Photoemission studies of high-temperature superconductors $YBa_2Cu_3O_{7-\delta}$, $GdBa_2Cu_3O_{7-\delta}$, and $EuBa_2Cu_3O_{7-\delta}$

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(Received 16 November 1987)

The electronic structures of three high-temperature superconducting materials, $YBa_2Cu_3O_{7-\delta}$, $GdBa_2Cu_3O_{7-\delta}$, and $EuBa_2Cu_3O_{7-\delta}$, were studied with angle-integrated photoemission. The effects of sample treatment and preparation, including mechanical scraping, ion sputtering, and temperature cycling, were examined. High-resolution spectra were obtained from samples prepared by mechanical scraping at 90 K in the vacuum chamber to minimize contamination and the loss of oxygen. The resonance behavior of the various valence and core states in the photoemission spectra was investigated to identify the atomic origin of the states. The Cu- and O-derived states dominated the valence-band region at low photon energies, as shown by a comparison of the energy distribution curves for all three compounds. The measured density of states at the Fermi edge was very low. All of the spectral features, including the valence bands, core levels, Fermi-edge emission, and the Cu $3d$ satellites did not show any noticeable changes as a function of sample temperature between 20 and 300 K.

I. INTRODUCTION

The understanding of the superconducting mechanism in the recently discovered copper-oxide-based high-temperature superconducting compounds[1-3] requires a detailed understanding of their electronic structure as a function of temperature. Here we report photoemission studies of three such compounds: $YBa_2Cu_3O_{7-\delta}$, $GdBa_2Cu_3O_{7-\delta}$, and $EuBa_2Cu_3O_{7-\delta}$ (for brevity, Y-Ba-Cu-O, Gd-Ba-Cu-O, and Eu-Ba-Cu-O, respectively). We have identified the electronic states of the constituents of each compound, and have monitored these states as a function of temperature through and well below the transition temperature. Also, we have made high-resolution measurements near the Fermi edge. At a temperature well below the transition temperature, the superconducting portion of the conduction electrons will be significant. If the superconducting gap is sizable and the pair density is sufficiently high, one might be able to observe the gap directly in the photoemission spectra. Furthermore, other subtle transition-related effects might show up. This work is an attempt to observe any unusual electronic properties of these materials which might be linked to their unusually high transition temperatures. These measurements can also offer help in checking band calculations, and can test some of the models proposed.[4-10]

There have been a number of photoemission studies on the Y-Ba-Cu-O compound.[11-22] In addition to providing the new studies on the two rare-earth compounds, the present work distinguishes itself from the previous results by a combination of several factors given below. We mechanically scraped the sample surface at low temperature (about 90 K) to expose a fresh surface of the superconducting material while minimizing influence from grain boundaries, contaminants, oxygen loss and/or other chemical modifications caused by other procedures of surface preparation. The properties of the samples were examined both before and after the photoemission measurements to ensure that the materials are in fact superconductors. Furthermore, some of the features in the electronic structure were identified by comparing photoemission spectra taken with a wide range of photon energies from all three materials.

II. EXPERIMENTAL DETAILS

The methods used for preparing the compounds are described elsewhere for the Y compound[23] and the Eu and Gd compounds.[24] The photoemission samples were disks about 5 mm in diameter and 3 mm thick, prepared by sintering powdered materials. The samples were stored in an oxygen atmosphere or a dessicator prior to insertion into the ultrahigh vacuum chamber. A magnetometer using a superconducting quantum interference device enabled us to verify the bulk superconductivity of the samples. Resistive measurements yielded onset temperatures of 92, 94.5, and 94.8 K, for Y-Ba-Cu-O, Gd-Ba-Cu-O, and Eu-Ba-Cu-O, respectively. Special care was taken to make these transition widths (10 to 90%) as sharp as possible (approximately 2 K). Figure 1 shows our resistivity-versus-temperature curves for the three materials. X-ray powder diffraction measurements revealed that the samples were single-phase compounds.[25]

