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W.K. Ford

Montana State University - Bozeman

C.T. Chen

AT&T Bell Laboratories, Murray Hill, New Jersey

J. Anderson

Montana State University - Bozeman

J. Kwo

AT&T Bell Laboratories, Murray Hill, New Jersey

Sy_Hwang Liou

University of Nebraska-Lincoln, sliou@unl.edu

See next page for additional authors

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Authors

W.K. Ford, C.T. Chen, J. Anderson, J. Kwo, Sy_Hwang Liou, M. Hong, G.V. Rubenacker, and J.E. Drumheller

Oxygen defect in $\text{YBa}_2\text{Cu}_3\text{O}_x$: An x-ray photoemission approach

W. K. Ford

Department of Physics, Montana State University, Bozeman, Montana 59717

C. T. Chen

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

J. Anderson

Department of Physics, Montana State University, Bozeman, Montana 59717

J. Kwo, S. H. Liou, and M. Hong

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

G. V. Rubenacker and J. E. Drumheller

Department of Physics, Montana State University, Bozeman, Montana 59717

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A combined x-ray photoemission and diamagnetic-susceptibility study of $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $x \approx 6$ and 7 has been performed, with emphasis on the oxygen defect and the effect of heating in vacuum. By comparing spectra taken at these two oxygen contents, the core levels observed in the O 1s and Ba 4d spectral range are identified. Peak-intensity analysis indicates (1) that the oxygen released during the *in situ* heating is derived from or near the Cu—O—Cu—O chains of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and (2) that there is a random distribution of oxygen defects in or near these chains leading to two chemically dissimilar barium atoms even in single-orthorhombic-phase samples.

The exciting discovery by Bednorz and Müller¹ of a new family of high-critical-temperature superconductors has captured the interest of the entire scientific community. The subsequent synthesis of alternate materials such as $\text{YBa}_2\text{Cu}_3\text{O}_x$,² which extend the critical temperature above the liquid-nitrogen condensation point, promises to affect technology and society in a positive fashion. Because the high- T_c phenomenon exists for a variety of chemical compositions, stoichiometries, and preparation methods, there remains much to be learned before the physical mechanism underlying the superconductivity is fully understood. Specifically, defects in the oxygen sublattice play a very important role in determining transport phenomena such as the critical current,³ as well as determining the crystal structure.⁴ We report herein the results of an element-specific, x-ray photoelectron spectroscopic study of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_x$ with x near the two extremes of the oxygen content, 6 and 7, placing an emphasis on the impact of varying the oxygen content by in-vacuum heating. Our data substantiate a proposal made earlier⁵ that the oxygen released during the heating is derived from the Cu—O—Cu—O chains of $\text{YBa}_2\text{Cu}_3\text{O}_7$; we also present evidence that there are two distinct barium sites in proximity to these chains even in orthorhombic, single-phase samples.

The Y—Ba—Cu—O compounds were prepared with a nominal composition of $\text{YBa}_2\text{Cu}_3\text{O}_x$, $x \approx 6.9$. They were derived from Y_2O_3 , BaCO_3 , and CuO powders pressed into pellets which were repeatedly ground and sintered at 950°C in air or O_2 for 10 h, and then slowly cooled in O_2 . After preparation the resistivity was measured as a function of temperature using a standard four-point

configuration by both ac and dc methods. The 10%–90% transitions were 94–92 K with zero resistance at 91 K. The structure of the superconducting phase was determined by both x-ray and electron diffraction to be orthorhombic.^{6,7} The samples were identified as consisting of a single phase, and were cut to rectangular shapes about 5 mm \times 7 mm \times 2 mm.

The photoemission experiments were performed in an experimental chamber equipped with an ESCA analyzer, a dual-anode x-ray source, and a helium-gas ultraviolet lamp. The electron analyzer lens system had a spot size of 3 mm, smaller than the sample surface extent. An Al $K\alpha$ anode with a photon energy of 1486.6 eV was used for the x-ray photoelectron spectroscopy (XPS) studies. In conjunction with the photoemission experiments, the existence of a superconducting phase in our samples was checked by observing the Meissner effect using a vibrating sample magnetometer. The sample magnetization was recorded as a function of temperature at low fields, typically 5 G. The magnetic phase diagram of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ material was also measured and is the subject of a separate report.⁸ In this report, our magnetization measurements serve as a point of contact between the bulk phenomena of superconductivity and our surface-sensitive XPS probe.

