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Single Crystal X-Ray Structure Analysis of $YBa_2Cu_3O_{6.5}$

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

The crystal structure of $YBa_2Cu_3O_{6.5}$ was refined from X-ray data of a twinned crystal with a domain ratio 5 : 1. The earlier proposed model of alternately filled and empty Cu–O chains is verified. On the basis of 1290 measured superstructure reflections averaged to 244 independent intensities a structure analysis was performed revealing systematic shifts of the strongly scattering atoms Y, Ba, and Cu compared to $YBa_2Cu_3O_{6.93}$.

1. Introduction

It is well known that T_c of $YBa_2Cu_3O_{7-x}$ depends on the oxygen content which is variable in the chain region of the structure, e.g., (*1, 2*). For $x = 1$ all oxygen is removed from the chains and the compound is nonmetallic. With increasing oxygen content, at $x = 0.6$, a semiconductor–metal transition occurs and the compound becomes superconducting. For $x = 0$ the highest T_c (93 K) is reached. Although different preparative routes lead to small deviations in the dependence of T_c on x, a two-plateau behavior of T_c versus x is well established (*2*). The Cu–O chains are considered to act as charge reservoirs for the CuO_2 planes (*3, 4*). In addition, it has been suggested that there is a connection between oxygen ordering, electronic properties, and T_c (*5, 6*) and it was assumed that the two plateaus correspond to two types of ordered orthorhombic phases, ortho I ($x = 0$) and ortho II ($x = 0.5$, model of alternating empty and filled chains). Theoretical calculations of T_c values based on these structural models show good agreement with experimental results (*7–9*). Except for the well characterized phases with $x = 0$ and $x = 1$, it is difficult to obtain structural information concerning oxygen ordering in samples with intermediate oxygen content.

The model of alternating empty and filled chains of compositions CuO_2 and CuO_3 in $YBa_2Cu_3O_{6.5}$ was proposed on the basis of electron diffraction studies (*10*) and was corroborated by neutron and X-ray diffraction. However, only a small number of superstructure reflections could be observed (*11–14*), which did not allow a more detailed structural analysis concerning the oxygen ordering. Very recently, 28 superstructure reflections were measured in a single crystal X-ray diffraction study (*15*). Besides the ordering of oxygen atoms into alternating empty and filled chains, a shift of the barium atoms was indicated. In a related study on $YBa_2Cu_3O_{6.35}$ only 8 independent superstructure reflections were detected. On this basis an "oxygen ordering copper displacement model" was proposed (*16, 17*).

We succeeded in collecting 244 independent superstructure reflections by X-ray diffraction in the Mo$K\alpha$ range from a YBa_2

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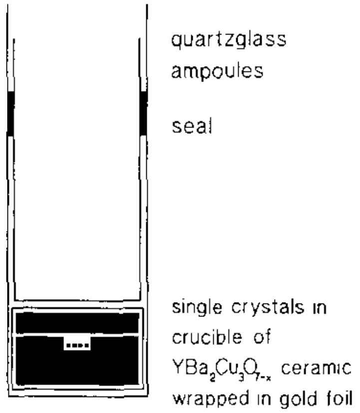

FIG. 1. Experimental setup for the preparation of $YBa_2Cu_3O_{7-x}$ single crystals with defined x.

$Cu_3O_{6.5}$ crystal and to refine details of the structure.

2. Preparation and Analytical Characterization

Single crystals of $YBa_2Cu_3O_{7-x}$ were grown from a CuO-rich flux. As described elsewhere (*18*) in more detail SnO_2 crucibles were used to prevent contamination. From such a batch $YBa_2Cu_3O_{6.93}$ crystals were selected. The controlled reduction of the oxygen content to the composition $YBa_2Cu_3O_{6.5}$ was carried out in a closed system as specified in Fig. 1; see also (*19*).

