Electron energy-loss spectroscopy of Sr$_2$CuO$_2$+$\delta$Cl$_2$–$y$: Overdoping and role of apical oxygen for high-$T_c$ superconductivity

H. Yang, Q.Q. Liu, F.Y. Li, C.Q. Jin, R.C. Yu *

Laboratory for Extreme Condition Physics, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, P.O. Box 603, Beijing 100080, PR China

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Abstract

By measuring O 1s and Cu 2p$_{3/2}$ absorption edges of Sr$_2$CuO$_2$+$\delta$Cl$_2$–$y$ using orientation-dependent high-energy electron energy-loss spectroscopy, the changes of the unoccupied electronic structure close to the Fermi level induced by stoichiometry variations have been explored. An interesting hole redistribution between the in-plane O 2p orbitals and apical O 2p orbitals induced by the doping level has been revealed in this system. For the low-doped samples in which superconductivity is absent, the holes reside predominantly on the oxygen sites of the CuO$_2$ plane, while for the high-doped samples in which superconductivity appears, considerable holes are found to enter the apical oxygen sites. This result reveals clearly that the apical O 2p holes play an important role in the occurrence of superconductivity in the ‘apical oxygen doped’ Sr$_2$CuO$_2$+$\delta$Cl$_2$–$y$ system.

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1. Introduction

Crystallographically hole-doped high-$T_c$ copper oxide superconductors consist of block stacking of charge reservoir and the CuO$_2$ conducting plane [1–3], and the connection between the charge reservoir and the CuO$_2$ conducting plane is apical oxygens (above or below the CuO$_2$ plane). Therefore, the existence of apical oxygens is generally regarded as one of the requirements for the occurrence of hole-doped superconductivity in high-$T_c$ copper oxide superconductors (although a few without any oxygen in apical sites were reported to be synthesized [4–6]). Much theoretical work has suggested that the apical oxygen $p_z$ states have an important effect of modifying the electronic structures of the CuO$_2$ plane and in this way govern optimum critical temperature $T_c^{\max}$ [7–10]. Experimentally the existence of O 2p holes in the $p_z$ orbitals of apical oxygen atoms has been shown in many high-$T_c$ copper oxide superconductors [11–14], and the prominent role of apical oxygen holes on superconductivity has also been underlined by experiments [13,14]. In this paper we report clear evidence that superconductivity in the “apical oxygen doped” copper oxychloride compound Sr$_2$CuO$_2$+$\delta$Cl$_2$–$y$ (SCOC) appears only if sufficient holes are also doped on the apical oxygen sites.

The parent compound Sr$_2$CuO$_2$Cl$_2$ with the apical sites outside the CuO$_2$ plane fully occupied by chlorine is an antiferromagnetic Mott insulator with a Néel temperature of 256 K [15]. There are three types of oxylahide cuprates with the K$_2$NiF$_4$-type structure, i.e., Sr$_2$CuO$_2$F$_3$, Ca$_2$CuO$_2$Cl$_2$ and Sr$_2$CuO$_2$Cl$_2$. Al-Mamouri et al. [4] reported that introducing interstitial F$^-$ ions into the Sr$_2$CuO$_2$F$_3$ compound yielded 46 K superconductivity, and Hiroi et al. [5] showed that 26 K superconductivity was rendered in the
Ca$_2$CuO$_2$Cl$_2$ compound by the substitution of Na$^+$ for Ca$^{2+}$. For these two K$_2$NiF$_4$-type oxyhalide cuprates, apical oxygen is seemingly not necessary for the occurrence of superconductivity. However, for the Sr$_2$CuO$_2$Cl$_2$, apical oxygen introduced by partial substitution of oxygen for apical chlorine (this doping mechanism is called “apical oxygen doping” [16]) would be one of the requirements for the occurrence of superconductivity since “apical oxygen doping” has been shown to be a unique effective way of hole doping in this compound [17,18]. Recently, this copper oxychloride compound has been successfully rendered superconductivity by “apical oxygen doping” using a high-pressure and high-temperature technique [19]. The structural characterization by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) suggested that the doped Sr$_2$CuO$_{2+y}$Cl$_{2-y}$ keeps well the structural properties of its parent compound Sr$_2$CuO$_2$Cl$_2$ (K$_2$NiF$_4$-type structure) [20]. Fig. 1 shows schematically the structure of this system.

It is interesting that superconductivity in the SCOC system appears only when overdoping of holes is achieved [19]. Study of the holes’ symmetry of the 30 K superconductor Sr$_2$CuO$_{2+y}$Cl$_{2-y}$ (nominal $y = 0.8$) using orientation-dependent high-energy electron energy-loss spectroscopy (EELS) revealed that the excess density of holes resides on the apical oxygen 2$p$ orbitals [21]. Since superconductivity in this system appears only when overdoping of holes is achieved, it is interesting to explore the changes of the electronic states close to the Fermi level induced by stoichiometry variations.

