

PREPARATION AND NEUTRON DIFFRACTION OF SUPERCONDUCTING “TETRAGONAL” AND NON-SUPERCONDUCTING ORTHORHOMBIC $Tl_2Ba_2Cu_1O_6$

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Many different samples of $Tl_2Ba_2Cu_1O_6$ have been prepared by different heat treatments at relatively low temperature. The material as first prepared is clearly orthorhombic and non-superconducting, but on annealing and quenching, the samples become almost tetragonal with high T_c . Various T_c values between <4 K and 70 K can thus be obtained, and the structure of these materials has been compared by neutron diffraction at 5 K and 300 K. For all samples 1/8th of the $Tl^{3+}O^{2-}$ atoms are missing, creating the electron holes apparently necessary for superconductivity. The main difference between the various samples appears to be that the non-superconducting material is orthorhombic, with a well ordered superstructure, while the superconducting material is pseudo-tetragonal, with disordered oxygen within the TlO plane, as for the higher superconducting members of the $Tl_2Ca_nBa_2Cu_{n+1}O_{2(n+3)}$ series. Superconductivity then appears to depend on the precise structural arrangement, and not just on stoichiometry and the number of electron holes.

1. Introduction

The structures of the high- T_c superconducting phases “2122” $Tl_2Ca_1Ba_2Cu_2O_8$ [1,2] and “2223” $Tl_2Ca_2Ba_2Cu_3O_{10}$ [3,4] have been found by X-ray and neutron diffraction to show only small deviations from the composition of the nominal formulae, with at most a few percent Tl-deficiency, and perhaps a few percent Ca-replacement by Tl. There is no evidence for extra oxygen.

This appears puzzling, because the nominal formulae imply all copper as Cu^{2+} , assuming Tl^{3+} and Ba^{2+} , whereas in the earlier high- T_c materials (La, Sr)₂CuO₄ and Y₁Ba₂Cu₃O₇ it is clear that electron holes are necessary for superconductivity, either as Cu^{3+} or as O^- , and indeed that T_c increases with an increasing numbers of holes [5]. Calculations of the apparent valence of copper in these earlier materials, from the observed Cu–O bond lengths, is in good agreement with the values implied by the formulae,

and from wet-chemical determinations of the number of holes.

However, calculations for the Cu–O distances observed in the Tl-materials imply a copper valence close to 2+ for a nominal oxygen valence of 2– [2], though T_c is higher than in the earlier materials. The only anomaly appears to be the low value obtained for the apparent valence of Tl, as if the holes were on the TlO-plane. High resolution analytical electron microscopy [6,7] indicates that as much as 1/3 of the Ca may be missing in these Tl-materials, and that the true formulae for the 2122 and 2223 phases may be $Tl_2Ca_{0.7}Ba_2Cu_2O_8$ and $Tl_2Ca_{1.5}Ba_2Cu_3O_{10}$. These formulae would imply a copper valence near 2.33, similar to that in Y₁Ba₂Cu₃O₇ [8]. Unfortunately, such formulae, with large amounts of Ca missing, are not supported by the X-ray and neutron structure determinations, unless the Ca is replaced by other atoms of similar scattering power.

If the Ca-deficient mechanism is valid, it is of in-

terest to inquire about the apparent Cu-valence in the 85 K superconducting 2021 phase $Tl_2Ba_2Cu_1O_6$, which contains no calcium! This was the purpose of these measurements.

2. Sample preparation and characterisation

Stoichiometric proportions of Tl_2O_3 , BaO_2 and CuO corresponding to the formula $Tl_2Ba_2Cu_1O_6$ were ground, pressed together, and heated in a 100 mm long by 8 mm diameter gold tube, pinched at the ends but not hermetically sealed. This permits loss of the excess oxygen produced by the decomposition of BaO_2 . BaO_2 was used, rather than BaO or $BaCO_3$, to reduce the reaction temperature. These samples were heated at $700^\circ C/h$ and held near $815^\circ C$ for 6 hours, then reheated at $50^\circ C/h$ to temperatures between 805 and $840^\circ C$. Several reheating cycles were tried according to table I, in either pinched gold tubes or open containers. The percentage weight loss was measured after each cycle, and was greatest in open containers, for which decomposition was observed after several hours at $750^\circ C$ with production of $BaCuO_2$ (table I).

