X-ray magnetic circular dichroism at rare-earth L\textsubscript{23} absorption edges in various compounds and alloys

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Abstract

Theoretical interpretations of X-ray magnetic circular dichroism (XMCD) at rare-earth (called R hereafter) L\textsubscript{23} absorption edges are reviewed using differing models, depending on the material under investigation. In the first chapter, we present an overview of recent developments for XMCD in XAS with a few general remarks, especially at R atom absorption edges. In Section 2, we first describe basic mechanism of XMCD at L\textsubscript{23} edges of R systems, and then we essentially discuss two examples of XMCD spectra in: (i) R\textsubscript{2}Fe\textsubscript{14}B metallic compounds, with the help of a cluster model, and (ii) RFe\textsubscript{2} Laves-phase compounds, using a tight-binding approximation for R 5d and Fe 3d conducting states. A good agreement between theory and experiment for R\textsubscript{2}Fe\textsubscript{14}B suggests that a cluster model provides a valuable method to quantitatively calculate XMCD spectra of R systems, even with quite complicated atomic arrangements. For RFe\textsubscript{2} systems the XMCD spectral shape, especially for the L\textsubscript{2} edge of heavy R elements, is more complicated than those of R\textsubscript{2}Fe\textsubscript{14}B systems, and this is explained by the competition of some different XMCD mechanisms.

In Section 3, we focus on special series of Ce systems, related to XAS and XMCD studies at the Ce L\textsubscript{23} edges. Two clearly differing cases are interpreted: (i) A well localized 4f\textsuperscript{1} system, i.e. CeRu\textsubscript{2}Ge\textsubscript{2}; (ii) A less localized 4f\textsuperscript{1} system, i.e. CeFe\textsubscript{2}, with a 3d partner. Then, from a more experimental point of view, we investigate the influence of substitution on the low temperature properties of CePd\textsubscript{3} compounds, i.e. Ce(Pd\textsubscript{1−x}Mn\textsubscript{x})\textsubscript{3} alloys where x is about 0.03, giving rise to (CePd\textsubscript{3})\textsubscript{3}Mn ordered structure. We give another example: Ce(Pd\textsubscript{1−x}Ni\textsubscript{x})\textsubscript{3} alloys with x taken up to about 0.25. Also the Ce L\textsubscript{23} XMCD signal measured in pure CePd\textsubscript{3} demonstrates that in the Ce based dense Kondo materials, only the 4f\textsuperscript{1} channel yields a magnetic response.

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Abbreviations: AES Auger electron spectroscopy; CF crystal field; DOS density of states; ED electric dipole; \(E_F\) Fermi energy; EQ electric quadrupole; \(E_{\text{exc}}\) exchange splitting energy; FL Fermi liquid; FWHM full width at half maximum; MCD magnetic circular dichroism; MV mixed valence; NM non-magnetic; R rare earth; \(R_E\) reduction factor of 4f–5d exchange energy; \(R_m\) reduction factor of Slater integrals; RXES resonant X-ray emission spectroscopy; RIXS resonant inelastic X-ray scattering spectroscopy; SIAM single impurity Anderson model; \(T_C\) Curie temperature; \(T_{\text{comp}}\) Compensation temperature; \(T_K\) Kondo temperature; TM Transition metal; VF valence fluctuation; XAS X-ray absorption spectroscopy; XES X-ray emission spectroscopy; XMCD X-ray magnetic circular dichroism; XPS X-ray photoelectron spectroscopy

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1. Introduction

X-ray magnetic circular dichroism (XMCD) represents the dependence of the spectral intensity on the relative orientation of the magnetization and photon helicity. Since the early 1990s this phenomenon has been widely used in a variety of X-ray spectroscopies for the element specific analysis of magnetic systems (Ebert and Schütz, 1996). XMCD is usually understood as the change in absorption when the photon helicity is reversed in a magnetic material. In the case of X-ray absorption spectroscopy (XAS) one could call this “MCD in XAS,” although the term XMCD is also widely accepted and we shall use it hereafter in the present paper. Before proceeding further, let us just also recall...
the existence of MCD in photoemission (XPS) which reflects the change in XPS spectrum when the photon helicity is reversed. Similarly MCD in Auger electron spectroscopy (AES) and X-ray emission spectroscopy (XES) is the change in the AES and XES spectra, respectively, when the photon helicity is reversed. However, in the present review, we shall focus essentially on XMCD, as defined above i.e. MCD in XAS. In the case of CeFe$_2$, we shall also report some results for MCD in resonant XES, i.e. RXES.

Actually XMCD is one of the most promising techniques to reveal local electronic and magnetic properties in a variety of magnetic materials, essentially because of its element as well as shell selectivities. In fact, with the help of circular polarized X-rays of good quality, arising from third-generation synchrotron facilities, a lot of data have been accumulated up to now on XAS and XMCD of transition-metal (TM) compounds and of rare-earth (called R hereafter) compounds. XMCD was first observed in X-ray absorption at the K threshold of Fe metal (Schütz et al., 1987). It has gained huge popularity due to the discovery of the sum rules (Thole et al., 1992; Carra et al., 1993a,b; Altarelli, 1993; Jo, 1993) which can be applied to obtain the ground state orbital and spin magnetic moments. In the present paper we review R inter-metallic systems (compounds and alloys) which contain mostly TM partners but not only. Also we focus on XMCD at the R L$^{23}$ edges, i.e. essentially 2p → 5d electronic transitions. Why do we consider these edges? Actually, XMCD at L$^{23}$ edges is an important tool to provide information on the R 5d electrons, separately from other shells, so that there are a lot of experimental data available. This kind of information is very difficult to obtain by other methods and thus crucial in order to understand the magnetic properties of the considered R based compounds.

In the first part of this paper (Section 2) we review rare earth compound series, mostly containing TM atoms, especially iron atoms. Some of them are good candidates for permanent magnets and exhibit a variety of magnetic properties. First of all we present the basic mechanism involved in XMCD spectra at L$^{23}$ edges and its various components which have to be taken into account to be able to interpret experiment properly (Section 2.1). For instance, during quite a long time, it has not been easy to draw instructive information from XMCD data (see for example, Baudelet et al., 1993): even the sign of XMCD intensities could not be predicted by a naive theory. After many challenges, Matsuyama et al. (1997) and Van Veenendaal et al. (1997) independently succeeded in explaining XMCD at R L$^{23}$ edges by introducing a novel role of the intra-atomic exchange interaction between R 5d and 4f electrons. One example of compounds is provided by the R$_2$Fe$_{14}$B metallic series (Section 2.2). Using a cluster model for the considered series of inter-metallic systems we underline the important roles of: (i) 4f–5d exchange interaction which includes the novel effect of enhancement of electric dipole (ED) intensity related to 2p → 5d transitions; and (ii) hybridization of R 5d states with spin polarized Fe 3d states of surrounding ions. For a quantitative comparison with XMCD data of these series of compounds, it was pointed out that this effect of the spin-polarized Fe 3d states has to be included. However and furthermore the electric quadrupole (EQ) transition (2p → 4f) has also to be accounted for (Fukui et al., 2001; Asakura et al., 2002). Another example of rare earth compound series is provided by RF$\text{E}_2$ type compounds in the Laves phase (Section 2.3). In the series of RF$\text{E}_2$ compounds (Section 2.3.2), the R 5d electrons exhibit a subtle exchange process between a major magnetic moment, i.e. the Fe 3d moment, and an additional one, i.e. the R 4f moment (Harada et al., 2004). The latter plays special roles in applications, in connection with magnetic anisotropy. In the present review we also consider the RA$\text{L}_2$ series (Section 2.3.5), especially when R = Sm still represents a light element of the series, i.e. SmAl$\text{L}_2$, in order to point out the role of the 4f exchange field when Fe 3d states are replaced by nonmagnetic Al 3p states. More generally, it is instructive to consider the following cases, each of which is a limiting case for the mechanism of XMCD at R L$^{23}$ edges: (i) SmAl$\text{L}_2$ (Section 2.3.5), (ii) LuFe$\text{E}_2$ (Section 2.3.4), (iii) RFe$\text{E}_2$ (Section 2.3.2) (especially, R = Gd to Tm which are the heavy elements of the series). The case (i) is a limiting case where only the effect of intra-atomic exchange interaction between 5d and 4f electrons is responsible for XMCD whereas in case (ii) the hybridization between R 5d and Fe 3d electrons is the only source to yield XMCD. In case (iii), both effects contribute to XMCD and give rise to a variety of XMCD shapes (Dartyge et al., 1998; Fujiwara et al., 2003). As far as comparison to experiment is concerned, it is to be noted that EQ contributions to the XMCD spectra ought to be also taken into account in addition to the usual ED ones. It is also to be mentioned that for XMCD at the L$_2$ edge of RFe$_2$ with heavy R elements all of three contributions, i.e. the ED contribution due to 5d–4f exchange interaction, the ED contribution due to R 5d–Fe 3d hybridization, and the EQ contribution, are weak and comparable in intensity, giving rise to a complicated spectral shape and its complicated temperature dependence.

As mentioned above, in order to understand the relationship between the XMCD spectra for R L$^{23}$ edges and the electronic and magnetic properties of R 5d, R 4f and Fe 3d states of R$_2$Fe$_{14}$B and RFe$_2$, it is essential to take into account the enhancement effect of the R 2p–5d ED transition intensity, as well as the EQ transition and the effect of R 5d–Fe 3d hybridization. On the other hand, the sum rules mentioned before cannot be applied to these XMCD spectra,
because the enhancement effect of the ED transition intensity breaks the sum rules. Therefore, no more discussion on the sum rules will be given in the present paper.

In the second part of the present review paper (Section 3) we focus on XAS and its magnetic counterpart, the XMCD at the Ce L23 edges, in order to study the specific case of Ce based systems. Especially magnetism of Ce intermetallic compounds is known to depend on the degree of localization of the 4f states and to exhibit a wide variety of behaviours from Kondo to mixed valence systems and from itinerant ferromagnets to strongly localized magnets. For many years these subjects have attracted a lot of interest of both experimentalists and theoreticians (see for example: Sereni et al., 1993; Degiorgi and Wachter, 1997; Razafimandimby et al., 1999). A very illustrative example of a manifold behaviour is magnetism of z and y phases in Ce metal (for theoretical works see Zöllf et al., 2001; Held et al., 2001). Other intriguing cases are Ce–Pd intermetallics. Let us give two examples: (i) A typical mixed valence system CePd7 (Beaurepaire et al., 1993) with a Kondo temperature \( T_K \) of about 1000 K and a Ce–Ce inter-atomic distance of 5.67 Å. Let us just recall that \( T_K \) is the temperature below which the local moment (4f in case of Ce) is compensated by the conduction electrons. (ii) A differing example is CePd3 which has a much lower \( T_K \) of about 240 K and a shorter Ce–Ce distance of 4.13 Å. In this compound 4f states are less hybridized with conduction electrons. However now, a non-negligible Ce–Ce inter-site magnetic exchange coupling is present, that could lead to a magnetic ordering of Ce moments under certain conditions.

Actually and first of all, we exhibit two clearly typical cases both from experimental and theoretical points of views: (i) A well localized 4f1 system, i.e. CeRu2Ge2 (Section 3.1), and a phenomenological interpretation of the corresponding XMCD spectra (Fukui et al., 1999): one negative peak at L3 edge and another positive peak at L2 edge. This kind of systems is characterized by \( n_f \approx 1 \) and generally magnetic ordering is developed at low temperature (\( T < 10 \) K). (ii) A less localized 4f system, i.e. CeF2 (Section 3.2) with a 3d partner (here it is Fe), and a theoretical interpretation of its XMCD spectra (Asakura et al., 2004a,b, 2005): a double peak structure (a replica of the edge). Moreover the sign of the dichroic signal is opposite to the preceding case. This kind of systems is characterized by \( n_f < 1 \) and by ferromagnetic order mainly due to the 3d TM electrons with a higher Curie temperature. Furthermore, theoretical calculations have also been performed by Asakura et al. (2005) for MCD in RXES in addition to the previously considered MCD in XAS for the mixed valence ferromagnetic compound CeFe2. It was shown that the excitation spectrum of Ce L3–M5 MCD in RXES is close to a less broadened version of the Ce L3 MCD in XAS, which reveals the structure originating from the Ce 4f5 configuration. Actually this structure is not visible by conventional Ce L3 MCD in XAS measurements.

Then (Section 3.3) we focus on CePd3 compounds which are indeed the most extensively studied Ce-based dense Kondo materials and we also study the alloying of the considered compounds with other substitutional TM elements (Mn or Ni), instead of Pd. It is generally accepted that the ground state of CePd3 can be described as a non-magnetic (NM) Fermi-liquid (FL). The electric resistivity \( \rho \) as a function of temperature shows a broad peak around 120 K, which is very close to the maximum in magnetic susceptibility. At lower temperatures, resistivity decreases, indicating the formation of a coherent FL state (Lawrence et al., 1996). This and other measurements (Arts et al., 1985; Kanai et al., 1998) suggest that the Kondo temperature of CePd3 is about 240 K, as already stated above. Moreover, resonant inverse photoemission spectra at the Ce 4d threshold (Kanai et al., 1998) show significant changes in 4f peak intensity in temperature range from 20 to 290 K. This observation indicates the tendency for the 4f electrons to become more localized at high temperatures, even though they are still itinerant around \( T_K \). Moreover here, we point out (Section 3.3.3) the remarkable Ce L23 XMCD signal measured in pure CePd3 which corresponds to a magnetic field induced effect due to the 5d paramagnetic susceptibility. It demonstrates the following result (Kappl et al., 2004): in the Ce based dense Kondo materials, only the 4f1 channel gives rise to a magnetic response. Also we investigate the influence of substitution (Singh and Dhar, 2003; Kappler et al., 2004) on the low temperature properties of CePd3 (Sections 3.3.1 and 3.3.2). At first we give an example: Ce(Pd1-xMnx)3 (Section 3.3.1) where \( x \) is about 0.03 giving rise to (CePd3)3Mn ordered compounds (Singh and Dhar, 2003). This special system is characterized by two phenomena: (i) Mn sublattice undergoes a ferromagnetic transition around 35 K; and (ii) Ce ions form a dense Kondo lattice and are in a paramagnetic state at least down to 1.5 K. Unfortunately up to now there is neither any XMCD data to confirm the previously considered results nor any corresponding theoretical analysis.

