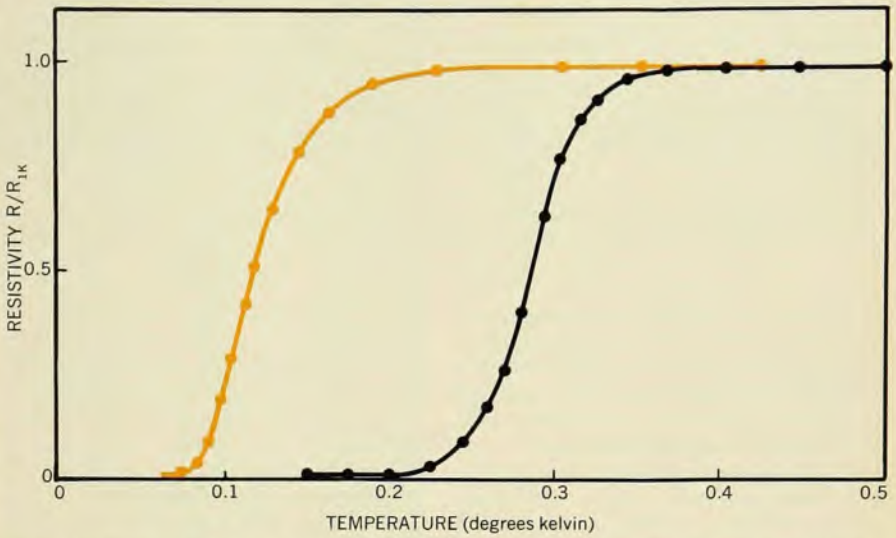
search & discovery

Superconductivity in novel sulfur-nitrogen polymer

Can a polymer of sulfur and nitrogen be metallic, even superconducting? Apparently yes, is the answer for polysulfur nitride, $(SN)_x$, a highly anisotropic, quasi-one-dimensional polymer that looks like a metal, has the transport properties of a metal and becomes superconducting at around 0.3 K. The idea of finding superconductivity in a new part of the periodic table is of course exciting, whether or not practical applications ever arise. So the important questions are the nature of the polymer—its transport properties, crystallographic structure and band structure—as well as speculations about future technological uses. Some of the facts about $(SN)_x$ were exchanged and clarified during a special session at the March meeting of The American Physical Society. At that meeting, which took place in Denver from 31 March to 3 April, two groups active in recent studies of the transport properties each described their work. One group is at IBM, San Jose (the group that first saw superconductivity); the other is at the University of Pennsylvania, Philadelphia. A third group actively studying $(SN)_x$ is at Temple University (Philadelphia).



Superconductivity in polysulfur nitride. The transition temperature of the sample, studied at IBM San Jose, decreases from about 0.2 K in the magnetic field of the earth (black) to about 0.07 K at a field of 335 G perpendicular to the fiber axis (shown in color). From reference 3.

The recent flurry of interest in $(SN)_x$ was inspired by the work of Mortimer Labes (Temple). He had reported unusual conductivity behavior in $(SN)_x$ in a 1973 paper[1] and in a talk at the 1974 Lake Arrowhead Symposium on Conducting Organic and Transition Metal Salts. The main topic at that meeting was TTF-TCNQ (tetrathiafulvalene tetracyanoquinodimethan), an organic quasi-one-dimensional conductor. Polysulfur nitride had been known since the early part of the century, but Labes and his colleagues were the first to measure the dc electrical conductivity of fibrous crystals of the polymer. It forms as a fibrous bundle of chains when S_4N_4 is pyrolyzed to form S_2N_2, and when S_2N_2 is then allowed to polymerize in the solid state. At the Lake Arrowhead meeting, Labes reported that his group had measured the dc electrical conductivity of $(SN)_x$ down to 4.2 K and found a low-temperature maximum but no ev-

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Electrons exhibit periodic density distribution

Although the electron distribution at the Fermi surface of a metal has long been considered to be well understood, some anomalies of electronic behavior such as magnetoresistivity have hinted that this understanding was not complete. In 1968 Albert W. Overhauser (Purdue University) proposed a model of a Fermi-surface instability that he called "charge density waves."[1] However, the validity of charge density wave theory has only now been established by the experimental observation of periodic structural distortions—unique consequences of this type of instability.

A charge density wave is a sinusoidal variation in the electron density with wave vector $\mathbf{q}_0$. The Coulomb attraction between the regions of electron concentration and the lattice ions produces a periodic structural distortion of the same wave vector. The formation of such distortions (often called superlattices) was identified in layered transition-metal dichalcogenides both in electron diffraction studies done by John A. Wilson, Frank DiSalvo and Subhash Mahajan, all of Bell Labs,[2] and in neutron scattering studies performed by David E. Moncton (MIT), John D. Axe (Brookhaven) and DiSalvo.[3] Similar distortions have also been observed[4] in the pseudo one-dimensional compound KCP—$K_2Pt(CN)_4Br_{0.3}xH_2O$.

