

Charge-density waves in transition-metal compounds

At low temperatures some crystals undergo a phase transition to a state in which the electron density displays periodic modulations incommensurate with the crystal lattice.

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The vast majority of compounds crystallize into a regular form in which a unit cell is repeated indefinitely, except for generally localized defects, impurities and boundaries. In a few compounds, however, at sufficiently low temperatures interactions between electrons and ions across unit cells make this regular array unstable with respect to small distortions. The stable state is one in which the charge density,^{1,2} the spin density,³ or the ion positions⁴ display long-period modulations. The period of these modulations may be incommensurate with the spacing of the underlying lattice, so that the material is no longer truly periodic, having two unrelated periods. In this article we shall focus on charge-density waves, in which the electron density and also the ion positions exhibit a periodic variation.

One-dimensional waves

The idea that the electronic energy of a metal could be lowered by a charge-density wave was first put forward some 20 years ago by Rudolf Peierls⁵ and Herbert Fröhlich.⁶ They considered the special case of a one-dimensional metal, in which the electrons are confined to move only in one dimension by, for example, confining them to a linear chain of atoms; the Fermi surface then consists of two parallel planes. A periodic lattice modulation whose wave vector exactly spans these two planes will couple electronic states across the Fermi surface through the electron-ion interaction. The additional periodic potential creates an energy gap at the Fermi surface because electrons whose momenta satisfy the Bragg condition scatter from the lat-

tice modulation. Electron states below the Fermi surface have their energy lowered, those above the Fermi surface are raised. At low temperatures, then, nearly all the states that are lowered are filled while those that are raised are empty, and the total energy of the distorted state is lower in energy than the normal or undistorted state. In this way Peierls and Fröhlich showed that a one-dimensional metal is inherently unstable against a charge-density wave. Subsequent work has shown that this instability is not restricted to one-dimensional systems. Albert Overhauser has suggested that the Coulomb interaction between electrons can also give rise to charge-density waves; however, this does not appear to be an important mechanism in the materials we are discussing.

For some time these theories remained a curiosity without experimental verification. In the last decade, however, charge-density waves have been observed in a number of compounds, leading to a renaissance of interest in the field. In the box on page 35 we list some of these compounds. Several have essentially one-dimensional structures, such as potassium cyanoplatinate, KCP for short, while others (TaSe₂, NbSe₂, TaS₂) are approximately two dimensional. A large class of organic compounds also display charge-density waves at low temperatures, but we will not discuss them here.

Putting aside the question of the microscopic origin of the instability for the moment, we start by discussing the phenomenon of charge-density waves in more detail. Consider the case of a uniform chain of atoms with spacing a . Suppose that the charge density in the crystal is given by

$$\rho(\mathbf{x}) = \rho_0(\mathbf{x})[1 + \rho_1 \cos(\mathbf{Q} \cdot \mathbf{x} + \varphi)] \quad (1)$$

that is, the electron density on each ion is

sinusoidally modulated, as shown in figure 1. The parameter ρ_1 denotes the amplitude of the charge modulation and $\mathbf{Q}$ is its wave vector; the phase φ describes the position of the charge density wave relative to the ions of the underlying lattice. For example, displacing the wave a distance $\mathbf{u}$ is entirely equivalent to a change in phase from φ to $\varphi + \mathbf{Q} \cdot \mathbf{u}$.

The modulation of charge causes each ion to see a different potential. The resulting forces in turn cause each ion to be displaced to a new equilibrium position. The modulation of ionic displacements u_n will have the form

$$u_n = u_0 \sin(nQa + \varphi) \quad (2)$$

where n is an integer defining the position of the ion. The amplitude u_0 must of course, be small compared to a if the crystal is not to be disrupted. The ion displacements are out of phase with the electron density. To see why, note that the force on an ion and hence its displacement arises from a difference of the charges on each side (for example, for an ion at a maximum in the charge-density wave the charge modulation is symmetric on the left and right; it will experience no net force and will not move).

The modulation of lattice sites may be detected by electron, x-ray or neutron diffraction. New diffraction satellites appear separated from each Bragg vector $\mathbf{G}$ of the underlying lattice by $m\mathbf{Q}$ where m is an integer. The location of these new satellites serves to determine the period of the wave, $2\pi/Q$, and for small u_0 the satellite intensity is proportional to $[(\mathbf{G} + m\mathbf{Q}) \cdot \mathbf{u}_0]^2$. John Wilson, Frank Di Salvo and Subash Mahajan, and C. B. Scruby, P. M. Williams and G. S. Parry at Imperial College, London, first observed diffraction satellites from layered compounds in an electron microscope and

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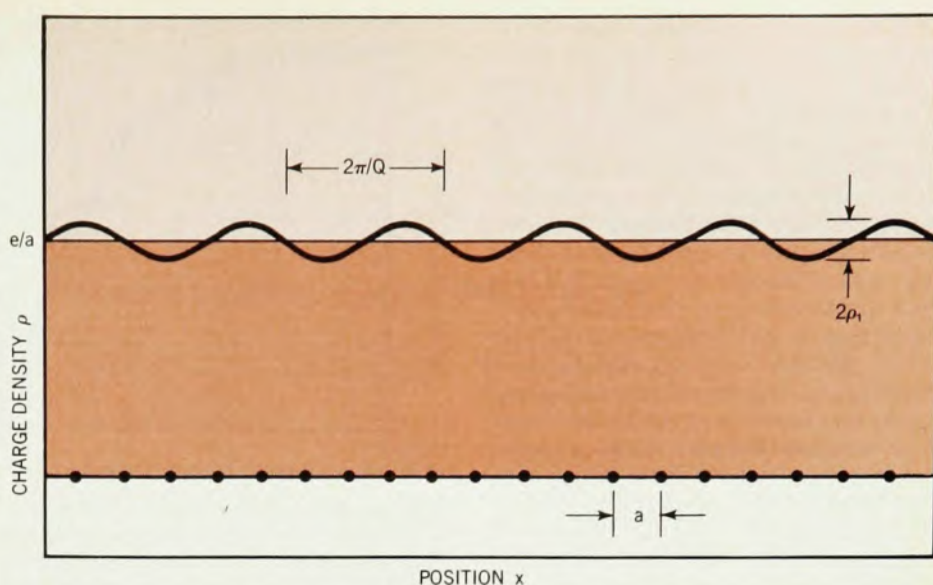
correlated their appearance with anomalies in various electronic properties, which also appeared at low temperatures. Figure 2 shows these new electron-diffraction spots. R. Comes, M. Lambert, H. Launois and H. R. Zeller observed similar diffraction satellites in the one-dimensional compound KCP by x-ray diffraction methods.

