Polarization dependence of resonant X-ray emission spectra in early transition metal compounds

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We calculate the polarization dependent spectra of resonant X-ray emission in TiF_3, VF_3 and Cr_2O_3, which have one, two and three $3d$ electron(s) in the ground state, respectively. We study the detailed mechanism of the spectral structures, comparing with a previous result of TiO_2. Then we discuss systematically the difference of spectra with the change of the $3d$ electron number from group theoretical consideration.

Keywords: resonant X-ray emission; polarization dependence; Wigner-Eckart theorem.

1. Introduction

Resonant X-ray emission spectroscopy (RXES) is a useful tool to analyze electronic structures of transition metal (TM) compounds (Kao *et al.*, 1996; Hill *et al.*, 1998; Jiménez-Mier *et al.*, 1999; Harada *et al.*, 2000) due to the recent development of high brightness synchrotron light sources. In RXES a core electron is excited near the threshold by an incident photon, and then the excited state decays by emitting an X-ray photon. Hence, the whole process of RXES is described by a coherent second order optical process (Tanaka *et al.*, 1991; Kotani & Shin, 2000).

The polarization dependence in RXES is a new interesting topic. Recently we analyzed the $2p \rightarrow 3d \rightarrow 2p$ RXES of TiO_2 and ScF_3 in "polarized" and "depolarized" configurations (Matsubara *et al.*, 2000). We call TiO_2 and ScF_3 "d^0 system", because formally tetravalent Ti and trivalent Sc have no $3d$ electron. The polarized configuration is the case where the polarization vector of the incident photon is perpendicular to the scattering plane and the depolarized configuration is the case where it is parallel. In both configurations the scattering angle is fixed to 90°, and the geometrical configuration is shown in Fig. 1.

The calculated results of (a) XAS and (b) RXES of TiO_2 are shown in Fig. 2. The indices from **a** to **h** denote the incident photon energies. We reasonably explained the spectral structures of RXES by means of group theoretical consideration: the elastic peak at 0 eV and the inelastic peak at 14 eV are bonding and anti-bonding states between the $3d^0$ and $3d^1\underline{L}$ configurations, where $\underline{L}$ denotes a ligand hole, respectively. The inelastic structure ranging from 5 eV to 10 eV appears in both polarized and depolarized configurations. The bonding and anti-bonding states have the same symmetry A_{1g} and non-bonding state has various symmetry except A_{1g}.

In the present paper we calculate the polarization dependent RXES of TiF_3, VF_3 and Cr_2O_3, which belong to $3d^1$, $3d^2$ and $3d^3$ systems, respectively, and give a systematic analysis for these early TM compounds.

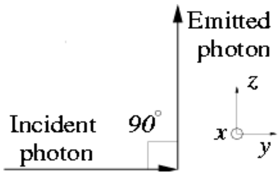

Figure 1 Assumed geometrical configuration. In the polarized configuration the polarization vector of the incident photon is taken in the x direction, while in the depolarized configuration it is in the z direction.

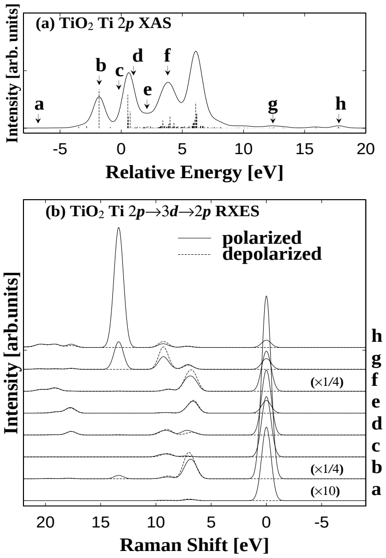

Figure 2 Calculated results of (a) Ti $2p$ XAS and (b) Ti $2p \rightarrow 3d \rightarrow 2p$ RXES for TiO_2. The spectra in the polarized configuration are plotted by solid lines, while those in the depolarized configuration by dashed lines. Indices from **a** to **h** denote the incident photon energies.

