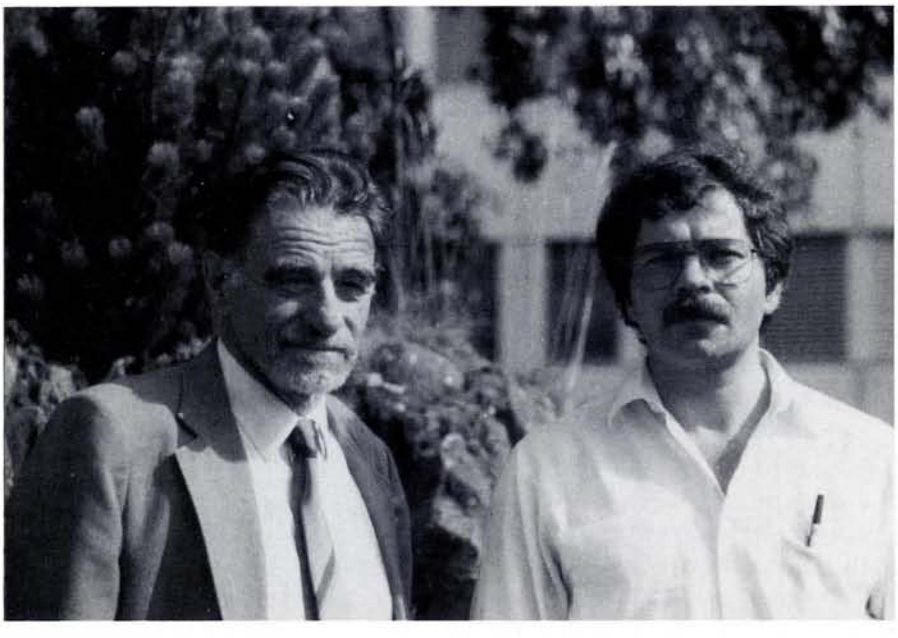
The Prizes of High T_c Superconductivity

The 1987 Nobel Prize in Physics was awarded to J.G. Bednorz and K.A. Müller, crowning a succession of awards that had included the 1988 Hewlett-Packard Europhysics Prize of EPS.*

Prizes in physics, as in any other field, are awarded for outstanding work and for work that is believed to be of lasting significance. Time, of course, does not always confirm the choices made and, on occasions, even Nobel prizes have seemed to owe more to sentiment or fashion than relevant and lasting worth. No-one, however, can question the importance of the discoveries of Johannes Georg Bednorz and K. Alex Müller, and few will doubt the wisdom of making the award so soon after their initial publications which triggered a world-wide research stampede into 'high temperature' superconducting oxides.

The 1987 award is remarkable not only for its immediacy. For the first time a single laboratory — certainly an industrial laboratory — has seen its scientists honoured in two successive years. In 1986 (in parallel with Ruska) it was the turn of Binnig and Rohrer for the scanning tunnelling microscope and in many places the question has been asked what is so special about the IBM Research Laboratory in Rüschlikon near Zurich. One of the answers is Alex Müller, a Swiss native who received his Ph.D. in solid state physics at the ETH Zurich and then spent five years at the Battelle Institute in Geneva. Ten years after joining IBM in 1973 at the age of 37, he was made Manager of the Physics Department and the vitality of the laboratory owes much to his skills in bringing the right people together in a productive environment. Müller, however, did not become just an administrator. Professor of the University of Zurich since 1972, he was made an IBM Fellow in April 1982 after which he was able to devote more of his time to his own ideas, in particular to exploring the low temperature behaviour of metal oxides which because of a strong electron phonon interaction might exhibit superconductivity. One of his most shrewd appointments to the laboratory was that of Georg Bednorz who joined IBM in 1982 at the age of 32. Although of German nationality and a graduate of Münster, Bednorz did his Ph.D. at the ETH, Zurich where he specialised in the preparation and crystal growth of highly refractive materials. The two men were complementary — Müller providing the physical insight and Bednorz the physico-chemical skills. Both were dedicated to the work they had set themselves and it was as much Bednorz as Müller who stiffened the resolve when the research seemed to be leading nowhere. The driving idea was that polaron formation accompanied by metallic conductivity in oxides might favour the onset of superconductivity, and, more specifically, compounds containing Ni^{3+} or Cu^{2+} states might well be possible candidates. They had no cut and dried theoretical framework for their belief — and in view of the current bafflement of physicists everywhere on the exact nature of the phenomenon, this is hardly surprising — and so they set about a systematic examination of compounds including the Ba-La-Cu-O system.

