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LETTER TO THE EDITOR

The character of doped holes in $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$: polarization-dependent x-ray fluorescence study at the O K edge

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Abstract. Orbital-resolved O K α x-ray fluorescence spectra of in-CuO₂-plane [O(1)] and apical [O(2)] oxygen atoms were obtained for $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ by making an appropriate choice of the energy of incident photons and the crystal orientation relative to the polarization vector of the incoming radiation. The site origin of 2p_{x,y} and 2p_z components in the Sr-doping-induced absorption prepeak near the O 1s edge, associated with states developed in the energy gap, was studied by O K α monitoring at the excitation energy of the prepeak. The spectral analysis, based on the O K α shape difference between inequivalent O sites, supports the assignment of the doping-induced 2p_{x,y} holes to the O(1) atoms but suggests that the 2p_z holes may have both O(2) and O(1) character in contrast to assignments in prior studies.

In p-type high- T_c superconducting cuprates, charge carriers were found to have mainly O 2p character [1]. This triggered a discussion on the role of in-CuO₂-plane oxygen and apical oxygen atoms, forming the Cu–O octahedra (pyramids), and their different Cu–O bonds in the high- T_c superconductivity mechanism.

While most of the theoretical models are based on Cu 3d_{x²-y²}-O(1) 2p_{x,y} σ -coupling, some emphasize the role of Cu 3d_{z²-r²}-O(2) 2p_z σ -bonding [2, 3]. A number of quantum-chemical calculations [4, 5] found the O(1) 2p_{x,y} π -contribution at E_F , thus suggesting an involvement of the Cu 3d_{xy}-O(1) 2p_{x,y} orbitals in the superconductivity mechanism. Some theoretical studies [6] indicated O(1) 2p_z-O(1) 2p_z overlap at E_F promoted by Cu 3d_{xz,yz}-O(1) 2p_z π -antibonding hybridization. It was argued that delocalized O(1) 2p_z-O(1) 2p_z π -bonds with a shallow ‘double-well’ potential parallel to the CuO₂ planes can be a basis for Cooper pairing.

In this uncertain situation, site-selective techniques, probing the local electronic structure, are of particular value. One such technique is x-ray fluorescence (XF) spectroscopy with tunable monochromatic photon excitation. As shown for some cuprates using O K α (2p \rightarrow 1s transitions) measurements [7, 8], the 2p states in the valence band belonging to different O sites can be selectively studied by virtue of large variations in the O 1s x-ray absorption (XA) cross-section for inequivalent sites at specific excitation energies as well as by taking advantage of 1s chemical shifts between the sites. And vice versa, the character of unoccupied states can be analysed on the basis of a difference in shape of the K α XF spectra between inequivalent sites.

For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the orbital character of the O 2p holes induced by Sr doping was studied by polarization-dependent XA spectroscopy at the O 1s edge [9, 10]. The observed

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O $2p_{x,y}$ and $2p_z$ components of the doping-induced prepeak, associated with charge carriers, were assigned to O(1) and O(2) atoms, respectively, on the basis of the chemical shift between these components in spectra with the polarization vector \mathbf{E} of incident photons perpendicular and parallel to the crystal c -axis. However, some uncertainty still remains, because the value of this shift (~ 0.3 eV) is smaller than the width of overlapping $2p_{x,y}$ and $2p_z$ XA prepeaks which also show some asymmetry.

While polarization-dependent XA spectroscopy probes the symmetry of unoccupied states relative to the crystal axes, the tunable-excitation XF technique provides information about the projections of these states onto inequivalent sites. In the prior study [7] on polycrystalline $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ it was found that the O $K\alpha$ shapes, which are a measure of the occupied O $2p$ density of states (DOS), are indeed very different for O(1) and O(2) atoms as predicted by band-structure calculations and O $K\alpha$ studies of model compounds, such as $\text{Ca}_{0.87}\text{Sr}_{0.13}\text{CuO}_2$ and La_2O_3 . These specific shapes can be used as a signature of O(1) and O(2) in probing the character of unoccupied p states.

If doping-induced holes, occupying in-plane (x, y) and out-of-plane (z) orbitals, belong to the O(1) and O(2) atoms, respectively, one can detect that by recording the angle-resolved O $K\alpha$ spectra of a single crystal at an excitation energy of the XA prepeak. In the latter case, different orientations of the crystal c -axis with respect to \mathbf{E} would lead to changes in the relative number of the core-excited O atoms of one or another type and, hence, to corresponding changes in the shape of the O $K\alpha$ spectrum as a result of subsequent core-hole radiative decay.

