

Electronic behavior of oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

W. K. Kwok,* G. W. Crabtree, A. Umezawa,† B. W. Veal, J. D. Jorgensen,
S. K. Malik,‡ L. J. Nowicki, A. P. Paulikas, L. Nunez

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 20 August 1987)

We have measured the resistivity, Meissner effect, and neutron powder diffraction on a series of samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ quenched into liquid nitrogen from temperatures between 400 and 900°C in order to study the dependence of the electronic and structural properties on oxygen content. The normal-state resistivity is linear only for samples with high superconducting transition temperatures, becoming concave upward for samples with low T_c , and semiconducting for nonsuperconducting samples quenched from high temperatures. Structural analysis shows dramatic movements of the bridging oxygen atom [O(4)] and the copper atom [Cu(2)] in the two-dimensional planes as the oxygen stoichiometry is reduced.

The properties of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ depend strongly on the oxygen content.¹⁻⁹ While chemical substitutions¹⁰⁻¹² induce rather modest variations in T_c , changes in the oxygen stoichiometry affect the electronic behavior of the normal state, the crystallographic structure, and the transition temperature over the range 0–93 K. Thus it is important to characterize the physical behavior of samples with varying oxygen contents. For $\delta \sim 0$, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is in the orthorhombic phase and exhibits superconductivity at 93 K. As the oxygen content is decreased, the transition temperature of the orthorhombic phase decreases, until for $\delta \sim 0.6$, the material enters the tetragonal phase and superconductivity is destroyed.¹ Several detailed aspects of this phase transition remain unexplored. It is not clear whether the loss of superconductivity is correlated with the structural phase transition. In the tetragonal phase the effect of the oxygen concentration on the normal-state electronic behavior is unknown. Finally, the structural changes which affect the electronic coupling of the one-dimensional chains and the two-dimensional planes as oxygen is removed are not well understood.

The oxygen-deficient structures of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ can

be produced in several ways. The equilibrium state with δ as large as 0.9 is obtained³ simply by raising the temperature in a controlled oxygen atmosphere. These structures can then be stabilized at room temperature by quenching into liquid nitrogen^{1,5} or by cooling in a partial oxygen atmosphere. Although there are slight differences between these metastable phases and the equilibrium high-temperature phase, their main structural features are nearly identical.¹ We have measured the resistivity, Meissner effect, superconducting transition temperature, and neutron powder diffraction in a series of oxygen-deficient samples produced by quenching into liquid nitrogen. In the orthorhombic phase, we find (with increasing δ) a continuous decrease of T_c and a transition from linear to concave upward behavior in the normal-state resistivity. In the tetragonal phase we observe the gradual appearance of semiconducting behavior. A continuous, dramatic shortening of the Cu(1)–O(4) bond and the lengthening of the Cu(1)–Cu(2) bond along the c direction occurs in both phases.

Samples were prepared from mixtures of Y_2O_3 , BaCO_3 , and CuO powders as reported elsewhere.¹ Quenching was carried out by placing the samples in a small platinum cup

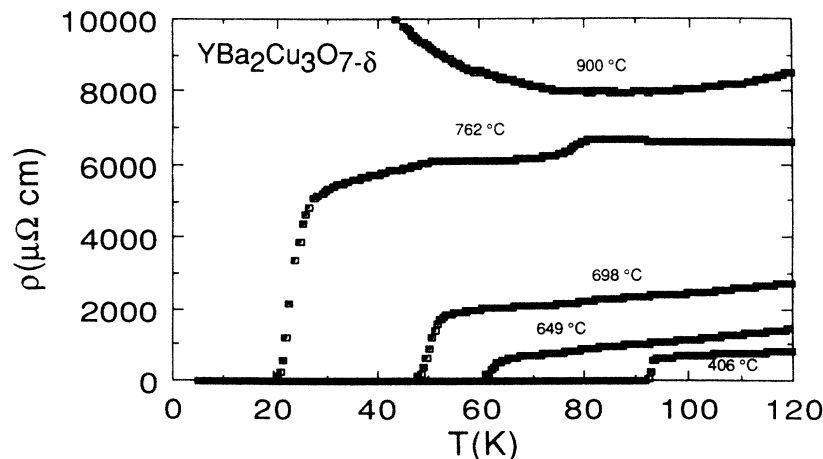


FIG. 1. Resistivity vs temperature for samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ quenched from various temperatures.

