

Orientations of oxygen hole states and ionicity of bismuth atoms in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

M. Faiz and G. Jennings

Argonne National Laboratory, Argonne, Illinois 60439

J. C. Campuzano

*Argonne National Laboratory, Argonne, Illinois 60439
and University of Illinois at Chicago, Chicago, Illinois 60680*

E. E. Alp

Argonne National Laboratory, Argonne, Illinois 60439

J. M. Yao and D. K. Saldin

University of Wisconsin, Milwaukee, Wisconsin 53211

Jaejun Yu

Sogang University, Seoul 100-611, Korea

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We report a study of the x-ray-absorption near-edge structure of the Bi L_3 and O K edges in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. A comparison with the Bi L_3 edges of Bi_2O_3 and KBiO_3 indicates that the Bi atoms are in a state close to a formal valency of +3 in the superconducting compound. We attribute the peaks below 529 eV in the O K -edge spectra of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ to holes on the O sites. We investigate the symmetries of these holes by using polarized x rays. By comparing the experimental spectra with simulations based on self-consistent electronic-structure calculations, we determine that the hole states at the O sites in the Cu-O and Bi-O planes do indeed lie in these planes, while those associated with the apical O atoms of the O pyramids in the structure are aligned along the c axis.

I. INTRODUCTION

Oxygen $2p$ holes in Cu-O bands are believed to play a crucial role in the high-temperature superconductivity of cuprate perovskites. A detailed study of the O $2p$ holes in the high- T_c superconductors is therefore essential to an understanding of the underlying physics. X-ray absorption¹⁻⁶ and electron-energy-loss spectroscopies^{7,8} directly probe these unoccupied states, and have been used extensively in the study of holes in the high- T_c cuprates. Most of the data from these experiments is fairly consistent, and has been interpreted to indicate that (a) there are strong electron-electron correlations due to the large Cu d - d Coulomb repulsion; (b) the states around the Fermi energy have mostly O $2p_{x,y}$ character; (c) holes of mainly in-plane s symmetry are present, although some experiments have detected small out-of-plane components as well. These experiments have been carried out on samples held at room temperature, and interpreted under the assumptions that there is a gap of approximately 2 eV around the Fermi energy in undoped samples, and that therefore the superconducting cuprates may be regarded as doped insulators. The experiments appear to indicate that the peak that appears above the Fermi energy in absorption spectroscopy is prominent only when the electric field of the photon is oriented along the a - b plane of the sample. The interpretation of the data has been entirely empirical, with no comparison to simulations of

the absorption spectra, except for our previous work on $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$.⁹ Furthermore, unless the experiment were sensitive mostly to the *bulk* of the sample, it would be misleading to interpret data from samples at room temperature, as it is now clearly established that the cuprates lose oxygen from the surface region when placed in a vacuum.⁹

In this work, we analyze polarized x-ray-absorption near-edge structure (XANES) from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ by comparing our results to computer simulations of the XANES incorporating the self-consistent potential of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ calculated using the full-potential linearized augmented plane-wave (FLAPW) method of density-functional electronic-structure calculations in the local-density approximation (LDA). The justification for this approach is that extensive ultraviolet photoemission studies of the valence band indicate that, in the immediate vicinity of the Fermi energy, not only the electronic energy levels,¹⁰ but also the wave functions¹¹ of the high- T_c superconductors are reasonably well described by the LDA. This is reflected in the excellent agreement of our XANES measurements to our simulations, which in turn allows us to determine the contribution of each Cu-O bond to the XANES spectra. Of course this approach is only valid in the superconducting regime, as the LDA calculations do not well describe the insulating state. The angle-resolved photoemission data so far does not support the idea that the electronic structure of the insulator

evolves continuously into that of the superconductor. On the contrary, it is found experimentally¹² that the Fermi-surface volume remains large as the doping is decreased, until suddenly, at the metal-insulator transition, it disappears. In the superconducting state, very strong photoemission final-state effects, and a good description of the photoemission spectra by first-principles, one-step photoemission calculations^{11,13} show that the empty levels' band dispersions are also reproduced reasonably well by the LDA. We therefore describe our absorption spectra from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ not in terms of an upper Hubbard band, but in terms of LDA quasiparticle states.

