Symmetry of unoccupied electronic states in the high-T_c superconductor $Sr_2CuO_{2+\delta}Cl_{2-y}$ studied by electron energy-loss spectroscopy

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(Received 3 May 2005; accepted 5 January 2006; published online 22 February 2006)

The symmetry of unoccupied electronic states at the O and Cu sites in the high-T_c superconductor $Sr_2CuO_{2+\delta}Cl_{2-y}$ has been studied by measuring O 1*s* and Cu $2p_{3/2}$ absorption edges using orientation-dependent high-energy electron energy-loss spectroscopy. Unlike many conventional superconductors, this superconducting material is found to have considerable O 2*p* holes at the apical oxygen sites (about 40% O 2*p* holes). About 60% O 2*p* holes are found to have $p_{x,y}$ symmetry in the CuO_2 planes. The unoccupied states on the Cu sites have predominantly in-plane $3d_{x^2-y^2}$ symmetry, probably with an admixture of about 14% $3d_{3z^2-r^2}$ symmetry. The Cu $2p_{3/2}$ absorption edge exhibits clearly divalent Cu(2) states, indicating that the doped holes would reside predominantly on O 2*p* orbitals. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2177359]

Recently, the high-T_c superconductor $Sr_2CuO_{2+\delta}Cl_{2-y}$ (T_c=30 K) has been synthesized with partial substitution of oxygen for apical chlorine by using the high-pressure technique.[1] Its crystallographic structure was determined to be of the tetragonal K_2NiF_4-type with a space group I4/mmm and lattice parameters $a=b=3.94$ Å, $c=15.64$ Å.[1,2] Figure 1 schematically shows the structure of the $Sr_2CuO_{2+\delta}Cl_{2-y}$. This superconducting material is very peculiar as compared with other superconductors. First, the hole concentration is very high. The average proportion of Sr, Cu, and Cl in atomic ratio is about 2:1:1.38 according to the characterization by transmission electron microscopy-energy dispersive x ray for a large number of perfect grains,[2] indicating that about 0.62 holes per unit cell were doped in the material if neglecting the oxygen deficiency. This hole concentration is much higher than the theoretically suggested optimal value, i.e., 0.35–0.38 holes per unit cell[3] for this oxychloride compound. Second, the bond lengths d_P [the Cu(*P*)–O(*P*) bond length] and d_A [the Cu(*P*)–O(*A*) bond length] are large. Although the d_P of $Sr_2CuO_{2+\delta}Cl_{2-y}$ (d_P=1.96 Å and d_A=2.9 Å) (Ref. 1) decreases from the d_P of the parent compound $Sr_2CuO_2Cl_2$ (d_P=1.99 Å) (Ref. 4) obtained at ambient pressure, it, as well as d_A, is still too large as compared with those of the same homologous copper–oxychloride superconductors such as $(Sr,Ca)_3Cu_2O_{4+\delta}Cl_{2-y}$ (d_P=1.93 Å and d_A=2.6 Å).[5] The bond lengths are regarded as the most direct measure of the magnitude of covalency since the hopping integrals are directly related to the bond lengths. Although many experiments have suggested that there is no correlation between T_c and d_P, d_A,[6] the influence of the bond length on the transfer of carriers cannot be neglected. Since this high-T_c superconductor $Sr_2CuO_{2+\delta}Cl_{2-y}$ shows some differences from other superconductors, researchers are very much interested in the nature of the states near the Fermi level in the material.

There is a general consensus that superconductivity in the CuO_2 plane-based superconductors is correlated with the concentration of holes in a nearly filled Cu 3*d*–O 2*p* valence band. The extra holes induced by doping are commonly considered to reside mainly on oxygen *p* orbitals due to a strong Hubbard repulsion on copper orbitals. There are several possibilities for oxygen *p* orbitals: $p\sigma_{x,y}$ orbitals in the CuO_2 planes which are σ bonded to Cu $d_{x^2-y^2}$ orbitals; $p\pi_{x,y}$ or $p\pi_z$ orbitals in the same plane which are π bonded to Cu d_{xy} or Cu $d_{yz,zx}$ orbitals. For the oxygen atom at the apical site above the Cu atom, one can have a p_z orbital forming a σ bond or a $p_{x,y}$ orbital forming a π bond. At present, there is no consensus about which one of the π orbitals at oxygen sites is doped with holes. For example, some theories assume that the doped holes may enter $p\sigma_{x,y}$ orbitals in the CuO_2 planes,[7,8] while some others consider $p\pi_{x,y}$ (Refs. 9 and 10) or $p\pi_z$ (Ref. 11) orbitals in the same plane. The existence of O 2*p* holes in the p_z orbitals of the apical oxygen atoms (above the Cu atoms) has also been discussed for some superconductors.[12]

