

Photoemission from single crystals of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ cleaved below 20 K: Temperature-dependent oxygen loss

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The first low-temperature photoemission spectra from well-oxygenated and characterized, cleaved single crystals of the 1:2:3-type superconductors, specifically $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$, are presented. In contrast with polycrystalline or higher-temperature single-crystalline studies, a distinct and very stable density of states is found at the Fermi edge below 20 K. As the crystal is warmed even to 80 K the emission is rapidly lost from both the upper and lower portions of the Cu-O hybrids. At room temperature there is a loss of intensity at the Fermi edge with an accompanying change in the Ba $4d$ core-level line shape and the presence of a charging effect indicative of an insulating surface. These results imply that upon warming from 20 K there is very rapid oxygen loss from the cleaved surface with a resulting loss of superconducting behavior. This suggests that future photoemission experiments, especially those investigating detailed band structure, should be performed at low temperatures.

I. INTRODUCTION

The understanding and characterization of the new class of high-temperature superconductors poses perhaps the greatest and most active challenge to the physics community at present. The potentially novel physics and overwhelming technological impact of these materials on society has led to an unparalleled intensification of both theoretical and experimental research.¹⁻³ The electronic structure of the new high-temperature superconductors has been a particularly active topic of investigation.⁴⁻⁶ An accurate measurement of the full valence-band spectrum is clearly of fundamental importance. Most band-structure calculations of the 1:2:3 superconductors predict an appreciable density of states, i.e., at least 10% of the peak valence-band density of states, near the Fermi edge. The lack of experimental verification of this density for the 1:2:3-type compounds by techniques such as photoemission⁷⁻¹⁰ has brought both the adequacy of the calculations and the validity of the experimental results into question. This absence of states within several kT_c of the Fermi edge is particularly disconcerting since it implies that these materials do not even exhibit normal metallic-type behavior, much less superconducting behavior.

As with all new materials, the new high-temperature superconducting samples have often been imperfect and inhomogeneous. Early photoemission results from cleaved polycrystalline samples have been shown to be strongly affected by poor oxygenation and contamination at the grain boundaries and surfaces.¹¹⁻¹⁴ The inhomogeneity is particularly important for photoemission studies since these materials have loosely bound oxygen which has been

observed to be depleted from the vacuum exposed surfaces.¹⁵ Since photoemission is intrinsically a surface sensitive probe, its application to such potentially oxygen-depleted surfaces is especially suspect.

II. EXPERIMENT

To resolve the issues of the Fermi edge, valence-band structure, and homogeneity near the surface, we have made every attempt possible to ensure the integrity of our samples during the photoemission measurements. Complications associated with grain boundaries of polycrystalline samples and the uncertain surface contamination from thin-film samples were avoided by cleaving single crystals *in situ*. Oxygen loss from the cleaved surfaces was prevented by cooling the samples to near liquid-helium temperatures. Obviously the high-quality growth and complete oxygenation of these crystals is also essential for these experiments. The single crystals of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ were grown at Los Alamos from molten melt flux which produced single crystals roughly $1 \times 1 \times 0.25 \text{ mm}^3$. Since large single crystals lack the porosity of polycrystalline samples, the oxygenation process is particularly difficult. Two different oxygenation techniques were used to compare their effectiveness. The first was a 1100 to 850 K anneal at an oxygen pressure of 1 atm for three days. The second involved the high-pressure (3 kbar) anneal at 800 K for three days developed at Sandia National Laboratories.¹⁶ The oxygenated samples were then characterized by Meisner-effect measurements in a field of 100 G. Both samples ex-

hibited a diamagnetic onset temperature above 92 K, but the extent of the diamagnetism varied greatly. The first sample was poorly oxidized with only a 10% diamagnetic signal below 10 K. From this an average oxygen stoichiometry significantly below 6.5 was inferred. The second sample exhibited over 90% diamagnetism at below 10 K with a diamagnet midpoint at 56 K, suggesting nearly complete bulk superconductivity and an average oxygen stoichiometry of approximately 6.7. While this bulk-oxygen content is not as high as used in some other polycrystalline studies, the surface oxygen content is among the highest reported in the literature.