The conventional picture of the electron distribution in simple metals assumes that the electrons have the same periodicity as the underlying ionic crystal and that the electronic ground state (for an ideal metal) consists of a filled Fermi sphere. By contrast, Overhauser demonstrated that under certain conditions the electrons can reach a still lower energy state by clustering together. The periodicity of the resulting charge density wave is determined primarily by the dimensions of the Fermi sphere of the metal, which bears no simple relation to the periodicity of the underlying lattice; it is incommensurate with the lattice. A further requirement of local charge neutrality leads to a modulation of the ionic periodicity. Overhauser notes that these incommensurate periodicities destroy the convenience of the concept of the unit cell because the unit cell—that volume over which the crystal structure repeats itself—now becomes the entire crystal.

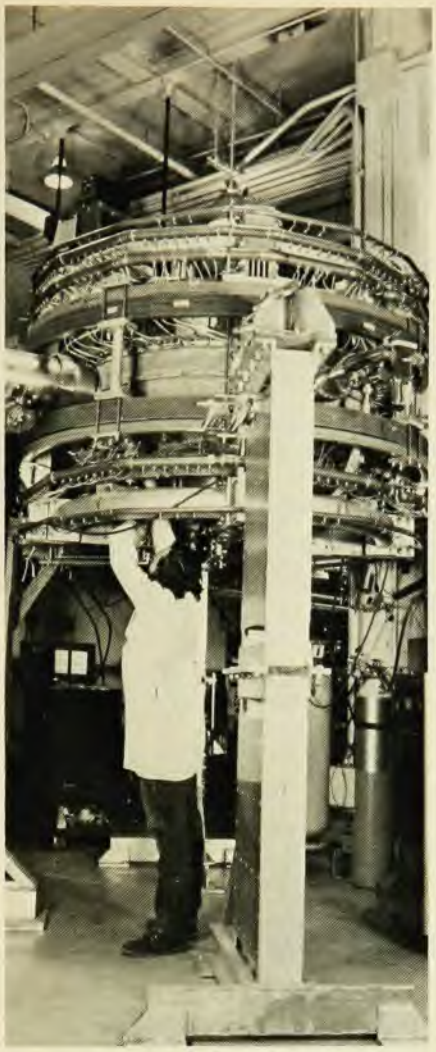
In layered compounds, the periodicity

"turbulent heating" of the ions can be achieved by stimulation of microinstabilities, which can have much stronger effects than collisions.

Recent experiments on the Alcator machine point to the identification of high ion temperatures (up to 1.2 keV) with just such a new and turbulent regime in the plasma. This so-called "slide-away" regime[1] seems to set in when the plasma density is low and the ratio of electron toroidal velocity to the thermal velocity is about 0.2 to 0.3. The strong ion heating that occurs under these conditions seems to correlate with the excitation of an ion plasma frequency mode.

The experimenters at Alcator have proposed a theoretical explanation for the behavior they observe in this region. The Thomson-scattering measurements[2] of the electron distributions in the slide-away regime suggests a combination of two distributions—one of non-current-carrying electrons, and the other of current-carrying electrons that circle around the toroid. The circulating electrons are held from running away collectively, under the influence of the applied electric field, by the same microinstability that heats the ions as well as by other microinstabilities that only affect the electrons and have been well identified experimentally. These slide-away electrons might be distinguished from the "run-away" electrons that are usually associated with unfavorable instabilities by the fact that they keep together in a large group and do not attain the high speed of runaways. The ion temperatures are measured by charge-exchange reactions and by emission of neutrons from fusion reactions.

Other, indirect experiments at Alcator indicate that it has an exceptionally clean plasma—an exceedingly important property for future Tokamak scaling. Coppi confesses that they do not yet know the exact reason for this purity but plan to determine its cause and measure the impurity concentrations. They also have deduced that, because the energy confinement time varies directly with density in Alcator, the product of density and containment time goes as the square of the density.



Alcator, the Tokamak-like device at MIT, features high values of current densities. Its magnetic field of 65 kG is being increased in steps; the coils have been tested to 100 kG.

