Chapter 2

# High-Temperature Superconductivity: A Progress Report

# CONTENTS



## *Boxes*



## *Figures*



## *Tables*

# Chapter 2

# High-Temperature Superconductivity: A Progress Report

No scientific discovery during the 1980s generated more worldwide excitement—and hype—than that of high-temperature superconductivity (HTS) in 1986. Four years later, the hype has died down, but the excitement remains. HTS appears less often in newspaper headlines, and it no longer commands the urgent attention of U.S. policy makers. But during the past several years there have been remarkable advances in HTS research.

This chapter provides a progress report on HTS, and an assessment of the R&D challenges that remain. For readers unfamiliar with the concepts and terminology of superconductivity, a brief primer is provided in appendix 2-A. Additional information on the science of HTS and its applications can be found in several studies[1,2,3] including an earlier OTA report.[4]

## PROGRESS REPORT

### *New HTS Materials*

Perhaps the most interesting development that has occurred in the past several years is the realization that HTS is a broader phenomenon than had been first thought. The initial discovery of copper oxides containing lanthanum ($T_c$ = 35 K) in 1986 was followed in 1987 by related compounds containing yttrium ($T_c$ around 93 K) and in 1988 by those containing bismuth (maximum $T_c$ of 110 K) and thallium (maximum $T_c$ of 125 K). Numerous variations on these basic layered copper-oxide compounds have also been found to exhibit superconductivity. This raises the hope that new materials may yet be discovered with even higher $T_c$s.

#### Room-Temperature Superconductivity

A superconductor operating at room temperature would be revolutionary. Provided that suitable manufacturing processes were available, and costs were comparable to ordinary conductors, room-temperature superconductors could replace normal conductors in virtually all devices involving electricity or magnetism. Over the past 2 years, there have been occasional reports of observations of room-temperature superconductivity, though none has been confirmed.[5]

No one knows yet whether room-temperature superconductivity is possible. At this writing, there are no accepted theoretical limitations on $T_c$. But even if a room-temperature superconductor is possible, practical applications may be difficult:

- To obtain critical fields and currents at levels high enough to be useful, superconductors are typically operated at temperatures substantially below $T_c$. For practical room-temperature (300 K) operation, a T, of 400 to 600 K (261 -621 'F) would be required (well above the temperature of boiling water).
- At elevated temperatures, vortex lattice pinning (see app. 2-A) becomes much more difficult, due to the higher ambient thermal energy. This could make it impossible for the room-temperature superconductor to carry useful currents even in small magnetic fields.

The search for new material with higher $T_c$s remains an important quest, along with research aimed at understanding the fundamental limitations of the performance of present materials. In this connection, further research on novel superconductors --e.g., organics--could lead to new insights.

### *Progress in Improving HTS Properties*

#### Thin Films

Films of superconductor, usually between 30 angstroms and 1 micrometer in thickness, can be deposited on a base material (called a substrate) to yield conductors used in a wide variety of sensors and electronic circuits. Several of the techniques for depositing the films-e. g., sputtering, molecular beam epitaxy, electron beam evaporation, and chemical vapor deposition—have much in common with

[1] Alan M. Wolsky et al., "The New Superconductors: Prospects and Applications," *Scientific American*, vol. 260, No. 2, February 1989, p. 61.

[2] National Academy of Sciences Committee on Science, Engineering, and Public Policy, *Research Briefing on High-Temperature Superconductivity* (Washington, DC: National Academy Press, 1987).

[3] C.P. Poole, T. Datta, and H.A. Farach, *Copper Oxide Superconductors* (New York, NY: John Wiley Interscience, 1988).

[4] U.S. Congress, Office of Technology Assessment, *Commercializing High-Temperature Superconductivity*, OTA-ITE-388 (Washington, DC: U.S. Government Printing Office, June 1988).

[5] "Room $T_C$ Reports Fail Verification," *Superconductor Week*, vol. 3, No. 4, Jan. 23, 1989, p. 1.

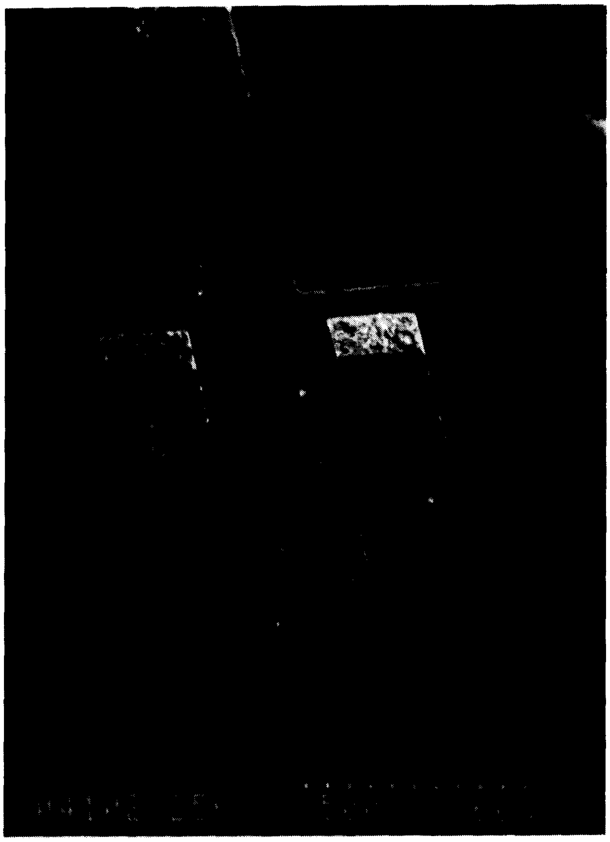


*Photo credit: IBM Research*

Electron micrograph of an edge-junction superconducting quantum interference device (SQUID) fabricated from $YBa_2Cu_3O_7$ thin films.

the techniques used in semiconductor manufacturing. New processes—e.g., laser ablation—are also being developed. These techniques permit control over the growth of the film, some down to a single atomic layer.

