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LETTERS TO THE EDITOR

The 125 K Superconductor $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$: A Tentative Structural Model

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The structure of the 125 K superconductor $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$ has been studied by X-ray powder diffraction and high-resolution electron microscopy. A structural model of this phase with tetragonal symmetry (a = 3.85 Å, c = 35.6 Å; *I4/mmm*) is proposed. The structure can be described as an intergrowth of oxygen-deficient triple perovskite layer $[ACuO_{3-y}]_3$ with triple-distorted sodium chloride-type layers $[A'O]_3$. © 1988 Academic Press, Inc.

The discovery of superconductivity in the systems Bi–Sr–Cu–O (*1*) and Bi–Sr–Ca–Cu–O (*2*) has suggested the possibility of replacing bismuth by a smaller trivalent cation such as Tl(III). Superconductivity above 100 K has indeed been observed in the system Tl–Ba–Ca–Cu–O (*3, 4*). Two phases, $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$, were assumed to be responsible for superconductivity at 108 and 125 K, respectively (*5*). The structure of the first one was recently studied (*6, 7*) and it appears, according to our observations, that the superconducting properties of this phase can be explained by the presence of intergrowth defects "$TlBa_2CaCu_2O_7$," involving thallium deficiency, in agreement with the formulation $Tl_{2-x}Ba_2CaCu_2O_8$. The structure of the oxide $Tl_2Ba_2Ca_2Cu_3O_{10}$ is not known, and the relationship between the presence of Cu(III) and superconductivity in this compound is so far not understood. The possibility of nonstoichiometry leading to the composition $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$ has to be considered. We report here the structural study of this phase.

The procedure for preparing $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$ is as follows: Appropriate amounts of Tl_2O_3, BaO_2, CaO, and CuO, corresponding to the nominal composition $Tl_2Ba_2Ca_2Cu_3O_{10}$, were mixed and ground in an agate mortar, then pressed into the form of bars. The bars were placed in an alumina crucible and heated in a sealed quartz tube at temperatures ranging from 750 to 900°C during times ranging from 3 to 12 hr. The sample was cooled slowly to room temperature. Under these conditions, the X-ray diffraction analysis shows that the resulting sample can be considered as a pure phase to within the precision of this method, i.e., for at least 90% of the sample.

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Resistance measurements and diamagnetism determination with a vibrating sample magnetometer by methods previously described (*7*) confirm a resistive transition at 125 K and a diamagnetic volume close to 15%.

The analysis of the electron diffraction patterns and X-ray diffractograms of this phase confirmed the parameters of the tetragonal cell and the reflection conditions, hkl: $h + k + l = 2n$; $a = 3.854$ Å, $c = 35.60$ Å.

In order to establish a structural model a high-resolution electron microscopy study was performed on crystals of this compound, with a Jeol 200 CX microscope ($C_s = 0.8$ mm).

The HREM images were recorded for different focus values (Fig. 1 is an example); a comparison with those obtained for $Tl_2Ba_2CaCu_3O_8$ (*7*) allowed a structural model to be proposed. Figure 2 shows examples of [010] HREM images for both oxides $Tl_2Ba_2CaCu_2O_8$ "2212" (Fig. 2a) and $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$ "2223" (Fig. 2b). The main contrast consists of quadruple staggered rows with thickness of about 6.6 Å of bright spots corresponding to the positions of the heavy cations (Tl and Ba); these rows are separated by parallel rows of smaller and less intense white spots, corresponding to copper layers: two rows in "2212" (Fig. 2a) and three rows, spaced about 11.2 Å, in "2223." Such layers and periodicity suggest the presence for the latter of a triple perovskite layer.

In order to check this model, the X-ray diffractogram of this phase was obtained with an Inel counter using Cu$K\alpha_1$ radiation. Thirty reflections, i.e., 58 *hkl* values, were used for intensity calculations, which were performed in the most symmetric space group, *I*4/*mmm*. Refining successively the atomic coordinates and the thermal and occupancy factors, the reliability factor calculated for the intensities could be lowered to $R = 0.07$ for the atomic coordinates and for the interatomic distances given in Tables I and II. Clearly, this study cannot be considered as an accurate structural determina-

