly to the wrong definition of the magnetic field direction in the previous investigation [750]. Moreover, for the whole series of compounds Salghetti-Drioli et al. [752] do not observe the double peak, found at approximately 3 eV in LaSe, as reported in Ref. [750]. Salghetti-Drioli et al. [752] argue that such a sharp absorption occurs right at the plasma minimum of respective La monochalcogenides and hence the Kerr rotation follows directly from the interplay between optical interband transitions and the plasma resonance [752]. Moreover, they were able to model the situation by applying the phenomenological Lorence-Drude fit. Salghetti-Drioli et al. [752] also suggested that the broad absorption developing at higher frequencies between 3 and 5 eV in LaTe is due to interband transitions into empty 4f states.

The energy band structure of lanthanum monochalcogenides have been investigated theoretically in Ref.s [753–757] using the LSDA approximation. The calculations have been devoted mostly to investigating the structural properties of La monochalcogenides. The total energy calculations for lanthanum monochalcogenides reported in Ref. [757] underestimate the experimental value of lattice constant by 1.9, 1.68, and 2.3 % in LaS, LaSe, and LaTe, respectively. The corresponding bulk modulus is overestimated when compared to the experimental data by 24 % and 35 % in LaS and LaTe, respectively. The electronic structure of LaS and the LaS/CdS interface have been studied in Ref. [756]. The observed low work function of LaS is well reproduced by the LSDA theory. As far as we know, there are no first principles theoretical investigations of the optical and MO properties of La monochalcogenides in the literature.

### **Electronic structure**

Figure 3.63 shows the fully relativistic energy band structure of LaS calculated in an external magnetic field. In these calculations the 4f states have been

considered as: (1) itinerant using the local spin-density approximation and (2) fully localized, treating them as core states, but unoccupied. The energy band structure of LaS without the 4 f states can be subdivided into three regions separated by energy gaps. The bands in the lowest region around -15 to -13.5 eV have mostly S s character with some amount of La sp character mixed in. The next six energy bands are S p bands separated from the s bands by an energy gap of about 7 eV. The width of the S p band is about 3.7 eV. The spin splitting of the S p bands is very small (about 0.03 eV at the X symmetry point (Fig. 3.63)). The highest region can be characterized as La spin-split d bands. La  $E_a$ d-states are shifted toward higher energy due to hybridization with S p states. It is important that the top of the S p bands is at -2.8 eV below the Fermi level since it means that all the interband transitions in the energy interval of 0.0 to 2.8 eV take part within the La d bands (see below). The LSDA calculations place the empty 4f states of La in LaS at 1 to 2 eV above the Fermi level. It is well known that LSDA usually gives a wrong energy position for the 4fstates in rare-earth compounds. For nonzero 4f occupation it places the 4fstates right at the Fermi level [623, 634] in contradiction with various experimental observations. In the case of La compounds the LSDA places the empty 4f states too close to the Fermi energy. For example, the LSDA calculations produce the empty 4 f states in pure La metal at 2.7 eV above the Fermi level [758], although according to the BIS measurements they are situated around 5.5 eV above the Fermi level [759, 760]. To put the La empty 4f energy states in right position we add a constant potential to the Hamiltonian which acts only on the 4f states. This potential shifts the fourteen on-site 4f energies upward by about 2 eV. We emphasize, however, that the 4f states are hybridized, and together with all other states their energy positions relax to self consistency. Fig. 3.63 presents the energy band structure of LaS calculated with shifted 4fstates. In such an approximation the La 4f empty states are situated around 3.5 eV above the Fermi level. Besides the upward shift of the La 4f states there are some other minor changes in the band structure, namely, the empty La 5dstates at the  $\Gamma$  symmetry point in the LSDA calculations become occupied in the approximation with shifted 4f states (Fig. 3.63).

Figure 3.64 shows the energy band structure and total DOS of LaSe and LaTe using an additional constant potential acting on the 4f states with the same value as was used for LaS. The main trend in the electronic structure of the sequence of LaX compounds (X = S, Se, or Te) results from the characteristic trend in the chalcogenide p and d wave functions and from the systematic change of the lattice parameters. The counteraction of screening by inner atomic shells and of relativistic effects leads to the characteristic trend in the position of the atomic p state and hence of the center of gravity of the chalcogenide p band, increasing from S to Te. The p bandwidth is monotonically increasing from S to Te due to the increasing extension of the atomic np

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*Figure 3.63.* Self-consistent fully relativistic energy band structure and total DOS (in states/(unit cell eV)) calculated with external magnetic field of 60 T for LaS.

wave function, although the lattice constant increases too. The direct energy gap between chalcogenide p and d bands decreases from LaS to LaTe (Fig. 3.64). The center of gravity of unoccupied 4f bands situated at 3.4, 3.2 and 2.9 eV above the Fermi level in LaS, LaSe, and LaTe, respectively. The degree of localization of La 4f states in the LaS–LaSe–LaTe row is increased due to increasing of La–La interatomic distances. The 4f states became narrower and besides are shifted toward the Fermi level in going from LaS to LaTe (see Fig.s (3.63) and (3.64)).



*Figure 3.64.* Self-consistent fully relativistic energy band structure and total DOS (in states/(unit cell eV)) calculated for LaSe and LaTe in an external magnetic field of 60 T with shifted 4f states.

#### **Optical spectra**

Figure 3.65 shows the calculated diagonal part of the optical conductivity  $\sigma_{1xx}$  and the optical reflectivity R of LaS, LaSe, and LaTe in the LSDA and with shifted 4f states approximations compared with the experimental data [750, 752]. The calculated spectra have been convoluted with a Lorentzian whose width is 0.3 eV to approximate a lifetime broadening. The most prominent discrepancy in optical conductivity spectra calculated using the conventional LSDA approximation is the extra peak situated at 2.3 and 2.1 eV in LaS and LaSe, respectively (Fig. 3.65). The corresponding structure is less pronounced in the case of LaTe. This peak is caused by extra structure present in the interband dielectric tensor. Responsible are interband transitions involving the hybridized empty 4f states, which in the LSDA approach exhibit a resonance too close to the Fermi energy. The peak is also responsible for the minimum in the optical reflectivity in LaS and LaSe at around 2.0 eV which is not observed in the experiment (Fig. 3.65). In the calculations with shifted 4fstates the transitions involving the 4f states do not take place at small photon energies any more, and the erroneous peak structure disappears from optical conductivity spectra.



*Figure 3.65.* Calculated diagonal part of the optical conductivity  $\sigma_{1xx}$  and the optical reflectivity R of LaS, LaSe, and LaTe in the LSDA (dotted line) and with shifted 4f states (solid line) compared with the experimental data [752] (circles) and [750] (triangles). There optical reflectivity spectrum of LaTe calculated for a 5/3 multilayered structure (slab) is also shown (see the explanation in the text).

On the basis of the results of the band structure calculation of lanthanum monochalcogenides, their observed optical reflectivity spectra (Fig. 3.65) can be sorted into the respective interband transition groups: (1) metallic high reflectivity below  $\sim 2 \text{ eV}$ , (2) a steep edge between  $\sim 2 \text{ and } \sim 2.5 \text{ eV}$ , and (3) above a minimum at  $\sim 2.7 \text{ eV}$  some less pronounced structures with a broad maximum of R between 5 and 9 eV mostly caused by  $3p \rightarrow 5d$  interband transitions.

The predominant structure of the lanthanum monochalcogenides spectra is the edge at 2.9, 2.7, and 2.3 eV in LaS, LaSe, and LaTe, respectively. This sudden drop is characteristic for metallic rare-earth chalcogenides and is due to a plasma oscillation interfering with interband excitations [628]. The energy of the conduction electron plasma resonance in the presence of the interband excitations is given by  $\varepsilon_{1xx}(\omega)=0$ .

We should mentioned one important discrepancy between the theory and the experiment. Namely, the edge in the optical reflectivity spectra which is caused by the plasma oscillations is deeper in the experimental spectra in comparison with the theoretically calculated one for all the three compounds. One of the possible reasons may be the influence of the surface. To model the surface effects we carried out band structure calculations using a tetragonal supercell

containing 4 unit cells of LaTe along z-direction in which 3 LaTe layers are replaced by 3 layers of empty spheres. The optical reflectivity spectrum of LaTe calculated for such a 5 layer slab separated by 3 layers of empty spheres (5/3 multilayered structure (MLS)) is in excellent agreement with the experimental measurements (Fig. 3.65). We also carried out the band structure calculations for a 9 layer slab separated by 3 layers of empty spheres (9/3 MLS) which gives results similar to those for 5/3 MLS.

Above 5 eV the theoretically calculated optical conductivity and reflectivity spectra of lanthanide monochalcogenides are larger in comparison with the experimental measurements. One of the possible reasons for this is a non-ideal sample surface, its roughness can reduce the optical reflectivity above 5 eV. As a result the experimental optical conductivity spectrum which has been derived from the reflectivity data through the Kramers-Kronig transformation has a lower intensity in comparison with the theoretical calculations (Fig. 3.65). We present two experimental measurements of the optical reflectivity in the case of LaSe in Fig. 3.65. It is clearly seen that even small deviation in the optical reflectivity spectra above 5 eV causes a great difference in the absolute value of the optical conductivity spectrum.

#### MO spectra

After consideration of the band structure and optical properties we turn to the magneto-optical spectra. In Fig. 3.66 we show the experimental [752]  $\theta_K(\omega)$  and  $\epsilon_K(\omega)$  MO Kerr spectra of LaS, as well as the spectra calculated with the LSDA, the 4*f* states in the core and the LSDA with shifted 4*f* states. This picture clearly demonstrates that the best description is given by the LSDA approach with shifted 4*f* states.

Due to the wrong position of the 4f bands in conventional LSDA calculations the off-diagonal part of the dielectric function  $\varepsilon_{xy}$  displays additional resonance structures at 1.0 and 2.4 eV which leads to a disagreement with the experimental Kerr spectra. The most prominent discrepancy in the LSDA Kerr rotation and ellipticity spectra is the negative peak at around 2 eV which is caused by the  $5d \rightarrow 4f$  interband transitions. In the LSDA approach with shifted 4f states the transitions involving the 4f states do not take place at these photon energies any more, and the erroneous peak structure around 2 eV disappears from Kerr spectra. The calculations in which the 4f states are treated as quasi-core are also not able to reproduce the correct MO spectra of LaS.

The LSDA calculations with shifted 4f states produce a single resonance minimum in the Kerr rotation spectrum in good agreement with the experimental measurements. The theoretical analysis of separate contributions of both the numerator, i.e.,  $\sigma_{xy}(\omega)$  and the denominator,  $D(\omega)$ , which factor together to give the Kerr angle shows that the shape of the Kerr ellipticity and Kerr rotation spectra in this compound are almost completely determined by the shape of the function  $[\omega D(\omega)]^{-1}$ . Off-diagonal  $\sigma_{1xy}(\omega)$  and  $\sigma_{2xy}(\omega)$  optical conductivity of LaS calculated in the LSDA approximation with shifted 4fstates show almost constant energy behavior below 3 eV. Fig. 3.67 shows the theoretically calculated Kerr rotation and ellipticity of LaS and the frequency dependence of real and imaginary parts of the function  $[\omega D(\omega)]^{-1}$  multiplied by a constant to normalize the spectra. Obviously the shape of the Kerr spectra in LaS results mostly from the resonance structure of the function  $[\omega D(\omega)]^{-1}$ below 3 eV. Although above this energy the shape of the Kerr spectra is determined by the interplay between optical interband transitions and the plasma resonance.

A similar situation is observed in the case of LaSe. The best description of the Kerr spectra of LaSe is given by the LSDA approach with shifted 4*f* states (Fig. 3.68). The resonance structure observed in the Kerr rotation spectrum is mostly determined by the resonance structure of the function  $[\omega D(\omega)]^{-1}$ . Although the high energy part of the Kerr spectra is affected also by the optical interband transitions.

Fig. 3.69 shows the experimental [752]  $\theta_K(\omega)$  and  $\epsilon_K(\omega)$  MO Kerr spectra of LaTe, as well as the spectra calculated in the LSDA approximation with shifted 4f states. Theory gives a much smaller resonance structure in the Kerr rotation spectrum and fails to produce a broader structure observed experimentally at higher energies between 3 and 5 eV [752]. This feature is well recognized only in LaTe. Salghetti-Drioli *et al.* [752] suggested that the broad absorption developing between 3 and 5 eV is due to interband transitions into empty 4f states. In our band structure calculations the center of gravity of empty 4f energy bands is shifted downwards by 0.4 eV going from LaSe to LaTe (Fig. 3.64). So a similar broad absorption in the Kerr rotation spectrum might be expected to be observed in LaSe starting at around 3.5 eV. Although there is a negative peak in the Kerr rotation spectrum of LaSe it occurs near 4.7 eV (Fig. 3.68) and has a much smaller intensity in comparison with the corresponding structure in LaTe.

There is another important discrepancy between the theory and the experiment. The MO measurements of lanthanum monochalcogenides [752] were performed in external magnetic fields up to 13.2 T. On the other hand, to achieve the same absolute value of the Kerr rotation in LaS and LaSe we used in our calculations an external magnetic field of 60 T. In other words, to achieve the same Zeeman splitting we need to use 5 times larger external magnetic field in comparison with the experimental conditions. The effective increase of the magnetic field may be caused by some amount of magnetic impurities. We can also imagine another, so called "self-magnetic" impurity mechanism. The ground state of lanthanum monochalcogenides have empty 4f states. The light absorption in the optical measurements leads to excited states of the La atom,



*Figure 3.66.* Calculated off-diagonal parts of the dielectric function  $\varepsilon_{xy}$  (in  $10^{29}$  s<sup>-2</sup>), Kerr rotation and Kerr ellipticity spectra (in degree) for LaS treating the 4*f* states as a core electrons, LSDA and LSDA with shifted 4*f* states compared with experimental data (circles) [752].

which may include  $5d \rightarrow 4f$  interband electron transitions. The exited electron in 4f state may exist quite a long time on the same site depending on the degree of the localization of the 4f states in the compound. Such a  $4f^1$  configuration decays to the ground state most probably through the Auger process emitting an addition electron from valence band. Due to energy balance it might be La *d* electron. An additional hole in *d* valence band will not influence the optical spectra due to its small life-time.



*Figure 3.67.* Calculated Kerr rotation and Kerr ellipticity spectra (in degree) for LaS in an external magnetic field of 60 T compared with experimental data [752]. The real and the imaginary parts of the function  $[\omega D(\omega)]^{-1}$  are also shown.



*Figure 3.68.* Calculated Kerr rotation and Kerr ellipticity spectra (in degree) for LaSe in an external magnetic field of 60 T treating the 4f states as a core electrons, conventional LSDA and LSDA with shifted 4f states compared with experimental data (circles) [752].



*Figure 3.69.* Calculated Kerr rotation and Kerr ellipticity spectra (in degree) for LaTe in an external magnetic field of 60 T compared with experimental data (circles) [752].

To model the situation we carried out two super-cell band structure calculations using the LSDA+U approximation with  $U_{eff} = 6$  eV. In the first calculations we used four unit cells in which one of four La atoms has a  $4f^1$  configuration. The second calculations have been carried out for 5/3 MLS with a 5 layered slab separated by 3 layers of empty spheres. For the surface La (first and fifth layers) we used a  $4f^1$  configuration and for the other 3 layers a  $4f^0$ configuration. The corresponding band structures and total density of states for LaTe are presented in Fig. 3.70. We found a ferromagnetic self-consistent solutions with the spin, orbital, and total magnetic moments equal to -0.455, 1.285, and 0.830  $\mu_B$ , and -0.658, 1.815, and 1.157  $\mu_B$  for the La site with a  $4f^1$  configuration in the bulk and slab, respectively. One should note also that the empty La 4f states of the surface layer are shifted toward  $E_F$  at around 0.5 eV in comparison with the bulk calculations. The partly occupied  $4f^1$  state is strongly hybridized with La 5d states and pinned to the Fermi level in both the calculations. The effect of localization of a  $4f^1$  state is much stronger for surface La atoms in the 5/3 MLS. In this case the La  $4f^1$  state is situated as close to the Fermi level as 0.05 eV with a half-width of around 0.04 eV for surface La atoms. The corresponding  $4f^1$  level in the bulk has a half-width of 0.10 eV, therefore a  $4f^1$  quasiparticle has a larger life-time at the surface than in the bulk.

The existence of the occupied  $4f^1$  state leads to a strong polarization of the system. Fig. 3.71 presents the Kerr rotation and ellipticity spectra calculated for the super-cell bulk approximation and for the 5/3 MLS. It can be seen that such a "self-magnetic" impurity mechanism increases the absolute value of the



*Figure 3.70.* The energy band structure and total DOS (in states/(unit cell eV)) of LaTe calculated in a super-cell for bulk and slab approximations with one of the La atoms having a  $4f^1$  occupation (see the explanation in the text).

Kerr rotation for LaTe by 4 times in the bulk and by one order of magnitude for the slab.

This mechanism may explain why in our band structure calculations we need to increase the value of the external magnetic field up to 5 times in comparison with the experimental conditions. Although our super-cell band structure calculations still do not produce the broad absorption between 3 and 5 eV in the MOKE spectra of LaTe (Fig. 3.69). The situation might be similar to that for CeSb, where the record Kerr rotation of 90° was observed [569]. Later on Salghetti-Drioli *et al.* [585] prepared well-characterized single crystals of CeSb, but could not reproduce the record Kerr rotation on a new crystal. Instead only a peak of  $-17^{\circ}$  was observed. Salghetti-Drioli *et al.* suggest that the observed 90° Kerr rotation might not be the intrinsic rotation of CeSb, but could be caused by a surface oxide layer. Possibly a similar situation is also happening in the case of LaTe.



*Figure 3.71.* Kerr rotation and Kerr ellipticity spectra (in degree) of LaTe calculated in supercell approximation for bulk and slab approximations with one of La atoms having a  $4f^1$  occupation (see the explanation in the text).

In conclusion, the LSDA calculations with shifted La 4f empty states reasonably describe the shape and magnitude of the optical and MO spectra in LaS in an external magnetic field and to a less extent the MO spectra in LaSe. The edge in the optical reflectivity spectra in La chalcogenides are deeper and the corresponding Kerr rotation spectra have narrower resonance structures in the experimental spectra in comparison with the theoretically calculated ones. One possible reason is the influence of surface effects. To achieve the same absolute value of the Kerr rotation in LaS and LaSe we must use in our calculations an external magnetic field 5 times larger than the experimental one. This might be associated with possible creation of the long-lived La  $f^1$  surface states which cause an additional polarization of the system. To accurately estimate the value of the life-time of such La  $4f^1$  surface quasiparticles further theoretical analysis is needed.

Theory fails to describe the broader structures in the MO spectra of LaTe between 3 and 5 eV. These structures might not be associated with the intrinsic rotation of LaTe, but could be caused by some additional surface structures. To clarify the nature of these features a new series of MO experiments with special attention to the surface conditions are highly desired.

# **3.2** Uranium compounds.

Intensive experimental and theoretical study over last three decades [761–768] has revealed that 5f magnetism is quite complex, because Coulomb, spinorbit, crystalline field and exchange energies in 5f systems are of the same order of magnitude. Today it is well established that many unusual physical properties of the light actinide metals are a reflection of the particular nature of the 5f electrons. Friedel [769] proposed many years ago that the bonding in these materials must involve the 5f electrons. The argument for 5f bonding can be understood as a consequence of the extended nature of the 5f wave function relative to the rare-earth 4f wave functions. This causes them to form a bandlike states [770].

The itinerant nature of the 5f electrons in the light actinide metals is well known [761, 762]. Their electronic structure and optical properties are well described by LSDA band structure calculations [771, 772]. On the other hand, the decreasing f-band width (W) and the increasing intra-atomic Coulomb energy (U) results in a Mott localization in between plutonium and americium [763, 773, 774] and the correlation effects are not properly described in the local density approximation [766, 767, 775].

Actinide compounds occupy an intermediate position between itinerant 3d and localized 4f systems [776, 777], and one of the fundamental questions concerning the actinide materials is whether their f states are localized or itinerant. This question is most frequently answered by comparison between experimental spectroscopies and the different theoretical descriptions.

Optical spectroscopy provides a powerful, widely used tool to investigate in much detail the electronic structure of actinides. Traditionally, one distinguishes the various existing kinds of spectroscopies according to the photon energy of the employed light, i.e., high-energy x-ray methods, and methods applying infrared, visible or medium-energy light ( $\hbar \omega < 10 \, \text{eV}$ ). X-ray photoemission spectroscopy (XPS) has been applied to determine the energy position of the 5f states below  $E_F$ , and angle-resolved XPS has been used to map out the energy bands in the Brillouin zone (see, e.g., [778]). Optical spectroscopy in the visible and infrared energy range has successfully been applied to many topics in the actinide research. Examples are the infrared absorption in the heavy-fermion state of URu<sub>2</sub>Si<sub>2</sub> [779] and UPd<sub>2</sub>Al<sub>3</sub> [780], reflectivity spectroscopy on intermediate valence and dense Kondo materials [602]. A particular useful spectroscopic technique is MO Kerr spectroscopy [7]. Reflectivity spectroscopy can be used to determine relative energy level positions, but Kerr spectroscopy has the additional advantage that it couples to both the spin and orbital polarization of the electron states [7]. Kerr spectroscopy is therefore ideally suited for studying magnetic actinide compounds. On the other hand, actinide compounds are also excellent subjects for MO research. The participation of the 5f states in bonding is reflected in strongly hybridized bands near the Fermi level, with a high density of states and significant  $f \rightarrow d$  oscillator strengths for optical transitions. The 5 f delocalization favors higher ordering temperatures. In fact, many uranium compounds have ordering temperatures which are one order of magnitude larger than those in similar lanthanide compounds [7, 575]. Regarding the magnitude of the MO effects

compared to rare-earth materials, an enhancement due to the larger spin-orbit energy can be expected and is in part experimentally verified [7, 575]. For actinide compounds the figure of merit  $R^{1/2}(\theta_K^2 + \epsilon_K^2)^{1/2}$ , where R is the optical reflectivity,  $\theta_K$  and  $\epsilon_K$  are Kerr angle and Kerr ellipticity, respectively, is one order of magnitude larger than for the best transition or rare-earth compounds [7]. Besides the issue of radioactivity (minimal for depleted uranium) a hindrance for successful application of actinide compounds in storage devices is that the typical Curie temperature are below room temperature. This is not a fundamental problem, and can probably be overcome by suitable alloying.

As we mention above one of the most intriguing aspects of actinide compounds is the great variability in the localization degree of the 5f electrons. Varying from one actinide compound to another, the 5f electrons may range from being nearly localized to being practically itinerant. In this work we consider two groups of actinide compounds. The optical and MO spectra of the first group which contains UFe<sub>2</sub>, U<sub>3</sub>X<sub>4</sub> (X=P, As, Sb, Bi), UCu<sub>2</sub>P<sub>2</sub>, UCuP<sub>2</sub>, UAsSe, and URhAl compounds can be properly described within the density functional theory in the local-density approximation, but such an approximation totally failed in the case UPd<sub>3</sub>, and UCuAs<sub>2</sub>. This result puts forward further evidence for at least partly itinerant electron behavior in the first group compounds and at least partly localized one in the second group.

## 3.2.1 UFe<sub>2</sub>

UFe<sub>2</sub> is one of the actinide compounds that has been intensively studied for several decades [781–786]. Below 160 K UFe<sub>2</sub> is a ferromagnet with a low magnetic anisotropy similar to that of pure iron. Interest in this compound arises from the fact that the total moment on the uranium site is very small as was first deduced from neutron diffraction experiments [787, 788]. Evidence for strong hybridization between the U 5f and Fe 3d electrons in UFe<sub>2</sub> was first theoretically provided by spin-polarized band structure calculations performed by Brooks et al. in Ref. [789]. They predicted that one consequence of the hybridization would be a reduction, as compared to the free-ion value in the orbital moment on the uranium. Using polarized neutrons and elastic scattering Wulff et al. [790] and Lebech et al. [791] showed that this was, in fact, the case. The orbital and spin moments are both of about 0.25  $\mu_B$ , but they are oppositely directed, and hence the net moment, which is the sum of the orbital and spin contributions, on the U site is close to zero. The neutron experiments [790, 791] on single crystals of UFe2 also showed that the Fe moment is 0.60 $\pm$ 0.03  $\mu_B$ , a substantial reduction from the 2.2  $\mu_B$  of pure Fe. Recently [792] the spin and orbital moments on the uranium site in UFe<sub>2</sub> have been deduced from x-ray magnetic circular dichroism data by using sum rules. It was found that  $M_L$ =0.21  $\mu_B$  and  $M_S = -0.20 \ \mu_B$  in agreement with the results given by polarized neutron scattering [791]. Spin moments were also

derived from the magnetic-Compton profile of UFe<sub>2</sub> in Ref. [793], and found to be equal to -0.20 and  $0.52 \mu_B$  at U and Fe sites, respectively. UFe<sub>2</sub> was also studied by means of photoelectron spectroscopy which showed a pronounced structure at the Fermi level that extends some 2–3 eV below  $E_F$  and originates from U 5*f* states [794, 795].

In order to examine how the hybridization between 5f electrons of uranium and the 3d electrons of iron affects the magnetic exchange parameters and spin-wave spectra, measurements of spin dynamics in UFe<sub>2</sub> were performed in Refs. [796, 797]. There are two important results emerging from these measurements. The first is the large Fe-Fe exchange parameter  $J_{\text{Fe-Fe}}$  (or equivalently the large spin-wave stiffness constant) deduced from the Fe spin-wave model. It is actually unprecedented that diluting Fe results in a larger Fe-Fe exchange. The increase in  $J_{\text{Fe-Fe}}$  must surely come from the 5f - 3d interaction. The second point is the absence of any scattering involving the uranium spins. The absence of, in particular, the acoustic U mode was attributed to the tendency of magnetic response of the 5f states to spread over ( $\omega$ , g) space because of hybridization with the 3d electrons of iron [796].

Paolasini et al. [798] measured the phonon dispersion curves in YFe<sub>2</sub>, UFe<sub>2</sub>, and CeFe<sub>2</sub> Laves phases by inelastic neutron scattering. The phonon dispersion curves and the generalized phonon densities of states were evaluated by a Born-von Karman model. Many differences in the phonon spectrum are found in UFe<sub>2</sub> with respect to the isostructural  $RFe_2$  compounds (R=rare earth). Compared to the expectation based on the knowledge of other  $RFe_2$ compounds, the Fe-Fe and U-Fe longitudinal force constants exhibit large increase in UFe<sub>2</sub>, whereas the U–U longitudinal force constants are substantially reduced. Furthermore, the Fe–Fe transverse force constants in UFe<sub>2</sub> are negative, whereas these parameter are usually near to positive and small in the Laves phases [798]. Normally a negative force constant indicates an incipient structural instability, but this is prevented by other interactions. It is tempting to ascribe these dramatic changes in the UFe<sub>2</sub> force constants, compared to those of the other materials, to electronic interactions. Such interactions, arising presumably from the hybridization of U 5 f and Fe 3d itinerant electrons, may also be responsible for the large magneto-elastic interactions found in UFe<sub>2</sub> [783].

The experimental measurements of the MO properties of  $UFe_2$  were recently reported by Kucera *et al.*. [799]

The fully relativistic spin-polarized LSDA energy band structure and total DOS of the ferromagnetic UFe<sub>2</sub> compound is shown in Fig. 3.72 [800]. The bands in the lowest region between -7.3 and -4.0 eV have mostly a Fe s character with some amount of U spd character mixed in. The energy bands between -4.0 and -0.3 eV are Fe 3d states. The U 5f energy bands are located above and below E<sub>F</sub> at about -0.4 to 2.0 eV. There is a strong hybridization



*Figure 3.72.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of UFe<sub>2</sub> [800].

	U			Fe			UFe <sub>2</sub>
	$M_s$	$M_l$	$M_t$	$M_s$	$M_l$	$M_t$	$M_t$
LSDA	-0.61	0.35	-0.26	0.68	0.06	0.74	1.22
LSDA+U(OP)	-0.71	0.72	0.01	0.71	0.08	0.79	1.59
LSDA+U	-1.83	3.08	1.25	1.14	0.20	1.34	2.59
LSDA [149]	-0.71	0.47	-0.24	0.75	0.07	0.82	1.40
LSDA+OP [149]	-1.03	0.88	-0.15	0.82	0.07	0.89	1.63
exper. [791]	-0.22	0.23	0.01	0.59	-	-	1.19
exper.[792]	-0.20	0.21	0.01	-	-	-	-
exper.[793]	-0.20	-	-	0.52	-	-	-

*Table 3.2.* The experimental and calculated [800] spin  $M_s$ , orbital  $M_l$ , and total  $M_t$  magnetic moments (in  $\mu_B$ ) of UFe<sub>2</sub>.

between the U 5f and Fe 3d states. Because of large spin-orbit interaction of 5f electrons, j = 5/2 and j = 7/2 states are roughly well separated and the occupied states are compoused mostly of the j = 5/2 states.

In magnets, the atomic spin  $M_s$  and orbital  $M_l$  magnetic moments are basic quantities and their separate determination is therefore important. Methods of their experimental determination include traditional gyromagnetic ratio measurements [801], magnetic form factor measurements using the neutron scattering [802], and magnetic x-ray scattering [803]. In addition to these, the recently developed x-ray magnetic circular dichroism combined with several sum rules [282, 283] has attracted much attention as a method of site and symmetry-selective determination of  $M_s$  and  $M_l$ . Table 3.2 presents the

comparison between calculated and experimental magnetic moments in UFe<sub>2</sub>. Polarized neutrons and elastic scattering [790, 791] as well as x-ray magnetic circular dichroism measurements [792] reveal that the orbital and spin magnetic moments on the U site are almost equal and oppositely directed, hence the U net moment, which is the sum of the orbital and spin contributions, is close to zero in UFe<sub>2</sub>. The LSDA calculations do not provide such a compensation (Table 3.2). The LSDA total magnetic moment on uranium in UFe<sub>2</sub> is equal to  $-0.26 \ \mu_B$  (Table 3.2) (with spin moment  $-0.61 \ \mu_B$  and orbital moment  $0.35 \ \mu_B$ ). The calculated uranium moment is dominated by 5*f* states: the 5*f* components of the spin and orbital moment are  $-0.50 \ \mu_B$  and  $0.34 \ \mu_B$ , respectively.

It is a well-known fact, however, that the LSDA calculations fail to produce the correct value of the orbital moment of uranium compounds [804, 148–150, 805]. In the LSDA, the Kohn-Sham equation is described by a local potential which depends on the electron spin density. The orbital current, which is responsible for  $M_l$ , is, however, not included into the equations. This means, that although  $M_s$  is self-consistently determined in the LSDA, there is no framework to determine simultaneously  $M_l$  self-consistently.

Numerous attempts have been made to better estimate  $M_l$  in solids. They can be roughly classified into two categories. One is based on the so-called current density functional theory [806–808] that is intended to extend density functional theory to include the orbital current as an extra degree of freedom, which describes  $M_l$ . Unfortunately an explicit form of the current density functional is at present unknown. The other category includes orbital polarization (OP) [148–150, 805], self-interaction correction (SIC) [809], and LSDA+U[134, 135] approaches, which provide a mean to calculate  $M_l$  beyond the LSDA scheme.

For a better description of  $M_l$ , the OP functional form of  $BL_z^2$  with the Racah parameter *B* has been deduced [148] from an atomic multiplet ground state without spin-orbit interaction (SOI), where *S* and *L* are given by Hund's rules. However, the OP method does not assure us that it will give a good description when the SOI is included and thus *S* and *L* are no longer good quantum numbers. The inclusion of the orbital polarization (OP) correction in Ref. [149] brings the calculated total U moment in UFe<sub>2</sub> to  $-0.15 \mu_B$ , in better agreement with experiment compared to the LSDA calculations (Table 3.2).

Solovyev at al. [134] argued that the key parameter responsible for the exchange-correlation enhancement of the orbital magnetic moments in solids is the "Hubbard U" rather than the intra-atomic Hund's second rule coupling, being consistent with a more general concept of the orbital polarization. This leads to a unified rotationally invariant LSDA+U prescription for the orbital magnetism.

Table 3.2 presents the calculated magnetic moments in UFe<sub>2</sub> using a generalization of the LSDA+U method which takes into account that in the presence of spin-orbit coupling the occupation matrix of localized electrons becomes non-diagonal in spin indexes [135]. The matrix elements of this method contain both  $F^0 = U$ , which provides the splitting of the localized states into "lower and upper Hubbard subbands", and the terms proportional to Slater integrals  $F^2$ ,  $F^4$ , and  $F^6$ , which are responsible for angular correlations within the localized shell. In the case when U is effectively screened and  $U_{eff} = U - J$ becomes small, the latter terms give the dominant contribution to the corresponding matrix elements. In our LSDA+U calculations [800] we used two sets of parameters: U=2.0 eV and J=0.5 eV and U = J = 0.5 eV. In the later case  $U_{eff}=0$  and the effect of the LSDA+U comes from non-spherical terms which are determined by  $F^2$ ,  $F^4$ , and  $F^6$  Slater integrals. In the following we will refer to calculations performed using the LSDA+U method with  $U_{eff} = 0$ as the LSDA+U(OP) calculations.

The LSDA+U(OP) calculations lead to almost complete cancellation of the spin and orbital magnetic moments at U site in agreement with the experimental data. At the same time the LSDA+U(OP) theory still strongly overestimates the absolute value of both the spin and orbital magnetic moments at the U site in UFe<sub>2</sub>. The total moment per formula unit becomes 1.59  $\mu_B$ , which is larger than the LSDA computed total moment of 1.22  $\mu_B$  and the experimental value of 1.19  $\mu_B$  [791].

The LSDA+U method with U=2.0 eV and J=0.5 eV strongly overestimates the spin and orbital magnetic moments at both the U and Fe sites and does not lead to the the cancellation of the spin and orbital magnetic moments at U site (Table 3.2). One can conclude that the on-site Coulomb repulsion on the U site is suppressed, most likely because of the strong hybridization between U 5f and Fe 3d states. As a consequence, U 5f electrons in UFe<sub>2</sub> demonstrate almost purely itinerant behavior.

In Fig. 3.73 we show the calculated and experimental MO Kerr spectra of UFe<sub>2</sub>. We have convoluted the calculated spectra with a Lorentzian whose width is 0.6 eV to estimate a lifetime broadening. The Kerr spectra of UFe<sub>2</sub> are significantly different from the spectra of pure bcc Fe. This difference arises predominantly from substantial reduction of the magnetic moment, higher population of 3d states and different location of the Fermi energy  $E_F$  in UFe<sub>2</sub> compared to bcc Fe. There exists rather good agreement between the experimental Kerr spectra of UFe<sub>2</sub> and the *ab initio* LSDA calculated one with the exception of a small blue shift of about 0.3 eV of the theoretically calculated prominent peak both in the Kerr rotation and ellipticity. The prominent peak at 0.6 eV in the Kerr rotation results from a combination of a deep resonance structure in the denominator  $D(\omega)$  and interband transitions contributing into  $\sigma_{2xy}$ . Away from the peak, for energies above 1.0 eV, the Kerr rotation and elliptic spectra and elliptic spectra between the experimental spectra between the peak, for energies above 1.0 eV, the Kerr rotation and elliptic spectra between the peak between the peak both in the term is a combination of a deep resonance spectra between the peak, for energies above 1.0 eV, the Kerr rotation and elliptic spectra between the peak between the peak both in the term is a both in the Kerr rotation and elliptic between the term is peak between the peak.

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*Figure 3.73.* Calculated [800] and experimental Kerr rotation and Kerr ellipticity (in degrees) spectra of the UFe<sub>2</sub> in comparison with the experimental data Ref. [799] and bcc Fe [324].

lipticity spectra are fully determined by the shape of  $\sigma_{2xy}$ . The LSDA+U(OP) approximation produces a slightly larger Kerr rotation spectrum in the whole energy interval in comparison with the LSDA calculations and the experiment. This might be connected with the overestimation of the U orbital magnetic moment in the LSDA+U(OP) calculations (Table 3.2).

# 3.2.2 $U_3X_4$ (X=P, As, Sb, Bi, Se, and Te)

## U<sub>3</sub>X<sub>4</sub> (X=P, As, Sb, and Bi)

The electronic and magnetic structures of  $U_3X_4$  (X=P, As, Sb) compounds have been investigated by Sandratskii and Kübler [777]. They obtained a noncolinear magnetic ground state for all three compounds. On the other hand the same authors found that the optical properties of  $U_3P_4$  are insensitive to the canting angle of the magnetic moment [810]. The theoretical investigation of the MO properties of  $U_3X_4$  (X=P, As, Sb, Bi, Se, and Te) compounds was carried out in Ref. [811]. The MO spectra measurements of these compounds were made in the presence of an external magnetic field (actually it was equal to 4 T in the case of  $U_3P_4$  and  $U_3As_4$  [812]) which can promote the transition from the noncolinear magnetic structure to a colinear one. To simplify the theoretical calculations we consider the  $U_3X_4$  compounds as having a collinear ferromagnetic structure.

As an example of the energy band structure of  $U_3X_4$  (X=P, As, Sb, and Bi) compounds Fig. 3.74 shows the fully relativistic spin-polarized energy band structure of ferromagnetic  $U_3As_4$ . The band structure of  $U_3As_4$  can be subdivided into several regions. The bands in the lowest region between -12.7 and -10 eV have mostly As *s* character with some amount of U *spd* character mixed in. Between -5.7 and -0.5 eV 24 As 4*p* states hybridize with the U



*Figure 3.74.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of  $U_3As_4$  [811].

6d states. The U 5*f* energy bands are located above and below E<sub>*F*</sub> at about -0.5 to 2.0 eV. There is a small overlapping in the  $\Gamma$  symmetry point between the As 4*p* states and U 5*f* energy bands. The highest region above the Fermi energy can be characterized as a antibonding U 6*d* states.

Let us consider the electronic structure of the other compounds. The main trend in the electronic structure of the sequence of  $U_3X_4$  compounds results from the characteristic trend in the pnictide p wave functions and from the systematic change of the lattice parameters. The counteraction of screening by inner atomic shells and of relativistic effects leads to the characteristic trend in the position of the atomic p state and hence of the center of gravity of pnictide p band, monotonically increasing from P to Bi. On the other hand the center of gravity for U 5 f bands is monotonically decreasing from  $U_3P_4$  to  $U_3Bi_4$ . The spin-orbit (SO) splitting at the centers of gravity are equal to 0.87 and 0.89 eV for U 5f and 6d states respectively for all four compounds. But SO splitting for pnictide p states shows a one order of magnitude increase from P (0.08 eV) to Bi (0.94 eV). The p bandwidth is monotonically increasing from  $U_3P_4$  to  $U_3Bi_4$  due to the increasing extension of the pnictide np atomic wave functions, although the lattice constant increases too. There is an energy quasigap between the pnictide p and U 5f states in U<sub>3</sub>P<sub>4</sub> and U<sub>3</sub>As<sub>4</sub> compounds. The quasigap decreases in  $U_3Sb_4$  and disappears in  $U_3Bi_4$  due to the changing widths and relative positions of pnictide p and U 5f bands.

In the case of  $U_3As_4$  and  $U_3Sb_4$  the Fermi level is situated near a deep minimum producing a rather small DOS at  $E_F$ . The LSDA calculation predicts the  $U_3Bi_4$  to be a semiconductor with a very small indirect energy gap about 0.001 eV and direct gap of 0.005 eV. This gap has a relativistic nature and closed after eliminating the SO interaction. The other three compounds



*Figure 3.75.* Calculated and experimental Kerr rotation and Kerr ellipticity (in degrees) spectra of the  $U_3P_4$  and  $U_3As_4$  compounds [811]. The experimental data are those of Ref. [812].

are nearly compensated semimetals. The analysis of the experimental Hall coefficient measurements in Refs. [813, 814] leads to a semimetallic state with carrier concentration per U atom as low as 0.026, 0.014, and 0.0079 for  $U_3P_4$ ,  $U_3As_4$  and  $U_3Sb_4$ , respectively, calculated with the assumption of a single band. Optical reflectivity measurements [812], on the other hand, suggest a conduction-electron concentration of 0.5 per U atom in  $U_3P_4$ . Such a large discrepancy would seem to be beyond experimental error even after accounting for all the approximations of the Drude fit. To explain such a discrepancy we should mention that the Hall coefficient measurements provides the number of carriers as a difference between hole and electron Fermi surface volumes while the optical measurement deals with all of the carriers. There are six sheets of the U<sub>3</sub>P<sub>4</sub> Fermi surface three hole and three electron sheets. The volume of all six sheets corresponds to 0.45 carriers/U atom in a good agreement with the estimations from the optical reflectivity measurements [812]. All the bands which cross the Fermi level have predominantly U 5f character [811] and if we assume that the electrons and holes of each sheet have the same mobility, then we may compare the carrier concentration derived from the Hall measurements with the LSDA results for the difference in hole and electron volumes: 0.089, 0.032, and 0.0065 carriers/U atom for U<sub>3</sub>P<sub>4</sub>, U<sub>3</sub>As<sub>4</sub> and U<sub>3</sub>Sb<sub>4</sub> respectively, The correspondence with the experimental values quoted above is quite reasonable.

After consideration of the bandstructure properties we turn to the magnetooptical spectra. In Fig. 3.75 we show the calculated and experimental[812] MO Kerr spectra of  $U_3P_4$  and  $U_3As_4$ . There exists rather good agreement between



*Figure 3.76.* Calculated Kerr rotation and Kerr ellipticity spectra (in degrees) of the  $U_3Sb_4$  and  $U_3Bi_4$  compounds [811].

the experimental Kerr spectra and the *ab initio* calculated one. Overall, the experimental features are excellently reproduced. In particular the theory displays the prominent peaks of  $U_3P_4$  at about 0.6 eV both in the Kerr rotation and Kerr ellipticity. With increasing energy, that is, for energies above 2.5 eV, the theoretical and experimental curves differ in detail and change sign at different energies. In the case of  $U_3As_4$  the agreement between theory and experiment is even better both in the shape and in the energy position of the sign change. We can conclude, therefore, that the behavior of the MO Kerr spectra in  $U_3P_4$  and  $U_3As_4$  is well described by the LSDA bandstructure theory.

The imaginary part of the inverse denominator (times the photon frequency),  $\text{Im}[\omega \text{D}]^{-1}$ , displays a double resonance structure at about 0.1 and 0.4 eV in U<sub>3</sub>P<sub>4</sub> [811]. The imaginary part of  $\omega \sigma_{xy}$ , i.e.  $\omega \sigma_{2xy}$  displays a very small value at 0.1 eV and a reasonable value at the second energy. Therefore the prominent peak in the Kerr rotation of U<sub>3</sub>P<sub>4</sub> at 0.6 eV results a combination of a deep resonance structure of the denominator and interband transitions contributing into  $\sigma_{2xy}$ . If one moves from U<sub>3</sub>P<sub>4</sub> to U<sub>3</sub>As<sub>4</sub> through the series, the real diagonal part of complex dielectric function  $\varepsilon_{1xx}$  crosses the energy axis at 0.42 and 0.17 eV in U<sub>3</sub>P<sub>4</sub> and U<sub>3</sub>As<sub>4</sub> respectively and, hence, the position of the resonance structure of the inverse denominator in U<sub>3</sub>As<sub>4</sub> shifts to smaller energies. As a consequence, in U<sub>3</sub>As<sub>4</sub> the main peak in the Kerr rotation is situated at 0.35 eV. The figure of merit  $R^{1/2}(\theta_K^2 + \epsilon_K^2)^{1/2}$  in U<sub>3</sub>As<sub>4</sub> has a maximum value of 6.0° at 0.35 eV which is much higher as in PtMnSb (0.83° at 1.57 eV).

The theoretically calculated plasma frequency was found to assume a small value of 0.97 eV in the  $U_3P_4$  and rapidly decreases through the series being to be equal to 0.53 and 0.20 eV in  $U_3As_4$  and  $U_3Sb_4$  respectively. The position of the prominent peaks in  $U_3Sb_4$  and  $U_3Bi_4$  is shifted to a far infrared energy



*Figure 3.77.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of  $U_3Se_4$  [811].

region (see Fig. 3.76). The absolute value of the Kerr rotation of  $U_3Sb_4$  extends to 7.5°.

#### U<sub>3</sub>Se<sub>4</sub> and U<sub>3</sub>Te<sub>4</sub>

The LSDA energy band structure and total DOS of  $U_3Se_4$  [811] is shown in Fig. 3.77. Due to one additional electron in the 4p shell of Se atom in comparison with pnictide atoms the 4p valence bands of  $U_3Se_4$  are fully occupied and shifted down. There is an energy gap of about 1.3 eV between Se p valence bands and U 5f bands. The energy band structure of  $U_3Te_4$  (not shown) is similar to  $U_3Se_4$ . Due to the increasing extension of the atomic 5p wave function of Te the p valence bands of  $U_3Te_4$  are slightly broader and the p bands also shifted upward decreasing the energy gap between Te 5p valence bands and U 5f bands up to 0.7 eV. The lattice constant of chalcogenide  $U_3Te_4$  (a=9.38 Å) is larger in comparison with the corresponding pnictide compound  $U_3Sb_4$  (a=9.112 Å).

It leads to an increase in the U-X interatomic distance (3.15 Å in U<sub>3</sub>Sb<sub>4</sub> and 3.25 Å in U<sub>3</sub>Te<sub>4</sub>). Together with the fact that in the chalcogenide compounds the *p* valence band is fully occupied and separated by the energy gap from the U 5*f* band allows one to assume a significant decrease of the hybridization between U 5*f* states and *p* valence states and an increase of the localization of the U 5*f* states in U<sub>3</sub>Se<sub>4</sub> and U<sub>3</sub>Te<sub>4</sub>. The Sommerfeld coefficient  $\gamma$  was calculated to be  $\gamma = 52.7$  mJ mol<sup>-1</sup>K<sup>-2</sup> in U<sub>3</sub>Te<sub>4</sub> which is more than four times larger in comparison with the corresponding pnictide compound U<sub>3</sub>Sb<sub>4</sub>. In addition, the calculations in the rigid muffin-tin approximation suggest that the electron-phonon coupling might enhance  $\gamma$  a factor  $\sim 1.5$  for uranium compounds [815]. We suspect that 5*f* electrons in the U<sub>3</sub>Se<sub>4</sub> and U<sub>3</sub>Te<sub>4</sub> have a



*Figure 3.78.* Calculated Kerr rotation and Kerr ellipticity spectra (in degrees) of the  $U_3Se_4$  and  $U_3Te_4$  compounds using LSDA and LSDA+U approaches [811].

quasilocalized nature and to give a proper description of the electronic structure and the optical and MO spectra, the intra-atomic Coulomb repulsion U of the 5f electrons must be taken into account.

The MO spectra of these compounds are shown in Fig. 3.78. There is a big difference between LSDA and LSDA+U calculated Kerr rotation spectra. The calculated Kerr spectra of  $U_3Se_4$  and  $U_3Te_4$  including intra-atomic Coulomb repulsion U of the 5f electrons are very similar to corresponding USe and UTe spectra [7] but with larger absolute values. To clarify the nature of 5f electrons in  $U_3Se_4$  and  $U_3Te_4$  experimental optical and MO spectra measurements are highly desired.

# 3.2.3 $UCu_2P_2$ , $UCuP_2$ , and $UCuAs_2$

The uranium pnictide ternary compounds with copper or nickel crystallize in a high-symmetry structure: UCuP<sub>2</sub>, UCuAs<sub>2</sub>, UNiAs<sub>2</sub> are tetragonal [816] and UCu<sub>2</sub>P<sub>2</sub> and UCu<sub>2</sub>As<sub>2</sub> are hexagonal [817]. The U-Cu ternaries order ferromagnetically in contrast to the U-Ni ternaries, which are all antiferromagnets [7]. The magnetic ordering temperatures are among the highest known so far for uranium compounds reaching 216 K for UCu<sub>2</sub>P<sub>2</sub> [818]. The energy dependence of the Kerr rotation and ellipticity of UCu<sub>2</sub>P<sub>2</sub> have been measured by Schöenes *et al.* [819].



*Figure 3.79.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of UCu<sub>2</sub>P<sub>2</sub> [811].



*Figure 3.80.* Calculated and experimental Kerr rotation and Kerr ellipticity (in degrees) spectra of  $UCu_2P_2$  [811]. The experimental data are those of Ref. [819].

