The differences between one-dimensional and three-dimensional semiconductors

At low temperatures, long-chain polymers and stacked flat molecules acquire a bandgap near the Fermi level that prevents them from being metallic conductors and gives them interesting properties.

Esther M. Conwell

The semiconductors with which we are most familiar, such as germanium and silicon, behave similarly in all three dimensions: Under most circumstances, electrons, for example, move equally well along the three crystal axes. There are, however, materials whose structure is so anisotropic that their properties as measured along one axis differ drastically from those measured in the other directions. In such materials the electrons may behave as if they were confined to move in only one or two dimensions. In particular, the quasi-one-dimensional materials have aroused a great deal of interest over the past decade. Thus, for example, a recent international conference on low-dimensional conductors at Abano Terme, Italy, in June 1984, had about 500 participants and almost as many papers discussing quasi-one-dimensional metallic, semiconducting, and superconducting materials. (As we shall see, these are for the most part the same materials under different conditions of temperature, doping or pressure.)

One fascination of the work in quasi-one-dimensional materials has been the unexpected overlap with other exciting areas of physics. One-dimensional states with fractional charge found in relativistic field theory have strong similarities to those predicted for polyacetylene and other quasi-one-dimensional conductors. Fractional charge and its ramifications have, of course, been eagerly researched since the discovery of the fractional quantum Hall effect. (See PHYSICS TODAY, July 1983, page 19.)

Another intriguing feature of quasi-one-dimensional materials is that they are a microcosm of condensed-matter physics. Apart from exhibiting a variety of phases and phase transitions, they are particularly sensitive to electron–electron correlations and to disorder. Carrier mobilities range from very low values, characteristic of hopping, to one of the highest values found in semiconductors—greater than 10^5 cm^2/V sec, in tetramethyltetraselenafulvalene hexafluorophosphate, $(TMTSF)_2PF_6$, at 4 K.[1] There is evidence[2] for the existence in quasi-one-dimensional semiconductors of highly mobile one-dimensional defects, solitons, which may contribute to transport properties. Studies of the dynamics and interactions of solitons and other nonlinear one-dimensional excitations provide fun for theorists. As additional incentives, polyacetylene and some of the other polymers have commercial prospects as conducting plastics and as rechargeable battery electrodes.

Organic materials

In a quasi-one-dimensional material, the overlap of electron wavefunctions is much larger in one crystallographic direction than in the others, allowing the electrons to move vastly more readily in that direction than in the others. Organic solids are more likely than inorganic materials to yield[3] quasi-one-dimensional materials. One class of such materials is that of the polymeric crystals, crystals formed from long-chain molecules (polymers) with an elementary repeat unit. The prototype of this class is polyacetylene, $(CH)_x$. Another class of such materials contains planar molecules stacked "like poker chips" in a linear array, with relatively close spacing between molecules within a stack and much larger spacing between molecules in the other directions; usually there are stacks of two different molecules involved. The prototypes are compounds of tetracyanoquinodimethane (TCNQ), tetrathiofulvalene (TTF) or molecules obtained from these by simple chemical modifications. A transfer of electrons from one type of molecule to another usually occurs within the crystal, leaving at least one set of chains with partially filled electron energy bands. Figure 1 shows samples of these materials. The large surface area that makes polyacetylene attractive for battery electrodes is clearly visible in figure 1c.

Although, as I have noted, these materials are not literally one-dimensional, the relatively weak electronic coupling transverse to the chains or stacks makes the electronic wavefunctions and atomic configurations along the chains much more deformable than in a tetrahedrally bonded crystal such

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as silicon. It is this deformability that makes for the significant differences between them and the three-dimensional semiconductors. The differences I will describe in this article are in the strong dependence of the semiconducting energy gap on temperature and impurities, the effect of added electrons on the lattice and the nature of defect levels in the gap. Unusual features connected with transport and the possible contributions from solitons will also be discussed.

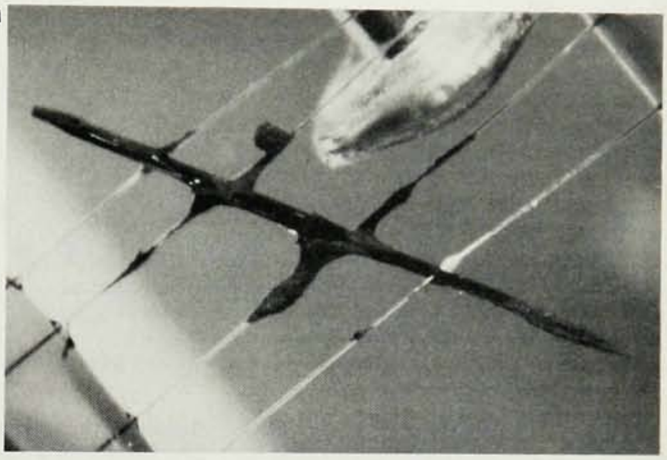
Typically these compounds are metals at high temperatures, in many cases to temperatures below 100 K. However, at low temperatures they generally become semiconductors, due to an inherent instability of one-dimensional materials first predicted by Rudolph Peierls and, independently, by Herbert Fröhlich in the 1950s.