High-energy EELS in transmission is a simple method to investigate the local density of unoccupied electronic states of high-$T_c$ superconductors. The unoccupied O 2$p$ and Cu 3$d$ states are probed by measuring O 1$s$ and Cu 2$p$ absorption edges, respectively. The information on the symmetry of the unoccupied states can be obtained by performing orientation-dependent measurements on single crystals.

2. Experimental

By controlling oxygen pressure provided by the oxidizer amount and changing chlorine content, we prepared a series of samples with the formula Sr$_2$CuO$_{2+y}$Cl$_{2-y}$, for nominal $y = 0.2$, 0.4, 0.6, 0.8, 1.0 and 1.2. All the samples were synthesized at 1050 °C for 1 h under a high-pressure of 6 GPa using Sr$_2$CuO$_3$ and Sr$_2$CuO$_2$Cl$_2$, prepared by conventional solid state reaction method under ambient pressure, as precursors. Details of the samples preparation are described in Ref. [19]. Thin samples for TEM and EELS studies were prepared by mechanical thinning, followed by argon ion milling. A liquid nitrogen cold stage was used during ion milling to reduce the damage by ion beams.

All the samples as-prepared were examined by XRD. The samples for nominal $y \leq 0.8$ showed nearly single-phase Cl-0201-type structure from the XRD data [19] (the following work was therefore performed on the samples for nominal $y \leq 0.8$). More detailed TEM investigation of these samples showed no trace of other phases with the similar 0201-type structure or higher member of the same homologous series, either. Therefore, the observed bulk superconductivity at 36 and 30 K, respectively, in the samples for nominal $y = 0.6$ and 0.8 [19] can be said to be caused by the “apical oxygen doped” Cl-0201 phase. Compositional analyses of the samples were carried out using energy dispersive analysis of X-ray (EDX). For each sample, 10 perfect grains were measured and the average proportion of Sr, Cu and Cl in atomic ratio was obtained. The results showed that the analyzed Sr and Cu contents agree well with their stoichiometric values in all the samples, and the Cl contents in $y$ in the samples Sr$_2$CuO$_{2+y}$Cl$_{2-y}$ for nominal $y = 0.2$, 0.4, 0.6 and 0.8 are 0.2, 0.38, 0.55 and 0.62, respectively. From the compositional analysis results, the total hole counts ($n_{total}$) in each sample can be obtained if neglecting the oxygen vacancy in the anion sites (this neglecting is reasonable as the samples were synthesized under a high oxidizing pressure). In addition, no obvious inhomogeneity of chemical composition was found in the perfect grains according to the characterization by EDX.

The O 1$s$ and Cu 2$p$ absorption edges were measured on a Tecnai F20 field-emission electron microscope operated at 200 kV. In our experiments, the scattering geometry with zero scattering angle $\theta$ has been used to measure the density and symmetry of unoccupied states. In this way, the momentum transfer $q$ is parallel to the electron beam and is determined by the energy-loss to be $q = q_0 = k_0 E/2E_0$, where $k_0$ and $E_0$ are the momentum and the energy of the incoming electron, respectively. More details on transmission EELS experiments are discussed elsewhere [22–24]. Spectra were acquired with a collection angle of about 0.2 mrad in diffraction mode. For this condition,
transitions mostly parallel to the electron beam are detected, and transitions with scattering vector perpendicular to the electron beam can be neglected.

We would point out that the “apical oxygen doped” Cl-0201 phase appeared to be stable under the illumination with weak electron beam, while exposed to the electron beam with high intensity this phase suffered from microstructure change [25]. Therefore, we tried our best, during the TEM and EELS experiments, not to expose the samples to the intense electron beam, so as to avoid the electron-irradiation effects on the samples.