A long time ago, Veenhuizen et al. (1987) already investigated the influence of substitutions on the low temperature properties of CePd3, especially in Ce(Pd1-xNix)3 alloys. On the basis of the temperature dependent susceptibility measurements the authors suggested that Ce has a tendency to a more localized 4f1 ground state with increasing Ni content up to 0.2. Magnetization measurements of Ce(Pd1-xNix)3 alloys recorded at 4.2 K in field up to 35 T was described by the following equation: \( M(B) = M_0 + \chi_{\text{intr}} B + bB^3 \), where \( \chi_{\text{intr}} \) is the intrinsic susceptibility of CePd3.
Fig. 1. Definition of the intensities $F^\pm(\omega)$.

and $M_0$ is the magnetization of the “Ni impurity” in saturation. It means that the intrinsic susceptibility of CePd$_3$ is not suppressed through substitution of Pd by Ni. However, Veenhuizen et al. do not give any indication about possible transition to a ferromagnetic phase in these systems. This kind of transitions has already been observed several years ago in CePd$_{1-x}$Ni$_x$ alloys, in which the Ce sublattice remains basically unchanged with the same CrB structure (Kappler et al., 1997). Furthermore the highly localized 4f$^1$ state of CePd leads to a ferromagnetic ordering below the Curie temperature $T_c = 6.5$ K, whereas CeNi shows the characteristic behaviour of a Kondo system. Thus, starting from CePd, $T_c(x)$ increases from 6.5 K, in the $0 < x < 0.5$ concentration range, to reach a plateau of about 10.5 K, in the $0.5 < x < 0.8$ range. Then, at higher Ni concentration, the $T_c$ values decrease and further steeply drop to zero near $x = 0.95$ (Nieva et al., 1988; Stewart, 2001). This system has been cited in Stewart’s review (2001) for its non-FL behaviour with $T_c$ suppressed to zero via Ni doping. Let us recall that, in general, the FL provides a good description of the low temperature measurable parameters of a metal as long as the electron interactions, while $T$ tends to zero, become temperature independent and are short ranged in both space and time. On the opposite, a non-Fermi-liquid behaviour is exhibited for a system with electron–electron interactions that are too strong to permit entry into the FL ground state at low temperatures. For the CePd$_{0.05}$Ni$_{0.95}$ system, an obvious explanation is probably given by the nearness to a magnetic instability in the phase diagram. In the present paper we would like to further investigate the low temperature properties of Ce(Pd$_{1-x}$Ni$_x$)$_3$ alloys (Kappler et al., 2004), when $x$ varies from 0 to 0.25 (Section 3.3.2). These systems have been characterized by magnetization measurements up to 4 T at low temperatures down to $T = 50$ mK. Temperature dependent specific heat measurements have been performed in the 0.5–20 K temperature range. Special attention is devoted to the Ce L$_{23}$ absorption edges (XAS) and the corresponding XMCD spectra in order to precise the electronic and magnetic ground state of Ce. Actually in Ce(Pd$_{1-x}$Ni$_x$)$_3$, the Ce L$_{23}$ absorption edges and XMCD study (a negative sign at L$_3$ and a positive one at L$_2$) reveals indeed a coexistence of a strong 4f hybridization and a ferromagnetic order. In Ce(Pd$_{1-x}$Ni$_x$)$_3$ alloys the main source of magnetism should be due to Ce atoms as in CeRu$_2$Ge$_2$.

Section 4 is devoted to a few concluding remarks on the series of rare earth compounds from both light and heavy sides, as far as the XMCD is concerned, with a special emphasis on the particular case of Ce compounds.

Before closing this chapter, we would like to make clear the definition of the sign of XMCD. As mentioned by Baudelet et al. (1993), the following definition of the sign of XMCD is important to avoid any confusion: we take the axis of quantization as $+z$ direction, which is also the direction of the photons wave vector, and the magnetic field $B$ is applied in the $-z$ direction to align the magnetization, as shown in Fig. 1. Then, the XMCD spectrum $\Delta F(\omega)$
is defined by
\[ \Delta F(\omega) \equiv F^+(\omega, B) - F^-(\omega, B), \] (1.1)
where \( F^+(F^-) \) is the XAS spectrum for the incident photon with \(+(-)\) helicity, and \( \omega \) is the incident photon energy. In the present paper, we use this convention. For the inverted magnetic field \(-B\), \( \Delta F(\omega) \) can also be written as
\[ \Delta F(\omega) = F^-(\omega, -B) - F^-(\omega, B) = F^+(\omega, B) - F^+(\omega, -B) = F^-\omega, -B) - F^+(\omega, -B). \] (1.2)
In the present paper, we write \( F^\pm(\omega, B) \) simply as \( F^\pm(\omega) \), unless it causes any confusion.

2. Rare earth series
2.1. Basic mechanism of XMCD at L\(_{23}\) absorption edges

2.1.1. Effect of 4f–5d exchange interaction
In this review, we focus our attention on XMCD spectra observed at \( L_{23} \) edges of R elements (Fischer et al., 1990; Baudelet et al., 1993). The main absorption originates through the ED transition from 2p core level to 5d states. It is to be noted that the 2p hole state left behind splits into 2p\(_{1/2}\) and 2p\(_{3/2}\) states due to a relatively large spin–orbit interaction. These states correspond to the \( L_2 \) and \( L_3 \) edges, respectively, which are supposed to be sufficiently far from each other to be discussed separately. Jo and Imada (1993) gave the first interpretation for a systematic trend of XMCD in \( L_{23} \) XAS edges of R atoms from Ce to Tm, assuming a 2p\(_{3/2}\) → 5d ED transition and a 4f state of trivalent R ion in the Hund’s rule ground state. For the series, the electron configuration is 2p\(^6\)4f\(^n\)5d\(^1\) (\( n = 1–13 \)) in the ground state and 2p\(^5\)4f\(^n\)5d\(^2\) in the final state, where the 5d electrons are in the conduction band with a semi-elliptical density of states. In this situation, Jo and Imada took into account the spin and orbital moments of the R 5d state induced through the intraatomic 4f–5d exchange interaction within a molecular field approximation. Based on these assumptions, the energy of the 5d state, specified by the \( z \) components of the orbital and spin quantum numbers, \( m_d \) and \( s_d \), respectively, is given by
\[ E_{d\mu} \equiv E(m_d, s_d) = -\sum_{k=1,3,5} \sum_{m, s} |c^k(2m_d, 3m_t)|^2 G^k n(m_t, s) \delta(s_d, s_t), \] (2.1)
where \( \mu \) denotes the combined indices of \( m_d \) and \( s_d \); \( c^k \) is proportional to the Clebsch–Gordan coefficient; \( G^k \) represents the 4f–5d Slater integrals; \( n \) is the number of 4f electrons corresponding to \( m_t \) and \( s_t \); \( \delta \) is the Kronecker delta function. We note that the energy \( E_{d\mu} \) depends on the number \( n \) of 4f electrons. Assuming a 5d band width of several eV, Jo and Imada calculated the integrated XMCD spectra. The calculated result was mostly consistent with experiments in the systematic variation of the integrated XMCD amplitude over the R elements, but the result failed to recover the exact sign for the intensity of the observed results (see for example Baudelet et al., 1993).\(^1\) As a consequence there was a need left for a more sophisticated interpretation of the spectra.

2.1.2. 4f–5d exchange interaction and enhancement of the ED transition intensity
In the case of Gd metal, in which the orbital magnetic moment is completely quenched, it has been pointed out that, according to band structure calculations, the spin dependent enhancement of the ED matrix element is crucial for predicting the correct XMCD sign (Carra et al., 1991; König et al., 1994). This is a consequence of the contraction of the radial part of the 5d orbital due to 4f–5d exchange interaction. This contraction effect in Gd was pointed out within band structure calculations (Harmon and Freeman, 1974), but applied to the XMCD of the Gd \( L_{23} \) edge was first done by Carra et al. (1991). Then, it is conceivable that, in other R elements having an open 4f shell, the magnitude of the enhancement depends not only on the 5d spin moment \( (s_d) \) but also on the 5d orbital moment \( (m_d) \) through the exchange energy \( E_{d\mu} \). Van Veenendaal et al. (1997) investigated the present problem assuming empty 5d states in the

\(^1\) Actually Jo and Imada (1993) claimed that their result agreed with experimental data including the sign of XMCD, but their definition of the sign of XMCD was opposite to the convention mentioned in Section 1.
Table 1
The ED transition intensity \( I^\pm(p_j; d_\mu) = \sum_{j_z} |M^\pm(p_jj_z; d_\mu)|^2 \)

<table>
<thead>
<tr>
<th>( m_d )</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>-1</th>
<th>-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ( I^+(p_3/2; d_\mu) )</td>
<td>( S_\Delta = 1/2 )</td>
<td>1</td>
<td>1/3</td>
<td>1/18</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>( -1/2 )</td>
<td>1/3</td>
<td>1/3</td>
<td>1/6</td>
<td>0</td>
</tr>
<tr>
<td>(b) ( I^-(p_3/2; d_\mu) )</td>
<td>( S_\Delta = 1/2 )</td>
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<td>0</td>
<td>1/6</td>
<td>1/3</td>
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<tr>
<td></td>
<td>( -1/2 )</td>
<td>0</td>
<td>0</td>
<td>1/18</td>
<td>1/3</td>
</tr>
<tr>
<td>(c) ( I^+(p_1/2; d_\mu) )</td>
<td>( S_\Delta = 1/2 )</td>
<td>0</td>
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<td>1/9</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>( -1/2 )</td>
<td>2/3</td>
<td>1/6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(d) ( I^-(p_1/2; d_\mu) )</td>
<td>( S_\Delta = 1/2 )</td>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>1/9</td>
<td>1/6</td>
</tr>
</tbody>
</table>

ground state. Also Matsuyama et al. (1997) phenomenologically introduced the enhancement effect by an enhancement factor \( \alpha \):

\[
F^\pm_j(\omega) = \sum_{\mu, j_z} |M^\pm(p_jj_z; d_\mu)|^2 (1 - \alpha E_{d_\mu}) \int_{E_F}^{W+E_{d_\mu}} d\varepsilon \rho_{d_\mu}(\varepsilon) L(\omega + E_p - \varepsilon), \tag{2.2}
\]

where \( F^\pm_j(\omega) \) represents the XAS spectrum with \( \pm \) helicity for the angular momentum \( j = 3/2, 1/2 \) of the 2p core state, \( M^\pm(p_jj_z; d_\mu) \) is the electric–dipole-transition matrix element for \( \pm \) helicity before taking into account the enhancement effect, \( \rho_{d_\mu}(\varepsilon) \) is the semi-elliptical density of state of the 5d \( (d_\mu) \) state with the band width \( W \) expressed as

\[
\rho_{d_\mu}(\varepsilon) = \frac{2}{\pi W^2} \sqrt{W^2 - (\varepsilon - E_{d_\mu})^2}, \tag{2.3}
\]

\( E_F \) is the FL, and \( L(\chi) \) is the Lorentzian

\[
L(\chi) = \frac{\Gamma / \pi}{\chi^2 + \Gamma^2}, \tag{2.4}
\]

with the lifetime broadening of the 2p hole, \( \Gamma \). XAS and XMCD spectra are given, respectively, by \( F^+_j(\omega) + F^-_j(\omega) \), and its magnetic counterpart \( F^+_j(\omega) - F^-_j(\omega) \), (Fig. 1). It is to be noted that \( M^\pm(p_jj_z; d_\mu) \) is expressed, apart from a constant factor, as

\[
M^\pm(p_jj_z; d_\mu) = \sum_{m_p, s_p} \langle 2m_p|1 \pm 1|m_p \rangle \langle 1m_p\frac{1}{2}sp|jj_z \rangle \delta(s_d, s_p), \tag{2.5}
\]

where \( \langle j_1m_1j_2m_2|JM \rangle \) is the Wigner coefficients. For discussions given below, we list in Table 1 the ED transition intensity

\[
I^\pm(p_j; d_\mu) = \sum_{j_z} |M^\pm(p_jj_z; d_\mu)|^2 \tag{2.6}
\]

for the \( \pm \) helicity lights and for the states from \( j = 3/2 \) or \( 1/2 \) to \( \mu = (m_d, s_d) \).

Matsuyama et al. (1997) calculated the integrated intensity of the XMCD spectrum (normalized by the integrated XAS intensity) \( \Delta \Gamma^{pj} \), for the entire series of trivalent R elements (Ce–Yb). The calculated results for \( \alpha = 0.0, 0.4 \) and 0.6 \((1/\text{eV})\) are shown in Fig. 2. The result for \( \alpha = 0.0 \) almost coincides with that by Jo and Imada (1993),
but by introducing \( \alpha \neq 0 \) (e.g. \( \alpha = 0.4 \) or 0.6 1/eV) the sign of the integrated XMCD changes in accord with experimental observations.

Let us first consider the case of Gd. The sign of \( \Delta I^{pj} \) is positive and negative for \( j = 3/2 \) and 1/2, respectively, by taking into account the enhancement effect. This is easily understood as mentioned in the following: with our convention, the magnetic field \( B \) is in the \(-z\) direction, so that all of seven 4f electrons occupy \( \uparrow \) spin states in the Hund’s rule ground state, where the spin quantization axis is in the \(+z\) direction. Therefore, by the 4f–5d exchange interaction the energy of 5d \( \uparrow \) spin states is lower than that of 5d \( \downarrow \) spin states, and the electric dipole transition amplitude is enhanced for the 2p to 5d \( \uparrow \) transition, instead of the 2p to 5d \( \downarrow \) transition. As seen from Table 1, the sign of XMCD is determined for L3 edge (\( j = 3/2 \)) mainly by the competition between the 2p to 5d \( \uparrow \) transition (the transition to \( (m_d,s_d) = (2,\uparrow) \)) by \(+\) helicity and the 2p to 5d \( \downarrow \) transition (most dominant is to \((-2,\downarrow)\)) by \(-\) helicity, and for L2 edge (\( j = 1/2 \)) mainly by the competition between the 2p to 5d \( \downarrow \) transition (most dominant is to \((2,\downarrow)\)) by \(+\) helicity and the 2p to 5d \( \uparrow \) transition (most dominant is to \((-2,\uparrow)\)) by \(-\) helicity. Therefore, by the enhancement of the 2p to 5d \( \uparrow \) transition matrix element, the transition by \(+\) and \(-\) helicity become dominant for L3 and L2 edges, respectively, giving rise to the positive and negative signs of XMCD. This is exactly the same situation as that shown by Carra et al. (1991) through the energy band calculation.\(^2\) From comparison with the result by Carra et al., the value of \( \alpha \) is estimated to be 0.4–0.6 1/eV.

