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Theory of X-ray absorption and resonant X-ray emission spectra by electric quadrupole excitation in light rare-earth systems

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Abstract

We have made precise theoretical calculations for both $2p_{3/2} \rightarrow 4f$ X-ray absorption spectroscopy (XAS) and $4d \rightarrow 2p_{3/2}$ resonant X-ray emission spectroscopy (RXES) by electric quadrupole excitations at the L_3 edge of light rare-earth elements, by means of atomic model with full multiplet effects. The calculation is based on the second-order optical formula, and the effect of the incident photon polarization is taken into account. It is shown that the $4d$–$4f$ interaction plays a more important role in $4d \rightarrow 2p_{3/2}$ RXES than the $4f$–$4f$ interaction does. Moreover, the calculated results of $4d \rightarrow 2p_{3/2}$ RXES show the strong polarization dependence, and it is originated from the spin multiplicity, which is derived from the $4d$–$4f$ interaction, of the RXES final states.

1. Introduction

X-ray absorption spectroscopy (XAS) at the $2p_{3/2}$ (L_3) edge of rare-earth (RE) elements gives rise to a strong white line due to the $2p_{3/2} \rightarrow 5d$ excitation corresponding to an electric dipole (ED) transition. At the same time, the electric quadrupole (EQ) transition is expected to cause a feature in the pre-edge region of the white line, but this feature is hardly observable in conventional XAS measurements, because of the weak transition intensity and the large spectral broadening due to the short lifetime of the $2p$ core hole.

High brightness synchrotron radiation sources have made the experimental detection of the EQ signal at the L_3 edge possible via resonant X-ray emission spectroscopy (RXES) [1–6]. Hämäläinen et al. [1] first detected the EQ signal of Dy compounds by measuring the RXES Dy $3d \rightarrow 2p_{3/2}$ excitation spectrum resulting from the $2p_{3/2} \rightarrow 4f$ EQ excitation. It consisted in monitoring the emitted photon intensity at the peak position of the Dy $3d_{5/2} \rightarrow 2p_{3/2}$ fluorescence spectrum as a function of incident photon energy. Tanaka et al. [7] and Carra et al. [8] first provided a theoretical interpretation of such an RXES process and also confirmed that the spectral broadening of the excitation spectrum observed by Hämäläinen et al. was limited by the $3d$ core-hole lifetime, rather than the much shorter $2p$ lifetime. Next, Veenendaal et al. [9] showed calculated results of $3d_{5/2} \rightarrow 2p_{3/2}$ RXES by EQ excitation for heavy RE elements.

More recently, Bartolomé et al. [6] observed the RE $4d \rightarrow 2p_{3/2}$ RXES at the L_3 pre-edge excitation of $RE_2Fe_{14}B$. They observed a double-peak structure in X-ray absorption magnetic circular dichroism (XAMCD) and RXES for these EQ excitations in the light RE systems Nd and Sm. And their experimental results show that these energy separations coincide within the experimental precision. This is, to the author's knowledge, the only experimental result of $4d \rightarrow 2p_{3/2}$ RXES by EQ excitation. Moreover, no theoretical study has been made on this optical process.

In this paper, we investigate theoretically the relation between $2p_{3/2} \rightarrow 4f$ XAS and $4d \rightarrow 2p_{3/2}$ RXES by EQ excitation in light RE systems. In particular, how these two spectra depend on the $4f$–$4f$ and $4d$–$4f$ interactions is shown. As a result, we can clearly see the importance of the $4d$–$4f$ interaction. Moreover, the calculated results of $4d \rightarrow 2p_{3/2}$ RXES show the strong polarization dependence, which is derived from the $4d$–$4f$ interaction.

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2. Model and formalism

In real metallic RE elements, $5d$–$4f$ interaction is very small, because $5d$ orbital forms broad energy bands. Therefore, we consider a system which consists of a RE $4f$ level and a core level (RE $2p$, $4d$ level), neglecting a RE $5d$ level. In other words, the calculations were performed using an atomic model for trivalent RE ions.

