RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 1 1 JANUARY 1988

X-ray and neutron-diffraction study of $La_1Ba_2Cu_3O_{9-\delta}$: Influence of the Cu—O structure on T_c

Yi Song, J. P. Golben, S. Chittipeddi, S. I. Lee,* R. D. McMichael,
X. D. Chen, J. R. Gaines,† and D. L. Cox
Department of Physics, Ohio State University, Columbus, Ohio 43210

A. J. Epstein
Department of Physics and Department of Chemistry, Ohio State University,
Columbus, Ohio 43210

(Received 2 September 1987)

X-ray and neutron diffraction studies on $La_1Ba_2Cu_3O_{9-\delta}$ demonstrate that the structure of this compound closely resembles that of $Y_1Ba_2Cu_3O_{9-\delta}$. The importance of oxygen ordering on the outer Cu planes for high-T_c superconductivity is stressed. Broadening in the diffraction peaks as T_c is decreased is indicative of greater disorder in the La or Ba sites and/or the oxygen configuration. Evidence for the existence of octahedral Cu—O configurations between unit cells, possibly associated with a Ba-doped $La_{3-x}Ba_{3+x}Cu_6O_{14+y}$ ($x=1$) phase, is minimal.

La-Ba-Cu-O is a unique high-temperature superconductor system where the empirical relationship between structure and superconductivity can be studied. The $La_{1.85}Ba_{0.15}CuO_4$ compound was found to have a zero resistance T_c near 20 K and a room-temperature structure similar to K_2NiF_4.[1,2] Recently, superconductivity with zero resistance T_c's as high as 75 K and onsets near 90 K have been reported in the $La_1Ba_2Cu_3O_{9-\delta}$ or 1:2:3 phase.[3-5] In contrast to the orthorhombic superconductor $Y_1Ba_2Cu_3O_{9-\delta}$, $La_1Ba_2Cu_3O_{9-\delta}$ appears tetragonal to within experimental error, especially in samples where $T_c < 60$ K.[5] It has been suggested that this La-based material has a different oxygen configuration (associated with the $La_{3-x}Ba_{3+x}Cu_6O_{14+y}$ or 3:3:6 phase) with none of the Cu—O chains present as in $Y_1Ba_2Cu_3O_{9-\delta}$.[6,7] This idea has received much attention[8] of late since it would define a new high-T_c superconducting phase in addition to the K_2NiF_4 and 1:2:3 phases.

We have performed x-ray and neutron-diffraction studies on two samples of composition $La_1Ba_2Cu_3O_{9-\delta}$ with $T_c=26$ and 43 K. Our results demonstrate that the 3:3:6 phase, if present, exists in very small amounts. Both samples are tetragonal to within experimental error. As T_c is raised the diffraction peaks sharpen implying that the disorder might be due to random placement of the La or Ba ions and/or oxygen vacancies. In light of recent data for the related $Y_1Ba_2Cu_3O_{9-\delta}$ compound,[9] the results suggest that as the oxygen vacancies tend toward ordering in lines, T_c increases.

The samples used in this study were prepared by the solid-state reaction method. Specific details for the preparation and characterization of these compounds are provided elsewhere.[10] The main variable in the present study was the sintering temperature which was 980 °C ($T_c=26$ K) and 1000 °C ($T_c=43$ K), respectively, for the two groups of samples. Both sets of samples were then slowly cooled to 500 °C and annealed in oxygen for 12 h. The T_c's for these samples were stable for a period of at least several weeks. Resistance measurements were made using the four-probe ac method.

The x-ray diffraction measurements were carried out on a Scintag diffractometer with the characteristic copper $K\alpha$ wavelength of 1.5409 Å. Neutron-diffraction measurements were conducted on the H-4S spectrometer at the Brookhaven High-Flux Beam Reactor. A PG(004) analyzer with a graphite filter was used with a neutron wavelength of 2.370 Å. Samples of 10 g were studied at room temperature in both sintered pellet and powder form.

