# Charge and Spin Density Waves

*Electrons in some metals arrange into crystalline patterns that move in concert, respond peculiarly to applied voltages and show self-organization*

by Stuart Brown and George Grüner

On a hot July afternoon the Mall in Washington, D.C., is overrun with sightseers. They move earnestly in zigzag patterns carrying their coolers, bouncing from museum to monument to cafeteria. Most of the streets bordering the lawns are flat, and as many tourists stroll in one direction as in the other. Suddenly a drumroll is heard: a marching band is assembling. On the roads, displacing the confused crowd, are gathering serried ranks of uniformed high school students. Soon the band is mustered in neat rows, hardly disturbed even by a child trying to hide between the trumpeters' legs from a pursuing parent. As the tourists watch, the band starts to play and then marches forward with a clash of cymbals.

The wanderers on the Mall imitate rather closely the behavior of electrons in common metals. On cooling to temperatures close to absolute zero, most metals remain in this state; that is, the electrons continue to wander. But in some metals the electrons organize themselves into regular patterns like the ranks of a marching band.

Such ordered ranks of electrons, otherwise known as charge-density waves, or CDWs for short, were envisaged by the theoretical physicist Rudolf E. Peierls in the early 1930s and discovered in the 1970s. A related phenomenon, spin-density waves, or SDWs, were predicted by Albert W. Overhauser in 1960, while at Ford Motor Company; the waves were also first seen in the 1970s. At one time, CDWs were suggested as being the agent of superconductivity. Today we know that superconductivity has a different origin, one in which the students dance in pairs rather than march; yet the many oddities of the marching bands themselves have kept researchers intrigued for decades. Charge-density waves may even find applications one day as tunable capacitors in electronic circuits and as extremely sensitive detectors of electromagnetic radiation.

Hook up a battery to the ends of a solid in which a CDW exists and apply a voltage across it. If the voltage is small enough, nothing happens: the shoes of the marchers are stuck to the road with chewing gum. (The sticking is weak, so charge-density waves have a "dielectric constant" several million times that of semiconductors, which allows them to store enormous amounts of charge—hence their potential use as capacitors.) But if you increase the voltage beyond a certain threshold, the shoes suddenly break free, and the band begins to march—there is a large current. The current is not proportional to the voltage, as in ordinary metals obeying Ohm's law; instead it increases vastly with small increases in voltage. Further, a small part of the total current oscillates in time, even if only a constant DC voltage is applied.

And charge-density waves exhibit a "self-organized" response to externally applied forces. In fact, the concept of self-organized criticality grew out of initial work on CDWs. This field attempts to understand the motions of complex systems such as sandpiles or earthquake fault networks. Let's say we dribble sand onto a surface. It piles up into a conical shape; the cone is so steep that often adding a single grain will cause an avalanche. Likewise, tectonic plates perpetually poise themselves on the brink of an earthquake. In some circumstances, charge-density waves so configure themselves that any slight change in an externally applied electric field leads to a drastic change. CDWs are thus a tabletop system in which we can test theories of self-organization.

Why do density waves form? The underlying cause is the interaction between the electrons in a metal. Normally the electrostatic repulsion between the negatively charged electrons is canceled out by the presence of positive ions (atoms that have lost one or more electrons and are therefore positively charged), which form the body of the metal. Then the electrons hardly notice one another. In such a situation, if we picture the electrons as the strolling crowd described earlier, the probability of finding a person—or electron—at any one spot is the same as at any other. So the electrons' charge density is uniform in space. Now suppose the electrons do interact—say by affecting the lattice in which the positive ions are arranged. The lattice can in turn influence the position of a second electron, effectively giving rise to an interaction between the electrons.

