

Effects of oxygen stoichiometry on the electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_x$

N. G. Stoffel and J. M. Tarascon

Bell Communications Research, Red Bank, New Jersey 07701-7020

Y. Chang, M. Onellion, D. W. Niles, and G. Margaritondo

*Department of Physics and Synchrotron Radiation Center,
University of Wisconsin, Madison, Wisconsin 53706*

(Received 19 June 1987)

Synchrotron-radiation photoemission was used to compare the electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($x=6.8$) which has a superconducting transition at 93 K, and semiconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($x=6.2$) which was prepared by vacuum annealing the $x=6.8$ material. The decrease in oxygen stoichiometry not only affects the intensity of two oxygen-related valence-band features, but also shifts the Fermi level upward and alters the shape of the Cu $3d$ satellite peak. The latter effect indicates a partial reduction to the Cu^{1+} valence state in the vacuum-annealed sample. The superconducting sample could also be modified *in situ* by an intense soft-x-ray beam, leading to oxygen desorption and to photoemission spectra much like the annealed sample.

INTRODUCTION

A common feature of the recently discovered high-temperature oxide semiconductors^{1,2} is a sensitivity of the critical temperature T_c to slight changes in oxygen stoichiometry. The kinetics of oxygen uptake and loss, and the associated effects upon transport properties have been studied in detail for $\text{La}_{2-y}\text{Sr}_y\text{CuO}_{4-x}$ (Ref. 3) and for $\text{YBa}_2\text{Cu}_3\text{O}_x$.⁴

The oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_x$ can be controlled over a wide range by annealing in an oxidizing or reducing ambient. Superconductivity above 90 K is associated with a high oxygen content ($x=6.8$) and is favored by annealing in oxygen, followed by slow cooling. Annealing in vacuum or inert gas above 420°C can reduce x by about 0.6, promoting an orthorhombic-to-tetrahedral phase transition without changing the basic layered structure of the compound. This removal of oxygen leads to resistance versus temperature behavior like that of a semiconductor. Neutron-diffraction studies⁵ have shown that changes in the occupancy of O sites on the central Cu-O plane account for nearly all of the stoichiometry difference.

Although the fundamental nature of the superconductive state has not been established, it is apparent that many of the proposed theoretical models are inherently sensitive to oxygen stoichiometry. The resonating valence-bond (RVB) model⁶ explicitly recognizes the importance of the copper oxidation state. Specifically, the RVB model postulates singlet pairs of electrons on adjacent Cu^{2+} ions. These pairs are immobile, yielding an insulating state, unless there is a sufficient concentration of holes in the form of Cu^{3+} ions. Assuming that oxygen is in the O^{2-} valence state, Cu^{3+} will be present for $x > 6.5$. The Cu valence state is also crucial for the excitonic model,^{7,8} which relies on a virtual transfer of charge between Cu and O to provide the binding force for Cooper pairs of electrons. A different point of view is provided by models which are based on band-structure calculations.⁹ Here the emphasis is less on specific valence states and more on

the position of various Cu-O bonding and antibonding bands relative to the Fermi level, which is in turn controlled by the doping effect of oxygen vacancies.

A number of workers have reported results of angle-integrated photoelectron spectroscopy on superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$.¹⁰⁻¹³ These studies have provided a consistent overall picture of the valence structure. Our purpose in this paper is to explore the electronic structure of nonsuperconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $x=6.2$, and to compare this with the superconducting compound. We find significant differences both in the valence state of Cu and the Fermi-level position as a function of oxygen content.

EXPERIMENTAL PROCEDURES

The preparation and characterization of the samples used in these experiments are described in detail in Ref. 4. Briefly, a dense, sintered pellet of the superconducting compound is prepared using CuO , BaCO_3 , and Y_2O_3 powders. This pellet is reannealed in oxygen at 940°C for two days and cooled in 5 h, resulting in a sample for which the midpoint of the resistive transition is 93 K. Thermal gravimetric analysis yielded an oxygen content of $x=6.8 \pm 0.1$.

