Magnetic circular dichroism of x-ray absorption spectroscopy at rare-earth $L_{2,3}$ edges in RE$_2$Fe$_{14}$B compounds (RE = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu)

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Magnetic circular dichroism (MCD) in the x-ray absorption spectroscopy (XAS) at the $L_{2,3}$ edges for almost entire series of rare-earth (RE) elements in RE$_2$Fe$_{14}$B (Ref. 1). Since the initial states, the 2$p_{1/2}$ core state for the $L_2$ edge and the 2$p_{3/2}$ core state for the $L_3$ edge which are split by the relatively large spin-orbit interaction, are well defined, we obtain from such a study detailed information on the final states, the 5$d$ conduction band for the electric dipole (ED) transition and the valence 4$f$ states for the electric quadrupole (EQ) transitions. It is usually very hard to observe the information on the weak spin and orbital polarization of the 5$d$ electron separately from others, although such information is important for understanding magnetic properties of these compounds since the 5$d$ electron mediates the inter-atomic exchange process between 4$f$-4$f$ electrons of RE’s on different sites as well as 4$f$-3$d$ electrons of RE and surrounding transition metal (TM) elements. Thus, a detailed study of the MCD spectra is one of the most ideal methods for this purpose because of the selectivity of an atom and a shell mentioned before.

I. INTRODUCTION

In recent years, much work has been accumulated on the magnetic circular dichroism (MCD) in x-ray absorption spectroscopy (XAS) in various ferromagnetic and ferrimagnetic materials, showing the unique and powerful ability of the method to reveal detailed information on electronic and magnetic properties of a selected atom and even of a selected shell. This method has become one of the most powerful methods for the purpose, thanks to the recent technical progress in x-ray sources which provide strong intensity and high tunability as well as high quality of circularly polarized photons.

In this paper, we treat the MCD spectra of XAS at the $L_{2,3}$ edges of almost entire series of rare-earth (RE) elements in metallic compounds, RE$_2$Fe$_{14}$B (Ref. 1). Since the initial states, the 2$p_{1/2}$ core state for the $L_2$ edge and the 2$p_{3/2}$ core state for the $L_3$ edge which are split by the relatively large spin-orbit interaction, are well defined, we obtain from such a study detailed information on the final states, the 5$d$ conduction band for the electric dipole (ED) transition and the valence 4$f$ states for the electric quadrupole (EQ) transitions. It is usually very hard to observe the information on the weak spin and orbital polarization of the 5$d$ electron separately from others, although such information is important for understanding magnetic properties of these compounds since the 5$d$ electron mediates the inter-atomic exchange process between 4$f$-4$f$ electrons of RE’s on different sites as well as 4$f$-3$d$ electrons of RE and surrounding transition metal (TM) elements. Thus, a detailed study of the MCD spectra is one of the most ideal methods for this purpose because of the selectivity of an atom and a shell mentioned before.

Unfortunately, however, there have been some problems in the interpretation of the MCD spectra at the $L_{2,3}$ edges of the RE elements: A naive theory $^{1}$ which takes
into account the polarization effect due to the $4f$-$5d$ exchange interaction, failed to explain the sign of the MCD integrated intensity of the experimental results, indicating the need for a more sophisticated interpretation of the spectra. One of the reasons for this failure comes from the pliability of the extended $5d$ states, which are the final states of the ED transition. The other comes from the ambiguity in estimating the contribution of the EQ transition to the $4f$ states. Carra and co-workers have suggested that the EQ transition is appreciable at the pre-edge region of these edges since the $4f$ level is pulled down to this region due to the strong Coulomb interaction between the core hole and the $4f$ states. And then, it has been tried to interpret the complicated structure as a consequence of the EQ contribution superimposed on the main ED component in a few RE-TM intermetallic compounds. However, these trials have not always succeeded in characterizing the EQ transitions, using, for instance, the angular dependence of the spectra. To overcome this limitation, the systematic measurements for almost entire RE elements will be a great help.

The purpose of this paper is to measure the MCD spectra of XAS at the $L_{2,3}$ edges of almost entire series of RE elements in metallic compounds, RE$_2$Fe$_{14}B$ and to make a theoretical analysis of these spectra in a systematic way. In our theoretical model, it is essential to take into account the enhancement of the $2p$-$5d$ dipole matrix elements due to the $4f$-$5d$ intra-atomic exchange interaction, which depends not only on the $5d$ spin state but also on the $5d$ orbital state. This effect is a consequence of the fact that according to the $4f$-$5d$ exchange interaction the radial part of the $5d$ wave function contracts and has a larger amplitude at the position of the $2p$ orbital. We note here that this effect solves a serious discrepancy in sign of the MCD integrated intensity mentioned above.

