

LOW-TEMPERATURE SUPERCONDUCTIVITY IS WARMING UP

Magnesium diboride defies the once conventional wisdom about what makes a good superconductor. It becomes superconducting near the relatively warm temperature of 40 kelvins—which promises a variety of applications

By PAUL C. CANFIELD AND SERGEY L. BUD'KO

IMAGINE walking around in your backyard and suddenly discovering a vein of gold in a corner you thought you knew well. Or imagine how Jed Clampett of the *Beverly Hillbillies* felt when oil started bubbling up through the ground. A similar sensation of incredulous excitement swept over the solid-state physics community in the early weeks of 2001, when researchers announced that magnesium diboride (MgB_2) superconducts—conducts electricity without resistance—at temperatures approaching 40 kelvins.

This simple compound had been studied in the 1950s and had been on the shelves in some laboratories for various mundane purposes for decades, with no one suspecting its enormously valuable hidden talent. Although 40 K (or -233 degrees Celsius) may sound rather low, it was nearly double the record for compounds made of metals (about 23 K for niobium-based alloys, which are widely used in research and industry). A transition temperature that high can be achieved by technologies that cost much less than those needed to bring about superconductivity in the niobium alloys. Possible applications include superconducting magnets and power lines.

Unlike high-temperature superconductors (copper oxide materials that superconduct at temperatures as high as 130 K), MgB_2 seems to be a traditional superconductor, albeit a novel variant. In their decades-long quest for superconductors with ever higher transition temperatures, physicists had developed rules of thumb regarding what kind of combinations of elements to try. In ad-

POLISHED CROSS SECTION of a magnesium diboride wire segment shows that the wire is essentially 100 percent dense and is made up of small, unoriented grains, which reflect light differently, giving rise to various colors. Such wires are useful for basic research into the material's superconductivity. The wire is 0.14 millimeter in diameter.

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dition, many suspected that 23 K was close to the maximum transition temperature possible for a traditional superconductor. To their great surprise, MgB_2 defied these rules and blew away the barrier to higher temperatures.

The speed with which understanding of MgB_2 grew was absolutely amazing. Jun Akimitsu of Aoyama Gakuin University in Tokyo announced the discovery at a meeting in mid-January 2001. Just two months later about 100 two-minute talks on the topic were presented at the American Physical Society's annual March meeting, and more than 70 research papers had been electronically posted on the arxiv.org preprint archive. This burst of activity happened for a few reasons. First, once you figure out how, it is fairly simple to make relatively pure MgB_2 . Second, in 2001 the condensed-matter physics community was more wired together by the Internet than ever before. These two ingredients, combined with the promise of a new, simple superconductor with a high transition temperature, formed an explosive intellectual mixture.

Confirming the Discovery

AT FIRST, news of Akimitsu's announcement spread only by word of mouth and e-mail. No research paper or electronic draft was available. When the news reached our group a few days after the meeting, we asked a series of questions: Can we make high-purity, solid

pieces of this stuff? (On the shelf, MgB_2 is a not so pure powder.) Does it really superconduct near 40 K? (There had been almost two decades' worth of USOs, or "unidentified superconducting objects"—compounds reported to have exceptionally high transition temperatures that other researchers could not replicate.) If MgB_2 does superconduct, can we uncover the mechanism of its superconductivity? And finally, can we delineate some of this compound's basic properties? Happily for one and all, the answer to each of these questions was yes.

The rumor of Akimitsu's discovery started a frantic and wonderful time for us and for other research groups. Our team specializes in studying the physical properties of metallic compounds, so as soon as we heard about the report, we emptied all of our furnaces of existing experiments and started trying to produce MgB_2 .

Making the compound was a tricky business initially. It is an example of an intermetallic compound, one made of two or more metallic elements. The simplest way of making intermetallic compounds—by just melting the elements together—was not possible in this case, because the two elements have very different melting points: 650 degrees C for magnesium and higher than 2,000 degrees C for boron. Because magnesium boils at just over 1,100 degrees C, the magnesium would evaporate before the compound could form, or, in the vernac-

ular, the magnesium would grow legs and walk away.

