Superconductivity and magnetism in organic metals

Some new, electrically conducting organic compounds show unexpected physical phenomena such as superconductivity, spin-density waves and a novel phase transition induced by an applied magnetic field.

Paul M. Chaikin and Richard L. Greene

Seven years ago Klaus Bechgaard of the University of Copenhagen synthesized a family of selenium-based organic compounds now known as Bechgaard salts (see figure 1). A few months later his collaborators at the University of Paris, Orsay, found[1] these materials to be superconducting below about 1.5 K, culminating the search for organic superconductivity that began in the early 1960s. (See PHYSICS TODAY, February 1981, page 17.)

Last year three groups developed[2] an organic superconductor with a much higher transition temperature—nearly 8 K—by chemically modifying a sulfur-based organic superconductor discovered[3] in 1983 at IBM, San Jose. Although this transition temperature is well below those of many inorganic materials—Nb_3Ge holds the record at 23.3 K—the rapid progress in raising the transition temperatures of organic superconductors has led many to hope that it will be possible to synthesize organic compounds with transition temperatures higher than those of inorganic materials. (For a review of superconducting materials, see PHYSICS TODAY, October 1984, page 60.)

Organic superconductors have attracted considerable interest because they exhibit many phenomena that do not appear in conventional superconductors or in nonsuperconducting materials. However, the study of organic superconductors is in its infancy and we are only beginning to understand the novel physics that appears to account for the anomalous physical properties of these materials. Organic superconductors show a remarkable variety of phase transitions, whose nature depends on the constituents of the compound and on external parameters such as pressure, temperature and magnetic field. At low temperatures, when the materials are in the ground state, there may be periodic spatial modulations of the charge density, spin density or molecular positions; the charge- and spin-density modulations compete with the superconducting state. Application of a magnetic field at low temperatures can induce a transition from a metallic (that is, conducting), nonmagnetic state to a semimetallic (poorly conducting), magnetic state—a type of transition never before observed in any material.

Most of the unusual properties of organic superconductors arise because the organic crystals are highly anisotropic, so that conductivity is negligible along one or two crystal axes. The physics of systems with such "reduced dimensionality" is one of the major themes in condensed-matter physics today. Research since the early 1970s has uncovered many novel properties of low-dimensional materials, both organic and inorganic. Progress in understanding these materials has required a highly interdisciplinary effort, with important contributions coming from synthetic and physical chemistry, materials science and theoretical and experimental condensed-matter physics. In this article we give an overview of the current understanding of organic superconductors and we look at some possible directions for future research—all from the perspective of experimental condensed-matter physics. A detailed treatment is available in the review articles cited in references 4–6.

Organic conductors

Understanding how organic compounds conduct electricity at all is the first step in appreciating the varied properties of organic superconductors. The charge-transfer salts, which are the subject of this article, are by far the largest and most diverse class of organic conductors, or "organic metals." Other organic conductors are graphite and its intercalation compounds (PHYSICS TODAY, March 1984, page 60) and certain doped polymers (PHYSICS TODAY, June, page 46). Charge-transfer salts are substances in which a donor molecule such as TTF transfers electrons to an acceptor molecule such as TCNQ to form a charge-transfer compound, TTF–TCNQ. Figure 2 shows these and other examples of donor (cation) molecules that combine with acceptor (anion) molecules to produce organic metals.

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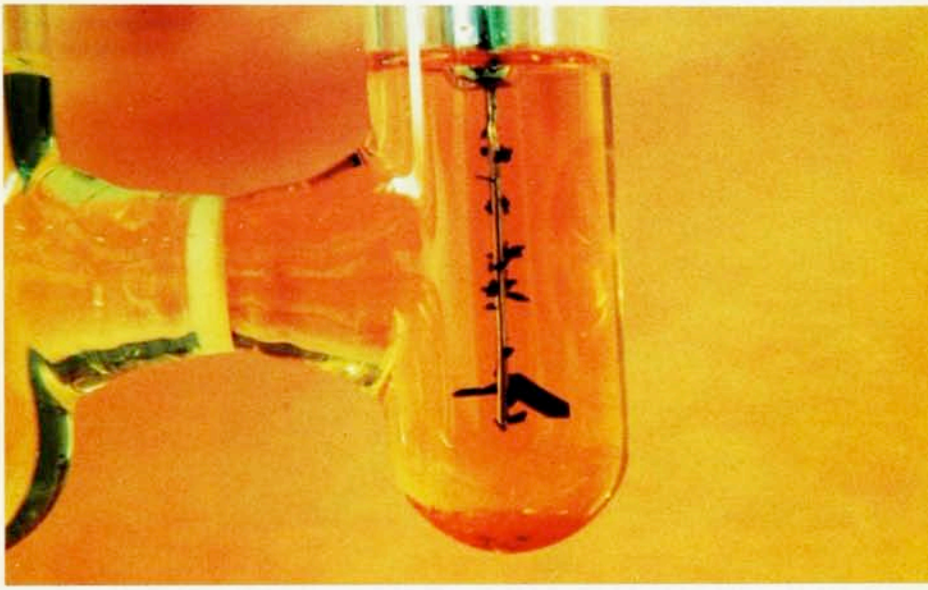

