Large, dispersive photoelectron Fermi edge and the electronic structure of YBa₂Cu₃O_{6.9} single crystals measured at 20 K

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We have performed angle-integrated photoemission measurements at 20 K on well-oxygenated $(T_c = 92 \text{ K})$ single crystals of YBa₂Cu₃O_{6.9} cleaved *in situ*, and find a relatively large, resolutionlimited Fermi edge which shows large amplitude variations with photon energy, indicative of bandstructure final-state effects. Some dispersion is seen even in our angle-integrated measurements. Our best estimate of $N(E_F)$ per Cu atom is that it is about 20% that of Cu metal with about a 20-80 mix of Cu 3d and O 2p orbitals. Dispersive and final-state effects are seen throughout the valence bands. The line-shapes of the spectra as a function of photon energy are very well reproduced by band-structure predictions, indicating a correct mix of 2p and 3d orbitals in the calculations, while the energy positions of the peak agree with calculated bands to within ≈ 0.5 eV. We conclude that a Fermi-liquid approach to conductivity is appropriate.

I. INTRODUCTION

While photoemission spectroscopy is, in general, a powerful tool for probing the electronic structure of materials,¹ it has proved somewhat erratic in the study of high- T_c superconductors. Because it is a surfacesensitive probe, the major experimental hurdle has been the preparation of high-quality surfaces in vacuum which are representative of the bulk. This is particularly true for the $(R)Ba_2Cu_3O_{6,9}$ materials (R = rare-earth element)whose surfaces have proved to be unstable in vacuum.²⁻⁵ The earlier photoemission work, primarily on scraped sintered powders, has been reviewed by Wendin^{6,7} and shows a notable lack of a Fermi edge which was a contributing factor to the general perception that a novel nonmetallic mechanism is responsible for the conductivity. This fact, combined with appearance of satellites in the photoelectron spectrum,^{8,9} as well as a 1 to 2 eV discrepancy between measured and calculated valence-band peaks $^{10-12}$ (whenever such a correspondence could be established) has cast serious doubt on the applicability of the one-electron model.¹³ Even measurements on cleaved single crystals failed to change the situation since the initial results obtained at room temperature were not

significantly different from those of sintered powders.¹⁴ We have recently shown,²⁻⁵ however, that the surface of a $(R)Ba_2Cu_3O_{6+x}$ superconductor remains quite stable in vacuum if the sample is kept at very low temperatures. For the first time, a very distinct and stable Fermi edge

was observed which, however, disappeared rapidly as the sample was warmed above ≈ 50 K. Changes upon warming were observed throughout the valence bands and core levels as well, and are interpreted in terms of oxygen loss in the near-surface region. Clearly, previous measurements at room temperature were not always probing the bulk electronic structure, and reports of temperature dependence¹⁵ possibly had their basis in a deteriorating surface.

Almost simultaneously with our discovery of stable metallic behavior in the 1:2:3 compounds, various researchers reported the existence of a distinct, albeit very weak, Fermi edge in the Bi-Ca-Sr-Cu-O materials.^{16,17} Apparently, these compounds are substantially more stable in vacuum than the 1:2:3 compounds. Quite recently, it is reported in the cubic perovskites as well,¹⁸ thus bringing a satisfying uniformity to the field of high- T_c superconductivity, and a conviction that we are at last probing the true bulk electronic structure. An ironic twist to the saga of the missing Fermi edge in the YBa₂Cu₃O_{6.9} compounds is that not only does it now exist, but it appears to be between two and ten times larger than in the related superconducting oxides as measured relative to the valence-band maximum.

Since our previous data were on EuBa₂Cu₃O_{6.7} crystals $(T_c \approx 70 \text{ K})$ which had less than optimum homogeneity, comparisons to calculations were not completely satisfactory. A thorough study of an O_{6.9} material is clearly called for, now that the method for surface stabilization is known. This is particularly true in view of the fact that

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most band calculations are for O_7 systems, $^{19-24}$ so that comparisons to $O_{6.7}$ will not suffice. While it is true that the gross features of the electronic structure, i.e., those probed by a photoemission measurement, will not yield the exact nature of the coupling mechanism, they must at some level influence this mechanism. It is essential then to resolve the many outstanding questions regarding the electronic structure of these materials.

