Paths to Higher Temperature Superconductors

Theodore H. Geballe

History shows right from the beginning that there has been no successful prediction of new families of superconductors. Discoveries in this field have been unexpected, even revolutionary, and not foreseen as simple and logical next steps in an ongoing scientific enterprise. The Bednorz-Müller discovery of superconductivity in the copper-oxide pervoskite family (*1*) was just such a revolutionary jump. But evolutionary research aimed at the synthesis and characterization of new compositions can also give insightful and even unexpected results. To this end, a 2-day workshop (*2*) was recently held in which a diverse group of researchers discussed the possibility of reaching substantially higher transition temperatures than are presently known.

The cuprate superconductors have in common planes or sheets of copper oxide (CuO_2) in which superconductivity is believed to occur. The saturation of the transition temperature (T_c) near 125 K in spite of the synthesis of dozens of new compounds might suggest that the limit of T_c has been reached. However trace signals—possibly associated with superconductivity—have been observed at much higher temperatures on many occasions in different laboratories. It is not trivial to establish their origin. Resistive and magnetic signals in inhomogeneous samples can mimic superconducting ones and have frequently been interpreted as such even though they are spurious and can easily be understood in terms of the topological characteristics of the inhomogeneity. More careful experiments are needed to track down the source of those that may be due to nontrivial causes.

An obvious and worthwhile approach is to synthesize new compounds in which the CuO_2 planes have new environments. They are, in all but one of the known families of superconductors, separated by intermediate layers. These layers serve the dual functions of providing lattice stability and providing itinerant charge carriers to the CuO_2 planes by the same type of charge transfer, which is known as "modulation" doping in semiconductor parlance. R. Cava (AT&T Bell Laboratories) pointed out that there are presently ten families of intermediate layers [for example, (La,Sr)O, CuO, and $(BiO)_2$], each of which has the potential of separating sequences of one to three CuO_2 sheets. It should be possible to introduce a much wider variety of intermediate "block" or "mushy" modulation doping layers between CuO_2 planes. In addition to the nontrivial problems associated with getting the composition right, very demanding processing paths are sometimes necessary. For instance, in the new families (presently nonsuperconducting) based on $La_{4+4n}Cu_{8+2n}O_{14+8n}$ building blocks, the $n = 2$ member is obtained only when it is quenched from a very narrow range of temperatures near 1000 K (*3*). A. W. Sleight (Oregon State University) pointed out that probably all the superconducting cuprates are metastable; consequently even systematic investigations made by varying the composition can easily miss key structures. Attention must be paid to the temperature- and time-dependent details of the synthesis.

Helpful Hints for Finding New Superconductors

1. Materials should be multicomponent structures with more than two sites per unit cell, where one or more sites not involved in the conduction band can be used to introduce itinerant charge carriers.

2. Compositions should be near the metal-insulator Mott transition.

3. On the insulating side of the Mott transition, the localized states should have spin-1/2 ground states and antiferromagnetic ordering of the parent compound.

4. The conduction band should be formed from antibonding tight-binding states that have a high degree of cation-anion hybridizaton near the Fermi level. There should be no extended metal-metal bonds.

5. Structural features that are desirable include two-dimensional extended sheets or clusters with controllable linkage, or both.

Z. Fisk (Los Alamos National Laboratory) discussed some unusual features in the 2-1-4 system, including the variation of T_c with carrier concentration. The question of what causes T_c to decrease with overdoping and how this relates to the phase diagram shows that there is still much about the doping process that is not understood. This was amplified by L. Gorkov (Florida State University). Is a large Fermi surface opened by an arbitrarily small doping level? Or are holes introduced into small pockets of a somewhat independent band while spins remain localized? Is the superconductivity attributable to carriers in the pockets interacting with spin fluctuations?

Perovskite phases are highly favored at high pressure. In general, coordination numbers are increased at high pressure and there is the possibility of obtaining unusual oxidation states and metastable phases by high-pressure quenches. B. A. Scott (IBM Yorktown Heights) emphasized that high-pressure phases can be used as precursors for the synthesis of new phases that cannot be reached by conventional paths.

