HIGH-TEMPERATURE SUPERCONDUCTIVITY (II—theory)

... and a Principle to Explain Them

Part II of a Special Report

by Edward Edelson
"In the old days," says Marvin Cohen of the University of California at Berkeley, "we just had phonons, and that explained all known superconductors. Now we have ten or fifteen new mechanisms proposed for two new superconductors. You know that in the future all these mechanisms are not going to be around. Phonons will still be there, and maybe one or two other mechanisms for the new materials."

This is the state of the theoretical art in the sudden new world of high-temperature superconductivity, where "the old days" are last year—before the September 1986 report by IBM researchers in Zurich of new superconducting metal oxides that work at higher temperatures. There are indeed 10 or 20 theories to explain what is happening inside the oxides that lose all their resistance at 40 or 95 degrees Kelvin, the temperature unit on a scale that begins at absolute zero—273.15 degrees below zero on the Celsius scale.

A hundred flowers bloom, and names blossom to match the new ideas: excitons, plasmons, magnons, spinons, bipolarons, and more. With the garden of theories so lushly overgrown, only a few familiar landmarks still are visible.

However, theorists can find where they are by triangulating on the one towering achievement of superconductivity theory—that developed in 1957 by John Bardeen, Leon N. Cooper, and J. Robert Schrieffer, then at the University of Illinois. Their BCS theory of superconductivity, for which they won the Nobel Prize, starts with a picture of a normally conducting metal or alloy whose atoms are arranged in a three-dimensional crystal structure. Some of the loosely held outer electrons drift away from their atoms (which thus become ions), forming an electron gas that is able to move through the lattice.

BCS

At room temperature, the electrons do not move with complete freedom. Sometimes they come up against imperfections in the lattice. At other times, the negatively charged electrons interact with the positively charged ions, bouncing off them as the ions vibrate. Because these interactions interfere with the movement of electrons, they cause electrical resistance. Higher temperatures have the effect of increasing resistance by increasing the vibrations.

The vibrations are called phonons because their frequency is in the acoustic range; when a person slaps his hand on the table, he creates phonons in the wood. The BCS theory says that at low temperatures in certain metals and alloys, interactions among electrons and phonons can result in paired electrons, called Cooper pairs.

One way to depict the interaction is to say that one negatively charged electron attracts the positively charged ions around it, causing a slight distortion in the lattice. The distortion produces a polarization, an area of increased positive charge. A second electron is attracted by this pocket of positive charge and becomes coupled to the first electron, accompanying it through the lattice.

Another way to depict the same phenomenon is to describe the electrons being coupled by the exchange of a virtual particle, the phonon. In this case too, the coupling allows the electrons to flow unhindered through the lattice.

Superconductivity is a collective phenomenon, however. The coherence length—the distance over which coupling extends—is such that each electron effectively belongs to a large number of pairs. But rather than producing a sea of independent electron pairs flowing through the lattice, the BCS theory has a highly correlated collection of Cooper pairs sweeping along. Or, in formal terms, instead of obeying Fermi rules of behavior, as electrons normally do, the aggregate of paired electrons now comes close to obeying Bose-Einstein rules: They condense into a sea of pairs with some of the properties of bosons—the ability, for instance, to move effortlessly through the lattice. Anything that destroys the Cooper pairs—the random thermal motions of electrons at high temperatures, for example—thereby destroys the superconductivity.

Adapting a theory

"We haven’t abandoned BCS, just conventional BCS," says physicist Michael Schluter of AT&T Bell Laboratories, speaking of the efforts to develop a compa-
tatable theory for the new superconducting materials. "Few people doubt that the general concept is correct, that the electrons have to be paired. But phonon energy is too weak to bind electron pairs for temperatures as high as one sees in the new materials."

In the BCS theory, the critical, or transition, temperature—the temperature at which a material becomes superconducting—depends among other things on three factors: the Debye frequency, or the highest phonon frequency in the lattice; the density of states, or energy levels that electrons can occupy, near the Fermi energy, which is the energy of the most energetic electrons possible in the superconducting material at zero temperature; and the strength of the electron-phonon coupling.

