Last January physicists discovered that an innocuous compound that had been sitting on the shelf for decades was, in fact, a record-breaking intermetallic superconductor

Magnesium diboride: one year on

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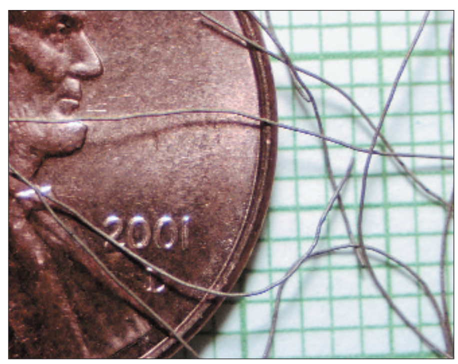
AT THE end of 2000 superconductivity in metal alloys and compounds appeared to remain trapped by a glass ceiling. Over the previous 10 years the temperature at which certain oxide-based compounds – such as bismuth strontium calcium copper oxide and mercury barium calcium copper oxide – lost their resistance to electric current had soared to well over 100 K. Meanwhile, the transition temperature, T_c, for carbon-based materials, including alkali-doped carbon-60 compounds, had risen close to the boiling point of liquid nitrogen (77 K). During the same period, however, the superconducting transition temperature of intermetallic compounds (materials made solely of metals and metal-like elements) remained close to 20 K – as it had been since the mid-1960s.


Segments of MgB_2 wire that were synthesized by exposing boron filament to magnesium vapour. The wires are shown next to a US penny for scale.

By February 2001 everything had totally changed. It was as if a firecracker had gone off in the tidy little ant hill of superconductivity research. For the first few months of 2001, groups all over the world raced to understand the properties of a new intermetallic superconductor. The substance that everyone was scrambling to buy or make, the substance that was causing this grand commotion, was magnesium diboride (MgB_2). This seemingly innocuous binary compound, which had been present in many labs for over half a century, had been discovered to superconduct just below 40 K.

So what?

Before going into the detailed properties of magnesium diboride; before presenting a brief history of our understanding of superconductivity; and before examining how we could miss superconductivity in MgB_2 for so long, we have to answer a question: so what?

Superconductors are not just strange compounds that only physicists play with. Superconducting materials are ideally suited to generating the high magnetic fields commonly required in research labs and in the magnetic resonance imaging (MRI) machines that are becoming so common in hospitals. The reason is that a solenoid made from superconducting wire can carry large currents, and thus generate large magnetic fields, without any dissipation (i.e. without any resistive heating).

In addition, superconducting power cables can carry many times the current density of normal cables. This means that the power capacity of a city can be increased dramatically by simply replacing copper cables with superconducting ones, rather than digging up the roads to lay new cables. Indeed, a test length of superconducting power cable made from ribbons of high-T_c oxide clad in silver was recently laid under the city of Detroit, and the installation of a second length is now being planned for Los Angeles.

But superconductors have to be cooled well below the transition temperature – to roughly about half of T_c – for use in applications. Typically, intermetallic superconductors operate in a bath of liquid helium (i.e. at a temperature of about 4 K) while cables that are made from high-T_c oxides are cooled by liquid nitrogen.

During the past 20 years, closed-cycle refrigerators – which are similar in principle to household refrigerators – have improved dramatically. In fact, it is now quite easy to cool objects to 20 K with no liquid cryogens. That said, the attractions of a new superconductor with a transition temperature of 40 K were clear to physicists. A material that could be cooled using a closed-cycle refrigerator would find many applications, provided it had good superconducting and material properties. These considerations – as well as the general enthusiasm of physicists with a new puzzle to solve – were the driving forces behind last year's excitement. Many groups all over the world are also currently in the process of filing patents, but whether any of these will prove to be valuable will ultimately depend on the properties of MgB_2.

Basic ideas and one equation

Superconductivity was discovered in 1911 by the Dutch physicist Heike Kamerlingh Onnes. Three years earlier, Onnes and colleagues had discovered how to liquefy helium, which they later used to cool mercury to below 4.2 K. At this temperature they found mercury lost its electrical resistance.