But the vaporization of magnesium suggested an alternative method: we could seal a piece of magnesium and some powdered boron inside a tantalum vessel, which is inert, and subject them to a temperature high enough to melt but not to boil the magnesium (say, 950 degrees C). Magnesium has a relatively high vapor pressure—indeed, one third of an atmosphere of magnesium vapor exists in equilibrium with the liquid metal at 950 degrees C. We expected that this dense vapor would diffuse into the solid boron, producing pellets of MgB_2 . Sure enough, we found that in as little as two hours this process produced very high purity MgB_2 in the form of a loosely sintered pellet (like sandstone). Within three days of hearing the rumors, we had made these pellets and were able to confirm superconductivity at near 40 K.

Having figured out how to make MgB_2 and confirmed that it is a superconductor, we asked the next burning question: Was it an old-fashioned superconductor whose behavior could be explained by a long-established theory called BCS theory (from the initials of its three discoverers' last names) or an example of a more exotic type [see box on page 86]? If it was an exotic type, that would be a profound scientific discovery. On the other hand, if it was a conventional BCS superconductor, the exceptionally high transition temperature would demand an explanation, but the prospects for using the material in applications would be more encouraging.

For several reasons, some researchers thought that MgB_2 was not a standard BCS superconductor. First, before high-temperature superconductors were discovered in 1986, two decades had gone by with the highest transition temperature stuck at around 20 K. This fact led some theorists to suggest that about 30 K was the maximum temperature possible for superconductivity in compounds that obey BCS rules. The high-temperature copper oxide superconductors far exceeded that limit, but they are not thought to be BCS superconductors.

Overview/Magnesium Diboride

- In 2001 researchers discovered that the seemingly unexceptional compound magnesium diboride superconducts below about 40 kelvins, nearly twice the temperature of other similar superconductors. Its maximum practical working temperature is about 20 to 30 kelvins.
- That temperature can be achieved by cooling with liquid neon or hydrogen or by closed-cycle refrigeration, all of which are much less expensive and troublesome than the liquid-helium cooling required by the niobium alloys that are widely used in industry at about four kelvins.
- When doped with carbon or other impurities, magnesium diboride roughly equals or betters niobium alloys at retaining its superconductivity in the presence of magnetic fields and when carrying an electric current. Potential applications include superconducting magnets, power lines and sensitive magnetic field detectors.

Second, MgB_2 's relatively high transition temperature, or critical temperature (T_c), violated one of the old rules of thumb in the search for intermetallic compounds having a higher T_c : the more electrons that could participate in the phase transition to the superconducting state, the higher the transition temperature would be. Neither magnesium nor boron brought particularly many electrons to MgB_2 .

A very direct experimental test can tell whether a superconductor is following the BCS theory. A key role in the theory is played by lattice vibrations. Imagine that the heavy positive ions of the crystal lattice are held in place by strong springs (the chemical bonds). Excitations such as heat manifest as vibrations of the ions at characteristic frequencies. BCS theory predicts that the transition temperature of a superconductor is proportional to the frequency of its lattice vibrations. As is the case with everyday objects such as wineglasses or guitar strings, objects made from lower-mass materials have higher characteristic frequencies than otherwise identical objects made from higher-mass materials. By using a different isotope of magnesium or boron, we can make MgB_2 out of atoms of different mass, which will alter the lattice vibration frequency, which in turn should alter T_c in a specific way.

Boron has two stable, naturally occurring isotopes: boron 10 and boron 11. The simplest prediction of the BCS model is that T_c should differ by 0.85 K for two samples of MgB_2 made with pure boron 10 and boron 11. With our first sintered pellets of MgB_2 , we discovered a shift of 1 K. The fact that the shift in T_c was a little larger than the simple prediction can be accommodated by BCS theory—it indicates that the boron vibrations are more important to the superconductivity than the magnesium vibrations [see box on page 87].