In this paper, then, we report on an extensive angleintegrated photoemission study of the valence bands of $YBa_2Cu_3O_{6.9}$ crystals cleaved in situ and measured at 20 K, in order to preserve the stoichiometry of the sample surface. Our purposes are to (a) characterize the photoemission intensity at E_F and obtain some rough estimate of $N(E_F)$, (b) determine the wave-function character at E_F , (c) compare the now rich valence-band spectra to calculations, (d) resolve outstanding issues regarding core level spectra as well as the -9-eV feature, and (e) characterize the resonance properties at the various absorption edges. Because of the very extensive nature of the data, and the desire to keep this manuscript to a manageable length, several items [e.g., (b) and (d)] will reported in greater detail elsewhere, 25 with only the most relevant conclusions reported here. Here we will show that for the $O_{6,9}$ material a large intensity at E_F is obtained which is now quite consistent with predictions of band theory. Indeed, the expectations from a traditional Fermi liquid²⁶ should be explored. This complements the recent positron annihilation results²⁷ which indicate the existence of a Fermi surface not too dissimilar from predictions.

II. EXPERIMENTAL DETAILS

The single crystals of $YBa_2Cu_3O_{6.9}$ were grown via an off-stoichiometry self-flux technique,²⁸ in contrast to our previous $EuBa_2Cu_3O_{6+x}$ crystals which were grown in a CuO-PbO flux. The latter technique may result in some residual Pb impurities (undetectable in photoemission) which could hinder complete oxygenation of the samples. In addition, recent phase diagram work by Hinks et al.²⁹ shows that while yttrium reacts to form a line compound in the 1:2:3 structure, other rare-earth elements such as europium have a range of compositions, with resulting serious consequences on T_c and homogeneity. In the $YBa_2Cu_3O_{6+x}$ crystals the oxygen stoichiometry was readily controlled (from 6.2 to 6.9) by annealing the samples at 500 °C in a flowing gas stream containing a predetermined mixture of O2 and N2 at atmospheric pressure. After equilibration at 500 °C for a minimum of 24 h, the samples were quenched in liquid nitrogen. Thus, our previous high-pressure techniques³⁰ were unnecessary. Microscopic examination of the O_{6.9} samples (our primary concern in this paper) revealed a high density of twins, with all the twin lines oriented along a single $\langle 110 \rangle$ direction. Typical sample dimensions were 1.5×1.5×0.05 mm. Magnetization measurements, taken with a SQUID magnetometer, indicated a T_c of 92 K with a transition width of ≈ 2 K. Samples were cooled in zero field, then magnetization data were taken in a measuring field of 2-5 Oe upon warming.

In order to enable us to cleave the crystals in the pho-

to emission chamber, the samples were mounted with epoxy between two 1-mm-diam aluminum rods oriented end to end. The sample c axis was parallel to the rods. One of the rods was attached to the cryostat cold finger so that cleaving was effected by prying on the free rod. The specimens cleaved quite readily at 20 K (or at 300 K), with a subsequent microscopic examination revealing large areas of mirrorlike surfaces.

The photoemission measurements were made at the Synchrotron Radiation Center in Stoughton, WI, using the Ames-Montana ERG/SEYA line as well as the newly commissioned Minnesota-Argonne-Los Alamos beamline (ERG). Overall instrument resolution using a double-pass cylindrical mirror analyzer (CMA) varied from 125 to 200 meV. The chamber pressure was maintained at $\approx 5 \times 10^{11}$ Torr throughout the measurements. Cooling to 20 K was accomplished via a closed-cycle He refrigerator.

The measurements reported here were done with the sample temperature maintained at 20 K since we have shown²⁻⁵ that warming the samples above 50 K results in a loss of the Fermi edge as well as irreversible changes throughout the valence band. Typically, the samples were held at 20 K for 48 h or more with no significant change in the spectra. The spectra were frequently monitored at hv = 50 eV to discern any changes, as well as at lower photon energies to detect the common adsorbates (O and CO). Some minor irreversible deterioration with time was observed due to photodesorbtion of oxygen (i.e., all deterioration ceased over-night with no photons impinging on the sample), as well as some very minor deterioration due to an overnight buildup of CO on the surface. The CO adsorbate caused no modification of the valence-band features and was, in any case, easily removed by flashing the sample to 50 K for less than 1 min so that no oxygen from the specimen was lost. A complete restoration of the last spectrum of the previous day was generally obtained. We might point out that this submonolayer adsorbate did not yield the now famous -9-eV feature, but rather the more familiar double peaks at -8 and -11 eV.

