

HIGH- T_c BICRYSTAL GRAIN BOUNDARIES

Among superconductors, the high-transition-temperature (high- T_c) cuprates, discovered 15 years ago by Georg Bednorz and Alex Mueller, are the most complex and fascinating. Since their discovery, three themes have been researched quite intensely: understanding the microscopic basis of the mechanism of superconductivity, advancing applications ranging from thin films used in superconducting quantum interference devices (SQUIDS) to wires for bulk applications, and discovering new superconducting compounds.

In conventional, noncuprate superconductors, the three themes are generally quite distinct. But in the high- T_c materials, the first two are frequently intertwined. For example, the physics of the symmetry of the superconducting wavefunction, the materials science of growth and defect control, and applications such as SQUIDS and wires are all closely connected. The cuprates are prototypical of a general trend in research: As materials become more complex, a close working relationship among physics, materials science, and applications becomes essential. Here we present a striking example of this interplay: grain boundaries in the cuprate superconductors.

The discovery of the high- T_c superconductors was immediately followed by frenetic activity to find materials with still higher transition temperatures. Amid this excitement, however, there was a growing and gnawing concern that applications of these materials would be exceedingly difficult to achieve. Two factors underpinned this doubt. First, the coherence length in the high- T_c materials is extremely short—only several angstroms, compared to 39 nm in niobium (a conventional superconductor) at 4.2 K. Such an ultrashort coherence length seemed to rule out the fabrication of device-quality Josephson junctions for SQUIDS. Second, the small critical current density J_c observed in these materials—a few hundred A/cm² at 4.2 K, compared to approximately a million A/cm² in conventional superconducting wires—appeared to preclude almost all thin-film and bulk applications.

During 1987–88, three papers changed the picture completely.¹ The first showed that the critical current densities of thin single-crystal films epitaxially deposited on single-crystal strontium titanate substrates are at least of the order of 10^5 – 10^6 A/cm² at 77 K, more than enough for practical applications. The second proved the suspicion, already alluded to in the first report of high- T_c superconductivity, that, in sharp contrast to conventional superconductors, the J_c in these materials is deleteriously determined by grain boundaries, the interfaces between crystallites in polycrystalline samples. The third paper showed that the strength of the superconducting coupling across a grain boundary is a function of the misorientation

Grain boundaries in high-temperature superconductors illustrate the interplay of physics, materials science, and applications in complex materials.

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the basic understanding of high- T_c superconductivity, to build devices, and to develop ingenious techniques for producing wires.² (See PHYSICS TODAY, March 1995, page 20, and March 1996, page 48.)

The bicrystal technique

There are many degrees of freedom in the choice of the relative orientations of two adjoining crystals and the location of the grain boundary between them. Although many grain-boundary geometries have been investigated with success, the most widely examined ones, which we focus on in this article, are in thin films designed so that only one externally controllable degree of freedom exists: the angle of rotation about the c -axis, normal to the planes of the high- T_c compounds (see figure 1).

The first experiments on bicrystal grain boundaries were carried out on samples prepared by fusing two SrTiO₃ crystals with a predetermined misorientation between them. The fused crystals, or bicrystals, were subsequently polished and used as a substrate for depositing epitaxially grown films of YBa₂Cu₃O_{7- δ} , shown schematically in figure 1a. The orientation of the deposited cuprate film followed that of the underlying substrate, so that the resulting epitaxial film had a single grain boundary with a prescribed orientation. The atomic-scale structure of a grain boundary fabricated with the bicrystal technology is shown in figure 1b. The interface is clean at an atomic level and is only a few angstroms wide.

Many groups have measured the current-carrying properties of grain boundaries prepared by the bicrystal technique. Figure 2a shows representative recent data of the variation in J_c as a function of the misorientation angle θ . The critical current density decreases exponentially by three to four orders of magnitude as θ increases to 45°. In addition, there is a substantial scatter in J_c for a given θ . The reasons why the decrease is exponential and why the scatter is present are topics of ongoing research.