All of the photoemission measurements were performed on the University of Illinois beam line at the Synchrotron Radiation Center in Stoughton, Wisconsin. Synchrotron radiation from the 1 GeV Aladdin storage ring was dispersed by an extended range grasshopper monochromator, and the photoelectrons were analyzed by a hemispherical energy analyzer. The overall energy resolution was between 0.075 and 0.25 eV, depending on the slit settings and photon energies used. The sample was clamped against the cold stage of a manipulator by tantalum
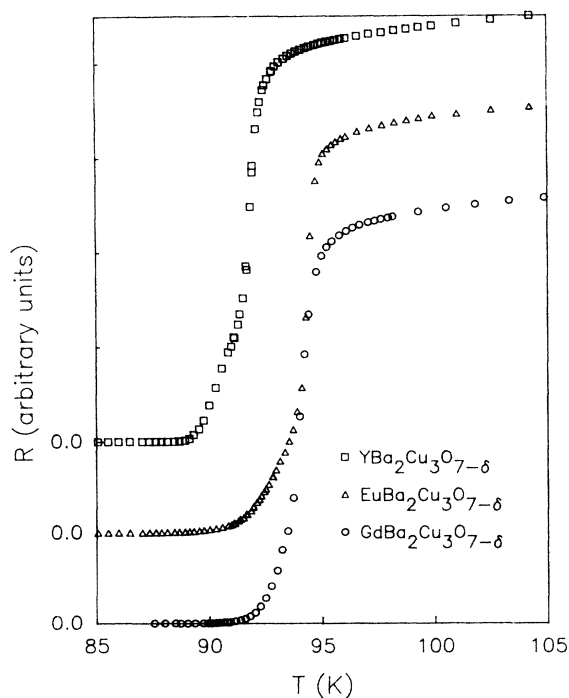
FIG. 1. Resistance as a function of temperature for the three materials. The points for the Y and Eu compounds are displaced upward for clarity.

sheets; indium was used to assure good thermal contact. The end of the manipulator could be cooled or warmed by exchange gas, liquid nitrogen, or liquid helium. Chromel-alumel thermocouples fixed to the backs of the sample allowed us to measure the sample temperature down to about 50 K. Below 50 K, the thermocouple response became quite insensitive to temperature variation, and therefore the temperature could not be determined accurately. With liquid-helium cooling, the sample mount was at about the He boiling temperature; but the sample surface was probably at a higher temperature. We estimated that the sample surface temperature was about 20 K. A gold foil in electrical contact with the samples provided the Fermi-level reference of the photoemission spectra.

III. RESULTS AND DISCUSSION

The line shapes of the photoemission spectra were observed to depend on the methods of treating the materials. (Some of the previously published results already showed this dependence.[11-22]) Untreated samples have a surface which, in addition to being contaminated, could have oxygen concentrations differing from bulk oxygen concentrations. Sputtered samples sometimes suffer from preferential sputtering of the constituents. This causes a deprivation of oxygen as well as the destruction of crystallinity, destroying the superconductivity in the region probed by the surface-sensitive method of photoemission. Annealing the sample changes the oxygen concentration, generally leading to a broadening of the transition.

To minimize the uncertainty of sample quality associated with sample treatment, we scraped the sample surface *in situ* at about 90 K to expose fresh superconducting grains. The reason for doing this at a low temperature was to minimize the loss of oxygen. Earlier studies by other groups indicated that oxygen leaves the surface in vacuum, even at room temperature; and it is known that oxygen deficiency could easily reduce the superconducting transition temperatures.[13] In this study, we found that the photoemission spectra taken from samples scraped and maintained at 90 K showed no noticeable changes over a period of about 2 h, indicating a negligible loss of oxygen. Spectra taken from different scrapes were very reproducible. The experiment on the temperature dependence started with a freshly scraped sample at 90 K. After the spectra were taken, the sample was further cooled to 20 K, where additional spectra were taken. The room-temperature data were taken last; the time for the measurement was kept short, so no noticeable oxygen loss was detected. In a separate experiment, we also sputtered these samples with argon ions for comparison; the spectra were significantly modified after this treatment, indicating changes of the surface chemical composition. In the following, only spectra obtained from samples scraped at 90 K will be presented.

After about one week of experimentation with the sample in the ultrahigh vacuum chamber, the superconducting transition was found to be broadened by a few degrees. This is perhaps due to a loss of some oxygen in the vacuum chamber during the chamber bakeout period; the bakeout was performed for 12 h at a temperature of 120 °C.

