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Site-specific unoccupied electronic structure of one-dimensional $SrCuO_2$

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The unoccupied electronic structure of $SrCuO_2$ single crystals has been studied using x-ray-absorption spectroscopy. By choosing the orientation of the single crystals with respect to the polarization vector of the synchrotron radiation, we are able to determine the hole occupation of the different O $2p$ and Cu $3d$ orbitals. We show that the intrinsic holes in the one-dimensional copper oxide zigzag chains mainly occupy planar Cu $3d_{y^2-z^2}$ orbitals, which closely resembles the situation in the undoped parent compounds of the high-temperature superconductors. Additionally, most of the oxygen states that are admixed to the upper Hubbard band are concentrated in the center of the chains most probably as a result of the larger number of nearest neighbors. Our results provide an important check for calculations of one-dimensional correlated Cu-O systems. [S0163-1829(97)51212-4]

The fundamental physical properties of low-dimensional and correlated systems have attracted a lot of interest in recent years. Ladder-type copper-oxide materials form an interesting class of compounds that combine a one-dimensional (1D) electronic network with electronic correlations resulting in unexpected magnetic ground-state properties.[1] Furthermore, following the homologous series $Sr_{n-1}Cu_{n+1}O_{2n}$, one is able to study the crossover from a one- to a two-dimensional (2D) Cu-O network and also gain important information on the physics of the cuprate-based high-temperature superconductors. Additionally, it has been predicted that ladder-type materials can be doped with holes, which might lead to new superconducting materials[2] and superconductivity with a transition temperature of about 12 K has recently been observed in $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ under high pressure (3 GPa).[3] One-dimensional $SrCuO_2$ is composed of two edge-sharing CuO_2 chains, which results in a zigzag copper-oxide network and represents the starting point for the series of ladder compounds (1D $SrCuO_2$ is a "one-leg ladder"). A detailed knowledge of its physical properties is therefore indispensable for an understanding of the ladder-type copper oxides. In Fig. 1 we show the structure of the Cu-O chains in $SrCuO_2$ and their orientation with respect to the orthorhombic unit cell. These chains are comprised of one copper and two symmetrically inequivalent oxygen atoms denoted as O(1) and O(2) (see Fig. 1). They are planar within the crystallographic **b-c** plane.

Only a few studies of 1D $SrCuO_2$ have been reported so far. From magnetic susceptibility measurements it has been concluded that $SrCuO_2$ is qualitatively different from the

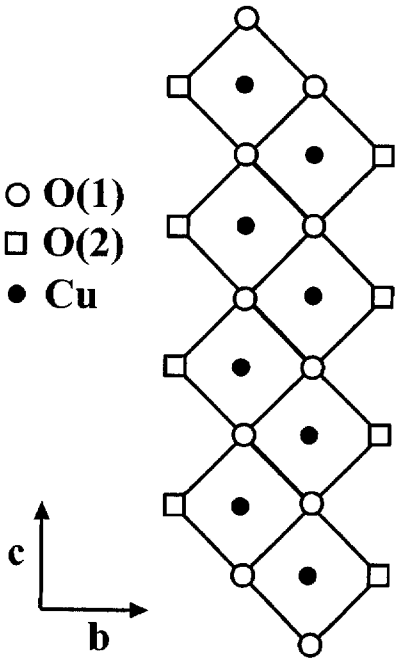

FIG. 1. Structure of the zigzag copper-oxide chains in $SrCuO_2$.

linear chain compound Sr_2CuO_3.[4] The existence of a diagonal intrachain spin-spin interaction causes frustration and prevents the observation of long-range magnetic order at low temperatures. Cu nuclear magnetic resonance (NMR) studies of polycrystalline samples report a clear difference between $SrCuO_2$ and Sr_2CuO_3 as regards the temperature dependence of the spin relaxation rate,[5] while single-crystal investigations find a very similar behavior for the two compounds.[6] Raman investigations have been interpreted in terms of a spin-liquid ground state for $SrCuO_2$.[7] Recently, angular-resolved photoemisssion spectroscopy studies have revealed evidence for spin-charge separation,[8] i.e., the existence of spinons and holons, a phenomenon that is expected for low-dimensional materials.