2. Model and formulation

We describe these compounds as an MX_6 (M = Ti, V, Cr and X = F, O) cluster model with O_h symmetry, and also consider the full multiplet structure. We take into account the hybridization $V(\Gamma)$ between M $3d$ and X $2p$ orbitals ($\Gamma = e_g, t_{2g}$ and for simplicity, $V(e_g) = -2V(t_{2g})$) and the crystal field splitting energy $10Dq$.

The charge transfer energy $\Delta = E(d^{n+1}\underline{L}) - E(d^n)$, where $E(d^n)$ and $E(d^{n+1}\underline{L})$ denote the configuration averaged energies of d^n and $d^{n+1}\underline{L}$ ($n = 1$ for TiF_3, $n = 2$ for VF_3 and $n = 3$ for Cr_2O_3), the Coulomb repulsion U_{dd} between the $3d$ electrons, and the attractive core-hole potential U_{dc} acting on the $3d$ electrons are also treated as adjustable parameters. These parameter values are determined to reproduce experimental results of XAS and RXES (Harada, 2000), and shown in Table. 1.

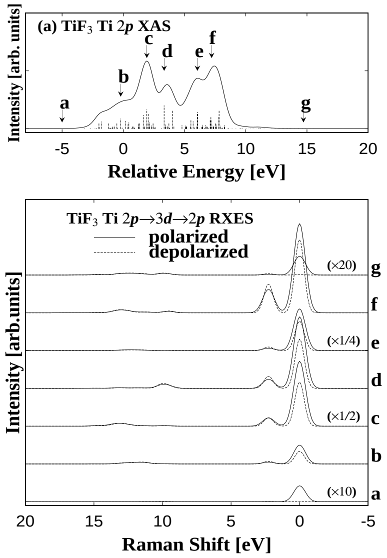

Figure 3 Calculated results of (a) Ti $2p$ XAS and (b) Ti $2p \rightarrow 3d \rightarrow 2p$ RXES for TiF$_3$. The spectra in the polarized configuration are plotted by solid lines, while those in the depolarized configuration by dashed lines. Indices from **a** to **g** denote the incident photon energies.

Table 1
Parameter values used in this calculation.

Compound	Δ	U_{dd}	U_{dc}	$V(e_g)$	$10Dq$
TiF$_3$	8.5	4.5	5.3	3.6	1.5
VF$_3$	8.0	4.5	5.3	3.2	1.4
Cr$_2$O$_3$	5.5	5.5	6.5	3.0	1.3

In the calculation of RXES, we use the following formula of the coherent second order optical process:

$$F(\Omega,\omega) = \sum_f \left| \sum_m \frac{\langle f|T_e|m\rangle\langle m|T_i|g\rangle}{\Omega + E_g - E_m - \mathrm{i}\Gamma_m} \right|^2 \delta(E_R + E_g - E_f), \quad (1)$$

where $|g\rangle$, $|m\rangle$ and $|f\rangle$ represent the ground, intermediate and final states of RXES with energies E_g, E_m and E_f, respectively. T_i and T_e are the electric dipole transition operators. The incident and emitted photon energies are represented by Ω and ω, respectively. E_R is the Raman shift energy, which is defined as the difference between incident and emitted photon energies, i.e. $\Omega - \omega$.

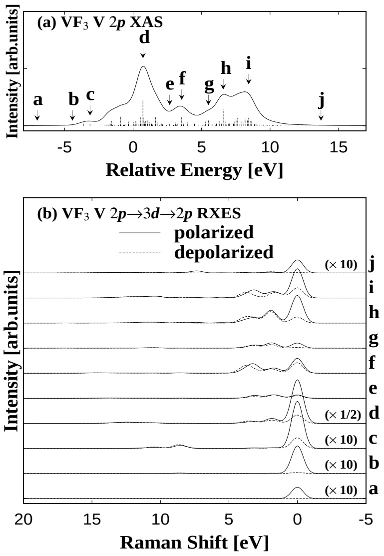

Figure 4 Calculated results of (a) V $2p$ XAS and (b) V $2p \rightarrow 3d \rightarrow 2p$ RXES for VF$_3$. The spectra in the polarized configuration are plotted by solid lines, while those in the depolarized configuration by dashed lines. Indices from **a** to **j** denote the incident photon energies.

