Oxygen "disorder" and the structures of high-T_c superconductors by neutron powder diffraction

by A. W. Hewat
E. A. Hewat
P. Bordet
J.-J. Capponi
C. Chaillout
J. Chenavas
J.-L. Hodeau
M. Marezio
P. Strobel
M. François
K. Yvon
P. Fischer
J.-L. Tholence

All of the high-T_c perovskite superconductors appear to show disorder of certain oxygen atoms. In $(La,Sr)_2CuO_4$ and perhaps also in $YBa_2Cu_3O_7$ this is associated with a structural transition. The Bi and Tl superconductors, for which we now have neutron structural data on four different phases, also show oxygen "disorder" which may be associated with valence fluctuations. In $Tl_2Ba_2CuO_6$, electron holes are created by the absence of 1/8 of the atoms in the TlO plane, producing a marked superstructure. However, this material is not superconducting if the superstructure is well ordered, with an orthorhombic (strictly monoclinic) structure. The T_c appears to depend on the disorder of the superstructure to produce a pseudotetragonal metric in which the oxygen atoms within the TlO plane are distributed over four equivalent sites about the center of the Tl square.

This paper is not concerned with the gross disorder observed in poorly prepared or partly reduced samples, especially at high temperature, but rather with microscopic disorder where oxygen appears distributed over several neighboring potential minima.

$(La,Sr)_2CuO_4$ undergoes a typical $SrTiO_3$ perovskite-type structural transition involving tilting of the CuO_6 octahedra **[Figure 1(a)]** below a temperature which decreases with Sr doping or increasing pressure (with a corresponding increase in T_c. Above this temperature, the CuO_6 apex oxygens are disordered over two potential minima, one of which will be occupied below the transition temperature [1]. This order–disorder transition produces a change of symmetry from orthorhombic to tetragonal. Axe et al. [1(d), (e)] have shown that tilting about a second axis can produce another structural transition for certain compositions of $(La,Ba)_2CuO_4$.

$YBa_2Cu_3O_7$ contains CuO chains of incomplete "octahedra" parallel to channels which in normal perovskite would be occupied by additional oxygen **[Figure 1(b)]**. Even at low temperature, the basal oxygen in these chains is strongly disordered in directions perpendicular to the chain axes, as evidenced by large thermal B-factors [2]. Using high-resolution neutron powder diffraction at many temperatures [3(a)], we have suggested the possibility of a disorder–order transition below some transition temperature, when these