A 1-mm-thick slice was cut from the superconducting sample for subsequent furnace annealing in a vacuum of 10^{-3} Torr. Annealing for 24 h at 420°C reduced the oxygen content of this sample to a value $x=6.2$, and resulted in semiconducting behavior. X-ray diffraction measurements showed both samples to be single phase, but the crystal structure converts from orthorhombic to tetragonal upon removal of oxygen.

The photoemission experiments were conducted at the University of Wisconsin Synchrotron Radiation Center. Angle-integrated photoelectron spectra were obtained with a cylindrical-mirror electron energy analyzer using photon energies between 40 and 160 eV. The samples

were mounted side by side on a copper holder which could be cooled to 50 K by a closed-cycle refrigerator. The sample temperature was below 70°C during the chamber bakeout to prevent inadvertent oxygen loss. The chamber base pressure was 2×10^{-10} Torr.

The photoemission results are sensitive to the method of surface preparation and to subsequent surface contamination. For this study fresh sample surfaces were prepared by scraping about 0.2 mm of material from the surface with a diamond-coated wheel. This treatment is expected to produce fractures within the grains, rather than just at grain boundaries. This grinding procedure does not result in noticeable outgassing of the sample at room temperature. Furthermore, we find essentially identical results when the sample is held at 50 K during the grinding and the photoemission measurements. This suggests that the surfaces of our samples are relatively stable and do not desorb oxygen spontaneously at room temperature.

In contrast, we find that oxygen is quickly desorbed by either the 2-keV electron beam used for Auger spectroscopy or the intense zero-order beam of white synchrotron radiation normally used to visually align the sample. This desorption has a profound effect on the photoelectron spectra. For this reason, except as noted, our photoelectron spectra were taken on freshly prepared surfaces which were only exposed to a relatively weak monochromatic beam of photons.

Auger spectroscopy revealed a significant carbon signal in our samples which increases toward the center of the samples. This is a residue of the BaCO_3 used in the synthesis of the compound, and is probably in the form of graphitic carbon at grain boundaries. We were not able to identify any contributions from this carbon to the valence-band spectra.

EXPERIMENTAL RESULTS

The photoelectron spectra obtained from the superconducting sample of $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $x=6.8$ are consistent with our previous results¹⁰ and those of other groups.¹¹⁻¹³ In Fig. 1 we present a set of photoelectron-energy distribution curves for selected photon energies, $\hbar\omega$. These results were recorded at room temperature, and essentially identical results were obtained at 50 K. The vertical scales are arbitrarily normalized, and the energy is referred to the Fermi level.

We call attention to the following features in Fig. 1. The intensity at the Fermi energy is quite small in spite of the metallic behavior of the conductivity for the $x=6.8$ sample. The main Cu $3d$ -O $2p$ bonding bands (B) appear between 2-7 eV below the Fermi energy, and a shoulder (A) appears near -2.5 eV. This shoulder is stronger at low photon energies, and becomes a distinct peak at energies below the range used in this study.¹¹ This intensity dependence has been interpreted as a signature of O $2p$ states, since the ratio of atomic O $2p$ and Cu $3d$ cross sections increases at lower photon energies. However, this is not conclusive evidence, since the valence wave functions are distorted and hybridized in the solid state.