During the course of our studies, the samples lost their superconducting phase when a large amount of the bulk oxygen was removed by heating in vacuum. It is known that they could be regenerated by heating them to 950°C in flowing O_2 at 1 atm for approximately 12 h and then cooled slowly to 500°C for several hours. The samples were weighed prior to and after the heating sequence to

estimate oxygen uptake. The samples thus regenerated display reproducible photoemission spectra and magnetization curves that matched those of the original samples.

All XPS lines were monitored during the course of heat treatment and demonstrated to be highly reproducible. Barium, oxygen, and to a lesser extent, copper showed important variations, whereas the Y $3p$ did not. In this paper, we shall only concentrate on the O $1s$ and Ba $4d$ levels since oxygen is the only element that desorbs into the vacuum during heat treatment and barium is the only element of which *all of its atoms* are directly influenced by the oxygen defects. The Ba $4d$ levels were selected since they are better resolved than the $3d$ states, which have a significantly greater natural linewidth. A detailed discussion of other core levels as well as the impact on XPS spectra by different sample surface preparation methods will be reported elsewhere.

Figure 1 displays the O $1s$ and Ba $4d$ core-level spectra after different stages of heat treatment. The binding energies were determined using the adventitious carbon line (not shown) and each spectrum is normalized to its maximum value. Curve (a) represents the sample immediately after insertion into the vacuum. The O $1s$ spectrum shows two peaks whereas the Ba $4d$ spectrum contains three peaks. The three-peak feature is the result of a superposition of two Ba $4d_{5/2}$, $4d_{3/2}$ doublets. This interpretation is based on consideration of the peak height ratio

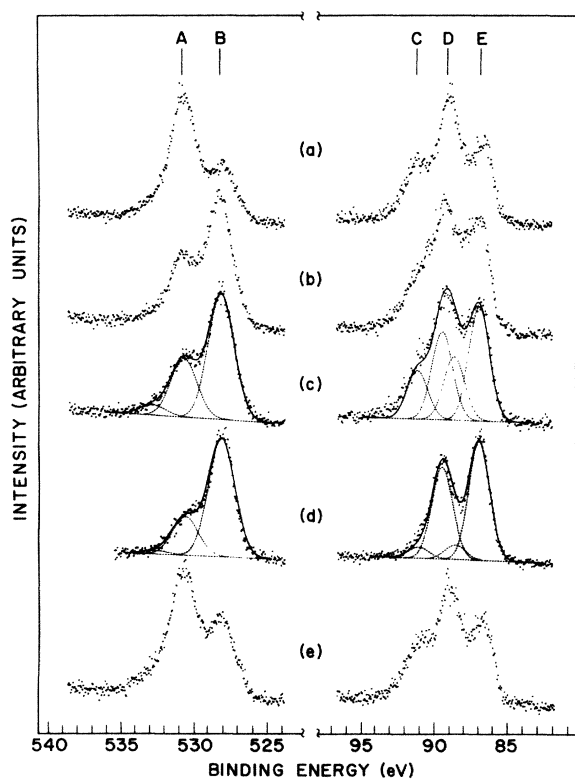


FIG. 1. O($1s$) and Ba($4d$) XPS spectra: (a) as inserted; (b) after first heating, ca. 0.6% oxygen loss; (c) after second heating, ca. 1.2% oxygen loss; (d) regenerated sample after heating, ca. 10% oxygen loss; (e) heated sample after exposure to atmosphere.

for the Ba $4d$ doublet. A simple multiplicity argument suggests a 3:2 ratio between the intensity of $4d_{5/2}$ and $4d_{3/2}$ levels; the measured ratios for Ba and BaO are 1.61 and 1.33, respectively.⁹ The intense central peak is due to the overlapping of the $4d_{3/2}$ level of the lower-binding-energy C - D doublet pair and the $4d_{5/2}$ level of the higher-binding-energy D - E doublet pair.