#### UCu<sub>2</sub>P<sub>2</sub>

The fully relativistic spin-polarized LSDA energy band structure and total DOS of the ferromagnetic UCu<sub>2</sub>P<sub>2</sub> compound is shown in Fig. 3.79. The bands in the lowest region between -12.4 and -10.1 eV have mostly a P *s* character with some amount of U *spd* character mixed in. The energy bands between -6.7 and -0.4 eV are P 3*p* states strongly hybridized with the Cu 3*d* states. The latter occupies the -5.5 to -4.0 energy region. The U 5*f* energy bands are located above and below E<sub>*F*</sub> at about -0.4 to 2.0 eV. The highest region above the Fermi energy can be characterized as a anti-bonding U 6*d* states.

In Fig. 3.80 we show the calculated [811] and experimental [819] MO Kerr spectra of the  $UCu_2P_2$ . We have convoluted the calculated spectra with a Lorentzian whose width is 0.4 eV to estimate a lifetime broadening. There



*Figure 3.81.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of UCuP<sub>2</sub> [820].

exists rather good agreement between the experimental Kerr spectra and the *ab initio* LSDA calculated one with the exception of a small shift of about 0.3 eV of the prominent peak both in the Kerr rotation and ellipticity. This peak results from a combination of a deep resonance structure in the denominator and interband transitions contributing into  $\sigma_{2xy}$ . Outside the peak, for energies above 1.0 eV, the Kerr rotation and elliptisity spectra are fully determined by the shape of  $\sigma_{2xy}$ . The two peaks at about 2.0 and 3.3 eV originate mostly from U  $6d \rightarrow 5f$  interband transitions. The interband transitions from Cu 3d to U 5f bands start above 4 eV. In the 1 to 5 eV energy region the theoretical and experimental curves deviate from one another in some details. The theoretically calculated figure of merit  $R^{1/2}(\theta_K^2 + \epsilon_K^2)^{1/2}$  in UCu<sub>2</sub>P<sub>2</sub> has a maximum value of  $2.5^{\circ}$  at 0.4 eV which is higher than that in PtMnSb (0.83° at 1.57 eV), although is smaller than in U<sub>3</sub>As<sub>4</sub>.

## UCuP<sub>2</sub>

UCuP<sub>2</sub> belongs to layered tetragonal ZrAl<sub>3</sub> type crystal structure with the space group I4/mmm (No. 139) with U at the 4*e* position, Cu at the 4*d* position, and P at the 4*c* and 4*e* positions. Phosphor atoms have two nonequivalent positions, the plane with  $P_1$  atoms is situated between uranium planes, whereas uranium and copper planes are separated by plane containing  $P_2$  atoms. The lattice constants are *a*=3.803, *c*=18.523 Å [820]. The unit cell of UCuP<sub>2</sub> contains 8 atoms.

The energy dependence of the Kerr rotation and ellipticity of  $UCuP_2$  have been measured by Funagalli *et al.* [821] The measurements have been done on a natural grown surface perpendicular to the *c*-axis.

The theoretical investigation of the energy band structure and MO spectra of  $UCuP_2$  was carried out in Ref. [820]. The fully relativistic spin-polarized



*Figure 3.82.* Calculated [820] and experimental [821] Kerr rotation and Kerr ellipticity (indegrees) spectra of UCuP<sub>2</sub>.

energy band structure of ferromagnetic UCuP<sub>2</sub>, shown in Fig. 3.81. The bands in the lowest region between -13.4 and -7.2 eV have mostly a P *s* character with some amount of U and Cu *spd* character mixed in. The energy bands between -7.2 and -0.4 eV are P 3*p* states strongly hybridized with the Cu 3*d* and U 6*d* states. There is a quasi gap between P *s* and *p* states. The Cu 3*d* states are fully occupied and situated around 5.0 eV below Fermi level. The U 5*f* energy bands are located above and below E<sub>*F*</sub> at about -0.4 to 3.0 eV. The highest region above the Fermi energy can be characterized as a anti-bonding U 6*d* states.

In Fig. 3.82 we show the calculated [820] and experimental [821] MO Kerr spectra of the UCuP<sub>2</sub> compound. There exists rather good agreement between the experimental Kerr spectra and the *ab initio* LSDA calculated one. Overall, the experimental features are reasonably well reproduced, except the theoretically calculated spectra have more sharp features in comparison with experimentally observed spectra. There is also a small red energy shift by about 0.1 eV in the position of the main Kerr rotation and ellipticity peaks in comparison with the experiment. We can conclude, therefore, that the spectral behavior of the MO Kerr spectra in UCuP<sub>2</sub> is well described by LSDA band-structure theory.

## UCuAs<sub>2</sub>

UCuAs<sub>2</sub> belongs to tetragonal AsCuSiZr crystal structure with the space group P4/nmm (No. 129) with U at the 2c position, Cu at the 2b position, and As at the 2a and 2c positions. The lattice constants are a=3.951, c=9.558Å [822]. The unit cell of UCuAs<sub>2</sub> contains 8 atoms. The nearest neighbor distance between uranium atoms is increased from 3.80 Å in UCuP<sub>2</sub> to 3.95



*Figure 3.83.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of UCuAs<sub>2</sub> calculated in the LSDA and LSDA+U approximations [822].

Å in UCuAs<sub>2</sub>, therefore, one would expect the increasing of 5f localization in going from UCuP<sub>2</sub> to UCuAs<sub>2</sub>.

The energy dependence of the Kerr rotation and ellipticity of UCuAs<sub>2</sub> have been measured by Schoenes *et al.* [819] The measurements have been made on a natural grown surface perpendicular to the *c*-axis in the energy range 0.55 to 5 eV and temperatures down to 2 K in an external magnetic field up to 10 T. Although UCuAs<sub>2</sub> has lower uranium concentration in comparison with UX and  $U_3X_4$  (X=P, As) compounds, its Kerr rotation reaches 1.75° (Ref. [819]) which is the largest among these compounds.

The fully relativistic spin-polarized energy band structure of ferromagnetic UCuAs<sub>2</sub> is shown in Fig. 3.83 calculated in the LSDA and LSDA+U approximations [822]. The energy bands in the lowest region between -13.6 and -7.5 eV have mostly As *s* character with some amount of U and Cu *spd* character mixed in. The energy bands between -7.5 and -1.0 eV are As 4*p* states strongly hybridized with the Cu 3*d* and U 6*d* states. There is a small energy gap between As *s* and *p* states. The Cu 3*d* states are fully occupied and situated



*Figure 3.84.* Calculated [822] and experimental Kerr rotation and Kerr ellipticity (in degrees) spectra of UCuAs<sub>2</sub>. The experimental data are those of Ref. [819].

around 5.0 eV below Fermi level. The highest region above the Fermi energy can be characterized by anti-bonding U 6*d* states. The U 5*f* energy bands in LSDA are located above and below  $E_F$  at about -0.5 to 1.5 eV.

In the LSDA+U band structure calculations [822] the self-consistent iterations were started from a  $5f^2$  configuration for the U<sup>4+</sup> ion with two on-site 5f levels shifted downward by  $U_{eff}/2$  and twelve levels shifted upwards by this amount. The energies of occupied and unoccupied 5f levels are separated by approximately  $U_{eff}$ . The LSDA+U energy bands and total density of states of UCuAs<sub>2</sub> for  $U_{eff}$ =1 eV are shown in Fig. 3.83. The Coulomb repulsion  $U_{eff}$  strongly influences the U 5f electronic states in UCuAs<sub>2</sub>.

In Fig. 3.84 we show the calculated [822] and experimental [819] MO Kerr rotation and ellipticity spectra of the UCuAs<sub>2</sub> compound. Better agreement between the calculated and the experimentally measured MO Kerr spectra was found when we used the LSDA+U approximation. The prominent peak at 1.2 eV in the Kerr rotation spectrum originates mostly from U  $5f \rightarrow 6d$  interband transitions (see Figs. 3.83). The interband transitions from Cu 3d to U 5f bands start above 4 eV. The LSDA calculations produce a two peak structure with the largest peak situated at 0.9 eV. The Coulomb repulsion  $U_{eff}$  shifts the energies of occupied 5f levels downwards and unoccupied ones upwards, as a result LSDA+U calculations correctly produce the shape and energy position of the prominent peak in both the Kerr rotation and ellipticity spectra (Fig. 3.84). On the other hand, theory both in the LSDA and LSDA+U approximations produces a blue energy shift by about 1 eV in the position of the local minimum and second high energy peak in the Kerr rotation and ellipticity spectra in comparison with the experiment.

Table 3.3 presents the comparison between calculated and experimental magnetic moments in UCuAs<sub>2</sub>. The LSDA total magnetic moment on ura-

		LSDA			LSDA+U		
atom	$M_s$	$M_l$	$M_{total}$	$M_s$	$M_l$	$M_{total}$	Exper.
U	-1.677	2.318	0.641	-2.135	4.123	1.988	1.27
Cu	-0.020	-0.002	-0.022	-0.017	-0.002	-0.019	
As <sub>1</sub>	-0.003	0.002	-0.001	0.003	0.005	0.008	
$As_2$	-0.010	-0.018	-0.028	-0.008	-0.016	-0.024	

*Table 3.3.* The experimental and LSDA calculated spin, orbital and total magnetic moments (in  $\mu_B$ ) of UCuAs<sub>2</sub>. The experimental datum is from Ref. [819].

nium in UCuAs<sub>2</sub> is only 0.641  $\mu_{\rm B}$  (Table 3.3) (with spin moment  $-1.677 \ \mu_{\rm B}$  and orbital moment 2.318  $\mu_{\rm B}$ ) which is considerably smaller than the experimental moment of about 1.27  $\mu_{\rm B}$ . [819] The calculated moment is dominated by 5*f* states: the 5*f* components of the spin and orbital moment are  $-1.569 \ \mu_{\rm B}$  and 2.283  $\mu_{\rm B}$ , respectively. On the other hand, the LSDA+*U* calculations overestimate the total magnetic moment in UCuAs<sub>2</sub> compound (Table3.3).

In conclusion, the spectral behavior of the MO Kerr spectra in UCuAs<sub>2</sub> is better described by LSDA+U bandstructure theory than by LSDA. This fact indicates that the U 5f electrons in the ternary UCuAs<sub>2</sub> are likely to be partly localized in contrast to UCuP<sub>2</sub> where U 5f electrons are itinerant. [820] This supports the conclusion drawn early by Schoenes *et al.* [819] that the localization of the f states is increased in going from UCuP<sub>2</sub> to UCuAs<sub>2</sub>.

# 3.2.4 UAsSe and URhAl

UAsSe crystallizes in the tetragonal PbFCl crystal structure (also called ZrSiS structure, P4/nmm space group) and orders ferromagnetically below  $T_C \approx 110$  K [823, 824]. Magnetic susceptibility measurements [825, 826] and photo-emission experiments [827] supplied evidence for localized 5*f* electrons in UAsSe. On the other hand, reflectivity and MO spectroscopy revealed a pronounced spectral intensity at small photon energies (< 2 eV) which was attributed to a 5*f* band located at the Fermi energy [575]. Also, the specific heat coefficient  $\gamma = 41$  mJ/mol K<sup>2</sup> indicates a tendency to itinerancy [828]. These apparently contradicting observations show that the behavior of the 5*f* electrons and the related magnetic properties of UAsSe are not yet well understood.

As in other uranium compounds with non-cubic structures such as, e.g., the ternary  $UT_2X_2$  compounds [829] there is the possibility of partially delocalized electrons in another sense. These compounds with a preferred *c*-axis tend to have the uranium atoms arranged in layers which leads to both anisotropic



*Figure 3.85.* Theoretical and experimental polar Kerr rotation and Kerr ellipticity spectra of UAsSe [830]. The experimental data  $(\Box)$  are after Reim (Ref. 5).

bonding and magnetic properties due to hybridization of 5f and p or d states. It is quite possible that the 5f electrons are delocalized in the planes but localized along the *c*-axis and we suspect that this may be the case in UAsSe. In this compound the uranium planes are perpendicular to the axis of the polar Kerr measurements, so that the polar MO Kerr effect selectively probes these planes which is a possible explanation of why the response appears to be due to itinerant electrons.

A comparison of the theoretical and experimental spectra in Fig. 3.85 proves that there is a very good agreement between the band theory and experimental data: Both the position and height of the main peak in the Kerr angle ( $\theta_K$ ) at 3 eV are properly given by theory, with the usual (small) dependence of the theoretical peak height on the broadening. Energy-band theory predicts also a smaller peak in the Kerr rotation at 1 eV, where there is only a shoulder seen in the measured Kerr angle. A Kramers-Kronig related peak structure is visible in the Kerr ellipticity ( $\varepsilon_K$ ) spectrum at 1.5 eV. In this energy region there will of course be the influence of the not included intraband conductivity which may change the pure interband spectra.

URhAl has also a layer crystal structure with U–Rh planes separated by Rh–Al planes. There are apparantly several contradicting experimental observations on the nature of 5f electron localization in URhAl. Inelastic neutron scattering experiments on URhAl revealed a peak at 380 meV, which could be the signature of an intermultiplet transition [831]. The value of 380 meV is quite close to the intermultiplet transition energy of 390 meV measured for UPd<sub>3</sub> [832]. There are, however, several other properties of URhAl that would



*Figure 3.86.* Experimental [836] and theoretical [595] Kerr spectrum of URhAl. The theoretical spectrum is calculated with the itinerant LSDA approach.

advocate rather delocalized 5*f* behavior in URhAl. A small U moment of only 0.94  $\mu_B$  was measured which does corresponds to the magnetic moment of neither a 5*f*<sup>2</sup> nor a 5*f*<sup>3</sup> configuration [833]. A significant amount of anisotropic 5*f*-ligand hybridization was reported [834]. Also, the measured specific heat  $\gamma = 60 \text{ mJ mol}^{-1}\text{K}^{-2}$  is not particularly small [835]. These contradictory observations demonstrate that the 5*f* behavior in URhAl is not yet understood.

In Fig. 3.86 we show the experimental Kerr spectrum [836] of URhAl together with the theoretical spectrum calculated using the itinerant LSDA approach [595]. The first spectral peak at 1 eV, and the second one at 2–3 eV in the Kerr angle are definitely reproduced in the theoretical spectrum. The theoretical Kerr rotation drops off between 4 and 5 eV, but it is not yet clear if this also occurs in the experimental  $\theta_{\rm K}$  spectrum. It can, nevertheless, be concluded that the itinerant 5*f* model explains the measured Kerr spectrum fairly well. Clearly, this supports the picture of delocalized 5*f* electrons in URhAl. The calculated electronic specific heat coefficient,  $\gamma$ = 41 mJ mol<sup>-1</sup>K<sup>-2</sup>, is quite reasonable since a many-body enhancement of 1.5 can be considered to be normal.

With respect to the signified intermultiplet transition, it could be speculated that the 5f's in URhAl divide into two groups, relatively delocalized, rather hybridized 5f's in the U–Rh plane, and more localized 5f's perpendicular to this plane, in accord with the observation of anisotropic f hybridization in

URhAl [834]. The possible intermultiplet transition might correspond to the localized 5f's, whereas Kerr spectroscopy in the polar geometry probes the MO response in the U–Rh plane.

In conclusion, we find that the MO Kerr spectra of UAsSe and URhAl can be excellently described by a LSDA band-structure approach to the 5f electrons.

## 3.2.5 UGa<sub>2</sub>

UGa<sub>2</sub> is one the most intensively studied intermetallic compounds of uranium with a non-transition metal. It is a ferromagnet with a Curie temperature of  $T_C$ = 125 K [837, 838]. There is a strong anisotropy of the paramagnetic susceptibility, with a much larger susceptibility along the easy direction [1120] than along the [0001] axis [837]. The magnetization isotherms below  $T_C$  are also very anisotropic. The magnetic moment, 2.7  $\mu_B/U$  was obtained from magnetization study [837, 838], which is close to 3.0  $\mu_B/U$ , determined from powder neutron diffraction study [839]. This large moment of about 3.0  $\mu_B/U$ , which is oriented along the [1120] direction in the basal plane, indicates that the 5*f* electrons are probably mainly localized at the uranium atomic sites.

The highly anisotropic magnetic susceptibility was analyzed on the basis of a  $5f^3$  (U<sup>3+</sup>)-crystalline electric field (CEF) scheme with exchange interaction [840]. The CEF interactions split the  ${}^{4}I_{9/2}$  multiplet into five doublets, with a overall CEF splitting of 713 K. This scheme explains well the temperature dependence of the magnetic susceptibility and produces the moment of 2.7  $\mu_B/U$  and the Curie temperature of 125 K.

There is also a suggestive report on the form factor obtained in polarized neutron scattering experiments, concluding that the uranium atoms are preferably in the U<sup>4+</sup> state, namely, the  $5f^2$  configuration, compared to the  $5f^3$  scheme but the observed form factor corresponds to a larger delocalization of the 5f electrons than that calculated in the Russel-Saunders coupling approximation [841].

In order to gain deeper understanding of the physical properties, it is essential to clarify the nature of the 5*f* electrons, namely, whatever they are localized or itinerant. The discussion is still controversial in the case of UGa<sub>2</sub>. Divis *et al.* [842] performed *ab initio* electronic structure calculations for UGa<sub>2</sub> using an optimized linear combination of atomic orbital method. Three separate calculations were done treating the uranium 5*f* states as band states and as localized states with occupation two and three, respectively. It was shown that the hybridization between itinerant 5*f* states and other valence states is rather small in comparison with intermetallics containing uranium and transition metals. The ferromagnetic ground state of UGa<sub>2</sub> originates entirely from 5*f* electrons which contribute almost 99 % to the calculated Stoner product. The uranium total magnetic moment which is obtained as a sum of spin  $(M_s = -1.52\mu_B)$  and orbital  $(M_l = 3.01\mu_B)$  magnetic moments underesti-

mates by factor two the experimental value. The calculated value of magnetocrystalline anisotropy (MAE) overestimates the experimentally obtained value by more than one order of magnitude. The Sommerfeld constant (from specific heat measurements) obtained from the itinerant ferromagnetic calculation exceeds the experimental value by a factor of 3.6. In the calculations assuming localized 5f behavior, a self-interaction correction for the 5f states was included. The anisotropic distribution of charge density in the crystal has been used to derive the crystal-field interaction, which splits the ground-state of two (three) localized 5f electrons into multiplets. The resulting CF parameters and the experimental value of the Curie temperature were then used to obtain the field dependence of the magnetization and the temperature dependence of the magnetic susceptibility. It was shown that such an approach provides fair comparability of the calculated values of total moments with experiment. The anisotropy of the magnetic susceptibility was slightly overestimated (strongly overestimated) in the case of  $5f^2$  ( $5f^3$ ) occupation. For both cases, the Sommerfeld constants are well below the experimental value.

To clarify the fundamental properties of UGa<sub>2</sub> a complex experimental and theoretical investigation was carried out recently by Honma *et al.* [843]. The electrical resistivity, elastic constants, thermal expansion coefficient, thermo-electric power, magnetic susceptibility and Hall coefficient indicate highly anisotropic properties, reflecting the hexagonal structure. They also performed the magnetoresistance and de Haas-van Alphen (dHvA) experiments to investigate the Fermi surface properties. Both data are very complicated, implying that the Fermi surface is a multiply-connected one. The cyclotron mass is rather light, ranging from 0.17 to 6.2  $m_0$ , which is consistent with the electronic specific coefficient of 5-11 mJ/K<sup>2</sup>mol. The dHvA measurements performed by Sakamoto *et al.* [844] also produces a rather small cyclotron masses about 0.2-3.3  $m_0$ .

We remark that most of the uranium compounds which order magnetically, have a moment of  $1-2 \mu_B/U$ . The magnetic moment of  $3 \mu_B/U$  in ferromagnetic state and a very low value of the electronic specific coefficient suggest that the 5f electrons in UGa<sub>2</sub> are localized at the uranium atomic site. Furthermore, the  $5f^2$  and  $5f^3$  configurations are easily distinguished by the experimental magnetoresistance data because UGa<sub>2</sub> is expected to be a compensated metal for  $5f^2$  and an uncompensated metal for  $5f^3$  as in LaGa<sub>2</sub>. But this simple description is, however, not applicable to the 5f-electron nature of UGa<sub>2</sub> [843]. The authors of Ref. [843] conclude that neither the localized  $5f^2$ - and  $5f^3$ -core models nor the spin-polarized 5f-itinerant band model can explain all the experimental data in UGa<sub>2</sub>. The results of the magnetoresistance are in agreement with the  $5f^3$ -core model, while the dHvA data are not explained by this model. On the other hand, the spin-polarized 5f-itinerant model is not consistent with either the magnetoresistance or dHvA data [843].

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*Figure 3.87.* Self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) calculated for UGa<sub>2</sub> in the LSDA approximation [845].

From the comparison among the various experimental and theoretical investigations listed above we can conclude that the nature of the 5f electrons in UGa<sub>2</sub> is not yet well established.

Another stringent test for the applicability of the itinerant LSDA approach to UGa<sub>2</sub> would be the description of the MO Kerr spectrum. The complex MO Kerr effect and optical reflectivity were studied experimentally with a UGa<sub>2</sub> single crystal over the 0.05 to 5.5 eV energy range in Ref. [846] in an external magnetic field applied normal to the sample surface. Rather large Kerr rotation and ellipticity spectra were found. A prominent peak in the Kerr rotation spectrum reaches  $-3^{\circ}$  around 0.5 eV and Kerr ellipticity is equal to  $1.5^{\circ}$  at 0.3 eV.

The fully relativistic spin-polarized LSDA energy band structure and total DOS of the ferromagnetic UGa<sub>2</sub> [845] is shown in Fig. 3.87. The bands in the lowest region between -10 and -7 eV have mostly Ga *s* character with a small amount of U *spd* character mixed in. The energy bands between -7 and -1 eV are predominantly Ga 4*p* states. The U 6*d* energy bands are located above and below  $E_F$  at about -0.9 to 7.0 eV. They are strongly hybridized with Ga 4*p* states. The characteristic feature of the LSDA band structure is a narrow peak of U 5*f*<sub>5/2</sub> states situated just at the Fermi level. U 5*f*<sub>7/2</sub> states are split off by strong SO coupling and form another narrow peak at 1.5 eV above  $E_F$ . It is important to note that U 5*f* states are situated in an otherwise low DOS region and hybridize only weakly with the Ga 4*p* and U 6*d* states. Because of this weak hybridization the width of the U 5*f*<sub>5/2</sub> peak is ~0.5 eV, which is smaller than both the SO splitting and the value of the on-site Coulomb repulsion U=2 eV.


*Figure 3.88.* Total (in states/(unit cell eV)) and partial (in states/(atom eV)) DOS of ThGa<sub>2</sub> calculated in the LSDA approximation [845].

In order to investigate the possible reason for very narrow of U 5f states in UGa<sub>2</sub> we performed calculations of the electronic structure of a model ThGa<sub>2</sub> compound keeping the lattice parameters and atomic sphere radii the same as for UGa<sub>2</sub> [845]. The valence band structure of ThGa<sub>2</sub> seems to provide a reasonable approximation for that of UGa<sub>2</sub> (with two localized 5f electrons) because the Th atom has two electrons less than U and the Th 5f states in ThGa<sub>2</sub> are above  $E_F$ . Fig. 3.88 shows the total and partial DOS of ThGa<sub>2</sub>. There is quite strong hybridization between Ga 4p and Th 6d electronic states. The Fermi level in this compound is situated in deep minimum of the DOS between Ga 4p and Th 5f and 6d states. The LSDA calculations position the 5f energy bands in UGa<sub>2</sub> at the Fermi level, therefore they do not overlap much with Ga 4p and U 6d states. It seems that from the LSDA point of view the possible localized behavior of U 5f electrons in UGa<sub>2</sub> is mainly caused by their very peculiar energy position which results in weak hybridization with other conduction states.

The energy band structure and total DOS of UGa<sub>2</sub> calculated within the LSDA+U approximation is shown in Fig. 3.89 [845]. The Coulomb repulsion splits partially occupied U  $5f_{5/2}$  states and the LSDA+U calculations give a solution with two localized 5f electrons. These localized 5f states are situated in the region of low DOS above the top of the Ga 4p bands and form a rather narrow peak at 0.5 eV below  $E_F$ . U 5f states just above the Fermi level are formed by the remaining  $5f_{5/2}$  states whereas the peak of  $5f_{7/2}$  states is pushed about 1 eV from its LSDA position.

Table 3.4 presents the comparison between calculated and experimental magnetic moments in UGa<sub>2</sub>. Powder neutron diffraction studies [839] reveal that the total magnetic moment on the U site is almost equal to 3.0  $\mu_B$ , while magnetization studies [837, 838] give 2.7  $\mu_B/U$ . The LSDA calculations do



*Figure 3.89.* Energy band structure and total DOS (in states/(unit cell eV)) calculated for UGa<sub>2</sub> in the LSDA+U approximation [845].

*Table 3.4.* The experimental and calculated [845] spin  $M_s$ , orbital  $M_l$ , and total  $M_t$  magnetic moments (in  $\mu_B$ ) of UGa<sub>2</sub>.

	LSDA	LSDA+U	LSDA[842]	LSDA+OP[843]	<i>exp</i> .[837]	exp.[839]
$M_s$	-2.08	-2.14	-1.52	-2.03	-	-
$M_l$	3.10	4.94	3.01	4.94	-	-
$M_t$	1.01	2.80	1.49	2.91	2.7	3.0

nor account for such a large magnetic moment (Table 3.4). The LSDA total magnetic moment on uranium in UGa<sub>2</sub> is equal to 1.01  $\mu_{\rm B}$  (Table 3.4) (with spin moment  $-2.08 \ \mu_{\rm B}$  and orbital moment  $3.10 \ \mu_{\rm B}$ ). The calculated moment is dominated by 5*f* states: the 5*f* components of the spin and orbital moment are  $-1.95 \ \mu_{\rm B}$  and  $3.04 \ \mu_{\rm B}$ , respectively. The LSDA+*U* calculations produce the total magnetic moment equal to 2.8  $\mu_{\rm B}$ ) in a good agreement with the experimental data (Table 3.4).

After consideration of the band structure we turn to the optical and magnetooptical spectra. In Fig. 3.90 we show the experimentally measured [846] optical reflectivity,  $\theta_K(\omega)$  and  $\epsilon_K(\omega)$  MO Kerr spectra of UGa<sub>2</sub>, as well as the spectra calculated with LSDA and LSDA+U approximations [845]. It can be seen that LSDA gives a better description of the optical reflectivity spectrum as well as the Kerr spectra of UGa<sub>2</sub> in the 0 to 1 eV energy interval. For higher energies the experimental Kerr rotation curve is situated someplace in between the curves obtained by the LSDA and LSDA+U approximations and overall agreement between theory and experiment became worse.



*Figure 3.90.* Calculated optical reflectivity, Kerr rotation and Kerr ellipticity spectra (in degree) for UGa<sub>2</sub> in the LSDA and LSDA+U approximations [845] compared with experimental data (circles) [846].

Although, the magnetic moment at the U site of UGa<sub>2</sub> is described better by the LSDA+U method, neither the localized LSDA+U model nor the spinpolarized LSDA 5f-itinerant band model can explain all the peculiarities of the experimental MO spectra in UGa<sub>2</sub>. The LSDA gives a better description of the optical and MO spectra of UGa<sub>2</sub> in the 0 to 1 eV energy interval, for higher energies the experimental Kerr rotation curve is situated someplace in between the curves obtained by the LSDA and the LSDA+U approximations. We conclude that the U 5f electrons in UGa<sub>2</sub> are occupied in an intermediate position between itinerant and localized character.

# 3.2.6 UPd<sub>3</sub>

UPd<sub>3</sub> is the only uranium based intermetallic compound in which 5f electrons are known to be localized, as determined by low-temperature specific heat [847] and inelastic neutron scattering [848, 849] data. This is also confirmed by dHvA measurements [850, 851] in which no orbits with heavy effective masses were found. According to photoemission spectroscopy (PES) experiments [852–854] localized U 5*f* electrons form a peak at binding energy of about -0.8 eV and there is no 5*f* spectral weight at the Fermi level. The study of the electronic structure of UPd<sub>3</sub> is interesting not only because of the localized character of 5*f* electrons but also because it can help to understand the intriguing properties of an isoelectronic uranium compound UPt<sub>3</sub> which exhibits a heavy fermion behavior and becomes superconducting at low temperatures. In U(Pd<sub>1-x</sub>Pt<sub>x</sub>)<sub>3</sub> alloys U 5*f* electrons remain localized for *x* smaller than 0.9 whereas a heavy quasiparticle peak develops at larger Pt concentrations. PES experiments [852] show that the U 5*f* peak shifts to higher

energies with the increase of Pt content and at x > 0.9 a second peak is formed just below the Fermi level indicating that 5f spectral weight appears at  $E_F$ .

The calculations of the electronic structure of UPd<sub>3</sub> performed using the local spin density approximation either for the experimentally observed dhcp or for fcc crystal structures [855–857] place partially occupied U 5*f* states exactly at the Fermi level and, thus, disagree qualitatively with the experimental data. Calculated cyclotron masses and the coefficient of the electronic specific heat are too high as compared to the experimental values. On the other hand, a reasonably good agreement between calculated and experimental angular dependence of dHvA frequencies is found in Ref. [858] in which two U 5*f* electrons were treated as core states. Recently, the electronic structure of UPd<sub>3</sub> has been calculated using self-interaction corrected (SIC) LSDA and a solution with two localized 5*f* electrons has been found [859].

**Electronic structure.** UPd<sub>3</sub> crystallizes in the hexagonal (dhcp) TiNi<sub>3</sub> type structure with the  $P6_3/mmc$  (No. 194) space group [860]. Each of two inequivalent U atoms occupying pseudo-cubic 2a ( $D_{3d}$ ) and hexagonal 2c ( $D_{3h}$ ) positions is surrounded by 12 Pd atoms, 6 of them being situated in the same and another 6 in the adjacent UPd<sub>3</sub> planes. The UPd<sub>3</sub> planes form *abac* sequence in *c* direction. The calculations were also performed for hcp and pseudo-cubic fcc-derived crystal structures with *abab* and *abc* stacking of UPd<sub>3</sub> planes, respectively. In these calculations the in-plane lattice constant and inter-plane spacing were kept the same as in the original dhcp structure which required application of small trigonal distortion to the fcc structure.

The effect of the Coulomb repulsion in the U 5*f* shell on the electronic structure of UPd<sub>3</sub> and UPd<sub>3-*x*</sub>Pt<sub>*x*</sub> have been studied in Ref. [135] by using the generalized LSDA+*U* method which takes into account that in the presence of spin-orbit coupling the occupation matrix of localized electrons becomes non-diagonal in spin indexes. The calculations were performed for U=2 eV derived from XPS measurements and J=0.5 eV.

The characteristic feature of the LSDA band structure of UPd<sub>3</sub> is a narrow peak of U  $5f_{5/2}$  states situated just at the Fermi level  $(E_F)$  1.5 eV above the top of Pd 4d states (Fig. 3.91). U  $5f_{7/2}$  states are split off by strong SO coupling and form another narrow peak 1 eV above  $E_F$ . It is important to note that U 5f states are situated in a low DOS region between Pd 4d and U 6d states [857, 856] and hybridize only weakly with the former. Because of this weak hybridization the width of the U  $5f_{5/2}$  and  $5f_{7/2}$  peaks is ~0.5 eV which is smaller than both the SO splitting and the value of their on-cite Coulomb repulsion U=2 eV derived from XPS and BIS spectra [854]. LSDA calculations performed for UPd<sub>3</sub> in fcc and hcp structures also place the U  $5f_{5/2}$  states just at  $E_F$ ; the width of the peak being almost the same as for dhcp UPd<sub>3</sub> [135]. It seems that from the LSDA point of view the localized



*Figure 3.91.* Band structure and the total DOS (in states/(unite cell eV)) of dhcp UPd<sub>3</sub> calculated using LSDA method [135].

behavior of U f electrons in UPd<sub>3</sub> is mainly caused by their very peculiar energy position which results in the weak hybridization with other conduction states.

The calculated occupation of U 5f states (2.924 for pseudo-cubic and 2.955 for hexagonal sites; see Table 3.5) is significantly larger than one would expect for U ion with  $f^2$  configuration. One can note, however, that apart from the two peaks of U 5f states at  $E_F$  there is a significant U 5f contribution to the DOS in the energy range between -6 and -2 eV which shows an energy dependence similar to that of Pd 4d DOS [135]. These states are apparently the so-called "tails" of Pd 4d states and arise as a result of the decomposition of the wave function centered at Pd atoms inside U atomic spheres. It is worth reminding that in ASA based calculations partial charges are defined as integrals of electron density over the volume of the AS surrounding the atom. In order to estimate the share of the Pd 4d "tails" in the calculated U 5f charges the calculations of the electronic structure of a model ThPd<sub>3</sub> compound keeping the lattice parameters and atomic sphere radii the same as for UPd<sub>3</sub> have been performed [135]. The band structure of ThPd<sub>3</sub> seems to provide a reasonable approximation for that of  $UPd_3$  with two localized 5f electrons because Th atom has two valence electron less than U and Th 5f states in ThPd<sub>3</sub> are above  $E_F$ .

Calculated Th and U partial charges are summarized in Table 3.5. The densities of Th 4d and 5f and Pd 4d states calculated for ThPd<sub>3</sub> in distorted fcc, dhcp, and hcp crystal structures. For all three structures the peak of atomic-like Th 5f states appears above  $E_F$  whereas the occupied Th states of f character are the above mentioned "tails" of predominantly Pd 4d states. Nevertheless, they sum up to give the 5f occupation of 0.9 electron inside Th sphere; most of it being acquired in the energy range below 8 eV corresponding to the top of Pd 4d DOS. It is interesting to note that the difference between f charges in and ThPd<sub>3</sub> in different crystal structures.[135]

structure	Th $d$	Th $f$	U $d$	U $f$	U $f-\operatorname{Th} f$
fcc	1.759	0.900	1.723	2.997	2.097
dhcp (cub)	1.802	0.877	1.804	2.924	2.046
dhcp (hex)	1.778	0.886	1.756	2.955	2.069
hcp	1.824	0.879	1.824	2.893	2.014

Table 3.5. The comparison of d and f charges in U and Th atomic spheres calculated for UPd<sub>3</sub>



*Figure 3.92.* Band structure and the total DOS (in states/(unite cell eV)) of dhcp UPd<sub>3</sub> calculated using LSDA+U method with spherically averaged U and J [135].

U and Th spheres is only slightly larger than 2, i.e., the occupied part of the U  $5f_{5/2}$  peak found at  $E_F$  in UPd<sub>3</sub> contains exactly the number of 5f electrons which, according to available experimental data, is supposed to be localized.

The results of LSDA calculations (see Fig. 3.91) with U 5f states forming the huge peak just at  $E_F$  contradict drastically the available experimental data which show that the electronic states at the Fermi level have relatively low effective masses whereas the U 5f states are localized and situated according to the XPS data [852, 861] at about 0.7 eV below  $E_F$ . This discrepancy between the calculations and experimental data is apparently due to the underestimation of the Coulomb repulsion between rather localized 5f electrons.

The energy bands calculated for UPd3 in experimentally observed dhcp crystal structure using spherically averaged Coulomb matrix elements are shown in Fig. 3.92. The bands below -1 eV are formed mainly by Pd 4d electrons hybridized at the bottom of the valence band with Pd 5s states. Occupied U 5f states with  $m_i = -5/2$  and -3/2 produce almost dispersionless bands at about -0.8 eV which is close to the binding energy of one of the bands ascribed to the localized U 5f electrons in ARPES measurements [853]. However, in contrast to the experimental data in which three groups of flat bands separated by  $\sim 0.3 \text{ eV}$  were observed, only one bunch of  $5f_{5/2}$  bands is found in the calculations. The remaining  $5f_{5/2}$  states form "spaghetti" of bands centered at about 0.5 eV above  $E_F$ . The bands located in the energy window between the split by the on-cite Coulomb interaction  $5f_{5/2}$  states show the dispersion very similar to the dispersion of the bands crossing the Fermi level in dhcp ThPd<sub>3</sub>. It is worth mentioning, that the Fermi surface cross-sections obtained from LSDA calculations for dhcp ThPd<sub>3</sub> reproduce very well those derived from the ARPES experiment [853].

The abovementioned self-consistent LSDA+U solutions are magnetic with a rather large U magnetic moment. This contradicts to the experimental data which show that the ordered magnetic moment in UPd<sub>3</sub> is only 0.01  $\mu_B$  per U atom [862]. This extremely small U magnetic moment is explained by the fact that according to a crystalline electric field (CEF) levels scheme derived from neutron scattering experiments the lowest CEF level of U<sup>4+</sup> ion in both hexagonal and quasi-cubic sites is a singlet [863] which leads to a nonmagnetic ground state of UPd<sub>3</sub>. LSDA+U is still a one electron approximation and can not fully account for the subtle many-body effects responsible for the small value of U magnetic moment in UPd<sub>3</sub>. It tries to obey the Hund's rules in the only way it is allowed to, i.e. by producing a magnetic solution. A possible way to overcome this discrepancy between the calculations and the experiment is to force a nonmagnetic ground state in LSDA+U calculations as it was done by H. Harima *et al* in Refs. [136, 862]. We have verified, however, that this leads to an increase of the total energy as compared to magnetic calculations.

In order to study the effect of Pt doping on the electronic structure of  $UPd_{3-x}Pt_x$  alloys the LSDA and LSDA+U calculations for model  $UPd_{1.5}Pt_{1.5}$  compound in dhcp and hcp crystal structures have been performed in Ref. [135]. The lattice constants and sphere radii in these calculations were kept the same as for UPd<sub>3</sub>. The desired composition was obtained by replacing one of inequivalent Pd atoms by Pt accompanied in the case of hcp structure by lowering the crystal symmetry to  $P\bar{6}m2$ . This results in an alloy which consists of alternating UPd<sub>3</sub> and UPt<sub>3</sub> planes forming *abc* or *abab* sequences along the crystallographic *c* direction. Two different compounds with the dhcp structure can be produced in this way. From the comparison of the LSDA total energies it was found that Pt substitution into the planes containing U atoms with the hexagonal local symmetry is more favorable and in the following only this compound will be considered.

The LSDA density of U 5*f* states in dhcp UPd<sub>1.5</sub>Pt<sub>1.5</sub> is similar to UPd<sub>3</sub> one. However, Th *f* charges calculated for a reference ThPd<sub>1.5</sub>Pt<sub>1.5</sub> compound show an average increase of 0.09 electrons as compared to ThPd<sub>3</sub> because of larger spatial extent of Pt 5*d* states. In UPd<sub>3-x</sub>Pt<sub>x</sub> alloys this leads to increased screening of the localized U 5*f* electrons which is confirmed by LSDA+U

calculations for dhcp and hcp UPd<sub>1.5</sub>Pt<sub>1.5</sub>. It was found a shift of two localized U 5*f* states from -0.8 to -0.6 eV going from UPd<sub>3</sub> to UPd<sub>1.5</sub>Pt<sub>1.5</sub>. This shift is apparently caused by stronger screening of the localized states by the part of *f* electron density coming from the *d* "tails" which increases due to larger contribution of extended Pt 5*d* states. The increased screening manifests itself in a 0.5 eV increase of  $\varepsilon_{\nu}$  for U 5*f* electrons upon Pt substitution. U *f* charge calculated for dhcp UPd<sub>1.5</sub>Pt<sub>1.5</sub> is 0.06 of an electron larger than in UPd<sub>3</sub>. The excessive charge is provided by the small increase of the occupation numbers of 5*f* states lying above the Fermi level.

Substitution of all Pd atoms by Pt leads to a further increase of Th f charge up to 1.061 in hcp ThPt<sub>3</sub>. Due to stronger screening by the density of the "tail"-like f electrons, the center of gravity of the occupied U  $5f_{5/2}$  states in UPt<sub>3</sub> obtained from LSDA+U calculations is pushed even closer to  $E_F$  as compared to hcp UPd<sub>1.5</sub>Pt<sub>1.5</sub>. As a result of the shift the bands originating from U  $|\frac{5}{2}, -\frac{3}{2}\rangle$  states start to cross the Fermi level and these states become only partially occupied with the occupation equal to 0.894.

Summarizing the results of LSDA+U calculations, the following scenario seems to provide a plausible explanation for the dependence of the binding energy of U f-derived peak in  $UPd_{3-x}Pt_x$  alloy on the Pt content observed in resonant PES experiment [852]. Because of larger spatial extent of Pt 5d wave function, an increase of the number of Pt nearest neighbors surrounding U atom upon Pt substitution causes a proportional increase of the part of felectron density at U site provided by the "tails" of Pd and Pt d states. The screening of the localized U 5f states by this delocalized density becomes stronger and they shift to higher energy. The change of the structure from dhcp to hcp, which occurs gradually for x between 1 and 2, provokes the increase of the density of band states below  $E_F$ , clearly seen from the results of the LSDA calculation for ThPd<sub>3-x</sub>Pt<sub>x</sub>, and a downward shift of the Fermi energy. In the PES experiment this manifest itself in an additional decrease of the binding energy of U 5f electrons. In Fig. 3.93 U 5f DOS calculated for  $UPd_xPt_{3-x}$ with x=0, 1.5, and 3 using the LSDA+U method are compared to the resonant PES spectra from Ref. [852]. The LSDA+U results reproduce quite well the observed shift of the U 5 f peak position towards the Fermi level with increased Pt content in the alloy. Considering the calculated density of unoccupied U 5 fstates we can suppose that if the proposed mechanism is correct a shift of a U 5 f derived peak away from  $E_F$  should be observed in BIS spectra.

**Optical and MO spectra.** After consideration of the band structure and PE spectra of UPd<sub>3</sub> we turn to the optical spectra. The optical reflectivity experiments have been conducted by Schoenes and Andres on single crystals of UPd<sub>3</sub> [864] in 0.03 to 12 eV energy interval. The optical conductivity spectra  $\sigma_{xx}(\omega)$  and imaginary part of the energy-loss function Im $[-1/\varepsilon(\omega)]$  were de-



*Figure 3.93.* The comparison of U 5*f* DOS calculated for UPd<sub>x</sub>Pt<sub>3-x</sub> using the LSDA+*U* method [135] to the resonant PES spectra (dotted lines) from Ref. [852]. DOS calculated for hcp and dhcp structures are shown by solid and dash-dotted lines, respectively.



*Figure 3.94.* Calculated optical reflectivity  $R(\omega)$ , diagonal part of the optical conductivity  $\sigma_{xx}(\omega)$ , and imaginary part of the energy-loss function Im $[-1/\varepsilon(\omega)]$  of ThPd<sub>3</sub> in the LSDA approach compared with the experimental data (open circles) [864].

rived from the reflectivity data using the Kramer-Kronig transformation. They also measured the optical spectra of polycrystalline ThPd<sub>3</sub> as a reference material.



*Figure 3.95.* Calculated optical reflectivity  $R(\omega)$  and diagonal part of the optical conductivity  $\sigma_{xx}(\omega)$ , of UPd<sub>3</sub> in the LSDA and LSDA+U approximations compared with the experimental data (open circles) [864].

Fig. 3.94 shows with the calculated optical reflectivity  $R(\omega)$  and diagonal part of optical conductivity  $\sigma_{xx}(\omega)$  and imaginary part of the energy-loss function Im $[-1/\varepsilon(\omega)]$  of ThPd<sub>3</sub> compared with the experimental data [864]. To incorporate the intraband contribution to the optical conductivity tensor it was used the phenomenological Drude model with intraband Drude relaxation time  $\gamma_D = 0.1$  eV. As can be seen, theory in LSDA and experiment agree very well. The predominant structure of the ThPd<sub>3</sub> reflectivity spectrum is the edge at 0.7eV. This sudden drop is due to a plasma oscillation interfering with interband excitations. The energy of the conduction electron plasma resonance in the presence of the interband excitations is given by  $\varepsilon_{1xx}(\omega)=0$ . In the particular case of ThPd<sub>3</sub> this condition is fulfilled at  $\hbar\omega$ = 0.7 eV. The LSDA theory produce a correct energy position of the plasma resonance in ThPd<sub>3</sub> (upper panel of Fig. 3.94). Above 3 eV theory gives a slightly larger reflectivity in comparison with experimental measurements. One of the possible reasons for this is a non-ideal sample surface, its roughness could reduce the optical reflectivity above 3 eV. As a result the experimental optical conductivity spectrum which has been derived from the reflectivity data through the Kramers-Kronig transformation has a lower intensity in comparison with the theoretical calculations (Fig. 3.94).

Fig. 3.95 shows the calculated optical reflectivity and conductivity spectra of UPd<sub>3</sub> compared with the experimental data [864]. Calculations were performed using both the LSDA and LSDA+U approximations. The intraband optical transitions in Drude form with inverse intraband Drude relaxation time  $\gamma_D = 0.1$  eV have been also included. This picture clearly demonstrates that



*Figure 3.96.* Decomposition of the complex polar Kerr spectra of UPd<sub>3</sub> in separate contributions. The left panel: calculated real and imaginary part of the off-diagonal optical conductivity function,  $\omega \sigma_{xy}$  (in 10<sup>20</sup> s<sup>-2</sup>). The middle panel: The imaginary and real part of  $[\omega D]^{-1}$ . The righ panel: The Kerr rotation and ellipticity spectra (in degrees) which results as a product of  $[\omega D]^{-1}$  and  $\omega \sigma_{xy}$ .

the better description is unambiguously given by the LSDA+U approach. The most prominent discrepancy in the LSDA spectra is the extra peak between 0 and 1 eV in the optical conductivity spectrum caused by interband transitions involving the hybridized 5f states, which in the LSDA approach exhibit a maximum resonance near  $E_F$ . In the LSDA+U approach, the occupied 5f state energies are shifted downward due to the on-site Coulomb interaction  $U_{eff}$ . As a result, the transitions involving the occupied 5f states do not take place at small photon energies, and the erroneous peak structure around 0 to 1 eV disappears from the optical conductivity spectrum.

The theoretically calculated optical conductivity and reflectivity spectra of  $UPd_3$  are larger above 3 eV in comparison with experimental measurements. The reason is possibly the same as it was in the case of  $ThPd_3$  - a non-ideal sample surface, which roughness could reduce the optical reflectivity above 3 eV.

After consideration of the band structure and optical properties we turn to the magneto-optical spectra. As we mentioned above, UPd<sub>3</sub> has a nonmagnetic ground state (the ordered magnetic moment is only 0.01  $\mu_B$  per U atom [862]) because the lowest crystalline electric field level of U<sup>4+</sup> ion in both hexagonal and quasi-cubic sites is a singlet [863]. Therefore Kerr rotation angle in UPd<sub>3</sub> is expected to be very close to zero. Although in an external magnetic field one would expect a nonzero Kerr effect.

Fig. 3.96 presents the theoretically calculated polar Kerr effect using the LSDA+U approach which gives a ferromagnetic solution for UPd<sub>3</sub>. To an-

alyze the nature of Kerr rotation we present in Fig. 3.96 also the separate contributions to the Kerr rotation and ellipticity spectra from both the numerator, i.e.,  $\sigma_{xy}(\omega)$  and the denominator,  $D(\omega) \equiv \sigma_{xx}(1 + \frac{4\pi i}{\omega}\sigma_{xx})^{1/2}$ , which factor together to give the Kerr effect in UPd<sub>3</sub>. The predominant structure of the UPd<sub>3</sub> reflectivity spectra is the edge at 0.7 eV. The existence of a narrow and strong plasmon peak at 0.7 eV leads to strong resonance structure in the inverse denominator  $[\omega D]^{-1}$  (middle panel of Fig. 3.96) at the same energy. On the other hand, the value of the off-diagonal optical conductivity  $\sigma_{xy}(\omega)$  is rather small at this particular energy. Therefore the large Kerr rotation and ellipticity at 0 to 1 eV results mostly due to a deep resonance structure of the denominator. On the other hand, the shape of Kerr rotation and ellipticity spectra beyond the plasma edge, i.e. above 1 eV almost completely determined by the shape of off-diagonal optical conductivity spectrum  $\sigma_{xy}(\omega)$  (Fig. 3.96). This page intentionally left blank

# Chapter 4

# XMCD PROPERTIES OF *d* AND *f* FERROMAGNETIC MATERIALS

In the following, results of recent theoretical investigations on the MXCD in various representative transition metal, 4f, and 5f systems will be presented. All these investigations deal with exclusively with the circular dichroism in x-ray absorption assuming a polar geometry.