In the case of \( \alpha = 0.0 \), we have no integrated intensity of XMCD if we disregard the 5d electron occupation in the ground state (as in the model by Van Veenendaal et al., 1997 and Goedkoop et al., 1997). But if we take into account the 5d electron occupation (as in the model by Jo and Imada, 1993 and by Matsuyama et al., 1997), the intensity of the 2p to 5d \( \uparrow \) transition becomes weaker than the 2p to 5d \( \downarrow \) transition because the 5d electron population is larger in the 5d \( \uparrow \) band due to the gain of the exchange energy \( E_{d\mu} \). Therefore, the sign of XMCD becomes negative and positive, respectively, for L3 and L2 edges, as shown in Fig. 2.

For other rare earth elements, it is seen from the results of \( \alpha = 0.4 \) and 0.6 (1/eV) in Fig. 2 that \( \Delta I^{pj} \) has large positive values for L3 (\( j = 3/2 \)) of heavy rare earths (Tb–Yb) and for L2 (\( j = 1/2 \)) of light rare earths (Ce–Sm), but it

\(^2\) Carra et al. (1991) published their paper before the papers by Jo and Imada (1993) and by Baudelet et al. (1993), and actually Jo and Imada, as well as Baudelet et al., referred the paper by Carra et al., but they did not notice the importance of the enhancement effect of the electric dipole transition intensity. Baudelet et al. stated “More importantly we obtain the wrong direction for the 5d magnetic moment.” on the sign of XMCD of Gd.
has much smaller values for \( L_3 \) of light rare earths (Ce–Sm) and for \( L_2 \) of heavy rare earths (Tb–Yb). The mechanism of this behaviour is more complicated than that of Gd, but the trend is understood in the following way. Looking at Table 1, we confine ourselves, for simplicity, to the following cases of largest ED transition intensity: for the \( L_3 \) edge the transition to \((m_d, s_d) = (2, \uparrow)\) by + helicity light and that to \((-2, \downarrow)\) by − helicity one, and for the \( L_2 \) edge the transition to \((2, \downarrow)\) by + helicity light and that to \((-2, \uparrow)\) by − helicity one. For light rare earths, the dipole transition intensity to \((m_d, s_d) = (2, \downarrow)\) is strongly enhanced by the exchange interaction with 4f states in the Hund’s rule ground state, but the dipole transition intensities to \((-2, \downarrow), (-2, \uparrow)\) and \((2, \uparrow)\) are not much enhanced. Therefore, in the \( L_2 \) edge the XAS intensity by the + helicity light is much larger than that by the − helicity light, and the XMCD has a large positive value, but in the \( L_3 \) edge the XAS intensities by the + and − helicities are comparable and the sign of XMCD is determined by higher order effects. For heavy rare earths, the dipole transition intensity to \((m_d, s_d) = (2, \uparrow)\) is strongly enhanced, but those to \((-2, \uparrow), (2, \downarrow)\) and \((-2, \downarrow)\) are not much enhanced. Therefore, the absorption intensity by + helicity light is much stronger than − helicity light for \( L_3 \), but the absorption intensities by + and − helicity lights are comparable for \( L_2 \).

As a conclusion it was stated that in addition to the previously considered spin and orbital polarization effect of the 5d states due to the 4f–5d exchange interaction, there was a novel effect of contraction in the radial part of the considered 5d wave functions which led to the enhancement of the 2p–5d ED matrix element.

### 2.1.3. Contribution of EQ transition

Furthermore the EQ contribution is also inevitable for a quantitative comparison of the calculated spectra with experiment. Then, Fukui et al. (2001) determined it using Cowan’s program (1981) based on an atomic model. The calculated integrated intensities of XAS and XMCD are shown in Fig. 3. The atomic calculation is a reasonable method since the 4f electrons, directly concerned with the EQ process, there was a novel effect of contraction in the radial part of the considered 5d wave functions which led to the enhancement of the 2p–5d ED matrix element.

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\(^3\) In the Hund’s rule ground state of Ce\(^{3+}\), for instance, the 4f electron with \((m_f, s_f) = (3, \downarrow)\) is occupied under the magnetic field \(B\) in the \(-z\) direction, so that the ED transition intensity to the state \((2, \downarrow)\) is much enhanced due to the gain in the exchange energy (Eq. (2.1)), but the transition to \((-2, \uparrow)\) is not enhanced.
are well localized. Many-body effects are crucial in this process, especially the interaction between the photo-excited 4f electron and the core hole left behind as well as between the other 4f electrons. However the lifetime effect of the 2p core hole smears out the detailed structure of the spectra.

The contribution of the EQ transition to XMCD is generally weaker than that of the ED transition mentioned in Section 2.1.2. However, the EQ contribution is somewhat lower in energy than the ED contribution, and especially, for the L3 XMCD of light rare earths and for the L2 XMCD of heavy rare earths, the EQ contribution can be important because the ED contribution is rather weak, as seen from Fig. 2.

### 2.1.4. 5d–3d hybridization between R(5d) and TM(3d) electronic states

Now, in order to determine XMCD spectra of R elements in intermetallic compounds containing TM, like for example R2Fe14B (Section 2.2) or RFe2 (Section 2.3), it is important to take into account another polarization effect of the 5d states due to the hybridization with spin polarized 3d states of surrounding TM ions (Fe in Sections 2.2 and 2.3), which occurs through the 2p–5d ED transition. Actually it is well known that the magnetic coupling between Fe 3d spin and R 4f spin always presents an antiferromagnetic alignment (via the R 5d conduction electrons) which makes them either ferromagnetic compounds for light rare earths (Ce–Sm) or ferrimagnetic compounds for half-filled (Gd) and heavy rare earths (Tb–Yb), because the R 4f spin moment is antiparallel and parallel, respectively, to the R 4f orbital moment (which is larger than the R 4f spin moment) for light and heavy rare earth elements.

On the contribution of R 5d–Fe 3d hybridization to XMCD, this effect must dominate the spectra for La or Lu compound, since there is no effect from the 4f electrons. For other rare earth elements, this effect is generally weaker than that of the ED contribution due to the R 4f–5d interaction mentioned in Section 2.1.2. However, for the L3 XMCD of light rare earths and for the L2 XMCD of heavy rare earths, this contribution can be important because the ED contribution by 4f–5d interaction is rather weak, as seen from Fig. 2. In the case of R2Fe14B, where Fe constitutes the majority of the magnetic moment, the contribution of R 5d–Fe 3d hybridization is large and determines almost the total L2 XMCD of heavy rare earth elements as will be shown in Section 2.2.6.

Since the R 4f and Fe 3d magnetic moments order ferromagnetically for light rare earth elements, the R 4f magnetization always aligns parallel to the external magnetic field, and hence the sign of the XMCD contributions from the ED contribution by R 4f–5d interaction, the EQ contribution and the ED contribution by R 5d–Fe 3d hybridization are easily determined, for instance as shown in Figs. 2 and 3. However, for heavy rare earth elements where the R 4f and Fe 3d magnetic moments are in the antiferromagnetic ordering, we have to pay attention to the following points: for R2Fe14B, where Fe constitutes the majority of the magnetic moment, (1) the sign of the ED contribution by R 4f–5d interaction is opposite to that in Fig. 2, (2) the sign of the EQ contribution is also opposite to that in Fig. 3, and (3) the sign of the ED contribution by R 5d–Fe 3d hybridization is the same as that of La2Fe14B. On the other hand, for RFe2, where R constitutes the majority of the magnetic moment; (1) the sign of the ED contribution by R 4f–5d interaction is the same as that in Fig. 2; (2) the sign of the EQ contribution is also the same as that in Fig. 3; and (3) the sign of the ED contribution by R 5d–Fe 3d hybridization is opposite to that of La2Fe14B.

### 2.1.5. Concluding remarks

Now, we are ready to review XMCD spectra in more details depending on the case under investigation. We shall report on recent theoretical works in relation with experimental spectra for a series of R elements in R2Fe14B (Section 2.2) and RFe2 compounds (Section 2.3). In contrast to RFe2 compounds, experimental data for almost all the R series in R2Fe14B are available. Also, the XMCD spectral structures in the R2Fe14B spectra are easier to understand as compared to RFe2 compounds. Furthermore less unsolved problems are left over. Therefore we shall next focus on R2Fe14B and afterwards on RFe2 compounds.

### 2.2. R2Fe14B metallic compounds

#### 2.2.1. R2Fe14B cluster model electronic structure

Quantitative and systematic calculations of XMCD in the series of R2Fe14B metallic compounds were first performed by Fukui et al. (2001) by including both ED and EQ transitions. First of all, for ED contribution, as already explained above, Fukui et al. took into account the 4f–5d exchange interaction which causes the magnetic polarization of 5d bands as well as the enhancement of 2p → 5d transition matrix element. Moreover, they pointed out the importance of the magnetic polarization of 5d bands due to the hybridization of R 5d states with spin-polarized Fe 3d states.
Fig. 4. Cluster model consisting of 10 R atoms (dark spheres) and 16 Fe atoms (light spheres).

(Section 2.1.3). Their results were in rather good agreement with experiment for almost the entire series of $R_2Fe_{14}B$ compounds. However, Fukui et al.’s model was too much simplified in the following two points:

(i) The density of states of R 5d bands was assumed to be given by a simple semi-elliptic function.

(ii) The XMCD due to hybridization between R 5d and Fe 3d bands has not been explicitly calculated. Instead, Fukui et al. simply added the XMCD spectrum observed experimentally for $La_2Fe_{14}B$ to the calculated XMCD spectrum of each R compound without the hybridization effect.

Afterwards a unified model was proposed by Asakura et al. (2002) to reproduce, in a more consistent and quantitative fashion, the XMCD spectra observed at $L_{23}$ edges of the $R_2Fe_{14}B$ series, improving the theory by Fukui et al. (2001). To this end, Asakura et al. adopted a cluster model, in which the band effects of Fe 3d and R 5d states are simulated. The mixing effect between 5d and 3d states was taken into account microscopically within the cluster model. Also taken into account in a mean-field approximation were the intra-atomic exchange effects on 5d states from 4f electrons as well as on 3d states from other 3d electrons. In the calculated spectra, the enhancement of the dipole matrix element due to 4f–5d exchange interaction was included in the way that was presented in Section 2.1.2.

It is known that a given $R_2Fe_{14}B$ compound has tetragonal symmetry and its unit cell contains 68 atoms (Herbst, 1991). Then, a cluster consisting of 10 R atoms including the central R (on the atomic site 0) and 16 Fe atoms surrounding the site 0 was adopted by Asakura et al. (2002) as shown in Fig. 4, where the R and Fe atoms are depicted with dark and light spheres respectively. Actually the considered cluster contains all R atoms up to the fifth nearest neighbours from site 0 and all Fe atoms up to the sixth nearest neighbours from site 0. The Hamiltonian of the cluster model
is expressed as

\[ H = \sum_i \sum_{\mu} \varepsilon_{5d}(\mu) d_{\mu,i}^+ d_{\mu,i} + \sum_j \sum_v \varepsilon_{3d}(v) D_{v,j}^+ D_{v,j} + \sum_{i \neq i'} \sum_{\mu, \mu'} [t_{i,j}(\mu, \mu') d_{\mu,i}^+ d_{\mu',i'} + v.c.] + \sum_{j \neq j'} \sum_v [t_{j,j'}(v, v') D_{v,j}^+ D_{v,j'} + v.c.] + \sum_{i \neq j} \sum_v [t(\mu, v) d_{\mu,i}^+ D_{v,j} + v.c.] \]  \tag{2.7}

where the operators \( d_{\mu,i}^+ \) (\( i = 0-9 \)) and \( D_{v,j}^+ \) (\( j = 1-16 \)) represent, respectively, the creation of an electron in the 5d state \( \mu \) of the R \( i \)th site and in the 3d state \( v \) of the Fe \( j \)th site. The indices \( \mu \) and \( v \) denote \((m_d, s_d)\) of R 5d and Fe 3d states, respectively. The 5d energy level \( \varepsilon_{5d} \) is essentially the same as the exchange energy \( E_{d\mu} \) in Eq. (2.1) but now we take into account the reduction factor \( R_E \) of the Slater integral \( G^k \):

\[ \varepsilon_{5d}(\mu) = R_E E_{d\mu}. \]  \tag{2.8}

On the other hand, the 3d energy level is expressed as

\[ \varepsilon_{3d}(v) = \Delta - E_{\text{exc}} s_{3d}, \]  \tag{2.9}

where \( \Delta \) is the Fe 3d–R 5d energy separation in nonmagnetic state and \( E_{\text{exc}} \) is the exchange splitting of the Fe 3d state. These values are taken \( \Delta = -2.6 \) eV and \( E_{\text{exc}} = 1.1 \) eV, and the Fermi energy is fixed at \(-2.0 \) eV with respect to the center of the 5d levels. The electron transfer integrals, \( t_{i,j}(\mu, \mu') \), \( t_{j,j'}(v, v') \) and \( t(\mu, v) \) are obtained from the Slater–Koster integrals given by the empirical formula by Pettifor (1977) (for more details, see Asakura et al., 2002).

In the case of Lu\(_2\)Fe\(_{14}\)B we show the calculated one particle density of states (DOS) in Fig. 5, where the partial DOSs are depicted for Lu 5d (projected on the central Lu site) and Fe 3d (averaged over all Fe sites) states with up (majority) and down (minority) spin components. The origin of the energy is taken at the Fermi level. The original discrete DOSs are broadened appropriately to give continuous bands. Here, let us briefly explain how Asakura et al.’s cluster calculation works. Firstly, we note that the overall shape of the DOS, especially of Fe 3d states shown in Fig. 5a, is similar to that calculated by the recursion method for Y\(_2\)Fe\(_{14}\)B (Inoue and Shimizu, 1986), except for fine structures. This is one of the main reasons why Asakura et al. (2002) found reasonable values of \( n_{3d} \), \( n_{5d} \) and \( M_s \) within a set of reasonable band parameters. Secondly, we would like to recall the fact that the hybridization between R 5d states and spin polarized Fe 3d states gives rise to a reasonable spin polarization in the R 5d bands, as will be discussed in the following. The effect of hybridization is seen most clearly in the Lu based compound, since in this case the polarization in Lu 5d bands comes only from the hybridization with Fe 3d states. Also, Asakura et al. (2002) considered the case where 4f electrons are partially filled, with Sm\(_2\)Fe\(_{14}\)B as an example. Now the energy of 5d levels depends on \( n_{5d} \) and \( \varepsilon_{5d} \) because of the exchange potential of 4f states, so that the partial DOSs are somewhat modified as compared to Lu\(_2\)Fe\(_{14}\)B, as shown in Fig. 5b.

