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.

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 ($\text{MgB}_2$). 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 $\text{MgB}_2$ 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 $\text{MgB}_2$.

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 known, 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 two 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 $k_B T_c = 1.13 \hbar \omega_d e^{-1/N(\epsilon_F)}$, where $k_B$ is the Boltzmann constant, $\hbar$ is the Planck constant divided by $2\pi$, $\omega_d$ is the Debye frequency, $V$ is the strength of the coupling between the electrons and the phonons, and $N(\epsilon_F)$ 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.

The final term in the BCS equation is $N(\epsilon_F)$, the density of states at the “Fermi surface”. Simply speaking, $N(\epsilon_F)$ 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 germainide, 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 Akimitsu’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 MgB2 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 MgB2 was probably an extreme example of standard, old-fashioned superconductivity. Either way, superconductivity at 40 K in MgB2 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 MgB2 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.

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 MgB2 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 MgB2 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 MgB2 could be made in as little as two hours. While we use this method in the laboratory to make 5–10 gramme samples of MgB2, industrial suppliers like Accuret 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 MgB2 wires by simply exposing boron filaments to magnesium vapour.

The reason we believed that this approach would work is because MgB2 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 MgB2 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 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 MgB2 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 MgB2 with isotopically pure boron. Indeed, the theory predicts a difference in the
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 \( H_{c1} \) and \( H_{c2} \) are inversely related to each other with \( H_{c2} \sim H_{c1}^2 \), and that \( H_{c1} \) can be very small. (In type-II superconductors, \( H^2 \) 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\(_3\)Sn), one of the reigning kings of the intermetallic superconductors. Although much higher critical current densities can be achieved in Nb\(_3\)Sn, 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 be-
come 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 resis-
tivity of magnesium diboride at 42 K is more than 20 times
close to that of Nb,Ge 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 ex-
isting 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 light-
weight – 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 require-
ments for magnetic separation as well (see “Superconduct-
vity 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 cap-
tal and operating savings for large colliders and other accel-
erators, 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 $H_{Jc}/H_c$ can be changed dramatically
– and, in some cases, increased significantly – with the judici-
ous 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 Madi-
son 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 re-
search into pinning mechanisms it should be possible to in-
crease the irreversibility field, critical current density and
upper critical field for bulk and wire samples as well (see Eom
et al. in further reading).

Before signing off, it is worth noting that there are very in-
teresting 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 aniso-
tropic 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 superconduc-
tor 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 out-lying 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 might even reveal other extreme superconductors.

**Further reading**


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