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Search for satellite reflections and low-temperature study of the 1223 and 2212 Tl–Ba–Ca–Cu–O superconductors

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Abstract. The structures of the 1223 and 2212 phases of the Tl–Ba–Ca–Cu–O system have been determined at 125 K. No satellite reflections were observed in extensive searches at both room and low temperature. The temperature dependence of the thermal parameters of the thallium atoms confirms the presence of a static disorder beyond that already incorporated in the refinements.

Introduction. The superconducting ceramics of the Tl–Ba–Ca–Cu–O system are the highest T_c materials known at present. A number of structure analyses have been reported, based on both powder (Cox, Torardi, Subramanian, Gopalakrishnan & Sleight, 1988) and single-crystal data (Subramanian, Calabrese, Torardi, Gopalakrishnan, Askew, Flippen, Morrissey, Chowdhry & Sleight, 1988; Torardi, Subramanian, Calabrese, Gopalakrishnan, Morrissey, Askew, Flippen, Chowdhry & Sleight, 1988; Subramanian, Parise, Calabrese, Torardi, Gopalakrishnan & Sleight, 1988). Electron diffraction studies show all but one of the known phases to be modulated, with satellite intensities weaker than those in the analogous Bi–Sr–Ca–Cu–O compounds (Parkin, Lee, Nazzal, Savoy, Beyers & LaPlaca, 1988; Zandbergen, Van Tendeloo, Van Landuyt & Amelinckx, 1988; Fitz Gerald, Withers, Thompson, Wallenberg, Anderson & Hyde, 1988), for which we have made a detailed analysis of the modulation (Gao, Lee, Coppens, Subramanian & Sleight, 1988). For not too large displacement amplitudes the effect of the modulation on the main reflections is very similar to that of the thermal motion (Petricek, Becker & Coppens, 1985). Thus, the unusually large anisotropies in the reported thermal parameters of the Tl compounds could constitute additional, indirect, evidence for the modulations, which may only fully condense at lower temperatures, as observed, for example, in TTF–TCNQ (Pouget, Khanna, Denoyer, Comes, Garito & Heeger, 1976; Coppens, Petricek, Levendis, Larsen, Paturle, Gao & LeGrand, 1987). This report describes a search for satellite reflections at both room and low temperatures, low-temperature (125 K) structure analyses of both the 1223 and the 2212 phases and a redetermination of the room-temperature (295 K) structure of the 2212 compound.

Sample preparation. 1223 *phase*. Single crystals of $TlBa_2Ca_2Cu_3O_{10}$ were grown from a copper-rich melt with oxides (Tl_2O_3, BaO_2, CaO_2 and CuO) in the molar ratio 1:2:2:4 (Tl:Ba:Ca:Cu) in a sealed gold tube. The mixture was heated to 1198 K, held for 6 h and cooled at 1 K min^{-1} to 373 K. Plate-like crystals found in the melt were mechanically separated and used for further characterization and structure determination. Flux-exclusion measurements on the crystals

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revealed a sharp T_c onset of ~110 K as reported earlier (Subramanian, Parise *et al.*, 1988).

2212 *phase.* Single crystals of $Tl_2Ba_2CaCu_2O_8$ were grown from a 2Tl–Ba–Ca–3Cu oxide mixture in a sealed gold tube. The mixture was heated to 1173–1193 K, held for 1 h and cooled at the rate of 2 K min^{-1} to 373 K. Plate-like crystals found in the melt were mechanically separated and used for further characterization and structure determination. Flux-exclusion measurements on the single crystals revealed a sharp superconducting transition at T_c ~110 K.

Search for satellites. 1223 *phase.* The crystal was mounted on a Nonius CAD-4 diffractometer and cooled to 125 K with a liquid-nitrogen gas stream. A systematic search of reciprocal space was conducted in the region $0<h,k<3.5$, $0<l<13$. ω–2θ scans were performed at intervals $\Delta h=\Delta k=0.1$ and $\Delta l=0.5$, using Mo $K\alpha$ radiation. No satellites were observed under these conditions. A long-exposure (60 h) Weissenberg $0kl$ photograph taken at room temperature also failed to show satellite reflections. Finally, the crystal was mounted at the SUNY X3 beamline at the National Synchrotron Light Source, Brookhaven. No satellites were observed under conditions at which the 110 reflections gave a peak height of about 400 000 counts s^{-1}. This corresponds to a satellite intensity which is less than about 4×10^{-4} times the intensity of the main reflection.