Before heat treatment, the samples are clearly not tetragonal. X-ray powder diffraction shows doubling of reflections ($h00$); ($0h0$), indicating an orthorhombic cell (fig. 1). After heat treatment and rapid cooling, the cell metric appears to become tetragonal: in fact the difference between the orthorhombic a - and b -axes is reduced depending on the heat treatment, while T_c becomes high when $a \approx b$ (table II).

This is to be compared with the results obtained by Iijima et al. [9], whose tetragonal sample was non-superconducting, and Torardi et al. [10], who found that T_c varied between 55 and 90 K, which they attributed to the annealing temperature, with higher T_c associated with higher annealing temperature.

Our results indicate that temperature is not the only factor in obtaining the "tetragonal" superconducting phase. T_c was determined by measurement of the a.c. susceptibility (fig. 2), as described earlier [8]. Sample #5, reheated to $750^\circ C$ and cooled quickly in an open container is "tetragonal" and superconducting ($T_c = 10$ K), while sample #1, reheated to a higher temperature ($805^\circ C$) in a pinched tube is not. Sample #3, after three cycles of heat treatment and rapid cooling is superconducting, with the highest T_c (70 K). In fact, a transition to a true tetragonal phase may occur at high temperature, and it may be necessary to quench the sample to obtain the "tetragonal" superconducting phase at low temperature.

Weight loss (table I) is much more rapid in the open container (sample #5) than in the pinched tube (sample #3). Weight loss is also small in an oxygen atmosphere (sample #7), but very large if the sample is heated to decomposition (sample #6). Weight losses of almost 11% in the production of the superconducting sample #3 are significant: they might be interpreted as the loss of thallium in a reduced volatile form such as Tl_2O , not produced in an enclosed oxygen environment.

We were therefore not surprised when the neutron diffraction results indicated that 1/8th of the atoms in the TlO -plane are missing, but this is also true for

Table I

Summary of the preparation conditions for seven different samples of $Tl_2Ba_2Cu_1O_6$. Samples #6 (decomposed) and #7 were not examined by neutron diffraction.

Sample	Preparation	Anneal conditions	Total weight loss	T_c	Symmetry
#1	8h, $820^\circ C$, gold tube	6h, $805^\circ C$, gold tube	not measured	< 4 K	Orthorhombic
#2	6h, $820^\circ C$, gold tube	none	-	< 4 K	Orthorhombic
#3	8h, $815^\circ C$, gold tube	7h, $840^\circ C$, gold tube 17h, $840^\circ C$, gold tube 21h, $840^\circ C$, gold tube quenched	10.72%	70 K	"Tetragonal"
#4	6h, $815^\circ C$, gold tube	none	-	< 4 K	Orthorhombic
#5	6h, $815^\circ C$, gold tube	5×30 min, $750^\circ C$, open boat	7.17%	10 K	"Tetragonal"
#6	6h, $820^\circ C$, gold tube	14h, $750^\circ C$, open boat	36%	-	decomposed
#7	6h, $815^\circ C$, gold tube	12h, $750^\circ C$, open boat, oxygen	not measured	< 4 K	Orthorhombic

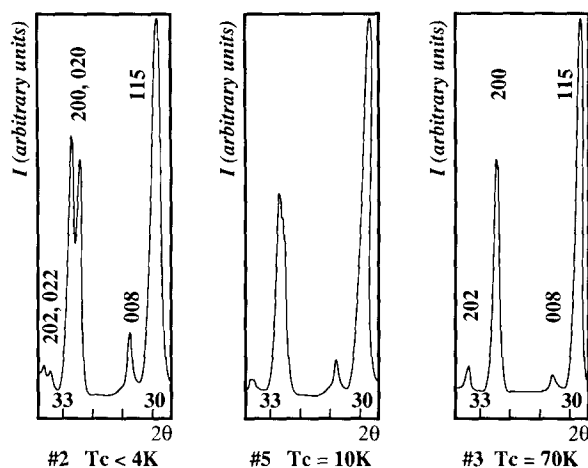


Fig. 1. X-ray powder diffraction line shapes for the orthorhombic sample #2, the almost "tetragonal" sample #5, and the "tetragonal" sample #3. Indexing is on the orthorhombic cell (5.45 Å, 5.51 Å, 23.20 Å).

