Structure of tetragonal superconducting $YBa_2Cu_{2.862}O_{6.62}$ single crystals with $T_c \approx 50$ K

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(Submitted 2 November 1987)
Pis'ma Zh. Eksp. Teor. Fiz. **46**, No. 11, 457–459 (10 December 1987)

The first data have been obtained on the crystal structure and superconductivity of single crystals of the tetragonal phase in the (1:2:3) Y-Ba-Cu-O system: $a = 3.869(1)$, $c = 11.723(1)$ Å, space group $P4/mmm$, $T_c \approx 50$ K.

It has been established[1,2] that the superconductivity with $T_c = 95$ K is due to an orthorhombic phase of $YBa_2Cu_3O_{7-\delta}$ with an oxygen concentration of approximately 7. The superconductivity of the tetragonal phase, in contrast, has remained an open question. According to Refs. 3 and 4, this phase is not a superconductor, but according to Refs. 5–7, it goes superconducting with $T_c \sim 50$–60 K. These superconducting properties of the tetragonal and orthorhombic phases depend on the oxygen concentration in the sample. It has been suggested that the value of δ for the tetragonal phase lies in the interval 1.0–0.5, while that for the orthorhombic phase is in the region $\delta < 0.5$. Tetragonal phases with $\delta > 0.5$ (Refs. 8–10) are semiconductors. Although tetragonal single crystals with $\delta = 0.2$ were described in Ref. 11, their properties were not studied there.

In this letter we report the first structural data on superconducting single crystals of the tetragonal phase. The single crystals were synthesized in two steps: 1) A mixture of Y_2O_3, $BaCO_3$, and CuO (0.5:2.5:6.5) was sintered at 950 °C in air for ~12 h. The resulting mass, with a large number of small-crystal inclusions, was ground and pressed into tablets under a pressure of several kilobars. 2) The tables were heated to ~1100 °C; the molten material was then cooled, first slowly (over ~6 h), to 800–850 °C and then rapidly, to room temperature. This process was carried out in an oxygen atmosphere at a pressure of 1.2–2.0 atm. The crystals which precipitated in the process were black wafers with a mirror-finish surface and maximum dimensions of $1 \times 0.7 \times 0.020$ mm.

The experimental x-ray material—a set of 3013 reflections in the backward hemisphere, $\sin\theta/\lambda \leqslant 1.00$ Å^{-1}—was obtained from a faceted crystal (Fig. 1) with dimensions of $0.310 \times 0.212 \times 0.009$ mm on an RÉD-4 automatic diffractometer [Mo Kα radiation; graphite monochromator; $\lambda = 0.71069$ Å; μ(Mo Kα) = 286 cm^{-1}]. The crystal was tetragonal with space group $P4/mmm$, $a = 3.869(1)$, $c = 11.723(1)$ Å, and $V = 175.53(8)$ Å^3. The width of the reflections at half-maximum in the region of the resolved α_1/α_2 doublets was 12′. When we scanned twinning-sensitive reflections

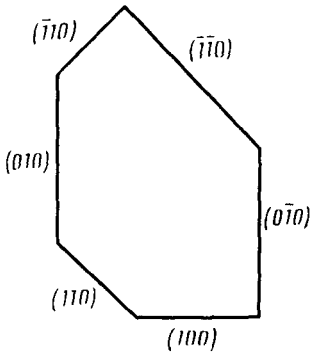

FIG. 1. Shape of the crystal from which the experimental x-ray data were obtained.

of the hh0 type over the angle ω, we observed no significant broadening of the peaks anywhere over the entire range of the azimuthal angle ψ.

To refine the structure, we used 417 reflections with $I > 3\sigma_I$, averaged over equivalent cases ($R_{av} = 2.0\%$). We used the method of least squares[12] in an all-matrix version, allowing for the anisotropy of the thermal vibrations of the atoms. Atomic-scattering curves corrected for anomalousness were taken from Ref. 13. In the final stage, we included the anharmonic components of the thermal vibrations of the atoms for a refinement. The most noticeable deviations from a harmonic law were seen in the thermal vibrations of the Cu1 atoms along the [110] and [1$\bar{1}$0] directions. The structure was refined to $R_W = 1.29\%$, $R = 1.33\%$.