3. Results and discussion

Fig. 2 shows the O 1s absorption edges of Sr₂CuO₂⁺yCl₂–y for various values of y (where y = 0 denotes the parent compound Sr₂CuO₂Cl₂ synthesized under ambient pressure). The spectra in Fig. 2a were obtained for momentum transfer q || a, b, while those in Fig. 2b were obtained for q || c. The solid lines are merely guides to the eye. The significant difference between both sets of spectra is seen on their low-energy part (E < 531 eV). In the q || a, b spectra we see the appearance of a clear pre-peak at about 528.3 eV for all the doped samples, while in the q || c spectra the appearance of a pre-peak at about 529.1 eV is clearly seen only for y = 0.55 and 0.62 (although a pre-peak is also visible for y = 0.38, its intensity is very weak). A large number of theories and experimental measurements have suggested that pre-peak on the low-energy part (usually E < 531 eV) of the O 1s absorption edge correspond to O 1s → O 2p transitions with the 2p holes near the Fermi level, and the intensities of the pre-peaks are proportional to the number of holes induced by doping. The momentum transfer for q || a, b probes the unoccupied states at the oxygen sites with 2pₓᵧ symmetry while that for q || c probes O 2p states. Therefore, the orientation-dependent O 1s EELS spectra can give information on the hole distributions in our samples and this will be discussed in detail in the following.

Fig. 3a and b shows, respectively, the q || a, b and q || c Cu 2p₃/2 (L₃) absorption edges of Sr₂CuO₂⁺yCl₂–y, for various values of y. The Cu 2p₃/2 edge corresponds to Cu(2p₃/2)3dₓ²→ₚₓᵧ → Cu(2p₃/2)3dₓ²→ₚₓᵧ transitions, where 2p denotes a 2p hole and Lₓᵧ denotes a ligand hole. A strong anisotropy is observed for all the samples. For q || a, b, a strong excitation into 3d orbitals parallel to the CuO₂ planes is observed at ~932 eV, indicating that most of the unoccupied 3d states have 3dₓ²→ₚₓᵧ symmetry. For q || c, there is a much smaller edge at almost the same energy, indicating that much less unoccupied 3d states, probably having 3dₓ²→ₚₓᵧ symmetry, are perpendicular to the CuO₂ planes. In addition, one can see that the q || a, b main line for all the doped samples shows a clear asymmetry which may be explained by the influence of holes on oxygen sites. A weak asymmetry of the main line was also observed in the X-ray absorption spectrum measured on La₁₋₈Sr₀.₁₃₋₀.₁₅ CuO₄ (Ref. [26]) and was interpreted in the same way. When comparing the Cu 2p₃/2 absorption edges of the doped samples with those of the parent sample, it turns out that all the doped samples, independent of the number of holes introduced to them, exhibit clearly divalent Cu(2) states. This means that the doped-holes reside predominantly on O 2p orbitals.

Now we focus on the discussion on the O 1s absorption edges. The pre-peak at ~528.3 eV, observed for q || a, b, is naturally explained as O 2pₓᵧ symmetry in the CuO₂ plane. The existence of apical O 2pₓᵧ holes’ symmetry can be discarded. It is remarked that the SCOC system is very simple having only two types of oxygen. One of them is the oxygen in the CuO₂ 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 O 2pₓᵧ orbitals are doped with holes, another pre-peak should appear on the low-energy
part or, at least, the pre-peak at ~528.3 eV should be split. No such evidence was observed in the $q || a, b$ O 1s absorption edges for all the doped samples (see Fig. 2). There are two types of O 2p$_{x,y}$ orbitals in the CuO$_2$ planes, one is called p$_x$ lying along the Cu–O bond, the other called p$_x$ lying perpendicular to it. Our measurements cannot differentiate between the in-plane O 2p$_{x,y}$ and the p$_x$ orbitals. However, it is reasonable to assume that the holes are located on O 2p$_{x,y}$ orbitals since the antibonding combination represents the highest occupied orbital, and will be the first one to be depleted when creating holes via doping.

The pre-peak at ~528.1 eV, observed for $q || c$, is ascribed to O 2p$_z$ symmetry at the apical oxygen atom 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 state 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 [27]. For all the doped samples, no pre-peak 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.