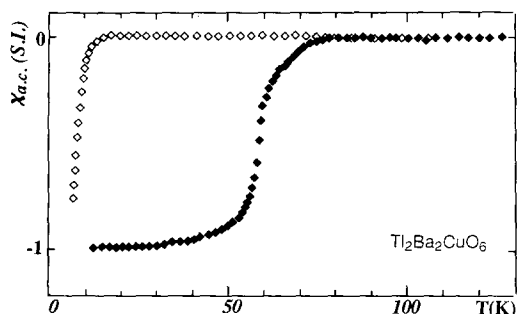


Fig. 2. Magnetic susceptibility of the superconducting 70 K "tetragonal" sample #3 and the 10 K almost "tetragonal" sample #5. The remaining orthorhombic samples were not superconducting above 4 K.

the non-superconducting preparations. Apparently it is unreacted thallium oxide that is responsible for the initial weight losses.

The surfaces of many of the samples, when examined at low resolution in the electron microscope, were seen to be contaminated with a fibrous crystalline Ba-containing material, probably $BaCO_3$. This contamination appeared to depend also on the preparation of the sample for microscopy. Neutron and X-ray powder diffraction showed that the total contamination was small, and contributed few peaks to the pattern. High resolution electron microscopy showed that intergrowth of other superconducting phases was rare.

3. Neutron diffraction

Neutron diffraction was performed on typically ~ 5 g samples at 5 K and a 300 K on D2B at ILL Grenoble as described earlier [2]. Five different samples were examined. Unlike the 2122- and 2223-phases, most of the samples were clearly orthorhombic. Only sample #3, the one with high T_c (70 K), was almost tetragonal. The observed and calculated diffraction patterns for this sample are shown in fig. 3.

Structure refinement in the orthorhombic space group A2aa, as used earlier for the Bi-2122 phase $Bi_2Ca_1Sr_2Cu_2O_8$ [11], gave satisfactory descriptions of all diffraction patterns. Table II shows that the difference between the a - and b -axes, virtually zero for the high- T_c sample #3, is as much as 1% for sample #4.

For all samples the occupation of both the Tl- and O-sites in the TlO layer appears to be only 7 sites out of 8. Table II shows that one-eighth or 12.5% TlO deficiency is well outside the error of 1–2% in the determination of these occupation numbers. Apparently for all samples, only 7/8 of the original Tl_2O reacts to form the 2021-phase, with the remaining unreacted Tl_2O and O_2 lost on heat treatment. It should be noted that 12.5% TlO_2 loss corresponds to a total weight loss of 7%, of the same order as the total weight loss observed in the best samples.

Table II shows that O3 oxygen within the TlO-plane is displaced from the ideal position ($\frac{1}{2}, \frac{1}{4}, z$) at the centre of the Tl-square, toward the Tl-ions. The displacement would be toward one of four single Tl-ions (and the space group would be Amaa) for $x = \frac{1}{2}$, which is almost true. This is similar to the observed oxygen displacement in $Bi_2Ca_1Sr_2Cu_2O_8$ [11], and in the 2122 and 2223 Tl-phases, except that the displacement in $Bi_2Ca_1Sr_2Cu_2O_8$ is toward one of four pairs of Bi-ions.

