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X-Ray Structural Investigation of an Untwinned Single Crystal of Orthorhombic $YBa_2Cu_3O_{6.93}$

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Crystals of $YBa_2Cu_3O_{6.93}$ were grown in a SnO_2 crucible. Parts of these crystals were untwinned and isolated for X-ray structure investigations at seven temperatures between 103 and 303 K. The positions of the chain atoms Cu(1) and O(4) are occupied at 100 and 93%, respectively. There is no evidence for oxygen atoms between the chains (site O(5) in ($\frac{1}{2}$ 0 0)). The temperature-dependent changes of the lattice constants and the positional shifts of O(1), Cu(2), and Ba are discussed. © 1988 Academic Press, Inc.

Single crystal structure investigations of the high-T_c superconductor, $YBa_2Cu_3O_{7-x}$, have suffered from two major problems. First, crystals easily incorporate components of the crucible material (e.g., Al from alumina crucibles) and, second, twinning occurs upon oxidation of the as-grown $YBa_2Cu_3O_6$ crystals.

The first problem was overcome by choosing SnO_2 as a crucible material. Thin platelets of edge length up to 1.5 mm were grown from a partially melting mixture of 66.7 mol% CuO, 26.7 mol% $BaCO_3$, and 6.7 mol% $YO_{1.5}$ (*1*) by heating in air at 1325 K for 3 hr and then cooling at a rate of 1.7 K/hr to 1123 K and finally at 10 K/hr to room temperature (*2*). No Sn was detected in the crystals by energy dispersive X-ray analysis (EDAX). Selected crystals without any additional oxygen treatment exhibited a T_c of 89 K and a transition width of approximately 4 K (Fig. 1). Concerning the second problem, in grazing incident light the characteristic diagonal striation pattern of the surface due to (110) twinning was observed for parts of a crystal. Upon rotation around an [001] axis other striated regions are encountered. However, some surface regions always stayed dark. Such a portion of a crystal was broken off and proved to be an untwinned orthorhombic single crystal, as determined by precession photographs. Untwinned portions were easily detected by Raman spectroscopy (*3*) in a number of other crystals.

The selected crystal formed a rectangular plate (0.074 × 0.098 × 0.014 mm^3). Full structure determinations were performed at T = 223, 243, 103, 263, 163, 283, and 303 K (±2 K). The given sequence of temperatures was chosen in order to ensure that no gradual change of the mosaic spread of the

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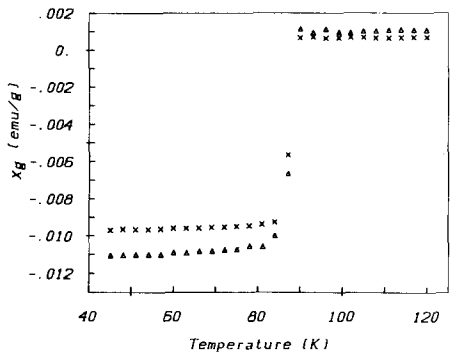

FIG. 1. Magnetic susceptibilities of two crystals (20 and 30 μg) of $YBa_2Cu_3O_{7-x}$ grown in SnO_2 crucibles from the same batch as the X-ray single crystal. The flux exclusion was measured in a field of 16 G perpendicular to the c-axis after cooling to 5 K at $B < 0.2$ G.

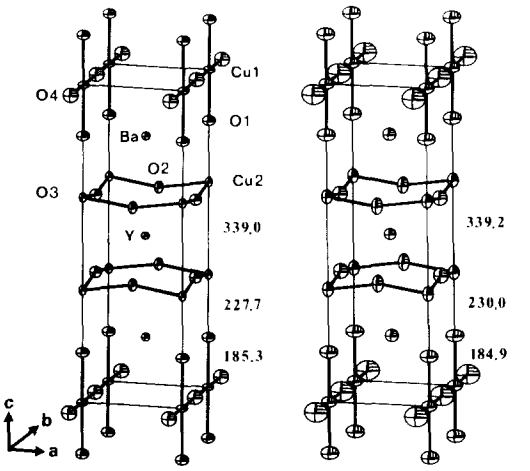

FIG. 2. Crystal structure of $YBa_2Cu_3O_{6.93}$ at 103 K (left) and 303 K (right). Ellipsoids are plotted at 95% probability. The given distances (pm) are discussed in the text.

crystal occurred during the investigation. Apart from the temperature variation, experimental conditions were kept the same. Intensities were collected in the $\omega/2\Theta$ mode (0.4–14.65° min^{-1}) on a $P21$ diffractometer in the range $3° < 2\Theta < 65°$ ($+h$, $\pm k$, $\pm l$), yielding 1405 (103 K) to 1413 (303 K) reflections. After correcting for absorption (analytic, 2560 grid points), these were averaged to sets of 399 symmetry independent reflections each.

Full matrix least-squares refinements resulted in the weighted residuals, R_w = 1.62% (303 K, 1.69% (283 K), 1.58% (263 K), 1.54% (243 K), 1.62% (223 K), 1.45% (163 K), and 1.37% (103 K)). To our knowledge, this structure investigation is the first performed on untwinned superconducting single crystals of $YBa_2Cu_3O_{7-x}$ ($x \approx 0.1$). Earlier investigations are summarized in (*4*), and discussed in detail with respect to twinning (*5*). Our investigation adds to the accuracy of the crystal structure determined and refined from neutron powder data at room temperature (*6*) and below (*7*, *8*).

