Incipient Modulation in the New High-Temperature Superconductor: $Tl_2Ba_2CaCu_2O_8$

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Electron diffraction patterns of the Tl-based superconductor $Tl_2Ba_2CaCu_2O_8$ display characteristic rings of diffuse intensity about space-group–forbidden reflections. There exists a close relationship between this diffuse intensity distribution and the incommensurate modulation observed in the structurally related Bi-based superconductor $Bi_2Sr_2CaCu_2O_8$.

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Recent developments in high-temperature superconductivity have produced two new structurally related superconducting materials of approximate composition $Bi_2Sr_2CaCu_2O_8$[1,2] and $Tl_2Ba_2CaCu_2O_8$,[3,4] hereafter referred to as BiSC and TlSC, respectively, The TlSC structure has been refined in $I4/mmm$ space group with cell parameters $a=3.8550(6)$ and $c=29.318(4)$ Å, and consists of two Cu-containing perovskite-related units separated by two thallium oxide units.[4] BiSC, however, differs from this simple "parent" structure in two ways. First, the basal plane of the average structure is expanded to an approximate $\sqrt{2}a_p\times\sqrt{2}a_p$ (p=perovskite) cell, refined as orthorhombic, $a=5.413(1)$, $b=5.421(3)$, $c=30.917(4)$ Å,[5] the space group of the average structure being either $Amaa$ or $A2aa$ ($Cccm$ or $Ccc2$ in the standard setting of the International Tables for Crystallography,[6] No. 66 or 37). Second, there exists an incommensurate modulation characterized by the primary modulation wave vector $\mathbf{q}=\mathbf{c}^*+\gamma(1,1,0)_p^*$ ($\gamma=0.105$).[5] The four-dimensional super-space group for this modulated structure is either N_{111}^{Amaa} (=66a.14.1 in the notation of de Wolff, Janssen, and Janner,[7] L_{111}^{Cccm} in the standard setting) or N_{111}^{A2aa} (=37a.14.1, L_{111}^{Ccc2}).[5]

Given the structural and chemical similarities between the two superconducting compounds, the reported[4] absence of the modulations in TlSC was surprising. Therefore, several specimens of stoichiometry $Tl_2Ba_2CaCu_2O_8$ were synthesized according to the methods described by Subramanian *et al.*[4] In our study, specimens were prepared in sealed Au vessels with various annealing and cooling regimes. The material described hereafter displayed properties typical of all the TlSC specimens prepared. It was annealed for 16 h at 900°C and quenched in liquid N_2. This material was well crystallized and reaction appeared to have reached equilibrium. X-ray powder diffraction gave a refined unit cell, tetragonal, $a=3.849(3)$ and $c=29.41(3)$ Å. Crushed fragments were examined via transmission electron microscopy.

Careful examination of heavily exposed electron diffraction patterns of our TlSC revealed the presence of a characteristic diffuse intensity distribution. Figure 1 shows an [001] zone-axis diffraction pattern. On our tilting slightly away from this [001] zone axis, diffuse intensity becomes apparent. This takes the form of rings of radius $\simeq\frac{1}{6}a_p^*$ [$=0.115\,|(1,1,0)_p^*|$] about those matrix reflections forbidden by the body-centering operation in the $[0\bar{1}1]$ zone-axis pattern in Fig. 2. Note, however, that these diffuse rings do not occur about the forbidden reflections in the [001] zone-axis pattern of Fig. 1. The 3D form of the diffuse intensity distribution is confirmed by the ⟨100⟩ zone-axis diffraction pattern of Fig. 3. The diffuse spots (arrowed) represent a cross section through the diffuse rings, around the forbidden reflection positions in Fig. 2. Other forms of diffuse intensity distribution (typically streaks and/or weak spots which also occur around positions of forbidden reflections) have also been observed, but, unlike the diffuse rings, were variable and not reproducible under our experimental conditions.