The difference between the Tl- and Bi-materials can be readily understood. In $Tl_2Ba_2Cu_1O_6$, each Tl already has two close oxygens (O2 and O3) above and below the TlO-plane, because of the relatively small distance (2.19 Å) between TlO planes. In $Bi_2Ca_1Sr_2Cu_2O_8$, the BiO planes are much further apart (3.28 Å), and only one oxygen (O2 from the BaO plane) is close to Bi: two additional short Bi-O bonds are then obtained if O3 moves toward a pair of Bi-ions. In either case, the result is that Bi and Tl

Table II

Atom co-ordinates (x, y, z), site "occupancies" (n) and vibrational amplitudes ($B=8\pi^2\langle u^2 \rangle \text{ \AA}^2$) for five different samples of $Tl_2Ba_2Cu_1O_6$ at 5 K and 300 K. The space group is A2aa, but the center of symmetry in Amaa has been retained ($x=0$ or $1/4$) for all atoms except O3 oxygen within the TlO plane, which when placed in a general position, moves to within 2.2 \AA of a Tl-atom (for Amaa O3(x) = $1/2$). Only the copper sites have been assumed to be fully occupied ($n=4$). The errors in the refined site occupancies are rather large, but clearly indicate that about 1 in 8 of the atoms in the TlO plane are missing.

	#4(5K)	#4(300K)	#2(5K)	#2(300K)	#1(5K)	#1(300K)	#5(5K)	#5(300K)	#3(5K)	#3(300K)
a	5.4491 (2)	5.4511 (3)	5.4504 (2)	5.4519 (3)	5.4547 (2)	5.4621 (1)	5.4610 (1)	5.4688 (2)	5.4598 (3)	5.4684 (4)
b	5.4965 (2)	5.5107 (2)	5.4958 (2)	5.5096 (3)	5.4740 (1)	5.4887 (1)	5.4716 (1)	5.4846 (2)	5.4645 (3)	5.4727 (4)
c	23.1484 (9)	23.1988 (11)	23.1496 (9)	23.1963 (12)	23.1354 (6)	23.1907 (6)	23.1459 (5)	23.2019 (7)	23.1869 (8)	23.2382 (9)
Tl										
(x)	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
(y)	0.2622 (8)	0.2544 (10)	0.2624 (7)	0.2446 (7)	0.2505 (8)	0.2489 (9)	0.2500 (7)	0.2529 (9)	0.2466 (10)	0.2456 (11)
(z)	0.4526 (1)	0.4526 (1)	0.4525 (1)	0.4519 (1)	0.4528 (1)	0.4529 (1)	0.4530 (1)	0.4530 (1)	0.4531 (1)	0.4532 (1)
(B)	1.17 (5)	1.68 (5)	1.20 (5)	1.12 (5)	1.16 (4)	1.58 (4)	1.16 (3)	1.72 (4)	0.96 (4)	1.74 (6)
(n)	7.24 (9)	7.17 (9)	7.31 (8)	6.91 (9)	7.14 (8)	7.06 (7)	7.15 (7)	7.26 (7)	7.00 (10)	7.35 (11)
Ba										
(x)	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
(y)	0.7480 (12)	0.7470 (13)	0.7514 (11)	0.7370 (14)	0.7520(13)	0.7510 (14)	0.7540 (12)	0.7527 (15)	0.7510 (18)	0.7515 (19)
(z)	0.3340 (1)	0.3344 (1)	0.3336 (1)	0.3334 (2)	0.3341 (1)	0.3336 (1)	0.3341 (1)	0.3338 (1)	0.3344 (2)	0.3335 (2)
(B)	0.86 (6)	1.17 (7)	0.85 (6)	1.54 (8)	0.84 (5)	1.17 (5)	0.76 (4)	1.07 (5)	0.82 (6)	1.50 (7)
(n)	8.15 (10)	8.12 (10)	8.12 (9)	7.99 (9)	7.90 (8)	7.82 (7)	7.76 (7)	7.64 (8)	7.59 (11)	8.23 (12)
Cu										
(x)	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
(y)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
(z)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
(B)	1.24 (7)	1.55 (8)	1.15 (7)	1.45 (8)	1.02 (5)	1.27 (5)	0.93 (5)	1.26 (6)	1.01 (7)	1.39 (8)
(n)	4.	4.	4.	4.	4.	4.	4.	4.	4.	4.
O1										
(x)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
(y)	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
(z)	0.2494 (3)	0.2503 (5)	0.2492 (3)	0.2553 (2)	0.2496 (5)	0.2497 (5)	0.2498 (5)	0.2501 (5)	0.2508 (5)	0.2507 (7)
(B)	0.83 (6)	1.37 (7)	0.91 (6)	0.89 (6)	0.62 (5)	1.08 (5)	0.49 (4)	0.89 (5)	0.41 (5)	1.19 (7)
(n)	8.54 (10)	8.59 (11)	8.67 (10)	8.64 (11)	8.10 (8)	8.17 (8)	7.80 (7)	7.78 (8)	7.52 (10)	8.07 (12)
O2										
(x)	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
(y)	0.2310 (7)	0.2340 (11)	0.2332 (8)	0.2580 (11)	0.2420(12)	0.2457 (13)	0.2457 (12)	0.2444 (14)	0.2452 (17)	0.2433 (17)
(z)	0.3667 (1)	0.3665 (1)	0.3667 (1)	0.3665 (1)	0.3665 (1)	0.3666 (1)	0.3661 (1)	0.3666 (1)	0.3666 (1)	0.3675 (1)
(B)	0.21 (5)	0.84 (7)	0.38 (5)	0.59 (6)	0.93 (5)	1.33 (5)	0.86 (4)	1.35 (6)	0.64 (6)	1.05 (8)
(n)	7.62 (10)	7.53 (9)	7.67 (9)	7.41 (9)	7.57 (8)	7.61 (8)	7.39 (8)	7.47 (8)	7.07 (11)	7.52 (12)
O3										
(x)	0.4645 (22)	0.4624 (19)	0.4595 (17)	0.4577 (12)	0.4602(15)	0.4595 (12)	0.4555 (14)	0.4570 (14)	0.4685 (28)	0.4755 (38)
(y)	0.3213 (10)	0.3160 (10)	0.3187 (9)	0.3127 (8)	0.3106 (9)	0.3051 (8)	0.3053 (10)	0.3006 (10)	0.3124 (15)	0.3111 (16)
(z)	0.4586 (3)	0.4585 (3)	0.4586 (3)	0.4604 (2)	0.4599 (2)	0.4604 (2)	0.4600 (2)	0.4606 (2)	0.4604 (2)	0.4605 (3)
(B)	3.65 (21)	3.49 (20)	2.99 (18)	2.94 (14)	2.68 (14)	3.02 (13)	2.75 (12)	3.14 (14)	2.20 (15)	2.01 (15)
(n)	7.03 (12)	6.94 (12)	6.90 (11)	7.01 (10)	6.98 (10)	7.02 (8)	7.13 (9)	7.19 (9)	7.25 (12)	7.14 (13)