From these initial electron-diffraction experiments it appeared that the materials undergo phase transitions as the temperature is lowered, with the low-temperature phase exhibiting a charge-density wave. However, the multiple scattering of electrons makes it difficult to determine the amplitude of the wave from the scattered intensities, even though the electron diffraction itself is sensitive to very small displacements. By contrast, neutrons and x-rays scatter only weakly from atoms, so that multiple scattering is less of a problem; the scattered amplitudes can thus readily be used to determine the amplitude u_0 of the lattice modulation. David Moncton, John Axe and DiSalvo⁸ used neutron scattering to study the 2H polymorph of tantalum selenide. Their results show no satellites in the diffraction pattern above an onset temperature ($T_0 = 122$ K in this case); below that temperature the satellite intensity rises abruptly and then levels off at lower temperatures, as shown in figure 3. Other compounds exhibit a similar behavior, but with different values of T_0 . In the layered compounds T_0 ranges from 30 K to 600 K.

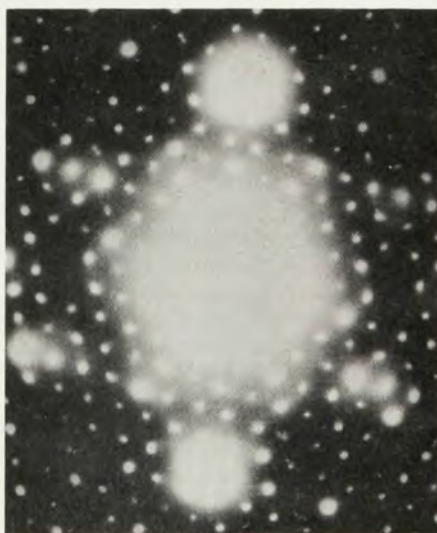
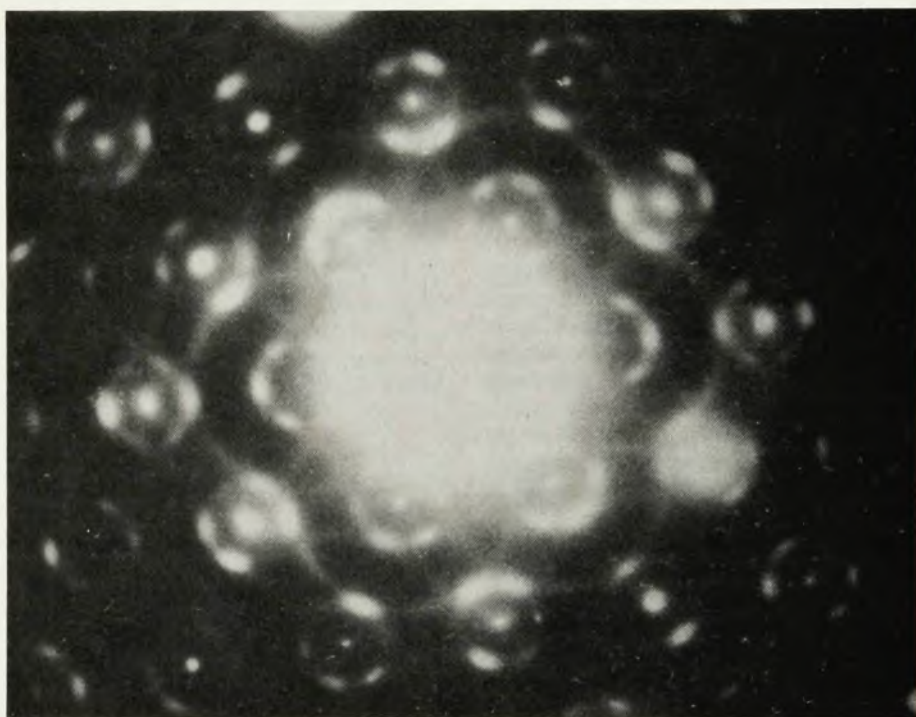
The data shown in figure 3 reflect another interesting aspect of the charge-density wave in 2H-TaSe₂. The wave vector $\mathbf{Q}$ of the distortion is commensurate with the lattice at low temperatures, having a value of one third the reciprocal lattice vector, $\mathbf{a}^*$. At 90 K there is an abrupt transition, shown in the figure as a decrease in intensity, in which $\mathbf{Q}$ changes from $\mathbf{a}^*/3$ to $\mathbf{a}^*/3 + \mathbf{q}$. At T_0 , $\mathbf{q}$ is $-0.02 \cdot \mathbf{a}^*/3$, and as the temperature is lowered the magnitude of $\mathbf{q}$ decreases, dropping discontinuously to zero at 90 K.

