The structure of superconducting $TlBa_2(Ca_{0.87}Tl_{0.13})Cu_2O_7$ single crystals with $T_c \sim 80$ K

N. N. Kolesnikov, V. E. Korotkov, M. P. Kulakov, G. A. Lagvenov, V. N. Molchanov, L. A. Muradyan, V. I. Simonov, R. A. Tamazyan, R. P. Shibaeva, and I. F. Shchegolev
Institute of Solid State Physics, Academy of Sciences of the USSR

(Submitted 7 April 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **50**, No. 1, 40–43 (10 July 1989)

The crystal structure of the single crystals of the 1212 phase has been determined in the Tl–Ba–Ca–Cu–O system; $a = 3.8472(5)$, $c = 12.721(3)$ Å, and space group $P4/mmm$. The chemical formula of this phase has been determined more accurately: $TlBa_2(Ca_{0.87}Tl_{0.13})Cu_2O_7$, $T_c \sim 80$ K, the Meissner effect is 75–80%.

Several new high-T_c superconductors of the Tl–Ba–Ca–Cu–O system, with the superconducting transition temperatures ranging from 80 K to 125 K, have recently been synthesized and their compositions and crystal structures have been determined.[1–8] The structural data for single crystals of all phases of the class

 0021-3640/89/130047-05$01.00

$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1,2,3$) have now been determined.[6,7,9] With regard to the phases of the class $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, the structure of only one phase ($n = 3$) of the four known phases ($n = 1,2,3,4$) has been determined from the single-crystal data.[10,11]

We are reporting here the first results of an x-ray diffraction study of single crystals of the 1212 phase: $TlBa_2CaCu_2O_7$.

The single crystals were grown by slowly cooling the melt in alundum containers in flowing oxygen. The starting material was a mixture of Tl_2O_3, CaO, BaO, and CuO powders; the composition of the charging material was $TlCaBa_2Cu_2O_x$. The cooling rates were 5, 150, and 250 deg/h in the temperature intervals 1250–1050 K, 1050–700 K, and 700–300 K, respectively. Upon termination of the process a solid, crystallized mass containing cavities of volume up to 0.5 cm^3 formed in the container. The single crystals were extracted from the cavity walls.

A fairly large single crystal was initially chosen for the experiment. A preliminary x-ray diffraction study of this single crystal by the photomethod showed that it is, according to the lattice constant c ($c = 12.7$ Å), a 1212 phase, that it is a single-phase

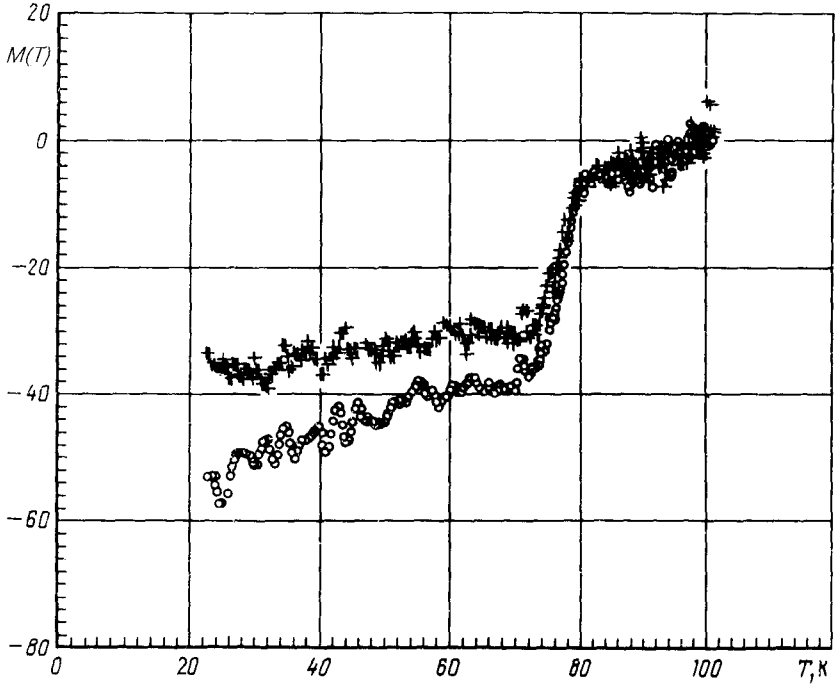

FIG. 1. Temperature dependence of the magnetic moment $M(T)$ of a single crystal of $TlBa_2(Ca_{0.87}Tl_{0.13})Cu_2O_7$ in a magnetic field $H = 10$ Oe. Diamagnetic screening curve (ZFC)—(0). Meissner expulsion curve (FC)—(+). [The magnetic moment $M(T)$ is given in arbitrary units, 20 (arb. unit) = 10^{-2} msu].

