Calculation of rare-earth 4*d* giant-absorption spectra with multiplet effects and decay processes

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The total and partial photoelectron yield spectra of all the trivalent rare-earth ions in the 4d giant resonance region are calculated with full multiplet effects. The decay processes are treated as coherent processes following photoexcitation. The results reproduce the over all features of experiments. It is obtained that the character of the giant-absorption is different between the light and heavy rare-earths. The multiplet effects play an essential role in the decay processes.

Keywords: rare-earth; **giant-absorption**; **giant resonance**; **XAS**; **multiplet**; **decay.**

1. Introduction

The x-ray photoabsorption spectra (XAS) of rare-earths in the region of 4d-edge exhibit strong asymmetric resonance called giant-absorption (Zimkina *et al.*, 1967). It is also found that a series of weak and sharp lines precede the giant-absorption (Fomichev *et al.*, 1967). These structures can basically be understood in terms of $4d^9 4f^{n+1}$ multiplet structure (Sugar, 1972) and decay to the continuum states (Dehmer & Starace, 1972). The theory of finite many-body system is applied in analogy to nuclear physics in several ways (Connerade *el al.*, 1987), and succeeded to describe the spectra in the context of collective excitations. These works, however, focused on the properties of the radial part of wave functions, so that the multiplet effects are paid less attention.

It has become known through the measurements of partial yields that there are differences in the character of the decay for light and heavy rare-earths (Prescher *et al.*, 1986; Dzionk *et al.* 1989; Richter *et al.*, 1989a; Richter *et al.*, 1989b; Nagata *et al.*, 1990: Baier *et al.*, 1993; Gottwald *et al.*, 1998). In the light rare-earths, photoexcitation process is described by the competition between $4d \rightarrow 4f$ photoabsorption and $4d \rightarrow \epsilon f$ photoionization, where these processes are strongly coupled by $< 4d^9 4f^{n+1}|1/r|4d^9 4f^n \epsilon f >$ configuration interaction (CI). The excited states are also coupled to $4f^{-1}$ and $5(s,p)^{-1}$ ionization continua by the CI processes $< 4d^9 4f^{n+1}|1/r|4d^{10} 4f^{n-1} \epsilon l >$ and $< 4d^9 4f^{n+1}|1/r|4d^{10} 4f^n 5(s,p)^{-1} \epsilon l >$ known as 4d-4f4f super-Coster-Kronig (sCK) and 4d-4f5(s,p) Coster-Kronig (CK) decay channels, respectively. In the same sence, the $< 4d^9 4f^{n+1}|1/r|4d^9 4f^n \epsilon f >$ CI can be regarded as a decay from $4d^9 4f^{n+1}$ states, which can naively be called $4f \rightarrow \epsilon f$ "tunneling" channel. On the other hand, in the heavy rare-earths, the photoexcitation process is well described by $4d \rightarrow 4f$ excitation and the sCK decay channel. It is also known from the spectra of solid state materials that the shape of giant-absorption of the light rare-earths is quite sensitive to the environment, while that of the heavy rare-earths is insensitive (Suzuki *et al.*, 1975; Olson & Lynch, 1982; Kalkowski *et al.*, 1985; Aita *et al.*, 1987).

The purpose of the present work is to investigate the differences in the character of the giant-absorption spectra, by calculating the total and partial photoelectron yield spectra, putting emphasis on the multiplet effects. The partial photoelectron yields refrect the decay probabilities from the excited states. The total photoelectron yields are regarded as photoabsorption spectra.

2. Formulation

The Hamiltonian of the system is written as

$$H = H_0 + V_r + V_a, \quad (1)$$

where H_0 describes the Coulomb, exchange and spin-orbit interactions, V_r the radiative dipole transition, V_a the non-radiative transition. H_0 represents multiplet effects, V_r photo excitation, V_a decay processes.

We take into account three decay channels, the 4d-4f4f sCK, the 4d-4$f(5s,5p)$ CK and the $4f \rightarrow \epsilon f$ "tunneling", explicitly. Other decay processes $(4d\text{-}(5s,5p)^2$ etc.) are included implicitly as a constant lifetime width (Γ) in the intermediate states.

