

Atomic structure of $Tl_2Ba_2CaCu_2O_8$ single crystals before and after the transition to the superconducting state

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The atomic structure of single crystals of the Tl 2212 phase at 296, 160, and 60 K has been refined by x-ray structural analysis. The superconducting transition is accompanied by significant displacements of the atoms of the TlO layer and by anomalous changes in the CuO_5 pyramids. The macroscopic symmetry of the crystal remains tetragonal as this phase transition occurs. The local orthorhombic distortions of the structure associated with displacements of Tl atoms occur before and after the phase transition.

Eight phases with the general chemical formula $Tl_m Ba_2 Ca_{n-1} O_{2n+m+2}$ ($m = 1, 2; n = 1, 2, 3, 4$) have been identified in the Tl - Ba - Ca - Cu - O system.¹⁻⁶ These phases have superconducting transition temperatures from 80 to 120 K. The lattice constants $a = b \approx 3.85 \text{ \AA}$ are approximately the same for all these phases, while the values of the lattice constant c differ sharply. Here are typical values for the various phases of composition $[m, n]$: 6.69 for $[1, 1]$, 12.73 for $[1, 2]$, 15.87 for $[1, 3]$, 19.10 for $[1, 4]$, 23.15 for $[2, 1]$, 29.39 for $[2, 2]$, 36.26 for $[2, 3]$, and 42.00 \AA for $[2, 4]$. Most of the structural studies of the Tl phases have been carried out on ceramic samples.^{5,7-9} The atomic restructuring which accompanies the superconducting phase transition for these phases is still being debated.

In this letter we are reporting an x-ray structural study of a $Tl_2Ba_2CaCu_2O_8$ single crystal with $T_c = 110 \text{ K}$, before and after the transition to the superconducting state. The crystals were grown and studied at the Institute of Solid State Physics, Russian Academy of Sciences. The growth methods, the results of the conductivity measurements, and the results of the structural studies at room temperature are reported in Ref. 10.

In the present study, the x-ray diffraction was carried out on a HUBER-5042 four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochromator, $\omega/2\theta$ scanning, $\sin \vartheta / \lambda \leq 1.22$), fitted with a Displex-202 closed-type helium attachment with two cooling cycles. The integral intensities were measured on a spherical sample 0.226 mm in diameter at temperatures of 290, 160, and 60 K. These measurements yielded 1844, 1408, and 1482 reflections, respectively. Analysis of the diffraction pattern confirmed the tetragonal symmetry group for this crystal, with $I4/mmm$. The lattice constants were found to be $a = 3.8545(3)$, $c = 29.317(2) \text{ \AA}$; $a = 3.8501$, $c = 29.261(2) \text{ \AA}$, and $a = 3.8486(4)$, $c = 29.232(2) \text{ \AA}$, respectively, at 296, 160, and

60 K. Satellite reflections indicating a modulation in the structures were observed by electron diffraction in several Tl superconductors in Refs. 5, 7, and 9. In our case, we did not observe satellite reflections in the x-ray diffraction, even when a special scan of reciprocal space was carried out.

The model of Refs. 11–14 was used as a starting point for refining the atomic structure of the $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (2212) single crystal. The structural parameters were refined by the method of least squares. The results were monitored with the help of difference syntheses of the electron density. The strongly correlated parameters were refined by step-by-step scanning.¹⁵ The final divergence factors—the ordinary factor and the weighted factor (R/R_w)—were found to be 0.0244/0.0232 (296 K), 0.0292/0.0272 (160 K), and 0.0307/0.0294 (60 K). The refined coordinates of the basic atoms and their equivalent thermal parameters are listed in Table I.

The results of this structural study can be summarized as follows. The Ca atoms in their (0, 0, 0) crystallographic sites are replaced isomorphically by Tl atoms with a probability of 0.12. The Tl atoms fill their basic site near the point (0.5, 0.5, 0.213) with a probability of 0.90. We do not rule out the possibility that 10% of the sites which are vacant in terms of Tl atoms are filled isomorphically by lighter Cu atoms, as

TABLE I. Coordinates of the basal atoms, site filling factors q , and equivalent thermal parameters B_{eq} . The first through third lines correspond to temperatures of 296, 160, and 60 K.