Previous researchers isolated the 3:3:6 phase, i.e., $La_{3-x}Ba_{3+x}Cu_6O_{14+y}$, which demonstrated metallic to insulating behavior in the range $0 \leq y \leq 1$.[11,12] In our study, $x=1$. Barium doped versions of this compound, such that $0 < x \leq 1$, have subsequently been reported to be superconducting.[6,7] Since the Cu—O configuration between the unit cells in this phase is proposed to be octahedral,[11,12] this has led to the suggestion that the Cu—O chains are not important for 90-K superconductivity.[6,7] The observance of tetragonal spectra is correlated to the symmetry of the octahedral oxygen configuration. In contrast, the tetragonal phase in the $Y_1Ba_2Cu_3O_{9-\delta}$ compound is actually nonsuperconducting.[9] Another study of the K_2NiF_4 phase of $La_{1.85}Ba_{0.15}CuO_4$ has shown that this compound undergoes a monoclinic phase transition near 150 K, well above T_c.[13] The majority of rare-earth substituted compounds $M_1Ba_2Cu_3O_{9-\delta}$ ($M=$Nd, Sm, Gd, Ho, Er, Lu, and Eu) have been shown to have slight orthorhombic distortions,[3,4,14] due to the linear placement of oxygens on the outer Cu planes (Refs. 15-17). $La_1Ba_2Cu_3O_{9-\delta}$ has also demonstrated orthorhombic shouldering in the x-ray data of samples with T_c's > 60 K.[5] Thus, a body of empirical evidence suggests that high-T_c superconductivity is favored in structures with lower than tetragonal symmetry.

X-ray diffraction data of the samples gave the lattice constants as $a=3.9085 \pm 0.0072$ Å, $b=3.9109 \pm 0.0110$ Å, and $c=11.7306 \pm 0.0281$ Å for the sample with

$T_c = 26$ K, and $a = 3.8995 \pm 0.0075$ Å, $b = 3.8977 \pm 0.0114$ Å, and $c = 11.7040 \pm 0.0293$ Å for the sample with $T_c = 43$ K. Though the samples appear tetragonal, a distortion of up to 0.0207 Å is within the limits of error. It is noted that disorder in the La^{3+} and Ba^{2+} sites should have little effect on the x-ray spectra since these ions are isoelectronic. However, disorder of the oxygen sites results in a large distribution of lattice distortions within the sample. This would be observed in the x-ray spectrum as a broadening of the spectral peaks. We observe this broadening to occur as T_c is reduced from 43 to 26 K. Another $La_1Ba_2Cu_3O_{9-\delta}$ sample which demonstrated metallic behavior down to a temperature of 5 K without going superconducting, and which appeared single-phased in the x-ray spectrum, demonstrated even more broadening in the peaks.

For $x = 1$, the metallic ion sublattices of the 1:2:3 and 3:3:6 phases are essentially identical, i.e., there is a stacked ordering of the Ba-La-Ba ions along the c-axis of the unit cell. The relative oxygen stoichiometry is also similar in the two phases. Hence, for $x = 1$, the 3:3:6 and 1:2:3 phases differ solely in the location and placement of oxygen deficiencies in the unit cell. Early studies on the 3:3:6 compound concluded that there were octahedral Cu—O coordinations between the unit cells along the c-axis (Fig. 1). The oxygen vacancy located on the outer Cu planes of the 1:2:3 structure is instead located on the Ba layer of this 3:3:6 structure. Consequently, in the 3:3:6 structure the unit cell must be defined with the lattice parameter $a_{336} = \sqrt{2} a_{123}$, where a_{123} is the (tetragonal) a lattice parameter for the 1:2:3 structure. In relating superconductivity to the structure of the 3:3:6 compound, it is noted that both of the mechanisms usually cited as important for superconductivity, i.e., the inner Cu—O planes and/or the outer Cu—O chains, are disrupted in this structure. The chains are missing due to the outer octahedral coordination and the planes are disrupted due to the alternate replacement of square pyramid and square planar coordinations across the a-b plane. It is also not clear that the 3:3:6 Cu—O coordination would remain intact when enough Ba^{2+} was substituted for La^{3+} to form the 2:4:6 stoichiometry since this doping would then change the valence structure.

We have looked for possible differences in the two configurations by the use of x-ray diffraction. However, the larger ions overshadow the specific oxygen contribution, negating any major observable difference in the x-ray spectra. We note that the intensity of the $(100)_{336}$ peak,[18] which has been singled out as a possible difference between the two structures as observed by x rays,[7] is within the noise level and is thus too weak to conclusively rule out either configuration.

For neutron diffraction the contribution from the oxygen atoms is comparable to other atoms in the unit cell. However, the different placements of the oxygen deficiencies between the 3:3:6 structure and the 1:2:3 structure involves only 2 atoms from the 1:2:3 unit cell and, therefore, the observed differences in the spectrum are subtle. Using the assumed 3:3:6 oxygen configuration, we calculated a finite intensity for the $(100)_{336}$ line at 24.8° and the $(101)_{336}$ line at 27.4°, which have no intensity under the assumption of the 1:2:3 configuration. In contrast, the $(201)_{336}$ line at 52.2° disappears in the 3:3:6 configuration, while it has significant intensity in the calculated 1:2:3 configuration, where it is indexed as $(111)_{123}$.

