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Orientation of the O 2p holes in $Bi_2Sr_2Ca_1Cu_2O_8$

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Unoccupied O 2p states are observed in $Bi_2Sr_2Ca_1Cu_2O_8$ near the Fermi level. They show up as a spike in the O 1s absorption edge at threshold ($h\nu = 528.2$ eV). The orientation of these O 2p states is determined via optical selection rules from the polarization dependence of the absorption using single crystals. The O 2p holes are found to have at least 95% $p_{x,y}$ character with x,y in the superconducting a-b plane.

Superconductivity in the CuO-based superconductors[1] is correlated with the concentration of holes[2] in a nearly filled Cu 3d-O 2p valence band. In the early models of high-temperature superconductivity[3] these holes are located on the Cu sublattice. They may spread to the oxygen sites via hybridization between the Cu 3d and O 2p valence states. Some models[4] assign a more dominant role to oxygen holes. If the hole-hole repulsion U_{dd} at the copper sites is large enough then any additional hole introduced by doping will prefer an oxygen site.[5] Thereby, it can participate in a superexchange interaction, which turns from an antiferromagnetic repulsion between equal spins on adjacent copper sites to an attraction when a hole is present at the mediating oxygen. The orientation of these oxygen hole orbitals is a sensitive probe of the Cu-O interaction. Several possibilities exist: For the oxygens in the CuO_2 plane (taken as the x-y plane) there are two types of in-plane orbitals, one along the Cu—O bond direction (σ bond) the other perpendicular to it (π bond). The out-of-plane p_z orbital can also form a π bond with the Cu. For the oxygens in the apex position above the Cu one can have a p_z orbital forming a σ bond or $p_{x,y}$ orbitals forming a π bond.

On the experimental side, O 2p holes were found via transitions from the O 1s core level. Absorption[6-9] and electron-energy loss[10-13] measurements exhibit a spike at threshold (see Fig. 1) that corresponds to O $1s \rightarrow$ O 2p transitions with the 2p holes near the Fermi level. The intensity of this spike is proportional[10,11] to the number of holes introduced via Sr doping in $La_{2-x}Sr_xCuO_4$ and via oxygen doping in $Y_1Ba_2Cu_3O_{7-y}$. In our work, we use dipole selection rules in optical absorption to identify the orientation of the O 2p holes. With the electric field vector E parallel to the x axis only transitions into p_x orbitals are allowed from an s level, and likewise for the other directions. For single crystals of $Bi_2Sr_2Ca_1Cu_2O_8$ cleaved along the ab-plane, we find that the O 2p holes are excited by E parallel to the surface. Thus, they have $p_{x,y}$ character with x,y in the superconducting a,b plane.

The choice of $Bi_2Sr_2Ca_1Cu_2O_8$ as model superconductor is motivated by its simple structure (all CuO_2 planes are equivalent) and by the high-quality surfaces that can be obtained owing to the weak bonding between the layers. In $Y_1Ba_2Cu_3O_7$ there are copper-oxygen chains and planes, leading to a more complex O 1s absorption edge[6,9,11,13] with at least two main near-edge features at 528.2 and 529.5 eV. Anisotropy has been observed[9,12,13] in $Y_1Ba_2Cu_3O_7$, but its interpretation has been difficult since various features with opposite anisotropies are superimposed. An early study[12] found the unresolved sum of the two features to have $p_{x,y}$ character. On the other hand, the lower energy feature (which scales with the hole concentration) was reported to have p_z character,[13] the upper feature $p_{x,y}$ character. Recent studies[9] identify up to four features with different polarization signatures. An additional problem with $Y_1Ba_2Cu_3O_7$ is the presence of Ba, which makes surfaces and grain boundaries very reactive and leads to $BaCO_3$ formation,[6,14] thereby obscuring

