RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 10 1 OCTOBER 1987

Structural and superconducting properties of orthorhombic and tetragonal $YBa_2Cu_3O_{7-x}$: The effect of oxygen stoichiometry and ordering on superconductivity

J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 9 July 1987)

The structural and superconducting properties of orthorhombic and tetragonal $YBa_2Cu_3O_{7-x}$ have been determined for a wide range of stoichiometries ($0.3 < x < 0.7$). In the orthorhombic phase, T_c decreases smoothly as x increases and reaches zero at the orthorhombic-to-tetragonal transition. Tetragonal $YBa_2Cu_3O_{7-x}$ is not superconducting at any stoichiometry. This systematic depression of T_c is correlated with the decrease in the oxygen content which alters the electronic structure of the Cu-O networks.

INTRODUCTION

In several recent papers it has been shown that $YBa_2Cu_3O_{7-x}$ exists in two forms which differ according to the overall oxygen stoichiometry and the ordering of oxygen vacancies. The orthorhombic phase [Fig. 1(a)], was originally synthesized for compositions in the range $0 < x < 0.2$, for which there are chains of nearly square planar CuO_{4-x} units sharing corners along the **b** direction.[1-6] It has been speculated that this one-dimensional Cu-O sublattice is responsible for the 92-K superconductivity observed in these compounds. The first direct evidence for the tetragonal phase [Fig. 1(b)] came from high-temperature x-ray powder diffraction data and from x-ray diffraction studies of samples quenched from high temperature.[7-12] Initial reports were unclear as to whether superconductivity was dramatically suppressed or completely absent in tetragonal $YBa_2Cu_3O_{7-x}$. Nevertheless, it was proposed that the transition from orthorhombic to tetragonal symmetry and the dramatic depression of T_c were the result of the destruction of the one-dimensional Cu-O chains.

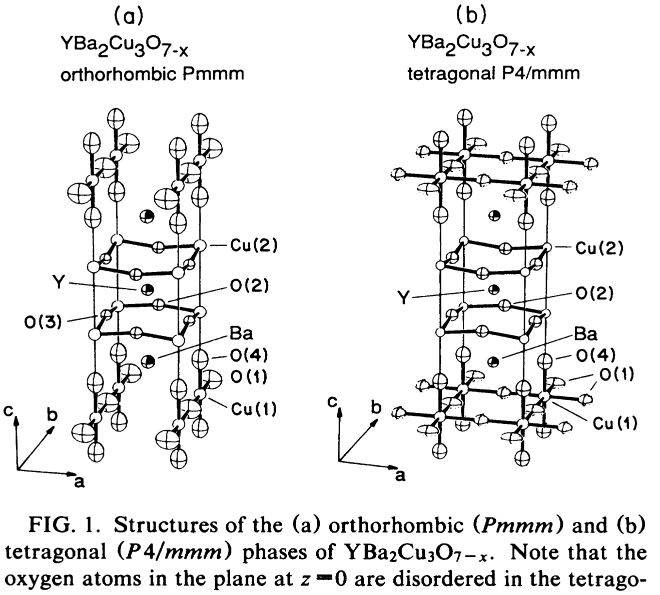

FIG. 1. Structures of the (a) orthorhombic (*Pmmm*) and (b) tetragonal (*P*4/*mmm*) phases of $YBa_2Cu_3O_{7-x}$. Note that the oxygen atoms in the plane at $z = 0$ are disordered in the tetragonal phase.

Initial neutron diffraction structural studies of the tetragonal phase were done on samples with compositions near $YBa_2Cu_3O_6$ in which the chain oxygen atoms [O(1) in Fig. 1(b)] had been completely removed.[13-15] In most cases, these samples were synthesized by cooling in an inert atmosphere (e.g., nitrogen, argon, or helium). A more recent *in situ* neutron powder diffraction study as a function of temperature and oxygen partial pressure has shown that the oxygen stoichiometry is a continuous function of temperature with the orthorhombic-to-tetragonal transition occurring at a composition near $YBa_2Cu_3O_{6.5}$.[16] Extensive thermogravimetric studies and chemical analysis have also shown that the oxygen stoichiometry is a continuous function of temperature and oxygen partial pressure.[17] These *in situ* results made it clear that both the orthorhombic and tetragonal phases of $YBa_2Cu_3O_{7-x}$ can be formed over a range of compositions: $0 < x < 0.5$ for orthorhombic $YBa_2Cu_3O_{7-x}$ and $0.5 < x < 1.0$ for tetragonal $YBa_2Cu_3O_{7-x}$. With increasing x, the one-dimensional chains in the orthorhombic phase are disrupted by an increasing number of oxygen vacancies at the O(1) site [at $(0,\frac{1}{2},0)$] accompanied by an increasing occupancy of the originally vacant site at $(\frac{1}{2},0,0)$. At the transition, the occupancy of the tetragonally equivalent oxygen sites at $(0,\frac{1}{2},0)$ and $(\frac{1}{2},0,0)$ is equal to 0.25, giving rise to a highly disordered two-dimensional Cu-O network in the basal plane.

