Charge-Density-Wave Conductors

Low-dimensional metals with moving lattice modulations display a host of unusual properties, including gigantic dielectric constants and the ability to 'remember' electrical pulse lengths.

Robert E. Thorne

When metals are cooled, they often undergo a phase transition to a state exhibiting a new type of order. Metals such as iron and nickel become ferromagnetic below temperatures of several hundred degrees Celsius; electron spins order to produce a net magnetization in zero field. Other metals, such as lead and aluminum, become superconductors at cryogenic temperatures; electrons form Cooper pairs of opposite spin and momentum, leading to electrical conduction with zero resistance and to expulsion of magnetic fields.

Since the mid-1970s, a wide range of quasi-one-dimensional metals have been discovered that undergo a different type of phase transition both above and below room temperature: They become charge-density-wave (CDW) conductors. These materials (examples of which are shown in figure 1) show strikingly nonlinear and anisotropic electrical properties, gigantic dielectric constants, unusual elastic properties and rich dynamical behavior. The ideas that explain these phenomena span much of contemporary condensed matter physics. For these and other reasons, CDW conductors rank among the most remarkable electrically conducting materials ever discovered.[1]

What is a charge-density wave?

A CDW is a modulation of the conduction electron density in a metal and an associated modulation of the lattice atom positions, as shown in figure 2. Although similar modulations are observed in many different types of solids, those that give rise to the unusual properties of quasi-one-dimensional metals have three special features: Like conventional superconductivity, they are caused by an instability of the metallic Fermi surface involving the electron–phonon interaction; they result in energy gaps at the Fermi surface; their wavelength λ_c is π/k_F, where k_F is the Fermi wavevector.

The mechanism by which CDWs might form was discussed by Rudolph Peierls in 1930.[2] Consider a quasi-one-dimensional metal consisting of chains of equally spaced atoms. The allowed conduction electron states form a band, as shown in figure 2. States inside the Fermi surface, with energies less than E_F and wavevectors less than k_F, will be occupied, and states outside the Fermi surface will be empty. If an energy gap is opened at $k = \pm k_F$, then the energies of the occupied states below E_F will be lowered, reducing the total electronic energy.

How might such a gap be produced? Most electronic energy gaps in solids arise from a Fourier component of the lattice potential in which the electrons move. Peierls pointed out that a modulation of the positions u_n of the lattice atoms of the form $\delta u_n = \delta u \cos[Qz + \phi]$ with wavevector $Q = 2k_F$ (and wavelength $\lambda_c = \pi/k_F$) would produce gaps at $\pm k_F$. In quasi-one-dimensional metals at low temperatures, the elastic energy cost to modulate the atomic positions is less than the gain in conduction electron energy, so the CDW state is the preferred ground state. At high temperatures the electronic energy gain is reduced by the thermal excitation of electrons across the gap, so the metallic state is stable. The second-order phase transition that occurs between the metallic and CDW states is known as the Peierls transition.[3]

The CDW state is characterized by a complex order parameter $\Psi = \Delta e^{i\phi}$. The magnitude Δ determines the size of the electronic energy gap and the amplitude δu of the atomic displacements. The phase ϕ determines the position of the CDW relative to the underlying lattice. Variations of ϕ and Δ can arise from collective excitations known as phasons and amplitudons, respectively.

CDW 'sliding'

Looking at the single-particle energy diagram in figure 2b, one might guess that CDW conductors are semiconductors: They have a band of filled states separated by an energy gap from a band of empty states. But like superconductors, CDW conductors have a collective charge transport mode. As shown in figure 3, when an electric field is applied, the CDW can "slide" relative to the lattice. The lattice atoms oscillate back and forth, producing a traveling potential, and the conduction electrons move with this potential, producing a current.

