Intriguing Properties Put Sodium Cobalt Oxide in the Spotlight

The compound is a good thermoelectric material. In hydrated form, it superconducts. And its structure is a theorist's dream.

Since the discovery 17 years ago of high-temperature superconductivity in such copper oxides as lanthanum strontium copper oxide, researchers have been taking a close look at related materials. If the copper oxides could surprise us in this way, they asked, what phenomena might lurk in other unexplored materials? Sodium cobalt oxide (Na_xCoO_2) has some answers.

First, this compound, which conducts like a conventional metal, performs much better than a metal as a thermoelectric material[1]—a material in which the flow of heat induces a flow of electricity, and vice versa. Next, a form of this transition-metal oxide with water molecules incorporated into its structure was recently found[2] to go superconducting below 5 K. Additional experimental and theoretical results now appear nearly daily on the e-print archive.

Most of the behavior seen so far suggests strong correlations between the electrons; it's inconsistent with the conventional Fermi-liquid picture, in which electrons are assumed to be relatively independent of one another. The sodium cobalt oxide system is thus one more intriguing playground for exploring the impact of strong correlations on electronic behavior in solids. (See the article by Yoshinori Tokura in PHYSICS TODAY, July 2003, page 50.)

Structurally, Na_xCoO_2 is very similar to the high-critical temperature (T_c) cuprates. In the stacked structure depicted in figure 1, Co and O atoms reside together in layers that alternate with layers of Na atoms, just as the copper–oxygen layers alternate with rare earth dopant layers in the cuprates. Charge is transported most readily within the two-dimensional plane of the Co–O layers. Furthermore, both Co and Cu atoms have a spin of ½. Such similarities have fueled speculation that the cobalt and copper oxides are governed by similar mechanisms of superconductivity.

One key structural difference is that the Cu atoms in the high-T_c materials form a square lattice, whereas Co atoms in Na_xCoO_2 make up a triangular array. The triangular lattice is "cool," exclaims experimentalist Robert Cava at Princeton University. "Theorists love it." That's because it's the lattice for which Princeton's Philip Anderson formulated his resonating valence bond (RVB) theory in the early 1970s. A number of theorists have tried to adapt that model to understand superconductivity on the square lattice of the cuprates. As Anderson comments, however, Na_xCoO_2 "is much more likely to show the true RVB behavior."

Thermoelectric properties

Na_xCoO_2 was first synthesized in the 1970s, but its thermoelectric properties were found only six years ago by Ichiro Terasaki and his team at Japan's Waseda University, using samples supplied by collaborators at Tokyo University.[1] For those samples, x was 0.5, but good thermoelectric behavior has been seen for x up to 0.75.

In metals and semiconductors, a charge current produced by an applied voltage leads to a heat current. Conversely, the heat current produced by a temperature gradient leads to a charge current. (See the article by Gerald Mahan, Brian Sales, and Jeff Sharp in PHYSICS TODAY, March 1997, page 42.)

Thermoelectric coolers exploit materials in which the ratio of the heat current to the charge current is very large. Experimenters determine this property by applying a thermal gradient to a sample and measuring the electric field caused by charge flow. The voltage per unit temperature difference between the ends of the sample is known as the thermopower, or Seebeck coefficient, S.

Materials used for thermoelectric cooling should have a large S. They should also have a low electrical resistivity, to allow the application of a large electrical current, and a low thermal conductivity, to hinder the flow of heat back to the sample. Gabriel Kotliar of Rutgers University notes that the big challenge is not just to make S larger but to reconcile in one material the often conflicting demands of high S, low resistivity, and low thermal conductivity.

Conventional metals have low resistivity, but unfortunately, they also have low values of S. That's because a thermal gradient causes both electrons and holes to diffuse toward the cooler end. This flow doubles the heat current but leads to the near cancellation of the charge current.

The resistivity of Na_xCoO_2 is as low as that of a metal, but its thermopower is ten times higher (see figure 2). At 1000 K, S approaches the values of the best-known thermoelectric materials. What gives Na_xCoO_2 this anomalously high thermopower? In most thermoelectric materials studied to date, the entropy transported by charge carriers derives from their kinetic entropy. The Waseda–Tokyo group speculated in 1997 that the high thermopower in Na_xCoO_2 might arise from spin fluctuations.