The sample was then heated to ca. 450°C for 1 min. This was sufficient to release a considerable amount of oxygen as measured in the residual gas analyzer. The spectra after heating are displayed in curve (b). Note that the lower-kinetic-energy O $1s$ peak, labeled A , and the highest-binding-energy Ba $4d$ peak, labeled C in Fig. 1, were severely affected. The sample was then heated a second time to 450°C for 1 min resulting in curve (c). Only a very little additional amount of oxygen was removed and only a slight reduction in the peaks A and C intensities was observed. The sample was subsequently removed from the vacuum and shown to be still superconducting with a 50% increase in volume magnetization. The sample was weighed and the oxygen stoichiometry was estimated to be 6.9. The sample was then regenerated using the procedure described above and returned to vacuum. Upon initial introduction to the vacuum and after the 450°C heating the sample produced spectra identical to (a) and (c), respectively.

The sample was next heated to 600°C . Curve (d) shows the effect of this heating. Sample charging caused line shifts of several volts in curve (d) resulting from a loss of conductivity. The energy scale was corrected by lining up the Y $3p$ level which is presumably less effected by the heating. The Ba $4d$ is now essentially a pure doublet. When this sample was checked in the magnetometer, there was no evidence of a superconducting diamagnetism down to 1.9 K. The oxygen content was determined by weighing to be approximately 6.1. Finally, curve (e) is characteristic of the spectra obtained after a vacuum-heated sample was withdrawn, exposed to atmosphere for about 2 min and then reinserted into the vacuum. We observed no contamination of the sample either upon heating or upon extended (24 h) presence in our chamber.

Peaks A , C , and D in curve (a) result from a combination of surface and bulk oxygen. After the initial 450°C heating of the sample peak A lost about 70% of its intensity (comparing the absolute intensities of the data) but after the second 450°C heating [curve (c)] the intensity of peak A remained essentially the same. The oxygen removed during this initial 450°C annealing is primarily from the thermal desorption of chemisorbed O_2 at the surface. Peak C , the Ba $4d_{3/2}$ level of the high-binding-energy doublet pair, lost its intensity concurrently with peak A . This indicates that part of the intensity C - D doublet is associated with the Ba atoms that react with surface adsorbates. This argument is further supported by curve (e) which shows that peaks A , C , and D regain essentially all of their original intensity when exposed once again to the atmosphere. In contrast to the changes observed in peaks A , C , and D , the intensities of peak B and the D - E doublet are unchanged during the heat treatments. It is also noteworthy that the C $1s$ spectra loses its intensity completely with heating. This is presumably due

to desorption of adsorbed species.

Curves (c) and (d) in Fig. 1 exhibit the interesting spectral modifications which occur when the sample is transformed from one containing a superconducting phase with $x \approx 6.9$ to the nonsuperconducting form with $x \approx 6.1$. A curve-fitting procedure has been performed to interpret these spectra. In fitting the O 1s spectra, all of the peak widths and all of the energy positions were constrained to be the same between curves (c) and (d). For the Ba 4d spectra, the energy separation and peak height ratio between the $4d_{5/2}$ and $4d_{3/2}$ lines were kept the same for the high- and low-binding-energy doublet pairs, as were the peak widths. Three kinds of line shapes, namely, Gaussian, Lorentzian, and an intermediate type, as well as different types of background functions were utilized. The dashed curves shown in Fig. 1 are the result of using Gaussian line shape and a linear background. However, the peak intensity ratios obtained by fitting with other line shapes and backgrounds were found to lie within 10% of the values quoted below.

