PERSPECTIVES: SUPERCONDUCTIVITY

Self-Organized One Dimensionality

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The latest installment in the mystery series entitled "High–Transition Temperature (T_c) Superconductivity" is called "Stripes" (*1*). Stripes are a complex form of electronic self-organization that occurs in close proximity to the superconductivity found in copper cuprates. Stripes are particularly well developed at low dopings where superconducting T_c's are relatively low and seem to fade away at the dopings at which the T_c's are highest. Although superconductivity and stripe order thus compete with each other to some extent, they are believed by many to reflect a common underlying physics. Two papers in this issue of *Science* report on some unusual electronic properties of fully developed stripes, providing novel clues on the physics behind superconductivity (*2*, *3*).

Zhou *et al.* (*2*) on page 268 present an ingenious analysis of photoemission data on a material that shows well-developed stripe order. Aspects of these data look quite similar to those of the best superconductors. The authors uncover structures that support the central hypothesis underlying the stripe interpretation: the notion that the strongly interacting two-dimensional electron system self-organizes into one-dimensional substructures. Noda *et al.* (*3*) on page 265 find indications that the stripe phase is a metal of the most peculiar kind. Their experiments hint at the possibility that a quantum liquid crystal is realized, a state of two-dimensional electronic matter that is metallic in one direction and insulating in the other.

What do these findings tell us about superconductivity? The photoemission work suggests that the gap in the electronic spectrum that was previously associated with superconductivity is actually more closely related to the stripes. This is hard to reconcile with the conventional Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity. Even more destructive for this still popular conventional picture would be the quantum liquid crystal: BCS theory insists that the competitor of the superconductor is the normal metallic state and nothing else.

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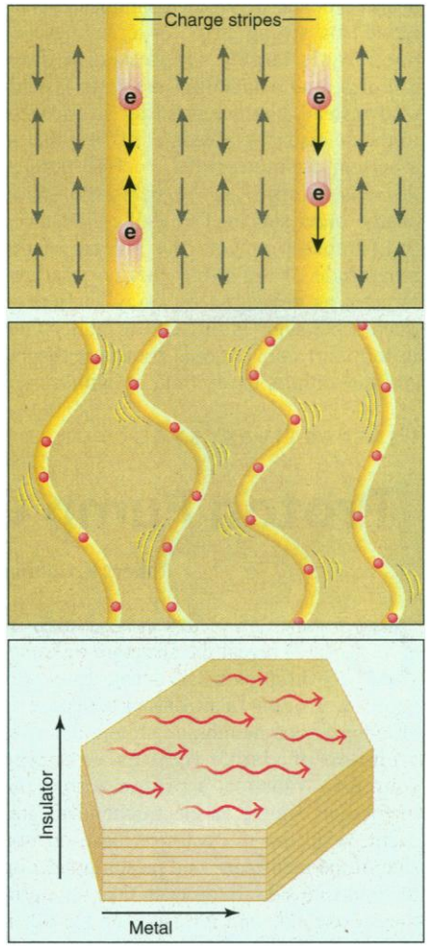
The stripe phase was first observed in 1995 by Tranquada *et al.* (*4*) by neutron scattering. The study suggested that the mobile charge carriers in the perovskite planes of cuprates are confined in narrow one-dimensional lines ("charge stripes"). These stripes are separated by insulating regions showing antiferromagnetic spin order, similar to the electronic state of the parent Mott insulators such as La_2CuO_4, in which the electron are localized because of strongly repulsive electron-electron interactions. These stripe patterns were previously predicted (*5*) as a generic outcome of mean-field theory, which has been successful in explaining other forms of electronic order (for example, the BCS theory of superconductivity). Although it appears to offer the right explanation for stripes in other doped transition metal oxides (*6*), mean-field theory falls short for stripes in cuprates for which it predicts insulating behavior, whereas cuprate stripes are metals or even superconductors. The reports by Zhou *et al.* and Noda *et al.* offer new clues: There appears to be an element of truth in the logic of mean-field theory, but crucial aspects of the real system behave completely differently.

According to mean-field theory, magnetic domains should act as potential barriers confining the low-lying electronic states to the one-dimensional charge stripes. One would therefore expect to see fingerprints of one-dimensional band structure (see the top panel in the figure). Using angular resolved photoemission, Zhou *et al.* find such a fingerprint, but only if they integrate their spectral functions over a large (0.5 eV) energy range, thereby determining the distribution of occupied momentum states. The observed momentum distribution is strikingly consistent with the expectation for the quarter-filled one-dimensional bands associated with the "half-filled" stripes deduced from neutron scattering (*6*). However, at lower energies, a strong dependence on the momentum perpendicular to the stripe direction is found. As a result, the momentum distribution at low energies looks two-dimensional, with pockets of low-lying states at certain locations in momentum space. In fact, these low-energy states look quite similar to those found in the best superconductors, with the only difference being that the so-called "nodal fermions" of the superconductors are absent in the striped cuprate.

How can the electrons that are one-dimensional at high energies rediscover the two-dimensional world at low energies? Within established electronic structure theory, this appears to be a paradox. However, the electrons may indeed be confined to the stripes and the stripes themselves may be subject to quantum meandering motions (see the middle panel in the figure). The trajectory of an electron moving on a



Stripes in motion. A possible interpretation of the photoemission and transport measurements in (*2*, *3*). (**Top**) At high energies (<0.5 eV) and short distances, the charge carriers are confined to the charge stripes, showing the fingerprints of one-dimensional quantum-mechanical delocalization. (**Middle**) At intermediate energies (<0.2 eV), the holes recover two-dimensional motion, which might be due to quantum meandering motions of the charge stripes, dragging around the holes on the stripes. (**Bottom**) On the macroscopic scale, the one-dimensional charge motions recover, giving rise to a system that is insulating in one direction and metallic in the other: the quantum liquid crystal that appears as a competitor of the superconducting state.

curved stripe would be longer than on a straight stripe, and its characteristic momentum would be smaller: This keeps the maximal Fermi momentum sharply defined. At the same time, coherent sideways motions of the stripes will give the appearance of coherent two-dimensional motions to the electrons propagating along the stripes.