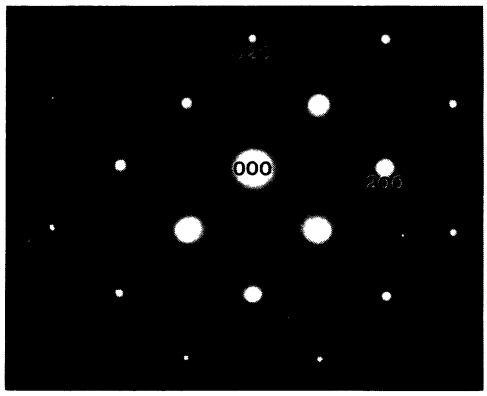

FIG. 1. [001] zone-axis electron diffraction pattern of TlSC. Note the absence of intensity about the forbidden $hk0$ ($h+k=2n+1$) matrix reflections.

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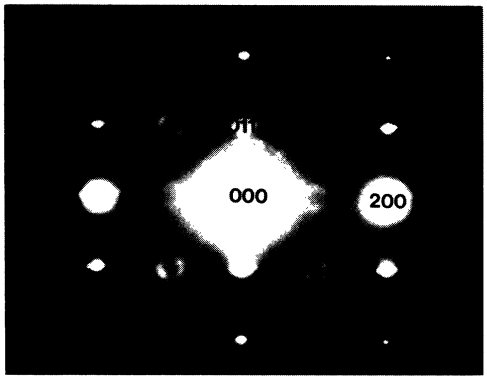

FIG. 2. [0$\bar{1}$1] zone-axis electron diffraction pattern of TlSC (obtained by tilting $\simeq 7.5°$ away from the [001] zone axis). Note the circles of diffuse intensity occurring around the Bravais-lattice–forbidden reflections.

For the following discussion of diffuse intensity we shall refer exclusively to the diffuse rings.

In the general case, the diffuse intensity distribution can only be observed at reciprocal-lattice positions $\mathbf{k}=\mathbf{G}+\mathbf{c}^*+A\mathbf{a}_p^*+B\mathbf{b}_p^*$, where $A^2+B^2\simeq(\frac{1}{6})^2$ and $\mathbf{G}$ is an allowed Bravais-lattice reciprocal-lattice vector. This describes circles of diffuse intensity of radius $\frac{1}{6}a_p^*$ surrounding the positions of forbidden matrix reflections. The intensity distribution within any one ring is not uniform, and the average intensity is not the same for all rings. Note the total absence of diffuse rings about forbidden reflections $hk0$, $h+k=2n+1$; see Fig. 1. There are obvious similarities between the diffuse intensity distribution in TlSC and the incommensurate satellite reflections in BiSC. If the ring of diffuse intensity in TlSC condensed on the position $A=B$ in the above formula, this would correspond to the incommensurate satellite reflections observed in BiSC.[5,8] A similar phenomenon of condensation of diffuse into discrete points occurs in $1T$-TaS_2.[9]

Single-crystal x-ray refinements of the average BiSC structure[1] and the TlSC structure[4] gave very large thermal parameters for atoms in the Bi oxide and Tl oxide layers, respectively. These results, together with the high-resolution electron microscope images of Matsui *et al.*,[8] suggest that the maximum disorder, compositional and/or displacive, occurs in these layers. This is further supported by the structure refinement of TlSC by Subramanian *et al.*[4] which has Ca substituting for Tl in this layer, and the refinement of BiSC by Matsui *et al.*[8] with Ca/Sr substituting for Bi. The incommensurate modulation present in the Bi-based superconductor, therefore, could arise from regular substitution of Ca/Sr for Bi with associated structural relaxation.