Appropriate amounts of powdered preanalyzed $YBa_2Cu_3O_{6.10}$ (47%) and $YBa_2Cu_3O_{6.93}$ (53%) were thoroughly mixed and pressed into two pellets. A few small untwinned crystals together with a larger twinned one were placed into a bore (1 mm diameter) in the center of one of the pellets. The second pellet was used as a lid. To avoid reactions between the ceramic and the quartz-glass tube, the pellets were wrapped in gold foil. The sample was transferred to a flat-bottomed quartz-glass ampoule with a diameter only slightly larger than the pellets, and a tightly fitting second ampoule minimized the inner volume essentially to that of the pellets. The ampoule system was sealed under 100 Torr Ar pressure approximately 4 cm above the water-cooled sample.

The sample was annealed for 25 days at 500°C. To ensure a well ordered structure it was cooled to room temperature at a rate of 3° per hr.

The oxygen content of the pellets was determined by volumetric titration as described elsewhere (*20*). It corresponds to the composition $YBa_2Cu_3O_{6.53(2)}$. The c-axis length determined with the modified Guinier technique (*21*) served as a check for homogeneity of the ceramic and its oxygen content. The value $c = 11.730(2)$ Å leads to the formula $YBa_2Cu_3O_{6.55(2)}$ (22). All experimental values closely correspond to the intended pellet composition $YBa_2Cu_3O_{6.54}$, powder data indicating a homogeneous product to have formed. Single crystals were characterized by measurements of magnetic susceptibility and X-ray diffraction using a precession camera and a four-circle diffractometer.

TABLE I

SUMMARY OF SINGLE CRYSTAL DATA AND X-RAY INTENSITY COLLECTION FOR $YBa_2Cu_3O_{6.5}$ (I)

Formula	$YBa_2Cu_3O_{6.5}$
Molar weight	658.2 $gmol^{-1}$
Lattice constants	$a = 3.834(1)$, $b = 3.878(1)$, $c = 11.740(2)$ Å
Space group	$Pmmm$, $Z = 1$
d_{calc}	6.241 gcm^{-3}
$\mu(MoK\alpha)$, λ	28.30 mm^{-1}, 0.71069 Å
Dimensions of the single crystal	0.1 × 0.15 × 0.02 mm
Data collection	four circle diffractometer $P2_1$, graphite monochromator, scintillation counter
Range of data, method	$4° \leq 2\theta \leq 70°$, ω-scan
Scan speed	variable, depending on I
Number of reflections	1316
Independent	479
Absorption correction	ψ-scans with 10 reflections
Refinement	SHELXTL program (*23*), full matrix least squares
Number of parameters	32
R(aniso)	2.74%
R_w(aniso)	2.00% weight: $1.0(\sigma(F))^{-2}$

TABLE II

ATOMIC PARAMETERS OF $YBa_2Cu_3O_{6.5}$ (I)

	x/a	y/b	z/c	U_{eq}
Y	0.5	0.5	0.5	0.0082(1)
Ba	0.5	0.5	0.18900(3)	0.0059(2)
Cu(1)	0	0	0	0.0095(2)
Cu(2)	0	0	0.3572(1)	0.0060(2)
O(1)	0	0	0.1554(4)	0.0136(6)
O(2)	0.5	0	0.3791(3)	0.0072(5)
O(3)	0	0.5	0.3781(3)	0.0076(5)
O(4)	0	0.5	0	0.0249(7)

Note. Equivalent isotropic U_{eq} [Å^2] are defined as one third of the trace of the orthogonalized U_{ij} tensor. Standard deviations in parentheses.

For one of the small untwinned single crystals (I) the refinement of the site occupation for the chain oxygen on the basis of diffractometer data (see also Tables I and II) leads to S.O.F. = 0.51(1). The O(5) position at ($\frac{1}{2}$ 0 0) is not occupied within one standard deviation. This corresponds to the composition $YBa_2Cu_3O_{6.51(1)}$. The finding is in agreement with our general experience that single crystals contain slightly less oxygen than the equilibrating ceramic environment.