Many ideas of CDWs were developed in early attempts to explain superconductivity. In 1941, John Bardeen suggested that "in the superconducting state there is a small periodic distortion of the lattice" that produces energy gaps, and that these gaps would lead to enhanced diamagnetism.[4] Bardeen abandoned this idea when he realized the difficulty of obtaining an appropriate arrangement of gaps on the three-dimensional Fermi surfaces of common superconductors. In 1954, Herbert Frohlich described a detailed theory of "one-dimensional superconductivity" that predicted CDW formation and collective charge transport.[5]

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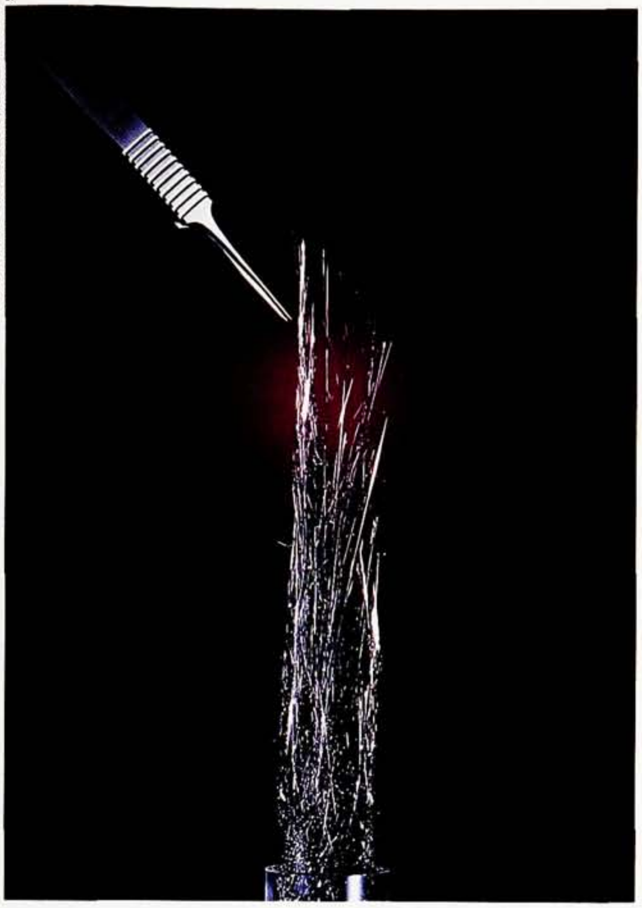

