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X-ray-diffraction study of a thermomechanically detwinned single crystal of $YBa_2Cu_3O_{6+x}$

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A twin-free single crystal of $YBa_2Cu_3O_{6+x}$ has been studied at room temperature and 115 K by x-ray-diffraction analysis. The crystal was grown from an Y-Ba-Cu-O melt in a gold crucible, leading to a 2% substitution of Au for Cu. Twins were removed from the as-grown crystal by a novel thermomechanical process, resulting in an orthorhombic (*Pmmm*), single-domain crystal. Oxygen positions and occupancies in the Cu-O basal plane have been refined, showing that the O(5) site is completely vacant, and the O(4) atoms are offset from the crystallographic mirror plane positions by 0.15 Å in a zig-zag fashion. Gold, which is a common impurity in crystals grown by the present technique, was found to occupy Cu(1) sites only. Weak superlattice reflections suggest a possible three-dimensional ordering of O and/or Au. To our knowledge, this paper reports the first high-resolution x-ray study of an intentionally detwinned, superconducting $YBa_2Cu_3O_{6+x}$ single crystal.

Knowledge of the structure of crystalline materials is essential for understanding their physical and chemical properties, controlling processing conditions, and developing applications. To date, structural models of the high-T_c superconductor $YBa_2Cu_3O_{6+x}$ have been formulated primarily using data from neutron powder diffraction on polycrystalline specimens[1-5] or single-crystal x-ray diffraction on twinned crystals.[6-8] The results of structural analyses of $YBa_2Cu_3O_{6+x}$ over the past two years have been intriguing and controversial. The unrecognized presence of twins caused early misidentification of the structure as tetragonal,[7,8] but the transmission electron microscopy results of Beyers *et al.*[9] provided evidence for orthorhombic symmetry as low as *2mm*. Later neutron powder diffraction studies[1-5] described the structure as orthorhombic, space group *Pmmm*, with the oxygen shifted from the O(4) sites in a direction along the *a* axis.[2,5] Recently, Siegrist *et al.*[6] determined the room-temperature electron density in a largely single-domain crystal containing 10% twins, and Simon *et al.*[10] examined an untwinned fragment from a twinned single crystal at temperatures from 103 to 303 K; in neither study, however, did they observe any statistically significant splitting of the O(4) position. Furthermore, a Raman-scattering investigation[11] showed the emergence of a weak symmetry-forbidden mode during cooling, suggesting the occurrence of a phase transition from *Pmmm* to *P2mm* between room temperature and 234 K.

The present analysis of an untwinned $YBa_2Cu_3O_{6+x}$ crystal was undertaken in order to resolve such issues as the proper space group, the disordering of oxygen O(4), and the existence of low-temperature, structural phase transformations. Untwinned crystals have recently become available via the development of a thermomechanical process for complete twin removal.[12] In the detwinning process, a uniaxial compressive stress is applied along a twinned *a*/*b* direction at 600 °C. For complete twin removal, a crystal must have a high degree of morphological perfection, as is typical of the crystals grown by the technique[13,14] employed in this investigation. The thermomechanical treatment leads to a ferroelastic-like domain switching associated with the migration of twin boundaries, which ultimately results in a single-domain crystal. The orthorhombic crystal used in this x-ray study had an onset T_c of $\simeq 54$ K and displayed forms $\{100\}$, $\{010\}$, and $\{001\}$ with $a \times b \times c$ dimensions of $130 \times 120 \times 52$ μm. This crystal was twin free as shown by polarized light optical microscopy (see Fig. 1) and by the absence of "split" reflections on x-ray precession photographs and diffractometric ω scans of the 400 and 040 peaks.

