Magnetic circular dichroism of resonant X-ray emission spectra at *L* edges of rare-earth compounds

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We study the resonant x-ray emission spectroscopy (RXES) and the magnetic circular dichroism (MCD) at the $L_{2,3}$ absorption edges of rare-earth elements, especially gadolinium ion. To this end, an atomic model is adopted and the multiplet coupling effect is taken into account. Using the formula of the coherent second order optical process which consists of the excitation process from the $2p$ core state to the empty $5d$ state and of the radiative decay from the $3d$ core state to the $2p$ core hole, we calculate RXES-MCD spectra. By inspection, we have confirmed that the enhancement of the $2p$-$5d$ dipole matrix element proposed for MCD of x-ray absorption spectroscopy. In addition, characteristic features of the spectra observed in gadolinium metallic compounds are reproduced by our calculations.

Keywords: resonant x-ray emission spectroscopy; **magnetic circular dichroism**; **rare earth L2,3 edges.**

1. Introduction

Resonant x-ray emission spectroscopy (RXES) has become one of the most powerful tools to study electronic and magnetic properties of a selected shell and a selected atom in solids, since new synchrotron radiation facilities with high brilliance have been realized. The polarization dependence of RXES gives us additional detailed information on the magnetic character: The magnetic circular dichroism (MCD) is one of the most popular examples.

Up to now, the systematic experimental study has been done on RXES-MCD at $L_{2,3}$ edges for Gd metallic compound (Krisch *et al.*, 1997; Iwazumi *et al.*, 1997; Iwazumi *et al.*, 2000), while some calculations have been done only for the normal x-ray emission spectroscopy (NXES) (de Groot *et al.*, 1997; Jo & Tanaka, 1998). Then, it is the purpose of this paper to discuss RXES and their MCD at the $L_{2,3}$ absorption edges of rare-earth in connection with the characteristics of the x-ray absorption spectra (XAS) and their MCD at these edges. Using the formula of the coherent second order optical process, we study in this paper the RXES which consists of the process of the XAS-type excitation from the $2p$ core state to the empty $5d$ state and of the radiative decay from the $3d$ core state to the $2p$ core hole.

It is known that, in XAS-MCD at $L_{2,3}$ edges of rare-earth elements, the enhancement of $2p$-$5d$ electric dipole transition matrix elements due to the $5d$-$4f$ exchange interaction is very important (Matsuyama *et al.*, 1997). Since the character of the intermediate state (which is the same as the final state of XAS) is reflected strongly to the spectral shape of RXES, the theoretical analysis of RXES-MCD experimental data is a critical test of the validity of the enhancement effect of the dipole transition matrix element. We formulate RXES-MCD taking this effect into account and perform numerical calculations of the spectra for the $L_{2,3}$-$M_{4,5}$ transition of a Gd^{3+} ion in an external magnetic field. The calculated results are compared with experimental data.

2. Model

Assuming the plus or the minus helicity for the incident photon while summing up both helicities for the emitted photons, we use the formula of the coherent second order optical process for RXES, which is represented by

$$F^{\rm h}_{\rm RXES}(\omega_1,\omega_2) = \sum_{\rm h'}\sum_{\rm f}\left|\sum_{\rm i}\frac{\langle {\rm f}|\,{\rm T}_2^{\rm h'}\,|{\rm i}\rangle\langle {\rm i}|\,{\rm T}_1^{\rm h}\,|{\rm g}\rangle}{E_{\rm i}-E_{\rm g}-\omega_1+{\rm i}\Gamma_{\rm i}}\right|^2 \times {\rm L}(E_{\rm f}+\omega_2-E_{\rm g}-\omega_1,\Gamma_{\rm f}), \quad (1)$$

where $|{\rm g}\rangle$, $|{\rm i}\rangle$ and $|{\rm f}\rangle$ are the ground, intermediate and final states with energies $E_{\rm g}$, $E_{\rm i}$ and $E_{\rm f}$, respectively; ω_1 and ω_2 are the incident and emitted photon energy; ${\rm L}(x,\Gamma)$ is the Lorentzian defined by ${\rm L}(x,\Gamma)=\Gamma/\pi(x^2+\Gamma^2)$ where $\Gamma_{\rm i}$ ($\Gamma_{\rm f}$) is the half width of the $2p$ ($3d$) core hole lifetime broadening of the L (M) shell, which is set to be 2.0 eV (0.5 eV).