Progress in improving the properties of thin films has occurred considerably faster than in bulk materials. This is apparently because the films grow as single crystals or as polycrystals having good alignment between their copper-oxygen planes, and because the vortex pinning strength is quite high. Already, critical current densities ($J_c$) above 1,000,000 Amps/cm$^2$ have been measured at 77 K in a magnetic field of 1 tesla—a level suitable for many electronics applications. Progress has also been made in producing films at temperatures below 600 °C (processing temperatures below about 500 °C are required to be compatible with manufacture of multilayer semiconductor devices) and in develop-

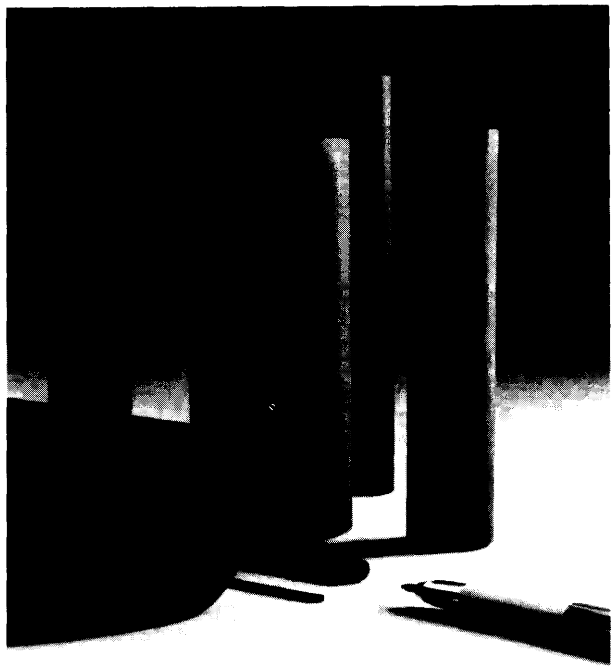


*Photo credit: ICI Advanced Materials*

Tubes fabricated from bulk high-temperature superconductors can be used for radio-frequency cavities and conductors.

ing new substrate materials that are less expensive and more practical.

## Bulk Superconductors

Bulk materials include thick films (>1 micrometer), wires, tapes, and three-dimensional shapes. Bulk conductor forms are used in large-scale applications, such as magnetic resonance imaging (MRI), maglev vehicles, etc. They are made by techniques common in metallurgy or ceramics: extrusion, tape casting, pressing, etc. Typically, they involve compaction and shaping of nonsuperconducting powders or precursors, followed by firing in an oven to consolidate the material and create the superconductor. This yields a polycrystalline material consisting of partially oriented crystalline grains separated by grain boundaries.

HTS bulk conductors have generally exhibited lower critical current densities than thin films, thought to be caused by weakened superconductivity at the grain boundaries. The critical current also falls off more rapidly with applied magnetic field than is the case with thin films. But recent advances in processing have raised the critical currents in short wires to several tens of thousands of Amps/cm$^2$

**Table 2-I—HTS R&D Challenges**

| Topic | Comment |
|---|---|
| Basic ***Research*** | |
| Theory/Mechanism of HTS | Abetter understanding will point the way to new materials, improvements in existing materials, and perhaps to new applications. |
| Search for New Materials | Synthesis and characterization of new HTS materials have been of tremendous value in guiding theory development, and will continue to be so. Further investigation of novel superconductors-e. g., organics-could provide important insights. |
| Structure/Property Relationships | Understanding properties such as critical current behavior is vital for virtually all applications. It involves not only basic physics issues but also the full complexity of the microstructure. |
| Appy ***Research*** | |
| Processing Science | Understanding the relationships among process variables, microstructure, and properties is critical for making better materials reproducibly. New, cheaper processes also need to be developed. |
| Thin Film Processes | Key goals include: reducing process temperatures below 500 °C so as to be compatible with semiconductor processing; finding suitable substrates and deposition processes-especially enabling deposition on semiconductors; developing processes for making films with extremely clean surfaces and strong superconductivity all the way up to the surface. |
| Bulk Processes | Key goals include: finding techniques for improving the superconductivity connection between adjacent crystal grains; introducing strong pinning sites for the magnetic vortex lattice; reducing alternating current (AC) losses; and making extremeiy thin filaments (several micrometers in diameter). |
| ***Applied Research-continued*** | |
| Chemical Stability | Some HTS materials are prone to react with atmospheric water and carbon dioxide, as well as with cladding and substrate materials. Some also readily lose oxygen from the crystal lattice. These reactions impair the superconductivity, and raise concerns about long-term stability. New approaches are needed to protect the materials and prevent these reactions. |
| Mechanical Properties | Mechanical properties such as brittleness, strength, and fatigue have received less attention than superconducting properties, but improvements are critical to reduce costs and increase reliability in actual applications. |
| ***Device Engineering R&D*** | |
| Thin Film Devices | Key goals include: demonstration of practical Josephson Junctions (JJs); development of a three-terminal device; patterning of multiiayer structures; developing low-resistance electrical contacts. |
| Bulk Devices | Key goals inciude: demonstration of long, flexible wires with 100,000 $Amps/cm^2$ in a magnetic fieid of 5 tesla; braiding and stabilization of composite cable; low-resistance electrical contacts and splicing of sections. |
| ***Manufacturing R&D*** | Includes making large numbers of JJs with uniform switching and threshold characteristics on a chip with high yield; long lengths of wire with reproducible properties; cost-effective nondestructive evaluation techniques. |
| ***Systems Development*** | Superconducting components have to be integrated into fully engineered systems, with refrigeration, auxiliary electronics, mechanical support, etc. |

SOURCE: Office of Technology Assessment, 1990.

at 77 K—within a factor of 10 of levels required for most applications. It should be noted, however, that these have been realized only in small samples of test material; reproducing them in long wires poses major engineering challenges.

## R&D CHALLENGES

While there has been considerable progress over the past several years, there remains along way to go before HTS can be widely used in practical applications. Table 2-1 gives examples of key remaining R&D challenges for both thin film and bulk HTS materials. These are grouped in five R&D categories: basic research; applied research; device engineering; manufacturing research; and systems development. They involve improving properties and processes, as well as integrating the superconducting components into larger systems.

*A strong, ongoing basic research effort is essential to support cost- effective development of applications.* At this writing, there is no commonly accepted theory of HTS. Thus, there is no way of predicting which materials should exhibit high critical temperatures, currents, or magnetic fields. Theory can also predict new phenomena. The Josephson effect, the basis of the device used in superconducting electronics, was predicted first by theory and later observed by experiment. If new phenomena are occurring in HTS, then new types of devices may be possible.

Basic research is also needed to establish the relationships among composition, microstructure, and properties-especially critical current density. In some cases, HTS presents new problems that

### Box 2-A—Superconducting Magnets

A superconducting magnet's major assets are its very high field strength, its ability to produce spatially uniform and temporally stable fields, its low power consumption, and its reliability. While a conventional electromagnet with an iron core can produce continuous fields up to around 2 tesla, superconducting magnets can routinely produce fields in excess of 12 tesla. A superconducting magnet consumes very little power except for refrigeration, while a nonsuperconducting magnet requires a large power source and extensive cooling.[1]

The superconductor used in magnets is much more than just a simple winding of wire. Typically, multifilamentary conductors are needed, with filament diameters of a few microns. These filaments are embedded in a normal metal matrix or tape, which stabilizes the superconductor and provides mechanical strength. If a section of the superconductor goes normal, then the current will be carried by the matrix, which has a lower resistivity than the superconductor in its normal state. Without the matrix, the normal spot would heat, causing adjacent areas of superconductor to go normal. The disturbance would propagate, causing the whole magnet to quench.

