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HIGH-TEMPERATURE SUPERCONDUCTING THIN FILMS

The recent discovery of superconducting oxides with high transition temperatures is a historic event already recognized by a Nobel Prize in physics. The complex behavior of those materials has attracted the attention of thousands of scientific researchers. The appearance of superconducting behavior above the boiling point of nitrogen has drawn in engineers and technologists, who are ready to exploit the phenomenon in applications ranging from microelectronics to lossless transmission lines and levitating transportation systems. This article will briefly describe those exciting developments and then discuss the research on high-temperature superconducting thin films and their possible applications in microelectronics at APL. The films are formed by the novel technique of laser ablation processing and are characterized by a number of methods, including the new technique of magnetically modulated microwave absorption. Both techniques, originally conceived and developed at APL, are described in some detail.

INTRODUCTION

The discoveries in late 1986 and early 1987 that certain copper-containing ceramic metal oxides become superconductive at temperatures well above the 15-year-old mark of 23 K in niobium–germanium launched a massive worldwide research effort. The new developments gave media-celebrity status to science (and some scientists), as the results of the superconductivity research were eagerly sought and rapidly disseminated by the international press. The reasons for that excitement are clear and manifold. First, there is the obvious scientific importance of those materials and the possibility that revolutionary new physics will be required to understand their superconductive behavior, which has attracted a multidisciplinary response from physicists, chemists, materials scientists, and ceramicists. Second, the engineering and technological communities see those materials as the potential realization of many applications of superconductivity that have thus far been economically impractical or even impossible at the extremely low temperatures required to achieve superconductivity. Electronics applications appear especially promising, given the successes already achieved in depositing superconducting ceramic films on a variety of materials. Indeed, it would be perilous for any technology-dependent society to ignore the economic implications of the applications of the developing technology. The combination of intellectual challenge, technological possibilities, and hoped-for economic payoff—all over less than two years—has fueled activity that shows no signs of abating.

The short history of superconducting ceramics with high transition temperatures began with the publication in the October 1986 issue of a relatively little-known German journal of an article by J. Bednorz and K. Müller[1] from the IBM laboratories in Zürich, describing the possible existence of superconductivity in La–Ba–Cu–O at $T_c = 35$ K. The resistance of the material dropped sharply at that temperature but did not quite go to zero. The paper was largely ignored.

At the December 1986 meeting of the Materials Research Society in Boston, K. Kitazawa[2] from the University of Tokyo confirmed the Bednorz–Müller results and further reported on the isolation and structure of the superconducting phase, $La_{1.85}Ba_{0.15}CuO_4$, which showed zero resistance as well as diamagnetism in the vicinity of 35 K. Less than two months later, at a press conference on 16 February 1987, Paul Chu from the University of Houston announced the observation of superconductivity at the astoundingly high temperature of 93 K, a result later confirmed and independently observed at a number of laboratories around the world. The material, revealed later in a publication,[3] was yet another perovskite structure, $YBa_2Cu_3O_7$, now commonly referred to as the (1–2–3) material. On the evening of 18 March 1987, at a specially organized session of the annual Solid-State Meeting of the American Physical Society in New York, the feverish worldwide activity on the subject became obvious when over a thousand scientists crammed into a hotel ballroom and surrounding corridors, under television lights and with the attention of international media, to present and discuss data on the above two superconducting oxides, as well as others obtained by substituting rare-earth elements for yttrium. The session lasted all night. *The New York Times* dubbed it the "Woodstock of Physics."

In the next ten months, results on the fabrication, atomic structure, and extensive chemical and physical characterization of the new materials poured in at a relentless pace. In November 1987, barely a year after the publication of their results, Bednorz and Müller were awarded the Nobel Prize in physics.

Just as the research activity in high-temperature superconductors seemed to be reaching an elevated plateau, A. Maeda of Tsukuba Laboratories announced at a press conference on 22 January 1988 the observation of the onset of superconductivity in Bi–Sr–Ca–Cu–O at 120 K with zero resistance occurring at 75 K.[4] Within days those results were confirmed at a number of laboratories. It has been established[5] that two different phases of the material prevail even in the single crystals of this system, with zero resistance observed between 70 K and 108 K. Whether the two phases can be separated, or how subtle the differences are between the two, are subjects of intense research.[6] Analogous to the atomic structure of rare-earth-based (1–2–3) superconducting oxides, the bismuth-based materials contain sheets of copper and oxygen, but in contrast to the former, they do not contain copper–oxygen chains.[5] The chemical sensitivity of the (1–2–3) materials was partially related to the facility with which oxygen moved in and out of the chains, making the materials unstable when exposed to air and water. The absence of chains in bismuth-based materials has indeed enhanced their chemical stability. Combined with their improved ductility, as compared with (1–2–3) oxides, they may prove to be the better candidates for superconducting applications.

