news and views

Search for organic superconductors

from A. D. Yoffe

A THEORETICAL paper published in 1964 by W. A. Little (*Phys. Rev.*, **134A,** 1416) dealt with the possibility of high temperature superconductivity particularly in solids formed from long chain organic molecules. The use of the term "high temperature" is of course a little ambiguous, but a realistic interpretation would put this in the vicinity of liquid nitrogen temperature (77 K) or higher. This theory was based on a particular kind of electron–phonon (vibrational) coupling and it naturally created considerable interest and excitement. First, there were the biological implications and second, there was the vision of a relatively cheap high temperature superconductor for both scientific and industrial use. It should be said that the paper was also greeted with a good deal of criticism and scepticism. This led to a hunt for organic-type solids which would be metals at room temperature and which would remain metals even when cooled to temperatures below that of liquid helium (4 K). This is not an easy problem to solve since pretty well all organic solids are insulators or semiconductors. One exception is of course graphite and the intercalate compounds formed from graphite with, say, alkali metal atoms such as potassium. They are metals in this sense, but they hardly qualify as organic solids.

Crystals of the organic charge transfer complexes such as TTF-TCNQ (tetrathiofulvene - tetracyanoquinodimethane) which are extremely anisotropic in their physical properties, do behave as metals with a conductivity in the region of 1,000 $ohm^{-1} cm^{-1}$ at room temperature when this is measured along one of the crystal axes. This is the direction along which the molecules are stacked. Further evidence for the metallic nature along this direction came from optical reflectivity experiments using polarised light. When the electric vector of the incident light is parallel to the direction of the stack of molecules (good conductivity direction) then typical metallic free carrier reflectivity is found. When the crystals are cooled below liquid nitrogen temperatures (round 60 K), however, the electrical conductivity begins to fall, and it seems that the solid changes to a small band gap semiconductor. The solid undergoes what is currently termed a Peierls transition, proposed for one-dimensional metals. In 1973 Heeger and his colleagues at the University of Pennsylvania published some rather startling results on the electrical conductivity for some of their crystals of TTF-TCNQ in which they found the conductivity rose to very high values approaching that for copper, just before the transformation temperature to the semiconducting state. There was talk of superconducting fluctuations and there can be little doubt that these experimental findings created quite a stir and led to the renewed interest in this and similar systems over the past few years.

TTF-TCNQ belongs to the class of solids built up from chain-like structures which are loosely called "one-dimensional conductors". Other examples are $K_2Pt(CN)_4.Br_{0.3}3H_2O$ (commonly abbreviated as KCP(Br)) and the sulphur nitrogen polymer, usually called $(SN)_x$ polymer. This polymer consists of helical chains of sulphur and nitrogen bound together in the crystal by relatively weak van der Waal's forces. The crystals have the appearance of brass, and in 1975 the IBM group (Greene, Street and Suter, *Phys. Rev. Lett.*, **34,** 577; 1975) reported that crystals of this material did in fact become superconducting, but at a relatively low temperature round 0.3 K. This is the first polymer to be shown to be a superconductor and although the result could be likened to a damp squib when we consider the magnitude of the transition temperature, it is important and provides the hope of synthesising other polymers which have higher superconducting transition temperatures.

Many research groups throughout the world with strong chemical support are at present attempting to synthesise such organic solids which behave as metals at all temperatures and which do not display the unfortunate characteristic of TTF-TCNQ at low temperatures. One interesting development has been the synthesis of the charge transfer complex HMTSF-TCNQ (hexamethylene tetraselenafulvalinium-tetracyanoquinodimethanide) which remains metallic below one degree Kelvin, although it does not become superconducting (Block, *et al., Phys. Rev. Lett.*, **34,** 1561; 1975). Another and rather better example is the organic complex radical anion salt 1,2-di (N-ethyl-4 pyridinium) ethylene^{2+} (7,7,8,8 - tetracyanoquinodimethane)$_4^{2-}$ discussed in this issue of *Nature* (page 201) by Ashwell, Eley and Willis.

A good deal of important physics and chemistry is coming out of this work on solids composed of chains of one kind or another. These crystals are extremely anisotropic in their physical properties, and we find that we are concerned with phenomena such as Peierls distortions, Kohn anomalies, soft phonon modes, superlattice formation, charge density waves and superconductivity. It is clear however that the real goal is the synthesis of organic solids which will become superconducting at reasonable temperatures. The experiments discussed above point the way in which future work might develop. □

NATURE

A hundred years ago

THE Ladies' Classes at University College, London, began on Monday last the second term of their eighth session. There was a slight decline in the number of students for the session 1874–75, but the first term of the session 1875–76 showed a considerable advance beyond the highest success hitherto attained. In the Michaelmas term, 1874–75, the whole number of individual students was 199; in the Michaelmas term, 1875–76, just elapsed, the number of individual students was 265. The whole number of tickets taken in Michaelmas term, 1874–75, was 257; in the same term of 1875–76 it was 367.
from *Nature*, **13,** 235; January 20, 1876