Solid-state physics

Liquid-nitrogen-temperature superconductors arrive

John Maddox

EVEN before last week's issue of *Nature* had been mailed to subscribers, last week's record high temperature for the transition to superconductivity, given by Strongin, Welch and Davenport as roughly 70 K (*Nature* **325**, 664; 1987), had been broken. On Monday, the *New York Times* announced that C.W. Chu and his associates at the University of Houston, last week's record-holders, had succeeded in preparing a ternary oxide that is superconducting at 98 K, well above the boiling point of liquid nitrogen at 77 K. One excited physicist wondered whether the US Department of Energy had not been over-hasty in agreeing to build a proton–proton collider using helium-cooled magnets.

These developments are every bit as important as Strongin, Welch and Davenport explained last week, when they also warned that it will be some time before these materials find their way into quite small devices, let alone into the power-carrying circuits of the big machines. During the past few months in which groups in the United States and Japan have been racing toward the goal of a liquid-nitrogen superconductor, they have had to make the best they can of specimens a few millimetres across which vary markedly in their properties from one to another.

Chu's technique (see Chu, C.W. *et al.* *Phys. Rev. Lett.* **58**, 405; 1987) requires that a mixture of the oxides of lanthanum, of calcium, barium or strontium, and of copper should be heated for hours on end at 900 °C and that the solid mass produced should be ground and sintered at 1,200 °C for another spell. There is no assurance that the resulting specimens are uniform solids, let alone regular crystals. Indeed, it has been possible to show that many of them are mixtures of two phases, each with a different crystal structure. Most specimens appear to be replete with empty voids, hardly suggestive of the purity and order that might be thought necessary for a superconductor. One of the goals ahead is the preparation of these materials in something like a well-ordered form.

What are they? And by what stretch of the imagination can an oxide be a super-conductor? In reality, the ternary oxides (or sulphides, for that matter) are more often semiconductors, which is credible enough. But one of the surprises of the past five years or so is that small changes of physical conditions or of chemical composition can profoundly change the nature of a material. Some may be ferromagnets

at low temperatures and semiconductors above some critical point. Ferroelectric characteristics are common.

The oxides in the forefront of people's minds in the past few months are materials that should ideally form crystals in which the two different kinds of cation (copper on the one hand and lanthanum and barium/strontium/calcium on the other) form planar sheets in each of which the atoms are linked together by oxygen atoms and which are then stacked on each other, first one kind and then the other.

Put differently, each copper ion is sur-rounded by a distorted octahedron of oxygen anions, giving tight binding within each copper plane but much looser binding in the direction perpendicular to the planes. The materials on which most interest has centred in recent weeks may be thought of as derived from $LaCuO_3$ or La_2CuO by the stoichiometric substitution of group II elements such as calcium for lanthanum atoms. But neither of the starting materials is a superconductor.

What seems to happen is that, especially in the short bonds between copper and oxygen atoms within the planes, bonding electrons acquire an unusual degree of de-localization, and hence mobility. On the face of things, the situation is a little like that in graphite, in which again there is a layered structure (based on a hexagonal network of carbon atoms) loaded with potentially mobile electrons — and it is no accident that there have been several attempts in the past few years to detect superconductivity in graphite at low temperatures and high pressures, all of them unsuccessful.

Part of the reason for this is that graphite is strictly a semiconductor, but one without a finite band-gap in the usual meaning of the term; instead, the density of electronic states as a function of energy tapers to a vanishingly small waist at the Fermi level, the energy of the most energetic occupied state when all the available electrons are fitted in most economically. The vanishingly small density of states at the Fermi level militates against superconductivity, dependent as that is on the interaction between mobile electrons and lattice vibrations. The electrons that matter will be those lying near the top of the occupied band, which can be excited into a conduction state by amounts of energy as small as those of lattice vibrational quanta (phonons); in graphite, the number of electrons available for conduc-

tion will be vanishingly small. Turning the argument around, the trick in making an oxide superconductor is to arrange that the density of electronic states as a function of energy is thick-waisted at the Fermi level.

The density of states at the Fermi level is not the only criterion that must be satisfied for superconductivity at high temperature to occur. It is also necessary that the electron coupling should be close, which is assured in these oxides by the proximity of neighbouring copper ions and by their capacity to exist in doubly or trebly charged form, which allows the exchange interactions to be strong. What remains to be puzzled out is why the coupling between the electron states and the lattice vibrations should be as strong as it appears to be; for that purpose, accurate crystal structures would be a boon, but they may not be easy to come by with materials made by sintering.

Several influences seem to matter in the design of the new materials. The substitution of a group II atom for lanthanum appears to be largely a way of influencing the electronic balance in the copper-carrying layers on either side, perhaps changing the electron affinity of the copper ions. In a sense, the group II elements among the lanthanums may be likened to the influence of the voltage on the grid of an old-fashioned triode valve.

Another way of changing the density of electronic states in the copper planes appears to be a stoichiometric deficiency of oxygen atoms, which explains why the properties of the oxide superconductors so far prepared appears to be sensitively influenced by the atmosphere in which they are prepared. In some cases, a reducing atmosphere will yield a superconductor whereas an oxidizing atmosphere will not; in others, the reverse is true.

So far, it seems, these empirical truths have been learned the hard way. People have prepared samples with very different compositions and have plotted selected measured quantities on diagrams in the hope that contour lines will lead them to an optimum composition. Now it may be possible to provide some explanation of what has happened. That is one problem that cries out to be tackled.

Another is that of controlling the composition of these materials more accurately than is possible by sintering at high temperatures. For even if, for the time being, oxide superconductors will be used only in small electronic devices (will the super-conducting magnetometers called SQUIDs be the first outlet for them?) the sheer mechanics of production will require uniform and reproducible raw material. That is another direction in which there will have to be progress if the potential of the new development is to be realized. □

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