The neutron spectrum for the $T_c = 43$ K sample is presented in Fig. 2. Close inspection of the neutron data reveals weak peaks near $2\theta = 25°$ in both samples. However, the relative magnitude of these peaks is much reduced in the $T_c = 43$ K sample as compared to the $T_c = 26$ K sample. By choosing the $(111)_{123}$ line as the signature of the 1:2:3 configuration and the $(100)_{336}$ line as the signature of the 3:3:6 configuration, a rough estimate of the

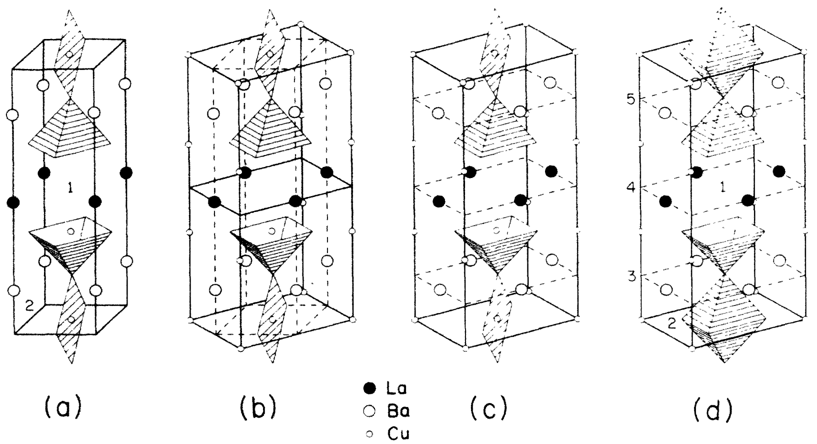

FIG. 1. The comparison of the 1:2:3 and 3:3:6 oxygen configurations. In all the representations oxygen is indicated at the corners of the square planar, square pyramid, and octahedral units. (a) In the 1:2:3 cell, an oxygen is missing from sites 1 and 2. This latter site represents four equivalent sites of $\frac{1}{4}$ oxygen each in the unit cell. (b) The 3:3:6 cell with twice the volume of the 1:2:3 cell is heavily outlined. The dashed line retains the 1:2:3 form. (c) The defined 3:3:6 cell enclosing the 1:2:3 oxygen configuration. (d) The final 3:3:6 configuration. Oxygens are missing from sites 1, 3, 4, and 5; these latter three sites represent four equivalent sites of $\frac{1}{4}$ oxygen each in the unit cell. Note that site 2 is now occupied, increasing the symmetry of the cell and negating the orthorhombic distortion.

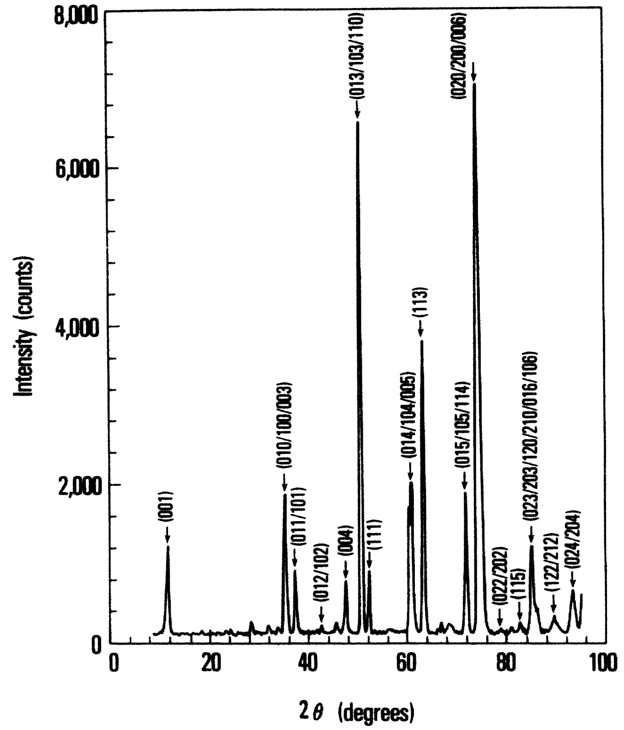

FIG. 2. The neutron spectrum for the $T_c = 43$ K sample at room temperature. All indexing pertains to the 1:2:3 structure.

