Atomic structure of $YBa_2Cu_3O_{7-\delta}$ single crystals with an intermediate oxygen concentration

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The atomic structures of the $YBa_2Cu_3O_{6.24}$, $YBa_2Cu_3O_{6.59}$, and $YBa_2Cu_3O_{6.97}$ crystals and the amounts of oxygen in them have been refined. It is concluded from the x-ray-diffraction reflections of the $YBa_2Cu_3O_{6.24}$ single crystals that structural blocks of tetragonal and orthogonal symmetry coexist. The compositions of these blocks are $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_{6.5}$. The O atoms in the $z = 0$ planes of all of the structures have an ordered arrangement.

The first data on the atomic structure of the phases of $YBa_2Cu_3O_{7-\delta}$ can be summarized by saying that at $\delta < 0.5$ the crystals have an orthorhombic symmetry, while at oxygen concentrations below 6.5 the symmetry becomes tetragonal. More-accurate research has shrunk the region with the tetragonal phase to [1,2] $\delta > 0.8$. The

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results reported below allow the assertion that a strictly tetragonal symmetry is a characteristic of only the $YBa_2Cu_3O_6$ phase and that any additional oxygen (above 6 atoms), even a small amount, goes to (0,1/2, 0) sites in the $z = 0$ planes in an ordered fashion, forming blocks of a local orthorhombic symmetry in two orientations.

A comprehensive x-ray structural study of $YBa_2Cu_3O_{6.24}$, $YBa_2Cu_3O_{6.59}$, and $YBa_2Cu_3O_{6.97}$ single crystals (whose synthesis and properties are discussed in Ref. 2) has made it possible to work from diffraction data to refine the amount of oxygen in each analyzed sample volume, $\sim 10^{-3}$ mm^3. The profiles and integral intensities of the diffraction reflections (RÉD-4 diffractometer, Ag$K\alpha$ radiation, $\lambda_{\alpha_1} = 0.5594$ Å, $\lambda_{\alpha_2} = 0.5638$ Å, graphite monochromator) have made it possible to determine the twinning laws and the ratio of the volumes of the twin components in these crystals. In samples with $O_{6.97}$ and $O_{6.59}$, it has been found that there is an ordinary twinning along (110) planes, with an approximately unit volume ratio of the twin components. The complex profile of the diffraction reflections of a crystal with $O_{6.24}$ has not yielded to the standard interpretation. Figure 1 shows profiles of the 040 and 400 reflections

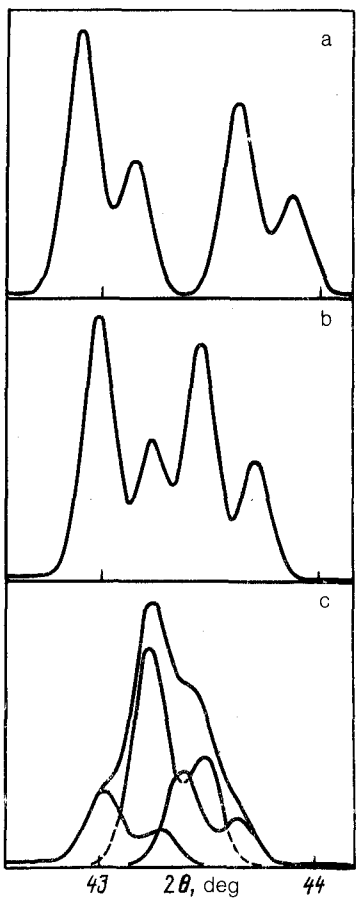

FIG. 1. Profiles of 040 and 400 x-ray diffraction reflections of twin crystals. a—$YBa_2Cu_3O_{6.97}$; b—$YBa_2Cu_3O_{6.59}$; c—$YBa_2Cu_3O_{6.24}$. In the latter case, the profile has been decomposed into components representing the scattering by the region of tetragonal symmetry and the two components of the orthorhombic twin.

for all three entities. The samples with $O_{6.97}$ yields reflections from various twin components, which are essentially completely resolved. In the case of the crystal with $O_{6.59}$, these reflections overlap significantly. The asymmetric profile of a reflection from a sample with $O_{6.24}$ has been interpreted only after a contribution from structural blocks of tetragonal symmetry was added to that from scattering by orthorhombic components. A decomposition of the profiles of the 400 (040) and 0016 reflections into components has made it possible to determine the parameters of the unit cells of the orthorhombic and tetragonal blocks separately for a $YBa_2Cu_3O_{6.24}$ sample. These blocks coexist in this crystal. The integral intensities of the corresponding scattering components have been used to determine the fractions of the volume occupied by the components of the orthorhombic twin and the tetragonal region of the crystal: 0.24, 0.19, and 0.57. The parameters of the unit cells of the $YBa_2Cu_3O_{7-\delta}$ crystals which were studied are summarized in Table I.

