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Orientation-dependent x-ray-absorption near-edge studies of high-T_c superconductors

S. M. Heald, J. M. Tranquada, A. R. Moodenbaugh, and Youwen Xu
Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973

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Orientation-dependent x-ray-absorption near-edge measurements have been made on the Cu and Y K edges in oriented $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_{7-x}$ superconductors. The orientation dependence of the Cu edges is quite similar to that for other Cu^{2+} planar compounds, and allows a clear identification of a number of near-edge features. The results also demonstrate the strong similarity of the Cu-O planes in the two materials, and clearly establish that Cu^{1+} is being formed on the linear-chain sites for $x = 0.77$.

X-ray-absorption near-edge measurements can provide detailed information about the bonding and valency of transition-metal atoms. A number of authors[1-9] have applied near-edge spectroscopy to the Cu site in the high-T_c superconductors to probe its electronic nature. For x-ray absorption at the K edge, 1s electrons are excited to unoccupied states with p symmetry. Direct transitions to d states are forbidden for dipole transitions, but d states are often observed as weak features due to quadrupolar transitions. The d-state configuration can significantly affect the edge, however, through screening. For Cu compounds the shift in going from $3d^{10}$ (Cu^{1+} ion in solution) to a $3d^9$ configuration (Cu^{2+} ion in solution) can be as much as 13 eV.[1]

In spite of a large amount of previous work, there still exists some controversy over the interpretation of the near-edge features in the high-T_c compounds. The Cu valence has been interpreted to be various combinations of Cu^{1+}, Cu^{2+}, and Cu^{3+}.[1-9] Lytle, Gregor, and Panson[6] have even reported that edge structure provides evidence for large amounts of Cu (Y) antisite disorder. An examination of the data in the above papers reveals that all report essentially the same spectra, and the disagreement lies in the interpretation of data. In this paper orientation-dependent measurements are used to clarify the origin of the various near-edge features in $YBa_2Cu_3O_{7-x}$ and $La_{1.85}Sr_{0.15}CuO_4$. This work benefits from previous work on the orientation dependence of the Cu edge in a number of planar compounds.[10-13] The orientation dependence of the Cu in both high-T_c compounds is found to be quite similar to other planar Cu^{2+} compounds, although the low-energy shakedown satellite feature commonly observed when the x-ray polarization vector $\hat{e}$ is perpendicular to the ligand plane is quite weak. The results seem to rule out large amounts of Cu (Y) antisite disorder. For $x = 0.77$ clear indications of Cu^{1+} are observed, and the orientation dependence confirms that the Cu^{1+} is located in the twofold-coordinated sites of the tetragonal structure as has been previously postulated on the basis of structural considerations.[14,15]

The orientation measurements became possible with the report that a strong magnetic field will orient powdered samples.[16] For the present work 400-mesh powders were mixed with 5-min epoxy (Duro TM-51) and cast into disks in an 8-T magnetic field at room temperature. The c axis orients along the field direction which was in the plane of the disks. Thus the polarization of the x-ray absorption could be measured by rotating the disks relative to the plane polarized synchrotron radiation used for the measurements. X-ray diffraction confirmed the high degree of orientation with an unoriented fraction estimated to be $\lesssim 5\%$. Analysis of the extended fine structure for $YBa_2Cu_3O_7$ found an unoriented signal of $\simeq 10\%$ probably due to a small unpolarized component of the x rays. An advantage of these samples over single crystals is the absence of Bragg-reflection-induced distortions in the spectra.

The samples were prepared from rare-earth oxides, alkaline-earth carbonates, and CuO using slight variations[17] on published procedures.[18,19] For $YBa_2Cu_3O_7$, the details of the final oxygen atmosphere heat treatment are 40 h at 970 °C, 8 h at 700 °C, and a furnace cool to below 100 °C. The measurements were made at beamline C-2 at the Cornell High Energy Synchrotron Source using Si(111) monochromator crystals. The slit size was $\simeq 0.25$ mm. Data were taken on the Cu edge in $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.23}$, and $La_{1.85}Sr_{0.15}CuO_4$, and on the Y edge in $YBa_2Cu_3O_7$. For the Cu edge a Cu foil sample was run simultaneously as an energy calibration, and all the spectra are referenced to the small peak halfway up the Cu foil edge. For the Y edge data a Y foil was used as a reference, with the energies being referenced to the inflection point of the edge.