Asakura et al.’s cluster calculation (2002) was performed as usual at zero temperature. Their subsequent calculated XMCD spectra also reflected situation at zero temperature. Actually, temperature dependence will be discussed later on in Section 2.2.6. Let us come back qualitatively on the hybridization effect. It is worth noticing that the calculated
energy bands reasonably yield an antiferromagnetic coupling between Fe 3d and R 5d spins. As is seen from the DOS of Fig. 5a, this result is thought to be a consequence of the fact that the hybridization between the spin polarized 3d and 5d states is stronger for the down spin band (minority) than for the up spin band (majority). As a matter of fact, 3d and 5d bands are energetically closer located in the former case than in the latter case. Then, the energy of a 5d electron having a down spin is pulled down more below the Fermi energy than when it has an up spin. Hence the number of the former is larger than that of the latter. Now the effect of 5d–3d hybridization on XMCD is obvious. The unoccupied 5d states are spin-polarized due to hybridization with 3d states, so that 2p → 5d XAS depends on the helicity of incident X-ray. Actually the absorption spectrum for X-rays with positive and negative helicities has been calculated at the central Lu site of the cluster.

Let us also comment on the case where 4f electrons are partially filled, i.e. Sm2Fe14B. In this case the energy of 5d levels depends on \( m_{5d} \) and \( s_{5d} \) because of the exchange potential of 4f states, so that the partial DOSs are changed with respect to Lu2Fe14B, as already stated. In this calculation, Asakura et al. (2002) used the values of the 4f–5d Slater integrals \( G^k \) obtained by the atomic Hartree–Fock calculations, and a reduction factor \( R_E \) of 0.8 for the overall spectrum. In the calculation of XMCD, Asakura et al. took into account the enhancement of the ED transition matrix element by a factor \( z \) taken to be 0.4 (1/eV).

2.2.2. Lu2Fe14B compound

The calculated XAS and XMCD for \( L_2 \) and \( L_3 \) edges of Lu2Fe14B compounds (Asakura et al., 2002) are shown with solid curves in Fig. 6a. In these calculations only ED process was assumed. Because of 2p core hole lifetime, a Lorentzian function was used to calculate the considered spectra. The corresponding spectral broadening (FWHM) due to lifetime effect was taken to be 4.0 eV. Furthermore each spectrum was then further convoluted with a Gaussian function of 1.5 eV width, simulating the instrumental resolution, in order to fit the actual experimental data. For XAS, a background was also assumed in an arctangent form to directly compare the result with experiment. This background, of course, does not affect XMCD. The experimental data are also shown in Fig. 6a with “×” for XAS and “+” for

![Fig. 6. (a) Calculated XAS and XMCD spectra (solid curves) at \( L_3 \) and \( L_2 \) edges of Lu2Fe14B by taking into account the ED contribution only. The results are compared with the experimental ones (× and + for XAS and XMCD, respectively). (b) Calculated XAS and XMCD spectra (solid curves) at \( L_3 \) and \( L_2 \) edges of Sm2Fe14B by taking into account the ED contribution only. The results are compared with the experimental ones (× and + for XAS and XMCD, respectively).](image-url)
Fig. 7. (a) XMCD spectra of the Sm L\textsubscript{2,3} XAS in Sm\textsubscript{2}Fe\textsubscript{14}B. Solid curves represent the calculated results consisting of the ED contribution (dashed curves) and the EQ contribution (dotted–dashed curves), while crosses represent the experimental data. (b) XMCD spectra of the Sm L\textsubscript{2,3} XAS in Sm\textsubscript{2}Fe\textsubscript{14}B. Solid curves are the sum of the three contributions: the ED contribution due to the 4f–5d exchange interaction (dashed curves), the ED contribution due to the Sm 5d–Fe 3d hybridization (dotted curves) and the EQ contribution (dotted–dashed curves).

XMCD and the calculated spectral shape of XMCD is in rather good agreement with experiment. It is interesting here to point out that the hybridization effect yields a correct sign of the XMCD spectrum, negative for L\textsubscript{2} edge and positive for L\textsubscript{3} edge, which is reasonable when it is considered that the hybridization effect polarizes the Lu 5d electrons antiferromagnetically with the Fe 3d electrons. However, the calculated amplitude of XMCD, which is defined by a percent value with respect to the maximum intensity of XAS, is much larger than the experimental one. Thus notice that the calculated XMCD is multiplied by 0.2 in Fig. 6a.

2.2.3. \textit{Sm\textsubscript{2}Fe\textsubscript{14}B} compound

In the calculation of the XMCD spectrum for this compound, Asakura et al. (2002) took into account the effects of polarization of 5d states due to 4f–5d exchange coupling as well as 5d–3d hybridization (Sections 2.1.1 and 2.1.4). Moreover the enhancement effect of ED transition amplitude was also accounted for by an enhancement factor defined in Section 2.1.2 and taken to be 0.4 (1/eV) according to Fukui et al. (2001). The calculated results for XAS and XMCD spectra for a typical example of light R elements, Sm\textsubscript{2}Fe\textsubscript{14}B, are shown in Fig. 6b, where the effect of EQ transitions is not taken into account. In Fig. 6b, the calculated XMCD has been again multiplied by a factor 0.22 to best fit to the experiment.

The remaining contribution to XMCD arises from EQ transitions (Section 2.1.3). In Fig. 7 the corresponding EQ contribution is shown as a dotted–dashed curve and it was obtained through a straightforward atomic full-multiplet calculation by Fukui et al. (2001). However the relative intensity between EQ and ED transitions was treated as an...
adjustable parameter. In Fukui et al. (2001) assumed that the ED contributions of R 4f–5d exchange interaction and R 5d–Fe 3d hybridization can be treated to be independent, but in Figs. 6b and 7a these contributions should not be exactly independent because they are automatically correlated through the calculated electronic structure of the Sm 5d states. However, Asakura et al. (2002) showed that their correlation is not very large. They calculated the following three contributions independently: (i) the ED contribution from Sm 4f–5d exchange interaction by putting $E_{\text{exc}} = 0$, (ii) that from the Sm 5d–Fe 3d hybridization by putting $R_{\text{E}} = 0$, and (iii) the EQ contribution. Then they compared the spectrum of (i) + (ii) + (iii) with the result shown in Fig. 7a, where the spectra (i), (ii), (iii) and (i) + (ii) + (iii) are shown in Fig. 7b with dashed, dotted, dash–dotted and solid curves, respectively.

From comparison of the solid curves in Figs. 7a and b, we find that they almost coincide with each other. Therefore, the contribution to XMCD from the Sm 4f–5d exchange interaction is almost independent of that from the Sm 5d–Fe 3d hybridization, and they can be almost additive. Furthermore, if we compare the solid curves of XMCD in Fig. 6a with the dotted curves in Fig. 7b, we find that they almost coincide with each other. These results indicate that the assumptions made by Fukui et al. (2001) are almost valid.

From Fig. 6b, it is seen that the relative intensity of (ii) vs. (iii) is comparable for both L3 and L2 edges and the relative intensities of L3 vs. L2 edges for (ii) and (iii) are also comparable. On the other hand, the intensity of (i) is much larger in the L2 edge than in the L3 edge, the reason of which has already been mentioned in Section 2.1.2 (see also Fig. 2). As a result, the intensities of (i), (ii) and (iii) are all comparable in the L3 edge, while the intensity of the L2 edge is mainly determined by (i).

2.2.4. Gd$_2$Fe$_{14}$B compound

Similar calculations have been performed for all other R elements of the series with fixed values of $(R_{\text{E}}, z)=(0.8, 0.4)$. The result for Gd$_2$Fe$_{14}$B, as an example, is shown in Fig. 8a. From Fig. 2, we see that the XMCD of Gd has considerably large positive value for L3 and very large negative value for L2. However, for Gd$_2$Fe$_{14}$B the Fe magnetic moment constitutes the majority of the total magnetic moment, so that the signs of XMCD should be inverted from those in Fig. 2. Thus we understand the considerably large negative XMCD for L3 and the very large positive XMCD for L2 which are shown in Fig. 8a. Here, most of XMCD spectra are determined by (i), and we see much smaller contributions from (iii), where the signs of the contributions (iii) are also inverted from those in Fig. 3. In Fig. 8a, we do not show the decomposition of the dashed curves to the contributions from (i) and (ii), but the contribution from (ii) is comparable with the MCD of Fig. 6a and it is much weaker than that from (i).

2.2.5. Er$_2$Fe$_{14}$B compound

Another example is given in Fig. 8b for a typical example of heavy R elements, Er$_2$Fe$_{14}$B (Asakura et al., 2002). Once more the calculated XMCD spectrum is in fair agreement with experimental data, although there are some discrepancies. In order to understand these results, we note that the signs of (i) and (iii) should be opposite to those in Figs. 2 and 3, because of the dominant Fe magnetic moment, while the sign of (ii) is the same as that of La$_2$Fe$_{14}$B. Actually, the L2 XMCD spectrum of Er$_2$Fe$_{14}$B is almost the same as that of La$_2$Fe$_{14}$B (see Fig. 5a), because the contribution from (ii) is much larger than (i) and (iii) (although (i) and (ii) are not decomposed in Fig. 8b). Here, it is to be noted that the contribution from (ii) is considerably large due to the large Fe magnetic moment of this material (compare with that of RFe$_2$ in Section 2.3) and that from (i) is small as seen from Fig. 2. On the other hand, the L3 XMCD spectrum consists of (i), (ii) and (iii) with comparable contributions. We remark that the contribution (i) in Er is much larger for L3 than for L2 (see Fig. 1) and the contribution (iii) in Er is also much larger for L3 than for L2 (see Fig. 3).

2.2.6. Discussion on the comparison with experimental results

In the preceding subsections, we have recalled Asakura et al.’s result (2002). Actually their calculated XMCD amplitude at zero temperature is much larger than the experimental results, although the calculated XMCD spectral shape is rather in good agreement with experiment. One of the reasons for this discrepancy in XMCD amplitude is that the experiment was performed at room temperature, so that R and Fe magnetic moments have been reduced due to thermal fluctuations. Another reason for the XMCD reduction would be the fluctuation in the magnetization directions for different magnetic domains. In Asakura et al.’s model, the Fe magnetic moment is controlled by the exchange parameter $E_{\text{exc}}$. Also the effect of the reduced 4f moment on 5d states can be effectively treated by decreasing the reduction factor $R_{\text{E}}$ as done by Fukui et al. (2001). Therefore, in order to compare with experiment at room temperature
Table 2

<table>
<thead>
<tr>
<th>R</th>
<th>La</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
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</thead>
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<td>0.12</td>
<td>0.16</td>
<td>0.40</td>
<td>0.12</td>
<td>0.12</td>
<td>0.20</td>
<td>0.12</td>
<td>0.08</td>
<td>0.04</td>
<td>–</td>
</tr>
</tbody>
</table>

The reduction factor ($R_E$) of the 4f–5d exchange energy $R_L a P r N dS mG dT bD yH oE r T mY bL u$ more systematically, calculations of the preceding subsections were used but by reducing $E_{\text{exc}}$ and $R_E$. Actually the value of $E_{\text{exc}}$ was fixed at 0.2 eV whereas the values of $R_E$ was taken as shown in Table 2.

The calculated XAS and XMCD for $L_3$ and $L_2$ edges are shown in Figs. 9(a) and (b), respectively, together with the experimental data (Chaboy et al., 1996). The overall agreement between calculated and experimental results is quite satisfactory in both XMCD shape and amplitude. The calculated XMCD involves the contributions of ED transitions with the effects of inter-atomic hybridization and intra-atomic exchange interaction, as well as EQ contributions. We note that, since each contribution to XMCD spectra is sometimes different in shape and sign, the total XMCD spectra show a variety of shapes. The mechanism of XMCD spectra for light ($R = \text{Pr–Sm}$) and heavy ($R = \text{Tb–Yb}$) rare earths is essentially the same as that of Sm$_2$Fe$_{14}$B and Er$_2$Fe$_{14}$B, respectively, which was explained in detail in the preceding subsection.
Let us comment a little bit on the reduction factor $R_E$ of the exchange energy in Table 2 with respect to the calculated results of Figs. 9a and b. There are two different origins for $R_E$:

(i) One is the correction from Hartree–Fock calculation of the exchange interaction between 4f and 5d states, namely the correction by intra-atomic configuration interaction, which results in the value of $R_E$ ($\approx 0.8$) at zero temperature.

(ii) The other one is the reduction of exchange energy by thermal fluctuations of 4f magnetic moment. In the comparison of calculated XMCD spectra with experiment at room temperature, this effect is important because the magnetic polarization of 5d states due to 4f–5d exchange interaction is reduced in proportion to the reduction of 4f magnetization. Actually, the magnetization of $R_2Fe_{14}B$ at room temperature is mainly carried by Fe 3d electrons. Also the magnetization of R 4f electrons is strongly reduced by thermal fluctuations (Herbst, 1991), except for Gd. In the case of Yb and Tm, the spectral shape of XMCD is similar to that of Lu which has no 4f magnetic moment. Therefore Asakura et al. suggested a drastic reduction of 4f magnetization and extremely small values of $R_E$ (0.04 and 0.08). For Gd, on the other hand, a considerable contribution from 4f magnetization to XMCD was seen, reflected in the reduction factor 0.4. It is to be noted that the rough trend of reduction factor $R_E$ (which takes a maximum at Gd and decreases in going away from Gd) is in qualitative agreement with the behaviour of $T_c$ in $R_2Fe_{14}B$ (Herbst, 1991). Of course, Asakura et al.’s treatment of $R_E$ is still phenomenological. Especially there is room for studying the XMCD temperature dependence from a microscopic point of view (Section 2.3.6). Nevertheless in the present section, we have reported a valuable extension of Fukui et al.’s theory (2001) by Asakura et al. (2002), which brings essentially two improvements: (1) a more realistic cluster model as well as (2) explicit calculations of XMCD.