A fully automated ENRAF-NONIUS CAD4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation was used for this investigation. Data collection was performed at room temperature (292 K) and at 115 K using a nitrogen gas stream cryostat. Lattice parameters were determined by least-squares analysis of the precisely centered positions of 25 reflections in the range $36° < 2\theta < 38°$. The integrated intensities were corrected for Lorentz, polarization, and extinction effects. An isometric grid absorption correction was also applied. At room temperature, reflections were measured from two octants related by an inversion (each Friedel pair was measured consecutively) in the range $2° < 2\theta < 60°$, and from one octant in the range $60° < 2\theta < 100°$. At 115 K, reflections were measured from all eight octants in the range $2° < 2\theta < 60°$, and from one octant in the range $60° < 2\theta < 120°$. Averaging all observed [$I > 3\sigma(I)$, where I and σ are intensity and standard deviation, respectively] symmetry-equivalent intensities, including Friedel pairs, produced residual factors $R(F)$ of 0.012 (292 K) and 0.026 (115 K). The ionic scattering factors for Y^{3+},

Ba^{2+}, Cu^{2+}, Au^{1+}, and O^{2-} were obtained from the International Tables.[15] All calculations were carried out using the ENRAF-NONIUS SDP structure determination package[16] and SHELX76 (Ref. 17) on a microVAX II computer.

Crystallographic data are as follows: $YBa_2Cu_{2.93}Au_{0.07}O_{6.7}$; orthorhombic, *Pmmm*, $z=1$; dimensions $0.130\times0.120\times0.052$ mm; graphite monochromatized MoK_α ($\lambda=0.71073$ Å), $\omega-2\theta$ scans; at 292 K, 1474 reflections measured, 1125 unique, 835 observed ($I>5\sigma$), $a=3.8336(7)$, $b=3.8828(5)$, $c=11.7503(12)$ Å, $R=0.0315$, $R_w=0.0452$; at 115 K, 3280 reflections measured, 1574 unique, 1141 observed ($I>5\sigma$), $a=3.8222(8)$, $b=3.8801(20)$, $c=11.7193(16)$ Å, $R=0.0383$, $R_w=0.0602$. Atomic positions and thermal parameters at 115 K are presented in Table I. Room-temperature data and geometric parameters are available from the authors. Figure 2 presents the structure; the general features agree with those of previous investigators.[1-5] The orthorhombic splitting factor, $2(b-a)/(b+a)$, shows the expected increase with decreasing temperature, but the values [0.0128(2) at 292 K and 0.0150(6) at 115 K] are less than those of Francois *et al.*[5] presumably due to the lower oxygen content in our crystal. All refinement models explored in this work are consistent with the Ba, Cu, Y, O(1), O(2), and O(3) atoms residing on an ordered, fully occupied centrosymmetric lattice of space group *Pmmm* at 292 and 115 K. At both temperatures, however, the occupancy of site O(4) refined to a value of 0.66(4), whereas the O(5) occupancy was zero. In addition, the apparent thermal motion of O(4) is anomalous even at 115 K. The values of all but one of the refined thermal tensor components (U_{ii}, $i=1,2,3$) are consistent with a

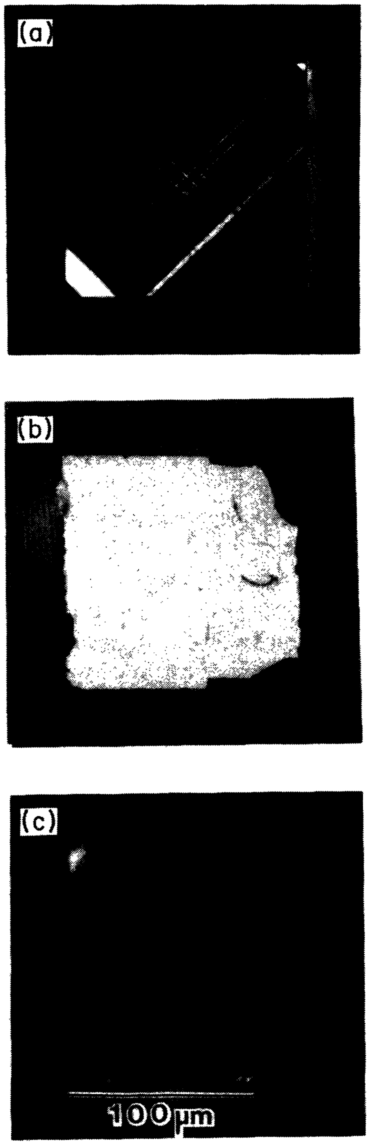

FIG. 1. Polarized light optical micrographs. (a) Twinned crystal exhibiting characteristic {110} type twin bands, (b) the same crystal after the detwinning treatment. The crystal has been rotated 90° from (b) to (c) showing the *a-b* anisotropy in the reflectivity associated with the orthorhombic structure.