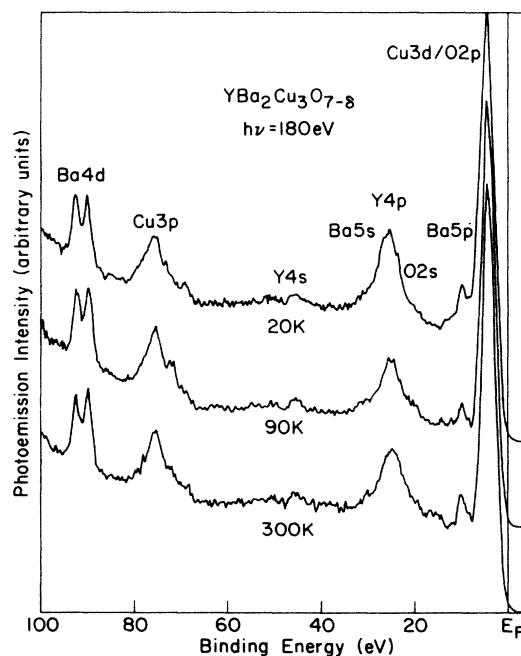Figures 2–4 show some of the photoemission spectra

FIG. 2. Photoemission spectra for Y-Ba-Cu-O taken with a photon energy of 180 eV at three temperatures; 20, 90, and 300 K. The binding energy scale is referred to the Fermi level at E_F. The electronic states are indicated.
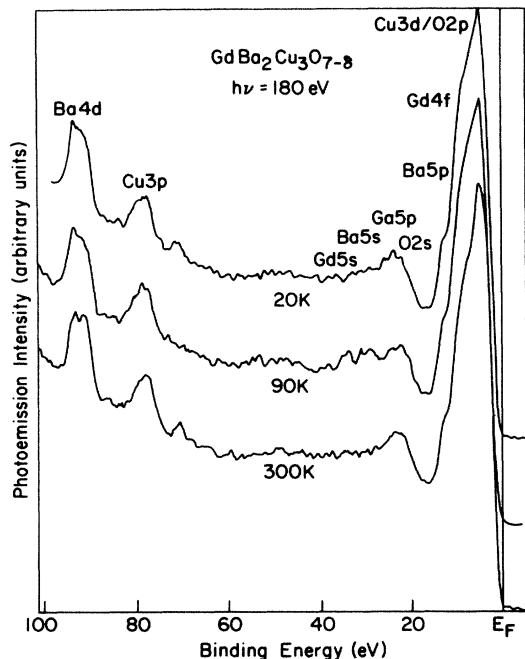
FIG. 3. Same as Fig. 2 except for Gd-Ba-Cu-O.

recorded using a photon energy of 180 eV for the three compounds. These measurements were made at room temperature (300 K), near the transition temperature (90 K), and well below the transition temperature (20 K). We have identified the atomic origin of the various spectral features, and have labeled them on the spectra. Table I gives a list of the measured binding energies of these states. The main valence-band feature, located 4.5 eV
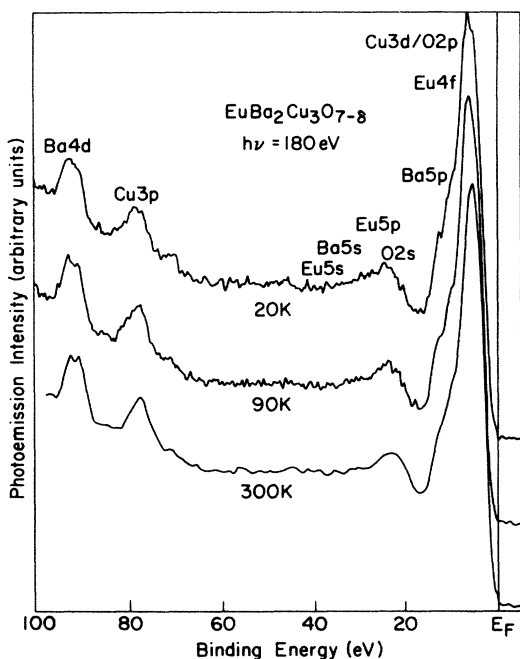

FIG. 4. Same as Fig. 2 except for Eu-Ba-Cu-O.