The closeness of this shift to the predicted 0.85 K revealed that MgB_2 is most likely a BCS superconductor, albeit an extreme example that has a much higher transition temperature than any other. The predictions of an approximate 30 K

Making Wires

Within a couple of weeks after the announcement of superconductivity in MgB_2 , we had devised a technique for making wire segments of this remarkable superconductor. MgB_2 can be formed by reacting magnesium vapor with boron, a process that can take place within hours at temperatures near 1,000 degrees Celsius: the boron essentially sucks the magnesium vapor out of the environment and becomes MgB_2 (swelling up dramatically in the process). Imagine a dry sponge sucking water vapor out of the air on a humid day. This process works with boron fibers that can be purchased in lengths of hundreds of meters; it has been applied to filaments with starting diameters ranging from 0.1 to 0.3 millimeter.

Wire segments such as these are very useful for basic research, allowing for the measurement of the intrinsic physical properties of MgB_2 . Before such wire segments could be used in practical applications, they would need to have a conductive, malleable sheath to provide structural support. (The conductive sheath also carries the current should the superconductivity fail, preventing catastrophic heating of the MgB_2 .) A suitable sheath has not yet been developed.

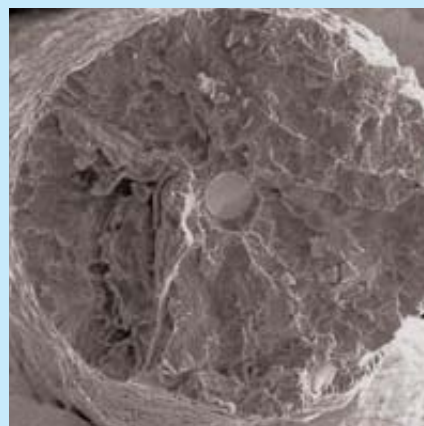
A more common method of wire synthesis is called "powder in a tube." This technique involves pouring powdered magnesium and boron or powdered MgB_2 into a tube, drawing the tube into a wire, and then reacting or annealing the wire to produce a solid structure. This technique has produced research samples that range from tens to hundreds of meters long.

Despite MgB_2 being a rather young superconductor, companies have been taking notice and are working toward commercializing it. Examples include Diboride Conductors and Hyper Tech Research, which are small companies focusing on making and improving the properties of MgB_2 wires, and Specialty Materials, which is a larger materials company with expertise in producing boron filaments.

—P.C.C. and S.L.B.



WIRES were made by reacting magnesium vapor and boron filaments.



CROSS SECTION of a snapped magnesium diboride wire segment reveals a central core of tungsten boride, 0.015 millimeter in diameter.

upper limit to BCS superconductivity were apparently not valid. This was good news, because standard intermetallic BCS superconductors are much easier to work with and can form useful wires much more readily than copper oxide-based superconductors can. In-

deed, it suddenly dawned on our group that we could form MgB_2 wires by simply exposing boron filaments to magnesium vapor [see box above]. Such wires are of greater use than sintered pellets for many measurements and for applications such as magnets.

A History of Superconductivity

Heike Kamerlingh Onnes discovered superconductivity in 1911 when he used liquid helium as a coolant to study the electrical properties of metals at low temperatures. To everyone's surprise, when mercury was cooled to about 4.2 kelvins, it suddenly lost all electrical resistance. This threshold is known as the critical temperature, or T_c .

Other materials having ever higher critical temperatures were discovered slowly but surely during the first five decades of superconductivity research. All these superconductors were either pure metallic elements or intermetallic compounds (made of two or more metallic elements). But from the 1960s through the mid-1980s the maximum value of T_c seemed to be stuck in the low 20s.

