Chemical Control of Underdoped and Overdoped States in Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$


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The chemical control of underdoped and overdoped states in the Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ compounds has been observed by high-resolution O K-edge X-ray-absorption near-edge-structure spectra. The chemical substitution of Sr for Ba in the fully-oxygenated Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ compounds gives rise to high hole concentrations within both the CuO$_2$ planes and the out-of-plane sites, leading to the overdoped state and the decrease in the superconducting transition temperature from 92 K for $y=0$ to 84 K for $y=0.8$. In contrast, an increase in the Sr content in the oxygen-deficient Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ compounds did not indicate superconductivity. The oxygen-deficient compounds exhibit the underdoped state due to the low hole concentration.

1. INTRODUCTION

Isovalent chemical substitution of Sr$^{2+}$ for Ba$^{2+}$ in the Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ ($\delta=0.7-0.9$) system reduces the $T_c$ value [1-12]. In contrast, replacement of Y$^{3+}$ by various 3$^+$/rare-earths (except Pr) has only minor effects on $T_c$. The series of Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ ($\delta=0.7-0.9$) compounds have been studied by means of X-ray diffraction [1,8-10,12], neutron diffraction [6,11], extended X-ray-absorption fine structure (EXAFS) [4], X-ray absorption near edge structure (XANES) [12], infrared spectra, and Raman scattering [7,11]. However, the reasons for the suppression of superconductivity in Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ have been a major puzzle in the cuprate superconductors.

A local perturbation of the structure in the neighborhood of the Sr sites (the oxygen vacancies along the CuO chains were induced by Sr doping) is well recognized to be the possible model for explaining the depression of superconductivity in Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ (\(\delta=0.9\)) [2]. However, Ganguli and Subramanian [9] found the decrease in $T_c$ in both series of Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ ($\delta=0.7$ and 1) with fixed oxygen contents. Their results indicate that the oxygen vacancies cannot be the cause of the fall in $T_c$ with Sr substitution. They also pointed out that the Sr substitution brings about a similar decrease in $T_c$ in the Tl$_2$Ba$_2$CuO$_6$ ($T_c=90$ K) high-$T_c$ superconductor [14]. Therefore, other factors are responsible for the depression of the $T_c$ in the Y(Ba$_{2-y}$Sr$_y$)Cu$_3$O$_6+\delta$ system.

It is well known that hole states play a pivotal role in the $p$-type cuprate superconductors. Therefore, a knowledge of the electronic structure near the Fermi level of these compounds is an important step toward unveiling the mechanism of superconductivity. The X-ray absorption spectra are determined by electronic transitions from a selected atomic core level to the unoccupied electronic states near the Fermi level. X-ray absorption near edge structure (XANES) is therefore a direct probe of the character and local density of hole states responsible for high-$T_c$ superconductivity.

To improve our understanding of the mechanism of $T_c$ suppression, a detailed study using the X-ray
absorption spectroscopy on \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) systems would be helpful. We therefore measure systematically the variations of electronic structure near the Fermi level for a series of \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta = 0.1 \) and 0.9) compounds by the XANES method. Although Song et al. [12] have conducted similar studies on the fully-oxygenated \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta = 0.9 \)) samples, they failed to observe the significant variation of the hole concentration as a function of the Sr doping. Moreover, in order to observe the intrinsic doping effect of Sr (rule out the contribution from the CuO chain sites), we also prepared a series of oxygen-deficient \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta = 0.1 \)) compounds. In this study, bulk-sensitive O 1s-edge X-ray fluorescence yield measurements in \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) for \( \delta = 0.1 \) and 0.9 were performed in order to investigate how the variation of hole states near the Fermi level induced by the Sr doping is related to the superconductivity.

2. EXPERIMENTAL

The samples of \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) were prepared by mixing powders of \( \text{Y}_2\text{O}_3, \text{BaCO}_3, \text{SrCO}_3, \) and \( \text{CuO} \). The mixtures were calcined at 950°C for 20 h in air. The resulting mixtures were ground and pressed into pellets. The pellets were sintered at 950°C for 20 h in air. The \( \delta = 0.9 \) (fully-oxygenated) samples were obtained when the sintered pellets were annealed at 400°C for 20 h in O\(_2\). Moreover, the \( \delta = 0.1 \) (oxygen-deficient) samples were achieved by annealing the sintered pellets at 730°C for 20 h in Ar then quenching into liquid nitrogen within 1 sec.