Table III

Bond lengths and resulting Zachariasen-Brown-Altermatt [12] valences V_i for $Tl_2Ba_2Cu_1O_6$ with parameters $r_0=1.996$ (Tl), 2.285(Ba), 1.679(Cu). The apparent Cu valence is larger than 2, indicating electron holes in the CuO layer, as in all other CuO-based superconductors, and as permitted by the removal of $Tl^{3+}O^{2-}$.

	#4(5K)	#4(300K)	#2(5K)	#2(300K)	#1(5K)	#1(300K)	#5(5K)	#5(300K)	#3(5K)	#3(300K)
Tl										
-O2	1.995	2.001	1.993	1.984	1.998	2.001	2.011	2.005	2.005	1.992
-O3	2.091	2.100	2.092	2.081	2.059	2.047	2.051	2.036	2.044	2.042
-O3	2.301	2.380	2.317	2.456	2.418	2.464	2.451	2.467	2.422	2.436
-O3	2.556	2.547	2.527	2.528	2.537	2.535	2.511	2.519	2.589	2.631
-O3	2.939	2.953	2.966	2.989	2.967	2.974	2.993	2.987	2.929	2.895
-O3	3.216	3.153	3.204	3.088	3.083	3.054	3.052	3.050	3.064	3.054
-V	2.55	2.44	2.55	2.47	2.52	2.50	2.49	2.52	2.51	2.52
Ba										
-O1x2	2.758	2.758	2.746	2.689	2.744	2.742	2.736	2.734	2.733	2.725
-O1x2	2.728	2.751	2.727	2.794	2.741	2.738	2.751	2.753	2.764	2.755
-O2x2	2.830	2.828	2.832	2.832	2.828	2.836	2.829	2.838	2.831	2.846
-O2	2.941	2.924	2.949	2.757	2.890	2.877	2.878	2.890	2.863	2.891
-O2	2.761	2.785	2.757	2.962	2.784	2.821	2.790	2.802	2.803	2.805
-V	2.07	2.03	2.08	2.05	2.07	2.04	2.25	2.21	2.22	2.21
Cu										
-O1x4	1.935	1.938	1.935	1.942	1.932	1.936	1.933	1.936	1.931	1.934
-O2x2	2.704	2.704	2.703	2.701	2.695	2.705	2.688	2.705	2.705	2.730
-V	2.13	2.11	2.13	2.09	2.15	2.12	2.14	2.12	2.15	2.13