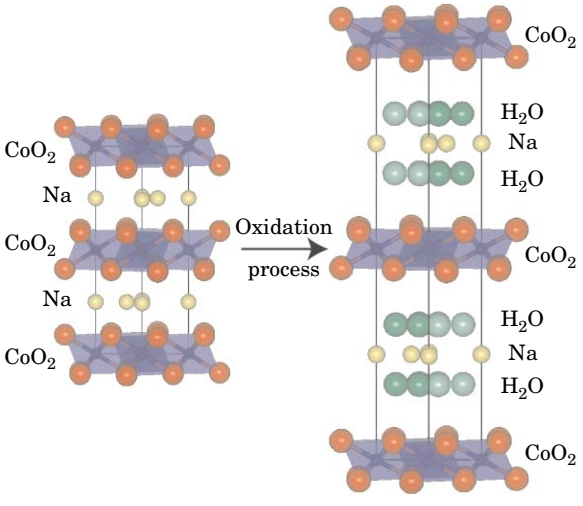

Figure 1. Structure of sodium cobalt oxide. At left, layers containing O (red) and Co atoms (blue) alternate with planes of Na atoms (yellow). After an oxidation process, water molecules (green) are intercalated between the Na and the Co–O layers. (Adapted from ref. 2.)

Three months ago, Yayu Wang, Nyrissa Rogado, Cava, and N. Phuan Ong of Princeton University showed experimentally[3] that the high thermopower in Na_xCoO_2 comes from the electronic spin entropy—the entropy associated with the oscillation of an electron between its two spin states. (Recall that the entropy of a system is related to the log of the system's degeneracy.) In the 1970s, Paul Chaikin and Gerardo Beni[4] had predicted that spin entropy contributes to the thermopower in materials with strong electron–electron repulsion; they applied their arguments to a class of organic conductors.

To demonstrate the role played by spin entropy, the Princeton team measured the thermopower of $Na_{0.68}CoO_2$ in the presence of a magnetic field. In a conventional metal, S is unaffected by a magnetic field. However, if S results from the electronic spin entropy, the thermopower should vanish when the field is strong enough to remove the spin degeneracy. That's exactly what the experimenters found.

The demonstration that spin entropy can strongly enhance thermopower might help guide the search for more promising thermoelectric materials. Terasaki and his coworkers are among those seeking compounds with high spin and orbital entropy, although he notes that some transition-metal oxides with those properties were nevertheless found to be poor thermoelectrics. Researchers hope to make thermoelectric materials viable—and more environmentally friendly—alternatives to conventional technologies for such applications as refrigerators or voltage generators.

Cava, Ong, and their coworkers also found that the magnetic susceptibility of $Na_{0.68}CoO_2$ was, in Ong's words, "surprisingly high." (Susceptibility is the ease with which a magnetic field can align the spins.) At 2 K, it's 100 times larger than the susceptibility of ordinary metals. Moreover, the temperature dependence of the susceptibility can be described by the Curie–Weiss relationship, which is characteristic of materials in which the spins are localized. Unlike the spins in a conventional metal, which are tied to delocalized electrons, the spins in this material "seem to be sitting in one place and responding to the field," explains Ong. The system is schizophrenic, having itinerant charges and localized spins.

