Structure of the single crystal of a nonstoichiometric phase with a high-temperature superconductivity ($Y_{1.4}BaCu_{1.6}O_5$)

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(Submitted 21 July 1987)
Pis'ma Zh. Eksp. Teor. Fiz. **46**, No. 5, 188–189 (10 September 1987)

The structure of the single crystal of the nonstoichiometric phase $Y_{1.4}BaCu_{1.6}O_5$ has been determined (the polycrystalline sample goes superconducting at 94–91 K). This phase corresponds to a filling of some of the positions of the Y atoms by Cu^{III} atoms.

It has recently been shown[1] that $LnBa_2Cu_3O_7$ compounds, where Ln = Y, Nd, Sm, Eu, Gd, Dy, Ho, or Yb, go superconducting at 80–96 K. In the course of a study of the conditions for the synthesis of $YBa_2Cu_3O_7$, by sintering in an O_2 flow for 0.5 h at 900–950 °C a mixture of Y_2O_3, $BaCO_3$ (BaO_2), and CuO, ground with ethyl alcohol and dried in air, we obtained single crystals of type I. We have carried out x-ray structural study of these crystals.

The dark-green, opaque, needle-shaped crystals of type I, with long dimension along the *b* axis, have an orthorhombic structure. At 150 K their lattice constants are $a = 12.161(6)$, $b = 5.664(4)$, and $c = 7.121(4)$ Å; we also find $Z = 4$, $Y_{1.4}BaCu_{1.6}O_5$, $d_{calc} = 6.00$ g/cm^3, and a space group *Pnma*. At 150 K we measured the intensities of 2101 *hkl* and $\bar{h}k\bar{l}$ reflections (λ MoK_α, $\theta/2\theta$ scanning, $2\theta_{max} = 70°$), using a Sinteks $R2_1$ diffractometer. Absorption was taken into account [$\mu(MoK_\alpha) = 320.9$ cm^{-1}]. The type I structure was refined to $R = 0.027$ ($Rw = 0.026$) on the basis of 926 independent reflections. The composition of the single crystal under study was refined in the course of a refinement of the structure through the fitting of *f* curves to minimize the *R*-factor. This minimum value of the *R*-factor corresponds to a structure in which there are Y and Cu^{III} atoms at YC1 and YC2 positions (Fig. 1) in the proportions 0.7Y + 0.3Cu. The single crystal of type I thus has the composition (YC1) (YC2) $BaCuO_5 = Y_{1.4}BaCu^{III}_{0.6}Cu^{II}O_5 = Y_{1.4}BaCu_{1.6}O_5$, which corresponds to an electrically neutral structure and to the occupation of some of the Y-atom positions by Cu^{III} atoms.

The Ba atom is coordinated with 11 oxygen atoms at distances of 2.600–3.243(5) Å; the coordination polyhedron is a prism with trapezoids at its bases and three additional vertices. Each of the trivalent YC1 and YC2 atoms is coordinated with seven O atoms at distances of 2.289–2.378(4) and 2.305–2.352(4) Å. Their polyhedra are trigonal prisms with a common additional vertex. The Cu atom is coordinated in a tetragonal pyramid with five O atoms; the Cu-O distances are 1.980–2.015(4) Å.

The polycrystalline sample of type I undergoes a transition to a superconducting state at 94–91 K (according to measurements by a four-probe method).

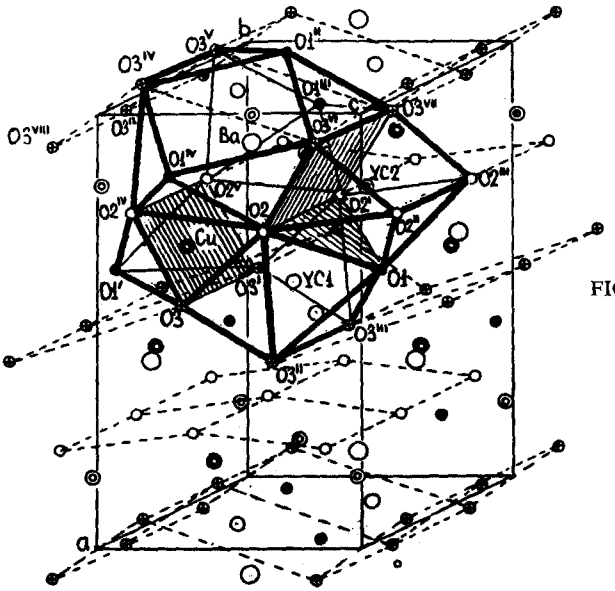

FIG. 1. Structure of the crystal of type I.

In addition to the single crystals of type I, the following structures have been identified in the Y-Ba-Cu-O system: a single-crystal structure $YBa_2Cu_3O_{8-x}$ with $x = 1.0(4)$ [$a = 3.827(1)$, $b = 3.877(1)$, $c = 11.708(6)$ Å, $Z = 1$, $d_{calc} = 6.37$ g/cm^3, space group *Pmmm*, incomplete occupation of the positions of one of the O atoms was established through a refinement of populations][2]; $YBa_2Cu_3O_{6+x}$ with $x \approx 0.5$ [$a = 3.859(3)$, $c = 11.71(1)$ Å, $Z = 1$, $d_{meas} = 5.93 \pm 0.22$ g/cm^3, space group $P\bar{4}m2$; the composition was found by a microprobe method][3]; and the stoichiometric phase Y_2BaCuO_5 ($Z = 4$, $d_{meas} = 5.65 \pm 0.5$ g/cm^3, space group *Pbnm*; the composition was found by a microprobe method),[3] which contains only divalent copper and which has the same structural motif as the nonstoichiometric phase of type I studied by us.

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Translated by Dave Parsons