Powder X-ray diffraction (XRD) analyses of the samples were performed using a SCINTAG (X1) diffractometer (Cu K\( \alpha \) radiation). Data for the Rietveld refinement were collected in the range 20-110° with step size of 0.02° and a count time of 10 s per step. The program of GSAS [15] was used for the Rietveld refinement in order to obtain information on the crystal structure of \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \). All the samples are in single phase. The fully-oxygenated \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta = 0.9 \)) samples were orthorhombic and could be indexed on the \( Pmmm \) space group. The oxygen-deficient \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta = 0.1 \)) samples were tetragonal with \( P4/mmm \) space group. The decrease in the cell volume with increasing the Sr content was found in both fully-oxygenated \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta = 0.9 \)) and oxygen-deficient (\( \delta = 0.1 \)) samples. This is simply a manifestation of smaller size of the substituting \( \text{Sr}^{2+} \) ions [1.36 Å for C.N. (coordination number) = 10] as compared to the \( \text{Ba}^{2+} \) ions (1.52 Å for C.N. = 10) [16].

Two chemical titration methods were used to determine the oxygen contents in the fully-oxygenated [17] and oxygen-deficient [18] samples which were found to be around 0.92 and 0.13, respectively. Magnetization data were taken from a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The chemical substitution of the \( \text{Sr}^{2+} \) ions for the \( \text{Ba}^{2+} \) ions in fully-oxygenated \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta = 0.9 \)) leads to a monotonic decrease in the superconducting temperature from \( T_c \sim 92 \) K for \( y = 0 \) to \( T_c \sim 84 \) K for \( y = 0.8 \). However, an increase in the Sr content in the oxygen-deficient \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta \sim 0.1 \)) compounds did not indicate superconductivity.

Using the 6-m high-energy spherical grating monochromator (HSGM) beamline, the X-ray absorption measurements were performed at the Synchrotron Radiation Research Center (SRRC) with an electron beam energy of 1.5 GeV and a maximum stored current of 240 mA. X-ray-fluorescence-yield spectra were recorded using a microchannel plate (MCP) detector [19]. This MCP detector is composed of a dual set of MCPs with an electrically isolated grid mounted in front of them. X-ray fluorescence yield measurement is strictly bulk sensitive with a probing depth of thousands of angstroms. During the X-ray fluorescence yield measurements, the grid was set to a voltage of 100 V while the front of the MCPs was set to \(-2000 \) V and the rear to \(-200 \) V. The negative MCP bias was applied to expel electrons before they entered the detector, while the grid bias ensured that no positive ions were detected. The MCP detector was located at \(-2 \) cm from the sample and oriented parallel to the sample surface. Photons were incident at an angle of 45° with respect to the sample normal. The incident photon intensity (\( I_0 \)) was measured simultaneously by a Ni mesh located after the exit slit of the monochromator. All the absorption spectra were normalized to \( I_0 \). The photon energy was calibrated using the known O K-edge absorption peaks of CuO. The energy resolution of the monochromator was set to \(-0.22 \) eV for the O K-edge X-ray absorption measurements. All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

In Fig. 1, the O K-edge X-ray absorption spectra for a series of fully-oxygenated \( \text{Y(Ba}_{2-y}\text{Sr}_y)\text{Cu}_6\text{O}_{16+\delta} \) (\( \delta \sim 0.9 \)) samples with \( y = 0 \)–0.8 are shown in the
Underdoped and Overdoped States in $Y(Ba_{2-y}Sr_y)Cu_3O_{6+\delta}$

The O K-edge X-ray absorption spectra for a series of fully-oxygenated $Y(Ba_{2-y}Sr_y)Cu_3O_{6+\delta}$ samples with $y = 0-0.8$.

Fig. 1. The O K-edge X-ray absorption spectra for a series of fully-oxygenated $Y(Ba_{2-y}Sr_y)Cu_3O_{6+\delta}$ samples with $y = 0-0.8$. Energy range of 525-540 eV obtained using a bulk-sensitive total X-ray fluorescence yield technique. The major features in the O 1s X-ray absorption spectrum of the sample with $y = 0.4$, as shown in Fig. 1, are three distinct prepeaks at -528.3, -529.3, and -530.5 eV, respectively, together with a shoulder at -527.7 eV, and a broad peak at 537 eV. The low-energy prepeaks with energy below 532 eV are ascribed to photoexcitation of the O 1s core electrons to holes with predominantly $2p$ character on the oxygen sites. Unoccupied states related to the Ba 4d and Y 5d states hybridized with O 2p states could be the origin for the enhanced peaks above 532 eV as observed in the O 1s X-ray absorption spectrum of the sample with $y = 0.4$. The O K-edge X-ray absorption spectra for various compounds with different $x$ values in Fig. 1 were normalized to the same height at the main peak of -537 eV.