Superstructure reflections could only be measured with the twinned crystal, which is about 30 times larger than the others. The temperature dependence of the susceptibility of this crystal was measured down to 4 K (SQUID magnetometer, applied fields 2, 20, 50, and 100 G). The measurement in the 2-G field is shown in Fig. 2. We found $T_{c(onset)}$ = 56 K and a transition width of 6 K. The amounts of Shielding and Meissner effect were approximately 40 and 25%, respectively. Both T_c and transition width strongly depend on the applied field. An increase to 20 G results in a significant broadening of the transition width. In a field of 100 G the temperature for the onset of superconductivity is lowered to 28 K.

3. Crystal Structure Investigation

The *hk*0 precession photograph of the investigated crystal (II) shows superstructure reflections in the a^* direction but none in the b^* direction. The diffraction pattern gives clear evidence for a doubling of the a-axis. Spots suggesting $b' = 2b$ only occur at small angles. All of them are interpreted as $\lambda/2$ reflections associated with very strong substructure reflections like 210.

The crystal is accompanied by a small domain generated by the usual twinning law in the Y123-system involving the (110) mirror plane (*24*). From the film intensities a domain ratio of approximately 5 : 1 is de-

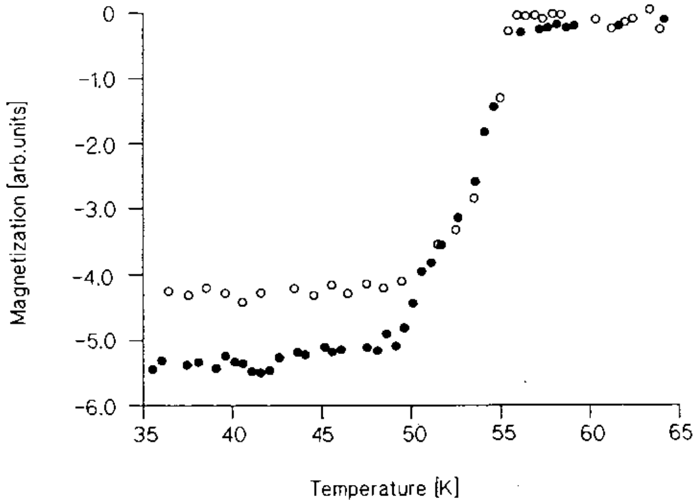

FIG. 2. Magnetic susceptibility of the $YBa_2Cu_3O_{6.5}$ crystal (II) (SQUID magnetometer, cooling in a 2-G field (open circles) and a zero field (solid circles)).

TABLE III

SUMMARY OF SINGLE CRYSTAL DATA AND X-RAY INTENSITY COLLECTION FOR $YBa_2Cu_3O_{6.5}$ (II)

Formula	$Y_2Ba_4Cu_6O_{13}$
Molar weight	1316.4 $gmol^{-1}$
Lattice constants	a = 7.655(5), b = 3.873(3), c = 11.735(9) Å
Space group	$Pmmm$, $Z = 1$
d_{calc}	6.241 gcm^{-3}
$\mu(MoK\alpha)$, λ	28.30 mm^{-1}, 0.71069 Å
Dimensions of the single crystal	0.7 × 0.48 × 0.04 mm
Data collection	four circle diffractometer CAD 4, graphite monochromator, scintillation counter
Range of data, method	$2° \leq 2\theta \leq 75°$, ω-2θ-scan
Scan speed	variable, depending on I
Number of reflections	3158 with 1290 $I > 3\sigma(I)$
Independent	244 with ($h = 2n + 1$, $n \neq 0$) $-13 \leq h \leq 13$; $-6 \leq k \leq 6$; $-18 \leq l \leq 18$
Scan width	$2.25° + 0.35 \tan \theta$
$F(000)$	580
Absorption correction	numerical R_{merge} = 9.64%
Refinement	SHELXTL program (*23*), full matrix least squares
Number of parameters	49
R(aniso)	8.46%