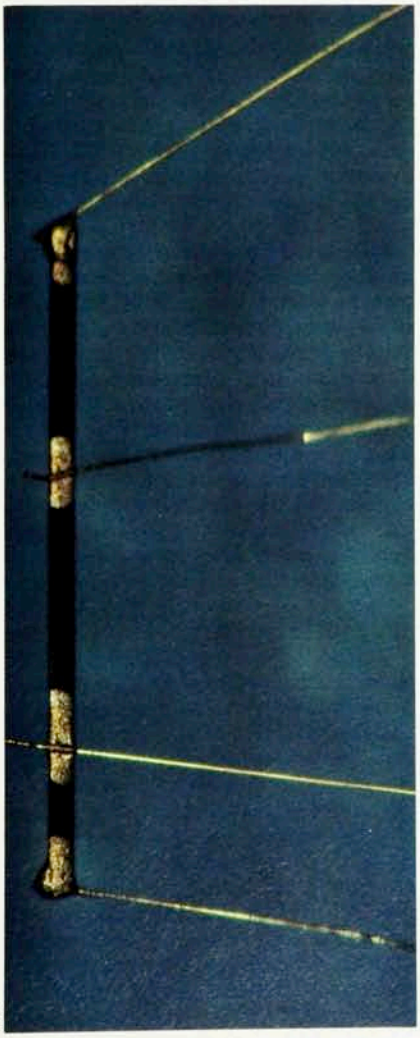

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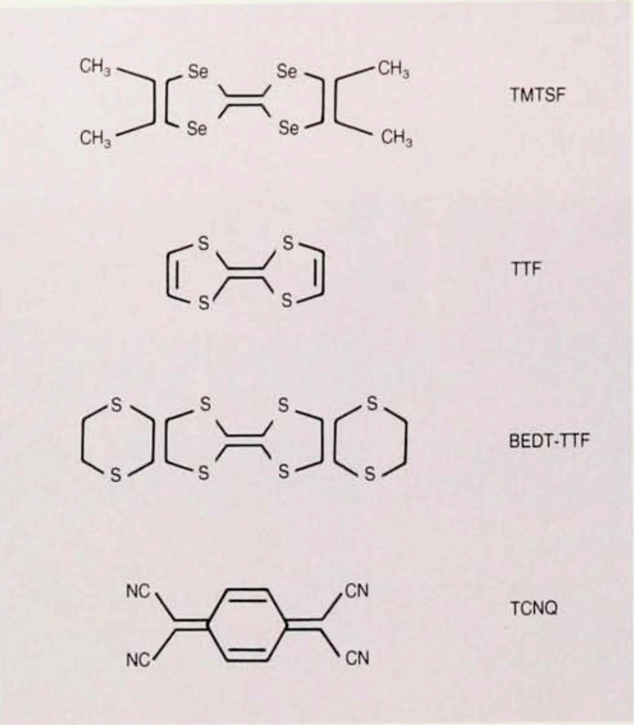
Organic metal. The dark material in the photograph at left is a single crystal of the organic metal (TMTSF)$_2$ClO$_4$. The four gold wires attached with gold paste are for electrical-conductivity measurements along the direction of highest conductivity. This typical crystal is 4 mm long, 0.2 mm wide and 0.05 mm thick. The crystals are prepared by electrochemical growth in solution, yielding very small single crystals that are perfect but quite brittle. The photo above shows crystals grown on a platinum electrode from a solution (highly diluted for the photo) of BEDT-TFF with triiodide anions. The largest crystal (lower right) is β-(BEDT-TTF)$_2$I$_3$. The black color is a result of the strong absorption of visible light in the crystalline state. (Upper photo courtesy of Jack M. Williams, Argonne National Laboratory.) Figure 1

The large planar molecules of the charge-transfer compound can stack on top of one another like pancakes (see figure 3), allowing the transferred charge to move easily along the separate donor and acceptor stacks. In charge-transfer compounds made from sulfur- or selenium-based molecules such as those shown in figure 2, a conduction band forms due to the overlap of electron wavefunctions in the sulfur or selenium atoms that are made neighbors by the stacking. The partial filling of this band with electrons by charge transfer from donor to acceptor leads to the observed metallic conduction levels.

The pancakelike stacking suggests that the charge-transfer salts are quasi-one-dimensional. The overlap of orbitals, and hence the electron hopping rate, is greater along the stacks of molecules than it is between them, making the conductivity greater along the stack than in other directions. The best organic conductors have a conductivity on the order of 2000 $\Omega^{-1}\mathrm{cm}^{-1}$ at room temperature, or about three orders of magnitude smaller than that of copper. Below room temperature, the metallic conduction is usually interrupted by a transition to a semiconducting or insulating state. This transition, as we shall see, is intimately connected with the one-dimensional character of the materials.

The first conducting charge-transfer salts were based on the TCNQ molecule and were discovered at DuPont in the early 1960s. These salts had, at best,



Molecules that form conducting charge-transfer salts. Among the important molecules that form donor–acceptor compounds are tetramethyltetraselenafulvalene (TMTSF), tetrathiafulvalene (TTF) and bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF), which are donors, and tetracyanoquinodimethane (TCNQ), which is an acceptor. Reference 7 describes all the molecules known to form conducting charge-transfer salts. Figure 2

room-temperature conductivities on the order of 100 $\Omega^{-1}\mathrm{cm}^{-1}$ and underwent a gradual transition to the insulating state below about 200 K. The synthesis of TTF–TCNQ in the early 1970s led to a dramatic increase in research on organic conductors. This salt was the first organic compound to display truly metallic properties and to exhibit, near 54 K, a sharp metal–insulator phase transition. The late 1970s saw the development of many analogous conducting organics.

Study of the properties of organic conductors resulted in a deeper understanding of the physical processes that can occur in quasi-one-dimensional metals. The realization that both the TTF and the TCNQ molecular stacks contribute to the conductivity stimulated work on the chemical modification of the TTF molecule and led to the synthesis of the TMTSF molecule. Bechgaard's active role in the work on TMTSF led him to the preparation of compounds of the form $(\mathrm{TMTSF})_2X$, where X is an inorganic anion such as $\mathrm{PF_6}^-$, $\mathrm{AsF_6}^-$, $\mathrm{ReO_4}^-$ or $\mathrm{ClO_4}^-$. The first of these salts to be studied, $(\mathrm{TMTSF})_2\mathrm{PF}_6$, had a metal–insulator transition at about 12 K, a temperature significantly lower than the transitions found in other organic conductors. Applying hydrostatic pressure to the $(\mathrm{TMTSF})_2\mathrm{PF}_6$ salt completely suppressed the metal–insulator transition and produced an organic superconductor—the first to be found. The behavior of many of the $(\mathrm{TMTSF})_2X$ compounds—the Bechgaard salts—was foreshadowed in these initial experiments. At ambient pressure the Bechgaard salts undergo metal–insulator transitions between 10 K and 200 K; at moderate pressures—about 10 kbar—most become superconducting below about 1.5 K.