More than 20 years of R&D went into learning how to manufacture appropriate conductors from LTS materials that are mechanically strong, flexible enough to be wound into a magnet, low-loss for AC currents[2], capable of high current densities, and stable against thermal, electrical, and magnetic fluctuations. Wire-drawing techniques are sufficient to produce thin filaments from ductile materials like niobium-titanium. But with more brittle materials such as niobium-tin, the process is trickier.[3] Because HTS materials are more brittle yet, fabrication of a suitable conductor will be a big challenge.[4]

Brittleness is also a concern for the reliability of a magnet. When a magnet is energized, the magnetic field exerts a force that tends to push the coils outward. This puts the coil materials in tension. Brittle materials like HTS tend to form cracks under tension. Therefore, HTS conductors will have to be supported by stiff structural materials designed so that the stresses on the superconductor fall within acceptable limits.

There are several other major problems with HTS composite conductors for magnets. The problem of low critical currents in HTS bulk conductors—especially in the presence of strong magnetic fields—has been mentioned in the text. HTS materials also react chemically with nearly all metals other than gold and silver, thus complicating the development of a good matrix/superconductor match. Finally, the layered structure of HTS materials can lead to differential thermal contraction, causing cracking during warm-up and cool-down cycles of the magnet.

As a result of these challenges, high-field HTS magnets should be considered to be long-term. A DOE report on the possibility of HTS accelerator magnets[5] estimates a minimum time of twelve years with a dedicated program to develop a multifilamentary conductor and winding technique, and to demonstrate a magnet. It notes that "a more aggressive program than assumed, while capable of reducing development risk, would not necessarily compress the schedule significantly." A commercial application requires development of auxiliary electronics and components, followed by testing and reliability demonstration. After the demonstration of the magnet, several years may be required for market acceptance.

[1]Comparing power requirements for an industrial high-gradient magnetic separator used in clay processing, the conventional version requires 270 kilowatts (kW) to produce the field and 30 additional kW for cooling, while the low-temperature superconducting magnet uses only 0.007 kW to produce the field and 60 kW for cooling. Argonne National Laboratory, *Advances in Applied Superconductivity: A Preliminary Evaluation of Goals and Impacts*, Report ANL/CNSV-64, January 1988.

[2]The AC losses are due to hysteresis, eddy currents, and resistance.

[3]The problem of brittleness of niobium-tin, a low-temperature superconductor, is avoided by using a ductile precursor form of niobium and tin for the wire-drawing and magnet winding steps. Only after all steps that require ductility and flexibility are completed is the wire heat-treated to react the niobium and tin to form the superconductor. The danger is that heat treatment after winding can cause breakdown of the insulator between conductors, thus causing a short circuit in the magnet.

[4]A process similar to that used for niobium-titanium (cf., footnote 3) is being tried with HTS materials by American Superconductor Corp. This startup company is forming ribbons of the metallic constituents and then oxidizing them to form the superconductor.

[5]Basic Energy Sciences Advisory Committee Report to U.S. Department of Energy, *Panel on High $T_c$ Superconducting Magnet Applications in Particle Physics*, December 1987.

never had to be faced with LTS. For instance, the performance of HTS materials is far more sensitive to impurities or minute changes in composition at surfaces and grain boundaries than is the case with LTS materials. This means that fabrication processes for HTS must be able to control the properties of these surfaces to a much higher degree.

To some extent, research in applied areas can be carried out in parallel with basic research. For

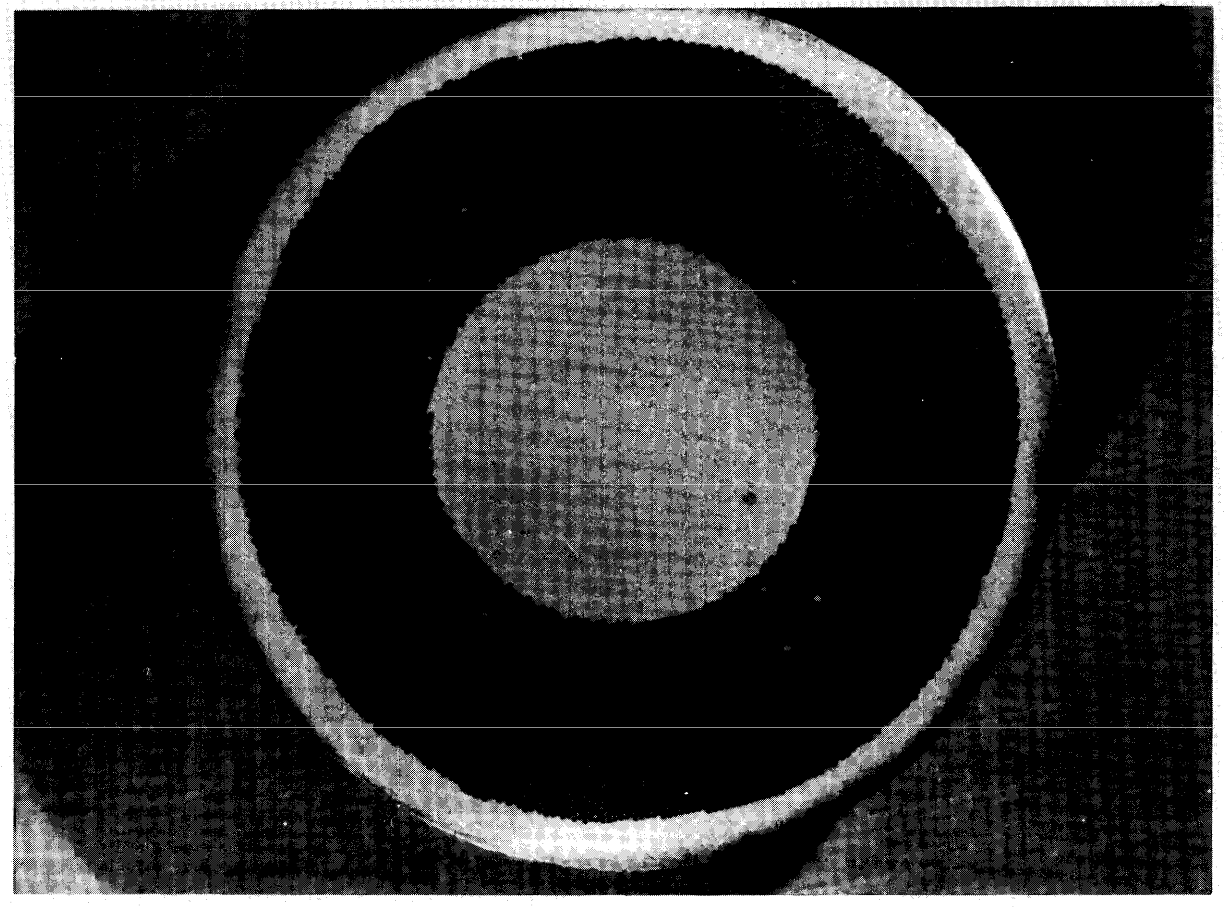


Photo credit: Supercon, Inc.