2212 *phase.* A room-temperature Weissenberg $h0l$ photograph was taken on a rotating-anode generator (Mo radiation, 50 kV, 100 mA). A 20 h exposure did not show any satellite reflections. An a-axis rotation photograph taken at liquid-nitrogen temperature with a conventional source showed no extra reflections when compared with a similar room-temperature photograph. Systematic searches at both room and low temperature (125 K) failed to give evidence for the occurrence of satellite reflections.

Data collection and refinement. The negative result of the satellite search indicates the absence of significant modulations in the bulk of our samples. Since the modulations are reported to be sample dependent and sensitive to heat treatment (Zandbergen *et al.*, 1988) it seemed important to establish that the apparent large anisotropic thermal motion was present in our samples. Furthermore, measurement of the thermal parameters at different temperatures can give information on the origin of the anomalies. A set of low-temperature (125 K) data was collected for the 1223 compound, while both room- and low-temperature data were collected for the 2212 phase. In each case three standard reflections were measured at regular intervals. Fluctuations were less than 2% of the average. Analytical absorption corrections were applied in all studies (Templeton & Templeton, 1978).* Cell dimensions (from a least-squares refinement of the positions of 25 reflections with $\theta<25°$) and data-collection parameters are summarized in Table 1, while refinement details are given in Table 2. The highest residual peaks in the final difference maps occur near the Tl atoms in 2212 (height 3.6 e $Å^{-3}$ at 125 K), and above and below O(4) in 1223 [height 5.9 e $Å^{-3}$ at 125 K, at about 0.4 Å from O(4)]. Structural disorder of the Tl atoms is also evident from the thermal parameters as discussed further below.

Discussion. Occupancies and positional and thermal parameters are listed in Tables 3 and 4. The two low-temperature studies confirm the earlier room-temperature results, including the large anisotropic values of the Tl thermal parameters. In both compounds, the Tl occupancy of the mixed Tl/Ca layers is higher than previously reported [1223: 10(1) *vs* 5%; 2212: 14(1) *vs* 10%]. In the region between room

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51537 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Data collection and processing summary*

Phase	1223	2212	2212
Temperature (K)	125	295	125
Reflections measured	1401	1261	1248
Octants	h,k,l and $h,k,-l$	h,k,l and $h,k,-l$	h,k,l and $h,k,-l$
$[(\sin\theta)/\lambda]_{max}$ ($Å^{-1}$)	0.81	0.81	0.81
Crystal dimensions (mm)	0.2×0.04×0.01	0.2×0.14×0.01	
Absorption coeff. (cm^{-1})	346.4	500.2	
Transmission factor	0.309–0.758	0.085–0.592	
Internal agreement factor	0.049	0.057	0.043
a (Å)	3.849(2) [3.853(1)]*	3.851(6)	3.843(1)
c (Å)	15.83(1) [15.913(4)]*	29.308(4)	29.263(9)
Space group	*P4/mmm*	*I4/mmm*	

*Room-temperature value (Subramanian, Parise *et al.*, 1988).

Table 2. *Refinement information*

$\Sigma\omega\Delta^2$ minimized with $\Delta=(F_o-k\|F_c\|)$ and $w=1/\sigma^2$; $\sigma(F)=1/(2F)\times[\sigma^2_{\text{counting}}+(0.02F^2)2]^{1/2}$.

	1223 (125 K)	2212 (295 K)	2212 (125 K)
Number of variables	26	22	22
Number of observations*	310	261	290
$R/\omega R(F)$	0.041/0.049	0.035/0.042	0.033/0.038
Goodness of fit S	1.36	1.23	0.84
Δ/σ, last cycle	<0.01	<0.01	<0.01

*All reflections with $I\geq 3\sigma(I)$ included.

