Unique identification of Zhang-Rice singlet excitation in $Sr_2CuO_2Cl_2$ mediated by the O 1*s* core hole: Symmetry-selective resonant soft x-ray Raman scattering study

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Zhang-Rice singlet excitation around 2 eV is observed, distinguished from Cu *dd* excitations, by a symmetry selective resonant soft x-ray Raman scattering (RSXRS) experiments at the O 1*s* edge excitation of $Sr_2CuO_2Cl_2$. Well below Néel temperature the initial state of $Sr_2CuO_2Cl_2$ is antiferromagnetic, and then the final state with the Zhang-Rice singlet is excited selectively when the photon polarization is conserved in the RSXRS process. We also observe a weak RSXRS structures around 0.5 eV in the controversial midinfrared region, taking advantage of extremely weak elastic scattering intensity in the O 1*s* edge. From its polarization dependence, it is interpreted to originate mainly from the two-spin-flip excitations.

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I. INTRODUCTION

Since the discovery of high-T_c superconductors (HTSC), the electronic properties of the cuprate family of compounds have been extensively studied with many experimental and theoretical techniques, yielding new concepts in solid-state physics. Characteristics of HTSC are often described by the *t-J* model,[1] where charge carriers are the so-called Zhang-Rice singlet (ZRS) states.[2] It is well accepted that the ZRS is a coupled state of a Cu 3*d* hole and an O 2*p* state on a CuO_4 plaquette and moves around on the Cu-O network, breaking the antiferromagnetic order of Cu 3*d* localized spins. Hence, it is quite important to investigate the characteristics of the ZRS.

Valence-band photoemission spectroscopy (PES) of undoped lamellar copper oxides such as La_2CuO_4 or $Sr_2CuO_2Cl_2$ gives indirect but essential information about the origin of HTSC because the final state of PES includes an additional hole in valence states, which can form the ZRS. Angle-resolved PES (ARPES) or electron-energy-loss spectroscopy (EELS) are also important tools to map the ZRS band dispersion using momentum conservation rule. Tjeng *et al.* performed a direct observation of the ZRS state in CuO by spin-resolved PES.[3] They have used a combination of circularly polarized light and electron-spin detection to unravel the local spin states. As far as we know, it was the first experiment to distinguish the ZRS state by its spin-singlet character. Another work to be noted was done by Duda *et al.*[4] They have reported the observation of the ZRS in the normal soft x-ray emission spectroscopy (NSXES) of $CuGeO_3$ excited above O 1*s* threshold. They have shown that for increasing excitation energies, the valence shoulder increases above the O 1*s* absorption threshold, and suggested that it was an evidence for the ZRS state formation.

We report an experimental method for the direct observation of the ZRS state in $Sr_2CuO_2Cl_2$ using symmetry-selective resonant x-ray Raman scattering (RSXRS) at the O 1*s* edge excitation. $Sr_2CuO_2Cl_2$ is suitable for exploring oxygen states only in the Cu-O plane due to the absence of apical oxygen atoms. It is highly stoichiometric and cannot be readily doped, which ensures that we are measuring a pure $Sr_2CuO_2Cl_2$ insulator. Wells *et al.* did a pioneering work of ARPES on $Sr_2CuO_2Cl_2$.[5] They reported the band structure with dispersions around 1 eV below the Fermi level and discussed the validity of the *t-J* model. Kim *et al.* suggest that an extended *t-J* model (t-t'-t''-J model) calculation including long range hopping interactions explains the full dispersion and the spectral intensity of the ''1 eV peak.''[6] Pothuizen *et al.* showed that the ''1 eV peaks'' in ARPES are the quasiparticles derived from the same O 2*p* states as ZRS.[7] The idea was also supported by Bala *et al.* using spin-fermion multiband models.[8]

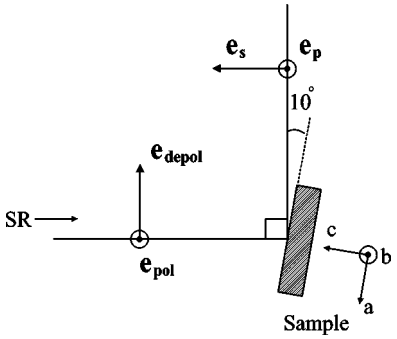

FIG. 1. Experimental geometry of the symmetry selective RSXRS. Incoming soft x ray is indicated as SR. A circle with dot represents a vector normal to the drawing. Arrows e_{pol} and e_{depol} show the polarization vector for the polarized and depolarized configurations, respectively. Crystallographic axes are also shown for the sample.