The Peierls distortion

Unless they are disordered or highly impure, at some temperature one-dimensional metals must fall victim to an instability in which the lattice suffers a periodic distortion (whose wavelength is, as we shall see, determined by the Fermi level of the crystal); this is accompanied by a new spatial periodicity in the electron distribution, that is, a charge-density wave. As a result, the conduction band acquires a gap at the Fermi level, so that the material becomes a semiconductor. Charge-density waves have since been observed[4] in both one- and two-dimensional compounds. In the family of compounds related to TMTSF (that is, TTF with four methyl groups and with sulfur replaced by selenium), an energy gap may also arise due to spin-density waves, ordering of the anionic chains or superconductivity. These compounds are more properly considered two-dimensional at the transition temperatures, however, and I will not consider them in this article. The Peierls distortion appears not only at low temperatures: Lightly doped polyacetylene may also be thought of as a Peierls-distorted crystal, as I shall show below.

To illustrate the Peierls instability, consider the case of a one-dimensional metal made up of a chain of atoms or molecules, with distance a between centers, each having one electron outside of closed shells. The uniform spacing requires that the electron wavefunction $\psi(x + a)$ must be the

a



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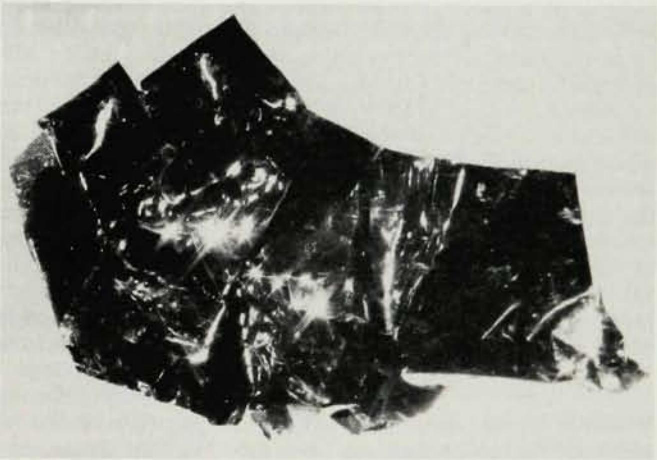

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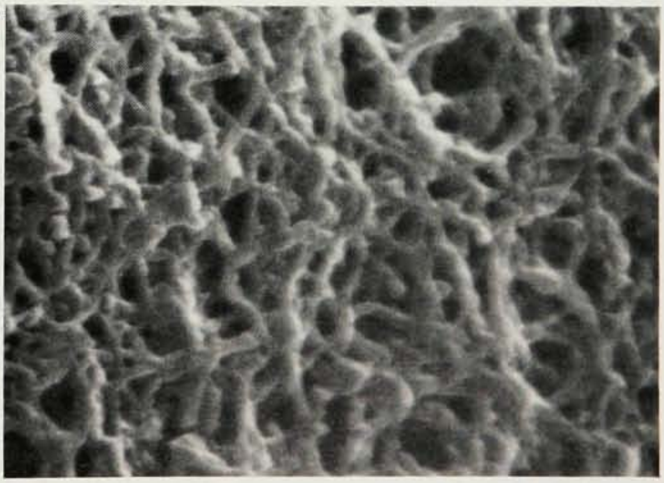
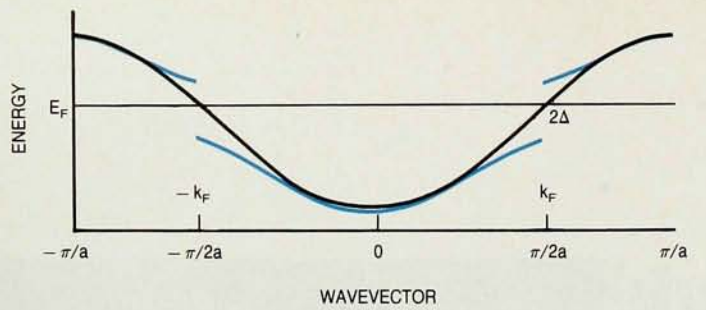


Organic semiconductors with a quasi-one-dimensional structure. At top (**a**) is a needle-shaped crystal of NMP-TCNQ, with attached wire leads for voltage and current measurements; the pinhead gives the scale of the photo. In the center (**b**) is a sample of polyacetylene film; its structure is shown in a scanning electron micrograph (**c**). Despite its solid, metallic appearance, the film consists of tangled fibrils, about 500 Å in diameter, and is mostly empty space. (Samples and micrograph courtesy of A.J. Epstein.) Figure 1 a



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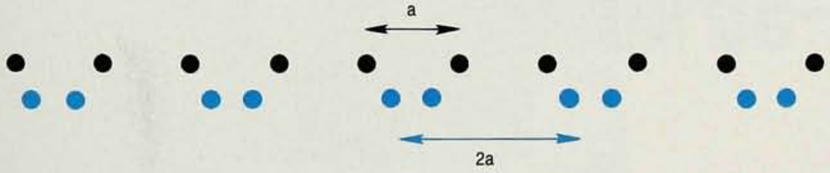


