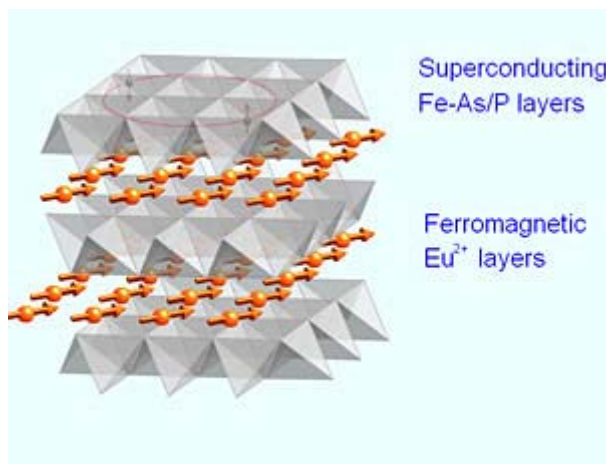


# An Iron Key to High-Temperature Superconductivity?

**The discovery that compounds known as iron pnictides can superconduct at 50 degrees above absolute zero has reignited physicists' quest for better high-temperature superconductors and may offer clues to unlocking a 20-year mystery**

Hideo Hosono's research group at the Tokyo Institute of Technology was not looking for a superconductor in 2006. Rather the team was trying to create new kinds of transparent semiconductors for flat-panel displays. But when the researchers characterized the electronic properties of their new substance--a combination of lanthanum, oxygen, iron and phosphorus--they found that below four kelvins, or -269 degrees Celcius, it lost all resistance to carrying an electric current; that is, it superconducted.



Although 4 K is far below the current laboratory record of 138 K (let alone the holy grail of "room temperature," or about 300 K), experimentalists with a new superconductor are like yachtsmen with a new boat design. The sailors want to know how fast they can make it go; the physicists, how hot any variant of the material can superconduct. Superconductors' uses in industry are hobbled by the need for expensive, complicated, space-hogging cooling systems. Any increase in operating temperature could ease those drawbacks for existing devices and make completely fresh applications technically and economically viable. Engineers envisage, for instance, lossless power cables carrying huge currents and compact superstrong magnets--for magnetic resonance imaging, levitated trains, particle accelerators and other wonders--all without the exorbitant expense and trouble of the liquid-helium cooling systems required by the old, cold, conventional superconductors.

So the Japanese group set about doping its material--adding a sprinkling of foreign atoms to the recipe--to try to raise the transition temperature. Replacing some of the oxygen atoms with fluorines brought on superconductivity at 7 K. Swapping arsenic for phosphorus resulted in superconduction up to 26 K, a temperature high enough to get physicists' attention all around the world and to spark a flurry of research when the group's arsenic paper appeared in late February 2008. By the end of March, groups in China had similar compounds superconducting just above 40 K. A month later, 56 K.

Although these impressive results were not close to challenging the records set over the past two decades by the copper oxide, or cuprate, superconductors, physicists were excited for several reasons. First, who knew where the rising temperatures would end? Second, they suspected that the iron compounds would be easier to work into technological applications than the cuprates, which are brittle and require complicated techniques to fashion into long wires such as for power cables or magnets.

Next, iron was a peculiar element to have in a superconductor because its atoms are strongly magnetic, and magnetism generally inhibits superconductivity. Indeed, along with perfect conduction, a defining characteristic of a superconductor is that it forces an applied magnetic field to skirt around it instead of passing through its interior. A field strong enough to enter the superconductor destroys the superconductor. Why was the magnetism of the iron atoms right inside the material not spoiling things? That puzzle remains unanswered.

But perhaps most interesting of all, the new iron compounds knocked the cuprates off their pedestal as a seemingly unique class of high-temperature superconductors. For more than 20 years the cuprates had resisted all attempts by researchers to formulate a theory explaining all of their properties, most particularly their high transition temperatures. Now with two species to compare and contrast, experimenters might finally uncover the vital clues that theorists could use to solve the mystery of high-temperature superconductivity.

### **Layered Structures**

Hope that the iron superconductors can offer clues about the cuprates is bolstered by the many similarities of the two kinds of compound. Both classes of material superconduct at warmer temperatures than all other known superconductors do. In both classes, each compound has a particular optimum level of doping that maximizes its transition temperature (the temperature below which the material becomes superconducting, also called the critical temperature). The temperature is lower for "underdoped" and "overdoped" samples, eventually falling to absolute zero when far enough from the optimum--in other words, a sample that is doped lightly or heavily enough does not superconduct at all [see box on page 67].