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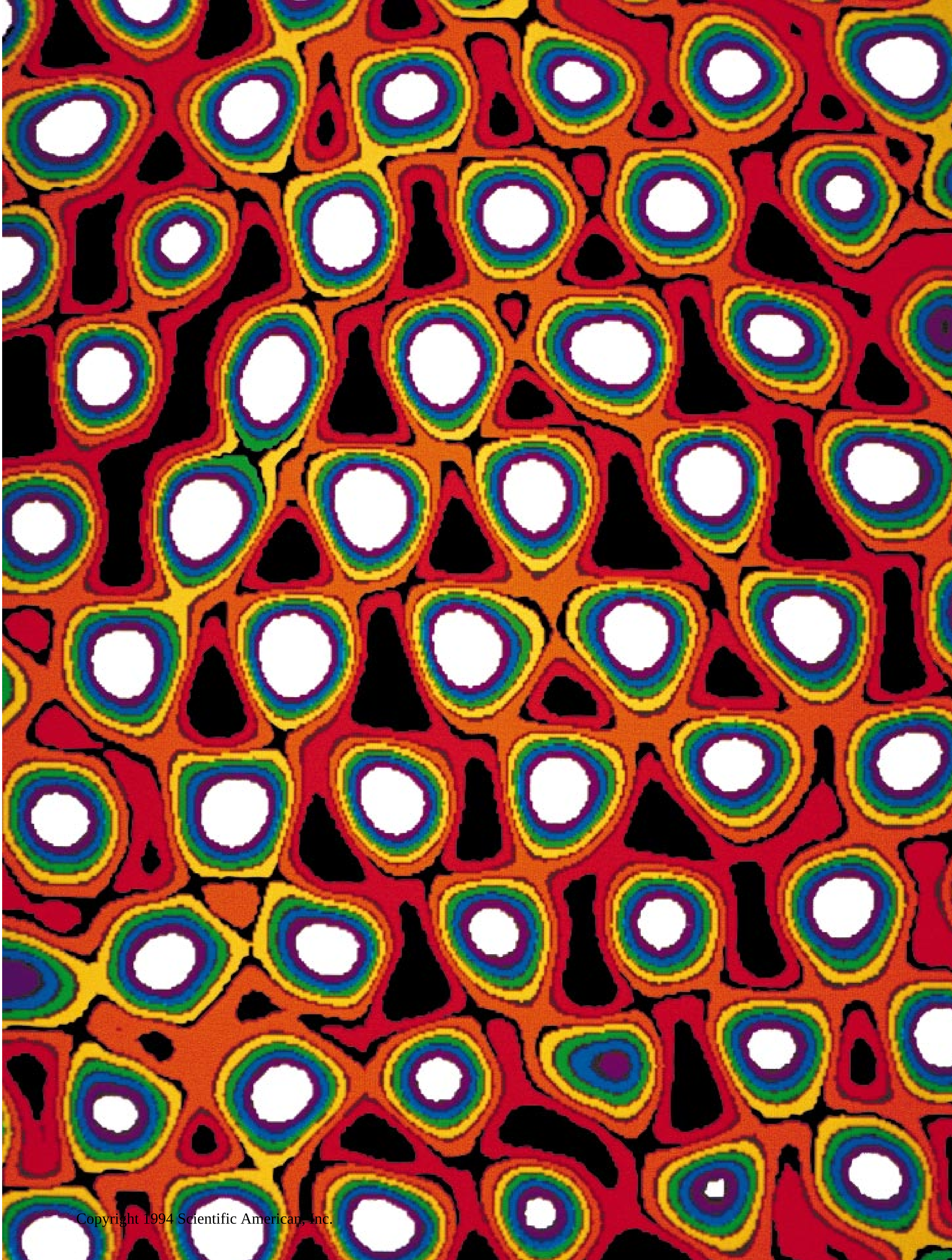
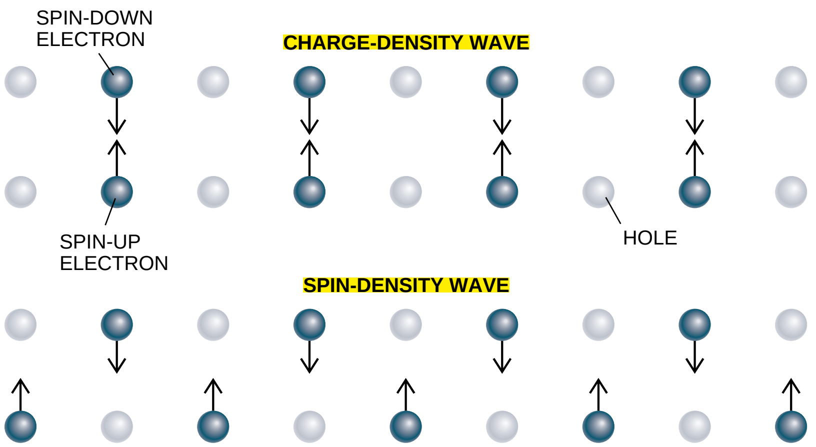
**REGULAR PATTERN of charge-density waves in the material tantalum disulfide is revealed by a scanning tunneling microscope. Peaks of high charge density (*white*) are spaced 12 angstroms apart in a hexagonal array. Robert V. Coleman and C. Gray Slough of the University of Virginia provided the scan.**



## Pairing States

Charge-density waves (*top*) can be thought of as electron-hole pairs as well as electron-electron pairs. (A hole is a vacant quantum-mechanical state; it acts much like a particle.) Looking at the array, we can think of an electron as being paired either with a hole to its right or left or with the electron opposite. (Superconductivity comes from yet another kind of electron-electron pairing.) In spin-density waves (*bottom*), the opposing electron is shifted, so that the total charge density is constant but the spin density goes up and down along the array.