Fig. 1 — K.A. Müller (left) and J.G. Bednorz whose partnership at the IBM Research Laboratory, Rüschlikon opened the door on to a whole new range of superconductors.



"Classical" superconducting alloys and compounds appeared to have reached the limit of the possible — a limit far from negligible in terms of critical field and current density even though critical temperatures were below 23 K and useful operating temperatures much lower. Historically one can regard the first generation superconductors as being typified by Nb-Ti alloys with a critical field of 12 T at $T = 0$ and a T_c of about 11 K. The second generation consisting of niobium compounds with Al, Ga, Sn, Ge as well as pseudo-binary alloys pushed the critical field up to 45 T and T_c to > 20 K although only Nb_3Sn was really suitable for magnet construction. Critical current densities associated with these alloys lie between 10^9 and 10^{10} A/m^2 at temperatures around 4 K. With the third generation typified by $PbMo_6S_8$, although T_c was nearer 15 K, the critical field was way up in the 60 T range. The theory based on Cooper pairing of electrons through phonon-mediated attraction looked solid; superconductors were well characterised; important interaction parameters could be obtained reliably from various types of ex-

* This prize will be presented during the 8th General Conference of the Condensed Matter Division to be held in Budapest, 6-9 April 1988.

periment; the electronic structures were well understood. Altogether the superconducting field seemed to be circumscribed.

That is until the appearance of the paper [1] by Bednorz and Müller — (received at the publishers on 17 April 1986) in which they reported that on cooling a Ba-La-Cu-O mixed phase alloy, its resistivity behaved like that of a very poor metal before dropping by up to three orders of magnitude (Fig. 2) "reminiscent of percolative superconductivity. The highest onset temperature is observed in the 30 K range". The tone was restrained, the claims modest and indeed only in the 10 K region did the resistance drop to zero. Significant, however, was the dependence of the onset temperature on measuring current — already a rather clear signal of superconductivity. In a second paper [2] published in *Europhysics Letters*, the authors together with M. Takashige presented the diamagnetic response of the same substance (Fig. 3). The effect was small (a few percent) but the message was clear and all over the world physicists turned their attention to this and similar systems.

In China, Japan, the USA and elsewhere in Europe, attempts were made to reproduce the Rüschlikon results and identify the phase responsible for the superconductivity. Quickly this was seen to be a perovskite-like layered structure of the K_2NiF_4-type, the presence of which had already been noticed by Bednorz and Müller in their multiphase samples. It was also found that Sr rather than Ba doping of La_2CuO_4 led to higher transition temperatures. But nobody knew where the superconducting took place — was it a volume effect, as hoped, or merely an interface effect, *e.g.* along grain boundaries? Resistance or AC susceptibility measurements cannot really distinguish between them whereas specific heat measurements at the phase transition can give an unequivocal answer. The experiment is difficult and the effect is almost swamped by the contribution from the lattice, but the signal was unmistakable. This really was bulk superconductivity that was being observed.

By the beginning of 1987, other substitutions, such as those tried by Paul Chu's group at Houston with yttrium for lanthanum had seen the critical temperature leap from the thirties to over 90 K — which while phenomenologically dramatic, initially added confusion to the scene as the lattice structure was not the same. Some reminiscence of perovskites remained in the arrangement, but

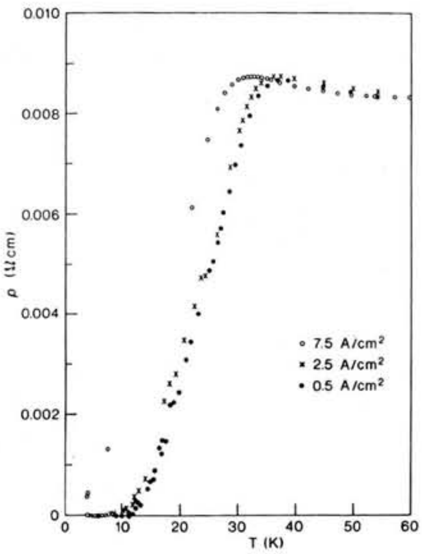


Fig. 2 — The signature of possibly high T_c superconductivity (from Ref. 1).