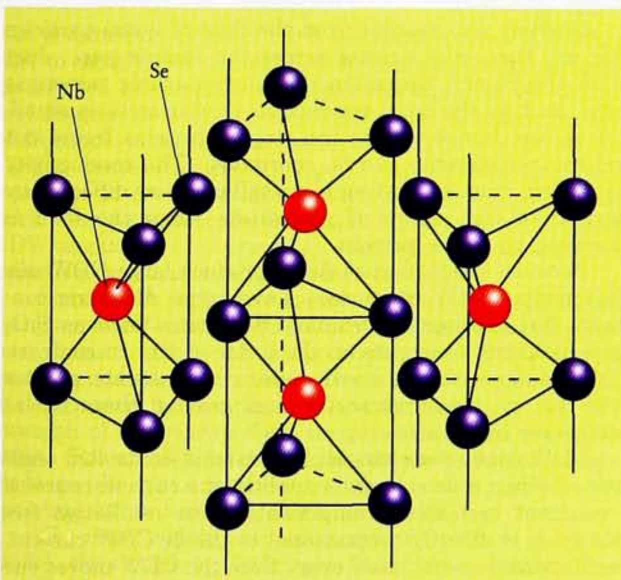

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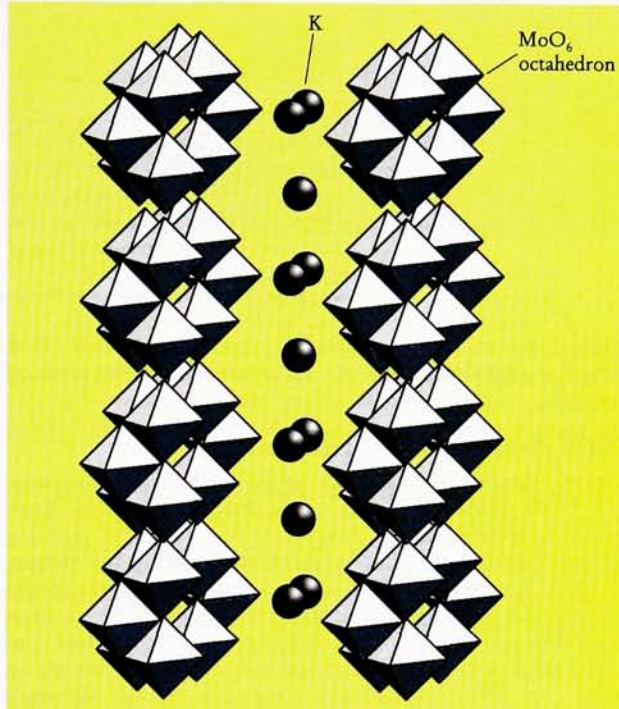
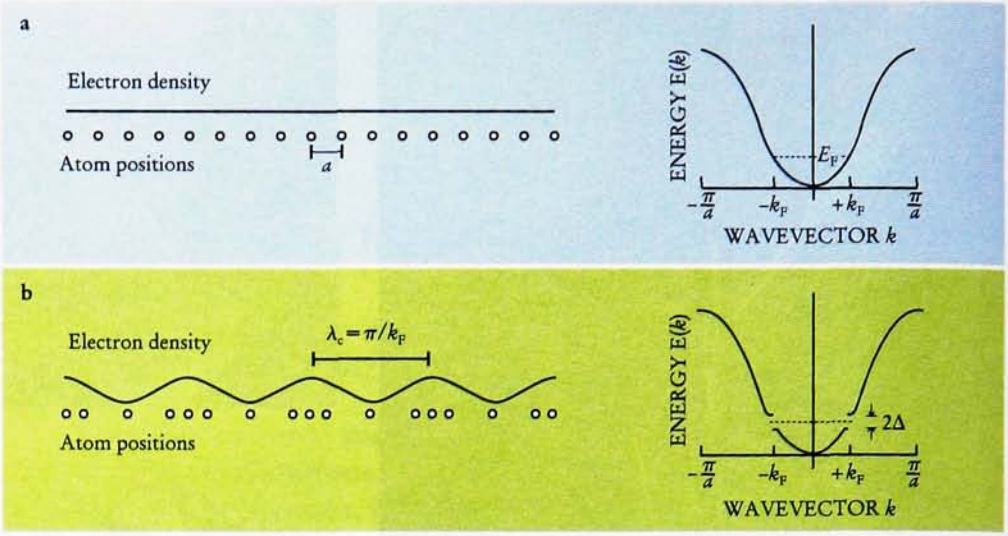


CDW MATERIALS and their structures.
a: Single-crystal whiskers of $NbSe_3$ grown by vapor transport. **b:** Centimeter-sized crystals of $K_{0.3}MoO_3$ ("blue bronze") grown by high-temperature electrochemistry. Despite widely varying crystal morphologies, CDW materials share a common architecture consisting of weakly coupled molecular chains. Electrons move easily along the chains and much less easily perpendicular to them, giving the quasi-one-dimensional character necessary for the formation of charge-density waves. FIGURE 1

Frohlich's theory bears a striking formal similarity to the BCS theory that followed three years later.

Real CDW conductors are not superconductors. Various mechanisms damp the collective motion at nonzero temperature, leading to finite resistance. More important, CDWs are pinned to the underlying lattice. If the CDW's wavelength λ_c is an integral multiple of the lattice period, then the CDW will have preferred positions relative to the lattice and when translated its energy will oscillate with a period λ_c. On the other hand, if the CDW's wavelength is incommensurate with the lattice period—as is the case in most quasi-one-dimensional metals—then it will be pinned by impurities and other lattice defects. In the presence of a single impurity, the CDW would minimize its energy by adjusting its position so as to place a crest or trough at the impurity. In the presence of many impurities, the CDW elastically deforms to optimize its impurity interaction energy, just as a heavy corrugated rubber sheet might respond when laid over a random bed of Teflon posts. As in the commensurate case, when the CDW is translated its energy oscillates with a period λ_c. In both cases the CDW remains pinned for small electric



FORMATION OF CDWS. A quasi-one-dimensional metal, as represented in **a**, can reduce its energy by developing a CDW, as in **b**. A CDW consists of coupled modulations of the conduction electron density and the atomic positions. The modulations have wavelength $\lambda_c = \pi/k_F$ and produce an energy gap at the Fermi surface $k = \pm k_F$. The modulations are usually quite small; atomic displacements are only about 1% of the interatomic spacing, and the conduction electron density varies by several percent. Fluctuations prevent CDW formation in strictly one-dimensional systems, and so some transverse coupling between one-dimensional chains is essential. **FIGURE 2**

fields, and it slides only with the application of fields that exceed a threshold field E_T determined by the pinning strength.