In this letter we present polarization-dependent and site-selective O $K\alpha$ XF measurements on a $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ single crystal using monochromatized synchrotron radiation for the tunable excitation. While the results support the conclusion of [9, 10] that doping-induced $2p_{x,y}$ holes belong to O(1) sites, they also suggest that the $2p_z$ holes may have both O(2) and O(1) character in contrast to previous assignments in the literature.

The $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ single crystal used in the present study had a size of $4 \times 4 \times 3$ mm³. Its growth has been described in detail elsewhere [11]. The sample characterization by various methods confirmed its good quality and its superconducting transition was found to occur at $T_c = 19$ K.

The experiment was performed at the undulator beamline BW3 [12] of HASYLAB, Hamburg, equipped with a modified SX-700 plane-grating monochromator. The XF measurements were carried out using a grazing-incidence multi-grating spectrometer with a multichannel-plate-based detector [13]. The experimental resolutions of the spectrometer and monochromator were set to about 0.5 and 0.7 eV, respectively. The energy calibration for the O $K\alpha$ spectra was done by recording the Zn $L\alpha, \beta$ lines of a Zn metal sample in the second order of diffraction. The manipulator with the sample holder and the spectrometer were mounted at a 90° angle with respect to each other in the vertical plane in an analysing chamber rotatable around the direction of the incoming radiation under ultrahigh-vacuum conditions [14]. The geometries used in present experiment are shown schematically in figure 1. The take-off direction was always perpendicular to the direction of the incident beam, so for any angle of incidence θ , the take-off angle is defined as $90^\circ - \theta$. To determine the excitation energies, O $1s$ XA spectra were measured in total-electron-yield mode with the resolution of ~ 0.3 eV.

The measured $\mathbf{E} \perp c$ and $\mathbf{E} \parallel c$ O $1s$ XA spectra of the $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ crystal (figure 2(a)) which reflect O p_{xy} and p_z contributions, respectively, are similar to those published in the literature [9, 10] and therefore are not discussed in detail here. The ratio between the xy - and z -components of the Sr-doping-induced prepeak at ~ 528.5 eV is approximately 5:1 [9, 10].

The O $K\alpha$ spectra recorded in experimental geometry 2 for various angles of incidence θ of the photon beam with respect to the sample surface are displayed in figures 2(b)–2(d) for three different excitation energies across the O $1s$ edge. The change in the excitation can