Which of the various pairing states occurs in a given material depends on the strength of the various interactions between the electrons. For instance, if direct electrostatic repulsion between electrons dominates, either a spin-density wave or a spin-parallel (or "triplet") superconducting state is favored. Electrons can also interact by distorting the lattice. The mediation of the lattice leads to attraction between electrons, and either a charge-density wave or a spin-antiparallel (or "singlet") superconducting state results.




The interactions often cause the electrons to become paired up; the pairs subsequently repel one another. Then each pair stays as far away as possible from all other pairs, and an ordered structure like that of the marching band is formed; the charge density becomes bumpy. If we take into account the wave nature of the electrons, a smooth variation of the charge density emerges. This smooth spatial variation of the charge is called a charge-density wave.

In addition to charge, electrons carry around with them something called spin. A spin is a magnetic moment associated with each electron; the moments can assume one of two states, labeled "up" and "down." If electrons with the same spin orientation repel one another, then each up spin wants to have a down spin as a neighbor. The result is a spin-density wave, or SDW. An SDW can be thought of as two CDWs, one for each spin state, superposed, with their peaks in alternate positions. Note that for a charge-density wave the charge varies in space, but not for a spin-density wave.

In general, how the electrons interact—and what kind of quantum-mechanical state is formed—depends on how the electrons' motion is confined. In three dimensions, electrons have the ability to avoid one another by simply moving out of the way. But if they are limited to traveling along a chain of atoms, the electrons cannot avoid one another and tend to interact more strongly. CDWs and SDWs occur mostly in such materials, in which the atoms are lined up in chains. (Many of these materials were first synthesized in the early 1970s.) In some circumstances, the electron pairs attract rather than repel one another, forming a superconducting state.

Chemists often design materials with a chainlike structure; however, they do not have much control over the nature of the electronic interactions. So whether the synthesized substance develops a CDW or an SDW or becomes superconducting cannot be predicted.

Electrons tend to pair at low temperatures. At absolute zero, each electron has its "mate," and the structure is fully ordered. As we warm up the material, some of the pairs become separated; they then induce other pairs to separate. With higher and higher temperatures, more and more pairs are divorced, until the last pair breaks up; above this critical temperature the material has only free electrons and is back to a metal. This process is known as a phase transition, as in the melting of an ice cube. If we reverse the process, cooling the material down from high temperatures, a CDW forms when we cross the phase-transition temperature. The electrons then get stuck. Because small electric fields can no longer dislodge them, and no current flows, the metal changes abruptly to an insulator. This sudden change in electric conductivity in fact signals the formation of a CDW.

Far more direct observations of CDWs have been made using scanning tunneling microscopes, which show the charge density even on atomic scale [*see illustration on preceding page*]. Further, a CDW is accompanied by distortions in the lattice. The distortion pattern, called a superlattice, can be seen by x-ray diffraction: the ions scatter x-rays onto photographic film, displaying a characteristic pattern that reveals their spacing. For example, if the superlattice wavelength is twice that of the lattice wavelength, the x-ray diffraction pattern will show additional spots halfway between the main spots coming from the lattice. (The intensity of the halfway spots relates to the size of the lattice deformation.) The first experiments of this type were performed by Robert Comes and his associates in Paris in the 1970s.

Since a spin-density wave leads neither to a charge fluctuation nor to a lattice distortion, detecting it is much harder. In principle, it could possibly be seen through the magnetic force microscope, an instrument that responds to variations of the spin, but the devices are not yet sensitive enough. The first demonstration of spin-density waves was made by scattering neutrons off chromium. (Neutrons, having spin and no charge, are useful for studying ordered spin structures.) In addition, indirect probes of the magnetic field, such as magnetic resonance—the same technique used in hospitals as a diagnostic tool—are now the only means of sensing the presence of SDWs.

