

STRUCTURE AND SUPERSTRUCTURE OF THE SUPERCONDUCTOR $Tl_2Ca_1Ba_2Cu_2O_8$ BY NEUTRON AND ELECTRON DIFFRACTION

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Neutron powder diffraction has been used to refine the structure of the high- T_c superconductor $Tl_2Ca_1Ba_2Cu_2O_8$ to determine the precise oxygen co-ordination and the effective valence of copper. The results are in excellent agreement with the Dupont X-ray structure, confirming the possible substitution of about 9% of the Ca-sites with Tl in our sample. The Tl-sites may be either 3% Tl-deficient or 7% Ca-substituted. The apparent valence of copper is 2.22. Oxygen in the center of the Tl square implies an average valence of less than 3 for Tl, and it is therefore not surprising that this oxygen is disordered toward the mid-point of the shortest Tl-Tl distance. High resolution electron images and diffraction reveal a quite different superstructure to the 5×5.4 Å superstructure seen in $Bi_2Sr_1Ca_2Cu_2O_8$. Very weak and diffuse superlattice spots may be due to a charge density wave in the TlO plane with period 6×3.8 Å.

Neutron powder diffraction has been used by Bor-det et al. [1] to decide between alternative X-ray models [2-4] for the structure of BiO layers in the 80 K superconductor $Bi_2Sr_1Ca_2Cu_2O_8$, and to obtain the effective Cu-valence as 2.33. The usual Aurivillius structure with an oxygen layer between a double Bi-layer [2] is not correct, and instead the oxygen is disordered within the Bi-layers, with an average NaCl-type structure. This latter model has now been used to describe the X-ray results [5] for $Tl_2Ca_1Ba_2Cu_2O_8$, and is confirmed in this paper by neutron diffraction from this material.

An attractive alternative structure, based mainly on chemical arguments involving dissociation of Bi^{3+} and Bi^{5+} , was proposed [6] for $Bi_2Sr_1Ca_2Cu_2O_8$, but these arguments presumably do not apply to the Tl-analogue, since the usual valences are Tl^{1+} and Tl^{3+} , with Tl^{5+} unknown.

The NaCl-type structure is, however, only the average structure of the BiO or TlO layers. Hewat et al. [7] have shown that in $Bi_2Sr_1Ca_2Cu_2O_8$ the superstructures involve waves of distortion along the b -axis. These waves are locked onto the lattice positions so that they have a local wave length of 4, 5 or 6 times the basic cell (5.4 Å). The superstructures

are composed of almost periodic combinations of these building blocks. For example, a combination of (4+5+5+5) gives a long period superlattice of 19×5.4 Å, with an average periodicity of $(4+5+5+5)/4 = 4.75 \times 5.4$ Å.

A fundamental question remains the effective valence of Cu, and how a valence in excess of 2 can be imposed by the structure, with perhaps cation deficiency [8], or oxygen excess and eventually dissociation of the valence of Bi (and Tl).

Tl_2O_3 , BaO_2 , CaO and CuO powder were mixed in an inert atmosphere and pressed into a pellet. The gross composition was $Tl_2Ba_2Ca_2Cu_3O_{10}$. The pellet was placed in a long alumina crucible together with, but separated from, Tl_2O_3 powder. The crucible with lid was placed in a silica tube with flowing O_2 . The temperature was kept at $750^\circ C$ for 2 hours, followed by 24 hours at $860^\circ C$. The pellet was re-ground and re-pressed, then reheated in flowing O_2 for 16 hours at $880^\circ C$, followed by $700^\circ C$ for 4 hours, and $550^\circ C$ for 2 hours, before finally being ground to a powder.

Figure 1 shows the Cu $K\alpha$ (1.5406 Å) X-ray powder diffraction pattern of the sample, taken with a Norelco diffractometer equipped with a graphite diffracted beam monochromator. The X-ray generator

