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X-ray magnetic circular dichroism at rare-earth $L_{2,3}$ edges in $R_2Fe_{14}B$ compounds (R=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 at the $L_{2,3}$ edges for almost the entire series of rare-earth (RE) elements in $R_2Fe_{14}B$ is studied experimentally and theoretically. By a quantitative comparison of the complicated MCD spectral shapes, we find that (i) the $4f$-$5d$ intra-atomic exchange interaction not only induces the spin and orbital polarization of the $5d$ states, but also it accompanies a contraction of the radial part of the $5d$ wave function depending on its spin and orbital states, which results in the enhancement of the $2p$-$5d$ dipole matrix element, (ii) there are cases where the spin polarization of the $5d$ states due to the hybridization with the spin polarized $3d$ states of surrounding irons plays important roles, and (iii) the electric quadrupole transition from the $2p$ core states to the $4f$ states is appreciable at the pre-edge region of the $2p$ to $5d$ dipole spectrum. Especially, our results evidence that it is important to include the enhancement effect of the dipole matrix element in the correct interpretation of the MCD spectra at the RE $L_{2,3}$ edges.

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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 the case of the rare-earth (RE) $M_{4,5}$ and transition metal (TM) $L_{2,3}$ absorption spectra the trend in the branching ratio has been very successfully quantified in terms of ground-state spin-orbit interaction and core-valence electrostatic interactions in early papers by Thole and van der Laan.[1,2]

In this paper, we treat the MCD spectra of XAS at the $L_{2,3}$ edges of almost entire series of RE elements in metallic compounds, $R_2Fe_{14}B$.[3] Since the initial states, the $2p_{1/2}$ core state for the L_2 edge and the $2p_{3/2}$ 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 $5d$ conduction band for the electric dipole (ED) transition and the valence $4f$ 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 $5d$ electron separately from others, although such information is important for understanding magnetic properties of these compounds since the $5d$ electron mediates the interatomic exchange process between $4f$-$4f$ electrons of RE's on different sites as well as $4f$-$3d$ electrons of RE and surrounding 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,[4] 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,[5] 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[6] 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. Since 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.[7–10] 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 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, $R_2Fe_{14}B$ 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 $2p$-$5d$ ED matrix element due to the $4f$-$5d$ intra-atomic exchange interaction,[11,12] 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 ferromagnetic (ferrimagnetic) compounds for the less-than-half-filled (half-filled or more-than-half-filled) RE ions. At room temperature, Fe moments predominantly contribute to bulk magnetization, which has been verified by the Fe K-edge MCD spectrum.[13] Since Fe constitutes the majority of the magnetic moment in $R_2Fe_{14}B$, 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 $La_2Fe_{14}B$ and $Lu_2Fe_{14}B$ observed are consistent with the result of the tight-binding calculation for $LaFe_2$.[14] Then, as a first step, we take this effect into account phenomenologically: the experimental MCD spectrum of $La_2Fe_{14}B$ is added complementally to the spectra of all other RE compounds, fixing its energy position and intensity. This contribution makes sometimes the shape of the MCD spectra complicated.

On the other hand, the EQ contribution is also inevitable for a quantitative comparison. Then, we calculate it using the Cowan's program[15] 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 EQ contribution on the ED one, we can reproduce, in a satisfactory manner, the experimental spectra for almost entire series of RE elements in $R_2Fe_{14}B$.

In the next section, the experimental details and resulting spectra for XAS MCD in $R_2Fe_{14}B$ are presented. The theoretical model is described and the results are compared with the experimental ones in Sec. III. 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 a series of RE elements in the metallic compounds, $R_2Fe_{14}B$ (R $=$La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu).[3]

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.[16] Powdered sample uniformly spread on the Scotch tape was used. X-ray intensity was monitored using an 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. A 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 $\Delta E/E\sim1.5\times10^{-4}$. Energy dependence of absorption coefficient was recorded at an energy interval of 1 eV, and data were accumulated every 2 sec 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 5–15 times.

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

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

$$\Delta\mu t=\ln\frac{I_0}{I_+}-\ln\frac{I_0}{I_-}, \tag{2}$$

where $I_+(I_-)$ represents the intensity of transmitted x ray with magnetization antiparallel (parallel) to the incident x-ray wave vector. The MCD spectrum was corrected by tilting angle and degree of circular polarization.