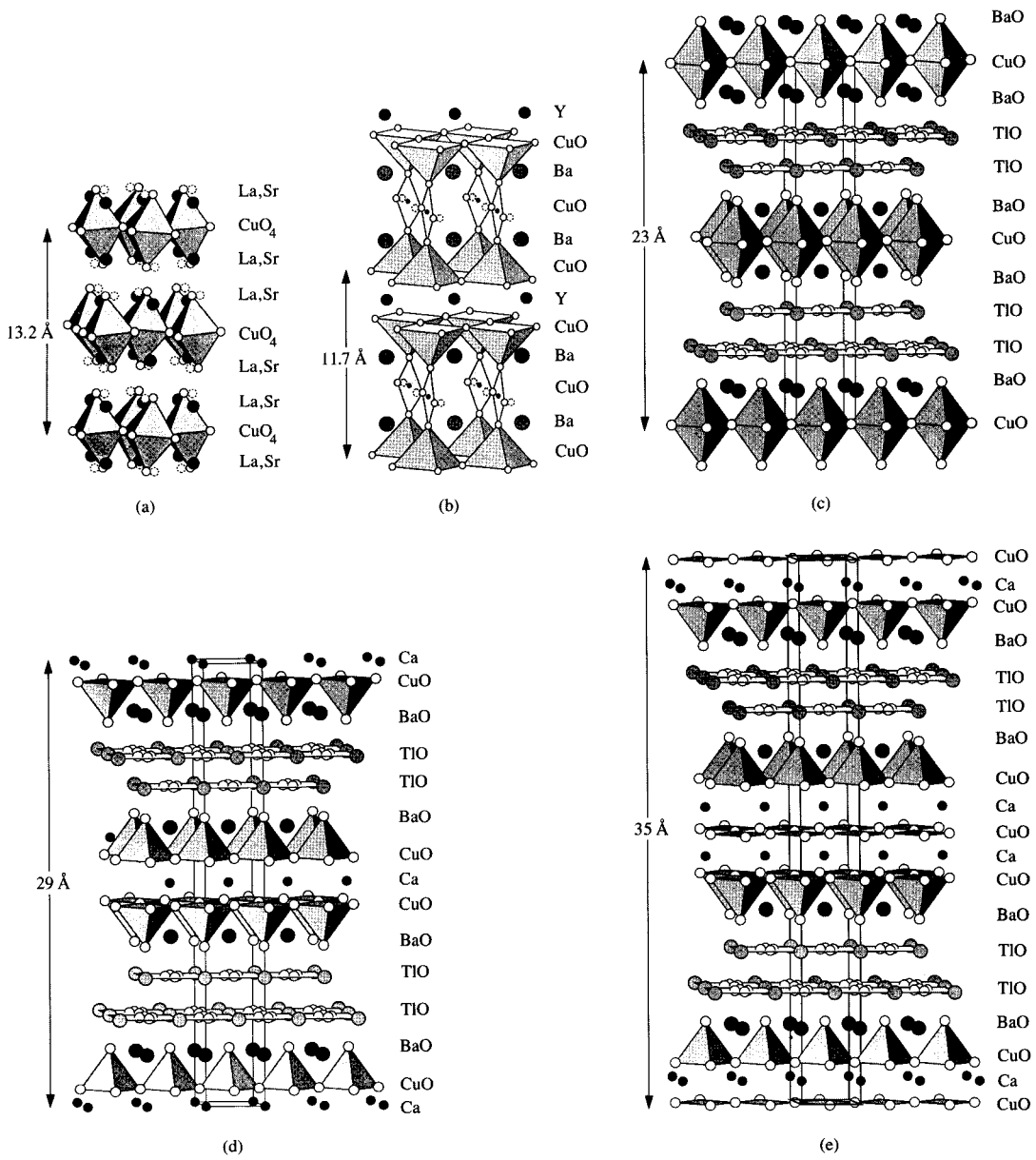

Figure 1

The structures of the various CuO superconductors, showing how similar they all are to the original Bednorz and Müller phase $(La,Sr)_2CuO_4$. (a) The 35 K superconductor $(La,Sr)_2CuO_4$, showing tilting of the CuO_6 octahedra in the orthorhombic phase, with the alternative oxygen positions in the high-temperature disordered tetragonal phase shown dotted [1]. (b) The 95 K superconductor $YBa_2Cu_3O_7$. Electron holes are distributed over both the chains and the planes, with apparent valences [2] Cu(chain) = 2.5 and Cu(plane) = 2.25. The oxygen in the chains may be disordered, or ordered over short distances to produce zigzag chains [3(a)]. (c) The "85 K" superconductor $Tl_2Ba_2CuO_6$ (2021) may be compared to $(La,Sr)_2CuO_4$; 1/8 of the TlO atoms are missing, producing a well-ordered superstructure in the nonconducting orthorhombic phase [4(g)]. This superstructure is disordered in the superconducting tetragonal phase, with oxygen in the TlO layers disordered over four equivalent sites [Figures 4(c), (d)]. (d) The "105 K" superconductor $Tl_2Ca_1Ba_2Cu_2O_8$ (2122) may be compared to $YBa_2Cu_3O_7$ with the CuO chains replaced by TlO layers. The structure is pseudotetragonal, with oxygen disordered in the TlO layer. The apparent Cu valence is 2.15 for the Cu pyramids. (e) The "125 K" superconductor $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2223), which appears to be strictly tetragonal, with disordered TlO-plane oxygen. The apparent Cu valence is 2.15 for the Cu pyramids, but only 2.0 for the Cu planes, which may serve merely to stabilize the tetragonal metric.

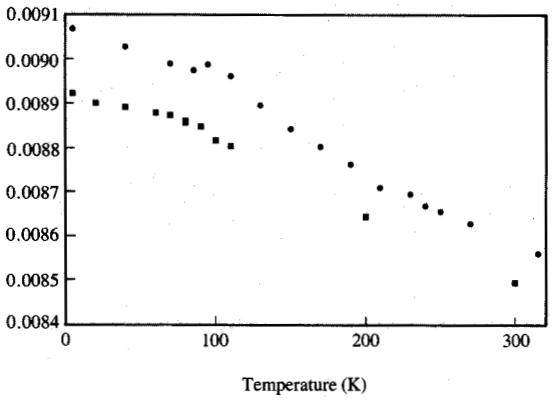

Figure 2

Orthorhombic distortion $(b - a)/(b + a)$ in two samples of $YBa_2Cu_3O_7$, as determined by neutron powder diffraction, showing an apparent anomaly near T_c in agreement with X-ray results [3].

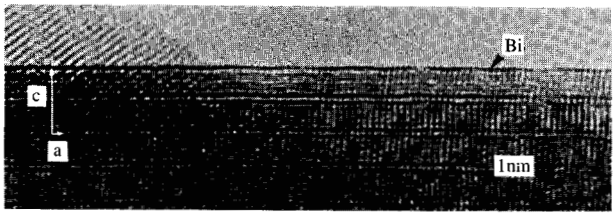

Figure 3

High-resolution electron image showing a single BiO plane at the surface of Bi 2122, showing that bonding is weak between BiO planes and implying that there are no Bi–O–Bi interplanar bonds, as in Aurivillius phases.

"incomplete octahedra" would be tilted against each other, producing zigzag CuO chains. A plot of the oxygen displacement from the chain axis shows a decrease with temperature, consistent with thermal vibration, but below T_c the displacement is constant at about 0.1 Å, implying static disorder. The coherence length would, however, be only about 50 Å, since every $1/x$th chain oxygen is missing for $YBa_2Cu_3O_{7-x}$, where typically $x \sim 0.1$. We are therefore unable to observe the superlattice reflections expected for this doubling of the b-axis, nor any lowering of the apparent symmetry from orthorhombic *Pmmm*.

