SUPERCONDUCTIVITY

Another December revolution?

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IN December 1986 I boarded a plane in San José, California, bound for Zürich, determined to unearth the facts behind the reports and rumoured confirmations of superconductivity at 30 K which had recently been published by Georg Bednorz and Alex Müller[1].

Eighteen hours later, I stumbled jet-lagged into the IBM Ruschlikon laboratory. There I found an agitated and preoccupied young man — Bednorz had just received the preprint of Kitazawa and Tanaka's confirmation[2], and, justifiably, was concerned that the rest of the world would run away with his discovery (although Bednorz and colleagues had submitted their magnetization results for publication a week before the Japanese in October, the paper[3] did not appear until February 1987).

Within half an hour, my travel weariness had disappeared. The amount and quality of the data my Swiss colleagues had accumulated was far beyond that generally known at the time, leaving no doubt that superconductors with T_c as high as 40 K really existed. I returned home a true believer, with the peace of my holiday delightfully shattered, ready to spread the good news to my colleagues in IBM Almaden.

I relate this story because in the middle of another December — last month — we again heard news of incredible advances in superconductivity. Within literally days of each other, two French laboratories reported evidence[4,5] suggesting that superconductivity may occur above 250 K, perhaps as high as 8 °C. But unlike in the 'December revolution' of 1986, it is not at all clear yet whether the barricades of superconductivity have been surmounted one more time.

The materials and methods of preparation could not be more different — the one common feature is that they are still copper oxides. The first report[4], from a Paris CNRS laboratory, describes the layer-by-layer deposition by molecular beam epitaxy of an eightfold sequence of CuO sheets interrupted by BiO intergrowths, a segment of what is commonly called the 'infinite layer' compound[6]. They observe a sharp drop in resistivity near 250 K in one sample, which seems to show a critical-current-induced shift in T_c when sample current is increased from 10^{-9} to 10^{-7} A. (The transport measurements are unorthodox; it seems that the current–voltage characteristics at various temperatures were used to obtain the resistivity plot.) These extraordinarily small currents are made necessary by the high sample resistance, which, although not explicitly stated, can reasonably be estimated to be as much as 3 MΩ just before the resistivity drop. I have sometimes observed just such a drop when the sample resistance became large enough with decreasing temperature to saturate the internal impedance of the current source[7]. Unfortunately, the paper gives almost no detail on how the transport measurement was made. The magnetization data also leave open questions not addressed in the paper. The signals are extremely weak and the apparent diamagnetism commences at 300 K, about 40 K above the resistive onset, a most unusual result even for a filamentary superconductor. My overall concern is the paucity of routine experimental details and vagueness as to reproducibility.

The second report[5] is from an experienced and well-known group based in Grenoble. Their samples were of the Hg-1223 compound (superconducting at 133 K)[8] and its extensions to four and five copper oxide layers, bulk-synthesized under an ambient oxygen pressure of 18,000 atm, a preparative technique now becoming widely used. Only resistivity data are given in the paper; however, the experimental conditions are more thoroughly addressed than was the case for the Paris workers. No magnetization plots are given, just a few rather nebulous statements about small diamagnetic shifts, suggesting a superconducting volume fraction of about 0.01 per cent, which are not connected in an obvious way with the samples on which the transport data were taken.

The most provocative evidence for an extraordinary transition temperature is their observation of a sharp drop to zero resistance at 235 K. This is reported in a curious way, implying that the sample was left for two days without remeasurement (they didn't actually go home for the weekend, did they?). When the measurement was repeated it was with 20 times more sample current and the drop did not reappear. A question I would like to have seen addressed is whether the authors monitored the quadrature phase signal during the original measurement. On occasion, I have seen the in-phase component of the sample voltage drop to zero in a.c. measurements when one of the contacts became suddenly capacitative as the temperature was lowered. Neither paper indicates that either the transport or magnetic measurements were reproducible without hysteresis over many temperature cycles, a test that most superconductivity experimentalist referees would demand. My final comment about the Grenoble resistivity data is that the 235 K drop is strikingly sharp and narrow for filamentary superconductivity, exhibiting neither a quasifluctuation rounding at the onset nor a tail as zero resistance is approached, the latter invariably associated with filamentary and non-bulk behaviour.

The years following the discovery of Bednorz and Müller gave rise to many sightings of Unidentified Superconducting Objects (USOs, an acronym which in Japanese means, I'm told, politely, 'error'). How then is one to judge reports of transient and ephemeral evidence suggestive of superconductivity? It is difficult. After all, in general there is no known theoretical reason why superconductivity cannot exist at almost any temperature: T_c in a neutron star is 10^9 K. For a given observation, the prime requirement has to be reproducibility, both in new sample preparation and remeasurement of original samples. For every association I have had with filamentary superconductors — from $(SN)_x$ to the original ambient-pressure Bechgaard salts, the early formulations of the high-T_c materials, the observation of superconductivity in undoped La_2CuO_4 and the glimmer of 125 K in the thallium copper oxides — rapid confirmation was achieved by groups equipped to do so, once all conditions of preparation and experimental technique were known.

Are the French scientists thus expanding the revolution begun in 1986, or are they, more in the spirit of the 1825 uprising against Nicholas I, mere Decembrists? We should know the answer anon. Both groups claim they have reproduced their results in several samples. Perhaps even as we go to press, they will be able to obtain confirmation by distributing these samples to colleagues with the ability to repeat their measurements independently.

Finally, in expressing caution, and yes, perhaps scepticism, about these reports, we must be careful not to discourage the continuing quest for new superconductors, for, to paraphrase the now famous opening line of the Bednorz–Müller paper, this search is by its very nature empirical, with few rules to guide us. But along our journey it is prudent to remember Richard Feynman's admonition that in science it is easy to be fooled, and the easiest one to fool is yourself. □

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1. Bednorz, J. G. & Müller, K. A. *Z. Phys.* **B64**, 189 (1986).
2. Uchida, S., Tagaki, H., Kitazawa, K. & Tanaka, S. *Jpn. J. appl. Phys.* **26**, L123 (1987).
3. Bednorz, J. G., Takashige, M. & Müller, K. A. *Europhys. Lett.* **3**, 379 (1987).
4. Laguës, M. *et al. Science* **262**, 1850–1852 (1993).
5. Tholence, J.-L. *et al. Phys. Lett.* **A184**, 215–217 (1994).
6. Siegrist, T., Zahurak, S. M., Murphy, D. W. & Roth, R. S. *Nature* **334**, 231–232 (1988).
7. Raminez, M. L., Vazquez, J. E. & Grant, P. M. *Internal IBM Rep.* RJ6457 (28 September 1988).
8. Schilling, A., Cantoni, M., Guo, J. D. & Ott, H. R. *Nature* **362**, 56–58 (1993).