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Electron energy-loss spectroscopy of $Sr_2CuO_{2+\delta}Cl_{2-y}$: Overdoping and role of apical oxygen for high-T_c superconductivity

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Abstract

By measuring O 1s and Cu $2p_{3/2}$ absorption edges of $Sr_2CuO_{2+\delta}Cl_{2-y}$ 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' $Sr_2CuO_{2+\delta}Cl_{2-y}$ system.

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Keywords: $Sr_2CuO_{2+\delta}Cl_{2-y}$; EELS; Apical oxygen

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 $Sr_2CuO_{2+\delta}Cl_{2-y}$ (SCOC) appears only if sufficient holes are also doped on the apical oxygen sites.

The parent compound $Sr_2CuO_2Cl_2$ 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 oxyhalide cuprates with the K_2NiF_4-type structure, i.e., $Sr_2CuO_2F_2$, $Ca_2CuO_2Cl_2$ and $Sr_2CuO_2Cl_2$. Al-Mamouri et al. [4] reported that introducing interstitial F^- ions into the $Sr_2CuO_2F_2$ compound yielded 46 K superconductivity, and Hiroi et al. [5] showed that 26 K superconductivity was rendered in the

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$Ca_2CuO_2Cl_2$ compound by the substitution of Na^+ for Ca^{2+}. For these two K_2NiF_4-type oxyhalide cuprates, apical oxygen is seemingly not necessary for the occurrence of superconductivity. However, for the $Sr_2CuO_2Cl_2$, 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 $Sr_2CuO_{2+\delta}Cl_{2-y}$ keeps well the structural properties of its parent compound $Sr_2CuO_2Cl_2$ (K_2NiF_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 $Sr_2CuO_{2+\delta}Cl_{2-y}$ (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 $2p_z$ 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 2p and Cu 3d states are probed by measuring O 1s and Cu 2p absorption edges, respectively. The information on the symmetry of the unoccupied states can be obtained by performing orientation-dependent measurements on single crystals.

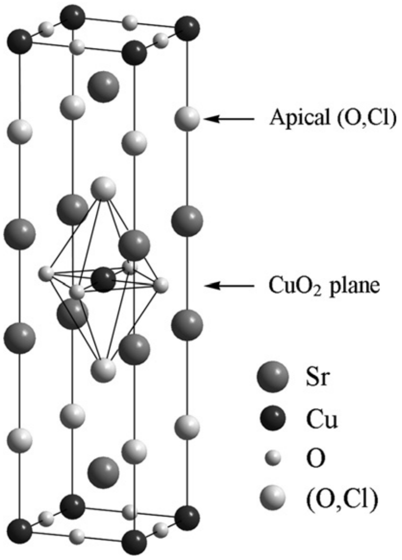

Fig. 1. Schematic view of the crystal structure of $Sr_2CuO_{2+\delta}Cl_{2-y}$.

2. Experimental

By controlling oxygen pressure provided by the oxidizer amount and changing chlorine content, we prepared a series of samples with the formula $Sr_2CuO_{2+\delta}Cl_{2-y}$ 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_2CuO_3 and $Sr_2CuO_2Cl_2$, 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 $y \leqslant 0.8$ showed nearly single-phase Cl-0201-type structure from the XRD data [19] (the following work was therefore performed on the samples for nominal $y \leqslant 0.8$). 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 $Sr_2CuO_{2+\delta}Cl_{2-y}$ 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 1s and Cu 2p absorption edges were measured on a Tecnai F20 field-emission electron microscope operated at 200 keV. In our experiments, the scattering geometry with zero scattering angle θ 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 $q = q_{\parallel} = k_0E/2E_0$, 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,