Organic Crystals: Hints of Extraordinary Conductivity

Most metals have to be cooled within a few degrees of absolute zero to become superconductors, and the highest temperature at which superconductivity has been found for compounds of several metals is 20.8°K. But new research has shown that an unusual class of organic solids, called charge transfer salts, behave in certain ways like metals, and one organic salt becomes highly conducting at a temperature of 58°K. That is still far colder than room temperature, but even a superconductor that could be cooled with liquid nitrogen (77°K) would be a significant advance beyond superconductors cooled with liquid helium (4.2°K).

Several key experiments with organic salts have been reported in the last year, and there appears to be no doubt that many unexpected properties have been found. But when assessing the likelihood that superconducting properties have been demonstrated, many scientists are cautious and a few are pointedly skeptical.

At a recent meeting of the American Physical Society, Alan J. Heeger, Anthony F. Garito, and associates at the University of Pennsylvania, Philadelphia, reported that the conductivity of an organic salt called (TTF)(TCNQ) rose to at least 500 times its conductivity at room temperature when the salt was cooled to 58°K (*1*). [TTF (tetrathiofulvalene) is the positive ion of the salt; TCNQ (tetracyanoquinodimethan) is the negative ion.] Approximately 70 crystals were grown and tested by the researchers at the University of Pennsylvania. They were typically quite small (0.7 by 0.1 by 0.033 mm). The conductivity of each crystal was measured with four probes of very fine gold wire (0.025 mm in diameter) that made contact to the crystal with silver paint. Out of the 70 crystals, three showed extraordinarily high conductivity. The rest had a maximum conductivity only about ten times greater than the room-temperature value. Heeger and his colleagues noted that the three special crystals had excellent morphologies and exceptionally smooth surfaces—in short they seem to be rare perfect crystals.

The true maximum conductivity of the three special crystals could not be measured because of the limitations of using silver paint to make electrical contact with the crystals. However, conductivty at temperatures nearing 58°K does rise very steeply (Fig. 1), and fits a functional form that diverges.

The researchers at Pennsylvania interpret the effect as a superconducting fluctuation and note that they have not been able to stabilize the superconducting state. Superconducting fluctuations are well known in conventional superconducting metals, and are observed as an excess of conductivity at temperatures nearing the superconducting transition. The specific signature is a temperature dependence ($T^{-3/2}$) which diverges at some critical temperature. In other systems where superconducting fluctuations have been found, the material goes on to become a superconductor, but (TTF) (TCNQ) does not. Heeger and his associates believe that a distortion of the crystal occurs just as it is about to make a superconducting transition, and causes it to become an insulator. The Pennsylvania

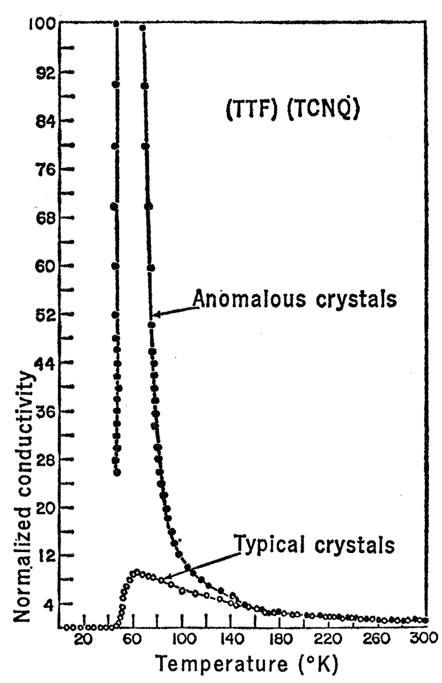

Fig. 1. A few anomalous crystals of the organic salt (TTF) (TCNQ) have been reported with extremely high conductivities at about 58°K. They are interpreted as near perfect crystals. For typical crystals, the maximum conductivity is about 10 times the value at room temperature, much greater than the maximum value for previously known organic solids.

researchers have suggested a program of alterations in the molecular structure that would possibly lead to stabilization of the superconducting state.

John Bardeen, at the University of Illinois, Urbana-Champaign, has proposed that the phenomena could be explained by a theory of superconductivity suggested by Herbert Fröhlich as early as 1954, rather than by the Bardeen-Cooper-Schieffer (BCS) theory of superconducting fluctuations. The Fröhlich theory has not been thoroughly developed, however, and Bardeen does not think that it can be used to make quantitative predictions yet.

The first attempt to reproduce the results of the Pennsylvania group is now in press and will soon be published. Dwaine Cowan, John Ferraris, and associates at Johns Hopkins University, Baltimore, Maryland, have studied a large number of (TTF) (TCNQ) crystals but found none with abnormally high conductivities.

Cowan and his associates were the first researchers to publish measurements of the conductivity of the salt (TTF)(TCNQ). In their original experiments (*2*), they found that the conductivity reached a maximum value (10^4 ohm^{-1} cm^{-1}) at about 60°K, but this is much less than the value (> 10^6 ohm^{-1} cm^{-1}) reported for the special crystals at Pennsylvania. (Normal conductivities for organic salts are 100 or 200 ohm^{-1} cm^{-1}.)