In this contribution we report a study of the site-specific unoccupied electronic structure of $SrCuO_2$ using polarization dependent x-ray absorption spectroscopy (XAS) in the fluorescence yield mode. This technique has proved to be highly effective in the study of the origin and character of the unoccupied electronic states in cuprate-based materials.[9] Here we show that, similarly to the 2D copper-oxide materials, the holes in $SrCuO_2$ have predominantly Cu $3d_{y^2-z^2}$ character. Furthermore, the two inequivalent oxygen sites differ markedly in the number of holes in their O $2p$ orbitals. Most of the holes are concentrated in the center of the zigzag chains. This is concluded to be a consequence of the different number of nearest Cu neighbors for the two oxygen sites.

$SrCuO_2$ single crystals were grown using the traveling-solvent-zone technique. Details are described elsewhere.[4] $SrCuO_2$ adopts an orthorhombic crystal structure[10] (space group *Cmcm*) with lattice parameters $a=3.577$ Å, $b=16.342$ Å, and $c=3.9182$ Å. The zigzag copper-oxide chains are oriented along the crystallographic **c** direction. The crystals were oriented for the experiment using an x-ray diffractometer and were cut using an ultramicrotome in order to obtain flat **a**-**b** and **a**-**c** surfaces, respectively. The XAS experiments were performed in the non-surface-sensitive fluorescence yield detection mode using linearly polarized light from the SX700/II monochromator at BESSY.[11] The energy resolution of the monochromator was set to be 280 and 660 meV at the O $1s$ and Cu $2p$ absorption thresholds, respectively.

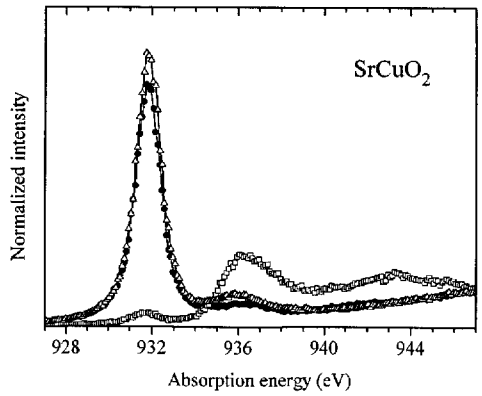

FIG. 2. Cu $2p_{3/2}$ absorption edges of $SrCuO_2$ for the light polarization vector **E** parallel to the crystal axes (□: **E**‖**a**; △: **E**‖**b**; ●: **E**‖**c**).

The measurements were carried out with synchrotron radiation at normal incidence, with the light polarization with respect to the single-crystalline sample being varied by rotating the sample (rotation axis is equal to sample normal). As dipole selection rules apply for XAS and due to the localized initial core states, our studies probe unoccupied O $2p$ and Cu $3d/4s$ electronic states in the case of O $1s$ and Cu $2p$ absorption, respectively. Using different orientations of the sample with respect to the light polarization vector **E** additionally allows one to choose between different final state orbitals, e.g., for **E**‖**a** only O $1s \rightarrow$ O $2p_x$ transitions are possible.

The data were corrected for the energy-dependent incident flux and for self-absorption effects according to a procedure described elswhere.[12] Additional measurements in the total-electron-yield mode have been performed at the Stanford Synchrotron Radiation Laboratory on freshly cleaved single crystals corroborating the results presented in the following.