Prototype composite superconductor containing 11,000 niobium-titanium filaments, designed for use in the Superconducting Super Collider.

example, the critical current can be improved empirically (applied research) without having fully characterized the material (basic research). Similarly, the full system has parts that can be designed, built, and tested without the superconducting component. For instance, the refrigeration requirements can be approximated early, and developed before the superconducting component is completed.

But until the basic parameters of the technology—e.g., the pinning mechanism—are understood, early resources spent on manufacturing technology and systems development may turn out to have been wasted in light of new developments. No amount of research on vacuum tube technology would have produced a supercomputer; it awaited the discovery of the transistor and of integrated circuits.

A better feel for all of the requirements that must be satisfied for HTS to be used in commercial applications can be gained by considering two key applications of LTS: high-field magnets and Josephson Junctions (JJs). These are the "building blocks' of many present superconductivity applications. JJs illustrate the challenges associated with thin film technology, while magnets illustrate the challenges of fabricating devices from bulk materials. These are discussed in boxes 2-A and 2-B.

***Box 2-B—Josephson Junctions***

**A Josephson Junction (JJ) is the basic building block of superconducting computers, digital electronics, and sensors. A JJ consists of two superconductors separated by a thin barrier layer of nonsuperconductor (see figure 2-1). As long as the current is not too large, pairs of superconducting electrons can tunnel through the barrier without any resistance; at some threshold current, however, the junction switches to a resistive state, with a resulting voltage across the barrier.**

**A JJ can be switched from the "off" (zero voltage) state to the "on" (finite voltage) state extremely rapidly (in about 1 picosecond) and with 100 times less power than a corresponding semiconductor transistor. The technology for producing JJs has been intensively developed using LTS films, and today LTS JJs are used in a variety of research instruments for astronomy, voltage measurement, and fast data sampling circuits. In principle, JJs could enable superconducting computers to be much smaller and faster than semiconductor-based computers. But although there has been extensive research on JJ computer components—first in the United States and more recently in Japan—the introduction of a general purpose computer using JJs does not appear to be imminent (see ch. 3).**

**HTS materials do exhibit the Josephson effect. In fact, polycrystalline HTS materials can be thought of as strongly superconducting grains coupled by weak Josephson links at the grain boundaries. These weak links appear to be the cause of the relatively low critical current densities observed to date in bulk materials.**

**Individual weak link junctions can be isolated relatively easily—simply by forming a narrow constriction in a thin film. These natural grain boundary JJs may be suitable for simple devices using one or two junctions, e.g., SQUIDS (see ch. 3). But for devices such as logic gates, that require many JJs be used together, more reproducible, deliberately fabricated junctions (e.g., the tunnel junction illustrated in figure 2-1) will be required.**

**The fabrication of large numbers of reproducible junctions was a major challenge with LTS, and could prove to be even more difficult with HTS. HTS junctions are likely to be 10 times more sensitive to imperfections at the superconductor-barrier interface than is the case with LTS materials, requiring far more precise control over the surface quality. The barriers must also be able to withstand the high processing temperatures required for HTS materials. These challenges guarantee that devices requiring large-scale integration of HTS JJs are many years away.**

## NEW OPPORTUNITIES

HTS materials are unique in having extremely high values of upper critical magnetic field ($H_{c2}$). At 0 K, $H_{c2}$ for $YBa_2Cu_3O_7$ is estimated to be many hundreds of tesla,[6] compared with around 14 tesla for niobium-titanium, the LTS material used most often in superconducting magnets. If the critical current density of HTS bulk conductors can be improved, the high $H_{c2}$ could enable an HTS magnet to operate as an insert inside another magnet, thus boosting the maximum field in the core.[7] [8] Use of HTS would also allow such magnets to operate at higher temperatures than present LTS magnets.

Another unique feature of HTS derives from the fact that the superconducting electron pairs are bound together more tightly than is the case for LTS (larger energy gap). Because the high frequency response of superconductors is limited to frequencies that do not disrupt the electron pairing, the stronger pairing could enable HTS 'devices to operate at frequencies up to 10 times higher than LTS devices. This could revolutionize the communications industry, making tens of thousands of new satellite broadcast channels available, and result in correspondingly higher rates of signal transmission and processing.

It is even possible that some of the "disadvantages of HTS materials could be turned into advantages. The sensitivity of the superconducting properties to oxygen content, crystal direction, and applied magnetic field could someday be the basis for new devices.

[6]For the magnetic field H parallel to the copper-oxygen planes. This estimate is only approximate, since it is based on extrapolation from measurements near 90 K.

[7]The highest continuous fields currently available are achieved using this type of hybrid magnet. They involve inserting a conventional water-cooled magnet inside a superconducting magnet.

[8]Explosive techniques, which destroy the magnet and sample, have reached fields of 100 to 1,000 tesla for a fraction of a second. However, the highest field strengths that are generally available at the Francis Bitter National Magnet Laboratory are 31.8 tesla continuous, and up to 68.4 tesla pulsed. Higher static and pulsed fields are available in Japan.

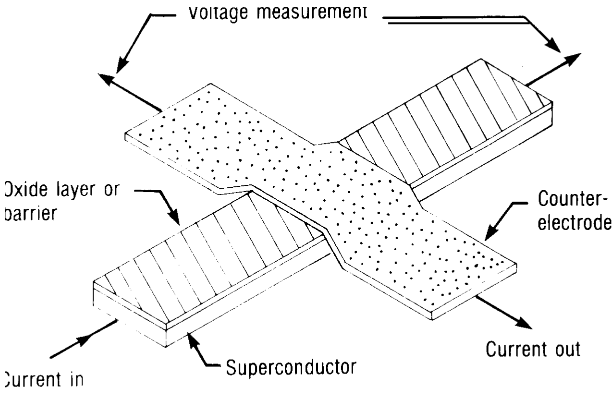
A particularly exciting prospect is the possibility of designing hybrid, layered devices that would combine different HTS materials with semiconductors, optoelectronic materials, and other superconductors to yield novel performance.

## CONCLUSION

In spite of some recent press reports that describe the new HTS materials as disappointing,[9] the past 3 years have seen rapid progress both in improving the superconducting properties of known materials and in finding new materials. Many observers remain optimistic that present problems can be solved and that both familiar applications and entirely new ones will occur—although the time scale for many of these is not short.