The Peierls instability. The graph (**a**) shows the energy ϵ_k as a function of wavenumber k for a one-dimensional crystal with lattice constant a. The possible values of k vary from $-\pi/a$ to $+\pi/a$; the periodicity of the chain makes larger values redundant. If there is one free electron per atom, the Fermi level E_F corresponds to a wavevector of $\pi/2a$. Distorting the lattice as shown in color in **b** results in opening a gap in the band at the Fermi energy, as shown by the colored curve in **a**. Figure 2

same as $\psi(x)$ to within a possible phase factor. As shown in standard texts on solid-state physics, this condition is satisfied by taking the wavefunction to be of the form $u_k(x)e^{ikx}$; here u_k is a periodic function of x with period a, and k is the electron wavevector. When the molecules are not too close together, which is usually true for the crystals we are considering, the functions u_k in the neighborhood of each molecule are nearly the same as the wavefunctions of the isolated molecule, and may be taken as equal to them. In this "tight binding" approximation, the energy ϵ_k of an electron with wavevector k is

$$\epsilon_k = -2t \cos ka$$

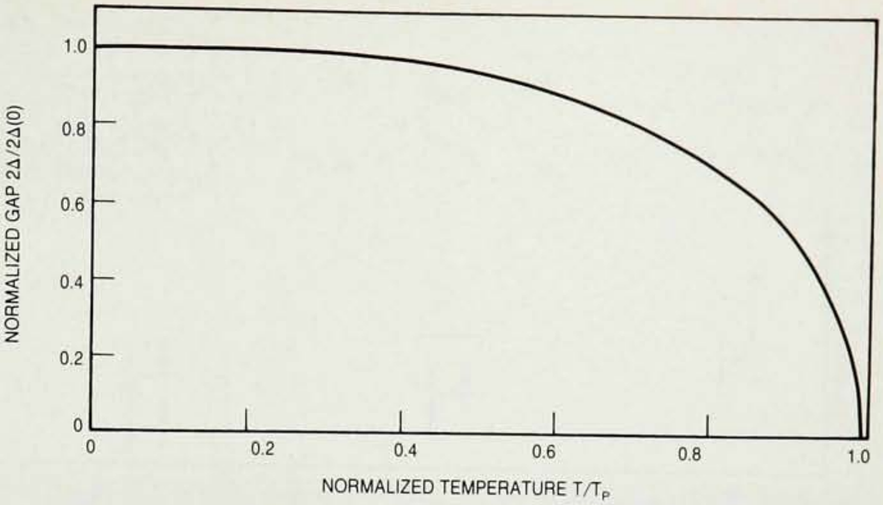
where t is the overlap integral for electron wavefunctions on nearest-neighbor molecules. Figure 2a shows a plot of ϵ_k as a function of k. For molecules with one electron outside of closed shells, exactly half the levels are filled, and at zero temperature there is a sharp division between empty and filled levels: The Fermi energy E_F is at midband. The wavevectors $\pm k_F$ that correspond to E_F are also indicated in figure 2a.

A distortion of the chain in which every molecule moves over a bit so that the lattice constant becomes $2a$ (figure 2b) leads to a small band gap opening at E_F. Peierls showed that at low temperatures, where almost all the electrons are in states below E_F, the decrease in electronic energy due to states being lowered to form the gap makes the distorted state the stable one, despite the cost in lattice energy.

It is more usual now to view the Peierls transition as the result of electron–phonon interaction, which had also been the approach originally used[5] by Fröhlich. In a material at low temperatures, the available states for electrons are all near the Fermi surface, which, in a one-dimensional material, consists of the points at $\pm k_F$. Although acoustic phonons (the quanta of the lattice vibrations) have very little energy compared to that of the electrons, they may have comparable momentum and can therefore readily scatter electrons from $\pm k_F$ to $\mp k_F$. There is thus a strong interaction of the electrons with acoustic phonons whose wavevector is $2k_F$. This produces a softening, or dip in frequency (called a Kohn anomaly), of the $2k_F$ phonons, an effect that has been seen experimentally for temperatures not far above the Peierls transition temperature, T_P, in TTF-TCNQ, for example. As the temperature of the material decreases to T_P, the frequency of the $2k_F$ phonons goes to zero. The lattice distortion at $2k_F$ thus becomes time invariant—it is "frozen in." If the wavelength associated with the $2k_F$ lattice distortion, π/k_F, is ma, an integer multiple of the lattice spacing a, the spatial period of the Peierls distortion is commensurate with the original lattice spacing. This is, for example, the case for the half-filled band, for which $m = 2$. Fröhlich's derivation shows that the Peierls gap increases with the strength of the electron–phonon coupling. The Peierls instability differs from superconductivity (which also results from an electron–phonon coupling that pairs charge carriers on opposite sides of the Fermi surface and having opposite spin) in that the former results from the pairing of electrons with holes rather than with other electrons.

