CONDENSED MATTER PHYSICS

Similarities Between Organic and Cuprate Superconductors

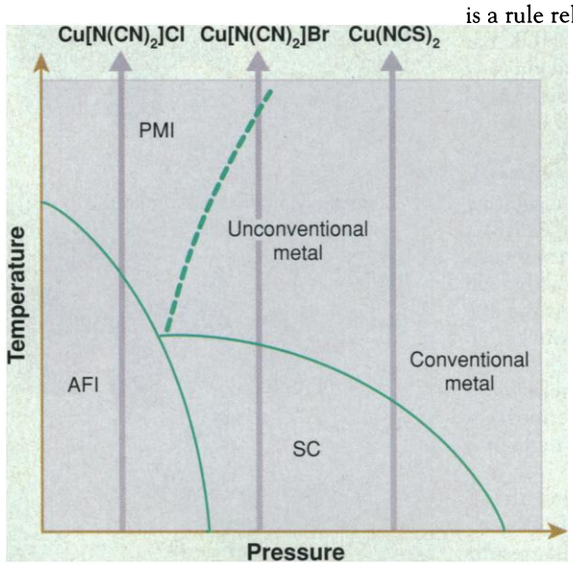
Ross H. McKenzie

One of the greatest challenges of condensed matter physics over the past decade has been the search for a correct theoretical description of the high-temperature cuprate superconductors. Organic superconductors have provided their fair share of puzzles too. When superconductivity was discovered in organic solids based on the bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) molecule (*1*), it was not clear if these peculiar materials were at all related to the equally unusual cuprates. However, recent work has shown that the organics exhibit some of the same interesting physics as the cuprates, including unconventional metallic properties.

The family (BEDT-TTF)$_2$X consists of conducting layers of BEDT-TTF molecules sandwiched between insulating layers of anions (X = Cu[N(CN)$_2$]Br, for example). The BEDT-TTF molecular is large and planar, and its different packing patterns are denoted by Greek letters (*1*). The basic unit of the packing pattern in the κ phase is a "dimer" consisting of two BEDT-TTF molecules stacked on top of one another. Each dimer has one electron less than a partially full electronic cloud because of charge transfer to the anions. The hole (missing electron) can hop from dimer to dimer within a layer much easier than it can between layers. Consequently, as in the cuprates, the layered structure leads to highly anisotropic electronic properties. For example, the conductivity parallel to the layers is two to five orders of magnitude larger than that perpendicular to the layers.

The family κ-(BEDT-TTF)$_2$X has a particularly rich phase diagram as a function of pressure, temperature, and anion (see figure) (*2–4*). Note that (i) antiferromagnetic and superconducting phases occur next to one another, (ii) recent experiments show that the metallic phase has properties that are quite distinct from conventional metals, and (iii) the diagram is quite similar to that of the cuprates if pressure is replaced with doping.

Nuclear magnetic resonance (NMR) can be used to probe the metallic state. The electrons cause a shift in the resonant frequency proportional to the electronic density of states (Knight shift). In a conventional metal, the Knight shift is independent of temperature. In contrast, in (BEDT-TTF)$_2$X with X = Cu[N(CN)$_2$]Br, it decreases significantly below about 50 K, suggesting a suppression of the density of states or "pseudogap" near the Fermi energy (*3–5*). If the nuclear spins are driven out of equilibrium, then the rate at which they realign with the external field is determined by their interactions with the electrons. The observed relaxation rate is 5 to 10 times larger than expected for a conventional metal and is strongly temperature-dependent (*5*). As the pressure is increased to 400 MPa, the NMR properties become more like those of a conventional metal (*3*). The temperature dependence of the NMR properties of the cuprates with small doping is similar (*6*).



Schematic phase diagram of the k-(BEDT-TTF)2X family of organic conductors. Superconducting (SC), insulating antiferromagnetic (AFI), and paramagnetic phases (PMI) are shown. The arrows denote the location of materials with different anions X at ambient pressure. As the pressure decreases, the properties of the metallic phase deviate from those of a conventional metal. This phase diagram is qualitatively similar to that of the cuprate superconductors, with doping playing the role of pressure.