Our basic understanding of the mechanism of superconductivity came over 40 years later thanks to a theory devised by John Bardeen, Leon Cooper and Robert Schrieffer. The BCS theory, as it became know, explains how electrons form pairs, known as Cooper pairs, that act as the building blocks of the superconducting state. This pairing takes place through an intermediary, namely a lattice vibration known as a phonon.

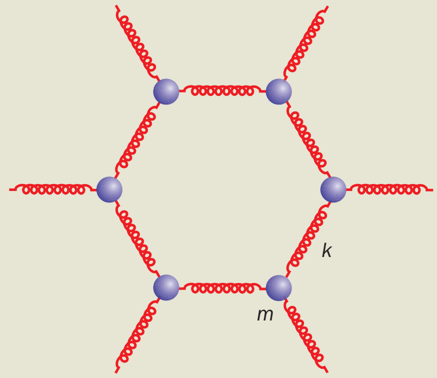
What initially sounds like the impossible attraction between two like-charged objects (i.e. electrons) can be understood at some level via partially inaccurate, but useful, analogies. Picture two people bouncing on a bed or a trampoline. Even though there is no attraction between these people on the ground, the depression left on the trampoline by one person can draw the other person closer. A microscopic example is an electron moving through a crystal lattice, drawing positively charged ions towards itself. This distortion – with its somewhat enhanced positive charge – attracts a second electron. This particular example is a somewhat static view of what is really a dynamic process, but it gives the basic picture.

The BCS theory has essentially three parameters, as can be seen in the equation for the superconducting transition temperature $k_B T_c = 1.13\hbar\omega_D e^{-1/VN(E_F)}$, where k_B is the Boltzmann constant, $\hbar$ is the Planck constant divided by 2π, ω_D is the Debye frequency, V is the strength of the coupling between the electrons and the phonons, and $N(E_F)$ is the density of states at the Fermi level.

The Debye frequency is the characteristic frequency of the lattice vibrations that couple the electrons in the superconducting state. Given that lattice vibrations mediate the Cooper pairs, it is not surprising that T_c is directly proportional to this characteristic vibrational frequency. Now let us invoke a grossly simplified, mechanical model of a crystal that regards the atoms as masses that are coupled together with little springs (see figure 1). The characteristic frequency of this system is $\omega = \sqrt{k/m}$, where k is the spring constant and m is the mass of the atom. Using this simplification we can see that the value of T_c should increase as the mass decreases. This gives rise to a prejudice that compounds containing lighter elements will have higher values of T_c than those composed of heavier elements.

The next parameter is V, the strength of the coupling between the electrons and the phonons. A high value of T_c can be achieved with large couplings as long as the crystal does not distort or loose stability. When the electron–phonon coupling becomes too strong, however, the structure of the crystal can distort to form a so-called charge-density wave at low temperatures. And for really large values of V, a given crystal structure may simply cease to exist in favour of a different one. In either case, the new or distorted structure tends not to be superconducting because it generally has fewer electrons available to participate in the superconducting ground state. For this reason, it was felt that higher transition temperatures would be found near structural phase transitions. Here the coupling is as strong as possible while a suitable crystal structure is maintained.

1 Model superconductor



A ball and spring model of a hexagonal lattice. Approximating the vibrational spectra of a boron-atom lattice by a single spring–mass system, with mass m and spring constant k, is a rather gross simplification. But it does capture the basic physics of how the critical temperature depends on the mass of the atoms and, more specifically, the isotope effect.

The final term in the BCS equation is $N(E_F)$, the density of states at the "Fermi surface". Simply speaking, $N(E_F)$ is a measure of the number of electrons that can take part in the superconducting ground state. In general, compounds containing transition metals – elements that have a partially filled "d-shell" – have a larger density of states at the Fermi surface, and thus a higher transition temperature, than non-transition-metal compounds. Before 2001 the reigning kings of the intermetallic superconductors were niobium germanide, vanadium silicide, niobium nitride and other transition-metal compounds. This led many physicists to believe that a high value for T_c could only be achieved in compounds that included transition metals to boost the density of states.

The BCS equation and, to some extent, these prejudices have helped to define the search for new superconductors over the past decades. While physicists and chemists have a rough idea of how to control the Debye frequency and the density of states, the electron–phonon coupling has remained a somewhat elusive parameter. Much of the search for new intermetallic superconductors has therefore focused on compounds that contain light elements and/or compounds with transition metals.