On the point (1), the DOSs of 5d states obtained in Fig. 5 are actually not semi-elliptic as assumed by Fukui et al. (2001). However, in XAS and XMCD spectra, the DOS structures are mostly smeared out by the large spectral broadening due to the 2p core hole lifetime. If the lifetime broadening effect is artificially reduced, the XMCD spectrum would reflect the 5d DOS structures. We would like to point out that experimental measurements of such detailed XMCD spectra with spectral broadening smaller than 2p lifetime width should be possible, in principle nowadays, especially with the help of Hämäläinen et al.’s technique (1991). These authors already succeeded in observing the pre-edge structure of the Dy L$_3$ XAS of Dy compounds without 2p core lifetime broadening by measuring the excitation spectrum of 3d to 2p resonant X-ray emission spectroscopy (RXES). This technique can also be applied to measure the XMCD spectrum (see Section 3.2.3). Then the present method of calculating XMCD structures, related to the detailed 5d DOS structures, should become more and more important. Actually, Asakura et al. (2004) have also performed theoretical calculations of XMCD in $R_2Fe_{14}B$ with the use of the R 5d and Fe 3d DOS obtained with the tight-binding energy-band model, instead of the cluster model which we have treated in the present section. They have shown that the results of XMCD calculated with the tight-binding model coincide almost perfectly with those calculated with the
cluster model, if we take into account the spectral broadening due to the 2p core hole lifetime. At the same time, they have shown that some more details of the R 5d band structure obtained with the tight-binding model should be reflected in the XMCD spectra, if the spectral broadening could be suppressed.

On the point (2), Asakura et al. (2002) succeeded in calculating XMCD spectra for Lu or La compounds on the basis of microscopic electronic states. Generally speaking, there is no reason why the contribution to XMCD from 4f–5d exchange interaction would be independent of that from 5d–3d hybridization, since both contributions are correlated to each other through 5d electronic structure. As far as Asakura et al.’s calculation is concerned, however, the two contributions can be shown to be almost independent as demonstrated for Sm$_2$Fe$_{14}$B (see Figs. 7a and b).

Now we turn to the RFe$_2$ series of compounds which present some new interesting aspects in addition to the previously considered features for R$_2$Fe$_{14}$B.

2.3. RFe$_2$ type Laves-phase compounds

2.3.1. Laves-phase electronic bands structure

In order to further discuss XMCD, we next report the electronic structure of RFe$_2$ Laves-phase type compounds calculated by Harada et al. (2004). To this end, these authors used a tight-binding method (Yamada et al., 1984) for the R 5d and Fe 3d states of RFe$_2$, which is known to provide reasonable electronic structure, including the hybridization between them. The effect of the 2p core hole was neglected for simplicity, since the photo-excited 5d electron is rather extended. The tight-binding Hamiltonian describing these states was then diagonalized using linear combinations of R 5d and Fe 3d states which are fairly hybridized. Also the effect of exchange field due to 4f electrons in the Hund’s rule ground state has been taken into account within the energies of 5d levels as well as the exchange field due to 3d–3d exchange interaction within the energies of 3d levels. The density of states (DOS) thus obtained is presented in Fig. 10a, at least, as far as one example of the Laves phase series (with a light element, R = Sm) is considered, i.e. in the case of SmFe$_2$. Harada et al. (2004) also considered the counterpart example of the RAl$_2$ series, i.e. SmAl$_2$, in order to extract the role of 4f exchange field, when Fe 3d states happened to be replaced by nonmagnetic Al 3p states (Fig. 10b). In such a case, they assumed another set of bands structure parameters adapted to the new compound under consideration. At last, they reported the calculated DOS of a compound at the end of the lanthanides series, i.e. LuFe$_2$ (Fig. 11).
Fig. 11. Calculated partial DOS in LuFe$_2$. The vertical dashed line denotes the Fermi energy. Up and down mean the spin directions.

From all these results, Harada et al. (2004) stated the following remarks:

(i) The DOS of R 5d bands show a characteristic peak at high energies for all three cases.
(ii) In SmAl$_2$, the hybridization between R 5d and Al 3p states is not significant, although the considered states are located relatively close in energy. This may be due to the symmetry of these states. Also 5d bands are polarized over the whole energy region by 4f exchange field.
(iii) In SmFe$_2$ and LuFe$_2$ the hybridization between R 5d and Fe 3d states is relatively strong, especially for the minority-spin band. As a consequence, the number of 5d electrons having down spin is larger than that of the electrons having up spin. This yields an antiferromagnetic spin arrangement of 5d and 3d moments. Thus, the tight-binding model reproduces a delicate energy dependence of the polarization in R 5d states, which directly affects XMCD spectra.
(iv) As far as the DOS of Sm 5d states in SmAl$_2$ compounds is concerned (Fig. 10b) it is rather different from that in SmFe$_2$ (Fig. 10a), not only near the Fermi energy but also along the whole energy region. The former is apparently due to the absence of spin polarization in Al 3p band while the latter originates from characteristics of Al 3p band (relative energy position as well as symmetry). It is to be noted that the states peaked in the highest energy region are polarized by intra-atomic exchange interaction. Thus, the polarization in the whole energy region of 5d bands will produce a broad XMCD spectrum.
(v) In LuFe$_2$ the spin polarization of Lu 5d bands is only due to hybridization with spin-polarized Fe 3d bands, so that the spin polarization of empty 5d bands is rather localized near the Fermi level with almost no spin polarization in the high energy region of 5d bands. Once the electronic bands structures have been obtained, Harada et al. (2004) were able to calculate the XAS spectrum for each incident X-ray polarization. The value of $\alpha$ (see Section 2.1.2) was assumed to be 0.6 (1/eV) for all R elements in the following. Whenever comparison was made between the calculated spectra and those observed from experiment, it was necessary to add the EQ contribution calculated using an atomic model (see Section 2.1.3).

2.3.2. RFe$_2$ Laves-phase compounds

Harada et al. (2004) calculated XMCD spectra of RFe$_2$ at the R atom L$_{2,3}$ edges for all trivalent R element series to see the trend of XMCD. Unfortunately, the experimental data for the light rare earths (La, Pr, Nd, Eu) compounds, as well as for Yb compound, are not available, in contrast to the preceding R$_2$Fe$_{14}$B series for which almost all experimental spectra are at hand. Then, they compared in Fig. 12(a) and (b) the calculated spectra for Gd and for the next heavy R (Tb, Dy, Ho, Er, Tm) compounds with the experimental ones (Dartyge et al., 1998). It is to be noted that the XMCD intensity calculated for each compound is much larger than the experimental results. Then, the previously considered intensities were reduced by a reduction factor 0.2 for all compounds, except for GdFe$_2$ where it was 0.6. Possible origins of that reduction were partially discussed in Section 2.2.6 (Fukui et al., 2001; Asakura et al., 2002).

From the calculated results of the series of heavy trivalent R elements (Fig. 12), a variety of spectral shapes was obtained depending on the R element and the considered absorption edge: roughly speaking, for heavy R compounds, the L$_3$ edge spectra consist of an intense positive peak at higher energies, coming from the ED contribution, and a weak negative peak at lower energies, arising from the EQ contribution, while the L$_2$ edge spectra are weak (except for Gd) and have a complicated shape. These characteristics are consistent with the experimental results, as shown in Fig. 12.
Fig. 12. Calculated (solid curve) and experimental (dotted curve) results of XMCD spectra at: (a) $L_3$ and (b) $L_2$ edges in $RFe_2$. The calculated XMCD intensity is reduced by a factor 0.2 except in the case of GdFe$_2$ where it is reduced by 0.6.

It is interesting to compare these results with those of $R_2Fe_{14}B$ shown in Section 2.2. In the $L_3$ edge of heavy $R$ elements, the behaviour of XMCD is similar for $RFe_2$ and $R_2Fe_{14}B$, if we invert the sign of XMCD, taking into account that the dominant magnetic moment is due to the $R$ 4f and Fe 3d contributions, respectively, for $RFe_2$ and $R_2Fe_{14}B$. This similarity of the XMCD behaviour is understood from the fact that the ED contribution (the contribution (i)) from the $R$ 5d–4f exchange interaction is dominant (as seen from Fig. 2) and much larger than the ED contribution from the $R$ 5d–Fe3d hybridization (the contribution (ii)). On the other hand, in the $L_2$ edge of heavy $R$ elements, both the ED contribution (i) and the EQ contribution (contribution (iii)) are very small (see Figs. 2 and 3). Therefore, for $RFe_2$ all the contributions (i), (ii) and (iii) become comparable with each other, so that the spectral shape of XMCD are complicated, as a characteristic feature of $RFe_2$. However, for $R_2Fe_{14}B$ the XMCD spectral shape is dominated by the contribution (ii), which is much larger than that of $RFe_2$ because of the much larger weight of Fe in the atomic
composition. In the case of RFe₂ with light R elements, the XMCD spectra at the L₂ edge show a strong positive peak coming from (i), while those at the L₃ edge exhibit a variety of shapes due to the small and comparable contributions (i), (ii) and (iii).

As shown in Fig. 12, the agreement between calculated and experimental spectra is fairly good if we except some discrepancies at the positive high-energy peak in L₂ spectra for Dy, Ho, Er and Tm (as well as the MCD amplitude). By inspection, it is found that the high-energy peak in the corresponding DOS could yield a relatively stronger positive peak at high energies, if an additional exchange splitting of the 5d bands would be introduced. A plausible origin of this additional splitting is the 5d–5d exchange interaction neglected so far, and a trial to improve the XMCD spectra by this interaction will be discussed in the next subsection.

2.3.3. Role of R 5d–R 5d exchange interactions

In the previous analyses, the effect of 5d–5d exchange interaction has been neglected. Although an overall trend of calculated XMCD spectra are fairly in agreement with those observed, we cannot reproduce a positive high energy peak, observed by Dartyge et al. (1998), at the L₂ edge of Dy, Ho, Er and Tm compounds.

In a recent paper, Fujiwara et al. (2006) have tried to improve XMCD spectra, taking into account 5d–5d exchange interactions within a mean-field approximation: they assumed the exchange field is proportional to the 4f magnetic moment for each R. The result is shown in Fig. 13. The improvement is evident although exchange field is rather weak.

The reason why the weak 5d–5d exchange interaction is however appreciable in XMCD spectra is that the sharp peak in 5d DOS at high energies is a characteristic of Laves phase compounds. Furthermore, Fujiwara et al. stated that the effect is not so significant in other cases (L₃ edge of these RFe₂ and L₂ and L₃ edges of R₂Fe₁₄B). It is to be noted that in the XMCD spectra at the L₂ edge of heavy RFe₂ the three contributions (i), (ii) and (iii) are all weak and hence relatively minor effects (such as the weak 5d–5d exchange interaction) comes up as an appreciable effect. We again stress that this is a consequence of the combined effect of 5d–5d exchange interaction and the sharp peak in 5d DOS at higher energies.

2.3.4. LuFe₂ Laves-phase compound

In order to clarify the variety of XMCD spectra in Fig. 12 and hence their origin, we investigate in the following rather simple cases. Firstly, we consider LuFe₂, where the R 4f shell is completely filled. In that case, since there is no effect from 4f electrons the only source to polarize the R 5d states is provided by hybridization with the spin-polarized Fe 3d states (see the partial DOS shown in Fig. 11). We note that the spin polarization of R 5d electrons is energy-dependent and is most prominent near the Fermi energy (see also the calculated result shown in Fig. 16). This explains the fact observed in LuFe₂ that the peak of the XMCD spectrum is located at lower energy than that of the corresponding XAS spectrum (Dartyge et al., 1998). Thus, XMCD is sensitive to the energy dependent polarization of the R 5d states, although a detailed structure is smeared out considerably by the lifetime broadening of the 2p core hole. As will be discussed in Section 3.2, the difference in energy of the XMCD and XAS peaks plays an important role in CeFe₂.
2.3.5. \( RaAl_2 \) Laves-phase compounds

In this subsection, we report the XMCD for one example of the \( RaAl_2 \) series with \( R = Sm \), a light element of the series, i.e. \( SmAl_2 \) \cite{Harada2004, Fujiwara2005}. In this compound there is an effect of \( Sm \, 4f \) electrons on \( Sm \, 5d \) states through the intra-atomic exchange interactions. As was discussed above, the effect of intra-atomic exchange interactions between 5d and 4f electrons generally dominate XMCD spectra (even in \( SmFe_2 \)). In certain cases, the energy-dependent enhancement of the ED matrix element changes the sign of XMCD spectra. This is seen in Fig. 14, where the XMCD spectra for \( SmAl_2 \) are shown for various values of \( \alpha \). At the L2 edge the sign of XMCD intensity changes with increasing \( \alpha \), while at the L3 edge, XMCD spectra are affected rather mildly. This fact remains true for all other light \( R \) elements, but the situation is changed for the heavy \( R \) elements, for which the effect of \( \alpha \) is more serious at the L3 than at the L2 edge.

In Fig. 15, we show the calculated XMCD spectra at the L3 edge of \( SmFe_2 \) and \( SmAl_2 \), and compare them with experimental results \cite{Mizumaki2004}. The value of \( \alpha \) is taken to be 0.6 \( 1/eV \), and the contributions (ii) and (iii) for \( SmFe_2 \) (contribution (iii) for \( SmAl_2 \)) are also taken into account. The lowest-energy negative peak for both materials is due to the EQ contribution (iii), which is located at the lower energy region with respect to the Fermi energy \( E_F \), chosen to be at zero energy. The other structures are due to the ED contribution (i) from the \( R \, 5d-4f \) exchange interaction even for \( SmFe_2 \). For the L3 edge of \( Sm_2Fe_{14}B \), we have shown that all the contributions (i), (ii) and (iii) are comparable in weight (see Section 2.2.3), but for \( SmFe_2 \) the contribution (ii) from the \( R \, 5d-Fe3d \) hybridization is weaker than the contributions (i) and (iii) because of the smaller weight of Fe in the atomic composition. The difference in the XMCD spectral shapes for \( SmFe_2 \) and \( SmAl_2 \) is caused by the different 5d band structure, instead by the contribution (ii) in \( SmFe_2 \). We can say that the agreement of the calculated and experimental results is quite good although the amplitudes of the XMCD spectra are reduced by 0.3 and 0.03 in \( SmFe_2 \) and in \( SmAl_2 \), respectively. Possible reasons for the discrepancy were discussed in Section 2.2.6. Thus, it is quite instructive to discuss the XMCD spectrum dividing the contributions, although these are not simply additive.

