Theory of oxygen 1*s* resonant X-ray emission spectroscopy in copper-based oxides

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Many-body effects on the oxygen 1*s* resonant x-ray emission spectrum (O 1*s* RXES) in copper-based oxides, such as Sr_2CuO_3 and La_2CuO_4, are discussed on the basis of cluster-model calculations. The Zhang-Rice singlet excitation, which is a typical many-body state in Cu-based oxide systems, can be detected at low temperatures where the antiferromagnetic correlation between the neighboring Cu spins is strong. Thus the present study emphasizes that the O 1*s* RXES can be a good tool to obtain information on the Cu 3*d* states. In particular the polarization-dependent RXES gives the symmetry-decomposed information.

Keywords: resonant X-ray emission; **Zhang-Rice singlet**; **polarization.**

1. Introduction

It is well accepted that resonant X-ray emission spectroscopy (RXES) gives the site- and orbital-selective information on the electronic structure of solids. In some experiments, this point was nicely utilized to distinguish the contributions from non-equivalent oxygen sites in layered Cu-oxide systems (Guo *et al.*, 1994; Butorin *et al.*, 1995; Duda *et al.*, 2000). So far, the spectra thus obtained were often compared only with the O 2*p* partial density of states obtained from the energy-band calculations, and the detailed spectral analysis has not been done so far. The first attempt to discuss the many-body effects on the O 1*s* RXES in $CuGeO_3$ has been done by Duda *et al.* (Duda *et al.*, 2000), though any theoretical analysis for their experiment has not been given. Very recently the present authors (Okada and Kotani, 2000) have analyzed their experiments on the basis of the cluster model calculations and have shown that the Zhang-Rice singlet (ZRS) state (Zhang and Rice, 1988), which is a typical many-body state in high-T_c-related cuprates, can be detected as an inelastic scattering peak at low temperatures in particular.

In the present study, we apply the cluster model analysis used for $CuGeO_3$ (Okada and Kotani,2000) to the corner-sharing cuprates, such as Sr_2CuO_3 and La_2CuO_4. The Cu-O-Cu bond angle in Sr_2CuO_3 and La_2CuO_4 is 180 degrees, since the square planar CuO_4 units are connected with each other, sharing their corners. Owing to this bond angle, the 2*p* hole state on each O site is highly polarized. This is in contrast to the O 2*p* hole states in edge-sharing $CuGeO_3$ and Li_2CuO_2. Accordingly, in the following, we show that the polarization dependence of the O 1s RXES is characteristic of the present corner-sharing cuprates. The polarization-dependent RXES gives symmetry-decomposed information on the many-body states.

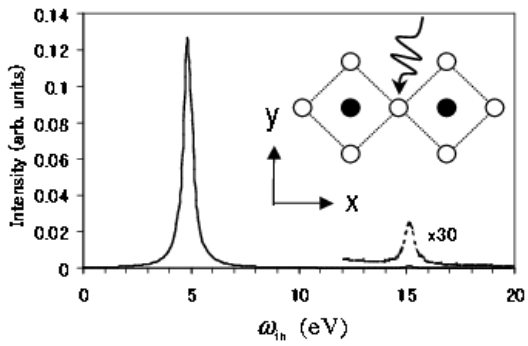

Figure 1
The O 1s XAS is plotted as a function of the incident photon energy ω_{in}. Since the one-body energy of 1*s* core hole is neglected, the origin of ω_{in} is arbitrary. The satellite region is enlarged 30 times. The illustration shows the cluster under consideration, where the open and closed circles represent the O and Cu atoms, respectively.

2. Model

We adopt a two-plaquette-cluster, $(Cu_2O_7)^{10-}$, and calculate the RXES process. The atomic configuration in $(Cu_2O_7)^{10-}$ is illustrated in the inset of Fig. 1. The Hamiltonian which describes this cluster is the *d*-*p* model, combined with the Coulomb interaction term between the O 1*s* and 2*p* holes. The relevant parameters which specify the Hamiltonian are the charge-transfer (CT) energy between Cu3*d* and O2*p* states (Δ=3.0 eV), the Cu3*d*-O2*p* hybridization ($pd\sigma$=−1.5 eV and $pd\pi$=$-pd\sigma/2$), the nearest-neighbor O2*p*-O2*p* hybridization ($pp\sigma$=0.5 eV and $pp\pi$=$-0.3pp\sigma$), the Cu3*d*-Cu3*d* Coulomb interaction (U_{dd}=8 eV), the O2*p*-O2*p* Coulomb interaction (U_{pp}=U_{dd}/2), and the O1*s*-O2*p* Coulomb interaction (U_{pc}=U_{pp}/0.8). The orbital and spin degeneracy in Cu3*d* and O2*p* orbits are taken into account. The multiplet coupling effect is taken into account only by introducing the diagonal part of the Cu 3*d*-3*d* exchange interaction (*J*=1.2 eV). These numerical values are close to those estimated for La_2CuO_4 (MacMahan *et al.*, 1988) and Sr_2CuO_3 (Okada *et al.*, 1996). In order to treat the many-body effects exactly, we numerically diagonalize the Hamiltonian by means of the Lanczos method (Heine, 1980).

