Resistance is useless

Chemistry holds the key to commercialisation of high-temperature superconductors that could revolutionise electrical power supply. Joe McEntee explores the challenges and the opportunities

For some researchers, high-temperature superconductivity ranks as one of the greatest discoveries in science. The ability of select materials to carry electrical current without loss – below the superconducting transition temperature (T_c) – when cooled by a cheap, practical cryogen opens up all sorts of possibilities. Chief among them: a family of enabling technologies – superconducting power cables, motors, generators and smart switches – that, if commercialised and deployed en masse, will transform the economics, efficiency and environmental impacts of electrical power generation and grid distribution.

High-T_c superconductivity, argue the true believers, could be a revolutionary technology. The dream is a compelling one, not least when considered against the backdrop of today's creaking electrical power networks. In the US alone, the Department of Energy (DoE) estimates that transmissions losses in the grid run at between seven and 10 per cent of the power delivered – equivalent to 40 power plants emitting 230 million tonnes of CO_2 per year. What's more, by 2030 demand for electricity is expected to grow by a whopping 100 per cent globally.

In short

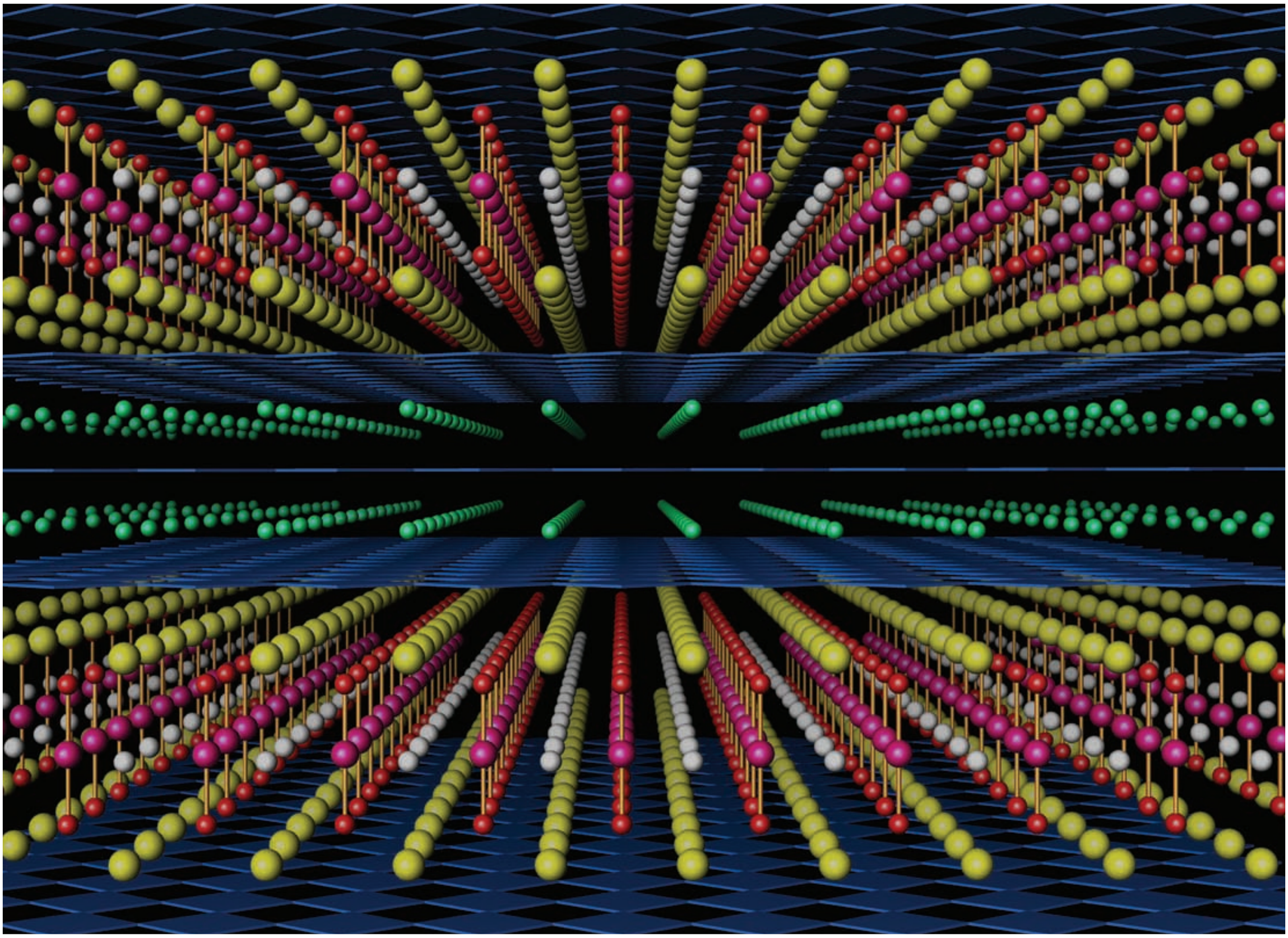
- **The underlying mechanisms of high-temperature superconductivity must be unravelled before it can be commercially exploited**
- **Multidisciplinary collaboration will be essential in the search for new classes of higher-T_c materials**
- **Commercial breakthroughs are imminent and prototypes are already successfully operating in the electric grid**

