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## LETTER TO THE EDITOR

**METALLIC, BAND-LIKE BEHAVIOR OF  $\text{EuBa}_2\text{Cu}_3\text{O}_{6.7}$  AS SEEN FROM UPS SPECTRA**  
**Comparison with band calculations**

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Valence band photoemission spectra of single crystals of  $\text{EuBa}_2\text{Cu}_3\text{O}_{6.7}$ , cleaved and measured at  $T = 20$  K, are presented. A stable Fermi edge is observed, whose amplitude is  $\approx 10\%$  of the maximum valence band intensity. This suggests metallic behavior. Except for a 1 eV shift toward higher binding energy, the results compare favorably with previous band calculations, and hint at a re-examination of theories based purely on a localized electronic structure. There is evidence for both Cu-3d and O-2p occupation at  $E_F$ , as predicted by band calculations.

**1. Introduction**

We have recently shown [1] that the vast majority of UPS photoemission data [2] taken at room temperature on  $(\text{RE})\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$  (where  $x > 0.5$ ) are probably not representative of bulk material. This is due to the rapid oxygen loss [3] which occurs at the surface in vacuum, and which is already evident at  $T < 80$  K even in single crystals cleaved at low temperatures. More likely these measurements are representative of  $x \approx 0$  assuming, of course, that no major reconstruction other than the orthorhombic to tetragonal transition occurs on the surface. We base this on our previous observation that after a few hours at room temperature in vacuum, a well-oxygenated, metallic single crystal surface becomes insulating as evidenced by a shift of the entire spectrum by as much as 0.5 eV toward higher binding energy. It is well known that the 1-2-3 materials are insulators [4] near  $x = 0$ . Such an insulating surface must have substantial thickness to sustain a charge, thus

even casting suspicion on any XPS measurements that were taken over a period of several days on the same sample surface. It is not surprising, then, that photoemission data vary so dramatically. Indeed the most consistently reported spectra (see, for example refs. [5-9], but the list is far from exhaustive) are entirely similar to our spectra on the insulating surface. It is also not surprising that all spectroscopic indications up to now were that the high- $T_c$  materials are not metallic, owing to the lack of a well-defined Fermi edge and the existence of satellites indicative of localized behavior. Many analyses of the data [5], and theories of high- $T_c$  superconductors [10], assume as a starting point that we are dealing with non-metallic, non-band-like materials.

Our recent experiments have shown, however, the UPS spectra on single crystals of  $\text{EuBa}_2\text{Cu}_3\text{O}_{6.6}$  ( $T_c$  midpoint = 55 K) cleaved at low temperatures ( $T < 20$  K) display a well-defined, stable, Fermi edge if the measurements are done at  $T \approx 20$  K, and that this Fermi edge rapidly disappears on

warming. This sensitivity to oxygen stoichiometry dictated that additional data be obtained on samples with  $x > 0.6$  and pointed to the need to completely reassess the data. In particular we felt the need to take another look at band calculations which predict [11–13] metallic Fermi surface and p–d hybridized bands at  $E_F$ , with oxygen p-character predominating. In this paper we report measurements on single crystals of  $\text{EuBa}_2\text{Cu}_3\text{O}_{6.7}$ , cleaved and measured at 20 K. The data are compared to band structure calculations to determine to what extent the electronic structure of these materials can be represented by such an approach. Surprisingly, we find substantial evidence that these materials are band-like, and that at  $E_F$  we have both Cu- and O-derived electronic structure. We believe that this should be a starting point for future models of high- $T_c$  superconductivity.

## 2. Experimental details

The single crystals of  $\text{EuBa}_2\text{Cu}_3\text{O}_{6.7}$  were grown from a flux and had typical dimensions of 1 mm  $\times$  2 mm  $\times$   $\approx$  0.1 mm. As grown, these materials are not superconducting, thus indicating a stoichiometry of  $x < 0.5$ . Because of their size they are difficult to oxygenate, requiring extreme conditions [14] of oxygen pressure (3 kbar) for at least 3 days at 500 °C. The oxygen stoichiometry is inferred from the midpoint of the superconducting transition temperature as measured by the diamagnetic susceptibility in a 10 G field on representative samples. While the transition was  $> 20$  K wide for the present samples, the midpoint was  $\approx 70$  K indicating that on the average  $x \approx 0.7$ . While this value may appear to be a small increment over our previous value of 0.6, the effect on the Fermi edge is substantial.