The photoemission experiments were performed at the National Synchrotron Light Source on beamline U-3 with a double-pass cylindrical mirror electron spectrometer. This provided an experimental resolution of 0.5 eV. The Fermi level was measured from an *in situ* sputtered Al substrate in electrical contact with the samples. The samples were epoxied onto and completely covered the end of aluminum sample holders. The sample holders were threaded into the copper cryostat. The crystals were cooled with a forced liquid cryostat employing either liquid helium or nitrogen. The sample temperatures were monitored by a thermocouple in good thermal contact with the copper tip of the cryostat. Sample temperatures were estimated to be less than 10 K higher than the thermocouple reading for the cryostat. With liquid-helium cooling the cryostat temperature was 10 K implying a sample temperature of less than 20 K. With liquid nitrogen we estimate a sample temperature of 80 K. Since the crystals were particularly small we tried to minimize any possible background signal from the cryostat by mounting the samples on the end of a 1-mm-diam, 5-mm-long aluminum rod. The samples were cleaved at either liquid-nitrogen or liquid-helium temperatures. The crystals were kept cold during the photoemission experiments, warmed and measured at progressively greater temperatures, and then cooled back down to examine the reversibility of any modifications. None of the observed changes were reversible with temperature. This indicates that irreversible oxygen loss, not a superconducting to normal phase transition, was responsible for the observed changes. The chamber pressure was kept in the low 10^{-10} to upper 10^{-11} torr range and no evidence of contamination was visible during the course of the experiment. The data presented below have been smoothed and scaled to equal peak intensity.

III. RESULTS

In Fig. 1 we present the photoemission spectra from near the Fermi edge of the well-oxygenated sample. The spectra show a strong and stable shoulder at the Fermi edge at both 20 and 80 K. The intensity of this shoulder is nearly 7% that of the peak intensity in the valence band. The sample was kept at 20 K for over 8 h with no change in the spectra, indicating that any residual adsorption from the ambient does not affect these states. Slight changes were apparent at the Fermi edge initially upon warming to 300 K. After 8 h at 300 K the Fermi edge

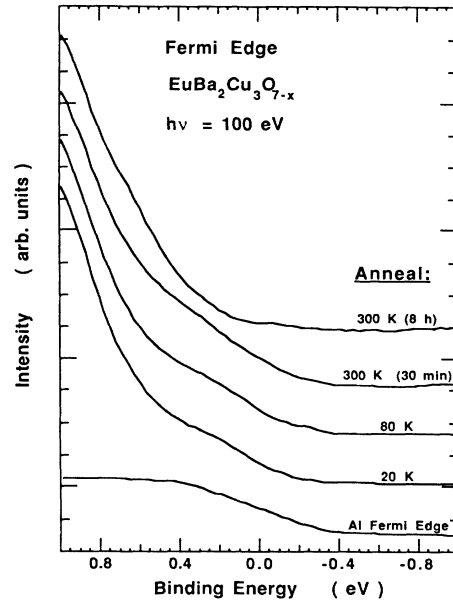


FIG. 1. Photoemission spectra from a well-oxygenated $\text{EuBa}_2\text{Cu}_3\text{O}_x$ crystal near the Fermi edge after various temperature-time anneals. A Fermi edge from a sputtered Al sample is also included for reference.

was no longer discernable. No Fermi edge was apparent for the poorly oxygenated sample (not shown).

The corresponding full valence-band spectra are shown in Fig. 2 and show very pronounced and irreversible temperature dependences. The spectrum from the 20 K, freshly cleaved sample shows strong emission from both the upper (2 eV) and lower (6 eV) portions of the Cu-O hybrid orbitals relative to the Eu 4*f* peak at 4 eV. The peak at 9 eV binding energy whose origin has been a continuing source of controversy, is only barely visible in this spectrum. Since the photon energy, 100 eV, is near the Ba 4*d* to 4*f* resonance we see quite pronounced emission from the Ba 5*p* levels. The resolved separation of the Ba 5*p*^{1/2} (14.8 eV) and Ba 5*p*^{3/2} (12.6 eV) components suggests the predominantly single-component nature of the Ba core levels. As the crystal is warmed from 20 to 80 K there is a