Bi is believed to have a formal valency close to +3 in the layered cuprate superconductor.¹⁴ Our measurements of the Bi L_3 absorption edge in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and the reference compounds, Bi_2O_3 and KBiO_3 , confirm this conclusion. Since Bi is in a +3 valence state in Bi_2O_3 , it may be speculated that the oxygen environment in the Bi-O layers in the superconductor is similar to that in the oxide. Therefore, we have also measured O K -edge absorption spectra in Bi_2O_3 in order to isolate the contribution of Bi-O bonds to the O K -edge spectra of the superconductor.

II. EXPERIMENT

The experiments were carried out at the Synchrotron Radiation Center (Stoughton, Wisconsin) using polarized x rays, monochromatized by an extended-range Grasshopper monochromator. A single crystal of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ was oriented such that the electric-field vector E of the x rays was in the ab (or basal) plane of the crystal at normal incidence. The crystal was cooled to 20 K before cleaving it in a vacuum of about 10^{-10} Torr in order to minimize any possible oxygen loss from the crystal surface. Oxygen K -edge absorption spectra were measured in the total electron yield mode for different values of angle (θ) between the electric-field vector E of the x rays and the c axis of the crystal. O K -edge absorption spectra from Bi_2O_3 were measured at room temperature. The energy resolution of the spectra from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ was 0.3 eV, whereas those from Bi_2O_3 was 0.5 eV. Bismuth L_3 absorption-edge measurements were carried out in the transmission mode at the X-18 beamline at NSLS (Brookhaven National Laboratory, New York). The energy resolution of the Si(220) monochromator was estimated to be about 3 eV at 13 419 eV.

III. RESULTS AND DISCUSSION

Figure 1 shows the Bi L_3 absorption edges of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, Bi_2O_3 , and KBiO_3 . We arbitrarily choose the energy zero in this figure to be at the midpoint of the main step in the Bi_2O_3 spectrum. The corresponding midpoint of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ spectrum is very close to that of Bi_2O_3 , while there is about a 1-eV shift between the main steps in the Bi_2O_3 and KBiO_3 spectra. Furthermore, a significant shoulder appears to the left of the midpoint of the main step only in the KBiO_3 spectrum. Since neutral Bi has an outer-shell configuration of $6s^2 6p^3$, it can be in either the +3 ionic state when only

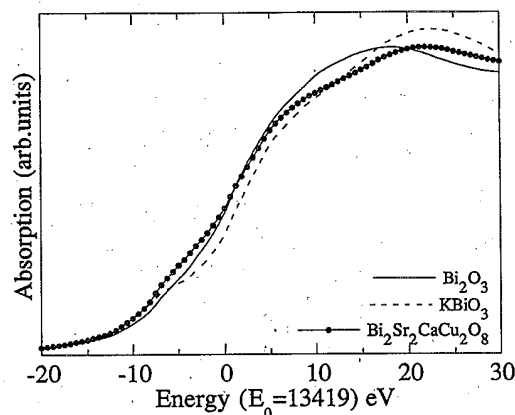


FIG. 1. Bismuth L_3 absorption edges of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, Bi_2O_3 , and KBiO_3 .

the $6p$ states are empty, or the +5 state when both the $6s$ and $6p$ states are empty. When the $6s$ states are empty, a $2p$ to $6s$ transition is allowed, as well as a $2p$ to $6d$, according to the selection rules of photoabsorption. It is known that Bi is in a pentavalent ionic state in KBiO_3 and a trivalent one in Bi_2O_3 .^{15,16} The low-energy shoulder on the KBiO_3 spectrum may thus be regarded as a signature of transitions into the unoccupied Bi $6s$ states in this (pentavalent) material, while its absence on the Bi L_3 edges in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and Bi_2O_3 suggests that the corresponding $6s$ states are occupied in the latter materials. Thus we may attribute a formal valency of Bi in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ close to +3.