The photoelectron yield spectrum $I(\omega)$ is calculated as

$$I(\omega) = \int d\epsilon F(\epsilon,\omega), \quad (2)$$

where $F(\epsilon,\omega)$ represents the resonant-photoemission spectrum. Here $F(\epsilon,\omega)$ is written as

$$F(\epsilon,\omega) = \sum_{k\beta} | < k\beta|T|g > |^2 \delta(\hbar\omega + E_g - E_{k\beta})\delta(\epsilon - \epsilon_k), \quad (3)$$

where $\hbar\omega$ is the incident photon energy, ϵ the kinetic energy of the emitted electron, $|g>$ (E_g) represents the ground state (energy), $|k\beta>$ $(E_{k\beta})$ the final states (energies) with a continuum electron.

We assume the final states $|k\beta>$ $(E_{k\beta})$ can be decoupled as $|k\beta> = |k>|\beta>$ $(E_{k\beta} = E_k + E_\beta)$. Here $|k>$ and E_k represents the ϵl continuum electron state and its energy, and $|\beta>$ and E_β the system after decay, respectively.

The operator T is the t-matrix

$$T = V_r + V_a \frac{1}{z - H_0} T \quad (4)$$

with

$$z = \hbar\omega + E_g + i\Gamma. \quad (5)$$

From eqs. (3) and (4), we obtain, after some algebra, the expression

$$F(\epsilon,\omega) = \sum_{k\beta} \Bigg| < k\beta|V_r|g > + \sum_{\alpha,\alpha'} < k\beta|V_a|\alpha >< \alpha|G|\alpha' > \times \left(< \alpha'|V_r|g > + \sum_{k'\beta'} \frac{< \alpha'|V_a|k'\beta' >< k'\beta'|V_r|g >}{z - E_{k'\beta'}} \right) \Bigg|^2 \times \delta(\hbar\omega + E_g - E_{k\beta})\delta(\epsilon - \epsilon_k), \quad (6)$$

where $|\alpha>$ (E_α) and $|\alpha'>$ $(E_{\alpha'})$ represent the excited states (energies) with $4d^9 4f^{n+1}$ configuration. The Green's function $< \alpha|G|\alpha' >$ is obtained numerically by matrix inversion from

$$< \alpha|\ G\ |\alpha' > = \frac{1}{z - E_\alpha}\delta_{\alpha\alpha'} + \frac{1}{z - E_\alpha} \times \sum_{k\beta,\alpha''} \frac{< \alpha|V_a|k\beta >< k\beta|V_a|\alpha'' >}{z - E_{k\beta}} < \alpha''|G|\alpha' > . \quad (7)$$

The ground state $|g>$ is taken to be the Hund's rule ground state. The reduced matrix elements required for the calculation are obtained by Cowan's program suit (Cowan, 1981). The required parameters such as Slater integrals F^k, G^k, R^k, the spin-orbit coupling constants ζ, and radial integrals $(nl|r|n'l')$, $(nl|r|\epsilon l')$ are obtained by the configuration averaged Hartree-Fock method with relativistic corrections. The kinetic energy of the continuum electron is determined so as to conserve the total average energy of the two configurations before and after decay. The Slater integrals are scaled from its original values in order to reproduce experiments well. $F^k(4f,4f)$, $F^k(4d,4f)$, $G^k(4d,4f)$ are reduced to 80%, 75% and 66%, respectively (Sugar, 1972). $R^k(4d\epsilon l,4f^2)$, $R^k(4d\epsilon l,4f5s)$, $R^k(4d\epsilon l,4f5p)$ and $R^k(4d4f,4d\epsilon l)$ are reduced to 100%, 60%, 60% and 70%, respectively. The spin-orbit coupling constants and radial integrals are not scaled.

In addition to these parameters, the $4d$ photoionization threshold energy is required, at which energy the continuum states ϵl for "tunneling" process start to rise. As this threshold energy is dependent on the environment of the rare-earth ion, it is taken as an arbitrary parameter.

3. Results and Discussion

The calculation was made for all of the rare-earth elements from La^{3+} to Yb^{3+}. These results reproduce the experimental photoabsorption spectra of the rare-earth trifluorides (Olson & Lynch, 1982) well. Selected results are shown below. The parameter values used are given in Table 1.