In experiments, O 2*p* holes are easily probed via transitions from the O 1*s* core level. A large number of theories and experimental measurements have suggested that the prepeaks on the low-energy part (usually $E<531$ eV) of the

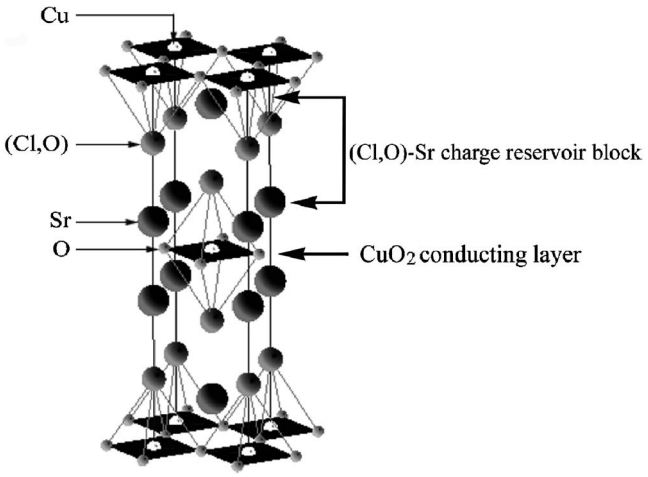

FIG. 1. Schematic of the structure of $Sr_2CuO_{2+\delta}Cl_{2-y}$. The (Cl, O)-Sr rock-salt charge reservoir block and the CuO_2 conducting layer are shown using thick arrows, respectively.

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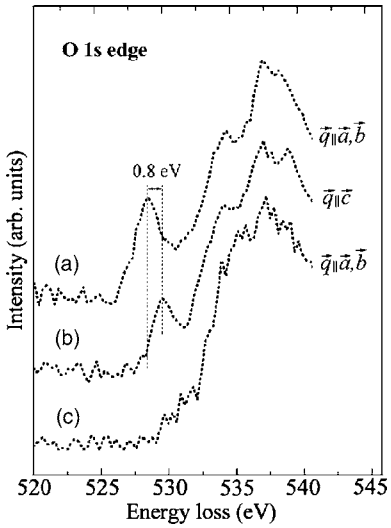

FIG. 2. The O 1*s* absorption edges of $Sr_2CuO_{2+\delta}Cl_{2-y}$ for momentum transfer $q\|a,b$ [curve (a)] and $q\|c$ [curve (b)]; and the O 1*s* absorption edge of $Sr_2CuO_2Cl_2$ for $q\|a,b$ [curve (c)].

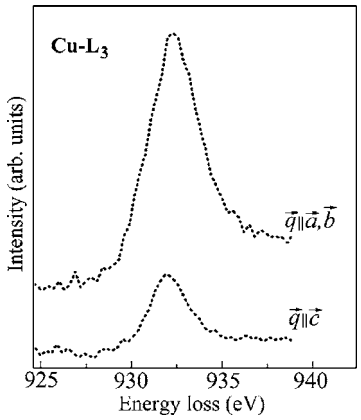

FIG. 3. Cu $2p_{3/2}$ absorption edges of $Sr_2CuO_{2+\delta}Cl_{2-y}$ for $q\|a,b$ and $q\|c$.

O 1*s* absorbtion edge correspond to O $1s \rightarrow$ O $2p$ transitions with the $2p$ holes near the Fermi level, and the intensities of the prepeaks are proportional to the number of holes induced by doping. The orientation of the O $2p$ holes can be identified using dipole selection rules in electron inelastic scattering. For example, with the momentum transfer q parallel to the x axis only transitions into p_x orbitals are allowed from an s level, and likewise for the other directions. The orientation-dependent electron energy-loss spectroscopy (EELS) studies of the holes' symmetry in high-T_c superconductors were reported in several papers.[13,14]

In transmission EELS, inelastically scattered electrons are detected and the energy loss is measured as a function of the scattering angle θ. In our experiment, the scattering geometry with zero scattering angle has been used to measure the local density of unoccupied states. More details on transmission EELS experiments are discussed elsewhere.[14–18] The primary energy of the incoming electrons was 200 keV.

