

which are not mentioned in the red books.

As one indication of what such surveys may reveal, four years of searching (1979–83) for primary freshwater fishes on the Malay peninsula, where 266 species had at one time been found, uncovered no evidence for the continued existence of an astonishing 54 per cent of those species¹⁰. Imboden's estimate¹ is that fewer than one-third of the world's bird species will qualify for a green list, defined by the criterion of "known not to be declining in numbers now, and unlikely to decline in

the next decade". Recent archaeological discoveries indicate that up to one-quarter of the bird species that existed a few millennia ago have been exterminated in modern times, but before they could be described by ornithologists, when humans colonized oceanic islands¹¹. Thus, the much-discussed extinction crisis is not a debatable future possibility: it is already well advanced. □

Jared M. Diamond is Professor of Physiology at the University of California Medical School, Los Angeles, California 90024, USA.

Cuprate superconductors

Structure and superstructure

Colin Greaves and Ted Forgan

PROGRESS in understanding the new rare-earth-free superconductors that we discussed in a recent News and Views article¹ has been rapid. We suggested then that the structure of Bi–Ca–Sr–Cu–O (BCSCO), which has superconducting transitions at 85 and 110 K, would soon be characterized. Several groups have now established that in the primary (85-K) phase, the metal ions are present in the approximate ratio 2:1:2:2. Veblen *et al.* report on page 334 of this issue² an electron-microscopy study that confirms the layered nature of this material, but clearly shows that the structure is anything but straightforward, as the basic building blocks seem able to fit together in slightly different ways, causing some disordering.

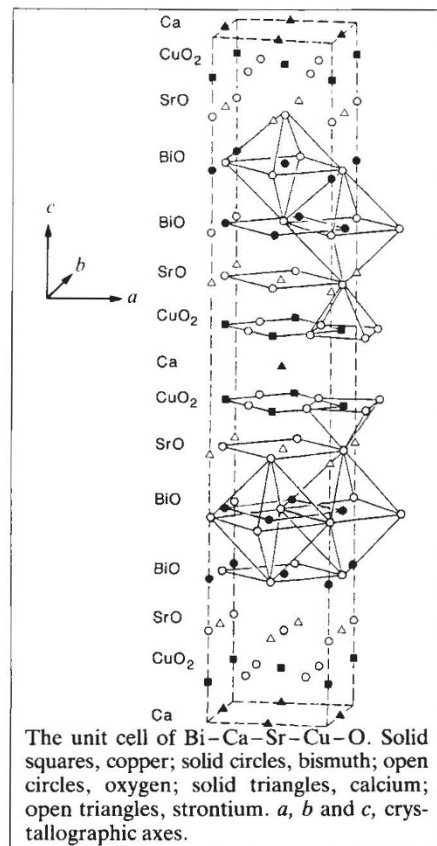
X-ray and neutron-diffraction studies of crystals with nominal composition $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+x}$ (ref. 3; S.A. Sunshine *et al.*, submitted to *Phys. Rev. Lett.*; J.M. Tarascon *et al.*, submitted to *Phys. Rev.*) reveal the same pseudo-tetragonal structure ($a=b=5.4$ Å; $c=30.8$ Å; see figure) for the basic building block that Veblen *et al.* find. Although structural relationships between this material and the Aurivillius phases⁴ are often emphasized, it is clear that two important differences exist.

First, Bi_2O_2 layers, which are a characteristic feature of the Aurivillius phases and actually consist of a Bi–O₂–Bi sandwich, are absent. In the superconducting phase, the central oxygen atoms of the sandwich have moved into the bismuth layers to form two BiO layers with a rock-salt (NaCl) type of structure. These layers are quite weakly bonded together to form the cleavage planes of this material⁵. Second, the perovskite-like structure, which interleaves the Bi_2O_2 layers in the Aurivillius phases, does not begin immediately adjacent to these layers in BCSCO. Instead, the rock-salt arrangement is extended on both sides by additional layers of SrO type.

Between the rock-salt structural blocks there are two CuO_2 layers separated by

calcium (Ca^{2+}) ions. Each copper atom has four coplanar oxygen neighbours. Another more distant oxygen atom in the adjacent SrO plane completes a square-pyramidal arrangement. The double copper layers are very similar to those found in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, in which Y^{3+} rather than Ca^{2+} is the bridging cation. These layers, therefore, increasingly seem to be important in the new superconductors, because the bismuth-containing material contains no copper chains analogous to those in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. We expect that the electrons responsible for the superconductivity belong to copper planes, and the copper ions have an average valence between two and three. It is also likely that the BiO planes are essentially insulating, so it would be no surprise if this material is even more two-dimensional than $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (see ref. 6). It is interesting to note the pronounced structural similarity between this new phase and the layer materials described in 1980 by Nguyen *et al.*⁷, for example $\text{La}_2\text{SrCu}_2\text{O}_6$, in which rock-salt blocks (La_2O_3) separate CuO_2 –Sr– CuO_2 double layers.

The high-resolution micrographs reported by Veblen *et al.* in this issue² reveal departures from the idealized structure shown in the figure. First, there is disorder along the c -direction (perpendicular to the planes), which is not unexpected in layer materials of this type, and seems to correspond to the exclusion or introduction of an extra unit about 4-Å thick. Along the b -direction, the structural features have a much greater length scale than the 5.4-Å repeat distance of the basic building block and are related to a commensurate or incommensurate superstructure with a lattice spacing five times larger^{3,5} (27 Å). This could be related to the unusual bismuth coordination in BCSCO. Although the oxygen atoms around this site form a slightly distorted octahedron, the lone pair of electrons on bismuth (Bi^{3+}) ions generally results in much less symmetrical environments. It is possible that distortions that



The unit cell of Bi–Ca–Sr–Cu–O. Solid squares, copper; solid circles, bismuth; open circles, oxygen; solid triangles, calcium; open triangles, strontium. a , b and c , crystallographic axes.

lower the site symmetry could lead to buckling of the BiO layers to form a superstructure associated with periodic displacements. The satellite peaks seen on either side of the principal peaks along the b -direction in the electron-diffraction pattern² seem compatible with such distortions, which could also reduce the local symmetry to monoclinic, as Veblen *et al.* suggest.

Finally, some words of caution concerning the deduction of microstructural features from electron micrographs. The samples examined by Veblen *et al.*² contain traces of the 110-K superconducting phase, which is formed only by heating the 85-K phase close to its melting point. Specimens prepared at lower temperatures may not show the same type or extent of structural disorder². Also, the specimens were prepared by finely grinding a sintered sample, and some disorder could have been introduced by this process. If this is so, it is itself an important observation, as any practical applications of these materials may depend on their mechanical strength and structural integrity. □

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Colin Greaves is in the Department of Chemistry and Ted Forgan is in the Department of Physics at the University of Birmingham, PO Box 363, Birmingham B15 2TT, UK.