

authority the Russians would deal with. The period was not without strain. Requests that Russian soldiers would desist raping women and children were threateningly dismissed as insults to the honor of the Red Army; Georgescu-Roegen was powerless to complain when his own sister-in-law was killed trying to escape from Russian soldiers. He was also head of the Romanian delegation negotiating the payment of the crushing reparations demanded by the Russians—\$300 million at 1938 prices. On the day fixed for signing the agreement, the Russians denounced the head of their own delegation as an impostor and the whole negotiation had to start over again.

Some months after these events, Georgescu-Roegen stowed away with his wife, Otilia, on a boat bound for Istanbul. He returned to Harvard, but the university could not immediately offer him a tenured position. At that stage, he wanted not to move again, and accepted a tenured post from Vanderbilt University. A symposium is being held there this month to mark his impending retirement after 27 years' service.

In conversation, Georgescu-Roegen speaks animatedly of his new theory and of the failure of the would-be critics among his colleagues to come out and debate with him. Asked the reason for his critics' muteness, he replies with a Romanian proverb—"Don't mention the cord in the house of the hanged." "I am very unpopular with economists," he says, comparing his attack on standard economics to the action of a man who confiscates marbles from children. "They will never forget that, but the next generation of economists will speak only my language."

Coming from a lesser man, the prediction might sound vainglorious. But Georgescu-Roegen inspires favorable reviews from independents and sky-high praise from those who agree with him. Economist

Kenneth Boulding, in a review of *The Entropy Law and the Economic Process* (*Science*, 10 March 1972), wrote that the book had real defects but that "If . . . the right 500 people were to read it, science perhaps would never be quite the same again." Joseph J. Spengler of Duke University, a past president of the American Economic Association, believes that this and Georgescu-Roegen's earlier book "will come to be recognized as two of the greatest books we have had in the first three quarters of this century." According to Herman Daly, a proponent of the steady-state economy, Georgescu-Roegen's new thesis has not yet been fully digested but when it has been, "it will win him a place as one of the most important economists of our time. What he has done is to tie economics back to its biophysical foundations—it is that divorce that has led to many of our current problems such as pollution."

Alvin Weinberg, director of the Institute for Energy Analysis and a man whose outlook on energy might be expected to make him an opponent of Georgescu-Roegen's, describes him as a "highly original thinker" whose views people are now beginning to take more seriously. But Weinberg begs off detailed discussion of the thesis, saying he is not an economist. Similarly economist Paul Samuelson professes incompetence to judge Georgescu-Roegen's ideas on entropy, but adds that his tennis partner, a scientist, informs him they are essentially sound. Samuelson finds "everything he writes extremely stimulating," but notes that, as with Malthus, "there is not much refutable about 'Just-you-wait' statements."

Georgescu-Roegen is willing to put more urgency into his "just-you-wait statements" in conversation than he is in print. He regards man's present place in history as being near the end of an unrepeatable bonanza of cheap fuel. "When the bonanza disappears, we may get into the kind of ex-

perience similar to that of species like fish which find they have to adapt to living in shallower waters. But in our case it would be a political and sociological change, not a biological modification. Evolution, even exosomatic evolution, is not reversible—man would rather die in the penthouse than live in the cave."

Pressed to say how and when the crisis may come, Georgescu-Roegen replies, "For the near future, I don't know. But in 50 or 60 years the world might find itself in a half anarchic state. I am not saying there will not be a government in the United States. But the tendency for the state to become more and more important in the individual's life will reverse. People will live in isolation from the state. These hippies may be an avant-garde pre-adaptation. People would have to educate their children at home because there would not be enough taxes for schools. The population might have to go down, I don't know how—it might be from the disorganization in the means of communication or of hospital care."

Whether or not this verbal presentiment turns out to be accurate, Georgescu-Roegen's general theory is a powerful and ambitious synthesis that would seem to deserve more attention than has yet been its lot. Though some of his general conclusions have been touched on by others (notably by Kenneth Boulding in his 1966 essay "The economics of the coming spaceship earth"), Georgescu-Roegen has developed the scholarly underpinning of a broad theoretical framework. The theory offers potential support to many of the ideas of ecologists, environmentalists, advocates of zero population growth, opponents of economic growth, alternative technologists, and other critics of the established economic order. Here at least, if not also among "standard" economists, Georgescu-Roegen should find an increasing following.—NICHOLAS WADE

RESEARCH NEWS

New Materials: A Growing List of Nonmetallic Metals

Two years ago, scientists working in materials research were extremely excited by the announcement that a certain organic salt—which contains no metallic elements—showed signs of superconductivity. The conductivity of this particular salt, called TTF-TCNQ, increased as it was cooled below room temperature, until a very high value was reached at 58°K. A superconducting material at that temper-

ature would have far outclassed the best of the "high temperature" superconducting metals which becomes lossless at 23°K.