In order to take into account the polarization of the incident photon, we adopt the usual *xyz* coordinates [10]. We assume that the momentum of the incident photon is anti-parallel to the x-direction, and the polarization vector of that is parallel to the z-direction. After the excitation of the core electron, photons are emitted in the direction specified by two angles θ and ϕ in the usual spherical coordinates. When the momentum of the emitted photon is parallel to the y-direction (so that $\theta = \phi = 90^\circ$), it is called the *polarized* configuration. On the other hand, when the momentum of the emitted photon is parallel to the z-direction (so that $\theta = 0^\circ$), it is called the *depolarized* configuration.

The $4d \to 2p_{3/2}$ RXES is given by

$$F(\Omega, \omega) = \sum_{p=\theta,\phi} \sum_{f} \delta(E_g + \Omega - E_f - \omega) \times \left| \sum_{q,q'} \sum_{m} \frac{\langle f | C^{(1)}_{q'} | m \rangle \langle m | C^{(2)}_{q} | g \rangle}{E_g + \Omega - E_m + \mathrm{i}\Gamma_m} B^{p}_{1q'} B_{2q} \right|^2, \tag{1}$$

where $|g\rangle$ is the ground state of the system with energy E_g, $|m\rangle$ and $|f\rangle$ are intermediate and final states with energies E_m and E_f, respectively, Ω and ω are incident and emitted photon energies, respectively. The constant factor Γ_m represents the spectral broadening corresponding to the lifetime of the $2p$ core hole. $C^{(2)}_q$ and $C^{(1)}_{q'}$ ($C^{(k)}_q$ denotes the normalized spherical harmonics with rank k) represent the EQ and ED transitions from $2p_{3/2}$ to $4f$ states and from $4d$ to $2p_{3/2}$ states, respectively. The polarization-dependent factor B_{2q} of the excitation process is given by

$$B_{2q} = \begin{cases} 1 & \text{for } q = +1, \\ -1 & \text{for } q = -1, \\ 0 & \text{for } q \neq \pm 1. \end{cases} \tag{2}$$

The other polarization-dependent factor $B^{p}_{1q'}$ of the de-excitation process is given by the pre-factors of Eqs. (2.10) and (2.11) of Ref. [10]. More details will be shown elsewhere [11].

3. Calculated results and discussion

As an example, we show the results for Nd. First, to see how the RXES depends on the $4f$–$4f$ and $4d$–$4f$ interactions, the calculated $4d \to 2p_{3/2}$ RXES are shown in Fig. 1. Fig. 1 shows contour maps (map of equi-intensity lines) of RXES in the two-dimensional plane of the incident photon energy Ω and emitted photon energy ω. Figs. 1(a) and (b) are calculated with the $4d$–$4f$ and $4f$–$4f$ interactions turned off in the RXES final state, separately. In these figures, the depolarized configuration is assumed. (The calculation in the polarized configuration gives similar results.) The origin of the incident and emitted photon energies is chosen arbitrarily. The spectral width of RXES final state is taken to be 0.7 eV half-width at half-maximum (HWHM) which corresponds to the lifetime broadening of the $4d$ core hole. It is much smaller than that of the $2p$ core hole (1.8 eV HWHM).

