First principles calculations for X-ray resonant spectra and elastic properties

by

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ABSTRACT

In this thesis, we discuss applications of first principles methods to x-ray resonant spectra and elastic properties calculation. We start with brief reviews about theoretical background of first principles methods, such as density functional theory, local density approximation (LDA), LDA+U, and the linear augmented plane wave (LAPW) method to solve *Kohn – Sham* equations. After that we discuss x-ray resonant scattering (XRMS), x-ray magnetic circular dichroism (XMCD) and the branching problem in the heavy rare earths *L*-edges. In the last chapter we discuss the elastic properties of the second hardest material *AlMgB₁₄*.

CHAPTER 1. INTRODUCTION

Since the interaction of electrons is the origin of the various material properties, a detailed understanding of electronic structure is of the utmost importance for providing new insights into vital problems in solid state physics and material science, making specific predictions for real materials and designing new materials. To reach detailed knowledge about the electronic structure, a theory based on the quantum physics is required. Density functional theory and the local density approximation (LDA) provide the theoretical foundation for modern first principles quantum calculations of materials. With increasing computational power and new algorithms, these microscopic parameter-free approaches have been applied successfully to various areas and have impacted, led, stimulated, and supported the development of experimental approaches. The main topic of this thesis is the application of the linear augmented plane wave (LAPW) method which is a first principles method for the calculation of the magnetic properties and elastic properties.

In chapter 2, we will briefly discuss the basic theory - density functional theory. Since the theory itself does not offer a prescription for determination of an exact functional, an approximation which determines the density functional has to be introduced for applying the theory to practical calculations. The local density approximation (LDA) is a well tested, most widely used and very successful method for this purpose. We will discuss the LDA and its supplements such as the local spin density approximation (LSDA), generalized gradient approximation (GGA), and the LDA+U method.

In chapter 3, we will discuss practical computational methods. We will start the discussion with the augmented plane wave method (APW) which is an all-electron method. The LAPW method will be discussed as an extension of the APW method.

Chapter 4 is about resonant x-ray spectra which is a fascinating method to study magnetic properties. We will discuss selection rules, x-ray resonant magnetic scattering (XRMS) and x-ray circular dichroism (XMCD). We will show the absorption coefficient is the imaginary part of the forward scattering amplitude so that the *Kramers–Kronig* relation can relate the XMCD results with the XRMS results which are obtained with specific polarization conditions. After that, we apply the LAPW method to investigate the branching ratio (BR) problem which is one of most outstanding problems in the field of magnetic X-ray scattering. In the X-ray absorption, the L3/L2 branching ratio is about 2 which can be simply explained by the statistical ratio of the core electrons. However in XMCD (XRMS) experiments with rare earth compounds, very various numbers of BR have been observed. To understand these phenomena, models which emphasize the importance of 4f-5d orbital-orbital interactions have been suggested in the atomic calculations which can not account the solid state effects. We will discuss these models, solid state effects and show the results of first principles calculation which suggests a different origin for the variation of the branching ratio (BR) in heavy rare earths compounds. We will compare the theoretical results with experimental results which have been obtained from XRMS spectra. The LAPW method is used to obtain the well converged 5d state wave functions which are critically important for obtaining accurate x-ray spectra.

In the last chapter, we will discuss the elastic properties calculation for the second hardest material, $AlMgB_{14}$. We will start the discussion with general methods and their application to cubic, hexagonal and orthorhombic structure. While, in the x-ray spectra calculation, accurate wave functions are important, the accuracy in total energy is the key for the elastic properties calculations. After the general method is discussed, we will discuss the structure, density of states, elastic constants, and relaxation of atomic positions of $AlMgB_{14}$.

CHAPTER 2. DENSITY FUNCTIONAL THEORY

It is important to develop a valid quantum-mechanical description to understand the physical properties of materials which are governed by the behavior of very tiny, almost mass-less electrons. In this quantum-mechanical description, it is necessary to solve the *Schrödinger* equation,

$$\hat{H}\Psi = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (2.1)$$

where the interaction Hamiltonian operator (H) acts on the N -particle wave function ($\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$). For the simpler systems such as single electron atoms, it might be possible to retrieve the desired information from the exact solutions of the equation. However, it is not only impossible but also unnecessary to obtain the exact solutions for the complex real solids that have an order of 10^{23} strongly interacting particles. Thus, it is unavoidable to introduce methods to approximate and reduce the size of the many body problem.

One of the important approximations is the *Born – Oppenheimer* adiabatic approximation which separates the effects of nuclei from electronic Hamiltonian. Since the nuclei are much heavier and slower than electrons, we can consider the electrons to be in a field of stationary nuclei. In this approximation, we can write the interaction Hamiltonian as

$$H = -\left(\frac{\hbar^2}{2m}\right) \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,\mu} \frac{e^2 Z^\mu}{|\mathbf{r}_i - \tau^\mu|} \quad (2.2)$$

where m and $\mathbf{r}_i$ denotes the electron mass and coordinates, τ^μ the nuclei coordinates, while eZ^μ is the charge of constituent nuclei. In this chapter we will discuss approaches for the ground state properties of an electron system.

2.1 Hartree-Fock Approximation

Hartree proposed an approximation(1; 2; 3; 4) which was based on the independent electron model, with which the one electron *Schrödinger* equation was not too unreasonable to describe the electrons in solids. In this approximation, electron-electron interactions are replaced by interaction between a given electron and the electric field which is made by other electrons assumed smooth distribution. And the complete many electron wave function (Ψ) is described as a product of single electron wave functions ($\phi(\mathbf{r}_i)$) which are assigned to each electron *i.e.*

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N) \quad (2.3)$$

The single electron wave functions are the solutions of *Hartree* equations as

$$-\frac{\hbar^2}{2m} \nabla^2 \phi_i(\mathbf{r}) + V_C(\mathbf{r})\phi_i(\mathbf{r}) + V_i(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}) \quad (2.4)$$

where the Coulomb potential energy V_C is originated from nuclei (V_C^{ion}), other electrons (V_C^{el}) and V_i is to compensate the self-interaction. While the functions ϕ_i which represent the self-consistent solution of *Hartree* equation minimize the energy functional, they are demanded to be improved to satisfy the *Pauli* principle.

The improvement can be achieved by using ,instead of a product wave function, a determinantal wavefunction, the so-called *Slater* determinant, which makes an anti-symmetric wave function and takes into account exchange effects. Using this wave function, from *Schrödinger* equation, we can obtain the *Hartree – Fock* equation as

$$-\frac{\hbar^2}{2m} \nabla^2 \phi_i(\mathbf{r}) + V_C(\mathbf{r})\phi_i(\mathbf{r}) - \sum_j \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r})\delta_{s_i s_j} = \varepsilon_i\phi_i(\mathbf{r}) \quad (2.5)$$

The last term on the left hand side describes the exchange interaction which is applied between parallel-spin electrons.

While the *Hartree – Fock* approximation is an effective method for the atomic electronic structure calculation, it has difficulties for the application to properties calculation for solids. Since it can not treat the screening effect in the solids properly, the interactions between electrons which are widely separated are overemphasized just by the long range effect of their

Coulomb field. In fact, the X_α method, which was proposed by Slater, was motivated to make better an approximation for this problem. Another source of the difficulty with the *Hartree – Fock* method is the correlation effects. The determinant wave function can take into account only the correlation for parallel-spin electrons but not for antiparallel-spin electrons. This shortcoming can be overcome by the configuration interaction (CI) method(8; 9).

For the X_α method(5; 6; 7), Slater suggested for the averaged exchange potential to use local electron density $n(\mathbf{r})$, to obtain

$$V_{XS}(\mathbf{r}) = -6 \left(\frac{3}{8\pi} n(\mathbf{r}) \right)^{1/3} \quad (2.6)$$

and proposed to introduce a fitting parameter α for the exchange potential as

$$V_{X_\alpha}(\mathbf{r}) = \alpha V_{XS}(\mathbf{r}) \quad (2.7)$$

Dimensionless parameter α can be determined by fitting the total energy to the result of *Hartree – Fock* approximation. The exchange potential which is derived from non-interacting homogeneous electron gas can be approximated with $\alpha = 1$ and interacting homogeneous electron case can be with $\alpha = 2/3$. Since it was the only simple method to construct the exchange part of potential, the X_α method became used widely for the early electronic structure calculations.

2.2 Density Functional Theory

The success of modern electronic structure calculation is based on a fundamental and powerful concept - density functional theory(10; 11; 12; 13; 14; 15) which is a theory of correlated many body systems. The theory which was originated by Hohenberg and Kohn considers the electron density as a *basic variable* to describe many body problems. And all properties of the system can be considered to be unique functionals of the ground state density. Historically, the idea to use the electron density as the basic variable for describing the properties of matter goes back to the *Thomas – Fermi* approximation(13; 15). In the *Thomas – Fermi* method, it is assumed that the variation in the potential on the electrons is sufficiently slow so that the kinetic energy of the system is approximated as that of a homogeneous free electron

gas with density equal to the local density at any given point. Before Dirac formulated the local approximation for exchange, this method had not included the exchange and correlation among the electrons. The *Thomas – Fermi* approach is a type of density functional theory and has the attraction that it deals with one equation for the density and not the full many body *Schrödinger* equation with $3N$ degrees of freedom. However, since its solution gives only a rough description of the electron density, the *Thomas – Fermi* approximation has been considered a rather oversimplified model for quantitative predictions in real physics.

In 1964, Hohenberg and Kohn(16) published two important theorems, contributing important advances of the *Thomas – Fermi* approximation. Modern density functional theory, which is based on the HK formalism, has become one of main theoretical tools for investigating the properties of matter. The essence of density functional theory is to replace the complex many particle wavefunction by the electron density $n(\mathbf{r})$ in the ground state. The ground state electron density is given as

$$n(\mathbf{r}) = \left\langle \Psi^{GS} \left| \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right| \Psi^{GS} \right\rangle \quad (2.8)$$

where Ψ^{GS} is the ground state wavefunction. In this section we will briefly review the foundations of density functional theory, the local density approximation, and various limitations and modifications.

Hohenberg-Kohn theorems

Hohenberg-Kohn (HK) theorems have established the single particle density $n(\mathbf{r})$ as a sufficient variable for a description of the ground state. Consider a system of electrons which are influenced by external potential $v(r)$ and the mutual Coulomb repulsion. The Hamiltonian has the form $H = T + V + U$, where T is the kinetic energy operator, V is the interaction with the external field, and U is the Coulomb repulsion.

Theorem1: The Density as Basic Variable - Assuming the ground state is nondegenerate, the external potential $v(\mathbf{r})$ of an interacting electron system is a unique functional of the ground state electron density $n(\mathbf{r})$, apart from a trivial additive constant.

Since the Hamiltonian that can give the many body wavefunctions for all states is fixed by the external potential this theorem implies that all ground state properties of the system are implicitly determined by the ground state electron density $n(\mathbf{r})$.

Theorem2: Variational Principle - Define a universal functional $F[n]$ as

$$F[n(\mathbf{r})] \equiv \langle \Psi | T + U | \Psi \rangle \quad (2.9)$$

With this definition, the energy functional E_v defined as

$$E_v[n] = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + F[n] \quad (2.10)$$

assumes its minimum value for the correct $n(\mathbf{r})$ which is corresponding to the external potential $v(\mathbf{r})$ and is restricted by the condition

$$N[n] \equiv \int n(\mathbf{r}) d\mathbf{r} = N \quad (2.11)$$

This minimum energy is the ground state energy and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density.

If $F[n]$ were a known and sufficiently simple function of n the problem of determining the ground state energy and density in a given external potential would be rather easy since it requires merely the minimization of a functional of the three dimensional density function. The major part of the complexities of the many electron problems are associated with the determination of the universal functional $F[n]$. As an alternative definition of a functional, Levy and Lieb's work (LL formulation)(17; 18; 19) is worth mentioning. They considered the class of many body wave functions Ψ that have the same density $n(r)$ and define the universal functional

$$F[n] = \min_{\Psi \rightarrow n(r)} \langle \Psi | T + U | \Psi \rangle \quad (2.12)$$

where the minimum is taken over all Ψ that give the density $n(r)$. With new $F[n]$, the minimized energy functional over the class of wavefunctions with the same density $n(r)$ is given as

$$E[n] = \langle \Psi_{min}^n | T + V + U | \Psi_{min}^n \rangle \quad (2.13)$$

where Ψ_{min}^n is the wavefunction that gives rise to $n(r)$ and minimizes $F[n]$. If the ground state is nondegenerate, $\Psi_{min}^{nGS} = \Psi^{GS}$, and if the ground state is degenerate Ψ_{min}^{nGS} gives one of the many ground state wavefunctions. While the HK formalism is a *V-representability* - the functional is defined only for densities that can be generated by some external potential, the LL formalism is a *N-representability* - the functional is defined for any density $n(r)$ derivable from a wavefunction Ψ_N for N electrons. While at the minimum of the total energy at a given condition, the functional of the LL formalism must equal the functional of the HK formalism, the LL formalism is not restricted to a nondegenerate ground state which the HK formalism is restricted to. Besides, it provides an in-principle way to determine the exact functional.

Since the original work by Hohenberg and Kohn analyzed only nondegenerate nonmagnetic ground states, some extensions(15; 20; 21; 22) have been suggested for more general cases such as degenerate ground states, magnetic cases and the finite temperature case. For instance, by using a grand potential functional of trial density matrices, Mermin(22) showed that the HK argument can be applied to the system which is in thermal equilibrium and concluded that not only the energy but also the electronic entropy, specific heat *etc.* are functionals of the equilibrium density.

Kohn-Sham ansatz : Derivation of single particle equation

The concern of the Kohn and Sham (KS)(23; 24) approach is how to derive the single particle *Schrödinger* equations which can replace the difficult interacting many body problem and can be solved completely and easily. For this purpose, they used the variational principle implied by the minimal properties of the energy functional in the HK formalism. Since the HK formalism does not provide a guidance as to the form of $E[n]$, some kind of approximations are necessary to apply the density functional theory to the investigation of physical systems. The key idea in the KS approach is separating the known physical quantities which can be expressed exactly from the others which have to be guessed or approximated. One then incorporates the latter terms into a exchange-correlation functional of the density. With separating the classical Coulomb energy from the universal functional $F[n]$, the ground state energy of an interacting

inhomogeneous electron gas can be written as

$$E[n] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + G[n] \quad (2.14)$$

where $n(\mathbf{r})$ is the density and $G[n]$ is a universal functional of the density. This expression is a minimum for the correct density $n(\mathbf{r})$. Here the exchange and correlation energy (E_{XC}) of an interacting system is introduced through separating the universal functional $G[n]$ into two parts

$$G[n] \equiv T_S[n] + E_{XC}[n] \quad (2.15)$$

where $T_S[n]$ is the kinetic energy of a system of noninteracting electrons with density $n(\mathbf{r})$ and $E_{XC}[n]$ is the exchange and correlation energy of an interacting system with density $n(\mathbf{r})$. At this point, KS assume that it is possible to choose the exactly soluble non-interacting system which has the same ground state density of the original interacting system. The stationary condition of the energy functional with a constraint

$$\int \delta n(\mathbf{r})d\mathbf{r} = 0 \quad (2.16)$$

leads to

$$\int \delta n(\mathbf{r}) \left(\phi(\mathbf{r}) + \frac{\delta T_S[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} \right) d\mathbf{r} = 0; \quad (2.17)$$

where

$$\phi(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2.18)$$

The single particle density

$$n(r) = \sum_{i=1}^N |\psi_i(r)|^2 \quad (2.19)$$

can be obtained from single particle *Schrödinger* equations to be solved self-consistently

$$\left(-\frac{1}{2} \nabla^2 + [\phi(r) + v_{XC}(r)] \right) \psi_i(r) = \varepsilon_i \psi_i(r) \quad (2.20)$$

where

$$v_{XC}(r) = \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} \quad (2.21)$$

It can be interpreted as the equation describing non-interacting electrons moving in the effective potential $V_{eff}(r)$ which is given by

$$V_{eff}(r) = v(r) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{XC}(r) \quad (2.22)$$

The ground state total energy is given by

$$E_{TOT} = \sum_i \varepsilon_i - \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - \int n(\mathbf{r})v_{XC}(\mathbf{r})d\mathbf{r} + E_{xc}[n] \quad (2.23)$$

The physical meaning of the eigenvalues ε_i which are introduced into the Kohn-Sham equation as Lagrange parameters is controversial and since there are some cases which are problematic to interpret the eigenvalues as excitation energies, the interpretation has to be done with caution. In fact, there is no rigorous justification to interpret eigenvalues as excitation energies or the wavefunctions as physical electron wavefunctions. Only their sum has significance as a part of expression for the ground state energy. And the so called *Slater – Janak* theorem(25) rigorously proves that the eigenvalue of the highest occupied *Kohn – Sham* orbital is precisely the chemical potential(26) or minus the ionization energy(12; 27; 28). However in many cases it has been successful to interpret excitation spectra with the eigenvalues and to understand the excited state properties of a system under consideration.

Local density approximation (LDA)

In principle, the density functional formalism can reproduce all ground states properties of any system with any accuracy if the exact exchange-correlation E_{XC} is given. However since the formalism to construct this functional (or the functional itself), which includes all many body effects has not been found, the utility of density functional theory depends on the discovery of sufficiently accurate approximations. The well tested, most widely used and very successful approximation is the local density approximation (LDA) which uses a functional depending only locally on the density for E_{XC} . The first method which used the local density for the exchange potential was the X_α method which Slater proposed. In this method, Slater simplified the non-local exchange energy in terms of the local $n(\mathbf{r})^{1/3}$ potential.

In a weakly inhomogeneous case, where $n(\mathbf{r})$ is sufficiently slowly varying, Kohn and Sham proposed that the $E_{xc}[n]$ can be written as

$$E_{xc}[n] = \int n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r})] d\mathbf{r} \quad (2.24)$$

where $\varepsilon_{xc}(n)$ is the exchange and correlation energy per electron of a uniform electron gas of density n . The exchange and correlation energy of a uniform electron gas have been calculated by several approaches such as many body perturbation theory(29), and the quantum Monte Carlo method(30).

Among a number of expressions for the exchange-correlation energy and potential, the most frequently employed parametrizations are those of Hedin and Lundqvist(29), von Barth and Hedin(20), Janak(31), Perdew and Zunger(32), Vosoko, Wilk and Nusair(33) and Perdew and Wang(34). Since neither DFT nor LDA contains any fitting parameters, it is impossible to analyze the accuracy of different approximations theoretically. Thus, the application of any approximation to the exchange-correlation potential in the real system is most frequently validated by an agreement between the calculation and experimental data.