Since it announced itself with a bang in the mid-1980s, however, the field of high-T_c superconductivity has, in some respects, struggled to live up to the early hype and breathless expectation. Subsequent scientific advances have been incremental in nature, rather than headline-grabbing breakthroughs. Dissenting voices have cited the slow rate of progress and a steady decline in the number of journal papers on high-T_c superconductivity as evidence that the field is a busted flush, with researchers following the money to more fashionable subjects like nanoscale science and technology. But the reality is much more complicated.

Certainly there is a long way to go in terms of the basic science of high-T_c superconductivity. At the theoretical level, for example, the mechanisms of high-temperature superconductivity remain obscure – which, in turn, imposes all sorts of practical restrictions on the chemists, materials scientists and physicists working to discover higher-T_c materials. Conversely, applied research, technology transfer and early-stage manufacturing are pushing on regardless, with all manner of prototypes and demonstration projects highlighting the commercial potential of high-T_c superconductivity in a range of utility, military and industrial applications.

A lasting legacy

The story of superconductivity – at least so far – is a tale of 100 years of scientific endeavour and of fundamental breakthroughs that have transformed our understanding of the forces that control atomic interactions within solids. There have been a few Nobel prizes along the way too.



The mercurocuprate $HgBa_2Ca_2Cu_3O_{8+x}$ has the highest T_c of any superconducting material (green spheres: calcium, yellow spheres: barium, pink spheres: mercury, white spheres: oxygen, blue sheets: copper-oxygen planes)

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It all started back in 1911 when Heike Kamerlingh-Onnes, a Dutch physicist who not long before had figured out how to liquefy helium, observed loss-free electrical flow in mercury at a slightly chilly 4.1 to 4.2K. For the discovery of low-T_c superconductivity, and the enabling breakthrough on helium liquefaction, Kamerlingh-Onnes landed the Nobel prize for physics in 1913.

The next big step forward came in 1957 with the elucidation of a theoretical framework to explain the fundamental workings of superconductivity. A trio of US researchers – John Bardeen, Leon Cooper and Robert Schrieffer (more commonly abbreviated to BCS in the literature) – showed that the superconducting state arises from the 'condensation' of electrons into so-called Cooper pairs.

Like quantum mechanics in general, BCS theory can be counter-intuitive. Instead of repelling, the two electrons in a Cooper pair come together through the exchange of phonons, quantised vibrational motions of the atoms in a solid that act as a kind of electron 'glue'.