The critical current across a grain boundary shows two limiting behaviors. Below angles of about 10°, the critical current is limited by the onset of flow of magnetic flux quanta along the boundary, whereas for larger angles, the boundary acts as a Josephson junction, with weak coupling between the grains and a supercurrent that depends on the phase difference between the grains' superconducting wavefunctions. These observations make clear that, for wires, θ should not exceed 10°; for Josephson devices, a desired value for J_c can be selected by choosing θ . These findings initiated a wide spectrum of applications, as illustrated in figure 3.

Many attempts have been made to explain the decrease in J_c with increasing θ . Such a change is expected

tion angle defining the grain boundary, and that large-angle grain boundaries, coupled by the Josephson effect, can potentially be used for devices. The findings described in these papers stimulated numerous research groups to contribute to and extend

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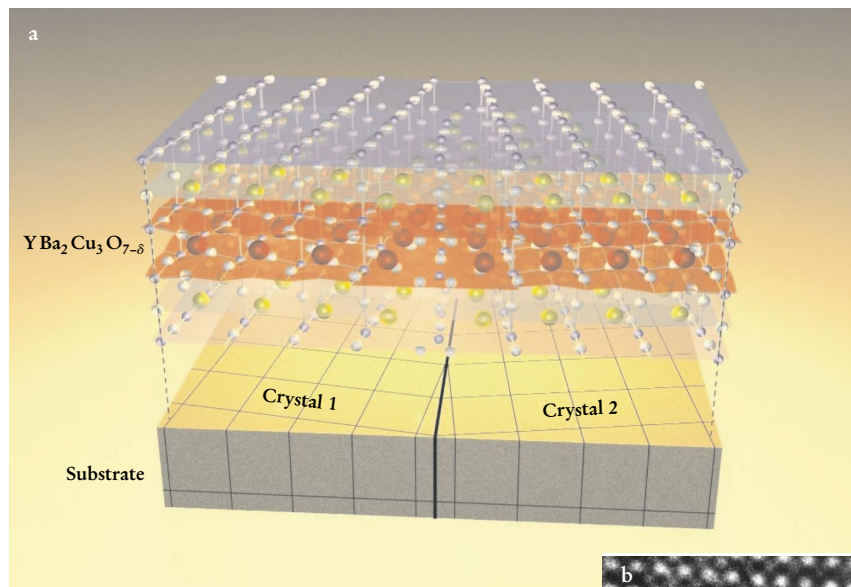


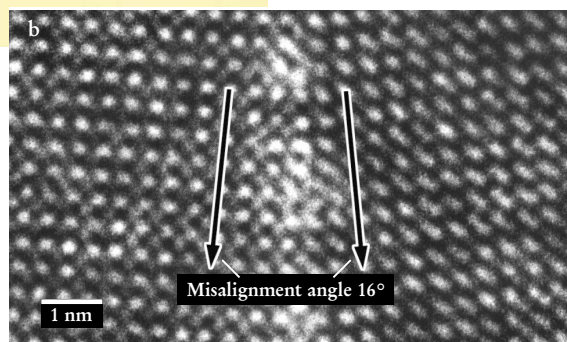
FIGURE 1. BICRYSTAL GRAIN BOUNDARY. (a) A single grain boundary is produced by fusing together two crystals, for example of SrTiO_3 . An epitaxial film of a high-temperature superconductor, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, is grown on top and replicates the grain boundary of the substrate. (Courtesy of G. Hammerl, University of Augsburg.) (b) A transmission electron microscope image of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundary produced by this method. (From J. G. Wen et al., *IEEE Trans. Appl. Supercond.* 9, 2046 [1999], © 1999 IEEE.)

in a superconductor with d -wave symmetry, in which the strength of the superconducting coupling is orientation-dependent (see *PHYSICS TODAY*, March 2000, page 17). However, the extent of the observed decrease in J_c is larger than expected. Topological defects are therefore generally believed to be responsible for a significant part of the suppression of the supercurrent flow across grain boundaries.

The current-carrying properties of all the grain boundaries in the cuprate superconductors are qualitatively similar. They do not depend on the details of how the boundaries are produced, or whether the material is a film or bulk. The current-voltage data measured across grain boundaries have provided various universal features.³ For example, if biased above their critical current, large-angle grain boundaries have a finite and relatively temperature-independent electrical resistance. Furthermore, some misorientations show steps in the current and a zero-bias anomaly with enhanced conductance. The current steps originate from resonances between the microwave radiation generated by the boundary due to the Josephson effect and the boundary's dielectric cavity modes. These so-called Fiske resonances suggest that the interface of a large-angle boundary acts as an insulating dielectric layer through which the current flows by tunneling. The zero bias anomaly is nowadays explained by the presence of electron states in the superconducting gap associated with d -wave symmetry.