That the rise of T_c (Fig. 1) is not yet over was clearly demonstrated once again when, in February 1988, A. Hermann of the University of Arkansas announced the discovery of a new compound, Tl–Ca–Ba–Cu–O, with zero resistance at 107 K and the onset of a broad transition at 125 K.[7] Reports of zero resistance at the later temperature have since appeared.[8] How detrimental the toxicity of thallium would prove to be in extensive research and, particularly, in limiting the uses of those materials, remains to be established. The bismuth- and thallium-based superconducting oxides were the subject of yet another long special evening session (dubbed "Woodstock II") at the annual Solid-State Meeting of the American Physical Society held in New Orleans on 21–25 March 1988.

Until now, the success in synthesizing materials with ever-increasing values of T_c has come exclusively from empirical approaches. Fundamental theoretical understanding of the underlying mechanism for superconductivity in these materials remains elusive and is one of the most exciting unsolved problems in the field. At the moment, it seems that even higher T_c's can be achieved by finding materials with an increasing number of Cu–O sheets in their unit cells.

The high value of T_c is not, however, the only desirable attribute of a superconductor. It is a crucial factor if one expects to use coolants that are cheaper and more easily managed than liquid helium or to entertain the possibility of entirely doing away with cooling systems.

In spite of the importance of higher values of T_c, the full potential of high-temperature superconducting ceramics cannot be realized unless they can be formed in appropriate shapes—thin films and wires—for small- and large-scale applications, respectively (Table 1). The fabrication of brittle ceramics into flexible wires that can form the basis of durable electrical and magnetic machinery and the deposition of thin films in patterned configurations on technologically useful substrates are only two of the challenges facing researchers interested in harnessing those fascinating new materials. The increasing understanding of the materials, methods that enhance stability at lower processing temperatures, rigorous chemical and mechanical testing of special structures, and the ability of such structures to carry high critical currents at temperatures around 0.7 T_c are all important factors whose successful resolution will determine the suitability of ceramic superconductors in technological applications (see the boxed insert). Although progress has been rapid, a long-term commitment will be essential to retain the momentum, to overcome many scientific problems, and to refine the many new processing techniques that have evolved in response to new materials.

The research on high-temperature superconductors at APL began in March 1987, after a conversation between

