Neutrons Clarify Superconductors

Neutron scattering experiments reveal a two-dimensional antiferromagnetic behavior that is consistent with an electron spin model of high-temperature superconductors

AMERICAN and Japanese researchers working at the Brookhaven National Laboratory High Flux Beam Reactor have found two-dimensional antiferromagnetic behavior of a type that is thought to be unique to the group of compounds that includes the new ceramic oxide high-temperature superconductors. Since high-temperature superconductivity also exists only in these compounds, the temptation is to link the two phenomena. Indeed, theorists, who had already devised models that do just this, are encouraged by the new finding.

"When two strange phenomena occur in the same place, they had better be connected," argues Philip Anderson of Princeton University, who is the architect of one of the major contending models of this type. "The two-dimensional antiferromagnetic correlations show that there are strong interactions and that we have to take them into account in any theory of superconductivity," adds theorist Victor Emery of Brookhaven.

But Anderson and his confreres in the theoretical physics community recognize that there is much more to do. "This is a first step in elucidating the role of spin fluctuations, but there are very important experiments yet to be performed before a direct link to superconductivity can be drawn," says Robert Schrieffer of the University of California at Santa Barbara, who is a co-author of the standard Bardeen-Cooper-Schrieffer (BCS) theory, which correctly describes conventional superconductors in considerable detail.

Given the rising tension as American and Japanese firms race to be the first to commercialize those ceramic oxide compounds that remain superconducting above liquid nitrogen temperature (77 K), it is worth noting that the new finding came about because of cooperation between researchers from the two countries. An essential part of the experiment was the availability of good quality single crystals. According to Robert Birgeneau of the Massachusetts Institute of Technology (MIT), separating out the two-dimensional character of the antiferromagnetic behavior would not have been possible without the crystals, which were provided by the Electrical Communications Laboratories of the NTT Corporation in Ibaraki, Japan. In addition to Birgeneau and a contingent from NTT, members of the collaboration included Gen Shirane of Brookhaven, Yasuo Endoh of Tohoku University in Sendai, and Marc Kastner of MIT.

The experiment itself involved neutron scattering. Neutrons scatter from both nuclei and magnetic moments in a crystalline material, but it is possible to isolate the magnetic component and thereby deduce the magnitude, dynamics, and location of the moments within the crystalline unit cell. Last spring, for example, a group from the Exxon Research and Engineering Company used the Brookhaven reactor to demonstrate the existence of antiferromagnetic ordering due to magnetic moments on the Cu^{2+} ions in polycrystalline powder samples of the compound La_2CuO_4. The moments are due to the spin of electrons in orbitals derived from atomic copper *3d* quantum states.

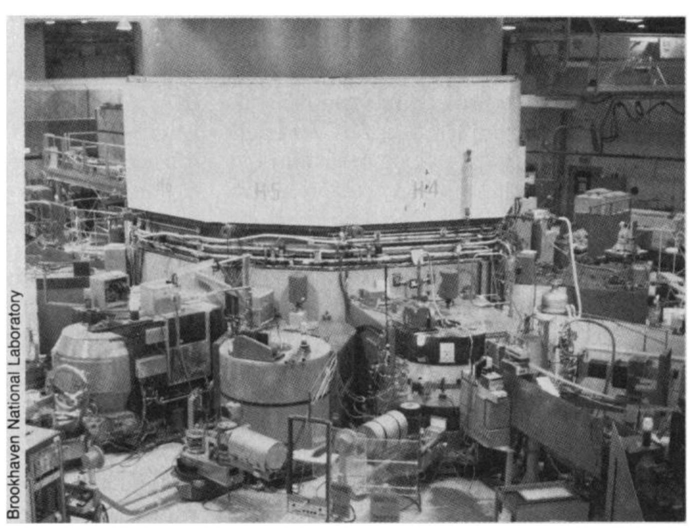
This compound is not usually superconducting, but the replacement of 15% or so of the lanthanum with strontium turns it into a superconductor with a critical temperature of about 40 K, so it serves as a reference whose properties are the starting point for models of the more complex superconductor. A characteristic structural feature of this compound is the existence of planes containing copper ions on the points of a rectangular (almost square) lattice and oxygen ions on the edges of the unit cell. According to the Exxon group, in the antiferromagnetic state the spins on the copper ions are aligned in these planes in such a way that spins on nearest neighbor copper ions within a plane point in opposite directions.