Before dealing with the theory of x-ray MO effects some comments of the XMCD spectroscopy seem to be appropriate. The first successful experimental XMCD investigations on transition metals have been done at the K edges of 3d elements [28] and the  $L_{2,3}$  edges of 5d elements [865]. These experiments in the energy range of around 7 and 15 keV, respectively, could be done in the transmission modes using film or powder samples without any special vacuum equipment. For the  $L_{2,3}$  edges of 3d elements at around 800 eV a number of technical problems had to be solved before the first investigations could be performed [9]. Among these the most serious one seems to be the detection method. While the transition mode supplies the most direct and reliable measure for the absorption coefficient it is applicable in the soft x-ray regime only if extremely thin samples can be prepared [9]. The alternative techniques, total electron yield and sample current detection give essentially the same spectrum but the corresponding signal is not strictly proportional to the absorption coefficient. In addition, they are surface sensitive because of the limited information depth of the secondary electrons. Fluorescence yield detection, on the other hand, is not surface sensitive but again supplies a signal that is not strictly proportional to the absorption coefficient. In addition, one has to note that experimental conditions may influence the intensify ratio of the  $L_{2,3}$  edges and therefore hamper or prevent a reliable application of the XMCD sum rules [866].

#### 4.1 3*d* metals and compounds

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At the core level edge XMCD is not only element-specific but also orbital specific. For 3d transition metals, the electronic states can be probed by the K,  $L_{2,3}$  and  $M_{2,3}$  x-ray absorption and emission spectra. The experimental investigations at the K edge of 3d transition metals are relatively unproblematic to perform. Because dipole allowed transitions dominate the absorption spectrum for unpolarized radiation, the absorption coefficient  $\bar{\mu}_K(E)$  reflects primarily the DOS of unoccupied 4p-like states of 3d transition metals. The corresponding matrix elements for the  $1s_{1/2} \rightarrow 4p_{1/2,3/2}$  transitions increase monotonically by nearly a factor 3 over the displayed range of energy in pure Fe and Ni [9]. Therefore there is no strict one-to-one correspondence  $\mu_K(E)$ and  $N_p(E)$ . Because of the extremely small exchange splitting of the initial 1s state the exchange and spin-orbit splitting of the final 4p-states that is responsible for the observed dichroism at the K edge. For this reason the dichroism in the terms of the difference in absorption  $\Delta \mu_K = \mu_K^+ - \mu_K^-$  for left and right circularly polarized radiation  $R_K = \Delta \mu_K / (2\bar{\mu}_K)$  is found to be only of order of 1%, being higest directly at the absorption adge [9].

Apart from the studies of XMCD spectra at the *K* edge on the pure elements Fe [28, 867–872], Co [872, 867], and Ni [870, 872], many different systems have been investigated so far. *K* edge studies supply valuable additional information, for example, on the exchange coupling in compounds (Mn in PtMnSb [867], Fe in Fe<sub>3</sub>Pt, FePt and FePt<sub>3</sub> [873], Fe<sub>2</sub>R with R= Ce, Sm, Gd, Tb, Tm, Lu [874], Fe<sub>2</sub>Gd [875], Fe<sub>n</sub>Gd<sub>m</sub> [874], Nd<sub>2</sub>Fe<sub>14</sub>B [870], Ce<sub>2</sub>Fe<sub>17</sub>H<sub>x</sub> [876], alloys (Fe and Co in Fe<sub>x</sub>Co<sub>1-x</sub> [867, 877], Fe and Ni in Fe<sub>x</sub>Ni<sub>1-x</sub>) [878], Fe in Fe<sub>x</sub>Pt<sub>1-x</sub> [867, 879] and multilayer systems (Fe in Fe/Co [877], Fe/Cu [880, 881], Fe/La [868], Fe/Ce [868], Fe/Nd [882, 883], Fe/Gd [884], Co in Co/Cu [880, 880, 885], Cu in Co/Cu [880, 881, 885], Fe/Cu [880, 881].

In contrast to the K edge, the dichroism spectra at the  $L_2$  and  $L_3$  edges are also influenced by the spin-orbit coupling of the initial 2p core states. In general, it gives rise to a very pronounced dichroism even if the local spinpolarization of the absorbing atom is rather small [9]. This was first demonstrated for the  $L_{2,3}$  spectra of 5d transition metals dissolved substantially in Fe [9]. In these systems a relative difference in absorption for left and right circularly polarized radiation  $R_{L_{2,3}}$  of up to 20% has been found. The first experimental investigation of XMCD at the  $L_{2,3}$  edge of pure Ni have been done by Chen *et al.* [31]. Many different systems have been investigated experimentally so far, such as various diluted and concentrated alloy systems (Fe in Fe<sub>x</sub>Pd<sub>1-x</sub> [886], Co in Co<sub>x</sub>Pd<sub>1-x</sub> [886], Ni in Ni<sub>x</sub>Pd<sub>1-x</sub> [886], Cr, Mn, Fe and Co in Ni [887]), compounds and multilayer systems (Fe and V in Fe/V [888, 889], Co in Co/Ni, Co/Pd, Co/Pt [890], Co and Cu in Co/Cu [506]). Ab initio calculations of the XMCD spectra of Fe, Co, and Ni at the K and  $L_{2,3}$  edges have been carried out by a number of researches [891, 892, 277, 893–897, 9]

In the following two sections the results of theoretical investigations on the XMCD in some representative transition metal systems will be presented in details. They are transition-metal alloys consisting of a ferromagnetic 3d element and Pt atom and Fe<sub>3</sub>O<sub>4</sub> and Mn-, Co-, or Ni-substituted magnetite. The later belongs to a strongly correlated system.

## 4.1.1 XPt<sub>3</sub> Compounds (X=V, Cr, Mn, Fe, Co and Ni).

Transition-metal alloys consisting of a ferromagnetic 3d element and Pt have drawn attention over the last years due to their wide variety of magnetic properties. In these intermetallic compounds, the Pt sites have induced magnetic moments due to the hybridization with the transition metal spin-polarized 3d states. The contribution of the orbital moment to the total moment on the Pt sites is expected to be important because the Pt atom is so heavy (atomic number Z=78) that the spin-orbit coupling of the Pt 5d electrons is fairly large (coupling constant  $\zeta_{5d}$ =0.5 eV). The 3*d*-Pt system also was found to have a good magneto-optical (MO) properties (see, e.g., Ref. [294-296]). Especially multilayers of Co and Pt or Pd are at present intensively studied because of their potential application as optical storage material in MO storage devices [297, 298]. Besides being of interest in applications, transition-metal platinum alloys XPt<sub>3</sub> and X<sub>3</sub>Pt are interesting because the 3d electronic states in the former compounds have less direct overlap and are expected to be more localized relative to the 3d states in the X<sub>3</sub>Pt materials. Also of interest is how the filling of the 3d band across the series affects the hybridization with the Pt 5d states and how this in turn affects the Pt spin and orbital moments.

The electronic structure, magnetic and MO properties of XPt<sub>3</sub> compounds have been investigated intensively both theoretically and experimentally. We briefly review the rather extensive number of studies below. Several band structure calculations within the local spin density approximation have been performed. Kübler calculated the spin magnetic moment of VPt<sub>3</sub> using the augmented spherical wave (ASW) method [898]. The electronic structure of several ordered phases of the Fe–Pt system, namely, Fe<sub>3</sub>Pt, FePt<sub>3</sub>, Fe<sub>2</sub>Pt<sub>2</sub>, and Fe<sub>3</sub>Pt<sub>5</sub> have been investigated by Podgorny using the LMTO method [899]. Spin-polarized band structures of MnPt<sub>3</sub> and FePt<sub>3</sub> were reported by Hasegawa [900]. Tohyama *et al.* studied the systematic trends in the electronic structure and magnetic moments of XPt<sub>3</sub> (X= Ti, V, Cr, Mn, Fe, and Co) based on their tight-binding calculations [901]. Suda *et al.* carried out APW band calculations for FePt<sub>3</sub> in the non-magnetic an anti-ferromagnetic phases [902]. Their calculated local magnetic moment at the Fe site agrees well with experiment. Shirai *et al.* performed spin-polarized band structure calculations

for XPt<sub>3</sub> (X=V, Cr, Mn, Fe, Co) using the scalar-relativistic version of the LAPW method [903]. They obtained good agreement between their calculated and the experimental spin magnetic moment at the transition metal site. On the other hand, the calculated spin moment of Pt atom differs significantly from the observed magnetic moment due to neglect of the spin-orbit interaction. The self-consistent band structure calculations of Fe<sub>3</sub>Pt were performed using a spin-polarized, scalar relativistic full-potential LAPW method in Ref. [904] to calculate the magnetic Compton profile. The orbital and spin magnetic moments of the  $Cu_3Au$ - type transition metal intermetallics XPt<sub>3</sub> (X= V, Cr, Mn, Fe, and Co) have been evaluated using the full-potential LAPW method with the spin-orbit interaction as a perturbation [905]. The calculation reproduced the experimental trend of the orbital and spin moments well. The orbital moment of Pt in CoPt<sub>3</sub> is, however, underestimated by a factor of about two. Energy band structure calculations for XPt<sub>3</sub> (X= V, Cr, Mn, Fe, Co) were performed in Ref.s [400, 906] to investigate their MO properties by means of relativistic ASW and LMTO methods using the local spin density approximation. The electronic structure, optical conductivity tensor and MO spectra of CoPt<sub>3</sub> and Co<sub>3</sub>Pt along with some other multilayered Co/Pt structures have been investigated experimentally and theoretically in Ref. [514].

Recently, Maruyama et al. measured magnetic circular x-ray dichroism for CrPt<sub>3</sub>, MnPt<sub>3</sub>, CoPt<sub>3</sub>, and ferromagnetic Fe<sub>3</sub>Pt and obtained an interesting variation in the orbital and spin magnetic moments on the Pt sites [907, 908]. The spin magnetic moment of Pt in CrPt<sub>3</sub> almost vanishes and the orbital moment is about  $-0.1 \mu_B$ , antiferromagnetically coupled with the Cr magnetic moment. On the other hand, the orbital moment of Pt in MnPt<sub>3</sub> vanishes almost completely and a small but positive spin component (of the order of 0.1  $\mu_B$  parallel to the transition metal moment) contributes to the Pt moment. In CoPt<sub>3</sub> and Fe<sub>3</sub>Pt, the Pt orbital and spin components are positive and relatively larger (in the range 0.1 to 0.3  $\mu_B$ ). Magnetic circular dichroism in the x-ray absorption spectrum in the 2p-3d excitation region of the transitionmetal element was also measured for ferromagnetic Cu<sub>3</sub>Au-type alloys, MnPt<sub>3</sub> , Fe<sub>3</sub>Pt and CoPt<sub>3</sub> in Ref. [399]. The x-ray magnetic circular dichroism and Faraday effect were studied in ordered and disordered Fe<sub>3</sub>Pt at K- and  $L_3$ edges in Ref. [909]. Angle dependent XMCD experiments have been performed at both Co and Pt  $L_{2,3}$  edges in two epitaxial (111) CoPt<sub>3</sub> thin films grown at 690 and 800K [910]. The analysis of the angular variations of the 3d orbital magnetic moment shows a strong perpendicular magnetocrystalline anisotropy (PMA) for the film grown at 690 K. It was related to the existence of anisotropic chemical local order yielding the formation of microscopic Corich and Co-poor planar local regions. In contrast, films grown above 800 K possess no PMA. These changes were correlated to their isotropic fcc structure of  $L1_2$  type. The MCD spectrum of ferromagnetic CoPt<sub>3</sub> was observed in

the photon energy range of 50 to 80 eV in Ref. [911]. MCD spectrum in the Pt  $N_{6,7}$  ( $4f \rightarrow 5d$ ) region shows very unusual features. This MCD spectral shape deviates significantly from the one expected by considering the conventional selection rule of the dipole transition. It was shown in the frame of the Anderson impurity model that the unusual line shape of the MCD is caused by a strong interference (Fano effect for resonant photoemission). X-ray Faraday rotation - the dispersive analogue of XMCD - has been measured near the platinum *L* edge of ferromagnetic disordered Fe<sub>3</sub>Pt [912].

The electronic structure, spin and orbital magnetic moments and XMCD spectra of the series XPt<sub>3</sub>, X= V, Cr, Mn, Fe, Co, Ni and X<sub>3</sub>Pt (X= Fe, Co, Ni) reported in Ref. [913]. The XAS and XMCD spectra were calculated at K,  $L_{2,3}$  and  $M_{2,3}$  edges for transition metals and  $L_{2,3}$ ,  $M_{2,3}$ ,  $M_{4,5}$ ,  $N_{2,3}$ ,  $N_{4,5}$ ,  $N_{6,7}$  and  $O_{2,3}$  edges at Pt sites.

**Magnetic moments.** Orbital and spin magnetic moments are determined by the interplay of hybridization, exchange, and Coulomb interactions, crystalfield and spin-orbit coupling. Table 4.1 presents the calculated spin  $(M_s)$  and orbital  $(M_l)$  magnetic moments in XPt<sub>3</sub> and X<sub>3</sub>Pt compounds. Our calculated results are in good agreement with those from the FLAPW calculations by Iwashita *et al.* [905]. The variation in the spin and orbital magnetic moments calculated inside the 3d transition metal and Pt atomic spheres in the  $XPt_3$ intermetallics is compared with the experimentally measured moments in Fig. 4.1. The magnetic moments of the  $XPt_3$  alloys were studied experimentally through neutron-scattering experiments already years ago [395, 914]. These experiments showed that CoPt<sub>3</sub> and MnPt<sub>3</sub> are ferromagnets, while CrPt<sub>3</sub> and VPt<sub>3</sub> are ferrimagnets, and FePt<sub>3</sub> is an anti-ferromagnet. The calculated spin magnetic moments of CoPt<sub>3</sub> and MnPt<sub>3</sub> at the 3d site are in good agreement with the experiment, and for CrPt<sub>3</sub> and VPt<sub>3</sub> the ferrimagnetic structure is in accordance with experiment, but the values of the moments are less accurately reproduced. Due to band filling, linear and symmetric behavior centered at MnPt<sub>3</sub> is clearly seen in the spin magnetic moments on the 3d transition metal sites (Fig. 1(a)).

The characteristic feature of the electronic structure of XPt<sub>3</sub> compounds is the strong hybridization of transition metal 3*d* and Pt 5*d* states, the later being much more delocalized. Fig. 4.2 shows the spin- and site-projected densities of the electronic states (DOS) for the transition metal site and the Pt site in XPt<sub>3</sub> compounds. Strong spin-orbit interaction in the Pt atomic sphere results in splitting of  $d_{3/2}$  and  $d_{5/2}$  states with the energy difference between their centers being ~1.5 eV. Inside the X atomic spheres the effect of the spin-orbit coupling is much weaker than the effect of the exchange field. The centers of both Pt  $d_{3/2}$  and  $d_{5/2}$  states lie at lower energies than the centers of the corresponding X *d* states. As a result of the X *d* – Pt *d* hybridization, the electronic



*Figure 4.1.* Theoretically calculated spin (a) and orbital (b) magnetic moments on the Pt sites (open circles) and X sites (open squares) [913] in comparison with the experimental data for XPt<sub>3</sub> and Fe<sub>3</sub>Pt compounds. The experimental Pt orbital moments (solid circles) for X= Cr, Mn and Fe are from Ref. [908], Co orbital (solid square) and Pt orbital for CoPt<sub>3</sub> are from Ref. [910], the experimental spin magnetic moments on X sites (solid squares) are from Ref. [395] and on Pt sites (solid circles) from Ref. [389].

states at the bottom of the valence band are formed mainly by Pt states while the states in the vicinity of the Fermi level  $(E_F)$  have predominantly transition metal d character with an admixture of Pt d states. The hybridization with the exchange split X d states leads to a strong polarization of Pt d states near  $E_F$ . The resulting difference in occupation numbers for Pt states with the opposite spin projections gives rise to the appearance of a comparatively large spin magnetic moment at the Pt site. A large energy splitting between the spin-up and spin-down bands is found only for states with predominant 3d character. The minority-spin 3d states form rather narrow bands located near the top of the Pt d band in XPt<sub>3</sub> compounds. It is definitely seen in Fig. 4.2 that, as one proceeds from the lighter to heavier 3d elements, the spin-up 3d band is first filled up to MnPt<sub>3</sub> and then electrons start to occupy the spin-down 3d band.

		X at	tom	Pt ato	om
	Х	$M_S$	$M_L$	$M_S$	$M_L$
	V	1.3751	0.0141	-0.0509	-0.0276
	Cr	2.6799	0.1789	-0.0300	-0.0558
XPt <sub>3</sub>	Mn	3.6985	0.0239	0.1244	-0.0014
	Fe	3.1370	0.1004	0.3045	0.0534
	Со	1.7079	0.0401	0.2384	0.0486
	Ni	0.4379	-0.0770	0.0780	0.0305
	Fe	2.5062	0.0870	0.2889	0.0522
X <sub>3</sub> Pt	Co	1.6379	0.0786	0.3153	0.0687
	Ni	0.5178	0.0198	0.2343	0.0866

*Table 4.1.* Calculated spin  $M_S$  and orbital  $M_L$  magnetic moments (in  $\mu_B$ ) of XPt<sub>3</sub> and X<sub>3</sub>Pt compounds [913].

This explains the linear and symmetric behaviors in the spin moments of the 3d atoms mentioned above.

The Pt spin moment reflects hybridization of the Pt 5*d* states with the 3*d* bands. At the beginning of 3*d* series (VPt<sub>3</sub> and CrPt<sub>3</sub>) and at the end (NiPt<sub>3</sub>) the spin magnetic moment at Pt sites is very small. The spin-up 3*d* bands in MnPt<sub>3</sub>, FePt<sub>3</sub>, and CoPt<sub>3</sub> are nearly filled, therefore the spin-down hole in the Pt *d* states mixes with the empty 3*d* bands. Due to stronger hybridization between the Pt *d* states and the empty 3*d* bands in FePt<sub>3</sub> and CoPt<sub>3</sub> (Fig. 4.2) the Pt spin moments are larger than in MnPt<sub>3</sub> where the largest 3*d* moment was found. The agreement between calculated spin magnetic moments at Pt sites and the experimentally derived moments is very good (Fig. 1(a)).

As can be seen from Fig. Fig. 1(b) the variation in the orbital magnetic moments on the Pt sites observed by Maruyama *et al.* in XMCD experiments [908] is well reproduced by our calculations. However, the interpretation of the orbital moments is more complicated than in the case of the spin moments. To understand better the formation of Pt and 3*d* transition metal orbital magnetic moments let us consider a site-dependent function  $dm_l(E)$  (see Eq. 2.1) and the integral of  $dm_l(E)$  given by Eq. 2.2. As we discussed above, the function  $dm_l(E)$  can be considered as the measure of unquenching of the orbital moment due to the SO interaction.

Both  $dm_l(E)$  and  $m_l(E)$  are defined in the local coordinate system chosen in such a way that z axis is directed along the magnetization. It is worth noting that the only nonzero matrix elements of the  $\hat{l}_z$  operator calculated between real harmonics with l = 2 are  $|\langle d_{x^2-y^2}|\hat{l}_z|d_{xy}\rangle| = 2$  and  $|\langle d_{xz}|\hat{l}_z|d_{yz}\rangle| = 1$ . Hence, the largest contribution to  $m_l(E)$  can be expected from the  $d_{x^2-y^2}$  and



*Figure 4.2.* Self-consistent fully relativistic, spin-polarized partial d-density of states of XPt<sub>3</sub> compounds (in electrons/atom eV) [913].



*Figure 4.3.* The  $dm_l(E)$ ,  $m_l(E)$  functions and partial densities of states (in electrons/atom eV spin) for l=2 in CoPt<sub>3</sub> [913].

 $d_{xy}$  orbitals. The  $m_l(E)$  function is proportional to the strength of the SO interaction and the value of the spin magnetic moment and it depends on the local symmetry. In the particular case of XPt<sub>3</sub> compounds the local symmetry for X atoms is O<sub>h</sub> and for Pt atom it is D<sub>4h</sub>. For the O<sub>h</sub> group, basis functions are  $E_g (d_{z^2}, d_{x^2-y^2})$  and  $T_{2g} (d_{xy}, d_{yz}, d_{xz})$  while for the D<sub>4h</sub> group they are A<sub>1g</sub>  $(d_{z^2})$ , B<sub>1g</sub>  $(d_{x^2-y^2})$ , B<sub>2g</sub>  $(d_{xy})$  and E<sub>g</sub>  $(d_{yz}, d_{xz})$ . So the largest contribution to  $m_l(E)$  can be expected in the case when we have simultaneously (at the same energy) a large contribution from the B<sub>1g</sub> and B<sub>2g</sub> states at Pt sites and the E<sub>g</sub> and T<sub>2g</sub> states at X sites in XPt<sub>3</sub> compounds.

Fig. 4.3 shows the functions  $dm_l(E)$  and  $m_l(E)$  calculated for Co and Pt sites together with the partial d density of states in CoPt<sub>3</sub> as an example. Here



*Figure 4.4.* The  $m_l(E)$  functions for l=2 in XPt<sub>3</sub> compounds [913].

and in the rest of the paper we will only consider the contribution coming from d orbitals to the  $m_l$  related functions. Both the  $dm_l(E)$  and  $m_l(E)$  functions show strong energy dependence. Although the variations of the functions at

Co site are significantly larger in comparison with those at Pt sites, Pt and Co d orbital moments  $M_l$  are almost equal (see Fig. 1(b) and Table 4.1).

When considering the  $m_l(E)$  (Fig. 4.4) as well as  $dm_l(E)$  (not shown) functions for XPt<sub>3</sub> compounds, one recognizes that especially those of CrPt<sub>3</sub>, MnPt<sub>3</sub>, FePt<sub>3</sub> and CoPt<sub>3</sub> are very similar for both the X and Pt sites respectively. In going from CrPt<sub>3</sub> to CoPt<sub>3</sub> the Fermi level is simply shifted upwards by filling the bands with electrons. In CrPt<sub>3</sub> the Fermi level crosses  $m_l(E)$ function at maximum and minimum at Cr and Pt sites respectively producing rather large Cr and Pt orbital moments with opposite sign (Fig. 1(b) and Table 4.1). In MnPt<sub>3</sub> due to filling the bands with one more electron, the Fermi level is situated at the local minimum in  $m_l^{Mn}(E)$  and at zero crossing in  $m_l^{Pt}(E)$ . As a result MnPt<sub>3</sub> has a very small orbital magnetic moment at the Mn site and almost a zero Pt orbital moment. Further shifting of the Fermi level in FePt<sub>3</sub> places the Fermi level at a local maximum at both the Fe and Pt sites, providing rather large Fe and Pt orbital moments with the same sign. We should also mentioned that absolute magnitude deviation of the  $m_l(E)$  function decreases at the beginning and end of the 3d row reflecting the decreasing of the spin magnetic moments in the compounds.

It is interesting to compare the electronic structure and orbital magnetic moments in the XPt<sub>3</sub> and X<sub>3</sub>Pt compounds. Fig. 4.5 shows *d* partial density of states in CoPt<sub>3</sub> and Co<sub>3</sub>Pt compounds at both the Co and Pt sites. In the CoPt<sub>3</sub> compound the transition metal site is surrounded by 12 Pt sites. On the other hand, in Co<sub>3</sub>Pt, 4 of the nearest neighbors are Pt sites and the other 8 are Co sites. This difference in Co–Co coordination has a dramatic effect on the width of the 3*d* spin down DOS near the Fermi level. The 3*d* spin up states are centered more in the middle of the energy range of the Pt 5*d* states and therefore the Co orbitals hybridize rather effectively with the 5*d* orbitals in both the CoPt<sub>3</sub> and Co<sub>3</sub>Pt compounds. On the other hand, 3*d* spin down states are centered in vicinity of the Fermi level where the Pt 5*d* DOS is rather small. As a result they have smaller 3*d*-5*d* hybridization. Thus the 3*d* spin down states are more localized in CoPt<sub>3</sub> and more itinerant in Co<sub>3</sub>Pt.

**XMCD spectra.** At the core level edge XMCD is not only element-specific but also orbital specific. For 3*d* transition metals, the electronic states can be probed by the *K*,  $L_{2,3}$  and  $M_{2,3}$  x-ray absorption and emission spectra whereas in 5*d* transition metals one can use the *K*,  $L_{2,3}$ ,  $M_{2,3}$ ,  $M_{4,5}$ ,  $N_{2,3}$ ,  $N_{4,5}$ ,  $N_{6,7}$ , and  $O_{2,3}$  spectra. As pointed out above, Eq. (1.201) for unpolarized absorption spectra  $\mu^0(\omega)$  allows only transitions with  $\Delta l = \pm 1$ ,  $\Delta j = 0, \pm 1$  (dipole selection rules). Therefore only electronic states with an appropriate symmetry contribute to the absorption and emission spectra under consideration (Table 4.2). We should mentioned that in some cases quadrupole transitions may play



*Figure 4.5.* Self-consistent fully relativistic, spin-polarized partial d-density of states of XPt<sub>3</sub> compounds (in electrons/atom eV) [913].

an important role, as it occurs, for example, in rare earth materials  $(2p \rightarrow 4f$  transitions) [915].

K edge of 3d transition metal elements. Fig. 4.6 shows the theoretically calculated XMCD in terms of the difference in absorption  $\Delta \mu_{\rm K} = \mu_{\rm K}^+ - \mu_{\rm K}^-$  for left and right circularly polarized radiation in XPt<sub>3</sub> (X=Mn, Fe, and Co) compounds. Because dipole allowed transitions dominate the absorption spectrum for unpolarized radiation, the absorption coefficient  $\mu_{\rm K}^0(E)$  (not shown) reflects primarily the DOS of unoccupied 4p like states  $N_p(E)$  of X above the Fermi level. Due to the energy dependent radial matrix element for the  $1s \rightarrow 4p$  there is no strict one-to-one correspondence between  $\mu_{\rm K}(E)$  and

Spectra	К	$L_2 \\ M_2 \\ N_2 \\ O_2$	$egin{array}{c} L_3 \ M_3 \ N_3 \ O_3 \end{array}$	$M_4 \ N_4$	$M_5 \ N_5$	$N_6$	$N_7$
Core level	$1s_{1/2}$	$\begin{array}{c} 2p_{1/2} \\ 3p_{1/2} \\ 4p_{1/2} \\ 5p_{1/2} \end{array}$	$\begin{array}{c} 2p_{3/2} \\ 3p_{3/2} \\ 4p_{3/2} \\ 5p_{3/2} \end{array}$	${3d_{3/2}}\over{4d_{3/2}}$	$\frac{3d_{5/2}}{4d_{5/2}}$	$4f_{5/2}$	$4f_{7/2}$
Valence states	$p_{1/2} \\ p_{3/2} \\ -$	$s_{1/2} \\ d_{3/2}$	$s_{1/2} \ d_{3/2} \ d_{5/2}$	$p_{1/2} \ p_{3/2} \ f_{5/2}$	$p_{3/2} \ f_{5/2} \ f_{7/2}$	$d_{3/2} \ d_{5/2} \ g_{7/2}$	$d_{5/2} \ g_{7/2} \ g_{9/2}$

*Table 4.2.* Angular momentum symmetry levels indicating the dipole allowed transitions from core states to the unoccupied valence states with the indicated partial density of states character.

 $N_p(E)$ . The exchange splitting of the initial 1s core state is extremely small [916] therefore only the exchange and spin-orbit splitting of the final 4p states is responsible for the observed dichroism at the K edge. For this reason the dichroism is found to be very small (Fig. 4.6). It was first pointed out by Gotsis and Strange [893] as well as Brooks and Johansson [917] that XMCD K spectrum reflects the orbital polarization in differential form  $d < l_z >/dE$  of the p states. As Fig. 4.6 demonstrates, where K XMCD spectra is shown together with dml(E) functions (Eq. 2.1), both quantities are indeed closely related to one another giving a rather simple and straightforward interpretation of the XMCD spectra at the K edge.

As in the case of absorption, K emission XMCD spectrum (not shown) is in close relationship with site- and l projected density of the expectation value of  $\hat{l}_z$ . Using the sum rule derived for K spectra in Ref. [896] we obtain a Mn 5p orbital magnetic moment of around -0.0019  $\mu_B$  in a good agreement with LSDA calculations (-0.0016  $\mu_B$ ).

 $L_{2,3}$  and  $M_{2,3}$  edges of 3d transition metal elements. Because of the dipole selection rules, apart from the  $4s_{1/2}$  states (which have a small contribution to the XAS due to relatively small  $2p \rightarrow 4s$  matrix elements [9]) only  $3d_{3/2}$  states occur as final states for  $L_2$  XAS for unpolarized radiation, whereas for the  $L_3$ XAS  $3d_{5/2}$  states also contribute (Table 4.2. Although the  $2p_{3/2} \rightarrow 3d_{3/2}$ radial matrix elements are only slightly smaller than for the  $2p_{3/2} \rightarrow 3d_{5/2}$ transitions the angular matrix elements strongly suppress the  $2p_{3/2} \rightarrow 3d_{3/2}$ contribution (see Eq. 1.201). Therefore in neglecting the energy dependence of the radial matrix elements, the  $L_2$  and  $L_3$  spectra can be viewed as a direct mapping of the DOS curve for  $3d_{3/2}$  and  $3d_{5/2}$  character, respectively.



*Figure 4.6.* Theoretically calculated 3d transition metal *K* XMCD absorption spectra in comparison with dml(E) function in XPt<sub>3</sub> alloys [913].

In contrast to the K edge, the dichroism at the  $L_2$  and  $L_3$  edges is also influenced by the spin-orbit coupling of the initial 2p core states. This gives rise to a very pronounced dichroism in comparison with the dichroism at the K edge. Fig. 4.7 shows the theoretically calculated 3d transition metal  $L_{2,3}$ XMCD spectra in XPt<sub>3</sub> alloys in comparison with the experimental data [399]. One finds that the theoretical XMCD spectra for the late transition metals to be in good agreement with experiment. For MnPt<sub>3</sub> the calculated magnetic dichroism is somewhat too high at the  $L_2$  edge. As one can see, the XMCD spectra for Fe<sub>3</sub>Pt, CoPt<sub>3</sub> and NiPt<sub>3</sub> are very similar with strong decreasing of the dichroism in NiPt<sub>3</sub> reflecting first of all the decrease of the spin magnetic moment in the later compound at the transition metal site (Table 4.1). The XMCD spectra of ferrimagnetic VPt<sub>3</sub> and CrPt<sub>3</sub> differ significantly at the  $L_3$  edge from the spectra of the ferromagnetic compounds. The former spectra have an additional positive peak in the low energy region.

The XMCD spectra at the  $L_{2,3}$  edges are mostly determined by the strength of the SO coupling of the initial 2p core states and spin-polarization of the final empty  $3d_{3/2,5/2}$  states while the exchange splitting of the 2p core states as well as the SO coupling of the 3d valence states are of minor importance for the XMCD at the  $L_{2,3}$  edge of 3d transition metals [9].

To investigate the influence of the initial state on the resulting XMCD spectra we calculated also the XAS and XMCD spectra of XPt<sub>3</sub> compounds at the  $M_{2,3}$  edge. The spin-orbit splitting of the 3p core level is of one order of magnitude smaller (from about 0.73 eV in V to 2.2 eV in Ni) than for the 2p level (from 7.7 eV in V to 17.3 eV in Ni) at the X-site in the XPt<sub>3</sub> compounds. As a result the magnetic dichroism at the  $M_{2,3}$  edge is much smaller than at the  $L_{2,3}$  edge (Fig. 4.7). Besides the  $M_2$  and the  $M_3$  spectra are strongly overlapped and the  $M_3$  spectrum in the region of the  $M_2$  edge. To decompose a corresponding experimental  $M_{2,3}$  spectrum into its  $M_2$  and  $M_3$  parts will therefore be quite difficult in general. It worth to mentioning that the shape of  $L_3$  and  $M_3$  XMCD spectra are very similar.

Pt  $L_{2,3}$  edges. As mentioned above, MXCD investigations supply information on magnetic properties in a component resolved way. This seems especially interesting if there is a magnetic moment induced at a normally nonmagnetic element by neighboring magnetic atoms. The underlying mechanism of the magnetic and magneto-optical properties of the systems considered here is the well known ability of transition metals to induce large spin polarization of Pt via strong 3d - 5d hybridization and exchange interaction. A very extreme example for this situation occurs for Pt in the XPt<sub>3</sub> compounds.

Results of the theoretical calculations for the circular dichroism at the  $L_{2,3}$  edge of Pt are shown in Figure 4.8 in comparison with the experimental data [908, 907]. As one can see, a rather pronounced XMCD is found. In ferromagnetic compounds MnPt<sub>3</sub>, Fe<sub>3</sub>Pt, and CoPt<sub>3</sub>, the XMCD spectrum is negative at the  $L_3$  and positive at the  $L_2$  edge as has been seen for the XMCD spectra at  $L_{2,3}$  edges of the 3*d* transition metals (Fig. 4.7). The XMCD in MnPt<sub>3</sub> at the  $L_3$  and  $L_2$  edges are of nearly equal magnitude, which suggest that an orbital magnetic moment almost vanishes in the Pt 5*d* states in this compound [908].



*Figure 4.7.* Theoretically calculated 3*d* transition metal  $L_3$  (full line),  $L_2$  (dotted line) and  $M_3$  (full line),  $M_2$  (dotted line) XMCD spectra in XPt<sub>3</sub> alloys [913] in comparison with experimental data (circles). [399]

In ferrimagnetically ordered VPt<sub>3</sub> and CrPt<sub>3</sub> the XMCD spectra at the  $L_3$  edge are positive with a double peak structure in a good agreement with the experimental measurements [907]. The experimental XMCD spectrum of CrPt<sub>3</sub> at the Pt  $L_2$  edge shows a positive sign although the theoretically calculated spectrum has additional negative components at both the low and high energy sides of the main peak (Fig. 4.8).

Pt M, N and O edges. To investigate the influence of the initial state on the resulting Pt XMCD spectra we calculated also the XAS and XMCD spectra of XPt<sub>3</sub> compounds at the  $M_{2,3}$ ,  $M_{4,5}$ ,  $N_{2,3}$ ,  $N_{4,5}$ ,  $N_{6,7}$ , and  $O_{2,3}$  edges. We found a systematic decreasing of the XMCD spectra in terms of  $R = \Delta \mu / (2\mu^0)$  in the row  $L_{2,3} - M_{2,3} - N_{2,3}$  edges. Although the magnetic dichroism at the  $O_{2,3}$  and  $N_{6,7}$  edges became almost as large as at the  $L_{2,3}$ edge. Besides, the lifetime widths of the core  $O_{2,3}$  and  $N_{6,7}$  levels are much smaller than  $L_{2,3}$  ones [918]. Therefore the spectroscopy of Pt atoms in the ultra-soft x-ray energy range at the  $O_{2,3}$  and  $N_{6,7}$  edges may be a very useful tool for investigating the electronic structure of magnetic materials.

Pt  $M_{4,5}$  and  $N_{4,5}$  spectra to some extent can be considered as an analog of the K spectrum. As it was mentioned above, K absorption spectrum at both sites reflects the energy distribution of empty  $p_{1/2}$  and  $p_{3/2}$  energy states (Table 4.2). The  $M_4$  ( $N_4$ ) absorption spectra due to the dipole selection rules occur for the transition from the  $3d_{3/2}$  ( $4d_{3/2}$ ) core states to the  $p_{1/2}$ ,  $p_{3/2}$ , and  $f_{5/2}$  valence states above Fermi level, whereas for the  $M_5$  ( $N_5$ ) XAS the  $p_{3/2}$ ,  $f_{5/2}$ , and  $f_{7/2}$  states contributes. Results of the theoretical calculations of the circular dichroism in absorption at the  $N_{4,5}$  edge of Pt in the XPt<sub>3</sub> (X= Cr, Mn and Fe) are shown in Figure 4.9. Comparing this spectra with the corresponding XMCD spectra of transition metals at the K edge (Fig. 4.6) one can see an obvious resemblance between these two quantities (the magnetic dichroism at the  $N_4$  edge has an opposite sign to the XMCD at the K and  $N_5$ edge). Such a resemblance reflects the similarity of the energy distribution of unoccupied p local partial densities of states  $N_p(E)$  just above the Fermi level at X and Pt sites (not shown). It occurs due to a strong X p - Pt p hybridization effect. The major difference is seen at 0 to 2 eV. It can be attributed to an additional contribution of the  $f_{5/2,7/2}$  energy states to the  $N_{4,5}$  spectra and to the difference in the radial matrix elements  $(1s \rightarrow p_{1/2,3/2})$  in K spectra and  $4d_{3/2,5/2} \rightarrow p_{1/2,3/2}$  in  $N_{4,5}$  spectra). Although the later plays a minor role due to the fact that radial matrix elements are smooth functions of energy.

It is interesting to compare Pt XAS and XMCD spectra at the  $L_{2,3}$ ,  $O_{2,3}$  and  $N_{6,7}$  edges. Due to the dipole selection rules, for unpolarized radiation (apart from the  $s_{1/2}$  states which have a small contribution to the XAS) only  $3d_{3/2}$  states occur as final states for  $L_2$  as well as for  $O_2$  spectra (Table 4.2). The  $L_3$  and  $O_3$  spectra reflect the energy distribution of both the  $3d_{3/2}$  and  $3d_{5/2}$ 



*Figure 4.8.* Theoretically calculated Pt  $L_{2,3}$  XMCD spectra in XPt<sub>3</sub> alloys (full line) [913] in comparison with the experiment (circles), the experimental data for CrPt<sub>3</sub> are from Ref. [907], MnPt<sub>3</sub> from Ref. [908], and CoPt<sub>3</sub> from Ref. [910].



*Figure 4.9.* Theoretically calculated Pt  $N_{4,5}$  XMCD spectra in XPt<sub>3</sub> alloys [913].

empty states. On the other hand, the  $N_7$  absorption spectrum reflects only the  $3d_{5/2}$  states (the density of the  $g_{7/2,9/2}$  states is really very small) whereas for the  $N_6$  XAS both the  $3d_{3/2}$  and  $3d_{5/2}$  states contribute. Therefore we have an inverse situation:  $N_6$  absorption spectra correspond to the  $L_3$  and  $O_3$  spectra, whereas the  $N_7$  is the analog of the  $L_2$  and  $O_2$  ones. This situation is clearly seen in Fig. 4.10 where the theoretically calculated XMCD spectra of XPt<sub>3</sub> compounds at the  $O_{2,3}$  and  $N_{6,7}$  edges is presented. The XMCD spectra at  $O_3$  edges are almost identical to the spectra at the  $N_6$  edges. The XMCD spectra at  $O_2$  edges are also very similar to the spectra at the  $N_7$  edges (but not identical because the energy distribution of Pt  $3d_{3/2}$  and  $3d_{3/2}$  states is not exactly the same due to SO interaction). The magnetic dichroism (e.g. in CoPt<sub>3</sub>) is negative at the  $O_3$  edge and positive at the  $O_2$  edge (as it was at  $L_{2,3}$ ) edges, see Fig. 4.8), but the XMCD is positive at the  $N_7$  edge and negative at the  $N_6$  one. However, we emphasize that  $O_3$  ( $O_2$ ) and  $N_6$  ( $N_7$ ) XMCD spectra are not identical to the  $L_3(L_2)$  ones. One can argue that at least for Pt the  $L_{2,3}$ spectra predominantly reflect atomic aspects of the valence band while for the



Figure 4.10. Theoretically calculated Pt  $O_{2,3}$  and  $N_{6,7}$  XMCD spectra in XPt<sub>3</sub> alloys [913].

 $O_{2,3}$  and  $N_{6,7}$  edge the itinerant aspects are more important. This is especially pronounced in ferrimagnetic VPt<sub>3</sub>, CrPt<sub>3</sub> and ferromagnetic MnPt<sub>3</sub> with more



*Figure 4.11.* Theoretically calculated Pt XAS and XMCD spectra at the  $O_{2,3}$  and  $N_{6,7}$  and Co  $O_{2,3}$  edge in CoPt<sub>3</sub> compound [913] in comparison with experimental data [911].

itinerant character of the valence states than in  $CoPt_3$  and  $NiPt_3$  with relatively more localized 3d states.

Because of the relatively small spin-orbit splitting of the 4f states of Pt (~3.3 eV), the  $N_6$  and the  $N_7$  spectra have an appreciable overlap. For this reason the  $N_7$  spectrum contributes to some extent to the structure of the total  $N_{6,7}$  spectrum in the region of the  $N_6$  edge, as can be seen from the Fig. 4.10. To decompose a corresponding experimental  $N_{6,7}$  spectrum into its  $N_6$  and  $N_7$  parts will therefore be quite difficult in general.

The only available experimental XMCD spectrum measured at the Pt  $N_{6,7}$  edge  $(4f \rightarrow 5d)$  is the spectrum of ferromagnetic CoPt<sub>3</sub> [911]. This spectrum was measured by the total photo-electron yield method. In contrast to

the high energy spectra of Pt ( $L_{2,3}$ ,  $M_{2,3}$  or  $M_{4,5}$  edge), for the ultra-soft xray energy region 50 to 80 eV the situation is complicated by the fact that due to small energy difference of Pt 5p, 4f and Co 3p core states, six spectra (Pt  $O_{2,3}$ , Pt  $N_{6,7}$ , and Co  $M_{2,3}$ ) appear simultaneously in a rather small energy range producing a very complicated spectrum for which interpretation is very difficult without a knowledge of the band structure and corresponding optical matrix elements. It is important to know the correct relative positions of these six spectra. The Dirac-Hartree-Fock-Slater one particle approximation used in this work to calculate the core states is not able to produce a correct energy position of the spectra (due to not taking into account a self-interaction correction, different kinds of relaxation processes and other many-particle effects), therefore we used the experimentally measured positions of the spectra from Ref. [911]. Note that the relative Pt  $O_{2,3} - N_{6,7}$  splitting in CoPt<sub>3</sub> [911] is reported significantly different (about 5 eV) from the corresponding value in pure Pt [919]. Fig. 4.11 shows the theoretically calculated Pt  $O_{2,3}$ , Pt  $N_{6,7}$ , and Co  $M_{2,3}$  XAS and XMCD spectra in CoPt<sub>3</sub> alloy in comparison with the experimental data [911]. There is reasonable agreement with the experimental results for Pt  $O_{2,3}$ ,  $N_{6,7}$  and Co  $M_3$  XMCD spectra. On the other hand, our one particle calculations were not able to reproduce additional resonance structures at 73 and 76.5 eV which is caused by a strong interference Fano effect [911]. There is also a deviation seen at the Pt  $O_{2,3}$  and Co  $M_2$  edge in the sense that the amplitude of the calculated XMCD spectra are too large. An additional peak at a low energy side of the  $M_3$  XMCD spectrum at ~61 eV is also not reproduced by theory.

Finally, we explored the anisotropy of the XMCD spectra with respect to the magnetization direction in these compounds. The influence of the direction of the magnetization on the XMCD spectra was found to be very small in  $XPt_3$  compounds. The comparatively small dependence of the XMCD spectra on the magnetization direction is related to the high degree of isotropy inherent to the Cu<sub>3</sub>Au structure.

**XMCD sum rules.** It is interesting to compare the spin and orbital magnetic moments obtained from the theoretically calculated XAS and XMCD spectra through the sum rules (Eq.s 1.204,1.204) with directly calculated LSDA values. In this case we at least avoid all the experimental problems.

Fig. 4.12 shows direct and sum rule derived spin and orbital magnetic moments from the theoretical XMCD  $L_{2,3}$  spectra. The number of the 3*d* and Pt 5*d* electrons is calculated by integrating the element and *lj* projected density of states inside each atomic sphere. The values  $n_{3d}$ = 3.644, 4.614, 5.606, 6.567, 7,776, 8.854 and  $n_{5d}$ = 8.302, 8.187, 8.213, 8.136, 8.138, 8.134 for VPt<sub>3</sub>, CrPt<sub>3</sub>, MnPt<sub>3</sub>, Fe<sub>3</sub>Pt, CoPt<sub>3</sub> and NiPt<sub>3</sub> respectively.



*Figure 4.12.* Theoretically LSDA calculated spin (a,c) and orbital (b,d) magnetic moments at the X and Pt sites (open circles)in comparison with estimated data using the sum rules (solid circles) for XPt<sub>3</sub> and Fe<sub>3</sub>Pt compounds [913].

As can be seen from Fig. 4.12, the general trend of the sum rule results is in a good agreement with the LSDA calculated spin and orbital magnetic moments for both the X and Pt sites. The orbital magnetic moments at X and Pt sites agree well with the direct calculations, but the spin magnetic moments deduced from the theoretical MXCD spectra are underestimated for VPt<sub>3</sub>, CrPt<sub>3</sub>, and MnPt<sub>3</sub> for both the transition metal and Pt sites. The disagreement at X sites reaches the 40% in VPt<sub>3</sub> and reduces to 19% in CrPt<sub>3</sub>, 15% in MnPt<sub>3</sub> and becomes less than 10% in Fe<sub>3</sub>Pt, CoPt<sub>3</sub> and NiPt<sub>3</sub> compounds. Such behavior arises because the sum rules ignore the  $p \rightarrow s$  transitions which play an essential role in the formation of the spin magnetic moments in early transition metals. In Fe, Co and Ni the relative contribution of the *s* states is reduced and the effect plays a minor role. Thus, first principles determinations of both the XMCD spectra and ground state properties ( $M_l$  and  $M_s$ ) are probably required for quantitative interpretation of the experimental results.

# 4.1.2 Fe<sub>3</sub>O<sub>4</sub> and Mn-, Co-, or Ni-substituted magnetite.

The interpretation of the experimental XMCD spectra of Fe<sub>3</sub>O<sub>4</sub> [480, 481] is very difficult due to the existence of three kinds of iron atoms, i.e. Fe<sup>2+</sup><sub>B</sub>,
$Fe_B^{3+}$  and  $Fe_A^{3+}$ . The substitution for one of the types of iron ions by another transition metal ion provides a possibility for distinguishing transitions from various sites. There are several such experimental studies in the literature. Koide and co-workers reported the XMCD spectra at the Fe M2.3 and Co  $M_{2,3}$  core-absorption edges in Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> [481]. For Fe<sub>3</sub>O<sub>4</sub> the  $M_{2,3}$ prethreshold MCD spectra were measured above and below the Verwey transition temperature. Van der Laan et al. [920] reported the XMCD spectra at the Ni  $L_{2,3}$  edges of NiFe<sub>2</sub>O<sub>4</sub> (trevorite). The Ni  $L_{2,3}$  edge magnetic circular dichroism measurements of ferrimagnetic  $Zn_xNi_{1-x}Fe_2O_4$  (x=0.0, 0.26, 0.50, and 0.75) were reported by Pong et al. [921]. Magnetic circular dichroism is reported for  $Mn_{2/3}Zn_{1/3}Fe_2O_4$  ferrite in Ref. [922] with the measurements performed on the 2p and 3p core levels of Mn and Fe. The electronic structure, spin and orbital magnetic moments and XMCD spectra of the series  $Fe_3O_4$ , CoFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>, and MnFe<sub>2</sub>O<sub>4</sub> presented in Ref. [923]. The XAS and XMCD spectra at K,  $L_{2,3}$  and  $M_{2,3}$  edges for transition metals sites were calculated.

**Fe**<sub>3</sub>**O**<sub>4</sub>. In Fig.s 4.13 and 4.14 the experimentally measured Fe  $L_{2,3}$  XMCD spectra [480] in Fe<sub>3</sub>O<sub>4</sub> are compared to the theoretical ones calculated within the LSDA and LSDA+U approaches. The dichroism at the  $L_2$  and  $L_3$  edges is influenced by the spin-orbit coupling of the initial 2p core states. This gives rise to a very pronounced dichroism in comparison with the dichroism at the K edge. Two prominent negative minima of Fe  $L_3$  XMCD spectrum are derived from iron ions at octahedral B sites. The major positive maximum is from Fe<sup>3+</sup><sub>A</sub> ions. In the LSDA+U calculations of the charge ordered Fe<sub>3</sub>O<sub>4</sub> the  $L_{23}$  XMCD spectra have slightly different shape for the Fe<sup>2+</sup><sub>B</sub> and Fe<sup>3+</sup><sub>B</sub> ions. The spectra from the LSDA calculations strongly underestimate the intensity of the first negative minimum (Fig. 4.13). On the other hand, the LSDA+U calculations are not able to produce the small positive shoulder at the high energy side of the main peaks of the Fe  $L_3$  XMCD spectrum.

The XMCD spectra at the  $L_{2,3}$  edges are mostly determined by the strength of the SO coupling of the initial 2p core states and spin-polarization of the final empty  $3d_{3/2,5/2}$  states, while the exchange splitting of the 2p core states as well as the SO coupling of the 3d valence states are of minor importance for the XMCD at the  $L_{2,3}$  edge of 3d transition metals [9].