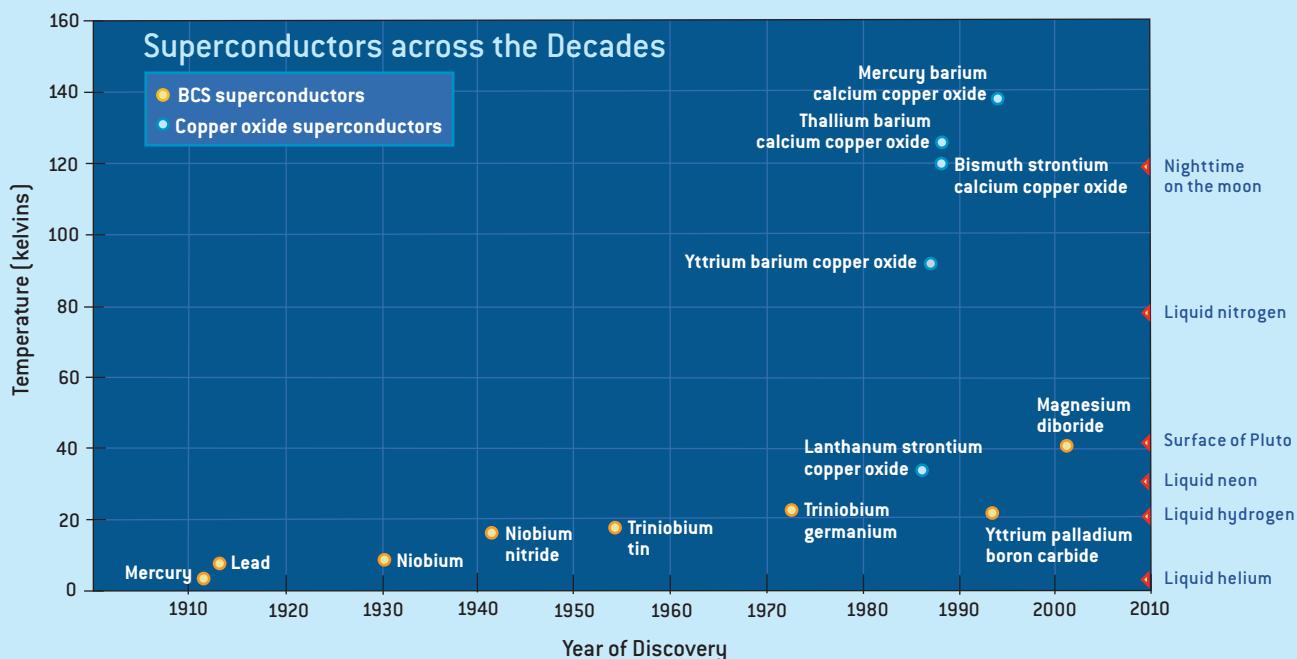
All this changed in 1986 with the discovery of high-temperature superconductivity in a slew of copper oxide-based compounds. During the first few years after this discovery, T_c values shot up, with mercury-barium-calcium-copper-oxide having a T_c of about 130 K. This was a fantastically exciting time, but it soon became clear that the leading theory of how superconductivity arises—known as BCS theory [see box on page 86]—does not explain the absence of resistance in these materials. Despite almost 20 years' worth of effort, there is still no definitive theory of how or why the copper oxide compounds superconduct.

These compounds also pose a multitude of physical challenges. Initially they were hard to make in either high-purity or single-crystal form, making the measurements of their fundamental properties difficult. In addition, the synthesis of wires is not easy: unlike the intermetallic superconductors, the individual grains that make up a piece of one of these oxides have to be aligned with respect to one another for the wire to have useful engineering properties. These problems left researchers and engineers wishing for a substance with the somewhat easier material properties of the intermetallic superconductors that also had a critical temperature significantly higher than 20 K.