Fossheim et al. [3(b)] review anomalies in the elastic properties and specific heat of $YBa_2Cu_3O_{7-x}$ which may be due to such subtle structural transitions. A plot of the orthorhombic distortion $(b - a)/(b + a)$ also shows an apparent anomaly near T_c (**Figure 2**) in agreement with the observation of Horn et al. [3(c)]. We find a smaller cusp for material with $x = 0.08$, and the anomaly is no longer apparent in a second sample with $x = 0.14$ except for a change in gradient near T_c. The orthorhombic distortion is very sensitive to oxygen deficiency or nonlinearity of the chains, since it is of course zero for tetragonal $YBa_2Cu_3O_6$ $(x = 1)$.

The structural anomaly for the basal chain oxygen is accompanied by smaller effects on the oxygen bridging the CuO chain to the CuO plane, and on the distance of this bridging oxygen from copper in the plane. Batlogg [3(d)] has pointed to the apparent importance of this bridging oxygen, with the Cu–O distance increasing with decreasing T_c due to reduction of the chain oxygen or to substitution of Cu. In the original structural work of Capponi et al. [2], the observed Cu–O distances were interpreted as evidence for the electron holes being distributed equally on both chain and plane copper sites. An alternative explanation, producing similar bond lengths, would put the holes mainly on the bridging oxygen.

$Bi_2Ca_1Sr_2Cu_2O_8$ is more complex. Neutron diffraction [4(a)–(c)] has been used to decide between different models for the BiO layers [4(d)–(f)]. Instead of oxygen between the Bi layers, as in the usual Aurivillius structure [4(f)], it is within the Bi layers. The two BiO layers are weakly bound together, being separated by the Bi lone-pair electrons, and the structure is seen to cleave readily between layers [4(g)]. (See **Figure 3**.) Not only is a marked superstructure evident within these layers, but the BiO oxygen appears disordered about the center of the Bi square **[Figure 4(a)]**. This is perhaps because the Bi–Bi distance is determined by the need to match the copper oxide perovskite layer, leaving too much space for oxygen within the BiO layer. The powder diffraction pattern shows that to a good approximation the cell metric is tetragonal, but if the space group is taken to be *F4/mmm*, this BiO oxygen appears distributed over four sites, closer to one of four pairs of Bi. However, the microscopic symmetry, as determined from convergent beam electron diffraction [4(h)] is orthorhombic, with space group *Amaa* or *A2aa*, subgroups of *F4/mmm*.

Refinement in noncentric *A2aa* implies an ordered structure, with oxygen occupying only one of the four equivalent sites of *F4/mmm* **[Figure 4(b)]**. Again, we might expect an order–disorder transition with increasing temperature, but the superstructure makes it difficult to study the details of this material.

This superstructure produces superlattice reflections at noncommensurable d-spacings of about 4.75 times the b-axis. We have shown by high-resolution electron microscopy [4(g)] that this superstructure is due to "blocks" of typically 5, 5, 5, 4 times the b-axis, yielding an average supercell of $19/4 = 4.75$ **[Figure 5]**. This superstructure is probably due to an imperfect match between the perovskite and BiO layers.