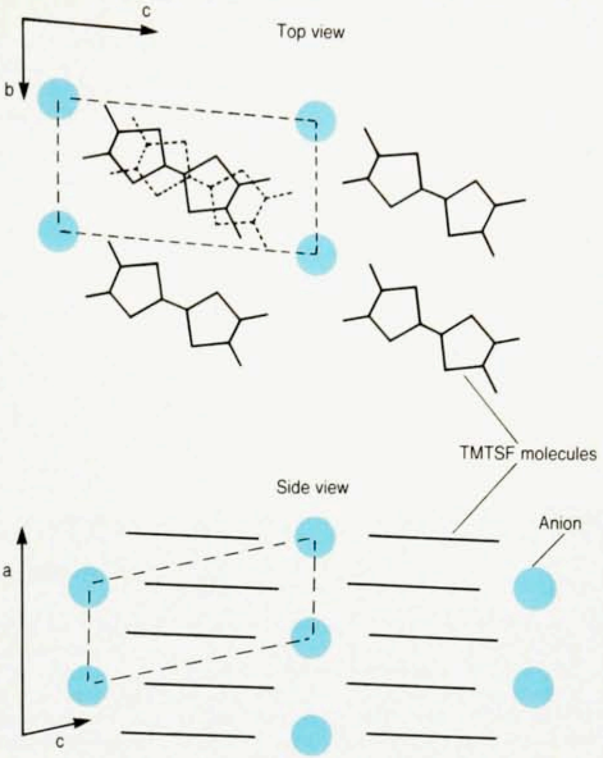
More recent research has resulted in another class of organic superconductors based on the BEDT-TTF molecule—abbreviated ET—shown in figure 2. The ET compounds are more two-dimensional than the Bechgaard salts and have significantly higher ambient-pressure transition temperatures. The physics of quasi-one-dimensional metals (see the box on page 28) helps explain the origins of the metal–insulator transition, the superconductivity and the other phenomena found in these two classes of organic metals.

TMTSF and ET Salts

The Bechgaard salts, $(\mathrm{TMTSF})_2X$, are isostructural, with only small differences in lattice parameters related to the sizes of the anions. Figure 3 shows the crystal structure schematically. The overlap of selenium π-orbitals of the TMTSF molecules along the a direction is responsible for the formation of a conduction band with a bandwidth of about 1 eV. The selenium-orbital overlap is about ten times smaller in the b direction and considerably weaker in the c direction because the anions form a sheet separating the array of TMTSF molecules in the ab plane. Figure 4b is a two-dimensional view of the Fermi surface.[8] The Fermi surface is heavily warped relative to that of the one-dimensional case, where the only interactions are in the a direction, but the surface can still "nest" at a wavevector $\mathbf{Q}$ of $(\pi/a, \pi/b)$. The Fermi surface is therefore susceptible to one-dimensional instabilities, which open a gap over the entire surface and produce a metal–insulator transition.

The anisotropy in the electrical conductivity σ and in other physical properties of the Bechgaard salts reflects the anisotropy in crystal structure. Typically one finds the conductivity ratio $\sigma_a:\sigma_b:\sigma_c$ to be $1:10^{-2}:10^{-5}$ with σ_a equal to 1000 $\Omega^{-1}\mathrm{cm}^{-1}$ at room temperature. The crystals are remarkably free from defects and disorder, the electron mobility exceeding 10^5 $\mathrm{cm^2/V\,sec}$ at 4.2 K, a value comparable to that found in highly pure semiconductors. However, the crystals are small and brittle (see figure 1), which has made some experimental measurements difficult.

Although the anions do not contribute to the conductivity, they play an important role in determining the low-temperature ground states of the various Bechgaard salts. All the organic metals known before the discovery of the Bechgaard salts exhibit a metal–insulator transition driven by the Peierls–Fröhlich mechanism to a charge-density-wave ground state. (See the box on page 28 for a description



Triclinic crystal structure of the (TMTSF)$_2X$ compounds, shown in two schematic views. The dashed lines indicate the unit cell, whose lattice constants a, b and c are approximately 7.3, 7.7 and 13.5 Å, respectively. Colored spots represent anions such as ClO_4^-, PF_6^- or ReO_4^-. The interplanar spacing of the TMTSF molecules along the a axis is about 3.6 Å. Figure 3

of charge-density waves and spin-density waves.) The surprising aspect of the (TMTSF)$_2X$ compounds, besides superconductivity, is the complete absence of the charge-density-wave transition. Instead, the insulating ground state is either a magnetic spin-density-wave state or a nonmagnetic state in which there is a new lattice periodicity caused by an anion rearrangement—an anion-ordering transition. The salts with octahedrally symmetric anions, such as PF_6^- or AsF_6^-, all have spin-density-wave ground states, as determined by measurements of magnetic susceptibility, antiferromagnetic resonance and nuclear magnetic resonance. Spin-density-wave transitions are rather rare among both inorganic and organic materials.