SQUID applications

Once the bicrystal experiments demonstrated the Josephson-junction behavior of high-angle grain boundaries, SQUIDs emerged as a natural application to pursue. Many early grain-boundary SQUID experiments² were performed at IBM in the late 1980s. The SQUIDs were almost exclusively so-called dc-SQUIDs, consisting of two Josephson junctions connected in a superconducting loop with a diameter typically around 50 μm . Since then, the research of prominent groups worldwide has led to low-noise high- T_c single-grain-boundary SQUID systems operating to temperatures as high as 110 K.⁴ Whereas many of these SQUID systems are based on grain boundaries fabricated with the bicrystal technique, others make use of



grain boundaries induced by the growth of high- T_c films on steps, crafted into the substrate surface (the so-called step-edge technique). And some SQUID systems use the biepitaxy technique, in which a seed layer is first deposited on part of the substrate; the high- T_c film subsequently deposited on the seed layer has a different orientation from the film deposited directly on the substrate. (The first commercially available SQUID used biepitaxially induced grain boundaries as the Josephson junction elements.) High- T_c SQUIDs are already in use in bio- and geomagnetometry, magnetic imaging, nondestructive materials evaluation, picovoltmeter measurements, and nuclear magnetic resonance spectroscopy.

In the medical sector, an important advantage of the high- T_c materials is the practicality of using liquid nitrogen over liquid helium. High- T_c SQUID magnetometers (which measure magnetic fields) and gradiometers (which measure magnetic field gradients) are currently being tested in clinical environments. The potential of these techniques is illustrated by figure 4, which displays two magnetocardiograms of a patient, the first taken immediately after a heart attack, the second one hour later. The magnetocardiogram reveals prominent changes in the heart signal following the attack, changes completely missed by the standard electrocardiogram. Although these specific measurements are of exploratory nature and need to be repeated and confirmed with many more patients, they clearly demonstrate a potential benefit of high- T_c SQUID systems in medical applications.

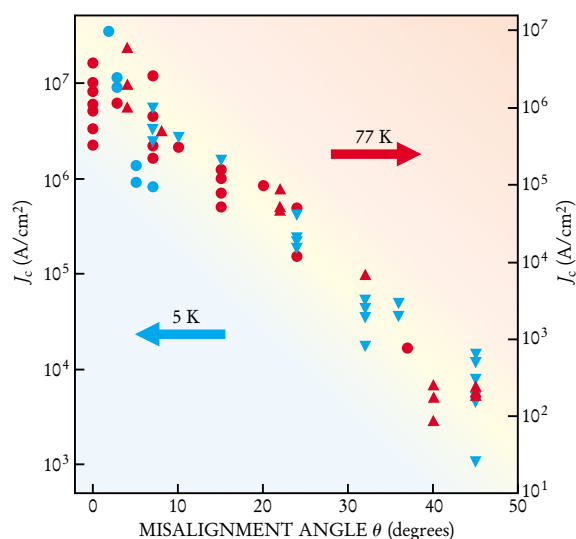


FIGURE 2. CRITICAL CURRENT DENSITY J_c measured as a function of the misorientation angle θ of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundaries. At both 5 K (blue) and 77 K (red), J_c shows scatter and an exponential decrease with angle. (Data from ref. 14.)

In the semiconductor industry, the bicrystal SQUID technology has found use in mapping out the magnetic field associated with the flow of current through metal lines in semiconductor chip packages, shown in figure 5. In this example, deviations from the expected current flow patterns were used to diagnose, at room temperature, wiring defects in multilayer packages of static random access memory chips made in a manufacturing line; such a diagnosis is not possible by other means.

The search for low-noise and high-speed radiation detectors and spectrometers is another active area of research. Superconducting Josephson junctions are, in many ways, ideal for these applications: They consume little power, generate relatively little noise at their low operating temperatures, and switch rapidly between superconducting and ohmic behavior. Single-boundary high- T_c junctions have been used for detection of radiation and for spectroscopy at frequencies up into the terahertz range.² An optical micrograph of a broadband logarithmically periodic antenna used for such studies is shown on the cover of this issue. The antenna uses a 30° bicrystal Josephson junction at its center as a detector.