Of the many other superconducting families, the three-dimensional ternary bismuthates stand out. These are based on +4 bismuth, which is unstable with respect to charge density wave formation (or disproportionation). Ternary compounds offer the advantage of being able to provide one site for doping that is not hybridized into the conduction band. For instance, substituting K on the nonconduction band Ba site of $BaBiO_3$ results in T_c(max) around 30 K, whereas substituting on the conduction band sites [$Ba(BiPb)O_3$] gives T_c(max) around 13 K. The extra degrees of freedom that ternary systems have to offer have yet to be fully exploited, and much more needs to be learned about the parameters that determine whether a dopant will produce a local or an itinerant carrier.

The need for a general database of materials properties for understanding metallic versus insulating behavior was stressed by J. Torrance (IBM Almaden).

D. W. Murphy (AT&T Bell Laboratories) and S. Kivelson (UCLA) discussed the fulleride superconductors. A wide spectrum of theoretical models of the superconducting pairing interaction responsible for the surprisingly high values of T_c, which range up to 30 K, involves interactions from purely electronic repulsive correlations to phonon-induced attraction. The situation is not dissimilar to the cuprates; however here the common structural feature is the buckyball. Charge is donated to the ball by the alkali metal (A) ions. The A_3C_{60} compounds are metals and superconductors with two distinct energy scales for excitations: one "intra" (that is, localized on a single buckyball) and the other "inter" (between the balls). The single ball molecular structure is rigid, and so phonon energies are high and the electron-phonon interaction should be weak. The inter-ball modes are very low in energy and would require unusually strong pairing to account for T_c. Models under consideration involve both energy scales. Strategies for obtaining higher T_c's include adjusting the inter-ball coupling.

J. Williams (Argonne National Labora-

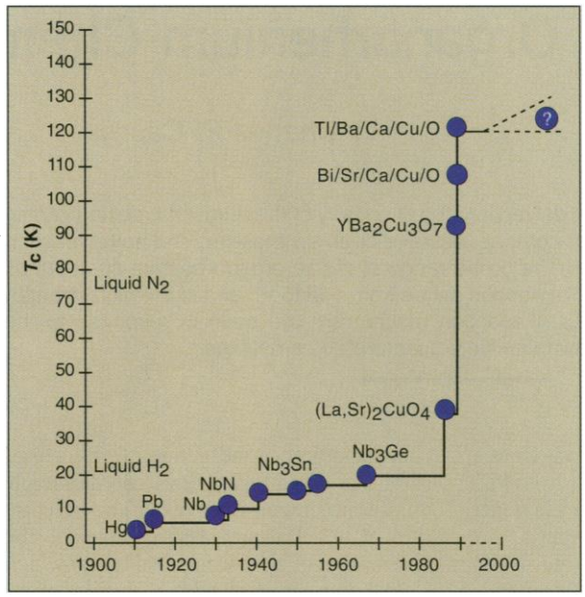
The author is in the Department of Applied Physics, Stanford University, Stanford, CA 94305.

tory) discussed the organic charge-transfer salt superconductors. In these systems, competing instabilities such as spin and charge density waves are prevalent. The richness of the competition is illustrated by the Et-based superconductors. In $k(Et)_2Cu[N(CN)_2]Cl$ the two-dimensional metallic organic layers support an antiferromagnetic transition at 45 K, followed by a weak ferromagnetic transition at 22 K (*4*) if cooled without strain. The application of a modest pressure (0.3 kbar) suppresses the magnetism completely, resulting in a 12 K superconducting transition. A survey of organic systems (*5*) allows one to conclude that two-dimensional materials are much more favorable for finding superconductivity than one-dimensional ones, probably because of the charge and spin density wave instabilities that cannot be suppressed easily in one-dimensional materials.

If an indiscriminate search were to be made for discoveries that are truly revolutionary, the odds are very bad because there is an infinite number of multi-component metastable compounds to choose from. One should be prepared to use all the hints that can be gleaned from experiment and theory as guides. As the experience of Bednorz and Müller shows, even a wrong hypothesis can prove to be a shining beacon (*6*). Further, Wu *et al.* were attempting to use cation substitution to simulate high pressures following the seminal studies of McWhan and co-workers (*7*) when they discovered 90 K superconductivity in an unknown and unanticipated phase (*8*).

