

## Parallel valence- and core-level photoemission studies of the metal-to-nonmetal transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

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Valence-level and Cu  $2p$  core-level photoemission spectra for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in both metallic ( $x < 0.5$ ) and nonmetallic ( $x > 0.5$ ) phases are presented together for the first time. The core spectra show evidence for holes in the hybrid Cu  $3d$ -O  $2p$  valence levels in the metallic state, but nonetheless the density of states at the Fermi energy seen in valence-level photoemission is at most 0.05 states/eV cell.

The so-called "1:2:3" defect perovskite phase  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $0 < x < 1$ ) has attracted widespread attention following the discovery of superconductivity in the quaternary Y-Ba-Cu oxide system.<sup>1,2</sup> For  $x=0.5$ , the copper is in the Cu II oxidation state with a nominal  $3d^9$  electron configuration. In the simplest picture the pure  $d^9$  configuration is localized by the electron-electron interaction, as in CuO itself.<sup>3</sup> However, there is some indication that metallic behavior and superconductivity can be maintained through  $x=0.5$  down to about  $x=0.6$ .<sup>4,5</sup> When  $x < 0.5$  charge neutrality is maintained in a phase of orthorhombic symmetry by introduction of holes into the strongly mixed Cu  $3d$ -O  $2p$  valence-band states and formally we now have Cu III present. The holes are itinerant, giving rise to metallic conductivity at room temperature and a transition to the superconducting state below 91 K.

There have by now been over 40 studies of the 1:2:3 phase by photoemission spectroscopy.<sup>6</sup> In core-level work a theme of particular interest has been to try to find evidence for Cu III in the metallic or superconducting state. Early work in this area was somewhat ambiguous,<sup>7-14</sup> but it now appears from careful studies of samples prepared *ex situ* with differing oxygen composition parameters that there is evidence in the Cu  $2p$  core-level spectra for two ligand hole final states associated with Cu III.<sup>15-17</sup> Nonetheless, the metallic phase is susceptible to oxygen loss under the UHV conditions of photoemission experiments, with consequent filling of the valence hole states. Such oxygen loss in the surface region provides one possible explanation of the recurring failure to find a measurable density of states at the Fermi energy in valence photoemission studies of the metallic 1:2:3 phase.<sup>9,18-29</sup> However, parallel monitoring of both core and valence levels is necessary before this explanation can be accepted.

We have recently developed the technique of *in situ* high-pressure oxygen annealing to prepare clean surfaces of the metallic 1:2:3 phase for photoemission studies.<sup>6</sup> In the present paper we extend the earlier work to produce an *in situ* metal-to-nonmetal transition within the 1:2:3 phase by vacuum annealing. Careful comparison of core-level data from metallic and nonmetallic phases provides evidence for two ligand hole structures in the metallic state. However, even though it follows that there must be

initial-state holes in the valence bands, photoemission spectra fail to show a metallic density of states at the Fermi energy.

Samples of the 1:2:3 compound were prepared by the standard solid-state route as described previously.<sup>6</sup> Note that long firing times at 950°C were used to ensure complete reaction of the  $\text{BaCO}_3$  used as a starting material, followed by slow cooling and extended anneals at 400°C under oxygen to allow complete oxygen uptake. The resulting metallic pellets gave the orthorhombic x-ray powder diffraction pattern characteristic of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x < 0.5$ ) free of reflections due to starting materials or secondary phases such as  $\text{Y}_2\text{BaCuO}_5$  or  $\text{BaCuO}_2$ . They exhibited sharp resistive transitions to a superconducting state with zero resistance at 91 K. Infrared reflection spectra measured in the range between 400 and 4000  $\text{cm}^{-1}$  gave up to 60% specular reflectivity at 400  $\text{cm}^{-1}$  with strong screening of the phonons around 600  $\text{cm}^{-1}$ , characteristic of the metallic state.<sup>30</sup>

Photoemission studies were conducted in a VG ESCALAB 5 Mark II spectrometer equipped with a double anode x-ray source (Mg  $K\alpha$  and Al  $K\alpha$ ) and a noble gas discharge lamp. The analyzer resolution was set at 0.4 eV for x-ray and He II photoemission measurements and at 0.1 eV for He I measurements. The position of the Fermi energy was established from measurements on a cleaned Ni stub. The spectrometer has a fast entry lock and a preparation chamber. The base pressure in the analysis chamber was  $5 \times 10^{-11}$  Torr.