Significantly, BCS theory also shows that the motion of these Cooper pairs is highly correlated through thousands of atomic lattice spacings within the solid – a manifestation of quantum mechanics that underpins zero resistance. It means that the electrons move freely through the space, rather than experiencing resistance from being bounced around within the lattice.

In 1972, Bardeen, Cooper and Schrieffer shared the Nobel prize for physics for their work on the theory of superconductivity.

Throughout the 1970s and early 1980s, the search for superconducting metals and intermetallic compounds with higher transition temperatures went on, topping out at a none-too-balmy 23K. For the most part, it was a field still dominated by physicists, materials scientists and engineers, with only a small number of solid-state chemists maintaining a watching brief.

Higher and higher

That all changed in 1986 when Alex Müller and Georg Bednorz, scientists at the IBM Research Laboratory in Rüschlikon, Switzerland, discovered superconductivity at 35K in a ceramic copper-oxide material (the La-Ba-Cu-O system). The discovery was as dramatic as it was unexpected – ceramics hardly being renowned for their electrical conductivity.

Things soon heated up further. Within months of the IBM announcement, other researchers were observing superconductivity in structurally similar ceramic cuprates at temperatures as high as 120K. Those higher T_cs were especially significant because they meant that cooling of superconducting materials was suddenly possible with liquid nitrogen, a cheap and widely used cryogen (boiling point 77K).

The field of high-T_c

superconductivity was born and, indicative of the seismic nature of their discovery, just a year later Bednorz and Müller were honoured with the Nobel prize for physics. It was at this point that the phenomenon of superconductivity truly entered the realm of chemistry, claims Peter Edwards, professor of inorganic chemistry at the University of Oxford, UK.

In a new book to honour the 75th birthday of the British chemist Sir John Meurig Thomas[1], Edwards and his Oxford colleague Vladimir Kuznetzov argue that high-T_c superconductivity 'was a pivotal event in the true dawning of the field of materials chemistry. For only through a detailed knowledge of the science of preparative solid-state chemistry could pure, single-phase materials be synthesised and studied in a definitive fashion'.

What they're referring to is the increasingly important role that materials chemists have played post-Bednorz/Müller, using a broad portfolio of approaches like sol–gel processing, chimie douce chemistry, electrochemistry, microwave chemistry, combustion and self-propagating methods to realise new high-T_c superconducting materials. Just as significant is the ability to chemically tune the material properties of these complex oxides through chemical substitution, such that small changes in composition can transform an antiferromagnetic insulator, for example, into a high-temperature superconductor.

Chemical intuition

More than 20 years on from that initial high-T_c discovery, over 50 other layered cuprates (with the same copper-oxygen planes) have been found, many showing substantially higher T_cs. The highest figure of merit to date is some 138K at ambient pressure (160K under pressure) in the mercurocuprate $HgBa_2Ca_2Cu_3O_{8+x}$, the head of a family of superconductors discovered by solid-state chemists at Moscow State University, Russia, and taken to this T_c value by physicists and materials scientists at ETH Zürich, Switzerland (see p52).

There have also been notable superconductor discoveries in non-copper oxides, organics, carbides, fullerides, borides, heavy fermions and other elements – a trend which suggests superconductivity may arise from multiple mechanisms. In contrast to the cuprates, though, none of these other classes of high-T_c materials has yet been found to exhibit superconductivity above the boiling point of liquid nitrogen.

'The grand challenge will be to map all of this onto the chemistry of the periodic table'

'This aspect is key to understanding why these exceptional properties occur, and it will be in the discovery of new high-T_c superconductors that chemists can make a significant contribution,' Edwards explains. 'This will require not only great experimental prowess, but an intuitive understanding of how this remarkable phenomenon comes about. I say "intuitive", since there simply is no universally agreed theory of high T_c.

'It's no exaggeration to say that understanding how high-T_c superconductivity works will be one of the most difficult and finest achievements of modern science. The trick – and the grand challenge – will be to map all of this onto the characteristic chemistry of the venerable periodic table of the elements.'

