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Anisotropy in the near-edge absorption fine structure of $YBa_2Cu_3O_{7-\delta}$

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We have observed orientational anisotropy of the near-edge absorption fine structure for the Cu $2p$ and O $1s$ excitations in single crystals of $YBa_2Cu_3O_{7-\delta}$ using electron-energy-loss spectroscopy. The O $1s$ absorption results suggest that O-derived holes near the Fermi level have $p_{x,y}$ symmetry. The Cu $2p$ edge is weakly anisotropic and consistent with some holes having d_{z^2} symmetry.

INTRODUCTION

Detailed characterization of the bulk properties of the recently discovered high-temperature superconductors has proven to be difficult due to the tendency of these materials to form polycrystalline, twinned, and highly-defect-density structures. Most experimental results are therefore averaged over many combinations of crystal orientation, composition, surface quality, and probably structure. Much detailed theoretical work, however, depends on restricted dimensionality or strong anisotropy. Recent experimental work on single crystals has confirmed anisotropy in measurements of magnetoresistance[1] and conductivity.[2] It would be useful, therefore, to have some experimental information on the symmetry and orientation of the band structure to guide the theoretical work.

We report results of inelastic scattering using high-energy electrons in well-characterized crystals of $YBa_2Cu_3O_{7-\delta}$. Within 20 eV of the absorption thresholds for the Cu $2p$ and the O $1s$ edges, we found anisotropic behavior on comparing results of scattering parallel to the a-b plane with results from scattering parallel to the c axis. From these results, we believe that we may make some basic observations regarding the symmetry of final-state holes near the Fermi level in the material.

MATERIAL CHARACTERIZATION

The $YBa_2Cu_3O_{7-\delta}$ material was prepared on a $SrTiO_3$ substrate as described elsewhere.[3] Briefly, coevaporation of Y, Ba, and Cu in a small partial pressure of O produced an amorphous film. Subsequent heat treating to 900 °C produced a polycrystalline film with the c axis largely oriented normal to the substrate plane. Characterization of the superconducting behavior was done by conductivity and Meissner experiments. This particular material has an exceptionally high critical current of about 10^5 A/cm^2. For the present experiment, it was convenient because it consisted of 0.3-μm-thick crystals which were orientated in one of two ways—with the c axis normal to the substrate plane or parallel to the substrate plane. The material was argon-ion milled to produce 20–100-nm-thick regions for electron microscopy and for the inelastic scattering experiments. Due to the possibility of damage in the presence of the ion milling, these experiments were repeated after reannealing of the thinned specimen. The results were not changed, so we believe that the experiments reflect the behavior of the undamaged material. The instrument used in these investigations was the VG Microscopes scanning transmission electron microscope (STEM), fitted with a high-resolution Wien filter electron spectrometer.[4] For these experiments, the energy resolution was about 0.3 eV and the probe size was varied from 2–10 nm depending on the specimen morphology. The acceleration voltage was 100 keV.

As a subject for other transmission electron microscope (TEM) investigations, the material has been rather well characterized.[5] As mentioned above, there are two basic morphologies present. Where the c axis points perpendicular to the film plane, 50-nm-wide twinned regions are present, confirming the orthorhombic structure. To obtain single-crystal data in these regions, the probe size in the energy-loss experiment was kept below 5 nm. Where the c axis lies parallel to the film plane, the crystals appear as 0.5-μm-wide plates having varying lengths. Since the twin planes are oriented parallel to the image plane, they are not visible in this region. Energy-loss spectra from this region are integrated over a few twinned regions.

EXPERIMENTAL GEOMETRY

The energy-loss scattering geometry in the STEM is illustrated approximately in Fig. 1. We have an incoming beam with wave vector $\mathbf{K}_0$ scattering through an angle θ into the final direction $\mathbf{K}_f$. The momentum $\mathbf{q}$ which is given up to the specimen has an orientation with respect to the specimen defined by the angle α. For the special condition $\theta_E = \Delta E/2E_0$ (where ΔE is the energy loss and E_0 is the incident energy), α equals 45°. At small scattering angles, α is nearly zero, producing excitations with the wave vector nearly parallel to the incident-beam direction. For large θ, α is nearly 90°, and the transferred wave vector is nearly perpendicular to the incident-beam direction. Thus, by controlling the scattering angle, the direction of wave-vector transfer in the material can be controlled, and anisotropy in the specimen can be detected. For instance, transitions from core states having s symmetry to final states having p symmetry are allowed in the dipole approximation only when the transferred wave vector $\mathbf{q}$ lies parallel to the spatial orientation of the final-state p orbit-