2.3.6. Comparison between \( SmFe_2 \), \( LuFe_2 \), \( SmAl_2 \) compounds

Keeping the above mentioned results in mind, the calculated results of \( SmFe_2 \) are compared with those of \( SmAl_2 \) and of \( LuFe_2 \) in Fig. 16 in more details. Discussion here is restricted to the ED contributions (i) and (ii). As was mentioned above, the XMCD spectrum of \( LuFe_2 \) reflects the spin polarization due to hybridization with the spin-polarized Fe 3d states (ii), being effective near the Fermi energy while that of \( SmAl_2 \) is the consequence of the spin and orbital polarization due to exchange field by R 4f electrons (i), spreading over the vacant 5d band. As is seen in Fig. 16, the XMCD spectrum of \( SmFe_2 \) seems to be the sum of both contributions (i) and (ii), although the positive peak is more intense than the sum. This discrepancy is probably due to a non-linear correlation of both polarization effects in the electronic structure of 5d states.
Fig. 15. Calculated XMCD spectra of SmFe$_2$ and SmAl$_2$ at L$_3$ edge. Experimental data are indicated by dots from M. Mizumaki and T. Nakamura (unpublished data).

Fig. 16. Comparison of calculated results of XMCD spectra at L$_3$ edge for SmFe$_2$, LuFe$_2$ and SmAl$_2$.

2.3.7. Temperature dependence: case of ErFe$_2$

So far, we have considered XMCD at zero-temperature. Now, it is relevant to investigate the temperature dependence of XMCD spectra in RFe$_2$ compounds because the mechanism of XMCD spectra at L$_{2,3}$ edges is quite subtle as we reported above (especially at the L$_2$ edge of heavy R elements) and each contribution to XMCD has its own temperature dependence.
Recently, Giorgetti et al. (2004) pointed out quite a new temperature dependent XMCD spectrum in the case of ErFe$_2$ at L$_2$ absorption edge. With increasing temperature, one of the peak intensity increases while the other peaks decrease monotonically. Let us recall that ErFe$_2$ is a ferri-magnetic compound with a compensation temperature $T_{\text{com}} = 486$ K and a Curie temperature $T_c = 587$ K. Actually it is quite natural to expect a decreasing XMCD intensity versus increasing temperature since the intensity is proportional to the magnetization. However, in the case under investigation, there are differing contributions: (i) ED due to R 5d–4f exchange interaction, (ii) ED due to R 5d–Fe 3d hybridization and (iii) EQ, each contribution having its own sign and temperature dependence. Fujiwara et al. (2006) pointed out the following remarks for the XMCD spectrum at L$_2$ edge of ErFe$_2$ (see Fig. 12(b)). The contributions (i)–(iii) have the same order of magnitude, and at the lower energy region (i) and (ii) have opposite sign and a considerable cancellation occurs (the sign of XMCD for (i) is negative and positive in low and high energy regions, respectively, that for (ii) is mainly positive, and that for (iii) is negative). At low temperatures the Er 4f magnetization is larger than the Fe 3d magnetization, but with increasing temperature towards $T_{\text{com}}$, the Er 4f magnetization decreases more rapidly than the Fe 3d magnetization, so that the amplitude of (i) decreases more rapidly than (ii). Thus, it is possible to have the increase of the positive contribution (ii) with increasing temperature due to the decrease of the cancellation with the negative contribution (i).

In Fig. 17, we show a result of preliminary calculations by Fujiwara et al. (2006) for the temperature dependence of the XMCD spectrum at the L$_2$ edge of ErFe$_2$. Some band parameters are modified, to some extent, to obtain a better agreement with the experimental XMCD spectra. In order to simulate the increase in temperature, the contributions of (i) and (iii) are reduced by introducing the reduction factor $R_m$, while no reduction is made for (ii). In the XMCD spectrum, the lowest energy peak with negative sign is due to (iii), the second-lowest-energy positive peak is mainly due to (ii) but overlaps with (i), the second-highest-energy negative peak is mainly due to (i) but overlaps with (ii), and the highest-energy positive peak is due to (i). This result is in considerable agreement with the experimental result (Giorgetti et al., 2004).

Finally, we would like to mention that it is quite promising to investigate the temperature dependence of the XMCD spectra experimentally and theoretically for obtaining more detailed information on magnetic materials.
2.3.8. Concluding remarks

In Section 2.3, we reviewed the mechanism of XMCD spectra at R L_{23} edges in R inter-metallic compounds, RFe_{2} in the Laves phase, by using a rather elaborated model. The band nature of R 5d and Fe 3d states, including the hybridization between them, was treated by a tight-binding approximation whereas the intra-atomic exchange interaction between 4f and 5d states was described by a mean-field arising from atomic 4f electrons in the Hund’s rule ground state. Then, the XMCD spectra happened to consist of both ED and EQ contributions: the former depends on the detailed polarization of R 5d states while the latter is dominated by rather localized 4f states. Beside the weak EQ contribution, we now comment on the ED contribution. For that contribution, the R intra-atomic exchange interaction generally dominates the polarization of R 5d electrons and hence the XMCD spectra depend on 4f states. Once more it is important to realize the novel role of intra-atomic exchange interaction, i.e. the enhancement of 2p → 5d dipole matrix element, which is indispensable for a proper interpretation of XMCD at R L_{23} edges. Especially for XMCD spectra of light R elements at L_{2} edge and of heavy R elements at L_{3} edge, this enhancement effect plays a crucial role.

Here we would like to focus on another important ED contribution arising from the hybridization of R 5d states with spin-polarized Fe 3d states, which is straightforward taken into account in tight-binding approximation. Especially for XMCD at L_{2} edge of RFe_{2} with heavy R elements, this ED contribution becomes comparable with other ED and EQ contributions, all of which are very weak, and the competition of the three contributions give rise to complicated XMCD spectral shape and its complicated temperature dependence. This situation is very interesting and characteristic of RFe_{2} systems, in strong contrast to the case of R_{2}Fe_{14}B where the XMCD at L_{2} edge of heavy R elements is determined only by R 5d–Fe 3d hybridization contribution. We can also see relatively detailed effects in the spectrum, leading to the information on relatively minor interactions in materials such as the effect of 5d–5d exchange interaction combined with the sharp peak in 5d DOS at higher energies. Before concluding this section, we would like to stress again that it is quite promising to investigate the temperature dependence of XMCD spectra experimentally and theoretically in order not only to study more detailed information on magnetic materials but also to confirm the subtle mechanism of XMCD.

We are now able to apply the present method to the analysis of XMCD spectra for various other R compounds and to discuss in details the role played by 5d electrons as far as their magnetic properties are concerned. Especially for R systems with complicated atomic arrangements, the present method will provide new powerful means to calculate XMCD spectra quantitatively. There is an interesting problem left for the future, i.e. to modify the present theory so as to apply it to insulating R compounds.

3. Ce systems

3.1. CeRu_{2}Ge_{2}: A well localized 4f^{1} system

3.1.1. General context and proposed model

These last decades, a variety of XMCD experiments have been performed, especially at L_{23} and M_{45} absorption edges of cerium, in various ferromagnetic inter-metallic compounds (Baudelet et al., 1990; Schütz, 1991; Carra et al., 1991; Giorgetti et al., 1993; Finazzi et al., 1996). These are motivated by interesting phenomena of 4f valence electrons of Ce; valence fluctuation (VF) or mixed valence (MV) phenomena. In the present subsection we first focus on XMCD in L_{23} XAS of CeRu_{2}Ge_{2}, as a typical example of trivalent Ce compounds (Rietschel et al., 1988; Severing et al., 1989; Jo and Imada, 1993). Other examples would be CePd, CeAl_{3}, CeRh_{3}B_{2} and so on. In such cases, the theory developed in the previous sections is applicable, assuming one 5d electron to exist in the ground state: the XMCD spectra are dominated by the 2p–5d ED transition combined with the effect of 4f–5d exchange interaction, where the 4f electrons are within Hund’s rule ground state. We notice that an enhancement of 2p–5d dipole matrix element (see Section 2.1.2) due to the effect of contraction in the radial part of 5d orbitals should be included in the corresponding calculation. Although the theoretical results are, in general, quite consistent with the experimental ones for other R elements (see Section 2), there still remain exceptional discrepancies in XMCD spectra of Ce compounds to be explained separately.

In this subsection, we study one of such examples, the Ce XMCD spectra of CeRu_{2}Ge_{2}. Within the simplest Ce^{3+} ionic model, a strong positive and a weak positive spectra are suggested by the theory, respectively, at L_{2} and L_{3} edges, while a strong positive and a weak negative spectra are observed, respectively, at L_{2} and L_{3} edges. As was mentioned before, at L_{2} edge the effect of enhancement of ED transition matrix element is crucial while at L_{3} edge, where the integrated XMCD intensity is weak, the cancellation occurs more or less among contributions from different 5d states,
where a ratio of two parameters $a$ and $b$ is determined by the strength of the tetragonal CF. Based on this 4f ground state, we try to reproduce the XMCD spectra by taking into account the 4f interactions and find out that the tetragonal CF plays an important role in solving the discrepancy in XMCD spectra of Ce$^{3+}$ in CeRu$_2$Ge$_2$. It is interesting to note that even in this simplest case of Ce$^{3+}$ compounds corresponding to 4f$^1$ configuration, our analysis needs detailed information on 4f states, which affect indirectly the ED transition ($2p \rightarrow 5d$) through 4f–5d exchange interaction.

3.1.2. Numerical results and comments

We performed a series of calculation of XMCD spectra for a reasonable value of $z$ taken to be 0.6 1/eV (Matsuyama et al., 1997), and for a variable ratio $b/a$ (of the above introduced CF parameters) taken from $\sqrt{3}$ (a cubic value) to 1.0. In Fig. 18 we show the results for $b/a = 1.0$ (a), 1.1 (b) and 1.2 (c), and it comes out that $b/a = 1.1$ (b) is the most appropriate choice to fit experimental spectra of CeRu$_2$Ge$_2$. Actually, in Fig. 18(b), the signs as well as the relative intensities of XMCD at L$_2$ and at L$_3$ appear to be consistent with experiment. The value of $b/a$ determined above seems to be reasonable since it is also reproduced when using a set of tetragonal CF parameters (see Fukui et al., 1999 for details) which yield the characteristic splittings, i.e. 43 meV and 65 meV for the first and second excited states, respectively, according to the specific heat measurements (Rietschel et al., 1988) of CeRu$_2$Ge$_2$. We note that this set of tetragonal CF parameters is not unique since the XMCD data alone are not sufficient to determine it.

3.1.3. Concluding remarks

So far we have seen that in the case of a trivalent Ce XMCD spectra are affected by details of 4f electron states, which, in ED transition ($2p \rightarrow 5d$), give rise not only to the polarization effect on the 5d ground state, but also to an effect of contraction in the radial part of 5d orbitals and hence an enhancement of the transition dipole matrix element through the 4f–5d exchange interaction. Also we have found that, in the case of Ce L$_3$ edge, more detailed information than Hund’s coupling on the 4f electron state is required. Especially to obtain a negative XMCD spectrum at L$_3$ edge it is essential to take into account the tetragonal CF, which mixes the states, $J_z = |−5/2⟩$ and $|3/2⟩$ in the $J = 5/2$ manifold split by the relatively large spin–orbit coupling, although the 4f electron is not directly concerned with the 2p–5d transition.

The sum rule (Thole et al., 1992) for XMCD is known to be useful to obtain information about orbital states. These orbital states are actually important in understanding magnetic anisotropy of rare-earth compounds. Unfortunately, sum rule is not straightforward applicable in our case, since the radial part of the transition matrix element depends on the $z$-component of the azimuthal quantum number as well as on the spin quantum number of the 5d electron. Discussions so far are restricted to the case of Ce$^{3+}$. It is well known that there are many Ce compounds showing VF or MV phenomena, and their XMCD spectra have also been observed (Baudelet et al., 1990, 1993). In order to study this problem, we are now reporting on a calculation based on a many-electron theory, taking into account the inter-atomic configuration interaction. The result is reported in the next subsection.

3.2. CeFe$_2$: a less localized $4f^1$ system

3.2.1. Brief presentation of the theoretical model and experimental results

Let us consider such a MV inter-metallic compound, CeFe$_2$, as an example. Other examples would be CeCo$_5$, Ce/Fe multi-layers and so on. CeFe$_2$ behaves as a ferromagnetic material but has anomalously small magnetic moment and a low Curie temperature ($T_c = 230$ K) as compared to other RFe$_2$ (see Section 2.1). However it is higher as compared to CeRu$_2$Ge$_2$ where $T_c = 9$ K. We ascribe the considered anomalous behaviour to the MV electronic state of Ce which can be satisfactorily described by the well known extended SIAM (single impurity Anderson (1961) model)(Kotani et al., 1988; Gehring, 2002), including various Coulomb interactions, i.e. $U_{ff}$, $U_{fc}$, $U_{fd}$, $U_{dc}$
Fig. 18. Calculated XMCD spectra of Ce$^{3+}$ L$_2$ and L$_3$ edges for the 4f electron state characterized by the ratio of the mixing coefficients $b/a$ between $|J_z = -5/2\rangle$ and $|J_z = 3/2\rangle$, (a) $b/a = 1.0$, (b) 1.1 and (c) 1.2. The inset in (b) shows the experimental result for CeRu$_2$Ge$_2$. 
Fig. 19. Calculated results (solid curves) and experimental ones (crosses) of XAS and XMCD at Ce L₃ edge of CeFe₂. Dashed curve represents the background contribution assumed in the calculation.

('c' means ‘core hole’). Here we combine it with a LCAO (Ce₁₇Fe₁₂) cluster calculation for Ce 5d and Fe 3d conduction states. Thanks to that cluster approach, the band nature of Fe 3d and Ce 5d states is well treated, as well as hybridization between both types of states. Also let us recall that in the considered model, we handle the three following electronic configurations: 4f⁰, 4f¹ and 4f². Let us also precise that, in CeFe₂, the hybridization of Ce 5d band with its Fe 3d partner is the origin of spin polarization of 5d states and then it happens to be crucial for XMCD at L₂,₃ edges. Furthermore, similarly to our calculation of Ce L₃ edge and 3d RXPS in CeRh₃ (Parlebas and Kotani, 2004), the effects of $U_{fd}$ and $-U_{dc}$ are also explicitly taken into account in the corresponding Hamiltonian (Asakura et al., 2004b, 2005), as already stated above.