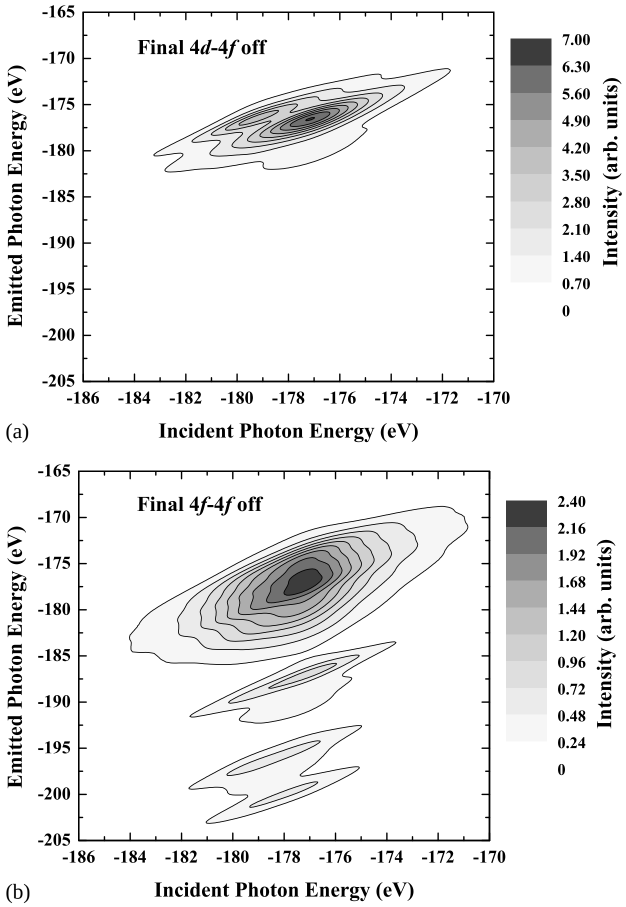

Fig. 1. Calculated $4d \to 2p_{3/2}$ RXES intensity in the depolarized configuration as a function of the incident photon energy Ω and the emitted photon energy ω for Nd^{3+} ion: (a) without $4d$–$4f$ interaction, (b) without $4f$–$4f$ interaction in the RXES final state.

In this $4d \to 2p_{3/2}$ RXES, the $4d$–$4f$ interaction is rather larger than the $4f$–$4f$ interaction in RXES final states. The RXES structures are, therefore, almost dominated by the $4d$–$4f$ interaction (see also Fig. 2(b)). Since the $4d$–$4f$ interaction produces multiplet structures largely depending on the spin direction between

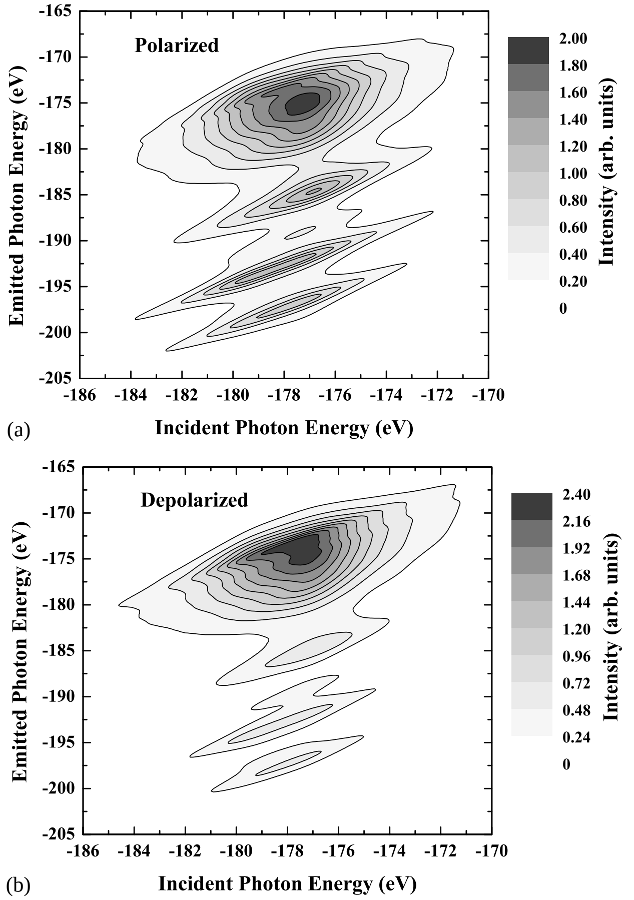

Fig. 2. Calculated $4d \rightarrow 2p_{3/2}$ RXES intensity as a function of the incident photon energy Ω and the emitted photon energy ω for Nd^{3+} ion: (a) polarized configuration, (b) depolarized configuration.