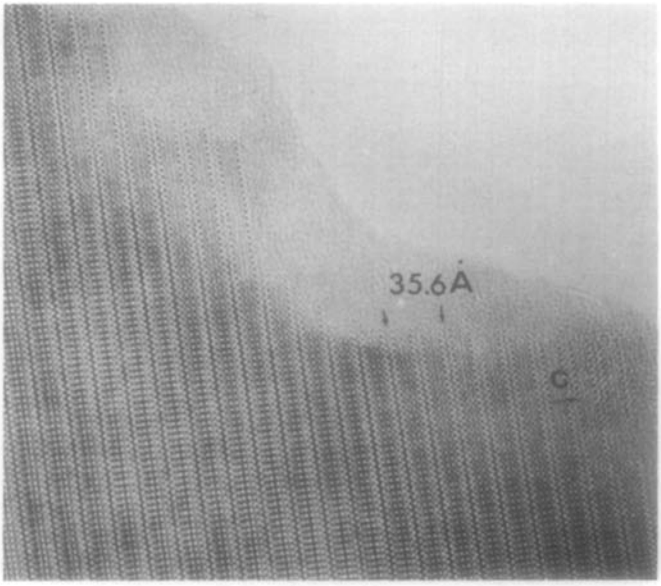

FIG. 1. $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$: [010] HREM image. The dark spots are equivalent to the ion positions.

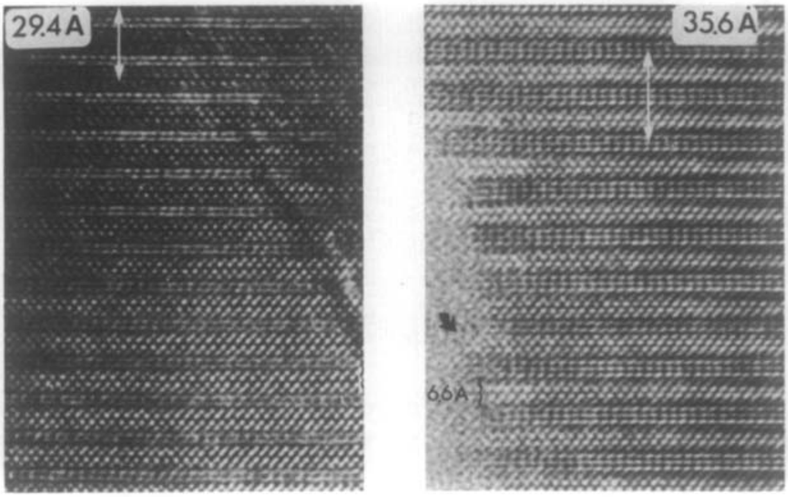

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FIG. 2. [010] images obtained for (a) $Tl_2Ba_2CaCu_2O_8$ "2212" and (b) $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$ "2223," assumed for the same focus value. Note the defect (black arrow) corresponding to the appearance of a "2212" inclusion in a "2223" matrix.

tion, but it allows a structural model to be proposed. Thus, the structure of the oxide $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$ (Fig. 3b) can be described as the intergrowth of an oxygen-deficient triple perovskite layer $[ACuO_{3-y}]_3$ with a triple-distorted sodium chloride-type layer $[A'O]_3$. The sodium chloride-type layers are built up from double layers $[TlO]_\infty$ separated by 2.2 Å, as in the $Tl_2Ba_2CaCu_2O_8$ structure (Fig. 3a), and surrounded with $[A'O]_\infty$ layers containing mainly barium, similar to the $[BaO]_\infty$ layers observed for $Tl_2Ba_2CaCu_2O_8$. In the triple perovskite layers the oxygen sites corresponding to the basal planes of the CuO_6 octahedra, i.e., parallel to (001), are fully occupied, as are the oxygen sites located at the same level as the barium ions. By contrast, the anionic sites

TABLE I

$Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$

		x	*y*	*z*	*B* (Å²)	
Tl	4(e)	0.0	0.0	0.2185(6)	0.1	0.879(9)
Ba	4(e)	0.0	0.0	0.6428(4)	0.2	1.0
Ca[a]	4(e)	0.0	0.0	0.5432(1)	0.4	1.0
Cu	2(a)	0.0	0.0	0.0	0.1	1.0
Cu	4(e)	0.0	0.0	0.0995(8)	0.1	1.0
O(1)	4(c)	0	0.5	0.0	1.0	1.0
O(2)	4(e)	0	0	0.049(6)	1.0	0.47(6)
O(3)	8(g)	0	0.5	0.095(3)	1.0	1.0
O(4)	4(e)	0	0	0.155(5)	1.0	1.0
O(5)	4(e)	0	0	0.718(8)	1.0	1.0

Note. $a = 3.854$ Å; $c = 35.6$ Å; *I4/mmm*; $x = 0.18$, $\delta = 0.47$. The *B* factors of oxygen atoms were fixed to 1 Å.

[a] 0.97 Ca and 0.03 Tl.