CDW materials and phenomena

A large number of materials undergo Peierls transitions to a CDW state. Only a small fraction of these have shown collective charge transport due to CDW motion, perhaps because pinning by defects is usually too strong. In 1973, Bardeen suggested that Frohlich's ideas might explain the unusual electrical properties of the quasi-one-dimensional organic conductor TTF–TCNQ, but the experimental results remained controversial for many years. In 1977, Nai-Phuan Ong and Pierre Monceau discovered[6] unusual transport properties in $NbSe_3$, synthesized two years earlier by Alain Meerchaut and Jean Rouxel; x-ray diffraction and nuclear magnetic resonance measurements confirmed that moving CDWs were responsible. CDW transport has since been observed in inorganic conductors such as TaS_3, $(TaSe_4)_2I$ and $K_{0.3}MoO_3$ and in organic conductors such as $(fluoranthene)_2PF_6$ and $(perylene)_2Au(maleonitriledithiolate)_2$.

As shown in figure 1, these materials generally consist of molecular chains that are weakly coupled together and along which electrons are highly delocalized. Above their Peierls transitions, they are anisotropic metals. Electrical conductivities along the chains are typically three orders of magnitude smaller than that of copper and one to three orders of magnitude larger than that perpendicular to the chains. In $NbSe_3$ and $K_{0.3}MoO_3$—the two most widely studied materials—CDWs form at 145 K and 180 K, respectively. In NbS_3, CDWs form at 340 K, and so CDW transport can be observed above room temperature.

CDW conductors are remarkable both for the diversity of phenomena they exhibit and for the ease with which many of these phenomena can be observed. Unlike in virtually all other bulk materials, electrical conduction in CDW metals is nonlinear at modest electric fields. As shown in figure 4, the CDW current is zero below a threshold field E_T and increases above it.[7] The threshold E_T is determined by the impurity concentration and can be less than 1 mV/cm in pure crystals. The energy a metallic electron could gain by traveling a mean free path in such a small electric field is orders of magnitude smaller than kT, confirming that E_T is a threshold for collective charge transport.

Current also results from the flow of quasi-particles that are thermally excited across the Peierls gap. Just below the Peierls transition the single-particle current is large, and so the total conduction nonlinearity is small. But at low temperatures the single particles freeze out and the nonlinearity can be enormous. The conductivity can switch from insulating to metallic values differing by more than ten orders of magnitude when the field is increased by a few percent.

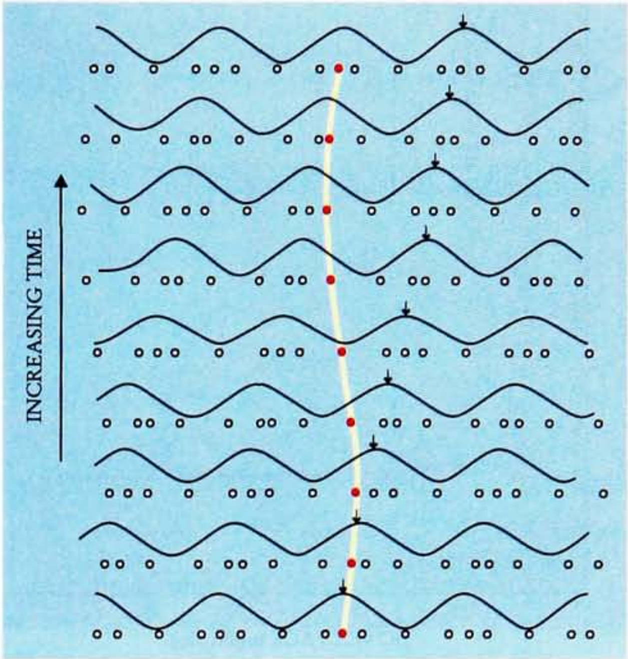
Because small electric fields produce large CDW displacements, CDW conductors have large dielectric constants but are lossy. Ordinary dielectrics such as SiO_2 have dielectric constants on the order of 10. In contrast, CDW conductors can have dielectric constants greater than 10^9 at low frequencies and greater than 10^3 at microwave frequencies.