The idea of the Peierls distortion must be generalized for quasi-one-dimensional crystals made up of large molecules such as TTF or TCNQ. Because such molecules have many phonon bands arising from internal vibrations, the coupling of the electrons to these internal modes is generally stronger than to the acoustic, or external, modes. As a result, the Peierls distortion in these materials may arise from freezing in some of the internal modes. For the case of a half-filled band, the Peierls-distorted state—and the resulting charge-density wave—is then due to variations, with period $2a$, in the shape of the molecules, rather than in their spacing. Striking evidence of this effect is the appearance[6] in the Peierls distorted state of strong absorption, at the frequency of the totally symmetric internal modes, for infrared radiation polarized parallel to the chains. Although the vibrations of these modes are essentially perpendicular to the chains, they receive a large dipole moment parallel to the chains from the phase oscillations (phonons) of the charge-density wave.

Note that Peierls's demonstration of the stability of the distorted state, as well as many of the other arguments above, are based on mean-field theory, that is, they neglect fluctuations in the values of the various quantities involved. One must be careful about applying such theories, particularly to one-dimensional systems, because fluctuations may have a strong effect on the behavior of the system. For example, fluctuations have been proven to prevent the occurrence of long-range order in a one-dimensional system whose elements interact through finite-range forces. Of course, the materials we are concerned with are actually three-dimensional. With even a small amount of coupling between chains or stacks, the lattice tends to order three-dimensionally near the mean-field transition temperature, leading to a true phase transition. The only material in which sizable fluctuations persist[7]



The Peierls gap as a function of temperature. The energy of the gap $2\Delta(T)$ is normalized to the value at 0 K, and the values of the temperature are normalized to the transition temperature, T_P. The shape of the curve is similar to that obtained for the gap in superconductors. Figure 3

above T_P is TTF-TCNQ. In any case, mean-field theory is widely used for calculations on quasi-one-dimensional materials and its predictions are generally at least qualitatively correct; one can expect the same for the Peierls instability.

The Peierls gap must decrease when the temperature rises, because the stability of the Peierls distorted state is caused by the electrons that populate the states below the gap. As the temperature rises from $T = 0$, electrons move into the upper band, and there is less and less energy to be gained by lowering the energy of the levels below the gap. To predict the variation of the gap with temperature, one uses mean-field theory to minimize the total energy, which leads to the behavior shown in figure 3, similar to that of a superconductor's gap. This type of variation, with a sharp cutoff at T_P, has been verified for many compounds of TCNQ and TTF (other than TTF-TCNQ) by measurements of the temperature variation of the internal-mode absorption—which, as I noted earlier, is due to the existence of the charge-density wave. Quantitatively, however, the theory does not do so well; the predicted values of T_P are usually larger by about a factor 2 than the observed values. It appears that at least a good part of the discrepancy is due to the presence of impurities and solitons, as I will discuss later.

It is interesting to compare the behavior of the gap described above with that of InSb, a small-gap three-dimensional semiconductor. Here, of course, the gap between the valence and conduction bands is due to the intrinsic structure of the crystal rather than a charge-density wave. At 0 K the gap for this material is 0.23 eV. If indium antimonide followed the behavior of the quasi-one-dimensional compounds, its gap would have vanished below 400 K. In actuality, the gap persists to at least 700 K, the highest temperature measured.