The MCD spectra at the $L_{2,3}$ edges in $R_2Fe_{14}B$ (R=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. The XAS intensity is normalized so that the maximum intensity

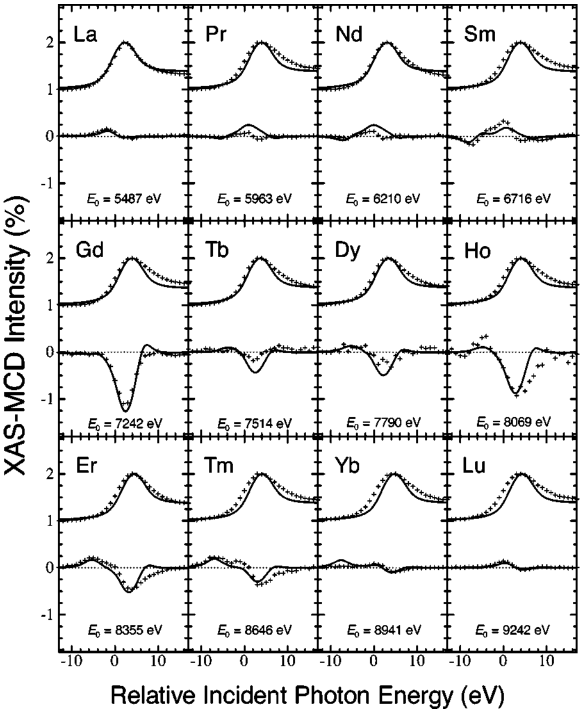

FIG. 1. The observed XAS and MCD spectra (crosses) at the RE L_3 edge in R_2Fe$_{14}$B compounds (RE: rare earth). The XAS spectra have been offset by unit for clarity and the MCD intensities (%) are normalized by the peaks of the XAS spectra. The origin of the energy axes represents the inflection point (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).

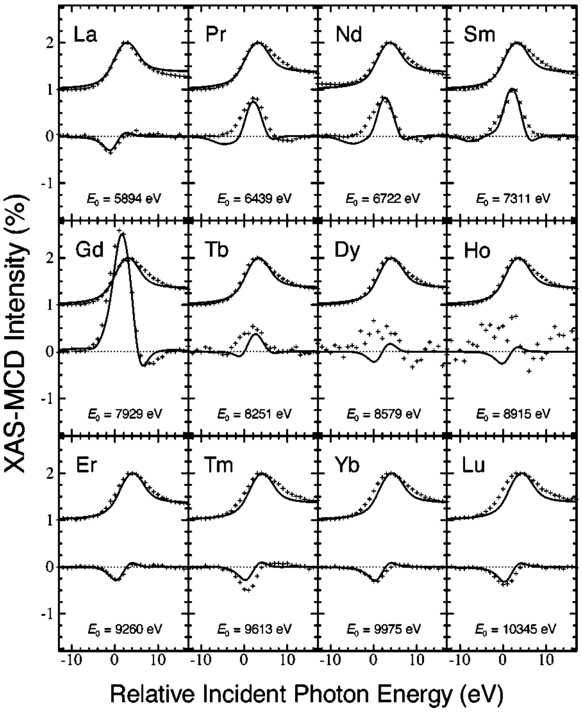

FIG. 2. The same as Fig. 1 but for RE L_2 edge.

is the same for all RE elements, and the MCD intensity (%) is normalized by the maximum intensity of each XAS spectrum.[17]

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 $2p^6 4f^n 5d^1$ to the final configuration $2p^5 4f^n 5d^2$. 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 semielliptic density of states. The Coulomb and exchange interactions are ignored within the $5d$ electrons. Furthermore, we assume a rectangular density of states following the above-mentioned semielliptic 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

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

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, $c^k(lm_l, l'm_{l'})$ 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[15] (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. Here 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 semielliptic 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 d symmetry in higher energies.

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

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. R_E denotes the reduction factor of the exchange energy for the spectrum calculation.