As it happens, the same copper-oxygen planes show up in the $RBa_2Cu_3O_7$ (where R is yttrium or a lanthanide rare earth) compounds that have critical temperatures above 90 K, although the three-dimensional crystal structures differ somewhat in the two classes of compounds. The notion that all the electronic action takes place on these planes has led many researchers to the belief that the same mechanism for superconductivity is operative in the two classes of compounds. "The physics cannot change drastically just by replacing lanthanum with yttrium," expresses the sentiment.

In the new Brookhaven experiments, the investigators first confirmed the earlier Exxon finding of antiferromagnetic ordering. The transition to the antiferromagnetic state occurred when the temperature dropped below 195 K in the NTT crystals. The basic new finding is that above the transition or Néel temperature a dynamic antiferromagnetic ordering dominates. At any instant, the copper spins are aligned antiferromagnetically over the considerable distance of 200 angstroms. But, from one instant to the

Brookhaven reactor

View of the experimental floor shows a variety of neutron scattering instruments surrounding the reactor.



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next, the orientation of the electron spins reverses. Because of this fluctuating orientation, the researchers refer to this state as a quantum spin fluid.

There are two other important differences between the conventional antiferromagnetic state and the quantum spin fluid. One is that the antiferromagnetic state is three-dimensional; that is, there is a definite relation between the orientation of the copper spins from one copper-oxygen plane to the next. But the quantum spin fluid is two-dimensional in that the instantaneous ordering is only within a plane; there is no correlation between planes. In neutron diffraction (elastic scattering), a two-dimensional antiferromagnet would show up as a pattern of diffraction rods perpendicular to the copper-oxygen planes rather than spots. But to see the rods associated with the dynamic quantum spin fluid, it is necessary to measure inelastic scattering in which the neutrons lose or gain energy when they interact with the dynamically fluctuating spins. This is the second difference.

The amount of energy transferred in inelastic scattering is a measure of the frequency or energy of the fluctuations. In any theory of superconductivity, the critical temperature scales with the energy of the physical process that mediates the transition to the superconducting state. In conventional superconductors, lattice vibrations (phonons) play this role. The comparatively hefty energy transfer associated with the spin fluctuations, which is about ten times that involved in inelastic neutron scattering from lattice vibrations, is therefore as important for high-temperature superconductivity as the mere existence of the fluctuations.

In the BCS theory of superconductivity, there are two key processes, which occur simultaneously. One is the formation of pairs of electrons with each member of the pair having equal but opposite momentum vectors and opposite spin orientations, and the other is the "condensation" of the pairs into a single quantum state, which is the superconducting state. To obtain pairing, it is necessary to overcome the natural coulomb repulsion between electrons. As originally worked out, the pairing mechanism in the BCS theory is the generation of an attractive force between electrons by means of electron interactions with phonons. However, pairing does not imply that the electrons are closely bound together. Often there are millions of other electrons in the volume occupied by one pair. In its present generalized form, the theory allows for a wide variety of pairing mechanisms and for more tightly bound pairs.

The spin-based models that have arisen as candidates to explain high-temperature superconductivity are rather subtle. For one thing, they make use of the repulsive coulomb force between nearby electrons rather than looking for another force to counteract it. In some cases, they allow pairing to occur before condensation; that is, at a higher temperature. Finally, it is even possible to dispense with pairing in the usual sense. In conventional superconductors, pairing of electrons is necessary to form composite "particles" that have an integer spin quantum number and are therefore bosons. Quantum mechanics allows bosons to condense into a single state, whereas particles, such as electrons, with half-integer spin quantum numbers (fermions) cannot.

Anderson's resonance valence bond (RVB) theory is the best known of the spin-based models, all of which are partial models in that they consider only what happens on the copper-oxygen planes. In the current version of the theory developed by Anderson and several Princeton colleagues, one considers a square lattice, each site of which is occupied by one electron. These electrons are in hybridized orbitals derived from copper $3d$ and oxygen $2p$ atomic states. Although the lattice points do not represent physical sites of copper or oxygen ions, they are plainly related.