To investigate the influence of the initial state on the resulting XMCD spectra we calculated also the XAS and XMCD spectra of  $Fe_3O_4$  at the  $M_{2,3}$  edge. The spin-orbit splitting of the 3p core level is about one order of magnitude smaller than for the 2p level in  $Fe_3O_4$ . As a result the magnetic dichroism at the  $M_{2,3}$  edge is smaller than at the  $L_{2,3}$  edge. In addition the  $M_2$  and  $M_3$  spectra are strongly overlapped and the  $M_3$  spectrum contributes to some ex-



*Figure 4.13.* Fe  $L_{2,3}$  XMCD spectra in Fe<sub>3</sub>O<sub>4</sub> calculated with the LSDA method [923] in comparison with the experimental data (circles) [480].

tent to the structure of the total  $M_{2,3}$  spectrum in the region of the  $M_2$  edge. To decompose a corresponding experimental  $M_{2,3}$  spectrum into its  $M_2$  and  $M_3$  parts will therefore be quite difficult in general.

In Fig.s 4.15 and 4.16 the experimentally measured Fe  $M_{2,3}$  XMCD spectrum [481] in Fe<sub>3</sub>O<sub>4</sub> is compared to the theoretical one calculated within the LSDA and LSDA+U approaches. Better agreement between the theory and the experiment was found when we used the LSDA+U approximation. The LSDA calculations underestimate the intensity of both the prominent negative minima and the second positive maximum at the Fe  $M_{2,3}$  edge. In Fe<sub>3</sub>O<sub>4</sub> the magnetic moments within the A and the B sublattices are ferromagnetically



*Figure 4.14.* Fe  $L_{2,3}$  XMCD spectra in Fe<sub>3</sub>O<sub>4</sub> calculated with the LSDA+U approximation [923] in comparison with the experimental data (circles) [480].

aligned while the two sublattices are antiferromagnetic with respect to each other. The XMCD spectra are positive at the  $M_3$  and negative at the  $M_2$  edge at the tetrahedral A sites and vice versa for the octahedral B ones. The interpretation of the experimental Fe  $M_{2,3}$  XMCD spectrum is very difficult without a knowledge of the band structure and corresponding transition matrix elements



*Figure 4.15.* Fe  $M_{2,3}$  XMCD spectra in Fe<sub>3</sub>O<sub>4</sub> calculated with the LSDA method [923] in comparison with the experimental data (circles) [481].

because this spectrum is a superposition of six  $M_{2,3}$  spectra (from Fe<sup>3+</sup><sub>A</sub>, Fe<sup>2+</sup><sub>B</sub> and Fe<sup>3+</sup><sub>B</sub> sites) appearing simultaneously in a rather small energy range.

Fig. 4.17 shows the theoretically calculated Fe K edge XMCD in terms of the difference in absorption  $\Delta \mu_K = \mu_K^+ - \mu_K^-$  for left and right circularly



*Figure 4.16.* Fe  $M_{2,3}$  XMCD spectra in Fe<sub>3</sub>O<sub>4</sub> calculated with the LSDA+U approximation [923] in comparison with the experimental data (circles) [481].

polarized radiation in Fe<sub>3</sub>O<sub>4</sub>. Because dipole allowed transitions dominate the absorption spectrum for unpolarized radiation, the absorption coefficient  $\mu_K^0(E)$  (not shown) reflects primarily the DOS of unoccupied 4p like states  $N_p(E)$  of Fe above the Fermi level. Due to the energy dependent radial matrix element for  $1s \rightarrow 4p$  transitions there is not an exact one-to-one correspondence between  $\mu_K(E)$  and  $N_p(E)$ . The exchange splitting of the initial 1s core state is extremely small, therefore only the exchange and spin-orbit splitting of the final 4p states is responsible for the observed dichroism at the K edge. For this reason the dichroism is found to be very small (Fig. 4.17). The main contribution to a total XMCD K spectrum of Fe<sub>3</sub>O<sub>4</sub> comes from the Fe<sub>A</sub><sup>3+</sup> ions.

In Fig. 4.17 we present the K XMCD spectra together with a site-dependent function  $dm_{tl}(E)$  given by Eq. 2.1. Fig. 4.17 demonstrates that the K XMCD spectrum and  $dm_l(E)$  function are closely related to one another giving a rather simple and straightforward interpretation of the XMCD spectra at the K edge.

**Co-, Ni- and Mn- substituted Fe**<sub>3</sub> $O_4$ . The electronic structure and XMCD spectra of Co-, Ni-, and Mn- substituted magnetite using the LSDA and LSDA+*U* methods have been calculated [923].

Fig. 4.18 shows the local partial density of states of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$ ions in  $\text{Fe}_A^{3+}[\text{Co}^{2+}\text{Fe}^{3+}]_B\text{O}_4^{2-}$ ,  $\text{Fe}_A^{3+}[\text{Ni}^{2+}\text{Fe}^{3+}]_B\text{O}_4^{2-}$ ,  $\text{Fe}_A^{3+}[\text{Mn}^{2+}\text{Fe}^{3+}]_B\text{O}_4^{2-}$ , respectively.

In contrast to LSDA, which produces the metallic solution in Co and Ni substituted magnetite, the LSDA+U gives an insulator in both cases. The energy gap of 0.63 eV in Co- substituted magnetite occurs between  $\operatorname{Co}_B^{2+} t_{2g\uparrow}$  (the top of valence band) and  $\operatorname{Fe}_B^{3+} t_{2g\uparrow}$  (bottom of empty conduction band) states at the  $\Gamma$  point. The gap in NiFe<sub>2</sub>O<sub>4</sub> is equal to 0.99 eV. It appears between Ni<sup>2+</sup><sub>B</sub>  $e_{g\downarrow}$  and  $\operatorname{Fe}_B^{3+} t_{2g\uparrow}$  states. In this compound Ni<sup>2+</sup><sub>B</sub>  $t_{2g}$  orbitals are fully occupied.

It is known that orbital and spin magnetic moments are determined by the interplay of hybridization, exchange and Coulomb interactions, crystal-field and spin-orbit coupling. The calculated spin  $(M_s)$  and orbital  $(M_l)$  magnetic moments on various atoms are given in Table 4.3 and compared with available experimental data.

Measurements indicate that the magnetic moment of an iron atom in Fe<sub>3</sub>O<sub>4</sub> on the A site is much smaller than the 5.0  $\mu_B$  of a pure Fe<sup>3+</sup> ion [498]. This is an indication of strong hybridization between the 3d orbitals of Fe<sub>A</sub>. As can be seen from Table 4.3 in all the compounds the magnetic moments within the A and the B sublattices are ferromagnetically aligned while the two sublattices are antiferromagnetic with respect to each other. Due to band filling, there is a systematic reduction of the spin magnetic moment from Mn<sub>B</sub><sup>2+</sup> to Ni<sub>B</sub><sup>2+</sup>



*Figure 4.17.* Fe K XMCD spectra in  $Fe_3O_4$  calculated with the LSDA+U approximation [923].

(Table 4.3). Using the XMCD sum rules, the authors of Ref. [920] found for the nickel in NiFe<sub>2</sub>O<sub>4</sub> an orbital to spin magnetic moment ratio  $M_l/M_s$ =0.27  $\pm 0.07$ . Our LSDA+U results give the ratio of 0.18 (Table 4.3) which is in a reasonable agreement with the experimental data [920].

The experimental measurements of the XMCD spectra at the Ni  $L_{2,3}$  edge are reported in Ref. [920]. The spectra were interpreted by atomic multiplet calculations for a 3*d* ground state including an octahedral crystal field splitting.



Figure 4.18. The LSDA+U partial DOS of Co-, Ni-, and Mn- substituted Fe<sub>3</sub>O<sub>4</sub> [923].

compound	ion	$M_s$	$\mathbf{M}_l$	$M_{\it total}$	Exper.	
Fe <sub>3</sub> O <sub>4</sub>	$\operatorname{Fe}_A^{3+}$ $\operatorname{Fe}_B^{2+}$ $\operatorname{Fe}_B^{3+}$	3.84 -3.54	0.02 -0.02	3.86 -3.56	3.82	
$Mn_A[Fe_2]_BO_4$	$\frac{\text{Fe}_B^{3+}}{\text{Mn}_A^{3+}}$ $\text{Fe}_B^{2+}$	-4.00 4.08 -4.05	-0.02 -0.01 -0.05	-4.02 4.07 -4.10	-	
$Fe_A[MnFe]_BO_4$	$ \begin{array}{c} \operatorname{Fe}_A^{3+} \\ \operatorname{Mn}_B^{2+} \\ \operatorname{Fe}_B^{3+} \end{array} $	3.99 -4.47 -4.24	0.01 -0.01 -0.15	4.00 -4.48 -4.39	- -	
$Fe_A[CoFe]_BO_4$	$egin{array}{c} { m Fe}_A^{3+} \ { m Co}_B^{2+} \ { m Fe}_B^{3+} \end{array}$	3.90 -2.57 -4.04	0.03 -0.01 -0.04	3.93 -2.58 -4.08	- - -	
$Fe_A[NiFe]_BO_4$	$egin{array}{c} { m Fe}_A^{3+} \ { m Ni}_B^{2+} \ { m Fe}_B^{3+} \end{array}$	3.99 -1.54 -4.09	0.02 -0.27 -0.03	4.01 -1.81 -4.12	- - -	

*Table 4.3.* The LSDA+U calculated spin and orbital magnetic moments (in  $\mu_B$ ) of Fe<sub>3</sub>O<sub>4</sub> [923]. The experimental data are from Ref. [498].

Results of the LSDA+U circular dichroism calculations for the  $L_{2,3}$  spectra of Fe and Ni are shown in Figure 4.19 with the experimental data for the Ni  $L_{2,3}$  edge [920]. As one can see, a rather pronounced XMCD is found. The XMCD spectrum is negative at the  $L_3$  and positive at the  $L_2$  edge at the Fe<sup>3+</sup><sub>B</sub> and Ni<sup>2+</sup><sub>B</sub> sites and vice versa for the Fe<sup>3+</sup><sub>A</sub> ones. For Fe<sup>3+</sup> ions the dichroism at the  $L_3$  edge is larger at tetrahedral A sites than at octahedral B ones. Due to their opposite signs and relative shift the total Fe XMCD  $L_3$  spectrum has a positive sharp peak with an additional negative shoulder on the high  $h\nu$  side of the main peak. The same feature (with the opposite sign) is observed for the experimentally measured Ni<sup>2+</sup> XMCD at the  $L_3$  edge (Fig. 4.19) with a strong negative peak and a 2-eV positive shoulder of the main peak. The positive shoulder was attributed in Ref. [920] to a singlet spin-flip state that appears as a result of the transition of a spin-down core electron into an empty spin-up Ni d state. This transition becomes allowed since the selection rule  $\Delta S = 0$  is broken by strong 2p spin-orbit interaction.

We should mention that the interpretation of the positive shoulder at 2 eV is controversial because the main peak of  $L_3$  white line region suffers seriously from self-absorption and saturation artifacts due to its large absorption cross section. It is also very difficult to isolate the positive MCD signal of the satellite peak at 2 eV higher energy from negative MCD signal of the main peak [921]. Further investigations are necessary in order to clarify the nature of the positive shoulder at 2 eV.

The XMCD spectra of  $\text{Co}^{2+}$  substituted magnetite have been reported for the Fe M<sub>2,3</sub> and Co M<sub>2,3</sub> core-absorption edges in Ref. [481]. In Fig. 4.20 the experimentally measured Fe and Co  $M_{2,3}$  XMCD spectra [481] in CoFe<sub>2</sub>O<sub>4</sub> are compared to the theoretical ones calculated within the LSDA+U approach. Site-preference calculations [924] pointed out that Co<sup>2+</sup> ions strongly prefer the octahedral *B* sites. The left column of Fig. 4.20 presents the theoretically calculated Fe and Co M<sub>2,3</sub> spectra with Co<sup>2+</sup> ions occupying only octahedral *B* sites (theory1) in comparison with the experimental measurements [481]. Two prominent negative minima *b* and *d* at 3 and 7 eV are derived from Fe<sup>3+</sup><sub>A</sub>  $M_3$  spectrum and Fe<sup>3+</sup><sub>B</sub>  $M_2$  one, respectively. The first positive maximum *c* at 4 to 5 eV is a sum of Fe<sup>3+</sup><sub>A</sub>  $M_2$  and Fe<sup>3+</sup><sub>B</sub>  $M_3$  spectra. The fine structure at 7 to 14 eV is from Co<sup>2+</sup><sub>B</sub> ions. The LSDA calculations (not shown) produce a similar XMCD spectrum except that the intensity of the first minimum at 3 eV is strongly underestimated by LSDA in comparison with the experiment.

Although the LSDA+U theory with  $\operatorname{Co}^{2+}$  ions occupying only octahedral B sites reasonably well describes all major features of the experimental spectrum it fails to produce the positive shoulders a and f at 2 and 10 eV and also underestimates the intensity of two prominent minima b and d at 3 and 7 eV, On the third panel from the top of the right column of Fig. 4.20 we present the theoretically calculated Fe and Co M<sub>2,3</sub> spectra with Co<sup>2+</sup> ions occupying only tetrahedral A sites (theory2). It is clearly seen that the shoulder a at 2 eV is derived from the Fe<sup>3+</sup><sub>B</sub> M<sub>3</sub> spectrum and the peak f at 10 eV mostly comes from the Co<sup>2+</sup><sub>A</sub> M<sub>2</sub> spectrum. Besides, the Fe<sup>3+</sup><sub>B</sub> M<sub>2</sub> and Co<sup>2+</sup><sub>A</sub> M<sub>3</sub> spectra



*Figure 4.19.* Fe and Ni  $L_{2,3}$  XMCD spectra in NiFe<sub>2</sub>O<sub>4</sub> calculated in the LSDA+U approximation [923] in comparison with the experimental data (circles) [920].

contribute to the *b* and *d* minima, respectively. The best agreement between the theory and experiment can be achieved if we assume that 80% of the  $Co^{2+}$  occupy the octahedral *B* sites and 20% occupy tetrahedral *A* sites (see theory3 on the fourth panel from the top of right column of Fig. 4.20).

The original idea in substituting  $Fe_B^{B+}$  ions by  $Co_B^{2+}$  ones was to simplify the XMCD spectra. It works for the  $L_{2,3}$  edge, but for the  $M_{2,3}$  edge the result



*Figure 4.20.* Co and Fe  $M_{2,3}$  XMCD spectra in CoFe<sub>2</sub>O<sub>4</sub> calculated in LSDA+U approximation [923] in comparison with the experimental data (circles) [481]. Theory1 presents  $M_{2,3}$  XMCD spectrum in Fe<sub>A</sub>[CoFe]<sub>B</sub>O<sub>4</sub> compound, theory2 for Co<sub>A</sub>[Fe<sub>2</sub>]<sub>B</sub>O<sub>4</sub> compound, and theory3 is a sum of 80% of the theory1 and 20% of the theory2.

is opposite: instead of 6 XCMD spectra for Fe<sub>3</sub>O<sub>4</sub> (see Fig. 4.16) we have ten  $M_{2,3}$  spectra in Co substituted magnetite (from Fe<sub>A</sub><sup>3+</sup>, Fe<sub>B</sub><sup>3+</sup> and Co<sub>B</sub><sup>2+</sup> sites in Fe<sub>A</sub>[CoFe]<sub>B</sub>O<sub>4</sub> and from Fe<sub>B</sub><sup>3+</sup> and Co<sub>B</sub><sup>2+</sup> sites in Co<sub>A</sub>[Fe<sub>2</sub>]<sub>B</sub>O<sub>4</sub>) appear simultaneously in a rather small energy range (Fig. 4.20).

Magnetic circular dichroism on the 2p and 3p core levels of Mn and Fe is reported for  $Mn_{2/3}Zn_{1/3}Fe_2O_4$  ferrite in Ref. [922]. Very large MCD signals were observed for both Mn and Fe with opposite sign for prominent features. As we mentioned above the  $Mn^{2+}$  ion may occupy both the tetrahedral A and octahedral B sites with preference to the A sites.



*Figure 4.21.* Mn  $L_{2,3}$  XMCD spectra in MnFe<sub>2</sub>O<sub>4</sub> calculated in the LSDA+U approximation [923] in comparison with the experimental data (circles) [922].

Fig. 4.21 presents the experimentally measured Mn  $L_{2,3}$  XMCD spectra [922] in Mn<sub>2/3</sub>Zn<sub>1/3</sub>Fe<sub>2</sub>O<sub>4</sub> in comparison with the theoretical calculations within the LSDA+U approach. The dichroism at the  $L_3$  edge is much larger for Mn<sup>2+</sup> ions at tetrahedral A sites than at B ones. The prominent negative minimum of  $L_3$  XMCD spectrum at around 4 eV is almost completely derived from Mn<sup>2+</sup> ions at tetrahedral A sites. The positive shoulder at 6 eV is due to Mn<sup>2+</sup><sub>B</sub> ions at octahedral B sites. The best agreement between the theory



*Figure 4.22.* Fe  $L_{2,3}$  XMCD spectra of MnFe<sub>2</sub>O<sub>4</sub> calculated with the LSDA+U approximation [923] in comparison with the experimental data (circles) [922].

and experiment can be achieved if we assume that 30% of the  $Mn^{2+}$  ions occupy the octahedral *B* sites and 70% occupy tetrahedral *A* sites (see theory on the third panel from the top of Fig. 4.21). Even with this Mn ion distribution, theory is not able to produce the second positive shoulder at 8 eV as well as a double structure at the  $L_2$  edge.

In Fig. 4.22 the experimentally measured Fe  $L_{2,3}$  XMCD spectra [922] in  $Mn_{2/3}Zn_{1/3}Fe_2O_4$  are compared to the theoretical calculations. Theory correctly produces a double peak structure at the  $L_3$  and  $L_2$  edges, although it was not able to produce additional negative component at the high energy side of the main double peak at 5 to 9 eV at the  $L_3$  edge.

If we assume that  $Mn^{2+}$  can occupy either the tetrahedral A or octahedral B sites there are three different types of Fe<sup>3+</sup> ion sites depending which site is occupied by the  $Mn^{2+}$  ions (Fig. 4.22). If  $Mn^{2+}$  ions occupy A sites there is only one type of Fe<sup>3+</sup> ion at the B sites with a positive double peak structure at the  $L_3$  edge and negative dichroism at the  $L_2$  edge. If  $Mn^{2+}$  ions occupy octahedral B sites there are two types of Fe<sup>3+</sup> ions at the A and B sites. These two iron ions are anti-ferromagnetically ordered and, hence, have opposite signs in the magnetic dichroism. The prominent positive maximum at around 3.5 eV at the  $L_3$  edge is derived mostly from the Fe<sup>3+</sup><sub>B</sub> ions with  $Mn^{2+}$  ions occupying octahedral B sites. The low energy peak at 2 eV is due to the Fe<sup>3+</sup><sub>B</sub> ions with  $Mn^{2+}$  ions occupying tetrahedral A sites, this peak is partly compensated by a negative dichroic signal from the Fe<sup>3+</sup><sub>A</sub> ions with  $Mn^{2+}$  ions at the B sites. The final theoretical spectrum on the fourth panel from the top of Fig. 4.22 is obtained from a sum of 70% Fe  $L_{2,3}$  spectra from  $Mn_A[Fe_2]_BO_4$  and 30% from Fe<sub>A</sub>[MnFe]\_BO\_4.

In Fig. 4.23 the experimentally measured Mn and Fe  $M_{2,3}$  XMCD spectra [922] in Mn<sub>2/3</sub>Zn<sub>1/3</sub>Fe<sub>2</sub>O<sub>4</sub> are compared to the theoretical ones calculated within the LSDA+U approach. As in the case of Co substituted Fe<sub>3</sub>O<sub>4</sub> (Fig. 4.20) Mn substituted magnetite has also ten  $M_{2,3}$  spectra at the  $M_{2,3}$  edge (from Mn<sup>2+</sup><sub>B</sub> and Fe<sup>3+</sup><sub>B</sub> sites in the Mn<sub>A</sub>[Fe<sub>2</sub>]<sub>B</sub>O<sub>4</sub> compound and from Fe<sup>3+</sup><sub>A</sub>, Fe<sup>3+</sup><sub>B</sub> and Mn<sup>2+</sup><sub>B</sub> sites in the Fe<sub>A</sub>[MnFe]<sub>B</sub>O<sub>4</sub> compound) (Fig. 4.23). The best agreement between the theory and experiment can be achieved if we assume that 70% of the Mn<sup>2+</sup> occupy the tetrahedral A sites and 30% occupy octahedral B sites (see theory on the sixth panel from the top of Fig. 4.23). In this case the agreement between theory and experiment is quite good except for being low at 0 to 2 eV and high in energy above the 11 eV tails where theory gives smaller dichroism in comparison with the experimental data. The prominent negative minimum at around the 4 eV is derived mostly from the Mn<sup>2+</sup>  $M_3$  spectrum at tetrahedral A site. The positive double peak at 5 to 6.5 eV is a superposition of Mn<sup>2+</sup><sub>A</sub>  $M_2$  and Mn<sup>2+</sup><sub>B</sub>  $M_3$  spectra suppressed by a negative signal from the Mn<sup>2+</sup>  $M_2$  spectrum. The features above 7 eV are completely derived from Fe ions on both sublattices.

Indeed, presented here results shows how sensitive the XMCD spectra can be for the same magnetic ions on different sites, and by comparing the experimental spectra with careful theoretical analysis a quantitative estimate for site occupancy may be easily obtained.



*Figure 4.23.* Mn  $M_{2,3}$  XMCD spectra in MnFe<sub>2</sub>O<sub>4</sub> calculated in the LSDA+U approximation in comparison with the experimental data (circles) [922].

#### 4.2 Rare earth compounds.

The astonishing variety of magnetic behaviors in rare-eart-3d transition metal (*R*-TM) intermetallics reflects the complexity of the exchange mechanism involving direct and indirect interaction mediated by the band states. These mechanisms are still not completely understood. X-ray magnetic circular dichroism, being element and orbital selective, offers the opportunity to probe the TM 4p and 3d band states by scanning through their K and  $L_{2,3}$  edges respectively. Information on the rare-earth ground state is usually obtained by performing XMCD measurements at the rare-earth M<sub>4,5</sub> edges since these edges involve the  $3d \rightarrow 4f$  transitions, i.e. they probe the electronic states of the 4f shell. On the other hand, L<sub>2,3</sub> edges of rare-earth ion provide the information on the R 5d band states through the  $2p \rightarrow 5d$  transitions. Such studies of XMCD have shown to be very useful and give new insite on both the magnetic properties of the *R*-TM compounds and the interpretation of the XMCD spectra.

Recently systematic studies have been performed on several series of R-TM intermetallic crystals, amorphous materials and insulating ferromagnetic oxides in order to extract the relevant physical effects which govern the XCMD of K,  $L_{2,3}$  and  $M_{4,5}$  edges. Giorgetti *et al.* [925] present the XMCD studies at the  $L_{2,3}$  edges of Ce and K edge of transition metals in CeFe<sub>2</sub>, Ce(Fe<sub>08</sub>Co<sub>0.2</sub>)<sub>2</sub>, CeCo<sub>5</sub>, Ce<sub>2</sub>Co<sub>17</sub>, CeRu<sub>2</sub>Ge<sub>2</sub>, Ce<sub>3</sub>Al<sub>11</sub>, CePd, CoFe<sub>2</sub>H<sub>3.8</sub> compounds. Suga and Imada [926] studied a dense Kondo material, Sm<sub>4</sub>As<sub>3</sub>. They performed the M<sub>4,5</sub> and N<sub>4,5</sub> XMCD at the Sm edges. The authors also measure XMCD spectra in the permanent magnet Nd<sub>2</sub>Fe<sub>14</sub>B at the M<sub>4,5</sub> and L<sub>2,3</sub> edges of Nd and Fe respectively. The shape of the spectra agree with atomic calculations.

XMCD at Er M<sub>4.5</sub> [927] was used to follow the H, T magnetic phase diagram of an amorphous  $Er_{12}$ -Fe<sub>73</sub> alloy. In these samples, macroscopic measurements of the magnetic moment show a strong evolution of the compensation temperature with the applied magnetic field. The variation of XMCD at Er M<sub>4.5</sub> is consistent with a magnetic structure of both the Er and Fe atoms. It shows the existence of temperature-induced, as well as field-induced, flip of the Er sub-lattice with respect to the direction of the magnetic field, evidenced by the change of sign of the dichroism. The authors of Ref. [928] present a XMCD study of a CeCuSi compound and a Ce/Fe multilayer performed at the Ce M<sub>4.5</sub> absorption edge. In the Ce/Fe MLS, Ce atoms are in the highly hybridized  $\alpha$  pase, characterized by a strong mixing between the 4f electrons with the valence band, and carry an ordered moment. XMCD experiments show the part of this moment is due to 4f electrons. The difference in the shape of the XMCD signals of a typical  $\gamma$ -like compound CeCuSi and of the Ce/Fe multilayer demonstrate that the XMCD spectra reflect the hybridization in the ground state of the cerium atoms in the multilayer. Ce  $M_{4,5}$  XMCD spectra in strongly correlated ferromagnetic systems CeCuSi, CeRh<sub>3</sub>B<sub>2</sub>, and CeFe<sub>2</sub> measured in Ref. [929]. By applying sum rules, it was shown that these

experiments are able to yield both the magnitude and the direction of the 4f magnetic moments on Ce.

A systematic XMCD study at the Fe K edge on  $RFe_{14}B$  series (R=rare earth and Y) performed in Ref. [930]. The study identifies the influence of the rare-earth magnetic state into the K edge XMCD signals in  $RFe_{14}B$  intermetallic compounds. This signal results from the addition of two components, each one being due to the magnetic contribution of both the iron and the rare-earth sublatices. The contribution of the R sublattice to the XMCD signal has been extracted yielding a direct correlation to the R magnetic moment. XMCD spectra has been measured in R-Co compounds (R=La, Tb, and Dy) at the Co K edge [931]. The experimental results have been interpreted within the multiple-scattering framework including the spin-orbit coupling. In the three systems, the XMCD spectra in the near edge region are well reproduced. Co K edge XMCD spectra in crystalline and amorphous Gd-Co alloys measured in Ref. [932]. The results analyses using a semi-relativistic full multiple scattering approach. It was shown that the spin polarization on Co atoms in GdCo<sub>5</sub> alloys is smaller than that in Co metal.

XMCD experiments have been performed in Ref. [933] at the  $R L_{2,3}$  (R=rare earth) and Ni K edges on single crystals of  $GdNi_5$  and  $TbNi_5$ . The spectra present huge and well-structured dichroic signals at both the  $R L_{2,3}$  and Ni K edges. In TbNi<sub>5</sub> the negative XMCD structure, observed 3 eV below the edge at the Tb  $L_3$  edge, was interpreted as the quadrupolar  $(2p \rightarrow 4f)$  transitions. A systematic study of XMCD, x-ray resonance magnetic scattering (XRMS), and resonance inelastic x-ray scattering (RIXS) at the  $L_{2,3}$  edges of Nd on Ni<sub>2</sub>Fe<sub>14</sub>B presented in Ref. [934] allowes to assign a dipole (E1) or quadrupole (E2) origin to different features appearing in the experimental spectra and to study the thermal dependence of the Nd moment orientation below the spin reorientation transition which take place at  $T_{SRT}$ = 135 K. A single crystal of Tb as a prototype system for a one-element magnet was used to investigate XMCD at the  $L_{2,3}$  edge [935]. The high resolution of the experimental data allows for a clear identification of the E1 and E2 transitions. On the basis of *ab initio* calculations a simple procedure for extracting of the E2 part from the experimental XMCD data was developed.

Fe  $L_{2,3}$  XMCD spectra on a single crystal of Fe<sub>17</sub>Dy<sub>2</sub> measured by Castro *et al.* in Ref. [936]. XMCD study at the *K* edge in the R<sub>6</sub>Fe<sub>23</sub> series (R=Ho and Y) presented in Ref. [937]. This study identifies the influence of the rare-earth magnetic state on the *K* edge XMCD signals. The results demonstrate that the contribution of both Fe and R to the *K* edge XMCD spectra can be easily isolated following its temperature-dependent behavior through compensation temperature and that they can be directly correlated to the Fe and R magnetic moments.

The distinguishing feature of the rare-earth elements in solids is the atomic character of the 4f levels, which lie relatively deep in the ion while having very small binding energies. It is this feature that account for the chemical similarity and magnetic diversity found in the series. A well-known consequence of this localized behavior is that a number of solid-state and spectroscopies involving the 4f electrons can be explained with the multiplet structure found from atomic calculations, with only small corrections being necessary to incorporate solid-state effects.

A 3d absorption process in rare-earth ions involves the electronic excitations to the 4f or the valence band (VB) levels, [938] i.e.,

$$3d^{10}4f^n(VB)^x \to 3d^94f^{n+1}(VB)^x.$$
 (4.1)

or

$$3d^{10}4f^n(VB)^x \to 3d^94f^n(VB)^{x+1}.$$
 (4.2)

The final-state configuration contains two open shells and due to strong 3d-4f overlap gives rise to large Coulomb and exchange correlation energies and produces a wide spread over the multiplet levels. The  $3d \rightarrow VB$  excitations (4.2) have much weaker strength in comparison with the first ones (4.1) not only due to low  $3d \rightarrow 6p$  cross section but also because near threshold the empty valence band states have mostly 5d character with a little hybridized 6p states. The total  $3d^94f^{n+1}$  multiplet structure is very complex and the total numbers of levels runs into thousands for many elements in the middle of the rare-earth series. There have been several calculations of the  $3d(4d)^94f^{n+1}$  multiplet structure in individual elements [939–950].

The theoretical analysis of magnetic circular dichroism of 4f photoemission spectra in Gd and Tb ions reported in Ref.s [948–950]. Imada and Jo calculate the  $M_{4,5}$  and  $N_{4,5}$  XAS spectra [947] for left and right circularly polarized light in trivalent rare earth ions. Thole *et al.* [944] measured and calculated in intermediate coupling the  $M_{4,5}$  XAS for all the rare-earth metals.

The energy band approximation was used in Ref. [951] to calculated XMCD spectra of  $Gd_5(Si_2Ge_2)$  compound. To treat the correlation effects at a simple level the LSDA+U method was used.

## 4.2.1 $Gd_5(Si_2Ge_2 \text{ compound})$

The family of intermetallic compounds  $Gd_5(Si_xGe_{1-x})_4$  have been known for over thirty years [952]. Recently  $Gd_5(Si_2Ge_2)$  and related  $Gd_5(Si_xGe_{1-x})_4$ phases, where  $x \leq 0.5$ , have attracted a great deal of attention mostly due to the discovery of a giant magnetocaloric effect (MCE) [953–955]. The effect is related to a first order phase transition from a high-temperature paramagnetic to a low-temperature ferromagnetic state at temperatures ranging from 130K (x=0.24) to 276K (x=0.5). It makes the Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>) a promising candidate material for near room temperature magnetic refrigeration [956–958]. A recent study of the Gd<sub>5</sub>(Si<sub>0.45</sub>Ge<sub>0.55</sub>)<sub>4</sub> alloy has revealed that on cooling the phase transition is associated with a first-order structural transition from a monoclinic (paramagnetic, space group  $P112_1/a$ ) to an orthorhombic (ferromagnetic, space group Pnma) symmetry [959]. A detailed crystal structure determination of both orthorhombic and monoclinic phases in a Gd<sub>5</sub>(Si<sub>0.5</sub>Ge<sub>0.5</sub>)<sub>4</sub> single crystal was carried out (see Ref. [960]). This magnetostructural transition can be induced reversibly by application of an external magnetic field, resulting in a colossal magnetostriction [961, 959] and a giant negative magnetoresistance [962–964]. Therefore these alloys may also be attractive in view of their potential technological applications for magnetostrictive/ magnetoresistive transducers.

The electronic structure, optical and magneto-optical spectra of  $Gd_5(Si_2Ge_2)$ in both low temperature orthorhombic and high-temperature monoclinic phases have been investigated in Ref. [965]. The standard LSDA approach places the Gd minority 4f energy bands at the Fermi level. This is a known problem with the LSDA approach and is associated with an inadequate treatment of the strongly correlated 4f electrons. To treat the correlation at a simple level the LSDA+U method was used to evaluate the optical properties. For the LSDA+U approach the Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure, and the 4f spin down levels are completely unoccupied and well above the Fermi level hybridized with Gd 5d states. Also LSDA+U theory predicts that the magneto-optical spectra can be used for the detecting of the structural  $\alpha \rightarrow \beta$  phase transition because the theoretical MO spectra are much more sensitive to the phase transition compared with the conventional optical measurements.

The XMCD offers valuable, element specific spectroscopic information about ordered magnetic moments, and because the detailed neutron scattering studies are precluded by the high absorption of Gd. The theoretically calculated XMCD spectra of  $Gd_5(Si_2Ge_2)$  within the LSDA+U approximation was presented in Ref. [951].

The structure of  $Gd_5(Si_2Ge_2)$  is very complicated containing 36 atoms per unit cell in both phases. For the low temperature phase (called  $\alpha$  hereafter) the crystal structure of  $Gd_5(Si_2Ge_2)$  is orthorhombic, the space group is *Pnma* (No. 62) and belongs to the  $Gd_5Si_4$  structure type [960]. The lattice parameters are *a*=7.5137, *b*=14.792, *c*=7.7858 Å [960]. Gd atoms in  $Gd_5(Si_2Ge_2)$ form quasi-infinite, two dimensional (3<sup>2</sup>434) nets. Two adjacent Gd (3<sup>2</sup>434) nets create a slab composed of distorted cubes and trigonal prisms sharing common faces. The distribution of Si and Ge atoms is random. However, in the band structure calculations of Ref. [951] was considered a specific positions for Si and Ge atoms, namely, Ge atoms were placed in T' positions (with x/a=0.84689, y/b=0.45984 z/c=0.52929) and Si atoms in the T positions (x/a=0.0235, y/b=0.75 z/c=0.1021 for the Si<sub>1</sub> atom, and x/a=0.2683, y/b=0.75 z/c=0.8711 for the Si<sub>2</sub> atom) [960]. In this case each ( $3^{2}434$ ) slab is connected to two adjacent slabs by Ge–Ge bonds (ca. 2.62 Å). The room temperature form of Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>) ( $\beta$  phase) crystallizes in the monoclinic space group  $P112_1/a$  (No. 14) with lattice constants equal to a=7.5891, b=14.827, c=7.7862 Å, angle  $\gamma=93.262^{\circ}$  [960]. The  $\beta$  phase involves nearly identical ( $3^{2}434$ ) slabs as seen in the  $\alpha$  phase, but with one-half of the Ge–Ge bonds connecting these slabs "broken", their GeGe<sub>2</sub>–GeGe<sub>2</sub> bond distance expands by 32.7% from 2.629 Å ( $\alpha$  phase at 243 K) to 3.488 Å ( $\beta$  phase at 292 K) [960]. This drastic structural change arises from a large shear movement of pairs of ( $3^{2}434$ ) slabs in the  $\alpha$  phase by ca. 0.8 Å along the +a or -a direction relative to one another.

For Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>), the electronic states can be probed by the K,  $L_{2,3}$ ,  $M_{2,3}$ ,  $M_{4,5}$ ,  $N_{2,3}$ ,  $N_{4,5}$ , and  $O_{2,3}$  x-ray absorption and emission spectra at Gd sites and by K and  $L_{2,3}$  ones at Si and Ge sites.

Fig. 4.24 shows the calculated XMCD spectra in terms of the difference in absorption  $\Delta \mu_{\rm K} = \mu_{\rm K}^+ - \mu_{\rm K}^-$  for left and right circularly polarized radiation at Gd, Si and Ge sites for both the low and high temperature phases. Because dipole allowed transitions dominate the absorption spectrum for unpolarized radiation, the absorption coefficient  $\mu_{\rm K}^0(E)$  (not shown) reflects primarily the DOS of unoccupied *p*-like states  $N_p(E)$  of X above the Fermi level. The exchange splitting of the initial 1s core state is extremely small [916] therefore only the exchange and spin-orbit splitting of the final *p* states is responsible for the observed dichroism at the *K* edge. For this reason the dichroism is found to be very small (Fig. 4.24).

The  $M_4$  ( $N_4$ ) absorption spectra due to the dipole selection rules occur for transitions from the  $3d_{3/2}$  ( $4d_{3/2}$ ) core states to the  $p_{1/2}$ ,  $p_{3/2}$ , and  $f_{5/2}$  valence states above Fermi level, whereas for the  $M_5$  ( $N_5$ ) XAS the  $p_{3/2}$ ,  $f_{5/2}$ , and  $f_{7/2}$  states contribute. Results of the calculations of the circular dichroism for absorption at the  $M_{4,5}$  and  $N_{4,5}$  edges of Gd in Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>) in both the low and high temperature phases are shown in Figure 4.25. We found that the dichroism at  $M_{4,5}$  and  $N_{4,5}$  edges involving transitions to empty Gd 4f states is of two orders of magnitude stronger than the dichroism at other core edges. The XMCD spectrum is positive at the  $M_4$  edge with a very tiny negative high energy shoulder and negative at the  $M_5$  edge are increased in intensity in comparison with the  $M_5$  and  $M_4$  ones. Through the  $\alpha \rightarrow \beta$  phase transition the dichroism at the  $M_4$  edges is increased.



*Figure 4.24.* Theoretically LSDA+U calculated K XMCD absorption spectra at Gd, Si and Ge sites for orthorombic and monoclinic Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>) [951].

We should mention here that a major shortcoming in band structure approximation is that the multiplet structure has not been included. For Ge and Si Kedges and for the Gd  $L_{2,3}$ ,  $M_{2,3}$ , and  $O_{2,3}$  edges this is probably not a major problem. However, for Gd  $M_{4,5}$  and  $N_{4,5}$  edges the core-valence electrostatic interactions might influence the line shape of the XAS and XMCD spectra. Thole *et al.* [944] measured and calculated in intermediate coupling the  $M_{4,5}$ XAS for all the rare-earth metals. Authors found that the number of  $3d^94f^{n+1}$ final-state levels reaches to 1077 in Gd<sup>3+</sup>. The XAS features are situated in two groups whose separation corresponds roughly to the  $3d_{3/2} - 3d_{5/2}$  spin-orbit splitting. Although the calculations indicate that very large number of lines have a small weight, nevertheless, this weight adds up to recognizable shoul-



*Figure 4.25.* Theoretically LSDA+U calculated  $M_{4,5}$  and  $N_{4,5}$  XMCD absorption spectra at Gd sites for orthorombic and monoclinic Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>) [951].

ders in the  $M_4$  and  $M_5$  spectra from high energy side. Therefore one could expect that the experimentally measured  $M_{4,5}$  XMCD spectra in Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>) might have a more complicated form in comparison with the calculated in band structure approximation presented in Fig. 4.25 without taking into account the multiplet structure. namely, might have an addition fine structures from the high energy site. The shape of  $N_{4,5}$  XMCD spectra in Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>) might be also distorted by the correspondent multiplet structure.

The theoretical method which include both the band structure and atomic like multiplet structure of rare earth metals and compounds is highly desired.

## 4.3 Uranium compounds.

Uranium compounds exhibit rich variety of properties to large extent because of the complex behavior of 5f electrons which is intermediate between the itinerant behavior of 3d electrons in transition metals and the localized one of 4f electrons in rear earth compounds. The dual character of 5f electrons alongside with the presence of strong spin-orbit (SO) coupling make the determination of the electronic structure of U compounds a challenging task because in many of them the width of 5f bands, their spin-orbit splitting, and the onsite Coulomb repulsion in the partially filled 5f shell are of the same order of magnitude and should be taken into account on the same footing. An interest to uranium compounds has recently been renewed, especially after the discovery of such unusual effects as heavy fermion superconductivity and coexistence of superconductivity and magnetism.

Because of the great number of papers which have been produced in recent years on actinide intermetallics, and in particular on heavy-fermion compounds, these would deserve one or more specialized review articles. Various aspects of these systems and of general heavy-fermion systems have already been reviewed in the past [966–978]. For this reason we will merely outline some general concepts relevant to uranium intermetallics, rather than doing a systematic review of all their physical properties.

For heavy-fermion compounds the attribute "heavy" is connected to the observation of a characteristic energy much smaller than in ordinary metals that reflects a thermal effective mass  $m^*$  of the conduction electrons orders of magnitude larger than the bare electron mass. These heavy masses manifest themselves, for example, by a large electronic coefficient  $\gamma$  of the specific heat C ( $\gamma = C/T for T \rightarrow 0$ ), an enhanced Pauli susceptibility, a huge  $T^2$  term in the electrical resistivity, and highly temperature-dependent de Haas-van Alphen oscillation amplitudes at very low temperatures. The large  $m^*$  value is usually believed to derive from the strong correlation electrons. While at high temperature these two subsets of electrons become strongly coupled, resulting in the formation of a narrow resonance in the density of states near the Fermi energy. Thus, at a sufficiently low temperature, the heavy-fermion compounds behave like a system of heavy itinerant electrons, the properties of which can be described in the framework of a Landau Fermi-liquid formalism.

Among uranium heavy-fermion compounds superconductivity is observed in UBe<sub>13</sub>, UPt<sub>3</sub>, URu<sub>2</sub>Si<sub>2</sub>, U<sub>2</sub>PtC<sub>2</sub>, UPd<sub>2</sub>Al<sub>3</sub>, and UNi<sub>2</sub>Al<sub>3</sub>. Superconductivity usually in these compounds coexists with AF order and this has led to the suggestion that the effective attractive interaction between the superconducting electrons may be mediated by spin fluctuations, rather than by the electron-phonon interaction. This is supported by the fact that the observed superconducting states are highly anisotropic, with nodes in the gap function not explainable by a s-wave theory.

A fascinating aspect of this class of compounds is the observation that, within the heavy-fermion regime, a wealth of ground states can occur. Although a myriad of experiments have been devoted to the characterization of these ground states, a comprehensive understanding of heavy-fermion properties at low temperature is still lacking. The heavy-fermion ground-state

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properties are highly sensitive to impurities, chemical composition, and slight changes of external parameters. This sensitivity indicates that a subtle interplay between different interactions produces a richness of experimental phenomena. It is widely believed that the competition between the Kondo effect (reflecting the interaction between the localized 5f moments and the conduction electrons) and the magnetic correlations between the periodically arranged 5f moments constitutes the key factor for as far as the magnetic properties of heavy-fermion compounds are concerned [966].

The x-ray magnetic circular dichroism technique developed in recent years has evolved into a powerful magnetometry tool to separate orbital and spin contributions to element specific magnetic moments. X-ray magnetic circular dichroism experiment consists of measuring the absorption by a sample of xrays with opposite (left and right) states of circular polarization. Study of the 5f electron shell in uranium compounds is usually performed by tuning the energy of the x-ray close to the M<sub>4.5</sub> edges of uranium (located at 3552 and 3728 eV, respectively) where electronic transitions between  $3d_{3/2.5/2}$  and  $5f_{5/2.7/2}$  states occur. Recently XMCD measurements have been successfully performed for uranium compounds such as US [979, 980], USb<sub>0.5</sub>Te<sub>0.5</sub> [981], U<sub>x</sub>La<sub>1-x</sub>S [982], UBe<sub>13</sub> and UPt<sub>3</sub> [983], UFe<sub>2</sub> [792, 984], UNi<sub>2</sub>Al<sub>3</sub> [985], UPd<sub>2</sub>Al<sub>3</sub> and URu<sub>2</sub>Si<sub>2</sub> [986], URhAl [987], UCoAl and UPtAl [988]. There are some features in common for all the uranium compounds investigated up to now. First, the dichroism at the  $M_4$  edge is much larger, sometimes of one order of magnitude, than at the  $M_5$  one. Second, the dichroism at the  $M_4$  edge has a single negative lobe that has no distinct structure, on the other hand, two lobes, a positive and a negative one, are observed at the M<sub>5</sub> edge. Concerning the line shape of the XMCD signal, the investigated metallic uranium compounds fall into two types according to a relative intensity of the positive and negative lobes observed at the M<sub>5</sub> edge. The two lobes have almost equal intensity for UP<sub>3</sub>, UPd<sub>2</sub>Al<sub>3</sub>, UPtAl, and UBe<sub>13</sub>. On the other hand, the positive lobe is smaller in comparison with the negative one for US, USb<sub>0.5</sub>Te<sub>0.5</sub>, UFe<sub>2</sub>, URu<sub>2</sub>Si<sub>2</sub>, UCoAl, and URhAl.

With the aim of undertaking a systematic investigation of the trends in uranium compounds we present the theoretically calculated electronic structure and XMCD spectra at  $M_{4,5}$  edges for the following uranium compounds: UPt<sub>3</sub>, URu<sub>2</sub>Si<sub>2</sub>, UPd<sub>2</sub>Al<sub>3</sub>, UNi<sub>2</sub>Al<sub>3</sub>, UBe<sub>13</sub>, UFe<sub>2</sub>, UPd<sub>3</sub>, UXAl (X=Co, Rh, and Pt), and UX (X=S, Se, and Te). The first five compounds belong to heavy-fermion superconductors, UFe<sub>2</sub> is widely believed to be an example of compound with completely itinerant 5*f* electrons, while UPd<sub>3</sub> is the only known compound with completely localized 5*f* electrons.



*Figure 4.26.* The LSDA partial  $5f_{5/2}$  and  $5f_{7/2}$  density of states (in states/(atom eV)) in UFe<sub>2</sub> [800].

# 4.3.1 UFe<sub>2</sub>

Fig. 4.26 shows the calculated fully relativistic spin-polarized partial 5f density of states of ferromagnetic UFe<sub>2</sub> [800]. Because of the strong spin-orbit interaction of 5f electrons, j = 5/2 and j = 7/2 states are well separated in energy and the occupied states are composed mostly of  $5f_{5/2}$  states whereas  $5f_{7/2}$  states are almost empty. One can note, however, that an indirect hybridization between j = 5/2 and j = 7/2 states via Fe 3d states is rather strong.

In order to compare relative amplitudes of  $M_4$  and  $M_5$  XMCD spectra we first normalize the corresponding isotropic x-ray absorption spectra (XAS) to the experimental ones taking into account the background scattering intensity as described in the Chapter I (see Eq. 1.203). Figure 4.27 shows the calculated isotropic x-ray absorption and XMCD spectra in the LSDA and LSDA+U(OP) approximations together with the experimental data [792]. The contribution from the background scattering is shown by dashed lines in the upper panel of Fig. 4.27.

The experimentally measured dichroic  $M_4$  line consists of a simple nearly symmetric negative peak that has no distinct structure. Such a peak is characteristic of the  $M_4$  edge of all uranium systems. The dichroic line at the  $M_5$ edge has an asymmetric s shape with two peaks – a stronger negative peak and a weaker positive peak. The dichroism at the  $M_4$  edge is more than two times larger than at the  $M_5$  one.

We recall that the  $M_4$  ( $M_5$ ) edge corresponds to  $3d_{3/2}(3d_{5/2}) \rightarrow 5f$  transitions. The created 3d core hole has electrostatic interaction with the 5f shell. However, in a first approximation, this interaction can be neglected since no clear multiplet structure is distinguished in the absorption spectra. This ap-



*Figure 4.27.* Isotropic absorption and XMCD spectra of UFe<sub>2</sub> at the uranium  $M_{4,5}$  edges calculated in the LSDA (solid lines) and LSDA+U(OP) (dashed lines) approximations [800]. Experimental spectra [792] (circles) were measured at 20 K and at magnetic field 2 T (the U  $M_4$  spectrum is shifted by -95 eV to include it in the figure). Upper panel also shows the background spectra (dashed line) due to the transitions from inner  $3d_{3/2,5/2}$  levels to the continuum of unoccupied levels.

proximation is supported theoretically since the Slater integrals  $F_k(3d, 5f)$  and  $G_k(3d, 5f)$  are small compared to the  $F_k(5f, 5f)$  integrals and 3d spin-orbit interaction [979]. Neglecting the core-level splitting the measured spectra reflect the density of states above the Fermi level weighted by the dipole transition probabilities. Since the XMCD technique uses circular polarized x-rays, the dichroism contains information about the character of the magnetic sub-levels in the DOS.