TABLE I. Measured binding energies of the various states relative to the Fermi level. Two energy values are listed for the p and d core levels that clearly show spin-orbit splittings.

Level	Binding energy (eV)
Cu $3d$/O $2p$	2.5
Cu $3d$/O $2p$	4.5
O	9.5
O $2s$	20.1
Cu $3p$	74.0
Ba $5p$	14.3, 16.0
Ba $5s$	30.0
Ba $4d$	92.7, 89.9
Y $4p$	24.0
Y $4s$	44.0
Gd $4f$	7.4
Gd $5p$	21.0, 26.3
Gd $5s$	36.0
Eu $4f$	9.6
Eu $5p$	22.0, 26.4
Eu $5s$	32.0

below the Fermi level (E_F), arises primarily from the Cu $3d$ and O $2p$ states. There are further contributions to this peak from the Gd $4f$ and Eu $4f$ on the higher binding energy side (Figs. 3 and 4). The Y-Ba-Cu-O compound does not have an occupied $4f$ level (Fig. 2), so the magnitude of the $4f$ contribution can be estimated by comparing these spectra. At this photon energy, the O $2p$ contribution is relatively weak, as suggested by studies done on Cu, CuO, and Cu_2O.[26,27] The O $2s$ state and the Cu $3p$ state can be identified at binding energies of 20.1 and 74 eV, respectively. Notice that the Cu $3p$ states, in addition to exhibiting a spin-orbit splitting, show chemical shifts and/or surface shifts, so the line shape is complicated and broadened.

The other common features of these spectra are the Ba-derived $4d$, $5s$, and $5p$ states. The Ba $4d$ states can be easily resolved at the binding energies of 92.7 and 89.9 eV; these states are broader in the rare-earth compounds, and we do not know the reason for this broadening. To enhance the photoemission intensity from the Ba $5s$ and $5p$ states, we made use of the resonant behavior of these levels at the Ba $4d$ photoabsorption threshold. The $4d$ level exhibits a broad resonance and a delayed onset, with photon energies ranging from about 100 to 130 eV. This resonance allows the unambiguous identification of Ba $5s$ level, at 30 eV, and of the Ba $5p$ levels at 14.3 and 16.0 eV.[28] Some of the spectra showing the Ba $5p$ resonance are shown in Figs. 5–7 for the three compounds. To conserve space, the spectra showing the resonance behavior of the Ba $5s$ are not shown here.

The Y levels do not exhibit any significant resonance enhancement in the photon energy range used. Figure 2 shows these levels to be at binding energies of 24.0 eV (Y $4p$) and 44.0 eV (Y $4s$); these peaks are not present in the spectra shown in Figs. 3 and 4. The rare-earth (Gd and Eu) states do exhibit a resonance behavior.[29] The Gd levels are strongly enhanced for the spectrum taken with a photon energy of 152 eV (Fig. 6), and similarly the Eu
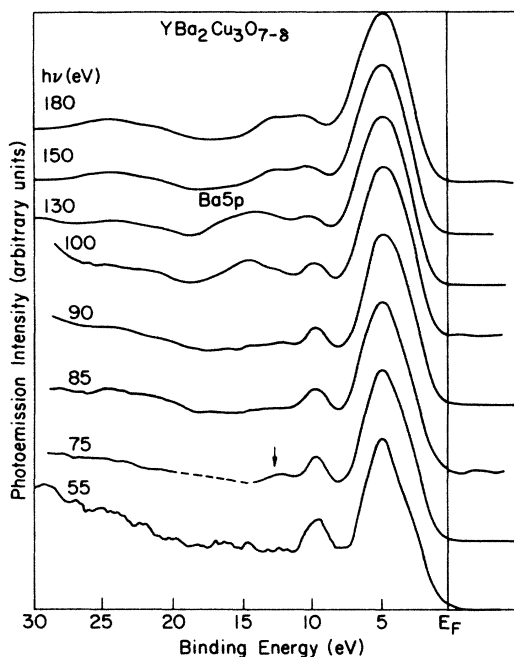
FIG. 5. Photoemission spectra of Y-Ba-Cu-O taken with various photon energies as indicated. The Ba $5p$ states resonate for photon energies near 130 eV. The arrow indicates the position of a Cu $3d$ satellite which resonates when the photon energy is near 75 eV. The Ba $4d$ core level excited by the second-order light from the monochromator shows up in the 75 eV spectrum; the part of the spectrum significantly distorted by this effect is replaced by an estimated smooth dashed curve.