The unusual properties of the metallic state are also seen in transport experiments. As the temperature decreases to about 100 K, the resistance increases, characteristic of a semiconductor. Below 100 K, it decreases rapidly, and from about 30 K down to the superconducting transition temperature, it decreases quadratically with temperature. This temperature dependence is characteristic of systems such as transition and heavy-fermion metals, in which the dominant scattering mechanism is the interactions of the electrons with one another. In transition and heavy-fermion metals, there is a rule relating the magnitude of the temperature dependence to the density of states deduced from the electronic specific heat. However, the observed scattering rate in the organics is several hundred times larger than predicted by this rule (*7*). Furthermore, the scattering is so strong that, above 30 K, the average distance an electron travels between collisions is less than the lattice spacing. This situation is inconsistent with conventional electronic transport.

In a conventional metal, the Hall resistance is a measure of the number of charge carriers and is independent of temperature. In contrast, recent measurements on the X = Cu[N(CN)$_2$]Cl salt showed a strong temperature dependence (*8*). However, the ratio of the longitudinal resistance to the Hall resistance has a simple quadratic temperature dependence up to 100 K. Similar behavior is found in the cuprates (*9*).

Experience with the cuprates suggests that the key physics involved in the above behavior is the layered structure and strong interactions between the electrons. The importance of the latter is supported by recent quantum chemistry calculations (*10*) and the large antiferromagnetic moment observed in the insulating phase (*11*). There is also increasing evidence that, like in the cuprates, the pairing of electrons in the superconducting state involves a different symmetry state than in conventional metals (*3*, *4*).

The theoretical challenge is to produce the simplest microscopic model that can reproduce the phase diagram shown in the figure. Kino and Fukuyama (*2*) recently made some progress in this direction. The key ingredients in their treatment were that they took the dimer structure and the strong interactions between electrons into account. The role of increasing pressure is to reduce the amount of dimerization and decrease the effect of the interactions between the electrons. Their model can describe the transi-

The author is in the School of Physics, University of New South Wales, Sydney 2052, Australia. E-mail: ross@newt.phys.unsw.edu.aut

tion from the insulating antiferromagnetic state to the metallic state and suggests the possibility of an intermediate metallic antiferromagnetic state. The limitations of their approach is that it involves many parameters, only treats the magnetic fluctuations in an average way, and does not predict superconductivity.

These findings show that the organics are worthy of more extensive study. Theoretical studies should focus on simplifying the model of Kino and Fukuyama and should take into account the magnetic fluctuations through techniques developed for the theory of cuprate superconductors. More experimental studies are needed to systematically characterize the unconventional properties of the metallic state.

References and Notes

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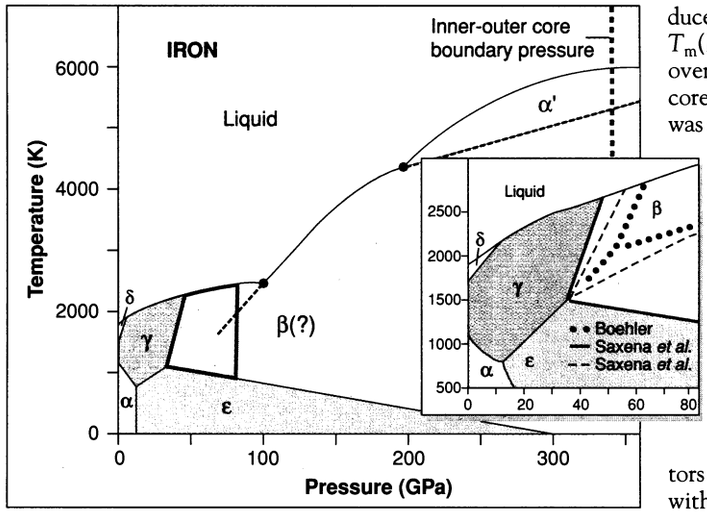
12. I thank the Australian Research Council for support.