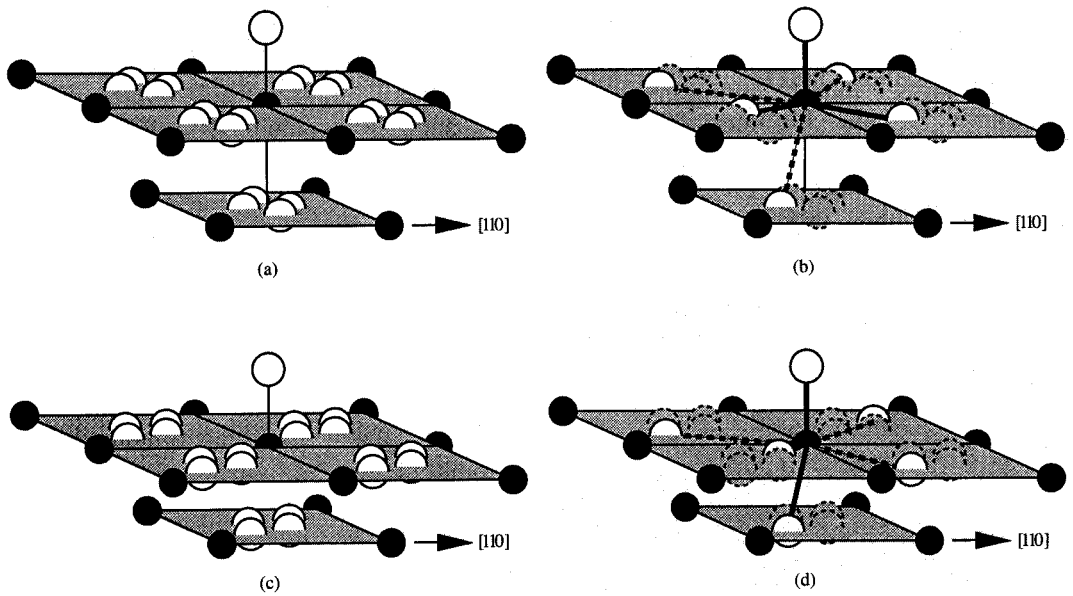

Figure 4

Structure of the BiO and TlO planes in the Bi and Tl (2122) phases. (a) Apparent oxygen disorder in the tetragonal space group *F4/mmm*. (b) Oxygen orders on one of the four sites equivalent in *F4/mmm*, if the microscopic symmetry satisfies the orthorhombic subgroup *A2aa*; the alternative oxygen sites are shown dotted. (c) Slightly different oxygen disorder in the thallium *Fmmm* phase. (d) Oxygen order to produce again three short Tl–O bonds, plus three long. The difference between Bi and Tl materials is that thallium has no lone-pair electrons which separate the BiO planes, so Tl forms a short bond to the second TlO plane. Oxygen within the plane moves toward a single Tl atom to complete its three short TlO bonds, rather than toward a pair of Bi atoms.

The superstructure is along a different direction, and much less pronounced in the Tl analog $Tl_2Ca_1Ba_2Cu_2O_8$ [5], which has an even higher T_c **[Figure 1(d)]**. A good fit to the data can be obtained in the tetragonal space group *I4/mmm*, but then oxygen again appears disordered over four sites within the TlO plane **[Figure 4(c)]**. Again, we can obtain an ordered structure **[Figure 4(d)]** by lowering the microscopic symmetry to orthorhombic *A2aa* or even centrosymmetric *Amaa*. However, ordering, if it exists, is probably of very short range, since the cell metric appears tetragonal rather than orthorhombic.

We found a situation similar to that of $Tl_2Ca_1Ba_2Cu_2O_8$ in the $T_c \sim 125$ K-phase $Tl_2Ca_2Ba_2Cu_3O_{10}$ **[Figure 1(e)]**, for which the cell metric appears strictly tetragonal, with even smaller oxygen disorder [5(b), (c)]. Again, electron diffraction reveals a subtle superstructure [5(c), (d)].

The coordination of Tl is slightly different from that of Bi. In the Bi compounds, oxygen is displaced from the center of the Bi square toward a *pair* of B atoms, so that each Bi atom has two oxygens at about 2 Å within the BiO plane, plus a third in the SrO layer above. There are three further oxygens at much larger distances, including one in the second BiO plane. The Bi lone-pair electrons are presumably between the BiO layers, explaining the ease with which the material cleaves. In the Tl materials, the TlO planes are much closer together, because there are no lone-pair electrons. Each Tl then already has two close oxygens, one from the perovskite plane and one from the second TlO layer. Oxygen within the TlO layer then moves toward a *single* Tl atom, so that again each Tl has three close oxygens plus three at greater distances.

This difference explains why it is relatively easy to produce single TlO-layer compounds (S. Parkin, [5(e)]), but probably impossible to produce single BiO-layer materials. The absence of lone-pair electrons permits Tl to form bonds to perovskite oxygen on both sides of a single TlO plane.

Our results for the first member of the series, $Tl_2Ca_0Ba_2Cu_1O_6$ **[Figure 1(c)]**, which also has the lowest T_c (<80 K), are perhaps the most interesting [5(f)]. We examined five samples after different heat treatment. Some were almost tetragonal and superconducting, while others were clearly orthorhombic and nonconducting! The former

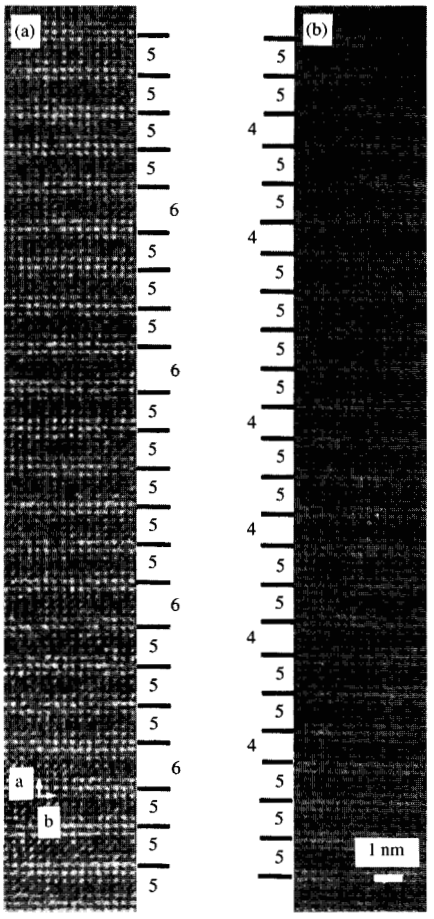

Figure 5

High-resolution electron image showing "blocks" of 4, 5, and 6 times the a-axis in Bi 2122 for two different samples, (a) and (b). A typical block sequence of 5, 5, 5, 4 produces an "incommensurable" superstructure of period $(5 + 5 + 5 + 4)/4 = 4.75 \times a$ [4(g)].

were produced by heat-treating the latter. This is reminiscent of orthorhombic superconducting $YBa_2Cu_3O_7$ and tetragonal semiconducting $YBa_2Cu_3O_6$, but the explanation for $Tl_2Ca_0Ba_2Cu_1O_6$ is not so simple. Neutron diffraction shows that about 1/8 of the TlO atoms are missing, producing a superstructure which can be seen with the electron microscope **[Figure 6(a)]**, with corresponding sharp superlattice spots **[Figure 6(b)]**. A model for this superstructure can be obtained by removing 1/8 of the TlO atoms along lines along [310] (**Figure 7**). It appears that the orthorhombic form of $Tl_2Ca_0Ba_2Cu_1O_6$ is produced when these Tl vacancies are ordered over large distances.