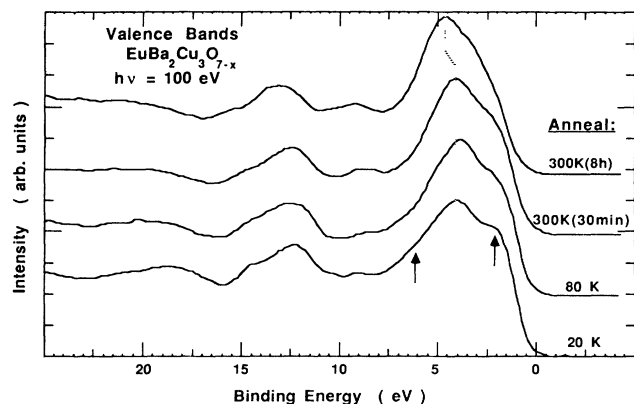


FIG. 2. Valence-band spectra from the well-oxygenated $\text{EuBa}_2\text{Cu}_3\text{O}_x$ crystal after indicated anneals.

very pronounced loss of intensity near both the upper (2 eV) and lower (6 eV) Cu-O hybrid orbitals. These changes are especially significant since the O $2p$ photoemission cross section at $h\nu=100$ eV is very small compared to that of Cu $3d$. A subsequent temperature increase to 300 K results in a continued narrowing of the Cu-O hybrid band and a growth of the controversial peak at 9 eV. After maintaining the crystal at 300 K for 8 h, there is essentially a rigid shift of the entire spectrum by 0.5 eV towards greater binding energy with further narrowing of the Cu-O hybrids and growth of the 9-eV feature indicating the charging of the region being sampled.

Figure 3 shows the corresponding photoemission spectra for the Ba $4d$ core levels along with those from the poorly oxygenated sample. The Ba core level is of particular interest since it has only one geometric site in the ideal, fully oxygenated structure and is in close proximity to the oxygen atoms in the Cu chains. As obtained by a least-squares-fitting algorithm, the well-oxygenated sample shows primarily a single-component structure with a Ba $4d^{5/2}$ binding energy of 88.2 eV. There is also a distinct shoulder on the low binding energy side of the primary peak with a binding energy of 87.3 eV. This shoulder has an intrinsic width of only 0.4 eV compared to the dominant component's width of 1.0 eV. As the sample is warmed to 80 K and even initially to room temperature, the Ba $4d$ spectra only broadens slightly with no appreciable change in line shape. After the 8-h room-temperature anneal the shoulder decreases in intensity and shifts by 0.5 eV towards greater binding energy while the dominant component broadens and shifts by 0.8 eV to greater binding energy. This final spectrum from the room-temper-

ature, well-oxygenated sample is similar to that of the freshly cleaved, 80 K, poorly oxygenated sample having two components each, shifted to greater binding energy than those in the freshly cleaved, well-oxygenated sample. As the poorly oxygenated sample is warmed to room temperature the main component of the Ba $4d$ spectra broadens further and shifts by an additional 0.4 eV towards greater binding energy with almost no discernable contribution from the low-binding-energy shoulder. Unfortunately the relatively poor resolution of our monochromator above the oxygen edge prevented us from obtaining meaningful O $1s$ core-level spectra.

IV. DISCUSSION

The general behavior of the above-mentioned temperature effects strongly suggests oxygen loss from the surface induced by warming. First, the shift of the Ba core levels to greater binding energy suggests the decreased screening efficiency of the Ba hole due to decreased oxygen coordination. While a loss of oxygen would be expected to result in a decrease of the ionization of the Ba and a consequent shift of the Ba levels to lower binding energy (a ground-state or initial-state effect), there is a compensating effect due to a decreased screening efficiency of the Ba core hole which could result in peak shifts to higher binding energy (final-state effects). Second, the loss of the photoemission intensity in the Cu-O hybrids would be expected from a loss of oxygen involved in the hybridization with the Cu. Third, the rigid shift of all the spectra by 0.5 eV towards greater binding energy following the 8-h, 300-K anneal can be explained by an electrostatic charging effect resulting from the oxygen loss near the vacuum interface. This shift provides compelling evidence that the surface has lost sufficient oxygen to be transformed from a superconductor into an insulator. The similarity of the Ba core-level line shape between our room-temperature, well-oxygenated sample and the cold, poorly-oxygenated sample also strongly supports an interpretation based on temperature-dependent oxygen loss. It is important to stress that the stability of the 20-K spectra for over 8 h and the rapid changes induced by warming confirm that the modifications we observe are temperature, not contamination, induced.