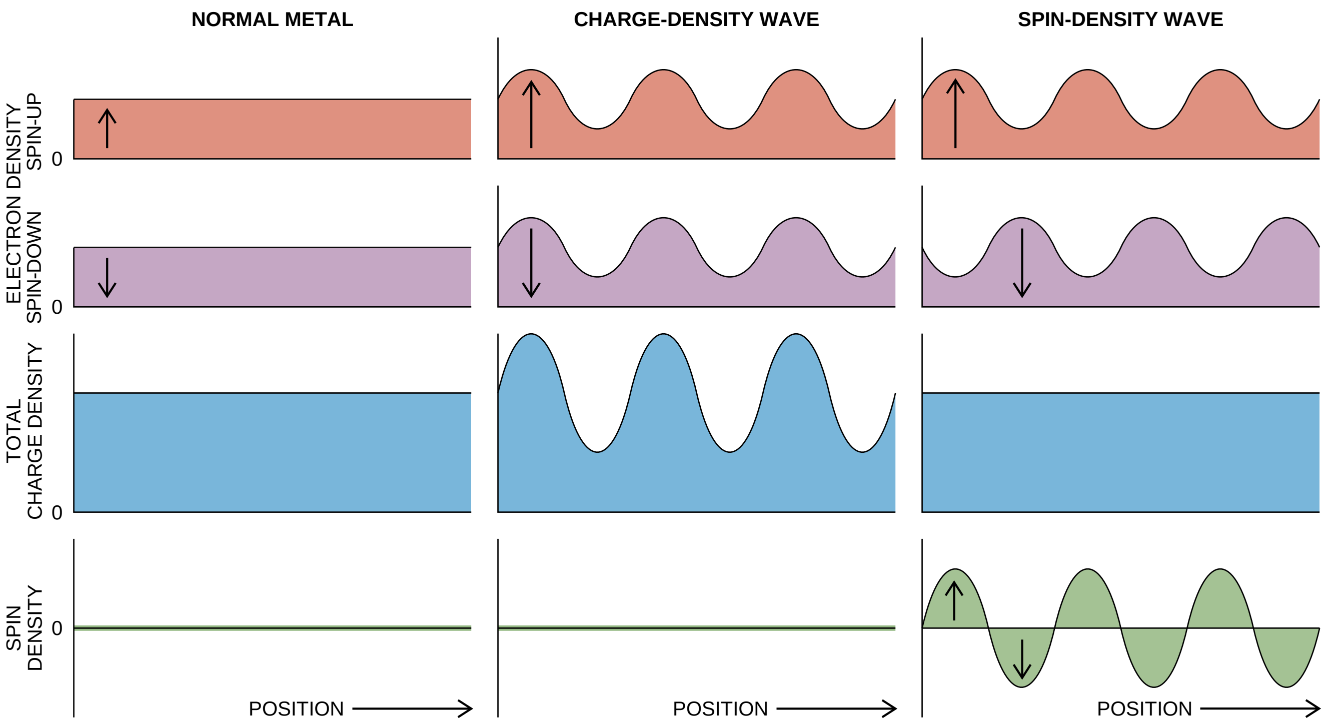
The effects of CDWs and SDWs may also be observed via the motions they perform as a body. These motions can be rather different depending on how the wavelength of the density wave relates to the underlying lattice spacing. The CDW wavelength changes with the number of electrons in the solid: if there are more electrons, the wavelength becomes smaller and, in particular, may not match the original lattice spacing of the ions in any neat way. Then the charge-density wave is said to be "incommensurate" with the original lattice spacing; it floats around unaffected by the lattice until pinned down by a defect. (A defect acts like a pothole—or chewing gum—in the electric potential surface, in which the CDW gets stuck.) But if the charge-density wave and the original lattice spacing are "commensurate" and fit neatly, then, for example, every other student stands in a depression in the road, and it is very hard to get the band moving. For this reason, incommensurate waves are much more intriguing in the varieties of behavior that they display. Commensurate waves—the ones originally envisioned by Peierls—are of largely historical interest.

There are two basic motions that charge-density waves can indulge in as a body, called collective modes. Quantum mechanics allows us to think of these modes as particles, which are then named by the suffix "on." The floating of the crests back and forth and their occasional bunching are a kind of collective mode known as a phason (it involves changing the "phase" of the density wave). For waves that do not fit well with the underlying lattice structure, the floating takes no energy at all (unless a defect pins the wave down), but the bunching takes some. The other way in which CDWs can change is that the crests can get higher. This motion, called an amplitudon, requires a lot of energy. The position and height of the crests may both vary, with variations over shorter distances having higher energies. The energies of these motions were first calculated by Patrick A. Lee, T. Morris Rice and Philip W. Anderson, then at AT&T Bell Laboratories. The SDWs share these collective motions with the CDWs and in addition have a purely magnetic mode that is related to changes in spin orientation. These excitations are called magnons.