Samples were mounted on platinum stubs and secured with platinum clips. Care was taken not to allow the clips to protrude onto the sample surface. Reference core-level photoemission spectra from uncleaned samples were usually taken prior to *in situ* cleaning. Sample cleaning was effected by filling the preparation chamber with pure oxygen and heating the platinum stub by coupling to the rf field provided by a water-cooled copper workcoil connected through a Leybold Heyraeus rf feedthrough to a Radyne 1.5-kW 400-kHz power supply. The cleaning cycle was designed to mimic the conditions of sample preparation and typically involved heating to around 600-700°C for 1 h, followed by cooling to 400°C over a period of several hours. After switching off the rf power, samples were allowed to cool to room temperature in oxygen and

the preparation chamber was then evacuated with the sequential aid of a sorption trapped rotary pump, a liquid-nitrogen trapped polyphenyl ether filled diffusion pump and a titanium sublimation pump. The base pressure in the preparation chamber deteriorated to around  $10^{-8}$  Torr as a result of oxygen filling, but samples could be transferred to the spectrometer main chamber within one hour of cleaning. The  $[C 1s]/[O 1s]$  intensity ratio for surfaces cleaned in this way was at most between 1/50 and 1/100, corresponding to carbonate levels as little as  $\frac{1}{4}$  monolayer. Additionally, it was found that high binding components of the Ba  $3d$  and O  $1s$  peaks whose intensity increased with decreasing angle of offtake of the photoelectrons relative to the surface plane were removed by the annealing procedure. The angle-dependent features are attributable to  $BaCO_3$  surface contamination. However, a residual shoulder did remain in the O  $1s$  region, but now with no enhanced intensity at shallow offtake angles. We believe this shoulder to be intrinsic to the metallic 1:2:3 phase.<sup>6</sup> A transition to a nonmetallic state was affected by vacuum annealing samples at  $600^\circ C$  for up to 24 h with the aid of the rf heater. Nonmetallic samples showed variable charging shifts in x-ray photoemission spectroscopy (XPS) and spectra were aligned relative to one another with reference to the Y  $3d$  level whose spectral profile is invariant on going through the metal-to-nonmetal transition. The nonmetallic state of vacuum-annealed samples was confirmed by *ex situ* resistivity and ir reflectance studies.<sup>31</sup>

Consider first the Cu  $2p_{3/2}$  structure shown in Fig. 1. Superficially, spectra from both metallic and nonmetallic phases resemble those from CuO, although the main peak in the spectrum from the orthorhombic metallic phase is noticeably broader than for CuO.<sup>32</sup> The spectrum of CuO has itself been the subject of some controversy. However, there is now a reasonable consensus that the main peak at 933 eV is due to the "well-screened"  $|2p^1 3d^{10} \underline{L}^1\rangle$  final state and the satellite at 942 eV is due to the "poorly screened"  $|2p^1 3d^9 \underline{L}^0\rangle$  final state (see, for example, Refs. 7-17). Here  $L$  refers to ligand oxygen and the bar denotes holes. The appearance of two final states is related to Cu  $3d-O2p(L)$  mixing in the initial state where the wave function for Cu(II) may be represented as  $|II\rangle$  where

$$|II\rangle = \alpha |3d^9 \underline{L}^0\rangle + \beta |3d^{10} \underline{L}^1\rangle.$$

However, the intensities of the two peaks in photoemission depend on values for core-valence Coulomb interactions and are not simply proportional to  $\alpha^2$  and  $\beta^2$ . For Cu I oxides the initial state is simply

$$|I\rangle = |3d^{10} \underline{L}^0\rangle.$$

Now only the final state  $|2p^1 3d^{10} \underline{L}^0\rangle$  is accessible and thus Cu<sub>2</sub>O shows no satellite peak due to poorly screened final states. Finally, for oxides where Cu is formally in the oxidation state III we have

$$|III\rangle = \gamma |3d^8 \underline{L}^0\rangle + \delta |3d^9 \underline{L}^1\rangle + \epsilon |3d^{10} \underline{L}^2\rangle.$$