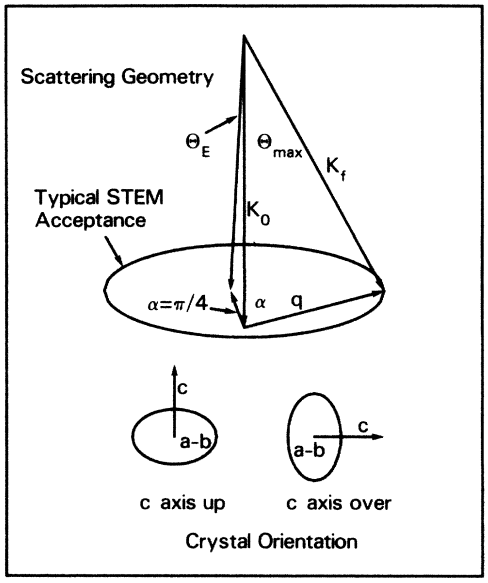

FIG. 1. Scattering geometry in the small-probe STEM instrument. Many scattering angles θ are integrated by axial apertures. Wave-vector transfer is favored to be in the directions perpendicular to the incident-beam direction, but some parallel component remains.

al. Thus transitions from the carbon 1*s* core level to the π^* levels in graphite require a wave-vector transfer parallel to the *c* axis, while transitions to the σ^* levels require transfer parallel to the graphitic planes. Angle-resolved experiments demonstrating this behavior have been conducted by others for conduction-band excitations in graphite[6] and for core excitations in boron nitride.[7] More complicated selection rules operate for $p \rightarrow d$ transitions,[8] leading to weaker expected scattering anisotropy. However, interpretation of observed anisotropy is similar to that for $s \rightarrow p$ transitions, because the orientation of the inner core state of *p* symmetry can be arbitrary, while the final states of *d* symmetry can have preferential orientation within the solid.

The geometry described in Fig. 1 is not wave-vector resolved, but is instead an integration over initial and final beam directions defined by two axial apertures as approximated by the single large aperture in the figure. Anisotropy of scattering intensity as a function of the transferred wave vector is expected, however, because θ_E is small with respect to the maximum scattering angle θ_{max} defined by the two apertures. We estimate the relative amount of scattering parallel and perpendicular to the incident beam by resolving the wave vector **q** in the two directions as a function of θ, and integrating over θ with appropriate phase space and scattering intensity weighting. In calculating the scattering intensity weighting, we have used the simple Born approximation in the dipole scattering limit.[9] We have ignored matrix-element and density-of-state effects. The ratio of scattering intensity in the perpendicular direction to that in the parallel direction was adjusted by selecting θ_{max} to be about 3:1 for the O 1*s* excitation (530 eV, $\theta_{max}=12$ mrad) and for the Cu 2*p* excitation (930 eV, $\theta_{max}=24$ mrad). We have verified this general behavior experimentally with the graphite 1*s* excitation at 285 eV.

EXPERIMENTAL RESULTS

Figure 2 shows the O 1*s* results. In this result, we have normalized the scattering intensity in a region several eV beyond the onset after subtraction of a smoothly varying background. This background largely consists of the high-energy tail of intensity associated with the Ba 4*d* absorption whose onset is at 94.5 eV. Since it is difficult to estimate the behavior of this intensity precisely, the magnitude of the oxygen absorption several eV beyond the edge is uncertain. Therefore, this study was limited to the extreme near-edge structure. We observe two overlapping edge structures, similar to those seen with x-ray absorption[10] in $YBa_2Cu_3O_{7-\delta}$ and to those seen in $La_{2-x}Sr_xCuO_4$ by electron energy loss.[11] The first, occurring near 527 eV, has been identified as being at or near the Fermi level by its dependence on Sr doping in the $La_{2-x}Sr_xCuO_4$. In this experiment, we find that this feature is strong when scattering is parallel to the *a-b* plane (*c* axis up) and weak when scattering in the *c* direction is allowed (*c* axis over). The magnitude of the observed anisotropy agrees relatively well with that predicted from the geometric scattering arguments above. Thus we conclude that holes near the Fermi level in the oxygen-derived orbitals have strong $p_{x,y}$ symmetry.