Figure 2 shows the measured O K edge of a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ single crystal at 20 K as a function of the angle θ . A straight line fitted to the region below 523.5 eV has been subtracted as background. The O K edge of Bi_2O_3 at room temperature is shown in Fig. 3. The spectrum also contains chromium L_2 and L_3 edges resulting from the coating on the monochromator Codling entrance slit. We exploit these edges to calibrate the energy scale, and to normalize the spectra. Since the Cr L edges

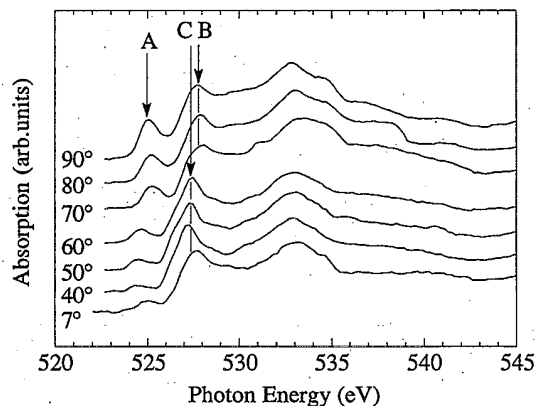


FIG. 2. Total electron yield due to x-ray absorption by O $1s$ electrons as a function of angle (θ) between the electric field and the c axis of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.

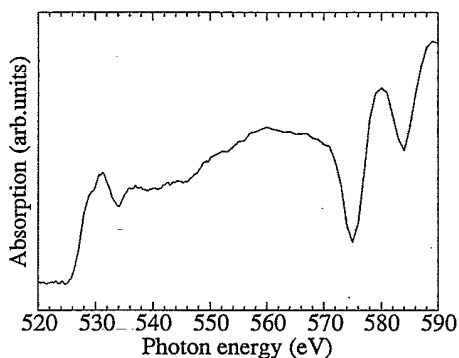


FIG. 3. Total electron yield due to x-ray absorption by O 1s electrons of Bi_2O_3 .

are caused by the monochromator, they are independent of the sample orientation. The spectra shown in our figures have not been smoothed in any way. Since we are observing the effects of electron transitions from O 1s core level, the selection rules of photoabsorption suggest that the XANES spectra in Figs. 2 and 3 are indications of the p -projected local density of unoccupied states on the O sites, and that the region very close to the absorption edge is a measure of O 2p hole concentration in the valence band. The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ K -edge spectra in Fig. 2 show the presence of three peaks (labeled *A*, *B*, and *C*) at 525.0 ± 0.3 , 527.8 ± 0.3 , and 527.3 ± 0.3 eV very close to the onset of the absorption edge. The peak *B* may be attributed to the Bi-O bands.¹⁷ There is significant dispersion of the empty states, although we have not been able to quantify it. From the spectrum of Fig. 3 it is unclear whether similar peaks are present near the O K edge of Bi_2O_3 due to the relatively poor energy resolution (0.5 eV rather than 0.3 eV) of our measurements.

We have attempted to understand the spectra on Fig. 2 by theoretical simulations. These were performed by the multiple-scattering code of Vvedensky, Saldin, and Pendry.¹⁸ Muffin-tin potentials were taken from the self-consistent FLAPW LDA calculations of Massidda, Yu, and Freeman.¹⁹ Figure 4 shows the results of these simulations for the same orientations, θ , of the electric-field

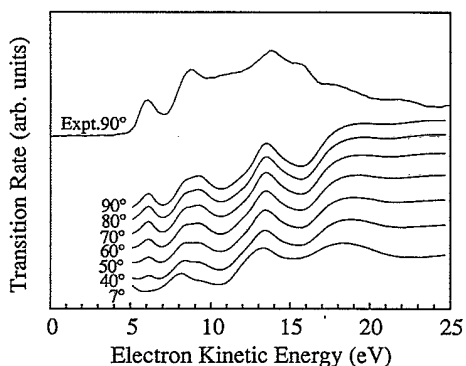


FIG. 4. Calculated XANES spectra of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ as a function of θ . An experimental spectrum is also shown above the calculated spectra for comparison. The experimental spectrum has been aligned with the calculated spectra.