The constant c and the degree of orthorhombic distortion, $(b-a)$, of the unit cells depend on the oxygen concentration in the them in approximately the same way as was found previously.[3] The relative volumes of the twin components and the parameters of the atomic models of all the crystals studied were refined on the basis of the diffraction data by the method of least squares. The refinement procedure was complicated by the strong correlation among some of the parameters being refined. We were able to refine the thermal factors B of the O2 and O3 atoms only by assuming $B_{O2}=B_{O3}$. In the case of the $YBa_2Cu_3O_{6.24}$ crystal, the pseudotetragonal nature of the bulk of the experimental data caused further difficulties in the refinement. The filling of the corresponding crystallographic positions by the basal atoms of the structures made it possible to independently determine the chemical composition of these single crystals. In all of the crystals, a defectiveness was observed only in terms of the O(4) atoms in (0,1/2,0) site. The coordinates of the basal atoms and the effective temperature factors B are summarized in Table II.

The divergence factors R_w, which characterize the overall accuracy of the structural models shown in Table II for the crystals with $O_{6.24}$, $O_{6.59}$, and $O_{6.97}$ are 2.60%, 1.99%, and 2.16%, respectively. As we mentioned earlier, as the x-ray diffraction studies have improved in accuracy, the orthorhombic distrotions have been detected in crystals with progressively larger values of δ, and the boundary in terms of the oxygen content between the orthorhombic and tetragonal phases is approaching six O atoms

TABLE I. The constants a, b, and c and the volumes V of the unit cells of $YBa_2Cu_3O_{7-\delta}$ crystals.

$7-\delta$	a, Å	b, Å	c, Å	V, Å^3	$b-a$, Å
6.97 (4)	3.820 (1)	3.886 (1)	11.688 (1)	173.5 (1)	0.066
6.59 (6)	3.835 (1)	3.878 (1)	11.740 (3)	174.6 (1)	0.043
6.24 (7)	3.841 (1)	3.873 (1)	11.750 (2)	174.8 (1)	0.032 } 1)
	3.858 (1)	3.858 (1)	11.795 (2)	175.6 (1)	–

1) Orthorhombic and tetragonal regions.

TABLE II. Coordinates and temperature factors B of the basal atoms of the $YBa_2Cu_3O_{7-\delta}$ structures.

Atom	x/a	y/b	z/c			B, Å^2		
			$O_{6.24}$	$O_{6.59}$	$O_{6.97}$	$O_{6.24}$	$O_{6.59}$	$O_{6.97}$
Y	1/2	1/2	1/2	1/2	1/2	0.39 (5)	0.27 (4)	0.45 (4)
Ba	1/2	1/2	0.1918 (1)	0.1889 (1)	0.1844 (1)	0.66 (4)	0.57 (3)	0.63 (3)
Cu1	0	0	0	0	0	0.77 (6)	0.46 (5)	0.52 (3)
Cu2	0	0	0.3589 (2)	0.3581 (2)	0.3553 (2)	0.71 (6)	0.41 (5)	0.44 (4)
O1	0	0	0.1545 (9)	0.1550 (9)	0.1572 (9)	1.2 (2)	0.9 (2)	0.9 (2)
O2	1/2	0	0.3794 (9)	0.3773 (7)	0.3795 (6)	0.7 (2)	0.6 (2)	0.7 (2)
O3	0	1/2	0.3797 (9)	0.3783 (7)	0.3779 (6)	0.7	0.6	0.7
O4	0	1/2	0	0	0	1.5 (9)	1.6 (6)	1.2 (3)

per cell.[3,4] The crystal chemistry of the Cu1 atoms, in the $z = 0$ plane of the $YBa_2Cu_3O_{7-\delta}$ structures, is of such a nature that a strictly tetragonal symmetry of the surroundings of these atoms is possible only in the $YBa_2Cu_3O_6$ phase where the O1 atoms form dumbbells with a Cu1 atom at their center. The placement of additional oxygen in the first coordination sphere of the Cu1 atoms conforms to the local orthorhombic symmetry.[5] Our discovery of the presence of structural units of tetragonal symmetry in the crystals which are most depleted in oxygen, $YBa_2Cu_3O_{6.24}$, leads to a composition $YBa_2Cu_3O_6$ for these blocks. This conclusion is supported independently by the constant value $c = 11{,}795$ Å (Table I). If we make use of the ratio found for the volumes of the orthorhombic blocks $[0.43(0.24 + 0.19)]$ and the tetragonal blocks (0.57) in this crystal, we find that the composition of the former is $YBa_2Cu_3O_{6.56}$. Taking into account the actual accuracy of the determination of the volume ratio of the blocks and the amount of oxygen on the basis of the diffraction data, we can assert that in this sample the composition is approximately $YBa_2Cu_3O_{6.5}$. Electron microdiffraction[6,7] has established an orthorhombic structure with a doubled constant a and an alternation of –O–Cu–O–Cu–O– and – –Cu– –Cu– – chains in the $z = 0$ plane for the phases of this composition. It is with this phase that the presence of the plateau $T_c = 50$–60 K on the plot of the superconducting transition temperature versus the oxygen content has been linked in the literature.[7] The doubling of the constant a has not yet been seen by x-ray methods, since it is associated with a change in the position of a single O atom, which is not detected against the background of the x-ray scattering by the heavy Ba, Y, and Cu atoms. The very existence of a plateau on the $T_c(\delta)$ curve in the region $0.5 > \delta > 0.2$ (Refs. 2 and 4) can be taken as a argument in favor of a structurally distinct phase with the composition $YBa_2Cu_3O_{6.5}$.