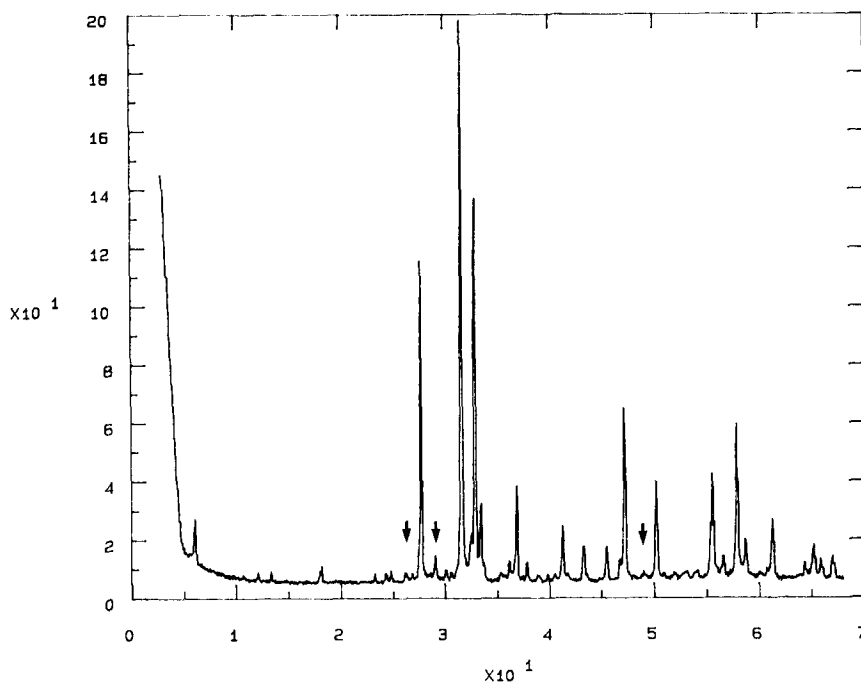


Fig. 1. X-ray powder diffraction pattern for $Tl_2Ca_1Ba_2Cu_2O_8$, with the strongest impurity phase lines indicated by arrows.

was run at 700 watts with with 2θ resolution 0.15° FWHM. The pattern corresponds to that for $Tl_2Ca_1Ba_2Cu_2O_8$ [5], with minor impurity phases identified as $Tl_2Ba_2Ca_2Cu_3O_{10}$ ($c=36 \text{ \AA}$) and CuO .

Figure 2 shows the magnetic flux exclusion for part of the sample pressed into a solid chip, showing a sharp drop with mid-point near 99 K. When the sample was powdered, the transition appeared much less sharp.

About 3 g of the sample was sealed in an aluminium can, and high resolution neutron powder data

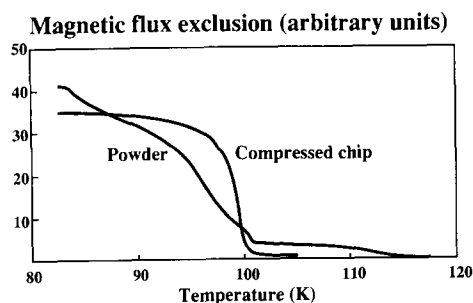


Fig. 2. Magnetic flux exclusion for $Tl_2Ca_1Ba_2Cu_2O_8$ as (a) loose powder, and (b) compressed chip.

collected on D2B at ILL Grenoble [9] with a wavelength of 1.5967 \AA to $2\theta=165^\circ$ in steps of 0.025° . Each point was averaged over 8 different detectors, with a total collection time of 12 hours. In fact the resolution was limited by the sample particle size, and similar results were obtained in 2 hours with the high flux geometry. Data were also collected at a wavelength of 3 \AA on D1A, to check that there was no deviation from tetragonal symmetry.

An early version [10] of the Rietveld profile refinement program was used with the X-ray structure [5] as the starting model. The background level was measured manually, and small regions containing peaks from the Al container or impurity phase excluded.

Figure 3 shows the observed and calculated profiles for the D2B data; the longer wavelength D1A data gave similar structural parameters, but less precision for the site occupancies and thermal vibrational amplitudes. The D2B data permitted the simultaneous refinement of site occupancies and anisotropic vibrational amplitudes for a total of 37 parameters.