Table 3. *Positional and thermal parameters* (Å^2) *for* 1223 (125 K)

	Occupancy	x	y	z		
Tl	0.95(2)	0.0894(6)	0	0		
Ba	0.92(1)	0.5	0.5	0.1738(1)		
Cu(1)	1.00	0	0	0.5		
Cu(2)	1.00	0	0	0.2994(1)		
Ca	0.90(1)	0.5	0.5	0.3956(2)		
Tl	0.10	0.5	0.5	0.3956		
O(1)	1.00	0	0.5	0.5		
O(2)	1.00	0	0.5	0.3025(5)		
O(3)	1.00	0	0	0.1254(9)		
O(4)	1.00	0.5	0.5	0		
		295 K*			125 K†	
	U_{11}	U_{22}	U_{33}	U_{11}	U_{22}	U_{33}
Tl	0.041(5)	0.022(3)	0.0046(8)	0.031(2)	0.016(1)	0.0024(7)
Ba	0.0056(6)		0.0125(8)	0.0022(4)	0.0022	0.0056(5)
Cu(1)	0.005(1)		0.005(1)	0.0007(7)	0.0007	0.003(1)
Cu(2)	0.004(1)		0.008(1)	0.0019(6)	0.0019	0.0064(9)
Ca/Tl	0.005(1)		0.015(1)	0.0034(9)	0.0034	0.012(1)
		B_{iso}			B_{iso}	
O(1)		0.9(3)			0.7(2)	
O(2)		1.1(2)			0.6(1)	
O(3)		0.6(3)			0.9(2)	
O(4)		2.6(7)			0.7(3)	

*Subramanian, Parise *et al.* (1988).

†The anisotropic temperature factor is defined as $\exp[-2\pi(h^2U_{11}+k^2U_{22}+l^2U_{33}+2hkU_{12}+2hlU_{13}+2klU_{23})]$.

temperature and 125 K the temperature parameters may be expected to be proportional to the absolute temperature, as a classical vibrational model is valid within a reasonable approximation, and zero-point vibrations are much smaller than the observed amplitudes [see, for example, Coppens & Vos (1971)]. With this model, results at the two temperatures (including the room-temperature study of 1223 by Subramanian, Parise *et al.*, 1988) can be used to estimate the static contribution to the U_{ij}, from which the static r.m.s. displacement can be derived. The following static r.m.s. displacements are significantly different from zero: 1223: Tl 0.15 and 0.11 Å in the **a** and **b** directions, respectively, and for 2212: Tl 0.11 and 0.08 Å in the **a**,**b** and **c** directions, Cu 0.06 Å in the **c** direction, and Ba 0.08 Å in the **c** direction. These results represent a disorder in addition to that obtained by moving the Tl atom in the 1223 phase out of one of the mirror planes by 0.344 Å (Table 3). Refinements with the Tl atoms in multiple positions of lower occupancy did not lead to agreement factors below those obtained with the more restricted model.

Torardi, Parise, Subramanian, Gopalakrishnan & Sleight (1988) have attributed the deviations from the more symmetric arrangement to a mismatch between the rather rigid geometry of the CuO planes and the bonding requirements in the Tl–O (respectively Bi–O) planes. While the deviations condense into a static displacement wave in several of the Bi compounds, they have no long-range order in the Tl phases studied in this work.

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Table 4. *Positional and thermal parameters* (Å^2) *for* 2212

	Occupancy		x		y	z	
	295 K	125 K	295 K	125 K		295 K	125 K
Tl	0.89(1)	0.88(1)	0.5		0.5	0.2133(1)	0.2133(1)
Ba	0.97(1)	0.97(1)	0.0		0.0	0.1213(1)	0.1212(1)
Cu	1.00		0.5		0.5	0.0538(1)	0.0538(1)
Ca	0.86(1)	0.86(1)	0		0	0	
Tl	0.14	0.14	0		0	0	
O(1)	1.00		0		0.5	0.0523(3)	0.0522(2)
O(2)	1.00		0.5		0.5	0.1458(6)	0.1456(5)
O(3)	1.00		0.588(8)	0.595(5)	0.5	0.280(1)	0.280(1)
		295 K			125 K		
	U_{11}	U_{22}	U_{33}	U_{11}	U_{22}	U_{33}	
Tl	0.0226(4)	0.0226	0.0075(4)	0.0169(3)	0.0169	0.0065(3)	
Ba	0.0055(4)	0.0055	0.0105(6)	0.0026(3)	0.0026	0.0081(4)	
Cu	0.0030(7)	0.0030	0.011(1)	0.0006(5)	0.0006	0.0068(8)	
Ca/Tl	0.005(1)	0.005	0.010(1)	0.0022(8)	0.0022	0.006(1)	
		B_{iso}			B_{iso}		
O(1)		0.6(1)			0.5(1)		
O(2)		1.4(3)			0.9(2)		
O(3)		2.0(6)			1.3(4)		

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