In the refinement process we varied the populations of atoms in the various atomic positions. Deviations from a complete population were established for the following atoms: Cu1 0.862(4), O1 0.35(1), and O3 0.96(1). The composition of the crystals studied turned out to be $YBa_2Cu_{2.862}O_{6.62}$. Here are the coordinates of the atoms, the effective isotropic temperature factors B, and the semiaxes of the thermal-vibration ellipsoids:

Y (1/2 1/2 1/2),	B = 0.45(1) Å^2, (0.072; 0.072; 0.082 Å) .
Ba (1/2 1/2 0.18931(2)),	B = 0.825(7) Å^2, (0.105; 0.105; 0.097 Å) .
Cu1 (0 0 0),	B = 0.93(2) Å^2, (0.120; 0.120; 0.081 Å).
Cu2 (0 0 0.35888(4)),	B = 0.48(1) Å^2, (0.064; 0.064; 0.101 Å) .
O1 (0 1/2 0),	B = 1.5(2) Å^2, (0.19; 0.10; 0.11 Å).
O2 (1/2 0 0.3782(2)),	B = 0.64(2) Å^2, (0.071; 0.090; 0.105 Å) .
O3 (0 0 0.1556(3)),	B = 1.7(1) Å^2, (0.159; 0.159; 0.114 Å) .

Here are the basic interatomic distances, in angstroms:

Y –	O2 x 8	2.404(1)	Cu1* –	O1* x 4	1.935(1)
Ba –	O1* x 4	2.944(1)		O3* x 2	1.824(4)
	O2 x 4	2.941(2)	Cu2 –	O2 x 4	1.948(1)
	O3* x 4	2.765(1)		O3* x 1	2.384(4)

Atoms with a population less than unity are marked with an asterisk.

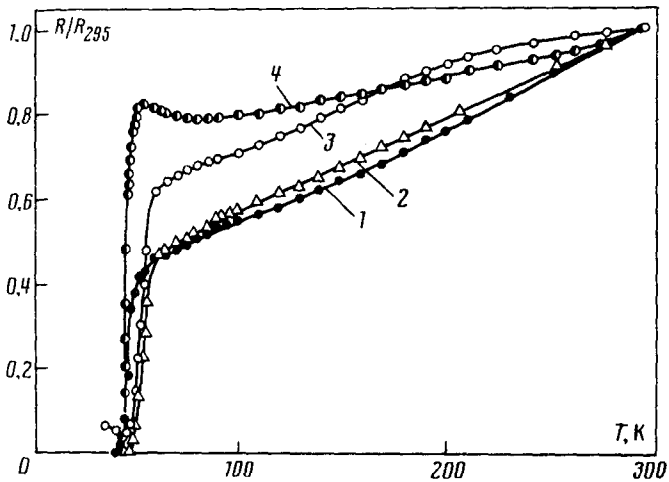

FIG. 2. Temperature dependence of the resistance for four single crystals.

Working from the structural data which have been published on the $YBa_2Cu_3O_{7-\delta}$ system, we traced the correlation between the amount of oxygen and the lattice constants. The lattice constant c turned out to be particularly sensitive. For crystals in which the amount of oxygen is 6.6–7.0, lattice constant c is essentially the same, 11.70 ± 0.02 Å; as the oxygen concentration is reduced from 6.6 to 6.0, this constant increases approximately linearly to 11.85 Å. The value of the parameter c might serve as a diagnostic tool for estimating the oxygen concentration. In our case, we used the diffractometer to measure the parameters of the unit cells for five single crystals. In all cases, the parameters were found to be the same, within the measurement errors. This agreement is evidence that we are dealing with a single tetragonal phase (single in terms of oxygen concentration).

The conductivity of the $YBa_2Cu_{2.862}O_{6.62}$ single crystals was measured in the *ab* plane by a four-contact method; the result is $\sigma_{195\,K} \approx 200$–$400$ S/cm. Figure 2 shows the temperature dependence of the resistance of four of the single crystals. In the resistance of all these crystals we see a similar metallic behavior; furthermore, their superconducting transition temperatures are identical, $T_c \approx 50$ K.

In summary, the tetragonal phases, like the orthorhombic phases, exhibit superconducting properties. Whether these properties are actually manifested depends on the oxygen concentration, which in turn is determined by the conditions under which the oxide phases are synthesized.

We wish to thank the participants of a seminar led by I. F. Shchegolev on high-temperature superconductivity at the Institute of Solid State Physics, Academy of Sciences of the USSR, for a discussion of these results.

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Translated by Dave Parsons