Probing the underlying physics

Knowing the underlying symmetry of the macroscopic quantum wavefunction is important in understanding properties of the high- T_c superconductors and in delineating which class of theories best describes these materials. Although the symmetry cannot establish the pairing mechanism, it can provide a check on proposed models.

Much of the early research into the high- T_c superconductors focused on the nature of the wavefunction of the paired electrons (see PHYSICS TODAY, January 1996, page 19). Many proposed that the pairs form a “ d -wave” state, with $d_{x^2-y^2}$ symmetry. In such a state, depicted in figure 3e, the superconducting wavefunction has four lobes of alternating sign. If two superconductors with $d_{x^2-y^2}$ symmetry are brought into contact at a Josephson junction, the phase difference across the junction is a function of the relative angle of rotation of the two superconductors and

the orientation of the junction plane. Bicrystal grain boundaries directly lend themselves to analyzing these effects and therefore provide a method of systematically exploring the symmetry of the order parameter. Indeed, they have been used with great success for this purpose.

If the orientation of the two crystals on either side of a grain boundary is such that the phase of the order parameter changes sign across the boundary, there is a corresponding change in phase across the junction by π . If two junctions, one of which has a phase change of π and the other not, are placed in a superconducting loop in series, the requirement that the phase difference around the loop be a multiple of 2π spontaneously produces a supercurrent that induces a phase shift of π to add to or subtract from that produced just by the junction geometry. This supercurrent flowing around the loop produces half of a quantum of magnetic flux, $1/2 (h/2e)$, which is measurable and is direct evidence for the existence of a junction with a π phase shift. Such experiments, using a scanning SQUID microscope, indeed revealed the presence of a half-integer flux (see figure 3g), proving $d_{x^2-y^2}$ symmetry⁵ at or near a grain boundary.

Superconducting electronics

The use of superconductivity in electronic applications has always had special appeal because of its inherent high speed and low power consumption. Josephson memory and logic applications were widely investigated during the 1970s. There have been two approaches to developing high- T_c electronics: applying electric or magnetic fields to very thin films of high- T_c materials to obtain three terminal devices, and building logic circuits using the flux quantum. In both approaches, grain-boundary junctions are used.

Researchers recognized very early that high- T_c materials have lower carrier concentrations than their conventional counterparts. This difference implied a larger electronic screening length, and therefore the possibility that an applied electric field could penetrate deep enough to produce a measurable change in the supercurrent and thus give rise to a field-effect transistor (FET).⁶ The grain boundary is generally believed to have an even lower carrier concentration, which could enable an electric field to modify the Josephson current across a grain boundary embedded in a superconducting drain-source channel, much as a gate voltage modifies the current through a semiconductor FET. Indeed, an electric field was observed⁷ to shift the T_c of a grain boundary by 10 K, with a correspondingly large change in J_c . The grain boundary thus behaved as a Josephson field-effect transistor (JoFET).

Two other ideas are being explored for producing three-terminal Josephson devices with grain boundaries: using quasiparticle injection into the boundary, and modulating the boundary’s resistance by a local magnetic field. These transistors are clearly research devices with exciting properties. Some of them show both current and voltage gain, and all have a superconducting “on” state (recent progress is documented in ref. 2).

Josephson junctions switch between superconducting and ohmic behavior at subpicosecond speeds, providing opportunities for ultrafast electronic devices.^{2,8} The most prominent architecture explored at present for superconducting digital circuitry is the rapid single-flux-quantum (RSFQ) technology. Here, information is represented by magnetic flux quanta, which are shifted between circuit elements at high speed. High- T_c RSFQ devices have predicted operating speeds exceeding 1 THz and dissipation levels of only microwatts per element. Small exploratory RSFQ logic circuits, including flip-flops, shift registers,

