Out-of-Plane Orbital Characters of Intrinsic and Doped Holes in La$_{2-x}$Sr$_x$CuO$_4$


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Bulk-sensitive, polarization-dependent O K- and Cu L-edge absorption spectra of single-domain La$_{2-x}$Sr$_x$CuO$_4$ with CuO$_2$ planes tilted off the sample surface were measured. A novel experimental configuration was utilized to achieve complete polarization geometry and eliminate optical path variations. Contrary to previous measurements, our data show for both intrinsic and doped holes a significant amount of O 2$p_z$ character, likely associated with apical O, but a very weak Cu 3$d_{x^2-y^2}$ character. These results impose strong constraints on superconductivity models invoking out-of-plane orbitals, and suggest that the apical O 2$p_z$ orbital may play an important role in high-$T_c$ phenomena.

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The electronic structure of high-$T_c$ superconducting cuprates has been intensively studied using electron spectroscopy techniques [1]. In particular, polarized inner-shell absorption measurements have provided valuable information on the local orbital character of the carriers in hole-doped cuprates [2–4]. These conducting holes were determined to contain predominately in-plane O 2$p_{x,y}$ and Cu 3$d_{x^2-y^2}$ orbital characters, thus supporting the two-dimensional nature of high-$T_c$ superconductivity. However, anomalies in the lattice dynamics have been interpreted to favor some out-of-plane orbitals [5], and a variety of models for the superconductivity have been proposed in which Cu 3$d_{x^2-y^2}$ and/or apical O 2$p_z$ orbitals play a key role [6–8]. On the other hand, a negative influence of the out-of-plane orbitals on superconductivity has been suggested recently [9]. So far, most of the polarized x-ray absorption and electron energy loss measurements have reported on the Cu 3$d_{x^2-y^2}$ character of the conducting holes. Because of differences in surface chemistry and spectroscopic probing depth, these experiments, using samples with the CuO$_2$ planes parallel to the surface, suffered from inevitable changes in surface sensitivity when measuring polarization dependency. Marked inconsistency has been found with a Cu 3$d_{x^2-y^2}$ to 3$d_{x^2-y^2}$ intensity ratio ranging from 5% to 20%, either with or without an energy shift [2,3]. Several polarized O K-edge absorption measurements have been reported but show no conclusive evidence for the presence of the apical O 2$p_z$ character except for the special case of YBa$_2$Cu$_3$O$_7$ where holes in the chains were measured [3,4].

In order to identify out-of-plane orbitals, and to help elucidate its relevancy to high-$T_c$ superconductivity, we have performed high-precision, bulk-sensitive, polarization-dependent fluorescence yield absorption measurements on La$_{2-x}$Sr$_x$CuO$_4$, maintaining a minimal yet constant surface sensitivity. Contrary to previous results, a significant amount of O 2$p_z$ character, ~15% of the O 2$p_{x,y}$ character and likely ascribed to apical O, has been observed for both intrinsic and doped holes. The Cu 3$d_{x^2-y^2}$ character is found to be very weak, ~1.5% of the Cu 3$d_{x^2-y^2}$ character. The quantitative results impose strong constraints on superconductivity models invoking out-of-plane orbitals, and suggest that the apical O 2$p_z$ orbital may play an important role in high-$T_c$ phenomena.

High-quality La$_{2-x}$Sr$_x$CuO$_4$ samples with $x=0.04$, 0.07, 0.15, and 0.34 were grown using off-axis sputter deposition on vicinal SrTiO$_3$ (101) substrates [10]. Single-domain (103) La$_{2-x}$Sr$_x$CuO$_4$ thin films, ~3500 Å thick with unidirectionally tilted CuO$_2$ planes, were obtained. The tilt angle between the c axis and the surface normal, $\theta_s$, is 46.3° for $x=0.07$ and 0.15 samples, and is 47.5° for $x=0.04$ and 0.34 samples. X-ray diffraction measured 5000:1, 700:1, 1400:1, and 50:1 for the population ratio of the (103) domain and (103') antiaxial ones in $x=0.04$, 0.07, 0.15, and 0.34 samples, respectively. The Sr content was determined by both Rutherford backscattering spectroscopy measurements and comparison with the photoabsorption data of ceramic La$_{2-x}$Sr$_x$CuO$_4$ samples [11]. Both methods gave a consistent $x$ within ± 0.005. Transport measurements showed a $T_c$ ($R=0$) of 5 and 30 K for $x=0.07$ and 0.15 samples, respectively.