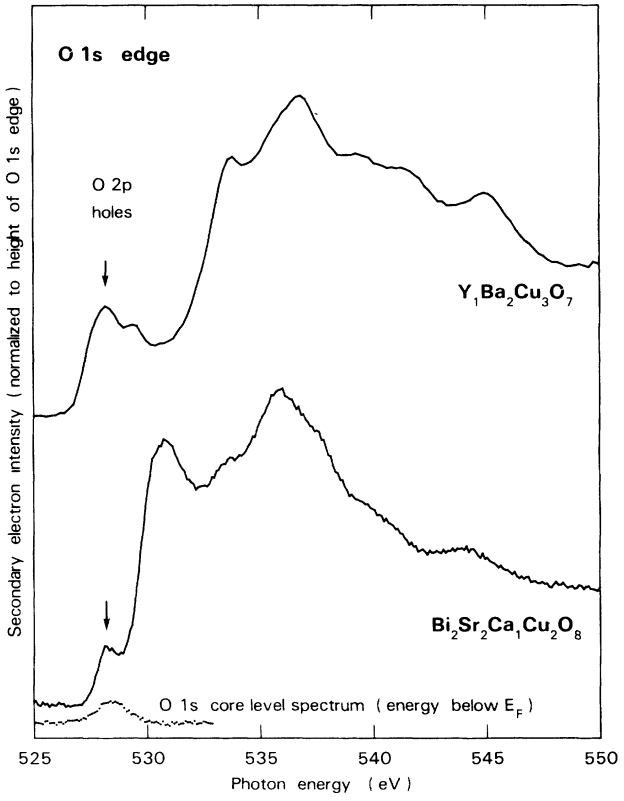

FIG. 1. O 1s absorption edges of $Y_1Ba_2Cu_3O_7$ (Ref. 6) and of $Bi_2Sr_2Ca_1Cu_2O_8$ (scraped in vacuum). In both materials one observes a spike at $h\nu = 528.2 \pm 1$ eV, which corresponds to transitions into unoccupied O 2p states near E_F. An O 1s core-level spectrum (dotted) is given for $Bi_2Sr_2Ca_1Cu_2O_8$.

surface-sensitive photoelectron spectra. $Bi_2Sr_2Ca_1Cu_2O_8$, on the other hand, exhibits less tendency to form surface carbonate (a more detailed account will be published elsewhere) and it cleaves easily, like layered compounds. We were able to use a tab technique to cleave it in ultrahigh vacuum (10^{-10}-Torr range) and obtain mirrorlike surfaces.

Single crystals of $Bi_2Sr_2Ca_1Cu_2O_8$ were grown from polycrystalline material of the composition $Bi_4Sr_3Ca_3Cu_4O_x$ maintained at about 875 °C for 40–50 h in air. The crystals (up to about $3\times3\times0.5$ mm^3 in size) were obtained as thin plates, with the c axis perpendicular to the plates. Typically, the onset of superconducting transition was about 84–85 K. An electron microprobe analysis indicated a composition near $Bi_{2.1}Sr_{1.6}CaCu_2O_{8.15}$. Single-crystal x-ray examination confirmed the incommensurately modulated $\sqrt{2}\times\sqrt{2}$ orthorhombic cell. Various methods for preparing clean surfaces were tried. Scraping produced clean surfaces, although the roughness increased upon prolonged scraping, such that the polarization effects became weaker. Surfaces cleaved in air gave already similar polarization effects as those cleaved in ultrahigh vacuum, but exhibited an extra contamination peak in the O 1s absorption edge at $h\nu=533.5$ eV, possibly due to the π^* resonance in CO (compare Ref. 15). The O 1s absorption edge was measured via the intensity of secondary electrons (0–6 eV kinetic energy), which is proportional to the absorption coefficient as long as the escape depth of the electrons (about 20 Å) is small compared to the absorption length of the photons (about 1000 Å). The O 1s core hole produced by an absorbed photon decays into an Auger electron, which in turn produces low-energy electron-hole pairs. As a consequence, the probing depth is given by the mean free path of the Auger electrons (10–20 Å at 500 eV kinetic energy), plus the mean free path of low-energy secondaries (about 10 Å).

Figure 1 establishes the energetic position of the empty O 2p states. A spike is observed in the O 1s absorption edge at $h\nu=528.2\pm1$ eV, corresponding to O 1$s\rightarrow$ O 2p transitions. This energy nearly coincides with the energy of the O 1s core level below the Fermi level. (The O 1s core-level spectrum of $Bi_2Sr_2Ca_1Cu_2O_8$ is inserted as a dotted curve in Fig. 1.) Neglecting excitonic effects[16] one concludes that the O 2p final states are located at the Fermi level. They may be viewed as holes in a heavily p-doped, O 2p-like valence band, whereas the main onset in the absorption ($h\nu=532$ eV in $Y_1Ba_2Cu_3O_7$, $h\nu=530$ eV in $Bi_2Sr_2Ca_1Cu_2O_8$) corresponds to the antibonding O 2p states in the conduction band. The situation is more complicated in $Y_1Ba_2Cu_3O_7$, because there exist several near-edge features and two O 1s core levels (the higher binding-energy core level probably due to carbonate contamination[6,14]). The lowest absorption feature is located at $h\nu=528.2$ eV, like in $Bi_2Sr_2Ca_1Cu_2O_8$, and it again is close to the (intrinsic) core-level binding energy. This feature also scales with the hole concentration,[11] whereas the upper one does not.

The polarization dependence of the O 1s absorption edge is demonstrated in Figs. 2 and 3 for the spike at threshold. To first order it can be approximated by a $\cos^2\theta$ law (Fig. 3, solid curve) which is expected from dipole selection rules for transition from the 1s to the $2p_{x,y}$ levels (x,y in the a-b plane). Transitions into $2p_z$ states would follow a $\sin^2\theta$ law. Adding a 5% p_z contribution gives the best fit to the data (dashed line in Fig. 3). However, the incomplete polarization of the synchrotron light[17] and the finite disorder of the sample surface can easily explain the 5% depolarization without having any $2p_z$ holes at all.