Compounds with tetrahedrally symmetric anions, such as ClO_4^- or ReO_4^-, often display structural phase transitions involving the orientational ordering of the anions. At room temperature the anions have random orientations, whereas at low temperature they orient to give various three-dimensional superstructures. If the periodicity of the anion superstructure matches that of the electrons at the Fermi energy, a gap will appear in the electron energy spectrum, producing an insulating ground state.[9]

For organic metals that are insulators at low temperatures, the application of modest hydrostatic pressure can depress the metal–insulator transition temperature and often eliminate the transition entirely, resulting in a metallic state at all temperatures. The phase diagram in figure 5 illustrates this for (TMTSF)$_2$PF$_6$. We see that the ambient-pressure spin-density-wave transition at a temperature $T_{\rm MI}$ of 12 K is suppressed at a pressure of about 6.5 kbar. The transition to superconductivity that normally appears at a temperature T_c of about 1.2 K is depressed by higher pressure. Similar phase diagrams are found for almost all the Bechgaard salts independent of the origin of the metal–insulator transition. For example, the ReO$_4$ salt, which undergoes an anion-ordering transition at a temperature $T_{\rm MI}$ of about 180 K, is driven to a metallic—and superconducting—state above 10 kbar. It is rather surprising that the spin-density-wave and anion-ordering transitions are suppressed in the same range of pressure because the strengths and natures of the interactions causing these transitions are very different. At present there is no detailed explanation of the mechanism by which pressure suppresses the metal–insulator transition.

The ET salts. The other class of organic materials that has superconducting members is the salts formed from the sulfur-based molecule BEDT-TTF, shown in figure 2. The superconducting ET compounds have a 2:1 stoichiometry—(ET)$_2X$—and a crystal structure rather similar to that of the Bechgaard salts, although the arrangement of the ET molecules in the ab plane is different.[10] This altered arrangement, along with the increased number of sulfur atoms per molecule, leads to roughly isotropic interactions between the ET molecules in the ab plane. The intervening plane of anions keeps the interaction weak in the third (c) direction. Thus, compared with the Bechgaard salts, the superconducting (ET)$_2X$ compounds have more two-dimensional electronic properties. However, the ET compounds have, for each anion X, a diversity of crystal phases with differing stoichiometries and crystal structures. These crystal phases have yet to be studied in detail, but among them one finds quasi-one-dimensional crystal structures that undergo metal–insulator transitions driven by the formation of charge-density waves and by anion ordering. Surprisingly, no spin-density-wave transitions have shown up in any ET salt.

We have touched only briefly on the variety of ground states and physical properties found in the two known classes of superconducting organic metals, the TMTSF salts and the ET salts. A major goal of current research on organic metals is to gain a fundamental understanding of the conditions under which these ground states are stable. Although research is making good progress, much is still not understood. At the end of this article we will return to the many unsolved problems. First, however, we look at two of the more interesting phases observed in these materials: the superconducting state

One-dimensional metals

Physicists have had a theoretical interest in one-dimensional structures since the early 1930s. However, it was only with the synthesis of real materials with quasi-one-dimensional metallic properties that the theory could be tested and further developed. The dominant feature of a one-dimensional system is its connectivity: On a line there is only one path between a point and any other point. If the path is broken there is no way for the second point to know what is happening at the first. This has two immediate consequences:

- Any disorder causes all electron states to be localized in one dimension because the disorder will eventually break the only available path.
- Without long-range forces there are no thermodynamic phase transitions in one dimension above zero temperature because thermally induced "breaks" decouple one end of the sample from the other end. However, at nonzero temperatures there will be short-range correlations, or fluctuations, associated with a phase transition.

In contrast, two- and three-dimensional systems have infinitely many paths connecting any two points and thus can have nonlocalized carriers and phase transitions above zero temperature.

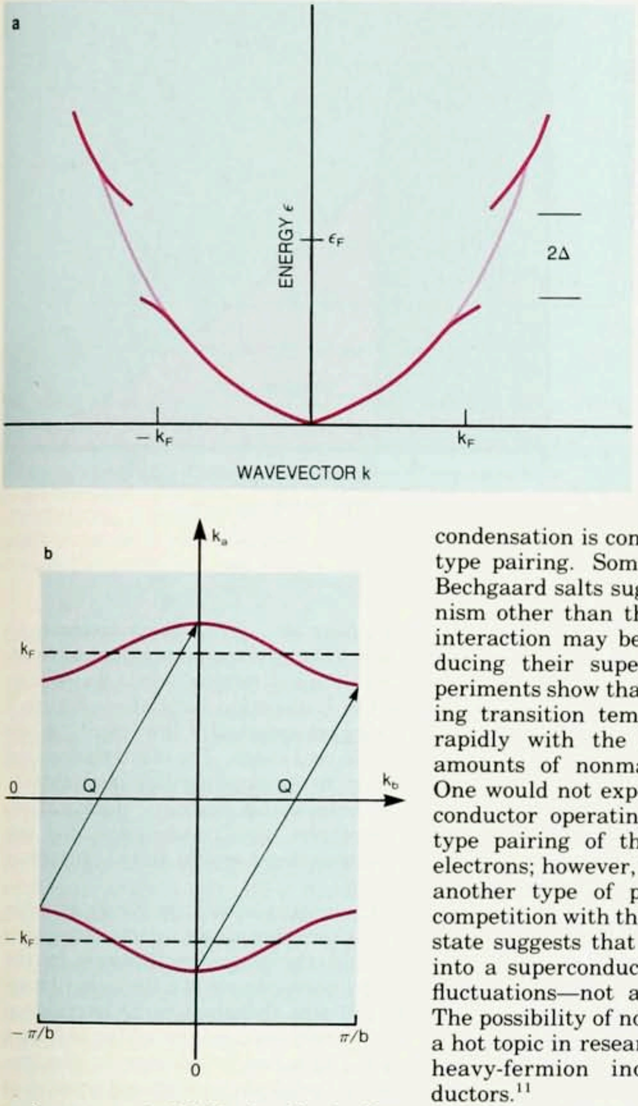
Conversely, one-dimensional metals are unstable against a variety of molecular rearrangements—distortions that lead to phase transitions. Electrons with wavevector k moving along a stack of equally spaced atoms have an energy $\epsilon(k)$. At zero temperature, the electron states are filled up to the Fermi energy level ϵ_F, or $\epsilon(k_F)$. Imagine applying a periodic potential with wavevector $\mathbf{Q}$ of magnitude $2k_F$, that is, a potential with a real-space periodicity $2\pi/Q$. This periodic potential couples states at $+k_F$ and $-k_F$, which have the same energy. Such degenerate states are split by the potential to form one state with higher energy than the original states and one state with lower energy. In one dimension *all* the states with energy ϵ_F, that is, all states on the Fermi surface, are located on two planes in reciprocal space; the planes are at $+k_F$ and $-k_F$ and are connected by the vector $\mathbf{Q}$ of magnitude $2k_F$. Thus the potential of wavevector $2k_F$ couples and splits these states and produces a gap in the energy spectrum at the Fermi energy ϵ_F, as figure 4a indicates, destroying the metallic state and producing an insulating state.