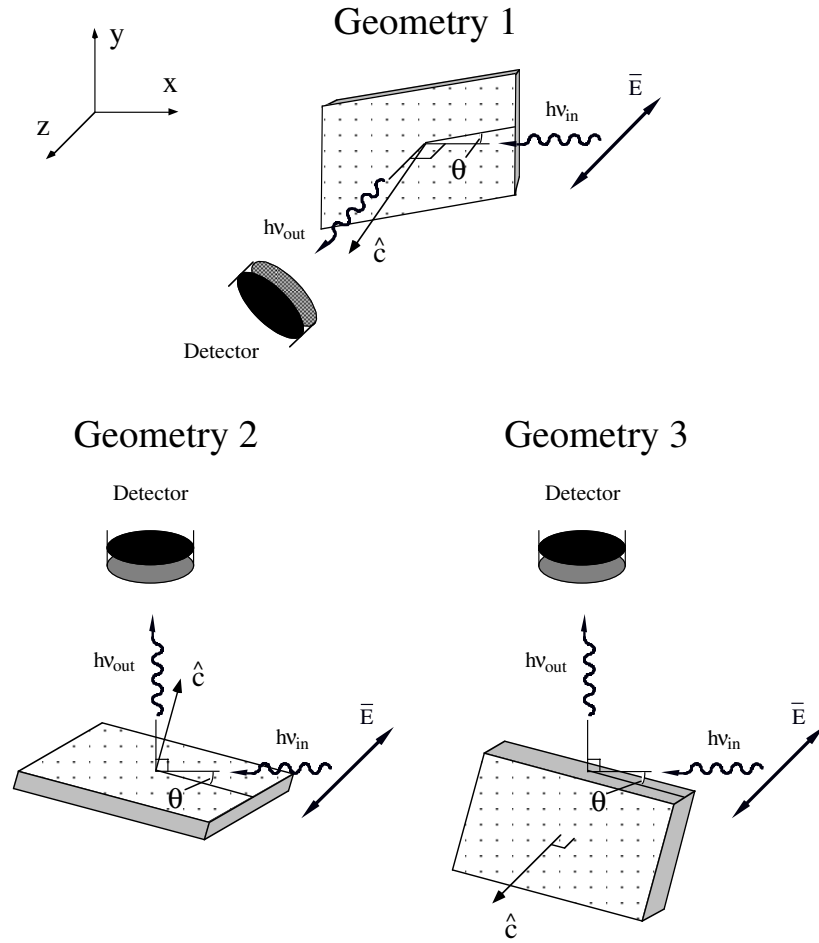


Figure 1. Different experimental geometries used for the excitation and detection of the x-ray fluorescence.

be easily monitored due to the presence of the peak from the elastically scattered radiation in all the spectra. In this geometry, the polarization vector \vec{E} of incident photons was always perpendicular to the c -axis for any θ , while the contributions of p_x , p_y , and p_z orbitals to the O $K\alpha$ spectra were defined by a specific choice of θ in accord with the following formula for spectral intensity (see e.g. reference [15] for details):

$$I(\omega, \theta) = I_{x,y}(\omega)[1 + \sin^2(90 - \theta)] + I_z(\omega) \cos^2(90 - \theta). \quad (1)$$

Since $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ has a tetragonal crystal structure, p_x and p_y contributions are indistinguishable in polarization-dependent XF measurements. For 528.5 eV incident photons with $\vec{E} \perp c$, the O $K\alpha$ spectra (figure 2(b)) are very similar to those of $\text{Ca}_{0.87}\text{Sr}_{0.13}\text{CuO}_2$ [8], containing only the O(1) type of oxygen. This indicates that 1s core holes are created only on O(1) atoms, thus allowing an orbital-resolved study by varying the angle θ . The $\theta = 15^\circ$ spectrum in figure 2(b) reflects mainly the O(1) $2p_{x,y}$ weight while the $\theta = 75^\circ$ spectrum consists of almost equal $I_{x,y}$ - and I_z -components. Hereafter, we will refer to it as the O(1) $2p_{x,z}$ weight, for brevity.