If the interpretation of the Hall measurements by Noda *et al.* (*3*) is correct, this "self-organized one dimensionality" restores itself in the ground state of the stripe phase. Noda *et al.* studied samples characterized by strong stripe order. Superconductivity is largely suppressed in these samples, and a metallic-like state is realized instead, characterized by an increase of the dc resistivity. Noda *et al.* find that in a certain doping regime, the Hall voltage decreases rapidly as soon as the stripe charge order sets in. The Hall conductance (σ_{xy}) tracks precisely the inverse of the magnitude of the stripe charge-order parameter as measured by x-ray scattering. Such a behavior is difficult to understand in terms of conventional transport theory, and the authors have come up with a very simple and appealing alternative interpretation. A prerequisite for the Hall effect is that the electrical currents flow in at least two dimensions. Noda *et al.* suggest that σ_{xy} reflects the degree of one dimensionality of the current flows in the striped system, with the one dimensionality imposed by the stripe order.

If this interpretation is correct, it would mean that the system of electrons collectivizes in a state that is insulating in one direction and metallic in the other (see the bottom panel in the figure). Such a state of electron matter was predicted by Kivelson *et al.* (*7*), who introduced the concept of quantum liquid crystals, quantum analogs of the classical liquid crystals familiar from liquid crystal displays. The existence of such a state can be demonstrated on the basis of general arguments. Kivelson *et al.* also came up with a specific example: Assuming the stripes to be internally metallic, they showed that stripe fluctuations of the type illustrated in the figure could prevent the system of stripes from becoming an overall insulator. However, Noda *et al.* present evidence suggesting that the quantum liquid crystal is associated with a stripe state that is insulating on the microscopic scale, like the stripes of mean-field theory (*6*). From the doping dependence of the stripe distance as measured by neutron scattering, Yamada *et al.* (*8*) deduced that at low doping levels, every hole stabilizes a piece of stripe exactly two unit cells long, indicating that the stripes are internally Mott insulating. In this doping regime, the Hall effect collapses. In contrast, above the critical doping level for which the neutron work suggests metallic stripes, the Hall effect is unremarkable. It remains to be understood why the insulating nature of the stripes on very small scales is apparently a condition for the quantum liquid crystal behavior on large scales.

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PERSPECTIVES: STRUCTURAL BIOCHEMISTRY

Proton Pump Caught in the Act

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On page 255 of this issue, Luecke *et al.* (*1*) reveal the structure of bacteriorhodopsin, an active transport protein, frozen in midstroke. Bacteriorhodopsin is a membrane protein that uses a photon of visible light as an energy source to transport a proton across the membrane against an electrochemical gradient, resulting in proton release on one side of the membrane and proton uptake on the opposite side. In order to take up a proton on one side and release it on the other, the affinity for the transported substance (a proton in this instance) must be altered along its path during the transport. Furthermore, a switch mechanism must assure that the pump is unidirectional. Some of the underlying molecular mechanisms are now revealed by the 2.0 Å resolution x-ray crystallographic structure of bacteriorhodopsin trapped in an intermediate state (*1*).

Bacteriorhodopsin is isolated from the purple membranes of an archaea, *Halobacterium salinarum*. The protein, although small (26 kD), contains seven transmembrane helices and a buried lysine residue that is covalently linked to a retinal molecule through a Schiff base; these motifs are also found in the eukaryotic visual pigments. Absorption of a photon by the protein-bound retinal in the initial state (BR) results in isomerization of the retinal, initiating a sequence of events as the protein adjusts and relaxes through a series of intermediates denoted K, L, M, N, and O. About 50 μs after a photon of light is absorbed, when the M state is forming, a proton is ejected on the extracellular side of the membrane. Several milliseconds later, a proton is taken up from the cytoplasmic side of the protein and, after a few more milliseconds, the protein relaxes back to the BR state, completing the photocycle (*2*, *3*). Light energy is hereby converted into a proton-motive force—a transmembrane proton electrochemical gradient that can be used to do work such as adenosine triphosphate biosynthesis. Bacteriorhodopsin is thus essentially a photosynthetic system—a light-harvesting protein that sets up a proton gradient—but without chlorophyll.

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Over the past two decades, methods have been devised for trapping the wild-type bacteriorhodopsin and its mutants in specific photo-intermediate states (*4*). The current work applies this technology to the $Asp^{96} \rightarrow Asn$ (D96N) mutant of bacteriorhodopsin in crystals formed by cubic lipidic phase crystallization, a crystallization procedure specifically designed for integral membrane proteins (*5*) that has resulted in several structures of bacteriorhodopsin at 2.9 to 1.55 Å resolution (*5*–*9*). The high quality of the crystals allows side chains and internal water molecules to be located with unusual accuracy.

Continuous illumination of the mutant D96N converts virtually 100% of the protein to one particular state, called M_N. In this state, the proton has already been ejected from the extracellular side of the protein because of marked shifts in the proton affinities of several residues, including the retinal chromophore, but the reprotonation of the retinal from the opposite side of the membrane is hindered by the point mutation.

The current study reveals that the movements performed by bacteriorhodopsin as it functions are small. A key role is played by internal water molecules that first help define the initial structure of the protein and then, after photoexcitation, redistribute themselves within the protein. These internal water molecules provide hydrogen

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