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Zhang-Rice singlet-state formation by oxygen 1*s* resonant x-ray emission in edge-sharing copper-oxide systems

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Resonant behavior of O 1*s* x-ray emission spectrum (XES) in Cu-based oxides, such as $CuGeO_3$ and Li_2CuO_2, is investigated through the model calculations using an edge-sharing Cu_2O_6 cluster. It is shown that the inelastic peaks that originate from the Cu *d-d* excitations and the Zhang-Rice singlet excitation can be observed on resonance, which indicates the importance of the many-body effects in discussing the O 1*s* resonant XES. It is shown that the Zhang-Rice singlet state can be excited in the O 1*s* XES final state when the Cu spins configuration around the irradiated O site is antiferromagnetic. Therefore the experiment at low temperatures is highly desired.

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I. INTRODUCTION

Resonant x-ray emission spectroscopy (RXES) is one of the powerful tools that give site-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.[1,2] Moreover, very recently, Duda *et al.* have shown that the O 1*s* RXES could provide us with information on the Cu 3*d* states, such as the *dd* excitations and Zhang-Rice singlet (ZRS) formation.[3,4] In other words, the O 1*s* RXES can be a tool to investigate the many-body states in cuprate systems. It is to be noted that the ZRS has not so far been confirmed in the valence-band photoemission spectrum (VB-PES).[5,6] The purpose of the present paper is therefore to analyze the O 1*s* RXES theoretically, paying particular attention to how the ZRS be detected in the O 1*s* RXES.

As is well known, the ZRS state is a coupled state of an O 2*p* hole and a Cu 3*d* one on a CuO_4 plaquette. How easily the ZRS state can move from a plaquette to the neighboring ones depends on the Cu-O-Cu bond angle, in other words, whether the plaquettes are connected with each other, sharing their edges or corners. As is well known, the mobility of the ZRS state between the plaquettes in edge-sharing $CuGeO_3$ and Li_2CuO_2 is quite low, since the Cu-O-Cu angle is far from 180°. As a result, the optical conductivity at the low-energy edge of the interband transition is quite low.[7] In the case of O 1*s* RXES, however, as shown below, the Cu 3*d* hole on a plaquette can be easily transferred to the neighboring plaquettes via O 1*s* core state, where it is essential that the core-hole has *s* symmetry. This point is quite important in the present edge-sharing system. The corresponding inelastic scattering (IS) process is illustrated in Fig. 1. We can expect that the ZRS excitation be detected as an IS peak with an appreciable intensity. In other words, the many-body effect is important in understanding the O 1*s* RXES.

II. THEORETICAL RESULTS

In order to simulate the one-dimensional (1D) CuO_2 chain structure in the edge-sharing Cu-O network systems such $CuGeO_3$ and Li_2CuO_2, we use an edge-sharing two-plaquette cluster model, $(Cu_2O_6)^{8-}$, shown in Fig. 2, the Hamiltonian of which is a so-called multi-band Hubbard model.[8] The present $(Cu_2O_6)^{8-}$ 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. In the ground state, the average 3*d* hole number is 0.71 per site and its character is almost $3d_{xy}$. The average hole number at the irradiated O site is 0.07. Extending the convention used in the single-site model analysis,[9] the ground state is mainly $|d^9;d^9\rangle$ electron configuration.

However, as is well known, the antiferromagnetic coupling between the neighboring Cu spins is quite weak, compared with that in the corner-sharing quasi-1D systems, such as Sr_2CuO_3. Therefore the initial state of the RXES at room temperatures must have a considerable amount of the statistical weight of the excited states with $S_z=1$. In the following, we show that the spin state of the initial state is quite important in discussing the many-body effects on the O 1*s* RXES.

First of all, let us see the O 1*s* XAS shown in Fig. 2. It consists of an intense main peak and a very weak satellite. A valence hole existing in the XAS final states occupies one of the O 2*p* and Cu 3*d* orbits. 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 2*p*) hole.