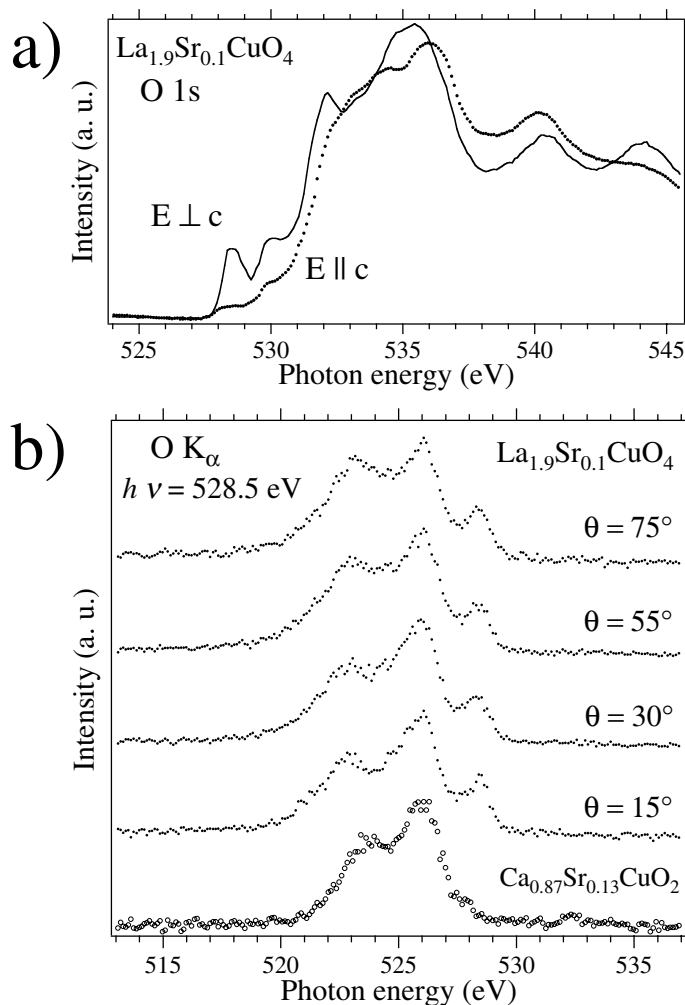


Figure 2. Polarization-dependent O 1s x-ray absorption of single-crystal $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ (a) and O $K\alpha$ x-ray fluorescence spectra selectively excited with $E \perp c$ at various values of θ ((b)–(d)). The multiple-ionization-satellite-free O $K\alpha$ spectra of polycrystalline $\text{Ca}_{0.87}\text{Sr}_{0.13}\text{CuO}_2$ and La_2O_3 are also shown for reference purposes.

The O(1) origin of the XF spectra in figure 2(b) is further verified by a comparison of experimental data with the p-orbital-resolved results of local-density-approximation calculations (LDA + U), incorporating effects of strong d–d Coulomb interaction. In the absence of this kind of calculation for $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$, the O 2p DOS of undoped La_2CuO_4 [16] was used, since the overall distribution of states over the valence band is modified little by Sr doping, according to photoemission measurements [17]. Indeed, the O(1) p_z weight, obtained experimentally as a difference between properly normalized $\theta = 75^\circ$ and $\theta = 15^\circ$ O(1) $K\alpha$ spectra from figure 2(b), resembles closely the calculated O(1) p_z DOS, as shown in figure 3. The latter figure also demonstrates good agreement between experiment and theory as regards O(1) $p_{x,y}$ orbitals (the peaks at ~ 0 eV in the experimental spectra are due to elastically scattered radiation). As a whole, the study of the radiative decay following selective 1s excitations into

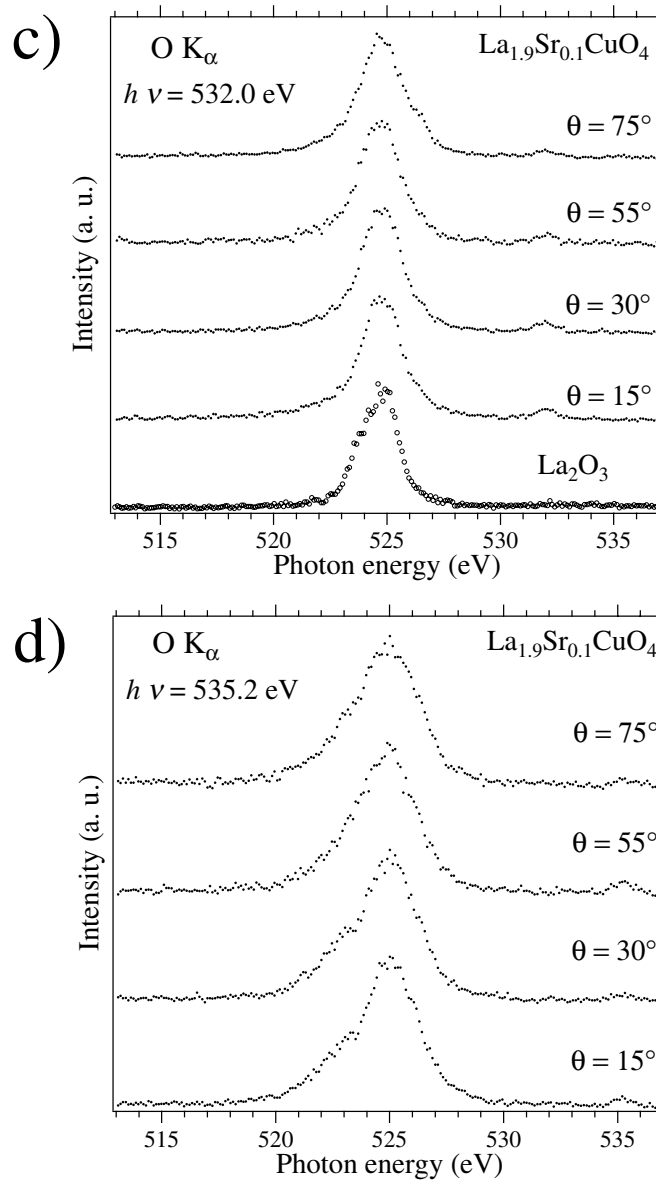


Figure 2. (Continued)

unoccupied states of $2p_{x,y}$ symmetry at 528.5 eV confirm that doping-induced $2p_{x,y}$ holes have O(1) character.