However, the term for the electron–phonon coupling remains important, and by noting that lead has one of the highest superconducting transition temperatures of all the elements (7.2 K) – even though it is very heavy and not a transition metal – we are forced to acknowledge that electron–phonon coupling plays an important role. And as we will see, the significance of this coupling is even more clearly demonstrated by MgB_2.

Pride and prejudice

Summarizing all of the prejudices from our whirlwind tour of BCS theory: to find an intermetallic compound that loses its resistance at relatively high temperatures, we clearly need to look for something that is made of light elements, preferably containing a transition metal, and that has strong phonon coupling. Many groups and individuals have tried to find such compounds over the decades with varying degrees of success.

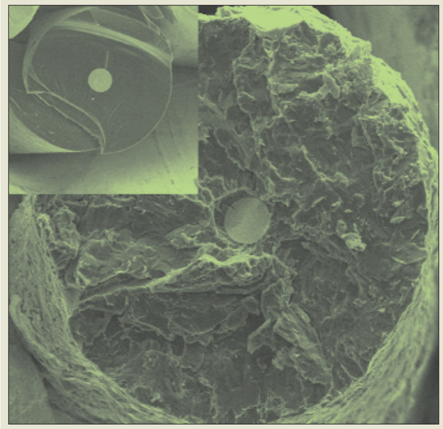
A recent attempt to find new intermetallic superconductors has involved mixtures of titanium, magnesium and boron. Since physicists knew relatively little about this ternary system, they thought it would be a good place to fish for new superconductors. After all, magnesium and boron atoms are light, while titanium is not too heavy and also provides the transition-metal d-shell electrons that are considered vital for a large density of states and, thus, a high transition temperature. It is a nice story with a good plot, but in this case the truth turned out to be stranger than fiction.

When Jun Akamitsu's group at Aoyama-Gakuin University in Tokyo studied this ternary system, they observed small hints of superconductivity near 40 K. After more research and some detective work, they discovered that it was actually the binary compound, magnesium diboride, that became superconducting (see Nagamatsu *et al.* in further reading). During a meeting in Sendai, Japan, in the second week of January 2001, superconductivity in MgB_2 was announced publicly. The clock started ticking.

The electronic grapevine started carrying hints of excitement, but no details. When our group heard – within about a week of the Sendai conference – no information was available. On hearing of a superconductor with a transition temperature near 40 K, many theorists and experimentalists immediately concluded that some exotic (i.e. not well understood) mechanism other than electron–phonon coupling must be at work. Indeed, they thought the physics might even be similar to the high-T_c oxide superconductors, which still lack an agreed theory. On the other hand, researchers familiar with intermetallic superconductors felt that MgB_2 was probably an extreme example of standard, old-fashioned superconductivity. Either way, superconductivity at 40 K in MgB_2 looked like an exciting proposition.

To give a measure of just how excited people were, our own group had posted its first paper on the Web by the end of January and had published three papers on MgB_2 in *Physical Review Letters* by mid-March. And at the American Physical Society's March meeting in Seattle, nearly 1000 physicists gathered late into the night to hear some 80 two-minute updates on the latest research.

2 Wires shape up



Cross sections of a boron filament some 100 microns in diameter, and the MgB_2 wire segments that were produced from it. The boron filament expands to a diameter of 150 microns as the magnesium vapour diffuses into the boron to make MgB_2.

Shape and size

As soon as we heard about the report at the Sendai meeting, we decided to make magnesium diboride, to test its superconducting transition temperature and, hopefully, to address some of the questions about the underlying mechanism involved. We emptied all of our furnaces and started trying to produce the compound – but making MgB_2 is a tricky business. The simplest way of making intermetallic compounds – by simply melting the elements together – was not an option open to us because of the high decomposition temperature of MgB_2 and the high vapour pressure of magnesium. In other words, the magnesium would just evaporate before the compound could form.