Experience gained from previous research on LTS—in processing techniques, characterization of materials, and design of integrated systems—will come in handy, though. And these problems are being addressed by large numbers of researchers around the world; since its discovery in 1986, more than 12,000 papers have been published on HTS. HTS is an area where continued diligence and patience could yield great dividends.

**Figure 2-l--Schematic of a Tunnel (or Josephson) Junction**




SOURCE ***Business Technology Research,*** "Superconductive Materials and Devices," 1988.

[9] See, for example, Robert Pool, ''Superconductivity: Is the Party Over?'' *Science*, vol. 244, No. 4907, May 26, 1989, p. 914.

# APPENDIX 2-A: SUPERCONDUCTOR PRIMER

As the temperature of a superconductor is lowered, a critical temperature $T_c$ is reached at which the material undergoes a transition from the normal state to the superconducting state (figure 2-2). The superconducting state is defined by two characteristics: the ability to conduct an electric current without loss; and the expulsion of magnetic field from the interior of the material (Meissner effect).

## *Zero Resistance*

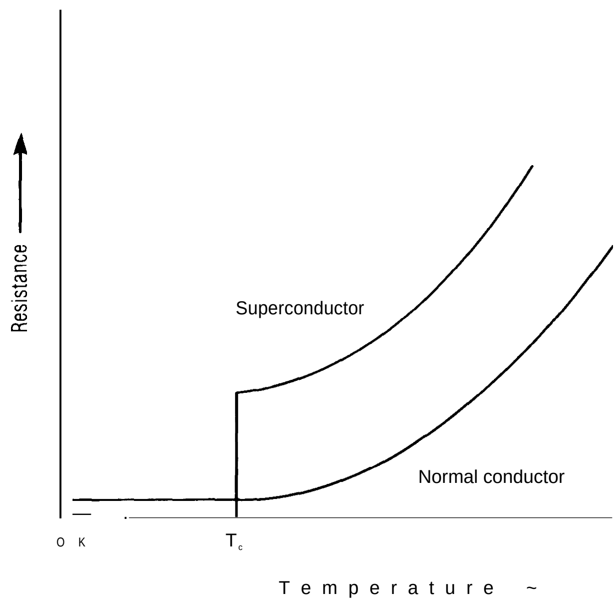
Ordinary conductors such as copper or aluminum present some resistance to the flow of electric current, causing some of the energy in the current to be dissipated into light and heat. Resistance is a useful property in light bulbs and toasters, but not for transmitting electricity from a power generating station to a factory. With zero electrical resistance, superconducting systems do not require a continuous supply of power to make up for losses. This has far-reaching consequences, enabling higher currents to be carried through wires, higher fields in magnets, and further miniaturization of computers.

Strictly speaking, the property of *zero* resistance obtains only under special conditions of direct (DC) currents. For alternating (AC) currents, such as the 60 cycle currents available from household wall outlets, superconductors do exhibit a small resistance. In general, this resistance is still lower than that of other common conductors such as copper and aluminum. However, the resistance of these metals decreases with temperature, dropping by roughly a factor of 6 between room temperature (300 K) and liquid nitrogen temperature (77 K). Thus, the advantage of a superconductor over a normal metal for a given application depends on how the superconductor's losses compare to those of normal wires at the relevant frequency and temperature.

## *Meissner Effect*

A superconductor expels magnetic fields from its interior by generating electrical currents on the surface. This property, known as the Meissner effect, is what causes a small magnet to float above a superconductor, and can be exploited, e.g., to produce frictionless bearings. This screening property also makes superconductors useful as magnetic shields; e.g., electronics can be shielded against electromagnetic interference from other nearby equipment. Although zero resistance is the property exploited in most superconductivity applications, the Meissner effect is considered the *sine qua non* of superconductivity; for while a drop in electrical resistance to a low value can occur in nonsuperconductors, the Meissner effect is unique to the superconducting state.

**Figure 2-2—Temperature Dependence of the Resistance of a Normal Conductor and a Superconductor (schematic)**




At $T_c$, the resistance of a superconductor drops to zero.

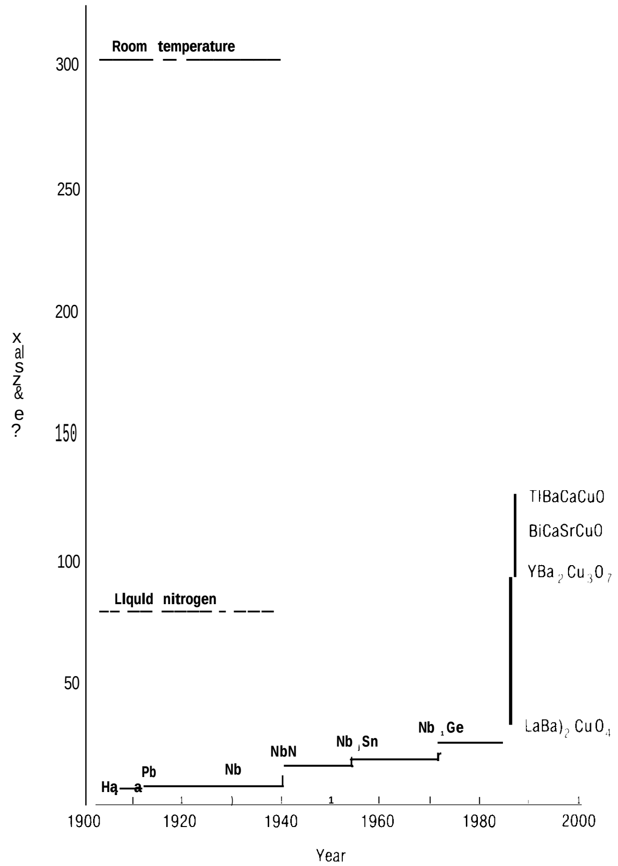
SOURCE: Office of Technology Assessment, 1990.

## *High-Temperature Superconductors*

In 1986, superconductivity was discovered in a new class of ceramic materials having the chemical composition $(La,Ba)_2CuO_4$ at 35 K (-396 °F). Prior to 1986, the highest known transition temperature was 23 K (–418 °F) for niobium-germanium (see figure 2-3). The transition temperature of the most commonly used LTS material—an alloy of niobium and titanium—is 9 K (–443 °F). These low-temperature superconductors (LTS) must be cooled with liquid helium at 4 K (–452 °F), which is expensive and difficult to work with. This is one reason why LTS materials have not been used widely in commercial applications.