which was suspended in a vertical tube furnace from a 0.005-in. nichrome wire. A separate platinum wire was used to invert the cup and drop the contents into liquid nitrogen. Samples were held at constant temperature in the furnace for at least 4 h (10 h for temperatures below 650°C) prior to quenching. The oxygen occupancy, unit-cell dimensions, and superconducting transition temperatures of these samples are reported elsewhere.¹

Resistivity was measured by an ac four-probe technique with 2.5 mA measuring current at 100 Hz. Copper wire leads were attached with silver paste. Data were taken in zero field from 4 to 300 K in a gas flow cryostat. The resistivity below 120 K of five samples quenched from 406, 649, 698, 762, and 900°C are plotted in Fig. 1. The sample quenched from 406°C has a midpoint transition temperature of 93.0 K and is comparable to samples prepared without quenching except that the resistivity at T_c is $625 \mu\Omega\text{cm}$ as compared to $350 \mu\Omega\text{cm}$ in the unquenched samples. The normal-state resistivity increases systematically with quench temperature (T_q) implying an increase in the electronic scattering rate or a decrease in the carrier concentration. The superconducting transition temperatures decrease systematically with increasing quench temperatures as shown in Fig. 2. The decrease in transition temperature correlates with a decrease in oxygen stoichiometry as determined by weight change and by powder neutron diffraction.¹ For quench temperatures below 500°C, T_c varies by only 0.5 K. For quench temperatures above 500°C, there is a continuous decrease in the transition temperature, with T_c going to zero in samples quenched at and above 800°C. The orthorhombic to tetragonal phase transition in quenched samples occurs very close to this quench temperature. However, the scatter in the T_c vs T_q data and the coarse grid of quench temperatures prevent a clear determination of whether the phase transition corresponds precisely to the destruction of superconductivity.

The phase transition occurs at $7-\delta \sim 6.44$ as shown in Table I. A continuous disordering of the chain oxygen atoms was observed as the transition is approached. The O(1) $(0, \frac{1}{2}, 0)$ site is depleted both by the reduced overall stoichiometry and by transfer of oxygen atoms into the

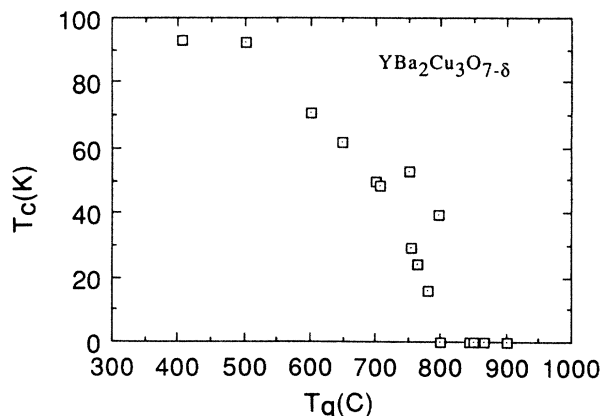


FIG. 2. Superconducting transition temperature T_c vs quench temperature T_q .

TABLE I. Oxygen occupancy vs quench temperature.

T_q (°C)	O(1) $(0, \frac{1}{2}, 0)$	O(5) $(\frac{1}{2}, 0, 0)$	O(4) $(0, 0, z)$	$7 - \delta$
605	0.68	0.04	1.99	6.71
650	0.61	0.02	1.97	6.60
705	0.53	0.05	1.96	6.54
755	0.46	0.07	1.91	6.44
775	0.43	0.11	1.92	6.46
805	0.40	0.12	1.93	6.45
850	0.55		1.88	6.43
900	0.45		1.87	6.32

O(5) $(\frac{1}{2}, 0, 0)$ sites (see Fig. 3 and Table I). The O(4) site occupancy is also reduced with increasing δ , varying from 1.99 for the $T_q = 605^\circ\text{C}$ sample to 1.87 for the $T_q = 900^\circ\text{C}$ sample. These O(4) site vacancies were not observed in the earlier measurements of the equilibrium structures at elevated temperatures.³ No detectable change in occupancies of the O(2) and O(3) sites was observed.