Guided by chemical and physical insights and intuition, coupled with ingenuity in chemical synthesis, Edwards reckons scientists are well set to discover high-T_c superconductivity in new classes of materials. And that could open the way to the panacea: superconducting materials at room

The search for the superconducting 'glue'

Thrashing out a unified theory of high-T_c superconductivity is like trying to complete a join-the-dots puzzle where some of the dots are still missing and some of the numbers are in the wrong order. Even so, progress continues on many fronts as scientists probe the 'glue' that binds electrons into superconducting pairs in high-T_c materials.

Researchers at Brown University, Providence, US, for example, recently reported that Cooper pairs not only form in superconductors but also in their opposite – electrical insulators (*Science,* 2007, **318**,1273).

'Our finding is quite counterintuitive,' said James Valles who led the research. 'Cooper pairing is not only responsible for conducting electricity with zero resistance, but it can also be responsible for blocking the flow of electricity altogether.'

In the study the team found Cooper pairs present in the insulator thin-film bismuth, as well as in superconductors, though they believe that the pairs behave differently in each instance. Taken further, the work could ultimately help scientists understand the limits of superconductivity.

Also in the US, further evidence has emerged to suggest that magnetism plays a key role in the formation of Cooper pairs. Scientists at the University of Tennessee and other centres carried out scanning-tunnelling microscopy measurements on the high-T_c copper-oxide superconductor PLCCO. Their data indicate that, rather than phonons (the interaction of electrons with the vibrational motions of the atoms in a solid), spin excitations appear to glue the electrons together(*Nature,* 2007, **450,** 1058).

'They say if it looks like a duck and quacks like a duck, then it's probably a duck,' said Pencheng Dai, a professor of physics at Tennessee. 'These findings add to the understanding that magnetism plays a role in creating [Cooper] pairs.'

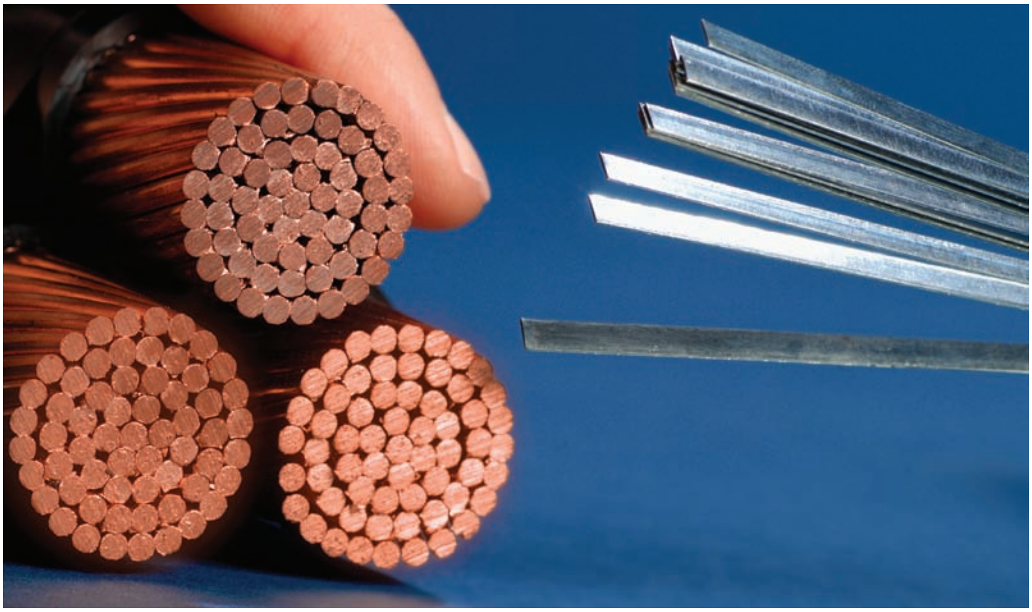
Finally, in a recent review published in *Nature* (2007, **450,** 1177), US and British scientists posit that superconductivity in certain materials can be achieved without phonons.