The data for $La_{1.85}Sr_{0.15}CuO_4$ are shown in Fig. 1. In this case a strong orientation dependence is seen, indicative of the strong anisotropy of the bonding at the Cu site in this material. For planar Cu^{2+} compounds a shoulder is always observed part way up the edge, which is enhanced when the x-ray polarization is perpendicular to plane. The data in Fig. 1 show a similar feature (B) which is most easily seen in the derivative spectra. The origin of this feature is generally attributed to transitions to $4p\pi^*$ states, where the asterisk indicates that the 1s-to-$4p\pi$ transition is accompanied by a shakedown transition associated with charge transfer from the ligands to the metal.[10-12,19] This charge transfer enhances the screening of the core hole, and lowers the transition energy from that associated with the p states which make up

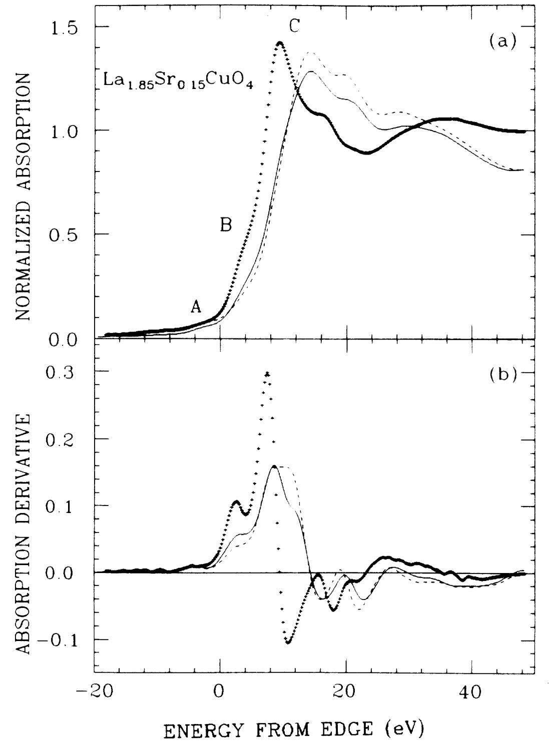

FIG. 1. Normalized Cu K near-edge absorption (a) and the absorption derivative (b) for unoriented (solid line) and an oriented sample of $La_{1.85}Sr_{0.15}CuO_4$ with $\hat{e}$ parallel to $\hat{c}$ (crosses) and $\hat{e}$ perpendicular to $\hat{c}$ (dashed line).

the main part of the edge. The strength of the feature in this case is significantly less than that found in other materials such as CuO and $CuCl_2 \cdot 2H_2O$. In previous work it has been suggested that a high degree of covalency will reduce the shakedown strength.[13] Another possibility is the existence of holes in the O 2p band which form the basis of a number of recent theories. Such holes can be expected to reduce the probability of charge transfer from the O 2p band, since such transfer would further deplete the band. Supporting evidence for this comes from studies on unoriented samples as a function of doping.[1] As the doping is increased, presumably increasing the number of holes, the intensity of the shakedown is reduced. The small pre-edge feature (A) is due to 1s-to-3d transitions. This feature is slightly enhanced for the in-plane spectrum reflecting the localization of initially empty 3d states in the a-b plane.

The main absorption feature (C) is seen to shift dramatically with orientation. This is the dipole-allowed direct transition to 4p states. For planar coordination these should be split into 4$p\pi$ and 4$p\sigma$ orbitals with the transition to the 4$p\pi$ orbitals allowed only for the polarization along the c axis, and the transition to the 4$p\sigma$ orbitals allowed for the polarization perpendicular to the c axis. This has been observed in other compounds, and just as for the present case, the 4$p\pi$ transition is observed to be ~5 eV lower in energy. The strong 4$p\pi$ signal is seen to be the origin of the upper shoulder in the unoriented spectrum. Thus, except for the weakness of the shakedown feature, the Cu spectrum in $La_{1.85}Sr_{0.15}CuO_4$ is seen to be quite similar to other Cu^{2+} planar compounds.

The spectra for $YBa_2Cu_3O_7$ are shown in Fig. 2. In this case the situation is complicated by the existence of two types of Cu sites. The Cu(1) sites are fourfold coordinated in a planar arrangement with oxygens in the b-c planes, while the Cu(2) sites are fivefold coordinated with four oxygens in the a-b plane and one at a longer distance along the c axis. Since the planes for the two sites are perpendicular, they will have different polarization dependence. When $\hat{e}$ is parallel to c, the Cu(1) σ and Cu(2) π orbitals will be excited. For polarization perpendicular to c the Cu(2) σ orbitals will be excited just as for $La_{1.85}Sr_{0.15}CuO_4$. For the Cu(1) sites the situation is complicated by the random orientation of the powder in the a-b plane. Thus, both the Cu(1) π and σ orbitals will be equally excited, significantly reducing the polarization dependence of the Cu(1) σ features. For the Cu(1) π features which are now only partially excited, the ~10% unpolarized component becomes important since it reduces the π component further when $\hat{e}$ is perpendicular to c, and adds a small π component for $\hat{e}$ parallel to c. The net result is a significantly reduced polarization dependence for the Cu(1) π feature as compared to the Cu(2) site.