Neutron diffraction shows that the superconducting form has essentially the same chemical composition as the nonconducting form, again with 1/8 of the TlO atoms missing. The difference is that these vacancies are now apparently disordered, or ordered over only short distances, producing a pseudotetragonal metric. Electron diffraction shows that the superlattice spots, which were very sharp in the well-ordered orthorhombic phase **[Figure 6(c)]**, are very diffuse in the tetragonal phase **[Figure 6(d)]**. In the nonsuperconducting orthorhombic phase, oxygen within the TlO planes will be ordered on one of the four positions [Figure 4(d)], while in the superconducting tetragonal phase it will be distributed over these four positions, which are then equivalent. Only this pseudotetragonal form is seen for the higher members of the series, where the perovskite metric dominates.

In conclusion, the structures of all of the perovskite high-T_c superconductors may permit structural transitions involving order–disorder of oxygen atoms. Since the oxygen-atom coordination determines the apparent valence on the metal ions, subtle changes in oxygen order imply changes in valence, and may be related to superconductivity in these materials.

References

1. (a) M. François, K. Yvon, P. Fischer, and M. Decroux, "Structural Phase Transition at 150 K in the High-Temperature Superconductor $La_{1.85}Sr_{0.15}CuO_4$," *Solid State Commun.* **63,** 35 (1987).
   (b) J. D. Jorgensen, H. Schuttler, D. G. Hinks, D. W. Capone, K. Zhang, M. B. Brodsky, and D. J. Scalapino, "Lattice Instability and High-T_c Superconductivity in $La_{(2-x)}Ba_{(x)}CuO_4$," *Phys. Rev. Lett.* **58,** 1024 (1987).
   (c) D. Mc. Paul, G. Balakrishnan, N. R. Berhoeft, W. I. F. David, and W. T. A. Harrison, "Anomalous Structural Behaviour of the Superconducting Compound $La_{1.85}Ba_{0.15}CuO$," *Phys. Rev. Lett.* **58,** 1976 (1987).
   (d) J. D. Axe, H. You, D. Hohlwein, D. E. Cox, S. C. Moss, K. Forster, P. Hor, R. L. Meng, and C. W. Chu, "Structural Phase Transformations and High-T_c Superconductivity," preprint (1988).
   (e) J. D. Axe, D. E. Cox, K. Mohanty, H. Moudden, A. R. Moodenbaugh, Youwen Xu, and T. R. Thurston, "A New Structural Modification of Superconducting $La_{2-x}M_xCuO_4$," *IBM J. Res. Develop.* **33,** 382 (1989, this issue).
2. J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournier, "Structure of the 100 K Superconductor $Ba_2YCu_3O_7$ Between (5–300) K by Neutron Powder Diffraction," *Europhys. Lett.* **3,** 1301 (1987).
3. (a) M. François, A. Junod, K. Yvon, A. W. Hewat, J. J. Capponi, P. Strobel, M. Marezio, and P. Fischer, "A Study of the Cu–O Chains in the High-T_c Superconductor $YBa_2Cu_3O_7$ by High Resolution Neutron Powder Diffraction," *Solid State Commun.* **66,** 1117 (1988).
   (b) K. Fossheim and T. Lægreid, "A Review of Elastic Properties of High-T_c Superconductors and Some Related C_p Results," *IBM J. Res. Develop.* **33,** 365 (1989, this issue).
   (c) P. M. Horn, D. T. Keane, G. A. Held, J. L. Jordan-Sweet, D. L. Kaiser, F. Holtzberg, and T. M. Rice, "Orthorhombic Distortion at the Superconducting Transition in $YBa_2Cu_3O_7$: Evidence for Anisotropic Pairing," *Phys. Rev. Lett.* **59,** 2772 (1987).
   (d) B. Batlogg, R. J. Cava, L. F. Schneemeyer, and G. P. Espinosa, "High-T_c Superconductivity in Bismuthates—How Many Roads Lead to High T_c?" *IBM J. Res. Develop.* **33,** 208 (1989, this issue).