The most obvious similarity, however, is that both the cuprates and the iron pnictides are made of alternating layers of atoms. Where cuprates feature copper oxide ( $\text{CuO}_2$ ) sheets, the new materials have sheets of an iron pnictide (pronounced "nik-tide")--iron bound to an element from nitrogen's group in the periodic table, such as phosphorus, arsenic or antimony. In Hosono's 26 K material, for instance, layers of lanthanum oxide ( $\text{LaO}$ ) alternate with iron arsenide ( $\text{FeAs}$ ).

The copper oxide and iron pnictide layers are the meat of these crystalline club sandwiches. They are where physicists believe superconductivity is produced. The "bread" layers merely contribute additional electrons to the meat or remove some electrons from it. With fluorine-doped  $\text{LaOFeAs}$ , for instance, each fluorine atom begins with one more electron than the oxygen it replaced, and these surplus electrons move to the  $\text{FeAs}$  layers, altering their electrical properties.

Viewed from above, the atoms in an  $\text{FeAs}$  layer would appear to be positioned on a nanoscale chessboard; one iron atom on each black square and an arsenic atom on every white one. The

cuprates'  $\text{CuCO}_2$  layers are similar but with only half the black squares occupied by a copper atom. Each  $\text{CuCO}_2$  layer is essentially flat; all the atoms lie in the same plane. In contrast, the arsenic atoms in an FeAs layer sit above and below the level of the iron atoms, four of them surrounding each iron atom at the vertices of a tetrahedron. As with almost every feature of the materials, whether it is the similarity or dissimilarity of the structures that is more important remains to be unraveled.

The layered structure profoundly affects the cuprate superconductors' properties, making them behave differently depending on whether a superconducting current, or supercurrent, is flowing parallel to the layers or perpendicular to them. For instance, the effect of a magnetic field on a supercurrent in a cuprate crystal depends on the direction of the field. The superconductivity can withstand a much stronger field when the field is aligned with the cuprate sheets than when it is perpendicular to them. That property has important ramifications because many applications of superconductivity involve generation of strong magnetic fields. These kinds of effects also serve as possible clues to deciphering why the cuprates superconduct.

Theorists took these clues deeply to heart and for 20 years they have largely focused on developing an explanation of how superconductivity could develop within a single cuprate sheet. That is, they have viewed the two-dimensionality as a crucial feature. This idea is reasonable from a theoretical standpoint because throughout mathematics and physics examples abound of systems that exhibit properties and phenomena unique to the two-dimensional case and absent or far more complicated in three dimensions. And in the specific case of the cuprates, many experiments have produced results that single out the  $\text{CuO}_2$  plane as being very special.

The first research on the iron pnictides seemed to be telling the same story, but in late July 2008, two groups of researchers--one led by Nan-Lin Wang of the Chinese Academy of Sciences, the other led by Paul C. Canfield of Iowa State University, with both groups including collaborators at Los Alamos National Laboratory--independently found that a particular iron pnictide superconductor responds very similarly to strong magnetic fields pointing in different directions. That is, this material, which has potassium-doped barium layers interleaved with FeAs and which can superconduct up to about 38 K, seems to have three-dimensional superconductivity.

In the words of Jan Zaanen, a theorist at Leiden University in the Netherlands, if the cuprates and the iron pnictides share the same "secret of high-temperature superconductivity," this experimental result implies that "two-dimensionality has been a red herring all along, causing theorists to look in wrong directions."

## **Quanta of Sound**

The "secret of high-temperature superconductivity" that Zaanen and other physicists want to extract by interrogating the cuprates and pnictides is a quite specific piece of information about what makes these materials superconduct. In particular, they want to know what interaction between the electrons involved leads to the superconducting state. An electric current in an ordinary metal is carried by the so-called conduction electrons, which are free to move through the material. These electrons, however, constantly collide with the positively charged metal ions,

which saps the energy of the current and heats the metal--this effect is the metal's electrical resistance.