Atom	q	x/a	y/b	z/c	B_{eq}
Tl	0,923(4)	0,516	0,516	0,21365(2)	1,57(2)
	0,888(4)	0,51075	0,51075	0,21350(2)	1,18(2)
	0,900(4)	0,5165	0,5165	0,21357(2)	0,98(2)
Ba	1,0	0,0	0,0	0,12157(2)	0,82(2)
	1,0	0,0	0,0	0,12138(1)	0,50(2)
	1,0	0,0	0,0	0,12147(2)	0,45(2)
(Ca,Tl)	0,88+0,12	0,0	0,0	0,0	0,74(4)
	0,89+0,11	0,0	0,0	0,0	0,41(5)
	0,87+0,13	0,0	0,0	0,0	0,40(4)
Cu	1,0	0,5	0,5	0,05402(4)	0,58(3)
	1,0	0,5	0,5	0,05395(3)	0,36(2)
	1,0	0,5	0,5	0,05387(4)	0,32(2)
O1	1,0	0,0	0,5	0,0526(1)	1,0(1)
	1,0	0,0	0,5	0,0526(1)	0,6(1)
	1,0	0,0	0,5	0,0526(2)	0,6(1)
O2	1,0	0,5	0,5	0,1456(3)	1,5(2)
	1,0	0,5	0,5	0,1448(2)	1,0(3)
	1,0	0,5	0,5	0,1452(3)	0,9(2)
O3 ²⁾	1,0	0,575(3)	0,575(3)	0,2808(5)	2,7(4)
	1,0	0,566(4)	0,566(4)	0,2821(3)	2,2(3)
	1,0	0,568(4)	0,568(4)	0,2815(7)	2,4(4)

*The thermal parameters of the O3 atom were refined in the isotropic approximation.

indicated in Ref. 10. However, our experimental data are not sufficiently accurate to reliably confirm that copper atoms or any other atoms occupy these sites. An important structural feature is the displacement of the Tl atoms away from the fourfold axis (Table I). In addition to these displacements of the Tl atoms, there are displacements of the O3 oxygen atoms, which coordinate the thallium and which are part of barium polyhedra. These displacements lower the local symmetry of the structure to orthorhombic. The orthorhombic regions of the crystal are rotated 90° with respect to each other. Statistically, they preserve a tetragonal symmetry for the macroscopic crystal. Formally, the situation is the same as ordinary twinning. However, our special analysis of the profiles of the diffraction reflections revealed no splitting of the peaks. A similar situation had been found previously¹⁶ in single crystals of a macroscopically tetragonal phase of the compound $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$. The absence of a splitting may be

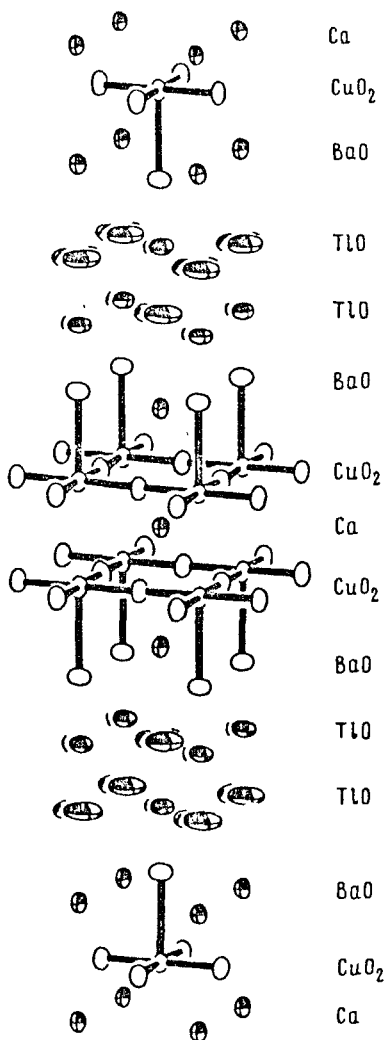


FIG. 1. Atomic structural model of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$.

attributed to a concentration of vacancies at block boundaries and to a relief of stress there. The methods which we used were not capable of determining the dimensions of the regions of a local orthorhombic symmetry.

The Tl atoms in this structure are in a distorted octahedron of O atoms with three pairs of Tl–O distances: ~ 2.00 , 2.35 , and 2.83 Å. This coordination is typical of thallium.^{13,17} The copper atoms are in tetragonal pyramids with Cu–O1 distances ~ 1.93 Å (these are the distances to the four oxygen atoms of the base of the pyramid). The Cu–O₂ distance, to the apical oxygen, is much larger, and has a far stronger temperature dependence. It has values $\sim 2.683(8)$ at $T = 296$ K, $2.658(8)$ at $T = 160$ K, and $2.670(7)$ Å at $T = 60$ K. The coordination polyhedron of the Ca atom is a truncated square prism, whose height is 0.55 Å smaller than the lateral edge. The largest (in volume) polyhedron in the structure is the [BaO₆] polyhedron, with a set of Ba–O distances from 2.78 to 2.89 Å. The nature of the thermal vibrations of the atoms in this structure is illustrated by the ellipsoids in Fig. 1.