By the dawn of the new millennium, then, the superconducting state could be achieved with varying degrees of ease and expense. In the oxides, superconductivity was practical near 77 K, which can be reached relatively easily by bathing the material in liquid nitrogen. The older intermetallic compounds such as triniobium tin were being used in the laboratory and as medical magnets operating at temperatures closer to 4 K, which can be reached with liquid helium.

The discovery in 2001 that the simple intermetallic compound magnesium diboride superconducts at 40 K, about double the temperature of the other intermetallics, was almost exactly what the doctor (or in this case, engineers) had ordered.

—P.C.C. and S.L.B.



Uses of Superconductors

ALTHOUGH IT OCCURS only at very low temperatures, superconductivity has a wide variety of present-day uses, as well as potential future applications. Some of the most obvious derive from superconductors' ability to carry high currents

with no energy losses or resistive heating. An example is superconducting magnets that can produce magnetic fields in excess of 20 tesla (about 500 times stronger than a typical refrigerator magnet). Low-temperature superconducting magnets such as these (and less strong ones) are used in

labs and in magnetic resonance imaging machines in hospitals. Sales of these magnets, crafted from niobium-based compounds and alloys, continue to grow.

Another high-current application that has been proposed is lossless power transmission lines, which can carry

much higher current densities than non-superconducting ones. To date, researchers have successfully tested several copper oxide-based prototypes that have been cooled to near 70 K with liquid nitrogen.

Generally speaking, to act as superconductors in practical applications, compounds need to be cooled substantially below their T_c , to about 0.5 to 0.7 T_c , because large electric currents or strong magnetic fields destroy the superconductivity closer to T_c . Consequently, a T_c of 20 K may imply an operating temperature of 10 K, which means that the superconductor has to be chilled by liquid helium, a costly and somewhat difficult option.

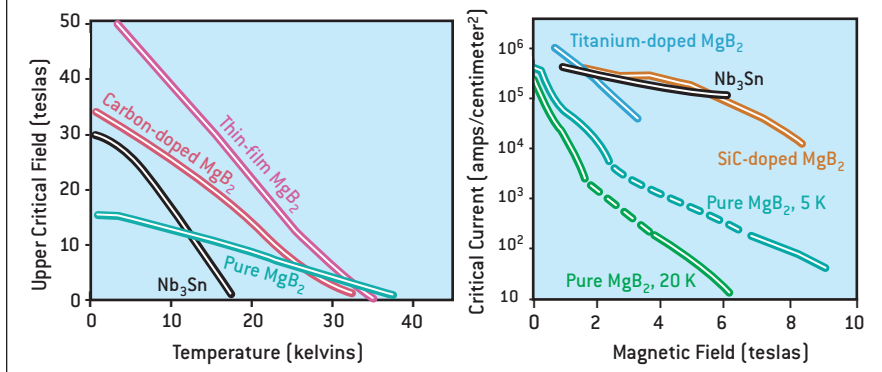
The applied research community is interested in MgB_2 because this material can be cooled to viable operating temperatures more easily than the lower- T_c niobium-based alloys and compounds that are employed today. MgB_2 can be cooled by liquid hydrogen or liquid neon or by fairly cheap, closed-cycle refrigerators that can readily reach below 20 K.

But if this vision is to become a reality, MgB_2 will need to have good superconducting properties. Researchers are paying particular attention to the superconductor's mixed phase, in which a magnetic field partially destroys the superconductivity—in most real applications, the material will be in this phase. Weak magnetic fields do not produce the mixed state; the superconductor excludes such fields from its interior and remains superconducting. At intermediate fields, however, the material allows the magnetic field to penetrate in the form of small tubes of magnetic flux known as vortices. The insides of these tubes are nonsuperconducting, but outside of them the material remains superconducting.

