

## Theoretical study of cluster size effects on X-ray absorption and resonant X-ray emission spectra in $d$ and $f$ electron systems

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Cluster size dependence of X-ray absorption spectra and resonant X-ray emission spectra are theoretically studied with a one-dimensional  $d$ - $p$  model, which describes qualitatively the effect of translational symmetry for nominally  $d^0$  (or  $f^0$ ) compounds such as  $\text{TiO}_2$  (or  $\text{CeO}_2$ ).

**Keywords:** resonant X-ray emission, X-ray absorption, one-dimensional  $d$ - $p$  model, Lanczos method.

### 1. Introduction

Study of resonant X-ray emission spectroscopy (RXES) has recently been a subject of remarkable progress with high brightness synchrotron radiation sources. In RXES, a core electron is excited by the incident X-ray photon to the absorption threshold and this excited state decays by emitting an X-ray photon. Therefore, RXES is a second order optical process, whose intermediate state is the same as the final state of the X-ray absorption spectroscopy (XAS), which is a typical first order optical process.

Theoretical analysis of XAS and RXES in  $d$  and  $f$  electron systems, such as transition metal compounds and rare earth compounds, has so far been made with a cluster model (or an impurity Anderson model) including a single cation (denoted hereafter as *single-cation model*). For nominally  $d^0$  and  $f^0$  systems,  $\text{TiO}_2$  and  $\text{CeO}_2$  for instance, XAS and RXES of  $\text{CeO}_2$  are well analysed by the single-cation model (see for instance a short review by Kotani (1997), but for  $\text{TiO}_2$  (Tezuka *et al.*, 1996) such an analysis for RXES breaks down even though it works well for the analysis of XAS (Okada & Kotani, 1993).

The spatial extension of the transition metal  $3d$  wave function is larger than that of the rare earth  $4f$  wave function. Therefore, it is expected that the RXES of transition metal compounds are more sensitive to the cluster size. Furthermore, it is interesting to compare the cluster size dependence of RXES and XAS. It is the purpose of this paper to perform a model study of cluster size effects on XAS and RXES.

### 2. Model

We consider the following one-dimensional  $d$ - $p$  Hamiltonian as a model of  $\text{TiO}_2$ :

$$H = \sum_{l,\sigma} [(\Delta + \varepsilon_p) d_{l\sigma}^\dagger d_{l\sigma} + \varepsilon_p p_{l\sigma}^\dagger p_{l\sigma}] + \sum_{\langle i,j \rangle} \sum_{\sigma} [v d_{i\sigma}^\dagger p_{j\sigma} + v^* p_{j\sigma}^\dagger d_{i\sigma}]$$

$$-U_{dc} \sum_l \left( \sum_{\sigma} d_{l\sigma}^\dagger d_{l\sigma} \right) \left( \sum_{\sigma'} c_{l\sigma'}^\dagger c_{l\sigma'} \right) + U_{dd} \sum_l d_{l\uparrow}^\dagger d_{l\uparrow} d_{l\downarrow}^\dagger d_{l\downarrow} + \sum_{l,\sigma} \varepsilon_c c_{l\sigma}^\dagger c_{l\sigma}. \quad (1)$$

Here,  $d_{l\sigma}^\dagger$  ( $p_{l\sigma}^\dagger$ ) is a creation operator of  $\sigma$  spin electron on the  $d$  ( $p$ ) site in  $l$ -th unit cell,  $\Delta$  is the charge-transfer energy between  $d$  and  $p$  orbitals,  $v$  is the nearest neighbor  $d$ - $p$  hopping,  $U_{dd}$  is the on-site  $d$ - $d$  Coulomb interaction, and  $U_{dc}$  is the intra-atomic core hole potential.  $c_{l\sigma}^\dagger$  ( $c_{l\sigma}$ ) is a creation (annihilation) operator of core electrons, and  $\varepsilon_c$  is the core electron energy. For simplicity, we disregard the orbital degeneracy of the  $d$ ,  $p$  and  $c$  states.