If the periodic potential comes from an electron–phonon interaction, then the result is a one-dimensional semiconducting state accompanied by a lattice distortion and by the formation of a charge-density wave (a sinusoidal modulation of the charge density along the stack). Thirty years ago Rudolf Peierls and Herbert Fröhlich showed theoretically the existence of this transition to the semiconducting state. (See PHYSICS TODAY, June, page 46.) If the Coulomb interaction between the electrons on a stack of organic molecules is greater than the electrons' interaction with the lattice phonons, then a transition to an insulating spin-density-wave state will be favored. A spin-density-wave state is a state in which the spins of electrons along the stack alternate between up and down; this arrangement of spins is like that in a one-dimensional antiferromagnet, but the periodicity of the spins is determined by the Fermi surface in the metallic state and can be commensurate or incommensurate with the underlying lattice of ions. This is of course also true for the periodic increase and decrease in electron charge density along a stack of organic molecules in the charge-density-wave state. Just as with three-dimensional metals, one-dimensional metals can become superconducting if they have not already become semiconducting because of charge-density-wave or spin-density-wave transitions.

We have a conundrum: One-dimensional metals are intrinsically unstable against a number of phase transitions but, as discussed above, one-dimensional systems cannot undergo phase transitions above zero temperature. In the organic materials this contradiction is resolved as a consequence of the fact that the one-dimensional stacks, or "chains," are surrounded by other one-dimensional stacks. If the molecular stacks are weakly coupled, they behave as one-dimensional chains and begin to develop local distortions consistent with their incipient instabilities. As the temperature decreases, the distorted regions grow, approaching infinite length as the temperature approaches zero. Their coupling to distortions on neighboring chains grows proportionately until the coupling energy is larger than the thermal energy. Hence the temperature of the phase transition—the critical temperature T_c—is determined not only by the intrachain interactions that cause the instability, but also by the interchain interactions. The intrachain interactions are characterized by a "mean-field" transition temperature T_{MF}, which is the temperature at which the transition would take place if the interchain interactions were equal to the intrachain interactions; the interchain interactions are similarly characterized by a temperature $T_\perp$. The actual superconducting transition temperature T_c is given approximately by the geometric mean $(T_{MF}T_\perp)^{1/2}$.

In the regime between the temperatures T_{MF} and T_c one expects to observe precursor effects, or fluctuation effects, associated with the phase transition. These fluctuations are significant only when the interchain interactions are much weaker than the intrachain interactions. On the other hand, if electron hopping between chains becomes too easy, the system becomes two- or three-dimensional and the one-dimensional instability is suppressed. However, the system is fairly robust: When the interchain hopping is not too large the system adjusts by changing the wavevector of the instability, as figure 4b illustrates. Thus in a low-dimensional system, the degree of "nesting"—the degree to which the two sections of the Fermi surface fit when translated along the wavevector $\mathbf{Q}$—is an important factor in determining whether or not a phase transition occurs to produce a ground state with charge or spin periodicity $2\pi/Q$.

Energy spectrum and Fermi surface. a: In the presence of a periodic potential with reciprocal-space wavevector $2k_F$, a one-dimensional energy band develops a gap (2Δ) at the Fermi energy ϵ_F. The colored lines indicate the energy band in the absence of a $2k_F$ potential. The bandwidth is determined by the electron hopping rate along the one-dimensional chain. **b:** Two-dimensional view of the open Fermi surface of a typical $(TMTSF)_2X$ compound. The dashed lines represent the planar one-dimensional Fermi surface when the interchain hopping rate is zero. The degree of "warping" of the Fermi surface is directly related to the electron hopping rate along the *b* crystal direction. (Based on the band-structure calculations in reference 8.) Figure 4



and a magnetic-field-induced spin-density-wave state.