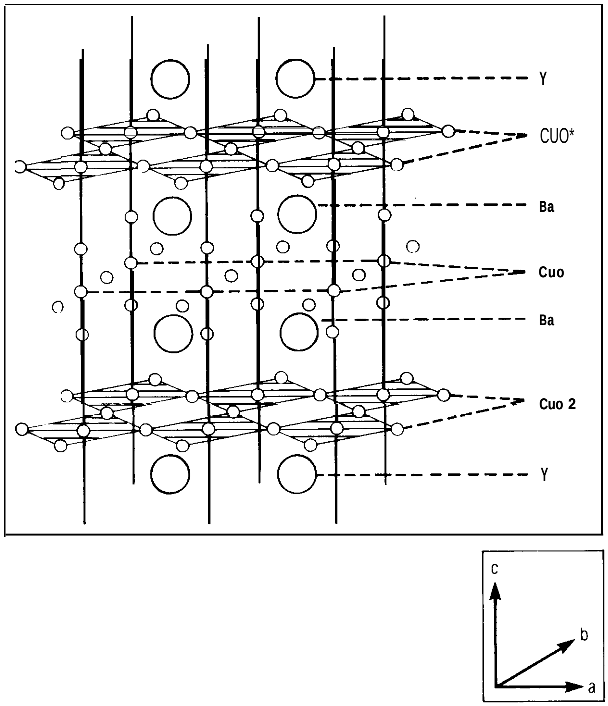
There are now three main types of superconducting compounds with transition temperatures above the boiling point of liquid nitrogen (77 K or –321 °F). In 1987, $YBa_2Cu_3O_7$ was discovered with $T_c$ = 92 K (–294 °F). In 1988, $Bi_2Sr_2Ca_nCu_{1+n}O_{2(3+n)}$ with n = 1 ($T_c$ = 85 K or –306 °F) and n = 2 ($T_c$ = 110 K or –261 °F) and $Tl_2Ba_2Ca_nCu_{1+n}O_{2(3+n)}$ with n = 0 ($T_c$ = 80 K or –315 °F), n = 1 ($T_c$ = 110 K or -261 °F), and n = 2 ($T_c$ = 125 K or –234 °F) were discovered. Numerous variations on these compounds have been found to be superconductors, all based on a layered, copper-oxygen structure (see

**Figure 2-3--Superconducting Critical Transition Temperature v. Year**




SOURCE: Office of Technology Assessment, 1990.

**Figure 2-4—Structure of $YBa_2Cu_3O_7$ Showing Successive Stacking Planes Along the C-axis**




The supercurrent is carried primarily in the $CuO_2$ planes.

SOURCE: Adapted from T.H. Geballe and J.K. Hulm, "Superconductivity—The State That Came In From the Cold," Science, vol. 239, No. 4838, Jan. 22, 1988, p. 370.

figure 2-4). At this writing, the thallium compound $Tl_2Ba_2Ca_2Cu_3O_{10}$ has the highest reproducible transition temperature (125 K).

The discovery of HTS materials with transition temperatures above the boiling point of liquid nitrogen aroused such great excitement because liquid nitrogen is cheaper, easier to handle, and has a higher cooling capacity than liquid helium. By operating at 77 K, both the system design and the refrigerator design can be simplified, and in principle, both capital and operating costs can be reduced. This revived hopes of widespread commercial applications of superconductivity.

## *History of Superconductivity*

Highlights of the history of superconductivity are shown in table 2-2. Superconductivity was first discovered in 1911 by Heike Kammerlingh Onnes in Leiden, The Netherlands. The Onnes group discovered that mercury lost all resistance to direct electric current flow when cooled to 4 K (-452 oF). This occurred soon after the successful liquefaction of helium, which allowed such very low temperatures to be reached.

Although the Leiden group immediately saw many applications for a lossless conductor, the superconductors they had found could only carry high current densities at low magnetic fields; as the fields were increased, they reverted to normal metals. This made them technologically useless.

Over the years, more than 6,000 elements, compounds, and alloys have been found to be superconductors. But for many years no one understood how to get the current-carrying capacity at high magnetic fields up into a useful range. The first materials capable of carrying high currents in high magnetic fields ("type II" materials—see below) were discovered in the Soviet Union in the 1950s.

It was not until 1957 that a theoretical understanding of superconductivity was achieved.[1] Using this theory, the Josephson Junction—a superconducting switching de-

[1] J. Bardeen, L.N. Cooper, and J.R. Schrieffer, *Physical Review B* vol. 106, p. 162 (1957); ibid., vol. 108, p. 1175 (1957).

*Photo credit: Argonne National Laboratory*

Electron micrograph of the grain boundary between crystals of HTS. Striations reflect the stacking of copper-oxygen planes. Because the supercurrent is carried primarily in the copper-oxygen planes, this kind of misalignment greatly reduces the current flow across the grain boundaries in the bulk material.

vice useful in electronic circuits and computers—was predicted and fabricated in 1962.[2] In 1955, the first practical supermagnet was produced at the University of Illinois, and in 1960 significant supermagnet advances were made at Bell laboratories. During the 1960s, commercial superconducting wire became available, and was soon used in large superconducting magnets for particle accelerators and nuclear fision experiments.

During the 1960s and 1970s, supermagnets largely displaced electromagnets for research, but it was not until superconductors appeared in magnetic field sensors in the 1970s and in MRI magnets in the early 1980s that they began to move out of a research environment. Since then, superconductors have slowly been making their way into commercial applications such as magnetic separators for removing impurities from kaolin clay and fast electronics for high-speed oscilloscopes (see ch. 3).

LTS is nearly 80 years old, while HTS is barely 3. The period between the discovery of LTS and the development of the first practical conductors (''type II' materials) was 50 years; it was another 20 years after that before LTS began to be used outside of a laboratory environment. This suggests that the widespread commercialization of HTS may take decades. To be sure, much has been learned from the development of LTS that may be applicable to HTS. But, as discussed below, HTS also presents some new challenges that will require real breakthroughs to solve—not just hard work.

**Table 2-2—Important Dates in the History of Superconductivity**

| Year | Event |
|---|---|
| 1911 | ... Superconductivity discovered (Onnes) |
| 1933 | ... Meissner effect discovered (Meissner) |
| 1934 | ... Phenomenological theory (London) |
| 1950 | ... Macroscopic quantum theory (Ginzburg-Landau) |
| 1957 | ... Prediction of type II materials (Abrikosov) |
| 1957 | ... Microscopic quantum theory (Bardeen-Cooper-Schrieffer) |
| 1950s | .. "A-15" materials (e.g., $Nb_3Sn$) discovered (Matthias et al.) |
| 1961 | ... High-field, high-current properties developed (Kunzler) |
| 1962 | ... Josephson effect predicted and discovered (Josephson) |
| 1986 | ... HTS ($T_c$ = 35 K) discovered (Bednorz-Mueller) |
| 1987 | ... HTS ($T_c$ = 93 K) discovered (Chu et al.) |
| 1988 | ... HTS ($T_c$ = 110 - 125 K) discovered (Maeda, Hermannn et al.) |

SOURCE: Off Ice of Technology Assessment, 1990.