Very recently, Okada and Kotani have predicted the possibility of symmetry-selective RSXRS across the O 1*s* excitation of undoped antiferromagnetic cuprates to distinguish the ZRS excitation from *dd* excitations.[9,10] In this process a Cu 3*d* hole is transferred to the neighboring Cu site mediated by an O 1*s* core hole in the intermediate state, to leave the ZRS in the final state. So the ZRS formation in RSXRS accompanies an extra electron mainly in the Cu 3*d* states, in contrast to the ZRS formation in PES. Their theory shows that the anisotropy at the O site is quite large in the low-dimensional cuprates such as $Sr_2CuO_2Cl_2$ and $CuGeO_3$, and which is the main reason for the remarkable polarization dependence of RSXRS. For this reason, the ZRS cannot be excited in a specific polarization geometry called the ''depolarized configuration,'' while it is excited in the ''polarized configuration.''

II. EXPERIMENT

The $Sr_2CuO_2Cl_2$ single crystals were grown from the melt, with typical dimensions around $4\times4\times0.5$ mm. Symmetry-selective RSXRS measurements on $Sr_2CuO_2Cl_2$ across the O 1*s* edge excitation were performed using a soft x-ray emission spectrometer[11] installed at the undulator beamline BL-2C at Photon Factory, KEK.[12] Synchrotron radiation is monochromatized using a varied-line spacing plane grating whose average groove density is 1000 lines/mm. The excitation energy accuracy is within 0.1 eV around the O 1*s* edge; the energy resolution is about 0.5 eV at 530 eV for the RSXRS and about 0.2 eV for the absorption spectra. The emission spectrometer is of the Rowland mount type with a laminar grating whose radius and groove density are 5 m and 1200 lines/mm, respectively. The total energy resolution of the system is 0.65 eV at 530 eV with a 20 μm incident slit width of the emission spectrometer. The experimental geometry is shown in Fig. 1.

The wave vectors of the incident and the emitted photons are in the plane normal to the sample surface, and the scattering angle is fixed to 90° When the polarization vector of the incident photon is parallel to the scattering plane, it is called the ''depolarized configuration,'' while when the polarization vector of the incident photon is perpendicular to the scattering plane, it is called the ''polarized configuration.'' It is noted that both the polarization-contained and the polarization-rotated components equally contribute to emission spectra in the polarized configuration, while only the polarization-rotated one is included in the depolarized configuration. The incidence angle of the soft x ray to the sample normal is about 10° in order to excite electrons in the Cu-O plane both in the polarized and depolarized configurations, and the incident polarization direction projected on the Cu-O plane is parallel to the Cu-O axis. Crystallographic axis orientation in the Cu-O plane was checked by Laue method using lattice parameters in the literature.[13] The sample was cleaved in N_2 gas flow just before introducing into vacuum chamber. The experiments were carried out at 40 K, well below the Néel temperature ($T_N=256$ K).[5] All the emission spectra reported here were collected within two hours of cleaving with the base pressure better than 7×10^{-10} Torr.

It is very important to calibrate emission energies precisely because we are to discuss small structures with low energy loss compared to the excitation energy. In this experiment, the absolute incident and emitted photon energies of each spectrum are carefully calibrated to within ±0.1 eV.

III. RESULTS AND DISCUSSION

Resonant emission spectra excited across the O 1*s* edge are displayed in Fig. 2. They are plotted as a function of the emission energy. The open circles and solid lines are the results for the polarized and depolarized configurations, respectively. The intensity of the spectra for both configurations is normalized by the O 1*s* NSXES. The spectrum labeled O 1*s* SXAS shows the soft x-ray absorption spectrum across the O 1*s* edge. The vertical bars on O 1*s* SXAS and on O 1*s* RSXRS show the position of the incident photon energy. The main broad structure around 524 eV (denoted by main band) is the contribution from the O 2*p* valence band. The main band is a superposition of the Raman component following the excitation energy (mainly below the absorption edge) and a fluorescencelike component (mainly above the absorption edge) smoothly connecting to the NSXES. At the high-energy side of the main band small structures exist that follow the excitation energy. These weak RSXRS spectra are the main interest of the present paper.