Superconductivity

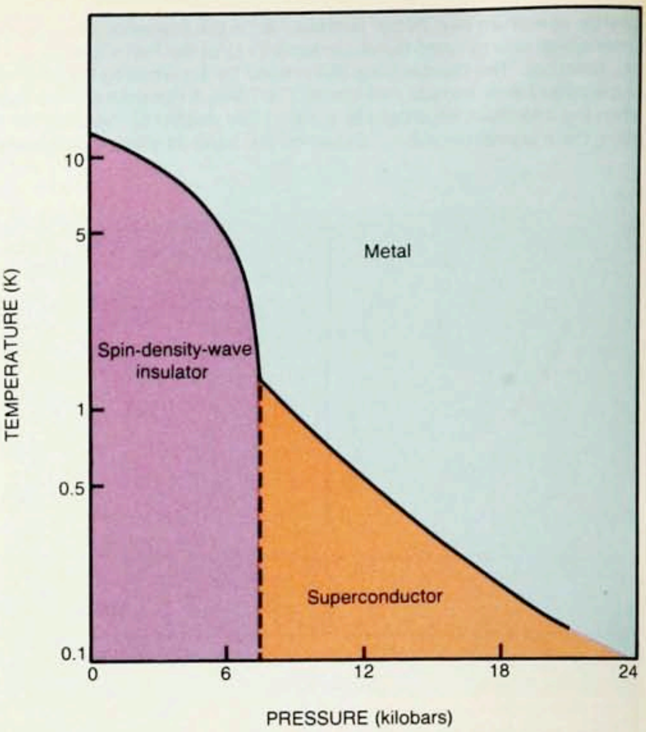
Superconductivity has now been established in many Bechgaard salts and in several ET salts by resistivity, specific-heat and Meissner-effect experiments. There is no compelling evidence to suggest that organic superconductors are in any way different from anisotropic three-dimensional inorganic superconductors with the usual Bardeen–Cooper–Schrieffer electron–phonon interaction, but interesting questions remain unanswered. All known superconductivity arises from an electron–phonon interaction that leads to the condensation of pairs of electrons with zero orbital angular momentum and opposed spins. This condensation is commonly known as s-type pairing. Some properties of the Bechgaard salts suggest that a mechanism other than the electron–phonon interaction may be important in producing their superconductivity. Experiments show that the superconducting transition temperature decreases rapidly with the addition of small amounts of nonmagnetic impurities. One would not expect this in a superconductor operating via the usual s-type pairing of the superconducting electrons; however, it could occur with another type of pairing. The close competition with the spin-density-wave state suggests that electrons can pair into a superconducting state via spin fluctuations—not an s-type coupling. The possibility of non-s-wave pairing is a hot topic in research on the so-called heavy-fermion inorganic superconductors.[11]

The quasi-one-dimensional nature of some of the electronic properties of the Bechgaard salts, in particular the metal–insulator transitions associated with one-dimensional instabilities, has led to the suggestion[4] that the mean-field superconducting transition temperature T_{MF}, which is determined by the intrachain interactions, is considerably higher than the actual superconducting transition temperature T_c of about 1–2 K observed by specific-heat experiments. If true, this would bolster hopes for higher superconducting transition temperatures in organic materials. Unfortunately the recent experimental data[5] are entirely consistent with a mean-field superconducting transition temperature on the order of 1–2 K. This simply means that the interchain hopping rate is high enough to eliminate any significant effect of superconducting fluctuations, yet low enough to retain an open quasi-one-dimensional Fermi surface, permitting a metal–insulator instability. On the other hand, normal-state properties such as the selenium nuclear magnetic-resonance relaxation rate, the far-infrared conductivity and the magnetoresistance are rather anomalous in the $(TMTSF)_2X$ salts and are not readily explained by theories based on noninteracting electrons. It appears that we do need to consider many-body effects of an as yet undetermined origin to explain the electronic properties of the Bechgaard salts. Any particular many-body effects on the superconducting state are still only conjectures.

The two-dimensional $(ET)_2X$ materials have significantly higher superconducting transition temperatures than the Bechgaard salts. The β phase of $(ET)_2I_3$ has a transition temperature T_c of about 8 K under 1.5 kbar of pressure, while β-$(ET)_2AuI_2$ has a transition temperature of about 4 K at atmospheric pressure.[2] At higher pressures, however, the transition temperatures of the $(ET)_2X$ materials drop even more rapidly than those of the $(TMTSF)_2X$ materials, for which we saw an example in figure 5. The suppression of superconductivity by pressure is much greater in the organic salts than it is in almost all inorganic superconductors.

The $(ET)_2X$ superconductors are now the focus of an international research effort. The present data are entirely consistent with what one would expect from two-dimensional superconductors driven by the usual BCS electron–phonon mechanism. Anomalous properties in the normal state of the $(ET)_2X$ superconductors have yet to be reported, although pressure cycling and iodine doping can induce wide variations in the superconducting transition temperatures T_c of some of the compounds. When more experimental data are available, we will be able to compare in detail the electronic properties of the

Pressure–temperature phase diagram for $(TMTSF)_2PF_6$. Note the rapid decrease with pressure of the transition temperatures to both the spin-density-wave state and the superconducting state. The phase boundary between the spin-density-wave state and the superconducting state (dashed line) has not yet been fully determined. Figure 5



$(TMTSF)_2X$ and $(ET)_2X$ materials. Then it may be possible to determine if and how the different interchain interactions in these two classes of materials influence the superconducting state, whether non-BCS interactions are occurring in organic superconductors and whether one can develop materials with higher transition temperatures.