The existence of two sites is clearly seen in the derivative spectra to cause a splitting of the 4$p\pi^*$ peak into two components (B and B′) with differing orientation dependence. B′ shows a strong polarization dependence, and is

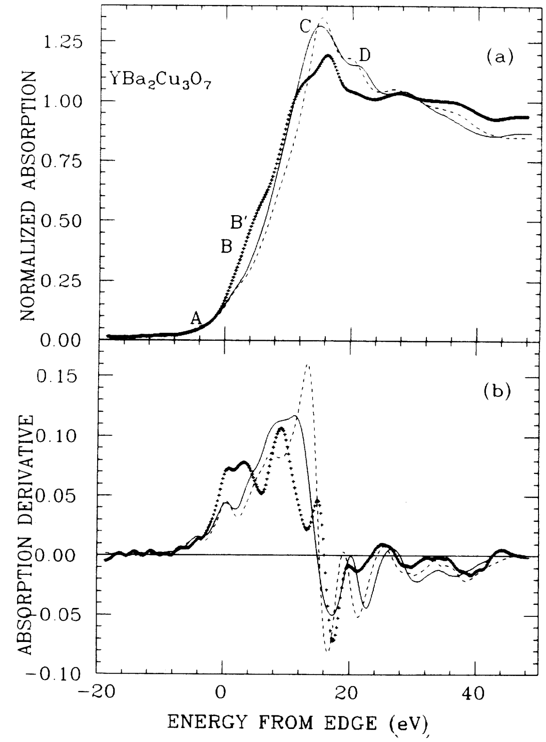

FIG. 2. Normalized Cu K near-edge absorption (a) and the absorption derivative (b) for unoriented (solid line) and an oriented sample of $YBa_2Cu_3O_7$ with $\hat{e}$ parallel to $\hat{c}$ (crosses) and $\hat{e}$ perpendicular to $\hat{c}$ (dashed line).

nearly absent for ê perpendicular to *c*. This strongly indicates that B′ is due to the Cu(2) sites as discussed above. For B the strong background from B′ makes it more difficult to quantify the polarization dependence, but it is clear that the dependence is weaker as expected for the Cu(1) sites. Confirmation for this assignment is also seen in a comparison of the unoriented spectrum with that for ê perpendicular to *c*. Feature B for the oriented spectrum shows the expected increase.

It is interesting to compare the position of these features with the same feature found in $La_{1.85}Sr_{0.15}CuO_4$. The $La_{1.85}Sr_{0.15}CuO_4$ transition is found to be quite close to the value of the Cu(2) transition and significantly higher than that for the Cu(1) sites. This suggests that the electronic environment of the Cu(2) site is similar to the Cu in $La_{1.85}Sr_{0.15}CuO_4$. In $La_{1.85}Sr_{0.15}CuO_4$ there are two *c*-axis bonds, but they are at a larger distance than the single *c*-axis bond found at the Cu(2) site, and therefore their net effect may be similar. This observation supports the notion that it is the Cu-O planes which are most important for superconductivity.

For the main part of the edge (C) the presence of two types of Cu complicates matters, and it is difficult to interpret the features as simply as for $La_{1.85}Sr_{0.15}CuO_4$. The single strong $4p\pi$ transition observed in $La_{1.85}Sr_{0.15}CuO_4$ when the polarization ê vector is along *c* is now split into two components. These are expected to be the Cu(2) $4p\pi$ and Cu(1) $4p\sigma$ transitions, with the $4p\pi$ transitions occurring at lower energy. For the polarization perpendicular to *c*, the strong feature is likely due to the Cu(2) $4p\sigma$ transition. This is shifted by ∼0.7 eV to lower energy from the Cu(1) $4p\sigma$ state reflecting somewhat longer (1.94 Å vs 1.85 Å) and weaker Cu—O bonds (note the absorption is probing the unoccupied or antibonding states).

More interesting is the feature D at about 20 eV. This has been interpreted as due to a Cu—O bond of about 2.5 Å, and indicating Cu (Y) antisite disorder since Cu in a Y site would have this bond length. However, the Y site is quite symmetric and features due to Cu in this site would show little orientation dependence. It is clear that the feature is nearly absent when the polarization is parallel to the *c* axis, contradicting this interpretation. The feature is most likely the low-energy part of the extended fine structure of a higher shell neighbor in the *a*-*b* plane. An essentially identical feature is observed for in-plane polarization in $La_{1.85}Sr_{0.15}CuO_4$.

Measurements on the Y edge are shown in Fig. 3, and support this view. Some orientation dependence is observed, but the main part of the edge is angle independent. The changes observed are of relatively high frequency as would be expected for contributions due to higher shell neighbors. These have a strong anisotropy, and their fine-structure contributions would be expected to cause such changes as are observed.