The possible final states are  $|2p^1 3d^8 \underline{L}^0\rangle$ ,  $|2p^1 3d^9 \underline{L}^1\rangle$ , and  $|2p^1 3d^{10} \underline{L}^2\rangle$ . From studies on the oxide NaCuO<sub>2</sub>

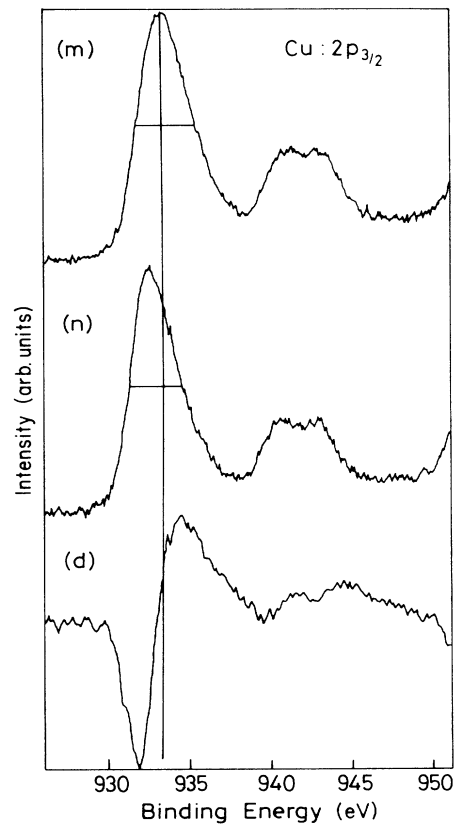


FIG. 1. Al  $K\alpha$  excited Cu  $2p_{3/2}$  core region spectra of metallic (m) and nonmetallic (n) phases of  $YBa_2Cu_3O_{7-x}$ . In the difference spectrum (d) the spectrum (n) has been subtracted from (m) following alignment of Y  $3d$  core-level peaks (not shown) and normalization of the areas of the complete  $2p_{3/2}$  structure. Satellite structure has been subtracted from the spectra which were accumulated over a wider range than shown to include the  $2p_{1/2}$  peaks. The horizontal lines delineate the full widths at half maximum height for the main core lines and the vertical line guides the eye as to the shift between (m) and (n).

(Refs. 11 and 12) it seems that the last of these configurations dominates the photoemission process, giving a peak to 2-eV higher binding energy of the well-screened peak of CuO. Again, it should be emphasized that the final-state intensities do not provide a direct measure of  $\gamma$ ,  $\delta$ , and  $\epsilon$  because ionization channels such as  $|3d^9 \underline{L}^1\rangle \rightarrow |2p^1 3d^{10} \underline{L}^2\rangle$  are opened by final-state relaxation effects. The broadening of the spectrum of  $YBa_2Cu_3O_7$  compared with that of CuO can therefore be attributed to an initial state with both Cu III and Cu II and the resulting accessibility of  $|2p^1 3d^{10} \underline{L}^2\rangle$  final states. Of course the bulk metallic behavior of  $YBa_2Cu_3O_7$  implies the valence-band holes are itinerant in the initial state. However, even in this situation, the strong core-valence Coulomb interaction will produce localized final states. On the other hand, the XPS does not rule out the possibility of localized initial states at the surface.

Upon vacuum annealing to give the nonmetallic tetragonal phase with nominal composition  $YBa_2Cu_3O_6$ , the well-screened peak of the Cu  $2p_{3/2}$  spectrum shifts to

lower binding energy and becomes narrower. At the same time the intensity of the poorly screened  $|2p^{-1}3d^9\bar{L}^n\rangle$  ( $n=0,1$ ) peak decreases. A difference spectrum between metallic and nonmetallic phases reveals an increase in spectral weight on the low binding energy side of the main peak and a decrease to the high binding energy side. This corresponds to a switchover between  $|2p^{-1}3d^{10}\bar{L}^2\rangle$  and  $|2p^{-1}3d^{10}\bar{L}^0\rangle$  final states as the initial state changes from a mixture of  $\frac{1}{3}\text{Cu II} + \frac{2}{3}\text{Cu I}$  to  $\frac{1}{3}\text{Cu I} + \frac{2}{3}\text{Cu II}$ . The nonmetallic behavior as  $x$  approaches 1 implies that there are now distinct localized valences throughout the bulk in the initial state.