	$\|\Delta E\|$	G^1	G^3	G^5	R_E
Pr^{3+}	7.86	1.293	1.021	0.773	0.15
Nd^{3+}	8.41	1.205	0.992	0.752	0.15
Sm^{3+}	9.30	1.184	0.946	0.718	0.20
Gd^{3+}	9.97	1.134	0.909	0.690	0.50
Tb^{3+}	10.23	1.114	0.893	0.677	0.15
Dy^{3+}	10.45	1.095	0.877	0.665	0.15
Ho^{3+}	10.62	1.078	0.862	0.654	0.25
Er^{3+}	10.76	1.062	0.849	0.643	0.15
Tm^{3+}	10.86	1.046	0.835	0.633	0.10
Yb^{3+}	10.93	1.032	0.822	0.622	0.05

$$F_{\pm}^{pj}(\omega)=\sum_{d\mu,j_z}|M_{pjj_z,d\mu}^{\pm}|^2(1-\alpha E_{d\mu})\times\int_{E_F}^{W+E_{d\mu}}\mathrm{d}\varepsilon\,\rho_{d\mu}(\varepsilon)\mathrm{L}(\hbar\omega+E_{pj}-\varepsilon), \qquad (4)$$

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

$$\Delta F^{pj}(\omega)=F_{+}^{pj}(\omega)-F_{-}^{pj}(\omega). \qquad (5)$$

Here $F_{+}^{pj}(\omega)[F_{-}^{pj}(\omega)]$ represents the absorption spectrum due to the ED transition of an x ray with positive (negative) helicity, whose matrix element is $M_{pjj_z,d\mu}^{+}(M_{pjj_z,d\mu}^{-})$ before taking into account the effect of the enhancement, and the factor, $(1-\alpha E_{d\mu})$, parameterizes this enhancement effect depending on $d\mu$.[11] This type of the enhancement factor is an extension of the actual observation in the band calculation[18] 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 2–30% larger than that for the $5d$ spin antiparallel to the $4f$ spin, which corresponds to that the value of α is 0.4–0.6 (1/eV). In this paper, we fix the value α to be 0.4 (1/eV) for all RE elements, whereas we scale down the magnitude of the exchange energy $E_{d\mu}$ with a reduction factor R_E. The value of R_E is treated as an adjustable parameter for each RE element to fit the calculated spectrum with the experimental one, as described later.

The Fermi energy denoted by E_F is determined so that one $5d$ electron exists in the ground state. E_{pj} is the energy of the core state specified by pj and L is the Lorentzian, $L(x)=(\Gamma/\pi)/(x^2+\Gamma^2)$, where 2Γ 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 $La_2Fe_{14}B$, since La has no $4f$ electron. The MCD spectra of $La_2Fe_{14}B$ exhibit the following characteristics: (i) They have the intensity only in the energy 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 $Lu_2Fe_{14}B$ and are supported by a tight-binding calculation for $LaFe_2$.[14] In our case, the interatomic 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 $La_2Fe_{14}B$ is added complementally to the calculated MCD spectrum (without the hybridization effect) of each RE compound, fixing its energy (with respect to the inflection point of each XAS spectrum) and intensity.

On the other hand, for the EQ transition, we carry out the calculation based on the atomic model[15] (with a reduction factor of 0.8 for the Slater integrals) since the states concerned with this transition, the initial state $2p^6 4f^n$ and the final state $2p^5 4f^{n+1}$, are well localized. Although the interactions between a photoexcited $4f$ electron and the core hole as well as other $4f$ electrons are crucial in this process, the lifetime effect of the $2p$ 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 energy difference $|\Delta E|$ between the ED and EQ spectra is estimated by the atomic Hartree-Fock calculation,[15] as listed in Table I. The variation of the intensity of the EQ contribution over the RE elements is also calculated by the atomic calculation, and the integrated intensities of XAS and its MCD are shown in Fig. 3. It is to be noted that the MCD of EQ transition has a strong angle dependence,[6,19] and we have fixed the angle θ between the z axis (magnetization direction) and the direction of the incident x-ray wave vector to be 45°, so as to fit to the experimental geometry. The relative intensity between EQ and ED transitions is chosen so as to reproduce the experimental MCD spectrum for Er (for other RE elements it is uniquely determined with the result in Fig. 3).

