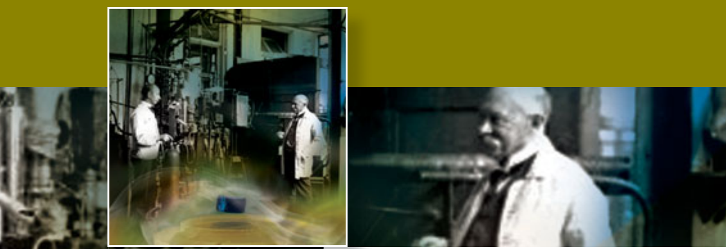

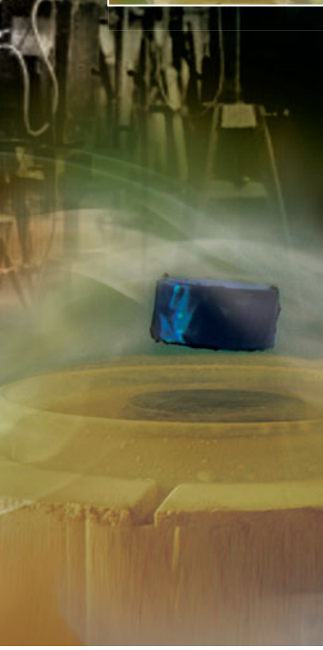

Superconductivity at 100—Where we've been and where we're going

David Larbalestier and Paul C. Canfield, Guest Editors

Basic scientific questions and tantalizingly revolutionary applications have been intertwined throughout the 100-year history of superconductivity. Within two years of his discovery of superconductivity in 1911, H. Kamerlingh Onnes imagined high-field applications for superconducting wires, only to have his hopes dashed by limitations of upper critical field and critical current density. Over the next 98 years, a scientific tango would play out repeatedly between (1) discovering and understanding new superconductors, often with higher transition temperature values and (2) improving these materials' upper critical field and critical current values while keeping manufacturing costs down. In this article, we take stock of where the field currently stands, with mature, developing, and recently discovered superconductors, and try to give a sense of where it may be going.

Introduction

In its 100 years, the history of superconductivity has been distinctly episodic, at times centered on applications, at times only on science, but, happily, currently emphasizing both. In this issue, we bring together articles that mostly cover the last decade, which started with the very unexpected discovery of the 39 K superconducting transition in the electron-phonon superconductor MgB_2 in 2001, and then followed in 2008 with the even more unexpected discovery of superconducting Fe-based compounds at 24 K, soon driven up to 56 K. We also review recent progress in applying useful cuprate conductors, especially $YBa_2Cu_3O_{7-x}$ coated conductors. These last 10 years combine exciting advances both in applications and discovery, with cuprates edging closer to truly transformational uses in electrotechnology, while science is grappling with the fascinating mechanisms of many new types of superconductivity, especially associated with Fe-based compounds.

New efforts to discover yet higher transition temperatures, T_c, have started, still grappling with the central question of all new superconductor searches: "What, besides my hunches, should define the best paradigm for my search?" Higher T_c inevitably means shorter coherence lengths for the superconducting state. Does this mean that as T_c increases, superconductivity is transitioning from the collective, high-carrier-density free-electron physics of most of the first century's superconductors to more localized, or bond-based, superconductors, where atomic-scale interactions dominate? The much lower carrier densities of the new higher-T_c compounds have lead to lowered ability to screen local regions of weak or no superconductivity, as may occur at stacking faults and above all at grain boundaries. Certainly the new superconductors have moved from isotropic, *s*-wave, electron-phonon dominated superconductivity to much more exotic and less isotropic interactions that may make applications more challenging.

In this article, we trace some aspects of the way that science and applications have been intimately combined in the first 100 years. Historically, we can chart superconductivity as falling into several distinct episodes that now overlap considerably, as the different generations of superconductors vie with each other for applications and scientific interest. We hope that this issue of *MRS Bulletin* conveys some of the great excitement and future potential of the science and applications of superconductivity as it celebrates its 100th birthday.