Table 1 lists the final parameters. The atom co-or-

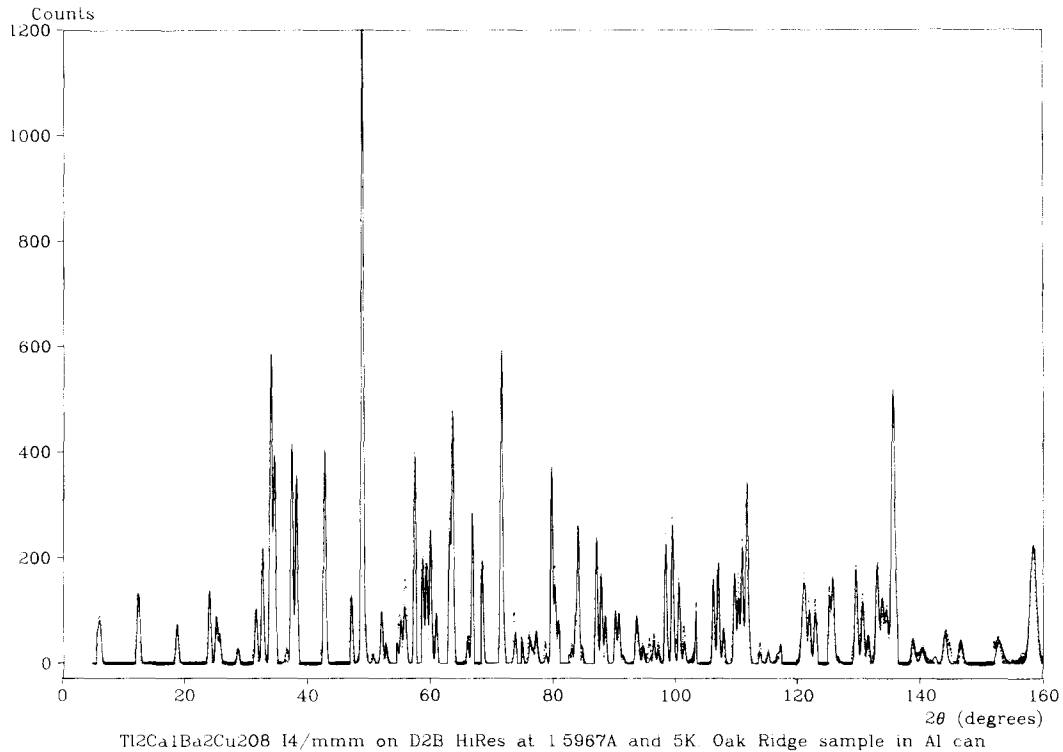


Fig. 3. Observed and calculated neutron powder diffraction patterns for $Tl_2Ca_1Ba_2Cu_2O_8$ at 1.5967 Å on D2B at ILL Grenoble.

dinates and anisotropic vibrational amplitudes are in good agreement with X-ray measurements [5], except that the displacement of the four-fold split O3 along the x -axis is now even larger. Relative to the assumed complete occupancy of the O1-site in the CuO plane, the Tl-site appears to be either 3% deficient in Tl or else 7% substituted by the weaker

scattering Ca. Again this is in approximate agreement with the X-ray results (on a different sample). Apart from the disorder of O3, the TlO plane may contain up to 9% extra oxygen. All other sites are probably fully occupied; one standard deviation in site occupancy is about 1%.

Table II lists the bond lengths and resulting va-

Table I

Atom co-ordinates (x, y, z), vibrational amplitudes ($B_{ij} = 8\pi^2 \langle u^2 \rangle \text{Å}^2$) and site "occupancies" n for $Tl_2Ca_1Ba_2Cu_2O_8$ with scattering lengths b at 300 K. The site occupancies indicate perhaps a transfer of Tl from the 4e-site to the 2a-site to replace 9% of Ca. The TlO planes may then be slightly deficient in Tl with a slight excess of oxygen; O3 is disordered along x toward the Tl-Tl closest distance. Only the oxygen site O1 within the CuO plane has been assumed fully occupied ($n=8$). Cell dimensions refined to $a=3.8558(1)$, $c=29.2596(9)$ in space group $I4/mmm$.

Atom	b	Site	n	x	y	z	B_{11}	B_{22}	B_{33}
Tl	8.89	4e	3.87(3)	1/2	1/2	0.2125(1)	1.93(6)	1.93(6)	1.60(12)
Ca	4.90	2a	2.15(3)	0	0	0	0.87(13)	0.87(13)	1.91(26)
Ba	5.25	4e	3.91(4)	0	0	0.1210(1)	0.67(9)	0.67(9)	1.53(20)
Cu	7.72	4e	3.92(4)	1/2	1/2	0.0551(1)	0.31(6)	0.31(6)	0.69(9)
O1	5.81	8g	8	0	1/2	0.0528(1)	0.57(8)	0.62(7)	0.74(11)
O2		4e	4.08(4)	1/2	1/2	0.1447(1)	0.72(8)	0.72(8)	2.23(18)
O3		16n/4	4.34(5)	0.6256(21)	1/2	0.2806(2)	6.58(70)	3.71(41)	1.22(26)