The truly dramatic motions occur when we apply an electric field to a solid containing a charge-density wave. A current-voltage relation very different from Ohm's law—in which conductivity is constant—was found in 1986 (in the material niobium triselenide) by Nai-Phuan Ong, Pierre Monceau and Alan M. Portis of the University of California at Berkeley. Since then, some CDW materials have displayed conductivities that vary by several orders of magnitude when very modest electric fields (of less than one volt per centimeter) are applied. We now know that this change in conductivity comes from the depinning and sudden motion of the entire density wave. Even more unusual is the variation of the current as time passes, even when only a constant (DC) voltage is applied. This was first observed by Robert M. Fleming and Charles C. Grimes of AT&T. Our recent measurements, and those of Denis Jérome, Silvia Tomić and others at the University of Paris South and Takashi Sambongi's group at Hokkaido University, have shown that spin-density waves behave much like charge-density waves in the presence of electric fields.

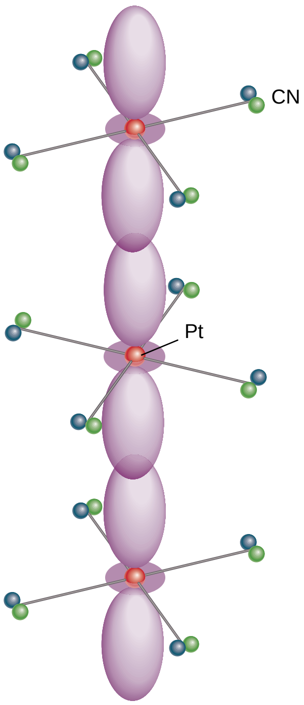
The simplest model that describes the behavior of density waves is called the classical particle model. It was proposed by one of us (Grüner) with Alfred Zawadowski and Paul M. Chaikin, then at the University of California at Los Angeles. The charge-density wave is represented by a single massive particle positioned at its center of mass. The behavior of this particle reflects that of the entire array. When there are no external electric fields, the particle sits on a ribbed surface, like a marble in a cup of an egg tray. This configuration corresponds to the crest of a CDW being stuck at a defect. If we move the CDW, the marble climbs over the edge of the eggcup and falls into the next one, which means that the next crest of the CDW gets stuck at the same defect.

This model allows us to understand much of the versatile behavior of CDWs. The marble is free to move around the bottom of the eggcup and can therefore readjust its position sensitively in re-



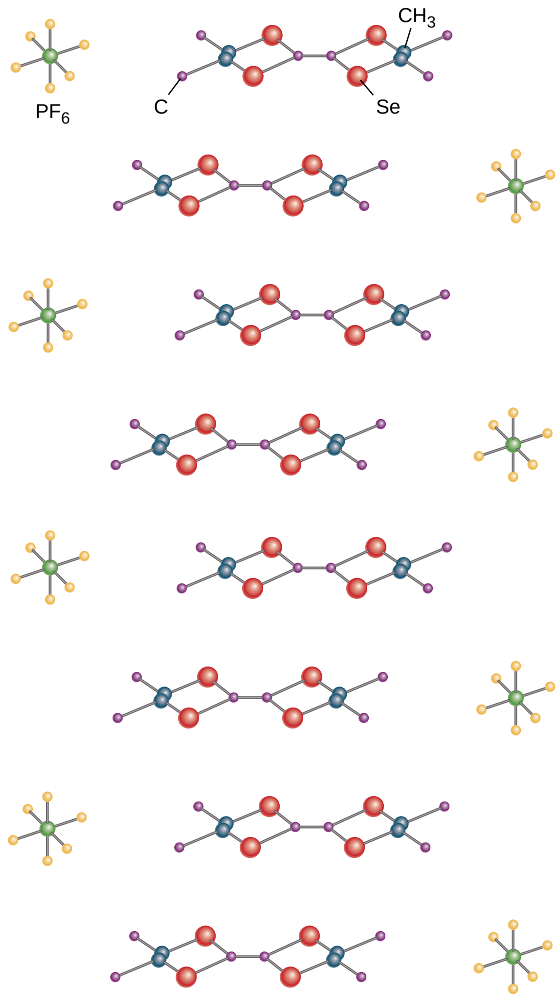

**CHARGE AND SPIN DENSITIES of electrons are shown in normal metals, charge-density waves and spin-density waves. The spin-up (*orange*) and spin-down (*purple*) electron densities vary with position within the crystal. They can be summed to yield the total charge density (*blue*); their difference yields the spin density (*green*).**