The measurements were done on the Ames–Montana beamline in Stoughton, WI, since the combined ERG–Saya monochromator gave us access to energies from 10 to 1000 eV. The low energies were essential in sorting out any oxygen resonance at 22 eV at  $E_F$ . The overall instrument resolution for the angle integrated measurements reported here ranged from 0.1 to 0.25 eV (com-

pared with our previous resolution of 0.5 eV). The chamber pressure was  $3 \times 10^{-11}$  Torr for all measurements below 300 K so that surface changes could not be induced by contamination within the time frame of the measurements. At elevated temperatures ( $T > 20$  K) only the specimen is heated while the cryostat continues to cryopump.

The samples were mounted with Torr-Seal epoxy to the end of a 1 mm diam.  $\times$  8 mm long Al rod, which was in intimate contact with the cryostat. A second Al rod was then mounted on top of the samples and the samples filed to conform to the rod cross-sections. Electrical contact was established via a coating of aqua-dag bridging the epoxy. The samples cleaved quite readily by prying on the top Al rod in situ at 20 K. Most of the spectra which we show here for comparison to band structure were taken within 4 h after cleaving, except for the spectrum at  $h\nu = 139$  eV. This was measured at 55 K after the sample was held for 12 h at 55 K. We point this out since some deterioration of the Fermi edge is already evident at this temperature as will be seen below from fig. 1.

## 3. Results and discussion

Because of the sensitivity of the spectra to oxygen content it is informative to dwell first on the time–temperature dependence which we previously measured [1] at  $h\nu = 100$  eV for  $x = 0.6$ . Here we show it for  $h\nu = 22$  eV, where we now access the 2s–2p absorption edge and amplify the oxygen-related features through resonance (or, as it turns out, an anti-resonance at  $E_F$ ).

Fig. 1 shows the spectra at resonance ( $h\nu = 22$  eV) on the same sample surface at various temperatures and times following a cleave (see figure caption for exact temperature–time variation). Clearly there is evidence for drastic time and temperature dependence which is irreversible. This would suggest that the failure of some UPS researchers to observe time-dependence in their data [5–9] is indicative of an already deteriorated starting surface.

The simplest indicator of a poor surface is the observation of the  $-9.5$  eV satellite which has

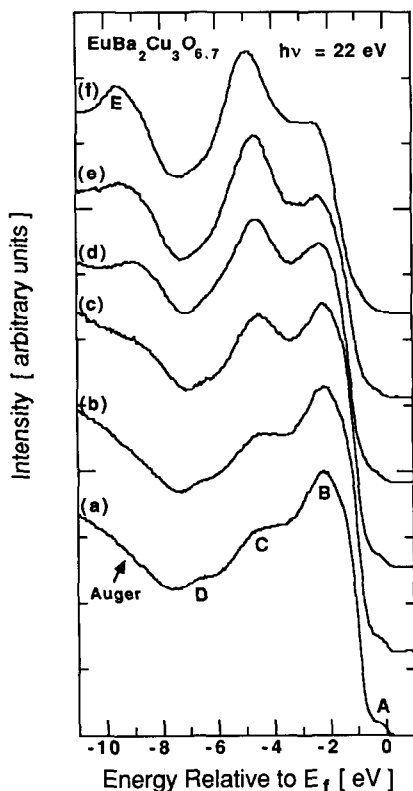


Fig. 1. Valence band photoemission spectra of  $\text{EuBa}_2\text{Cu}_3\text{O}_{6.7}$ , with  $h\nu = 22$  eV, taken at different times and temperatures after a cleave. (a) Fresh cleave at  $T = 20$  K; (b)  $T = 55$  K, 2 h after cleave. The crystal now set for 12 h at 55 K before taking the next three spectra in rapid successions: (c)  $T = 55$  K; (d)  $T = 150$  K; (e)  $T = 300$  K. The crystal was held for 12 more hours at 55 K before taking spectrum (f) at  $T = 300$  K. Note that an Eu-4f Auger peak coincides with the satellite peak E.