The relevant part of the RXES spectral function is given by the following expression:[10]

$$I_{\mu\nu}(\omega_{in},\omega_{out})=\sum_f\left|\sum_{m,\sigma}\frac{\langle f|s_\sigma^\dagger p_{\nu\sigma}|m\rangle\langle m|p_{\mu\sigma}^\dagger s_\sigma|g\rangle}{E_g+\omega_{in}-E_m-i\Gamma_m}\right|^2 \times\delta(E_g+\omega_{in}-E_f-\omega_{out}), \quad (2.1)$$

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), inter-

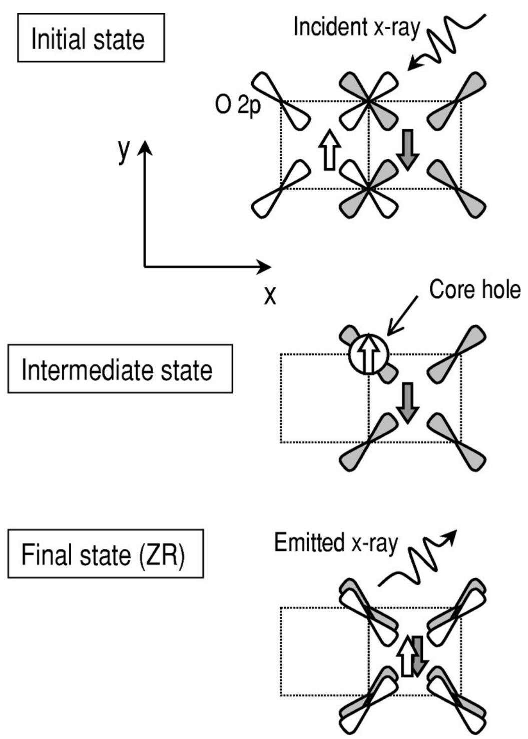

FIG. 1. The IS process, which leaves a ZRS state in the final state, is shown schematically by using a two-plaquette $(Cu_2O_6)^{8-}$ cluster model. Two squares (dotted lines) represent CuO_4 plaquettes. The O $2p$ component of the valence holes and the O $1s$ core hole are shown on the corners of the plaquettes. In the ground state, the valence holes occupy the coupled states of the Cu $3d_{xy}$ orbit and the O $2p$ ones shown in this figure, where the x axis is along the CuO_2 chain structure. It is assumed that, in the initial state, the left (right) plaquette has an up- (a down-) spin valence hole and that the up-spin valence hole is converted to the O $1s$ core hole in the intermediate state. By emitting an x ray, the O $1s$ core hole makes transition to the valence state on the right plaquette.

mediate, 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).

It is to be noted in Eq. (2.1) that all the O $2p$ electrons have the same transition matrix element to the O $1s$ hole state existing in the intermediate state, since the O $1s$ wave function is isotropic. In other words, the symmetry of the O $2p$ hole state may differ between the initial and final states of the RXES process, which can be an origin of the IS.

The RXES shown in Fig. 3 is $I_{xx}+I_{xy}+I_{xz}$ for the ground state with $S_z=0$, where only the IS peaks are plotted and the position of the elastic peak is traced by a straight line. The RXES is enhanced at the narrow ω_{in} range where the XAS intensity is high. In this energy range, the position of each IS peak shifts with increasing ω_{in}, which means that all IS peaks behave Raman-scattering-like. This point is important in comparing the calculated results with the experiment. If there is an extra continuum in the XAS as shown by the broken line in Fig. 2, the corresponding XES behaves normal-XES-like as a function of ω_{in}. Therefore, when the normal-XES contirbution is large, it is difficult to separate the true RXES component even in the resonance condition. In this sense, the on-resonance spectra of the main O $2p$ band in Duda *et al.*'s data[3,4] appears to be appreciably contaminated with such normal-XES contributions, as mentioned later.