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 elements in $R_2Fe_{14}B$ in Figs. 1 and 2. The agreement between the calculated and experimental results is satisfactory for most of RE elements. The values of R_E used in the analysis are listed in Table I, and some discussion on them is given in the next section. In order to see the spectral structure in more detail, we present the results for $Sm_2Fe_{14}B$ (Fig. 4), $Gd_2Fe_{14}B$ (Fig. 5), and $Er_2Fe_{14}B$ (Fig. 6), which are typical examples of less-than-half-filled RE (Sm), of half-filled case (Gd), and of more-than-half-filled RE (Er).

In these spectra, we see the following: The ED contribution is decomposed into two components, (i) the effect due to the $4f$-$5d$ exchange interaction (the dashed curve in Figs. 4–6) and (ii) the effect of hybridization between the RE $5d$ and Fe $3d$ bands (the dotted curve). In the contribution (i), the enhancement effect of the ED matrix element is domi-

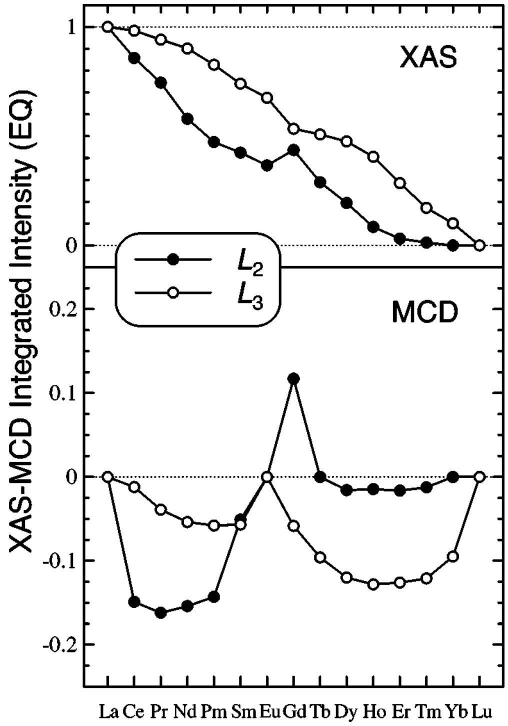

FIG. 3. The integrated intensities of RE $L_{2,3}$ XAS-MCD concerning the $2p$-$4f$ EQ transition for the entire series of RE^{3+} free ion by the full-multiplet calculation, when the incident angle is 45°. These are normalized at the values of La XAS for L_2 (closed circles) and L_3 (open circles), respectively.

nant compared with the magnetic polarization effect of the $5d$ band.[11] 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. 6) 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 $4f$-$5d$ exchange effect is originally small to the MCD integrated intensities in these cases.[11] 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 the more-than-half-filled RE elements, the EQ signal is very small. We will discuss this in the next section.

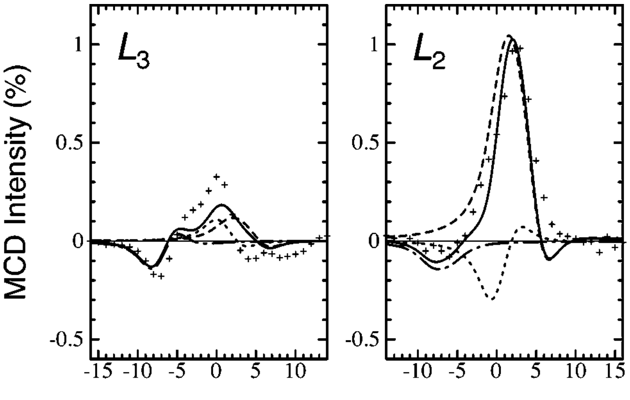

FIG. 4. MCD spectra of $L_{2,3}$ XAS for Sm^{3+} in Sm$_2$Fe$_{14}$B, as a typical example of less-than-half-filled RE elements. The origin of the energy is chosen as E_0. The solid curves are the calculated results, which consist of the ED contribution due to the $4f$-$5d$ exchange interaction (the 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.