In Fig. 2 we show the Cu $2p_{3/2}$ absorption edges of $SrCuO_2$ for **E** parallel to the three crystallographic axes. The data are normalized in an energy region of 1000–1010 eV where the final states are nearly free-electron-like and therefore essentially isotropic. As transitions into Cu $4s$ states are weak, these measurements probe mainly the hole distribution in the Cu $3d$ orbitals. As can be seen from Fig. 2, the spectra consist of three different features located at 931.7, 936.2, and 943.1 eV. The intensity of these features is strongly anisotropic.

While the data for **E**‖**b** and **E**‖**c** are almost identical, a clear variation is observed going to **E**‖**a**. The first feature is strongly suppressed for **E**‖**a** but the second and the third features are higher in intensity when compared to the other polarization directions. This observation is analogous to that made for two-dimensional CuO_2 planes in cuprate superconductors or their parent compounds.[9] For **E**‖**a**, where only Cu

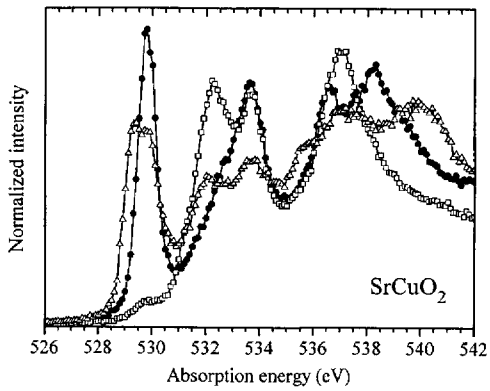

FIG. 3. O $1s$ absorption edges of $SrCuO_2$ for the light polarization vector **E** parallel to the crystal axes (□: **E**‖**a**; △: **E**‖**b**; ●: **E**‖**c**).

$3d_{3x^2-r^2}$ final states can be reached, the small peak at 931.7 eV shows that less than 5% of the holes occupy these orbitals. In this evaluation, the different cross sections for transitions into Cu $3d_{y^2-z^2}$ and Cu $3d_{3x^2-r^2}$ states[9] and the small deviation (~ 3%) from perfect light polarization have been taken into account. The anisotropy of the spectra demonstrates that, as in the 2D cuprates, the holes predominantly occupy "planar" Cu $3d_{y^2-z^2}$ orbitals (which are the analogous to Cu $3d_{x^2-y^2}$ orbitals in the usual notation used for the 2D cuprates). This is a result of the noncubic crystal field at the Cu sites, which leads to a lifting of the twofold degeneracy of the Cu $3d$ states with e_g symmetry. Consequently, it is also possible to restrict oneself to the "in-plane" orbitals in cluster calculations of $SrCuO_2$. The two broad features above 933 eV, mainly visible for **E**‖**a**, have also been observed in many other cuprate systems for **E** perpendicular to the CuO_2 planes[9] and have been assigned to orbital combinations that involve Cu $3d_{3x^2-r^2}$ states together with other copper or oxygen states.[9,13,14]

Important information can be obtained from the O $1s$ absorption edges, which are shown in Fig. 3. These measurements probe empty electronic states located in the O $2p_x$ (**E**‖**a**), O $2p_y$ (**E**‖**b**), and O $2p_z$ (**E**‖**c**) orbitals. The data are again normalized in an energy range far above the absorption edge (600–610 eV) where the final states have nearly free-electron character. The three spectra are rich in structure. The features above 531 eV are caused by transitions into O $2p$ orbitals that are hybridized with Sr $5s$, Sr $4d$, Cu $4s$, or Cu $4p$ states. The most pronounced features that are common to the **E**‖**a** and **E**‖**c** spectra (at about 533.5 and 536.6 eV) most likely arise from a combination of O(2) $2p_{x,z}$ orbitals with Sr $4d$ states in the Sr-O plane perpendicular to **b**. The other higher-lying maxima can be assigned to orbital combinations within the Cu-O network.

