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Bandlike and excitonic states of oxygen in $CuGeO_3$: Observation using polarized resonant soft-x-ray emission spectroscopy

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Polarized resonant x-ray fluorescence spectroscopy at O 1s resonances was used to study $CuGeO_3$. Two distinct spectral contributions are identified, i.e., an intense ''main band'' of soft-x-ray fluorescence, reflecting primarily bandlike O 2p states, and resonant inelastic x-ray scattering (RIXS) characterized by spectral features that disperse linearly with excitation energy and resonate at the O 1s pre-edge peak. RIXS reflects excitoniclike (''optical'') final states and has previously only been observed for metal-ion core edges. Moreover, analysis of the excitation energy and polarization dependence of the main band allows the identification of features deriving from the site-specific partial density of states as well as strong evidence for the observation of a two-hole state (Zhang-Rice singlet).

The electronic structure of cuprates is determined by the interplay of the narrow Cu 3d band localized on the Cu sites and the predominantly itinerant O 2p band. The bonding of the Cu-O octahedra themselves and their coupling (e.g., edge- or vertex-sharing plates or chains) are keys to the type of macroscopic low-temperature behavior of these compounds, be it superconductivity or, as in the case of $CuGeO_3$, a spin-Peierls state ($T_{SP}=14$ K). Although the past decade has seen a vast amount of literature dedicated to the understanding of high-T_c superconductivity, the underlying mechanism is still not fully understood. Spin-Peierls states are unusual for inorganic materials and it is interesting to note that the one-dimensional edge-sharing CuO_4 chains of $CuGeO_3$ are coupled along its crystallographic c axis, in contrast to high-T_c cuprates that have vertex-sharing chains. Therefore it is important to gain detailed experimental knowledge of the electronic structure and in particular of the valence band of these Cu-O units.

$CuGeO_3$ is an orthorhombic antiferromagnetic insulator at room temperature with the lattice parameters $a=4.81$ Å, $b=8.47$ Å, and $c=2.94$ Å. Early band structure calculations[1,2] predicted a metallic ground state, whereas more sophisticated techniques[3,4] yielded gap values comparable to the value found in optical absorption (3.7 eV). Although the O 2p electrons are much less correlated than the Cu 3d electrons, the theoretical partial density of states (PDOS) appears to depend strongly on the calculational methods used. The O 2p electrons are expected to have both itinerant character forming a wide valence band but also some localized character due to bonding to the central Cu atom and thus hybridization with 3d electrons. The aim of this paper is to experimentally examine the different roles played by the oxygen-specific valence band electrons.

A recent valence-band photoemission spectroscopy (VB-PES) study of $CuGeO_3$ (Refs. 5 and 6) revealed rather complex spectra due to overlapping contributions from different sites as well as from both bandlike and localized states. Moreover, the removal of an electron by PES induces a strong perturbation to the system and therefore the nature of localized states cannot be studied close to the ground state. Soft-x-ray fluorescence spectroscopy (SXFS), on the other hand, is a bulk-sensitive core level technique (thus chemically specific) and subject to dipole selection rules. Moreover, SXFS is insensitive to charging effects (which plagues electron spectroscopies of insulators such as $CuGeO_3$) because it does not involve the detection of electrons. The final state of a SXF process consists of a valence electron-hole pair, in which both electron and hole have the same orbital character. Thus the SXF spectrum will only resemble the PDOS of the unperturbed system *if correlation effects such as final-state interactions are negligible* and it will depend little on the excitation energy if the core electron is excited to a delocalized state. However, recent resonant SXF experiments at cuprate *copper core resonances* show that the SXF spectra are dominated by excitonic states that disperse linearly with excitation energy.[7–9] This may be interpreted as resonant inelastic x-ray scattering (RIXS), described by the second-order Kramers-Heisenberg scattering formula,[10] and the observed states are crystal field or *dd* excitations, as well as charge transfer (CT) excitations, involving an O 2*p*-Cu3*d* transition.