A remarkable feature of the normal-state resistivity of the quenched samples is a continuous evolution from the linear behavior characteristic of unquenched samples to a concave upward behavior that is typical of metals. This trend is illustrated in Fig. 4. The concave upward behavior first becomes evident in the temperature range below 150 K for samples still in the orthorhombic phase with finite but low superconducting transition temperatures. For quench temperatures near 800°C where superconductivity is severely depressed or absent, no evidence of the linear resistivity can be seen. Thus, high- T_c superconductivity and the distinctive linear normal-state resistivity ap-

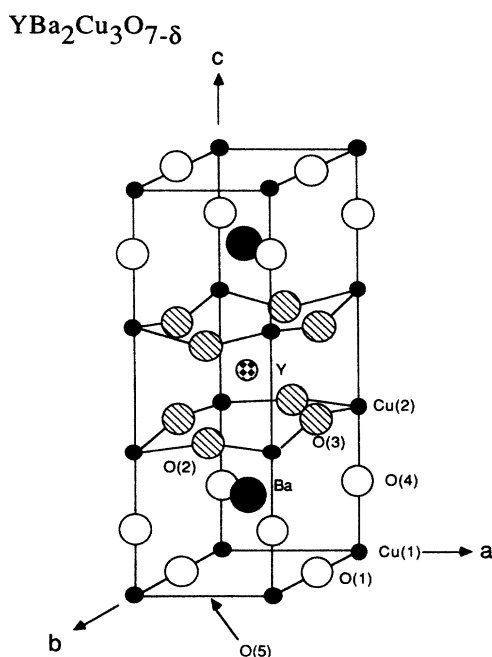


FIG. 3. Structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$.

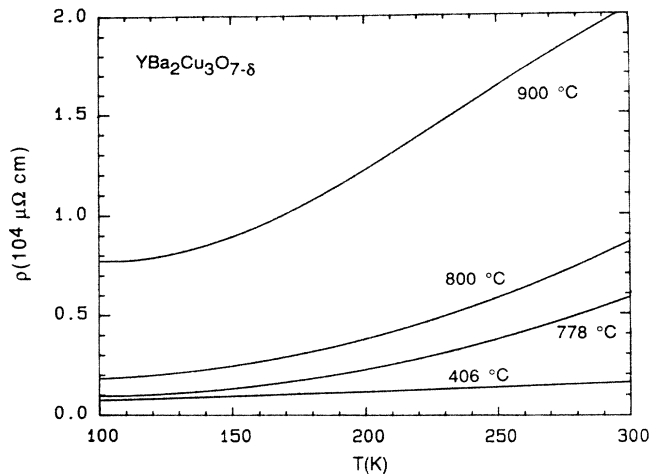


FIG. 4. Resistivity vs temperature from 300 to 100 K for quenched samples showing a gradual transformation in the normal-state resistivity from linear to concave upward behavior.

pear to be closely associated phenomena.

The concave upward trend in the resistivity which begins in the orthorhombic phase signals the beginning of a continuous shift from metallic to semiconducting behavior. The semiconducting behavior is clearly evident in samples quenched from high temperature as illustrated in Fig. 1. The sample quenched from 900°C is typical of most samples in the tetragonal phase in that its resistivity has a positive slope near room temperature and a negative slope at low temperature. Although there is a continuous evolution of metallic to semiconductorlike behavior as the quench temperature is raised, superconductivity is clearly limited to the metallic region. A sample quenched from 800°C, very close to the orthorhombic to tetragonal phase transition, showed metalliclike behavior down to 4 K with no evidence of superconductivity. This sample shows that there is a narrow nonsuperconducting metallic region with a typical concave upward normal resistivity curve separating the superconducting and semiconducting states.

The Meissner effect was measured in a commercial SQUID magnetometer by the following procedure. Samples were crushed and placed in a Al-Si bucket and positioned in a field of 53 Oe at 120 K. The temperature was

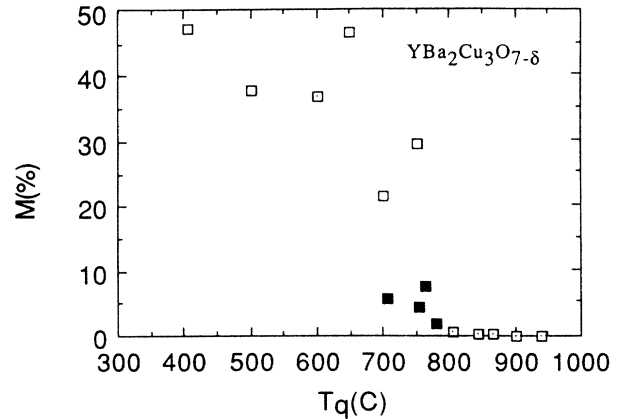


FIG. 5. Meissner effect expressed as a fraction of $-1/4\pi$ vs quench temperature T_q . The solid symbols are samples with broad superconducting transitions or anomalously high normal-state resistivities.