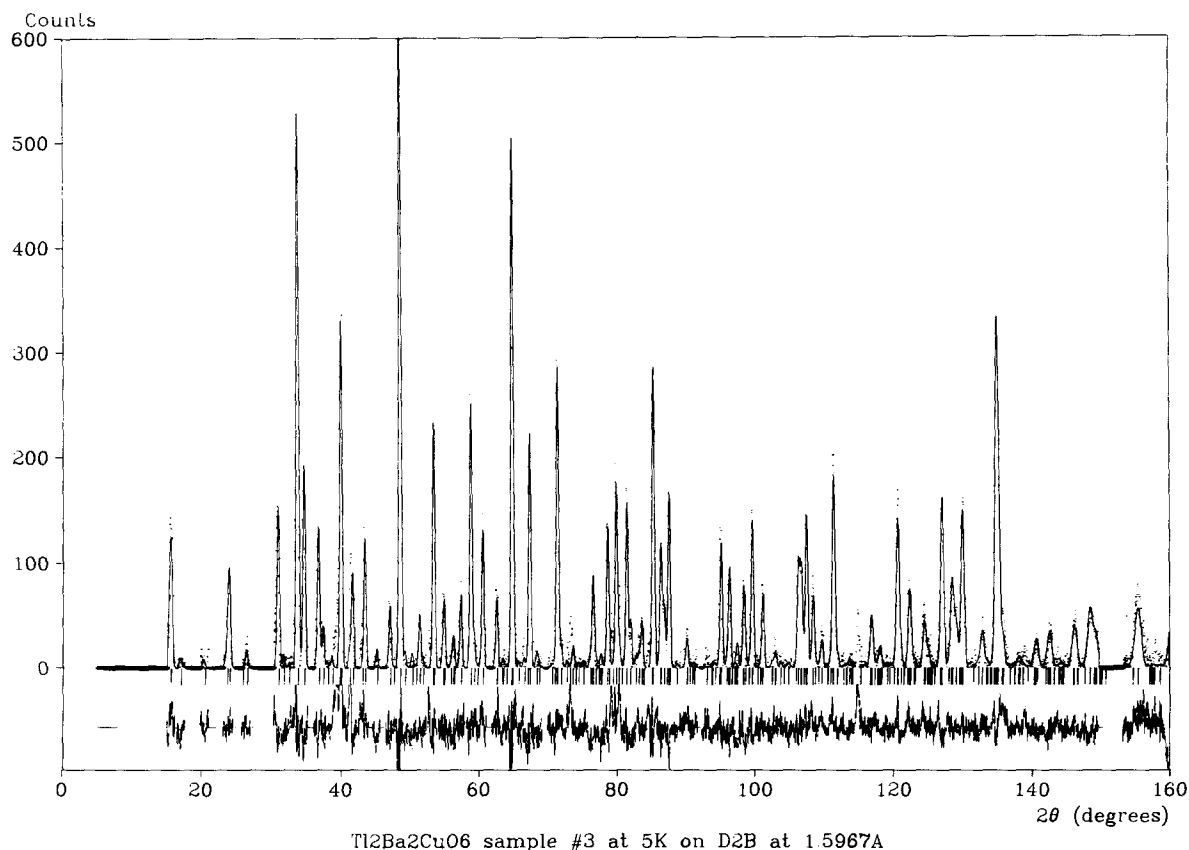


Fig. 3. Observed and calculated neutron powder diffraction patterns for superconducting $Tl_2Ba_2Cu_1O_6$ sample #3, with the difference pattern below. The vertical bars under the main plot indicate reflection positions.

have three relatively short bonds to oxygen opposite three relatively long bonds (table III).

