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Superconducting $Tl_2Ba_2CuO_6$: The Orthorhombic Form

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The structure of an orthorhombic variant of $Tl_2Ba_2CuO_6$ ($Z = 4$), with a superconducting onset at 90 K, has been studied using neutron powder diffractometry at 12 K (a = 5.4834(3), b = 5.4586(3), c = 23.198(1) Å), 60 K (a = 5.4834(3), b = 5.4585(3), c = 23.199(1) Å), and 293 K (a = 5.4967(3), b = 5.4651(3), c = 23.246(1) Å). The distortion from *I4/mmm* symmetry, reported in single-crystal X-ray investigations, to *Abma* is manifested in the Tl–O layer. At the temperatures studied, the coordination of Tl to oxygen is (2 + 1 + 2) square pyramidal rather than octahedral. At lower temperatures, distortion decreases but does not disappear. Despite the orthorhombic symmetry the CuO_2-layers remain flat.

Introduction

The compound $Tl_2Ba_2CuO_6$ is the structural end member of a family of oxide superconductors (*1–6*) with the general composition $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$. Here n is the number of consecutive Cu–O layers stacked along the c-crystallographic axis; values ranging from 1 to 5 have been reported in either bulk samples or as intergrowths (*4–7*). The superconducting transition temperature, T_c, varies from 85 K for the n = 1 phase to 125 K for n = 3. These materials have been characterized using single-crystal X-ray data (*4–6*) while $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ have also been refined using neutron powder diffraction data. The unit cells are tetragonal, *I4/mmm*, with $a \sim 3.85$ and $c \sim 23.2$, 29.3, and 35.9 Å for the one-, two-, and three-layer materials, respectively. The structures are composed of either one, two, or three layers of Cu, in square planar coordination, interleaved with NaCl-type Tl–O slabs two octahedra in thickness. Recently, reports of compounds of this type containing just single layers of Tl have been reported (*8*). Charge compensating Ca^{2+} (in the n = 2 and n = 3 materials) is located between adjacent copper sheets, and Ba^{2+} is located between the copper sheets and Tl–O slabs. There are considerable displacements of both oxygen and thallium within the Tl–O sheets, and these displacements have been modeled in *I4/mmm* as a split atom in the case of oxygen: four equivalent sites, each displaced about 0.4 Å from the ideal position.

Prior to this study, no evidence for either an enlarged cell (a = 5.44 Å) or symmetry

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lower than tetragonal was reported. We find an orthorhombic distortion in $Tl_2Ba_2CuO_6$ ($n = 1$) at 293 K (room temperature), 60 K, and 12 K.

Experimental Details

Neutron powder diffraction measurements were made on a triple axis diffractometer at the Brookhaven HFBR equipped with a pyrolytic graphite monochromator and analyzer in the (002) and (004) settings, respectively. The collimation was 20′ in-pile, 40′ monochromator-sample, 40′ sample-analyzer, and 20′ analyzer-detector. The wavelength was 2.370 ± 0.001 Å, and the higher order harmonics were eliminated with a pyrolytic graphite filter.

The synthesis procedures were previously reported. Flux exclusion measurements showed a sharp superconducting transition onset at 90 K. About 20 g of material, in the form of pressed pellets, was placed in an aluminum sample holder in a closed-cycle He cryostat.

Extended data sets were collected by step scanning at 0.1° intervals over the angular range $5° \leq 2\theta \leq 138.0°$.

The orthorhombic symmetry for $Tl_2Ba_2CuO_6$ is indicated by the presence of a doublet (Fig. 1) for the (220) reflection indexed according to the $a = 3.85$ Å tetragonal cell. A unit cell with $a > b \simeq \sqrt{2}a_{\text{tetragonal}}$ was chosen for structure refinement. The presence of weak intensities of the type hkl, $h + l \neq 2n$ suggested an A-centered unit cell. While two other weak peaks were observed close to positions expected for diffraction from (013) and (015), they were displaced from those positions by ~0.4 Å. On this basis space group *Amaa* was rejected and the structure refinement carried out in space group *Abma*. The d-spacings (Å) and intensity (normalized to the strongest peak in the pattern assigned as $I = 100$) for those weak intensities not accounted for by the orthorhombic cell, space group *Abma*, are 7.21(1.4), 4.50(0.7), 3.59(0.4).