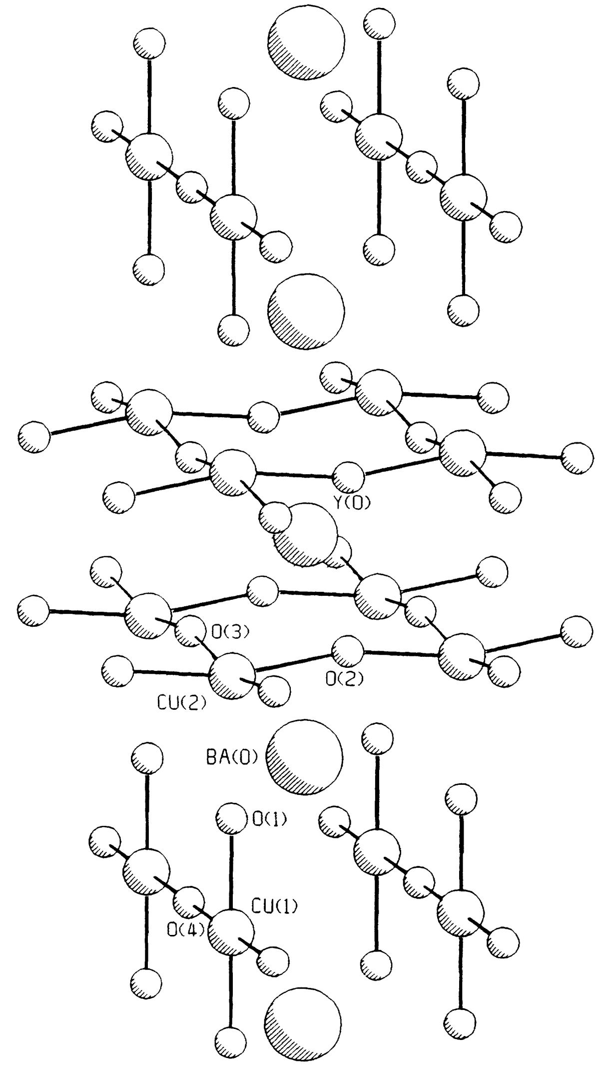

FIG. 2. Crystal structure of $YBa_2Cu_3O_{6+x}$. The O(5) site, ($\frac{1}{2}00$), is vacant, and the O(4) atoms in the actual structure are displaced 0.15 Å off the *b* axis in the *a* direction, leading to a zig-zag Cu(1)-O(4)-Cu(1) chain.

TABLE I. Atomic and thermal parameters at 115 K.

Atom	x	y	z	U_{11}	U_{22}	U_{33}
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.188 35(3)	0.006 19(9)	0.003 06(7)	0.006 17(7)
Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0035(2)	0.0020(2)	0.0046(2)
Au/Cu	0	0	0	0.0049(2)	0.0047(2)	0.0025(2)
Cu(2)	0	0	0.357 38(6)	0.0032(2)	0.0019(2)	0.0054(2)
O(1)	0	0	0.1586(4)	0.010(1)	0.011(2)	0.008(1)
O(2)	$\frac{1}{2}$	0	0.3784(4)	0.005(1)	0.004(1)	0.009(1)
O(3)	0	$\frac{1}{2}$	0.3782(4)	0.006(1)	0.0018(9)	0.008(1)
O(4)	0[a]	$\frac{1}{2}$	0	0.026(6)	0.005(3)	0.007(2)

[a] Refined to 0.036(1) in the disordered model, with U_{11} fixed at 0.007.

decrease to nearly isotropic thermal motion of all atoms at 115 K. However, at 115 K, U_{11} for atom O(4) is more than twice that of the next largest component [U_{22} for O(1)], and implies an rms displacement of 0.16(1) Å along the a lattice direction. Damped, full matrix, least-squares refinement of a doubly occupied disordered model converged to nearly the same value: 0.14(1) Å. All attempts to refine three settings of noncentrosymmetric models of $P2mm$ failed.