HIGH-PRESSURE GEOPHYSICS

Iron: Beta Phase Frays

Orson L. Anderson

Geoscientists are interested in the properties of iron at high pressure in order to understand Earth's core, which is constituted almost entirely of iron. The phase diagram, a fundamental property of iron, has four accredited solid phases (α, γ, ε, and δ) mapped as high as 50.2 GPa and 2000 K (*1*) (see figure inset). Currently there is a dispute about whether the number of solid phases should be raised to five. Experimental data reported by Andrault *et al.* on page 831 of this issue (*2*) favor the validity of a fifth phase, called β, discovered and named by Saxena *et al.* (*3*, *4*). If authenticated, β would replace ε at the pressure and temperature conditions of Earth's inner core. The crystallographic structure of the inner core would change correspondingly, requiring a new look at theories of how Earth's core functions and affecting such fields as magnetogeodynamics, cosmochemistry, seismology, and first-principles calculations.



Iron's phases. The phase diagram of iron, which conforms to the latest melting temperature curve (*21*), upon which the proposed β phase (yellow) is placed. In the absence of β iron, ε iron, now hcp (hexagonal close packed) (pink) would extend to the high pressures and temperatures near Earth's core conditions. The region outlined in red shows where experiments testing for the presence of the β phase are currently done. (**Inset**) The boundaries for all established phases and three sets of boundaries for the proposed β phase. Phases: γ iron is fcc (face-centered cubic) (violet), α iron is bcc (magnetic body-centered cubic) (green), and δ iron is bcc (nonmagnetic body-centered cubic) (white). Another hypothetical iron phase, α′ (light yellow), is proposed to be bcc.

The fitful progress in discovering the complexities of the phase diagram of iron, characterized by contention followed by a big advance in experimental accuracy, exemplifies the aphorism of P. W. Bridgman, the patriarch of high-pressure physics: ". . . we never have perfectly clean-cut knowledge of anything, but all our experience is surrounded by a twilight zone, a penumbra of uncertainty. . . . the penumbra is to be penetrated by improving the accuracy of measurement." (*5*, pp. 33–34.)

In the late 1960s, a new experimental pressure device, the diamond-anvil cell, was developed. By the early 1990s, subsequent innovations allowed the temperature of experiments to be extended above 2000 K. This range permitted the determination of melting temperature T_m of iron at high pressure (above 50 GPa). Measurement of T_m was achieved by detecting a jump in a physical property such as electrical resistivity or optical reflectivity. The melting curve as a function of pressure P was measured to 43 GPa (*6*), then to 100 GPa (*7*), and finally to 197 GPa (*8*) at 3900 K by Boehler's group at Mainz. A competing measurement made by the Berkeley group (*9*) produced much higher values of $T_m(P)$, leading to a controversy over the temperature of Earth's core that lasted a decade. There was a standoff between the two groups because the measurement methods led to subjective conclusions about the value of T_m.

An absolute measure of the onset of the liquid state, showing where crystal structure diffraction patterns disappeared, was needed. X-ray diffraction arising from laboratory generators had been successfully used with the diamond-anvil cell, but at the high temperatures required for iron melting, the intensity of the diffracted lines weakened, giving inconclusive results.

When the diamond-anvil cell was attached to a terminus of a synchrotron beamline, the resulting intense x-rays provided high-quality, in situ diffraction patterns of iron structure even at quite high temperatures. Thus, the controversy about $T_m(P)$ was resolved in favor of the Mainz group, because the liquid structure of iron was found below the Berkeley melting curve and above the Mainz melting curve (*10*). The synchrotron radiation experiment described above was performed at the National Synchrotron Light Source at Brookhaven National Laboratories.

The diamond-anvil cell on the synchrotron beamline thus became a tool to explore

The author is at the Institute of Geophysics and Planetary Physics and Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095–1361 USA. E-mail: olanderson@adam.igpp.ucla.edu