3.1. light rare-earths

The calculated results of total and partial photoelectron yields for a Pr^{3+} ion are shown in Fig.1 as a representative of the light rare-earths. The dotted, dashed, dash-dotted, and solid curves corresponds to the partial photoelectron yields of $4f^{-1}$, $5s^{-1}$, $5p^{-1}$, and $4d^{-1}$, respectively. The thick solid curve represents total photoelectron yield and can be regarded as photoabsorption spectrum. The intensities of these spectra are proportional to the probabilities of their decay channels. The origin of abscissa is set to the average energy of all the multiplets. The dipole allowed states exist high above the average energy. The asymmetric Fano profile lacks a Fano minimum in the lower energy side, because the continuum state of the $4d^{-1}$ channel which causes the interference is cut at the threshold.

It can be seen from the partial photoelectron yields that there are strong preference of the decay channels for each multiplet. Among the three strong multiplet lines, the highest energy line decays almost exclusively by $4f \rightarrow \epsilon f$ "tunneling" channel, because the sCK and CK channels are forbidden from the symmetry. The second line is allowed for the "tunneling" and CK channels and the lowest line is allowed for all the three decay channels.

It is generally observed in the light rare-earths that the sCK and CK channels are suppressed for high energy multipltes, while the "tunneling" channel is suppressed for low energy states by threshold. The "tunneling" channel has large decay probabilities for higher energy multiplets, because the exchange interaction in $< 4d^9 4f^{n+1}|H_0|4d^9 4f^{n+1} >$ Hamiltonian matrix elements and the "tunneling" CI $< 4d^9 4f^{n+1}|V_a|4d^9 4f^n \epsilon f >$ matrix elements have a similar form.

It is also found that the position of threshold has strong influence on the shape of giant-absorption. We will investigate it in the later subsection.

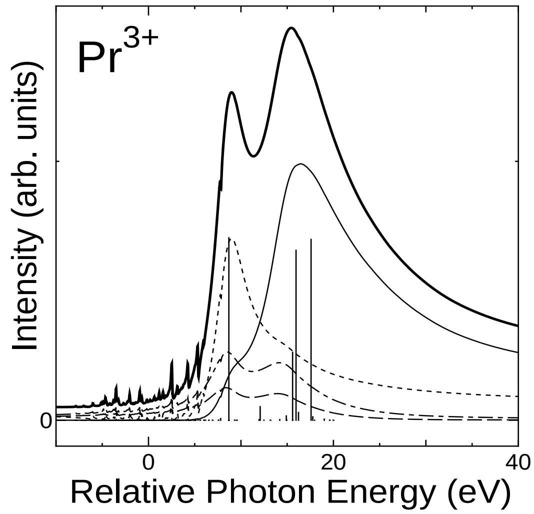

Figure 1
The calculated results of total and partial photoelectron yields for Pr^{3+}. The thick solid curve represents total photoelectron yield. The dotted curve represents $4f^{-1}$ partial photoelectron yield, dashed $5s^{-1}$, dash-dotted $5p^{-1}$ and solid $4d^{-1}$. The vertical bars represent the transition probabilities to the $4d^9 4f^{n+1}$ multiplets.

3.2. heavy rare-earths

The calculated results for an Er^{3+} ion is shown in Fig.2 as a representative of the heavy rare-earths. In this case, the most dominant decay channel is $4d$-$4f4f$ sCK (Ogasawara & Kotani, 1995). The asymmetric Fano profile is clearly seen. The "tunneling" decay channel has only a minor contribution, because the positions of dipole allowed multiplets are lower than threshold. The crossover of the dominant decay channels from the "tunneling" to sCK takes place near Sm^{3+}.

The intensity ratios between the $4d$-$4f4f$ sCK and $4d$-$4f5(s,p)$ CK channels change roughly proportional to ${}_nC_2$ over $(2,6) \times n$ for the heavy rare-earths, where n is the $4f$ number in the excited states.

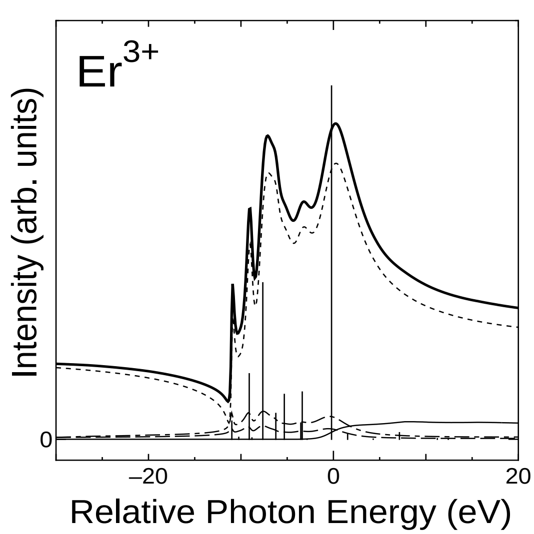

Figure 2
The calculated results of total and partial photoelectron yields for Er^{3+}.