However, we realized that if exactly the right proportions of magnesium and boron were sealed in an inert tantalum vessel and reacted at a high enough temperature (950 °C), then polycrystalline pellets of MgB_2 could be made in as little as two hours. While we use this method in the laboratory to make 5–10 gramme samples of MgB_2, industrial suppliers like Accumet Materials use a similar technique to make 10–100 kg quantities of the compound.

Within three days of hearing the rumours, we had made high-purity pellets of magnesium diboride and were able to confirm superconductivity near 40 K. Although the transition temperature can be measured on sintered pellets of this kind, many other measurements and applications require the superconductor to be in a denser form with a better defined geometry. It then suddenly dawned on us that we might be able to form MgB_2 wires by simply exposing boron filaments to magnesium vapour.

The reason we believed that this approach would work is because MgB_2 is composed of just two elements, and because magnesium has a relatively high vapour pressure (i.e. it readily turns into a gas). Indeed, one third of an atmosphere of magnesium vapour exists in equilibrium with the liquid metal at 950 °C. This simple idea was rapidly put to the test and we soon found that we could produce segments of MgB_2 wire up to 0.4 mm in diameter from lengths of boron filament (see figure 2 and Canfield *et al.* in further reading). Such boron filaments are found in a variety of composite materials – ranging from fibre in military garments to high-performance sports equipment. Moreover, they can be up to several kilometres in length, which bodes well for future applications. The same technique is also being exploited by our group and others, including Hans Christen and co-workers at the Oak Ridge National Laboratory, to turn boron films into magnesium-diboride films.

Starting with boron filament is one particularly elegant method of making wire-like samples, but there is another tried and trusted way to produce superconducting wires from a wide variety of materials – the "powder-in-a-tube" method. In this approach, magnesium-diboride powder is poured into a tube that is then made thinner and longer. This method has been used by a variety of groups around the world, including Sungho Jin and co-workers at Lucent Technologies in the US and Edward Collings' group at Ohio State University (see Jin *et al.* in further reading).

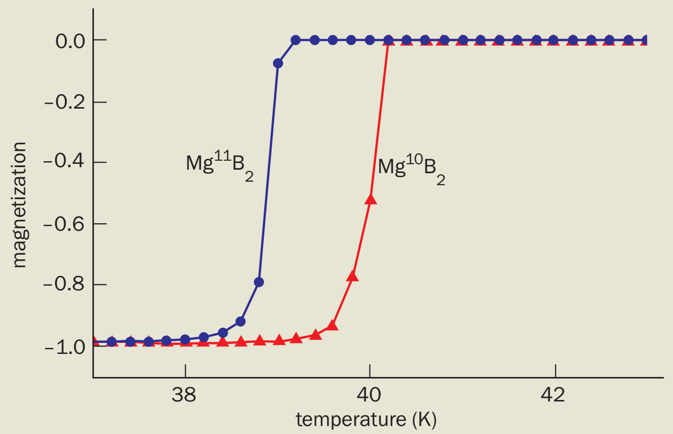
Already wires ranging in length from 10 m to 100 m have been made, or are in the process of being made. At this stage it is not clear which approach will ultimately produce the best results, but it is fairly clear that magnesium-diboride wires will be made and utilized in the foreseeable future. But this is putting the cart before the horse. First let us review some of the basic properties of MgB_2 and then return to the applications.

What makes it tick?

So is magnesium diboride an old-fashioned superconductor that can be explained by BCS theory or is it more exotic? Bardeen, Cooper and Schrieffer showed that the transition temperature of a superconductor is proportional to the frequency of the lattice vibrations. And earlier in this article we showed that a simple model of the lattice predicts that higher transition temperatures can be achieved for compounds with lighter atoms. But how can we change the mass of the atoms without changing the compound itself? The answer is isotopes!

Now we start to see just how important light elements are. Boron has two stable naturally occurring isotopes: boron-10 and boron-11. The simple predictions of the BCS model can be tested by making two samples of MgB_2 with isotopically pure boron. Indeed, the theory predicts a difference in the

3 Classic traits of a conventional superconductor



The magnetization $Mg^{11}B_2$ (blue) and $Mg^{10}B_2$ (red) as a function of temperature. The sudden change in magnetization (as well as resistivity and specific heat), which signals the onset of superconductivity, occurs 1 K higher in the lighter compound (see Bud'ko *et al.* in further reading). Later data from David Hinks's group at the Argonne National Lab confirmed these results and showed additionally that there is virtually no shift associated with magnesium isotopes (see Hinks *et al.* in further reading). The results are consistent with boron vibrations being the key to superconductivity in MgB_2.

value of T_c of 0.85 K between the two different compounds. With our first sintered pellets of magnesium diboride, we discovered a shift of 1 K in the resistivity, magnetization and specific-heat measurements (see figure 3 and Bud'ko *et al.* in further reading).