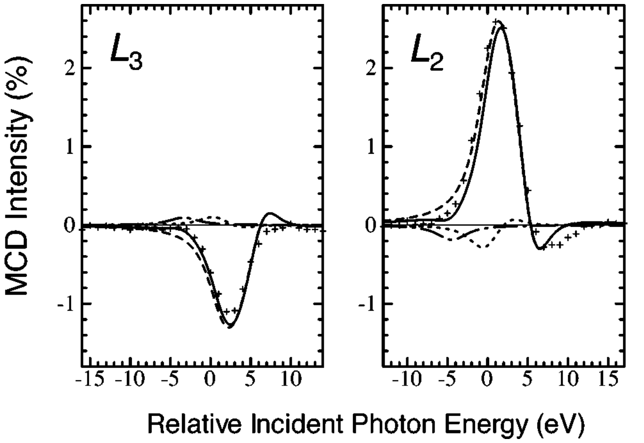

FIG. 5. MCD of $L_{2,3}$ XAS spectra for Gd^{3+} having no $4f$ orbital moment. Others are the same as in Fig. 4.

IV. SUMMARY AND DISCUSSIONS

We have analyzed the MCD spectra observed at the $L_{2,3}$ edges for almost entire series of RE elements in R_2Fe$_{14}$B, taking into account for the ED transition (i) the enhancement

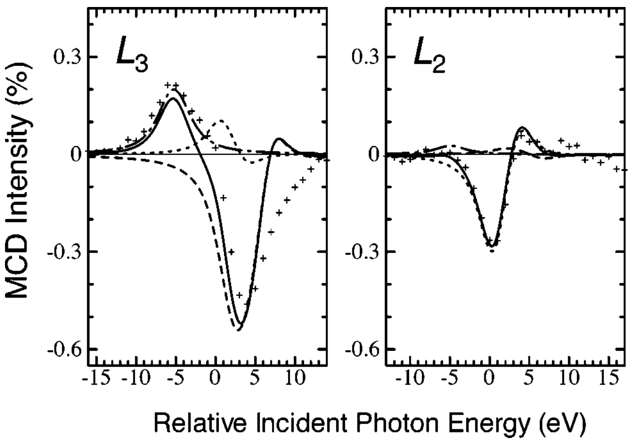

FIG. 6. MCD of $L_{2,3}$ XAS spectra for Er^{3+} as a typical example of more-than-half-filled RE elements. Others are the same as in Fig. 4.

of the $2p$-$5d$ ED transition matrix element caused by the $4f$-$5d$ intra-atomic exchange interaction and (ii) the spin and orbital polarization of the $5d$ states due to this interaction as well as the hybridization with the spin polarized $3d$ states of the surrounding Fe ions, and (iii) the EQ transition at the pre-edge region.

The main parameters in our calculation are α, R_{E}, and the EQ-ED intensity ratio. Considering that the adjustable parameters are only R_{E} (for each RE element) and the EQ-ED intensity ratio (for Er), the agreement between the calculated and experimental MCD spectra is quite good for all RE elements except for the L_2 edge of Dy and Ho. The reason for the disagreement for the L_2 edge of Dy and Ho is not clear at present, but the scattering of the experimental MCD intensity for these spectra is exceptionally large, and more detailed investigation is necessary both theoretically and experimentally.

Now we would like to give some discussion on the reduction factor R_{E}. It is well known that the Slater integrals obtained by the Hartree-Fock calculation is in general too large, and usually some reduction factors are introduced to represent empirically the effect of the configuration interaction (note that we have used the reduction factor 0.8 for the calculation of spectra due to the EQ transition). Therefore one of the origins of R_{E} is the reduction of the Slater integrals G^k. However, the reduction factor of the Slater integral is considered to be larger and less RE element sensitive compared with R_{E} in Table I.