In Fig. 3, we show results for the Cu 2*p* edge, compared with results from CuO. We have not attempted here to scale the absolute scattering intensities (due in part to the large background intensity that must be stripped away), but observe that in general, the CuO scattering is about five times stronger than that in the $YBa_2Cu_3O_{7-\delta}$. This behavior is probably a reflection of the lower density of Cu in the $YBa_2Cu_3O_{7-\delta}$. The narrow peak at the absorption edge has been investigated by others for a range of transition-metal oxides.[12] Its presence is linked to the large density of states presented by the partially filled *d*

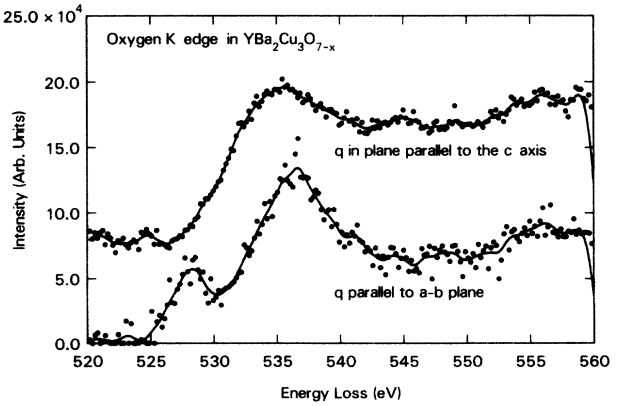

FIG. 2. O 1*s* absorption in the *c*-axis-up and *c*-axis-over orientations. The results of two separate experimental comparisons are shown. The pre-edge structure variation is understood in terms of final state holes with $p_{x,y}$ symmetry. The STEM energy was 100 keV and the half angle was 16 mrad.

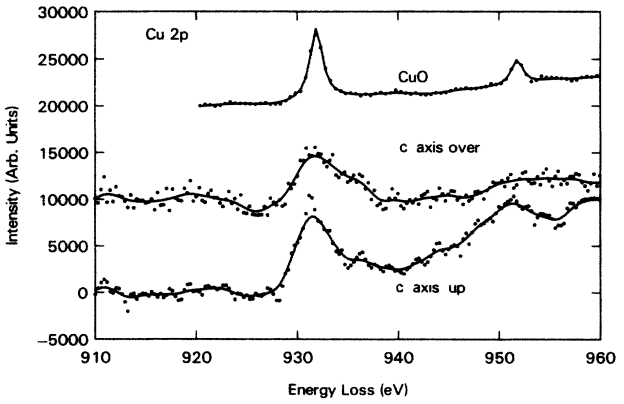

FIG. 3. Cu $2p$ absorption edge for CuO and $YBa_2Cu_3O_{7-\delta}$ in the c-axis-up and c-axis-over orientations. Only weak anisotropy is observed.

bands in the transition metals and their oxides. In the Cu metal, with a filled d band, the peak is absent, appearing only in the oxide due to charge transfer from Cu to O accompanied by hybridization of the Cu d with the O p orbitals. The peak observed in this experiment therefore indicates that the Cu d orbitals are partially empty and that they retain their narrow character. Interestingly, the width of the peak is about 2 eV in the CuO and closer to 4 eV in the new material. We speculate that this is a result of disorder in the Cu environment, possibly due to the incomplete coordination of the Cu by oxygen. The broadening would then be a clue as to a shift in the final-state band energy between the CuO planes and the chains. Little anisotropy is present in the magnitude of this onset peak. This is consistent with estimates of the transition-matrix elements for Cu $2p \rightarrow d_{z^2}$ and Cu $2p \rightarrow d_{x^2-y^2}$ scattering.[13] The small anisotropy that exists is therefore difficult to interpret.

In some regions of this specimen having the c-axis-up orientation, the Cu $2p$ onset peak disappears entirely. These regions were found to be not $YBa_2Cu_3O_{7-\delta}$ but some compound composed of Y, Ba, Cu, O, and C. For the core losses other than C and Cu, this material exhibited similar edge positions and shapes, leading to difficulty in identification for obtaining the Cu $2p$ anisotropy. We are still pursuing the identity of this material. It should be emphasized that this material system displays many morphologies and stoichiometries intermixed in the bulk. Extreme care must be exercised to avoid contamination of experimental data with results which are not characteristic of the material of interest. Further work must also be undertaken with a wider range of materials, and with more closely controlled wave-vector transfers. Thus far, however, the scattering data support the conclusion that $YBa_2Cu_3O_{7-\delta}$ is highly anisotropic close to the Fermi level, and provide evidence for quantifying this anisotropy for band-structure calculations.

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