Because of the electric dipole selection rules ( $\Delta l = \pm 1$ ;  $\Delta j = 0, \pm 1$ ) the major contribution to the absorption at the  $M_4$  edge stems from the transitions  $3d_{3/2} \rightarrow 5f_{5/2}$  and that at the  $M_5$  edge originates primarily from  $3d_{5/2} \rightarrow 5f_{7/2}$  transitions, with a weaker contribution from  $3d_{5/2} \rightarrow 5f_{5/2}$  transitions. For the later case the corresponding  $3d_{5/2} \rightarrow 5f_{5/2}$  radial matrix elements are only slightly smaller than for the  $3d_{5/2} \rightarrow 5f_{7/2}$  transitions. The angular matrix elements, however, strongly suppress the  $3d_{5/2} \rightarrow 5f_{5/2}$  contribution. Therefore the contribution to XMCD spectrum at  $M_5$  edge from the transitions

#### Table 4.4.

The dipole allowed transitions from core  $3d_{3/2,5/2}$  levels to the unoccupied  $5f_{5/2,7/2}$  valence states for left ( $\lambda = +1$ ) and right ( $\lambda = -1$ ) polarized x-rays.

Edge	$\lambda = +1$	$\lambda = -1$	
	$-5/2 \rightarrow -3/2$	$-5/2 \rightarrow -7/2$	
	$-3/2 \rightarrow -1/2$	$-3/2 \rightarrow -5/2$	
$M_5$	$-1/2 \rightarrow +1/2$	$-1/2 \rightarrow -3/2$	
	$+1/2 \rightarrow +3/2$	$+1/2 \rightarrow -1/2$	
	$+3/2 \rightarrow +5/2$	$+3/2 \rightarrow +1/2$	
	$+5/2 \rightarrow +7/2$	$+5/2 \rightarrow +3/2$	
	$-3/2 \rightarrow -1/2$	$-3/2 \rightarrow -5/2$	
$M_4$	$-1/2 \rightarrow +1/2$	$-1/2 \rightarrow -3/2$	
	$+1/2 \rightarrow +3/2$	$+1/2 \rightarrow -1/2$	
	$+3/2 \rightarrow +5/2$	$+3/2 \rightarrow +1/2$	

with  $\Delta j = 0$  is about 15 times smaller than the transitions with  $\Delta j = 1$  (see Eq. 1.201).

The selection rules for the magnetic quantum number  $m_j$  ( $m_j$  is restricted to -j, ... + j) are  $\Delta m_j = +1$  for  $\lambda = +1$  and  $\Delta m_j = -1$  for  $\lambda = -1$ . Table 4.4 presents the dipole allowed transitions for x-ray absorption spectra at  $M_5$ and  $M_4$  edges for left ( $\lambda = +1$ ) and right ( $\lambda = -1$ ) polarized x-rays.

To go further, we needs to discuss the characteristic of the 5*f* empty DOS. Since *l* and *s* prefer to couple antiparallel for less than half-filled shells, the j = l - s = 5/2 has a lower energy than the j = l + s = 7/2 level. Due to the intra-atomic exchange interaction the lowest sublevel of the j = 5/2 will be  $m_{5/2} = -5/2$ , however, for the j = 7/2 the lowest sublevel will be  $m_{7/2} = +7/2$ . This reversal in the energy sequence arises from the gain in energy due to alignment of the spin with the exchange field [983].

The  $5f_{7/2}$  states are almost completely empty in all the uranium compounds. Therefore all the transitions listed in Table 4.4 are active in the  $M_5$  absorption spectrum. The contribution from the first four transitions for  $\lambda = +1$  cancels to a large extent with the contribution of the opposite sign from the last four transitions for  $\lambda = -1$  having the same final states. Thus the XMCD spectrum of U at the  $M_5$  edge  $(I = \mu^- - \mu^+)$  can be roughly approximated by the following sum of  $m_j$ -projected partial densities of states [800]:  $(N_{-7/2}^{7/2} + N_{-5/2}^{7/2}) - (N_{7/2}^{7/2} + N_{5/2}^{7/2})$ . Here we use the notation  $N_{m_j}^j$  for the density of states with the total momentum j and its projection  $m_j$ . As a result, the shape of the  $M_5$  XMCD spectrum contains of two peaks of opposite signs – a negative peak at lower energy and a positive peak at higher energy. As the separation of the peaks is smaller than the typical lifetime broadening, the peaks cancel each other to a large extent, thus leading to a rather small signal. Since the splitting of states with  $m_j = \pm |m_j|$  increases with the increase of the magnetization at the U site, the amplitude of the  $M_5$  spectrum should be proportional to the U magnetic moment.

A rather different situation occurs in the case of the  $M_4$  x-ray absorption spectrum. Usually in uranium compounds the U atom is in  $5f^3$  (U<sup>+3</sup>) or  $5f^2$ (U<sup>+4</sup>) configurations and has partly occupied  $5f_{5/2}$  states. In the first case the  $5f_{5/2}$  states with  $m_j = -5/2$ , -3/2, and -1/2 are usually occupied. The dipole allowed transitions for  $\lambda = +1$  are  $-1/2 \rightarrow +1/2$ ,  $+1/2 \rightarrow +3/2$ , and  $+3/2 \rightarrow +5/2$  and those for  $\lambda = -1$  are  $+3/2 \rightarrow +1/2$ . The transitions with the same final states  $m_j$ =+1/2 mostly cancel each other and the XMCD spectrum of U at the  $M_4$  edge can be roughly represented by the sum [800]  $-(N_{3/2}^{5/2} + N_{5/2}^{5/2})$ . The corresponding analysis for the  $5f^2$  (U<sup>+4</sup>) configuration with occupied  $f_{5/2,-5/2}$  and  $f_{5/2,-3/2}$  states shows that the dipole allowed transitions for  $\lambda = +1$  are  $-3/2 \rightarrow -1/2$ ,  $-1/2 \rightarrow +1/2$ ,  $+1/2 \rightarrow +3/2$ , and  $+3/2 \rightarrow +5/2$  and for  $\lambda = -1$ :  $+1/2 \rightarrow -1/2$  and  $+3/2 \rightarrow +1/2$ . Again, the XMCD spectrum of U at the  $M_4$  edge can be approximated by  $-(N_{3/2}^{5/2} + N_{5/2}^{5/2})$  [800]. This explains why the dichroic  $M_4$  line in uranium compounds consists of a single nearly symmetric negative peak.

We should note, however, that the explanation of the XMCD line shape in terms of  $m_i$ -projected DOS's presented above should be considered as only qualitative. First, there is no full compensation between transitions with equal final states due to difference in the angular matrix elements; second, in our consideration we neglect cross terms in the transition matrix elements; third, there is no pure  $5f^3$  or  $5f^2$  configurations in uranium compounds. It is always difficult to estimate an appropriate atomic 5f occupation number in band structure calculations. Such a determination is usually obtained by the integration of the 5f electron charge density inside of the corresponding atomic sphere. In the particular UFe<sub>2</sub> case, the occupation number of U 5f states is around 2.9 in the LSDA calculations. We, however, should keep in mind that some amount of the 5f states are derived from the so-called "tails" of Fe 3dstates arising as a result of the decomposition of the wave function centered at Fe atoms. The careful analysis in the case of UPd<sub>3</sub> presented in Ref. [135] shows that the occupation number of the "tails" of Pd 4d states sum up to give the 5f occupation of 0.9 electrons in the U atomic sphere. We should also note that due to the strong hybridization between U 5 f and Fe 3d states, the U  $5f_{7/2}$  states in UFe<sub>2</sub> are not completely empty, some of them are occupied, also some amount of U  $5f_{5/2}$  states, which we have been considering as fully occupied, are partially empty.

The overall shapes of the calculated and experimental uranium  $M_{4,5}$  XMCD spectra correspond well to each other (Fig. 4.27). The major discrepancy between the calculated and experimental XMCD spectra is the size of the  $M_4$  XMCD peak. The LSDA underestimates the integral intensity of the XMCD at the M<sub>4</sub> edge. As the integrated XMCD signal is proportional to the orbital moment [282] this discrepancy may be related to an underestimation of the orbital moment by LSDA-based computational methods (Table 3.2). On the other hand, the LSDA+U(OP) approximation gives larger intensity for the M<sub>4</sub> XMCD spectrum in comparison with the experimentally measured one. It reflects the overestimation of the orbital moment at U site in the LSDA+U(OP) calculations (Table 3.2). In the case of the M<sub>5</sub> XMCD spectrum, the LSDA reproduces the amplitude of the positive peak and overestimates the amplitude of the negative peak.

To investigate the influence of the initial state on the resulting U XMCD spectra we calculated also the XAS and XMCD spectra of UFe<sub>2</sub> compound at the  $N_{4,5}$  and  $O_{4,5}$  edges (not shown). We found a substantial decrease of the XMCD in terms of  $R = \Delta \mu / (2\mu^0)$  at  $N_{4,5}$  edges in comparison with the  $M_{4,5}$  ones. The theoretically calculated dichroic  $N_4$  line consists of a simple nearly symmetric negative peak that has no distinct structure as was observed at the  $M_4$  XMCD spectrum. The LSDA calculations give much smaller dichroic signal at the  $N_4$  edge in comparison with the LSDA+U(OP) calculations. The dichroic line at the  $N_5$  edge is reminiscent of the corresponding  $M_5$  spectrum and has an asymmetric s shape with two peaks – a stronger negative peak and much weaker positive peak. In contrast to the dichroism at the  $M_{4,5}$  edges where XMCD at  $M_4$  edge is more than two times larger than at the  $M_5$  one, the dichroism at the  $N_4$  edge has almost the same intensity as at the  $N_5$  edge.

Due to MO selection rules the  $O_4$  XMCD spectrum resembles the  $M_4$  spectrum, whereas the  $O_5$  spectrum is similar to the  $M_5$  one. Because of the relatively small spin-orbit splitting of the 5d states of U (~ 11 eV), the  $O_4$  and  $O_5$  spectra almost overlap each other. The magnetic dichroism at quasi-core  $O_{4,5}$  edges is of one order of magnitude larger than the dichroism at the  $N_{4,5}$  edges and become almost as large as that at the  $M_{4,5}$  edge. Besides, the lifetime broadening of the core  $O_{4,5}$  levels is much smaller than the broadening of the  $M_{4,5}$  ones [918]. Therefore the spectroscopy of U atoms in the ultra-soft x-ray energy range at the  $O_{4,5}$  edges may be a very useful tool for investigation of the 5f electronic states in magnetic U materials.

The XAS spectra at the  $M_{4,5}$ ,  $N_{4,5}$ , and  $O_{4,5}$  edges involve electronic transitions between  $nd_{3/2,5/2}$  (n=3,4, and 5) and  $5f_{5/2,7/2}$  states and therefore are used to study of the 5f empty electronic states in uranium compounds. To investigate the 6d states of U one should tune the energy of the x-ray close to the



*Figure 4.28.* XMCD spectra of UFe<sub>2</sub> at the uranium  $M_{2,3}$ ,  $N_{2,3}$ ,  $O_{2,3}$  and  $N_{6,7}$  edges calculated in the LSDA approximation [800]. All the XMCD spectra are multiplied by a factor  $10^2$ . (The  $M_2$  and  $N_2$  spectra are shifted by -800 eV and -150 eV, respectively, to include them in the figure).

 $M_{2,3}$ ,  $N_{2,3}$ ,  $O_{2,3}$ , or  $N_{6,7}$  edges of uranium. The first three doublets are due to the  $np_{1/2,3/2} \rightarrow 6d_{3/2,5/2}$  (n=3,4, and 5) interband transitions.

Fig. 4.28 presents the theoretically calculated XMCD spectra of U  $M_{2,3}$ ,  $N_{2,3}$ , and  $O_{2,3}$  edges. The XMCD signals at these edges are two order of magnitude less than the corresponding signals at the  $M_{4,5}$  edges.

Because of the dipole selection rules, apart from the  $ns_{1/2}$  states (which have a small contribution to the XAS's due to relatively small  $np \rightarrow 7s$  matrix elements only  $6d_{3/2}$  states occur as final states for the  $M_2$ ,  $N_2$ , and  $O_2$  XAS's for unpolarized radiation, whereas for the  $M_3$ ,  $N_3$ , and  $O_3$  XAS's the  $6d_{5/2}$ states also contribute. Although the  $np_{3/2} \rightarrow 6d_{3/2}$  radial matrix elements are only slightly smaller than for the  $np_{3/2} \rightarrow 6d_{3/2}$  contribution (see Eq. 1.201). Therefore, neglecting the energy dependence of the radial matrix elements, the  $M_2$ ,  $N_2$ , and  $O_2$  absorption spectra can be viewed as a direct mapping of the DOS curve for  $6d_{3/2}$ , and the  $M_3$ ,  $N_3$ , and  $O_3$  XAS's reflect the DOS curve for  $6d_{5/2}$  states. The shape of  $X_3$  (X = M, N, or O) XMCD spectra consists of two peaks of opposite sign - a negative peak at lower energy and a positive peak at higher energy. The shape of  $X_2$  (X = M, N, or O) XMCD spectra also have two peaks of an opposite sign, but the negative peaks situated at higher energy and the positive peak at lower energy (Fig. 4.28).

Figure 4.28 also presents the theoretically calculated XMCD spectra at U  $N_{6,7}$  edges. Because of the electric dipole selection rules the major contribution to the absorption at the  $N_7$  edge stems from the transitions  $4f_{7/2} \rightarrow 6d_{5/2}$  and that at the  $N_6$  edge originates primarily from  $4f_{5/2} \rightarrow 6d_{3/2}$  transitions (the contribution from  $4f_{5/2} \rightarrow 6d_{5/2}$  transitions are strongly suppressed by the angular matrix elements). The XMCD signals at these edges are even smaller than the corresponding signals at the  $X_{2,3}$  (X = M, N, or O) edges. Because of the relatively small spin-orbit splitting of the 4f states of U, the  $N_6$  and  $N_7$  spectra have an appreciable overlap. Besides, in the case of  $N_{6,7}$  XAS one would expect a strong electrostatic interaction between the created 4f core hole and the valence states. It can lead to an additional multiplet structure in the XAS and XMCD spectra at the  $N_{6,7}$  edges. We have not considered multiplet structure in our XMCD calculations. This structure can be captured using full atomic multiplet structure calculations.

We also calculated the x-ray magnetic circular dichroism at the Fe K,  $L_{2,3}$ , and  $M_{2,3}$  edges, with the results being presented in Fig. 4.29. For comparison we also show the XMCD spectra in bcc Fe. Although the XMCD signal at the Fe K edge has almost the same amplitude both in bcc Fe and UFe<sub>2</sub>, their shapes are quite different (Fig. 4.29). It was first pointed out by Gotsis and Strange [893] as well as Brooks and Johansson [917] that XMCD K spectrum reflects the orbital polarization in differential form  $d\langle l_z \rangle/dE$  of the p states.



*Figure 4.29.* XMCD spectra of UFe<sub>2</sub> at the Fe K,  $L_{2,3}$ , and  $M_{2,3}$  edges in bcc Fe and Fe in UFe<sub>2</sub> calculated in the LSDA approximation [800]. The XMCD spectrum at the K edge has been multiplied by a factor  $10^2$ .

It gives a rather simple and straightforward interpretation of the Fe XMCD spectrum at the K edge [623].

The dichroism at Fe  $L_2$  and  $L_3$  edges is influenced by the spin-orbit coupling of the initial 2p core states. This gives rise to a very pronounced dichroism in comparison with the dichroism at the K edge. Figure 4.29 shows the theoretically calculated Fe  $L_{2,3}$  XMCD spectra in UFe<sub>2</sub> and bcc Fe. The

dichroism at the  $L_3$  edge has a negative sign and at the  $L_2$  edge a positive one. The XMCD dichroic signals at the Fe  $L_{2,3}$  and  $M_{2,3}$  edges are three times smaller in UFe<sub>2</sub> than the corresponding XMCD in bcc Fe due to strongly reduced magnetic moment at the Fe site in UFe<sub>2</sub> in comparison with pure Fe. Besides, the shape of the spectra is more asymmetrical in UFe<sub>2</sub>.

The magnetic dichroism at the Fe  $M_{2,3}$  edges is much smaller than at the  $L_{2,3}$  edges (Fig. 4.29). Besides the  $M_2$  and the  $M_3$  spectra are strongly overlapped and the  $M_3$  spectrum contributes to some extent to the structure of the total  $M_{2,3}$  spectrum in the region of the  $M_2$  edge. To decompose a corresponding experimental  $M_{2,3}$  spectrum into its  $M_2$  and  $M_3$  parts will therefore be quite difficult in general. It worth mentioning that the shape of Fe  $L_3$  and  $M_3$  XMCD spectra are very similar.

#### 4.3.2 US, USe, and UTe

The uranium compounds US, USe, and UTe belong to the class of uranium monochalcogenides that crystallize in the NaCl structure and order ferromagnetically (on the uranium sublattice) at Curie temperatures of 178, 160, and 102 K, respectively (see, e.g., the review [967]). These uranium compounds exhibit several unusual physical phenomena, which are the reason for a continuing on-going interest in these compounds. Despite their relatively simple and highly symmetrical NaCl structure, it has been found that the magnetic ordering on the uranium atoms is strongly anisotropic [989, 990], with the uranium moment favoring a [111] alignment. The magnetic anisotropy in US, e.g., is one of the largest measured in a cubic material, with a magnetic anisotropy constant  $K_1$  of more than  $2 \times 10^8$  erg/cm<sup>3</sup> [991]. Also the magnetic moment itself is unusual, consisting of an orbital moment that is about twice as large as the spin moment, and of opposite sign [992, 993, 148]. A bulk magnetization measurements [990] yields an ordered moment of 1.55  $\mu_B$  per unit formula and neutron scattering measurements [994] show a slightly larger value of 1.70  $\mu_B$ , which is assigned to the 5f magnetic moment. These values are far smaller than that expected for the free ion, indicating that some sort of "solid state effect" takes place with the 5f states. From several experimental results (for instance, photoemission [995], electrical resistivity [996], pressure dependence of Curie temperature [997], and specific heat measurements [998, 999]), the 5 f electrons of US are considered to be itinerant.

It has been suggested that uranium monochalcogenides are mixed valence systems [1000]. Low-temperature ultrasonic studies on USe and UTe were performed in the context of questioning the possibility of the coexistence of magnetism and intermediate valence behavior [1001]. They found a monotonic trend of the Poisson's ratio, which decreases with increasing chalcogenide mass, and is positive in US, negative in USe and UTe. This indicates the possibility of intermediate valence in the last two compounds. Indeed, a negative Poisson's ratio, i.e. a negative  $C_{12}$  elastic constant, is quite common for intermediate valence systems, and its occurrence seems to be due to an anomalously low value of the bulk modulus. A negative  $C_{12}$  means that it costs more energy to distort the crystal from cubic to tetragonal structure, than to modify the volume. Thus, when uniaxially compressed along a [100] direction, the material will contract in the [010] and [001] directions, trying to maintain a cubic structure. An explanation for a negative  $C_{12}$  may be given through a breathing deformability of the actinide ion due to a valence instability [1002].

The dependence of the Curie temperatures  $T_c$  of US, USe and UTe on hydrostatic pressure up to 13 GPa has been determined in Ref. [1003]. For USe and UTe,  $T_c$  initially increases with applied pressure, passing through maxima at pressure of about 6 GPa and 7 GPa, respectively. For US,  $T_c$  decreases monotonically with pressure, which is compatible with pressure-dependent itinerant electron magnetism. Pressure increases the bandwidth and correspondingly decreases the density of states at the Fermi level, which leads to a decrease of  $T_c$ . The behavior of USe and UTe is suggestive of localized interacting 5fmoments undergoing Kondo-type fluctuations, which begin to exceed the magnetic interaction when  $T_c$  passes through maximum. A theoretical analysis of these experiments is given in Ref. [1004] On the basis of band structure calculations it is argued that the non-monotonic behavior of  $T_c$  under pressure is solely the result of pressure-driven increased 5f itineracy.

It must be remarked that the behavior of uranium monochalcogenides cannot be explained entirely by a simple trend of increasing localization with increasing chalcogen mass [966]. Whereas such a trend is evident in the dynamic magnetic response, in the pressure-dependence of the Curie temperatures and in the value of the ordered moment, the behavior of Poisson's ratio and of the Curie temperature is the opposite from what one would naively expect.

There are several band structure calculations of uranium monochalcogenides in literature [148, 1005–1014]. Kraft *et al.* [1008] have performed the LSDA calculation with the spin-orbit interaction (SOI) in a second variational treatment for ferromagnetic uranium monochalcogenides (US, USe, and UTe) using the ASW method, and have shown that the magnitude of the calculated orbital magnetic moment  $M_l$  is larger than that of spin moment  $M_s$  and they couple in an antiparallel way to each other. However, the magnitude of the total magnetic moment ( $M_s+M_l$ ) is too small compared to the experimental data, indicating that the calculated  $M_l$  is not large enough.

The optical and MO spectra of uranium monochalcogenides have been investigated theoretically in Ref.s [1005, 1006, 1008, 1010]. These theoretical spectra are all computed from first principles, using Kubo linear-response theory, but it appears that there are large differences among them. Cooper and co-worker [1007] find good agreement with experiment for the real part of the diagonal conductivity ( $\sigma_{xx}^{(1)}$ ) of UTe, but the much more complicated off-

diagonal conductivity  $(\sigma_{xy}^{(2)})$  of US and UTe is about 4 times larger than experiment and also the shape of their spectrum is different from the experimental one. Halilov and Kulatov [1005] also find an off-diagonal conductivity which is much larger than the experimental one, but they additionally obtain a diagonal conductivity  $\sigma_{xx}^{(1)}$  that differs substantially from experiment. Gasche [1006] find a Kerr rotation spectrum of US that is quite different from experiment, and subsequently consider the effect of an orbital polarization term to improve the ab initio Kerr spectra. Kraft et al. [1008] obtained for US, USe, and UTe reasonable agreement with experiment for the absolute value of the Kerr spectra. However, the shape of the Kerr spectra is not reproduced by LSDA theory, since the theoretical spectra exhibit a double-peak structure, but experimental spectra have only a one-peak structure. The LSDA+U calculations presented in Ref. [1010] take into account the strong Coulomb correlations among the 5f orbitals and are greatly improve the agreement between theory and experiment for all three materials. This finding appears to be consistent with the quasilocalized nature of the 5f electrons in these compounds.

**Band structure.** All the three chalcogenides, namely, US. USe, and UTe crystallize in the NaCl type structure (B1) with space group symmetry Fm3m. The uranium atom is positioned at (0,0,0) and chalcogen at (1/2,1/2,1/2).

The LSDA energy band structure of US (Figure 4.30) can be subdivided into three regions separated by energy gaps. The bands in the lowest region around -15 eV have mostly S s character with a small amount of U sp character mixed in. The next six energy bands are S p bands separated from the s bands by an energy gap of about 6 eV. The width of the S p band is about 4 eV. U 6d bands are broad and extend between -2.5 and 10 eV. The sharp peaks in the DOS just below and above the Fermi energy are due to  $5f_{5/2}$  and  $5f_{7/2}$  states, respectively. Fig. 4.30 also shows the energy bands and total density of states of US in the LSDA+U approximation [1014]. The Coulomb repulsion splits partially occupied U  $5f_{5/2}$  states and the LSDA+U calculations give a solution with three localized 5f electrons in US. U 5f states just above the Fermi level are formed by the remaining  $5f_{5/2}$  states whereas the peak of  $5f_{7/2}$  states is pushed about 1 eV upward from its LSDA position.

Table 4.5 presents the comparison between calculated and experimental magnetic moments in uranium monochalcogenides. For comparison, we list also the results of previous band structure calculations. Our LSDA results obtained by fully relativistic spin-polarized LMTO method are in good agreement with the ASW Kraft *et al.* results [1008]. The LSDA calculations for ferromagnetic uranium monochalcogenides (US, USe, and UTe) give the magnitude of the total magnetic moment  $M_t$  too small compared to the experimental data, indicating that the calculated  $M_l$  is not large enough.

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*Figure 4.30.* Self-consistent fully relativistic energy band structure and total DOS (in states/(unit cell eV)) of US calculated within the LSDA and LSDA+U approximations with U=2 eV and J=0.5 eV [1014].

It is a well-known fact, however, that the LSDA calculations fail to produce the correct value of the orbital moment of uranium compounds [804, 148–150, 805]. In LSDA, the Kohn-Sham equation is described by a local potential including the spin-dependent electron density. The electric current, which describes  $M_l$ , is, however, not included. This means, that although  $M_s$ is self-consistently determined in LSDA, there is no framework to simultaneously determine  $M_l$  self-consistently.

Using the LSDA+OP method Brooks [148] obtained larger magnitude of  $M_l$  and improvement in  $M_t$ . However, they have stated that the individual magnitudes of  $M_s$  and  $M_l$  are considered to be too large from the analysis of the magnetic form factor and the ratio  $M_l/M_s$  is still far from the experimental value for all the three uranium monochalcogenides (Table 4.5).

Table 4.5 presents the calculated magnetic moments in uranium monochalcogenides using a generalization of the LSDA+U method [134, 135]. In this calculations we used U = 2.0 eV and J = 0.5 eV. Table 4.5 presents also the LSDA+U calculated magnetic moments with U = J = 0.5 eV (the LSDA+U(OP) approximation).

Fig. 4.31 shows  $5f_{5/2}$  partial density of states in US calculated within the LSDA, LSDA+U(OP) and LSDA+U approximations [1014]. The
#### Table 4.5.

The experimental and calculated spin  $M_s$ , orbital  $M_l$ , and total  $M_t$  magnetic moments at uranium site (in  $\mu_B$ ) of US, USe, and UTe [1014].

Compound	method	M	M	M+	-M/Ma	
compound	LSDA	-1.53	2.14	0.60	1.41	
	LSDA+U(OP)	-1.48	3.21	1.72	2.17	
	LSDA+U	-1.35	3.42	2.07	2.53	
US	LSDA [1008]	-1.6	2.5	0.9	1.6	
	LSDA+OP [148]	-2.1	3.2	1.1	1.5	
	OP scaled HF [150]	-1.51	3.12	1.61	2.07	
	HF(TB) [1012]	-1.49	3.19	1.70	2.14	
	exper. [994]	-1.3	3.0	1.7	2.3	
	exper. [990]	-	-	1.55	-	
	LSDA	-1.75	2.54	0.79	1.45	
	LSDA+U(OP)	-1.65	3.65	2.00	2.21	
	LSDA+U	-1.96	4.61	2.65	2.35	
USe	LSDA [1008]	-1.8	2.8	1.0	1.5	
	LSDA+OP [148]	-2.4	3.4	1.0	1.4	
	exper. [994]	-	-	2.0	-	
	exper. [990]	-	-	1.8	-	
	LSDA	-2.12	3.12	1.00	1.47	
	LSDA+U(OP)	-1.91	4.09	2.17	2.14	
	LSDA+U	-2.13	4.95	2.81	2.32	
UTe	LSDA [1008]	-2.2	3.4	1.2	1.5	
	LSDA+OP [148]	-2.6	3.4	0.8	1.3	
	exper. [1015]	-1.57	3.48	1.91	2.21	
	exper. [994]	-	-	2.2	-	
	exper. [990]	-	-	1.9	-	

LSDA+U(OP) approximation strongly affects the relative energy positions of  $m_j$  projected 5*f* density of states and substantially improve their orbital magnetic moments (Table 4.5). For example, the ratio  $M_l/M_s$  in the LSDA+U(OP) calculations is equal to -2.17 and -2.14 for US and UTe, respectively. The corresponding experimental value are -2.3 for US from the neutron measurements [994] and -2.21 for UTe from the magnetic Compton profile measurements [1015].

The 5f spin  $M_s$  and orbital  $M_l$  magnetic moments in US have been also calculated in Ref. [1012] on the basis of the HF approximation for an extended Hubbard model. The tight-binding model includes the intra-atomic 5f - 5f multipole interaction and the SOI in the 5f state. The parameters involved in the model were determined by fitting with the energy of Bloch electrons in



*Figure 4.31.* The partial  $5f_{5/2}$  density of states (in states/atom eV) in US, USe, and UTe calculated within the LSDA, LSDA+U(OP), and LSDA+U approximations [1014].

the paramagnetic state obtained in the LDA band structure calculation. The calculated ratio of the moments  $M_l/M_s$  of -2.14 and  $M_l$  of  $-3.19\mu_B$  are in good agreement with available experimental results (Table 4.5).

We should mentioned that the results of the LSDA+U(OP) calculations are in close agreement with the results obtained using the HF approximation for an extended Hubbard model [1012] (Table 4.5). Both the approximations take into account the SOI and the intra-atomic 5f - 5f Coulomb interaction in Hubbard model. The small differences in magnetic moments are due to slightly different values of  $U_{eff}$ . In our calculations we used U = J = 0.5 eV, which gives  $U_{eff}=0$ . Authors of Ref. [1012] used U = 0.76 eV and J = 0.5 eV, which gives  $U_{eff}=0.26$  eV. Besides, there are some small differences in F<sup>2</sup>, F<sup>4</sup> and F<sup>6</sup> Slater integrals in two the calculations.

Fig. 4.31 also shows the  $m_j$  projected  $5f_{5/2}$  density of states in US calculated in the LSDA+U approximation with U = 2.0 eV and J = 0.5 eV [1014]. The corresponding partial DOS's for USe and UTe are presented in Fig. 4.32. The degree of localization of occupied  $5f_{5/2}$  states is increasing going from US to UTe. In US the  $5f_{5/2}$  states with  $m_j = -5/2$  is strongly hybridized with



*Figure 4.32.* The partial  $5f_{5/2}$  density of states (in states/atom eV) in US, USe, and UTe calculated within the LSDA+U approximation [1014].

other occupied states, while the hybridization in USe and particularly in UTe almost vanishes. The  $5f_{5/2}$  states with  $m_j = -5/2$  are responsible for the narrow single peak in UTe (Fig. 4.32). The orbital magnetic moments calculated in the LSDA+U approximation are larger than calculated in the LSDA+U(OP) approximation, which leads to slightly overestimated ratio  $M_l/M_s$  in comparison with the experimental data for the LSDA+U calculations (Table 4.5).

**XMCD spectra.** Fig. 4.33 shows the XMCD spectra of US, USe, and UTe at the uranium  $M_{4,5}$  edges calculated within the LSDA and LSDA+U approximations [1014]. It is clearly seen that the LSDA calculations give inappropriate results. The major discrepancy between the LSDA calculated and experimental XMCD spectra is the size of the  $M_4$  XMCD peak. The LSDA underestimates the integral intensity of the XMCD at  $M_4$  edge. As the integrated XMCD signal is proportional to the orbital moment [282] this discrepancy could be related to an underestimation of the orbital moment by LSDA-based computational methods (Table 4.5). On the other hand, the LSDA+U approximation produces good agreement with the experimentally measured intensity for the  $M_4$  XMCD spectrum. In the case of the  $M_5$  XMCD spectrum, the LSDA strongly overestimates the value of the positive peak. The LSDA+U(OP) approximation gives a good agreement in the shape and intensity of the XMCD spectrum at the  $M_5$  edge.



*Figure 4.33.* The XMCD spectra of US, USe, and UTe at the uranium  $M_{4,5}$  edges calculated within the LSDA (dashed lines), LSDA+U(OP) (dotted lines), and LSDA+U (solid lines) approximations [1014]. Experimental spectra of US [988] (circles) were measured at magnetic field 2 T. (U  $M_4$  spectra are shifted by -95 eV to include them in the figure).

The behavior of the 5f electrons ranges from nearly delocalized to almost localized: US is considered to be nearly itinerant [1016], while UTe is considered to be quasilocalized [1017]. So the failure of LSDA description of XMCD spectra in US comes as a surprise, because, if the 5f electrons are itinerant, one would expect the delocalized LSDA approach to be applicable. However, as the integrated XMCD signal is proportional to the orbital moment [282] this discrepancy could be related to an underestimation of the orbital moment by LSDA-based computational methods.

It is interesting to note, that the LSDA+U(OP) and LSDA+U calculations give similar results for XMCD spectrum at the  $M_5$  edge in the case of US and became relatively more different going through USe and UTe, probably, reflecting the increase of degree of localization of 5*f* electrons. Besides, the relative intensity of the  $M_5$  and  $M_4$  XMCD spectra is strongly increased going from US to UTe. The experimental measurements of the XMCD spectra in USe and UTe are highly desired.

## 4.3.3 UXAl (X=Co, Rh, and Pt)

The group of ternary uranium compounds with composition UTX, where T is a transition metal (Fe-Ni and 4d, 5d equivalents) and X a p element (Al, Ga, Ge, Sn), has recently attracted attention [1018]. These compounds provide wide possibilities for study via the variation of atom types. The compounds forming with atoms to the left of the transition metal series (Fe, Co, and Ru) are paramagnetic - although UCoAl is metamagnetic - while URhAl, UIrAl and UPtAl are ferromagnetic and UNiAl is antiferromagnetic.

One of the key questions to be addressed when discussing actinide compounds is the degree of localization of the 5f electrons, which may range from nearly localized to practically itinerant, depending on the specific compound. Since the 5f electrons are simultaneously involved in the chemical bonding and magnetism, a broad variety of physical properties may emerge from the degree of 5f localization. UTA1 (T=Co, Rh, and Pt) compounds have been also considered in this respect [988, 1019, 1020, 833, 831].

UCoAl shows no magnetic ordering down to the lowest temperatures, but in a relatively low magnetic field, of about 0.7 T, applied along the *c* axis a metamagnetic transition to a ferromagnetic state is observed at low temperatures. The metamagnetic transition in UCoAl is attributed to band metamagnetism [988]. The metamagnetism is induced only when the magnetic field is applied along the *c* axis, whereas in fields in a perpendicular direction UCoAl behaves like a Pauli paramagnet and no metamagnetic transition is observed in magnetic fields up to 42 T [1019]. The strong uniaxial magnetic anisotropy is preserved in UCoAl, at least up to room temperature. It is of interest to note a rather low ordered magnetic moment of UCoAl which amounts to  $0.30\mu_B/f.u.$  at 4.2 K, above the metamagnetic transition. The moment steadily increases with magnetic field, showing no saturation tendency up to 35 T where it reaches the value of  $0.6\mu_B/f.u.$  [1019, 1020].

The UPtAl compound is an appropriate reference system for the same structure and with composition and bonding similar to that of UCoAl. It orders ferromagnetically below a  $T_C$  of 43 K with a saturated magnetization of  $1.38\mu_B$ per formula unit at 2 K in fields applied along the *c* axis [1021]. The strong uniaxial anisotropy is manifested by the fact that the magnetization measured along the *a* axis is much smaller and has no spontaneous component. In fact, it resembles the magnetic response of a paramagnet exhibiting  $0.28\mu_B/f.u.$  at 40 T.

As for the URhAl compound, a sizable induced moment of  $0.28\mu_B$  on the Rh atom within the basal uranium plane was detected in a polarized neutron study, whereas, interestingly, only a very small induced moment of  $0.03\mu_B$ 

was detected on the equally close Rh site out of the plane [833]. The large anisotropy in the induced Rh moments clearly reflects the anisotropy of the U(5f)-Rh(4d) hybridization: a strong hybridization occurs between the valence orbitals of the U and Rh atoms within the basal plane, but the hybridization between the valence orbitals of the U atom and those of the equally close Rh atom in the adjacent plane is much smaller.

Later, inelastic neutron-scattering experiments found a peak at 380 meV, which was interpreted as the signature of an intermultiplet transition [831], thus promoting the localized picture. The 380-meV peak occurred at the same energy where a uranium intermultiplet transition was observed [832] in UPd<sub>3</sub>, which is one of the uranium compounds where the 5f electrons are undoubtedly localized.

Five electronic band structure calculations for URhAl were carried out recently [595, 1022, 1023, 988, 1024]. These indicated, first, that the bonding and magnetism are governed by the U 5f – Rh 4d hybridization [1022] and, second, that the calculated magneto-optical Kerr spectrum [595] – based on the assumption of delocalized 5f's – compares reasonably well to the experimental Kerr spectrum. Besides, the authors of Ref. [1023] were able to describe satisfactory the equilibrium volume, bulk modulus, and magnetocrystalline anisotropy in URhAl using the LSDA-based full potential relativistic LAPW method. Somewhat less well explained were the uranium orbital moment and the XMCD spectra.

Experimental and theoretical x-ray magnetic circular dichroism XMCD studies of the intermetallic compounds UCoAl and UPtAl at the uranium  $M_4$  and  $M_5$  edges are reported in Ref. [988]. The results show that the orbital-to-spin moment ratio is of comparable value,  $M_l/M_s \sim -2$ , for both compounds. The reduction of the  $M_l/M_s$  ratio compared to the U<sup>3+</sup> (5f<sup>3</sup>) free ion value of -2.57, and the sizable decrease of orbital and spin moments, especially for UCoAl, indicate a significant delocalization of the 5f electron states in these compounds.

**Band structure.** UTAl (T=Co, Rh, or Pt) crystallize in the hexagonal Zr-NiAl structure (Fe<sub>2</sub>P type), which contains three formula units per unit cell. The ZrNiAl structure has a layered structure, consisting of planes of uranium atoms admixted with one-third of the T atoms, that are stacked along the c axis, while two adjacent uranium planes are separated from one another by a layer consisting of the remaining T atoms and the Al atoms. The uranium atoms have transition metal nearest neighbors and vice versa, so both uranium and Tatoms are well separated from atoms of the same type. The uranium interlayer exchange coupling is relatively weak and depends sensitively on the specific Telements, which gives rise to a variety of magnetic behaviors observed in the UTX compounds [1018].

The fully relativistic spin-polarized LSDA energy band structure and total density of states (DOS) of the ferromagnetic UTAl (T=Co, Rh, and Pt) compounds are shown in Fig. 4.34 [1024]. The bands in the lowest region of UPtAl, between -9.2 and -6.0 eV, have mostly Al s character with a small amount of U spd and Al p character mixed in. The energy bands between -6.0and -3.0 eV are predominantly Pt 5d states. Due to increasing of the spatial expansion of valence transition metal d states in going from Co to Pt the corresponding d energy widths are increased and shifted downwards. Co 3d energy bands are occupied in the -1.2 to -2.8 eV energy interval in UCoAl, the 4d bands of Rh in URhAl are situated in the -2.0 to -4.5 eV energy range, and Pt 5d bands are in the -3.0 - 6.0 eV interval. Therefore the valence d energy band widths are equal to 1.6, 2.5, and 3.0 eV in UCoAl, URhAl, and UPtAl, respectively (Fig. 4.34). The U 5f energy bands occupy the same energy interval above and below  $E_F$  in all the compounds under consideration, namely, about -1.0 to 2.0 eV. There is a strong hybridization between the U 6d, transition metal d, and Al p states.

The itinerant character of electron states usually implies a strong reduction of the orbital magnetic moment with respect to the free-atom expectation value. Nevertheless, in contrast to 3d electrons in transition metals, sizable orbital magnetic moments are observed in U intermetallic compounds with apparently strongly delocalized 5f electrons. It is the very strong spin-orbit coupling present in actinides that enhances an orbital moment in the case of itinerant 5f electron states. Analyzing spin and orbital magnetic moments in various actinide compounds, Lander et al. suggested that the ratio of the orbital to the spin moments provides information on the strength of 5f ligand hybridization, and consequently the delocalization of the 5f electrons [1025]. The individual values of orbital and spin components, however, contain essential information, and therefore relevant experiments and first-principles electronic structure calculations which independently evaluate orbital and spin moments become an important issue for 5f electron compounds. The recently developed x-ray magnetic circular dichroism experimental method combined with several sum rules [282, 283] has attracted much attention as a site- and symmetry-selective way to determine  $M_{s}$  and  $M_{l}$ . It should be mentioned, however, that the reported quantitative results inferred from the XMCD spectra are based on a sum rule analysis of the spin-orbit split spectra of the core levels of uranium. The sum rules enable one to estimate the spin and orbital components of the uranium ions, however, the values of magnetic moments rely on theoretical inputs such as the number of holes in the 5f subshell and a value of the dipolar term. In particular, the spin moment is retrieved with a higher relative error. Comparing the XMCD-derived moments with the results of polarized neutron diffraction and first-principles calculations, one usually obtains smaller moments from the XMCD sum rules for uranium compounds [1023, 988]. A

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The LSDA self-consistent fully relativistic, spin-polarized energy band structure *Figure* 4.34. and total DOS (in states/(unit cell eV)) of UCoAl, URhAl, and UPtAl [1024].

more reliable quantity that can be extracted from the sum rule analysis is the ratio between orbital and spin moments and their relative orientation.

Table 4.6 lists the calculated spin  $M_s$ , orbital  $M_l$ , and total  $M_t$  magnetic moments (in  $\mu_B$ ) of UTAl (T=Co, Rh, and Pt) as well as the ratio  $M_l/M_s$ [1024]. Our LSDA results are in good agreement with previous LSDA-based calculations [1023, 988]. All the LSDA calculations strongly underestimate the orbital moment in the compounds. The inclusion of the orbital polarization (OP) correction in Ref. [1022] brings the calculated total U moment in URhAl to 0.60  $\mu_B$ , in better agreement with experiment (0.94  $\mu_B$  according to Ref. [833]) in comparison with the LSDA calculations (Table 4.6).

#### Table 4.6.

The experimental and calculated spin  $M_s$ , orbital  $M_l$ , and total  $M_t$  magnetic moments at uranium site (in  $\mu_B$ ) of UCoAl, URhAl, and UPtAl [1024].

Compound	method	$M_s$	$M_l$	$\mathbf{M}_t$	$-M_l/M_s$
UCoAl	LSDA	-0.92	1.09	0.17	1.18
	LSDA+U(OP)	-1.14	2.29	1.15	2.01
	LSDA+U	-1.50	3.47	1.97	2.31
	LSDA [988]	-1.01	1.19	1.18	1.18
	exper. [988]	-	-	-	1.95
URhAl	LSDA	-1.23	1.72	0.49	1.40
	LSDA+U(OP)	-1.40	2.94	1.54	2.10
	LSDA+U	-1.66	3.83	2.17	2.31
	LSDA [988]	-1.22	1.59	0.37	1.30
	LSDA [1023]	-1.24	1.63	0.39	1.31
	LSDA+OP [1022]	-1.01	1.61	0.60	1.59
	exper. [833]	-1.16	2.10	0.94	1.81
UPtAl	LSDA	-1.63	2.08	0.45	1.28
	LSDA+U(OP)	-1.60	3.32	1.72	2.08
	LSDA+U	-1.85	4.26	2.41	2.30
	LSDA [988]	-1.63	2.06	0.43	1.26
	exper. [988]	-	-	-	2.10

As mentioned, we also carried out energy band structure calculations for the UTAl compounds using a generalization of the LSDA+U method [135]. In these calculations we used U = J = 0.5 eV, which gives  $U_{eff}=0$  (the LSDA+U(OP) approximation) as well as U = 2.0 eV and J = 0.5 eV. Fig. 4.35 shows the  $5f_{5/2}$  partial density of states in UPtAl calculated in the LSDA, LSDA+U(OP), and LSDA+U approximations. As can be seen from Fig. 4.35 the LSDA+U(OP) approximation, which takes into account the correlations between spin and orbital magnetic moment directions, strongly affects the relative energy positions of  $m_j$  projected 5f density of states and substantially improves their orbital magnetic moments (Table 4.6). The ratio  $M_l/M_s$  in the LSDA+U(OP) calculations is equal to 2.01, 2.10, and 2.08 for UCoAl, URhAl, and UPtAl, respectively. The correspondent experimental data are 1.95, 1.81, and 2.10 estimated from the XMCD measurements [988].

The orbital magnetic moments calculated in the LSDA+U approximation with U = 2.0 eV and J = 0.5 eV are larger than those calculated using U = J = 0.5 eV, which leads to slightly overestimated ratio M<sub>l</sub>/M<sub>s</sub> in comparison with the experimental data (Table 4.6).



*Figure 4.35.* The partial  $5f_{5/2}$  density of states (in states/atom eV) in UPtAl calculated in the LSDA and LSDA+U(OP) approximations [1024].

**XMCD spectra.** Fig. 4.36 shows the calculated x-ray isotropic absorption and XMCD spectra in the LSDA, LSDA+U(OP), and LSDA+U approximations for UPtAl [1024] together with the experimental data [988]. To calculate the x-ray isotropic absorption M<sub>4,5</sub> spectra we take into account the background intensity which appeares due to the transitions from inner levels to the continuum of unoccupied levels [280].

Due to underestimation of the orbital magnetic moment the theory produces much smaller intensity of the XMCD spectrum at the  $M_4$  edge in comparison with the experiment in the LSDA calculations and simultaneously gives a larger dichroic signal at the  $M_5$  edge of UPtAl (Fig. 4.36). On the other hand, the LSDA+U(OP) approximation produces an excellent agreement not only for the value of the magnetic moments but also in the shape and intensity of XMCD spectra both at the  $M_4$  and  $M_5$  edges. The LSDA+U approximation with U = 2.0 eV and J = 0.5 eV overestimates the negative signal at the  $M_4$ edge due to the overestimation of the U orbital magnetic moment. This ap-



*Figure 4.36.* Isotropic absorption and XMCD spectra of UPtAl at the uranium  $M_{4,5}$  edges calculated in the LSDA (dotted lines) and LSDA+U(OP) (solid lines) approximations [1024]. Experimental spectra [988] (circles) were measured at 10 K and at magnetic field 2 T (the U  $M_4$  spectrum is shifted by -95 eV to include it in the figure).

proximation also underestimates the positive peak and strongly overestimates the negative one at the  $M_5$  edge (Fig. 4.36).

In the case of URhAl the LSDA+U(OP) approximation also produces an XMCD spectrum at the  $M_4$  edge in excellent agreement with experiment, but slightly overestimates the value of the positive shoulder at the  $M_5$  edge (Fig. 4.37). The LSDA+U approximation with U = 2.0 eV and J = 0.5 eV overestimates the negative signal at the  $M_4$  edge, although, slightly improves the agreement with the experimental spectrum at U  $M_5$  edge (Fig. 4.37).

The LSDA+U(OP) approximation overestimates and the LSDA+U one strongly overestimates the intensity of XMCD signal at the  $M_4$  edge in UCoAl, probably due to the fact that the measured spontaneous magnetic moment of UCoAl is far from the saturation in the experimentally applied external magnetic field of 7 T [988]. One would expect, therefore, that in a higher magnetic field UCoAl will have larger orbital magnetic moment and, hence, larger dichroism at the  $M_4$  edge. As was the case for URhAl, the LSDA+U calculations with U = 2.0 eV and J = 0.5 eV give a better description of the positive peak at the  $M_5$  edge in UCoAl (Fig. 4.37).



*Figure 4.37.* The XMCD spectra of UCoAl and URhAl at the uranium  $M_{4,5}$  edges calculated in the LSDA (dashed lines) and LSDA+U(OP) (solid lines) approximations [1024]. Experimental spectra for UCoAl [988] (circles) were measured at magnetic field 7 T. Experimental data for URhAl is from Ref. [987]. (U  $M_4$  spectra are shifted by -95 eV to include them in the figure).



*Figure 4.38.* Uranium M<sub>5</sub> XMCD spectrum of UCoAl calculated in the LSDA+UOP) approximation (full line) and spectra calculated with  $[N_{7/2}+N_{5/2}]$  and  $[N_{-7/2}+N_{-5/2}]$  DOS's artificially shifted by 10 meV (dashed line) and 20 meV (dotted line) [1024].

The  $5f_{7/2}$  states are almost completely empty in all the uranium compounds, therefore the XMCD spectrum of U at the  $M_5$  edge can be roughly represented by the following  $m_j$  projected partial density of states [800]:  $[N_{-7/2}^{7/2} + N_{-5/2}^{7/2}]$ 

 $[N_{7/2}^{7/2}+N_{5/2}^{7/2}]$ . Thus the shape of  $M_5$  XMCD spectrum consists of two peaks of opposite sign - a negative peak at lower energy and a positive peak at higher energy. The XMCD spectrum of U at the  $M_4$  edge can be represented by the  $-[N_{3/2}^{5/2}+N_{5/2}^{5/2}]$  DOS's, [800] thus it consists of a single negative peak.

In UCoAl (above the metamagnetic transition) the dichroic line at the  $M_5$ edge has an asymmetric s shape with two peaks - a stronger negative peak and a weaker positive peak. The shape of the  $M_5$  XMCD spectrum strongly depends on the value of the external magnetic field, the positive peak is increased relative the negative one upon increasing the external magnetic field from 0.9 T to 7 T (see Fig. 2 in Ref. [988]). From the qualitative description of the  $M_5$  XMCD spectra in terms of partial density of states we can conclude that the shape of the  $M_5$  XMCD spectrum depends on the relative energy positions of the  $[N_{7/2}^{7/2}+N_{5/2}^{7/2}]$  and  $[N_{-7/2}^{7/2}+N_{-5/2}^{7/2}]$  partial DOS's which depend on the value of crystal field and Zeeman splittings of the  $5f_{7/2}$  electronic states [800]. Upon increasing of the external magnetic field the Zeeman splitting is increased, leading to larger separations between the  $m_i$  projected partial DOS's. Fig. 4.38 shows uranium M<sub>5</sub> XMCD spectrum of UCoAl calculated in the LSDA+U(OP) approximation and the spectra calculated with  $[N_{7/2}^{7/2}+N_{5/2}^{7/2}]$ and  $[N_{-7/2}^{7/2}+N_{-5/2}^{7/2}]$  DOS's artificially shifted by 10 and 20 meV. It is clearly seen that model calculations correctly reproduce the experimental tendency in the shape of UCoAl M<sub>5</sub> XMCD spectrum in the external magnetic field.