The photoabsorption measurements were performed using the AT&T Bell Laboratories Dragon beam line at the National Synchrotron Light Source [12]. The monochromator resolution was set at ~0.15 and ~0.45 eV for the O K edge and Cu L edge, respectively. Bulk-sensitive (~2000 Å probing depth) fluorescence yield (FY) spectra were recorded using a high-sensitivity seven-element germanium array detector. To achieve complete polarization geometry and eliminate optical path variations, an azimuthal rotation method was used; its schematic is shown in Fig. 1. For E$_\parallel$|c, the $b$, $c$, and $a$ axes of the La$_{2-x}$Sr$_x$CuO$_4$ thin film are oriented parallel to the incident photon direction, majority polarization vector (E$_b$), and the minority polarization vector (E$_c$), respectively. Complete E$_b$⊥c geometry is achieved by rotating the sample about its surface normal, $\mathbf{n}$, by ~150° (exact value depending on $\theta$). The fluorescence detector is fixed along the $c$ axis, shown in the figure before rotation, with a collection cone of ±25°. In this arrangement, the optical paths are fixed at non-grazing angles, thus maintaining a minimal yet constant surface sensitivity. Polarization-dependent absorption spectra were then recorded at room temperature as a function of the azimuthal angle $\phi$. After normalization to the incident photon flux, the spectra of different $\phi$ show nearly identical fluores-
FIG. 1. Geometric arrangement for the $E_a \perp c$ absorption measurements on single-domain (103) La$_{2-x}$Sr$_x$CuO$_4$. The $E_a \perp c$ geometry can be achieved by rotating the sample about its surface normal, $n$.

ence yields at 10 eV below and 100 eV above the edge, where no significant polarization effect is expected. A high degree of linear polarization, $(|E_a|^2 - |E_c|^2)/(|E_a|^2 + |E_c|^2)$, is obtained by closing the vertical angular acceptance of the synchrotron radiation down to 0.2 mrad. Its upper limit is calculated to be 99%. An independent measurement using a crystal polarimeter at 650-eV photon energy gives a linear polarization of $(98.3 \pm 0.4)\%$.

Figure 2(a) shows the O $K$-edge normalized fluorescence yield absorption spectra for the $x = 0.15$ sample taken with $E_a \perp c$ and $E_a \parallel c$. Expanded spectra for the low-energy region (peaks labeled $A$ and $B$) as a function of $\phi$ are displayed in Fig. 2(b), showing systematic evolution of the peak intensities. As discussed previously [11,12], peak $A$ stems from doping-induced holes, and results mainly from a $3d^9L \rightarrow 1L3d^9$ transition; peak $B$ is associated with the “upper Hubbard band” and results from a $3d^9 \rightarrow 1L3d^{10}$ transition of the undoped material, which is allowed due to the admixture of $3d^{10}L$ with $3d^8$ in the ground state. Here $L$ and $1L$ denote the O $2p_{x,y}$ ligand hole and O 1$s$ core hole, respectively. As $\phi$ is changed from $E_a \perp c$ to $E_a \parallel c$, the intensities of peaks $A$ and $B$ decrease and new peaks (labeled as $A'$ and $B'$) appear at $\sim 0.4$ eV lower photon energies, developing full strength at $E_a \parallel c$. A dipole transition analysis shows that peak $A$ ($A'$) contains exclusively $2p_{x,y}$ ($2p_z$) character, and gives very good agreement with the observed intensity evolution as a function of $\phi$. The net intensity gain between the $E_a \parallel c$ and $E_a \perp c$ spectra near 526.8-eV photon energy excludes the possibility of peak $A'$ being an absorption feature due to surface contaminations. The appearance of peak $A'$ clearly demonstrates that the doped holes in La$_{2-x}$Sr$_x$CuO$_4$ contain a significant amount of O $2p_z$ character.

Figure 3(a) shows the copper $L_{2,3}$ absorption spectra for the $x = 0.15$ sample taken at $E_a \perp c$ and $E_a \parallel c$. The $L_3$ spectral region as a function of $\phi$ has been magnified in

FIG. 2. O $K$-edge fluorescence yield photoabsorption spectra of La$_{1.85}$Sr$_{0.15}$CuO$_4$. (a) Wide range spectra for $E_a \perp c$ ($\phi = 156^\circ$) and $E_a \parallel c$ ($\phi = 0^\circ$); (b) expanded spectra in the low-energy region of (a) and of those taken with intermediate angles. These $\phi$ were chosen such that the value of $|E_a \times c|^2/|E_a|^2$ corresponds to 1.0, 0.9, 0.8, 0.6, 0.4, 0.2, 0.1, and 0.0, respectively.