rived. The superstructure reflections of the larger domain can be measured without interference from the smaller domain as the twinning does not produce overlapping superstructure reflections. The superstructure reflections appear as sharp spots on the $hk0$ precession photograph, indicating a high degree of order. Q-scans along the directions of all three axes, however, reveal rather anisotropic peak shapes. Whereas the peak width (full width at half maximum) for the 100 reflection in the b^* direction is as narrow as for the substructure reflections 200 and 210, it is twice as broad in the a^* direction and nearly six times broader in the c^* direction. Clearly, ordering is rather perfect parallel to (001), particularly in the chain direction along [010], but poor along [001]. This result is in agreement with earlier findings (*15*). Last but not least, a special feature of the $hk0$ precession photograph is noteworthy. The superstructure reflections have particularly larger intensities at high θ values. This observation indicates that besides the oxygen atoms the strongly scattering atoms contribute to the intensities of these reflections via small displacements from their positions compared to $YBa_2Cu_3O_{6.93}$.

For the structure analysis the full Ewald sphere was measured in the Mo$K\alpha$ range up to $2\theta = 75°$, leading to 3158 superstructure reflections which merged into 352 independent reflections with $I > 3\sigma$ (I) and R_{merge} = 9.64%. To reduce interference with $\lambda/2$ contributions from the strong substructure reflections the range $|h| < 3$ was omitted from refinements. The crystal data are summarized in Table III. The positions of the Y and Ba atoms were derived from a Patterson synthesis and after isotropic refinement of all heavy atoms the oxygen atoms could be

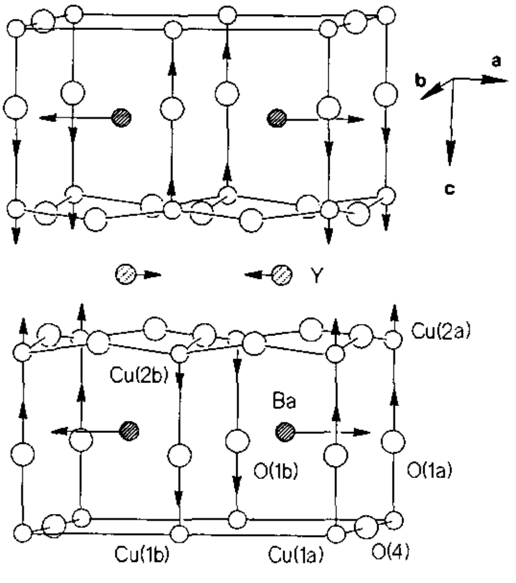

FIG. 3. Unit cell of $YBa_2Cu_3O_{6.5}$ with alternating empty and filled chains. The shifts of the atoms relative to $YBa_2Cu_3O_{6.93}$ are marked by arrows, the lengths of which indicate the amount of shift.

TABLE IV

ATOMIC PARAMETERS OF $YBa_2Cu_3O_{6.5}$ (II)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{13}
Y	0.2535(2)	0.5	0.5	0.010(3)	0.012(7)	0.013(8)	0
Ba	0.2413(1)	0.5	0.1887(3)	0.003(1)	0.001(1)	0.002(1)	0.0001(2)
Cu(1a)	0	0	0	0.005(1)	0.003(2)	0.007(2)	0
Cu(1b)	0.5	0	0	0.013(2)	0.012(4)	0.022(3)	0
Cu(2a)	0	0	0.3594(5)	0.028(2)	0.028(3)	0.021(3)	0
Cu(2b)	0.5	0	0.3518(5)	0.027(2)	0.029(3)	0.020(3)	0
O(1a)	0	0	0.166(1)	0.008(5)	0.004(7)	0.00(1)	0
O(1b)	0.5	0	0.151(2)	0.003(5)	0.02(1)	0.03(2)	0
O(2)	0.249(2)	0	0.389(4)	0.04(3)	0.02(6)	0.01(5)	0.005(5)
O(3a)	0	0.5	0.385(2)	0.028(9)	0.01(1)	0.02(2)	0
O(3b)	0.5	0.5	0.383(3)	0.005(2)	0.03(2)	0.02(2)	0
O(4)	0	0.5	0	0.01(1)	0.01(1)	0.00(1)	0

Note. The anisotropic displacement parameters [Å^2] are defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots\ldots + 2U_{23}klb^*c^*)]$.