Experimental results of XAS ($\times$) and XMCD ($+$) for Ce L₃ and L₂ edges of CeFe₂ are shown in Figs. 19 and 20, respectively (Giorgetti et al., 1993; Schille et al., 1994). The double-peak structure of XAS is a characteristic feature of MV Ce compounds and usually explained by 4f⁰ (higher energy peak) and 4f¹ (lower energy peak) components in the final state.

Corresponding to them XMCD spectra also exhibit a double-peak structure. The sign of XMCD is positive for L₃ and negative for L₂, similar to that in LuFe₂, so that we expect that XMCD in CeFe₂ is caused mainly by the spin polarization of Ce 5d bands due to hybridization with spin-polarized Fe 3d bands, as in the case of LuFe₂. This is reasonable because the spin and orbital polarization of Ce 4f states would be very small due to the MV character. However, there remain some features to be solved theoretically: (1) The energy positions of the two peaks in XAS are
different from those of XMCD. The difference is larger for the lower energy peak (4f$^1$ peak) than the higher energy one (4f$^0$). (2) The widths of the two XMCD peaks are different; the lower energy peak is broader than the high energy one. (3) It is not clear where we can see the contribution from the 4f$^2$ configuration.

Theoretical calculations have been made to solve these problems (Asakura et al., 2004b, 2005).

### 3.2.2. Numerical results and comments

We consider a Ce$_{17}$Fe$_{12}$ cluster model to describe Ce 5d and Fe 3d states, because the cluster with finite size is more convenient to be combined with SIAM. The Hamiltonian of the cluster is given by Eq. (2.7), and diagonalized in the form

$$H_c = \sum_\ell \varepsilon_\ell \sigma_\ell^+ \sigma_\ell,$$  

(3.2)

by the transformation

$$a_\ell^+ = \sum_{\mu,i} (\mu,i|\ell)a_{\mu i}^+ + \sum_{\nu,j} (\nu,j|\ell)a_{\nu j}^+.$$  

(3.3)

The mixed Ce 5d–Fe 3d states are combined with Ce 4f states in the frame of an extended SIAM. The Hamiltonian of the extended SIAM in the initial state of XAS is written as

$$H_g = \varepsilon_4 \sum_\lambda a_{4 \lambda}^+ a_{4 \lambda} + U_{44} \sum_{\lambda > \lambda'} a_{4 \lambda}^+ a_{4 \lambda'} a_{4 \lambda'}^+ a_{4 \lambda} + \sum_\ell \varepsilon_\ell a_{\ell}^+ a_{\ell} + \sum_{\ell,\ell'} (V_{\ell \ell'} a_{\ell}^+ a_{\ell'} + h.c.),$$  

(3.4)

where $\lambda$ represents the combined spin and orbital quantum numbers of the Ce 4f state, $U_{44}$ is the Coulomb interaction of Ce 4f states and $V_{\ell \ell'}$ is the hybridization between 4f ($\lambda$) and $v(\ell)$ states. In the final state of XAS, the 2p core electron
Fig. 21. Calculated results of XAS and XMCD at L₃ edge for various values of \( U_{dc} \) in the limit of 4f⁰ configuration. The peak position of XMCD is taken as the origin of the relative energy.

is excited to the 5d band and the 4f level is pulled down due to the core hole potential \(-U_{fc}\). Furthermore, 5d electrons on the core hole site \((j = 0)\) interact with the 4f electron through the Coulomb interaction \( U_{fd} \) and the core hole through \(-U_{dc}\). Therefore, the Hamiltonian in the final state is given by

\[
H_f = H_g - U_{fc} \sum_{\lambda} a_{f,\lambda}^+ a_{f,\lambda} - U_{dc} \sum_{k,k'} C_{k,k'} a_{f,\lambda}^+ a_{f,\lambda} + U_{fd} \sum_{k,k',\lambda} C_{k,k'} a_{f,\lambda}^+ a_{f,\lambda} a_{v,k'}^+ a_{v,k'},
\]

(3.5)

where

\[
C_{k,k'} = \sum_v \langle k|v, 0\rangle \langle v, 0|k'\rangle.
\]

(3.6)

The Hamiltonians \( H_g \) and \( H_f \) are diagonalized by taking into account the three configurations 4f⁰, 4f¹ and 4f². In diagonalizing \( H_f \) it is assumed that only a photoexcited electron is affected by the Coulomb interactions \(-U_{dc}\) and \( U_{fd}\). By the calculation CeFe₂ is shown to be in the MV state with an average 4f electron number in the ground state \( n_f = 0.64\). The calculated results of XAS and XMCD are shown in Figs. 19 and 20 by solid curves, where the dashed curve is the background contribution to XAS. The values of \( U_{dc} \) and \( U_{fd} \) are taken to be 2.0 and 1.7 eV, respectively. The agreement between calculated and experimental results is satisfactory both for XAS and XMCD at both L₂ and L₃ edges.

In order to see the mechanism determining the relative peak positions of XAS and XMCD, the effect of the core-hole potential \(-U_{dc}\) on XAS and XMCD is calculated for 4f⁰ peak, disregarding 4f¹ and 4f² contributions. The results are shown in Fig. 21. In the case of \( U_{dc} = 0\), the peak of XMCD is shifted by about 4 eV towards lower photon energy with
respect to that of XAS, and its width is smaller. The reason for this is as follows: since the XAS peak occurs by optical transition of the $2p_{3/2}$ core electron to the Ce 5d conduction bands above the Fermi level, the position and width of the XAS peak correspond to the center and the width of the unoccupied part of Ce 5d bands. On the other hand, XMCD is caused only by the spin polarized part of the unoccupied Ce 5d bands. The spin polarization of Ce 5d bands is induced by Fe 3d spin polarization through hybridization between Ce 5d and Fe 3d states, but Fe 3d bands are mainly located at the lower energy side of Ce 5d bands, so that the spin polarization of the empty states of Ce 5d bands is limited to the states near the FL. With increasing $U_{dc}$, on the other hand, the oscillator strength of XAS is transferred to the lower energy side (toward the FL, which is the peak position of XMCD), and therefore the energy difference of XAS and XMCD peaks decreases. This explains that the positions of the higher energy peak (4f$^0$ peak) of XAS and XMCD are close to each other in Fig. 19.

For the lower energy peak (mainly 4f$^1$), on the other hand, we have to take into account the effect of Coulomb interaction between 4f and 5d states $U_{fd}$, too. Then, the effects of attractive $-U_{dc}$ and repulsive $U_{fd}$ almost cancelled each other, so that the situation becomes similar to the case of $U_{dc} = 0$ in Fig. 21. Therefore, the effect of $-U_{dc}$ and $U_{fd}$ is essential in understanding the relative positions of the two peaks in XAS and XMCD in CeFe$_2$. More generally we notice that our parameter values are comparable to those used for 3d XPS spectra (Konishi et al., 2000).

The difference in the spectral widths of the two XMCD peaks, as well as the difference in the spectral widths of XAS and XMCD peaks, is also caused mainly by the effect of $-U_{dc}$ and $U_{fd}$, as seen from Figs. 19 and 21. For the contribution from the 4f$^2$ configuration, a detailed discussion will be given in the next subsection.

### 3.2.3. MCD in resonant X-ray emission spectra

Here we consider resonant X-ray emission spectroscopy (RXES) and its MCD (MCD-RXES) for CeFe$_2$, where the Ce 3d$_{5/2}$ to 2p$_{3/2}$ radiative transition occurs following the Ce 2p$_{3/2}$ to 5d radiative excitation. Through the calculations of RXES and MCD-RXES, we would like to discuss where is the 4f$^2$ contribution in the Ce L$_3$ XAS of CeFe$_2$ (Kotani et al., 2005). The RXES spectrum is given by

$$
F^{(\lambda_1, \lambda_2)}_{\text{RXES}}(\Omega, \omega) = \sum_{j} \left| \sum_{i} \langle j | T^{2}_{2} | i \rangle \langle i | T^{\lambda_1}_{1} | g \rangle \right|^2 \frac{\Gamma_{M}/\pi}{(E_g + \Omega - E_i + i\Gamma_L)^2 + \Gamma_M^2},
$$

where $\Omega$ and $\omega$ are energies of the incident and emitted photons with helicities $\lambda_1$ and $\lambda_2$, respectively, $|g\rangle$, $|i\rangle$ and $|j\rangle$ are the ground, intermediate and final states with energies $E_g$, $E_i$ and $E_j$, respectively, and $T^{\lambda_1}_{1}$ and $T^{\lambda_2}_{2}$ are the operators of optical transitions. MCD-RXES is a newly developed field of spectroscopy, which gives important information on the magnetic polarization of electronic states in ferromagnetic materials. MCD-RXES is defined by the difference of RXES spectra for the circular polarized incident X-ray with $+$ and $-$ helicities, where the polarization of the emitted X-ray is not detected.

Therefore, the MCD-RXES spectrum $\Delta F_{\text{RXES}}(\Omega, \omega)$ is described by

$$
\Delta F_{\text{RXES}}(\Omega, \omega) \equiv \sum_{\lambda_2} \left[ F^{(+, \lambda_2)}_{\text{RXES}}(\Omega, \omega) - F^{(-, \lambda_2)}_{\text{RXES}}(\Omega, \omega) \right].
$$

In the calculations presented in this section, we assume that the incident X-ray beam is antiparallel to the magnetization of CeFe$_2$ and the angle between the emitted and incident X-ray directions is fixed at 54.7° (magic angle).

As seen from the expression of RXES spectrum given above, the spectral broadening of RXES (as well as MCD-RXES) is given by $\Gamma_M$, the lifetime broadening of the Ce 3d core hole in the final state of RXES. Actually $\Gamma_M$ is much smaller than $\Gamma_L$, the lifetime broadening of the Ce 2p core hole in the final state of XAS (intermediate state of RXES). The value of $\Gamma_M$ is estimated to be about 0.7 eV, while $\Gamma_L$ is about 3.0 eV from the fitting of the experimental Ce L$_3$ XAS spectrum in Fig. 19. Therefore, we expect that RXES (and MCD-RXES) spectra exhibit more precise structures than XAS (and XMCD). The calculations of RXES and MCD-RXES are performed with the extended SIAM for the incident X-ray energy tuned to the positions a to m in Fig. 19, and the results are shown in Fig. 22 with the solid (RXES) and dashed (MCD-RXES) curves, where the background contribution to RXES is disregarded.

The calculated MCD-RXES spectra for the excitation energies a–e exhibit two peaks, which correspond to the 4f$^2$ (higher energy peak) and 4f$^1$ (lower energy one) configurations. For f to m, another peak occurs on the lower photon
energy side, corresponding to the $4f^0$ configuration. Therefore, we obtain the signal of the $4f^2$ configuration in the MCD-RXES spectrum.

A more direct way to detect $4f^2$ contribution in $L_3$ edge of XAS is to calculate the excitation spectrum of RXES (especially MCD-RXES) for a fixed emitted X-ray energy at the energy difference of the $3d_{5/2}$ and $2p_{3/2}$ core levels, $\Delta_{dp}$. Namely, the amplitude of RXES (MCD-RXES) is calculated by fixing the emitted X-ray energy at $\Delta_{dp}$, which is taken as the origin of the abscissa in Fig. 22, as a function of the incident X-ray energy. The results of the excitation spectra are shown in Fig. 23. By comparing the calculated results in Figs. 19 and 23, we note that the results in Fig. 23 correspond to a less broadened version of those in Fig. 19. Actually, by calculating the XAS and XMCD spectra with smaller spectral broadening $\Gamma_M = 0.7$ eV, we can check that the result coincides almost completely with those in Fig. 23. Then, owing to the reduced spectral broadening, we can find the $4f^2$ contribution which is hidden in the conventional $L_3$ XAS. Namely, we find that the lower energy peak of XMCD split into two peaks in Fig. 23, which correspond to $4f^1$ (higher photon energy one) and $4f^2$ (lower photon energy one) contributions, although the splitting is not very clear in XAS.

We would like to emphasize that the excitation spectrum of MCD-RXES is a powerful tool to detect the contribution of Ce $4f^2$ configuration in Ce $L_3$ edge of the X-ray spectroscopy.
In summary we have shown theoretically that the technique of the excitation MCD-RXES spectrum is very useful to observe fine structures of XMCD beyond the lifetime broadening of the L3 core hole. This technique is an extension of the technique of the excitation spectrum of RXES by Hämäläinen et al. (1991) to MCD-RXES. Hämäläinen et al. succeeded in measuring the signal of weak electric quadrupole excitation at L3 edge of Dy compounds by observing the excitation spectrum of RXES. After the experiments, Tanaka et al. (1994) explained that the excitation spectrum of RXES corresponds to a less broadened version of XAS. It is highly desirable that the present theoretical prediction of observing the Ce 4f² signal by the excitation spectrum of MCD-RXES will be confirmed by experimental observations, and that the present technique will be used more generally in order to get high resolution MCD spectra. Let us just add that quite recently, the detection of 4f² contribution in L3 XAS for Ce–Th and Ce–Sc alloys has been reported by Rueff et al. (2004) taking advantage of resonant inelastic X-ray scattering spectroscopy (RIXS).

3.3. CePd₃: a dense Kondo material

We have so far discussed the XMCD behaviour of two typical classes of Ce compounds; a typical trivalence Ce compound CeRu₂Ge₂ and a typical mixed-valence Ce compound CeFe₂. In this section we describe experimental results of XMCD behaviour of another class of Ce compounds, CePd₃ and its alloy with TM elements, with no theoretical interpretation up to now.

3.3.1. Ce(Pd₃−ₓMnₓ)₃: experimental results for Mn substitution

Before treating the case of Ni impurities in CePd₃ in more details, we would like to mention another example of TM impurities in the same compound, i.e. Mn impurities. Unfortunately from the available literature (Singh and Dhar, 2003), only a concentration of about 3% of Mn has been considered. At that concentration the Mn ions form a sublattice with a large Mn–Mn distance of 8.5 Å and give rise to an ordered compound the chemical formula of which is CePd₃₈Mn. From the study of a field dependent magnetization \( M(H) \), Singh and Dhar could not find any saturation, even at low temperature (2.8 K) and high magnetic field (120 KOe). Instead they got an almost linear variation of \( M(H) \) with respect to \( H \), which they attributed to the contribution of Ce atoms in a paramagnetic state. Also from Arrots plots, due to the presence of Mn impurities, they could estimate a Curie temperature \( T_c \) between 30 and 40 K.