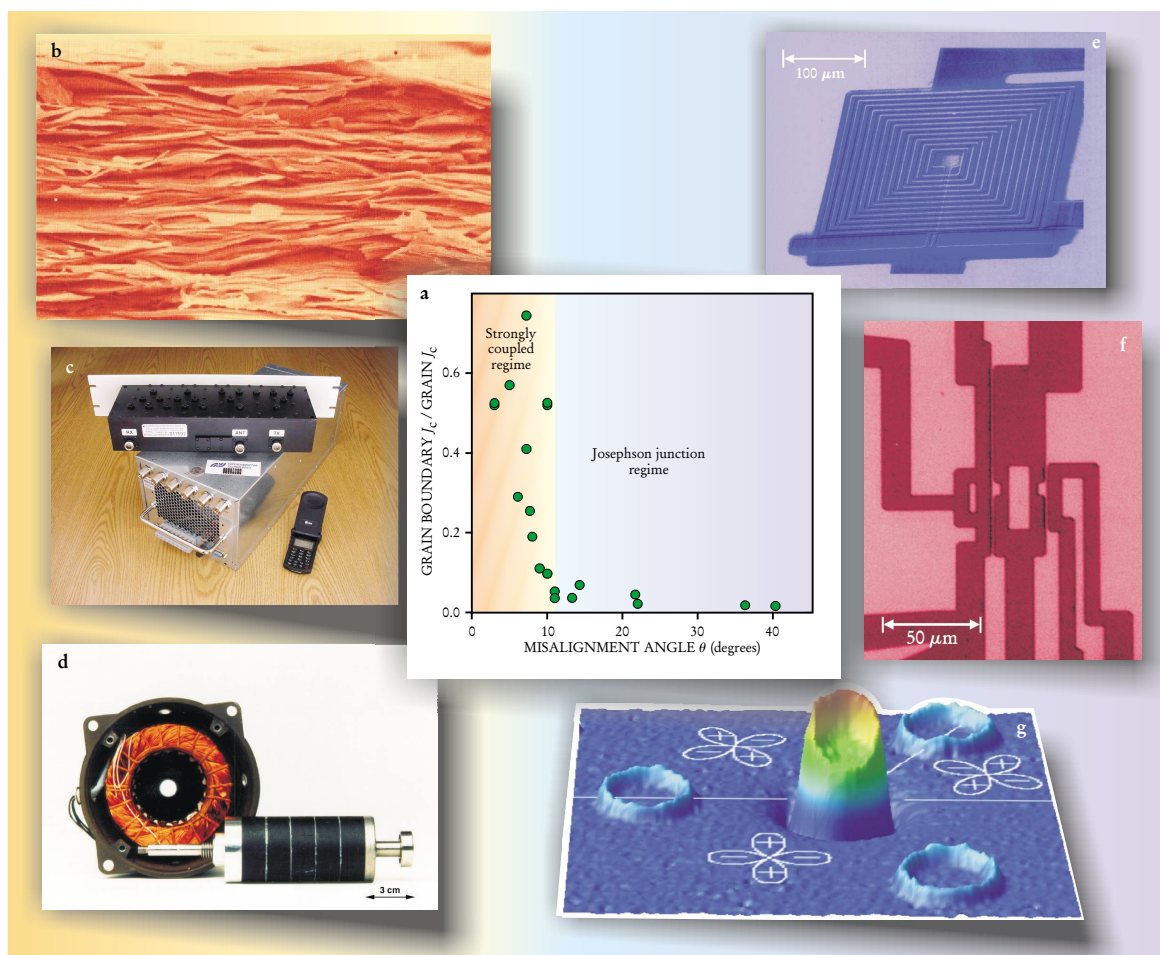


FIGURE 3. HIGH- T_c GRAIN BOUNDARIES fall into two categories of behavior, as shown in (a). To the left (b–d) are applications requiring that, at most, low-angle grain boundaries be present; in applications that only require lengths of superconductor less than a meter or so (such as c and d), grain boundaries may be avoided almost completely. (b) Micrograph of a high- T_c cable made by the powder-in-tube method. (Courtesy of K. Watanabe, Tohoku University, Japan.) (c) Epitaxial film used for a microwave filter in a cell-phone system. (Courtesy of A. Cardona and D. Scalapino, Superconducting Technologies Inc.) (d) Hysteresis motor, in which a rotating magnetic field produces a torque on the rotor formed from a cylinder of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. (Courtesy of T. Habisreuther and E. Hoenig, Institute for Physical High Technology, Jena, Germany.) To the right (e–g) are applications based on large-angle Josephson-coupled grain boundaries in thin films, produced in the manner sketched in figure 1. (e) Bicrystal SQUID with a high- T_c input coil. (Courtesy of H. Hilgenkamp, University of Twente, the Netherlands.) (f) Rapid single-flux-quantum circuit incorporating four bicrystal Josephson junctions. (From G. Y. Sung et al., *IEEE Trans. Appl. Supercond.* **9**, 3921 [1999], © 1999 IEEE.) (g) Results of a grain-boundary experiment probing the order-parameter symmetry of the high- T_c superconductors, which determined that, at grain boundaries, the superconductors have $d_{x^2-y^2}$ symmetry as shown in white. The inherent phase change around the superconducting loop in the middle where the three grains meet results in a current flowing around the loop, producing the local magnetic field shown as the peak there. (Courtesy of C. C. Tsuei and J. Kirtley, IBM.)

and analog-to-digital converters, have been implemented, some using bicrystal technology (see figure 3f). Likewise, prototypes of voltage standards based on the Josephson effect use bicrystal junctions, in some cases several hundreds of them simultaneously. There are two serious problems with these devices, however: the difficulty of getting junctions with the same critical current densities and the inability to fabricate junctions where needed, rather than where the boundaries lie.

Quantum computers manipulate coherent quantum states, which are made up of a superposition of, say, two states such as spin up or down. Such a two-state system

is the quantum equivalent of the classical binary bit, and is called a quantum bit or qubit. In principle, many ways exist of generating qubits. One approach is to use circuits made out of conventional superconductors in which Josephson junctions are connected in loops. In these circuits, a precisely controlled magnetic field corresponding to half a flux quantum is applied to produce degenerate quantum states to serve as qubits.

The use of high- T_c superconductors provides an attractive alternative: If the loop encloses a Josephson junction with a π phase shift, then half a flux quantum is produced spontaneously. This approach has two advan-