U_{33} for O(1a) and O(4) is refined to nonpositive definite. $U_{12} = U_{23} = 0$.

located from a ΔF synthesis. The site occupation of the chain oxygen O(4) refines to S.O.F. = 1.08(15); i.e., the position is fully occupied, whereas the position at ($\frac{1}{2}$ $\frac{1}{2}$ 0) is not occupied. This corresponds to a composition $YBa_2Cu_3O_{6.54(6)}$. The full matrix least-squares refinement converged to R = 8.46%, which is nearly identical with R_{merge}. The atomic parameters are summarized in Table IV; some interatomic distances are presented in Table V.

4. Results and Discussion

The crystal structure of $YBa_2Cu_3O_{6.5}$ is shown in Fig. 3. The arrows indicate extent and direction of the parameter shifts compared to the structure of $YBa_2Cu_3O_{6.93}$. The structure model with alternating empty and filled chains in $YBa_2Cu_3O_{6.5}$ is verified. The oxygen position O(4) between Cu(1a) type atoms is fully occupied and the position between Cu(1b) type atoms is empty on the significance level of one standard deviation. The observed position of the O(1) type atoms, although less certain according to the larger standard deviations, is in line with the chemical argument that O(1a) coordinates Cu^{III} and O(1b) coordinates Cu^{I}. The Cu–O distances of 1.95(2) Å and 1.78(2)Å compare with those observed in $YBa_2Cu_3O_{6.93}$(1.85 Å (*25*)) and $YBa_2Cu_3O_{6.0}$ (1.79 Å (*26*)), respectively.

TABLE V

ATOMIC DISTANCES OF $YBa_2Cu_3O_{6.5}$ (II)

Cu(1a)–O(1a)	1.95(2)	Y–O(2)	2.33(3)
Cu(1a)–O(4)	1.94(1)	Y–O(3a)	2.36(2)
Cu(1b)–O(1b)	1.78(2)	Y–O(3b)	2.34(3)
Cu(2a)–O(1a)	2.27(2)	Ba–O(1a)	2.69(1)
Cu(2a)–O(2)	1.94(2)	Ba–O(1b)	2.80(1)
Cu(2a)–O(3a)	1.96(1)	Ba–O(2)	3.05(4)
Cu(2b)–O(1b)	2.35(3)	Ba–O(3a)	2.96(3)
Cu(2b)–O(2)	1.98(2)	Ba–O(3b)	3.02(3)
Cu(2b)–O(3b)	1.97(1)	Ba–O(4)	2.88(1)

Note. All bond lengths are given in [Å].

A remarkable result of our investigation are somewhat coupled shifts of the heavy atoms when compared with their positions in $YBa_2Cu_3O_{6.93}$. The Ba atom shifts by nearly 0.07 Å towards the filled chain. The shift of the Y atom in the opposite direction is less pronounced but still significant ($\approx$0.03 Å). The observed shifts of the Cu(2) type atoms should be of some relevance for the electronic balance in the CuO_2 planes. Due to the displacements in c direction the buckling of the plane is slightly reduced for Cu(2a) and increased for Cu(2b), leading to closest distances between Cu atoms in adjacent planes of 3.30 and 3.46 Å, respectively.

The slight differences in the coordinations of Cu(2a) and Cu(2b) might indicate marginally varied doping levels for these two kinds of atoms (*27*). However, simple electrostatics seems to offer a more evident explanation. Coulombic attraction will shift the Ba cation into a region with increased coordination by oxygen anions (although there also will be a stronger repulsion by Cu(1a) than by Cu(1b)). In turn, Cu(2a) moves away from Ba and exerts a stronger repulsion on Y. The circle is closed with the downward shift of Cu(2b) atoms.

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Note Added in Proof. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository numbers CSD-390000(I) and CSD-390001(II), the names of the authors, and the journal citation.

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