In conclusion, the LSDA+U approximation with U = 2.0 eV and J = 0.5 eV overestimates the negative signal at the  $M_4$  edge for all the compounds under the consideration due to the overestimation of the U orbital magnetic moment. This approximation provides poor description of the XMCD spectrum at the  $M_5$  edge in UPtAl, but gives rather good agreement with the experiment in the case of URhAl and UCoAl. One can conclude that the U 5f states in UPtAl have more itinerant character than those in URhAl and UCoAl.

#### 4.3.4 UPt<sub>3</sub>

UPt<sub>3</sub> is a well known heavy fermion system [1026, 1027]. The Sommerfeld coefficient of the linear low-temperature specific heat is strongly enhanced, i.e.,  $\gamma$ =420 mJ/(mol U  $K^2$ ). Strong electron-electron correlations are also manifest in a  $T^3 \log T$  term in the low temperature specific heat, which is believed to be due to spin fluctuations. At low temperature UPt<sub>3</sub> is a superconductor, with a  $T_c$  of 0.54 K [977]. UPt<sub>3</sub> is the archetype of a heavy-fermion system. It has the qualitative properties of a Fermi liquid, but the magnitude of the effective masses, reflected in the specific heat and magnetic susceptibility, is very much larger than the free-electron value. The heaviness of the electrons is gener-

ally attributed to electron correlations which come from the strong Coulomb interactions among the localized 5f electrons on the U sites.

UPt<sub>3</sub> has attracted a great deal of interest from band-structure theorists [1028–1032], particularly when it became clear that reliable experimental information on the Fermi surface could be obtained by measurements of the de Haas – van Alphen (dHvA) effect [1033–1035]. These experiments unambiguously confirm that UPt<sub>3</sub> has to be regarded as a strongly correlated Fermi liquid. Although a detailed picture of the low-temperature phase of UPt<sub>3</sub> has emerged, a comprehensive theoretical picture of the heavy quasiparticles is still missing.

It has been considered a success of the LSDA that the dHvA frequencies could be related to extremal orbits on the Fermi surface obtained by bandstructure calculations which treat the U 5*f* states as itinerant. There are good reasons that standard band-structure calculations reproduce well the complex topology of the Fermi surface in UPt<sub>3</sub>. In great contrast, however, no such agreement is found for the measured cyclotron masses. The calculated energy bands are too broad for explaining the effective masses: dHvA masses are by a factor of order 20 bigger than the band masses  $m_b$  obtained from the LSDA calculations [1030–1032]. This is of course the defining characteristic of a heavy-fermion compound and is due to the strong electron-electron correlations not included in the band-structure calculations. It is interesting that even in the presence of such strong correlations, there is no evidence of any breakdown of Fermi-liquid theory. The standard Lifshitz-Kosevich formula for the field and temperature dependence of the amplitude of quantum oscillations is perfectly verified down to 10 mK and up to 18 T [977].

UPt<sub>3</sub> shows a static antiferromagnetic order below about  $T_N$ =5 K with a very small staggered moment of order  $0.01\mu_B/U$  atom. This ordering was first noticed in muon spin relaxation measurements by Heffner *et al.* [1036] and was soon confirmed by neutron scattering [1037]. The magnetic order is collinear and commensurate with the crystal lattice, with a moment aligned in the basal plane. It corresponds to antiferromagnetic coupling within planes and ferromagnetic coupling between planes. All aspects of this ordering were reproduced by later neutron studies on a different crystal [1038, 1039] and by magnetic x-ray scattering [1040]. The moment at lower temperatures grows to a maximum magnitude of  $0.02-0.03\mu_B/U$  atom.

**Band strucure.** UPt<sub>3</sub> crystallizes in the MgCd<sub>3</sub> type structure. The uranium atoms form a closed-packed hexagonal structure with the platinum atoms bisecting the planar bonds. There are two formula units per unit cell. The compound belongs to the space group  $P6_3/mmc$  and the point group  $D_{6h}$ . The lattice parameters are a=5.753 Å and c/a=4.898. The nearest U-U distance

is between atoms in adjacent layers, equal to 4.132 Å, and the conductivity is greatest along the c axis.

The fully relativistic spin-polarized LSDA energy band structure and total DOS of the ferromagnetic UPt<sub>3</sub> compound is shown in Fig. 4.39 [1041]. The occupied part of the valence band is formed predominantly by Pt 5*d* states. The characteristic feature of the LSDA band structure is a narrow peak of U  $5f_{5/2}$  states situated just at the Fermi level ( $E_F$ ) 1.0 eV above the top of Pt 5*d* states. U  $5f_{7/2}$  states are split off by strong SO coupling and form another narrow peak 1 eV above  $E_F$ .

Fig. 4.39 also shows the band structure of UPt<sub>3</sub> calculated in the LSDA+U approximation with U=2.0 eV and J=0.5 eV [1041]. The Coulomb repulsion splits partially occupied U  $5f_{5/2}$  states and the LSDA+U calculations give a solution with two localized 5f electrons. These localized 5f states are situated above the top of Pt 5d and form a rather narrow peak at 0.2 eV below  $E_F$ . The position of the peak agrees well with the results of recent resonant photo-emission spectroscopy (PES) [852] and angular resolved PES (ARPES) [853] measurements. U 5f states just above the Fermi level are formed by the remaining  $5f_{5/2}$  states whereas the peak from the  $5f_{7/2}$  states is pushed from its LSDA position at 1 eV above  $E_F$  to 2.3 eV.

An orbital resolved DOS corresponding to the orbitals with the largest occupation numbers is shown in Fig. 4.40 for UPt<sub>3</sub> and for UPd<sub>3</sub> as a reference material. Two peaks at -1.0 to -0.5 eV in UPd<sub>3</sub> are formed by  $5f_{5/2}$  states with  $m_j = -5/2$  and  $m_j = -3/2$ . Their occupation numbers are  $n_{\frac{5}{2}}=0.988$ and  $n_{\frac{3}{2}}=0.982$ , which corresponds to an  $f^2$  configuration of the U ion [135]. The corresponding states in UPt<sub>3</sub> are situated in -0.5 to 0.2 eV energy range, very close to the Fermi level and partially occupied. Such a different energy position of occupied  $5f_{5/2}$  states in UPd<sub>3</sub> and UPt<sub>3</sub> can be explained by the larger spatial extent of Pt 5*d* wave functions as compared to the Pd 4*d* states which causes a proportional increase of the part of *f* electron density at U site provided by the "tails" of *d* states. The screening of the localized U 5*f* states by this delocalized density becomes stronger in UPt<sub>3</sub> and their occupied  $5f_{5/2}$ states shift to higher energy [135].

The above-mentioned self-consistent LSDA+U solutions for UPd<sub>3</sub> and UPt<sub>3</sub> are magnetic with a rather large U magnetic moment. This is contrary to the experimental data which show that the ordered magnetic moment is only 0.01  $\mu_{\rm B}$  and 0.02–0.03 $\mu_{B}$  per U atom in UPd<sub>3</sub> and UPt<sub>3</sub>,respectively [862, 1038–1040]. This extremely small U magnetic moment is explained by the fact that according to the crystalline electric field (CEF) level scheme derived from neutron scattering experiments, the lowest CEF level of U<sup>4+</sup> ion in both compounds is a singlet [863, 1040] which leads to a nonmagnetic ground state for these compounds. The LSDA+U is still a one electron approximation and can



*Figure 4.39.* The self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of UPt<sub>3</sub> calculated in the LSDA and LSDA+U approximations [1041].



*Figure 4.40.* The partial  $5f_{5/2}$  density of states (in states/atom eV) in UPt<sub>3</sub> and UPd<sub>3</sub> calculated in the LSDA+U approximation.

not fully account for the subtle many-body effects responsible for the small value of the U magnetic moment in the UPd<sub>3</sub> and UPt<sub>3</sub>. It tries to obey the Hund's rules in the only way it is allowed to, i.e. by producing a magnetic solution. A possible way to overcome this discrepancy between the calculations and the experiment is to force a nonmagnetic ground state in the LSDA+U calculations as it was done by H. Harima *et al.* in Refs. [136, 862]. We have verified, however, that this leads to an increase of the total energy as compared to magnetic states obtained in the calculations.

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It should be mentioned that depending on the starting conditions another self-consistent LSDA+U solution very close in total energy can obtained for UPd<sub>3</sub> as well as for UPt<sub>3</sub>. This solution also results in two localized U 5f electrons but in this case the occupied states are  $|\frac{5}{2}, -\frac{5}{2}\rangle$  and  $|\frac{5}{2}, -\frac{1}{2}\rangle$  (here we used the notation  $|j, m_j\rangle$  for the state with the total momentum j and its projection  $m_j$ ) [1041]. The existence of two almost degenerate solutions can be understood if one compares the matrix elements of Coulomb interaction  $U_{m_j,m'_j}$  calculated between  $5f_{5/2}$  states with different  $m_j$  [135]. The matrix elements  $U_{\frac{5}{2},\frac{3}{2}}$  and  $U_{\frac{5}{2},\frac{1}{2}}$  are equal and the energy difference is caused not by the on-site Coulomb interaction but instead by a difference in the hybridization between U  $5f_{5/2}$  and conduction electrons. Also, the lowest unoccupied 5f state, which is either  $|\frac{5}{2}, -\frac{1}{2}\rangle$  or  $|\frac{5}{2}, -\frac{3}{2}\rangle$ , feels the same Coulomb repulsion of the localized electrons. Total energy calculations, however, show that lower energy solution is associated with  $|\frac{5}{2}, -\frac{3}{2}\rangle$  occupied states.

**XMCD spectra.** As we mentioned above, for the  $5f^2$  configuration in UPt<sub>3</sub> we have two solutions with close total energies, in the first case the  $5f_{5/2}$ states with  $m_i = -5/2$  and -3/2 are occupied, in the second case the occupied states are  $m_i = -5/2$  and -1/2. In the first case the dipole allowed transitions for left circularly polarized light,  $\lambda = +1$  are  $-3/2 \rightarrow -1/2$ ,  $-1/2 \rightarrow +1/2, +1/2 \rightarrow +3/2$ , and  $+3/2 \rightarrow +5/2$  and for right circularly polarization  $\lambda = -1$ :  $+1/2 \rightarrow -1/2$  and  $+3/2 \rightarrow +1/2$ . The transitions with equal final states  $m_i = -1/2$  and  $m_i = +1/2$  mostly cancel each other and the XMCD spectrum of U at the  $M_4$  edge  $(I = \mu^- - \mu^+)$  can be roughly represented by  $-[N_{3/2}^{5/2} + N_{5/2}^{5/2}]$  partial density of states [800]. In the second case, however, the dipole allowed transitions for  $\lambda = +1$  are  $-1/2 \rightarrow +1/2$ ,  $+1/2 \rightarrow +3/2$ , and  $+3/2 \rightarrow +5/2$  and for  $\lambda = -1$ :  $-1/2 \rightarrow -3/2$  and  $+3/2 \rightarrow +1/2$ . Therefore U  $M_4$  XMCD spectrum can be roughly represented by  $N_{1/2}^{5/2} - [N_{3/2}^{5/2} + N_{5/2}^{5/2}]$  partial density of states. One would expect there-fore smaller intensity of dichroic signal at the  $M_4$  edge for the second case in comparison with the first one due to the compensation between  $N_{1/2}$  and  $[N_{3/2} + N_{5/2}]$  partial density of states in the second case.



*Figure 4.41.* The model representation of the M<sub>5</sub> (a) and M<sub>4</sub> (b) XMCD of UPt<sub>3</sub> for two solutions with  $|\frac{5}{2}, -\frac{3}{2}\rangle$  occupied states (full lines) and  $|\frac{5}{2}, -\frac{1}{2}\rangle$  ones (dashed lines): (a) presents the partial densities of states  $[N_{-7/2}^{7/2} + N_{-5/2}^{7/2}] - [N_{7/2}^{7/2} + N_{5/2}^{7/2}]$ , (b)  $-[N_{3/2}^{5/2} + N_{5/2}^{5/2}]$  (full line) and  $N_{1/2}^{5/2} - [N_{3/2}^{5/2} + N_{5/2}^{5/2}]$  (dashed lines) [1041] (see the explanation in the text).

The  $5f_{7/2}$  states are almost completely empty in all the uranium compounds. Therefore the XMCD spectrum of U at the  $M_5$  edge can be roughly represented by the  $m_j$  projected partial density of states [800]:  $[N_{-7/2}^{7/2} + N_{-5/2}^{7/2}] - [N_{7/2}^{7/2} + N_{5/2}^{7/2}]$ . As a result, the shape of the  $M_5$  XMCD spectrum consists of two peaks of an opposite sign - a negative peak at lower energy and a positive peak at higher energy. As the separation of the peaks is smaller than the typical lifetime broadening, the peaks cancel each other to a large extent, thus leading to a rather small signal.

Although we neglect cross terms in the transition matrix elements and there is no full compensation between transitions with equal final states due to difference in the angular matrix elements, such a simple representation qualitatively reproduces all the peculiarities of the experimentally measured XMCD spectra in UPt<sub>3</sub>. It gives a simple, slightly asymmetric negative peak at the  $M_4$  edge and an s shaped two peak structure at the  $M_5$  edge (Fig. 4.41). It also correctly gives the dichroism at the  $M_4$  edge of approximately one order of magnitude larger than at the  $M_5$  one. The spectrum at the  $M_4$  edge is very sensitive to the character of the occupied  $5f_{5/2}$  states and has larger intensity for the solution with occupied  $|\frac{5}{2}, -\frac{3}{2}\rangle$  states.

Fig. 4.42 shows the calculated XMCD spectra in the LSDA and LSDA+Uapproximations for UPt<sub>3</sub> [1041] together with the experimental data [983]. The intrinsic broadening mechanisms have been accounted for by folding the XMCD spectra with a Lorentzian of 3.2 and 3.4 eV for  $M_5$  and  $M_4$  spectra, respectively. The overall shapes of the calculated and experimental uranium  $M_{4.5}$  XMCD spectra correspond well to each other. The major discrepancy between the calculated and experimental XMCD spectra is the size of the  $M_4$ XMCD peak. The LSDA theory produces a much smaller intensity for the XMCD spectrum at  $M_4$  edge in comparison with the experiment and simultaneously gives a larger dichroic signal at  $M_5$  edge. On the other hand, the LSDA+U approximation produces excellent agreement in the shape and intensity of XMCD spectra both at the  $M_4$  and  $M_5$  edges for the solution with the  $\left|\frac{5}{2},-\frac{3}{2}\right\rangle$  state occupation. The solution with  $\left|\frac{5}{2},-\frac{1}{2}\right\rangle$  occupation produces a smaller intensity for the XMCD spectrum at the  $M_4$  edge in comparison with the experiment. This observation is consistent with the total energy calculations which show that the lowest energy state has the solution with  $\left|\frac{5}{2}, -\frac{3}{2}\right\rangle$ states occupied.

The LSDA+U(OP) approximation, which describes the correlations between spin and orbital magnetic moment directions ( $U_{eff}=0$ ) gives a correct value of the XMCD spectrum at U  $M_4$  edge, but slightly overestimates the positive peak and underestimates the negative one at the  $M_5$  edge (not shown).

Fig. 4.42 shows also the XMCD spectra in UPd<sub>3</sub> calculated using the LSDA+U approximation for the solution with occupied  $|\frac{5}{2}, -\frac{3}{2}\rangle$  states [1041]. The XMCD spectra of UPd<sub>3</sub> and UPt<sub>3</sub> are very similar, except, the positive peak at the  $M_5$  edge is slightly less pronounced in UPd<sub>3</sub> than in UPt<sub>3</sub>. Experimental measurements of XMCD spectra in UPd<sub>3</sub> are highly desired.

### 4.3.5 URu<sub>2</sub>Si<sub>2</sub>

The heavy-fermion superconductor URu<sub>2</sub>Si<sub>2</sub> has attracted continuous attention in the last decade for its unusual ground-state properties. URu<sub>2</sub>Si<sub>2</sub> crystallizes in the body-centered tetragonal ThCr<sub>2</sub>Si<sub>2</sub> structure with lattice constant a=4.126 Å and c/a=2.319. At  $T_N$ =17.5 K the system undergoes an antiferromagnetic phase transition which is accompanied by a sharp peak in the specific heat [1042, 1043] and thermal expansion [1044]. A second transition occurs at  $T_c$ =1.2 K and indicates the onset of superconductivity which coexists with the antiferromagnetic order. Neutron-scattering measurements [1045, 1046] revealed a simple antiferromagnetic structure with a tiny ordered moment of (0.04±0.01)  $\mu_B$ /U atom, oriented along the c axis of the tetragonal crystal structure. The formation of an energy gap in the magnetic excitation spectrum is reflected by an exponential temperature dependence of the specific



*Figure 4.42.* The XMCD spectra of UPt<sub>3</sub> and UPd<sub>3</sub> at the uranium  $M_{4,5}$  edges calculated in the LSDA, LSDA+U(OP), and LSDA+U approximations [1041]. Experimental spectra for UPt<sub>3</sub> [983] (circles) were measured in a magnetic field of 5 T at 20 K. (U  $M_4$  spectra are shifted by -95 eV to include them in the figure).

heat [1042, 1043], the thermal expansion [1044] and the NMR and nuclear quadruple-resonance NQR relaxation rates [1047] in the ordered state. Electrical resistivity [1048] and point-contact spectroscopy measurements [1049] show a similar energy gap, indicating a strong scattering of the conduction electrons by the magnetic excitations. Magnetization measurements in high magnetic fields [1050, 1051] show a suppression of the heavy-fermion state in three consecutive steps at 35.8, 37.3, and 39.4 T for fields along the easy axis  $(B \parallel c)$ . These transitions have been confirmed in high-field measurements of the magnetoresistance and Hall coefficient [1052].

There are several LSDA band structure calculations of URu<sub>2</sub>Si<sub>2</sub> in the literature [1053–1056]. A self-consistent calculation of electronic band structure for antiferromagnetically ordered URu<sub>2</sub>Si<sub>2</sub> was performed using an all-electron fully relativistic spin-polarized LAPW method by Yamagami and Hamada [1056]. They obtained a magnetic moment at the uranium site with a tiny value of  $0.09\mu_B$  due to cancellation between the spin and the orbital moments. The theoretically calculated frequencies as functions of the direction of applied magnetic field are in reasonable agreement with the dHvA frequencies measured by Ohkuni *et al.* [1057]. The electronic band structure and the Fermi surface of paramagnetic URu<sub>2</sub>Si<sub>2</sub> have been studied also with high-resolution angle-resolved photoemission spectroscopy in Ref. [1058]. It was found that Ru 4*d* bands form the main body of the valence band and exhibit a remarkable energy dispersion in qualitatively good agreement with the band structure calculations. In addition to the dispersive Ru 4*d* bands, a less dispersive band was found near the Fermi level, which can be assigned to the U 5*f* - Ru 4*d* hybridized band.

**Band strucure.** Self-consistent LSDA calculations produce an antiferromagnetic ground state in  $URu_2Si_2$  [1041] in agreement with the experimental observation [1044]. The spin moment at the U site is obtained as  $-0.04\mu_B$ , the orbital moment is  $0.09\mu_B$ . The total magnetic moment is, therefore,  $0.05\mu_B$ . This is in a good agreement with the magnetic moment of  $0.04\mu_B$  observed by neutron-scattering measurements [1045, 1046]. The fully relativistic spinpolarized LSDA energy band structure and total DOS of the antiferromagnetic URu<sub>2</sub>Si<sub>2</sub> is shown in Fig. 4.43. Fig. 4.44 shows the LSDA partial density of states of URu<sub>2</sub>Si<sub>2</sub> [1041]. Si 3s states are located mostly at the bottom of the valence band in the -11 to -8 eV energy interval. Si 2p states hybridize strongly with Ru 4d, U 6d and U 5f valence states and occupy a wide energy range from -6.5 to 11 eV. There is an energy gap of around 0.5 eV between Si 3s and 3p states. Ru 4d states are situated below and above Fermi level in the -6.5 to 3.5 eV range. The Fermi level falls in the local minimum of Ru 4d states (Fig. 4.44). U 6d states are strongly hybridized with Ru 4d as well as Si 3p and even Si 3s states. A narrow peak of U  $5f_{5/2}$  states situated just at the Fermi level  $E_F$ . U  $5f_{7/2}$  states are split off by strong SO coupling and form another narrow peak 1.2 eV above  $E_F$ . Because U 5f states are situated at the local minimum of Ru 4d states there is rather week U 5f – Ru 4d hybridization.

Fig. 4.43 also shows the band structure of URu<sub>2</sub>Si<sub>2</sub> calculated in the LSDA+U approximation with U=2.0 eV and J=0.5 eV [1041]. The Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure of URu<sub>2</sub>Si<sub>2</sub>. The occupied on-site 5f energies are shifted downward by  $U_{eff}/2$  and the unoccupied levels are shifted upwards by this amount. As a result both the occupied and empty U 5f states move to a position with large Ru 4d DOS and the degree of U 5f – Ru 4d hybridization increases going from the LSDA to the LSDA+U solution. In the Hartree-Fock like LSDA+U solution with nonspherical correction to Coulomb matrix elements, three particular  $5f_{5/2}$  states ( $m_j = -5/2$ ,  $m_j = -3/2$ , and  $m_j = -1/2$ ) are occupied which leads to large spin (-2.01  $\mu_B$ ) and orbital (4.78  $\mu_B$ ) magnetic moments for the U atom. U 5f states just above the Fermi level are formed by the remaining  $5f_{5/2}$  states whereas the peak of  $5f_{7/2}$  states is pushed from its LSDA position above  $E_F$  by 2.8 eV.



*Figure 4.43.* The self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of URu<sub>2</sub>Si<sub>2</sub> calculated in the LSDA and LSDA+U approximations [1041].

**XMCD spectra.** Fig. 4.45 shows the calculated x-ray isotropic absorption and XMCD spectra in the LSDA and LSDA+U approximations for URu<sub>2</sub>Si<sub>2</sub> [1041] together with the experimental data [986]. To calculate the x-ray isotropic absorption M<sub>4,5</sub> spectra we take into account the background intensity which appears due to transitions from occupied levels to the continuum of unoccupied levels [280].

The theory [1041] produces a much smaller intensity of the XMCD spectrum at the  $M_4$  edge in comparison with the experiment in the LSDA calculations. It also gives a larger positive peak and a two times smaller negative peak at the  $M_5$  edge (Fig. 4.45). The LSDA+U approximation with J=2.0 and J=0.5 eV and nonspherical corrections to Coulomb matrix elements [986] produces excellent agreement in shape and intensity for the XMCD spectra both at the  $M_4$  and  $M_5$  edges. This can be considered as evidence in favor of a picture of partly localized U 5f states in URu<sub>2</sub>Si<sub>2</sub>.

One should mentioned that the LSDA+U(OP) calculations ( $U_{eff}=0$ ) underestimate the negative XMCD peak and overestimate the positive one at the  $M_5$ edge (not shown). This approximation also slightly underestimates the XMCD signal at the  $M_4$  edge.



*Figure 4.44.* The partial density of states in URu<sub>2</sub>Si<sub>2</sub> calculated in the LSDA approximation [1041] (the 6*d* partial DOS has been multiplied by factor 3 for clarity).

## 4.3.6 UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub>

The most recently discovered heavy-fermion superconductors UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub> [1059, 1060] exhibit coexistence between superconductivity and a magnetic state with relatively large ordered magnetic moments. UPd<sub>2</sub>Al<sub>3</sub> was found to exhibit a simple antiferromagnetic structure [wave vector  $\mathbf{q}=(0,0,1/2)$ ] below  $T_N \sim 14.5$  K and static magnetic moments of U lying in the basal plane [1061]. The neutron-scattering data are consistent with an ordered magnetic moment  $M_t \sim 0.85 \mu_B$ , reduced compared to the effective moment obtained from the high-temperature susceptibility, but exceeding by up to two orders of magnitude the small moments found, for example, in UPt<sub>3</sub>. Hence, in contrast to UPt<sub>3</sub>, a picture of local-moment magnetism seems to describe the magnetic state in UPd<sub>2</sub>Al<sub>3</sub>. Surprisingly, this large-moment magnetism was found to co-

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*Figure 4.45.* Isotropic absorption and XMCD spectra of URu<sub>2</sub>Si<sub>2</sub> at the uranium M<sub>4,5</sub> edges calculated in the LSDA (dashed lines) and LSDA+U (full lines) approximations [1041]. Experimental spectra [986] (circles) were measured at 50 K and in a magnetic field of 5 T (U  $M_4$  spectra are shifted by -95 eV to include them in the figure).

exist with heavy-fermion superconductivity exhibiting the highest  $T_c$  reported to date for this class of materials.

The electronic structure and Fermi surface of the antiferromagnetic UPd<sub>2</sub>Al<sub>3</sub> were calculated using the LSDA approximation in Ref.s [1062–1064]. The calculated magnetic moment was in good agreement with experiment as was the calculated magnetocristalline anisotropy. The calculations reveal the importance of hybridization of the U 5*f* states with the valence states of Pd and Al even though this hybridization appears to be rather weak and to influence only a restricted energy interval in the U 5*f* bands. The calculated de Haas-van Alphen (dHvA) frequencies are found to be in good agreement with the experimental data. However, the observed heavy masses cannot be obtained within the LSDA [1064].

The measured (in Ref. [1065]) x-ray photoemission and bremsstrahlung isochromat spectra of UPd<sub>2</sub>Al<sub>3</sub> are well reproduced by the LSDA calculated U 5f density of states. On the other hand, the resonance photoemission spectra of UPd<sub>2</sub>Al<sub>3</sub> does not match the calculated U 5f DOS in shape or position, while the calculated Pd 4*d* DOS matches very well with the off-resonance spectrum [1066].

The superconducting and magnetic properties of UNi<sub>2</sub>Al<sub>3</sub> are not so well documented compared to those of UPd<sub>2</sub>Al<sub>3</sub> owing to the difficulties of preparing good single crystals [985]. UNi<sub>2</sub>Al<sub>3</sub> undergoes transitions to antiferromagnetism at  $T_N \sim 4.6$  K and to superconductivity at  $T_C \sim 1.2$  K [1060]. Muon spin rotation ( $\mu$ SR) experiments [1067] on polycrystalline UNi<sub>2</sub>Al<sub>3</sub> showed evidence for antiferromagnetism with an ordered moment of the order of 0.1  $\mu_B$ . Elastic neutron scattering from a single-crystal sample of UNi<sub>2</sub>Al<sub>3</sub> has revealed the onset of long-range order magnetic order below  $T_N$ =4.6 K [1068]. The order is characterized by wave vector of the form ( $\frac{1}{2} \pm \tau, 0, \frac{1}{2}$ ), with  $\tau$ =0.110±0.0003, indicating an incommensurate magnetic structure within the basal plane, which is simply stacked antiferromagnetically along *c* to form the full three-dimensional magnetic structure. The maximum amplitude of the order of the order of the order dimensional magnetic structure.

**Band strucure.** UPd<sub>2</sub>Al<sub>3</sub> and UPd<sub>2</sub>Al<sub>3</sub> crystallize in a rather simple hexagonal structure P6/mmm (D<sup>1</sup><sub>6h</sub>, PrNi<sub>2</sub>Al<sub>3</sub>-type structure) with lattice constant a=5.365 Å and c/a=4.186 for UPd<sub>2</sub>Al<sub>3</sub> and a=5.207 Å and c/a=4.018 for UNi<sub>2</sub>Al<sub>3</sub>.

The fully relativistic spin-polarized LSDA energy band structures and total DOS's of the antiferromagnetic UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub> are shown in Fig. 4.46 [1041]. The results of our band structure calculations of UPd<sub>2</sub>Al<sub>3</sub> are in good agreement with previous calculations of Sandratskii et al. [1063]. Al 3s states are located mostly at the bottom of the valence band in the -9.7 to -5 eV energy interval. Al 3p states occupy wide energy range from -6 to 11 eVhybridized strongly with Pd 4d, U 6d and U 5f valence states. Pd 4d states are almost fully occupied and situated below Fermi level in the -5 to -2.5eV range. The magnetic moment at the Pd site, therefore, is extremely small. U 6d states are strongly hybridized with Pd 4d as well as Al 3p states. The characteristic feature of the LSDA band structure is a narrow peak of U  $5f_{5/2}$ states situated just at the Fermi level  $E_F$ . U  $5f_{7/2}$  states are split off by strong spin-orbit coupling and form another narrow peak 1.2 eV above  $E_F$ . Because Pd 4d states are located far below the Fermi level, there is rather week U 5f - Pd 4d hybridization. We should mention, however, that this hybridization is of primary importance and influences greatly the form and width of the 5fpeaks (the analysis of the hybridization effects in UPd<sub>2</sub>Al<sub>3</sub> are presented in Ref. [1063]).

In agreement with experiment [1061] we found the basal plane of the hexagonal structure to be the plane of easy magnetization in UPd<sub>2</sub>Al<sub>3</sub>. The magnetic structures with magnetic moments lying in the xy plane possess lower energy than those with atomic moments along the z axis. A rotation of the magnetic moment within the xy plane does not noticeably change the energy of the configuration as well as the value of the spin and orbital magnetic moments.



*Figure 4.46.* The self-consistent fully relativistic, spin-polarized energy band structure and total DOS (in states/(unit cell eV)) of UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub> calculated in the LSDA approximation [1041].

Our calculations, unfortunately, yield for the total energy of the in-plane ferromagnetic structure a slightly lower value than for the energy of the corresponding antiferromagnetic structure, although the difference of the total energy of the ferromagnetic and antiferromagnetic in-plane solutions is very small, about 9 meV per formula unit, and is close to the accuracy limit of our LMTO–LSDA calculations. This disagrees with experiment which shows the ground state magnetic structure to be antiferromagnetic [1061]. The same results were obtained by Sandratskii *et al.* in Ref. [1063].

The energy band structure of  $UNi_2Al_3$  and  $UPd_2Al_3$  are very similar (Fig. 4.46) [1041]. The major difference is in the energy location and width of the transition metal bands. Due to less spatial expansion of Ni 3d wave functions compared to Pd 4d wave functions the Ni 3d energy band is 1.5 times narrower than the corresponding 4d band in  $UPd_2Al_3$ . The Ni 3d energy band is situated in the -3 to -1.2 eV energy interval. Due to a shift of the Ni 3d band toward the Fermi level, the U 5f - Ni 3d hybridization in  $UNi_2Al_3$  is increased in comparison with the U 5f - Pd 4d hybridization in  $UPd_2Al_3$ . A stronger interaction between 5f and conduction electrons when replacing Pd by Ni is manifested in a shift toward higher temperatures of the maxima of both the resistivity and the susceptibility together with the decrease of the

#### Table 4.7.

The experimental and calculated spin  $M_s$ , orbital  $M_l$ , and total  $M_t$  magnetic moments at uranium site (in  $\mu_B$ ) of UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub>. The magnetic moments calculated for easy magnetic axes, namely, hexagonal plane in UPd<sub>2</sub>Al<sub>3</sub> and *c* axis in UNi<sub>2</sub>Al<sub>3</sub> [1041].

Compound	method	$M_s$	$\mathbf{M}_l$	$\mathbf{M}_t$	$-M_l/M_s$
	LSDA	-1.38	2.22	0.84	1.61
	LSDA [1063]	-1.62	2.49	0.87	1.54
UPd <sub>2</sub> Al <sub>3</sub>	LSDA+U(OP)	-1.59	3.73	2.14	2.34
	LSDA+U	-1.92	4.61	2.69	2.40
	exper. [1061]	-	-	0.85	-
	exper. [985]	-	-	-	2.01
	exper. [986]	-	-	-	1.91
	LSDA	-0.47	0.54	0.07	1.15
UNi2Al3	LSDA+U(OP)	-1.22	2.90	1.68	2.38
	LSDA+U	-1.74	4.46	2.72	2.56
	exper. [1061]	-	-	0.2	-
	exper. [985]	-	-	-	2.49

magnetic ordering temperature  $T_N$ , the superconductivity temperature  $T_C$ , the antiferromagnetic moment and the smaller entropy change at  $T_N$  [985].

Fig. 4.47 shows  $m_j$  projected  $5f_{5/2}$  density of states in UPd<sub>2</sub>Al<sub>3</sub> calculated in the LSDA and LSDA+U approximations [1041]. We performed two LSDA+U band structure calculations. In the first calculation we used U = J = 0.5 eV, which gives  $U_{eff}=0$  (the so called LSDA+U(OP) approximation). In the second one U = 2.0 eV and J = 0.5 eV. The LSDA approximation places the  $5f_{5/2}$  density of states in close vicinity of the Fermi level at -0.5 to 0.5 eV with strong hybridization between states with different  $m_j$ . The Coulomb repulsion  $U_{eff}$  strongly influences the electronic structure of UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub>. In the Hartree-Fock like LSDA+U solution with nonspherical corrections to Coulomb matrix elements, three particular  $5f_{5/2}$ states ( $m_j = -5/2$ ,  $m_j = -3/2$ , and  $m_j = -1/2$ ) are almost completely occupied producing the  $5f^3$  configuration for U in UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub>.

Table 4.7 lists the calculated spin  $M_s$ , orbital  $M_l$ , and total  $M_t$  magnetic moments at uranium site (in  $\mu_B$ ) as well as the ratio  $M_l/M_s$  for UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub> [1041]. Our LSDA results are in good agreement with previous LSDA calculations [1063]. Surprisingly, LSDA calculations produce the *total* magnetic moments in UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub> in good agreement with the experimental data. On the other hand, the LSDA calculations strongly under-



*Figure 4.47.* The partial  $5f_{5/2}$  density of states (in states/atom eV) in UPd<sub>2</sub>Al<sub>3</sub> [1041].

estimate the ratio  $M_l/M_s$  (especially in UNi<sub>2</sub>Al<sub>3</sub>) due to the underestimation of the orbital moment by LSDA-based computational methods. The ratio  $M_l/M_s$  in the LSDA+U(OP) calculations is in reasonable agreement with the experimental data for both the compounds.

**XMCD spectra.** Fig. 4.48 shows the calculated XMCD spectra in the LSDA, LSDA+U(OP) and LSDA+U approximations for UPd<sub>2</sub>Al<sub>3</sub> [1041] together with the corresponding experimental data [986]. The overall shapes of the calculated and experimental uranium  $M_{4,5}$  XMCD spectra correspond well to each other. The major discrepancy between the calculated and experimental XMCD spectra is the size of the  $M_4$  XMCD peak. The LSDA theory produces much smaller intensity for the XMCD spectrum at the  $M_4$  edge in comparison with experiment and simultaneously strongly overestimates the negative peak at the  $M_5$  edge. On the other hand, the LSDA+U(OP) approximation produces an excellent agreement in the shape and intensity of the XMCD spectra both at the  $M_4$  and  $M_5$  edges. The LSDA+U calculations with U=2.0 eV slightly overestimate the intensity of the dichroic signal at the  $M_4$  edge and produce a larger negative peak and smaller positive one at the  $M_5$  edge.



*Figure 4.48.* The XMCD spectra of UPd<sub>2</sub>Al<sub>3</sub> and UNi<sub>2</sub>Al<sub>3</sub> at the uranium M<sub>4,5</sub> edges calculated in LSDA and LSDA+U approximations [1041]. Experimental spectra for UPd<sub>2</sub>Al<sub>3</sub> [986] were measured in a magnetic field of 5 T and 35 K. The experimental data for the U  $M_4$  XMCD spectrum of UNi<sub>2</sub>Al<sub>3</sub> is from Ref. [985]. (U  $M_4$  spectra are shifted by -95 eV to include them in the figure).

Fig. 4.48 shows also the XMCD spectra for  $UNi_2Al_3$  [1041]. The experimental data exist only for the  $M_4$  edge in this compound [985]. For the LSDA calculations the theory produces a smaller intensity of the XMCD spectrum at the  $M_4$  edge in comparison with the experiment. On the other hand, the intensity of the experimentally measured  $M_4$  XMCD spectrum is in between the results obtained by LSDA+U(OP) and LSDA+U approximations.

### 4.3.7 UBe<sub>13</sub>

The system UBe<sub>13</sub> was the first U-based heavy-fermion superconductor discovered [1069] and, similar to UPt<sub>3</sub>, it shows peculiar properties, pointing to an unconventional superconducting order parameter. UBe<sub>13</sub> is certainly the most anomalous of the heavy-fermion superconductors.

The specific heat in UBe<sub>13</sub> is very weakly dependent upon magnetic field and highly sensitive to pressure [1070]. The low-temperature value of the electronic specific heat coefficient,  $\gamma$  is of order 1000 mJ mol<sup>-1</sup> K<sup>-2</sup>, corresponding to an effective mass of several hundred free-electron masses. The magnetic susceptibility is weakly pressure dependent in comparison with the specific heat and under pressure has a completely different temperature dependence [1071]. Doping on the U sublattice which drives away the specific heat anomaly leaves the low-temperature susceptibility essentially unchanged. The magnetization is linear in fields up to 20 T [1070].

The dynamic magnetic susceptibility reveals no significant structure on the scale of 1 meV as is evidenced in C/T and instead shows a broad "quasielastic" response on the scale of 15 meV as evidenced in both neutron scattering and Raman spectra. Concomitant with the peak in  $\chi''$  is a Schottky anomaly in the specific heat, suggesting that the 15 meV peak represents highly damped crystal-field levels for which further evidence appears in the nuclear magnetic relaxation of the <sup>9</sup>Be sites. This dynamic susceptibility peak integrates to give 80% of the static susceptibility up to the experimental cut-off. This places a stringent bound on any hypothetical moment-carrying state in the low-frequency region; given a 10 K Kondo scale, to explain the residual susceptibility the effective squared moment must be less than  $0.25\mu_B$ , which would appear to rule out an interpretation in terms of a  $5f^3 \Gamma_6$  ground state [1070].

There are several different interpretations of these experimental data in literature. Miranda and coworkers suggested the non-Fermi-liquid (NFL) behavior of UBe<sub>13</sub> could be driven by disorder [1072]. Cox proposed, based on symmetry grounds, the NFL behavior can be explained by the two-channel Kondo model description [1073]. More recently, Anders *et al.* tackled the problem for the corresponding lattice model [1074]. They also performed a calculation of the optical properties within such a two-channel Anderson lattice model for which the suppression of the low-frequency Drude component and the development of a mid-infrared absorption in the excitation spectrum at low temperatures have been suggested [1074].

One framework for describing the low-temperature properties of  $UBe_{13}$  characterizes the material's behavior in terms of its energy scales. Whereas common metals may be characterized by a single energy scale (the Fermi energy),  $UBe_{13}$  appears to require several. One may considered four energy scales [1070]: a crystal field splitting of 150-189 K, a Kondo temperature of about 25 K, a spin-fluctuation temperature of about 2 K, and the superconducting transition temperature of about 0.8 K.

The energy band structure and Fermi surface of UBe<sub>13</sub> have been investigated in Ref.s ([1075–1078]) in a frame of the LSDA approximation. It was shown [1078] that the hybridization between the U 5*f* states and the Be 2*p* states occurs in the vicinity of the Fermi level. The sheets of the Fermi surface are all small in size and closed in topology. The cyclotron effective mass calculated for the dHvA branches in the three symmetry directions varies from  $1.08m_0$  to  $4.18m_0$ . The theoretical electronic specific-heat coefficient  $\gamma_{band}^{LDA}$  is  $13.0 \text{ mJ/K}^2 \text{ mol [1078]}$ . The theoretical results for the electronic specific-heat



*Figure 4.49.* Crystal structure of UBe<sub>13</sub>.

coefficient are much less than the experimental ones, suggesting a large enhancement due to many-body effects. This disagreement between theory and experiment might be ascribed to the enhancements due to the electron correlations and/or the electron-phonon interaction which the LDA fails to take into account.

**Band structure.** UBe<sub>13</sub> crystallizes in the NaZn<sub>13</sub>-type fcc structure with the space group  $O_h^6-Fm3c$  (No 226) and contains 28 atoms per unit cell. There are two distinct Be sites, Be<sub>1</sub> and Be<sub>2</sub>, with the 24 Be<sub>2</sub> sites having a very low site symmetry (only a mirror plane). The U atoms are surrounded by cages of 24 Be<sub>2</sub> atoms (Fig. 4.49) at the distance of 3.02 Å. Eight Be<sub>1</sub> atoms are separated from the U atom by 4.443 Å. This ensures that the U atoms widely separated. The U atoms form a simple cubic sublattice with a large U-U nearest-neighbor distance of a/2=5.13 Å, which guarantees that the f - f overlap is negligible. Therefore, all broadening of the U 5*f* states into bands results entirely from hybridization with the conduction bands, rather than partially from direct f - f overlap, as occurs in many U compounds.

Self-consistent LSDA calculations produce a nonmagnetic ground state in UBe<sub>13</sub> [1041]. To calculate the electronic structure and XMCD spectra of UBe<sub>13</sub> in the LSDA approximation, the term  $2\mu_{\rm B}\mathbf{B} \cdot \mathbf{s}$  which couples the spin of an electron to the external magnetic field was added to the Hamiltonian at the variational step. The fully relativistic spin-polarized LSDA energy band structure and total DOS of UBe<sub>13</sub> is shown in Fig. 4.50 calculated in an external magnetic field of 20 T [1041]. The occupied part of the valence band is formed predominantly by Be 2s and 2p states. U  $5f_{5/2}$  states are situated just



*Figure 4.50.* The energy band structure and total density of states (in states/unite cell eV) in  $UBe_{13}$  calculated in the LSDA and LSDA+U approximations [1041].

at the Fermi level 1.0 eV above the top of Be 2p states. U  $5f_{7/2}$  states are split off by strong SO coupling and form another narrow peak 1 eV above  $E_F$ . Be 2s states are located mostly at the bottom of the valence band. Be 2p states are strongly hybridized with U 6d states in the -6 to -1 eV energy interval. On the other hand there is quite large U 5f – Be 2p hybrization in vicinity of the Fermi level in the -0.6 to 1.4 eV energy range. Although every individual Be atom produces a quite small 2p partial density of states, due to the large number of Be atoms they sum up to a 2p DOS comparable in intensity with the U 5f DOS (Fig. 4.50).

Fig. 4.50 also shows the band structure of UBe<sub>13</sub> calculated in the LSDA+U approximation with U=2.0 eV and J=0.5 eV. Partially occupied U  $5f_{5/2}$  states split due to the Coulomb repulsion and the LSDA+U calculations give a solution with three localized 5f electrons. These localized 5f states form a rather narrow peak at 0.6 eV below  $E_F$ . U 5f states just above the Fermi level are formed by the remaining  $5f_{5/2}$  states whereas the peak of  $5f_{7/2}$  states is pushed from its LSDA position at 1.2 eV above  $E_F$  to 2.2 eV.

Fig. 4.51 shows  $m_j$  projected  $5f_{5/2}$  and total  $5f_{7/2}$  density of states in UBe<sub>13</sub> calculated in the LSDA and LSDA+U approximations [1041]. We per-



*Figure 4.51.* The  $m_j$  projected  $5f_{5/2}$  and total  $5f_{5/2}$  density of states in UBe<sub>13</sub> calculated in the LSDA and LSDA+U approximations [1041].

formed two LSDA+U band structure calculations both with U=2.0 eV and J=0.5 eV. In the first calculation we used the LSDA+U method with nonspherical corrections to the Coulomb matrix elements [135]. The effect of a less asymmetric density of localized 5f electrons can be simulated by replacing the matrix elements  $U_{mmm'm'}$  and  $J_{mm'm'm}$  by averaged Coulomb U and exchange J integrals, respectively, and setting all other matrix elements to zero [135]. In the non-relativistic limit this would correspond, except for the approximation to the double counting term, to the original version of the LSDA+U method proposed in Ref. [129]. In this case all unoccupied U 5f electrons independently of their angular momentum experience the same Coulomb repulsion as the localized ones. In the Hartree-Fock like LSDA+U solution with nonspherical corrections to the Coulomb matrix elements three particular  $5f_{5/2}$  states ( $m_j = -5/2$ ,  $m_j = -3/2$ , and  $m_j = -1/2$ ) are occupied which leads to i) large spin (-1.95  $\mu_B$ ) and orbital (4.47  $\mu_B$ ) magnetic moments of U atom and ii) strongly anisotropic Coulomb interaction of the



*Figure 4.52.* Comparison of the calculated U partial 5f DOS in the LSDA (dotted line), LSDA+U approximations with the experimental BIS spectrum (circles) of UBe<sub>13</sub> [1079]. Dashed line presents DOS calculated with nonspherical correction to Coulomb matrix elements whereas full line are calculated with averaged U and J [1041].

remaining 5f electrons with the occupied ones. In the calculations using the LSDA+U method with spherically averaged U and J an unoccupied U 5f electrons feel a much more isotropic repulsive potential and is situated closer to the Fermi energy. This gives smaller magnetic moments (spin moment is equal to  $-1.82 \ \mu_B$  and orbital moment 4.08  $\mu_B$ ) in comparison with the nonspherial solution. The  $5f_{5/2}$  states with  $m_j = -1/2$  became partly empty for the calculations with spherically averaged U and J and the main peak of  $N_{-1/2}$  DOS is situated just above the Fermi level (Fig. 4.51).

The three calculations presented in Fig. 4.51 produce rather different energy locations for the empty 5f states [1041]. The principal question of the energy position of the empty 5f states is usually answered by bremsstrahlung isochromat spectroscopy (BIS) measurements. Fig. 4.52 shows the experimental BIS spectrum of UBe<sub>13</sub> [1079] compared with the calculated energy distribution for the unoccupied partial U 5f density of states in the LSDA and LSDA+U approximations. The LSDA places empty 5f states too close to the Fermi level (Fig. 4.52). The LSDA+U calculations with nonspherical solution place the maximum of empty 5f states more than 1 eV higher than the experiment. The LSDA+U calculations with spherically averaged U and J give the correct position of empty 5f states within the experimental resolution (Fig. 4.52). The use within the experimental resolution (Fig. 4.52). The main peak in the BIS spectrum is derived from the U  $5f_{7/2}$  states, while the low energy shoulder split off from the main peak is from the  $5f_{5/2}$  states.

**XMCD spectra.** Fig. 4.53 shows the UBe<sub>13</sub> x-ray isotropic absorption and XMCD spectra calculated in the LSDA and LSDA+U approximations [1041] together with the experimental data [983]. The LSDA calculations produce much smaller intensity of the XMCD spectrum at the  $M_4$  edge in comparison



*Figure 4.53.* Isotropic absorption and XMCD spectra of UBe<sub>13</sub> at the uranium  $M_{4,5}$  edges calculated in the LSDA (dotted lines), and LSDA+*U* approximations. The dashed line presents XMCD spectra calculated with nonspherical corrections to Coulomb matrix elements whereas the full line results are calculated with averaged *U* and *J* [1041]. Experimental spectra [983] (circles) were measured at 12 K and in a magnetic field of 5 T (the U  $M_4$  spectrum is shifted by -95 eV to include it in the figure).

with the experiment and simultaneously give larger dichroic signal for the negative peak and do not produce the positive shoulder at the  $M_5$  edge (Fig. 4.53). On the other hand, the LSDA+U calculations improve the agreement between the theory and the experiment in the shape and intensity of XMCD spectra both at the  $M_4$  and  $M_5$  edges. The LSDA+U method with nonspherical corrections to the Coulomb matrix elements slightly overestimates the dichroic signal at the  $M_4$  edge, underestimates the intensity of the positive peak and strongly overestimates the negative peak at the  $M_5$  edge. The LSDA+U calculations with averaged U and J give a correct value of the positive peak at the  $M_5$  edge and the negative peak at the  $M_4$  one but still overestimate the intensity of the negative peak at the  $M_5$  edge.