CDW conductors can act like current-controlled oscillators. When a dc voltage is applied, the current contains a coherent oscillating component.[7] The oscillation frequency ω_c is directly proportional to the dc CDW current. Oscillations occur because every time the CDW moves one wavelength, the local forces that it feels due to each impurity complete one cycle. Consequently, the CDW's configuration evolves periodically in steady-state sliding, and the frequency ω_c is determined by the CDW velocity $v = \lambda_c\omega_c/2\pi$ and thus by the CDW current. Analogous oscillations due to the ac Josephson effect are observed in superconducting tunnel junctions.

When ac and dc voltages are applied together, the dc current–voltage characteristic exhibits steps of constant CDW current. These steps are analogous to Shapiro steps observed in Josephson junctions, and are due to mode locking of the internal CDW frequency ω_c with a rational multiple of the applied ac frequency ω. Harmonic steps with $\omega_c/\omega = p$ are observed, as are subharmonic steps with $\omega_c/\omega = p/q$, where p and q are integers. Hundreds of subharmonic steps with p/q as small as 1/30 can be seen in high-quality single crystals, as shown in figure 5. At some temperatures the simple mode-locking behavior gives way to a period-doubling route to chaos.[8] This surprisingly complex yet clean behavior is observed in bulk material, and is due to CDW interaction with random impurities.

CDW conductors can "remember" previous inputs. For example, if a series of current pulses are applied, the CDW response to a given pulse depends upon the sign of the preceding pulse. Memory effects result because a static CDW interacting with randomly distributed impurities can assume many different metastable configurations; the particular configurations assumed depend upon past inputs. CDW conductors also have unusual electromechanical properties.[9] CDW depinning can change a CDW conductor's elastic moduli by up to 20%, and can produce metastable changes in the conductor's length.

Similar properties have been observed in spin-density-wave conductors[10] such as $(TMTSF)_2PF_6$. Spin-density waves are close cousins of CDWs that arise in quasi-one-dimensional metals where there are strong electron–electron interactions. A spin-density wave can be considered to consist of two CDWs of opposite spin displaced relative to each other by half a wavelength, producing an antiferromagnetic variation of the conduction electron spin. A spin-density wave has almost no electronic charge modulation and no measureable lattice modulation. However, it does produce an energy gap at the Fermi surface, is pinned by impurities and can slide when depinned by electric fields.



CDW 'SLIDING.' When an electric field is applied, the conduction electron wave moves with the traveling lattice wave, illustrated in these snapshots at successive times. This sliding results in collective charge transport. More detailed considerations show that the current associated with a given wave velocity is determined by the total conduction electron charge density, not the modulation charge density. FIGURE 3

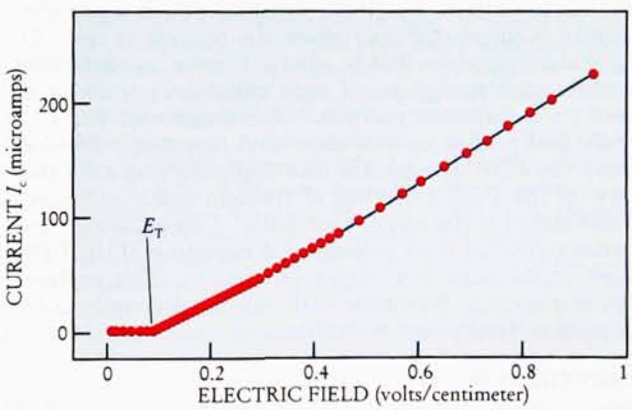
Models of CDW transport

The diverse properties of CDW conductors are due in large part to the physics of how a CDW interacts with randomly distributed impurities. The essential ingredients—damping, disorder and elastic interactions among many degrees of freedom—underlie the behavior of many systems including vortex lattices in type-II superconductors, fluid interfaces in porous media, domain walls in magnets, magnetic bubble arrays and earthquake faults. For this reason, CDW conductors have served as a model system for studying collective dynamics in the presence of disorder.