TABLE I. The coordinates of the atoms, their thermal parameters B_{equiv} (Å^2), and the semiaxes of the ellipsoids of the thermal vibrations (Å) along the a, b, and c directions.

Atom	x/a	y/b	z/c	B_{equiv}	Semiaxes of thermal. vibr. ellipsoids		
					a	b	c
Tl	0.0877 (4)	0	0	1.76 (4)	0.202 (3)	0.143 (2)	0.075 (2)
Ba	0.5	0.5	0.2155 (1)	0.55 (1)	0.079 (1)	0.079 (1)	0.092 (2)
Cu	0	0	0.3740 (1)	0.44 (2)	0.066 (2)	0.066 (2)	0.089 (3)
Ca(Tl)	0.5	0.5	0.5	0.47 (4)	0.075 (4)	0.075 (4)	0.081 (5)
O1	0.5	0	0.3797 (5)	0.69 (8)	0.086 (7)	0.086 (7)	0.11 (1)
O2	0	0	0.1582 (7)	1.1 (1)	0.129 (8)	0.129 (8)	0.09 (2)
O3	0.5	0.5	0	2.6 (3)	0.21 (7)	0.21 (7)	0.09 (3)

sample, and that the quality of this sample is such that it can be used to obtain experimental x-ray data. We have then cut out from this sample a wafer measuring $0.25\times0.25\times0.04$ mm, which was used in the experiment.

The superconducting transition of the wafer cut out from the single crystal was detected from the temperature dependence of the magnetic moment. To measure the magnetic moment, we used a magnetometer based on an rf SQUID with a sensitivity of 5×10^{-3} emu for a sample with dimensions $0.5\times0.5\times0.25$ mm in a 10-Oe magnetic field. Figure 1 shows the results on diamagnetic screening (ZFC) of a test single crystal in a magnetic field $H = 10$ Oe (0) and on the Meissner expulsion of the magnetic flux (FC) (+). Since the volume of the crystal is small, the ZFC and FC curves do not stand out too prominently against the background of the magnetometer noise. We see that the superconducting transition begins at 80 K and that the transition width is 10 K. The ratio of the Meissner-expulsion signal to the diamagnetic-screening signal is 75–80%.

The experimental data were obtained with a RÉD–4K automatic diffractometer (Mo $K\alpha$ radiation, graphite monochromator, ω and $\omega/2\theta$ variable-speed scanning, $\sin\theta/\lambda\leqslant0.8$). We measured a total of 2509 reflections, of which 284 reflections with

TABLE II. Atomic spacings (in Å) for $TlBa_2(Ca_{0.87}Tl_{0.13})Cu_2O_7$.

Cu – O1	1.924 (3) × 4	Ca(Tl) – O1	2.458 (4) × 8
Cu – O2	2.745 (9) × 1	Ba – O1	2.839 (5) × 4
Tl – O2	2.040 (9) × 2	Ba – O2	2.816 (2) × 4
Tl – O3	2.493 (1) × 2	Ba – O3	2.741 (1) × 1
Tl – O3	2.968 (1) × 2		