Since the intensity of the pre-peak is proportional to the number of doped-holes, we give estimates of the relative contributions of the in-plane O 2p$_{x,y}$ and apical O 2p$_z$ orbitals to further discuss the electronic structure. In order to get a better impression of the changes of the pre-peak which occur with $y$, we show in Fig. 4 the $q || a, b$ (left part) and $q || c$ (right part) difference spectra with the $q || a, b$ O 1s absorption edge of the parent sample Sr$_2$CuO$_2$Cl$_2$. To obtain these difference spectra we normalized each spectrum in Fig. 2a and b to have the same integrated area between 532 and 545 eV and then subtracted the $q || a, b$ edge of the parent sample. These difference spectra were then smoothed by splines. Assuming the average proportion of Sr, Cu and Cl in atomic ratio analyzed by TEM-EDX for each doped sample is the real one and neglecting the oxygen deficiency, the total hole counts $n_{\text{total}}$ doped in each sample were obtained. The doped-holes were verified by the Cu 2p$_{3/2}$ data to reside predominantly on O 2p orbitals, and the hole distribution between the in-plane O 2p$_{x,y}$ and apical O 2p$_z$ orbitals was derived approximately from the intensity ratio of the $q || a, b$ and $q || c$ pre-peaks. The number of holes $n_{\text{plane}}$ and $n_{\text{apex}}$ for the samples obtained from the difference spectra data (see Fig. 4) is listed in Table 1 along with the $T_c$ values. From the table, we first note an interesting change of hole distributions which occur with the doping level for the SCOC system. For the low-doped samples Sr$_2$CuO$_2$.55Cl$_1.45$ and Sr$_2$CuO$_2$.38Cl$_1.62$ the holes are located predominantly on the CuO$_2$ plane, while for the high-doped samples Sr$_2$CuO$_2$.55Cl$_1.45$ and Sr$_2$CuO$_2$.62Cl$_1.38$ considerable holes are found to be on the apical oxygen sites. This hole redistribution between the CuO$_2$ plane and apical sites induced by the doping level could be explained by the increase of the bond length of apical O–in-plane Cu ($d_A$), since the $d_A$ increases with the increase of number of holes [19]. The hole redistribution caused by the change of bond length $d_A$ is also observed in other superconductors. For example, the in-plane hole concentration of YBa$_2$Cu$_4$O$_8$ increases significantly due to the reduction of the $d_A$ caused by pressure [28,29]. The redistribution of charges between CuO$_2$ plane and other planes has been also observed in YBa$_2$Cu$_{3-x}$O$_{7-x}$ when the bond length $d_A$ changes with the variation of $\delta$ (but not due to pressure) [30].

The data in Table 1 show that for the Sr$_2$CuO$_2$.38Cl$_1.62$, Sr$_2$CuO$_2$.55Cl$_1.45$ and Sr$_2$CuO$_2$.62Cl$_1.38$ samples the $n_{\text{plane}}$ is very close and can be regarded as the same doping level, but only the latter two samples exhibit superconductivity. This phenomenon can be reasonably explained by the differences of their $n_{\text{apex}}$, i.e., in the superconducting samples considerable holes are doped in the apical oxygen sites, while in the nonsuperconducting sample few holes are doped in the apical oxygen sites. This leads to a result: for the “apical oxygen doped” SCOC system, holes on the CuO$_2$ planes alone could not induce superconductivity if there were not also sufficient holes-doped on the apical oxygen sites. The prominent role of apical holes on superconductivity has also been revealed in some other hole-doped high-$T_c$ superconductors such as the Ca-doped YBCO system [13,14]. These experimental results may prove that the inclusion of next-nearest-neighbor hopping of doped-holes in the band models [7–10] is important.

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**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n_{\text{plane}}$</th>
<th>$n_{\text{apex}}$</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$CuO$_2$.3Cl$_1$.8</td>
<td>0.20</td>
<td>0</td>
<td>~ —</td>
</tr>
<tr>
<td>Sr$_2$CuO$_2$.35Cl$_1$.62</td>
<td>0.33</td>
<td>0.05</td>
<td>30</td>
</tr>
<tr>
<td>Sr$_2$CuO$_2$.55Cl$_1$.45</td>
<td>0.35</td>
<td>0.20</td>
<td>36</td>
</tr>
<tr>
<td>Sr$_2$CuO$_2$.62Cl$_1$.38</td>
<td>0.37</td>
<td>0.25</td>
<td>30</td>
</tr>
</tbody>
</table>

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Fig. 4. Smoothed difference spectra of the $q || a, b$ (left part) and $q || c$ (right part) O 1s absorption edges of Sr$_2$CuO$_2$.55Cl$_1$.45 with respect to the $q || a, b$ O 1s edge of the normal sample Sr$_2$CuO$_2$Cl$_2$ as a percentage of the mean height between 532 and 545 eV.
4. Conclusion

We have studied the O 1s and Cu 2p\textsubscript{3/2} absorption edges of Sr\textsubscript{2}CuO\textsubscript{2+y}Cl\textsubscript{2−y} by means of orientation-dependent high-energy electron energy-loss spectroscopy, and the changes of the unoccupied electronic structure close to the Fermi level, which occur with the doping level, have been revealed in this system. For the low-doped samples in which superconductivity is absent, the doped-holes are found to reside predominantly on the oxygen sites of the CuO\textsubscript{2} plane; while for the high-doped samples in which superconductivity appears, considerable holes are found to enter the apical oxygen sites. Our studies reveal a clear picture about the superconductivity in the “apical oxygen doped” SCOC system: holes on the CuO\textsubscript{2} planes alone could not induce superconductivity if there were not also sufficient holes-doped on the apical oxygen sites.

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