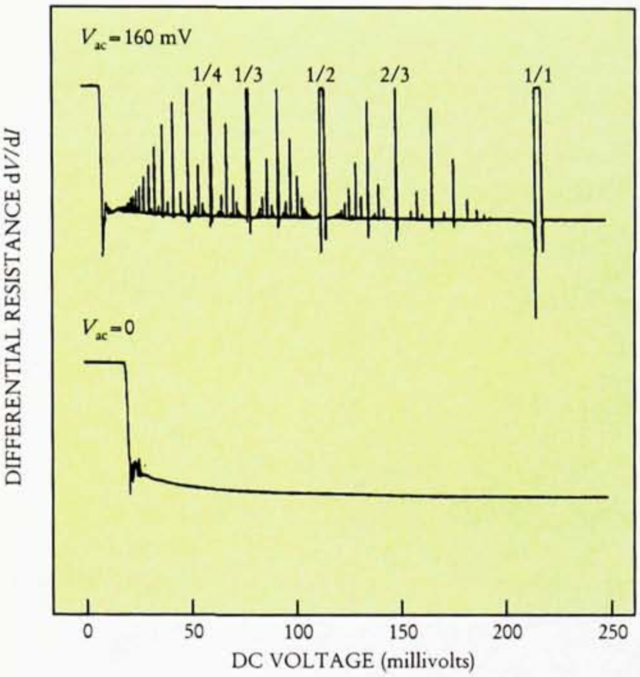
Some CDW properties can be qualitatively reproduced using a model that treats the CDW as a single overdamped particle moving in a periodic potential, much like a marble on a corrugated metal sheet. The strength of the pinning is determined by the depth of the corrugations, and the strength of the electric field corresponds to the tilt of the sheet. For small tilts the marble displaces in its trough; for large tilts it can roll from trough to trough, periodically speeding up and slowing down as it rolls.

The most widely studied model of CDWs is the FLR model, developed by Hidetoshi Fukuyama, Patrick Lee and T. Maurice Rice.[11] This model treats the CDW as a classical extended elastic medium (a rubber sheet) that interacts with random impurities and couples to an electric field. Large-scale numerical simulations and analytic calculations using this and related models have provided insight into many experimental phenomena.[12] Quantitative comparisons between calculations and experiment have met with less success, and experiments have not probed the short-length-scale dynamics predicted to underlie macroscopic properties.

Much attention has focused on the CDW response near the depinning threshold.[12,13] Daniel Fisher suggested in 1983 that CDW depinning can be viewed as a dynamical phase transition. Above threshold a velocity–velocity correlation length characterizes the scale on which local CDW motions are correlated; below threshold a second correlation length characterizes the size of the regions that respond when the CDW is locally perturbed. As in conventional thermodynamic phase transitions, these correlation lengths diverge as the critical point—the threshold field—is approached (as illustrated in figure 6), and scaling forms characterize static and sliding state quantities in terms of a reduced field $f = (E - E_T)/E_T$. Early experiments seemed consistent with the predicted form for the CDW velocity $v_c \propto f^{\beta}$. But subsequent theoretical and experimental work has shown that the critical regime occurs extremely close to threshold ($|f| < 0.01$), and that experimental systems are sufficiently "small" that finite-



CURRENT-FIELD CHARACTERISTIC of a CDW conductor. For electric fields less than a threshold E_T, the CDW remains pinned to impurities. Above E_T the CDW depins and slides relative to the lattice. Data are for $NbSe_3$ at 120 K. FIGURE 4



MODE LOCKING of CDWs. When ac and dc voltages are applied together, the dc current–voltage characteristic exhibits steps of constant CDW current. These steps appear as peaks in the differential resistance dV/dI, which rise toward the value of the single-particle resistance that shunts the CDW. The steps (peaks) are due to mode locking of the internal CDW frequency ω_c with a rational multiple of the applied ac frequency ω—that is, $\omega_c/\omega = p/q$. Data are for $NbSe_3$ at 120 K. FIGURE 5

size effects make the critical regime unobservable. These ideas developed for CDW systems have been applied in analyzing other dynamical systems, and experimental tests are in progress.