Thin samples for EELS measurements were prepared by mechanical thinning, followed by argon ion milling. A liquid-nitrogen cold stage was used during ion milling to reduce ion beam damage. A Tecnai F20 electron microscope with a field emission gun was used for the EELS experiments.

Curves (a) and (b) in Fig. 2 show the O 1*s* absorption edges of a $Sr_2CuO_{2+\delta}Cl_{2-y}$ single crystal for momentum transfers $q\|a,b$ and $q\|c$, respectively. A clear anisotropy is observed and the prepeaks at ~528.3 and ~529.1 eV are clearly seen in the edges for $q\|a,b$ and $q\|c$, respectively. As mentioned above, the prepeaks on the low-energy part are related to the holes on O $2p$ orbitals and the momentum transfer for $q\|a,b$ probes the unoccupied states at the O sites with $2p_{x,y}$ symmetry, while that for $q\|c$ probes O $2p_z$ states. The O 1*s* edge of a normal compound $Sr_2CuO_2Cl_2$ single crystal for $q\|a,b$ is also shown by Curve (c) in Fig. 2 for comparison, where no obvious hole-related prepeak is observed in the edge.

The prepeak at ~528.3 eV, observed for $q\|a,b$, is naturally explained as O $2p_{x,y}$ symmetry in the CuO_2 plane. The existence of apical O $2p_{x,y}$ holes' symmetry can be discarded. It is remarked that the $Sr_2CuO_{2+\delta}Cl_{2-y}$ system is very simple; having only two types of oxygen. One of them is the oxygen in the CuO_2 plane, and the other is the oxygen incorporated in the apical sites (see Fig. 1). The in-plane and apical oxygen atoms should have different binding energies of the O 1*s* level, although no information on their exact values is available. If the apical O $2p_{x,y}$ orbitals are doped with holes, another prepeak should appear on the low-energy part or, at least, the prepeak at ~528.3 eV should be split. But no such evidence was observed in the O 1*s* absorption edge for $q\|a,b$. There are two types of O $2p_{x,y}$ orbitals in the CuO_2 planes, one is called $p\sigma_{x,y}$ lying along the Cu–O bond, the other called $p\pi_{x,y}$ is perpendicular to it. Since the antibonding combination represents the highest occupied orbital, and will be the first one to be depleted when creating holes via doping, it is reasonable to assume that the holes are located on O $p\sigma_{x,y}$ orbitals, but the possibility of having holes on the perpendicular $p\pi_{x,y}$ orbitals has also been discussed for other superconductors.[9,10] Our measurements, however, cannot differentiate between the in-plane O $p\sigma_{x,y}$ and the $p\pi_{x,y}$ holes.

The prepeak at ~529.1 eV, observed for $q\|c$, is ascribed to O $2p_z$ symmetry at the apical oxygen site. The out-of-plane π holes in the CuO_2 planes can be excluded, for if O $2p_z$ orbitals in the CuO_2 planes are doped with holes, the final states from the O 1*s* level for $2p_z$ symmetry would have an energy lower than that for $2p_{x,y}$ symmetry, as suggested for other superconductors.[19] No prepeak related to the out-of-plane π holes in the CuO_2 planes is observed for $q\|c$ at the energies lower than ~528.3 eV (see Fig. 2). The obvious anisotropy observed for the O 1*s* absorption edges suggests that the O atoms at the apical sites have a bonding energy of the O 1*s* level higher than those in the CuO_2 planes. The intensity ratio of the prepeak for $q\|a,b$ to that for $q\|c$ is obtained to be about 1.5 by subtracting (for $E<531$ eV) the $q\|a,b$ edge of $Sr_2CuO_2Cl_2$ from the $q\|a,b$ and $q\|c$ edges of $Sr_2CuO_{2+\delta}Cl_{2-y}$. This means that about 60% of the doped holes have O $2p_{x,y}$ symmetry, and 40% have O $2p_z$ symmetry.

