Number of Organic Superconductors Grows

New discoveries suggest that the superconductivity of certain organic salts is a general phenomena

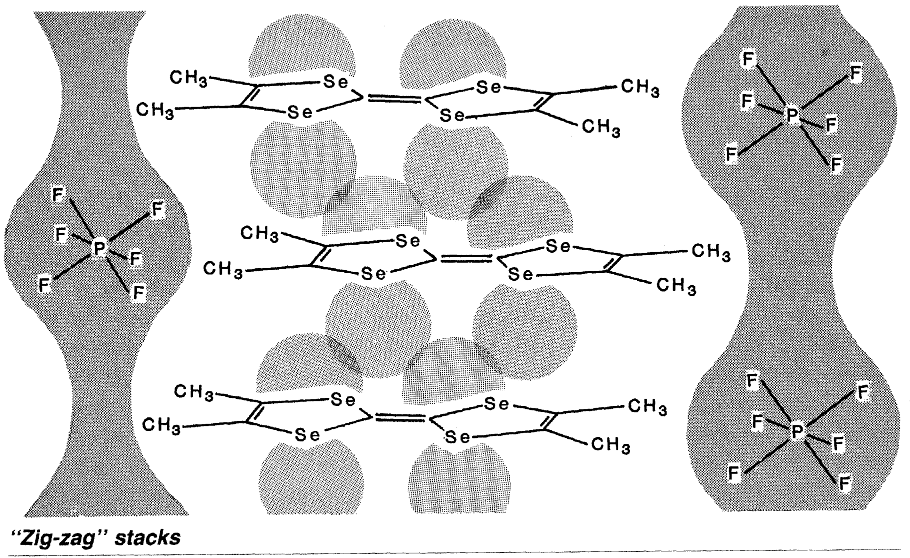
Superconductivity—the complete absence of electrical resistance—has long been assumed to have great industrial potential. Power transmission without any loss of energy would increase the efficiency of the national electrical grid and would make possible more efficient electric motors and much more powerful electromagnets. The absence of heat generation would make possible much larger, more powerful computers. And the ability of a superconductor to expel an external magnetic field (the Meissner effect) could make it possible to "float" a vehicle above a superconducting roadway for smooth and efficient transportation.

The problem with all of these potential applications is that superconductivity in metals requires very low temperatures and, thus, expensive cooling equipment. The highest recorded critical temperature (the temperature at which a material passes from conducting to superconducting) is 23.2 K for the alloy Nb_3Ge. Since that critical temperature was discovered in 1973 and no higher one has yet been observed, many investigators have concluded somewhat reluctantly that metallic alloys with significantly higher critical temperatures will probably not be observed soon. Some of these people have turned to organic materials in the hope that a material with a higher critical temperature can be rationally designed. In 1979, Klaus Bechgaard of the University of Copenhagen and Denis Jérome of the University of Paris-South at Orsay found a family of selenium-based organic chemicals that are superconducting. Earlier this year, Edward M. Engler, Richard L. Greene, and their colleagues at the IBM San Jose Research Laboratory reported the discovery of a sulfur-containing organic superconductor. This result dispelled fears that the French results might represent an anomaly rather than a general phenomenon.

The first stable conducting organic material was synthesized in 1960 at the Du Pont Company. The new compound was 7,7,8,8-tetracyano-*p*-quinodimethane, usually abbreviated TCNQ. This material is not itself conductive, but in salts such as $Cs_2(TCNQ)_3$, some of the TCNQ molecules become negatively charged and electrons can move from charged molecules to neutral ones, carrying a current in the process. The best organic conductors have a conductivity of about 1000 to 2000 ohm^{-1} $centimeter^{-1}$ at room temperature, compared to 10^5 ohm^{-1} $centimeter^{-1}$ for copper.

Organic conductors like $Cs_2(TCNQ)_3$ typically undergo a phase change at low temperatures, where they are converted from conductors to insulators. Nonetheless, they share two key characteristics with the subsequently discovered superconductors. The organic portion of the conductor is composed of large, planar molecules with extended π-electron systems above and below the planes. The energy cost of partially filling or partially opening the valence bands is small, and the molecules can become stacked one over the other like pancakes so that electrons can propagate from plane to plane along the stack. The counterions occupy the spaces between the stacks. These arrays are highly anisotropic—that is, the electrical conductivity is much greater (often as much as 500 times greater) in the direction parallel to the stacks than in a direction perpendicular to them.