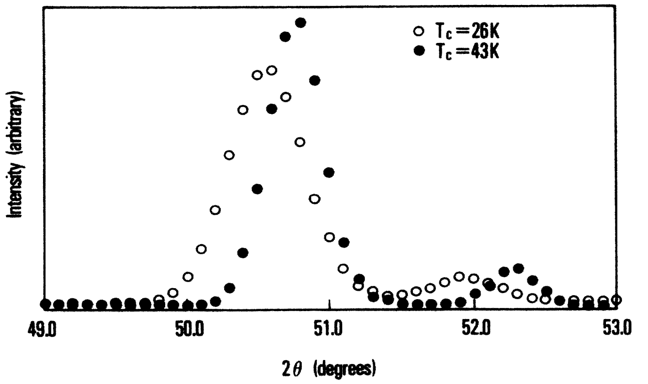

FIG. 3. Overlay of the neutron spectrum for the $T_c = 26$ K sample (white dots) and $T_c = 43$ K sample (black dots). Several important features are displayed. The displacement of the left peak [indexed as $(013/103/110)_{123}$] and the right peak [indexed as $(111)_{123}$] as T_c increases is indicative of the change in the lattice parameters. Broadening in the peaks as T_c decreases demonstrates an increase in oxygen and/or La-Ba disorder. The $(111)_{123}$ peak is a signature of the 1:2:3 configuration, and hence its intensity indicates the amount of this configuration present in the sample. The spectrum calculation based on Er-Rakho *et al.*'s 3:3:6 configuration (with a further assumption of a 2:4:6 stoichiometry), predicts zero intensity for this line.

percent amount of each configuration present was obtained. The standard for both configurations was the $(013/103/110)_{123}$ line which is indexed as $(113/200)_{336}$ in the 3:3:6 structure (Fig. 3). The observed $(111)_{123}$ to $(013/103/110)_{123}$ ratio was 0.112 and 0.127 for the $T_c = 26$ K and $T_c = 43$ K samples, respectively. When compared with the calculated ratio of 0.135 for the $La_1Ba_2Cu_3O_{6.8}$ compound, this resulted in estimates of 83.0% and 94.1%, respectively, for the 1:2:3 configuration in these samples. The observed $(100)_{336}$ to $(113/200)_{336}$ ratio was 6.8×10^{-3} and 1.9×10^{-3} for the $T_c = 26$ K and $T_c = 43$ K samples, respectively. Compared to the calculated ratio of 4.6×10^{-2}, derived from the unit-cell information given by Er-Rakho, Michel, Provost, and Raveau,[11] this resulted in estimates of 15% and 4.1%, respectively, for the 3:3:6 configuration in these samples.

Similar to the x-ray spectra, the major peaks in the neutron spectra were broader in the $T_c = 26$ K sample as opposed to the $T_c = 43$ K sample. However, in the case of the neutron scattering, the broadening of the peaks could be attributed to either oxygen disorder and/or La–Ba disorder. Recent studies by Jorgensen and co-workers[9,17] on oxygen ordering and the orthorhombic-tetragonal phase transition in $Y_1Ba_2Cu_3O_{9-\delta}$ conclude (i) that T_c can be reduced in versions of this compound simply due to the disordering of oxygen atoms and/or the elimination of Cu^{3+} ions, and (ii) that the existence of one-dimensional Cu–O chains is necessary to achieve a transition temperature near 90 K. The observed disorder in the $La_1Ba_2Cu_3O_{9-\delta}$ samples is consistent with both of the above conclusions.

The lattice constants obtained from the neutron data of $a = 3.9148 \pm 0.0038$ Å and $c = 11.7389 \pm 0.0097$ Å for the $T_c = 26$ K sample, and $a = 3.9045 \pm 0.0040$ Å and $c = 11.7316 \pm 0.0095$ Å for the $T_c = 43$ K sample compare well with the parameters obtained from x-ray diffraction data given earlier. Though our x-ray and neutron-diffraction studies are best interpreted in terms of a tetragonal unit cell, the possibility that a small orthorhombic distortion exists. This point is also made in light of the work by Jorgenson *et al.*, which demonstrated that the tetragonal phase of the related $Y_1Ba_2Cu_3O_{9-\delta}$ compound was not superconducting. The comparison of one graph showing T_c as related to the quenching temperature with another graph showing the orthorhombic distortion as related to the quenching temperature, strongly indicates a direct correlation between the size of the orthorhombic distortion and T_c.[9] The correlation may be less pronounced in $La_1Ba_2Cu_3O_{9-\delta}$. Another empirical relation between the lattice constants and T_c, namely, the tendency for the a lattice constant to decrease as T_c is raised, as found in the superconducting compounds $[La_{1-x}(Ba,Sr,Ca)_x]_2CuO_{4-\delta}$,[19] and recently in $Y_1Ba_2Cu_3O_{9-\delta}$,[9] is confirmed for this compound.