 $UBe_{13}$  is unlike the other heavy-fermion compounds in that the better description of its XMCD and BIS spectra requires spherically averaged U and J values. The physical reason for that is not clear, however there are some

indications from the calculations. Compare the orbital resolved  $5f_{5/2}$  DOS's shown in Fig. 4.51 one can see that in the LSDA+U solution with nonspherical corrections to the Coulomb matrix elements, three particular  $5f_{5/2}$  states  $(m_j = -5/2, m_j = -3/2, \text{ and } m_j = -1/2)$  are fully occupied which leads to a pure  $5f^3$  configuration. The calculations using the spherically averaged U and J values give a solution with partly empty  $m_j = -1/2$  states with the main peak of the  $N_{-1/2}$  DOS very close to the Fermi level (Fig. 4.51). This is the typical situation for a system with mixed valence [634, 679]. One should mention that the LSDA+U method which combines LSDA with a basically static, i.e., Hartree-Fock-like, mean-field approximation for a multi-band Anderson lattice model does not contain true many-body physics and cannot treat a systems with mixed valence properly. The evaluation of the electronic structure of UBe<sub>13</sub> needs further theoretical investigations.

# 4.3.8 Conclusions

There are some features in common for all the uranium compounds investigated up to now. First, the dichroism at the  $M_4$  edge is much larger, sometimes of one order of magnitude, than at the  $M_5$  one. Second, the dichroism at the  $M_4$ edge has a single negative peak that has no distinct structure, on the other hand, two peaks, a positive and a negative one, are observed at the  $M_5$  edge. The peculiarities of the XMCD spectra can be understood qualitatively considering the partial density of states and the electric dipole selection rules.

Since l and s prefer to couple antiparallel for less than half-filled shells, the j = l - s = 5/2 has a lower energy than the j = l + s = 7/2 level. Due to intra-atomic exchange interaction the lowest sublevel of the j = 5/2will be  $m_{5/2} = -5/2$ , however, for the j = 7/2 the lowest sublevel will be  $m_{7/2} = +7/2$ . This reversal in the energy sequence arises from the gain in energy due to alignment of the spin with the exchange field [983].

Because of the electric dipole selection rules  $(\Delta l = \pm 1; \Delta j = 0, \pm 1)$  the major contribution to the absorption at the  $M_4$  edge stems from the transitions  $3d_{3/2} \rightarrow 5f_{5/2}$  and that at the  $M_5$  edge originates primarily from  $3d_{5/2} \rightarrow 5f_{7/2}$  transitions, with a weaker contribution from  $3d_{5/2} \rightarrow 5f_{5/2}$  transitions. For the later case the corresponding  $3d_{5/2} \rightarrow 5f_{5/2}$  radial matrix elements are only slightly smaller than for the  $3d_{5/2} \rightarrow 5f_{7/2}$  transitions. The angular matrix elements, however, strongly suppress the  $3d_{5/2} \rightarrow 5f_{5/2}$  contribution. The selection rules for the magnetic quantum number  $m_j$  ( $m_j$  is restricted to -j, ... + j) are  $\Delta m_j$ =+1 for  $\lambda = +$  and  $\Delta m_j = -1$  for  $\lambda = -$ .

The  $5f_{7/2}$  states are almost completely empty in all the uranium compounds. Therefore the XMCD spectrum of U at the  $M_5$  edge  $(I = \mu^- - \mu^+)$  can be roughly represented by the following  $m_j$  projected partial density of states :  $[N_{-7/2}^{7/2}+N_{-5/2}^{7/2}]-[N_{7/2}^{7/2}+N_{5/2}^{7/2}]$ . As a result, the shape of  $M_5$  XMCD spectrum
stems in two peaks of an opposite sign - a negative peak at lower energy and a positive peak at higher energy. As the separation of the peaks is smaller than the typical lifetime broadening, the peaks cancel each other to a large extent, thus leading to a rather small signal. Uranium compounds have partly occupied  $5f_{5/2}$  states and XMCD spectrum of U at the  $M_4$  edge can be roughly represented by following  $m_j$  projected partial density of states:  $-[N_{3/2}^{5/2}+N_{5/2}^{5/2}]$ . It explains why the dichroic  $M_4$  line in uranium compounds consists of a single nearly symmetric negative peak.

The overall shapes of the calculated and experimental uranium  $M_{4,5}$  XMCD spectra correspond well to each other. The major discrepancy between the calculated and experimental XMCD spectra is the size of the  $M_4$  XMCD peak. The LSDA theory produces usually much smaller intensity for the XMCD spectrum at the  $M_4$  edge in comparison with the experiment and simultaneously gives inappropriate dichroic signal strength at the  $M_5$  edge. It fails to produce a correct intensity of dichroic signal at the  $M_4$  edge even in UFe<sub>2</sub> which is widely believed to have itinerant 5f electrons. As the integrated XMCD signal is proportional to the orbital moment this discrepancy could be related rather to an underestimation of the orbital moment by LSDA-based computational methods rather than to a failure in the description of the energy band structure of the itinerant 5f systems. The LSDA+U approximation gives much better agreement in the shape and intensity of the XMCD spectra both at the  $M_4$  and  $M_5$  edges in uranium compounds.

Concerning the best description of line shape and intensity of the XMCD spectra, the investigated metallic uranium compounds fall into two groups according to the type of LSDA+U method used. The LSDA+U(OP) approximation ( $U_{eff}$ =0) better describes the XMCD spectra in UFe<sub>2</sub>, UXAl (X=Co, Rh, and Pt), UPd<sub>2</sub>Al<sub>3</sub>, and UNi<sub>2</sub>Al<sub>3</sub> compounds. But the XMCD spectra of UPt<sub>3</sub>, URu<sub>2</sub>Si<sub>2</sub>, and UBe<sub>13</sub> are better described by the LSDA+U method with U=2.0 eV and J=0.5 eV. It might be concluded to some extent that the last three compounds have a larger degree of localization than the compounds from the first group.

# Appendix A Linear Method of MT Orbitals

#### A.1 Atomic Sphere Approximation

One of the first band theory calculation methods was that proposed by Wigner and Seitz in 1933 [1080]. In this method the crystal is divided into polyhedral Wigner–Seitz cells inside which the potential is assumed to be spherically symmetric. This approximation is reasonable for close–packed crystal structures with 8–12 nearest neighbors on a central atom. In this case, the solution of Schrödinger's equation for arbitrary energy E may be represented by the partial waves

$$\Phi_L(E, \mathbf{r}) \equiv u_l(E, r) \mathbf{i}' Y_L(\hat{\mathbf{r}}) , \qquad (A.1)$$

where the index L is a combination of the quantum numbers  $l, m; u_l$  is the solution of the radial Schrödinger equation.

The wave function of a valence electron in a crystal has the form

$$\Psi_{\mathbf{k}}(\mathbf{r}, E) = \sum_{L} C_{L}(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \theta(\mathbf{r} - \mathbf{R}) \Phi_{L}(E, \mathbf{r} - \mathbf{R}) \quad . \tag{A.2}$$

Here, **R** is the lattice vector;  $\theta(\mathbf{r})$  is the function equal to unity inside the cell located at the coordinate origin and equal to zero outside the cell.

If, for a given E and wave vector  $\mathbf{k}$  we find the coefficients  $C_L$  so that  $\Psi_{\mathbf{k}}(\mathbf{r}, E)$ , and its derivative are continuous functions on passing from one Wigner–Seitz cell to the other, (A.2) is the solution of the Schrödinger equation in the crystal, and E is the energy eigenvalue for the wave vector  $\mathbf{k}$ . Obviously, these boundary conditions depend on  $\mathbf{k}$  and crystal structure. In the atomic sphere approximation (ASA), when the Wigner–Seitz cell is replaced by a sphere of equivalent volume, this condition reduces to that specified for the radial logarithmic derivatives

$$D_l(E) \equiv su'_l(E,s)/u_l(E,s) , \qquad (A.3)$$

where the sphere radius is defined from the condition  $s = (3\Omega_0/4\pi)^{1/3}$ ;  $\Omega_0$  is the volume of the Wigner–Seitz cell.

For a common point  $\mathbf{k}$ , the boundary condition in the Wigner–Seitz method can almost never be satisfied, while the spherical approximation of an isotropic  $\mathbf{k}$ -space is very crude. For this reason, this method was rarely used for 40 years.

To overcome these difficulties, in 1937, Slater proposed to use touching "muffin tin" (MT) spheres [1081]. In the MT model, the potential inside the spheres is spherically symmetric,

while in the interstitial region it is assumed to be equal to a constant,  $V_c$ . In this region, which for close–packed structures takes up approximately 30% of the cell volume, the kinetic energy of an electron equals

$$q_0^2 = E - V_c$$
 . (A.4)

Slater based his development of the Augmented Plane Wave (APW) method on the expansion of the wave function in this interstitial region in plane waves, augmented inside the MT-spheres by an angular momentum expansion. For the purposes of explaining the band structure method used in this book, the relevant chain of development is in terms of the multiple scattering formalism starting with the KKR method. The major difficulty of the KKR method equations

$$\det[A_{L'L}^{\mathbf{k}}(E) + \delta_{L'L} q_0 \cot \eta_l] = 0 \quad , \tag{A.5}$$

written in the notation of phase shifts, is the dependence of the structure constants  $A_{L'L}^{\mathbf{k}}$  on the energy E. Here L is a generalized notation representing both l and m quantum numbers. The potential function in KKR

$$q_0 \cot \eta_l = q_0 \frac{n_l(q_0 s) D_l(E, s) - q_0 s n_l'(q_0 s) / n_l(q_0 s)}{j_l(q_0 s) D_l(E, s) - q_0 s j_l'(q_0 s) / j_l(q_0 s)}$$
(A.6)

also depends strongly on  $q_0$ . However, the dependence of the structure constants and potential function on  $q_0$  to a large extent cancel each other out, as was shown in the derivation of a parametric representation of the Fermi surface of transition metals [1082, 1083]. This is part of the reason 40 years after the proposal of the cellular method that Andersen proposed to return to the atomic sphere approximation, (ASA), but in the multiple scattering formalism [1084]. In the atomic sphere approximation, the volume of the interstitial region is zero, so that only one condition is specified for  $q_0^2$ , i.e., it should approximate the kinetic energy of an electron in all outer regions of the atomic spheres. Andersen used  $q_0^2 = 0$ . This condition significantly simplifies the KKR equations,

$$\det|S_{L'L}^{\mathbf{k}} - \delta_{L'L}P_l(E)| = 0 , \qquad (A.7)$$

where the potential function is

$$P_l(E) = 2(2l+1)\frac{D_l(E) + l + 1}{D_l(E) - l} ; (A.8)$$

and the structure constants are

$$S_{L'L}^{\mathbf{k}} = \sum_{\mathbf{R} \neq 0} e^{i\mathbf{k}\mathbf{R}} S_{L'L}(\mathbf{R}) \quad ; \tag{A.9}$$

$$S_{L'L}(\mathbf{R}) = -\frac{8\pi(2l+2l'-1)!!}{(2l-1)!!(2l'-1)!!} \times \sum_{L''}^{l''=l+l'} C_{LL''L'}(-\mathbf{i})^{l''} \left(\frac{R_s}{s}\right)^{-l''-1} Y_{L''}(\hat{\mathbf{R}}) ; \quad (A.10)$$

and  $C_{LL''L'}$  are the Gaunt coefficients,

$$C_{LL'L''} = \int Y_L(\hat{\mathbf{r}}) Y_{L'}^*(\hat{\mathbf{r}}) Y_{L''}(\hat{\mathbf{r}}) d\Omega.$$
 (A.11)

Equations (A.7-A.10) are important because the structure constants (A.9) do not depend on energy. All the information about the crystal potential is contained only in the potential function, while the data on the crystalline structure are contained in the structure constants. Clearly, such a separation considerably simplifies and accelerates the calculation of the band structure. If the contribution of the interstitial region the kinetic energy of an electron is neglected, the error in the eigenvalues does not exceed several percent of the valence band width. Equation (A.7) is obtained as the limit  $q_0 \rightarrow 0$  from the KKR expression (A.5) and is called the KKR-ASA equation. This expression can also be obtained in another way, i.e., by introducing the so-called MT orbitals, to which we now turn.

#### A.2 MT orbitals

Let us first consider a unit atomic sphere. Assume that inside this sphere the potential is spherically symmetric, while outside it  $q_0^2 = E - V_c = 0$ . Then, inside the sphere, the wave function of an electron will satisfy the Schrödinger equation allowing the separation of variables. Outside the sphere, we have the Laplace equation  $\nabla^2 \Psi = 0$ . In a general case, the radial part of this solution has the form  $\Phi_l = a_l r^l + b_l r^{-l-1}$ . The coefficients  $a_l$  and  $b_l$  are determined from the condition of continuity and differentiability of the wave function on the sphere surface. Thus, the radial wave function is

$$\Phi_l(r,E) = \begin{cases} u_l(r,E), & r \le s \\ \left[\frac{D_l+l+1}{2l+1} \left(\frac{r}{s}\right)^l + \frac{l-D_l}{2l+1} \left(\frac{r}{s}\right)^{-l-1}\right] u_l(s,E), & r > s \end{cases},$$

where  $u_l(r, E)$  is the solution of the normalized radial Schrödinger equation in the atomic sphere of the radius s.

These functions are not used as basis functions since the solution for r > s contains a diverging wave. Therefore, we write new functions

$$\bar{\Phi}_{l}(r,D) = \begin{cases} \Phi_{l}(r,D) - \frac{D+l+1}{2l+1} \frac{\Phi_{l}(s,D)}{\Phi_{l}(s,l)} \Phi_{l}(r,l), & r \leq s \\ \frac{l-D}{2l+1} \left(\frac{r}{s}\right)^{-l-1} \Phi_{l}(s,D), & r > s \end{cases}$$
(A.12)

This expression is obtained from  $\Phi_l(r, E)$  by subtracting the diverging wave  $\frac{(D+l+1)}{(2l+1)}(r/s)^l$ . Also, for  $r \leq s$ , instead of  $(r/s)^l$  the function  $\Phi_l(r, l)/\Phi_l(s, l)$  is used, and the variable E is replaced by the logarithmic derivative D for the corresponding energy E. This may always be done if the number of nodes of the wave function is known. The function (A.12) is, thus far, not the solution of the Schrödinger equation inside the atomic sphere, however, it is continuous and smooth over the entire space and decreases outside the sphere. Therefore, we can use it to write the basis function

$$\bar{\Phi}_L(\mathbf{r}, D) = \mathrm{i}^l Y_L(\hat{\mathbf{r}}) \bar{\Phi}_l(r, D) \quad . \tag{A.13}$$

Now, let us form a crystal by surrounding every atom with a sphere equivalent to the Wigner–Seitz cell, i.e., use the ASA. For simplicity, we consider one atom per unit cell. In deriving the basis function, it is necessary to include all the tails of the functions contributing into the central sphere coming from sites situated at  $\mathbf{R}$  with respect to the central sphere.

We write the Bloch sum

$$\chi_L^{\mathbf{k}}(\mathbf{r}, D) = \sum_{\mathbf{R} \neq 0} e^{i\mathbf{k} \cdot \mathbf{R}} \bar{\Phi}_L(\mathbf{r} - \mathbf{R}, D) \quad . \tag{A.14}$$

The tail coming from the site at R, is

$$\bar{\Phi}_L(\mathbf{r} - \mathbf{R}, D) = i^l Y_L(\hat{\mathbf{r}} - \hat{\mathbf{R}}) \left| \frac{\mathbf{r} - \mathbf{R}}{s} \right|^{-l-1} \frac{l-D}{2l+1} \Phi_l(s, D) \quad .$$
(A.15)

We decompose this function in terms of the angular momentum relative to the center by means of the theorem of additivity [1085]:

$$i^{l}Y_{L}(\hat{\mathbf{r}} - \hat{\mathbf{R}}) \left| \frac{\mathbf{r} - \mathbf{R}}{s} \right|^{-l-1} = 4\pi \sum_{L''L'}^{l''=l+l'} C_{LL''L'} \frac{(2l''-1)!!}{(2l-1)!!(2l'+1)!!} \times (-i)^{l''} \left(\frac{R}{s}\right)^{-l''-1} Y_{L''}^{*}(\hat{\mathbf{R}}) \times i^{l'} \left(\frac{r}{s}\right)^{l'} Y_{L'}(\hat{\mathbf{r}}) \qquad . \quad (A.16)$$

For the function to be continuous and differentiable on the sphere surface, we must carry out an augmentation, i.e., use  $\Phi_{l'}(r, l')/\Phi_{l'}(s, l')$  instead of  $(r/s)^{l'}$  in (A.16). Finally, we have the basis functions

$$\chi_{L}^{\mathbf{k}}(\mathbf{r}, D) =$$

$$= \begin{cases} \Phi_{L}(\mathbf{r}, D) - \Phi_{l}(s, D) \frac{l-D}{2l+1} \sum_{L'} \left[ S_{L'L}^{\mathbf{k}} - \frac{l+1+D}{l-D} 2(2l+1) \delta_{L'L} \right] \\ \times \Phi_{L'}(\mathbf{r}, l') \frac{1}{\Phi_{l'}(s, l') 2(2l'+1)}, & r \leq s , \\ \Phi_{l}(s, D) \frac{l-D}{2l+1} \left[ i^{l} Y_{L}(\mathbf{r}) \left( \frac{r}{s} \right)^{-l-1} + \sum_{L'} S_{L'L}^{\mathbf{k}} \\ \times i^{l'} Y_{L'}(\hat{\mathbf{r}}) \left( \frac{r}{s} \right)^{l'} \frac{1}{2(2l'+1)} \right], & r > s , \end{cases}$$

$$(A.17)$$

where  $S_{L'L}^{\mathbf{k}}$  are defined in (A.9). These are the MT orbitals. The obtained functions can be used as basis function in, for example, the Ritz variational methods.

Note that for the linear combination

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{L} C_{L}(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \chi_{L}(\mathbf{k}, \mathbf{r} - \mathbf{R}, D_{l}(E))$$
(A.18)

of MT orbitals to be the solution of the Schrödinger equation for the entire crystal, it must be equivalent to (A.2). In other words, inside the central sphere (hence, inside any other sphere), the sum of tails coming from all the other atomic positions are mutually canceled with the unphysical terms of the central MT orbital proportional to  $i^l Y_L(\hat{\mathbf{k}})r^l$ , i.e., in (A.17), the second term for  $r \leq s$  should go to zero. This condition leads to a set of linear homogeneous equations

$$\sum_{L} [S_{L'L}^{\mathbf{k}} - \delta_{L'L} P_l(E)] \Phi_l(s, D_l) C_L(\mathbf{k}) = 0 \quad , \tag{A.19}$$

with the potential function and structure constants defined in (A.8,A.9). We again obtain the KKR–ASA equations.

The problem of calculating the band structure reduces to the determination of eigenvalues and eigenvectors for a unit atomic sphere with a spherically symmetric potential with kdependent boundary conditions imposed by the surroundings. The atom sizes and crystal potential are contained in the logarithmic derivatives  $D_l(E)$ , while those of the crystal structure are in the energy independent structure constants  $S_{l'm';lm}(\mathbf{k})$  which also do not depend on the lattice constant.

### A.3 Relativistic KKR–ASA

The relativistic KKR–ASA equation is derived just as in the nonrelativistic case. Consider, first, a unit atomic sphere inside which the potential is spherically symmetric and outside of which the electron kinetic energy  $q_0^2 = E - V_c = 0$ .

Now, however, the Schrödinger equation is replaced by the Dirac equation

$$[c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2/2 + V(\mathbf{r})]\Psi_{\mathbf{k}}(\mathbf{r}) = (c^2/2 + E)\Psi_{\mathbf{k}}(\mathbf{r}) \quad (A.20)$$

where c is the velocity of light (in atomic units, c = 274.0746);  $\mathbf{p} = -i\nabla$  is the momentum operator;  $\boldsymbol{\alpha}$  is the Dirac four-dimensional matrix

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} =$$

 $\sigma$  corresponds to the set of Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

and the  $\beta$ -matrix is

$$\beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

The solution of the Dirac equation with a spherically symmetric potential is

$$\Phi_K(\mathbf{r}, E) = i^l Z_K(\hat{\mathbf{r}}) \Phi_\kappa(r, E) \quad , \tag{A.21}$$

where, as usual,  $K = (\kappa, \mu)$ ;  $\kappa$  is the relativistic quantum number;  $\Phi_{\kappa}(r, E)$  is the matrix of radial solutions,

$$\Phi_{\kappa}(r, E) = \begin{pmatrix} g_{\kappa}(r, E) \\ \mathrm{i}f_{\kappa}(r, E) \end{pmatrix} ; \qquad (A.22)$$

 $Z_K(\hat{\mathbf{r}})$  is the matrix of the spin-angular functions,

$$Z_{K}(\hat{\mathbf{r}}) = \begin{pmatrix} \chi^{\mu}_{\kappa}(\hat{\mathbf{r}}) & 0\\ 0 & \chi^{\mu}_{-\kappa}(\hat{\mathbf{r}}) \end{pmatrix} ; \qquad (A.23)$$

$$\chi^{\mu}_{\kappa}(\hat{\mathbf{r}}) = \sum_{m=\pm 1/2} C^{j\mu}_{l,\mu-m,1/2,m} Y_{l,\mu-m}(\hat{\mathbf{r}}) \chi(m) \; ; \tag{A.24}$$

 $C_{l,\mu-m,1/2,m}^{j\mu}$  are the Clebsch–Gordan coefficients;  $Y_{lm}(\hat{\mathbf{r}})$  are the spherical harmonics; j is the eigenvalue of the operator of the total angular momentum  $j = l \pm 1/2$ ;

$$\chi\left(\frac{1}{2}\right) = \begin{pmatrix} 1\\0 \end{pmatrix}, \quad \chi\left(-\frac{1}{2}\right) = \begin{pmatrix} 0\\1 \end{pmatrix}$$

are the Pauli spinors.

The spin-angular functions are orthogonal and normalized according to

$$\int d^2 \hat{\mathbf{r}} Z_{K'}(\hat{\mathbf{r}}) Z_K(\hat{\mathbf{r}}) = I \delta_{K'K} . \qquad (A.25)$$

The radial wave functions are normalized in a sphere of radius s:

$$\langle \Phi_{\kappa}(r,E) | \Phi_{\kappa}(r,E) \rangle = \int_{0}^{s} dr r^{2} (g_{\kappa}^{2}(r,E) + f_{\kappa}^{2}(r,E)) = 1$$
 (A.26)

The relativistic analog of the logarithmic derivative for the radial wave function  $\Phi_{\kappa}(r, E)$  has the form

$$D_{\kappa}(E) = s \frac{cf_{\kappa}(s, E)}{g_{\kappa}(s, E)} - \kappa - 1 \quad . \tag{A.27}$$

Assume  $E = V_c = 0$  in the region outside the atomic sphere. Here, the radial Dirac equations for free electrons

$$\left(\frac{d}{dr} + \frac{1-\kappa}{r}\right)\widetilde{f}_{\kappa}(r) = 0 ,$$
  
$$\left(\frac{d}{dr} + \frac{1+\kappa}{r}\right)\widetilde{g}_{\kappa}(r) - c\widetilde{f}_{\kappa}(r) = 0 .$$
(A.28)

have the solutions [1086]

$$\widetilde{\Phi}_{\kappa}(r,D) = \begin{pmatrix} g_{\kappa}(D,r) \\ \mathrm{i}f_{\kappa}(D,r) \end{pmatrix} = \begin{pmatrix} (r/s)^{\kappa} \\ \mathrm{i}(2\kappa+1)/cs\,(r/s)^{\kappa-1} \end{pmatrix}, \quad D = \kappa , \qquad (A.29)$$

$$\widetilde{\Phi}_{\kappa}(r,D) = \begin{pmatrix} g_{\kappa}(D,r) \\ if_{\kappa}(D,r) \end{pmatrix} = \begin{pmatrix} (r/s)^{-\kappa-1} \\ 0 \end{pmatrix}, \quad D = -\kappa - 1 , \quad (A.30)$$

and

$$\widetilde{\Phi}_{K}(\mathbf{r}, D) = \mathrm{i}^{l} Z_{K}(\widehat{\mathbf{r}}) \widetilde{\Phi}_{\kappa}(r, D) \quad . \tag{A.31}$$

The commonly used expression for the singular solutions at the origin (A.29,A.30) has the form

$$\widetilde{\Phi}_{K}(\mathbf{r}, -l-1) = i^{l} Z_{K}(\widehat{\mathbf{r}}) \begin{pmatrix} (r/s)^{-l-1} \\ i(-l-1+\kappa+1)/sc(r/s)^{-l-2} \end{pmatrix} , \qquad (A.32)$$

and for regular solutions

$$\widetilde{\Phi}_{K}(\mathbf{r},l) = \mathrm{i}^{l} Z_{K}(\widehat{\mathbf{r}}) \begin{pmatrix} (r/s)^{l} \\ \mathrm{i}(1+\kappa+1)/sc \left(r/s\right)^{l-1} \end{pmatrix} \quad . \tag{A.33}$$

Thus, in the region outside the sphere, the solution to the Dirac equation, matching continuously at the surface the solution inside the sphere, will be

$$\Phi_{K}(\mathbf{r}, D) = \mathbf{i}^{l} Z_{K}(\hat{\mathbf{r}})$$

$$\times \begin{cases} \begin{pmatrix} g_{\kappa}(r, D) \\ \mathbf{i} f_{\kappa}(r, D) \end{pmatrix}, & r \leq s, \\ \begin{pmatrix} \frac{D+l+1}{2l+1} \widetilde{\Phi}_{\kappa}(r, l) + \frac{l-D}{2l+1} \widetilde{\Phi}_{\kappa}(r, -l-1) \end{pmatrix} g_{\kappa}(s, D), & r > s. \end{cases}$$
(A.34)

By analogy with (A.12), we write new functions by subtracting the diverging wave from the Dirac equation solution inside and outside the sphere

$$\bar{\Phi}_{K}(\mathbf{r}, D) = i^{l} Z_{K}(\hat{\mathbf{r}})$$

$$\times \begin{cases}
\Phi_{\kappa}(r, D) - \frac{D+l+1}{2l+1} \frac{g_{\kappa}(s, D)}{g_{\kappa}(s, l)} \widetilde{\Phi}_{\kappa}(r, l), & r \leq s , \\
\frac{l-D}{2l+1} \widetilde{\Phi}_{\kappa}(r, -l-1) g_{\kappa}(s, D), & r > s .
\end{cases}$$
(A.35)

We use these functions to form the Bloch summation

$$\chi_K^{\mathbf{k}}(\mathbf{r}, D) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} \bar{\Phi}_K(\mathbf{r} - \mathbf{R}, D) \quad , \tag{A.36}$$

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and expand the tail of the function coming from the site situated at  $\mathbf{R}$  about the zero center. For this, we use the generalized theorem of additivity

$$\mathbf{i}^{l} Z_{K}(\hat{\mathbf{r}}) \widetilde{\Phi}_{\kappa}(|\mathbf{r} - \mathbf{R}|, -l-1) = \sum_{K'} \mathbf{i}^{l'} Z_{K'}(\hat{\mathbf{r}}) \widetilde{\Phi}_{\kappa'}(r, l') \frac{S_{K'K}(\mathbf{R})}{-2(2l'+1)} , \qquad (A.37)$$

where

$$S_{K'K}(\mathbf{R}) = \sum_{LL'L''}^{l''=l+l'} \left(-\frac{1}{2}\right) \frac{4\pi (2l''-1)!!}{(2l-1)!!(2l'-1)!!} C_{l',\mu'-m,1/2,m}^{j'\mu'} \\ \times C_{L''L'L}(-i)^{l''} \left(\frac{R}{s}\right)^{-l''-1} Y_{L''}^{*}(\mathbf{R}) C_{l,\mu-m,1/2,m}^{j\mu} ; \quad (A.38)$$

and  $C_{L''L'L}$  are again the Gaunt coefficients.

We carry out the augmentation by analogy with the nonrelativistic case to obtain the expressions for the exact relativistic MT orbital inside the central sphere (hence, inside any other sphere):

$$\chi_{K}^{\mathbf{k}}(\mathbf{r}, D) = i^{l} Z_{K}(\hat{\mathbf{r}}) \Phi_{\kappa}(r, D) - \frac{D-l}{2l+1} g_{\kappa}(s, D) \\ \times \sum_{K'} i^{l'} Z_{K'}(\hat{\mathbf{r}}) \Phi_{\kappa'}(r, l') \frac{1}{g_{\kappa}(s, l')} \left(-\frac{1}{2} \frac{1}{2l'+1}\right) \\ \times \left(S_{K'K}^{\mathbf{k}} - \delta_{K'K} \frac{D+l+1}{D-l} 2(2l+1)\right) .$$
(A.39)

Here

$$S_{K'K}^{\mathbf{k}} = \sum_{\mathbf{R}\neq 0} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}} S_{K'K}(\mathbf{R}) \quad ; \tag{A.40}$$

$$S_{K'K}^{\mathbf{k}} = \sum_{m=\pm 1/2} C_{l',\mu'-m,1/2,m}^{j'\mu'} S_{l',\mu'-m,l,\mu-m}^{\mathbf{k}} C_{l,\mu-m,1/2,m}^{j\mu} ; \qquad (A.41)$$

 $S_{L'L}^{\mathbf{k}}$  are the structure constants of the nonrelativistic KKR–ASA method. For the linear combination of MT orbitals (A.39) to satisfy the Dirac equation over the entire space, it is required that, inside the central sphere, the sum of tails coming from all other positions be mutually canceled with the nonphysical term of the central MT orbital. This condition leads to the set of linear homogeneous equations

$$\sum_{K'} \left( S_{K'K}^{\mathbf{k}} - \delta_{K'K} 2(2l+1) \frac{D_{\kappa}(E) + l + 1}{D_{\kappa}(E) - l} \right) g_{\kappa}(s, D_{\kappa}) C_{K}(\mathbf{k}) = 0 \quad , \qquad (A.42)$$

where the energy E may take on only those values for which the secular determinant equals zero:

$$\det \left| S_{K'K}^{\mathbf{k}} - \delta_{K'K} 2(2l+1) \frac{D_{\kappa}(E) + l + 1}{D_{\kappa}(E) - l} \right| = 0 \quad . \tag{A.43}$$

Like in the nonrelativistic case, the relativistic KKR–ASA method has all the information concerning the crystal potential function within  $P_{\kappa}(E)$ , while crystal structure information is contained in the structure constants which do not depend on energy. The relativistic structure constants may easily be calculated from the nonrelativistic analogs by using (A.41).

# A.4 Linear Method of MT Orbitals (LMTO)

We can use the MT orbitals (A.17) or their relativistic analogs (A.39) as the trial functions in the Ritz variational procedure to find the linear combination of MT orbitals

$$\det |\langle \chi_{L'}^{\mathbf{k}}(\mathbf{r} - \mathbf{R}_I')|\mathbf{H} - E|\chi_L^{\mathbf{k}}(\mathbf{r} - \mathbf{R}_I')\rangle| = 0 \quad . \tag{A.44}$$

This method is not more complicated than the KKR method and, moreover facilitates allowing for non-MT crystal potentials and frequently yields better convergence than KKR. However, because the MT orbitals implicitly depend on energy, the computational demands of this method become comparable to the original APW and KKR methods. The situation becomes much simpler if we use energy independent MT orbitals. Below we follow primarily the development as given in reference [1087].

#### A.4.1 Basis functions

Let us represent the basis radial wave function as an expansion in a Taylor series about an arbitrary point  $E_{\nu}$  and limit ourselves to the linear term

$$\Phi(D,r) = \Phi_{\nu}(r) + \omega(D)\dot{\Phi}_{\nu}(r) \quad (A.45)$$

where

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$$\Phi_{\nu}(r) \equiv u_l(E_{\nu}, r); \quad \dot{\Phi}_{\nu}(r) \equiv \left. \frac{\partial u_l(E, r)}{\partial E} \right|_{E=E_{\nu}}$$

The functions  $\Phi_{\nu}(r)$  are normalized to unity in the sphere of the radius s. The coefficient  $\omega(D)$ , like  $\Phi(D, r)$ , depends on the logarithmic derivative which is chosen by the requirement that  $\Phi(D, r)$  should have the logarithmic derivative on the sphere

$$\omega(D) = -\frac{\Phi_{\nu}(s)}{\Phi_{\nu}(s)} \frac{D - D_{\nu}}{D - D_{\dot{\nu}}} \quad (A.46)$$

Here

$$D_{\nu} = S\Phi'_{\nu}(s)/\Phi_{\nu}(s)$$
; (A.47)

$$D_{\dot{\nu}} = S \dot{\Phi}'_{\nu}(s) / \dot{\Phi}_{\nu}(s)$$
 . (A.48)

The amplitude of the function (A.45) on the sphere surface  $\Phi(D, s) \equiv \Phi(D)$  is defined by

$$\Phi(D) = \Phi_{\nu}(s) \frac{D_{\nu} - D_{\dot{\nu}}}{D - D_{\dot{\nu}}} .$$
 (A.49)

In the basis set of the functions

$$\Phi_L(D, \mathbf{r}) = i^l Y_L(\hat{\mathbf{r}}) \Phi_l(D, r)$$
(A.50)

the Hamiltonian matrix elements and overlap matrices inside the sphere obviously have the form

$$\langle \Phi_{L'}(D') | \mathbf{H} - E_{\nu} | \Phi_L(D) \rangle = \delta_{L'L} \omega_l(D) , \qquad (A.51)$$

$$\langle \Phi_{L'}(D') | \Phi_L(D) \rangle = \delta_{L'L} (1 + \langle \dot{\Phi}_{\nu l}^2 \rangle \omega_l(D)) \quad . \tag{A.52}$$

In what follows we shall use the abbreviated notations  $\Phi_{\nu} \equiv \Phi_{\nu}(s)$ ;  $\dot{\Phi}_{\nu} \equiv \dot{\Phi}_{\nu}(s)$ .

Until now we have always considered a unit sphere. Below, when we deal with crystals, the influence of each of the spheres on the energy spectrum will be defined by the combination of potential parameters, e.g.  $D_{\nu}$ ,  $s\Phi_{\nu}^{2}$ ,  $s\Phi_{\nu}\dot{\Phi}_{\nu}$  and  $\langle\dot{\Phi}_{\nu}^{2}\rangle$ .

#### APPENDIX A: Linear Method of MT Orbitals

However, the first three parameters depend considerably on the selection of  $E_{\nu}$ . Therefore, in practice it is more convenient to use  $\omega(D_1)$ ,  $s\Phi^2(D_1)$  and  $\Phi(D_1)/\Phi(D_2)$ , where  $D_1 = -l - 1$ ,  $D_2 = l$ . Actually the transition from the first set of parameters to the second with  $D_1$ and  $D_2$  means that we must use a secant of the energy rather than a tangent. This may bring about various results, but, in most cases the differences are minor. The second combination of parameters appears to be easier to use [see (A.63)]. Note that in this case (A.45,47,A.48) acquire the following forms, respectively,

$$\Phi_{l}(r,D) = \frac{\omega_{l}(D) - \omega_{l}(-l-1)}{\omega_{l}(l) - \omega_{l}(-l-1)} \Phi_{l}(l,r) + \frac{\omega_{l}(D) - \omega_{l}(l)}{\omega_{l}(-l-1) - \omega_{l}(l)} \Phi_{l}(-l-1,r) , \qquad (A.53)$$

$$\frac{\omega_l(D) - \omega_l(-l-1)}{\omega_l(D) - \omega_l(l)} = \frac{\Phi_l(s, -l-1)}{\Phi_l(s, l)} \frac{D+l+1}{D-l} , \qquad (A.54)$$

$$\Phi_l(s,D) = \frac{(2l+1)\Phi_l(s,-l-1)\Phi_l(s,l)}{(D+l+1)\Phi_l(s,-l-1) - (D-l)\Phi_l(s,l)} .$$
(A.55)

It can also be shown that the following are true

$$\frac{\omega_l(D) - \omega_l(-l-1)}{\omega_l(l) - \omega_l(-l-1)} = \frac{D+l+1}{2l+1} \frac{\Phi_l(s,D)}{\Phi_l(s,l)} , \qquad (A.56)$$

$$\frac{\omega_l(l) - \omega_l(D)}{\omega_l(l) - \omega_l(-l-1)} = \frac{l-D}{2l+1} \frac{\Phi_l(s,D)}{\Phi_l(s,-l-1)} .$$
(A.57)

Then, in the Andersen approximation, the MT orbital (A.17) is

$$\chi_L^{\mathbf{k}}(\mathbf{r}, D) \simeq \frac{\omega_l(l) - \omega_l(D)}{\omega_l(l) - \omega_l(-l-1)} \chi_L^{\mathbf{k}}(\mathbf{r}) = \alpha_l(D) \chi_L^{\mathbf{k}}(\mathbf{r}) , \qquad (A.58)$$

where the MT orbital  $\chi_L^{\mathbf{k}}(\mathbf{r})$  does not depend on energy,

$$\chi_{L}^{\mathbf{k}}(\mathbf{r}) = \Phi_{L}(\mathbf{r}, -l-1) - \Phi_{l}(s, -l-1) \\ \times \sum_{L'} S_{L'L}^{\mathbf{k}} \frac{\Phi_{L'}(\mathbf{r}, l')}{2(2l'+1)\Phi_{l'}(s, l')} .$$
(A.59)

Here,  $S_{L'L}^{\mathbf{k}}$  are the structure constants (A.9) which can be represented [1087]

$$S_{L'L}^{\mathbf{k}} = g_{L'L} \Sigma_{\lambda\mu}^{\mathbf{k}}$$

where  $\lambda = l' + l$ ;  $\mu = m' - m$ ;

$$g_{L'L} = (-1)^{m+1} 2 \left( \frac{(2l'+1)(2l+1)}{2\lambda+1} \times \frac{(\lambda+\mu)!(\lambda-\mu)!}{(l'+m')!(l'-m')!(l+m)!(l-m)!} \right)^{1/2}$$
  
$$\Sigma_{\lambda\mu}^{\mathbf{k}} = \sum_{\mathbf{R}\neq 0} e^{i\mathbf{k}\mathbf{R}} \left( \frac{s}{R} \right)^{\lambda+1} \left[ \sqrt{4\pi} i^{\lambda} Y_{\lambda\mu}(\hat{\mathbf{R}}) \right]^{*}.$$

In (A.59), the second term is the sum of the tails coming from all the remaining atoms of a crystal.

The representation of the MT orbitals as a product of  $\alpha_l(D)$  and the energy independent orbital is very convenient since it allows the use of  $\chi_L^{\mathbf{k}}(\mathbf{r})$  instead of  $\chi_L^{\mathbf{k}}(\mathbf{r}, D)$ . It may be easily shown that this does not cause a change in the energy eigenvalues, but affects rather the normalization of the wave functions.

# A.4.2 Hamiltonian and overlap matrices

A more general expression for the LMTO basis function (A.59) can be written as

$$\chi_L^{\mathbf{k}}(D_{l_2}, \mathbf{r}) = \Phi_L(D_{l_2}, \mathbf{r}) - \sum_{L'} \frac{\Phi_{L'}(l', \mathbf{r})}{\omega_{l'}(D_{l'_2}) - \omega_{l'}(l')} T_{L'L}^{\mathbf{k}} .$$
(A.60)

Here,  $D_{l_2}$  is an arbitrary logarithmic derivative not equal to l and  $T_{L'L}^{\mathbf{k}}$  is the matrix

$$T_{L'L}^{\mathbf{k}}(D_{l'_{2}}, D_{l_{2}}) = \sqrt{\frac{s}{2}} \Phi_{l'}(s, D_{l'_{2}}) \times \left\{ -2(2l+1)\frac{D_{l_{2}}+l+1}{D_{l_{2}}-1} + S_{L'L}^{\mathbf{k}} \right\} \sqrt{\frac{s}{2}} \Phi_{l}(s, D_{l_{2}}) .$$
(A.61)

If in practical calculations the value  $D_{l_2} = D_{l\nu}$  is used, the expression for the LMTO basis function becomes

$$\chi_{L}^{\mathbf{k}}(D_{l\nu},\mathbf{r}) = \Phi_{L}(D_{l\nu},\mathbf{r}) + \sum_{L'} \frac{\Phi_{L'}(l',\mathbf{r})}{\omega_{l'}(l')} T_{L'L}^{\mathbf{k}} ,.$$
(A.62)

and the matrix (A.61) simplifies to

$$T_{L'L}^{\mathbf{k}} = \sqrt{\frac{s}{2}} \Phi_{l'}(s, D_{l'\nu}) [P_l(D_{l\nu})\delta_{LL'} - S_{L'L}^{\mathbf{k}}] \sqrt{\frac{s}{2}} \Phi_l(s, D_{l\nu}) , \qquad (A.63)$$

were

$$P_l(D_{l\nu}) = -2(2l+1)\frac{D_{l\nu} + l + 1}{D_{l\nu} - l}, \qquad (A.64)$$

The Hamiltonian and overlap matrices of the LMTO eigenvalue problem

$$\mathbf{H} - E\mathbf{O} = 0 , \qquad (A.65)$$

are then

$$H_{L'L}^{\mathbf{k}} = \langle \chi_{L'}^{\mathbf{k}} | \mathbf{H} | \chi_{L}^{\mathbf{k}} \rangle = H_{l'}^{(1)} \delta_{L'L} + (H_{l'}^{(2)} + H_{l}^{(2)}) T_{L'L}^{\mathbf{k}} + \sum_{L''} T_{L'L''}^{\mathbf{k}} H_{L''}^{(3)} T_{L''L}^{\mathbf{k}} , \qquad (A.66)$$

$$O_{L'L}^{\mathbf{k}} = \langle \chi_{L'}^{\mathbf{k}} | \chi_{L}^{\mathbf{k}} \rangle = O_{l'}^{(1)} \delta_{L'L} + (O_{l'}^{(2)} + O_{l}^{(2)}) T_{L'L}^{\mathbf{k}} + \sum_{L''} T_{L'L''}^{\mathbf{k}} O_{l''}^{(3)} T_{L''L}^{\mathbf{k}} , \qquad (A.67)$$

where

$$\begin{aligned}
 O_l^{(1)} &= 1; \\
 O_l^{(2)} &= \omega_l^{-1}(l); \\
 O_l^{(3)} &= \omega_l^{-2}(l) + \langle \Phi_{\nu l}^2 \rangle; 
 \end{aligned}$$
 (A.68)

$$H_{l}^{(1)} = E_{\nu l} O_{l}^{(1)} ;$$
  

$$H_{l}^{(2)} = \frac{1}{2} + E_{\nu l} O_{l}^{(2)} ;$$
  

$$H_{l}^{(3)} = \omega_{l}^{-1}(l) + E_{\nu l} O_{l}^{(3)} .$$
  
(A.69)

In these expressions, the components with  $S_{L'L}^0$ ,  $S_{L'L}^1$  and  $S_{L'L}^2$  in (A.66,A.67) may be considered to be one-, two- and three-center integrals respectively. Equations (A.66,A.67) are the fundamental expressions of the LMTO method in the atomic sphere approximation (LMTO–ASA). In fact, this method is similar to the linear combination of atomic orbitals (LCAO). For the LMTO–ASA method, when the basis functions, i.e., energy independent MT orbitals are correctly chosen the multicenter integrals are easily calculated through the corresponding matrices.

### A.4.3 Valence electron wave function in a crystal

Let us assume that  $C_L^{j\mathbf{k}}$  is the eigenvector corresponding to an egenvalue  $E_{j\mathbf{k}}$  obtained after diagonalization of the eigenvalue problem (A.65). Then, the valence electron wave function can be written as

$$\Psi_{j\mathbf{k}}(\mathbf{r}) = \sum_{L} C_{L}^{j\mathbf{k}} \chi_{L}^{\mathbf{k}}(\mathbf{r}, D_{l\nu}) . \qquad (A.70)$$

Substituting the expression (A.62) for  $\chi_L^{\mathbf{k}}(\mathbf{r}, D_{l\nu})$  one obtaines a one–center expansion

$$\Psi_{j\mathbf{k}}(\mathbf{r}) = \sum_{L} [\pi_{L}^{j\mathbf{k}} \Phi_{\nu L}(\mathbf{r}) + \Omega_{L}^{j\mathbf{k}} \dot{\Phi}_{\nu L}(\mathbf{r})] , \qquad (A.71)$$

where

$$\pi_L^{j\mathbf{k}} = C_{L'}^{j\mathbf{k}} + \omega_l^{-1}(l) \sum_{L'} T_{LL'}^{\mathbf{k}} C_{L'}^{j\mathbf{k}} , \qquad (A.72)$$

$$\Omega_L^{j\mathbf{k}} = \sum_{L'} T_{LL'}^{\mathbf{k}} C_{L'}^{j\mathbf{k}} .$$
(A.73)

As shown in [1087], these expressions for the wave function are accurate up to terms in  $(E - E_{\nu})$ , while the energy eigenvalues  $E_{j\mathbf{k}}$  and the corresponding eigenvectors  $C_L^{j\mathbf{k}}$  are determined to within  $(E - E_{\nu})^3$ . To be able to write  $\Psi_{\mathbf{k}}(E_j, \mathbf{r})$  also to within  $(E - E_{\nu})^3$  one can substitute  $\Phi_L(\mathbf{r}, -l-1)$  in (A.70) by the exact energy dependent MT orbitals (A.17).

#### A.4.4 Density matrix

If spin polarized LMTO calculations are performed the radial solution of the Schrödinger equation inside the sphere acquires an additional spin index

$$\Phi_{L\sigma}(\mathbf{r}) = u_{l\sigma}(r)i^{l}Y_{lm}(\hat{r})\chi_{\sigma}$$
(A.74)

where  $\chi_{\sigma}$  is the eigenfunction of the spin operator corresponding to the spin projection  $\sigma$ . Substituting the one center expansion of the LMTO wave function (A.71) into the definition of the charge density

$$\rho(\mathbf{r}) = \sum_{j\mathbf{k}} f(E_{j\mathbf{k}}) |\Psi^{j\mathbf{k}}(\mathbf{r})\rangle \langle \Psi^{j\mathbf{k}}(\mathbf{r})| = \sum_{j\mathbf{k}} f(E_{j\mathbf{k}}) |\Psi^{*j\mathbf{k}}(\mathbf{r})|^2 , \qquad (A.75)$$

where f(E) is the Fermi function, one can write the elements of the spin density matrix

$$\rho_{\sigma,\sigma'}(\mathbf{r}) = \sum_{j\mathbf{k}} f(E_{j\mathbf{k}}) \sum_{lm,l'm'} i^{l+l'} Y_{lm}(\hat{r}) Y_{l'm'}^{*}(\hat{r})$$

$$\times \left[ \pi_{lm\sigma}^{j\mathbf{k}} u_{\nu l\sigma}(r) + \Omega_{lm\sigma}^{j\mathbf{k}} \dot{u}_{\nu l\sigma}(r) \right]$$

$$\times \left[ \pi_{l'm'\sigma'}^{*j\mathbf{k}} u_{\nu l'\sigma'}(r) + \Omega_{l'm'\sigma'}^{*j\mathbf{k}} \dot{u}_{\nu l'\sigma'}(r) \right]. \quad (A.76)$$

Taking the elements of the spin density matrix from the projection of the wave function onto the  $Y_{lm}$  subspace gives

$$\rho_{lm\sigma,l'm'\sigma'}(r) = \sum_{j\mathbf{k}} f(E_{j\mathbf{k}}) \left[ \pi_{lm\sigma}^{j\mathbf{k}} u_{\nu l}(r) + \Omega_{lm\sigma}^{j\mathbf{k}} \dot{u}_{\nu l}(r) \right] \\ \times \left[ \pi_{l'm'\sigma'}^{*j\mathbf{k}} u_{\nu l'}(r) + \Omega_{l'm'\sigma'}^{*j\mathbf{k}} \dot{u}_{\nu l'}(r) \right].$$
(A.77)

Here it is assumed for simplicity that the radial functions  $u_{\nu l}$  and  $\dot{u}_{\nu l}$  do not depend on spin indices. Finally, keeping only the l' = l part of the spin density matrix and performing the radial integration one obtains the expression for the occupation matrix which enters the LDA+U energy functional (1.43)

$$n_{lm\sigma,lm'\sigma'} = \sum_{j\mathbf{k}} f(E_{j\mathbf{k}}) \left( \pi_{lm\sigma}^{j\mathbf{k}} \pi_{lm'\sigma'}^{*j\mathbf{k}} + \Omega_{lm\sigma}^{j\mathbf{k}} \Omega_{lm'\sigma'}^{*j\mathbf{k}} \langle \dot{\Phi}_l^2 \rangle \right) .$$
(A.78)

Usually, the occupation matrix is diagonal in spin indices. However, nondiagonal elements appear if the spin-orbit coupling is included into the Hamiltonian or non-collinear magnetic structures are considered.