The observation of diffuse rings in TlSC is consistent with a modulation which is randomly oriented in the basal plane but with a discrete wavelength. The modulation wave vector in both BiSC and TlSC is $\sim 0.1\,|(1,1,0)_p^*|$. If one in ten Bi or Tl were replaced by Ca or Sr, then such a wave vector would not be unexpected. This level of substitution coincidentally has been reported by Subramanian *et al.* for TlSC.[4]

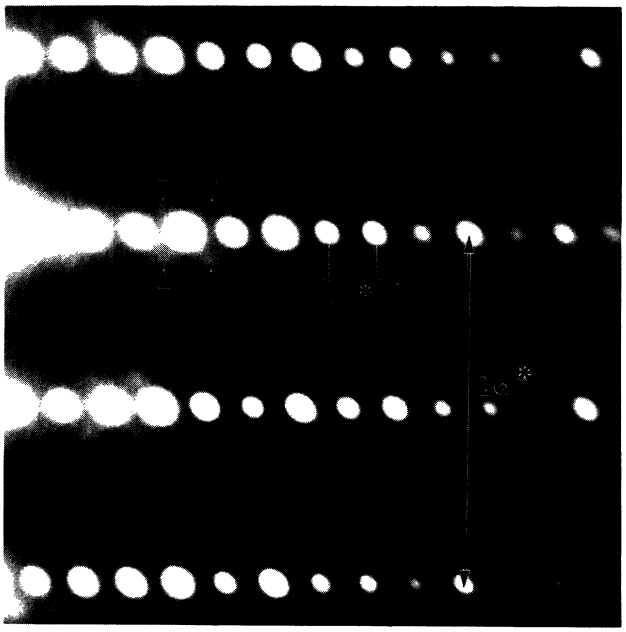

FIG. 3. A portion of a ⟨100⟩ zone-axis electron diffraction pattern. The diffuse spots around the forbidden matrix reflections are arrowed.

The facts that the modulation wave vectors are $\mathbf{q}=\mathbf{c}^*+A\mathbf{a}_p^*+B\mathbf{b}_p^*$ and that $\mathbf{q}\cdot\frac{1}{2}(\mathbf{a}_p+\mathbf{b}_p+\mathbf{c})\simeq\frac{1}{2}$ imply that the modulation in those Bi or Tl layers related by the body-centering operation are π out of phase. The observation that the diffuse intensity in TlSC is not observed in the [001] zone-axis pattern means that in this projection the modulated structure is the same as the average structure. Thus the modulation in those Tl layers related by a mirror plane perpendicular to the c axis are π out of phase. In other words, in Fig. 4, if atom 1 tends to be the Ca/Sr so also will atom 2, while atoms 3

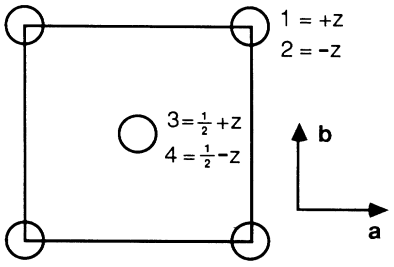

FIG. 4. [001] projection of the Tl atom positions in TlSC for which the value of z was refined (Ref. 4) as 0.2136. Bi atom positions in BiSC can be approximated with the same geometry with $z=0.1977$ (recalculated from refinement of BiSC, Ref. 1).

and 4 will tend to be Bi or Tl. Within one Tl layer, the average distance separating Ca atoms will be $\simeq 6a_p$ in TlSC.

Common to all the reported high-temperature superconductors, $La_{2-x}(Ba,Sr)_xCuO_4$, $YBa_2Cu_3O_{\sim 7}$, $Bi_2Sr_2CuO_6$, BiSC, and TlSC, is the copper-containing perovskite-related unit with in-plane dimension $\simeq 3.85$ Å. In the case of the latter two, these perovskitelike units are separated by Bi oxide and Tl oxide units, respectively. The basal-plane periodicities of these oxide units must match the perovskite dimension. If these two periodicities are not commensurate with each other, the structure cannot form. We propose that the substitution of Ca/Sr, or even possibly Cu, for Bi and Tl facilitates commensurability of the two structural units by adding flexibility to the basal plane dimension, and that the modulation has its origins in this substitution, with the displacive component of the modulation being a basic consequence. The similarity of wavelengths for the modulation in BiSC and TlSC implies a similarity in the level of substitution required to achieve this commensurability.

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[1]M. A. Subramanian, C. C. Torardi, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Science **239**, 1015–1017 (1988).