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A strong coulomb repulsion between electrons prevents two electrons from occupying the same site, but each electron is paired with one of its neighbors in the sense that their spins are opposite, which gives a net spin for the pair equal to zero (singlet). There need not be any correlation between the spins of an electron and its three other neighbors. This pairing is the effect of the valence bond. Since all possible pairing configurations are equally likely, the actual quantum state is a combination of all of them; this is the resonance part.

The physical realization of the resonance is a dynamic shifting of valence bonds between different pairs of neighboring electrons. The dynamically fluctuating spins associated with the electrons on each site are exactly what the neutron scattering results show. Anderson proposes that the apparent long-range 200-angstrom order is not truly antiferromagnetic but is actually a manifestation of another aspect of his theory, a so-called pseudo-Fermi surface. He suggests that more extensive inelastic neutron scattering measurements could verify this contention.

Because of the coulomb repulsion that prevents occupancy of a site by two electrons, there is no net electron motion, and the RVB state is not even metallic, much less superconducting. However, as pointed out by Steven Kivelson of the State University of New York at Stony Brook and Daniel Rokhsar and James Sethna of Cornell University, there are special defects called solitons that can exist in the RVB state. There is evidence for analogous solitons in one-dimensional physical systems, such as the polymer polyacetylene.

A soliton can form during the dynamic fluctuating of the valence bonds when one site in a local region of the lattice is left unpaired. With the formation of this defect, the unpaired site is still occupied by one electron, so the excess electrical charge associated with the defect is 0 while the spin quantum number changes to 1/2. This unusual charge-spin combination is the mark of a soliton. Moreover, for every strontium atom that replaces a lanthanum atom in the superconducting compound $La_{2-x}Sr_xCuO_4$, one electron is removed. If the electron is missing from the defect site, the effective charge is +1 but the spin is now 0; that is, there is an electrically charged boson, which is also a soliton.

One possible mechanism for a transition from the RVB to the superconducting state is by means of a condensation of these charged defects, which, as bosons, do not have to form pairs first. Since the bosons are topological defects in an underlying physical system of paired electrons, however, it is not strictly true that no pairing of any kind is involved. In any case, there has not been enough work on the RVB model to tell whether the bosons condense directly or pair first. It might be that condensation both with and without pairing are possible, depending on the value of parameters in the theory.

One spin-based model that preserves a more conventional pairing is that of Emery at Brookhaven. A variation of this model has also been proposed by Jorge Hirsch of the University of California at San Diego. Emery's version starts with a consideration of the occupancy by electrons of orbitals associated separately with the copper and with the oxygen sites in the copper-oxygen planes. Only a few electron orbitals play a role. At the start, copper ions have a random array of spins, each of which is associated with an orbital occupied by a single electron, whereas there is no spin on the oxygen ions, whose orbitals are each occupied by two electrons. In contrast to the RVB model, any electron vacancies (holes) added by, for example, substituting strontium for lanthanum will end up on the oxygen ions. The presence of a hole on an oxygen ion generates a spin because there is now an odd number of electrons there. The entities that pair to form bosons that can condense into the superconducting state are the electrons on the oxygen ions, but it is more convenient to think in terms of holes.

In the language of quantum field theory as applied to conventional superconductors, the attractive force that pairs electrons arises when the electrons exchange a phonon. The same idea applies in Emery's theory, except that the exchanged quantity is called a spin excitation. Consider a copper ion flanked by two oxygen ions that are occupied by holes with opposite spins. Spin excitation refers to the flipping of the spin on the copper ion when the holes on the oxygen ions exchange their spin. It takes place in two steps. Spins can migrate through a lattice by exchanging sites with a neighboring spin of opposite orientation. First, the copper ion and that oxygen with a spin opposite to the copper exchange spins. Then the copper and the second oxygen exchange spins, returning the copper spin to its original orientation. Unfortunately, there is no simple classical picture of why this exchange causes an attraction between the holes.