The blocks of orthorhombic and tetragonal symmetry which coexist in a single crystal (Fig. 2) can be seen most clearly in an analysis of the profiles of the diffraction reflections from $YBa_2Cu_3O_{6.25}$ crystals. In samples whose oxygen content deviates significantly from 6.25 it is more complicated to establish the coexistence of blocks with different symmetries, since blocks of one symmetry begin to predominate in the

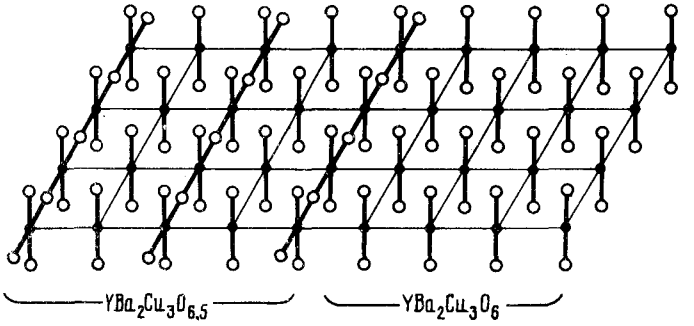

FIG. 2. Model for the joining of $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_3O_6$ blocks in a $YBa_2Cu_3O_{6.24}$ crystal. The $z = 0$ plane of the structure is shown. ●—Cu1 atoms; ○—O1 atoms, which form vertical dumbbells, and O4 atoms, which are part of –O4–Cu1–O4–Cu1–O4 chains. The twinning of the $YBa_2Cu_3O_{6.5}$ blocks is not shown.

volume of the crystal. An important point is that additional oxygen, even in small amounts, becomes distributed in an ordered way among (0,1/2,0) positions in the $z = 0$ planes of the Y phases. In practice, however, the structure and properties of a specific sample vary strongly with the methods used to synthesize and process it. In all cases, a stable structural skeleton of $YBa_2Cu_3O_6$ determines the base of the Y phases with intermediate amounts of oxygen. Only additional oxygen is unstable in these phases. Our results show that the crystals with 6 to 6.5 oxygen atoms, which were characterized in Ref. 2, break up into to tetragonal and orthorhombic structural units with the respective compositions $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_{6.5}$. At the oxygen concentration $O_{6.5}$ the entire crystal may consist of twin blocks of orthorhombic symmetry. It is with this phase that the appearance of a superconductivity with $T_c = 50$–60 K has been linked.[7] As the crystal becomes saturated further with oxygen, local regions with a composition $YBa_2Cu_3O_7$ appear, and the transition temperature $T_c = 50$–60 K is retained.[5] As the amount of oxygen over the entire crystal approaches O_7, the structure is found to consist of orthorhombic twin blocks of $YBa_2Cu_3O_7$, and T_c reaches its second limit ~ 90 K.

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[1]R. J. Cava, B. Batlogy, C. H. Chen *et al.*, Nature **329**, 423 (1987).
[2]I. V. Aleksandrov, A. B. Bykov, I. P. Zibrov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 449 (1988) [JETP Lett. **48**, 493 (1988)].
[3]A. Pietraszko, M. Wolcyrz, R. Horyn *et al.*, Cryst. Res. Technol. **23**, 351 (1988).
[4]W. E. Farneth, R. K. Bordia, E. M. McCarron III *et al.*, Solid State Commun. **66**, 953 (1988).
[5]V. I. Simonov, L. A. Muradyan, V. N. Molchanov, and É. K. Kov'ev, Kristallografiya **33**, 621 (1988) [Sov. Phys. Crystallogr. **33**, 366 (1988)].
[6]T. Ichihashi, S. Iijima, Y. Kubo, and J. Tabuchi, Jpn. J. Appl. Phys. **27**, L1187 (1988).
[7]Y. Kubo, T. Ichihashi, T. Manako *et al.*, Phys. Rev. **B37**, 7858 (1988).
[8]D. C. Mattis, Mod. Phys. Lett. **B2**, 577 (1988).

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