been the source of much discussion. This satellite is definitely oxygen-derived (it resonates at the  $h\nu = 22$  eV oxygen resonance) and grows dramatically with time and temperature. It is *extremely weak* in our freshly cleaved, well-oxygenated sample suggesting that it is probably totally absent for  $x = 0.9$ . At this point the reader may be confused by the apparent satellite in spectra (a) and (b) in fig. 1. It is unfortunate that in our Eu-based samples an Auger feature, which seems to be related to the Eu-5p absorption edge [16], occurs at  $-9.5$  eV for the resonant photon energy of 22 eV. The satellite intensity seen at other photon energies from a freshly-cleaved surface is nearly

zero. The actual oxygen satellite first becomes substantial in spectrum (c) of fig. 1 after the sample sat for 2 h at 55 K. Note that it is shifted from the Auger feature by  $\approx 1$  eV, and that its position in energy is also slightly time-temperature-dependent.

As the oxygen satellite increases in intensity (spectra (c-f)) there is a corresponding drop in intensity of feature B at  $-2$  eV which also resonates (relative to peak C) at  $h\nu = 22$  eV and hence contains substantial O-2p character. Likewise the signal at the Fermi edge dramatically decreases in intensity after 12 h at 55 K (spectrum (c)), and disappears altogether upon warming to 150 K (spectrum (d)). Feature D is already no longer evident after 12 h at 55 K (spectrum (c)).

Spectra (e) and (f) in fig. 1 were taken at room temperature and are similar to spectra most often reported in the literature [5-9]. Note that (f) is shifted relative to (e) by about 0.25 eV, indicating charging and hence an insulating surface. The difference between (e) and (f) is that the sample was held for 12 additional hours at 55 K before remeasuring at 300 K. Shifts as large as 0.5 eV are obtained after 12 h at room temperature. These results demonstrate that the Fermi edge disappears long before the surface becomes insulating, and that even at 55 K the surface deterioration and transformation eventually result in an insulating surface, albeit at a slower rate. It may be that the final insulating state is approached at all temperatures at different rates. Thus we emphatically state that all UPS measurements not taken below  $\approx 60$  K on a freshly cleaved surface are to be carefully scrutinized for surface deterioration. This is especially true for data claiming no temperature dependence, and may even hold for Bi- and Tl-based materials where a faint Fermi edge has been observed [17] at room temperature. This edge would probably be substantially larger if surface deterioration is prevented.

We obtain a hint of the nature of the surface transformation by comparing the above results to spectra from a freshly-cleaved surface of an as-grown, non-superconducting crystal (i.e.  $x < 0.5$ ). Space considerations preclude the presentation of a figure. Nevertheless, the spectrum, while not indicative of an insulating surface, agrees much

more closely with the present room temperature results (e.g. it has a large  $-9.5$  eV satellite intensity). This would seem to substantiate the supposition that our insulating surface consists merely of an  $x \approx 0$  material whose valence band is dramatically different from that of  $x = 0.7$ .