Among the materials that appear capable of superconductivity without phonons are the so-called heavy-electron superconductors, certain organics and the copper-oxide materials.

'If we ever find a material that superconducts at room temperature, it will be within this class of materials,' said David Pines, a co-author of the work from Los Alamos National Laboratory, New Mexico, US. 'This research shows you the lamp-post under which to look for new classes of superconducting materials.'

High-T_c superconductors could make power blackouts a thing of the past

AP PHOTOS



AMERICAN SUPERCONDUCTOR

2G superconducting tapes (right) have power densities 150 times higher than copper wires

temperature and above.

'I regard high-T_c superconductivity as one of the greatest ever discoveries in science,' says Edwards. 'As far as I am aware, there are no theoretical limits to T_c, but it is important to stress that this endeavour will require expertise in all sister disciplines of chemistry, physics and materials science.'

Joined-up thinking

Yet the reality is that scientists working on superconductivity today are not so different to Kamerlingh-Onnes back in 1911. In superconductivity, it seems, serendipity still goes with the turf. Despite all the progress of the intervening years, and the accumulated experience with many different kinds of superconductors, researchers do not yet know how to predict the occurrence of superconductivity or to design a material with given superconducting properties.

The supercable project

In Spain, a collaborative project between industry and academia will set a superconducting precedent in Southern Europe. The 'Supercable Project' – a joint initiative between the Autonomous University of Barcelona's Department of Physics, the Institute of Material Science in Barcelona and the French cable manufacturer Nexans – will develop a 30 metre superconducting cable made from the ceramic BSCCO.

The project recently received a €500 000 energy efficiency award from the Spanish Energy company EDESA, which will fund the manufacture and installation of the cable, the construction of which should be complete by 2010.

The aim is to validate the practicality of superconductor cables. The collaboration will also continue to develop and test new superconducting materials based on 2G YBCO technology.

Moving from 'materials by serendipity' to 'materials by design' is one of the headline goals laid out in a recent workshop report, *Basic Research Needs for Superconductivity*, published by the US DoE's Office of Basic Energy Sciences.[2]

The priority, the report concludes, is to establish a 'family tree' of superconductivity by identifying new classes of superconductors and isolating the factors promoting superconductivity, with special emphasis on finding a room-temperature superconductor. For chemists working in the field, that means 'extending the search for superconductivity to new materials, including ternary, quaternary and high-order compounds with increasingly complex chemical compositions and structures'.

Out of the lab, into the grid

Many questions remain unanswered when it comes to the basic science of high-T_c superconductivity. The long-term commercial opportunity is such, however, that the technology push is already well under way, with a posse of established, diversified manufacturers (among them Siemens, Sumitomo, Nexans and Southwire) lining up alongside 'pure-play' superconductor companies (the likes of American Superconductor, SuperPower and Zenergy).

In the main, the commercial R&D effort is concentrated on power-grid technologies, with government-sponsored prototypes and demonstration projects spanning applications such as high-capacity power cables, transformers, reactive power generators and motors, and fault-current limiters (which exploit the abrupt transition of superconducting materials to a resistive state above a critical current level). Here, first generation (1G) superconducting wires – a prohibitively expensive format based on Bi-Sr-Ca-Cu-O (BSCCO) powder packed into a silver tube – have been superseded by state-of-the-art 2G wires based on $YBa_2Cu_3O_7$ (YBCO).