The main point we wish to emphasize then is that our data agree with the most recent work of others<sup>15-17</sup> in pointing to Cu III in the initial state for the metallic 1:2:3 phase even though we are working in an ultrahigh vacuum environment. Oxygen loss to give a nonmetallic tetragonal phase with  $x > 0.5$  is not spontaneous in UHV at room temperature and can only be achieved by prolonged heating. This view is reinforced by the observations that base pressures below  $10^{-10}$  Torr can be maintained while working on  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and that pellets retain characteristically metallic infrared reflectivities even after prolonged periods in UHV.

It is informative now to turn to the valence level photoemission spectra shown in Figs. 2 and 3. The data from the metallic 1:2:3 phase are in broad agreement with those from scraped<sup>19,20,22-24,26,27</sup> or fractured<sup>18,21,22,24</sup> ceramic samples and with those from cleaved single crystals.<sup>25,33</sup> The definition of spectral features in our own work is as

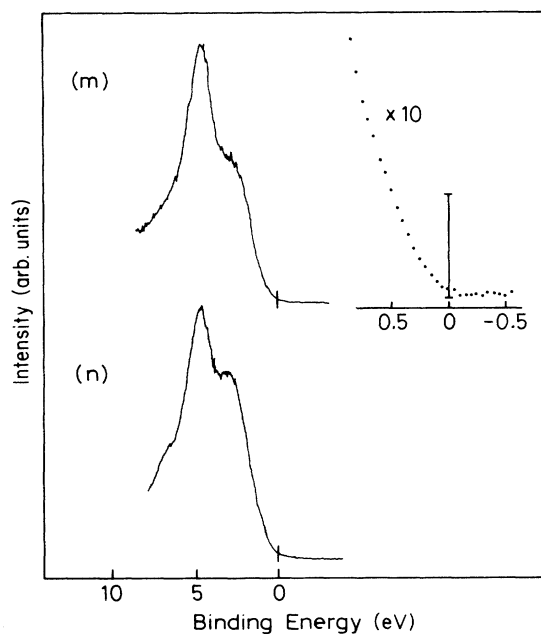


FIG. 2. He I photoelectron spectra ( $h\nu=21.2$  eV) of metallic ( $m$ ) and nonmetallic ( $n$ ) phases of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . The inset to the spectrum of the metallic phase shows an expanded scan around the Fermi energy following subtraction of structure due to He I  $\beta$  satellite radiation. The solid line delineates the Fermi edge threshold height corresponding to 0.5 states/eV cell (see text).

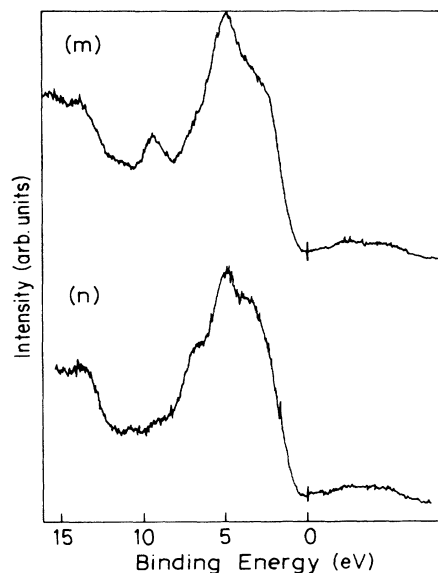


FIG. 3. He II photoelectron spectra ( $h\nu=40.8$  eV) of metallic ( $m$ ) and nonmetallic ( $n$ ) phases of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Structure apparently above the Fermi energy is excited by He II  $\beta$  satellite radiation.

good as in this latter. Our data show nicely the relationship between spectral features for metallic and nonmetallic samples. In both He I and He II spectra we find that the central peak at 4.8 eV in the valence-band photoemission decreases in intensity relative to shoulders at 2.6 and 7.3 eV upon oxygen loss. This suggests that a significant contribution to the intensity of the central feature is associated with the oxygen atoms that complete the Cu-O-Cu chains. It is these atoms that are lost upon vacuum annealing to produce the nonmetallic tetragonal phase.