The first features directly above the absorption onset (i.e., below 531 eV) can be assigned to transitions into O $2p$ orbitals that are hybridized with Cu $3d$ states forming the so-called upper Hubbard band. In the case of $SrCuO_2$, the spectra are highly anisotropic in this energy range as regards both their shape and intensity. For **E**‖**a**, the intensity is very low, confirming the almost negligible fraction of "intrinsic" (Cu $3d^9$) holes occupying orbitals that are perpendicular to the Cu-O network, as discussed above. In contrast to the Cu $2p$ edges shown in Fig. 2, the O $1s$ absorption is considerably different for **E**‖**b** and **E**‖**c**. This has its origin in the fact that the zigzag copper-oxide chains in $SrCuO_2$ contain two inequivalent oxygen sites (see Fig. 1), which differ in the number of neighboring copper atoms. While the O(1) site is surrounded by two copper atoms in the **c** and one in the **b** direction, the O(2) site has only one adjacent copper along **b**. Thus, for **E**‖**c** one would expect O $1s \rightarrow$ O $2p_z$ transitions only at the O(1) site, but for **E**‖**b** O $1s \rightarrow$ O $2p_y$ transitions can occur at both oxygen sites. Indeed, a single absorption feature at 529.8 eV is observed for **E**‖**c**, while for **E**‖**b** two near-edge absorption structures are visible that are located at 529.3 and 529.8 eV. Owing to the almost square oxygen network in the Cu-O chains the hybridization of O $2p$ and Cu $3d$ orbitals is barely direction dependent, i.e., the energy of the respective unoccupied states is virtually the same. We therefore expect O $1s \rightarrow$ O $2p_y$ and O $1s \rightarrow$ O $2p_z$ transitions at the O(1) site to occur at roughly the same energy. Consequently, we ascribe the features at 529.8 eV to transitions at the O(1) site and that at 529.3 eV to transitions occuring at O(2). As can be seen in Fig. 3, the spectral weight of the two low-lying absorption features for **E**‖**b** and thus the hybridization of O $2p_y$ orbitals of O(1) and O(2) to Cu $3d_{x^2-y^2}$ states is very similar, while the higher intensity of the single peak for **E**‖**c** reflects larger hybridization of O $2p_z$ orbitals at the O(1) site, which might be due to the difference in the copper next-nearest-neighbor environment along these directions. From this it is clear that the hole occupancy is different for the two oxygen sites, O(1) and O(2), which leads to the interesting picture in which most of the holes with oxygen character are concentrated in the center of the copper oxide zigzag chains [O(1), about 70%] and only ~30% are sitting on the outer corners [O(2)]. Recently, a similar hole distribution has been predicted from cluster calculations for linear Cu-O chains.[15] This is mainly a consequence of the differnt numbers of Cu neighbors for the two oxygen sites.

The fact that a two-peak structure is observed near the absorption onset for **E**‖**b** most likely arises from a different binding energy of the O $1s$ core levels at the two oxygen sites. This might be a consequence of the different neighborhood and bonding for the two sites. A similar observation has been made for $YBa_2Cu_4O_8$, which also contains Cu-O zigzag chains.[16] A complete description of absorption energies, however, requires a detailed understanding of the complicated combination of different (i) binding energies and (ii) final-state screening processes at the O(1) and O(2) sites. An analysis with the help of calculations would be necessary to deduce the relative importance of these quantities. Furthermore, intriguing questions arise about how the hole distribution in the Cu-O zigzag chains influences the super-exchange integral J and how it might change as a function of doping. For example, about half of the doped holes reside on the chains in the hole-doped superconductor $YBa_2Cu_4O_8$ with an almost equal distribution between the two chain oxygen sites.[16]

To summarize, we have studied the unoccupied electronic structure of the one-dimensional cuprate-based compound $SrCuO_2$. The distribution of the intrinsic hole ("Cu $3d^9$") between the different O and Cu orbitals has been determined. Analogous to 2D cuprates, the holes have predominantly

planelike character. The majority is concentrated in the center of the copper oxide zigzag chains giving rise to hole stripes in the middle of the chains.

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