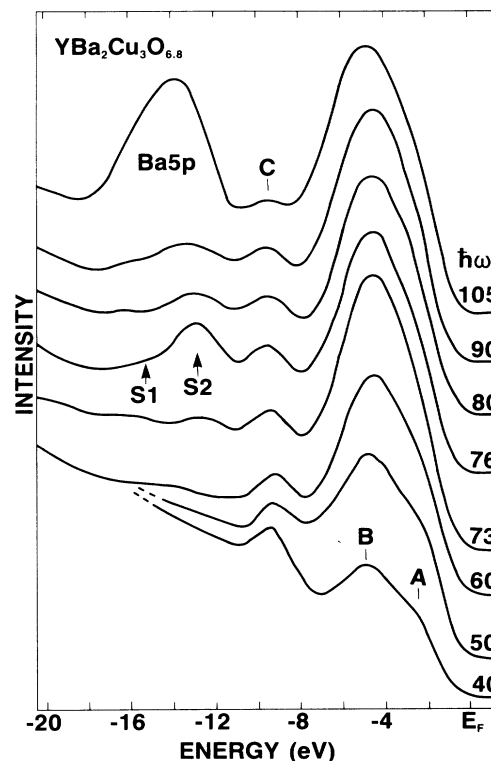


FIG. 1. Room-temperature valence-band photoelectron spectra of the 93-K superconducting compound with $x=6.8$ at the indicated photon energies $\hbar\omega$.

A sharp feature (C) appears at -9.5 eV, which is also relatively stronger at low photon energies. This peak is reported to be resonantly enhanced at the Cu $3p$ absorption threshold,¹² but we do not observe a definite effect at that energy. The shallow Ba $5p$ core level is resonantly enhanced above the Ba $4d$ threshold, and produces the strong features near -15 eV in the $\hbar\omega=105$ -eV spectrum.

Finally, an important feature (S2) appears for photon energies just above the Cu $3p$ photoabsorption threshold at $\hbar\omega=74$ eV. This peak is a satellite of the Cu $3d$ band which is resonantly enhanced by an interaction between a $3p$ - $3d$ - $3d$ Auger transition and a $3d$ shakeup excitation. The energy position of this satellite conveys information about the valence state of Cu atoms. In Fig. 1, the arrow above S2 shows the position of the satellite for Cu^{2+} in CuO as reported in Ref. 14 (-12.9 eV). Similarly, S1 denotes the energy of the satellite due to Cu^{1+} measured in Cu_2O (-15.3 eV). The large peak at S2 at resonance is indicative of a high percentage of Cu^{2+} in the $x=6.8$ compound, but is difficult to estimate this fraction. We do not know the characteristic satellite shape for Cu^{3+} .

The Cu $3d$ satellite is markedly different in the furnace annealed $x=6.2$ sample, as seen in Fig. 2. Comparing the spectra taken below and above the Cu $3p$ threshold, $\hbar\omega=73$ and 76 eV, we find that the satellite exhibits similar intensity at -12.9 and -15.3 eV. The weak struc-

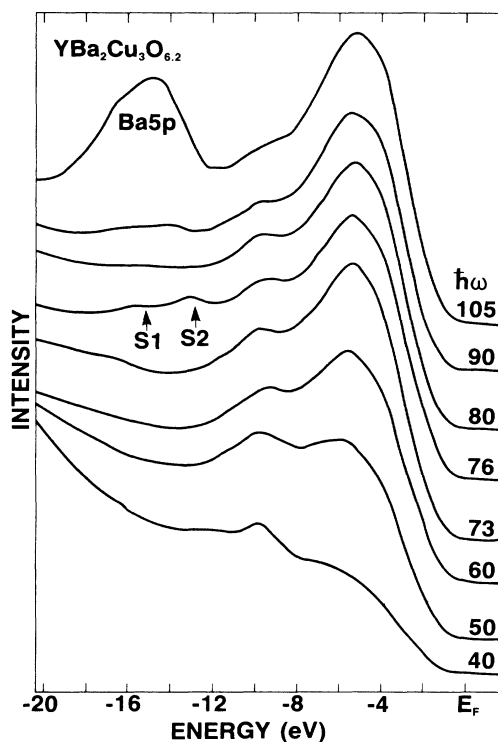


FIG. 2. Photoelectron spectra from the sample for which x has been reduced to 6.2 by vacuum annealing at 420°C.

ture at $S1$ signifies the presence of Cu^{1+} , but the decrease in the total intensity of the satellites is surprising.