The relevant part of the RXES spectral function is given by the following expression:

$$I_{\mu\nu}(\omega_{in},\omega_{out}) = \sum_f \left| \sum_{m,\sigma} \frac{\langle f|s_\sigma^\dagger p_{\nu\sigma}|m\rangle\langle m|p_{\mu\sigma}^\dagger s_\sigma|g\rangle}{E_g+\omega_{in}-E_m-i\Gamma_m} \right|^2 \times \delta(E_g+\omega_{in}-E_f-\omega_{out}), \quad (1)$$

where ω_{in} and ω_{out} are the incident and emitted photon energy and μ and ν are their polarization directions, respectively. $|g\rangle$, $|m\rangle$ and $|f\rangle$ represent the ground (initial), intermediate and final states of the system, respectively, and the corresponding energies are E_g, E_m and E_f. The core-hole lifetime broadening effect in the intermediate state is taken into account by a constant parameter Γ_m (=0.5 eV).

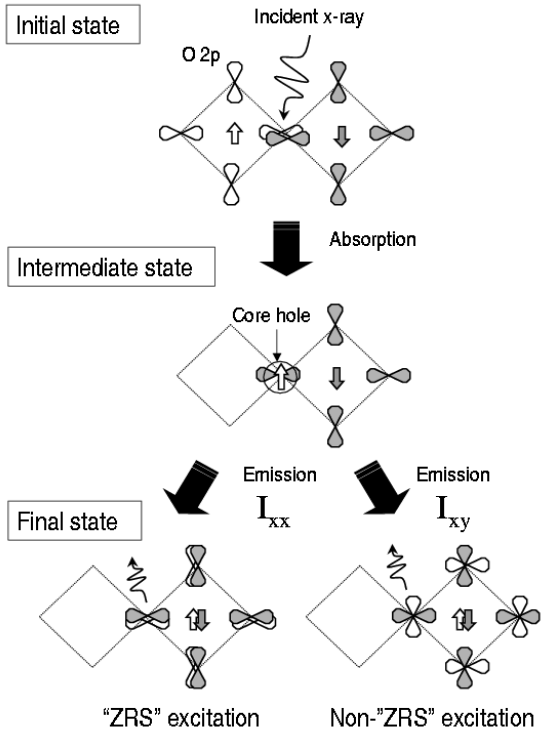

Figure 2
The RXES process is schematically shown. For simplicity it is assumed that the up-spin (down-spin) hole is in the left-hand-side (right-hand-side) plaquette.

3. Results of calculation

The present $(Cu_2O_7)^{10-}$ cluster has two valence holes, and the spin state is specified by the z component of the total spin (S_z). In the present case, the ground state is of S_z=0, which indicates that the spins localized mainly on the Cu sites are aligned antiferromagnetically. As shown later, this spin-configuration in the initial state is quite important in discussing the many-body effects on the O 1s RXES. In the ground state, the average 3d hole number is 0.68 per site and its character is almost $3d_{x^2-y^2}$. Extending the convention used in the single-site model analysis (Van der Laan *et al.*, 1981), the ground state is mainly $|d^9; d^9\rangle$ electron configuration.

On the other hand, the symmetry of the O 2p holes in the ground state is almost polarized to p_x or p_y, as schematically illustrated in Fig. 2. Accordingly, we can selectively excite the non-equivalent O sites by using the polarized incident X-ray. For instance, the average hole number at the O site which connect two Cu ions is 0.20 and its symmetry is almost p_x. The O 1s XAS at this O site is shown in Fig 1. The spectrum consists of an intense main peak at 4.85 eV and a very weak satellite at 15.1 eV. The final state which corresponds to the main peak is the $|d^{10}; d^9\rangle$ final state and the satellite is $|d^{10}; d^{10}\underline{L}\rangle$, where $\underline{L}$ denotes a ligand (O 2p) hole.

In Fig. 3 (a), I_{xx}, I_{xy}, I_{xz} and $I_{xx} + I_{xy} + I_{xz}$ on reosonace (ω_{in}=4.85 eV) are plotted as a function of the Raman shift. Each spectrum consists of only several peaks owing to the finite-size cluster calculations. They can be classified into four groups, which are denoted as "d^8", "O 2p main band", "ZRS", and "dd". If the electron correlation is negligible, the "O 2p main band" corresponds to the O 2p partial density of states in the energy-band calculation. We expect that the line shape of the O 2p main band becomes smooth with increasing the cluster size.