Some investigators reasoned that conductivity could be improved by incorporating atoms with more *d*-electrons into the planar arrays. In the early 1970's, Fred Wudl, now at the University of California, Santa Barbara, synthesized tetrathiafulvalene (TTF), which contains four sulfur atoms and which readily gives up an electron to form a stable, positively charged structure. Wudl found that TTF could be combined with chlorine atoms to produce a highly conductive material. Subsequently, Dwaine O. Cowan and his colleagues at Johns Hopkins University and Alan J. Heeger and his associates at the University of Pennsylvania independently combined TTF and TCNQ to form the first "organic metal." Neither material, however, gave any hint of superconductivity.



"Zig-zag" stacks

In Bechgaard salts such as $(TMTSF)_2PF_6$, *the planar organic molecules are stacked like pancakes with every other molecule slightly offset. This provides niches in which the inorganic salts sit. The shaded areas represent regions of charge density.*

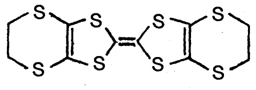
To modify the electron-donating properties of TTF, some investigators tried to make selenium analogs. Bechgaard, then a postdoctoral fellow with Cowan at Johns Hopkins, synthesized tetramethyltetraselenafulvalene or TMTSF. Crystals of TMTSF and TCNQ can be either conductors or insulators at room temperature, depending on how the crystals are prepared, but the conductor becomes an insulator below 60 K. Bechgaard and Jérome next prepared the analogous salt of TMTSF and 2,5-dimethyl-TCNQ (DMTCNQ). Following up on a suggestion by Meir Weger of the Hebrew University of Jerusalem, they subjected the TMTSF-DMTCNQ to a pressure of 10,000 atmospheres (10 kbar) before cooling it. This produced a stabilization of the conductivity at low temperatures but not the hoped-for superconductivity.

Encouraged by the stabilization of

conductivity at low temperatures, Bechgaard and Jérome began studying other salts of TMTSF. In December 1979, they observed that $(\mathrm{TMTSF})_2\mathrm{PF}_6$, when subjected to a pressure of 12 kbar and cooled slowly, lost all electrical resistance at 0.9 K. Wudl and Klaus Andres, both of whom were then at Bell Laboratories, subsequently showed that the compound exhibits the Meissner effect, confirming that it is superconducting.

Since then, Bechgaard and Jérome have observed superconductivity in crystals with the general formula $(\mathrm{TMTSF})_2X$, where X is hexafluoroarsenate ($\mathrm{AsF_6}^-$), hexafluoroantimonate ($\mathrm{SbF_6}^-$), hexafluorotantalate ($\mathrm{TaF_6}^-$), perrhenate ($\mathrm{ReO_4}^-$), and perchlorate ($\mathrm{ClO_4}^-$). These materials, now known as Bechgaard salts, exhibit superconductivity at high pressures and low temperatures. The sole exception is $(\mathrm{TMTSF})_2\mathrm{ClO}_4$, which becomes superconductive at 1.2 K at normal atmospheric pressure.

For some time, it was believed that the Bechgaard salts might be the only class of organic materials that could be made superconducting. Earlier this year, however, the IBM group reported the discovery of a second class of superconductors based on sulfur compounds. The organic component of the new superconductor is *bis*(ethylenedithiolo)tetrathiafulvalene or BEDT-TTF:



This material forms at least three distinct compounds with perrhenate; one of these, $(\mathrm{BEDT\text{-}TTF})_4(\mathrm{ReO}_4)_2$, becomes superconducting at a temperature of about 2 K under a pressure of at least 4 kbar.

The structure of $(\mathrm{BEDT\text{-}TTF})_4(\mathrm{ReO}_4)_2$ bears some similarity to that of the Bechgaard salts. In particular, the BEDT-TTF molecules are "zig-zagged" along the main axis, providing cages in which the perrhenate anions sit, and thereby determining the stoichiometry of the material. There is also the possibility of strong S–S bonding between BEDT-TTF molecules along an axis perpendicular to the main axis. This bonding may be more important in BEDT-TTF since it contains twice as many chalcogenide atoms as TMTSF.

