Superconducting ceramics

High-temperature anomalies

David Caplin

Two strands are emerging in the helter-skelter race to find higher transition temperatures for superconductivity. One is the application of textbook scientific method in the communal verification of extraordinary results. Once the scientific community woke up to the implications of J.G. Bednorz and K.A. Muller's report (*Z. Phys.* **B64**, 189–193; 1986) of superconductivity above 30 K in $(La, Sr)_2CuO_4$ compounds, anyone who wished to could reproduce the results within a couple of days. There is the story, perhaps apocryphal, that having received the manuscript announcing the discovery of the $YBa_2Cu_3O_7$ 90-K superconductor (Wu, M.K. *et al. Phys. Rev. Lett.* **58**, 908–911; 1987) in the morning postal delivery, one of the referees had confirmed the transition temperature before midnight.

On the other hand, there are now at least a dozen reports, including one from Huang *et al.* on page 403 of this issue, of anomalies that indicate superconductivity in the same materials at far higher temperatures, but even the authors themselves are unable to reproduce their results from one sample to another. Often, the electrical resistivity appears to drop by several orders of magnitude, or the magnetic susceptibility suddenly becomes strongly diamagnetic.

It is not that careful scientists find the reproducible data and the careless find the anomalies, for several groups have produced both species. The common feature of reports of high-temperature anomalies, at 155 K (Ovshinsky, S.R. *et al. Phys. Rev. Lett.* **58**, 2579–2581; 1987), at 'room temperature' (Sumitomo Electric Co; see *Nature* **328**, 98; 1987) and at 230 K (Huang *et al.* on page 403), appears to be that the superconducting phase lives for a few hours or days at most, and that it constitutes only a small proportion of the total volume.

An important point, well known in conventional superconductivity, is that a minute amount of superconducting phase can provide zero-resistance percolative paths in a non-superconducting matrix. Grain boundaries, to which minority phases tend to segregate anyway, are particularly favourable locations. Magnetic tests for superconductivity can be equally misleading, because any closed path of zero resistance will exclude flux changes from its interior, and so give a large diamagnetic signal. (This is often described, misleadingly and incorrectly, as an observation of the Meissner effect; the latter is the *expulsion* of magnetic flux from a superconductor as it is cooled, in a magnetic field, through its superconducting transition.)

In many cases the samples showing the anomaly had been prepared by a slight variation on the known optimum recipe for the $YBa_2Cu_3O_7$ compound, for example by replacing some oxide with fluoride (Ovshinsky *et al.*) or by exposing the material to argon at 300 K (Huang *et al.*), which would presumably cause the sample to lose a small amount of oxygen.

This circumstantial evidence suggests that the material that is responsible for the high-temperature effects is not a true bulk phase, in which case endeavours to isolate it are doomed to failure (but who knows what may have happened by the time these comments appear in print). It could be instead that in special circumstances, there is some kind of two-dimensional superconductivity at grain boundaries. This would not be inconsistent with what is known already about the bulk high-temperature superconductors: the active regions in these perovskite-related structures are the Cu–O planes, and the superconducting properties are extremely sensitive to occupancy of the oxygen sites.

Oxygen diffusion rates in these compounds are high (they are well known to be superionic conductors at 400°C and above), but are far from being high enough to allow significant structural change in bulk material at room temperature. The ceramic superconductors as presently prepared are porous, however, and the diffusion rate for oxygen along grain boundaries could well be orders of magnitude higher than the bulk value. Thus, it is not unreasonable that during hours or days at room temperature, the oxygen stoichiometry of a superconducting intergranular region could change significantly.

The irreproducible effects that are being seen in the superconducting oxides resemble the anomalies reported 10 years ago (Brandt, N.B. *et al. JETP Lett.* **27**, 33–38; 1978) in CuCl under pressure. These were then investigated in considerable detail (Chu, C.W. *et al. Phys. Rev.* **B18**, 2116–2123; 1978), but very little in the way of systematic behaviour could be identified. Various mechanisms were considered, including superconductivity induced at an interface by an excitonic mechanism, but without any firm conclusion.

Reports of possible, if transient, superconductivity at these higher temperatures should not be brushed aside. It is vital to discover a reliable way of preparing the material that displays these anomalies; there will then be much hard work to understand their origin. It may be that to create room-temperature superconductors we have to replicate on a macroscopic scale the microscopic structure of grain boundaries, perhaps using the techniques of molecular-beam epitaxy. ☐

David Caplin is in the Department of Physics, Imperial College of Science and Technology, Prince Consort Road, London SW7 2BZ, UK.

Quasars

Probing the early Universe

R.F. Carswell

For those interested in the history and the ultimate fate of the Universe, quasars have been a source both of hope and of frustration. Hope because quasars are so bright, and seen at such large distances, that in the highest-redshift cases we see them as they were when the Universe was at most one-fifth of its present age. Thus the study of quasars should allow us to infer some of the properties of the early Universe, and particularly any changes in the rate of expansion since then. Frustration because quasars show such diverse behaviour, most importantly in their intrinsic luminosities, that any effects caused by the expansion of the Universe are completely masked. The prospect of disentangling the evolution of quasars from changes in the expansion of the Universe is remote today. But there is another use for quasars: to probe gas clouds that intervene between us and them. This was the subject of a recently held workshop*.

The spectra of all high-redshift quasars show atomic-absorption lines arising in gas clouds with redshifts, and hence distances and ages, up to that of the quasar itself. Mostly we detect only the lines of neutral hydrogen, the most abundant element in the Universe. In a few cases, though, heavy elements are found, indicating some nuclear processing in stars. Recently, high-quality, high-resolution spectroscopy has enabled astronomers to address detailed problems concerning the nature of these quasar-absorbing clouds.

Detailed work by A.M. Wolfe (Pittsburgh Univ.) and his collaborators shows that if the regions that contain heavy elements are in galaxies, then the galaxies must have been considerably larger in the past than they appear to be now. This

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**QSO Absorption Lines: Probing the Universe* Space Telescope Science Institute, Baltimore, 10–21 May 1987.