Figure 3 shows the same spectra plotted as a function of the Raman shift, the energy loss from the incident photon energies, so as to distinguish the Raman component. It is remarkable that clear polarization dependence is found both in the elastic scattering and the energy-loss structure around 2 eV, as well as the O 2*p* main band. First we discuss the structure around 2 eV. It is clearly seen that the intensity of the 2 eV structure is stronger in the polarized configuration than in the depolarized configuration. Kuiper *et al.* determined the absolute Cu *dd* excitation energies of $Sr_2CuO_2Cl_2$ by RSXRS spectra across the Cu 3*p* edge.[14] The single hole at copper site in the ground state is ascribed to $d(x^2-y^2)$ and from their analysis, $d(3z^2-r^2)$, $d(xy)$, and $d(xz)$ $[d(yz)]$ states are positioned at 1.5 eV, 1.35 eV and 1.7 eV above the ground state, respectively.

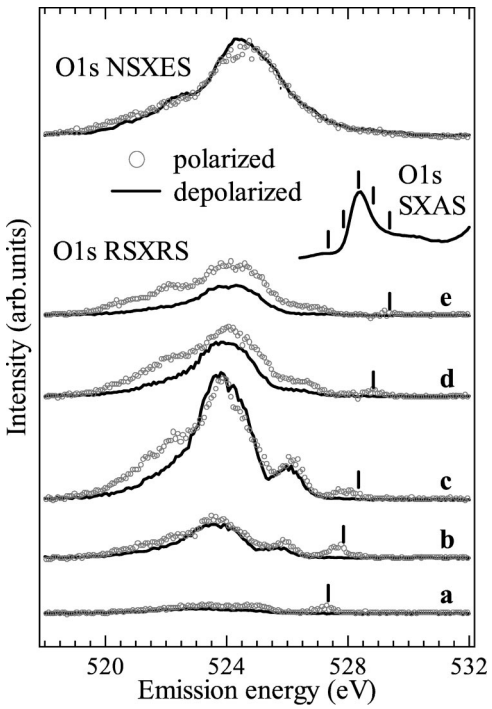

FIG. 2. Soft x-ray emission spectra of $Sr_2CuO_2Cl_2$ across the O 1*s* excitation. The open circles and the solid lines are the results for the polarized and depolarized configuration, respectively. O 1*s* NSXES shows the emission spectrum excited at 600 eV. O 1*s* RSXRS shows a series of the emission spectra across the O 1*s* resonant excitation. O 1*s* soft x-ray absorption spectroscopy (SXAS) shows a soft x-ray absorption spectrum across the O 1*s* edge. Vertical bars on O 1*s* SXAS and O 1*s* RSXRS show the position of the incident photon energy.

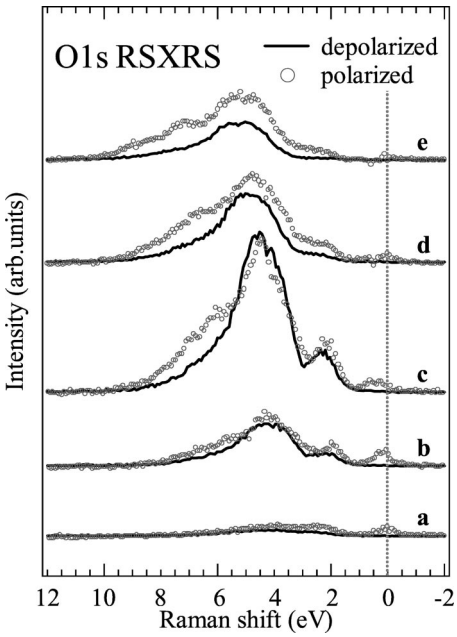

FIG. 3. Soft x-ray emission spectra in the Raman shift representation. The excitation energies are indicated by alphabets following Fig. 2.