In this paper, we report resonant SXF spectroscopy at O 1*s* resonances of $CuGeO_3$ and show that O 1*s* SXF reflects oxygen-specific valence states with both bandlike as well as localized character. The localized states are observed as RIXS features that resonate *only* at the pre-edge peak (associated with the upper Hubbard band) of O 1*s* absorption. By analyzing the excitation-energy and polarization dependence of our O 1*s* SXF spectra we can separate features derived from the symmetry-projected 2*p* DOS at different oxygen sites. Moreover, we argue that the high-energy shoulder of in-plane excited spectra is evidence for the occurrence of a Zhang-Rice singlet,[11] which could not be identified in photoemission spectra of $CuGeO_3$.[5,6]

The experiments were performed at beamline X1B of the National Synchrotron Light Source, Brookhaven National Laboratory. A grazing incidence Rowland mounted spherical grating spectrometer was used to analyze the soft-x-ray fluorescence.[12] We used the first-order diffraction of a grating with 5 m radius and 1200 *l*/mm spacing and set the slit width to 15 μm which gives a resolution of better than 0.6 eV. The energy scale was obtained by recording the spin-orbit split Zn $L_{2,3}$ fluorescence[13] in second order of diffraction from the spectrometer grating. The monochromator energy bandpass was about 0.8 eV so that the combined resolution, relevant for the inelastic scattering, was about 1 eV. High-quality $CuGeO_3$ single crystals, several centimeters long, were grown from the melt by a floating zone technique.[14] Platelike samples were easily cleaved along the *bc* plane just before inserting into the experimental vacuum chamber for x-ray measurements. Typical dimensions were about 1 cm along the *c* axis, 0.5 cm along the *c* axis, and a thickness of 1 mm.

Figure 1(a) shows SXF at two different excitation energies—(*A*) 531.7 eV and (*B*) 533.9 eV—and three different sample geometries. The detection direction of the x-ray fluorescence was always in the $\hat{e}_{inc}$ direction, where $\hat{e}_{inc}$ denotes the polarization vector of the incoming beam. We observe a strong energy and polarization dependence of the main band that we attribute to the existence of inequivalent oxygen sites. The excitation energies were chosen based on O 1*s*-fluorescence-yield spectra [also shown in Fig. 1(a)] recorded with the same grazing incidence angle of the excitation beam as used when recording x-ray fluorescence spectra. Our normal-incidence electron yield O 1*s*-absorption spectra (not shown) match recently published data by others.[15]

Figures 1(b) and 1(c) show details of the spectra excited at 531.7 eV (*A*) on an energy loss scale, for comparison to high-resolution (~0.6 eV) Cu 2*p* RIXS of $CuGeO_3$. Cu 2*p* RIXS shows the elastic peak (0 eV), a *dd* excitation energy loss peak (2.02 eV), and a band of CT excitations (3.5–8 eV).

Figure 2 displays SXF spectra resonantly excited at various energies close to the two first absorption maxima. Note that we plotted the spectra against an energy loss scale so that RIXS features appear at constant loss energies (solid vertical lines) and SXF disperses apparently to larger energy losses (dashed lines) with increasing excitation energy. We associate the peak with the lowest-energy loss (about 1.85 eV) with *dd* excitations, resonating when tuning across the pre-edge peak (531.7 eV). The strong energy-dependent spectral shape of the main band is partly due to weight shifts of SXF from inequivalent sites. However, a shoulder on the low-energy-loss flank develops at higher excitation energies and has no correspondence in the O 2*p* DOS. We interpret this as a signature for a Zhang-Rice singlet which is generally expected in cuprates. Moreover, a shoulder at an energy loss of about 9 eV, tentatively marked with a vertical line at 9.0 eV in Fig. 2, is also registered, probably due to CT excitations as suggested by their observation in Cu 2*p* fluorescence. To summarize our observations, we may say that the energy and polarization dependences of our O 1*s* SXF spectra suggest that we must explain our observations in terms of both (I) bandlike states (main fluorescence band) and (II) localized excitonic states (inelastic scattering).