The MIT device is a university experiment, as distinguished from more heavily funded projects such as those at national laboratories. But its work lies midway between the exploratory area of pure research, typical of university projects, and its "national-laboratory" role of determining parameters in a new and interesting region. Thus it will be especially useful as a research tool to explore plasma physics relevant to thermonuclear reactors; its wide range of parameters and high magnetic field enhance this role for it. However, it was not designed strictly as a research reactor—it has neither the flexibility nor the space for multiple diagnostic experiments—and at least one observer commented to us that Alcator should not be overlooked as a potential source of a set of plasma containment parameters that work. —BGL

Machine operating conditions

Major radius = 54 cm
Minor radius = 9.5 cm
Toroidal field = 65 kG
Pressure = 3×10^{-9} Torr

Plasma operating conditions

Average density:
2×10^{12} to 2×10^{14} cm^{-3}

Peak density:
up to 3.5×10^{14} cm^{-3}

Plasma current: 20 to 200 kA

Electron temperature:
0.1 to 1.8 keV

Ion temperature: up to 1.2 keV

Confinement time: 0.5 to 15 msec

Plasma current pulse: ≤ 400 msec

Beta (poloidal): 0.05 to 1.0

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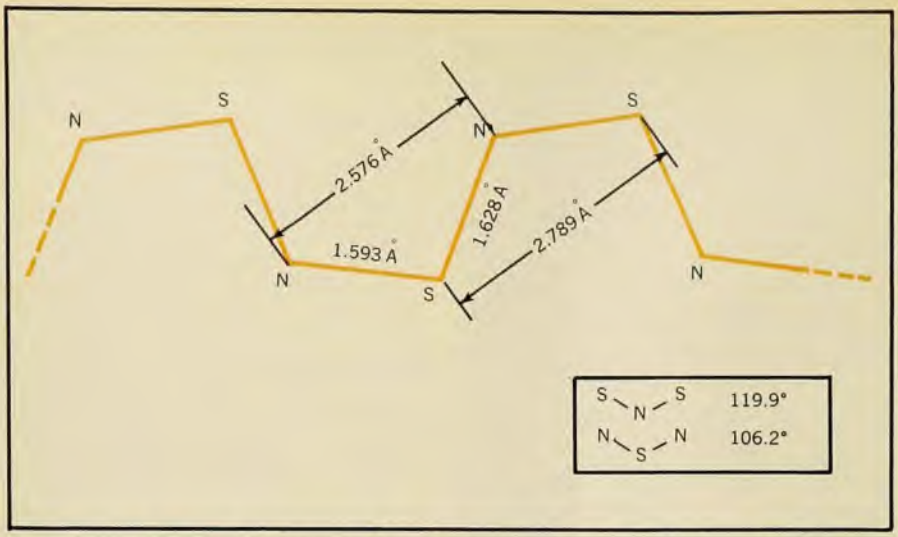
idence of a metal–insulator (Peierls) transition; other pseudo-one-dimensional conductors, such as TTF–TCNQ, undergo such transitions. In other words, the metallic properties of this inorganic polymer appeared to persist down to much lower temperatures than the metallic properties of the organic conductors.

At IBM, San Jose, Richard Greene, Paul Grant and Bryan Street prepared their own crystals of $(SN)_x$ and reported low-temperature (10 K–1.5 K) specific-heat measurements.[2] The results below 3.2 K, taken together with their measurements of other transport properties, indicated that the metallic properties persisted down as far as 1.0 K, with a conduction band width of at least 0.9 eV. A few months later, Greene and Street, along with Laurance Suter (Stanford University) saw superconductivity at 0.26 K in single crystals of $(SN)_x$.[3] (See figure, page 17.)

Any question of "dimensionality"of the system is of course largely semantic rather than basic: If the material were completely one-dimensional, fluctuations would prevent any three-dimensional superconducting transition. The considerable degree of anisotropy, however, has been clearly established. Labes and his coworkers had reported on the anisotropy of the electrical conductivity, finding a factor of 500 to 1 at 20 K.[4] They also showed that thin films could be prepared. The Pennsylvania group (Arthur Bright, Marshall Cohen, Anthony Garito, Alan Heeger, Alan MacDiarmid, Chester Mikulski and Peter Russo) measured the optical reflectivity of $(SN)_x$ films from the near ultraviolet to the far infrared (from 30 000 cm^{-1} through 500 cm^{-1}).[5] They found metallic reflectivity that they attributed to the component of light polarized parallel to the principal conducting axis.

This work, as well as similar optical studies on single crystals, was described by the Penn group at the Denver meeting. Both sets of data were analyzed according to the Drude model, appropriate for a metal.[6] An interesting result from the Penn experiments is the achievement of fully oriented epitaxial



X-ray structure of polysulfur nitride $(SN)_x$, as determined by Alan MacDiarmid and his colleagues at the University of Pennsylvania. The almost planar chain of alternating sulfur S and nitrogen N atoms has intrachain distances and bond angles as shown above. From ref. 7.

thin films on Teflon, Mylar and polyethylene. This is the first reported case of fully oriented thin films of any polymer, Garito tells us, and is of potential technological interest because of the anisotropic optical and electronic properties of $(SN)_x$.