Superconductivity occurs when conduction electrons become linked together in pairs, which are known as Cooper pairs. The Cooper pairs gather en masse in a single quantum state, a process known as Bose-Einstein condensation. This swarm of charged particles is able to move through the material in lockstep without losing energy in collisions with the metal ions; the resistance drops to zero. Measurements confirm that in both cuprate and iron pnictide superconductors, the carriers of electric current have twice the charge of an electron--the carriers are Cooper pairs. But theory must also explain the mechanism that forms these Cooper pairs. According to the classic explanation of conventional superconductivity--the BCS theory, developed by John Bardeen, Leon N. Cooper and J. Robert Schrieffer in 1957--a very prosaic entity plays this role: sound.

Sound is made of vibrations. The quantum of vibration in a solid is the phonon, named by analogy with the photon, the quantum of light (or, if you like, the quantum of electromagnetic vibrations). An interaction between two conduction electrons, mediated by phonons, can be visualized as follows: the first electron's electric field tugs on the metal's positively charged ions as it passes near them. The electron leaves in its wake a temporary region of distorted lattice--the very stuff of phonons. A second electron will experience a small attractive force toward the momentarily distorted region because of the slightly increased density of positive charge there. This small, indirect attractive force is enough to produce Cooper pairs and superconductivity, so long as the temperature is low enough that thermal vibrations do not overwhelm the effect. The BCS theory puts this approximate heuristic picture on a firm mathematical basis that allows calculation of a material's transition temperature based on the material's other properties.

One of the classic verifications of the BCS theory is the observation that transition temperatures of two isotopes of a superconducting material are different by about the right proportion. Thus, mercury 198 superconducts when it is colder than 4.18 K, but mercury 202 only does so below 4.14 K. The slightly heavier mercury 202 atoms vibrate less and at a lower pitch, and thus in mercury 202 the electron-phonon force is weaker, the Cooper pairs are more fragile and less thermal energy suffices to overwhelm the superconductivity.

Studies of cuprates, however, revealed virtually no isotope effect--phonons could not be the principal binder of Cooper pairs in those materials. In many respects this result was no surprise because the cuprates superconducted far above 30 K and theorists had long ago computed that the electron-phonon interaction described by the BCS model would not be strong enough to hold Cooper pairs together at such high temperatures in any plausible material.

An exception to this 30 K rule did come along in 2002, in the form of magnesium diboride, which superconducts at 39 K [see "Low-Temperature Superconductivity Is Warming Up," by Paul C. Canfield and Sergey L. Bud'ko; *SCIENTIFIC AMERICAN*, April 2005]. Magnesium diboride does show the isotope effect and is understood to be a BCS superconductor, albeit a peculiar variant of the theme. Its unusually high transition temperature results from exceptionally strong coupling between certain electrons and lattice vibrations and from it managing to have two populations of electrons that each form a distinct condensate of Cooper pairs.

What of the new iron-based superconductors? Only a few weeks after Hosono's discovery that fluorine-doped LaOFeAs superconducts at 26 K was published on the Web, theorists released a preprint calculating that the electron-phonon coupling in that material, acting in the manner described by the BCS theory, could not be the glue holding the Cooper pairs together. Lilia Boeri of the Max Planck Institute of Solid State Physics in Stuttgart, Germany, and her co-workers calculated that the transition temperature would be below 1 K if phonons were responsible in the conventional way.

Remarkably, however, researchers have seen some isotope effects, just as the BCS theory would predict. This past May, Xian Hui Chen of the University of Science and Technology of China and his collaborators reported observing a strong effect on the transition temperature of iron arsenide superconductors made with two different isotopes of iron. Thus, the electron-phonon coupling seems to play a role, but other interactions, not included in the BCS theory or the calculations by Boeri and her co-workers, must also be important. Those other interactions could also be behind the cuprates' Cooper pairs and thus might be "the shared secret" of high-temperature superconductivity.

### **Competing Processes**

Clues to the additional physical processes important for high-temperature superconductivity may come from studying how the transition temperature varies with the level of doping for each iron pnictide and from examining the properties the material exhibits when it is not superconducting. Physicists map this information in so-called phase diagrams, which are analogous to the phase diagrams that record how a substance such as water changes its physical state when the temperature and pressure vary [see box on preceding page].

With the amount of doping plotted along the horizontal axis, the superconducting state of a cuprate or an iron pnictide forms a roughly semicircular region at the bottom of the graph. The limits of that region show that if the doping is too low or too high, the material does not superconduct even at absolute zero. The highest part of the semicircle shows the maximum transition temperature, which is attained by some optimal amount of doping.