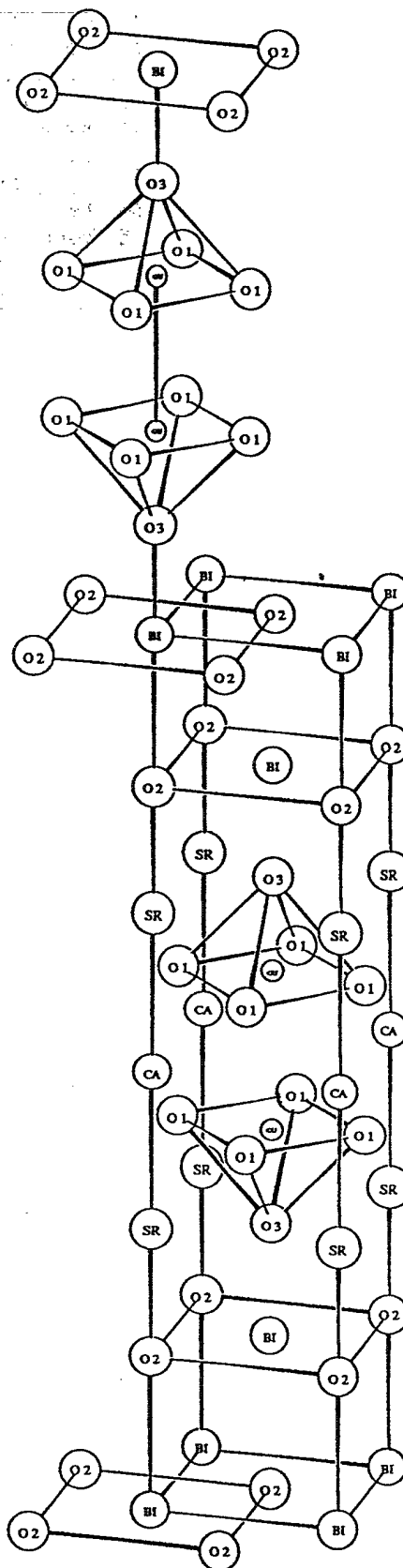


FIG. 5. Crystal structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.

vector of the x radiation from the crystal's c axis. An experimental spectrum is also shown in the same figure, above the calculated spectra, for comparison. The experimental spectrum has been aligned with the calculated spectra. Note that the peaks closest to the absorption edge on the calculated spectra seem to be dispersing in the same way as on the experimental data (Fig. 2). Also, the relative positions and intensities of the peaks seem to be consistent with our data, within the experimental accuracy.

Given that the O atoms in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ occur in three different environments (see Fig. 5), a XANES spectrum without a detailed theoretical simulation is a rather