tages: With no need for an applied magnetic field, noise from external sources is minimized; and the behavior is much less sensitive to the exact properties of the loops and the junctions, which places less stringent demands on lithographic control. Grain boundaries are a natural choice for producing these π junctions. But such an approach has two inherent problems: *d*-wave superconductors have a large density of excitable quasiparticles at the nodes where the superconducting wavefunction goes to zero, and grain-boundary junctions have a finite resistance. Both can cause decoherence of the wavefunction and lead to intolerable errors. Dennis Newns of IBM has proposed that, at the very low temperatures at which quantum computers would have to operate, the effect of a node is small and can be ignored. The second problem, that of decoherence at the grain boundaries, can be addressed by making the grain boundary insulating, as discussed later.

The strongly coupled regime

Our discussion so far has focused on the use of Josephson coupling, observed across a large-angle boundary. For a number of other applications, the presence of Josephson coupling is undesirable, and hence either no boundaries or, at best, only low-angle ones can be tolerated. An example of an important commercial application of zero grain-boundary tolerance is in high-*Q* filters in base stations for wireless communication. Several hundred base stations in the US currently use this technology, in which only epitaxial films deposited on single-crystal substrates are used. (The films themselves are not perfect single crystals. They contain very low-angle grain boundaries and, frequently, twins, which are 90° rotations within the layers. Neither of these classes of defects significantly affects the critical current densities.)

For bulk applications such as wires, it would be prohibitively expensive to produce a single-crystal material, and low-angle grain boundaries are tolerated. Note that the detrimental effect of grain boundaries in high-*T_c* wires contrasts with the situation in conventional superconductors, in which grain boundaries are sometimes deliberately introduced to increase *J_c* through enhanced pinning of magnetic vortices. To pursue these applications, several fabrication techniques have been developed to produce high-*T_c* conductors—both flat tapes and round wires—that contain only low-angle boundaries. These techniques fall into two general categories: powder-in-tube methods^{9,10} or coated-conductor technologies.^{11,12}

Deformation of large-grained crystalline materials changes an initially random distribution of the orientations of grains to one that can have pronounced orientational order—a process known as texturing. The texture that develops is controlled by the material's crystal structure and the method of deformation. Within the layered high-*T_c* materials, bismuth-based superconductors such as Bi₂Sr₂CaCu₂O_{8+δ} are particularly anisotropic, with coupling between the layers dominated by Van der Waals' forces. When these materials, in powder form, are placed in a silver tube and extruded, they develop a desirable texture: The microstructure produced in this powder-in-tube method is lamella-like, with the layers lying parallel to the extrusion direction and with a good fraction of the near-neighbor misorientation below 15° (see figure 3a).