For the polarized and depolarized configurations eq. (1) is transformed into the following form (Matsubara *et al.*, 2000):

$$\begin{aligned} F(\Omega,\omega) &= \sum_f \left| \sum_{q,q'=\pm1} \sum_m \frac{\langle f|C_q^{(1)}|m\rangle\langle m|C_{q'}^{(1)}|g\rangle}{\Omega + E_g - E_m - \mathrm{i}\Gamma_m} \right|^2 \\ &\quad \times \delta(E_R + E_g - E_f) \quad (\text{polarized}), \end{aligned} \quad (2)$$

$$\begin{aligned} F(\Omega,\omega) &= \sum_f \left| \sum_{q=\pm1} \sum_m \frac{\langle f|C_q^{(1)}|m\rangle\langle m|C_0^{(1)}|g\rangle}{\Omega + E_g - E_m - \mathrm{i}\Gamma_m} \right|^2 \\ &\quad \times \delta(E_R + E_g - E_f) \quad (\text{depolarized}). \end{aligned} \quad (3)$$

3. Calculated results and discussion

In Figs. 3, 4 and 5, we show the calculated results of (a) Ti, V and Cr $2p$ XAS and (b) Ti, V and Cr $2p \rightarrow 3d \rightarrow 2p$ RXES of TiF$_3$, VF$_3$ and Cr$_2$O$_3$, respectively. The indices **a, b,** ... indicate the incident photon energies. The spectra of both polarized (solid line) and depolarized (dashed line) configurations are plotted as a function of Raman shift, i.e. 0 eV corresponds to the elastic scattering (Rayleigh line). In addition to the elastic peak, two sets of inelastic peaks are seen in all RXES spectra: one ranges from about 1 eV to 5 eV, and the other from about 7 eV to 14 eV. The former results from so-called *d-d* excitation, and the latter from the charge transfer excitation. In the d^3 system the elastic peak is seen only in the polarized configuration as in the case of the d^0 system, while in d^1 and d^2 systems it has considerable intensity in both configurations.

Furthermore, remarkable enhancement of the intensity of the anti-bonding state, which is seen in the d^0 system when incident photon energies are set at satellite structures of XAS is hardly seen in the d^1, d^2 and d^3 systems.

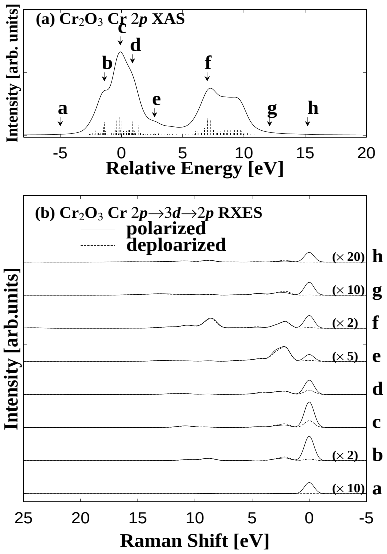

Figure 5 Calculated results of (a) Cr 2*p* XAS and (b) Cr $2p \rightarrow 3d \rightarrow 2p$ RXES for Cr_2O_3. The spectra in the polarized configuration are plotted by solid lines, while those in the depolarized configuration by dashed lines. Indices from **a** to **h** denote the incident photon energies.