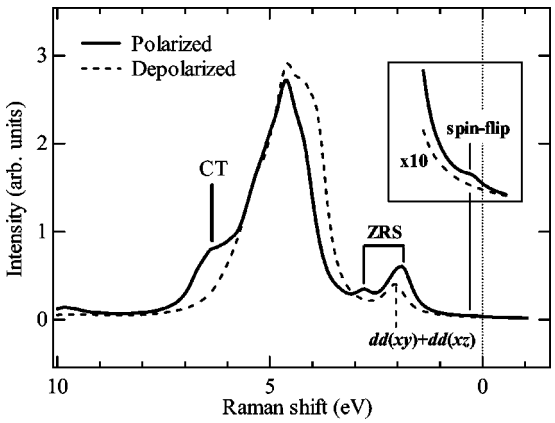

FIG. 4. Theoretical O 1*s* RSXRS obtained by a one-dimensional Cu_4O_{13} cluster model. In the polarized spectrum, the elastic component is removed. Each spectrum is convoluted with a Lorentz function of width 0.5 eV and normalized by the integrated intensity. In the inset, each spectrum is enlarged ten times.

According to Abbamonte *et al.*,[15] resonant x-ray Raman scattering spectra across the Cu 1*s* edge of $Sr_2CuO_2Cl_2$ exhibits a small and broad peak around 2 eV. Hill *et al.*[16] and Idé and Kotani[17] showed that the lowest energy inelastic peak of resonant x-ray Raman scattering across the Cu 1*s* edge of Nd_2CuO_4 corresponds to the ZRS excitation. Therefore, the possible origin of the 2 eV structure in Fig. 3 might be the ZRS excitation or the *dd* excitation (or the two excitations overlap each other). Okada and Kotani predicted that the ZRS and the *dd* excitations have a comparable intensity in RSXRS at the O 1*s* edge, whereas the former is dominant at the Cu 3*p* edge and the latter is dominant at the Cu 1*s* edge. An important point that Okada and Kotani predicted is that the ZRS and the *dd* excitations in RSXRS at O 1*s* edge can be discriminated by selection rules of the polarization dependence.

As Okada and Kotani showed, the ZRS excitation in the O 1*s* RSXRS is allowed only for the polarized configuration. Also, from a simple consideration of symmetry, the *dd* excitation of the $d(xy)$ state, which we call as $dd(xy)$ excitation hereafter, is allowed for the depolarized configuration, while the $dd(3z^2-r^2)$ excitation is allowed for the polarized one. The $dd(xz)$ excitation is allowed for both configurations. According to a recent cluster-model calculation,[18] the intensity of the $dd(3z^2-r^2)$ and $dd(xy)$ excitation is nearly the same. In other words, without ZRS contribution, the intensity of the 2 eV structure does not depend on the experimental geometry. Therefore we conclude that the enhanced 2 eV structure in the polarized configuration is caused by the ZRS contribution.

For comparison, we show a theoretical O 1*s* RSXRS in Fig. 4, which is obtained by applying a numerically exact diagonalization technique to a one-dimensional Cu_4O_{13} cluster model.[19] It is evident that the intensity of the 2 eV structure in the polarized spectrum is larger than that in the depolarized spectrum. In the 2 eV structure region of the polarized spectrum, there are two peaks at 1.8 eV and 2.7 eV, which are mainly due to the ZRS excitation. The splitting of

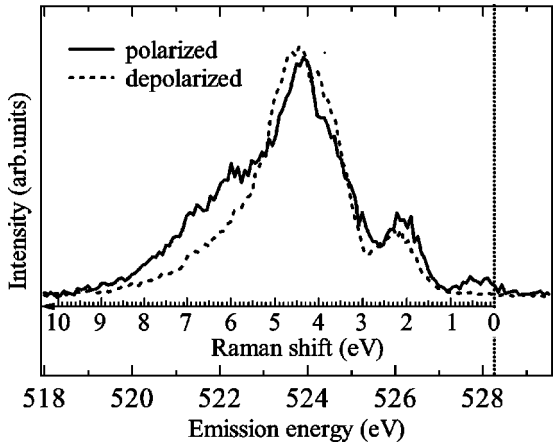

FIG. 5. Expanded scale of spectrum (c) in Fig. 3.

the ZRS excitation represents the ZRS bandwidth along the one-dimensional chain direction. The $dd(3z^2-r^2)$ excitation is hidden in between the two ZRS peaks in the present result, though it is coupled with the ZRS excitation to some extent due to the same symmetry in the Cu_4O_{13} cluster. However, the 2 eV peak in the depolarized spectrum originates from the $dd(xy)$ and $dd(xz)$ excitations with nearly the same intensity.