When the charge-density wave is commensurate, the distortion of charge and atomic displacement simply gives the crystal a larger unit cell. Specifically if $\mathbf{Q} = \mathbf{a}^*/3$, then the new unit cell is three times the old unit cell and the crystal is periodic. When $\mathbf{Q}$ is incommensurate no unit cell can contain an exact period of both the wave and the underlying crystal structure. The material is no longer periodic; the whole sample is the unit cell.

Electron diffraction patterns from various crystal polymorphs: (a) 1T-(Ta_{0.6}Nb_{0.4})S₂, (b) 4Hb-TaS₂, (c) 1T-TaSe₂. In each case the bright central spots are due to Bragg scattering; in (a) the streaks and the spots they connect are due to an incommensurate wave; in the other pictures the small satellites are due to commensurate charge-density waves. Figure 2



A charge-density wave in a one-dimensional metal. The graph shows the sinusoidally modulated density of conduction electrons. The dots on the axis represent the ions. Forces due to the nonuniform electron density distort the lattice slightly. Figure 1



While these experiments were able to show that the ions move, they did not directly show that the local charge at each ion is modulated. To measure this local charge one needs a probe sensitive to the distribution of conduction electrons. X-ray spectroscopy is such a probe, since by measuring the absolute energy of a core level it samples the local electronic environment of the ion. Groups at Bell Labs and IBM have used this technique to show that in the 1T polymorph of TaSe₂ ($T_0 = 600$ K) there is a modulation of roughly one electronic charge per atom at room temperature, as if different tantalum ions had different valences ranging between Ta⁵⁺ and Ta³⁺. At the same temperature the largest displacement of the ions is 0.23 Å. (The Ta-Ta intralayer spacing is 3.3 Å.) Another probe that can give information about electron densities is nuclear magnetic resonance. The nuclear resonance frequency is determined not only by the applied magnetic field but also by the internal magnetic fields due to the spin and orbital moments of the conduction electrons. These fields give rise to a small shift in the resonance frequency of each nucleus, called the Knight shift, which is proportional to the conduction electron density at each nucleus. Furthermore, if the nuclear spin is greater than $\frac{1}{2}$, satellites may appear around the main resonance due to the splitting of nuclear quadrupole levels by local electric fields. Eitan Ehrenfreund and Arthur Gossard at Bell Labs and Fred Gamble, then at Synvar, using Knight shift and electronic data, estimated the charge modulation, $2\rho_1/\rho_0$, in the 2H polymorph of NbSe to be about 10%. For 2H-NbSe, the onset temperature is 33 K; it thus appears that ρ_1 scales with T_0 .

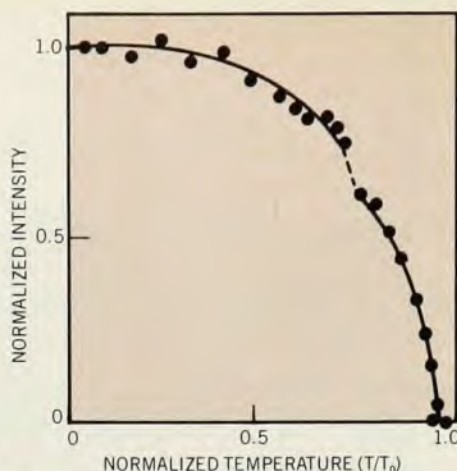
The Landau theory

Second-order or weakly first-order (small latent heat) phase transitions can be usefully, though empirically, described by the Landau theory.⁹ The key concept in the theory is the existence of an "order parameter" that vanishes for temperatures above the phase transition temperature T_0 and, in the case of a second-order transition, grows smoothly from zero for temperatures below T_0 . In our case the order parameter may be the conduction-electron charge density itself or, equivalently, the lattice distortion. A description of the charge-density wave must include not only its amplitude but also its phase, and we therefore introduce a complex order parameter ψ based on the charge density

$$\rho_1(\mathbf{r})\cos(\mathbf{Q} \cdot \mathbf{r} + \varphi) = \text{Re}[\psi(\mathbf{r})\exp(i\mathbf{a}^* \cdot \mathbf{r}/3)] \quad (3)$$

For the materials we are considering, $\mathbf{Q}$ is approximately $\mathbf{a}^*/3$, so that $\psi(\mathbf{r})$ will only vary slowly in space.

Landau argued that the difference in free energies between the normal (undistorted) and distorted states could be



The intensity of a first-order diffraction satellite in 2H-TaSe₂ below the transition temperature as observed by neutron diffraction. The dotted line marks the transition from an incommensurate to a commensurate wave. Figure 3

written as a power series in the order parameter, and because the magnitude of the order parameter approaches zero as the temperature approaches the transition temperature from below, only the first few terms of the series need be retained when T is near T_0 . Further, only those terms that are invariant under the symmetry operations of the undistorted crystal are nonzero. For charge-density waves in 2H-TaSe₂ the free energy difference, ΔF , between the normal and distorted states is, according to these rules,

$$\Delta F = \int d^3r [a(T - T_0)|\psi(\mathbf{r})|^2 + b|\psi(\mathbf{r})|^4 + c|(\nabla - i\mathbf{q})\psi(\mathbf{r})|^2 + d\text{Re}[\psi^3(\mathbf{r})]]$$

The coefficients a through d are phenomenological constants. The first two terms in this expansion can produce a ground-state energy lower than the undistorted state ($\Delta F < 0$) with $\psi \neq 0$ if a and b are positive and $T < T_0$. The third term is minimized when the wave vector

is incommensurate ($\mathbf{Q} = \mathbf{a}^*/3 + \mathbf{q}$), while the last term represents the energy gained by making the wave commensurate ($\mathbf{Q} = \mathbf{a}^*/3$). The interplay of the last two terms determines the nature and occurrence of the commensurate-incommensurate transition. Consider for example the two simplest choices

► $\psi(\mathbf{r}) = \psi_0 \exp i(\mathbf{q} \cdot \mathbf{r} + \varphi)$ which corresponds to a simple incommensurate wave with $\mathbf{Q} = \mathbf{a}^*/3 + \mathbf{q}$.