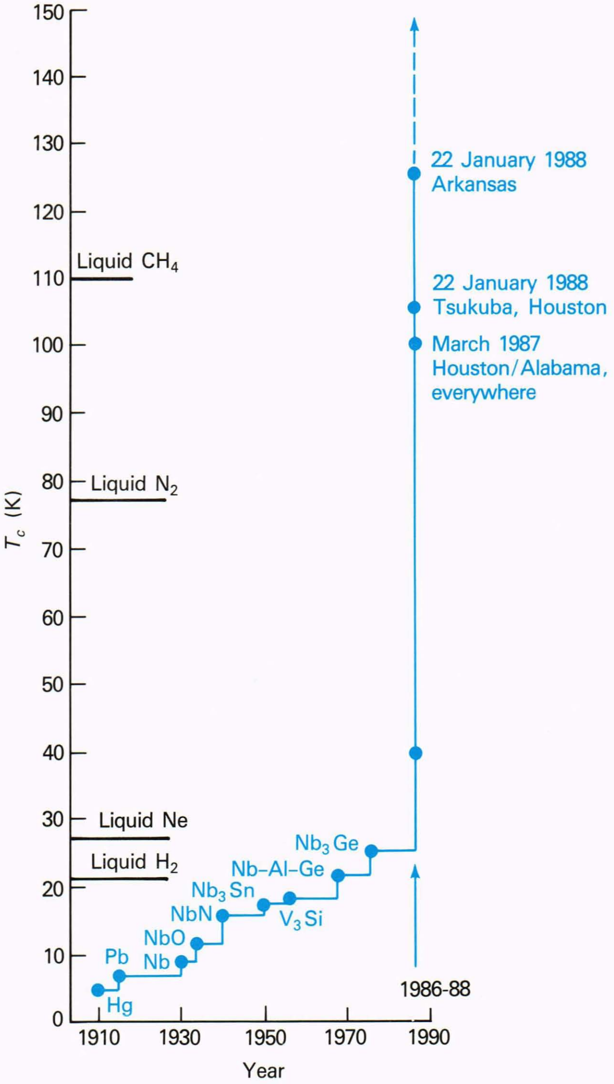
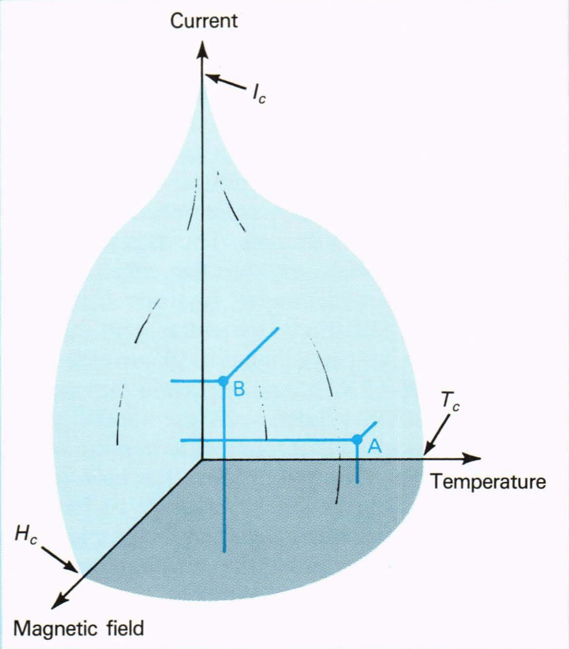


Figure 1—Evolution of superconducting materials with higher transition temperatures.

Table 1—Fields of application and characteristics demanded of high T_c superconductors.

Characteristics	*Energy*	*Traffic/ Transportation*	*Information/ Communication*	*Ocean/ Space*	*Advanced Processing*	*Medical*	*Research and Development*
High current	•	•	•	•	•	•	•
High magnetic fields	•	•			•	•	•
Connection	•	•		•	•	•	•
Strength	•	•		•	•	•	•
Long unit length	•	•		•	•	•	•
Plastic deformation	•	•		•	•	•	•
Thin-film deposition			•	•	•	•	•
High integration			•				
Insulation film			•				
Flexibility	•	•		•	•	•	•
Resistance to strain	•	•		•	•	•	•
Resistance to radiation	•		•	•			•

The superconducting state of a particular material can be described parametrically as falling within the envelope defined by three parameters: temperature, current, and magnetic field. If any one of these parameters exceeds a critical value (T_c, I_c, and H_c, respectively), the superconducting state will be destroyed. This fact is illustrated by the figure shown below. A small-scale superconducting device could operate near T_c (point A) because it requires small currents and magnetic fields. A large-scale superconducting device, however, requires large currents and fields and must therefore operate at temperatures well below T_c (point B).



K. Moorjani of APL and L. Bennett of the National Bureau of Standards regarding the possibilities of forming nanometer composites from the new materials. The National Bureau of Standards provided bulk samples, and efforts were soon afoot to form thin films, using our experience with sputtering techniques and the excimer laser (newly acquired in the microphysics program) that had already been used to form microstructures. That work had led to the concept of a novel technique for laser deposition[9] that seemed well suited to deposit superconducting ceramic films. Before describing that technique, let us say a few words about processing with photon beams.

LASER PROCESSING OF MATERIALS

One of the aims of the microphysics program when it started in 1984 was to investigate the use of intense photon beams for materials processing. The directionality and the highly collimated nature of laser beams offer a number of advantages, including the important consequence that large amounts of energy can be conveniently manipulated to almost any location. Those factors have been fully exploited in the traditional industrial application of lasers. Another point of interest in the area of advanced technologies is the fact that a laser beam can be focused to dimensions whose lower limit is essentially as small as the wavelength employed. Thus, extremely high photon fluxes can be constricted to small volumes to carry out a variety of processes of interest in microelectronics and integrated devices. Such tools are expected to provide a unique single-step method in patterning materials via localized deposition, doping, etching, and growth. Besides their obvious importance in processing techniques, photon beams allow for fundamental studies at micron and submicron dimensional levels, which can eventually be extended to even smaller dimensions when coherent sources of photons at shorter wavelengths become available.