A comparison of intensities of spectral features under He I and He II excitation further supports these ideas. As we go from 21.2 to 40.8 eV excitation, the O  $2p$ -Cu  $3d$  cross section decreases from about 0.35 to 0.2.<sup>33</sup> Thus, the decrease in relative intensity of the central feature with increasing photon energy suggests that the central peak relates to states of dominant O  $2p$  character. However, the intensity changes are much weaker than for most other transition-metal oxide systems, suggesting that there is very strong Cu  $3d$ -O  $2p$  mixing.

Early band-structure calculations on  $\text{YBa}_2\text{Cu}_3\text{O}_7$  gave density-of-states profiles at variance with experimental data in that a dip rather than a peak appeared in the middle of the valence band.<sup>34</sup> Also, the maximum in the Cu  $3d$  partial density of states was found at the bottom of the valence band.<sup>34,35</sup> However, recent work by Richert and Allen<sup>36</sup> using a simple parametrized tight-binding model gives a band structure for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  conforming in most respects to our experimental data. In particular, the O  $2p$  density of states peaks strongly in the middle of the valence band, with a strikingly sharp central contribution from the oxygen chain atoms. The Cu  $3d$  partial density of states appears mainly at the top of the valence band, but with a significant weighting at the bottom where there is strong  $\sigma$ -type Cu-O covalency.

In comparing photoemission data with band-structure calculation, we recognize that the "Cu 3d" structure appearing in the main valence-band region probably relates to 3d ionization strongly screened by charge transfer from oxygen, as is now well documented for NiO.<sup>37-39</sup> This represents a breakdown of a simple one-electron picture. The present data cannot be reconciled with one-electron calculations in two further respects. First, the prominent peak at 9.3 eV in the HeII spectrum of the metallic phase does not appear in any calculated density of states. The origin of the peak has recently been discussed in detail by Margaritondo and co-workers.<sup>25,33</sup> They conclude that the 9.3-eV feature is a two-hole satellite of the leading valence-band shoulder. In fact, the satellite appears at almost exactly the same energy below the Fermi level as the satellite in NiO ascribed to the unscreened  $d^7$  configuration produced by ionization of the localized  $d^8$  initial state.<sup>37-39</sup> In the 1:2:3 compound, the satellite shows strong resonance enhancement at the Cu 3p core threshold,<sup>10,23</sup> just as for the NiO satellite.<sup>40,41</sup> This leads us to believe that the 9.3-eV satellite is due to an unscreened  $3d^7$  final state associated with Cu III in the initial state. Similar unscreened satellites for initial state Cu II or Cu I occur at 12.9 and 15.3 eV, respectively, in CuO and Cu<sub>2</sub>O.<sup>42</sup> On the basis of our interpretation, it is easy to understand the disappearance of the 9.3-eV feature on going into the nonmetallic state where there is no Cu III.

The second and most surprising feature of the photoemission spectra is that there is no well-defined metallic Fermi edge. Band-structure calculations suggest a Fermi edge density of states between 3 and 6 states/eV cell.<sup>34-36</sup> To compare our experimental data with these estimates we adopt the following *ad hoc* procedure. Due to strong Cu 3d-O 2p mixing the atomic character of states varies relatively weakly across the valence bands. Thus, to a first approximation we can ignore variation in ionization ma-

trix elements across the band. Also, assuming no modulation with electron energy in the density of final states available to valence-band electrons, we can normalize the area of the valence band in He I photoemission to the total number of states per YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> cell, that is 34 states/cell. It is then possible to transfer a vertical line onto the experimental spectrum representing a density of states in states/eV cell, as shown in Fig. 2.<sup>43</sup> From comparison with the experimental data we can put an upper limit of around 0.05 states/eV cell for the density of states at the Fermi energy seen by photoemission.

The reasons for the low density of states are not obvious. Despite the Cu 2p core-level data there must be residual fears about the possibility of surface oxygen loss. A radical alternative suggestion is that the surfaces seen in photoemission are intrinsically nonmetallic even when oxygen stoichiometry is maintained. This situation could arise from band narrowing at the surface due to the reduced coordination with consequent localization of Cu III and Cu II valences in polaronic states. This idea has been widely used to account for the electrochemical behavior of narrow-band metallic systems such as ternary Ru IV oxides where cyclic voltammetry implies the existence of localized Ru III and Ru V surface states.<sup>44</sup> Further experiments directed toward investigation of the metallicity of atomically clean YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> surfaces under high overpressures of oxygen are necessary to clarify these ideas.

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