TABLE II

INTERATOMIC DISTANCES (Å) OF $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$

Tl–O(5)	2.72 × 4	Cu(1)–O(1)	1.92 × 4
Tl–O(4)	2.27 × 1	Cu(1)–O(2)	1.76 × 2δ
Tl–O(5)	2.25 × 1		
		Cu(2)–O(3)	1.93 × 4
Ba–O(3)	2.57 × 4	Cu(2)–O(4)	1.98 × 1
Ba–O(4)	2.76 × 4	Cu(2)–O(2)	1.78 × δ
Ba–O(5)	2.67 × 1		
Ca–O(1)	2.46 × 4		
Ca–O(2)	2.73 × 4δ		
Ca–O(3)	2.66 × 4		

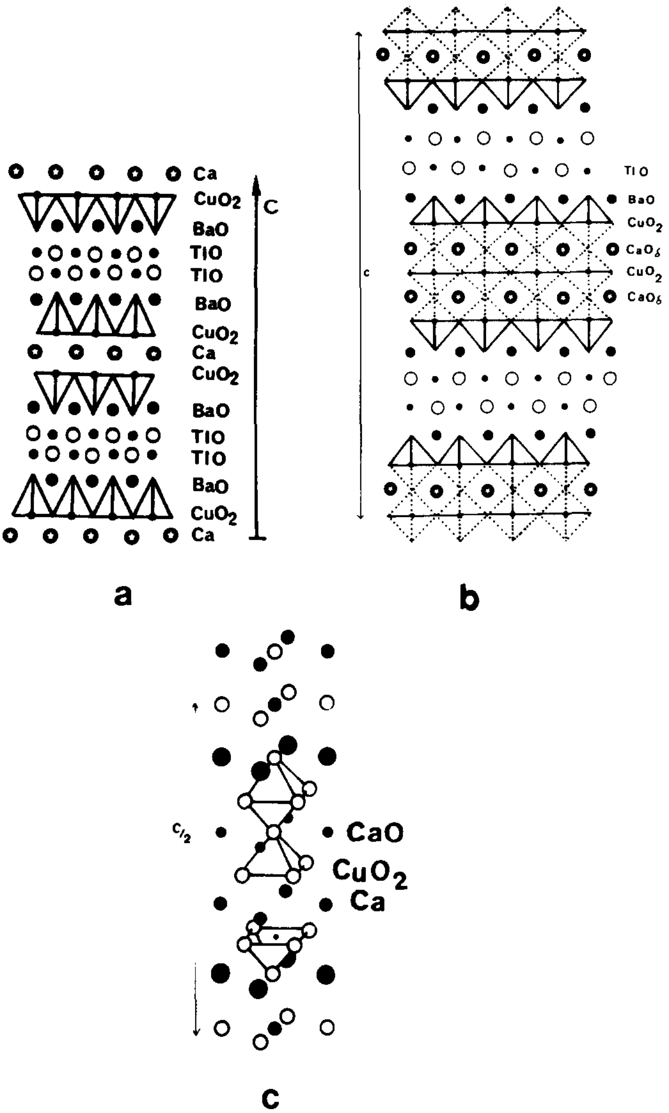

FIG. 3. Idealized models of (a) $Tl_2Ba_2CaCu_2O_8$; (b) $Tl_{2-x}Ba_2Ca_2Cu_3O_{10+\delta}$; (c) limiting model for $\delta = 1$: $Tl_{2-x}Ba_2Ca_2Cu_3O_{11}$ (note that the two possible positions of the additional oxygen, symmetric with respect to the middle Cu(1) atom, lead to equivalent models).

located at the same level as the calcium ions were found to be only 50% occupied. Thus, such an oxygen distribution could be interpreted as resulting from the existence of single layers of CuO_5 pyramids and double layers of CuO_5 pyramids and CuO_6 octahedra interleaved with calcium ions (Fig. 3c). This structure is closely related to that of $Tl_2Ba_2CaCu_2O_8$: it exhibits similar $[BaO]_\infty$ and $[TlO]_\infty$ layers and differs from this latter oxide by the introduction of one $[CuO_2]_\infty$ layer and additional oxygen between two pyramidal layers. Although rather short, the distance between the copper plane, close to 3.6 Å, is much longer than that observed for $Tl_2Ba_2CaCu_2O_8$ so that the additional oxygen can be intercalated at the same level as the calcium ions, in contrast to this latter oxide.

The deviation from stoichiometry deduced from the refinements of the structure, corresponding to the formulation $Tl_{1.8}Ba_2Ca_2Cu_3O_{10+\delta}$, is not accurately determined. However, it may be considered as significant with respect to the high Cu(III) content of this oxide, consistent with its high critical temperature.

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