Band-structure calculations based on the local-density approximation (LDA) have been successful to calculate the electronic structure of the cuprate superconductors [20]. According to the LDA band-structure calculations in $YBa_2Cu_3O_{6+\delta}$ ($\delta = 0.9-1$), the O(2,3) atoms in the CuO$_2$ planes and the O(1) atom in the CuO chain are predicted to have the largest and the lowest binding energy of the O 1s level, respectively. Moreover, based on the polarization-dependent X-ray absorption measurements on a single crystal of $YBa_2Cu_3O_{6+\delta}$ ($\delta = 0.9-1$), it was found that O(2,3) [in the Cu(2)O$_2$ planes] 1s level is about 0.8 eV lower in energy than the O(4) [in the BaO planes] 1s level [22]. The O(1) [in the Cu(1)O chain] 1s binding energy is in between those of O(4) and O(2,3). These results are consistent with the theoretical prediction.

In O K-edge X-ray absorption spectra of $Ba_2Cu_3O_{6+\delta}$ ($\delta = 0.9-1$), the prepeaks at -527.8 eV are attributed to transitions into O 2p holes in the CuO$_2$ ribbons [apical oxygen O(4) sites and Cu(1)O(1) chains sites]. The high-energy prepeak at -528.5 eV is ascribed to transitions into O 2p hole states within the Cu(2)O(2,3)$_2$ planes [22,23].

The orthorhombic $Y(Ba_{2-y}Sr_y)Cu_3O_{6+\delta}$ ($\delta = 0.9-1$) compounds are isomorphic with $YBa_2Cu_3O_{6+\delta}$ ($\delta = 0.9-1$) (space group Pmmm). With the increase in the Sr content in $Y(Ba_{2-y}Sr_y)Cu_3O_{6+\delta}$ ($\delta = 0.9-1$), the compounds still keep the orthorhombic form. We did not observe any phase transition (from orthorhombic to tetragonal) at a particular Sr concentration in the $Y(Ba_{2-y}Sr_y)Cu_3O_{6+\delta}$ ($\delta = 0.9-1$) system. As shown in Fig. 1, the O 1s X-ray absorption spectrum of $Y(Ba_{2-y}Sr_y)Cu_3O_{6+\delta}$ ($\delta = 0.9-1$) with $y = 0.4$ exhibits similar features as observed in $YBa_2Cu_3O_{6+\delta}$ ($\delta = 0.9-1$). We therefore adopt the same assignment scheme for the O 1s X-ray absorption spectra of $Y(Ba_{2-y}Sr_y)Cu_3O_{6+\delta}$ ($\delta = 0.9-1$). The high-energy prepeak at -528.5 eV is attributed to the excitation of O 1s electrons to O 2p holes in the Cu(2)O(2,3)$_2$ planes. The low-energy prepeaks at -527.7 eV in Fig. 1 are due to the superposition of O 2p hole states in the apical oxygen sites [O(4) and the Cu(1)O(1)] chains. The peaks at 527.7 and 528.3 eV corresponds to the transitions from O 1s state into the valence band.

The peak at about 529.3 eV is ascribed to transitions into the conduction band (upper Hubbard band), which is predominantly formed by the hybridization in the ground state of the Cu3$d^9$ and Cu3$d^{10}$L states, where L is a ligand hole from the O 2p band [22,23]. Due to the strong on-site correlation effects on the copper sites in the cuprate superconductors, the upper Hubbard band (UHB) has always been assumed to exist. Moreover, the peak at -530.5 eV (as shown in Fig. 1) is due to the transition...
Liu, Chang, Chen, and Liu

Fig. 2. The integrated intensity of each prepeak, normalized against that of the main peak at \(-537\) eV, is plotted as a function of Sr content \(y\) in \(\text{Y(Ba}_2\text{Sr}_y\text{Cu}_3\text{O}_{6+x}(\delta\sim0.9)}\).