Field-induced transitions

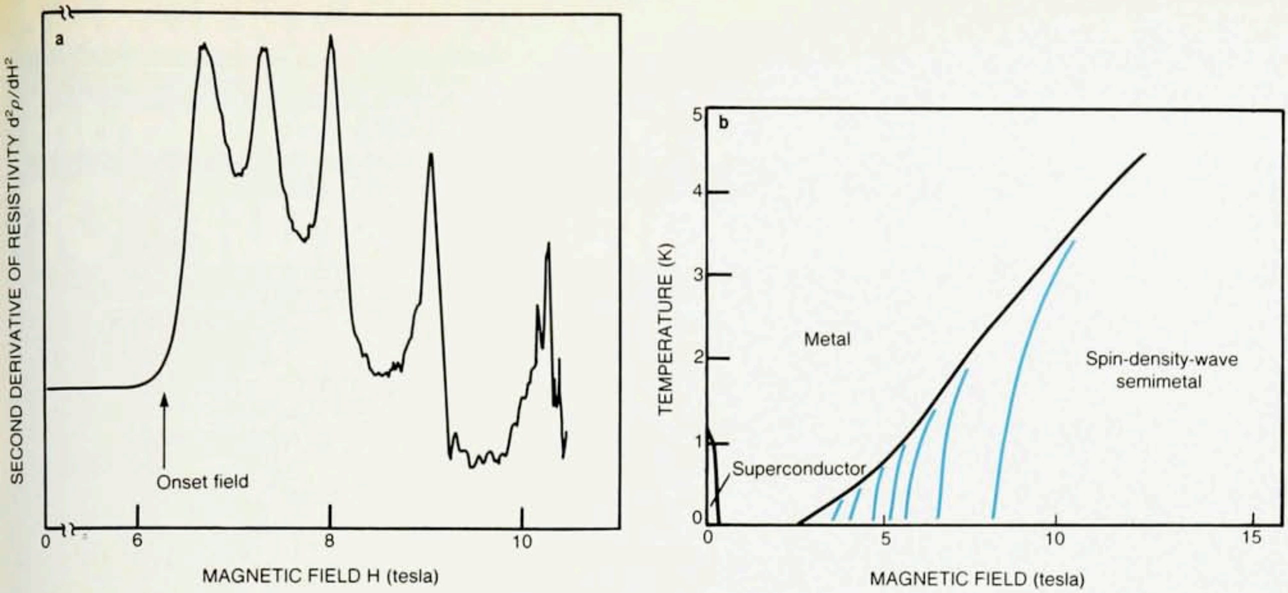
Perhaps the most unusual new phenomenon found in the Bechgaard superconductors is a magnetic-field-induced transition from a metallic, nonmagnetic state to a semimetallic, spin-density-wave state. This transition is observed at low temperatures in salts that are just on the superconducting side of the boundary between the spin-density-wave phase and the superconducting phase (see figure 5). James Kwak and his coworkers at Sandia Laboratories and IBM discovered[12] the transition during magnetoresistance experiments on $(TMTSF)_2PF_6$ under pressure. Figure 6a shows some of the original data. A theoretical model proposed[14] in 1984, three years after the experimental finding, appears to explain the origin of this unique phase transition.

The magnetic field at which the phase transition occurs depends only on the component of the field perpendicular to the *ab* plane. One would expect the magnetic field to affect the spins of the electrons essentially isotropically, so the transition must be caused by changes in the orbits of the electrons driven by the magnetic field. Such orbitally induced phase transitions are quite rare in nature.

In conventional materials one sees strong magnetic-field effects when the electrons form closed orbits in reciprocal space. Because a magnetic field exerts a force perpendicular to the motion of a charged particle, it cannot change the energy of the particle, only its direction. Thus an electron on the Fermi surface subjected to a magnetic field travels along the Fermi surface in a plane perpendicular to the field. For a circular or spherical Fermi surface the electron simply circulates periodically in a closed orbit. Because the velocity of an electron is always perpendicular to the Fermi surface, the real-space motion of the electron is a closed path, as figure 7 indicates.

A fundamental principle of quantum mechanics is the quantization of periodic orbital motions, which produces discrete energies; for orbits in a magnetic field these energies are called Landau levels. The spacing between the Landau levels is proportional to the magnetic field. The quantization gives rise to a wealth of phenomena as the Landau levels all increase in energy and cross the Fermi energy one by one with increasing magnetic field. The deHaas–van Alphen effect and the quantized Hall effect (see PHYSICS TODAY, December, page 17) are two examples. In the Bechgaard superconductors, however, there are no closed orbits! The electrons merely traverse the Fermi surface from $-\pi/b$ to π/b and then reappear at $-\pi/b$. Each electron always has a positive component of velocity in the *a* direction, while its velocity in the *b* direction oscillates. Figure 7 shows schematically the resulting motion in real space. The electron does not return to the same position periodically, so there is no Landau quantization. Hence one would anticipate that the magnetic field would have very little effect.

The observation[12] by Kwak and his coworkers that above a certain magnetic field there are oscillations in the magnetoresistance of a Bechgaard compound was therefore quite surprising. If this field-induced transition is from a metal to a semiconductor or semimetal—a metal with a reduced number of carriers—then the decrease in the carrier concentration should be readily observed as an increase in the Hall resistance, which in the simplest case is given by H/ne, the ratio of the magnetic field to the product of the electron concentration and the electron charge. Two groups independently measured[15] the Hall resistance at low temperature in the Bechgaard ClO_4 salt. At the field marking the onset of the transition, the Hall resistance abruptly increased, indicating a substantial loss of carriers. However, above the onset field, the Hall resistance showed unexpected behavior: Rather than increasing linearly with the field, it increased in a series of steps reminiscent of the quantum Hall effect. The temperature dependence suggests that each of these steps corresponds to a separate phase transi-



Magnetic-field effects on TMTSF compounds. **a:** The second derivative of the *a*-axis resistivity with respect to magnetic field in the metallic state of $(TMTSF)_2PF_6$ under pressure and at low temperature, with the magnetic field perpendicular to the crystal *ab* plane. The arrow indicates the field above which there are unusual oscillations. Experiments have shown[13] that the transition at this field is from a nonmagnetic, metallic state to a spin-density-wave state. The oscillations in the magnetoresistance result from a series of phase transitions that occur as the magnetic field is increased. **b:** Schematic temperature–magnetic field phase diagram for $(TMTSF)_2ClO_4$ at ambient pressure for a magnetic field perpendicular to the *ab* plane. The black curve represents the second-order phase transition to the spin-density-wave state. The colored curves represent the phase transitions at higher fields. The suppression of superconductivity at lower fields is also shown. Figure 6

tion. More recent work on magnetization[16] and specific heat[17] has confirmed the conjectured series of phase transitions. Figure 6b is a schematic phase diagram based on the magnetization data.