This mixed phase still manifests many of superconductivity's useful characteristics. As the strength of the applied magnetic field increases, the percentage of the material occupied by the flux tubes increases until they overlap fully, at which point the whole material is nonsuperconducting. The field strength at which superconductivity is lost is referred to as the upper critical

IMPROVING PERFORMANCE

Maintaining superconductivity in a magnetic field and when carrying a current is crucial for applications. The plotted data show how doping with impurities has improved the performance of MgB_2 ; it now equals or exceeds that of the industrially favored triniobium tin (Nb_3Sn). The graph at the left shows that wire segments of carbon-doped MgB_2 and a thin film of MgB_2 with an unknown level of impurities withstand a higher magnetic field ("upper critical field") than Nb_3Sn at all temperatures. The data at the right (taken at about 4 K except where noted) show that MgB_2 doped with silicon carbide (SiC) equals the current-carrying capacity of Nb_3Sn , but other variants are significantly inferior. Dashed lines are interpolations.



field and is a key property that determines how useful a superconductor will be in practice.

Most applications will involve intermediate fields (the field is strong enough to be useful but not so strong as to destroy superconductivity altogether), so the goal becomes maximizing the range of temperatures and magnetic fields in which the superconducting mixed phase survives. Temperature also plays a role in these considerations because the upper critical field of a superconductor varies with temperature. Just below T_c , the upper critical field is close to zero—that is, even the weakest field destroys the superconductivity. At lower temperatures the superconductivity can resist stronger fields [see box above].

Fortunately, the upper critical field of

a material can be tuned by making the compound in differing ways, generally by adding certain impurities. For example, when some carbon is substituted for boron in MgB_2 , the upper critical field is dramatically improved. Our group and others have shown that for about a 5 percent substitution of carbon, the upper critical field of MgB_2 can be more than doubled—a fantastic and important improvement in bulk samples.

In addition, the group of David C. Larbalestier at the University of Wisconsin–Madison has shown that thin films of MgB_2 have even higher values of the upper critical field, well above those of triniobium tin (Nb_3Sn). The thin-film data present a vital mystery: What is giving rise to the high values? Is it small amounts of oxygen? Is it some other element sneaking

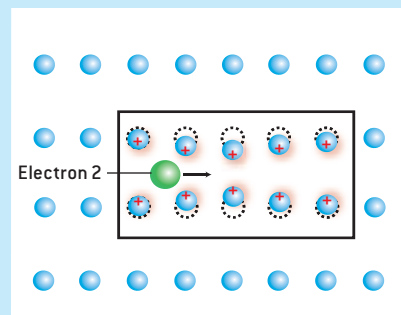
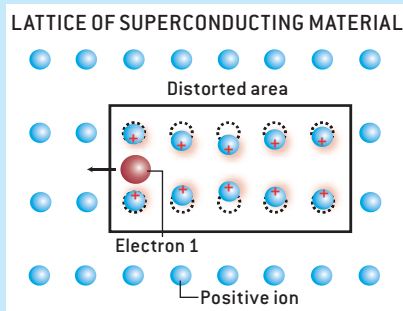
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Predictions of BCS Theory

In 1957 physicists John Bardeen, Leon N. Cooper and J. Robert Schrieffer proposed an explanation of the mechanism underlying superconductivity of metals in a theory that bears their initials. In a normal, nonsuperconducting metal, electrons scatter off of defects and imperfections, which generates resistance. According to BCS theory, superconductivity takes place when the electrons instead act as a single extended collective object that can move without scattering.

The building blocks of this new electronic state are pairs of electrons, called Cooper pairs, in which the partners are weakly attracted to each other. This attraction between two like-charged particles, at first sight seemingly impossible, occurs because the metal is composed of positively charged ions as well as electrons. As one member of the Cooper pair moves through the metal, it leaves a positively charged ionic distortion in its wake. This fleeting net positive charge attracts a second electron. In this way, the lattice distortion loosely couples the electrons. (More precisely, lattice vibrations of a specific frequency are involved in the coupling.) A rather gross analogy is that of two kids bouncing on a large trampoline. Even though there is no direct attraction between the kids, they will tend to bounce toward each other