FIG. 6. Same as Fig. 5 except for Gd-Ba-Cu-O.

levels are strongly enhanced for the spectrum taken with a photon energy of 145 eV (Fig. 7). The relevant binding energies are given in Table I.

From the dependence of the $4f$ partial cross sections on photon energy, we conclude that the spectra shown in Figs. 5–7 contain little rare-earth $4f$ contributions in the valence-band region when the photon energy is lowered to 55 eV. The similarity between the spectra for the three compounds at this photon energy also leads to the same conclusion; thus, the emission in the valence-band region is dominated by the Cu $3d$ and O $2p$ states. At low photon energies, a shoulder is apparent at a binding energy of 2.5 eV. This shoulder may be related to features in the density of states or band structure; it is mainly derived from the O $2p$ states. The comparison of the experimental valence-band spectra with various theoretical band calculations has been discussed by Redinger, Freeman, Yu, and Massidda.[5] They point out that there is approximately a 2 eV shift between the theoretical and experimental valence bands. They attribute this shift to the lack of metallic screening of the Cu d hole after photoemission; in other words, many-body effects are important in these materials.

The peak in the valence-band region at a binding energy of 9.5 eV shows an intensity which is about the same in all three compounds. This peak cannot be identified as emission from any single-particle state based on the known core level binding energies and calculated band
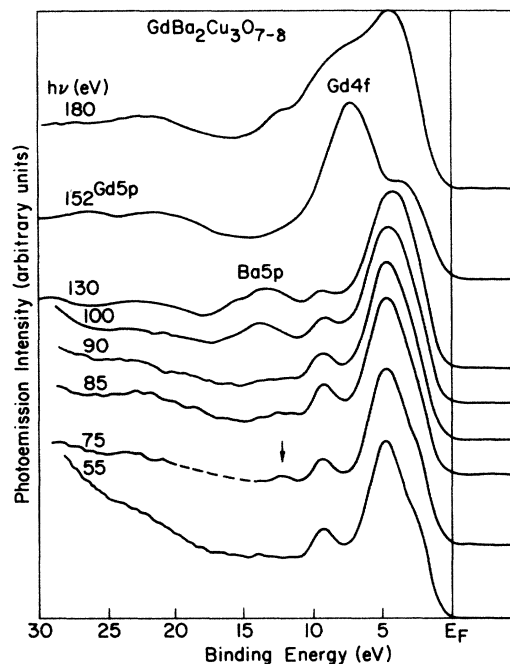
structure of these materials. It lacks any resonance behavior in the range of photon energies used, so it is not a Cu-, Ba-, Y-, Gd-, or Eu-derived state. Again the similarities of its line shape for all three compounds lead us to identify this peak as most likely an O-derived feature, and it is conjectured that it may be a multielectron feature. Earlier studies by other groups indicated that this feature
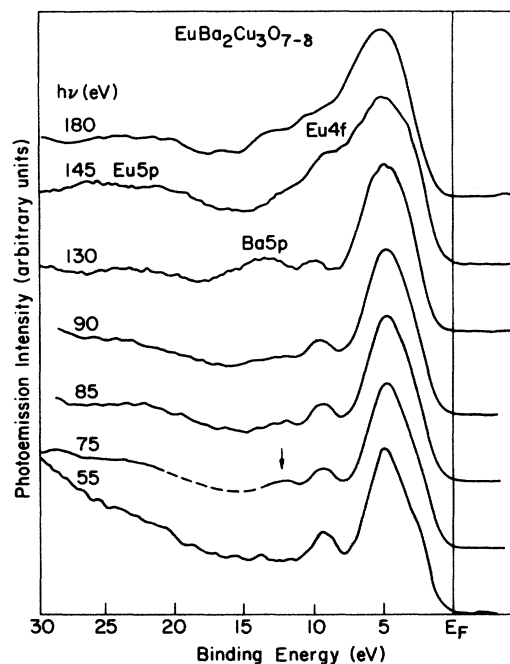

FIG. 7. Same as Fig. 5 except for Eu-Ba-Cu-O.