We define RXES-MCD by the difference of the spectra for the incident photon having the different helicities:

$$\Delta F_{\rm RXES}(\omega_1,\omega_2) = F^{+}_{\rm RXES}(\omega_1,\omega_2)-F^{-}_{\rm RXES}(\omega_1,\omega_2). \quad (2)$$

Incidentally, XAS spectrum is represented as

$$F^{\rm h}_{\rm XAS}(\omega_1)=\sum_{\rm i}\left|\langle {\rm i}|\,{\rm T}_1^{\rm h}\,|{\rm g}\rangle\right|^2{\rm L}(E_{\rm i}-\omega_1-E_{\rm g},\Gamma_{\rm i}), \quad (3)$$

where the notation is the same as that in eq. (1). The transition matrix element $\langle 5d|\,{\rm T}_1^{\rm h}\,|2p\rangle$ is proportional to $(1-\alpha E(m_d,s_d))^{1/2}$, in which $E(m_d,s_d)$ is the $5d$-$4f$ exchange energy specified by the z-component of the orbital and spin quantum number (m_ℓ, m_s) (Matsuyama *et al.*, 1997):

$$E(m_d,s_d) = -\sum_{k=1,3,5}\sum_{m_f,s_f}|c^k(2m_d,3m_f)|^2G^k(4f,5d) \times n(m_f,s_f)\delta(s_d,s_f). \quad (4)$$

Here $\delta(x,y)$ is the Kronecker's delta; $G^k(4f,5d)$ represents the $4f$-$5d$ Slater integrals given by the atomic Cowan's program; $n(m_f,s_f)$ is the occupation number of $4f$ electron in each state.

In the case of Gd^{3+}, $4f$ electrons are completely spin polarized (spin-up state), so that the exchange energy of the $5d$ electron depends only on the $5d$ spin state and the so-called exchange splitting, $E_\uparrow-E_\downarrow$, takes the value of -1.13 eV, which almost coincides with that obtained by an energy band theory for the ferromagnetic Gd metal (Harmon & Freeman, 1974).

On the other hand, the density of states of the $5d$ band is simply assumed to be a semi-elliptic with the half width W = 3.5 eV for each orbital and spin state, and further one electron is assumed to exist in the $5d$ bands. We believe that the simple shape of the density of states for $5d$ bands works because of the relatively large life-time broadening of the $2p$ and $3d$ core holes. In order to deal with the NXES spectra, we also assume a continuum d band with a constant rectangular density of states above the semi-elliptic bands, which gives the height of edge jump and no contribution to the integrated intensity of their MCD. We take into account an integration over the kinetic energy of the excited d electron to reproduce not only the Raman component but also the NXES component in the

spectra of RXES and its MCD. Additionally, the lifetime broadening of the final state is considered with Lorentzian as previously described, and all calculated spectra are convoluted by the Gaussian function with the width of 0.75 eV, representing the instrumental resolution.