In addition to this, we point out another important polarization effect of the $5d$ state due to the hybridization with the spin polarized $3d$ states of surrounding Fe ions. It has been well known that the magnetic coupling between Fe $3d$ spin and RE $4f$ spin is always antiferromagnetic alignment via the conduction electrons, such as RE $5d$ electrons in the RE-TM intermetallic system, which makes them the ferro-magnetic (ferri-magnetic) compounds for the less-than-half (half-filled or more-than-half) RE ions. At room temperature, Fe moments predominantly contribute to bulk magnetization, which has been verified by the Fe $K$-edge MCD spectrum. Since Fe constitutes the majority of the magnetic moment in RE$_2$Fe$_{14}B$, it is not difficult to realize that the effect is important in the MCD spectra at the RE $L_{2,3}$ edges. In the case of La or Lu compound, this effect must dominate the spectra, since there is no effect from the $4f$ electrons. In fact, the MCD spectra in La$_2$Fe$_{14}B$ and Lu$_2$Fe$_{14}B$ observed are consistent with the result of the tight binding calculation for LaFe$_2$. Then, as a first step, we take this effect into account phenomenologically: the experimental MCD spectrum of La$_2$Fe$_{14}B$ is added complementally to the spectra of all other RE compounds, adjusting the amplitude and fixing the relative energy position. This contribution makes sometimes the shape of the MCD spectra complicated.

On the other hand, the quadrupole contribution is also inevitable for a quantitative comparison. Then, we calculate it using the Cowan’s program based on the atomic model, which is reasonable since the $4f$ electrons directly concerned with this process are well localized. Many body effects are crucial in this process but the lifetime effect of the $2p$ core hole smears out a detailed structure of the spectra. Superposing the electric quadrupole contribution on the dipole one, we reproduce the experimental spectra for the entire series of RE elements in RE$_2$Fe$_{14}B$.

In the next section, the experimental details and resulting spectra for XAS-MCD in RE$_2$Fe$_{14}B$ are presented. The theoretical model is described and the results are compared with the experimental ones in Sec. II. In the last section, we summarize our results and give brief discussions on them.

II. EXPERIMENTAL RESULTS

In this section, we describe the experimental conditions and present the observed spectra at the $L_{2,3}$ edges for almost entire series of RE elements in the metallic compounds, RE$_2$Fe$_{14}B$ (RE = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu).

MCD measurements were made at room temperature in transmission mode using left-circularly polarized x-rays (+ helicity) emitted from an elliptical multipole wiggler on the beamline 28B of the Photon Factory at KEK. The beamline is composed of a fixed-exit double crystal monochromator equipped with Si(111) and Si(220) and two doubly focusing mirrors. Powdered sample uniformly spread on the Scotch tape was used. X-ray intensity was monitored using ionization chamber filled with N$_2$ gas before and after the sample. Here we denote that $I_0$ is the intensity of incident beam while $I$ is that of transmitted beam. Magnetic field of 0.6 T was applied antiparallel or parallel to the direction of the incident x-ray wave vector, while the helicity was fixed. The sample plane was tilted 45° away from the direction of the incident beam. Degree of circular polarization $P_C$ was estimated to be 0.35 ~ 0.6 in the photon energy range studied. Energy resolution has been assessed to be $\Delta E/E \sim 1.5 \times 10^{-4}$. Energy dependence of absorption coefficient was recorded at an energy intervals of 1 eV, and data were accumulated every 2 seconds in order to minimize any time dependent drift, while the magnetic field was reversed twice for each energy point. Such a measurement was repeated for 5 to 15 times.

XAS and MCD spectra are defined, respectively, as follows:

$$
\mu t = \frac{1}{2} \left( \ln \frac{I_0}{I_+} + \ln \frac{I_0}{I_-} \right),
$$

(1)
\[
\Delta \mu = \ln \frac{I_0}{I} - \ln \frac{I_0}{I_-},
\]

where \(I_+(I_-)\) represents the intensity of transmitted x-ray with magnetization antiparallel (parallel) to the incident x-ray wave vector. The XAS spectrum was normalized by absorption coefficient at higher energy side to obtain a thickness-independent spectrum, and the MCD spectrum was also subjected to the normalization and correction by tilting angle and degree of circular polarization.