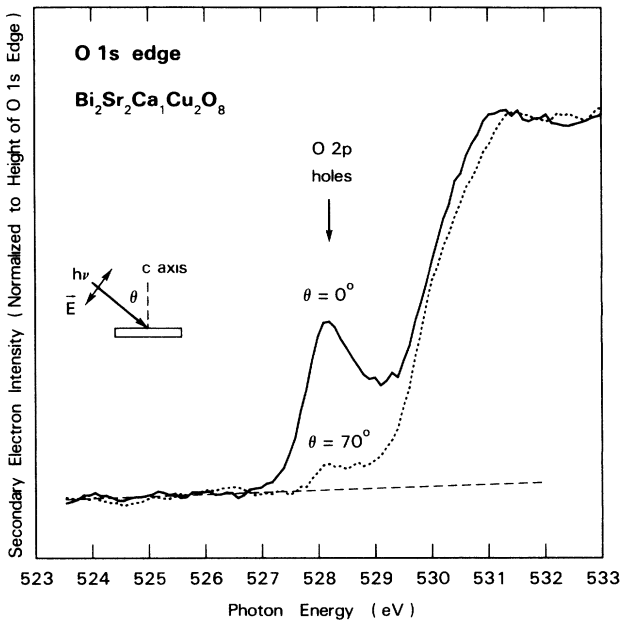

FIG. 2. Polarization dependence of the O 1s edge for a $Bi_2Sr_2Ca_1Cu_2O_8$ single crystal cleaved in vacuum. The O 2p spike at $h\nu=528.2$ eV is excited by the component of the electric field vector **E** parallel to the a-b plane.

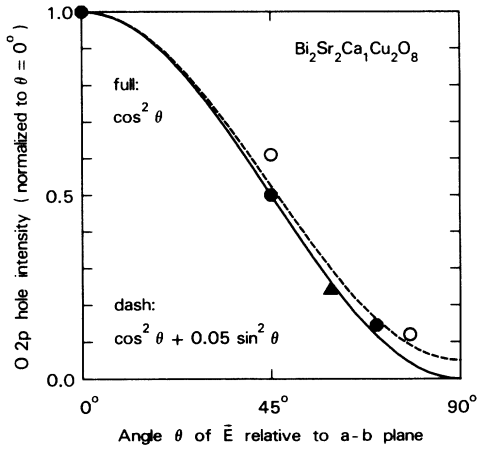

FIG. 3. Polarization dependence of the O 1$s\rightarrow$ O 2p transition intensity at $h\nu=528.2$ eV for a variety of samples (different symbols). An O $2p_{x,y}$ orbital (x,y in the a-b plane) gives a $\cos^2\theta$ dependence (full line) using optical dipole selection rules. Up to 5% of additional O $2p_z$ states can be accommodated (dashed line). However, the data are consistent with the absence of O $2p_z$ holes taking incomplete polarization of the light and sample disorder into account.

There is a natural explanation for the $p_{x,y}$ character of the O $2p$ holes using a widely adopted bonding concept for the CuO_2 planes. The (Cu $3d_{x^2-y^2}$) orbital has lobes pointing towards the in-plane oxygen that interact strongly with the O $2p_{x,y}$ orbitals. Their antibonding combination represents the highest occupied orbital, and will be the first one to be depleted when creating holes via doping. Note that there are two types of O $2p_{x,y}$ orbitals, one along the Cu-O bond, the other perpendicular to it. In the standard model the O $2p$ holes are located in the Cu-O σ bond, but the possibility of having the holes in the perpendicular π-bonding orbital has also been proposed.[18] Our experiment averages over these two directions and cannot distinguish between them. However, we can rule out a π bond formed by the p_z orbital as location of the holes. In the context of the measurements[9,13] on $Y_1Ba_2Cu_3O_7$ the existence of O $2p$ holes in the p_z orbital of an apex oxygen (above the Cu atoms) has been discussed. We can rule out this possibility for $Bi_2Sr_2Ca_1Cu_2O_8$.

For $Bi_2Sr_2Ca_1Cu_2O_8$ there is another explanation for the $p_{x,y}$ character of the oxygen holes to be considered. Several one-electron band calculations[19] stress the importance of the interaction between Bi and the O in the BiO planes for the doping of this material. A Bi $6p_{x,y}$,O $2p_{x,y}$ band is found to extend from 4 eV above the Fermi level E_F down to 1 eV below E_F. The electrons in this band are taken from the CuO_2 planes, where they create extra holes. In principle, our measurement can distinguish between oxygen $p_{x,y}$ holes in the BiO and in the CuO_2 planes. In the first case, there is a p_z counterpart at higher energy, in the second case, the remainder of the spectrum is unpolarized. We find no evidence for such higher-lying p_z states. However, we cannot discard their existence completely, since they are difficult to discriminate against the large unpolarized background from the other conduction-band states.

Note added in proof. Recently, we received papers by P. Kuiper *et al.* [Phys. Rev. B **38**, 6483 (1988)] and by N. Nücker *et al.* [Phys. Rev. B (to be published)] on the O $1s$ absorption edge in high-temperature superconductors. The latter reports $p_{x,y}$ character for the O $2p$ holes in $Bi_2Sr_2Ca_1Cu_2O_8$, in agreement with our results.

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