Table II

Bond lengths and resulting Brown–Altermatt–Zachariasen [12] valences V_i for $Tl_2Ca_1Ba_2Cu_2O_8$ [with $r_0=2.285$ (Ba), 1.967 (Ca), 1.679 (Cu), 1.95 (Tl by comparison with Tl oxides)]. Clearly the Tl–O3 distances in the TlO plane are too long (or too few) to satisfy a Tl valence of 3, even with this disordered structural model. By comparison, the Ca–O and Ba–O co-ordination is satisfactory, and the average Cu valence is larger than 2, as in all other CuO superconductors.

Tl–O2	1.985	×1	Ca–O1	2.470	×8	Cu–O1	1.929	×4
Tl–O3	2.051	×1				Cu–O2	2.622	×1
Tl–O3	2.417	×2	Ba–O1	2.775	×4			
Tl–O3	3.094	×2	Ba–O2	2.813	×4			
$V(Tl)$	2.33		$V(Ca)$	2.05		$V(Cu)$	2.11	
			$V(Ba)^*$	2.02		$Z(Cu)$	2.22	

*If Ba–O3=2.918 Å is included, the apparent valence of Ba increases by 0.18.

lences according to the Brown–Altermatt–Zachariasen [12] formula summing over the cation–oxygen bond lengths r_{ij} with empirical parameter $B=0.37$,

$$V_i = \sum_j \exp\{(r_0 - r_{ij})/B\}.$$

The parameters r_0 for each atom pair are obtained [12] for compounds in which the valence state is well known. Unfortunately, no value is given for $Tl^{3+}-O$, but a value of $r_0=1.95$ has been obtained from the Tl–O distances reported in ref. [11]. This value could be improved by a comparison with a larger number of Tl-compounds.

The co-ordination of Ca and Ba is quite normal, yielding apparent valences of 2 for both. The co-ordination of Cu is similar to that found in other CuO superconductors, with an apparent valence greater than 2. If the original Zachariasen formula is used [13], the Cu-valence increases to 2.22.

The co-ordination of Tl is of course quite unusual. The 2 Å out-of-plane distances Tl–O2 and Tl–O3 to the second layer are normal, but if O3 is placed in the center of the Tl-square (fig. 4) the ×4 Tl–O3 distances (2.73 Å) within the layer are too long (or too few), giving a valence sum of only 2.16 for Tl. (The valence Tl^{2+} does not exist: compounds where the formula would indicate this valence state actually contain Tl^{1+} and Tl^{3+} .) On the other hand, if O3 is placed between the closest Tl–Tl, the ×4 Tl–O3 distances ($a/2=1.93$ Å) are too short (or too many), giving a valence sum of nearly 6! It is then physically reasonable that when O3 is permitted to move off the high symmetry site, it moves toward the Tl–Tl line to reduce the Tl–O3 distance and increases the apparent Tl valence, but even with this