## Superconductivity Theory

In 1957, Bardeen, Cooper, and Schreiffer, who received the Nobel prize for their theory (known as the "BCS" theory), proposed that electrons form pairs (known as Cooper pairs) in the superconductor and that these pairs are able to carry currents without loss. In the superconducting state, the electrons-which are normally repelled from one another due to their same electric charge-feel a net attraction through interaction with vibrations of the crystal lattice, resulting in the formation of Cooper pairs. BCS theory has proven applicable to all known low-temperature superconductors with only minor modifications. As yet, it is not clear whether BCS theory can be adapted to explain the new HTS materials.

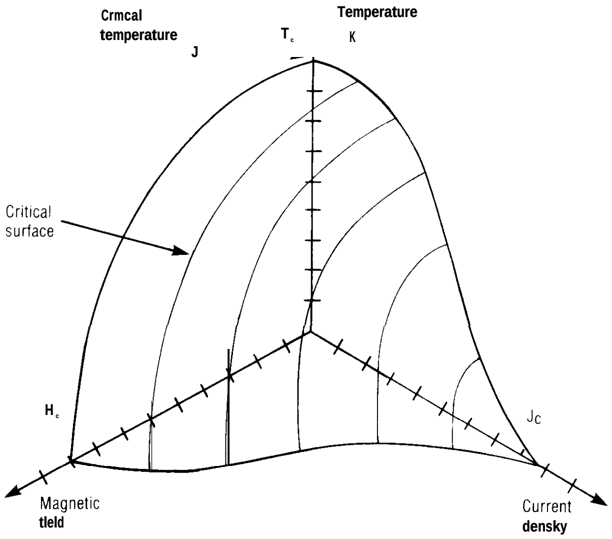
## Critical Properties

A transition from the superconducting state back to the normal state can occur in any of three independent ways: by raising the temperature above the critical transition temperature ($T_c$); by raising the current flow above the critical current density ($J_c$); or by raising the applied magnetic field above the critical magnetic field strength ($H_{c2}$). Alternatively, lesser changes in these variables can cause the transition if they occur in combination.

For a typical superconducting material, the parameters $T_c$, $J_c$, and $H_{c2}$ define the boundaries within which the material if in the superconducting state, and outside of which the material is in its normal resistive state (see figure 2-5). In general, the actual values of these parameters depend not only on the type of material, but also on its processing history, impurities, etc. For a given superconducting material, an application is only feasible if the operating temperature, current, and magnetic field fall well within these boundaries. To obtain usefully high

[2] B.D. Josephson, "Possible New Effects in Superconductive Tunneling," *Physical Review Letters*, vol. 1, July 1962, pp. 251-253.

**Figure 2-5—Superconducting State Boundaries Defined by Temperature, Field, and Current**

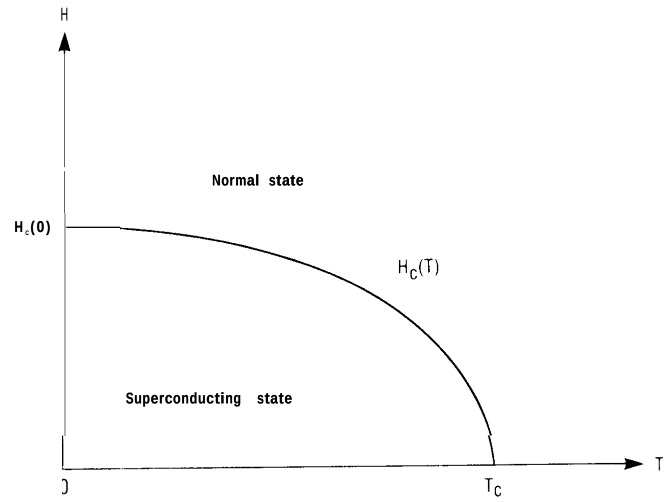



Material must be maintained below the "critical surface" to remain superconducting.

SOURCE: *Business Technology Research, "Superconductive Materials* and Devices," 1988.

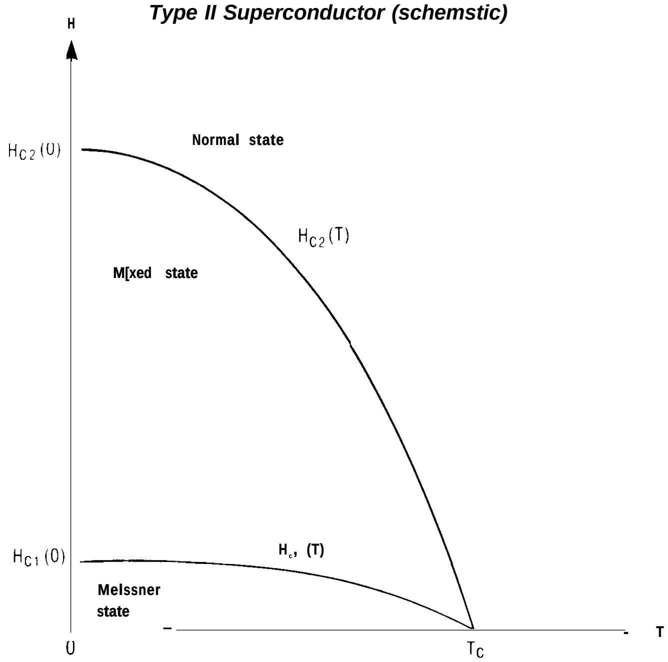
**Figure 2-6—Critical Magnetic Field (H) v. Temperature Boundary**

***Type I Superconductor***




Material must beat afield and temperature below the $H_c(T)$ line to remain superconducting.

***Type II Superconductor (schemstic)***




Magnetic flux lines enter the material for fields above $H_{c1}(T)$. Material remains superconducting below upper critical field $H_{c2}(T)$.

SOURCE: *Business Technology Research*, "Superconductive Materials and Devices," 1988.

values of current and magnetic field, superconductors are generally operated well below TC—ideally below about 1/2 T . Thus, for operation at 77 K, a $T_C$ of approximately 150 ~ is desirable, higher than the $T_C$ of any presently known material. Accordingly, room-temperature operation would require a $T_C$ around 600 K, about 621 oF.