Refinement was carried out using a modified version of the Rietveld–Hewat program (*9, 10*). Background values were obtained by linear interpolation of estimated values between the peaks. Initially, Gaussian peak shapes were assumed. In the final stages of refinement, a slight improvement to the fit was obtained by modeling a Lorentzian component to the peak width of the type $x \tan \theta$; x is a refinable parameter. The total number of peaks in each data set was 101.

The starting model was derived from the recently reported structure solution and refinement of Torardi *et al.* (*5*). Twenty two parameters were varied; these comprised seven profile variables (three halfwidth, three unit cell, and the zero point) and 15 structural parameters (atomic positions, isotropic thermal factors, and a scale factor). Refinement converged quickly for all three data sets. All but the positions of O(3) were close (within 3 standard deviations) to the ideal values expected for *I4/mmm* symmetry (*5*).

The large isotropic thermal parameters for O(3) and Tl (5.4 and 1.5 Å^2) were relatively temperature independent and suggestive of static displacements. A series of refinements lead to the conclusion that this positional disorder could be adequately modeled by a single anisotropic atom with refinable B_{11} and B_{22} components. The small B_{33} component (0.2 Å) was fixed for all three temperatures and B_{13} was fixed equal to zero. Refinement of two additional parameters, compared with the model employing fully isotropic thermal parameters, resulted in a sizable improvement in the residual (*11*), S_I^2, for example, from 6.4 to 5.2 in the case of the 293 K data set. This residual is based on integrated intensities and is arguably a more realistic goodness-of-fit indicator (*11*).

In the final stages of refinement, atomic

TABLE I

RESULTS OF RIETVELD REFINEMENT FOR $Tl_2Ba_2CuO_6$ SCATTERING AMPLITUDES FOR Tl, Ba, Cu, and O WERE TAKEN AS 0.879, 0.525, 0.7718, AND 0.5805 × 10^{-12} cm, RESPECTIVELY (9)

Atom	x	y	z	B or B_{11}[a] (Å²)	B_{22}[a] (Å²)
			0.2018(1)	3.1(2)	1.0[a](2)
Tl	0	0	0.2023(1)	2.1(2)	0.9(2)
			0.2022(1)	2.2(2)	0.7(2)
	0.00		0.0822(2)	0.9(1)	
Ba	0.00	½	0.0829(2)	0.7(2)	—
	0.00		0.0832(2)	0.7(2)	
				0.6(1)	
Cu	0	0	0	0.4(1)	—
				0.6(1)	
				0.2(1)	
O(1)	¾	¼	0.000	0.2(1)	—
				0.1(1)	
			0.1161(2)	1.1(1)	
O(2)	0	0	0.1169(2)	0.2(2)	—
			0.1160(2)	0.2(1)	
	0.045(3)		0.2887(3)	12.1(10)	6.0(5)
O(3)	0.039(4)	0	0.2881(3)	14.6(10)	7.5(6)
	0.043(3)		0.2886(3)	13.2(8)	6.6(5)

Temperature (K)	293	60	12
R_I	0.069	0.061	0.063
R_{wp}	0.098	0.092	0.089
R_e	0.077	0.071	0.070
S_p^2	1.62	1.68	1.62
a(Å)	5.4967(3)	5.4834(3)	5.4834(3)
b(Å)	5.4651(3)	5.4585(3)	5.4586(3)
c(Å)	23.246(1)	23.199(1)	23.198(1)

Note. The three entries per atom at values at 293, 60, and 12 K, respectively.

[a] Refined anisotropic thermal parameters for Tl and O(3). B_{33} for Tl and O(3) fixed equal to 0.2 Å for these refinements; $B_{13} = 0.0$.

positional parameters less than 1 standard deviation from an ideal position were fixed at that position. In particular O(1), which, along with Cu, makes up the Cu–O square planar sheet, was fixed at (¾, ¼, 0.00) for all three refinements. In this way the reflection/structural parameter ratio was greater than 7 for all three sets of data.