Geometry of the system is shown, for instance, at the top of Figs. 1(a) and 1(b) for  $d_1p_2$  and  $d_6p_6$  clusters, respectively. We set the number of valence electrons in the ground state as  $2N$  for the  $d_Np_N$  cluster. The  $d_1p_2$  cluster with the *open boundary condition* is used as a reference system representing the single-cation cluster, and the effect of larger clusters is studied using the  $d_Np_N$  clusters with the *periodic boundary condition*.

Although we do not explicitly consider the orbital degeneracy, its effect on the  $d$ - $p$  hopping can partly be taken into account by putting  $v = \sqrt{[2V(e_g)^2 + 3V(t_{2g})^2]}/2$ , where  $V(e_g)$  and  $V(t_{2g})$  are hybridization strengths of  $\text{TiO}_6$  cluster model. Using the parameter values  $V(e_g)=3.0$  and  $V(t_{2g})=-1.5$  (in units of eV) after Okada & Kotani (1993), we have  $v=3.5$  eV. Other parameters are chosen to be  $\Delta=4.0$ ,  $U_{dd}=4.0$  and  $U_{dc}=6.0$  (in eV). These will be referred to as “ $\text{TiO}_2$ -like” parameters.

The present model can also be used for the  $\text{Ce } 4f$ - $3d$  RXES calculation of a “ $\text{CeO}_2$ -like” system by regarding  $d$ ,  $p$  and  $c$  as  $\text{Ce } 4f$ ,  $\text{O } 2p$  and  $\text{Ce } 3d$  orbitals, respectively, and by taking appropriate values for the model parameters.

The RXES spectrum is calculated by using the coherent second order optical formula and by taking into account the optical dipole transition between  $c$  and  $d$  states. Numerical calculations are made using the Lanczos method.

### 3. Calculated Results

Figures 1(a) and 1(b) show the calculated XAS and RXES spectra for the  $\text{TiO}_2$ -like parameters in  $d_1p_2$  and  $d_6p_6$  clusters, respectively. It is seen that the cluster size dependence of XAS is small. With the increase of the cluster size, some fine absorption structures come arise on the high energy tail of the main peak. The calculated RXES are shown with the incident photon energy  $\Omega$  tuned to the XAS energy positions 1, 2, 3, and so on. In the present calculation of RXES, we confine our interest to the study of inelastic X-ray scattering (IEXS) components with  $\omega \neq \Omega$  ( $\omega$  being the emitted photon energy), and for elastic scattering component ( $\omega = \Omega$ ) we show only their emitted photon energies by arrows in the figures of RXES.

In the case of the  $d_1p_2$  system, IEXS peaks are caused by the local charge transfer excitation, and their energy  $\omega$  moves in parallel with  $\Omega$ . The first IEXS peak corresponds to a single-electron charge transfer excitation (anti-bonding state between  $d^0$  and  $d^1p$  configurations), while the second one mainly to a two-electrons charge transfer state. For the  $d_6p_6$  cluster, on the other hand, the energy  $\omega$  of the strongest RXES peak does not follow  $\Omega$  but is rather constant, and it oscillates, in more precise, with the change of  $\Omega$ . Thus the cluster size effect is very important for RXES.

Similar calculations have also been made for the  $\text{CeO}_2$ -like system, although the result is not shown here. It is found that the

cluster size dependence of XAS and RXES for the CeO<sub>2</sub>-like system is much smaller than that of the TiO<sub>2</sub>-like system, and the single-cation cluster model works well in describing both XAS and RXES.