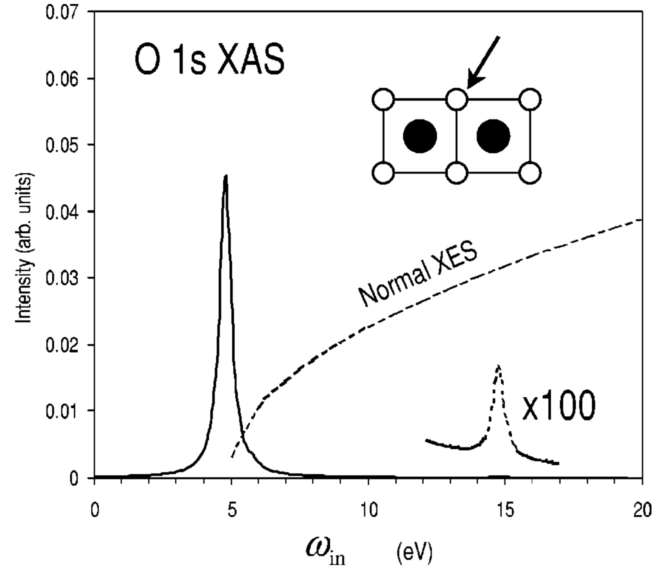

FIG. 2. The O $1s$ XAS in $(Cu_2O_6)^{8-}$ is shown by the solid curve as a function of incident photon energy ω_{in}. Note that the origin of ω_{in} is arbitrary, since the one-body energy of the core hole is not included explicitly in our numerical calculations. A weak correlation satellite seen at $\omega_{in}=15$ eV is enlarged 100 times. The broken line represents the continuum state often seen in the experimental O $1s$ XAS. The excitation of the $1s$ core electron to this continuum gives the fluorescence-like (normal-XES-like) contribution to the XES, though not included in the present calculation. The inset shows the cluster schematically, where the open and closed circles represent the O and Cu ions, respectively, and the irradiated O site is indicated by an arrow.

The XES on resonance is also shown by the solid curve in Fig. 4(a), where the abscissa is the Raman shift, $\Delta\omega=\omega_{out}-\omega_{in}$. The spectral structures can be classified into four components: The first one $|d^{10};d^9\underline{L}\rangle$ is the main structure centered at $\Delta\omega=-5$eV, which reflects the density of states of

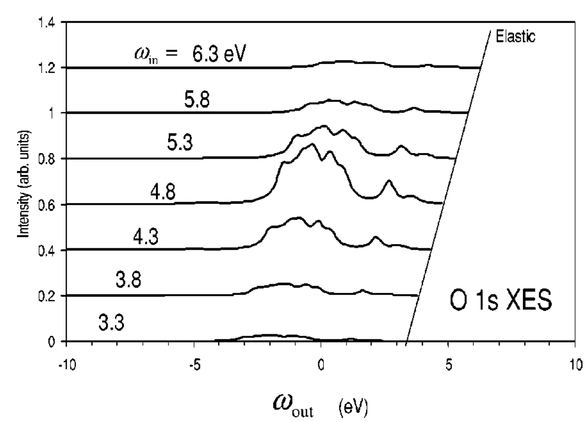

FIG. 3. The O $1s$ RXES in $(Cu_2O_6)^{8-}$ is shown as a function of ω_{out} for various ω_{in}.

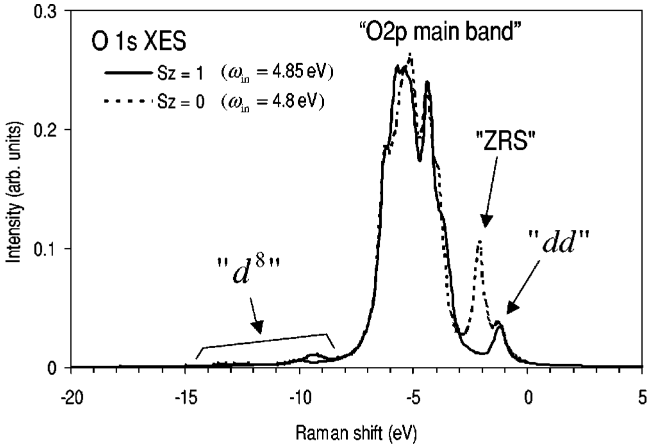

FIG. 4. The on-resonance O 1s XES in $(Cu_2O_6)^{8-}$ is calculated for $S_z=0$ ($\omega_{in}=4.8$ eV) and $S_z=1$ ($\omega_{in}=4.85$ eV) as a function of the Raman shift ($\Delta\omega$).