Wires must not only have the requisite critical current densities but the cables formed from them must pass economic and reliability measures, such as mechanical strength. Prototype systems built in Europe, Japan, and the US show an encouraging trend in both these criteria.¹⁰ The critical current densities of cables are in the range of

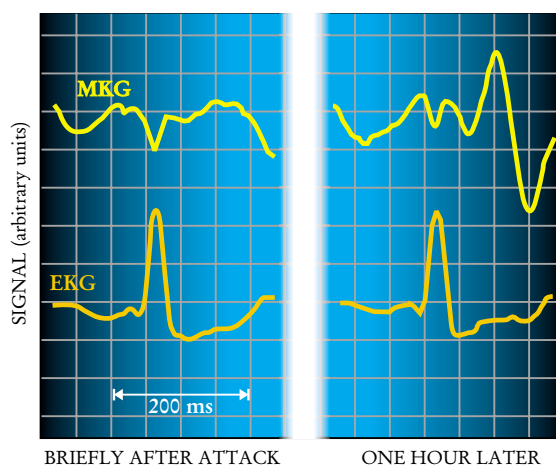


FIGURE 4. SQUID SYSTEMS operating at 77 K are being used for medical applications. Here are two successive electrocardiograms (EKGs) and magnetocardiograms (MKGs) of a patient taken after an interval of one hour following a heart attack. The MKG shows pronounced changes. (Courtesy of P. Seidel, University of Jena, Germany.)

10⁴ A/cm² at 77 K, dropping approximately by half in a magnetic field of 1 T applied parallel to the tape surface. The cable systems are designed for high-power, 25 MVA–5 GVA applications (5 GVA is the output power of a very large nuclear power plant).

Another method of texturing is to provide a template that has a textured surface on which the high-*T_c* materials are deposited.^{11,12} When tapes of nickel-based alloys are rolled and suitably heat-treated, the Ni grains become textured along two of their main crystal axes, so that grain boundaries are aligned in all directions. On this surface, a buffer layer and then a high-*T_c* material, typically YBa₂Cu₃O_{7-δ}, are deposited. As in the bicrystal experiments, the epitaxial high-*T_c* film reproduces the microstructure of the buffer layer, which in turn replicates that of the Ni alloy. The thickness of the superconducting films is in the range of a few microns, with the entire tapes being 25–50 μm thick. This process, known as the rolling-assisted biaxially textured substrate technique (RABiTS),¹² produces low-angle boundaries (2–5°); consequently, the *J_c* reaches values well above 10⁵ A/cm² at 77 K and 1 T.

Texturing can also be induced in the buffer layer, either by ion-beam-assisted deposition or deposition under a glancing angle.¹¹ The critical current densities of superconductor films grown on textured buffer layers exceed 10⁶ A/cm² at 77 K and zero external magnetic field. Tapes 1 cm wide carry well above 100 A at this temperature. The length of the tapes is limited currently to several meters, but deposition systems capable of producing longer tapes are being built.

Coated conductor processes solve the grain boundary problem by aligning the grains and thereby exploiting the full potential of high-*T_c* superconductors. The main challenges are reducing the cost of fabricating wires, maintaining a large *J_c* in thick films to meet practical requirements, and fabricating wires of sufficient length. But further progress is anticipated. For example, deposition of high-*T_c* films on metallic tapes by non-vacuum techniques such as dip-coating is showing increasing success, with Takeshi Araki and colleagues at the International Super-

conducting Technology Center in Nagoya, Japan, reporting J_c values already exceeding 10^6 A/cm² at 77 K.