In order to investigate the variation of the hole states among different oxygen sites as a function of the Sr doping, these pre-edge features were analyzed by fitting Gaussian functions to each spectrum. In Fig. 2 the relative integrated intensity of each prepeak as analyzed by the curve fitting, normalized against that of the main peak at \(-537\) eV, is plotted as a function of Sr content \(y\) in \(\text{Y(Ba}_2\text{Sr}_y\text{Cu}_3\text{O}_{6+x}(\delta\sim0.9)}\). As seen in Fig. 2, the hole contents from the CuO planes and apical and chain sites increase with increasing Sr doping for \(y < 0.6\) and saturate for \(y > 0.6\). This clearly reveals that the overdoped state among the plane, apical, and chain oxygen sites can be achieved by Sr doping in the fully-oxygenated \(\text{Y(Ba}_2\text{Sr}_y\text{Cu}_3\text{O}_{6+x}(\delta\sim0.9)}\) sample. Higher Sr doping level will give rise to a heavier doped hole state of the sample and lead to the depression of \(T_c\) in \(\text{YBa}_2\text{Cu}_3\text{O}_{6+x}(\delta\sim0.9)}\). It is also worth pointing out that the intensity for the upper Hubbard bands also increases with Sr doping. This phenomenon is not clear at this stage.

In order to remove the contribution from the Cu(1)O(4) chain, the intrinsic contribution of Sr doping in the oxygen-deficient \(\text{Y(Ba}_2\text{Sr}_y\text{Cu}_3\text{O}_{6+x}(\delta\sim0.1)}\) can fit the goal. In Fig. 3, the O K-edge X-ray absorption spectra for a series of fully-oxygenated \(\text{Y(Ba}_2\text{Sr}_y\text{Cu}_3\text{O}_{6+x}(\delta\sim0.1)}\) samples with \(y = 0-1.0\) are shown in the energy range of 525-540 eV obtained using a bulk-sensitive total X-ray fluorescence yield method. The major features in the O 1s X-ray absorption spectrum of such samples, as shown in Fig. 3, are similar to those in Fig. 1. We therefore apply a similar approach to analyze the variation of the hole states among different oxygen sites as a function of the Sr doping. In Fig. 4 the integrated intensity of each prepeak, normalized against that of the

Fig. 3. The O K-edge X-ray absorption spectra for a series of fully-oxygenated \(\text{Y(Ba}_2\text{Sr}_y\text{Cu}_3\text{O}_{6+x}(\delta\sim0.1)}\) samples with \(y = 0-1.0\).

Fig. 4. The integrated intensity of each prepeak, normalized against that of the main peak at \(-537\) eV, is plotted as a function of Sr content \(y\) in \(\text{Y(Ba}_2\text{Sr}_y\text{Cu}_3\text{O}_{6+x}(\delta\sim0.1)}\).
main peak at ~537 eV, is plotted as a function of Sr content \(y\) in \(\text{Y(Ba}_{2-y}\text{Sr}_y\text{Cu}_3\text{O}_{6+s}}\ (\delta \sim 0.1)\).

Based on the results in Fig. 4, we can conclude that the hole concentration within the plane, apical, and chain oxygen sites can be increased by increasing the Sr content in the oxygen-deficient \(\text{Y(Ba}_{2-y}\text{Sr}_y\text{Cu}_3\text{O}_{6+s}}\ (s \sim 0.1)\) samples. This again confirms that the Sr doping can effectively increase the hole concentration in the cuprate superconductors. Because the parent \(\text{YBa}_{2}\text{Cu}_3\text{O}_{6+s}\) (without the hole contribution from the CuO chain) is in the underdoped state, no superconductivity has been found in the oxygen-deficient Sr-doped samples.

4. CONCLUSIONS

In this study, we reported the O 1s-edge X-ray absorption spectra for a series of \(\text{Y(Ba}_{2-y}\text{Sr}_y\text{Cu}_3\text{O}_{6+s}}\ (s \sim 0.1\) and 0.9) compounds. Near the O 1s edge, the multiple prepeaks are related to the different O 1s binding energies of the nonequivalent oxygen sites in the crystal structure. As deduced from the O 1s X-ray absorption spectra, the hole concentrations originating from the CuO planes and CuO3 ribbons can be increased in \(\text{Y(Ba}_{2-y}\text{Sr}_y\text{Cu}_3\text{O}_{6+s}}\ (\delta \sim 0.1\) and 0.9) by increasing the Sr doping. The present XANES results clearly demonstrate that the suppression of superconductivity with Sr substitution in fully-oxygenated \(\text{Y(Ba}_{2-y}\text{Sr}_y\text{Cu}_3\text{O}_{6+s}}\ (\delta \sim 0.9)\) arises predominantly from overdoping.

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