Our observation of a static disorder in $YBa_2Cu_3O_{6+x}$ is consistent with the neutron-scattering results of Francois *et al.*[5] Furthermore, the displacement of the O(4) atom determined in this study is comparable to that reported by Francois *et al.* in a polycrystalline sample (0.12–0.13 Å at 110 K).[5] At 115 K, atom O(4) occupies positions $x \simeq 0.15$ Å on either side of the crystallographic mirror plane, so that the Cu(1)-O(4)-Cu(1) chain is not linear but "zig-zag." The existence of ordered domains of this type would explain persistent observations of symmetry lower than *mmm* and the existence of weak superlattice reflections noted in the present and other investigations.[18] However, long-range misregistration of adjacent zig-zag chains would produce the disordered, higher symmetry material.

Weak superlattice reflections were observed for all forms of $\{\frac{1}{2}\frac{1}{2}0\}$, $\{\frac{1}{2}0\frac{3}{2}\}$, $\{\frac{1}{2}1\frac{3}{2}\}$, and $\{1\frac{1}{2}\frac{3}{2}\}$. These superlattice reflections could result from ordering of O and/or Au atoms. Further investigations of the exact nature of the superlattice are in progress.

The presence of Au, substituted only at the Cu(1) site, was first detected as significant residual electron density in a difference Fourier map and subsequently refined to 6.9(4)%. The gold was incorporated into the $YBa_2Cu_3O_{6+x}$ crystal during growth from Y-Ba-Cu-O melts in gold crucibles. The level of gold determined in the refinement is consistent with electron microprobe measurements on similar crystals prepared by this technique.[14] It should be noted that the low T_c value (54 K) of this crystal results from the depletion of oxygen at the O(4) site rather than the presence of Au. Gold-containing crystals[14] and ceramic samples with 10% of the Cu replaced by Au (Ref. 19) exhibit sharp superconducting transitions at 90 K. Although it is known that Au can exist in both Au(I) and Au(III) states, it is not possible to conclude in the present structure whether a Au(I), Au(III), or mixed Au(I)/Au(III) state is most appropriate. When Au(I) was assumed, the x value in the above formula was found to be 0.66 and 10% of the Cu(I) sites [equivalent to 7% of the Cu(1) sites] are substituted with Au(I).

In summary, an untwinned single crystal of $YBa_2Cu_3O_{6+x}$ has been studied by x-ray diffraction at 292 and 115 K. Oxygen positions in the superconducting basal plane have been refined, showing significant (0.15 Å) displacement from the $[0\frac{1}{2}0]$ lattice positions. Oxygen occupancy at $[\frac{1}{2}00]$ sites was found to be zero. These results may contribute to our understanding of important physical phenomena in these materials such as oxygen diffusion and anisotropy of physical properties, as well as theories of high-temperature superconductivity.

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

[2] S. Miraglia, F. Beech, A. Santoro, D. Tran Qui, S. A. Sunshine, and D. W. Murphy, Mater. Res. Bull. **22**, 1733 (1987).

[3] 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).

[4] 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).

[5] M. Francois, A. Junod, K. Yvon, A. W. Hewat, J. J. Capponi, P. Strobel, M. Marezio, and P. Fischer, Solid State Commun. **66**, 1117 (1988).

[6] T. Siegrist, S. Martin, P. Marsh, A. T. Fiory, R. M. Fleming, L. F. Schneemeyer, S. A. Sunshine, and V. Waszczak, in *High Temperature Superconductivity: The First Two Years*, edited by R. Metzger (Gordon and Breach, New York, 1988), p. 83.