then lowered to 5 K and the magnetization was measured. The Meissner-effect measurements are reported in Fig. 5 as the measured susceptibility normalized by $-1/4\pi$. The Meissner effect is generally large for samples in the orthorhombic phase and drops sharply near the orthorhombic to tetragonal phase transition. This indicates that even the samples with low T_c in the orthorhombic phase are bulk superconductors. The scatter in Fig. 5 can be explained by sample quality. In particular, the superconducting samples with a Meissner effect less than 10% also displayed broad (> 5 K) superconducting transitions or unusually high normal-state resistivities. If only those samples with narrow superconducting transitions are considered, then there is a sharp drop in the Meissner effect near the orthorhombic to tetragonal phase transition where superconductivity vanishes.

The gradual change from the orthorhombic to tetragonal phase is accompanied by a dramatic shift in the position of the bridging O(4) oxygen atom toward the one-dimensional chain and away from the corrugated two-dimensional Cu-O plane. Some reduction in the corrugation in the Cu-O plane occurs since the vertical position $z(\text{Cu}(2))$ increases while $z(\text{O}(2))$ and $z(\text{O}(3))$ are rela-

TABLE II. Atomic positions for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ determined by Rietveld refinement of neutron powder diffraction data.

T_q (°C)	Cu(2) z	O(2) z	O(3) z	O(4) z	Ba z	a (Å)	b (Å)	c (Å)
605	0.3573	0.3776	0.3787	0.1575	0.1872	3.8352	3.8901	11.6847
650	0.3573	0.3784	0.3784	0.1565	0.1877	3.8313	3.8845	11.7199
705	0.3586	0.3783	0.3783	0.1561	0.1893	3.8437	3.8845	11.7055
755	0.3592	0.3789	0.3781	0.1555	0.1903	3.8518	3.8773	11.7174
775	0.3597	0.3810	0.3766	0.1553	0.1907	3.8573	3.8743	11.7094
805	0.3596	0.3805	0.3767	0.1549	0.1909	3.8585	3.8741	11.7292
850	0.3602	0.3786	...	0.1546	0.1916	3.8668	...	11.7310
900	0.3605	0.3785	...	0.1543	0.1919	3.8676	...	11.7411

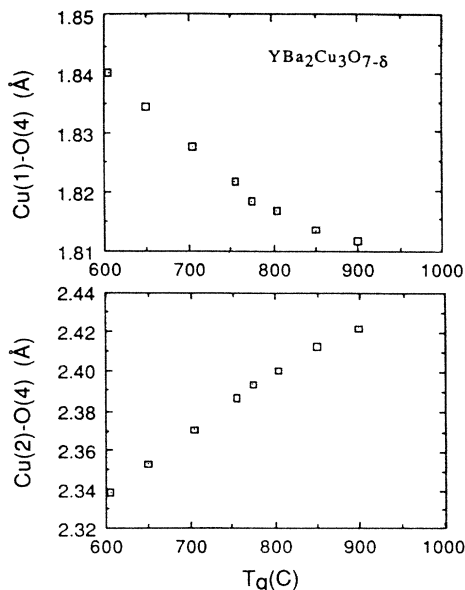


FIG. 6. Cu(1)–O(4) and Cu(2)–O(4) atomic distance vs quench temperature T_q . There is a systematic change in bond length even in the tetragonal phase.

tively unchanged or show some reduction. The Ba atom is displaced toward the Cu–O plane (see Table II). In unquenched samples, the Cu(1)–O(4) bond length is 1.85 Å, smaller than any other Cu–O bond in the structure. In the quenched samples, this bond gets systematically shorter as shown in Fig. 6. Qualitatively, this bond shortening may be understood as a compensation for the reduced coordination of Cu(1) as the occupancy of the O(1) site diminishes. This reduction of the Cu(1)–O(4) bond length is accompanied by an expansion of the Cu(1)–Cu(2) distance. The effect of the shorter Cu(1)–O(4) bond length and the longer Cu(1)–Cu(2) distance is to

reduce the coupling of the one-dimensional chains to the two-dimensional planes. This reduced coupling could have a large effect on the electronic structure^{13–15} of the compound and might be involved in the reduction of T_c . There is significant movement of the O(4) atoms at all quench temperatures in both the orthorhombic and tetragonal phases. Thus bonding of the O(4) atom could play an essential role in determining the systematic behavior of the superconducting transition temperatures and the normal-state resistivities as a function of quench temperature.