The heady first two years (1911–1913)

The superconducting state was discovered, to total surprise, on April 8, 1911 by Heike Kamerlingh Onnes, a man with both a pronounced scientific *and* technological vision. In 1913, just two years after his discovery that Hg entered the superconducting state at 4.2 K, he went to Chicago to the International

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Institute of Refrigeration to present a detailed vision for how to use superconductors to create fields of 10 T, a feat that he analyzed to be quite impossible if he had to cool Cu windings with liquid air, which he had analyzed would cost about as much as a cruiser! A few words from his paper[1] describing his first, not-yet-quite-perfected test quickly convey his excitement and hope for rapid progress toward his goal:

> "I think it will be possible to come to a higher current density . . . if we secure better heat conduction from the bad places in the wire to the liquid helium . . . in a coil of bare lead wire wound on a copper tube the current will take its way when the whole is cooled to 1.5 K practically exclusively through the windings of the superconductor. If the projected contrivance succeeds and the current through the coil can be brought to 8 amperes . . . we shall approach to a field of 10,000 gauss. The solution of the problem of obtaining a field of 100,000 gauss could then be obtained by a coil of say 30 cm in diameter and the cooling with helium would require a plant which could be realized in Leiden with a relatively modest financial support . . . When all outstanding questions will have been studied and all difficulties overcome, the miniature coil referred to may prove to be the prototype of magnetic coils without iron, by which in future much stronger and . . . more extensive fields may be realized than are at present reached in the interferrum of the strongest electromagnets. As we may trust in an accelerated development of experimental science this future ought not to be far away."

Back to basic science (1914–1961)

Note especially the optimism of his last sentence. Sadly, and without yet realizing it, Onnes had just come up against a fundamental characteristic of pure metal superconductors that determines that they remain superconducting only in very weak fields. When Onnes put his pure metal wires in an external magnetic field the next year,[2] he found that superconductivity was destroyed at a very low critical field H_c of only about 500 gauss (or 50 mT in today's units), forcing him to put away his technology dreams. Some dozen years later, late in his career, Onnes planned a great electromagnet for Leiden, a huge iron pole-piece magnetized by 400 kW of copper windings to generate 2 T, just one-fifth the strength of his original superconducting dream. This magnet, at the time the second most powerful in the world, was commissioned from Siemens and Halske and delivered in 1932, after Onnes's death. It was productively used by the next director of the Leiden laboratory, W.J. de Haas. Superconducting magnets that could extend this field range had to wait more than 30 years.

Even without technological possibilities, superconductivity continued to fascinate, attracting many of the leading physicists of the era to attempt a theory of superconductivity. But there was no quick breakthrough. Only 21 years after the discovery of zero resistivity did it become clear that the diamagnetism of the superconducting state, not its zero resistivity, was the more fundamental property[3] and one that enabled a thermodynamic description that clearly distinguished a perfect conductor from a superconductor. Materials studies had been renewed in the late 1920s in Leiden, but the inhomogeneities produced by cold working and the poorly controlled phase state of most samples inhibited understanding of their essential properties.[4] Nonetheless, de Haas found that eutectic Pb-Bi alloys could exhibit zero resistance in fields up to 2 T,[5–7] but not at critical current densities J_c anywhere near high enough to reignite Onnes's dreams.

In fact, the breakthrough was at hand—but was not to be recognized. The gifted crystal grower Lev Shubnikov, a member of the Leiden laboratory from 1926 to 1930, had returned to Kharkov in the Soviet Union in 1930 to set up helium liquefaction capabilities and to continue some of the Leiden alloying studies. Making a series of solid-solution Pb-Tl single crystals, he showed that alloying produced a progressive and quite clear separation between the loss of full diamagnetism at a lower critical field H_{c1} and the restoration of resistance at a significantly higher upper critical field H_{c2}.[4,8,9] These truly breakthrough observations demonstrated the role of normal-state electron scattering in suppressing H_{c1} and raising H_{c2}, while scarcely changing either T_c or H_c. This showed how the scientifically interesting, but not very useful, pure-metal, Type I behavior could be transformed into a much higher field Type II superconductivity.

Coupled to de Haas's earlier observations[5–7] that low-J_c behavior persisted in eutectic Pb-Bi alloys up to 2 T, it seems that Onnes's vision of superconducting wires could have made giant iron electromagnets of the Leiden type obsolete before World War II. But the import of Shubnikov's results was not appreciated, or was simply ignored. Unfortunately, his strong links to the West, a result of his stay in Leiden, and the openness of his laboratory to foreigners, led to charges of espionage. In 1937, he was arrested and quickly shot. For decades, his truly outstanding breakthrough went quite unrecognized.

Superconducting studies then relaxed back to pure science. Ginzburg and Landau (G-L) presented a powerful phenomenological theory of the superconducting state in 1950.[10] Again, there was a tantalizing opportunity for a path to applications that was not taken. A central feature of the theory is the energy of the interface between the superconducting and normal state. This energy changes from positive to negative when the dimensionless parameter κ exceeds $1/\sqrt{2}$. (The Ginzburg-Landau parameter κ is now understood to be the ratio of the superconducting state penetration depth λ of magnetic fields to the coherence length ξ of the superconducting state itself.) This corresponds exactly to the transition from a Type I to a Type II superconductor observed by Shubnikov.