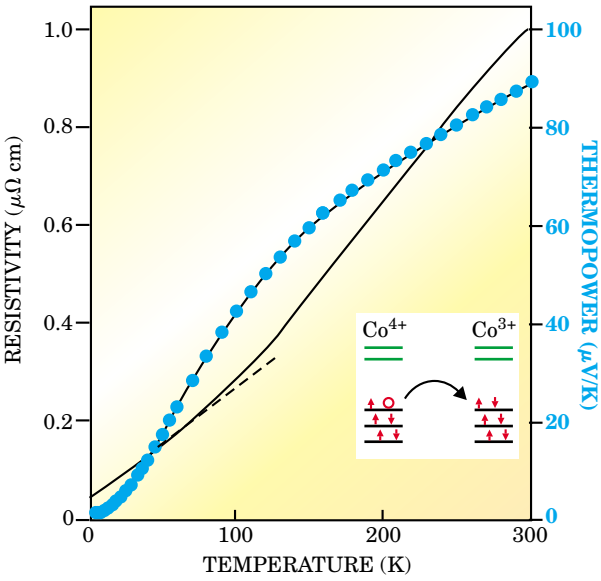

Figure 2. Properties of sodium cobalt oxide, as a function of temperature. The resistivity (black curve) behaves like that of most metals, whereas the thermopower (blue) is much higher. **(Inset)** Energy levels occupied by the outer 3*d* electrons (red arrows) in Co^{4+} and Co^{3+} ions in Na_xCoO_2. Electrons donated by Na atoms change Co^{4+} ions to Co^{3+}. A hole (open circle) can hop from one to the other, as sketched. (Adapted from ref. 3.)

Superconducting behavior

Sodium cobalt oxide attracted even more interest this past March when Kazunori Takada and his colleagues at the National Institute for Materials Science in Tsukuba, Japan, reported it to be superconducting.[2] The discovery was a bit serendipitous. Takada's team had been working with individual layers of transition-metal oxides. To help separate the layers so they could be peeled off, the experimenters were intercalating various substances into the bulk structure. In one experiment, they intercalated water into $Na_{0.35}CoO_2$ through an oxidation process.

Motivated by discussions with a colleague, Takada and his coworkers measured the magnetism of the water-intercalated Na_xCoO_2 in the faint hope of seeing superconductivity. They were surprised to see its susceptibility turn sharply negative just below 5 K, as seen in figure 3a. Such strong diamagnetism—caused by the expulsion of magnetic flux by a supercurrent—is a classic signature of the onset of superconductivity. The resistivity of this material also drops precipitously below 5 K (see figure 3b).

The hydrated form of sodium cobalt oxide is written as $Na_xCoO_2{\cdot}yH_2O$. In the Tsukuba experiment, $x \approx 0.35$ and $y \approx 1.3$. As shown recently by Cava and colleagues from Princeton and Gdansk University,[5] T_c varies with the dopant level x of Na in the compound, rising to its highest value ($T_c = 5$ K) near $x = 0.3$. A similar dependence of T_c on x is seen in the high-T_c copper oxides.

The T_c for $Na_{0.3}CoO_2{\cdot}yH_2O$ is far below values of 100 K or more seen in the copper oxides, so no one is talking about practical applications. Still researchers hope that studies of this new compound will yield valuable clues to the mechanisms of superconductivity in the cuprates.

Does the superconductivity in hydrated sodium cobalt oxide result from the conventional phonon-mediated Bardeen-Cooper-Schrieffer (BCS) theory? In Na_xCoO_2, cobalt's outer electrons occupy 3*d* orbitals; Takada notes that the few other 3*d* transition metal oxides that superconduct are understood essentially as BCS superconductors. Or do strong electron correlations make the cobalt compound behave more like the high-T_c cuprates, in which the spins of the copper atoms, rather than the phonons, are thought to play a dominant role in Cooper pair formation?

A major clue to the mechanism of superconductivity is the symmetry of the Cooper-pair wavefunction. For BCS-like superconductors, electrons orbit one another with zero angular momentum (*s*-wave pairing). For the cuprates, electrons are paired in a *d*-wave state (with an angular momentum quantum number of 2). Strontium ruthenate, which bears some resemblance to Na_xCoO_2, has *p*-wave pairing.

A number of theorists lean toward a complex *d*-wave-type pairing, a prediction that emerges from Anderson's RVB approach.[6] Others think the proximity to a ferromagnetic state suggests that *p*-wave pairing is involved.[7] Experimenters are reporting preliminary results but it's too early for a consensus to develop.

Picture of cobalt atoms

Let's look closer at the electronic structure of the Co atoms in Na_xCoO_2. When one has simply CoO_2 without Na, each Co atom is in the Co^{4+} valence state; five electrons occupy the 3*d* orbitals, whose energy levels are sketched in figure 2. Only the outermost 3*d* electron is unpaired, and Co^{4+}