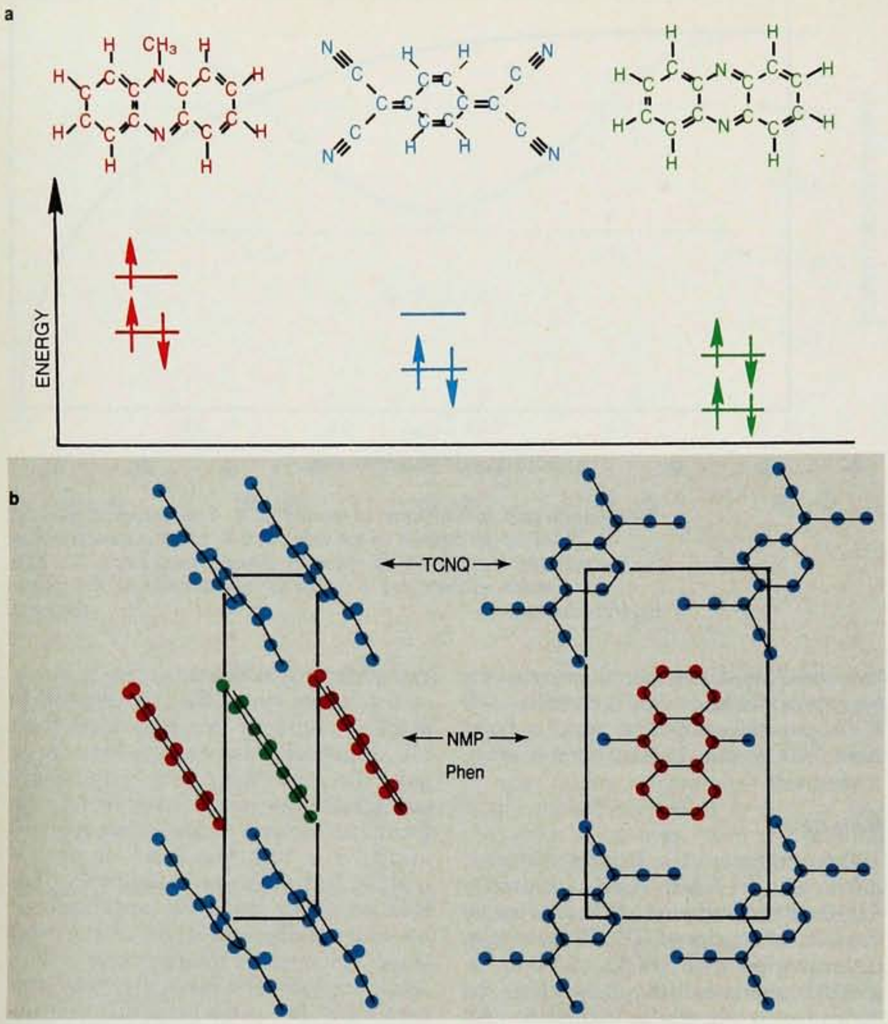
Materials

One example of a Peierls distorted material is NMP-TCNQ, suitably doped. Before doping, this compound consists of stacks of TCNQ molecules intermingled with stacks of NMP (n-methyl phenazinium) molecules; the structure is shown in figure 4. An NMP molecule has one unpaired electron whose energy is above the lowest empty TCNQ level. Thus in the crystal electrons are transferred from the NMP molecules to the TCNQ molecules (such materials are called charge-transfer salts). Joel S. Miller showed that one can control the amount of charge transfer by replacing some of the NMP molecules with phenazine molecules, thereby making the alloy $(NMP)_x(Phen)_{1-x}(TCNQ)$. Although the phenazine molecule is quite similar to NMP (otherwise it could not substitute for NMP), it cannot give an electron to the TCNQ chain. One can thus vary the number of conduction electrons, or the degree of conduction-band filling, on the TCNQ chain by varying x. (In other words, one can make the molecules of the TCNQ chain show different valences.) In that sense, this is one of the few quasi-one-dimensional molecular crystals that can be doped.

The alloy compositions around $x = 0.5$ are of particular interest: At this doping level, the transfer results in one conduction electron for every two TCNQ molecules, so the conduction band is 1/4 filled, which should put the Fermi wavevector k_F 1/4 of the way into the band. However, it turns out that in this material the repulsion U between two electrons on the same site is large, so that those states that correspond to double occupancy are separated from the single-occupancy states by a large gap. Because there are only singly occupied states in the lower band, the Fermi wavevector, rather than being 1/4 of the way into the band, is at the middle, just as shown in figure 2a. This location of k_F has been corroborated[8] by x-ray studies and is in fact the most direct evidence for a large value of U in these crystals. The large magnetic susceptibility, the behavior of the thermoelectric power and considerations of screening also lead to the conclusion[9] that on-site electron–electron correlations are important at this band filling.

With only singly occupied states allowed, electron spin becomes unimportant (the electron spin and translational degrees of freedom become uncoupled for large on-site repulsions, U), and we may think[10] of the conduction band in this material as a half-filled band of spinless fermions. The large repulsion between electrons on the same TCNQ molecule need not hinder the motion of electrons along the chain, so this material should be a metal. Conductivity and optical data of Rich McCall, David Tanner and Arthur Epstein show, however, that a gap exists at the Fermi energy at temperatures up to room temperature, the highest temperature for which there are measurements. The appearance in infrared absorption of the symmetric modes of the TCNQ molecule indicates that the gap is due to a Peierls transition, in particular, one due to internal modes. Thus $(NMP)_{0.5}(Phen)_{0.5}(TCNQ)$ is a spinless analogue of the Peierls distorted material with a half-filled band, which was discussed earlier.

Trans-polyacetylene is a planar compound consisting of CH units coupled



Structure of $(NMP)_x(Phen)_{1-x}(TCNQ)$. The chemical structures of the molecules and the relative positions of the energy levels of the valence electrons are shown in **a**. The diagrams at the bottom of the figure (**b**) show two views of the crystal structure: At left is a view down the b axis of the crystal, and at right is a view down the highly conducting a axis. There appear to be two methyl groups on NMP in the view along a because the NMP molecules' orientation alternates along the a axis. Figure 4

by alternating single and double bonds (figure 5), arranged in a linear structure akin to the cyclic structures seen in aromatic compounds. The bonding orbitals are hybrids of the carbon atom's 2s and 2p orbitals: The linear combination of the 2s orbital with the two in-plane 2p orbitals produces three molecular orbitals, called σ orbitals, for (in-plane) covalent bonds at 120° to each other. These three σ bonds connect each carbon atom with two neighboring carbons and a hydrogen. The third 2p orbital on each C atom, the orbital perpendicular to the plane, forms what is called a π bond with the corresponding 2p orbital on one of the atom's two neighbors.