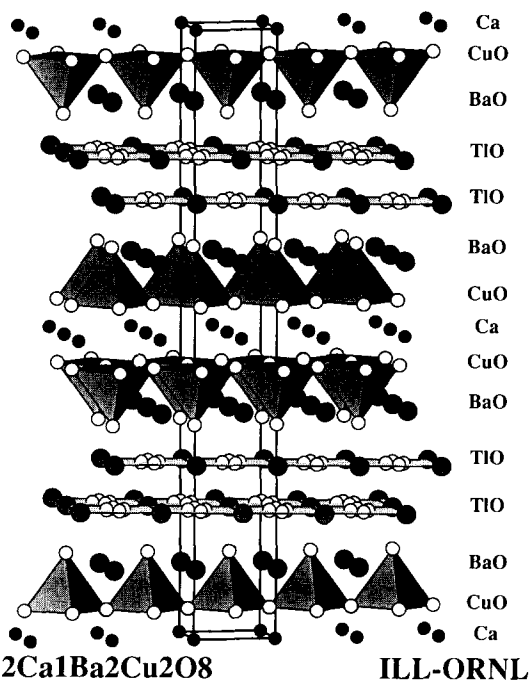
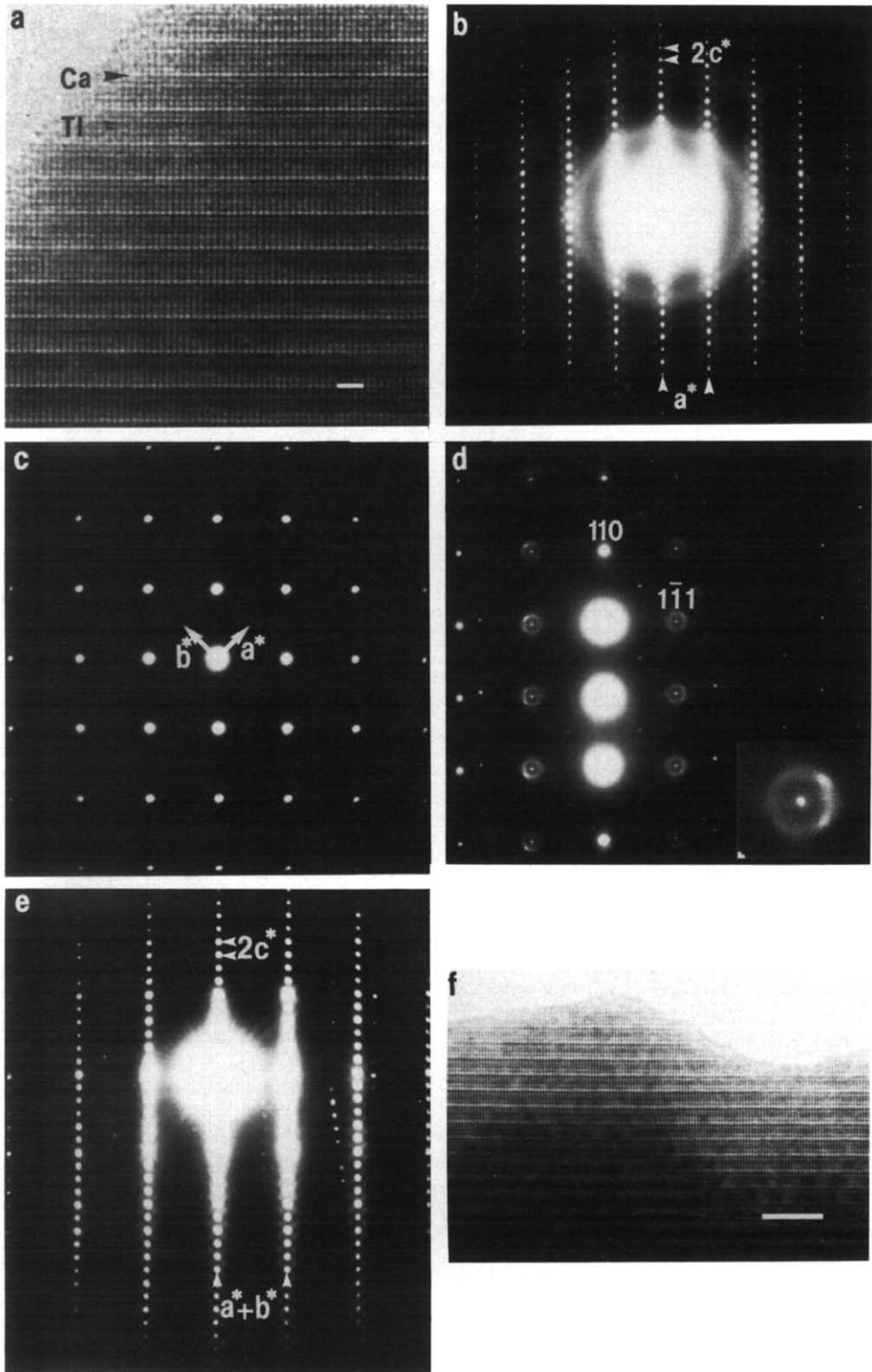


Fig. 4. The structure of $Tl_2Ca_1Ba_2Cu_2O_8$ showing the O3 atoms disorderly displayed toward the line joining Tl–Tl to reduce the Tl–O3 distance, which is too long for Tl^{3+} .

simple disordered model the valence sum is too small, supposing of course that all are Tl^{3+} and none are Tl^{1+} .

This is an important question, because if Tl^{1+} were present, it would explain why the valence of Cu could be larger than 2, without the need for cation deficiency or oxygen excess. Unfortunately, we do not yet have a model for the local environment of Tl consistent with the apparent disorder observed with X-



rays and neutrons, and the superstructure observed with electrons.