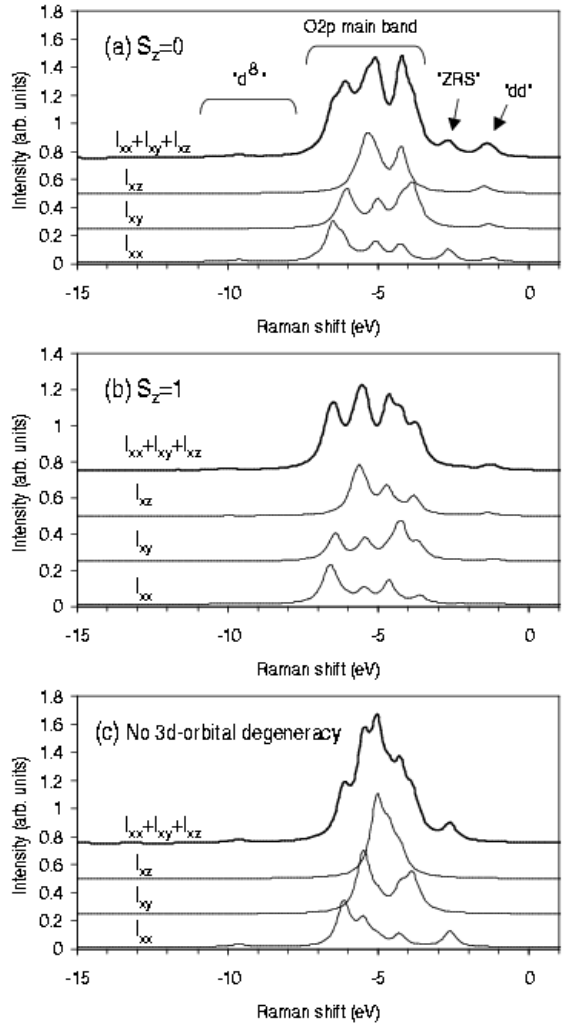

Figure 3
The O 1s RXES (I_{xx}, I_{xy}, I_{xz} and $I_{xx} + I_{xy} + I_{xz}$) are plotted as a function of the Raman shift. These spectra are convoluted with a Lorentzian function of with 0.5 eV. In (a), the ground state with S_z=0 is used as the initial state of the RXES, while the lowest-energy state with S_z=1 is used in (b). In (c), the S_z=0 ground state is used, but the 3d orbits with $3z^2 - r^2$, xy, yz or zx symmetry are removed from the basic wavefunctions.

The structures which are indicated as "d^8", "ZRS", and "dd" are understood as follows: The RXES process shown in Fig. 3 (a) is schematically shown in Fig. 2. Suppose that a 1s core electron with up spin is excited by absorbing an incident X-ray, as illustrated in Fig. 2. The 1s core hole thus created may be filled with a $2p_x$, $2p_y$ or $2p_z$ electron. If the $2p_x$ hole created in the final state is extended onto the left-hand-side plaquette, we detect the elastic scattering or the $x^2 - y^2 \rightarrow 3z^3 - r^2$ orbital excitation which contributes to the "dd" structure. If the $2p_x$ hole created in the final state is extended onto the right-hand-side plaquette, we detect the "ZRS" excitation ($|d^{10}; d^9\underline{L}\rangle$) or the "$d^8$" state ($|d^{10}; d^8\rangle$). Obviously, the ZRS can be detected only in the final state of I_{xx}, as can be seen in Fig. 2.

The structure assignments given above can be easily confirmed

by calculating the RXES assuming the $S_z = 1$ initial state, which are shown in Fig. 3 (b). Since $S_z = 1$, the ZRS cannot be realized. Accordingly, the ZRS structure is missing in I_{xx}. In order to clarify the role of the orbital excitations, in Fig. 3 (c), we show the RXES calculated by removing the 3*d* orbits with $3z^2 - r^2$, *xy*, *yz* and *zx* symmetry. In this case, the *dd* excitation does not occur. Indeed, the "*dd*" structure is missing in Fig. 3 (c).

4. Concluding remarks

The present study shows that the O 1*s* RXES directly reflects the Cu 3*d* states, where the many-body effect caused by the inter-plaquette charge-transfer is important. In the case of the corner-sharing system under consideration, the polarization-dependent XAS is site-selective. Moreover, the many-body states reached through the subsequent emission process is quite symmetry-sensitive. Thus we can get the symmetry-decomposed information from the polarization-dependent RXES. Obviously, the symmetry-sensitivity and the site-sensitivity depend on the crystal structure. Although in the present study the RXES is calculated only for the two-plaquette cluster which simulates the quasi-one-dimensional system, a similar polarization-sensitive RXES can be expected for the layered corner-sharing cuprate systems. The polarization dependence of the RXES in the edge-sharing systems differs somewhat from the present corner-sharing systems (Okada and Kotani, 2000).

Finally, we consider that the temperature dependence of the RXES is quite important. At room temperature, it seems that the RXES is a linear combination of Figs. 3 (a) and (b). With decreasing the temperature, the statistical weight of $S_z = 0$ will increase. In other words, the ZRS peak becomes intense with increasing antiferromagnetic correlation between the neighboring Cu sites. Therefore the experimental observation of the temperature-dependent RXES is interesting and highly desired.

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