Band-structure calculations show that electrons in the σ bonds occupy deep-lying filled bands; we shall thus not be concerned with them here. Because the carbon atoms are quite close together—their spacing is less than 1.5 Å—there is a large overlap of the wavefunctions for electrons in the π bonds, resulting in a wide conduction band. If the bonds shown in figure 5 were of equal length, polyacetylene, with each CH unit supplying one π electron, would be similar to the chain of one-electron atoms. Polyacetylene crystals would then have a half-filled band and be metallic. In fact, $(CH)_x$ is observed to be a semiconductor unless it is very heavily doped. The gap was first attributed entirely to large repulsions between electrons on the same CH unit. Although many people adduced evidence—from optical spectra,[11] for example—that the bonds were of different lengths, it took some years before x-ray measurements[2] showed that the double bond is about 0.03 Å shorter. The alternating short and long bonds can be thought of as a Peierls distortion, producing a gap at the Fermi energy, just as shown in figure 2. Nevertheless, as the quantum chemists have insisted all along, electron–electron correlations may not be neglected in this material. The present thinking is that these interactions contribute to the gap in polyacetylene as well as the Peierls distortion.

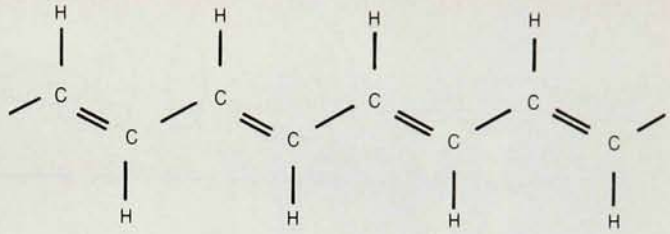
The effects of doping: solitons

In three-dimensional semiconductors many different atoms can substitute for an atom of the host, or go into an interstitial position in the lattice, and can act as donors of extra electrons or holes to the lattice. At low temperatures the extra electrons or holes are bound to the impurity in orbits that may be large—covering many lattice constants—or small, depending on the nature of the impurity. Efforts to apply models of this sort for doping of quasi-one-dimensional semiconductors met with no success.

We have seen earlier that $(NMP)_{0.5}(Phen)_{0.5}(TCNQ)$ may be doped by replacing phenazine molecules with NMP molecules. The extra NMP molecules transfer their electrons to the TCNQ chain, and one might expect that the added electrons would be free to move on that chain, resulting in an increase in k_F from $\pi/2a$. This increase in k_F would in turn lead to an increase in the wavevector for the distortion, according to Peierls's recipe for minimizing the free energy at low temperatures. This change in the wavevector of the charge-density wave should have been observed by x rays. In fact, however, k_F was observed[8] not to change until x reached values near 0.59. This suggests that electrons in excess of 0.5/molecule—up to about 0.59/molecule—are accommodated in localized states.

One way of producing this result had been suggested earlier by Akio Kotani

Trans-polyacetylene. The alternating single and double bonds do not have the same lengths. Although the two structures having the double bonds in the two possible positions have the same energy, it is almost impossible to switch from one to the other because all the bonds must be flipped simultaneously. Figure 5



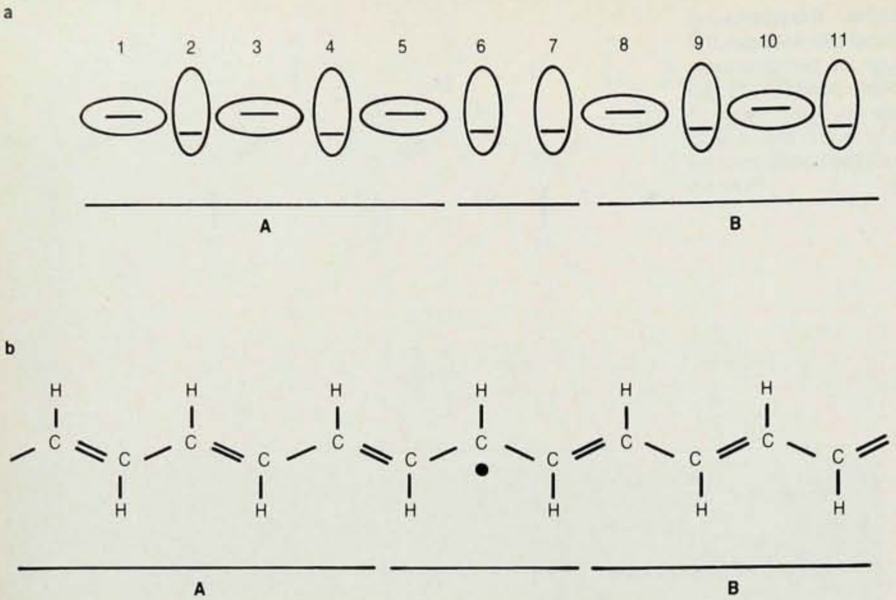
and was developed further by Michael Rice and by Wu Pei Su, J. Robert Schrieffer and Alan Heeger.[12] To obtain the periodicity $2a$, one needs molecules of two different shapes, which we may represent schematically as "fat" and "thin," at alternating sites in the chain (figure 6). There are two degenerate arrangements of such a chain. The arrangement A, with fat molecules at odd sites and thin ones at even sites, is degenerate with the arrangement B, where thin molecules are at odd sites and fat ones at even sites. One can then imagine a situation such as that shown in figure 6, where A and B exist in different parts of the chain with a transition region or domain wall between. Defects of this kind could be created thermally; the energy required to create[10] one is the gap energy divided by 2π. They must, however, be created in pairs, resulting in an arrangement of the form $A|B|A$ or $B|A|B$, so that their creation does not result in a change of the boundary conditions. In real situations, one expects[10,12] the molecules to change shape gradually, with the transition region extending over a number of lattice sites—over a distance approximately twice the bandwidth divided by the gap. For $(NMP)_x(Phen)_{1-x}(TCNQ)$ the transition is expected to cover about five lattice sites. The gradualness of the change suggests that the domain wall could move easily while maintaining its overall shape, which would make it, in a loose definition of the term, a soliton. In fact there is good evidence[2] in polyacetylene, where, as we shall see, such domain walls also exist, that they are mobile.