There are, however, two important differences in structure. Whereas the TMTSF molecule is almost planar, the terminal methylene groups at either end of the BEDT-TTF molecule are positioned well out of the plane of the rest of the molecule. This might be expected to limit interactions of the π-electrons by holding the molecules farther apart than would be the case with the planar compounds. Also, the perrhenate anions in the IBM compound are ordered at room temperatures, whereas none of the anions in the Bechgaard salts are ordered. The significance of this observation is not yet clear. The fact that BEDT-TTF forms more than one salt with perrhenate can be a major advantage, argues Engler, since it should make it possible to examine the influence of structure on superconductivity.

The IBM group has synthesized a series of sulfur compounds that are more planar than BEDT-TTF, but none of the series has yet been shown to be a superconductor. In fact, says Greene, their electrical properties depend strongly on the stoichiometry of their salts. The organic compounds that form a 1:1 complex with the anion tend to be insulators, while those that form a 2:1 complex tend to be metallic in nature. Those with a 3:2 stoichiometry tend to be metallic at room temperature but undergo a phase change to become an insulator at temperatures between 100 and 200 K.

Meanwhile, the possibility of raising the critical temperature of the organic superconductors remains somewhat controversial. The highest temperature observed so far is about 3 K at 7 kbar for $(\mathrm{TMTSF})_2\mathrm{FSO}_3$, observed by Wudl and Paul Chaikin of the University of Pennsylvania. Bechgaard and Jérome have not observed superconductivity in this salt, but in October, Andres and his colleagues at the Institute for Low-Temperature Research in Garching, Germany, measured the Meissner effect for the salt, confirming that it is superconducting. Bechgaard and Jérome, meanwhile, have interpreted some of their results to indicate that small regions of the Bechgaard salt crystals become superconducting between 15 and 20 K, indicating, they argue, that the materials "want" to become superconducting at those temperatures; only slight modifications may be necessary, they say, to increase the critical temperature. Greene and Chaikin argue, however, that the evidence for these fluctuations is very weak and that the effect is probably not real. For the moment, most American investigators appear to agree with Greene and Chaikin, while most Europeans agree with Bechgaard and Jérome.

Most investigators agree, though, that the best chance for finding higher critical temperatures lies in the use of tellurium compounds, which have still more electrons and thus a larger conduction band. The synthesis of tellurium compounds has proved exceptionally difficult, primarily because there is little prior recorded data about the chemistry of tellurium. The few tellurium compounds prepared so far have not been superconducting. No one has yet reported the tellurium analog of TMTSF, however.

A partial explanation for some of the behavior of the Bechgaard salts has been offered by Jack M. Williams and Mark Beno of the Argonne National Laboratory, and is based on x-ray structures of the salts. They have found that the selenium-selenium distance between adjacent stacks may be a major factor in controlling whether or not the material will be superconducting. The best arrangement occurs with the perchlorate salt, which is superconducting at room pressure. Most of the other anions that have been used are larger than perchlorate and therefore pressure is required to "squeeze" the salts so that the stacks contract to the proper distances.

J. P. Pouget of Orsay has shown that ordering of the anions is important. At room temperature, the perchlorate anion in $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ adopts random orientations. If the salt is cooled rapidly, these orientations are frozen in and the salt does not become superconducting. But if the salt is cooled slowly, the perchlorate anions become oriented and the salt becomes superconducting. This orientation, Williams says, is controlled primarily by a strong hydrogen-bonding interaction between the perchlorate oxygens and hydrogens of methyl groups on the organic portion of the salts. Pouget and Jérome, in contrast, argue that the strong interaction between oxygen anions and the selenium atoms is responsible for ordering. In either case, it is important to have oxygen-containing anions to form strong hydrogen bonds. On the basis of his interpretation, Williams is now making new materials that he predicts will also be superconducting at normal pressure.

Other aspects of the behavior of the materials is less readily explainable. One of the most unusual things about the salts is that application of a strong magnetic field while the materials are conductors (not superconductors) converts them into insulators. This behavior is unprecedented, says Chaikin: "There is nothing else like this," and no explanation for why it happens. There are other nonlinear electrical effects that have also been observed, and most investigators argue that a more extensive study of these effects will provide a better understanding of how the salts work and how they might be improved.

—**Thomas H. Maugh II**