While temperature-dependent phenomena are not within the scope of this paper (again, they have been thoroughly reported by us previously $^{2-5}$), we wish to point out that all samples were eventually heated to room temperature and monitored for any spectral changes. Just as previously reported, an irreversible loss of the Fermi edge rapidly occurred in each case, as well as a buildup of the -9-eV oxygen-related feature. However, it was found that the deterioration of the $Y-O_{6.9}$ specimens was substantially slower than that of our previous $Eu-O_{6.7}$ samples (hours versus minutes). Also, within the YBa₂Cu₃O_{6.9} system, the rate of oxygen loss was a function of oxygen stoichiometry as well; i.e., it increased somewhat with decreasing oxygen content. While it may be that the same mechanism responsible for poor oxygen uptake may act to enable a rapid oxygen loss in the near surface region, other possibilities should be considered. In particular, if oxygen diffuses from the crystal in the ab plane rather than along the c axis,³¹ then a highly stepped surface provides a much shorter escape path for

oxygen versus a smooth mirrorlike surface. Our previous cleaved surfaces were, indeed, highly stepped.

III. RESULTS AND DISCUSSION

A. The intensity at E_F

The largest intensity at E_F (relative to the valence-band maximum) observed to date in an oxide superconductor is shown in the spectrum in Fig. 1, taken at 20 K and hv=50 eV for YBa₂Cu₃O_{6.9} (sample A). It equals more than 20% of the maximum valence-band intensity. Superimposed in the figure is the spectrum for Cu metal taken at hv=40 eV (Ref. 32) for purposes of comparison. (All other oxide superconductors reported thus far have relative intensities at E_F that are even smaller than that of the Cu metal in Fig. 1.)

One must not, of course, conclude from Fig. 1 that $N(E_F)$ for YBa₂Cu₃O_{6.9} is larger than for Cu metal. Indeed, to obtain an estimate of $N(E_F)$ for YBa₂Cu₃O_{6.9} relative to Cu from Fig. 1 requires several assumptions and approximations in normalizing the spectra. By normalizing the two spectra to the integrated Cu 3d intensity, it should, in principle, be possible to obtain an estimate of $N(E_F)$ per Cu atom relative to that of Cu metal. The various assumptions are (a) the photocurrents due to Y 4d and 5s, Ba 6s, and Cu 4s emission are more than an order of magnitude smaller than that due to Cu d and O

2p and can thus be ignored, (b) we assume a Cu $3d^9$ and O $2p^6$ configuration so that the ratio of d to p electrons is 27/42, (c) we analyze the data at hv = 50 eV where the cross sections σ_{3d} and σ_{2p} are nearly equal, so that 40% of the integrated intensity in Y 1:2:3 comes from Cu 3d, (d) we use the calculated atomic cross sections³³ since it has been shown¹⁰ that they are not too different from those actually calculated for Y 1:2:3, and (e) the magnitude of σ_{4s} is estimated from the Cu spectrum to be about 8% that of σ_{3d} . After normalizing, it is estimated from the ratio of the intensities at E_F that $N(E_F)$ per Cu atom in Y 1:2:3 is about 20% of that in Cu metal. Band calculations²³ yield $N(E_F)$ in O₇ material that is twice that of Cu metal. While much of the discrepancy can probably be traced to the rough approximations, a large part reflects the fact that our intensity at E_F is still two to five times lower than various calculations (see Fig. 5). $^{34,19-24}$

Figure 2 shows the Fermi edge in another sample (B) of $YBa_2Cu_3O_{6.9}$ for a number of different photon energies. We distinguish between samples because the intensity at E_F is somewhat cleave dependent. That of sample B, for example, is $\approx 20\%$ smaller (relative to the valence-band maximum) than sample A, although both samples were nominally $O_{6.9}$. The spectra in Fig. 2 were normalized to integrated intensities of the valence bands. A more correct normalization would take into account the varying relative cross sections of the 3d and 2p electrons; i.e., at each photon energy the integrated intensity should be proportional to $[42\sigma_{2p}(h\nu)+27\sigma_{3d}(h\nu)]$. However, this





FIG. 1. Valence-band spectrum for YBa₂Cu₃O_{6.9} (sample A) at hv = 50 eV. The sample was cleaved and measured at T = 20 K. The intensity at E_F is more than 20% of the maximum valence-band intensity. Superimposed in the figure for comparison is the valence-band spectrum of Cu metal taken from Ref. 32.