Fig. 3(b). No energy shift greater than 30 meV is observed at the $L_3$ white line as its intensity reduces by nearly 2 orders of magnitude in going from $E_a \perp c$ to $E_a \parallel c$ geometry. The raw data of the $L_3$ white line give a $3d_{3/2} \rightarrow 2p_z$ intensity ratio of 4.5%. After being corrected for the FY saturation effect, this ratio is reduced down to 3% [13]. Figure 3(c) shows the difference spectra obtained by subtracting a small percentage of the intensities of the $E_a \perp c$ spectra from those of the $E_a \parallel c$ spectra in the $L_2$ white line region. The raw data clearly show that $\sim 3\%$ of the $E_a \perp c$ spectrum is sufficient to remove the barely visible $L_2$ white line shown in the $E_a \parallel c$ spectra, in excellent agreement with that obtained from the $L_3$ white line with the FY saturation correction. After correction for nonperfect linear polarization $|E_a|^2/|E_a|^2 = (0.9 \pm 0.2)\%$, analysis of both the $L_3$ and $L_2$ white lines then results in a final value $(2 \pm 0.5)\%$ for the $3d_{3/2} \rightarrow 2p_z$ intensity ratio, which is much smaller than previously reported in studies employing different experimental techniques [2,3].

To illustrate the evolution of the O $2p_{x,y}$ and $2p_z$ characters as functions of Sr concentration, Fig. 4(a) shows the low-energy region of the O $K$-edge $E_a \perp c$ and $E_a \parallel c$ spectra. In the $E_a \perp c$ spectra, with increasing Sr doping, peak $A$ gains intensity by introducing holes into the
valence states as well as transferring spectral weight from peak B [11]. A similar effect is also observed between peaks A’ and B’ in the $E_{\text{g}}\text{l}_{\text{c}}$ spectra. The $2p_z$ to $2p_{x,y}$ ratio (peaks $A', A$) is large and varies as $(14 \pm 1)\%$, $(13 \pm 1)\%$, $(16 \pm 1)\%$, and $(34 \pm 2)\%$ for $x = 0.04, 0.07, 0.15$, and 0.34 samples, respectively. Interestingly, this ratio is largest in the sample with highest Sr content.

The $2p_z$ to $2p_{x,y}$ intensity ratios for the “upper Hubbard band” (peaks $B', B$) are found to be $(16 \pm 2)\%$ for $x = 0.04, 0.07$, and 0.15 samples; an extrapolation suggests a similar ratio also for the undoped sample ($x = 0$).

According to band-structure calculations [14], one may ascribe the $2p_z$ character to apical O, and the $2p_{x,y}$ to in-plane O. The analogous spectral weight transfer from $B'$ to $A'$ ($2p_z$ character), and that from $B$ to $A$ ($2p_{x,y}$ character), strongly suggests that the apical O $2p_z$ mixes with the in-plane O $2p_{x,y}$ and Cu $3d_{x^2-y^2}$ in the ground state, instead of forming a separate band. The $0.3 - 0.5$ eV energy shifts between $2p_z$ and $2p_{x,y}$ character might be due to the differences in the chemical shifts and screening between the apical and in-plane O 1s photoabsorption processes.

To investigate the Cu $3d_{x^2-y^2}$ character, Fig. 4(b) shows the Cu $L_3 E_{\text{g}}\text{l}_{\text{c}}$ and $E_{\text{g}}\text{l}_{\text{c}}$ spectra for these four samples. Upon Sr doping, the $L_3$ white line in the $E_{\text{g}}\text{l}_{\text{c}}$ spectra reduces slightly its peak height and a doping-induced satellite peak (the shoulder indicated as $L_1$) develops at $\sim 1$ eV above the white line. The major configuration involved in the x-ray absorption for the white line and the satellite peak are $3d^9 \rightarrow 2p_{3/2}3d_{10}$ and $3d^9L \rightarrow 2p_{3/2}3d_{10}L$, respectively. Using the aforementioned analysis procedure for the $L_3$ and $L_2$ white lines, the $3d_{x^2-y^2}$ to $3d_{x^2-y^2}$ intensity ratios for the white line are found to be $(2 \pm 0.5)\%$ for $x = 0.04, 0.07$, and 0.15 samples. For the $x = 0.34$ sample, the ratio increases to $(7.5 \pm 1)\%$, taking into account the presence of $\sim 2\%$ (103) antdomains. By normalizing and subtracting the $L_3$ spectra of the $x = 0.04$ sample from those of the other three samples, the $3d_{x^2-y^2}$ to $3d_{x^2-y^2}$ intensity ratios of the doping-induced satellite peak ($L_1$) were estimated to be $(2.5 \pm 1)\%$ for $x = 0.07$ and 0.15 and $(8.5 \pm 2)\%$ for the $x = 0.34$ samples.