The IBM group presented heat capacity and optical data at the meeting, both types of data indicating to them that the conduction bands are wider than in TTF–TCNQ. The IBM and Penn optical results, both of which indicate that $(SN)_x$ has more interchain coupling and less one-dimensional character than TTF–TCNQ, are compatible with band-structure calculations presented at the Denver meeting. These calculations, done independently at IBM (William Rudge), at the University of British Columbia (W. I. Friesen, A. J. Berlinsky, B. Bergersen, L. Weiler) and Simon Fraser University (T. M. Rice), and at the University of Pennsylvania (Paul Soven and Arthur Bright), suggest that $(SN)_x$ is a semimetal with pockets of electrons and holes. However, the first two calculations were based on electron-diffraction structural studies that are now believed to be somewhat inaccurate. X-ray results are usually considered more reliable than those obtained from electron-diffraction studies. Analytically pure single crystals suitable for x-ray studies have been prepared by MacDiarmid at Penn, and the x-ray structure analyses have been completed. The Pennsylvania x-ray structure has several major differences from that of the electron-diffraction study: the S–N bond distances along the chain are equal, rather than alternating; the S and N bond angles are qualitatively different; the position of one chain relative to its neighbor is shifted.[7] (See figure above.)

Greene points out to us that at least some of the interest in working with the chainlike material comes from William Little's suggestion, made several years ago, for forming high-temperature superconductors by adding polarizable groups to a conducting backbone. Polysulfur nitride offers such a backbone, but Greene feels that such ideas are still quite speculative for $(SN)_x$. According to Garito, it is probably incorrect to consider $(SN)_x$ in the class of one-dimensional conductors; a better way to think of it may be as the forerunner of an entirely new class of metallic polymers.

What then, is the significance of $(SN)_x$? The widespread opinion is that $(SN)_x$ is important not only for itself but also for the insight it may give into the behavior of the structurally more versatile organic materials: How do the multidimensional interchain interactions become sufficiently significant to lead to a three-dimensional transition to the superconducting state? Why is there no Peierls transition to the insulating state? Why is there a broad maximum in the normal-state conductivity that appears to be a function of temperature and crystal purity? Once more is known about the structural requirements for these phenomena to occur, the flexibility of organic synthesis could be exploited to achieve chemical control of the electronic properties. (Aaron Bloch of Johns Hopkins University, Baltimore, tells us that he and Dwaine Cowan have been studying a new organic material, known as HMTSF–TCNQ, that also does not undergo a metal–insulator transition.[8] But, as of early May, no superconducting transition had been observed.)

Along with any new participants that may have been inspired to work with $(SN)_x$ by the Denver meeting, the Penn, IBM and Temple groups are continuing their experiments. The Penn group, in collaboration with Robert Pohl and Liang Fu Lou (both of Cornell), has now confirmed the observation of superconductivity in $(SN)_x$, as they reported at the Denver meeting. Garito tells us that at Penn, activity is now focussed on the optical, magnetic and transport properties of single crystals and epitaxial films, and that tunneling experiments are now being carried out. At IBM, Street has been able to modify the $(SN)_x$ crystallization procedure to obtain crystals of greater perfection and higher resistivity ratio—the ratio R_{300K}/R_{4K} is now about 100 instead of ranging between 5 and 20. Some critical-field measurements have been done, as well as studies of the behavior of $(SN)_x$ under pressure; both kinds of measurements have given only preliminary results. Greene notes that the values of H_c appear to be high for a material with such a low T_c (most recently 0.34 K) and are much greater parallel to the fiber axis than perpendicular to it. And William Gill and Greene have found that T_c appears to increase with pressure, whereas most S- and P-electron superconductors show a decrease in T_c with increasing pressure. They tentatively interpret this result in terms of the pressure change causing a change in the band structure rather than simply stiffening the lattice, as in other S–P systems, and hope that this kind of measurement will be useful in finding out what happens when $(SN)_x$ undergoes its transition.

Labes and his colleagues have also confirmed the superconductivity in $(SN)_x$. They are continuing to try to incorporate $(SN)_x$ chains into the canals of organic inclusion compounds in an approach to the Little model. Chemical modification, Labes, explained to us, is not possible here, because such modification of the $(SN)_x$ chain destroys the metallic conductivity.

—MSR

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