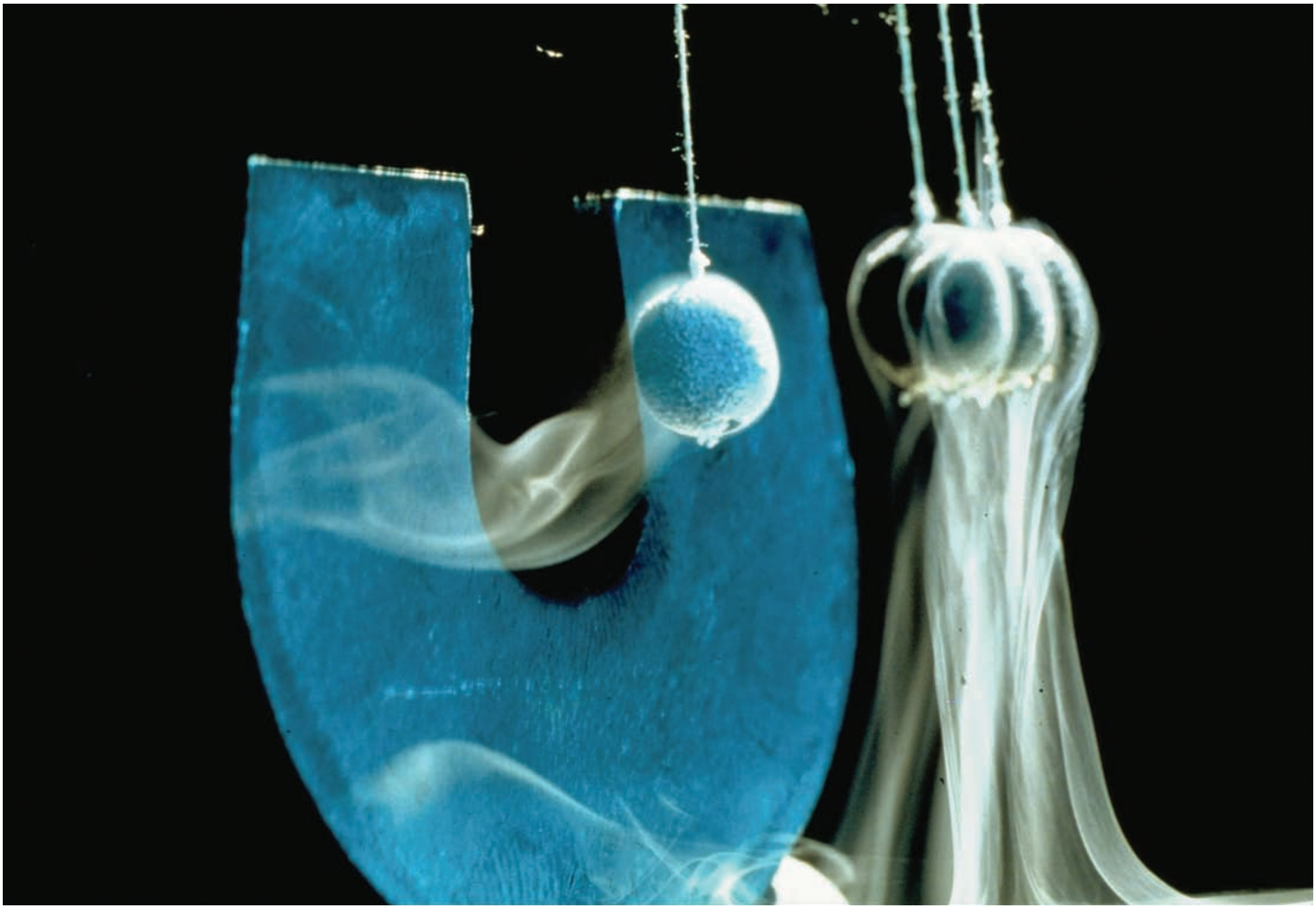
These 2G wires are capable of carrying up to 10 times the current of copper in power cables of the same cross-section, making them vastly easier to install in dense urban environments, and they provide significant efficiency benefits as well. YBCO tapes up to 500m long are now being manufactured with power densities 150 times higher than copper wires.