To selectively measure O(2) $K\alpha$ spectra, almost free of the O(1) contribution, the 532.0 eV excitation was chosen, in view of findings from the prior study [7]. Calculations predict that a steep rise of the main O 1s edge is due to unoccupied O p states admixed with La 5d, 4f states. Indeed, the recorded O $K\alpha$ spectra (figure 2(c)) are similar to those of La_2O_3 , reflecting La–O bonding, and in agreement with LDA + U calculations [16]. For O(2) atoms, the predominant contribution to the spectral weight comes from weakly bonding and non-bonding

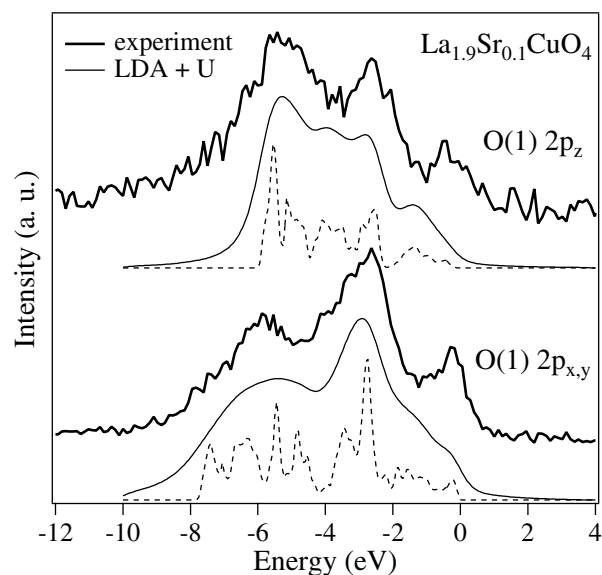


Figure 3. Orbital-resolved O(1) $K\alpha$ spectra of $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ together with the results of LDA + U calculations which were broadened to account for the varying valence 2p hole lifetime and experimental resolution.

states, forming an essentially narrow band in the occupied $2p_{x,y}$ DOS. An enhanced relative $2p_z$ contribution to the $\theta = 75^\circ$ $K\alpha$ spectrum in figure 2(c) gives rise to a distinct high-energy structure at ~ 526.5 eV which is in agreement with the peaking O(2) σ -DOS close to the top of the valence band, as calculated in reference [16].

According to polarization-dependent measurements, intensities of transitions to the states of $p_{x,y}$ and p_z symmetry in O 1s XA spectra and, consequently, the absorption and ionization cross-section for inequivalent O atoms become comparable at energies higher than 533 eV [10], due to La 5d, 4f–O p and Cu s, p–O p hybridization in the conduction band. This leads to a similarity of O $K\alpha$ spectra recorded for excitation energies at the main O 1s XA edge ($h\nu \geq 533$ eV) to those obtained at excitation energies set far above the XA edge [7]. The effect is demonstrated for 535.2 eV incident photons in figure 2(d).

To study the radiative decay for core excitations to unoccupied states of $2p_z$ symmetry at E_F in $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$, experimental geometries 1 and 3 (figure 1) were used which allow the polarization vector \mathbf{E} of incident photons to be parallel to the c -axis of the crystal. For geometry 1, this condition is fulfilled only for small θ while, for geometry 3, it is valid for any θ -value. For geometry 1, the contributions of the p_x , p_y , and p_z orbitals to the O $K\alpha$ spectra are defined by equation (1) while, for geometry 3, the spectra consist of equal $I_{x,y}$ - and I_z -components. In the case of 528.5 eV incident photons, the O $K\alpha$ spectra (figure 4) obtained in geometries 1 and 3 are wider than those of O(2) (see figure 2(c)), thus suggesting some O(1) contributions.