Very recently the researchers at Johns Hopkins have measured the conductivities of many more crystals by using a mirowave technique that eliminates the fine wire probes (*3*). The microwave measurements are consistent with the earliest measurements at Johns Hopkins, as are the Pennsylvania data for the 67 normal crystals. So the outstanding question is, what makes the anomalous crystals anomalous? Anthony Garito, one of the Pennsylvania researchers, thinks that "severe materials differences" probably account for the different results of the two experiments.

However, the Johns Hopkins researchers also measured the conductivity of an analog of the (TTF) (TCNQ) compound. Neither group has been able to make single crystals of the analog. The Pennsylvania researchers measured the conductivity of a polycrystalline form of the analog compound and reported it seemed to diverge; the Johns Hopkins experiments with microwave techniques showed a steep rise in conductivity but no divergence. Cowan points out that the discrepancy between these two results cannot be due to barriers in the crystals.

Perhaps the most critical estimate of the reported evidence for superconducting effects comes from Bernd Matthias, at the University of California, La Jolla, who suspects that the results for the special crystals and for the analog compound are simply wrong. Matthias, who discovered the superconductor that functions at 20.8°K, suggests that the crystals being studied are ferroelectric, and that for such materials, conductivity maxima near certain critical temperatures are not unusual. Several researchers have objected to the fact that Heeger has so far been unwilling to lend any of the special crystals to other laboratories for testing.

(At Pennsylvania, Garito says that he and his co-workers have an open laboratory where anyone is welcome to collaborate, and that they have lent a batch of crystals to Paul Chaiken, at the University of California, Los Angeles, who was formerly a student with the Pennsylvania group. Follow-up experiments with the special crystals are probably not possible now, according to Heeger, because the crystals are quite fragile and partially coated with silver paint.)

Whether or not superconducting properties are ultimately confirmed, it is clear that (TTF)(TCNQ) and related (TCNQ) compounds have extraordinary conduction properties, and that only a few of the possible crystals have been studied. Because of the relative ease with which many variations of organic compounds can be synthesized, it is possible that the properties of organic superconductors could be tailored to fit many needs. The National Bureau of Standards, the Bell Telephone Laboratories, Monsanto Research and Development Laboratories, and the International Business Machines Watson Research Center are all beginning to study organic solids.

Concerning the three special crystals reported by Heeger and his associates, the consensus of other researchers seems to be "If he's right, he's got something fantastic."—WILLIAM D. METZ

References and Notes

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Influenza: The Last of the Great Plagues

Never, before influenza, has control of an infectious disease been contingent upon an understanding of the molecular biology of its agent. Control of cholera, for example, depends only upon a separation of sewage and drinking water; control of malaria depends primarily upon the eradication of mosquitos; and control of viral diseases such as yellow fever, smallpox, poliomyelitis, and measles depends upon isolation of the virus and production of vaccines. Yet 40 years after isolation of its causative virus and 30 years after development of a vaccine effective against it, influenza remains an embarrassing anachronism—the only infectious disease that appears periodically in life-threatening pandemics (global epidemics).

Influenza's persistence results from a unique genetic plasticity that enables the viral agent to undergo two types of antigenic shift: frequent (once every year or two), minor mutations that give the new variant a somewhat increased resistance to prevailing antibodies, and less frequent (once every 10 to 12 years), major antigenic shifts that circumvent nearly all preexisting immunity. The effects of these shifts can be devastating. During the winter of 1968–1969, there were more than 51 million reported cases of influenza in the United States attributed to a major new influenza variant first isolated in Hong Kong, and at least 20,000, and perhaps as many as 80,000, excess deaths attributed to influenza and its side effects. (Excess deaths are those beyond the number that would be expected in the absence of an epidemic.)

Even during the past winter, when only a minor variant—the so-called London flu—emerged, at least 2200 excess deaths in 122 U.S. cities were attributed to influenza and its side effects, especially pneumonia. In terms of the number of deaths each year, the combination of influenza and pneumonia is the fifth most serious public health problem in the United States, and in terms of days of work missed, it is the most serious.

Chills, Fever, and a Running Nose

Although the term "influenza" is used loosely by both physicians and patients, it should not be confused with the common cold, with other, less severe infections of the respiratory tract, or with gastrointestinal infections. Influenza is a brief, but severely incapacitating disease with an incubation period of 24 to 72 hours. Its abrupt onset is marked by chills, fever, headache, aching muscles, and extreme fatigue, followed by a running nose and a sore throat. A cough is nearly universal, and often severe. The disease usually runs its course in about 3 to 7 days, although fatigue may last longer. As with other viral infections, there is no specific treatment after the onset of symptoms.

Uncomplicated influenza is rarely fatal, except in patients with chronic diseases of the heart or lungs. Most influenza-mediated deaths arise from bacterial pneumonia or other severe infections that occur when the patient is weakened by influenza. These secondary infections can be largely controlled now, but were the cause of many deaths before the advent of antibiotics. An estimated 20 million people worldwide and more than 500,000 in the United States died of such complications during the influenza pandemic of 1917–1918.

Influenza vaccines have moderated the severity of epidemics in recent years, but the commonly used killed virus vaccines have several important deficiencies. One problem is that such vaccines, many scientists believe, are inherently less effective than those produced with attenuated viruses, and are thus only partially effective to begin with. A greater problem in the past has been the length of time required for adaptation of newly emerged human influenza viruses to growth in chick embryos for preparation of vaccines. Influenza spreads so rapidly that epidem-