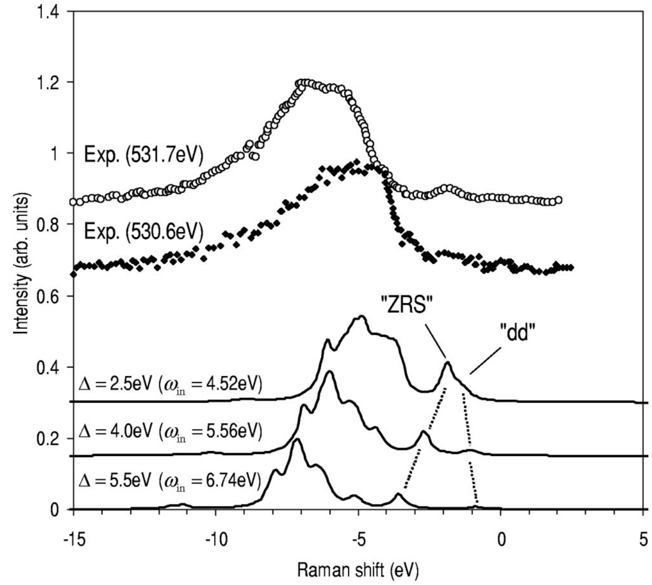

FIG. 5. The on-resonance O 1s XES ($I_{yx}+I_{yy}+I_{yz}$) in $(Cu_2O_6)^{8-}$ with $S_z=0$ is calculated for Δ=2.5, 4.0, and 5.5 eV. The incident photon energies for the experiment (Ref. 4) shown here are 530.6 eV and 531.7 eV. The latter corresponds to the on-resonance condition. The XES intensity in the experiment is normalized, while that in the theory is not.

the unhybridized O 2p bands. (Hereafter, this structure is called the ''O 2p main band.'') The second one $|d^9;d^9\rangle$ is a weak shoulder structure at $\Delta\omega=-1.2$ eV, which is due to the excitation from Cu 3d_{xy} to 3$d_{3z^2-r^2}$. The third one $|d^{10};d^9\underline{L}\rangle$ is a weak peak at $\Delta\omega=-2.4$ eV, which is due to the ZRS excitation. (Hereafter, this peak is called the ''ZRS'' peak.) The IS process that leads to the ZRS peak is shown schematically in Fig. 1. The last one $|d^{10};d^8\rangle$ is a weak and broad structure ranging from $\Delta\omega=-9$ to -14 eV. Its origin is found to be the Cu 3d^8 electron configuration, since the position of this structure is sensitive to the Cu 3d-3d Coulomb interaction strength (U_{dd}).

For comparison, the XES for the $S_z=1$ initial state is shown by the solid line in Fig. 4, where the ZRS peak is suppressed, as we expect. In other words, the Cu spin configuration strongly affects the line shape of the O 1s RXES. It is to be noted here that the difference in the integrated intensity of the IS structures is not so large for $S_z=0$ and $S_z=1$. In the present O 1s RXES, the integrated intensity strongly depends on the absorption intensity from the initial to intermediate states and it is determined by the O 2p hole number (n_{2p}) at the irradiated O site in the initial state. Our result that the difference in the integrated intensity is small for $S_z=0$ and $S_z=1$ indicates that the valence hole distribution in the cluster does not depend on the Cu spin configuration remarkably. Instead, the difference in the RXES line shape is due to the final state effects.