But Shubnikov's studies were forgotten, even though Landau had been in Kharkov with Shubnikov, and the physical significance of the negative surface-energy solutions of the equations for $\kappa > 1/\sqrt{2}$ was dismissed. Shortly after, Abrikosov solved the G-L equations in this "unphysical" extreme Type II

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superconductor, high-κ limit. He showed that superconductivity could be stable in very high fields if the Type II superconductivity, identified by Shubnikov 21 years before, was characterized by a partially diamagnetic state. In this state, the magnetic field partially penetrates the superconductor as quantized vortices, but leaves a connected superconducting matrix intact.[11]

In spite of Abrikosov referencing Shubnikov's work, the crucial route to applications still did not emerge. Landau was not persuaded of the value of Abrikosov's solution, and publication was delayed until 1957,[12] at which point all of the scientific excitement about superconductivity seemed to be taken up by the wonderful explanation of the mechanism of superconductivity given by Bardeen, Cooper, and Schrieffer,[13] who showed how the electron-phonon interaction could lead to the superconducting state.

Applications take off (1961–present day)

In 1986, Ted Berlincourt gave an excellent description of the slow awakening of technological interest in superconductivity in the 1950s at the Applied Superconductivity Conference, which celebrated the 75th anniversary of superconductivity.[14] The 1950s had seen higher-T_c superconductors being discovered in the A15 crystal structure, first V_3Si at 17 K,[15] then many others, especially Nb_3Sn,[16] at 18 K. A few industrial scientists saw that high critical current densities J_c could be attained by cold-working wires of Nb and the solid solution of Mo-Re, even if there was no expectation that high-field, high J_c operation would be possible. In fact, superconductivity was still seen as a scientific curiosity, even though T_c values were well above liquid He temperatures.

All of this changed in late 1960 when a metallurgical group (Kunzler, Buehler, Hsu, and Wernick) at Bell Labs[17] placed samples of Nb_3Sn into an 8.8 T Bitter magnet, and to their enormous surprise, and everyone else's, found that a primitive wire carried a current density J_c of $>10^5$ A/cm^2 at the highest field available. The essential, quite unique advantages of using superconductors for generating strong magnetic fields, first described by Onnes, were finally realized. There was then an explosion of applications that brought the first magnets to market using Nb_3Sn and more conveniently the ductile bcc alloys, first Nb-Zr and then Nb-Ti.

Magnets made from Nb-Ti and Nb_3Sn have given us MRI machines, very-high-field NMR (up to 1 GHz proton resonance), many types of laboratory magnets, and huge accelerators, of which the Large Hadron Collider at CERN and the ITER fusion reactor now under construction are mammoth examples[18] (see **Figure 1**). But all of these magnets operate in a narrow temperature window between about 2 and 6 K, since the T_c values of Nb-Ti and Nb_3Sn are only 9 and 18 K, respectively. Such low-T_c superconductors remain valuable because they fulfill the key requirement of any technology—they find a means to do things that cannot be done any other way. Generating fields higher than 1–2 T in large volumes with non-superconducting wires requires hundreds of kW or even MW, whereas superconductors that can operate at current densities of ~10^5 A/cm^2 in fields up to about 10 T (as Nb47wt%Ti can) can avoid such losses completely.

A modern 3 T MRI magnet made out of Nb47wt%Ti runs in persistent mode without any significant electrical power loss for years. Although initially cooled with ~1000 liters of liquid helium, it may never need to be refilled, because the He boil-off caused by its small room-temperature heat leak is recondensed by a small refrigerator. The 400 kW Leiden magnet produced only 2 T in a few-cm-wide gap, whereas the modern MRI magnet produces a 3 T central field of great homogeneity in about a 1 meter bore with the expenditure of a few kW at the room-temperature wall plug for the cryogenic shield cooler. This is a technological feat that surpasses Onnes's wildest dreams.

High-temperature superconducting cuprates (1986–present day)

When cuprate-based, high-temperature superconductors burst onto the scene, first in 1986 with the La_2CuO_4 family of compounds, and then in 1987 with $YBa_2Cu_3O_{7-x}$ and its T_c of 92 K, there were feverish dreams of a zero-resistance utopia that would soon extend to room temperature and beyond. In an explosion of discovery, more than 100 structurally related compounds were found to superconduct, the highest being a Hg-cuprate with a T_c of 135 K. For a few years, the hopes that superconductivity would replace Cu and Fe in electrotechnology became utterly pervasive.