In order to explain this behavior of spectral structures due to the difference of the 3*d* electron number, we use group theoretical consideration. According to the Wigner-Eckart theorem, the optical transition matrix element is described as the Clebsch-Gordan (CG) coefficient. The transition occurs only when the CG coefficient is nonzero. The ground state symmetry Γ_g of the d^1, d^2 and d^3 systems are T_{2g}, T_{1g} and A_{2g} states, respectively. By using this, the final state symmetry $\Gamma_{f,p}$ ($\Gamma_{f,d}$) of the polarized (depolarized) configuration is obtained as follows:

$$\Gamma_{f,p} = \sum_{\gamma'=x,y} \Gamma_g \otimes T_{1u,x} \otimes T_{1u,\gamma'} \quad \text{(polarized)}, \qquad (4)$$

$$\Gamma_{f,d} = \sum_{\gamma'=x,y} \Gamma_g \otimes T_{1u,z} \otimes T_{1u,\gamma'} \quad \text{(depolarized)}. \qquad (5)$$

The result is shown in Table. 2. In d^1 and d^2 systems, the ground state symmetry, T_2 for d^1 and T_1 for d^2, is found in the final state of both polarized and depolarized configurations. This is why the elastic peaks in d^1 and d^2 systems are allowed in both polarized and depolarized configurations.

Table 2
The ground state symmetries and the allowed final state symmetries of each compound.

Compound	ground (Γ_g)	final(polarized) ($\Gamma_{f,p}$)	final (depolarized) ($\Gamma_{f,d}$)
TiF_3 (d^1)	T_2	A_1, A_2, E, T_1, T_2	A_1, A_2, E, T_1, T_2
VF_3 (d^2)	T_1	A_1, A_2, E, T_1, T_2	A_1, E, T_1, T_2
Cr_2O_3 (d^3)	A_2	A_2, E, T_1, T_2	T_1, T_2

In the d^3 system, however, the ground state can be reached only in the final state of the polarized configuration as in the case of the d^0 system. Therefore, the elastic peak is only seen in the polarized configuration. Note that the elastic peak intensity in the depolarized configuration is slightly seen in Fig. 5 due to the spin-orbit interaction, which is not taken into account in this group theoretical consideration. Also, the inelastic peak corresponding to the anti-bonding final state, which appeared in the d^0 system, is hardly seen in d^1, d^2 and d^3 systems due to the effects of the multiplet coupling and relatively weak hybridization.

The present results are in fair agreement with recent experimental data by Harada (2000).

4. Conclusion

In conclusion, we have calculated and made a systematic analysis for the polarization dependent RXES of TiF_3, VF_3 and Cr_2O_3, which have one, two and three 3*d* electron(s), respectively, by using the MX_6 cluster model. The calculated results show that the behavior of the spectral intensity, especially the elastic peak intensity, in the d^1 system resembles that in the d^2 system, while that in the d^3 system resembles the d^0 system. This result is reasonably explained by the selection rule using group theoretical consideration.

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References

Harada, Y. (2000). *Thesis, Univ. of Tokyo*.
Harada, Y., Kinugasa, T., Eguchi, R., Shin, S., Matsubara, M. & Kotani, A. (2000). *Phys. Rev.* B**61**, 12854–12859.
Hill, J. P., Kao, C.-C., Caliebe, W. A. L., Matsubara, M., Kotani, A., Peng, J. L. & Greene, R. L. (1998). *Phys. Rev. Lett.* **80**, 4967–4970.
Jiménez-Mier, J., van Ek, J., Ederer, J. D., Callcott, T. A., Jia, J. J., Carlisle, J., Terminello, L., Asfaw, A. & Perera, R. C. (1999). *Phys. Rev.* B**59**, 2649–2658.
Kao, C.-C., Caliebe. W. A. L., Hastings, J. B. & Gillet J.-M. (1996). *Phys. Rev.* B**54**, 16361–16364.
Kotani, A. & Shin, S. (2000) to be published in *Rev. Mod. Phys*.
Matsubara, M., Uozumi, T., Kotani, A., Harada, Y. & Shin, S. (2000). *J. Phys. Soc. Jpn*, **69**, 1558–1565.
Tanaka, S., Okada, K. & Kotani, A. (1991). *J. Phys. Soc. Jpn*, **60**, 3893–3903.

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