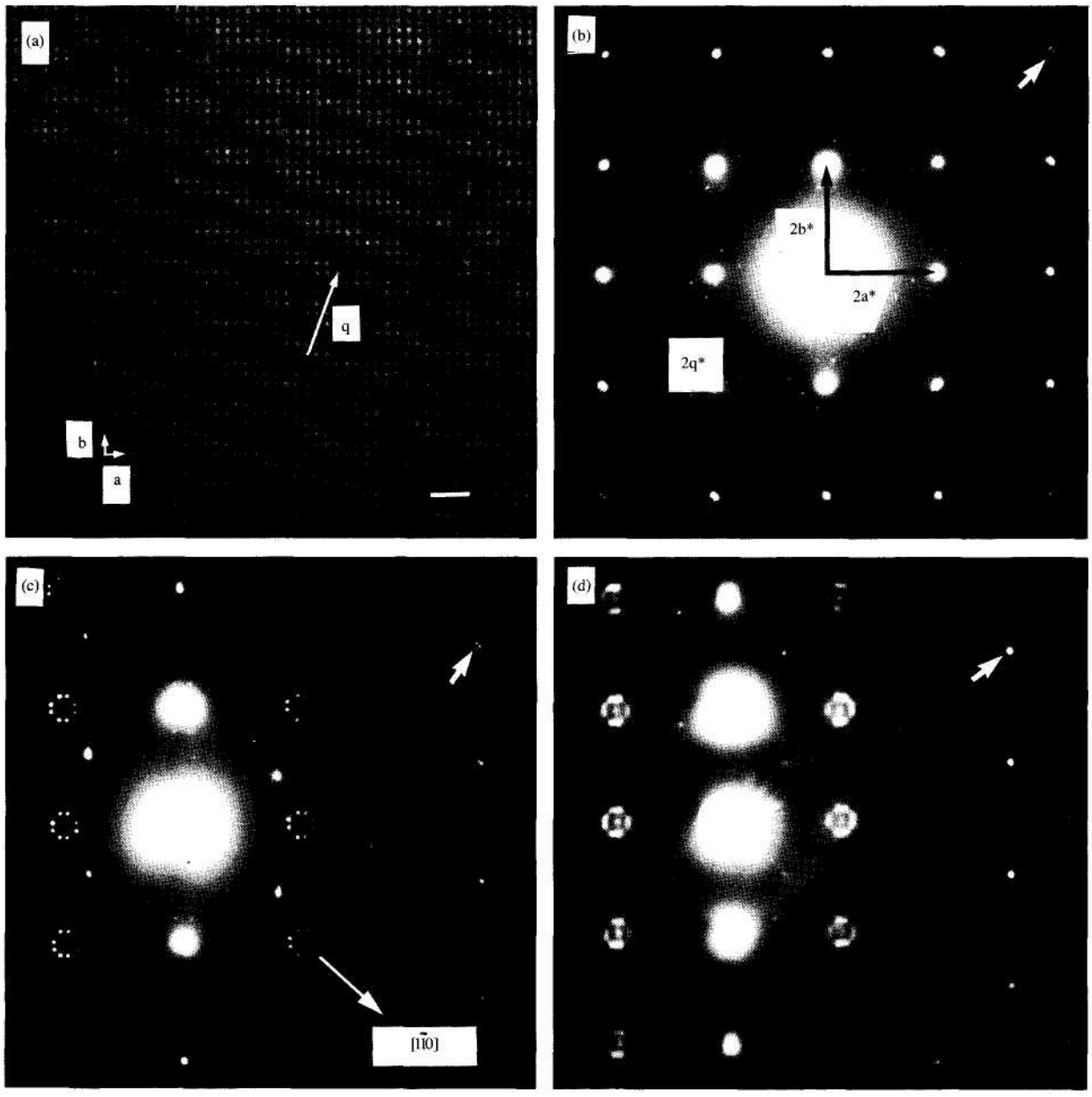

Figure 6

(a) High-resolution [001] electron image of the superstructure in orthorhombic Tl 2021. This image can be interpreted as a systematic absence of 1/8 of the TlO atoms (Figure 7), as required by the neutron diffraction results [5(f)]. (b) The corresponding electron diffraction pattern, showing superlattice spots. (c) The superlattice spots are sharp, indicating long-range order in the orthorhombic nonsuperconducting material. (d) The superlattice spots are diffuse, indicating only very short-range order in the pseudotetragonal superconducting material.

4. (a) H. G. von Schnering, L. Walz, M. Schwarz, W. Becker, T. Hatweg, B. Popp, B. Hettich, P. Müller, and G. Kämpf, "The Crystal Structures of the Superconducting Oxides $Bi_2(Sr_{1-x}Ca_x)_2CuO_{8-\delta}$ and $Bi_2(Sr_{1-y}Ca_y)_3Cu_2O_{10-\delta}$ Where $0 \le x \le 0.3$ and $0.16 \le y \le 0.33$," *Angew. Chem. Int. Ed. Engl.* **27,** 574 (1988).
(b) P. Bordet, J. J. Capponi, C. Chaillout, J. Chenavas, A. W. Hewat, E. A. Hewat, J. L. Hodeau, M. Marezio, J. L. Tholence, and D. Tranqui, "Powder X-Ray and Neutron Diffraction Study of the Superconductor $Bi_2Sr_2CaCuO_8$," *Physica C* **153,** 623 (1988).
(c) P. Bordet, J. J. Capponi, C. Chaillout, J. Chenavas, A. W. Hewat, E. A. Hewat, J. L. Hodeau, M. Marezio, J. L. Tholence, and D. Tranqui, "A Note on the Symmetry and Bi Valence of the Superconductor $Bi_2Sr_2Ca_1Cu_2O_8$," *Physica C* **156,** 189 (1988).
(d) J. M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H.