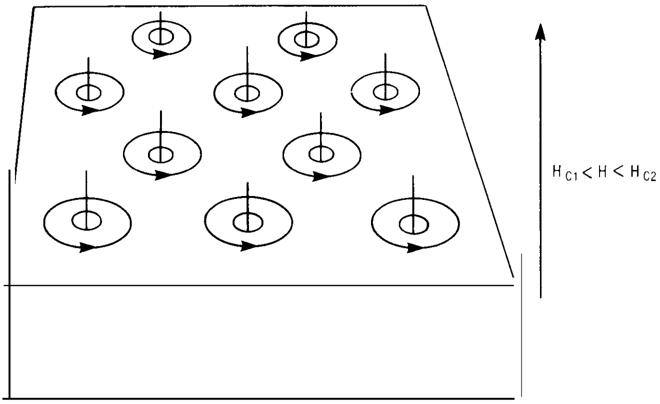
## Behavior of Superconductors in a Magnetic Field

Superconductors are classified in two types according to their behavior in an applied magnetic field (see figure 2-6). Type I superconductors, which include most pure metal superconductors, exclude magnetic flux until a maximum field ($H_C$) is exceeded at which point the material loses its superconductivity. In general, type I superconductors are not technologically important because $H_C$ is very low—100 to 1,000 gauss (0.01 to 0.1 tesla).[3] By comparison, the field of a typical magnet used in an MRI system is around 15,000 gauss. None of the type I superconductors remains superconducting in such a high field.

Virtually all superconductors of technological importance are type II, including the new HTS materials. Type II superconductors have two critical fields, $H_{C1}$ and $H_{C2}$. They behave like type I materials at low magnetic fields, below $H_{C1}$. At fields above $H_{C2}$, the superconductor is driven into its normal state. For fields between $H_{c1}$ and $H_{c2}$, the magnetic field penetrates the superconductor,

[3] One tesla (T) equals 10,000 gauss (G). The Earth's magnetic field at Washington, DC, is 0.57 gauss.

**Figure 2-7--Schematic Representation of Flux Vortices in a Type II Superconductor**




When the applied magnetic field is between $H_{c1}$ and $H_{c2}$, lines of magnetic flux penetrate the superconductor, surrounded by supercurrent "whirlpools." As long as these flux lines remain "pinned" at fixed sites, the superconductivity is not impaired.

SOURCE: *Business Technology Research*, "Superconductive Materials and Devices," 1988.

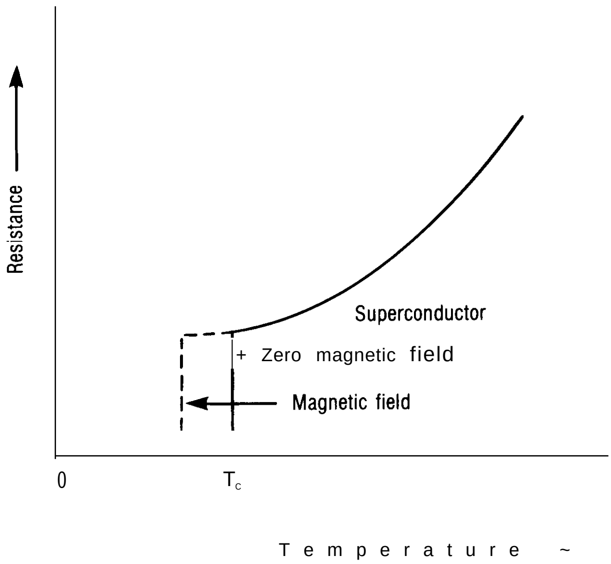
forming a lattice of vortices or supercurrent 'whirlpools' (see figure 2-7). These vortices repel one another, and arrange themselves in a regular array so as to be as far from one another as possible. As the magnetic field increases toward $H_{c2}$, more vortices are formed, the lattice spacing is decreased, until at $H_{cz}$, the superconductivity disappears.

HTS materials are unusual in having much higher values of $H_{c2}$ than LTS materials. For instance, at 4 K, $H_{c2}$ for $Nb_3Sn$ is about 20 tesla, compared with an extrapolated value for $YBa_2Cu_3O_7$ of around 200 tesla. It is not yet clear how these higher values of $H_{c2}$ may be exploited.

## Critical Current Density

The current density is defined as the amount of electric current passing through a unit cross section of conductor. In many applications—e.g., magnets—superconductors have to be able to sustain high current densities (typically $10^5$ to $10^6$ Amps/cm$^2$). Even on electronic circuit boards, where the absolute currents are only on the order of milliamps, the current density is high because the cross section of the conductors carrying the current is so small. The maximum current density that a superconductor can carry, the critical current density ($J_c$), depends not only on the composition of the material, but also on details of the microstructure, such as the presence of impurities and defects in the crystal lattice.

**Figure 2-8-Effect of Magnetic Field on Superconducting Transition (schematic)**




An applied magnetic field causes resistance to appear in HTS materials below $T_c$.

SOURCE: Office of Technology Assessment, 1990.

There is a theoretical limit on the amount of current that can be carried by any superconductor.[4] But, in practice, type II superconductors in a magnetic field typically exhibit $J_c$s that are a factor of 10 below this theoretical limit. The reason is that the flow of electric current exerts a force (Lorentz force) on the vortex lattice, and this force gets stronger as the electric current increases. Resistance appears when this force becomes strong enough to dislodge the vortex lattice from the pinning sites to which it is attached.

A significant fraction of the vortices are pinned in place by defects, grain boundaries, and other points of weakened superconductivity. Also, because of their mutual repulsion, the unpinned vortices are locked in place. Collectively, this local site pinning and the lattice locking are known as the pinning force in the superconductor. At the critical current the Lorentz force overcomes the pinning force and vortices begin to move. This movement constitutes resistance, and eventually quenches the superconductivity. An understanding of how to fabricate LTS conductors with the strongest possible pinning forces has been reached only after 20 years of research.

Increasing temperature can also act to disrupt the superconductivity in type 11 materials. At low temperatures (around 4 K), the ambient thermal energy is not large

[4]The thermodynamic critical current is the amount of current that will produce a magnetic field that exceeds the thermodynamic critical field locally. The thermodynamic critical current causes depairing of the Cooper pairs, thus destroying the superconductivity.

enough to dislodge pinned vortices. Therefore, thermally activated vortex movement has not been a problem with LTS materials. At higher temperatures, though, the higher thermal energy in the crystal can overcome the pinning forces, causing vortices to jump from one site to another (flux creep).

In the presence of a magnetic field, HTS materials exhibit a small residual resistivity at temperatures considerably *below* $T_c$ (see figure 2-8). This phenomenon is not observed in LTS, and may require HTS materials to be operated substantially below $T_c$ for applications in a magnetic field, i.e., at temperatures of 20 to 30 K rather than 77 K. This residual resistivity is due both to poor coupling between individual grains of HTS and to weak vortex pinning vis-a-vis thermal energy. Better processing techniques will eventually lead to improved intergranular coupling. New and stronger pinning mechanisms will have to be found to counteract the higher thermal energy at higher operating temperatures. Some hope may be derived from the fact that *thin* films of HTS exhibit far higher critical currents in the presence of magnetic fields than do bulk single crystals. This suggests that the low critical currents in bulk materials may not be intrinsic, but may be improved by creating microstructure similar to those in thin films. In any case, materials with higher $T_c$ do not necessarily have higher pinning strength, and therefore are not necessarily more attractive for practical applications.