The sample preparation and techniques for electron microscopy on similar superconductors have been described earlier [14]. High resolution images of well ordered crystals were obtained at 200 kV on the JEOL 200CX microscope (fig. 5a). A very weak centered superstructure is observed in [100] projection images, and in the diffraction pattern (fig. 5b). Satellite peaks are observed displaced from each lattice reflection by $\langle \frac{1}{6}, 0, 1 \rangle$. They vary in intensity from region to region in the crystal, and only the first order satellites are ever seen. In the exact [001] orientation, no satellites are visible, except at higher angles (fig. 5c). Tilting away from the exact [001] orientation reveals four distinct satellites joined by a circle of diffuse intensity about each lattice reflection (see the [1-1-2] pattern in fig. 5d). The [110] pattern also reveals the satellites in some regions (fig. 5e). In this pattern, diffuse satellites corresponding to the circular diffuse regions seen in fig. 5d are sometimes visible (in fig. 5e, the satellites seen at some distance from the direct beam are actually the $\langle \frac{1}{6}, 0, 1 \rangle$ satellites picked up by the curvature of the Ewald sphere.) The [110] lattice images also display a weak and variable superstructure. (In fig. 5f the dark zones are located on an approximately face-centered superlattice).

The diffuse circles indicate that the ordering is essentially short-range in nature, and that it is imperfectly aligned along the [100] direction. The superlattice modulation vectors are presumably rotated about [001] from one region to another. It is not clear whether the superstructure modulation exists simultaneously on both (100) and (010) planes, or whether the modulation is unidirectional in any given small region. The modulation is most strongly seen in the TlO planes. These results are essentially in agreement with those of ref. [15]. However, those authors did not observe ordering in the [110] images.

In conclusion, the neutron results confirm the X-ray structure [5], which is similar to that of $Bi_2Sr_1Ca_2Cu_2O_8$, with oxygen within the Tl (or Bi) planes [1], and not between them as in the usual Aurivillius structure [2]. However, the electron results show that the superstructure is quite different, and much less evident than that in $Bi_2Sr_1Ca_2Cu_2O_8$ [7]. About 9% of Ca-sites may be occupied by Tl, and either 3% of Tl-sites are empty, or perhaps 7% are occupied by Ca. The remaining sites are fully occupied, except for perhaps as much as 9% extra oxygen within the TlO layers. The $Bi_2Sr_1Ca_2Cu_2O_8$ results were not sufficiently precise to obtain similar information on site occupancies in that material. In particular, no Ba-deficiency was observed to compare with the Sr-deficiency observed for some samples of $Bi_2Sr_1Ca_2Cu_2O_8$ [8]. The cation coordinations and implied valences are also consistent with fully occupied sites, except for Tl, where even when O3 is disordered from the center of the Tl-square, the Tl-O3 bonds are so long (or so few) that the average valence of Tl appears closer to 2 than to 3. The valence of Cu, at 2.22 is similar to that found in other copper oxide superconductors. The superstructure observed with electrons is probably due to displacements with the TlO layer, as in $Bi_2Sr_1Ca_2Cu_2O_8$ [7].

Note added in proof

After the completion of these measurements, we found that similar neutron results have been obtained at Brookhaven [16], though the longer wavelength used (2.4 Å) meant that only about 1/3 as many reflections were obtained.

Fig. 5(a) [110] image of $Tl_2Ca_1Ba_2Cu_2O_8$. The bright lines correspond to the Ca-planes, and the double dark lines to the Tl-planes. The scalar bar represents 10 Å. (b) [100] electron diffraction pattern (EDP) of $Tl_2Ca_1Ba_2Cu_2O_8$. Note the weak satellite reflections at $\langle 1/6, 0, 1 \rangle$ relative to the main reflections. (c) [001] EDP. The superlattice reflections are only seen at high angle. (d) [1-1-2] EDP showing groups of 4 satellite reflections connected by a circle of diffuse scattering (see inset). (e) [110] EDP showing very weak satellites corresponding to the diffuse circles in (d). The satellites seen at some distance from the direct beam are actually the $\langle 1/6, 0, 1 \rangle$ satellites picked up by the curvature of the Ewald sphere. (f) Low magnification [110] image showing variable, approximately face-centered superstructure. The scale bar represents 50 Å.

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