The original BCS theory described metals with weak electron-phonon coupling energy. It accurately described results seen with superconductors such as aluminum, which have a very low transition temperature. However, deviations from the results predicted by the BCS theory were later seen in other superconductors, such as lead and niobium.

A modification of the original theory, called the Eliashberg theory (after the Soviet physicist who first developed it), explained those deviations by adding a more accurate description of the electron-phonon interactions.

Unconditional theory

Conventional BCS theory assumed instantaneous interactions among electrons and phonons. The Eliashberg theory, as refined by J. Robert Schrieffer and others in the United States, took into account the retardation in the interaction; instead of interacting at the speed of light, electrons and phonons interact at the speed of sound. "That is a much longer time, and it has important effects on the strength of electron pairing," says theorist Bernd Schuttler, formerly of Argonne National Laboratory and now at the University of Georgia. "In a more generalized formalism that involves phonon frequency, coupling strength and Fermi velocity [how fast electrons move at the Fermi energy], it can explain deviations from the weak coupling theory."

Two recent sets of closely related experiments, at Bell Laboratories and the University of California at Berkeley, seem to have set a limit on the role of phonons in electron pairing in the new materials. The experiments hinged on what is called the isotope effect. Phonon frequencies depend on the mass of the ions in the lattice; as the mass increases, the frequencies go down and so should the transition temperature of the material. (It was the observation in 1950 that transition temperature decreases as atoms in the material are replaced by heavier isotopes that helped lead to the BCS theory.)

The researchers at both Bell Laboratories and Berkeley did experiments in which oxygen-16 atoms in the new superconducting oxides were replaced in large measure by oxygen-18 atoms. BCS theory predicted that replacement should cause a decrease of about 5 degrees Kelvin in the transition temperature of the compound yttrium-barium-copper oxide, which becomes superconducting at over 90 degrees Kelvin. Both the Bell Laboratories researchers, led by Bertram Batlogg, and the Berkeley experimenters, led by Alex Zettl, reported essentially the same findings. Both found a 4 percent decrease in the frequency of the oxygen vibrations but "very little, if any, of an isotope effect" on transition temperature, in the words of the Bell report. However, both groups did find a small isotope effect in lanthanum-strontium-copper oxide, which is superconducting at 40 degrees Kelvin.

The general interpretation of the oxygen isotope experiments is that they set drastic limits on the role of phonons in the new materials. "It leaves open a few loopholes in principle," says Michael Schluter. "In practice, it would require cancellation of other factors to very high accuracy to explain coupling by phonons alone. So phonons in the simple sense are out," he declares.

Says Victor J. Emery of Brookhaven National Laboratory, "If you assume a dominant electron mechanism with a little bit of phonons, you can explain the isotope effect with enough interaction to give you a transition temperature of one to ten degrees Kelvin. I did a back-of-the-envelope calculation that came up with one degree Kelvin. Someone else did a computer calculation that came up with ten degrees Kelvin. Either way, phonons make a minor contribution."

Some physicists still are cautious about the isotope experiments. They note that there are superconductors in which the isotope effect has not been seen, even though phonons are known to be responsible for electron pairing. "We need the experiments repeated," says Georgia's Bernd Schuttler.

New theories

Nevertheless, most physicists believe new theories are necessary for the new material. Perhaps the most provocative point of view is held by Philip Anderson, a Nobel laureate in physics at Princeton University. Anderson believes that a completely different ap-
Giants in superconducting. John Bardeen, Leon Cooper, and J. Robert Schrieffer (left to right) won a Nobel Prize for 1957 theory.

The basic ingredient for attraction is that you have to polarize something. In the electron-phonon interaction, the electron polarizes the lattice. There are two other things you can polarize, charge or spin.