We consider that the other origin of R_{E}, which is element sensitive, is due to the thermal fluctuation of the $4f$ magnetic moment. As mentioned in Sec. I, the bulk magnetization of $R_2\mathrm{Fe}_{14}\mathrm{B}$ is predominantly caused by the Fe $3d$ moment, and at room temperature the thermal fluctuation of the RE $4f$ moment is large.[20] In order to compare our calculation, which is formulated essentially at zero temperature, with experimental data obtained at room temperature, it is necessary to introduce a reduction of the exchange energy $E_{d\mu}$ due to the thermal reduction of the $4f$ magnetic moment. It is to be noted that the factor R_{E} should be larger for the RE element with higher Curie temperature (T_{C}), because the thermal fluctuation of the $4f$ magnetic moment should be smaller at room temperature. According to Table I, the value of R_{E} is largest for Gd, and decreases in going away from Gd, as a rough trend. This is in qualitative agreement with the behavior of T_{C} in $R_2\mathrm{Fe}_{14}\mathrm{B}$.[20] It is a problem left in the future investigation to study quantitatively the values of R_{E} and α. In this paper we have fixed α to be 0.4 (1/eV), but if we change the value of α, the value of R_{E} will also be changed. There has been no microscopic estimation of α for $R_2\mathrm{Fe}_{14}\mathrm{B}$. In the present work, we tried to analyze the experimental data by using the value of α from 0.3 to 0.6, and found that the result with α around 0.4 is the best. In order to discuss the values of α and R_{E} quantitatively, microscopic calculations of these quantities are required.

In the following, we give some remarks on the points (i), (ii), and (iii) mentioned above. We note that the $5d$ electron in the initial state introduces much varieties to MCD spectra: The $5d$ electron in the initial state occupying the low-energy state blocks $2p$-$5d$ ED 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 $4f$-$5d$ intra-atomic exchange interaction (including the enhancement effect), we can say the following: In the case of less-than-half filled 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. 5). On the other hand, in more-than-half-filled RE elements, the MCD spectra at the L_3 edge show a similar behavior to that in the L_2 edge of less-than-half-filled RE elements except for the reversed signs. The intensity of MCD at the L_3 edge of less-than-half-filled RE elements and the L_2 edge of more-than-half-filled 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. 4 (L_3) and Fig. 6 (L_2).

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 MgCu_2-type Laves phase compounds $R\mathrm{Fe}_2$ supports these characteristics.[14] Since this effect is free from the enhancement of the ED matrix element, this gives rise to the contribution with the different signal to the MCD spectra than the contribution from the $4f$-$5d$ intra-atomic exchange interaction. These observations are quite consistent with experimental results.

Our treatment for the RE $5d$-Fe $3d$ hybridization contribution is crude, and it is necessary to improve this. As mentioned above, we are performing some improved calculations, where RE $5d$ and Fe $3d$ states are treated by the tight-binding band method, in the case of $R\mathrm{Fe}_2$ systems.[14] According to our preliminary result for $R\mathrm{Fe}_2$ (for instance for HoFe_2), two MCD contributions from the RE $4f$-$5d$ exchange interaction and the RE $5d$-Fe $3d$ hybridization is almost additive. Therefore we expect that this is also the case in $R_2\mathrm{Fe}_{14}\mathrm{B}$. We will publish the results of improved calculations in the near future.

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.[15] Each spectrum of less-than-half-filled RE elements consists of two groups, which correspond to the final states having a parallel spin and an antiparallel spin of the photoexcited electron to the $4f$ spin in the initial state. In the case of more-than-half-filled 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 $2p$ core hole and the spectra in fact show a very simple Lorentzian-like shape. In the experimental MCD spectra, the EQ transition is apparent at the L_3 edge, while the traces of the EQ transition are not found at the L_2 edge in the more-than-half-filled RE elements. This is consistent with our calculations (see Fig. 3). If the angle θ is changed to $0°$, according to the theoretical calculation,[21] the MCD intensity of the EQ transition should be increased for Tb at the L_2 edge. It is desirable that this is confirmed by experimental observations in future.

The x ray emission spectroscopy (XES), in which the final state of XAS is the intermediate state and then the $3d$ core electron fills the $2p$ core hole with emitting x ray, is another tool to identify the EQ contribution experimentally since the broadening of the spectra is reduced by virtue of the relatively long lifetime of the $3d$ core hole to the $2p$ core hole.[22] Observation of XES at the L_2 edge is desired.

In conclusion, we have confirmed the important role of the $4f$-$5d$ exchange interaction, which leads to the spin and orbital dependent enhancement of the $2p$-$5d$ ED matrix element in addition to the usual polarization effect in MCD. We find that, in some cases, the hybridization of the $5d$ states with the spin polarized $3d$ states of the surrounding Fe ions plays a vital role. Furthermore, the EQ transition is appreciable, especially, at the L_3 edge.

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