FIG. 2. Blowup of the Fermi edges in YBa₂Cu₃O_{6.9} (sample B) at various photon energies. Note the large amplitude variations with hv. A double shoulder is evident at E_F for hv=26 and 28 eV, indicative of dispersion.

results in a montonic decrease of absolute intensity which is undesirable for purposes of display. Since we wish to focus primarily on the rapid changes of intensity in small energy windows, the normalization presented here is quite adequate. A detailed study of the hv dependence of the Fermi edge is quite extensive and will be given in a separate publication.^{25,35} Here we merely wish to point out that the amplitude decreases with hv more slowly than σ_{2p} $(h\nu)$, indicating a substantial Cu 3d contribution at E_f . The result of the best fit to the amplitude dependence yields approximately a 20-80 mix of Cu 3d and O 2p orbitals at E_F . In a more traditional experiment to determine the orbital character of photoemitted electrons (i.e., Fano resonance at a core absorption edge), a recent publication³⁶ shows only a very small intensity enhancement at E_F in YBa₂Cu₃O_{6.9} and La_{2-x}Sr_xCuO₄ at the Cu 3p absorption edge (hv = 74 eV), and none at all



FIG. 3. Valence-band spectra for YBa₂Cu₃O_{6.9} (sample B) for a series of photon energies normalized to equal maximum intensities. The clearly identifiable peaks are labeled A through F. Many final state peaks are evident below hv=24 eV, which shift to apparent higher binding energies with hv. One set of these is labeled by the arrows. Much of the O 2p intensity is concentrated in peaks A and B, while the Cu 3d intensity is centered on peak D (more clearly seen in Fig. 4 at hv=70 eV), but is distributed throughout the valence bands. The differences between sample A and sample B probably reflect differences in orientation from residual angle-resolved effects.

in Bi-Ca-Sr-Cu-O. We would, however, caution the reader that a null resonance experiment at the 3p edge is inconclusive in view of the fact that the entire valence band shows only a weak, or no resonance. Most of the resonant intensity is in the -12-eV satellite (see Sec. III C). Thus a similar cross-section study as done on YBa₂Cu₃O_{6.9} is desirable on Bi-Sr-Ca-Cu-O compounds.

In this paper we wish focus attention on the various apparent resonances at E_F at photon energies of 14, 18, 20, 26, and 50 eV. (The 14-eV enchancement is seen in Fig. 3.) The 18-eV enchancement at E_F has been observed in other systems¹⁶ and has been attributed to a Fano resonance at the O 2s absorption edge. While we are not prepared to state that this is or is not the actual enhancement mechanism, we would alert the reader to obvious complications in the form of the enhancements at the other stated photon energies. We cannot rule out the possibility, for example, that 18 eV enhancement has its origin in the same mechanism responsible for intensity enhancements at other hv, namely, van Hove singularities in the joint density of states. We state this for the following reasons: (a) the O 2s absorption edge, at least in EuBa₂Cu₃O_{6.7}, occurs at 22 eV and not at 18 eV, as evidenced by the resonance of the predominantly 2p-like features⁵ at -2 eV, as well as the nearly pure oxygen impurity peak at -9 eV (see Sec. III C), (b) we know of no other mechanisms that can produce enhancements at the other photon energies, (c) there is a satisfying correlation between the 18- and 50-eV intensity enhancements if we assume a free-electron parabolic final-state band.³⁷ In this model, the 18-eV enchancement comes from the second Brillouin zone, while that at 50 eV is due to the same van Hove singularity in the 3d zone, and (d) various final-state peaks in the secondary electron spectrum are observed near the secondary cutoff (see Sec. III B and Fig. 3).

In a true angle-integrated photoemission measurement one would generally not expect k-dependent spectral manifestations from individual bands. However, we are measuring the photocurrent from single crystals with an energy analyzer (CMA) which admits only a limited number of electron trajectories. In particular, one of the trajectories accepted is that of normal emission, which may dominate over other spectral features. If van Hove singularities are present, they will further enhance this dominance. Thus it is entirely possible to observe residual angle-resolved effects in an angle-integrated measurement, if single-crystal specimens are used.

Finally we discuss a feature in Fig. 2 which likewise has its origin in angle-resolved phenomena, and is perhaps most significant. In particular, we focus attention on the Fermi edges for $h\nu=26$ and 28 eV where a clear double shoulder characterizes the Fermi edge. The peak in the spectral density is clearly below E_F by an amount greater than our instrument resolution of ≈ 125 meV at this photon energy. At other $h\nu$ the peak is at E_F to within instrument resolution. We are clearly observing dispersion in the band that crosses E_F even in our angle-integrated measurement. Takahaski *et al.*¹⁶ have observed dispersion at E_F in Bi₂CaSr₂Cu₂O₈ in their angle-resolved experiment along the k_x and k_y directions. Our data complement their experiment well and suggests that the bandlike nature of the carriers at E_F is universal in high- T_c materials. Thus we are observing what appear to be traditional metallic bands crossing E_F . Photoemission measurements on the newly discovered^{38,39} electrondoped cuprate superconductors should prove very interesting. Indeed, it may be possible to establish whether the concept of a doped semiconductor has validity since in that case a band gap should be observed near E_F in contrast to the preceding situation. The discovery of these materials at first glance, however, reinforces for us a more traditional band picture, where in a metallic system the behavior of electrons and holes is interchangeable.