Due to electron–phonon coupling, a distortion of the molecule changes the electron energy, making it lower for one shape of molecule—the thin one, let us say. The arrangement shown in figure 6 will then accommodate an extra electron in the domain wall—or soliton. Thus there is one electron more in the region than there would have been if either arrangement A or arrangement B had continued uninterrupted. (A domain wall with two fat molecules together would accommodate a hole.) Because the extra electron is localized, it has an energy level in the gap; by symmetry (if we neglect the positive charge on the NMP that gave rise to it) it is halfway between conduction and valence bands. Extra electrons due to NMP doping at levels x above ½ can thus be disposed of in the domain walls, leaving the rest of the chain with $k_F = \pi/2a$. Each extra electron requires the creation of a pair of solitons, which costs an energy $2\Delta/\pi$, less than the energy Δ that would be required to put an electron into the conduction band.

Interestingly, the solitons—for this case of spinless fermions—would have fractional charge.[10] To form a pair of solitons, one state must be removed from the conduction band and one, with its electron, from the valence band in the vicinity of the soliton. The removal of the electron results in an uncompensated charge of $+e/2$ on each soliton. To minimize energy, the electron is put on one of the solitons, resulting in a pair with charges $+e/2$ and $-e/2$. These results are[13] entirely analogous to those obtained by Roman Jackiw and Claudio Rebbi in studying a relativistic field theory for a one-dimensional spinless Fermi field coupled to a Bose field with broken symmetry (the analogue of the broken symmetry due to the Peierls distortion). Fractional charges have also been predicted for other cases involving commensurate Peierls distortions, although not in the wide variety found in the fractional quantum Hall effect.

There is an additional feature that must be considered in crystals: the interaction with other chains. This interaction can remove the degeneracy of the A and B regions, making it energetically advantageous to shorten one type of region at the expense of the other, and thereby "confining" the solitons. For $(NMP)_x$ $(Phen)_{1-x}$ $(TCNQ)$, with x near ½, the NMP^+ molecules are more or less on alternate sites and energy is minimized by having the phase with the thin molecules (where the electrons are preferentially located) opposite the NMP^+ as long as possible. In this situation the stable excitation is no longer a soliton, but one may think[14] of it as a superposition of two solitons with appropriate phases. This excitation is called a polaron because, like the well-known polaron in ionic crystals, it consists of an electron dressed by lattice vibrations. Despite some efforts, fractional charges have not been detected in quasi-one-dimensional conductors; it may be that they do not survive interchain potentials.

In polyacetylene the weak interchain binding allows large numbers of impurities to be inserted between the chains, much larger numbers than are found in the usual three-dimensional semiconductors. Typical acceptors are AsF_6 and I; typical donors are Na and K. There is a great deal of evidence[2] that the extra electrons or holes are accommodated in soliton levels; interchain potentials appear to be small enough that the "confinement" effect may be significant only at quite low temperatures. In



Domain walls in a one-dimensional lattice consisting of two different kinds of units: "fat" and "thin" (above) and single and double bonds (below). (The bars in the fat and thin molecules indicate the electronic energy levels.) The dot indicates the localized extra electron in the domain wall in polyacetylene. Figure 6

this case, long (single) and short (double) bonds replace fat and thin molecules (figure 6b), and because the fermions in $(CH)_x$ are not spinless, each soliton can accommodate up to two electrons. The argument used above now leads to the conclusion that the possible charges on a soliton in polyacetylene are zero and $\pm$e. The neutral soliton, having one electron (screened by one positive charge) has spin ½; the charged solitons have no spin. The reversal of the charge–spin relations from those usually found has been the subject of much comment. I will say more about some of the consequences in the next section.