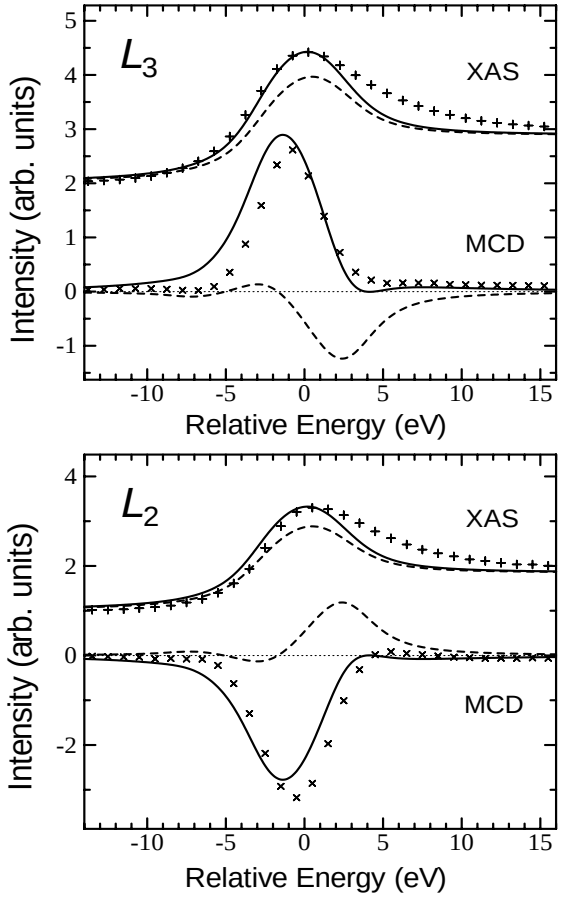

Figure 1
XAS and its MCD spectra at L_2 and L_3 edges calculated using $\alpha = 0$ (dashed) and 0.6 /eV (solid), with the experiments (shown with crosses) in $Gd_{33}Co_{67}$ amorphous (Iwazumi *et al.*, 2000). The origin of the energy is chosen as the peak of the white line.

3. Results and Discussion

The calculated spectra of $L_{2,3}$ XAS and its MCD for a Gd^{3+} ion are shown in Fig. 1, and compared with experimental results for $Gd_{33}Co_{67}$ (Iwazumi *et al.*, 2000). The solid curve is obtained for a finite α (= 0.6 /eV), and the dashed curve is for $\alpha = 0$, respectively. It is seen that the calculated MCD spectrum is strongly enhanced on the lower energy side of the white line, because in this region the $5d\uparrow$ density of states (we take the ferromagnetic $4f$ spin direction as $\uparrow$) is higher than the $5d\downarrow$ one (due to the $5d$-$4f$ exchange interaction by eq. (4)), so that the dipole transition amplitude is enhanced by the exchange interaction.

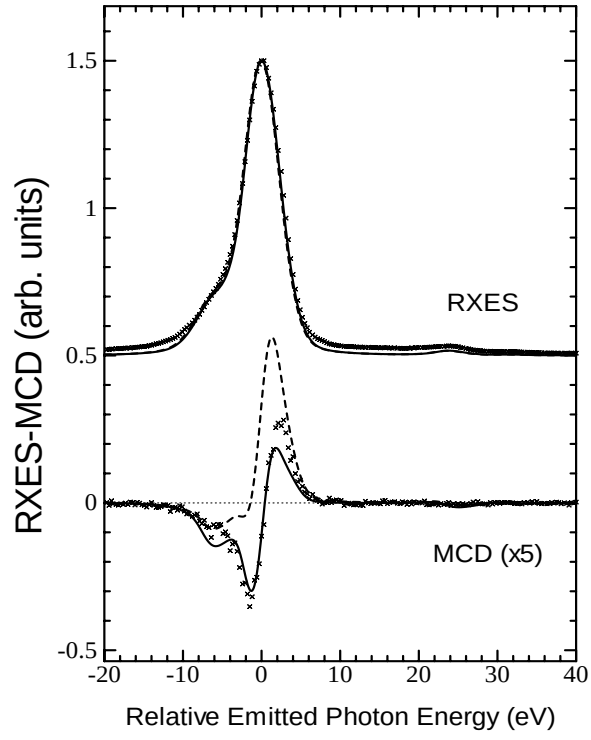

Figure 2
Calculated L_2-M_4 RXES and its MCD spectra using $\alpha = 0$ (dashed) and 0.6 /eV (solid) for the incident photon energy 0.5 eV in Fig. 1. The calculated spectra are normalized so that the RXES peak intensity coincides with the experimental one. Experimental results (Iwazumi *et al.*, 2000) are shown with crosses.