In Fig. 3 we compare the spectra taken at $\hbar\omega = 76$ eV near the Cu $3p$ resonance energy. Curves *a* and *b* are from surfaces of the $x = 6.8$ sample which were prepared and measured at room temperature and at 50 K, respectively. The differences in these curves are not significant. Spectrum *c* was taken on the $x = 6.8$ sample after it was exposed to intense synchrotron light for 15 min *in situ*. This procedure removes oxygen from the surface either through thermal or electronic desorption mechanisms. The satellites of both the Cu^{1+} and Cu^{2+} valence states are apparent in this spectrum and also in curve *d* taken on the $x = 6.2$ sample. Curves *c* and *d* share some other features which distinguish them from curves *a* and *b*. Note that the shoulder *A* and the feature *C* are weak or absent in the partially reduced samples. This supports the assignment of both features to oxygen-derived states.

A comparison of Figs. 1 and 2 reveals a definite shift towards higher binding energy for the valence bands, the satellite peaks, and the Ba $5p$ core levels in the $x = 6.2$ sample. Although we find some differences in the line shapes of the core and valence features between the various samples, the main underlying effect of the change in oxygen stoichiometry is clearly an almost-rigid shift of the electronic states. The shift of the Ba $5p$ core level is 0.9 ± 0.2 eV, while the Ba $4d$ levels (not shown) are 0.9 ± 0.1 eV lower in the $x = 6.2$ sample. Shifts also occur in the *in situ* annealed surfaces, but are smaller than in the furnace

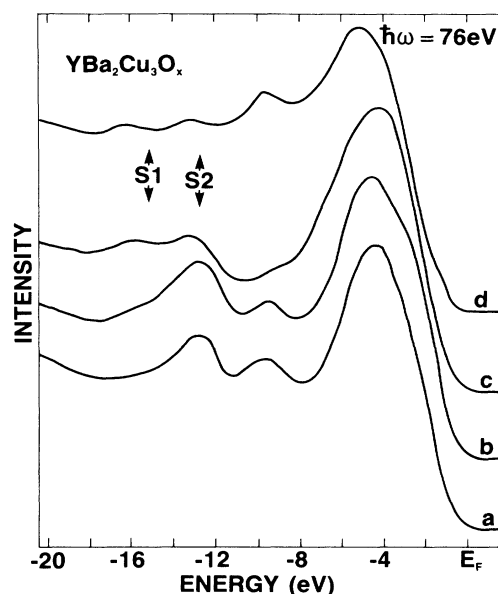


FIG. 3. A comparison of spectra taken at the Cu $3p$ resonance photon energy on the superconducting sample at 300 K (*a*), at 50 K (*b*), and after *in situ* annealing (*c*). *d* is the annealed $x = 6.2$ sample. The Cu $3d$ satellites $S1$ and $S2$ are particularly affected by annealing.

annealed sample, and the magnitude of the shift depends on the length and intensity of the soft-x-ray exposure.

DISCUSSION AND CONCLUSIONS

The annealing-induced binding energy shifts can be interpreted either in the context of band-structure or localized electronic states. A nearly rigid shift of the spectral features is a commonly observed effect of semiconductor doping or surface band bending, where the Fermi level E_F is varied through the band gap. The primary effect on the photoemission spectrum is a general electrostatic shift of all electronic states, while changes in the density of states occur as a second-order effect. The upward shift of E_F is to be expected with the removal of O, since oxygen vacancies should act as donors. The magnitude of the shift, almost 1 eV, confirms that the density of states is quite low at and above E_F in the superconducting compound.¹⁵