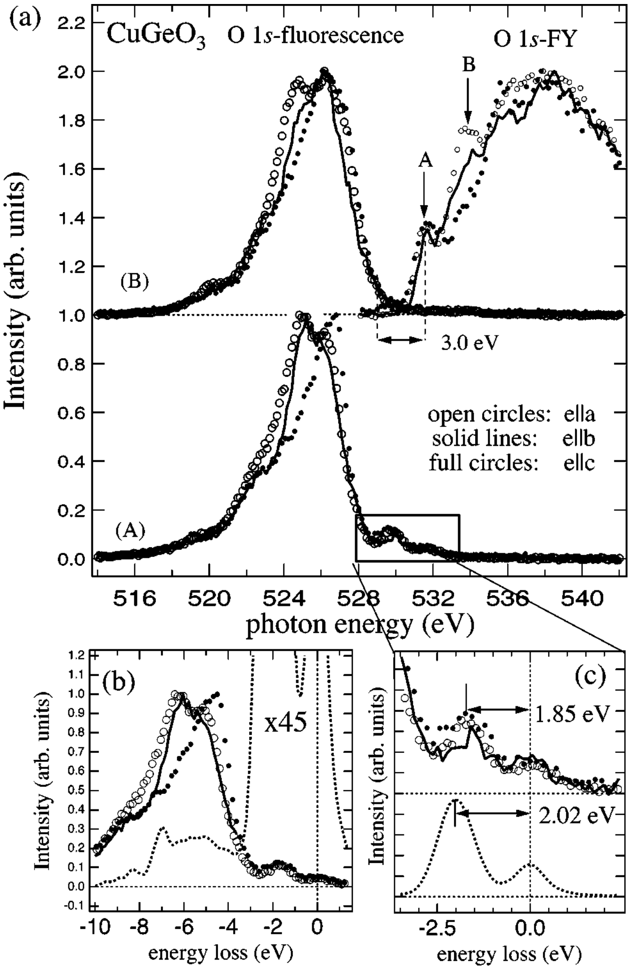

FIG. 1. (a) $CuGeO_3$ resonant O 1*s* SXF excited at (*A*) 531.7 eV and (*B*) 533.9 eV for three different geometries. The O 1*s* fluorescence yield (FY) spectra (absorption) in corresponding geometries is shown on the top. The two vertical arrows indicate the excitation energy positions. (b) and (c) show details of the *A* spectra on an energy-loss scale. For comparison Cu 2*p* RIXS is also displayed (dashed lines) with an arbitrary relative intensity scaling.

I. BANDLIKE O 2*p* VALENCE STATES

From Fig. 1 we find that the bandwidth of the oxygen 1*s* SXF (excited at the higher energy) is about 8.5 eV and the

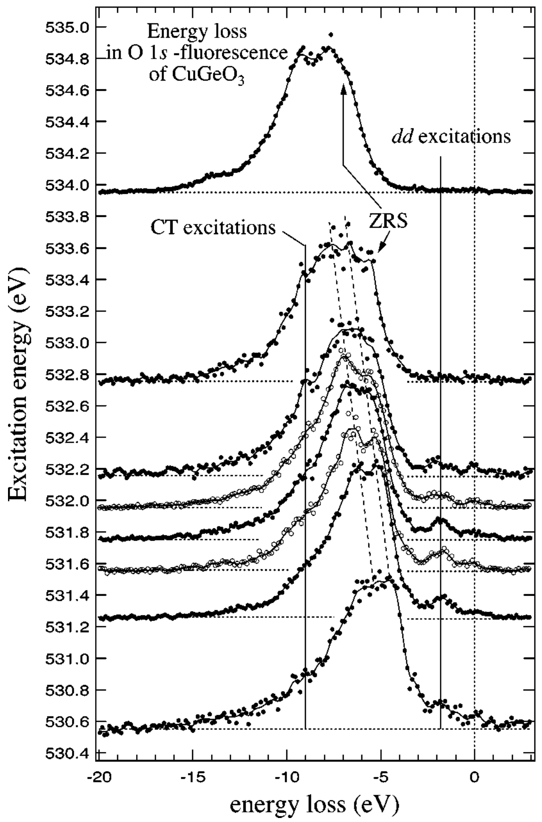

FIG. 2. $CuGeO_3$ O 1*s* SXF spectra excited at various energies ($e\|a$ geometry) plotted against an energy-loss scale. Zero energy corresponds to elastic scattering; losses have negative energies. The raw spectra are shown as circles and the superimposed solid lines are corresponding three-point binomially smoothed spectra. The spectra are vertically offset by the excitation energy for clarity.

oxygen band gap, indicated by the double-arrow line, is about 3.0 eV. Both observations are similar to what is found in recent band structure calculations.[3,4] Therefore it is reasonable to assume that this spectrum indeed reflects the bandlike O 2*p* states.