## Density-Wave Materials




Two very different types of materials, organic and inorganic, show density waves. The inorganic materials are characterized by chains of transition-metal ions, such as platinum. Within a crystal, each chain is well separated from its neighbors. The electrons move freely along the chains, but the large separation between chains impedes transverse motion, so that the electric conductivity might be from 10 to 1,000 times greater in the chain direction than across. A typical linear-chain compound of the inorganic variety, $K_2Pt(CN)_4Br_{0.3}3H_2O$, or KCP for short, is shown at the left. The vertical lobes (*purple*) show electron orbitals overlapping along the chain. Some other linear-chain compounds having so-called incommensurate charge-density waves are $NbSe_3$, $(TaSe_4)_2I$ and $K_{0.3}MoO_3$.

The other types of CDW materials are grown from flat organic molecules such as the synthetic one, tetramethyltetraselenafulvalene, or TMTSF. Several of these molecules are stacked on one another to form a crystal together with embedded $PF_6$ ions, as shown at the right. Electrons are free to move up and down the stack but not from one stack to the next; thus, the conductivity is again highly anisotropic.




These organic materials are of particular importance in studying electrons in solids because their properties can be fine-tuned. For example, an entire family of TMTSF-based salts can be created by replacing the $PF_6$ anion with $ReO_4$, Br, SCN or $AsF_6$, among others. Each new salt has slightly different interaction strengths between the electrons; these variations can have profound effects. The crystal $(TMTSF)_2ClO_4$, if cooled slowly down to one kelvin, becomes a superconductor, whereas rapid cooling gives a spin-density wave.

sponse to applied electric fields. Because the marble—that is, the charge-density wave—carries charge, its position affects the electric field within the medium. The marble usually adjusts its position so as to reduce the electric field acting on it. Thus, materials with charge-density waves have a large "dielectric constant," so large that they could be called superdielectrics. Our measurements on both charge- and spin-density waves give values for the dielectric constant more than one million times larger than that of ordinary semiconductors.

What happens if we apply a DC voltage? The egg tray on which the marble lies will tilt. If the tilt—that is, the voltage—is great enough, the marble can roll out of the eggcup and down the egg tray. The marble slows down when it climbs up an edge and speeds up when it falls down one. Consequently, its speed, and the electric current, goes up and down with time. These current oscillations, which we have mentioned earlier, are widely observed. The average current is higher if the tilt in the egg tray—that is, the DC voltage—is higher.

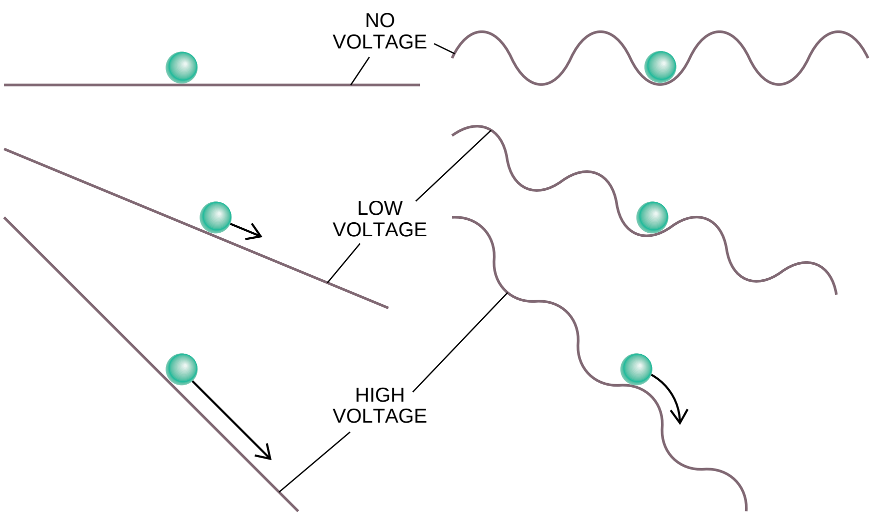
Now suppose that instead of a DC voltage, an AC voltage is applied, in which case the egg tray is rocked back and forth like a seesaw. The marble oscillates back and forth in its cup. This sloshing of the entire density wave scatters light of certain colors, allowing its detection in optical experiments at micron and millimeter wavelengths, as conducted at U.C.L.A. (Conversely, the CDW can sensitively detect electromagnetic radiation.) If we apply both a DC field and an AC field, the former makes the egg tray tilt to one side, whereas the latter makes it jiggle from side to side. Suppose the marble is rolling down the egg tray. If the time the marble takes to go from one eggcup to the next is nearly the same as the time for which the egg tray is tilted "up" by the AC voltage, it will hop between eggcups once each cycle of the AC field. When the marble is hopping down the egg tray with the help of the AC field, augmenting the average tilt of the egg tray by increasing the DC voltage does not change the average current. So if we plot the current versus the DC voltage (in the presence of an AC voltage), we will see the current generally increasing with DC voltage except for certain plateaus where we have a "mode locking" [*see bottom illustration on this page*].