Several other features of pnictides and cuprates at particular temperatures and levels of doping show great similarity. Both enter a magnetic state known as antiferromagnetism at doping levels too low for superconductivity. A familiar magnetized piece of iron is a ferromagnet--each atom in the material tends to orient its individual magnetic moment, its individual little "compass needle" of magnetism, in the same direction as its nearest neighbors. All of these magnetic moments thus combine to produce the field of the magnet as a whole. In an antiferromagnet, in contrast, the nearest neighbor atoms tend to point their magnetic moments in opposite directions and the material as a whole produces no magnetic field.

For the cuprates, the undoped materials are typically antiferromagnetic up to temperatures well above the highest superconducting transition temperature of the doped material. But as the doping level increases, the temperature for antiferromagnetism plunges to zero before superconductivity appears. Physicists interpret this as a sign that these two different kinds of ordering--antiferromagnetic alignment of the atoms' magnetic moments and the formation of a

condensate of Cooper pairs--are incompatible and competing. The interaction that generates superconductivity in these materials has to overcome the antiferromagnetism.

The pnictides show similar behavior, with the undoped materials exhibiting an antiferromagnetism that is not present in the superconducting state. In December a collaboration of researchers at several laboratories in the U.S. and China found that the antiferromagnetism in the iron pnictide that they studied--cerium oxygen iron arsenide (CeOFeAs) doped with fluorine--disappeared rapidly with increasing doping, much as in the cuprates.

The group also looked at a structural transition that occurred. In the FeAs planes, each Fe atom is surrounded by four As atoms arranged at the vertices of a tetrahedron. At low doping and low temperatures, those tetrahedrons are distorted. At the amount of doping yielding the highest transition temperature, the distortion completely disappeared, suggesting that the good tetragonal symmetry could be important for the pnictide's superconductivity. Tetragonal symmetry is not a factor in the cuprates'  $\text{CuO}_2$  planes, which at most deviate only slightly from being completely flat.

In the cuprates, the antiferromagnetic state is an electrical insulator, but for the pnictides it is a conductor, albeit a poorer conductor than a typical metal. Which is more important in understanding these two materials: the similarity of the antiferromagnetism or the dissimilarity of the conductivity of that state? As with so many features, a conclusive answer to that question remains hidden.

## **Catching Waves**

Another issue of great importance for efforts to unravel the cause or causes of high-temperature superconductivity is the symmetry of the Cooper pairs. In BCS materials, the Cooper pairs have so-called spherical symmetry--a shape that, like a sphere, looks the same in all directions. Also termed s-wave symmetry, it is analogous to the perfectly symmetrical shape of a hydrogen atom in its ground state. (Both examples involve two fermions bound together--two electrons in the case of the Cooper pairs, a proton and an electron in the case of a hydrogen atom.)

The type of symmetry in cuprate Cooper pairs was long a controversial subject, and only after many years did experiments finally resolve it as a kind of symmetry called d-wave with some s-wave mixed in as well. The d-wave symmetry somewhat resembles a four-leaf clover, but with two colors of leaves (actually, "positive" and "negative" lobes) alternating around the stalk. Early experiments on pnictides pointed to s-wave symmetry, leaving open the possibility that those materials really do behave, somehow, as BCS superconductors. Results reported in December and January, however, show that the pnictide's s-wave has an unconventional feature, with positive regions on the opposite side of negative regions instead of the whole sphere being the same sign. Thus, once again the pnictides and cuprates seem to be similar but different.

These studies of the iron pnictides continue at a frenetic pace--in their 20 years of investigating the cuprates, experimenters have built up a veritable arsenal of techniques to bring to bear on the new materials. But the picture emerging from experiments so far is at least as puzzling as that of the cuprates. How much the two puzzles are related and how the commonalities might lead to

insights that could be useful for developing room-temperature superconductivity may not be clear for some time.

Meanwhile the instigator of the field, Hosono, has added another curiosity to be explained. In March he reported finding that strontium iron arsenide ( $\text{SrFe}_2\text{AS}_2$ ) superconducts not only when doped with cobalt but also when the undoped compound is exposed to water vapor. Furthermore, differences in the features of the two cases suggest to him that a different superconducting mechanism is at work in each.

If the history of the cuprates is any guide, expect researchers to keep uncovering more puzzles than answers for some years to come.