The crystal structure of $CuGeO_3$ reveals[16] that there are two inequivalent oxygen sites: in-plane oxygen and apical oxygen. The authors of a very recent polarization-dependent x-ray absorption study[15] assigned the spectral structures to contributions from the empty O 2*p* bands from different sites. The excitation energy dependence of the x-ray fluorescence band (Fig. 1) can also be partly explained by site selectivity. This means, with the lower excitation energy, only O 1*s* SXF from the in-plane oxygen is emitted since it is below the threshold for apical oxygen 1*s* SXF. At high-energy excitation O 1*s* SXF from both sites are superposed with different weights and energy offsets. Our x-ray fluorescence spectra show the existence of at least three contributions to the oxygen valence band at 526.3 eV, 524.7 eV, and 520.2 eV. A ground-state band structure calculation[4] using the ''LDA+U''-scheme[17] shows the O 2*p*-projected states with very similar structures as we observe. We can also compare our results to valence-band photoemission spectra[6] that show three oxygen-related structures at 4 eV, 5 eV, and 8 eV binding energy, respectively.

The polarization dependence of the oxygen 1*s* SXF spectra in Fig. 1 reflects the difference in spectral weight from O $2p_{x,y}$ and $2p_z$ orbitals, respectively. The crystal structure of $CuGeO_3$ is such that there exist two orientations of Cu-O-octahedra with their *z* axis, defined by a line connecting the two apical oxygen sites, that has an angle of (nearly) ±45° to the surface plane. These octahedra alternate along the crystallographic *b* axis. Therefore it is not possible to orient the polarization vector of the exciting x rays, $\hat{e}_{inc}$, parallel to all *z* axes simultaneously. On the other hand, one may align the $\hat{e}_{inc}$ with the plane defined by the other four oxygen sites by having $\hat{e}_{inc}$ parallel to the *c* axis. Spectra with $\hat{e}_{inc}\|b$ and $\hat{e}_{inc}\|a$ will contain mixtures of purely out-of-plane and in-plane components. By taking the above effects into account we can therefore identify spectral components with in-plane and out-of-plane character.

The top pair of spectra (excited at the higher energy) in Fig. 1 shows an apparent narrowing when excitation is changed from $e\|a$ and $e\|b$, having out-of-plane contributions, to ($e\|c$), having a purely in-plane contribution. Thus the in-plane O 2*p* states are found to have more spectral weight at energies closer to the valence-band top in accordance with the a recent multiband Hubbard Hamiltonian calculation.[6] According to Ref. 15 one can only excite in-plane oxygen at the lower excitation energy (bottom pair of oxygen 1*s* SXF spectra in Fig. 1). However, this is in contradiction to our observation of out-of-plane contributions in the polarization-dependent O 1*s* SXF spectra and calls for a reinterpretation of the O 1*s* absorption spectrum. Finally, we note that the low-energy excited spectra have contributions from localized oxygen states [Fig. 1(c)] discussed in the next section.

II. RESONANT INELASTIC SCATTERING: EXCITONIC STATES AT THE O SITES

Recent RIXS experiments on cuprates at the Cu *p* edges[7] revealed both *dd* and CT excitations and Cu 1*s* RIXS (Ref. 9) showed a clear indication of a CT excitation. The transitions for Cu *p*-edge RIXS are predominantly $d^9 \rightarrow \underline{c}d^{10} \rightarrow d^{9*}$ (*dd* excitations) and $d^9 \rightarrow \underline{c}d^{10} \rightarrow d^{10}\underline{L}$ (CT excitations), where $\underline{c}$ stands for a Cu *p*-core hole and $\underline{L}$ for a ligand hole. One can assume that the ground-state Cu 3*d* hole has x^2-y^2 symmetry and the excitation energy of this hole to orbitals of different symmetry (denoted as d^{9*}) has been found[8] to be about 1.3–1.7 eV for cuprates. Not unexpectedly, therefore, the resonant Cu 2*p* RIXS spectra of $CuGeO_3$ (Ref. 18) turn out to be very similar to those measured for other cuprates, such as La_2CuO_4.[7] An early optical *reflectivity* study on $CuGeO_3$ (Ref. 19) using a Kramers-Kronig transformation found a reversed energy ordering of the *dd* and the CT excitations, while later a direct optical *absorption* measurement[20] determined these excitations to be at similar energies as we find in Cu *p*-edge RIXS (Fig. 1).