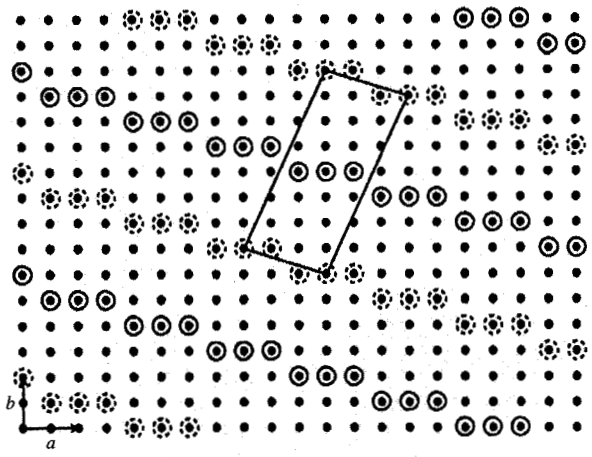

Figure 7

Schematic representation of the proposed model for the superstructure of the orthorhombic phase. (• = thallium atoms in one TlO bilayer; ○ = thallium vacancies on one TlO bilayer; ◌ = thallium vacancies on the succeeding bilayer.) Compare with Figure 6(a). The oxygen atom vacancies are presumably associated with the Tl vacancies. In this model 1/8 of the thallium atoms are missing. The structure is orthorhombic (strictly monoclinic) when the superstructure is well ordered, but pseudotetragonal when the TlO vacancies are disordered, or when the structure is constrained by additional CuO layers in the higher-order compounds.

Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Hwang, "Crystal Substructure and Physical Properties of the Superconducting Phase $Bi_4(Sr,Ca)_6Cu_4O_{16+x}$," *Phys. Rev. B* **37,** 9382 (1988).
(e) S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover, R. M. Fleming, S. H. Glarum, S. Nakahara, R. Farrow, J. J. Krajewski, S. M. Zahurak, J. V. Waszczak, J. H. Marshall, P. Marsh, L. W. Rupp, and W. F. Peck, "Structure and Physical Properties of Single Crystals of the 84-K Superconductor $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_{8+\delta}$," *Phys. Rev. B* **38,** 893 (1988).
(f) 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, "A New High-Temperature Superconductor: $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$," *Science* **239,** 1015 (1988).
(g) E. A. Hewat, M. Dupuy, P. Bordet, J. J. Capponi, C. Chaillout, J. L. Hodeau, and M. Marezio, "Superstructure of the Superconductor $Bi_2Sr_2CaCu_2O_8$ by High-Resolution Electron Microscopy," *Physica C* **153,** 619 (1988); see also *Nature* **333,** 53 (1988).
(h) R. L. Withers, J. S. Anderson, B. G. Hyde, J. G. Thompson, L. R. Wallenberg, J. D. FitzGerald, and A. M. Stewart, "An Electron Diffraction and Group Theoretical Study of the New Bi-Based High-Temperature Superconductor," *J. Phys. C* **21,** 53 (1988).
5. (a) A. W. Hewat, E. A. Hewat, J. Brynestad, H. A. Mook, and E. D. Specht, "Structure and Superstructure of the Superconductor $Tl_2Ca_1Ba_2Cu_2O_8$ by Neutron and Electron Diffraction," *Physica C* **152,** 438 (1988).
(b) D. E. Cox, C. C. Torardi, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, "Structure Refinements of Superconducting $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ from Neutron Diffraction Data," *Phys. Rev.* **38,** 6624 (1988).
(c) J. J. Capponi, P. Bordet, C. Chaillout, J. Chenavas, A. W. Hewat, E. A. Hewat, J. L. Hodeau, and M. Marezio, "Neutron and Electron Diffraction from $Tl_2Ca_2Ba_2Cu_3O_{10}$, and Its Relation to $Tl_2Ca_1Ba_2Cu_2O_8$," 1988, unpublished.
(d) R. B. Beyers, S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. J. Savoy, G. L. Gorman, T. C. Huang, and S. J. La Placa, "Tl–Ca–Ba–Cu–O Superconducting Oxides," *IBM J. Res. Develop.* **33,** 228 (1989, this issue).
(e) S. S. P. Parkin, presented at the IBM Europe Institute Workshop on High-Temperature Superconductivity, Oberlech, Austria, August 8–12, 1988.
(f) E. A. Hewat, P. Bordet, J. J. Capponi, C. Chaillout, J. Chenavas, M. Godinho, A. W. Hewat, J. L. Hodeau, and M. Marezio, "Electron Microscopy of Superconducting "Tetragonal" and Non-Superconducting Orthorhombic $Tl_2Ba_2Cu_1O_6$," *Physica C* **156,** 375 (1988).
(g) A. W. Hewat, P. Bordet, J. J. Capponi, C. Chaillout, J. Chenavas, M. Godinho, E. A. Hewat, J. L. Hodeau, and M. Marezio, "Preparation and Neutron Diffraction of Superconducting "Tetragonal" and Non-Superconducting Orthorhombic $Tl_2Ba_2Cu_1O_6$," *Physica C* **156,** 369 (1988).