According to Frank Di Salvo (Cornell University), $BaCoS_2$ is a compound with potential for opening new insights. This compound has a layered structure in which the CoS_2 sheets are formed by edge-sharing square prisms. Compare this with the copper oxides, where the CuO_2 layers are corner-sharing square prisms. It is a Mott insulator, and if it can be doped into a metallic state will it become superconducting?

Relatively few nitrides have been synthesized, and little is known about solid-state nitrides compared with the oxides, halides, sulfides, phosphides, or carbides. Di Salvo has discovered ways of synthesizing nitrides by using electropositive metals in ternary systems. $LiMoN_2$, for example, is a layered structure similar to lithium intercalated MoS_2. Band calculations on this material by D. Singh *et al.* (Naval Research Laboratory) show large contributions to the density of states at the Fermi level by the nitrogen anions. $LiMoN_2$ is apparently an ionic metal reminiscent of the cuprates. Investigations of the transport properties are under way. Di Salvo further noted that mixed nitride-fluoride systems, from the valence point of view, average to oxygen. The opportunity to employ anion doping by varying the ratio of nitrogen to fluorine offers possibilities in addition to more usual cation doping to move away from an insulating state.



Going up? This plot of the highest transition temperature versus year has not changed since 1988.

D. Mitzi (IBM Yorktown Heights) discussed the intercalation of mono- and dialiphatic amines and aromatic species in between inorganic perovskite layers, including a copper bromide perovskite layer in which the copper is sixfold coordinated by bromine. This class has structural similarities to the high-T_c cuprates. Here, however, the inorganic intermediate layer is replaced by an organic "mushy" layer, thereby providing more flexibility to tune to properties of the active perovskite layer.

A. Stacy (University of California, Berkeley) discussed the use of molten oxides as fluxes from which cuprates can be grown at temperatures lower than for other methods. Entirely new compounds have been discovered using the molten salt technique. For instance, $La_{1.88}Na_{0.12}CuO_{4-x}$ with a T_c of 26 K was found to separate out at 320°C.

Vapor phase deposition with advanced molecular beam epitaxy techniques has been adapted with much success to fabricate oxide structures. Layer-by-layer growth has produced artificial BiSrCaCuO structures with $(CuO_2)_{n+1}(Ca)_n$ sequences for n = 1 to 7 (*9*). T_c probably decreases below the 110 K maximum for n = 3. It is likely that T_c decreases for n greater than 3 because the inner layers are underdoped. It is, however, possible to directly dope the inner layers with holes if vacancies or monovalent cations such as K are substituted for the Ca ions. A particularly interesting system where this has been done to some extent is the metastable structure with no intermediate layering, the so-called infinite layer structure, which consists only of $(CuO_2)_{n+1}(A)_n$ planes (for A divalent and/or trivalent). Such structures have been obtained by pressure quenching as well as by epitaxial film growth. These systems have possibilities of being either p-type, with T_c's up to 90 K (when doped with monovalent A ions or vacancies), or n-type, with T_c's up to 40 K (when doped with trivalent A ions). They also have been reported but not confirmed to show trace signals of T_c greater than 130 K.

In view of all of the possibilities discussed at the workshop, certain general goals can be enumerated. We should learn how to introduce carriers into Mott insulators. We need to find methods of doping that minimize disorder. We can look for systems where more than one energy scale can come into play and where each can be separately manipulated. We should study systems with identifiable substructures that can be lower dimensional entities connected by variable links. We should develop a better theoretical understanding of highly correlated systems, which R. Laughlin (Stanford University) emphasized requires quantitative measurements on high-quality samples.

But what is essential? R. C. Dynes (University of California, San Diego) noted seemingly opposite criteria: localized versus delocalized, stable versus metastable, defect-free versus doped, cluster versus uniform, reduced dimensionality versus three-dimensional, and simplicity versus complexity. All may be relevant in crucial ways. By definition, logical pathways are evolutionary. For the truly revolutionary discoveries that open entirely new vistas, expert opinion is inadequate. However, imaginative research inspired by logical (though not necessarily correct) ideas has led to revolutionary results in the past. The hope is that with good experiments, good intuition, and good luck, it can happen again.

References and Notes

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