Bonding in the structure involving the O(4) atom implies an electronic connection between the chains and the planes. This connection is manifested in the observed evolution of the normal-state resistivity as the oxygen content is reduced. If the planes provide the dominant conduction path and it is independent of the chains, then one cannot readily explain the gradual appearance of semiconducting behavior in the tetragonal phase as oxygen vacancies appear in the chains. Alternatively, the metallic behavior near the orthorhombic to tetragonal phase transition where the chains are severely disrupted suggests that the planes do contribute significantly to the conduction process. Therefore the chains and planes must be viewed as a single interacting electronic system whose properties vary continuously with oxygen content. The semiconducting behavior of the tetragonal phase is contrary to predictions of metallic behavior by electronic band-structure calculations.^{13,16,17} This discrepancy suggests that correlation effects leading to localization, charge density waves, or spin density waves are important.

This work was supported by the U.S. Department of Energy, Basic Energy Science-Materials Science under Contract No. W-31-109-ENG-38. The work of one of us (A.U.) was partially supported by the Natural Sciences and Engineering Research Council Grant No. PGS3 (Canada).

*Also at Department of Physics, Purdue University, W. Lafayette, IN 47907.

†Also at Department of Physics, University of Alberta, Edmonton, Canada.

‡Permanent address: Tata Institute of Fundamental Research, Bombay, India.

¹J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, A. P. Paulikas, *Phys. Rev. B* **36**, 5731 (1987).

²A. M. Kini, U. Geiser, H.-C. I. Kao, D. Carlson, H. H. Wang, M. R. Monahan, and J. M. Williams, *Inorg. Chem.* **26**, 1834 (1987).

³J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, M. S. Kleefisch, *Phys. Rev. B* **36**, 3608 (1987).

⁴K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, K. Fueki, *Jpn. J. Appl. Phys. Lett.* **26**, L1228 (1987).

⁵J. van den Berg, C. J. van der Beek, P. H. Kes, G. J. Nieuwenhuys, J. A. Mydosh, H. W. Zandbergen, F. P. F. van Berkel, R. Steens, and D. J. W. Ijdo, *Neurophysiol. Lett.* **4**, 737 (1987).

⁶A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Shneemeyer, J. V. Waszczak, *Mater. Res. Bull.* **22**, 1007 (1987).

⁷P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, *Mater. Res. Bull.* **22**, 995 (1987).

⁸C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, J. L. Hodeau, and M. Marezio, *Phys. Rev. B* **36**, 7118 (1987).

⁹R. Beyers, G. Lim, E. M. Engler, V. Y. Lee, M. L. Ramirez, R. J. Savoy, R. D. Jacowitz, T. M. Shaw, S. La Placa, R. Boehme, C. C. Tsuei, Sung I. Park, M. W. Shafer, and W. J. Gallagher, *Appl. Phys. Lett.* **51**, 614 (1987).

¹⁰E. M. Engler, V. Y. Lee, A. I. Nazzari, R. B. Beyers, G. Lim, P. M. Grant, S. S. P. Parkin, M. L. Ramirez, J. E. Vazquez, and R. J. Savoy, *J. Am. Chem. Soc.* **109**, 2848 (1987).

¹¹Z. Fisk, J. D. Thomson, E. Zirngiebl, J. L. Smith, and S. W. Cheong, *Solid State Commun.* **62**, 743 (1987).

¹²B. W. Veal, W. K. Kwok, A. Umezawa, G. W. Crabtree, J. D. Jorgensen, J. W. Downey, L. J. Nowicki, A. W. Mitchell, A. P. Paulikas, and C. H. Sowers, *Appl. Phys. Lett.* **51**, 279 (1987).

¹³M. H. Whangbo, M. Evain, M. A. Beno, U. Geiser, and J. M. Williams, *Inorg. Chem.* **26**, 2566 (1987).

- ¹⁴S. Massidda, J. Yu, A. J. Freeman, and D. D. Koelling, *Phys. Lett.* **122**, 198 (1987).
- ¹⁵J. Yu, S. Massidda, A. J. Freeman, and D. D. Koelling, *Phys. Lett.* **122**, 203 (1987).
- ¹⁶J. Yu, A. J. Freeman, S. Massidda, in *Proceedings of the In-*

- ternational Workshop on Novel Mechanisms of Superconductivity, June 22–26, 1987, Berkeley, California*, edited by S. A. Wolf and V. L. Kresin (Plenum, New York, 1987).
- ¹⁷F. Herman, R. V. Kasowski, and W. Y. Hsu, *Phys. Rev. B* **36**, 6904 (1987).