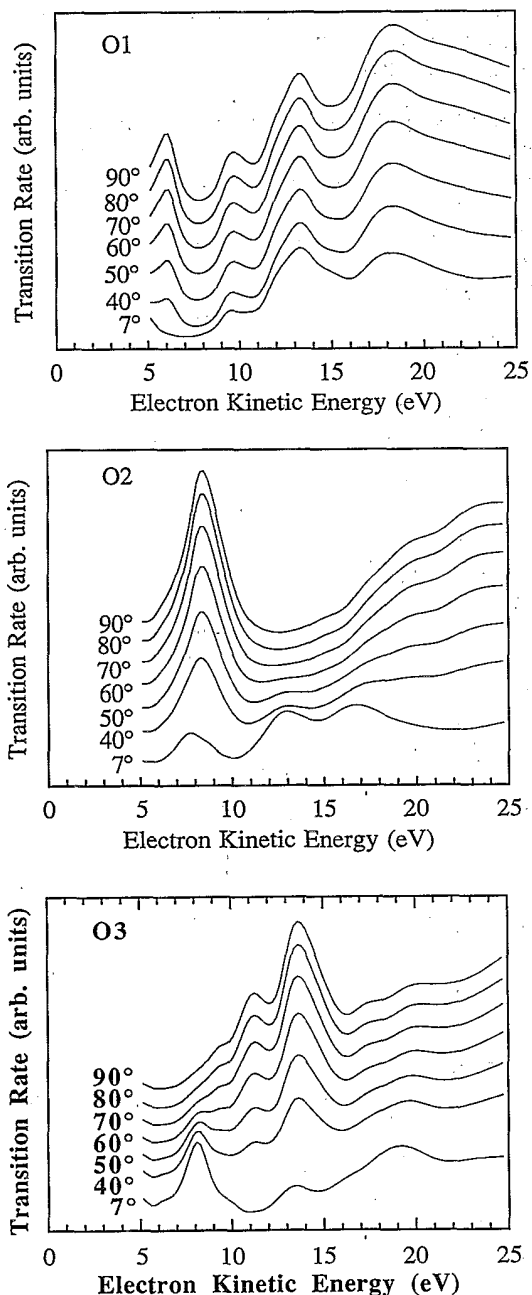


FIG. 6. Decomposition of the calculated total absorption cross section, as a function of θ , into the components due to holes on (a) O(1), (b) O(2), and (c) O(3) sites in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.

blunt tool. However, our calculations allow the decomposition of the computed total absorption cross section, as a function of θ , into the contributions from the excitations from the O atoms from the three different types of site, O(1), O(2), and O(3), shown in Fig. 5. These site-localized spectra are plotted in Figs. 6(a), 6(b), and 6(c), respectively. It can be seen that peaks *A*, *B*, and *C* arise from core-electron excitations from O(1), O(2), and O(3) atoms, respectively. The increase in the magnitude of the peak *A* as the electric field E is moved towards the Cu-O plane is a clear indication that it arises from the holes in the planar Cu-O orbitals. Similarly, one may argue that the peak *B* arises from the holes in the planar Bi-O orbitals. In contrast, the magnitude of the peak *C*, associated with the O(3) sites, increases as the electric field E is moved towards the c axis of the crystal. These results are consistent with the electronic-structure calculations of Marksteiner *et al.*,²⁰ who found that although the O(1) atoms were hybridized with the Cu atoms in their Cu-O basal planes, the Bi p states hybridize with both the O p states from the O(2) atoms in their own basal planes as well as the O(3) atoms displaced along the c axis and lying in the neighboring Sr-O planes. The last, of course, are not usually implicated in the flow of the supercurrents.

IV. CONCLUSION

We have compared the Bi L_3 x-ray-absorption near-edge structure from the high-temperature superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ with that from the trivalent Bi ion in Bi_2O_3 and the pentavalent one in KBiO_3 . The similarity of the spectra from the first two materials and their dissimilarity with the third suggests a formal valency of the Bi ions in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ of close to +3.

We have also made a systematic XANES study of the O K edge in single crystal $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, with a view to determining experimentally the orientations of the O holes, suspected of being associated with the high-temperature superconductivity in the cuprates. We are able to identify the contributions to the spectra of holes on all three O sites, and find direct experimental evidence that the holes of basal-plane symmetry lie in both the Cu-O and the Bi-O planes. In contrast, the holes associated with the O atoms [the O(3) atoms] at the apices of the oxygen pyramids in the structure occur in orbitals aligned along the c axis.

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