We also examined briefly the Cu $2p_{3/2}$ (L_3) absorption edges of $Sr_2CuO_{2+\delta}Cl_{2-y}$ for $q\|a,b$ and $q\|c$ and the results are shown in Fig. 3. Enough information about the unoccupied states at the Cu sites can be obtained using Cu $2p_{3/2}$ edge which is related to the transitions of Cu $2p_{3/2}$ core electrons from the $(2p_{3/2})3d^9\underline{L}$ ground states to the $(\underline{2p}_{3/2})3d^{10}\underline{L}$ excited states, where $\underline{2p}$ denotes a $2p$ hole and $\underline{L}$ denotes a ligand hole. For $q\|a,b$, a strong excitation into $3d$ orbitals parallel to the CuO_2 planes is observed at ~932 eV, indicat-

ing that most of the unoccupied $3d$ states have $3d_{x^2-y^2}$ symmetry. For $q \| c$, there is a much smaller edge at almost the same energy, indicating that much less unoccupied $3d$ states, probably having $3d_{3z^2-r^2}$ symmetry, are perpendicular to the CuO_2 planes. The intensity for $q \| c$ is about 20% of that for $q \| a,b$. If only e_g states were considered and the lower lying t_{2g} states were neglected, we can attempt and estimate of the percentage character of the Cu $3d$ states based on the relative weights of the corresponding transitions in $Bi_2Sr_2CaCu_2O_8$ reported in Ref. 14. This estimation gives the result that about 14% of the unoccupied $3d$ states have $3d_{3z^2-r^2}$ symmetry and the rest have $3d_{x^2-y^2}$ symmetry. It should be noted that this evaluation is based on the neglect of t_{2g} states. In fact, we cannot exclude the admixture of t_{2g} states. According to the theoretical model for high-T_c superconductivity based on d-d excitations,[20] this admixture may play an important role in the pairing of holes which results in superconductivity. In addition, the main line for $q \| a,b$ shows an asymmetry which may be explained by the influence of holes on O sites. A weak asymmetry of the main line was also observed in the x-ray absorption spectrum measured on $La_{1.85}Sr_{0.15}CuO_4$ (Ref. 21), and was interpreted in the same way. In spite of the different symmetry obtained, the Cu $2p_{3/2}$ absorption edge is similar to that measured by x-ray photoelectron spectroscopy on the normal compound $Sr_2CuO_2Cl_2$ (Ref. 22), indicating that the doped superconductor $Sr_2CuO_{2+\delta}Cl_{2-y}$ also exhibits divalent Cu(2) states. This means that the doped holes reside predominantly on O $2p$ orbitals.

The orientation-dependent EELS spectra give *direct* information on the hole distributions in our sample. Assuming the total hole concentration ($\sim$0.62 holes per unit cell) analyzed in Ref. 2 is the real one, there will be about 0.37 holes ($\sim$60%) having O $p_{x,y}$ symmetry in the CuO_2 planes and 0.25 holes ($\sim$40%) having O p_z symmetry at the apical site of oxygen. Unlike many conventional superconductors, this superconducting material has many O $2p$ holes at the apical oxygen. It is noted that the bond lengths d_P and d_A of the $Sr_2CuO_{2+\delta}Cl_{2-y}$ are large compared with those of many other superconductors. The large bond length of apical O–in-plane Cu (d_A) possibly influences the transfer of holes from the apical oxygen sites to the CuO_2 planes. This view can be verified from the hole redistribution caused by the change of bond length d_A in other superconductors. For example, the in-plane hole concentration of $YBa_2Cu_4O_8$ increases significantly due to the reduction of the d_A caused by pressure.[23,24] The redistribution of charges between CuO_2 plane and other planes has been also observed in $YBa_2Cu_3O_{7-\delta}$ when the bond length d_A changes with the variation of δ (but not due to pressure).[25] So, the large number of holes observed in the material, which are located in the $2p_z$ orbitals of the apical oxygen, can be reasonably explained.

It should be noted that the superconductor $Sr_2CuO_{2+\delta}Cl_{2-y}$ is obviously overdoped as compared with the theoretically proposed doping level.[3] The excess density of holes ($\sim$0.25) is identified to reside on the apical oxygen. On the other hand, superconductivity in $Sr_2CuO_{2+\delta}Cl_{2-y}$ appears only when overdoping of holes is achieved.[1] This indicates that, besides the hole concentration in the CuO_2, the holes at the apical O sites may also play an important role in the occurrence of superconductivity in this material. The evidence for the prominent role of apical holes in superconductivity was also reported in some other hole-doped high-T_c superconductors, such as the $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ system.[26] These experimental results may prove that the inclusion of next-nearest-neighbor hopping of doped holes in the band models[6,27–30] is important.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50471053, 50321101, 50332020, and 5041009) and the State Key Development Program for Basic Research of China (Grant Nos. 2005CB623602 and 2005CB724402).

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