Using (A.71) Eq. (A.78) can be rewritten as

$$n_{lm\sigma,lm'\sigma'} = \sum_{j\mathbf{k}} f(E_{j\mathbf{k}}) (\langle u_{\nu l} Y_{lm} \chi_{\sigma} | \Psi^{j\mathbf{k}} \rangle \langle \Psi^{j\mathbf{k}} | u_{\nu l} Y_{lm'} \chi_{\sigma'} \rangle + \langle \dot{\Phi}_l^2 \rangle^{-1} \langle \dot{u}_{\nu l} Y_{lm} \chi_{\sigma} | \Psi^{j\mathbf{k}} \rangle \langle \Psi^{j\mathbf{k}} | \dot{u}_{\nu l} Y_{lm'} \chi_{\sigma'} \rangle).$$
(A.79)

The variation of  $n_{lm\sigma,lm'\sigma'}$  with respect to  $\Psi^{*j{\bf k}}$ 

$$\frac{\delta n_{lm\sigma,lm'\sigma'}}{\delta \Psi^{*j\mathbf{k}}} = [|u_{\nu l}Y_{lm'}\chi_{\sigma'}\rangle\langle u_{\nu l}Y_{lm}\chi_{\sigma}| + \langle \Phi_l^2 \rangle^{-1} |\dot{u}_{\nu l}Y_{lm'}\chi_{\sigma'}\rangle\langle \dot{u}_{\nu l}Y_{lm}\chi_{\sigma}|] \Psi^{j\mathbf{k}}$$
(A.80)

defines the projector which appears in the Kohn-Sham equations (1.59) of the LDA+U method (see section 1.2.4).

#### A.5 Relativistic LMTO Method

Andersen [1087] derived the relativistic generalization of the LMTO method based on the Pauli Hamiltonian. Here, we proceed from a more general approach based on the solution of the Dirac equation [1086].

The trial function with arbitrary logarithmic derivative D is written similarly to (A.45)

$$\Phi_{K}(D,\mathbf{r}) = i^{l} \begin{pmatrix} g_{\kappa}(D,r) & \chi_{K}(\mathbf{r}) \\ if_{\kappa}(D,r) & \chi_{\bar{K}}(\mathbf{r}) \end{pmatrix} , \qquad (A.81)$$

$$a_{r}(D,r) = a_{rrr}(r) + \omega_{r}(D)\dot{a}_{rrrr}(r)$$

$$g_{\kappa}(D,r) = g_{\nu\kappa}(r) + \omega_{\kappa}(D)g_{\nu\kappa}(r) ,$$
  

$$f_{\kappa}(D,r) = f_{\nu\kappa}(r) + \omega_{\kappa}(D)\dot{f}_{\nu\kappa}(r) ,$$
(A.82)

where  $K = (\kappa, \mu)$ ;  $\bar{K} = (-\kappa, \mu)$ ;  $\dot{g}_{\nu\kappa} \equiv \partial g_{\kappa}/\partial E|_{E=E_{\nu}}$ ; the radial wave functions are normalized according to the condition (A.26); the logarithmic derivative is defined in (A.27);  $\chi_K$  is the spin–angular functions defined in (2.58);

$$\omega_{\kappa}(D) = -\frac{g_{\nu\kappa}}{g_{\nu\kappa}} \frac{D - D_{\nu\kappa}}{D - D_{\nu\kappa}} ; \qquad (A.83)$$

$$g_{\kappa}(D) = g_{\nu\kappa} \frac{D_{\nu\kappa} - D_{\nu\kappa}}{D - D_{\nu\kappa}} . \tag{A.84}$$

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The matrix elements of the Hamiltonian and overlap matrix in the basis set (A.81) for a unit sphere of radius s have the form

$$\langle \Phi_{K'}(D',\mathbf{r})|\mathbf{H} - E_{\nu\kappa}|\Phi_K(D,\mathbf{r})\rangle = \omega_\kappa(D)\delta_{K'K} \quad , \tag{A.85}$$

$$\langle \Phi_{K'}(D',\mathbf{r})|\Phi_K(D,\mathbf{r})\rangle = [1 + \omega_\kappa(D)\omega_\kappa(D')\langle|\dot{\Phi}_{\nu\kappa}|^2\rangle]\delta_{K'K} .$$
(A.86)

We use the expression

$$\int_{\Omega} X^{+} \boldsymbol{\alpha} \cdot \mathbf{p} Y d^{3} \mathbf{r} = \int_{\Omega} (Y^{+} \boldsymbol{\alpha} \cdot \mathbf{p} X)^{*} d^{3} \mathbf{r} - i \int_{S} X^{+} \boldsymbol{\alpha} \cdot \mathbf{n} Y d^{2} S \quad , \tag{A.87}$$

where n is the vector normal to the sphere, and obtain an important relation,

$$sg_{\nu\kappa}g_{\nu\kappa}(D_{\nu\kappa}-D_{\nu\kappa})=1 \quad . \tag{A.88}$$

Let us select two arbitrary logarithmic derivatives  $D_1$  and  $D_2$  as the parameters. It can be easily shown that the following relation holds:

$$sg_{\kappa}(D_1)g_{\kappa}(D_2) = -\frac{\omega_{\kappa}(D_2) - \omega_{\kappa}(D_1)}{D_2 - D_1}$$
(A.89)

and, for the case  $D_1 = -l - 1$ ,  $D_2 = l$ 

$$(2l+1)sg_{\kappa}(-l-1)g_{\kappa}(l) = \omega_{\kappa}(-l-1) - \omega_{\kappa}(l) \quad . \tag{A.90}$$

The energy independent relativistic MT orbital (RMTO) in the region outside the atomic sphere is a solution of the Dirac equation for  $E = V_c = 0$  possessing the logarithmic derivative  $\widetilde{D}_{\kappa}(0) = \widetilde{D}_{0\kappa}$  where the tilde indicates the function for free electrons. The radial solutions of the Dirac equations for free electrons, singular and regular at the origin, have the forms of (A.32,A.33), respectively.

The relativistic MT orbital  $\chi_K(\mathbf{r})$ , inside the sphere on which it is centered, equals  $\Phi_K(-l-1, \mathbf{r})$ . In the interstitial region it is proportional to  $\widetilde{\Phi}_K(-l-1, \mathbf{r})$  and, inside any other sphere shifted by the lattice translation vector  $\mathbf{R}$ , it is the linear combination of  $\Phi_K(l', \mathbf{r} - \mathbf{R})$  with coefficients that ensure continuity and differentiability of the RMTO over the entire space.

The Bloch sum of orbitals

$$\chi_{K}^{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \chi_{K}(\mathbf{r} - \mathbf{R})$$
(A.91)

can be represented by using the generalized theorem of additivity (A.37) as

$$\chi_{K}^{\mathbf{k}}(\mathbf{r}) = \Phi_{K}(-l-1,\mathbf{r}) - \sum_{K'} \frac{\Phi_{K'}(l',\mathbf{r})}{2(2l'+1)} \frac{g_{\kappa}(-l-1,s)}{g_{\kappa'}(l',s)} S_{K'K}^{\mathbf{k}} , \qquad (A.92)$$

where  $S_{K'K}^{\mathbf{k}}$  is defined in (A.41). The second term in this expression is the sum of the RMTO tails coming from all other atoms in the crystal.

We use (A.90) to rewrite (A.92)

$$\chi_{K}^{\mathbf{k}}(\mathbf{r}) = \Phi_{K}(-l-1,\mathbf{r}) - \sum_{K'} \frac{\Phi_{K'}(l',\mathbf{r})}{\omega_{\kappa'}(-l'-1) - \omega_{\kappa'}(l')} \times \frac{s}{2} g_{\kappa'}(-l'-1,s) g_{\kappa}(-l-1,s) S_{K'K}^{\mathbf{k}} .$$
(A.93)

Taking (A.85,A.86) into account, we obtain the relativistic LMTO–ASA elements of the Hamiltonian and overlap matrices

$$\begin{aligned} H_{K'K}^{\mathbf{k}} &= \langle \chi_{K'}^{\mathbf{k}} | \mathbf{H} | \chi_{K}^{\mathbf{k}} \rangle = H_{\kappa'}^{(1)} \delta_{K'K} + \left[ -(H_{\kappa'}^{(2)} + H_{\kappa}^{(2)}) S_{K'K}^{\mathbf{k}} \right. & (A.94) \\ &+ \sum_{K''} S_{K'K''}^{\mathbf{k}} H_{\kappa''}^{(3)} S_{K''K}^{\mathbf{k}} \right] \frac{s}{2} g_{\kappa'} (-l'-1,s) g_{\kappa} (-l-1,s) \ , \\ O_{K'K}^{\mathbf{k}} &= \langle \chi_{K'}^{\mathbf{k}} | \chi_{K}^{\mathbf{k}} \rangle = O_{\kappa}^{(1)} \delta_{K'K} + [-(O_{\kappa'}^{(2)} + O_{\kappa}^{(2)}) S_{K'K}^{\mathbf{k}} \\ &+ \sum_{K''} S_{K'K''}^{\mathbf{k}} O_{\kappa''}^{(3)} S_{K''K}^{\mathbf{k}} \right] \frac{s}{2} g_{\kappa'} (-l'-1,s) g_{\kappa} (-l-1,s) \ , \end{aligned}$$

where

$$O_{\kappa}^{(1)} = 1 + \langle \Phi_{\nu\kappa} | \Phi_{\nu\kappa} \rangle \omega_{\kappa}^{2}(-l-1) ,$$

$$O_{\kappa}^{(2)} = \frac{1 + \langle \Phi_{\nu\kappa} | \Phi_{\nu\kappa} \rangle \omega_{\kappa}(-l-1) \omega_{\kappa}(l)}{\omega_{\kappa}(-l-1) - \omega_{\kappa}(l)} ,$$

$$O_{\kappa}^{(3)} = \frac{1 + \langle \Phi_{\nu\kappa} | \Phi_{\nu\kappa} \rangle \omega_{\kappa}^{2}(l)}{2s[(2l+1)g_{\kappa}(l)]^{2}} ,$$

$$H_{\kappa}^{(1)} = \omega_{\kappa}(-l-1) + E_{\nu\kappa}O_{\kappa}^{(1)} ,$$

$$H_{\kappa}^{(2)} = \frac{1}{2} + \frac{\omega_{\kappa}(l)}{\omega_{\kappa}(-l-1) - \omega_{\kappa}(l)} + E_{\nu\kappa}O_{\kappa}^{(2)} ,$$

$$H_{\kappa}^{(3)} = \frac{\omega_{\kappa}(l)}{2s[(2l+1)g_{\kappa}(l)]^{2}} + E_{\nu\kappa}O_{\kappa}^{(3)} .$$
(A.96)

In (A.94,A.95), the terms with the indices 1,2 and 3 are one-, two- and three-center integrals, respectively.

# A.6 Relativistic Spin-Polarized LMTO Method

The most widely used approach to treat simultaneously relativistic and the magnetic field effect on electrons in solids is based on a scheme proposed by MacDonald and Vosko [1088]. In this approach the Dirac equation for a spin-dependent potential has the form

$$[H(\mathbf{r}) - E]\Psi(\mathbf{r}) = 0 \tag{A.97}$$

$$H(\mathbf{r}) = H^0(\mathbf{r}) + H^M(\mathbf{r}) \tag{A.98}$$

where  $H^0(\mathbf{r})$  is the Dirac operator for the spin-independent part of the potential

$$H^{0}(\mathbf{r}) = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^{2}/2 + \mathbf{I}V(\mathbf{r}) , \qquad (A.99)$$

whereas the spin-dependent part of the Hamiltonian,

$$H^{M}(\mathbf{r}) = \beta \boldsymbol{\sigma} \mathbf{B}(\mathbf{r}) , \qquad (A.100)$$

contains an effective magnetic field  $\mathbf{B}(\mathbf{r})$ ,

$$\mathbf{B}(\mathbf{r}) = \mu_B[\mathbf{B}_{xc}(\mathbf{r}) + \mathbf{B}_{ext}(\mathbf{r})], \qquad (A.101)$$

which couples to the spin of the electron. Here  $\mathbf{B}_{ext}$  is an external field and the subscript xc refers to the exchange-correlation potential,

$$V_{xc}(\mathbf{r}) = \frac{\delta}{\delta n} E_{xc}[n, \mathbf{m}], \ \mathbf{B}_{ext}(\mathbf{r}) = \frac{\delta}{\delta \mathbf{m}} E_{xc}[n, \mathbf{m}],$$
(A.102)

where  $n(\mathbf{r})$  and  $\mathbf{m}(\mathbf{r})$  are the electron and the spin magnetization densities, respectively.

The most accurate solution to the spin-polarized relativistic band structure problem can be obtained by setting up the relativistic MTO's by using proper solutions to the single-site Dirac equation for a spin-dependent potential. Spin-polarized fully relativistic LMTO (SPR RLMTO) methods have been developed by Ebert [1089], Solovyev *et al.* [1090], and Krasovskii [563].

As shown by Feder *et al.* [1091], Strange *et al.* [1092], and also Cortona *et al.* [1093], the spin-dependent potential in the Dirac equation results in a set of an infinite number of coupled equations for the radial functions. The usual approximation is to neglect the weak spin-orbit coupling of the order of  $(1/c^2)(1/r)[dB(r)/dr]$  between the states with  $\Delta l = \pm 2$  and  $\Delta j = \pm \frac{1}{2}$  so that the infinite set decomposes into independent sets of four (for  $|\mu| \le l - 1/2$ ) or two (for  $|\mu| = l + 1/2$ ) coupled equations for each  $l\mu$ .

Therefore the solution of Eq. A.97 inside the atomic sphere is chosen as

$$\Psi(E,\mathbf{r}) = \sum_{ls\mu} \sum_{\eta=1,2} c^{\eta}_{l\mu} \varphi^{s,\eta}_{l\mu}(E,\mathbf{r}), \qquad (A.103)$$

where the partial solution takes the form

$$\varphi_{l\mu}^{s,\eta}(E,\mathbf{r}) = i^{l} \begin{pmatrix} g_{l\mu}^{s,\eta}(E,r) & \chi_{l,\mu}^{s}(\hat{r}) \\ i f_{l\mu}^{s,\eta}(E,r) & \chi_{l+2s,\mu}^{-s}(\hat{r}) \end{pmatrix} .$$
(A.104)

Similar to the conventional RLMTO method, the expression for the wave function with an arbitrary logarithmic derivative *D* reads [563]

$$\Phi_{l\mu}^{s}(D,\mathbf{r}) = \sum_{\eta} [a_{l\mu}^{\eta}(D)\varphi_{l\mu}^{s,\eta}(E_{\nu},\mathbf{r}) + b_{l\mu}^{\eta}(D)\dot{\varphi}_{l\mu}^{s,\eta}(E_{\nu},\mathbf{r})].$$
(A.105)

In principle, one could go on completely analogously to the conventional LMTO method to construct spin-polarized relativistic MTO's. This approach results, however, in a very inconvenient form of the Hamiltonian and overlap matrix elements. An alternative way [1089] to set up the MTO's is simply to augment smoothly the interstitial solutions  $n_{l\mu}(\mathbf{r})$  within the central cell by  $\Phi_{l\mu}(-l-1, \mathbf{r})$  and in all other spheres by linear combinations of  $\Phi_{l\mu}(l', \mathbf{r})$ . These functions  $\Phi_{l\mu}(D, \mathbf{r})$  are now found by smoothly matching linear combinations of the solutions  $\varphi_{l\mu}^{s,\eta}(E_{\nu}, \mathbf{r})$  and their energy derivatives  $\dot{\varphi}_{l\mu}^{s,\eta}(E_{\nu}, \mathbf{r})$  to the Neumann solutions  $n_{l\mu}(\mathbf{r})$ for D = -l - 1 and to the Bessel solutions  $j_{l\mu}(\mathbf{r})$  for D = +l, respectively.

# A.6.1 Perturbational approach to the relativistic spin-polarized LMTO method

A less accurate but much easier way to deal with the full Hamiltonian operator for a spindependent potential is to take into account of the spin-dependent part  $H^M(\mathbf{r})$  of  $H(\mathbf{r})$  within the variational step [1089]. This means that the RLMTO basis functions are constructed starting form solutions of the Dirac equation in the spin-independent part of the potential. Then, the approximate RLMTO Hamiltonian matrix  $H^{0\mathbf{k}}_{K'K}$  is constructed just as for the non-spin-polarized case, and the matrix

$$H_{K'K}^{M\mathbf{k}} = \langle \chi_{K'}^{\mathbf{k}} | H^{M}(\mathbf{r}) | \chi_{K}^{\mathbf{k}} \rangle , \qquad (A.106)$$

can be easily expressed in terms of matrix elements of  $H^M(\mathbf{r})$  taken between the functions  $\Phi_K(D, \mathbf{r})$ . These, in turn, are given by [1089]

$$\langle \Phi_{\kappa'}(D', \mathbf{r}) | H^M(\mathbf{r}) | \Phi_{\kappa}(D, \mathbf{r}) \rangle = G(\kappa', \kappa, \mu) [B\{g_{\kappa'}, g_{\kappa}\} + \omega_{\kappa}(D)B\{g_{\kappa'}, \dot{g}_{\kappa}\} + \omega_{\kappa'}(D')B\{\dot{g}_{\kappa'}, g_{\kappa}\} + \omega_{\kappa'}(D')\omega_{\kappa}(D)B\{\dot{g}_{\kappa'}, \dot{g}_{\kappa}\}] + G(-\kappa', -\kappa, \mu) [B\{f_{\kappa'}, f_{\kappa}\} + \omega_{\kappa}(D)B\{f_{\kappa'}, \dot{f}_{\kappa}\} + \omega_{\kappa'}(D')B\{\dot{f}_{\kappa'}, f_{\kappa}\} + \omega_{\kappa'}(D')\omega_{\kappa}(D)B\{\dot{f}_{\kappa'}, \dot{f}_{\kappa}\}],$$
(A.107)

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with

$$\langle \chi_{\kappa'}^{\mu'} | \sigma_z | \chi_{\kappa}^{\mu} \rangle = \delta_{\mu\mu'} G(\kappa', \kappa, \mu) = \delta_{\mu\mu'} \begin{cases} -\frac{\mu}{\kappa + \frac{1}{2}}, \ \kappa = \kappa' \\ -[1 - (\frac{\mu}{\kappa + \frac{1}{2}})^2]^{1/2}, \ \kappa = -\kappa' - 1 \\ 0, - \text{ otherwise} \end{cases}$$

and

$$B\{\dot{g}_{\kappa'},g_{\kappa}\} = \int dr r^2 B(r) \dot{g}_{\kappa'}(r) g_{\kappa}(r), \qquad (A.108)$$

and similar for all other functions  $B\{\alpha_{\kappa'}, \beta_{\kappa}\}$  with  $\alpha, \beta = (g, \dot{g}, f, \dot{f})$ .

Due to the properties of the angular part  $\langle \chi_{\kappa'}^{\mu'} | \sigma_z | \chi_{\kappa}^{\mu} \rangle$ , the matrix elements  $H_{K'K}^{M\mathbf{k}}$  are only diagonal in l and  $\mu$ , which means, apart from the coupling between functions with  $\kappa = \kappa'$ , there is a coupling for  $\kappa = -\kappa' - 1$ . However, this coupling produces no remarkable difficulties to setting up the matrix  $H_{K'K}^{\mathbf{k}}$ . Because all further steps within this perturbational approach are completely identical to a conventional RLMTO calculations, this method provides a very simple way to perform spin-polarized relativistic band structure calculations. In spite of this approximation used, this scheme nevertheless gives results in very good agreement with the SPR RLMTO one, while being very simple to implement [1089].

# Appendix B Optical matrix elements

Now let us consider in details the evaluation of the matrix elements (1.245) in the fully relativistic Dirac representation in the framework of the RLMTO method.

# **B.1** ASA approximation

The Bloch-sum of SPRLMTO's has the following one-center expansion inside an arbitrary atomic sphere, R', with radius  $S_{R'}$ :

$$\chi_{RK}^{\mathbf{k}}(\mathbf{r}) = \sum_{K'} \left[ \Pi_{RK,R'K'}^{\mathbf{k}} \Phi_{R'K'}(\mathbf{r} - \mathbf{R}', E_{\nu}) + \Omega_{RK,R'K'}^{\mathbf{k}} \dot{\Phi}_{R'K'}(\mathbf{r} - \mathbf{R}', E_{\nu}) \right] \quad \text{for } |\mathbf{r} - \mathbf{R}'| \le S_{R'}, \tag{B.1}$$

where  $\Phi_{RK}(\mathbf{r}, E)$  is given in (A.104) or (A.21), matrices  $\Pi^{\mathbf{k}}$  and  $\Omega^{\mathbf{k}}$  are given in terms of the canonical structure constants by Eqs. (A.72,A.73); although in the *lm*-rather in the  $\kappa\mu$  representation. The desired result is obtained by the unitary transformation specified by Eq. (A.24).

Introducing new coefficients

$$A_{RK,n}^{\mathbf{k}}(\mathbf{r}) = \sum_{R'K'} \prod_{RK,R'K'}^{\mathbf{k}} C_{R'K',n}^{\mathbf{k}}$$
(B.2)

$$B_{RK,n}^{\mathbf{k}}(\mathbf{r}) = \sum_{R'K'} \Omega_{RK,R'K'}^{\mathbf{k}} C_{R'K',n}^{\mathbf{k}}$$
(B.3)

we can express the valence electron wave function in a crystal as

$$\Psi_{n}^{\mathbf{k}}(\mathbf{r}) = \sum_{K} \left[ A_{RK,n}^{\mathbf{k}} \Phi_{RK}(\mathbf{r} - \mathbf{R}, E_{\nu}) + B_{RK,n}^{\mathbf{k}} \dot{\Phi}_{RK}(\mathbf{r} - \mathbf{R}, E_{\nu}) \right] \quad \text{for } |\mathbf{r} - \mathbf{R}| \le S_{R},$$
(B.4)

The optical matrix element is an integral over the primitive cell. With RLMTO's as a basis functions, we express this integral in the standard way as the integral over the interstitial region,

where the RLMTO's are free-space solutions, plus the sum of integrals over the atomic spheres, i.e.:

$$\langle \Psi_{n'}^{\mathbf{k}} | c\alpha | \Psi_{n}^{\mathbf{k}} \rangle = \langle \Psi_{n'}^{\mathbf{k}} | c\alpha | \Psi_{n}^{\mathbf{k}} \rangle_{I} + \sum_{R} \langle \Psi_{n'}^{\mathbf{k}} | c\alpha | \Psi_{n}^{\mathbf{k}} \rangle_{R}.$$
(B.5)

For the integral over the atomic sphere at  $\mathbf{R}$ , we obtain from the one-center expansion (B.4)

$$\langle \Psi_{n'}^{\mathbf{k}} | c \alpha | \Psi_{n}^{\mathbf{k}} \rangle_{R} = \sum_{KK'} \left[ A_{RK',n'}^{*\mathbf{k}} A_{RK,n}^{\mathbf{k}} I_{K'K}^{\alpha \alpha} + A_{RK',n'}^{*\mathbf{k}} B_{RK,n}^{\mathbf{k}} I_{K'K}^{\alpha \beta} \right.$$

$$\left. + B_{RK',n'}^{*\mathbf{k}} A_{RK,n}^{\mathbf{k}} I_{K'K}^{\beta \alpha} + B_{RK',n'}^{*\mathbf{k}} B_{RK,n}^{\mathbf{k}} I_{K'K}^{\beta \beta} \right] .$$

$$(B.6)$$

Here

$$I_{K'K}^{\alpha\beta} = \langle \Phi_{K'}^{\alpha} | c\alpha | \Phi_{K}^{\beta} \rangle_R \quad , \tag{B.7}$$

with  $\Phi^{\alpha} \equiv \Phi$  and  $\Phi^{\beta} \equiv \dot{\Phi}$ .

Using the relations  $\alpha = \tau \sigma = \tau \sigma_r \left(\frac{\mathbf{r}}{r} + \left[\widehat{K}, \frac{\mathbf{r}}{r}\right]\right)$  we have [344]

$$I_{K'K}^{\alpha\beta} = i\langle K' | \hat{\mathbf{r}} | K \rangle \int_{0}^{S} \left\{ [\kappa' - \kappa - 1] g_{\kappa'}^{\alpha}(r) f_{\kappa}^{\beta}(r) + [\kappa' - \kappa + 1] f_{\kappa'}^{\alpha}(r) g_{\kappa}^{\beta}(r) \right\} cr^{2} dr, \qquad (B.8)$$

with

$$\langle \kappa' \mu' | \, \hat{r} \, | \kappa \mu \rangle \equiv i^{l-l'} \int \int \chi^*_{\kappa' \mu'}(\hat{\mathbf{r}}) \, \hat{\mathbf{r}} \, \chi_{\kappa \mu}(\hat{\mathbf{r}}) d \, \hat{\mathbf{r}} \,. \tag{B.9}$$

The integral over the interstitial region is

$$\langle \Psi_{n'}^{\mathbf{k}} | c\alpha | \Psi_{n}^{\mathbf{k}} \rangle_{I} = \sum_{R'K'} \sum_{RK} C_{R'K',n'}^{*\mathbf{k}} \langle \chi_{R'K'}^{\mathbf{k}} | c\alpha | \chi_{RK}^{\mathbf{k}} \rangle_{I} C_{RK,n}^{\mathbf{k}} .$$
(B.10)

The expression (A.87) is equivalent to

$$\int_{I} X^{+} \mathrm{H}Y d^{3}r = \int_{I} (Y^{+} \mathrm{H}X)^{*} d^{3}r - \mathrm{i} \int_{S} X^{+} c\alpha \cdot \mathbf{n}Y d^{2}r \quad , \tag{B.11}$$

where **n** is the vector in the direction of the outward normal to the surface, in our case the surface is a sphere, therefore  $\mathbf{n} = \hat{r} \equiv \mathbf{r}/r$ ; H is the Dirac Hamiltonian; X and Y are the solutions of Dirac equation  $HX = W_x X$ ,  $HY = W_y Y$ , W is the total electron energy including the rest energy  $W = E + c^2/2$ . Substituting  $Y = c\alpha Z$  to (B.11) and using the relations  $[H, \alpha]_+ = 2c\mathbf{p}$ we obtain

$$(W_x + W_z) \int_I X^+ c\alpha Z d^3 r =$$
  
$$\int_I (X^+ 2\mathbf{p}c^2 Z) d^3 r + \mathbf{i} \int_S X^+ c(\alpha \hat{r}) c\alpha Z d^2 r \quad . \tag{B.12}$$

To evaluate the volume integral in the right side of the (B.12) we can use the same trick substituting to the (B.11)  $Y = 2c^2 \mathbf{p}Z$ . The final expression is

$$\left(1 + \frac{E_x + E_z}{c^2}\right)(E_x - E_z) \int_I X^+ c\alpha Z d^3 r = i(E_x - E_z) \times \\ \times \int_I (X^+(\alpha \widehat{r})\alpha Z) d^2 r + i \int_S X^+ c(\alpha \widehat{r}) 2\mathbf{p} c Z d^2 r \quad .$$
(B.13)

Let us introduce the envelope functions. In the general case, the we should consider the solution of the Helmholtz equation outside the sphere  $\nabla^2 \Psi \pm q^2 \Psi = 0$  unlike the conventional LMTO method in which the energy independent MT orbitals are the solution of the Laplace equation. In the general case, the regular and irregular envelope functions have the form [344]

$$N_{RK}(\mathbf{r}_{R},q) = \begin{pmatrix} 1\\ \frac{1}{c}\sigma\mathbf{p} \end{pmatrix} N_{Rl}(\mathbf{r}_{R},q)\chi_{\kappa\mu}(\widehat{r}_{R}) = \\ = -\left(\frac{w}{S_{R}}\right)^{1/2} \frac{(qS_{R})^{l+1}}{(2l-1)!!} \begin{pmatrix} n_{Rl}(r_{R}q)\chi_{\kappa\mu}\\ \frac{i}{c}s_{\kappa}qn_{R\lambda}(r_{R}q)\chi_{-\kappa\mu} \end{pmatrix} , \qquad (B.14)$$

$$J_{RK}(\mathbf{r}_{R},q) = \begin{pmatrix} 1\\ \frac{1}{c}\sigma\mathbf{p} \end{pmatrix} J_{Rl}(\mathbf{r}_{R},q)\chi_{\kappa\mu}(\widehat{r}_{R}) =$$
$$= \left(\frac{w}{S_{R}}\right)^{1/2} \frac{(2l-1)!!}{2(qS_{R})^{l}} \begin{pmatrix} j_{Rl}(r_{R}q)\chi_{\kappa\mu}\\ \frac{i}{c}s_{\kappa}qj_{R\lambda}(r_{R}q)\chi_{-\kappa\mu} \end{pmatrix} , \qquad (B.15)$$

where  $n_l$  and  $j_l$  are spherical Neuman and Bessel functions,  $\lambda = l - 1$  for  $\kappa > 0$  and  $\lambda = l + 1$  for  $\kappa < 0$ ;  $s_{\kappa} = \text{sign}(\kappa)$ ;  $S_R$  is the radius of the atomic sphere, centered at **R**; w is the average Wigner-Seitz radius, i.e.  $(4\pi/3)w^3$  equals to the volume of the primitive cell, divided by the number of atoms (spheres) per cell. To obtain the (B.14) and (B.15) we used expressions [1094]

$$\sigma \mathbf{p} = -i(\sigma \,\widehat{\mathbf{r}}) \left( \frac{d}{dr} + \frac{1+\widehat{\kappa}}{r} \right),$$

$$\widehat{\kappa}\chi_{\kappa\mu} = \kappa\chi_{\kappa\mu}, \ \ (\sigma \ \widehat{\mathbf{r}})\chi_{\kappa\mu} = -\chi_{-\kappa\mu}$$

and recurrent relations

$$\frac{d}{dr}f_l(qr) = -\frac{\kappa+1}{r}f_l(qr) + s_\kappa q f_l(qr), \qquad (B.16)$$

where  $f_l(qr)$  is the spherical Bessel or Neuman function.

The radial envelope relativistic functions at  $q^2 = 0$ ,

$$N_{R\kappa}(r_R) = \lim_{q^2 \to 0} N_{R\kappa}(r_R, q), \ \ J_{R\kappa}(r_R) = \lim_{q^2 \to 0} J_{R\kappa}(r_R, q)$$

and their energy derivatives

$$\dot{N}_{R\kappa}(r_R) = (d/dq^2) N_{R\kappa}(r_R, q)|_{q^2 = 0}$$

and

$$\dot{J}_{R\kappa}(r_R) = (d/dq^2) J_{R\kappa}(r_R,q)|_{q^2=0}$$

are equal to

$$N_{RK}(\mathbf{r}_R) = \left(\frac{w}{S_R}\right)^{1/2} \begin{pmatrix} (r_R/S_R)^{-l-1} \\ i\frac{-l-1+\kappa+1}{cS_R} \begin{pmatrix} r_R \\ S_R \end{pmatrix}^{-l-2} \end{pmatrix} ,$$
(B.17)

$$J_{RK}(\mathbf{r}_{R}) = \left(\frac{w}{S_{R}}\right)^{1/2} \frac{1}{2(2l+1)} \left(\frac{(r_{R}/S_{R})^{l}}{i\frac{l+\kappa+1}{cS_{R}} \left(\frac{r_{R}}{S_{R}}\right)^{l-1}}\right) ,$$
(B.18)

$$\dot{N}_{RK}(\mathbf{r}_R) = \left(\frac{w}{S_R}\right)^{1/2} \frac{S_R^2}{2(2l-1)} \left(\frac{(r_R/S_R)^{-l+1}}{i\frac{-l+1+\kappa+1}{cS_R} \left(\frac{r_R}{S_R}\right)^{-l}}\right) ,$$
(B.19)

$$\dot{J}_{RK}(\mathbf{r}_R) = -\left(\frac{w}{S_R}\right)^{1/2} \frac{S_R^2}{4(2l+1)(2l+3)} \left(\frac{(r_R/S_R)^{l+2}}{i\frac{l+2+\kappa+1}{cS_R} \left(\frac{r_R}{S_R}\right)^{l+1}}\right) .$$
(B.20)

The relativistic logarithmic derivative is  $D_{\kappa} = S_R(cf_{\kappa}/g_{\kappa}) - \kappa - 1$ . From (B.17) – (B.20) the corresponding logarithmic derivatives are equal to

$$D_{\kappa}\{N\} = -l - 1, \ D_{\kappa}\{J\} = l, \ D_{\kappa}\{\dot{N}\} = -l + 1, \ D_{\kappa}\{\dot{J}\} = l + 2.$$

The one-center expansion of the relativistic envelope function is

$$N_{RK}(\mathbf{r}_{R}, q) = N_{R'K}(\mathbf{r}_{R'}, q)\delta_{R'R} - \sum_{R'K'} J_{R'K'}(\mathbf{r}_{R'}, q)S_{R'K', RK}(q)$$
(B.21)

The integral over the interstitial region in the (B.5) can be evaluated using the common expression (B.13). In this case  $X \equiv N_{R'K'}(\mathbf{r}_{R'},q'), Z \equiv N_{RK}(\mathbf{r}_R,q), E_x \equiv q'^2, E_z \equiv q^2$ . Let us set in (B.13),  $q^2 = 0$  take the derivative with respect to q' and set  $q'^2 = 0$  afterward. Changing the sign of the unit vector,  $\mathbf{r}$ , which in Eq.(B.13) is inside of atomic sphere. As a result we obtained

$$\begin{split} &\langle \chi_{R'K'} | c\alpha | \chi_{RK} \rangle_I = -i\chi_{R'K'} (D_{l'}) \sqrt{s_{R'}/w} \times \\ &\times \Biggl\{ \Biggl( W_1 \{N, N\}_{R'K'K} + W_2 \{\dot{N}, N\}_{R'K'K} \Biggr) \delta_{R'R} - \\ &- \sum_{K''} \Biggl[ S_{R'K', RK''} \Biggl( W_1 \{J, N\}_{RK''K} + W_2 \{\dot{J}, N\}_{RK''K} \Biggr) + \\ &+ \Biggl( W_1 \{N, J\}_{R'K'K''} + W_2 \{\dot{N}, J\}_{R'K'K''} \Biggr) S_{R'K'', RK} + \end{split}$$

$$+\dot{S}_{R'K',RK''}W_{2}\{J,N\}_{RK''K}\right] + \sum_{R''K''K'''}S_{R'K',R''K''} \times \\\times \left[ \left( W_{1}\{J,J\}_{R''K''K'''} + W_{2}\{\dot{J},J\}_{R''K''K'''} \right) S_{R''K''',RK} + \\+\dot{S}_{R'K',R''K''}W_{2}\{J,J\}_{R''K''K'''}S_{R''K''',RK} \right] \right\} \chi_{RK}(D_{l})\sqrt{s_{R}/w},$$
(B.22)

 $S_{R'K',RK}$  are the structural constants;  $\dot{S}_{R'K',RK}$  is the energy derivative of structure constants:

$$\dot{S}_{R'K',RK} = \frac{d}{dq^2} S_{R'K',RK}(q)|_{q^2=0}.$$

$$W_1\{X,Z\}_{RK'K} = \int_S X^+ \left(\alpha \,\widehat{\mathbf{r}}\right) \alpha Z dS; \qquad (B.23)$$

$$W_2\{X,Z\}_{RK'K} = \int_S X^+ \left(\alpha \,\widehat{\mathbf{r}}\right) 2\mathbf{p}\mathbf{c}\mathbf{Z}dS. \tag{B.24}$$

The first "Wronskian" can be evaluated by direct substitution of the (B.23) for the solution of Dirac equation and using the relations [1094]  $(\alpha \hat{\mathbf{r}})\alpha = \hat{\mathbf{r}} + [\kappa, \hat{\mathbf{r}}]$  and  $cf_{\kappa} = (g_{\kappa}/S_R)(D_{\kappa} + \kappa + 1)$ :

$$W_{1}\{X, Z\}_{RK'K} = S_{R}^{2}g_{R\kappa'}\{X\}g_{R\kappa}\{Z\}\left((1+\kappa'-\kappa)+\frac{1}{c^{2}}\frac{1}{S_{R}^{2}}(1-\kappa'+\kappa)(D_{\kappa'}\{X\}+\kappa'+1)(D_{\kappa}\{Z\}+\kappa+1)\right)\times \times \langle K'|\hat{\mathbf{r}}|\mathbf{K}\rangle \simeq S_{R}^{2}g_{R\kappa'}\{\mathbf{X}\}g_{R\kappa}\{\mathbf{Z}\}(1+\kappa'-\kappa)\langle \mathbf{K}'|\hat{\mathbf{r}}|\mathbf{K}\rangle.$$
(B.25)

The second "Wronskian" can be evaluated using the relations [1094]

$$\left(\alpha \,\widehat{\mathbf{r}}\right)\mathbf{p} = -\mathrm{i}\tau(\sigma \,\widehat{\mathbf{r}}) \left\{\widehat{\mathbf{r}}\frac{d}{dr} + \frac{1}{r}\left(\widehat{\mathbf{r}} - \frac{1}{2}[\widehat{\mathbf{l}}^{2}, \widehat{\mathbf{r}}]\right)\right\},$$

$$\left(\alpha \,\widehat{\mathbf{r}}\right) \bigtriangledown \left(\alpha \,\widehat{\mathbf{r}}\right) = \bigtriangledown + \frac{1}{r}[\kappa, \,\widehat{\mathbf{r}}], \quad \frac{d}{dr}g_{\kappa} = S_{R}^{-1}g_{\kappa}D_{\kappa},$$
and
$$\frac{d}{dr}cf_{\kappa} = S_{R}^{-2}g_{\kappa}(\kappa - 1)(D_{\kappa} + \kappa + 1):$$

$$W_{2}\{X, Z\}_{RK'K} = 2g_{R\kappa'}\{X\}g_{R\kappa}\{Z\}\left[D_{\kappa'}\{X\}D_{\kappa}\{Z\} + 1\right]$$

$$+2D_{\kappa}\{Z\} - l(l+1) + (D_{\kappa'}\{X\} - D_{\kappa}\{Z\} + 1) \times \\ \times \left(\delta_{l',l-1}(l+1) - \delta_{l',l+1}l\right) \Big] \langle K'|\hat{\mathbf{r}}|\mathbf{K} \rangle.$$
(B.26)

Making the trivial transformations we obtain:

$$W_1\{N,N\}_{R'K'K} = wS_{R'}(1+\kappa'-\kappa)\langle K'|\hat{\mathbf{r}}|\mathbf{K}\rangle\delta_{\mathbf{R'R}},$$

$$\begin{split} W_{2}\{\dot{N},N\}_{RK'K} &= -2wS_{R'}\langle K'|\hat{\mathbf{r}}|\mathbf{K}\rangle\delta_{\mathbf{R'R}}\delta_{\mathbf{l'},\mathbf{l}+1}, \\ W_{1}\{J,N\}_{RK''K} &= wS_{R}\frac{1}{2(l''+1)}(1+\kappa''-\kappa)\langle K''|\hat{\mathbf{r}}|\mathbf{K}\rangle, \\ W_{2}\{\dot{J},N\}_{RK''K} &= wS_{R}\frac{2l+1}{2(2l+3)}\langle K''|\hat{\mathbf{r}}|\mathbf{K}\rangle\delta_{\mathbf{l''},\mathbf{l}+1}, \\ W_{1}\{N,J\}_{R'K'K''} &= wS_{R'}\frac{1}{2(l''+1)}(1+\kappa'-\kappa'')\langle K'|\hat{\mathbf{r}}|\mathbf{K}''\rangle, \\ W_{2}\{\dot{N},J\}_{R'K'K''} &= -\frac{1}{2}wS_{R'}\langle K'|\hat{\mathbf{r}}|\mathbf{K}''\rangle\delta_{\mathbf{l''},\mathbf{l''}-1}, \\ W_{2}\{J,N\}_{RK''K} &= -\frac{w}{S_{R}}(2l+1)\langle K''|\hat{\mathbf{r}}|\mathbf{K}\rangle\delta_{\mathbf{l''},\mathbf{l}+1}, \\ W_{1}\{J,J\}_{R''K''K'''} &= wS_{R''}\frac{1+\kappa''-\kappa'''}{4(2l''+1)(2l'''+1)}\langle K''|\hat{\mathbf{r}}|\mathbf{K}'''\rangle, \\ W_{2}\{J,J\}_{R''K''K'''} &= 0, \\ W_{2}\{\dot{J},J\}_{R''K''K'''} &= -\frac{wS_{R''}}{4(2l''-1)(2l'''+1)} \end{split}$$

where

$$\langle K' | \hat{\mathbf{r}} | \mathbf{K} \rangle \equiv i^{l-l'} \int \int \chi^*_{\kappa'\mu'}(\hat{\mathbf{r}}) \, \hat{\mathbf{r}} \, \chi_{\kappa\mu}(\hat{\mathbf{r}}) \, d \, \hat{\mathbf{r}} = i^{l-l'} (4\pi/3)^{1/2} \times \\ \times \sum_{m_s = \pm \frac{1}{2}} C^{l'1/2j'}_{\mu'-m_s,m_s} C^{l\mu-m_s}_{1\mu'-\mu,l'\mu'-m_s} C^{l1/2j}_{\mu-m_s,m_s}$$
(B.28)

 $\langle K^{\prime\prime}|\hat{\mathbf{r}}|\mathbf{K}^{\prime\prime\prime}\rangle\delta_{\mathbf{l}^{\prime\prime},\mathbf{l}^{\prime\prime\prime}-1}.$ 

$$C_{l'm',lm}^{l''m''} \equiv \int \int Y_{lm}^* Y_{l'm'} Y_{l''m''} d\,\widehat{\mathbf{r}} = C_{l'm-m'',lm'}^{l''m''}$$
(B.29)

Substitution of the (B.27) to the expression (B.22) and making the Bloch summation we obtain the final expression [344]

$$\left\langle \chi_{R'K'}^{\mathbf{k}} | c\alpha | \chi_{RK}^{\mathbf{k}} \rangle_{I} = -i\chi_{R'K'}(D_{l'})\sqrt{s_{R'}/w} \times \left\{ \left\langle K' | \widehat{\mathbf{r}} | \mathbf{K} \right\rangle \delta_{\mathbf{R}'\mathbf{R}} \left( 1 + \kappa' - \kappa - 2\delta_{l',l+1} \right) w \mathbf{S}_{\mathbf{R}} - \sum_{K''} \left[ S_{R'K',RK''}^{\mathbf{k}} \left( \frac{1 + \kappa'' - \kappa}{2(2l''+1)} + \frac{2l+1}{2(2l+3)} \delta_{l'',l+1} \right) \times \left\langle K'' | \widehat{\mathbf{r}} | \mathbf{K} \right\rangle w \mathbf{S}_{\mathbf{R}} + w \mathbf{S}_{\mathbf{R}'} \left\langle \mathbf{K}' | \widehat{\mathbf{r}} | \mathbf{K}'' \right\rangle \left( \frac{1 + \kappa' - \kappa''}{2(2l''+1)} - \frac{1}{2} \delta_{l',l''-1} \right) \times \left\langle S_{R'K'',RK}^{\mathbf{k}} - \dot{S}_{R'K',RK''}^{\mathbf{k}} \delta_{l'',l+1} \left\langle K'' | \widehat{\mathbf{r}} | \mathbf{K} \right\rangle (2l+1) \frac{w}{\mathbf{S}_{\mathbf{R}}} \right] + \sum_{R''} \sum_{K''} \sum_{K'''} \sum_{K'''} S_{R'K',R''K''}^{\mathbf{k}} w S_{R''} \left\langle K'' | \widehat{\mathbf{r}} | \mathbf{K}'' \rangle \times \left( \frac{1 + \kappa'' - \kappa'''}{4(2l''+1)(2l'''+1)} - \frac{\delta_{l'',l'''-1}}{2[4(l''')^{2}-1]} \right) S_{R''K''',RK}^{\mathbf{k}} \right\} \times \chi_{RK}(D_{l}) \sqrt{s_{R}/w}.$$

$$(B.30)$$

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(B.27)

# **B.2** Combined-correction term.

Using the expression (B.11) we can obtain

$$(E_x - E_z) \int_I X^+ Z d^3 r = i \int_S X^+ c(\alpha \,\widehat{\mathbf{r}}) Z d^2 r \,. \tag{B.31}$$

To obtain the combined-correction terms we have to use the relativistic envelope functions:

$$X \equiv N_{R'K'}(\mathbf{r}_{R'}, q'), \ Z \equiv N_{RK}(\mathbf{r}_R, q), \ E_x \equiv q'^2, \ E_z \equiv q^2,$$

and their one-center expansion (B.21). Let us set in (B.31)  $q^2 = 0$ , take the derivative with respect to  $q'^2$  and set  $q'^2 = 0$  afterward. Change the sign of the unit vector  $\hat{\mathbf{r}}$  which direct in (B.31) inside of atomic sphere. As a result the combined correction term is

$$\begin{split} &\langle \chi_{R'K'} | c\alpha | \chi_{RK} \rangle_{I} = -\chi_{R'K'} (D_{l'}) \sqrt{s_{R'}/w} \times \\ &\times \Biggl\{ W\{\dot{N}, N\}_{R'K'K} \delta_{R'R} - \sum_{K''} \Bigl[ S_{R'K',RK''} W\{\dot{J}, N\}_{RK''K} + \\ &+ W\{\dot{N}, J\}_{R'K'K''} S_{R'K'',RK} + \dot{S}_{R'K',RK''} W\{J, N\}_{RK''K} \Bigr] + \\ &\sum_{R''K''K'''} \Biggl[ S_{R'K',R''K''} W\{\dot{J}, J\}_{R''K''K'''} S_{R''K''',RK} + \\ &+ \dot{S}_{R'K',R''K''} W\{J, J\}_{R''K''K'''} S_{R''K''',RK} \Biggr] \Biggr\} \chi_{RK} (D_{l}) \sqrt{s_{R}/w} , \end{split}$$

$$(B.32)$$

where

$$W\{X, Z\}_{RK'K} = \int_{S} X^{+} c(\alpha \widehat{\mathbf{r}}) Z d^{2} r = S_{R} g_{R\kappa'} \{X\} g_{R\kappa} \{Z\} \times \left(D_{\kappa} \{Z\} + \kappa - D_{\kappa'} \{X\} - \kappa'\right) \langle K'|K \rangle =$$
$$= S_{R} g_{R\kappa'} \{X\} g_{R\kappa} \{Z\} \left(D_{\kappa} \{Z\} - D_{\kappa'} \{X\}\right) \delta_{K'K} .$$
(B.33)

Using the expressions for the relativistic envelope functions, their energy and logarithmic derivatives (B.17)-(B.20) we can obtain the certain Wronskians:

$$W\{\dot{N},N\}_{R'K'K} = -wS_{R'}^2 \frac{1}{2l-1}\delta_{K'K},$$

$$W\{\dot{J}, N\}_{RK''K} = wS_R^2 \frac{1}{4(2l+1)} \delta_{K''K},$$

$$W\{\dot{N}, J\}_{R'K'K''} = wS_{R'}^2 \frac{1}{4(2l'+1)} \delta_{K'K''}$$

$$W\{J,N\}_{RK''K} = -\frac{1}{2}w\delta_{K''K},$$
  

$$W\{J,J\}_{R''K''K'''} = \frac{wS_{R''}^2}{4(2l''+3)(2l''+1)^2}\delta_{K''K'''},$$
  

$$W\{J,J\}_{R''K''K'''} = 0.$$
(B.34)

Substituting the expression (B.34) to the (B.32) and making the Bloch summation we obtain the final expression for combine-correction term:

$$\begin{split} \langle \chi_{R'K'}^{\mathbf{k}} | \chi_{RK}^{\mathbf{k}} \rangle_{I} &= \chi_{R'K'}(D_{l'}) \sqrt{s_{R'}/w} \left[ \frac{wS_{R}^{2}}{2l-1} \delta_{R'R} + \right. \\ &+ \left( \frac{wS_{R'}^{2}}{4(2l'+1)} + \frac{wS_{R}^{2}}{4(2l+1)} \right) S_{R'K',RK}^{\mathbf{k}} - \frac{w}{2} \dot{S}_{R'K',RK}^{\mathbf{k}} - \\ &- \sum_{R''} \sum_{K''} S_{R'K',R''K''}^{\mathbf{k}} \frac{wS_{R''}^{2}}{4(2l''+3)(2l''+1)^{2}} S_{R''K'',RK}^{\mathbf{k}} \right] \times \\ &\times \chi_{RK}(D_{l}) \sqrt{s_{R}/w}. \end{split}$$
(B.35)

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