The greatest successes of the FLR model have come in accounting for phenomena where the CDW's many elastic degrees of freedom are essential in predicting features qualitatively. For example, the subharmonic steps observed on the dc I–V characteristic when ac and dc excitations are applied together are not predicted in simple models. In the FLR model, they arise from spatial structure in the dynamics of the moving CDW: Different regions advance at different times during the period of the motion.

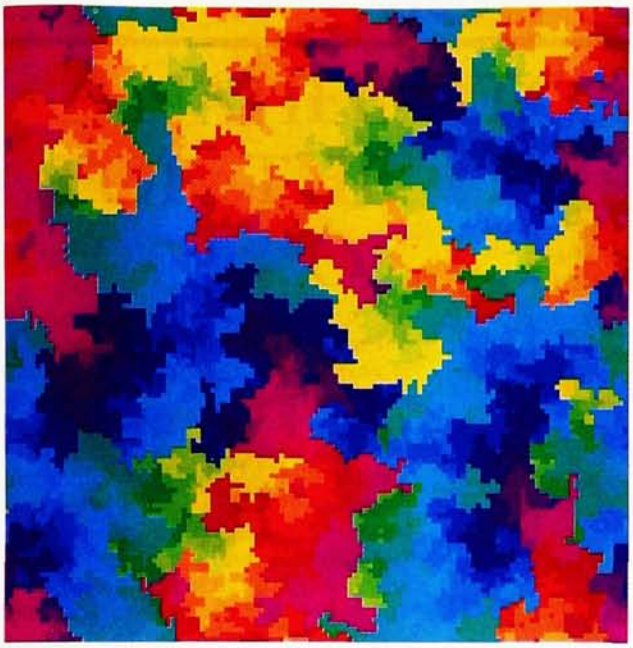
Perhaps the most striking example is the pulse-duration memory effect.[14] When a series of equal-length voltage pulses is applied to a CDW conductor, the CDW current oscillates due to the locally periodic CDW interaction with impurities. Remarkably, for a broad range of experimental conditions, the current at the end of each pulse is always increasing, regardless of the pulse length. The CDW thus "remembers" or "learns" the length of the pulses. This effect is not shown by a single overdamped particle moving in a periodic potential. Such a particle's velocity is increasing only when the particle is near the top of the potential—that is, when it is near its least-stable position—but at the end of each pulse the particle finds itself in a different position. Simulations of the FLR model and related models show that repeated pulses can cause the CDW to organize into configurations such that most of the CDW's degrees of freedom reach minimally stable states at the end of each pulse. The pulse-duration memory effect is thus considered a signature of the CDW being on the edge of its region of stability. This explanation of a seemingly esoteric CDW effect led directly to the ideas of self-organized criticality.

Current research issues

Despite substantial experimental and theoretical progress during the last 15 years, many aspects of CDW systems remain obscure. Although nearly all calculations of CDW transport properties have assumed that the CDW is perfectly elastic and does not tear, many experiments indicate that the CDW is plastic and can tear rather easily.[15] CDWs can be viewed as simple crystals, and, like ordinary crystals, they exhibit dislocations and other defects. When electric fields are applied, the stresses that develop as the CDW elastically deforms can generate dislocations and cause them to climb and glide. This results in conversion between CDW charge and single-particle charge, in a process analogous to phase slip in superconductors and superfluids. CDW dislocations can have large effects on the CDW I–V characteristic near threshold and can result in enormous low-frequency noise with a $1/f$-like spectrum. The details of how CDW dislocations form and move and how they affect CDW dynamics are not understood.