$I \geqslant 3\sigma(I)$ were independent reflections. The correction for the absorption was introduced numerically, $\mu = 411.7$ cm^{-1}. We used a tetragonal crystal with a space group $P4/mmm$, $a = 3.8472(5)$, $c = 12.721(3)$ Å, and $Z = 1$. The model of the structure, determined from the analysis of the Patterson function, is the same as the model found from the powder data.[12] A refinement of this model by the method of least squares with a Tl atom in the 000 site proved, however, to be unsatisfactory. With anomalously large thermal parameters of Tl in the *ab* plane, the minimum value of the R factor, with allowance for the anisotropy of the thermal vibrations of the atoms, was 24%. The value of the R factor decreased appreciably (to 5%) upon equiprobable statistical distribution of the Tl atom among the four sites situated 0.34 Å from the 000 point. The magnitude of the displacement was determined from an analysis of the electron-density differencing synthesis. A more accurate determination of the degree to which the atoms fill their sites showed that there is a partial presence of Tl in the 1/2 1/2 1/2 site. As a result, we were able to refine the formula for the 1212 phase: $TlBa_2(Ca_{0.87}Tl_{0.13})Cu_2O_7$. The structure was also determined more accurately: $R = 3.4\%$ and $R_w = 3.2\%$. The atomic coordinates, the thermal parameters of the atoms, B_{equiv}, and the semiaxes of the thermal-vibration ellipsoids (in Å) along the *a*, *b*, *c* directions are listed in Table I. The main atomic spacings are given in Table II.

Figure 2 shows the crystal structure of $TlBa_2(Ca_{0.87}Tl_{0.13})Cu_2O_7$. In this structure the coordination polyhedra Ba, Ca, and Cu are similar in configuration to the polyhedra Ba, Y, and Cu(2), respectively, in the $YBa_2Cu_3O_7$ structure.[10] In contrast with the latter structure, however, in which the Cu(2) atom deviates from the oxygen plane by 0.266 Å, the undulation of the cuprate layer CuO_2 in 1212 structure is less pronounced: The Cu atom deviates from the plane of the four oxygens by 0.07 Å. The coordination polyhedron of the Tl atom is a strongly distorted octahedron, whose distortion is similar to that in the 1223, 2223, and 2212 structures,[6,7,10] although in the

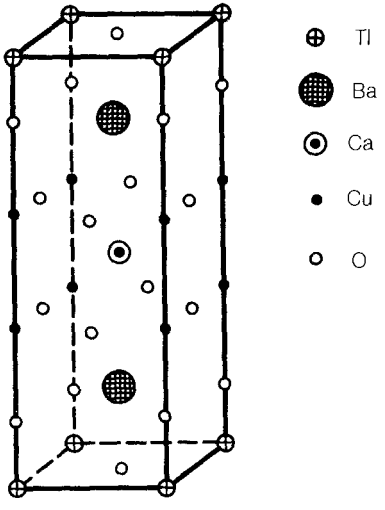

FIG. 2. The crystal structure of $TlBa_2(Ca_{0.87}Tl_{0.13})Cu_2O_7$.

last two structures the distortion of the polyhedron stems from the statistical displacement of the oxygen atom, rather than the Tl atom. The structural feature of all phases of the $TlBa_2Ca_{n-1}Ca_nO_{2n+3}$ system may possibly be this sort of disorder of the Tl atom, while the structural feature of all phases of the $Tl_2Ba_2Ca_{n-1}Ca_nO_{2n+4}$ system may be the statistical disorder of the oxygen atom. It should not be ruled out that these structural features could be caused by the modulated structure in the Tl crystals.[3,8]

We are deeply grateful to P. A. Kononovich for assistance with this study and for a discussion of the results.

[1]Z. Z. Sheng and A. M. Hermann, *Nature* **332**, 55 (1988).
[2]Z. Z. Sheng and A. M. Hermann, *Nature* **332**, 138 (1988).
[3]R. M. Hazen *et al.*, Phys. Rev. Lett. **60**, 1657 (1988).
[4]S. S. P. Parkin *et al.*, Phys. Rev. Lett. **60**, 2539 (1988).
[5]S. S. P. Parkin *et al.*, Phys. Rev. Lett. **61**, 750 (1988).
[6]C. C. Torardi *et al.*, Science **240**, 631 (1988).
[7]M. A. Subramanian *et al.*, *Nature* **332**, 420 (1988).
[8]S. S. P. Parkin *et al.*, Phys. Rev. B **38**, 6531 (1988).
[9]C. C. Torardi *et al.*, Phys. Rev. B **38**, 225 (1988).
[10]M. A. Subramanian *et al.*, J. Sol. State Chem. **77**, 192 (1988).
[11]B. Morosin *et al.*, Physica C **12**, 587 (1988).
[12]M. Hervien *et al.*, J. Sol. State Chem. **75**, 212 (1988).
[13]M. A. Beno *et al.*, Appl. Phys. Lett. **51**, 367 (1987).

Translated by S. J. Amoretty