Three new photon beam-processing techniques have been developed at APL. Of particular interest to the fabrication of superconducting thin films is the method termed laser ablation processing.[10] In that method (Fig. 2), a pulsed beam from an excimer laser is focused onto a pressed pellet of the superconducting oxide that is mounted in a vacuum cell, and the ablated material is collected on a substrate. The excimer laser operates at 193 nm, in the ultraviolet region of the spectrum, with a pulse frequency of 10 Hz and with an energy of approximately 150 mJ per pulse. During the deposition, the sample is translated stepwise so that the beam focal spot of approximately 0.5 mm^2 resides at any single location on the target material for 1 min.

The laser ablation processing technique has been used to deposit thin films of La–Sr–Cu–O, Y–Ba–Cu–O,[10] and Bi–Sr–Ca–Cu–O[11] on a variety of substrates that include fused quartz, crystalline silicon, sapphire, and oriented crystals of strontium titanate and zirconium oxide. The quality of the film depends on the substrate as well as the deposition parameters, such as the substrate temperature T_s during deposition, and the post-deposition annealing temperature T_a. We shall discuss those features below. It has become clear that the laser ablation processing technique offers several advantages over conventional evaporation and sputtering methods. The proper stoichiometry for superconducting films is easily obtained from a single target, the method is clean and cheap, and it can be upscaled and automated with relative ease.

CHARACTERIZATION

The bulk samples of superconducting oxides used as targets in the laser-ablation-processing cell, as well as the thin films obtained from them, have been characterized by structural, electrical, and magnetic measurements.[10-13] Additionally, a new technique of magnetically modulated microwave absorption (MAMMA) has been developed at APL[10,14] to investigate superconducting transitions and properties. This highly sensitive tool, described below, has been used extensively to study a variety of phenomena related to superconductivity.[15]

MAMMA (MAGNETICALLY MODULATED MICROWAVE ABSORPTION) METHOD

The most dramatic signature of superconducting behavior is seen in the variation of the DC resistance of a superconducting material with temperature. As the superconducting transition temperature T_c is approached, the DC resistance falls abruptly and the material exhibits zero resistance below T_c (Fig. 3). This simple measurement is limited to studying superconductivity in electrically continuous samples. Furthermore, it is only indicative (but not definitive) of superconductivity, because metal–insulator transitions, which are common in metal oxides, can give false positives. Alternatively, one can study superconducting transitions at high (microwave) frequencies using well-established methods. Although a superconducting transition, as seen in the DC-resistance measurement, becomes less abrupt with increasing frequency, the microwave method has a number of advantages, since it probes the entire sample (at least within the penetration depth) and provides a tool for investigating superconductivity even in discontinuous samples that cannot be studied by conventional resistance measurements.

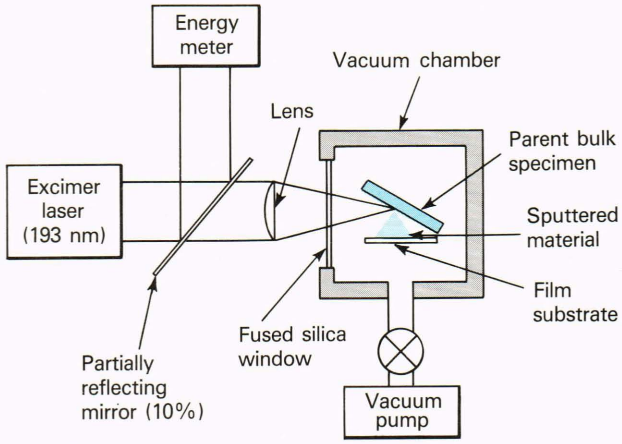


Figure 2—Schematic diagram of apparatus for thin-film deposition by laser ablation of bulk material. (Reproduced by permission, Mater. Res. Soc.)