An example of a theory based on charge polarization is the excitonic mechanism, first outlined by Vitaly Ginzburg of the Soviet Union and independently by William Little of Stanford University. It was later developed by David Allender, James Bray, and John Bardeen at the University of Illinois.

The excitonic theory pictures electrons as being paired by exchange of a virtual particle, the exciton. An exciton comes into existence when an electron moves to a higher energy state, creating a hole, or vacancy, then drops back to the lower energy state. Put another way: The electron creates a polarization cloud by pushing nearby electrons away because of the Coulomb repulsion between similarly charged particles; a second electron has its energy lowered because of the polarization cloud and forms a pair with the first.

An example of spin polarization theory, credited to P. G. DeGennes, a French theorist, assumes the production of virtual particles called magnons. The process starts with a nonsuperconducting material in the antiferromagnetic state, with neighboring electrons having spin of opposite orientation.

"When the material is doped by the addition of another element, holes are created that also carry a spin," Schüttler says. "Each hole wants to spin antiparallel to the electrons, but it also wants to delocalize—spread its wave function to other sites. But it sees antiferromagnetic electrons whose spins are aligned parallel with it at these other sites. So it tries to cant their spin a bit and also cant its own spin a bit, so it can delocalize to some degree and still have a favorable alignment of its spin with the antiferromagnetic electrons. Now we have a spin polarization cloud. A second electron sees the polarization cloud and experiences effective attraction to the hole. The crucial difference is that the interaction is mediated by polarizing spin degrees of freedom."

Different pictures

To a large degree, the charge polarization and spin polarization theories are based on two sharply different pictures of the electron structure of the material. The BCS theory assumed that the conduction electrons, those that formed Cooper pairs, were delocalized and moved relatively independently. Charge
polarization theories also are based on this picture of band structure, so called because the conduction electrons are in an energy band of delocalized states.

Many spin polarization theories assume a strikingly different structure, called the Mott-Hubbard picture. As described by Nevill Mott, a British Nobel laureate in physics, and John Hubbard, a Briton who was with IBM at San Jose before his death, the Mott-Hubbard picture assumes that the electrons are in a more ordered, localized structure, in which they are strongly correlated. In the Mott-Hubbard construct, the atoms in the lattice have outer electron shells that are almost exactly half-filled, so that there is one conduction electron per atom and the material is an insulator. The collective movement responsible for the material's transition to superconductivity can occur through correlations of the electron spins.

The Mott-Hubbard picture has not been proposed for any conventional metallic superconductor, although it has been invoked for a new group of organic superconductors and for the puzzling group of compounds called heavy fermion metals. (See “Turmoil in the Solid State” by Arthur Fisher, Mosaic Volume 18 Number 3 1987.) It has been proposed for the oxide superconductors because, as Michael Schluter describes it, the band structure, “straightforward as it is, is in a slight crisis.”

The observation of antiferromagnetism in lanthanum-copper-oxide, which was not known to be superconducting itself but does become superconducting when doped with barium, “is a fact that band theory has some trouble with,” Schluter says. Antiferromagnetism generally is assumed to indicate an ordered state of electrons that is often at odds with the results of pure band theory for this material. “Band theory,” says Schluter, “could explain the fact that the new materials are semiconducting when they are in a pure phase. But it would require a frozen-in lattice distortion, which hasn’t been observed.”

No rose garden

So far, it can be said that every new theory has its problems. One example will suffice: The problem with the excitonic mechanism is that the transition temperatures it predicts are too high—hundreds or even thousands of degrees Kelvin, much higher than have been observed. Nonetheless, the challenge of explaining the new materials has led to a number of inventive theories.

Victor Emery of Brookhaven has a spin polarization theory based on the Hubbard model. In his theory, there is strong coupling of the electrons based on antiferromagnetic spin fluctuations. The charge carriers are holes—missing electrons—that are created as barium is added to lanthanum-copper oxide. Cooper pairing occurs as a result of interactions between the spins of the holes and neighboring electrons.