Controlling the boundaries

So far in our discussion, the naturally occurring properties of grain boundaries in the high- T_c cuprate materials have been accepted as given. Either the boundaries have been exploited or ways have been found of avoiding their detrimental behavior. But in recent experiments, the properties of grain boundaries have been deliberately modified. There are two application areas—almost two extremes—in which modification is desirable: qubits and wires. Qubits require an insulating grain boundary; wires require strong superconducting coupling, which will reduce the cost of fabrication of cables by relaxing the stringent need to control their microstructure.

Many attempts have been made to modify the properties of grain boundaries. The most significant of these have been the recent studies of chemical doping, at or near the boundaries, that enhances the boundaries' J_c without lowering the T_c of the bulk material¹³ (see PHYSICS TODAY, October 2000, page 21). This approach has its genesis in the large electric screening length of the high- T_c superconductors. In these materials, grain boundaries are electronically active, creating near the boundary either depletion layers with a reduced number of superconducting charge carriers or enhancement layers with excessive carrier density. Reducing the structure-induced positive grain-boundary charge, such as by replacing some of the Y^{3+} ions by Ca^{2+} in $YBa_2Cu_3O_{7-\delta}$, should therefore enhance J_c . However, this replacement has to be done not only in a process compatible with large-scale production but with nanometer accuracy at the interface only, because the substitution causes an undesirable reduction of the T_c within the grains.

This obstacle was overcome by using multilayers of $YBa_2Cu_3O_{7-\delta}$ and $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films: Calcium atoms diffuse right along the grain boundary into the $YBa_2Cu_3O_{7-\delta}$ layer, enhancing J_c by a factor of six at 77 K for 24° boundaries. This technique may ease the requirement of grain alignment faced by the coated conductor technologies. If doping of the grain boundaries can enhance coupling, then, in principle, it can also be used to make it insulating. This development would be very desirable for implementing qubits and for devices utilizing hysteretic Josephson junctions.

A new paradigm

The experiments on grain boundaries in the high-temperature cuprate superconductors illustrate the close interplay of physics, materials, and applications. The epitaxial growth of $YBa_2Cu_3O_{7-\delta}$ films enabled the bicrystal technology and the fabrication of electromagnetic detectors, such as radio-frequency spectrometers and SQUIDs for such diverse fields as medicine and nondestructive testing. The identification of the coupling across grain boundaries into flux-flow and Josephson-coupled regimes had a direct effect on science and applications, including producing superconducting cables with high critical current densities and designing experiments that established the symmetry of the superconducting order parameter at the grain boundaries.

The close connections among physics, materials, and applications has motivated research and produced remarkable progress in all three areas. We believe that as the complexity of materials grows, knowledge of science and its application will be increasingly required, if not essential.

One of the authors (Chaudhari) has benefited enormously from a group of visiting scientists who worked with him on

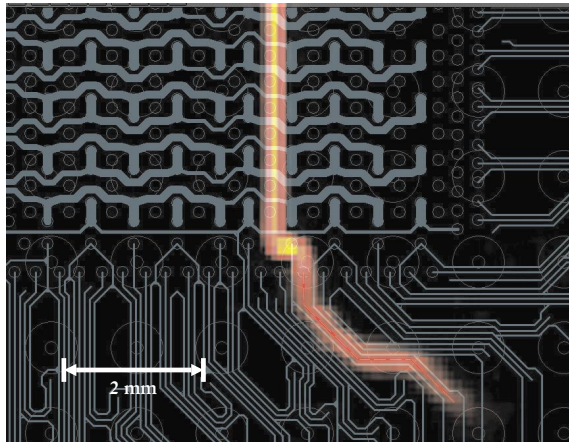


FIGURE 5. SCANNING SQUID PHOTOGRAPH of a section of a package for a commercial static random access memory chip. The current flowing through a short from a bitline to ground is imaged by the magnetic field it generates. This technique is used for the room-temperature detection of defects in packages in a manufacturing environment. (Courtesy of L. Knauss and T. Venkatesan, Neocera Inc.)

high-temperature superconductivity. They gave freely. They are Duane Dimos, Rudolf Gross, Masashi Kawasaki, Ettore Sarnelli, Neeraj Khare, Shawn-Yu Lin, and the coauthor of this article (Mannhart). Mannhart thanks Hans Hilgenkamp for longtime, fruitful collaboration and the BMBF for support of the EKM-project 13N6918.

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