In summary, x-ray and neutron-diffraction studies on samples of $La_1Ba_2Cu_3O_{9-\delta}$ show evidence of greater oxygen disorder in the samples with progressively lower T_c's and possible disorder in the La and Ba atomic sites. Estimates of the 1:2:3 and 3:3:6 configurations present in the $T_c = 43$ K sample were 94% and 4%, respectively. These estimates were 83% and 15%, respectively, for the $T_c = 26$ K sample. The results correlate with recent data on $Y_1Ba_2Cu_3O_{9-\delta}$, which demonstrated that T_c was reduced when the outer Cu–O chains were disrupted and hence when the oxygen disorder increased.

Noted added. After this manuscript was completed, we learned of a similar study being conducted by D. B. Mitzi *et al.* at Stanford University. We are grateful to them for communicating their results prior to publication.

We would like to thank Alan Goldman, Roy S. Tucker, and Scott Coburn for technical assistance. The financial support of the National Science Foundation through Grant No. DMR 83-16989 to the Ohio State University Materials Research Laboratory and Grant No. DMR 84-05403 is gratefully acknowledged. One of the authors (S.C.) would like to acknowledge support from the U.S. Department of Energy, Division of Materials Science, Grant No. DE-FG02-86ER45271.A000.

---

[*] Present address: Department of Physics, Pohang Institute of Science and Technology, Pohang, South Korea.

[†] Present address: Department of Physics, University of Hawaii at Manoa, Honolulu, HI 96822.

[1] J. G. Bednorz, M. Takashige, and K. A. Müller, Europhys. Lett. **3**, 379 (1987).

[2] H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L123 (1987).

[3] P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).

[4] D. W. Murphy, S. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, Phys. Rev. Lett. **58**, 1888 (1987).

[5] S. I. Lee, J. P. Golben, S. Y. Lee, X. D. Chen, Y. Song, T. W. Noh, R. D. McMichael, J. R. Gaines, D. L. Cox, and B. R. Patton, Phys. Rev. B **36**, 2417 (1987).

[6] D. B. Mitzi, A. F. Marshall, J. Z. Sun, D. J. Webb, M. R. Beasley, T. H. Geballe, and A. Kapitulnik (unpublished).

[7] Presentation of the Stanford group at the Berkeley Conference, 1987. Referred to by T. H. Geballe, in *Novel Superconductivity,* Proceedings of the International Workshop on Novel Mechanisms of Superconductivity, Berkeley, 1987, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 1105.

[8] A. L. Robinson, Science **237**, 248 (1987).

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

[10] X. D. Chen, S. Y. Lee, J. P. Golben, S. I. Lee, R. D. McMichael, Yi Song, T. W. Noh, and J. R. Gaines, Rev. Sci. Instrum. **58**, 1565 (1987).

[11] L. Er-Rakho, C. Michel, J. Provost, and B. Raveau, J. Solid State Chem. **37**, 151 (1981).

[12] J. Provost, F. Studer, C. Michel, and B. Raveau, Synth. Met. **4**, 147 (1981).

[13] S. C. Moss, K. Forster, J. D. Axe, H. You, D. Holhwein, D. E. Cox, P. H. Hor, R. L. Meng, and C. W. Chu (unpublished).

[14] J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, Phys. Rev. B **36**, 226 (1987).

[15] M. A. Beno, L. Soderholm, D. W. Cappone II, D. G. Hinks, J. D. Jorgensen, and I. K. Schuller, Appl. Phys. Lett. **51**, 57 (1987).

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

[17] J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. V. George, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[18] The subscript refers to the unit-cell indexing. The 3:3:6 structure used here is discussed in Ref. 11.

[19] K. Kishio, K. Kitazawa, N. Sugii, S. Kanbe, K. Fueki, H. Takagi, and S. Tanaka, Chem. Lett. **1987**, 635 (1987).