► $\psi(\mathbf{r}) = \psi_c e^{i\varphi}$ which represents a commensurate wave.

In both cases ΔF is minimized with respect to the amplitude of the wave, ψ_0 or ψ_c , and the phase φ . In the former case the free energy density is, for $T < T_0$

$$\Delta F/V = a^2(T - T_0)^2/4b$$

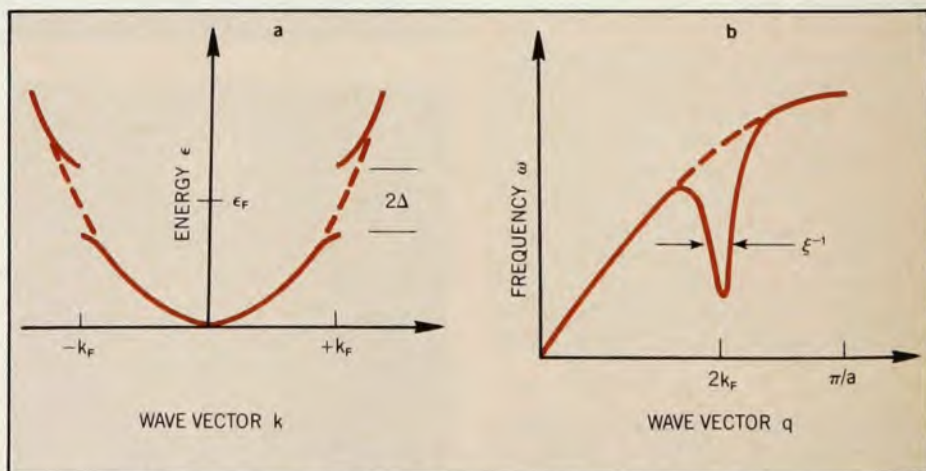
Note that the contributions to ΔF from the last two terms both vanish, so that the energy is independent of the choice of φ . When the periods of the charge density wave and the lattice are incommensurate it does not matter where in the lattice the wave sits.

In the commensurate case the last term forces the choice $\cos 3\varphi = \pm 1$, and we say that the phase is "pinned." In this case the free energy difference takes on a more complex form than for the incommensurate waves. A comparison of the free energies determines which phase is stable. The phase transition is first order in this model.

In their neutron-scattering studies of 2H-TaSe₂ Moncton, Axe and DiSalvo noticed that the incommensurate state was modified by the appearance of harmonics when the commensurate state was approached. They pointed out that if the order parameter is of the form

$$\psi(\mathbf{r}) = \psi_0 \exp i(\mathbf{q} \cdot \mathbf{r} + \varphi) + \psi_1 \exp [-2i(\mathbf{q} \cdot \mathbf{r} + \varphi)]$$

the crystal can gain energy from the lock-in term, even in the incommensurate state; the transition to the commensurate



Energy relations in the presence of charge-density waves. (a) In the presence of a lattice distortion with wave vector $2k_F$, the energy band develops a gap at the Fermi energy, ϵ_F . (b) At temperatures above the transition temperature T_0 the spectrum of acoustical-phonon frequencies ω , shows a marked dip near $2k_F$. In a simple model the energy, $\hbar\omega$, decreases to zero at T_0 ; the resulting static lattice distortion is accompanied by the energy gap shown in graph (a). Figure 4

state, however, remains first order. W. L. McMillan⁹ realized that an even lower free energy could be attained by allowing a phase variation $\varphi(\mathbf{r})$, which introduces a large number of harmonics. Actually, the problem in which only the phase varies can be solved exactly; 30 years ago F. C. Frank and J. H. van der Merwe¹⁰ obtained, in another context, a solution in terms of incomplete elliptic functions. The key feature of their solution is a continuous transition to the commensurate state; close to the transition there are commensurate regions separated by regions in which the phase varies rapidly through $2\pi/3$. McMillan introduced the term "discommensuration" to describe these "kinks" in the phase. The resulting picture is of a continuous transition proceeding through a continuous decrease in the number of discommensurations. Including amplitude modulation and dynamical effects does not change the picture.^{11,12} In 2H-TaSe₂ there are, however, three coexisting charge density waves whose $\mathbf{Q}$ -vectors point at 120° with respect to each other. The structure that results is therefore periodic in several directions, much like the three-dimensional periodicity of the atoms in a crystal. Including the three wave vectors in the model restores the first-order phase transition.¹³

While the phase of a low-order commensurate wave is readily locked into the crystal lattice, it can be shown that the strength of the lock-in term drops off exponentially with increasing size of the superlattice unit cell. What then determines the phase of the incommensurate charge density wave? Impurities couple strongly to distortions in the charge distribution. Take, for example, an impurity with an attractive potential. Clearly it will be favorable to have one of the maxima of the charge density coincide with the impurity, and this leads to a linear coupling of the impurity to the phase φ . This contrasts with the case of foreign atoms in a crystal, which couple only to the deformation or strain, which in turn is determined by the derivative of the phase. The analogy is rather that the lattice acts as a substrate and one is dealing with crystallization onto an imperfect substrate determined by the impurities. Yoseph Imry and Shang-Teng Ma, at Brookhaven, and Lu Sham and Bruce Patton, at La Jolla, showed that such linear coupling in fact could destroy the three-dimensional long-range order associated with a charge-density wave. A dimensional argument shows how this comes about. Suppose that the length scale for phase variation is L ; the free energy of a volume L^3 then has two terms: first, a repulsive term arising from the positive gradient terms proportional to L ; second, impurities contribute an attractive term, but because one cannot adjust the phase to take advantage of all impurities if they are randomly distributed,

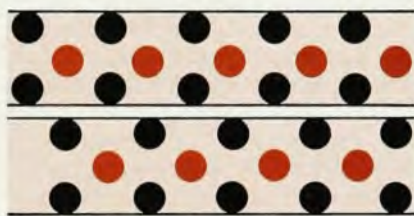
the average coupling energy is proportional to the square root of number of impurities, or $L^{1.5}$. Clearly, when the energy is minimized by balancing these two terms, the length scale of the short-

range order is also determined. This argument applies as well in one and two dimensions with the same result. All these theories show that the local value of the phase is pinned by impurities.