Figure 1. The central coil of the ATLAS solenoid (before being placed in its cryostat), a key component of the ATLAS interaction region at the Large Hadron Collider at CERN. It is the smallest coil in a complex superconducting magnet system containing 24 larger toroidal magnets.

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But like all new technology dreams, an essential reality is that doing something that cannot be done any other way (i.e., generating multi-tesla fields in large volumes with minimal energy dissipation) is much easier than replacing existing technology, such as the motors, generators, transmission cables, transformers, and other electrotechnology components made from Cu and Fe. Not only must the essential combination of high J_c in high field be possible, but so too must system costs, reliability, and operation be attractive enough to compete with a century-old technology made of cheap materials whose long-term reliability is well understood. It was soon seen that cuprates were very complex, sensitive to defects (especially grain boundaries), and resistant both to theoretical understanding and to widespread application. Malozemoff discusses this in his article in this issue, a story that provides the context as well as the benchmarks for the more recent discoveries made over the past decade.

MgB_2, iron-based superconductors, and the ongoing search for new superconductors (2001–present day)

The complexity and concomitant difficulties associated with the cuprates explain much of the excitement that came in 2001 when a "simple" binary compound, MgB_2, was found to superconduct at 39 K, about twice the T_c of the highest-T_c A15 compound, Nb_3Ge, with a T_c of 23 K. In addition to its high T_c value, MgB_2 was a welcome return to the well-understood electron-phonon coupling. Working with this metallic, high-carrier density superconductor, grain boundaries were found NOT to be intrinsic barriers to current flow, which allowed use of simpler and cheaper methods of creating wires developed for Nb_3Sn and Nb-Ti.

This simplicity is driving a very real potential for application in the biggest superconducting market, for MRI. As the articles of Putti and Grasso and of Tarantini and Gurevich suggest, there are good reasons for great interest in MgB_2. It is made from raw materials that are inherently inexpensive, and it can be made into conductors using standard mechanical working technology that is used for Nb-Ti and Nb_3Sn. Strangely, and to its disadvantage, it has some of the characteristics of the pure metals discovered by Onnes. Although a Type II superconductor, it is a stoichiometric line (ordered) compound with very little intrinsic scattering, thus, in pure form, possessing a small upper critical field H_{c2}. Therefore, even though it has twice the T_c of Nb_3Sn (39 K versus 18 K), its H_{c2} is less than half. But it is a two-band superconductor, and the way that alloying can enhance H_{c2} is a very important part of the MgB_2 story; with judicious carbon substitution on the B-site, H_{c2} can be doubled in bulk MgB_2 with minimal loss in T_c value. Efforts to improve J_c and reduce the superconducting anisotropy are yielding very promising results.

An even more remarkable discovery was made in 2008: superconductivity in Fe-based compounds. Here there are not just two bands but perhaps as many as five that are vital to developing superconductivity. These multiple bands also greatly enhance the capability of developing high H_{c2}. Although these compounds have a maximum T_c of only 56 K, compared to a maximum of 135 K in the cuprates, they develop very high H_{c2} values and have relatively low anisotropy, fulfilling several of the key requirements for application-ready materials. Like the cuprates before them, dozens of structurally related compounds have been found to superconduct, with a steady stream of them still being found three years after the initial discovery. Another similarity to the cuprate superconductors is the fact that the superconducting Fe-based compounds lie in close proximity to an antiferromagnetic phase transition and only achieve their maximal transition temperatures once this antiferromagnetism is suppressed. The articles by Ni and Bud'ko and by Sefat and Singh outline our current understanding of when and why these compounds superconduct by outlining our empirical as well as band-structural understanding.

Conclusions

Having reviewed the three ages of superconductivity: well understood, industrially utilized materials (Nb-based technology); materials that are transitioning from basic and applied research to industrial use (cuprates and MgB_2); and newly discovered materials with possible industrial use (Fe-based materials), we are left with the question: "What of even better (not always higher-T_c) materials?" A special characteristic of the search for new materials is that it requires a certain kind of passionate optimism because there is no recipe for finding new materials that may manifest new types of superconductivity. As Beasley's article shows, though, the physics of superconductivity imposes some inevitable correlations and constraints on the properties of the superconducting state. Indeed, finding new superconductors with improved, technologically appealing properties may well be a complex, multi-parameter exercise in finding a "sweet spot" in compositional as well as physical phase space. Whatever the potential for applications, the science will be fascinating, and we hope that Nature (Mother, not the journal) will again serve us many surprises that lead to both fascinating science and wonderful technology.

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