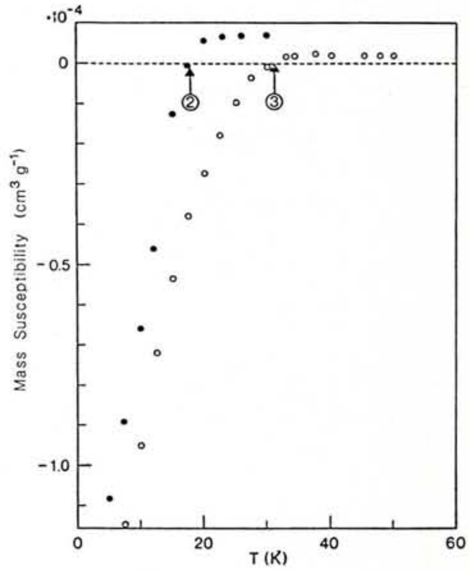


Fig. 3 — Not only a fall in resistance, but diamagnetism too (from Ref. 2).

in addition to layers consisting of puckered planes of copper and oxygen atoms on a square lattice, other Cu atoms form chains with O atoms, leaving vacant sites in the perpendicular direction. The barium and yttrium lie in intermediate planes. The microstructure proved to be very complicated and it was then found that single phase grains are heavily twinned, a consequence of a tetragonal to orthorhombic transition in the solid state.

Very soon the techniques for producing high T_c superconducting ceramics and even thin films and minute single crystals became established and 'do it yourself' recipes (that worked) appeared in the literature. These fourth generation materials typified by $YBa_2Cu_3O_7$ showed sharp transitions to the superconducting state at 90 K plus, but from a practical point of view they have serious limitations. Apart from the problems posed by the strong anisotropy of the critical fields and the critical currents, the latter have proved to be low.

To arrive at a high T_c, the location and concentration of the oxygen atoms is critical. Raising the quench temperature of a $YBa_2Cu_3O_{7-x}$ sample from 400°C up to 800°C sees the T_c change from 93 K to zero. Neutron diffraction studies on the same specimens show a direct correlation between those results and the fractional site occupancy of the oxygen atoms in the chains. As the quench temperature is raised, less oxygen is retained and by 800°C the orthorhombic has given way to the tetragonal phase which is no longer metallic.

Plotting the phase diagram of a quaternary compound is notoriously difficult and a great deal of work is going to be needed in order to construct a convincing picture. Band structure calculations reveal again a very complex situation, but it can be inferred that whilst the density of electron states seems to be built up of contributions from copper and oxygen sites, the overall density of states at the Fermi level is surprisingly low.

Much discussion is currently going on about the role of phonons in these materials. It is known that the density of phonon states extends to about double the energies encountered in most metals and some of the highest values can be attributed to particular oxygen modes. Is the coupling between these and the conduction electrons so strong that the high T_c could be explained? This is not known at present. In conventional superconductivity, clear answers are given by substituting an isotope of the critical element, so altering the phonon frequences without upsetting the lattice structure, but when the normal ^{16}O is exchanged for ^{18}O in the new materials, the effect, when it is seen, is too small to be accepted as evidence that phonons play the dominant role. Other proposed mechanisms still await the verdict of a crucial experiment.

Infrared reflectivity and tunnelling measurements looking for the characteristic energy gap of superconductors have revealed unusually large gap values in the high T_c oxides which suggests that the coupling is very strong although from other experiments the opposite conclusion can be drawn. One exceptional property is, however, well established. On substituting Y by trivalent magnetic rare earths, instead of the superconductivity being suppressed, a high T_c is still found. This suggests no interaction between the itinerant electrons and the rare earth ions.

At present, one of the most awkward problems is connected with the complex microstructure leading to a kind of superconducting "glass state". Measurements very close to T_c show completely reversible magnetization curves and reveal most extreme type II superconductivity in terms of the Ginzburg-Landau parameter. At lower temperature, the magnetic hysteresis observed in small single crystals indicates substantial pinning in moderate fields so encouraging optimism over the current densities that might be realised in bulk specimens even though the transport currents measured to date are orders of magnitude below. Much patience and hard work is going to be needed to produce high field magnets with the new materials, but it is predicted that they will come this century. In the meantime, quite rapid exploitation in micro-electronics, where thin films plays a big role, is confidently expected.

To what extent the forecasts prove accurate, only time will tell but with more than a thousand publications already devoted to the high T_c materials, no-one need fear that the new physics that Bednorz and Müller launched may prove to be just a passing fashion after all.

The latter part of this article was based on a survey of high T_c developments given by Prof. J. Müller of Geneva University to the EPS Associate Members on the occasion of their meeting with the Executive Committee on 26 November 1987.

REFERENCES

[1] Bednorz J.G. and Müller K.A., 'Possible High T_c Superconductivity in the Ba-La-Cu-O System', *Z. Phys. B.* **64** (1986) 189.

[2] Bednorz J.G., Takashige M. and Müller K.A., 'Susceptibility Measurements Support High T_c Superconductivity in the Ba-La-Cu-O System', *Europhys. Lett.* **3** (1987) 379.