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depended on the sample treatment;[13] this observation is consistent with the conclusion that this peak is oxygen related. In our experiment, this peak is extremely reproducible for different scrapes, suggesting that it is in fact an intrinsic feature of the material.

An issue of interest is the Cu valence in the high-temperature superconductors. Some models predict charge fluctuations of the copper ions, corresponding to the different valence states of Cu present in the system. For photon energies at or somewhat above 72 eV, the shake up satellites of Cu $3d$, corresponding to the simultaneous excitation of two $3d$ electrons, are known to show large resonance enhancement.[26,27] The positions of the satellites depend on the charge state of the Cu atom, and have been experimentally determined in CuO and Cu_2O.[27] The binding energies of the satellites are measured to be 10.5 and 12.9 eV for CuO and 15.3 eV for Cu_2O. We therefore determined the Cu valence state by tuning the photon energies through the resonance. The spectra in Figs. 5–7 show the position of a satellite feature at 12.3 eV, indicated by arrows. Although the companion peak (presumably at 9.9 eV) is obscured by overlapping peaks, the result unambiguously indicates that the Cu is in a 2+ valence state in all three compounds. A similar study rules out the trivalent valence state of copper in Y-Ba-Cu-O,[30] and a Mössbauer study rules out charge fluctuations for the Eu-Ba-Cu-O compound.[31]

We have examined the 2+ Cu valence state of these samples as a function of temperature to see if the superconducting transition causes any unusual behavior of the Cu valence. The results for Gd-Ba-Cu-O and Eu-Ba-Cu-

FIG. 9. Same as Fig. 8 except for Eu-Ba-Cu-O.

O are shown in Figs. 8 and 9, respectively. The result for Y-Ba-Cu-O is similar, so it is not shown here. The satellite features, indicated by the arrows, do not show any noticeable temperature dependence. The two additional peaks at 16.6 and 19.0 eV in Figs. 8 and 9 are derived from Ba $4d$ photoelectrons which are excited by the second-order light from the monochromator.

There are additional broad and weak features in the spectra which cannot be unambiguously assigned. For ex-
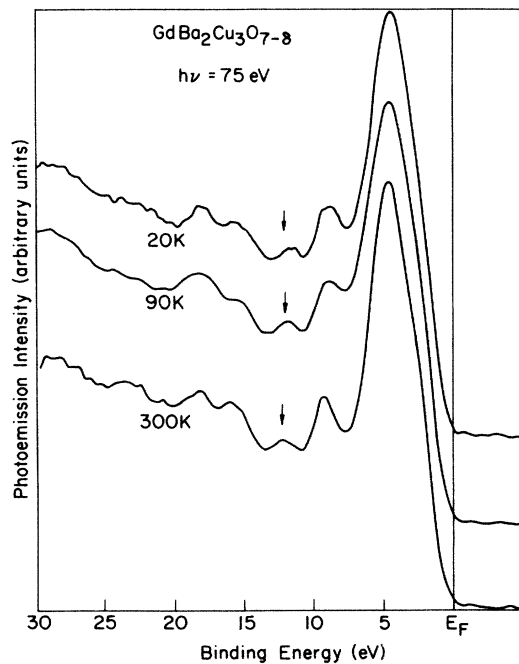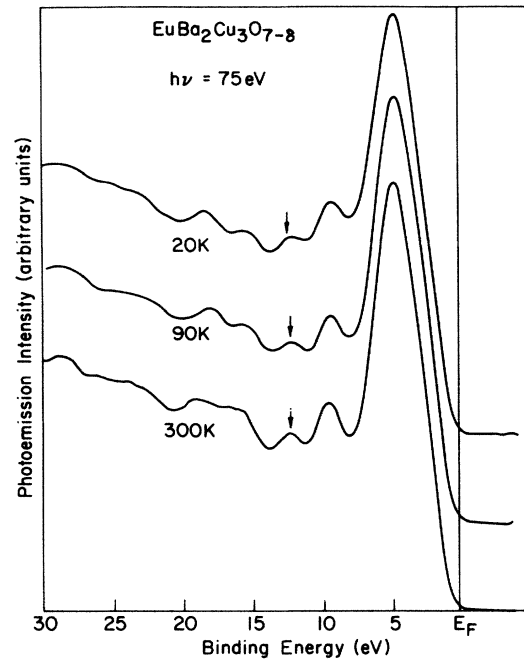