[7] Y. LePage, W. R. McKinnon, J. M. Tarascon, L. H. Greene, G. W. Hull, and D. M. Hwang, Phys. Rev. B **35**, 7245 (1987).

[8]R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, H. K. Mao, C. G. Hadidiacos, P. H. Hor, R. L. Meng, and C. W. Chu, Phys. Rev. B **35**, 7238 (1987); **36**, 3966(E) (1987).

[9]R. Beyers, G. Lim, E. M. Engler, R. J. Savoy, T. M. Shaw, T. R. Dinger, W. J. Gallagher, and R. L. Sandstrom, Appl. Phys. Lett. **50**(26), 1918 (1987).

[10]A. Simon, J. Köhler, H. Borrmann, B. Gegenheimer, and R. Kremer, J. Solid State Chem. **77**, 200 (1988).

[11]M. Zhang, C. Qiang, S. Dakun, J. Rong-fu, Q. Zheng-hao, Y. Zheng, and J. F. Scott, Solid State Commun. **65**(6), 487 (1988).

[12]D. L. Kaiser, F. W. Gayle, R. S. Roth, and L. J. Swartzendruber, J. Mater. Res. **4**, 745 (1989).

[13]D. L. Kaiser, F. Holtzberg, B. A. Scott, and T. R. McGuire, Appl. Phys. Lett. **51**, 1040 (1987).

[14]D. L. Kaiser, F. Holtzberg, M. F. Chisholm, and T. K. Worthington, J. Cryst. Growth **85**, 593 (1987).

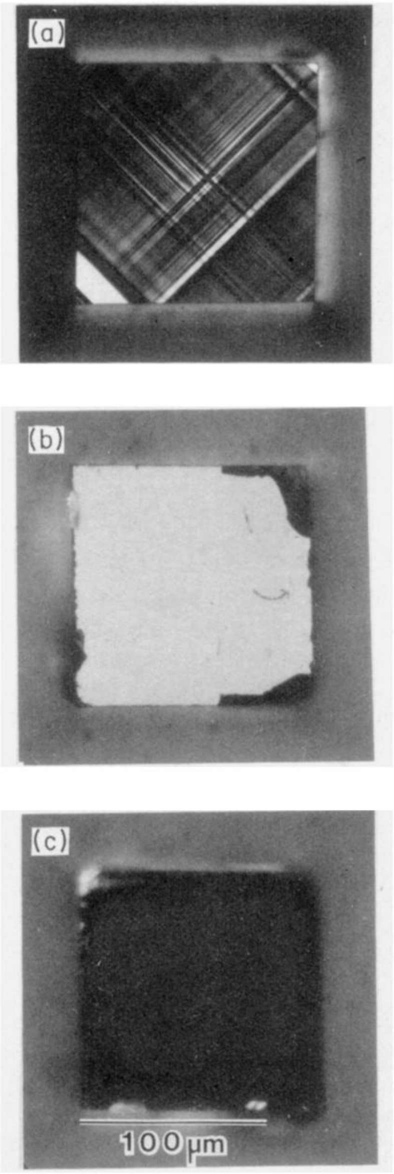
[15]*International Tables for X-ray Crystallography,* edited by J. A. Ibers and W. C. Hamilton (Kynoch, Birmingham, 1974), Vol. IV.

[16]B. A. Frenz, in *Computing in Crystallography,* edited by H. Schenk, R. Olthof-Hazelkamp, H. van Konigsveld, and G. C. Bassi (Delft University Press, Delft, 1978), p. 64.

[17]G. M. Sheldrick, SHELX76—*A Program for Crystal Structure Determination* (University of Cambridge, Cambridge, 1976).

[18]R. M. Fleming, L. F. Schneemeyer, P. K. Gallagher, B. Batlogg, L. W. Rupp, and J. V. Waszczak, Phys. Rev. B **37**, 7920 (1988).

[19]J. J. Pouch, A. F. Hepp, J. R. Gaier, and P. D. Hambourger,



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