The promise of superconductivity for TTF-TCNQ was never realized, but the material nevertheless enticed many researchers to study nonmetallic metals. The conduction properties of organic crystals were largely unknown at the time, and the novel behavior of TTF-TCNQ, plus the

possibility of synthesizing many related salts by the techniques of organic chemistry, were more than enough to stimulate further research. That research has certainly borne fruit, as there are now nearly a dozen similar materials known. Besides being unusual for the fact that they are conducting at all, these materials behave like one-dimensional metals in that they conduct strongly in one direction but not in

others. Lastly, the possibility of superconductivity has not proved irrelevant. One material, a polymer of sulfur and nitrogen, does undergo a transition into a superconducting state—albeit at 0.3°K.

Although the organic salts and the sulfur-nitrogen polymer are not perfectly analogous, they nevertheless have many similarities. The polymer is a long chain of alternating atoms of sulfur and nitrogen, in which the predominant direction for conduction is up and down the chain. The individual polymer chains can bond together loosely to form a crystal. Covalent bonds connect the atoms in each polymer, and weaker bonds align the polymers with each other in such a fashion that sulfur and nitrogen atoms alternate in an orderly crystal structure.

Family of TCNQ Salts

The organic salts are composed of the elements nitrogen, hydrogen, carbon, and sulfur or one of its possible replacements from the same column of the periodic table. The organic salts are not, strictly speaking, polymers, but they also tend to conduct in a single direction, which is along a backbone formed by stacks of repeated units in the crystal structure. Most organic crystals studied so far have been salts of TCNQ (tetracyanoquinodimethane) in which the positive ion was TTF (tetrathiofulvalene) or a variation of it. Both these molecular forms are planar so that they can be easily stacked, and the structure of the TTF-TCNQ crystal is generally thought to consist of parallel columns of separately stacked TTF and TCNQ molecules.

Because of the long repeated structures of the polymer of sulfur and nitrogen, $(\text{SN})_x$, and the TCNQ salts, they are highly anisotropic. Both classes of materials have ratios of 100:1 or more for measured conductivity parallel to the structural axis versus conductivity perpendicular to it. This property suggests a number of possible industrial applications, particularly as a polarizer that could be used in integrated optical communications circuitry. The superconductivity discovered in $(\text{SN})_x$ is of course at too low a temperature to conceivably be useful, since even liquid helium refrigerators do not routinely cool materials to 0.3°K.

The present burst of activity in the study of exotic, quasi-one-dimensional metals began in 1973. In April of that year, Alan J. Heeger, Anthony F. Garito, and associates at the University of Pennsylvania, Philadelphia, announced that three of seventy crystals of TTF-TCNQ that they had tested showed superconducting fluctuations at 58°K [*Science* **180**, 1041 (1973)]. Superconducting fluctuations occur when

small regions in a crystal are fluctuating between the superconducting state and the normally conducting one. Many materials show superconducting fluctuations, then go on to become completely superconducting at still lower temperatures. However, TTF-TCNQ changes into an insulator at temperatures below 58°K. The very high conductivity peaks that were interpreted as the evidence for superconducting fluctuations were not confirmed by other researchers. Many solid-state scientists think the original high conductivity peaks were an artifact of the particular experimental method used. Nevertheless, the hints of extraordinary properties were sufficiently strong that at least six laboratories in the United States began to devote considerable effort to the study of TTF-TCNQ and related compounds.

At least eight TCNQ salts have now been synthesized with donor molecules (forming positive ions) similar to TTF, which has two coupled five-member rings, each containing a pair of sulfur atoms. Many of the variations have been synthesized by Dwaine Cowan, Aaron Bloch, Ted Poehler, and associates at Johns Hopkins University, Baltimore, Maryland, where research on organic conductors started at least 4 years ago. Extensive research on materials of the TTF-TCNQ type has also been done at the International Business Machines (IBM) laboratories in Yorktown Heights, New York, where Bruce Scott and his co-workers synthesized the first selenium analog of the TTF molecule, and by other groups.

The more highly conducting organic crystals are those in which the donor and acceptor molecules form separate conducting stacks. These are technically semimetals, since the conduction band energies for the two stacks are only weakly overlapping. In the semimetal category, the more conducting crystals are thought to be those with small and easily polarizable donor molecules. In addition, both donor and acceptor molecules should be symmetric, according to Aaron Bloch, so as not to become structurally disordered at low temperatures and thus undergo a transition to become an insulator. Most of the TCNQ salts undergo a metal-insulator transition (Peierls transition) at temperatures in the range 40° to 80°K.

