STRUCTURE AND SUPERSTRUCTURE OF THE SUPERCONDUCTOR Tl₂Ca₁Ba₂Cu₂O₈ BY
NEUTRON AND ELECTRON DIFFRACTION

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Neutron powder diffraction has been used to refine the structure of the high-Τ_c superconductor Tl₂Ca₁Ba₂Cu₂O₈ 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 TI square implies an average valence of less than 3 for Tl, and it is therefore not surprising that this oxygen is desordered 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 Bi₂Sr₂Ca₂Cu₂O₈. Very weak and diffuse superlattice spots may be due to a charge density wave in the TIO 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 Bi₂Sr₂Ca₂Cu₂O₈, and to obtain the effective Cu-valence as 2.33. The usual Aurivillus 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 Tl₂Ca₁Ba₂Cu₂O₈, and is confirmed in this paper by neutron diffraction from this material.

An attractive alternative structure, based mainly on chemical arguments involving dissociation of Bi³⁺ and Bi⁵⁺, was proposed [6] for Bi₂Sr₂Ca₂Cu₂O₈, but these arguments presumably do not apply to the Tl-analogue, since the usual valences are Tl¹⁺ and Tl³⁺, with Tl⁵⁺ 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 Bi₂Sr₂Ca₂Cu₂O₈ 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 × 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).

Tl₂O₃, BaO₂, CaO and CuO powder were mixed in an inert atmosphere and pressed into a pellet. The gross composition was Tl₂Ba₂Ca₂Cu₂O₁₀. The pellet was placed in a long alumina crucible together with, but separated from, Tl₂O₃ powder. The crucible with lid was placed in a silica tube with flowing O₂. The temperature was kept at 750°C for 2 hours, followed by 24 hours at 860°C. The pellet was re-ground and re-pressed, then reheated in flowing O₂ for 16 hours at 880°C, followed by 700°C for 4 hours, and 550°C for 2 hours, before finally being ground to a powder.

Figure 1 shows the Cu Kα (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

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Fig. 1. X-ray powder diffraction pattern for Tl₂Ca₁Ba₂Cu₂O₈, 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 Tl₂Ca₁Ba₂Cu₂O₈ [5], with minor impurity phases identified as Tl₂Ba₂Ca₂Cu₃O₁₀ (c=36 Å) 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 collected on D2B at ILL Grenoble [9] with a wavelength of 1.5967 Å to 2θ=165° 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 Å 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 AI 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-
coordinates and anisotropic vibrational amplitudes are in good agreement with X-ray measurements [5], except that the displacement of the four-fold split $O_3$ along the $x$-axis is now even larger. Relative to the assumed complete occupancy of the $O_1$-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 $O_3$, the TIO 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>
<thead>
<tr>
<th>Atom</th>
<th>$b$</th>
<th>Site</th>
<th>$n$</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{11}$</th>
<th>$B_{22}$</th>
<th>$B_{33}$</th>
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<tbody>
<tr>
<td>Tl</td>
<td>8.89</td>
<td>4e</td>
<td>3.87(3)</td>
<td>1/2</td>
<td>1/2</td>
<td>0.212(5)</td>
<td>1.93(6)</td>
<td>1.93(6)</td>
<td>1.60(12)</td>
</tr>
<tr>
<td>Ca</td>
<td>4.90</td>
<td>2a</td>
<td>2.15(3)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.87(13)</td>
<td>0.87(13)</td>
<td>1.91(26)</td>
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<tr>
<td>Ba</td>
<td>5.25</td>
<td>4e</td>
<td>3.91(4)</td>
<td>0</td>
<td>0</td>
<td>0.121(1)</td>
<td>0.67(9)</td>
<td>0.67(9)</td>
<td>1.53(20)</td>
</tr>
<tr>
<td>Cu</td>
<td>7.72</td>
<td>4e</td>
<td>3.92(4)</td>
<td>1/2</td>
<td>1/2</td>
<td>0.055(1)</td>
<td>0.31(6)</td>
<td>0.31(6)</td>
<td>0.69(9)</td>
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<tr>
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<td>5.81</td>
<td>8g</td>
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<td>0</td>
<td>1/2</td>
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<td>0.57(8)</td>
<td>0.57(8)</td>
<td>0.74(11)</td>
</tr>
<tr>
<td>O2</td>
<td>4.08</td>
<td>4e</td>
<td>4.08(4)</td>
<td>1/2</td>
<td>1/2</td>
<td>0.144(1)</td>
<td>0.72(8)</td>
<td>0.72(8)</td>
<td>2.23(18)</td>
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<tr>
<td>O3</td>
<td>4.34</td>
<td>16n/4</td>
<td>0.6256(21)</td>
<td>1/2</td>
<td>1/2</td>
<td>0.280(2)</td>
<td>6.58(70)</td>
<td>3.71(41)</td>
<td>1.22(26)</td>
</tr>
</tbody>
</table>

Fig. 3. Observed and calculated neutron powder diffraction patterns for Tl$_2$Ca$_1$Ba$_2$Cu$_2$O$_8$ at 1.5967 Å on D2B at ILL Grenoble.
Table II
Bond lengths and resulting Brown–Altermatt–Zachariasen [12] valences $V_i$ for Tl$_2$Ca$_1$Ba$_2$Cu$_2$O$_8$ [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 Tl0 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.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>$V_i$</th>
<th>Bond</th>
<th>Length (Å)</th>
<th>$V_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl–O2</td>
<td>1.985</td>
<td>1</td>
<td>Ca–O1</td>
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<tr>
<td>Tl–O3</td>
<td>2.051</td>
<td>1</td>
<td>Ba–O1</td>
<td>2.775</td>
<td>4</td>
</tr>
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<td>2.417</td>
<td>2</td>
<td>Ba–O2</td>
<td>2.813</td>
<td>4</td>
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<td>Tl–O3</td>
<td>3.094</td>
<td>2</td>
<td>Cu–O2</td>
<td>2.622</td>
<td>1</td>
</tr>
<tr>
<td>$V(Tl)$</td>
<td>2.33</td>
<td></td>
<td>$V(Ca)$</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>$V(Ba)^*$</td>
<td>2.02</td>
<td></td>
<td>$V(Cu)$</td>
<td>2.11</td>
<td></td>
</tr>
</tbody>
</table>

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

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

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

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$^{3+}$ 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 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-
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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 TiO 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\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_8\), with oxygen within the Ti (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\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_8\) [7]. About 9% of Ca-sites may be occupied by Ti, and either 3% of Ti-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 TiO layers. The Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_8\) 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\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_8\) [8]. The cation coordinates and implied valences are also consistent with fully occupied sites, except for Ti, where even when O3 is disordered from the center of the Ti-square, the Ti–O3 bonds are so long (or so few) that the average valence of Ti 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 TiO layer, as in Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_8\) [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 Ti\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_2\)O\(_8\). The bright lines correspond to the Ca-planes, and the double dark lines to the Ti-planes. The scalar bar represents 10 Å. (b) [100] electron diffraction pattern (EDP) of Ti\(_2\)Ca\(_2\)Ba\(_2\)Cu\(_2\)O\(_8\). 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 bare represents 50 Å.
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References