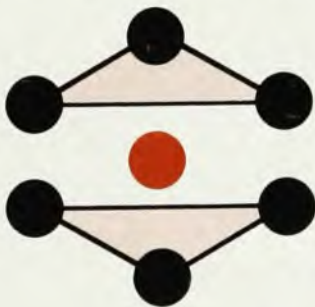
Compounds exhibiting charge-density waves

Charge-density waves have been observed in both one- and two-dimensional structures.

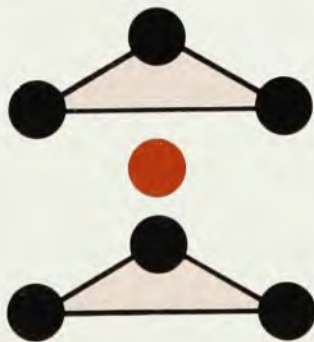
The "two-dimensional" compounds have the composition MX_2 , where M is vanadium, niobium, or tantalum, and X is one of the chalcogenides: sulfur, selenium, or tellurium. The atoms are strongly bonded into layers three atoms thick, with a close-packed sheet of M atoms (color) sandwiched between two close-packed sheets of X atoms (black).



The layers are weakly bonded to each other, mainly through chalcogen-chalcogen van der-Waals interactions. Tantalum disulfide has such a layered structure, and it can be prepared in a number of polymorphs. These polymorphs differ from each other in the stacking arrangement of the layers and by the metal coordination within a given layer. The two observed coordinations are octahedral, in which chalcogens alternate

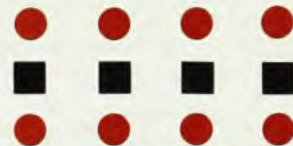


and trigonal prismatic, in which the chalcogens are aligned above each other in each layer.

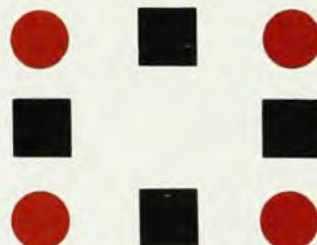


The simplest polymorphs are the 1T, which have one layer per unit cell, octahedral coordination and overall trigonal symmetry, such as 1T-TaS₂; and the 2H, which have two layers per unit cell, trigonal prismatic coordination, and overall hexagonal symmetry, such as 2H-TaS₂. The designations, such as 1T or 2H, of the polymorphs come from the initial letters of the overall symmetry classes.

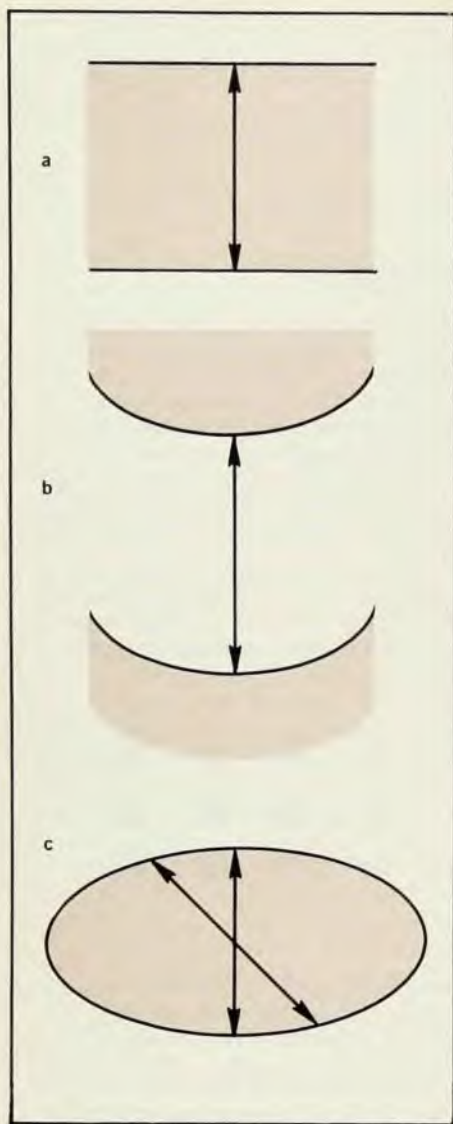
The "one-dimensional" compounds have a structure consisting of strings of electrically conducting atoms or molecules (color), separated by nonconducting ions or molecules (black).



In some cases the "insulating" species are also conducting but the wave function overlap between the two different kinds of molecules is very small. The structure viewed along a string is



The region in the center may be filled with a conducting chain or with some other ions or molecules. An example of the latter is KCP with bromine, $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$, where the conducting chains are made of platinum atoms, the insulating chains of potassium and cyanide; bromine atoms fill the central region. Some organic materials form structures in which two different chains alternate, so that the central region is filled with a "conducting" linear molecule. With some organic materials, both molecular chains are conductors, and the insulation between chains arises because their wave functions do not overlap to any appreciable extent. Niobium trichalcogenides, such as NbSe₃, have a similar structure, but overlap of the atomic wave functions makes their behavior more nearly two-dimensional.