Very recently, the researchers at Johns Hopkins have found a new organic charge transfer salt which has the highest room-temperature conductivity of any known organic substance. Perhaps more importantly, the new salt, HMTSF-TCNQ, is the first organic conductor based on the TTF-TCNQ prototype that does not undergo a metal-insulator transition. Work by the Johns Hopkins group has shown

that HMTSF-TCNQ behaves electrically as a metal in the temperature range from 1.1° to 300°K, and they, in cooperation with R. L. Greene of the IBM laboratories in San Jose, California, and his co-workers at Stanford University have extended the result down to 0.008°K. The new donor molecule, HMTSF (hexamethylenetetraselenafulvalenium), represents a considerable success because the insulator state has been suppressed. However, HMTSF-TCNQ does not appear to become superconducting, even at very low temperatures, according to Greene and his co-workers.

Even though the flexibility of organic chemistry offers the hope of fine control over conduction properties in a way that is not possible with elemental metals, the logical progressions for synthesizing new materials have not proved simple in practice. One reason is that HMTSF is considerably more difficult to synthesize than TTF because less is known about the preparative chemistry of selenium than sulfur, and because selenium is very toxic. Tellurium substitutions might yield even better conduction properties than selenium substitution, but work with tellurium is "really grim," according to the Johns Hopkins researchers.

Unlike the TCNQ salts, which were first synthesized by Du Pont researchers in the 1960's, $(\text{SN})_x$ had been known for more than 50 years. In 1910, Frank Playfair Burt, then at the University College, London, reported that "a new sulphide" of nitrogen which he identified as $(\text{SN})_x$ afforded "an interesting example of inorganic polymerism." However, the conducting properties of $(\text{SN})_x$ were not investigated until 1962 when Mortimer Labes at Temple University in Philadelphia measured the d-c conductivity of fibrous crystals of the polymer. When Labes reported this work at the 1974 Lake Arrowhead Symposium on Conducting Organic and Transition Metal Salts, where most of the researchers studying TTF-TCNQ heard it, the two research efforts merged.

First Superconducting Polymer

What Labes found was that $(\text{SN})_x$ remained conducting from room temperatures down to 4.2°K, without undergoing a Peierls transition. Within a short time, researchers at IBM, San Jose, had prepared their own crystals of $(\text{SN})_x$ and made low-temperature (10° to 1.5°K) specific heat measurements that indicated the polymer would remain metallic at even lower temperatures. Shortly afterward, Greene, and Bryan Street, along with Laurence Suter of Stanford University, Palo Alto, California, established that the tran-

sition to the superconducting state occurred between 0.25° and 0.28°K for three different crystal samples. The discovery was the first time superconductivity had been found in a polymer.

The discovery was perhaps less shocking to those who had seen $(\text{SN})_x$ crystals, which are shiny, with a bronze metallic luster, and are almost as conducting as mercury.

The new superconductor grows as a bundle of crystal fibers. To grow the fibrous crystals is a fairly tricky process that starts with the vacuum sublimation of S_4N_4 . According to the University of Pennsylvania group, the material is deposited as a dimer, S_2N_2 , which is in crystalline form. The S_2N_2 structure is a square planar ring. Over the course of many hours at room temperature polymerization takes place, as one bond on the square ring breaks and attaches to an adjoining S_2N_2 molecule. The result is a long chain of repeated SN monomers.

Considerable variation is found in the properties of different samples of $(\text{SN})_x$. The bulk crystal separates into many fibers because of large-scale defects in the crystal structure, but, according to Ray Baughman at the Allied Chemicals laboratories in Morristown, New Jersey, the process of solid-phase polymerization also introduces many molecular-scale defects. According to Baughman, the spatial symmetries of the S_2N_2 and $(\text{SN})_x$ crystals are similar, but the unique axis of the polymer does not correspond to the unique axis of the dimer. Therefore, a flipping of the axis must occur during polymerization. There are two ways in which the final crystal can be formed, and this bifurcation introduces a randomness to the reaction that results in many chains that are not in their natural positions in the crystal lattice. According to Baughman and co-workers at Allied Chemicals and University of Pennsylvania, in the final state as many as 27 percent of the chains are in disordered positions.

The amount of molecular-scale crystal disorder is an important variable that may conceal the intrinsic conducting and superconducting properties of $(\text{SN})_x$. The crystal defects along the axis of the fibers add to the electrical resistance of a sample of $(\text{SN})_x$, and the defects also give rise to residual resistance that is present in some samples even after the crystal has clearly made a transition to a superconducting state.