The more detailed consideration of our spectra using a fitting algorithm, especially in comparison with other spectra in the literature, provides valuable additional insight. Most notably, the position of the Ba core levels seems to indicate that most other photoemission experiments have examined oxygen-depleted surfaces. In particular, the binding energies of our well-oxygenated Ba $4d^{5/2}$ (87.3 and 88.2 eV) and Ba $5p^{3/2}$ (11.7 and 12.6 eV) core levels can be used to gauge the oxygenation of the sample surfaces. It is not surprising that some of the apparently well-oxygenated samples reported in the literature were measured by less surface sensitive x-ray photoelectron spectroscopy.^{17,18} In particular our well-oxygenated Ba $4d$ core-level spectrum is very similar to Steiner's in both absolute position and relative intensity. Our low-binding-energy shoulder component is slightly diminished relative to Steiner's most probably due to our in-

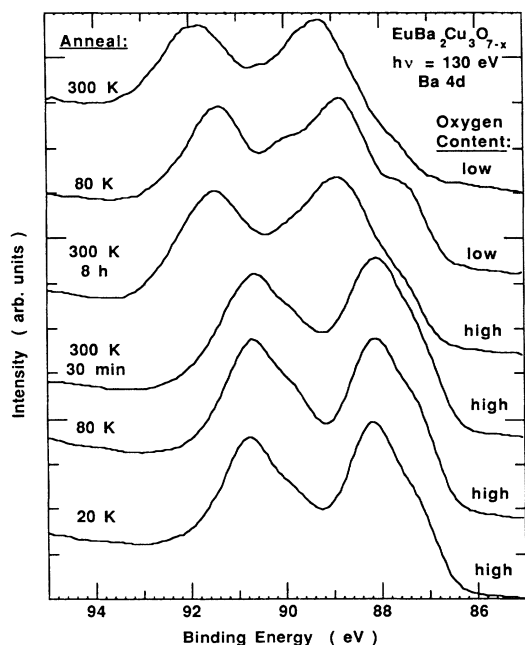


FIG. 3. Ba $4d$ core-level photoemission spectra for both a well and poorly oxygenated $\text{EuBa}_2\text{Cu}_3\text{O}_x$ crystal after specified anneals.

complete initial oxygenation and greater surface sensitivity. The low-energy shoulder and dominant peak in the well-oxygenated sample can be attributed to local oxygen coordinations of 10 and 9, respectively. Such an assignment is also consistent with our bulk magnetization estimate of the stoichiometry. It is interesting to note that upon annealing for 8 h at 300 K, the dominant peak is observed to chemically shift by 0.3 eV towards greater binding energy even after accounting for the 0.5-eV electrostatic shift. This is probably due to greater oxygen loss around the Ba atom. Surface contamination would also give rise to a shifted component, but this identification seems unlikely due to the stability of our surface at 20 K and the similar presence of a deeper binding energy component in the freshly cleaved, cold, poorly oxygenated sample.

Most other valence-band photoemission spectra in the literature, including recent room-temperature, single-crystal work,¹⁹ have a well-defined peak at a binding energy of approximately 9 eV. Since in our spectra this peak is absent in the well-oxygenated sample, grows with increasing oxygen loss, and is also apparent in the poorly oxygenated sample, it is most likely attributable to poorly oxygenated material. This dependence is opposite to that which would be predicted for a state arising from double ligand hole occupation.^{3,17} The correlation of the growth of this peak with the reduction of the Cu-O hybrid states suggests that some of the remaining oxygen electrons are becoming less bandlike and more localized in atomiclike orbitals. Finally, we note that our low-temperature Cu-O

hybrid width is significantly greater than either our higher temperature or other experimental results. This not only impacts band-structure calculations, but also has import in the Hamiltonian used to describe such systems.

In summary, the first near liquid-helium temperature photoemission measurements of *in situ* cleaved single crystals of the 1:2:3-type superconductors have been attained. The photoemission spectra are stable for many hours at 20 K, exhibit a distinct Fermi edge, and are extremely sensitive to warming with a loss of the upper and lower Cu-O hybrid orbital intensity at 80 K and a complete loss of the Fermi edge and radical changes in the Ba 4*d* line shapes at room temperature. By comparing the results of well-oxygenated and poorly oxygenated samples, strong evidence for an irreversible, temperature-dependent oxygen loss from the surface is found. Such evidence implies that photoemission measurements from samples at room temperature or even at liquid-nitrogen temperature may not be representative of the superconducting phase of the 1:2:3 materials.

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