While the purpose of this paper is to discuss primarily the electronic structure of the well-oxygenated $(T_c = 92)$ K) $YBa_2Cu_3O_{6,9}$ material, we have also measured the spectra on materials with lower oxygen content and hence lower T_c 's. A detailed discussion of those results is beyond the scope of this paper and will form the basis of a separate manuscript.⁴⁰ Nonetheless we wish to point out that the intensity at E_F decreases anomalously rapidly with T_c and may have its basis in the strong coupling model,⁴¹ consistent with the finding of Imer et al.⁴² that the gap $2\Delta = 8 kT_c$. We mention this fact here because of our observation that all published values^{8, 16, 18} of Fermi edges in related superconducting oxides (including the cubic perovskites) appear to be anomalously low relative to our large intensity in YBa₂Cu₃O_{6.9}. In all cases the samples measured had T_c 's lower than 92 K. It will clearly be essential to measure the spectrum of the 120 K compound once the metallurgical problems are overcome. From the strong-coupling model one would anticipate a large $N(E_F)$.

B. Valence bands --- comparison to band calculations

The full valence-band spectra taken at different photon energies in sample B are displayed in Fig. 3. (Although the intensity at E_F is smaller for sample B versus sample A, the counting statistics, due to a change in beamlines, are superior in sample B.) The spectra differ substantially from most reported in the literature, and contain more structure than even our previously reported²⁻⁵ results on EuBa₂Cu₃O₆₇. Again, because of our partially angleresolved measurement, we are observing a spectrum not totally representative of the density of states. This is particularly true at low photon energies $(h\nu < 24 \text{ eV})$ where at first glance there appears to be substantial dispersion in the valence-band peaks. While some dispersion actually exists, the bulk of the apparent shifts is again a result of final-state enchancements in valence-band emission from certain bands at the those values of hv which allow direct transitions at van Hove singularities in the joint density of states (usually at Brillouin-zone boundaries). Thus much of the apparent dispersion is caused by a series of these final-state enhancements shifting by 1 eV in the spectrum each time the photon energy shifts by 1 eV. (Note one set of these enhancements marked by the arrows.) They are extremely useful in verifying the existence of a feature which may otherwise be unobservable

due to a weak cross section. In this manner, besides the peak at E_F , we identify six other peaks in the spectra which we label A through F in the figure. The 19-eV spectrum, for example, confirms the existence of feature C, while the 20-eV spectrum clearly enhances feature D, albeit both (not surprisingly) with some dispersion. The identifiable peaks are located at -1.5, -2, -3, -4, -5, and -6.5 eV. Peak A has the highest intensity at low hvand rapidly decreases in intensity as hv increases. Hence, we associate A with primarily O 2p bands. This is consistent with our previous observation that as the surface deteriorates with oxygen loss, most of the intensity is lost in the region of peak A. Peak B is similar, but clearly has more Cu 3d admixture (slower hv dependence). The centroid of Cu 3d intensity is at -4 eV (peak D) where peaks C, D, and E grow rapidly with increasing hv and coalesce into a single feature at large hv. This growth is seen more clearly in Fig. 4 where only four spectra are shown but with the background subtracted.

Superimposed on the spectra in Fig. 4 are calculated spectra (dotted lines) of Redinger *et al.*¹⁰ obtained by appropriately broadening the density of states (DOS) and convoluting each partial density of states (PDOS) with appropriate cross sections. We have shifted them to



FIG. 4. Valence-band spectra for YBa₂Cu₃O_{6.9} (sample *B*) at a limited number of $h\nu$ with the background subtracted. Superimposed on the spectra are the calculated spectra (dashed lines) of Redinger *et al.*¹⁰ The latter have been shifted to higher binding energies by 0.5 eV. Note that the line shapes correspond well at both low and high photon energies. The peaks in the calculated spectra are labeled *A* through *F*, and correspond with those in Fig. 3.

higher binding energies by only 0.5 eV in order to get coincidence with peaks A and B. We also note that the calculated spectra are for the stoichiometric compound YBa₂Cu₃O₇. We have made such a comparison to calculations in our earlier work⁴ on EuBa₂Cu₃O_{6.7}, but in that earlier work we were unable to resolve peaks A, C, and Din the data. Consequently, we matched the large calculated Fermi edge with the leading edge of the valence bands (at -1 eV) and concluded that we have a 1-eV discrepancy between calculation and experiment. Our present data, however, allow us to obtain a one-to-one correspondence with peaks A through E between experiment and calculations (including correct energy positions) if the above-mentioned 0.5-eV rigid shift is employed.