FIG. 8. Photoemission spectra of Gd-Ba-Cu-O taken with a photon energy of 75 eV, for which the Cu satellite feature (indicated by the arrows) is strongly enhanced. The three spectra were taken at 20, 90, and 300 K as indicated.
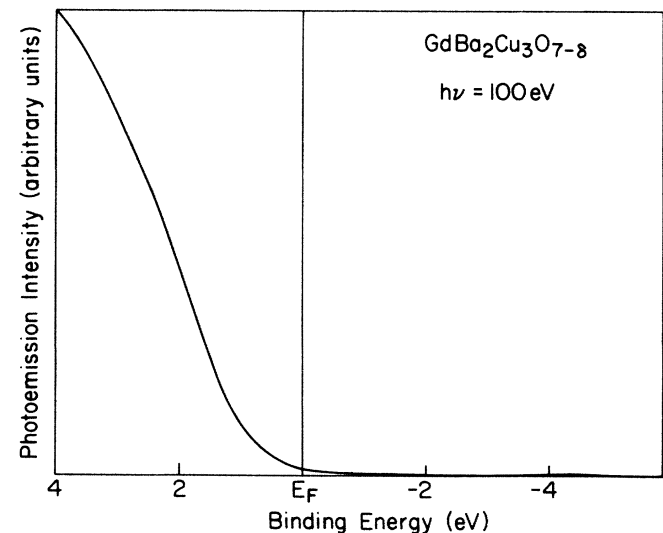

FIG. 10. Photoemission spectrum of Gd-Ba-Cu-O taken with a photon energy of 100 eV, showing the density of states near the Fermi level. The overall instrumental resolution was 0.075 eV. The sample temperature was 20 K.

ample, a very broad feature centered at about 50 eV binding energy can be seen in Figs. 2–4. This is perhaps a many-electron feature.

Several careful high-resolution scans at the Fermi level were taken at different temperatures for each compound. Figure 10 shows one typical spectrum for Gd-Ba-Cu-O taken at 20 K, greatly expanded to show details. It is evident that there is a very low density of states at the Fermi level. Within the resolution of our instrument, we observed no fine structures near the Fermi edge, although some theoretical results predicted the presence of some fine structures. The measured density of states did not show any noticeable temperature dependence. The results for the other compounds were similar, so they are not shown here.

IV. SUMMARY

In this study, we examined the electronic structure of three closely related high-temperature superconducting materials: Y-Ba-Cu-O, Gd-Ba-Cu-O, and Eu-Ba-Cu-O. We searched for any unusual behavior or electronic properties of the system that might help explain the unusually high transition temperatures. Although the gap energy is expected to be relatively large in these materials, we found no effect of the transition on the photoemission spectra. To ensure that we were probing the superconducting materials with the correct chemical composition, we scraped the surface of each sample at 90 K. Since the transition is thought to be second order, the sample temperature was cooled to 20 K, well below the transition temperature to convert a significant fraction of the conduction electrons to the superconducting state. However, the results show that all spectral features, including the region near the Fermi edge, valence-band region, core levels, and multielectron features, do not show any significant temperature dependence. The $4f$ states in the rare-earth compounds are mainly located at roughly 7–10 eV below the Fermi level, as expected for most rare-earth salts. By comparing the spectra for the three compounds over a wide range of photon energy, we identified the atomic origins of the various spectral features.

Although scraping the surface at low temperatures should expose materials with the correct stoichiometry, there is yet no guarantee that the near-surface region is in fact superconducting at low temperatures. The surface acts as a perturbation to the electronic properties of these materials, and this perturbation could ruin the superconductivity near the surface. This possibility is related to the question as to whether or not there is a significant overlap between the photoemission probing depth (about 5 Å) and the wave functions of the superconducting electrons in the bulk. In view of these considerations, the absence of any temperature dependence of the data is not necessarily a conclusive indication of the relation between the superconducting transition and the modification of electronic properties. The same problem will arise even for experiments performed on single-crystal surfaces.

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