Local spin density approximation (LSDA)

In the HK, KS approach, the external potential is considered as a local, scalar and non-relativistic one and the wavefunction for the system of particles is spinless, one component and non-degenerate in the ground state. There are a number of studies to generalize these limitations. Spin density functional theory is a generalization for describing magnetic properties. In order to describe magnetic effects, the electron density ($n(\mathbf{r})$) in DFT has to be replaced by the electron density ($n(\mathbf{r})$) plus the magnetization density ($\mathbf{m}(\mathbf{r})$) as fundamental variables. This leads to an energy functional

$$E = E_{HK}[n, \mathbf{m}] \quad (2.25)$$

The formalism can be also represented using a four component density matrix $\rho_{\alpha\beta}(\mathbf{r})$ instead of $n(\mathbf{r})$ and $\mathbf{m}(\mathbf{r})$. With introducing two component *Pauli* wavefunctions and corresponding

electron and magnetic density ;

$$\psi_i(\mathbf{r}) = \begin{pmatrix} \psi_{1,i}(\mathbf{r}) \\ \psi_{2,i}(\mathbf{r}) \end{pmatrix} \quad (2.26)$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \quad (2.27)$$

$$\mathbf{m}(\mathbf{r}) = \sum_{i=1}^N \psi_i^*(\mathbf{r}) \boldsymbol{\sigma} \psi_i(\mathbf{r}) \quad (2.28)$$

the variational principle generates single particle *Schrödinger – Pauli* equations.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r}) + \boldsymbol{\sigma} \cdot \mathbf{B}_{eff}(\mathbf{r}) \right] \psi_{\sigma,i}(\mathbf{r}) = \varepsilon_{\sigma,i} \psi_{\sigma,i}(\mathbf{r}) \quad (2.29)$$

where the effective magnetic field $\mathbf{B}_{eff}(\mathbf{r})$ is given as

$$\mathbf{B}_{eff}(\mathbf{r}) = \mathbf{B}_{xc}(\mathbf{r}) + \mathbf{B}_{ext}(\mathbf{r}) \quad (2.30)$$

$$\mathbf{B}_{xc}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r}), \mathbf{m}(\mathbf{r})]}{\delta \mathbf{m}(\mathbf{r})} \quad (2.31)$$

In this case, the LDA also has to be generalized to LSDA for constructing a spin dependent exchange correlation energy. The exchange correlation energy is approximated locally as the exchange correlation energy of a uniform interacting electron gas which has the same electron and magnetization density :

$$E_{XC}^{LSDA}[n(\mathbf{r}), m(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r}), m(\mathbf{r})) d\mathbf{r} \quad (2.32)$$

In the cases of collinear magnetism, the single particle equations can be diagonalized by choosing the z – *axis* as the magnetic moment direction and two spin components are completely decoupled. By solving these decoupled equations separately, spin dependent observables can be obtained.

The formalism can be extended to the fully relativistic case by constructing single-particle equations based on the *Dirac* equation instead of the *Schrödinger – Pauli* equations. The relativistic case will be discussed in a later chapter.

Extensions & modifications of L(S)DA

L(S)DA has been successful in describing the ground state properties of a large range of physical systems. Even for the excited state properties, in a lot of cases it can be successfully applied. It has become a valuable tool of first principles calculations in solid-state physics and has contributed significantly to the understanding of material properties. However, as an approximation, L(S)DA is not successful for all systems although the exact DFT should be capable of obtaining ground state properties. There are some systematic errors which have been observed when using the L(S)DA. It overestimates cohesive energies (bonding) for almost all elemental solids and underestimates the lattice parameters in many cases. It also underestimates the band-gaps in semiconductors and insulators. It fails to describe the properties of highly correlated systems, such as Mott insulators and certain f -band materials. There have been several modifications of LSDA to circumvent these difficulties such as the generalized gradient approximation (GGA)(35; 36; 37; 38), the self interaction correction (SIC)(15; 39), the GW approximation(40; 41) and the LDA+U approach(10; 45; 46; 47; 48). In this section, we will briefly touch on just two cases - GGA and LDA+U.

Generalized gradient approximation (GGA)

For the L(S)DA formalism, Kohn-Sham assumed a sufficiently slowly varying charge density. Therefore, it is expected that the formalism has to be modified for the case which the charge density has a large gradient. The gradient expansion approximation (GEA) was suggested for systematic correction for this limitation and included the gradient terms of the charge density. However it did not lead to a consistent improvement in the L(S)DA result. In some cases it is worse than the L(S)DA and it does violate some conditions such as *sum - rules*(49; 50).

The GGA also includes gradient terms in the exchange correlation energy. However, in this case, the function has been designed to modify the behavior at large gradients for preserving certain constraints. The GGA exchange correlation functional(37; 38) is given as

$$E_{XC}^{GGA}[n^\uparrow, n^\downarrow] = \int n(\mathbf{r}) \varepsilon_{xc}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow, \dots) d\mathbf{r}$$

$$= \int n(\mathbf{r}) \varepsilon_{xc}^{hom}(r_s) F_{xc}(r_s, \zeta, s) d\mathbf{r} \quad (2.33)$$

where $\varepsilon_{xc}^{hom}(r_s)$ is the exchange energy per particle of the unpolarized uniform electron gas and $F_{xc}(r_s, \zeta, s)$ is called the *enhancement factor* which depends on the density parameter r_s

$$r_s = \left(\frac{3}{4\pi n} \right)^{1/3} \quad (2.34)$$

the local relative spin polarization $\zeta = \zeta(\mathbf{r})$,

$$\zeta(\mathbf{r}) = \frac{n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r})}{n(\mathbf{r})} \quad (2.35)$$

and the local inhomogeneity parameter, $s = s(\mathbf{r})$, or reduced density gradient,

$$s(\mathbf{r}) = \frac{|\nabla n|}{2k_F n} = \frac{3}{(18\pi)^{1/3}} |\nabla r_s| \quad (2.36)$$

Since the construction of the GGA is not unique, it has to be justified by comparison of the calculated results for real systems with experimental data.

L(S)DA + U

The L(S)DA+U method has been suggested to solve the deficiency which L(S)DA has in calculations involving strongly correlated materials. The L(S)DA method has difficulty to describe the localization of charge and spin of the correlated electrons properly. This difficulty originates from strongly correlated systems, where the Coulomb correlations inside atoms are strong as was pointed out by Hubbard (Hubbard U (42; 43; 44)) and is responsible for the localization of electrons and magnetism. On the other hand the L(S)DA functional originated from the homogeneous electron gas and the spin dependence has its origin in the exchange. As a possible approach, Anisimov *et al.* (45; 47) suggested to add a Hubbard like U -potential, an orbital dependent correction, that approximately accounts for strong electron correlations in localized $d(f)$ shells to the LDA potential.

The main idea of the L(S)DA+U method is to separate the electrons into two subsystems: localized $d(f)$ electrons for which the Coulomb $d-d(f-f)$ repulsion should be taken into account by a term $\frac{1}{2}U \sum_{i \neq j} n_i n_j$ (n_i are $d(f)$ -orbital occupancies) as in a mean field (Hartree-Fock) approximation, and delocalized s, p electrons which could be described by using an orbital

independent one-electron potential (LDA). For an open system with a fluctuating number of $d(f)$ electrons, the correct formula for Coulomb energy $d - d(f - f)$ interactions as a function of the $d(f)$ electrons N is $E = UN(N - 1)/2$. With this correction term and a Hubbard-like term, the new energy functional is given as

$$E = E^{LDA} - UN(N - 1)/2 + \frac{1}{2}U \sum_{i \neq j} n_i n_j \quad (2.37)$$

The orbital energies ε_i are

$$\varepsilon_i = \frac{\partial E}{\partial n_i} = \varepsilon^{LDA} + U\left(\frac{1}{2} - n_i\right) \quad (2.38)$$

and orbital dependent potential is

$$V_i(\mathbf{r}) = \frac{\delta E}{\delta n_i(\mathbf{r})} = V^{LDA}(\mathbf{r}) + U\left(\frac{1}{2} - n_i\right) \quad (2.39)$$

where n_i is the orbital occupation. This simple formula shifts the LDA orbital energy by $-U/2$ for occupied orbitals ($n_i = 1$) and by $+U/2$ for unoccupied orbitals ($n_i = 0$). And the discontinuous behavior is restored in the potential which is a characteristic that LDA has lost from the exact DFT(51). In its most generalized form, the L(S)DA+U functional is defined as

$$E^{L(S)DA+U}[\rho^\sigma(\mathbf{r}), \{n^\sigma\}] = E^{L(S)DA}[\rho^\sigma(\mathbf{r})] + E^{DC}[\{n^\sigma\}] - E^U[\{n^\sigma\}] \quad (2.40)$$

where $E^{L(S)DA}$ is the L(S)DA energy functional, E^U is the electron-electron interaction energy of the localized electron, E^{DC} is the double counting term, $\rho^\sigma(\mathbf{r})$ is the charge density for spin σ electrons and $\{n^\sigma\}$ is the occupation matrix. The electron-electron interaction energy E^U is determined by

$$\begin{aligned} E^U[\{n\}] = & \frac{1}{2} \sum_{\{m\}, \sigma, \sigma'} (n_{\sigma m_1, \sigma m_2} U_{m_1 m_2 m_3 m_4} n_{\sigma' m_3, \sigma' m_4} \\ & - n_{\sigma m_1, \sigma' m_2} U_{m_1 m_4 m_3 m_2} n_{\sigma' m_3, \sigma m_4}) \end{aligned} \quad (2.41)$$

where $U_{m_1 m_2 m_3 m_4}$ are the matrix elements of the on-site Coulomb interaction. The on-site Coulomb interaction can be determined from LSDA calculation and given, with screened Slater integrals F^k , as

$$U_{m_1 m_2 m_3 m_4} = \sum_{k=0}^{2l} a_{m_1 m_2 m_3 m_4}^k F^k \quad (2.42)$$

where the $a_{m_1 m_2 m_3 m_4}^k$ are given as

$$a_{m_1 m_2 m_3 m_4}^k = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle l m_1 | Y_{kq} | l m_2 \rangle \langle l m_3 | Y_{kq}^* | l m_4 \rangle \quad (2.43)$$

The matrix elements $U_{mm'm'}$ and $U_{mm'm}$ can be identified as pair Coulomb and exchange integrals

$$U_{mm'm'} = U_{mm'}, \quad U_{mm'm} = J_{mm'}. \quad (2.44)$$

If parameters U and J are set to be the average of the matrices $U_{mm'}$ and $U_{mm'} - J_{mm'}$ over all possible pairs of m, m' ,

$$U = \frac{1}{(2l+1)^2} \sum_{mm'} U_{mm'} \quad (2.45)$$

$$U - J = \frac{1}{2l(2l+1)} \sum_{mm', m \neq m'} U_{mm'} - J_{mm'} \quad (2.46)$$

the double counting term $E^{DC}[\{n^\sigma\}]$ can be expressed

$$E^{DC}[\{n^\sigma\}] = \frac{1}{2} U N(N-1) - \frac{1}{2} J [N^\uparrow(N^\uparrow - 1) + N^\downarrow(N^\downarrow - 1)] \quad (2.47)$$

While it is an expression for LSDA, using $N^\uparrow = N^\downarrow = \frac{N}{2}$, it is possible to obtain the expression for LDA

$$E^{DC}[\{n^\sigma\}] = \frac{1}{2} U N(N-1) - \frac{1}{4} J N(N-2) \quad (2.48)$$

By using the above expressions for E^U, E^{DC} , the energy functional is

$$\begin{aligned} E^{L(S)DA+U}[\rho^\sigma(\mathbf{r}), \{n^\sigma\}] &= E^{L(S)DA}[\rho^\sigma(\mathbf{r})] \\ &+ \frac{1}{2} U N(N-1) - \frac{1}{2} J [N^\uparrow(N^\uparrow - 1) + N^\downarrow(N^\downarrow - 1)] \\ &+ \frac{1}{2} \sum_{m, m', \sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} \\ &+ \frac{1}{2} \sum_{m \neq m', \sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma} \end{aligned} \quad (2.49)$$

In principle, the screened Coulomb U and exchange J integrals can be determined from supercell L(S)DA calculation using Slater's transition state technique or from constrained L(S)DA calculations. Alternatively, it is possible for these parameters to be estimated from experiments such as photoemission and inverse-photoemission. The LDA+U approach will be used later in the thesis to treat the electronic structure of the 4f states in the heavy rare earth metals.

CHAPTER 3. COMPUTATIONAL METHOD - LAPW

In the previous chapter, we discussed how the difficulty of many body problems can be circumvented through density functional theory and obtained, with the *LDA*, the *Kohn – Sham* equations which are the single particle *Schrödinger* equations. In this Chapter, we will discuss solving the *Kohn – Sham* equations and as their application, we discuss a practical computation method - the LAPW which is an accurate but computationally demanding method.

3.1 Solving The Kohn-Sham Equations

In most computational approaches that have been proposed for solids, the first step for solving problems is the construction of a basis set to represent the wave functions

$$\psi(\mathbf{r}) = \sum C_i \phi_i(\mathbf{r}) \quad (3.1)$$

where the $\phi_i(\mathbf{r})$ are the basis functions and the C_i are expansion coefficients. With a given basis, the Hamiltonian (H) and overlap matrices (O) are constructed and yield the eigenvalue equations

$$\sum_i (H_{ij} - EO_{ij})C_j = 0, j = 1, 2, \dots, N \quad (3.2)$$

where N is the number of basis functions and

$$H_{ij} = \int \phi_i^*(\vec{r}) \mathbf{H} \phi_j(\vec{r}) d\vec{r} \quad (3.3)$$

$$O_{ij} = \int \phi_i^*(\vec{r}) \phi_j(\vec{r}) d\vec{r} \quad (3.4)$$

These secular equations are solved at each $\mathbf{k}$ -point in the irreducible wedge of the Brillouin zone. The function $E(\mathbf{k})$ is defined by secular determinant zeros

$$\det |H_{ij}(k) - E(k)O_{ij}(k)| = 0 \quad (3.5)$$

In principle, an infinite number of basis functions have to be used to construct exact wave functions. However in practice, one works with a limited number of basis functions and with such a limited basis, one could try to find a basis set that can generate a function that is “close” to the ψ_i . The larger number of basis functions gives the better approximation of the eigenfunction, but is more time-consuming for the diagonalization of the matrix equation. Thus, the number of basis functions should be chosen to achieve a given level of convergency. In fact, an important step for computational condensed matter physics is to find a basis set that is simultaneously efficient and unbiased. Computations using different band theory methods differ only in the selection of the basis functions ϕ_i and can usually be derived from the same variational functional. Thus the choice of a particular method is often governed by the desired convergence, the convergence stability, and the rate of convergence.

3.2 Augmented Plane Wave Method (APW)

Since the electron wave functions are varying very quickly near the core, the methods which use plan-waves basis functions have difficulty to construct accurate wave functions near the core. The APW method(52; 53) was suggested to solve this difficulty by using atomic-like radial wave functions as a part of basis functions. This approach divides space into non-overlapped atom centered spheres, the so-called muffin-tins and the remaining interstitial region and uses different potentials and basis functions in each region. In the muffin-tins, a spherically symmetric potential is assumed and the radial solutions of *Schrödinger* equation of this potential are used as the basis functions. In the interstitial region, a constant potential is assumed and plane waves which are solutions of *Schrödinger* equation with constant potential are used as the basis functions. Thus the single particle wavefunctions can be represented in terms of the following basis functions:

$$\phi(\mathbf{r}) = \begin{cases} \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & \text{interstitial region} \\ \sum_{lm} A_{lm} u_l(r) Y_{lm}(\hat{\mathbf{r}}) & \text{muffin-tin region} \end{cases} \quad (3.6)$$

where ϕ is a wavefunction, Ω is the cell volume, $\mathbf{G}$ is a reciprocal lattice vector, $C_{\mathbf{G}}$ and A_{lm} are expansion coefficients. u_l is the regular solution of

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} l(l+1) + V(r) - E_l \right\} r u_l(r) = 0 \quad (3.7)$$

where E_l is an energy parameter and $V(r)$ is the spherical component of the potential. The constraint which requires the continuous wave function is done by defining the A_{lm} in terms of the $C_{\mathbf{G}}$ as

$$A_{lm} = \frac{4\pi i^l}{\Omega^{1/2} u_l(R)} \sum_{\mathbf{G}} C_{\mathbf{G}} j_l(|\mathbf{k} + \mathbf{g}| R) Y_{lm}^*(\mathbf{k} + \mathbf{G}) \quad (3.8)$$

where the origin is taken at the center of the sphere and R is the sphere radius.

With a fixed parameter E_l , APWs can be used as a basis and lead to a standard secular equation for the band energies and wave functions. Unfortunately, if the E_l are kept fixed, the APWs which are solution of *Schrödinger* equation only at the energy E_l can not offer enough variational freedom so that E_l must be set equal to the band energy to achieve an accurate description. Thus the energy band cannot be obtained from a single diagonalization. Since the radial function u_l depends on the band energy, the solution of the secular equation becomes a nonlinear problem which requires much more demanding computational procedure.

A further difficulty of the APW method is that since, with the general crystal potential, the optimum variational choice of E_l is no longer given by band energy, it is difficult to extend APW method for the general potential case. Another difficulty is the so-called “asymptote problem”. Since $u_l(R)$ appears in the denominator of the matching coefficient, A_{lm} , the plane waves and radial functions are decoupled at the energy parameter E_l for which u_l vanishes on the sphere boundary. The asymptote problem leads to numerical difficulties with the bands near an asymptote energy.

3.3 Linear Augmented Plane Wave Method (LAPW)

There were several proposed modifications of the APW method(54; 56). The basic idea of the modifications of the APW method is to improve the APWs basis to offer enough variational freedom so that it is not necessary to set the energy parameter E_l equal to the band energy. The

LAPW method originated from Anderson's suggestion(55) uses not only the radial solution of the *Schrödinger* equation but also its derivative with respect to the energy. The first numerical code which implemented LAPW method(56) was by Koelling and Arbman. The LAPW method solved APW problems successfully and became a flexible and accurate band structure method(57; 58; 59).

While the basis functions which the LAPW method is using in the interstitial region are same as the APW's, the basis functions inside the spheres are linear combinations of radial functions $u_l(r)$ and their energy derivatives. Using these basis functions, the wave functions are

$$\phi(\mathbf{r}) = \begin{cases} \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & \text{interstitial region} \\ \sum_{lm} [A_{lm} u_l(r) + B_{lm} \dot{u}_l(r)] Y_{lm}(\hat{\mathbf{r}}) & \text{muffin-tin region} \end{cases} \quad (3.9)$$

where the B_{lm} are coefficients for the energy derivative, analogous to the A_{lm} . The radial wave function $u_l(r)$ is given as same as the APW's and the energy derivative, $\dot{u}_l(r)$ satisfies

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} l(l+1) + V(r) - E_l \right\} r \dot{u}_l(r) = r u_l(r) \quad (3.10)$$

When the energy parameter E_l differs slightly from the real band energy ϵ , LAPWs can reproduce radial wave function constructed at the band energy with ignorable error, while APWs fail. The radial wave function can be expanded into

$$u_l(\epsilon, r) = u_l(E_l, r) + (\epsilon - E_l) \dot{u}_l(r) + O((\epsilon - E_l)^2) \quad (3.11)$$

where $O((\epsilon - E_l)^2)$ denotes error that are quadratic in this energy difference. The LAPW method introduces errors of order $(\epsilon - E_l)^2$ in wave functions; This yields errors of order $(\epsilon - E_l)^4$ in the band energy. Since the errors are high order, the linearization works very well over a rather broad energy range so that it is often possible to treat all valence bands with a single energy parameter E_l . The LAPW method gives accurate energy bands (at a given k-point) with a single diagonalization, while, in the APW method, at least one diagonalization is needed for each band.