In general, there is a great deal of agreement between various band calculations.¹⁹⁻²⁴ There are, however, small differences such as, for example, the intensity at E_F which is smaller in the calculations of Ching *et al.*²¹



FIG. 5. (a) Density of states for YBa₂Cu₃O₇ taken from Ref. 22. The peaks labeled A through F correspond with the labeled peaks in the spectra of Figs. 3 and 4. (b) Blowup of the band structure near E_F , taken from Ref. 19. Band 4, due to the chains, should be filled for O_{6.9}.

versus that of Yu *et al.*,¹⁹ and which is in much closer agreement with our experiment. We are not prepared, however, to distinguish between the various calculations on the basis of these small differences. We refer the reader to the excellent review by Pickett²³ for further information and references. For comparative purposes we show in Fig. 5(a) the DOS taken from Ching *et al.*,²¹ and in Fig. 5(b) a blowup of the four bands near E_F , taken from Yu *et al.*¹⁹

Peak F does not appear in the calculated spectra of Fig. 4, but it is present as a weak feature in the original DOS as shown in Fig. 5(a). Thus, all experimental peaks A through F are here clearly identified (and labeled) with corresponding peaks in the DOS. Nearly exact agreement with our spectra is obtained by shifting E_F to +0.5 eV, with the exception of the relatively intense sharp structure producing the large Fermi edge in the calculated DOS of Yu et al. This sharp edge is due to band 4 in Fig. 5(b), a relatively flat hybrid band due to $Cu(1)(d_{yz})-O(1)(p_z)-O(4)(p_y)$ orbitals. It has a charge density highly localized on the one-dimensional chains. Bands 2 and 3 are due to Cu O planes while band 1 also comes from chains. We note that while band 4 crosses E_F for the stoichiometric compound YBa₂Cu₃O₇, Yu et al.¹⁹ state that band 4 is actually filled for $O_{6.9}$. Thus a sharp peak just below E_F with considerable Cu character would be expected in the data. Instead a sharp peak is observed precisely at E_F with intensity more in keeping with Fig. 5(a). It is as if a weakened version of band 4 has been pulled up in energy by 0.5 eV relative to the rest of the bands.

With the above exception, the one-electron band calculation actually captures most of the essential features of our spectra. Consequently, we feel it deserves a closer look. In particular, the role of oxygen vacancies needs to be better understood. We might point out an interesting historical trend relating to comparison with band calculations. The initial results on sintered powders¹¹ (see also Redinger *et al.*¹⁰) were in disagreement with calculations by a full 2 eV. Even after such a large shift was conducted, the correspondence was more imaginary than real.



FIG. 6. Extended valence-band spectra for $O_{6.9}$ (sample A) and $O_{6.25}$ crystals. Note the absence of a Fermi edge and the narrower bandwidth for $O_{6.25}$. Note also the absence of the -9-eV satellite in both spectra.

As the samples improved, the agreement improved, both in peak position and line shape, until we now reproduce the line shape reasonably well (Fig. 4) and the peak position to within 0.5 eV. The trend seems to favor the calculated band structure. The residual 0.5-eV shift, however, is currently still a problem. Some of the possible causes are (a) correlation effects, (b) shift in E_F due to filling of holes in $O_{6,9}$ material, (c) an error in calculations in placing E_F , or (d) residual experimental problems, such as surface effects, which have not yet been addressed. The general agreement between various band calculations^{18–24} would seem to rule against c, while our experiments show a relatively small (< 0.1 eV, see Fig. 6) shift in E_F as holes are filled at still lower oxygen concentrations (down to $O_{6,25}$). The samples have reached a state of perfection where any improvements are likely to be insignificant. Thus, most researchers⁴³ put the onus on correlation effects which seems quite plausible in view of the existence of valence-band satellites. However, we are