These results suggest that the single-cation model can well describe XAS for both Ti and CeO<sub>2</sub>, and justify previous theoretical analyses of Ti 2pXAS of TiO<sub>2</sub> (Okada & Kotani, 1993) and Ce 3dXAS of CeO<sub>2</sub> (Kotani, 1997, and references therein). For RXES, on the other hand, the cluster size dependence is very important for the TiO<sub>2</sub>-like system, while the single-cation model works as a fairly good model for the CeO<sub>2</sub>-like system. According to the Ti 3d-2p RXES spectra of TiO<sub>2</sub> measured experimentally by Tezuka *et al.* (1996), strong IECS spectra whose energy  $\omega$  do not follow

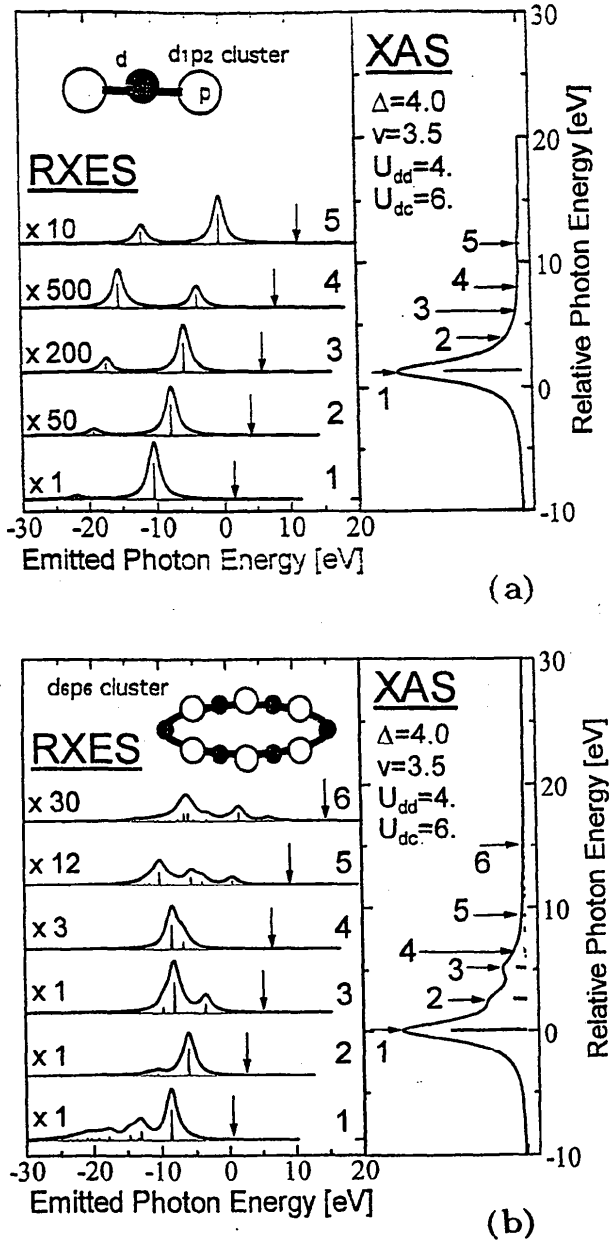
the change of  $\Omega$  were observed. These spectra cannot be explained with the single-cation model, but are qualitatively consistent with the results of the d<sub>6</sub>p<sub>6</sub> cluster. The mechanism of the cluster size dependence of RXES in the TiO<sub>2</sub>-like system will be discussed in detail in a separate paper (Idé & Kotani, 1998).

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**References**

Idé, T. & Kotani, A. (1998). *J. Phys. Soc. Jpn.* In the press.  
 Kotani, A. (1997). *Proceedings of the 9th International Conference on X-Ray Absorption Fine Structure*, (Grenoble, 1996) *J. Phys. IV France* 7, C2 1-8.  
 Okada, K. & Kotani, A. (1993). *J. Electron Spectrosc. Relat. Phenom.* 62, 131-140.  
 Tezuka, Y., Shin, S., Agui, A., Fujisawa, M. & Ishii, T. (1996). *J. Phys. Soc. Jpn.* 65, 312- 317.

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**Figure 1** Calculated XAS and RXES spectra for TiO<sub>2</sub>-like parameters with (a) d<sub>1</sub>p<sub>2</sub> and (b) d<sub>6</sub>p<sub>6</sub> clusters, the geometry of which is shown in the inset.