The data for $YBa_2Cu_3O_{6.23}$ are shown in Fig. 4. The oxygen vacancies in this case lead to some of the Cu(1)

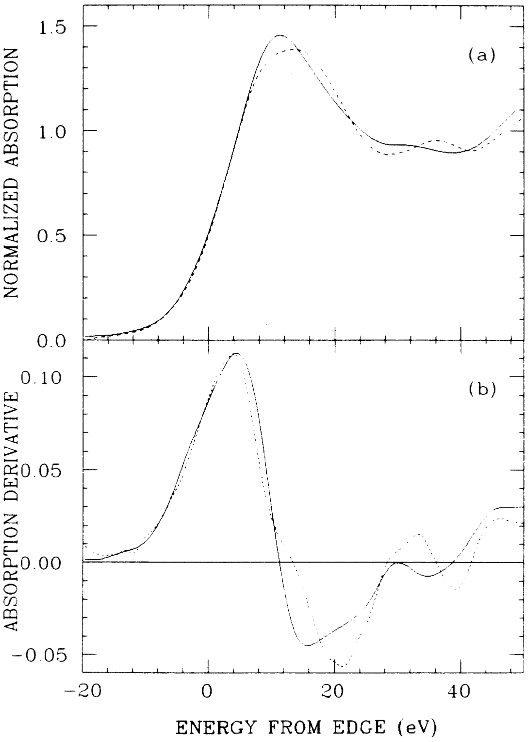

FIG. 3. Normalized Y *K* near-edge absorption (a) and the absorption derivative (b) for an oriented sample of $YBa_2Cu_3O_7$ with ê parallel to ĉ (dashed line) and ê perpendicular to ĉ (solid line).

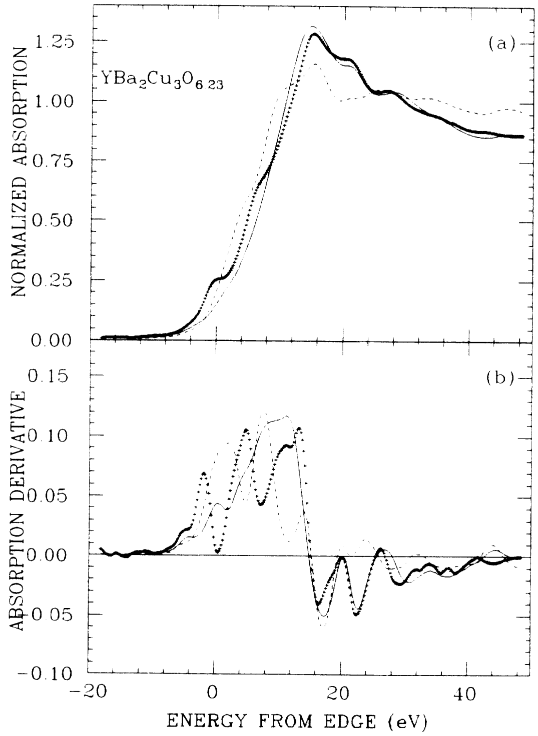

FIG. 4. Normalized Cu *K* near-edge absorption (a) and the absorption derivative (b) for an oriented sample of $YBa_2Cu_3O_{6.23}$ with ê perpendicular to ĉ (crosses) and ê parallel to ĉ (dashed line). The solid line is the spectrum from an unoriented $YBa_2Cu_3O_7$ sample for comparison.

sites becoming twofold coordinated with the bonds along the c axis.[14,15] As can be seen this results in a number of changes in the edge features. The most obvious is the appearance of a new peak near 0 eV, which is characteristic of Cu^{1+}. The low-lying transition for linear Cu bonding is of $4p\pi$ character (shakedown is eliminated by the absence of d holes), and will be enhanced when the polarization is oriented perpendicular to the bond direction. Thus, the existence of the feature only for the polarization perpendicualr to c axis clearly locates the Cu^{1+} in the Cu(1) sites as expected from chemical considerations.

It has been shown that orientation-dependent x-ray absorption can help unravel the complexities of the near-edge spectra for these materials. The planar Cu(2) sites in $YBa_2Cu_3O_7$ are found to be quite similar to the Cu sites in $La_{1.85}Sr_{0.15}CuO_4$, suggesting that the Cu-O planes are the dominant factor in high-T_c superconductivity. Both materials have weak shakedown features which may be a consequence of holes in the O $2p$ band. For oxygen-deficient $YBa_2Cu_3O_{6.23}$, Cu^{1+} is observed, which resides entirely on the linear Cu(1) sites. Finally, no indications for Cu (Y) antisite disorder can be observed in the near-edge structure.

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