Considering the larger experimental uncertainties, these ratios are essentially the same as those obtained from the $L_3$ white line, and an extrapolation suggests a similar ratio for the $x = 0.04$ sample as well. Figure 5 summarizes the apical O $2p_z$ to in-plane O $2p_{x,y}$ and the Cu $3d_{x^2-y^2}$ to $3d_{x^2-y^2}$ intensity ratios of doping-induced peaks.

A careful analysis is required to relate the x-ray absorption intensities to the hole orbital character (occupation numbers) in the ground state. For Cu $3d_{x^2-y^2}$ to $3d_{x^2-y^2}$ character ratio, the “3/4” factor between $p_{3/2,Z} \rightarrow d_{x^2-y^2}$ and $p_{3/2,Z} \rightarrow d_{x^2-y^2}$ full dipole transition strength needs to be taken into account. After this renormalization, both the intrinsic and doped holes show an apical O $2p_z$ to in-plane O $2p_{x,y}$ character ratio of
\[ \sim 15\% \text{ and a } Cu \ 3d_{3z^2-r^2} \text{ to } 3d_{x^2-y^2} \text{ character ratio of } \\
\sim 1.5\% \text{ in superconducting samples. Coupling these ratios with the calculated admixture of Cu } 3d_{3z^2-r^2} \text{ and in-plane O } 2p_{x,y} \text{ character, one can estimate the Cu } \\
3d_{3z^2-r^2} \text{ to apical O } 2p_z \text{ character ratio. For intrinsic holes, the calculated admixture is roughly } 70\% \text{ Cu } \\
3d_{3z^2-r^2} \text{ and } 30\% \text{ in-plane O } 2p_{x,y} \text{ [11,14], giving a } \sim 1\% \text{ Cu } 3d_{3z^2-r^2} \text{ and a } \sim 4\% \text{ apical O } 2p_z \text{ character. The analysis for the doped holes is more complicated, because it} \\
\text{involves a large spectral weight transfer and requires detailed information on the hybridization of various} \\
\text{configurations. Nevertheless, knowing that the doped holes contain more in-plane O } 2p_{x,y} \text{ than Cu } 3d_{3z^2-r^2} \text{ character (roughly a } 3:1 \text{ ratio) [11,14], our results indicate} \\
\text{that the apical O } 2p_z \text{ is the overwhelmingly predominant out-of-plane orbital for doping-induced holes.} \\
\text{Although the role of the apical O } 2p_z \text{ orbital in high-} \\
T_c \text{ phenomena is not clear at this time, its prominent appearance and progressive increase relative to the in-plane} \\
O \ 2p_{x,y} \text{ character with Sr doping could have profound physical implications. For instance, the increase in apical O } 2p_z \text{ to in-plane O } 2p_{x,y} \text{ ratio can enhance the coupling} \\
between layers, thus providing an appealing explanation for the rapid increase in out-of-plane to in-plane conductiv-} \\
ty ratio with doping [15]. \text{The apical O } 2p_z \text{ orbital may also link directly to the pressure-dependent transport} \\
properties [5\text{–}8]. \text{Although our data indicate that too} \\
too large a } 2p_z \text{ to } 2p_{x,y} \text{ ratio may suppress the superconductivity, the arguments on out-of-plane orbitals having a} \\
negative influence on superconductivity [9] must confront the significant amount of apical O } 2p_z \text{ character observed} \\
in the superconducting samples. The observed very weak Cu } 3d_{3z^2-r^2} \text{ character, on the other hand, imposes a} \\
strong constraint on theories requiring a considerable amount of Cu } 3d_{3z^2-r^2} \text{ character, such as in } d-d^* \text{ excitation} \\
\text{and triplet hole} [8] \text{ models.} \\
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I_n(I_{\text{sat}} - I_n)/I_{\text{sat}} \text{ functional form correction for the FY} 
saturation effect is needed. Three different methods were utilized and a consistent } I_n \text{ of } \sim 3 \text{ times the peak} 
\text{height of the } L_3 \text{ white line was obtained. For the low-energy peaks at the } 
O K \text{ edge and for the Cu } L_2 \text{ white line, this correction is} 
\text{not essential because their absorption cross sections are quite small compared to the total absorption cross} 
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