Since usually if $u_l(r) = 0$ both its radial derivative and $\dot{u}_l(r)$ will not be zero, the LAPW method does not have the asymptote problem. And the flexibility of LAPWs inside the spheres

allows extension of the method for non-spherical potentials inside the spheres. However the requirement that the basis functions have continuous derivatives demands higher planewave cutoffs to achieve a given level of convergence.

3.4 Scalar Relativistic Approximation

Relativistic effects are more important in heavier elements and compounds so that the effects have to be included in the theoretical calculation. For this calculation, the band structure problem with the four-component formalism of the *Dirac* equation has to be set up and solved numerically. The *Kohn – Sham* equation has the form of a single particle *Dirac* equation

$$\left\{ c\boldsymbol{\alpha}(\boldsymbol{\sigma}) \cdot \mathbf{p} + [\beta(\sigma) - 1]mc^2 + V^{eff}(\mathbf{r}) \right\} \Psi = E\Psi \quad (3.12)$$

where $\boldsymbol{\sigma}$ is the vector of *Pauli* matrices, $\mathbf{p}$ is the momentum operator and V^{eff} is effective potential. Ψ is the relativistic four component wave function. Since the calculations which deal with these four component Ψ with high accuracy are computationally demanding, even working with modern computers it is reasonable to introduce some kind approximation for more efficiency.

The scalar-relativistic approximation(61) solves the *Dirac* equation which by dropping the spin-orbit interaction allows all other relativistic kinetic effects to be included. In the case that spin-orbit interaction is important, the spin-orbit effect can be included by a perturbation method. Solution of the *Dirac* equation inside the muffin tin sphere is of the form

$$\Psi = \Psi_{\kappa\mu} = \begin{bmatrix} g_{\kappa}(r)\chi_{\kappa\mu} \\ -if_{\kappa}(r)\sigma_r\chi_{\kappa\mu} \end{bmatrix} \quad (3.13)$$

where f_{κ} and g_{κ} satisfy the following radial equations:

$$\frac{\partial f_{\kappa}(r)}{\partial r} = \frac{1}{c}(V - E)g_{\kappa}(r) + \left(\frac{\kappa - 1}{r}\right) f_{\kappa}(r) \quad (3.14)$$

$$\frac{\partial g_{\kappa}(r)}{\partial r} = -\frac{(\kappa + 1)}{r}g_{\kappa}(r) + 2Mc f_{\kappa}(r) \quad (3.15)$$

and

$$M \equiv m + \frac{1}{2c^2}(E - V(r)) \quad (3.16)$$

In these equations κ is the relativistic quantum number and $\chi_{\kappa\mu}$ is two-component spinor. From these equations, we can obtain

$$\begin{aligned} & -\frac{1}{2M} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dg_{\kappa}}{dr} \right) + \left[V + \frac{1}{2M} \frac{l(l+1)}{r^2} \right] g_{\kappa} \\ & - \frac{1}{4M^2 c^2} \frac{dV}{dr} \frac{dg_{\kappa}}{dr} - \frac{1}{4M^2 c^2} \frac{dV}{dr} \frac{(1+\kappa)}{r} g_{\kappa} = E g_{\kappa} \end{aligned} \quad (3.17)$$

The formal mass term M is called the *mass – velocity* term, the term $(dV/dr)/(dg/dr)$ is the *Darwin*-term and the last term of the left-hand side is the *spin – orbit coupling* term which depends on the sign of κ . Defining a new function ϕ_{κ} by

$$\phi_{\kappa} \equiv \frac{1}{2Mc} \frac{dg_{\kappa}}{dr} \quad (3.18)$$

and dropping the last term which causes coupling of spin up and spin down contributions, we obtain

$$\frac{d\phi_l}{dr} = -\frac{2}{r} \phi_l + \left[\frac{l(l+1)}{2Mc r^2} + \frac{1}{c} (V - E) \right] g_l \quad (3.19)$$

where the κ index has been replaced by l since there is no longer any j dependence. Now, the solution of the *Dirac* equation is rewritten with the usual *lms* quantum numbers as

$$\Psi_{lms} = \begin{bmatrix} g_l Y_{lm} \chi_s \\ \frac{i}{2Mc} \sigma_r \left(-\frac{dg_l}{dr} + \frac{1}{r} \sigma \cdot \mathbf{L} \right) Y_{lm} \chi_s \end{bmatrix} \quad (3.20)$$

After the functions g_l and ϕ_l are replaced by new functions which are defined as

$$P_l = r g_l \quad (3.21)$$

$$Q_l = r c \phi_l \quad (3.22)$$

the scalar relativistic equations may be written as

$$\frac{dP_l(r)}{dr} = 2MQ(r) + \frac{1}{r} P_l(r) \quad (3.23)$$

$$\frac{dQ_l(r)}{dr} = -\frac{1}{r} Q_l + \left[\frac{l(l+1)}{2Mr^2} + (V - E) \right] P_l \quad (3.24)$$

These can be solved numerically in the same way as for the non-relativistic *Schrödinger* equation.

CHAPTER 4. X-RAY RESONANT SPECTRA

With the new generation of photon sources, x-ray measurement techniques such as x-ray resonant magnetic scattering (XRMS)(62; 63; 64; 65; 66; 67; 68; 69; 70; 71) and x-ray magnetic circular dichroism (XMCD)(62; 72; 73; 74) have become powerful tools to investigate magnetic systems. While, for absorption, a core electron is promoted into an unoccupied state above the Fermi level (Fig.4.1), in resonant scattering, the promoted electron recombines with the core hole (Fig.4.2). Since the absorption (resonant scattering) involves transitions from well understood core levels, the spectra can yield information about the spin polarization and spin-orbit coupling of final (intermediate) states. Furthermore the information obtained is element and orbital specific since the technique requires scanning through specific absorption edges such as the *K*-edge, *L*-edge, *M*-edge. Element specificity is one of the advantages for using energy tunable x-rays since most conventional techniques (laser based) used for the study of magnetic materials measure the total optical response which contains contributions from the various magnetic elements for complex materials.

In this chapter, we will discuss basic concepts and formulas of XRMS and XMCD. After that we will describe the theoretical results of L_3, L_2 edge spectra for heavy rare earths.

4.1 Selection Rules

Selection rules are the relations between quantum numbers of initial and final (intermediate) states, which permit the transition matrix elements not to be zero in the transition process. If we have the transition matrix element formula we may infer them easily. However, since it is very convenient to derive the transition matrix formula with these rules we start this chapter with the selection rules. In x-ray spectra, the selection rules have two independent

Figure 4.1 Resonant absorption at the L_3 edge of a rare earth element. A core electron which absorbs an incoming photon excites to an empty conduction band which satisfies selection rules and leaves a hole in the core state.

Figure 4.2 Resonant scattering at the L_3 edge of a rare earth element. In this case, the excited electron recombines with the core hole.

sources - one is a conservation principle and another is the geometrical relationship between the polarization of photon and the direction of magnetic moment. While the selection rules which originate from conservation laws restrain the transition itself, geometrical relationships restrict the observation of the scattering intensity.

The most important principle behind the selection rules in x-ray spectra is the conservation of angular momentum. The allowed change of the angular momentum of the electron which participates in the transition depends on the helicity of photon which is absorbed (emitted) in the process. The angular momentum carried by the photon is determined by its polarity, which is $+1$ (-1) for the right (left) circular polarized photon. Therefore, an electron which absorbs a right (left) circular polarized photon which propagates parallel to the magnetic field direction is able to excite only if there are available empty states that have one increased (decreased) total angular momentum quantum number. Because the number of available empty states depends on the quantum states - m_l is the important quantum number, the transition probability depends on the photon's polarity (See Fig.4.3). If the total angular momentum of the initial (final) state is $J(J')$ and the photon angular momentum is σ , it is possible to present their relation with the vector sum.

$$\mathbf{J}' = \mathbf{J} + \sigma \quad (4.1)$$

which gives a selection rule

$$\Delta j = j' - j = 0, \pm 1 \quad (4.2)$$

Since it can not satisfy the triangular rule of vector sum, the transition, $j' = j = 0$, is not allowed. If the orbital and spin angular momenta are good quantum numbers, there are additional selection rules - orbital, spin momentum selection rules. If we can ignore the relativistic spin flip term, the quantum number for spin should be conserved. It can be expressed as a selection rule,

$$\Delta s = 0. \quad (4.3)$$

Figure 4.3 A transition diagram in which electronic states are simplified to emphasize the role of the photon polarity in transition without spin consideration. The empty state which fulfills the selection rules is required for the electron transition. From Ref.(62)

With the relation between $\mathbf{J}$, $\mathbf{L}$, $\mathbf{S}$

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (4.4)$$

we can write the selection rule for orbital momentum as

$$\Delta l = \Delta j = 0, \pm 1 \quad (4.5)$$

However the transition with $\Delta l = 0$ is restricted by the parity argument(75). It is possible to define the selection rules as

1. **Total angular momentum** $(j, m_j) : \Delta j = 0, \pm 1, \Delta m_j = 0, \pm 1$
2. **Spin angular momentum** $(s, m_s) : \Delta s = 0, \Delta m_s = 0$
3. **Orbital angular momentum** $(l, m_l) : \Delta l = \pm 1, \Delta m_l = 0, \pm 1$

While the charge scattering conserves the photon polarization, the magnetic scattering causes a change in the polarization of scattered photon. This property that is combined with the sensitivity of scattering geometry has been used to separate magnetic signals from charge signals. Fig.4.4 shows a conventional coordinate system(69; 76) for XRMS. In this coordinate system, the relevant vectors can be written as :

$$\mathbf{k} = k \begin{pmatrix} \cos \theta \\ 0 \\ -\sin \theta \end{pmatrix} \quad (4.6)$$

$$\mathbf{k}' = k \begin{pmatrix} \cos \theta \\ 0 \\ \sin \theta \end{pmatrix} \quad (4.7)$$

$$\hat{\varepsilon} = \varepsilon_\sigma \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix} + \varepsilon_\pi \begin{pmatrix} -\sin \theta \\ 0 \\ -\cos \theta \end{pmatrix} \quad (4.8)$$

Figure 4.4 Scattering geometry used for the resonant scattering amplitude after Ref.(69). $\mathbf{e}_2$ is perpendicular to the scattering plane, which contains the vectors $\mathbf{k}$, $\mathbf{k}'$, $\mathbf{e}_1$, and $\mathbf{e}_3$.

$$\hat{\varepsilon}' = \varepsilon'_\sigma \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix} + \varepsilon'_\pi \begin{pmatrix} \sin \theta \\ 0 \\ -\cos \theta \end{pmatrix} \quad (4.9)$$

where ε_σ and ε_π describe the components of polarization vector which are perpendicular and parallel to the scattering plane, with $|\varepsilon_\sigma|^2 + |\varepsilon_\pi|^2 = 1$. Since the details of the geometry dependent scattering intensity will be discussed in the XRMS section, we briefly touch on the polarization dependence of the scattering length of which the absolute square gives the cross section of the scattering and which will be derived as eq.(4.44). The scattering length of eq.(4.44) is composed of three terms as

$$f(E) = f_0(E) + f_{circ}(E) + f_{lin}(E) \quad (4.10)$$

Each term of scattering length has a different polarization dependence given by

$$f_0(E) \propto (\hat{\varepsilon}' \cdot \hat{\varepsilon})[F_{+1}^1 + F_{-1}^1] \quad (4.11)$$

$$f_{circ}(E) \propto (\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{\mathbf{m}}[F_{+1}^1 - F_{-1}^1] \quad (4.12)$$

$$f_{lin}(E) \propto (\hat{\varepsilon}' \cdot \hat{\mathbf{m}})(\hat{\varepsilon} \cdot \hat{\mathbf{m}})[2F_0^1 - F_{+1}^1 - F_{-1}^1] \quad (4.13)$$

$$\hat{\varepsilon}' \cdot \hat{\varepsilon} = \begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix} \quad (4.14)$$

$$(\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{\mathbf{m}} = \begin{pmatrix} 0 & m_1 \cos \theta + m_3 \sin \theta \\ -m_1 \cos \theta + m_3 \sin \theta & -m_2 \sin 2\theta \end{pmatrix} \quad (4.15)$$

$$(\hat{\varepsilon}' \cdot \hat{\mathbf{m}})(\hat{\varepsilon} \cdot \hat{\mathbf{m}}) = \begin{pmatrix} m_2^2 & m_2(-m_1 \sin \theta + m_3 \cos \theta) \\ m_2(m_1 \sin \theta + m_3 \cos \theta) & m_1^2(\cos^2 \theta - 1) + m_3^2 \cos^2 \theta \end{pmatrix} \quad (4.16)$$

In these expressions E is the photon energy, ε and ε' are the polarization vectors of the incident and scattered beams, $\hat{\mathbf{m}}$ represents the local moment direction and F_ν^1 are the strongly energy-dependent dimensionless resonant strengths for dipole transitions. The polarization dependence of the resonant scattering that is represented in a matrix is

$$\begin{pmatrix} \varepsilon'_\sigma \\ \varepsilon'_\pi \end{pmatrix} = \begin{pmatrix} f_{\sigma\sigma} & f_{\sigma\pi} \\ f_{\pi\sigma} & f_{\pi\pi} \end{pmatrix} \begin{pmatrix} \varepsilon_\sigma \\ \varepsilon_\pi \end{pmatrix} \quad (4.17)$$

If only eq(4.12) is considered, the resonant scattering which will be discussed later can be represented as

$$\begin{pmatrix} \varepsilon'_\sigma \\ \varepsilon'_\pi \end{pmatrix} = \mathbf{M}_T \begin{pmatrix} 0 & m_1 \cos \theta + m_3 \sin \theta \\ -m_1 \cos \theta + m_3 \sin \theta & -m_2 \sin 2\theta \end{pmatrix} \begin{pmatrix} \varepsilon_\sigma \\ \varepsilon_\pi \end{pmatrix} \quad (4.18)$$

where $\mathbf{M}_T = F_{+1}^1 - F_{-1}^1$ is the contribution of transition matrix elements. As the above equation shows, it is possible to determine the polarization character of the scattered photons with the incident photon's polarization, magnetic moment and scattering geometry. For example, with a σ polarized incident photon, only a π polarized scattered photon is possible.

4.2 X-ray Resonant Magnetic Scattering (XRMS)

Considering the ratio of magnetic to charge scattering is less than $\approx 10^{-5}$, the application of x-ray magnetic scattering to study magnetic materials is challenging. In fact, it was a main

hindrance for the progress in using x-ray scattering for the investigation of magnetic properties after the first measurement by de Bergenvin and Brunel(77). However, the advent of high intensity, highly polarized, photon sources opens the gate to use x-rays as an alternative source to investigate magnetic properties. The observation of the resonant enhanced magnetic satellites in antiferromagnetically ordered Ho(64) with successful model calculations(67) demonstrated how weak magnetic scattering can be observed with new synchrotron radiation sources and stimulated experimental investigation of the polarization dependence of near-edge x-ray absorption and scattering. With polarization studies using higher degree of linear polarization incident beams, it has been possible to distinguish between charge peaks, arising from lattice modulation, and magnetic peaks, in a spiral magnetic structure(78; 79)-while the polarization of photons which interact with charge is not changed it is possible to produce polarization change in the magnetic scattering. Furthermore, it has been suggested that it should be possible to measure separately the spin and orbital contributions to the cross section(66; 76; 80).

The large enhanced magnetic peaks can be understood from the resonant process of the low order electric multi-pole transition between a core level and unoccupied conduction states. Since, in systems which have net magnetic moments the unoccupied states are split by the exchange interaction, transitions should be sensitive to magnetization (exchange splitting). Even in the antiferromagnetically ordered system which have no energy splitting in the final energy eigenstates, since, locally at one site, the projected density of states can be different for up and down states transitions can prove these differences. In the case of the L_3 , L_2 edge transition of rare-earths, since atomic-level transitions are dominated by electric dipole (E1) and electric quadrupole (E2) characters that involve the $2p_{3/2}, 2p_{1/2}$ to $5d$ or $4f$ states respectively, spectra can attain $5d$ or $4f$ magnetization information. In this section, we discuss the basic formula for the cross section and scattering length in XRMS.

The cross section for scattering from an initial state, $|a\rangle$, into a final state, $|b\rangle$ can be calculated from the interaction Hamiltonian using a perturbation expansion(66) as

$$\frac{d^2\sigma}{d\Omega dE'} = \left(\frac{e^2}{mc^2}\right)^2 \left| \left\langle b \left| \sum_j e^{\mathbf{Q} \cdot \mathbf{r}_j} \right| a \right\rangle \right|^2 \hat{\epsilon}' \cdot \hat{\epsilon}$$

$$\begin{aligned}
& -i \frac{\hbar \omega}{m c^2} \left\langle b \left| \sum_j e^{\mathbf{Q} \cdot \mathbf{r}_j} \mathbf{s}_j \right| a \right\rangle \cdot (\hat{\varepsilon}' \times \hat{\varepsilon}) \\
& + \frac{\hbar^2}{m} \sum_{|c\rangle} \frac{\langle b | \Omega^\dagger(\mathbf{k}', \hat{\varepsilon}') | c \rangle \langle c | \Omega(\mathbf{k}, \hat{\varepsilon}) | a \rangle}{E_a - E_c + \hbar \omega_k - i\Gamma/2} \\
& + \frac{\hbar^2}{m} \sum_{|c\rangle} \frac{\langle b | \Omega(\mathbf{k}, \hat{\varepsilon}) | c \rangle \langle c | \Omega^\dagger(\mathbf{k}', \hat{\varepsilon}') | a \rangle}{E_a - E_c - \hbar \omega_k} \Bigg|^2. \\
& \delta(E_a + \hbar \omega_k - E_b - \hbar \omega_{k'})
\end{aligned} \tag{4.19}$$

where $\mathbf{k}(\mathbf{k}')$ is the wave vector and $\hat{\varepsilon}(\hat{\varepsilon}')$ is the polarization for the incoming(outgoing) photon. $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$ stands for the scattering vector and Γ is for taking into account the core hole lifetime broadening. The generalized transition operator, $\Omega(\mathbf{k}, \hat{\varepsilon})$ can be represented as

$$\Omega(\mathbf{k}, \hat{\varepsilon}) \equiv \sum_j \left(\frac{\hat{\varepsilon} \cdot \mathbf{P}_j}{\hbar} - i(\mathbf{k} \times \hat{\varepsilon}) \cdot \mathbf{s}_j \right) e^{i\mathbf{k} \cdot \mathbf{r}_j} \tag{4.20}$$

where $\mathbf{P}_j$ is the momentum, $\mathbf{r}_j$ is the position and $\mathbf{s}_j$ is the spin of j -th electron. The $\sum_j$ is for sum over all the electrons in the solid. It is possible to express explicitly the contribution of each atom in $\Omega(\mathbf{k}, \varepsilon)$ as

$$\Omega(\mathbf{k}, \hat{\varepsilon}) \equiv \sum_N e^{i\mathbf{k} \cdot \mathbf{R}_N} \sum_{j'} \left(\frac{\hat{\varepsilon} \cdot \mathbf{P}_{j'}}{\hbar} - i(\mathbf{k} \times \hat{\varepsilon}) \cdot \mathbf{s}_{j'} \right) e^{i\mathbf{k} \cdot \mathbf{r}_{j'}} \tag{4.21}$$

by using the reduced position vector

$$\mathbf{r}_j = \mathbf{R}_N + \mathbf{r}_{j'}$$

where $\mathbf{R}_N$ is the position vector for N -th atom and $\mathbf{r}_{j'}$ is the electron's position vector with respect to the atom. It is possible for this expression to become problematic when the electronic states can not be associated with a particular atomic site. However, since it is safe in the considered cases, we will keep using it. If the plane exponential is expanded as

$$e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1 + i\mathbf{k} \cdot \mathbf{r} + \frac{i^2}{2}(\mathbf{k} \cdot \mathbf{r})^2 + \dots$$

the multi-pole expression for the transition operator is given as

$$\Omega(\mathbf{k}, \hat{\varepsilon}) \equiv \sum_N e^{i\mathbf{k} \cdot \mathbf{R}_N} \sum_{j'} \left(\frac{\hat{\varepsilon} \cdot \mathbf{P}_{j'}}{\hbar} - i(\mathbf{k} \times \hat{\varepsilon}) \cdot \mathbf{s}_{j'} \right) \left(1 + i\mathbf{k} \cdot \mathbf{r}_{j'} + \frac{i^2}{2}(\mathbf{k} \cdot \mathbf{r}_{j'})^2 \right) \tag{4.22}$$

Before going further, it might be a good place to discuss the limitations (assumptions) that we have in this study.