Fermi-surface nesting. Diagrams (a) and (b) show sections of Fermi surfaces that are perfectly nested, spanned by the wave vectors represented by arrows; such surfaces give rise to divergent susceptibilities $\chi(q)$. (c) A Fermi surface that produces a large, but not divergent susceptibility $\chi(q)$. Figure 5

Can a charge-density wave be induced to move and carry a current? This idea goes back to some of the earliest work on these states; indeed, Fröhlich was trying to construct a theory of superconductivity based on charge-density waves in his early papers on the subject. His argument went as follows. At zero temperature the presence of a periodic distortion in a one-dimensional metal completely truncates the Fermi surface and there are no simple-particle states left. However, if we move all the electrons, we end up moving the charge-density wave itself and do not lose the energy gained by forming the wave. There is no barrier to moving an incommensurate wave, so Fröhlich hoped that states with charge-density waves would be highly conducting. Alternatively, this conductivity can be understood as arising from collective modes of the phase, known as "phasons," which are just the vibrational modes of the dis-

torted charge distribution, that is, of the charge-density wave itself. The long-wavelength limit of the longitudinal acoustic phonon mode describes the translational degree of freedom of the charge-density wave. However, as we have seen, the phase is pinned by commensurability with the lattice or by impurities and this implies a local restoring force for the oscillations, or a barrier against movement of the charge-density wave. We are thus led to conclude that the distorted state in a one-dimensional system is insulating, not conducting. The phase oscillations should show up as infrared-active low-lying modes, and indeed infrared reflectivity studies of KCP by P. Bruesch, S. Strässler and H. R. Zeller at Brown-Boveri have shown these modes unambiguously.

Actually the description we have given is not complete, because when a charge-density wave carries a current the associated phase modulations will produce localized charge accumulations, leading to long-range forces in systems such as KCP. Although these forces modify the results, they do not change the basic conclusions that impurities have a drastic effect on conductivity in the distorted state. Several groups have investigated KCP with neutron-scattering methods and have seen the effects of both long-range forces and impurities.

Another issue now under active exploration is the possibility that an electric field may free the phase of a charge-density wave, so that the wave is no longer pinned to the lattice. This "de-pinning" would give rise to a non-linear current response to the field. This mechanism may be responsible for the large deviations from Ohm's law that Nai-Phuan Ong and P. Monceau observed in NbSe_3 at fields as low as 0.1 V/cm. Patrick Lee and Maurice Rice at Bell Labs have estimated the field required to de-pin an incommensurate charge-density wave from impurity sites and found that it could be this low.

Microscopic theories

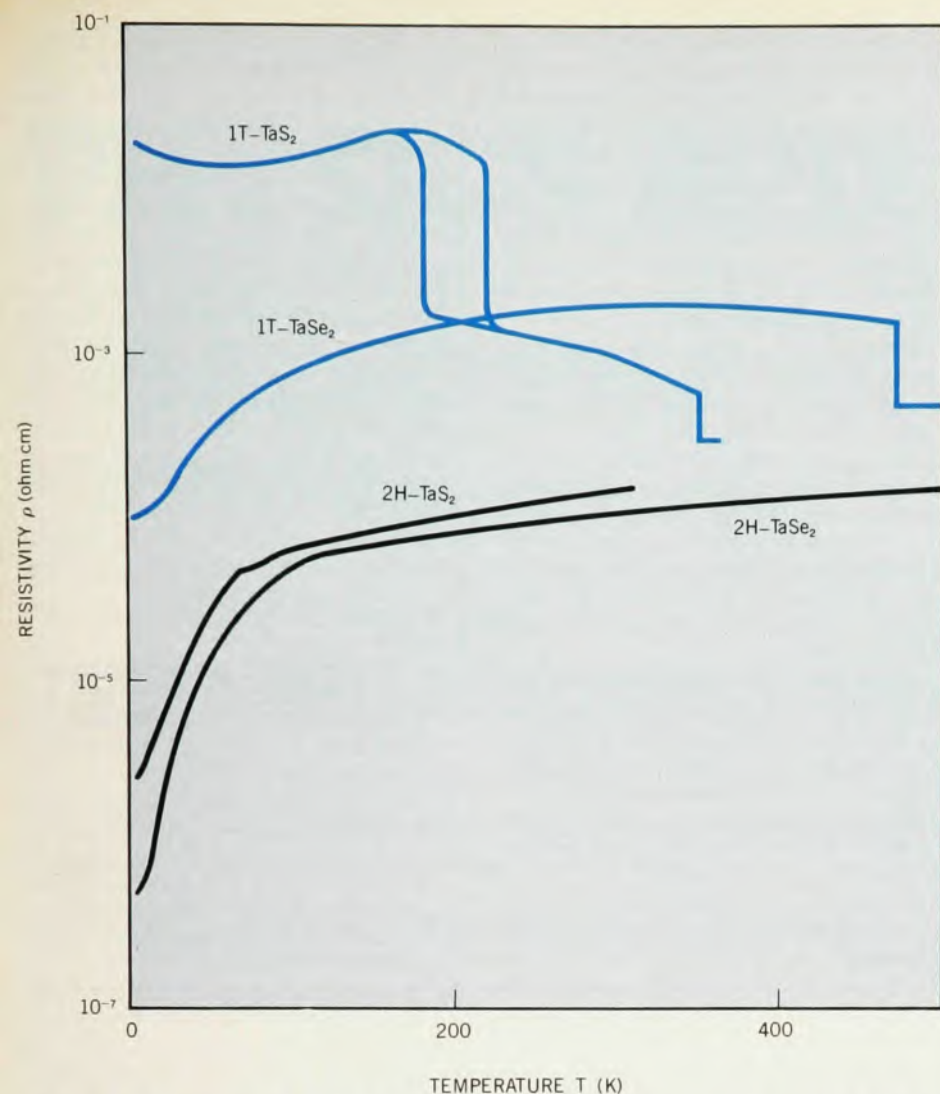
Having discussed phenomenological theories and the experimental observations of incommensurate lattice distortions, let us now consider the microscopic mechanisms responsible for charge-density waves. The simplest model is that due originally to Peierls⁵ and Fröhlich,⁶ who considered noninteracting electrons moving in the potential due to the ions in a one-dimensional metal; the mean-field approximation makes the problem readily soluble. Although this approach leaves out fluctuation effects that are important in one dimension, it captures the essential physics of higher-dimensional systems.