According to this prescription, the binding energies for peaks *A* and *B* are 530.6 and 528.0 eV, respectively. The binding energies for the $4d_{5/2}$ levels in the *C-D* doublet and *D-E* doublet pairs are 88.4 and 86.7 eV, respectively, which manifests a 1.7 eV chemical shift. The energy separation for the doublet is found to be 2.47 eV, in good agreement with that of BaO, 2.5 eV.⁹ The widths for the O 1s and Ba 4d peaks are 2.1 and 1.7 eV, respectively. The peak height ratio for Ba 4d doublet is found to be 1.3 which is also in good agreement with that of BaO, 1.33.⁹

The peak *A*-to-*B* intensity ratios were found to be 0.47 for spectrum (c) and 0.33 for spectrum (d). This result and the fact that peak *B* retained its intensity during the heat treatment implies that peak *A* loses 30% of its intensity during the 600°C annealing, calculated as $(0.47-0.33)/0.47$. After this oxygen loss the sample shows no superconductivity and the oxygen content is reduced from 6.9 to 6.1. It is, therefore, evident that this oxygen loss is primarily derived from the bulk. Notice that this difference is very close to that obtained via the weighing measurements.

The analysis of neutron powder diffraction measurements has suggested that this material undergoes a structural phase transition from orthorhombic-to-tetragonal symmetry as the oxygen defect is increased.¹⁰ Figure 2 displays the tripled perovskite superconductivity-related orthorhombic structure of the $YBa_2Cu_3O_7$. The O(2) and O(3) atoms should have nearly degenerate 1s core levels because their chemical environments are very similar in the orthorhombic phase and are identical in the tetragonal phase. This is also true for the O(1) and O(4) atoms. If one assumes that peak *A* is associated with the O(2,3) atoms with the others remaining intact upon heating, the intensity loss between curves (c) and (d) is calculated to be 20%, 3.9 O(2,3) atoms when $x \approx 6.9$ vs 3.1 O(2,3) atoms when $x \approx 6.1$. Alternatively, if we assume that peak *A* is due solely to the O(1,4) atoms then the intensity loss is 28%, 2.9 O(2,3) atoms when $x \approx 6.9$ vs 2.1 O(2,3) atoms when $x \approx 6.1$, the latter value is within the error of our measurement, $30 \pm 3\%$. Qualitatively, that peak *B* is more intense

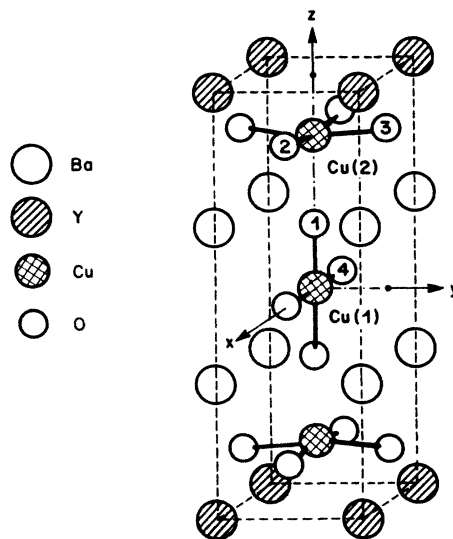


FIG. 2. The tripled perovskite structure of $YBa_2Cu_3O_7$. The O(1), O(2), O(3), and O(4) are labeled for reference in the text.

than peak *A* is also consistent with the unit-cell occupancy numbers between O(2,3) and O(1,4). With this assignment the discrepancy between the observed and calculated *A* to *B* intensity ratios, 0.47 vs 0.72 for spectra (c) and 0.33 vs 0.53 for spectra (d), could come from surface oxygen whose intensity is enhanced by the surface sensitivity characteristic of the XPS probe. This strongly bonded surface oxygen may be either completed CuO perovskite microstructures at the surface or YO configurations. Due to their stability, they remain intact during the entire heat treatment. To summarize, our O 1s data favor the peak assignment that peak *A* contains the 1s levels of O(1,4) and peak *B* contains the 1s levels of O(2,3). The oxygen released during the 600°C heating is derived from O(1,4).