On the other hand, the discrete satellite binding energies observed in the reduced samples support the assignment of a specific localized valence state for the Cu ions. Cu is nominally in a Cu^{2+} valence state for a value of $x = 6.5$. Our results show significant Cu^{1+} in the $x = 6.2$ sample and in the *in situ* annealed sample for which x is unknown. This result is consistent with the analysis of neutron-diffraction data.⁵

Photoabsorption at the Cu $2p$ threshold¹⁶ and Cu $2p$ photoelectron spectra¹⁷ have been interpreted as evidence for a valence greater than +2. We do not know if it is possible to see Cu^{3+} directly in the valence-band spectra of Cu compounds, but there are no unassigned resonance

structures in our data which would be candidates for the Cu^{3+} satellite.

Both the valence state of Cu and the Fermi energy position affect the oxygen-induced semiconductor-to-superconductor transition, and our data demonstrate dramatic effects of oxygen content on these parameters. However, the electronic structure very near the Fermi level is almost certainly crucial for the superconducting pairing, and angle-resolved photoemission on single crystals will be required to provide details of this structure. In addition to electronic effects, structural effects, such as the formation

of one-dimensional Cu-O chains and the orthorhombic phase transformation, could also play a role.

ACKNOWLEDGMENTS

This work is supported by the NSF, Grant No. DMR-84-21212, by the Office of Naval Research, Contract No. N00014-80-C-0908, and by the Wisconsin Alumni Research Foundation. Helpful discussions with B. G. Bagley, H. H. Farrell, L. H. Greene, and E. Yablonovitch are gratefully acknowledged.

-
- ¹J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189, (1986).
²M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987).
³J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull, and T. H. Geballe, *Science* **235**, 1373 (1987).
⁴J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, *Phys. Rev. B* **36**, 226 (1987).
⁵J. E. Greedan, A. O. O'Reilly, and C. V. Stager, *Phys. Rev. B* **35**, 8770 (1987).
⁶P. W. Anderson, *Science* **235**, 1196 (1987).
⁷C. M. Varma, S. Scmitt-Rink, and E. Abrahams, *Solid State Commun.* **62**, 681 (1987).
⁸J. P. Collman, J. T. McDevitt, and W. A. Little, *Phys. Rev. B* (to be published).
⁹S. Massida, Jaejun Yu, A. J. Freeman, and D. D. Koelling, *Phys. Lett.* (to be published).
¹⁰M. Onellion, Y. Chang, D. W. Niles, R. Joynt, G. Margaritondo, N. G. Stoffel, and J. M. Tarascon, *Phys. Rev. B* **36**, 819 (1987).
¹¹P. D. Johnson, S. L. Qiu, L. Jiang, M. R. Ruckman, M. Stron-
gin, S. L. Hulbert, R. F. Garret, B. Sinkovic, N. V. Smith, R. J. Cava, C. S. Lee, D. Nichols, E. Kaczanowicz, R. E. Salamon, and J. E. Crow, *Phys. Rev. B* **35**, 8811 (1987).
¹²R. L. Kurtz, R. L. Stockbauer, D. Mueller, A. Shih, L. E. Toth, M. Osofsky, and S. A. Wolf, *Phys. Rev. B* **35**, 8818 (1987).
¹³A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **35**, 8814 (1987).
¹⁴M. R. Thuler, R. L. Benbow, and Z. Hurych, *Phys. Rev. B* **26**, 669 (1982).
¹⁵R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zaharuk, and G. P. Espinosa, *Phys. Rev. Lett.* **58**, 1676 (1987).
¹⁶Y. Jeong, F. Lu, H. Jhans, S. A. Shaheen, M. Croft, P. Ansari, M. Greenblatt, L. H. Greene, and J. M. Tarascon (unpublished).
¹⁷H. Ihara, M. Hirabayashi, N. Terada, Y. Kimura, K. Senzaki, M. Akimoto, K. Bushida, F. Kawashima, and R. Uzuka, *Jpn. J. Appl. Phys.* **26**, L460 (1987).