$4d$ core and $4f$ electrons, it is very interesting how the $4d$–$4f$ interaction affects the polarization dependence of RXES.

The calculated results of $4d \rightarrow 2p_{3/2}$ RXES in the polarized and depolarized configurations are shown in Figs. 2(a) and (b), respectively, which include both the $4d$–$4f$ and $4f$–$4f$ interactions. Though the energy positions of these RXES structures are almost the same, the intensity distribution shows the strong polarization dependence. In polarized (depolarized) configuration, the intensity of lower (higher) emitted photon energy is relatively enhanced. The reason for this is as follows : In $4d \rightarrow 2p_{3/2}$ RXES final state of Nd^{3+} ion, $4d^9$ and $4f^4$ electrons exist. Since the $4d^9$ core state with parallel (anti-parallel) spin direction to the $4f^4$ state lies at lower (higher) energy, the transition to the state has higher (lower) emitted photon energy. First, in $2p_{3/2} \rightarrow 4f$ absorption process, the quadrupole transition operator $C^{(2)}_{-1}$ mainly brings the transition to $4f$ states with down-spin and negative magnetic quantum number. Next, in $4d \rightarrow 2p_{3/2}$ emission process, the dipole transition operators are partly given by $C^{(1)}_0$ $(C^{(1)}_1 + C^{(1)}_{-1})$ in the polarized (depolarized) configuration (see Eq. (2.10) of Ref. [10]). After the $4d \rightarrow 2p_{3/2}$ emission, the $4d$ hole with both up- and down-spins and negative magnetic quantum number is left by $C^{(1)}_0$ and $C^{(1)}_1$ operators. Thus, both the strong transition to the anti-parallel state and the rather weak transition to the parallel spin state can be seen. On the other hand, the $4d$ hole with up-spin and positive magnetic quantum number is dominantly left by $C^{(1)}_{-1}$ operator. Thus, only the transition to the parallel spin state can be seen. (Similar discussion is also held for the quadrupole excitation operator $C^{(2)}_1$.) The transition to the anti-parallel (parallel) spin state is, therefore, rather strong in the polarized (depolarized) configuration. In other words, $4d \rightarrow 2p_{3/2}$ RXES shows the strong polarization dependence derived from the $4d$–$4f$ interaction.

Usually, RXES is represented by keeping Ω fixed, while varying ω, so that it corresponds to the cross-section parallel to the ω-axis in Fig. 2. On the other hand, the excitation spectrum is the cross-section parallel to the Ω-axis. In addition to these spectra, XAS, if it could be recorded directly with reduced spectral broadening, would correspond approximately to a cross section taken parallel to the Ω-axis with $\omega = -177$ eV in Fig. 1(a). It is not the cross section shown in Fig. 2, because the $4d$–$4f$ interaction does not intervene in the XAS process. Therefore, the energy separation of a double-peak structure observed by $2p_{3/2} \rightarrow 4f$ XAS (and also its MCD) generally does not agree with that determined from $4d \rightarrow 2p_{3/2}$ RXES, in contrast to recent experimental results by Bartolomé et al. [6]. The reason is that the energy separation in XAS is determined only by the $4f$–$4f$ interaction, while that in RXES (for instance, its excitation spectrum) is determined by both $4f$–$4f$ and $4d$–$4f$ interactions.

Though the strength of the $3d$–$4f$ and $4f$–$4f$ interactions are comparable in the RE $3d \rightarrow 2p_{3/2}$ RXES final state, the $3d$–$4f$ interaction has important effects on the excitation spectrum [7,12]. Since the $4d$–$4f$ interaction is rather larger than the $4f$–$4f$ interaction in $4d \rightarrow 2p_{3/2}$ RXES final states, the excitation spectrum, in general, cannot be regarded as essentially the same as XAS with a narrower spectral width.

In this paper, we showed only the calculated results for Nd as an example. All other light RE elements show similar behavior of the $4d$–$4f$ and $4f$–$4f$ interaction dependence and the polarization dependence.

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