The barium chemical environment is radically altered when the superconducting phase is lost. The ratio of the *C-D* to the *D-E* Ba 4d doublets changes from 0.56 in spectrum (c) to 0.12 in spectrum (d). Presumably spectrum (d) represent this material in its tetragonal phase¹⁰ and the shift of the Ba 4d spectral strength to the lower-binding-energy doublet is a manifestation of this. An initial-state effect could also be operative. That is, with the reduction of electronegative oxygen coordination, a reduced charge transfer from the barium sites occurs. In either case, the shift of the spectral weight from the high-binding-energy doublet to the low-binding-energy one is consistent with the picture that the O(1,4) atoms of the Cu—O—Cu—O chains are lost during heating. Referring to Fig. 2, it is these atoms which are nearest to the barium sites.

The Ba 4d spectrum (d) also suggests that the nonsuperconducting sample is multiphase $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$. With an oxygen content $x \approx 6.1$, 10% of the sample being $YBa_2Cu_3O_7$, and 90% being $YBa_2Cu_3O_6$, the Ba 4d *C-D* to *D-E* peak ratio should be 0.11, very

close to the observed 0.12. But this should also lead to a chemical shift of the low-binding-energy peak which is not observed. Alternatively, the 0.9 oxygen defect may be randomly distributed over the sample. In this case, the ratio would be 0.25, which is not in reasonable agreement with our measurements. A TEM study could perhaps clarify this point.

More intriguing is the fact that the superconducting material has two distinct barium sites; cf. Fig. 1, curve (c). The *C-D* to *D-E* Ba *4d* double ratio of 0.56 cannot be explained in this case by invoking a multiphase sample. That is, an oxygen content of $x \approx 6.9$ would require 90% of the sample to be $x = 7$ and 10% to be $x = 6$, leading to a ratio of 0.11. Conversely, a random distribution of defects over the lattice would give rise to a ratio of 0.25 for an oxygen concentration of $x \approx 6.9$. Our results are in agreement with earlier XPS work that noted the existence of two barium sites in more poorly resolved spectra.⁵

Several explanations of this observation have been considered. Surface contamination immediately comes to mind. However, we obtain similar spectra no matter whether we apply our heat treatment or scrape the surface with a diamond file to clean it prior to our photoemission measurements. Whereas, scraping does not guarantee that surface contamination effects are important, the success of other photoemission studies, e.g., Refs. 5 and 6, suggests that such effects are minimized. It should also be noted that the high photoelectron kinetic energies experienced in XPS, ≥ 1000 eV, make this technique more bulk sensitive than many other surface probes. Second, an inhomogeneous surface stoichiometry may be present. Scraping the surface revealed that there seemed to be no elemental gradients at the surface of our regenerated samples. Third, the oxygen may be contained in various C–O bonds. However, although detectable there was negligible carbon contamination in the regenerated samples. This

would argue against residual raw materials, e.g., CO and BaCO_3 , remaining after the initial sample growth. Considering that the Ba *4d* photoelectron escape depth at XPS energies is in excess of 30 Å, equating to averaging over 3–8 unit cells, and that the spectra have been reproduced repeatedly on different samples we infer that our observation of two chemical barium sites is characteristic of the bulk single-phase, polycrystalline material and not an experimental artifact.

We choose to interpret the two barium sites as arising from variations in the Cu–O–Cu–O chain. This chain will kink and change directions if in any unit cell one O(4) atom, cf. Fig. 2, is repositioned to lie on the *y* axis. This placement is presumably not energetically hindered since the *y*-axis and *x*-axis sites have the same coordination. Interaction with the other O(4) atom would be minimal due to the localization of the Cu–O bond. From a crude calculation we estimate that as little as roughly 10%–20% of the unit cells would have to undergo this chain kink to make agreement with the XPS data. Although it is energetically less favorable, the reposition of O(1) to the *x-y* plane cannot be excluded. Such a repositioning could be either periodic or random. A periodic distribution would appear as faint additional features in the diffraction measurements. This picture appears to disagree with that derived from the neutron and x-ray structure determination.^{6,10,11} However, those techniques are not as element specific and chemical environment sensitive as XPS and the observations of actual distribution of kinks may be made infeasible by their experimental detectability limits.

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