The model we have described, and the equations it implies for the marble's motion, turns out to be applicable in quite diverse situations. For example, it describes a Josephson junction (that between two superconductors), the motion of ions in solids, a pendulum in a gravitational field and certain electronic circuits. Although the equations look simple, they display a variety of solutions, including chaotic behavior.

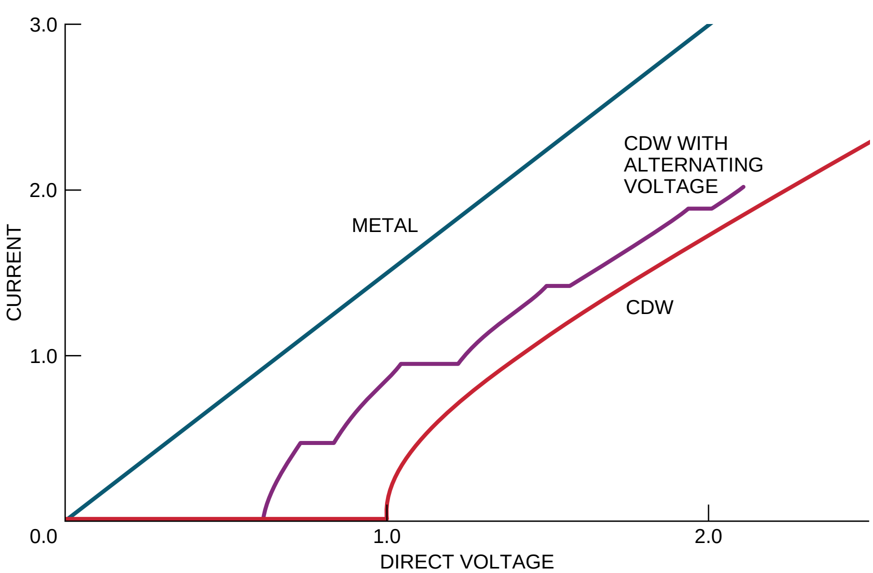
Other behaviors are not so simple to understand. By cooling materials that contain spin-density waves down to almost absolute zero, we find a peculiar phenomenon that has been interpreted as the marble's tunneling through to the next eggcup instead of climbing over its edge. This purely quantum-mechanical effect has since been confirmed by other groups. Tunneling has been predicted by Kazumi Maki of the University of Southern California and by the late John Bardeen of the University of Illinois, but it is too early to tell whether their model applies to our low-temperature experimental findings about SDWs.

Perhaps the most bizarre behavior of all is that of self-organization [see "Self-Organized Criticality," by Per Bak and Kan Chen; SCIENTIFIC AMERICAN, January 1991]. Susan N. Coppersmith and Peter B. Littlewood of AT&T and Kurt A. Wiesenfeld and Per Bak of Brookhaven National Laboratory were the first to deduce this phenomenon, from experiments on CDWs performed by researchers at AT&T and by us at U.C.L.A. Self-organization is a phenomenon that charge-density waves have in common with earthquakes. Just as two tectonic plates rubbing on each other get stuck at ragged edges and then suddenly unstick (with catastrophic consequences), charge-density waves, in the presence of some electric fields, get stuck on defects and suddenly unstick. But the analogy goes deeper. Earthquakes and charge-density waves tend to settle into configurations in which a small disturbance will cause a violent change: they organize themselves into a critical state. The marble balances itself exactly on the thin edge between two eggcups.