FIG. 7. Resonance properties of slightly deteriorated $\text{EuBa}_2\text{Cu}_3O_{6,x}$ at the O 2s (left panel) and the Cu 3p (right panel) absorption edges. Deterioration allows the observation of the -9-eV peak. The maximum enhancement of both the -9-eV peak and the feature at -2 eV (peaks A and B are not resolved here) occurs at hv=22. An incidental Eu 4f resonance at -5 eV occurs in the 18-eV spectrum. The two Cu 3d satellites (right panel) are marked by arrows. The large increase in the background at 74 eV is due to the MVV Auger peak. There is little or no resonance in the Cu valence-band spectrum. The insets in both panels are a blowup of the spectra around E_F .

puzzled by the rigid nature of the shift of the entire DOS, including the supposedly more extended O 2p orbitals shifting equally with the presumably more localized Cu 3d orbitals, while at the same time the relatively flat band 4 (where larger correlations might be expected) remains pinned at E_F (note the sharp peak at E_F in Fig. 1). Perhaps the issue can be resolved within the Hubbard model. Any plausible model of the electronic structure, however, will have to incorporate the essential features of the one-electron DOS, including the fact that the 3dbandwidth is much broader than it is in Cu metal, and that most of the O 2p intensity actually exists in a relatively narrow (2-eV wide) band near E_F , as seen from the 20-eV spectrum in Fig. 4.

The major disagreement between band calculations and experiment exists, of course, for the O_6 material where the one-electron theory obtains¹⁹⁻²³ metallic behavior versus the measured insulating behavior. Figure 7 shows spectra at hv = 50 eV for O_{6.9} and O_{6.25} material and it is clear that the latter spectrum has negligible intensity at E_F . It is widely believed that it is the magnetic transition, present at oxygen stoichiometries below 6.4, which results in the insulating gap. Several workers²⁴ have succeeded in obtaining a magnetic transition in their calculations. We, of course, cannot discern that from our data. What we can observe is that the bandwidth of the $O_{6.25}$ material is substantially narrower than that of the $O_{6.9}$ material which would indicate that the entire valence band undergoes changes as oxygen is lost. This would argue against the concept of a doped Mott insulator, and would seem to conform with the suggestion by Kasowski²⁰ and others that the effect of oxygen vacancies is to cause a band narrowing which eventually contributes to the formation of magnetism.

C. Resonances and core levels

In addition to valence-band measurements, we have performed extensive measurements on the Ba and O core levels in order to sort out some of the conflicting reports regarding satellites. A full description is, again, beyond the scope of this paper and will form the basis of a separate publication. However, it is useful to quote some of the conclusions reached in that publication since they have a direct bearing on the electronic structure of the $O_{6.9}$ material.

We focus our attention again on Fig. 6 and note that neither the $O_{6.9}$ nor the $O_{6.25}$ spectra display the oxygenrelated feature at -9 eV. This peak, as many have suspected,¹² is not intrinsic to the 1:2:3 structure. The feature is absent as long as the sample remains cold (we have held the samples up to 48 h without deterioration). At the same time a single O 1s core line¹² is seen at -528eV as long as the sample remains cold. Upon warming, the -9-eV peak begins to grow, faster for the low oxygen materials, and slower for $O_{6.9}$. This suggests that it is due to oxygen coming out of the bulk and sitting either adsorbed on the surface or in some interstitial location in the near-surface region. The fact that it is an oxygen feature can be discerned from Fig. 7(a), where the -9-eV peak, observed in a partially degraded sample, clearly resonates at hv=22 eV. Coincident with the growth of the -9-eV peak is also the growth of a second O 1s core level at -531 eV which we likewise associate with adsorbed oxygen coming from the deteriorating nearsurface region. We differ from those^{12,18} who call it a surface impurity only in terms of the source of that impurity—namely, the deteriorating sample itself.

Two sets of Ba 4d and 5p core levels doublets are often seen in published data⁴⁵⁻⁴⁷ with varying relative intensities and interpretations. Our extensive hv-dependent measurements clearly show that the lower-bindingenergy, spin-orbit split doublet is a surface shifted component whose intensity is dependent on surface perfection, and is totally unrelated to the number of oxygen holes.⁴⁵ The best samples at all oxygen concentrations show a surface component having equal intensity with the bulk component.