Whether pairing of the holes occurs at a higher temperature than condensation of the pairs is directly related to the ratio of the distances between the members of the pair and between pairs. In conventional superconductors, where pairing and condensation occur together, this ratio is large, whereas a small ratio favors pairing before condensation. Although the question remains to be answered by experiment, Emery believes that the ratio of distances in the ceramic oxides is large enough for pairing and condensation to occur together.

All in all, the origin of superconductivity in the ceramic oxides is a very difficult problem for theorists and experimentalists alike. Birgeneau says, "This is the first problem I've encountered in 10 years where you have to know all of solid-state physics to work on it." But everyone agrees that the best way to determine if spin fluctuations really do underlie high-temperature superconductivity in these compounds would be to extend neutron scattering measurements to good quality single crystals of superconductors. This is not a trivial requirement because neutron scattering requires rather large samples, such as the 0.5-cubic-centimeter crystals of La_2CuO_4 grown at NTT.

■ ARTHUR L. ROBINSON

How Big Can a Species Be?

"People will probably accuse us of flogging a dead horse," says John Eadie of the University of British Columbia. "Maybe we are, but we want to flog it until someone smells it." The terminated equine to which Eadie refers is the business of species-size ratios in nature, a phenomenon whose apparent significance held ecologists in its thrall for some 20 years. During the past few years, however, the perceived implication of size ratios—specifically, the importance of competition in communities—came under attack, and promptly withered. "What we have been looking at," says Eadie, "is something that might be even more fundamental."

Working in conjunction with Louis Broekhoven and Patrick Colgan of Queen's University, Ontario, Eadie concludes that the existence of the long-discussed size ratios is the inevitable outcome of the distribution of species' sizes in nature. That distribution—described statistically as lognormal—is like a bell-shape curve in which the right-hand tail is extended. "The interesting question to ask," says Eadie, "is, what underlies the lognormal distribution?"

Species' sizes and the differences between them has long been a subject of concern to ecologists, but it became enshrined in the theory of the subject when, in 1959, Evelyn Hutchinson observed that similar species subsisting at similar trophic levels were separated in size by a ratio close to 1.3. (The size ratio might apply to the body as a whole or to the structure the organism used in making a living, such as beaks in birds.) Hutchinson proposed that competition pushed species apart, and a difference of 1.3 in size represented a boundary at which coexistence was possible. "The notion became so entrenched in the ecological literature that the mere observation of a ratio near 1.3 . . . was often taken as prima facie evidence that communities were organized according to the principles of [competition]," note Eadie and his colleagues.

In fact, when the putative link between size ratios and competition was examined critically—principally at the instigation of Daniel Simberloff, of Florida State University, and his associates—it began to look very tenuous indeed. And, as several authors have pointed out, size ratios of around 1.3 are very common in the world, among objects both animate and inanimate. "Although these criticisms point out the limited utility of size-ratio analyses," note Eadie and his colleagues, "they do not present a mechanism to explain how such artifacts could arise."

The Canadian researchers analyzed a series of 33 ecological studies that encompassed 439 assemblages of species. In 93% of cases the size distribution was most accurately described as lognormal, out of which the 1.3 ratio inevitably falls. (In addition, the variances are small.) "Hutchinson's constant, then, may simply be an inadvertent artifact of a lognormal distribution of animal sizes in nature," they note.

The question then becomes, what governs the original lognormal distribution? "It is not unreasonable to think of a trait such as body size evolving in response to a large number of independent, selective pressures among which competitive ability is only one," suggest Eadie and his colleagues. In other words, when one is dealing with a measure—body size in this case—that is the product of the interaction of a multiplicity of influences, a lognormal distribution inevitably results: and this holds whether you are dealing with canaries or cookie cutters.

Eadie and his colleagues are clearly not saying that the 1.3 Hutchinsonian ratio does not exist, and neither are they suggesting that competition is not sometimes an important component of species assemblages. What they are saying is that competition is just one of many factors that influence the shapes of those communities, that there are other, perhaps more fundamental factors involved. "I'm hoping that people will see beyond the dead horse," notes Eadie. "Maybe there was an important question that we all forgot to ask right at the beginning." ■

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ADDITIONAL READING

J. McA. Eadie *et al.*, "Size ratios and artifacts: Hutchinson's rule revisited," *Am. Nat.* **129**, 1 (1987).