The low-energy structures in O 1*s* RIXS seen in Fig. 1(b) and 1(c) are the elastic peak and a loss peak at an energy similar to the *dd* excitations observed in Cu 3*p* RIXS.[8] We point out that the energy of the inelastic peak is 1.85 eV and therefore slightly lower than the *dd*-excitations found in our Cu 2*p* RIXS (2.02 eV). The oxygen 1*s* absorption prepeak—observed for Cu^{2+} systems and taken as evidence for the upper Hubbard band which has predominantly Cu $3d$ character—has been explained[21] by mixing of ligand-hole states ($d^{10}\underline{L}$) into its ground state. The ligand hole is filled in the absorption process, leaving a d^{10} intermediate state in the RIXS process which subsequently decays into a mixture of $d^{10}\underline{L}$ and $d^{9}*$ states. The shift between the RIXS peaks at the O $1s$ and Cu $2p$ resonances indicates that oxygen holes preferentially couple to Cu $3d$ orbitals with in-plane character that are expected to have lower excitation energies.

It is natural to expect signatures for double-hole states (i.e., a mixture of $d^{9}\underline{L}$, d^{8}, $d^{10}\underline{L}^{2}$, called the Zhang-Rice singlet) in resonant SXF spectra of cuprates, but this process requires the excited electron to leave the atom. The intermediate state at pre-peak excitation is rather localized which would make such a transition less appear less likely than the transitions to a bound state (dd excitations). However, in the SXF spectra at higher excitation energies [top panel of Fig. 1(a)] we observe a shoulder on the high-energy side of the main band that has no counterpart in the O $2p$ DOS and shows the same polarization dependence as the in-plane oxygen part of the bandlike states. This feature appears only when tuning to excitation energies that promote the electron into a delocalized oxygen orbital. Although possible, it seems unlikely that additional states close to the top of the valence band, located at about 528.8 eV emission energy, would appear in the DOS of apical oxygen. Together, this may be taken as strong evidence for this feature to be a Zhang-Rice singlet (ZRS). The ZRS has only been able to be identified in PES of CuO, although according to theoretical expectations, the ZRS should be a general feature and first ionization state in cuprates. Several reasons may be invoked to explain this discrepancy, including charging or other surface effects and the fact that elemental selectivity is weak in PES.

The energy-loss feature marked with a vertical line at about 9.0 eV in Fig. 2 is attributed to a CT excitation of O $2p$ character, although the overlap with SXF makes the exact energy assignment difficult. The authors of Ref. 9 found a broad feature at 6 eV in Cu $1s$ RIXS attributed to CT excitations but did not report RIXS at larger energy losses. On the other hand, the authors of an EELS study[5] reported a loss feature at 9.4 eV, possibly being the same excitation that we observe. Since the energy difference between these two high-energy-loss features is close to the observed band gap, our 9.0 eV loss feature might be the result of a double-electron excitation, i.e., a CT excitation with an extra electron excited into the O conduction band. Figure 1(b) shows that CT transitions with Cu $3d$ character observed in Cu $2p$ RIXS (Fig. 1) have energy losses that strongly overlap with the position of the strong SXF main bands. Therefore, it is likely that some of the excitation energy dependence and polarization dependence observed for the O $1s$ SXF main band is due to the occurrence of RIXS from CT excitations. This may be tested in the future, for instance, by a further narrowing of the excitation-energy bandwidth, resulting in a relative enhancement of RIXS over SXF.

In conclusion, we have unraveled information about *oxygen-specific* bandlike and excitonic states by taking advantage of the polarization and energy dependence of resonant O $1s$ SXF of $CuGeO_3$. Resonant inelastic x-ray scattering has been found at a cuprate O $1s$-absorption pre-edge peak, directly revealing its localized character. We have presented an initial interpretation of the observed structures and found evidence for the formation of a Zhang-Rice singlet state in $CuGeO_3$. We believe that O $1s$ RIXS is a novel source of information for the electronic structure of many doped, as well as pure, correlated oxide materials. The very low x-ray fluorescence yield at the metal core edges of many important $4d$ oxides (for instance, low-dimensional Mo bronzes,[22] W bronzes, and ruthenates) makes it extremely difficult to study dd excitations other than at O $1s$ resonances. Modern synchrotron radiation sources offer the possibility for studying effects of many low-temperature transitions in correlated materials at the necessary high spectral resolution.

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