The MCD spectra at the \(L_{2,3}\) edges in RE\(_2\)Fe\(_{14}\)B (RE = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) thus obtained are shown with crosses in Fig. 1 (\(L_3\)) and Fig. 2 (\(L_2\)). In these figures, the origin of the abscissa is taken to be the energy of the absorption edge \(E_0\), which is determined as the energy at the first inflection point of XAS spectrum.

### III. Model and Calculated Results

In this section, we describe our model to calculate the XAS-MCD spectra at the \(L_{2,3}\) edges of the RE elements, which are composed of two contributions; ED and EQ ones. Then we discuss them separately in the following.

First, we are concerned with the ED transition from the initial configuration \(2p^64f^\pm 5d^l\) to the final configuration \(2p^54f^\mp 5d^l\). In the calculation of the XAS process, we make the following simplifications: (i) The \(5d\) states are so extended that they constitute the energy band having a simple semi-elliptic density of states of the Coulomb and exchange interactions are ignored within the \(5d\) electrons. Furthermore, we assume a rectangular density of states following the above-mentioned semi-elliptic one, simulating higher energy \(d\)-symmetry states other than the \(5d\) states of RE. In this sense, we take a one-body picture for the \(5d\) electrons. (ii) On the other hand, the electron correlation within the \(4f\) electrons is so strong that the Hund’s-rule ground state is realized. (iii) Then, the intra-atomic exchange interaction between the \(4f\) and \(5d\) electrons is considered as a mean-field while the intra-atomic Coulomb interaction between them is neglected since it does not affect the MCD spectra seriously.

Based on the assumptions (ii) and (iii), the energy of the \(5d\) state specified by the \(z\)-component of the azimuthal quantum number, \(m_d\), and that of the spin quantum number, \(s_d\), is given by

\[
E_{d\mu} = E(m_d, s_d) = - \sum_{k=1,3,5} \sum_{m_f, s_f} |c^k(2m_d,3m_f)|^2 G^k \times n_{m_f, s_f} \delta(s_d, s_f),
\]

where \(d\mu\) denotes the combined indices of \(m_d\) and \(s_d\), \(m_f\) and \(s_f\) denote, respectively, the \(z\)-component of the azimuthal quantum number and that of the spin quantum number for \(4f\) electrons, \(c^k(lm_f,lm'_{\nu})\) is proportional to the Clebsch-Gordan coefficients, \(G^k\) \((k = 1, 3, 5)\) represent the \(4f\)-\(5d\) Slater integrals which have been calculated using the Cowan’s program[6] (Table I), \(n_{m_f, s_f}\) is the number of the \(4f\) electrons in the state specified by \(m_f\) and \(s_f\), and \(\delta(x, y)\) is the Kronecker delta function.

We note that the energy \(E_{d\mu}\) depends on the number and their quantum numbers of the \(4f\) electrons.

As was mentioned above, the \(5d\) states are assumed to form an energy band with the semi-elliptic density of states, \(\rho_{d\mu}(\epsilon) = 2\sqrt{W^{2} - (\epsilon - E_{d\mu})^2}/\pi W^2\), where \(W\) denotes the bandwidth (3.5 eV), followed by the constant density of states having the \(d\)-symmetry in higher energies.

Denoting the core hole state as \(p_j\) \((j = 1/2, 3/2)\) and the photo-excited \(5d\) state as \(d\mu\), we calculate the absorption spectrum for the left- and right-circular polarized x-rays as

\[
F_\pm^{p_j}(\omega) = \sum_{d\mu,p_j} \left| M_{p_jz,d\mu}^{\pm} \right|^2 (1 - \alpha E_{d\mu}) \times \int_{E_\gamma}^{W + E_{d\mu}} d\epsilon \rho_{d\mu}(\epsilon) (\hbar \omega + E_{p_j} - \epsilon),
\]

and the corresponding MCD spectrum whose definition is consistent with the experimental condition as

\[
\Delta F_\pm^{p_j}(\omega) = F_+^{p_j}(\omega) - F_-^{p_j}(\omega).
\]