To estimate contributions of inequivalent sites, the data in figure 4 were simulated by a linear combination of orbital-resolved O $K\alpha$ spectra recorded in geometry 2. The change in the angle between the polarization vector \mathbf{E} of the incident photon and the direction of the emitted photon from 0° to 90° on going from geometry 1 to geometries 2 and 3 is expected to have no significant influence on the O $K\alpha$ shape, except for as regards the strength of the elastic peak. Furthermore, our estimations of self-absorption effects for different geometries

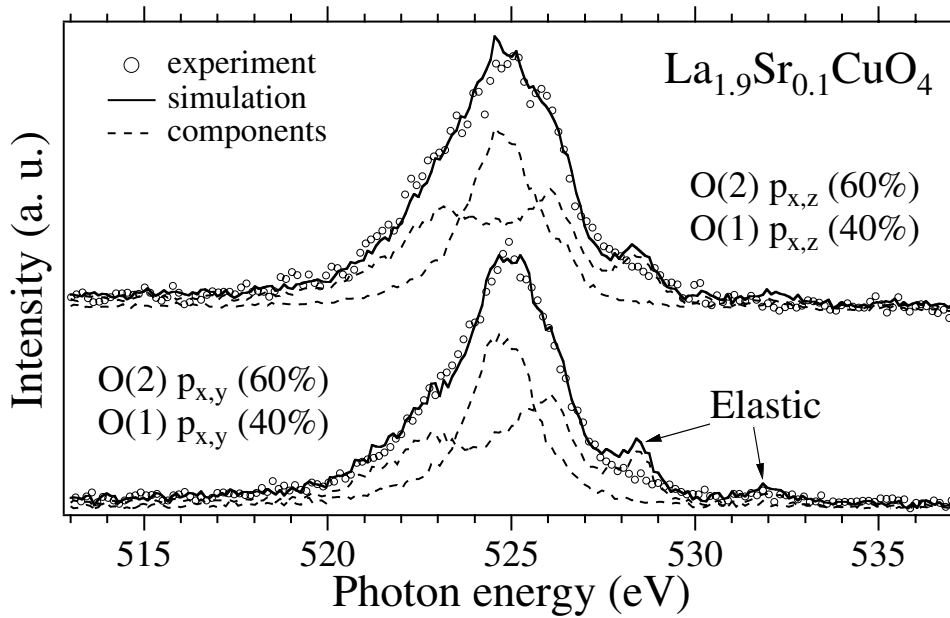


Figure 4. O $K\alpha$ x-ray fluorescence spectra of single-crystal $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ recorded in geometries 1 ($\theta = 10^\circ$) and 3 ($\theta = 15^\circ$) for 528.5 eV incident photons with $\mathbf{E} \parallel \mathbf{c}$, and their simulation by a linear combination of orbital-resolved O(1) and O(2) $K\alpha$ spectra obtained in geometry 2.

and θ suggest that they do not have a substantial influence on the shape analysis presented here.

The two O $K\alpha$ spectra in figure 4 were recorded at specific crystal orientations so that they represent mainly $2p_{x,y}$ (geometry 1, $\theta = 10^\circ$) and $2p_{x,z}$ (geometry 3, $\theta = 15^\circ$) orbitals, respectively. The shape of the former spectrum is very well reproduced by a superposition of $\theta = 15^\circ$ spectra from figures 2(b) and 2(c), i.e. by a superposition of O(1) and O(2) $2p_{x,y}$ components, while the latter can be reconstructed as a linear combination of $\theta = 75^\circ$ spectra for O(1) and O(2), reflecting mainly $2p_{x,z}$ contributions of inequivalent sites. In both cases, the O(1) and O(2) fractions are 40% and 60% (figure 4), respectively, thus suggesting the presence of an O(1) $2p_z$ component in the ~ 528.5 eV XA structure. It is difficult to make a precise quantitative analysis for the distribution of doped z -holes over O(1) and O(2) sites due to experimental factors, such as the incomplete linear polarization of the incident radiation and a certain width of excitation. However, significant O(1) contributions used in simulations of the spectra in figure 4 cannot be entirely ascribed to these experimental factors, and therefore suggest that some of the induced holes are located in the O(1) $2p_z$ orbitals.

In conclusion, the present results do not support the description of the Sr-doping-induced $2p_z$ weight in O 1s XA spectra of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as belonging to only O(2) sites. Although the offset of the $2p_z$ component in the ~ 528.5 eV XA peak is somewhat shifted relative to that of the $2p_{x,y}$ component, the former has a considerable width and asymmetry, and substantially overlaps with the latter. Therefore, the $2p_z$ component can have both O(2) and O(1) contributions. The presence of O(1) $2p_z$ holes should not be *a priori* disregarded; they may provide some basis for the three dimensionality of the high- T_c superconductivity phenomenon.

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