Finally from the study of the temperature dependent specific heat of (CePd₃)₈Mn, Singh and Dhar (2003) exhibited a peak at 32 K (i) in accord with the \( T_c \) estimated from the previously considered Arrots plots and (ii) in relation with a ferro-magnetic order of the Mn sublattice. Furthermore from their estimation of a specific heat coefficient as high as 275 mJ/mol K², Singh and Dhar concluded that (CePd₃)₈Mn behaves as a dense Kondo lattice. Of course this
study should be completed by selective XMCD measurements as well as a complementary investigation of a series of Ce(Pd$_{1-x}$Mn$_x$)$_3$ alloys with various $x$ contents. Such a detailed experimental work has been done for Ni impurities in CePd$_3$ (Kappler et al., 2004) and is reported in the next subsection.

3.3.2. Ce(Pd$_{1-x}$Ni$_x$)$_3$: experimental results for Ni substitution

First of all Kappler et al. (2004) made a full study of lattice parameters of various Ce(Pd$_{1-x}$TM$_x$)$_3$ alloys with TM = Ni, Ag: (i) as a function of Ni concentration $x$, with $x$ taken up to 25 at % Ni, the solubility limit of Ni in CePd$_3$; (ii) as a function of Ag concentration $x$, with $x$ taken up to 13 at % Ag. At low concentration, up to $x = 0.05$, the Ni substitution drives the Ce atoms towards the 4f$^1$ state limit. The lattice parameter reaches a broad maximum around $x = 0.05$ and then decreases with increasing concentration, showing a complex behaviour of the Ce–4f configuration. Of course in the case of Ag substitution the concentration dependent lattice parameter is almost linear and there is no maximum at all. Also magnetization was studied by Kappler et al. for $x < 0.20$ in the 2–20 K temperature range and for $x \geq 0.20$ down to $T = 50$ mK in fields up to 4 T. Especially they showed magnetization curves measured for Ce(Pd$_{0.75}$Ni$_{0.25}$)$_3$. As the temperature is lower than 2 K the saturation of the magnetization is observed with a corresponding opening of an hysteresis loop with a coercive field of about 0.1 T. These results evidence the existence of a ferromagnetic state below the Curie temperature $T_C \approx 2$ K. The saturated magnetic moment extracted from the magnetization measurements at 50 mK is about $M_S = 0.15 \mu_B$/f.u. This low $M_S$ value can be explained by the Kondo effect acting on the Ce ground state, reducing the moment of the $I_7$ state in a cubic crystalline field, expected to be equal to 0.7 $\mu_B$. A similar magnetic behaviour is also observed for a solid solution with $x = 0.20$.

In addition Kappler et al. studied the overall behaviour of the temperature dependent specific heat $C_M(T)$ in the 0.5–20 K temperature range for the series of Ce(Pd$_{1-x}$Ni$_x$)$_3$ samples and in comparison to a Ce(Pd$_{0.87}$Ag$_{0.13}$)$_3$ alloy. Within their temperature dependent specific heat measurements a very interesting feature is the almost fixed and pronounced peak which appeared at $T = 1.45$ K for the various $C_M(T)$ curves of all samples with $x \geq 0.1$. The amplitude of this peak increased with Ni concentration but was absent in pure CePd$_3$. Thus it should be directly related to the Ni effect on a CePd$_3$ compound and more precisely to a magnetic transition, as illustrated by the magnetization measurements at low temperatures. Compared to CePd$_3$ one may conclude that by increasing the Ce–Ce spacing a little bit from 4.126 Å for CePd$_3$ to a maximum of 4.140 Å for Ce(Pd$_{0.95}$Ni$_{0.05}$)$_3$ does not prevent the disappearance of the nonmagnetic FL behaviour and the creation, instead, of a magnetically ordered state. Probably the d conduction band as well as the $4f$–$d$ hybridization change sufficiently from a Ce–Pd to a Ce–Ni environment to give rise to these different behaviours. Kappler et al. also presented $C_M(T)$ results for a Ce(Pd$_{0.87}$Ag$_{0.13}$)$_3$ alloy. The significant increase of the electronic specific heat coefficient term, defined as the limit $(C/T)_{T \rightarrow 0}$ (about 150 mJ/K$^2$ mol for this alloy, compared to 38 mJ/K$^2$ mol for CePd$_3$) suggests that a heavy fermion state characterized Ce(Pd$_{0.87}$Ag$_{0.13}$)$_3$ in contrast to the specific effect of Ni impurities in CePd$_3$. The magnetic transition, with almost constant lattice parameters suggests that this transition comes more from an electronic effect rather than from a chemical pressure effect.

The Ce L$_2$3 XAS spectra in CePd$_3$ (see Section 3.3.3) and in Ce(Pd$_{0.75}$Ni$_{0.25}$)$_3$ are reproduced in Fig. 24. As expected they exhibit a double peak structure which is characteristic of highly correlated Ce systems: the ground state is a mixture of $|4f^1\rangle$ and $|4f^0\rangle$ states.

For the Ni doped alloy it is remarkable to note that, despite the magnetic state of this sample, the double peak structure is still observed. However, as illustrated in Fig. 24, a decrease of $4f^0/4f^1$ intensity ratio leads to a $n_f$ increasing of about 5%, when going from CePd$_3$ to an alloy with $x = 0.25$.

In both L$_{23}$ edges of Ce(Pd$_{0.75}$Ni$_{0.25}$)$_3$ alloy the magnetic dichroism consists of a main structure and possibly some tiny structures at high energy (see Fig. 24). Each main peak points 2 eV before the edge maximum, with a line width ($\approx 5$ eV) much narrower than the edge line ($\approx 10$ eV). The sign of the dichroic response is positive (negative) at the L$_2$ (L$_3$), which corresponds to a 5d moment parallel to the applied magnetic field. The normalized amplitudes of the dichroic signals are about $2 \times 10^{-3}$ and $8 \times 10^{-3}$ at L$_2$ and L$_3$ edges, respectively. The integrated XMCD signals at L$_{23}$ edges give a 5d-XMCD branching ratio close to $-4$. This reproduces the expected behaviour for a well localized 4f$^1$ system, as in CeRu$_2$Ge$_2$ compounds, and consequently demonstrates that the main source of magnetism, in the Ce(Pd$_{1-x}$Ni$_x$)$_3$ system, is due to Ce atoms.

3.3.3. Pure CePd$_3$: experimental situation

The observation (Fig. 24) at Ce L$_2$ edge of a dichroic signal in a pure CePd$_3$ compound shows the extreme sensitivity of XMCD technique. The signal corresponds to a magnetic field induced effect only due to the 5d paramagnetic
susceptibility which is a part of the total susceptibility. The small amplitude (only $1.8 \times 10^{-3}$) at L$_2$ edge explains the lack of signal at L$_3$ edge. Indeed if we suppose a branching ratio of about $-4$, as observed for Ce(Pd$_{0.75}$Ni$_{0.25}$)$_3$, the amplitude of L$_3$ signal should be approximately $-0.5 \times 10^{-3}$. To detect such a tiny signal would require by far much more beam time than used for the present experiment. The magnetic field dependence of the maximum dichroic signal, presented in the inset of Fig. 24, demonstrates, if needed, the validity of these experiments, as they well reproduce the magnetic character of the different samples, specially the linear variation for CePd$_3$. Let us highlight that the observation of only one magnetic peak corresponding to the main 4$f^1$ final state points out that only this channel leads to a magnetic response. It has been already discussed that the sum rules (Carra et al., 1993a) do not apply in the case of 5d bands of R systems, due to 4f exchange. However, it is possible to make a rough comparison of the dichroic signals with those of CeRu$_2$Ge$_2$ where the $M_{5d}(4K)$ moment is known to be $\approx 0.1 \mu_B$. As the ratio between the two dichroic signals is about 10, $M_{5d}$ is approximately $0.01 \mu_B$ in Ce(Pd$_{0.75}$Ni$_{0.25}$)$_3$ and $4 \times 10^{-3} \mu_B$ in CePd$_3$.

Summarizing, the XAS spectrum of Ce(Pd$_{1-x}$Ni$_x$)$_3$ and CePd$_3$ systems has a double-peak structure corresponding to 4$f^1$ and 4$f^0$ configurations but their XMCD spectrum exhibits almost a single-peak structure corresponding to 4$f^1$ configuration. This is in strong contrast to trivalence compounds like CeRu$_2$Ge$_2$ and the mixed valence compounds like CeFe$_2$, where both XAS and XMCD spectra display a single peak (4$f^1$ peak) for the trivalent compounds and double peaks (4$f^1$ and 4$f^0$) for the mixed valence compounds. Theoretical interpretations for the characteristic behaviours of XMCD in Ce(Pd$_{1-x}$Ni$_x$)$_3$ and CePd$_3$ are left to future investigations.

4. Summary

In the present paper, theoretical interpretations of XMCD at rare-earth L$_{23}$ absorption edges were reviewed using differing models, depending on the material under investigation. In the first chapter, as an introduction, some recent developments were briefly recalled for XMCD at R atom L$_{23}$ XAS edges with a few general remarks. Then (Section 2), after having presented an overview of the basic mechanism of XMCD at L$_{23}$ absorption edges and after having clarified the definition of XMCD sign, we essentially discussed two examples of XMCD spectra in: (i) $R_2$Fe$_{14}$B metallic compounds, with the help of a cluster model; and (ii) $R$Fe$_2$ Laves-phase compounds, using a tight-binding approximation for $R$ 5d and Fe 3d conducting states.

A good agreement between theory and experiment for $R_2$Fe$_{14}$B compounds suggests that a cluster model provides a valuable method to quantitatively calculate XMCD spectra of $R$ systems, even with quite complicated atomic
arrangements as it is the case for $\text{R}_2\text{Fe}_{14}\text{B}$. Actually, for the considered series of $\text{R}_2\text{Fe}_{14}\text{B}$ metallic systems we underlined the important roles of (i) 5d–4f exchange interaction which includes the novel effect of enhancement of ED intensity related to $2p \rightarrow 5d$ transitions and (ii) hybridization of R 5d states with spin polarized Fe 3d states of surrounding ions. From a quantitative comparison with XMCD data of these series of compounds, it was pointed out that the effect of spin-polarized Fe 3d states had to be included. However and furthermore the EQ transition ($2p \rightarrow 4f$) had to be accounted for as well. Also, there is no reason why the contribution to XMCD from 5d–4f exchange interaction would be independent of that from 5d–3d hybridization, since both contributions are correlated to each other through 5d electronic structure. However, the two contributions have been shown to be almost independent, as it is the case for $\text{Sm}_2\text{Fe}_{14}\text{B}$.

In the series of $\text{RFe}_2$ compounds, it appeared some new interesting features in addition to the previously considered aspects of $\text{R}_2\text{Fe}_{14}\text{B}$ systems. The most interesting feature in $\text{RFe}_2$ is that the ED contribution due to the R 5d–4f exchange interaction, that due to the R 5d–Fe 3d hybridization and the EQ contribution to the XMCD at the L$_2$ edge of heavy R elements are all weak and comparable in intensity, so that by their competition, the XMCD spectra exhibit complicated shapes and complicated temperature-dependence. In this situation, we can see the effect of relatively minor interactions in materials such as the 5d–5d exchange interaction. It is also interesting to compare the XMCD features for $\text{RFe}_2$ and $\text{RAI}_2$.

In Section 3, we focused on the special case of Ce systems, related to XAS and XMCD studies at the Ce L$_{23}$ edges. Two clearly differing cases were interpreted: (i) A well localized 4f$^1$ system, i.e. CeRu$_2$Ge$_2$; (ii) A less localized 4f$^1$ system, i.e. CeFe$_2$, with a 3d partner. In the case of a trivalence Ce, as it is the case for CeRu$_2$Ge$_2$, the XMCD spectra was affected by details of 4f electron states, which, in the ED transition ($2p \rightarrow 5d$), gave rise not only to the polarization effect on the 5d ground state, but also to an effect of contraction in the radial part of 5d orbitals and hence an enhancement of the transition dipole matrix element through 4f–5d exchange interaction. Already in previous works the latter effect has been introduced by a phenomenological parameter $\alpha$. Also we have recalled that, in the case of Ce, more detailed information than Hund’s rule coupling on 4f electron states is required. Especially to obtain a negative XMCD spectrum at the L$_3$ edge it was essential to take into account the tetragonal CF. As a matter of fact, the 4f orbital state is sensitively reflected in XMCD spectra, although the 4f electron is not directly concerned with the 2p → 5d transition.

In the case of a less localized 4f$^1$ systems, like CeFe$_2$, the effect of hybridization between the Ce 5d and spin polarized Fe 3d states plays a main role in the XMCD spectrum. Then the effects of attractive $-U_{dc}$ and repulsive $U_{1d}$ interactions have been shown to be essential in understanding the relative positions of the two peaks in the corresponding XAS and XMCD spectra. Also the difference in the spectral widths of the two XMCD peaks, as well as the difference in the spectral width of XAS and XMCD peaks were also caused mainly by the effect of $-U_{dc}$ and $U_{1d}$. For the contribution from the 4f$^2$ configuration, a detailed discussion could be provided through MCD in RXES. Theoretically we have shown that the technique of the excitation spectrum of MCD-RXES is very useful to observe fine structures of XMCD beyond the lifetime broadening of the L$_3$ core hole. This technique is actually an extension of the technique of RXES excitation spectrum by Hämäläinen et al. to MCD-RXES. Then, from a more experimental point of view, we reported the influence of impurity substitution on the low temperature properties of CePd$_3$ compounds, i.e. Ce(Pd$_{1-x}$Mn$_x$)$_3$ alloys where $x$ is about 0.03, giving rise to a (CePd$_3$)$_8$Mn ordered structure. In this system Mn sublattice undergoes a ferromagnetic transition whereas Ce ions form a dense Kondo lattice and are in a paramagnetic state. We gave another differing example: Ce(Pd$_{1-x}$Ni$_x$)$_3$ alloys with $x$ taken up to about 0.25. In this alloy series thermal and magnetization measurements exhibited a transition from a non-magnetic state (pure CePd$_3$) to a ferromagnetic state for $x > 0.05$, with a Curie temperature $T_c \approx 2$ K. The Ce L$_{23}$ absorption edges and magnetic circular dichroism studies revealed the coexistence of strong 4f hybridization and ferromagnetic order essentially due to Ce atoms. Also the Ce L$_{23}$ XMCD signal measured in pure CePd$_3$ pointed out that in Ce based dense Kondo materials, only the 4f$^1$ channel yields a magnetic response.

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