Here \(F_\pm^{p_j}(\omega)\) \((F_\pm^{p_j}(\omega))\) represents the absorption spectrum due to the electric-dipole transition of an x-ray with positive (negative) helicity, whose matrix element is \(M_{p_jz,d\mu}^{\pm}(M_{p_jz,d\mu}^{\pm})\) before taking into account the effect of the enhancement, and the factor, \((1 - \alpha E_{d\mu})\), parameterizes this enhancement effect depending on \(d\mu\) (Ref. 9). This type of the enhancement factor is an extension of the actual observation in the band calculation[4] for Gd whose \(4f\) electrons have only spin moments: The \(2p\)-\(5d\) ED matrix element for the \(5d\) spin parallel to the \(4f\) spin is 30% larger than that for the \(5d\) spin antiparallel to the \(4f\) spin. We fix the parameter value \(\alpha\) to be 0.6 for all RE elements, which yields the 30% enhancement of the ED matrix element in the case of Gd metal. The Fermi energy denoted by \(E_F\) is determined so that one \(5d\) electron exists in the ground state. \(E_{p_j}\) is the energy of the core state specified by \(p_j\) and \(L\) is the Lorentzian, \(L(x) = (\Gamma/\pi)/(x^2 + \Gamma^2)\), where \(2\Gamma\) denotes the spectral broadening due to the lifetime of the \(2p\) core hole and is set to be 4.0 eV. The spectrum thus obtained is further convoluted with a Gaussian function of the width (1.5 eV) simulating the instrumental resolution to obtain the full spectrum.

As was mentioned in the introduction, we next consider the additional spin polarization effect of \(5d\) states owing to the hybridization with the spin polarized \(3d\) states of surrounding Fe ions. This effect dominates the MCD spectra of La\(_2\)Fe\(_{14}\)B, since La has no \(4f\) electron. The MCD spectra of La\(_2\)Fe\(_{14}\)B exhibit the following characteristics: (i) They have the intensity only in the energy

\[
\Delta \mu = \ln \frac{I_0}{I} - \ln \frac{I_0}{I_-},
\]
range near the inflection point of XAS spectrum, (ii) The MCD spectrum at the $L_3$ edge is mostly positive while the one at the $L_2$ edge is mostly negative. These characteristics are hold in Lu$_2$Fe$_{14}$B and are supported by a tight-binding calculation for La$_2$Fe$_{14}$B. In our case, the inter-atomic hybridization as well as the intra-atomic exchange interaction contribute to the spin polarization of the $5d$ states. In this paper, we take into account the hybridization effect phenomenologically: The MCD spectrum observed experimentally at each edge of La$_2$Fe$_{14}$B is added complementarily to the calculated MCD spectrum (without the hybridization effect) of each RE compound, where the relative intensity of the two MCD spectra is treated as an adjustable parameter, while the energy position of the hybridization contribution is fixed with respect to the inflection point of each XAS spectrum.

On the other hand, for the EQ transition, we carry out the calculation based on the atomic model with a reduction factor of 0.8 for the Slater integrals since the states concerned with this transition, the initial state $2p^6f^{n}$ and the final state $2p^4f^{n+1}$, are well localized. In our calculation, we ignore the existence of a 5$d$ electron in the ground state for simplicity. Although the interactions between a photo-excited 4$f$ electron and the core hole as well as other 4$f$ electrons are crucial in this process, the lifetime effect of the 2$p$ core hole smears out a detailed structure of the spectra. Then, we superpose the ED spectrum and the EQ spectrum, obtaining the total one; the relative energies of these spectra have been estimated by the atomic Hartree-Fock calculations while their intensity ratio is regarded as a fitting parameter. It is to be noted that the MCD of EQ transition has a strong angle dependence and we have fixed the angle $\theta$ between the z-axis (quantization axis) and the direction of the incident x-ray wave vector to be 45°, so as to fit to the experimental geometry.

Now, we are ready to compare the total MCD spectra, which are the superposition of the ED and EQ contributions, with the experimental spectra for a series of RE compounds in Figs. 1 and 2. Here, the calculated spectra of both XAS and MCD are adjusted so that the calculated maximum intensities of these spectra coincide with the corresponding experimental ones. The agreement is quite good for all RE elements. In order to see the spectral structure in more detail, we present the results for Nd$_2$Fe$_{14}$B (Fig. 3), Gd$_2$Fe$_{14}$B (Fig. 4), and Er$_2$Fe$_{14}$B (Fig. 5), which are typical examples of the light RE (Nd), of the half-filled case (Gd), and of the heavy RE (Er). In these figures, we use the values of the energy difference $|\Delta E|$ between the ED and EQ transitions for the trivalent RE ions tabulated in Table I, which have been calculated based on the atomic model.