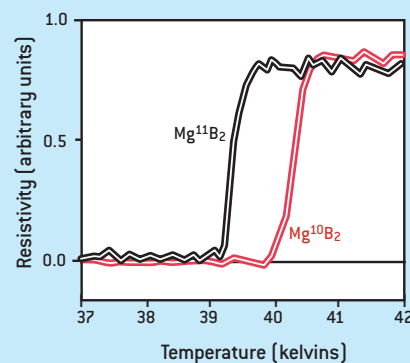


FORMATION OF ELECTRON PAIRS known as Cooper pairs (*above*) ultimately leads to superconductivity. One electron leaves in its wake a distortion of the lattice of positively charged ions in a metal (*left panel*). Shortly thereafter, the second electron is attracted by the resulting concentration of positive charge (*right panel*). In effect, the two electrons are weakly attracted to each other.

because of the distortion that the other causes in the tarp beneath their feet.

The Cooper pairs overlap one another, and below the critical temperature (T_c) they form an extended electronic state that no longer experiences any electrical resistance.

A simplified version of the BCS theory predicts that T_c depends on three properties of the material in question: the number of electrons that can participate in the superconducting state (the more electrons that can participate, the higher the T_c); the characteristic frequency of lattice vibrations involved in coupling the electrons in the Cooper pair (the higher the frequency, the higher the T_c); and the strength of the coupling between the lattice distortion and the electrons (the stronger this coupling, the higher the T_c). For decades, the search for higher T_c values focused on optimizing these three related properties, with a preference for



ELECTRICAL RESISTIVITY of MgB_2 drops to zero as the material is cooled below its critical temperature of about 40 K. The critical temperature is different for samples made with pure boron 10 and boron 11. This clear isotope shift is predicted by BCS theory and thus indicates that the superconductivity in MgB_2 is traditional BCS superconductivity.

trying to improve the first two. MgB_2 seems to have a high T_c because of its stronger electron-lattice coupling, the third property. —P.C.C. and S.L.B.

in and doping in unknown ways? Is it strain in the structure of the MgB_2 in the films? Whatever the answers to those questions, clearly MgB_2 is a promising material for superconducting magnets that can function at higher temperatures and possibly even in higher fields than triniobium tin, which is currently the preferred compound for such magnets.

The second superconducting property of particular interest for applied physics is the critical current density. This quantity delineates the maximum amount of current that a superconductor can carry and still maintain zero resistance. For current densities above the critical current density, the vortices (the

small nonsuperconducting regions of the sample) start to slip or move. Once these regions start moving, energy losses occur—that is, the material has a nonzero resistance. To counter this effect, the vortices can be pinned (in essence, nailed down) by introducing the right type of defect into the superconductor. Often the vortex pinning can be increased by making the individual crystallites (or grains) of the material smaller, thus increasing the surface area associated with grain boundaries, where vortices get pinned. Another method of increasing vortex pinning involves adding microscopic inclusions of some second material such as yttrium oxide or titanium diboride.

Currently one of the major challenges associated with making MgB_2 a useful superconducting material is to increase its critical current density at higher magnetic fields. The critical current density of pure MgB_2 is comparable to that of triniobium tin at low magnetic fields but falls off much more rapidly at higher fields. This is not good news if the goal is to use MgB_2 in magnets, which are meant to produce a strong field. On the other hand, in the four years since the discovery of superconductivity in this compound, the research community has made considerable improvements in critical current density, both in the low-field value and, perhaps more important,

in the higher-field values. Research in this area is very active, and it appears that physicists will soon make further improvements and achieve a better understanding of what will provide a good pinning site in MgB_2 .

Past, Present and Future

THE DISCOVERY of superconductivity in MgB_2 is simultaneously the fruition of decades of focused research and a stark reminder that nature does not always heed the rules of thumb we make up in our often vain attempts to describe her. Although MgB_2 was known to exist for about 50 years, it was never tested for superconductivity, partly because it did not fit our image of a likely intermetallic superconductor. Luckily, in the search for new materials and properties, nature's voice can still be heard over the din of our prejudices.