3.3. threshold energy

Calculated results for a Sm^{3+} ion for two different 4*d* ionization energies are shown in Fig.3. It can be seen that the $4d$-$4f4f$ sCK and the $4f \to \epsilon f$ "tunneling" have comparable decay probabilities and that the ratio between them depends on the threshold energy.

The deep dip in the giant-absorption in Fig.3 (a) is smeared out in Fig.3 (b), while the structures below the threshold are scarcely affected. This is due to the increase of the $4f \to \epsilon f$ "tunneling" decay probability, which can clearly be seen from the partial photoelectron yields.

The sensitivity of the shape of giant-absorption in the light rare-earth can be explained from the fact that their dominant decay channel is the $4f \to \epsilon f$ "tunneling" one, where the continuum electron is emitted to the electronic states with small kinetic energies, so that strong material dependence is expected. On the other hand, the insensitivity in the heavy rare-earth can be understood from the fact that their dominant decay channel is $4d$-$4f4f$ sCK, where the continuum electron is emitted to free electron-like high kinetic energy (>100eV) states.

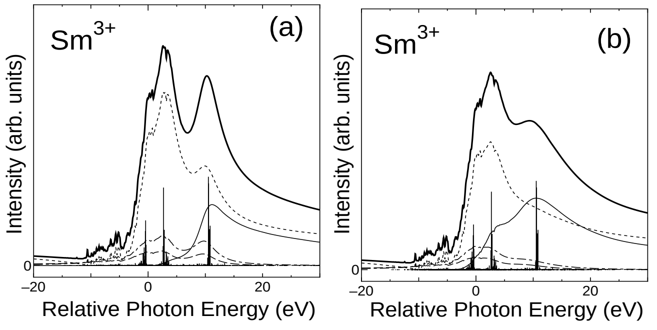

Figure 3
The calculated results of total and partial photoelectron yields for Sm^{3+} with 4*d* ionization threshold energy of (a) 3eV and (b) −3eV.

Table 1
Slater integrals and spin-orbit coupling constants required for multiplet effects are shown for the ground states and photoexcited states.

	Pr^{3+}	Sm^{3+}	Er^{3+}
$F^2(4f,4f)$	9.78 (eV)	10.92 (eV)	12.87 (eV)
$F^4(4f,4f)$	6.14	6.85	8.08
$F^6(4f,4f)$	4.41	4.93	5.81
ζ_{4f}	0.10	0.16	0.30
$F^2(4f,4f)$	9.98	11.07	12.98
$F^4(4f,4f)$	6.27	6.95	8.15
$F^6(4f,4f)$	4.51	5.00	5.86
ζ_{4f}	0.11	0.16	0.31
ζ_{4d}	1.38	1.83	3.05
$F^2(4d,4f)$	10.59	11.66	13.55
$F^4(4d,4f)$	6.77	7.45	8.66
$G^1(4d,4f)$	11.06	12.13	14.01
$G^3(4d,4f)$	6.92	7.61	8.82
$G^5(4d,4f)$	4.88	5.38	6.24

4. Concluding Remarks

In conclusion, comparing the results for the whole rare-earth series, it is observed that the characteristics of the decay are qualitatively different between the light and heavy rare-earths. In the light rare-earths the $4f \to \epsilon f$ "tunneling" channel is important, where the continuum state ϵf is just above threshold. The shape of giant-absorption of the light rare-earths reflects the density of states near the threshold, so that the spectra may depend on environment. On the other hand, the shape of giant-absorption of the heavy rare-earths is determined by $4d$-$4f4f$ sCK channel, where the free electron like continuum states with high kinetic energy are involved. Thus the shape of giant-absorption of the heavy rare-earths is less dependent on environment.

The change of the dominant decay channels are due to the increase of $4f$ numbers, which is an arithmetic factor, and to the shift of 4*d* ionization threshold, which is a radial part effect. However it is found that the decay channels are also dependent on the multiplet terms, which is an angular factor. Therefore it is essential to consider the multiplet structures for the full understanding of the decay processes.

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