With the above as a warning prelude, we now discuss the data measured at 55 K and below within 4 h after cleaving. In fig. 2 we show six spectra spanning the range  $h\nu = 22$  eV to  $h\nu = 139$  eV, and compare them to theoretical spectra of Redinger et al. [18], published in 1987. The corresponding calculated and measured photon energies are not always identical, but they are sufficiently close that meaningful comparisons are possible. The spectra in the left panel were taken at 20 K, while those in the right panel were taken at 55 K. The 12 h delay for the 139 eV spectrum has already been mentioned. The secondary background was subtracted in our data in the usual fashion by assuming that the secondary intensity at any binding energy  $E$  is proportional to the total integrated signal from  $E_F$  to  $E$ . This enables

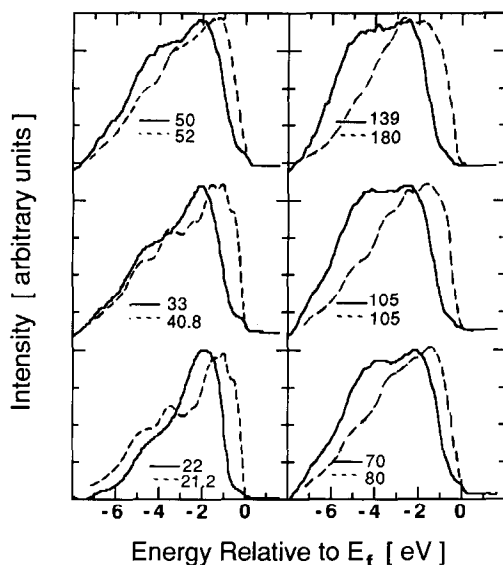


Fig. 2. Comparison of spectra at various photon energies to spectra predicted (ref. [18]) from a band calculation. Data in the left panel were taken at 20 K and at 55 K in the right panel. The  $h\nu = 139$  eV spectrum was then  $\approx 18$  h after the cleave and showed some deterioration. The Eu-4f contribution is non-negligible above 50 eV.

a more direct comparison with calculations. The solid lines are our data while the dashed lines are calculated spectra of Redinger et al. [18]. First we call the reader's attention to the very distinct Fermi edge in all experimental spectra which is about a factor of 2 larger here than in all previous copper oxide spectra. (Parenthetically, we would rule against photon-stimulated desorption as the primary cause of surface oxygen loss, since the spectra are stable at low temperatures regardless of exposure to photons.) The Fermi edge is seen at  $h\nu = 22$  eV where the O-2p cross section is three times larger than that of Cu-3d, and it is also seen with almost equal intensity at  $h\nu = 139$  eV where the relative cross-sections are almost reversed. This indicates contributions from both O-2p and Cu-3d bands at  $E_f$ . The  $h\nu = 22$  eV spectrum is most representative of the O-2p density, while the  $h\nu = 139$  eV spectrum should be primarily associated with Cu-3d emission. The 139 eV photon energy was chosen for comparison because at this photon energy the Eu-4f emission is at an anti-resonance and hence substantially (but not totally) suppressed, so that the underlying Cu-3d emission is more clearly revealed. Unfortunately the 12 h delay in the measurement of this spectrum has resulted in a total suppression of the  $-6.5$  eV shoulder.

An important point to note is that, besides the Cu-3d intensity at  $E_F$ , there are three additional Cu-derived features in the spectra (not counting the 12 eV satellite) which strongly argue against a localized Cu-3d level. The Cu features are spread throughout the 7 eV wide valence band in good agreement with band calculations. The observed maximum is at  $-4.5$  eV, however, vs. the calculated  $-3$  eV. This may not be a serious problem since the  $-4.5$  eV peak is seen to grow with oxygen loss at the expense of the  $-2$  eV and  $-6.5$  eV features. A strong narrow peak at  $-4.5$  eV appears indicative of an oxygen-deficient surface. This suggests a narrowing of the d-band so that the localized picture may be more appropriate for  $x = 0$ .

A glance at fig. 2 shows that the trends with  $h\nu$  and the shapes of the experimental spectra are very similar to those predicted by the calculation. The major discrepancies are a persistent 1 eV shift

of the experimental results to higher binding energies and an underestimate of Cu intensity at  $-4.5$  eV. The latter discrepancy, as noted, is probably indicative of a slightly oxygen-deficient sample (i.e.  $x = 0.7$ ). Moreover, at higher photon energies there is an increasing contribution from Eu-4f emission near  $-5$  eV. This strongly suggests that, except for the 1 eV shift, *the band calculations are fundamentally correct.*

We do not dismiss lightly the 1 eV shift as simply being due to an inaccuracy in the calculation. There may be important underlying reasons for the discrepancy. We are aware that some calculations [13] place the Fermi energy in a low density region 2 eV above the first strong peak. While we are happy with the placement of the Fermi energy, these same calculations place the bulk of the Cu-3d density into the peak at  $-2$  eV, clearly in contradiction with our data.