The phase transition to a superconducting state is not accompanied by a change in symmetry or a change in the metric of the crystal lattice. Some of the structural properties nonetheless exhibit an anomalous temperature dependence near the phase transition. The behavior of the basic interatomic distances in the structure as the temperature is varied, before and after the phase transition, is shown in Table II. The greatest transition-related change is in the Cu–O2 distance. Upon cooling from 296 to 160 K, this distance naturally decreases from $2.683(8)$ to $2.658(8)$ Å. Upon the transition to the superconducting state, it increases again, to $2.670(7)$ Å at $T = 60$ K. Another anomaly in the behavior of the interatomic distances is seen in the relative arrangement of neighboring CuO₂ layers. At temperatures of 296 , 160 , and 60 K, the distances between the layers in the structure are 3.084 , 3.076 , and 3.077 Å. The excursion of Cu atoms from their oxygen layer decreases monotonically with decreasing temperature: 0.042 Å to 0.041 Å and (more sharply) to 0.036 Å. The Cu–O2 distance in the literature tells us that the excursion of Cu atoms from the oxygen layer and the temperature of the superconducting phase transition are strongly correlated with each

TABLE II. Basic interatomic distances in the Tl₂Ba₂CaCu₂O₈ structure.

Cation	Anion	Distance			Number of bonds
		296 K	160 K	60 K	
Tl	O2	1.998(8)	2.012(6)	2.000(6)	1
	O3	2.00(1)	2.03(1)	2.00(1)	1
	O3	2.32(2)	2.37(1)	2.355(9)	2
	O3	2.85(1)	2.81(1)	2.840(8)	2
Ba	O1	2.793(3)	2.786(2)	2.784(1)	4
	O2	2.815(2)	2.807(3)	2.808(1)	4
	O3	2.89(2)	2.85(1)	2.86(1)	1
Cu	O2	2.683(8)	2.658(8)	2.670(7)	1
	O1	1.928(1)	1.926(1)	1.925(1)	4
Ca	O1	2.468(3)	2.464(2)	2.464(2)	8

other. These structural properties are determined by the valence states of the Cu and O atoms. In the crystal structure $\text{TlBa}_2\text{LaCu}_2\text{O}_7$ (Ref. 17), for example, which does not go superconducting (the formal valence of the copper atom is Cu^{2+}), the Cu–O2 distance is $2.452(5) \text{ \AA}$ —far shorter than the corresponding distances in crystals which do go superconducting. The excursion of the Cu atom from the oxygen layer in the $\text{TlBa}_2\text{LaCu}_2\text{O}_7$ structure, 0.180 \AA , is substantially larger than that in the superconducting phases. Similar changes in the structural parameters characterizing the structure of the CuO_2 layer and the distance of the apical oxygen, O2, are associated with the superconducting phase transition and can be detected reliably by x-ray diffraction. In analyzing the structural changes, one must examine the behavior of the CuO_2 layer in association with the apical oxygen O2.

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- ¹Z. Z. Sheng and A. M. Hermann, *Nature* **332**, 138 (1988).
- ²R. M. Hazen, L. W. Finger, R. J. Angel *et al.*, *Phys. Rev. Lett.* **60**, 1657 (1988).
- ³S. S. Partsein, V. Y. Lee, E. M. Engler *et al.*, *Phys. Rev. Lett.* **60**, 2539 (1988).
- ⁴C. C. Torardi, M. A. Subramanian, J. C. Calabrese *et al.*, *Science* **240**, 631 (1988).
- ⁵S. S. P. Parkin, V. Y. Lee, A. I. Nazzal *et al.*, *Phys. Rev. Lett.* **61**, 750 (1988).
- ⁶M. Hervieu, A. Maignan, C. Martin *et al.*, *Mod. Phys. Lett. B* **2**, 1103 (1988).
- ⁷S. S. P. Parkin, V. Y. Lee, A. I. Nazzal *et al.*, *Phys. Rev. B* **38**, 6531 (1988).
- ⁸K. Yvon and M. Francois, *Z. Phys. B* **76**, 413 (1989).
- ⁹R. B. Beyers, S. S. P. Parkin, V. Y. Lee *et al.*, *IBM J. Res. Dev.* **33**, 228 (1989).
- ¹⁰L. A. Muradyan, V. N. Molchanov, R. A. Tamazyan *et al.*, *Sverkhprovodimost' (KIAE)* **4**(2), 277 (1991) [*Superconductivity* **4**(2) 237 (1991)].
- ¹¹M. A. Subramanian, J. C. Calabrese, C. C. Torardi *et al.*, *Nature* **332**, 420 (1988).
- ¹²M. Onoda, S. Kondon, K. Fukuda, and M. Sato, *Jpn. J. Appl. Phys.* **27**, L1234 (1989).
- ¹³Y. Gao, R. Li, P. Coppens *et al.*, *Acta Cryst. A* **45**, FC11 (1989).
- ¹⁴D. E. Cox, C. C. Torardi, M. A. Subramanian *et al.*, *Phys. Rev. B* **38**, 6624 (1988).
- ¹⁵L. A. Muradyan, S. F. Radaev, and V. I. Simonov, *Methods of Structural Analysis*, Nauka, Moscow, 1989, p. 5.
- ¹⁶V. N. Topnikov, V. I. Simonov, L. A. Muradyan *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **46**, 457 (1987) [*JETP Lett.* **46**, 577 (1987)].
- ¹⁷V. N. Molchanov, R. A. Tamazyan, V. I. Simonov *et al.*, *Kristallografiya* (in press).

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