Electrons moving along a chain of equally spaced atoms with wave number k have an energy $\epsilon(k)$. At zero temperature the states are filled up to the Fermi energy, $\epsilon_F = \epsilon(k_F)$ and are empty above

that level. Applying a periodic potential with wave vector $Q = 2k_F$ creates a gap in the energy spectrum at ϵ_F as shown in figure 5(a), because the periodic potential couples states at $+k_F$ and $-k_F$ in first order. One way of producing such a potential is by a periodic distortion of the lattice, such as that given by equation 2. The resulting electron density is modulated as in equation 1. The states near the gap below ϵ_F , which are pushed down in energy, are occupied while those that are raised are empty; the total electronic energy is therefore lowered. If the electronic energy gain is larger than the potential energy cost of the lattice distortion, a charge-density wave will spontaneously appear. At zero temperature such a distortion always occurs in a one-dimensional system, no matter how weak the electron-ion coupling. As the temperature is increased, some electrons will be thermally excited across the gap at ϵ_F , thus reducing the electronic energy gained by creating the distorted state. Finally, the transition temperature T_0 is reached, where the gap closes entirely. The mathematical structure is identical to the familiar Bardeen-Cooper-Schrieffer theory of superconductivity but was worked out by Fröhlich and G. C. Kuper¹⁵ some years earlier. For weak coupling the energy gap obeys the BCS relation $2\Delta = 3.5k_B T_0$.

Above the transition temperature the processes that give rise to the crystal and charge distortion are still active. Although they can no longer give rise to a stable distortion of the lattice, they do produce an anomaly in the behavior of longitudinal acoustic phonons, called a "giant Kohn anomaly," in that the energy of the phonons shows a decrease as the wave number is increased through $2k_F$. The simple model outlined above predicts that as the temperature is decreased to T_0 the phonon energy at $2k_F$ decreases to zero. Below T_0 the phonon energy is zero at $2k_F$, and this phonon becomes "frozen in" as a static distortion. In most systems, however, one finds experimentally that the static distortion appears before the phonon energy at $2k_F$ has dropped all the way to zero (this is called the "central mode problem").

None of the materials studied to date are truly one dimensional; they are bulk three-dimensional crystals. However, there are many materials with linear or planar arrangements of molecules that give rise to highly anisotropic behavior of properties such as the electrical conductivity. In the "quasi-one-dimensional" systems the conductivity in one direction is typically 10^3 to 10^5 times higher than in perpendicular directions. In the "quasi-two-dimensional" metallic layered compounds the anisotropy is much smaller; the conductivity parallel to the layers is typically 30 times the perpendicular conductivity. These systems have a Fermi surface that reflects the one- or



The electrical resistivity of several layered tantalum dichalcogenides shows anomalies due to charge-density waves. Note the differences in behavior of the two polymorphs. Figure 6

two-dimensional character of the material. A charge-density wave will most likely occur in those cases where the shape of the Fermi surface is such that many states on the surface can be connected by the same wave vector $\mathbf{Q}$. In figures 6(a) and (b) we show examples of such "nested" surfaces. A periodic distortion having wave vector $\mathbf{Q}$ will then produce gaps at the portions of the Fermi surface connected ("spanned") by $\mathbf{Q}$. If many states are connected, the energy gained by creating gaps at the Fermi surface may overcome the potential energy cost of the lattice distortion and the distortion will be stable.

The nested Fermi surfaces that give rise to stable lattice distortions also affect the wave-vector dependence of the electric susceptibility, $\chi(\mathbf{q})$. In one dimension $\chi(\mathbf{q})$ diverges logarithmically at $\mathbf{q} = \mathbf{Q}$. If the Fermi-surface nesting is not perfect, as in figure 6(c), the susceptibility does not diverge and a charge-density wave is stable only if the electron-ion interaction is large enough. That the Fermi-surface shape is important in determining the instability conditions was first shown by W. M. Lomer for the case of chromium

metal, where the exchange interaction dominates the electron-ion interaction and leads to a spin-density wave.

The energy gap that gives rise to charge-density waves will also produce changes in all of the thermodynamic and transport properties of the crystal at and below T_0 . Thus, for example, we would predict that at T_0 the specific heat has a finite discontinuity whose magnitude is influenced by fluctuations in the lattice distortion. The electrical resistivity may increase or decrease below T_0 ; on the one hand, the effective carrier density is reduced by the gap, but on the other hand, the scattering rate may be dramatically changed by the elimination of some Fermi surface sections. The magnetic susceptibility should decrease below T_0 , since the gap will reduce the paramagnetic Pauli susceptibility, which is proportional to the density of conduction electron states at the Fermi level.

The coherence length of a wave is roughly the minimum length over which its amplitude can vary appreciably. We can estimate the magnitude of the coherence length ξ of a charge-density wave from the uncertainty principle as follows.