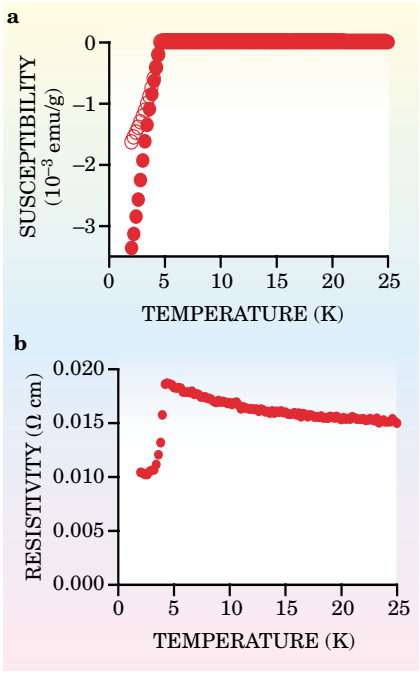

Figure 3. Superconductivity appears in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ below about 5 K. **(a)** Magnetic susceptibility drops precipitously there in the presence and absence of a magnetic field (open and filled circles, respectively). **(b)** Resistivity also falls steeply near 5 K. (Adapted from ref. 2.)

has a spin of ½. When Na atoms are added to this compound, each contributes one electron, thereby changing Co^{4+} to a spinless Co^{3+} state.

The thermoelectric material, with $x \approx 0.7$, has, on average, 30% Co^{4+} and 70% Co^{3+}. To make the superconducting form, Takada and company managed to coax more Na atoms to leave the material and thereby decreased the doping to $x \approx 0.3$. The lighter doping reverses the previous picture so that 70% of the sites are occupied by spins. As holes hop around, the spinless Co^{3+} ions appear to move in a sea of Co^{4+} sites, effectively becoming charge carriers with no spin.

The CoO_2 lattice is known as a Mott insulator—a structure in which each electron is localized on a single site by strong electron–electron interactions. The tendency for nearest neighbors to align their spins in the opposite directions is nearly frustrated by the triangular geometry. This Mott insulator is the starting point for Anderson's RVB model. The resonating bond is the fluctuating singlet pairing of adjacent electrons.

One gets a superconducting state by doping the Mott insulator with Na atoms. If adding Na is equivalent to electron doping, what role is played by the water, which so far seems essential to achieving superconductivity? Experimenters are already trying to answer this question. Some theorists postulate that the water screens Co atoms from the strong Coulomb force of the Na atoms.

The hydrated form of Na_xCoO_2 has been available mostly as a powder and is readily dehydrated in air. A group at Oak Ridge National Laboratory has now shown that one can grow single crystals of the compound by conventional methods.[8] An MIT group recently developed an electrochemical technique that enables them to grow single crystals[9] and to have more precise control over the doping level x. With such improved samples, we can look forward to more definitive results.

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Band on the Run: Light Meets Shock Fronts in Virtual Photonic Crystals

When light interacts with dynamically changing photonic structures, the results can be surprising—and in some cases unprecedented.

When the Schrödinger equation is solved for periodic potentials, the allowed energies are confined to a series of energy bands. That predicted energy structure is familiar from metals, semiconductors, and insulators. A similar but less well-known prediction follows when Maxwell's equations are applied to materials in which the dielectric function varies periodically: The frequencies of light that can propagate through the medium are confined to prescribed bands. Light with frequencies in the gaps between those photonic bands reflects off the medium's surface.

Materials with periodic dielectric structures are called photonic crystals, and they have been constructed with periodicities in one, two, and three dimensions. In dimensions greater than one, a considerable challenge is to fabricate structures that block the propagation of light in all directions. The challenge has been met, first by UCLA's Eli Yablonovitch in 1991. Since then, and especially in the past five years, the technology for making dielectric crystals has advanced impressively. Physicists now have a great deal of control over the periodicity of photonic crystals.

Until a few months ago, work on photonic crystals had generally involved static structures with fixed dielectric period. But earlier this year, MIT postdocs Evan Reed and Marin Soljačić, along with group leader John Joannopoulos, investigated materials in which the dielectric function varied with time.[1] In their analytical and computer studies, a shock wave propagated through a one-dimensional dielectric and reduced the period of the dielectric function in the shocked region.

When the MIT group explored the interaction of light with the moving shock wavefront, the results they discovered were quite unexpected. "Who would have guessed," noted Yablonovitch, "that out of plain old Maxwell's equations, so much richness would emerge?"

Ratchets and funnels

Reed and company conducted simulations in which light interacted with advancing shock fronts moving at