The lattice constants determined with 50 selected reflections from the entire sphere in reciprocal space are summarized in Table I. The data show that the change of the c-axis as a function of temperature is largest, followed by the a- and b-axis (3.4, 1.9, and 1.4% contraction from 303 to 103 K). There is evidence for a significant increase of the temperature-dependent orthorhombic strain, $2(b - a)/(a + b)$, between 163 and 103 K, compared to the range 303 to 163 K, as first reported in Ref. (*9*).

TABLE I

LATTICE CONSTANTS (pm) FOR A SINGLE CRYSTAL OF $YBa_2Cu_3O_{6.93}$ AT DIFFERENT TEMPERATURES

	103 K	163 K	223 K	243 K	263 K	283 K	303 K
a	380.92(4)	381.08(3)	381.25(4)	381.31(4)	381.43(4)	381.54(5)	381.66(3)
b	387.98(4)	388.01(3)	388.12(4)	388.22(3)	388.32(4)	388.40(5)	388.52(3)
c	1165.02(11)	1166.22(9)	1166.80(10)	1167.25(10)	1167.84(12)	1168.39(15)	1169.01(9)

Note. Standard deviations are in parentheses.

TABLE II

ATOMIC PARAMETERS OF $YBa_2Cu_3O_{6.93}$ AT 103 K (BOLDFACED) AND 303 K

Atom	Position	K	z/c	z/c	U_{11}	U_{11}	U_{22}	U_{22}	U_{33}	U_{33}
Ba	2*t*	**0.25**	0.18411(2)	**0.18382(2)**	770(14)	**314(12)**	659(16)	**313(13)**	685(15)	**279(12)**
Y	1*h*	**0.125**	0.5	**0.5**	610(27)	**291(22)**	577(32)	**302(25)**	520(30)	**217(24)**
Cu(1)	1*h*	**0.125**	0	**0**	1011(38)	**540(29)**	692(42)	**367(33)**	467(42)	**199(29)**
Cu(2)	2*q*	**0.25**	0.35492(5)	**0.35452(4)**	499(25)	**227(20)**	473(28)	**271(23)**	860(30)	**390(24)**
O(1)	2*q*	**0.25**	0.15818(31)	**0.15907(26)**	1450(155)	**760(117)**	1189(175)	**790(137)**	629(135)	**380(109)**
O(2)	2*s*	**0.25**	0.37861(31)	**0.37861(25)**	493(137)	**300(113)**	858(175)	**741(143)**	1179(146)	**614(114)**
O(3)	2*r*	**0.25**	0.37852(31)	**0.37809(25)**	957(148)	**652(120)**	535(168)	**375(137)**	946(140)	**520(112)**
O(4)	1*e*	**0.116(2)**	0	**0**	2468(296)	**1046(192)**	663(274)	**456(210)**	1625(280)	**839(201)**

Note. The thermal parameters [$pm^2 \times 10^5$] are defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$.

Table II summarizes the refined structural parameters for 103 and 303 K. The site occupation for O(4) is 0.93(2), which corresponds to a formula $YBa_2Cu_3O_{6.93}$. Within one standard deviation no oxygen occupies the O(5) position at ($\frac{1}{2}$ 0 0). The Cu(1) position is fully occupied, in contrast to earlier reported "deficiencies" due to preferred substitution of this position by Al in the case of crystals grown in alumina crucibles (*10*). Figure 2 compares the thermal ellipsoids of the atoms at 103 and 303 K. The change of the vibrational amplitudes for the O(4) atoms in (0 $\frac{1}{2}$ 0), in particular, clearly indicates the dynamic rather than static disorder of these weakly bonded atoms. The orientations of all ellipsoids correspond to the hierarchy of bond strengths and are closely related to the anisotropy of the thermal lattice expansion.

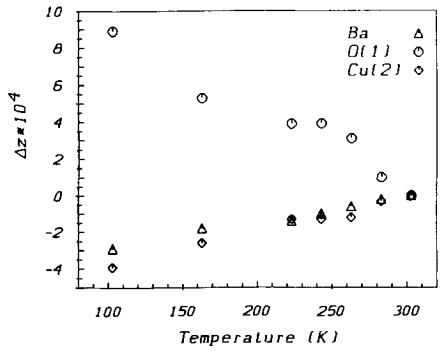

FIG. 3. Shifts of atomic parameters z of Ba, O(1), and Cu(2) as a function of temperature. The changes refer to the structure at 303 K.

Significant changes of the positional parameters are observed for Ba, Cu(2), and O(1). As plotted in Fig. 3, with decreasing temperature O(1) moves toward larger *z*, while Ba and Cu(2) show opposite shifts. One is left with the impression that the weak O(1)–Cu(2) interaction is strengthened at the expense of the O(1)–Cu(1) bond. However, the changes in *z* just compensate for the changes in *c* in order to keep the Cu(1)–O(1) bond length (185 pm), as well as the Cu(2)–Cu(2) distance (339 pm), constant. The thermal contraction of the *c*-axis is essentially based on the contraction of the space between the $Cu(2)O_2$ plane and the plane formed by Ba and O(1) atoms. This result might be expected as a result of the relatively weak bonding between O(1) and Cu(2), and among Ba, O(2) and O(3).

The remarkable movement of the Ba atoms is rationalized by a rather trivial explanation. Due to the thermal contraction the Y^{3+} ions pairwise exert pressure on the pair of Ba^{2+} ions between them. In terms of a simple electrostatic argument, taking only the Coulomb repulsion, $e_1 \cdot e_2/d^2$, into account, the equilibrium position of Ba^{2+} is such that twice the repulsive force between 2+/3+ ions compensates the repulsion between 2+/2+ ions.

Unfortunately we have not yet succeeded in measuring diffraction data at a comparable level of accuracy below T_c. Such measurements are being planned.

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