The properties of CDW conductors at low temperatures are also poorly understood.[16] Below roughly one-third of the Peierls transition temperature, the I–V characteristic develops a second characteristic field E_T^* well above E_T, below which the CDW conductivity "freezes out" with decreasing temperature and above which it increases abruptly with decreasing temperature. The CDW's dielectric properties change dramatically, and at liquid-helium temperatures the electrical and thermal properties exhibit many features characteristic of a glass. These effects are thought to arise from the freeze-out of single-particle excitations. Pinning-related CDW compressions and expansions change the CDW charge density, and at high temperatures these density variations are screened by thermally excited single particles. At low temperatures the single-particle density is very low and the screening is ineffective, so the CDW is stiffened by Coulomb interactions. Although calculations have reproduced some important qualitative features of some experiments, quantitative discrepancies are very large, and many other qualitative features have yet to be explained.

Compared with other conducting materials studied in bulk form, CDW conductors show an extremely rich variety of properties. Could these properties be put to use in practical applications? CDW memory devices, switches, rectifiers, mixers and optical detectors have all been proposed. At present it is not clear that such devices would have advantages over existing technologies, or that any advantages would be sufficient to warrant the investment needed for commercialization. Evaluating the potential of CDW a



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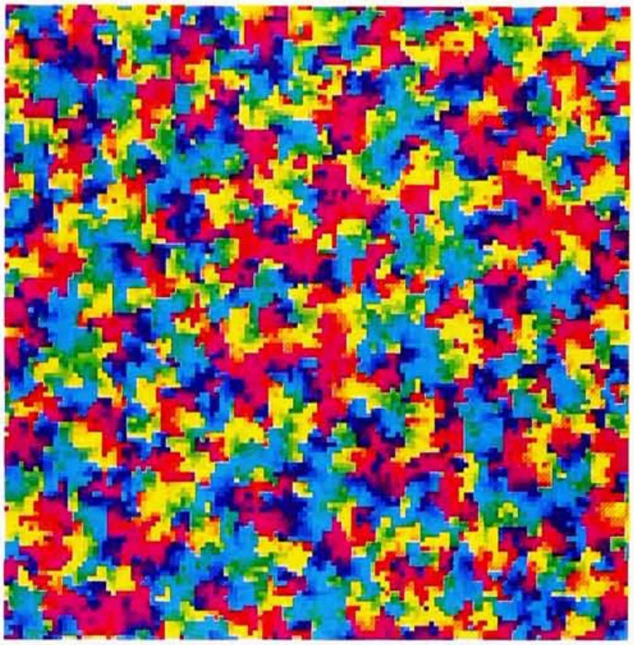

MANY-DEGREE-OF-FREEDOM DYNAMICS. If CDW defects are not allowed, simulations of the FLR model show that the CDW's configuration evolves periodically in the sliding state. The spatiotemporal pattern of motion during each period is complex, and different regions advance at different times. Here, the advance times in a two-dimensional simulation are indicated using a periodic color map. The characteristic size of the regions in which CDW motion is correlated is large very close to the depinning threshold (**a**) and decreases away from threshold (**b**) as the CDW moves faster. (Adapted from Myers and Sethna, ref. 12.) **FIGURE 6**

conductors has been difficult because experiments have been confined to single crystals, which grow in inconvenient shapes and sizes, are often difficult to contact electrically and have imperfections that corrupt measured properties.

Two recent developments promise to change the direction of CDW research and to integrate it into the mainstream of research on conducting materials. First, a three-terminal CDW device—a MOSFET-like heterostructure in which the channel is formed by a CDW conductor—has been fabricated.[17] An applied gate voltage modulates the collective CDW conductance and can be used to change the CDW wavelength and energy gap. Second and more significant, Herre van der Zant, Cees Decker and their coworkers at the Delft University of Technology have synthesized oriented films of a sliding CDW material.[18] Standard film-patterning techniques should permit a sample's geometry to be precisely controlled, and allow unprecedented study of meso- and microscale aspects of CDW physics. Furthermore, CDW films will permit new types of heterostructures and devices involving novel interactions between electronic states. The opportunities these developments provide should ensure that CDW conductors remain a productive venue for pursuing the electronic properties of condensed matter for many years to come.

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