Cost, however, remains the biggest issue – still an order of magnitude higher in 2G YBCO wires versus conventional copper technology. The complexity of the manufacturing process is a major contributing factor, requiring sequential deposition of many layers on a flexible metal substrate while maintaining inter-layer alignment.

Transitioning to volume manufacture will undoubtedly yield economies of scale, but this alone is unlikely to be enough. As the DoE report notes, making 2G technology commercially competitive will also require 'innovative materials science to find deposition processes that achieve the fundamental goals of epitaxial orientation, preventing compositional contamination of the superconductor, and protecting against thermal damage in the event of an accidental loss of superconductivity'.

Making the breakthrough

Commercial developers – in particular, their R&D chemists and materials scientists – are already on the case, says Alexis Malozemoff, chief technology officer of American Superconductor, a high-T_c superconductor company based in Devens, Massachusetts. 'A deeper understanding of the phase relationships in the YBCO family of materials continues to be important as new compositions are developed to increase the current-carrying capability of 2G wires,' he says.



GETTY IMAGES

Superconductors also exclude magnetic fields – here a superconductor on a string swings away from a magnet (the Meissner Effect)

For example, the metal-organic deposition process, involving the use of liquid-phase chemical precursors applied onto flexible tapes of textured template, is a leading approach to low-cost, high-temperature superconductor wire. 'Developing ways to increase thickness and control the phase structure of these films is critical to achieving further improvements in wire performance,' he explains.

Malozemoff reckons high-T_c superconductor science and technology is progressing at a 'healthy rate as recognition spreads of the potential impact of the technology in utility, military and other commercial sectors'. Real-world demonstration projects play a key role in this regard, both as a necessary precursor to full-scale technology transfer, while providing the ultimate in-situ measure of superconductor reliability.

To date, many hundreds of kilometres of 1G wires have been deployed for demonstration purposes, and projects with 2G wires are starting. In the US, for example, high-T_c superconducting distribution cables are now in operation in the electricity grids in Columbus, Ohio, and Albany, New York. The Department of Homeland Security (DHS) is backing a project to install a superconductor cable with fault-current limiting capability in the New York grid by 2010; the cable will protect supply if a current surge occurs as a result of a grid short-circuit. The US Navy is also working with industrial partners on high-Tc superconducting motors for its next generation destroyer.[3]

Meanwhile, public investment in high-Tc superconductivity remains strong, as illustrated by successful 2007 stock offerings by American Superconductor (market capitalisation \$1.08 billion (£550 million)) and Zenergy (market capitalisation \$280 million). Governmental support is also robust, with significant programmes at the DoE, DHS, Department of Defense and Department of Commerce in the US, and also in Japan, Korea, China and Europe. Globally, it's estimated that government/industrial funding of high-T_c R&D is running at around \$1 billion per year.[4]

'The commercial adoption of these materials is now a question of when rather than if'

For the true believers out there in industry, it seems, the commercialisation of high-Tc superconductivity long ago ceased to be a question of if, rather than when. What's more, Malozemoff reckons technology push will soon be met with market pull: 'The next big breakthrough for high-T_c superconductor technology will be its commercial adoption by utilities, the military and in motors and generators for a range of industrial applications,' he says. 'A broad array of prototypes are already successfully operating in-grid and this breakthrough is imminent.'

Joe McEntee is a science and technology writer based in Bristol, UK.

Further reading

1 K D M Harris and P P Edwards Eds, *Turning Points in Solid-State, Materials and Surface Science: a Book in Celebration of the Life and Work of Sir John Meurig Thomas*, 51-75. Cambridge, RSC Publishing, 2008

2 *Basic Research Needs for Superconductivity*, US DOE Office of Basic Energy Sciences workshop report: http://www.sc.doe.gov/bes/reports/list.html

3 A Malozemoff, *Nature Materials*, 2007, **6**, 617

4 S Foltyn *et al*, *Nature Materials*, 2007, **6**, 631