Restriction 1 : We have confined our discussion to only the resonant phenomena.

As given in eq.(4.19) , the terms in the cross section are interpreted as a Thompson scattering term, a non-resonant magnetic scattering term, a resonance scattering term. However, this study has been limited in the photon energy range in that $\hbar\omega_k \cong E_a - E_c$ so that anomalous dispersion effects occur and the third term dominates over the second and forth terms, Also, even if the first term is much larger than resonant term, we have assumed the charge Bragg peaks can be well separated from magnetic Bragg peaks and have not considered the cross-term.

Restriction 2 : We have confined our discussion to only the core states which have well splitted spin-orbit partners.

The electrons which participate in the transition come from only well localized core level states. They have total angular momentum j as a good quantum number. The spin-orbit interactions of these states are strong so that the splitting between the states, called spin-orbit partners, can be very large and easy to resolve in the spectra. The summation over occupied electrons should be limited to the core states that participate in the transition.

Restriction 3 : We have confined our discussion to only the single electron approach.

The x-ray spectra can have features that originate from many body interactions such as final state effects(81; 82). However in the most cases it is believed that these many body effects are just secondary so that the single electron approximation gives a reasonable explanation for the significant structure of spectra in the rare-earth L -edges. The single electron wave functions of the core and valence band have been used for the initial, final, and intermediate states.

Restriction 4 : We confine our discussion to only elastic scattering.

X-ray scattering spectra study does not have to be limited to elastic phenomena. As a matter of fact, inelastic scattering(83; 84; 85) is a good tool to study the higher order terms - particularly the quadrupole transitions at the rare-earth L -edges. However we have considered only elastic, $\omega_k = \omega_{k'}$, scattering processes and that the initial and final electronic states are identical $|a\rangle = |b\rangle$. In the next chapter, since the relevant matrix elements are related, we will discuss XMCD which is not the elastic scattering but absorption.

Restiction 5 : We have confined our discussion to only the electric dipole interaction.

Even though $\mathbf{k} \cdot \mathbf{r}$ is not so small to be ignored easily in the x-ray wavelength region and quadrupolar terms have been observed, since, in most case, quadrupolar term's contribution is about 1% of dipole term's it is reasonable to consider the electric dipole interaction as a main contributor of x-ray spectra. With only the electric dipole interaction, the transition operator eq.(4.22) can be simplified as

$$\Omega(\mathbf{k}, \hat{\varepsilon}) = \sum_N e^{i\mathbf{k} \cdot \mathbf{R}_N} \sum_{j'} \frac{\hat{\varepsilon} \cdot \mathbf{P}_{j'}}{\hbar} \quad (4.23)$$

With the restrictions above, we can obtain much simpler equation for the XRMS cross section and scattering amplitude.

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{XRMS} = |F_{XRMS}|^2 \quad (4.24)$$

$$\begin{aligned} F_{XRMS} &= \left(\frac{e^2 \hbar^2}{m^2 c^2} \right) \sum_{|c\rangle} \frac{\langle a | \Omega^\dagger(\mathbf{k}', \hat{\varepsilon}') | c \rangle \langle c | \Omega(\mathbf{k}, \hat{\varepsilon}) | a \rangle}{E_a - E_c + \hbar\omega_{\mathbf{k}} - i\Gamma/2} \\ &= \left(\frac{e^2 \hbar^2}{m^2 c^2} \right) \sum_{|c\rangle} \frac{\langle a | \sum_N e^{-i\mathbf{k}' \cdot \mathbf{R}_N} \sum_{j'} \frac{\hat{\varepsilon}' \cdot \mathbf{P}_{j'}}{\hbar} | c \rangle \langle c | \sum_N e^{i\mathbf{k} \cdot \mathbf{R}_N} \sum_{j'} \frac{\hat{\varepsilon} \cdot \mathbf{P}_{j'}}{\hbar} | a \rangle}{E_a - E_c + \hbar\omega_{\mathbf{k}} - i\Gamma/2} \\ &= \left(\frac{e^2 \hbar^2}{m^2 c^2} \right) \sum_N e^{-i\mathbf{Q} \cdot \mathbf{R}_N} \sum_{j'} \sum_{|c\rangle} \frac{\langle a | \frac{\hat{\varepsilon}' \cdot \mathbf{P}_{j'}}{\hbar} | c \rangle \langle c | \frac{\hat{\varepsilon} \cdot \mathbf{P}_{j'}}{\hbar} | a \rangle}{E_a - E_c + \hbar\omega_{\mathbf{k}} - i\Gamma/2} \\ &= \sum_N e^{-i\mathbf{Q} \cdot \mathbf{R}_N} F_{XRMS,N} \end{aligned} \quad (4.25)$$

where $F_{XRES,N}$ is the scattering amplitude that is calculated at one isolated atom,

$$F_{XRES,N} = \left(\frac{e^2 \hbar^2}{m^2 c^2} \right) \sum_{j'} \sum_{|c\rangle} \frac{\left\langle a \left| \frac{\vec{\varepsilon}' \cdot \mathbf{P}_{j'}}{\hbar} \right| c \right\rangle \left\langle c \left| \frac{\vec{\varepsilon} \cdot \mathbf{P}_{j'}}{\hbar} \right| a \right\rangle}{E_a - E_c + \hbar \omega_{\mathbf{k}} - i\Gamma/2} \quad (4.26)$$

This reduced expression of the scattering amplitude can be used for theoretical study of the resonant spectra. From the computational point of view, since calculation of the transition matrix elements (ME) is the most complex and computational demanding step, we will start the discussion of the spectra calculation with ME.

A matrix element consists of three parts - initial, intermediate and final state wave functions and a transition operator. The wave functions in ME can be represented either in a $|j, m_j\rangle$ or in a $|l, m_l, s, m_s\rangle$ basis. With the $|j, m_j\rangle$ basis, while the transition from fully relativistic core states might be straight forward, the spin dependent character is not clear because the spin is not a good quantum number in this representation. The $|l, m_l, s, m_s\rangle$ basis is required to express the spin dependent character explicitly. It is possible to transform from one basis representation to another using *Clebsch – Gordan* coefficients as

$$|j, m_j\rangle = R_{n,j}(r) \sum_{m_l, m_s, m_l+m_s=m_j} C_{l, m_l, s, m_s}^{j, m_j} Y_{l, m_l} \chi_{s, m_s} \quad (4.27)$$

where

$$C_{l, m_l, s, m_s}^{j, m_j} = (-1)^{l-s+m_j} \sqrt{2j+1} \begin{pmatrix} l & s & j \\ m_l & m_s & -m_j \end{pmatrix} \quad (4.28)$$

Keeping this in mind, we may write the initial (final) state wave functions as

$$\begin{aligned} |a\rangle &= R_{n,j}(r) \psi_{j, m_j}(\hat{r}) \\ &= R_{n,j}(r) \sum_{m_l, m_s, m_l+m_s=m_j} C_{l, m_l, s, m_s}^{j, m_j} Y_{l, m_l}(\hat{r}) \chi_{s, m_s} \\ &\equiv \sum_{m_l, m_s, m_l+m_s=m_j} \left| n, j, m_j, l, m_l, \frac{1}{2}, m_s \right\rangle \end{aligned} \quad (4.29)$$

The intermediate conduction band states can be expressed as a product of radial, angular and spin terms as

$$|c\rangle = \Psi_{\Lambda} \chi_{m'_s}$$

$$\begin{aligned}
&= \sum_{l'=0}^{\infty} \sum_{m'_l=-l'}^{l'} R_{\Lambda,l',m'_l,m'_s}(r) Y_{l',m'_l}(\hat{r}) \chi_{m'_s} \\
&= \sum_{l'=0}^{\infty} \sum_{m'_l=-l'}^{l'} \left| l', m'_l, \frac{1}{2}, m'_s \right\rangle
\end{aligned} \tag{4.30}$$

If the spin-orbit interaction in the intermediate state is not too weak to be ignored, spin states can not be separated so that summation over spin states should be added as

$$\begin{aligned}
|c\rangle &= \sum_{m'_s} \Psi_{\Lambda} \chi_{m'_s} \\
&= \sum_{m'_s} \sum_{l'=0}^{\infty} \sum_{m'_l=-l'}^{l'} R_{\Lambda,l',m'_l,m'_s}(r) Y_{l',m'_l}(\hat{r}) \chi_{m'_s} \\
&= \sum_{m'_s} \sum_{l'=0}^{\infty} \sum_{m'_l=-l'}^{l'} \left| l', m'_l, \frac{1}{2}, m'_s \right\rangle
\end{aligned} \tag{4.31}$$

Now the transition operator should be modified to a new form so that it can be evaluated in real space. Most x-ray literatures use a simple relation between the momentum operator $\mathbf{p}$ and radial vector $\mathbf{r}$. The transition operator can be re-expressed as

$$\begin{aligned}
\langle c | \hat{\varepsilon} \cdot \mathbf{P} | a \rangle &= \frac{im(E_c - E_a)}{\hbar} \langle c | \hat{\varepsilon} \cdot \mathbf{r} | a \rangle \\
&= im\omega_k \langle c | \hat{\varepsilon} \cdot \mathbf{r} | a \rangle
\end{aligned} \tag{4.32}$$

with

$$\langle \alpha | \mathbf{P} | \beta \rangle = \frac{im(E_{\alpha} - E_{\beta})}{\hbar} \langle \alpha | \mathbf{r} | \beta \rangle \tag{4.33}$$

The dot product of polarization and radial vector is

$$\begin{aligned}
\hat{\varepsilon} \cdot \mathbf{r} &= (\varepsilon_x \sin \theta \cos \phi + \varepsilon_y \sin \theta \sin \phi + \varepsilon_z \cos \theta) r \\
&= r \sqrt{\frac{4\pi}{3}} \sum_{M=-1}^1 \varepsilon_M Y_{1M}
\end{aligned} \tag{4.34}$$

and

$$\begin{aligned}
&\left\langle l', m'_l, \frac{1}{2}, m'_s \left| \hat{\varepsilon} \cdot \mathbf{r} \right| n, j, m_j, l, m_l, \frac{1}{2}, m_s \right\rangle \\
&= \int dV (R_{\Lambda,l',m'_l,m'_s}(r) Y_{l',m'_l}(\hat{r}) \chi_{m'_s})^{\dagger} (r \sqrt{\frac{4\pi}{3}} \sum_{M=-1}^1 \varepsilon_M Y_{1M}) (R_{n,j}(r) C_{l,m_l,s,m_s}^{j,m_j} Y_{l,m_l}(\hat{r}) \chi_{m_s}) \\
&= \sqrt{\frac{4\pi}{3}} (\int_0^{\infty} r^2 dr R_{\Lambda,l',m'_l,m'_s}^{\dagger}(r) r R_{n,j}(r)) (\int d\Omega Y_{l',m'_l}^{\dagger}(\hat{r}) \sum_{M=-1}^1 \varepsilon_M Y_{1M} Y_{l,m_l}(\hat{r}) C_{l,m_l,s,m_s}^{j,m_j} \chi_{m'_s} \chi_{m_s})
\end{aligned} \tag{4.35}$$

Using the $3j$ symbol for the spherical harmonics integration

$$\begin{aligned}
\int d\Omega Y_{l',m'}^\dagger Y_{k,q} Y_{l,m} &= \sqrt{\frac{2k+1}{4\pi}} \delta_{q,m'-m} c^k(l', m', l, m) \\
&= \sqrt{\frac{2k+1}{4\pi}} \delta_{q,m'-m} (-1)^{-m'} \sqrt{(2l'+1)(2l+1)} \cdot \\
&\quad \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & q & m' \end{pmatrix} \quad (4.36)
\end{aligned}$$

and separating the radial matrix elements

$$\begin{aligned}
&\langle l', m'_l, \frac{1}{2}, m'_s | \hat{\varepsilon} \cdot \mathbf{r} | n, j, m_j, l, m_l, \frac{1}{2}, m_s \rangle \\
&= \Re_{l',m'_l,m'_s}^j c^1(l', m'_l, l, m_l) C_{l,m_l,s,m_s}^{j,m_j} \delta_{m'_s,m_s} \sum_{M=-1}^1 \varepsilon_M \delta_{M,m'_l-m_l} \quad (4.37)
\end{aligned}$$

where

$$\Re_{l',m'_l,m'_s}^j = \int_0^\infty r^2 dr R_{\Lambda,l',m'_l,m'_s}^\dagger(r) r R_{n,j}(r) \quad (4.38)$$

we can obtain the equation

$$\begin{aligned}
\langle c | \hat{\varepsilon} \cdot \mathbf{r} | a \rangle &= \sum_{m'_s} \sum_{l'=0}^\infty \sum_{m'_l=-l'}^{l'} \left\langle l', m'_l, \frac{1}{2}, m'_s \right| (\hat{\varepsilon} \cdot \mathbf{r}) \sum_{m_l, m_s} \left| n, j, m_j, l, m_l, \frac{1}{2}, m_s \right\rangle \\
&= \sum_{m'_s} \sum_{l'=0}^\infty \sum_{m'_l=-l'}^{l'} \sum_{m_l, m_s} \left\langle l', m'_l, \frac{1}{2}, m'_s \right| (\hat{\varepsilon} \cdot \mathbf{r}) \left| n, j, m_j, l, m_l, \frac{1}{2}, m_s \right\rangle \\
&= \sum_{m'_s} \sum_{l'=0}^\infty \sum_{m'_l=-l'}^{l'} \sum_{m_l, m_s} \Re_{l',m'_l,m'_s}^j c^1(l', m'_l, l, m_l) C_{l,m_l,s,m_s}^{j,m_j} \delta_{m'_s,m_s} \sum_{M=-1}^1 \varepsilon_M \delta_{M,m'_l-m_l} \quad (4.39)
\end{aligned}$$

The dipole selection rules constrain the l', l, m'_l, m_l so that the indices in the summation are simplified as

$$\langle c | \hat{\varepsilon} \cdot \mathbf{r} | a \rangle = \sum_{m'_l, m_l, m_s} \sum_M \varepsilon_M \delta_{M, m'_l-m_l} \Re_{l',m'_l,m'_s}^j c^1(l', m'_l, l, m_l) C_{l,m_l,s,m_s}^{j,m_j} \delta_{m'_s,m_s} \quad (4.40)$$

Therefore, the scattering amplitude of a single resonant atom, N , is

$$\begin{aligned}
F_{XRMS,N} &= \left(\frac{e^2 \omega_k^2}{c^2} \right) \sum_{\Lambda} \sum_{m_j} \frac{\langle a | \hat{\varepsilon}'^\dagger \cdot \mathbf{r} | c \rangle \langle c | \hat{\varepsilon} \cdot \mathbf{r} | a \rangle}{E_{|n,j,m_j,l\rangle} - E_{|\Lambda,m'_s\rangle} + \hbar \omega_k - i\Gamma/2} \\
&= \left(\frac{e^2 \omega_k^2}{c^2} \right) \sum_{m_s} \sum_{m_j} \sum_{M=-1}^1 (\varepsilon_M'^\dagger \cdot \varepsilon_M) \Re_{l',m'_l,m'_s}^j \left| c^1(l', m'_l, l, m_l) \right|^2 \left| C_{l,m_l,s,m_s}^{j,m_j} \right|^2 \\
&= \sum_{M=-1}^1 (\varepsilon_M'^\dagger \cdot \varepsilon_M) \cdot F_{1M} \quad (4.41)
\end{aligned}$$

where

$$\mathfrak{S}_{l',m'_l,m'_s}^j = \sum_{\Lambda} \frac{|\Re_{l',m'_l,m'_s}^j|^2}{E_{|n,j,m_j,l\rangle} - E_{|\Lambda,m'_s\rangle} + \hbar\omega_k - i\Gamma/2} \quad (4.42)$$

and

$$F_{1M} = \left(\frac{e^2\omega_k^2}{c^2} \right) \sum_{m_s} \sum_{m_j} \mathfrak{S}_{l',m'_l,m'_s}^j \left| c^1(l', m'_l, l, m_l) \right|^2 \left| C_{l,m_l,s,m_s}^{j,m_j} \right|^2 \quad (4.43)$$

If $\varepsilon_M^{\dagger} \cdot \varepsilon_M$ is represented with the polarization vector $(\hat{\varepsilon}, \hat{\varepsilon}')$ and the unit vector $\hat{\mathbf{m}}_N$ which describes the local magnetic moment direction at the N -th atom, the transition matrix elements have the new form

$$\begin{aligned} F_{XRMS,N} &= (\hat{\varepsilon}'^{\dagger} \cdot \hat{\varepsilon}) [F_{11} + F_{1-1}] \\ &\quad - i(\hat{\varepsilon}'^{\dagger} \times \hat{\varepsilon}) \cdot \hat{\mathbf{m}}_N [F_{11} - F_{1-1}] \\ &\quad + (\hat{\varepsilon}'^{\dagger} \cdot \hat{\mathbf{m}}_N)(\hat{\varepsilon} \cdot \hat{\mathbf{m}}_N) [-F_{11} + 2F_{10} - F_{1-1}] \\ &= f_0(E) + f_{circ}(E) + f_{lin}(E) \end{aligned} \quad (4.44)$$

We have obtained the analytical expression for the scattering amplitude by using the simple commutation relation between two operators $\mathbf{p}, \mathbf{r}$. Alternatively, it is possible to obtain same results by treating the momentum operator as the optical (gradient) operator and using the gradient integration formula(86). This is useful, because, through this method, we can show more explicitly that x-ray spectra have a common physics formalism with other optical spectra. This will be discussed in a later section.