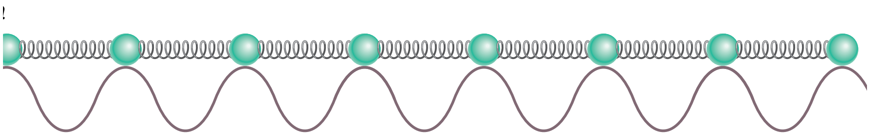
To study the self-organizing behavior, we have to refine our model slightly. Self-organization comes from self-interactions, so our model has to include the push-and-pull between the different regions of the CDW. One marble at the center of mass is no longer enough; we now need a series of marbles attached to their neighbors by springs. This arrangement represents the elasticity of the density wave. Suppose we repeatedly turn on a DC electric field for some time and then turn it off. The marbles move some distance during the "on" time and roll to the bottoms of eggcups when the field is turned off. We would expect them to move farther if the "on" time is longer. But what happens is actually quite different, as was found in simulations by Coppersmith. Just before the field is turned on, the marbles are positioned in neighboring eggcups. When the field is turned off, each is found to be exactly balanced on an edge between two eggcups—no matter how long the field is kept on [*see illustration on next page*]. (After the field is turned off, the marbles roll into eggcups, sometimes to their right and sometimes to their



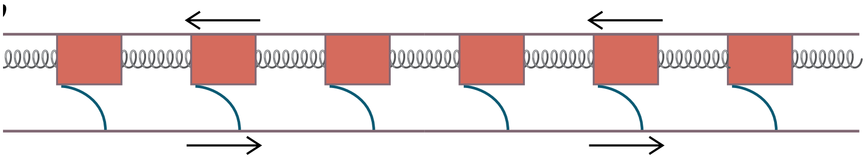

**CHARGED-PARTICLE MODEL shows how current flow in charge-density waves differs from that in normal metals. In a metal (*left*) the particle rests on a flat (electrical potential) surface. If we apply a voltage, the surface tilts, and the particle starts to move: there is a current. For a charge-density wave (*right*), the surface is ribbed. If the applied voltage is low—that is, the tilt is small—the particle changes position only slightly, and there is no current. If the tilt is large enough to get the particle over the barrier, the particle runs down the ribbed surface. Then the current goes up and down in time as the particle climbs over each barrier.**




**CURRENT VERSUS VOLTAGE is plotted for metals and charge-density waves. In a metal (*blue*) the current increases linearly with voltage. For a charge-density wave, there is no current until the voltage increases to a critical value; only then does the current start to flow (*red*). If in addition to a direct voltage we apply an alternating one, the curve shows plateaus (*purple*). The plateaus correspond to a "mode locking" when the flow of the charge-density wave matches the alternating frequency.**



CHARGE-DENSITY WAVE MODEL



EARTHQUAKE MODEL

**SELF-ORGANIZED BEHAVIOR is compared for models of charge-density waves and earthquake faults. The particles attached by springs represent the position and elasticity of the charge-density wave (*a*). The particles rest on a ribbed surface. If one turns an electric field on and off repeatedly, the marbles are found to sit in the most unstable position possible: each on top of a hill. In the earthquake model (*b*) the blocks are attached to a surface moving sideways with respect to the lower surface. The lower surface has metal strips that drag on the blocks; the blocks are also connected by springs. After some arbitrary (unpredictable) time, the accumulated strain makes the blocks rearrange their positions catastrophically. But the new positions are again unstable. The photograph shows the San Andreas fault in Carrizo Plain, east of San Luis Obispo, Calif.**

left.) This bizarre self-regulatory behavior is easier to study in charge-density waves than in earthquakes. It has given the former a particular use in testing complex dynamical theories.

In fact, the density-wave states are probably just the simplest periodic configurations of electrons we can hope to find. Several theories suggest a hierarchy of more complex arrangements. One suggestion came from theoretical physicist Eugene Wigner in 1939. Wigner showed that if the density of electrons is low enough—say in a collection of electrons moving freely in two dimensions—they would settle into a crystalline pattern. Since then, many researchers have searched for "Wigner crystals." In the early 1980s Grimes and Gregory Adams, also at AT&T, showed that electrons deposited on the surface of liquid helium form just such a crystal. Evidence of their presence in solid-state systems has come from groups at Saclay, France, AT&T and elsewhere.

The various properties of density-wave materials have yet to be applied toward enhancing our comfort. Still, plans abound. The dielectric constants of CDW materials, besides being enormous, also change with the electric field; they could be implemented in circuits as tunable capacitors. The strong response of charge-density waves to electromagnetic radiation could make them useful as light detectors; at low temperatures, this sensitivity would ultimately be limited by quantum mechanics. Bardeen, better known for the theory of superconductivity and the invention of the solid-state transistor, worked out the theory of the quantum transport of density waves. Whether quantum detectors such as he envisaged can be built and put to practical use remains to be seen. Right now, we are happy enough just to learn more about the idiosyncracies of charge- and spin-density waves.

FURTHER READING

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