A reason often cited [5–9,18] for the 1 eV discrepancy is incomplete screening of the photoemission-created hole due to the highly correlated Fermi liquid. While this may be the most plausible explanation in view of the  $-12$  eV correlation satellite, there are other considerations. (Recall that we have ruled out the  $-9.5$  eV satellite as being intrinsic to the 1-2-3 material.) First of all, the measured d-band width is substantially broader than in Cu metal. Then, also, we have observed that the intensity of the  $-12$  eV satellite decreases with oxygen loss and hence seems to be more closely associated with good band states. While the Anderson impurity mode [15,19] for localized 3d levels would also predict that the satellite intensity should decrease as the p–d hybridization is weakened, we do not know how to reconcile the model with good band states. We do not rule out correlation. Indeed, we believe the problem may be similar to heavy fermions [20] where correlations within a well-defined band structure lead to photoemission satellites in the valence bands [21]. Even NiO is now being interpreted in this fashion [22]. On the other hand a two-hole bound-state satellite such as is found in Ni [24] cannot be ruled out as a viable alternative explanation for the  $-12$  eV satellite.

Another possible explanation for the 1 eV shift is that already stated in the paper by Yu, Freeman

and Massidda [25]. Their calculations are for the stoichiometric material,  $x = 1.0$ . They point out that the bulk of the density at  $E_F$  arises from the partially occupied  $\pi$ -bonding band which is a Cu1–O1–O4 hybrid. For  $x \leq 0.9$  this band is fully occupied and pushed below  $E_F$ . Recall that our measurements are for  $x = 0.7$ . This question then will easily be resolved by making measurements on crystals with  $x = 0.9$  and noting the intensity near and at  $E_F$ . If band calculations are correct, the intensity at the Fermi level should continue to increase with  $x$ . There is some consistency in this approach in that the above hybrid comes from the chains in the crystal structure and oxygen loss is believed to first occur in the chains. One might at first conclude that the question is already settled since our intensity at  $E_F$  is substantially larger for the present  $x = 0.7$  sample vs. our previous  $x = 0.6$  sample. However, due to sample inhomogeneities as evidenced by the broad superconducting transition, we cannot be certain that the intensity at  $E_F$  scales with  $x$  in the observed fashion.

There is finally the question of the  $x = 0$  results. Assuming that the surface of our crystals eventually transforms to the tetragonal EuBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> as oxygen is lost, we are faced with the problem of an insulating surface where most calculations predict a metallic state. To overcome this difficulty it has already been suggested [25,26] that while the calculations may be correct, an anti-ferromagnetic gap may induce a metal–non-metal transition in systems with high oxygen vacancies. The role of the vacancies is first to dramatically narrow the bands, with magnetism then occurring within these bands. Our data would support the band narrowing hypothesis as evidenced by the build-up of the  $-4.5$  eV peak with time. From this point of view the magnetic phase diagram of the cuprates is not so difficult to understand.

#### 4. Conclusions

We recapitulate here the following observations:

- (1) Rapid oxygen loss from the sample surface at  $T > 20$  K drastically changes the surface band

structure of the (RE)Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> materials and results in an insulating surface.

- (2) The shapes and photon energy dependencies of the UPS spectra taken at  $T \leq 55$  K within 4 h after a fresh cleave agree very closely with calculated spectra except for a 1 eV shift. Band calculations appear to be fundamentally correct.
- (3) A substantial Fermi edge is observed at all photon energies in freshly-cleaved  $x = 0.7$  samples, indicating metallic conductivity, and the occupation of both Cu-3d and O-2p orbitals at  $E_F$ .

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