The results of the refinements are presented in Table I. The fit of the calculated pattern profile to the observed neutron powder for the 293 K data is shown in Fig. 1.

Discussion

Bulk $Tl_2Ba_2CuO_6$ prepared as herein described is orthorhombic. Although the deviation from tetragonal symmetry is small, it is easily seen at high angles (Fig. 1). The magnitude of the orthorhombic distortion decreases with decrease in temperature (Table I). The difference in a and b unit cell parameters varies from 0.032 Å at 293 K to 0.025 Å at 12 K.

The deviation from ideal *I4/mmm* symmetry is essentially restricted to the Tl–O(3) sheets which make up the Tl–O slab (Fig. 2). For thallium in the 3+ oxidation state, a variety of coordination environments has been reported, including square planar (*12*), tetrahedral (*13*), octahedral (*14*), and a distorted octahedral arrangement (*15*) in Tl_2O_3. In $Tl_2Ba_2CuO_6$, Tl is in (2 + 1 + 2) square pyramidal coordination (Fig. 2, Table II). The Tl–O distances are relatively independent of temperature. The shortest of these (Tl–O(2) and Tl–O(3) in Table II) are arranged along the c axial direction while short (Tl–O(3)[a]) and long (Tl–

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) FOR $Tl_2Ba_2CuO_6$ AT 12, 60, AND 393 K

Distance	293 K	60 K	12 K
Cu–O(1)	1.938	1.934	1.934
Cu–O(2)	2.698(5)	2.711(5)	2.691(5)
Tl–O(2)	1.994(6)	1.982(6)	1.998(6)
Tl–O(3)	2.034(7)	2.003(8)	2.019(8)
Tl–O(3)[a]	2.512(17)	2.535(20)	2.516(22)
Tl–O(3)[b] × 2	2.752(2)	2.747(1)	2.747(1)
Tl–O(3)[c]	3.002(17)	2.966(20)	2.984(22)
⟨Tl–O⟩	2.51	2.48	2.50

Note. Superscripts refer to the following symmetry transformations: [a] $x - \frac{1}{2}, -y, \frac{1}{2} - z$; [b] $-x, \frac{1}{2} + y, \frac{1}{2} - z$; [c] $\frac{1}{2} - x, -y, \frac{1}{2} - z$.