In these spectra, we see the following: The ED contribution is decomposed into two components, (i) the effect due to the 4$f$-5$d$ exchange interaction (the dashed curve in Figs. 3-5) and (ii) the effect of hybridization between the RE 5$d$ and Fe 3$d$ bands (the dotted curve). In the contribution (i), the enhancement effect of the dipole matrix element is dominant compared with the magnetic polarization effect of the 5$d$ band (see Ref. [1]). On the other hand, the EQ contribution (the chain curve) is appreciable in the MCD spectra only at the $L_3$ pre-edge region. For the ED contribution, there are cases where the signs of the MCD spectra due to the enhancement and the hybridization effects are opposite. This situation is clearly found at Er (the left panel of Fig. 5) or Tm $L_3$ edge. The enhancement effect is dominant in the $L_2$ edge of Pr, Nd, Sm, Gd, and in the $L_3$ edge of Gd, Tb, Dy, Ho, Er, Tm. The MCD signals have the peak near the white line but slightly below the maximum of XAS spectra. On the other hand, the hybridization effect is well recognized not only in the La and Lu $L_{2,3}$ edges but also in the $L_2$ edge of Er, Tm, Yb, and in the $L_3$ edge of Pr, Nd, Sm, Yb, since the contribution of the 4$f$-5$d$ exchange effect is originally small to the MCD integrated intensities in these cases. The EQ contribution is recognized in the MCD spectra at the $L_3$ pre-edge of several RE’s and has an opposite sign to the ED one by the enhancement effect. In the $L_2$ edge of heavy RE elements, the EQ signal is very small. We will discuss this in the next section.

IV. SUMMARY AND DISCUSSIONS

We found that the MCD spectra observed at the $L_{2,3}$ edges for almost entire series of RE elements in RE$_2$Fe$_{14}$B are well reproduced if we take into account for the ED transition (i) the enhancement of the 2$p$-5$d$ ED transition matrix element caused by the 4$f$-5$d$ intra-atomic exchange interaction and (ii) the spin and orbital polarization of the 5$d$ states due to this interaction as well as the hybridization with the spin polarized 3$d$ states of the surrounding Fe ions, and (iii) the EQ transition at the pre-edge region. The fine structure of the density of states of the 5$d$ conduction band is considered to be smeared by the large spectral width due to the lifetime of the deep 2$p$ core hole, although the hybridization effect might reflect more or less the band structure of the 5$d$ and 3$d$ states.

In addition, we note that the 5$d$ electron in the initial state introduces much varieties to XAS-MCD spectra: The 5$d$ electron in the initial state occupying the low energy state blocks 2$p$-5$d$ dipole excitation to the lower energy states, while the enhancement factor becomes larger for the lower energy states and eventually overcomes the blocking effect in our calculation. If we consider only the 4$f$-5$d$ intra-atomic exchange interaction (including the enhancement effect), we can say the following: In the case of light RE elements, the positive MCD spectra in lower energy range are enhanced significantly and this results in the large positive integrated intensity of MCD at the $L_2$ edge. For the half-filled case (Gd), the enhancement effect causes the large positive and negative MCD in the $L_2$ and $L_3$ edges, respectively (see Fig. 4). On the
other hand, in heavy RE elements, the MCD spectra at the L₃ edge show a similar behavior to that in the L₂ edge of light RE elements except for the reversed signs. The intensity of MCD at the L₃ edge of light RE elements and the L₂ edge of heavy RE elements is small, because it is determined by a delicate balance of the positive and negative contributions. Then the hybridization effect with the 3d electrons becomes very important, as seen in Fig. 3 (L₃) and Fig. 5 (L₂).

Now, let us consider the hybridization effect qualitatively. It has been mentioned that this effect occurs in the restricted energy range near the inflection point of XAS, which is reasonable since the 5d energy band only near the Fermi energy is strongly affected by the hybridization effect. Also it is interesting to point out that this effect yields the sign of the MCD spectrum, being consistent with what we expect in the case where the spin of the 5d electron is antiparallel to that of the Fe 3d electrons. Our preliminary tight-binding calculation for MgCu₂-type Laves phase compounds supports these characteristics. Since this effect is free from the enhancement of the ED matrix element, this gives rise to the contribution from the 4f-5d intra-atomic exchange interaction. These observations are quite consistent with experimental results.