Received November 11, 1988; accepted for publication December 12, 1988

Alan W. Hewat *Institute Max von Laue–Paul Langevin, 156X, 38042 Grenoble Cedex, France.* Dr. Hewat has been a staff scientist at the European High Flux Reactor Laboratory (ILL) since 1973. Previously he had worked in the Materials Science Division, AERE Harwell, U.K. Dr. Hewat has a Ph.D. in physics from the University of Melbourne, Australia, and an honorary doctorate in chemistry from the University of Uppsala, Sweden. His main interest is the study of phase transitions using neutron scattering.

Elizabeth A. Hewat *CEA, IRDI, D. Leti, CENG, 85X, and CNRS Laboratoire de Cristallographie 155X, 38041 Grenoble Cedex, France.* Dr. Hewat has an M.Sc. from the University of Melbourne, Australia, and a Ph.D. in metallurgy from Oxford University, Oxford, U.K. She has a joint appointment with the CEA and CNRS Grenoble laboratories, and works on electron diffraction and high-resolution image reconstruction of the structures of semiconductors and superconductors.

Pierre Bordet *CNRS Laboratoire de Cristallographie 155X, 38041 Grenoble Cedex, France.* Dr. Bordet has a doctorate from the University of Grenoble, and has worked on magnetism, superconductivity, and phase transitions using X-ray and neutron diffraction.

Jean-Jacques Capponi *CNRS Laboratoire de Cristallographie 155X, 38041 Grenoble Cedex, France.* Dr. Capponi has a doctorate from the University of Grenoble. He has studied high-pressure synthesis of new materials and high-temperature X-ray diffractometry. He now concentrates on the synthesis of new superconductors and their crystal structures using X-ray diffraction.

Catherine Chaillout *CNRS Laboratoire de Cristallographie 155X, 38041 Grenoble Cedex, France.* Dr. Chaillout has a doctorate from the University of Grenoble. She has worked on neutron diffraction at the National Bureau of Standards, Washington, D.C., and at the AT&T Bell Laboratories, Murray Hill, New Jersey. Her main interests are electron diffraction and microscopy.

Jean Chenavas *CNRS Laboratoire de Cristallographie 155X, 38041 Grenoble Cedex, France.* Professor Chenavas obtained his doctorate from the University of Grenoble. He is investigating the high-temperature synthesis of new materials, phase transitions, and crystal-structure determination by X-ray diffraction techniques.

Jean-Louis Hodeau *CNRS Laboratoire de Cristallographie 155X, 38041 Grenoble Cedex, France.* Dr. Hodeau obtained his doctorate from the University of Grenoble. For his thesis research he investigated the structures of the magnetic/superconducting rare-earth Rh–Sn compounds—particularly the re-entrant superconductor $Er_4Rh_6Sn_{19}$. His primary interest is the study of ordered/disordered compounds using X-ray, electron-, and neutron-diffraction techniques.

Massimo Marezio *CNRS Laboratoire de Cristallographie 155X, 38041 Grenoble Cedex, France.* Professor Marezio is the Director of the CNRS Laboratoire de Cristallographie; he has a joint appointment to AT&T Bell Laboratories, Murray Hill, New Jersey. Professor Marezio has a doctorate from the University of Rome. He has been studying mixed valences and superconductivity and their relation to magnetism.

Pierre Strobel *CNRS Laboratoire de Cristallographie 155X, 38041 Grenoble Cedex, France.* Dr. Strobel has a doctorate from the University of Strasbourg; he has been working on the synthesis, crystal growth, and characteristics of transition-metal oxides at the CNRS Laboratoire in Grenoble. He has also collaborated with Dr. A. Wold at Brown University, Dr. M. Greenblatt at Rutgers University, Dr. C. Hurd at the National Research Council, Ottawa, and Dr. F. Holtzberg at the IBM T. J. Watson Research Center.

Michel François *Laboratoire de Cristallographie, Université de Genève, CH-1211, Genève, Switzerland.* Dr. François has a doctorate from the University of Nancy (France), and is currently at the Laboratoire de Cristallographie at the University of Geneva investigating the crystal structures of superconductors.

Klaus Yvon *Laboratoire de Cristallographie, Université de Genève, CH-1211, Genève, Switzerland.* Professor Yvon has a Ph.D. in physics and physical chemistry from the University of Vienna. He is currently Professor of crystallography at the University of Geneva and Professor of physical chemistry at the University of Graz (Austria). His main interests are the structure and properties of metallic compounds.

Peter Fischer *Labor für Neutronenstreuung, ETHZ, c/o Paul Scherrer Institut, CH-5232, Villigen PJI, Switzerland.* Dr. Fischer has a doctorate from the ETH, Zürich; he is currently at the Swiss neutron-scattering laboratory ETHZ at Würenlingen. His main interests are neutron scattering, magnetism, and structure determination.

J.-L. Tholence *CRTBT CRNS, 166X, 38042 Grenoble Cedex, France.* Dr. Tholence obtained his doctorate from the University of Grenoble. He has studied primarily the magnetic properties of Kondo systems, spin glasses, amorphous magnetic materials, heavy fermions, and Chevrel phases. Recently he has been measuring the ac susceptibility, high-field magnetization, and critical current densities of high-T_c superconductors.