In the case with S_z=0 shown in Fig. 4, the relative intensity of the ZRS peak is about 10% of the total IS intensity. It is to be mentioned that the intensity of this kind of many-body peaks is much weaker in the VB-PES.[11] This difference is due to the selection rule for the transition processes. The total spin of the material system is conserved during the O 1s RXES process. Accordingly, if the initial state is spin singlet, the final states must be spin singlet and the triplet final states are forbidden. On the other hand, in the case of VB-PES for $(CuO_4)^{6-}$ cluster for instance, the spin-triplet final states are three times stronger than the spin-singlet ones according to their statistical weights. In this sense, the O 1s RXES can be a novel tool to detect the ZRS excitation in the edge-sharing Cu-O chain systems.

In order to compare the experiment with our results quantitatively, our parameter values used in the calculation may need readjusting. In particular, the CT energy between the Cu 3d and O 2p states (Δ) is a key parameter that determines the Raman shift of the ZRS peak as well as that of the O 2p main band, as seen in Fig. 5. According to Mizuno *et al.*,[7] Δ in $CuGeO_3$ (=4.9 eV) is fairly larger than that in Li_2CuO_2 (=3.2 eV). Our Δ used in the present results shown above (=3.0 eV) is close to the latter. The Δ dependence of the O 1s RXES on resonance is shown in Fig. 5. It is found that, with increasing Δ, the ZRS peak together with the O 2p main band shifts to the lower energy side.

In Fig. 5, we have shown two experimental results taken at different ω_{in}.[4] The on-resonance condition corresponds to 531.7 eV. It is obvious that the O 2p main band shifts with increasing ω_{in}, which indicates that the normal XES component dominates the spectrum at 531.7 eV. Therefore we cannot directly compare our theoretical result with the experiment at 531.7 eV. Instead, we can use the spectrum at 530.6 eV in order to discuss the position of the O 2p main band [note that the position of the O 2p main band is almost independent of ω_{in} in our calculation (see Fig. 3)]. Compared with the theoretical results, the main structure in the experiment is highly asymmetric. The intensity at the lower-energy side of the main structure is too large to be ascribed to the 3d^8 final states. According to the energy-band calculation,[12] it is caused by the hybridization between Ge 4sp and O 2p bands. Therefore it impossible to reproduce the whole line shape by means of the present cluster model, since the Ge 4sp bands are not taken into account in the present calculations. However, by estimating the center of gravity of the main structure, we can discuss the numerical value of Δ and we conclude that Δ in $CuGeO_3$ be less than 4 eV.

It is to be noted in Fig. 5 that the ZRS is always split off from the O $2p$ main band irrespective of Δ. This is in contrast to the interpretation of Duda *et al.* that the ZRS is not split off. As seen in Fig. 5, we expect that the ZRS be detected at the Raman shift of $\Delta\omega \sim -2$ eV for $\Delta \sim 2.5$ eV. In the experiment at 531.7 eV, a clear peak is confirmed at $\Delta\omega \sim -2$ eV. It is to be stressed that this peak is not affected by the normal XES, because its energy is higher than the normal XES by about 3 eV. Even in the experiment at 530.6 eV, we find a considerable amount of intensity at this peak energy. Although Duda *et al.* ascirbed this peak to the dd excitation, our interpretation is that this peak is mainly caused by the ZRS, although the dd excitation may also contribute to some extent to this peak as in the calculated result for $\Delta = 2.5$ eV. We hope more detailed experiments in this energy region in order to separate the ZRS and the dd excitations. We propose the measurements of the temperature dependence for this inelastic peak. To identify the ZRS is important also in determining the optical gap, since the position of the ZRS corresponds to the optical gap. It will resolve the controversy on the optical gap[13,14] and will give important information in discussing why the ZRS has not so far been confirmed in the VB-PES.[5,6]

In summary, the present study shows that the O $1s$ RXES directly reflects the Cu $3d$ states, where the many-body effect caused by the inter-plaquette CT is important. In the case of the edge-sharing system, the CT path via the core hole state is essential. To examine our results experimentally, the detailed observation is desired, varying ω_{in} around the XAS peak. The temperature dependence is quite important. Such experiments will open new aspects of the O $1s$ RXES.

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