4. Conclusion

Neutron diffraction has shown that the chemical compositions of superconducting and non-superconducting $Tl_2Ba_2Cu_1O_6$ are surprisingly similar, with 1 in 8 atoms in the TlO plane missing. The difference is that the annealed superconductor is almost tetragonal, while the non-superconducting material as first prepared is definitely orthorhombic. Removal of $Tl^{3+}O^{2-}$, will of course create electron holes, and permit the apparent copper valence to increase above 2+ in both the superconducting and non-superconducting material, as confirmed by the observed Cu-

O bond lengths. Electron microanalysis on these same samples by Cheetham et al. [13], agree that all are of similar composition; the amount of Tl-deficiency is estimated at less than 1 in 8, but our results are within the error limits of the electron microanalysis given the difficulties with surface contamination observed in the microscope.

Our results are also supported by electron microscopy and diffraction [14], which reveal a clear superstructure that can be explained by removing every 1/8th line of thallium atoms. In the orthorhombic phase, these lines of vacancies are ordered over long distances, while in the "tetragonal phase" the more diffuse electron diffraction superlattice spots indicate only short range order.

Since the composition of all samples is similar, and only the cell metric changes from orthorhombic to

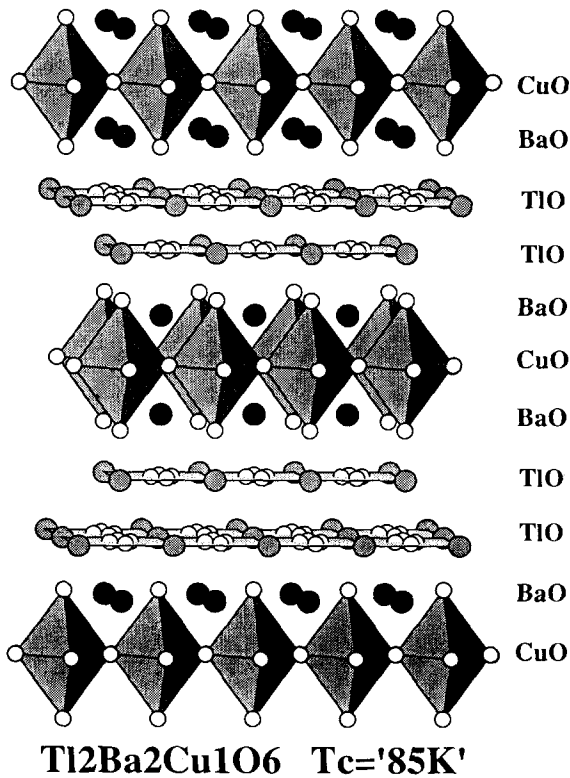


Fig. 4. Structure of $Tl_2Ba_2Cu_1O_6$, showing schematically the displacement of oxygen O3 in the TlO-plane toward thallium, but not showing the superstructure produced by the 1 in 8 TlO vacancies.

“tetragonal”, chemical composition and electron hole concentration may be a necessary but not sufficient condition for superconductivity. Details of the structure, and the superstructure, determined by the heat treatment, are apparently also important. In $Tl_2Ba_2Cu_1O_6$ a transition to a tetragonal structure may occur at high temperature, as in the similar La_2CuO_4 structure where tilting of the octahedra are involved, and it may be necessary to quench the material from above this temperature to obtain the superconducting “tetragonal” phase.

Superconductivity does seem to depend in all of these Bi- and Tl-phases, on obtaining a pseudotetra-

gonal metric, with oxygen within the TlO or BiO plane apparently disordered between four close equivalent positions (fig. 4). It is possible to draw comparisons between oxygen disorder in these materials and in the earlier high- T_c structures [15].

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