4.3 X-ray Magnetic Circular Dichroism (XMCD)

X-ray absorption depends on the polarization of x-rays in magnetic materials. XMCD (XMLD) is the absorption difference of circular (linear) polarized light. XMLD was calculated and observed at M_4, M_5 edges of rare earth compounds by Thole *et al.*(87) and van der Lann *et al.*(88), but has been restricted by the small number of materials and edges where it can be observed. The first theoretical formulation of XMCD was done by Erskine *et al.*(89), who described the excitation at M_2, M_3 edges of Ni in 1975. And the first experimental observation was performed by Schultz *et al.*(90) at the Fe K -edge. They could interpret their observation

as the difference of unoccupied final spin density of states (DOS). With Fermi's *Golden rule*, the photo-absorption coefficient μ in the expression $I(z) = I_0 e^{-\mu z}$ can be written as

$$\mu(E) = \sum_{i,f} |M_{fi}(E)|^2 \rho(E) \quad (4.45)$$

where $M_{fi}(E)$ is the matrix elements for photon transition of the initial state $|i\rangle$ into the final state $|f\rangle$. With simplified assumptions such as the matrix elements $M_{fi}(E)$ for all possible photoelectron final state are constant, from the definition of XMCD spectra

$$\mu_c = \mu^+ - \mu^- \quad (4.46)$$

where μ^+ (μ^-) is the absorption coefficient of right (left) circularly polarized photon, they obtained the normalized spin-dependent photo-absorption coefficient

$$\frac{\mu_c}{\mu_0}(E) = P_e \frac{\Delta\rho}{\rho}(E) \quad (4.47)$$

where μ_c (μ_0) is spin dependent (independent) contribution for the absorption coefficient μ . The final state density can be separated into states with spin parallel ($\rho^\uparrow(E)$) and antiparallel ($\rho^\downarrow(E)$) to the photon spin and given as

$$\rho(E) = \rho^\uparrow(E) + \rho^\downarrow(E).$$

The spin density of states in the absorption process are given by

$$\frac{\Delta\rho}{\rho}(E) = \frac{\rho^\uparrow(E) - \rho^\downarrow(E)}{\rho^\uparrow(E) + \rho^\downarrow(E)}.$$

$P_e = [n^\uparrow - n^\downarrow]/[n^\uparrow + n^\downarrow]$ is the degree of photoelectron polarization from the light source where $n^\uparrow$ and $n^\downarrow$ are probabilities to create a photoelectron of a given spin. With this straightforward, simple interpretation, their observation of rather large signals at the L -edges of ferromagnetic Gd and Tb metal(91) was enough to attract attention and establish XMCD as a useful probe of magnetic properties. However, when this simple model was applied to the rare earths L -edges it failed to explain the sign and the magnitude of the signals - the direction of $5d$ polarization deduced from XMCD spectra is wrong when this simple model is used. To solve this so-called

“sign problem” , the spin dependence, instead of constant, matrix elements was taken into account(92). The XMCD signal is better approximated by the expression

$$\begin{aligned}\frac{\mu_c}{\mu^+ + \mu^-} &= \frac{\mu^+ - \mu^-}{\mu^+ + \mu^-} \\ &= P_E \left(\frac{\Delta M}{M} + \frac{\Delta \rho}{\rho} \right)\end{aligned}\quad (4.48)$$

where $\Delta M = M^\uparrow - M^\downarrow$ is the difference between the spin dependent radial parts of the matrix elements and μ^+ (μ^-) is the absorption coefficient of right (left) polarized photon.

In absorption measurements, the absorption coefficient μ is defined by

$$I(z) = I_0 e^{-\mu z} \quad (4.49)$$

where the light is assumed to propagate along the z-direction and I_0 is the incident intensity of the light. In the absence of any net sample magnetization, the transmitted beam is simply attenuated by a factor $\exp(-\mu d)$, where d is sample thickness. However magnetizing of the sample modifies the absorption coefficients μ by small amount which is increased or decreased depending on the sample's magnetization and the photon's helicity, either right (+) or left (-). By definition, the XMCD spectra , μ_c are related to absorption spectra (I^+ , I^-) by

$$\mu_c \sim \ln \left(\frac{I_0^+}{I^+} \right) - \ln \left(\frac{I_0^-}{I^-} \right) \quad (4.50)$$

where $I_0^\pm$ are the incident intensities for right (+) and left (-) circularly polarized photons.

From interaction Hamiltonian,

$$H_{int} = - \sum_j \frac{e}{mc} \mathbf{p}_j \cdot \mathbf{A}(\mathbf{r}_j, t) \quad (4.51)$$

where m and $\mathbf{p}$ denote the electron mass and momentum, Carra *et al.*(93; 94) obtained that the absorption coefficient, for an electric 2^L pole transition, is proportional to

$$W_{EL} = 2\lambda \sum_{M=-L}^L \left| \hat{\mathbf{e}} \cdot \mathbf{Y}_{LM}^{(el)}(\hat{\mathbf{k}}) \right|^2 w_{LM}^{(el)}(\mathbf{k}) \quad (4.52)$$

where $\hat{\mathbf{k}}, \hat{\mathbf{e}}$ stand for the unit vector of the photon momentum and polarization. Also assuming $kr \ll 1$ and $T = 0$,

$$w_{LM}^{(el)}(\mathbf{k}) = 4\pi^2 e^2 \sum \left[\frac{L+1}{L[(2L+1)!!]^2} \right] k^{2L} \left| \left\langle \eta \left| \sum_j r_j^L Y_{LM} \right| \alpha \right\rangle \right|^2 \delta(\varepsilon_\alpha - \varepsilon_\eta - \varepsilon) \quad (4.53)$$

where α, η denote the ground and excited electronic states. From this, the dipole XMCD can be expressed as

$$\mu_c^{E1}(k) = \frac{6\pi N}{k} [w_{11}^{(el)} - w_{1-1}^{(el)}] \cos \theta \quad (4.54)$$

where $\cos \theta = \hat{\mathbf{k}} \cdot \hat{\mathbf{z}}$ with $\hat{\mathbf{z}}$ the unit vector in the direction of the local magnetization; N represents the number of atoms per unit volume.

Alternatively, it is possible to calculate the absorption coefficient from a relation between the absorption coefficient μ and the imaginary part of the dielectric constant $Im(\epsilon)$. From optical properties,

$$\begin{aligned} \mu &= Im(\epsilon) \frac{\omega}{c} \\ &= \frac{4\pi}{c} Re(\sigma(\omega)) \end{aligned} \quad (4.55)$$

where $Re(\sigma(\omega))$ is the real part of the so-called optical conductivity. With a general expression for $Im(\epsilon)$,

$$Im(\epsilon) = \frac{4\pi^2 e^2}{m^2 \hbar \omega} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{mm'} D_{mm'}(\mathbf{k}) \delta(E_n(\mathbf{k}) - E_{n'}(\mathbf{k}) - \hbar\omega) \quad (4.56)$$

where

$$D_{mm'}(\mathbf{k}) = \frac{f(E_{n'}(\mathbf{k})) - f(E_n(\mathbf{k}))}{E_n(\mathbf{k}) - E_{n'}(\mathbf{k})} |\langle n, \mathbf{k} | \mathbf{p} | n', \mathbf{k} \rangle|^2 \quad (4.57)$$

the absorption coefficient is given as

$$\mu_{\pm}^j = \frac{4\pi\omega e^2}{m^2 c V} \sum_{\Psi'jm} \delta(E_{\Psi'jm}(\mathbf{k}) - E_{\Psi}(\mathbf{k}) - \hbar\omega) \frac{|\langle \Psi | \mathbf{p}^{\pm} | \Psi'jm \rangle|^2}{(E_{\Psi'jm} - E_{\Psi})^2} \quad (4.58)$$

where $|\Psi\rangle$ is the ground state, $|\Psi'jm\rangle$ is the final state with a core hole of quantum numbers jm and the function $f(E)$ is *Fermi - Dirac* distribution function.

After the first XMCD observation was reported, the technique has been used to study magnetic properties of various systems(95; 96; 97; 98; 99; 100; 101). Along with the progress of experimental measurements, theoretical calculations have progressed to interpret and understand the detailed mechanisms producing the spectra - atomic model calculations(102; 103; 104; 105) and first principles band structure calculations(92; 94; 106; 107; 108). A great attraction of the XMCD technique is due to the successful extension of optical sum-rules into the x-ray region. Sum-rules(10) which were formulated by Thole *et al.*(109) and Carra *et al.*(110) related

the integrated intensity to the magnetic moment of the ground states. With sum rules, the XMCD technique is able to obtain the quantitative shell specific information of the orbital and spin part of the local magnetic moment separately. The ground state expectation value of the orbital angular momentum per hole is given by

$$\frac{\int_{j_++j_-} d\omega(\mu^+ - \mu^-)}{\int_{j_++j_-} d\omega(\mu^+ + \mu^- + \mu^0)} = \frac{1}{2} \frac{l(l+1) + 2 - c(c+1)}{l(l+1)(4l+2-n)} \langle L_z \rangle \quad (4.59)$$

For the spin dependent part of the local magnetic field per hole, sum rule is given as

$$\begin{aligned} \frac{\int_{j_+} d\omega(\mu^+ - \mu^-) - [(c+1)/c] \int_{j_-} d\omega(\mu^+ - \mu^-)}{\int_{j_++j_-} d\omega(\mu^+ + \mu^- + \mu^0)} &= \frac{l(l+1) - 2 - c(c+1)}{3c(4l+2-n)} \langle S_z \rangle \quad (4.60) \\ &+ \frac{l(l+1)[l(l+1) + 2c(c+1) + 4] - 3(c-1)^2(c+2)^2}{6lc(l+1)(4l+2-n)} \langle T_z \rangle \end{aligned}$$

Here $T = \mathbf{s} - 3\mathbf{r}(\mathbf{r} \cdot \mathbf{s})/|\mathbf{r}|^2$, $j_{\pm} = c \pm 1/2$ and c is the orbital quantum number of the core state which participates in the transition. The expectation value of the magnetic dipole operator $\langle T_z \rangle$ accounts for the anisotropy of the field of the spins when the atomic cloud is distorted by crystal field or spin-orbit coupling. For cubic transition metals (3d shell), the sum rule can give accurate $\langle S_z \rangle$ information with neglecting $\langle T_z \rangle$ which is sufficiently smaller than $\langle S_z \rangle$. For 5d transition metals, or non-cubic systems $\langle T_z \rangle$ is rather significant, and neglecting $\langle T_z \rangle$ gives only qualitatively correct $\langle S_z \rangle$. However the sum rules fail to give correct information for the moments of the rare earth 5d shell. A number of studies that investigated the validity of sum rules have been carried out with 3d, 5d elements and various results have been reported(111; 112; 113; 114). These various results contain a number of assumptions which were made to derive the sum rules such as ignoring the exchange splitting for core levels, using the classical interaction operator($\nabla \cdot \mathbf{a}_\lambda$), ignoring the anisotropy of the core states, ignoring $p \rightarrow s$ transitions, ignoring the relativistic correction to radial part, and ignoring inter atomic hybridization. Some of them are reasonably good but others are problematic. Especially, one of the serious assumptions is the last one. With this assumption, one is ignoring the energy dependence of the radial matrix elements(110), therefore it is hard to expect sum rules to be reasonably applied to rare earths compounds.

4.4 Transition Matrix Elements at L_3 , L_2 edges with the LAPW Method

In this section, we apply the results of previous sections to the L_3 , L_2 edge of rare earths which exhibit very interesting phenomena. In these spectra, the dipole transitions are predominantly from the $2p_{1/2}$ and $2p_{3/2}$ core levels to the unoccupied spin polarized states with $5d$ character. In this section, for simplification, we have discuss only the transitions from $2p$ to $5d$ states, while the computational results included all allowed dipole transitions to $5d$ and $6s$ states. We have derived the transition matrix elements formula analytically using LAPW basis functions. The XMCD spectra formula also have been derived in simplified form.

The LAPW method splits space into MT spheres and an interstitial region and uses different basis functions in each. However, in x-ray spectra calculations since we are only interested in the region where the core and valence wave functions are overlapped, it is reasonable to consider only the MT sphere region for the matrix elements. The wave functions inside the MT sphere region are represented as :

$$\psi_{n,k}(r) = \sum_{l,m_l,m_s} [A_{l,m_l}^{m_s}(n,k)u_l^{m_s}(r) + B_{l,m_l}^{m_s}(n,k)\dot{u}_l^{m_s}(r)]Y_{l,m_l}(\hat{r})\chi_{m_s} \quad (4.61)$$

where n is band index, and

$$\dot{u}_l^{m_s} = \left(\frac{\partial u_l^{m_s}}{\partial E} \right)_{E_0} \quad (4.62)$$

Since for ME we are primarily interested in $d(l=2)$ states, the wave function can be simplified as

$$\psi_{k,n}(r) = \sum_{m_l,m_s} [A_{l=2,m_l}^{m_s}(k,n)u_{l=2}^{m_s}(r) + B_{l=2,m_l}^{m_s}(k,n)\dot{u}_{l=2}^{m_s}(r)]Y_{l=2,m_l}(\hat{r})\chi_{m_s} \quad (4.63)$$

If we use m instead of m_l and leave out " $l=2$ ", the notation becomes

$$\psi_{k,n}(r) = \sum_{m,m_s} [A_m^{m_s}(k,n)u^{m_s}(r) + B_m^{m_s}(k,n)\dot{u}^{m_s}(r)]Y_{2,m}(\hat{r})\chi_{m_s} \quad (4.64)$$

The core state wave functions can be represented as

$$\begin{aligned} \psi_c &= \sum_{m'_l,m'_s} C_{m'_l,m'_s} R_{l'}^{m'_s}(r) Y_{l',m'_l}(\hat{r}) \chi_{m'_s} \\ &= \sum_{m',m'_s} C_{m',m'_s} R^{m'_s}(r) Y_{1,m'}(\hat{r}) \chi_{m'_s} \end{aligned} \quad (4.65)$$

In the last equation we used m' instead of m'_l , omitted $l' = 1$ and represented *Clebsch–Gordan* coefficients as C_{m',m_s} .

Now we can use these wave functions to evaluate the transition matrix elements given as

$$M_{if}^{\pm 1} = -\hbar^2 \sum_c \sum_k \sum_n M_{c,k,n}^{\pm 1*} \cdot M_{c,k,n}^{\pm 1} \quad (4.66)$$

$$\begin{aligned} M_{c,k,n}^\mu &= \int dV \psi_c^*(l'=1) \nabla_\mu \psi_{k,n}(l=2) \\ &= \sum_{m',m,m_s} \Re_{l=2,m_s}^{l'=1} (-1)^{m'} \frac{\begin{pmatrix} 1 & 1 & 2 \\ -m' & \mu & m \end{pmatrix}}{\begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix}} C_{m',m_s} \chi_{m'_s} \chi_{m_s} \delta_{m'_s,m_s} \\ &= \sum_{m',m,m_s} \Re_{l=2,m_s}^{l'=1} (-1)^{m'} C_{m',m_s} \chi_{m'_s} \chi_{m_s} \delta_{m'_s,m_s} \frac{Gaunt(1,1,2,m',\mu,m)}{Gaunt(1,1,2,0,0,0)} \end{aligned} \quad (4.67)$$

where $\mu = \pm 1$, and $\Re_{l=2,m_s}^{l'=1}$ is the reduced matrix element, which is given as

$$\begin{aligned} \Re_{l=2,m_s}^{l'=1} &= \langle R^{m_s} | \nabla_0 | A_{m_s}^{m_s}(\mathbf{k}, n) u^{m_s}(r) + B_{m_s}^{m_s}(\mathbf{k}, n) \dot{u}^{m_s}(r) \rangle \\ &= \frac{2}{\sqrt{5}} \int r^2 dr [R^{m_s}(r) \left(\frac{\partial}{\partial r} + \frac{3}{r} \right) (A_{m_s}^{m_s}(\mathbf{k}, n) u^{m_s}(r) + B_{m_s}^{m_s}(\mathbf{k}, n) \dot{u}^{m_s}(r))] \\ &= \frac{2}{\sqrt{5}} [H^{m_s} A_{m_s}^{m_s}(\mathbf{k}, n) + \dot{H}^{m_s} B_{m_s}^{m_s}(\mathbf{k}, n)] \end{aligned} \quad (4.68)$$

where

$$H^{m_s} = \int r^2 dr R^{m_s}(r) \left(\frac{\partial}{\partial r} + \frac{3}{r} \right) u^{m_s}(r) \quad (4.69)$$

$$\dot{H}^{m_s} = \int r^2 dr R^{m_s}(r) \left(\frac{\partial}{\partial r} + \frac{3}{r} \right) \dot{u}^{m_s}(r) \quad (4.70)$$

The summation can be simplified using the selection rules, such as $m' = m + \mu$.

Before discussion of the L_3 edge transition, it is worth while to make some practical remarks.

1. With spin-orbit coupling, the wave function which has a band index is a mixed state of spin up and down. Therefore, like atomic model calculations, the approaches that characterize wave functions as only spin up and down are only appropriate for the case that the spin-orbit coupling is negligible.

Table 4.1 Gaunt factors for the transition from $l' = 1$ to $l = 2$.

k	l'	l	q	m_l	m_l	Gaunt factor
1	1	2	-1	-1	0	-0.126157
1	1	2	-1	0	1	-0.218510
1	1	2	-1	1	2	-0.309019
1	1	2	0	-1	-1	0.218510
1	1	2	0	0	0	0.252313
1	1	2	0	1	1	0.218510
1	1	2	1	-1	-2	-0.309019
1	1	2	1	0	-1	-0.218510
1	1	2	1	1	0	-0.126157

2. Gaunt factors - Gaunt factors are defined as the integration of the product of three spherical harmonic functions as

$$Gaunt(l', k, l, m_l', q, m_l) = \int d\Omega Y_{l', m_l'}^\dagger Y_{k, q} Y_{l, m_l} \quad (4.71)$$

For dipole transitions from $l' = 1$ to $l = 2$, they can be tabulated as in Table 4.1.