[2]R. M. Hazen, C. T. Prewitt, R. J. Angel, N. L. Ross, L. W. Finger, C. G. Hadidiacos, D. R. Veblen, P. J. Heaney, P. H. Hor, R. L. Meng, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, Z. J. Huang, L. Gao, J. Bechtold, and C. W. Chu, Phys. Rev. Lett. **60**, 1174 (1988).

[3]Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 55 (1988).

[4]M. A. Subramanian, J. C. Calabrese, C. C. Torardi, J. Gopalakrishnan, T. R. Askew, R. B. Flippen, K. J. Morrisey, U. Chowdrey, and A. W. Sleight, Nature (London) **332**, 420–422 (1988).

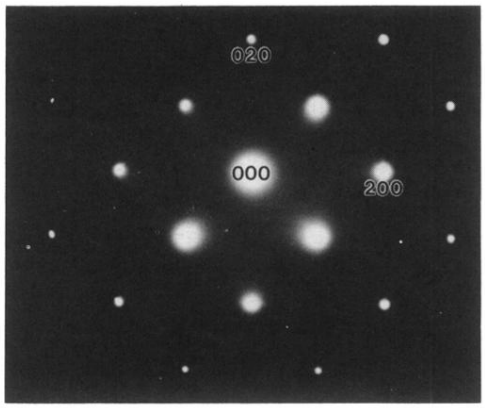
[5]R. L. Withers, J. S. Anderson, B. G. Hyde, J. G. Thompson, L. R. Wallenberg, J. D. Fitz Gerald, and A. M. Stewart, to be published.

[6]*International Tables for Crystallography,* edited by Th. Hahn (Reidel, Hingham, MA, 1983), Vol. A, p. 302.

[7]P. M. de Wolff, T. Janssen, and A. Janner, Acta Crystallogr., Sect. A 37, 625 (1981).

[8]Y. Matsui, H. Maeda, Y. Tanaka, and S. Horiuchi, to be published.

[9]R. L. Withers and T. R. Welberry, J. Phys. C **20**, 5975 (1987).



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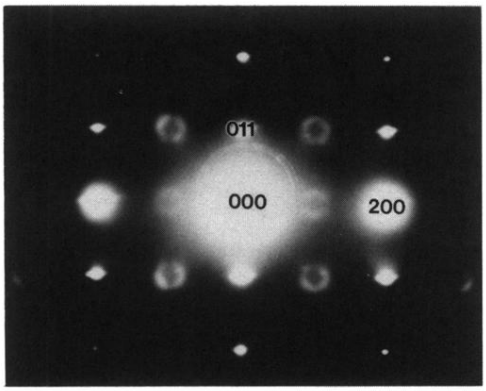

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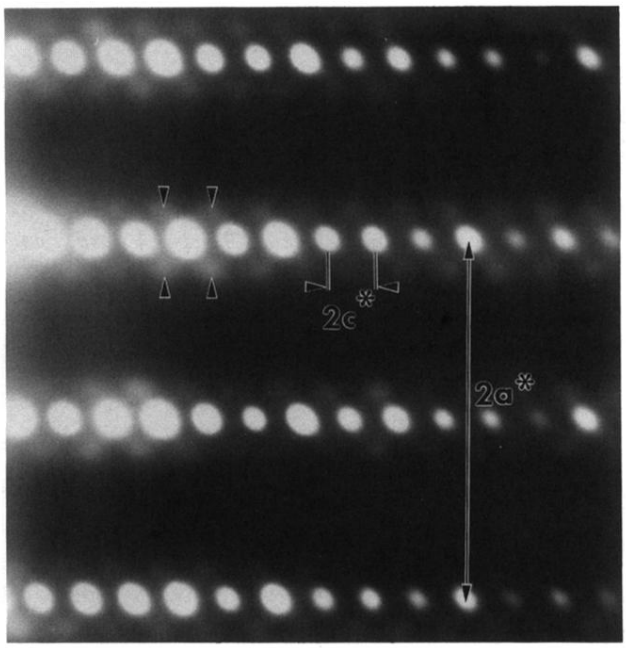

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