How does such interesting behavior arise in an open-orbit system that conventionally should have a simple dependence on the magnetic field? The answer is, as usual, simple in hindsight and relates to the very nature of the instability of low-dimensional systems discussed at the beginning of this article. In the absence of a magnetic field the velocity of electrons on the Fermi surface can be in any direction, and hence the electrons can explore the entire two-dimensional space of the *ab* plane. In the presence of a magnetic field, however, they must move on the trajectories shown in figure 7: They can move as far as they want in the *a* direction, but they have limited excursion in the *b* direction. The presence of the magnetic field has made the electron motion effectively one-dimensional—infinite range in *a*, restricted range in *b*. As the magnetic field is increased, the frequency with which the electron goes from $-\pi/b$ to π/b in figure 4b increases and the width w of the traverse along *b* in figure 7 decreases, as does the wavelength λ of the motion along *a*. In a sense the system becomes more one-dimensional as the field increases, although strictly speaking it is one-dimensional in any field.

We now know that one-dimensional systems are susceptible to a number of phase transitions that open a gap at the Fermi surface. If the system is two-dimensional but has open orbits, the magnetic field makes it one-dimensional and again we have a phase transition with a gap. This is the physical origin of the instability in the presence of a magnetic field. Once the instability occurs the system has a new periodicity, $2k_F$. What happens at magnetic fields above this point is still a matter of conjecture, and researchers have suggested[14,18] several possibilities. The problem is particularly intriguing because several periodicities are present: the lattice period, the wavelength π/k_F associated with the Fermi wavevector and the variable period λ set by the magnetic field for the electron motion along *a*, all of which may be incommensurate with one another. The system itself must find a way to balance these competing lengths and decide on its own periodic distortion. The results of experiments on the phase transitions of the Bechgaard salts in magnetic fields have been quite spectacular and a very active research effort is now aimed at understanding these transitions.

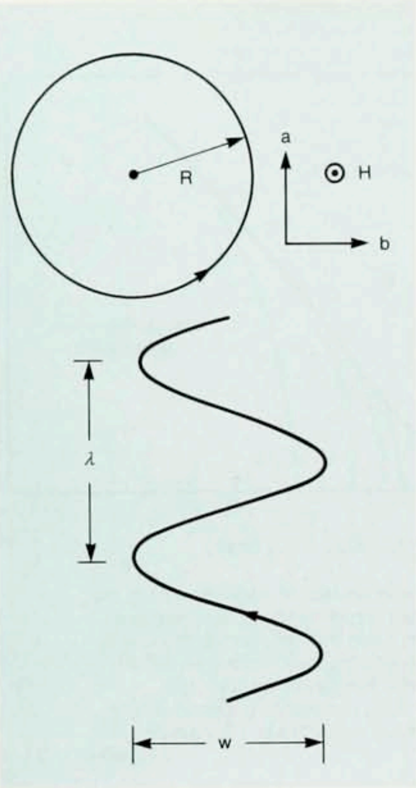
Future issues

Our discussion makes clear that many fundamental issues concerning organic superconducting materials remain unresolved:

▶ Perhaps the most basic question is whether we can use organic chemistry more effectively in synthesizing better superconductors. This will require a much deeper understanding of the relationship between crystal structure, stoichiometry and molecular properties and the actual physical properties of the crystal. Currently only some phenomenological ideas are available to guide the chemist in making materials that have superconducting, magnetic or insulating ground states. Thus far only charge-transfer organic solids and a few graphite-intercalation compounds have exhibited superconductivity, but there seems to be no fundamental reason to exclude the occurrence of superconductivity in other organic materials, such as polymers.

▶ As we have suggested, very little is known about the mechanism of superconductivity in the organic metals. Is an interaction other than the conventional electron–phonon interaction leading to the electron pairing? A better understanding of the relevant interactions may lead to means of raising the superconducting transition temperature above that found in inorganic superconductors.

▶ What aspects of the theory of one-dimensional metals are relevant to the properties of organic superconductors? So far the theoretical models have been able to account for the diversity of low-temperature phases in terms of competition among a few interactions, predominantly the Coulomb and electron–phonon interactions. Now we should ask for more. Can the theory give us a quantitative understanding that will allow us to predict when a spin-density-wave, charge-density-wave, anion-ordered or superconducting ground state



Electron motion. The diagrams indicate the real-space motion of an electron in a crystal in a magnetic field perpendicular to the *ab* plane for a Fermi surface with closed and open orbits. In the case of a closed orbit, the cyclotron radius R is inversely proportional to the external magnetic field H; similarly, in the case of an open orbit, the amplitude w of b-axis motion and the magnetic length λ are inversely proportional to the external magnetic field. Figure 7

will occur?

▶ What of the fundamental characteristics of low-dimensional systems? How are the effects of impurities and localization so easily suppressed to yield materials with mobilities that rival those of the most perfect semiconductors? How does the disorder associated with impurities or incomplete anion ordering affect the phase transitions and electronic properties of one-dimensional materials? Do one-dimensional fluctuations influence any properties significantly?

▶ Finally, we lack a detailed understanding of the effect of magnetic fields on the low-temperature electronic properties of low-dimensional metals. In particular we do not completely understand the large magnetotransport coefficients and the unique series of phase transitions at high magnetic fields. Further theoretical and experimental investigation of organic and other low-dimensional metals should elucidate many of the novel properties of an interacting two-dimensional electron gas in a magnetic field, a topic of considerable interest since the discovery of the quantum Hall effect and the fractional quantum Hall effect in other materials.

With so many fundamental questions about the normal metallic state of organic conductors still unanswered, we anticipate that the properties of organic superconductors and other conducting materials of reduced dimensionality will be active areas of research for some time. Although the technological impact of organic metals has been minimal so far, the hope for technological application, as well as the quest for basic understanding, motivates the research. The prospects for scientific and technological progress must be viewed quite optimistically in light of the surprising discoveries of the past seven years.

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