L_3 edge transition matrix elements

With *Clebsch – Gordan* coefficients, the components of $2p_{3/2}$ core level can be expressed as

$$\begin{aligned}
\left| \frac{3}{2}, \frac{3}{2} \right\rangle &= R^\uparrow(r) Y_{1,1} |\uparrow\rangle \\
\left| \frac{3}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{2}{3}} R^\uparrow(r) Y_{1,1} |\uparrow\rangle + \sqrt{\frac{1}{3}} R^\downarrow(r) Y_{1,-1} |\downarrow\rangle \\
\left| \frac{3}{2}, -\frac{1}{2} \right\rangle &= \sqrt{\frac{1}{3}} R^\uparrow(r) Y_{1,1} |\uparrow\rangle + \sqrt{\frac{2}{3}} R^\downarrow(r) Y_{1,-1} |\downarrow\rangle \\
\left| \frac{3}{2}, -\frac{3}{2} \right\rangle &= R^\downarrow(r) Y_{1,-1} |\downarrow\rangle
\end{aligned}$$

The transition formula from each core state with right circular polarized (ε_{+1}) photons are given by

$$M_{1,k,n}^{+1} = \left\langle \frac{3}{2}, \frac{3}{2} \left| \nabla_{+1} \right| \psi_{k,n}(r) \right\rangle$$

$$\begin{aligned}
&= (H^\dagger A_0^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_0^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, 1, 1, 0)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
M_{2,\mathbf{k},n}^{+1} &= \left\langle \frac{3}{2}, \frac{1}{2} | \nabla_{+1} | \psi_{\mathbf{k},n}(r) \right\rangle \\
&= \sqrt{\frac{2}{3}} (H^\dagger A_{-1}^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_{-1}^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, 0, 1, -1)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
&+ \sqrt{\frac{1}{3}} (H^\dagger A_0^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_0^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, 1, 1, 0)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
M_{3,\mathbf{k},n}^{+1} &= \left\langle \frac{3}{2}, -\frac{1}{2} | \nabla_{+1} | \psi_{\mathbf{k},n}(r) \right\rangle \\
&= \sqrt{\frac{1}{3}} (H^\dagger A_{-2}^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_{-2}^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, -1, 1, -2)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
&+ \sqrt{\frac{2}{3}} (H^\dagger A_{-1}^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_{-1}^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, 0, 1, -1)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
M_{4,\mathbf{k},n}^{+1} &= \left\langle \frac{3}{2}, -\frac{3}{2} | \nabla_{+1} | \psi_{\mathbf{k},n}(r) \right\rangle \\
&= (H^\dagger A_{-2}^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_{-2}^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, -1, 1, -2)}{Gaunt(1, 1, 2, 0, 0, 0)}
\end{aligned}$$

and with left circular polarized(ε_{-1}) photon,

$$\begin{aligned}
M_{1,\mathbf{k},n}^{-1} &= \left\langle \frac{3}{2}, \frac{3}{2} | \nabla_{-1} | \psi_{\mathbf{k},n}(r) \right\rangle \\
&= (H^\dagger A_2^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_2^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, 1, -1, 2)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
M_{2,\mathbf{k},n}^{-1} &= \left\langle \frac{3}{2}, \frac{1}{2} | \nabla_{-1} | \psi_{\mathbf{k},n}(r) \right\rangle \\
&= \sqrt{\frac{2}{3}} (H^\dagger A_1^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_1^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, 0, -1, 1)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
&+ \sqrt{\frac{1}{3}} (H^\dagger A_2^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_2^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, 1, -1, 2)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
M_{3,\mathbf{k},n}^{-1} &= \left\langle \frac{3}{2}, -\frac{1}{2} | \nabla_{-1} | \psi_{\mathbf{k},n}(r) \right\rangle \\
&= \sqrt{\frac{1}{3}} (H^\dagger A_0^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_0^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, -1, -1, 0)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
&+ \sqrt{\frac{2}{3}} (H^\dagger A_1^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_1^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, 0, -1, 1)}{Gaunt(1, 1, 2, 0, 0, 0)} \\
M_{4,\mathbf{k},n}^{-1} &= \left\langle \frac{3}{2}, -\frac{3}{2} | \nabla_{-1} | \psi_{\mathbf{k},n}(r) \right\rangle \\
&= (H^\dagger A_0^\dagger(\mathbf{k}, n) + \dot{H}^\dagger B_0^\dagger(\mathbf{k}, n)) \frac{Gaunt(1, 1, 2, -1, -1, 0)}{Gaunt(1, 1, 2, 0, 0, 0)}
\end{aligned}$$

L₂ edge transition matrix elements

With *Clebsch – Gordan* coefficients, the components of $2p_{1/2}$ core level can be expressed as

$$\begin{aligned} \left| \frac{1}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{1}{3}} R^\dagger(r) Y_{1,1} |\uparrow\rangle - \sqrt{\frac{2}{3}} R^\dagger(r) Y_{1,-1} |\downarrow\rangle \\ \left| \frac{1}{2}, -\frac{1}{2} \right\rangle &= \sqrt{\frac{2}{3}} R^\dagger(r) Y_{1,1} |\uparrow\rangle - \sqrt{\frac{1}{3}} R^\dagger(r) Y_{1,-1} |\downarrow\rangle \end{aligned}$$

The transition formula from each core state with right circular polarized (ε_{+1}) photon are given

$$\begin{aligned} M_{1,k,n}^{+1} &= \left\langle \frac{1}{2}, \frac{1}{2} | \nabla_{+1} | \psi_{k,n}(r) \right\rangle \\ &= \sqrt{\frac{1}{3}} (H^\dagger A_{-1}^\dagger(k, n) + \dot{H}^\dagger B_{-1}^\dagger(k, n)) \frac{Gaunt(1, 1, 2, 0, 1, -1)}{Gaunt(1, 1, 2, 0, 0, 0)} \\ &\quad - \sqrt{\frac{2}{3}} (H^\dagger A_0^\dagger(k, n) + \dot{H}^\dagger B_0^\dagger(k, n)) \frac{Gaunt(1, 1, 2, 1, 1, 0)}{Gaunt(1, 1, 2, 0, 0, 0)} \\ M_{2,k,n}^{+1} &= \left\langle \frac{1}{2}, -\frac{1}{2} | \nabla_{+1} | \psi_{k,n}(r) \right\rangle \\ &= \sqrt{\frac{2}{3}} (H^\dagger A_{-2}^\dagger(k, n) + \dot{H}^\dagger B_{-2}^\dagger(k, n)) \frac{Gaunt(1, 1, 2, -1, 1, -2)}{Gaunt(1, 1, 2, 0, 0, 0)} \\ &\quad - \sqrt{\frac{1}{3}} (H^\dagger A_{-1}^\dagger(k, n) + \dot{H}^\dagger B_{-1}^\dagger(k, n)) \frac{Gaunt(1, 1, 2, 0, 1, -1)}{Gaunt(1, 1, 2, 0, 0, 0)} \end{aligned}$$

and with left circular polarized (ε_{-1}) photon,

$$\begin{aligned} M_{1,k,n}^{-1} &= \left\langle \frac{1}{2}, \frac{1}{2} | \nabla_{-1} | \psi_{k,n}(r) \right\rangle \\ &= \sqrt{\frac{1}{3}} (H^\dagger A_1^\dagger(k, n) + \dot{H}^\dagger B_1^\dagger(k, n)) \frac{Gaunt(1, 1, 2, 0, -1, 1)}{Gaunt(1, 1, 2, 0, 0, 0)} \\ &\quad - \sqrt{\frac{2}{3}} (H^\dagger A_2^\dagger(k, n) + \dot{H}^\dagger B_2^\dagger(k, n)) \frac{Gaunt(1, 1, 2, 1, -1, 2)}{Gaunt(1, 1, 2, 0, 0, 0)} \\ M_{2,k,n}^{-1} &= \left\langle \frac{1}{2}, -\frac{1}{2} | \nabla_{-1} | \psi_{k,n}(r) \right\rangle \\ &= \sqrt{\frac{2}{3}} (H^\dagger A_0^\dagger(k, n) + \dot{H}^\dagger B_0^\dagger(k, n)) \frac{Gaunt(1, 1, 2, -1, -1, 0)}{Gaunt(1, 1, 2, 0, 0, 0)} \\ &\quad - \sqrt{\frac{1}{3}} (H^\dagger A_1^\dagger(k, n) + \dot{H}^\dagger B_1^\dagger(k, n)) \frac{Gaunt(1, 1, 2, 0, -1, 1)}{Gaunt(1, 1, 2, 0, 0, 0)} \end{aligned}$$

Intensity of XMCD spectra at L₃, L₂ edge

Since the spin-orbit coupling (SOC) mixes the spin states, the formula for intensity of spectra are very complex with cross terms. However, if we consider the terms that give the

primary contribution, the intensity formula can be simplified, and given , with the radial transition matrix elements (M^{ms}) and the density of states ($D_{m_l}^{ms}$), as

$$I_{L_3}(E) \sim \quad (4.72)$$

$$\begin{aligned} & (1.226)^2 \left[\frac{1}{3} M^{\uparrow 2}(E) D_{-2}^{\uparrow}(E) - M^{\uparrow 2}(E) D_2^{\uparrow}(E) \right. \\ & \quad \left. + M^{\downarrow 2}(E) D_{-2}^{\downarrow}(E) - \frac{1}{3} M^{\downarrow 2}(E) D_2^{\downarrow}(E) \right] \\ & + (0.869)^2 \left[\frac{2}{3} M^{\uparrow 2}(E) D_{-1}^{\uparrow}(E) - \frac{2}{3} M^{\uparrow 2}(E) D_1^{\uparrow}(E) \right. \\ & \quad \left. + \frac{2}{3} M^{\downarrow 2}(E) D_{-1}^{\downarrow}(E) - \frac{2}{3} M^{\downarrow 2}(E) D_1^{\downarrow}(E) \right] \\ & + (0.500)^2 \left[\frac{2}{3} M^{\uparrow 2}(E) D_0^{\uparrow}(E) - \frac{2}{3} M^{\downarrow 2}(E) D_0^{\downarrow}(E) \right] \end{aligned}$$

$$I_{L_2}(E) \sim \quad (4.73)$$

$$\begin{aligned} & (1.226)^2 \left[\frac{2}{3} M^{\uparrow 2}(E) D_{-2}^{\uparrow}(E) - \frac{2}{3} M^{\downarrow 2}(E) D_2^{\downarrow}(E) \right] \\ & + (0.869)^2 \left[\frac{1}{3} M^{\uparrow 2}(E) D_{-1}^{\uparrow}(E) - \frac{1}{3} M^{\uparrow 2}(E) D_1^{\uparrow}(E) \right. \\ & \quad \left. + \frac{1}{3} M^{\downarrow 2}(E) D_{-1}^{\downarrow}(E) - \frac{1}{3} M^{\downarrow 2}(E) D_1^{\downarrow}(E) \right] \\ & + (0.500)^2 \left[-\frac{2}{3} M^{\uparrow 2}(E) D_0^{\uparrow}(E) + \frac{2}{3} M^{\downarrow 2}(E) D_0^{\downarrow}(E) \right] \end{aligned}$$

4.5 X-ray Spectra of Heavy Rare Earths at the L_3 , L_2 edges

Introduction

At the L -edge of the rare earths, the x-ray spectra contain information about magnetic states involving $5d$ electrons. This information is important because the $5d$ electrons play an essential role in coupling the $4f$ moments with each other (the RKKY mechanism), which results in the often exotic magnetic structures exhibited by rare earth materials. In principle, XMCD (XRMS) can yield a profile of magnetic character of the $5d$ electrons near each rare earth atom in a magnetic material. However, the XMCD sum rules for orbital(109) and spin moments(110), which have been valuable for obtaining insight into $3d$ magnetic states for transition metal magnets, are not applicable, and systematic studies are needed to sort out the precise way the XMCD (XRMS) spectra are related to the $5d$ electronic structure(115; 116).

This is not a easy task, since there are strong exchange effects (with $4f$ electrons), a significant spin-orbit interaction, crystal field and band structure effects, all contributing to the final spectra.

One of the most intriguing and not well understood issues is the so-called “branching ratio (BR)” problem in the rare earths(117). This is the L_3/L_2 XMCD (XRMS) intensity ratio and without spin-orbit coupling (SOC) in the $5d$ states it is expected to have a value of -1 (1) in the case of $2p \rightarrow 5d$ transitions. However the measured values are quite different - for heavy rare earths the L_3 intensity is significantly larger than the corresponding L_2 intensity and for light rare earths the inverse is true. To evaluate the L_3 and L_2 spectra there have been several atomic model calculations which used parameters and concluded that the primary influence on the ratio was interaction between the partially unfilled $4f$ orbitals and $5d$ states(103; 104; 105). However, rather than resort to a parameterized atomic calculation, it is not just of interest but also important to see if a straight forward first principles band structure calculation can reproduce the experimental results and establish what causes the large variation in the ratio and its relation to the underlying electronic structure

Computational details

The calculations were performed using the self-consistent scalar relativistic full potential LAPW method with the LSDA+U approach for consideration of the local $4f$ electronic orbitals(118). The SOC was added in the self-consistent iteration by the second variation method. To obtain accurate wave functions (including the empty valence states) the calculations were well converged by using $R_{MT} = 3.2a.u.$ and $R_{MT}K_{max} = 9.0$ with 1008 k -points in the irreducible Brillouin zone (IBZ). These parameters have been used during all the calculations.

The experimental data discussed in this paper were obtained using XRMS for an incommensurate magnetically ordered state in $RENi_2Ge_2$ ($RE = Gd, Tb, Dy, Ho, Er, Tm$)(119). Because the incommensurate ordering is problematic for direct band structure techniques we restricted ourselves to evaluating the magnetic ground state for hcp heavy rare earth elements

with the experimental lattice constants for the ferromagnetic state (for XMCD) and for XRMS a fictitious antiferromagnetic state was used. In this way we are missing some of the crystal specific band structure effects. However the on-site $4f - 5d$ exchange, the spin effects on the radial matrix elements and the spin orbit coupling should all be reasonably independent of crystal structure.

The values of the on-site Coulomb U -potentials for the $4f$ local orbitals were chosen with two aspects in mind. Firstly, the unoccupied $4f$ states should be pushed up above the Fermi level, and secondly, the U influence on the occupied $4f$ states was fixed so that the occupied m_l states had a net orbital moment of zero for all the heavy rare earth elements. While, except Gd, this does not yield the proper Hund's rule ground state, it allows us to exclude the $4f$ orbital effects on the spectra and to isolate the influence of SOC within the $5d$ states. We used a Lorentzian broadening to take account of the core hole lifetime which is about $3 \sim 4$ eV for the L_3 and L_2 edges in heavy rare earth elements(120). A Gaussian smearing of about 2 eV was included to account for instrumental resolution.

We have not included E2 or quadrupole transitions, which are considerably smaller than the dipole transitions considered. With the x-ray energy tuned near the L -edges, an electron in a $2p$ state is excited to an empty d or s state and leaves a core hole state. For transition metals (Fe, Ni) the final state effects caused by the presence of the core hole have been invoked to explain some discrepancies between calculation and experiment(121; 122). We believe any such effects will be much smaller for $5d$ states because the bands are in general much broader (~ 10 eV) than the more local $3d$ states of Ni and Fe. These effects have not been included in the calculation.

Results & discussion

Early first principles band structure calculations for XMCD spectra at the L_3 and L_2 edges of Gd metal(92; 94) gave good results when compared with experiment for the sign, shape and magnitude of the spectra. The sign of the spectra was reversed from what would be expected from a simple argument involving more unoccupied spin down $5d$ states compares

Figure 4.5 Typical radial densities of the spin-polarized 5d wave functions, showing overlap with the 4f and 2p states.

to unoccupied spin up states. However, this was explained by the spin up radial functions being more localized and having a considerably larger magnitude in the region of the 2p radial functions(92; 123; 124). Fig.4.5 shows clearly that the spin up 5d radial functions are pulled in relative to the spin down functions because of their stronger exchange interaction with the localized 4f orbitals and have a larger overlap region with the 2p radial functions. This larger overlap region causes larger matrix elements for transitions to spin up bands. The difference between spin up and down radial matrix elements can be as large as 30% in rare earth compounds. Because these interactions occur deep within the rare earth atoms, they will not be affected by the crystal environment and should be essentially the same for all rare earth compounds. Since the contraction of spin up radial wave functions originates from the 4f – 5d exchange interaction we can expect the the difference in the spin up and spin down 5d radial functions is proportional to the net spin moment of the 4f states. It is also expected that in the heavy rare earths the difference between the spin up and down radial matrix elements decreases with increasing 4f electrons just like the conduction electron magnetization. Fig.4.6 shows the energy dependence of the radial dipole matrix elements calculated for Gd and Er. It clearly shows that Gd which has “7” 4f electrons has not only larger matrix elements than

Figure 4.6 The energy dependence of the radial dipole matrix elements calculated for Gd (red) and Er (blue). It clearly shows the radial matrix elements depend on the magnetic states. In this figure, Fermi energy is located 0eV

Er which has “11” 4f electrons but also there is a larger difference between the spin up and down matrix elements. The figure also demonstrates the strong dependence of radial wave functions on band energy. The lower energy states have bonding character, while the empty states above the Fermi energy develop antibonding character, and near the top of the 5d band they are more strongly localized and have the largest dipole matrix elements with 2p states. The atomic models do not contain this solid states effect, but they did include a parameterized spin dependence, a so-called “breathing” parameter(103), to solve the “sign problem”.

Besides being spin polarized, the band structure calculations must be relativistic so that SOC is included when obtaining the conduction electron states. Without SOC, m_l partial density of states are symmetric so that

$$D_{m_l=-2}^{m_s} = D_{m_l=2}^{m_s}$$

$$D_{m_l=-1}^{m_s} = D_{m_l=1}^{m_s}$$

With these conditions (no SOC), we can obtain the L_3, L_2 intensity expression from eq.(4.72),

eq.(4.73) as

$$\begin{aligned}
 I_{L_3}(E) &\sim (1.226)^2 \left(\frac{2}{3}\right) [-M^{\uparrow 2}(E) D_{-2}^{\uparrow}(E) + M^{\downarrow 2} D_{-2}^{\downarrow}(E)] \\
 &+ (0.500)^2 \left(\frac{2}{3}\right) [M^{\uparrow 2}(E) D_0^{\uparrow}(E) - M^{\downarrow 2} D_0^{\downarrow}(E)] \\
 I_{L_2}(E) &\sim (1.226)^2 \left(\frac{2}{3}\right) [M^{\uparrow 2}(E) D_{-2}^{\uparrow}(E) - M^{\downarrow 2} D_{-2}^{\downarrow}(E)] \\
 &+ (0.500)^2 \left(\frac{2}{3}\right) [-M^{\uparrow 2}(E) D_0^{\uparrow}(E) + M^{\downarrow 2} D_0^{\downarrow}(E)]
 \end{aligned}$$

from which it is easy to show

$$I_{L_3}(E) = -I_{L_2}(E)$$

Indeed, with just exchange and without SOC in the $5d$ states, the L_3/L_2 ratio is exactly $1 : -1$ for XMCD. This result assumes the $2p_{1/2}$ and $2p_{3/2}$ radial functions are the same. Relaxing this approximation and using the actual radial function for the $2p$ core states results in larger intensity in L_2 than in L_3 but the difference is less than 1%.

Fig.4.7 shows the integrated intensity squared for XMCD spectra (normalized to the Gd L_3 value) vs. the $de - Gennes$ factor for heavy rare-earth metals. It is the $4f - 5d$ exchange interaction that gives the over-all trend of the intensity proportional to the $de - Gennes$ factor. The SOC makes L_3, L_2 intensity unequal and gives rise to a branching ratio differing from unity. For Gd the SOC is considerably smaller than exchange, while for Er and Tm the SOC is comparable or even larger than the exchange splitting (Fig.4.9). With SOC the L_3/L_2 ratio becomes comparable with the experimental values (Fig.4.10). It is interesting to compare the intensities of the spectra which are calculated for the ferro (Fig.4.7) and anti-ferro (Fig.4.8) magnetic ordered states. Since they have quite different $5d$ empty states - density of states and magnetic moments (See Table 4.2, Fig.4.11, and Fig.4.12), it would be expected that the intensities of spectra are also very different. However, surprisingly, they have quite similar over-all trends. This provides some evidence that the contribution of the radial transition matrix elements is local and dominant component to other details of the electronic structure. As discussed above, while the number of $5d$ empty states are affected somewhat by magnetic ordering, the radial wave functions in the core region (inside the $4f$ orbital) need not be greatly affected.