Over the past four years, humankind's understanding of superconductivity in MgB_2 has evolved at breakneck speed. We have a clear idea of the properties of high-purity MgB_2 , and we are learning how to modify the material so as to improve the ranges of magnetic field and current density over which it can be useful. The properties at 20 to 30 K have improved to the point that it appears high-current-density applications, such as magnets, can be made to operate either with cryogenics such as liquid hydrogen or liquid neon or with closed-cycle refrigerators. Prototype coated wires and even some initial magnets have been made, but more work is needed to optimize the superconductor's properties and to understand its metallurgy as well as that of possible wire-coating materials.

On the whole, the future for MgB_2 looks quite promising. Indeed, if a shift toward a hydrogen-based economy occurs, then MgB_2 could truly come into its own. If large quantities of hydrogen are to be produced, for example, at small pebble-bed reactors [see "Next-Generation Nuclear Power," by James A. Lake, Ralph G. Bennett and John F. Kotek; *SCIENTIFIC AMERICAN*, January 2002], the hydrogen will have to be transported in some manner. One way

Structure and Bonding

One of the primary reasons for the surprisingly high transition temperature of MgB_2 is the strength of the interaction between certain electrons and certain lattice vibrations. The strong interaction arises because of the material's structure and bonding.

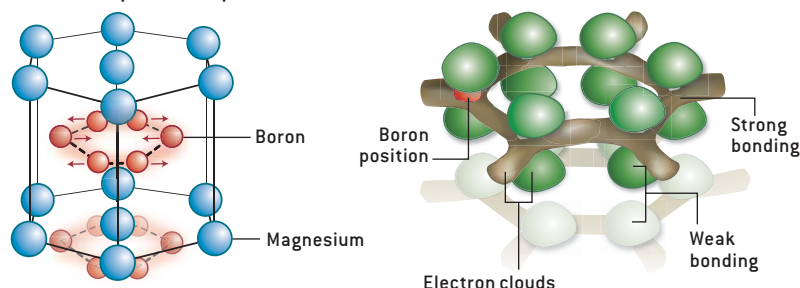
The boron atoms in MgB_2 form a hexagonal honeycomb pattern (red, left). In MgB_2 these layers are separated by layers of magnesium (blue). The electrons responsible for the ordinary electrical conductivity and also the superconductivity are associated with the boron layers and are involved in one of two different types of bonding in the material (right). A very strong bonding occurs within the hexagonal plane, and a much weaker bonding occurs between the boron layers.

The conduction electrons of the planar bonds are very strongly affected by in-plane lattice vibrations (arrows, left). This strong interaction, or coupling, results in a state that remains superconducting at higher temperatures.

MgB_2 has revived a very exciting basic physics question: Can a superconductor have superconductivity involving two distinct collections of electrons (green and gold) forming two distinct seas of Cooper pairs?

Experimental evidence suggests that this is the case in MgB_2 , which would be the first clear example of this phenomenon.

—P.C.C. and S.L.B.



would be through insulated, liquid-carrying pipes that would maintain temperatures below hydrogen's 20 K boiling point. These pipes could constitute the cryogenic system for lossless power cables made of MgB_2 sharing the space inside the thermal insulation. Although such a system currently sounds more like science fiction than an engineering reality, it has been proposed for serious study.

After the discovery of the first copper oxide-based superconductor, researchers found scores of other superconduct-

ing copper oxides. Yet four years after the discovery of MgB_2 , no other related compounds have been found to have anomalously high T_c values. The discovery of superconductivity in the oxides was akin to discovering a whole new continent (with wide expanses to be explored). The discovery of superconductivity in MgB_2 , on the other hand, was more like the discovery of an outlying island in a well-explored archipelago. We do not know if this is the final member of the chain or if yet another surprise awaits us out there. SA

MORE TO EXPLORE

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