These simple measurements immediately changed the nature of the discussions about magnesium diboride. They revealed that MgB_2 is most likely an extreme example of a traditional superconductor with a low density of states, a high Debye frequency, a large electron–phonon coupling and a very high value of T_c. This was extremely good news. Standard intermetallic superconductors are much easier to work with, and can form useful wires much more easily than the high-temperature oxide superconductors.

Basic properties

Having addressed the mechanism that underlies superconductivity in MgB_2 (at least to some extent), and having devised a way to make samples in a variety of shapes and sizes, physicists started to address the basic properties of MgB_2. By mid January we knew that magnesium diboride lost its resistance below 40 K, but over what range of temperatures and applied magnetic fields would it superconduct? And, even more importantly for applications, under what conditions would it be a *useful* superconductor?

At this point it is prudent to review some of the characteristic features of superconductors. There are two basic types of superconductors: type-I and type-II. The difference, in poetic terms, is essentially diplomatic, and refers to the way the superconducting state reacts to an applied magnetic field.

Type-I superconductors simply refuse to compromise with the applied field in any way, shape or form. They only superconduct in magnetic fields below a certain critical value, H_c. Above this critical field, superconductivity is destroyed and the sample returns to its normal state.

The situation is quite different for type-II superconductors, which can still conduct without resistance in relatively large applied magnetic fields. In this case, there are two important field scales: a lower critical field, H_{c1}, below which the material behaves just like a type-I superconductor, and an upper critical field, H_{c2}, above which the sample is a normal conductor. For fields between H_{c1} and H_{c2}, magnetic field lines, known as vortices, penetrate the sample to produce a "mixed state" that can still superconduct. At the core of these vortices, the material reverts to its normal conducting state – at H_{c1} the vortices are few and far between, while at H_{c2} they overlap to such an extent that the whole sample becomes normal.

The advantages of type-II superconductors are that H_{c2} and H_{c1} are inversely related to each other with $H_{c2} \sim H_c^2/H_{c1}$, and that H_{c1} can be very small. (In type-II superconductors, H_c^2 is an energy scale that is proportional to the binding energy of the Cooper pairs.) As a result, the upper critical field can often significantly exceed 10 T. A large upper critical field is vital in many applications: in magnets, for example, it defines the largest field that can possibly be generated by a superconducting solenoid.

But in the spirit of the old American idiom "there ain't no such thing as a free lunch", there is a price associated with high values of H_{c2}. The sample will only have zero resistance in the mixed state if the magnetic flux vortices are "pinned" or restrained from moving. Pinning is an extrinsic effect, and optimizing the pinning without severely degrading the superconducting properties is one of the dark arts in the field of applied superconductivity. Examples of pinning sites include grain boundaries and clusters of impurities called precipitates. In the simplest picture, these sites reduce the energy needed to drive the sample into the normal state, thereby pinning the vortex core.

Two simple quantities – known as the irreversibility field, H_{irr}, and the critical current density, J_c – measure how well the vortices are pinned. For fields above H_{irr}, or currents above J_c, the vortices start to move and a finite resistance develops. The irreversibility field and the critical current density therefore set the practical upper limits for magnet or power-distribution applications. In both these applications, we are greedy and want as large a current density or field as possible.

So how does magnesium diboride shape up? Our group has measured the response of MgB_2 as a function of temperature and in various magnetic fields (figure 4 and Finnemore *et al.* and Bud'ko *et al.* in further reading). We found that, at low temperatures, the upper critical field of wire segments is almost 16 T, while the irreversibility field is close to 7 T. Taking a value somewhat less than H_{irr} as a safe operating field, we expect to be able to produce a 3 T magnet from MgB_2 wire cooled to 20 K.