Figure 4.7 The integrated intensity of XMCD spectra of the ferromagnetic ordered rare earths. For comparison with XRMS, the values are obtained by integration the sums of the squared real and imaginary parts of the XMCD spectra which are related by the K-K relation and normalized to the Gd L_3 value. The middle green diamonds represent results without SOC which yield $L_3 = L_2$. With SOC, while L_2 (red triangles) intensities are decreased, the intensity of L_3 (blue squares) are increased.

Figure 4.8 The integrated intensity of XRMS spectra for the anti-ferro magnetic ordered rare earths.

Figure 4.9 The comparison of the exchange energy and spin-orbit coupling energy in heavy rare earth atoms. They have been calculated using an atomic code.

Figure 4.10 Branching ratio vs. de Gennes factor for heavy rare earths. The experimental data (blue squares) were obtained for $ReNi_2Ge_2$ (119). The calculational results with SOC (red circles) are comparable with the experimental values. The green circles are the results without SOC

Table 4.2 The 5*d* magnetic moments (μ_B) of the heavy rare earths in the ferro, and anti-ferro magnetically ordered states.

	FERRO	ANTI-FERRO
Gd	0.4485	0.3491
Tb	0.4247	0.3011
Dy	0.3981	0.2492
Ho	0.3665	0.2200
Er	0.3159	0.1457

Figure 4.11 Gd 5*d* density of states in the ferro, and anti-ferro magnetic ordered states at a single site. Red represents the spin up states and blue is for spin down states. It shows clearly the ferromagnetic state has larger exchange splitting than the anti-ferromagnetic state.

Figure 4.12 The $m_l = \pm 2$ components of Gd 5d density of states in the ferro, and anti-ferro magnetic ordered states are shown. Red and blue represent spin up and down states respectively.

Figure 4.13 The Gd and Er spectra which arise from the $m_l = \pm 2$ components (blue lines). For comparison, the spectra calculated with all components of the wave function (red lines) are included. It shows the importance of $m_l = \pm 2$ components.

Figure 4.14 XMCD spectra of Er which is calculated with two hypothetical tetragonal structures. Type (a), blue, has $a=b=6.55$ a.u., $c=10.00$ a.u. and type (b), red, has $a=b=8.10$ a.u., $c=6.55$ a.u..

One intriguing result (Fig.4.13) is that when we calculated the optical spectra using only the $m_l = \pm 2$ components of the unoccupied $5d$ conduction band states, 90% of the full spectra is reproduced, indicating the dominance and importance of these components. This result suggests that crystal field effects and moment direction (which influence the position and occupation of angular momentum components of the $5d$ states) may be important and detailed analysis for other crystal structures and magnetic orderings will need further study if the XMCD and XRMS spectra are to be fully exploited. As a preliminary calculation for addressing the influence of crystal field, we have calculated the XMCD spectra of Er which has two hypothetical structures (Fig.4.14). Both structures are tetragonal but type(a) has a larger c -lattice constant ($c/a = 1.53$) and type(b) has a smaller c -lattice constant ($c/a = 0.81$). It shows the sensitivity of the spectra to the crystal structure.

With this result, we can further simplify the XMCD intensity formula just using $m_l = \pm 2$

components. From eq.(4.72), eq.(4.73) we obtain

$$I_{L_3}(E) \sim (1.226)^2 \left[\frac{1}{3} M^{\uparrow 2}(E) D_{-2}^{\uparrow}(E) - M^{\uparrow 2}(E) D_2^{\uparrow}(E) \right. \\ \left. + M^{\downarrow 2}(E) D_{-2}^{\downarrow}(E) - \frac{1}{3} M^{\downarrow 2}(E) D_2^{\downarrow}(E) \right] \quad (4.74)$$

$$I_{L_2}(E) \sim (1.226)^2 \left[\frac{2}{3} M^{\uparrow 2}(E) D_{-2}^{\uparrow}(E) - \frac{2}{3} M^{\downarrow 2}(E) D_2^{\downarrow}(E) \right] \quad (4.75)$$

A different form of this result can be obtain by using two parameters α, β instead of the spin dependent radial transition matrix elements. It is possible to express the intensity using partial density of states with these parameters:

$$I_{L_3}(E) \sim \alpha \left[\frac{1}{3} D_{-2}^{\uparrow}(E) - D_2^{\uparrow}(E) + \beta D_{-2}^{\downarrow}(E) - \frac{1}{3} \beta D_2^{\downarrow}(E) \right] \\ \sim \alpha \left[\frac{1}{3} (D_{-2}^{\uparrow}(E) - \beta D_2^{\downarrow}(E)) - (D_2^{\uparrow}(E) - \beta D_{-2}^{\downarrow}(E)) \right] \\ I_{L_2}(E) \sim \frac{2}{3} \alpha (D_{-2}^{\uparrow}(E) - \beta D_2^{\downarrow}(E))$$

where α replaces the spin up radial matrix elements and β represents the ratio between spin up and down radial matrix elements. Fig.4.15 shows L_3, L_2 Gd spectra calculated with two values of α and four values of β to compare their effect on the intensity. The α values are 120, 150 and β values are 0.80, 0.82, 0.84 and 0.86 (a range comparable to Gd). For clearness, we also include the full component spectra (black) and the spectra (red) calculated for $m_l = \pm 2$. The intensities are increased with α as we expected. The interesting result is the trends related to β . With increasing β , while the L_3 spectra moved downward the L_2 spectra move upward. β can take the value between 1.0, which is the maximum when the spin up and down radial matrix elements are equal. This is the case when the spin up $5d$ wave function is not contracted by the $4f - 5d$ exchange interaction. The β and the breathing parameter in atomic calculations have some similarities. In the atomic calculation, a smaller $4f - 5d$ exchange interaction results in a smaller breathing parameter and dispersive spectra, and this corresponds to a larger β parameter. In the comparison to experimental results, it is possible that these parametrization approaches reproduce similar or better intensity results than the real band calculations. However the physical meaning of these parameters are not clear and it is hard to consider these constant parameters are able to take into account the band energy dependent radial transition matrix elements properly.

Figure 4.15 The trend of spectra with parameters α and β (See text). The spectra are calculated with $\alpha = 120, 150$ and $\beta = 0.80, 0.82, 0.84$ and 0.86 . For the comparison, the full spectra (black) and the $m_l = \pm 2$ spectra (red) are included. While the parameter α determines the peak intensity, β determines the asymmetry shape of the spectra.

Conclusion

By restriction the $4f$ orbital moment to zero and considering the influence of the spin orbit coupling (SOC) in the valence bands we have been able to demonstrate for the heavy rare earth series the very strong dependence of the L_3/L_2 branching ratio on the SOC across the heavy rare earth series elements. We note that our results do not explain the inverted trend in the light rare earths where L_2 is larger than L_3 . Here we have found the influence of the $4f$ unoccupied states with non-zero net orbital angular momentum can greatly influence the magnetic spectra through hybridization with the empty $5d$ states. This effect is not part of atomic models, but can be quite complicated in full band structure calculations. The influence of the hybridization also demands further detailed analysis.

CHAPTER 5. ELASTIC PROPERTIES CALCULATION OF $AlMgB_{14}$

5.1 Introduction

The discussion in this chapter is based on the published paper(125) titled “First Principles Calculation of Elastic Properties of $AlMgB_{14}$ ”.

Since their discovery(126), boron rich compounds that consist of B_{12} icosahedra have been the subject of numerous investigations because of their novel scientific properties and potential technical applications. Their common properties originate from B_{12} icosahedra while their individual character is determined by interstitial atoms. A common character is the refractory nature of boride compounds(127) and many practical applications of boron-rich compounds are related to this property-with uses in the field of nuclear energy, aerospace and the military(128). Recently, Ames Laboratory scientists discovered an interesting mechanical property of $AlMgB_{14}$. Its hardness reached that of the second hardest material, cubic $BN(c - BN)$ with small chemical additions- TiB_2 additions gives $35 - 46 \text{ GPa}$ hardness and Si doping gives $32 - 37 \text{ GPa}$ (129). This observation is very intriguing because $AlMgB_{14}$ is far from the conventional paradigm for ultrahard materials, lacking the usual high symmetry, small unit cell, and small bond lengths. Scientifically, it might provide a good example to investigate how hardness can be enhanced by microstructural complexity and chemical doping. It may also prove very useful because it may replace the expensive $c - BN$ for technical applications.

The structure of $AlMgB_{14}$ had been reported by Matkovich and Economy(130) and after that there have been several additional publications about its crystal structure(131; 132; 133), optical and electric properties(134; 135). These studies were experimental. Although electronic structure investigations are very important for understanding material properties, the

complexity of this material is quite formidable even for modern computational methods, and to our knowledge no previous calculations have been reported. $AlMgB_{14}$ has the orthorhombic structure with lattice constants $a = 0.5848nm$, $b = 1.0312nm$, $c = 0.812nm$, space group $Imma$, and four formula units per cell. Additionally, it has vacancies (two per cell) at the metal sites. With new parallelized computational band structure techniques, we have been able to investigate the electronic structure for this complex material and have calculated its elastic constants.

5.2 Elastic Constants

Elastic constants contain some of the more important information which can be obtained from ground state total energy calculations. A given crystal structure cannot exist in a stable or metastable phase unless its elastic constants obey certain relationships. And the elastic constants also determine the response of the crystal to external forces, as characterized by bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, and so play an important part in determining the strength of a material. Especially, the bulk and shear moduli are frequently calculated for materials when investigating their hardness. The bulk modulus calculation for a single crystal is easier than the shear modulus calculation because hydrostatic pressure does not change the crystal symmetry. However, the correlation between material hardness and shear modulus exhibits better consistency than for the bulk modulus(136). Furthermore, the whole set of elastic stiffness constants (ESCs), or elastic compliance constants (ECCs), have to be calculated to extract the theoretical polycrystalline bulk modulus and shear modulus. And, because the number of these constants increases as the crystal symmetry decreases the polycrystalline bulk and shear modulus calculations for low symmetry materials can be computationally demanding.

The elastic strain tensor ε_{ij} is related to the stress σ_{ij} by Hook's law

$$\sigma_{ij} = \sum_{k,l=1}^3 c_{ijkl} \varepsilon_{kl} \quad (5.1)$$

Using Voigt's contraction(137), this is usually written as:

$$\sigma_{\alpha} = \sum_{\beta=1}^6 c_{\alpha\beta} \varepsilon_{\beta} \quad (5.2)$$

where

$$\sigma_{\alpha} = \sigma_{ij}$$

if $\beta = 1, 2, 3$

$$\varepsilon_{\beta} = \varepsilon_{kl}$$

if $\beta = 4, 5, 6$

$$\varepsilon_{\beta} = 2\varepsilon_{kl}$$

The number of independent components of the ESC tensor $c_{\alpha\beta}$ depends on crystal symmetry. This number is 3 for a cubic material, 5 for a hexagonal one, 9 for an orthorhogonal one, and 21 for triclinic materials(137).

First principles calculations that use periodic boundary conditions assume the existence of single crystals. The calculated elastic constants can be directly compared to the experimental results if there are available single crystal data. However it is still worth while to we have approximations for polycrystalline data. There are two approximations used to calculate the extreme bulk and shear modulus for a statistically isotropic polycrystalline single phase material - the Voigt method and the Reuss method(137). The first one assumes a uniform strain and gives the bulk (B_V) and shear (G_V) moduli as functions of the ESCs.

$$B_V = \frac{1}{9}(c_{11} + c_{22} + c_{33}) + \frac{2}{9}(c_{12} + c_{23} + c_{13}) \quad (5.3)$$

$$G_V = \frac{1}{15}(c_{11} + c_{22} + c_{33}) - \frac{1}{15}(c_{12} + c_{13} + c_{23}) + \frac{1}{5}(c_{44} + c_{55} + c_{66}) \quad (5.4)$$

The second one assumes a uniform stress and gives B_R and G_R as function of the ECCs.

$$\frac{1}{B_R} = (s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{23} + s_{13}) \quad (5.5)$$

$$\frac{1}{G_R} = \frac{4}{15}(s_{11} + s_{22} + s_{33}) - \frac{4}{15}(s_{12} + s_{13} + s_{23}) + \frac{3}{15}(s_{44} + s_{55} + s_{66}) \quad (5.6)$$

If they are applied to calculate average isotropic elastic moduli for polycrystalline samples using the anisotropic single crystal elastic constants, they give the theoretical maximum (Voigt method) and minimum (Reuss method) values of isotropic elastic moduli(138). Frequently, their arithmetic averages $B = (B_V + B_R)/2$, $(G_V + G_R)/2$ are taken for an estimation of the elastic properties. The other two elastic constants describing an isotropic polycrystalline material, the Young modulus (E) and the Poisson ratio (ν), can be expressed as

$$E = \frac{9BG}{3B + G} \quad (5.7)$$

$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (5.8)$$

Additionally, we remark that the limiting values of the Voigt and Reuss approximations are the same for a polycrystalline sample of isotropic crystallites, but a difference is expected for an aggregate of anisotropic crystallites. The magnitude of the difference is a function only of the degree of elastic anisotropy possessed by the crystal under consideration. Therefore, it is useful to evaluate the percent of elastic anisotropy of materials(138). For bulk (A_B) and shear (A_G) moduli, this can be defined as

$$A_B = \frac{B_V - B_R}{B_V + B_R} \quad (5.9)$$

The elastic anisotropy of materials is a primary cause for detrimental microcracks that are induced in ceramics(139; 140).

Because the ESC tensor $\mathbf{c}$ is related to the ECC tensor $\mathbf{s}$ by

$$\mathbf{cs} = I_6$$

the polycrystalline elastic moduli for both approximations can be calculated by knowing either tensor. The ESCs can be obtained from the calculation of the materials's response to structure distortion. In first principles calculation, this information can be deduced from total energy variation with structure distortion. In fact, to calculate elastic constants, it is necessary to apply small strains to the equilibrium lattice and determine the resulting change in the total energy. The elastic constants are proportional to the coefficient of the second order in a polynomial fit of the total energy as a function of the distortion parameter δ (141).

Table 5.1 Independent parameters describing elastic properties

Crystal Structure	Parameters
Cubic	c_{11}, c_{12}, c_{44}
Hexagonal	$c_{11}, c_{12}, c_{13}, c_{33}, c_{55}$
Tetragonal	$c_{11}, c_{12}, c_{13}, c_{33}, c_{44}, c_{66}$
Trigonal	$c_{11}, c_{12}, c_{13}, c_{14}, c_{33}, c_{44}$
Orthorhombic	$c_{11}, c_{12}, c_{13}, c_{22}, c_{23}, c_{33}, c_{44}, c_{55}, c_{66}$
Monoclinic	$c_{11}, c_{12}, c_{13}, c_{22}, c_{23}, c_{33}, c_{44}, c_{51}, c_{52}, c_{53}, c_{55}, c_{64}, c_{66}$

After choosing the strain components corresponding to each ESC, we established the corresponding distortion matrix $\mathbf{D}$ for each structure. With different values of the distortion parameter, these symmetric distortion matrices transform the original lattice vector set to new distorted lattice vector sets $\mathbf{R}' = \mathbf{R}\mathbf{D}$. We calculated the total energies of these distorted crystal structures for several different distortion magnitudes. In order to remain within the elastic limit of the crystals, it is necessary to keep only small lattice distortions. The internal energy of the crystal under strain, δ , can be expanded in powers of the strain tensor with respect to the initial internal energy of the unstrained crystal in the following way:

$$E(V, \delta) = E(V_0, 0) + V_0 \left(\sum_{i=1}^6 \tau_i \xi_i \delta_i + \frac{1}{2} \sum_{i,j=1}^6 c_{ij} \delta_i \xi_i \delta_j \xi_j \right) + O(\delta^3) \quad (5.10)$$

The volume of the unstrained system is denoted V_0 and $E(V_0, 0)$ is the corresponding total energy. The τ_i in the linear term represents an component in the stress tensor. The Voigt notation has been employed for conciseness. It replaces xx, yy, zz, yz, xz and xy by 1, 2, 3, 4, 5 and 6. To take into account the symmetry of δ using the Voigt notation we introduced the factor ξ_i which takes the value 1 if the Voigt index is 1, 2, or 3 and the value 2 for 4, 5, or 6.

Since the number of independent elastic constants depends on the crystal structure, the number of strains which have to be chosen also depends on the crystal structure. The independent elastic constants with several chosen crystal structures are given Table 5.1.

In the following , we show the formula to calculate the elastic constants for three different crystal structures - cubic, hexagonal and orthorhombic.

Cubic structure

Hook's law, in cubic elastic symmetry, has the form

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix}$$

The three elastic constants (c_{11}, c_{12}, c_{44}) of cubic materials(143; 142; 144; 145) can be obtained by calculating the bulk modulus $B = (c_{11} + 2c_{12})/3$, and two shear moduli, $c_{11} - c_{12}$ and c_{44} . The bulk modulus is related to the curvature of $E(V)$,

$$B(V) = VE''(V) = V \frac{d^2 E(V)}{dV^2}$$

where V is the volume of the unit cell, $E(V)$ is the energy/unit cell at volume V . Since the calculations only provide a set of energies $E(V_i)$ for a limited number of volumes V_i , the second derivative $E''(V)$ must be approximated. It can be calculated by making a least squares fit of the computed energies.

The shear moduli require knowledge of the derivative of the energy as a function of a lattice strain. In the case of a cubic lattice it is possible to choose this strain so that the volume of the unit cell is preserved. For the calculation of the modulus $c_{11} - c_{12}$, the distortion matrix D_1 can be chosen as

$$D_1 = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & \frac{\delta^2}{(1+\delta)^2} \end{pmatrix}$$

With this distortion matrix, the expansion of energy in powers of the strain contains only even powers. The application of this strain changes the total energy from its unstrained value to

$$E(\delta) = E(0) + 3(c_{11} - c_{12})V\delta^2 + O[\delta^4]$$

where V is the volume of the unit cell and $E(0)$ is the energy of the unstrained lattice at volume V . For the elastic modulus c_{44} , the distortion matrix D_2 can be chosen as

$$D_2 = \begin{pmatrix} 1 & \delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & \frac{1}{(1-\delta)^2} \end{pmatrix}$$

which changes the total energy to

$$E(\delta) = E(0) + 2c_{44}V\delta^2 + O[\delta^4]$$

Since these strains are constructed so that $\Delta V = 0$, the energy expansions do not have pressure or stress terms.