Having stated that the -9-eV oxygen-related feature is not intrinsic to the 1:2:3 material, we now wish to point out that a weak Cu 3d related feature exists at $\approx -10 \text{ eV}$ which is intrinsic to the 1:2:3 electronic structure, but which is usually not discernible in a measurement because of coincidence with the large -9-eV contamination peak. This satellite exists in addition to the commonly observed -12-eV peak. Both of these satellites resonate strongly at the Cu 3p edge at 74 eV as shown in Fig. 7(b). [Note that the spectra in Fig. 7(b), where the two satellites in question are marked by arrows, are for EuBa₂Cu₃O_{6.7} and not YBa₂Cu₃O_{6.9}.] The existence of the second satellite has been postulated¹² previously, since it is expected within the d^8 multiplet structure, and is observed both in Cu and Ni metals.^{48,49} The observation of the resonance, however, confirms its existence. The bulk of the 3d bands show only an extremely weak resonance at the 3p edge. This is very much reminiscent of Ni metal where one also observes^{49,48} a strong satellite resonance (the well-known two-hole bound state) with almost no accompanying resonance in the valence bands. Indeed, it would seem to confirm one more time that the ground state of Cu is in the d^9 configuration.

Satellites, in general, are an indication of electron correlation in materials,⁵⁰ and hence correlation effects are likely in this material. However, our measurements show that most of the results of the one-electron model are valid for YBa₂Cu₃O_{6.9}, just as they are valid in Cu and Ni. The similarity to heavy-fermion systems, where band theory (at least in uranium compounds) captures the essential features of the DOS but does not address the question of satellites, correlation, and coupling,^{51,52} is striking. What we find interesting is the extremely strong resonance of the -12 eV satellite, which in our measurements is stronger than any reported in literature for any cuprate. Such a strong 3d Fano resonance suggests the existence of empty Cu 3d states and a super-Coster-Kronig (SCK) autoionization process. If the number of empty 3d states decreases, then the strength of this resonance should likewise decrease since only a weaker Coster-Kronig-Auger process is possible. In Cu metal, where the d band is filled, the resonance is very weak, the available empty states being in the fourth principal quantum shell rather than the third. In Y 1:2:3, the resonance

does not measurably weaken as the oxygen stoichiometry is varied down to $O_{6.25}$. It does, however, decrease dramatically as the surface deteriorates. This would suggest the existence of empty 3d states down to low oxygen stoichiometries, again consistent with calculations.⁵³ As the surface deteriorates, however, a substantial amount of Cu forms in the d^{10} configuration.

Finally, we consider the oxygen resonance (2s absorption edge) shown in Fig. 7(a). We show spectra for a slightly deteriorated surface of $EuBa_2Cu_3O_{6+x}$ as we tune the photon energy through this edge in order to show the resonant behavior of the -9-eV satellite at hv=22 eV which has been shown to be of purely oxygen origin.⁴³ It will be seen that this is the same photon energy at which the resonance of the -2-eV peak in the valence bands is manifested. The point we wish to make is that the O 2s to 2p resonance is at hv=22 eV, and not at 18 eV as one might conclude from a cursory glance at the Fermi edge enhancements. While we cannot state that the resonance occurs at 22 eV in other cuprates, we wish to leave the reader with two points regarding resonance experiments at E_F (1) the numerous enchancements in the Fermi edge at low hv diminish the usefulness of the O 2s edge to confirm the occupancy of O 2p orbitals at E_F , and (2) the lack of resonance at E_F for hv = 74 eV does not preclude Cu 3d occupancy at E_F since the entire valence band (27) 3d electrons) fails to resonate at this edge.

IV. CONCLUSION

We have reexamined the electronic structure of YBa₂Cu₃O_{6.9} single crystals via photoemission spectroscopy, making the measurements at 20 K in order to maintain surface oxygen stoichiometry. We find that typical spectra display a large, sharp (resolution limited) Fermi edge consistent with metallic behavior. $N(E_F)$ per Cu atom is very roughly estimated to be as large as 20% of that of Cu metal and contains about a 20-80 mix of Cu 3d and O 2p orbitals. Dispersion and final-state enhancements, phenomena associated with well-defined bands, are observed at E_F and throughout the valence bands. We find excellent agreement with a calculated DOS if the DOS is shifted to higher binding energies by $\approx 0.5 \text{ eV}$ (except for the feature at E_F). Not only peak positions, but also line shapes of the spectra appear to agree with previous calculations, which would indicate that the calculations contain the correct mix of 3d and 2p orbitals throughout the valence bands. Thus, much of the O 2pintensity is peaked in a narrow, 2-eV wide band near E_F with a long tail extending to -7 eV, while the Cu 3d band is centered at -4 eV and extends through the valence bands. Our results complement well the angleresolved measurements of Takahashi, which likewise point to a hybridized bandlike behavior of the superconducting oxides. The very large resonance of the -12-eV satellite, which decreases in intensity relative to the valence bands as the surface deteriorates, is a result of a SCK autoionization process and points to the existence of empty Cu 3d states.

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