This paper reports initial results of a detailed study of the preparation, resistivity, oxygen vacancy distribution (as determined by neutron powder diffraction), and superconductivity of a series of orthorhombic and tetragonal samples of $YBa_2Cu_3O_{7-x}$ produced by quenching into liquid nitrogen. Samples cover the composition range $x = 0.3–0.7$. The principal findings are (1) the superconducting transition temperature decreases smoothly in the orthorhombic phase with increasing quenching temperature or, equivalently, decreasing oxygen concentration; (2) the superconducting transition temperature goes to zero at or near the tetragonal-to-orthorhombic phase transition, with the tetragonal phase being nonsuperconducting; and (3) the principal structural differences among the quenched samples are the decreasing occupancy of the

(0,$\frac{1}{2}$,0) site in the Cu-O chains, and, near the phase transition, increasing occupancy of the ($\frac{1}{2}$,0,0) site. These sites are symmetry equivalent in the tetragonal phase. There is no significant change in the Cu-O atomic arrangement or occupancy of the two-dimensional dimpled planes.

EXPERIMENTAL PROCEDURE

Large samples of 40–50 g of $YBa_2Cu_3O_{7-x}$ were prepared from Y_2O_3, $BaCO_3$, and CuO powders. The powders were mixed and ground, pressed into pellets, fired at 940 °C for 24 h in flowing O_2, cooled in air, reground with mortar and pestle or vibrating ball mill, screened (200 mesh), and mixed and fired a second time at 940 °C for 24 h. The temperature was then reduced to 680 °C and held for an additional 24 h and then cooled to ambient at a rate of 50 °C/h. This procedure produced samples with resistively measured superconducting transitions with a midpoint of 93 K and a width of 2 K from onset to zero resistance.

For the quenching experiments, 8–10 g of small pieces of these samples were placed in a small platinum cup and suspended in a vertical tube furnace on a 5-mil 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. For resistivity and weight-loss measurements, each quenched sample also contained a small sintered bar of typical dimensions 1×2×10 mm.[3] These bars were weighed before and after each quenching experiment as a check of the oxygen stoichiometry. ac resistivity measurements to determine the superconducting transition temperatures were performed by a four-point technique using 2.5-mA current at 100 Hz.

Neutron powder diffraction measurements were performed to determine the structures, overall oxygen stoichiometry, degree of oxygen vacancy ordering, and homogeneity for samples quenched from a number of temperatures extending from 605 to 900 °C. In each case the data were refined by the Rietveld technique.[18] The oxygen stoichiometries obtained from neutron diffraction were compared with those obtained from weight-loss measurements and found to agree within experimental uncertainties.

RESULTS AND DISCUSSION

The Rietveld refinements of the neutron diffraction data show that quenched samples exhibit a transition from the orthorhombic to the tetragonal structure similar to that observed *in situ* at high temperature.[16] In the quenched samples, the transition appears at a quench temperature of about 800 °C, 50–100 °C higher than the transition temperature observed for *in situ* samples.[19] In addition, the quenched samples show a small number of oxygen vacancies on the O(4) sites which do not appear in the *in situ* samples. The shift in the transition temperature between the two preparation techniques may be due to the additional O(4) vacancies. Clearly, the preparation technique plays a role in determining the exact oxygen stoichiometry, but the fundamental characteristics of samples produced by the two techniques are nearly identical, as shown below.

The Rietveld refinements on quenched samples give a lattice parameter variation which is qualitatively the same as that of the *in situ* samples as shown in Fig. 2. The continuous disordering of the chain oxygen atoms as the transition is approached is shown in Fig. 3. This behavior is essentially identical to that observed at high temperature[16] except that the transition is shifted to about 800 °C. This temperature corresponds to an overall oxygen stoichiometry (refined for the sample quenched from 805 °C) of 6.44(4). The combined occupancy of the ($\frac{1}{2}$,0,0) and (0,$\frac{1}{2}$,0) sites is 0.51(4), while the occupancy of the O(4) site is 1.93(2). This small oxygen vacancy concentration at the O(4) site, which has not been reported for previous refinements of tetragonal $YBa_2Cu_3O_6$, is consistently observed in the quenched samples. The refined occupancies for O(4) vary monotonically from 1.99(3) for the sample quenched from 605 °C to 1.87(2) for the sample quenched from 900 °C.