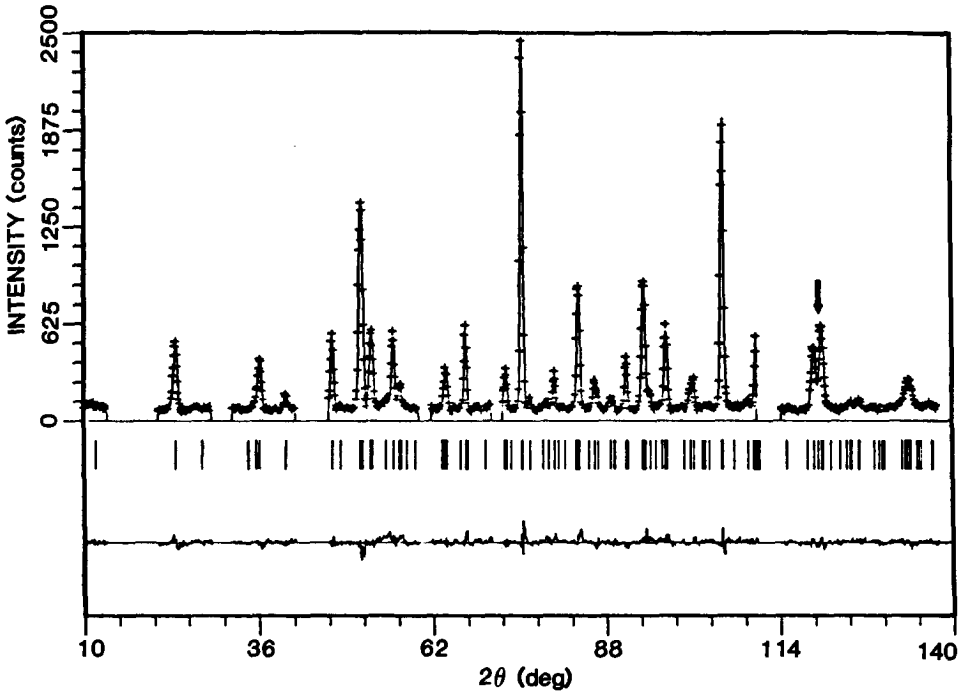

FIG. 1. Profile fit and difference plot for $Tl_2Ba_2CuO_6$ at 293 K. Short vertical markers below the pattern represent allowed reflections. Peaks from impurity phase (see text) and Al sample holder have been excluded. The peaks indicated by the arrow (the (400) and (040) reflections) are in the vicinity of the position expected for the (220) reflection if the true symmetry was tetragonal, *I4/mmm*.

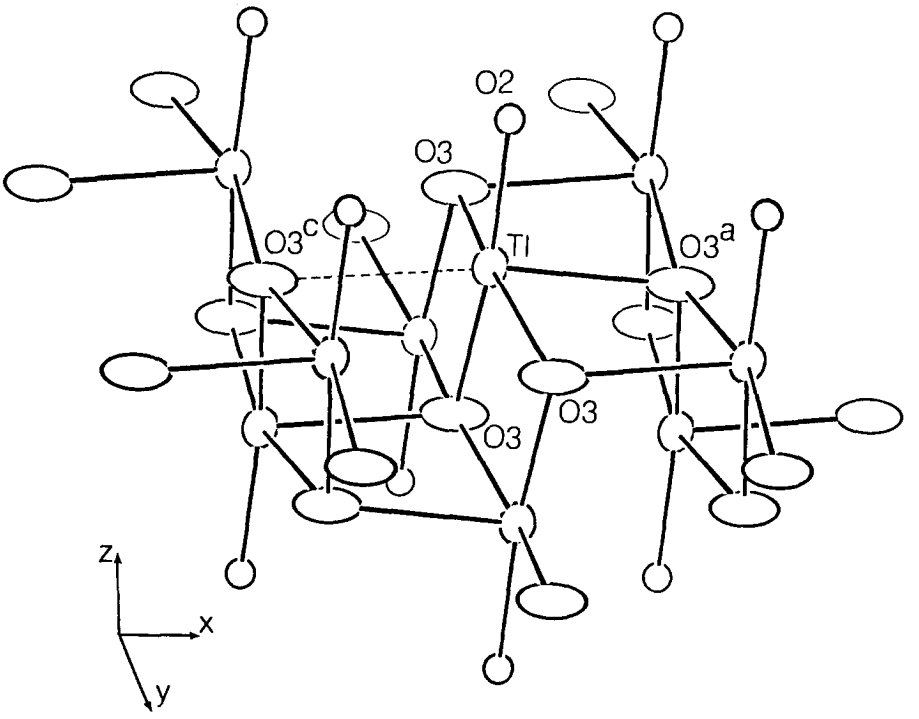

FIG. 2. Tl–O slab in $Tl_2Ba_2CuO_6$ (orthorhombic form).

O(3)[3]) distances alternate along the *a*-axis (Fig. 2). Over the temperature range studied the average Tl–O distance (Table II) remains constant (~2.50 Å).

For the three temperatures studied, the CuO plane remains relatively unchanged, with Cu and O(1) on ideal positions. Any deviation from square planar geometry is simply that imposed by the orthorhombic unit cell. The CuO_2-layer is flat, in contrast to other superconductors containing one CuO_2-layer possessing orthorhombic symmetry.

In conclusion, $Tl_2Ba_2CuO_6$ possesses orthorhombic unit cell symmetry, a structural aspect it shares with all other copper oxide-based superconductors except the $n = 2$ and $n = 3$ thallium materials. Essentially, the orthorhombic distortion manifests itself in the Tl–O slab as a displacement from the ideal position of a single oxygen atom O(3). There is no distortion of the CuO_2-layer, which remains flat.

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