The general formula for the polycrystalline aggregation bulk, and shear moduli can be much simpler in cubic symmetry. They are, for the Voigt method,

$$\begin{aligned} B_V &= \frac{(c_{11} + 2c_{12})}{3} \\ G_V &= \frac{(c_{11} - c_{12} - 3c_{44})}{5} \end{aligned}$$

and, for the Reuss method,

$$\begin{aligned} B_R &= \frac{(c_{11} + 2c_{12})}{3} \\ G_R &= \frac{5(c_{11} - c_{12})c_{44}}{[4c_{44} + 3(c_{11} - c_{12})]} \end{aligned}$$

Besides the Reuss and Voigt methods for determination of general bounds of B and G , Hashin and Shtrikman(146) found improved bounds for the polycrystalline cubic systems. In isotropic materials, the shear modulus is related to the elastic moduli by

$$G^I = c_{44}^I = \frac{c_{11}^I - c_{12}^I}{2}$$

but in real crystals the anisotropy constant

$$A = \frac{2c_{44}}{c_{11} - c_{22}}$$

is not unity. In this case, it is possible only to bound the shear modulus of the aggregate which is given by

$$G_1 = G_1^* + \frac{3(G_2^* - G_1^*)}{5 - 4\beta_1(G_2^* - G_1^*)}$$

and

$$G_2 = G_2^* + \frac{2(G_1^* - G_2^*)}{5 - 6\beta_2(G_1^* - G_2^*)}$$

where

$$G_1^* = \frac{1}{2}(c_{11} - c_{12}), G_2^* = c_{44}$$

and

$$\beta_1 = -\frac{3(B + 2G_1^*)}{5G_1^*(3B + 4G_1^*)}, \beta_2 = -\frac{3(B + 2G_2^*)}{5G_2^*(3B + 4G_2^*)}$$

The Shtrikman bound G_S is designed as the smaller of G_1 and G_2 while the Hashin bound G_H is the larger.

Hexagonal structure

For a hexagonal structure(147; 148), there are five independent elastic constants, usually referred to as $c_{11}, c_{12}, c_{13}, c_{33}, c_{55}$. Hook's law, in hexagonal structure, has the form

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{55} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & (c_{11} - c_{12})/2 \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix}$$

The theoretical treatment of the elastic constants of hexagonal systems is thus considerably more involved than for cubic materials. Since five different strains are required to determine five independent elastic constants, five distortions which are described below have to be employed for the investigation of hexagonal elastic constants. The first distortion matrix (D_1) is written as

$$D_1 = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

It changes the size of the basal plane, while keeping the z -axis constant. The symmetry of the strained lattice is still hexagonal. The energy associated with this distortion can be given

as

$$E(V, \delta) = E(V_0, 0) + V_0[(\tau_1 + \tau_2)\delta + (c_{11} + c_{12})\delta^2]$$

The second distortion matrix (D_2) is written as

$$D_2 = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 - \delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This distortion changes the x and y lattice in opposite direction while z lattice is kept in constant and the resulting distorted structure has monoclinic symmetry. The energy is expressed as

$$E(V, \delta) = E(V_0, 0) + V_0[(\tau_1 - \tau_2)\delta + (c_{11} - c_{12})\delta^2]$$

The third distortion matrix (D_3) is given as

$$D_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 + \delta \end{pmatrix}$$

and the energy is

$$E(V, \delta) = E(V_0, 0) + V_0(\tau_3\delta + \frac{c_{33}}{2}\delta^2)$$

The fourth distortion matrix (D_4) is written as

$$D_4 = \begin{pmatrix} 1 & 0 & \delta \\ 0 & 1 & 0 \\ \delta & 0 & 1 \end{pmatrix}$$

This distortion reduces the symmetry and produces the triclinic structure. The energy can be written as

$$E(V, \delta) = E(V_0, 0) + V_0(\tau_5\delta + 2c_{55}\delta^2)$$

The last elastic constant c_{13} can be obtained by hydrostatic compression which is expressed by the distortion matrix

$$D_5 = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & 1 + \delta \end{pmatrix}$$

The energy is given as

$$E(V, \delta) = E(V_0, 0) + V_0[(\tau_1 + \tau_2 + \tau_3)\delta + \frac{1}{2}(c_{11} + 2c_{12} + 4c_{13} + c_{33})\delta^2]$$

Since the hydrostatic compression is also related to the bulk modulus, it is possible to represent the bulk modulus with these elastic constants. The bulk modulus is defined by

$$\begin{aligned} B &= V_0 \frac{d^2 E}{dV^2} \\ &= \frac{1}{9V_0} \frac{d^2 E}{d\delta^2} \\ &= \frac{2}{9}(c_{11} + c_{12} + 2c_{13} + \frac{1}{2}c_{33}) \end{aligned}$$

The Voigt and Reuss bounds, when expressed in c_{ij} , take the form

$$\begin{aligned} B_V &= \frac{1}{9}[2(c_{11} + c_{12}) + c_{33} + 4c_{13}] \\ G_V &= \frac{1}{30}[12c_{66} + 12c_{44} + c_{11} + c_{12} + 2c_{33} - 4c_{13}] \\ B_R &= \frac{(c_{11} + c_{12})c_{33} - 2c_{13}^2}{c_{11} + c_{12} + 2c_{33} - 4c_{13}} \\ G_R &= \frac{5}{2} \left[\frac{c_{44}c_{66}[(c_{11} + c_{12})c_{33} - 2c_{13}^2]}{(c_{44} + c_{66})[(c_{11} + c_{12})c_{33} - 2c_{13}^2] + 3B_V c_{44}c_{66}} \right] \end{aligned}$$

Orthorhombic structure

An orthorhombic structure(140) has 9 independent elastic constants which are referred to as $c_{11}, c_{12}, c_{13}, c_{22}, c_{23}, c_{33}, c_{44}, c_{55}, c_{66}$. Hook's law, in hexagonal structure, has the form

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{13} & c_{23} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix}$$

Since the number of required strain and deformation matrices is the same as the number of independent elastic constants, we have to construct nine deformation matrices for the orthorhombic structure. In this case, we can classify the distortion matrices in three groups. The first distortion group preserves the symmetry but changes the volume, the second group is volume conserving monoclinic shear distortions and the last is volume conserving orthorhombic distortions which conserve not only volume but also symmetry. The three elastic constants c_{11}, c_{22}, c_{33} are included in the first group, c_{44}, c_{55}, c_{66} are included in second, and c_{12}, c_{13}, c_{23} are included in the last group. For the first group, distortion matrices and energy relations are given as

$$D_1 = \begin{pmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$D_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1+\delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and

$$D_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\delta \end{pmatrix}$$

$$E(V, \delta) = E(V_0, 0) + V_0 \left(\tau_1 \delta + \frac{c_{11}}{2} \delta^2 \right),$$

$$E(V, \delta) = E(V_0, 0) + V_0 \left(\tau_2 \delta + \frac{c_{22}}{2} \delta^2 \right)$$

and

$$E(V, \delta) = E(V_0, 0) + V_0 \left(\tau_3 \delta + \frac{c_{33}}{2} \delta^2 \right)$$

They correspond to straining the lattice along the x , y , and z axis, respectively. For the second group,

$$D_4 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & \frac{\delta}{(1-\delta^2)^{1/3}} \\ 0 & \frac{\delta}{(1-\delta^2)^{1/3}} & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix},$$

$$D_5 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & \frac{\delta}{(1-\delta^2)^{1/3}} \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ \frac{\delta}{(1-\delta^2)^{1/3}} & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$$

and

$$D_6 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & \frac{\delta}{(1-\delta^2)^{1/3}} & 0 \\ \frac{\delta}{(1-\delta^2)^{1/3}} & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$$

$$E(V, \delta) = E(V_0, 0) + V_0 \left(2\tau_4 \delta + 2c_{44} \delta^2 \right),$$

$$E(V, \delta) = E(V_0, 0) + V_0 \left(2\tau_5 \delta + 2c_{55} \delta^2 \right)$$

and

$$E(V, \delta) = E(V_0, 0) + V_0 \left(2\tau_6 \delta + 2c_{66} \delta^2 \right)$$

For the last,

$$D_7 = \begin{pmatrix} \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix},$$

$$D_8 = \begin{pmatrix} \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} \end{pmatrix}$$

and

$$D_9 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} \end{pmatrix}$$

$$E(V, \delta) = E(V_0, 0) + V_0 \left[(\tau_1 - \tau_2)\delta + \frac{1}{2}(c_{11} + c_{22} - 2c_{12})\delta^2 \right],$$

$$E(V, \delta) = E(V_0, 0) + V_0 \left[(\tau_1 - \tau_3)\delta + \frac{1}{2}(c_{11} + c_{33} - 2c_{13})\delta^2 \right]$$

and

$$E(V, \delta) = E(V_0, 0) + V_0 \left[(\tau_2 - \tau_3)\delta + \frac{1}{2}(c_{22} + c_{33} - 2c_{23})\delta^2 \right]$$

The elastic constants c_{12} , c_{13} , c_{23} are given with the superposition of the already calculated elastic constants c_{11} , c_{22} , c_{33} .

5.3 Computational Details & Results

For $AlMgB_{14}$ we used the parallelized full-potential, linear augmented plane wave method (FPLAPW)(149) within the local-density approximation with the *Hedin–Lundqvist* exchange correlation potential(29). Most of these calculations were performed using the SP machine at NERSC. We iterated with the equivalent of 64 k -points in the whole Brillouin zone to calculate self-consistent total energies. The number of augmented plane waves for these calculations was about 3500. The muffin-tin radius is 1.5 *a.u.* for B atoms, 2.2 *a.u.* for Al atoms and 2.7 *a.u.* for Mg atoms. The value of the plane-wave cutoff $KR_{max} = 6.0$ was determined by the radius of the B atoms because they have a much smaller muffin-tin radius than the metal atoms. We calculated both the 64 atoms per cell case and 62 atoms per cell case, which has two vacancies at metal sites(130; 132). As shown in Fig.5.1 one vacancy is at the Al site (0.0, 0.5, 0.0) and another is at the Mg site (0.75, 0.5, 0.391).

Figure 5.1 Crystal structure of $AlMgB_{14}$ with two vacancies at metal sites. The red spheres are Mg atoms, blue are Al atoms, white are vacancy sites and green are boron atoms and icosahedra. The vertical direction is along $(0, 1, 0)$ and the horizontal direction is along $(0, 0, 1)$

Figure 5.2 Calculated density of states for $AlMgB_{14}$ with 62 atoms/cell. The Fermi level lies below a band gap of about 1eV and there is one hole per cell. The states below the gap are predominantly due to boron, while the states above the gap are primarily due to Al and Mg.

Calculations for the full 64 atoms per cell structure show that the *Fermi* level lies in states above a band gap of about 1eV. With the observed 25% vacancies on the Al and Mg sites, calculations indicate that the *Fermi* level falls below the gap, near the top of a broad set of bands having predominantly boron character (see Fig.5.2). The vacancies lower the total energy per atom below that of the 64 atoms per cell structure. For the 62 atoms case, the top most valence band is half full (one hole per unit cell), and thus ordered vacancies, the scattering of electrons near the top of occupied boron bands at the *Fermi* level can be very high and some of the electronic states could become localized. One would thus expect transport properties such as electrical resistivity to be sensitive to sample preparation methods since processing parameters such as cooling rate will determine the degree of ordering of the vacancies and induce other microstructural defects affecting scattering. It is also possible that the vacancies could cluster locally (*e.g.* near defects or grain boundaries) and thus affect the local electronic structure, causing some parts to be ceramic like and others parts to have some degree of metallic behavior. Chemically doping the sample, for example with Si, would add electrons to the valence band. It is expected that when the valence bands are completely filled and the *Fermi* level lies within the gap, the material will have maximum resistivity, and properties may change rapidly as the nature of the electronic states at the *Fermi* level change quickly with doping. Fig.5.3 shows the *DOS* for the sample which has one Si atom at a Al site and two vacancies at metal sites. The *Fermi* level lies in the gap. There are *Si* impurity states in the original 1eV gap.

With vacancies, the positions of atoms surrounding each vacancy are slightly shifted from the ideal lattice coordinates. The new relaxed position can be ascertained using total force calculations(150; 151). Although this results in lower total energy, it is well known that atomic position relaxation usually gives smaller elastic constants than for unrelaxed case(152). Since the atoms which are on the relaxation resulted positions have the optimized (minimized) forces which respond the structure distortions, it is possible that the relaxation decreases elastic constants. Fig.5.4 is the *DOS* for the 62 atoms per cell case with optimized atomic positions. For this calculation, the 62 atoms are relaxed until the force components exerted on each atom

Figure 5.3 Calculated unrelaxed density of states for AlMgB_{14} with Si doping. One Si atom replaces one Al atom with two vacancies at metal sites. The Fermi level lies in the gap. There are Si impurity states in the original 1 eV gap.

Figure 5.4 Calculated density of states for $AlMgB_{14}$ with relaxed 62 atoms/cell. It shows the decreased number of states near the Fermi level compared to the unrelaxed case.

Table 5.2 Calculated elastic stiffness constants for both 64 atoms/cell and 62 atoms/cell $AlMgB_{14}$ (the numbers within parentheses are fitting errors.)

	64 atoms (GPa)	62 atoms (GPa)
c_{11}	545(1.89)	503(1.45)
c_{22}	538(0.81)	500(1.63)
c_{33}	531(2.27)	496(2.86)
c_{44}	199(0.03)	183(0.00)
c_{55}	254(0.67)	252(0.10)
c_{66}	221(0.04)	211(0.06)
$c_{11} + c_{22} - 2c_{12}$	1011(14.93)	936(11.23)
$c_{11} + c_{33} - 2c_{13}$	929(8.79)	844(0.78)
$c_{22} + c_{33} - 2c_{23}$	988(16.2)	927(8.79)
c_{12}	36(8.82)	33.5(7.16)
c_{13}	73.5(6.48)	77.5(2.55)
c_{23}	40.5(9.64)	34.5(6.64)

are decreased to $< 0.014(eV/\text{\AA})$. Compared with the unrelaxed case, the total energy is lower and the DOS is decreased near *Fermi* level (see Fig.5.2). Although the relaxed structure is more stable than the unrelaxed one, preliminary calculation for relaxed $AlMgB_{14}$ shows that the elastic constants do not change much in the optimized case.

Table 5.2 shows the ESCs obtained by polynomial fits to the total energy and Table 5.3 gives the calculated elastic properties for both the 64 and 62 atom case. Included in Table 5.3 are the two extreme values (Voigt and Reuss), and the average. Most of the constants are

Table 5.3 Elastic properties-bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson ratio (ν)-of polycrystalline $AlMgB_{14}$ calculated with the Voigt and Reuss methods

	64 atoms	62 atoms
B_V (GPa)	212.67	198.89
B_R (GPa)	212.13	184.03
B_{ave} (GPa)	212.40	191.46
G_V (GPa)	232.40	219.43
G_R (GPa)	230.12	211.98
G_{ave} (GPa)	231.26	215.71
E (GPa)	509.04	470.45
ν	0.1	0.09

Table 5.4 Percentage anisotropy of bulk (A_B) and shear (A_G) are given along with the calculated longitudinal (C_L), transverse (C_T), and average (C_M) sound velocities. The transverse modes are degenerate in isotropic polycrystalline materials

	64 atoms	62 atoms
$A_B(\%)$	0.13	3.88
$A_G(\%)$	0.49	1.73
$C_L(km/s)$	13.8	13.4
$C_T(km/s)$	9.17	9.01
$C_M(km/s)$	10.03	9.84

slightly decreased with the presence of vacancies. The calculated bulk and shear moduli are not as big as those for superhard materials, which is to be expected for $AlMgB_{14}$, because the superhardness of $AlMgB_{14}$ compounds is attained only by chemical and microstructural modification. The measured Vicker's hardness of $AlMgB_{14}$ is 27 – 28 GPa for a single crystal(133) and 32 – 35 GPa for a polycrystalline sample(129). The calculated value of the shear modulus of $AlMgB_{14}$ (215 GPa) is similar with those of B_6O (204 GPa), rutile- SiO_2 (220 GPa), and SiC (196 GPa). The corresponding microhardnesses are 35, 33, 29 GPa. $AlMgB_{14}$ has a reasonable position on the shear modulus *v.s.* hardness plot (Fig.5.5)(136). Another interesting quantity given in Table 5.3 is the Poisson ratio. This has been used to characterize bonding, with $\nu = 0.25$ suggested as the low limit for a central force solid(140). The low Poisson ratio(~ 0.1) of $AlMgB_{14}$ and the large value of the ratio of the shear modulus to bulk modulus ($G/B = 1.13$) suggest that this material has noncentral, directional covalent bonds(153).

Table 5.4 shows the calculated anisotropy and elastic wave velocity in $AlMgB_{14}$, with the assumption that this material is isotropic polycrystalline. The relationships between the sound wave velocity and the elastic constants are

$$C_L = \left[\frac{B + \frac{4}{3}G}{\rho} \right]^{1/2} \quad (5.11)$$

$$C_T = \left[\frac{G}{\rho} \right]^{1/2} \quad (5.12)$$

and their average is

$$C_M = \left[\frac{1}{3} \left(\frac{2}{C_T^3} + \frac{1}{C_L^3} \right) \right]^{-1/3} \quad (5.13)$$

Figure 5.5 Plot of microhardness *vs.* shear modulus for various materials (see Ref.(136)). The filled circle shows the position of $AlMgB_{14}$.

The transverse modes are degenerate in isotropic polycrystalline materials(137). One interesting observation is that the sound wave velocity approaches that of the diamond. Even though there are vacancies, $AlMgB_{14}$ has nearly isotropic elastic properties. This might be explained by consideration of the role of icosahedra in boron-rich solids. The nearly isotropic elastic properties of boron rich solids could be a common character that might be attributed to the icosahedra skeleton. The icosahedra are centered at $(0.25, 0.25, 0.25)$, $(0.25, 0.75, 0.25)$, $(0.75, 0.25, 0.75)$ and $(0.75, 0.75, 0.75)$ in $AlMgB_{14}$ and are highly symmetric (see Fig.4.1).

In summary, we have calculated elastic properties: elastic constants, elastic anisotropy and elastic wave velocities for $AlMgB_{14}$. The elastic moduli and the measured microhardness are consistent with other hard materials, but there is little that can be directly related to the dramatic increase in hardness caused by Si doping. The microstructure of these chemically modified samples needs to be investigated. Experiments on the optical properties and even the electrical conductivity would help elucidate the electronic structure and the possible role of defects and doping.

CHAPTER 6. CONCLUSION

In this thesis, we have applied first principles methods to the investigation of interesting and important physical questions. In the x-ray spectra, we have established the importance of spin-orbit coupling in the branching ratio problem of the heavy rare-earth series L -edges and obtained results which are in reasonable agreement with the experimental results. In the elastic properties calculation, we have also obtained reasonable position for $AlMgB_{14}$ in the materials trend of shear modulus *vs.* hardness. However, in this thesis work, we have raised more questions which have to be answered than which have been answered. The influence of crystal field is the one of questions which have to be considered. And the non-collinear calculation has to be performed for considering specific magnetic orderings. The influence of the hybridization of $5d$ and $4f$ unoccupied states with non-zero net orbital angular momentum on the spectra also demands careful study. The final state calculations with supercells are worth performing to accounting for the core-hole effects. The light rare-earths cases are much more problematic the the heavy rare-earth cases. We hope our insights are valuable and lead to further investigations toward a more complete understanding of the variations in branching ratio.

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He gives power to the weak, and to those who have no might He increases strength. Even the youths shall faint and be weary, and the young men shall utterly fall, but those who wait on the LORD shall renew their strength; they shall mount up with wings like eagles, they shall run and not be weary, they shall walk and not faint. (ISAIAH 41:29)

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I would like to thank to and share this happy moment with my family - Hyejin, David, and Jennie. They were willing to bear the hard, boring time with a physics graduate student. I am sure I could not come this moment without their love and patient support.

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