We now turn to the case of the EQ contribution. In this case, the 4f electrons play a direct role since the 2p electron is excited to the 4f state. The most important interaction is surely the Coulomb and the exchange interactions among 4f electrons, resulting in forming the multiplet structure which can be calculated with the aid of the atomic Cowan’s program. Each spectrum of light RE elements consists of two groups, which correspond to the final states having a parallel spin and an antiparallel spin of the photo-excited electron to the 4f spin in the initial state. In the case of heavy RE elements, there is only one kind of spin in unoccupied 4f states so that the structure in the spectra is not simply divided into two groups. The fine structures discussed above is unfortunately smeared by the short lifetime of the deep core hole.

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11 J. Chaboy, H. Maruyama, L. M. García, F. Bartolomé, K. Kobayashi, N. Kawamura, A. Marcelli, and L. Bozukov, Phys. Rev. B54, R15637 (1996).
12 H. Ogasawara, K. Fukui, I. Harada, and A. Kotani, Meeting Abstracts of Phys. Soc. Jpn. 55, Issue 2, Part 4, 603 (2000).
13 R. D. Cowan, The Theory of Atomic Structure and Spectra (University of California Press, Berkeley, 1981).
14 T. Iwazumi, A. Koyama, and Y. Sakurai, Rev. Sci. Instrum. 66, 1691 (1995).
15 H. König, X. Wang, B. N. Harmon, and P. Carra, J. Appl. Phys. 76, 6474 (1994).
16 M. van Veenendaal and R. Benoist, Phys. Rev. B58, 3741 (1998).
17 K. Fukui, doctoral thesis, Okayama University, 2000.
18 F. Bartolomé, J. M. Tonnerre, L. Sève, D. Raoux, J. Chaboy, L. M. García, M. Krisch, and C. C. Kao, Phys. Rev. Lett. 79, 3775 (1997).
FIG. 1. The observed XAS and MCD spectra (crosses) at the RE $L_3$ edge in RE$_2$Fe$_{14}$B compounds (RE: rare-earth). The normalized XAS spectra have been offset by unit for clarity. The MCD intensities are also normalized by the peaks of the XAS spectra and are multiplied by a factor noted in each panel. The origin of the energy axes represents the inflection point ($E_0$) of each XAS spectrum. The solid curves are calculated spectra of $L_3$ XAS and MCD spectra for RE$^{3+}$ but the curves of MCD for La and Lu are not the calculated ones (see text).
FIG. 2. The same as Fig. 1 but for RE $L_2$ edge.
FIG. 3. $L_{2,3}$ XAS and MCD for Nd$^{3+}$ in Nd$_2$Fe$_{14}$B, as a typical example of light RE elements. The origin of the energy is chosen as $E_0$. The solid curve is the calculated result, which consists of the ED contribution due to the 4f-5d exchange interaction (the dashed curve), the ED contribution due to the hybridization with the Fe 3d electrons (the dotted curve) and the EQ contribution (the chain curve), while the crosses represent the experimental results.

FIG. 4. $L_{2,3}$ XAS and MCD for Gd$^{3+}$ as a typical example of having no 4f orbital moment. Others are the same as in Fig. 3.

FIG. 5. $L_{2,3}$ XAS and MCD for Er$^{3+}$ as a typical example of heavy RE elements. Others are the same as in Fig. 3.

|     | $|\Delta E|$ (eV) | $G^1$ | $G^3$ | $G^5$ |
|-----|-----------------|-------|-------|-------|
| Pr$^{3+}$ | 7.86           | 1.293 | 1.021 | 0.773 |
| Nd$^{3+}$ | 8.41           | 1.205 | 0.992 | 0.752 |
| Sm$^{3+}$ | 9.30           | 1.184 | 0.946 | 0.718 |
| Gd$^{3+}$ | 9.97           | 1.134 | 0.900 | 0.690 |
| Tb$^{3+}$ | 10.23          | 1.114 | 0.893 | 0.677 |
| Dy$^{3+}$ | 10.45          | 1.095 | 0.877 | 0.665 |
| Ho$^{3+}$ | 10.62          | 1.078 | 0.862 | 0.654 |
| Er$^{3+}$ | 10.76          | 1.062 | 0.849 | 0.643 |
| Tm$^{3+}$ | 10.86          | 1.046 | 0.835 | 0.633 |
| Yb$^{3+}$ | 10.93          | 1.032 | 0.822 | 0.622 |

TABLE I. The atomic values of the Slater integrals $G^k$ (eV) for the 4f-5d exchange interaction and the energy difference $|\Delta E|$ (eV) between the term-averaged energies of the 2p-5d ED and 2p-4f EQ transition in RE$^{3+}$ ion. These are calculated using the atomic Cowan’s program based on the Hartree-Fock method.