The range of momentum states (Δk) affected by the wave is bounded by $\epsilon_F \pm \Delta$, where Δ is the energy of the gap introduced by the charge density wave. If Δ is small compared to the Fermi energy, the range of affected states is proportional to the gap—that is, we are approximating the undistorted $\epsilon(k)$ relationship with a linear one. In that case

$$\Delta k/k_F \cong \Delta/\epsilon_F$$

so that the uncertainty in position is

$$\Delta x = \xi = 1/\Delta k = \left(\frac{\epsilon_F}{\Delta}\right) \cdot \frac{1}{k_F}$$

The coherence length of the charge-density wave, or equivalently, Δk , can be observed as the width of the Kohn anomaly or of the peak in electric susceptibility.

If, as we assumed, Δ is much smaller than ϵ_F , the coherence length is large compared to $1/k_F$. Systems in which the conduction electrons are free to move in three dimensions are then adequately described by a mean-field theory, and fluctuations in the order parameter are negligible. When the coherence length is on the order of k_F the fluctuations are not negligible even in three dimensions and the theory becomes much more difficult.

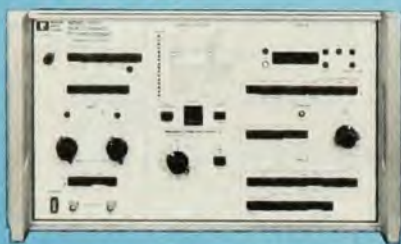
Metallic layered compounds

As a concrete example we consider some of the metallic layered compounds. As we indicated earlier, the observed size of the anomalies in the physical properties or deviations from the behavior extrapolated from above the transition temperature increases with increasing T_0 . The 2H polymorph of NbSe₂ has the lowest transition temperature (33 K) of these compounds and the size of the anomalies found here can be used to estimate the anomalies expected in similar compounds. The charge-density wave in 2H-NbSe₂ is always incommensurate; the wavelength⁸ is about 3% greater than three times the Nb-Nb intralayer separation of 3.3 Å. At 4.2 K the amplitude of the niobium lattice distortion is only 0.05 Å and, as we previously pointed out, the amplitude of the charge-density wave $2\rho_1/\rho_0$ is about 10%. The effect of this distortion on physical properties is small. The resistivity increases by approximately 5% over that extrapolated from above T_0 ; the specific heat shows a small peak at T_0 with a height of about 5% and an integrated enthalpy of about 2.0 joules/mole.

The physical properties of some layered compounds with higher transition temperatures become quite complicated. As an example, consider the 1T and 2H polymorphs of TaS₂ and TaSe₂. We show the electrical resistivity for current parallel to the layers in figure 7. Both 2H compounds show similar behavior, with the resistivity decreasing rapidly below the transition temperature. Note that the resistivity above T_0 is on the order of 10^{-4} ohm-cm, a point we discuss later.

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The properties of the 1T polymorphs are dramatically different from those of the 2H. For these, the transition temperature is around 600 K. The transitions to the commensurate state are first-order phase transitions and are accompanied by large increases in resistivity. As can be expected from the high transition temperatures, the charge-density wave amplitude at 300 K and below is close to one electron per atom.

Both 1T polymorphs also exhibit interesting properties that illustrate some of the theoretical points we discussed earlier. The Fermi surface of 1T-TaS₂ is made up of sections similar to those shown in figure 6(c), so that $\chi(q)$ is large but does not diverge. As final evidence that the wavelength is determined by the Fermi surface, the magnitude of Q can be changed by alloying with transition elements of different electron number, as in 1T-Ta_{1-x}Ti_xS₂.

The measured wavelength of the distortions in 1T-TaSe₂ is 12.2 Å, very close to that predicted by the band structure calculations of, for example, L. F. Mattheiss.¹⁹ An interesting feature of 1T-TaS₂ is that it exhibits two phase transitions below T_0 before the commensurate state is reached below 200 K. K. Nakanishi and H. Shiba were able to explain this double transition within the Landau theory.¹¹

All the transition-metal compounds that exhibit charge-density waves have resistivities above T_0 on the order of 10^{-4} ohm-cm or greater. This value is more than two orders of magnitude larger than that of copper metal at a similar temperature. Such a large value of resistivity means that the scattering times of the conduction electrons are extremely short (about 2×10^{-15} sec), or equivalently, the mean free path is only a few atomic distances. Such values are characteristic of transition-metal compounds with large electron-phonon interactions, and suggest that the incoherent electron-phonon scattering rate determines the energy scale in these materials. The large amplitudes of the distortions in materials such as 1T-TaS₂ and 1T-TaSe₂ also suggest a strong coupling between electrons and phonons. Current theories apply to the charge-density waves in metals with weak coupling and special Fermi surfaces, and a complete strong-coupling theory has yet to be developed.

As William McMillan pointed out,²¹ the layered compounds, even those with moderate transition temperatures such as 2H-TaSe₂, have short coherence lengths. A variety of experiments including the width of the anomaly in the acoustic phonon branch and the large fluctuation contribution to the specific heat near T_0 show²² that ξ in 2H-TaSe₂ is only about 5 Å. Such a short coherence length means that the simple models we discussed previously will not be adequate to explain the observed behavior fully. In particular,

the transition temperature and the thermodynamic behavior will not be determined simply by electron excitation across the gap associated with a charge-density wave. Changes in the phonon entropy will make an important contribution to the free energy, because a large portion of the longitudinal acoustical-phonon branch of width approximately $1/\xi$ is affected by the lattice distortion.

The concept of a lattice of electrons is an old one, dating back to Eugene Wigner's classic paper on the electron gas in 1934. While the models discussed here differ in several ways from Wigner's ideas, the charge-density waves are in essence charged lattices that form with their own period inside certain crystals. They are a lattice within a lattice, and the study of their dynamics and motion is an intriguing problem for the future.

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