Symmetry of unoccupied electronic states in the high-$T_c$ superconductor Sr$_2$CuO$_2$+$\delta$Cl$_{2-y}$ studied by electron energy-loss spectroscopy

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The symmetry of unoccupied electronic states at the O and Cu sites in the high-$T_c$ superconductor Sr$_2$CuO$_2$+$\delta$Cl$_{2-y}$ has been studied by measuring O 1s 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 2p holes at the apical oxygen sites (about 40% O 2p holes). About 60% O 2p 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% $3d_{z^2}$ symmetry. The Cu 2P$_{3/2}$ absorption edge exhibits clearly divalent Cu(2) states, indicating that the doped holes would reside predominantly on O 2p orbitals. © 2006 American Institute of Physics, [DOI: 10.1063/1.2177359]

Recently, the high-$T_c$ superconductor Sr$_2$CuO$_2$+$\delta$Cl$_{2-y}$ ($T_c=30$ K) has been synthesized with partial substitution of oxygen for apical chlorine by using the high-pressure technique. Its crystallographic structure was determined to be of the tetragonal K$_2$NiF$_4$-type with a space group I4/mmm and lattice parameters $a=b=3.94$ Å, $c=15.64$ Å. Figure 1 schematically shows the structure of the Sr$_2$CuO$_2$+$\delta$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 Sr$_2$CuO$_2$+$\delta$Cl$_{2-y}$ is correlated with the hole 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 $\sigma$ bonded to Cu $d_{x^2-y^2}$ orbitals; $p\pi_{x,y}$ or $p\pi_z$ orbitals in the same plane which are $\pi$ bonded to Cu $d_{x^2-y^2}$ or Cu $d_{y^2}$ orbitals. For the oxygen atom at the apical site above the Cu atom, one can have a $p_z$ orbital forming a $\sigma$ bond or a $p_{x,y}$ orbital forming a $\pi$ bond. At present, there is no consensus about which one of the $\pi$ 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, while some others consider $p\sigma_{x,y}$ orbitals (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.

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 pre-peak on the low-energy part (usually $E<531$ eV) of the

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FIG. 1. Schematic of the structure of Sr$_2$CuO$_2$+$\delta$Cl$_{2-y}$. The (Cl, O)-Sr rock-salt charge reservoir block and the CuO$_2$ conducting layer are shown using thick arrows, respectively.
O 1s absorption edge correspond to O 1s → 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 \( \theta \). 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 1s absorption edges of a \( \text{Sr}_2\text{CuO}_2\text{Cl}_2 \) single crystal for momentum transfers \( q||a, b \) and \( q||c \), respectively. A clear anisotropy is observed and the prepeaks at \( \sim 528.3 \) and \( \sim 529.1 \) 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 \( 2p \) 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 \( 2p_z \) states. The O 1s edge of a normal compound \( \text{Sr}_2\text{CuO}_2\text{Cl}_2 \) 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 \( \sim 528.3 \) eV, observed for \( q||a, b \), is naturally explained as \( 2p_{x, y} \) symmetry in the \( \text{CuO}_2 \) plane. The existence of apical \( 2p_{x, y} \) holes’ symmetry can be discarded. It is remarked that the \( \text{Sr}_2\text{CuO}_2\text{Cl}_2 \) system is very simple; having only two types of oxygen. One of them is the oxygen in the \( \text{CuO}_2 \) 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 1s level, although no information on their exact values is available. If the apical \( 2p_{x, y} \) orbitals are doped with holes, another prepeak should appear on the low-energy part or, at least, the prepeak at \( \sim 528.3 \) eV should be split. But no such evidence was observed in the O 1s absorption edge for \( q||a, b \). There are two types of \( 2p_{x, y} \) orbitals in the \( \text{CuO}_2 \) planes, one is called \( \pi \) lying along the \( \text{Cu}–\text{O} \) bond, the other called \( \pi^* \) 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 \( \text{O} \pi \) orbitals, but the possibility of having holes on the perpendicular \( \pi^* \) orbitals has also been discussed for other superconductors.\(^9\)\(^{10}\) Our measurements, however, cannot differentiate between the in-plane \( \text{O} \pi \) and the \( \pi^* \) holes.

The prepeak at \( \sim 529.1 \) eV, observed for \( q||c \), is ascribed to \( 2p_z \) symmetry at the apical oxygen site. The out-of-plane \( \pi \) holes in the \( \text{CuO}_2 \) planes can be excluded, for if \( 2p_z \) orbitals in the \( \text{CuO}_2 \) planes are doped with holes, the final states from the O 1s level for \( 2p_z \) symmetry would have an energy lower than that for \( 2p_{x, y} \) symmetry, as suggested for other superconductors.\(^9\)\(^{10}\) No prepeak related to the out-of-plane \( \pi \) holes in the \( \text{CuO}_2 \) planes is observed for \( q||c \) at the energies lower than \( \sim 528.3 \) eV (see Fig. 2). The obvious anisotropy observed for the O 1s absorption edges suggests that the O atoms at the apical sites have a bonding energy of the O 1s level higher than those in the \( \text{CuO}_2 \) 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 \( \text{Sr}_2\text{CuO}_2\text{Cl}_2 \) from the \( q||a, b \) and \( q||c \) edges of \( \text{Sr}_2\text{CuO}_2\text{Cl}_2 \). This means that about 60% of the doped holes have \( 2p_{x, y} \) symmetry, and 40% have \( 2p_z \) symmetry.

We also examined briefly the Cu 2p\(_{3/2}\) (\( L_3 \)) absorption edges of \( \text{Sr}_2\text{CuO}_2\text{Cl}_2 \) 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 electron from the \( 2p_{3/2}\) ground states to the \( 2p_{3/2}\) excited states, where \( 2p \) denotes a 2p hole and \( L \) denotes a ligand hole. For \( q||a, b \), a strong excitation into 3d orbitals parallel to the \( \text{CuO}_2 \) planes is observed at \( \sim 932 \) eV, indicating...
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_{x^2-y^2} symmetry, are perpendicular to the CuO₂ planes. The intensity for q||c is about 20% of that for q||a, b. If only ε_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 Bi₂Sr₂CuO₄ reported in Ref. 14. This estimation gives the result that about 14% of the unoccupied 3d states have 3d_{x^2-y^2} symmetry and the rest have 3d_{3z^2-r^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, 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 La₁.₈₅Sr₀.₁₅CuO₄ (Ref. 21), and was interpreted in the same way. In spite of the different symmetry obtained, the Cu 2pₓ/₂₂/₂ absorption edge is similar to that measured by x-ray photoelectron spectroscopy on the normal compound Sr₂CuO₂Cl₂ (Ref. 22), indicating that the doped superconductor Sr₂CuO₂⁺Cl₂₋₋ 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 (≈0.62 holes per unit cell) analyzed in Ref. 2 is the real one, there will be about 0.37 holes (≈60%) having O pₓ₋₋₋ symmetry in the CuO₂ planes and 0.25 holes (≈40%) having O pₓ 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 Sr₂CuO₂Cl₂₋₋ 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 CuO₂ 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 YBa₂Cu₃O₆₆ increases significantly due to the reduction of the \( d_A \) caused by pressure. It is noted that the superconductor Sr₂CuO₂Cl₂₋₋ is obviously overdoped as compared with the theoretically proposed doping level. The excess density of holes (≈0.25) is identified to reside on the apical oxygen. On the other hand, superconductivity in Sr₂CuO₂Cl₂₋₋ appears only when overdoping of holes is achieved. This indicates that, besides the hole concentration in the CuO₂, 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 Y₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋(suite continued)