The resistively measured superconducting transition temperatures T_c for all of the quenched samples studied by neutron diffraction, plus some additional samples, are plotted as a function of quench temperature in Fig. 4. It is clear that superconductivity does not exist in the tetragonal phase at any oxygen stoichiometry. Within the precision of these measurements, in the orthorhombic phase T_c decreases smoothly as the structural transition is approached and reaches zero at or near the orthorhombic-to-tetragonal phase transition.

The results presented above clarify the superconducting behavior of orthorhombic and tetragonal $YBa_2Cu_3O_{7-x}$. There is a systematic decrease in T_c in the orthorhombic phase as the oxygen stoichiometry is lowered, and T_c is zero in the tetragonal phase. The phase transition occurs when the occupancy of the O(1) site is equal to 0.5, and

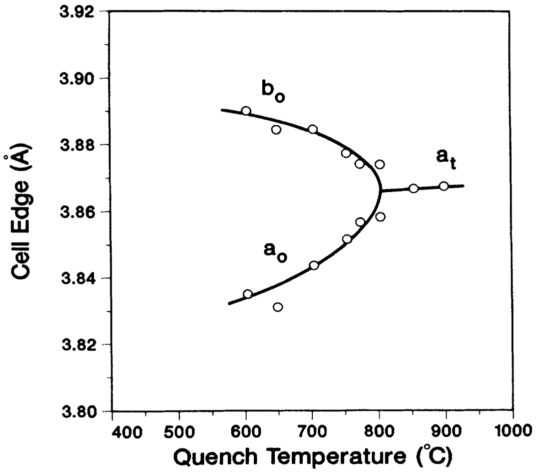

FIG. 2. Orthorhombic and tetragonal lattice parameters as a function of quench temperature determined from Rietveld refinement of neutron powder diffraction data.

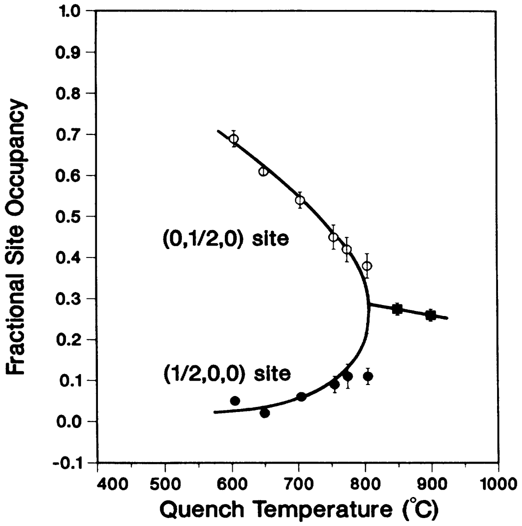

FIG. 3. Fractional site occupancies of the $(0,\frac{1}{2},0)$ and $(\frac{1}{2},0,0)$ sites in $YBa_2Cu_3O_{7-x}$ vs quench temperature. Note that because the two sites become symmetry equivalent in the tetragonal phase (above 800 °C), the fractional occupancy must be doubled to yield the number of oxygen atoms per unit cell.

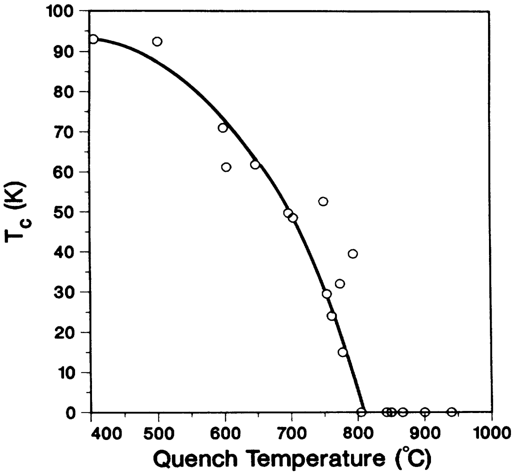

FIG. 4. Resistively measured superconducting transition temperatures T_c vs quench temperature for $YBa_2Cu_3O_{7-x}$ samples quenched into liquid nitrogen.

the total oxygen stoichiometry is slightly below 6.5. There are a small number of vacancies on the O(4) site in quenched samples that do not appear in the *in situ* samples.