The other feature to be noted in Fig. 4 is a 6 eV shoulder in the polarized spectrum. It is caused by Cu $3d(x^2-y^2)$–O $2p$ charge transfer. This excitation is the same as that observed in the Cu $1s$ resonant x-ray Raman scattering study.[15]

Figure 5 shows an expanded scale of the emission spectra at the lower Raman shift region. In the spectra excited 1 eV below the absorption peak [spectrum (a) in Figs. 2 and 3], the elastic peak with very weak shoulders exhibits polarization dependence. At peak excitation [Fig. 5 and spectrum (c) in Fig. 3], however, the elastic peak vanishes and only the energy-loss structures around 0.5 eV grow up to show clear polarization dependence. These structures have been confirmed not to originate from an elastic component due to a wrong energy calibration. It is found from Fig. 5 that the 0.5 eV peak is allowed only for the polarized configuration. We note that this polarization dependence is confirmed in the theoretical result shown in Fig. 4. We interpret it as the two-magnon excitation.[20] However, the present calculation does not reproduce the intensity successfully, probably due to the finite-size-cluster effect. It is to be emphasized that the observation of the 0.5 eV peak is impossible in the Cu $3p$ RSXRS because of the existence of the strong elastic peak, but it becomes possible in the present study by taking advantage of extremely weak elastic scattering intensity in the O $1s$ edge.

We give some remarks on the main band contribution. The O $2p$ main band in the O $1s$ excitation has so far been studied by NSXES, but Okada and Kotani proposed to study its Raman component in order to get more information on the O $2p$ band. They predicted that the Raman component of the main band should have characteristic polarization dependence. In the present measurements, clear polarization dependence around 6 eV is observed. We believe this polarization dependence to originate from the symmetry selection rule of RSXRS for the final states with Cu $3d(x^2-y^2)$–O $2p$ charge transfer, similar to the symmetry selection rule for the final states with the ZRS and the dd excitations. We note that Okada and Kotani also predicted temperature dependence of ZRS excitation as well as the Raman component of the main band, the latter especially for the corner-sharing cuprates such as $Sr_2CuO_2Cl_2$. Measurements for temperature dependence of the O $1s$ RSXRS on $Sr_2CuO_2Cl_2$ are now in progress, which will be reported in the near future.

IV. CONCLUSIONS

In summary, we have applied symmetry-selective soft x-ray Raman scattering to the study of electronic structures near the Fermi edge in an undoped antiferromagnetic insulator belonging to the cuprate family. The following two points are unraveled by the polarization dependence, which may be related to the electronic conduction in antiferromagnetic background.

(a) The enhancement of the 2 eV structure in the polarized configuration is caused by the ZRS excitation. This result is consistent with that of the optical absorption and EELS. However, the crystal-field splittings for $d(3z^2-r^2)$, $d(xy)$, $d(yz)$, and $d(zx)$ may be somewhat larger than those estimated by Kuiper *et al.*

(b) The 0.5 eV structure exhibits clear polarization dependence, and is interpreted to be due to the two-magnon excitation.

Our results open a new possibility of symmetry-selective RSXRS to provide a full set of important microscopic parameters for strongly correlated systems, namely, charge-transfer energy Δ, Coulomb interaction U, hopping energy t, and spin-exchange interaction J.

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[19] The Cu_4O_{13} cluster in the present study is described by O $1s$, O $2p$, and Cu $3d$ orbitals. The relevant parameters that characterize the Hamiltonian are as follows. The charge-transfer energy Δ is 3 eV for Cu $3d(x^2-y^2)$ and 2.5 eV for the other Cu $3d$ orbitals. The hopping strength between Cu $3d$ and O $2p$ is 1.3 eV for x^2-y^2, 0.45 eV for $3z^2-r^2$, and 0.42 eV for xy, yz, and zx. The on-site dd Coulomb interaction U is taken at 8 eV.

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