We also compared the critical current density of magnesium diboride with niobium tin (Nb_3Sn), one of the reigning kings of the intermetallic superconductors. Although much higher critical current densities can be achieved in Nb_3Sn, it has to be cooled to much lower temperatures before it even loses its resistance. Indeed, at 20 K, niobium tin is essentially in its normal conducting state. If you recall that superconductors become useful at temperatures below $\frac{1}{2}T_c$ – i.e. below about 20 K for MgB_2 – and that such temperatures can easily be reached using a closed-cycle refrigerator, then magnesium diboride suddenly becomes a much more interesting superconductor.

On top of all this, MgB_2 has a very low normal-state resistivity. This is important because superconducting magnets can sometimes suddenly become normal conductors if either the critical current or the irreversibility field is exceeded, or if the magnet is bumped or disturbed at high fields. At this point, what used to be a zero-resistance coil can suddenly become a toaster. This dramatic event is called "quenching".

Quenching is a runaway process in which a small normal-conducting region heats up and turns a far greater part of the magnet into a normal conductor. It mainly occurs because many superconducting materials have quite high resistivities in the normal state. In order to protect against this normal-state heating, most superconducting wires are encased in highly conducting sheaths. In contrast, the resistivity of magnesium diboride at 42 K is more than 20 times smaller than that of Nb_3Ge in its normal state, and only a little greater than that of copper wire. This means that MgB_2 will be able to handle a quench much more readily than existing superconducting materials and will therefore require less protective sheathing.

Wires, films and the future

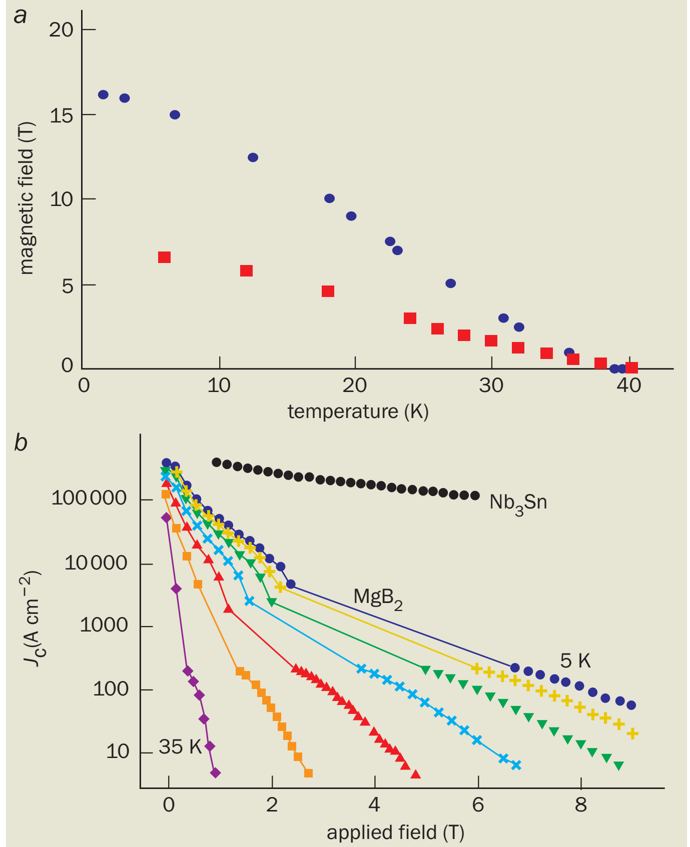
So what could be done with a superconductor that has all the properties of magnesium diboride? If arbitrary lengths of MgB_2 wires could be synthesized with the properties shown in figure 4, then there would be immediate uses for them in magnets for medical, industrial and research applications. Such magnets would be particularly appealing for magnetic-resonance-imaging applications because they would be lightweight – due to the low density of MgB_2 and the reduced need for cladding to protect against quenches – and could be cooled via a closed-cycle refrigerating unit. A similar magnet with a field of 2–3 T at 20 K would meet industrial requirements for magnetic separation as well (see "Superconductivity leaves the lab" *Physics World* October 2000 p23).