“There are two important things about antiferro-magnetic correlations,” the Brookhaven scientist says. “One is that they confirm you have the strong short-term repulsions of the kind that you build into the Hubbard model.

“Less directly, experiments with lanthanum-copper oxide show that the density of carriers is the density of dopants. In the simple-band picture, you would say that the number of carriers is the number of coppers as modified by the dopant. The reason seems to be that lanthanum-copper oxide itself is an antiferromagnetic insulator that has an insulating gap in its electron spectrum and that the gap persists when you dope.”

Arthur J. Freeman, a theorist at Northwestern University, has a completely different picture, based on detailed, precise energy-band calculations. His calculations show evidence of the strong charge polarizations expected for an excitonic mechanism.

“In these ionic metals,” says Freeman, “our calculations show that there are important charge transfer excitations, or excitons, from localized copper-oxygen states bonded perpendicularly to the copper-oxygen chains and planes to itinerant—that is metallic—copper-oxygen states bonded in the chains or planes. These excitations enhance the electron pairing via exchange of excitons and serve to raise the materials’ transition temperature.”

Recent experiments at the University of Geneva support that theory, Freeman notes. The experiments measured anisotropic Fermi surface—a phenomenon found only in metals—whose parameters “are in very good agreement with our calculations.”

In a recent review paper, Nevill Mott asked the rhetorical question, “Is there an explanation?” and wrote, “The short answer is that there are many, perhaps as many as there are theorists in the field.” He then proceeded to give his own explanation, based on the existence of bipolarons.

A polaron is an electron that sits in a pocket of positive charge in a lattice; a bipolaron is a pair of such electrons. Mott pointed out that bipolarons can undergo a Bose condensation if electron structure of the material meets certain conditions. Those conditions are most likely to occur in layered material such as the new oxide superconductors, he says, and his theory also explains the anisotropy of current flow observed in these radical new materials.

In the works

Philip Anderson and his colleagues at Princeton have a theory that is strikingly different from all others; it assumes no polarization of any kind. Anderson cheerfully admits that his theory is not yet fully developed, but he says the answer is in the works.

Anderson’s resonating valence bond, or RVB, theory starts with a different, dynamic picture of antiferromagnetism. Its starting point is a theory developed by Nobelist Linus Pauling of Stanford University to explain the way atoms can bind to form molecules. As Anderson developed the theory, it assumes that antiferromagnetism in some materials does not result in spin correlations of electrons in a highly ordered array, with each electron interacting with its neighbor. Instead, the electrons can be described as being in a kind of square dance, in which overall order is maintained even though each dancer constantly changes partners. In formal terms, there is a spin liquid instead of a spin crystal.

A key element of RVB theory is that electron pairs can exist in material that is not superconducting. Superconductivity occurs when the material is doped to create holes in it. The holes then form pairs and undergo Bose condensation, making superconductivity possible.

“These are very strange objects,” says Anderson. “They also have the peculiar property that they are confined to individual atomic planes and cannot tunnel coherently back and forth between planes. This is shown by recent experimental results that demonstrate that the material is not a metal for conduction perpendicular to the planes. In order to...
move in that direction, these charge carriers have to pair up, so that superconductivity appears when the substance becomes a three-dimensional metal instead of just a two-dimensional metal. We have developed an equivalent of the gap equation of the BCS theory for this process, and it gives some very strange results that we are still in the process of working out in detail."

Experiment and observation

"So far, I've been trying to work out the mathematics for all of these theories," says Marvin Cohen. "The problem is not that they don't work but that they all work, because we don't have enough experiments. We need more experimental evidence."

Many experiments are being done, but the results so far are not decisive. At Brookhaven National Laboratory, for example, a team including researchers from Brookhaven, the Massachusetts Institute of Technology, and Nippon Telephone and Telegraph has looked for the breathing mode postulated by Freeman's soft phonon theory (and variations on the theme proposed by other theorists) but has not found them. Yet Freeman says he has experimental evidence and simulations that he has done on supercomputers to support his theoretical picture.