The reduction in T_c correlates with the observed reduction in the oxygen stoichiometry and the associated disordering of the Cu-O chains. In an ionic picture, the oxygen stoichiometry can be related to the Cu valence by a simple charge balance argument. Superconductivity disappears near the oxygen stoichiometry ($YBa_2Cu_3O_{6.5}$) corresponding to an average valence of 2+ for the copper ions. In a metallic picture the oxygen stoichiometry affects the electronic behavior by shifting the Fermi level and by altering the underlying band structure. In a simple rigid-band picture, removal of oxygen increases the number of conduction electrons and raises the Fermi level. (This increase in the Fermi level is equivalent to a decrease in the average Cu valence in an ionic picture.) If the density of states at the new Fermi level were lowered, the superconducting transition temperature would be expected to fall. Band-structure calculations[20] of $YBa_2Cu_3O_{7-x}$ indicate that the density of states falls approximately a factor of 2 as x changes from 0 to 0.5, possibly enough to cause a substantial reduction of T_c. In addition to a shift of the Fermi level, oxygen vacancies will cause a change in the band structure itself, since the vacancies remove an important overlap in the one-dimensional metallic Cu-O chains. In general, one expects the one-dimensional band associated with the chains to narrow, leading to a higher density of states. Both a Fermi-level shift and changes in the band structure due to oxygen vacancies play a role in determining the final density of states. It should also be noted that the mechanisms governing superconductivity in the high-T_c oxides are not understood so that effects other than variations in the density of states may be important. Nonetheless, it is likely that the reduction in T_c and the structural phase transition itself are driven by the electronic energy of the system.

It is a remarkable feature of the quenched samples that the geometry of the two-dimensional Cu-O planes [Cu(2), O(2), O(3) in Fig. 1] is relatively unaffected as the quench temperature is varied. It is therefore tempting to conclude that only the chains are involved in the superconductivity. However, there are important electronic interactions between the chains and planes mediated by the bridging oxygen on the O(4) site. Thus, changes in electronic structure caused by the oxygen vacancies in the chains may affect the electronic behavior of the planes in a way that is detrimental to superconductivity. Therefore, the role of the two-dimensional planes in superconductivity cannot be directly addressed with these results. In contrast, the role of the chains is clear: Superconductivity is weakened as the one-dimensional chains are disrupted, and the transition temperature goes to zero when the $(0,\frac{1}{2},0)$ and $(\frac{1}{2},0,0)$ sites become symmetry equivalent and reach an average occupancy of 25%. The presence of the chains is essential for achieving a high transition temperature.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy, Basic Energy Sciences–Materials Sciences, under Contract No. W-31-109-ENG-38. Useful discussions with D. G. Hinks, I. K. Schuller, M. A. Beno, C. U. Segre, and L. Soderholm are acknowledged. We are also grateful to numerous colleagues in other laboratories for sending copies of their unpublished results.

---

[1] M. A. Beno, L. Soderholm, D. W. Capone II, D. G. Hinks, J. D. Jorgensen, J. D. Grace, I. K. Schuller, C. U. Segre, and K. Zhang, Appl. Phys. Lett. **51**, 6 (1987).

[2] J. E. Greedan, A. O'Reilly, and C. V. Stager, Phys. Rev. B **35**, 8770 (1987).

[3] J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournier, Europhys. Lett. **3**, 1301 (1987).

[4] W. I. F. David, W. T. A. Harrison, J. M. F. Gunn, O. Moze, A. K. Soper, P. Day, J. D. Jorgensen, D. G. Hinks, M. A. Beno, L. Soderholm, D. W. Capone II, I. K. Schuller, C. U. Segre, K. Zhang, and J. D. Grace, Nature **327**, 310 (1987).

[5] F. Beech, S. Maraglia, A. Santoro, and R. S. Roth, Phys. Rev. B **35**, 8778 (1987).

[6] S. Katano, S. Funahashi, T. Hatano, A. Matsushita, K. Nakamura, T. Matsumoto, and K. Ogawa, Jpn. J. Appl. Phys. **26**, L1046 (1987).

[7] I. K. Schuller, D. G. Hinks, M. A. Beno, D. W. Capone II, L. Soderholm, J.-P. Locquet, Y. Bruynseraede, C. U. Segre, and K. Zhang, Solid State Commun. **63**, 385 (1987).

[8] A. 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).

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

[10] P. Strobel, J. J. Capponi, C. Chaillout, M. Marezio, and J. L. Tholence, Nature **327**, 306 (1987).

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

[12] M. O. Eatough, D. S. Ginley, B. Morosin, and E. L. Venturini, Appl. Phys. Lett. **51**, 367 (1987).

[13] A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Schneemeyer, and J. V. Waszczak, Mater. Res. Bull. **22**, 1007 (1987).

[14] S. Katano, S. Funahashi, T. Hatano, A. Matsushita, K. Nakamura, T. Matsumoto, and K. Ogawa, Jpn. J. Appl. Phys. **26**, L1049 (1987).

[15] A. W. Hewat, J. J. Capponi, C. Chaillout, M. Marezio, and E. A. Hewat (unpublished).

[16] J. 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, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[17] K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. **26**, L1228 (1987).

[18] R. B. VonDreele, J. D. Jorgensen, and C. G. Windsor, J. Appl. Crystallogr. **15**, 581 (1982).

[19] J. 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 (unpublished).

[20] S. Massidda, J. J. Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987).