From both electron diffraction studies and x-ray diffraction studies, models of the crystal structure of $(\text{SN})_x$ have been proposed, first by M. Boudelle at the Claude Bernard University in Lyon, France, and more recently by the University of Penn-

sylvania group. The two structures are very similar. The polymer is almost planar but not at all straight, as the atoms in the ring structure of S_2N_2 do not move very far during polymerization.

Using either crystal structure, the conduction band energies of $(\text{SN})_x$ can be calculated, with the general result that $(\text{SN})_x$ has a conduction band that is about 1 electron volt wide and has the properties of a semimetal with pockets of electrons and holes. From consideration of the crystal structure, it is not yet clear whether $(\text{SN})_x$ is one-dimensional or not. There are weak interchain bonds that may contribute to electrical communication between polymer chains.

Dispute over Dimensionality

From consideration of the conducting properties, it is clear that $(\text{SN})_x$ cannot be perfectly one-dimensional, or it would not become superconducting at all. Fluctuations occur randomly throughout any material that is approaching a superconducting transition, and "normal" regions are only locked into the superconducting state by the influence of neighboring regions. But in a chain, one "normal" link stops such communication completely, and there would be no way for the number of normal regions to steadily decrease. Calculations of the band structure by several research groups tend to support a two- or three-dimensional system. Optical measurements including reflectivity and plasma studies by the University of Pennsylvania group and others also indicate an anisotropy characteristic of three-dimensional systems; researchers at Temple and Brown universities, however, report evidence of a one-dimensional system.

Where the debate over the dimensionality of $(\text{SN})_x$ will lead is uncertain. A number of researchers had suggested that $(\text{SN})_x$ offered the first opportunity to test theories of superconductivity in a one-dimensional system. It is generally expected that $(\text{SN})_x$ will obey the conventional Bardeen-Cooper-Schrieffer theory of superconductivity that has been so successfully used to explain metals; other superconducting theories might also be tested.

Although most tests of $(\text{SN})_x$ have been carried out on bulk crystals, usually a few millimeters long and fractions of a millimeter wide or high, the growth of thin films of the polymer has also been reported. At the University of Pennsylvania, Heeger, Alan MacDiarmid, and Garito have prepared the first fully oriented crystal films. The films were produced by epitaxial growth on various materials including Mylar, Teflon, and polyethylene,

and are reported to be analytically pure and free of trace S_2N_2 contaminants. Epitaxial growth is a form of crystal deposition in which the structures of the substrate and its growing crystal are sufficiently similar that one can be used to form a pattern for the other.

The thin films of $(\text{SN})_x$ could be particularly useful as polarizers, because light rays polarized parallel to the conducting axis of the film (which is the same as the fiber axis) are reflected more strongly than rays polarized perpendicular to the axis. Since the usefulness of $(\text{SN})_x$ as a polarizer is derived from the anisotropic conduction properties of the material rather than from its superconducting properties, the salts based on TTF-TCNQ might also have optical applications.

Industrial support for research on exotic one-dimensional conductors has followed a pattern in the last few years that also suggests that optical properties may be the most useful aspects at present. Four years ago Monsanto researchers began studying TTF-TCNQ because of its high thermoelectric power capability. Most of the organic conductors produce electrical power when heated, and this property can be used for refrigerators and small power sources. (Propane-fired lead telluride units have been marketed for use in place of batteries.) Monsanto was reassessing its research in 1973 when the superconducting fluctuations of TTF-TCNQ were announced and decided to continue. But it has now stopped all research on the exotic one-dimensional conductors. Monsanto researchers concluded that the most likely applications were in electronics or optics, which are not fields where Monsanto has had a traditional interest. Du Pont showed some interest and then dropped the subject.

The interest in basic research on these materials remains quite strong, however. Most laboratories have emphasized research on $(\text{SN})_x$ over TCNQ salts during the last 6 months, but there is evidence now that they are returning to a program that balances research on organic and inorganic conductors more evenly. At the Bell Laboratories in Morristown, New Jersey, Fred Wudl is experimenting with different acceptor molecules, to possibly replace TCNQ. Others are trying to think of ways to synthesize structures similar to $(\text{SN})_x$, such as the replacement of sulfur with selenium in that molecule. Still others talk of the possibility of synthesizing organic conducting polymers.

Behind it all may be the hope of unusual superconductivity, and there is no doubt that this class of compounds has many novel properties that are worthy of further study.—WILLIAM D. METZ