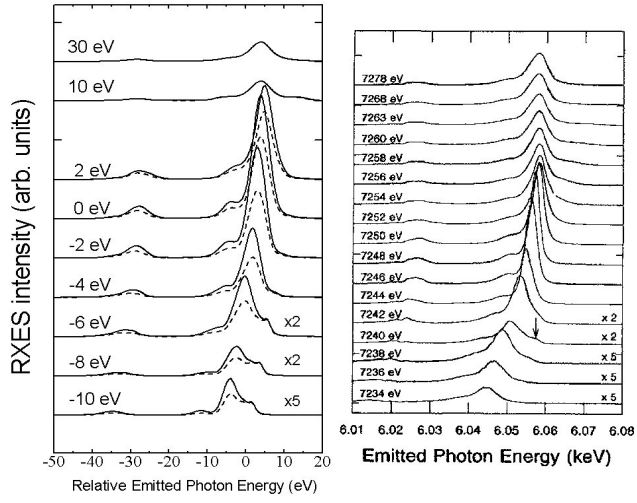

Figure 3
Calculated L_3-$M_{4,5}$ RXES spectra (left panel) using $\alpha = 0$ (dashed) and 0.6 /eV (solid) compared with the experiments (Iwazumi *et al.*, 1997) (right panel) for various values of the incident photon energy (ω_1). The value of $\omega_1 = 0$ eV in the left panel corresponds to 7248 eV in the right panel.

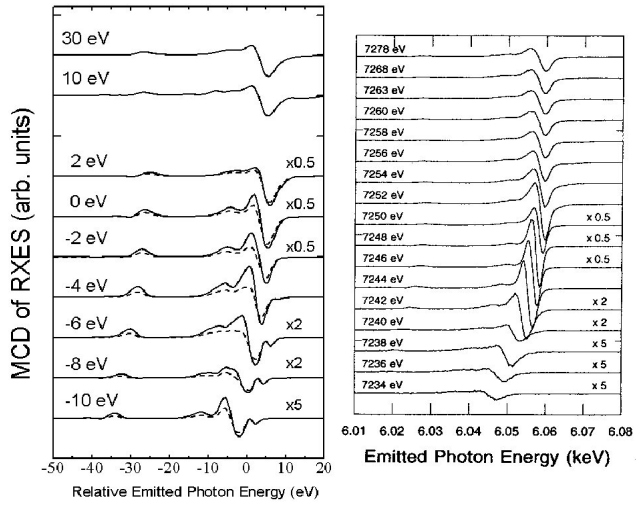

Figure 4
MCD spectra for Fig. 3.

Figure 2 shows the calculated L_2-M_4 RXES spectrum and its MCD for $\alpha = 0.6$ /eV and 0. The experimental results are also shown with the crosses. The MCD spectrum exhibits a dispersive shape with positive and negative MCD for higher and lower energy sides, respectively. The positive (negative) MCD corresponds to the process where a $2p\downarrow(\uparrow)$ electron is more strongly excited to the $5d\downarrow(\uparrow)$ band and a $3d\downarrow(\uparrow)$ electron makes a transition to the $2p\downarrow(\uparrow)$ state. For $\alpha = 0$, the intensity of the negative MCD part is smaller than the experimental result. When we switch on the effect of α, the part of the negative MCD is strongly enhanced because of the enhancement of the $2p\uparrow$ to $3d\uparrow$ transition matrix element. The agreement with the experiment is much improved by the effect of α.

In Figs. 3 and 4, respectively, the calculated L_3-$M_{4,5}$ RXES spectra and their MCD are shown for various values of the incident photon energy. It is found that the Raman-like behavior of RXES changes to the fluorescence-like one with increasing ω_1. At the pre-threshold resonance, the $2p$-$4f$ quadrupole excitation gives rise to a structure (indicated by the arrow in Fig. 3) on the high emitted photon energy side of RXES. These features are well reproduced in our calculations. The effect of α is clearly seen in the RXES-MCD, and the enhancement of the positive MCD part improves greatly the agreement with the experimental results.

4. Concluding Remarks

Our analysis shows that the enhancement effect of the dipole transition matrix element by the $5d$-$4f$ exchange interaction plays an important role at the gadolinium $L_{2,3}$ edges. Also the quadrupole excitation plays a role in the pre-threshold resonance.

Similar calculations of RXES-MCD have been made for a Sm^{3+} ion, and the results are in good agreement with recent experimental data by Nakamura (2000). The calculated and experimental results will be published elsewhere.

We thank Dr. T. Iwazumi and Dr. T. Nakamura for providing us with the experimental data. The computation in this work was achieved using the facilities at the Supercomputer Center, Institute for Solid State Physics, University of Tokyo.

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