Transport properties

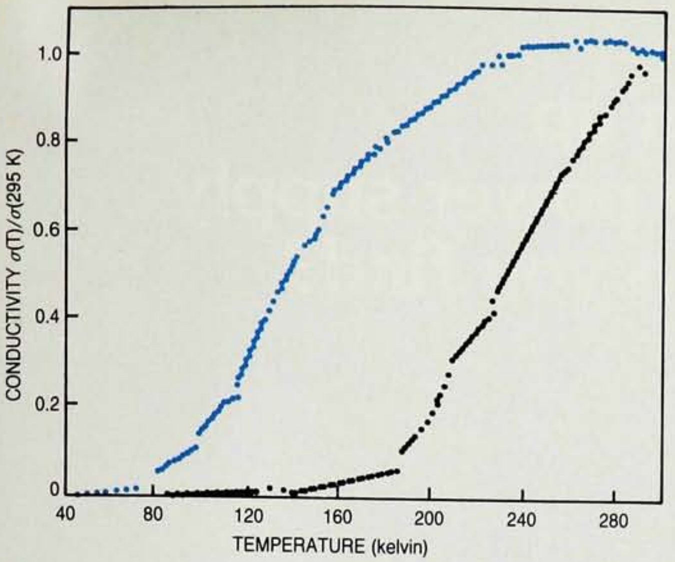
Just as for three-dimensional semiconductors, doping may have a great effect on the conductivity σ of quasi-one-dimensional semiconductors. Figure 7 shows the conductivity as a function of temperature for two samples of $(NMP)_x(Phen)_{1-x}(TCNQ)$; at all temperatures σ is much larger for $x = 0.54$ than for $x = 0.51$. An obvious thought is that this difference is due to different numbers of polarons contributing to transport in the two samples. However, this is apparently not the case: The number of polarons in the sample with $x = 0.54$ could be at most four times what it is when $x = 0.51$ (thermal generation would make this number even smaller), whereas at 180 K, for example, the conductivity σ of the 0.54 sample is larger by a factor of 20. More importantly, the temperature variation of the conductivity for the lightly doped sample, but not for the heavily doped sample, more or less follows the variation one expects in the number of conduction electrons and holes, given the fairly small gap in this compound, 0.15 eV. The explanation[15] for the greatly enhanced conductivity of the sample with $x = 0.54$ is the decrease of the Peierls gap due to doping: With greater doping there are more electrons in the conduction band for a given temperature, thus destabilizing the Peierls gap.

In lightly doped trans-polyacetylene, where the gap is much larger and free carriers are not expected, there is good evidence that both intersoliton hopping and free-soliton motion contribute to the electric current in appropriate situations. The ac and dc conductivities and the thermoelectric power for very lightly doped samples are well described[2] by a model of intersoliton hopping due to Steve Kivelson. There is good evidence that the photoconductivity observed in pristine samples is due to photoinduced, charged, moving solitons. Solitons might[16] thus play a role in the conductivity of p–n junctions or Schottky barriers that use polyacetylene.

More highly doped samples of polyacetylene, with donors or acceptors in the range 1–5%, are characterized by conductivities as high as $10^2\ \Omega^{-1}\mathrm{cm}^{-1}$. They are still semiconductors, as indicated by the increase in σ with increasing T throughout the temperature range and by their optical absorption.[2] The magnetic susceptibility in this range is, surprisingly, very much lower[2] than one would expect in a metal of similar conductivity. This observation has led to the suggestion that here also the conduction is due to moving solitons, because, as noted earlier, charged solitons have no spin. However, the charged solitons in doped polyacetylene are strongly pinned by the Coulomb attraction of the donors or acceptors—at low concentrations, at least. Thus, one current model involves soliton tunneling through the impurity barriers. Less exotic models have also been presented to account for these phenomena. Epstein, for example, has shown[17] that variable-range hopping of holes can account well for both the conductivity and the susceptibility of at least some of the samples in this doping range. It is also possible that, due to the large spread of the soliton levels within the gap at high impurity concentrations, there are enough free carriers to account for at least some of the observed conductivity. All this promises an interesting time ahead in the investigation of these materials.

Contrasts

The differences between quasi-one-dimensional and three-dimensional semiconductors can be attributed to the fact that the gap in the quasi-one-dimensional materials has its origin in the electron–phonon interaction rather than in a separation of energy levels having different atomic origins, as in the three-dimensional case. As a result, the materials differ in many ways, including the sensitivity of the gap to temperature and impurities. For quasi-one-dimensional conductors with small gaps—up to a few tenths of an electron volt—a transition to the me-



Conductivity as a function of temperature for two samples of $(NMP)_x(Phen)_{1-x}(TCNQ)$, with $x = 0.51$ (black) and with $x = 0.54$ (color). The values of the conductivity are normalized to the values at room temperature (295 K): 37 $\Omega^{-1}cm^{-1}$ for $x = 0.54$ and 5 $\Omega^{-1}cm^{-1}$ for $x = 0.51$. Figure 7

tallic state generally occurs at fairly low temperatures. Impurities decrease the gap and may cause it to disappear at temperatures well below where it would otherwise still exist. This is in contrast to three-dimensional semiconductors, where, for example, a high concentration of shallow impurity levels could cause the activation energy for conductivity to disappear while the gap still remains.

In contrast to the situation in three-dimensional materials, an electron (or hole) from a donor (or acceptor) introduced into a quasi-one-dimensional semiconductor results in a deformation of the chain that provides a level in the gap for the added electron (hole). The deformations may be mobile and contribute to transport in the quasi-one-dimensional material. I have here discussed the detailed nature of these distortions for materials that would have been metals with half-filled bands were there no Peierls distortion. Undoubtedly, other unusual properties of quasi-one-dimensional crystals and polymers will emerge as they continue to be the objects of active study pursued by many groups in the US and abroad.

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