Already, experiments are putting bounds on theories. For example, any theory must explain not only the high temperature at which superconductivity occurs and the antiferromagnetic observations, but also some other properties of the new materials, says Bernd Schützler. One such property is the specific-heat behavior of the high-temperature superconductor. Specific heat is the quantity of heat needed to raise the temperature of a material by a given amount. In most materials, specific heat decreases steadily as the temperature goes down. In all superconducting materials, including the new ones, specific heat decreases steadily with the temperature until the sample reaches its superconducting transition temperature; its specific heat goes up slightly at that point before starting to go down again.

There is also an unusual temperature dependence of electrical resistivity in the new materials. In an ordinary metal, higher temperature causes an increase in resistivity by increasing lattice vibrations. When one cools a metal such as copper, resistance decreases linearly at high temperatures, then flattens out at lower temperatures. In the new materials, the resistance is linear over the entire range studied—even to the highest temperatures at which the material remains stable as a compound.

Another unusual observation concerns the temperature dependence of NMR, or nuclear magnetic resonance, relaxation rates in the materials. In NMR, properties are measured by placing a sample in a magnetic field, beaming in radio waves of appropriate frequency, and measuring the relaxation time of nuclei as they give up the absorbed energy. In a classic BCS superconductor, there is a slight hump in the relaxation rate (the inverse of the relaxation time) at the transition temperature. In the new materials, the hump is not seen.

The gap question

The NMR measurements are important because they bear on one of the major questions about the new materials: Is
there a superconducting gap? “Gap” in this respect is used to refer to the minimum energy required to create an electronic excitation in a superconductor.

There can be gapless superconductivity even in conventional materials. If an ordinary superconductor is doped with magnetic impurities, the transition temperature goes down. There is a critical concentration of impurities above which the material is not superconducting, no matter how low the temperature. Just a little below that critical concentration, the material exhibits true superconductivity, but measurements detect no gap. In that case, says Schüttler, “it comes from the coupling of spins of conduction electrons to the spins of the magnetic impurity.” The existence of a gap, and its size if it does exist, is of obvious importance to theorists.

One quantity used to describe a superconducting material is a dimensionless number derived by multiplying the low-temperature limit of the gap by two and dividing it by a constant (the Boltzmann constant) multiplied by the transition temperature. In the classic BCS theory, the value of this expression is about 3.5. A number significantly larger than that would indicate very strong electron coupling.

Values for this ratio can be obtained in several ways. Using NMR data, the values for the yttrium-barium-copper oxide are in the range of 3 to 8. Using infrared spectroscopy, experimenters have gotten values below 3.5, but reinterpretation of the data has given values between 4 and 5. Another method used is tunneling, in which a voltage is applied to a metal tip in contact with the superconducting material; if the voltage is sufficient to break the Cooper pairs, electrons will tunnel through, and the applied voltage where that happens is thus a measure of the superconducting gap. Tunneling experiments have given values for the ratio ranging from 4 to 20.

Recent experiments by Bill Warren and Russ Walsteat at Bell Laboratories indicate there is a superconducting gap in the new materials, Bertram Batlogg says. The experiments show that the gap is different at various sites in the unit cell of the material; it is found in the chains, but not in the planes, he says.

“That’s an example of the difficulties that experimenters face these days,” says Bernd Schüttler. “The experiments seem to give contradictory results. But it’s not even clear that the results are inconsistent. It could be that the gap measurement in tunneling is different than in NMR. It’s possible that you get a different gap when you measure by one method rather than by another.

“Or it could be impurity phases on the surface of the sample in the tunneling or infrared experiment.”

The field obviously still is in flux, with theorists waiting eagerly for the results of experiments designed to separate the theoretical wheat from the chaff. It took more than a half-century after the first observation of superconductivity to develop a satisfactory theoretical explanation of the phenomenon. Few anticipate that a theory of the new high-temperature superconductors will take that long now. Nonetheless, everyone knows the quest has just begun.

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