Other uses could include magnets in university labs and other research settings, and for the really large magnets required to focus and bend particle beams at accelerators. After attending a recent seminar on MgB_2, Peter Limon, head of the technical division at Fermilab, stated: "The promise of MgB_2 is that it is a potentially inexpensive superconductor that can operate at elevated temperature, thereby simplifying costly and complex cryogenic systems. This may lead to capital and operating savings for large colliders and other accelerators, and, possibly more important, could lead to greater reliability and availability." Such factors could also allow the construction of the next generation of accelerators.

Clearly any improvement in the critical current density or the irreversibility field would only increase the appeal of MgB_2 as a useful superconductor. While this may appear to be a blithe and somewhat optimistic statement, it actually indicates the research direction that many groups are currently taking.

The pinning of vortices is an extrinsic effect: it can often be increased by adding the "right sort" of impurity or defect. Moreover, the ratio of H_{c2}/H_{c1} can be changed dramatically – and, in some cases, increased significantly – with the judicious addition of defects. (In contrast, the thermodynamic critical field, H_c, tends not to change as much.) Indeed, initial results on thin films of MgB_2 by Chang-Beom Eom and David Larbalestier of the University of Wisconsin at Madison and co-workers indicate that some films that appear to be contaminated – probably with magnesium oxide – have almost double the irreversibility field, critical current density and upper critical field compared with clean samples. The values that can be extracted from clean samples (figure 4) should therefore be treated as lower limits. With more research into pinning mechanisms it should be possible to increase the irreversibility field, critical current density and upper critical field for bulk and wire samples as well (see Eom *et al.* in further reading).

4 Critical properties



(*a*) The upper critical field (blue) and the irreversibility field (red) of MgB_2 as a function of temperature. (*b*) The superconducting critical current density, J_c, of MgB_2 as a function of applied magnetic field for various temperatures. The critical current density of niobium tin (black) at 4.2 K is shown for comparison.

Before signing off, it is worth noting that there are very interesting basic-physics questions that remain to be answered about MgB_2. If MgB_2 proves to be an extreme example of phonon-mediated BCS superconductivity, then are any of its properties novel? To date several interesting features have come to light. It now appears that MgB_2 has a highly anisotropic critical field (rather than an isotropic one) that can vary by almost a factor of five depending on the orientation of the applied field with respect to the individual grains. Indeed, measurements on the very first tiny single crystals of MgB_2 appear to have similarly large anisotropies.

Another fascinating possibility is that MgB_2 may have two superconducting gaps associated with its superconducting ground state, rather than one. The superconducting gap is a measure of how strongly the electrons are bound inside the Cooper pairs. The details and full implications of these features are still being examined and are certainly beyond the scope of this article.

Another question is whether there are more "surprise" superconductors like MgB_2 waiting to be found. Indeed, MgB_2 is a notable example of an intermetallic superconductor that has a fantastically high value of T_c yet a remarkably small density of states. The existence of such a conspicuous material will guide new searches for superconductors with comparable – or even higher – values of T_c. Physicists should be looking for compounds with large characteristic frequencies and strong electron–phonon couplings, without worrying too much about the density of states at the Fermi surface. Over the next few years we will see what these searches turn up.

The best of all worlds

MgB_2 has everything that could have been hoped for from an intermetallic superconductor. It has a remarkably high critical temperature, it has a low normal state resistivity, it is lightweight and it is made from elements that are abundant in nature. In terms of basic physics, MgB_2 seems to be an outlying example of phonon-mediated BCS superconductivity, which is consistent with the fact that it seems to be relatively easy to make prototype MgB_2 wires that manifest excellent critical current densities and irreversibility fields. The potential uses for MgB_2 include superconducting magnets and perhaps even cables for power transmission. The question of whether thin films of MgB_2 will be useful in applied situations still has to be addressed but, given the high value of T_c and the ease of making films, this too seems likely.

One point does have to be kept in mind, however. Even though we already know an amazing amount about MgB_2, our knowledge of superconductivity in this compound is only one year old. There is therefore the very real potential to improve its critical properties. In a similar vein, it is almost certain that our understanding of this extreme example of intermetallic superconductivity will greatly improve over the next few years and may even reveal other extreme superconductors.

Further reading

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