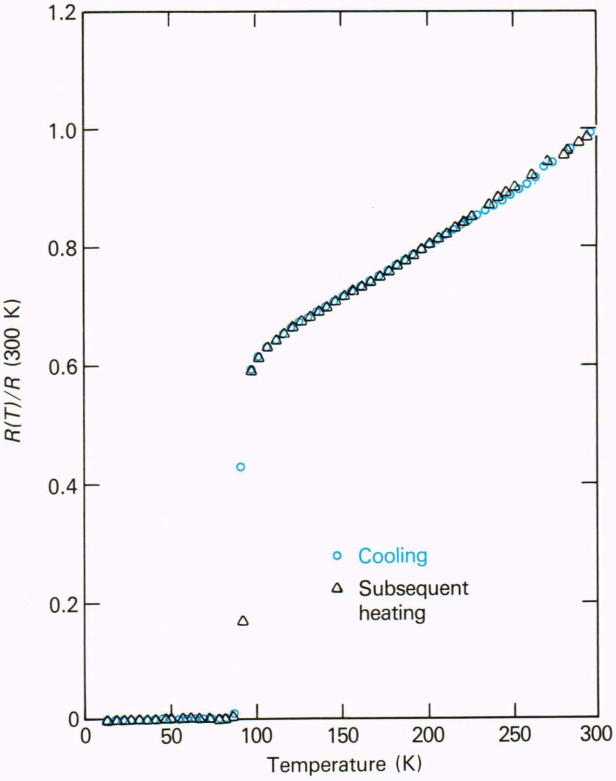


Figure 3—Resistance versus temperature and the superconducting transition in $YBa_2Cu_3O_{7-\delta}$.

The measurement of microwave absorption generally involves monitoring the quality factor Q of a microwave resonator. The reflected power from a microwave resonant cavity in a bridge is recorded and its variations provide a measure of corresponding changes in the *Q* of the cavity, which are affected by absorption of energy by the sample via the cavity fields. Thus, the reflected power as a function of the sample temperature indicates changes, superconducting and otherwise, in the sample's DC resistance.

The MAMMA technique refines and differs from conventional microwave techniques in that it is specific for detecting superconducting transitions because only magnetic-field-induced changes in the sample's microwave loss as a function of temperature are observed. This is accomplished by applying a small AC magnetic field to the sample and phase-detecting the microwave power reflected from the cavity at the AC-field modulation frequency. Besides having the usual desirable features of microwave methods, it has a number of other advantages. One is high sensitivity, stemming from noise reduction by narrowband amplification and phase-sensitive detection, so that superconductivity can be easily detected in small samples weighing as little as 0.1 mg. Second, and most important, only those changes in sample resistance and microwave loss that are magnetic-field-dependent will be observed. This last condition is characteristic of a superconducting transition, and it eliminates spurious responses from other sources of temperature-dependent changes in sample resistivity. Finally, the superconducting transition in the MAMMA method is recorded as a derivative peak, allowing a well-defined critical temperature measurement and permitting easy resolution of multiple superconducting phases. Those advantages make it easy to investigate important parameters of superconductors such as critical fields, anisotropic effects, granularity, and London penetration depth.

A further advantage of the MAMMA technique is that it is closely related to that of electron spin resonance and thus can be carried out on readily available instruments such as the homodyne-type, X-band (9.1 GHz) electron-spin-resonance spectrometer. That is because MAMMA is based on observing that part of the change in the resistive microwave loss that is produced by application of a small AC magnetic field (0.5 mT (5 G) or less), whereas electron spin resonance observes analogous changes in magnetic microwave loss in a paramagnetic sample. Both observations are readily made by the electron-spin-resonance spectrometer's standard operating mode, which phase-detects the microwave power reflected from the cavity at the AC-field modulation frequency. The AC field is superimposed on a DC magnetic field—which can be varied over a wide range, thus permitting observations of DC magnetic field effects—but is always large enough so that the combined AC plus DC field never changes sign, since that would complicate the phase-detection process. The response (Fig. 4) is proportional to the product of the temperature derivative of the resistance $\partial\rho/\partial T$ and the field derivative of the critical temperature $\partial T_c/\partial H$. The latter factor assures that only the field-dependent transitions (which superconducting transitions are) are observed while the factor $\partial\rho/\partial T$ results in a peak signal. This is illustrated in Fig. 5 for niobium, a conventional superconductor, which indeed exhibits a peak at $T_c = 9.3$ K. Figure 6 shows the conventional microwave absorption in V_2O_3, with an abrupt fall at approximately 155 K because of its well-known insulator– metal transition and a lack of magnetic-field-modulated microwave absorption (since that transition is not magnetic-field-dependent). Thus, the method provides an exquisite tool for differentiating between superconducting and nonsuperconducting transitions. In addition, the technique provides more subtle characterization of superconductors by allowing a measure of their granularity, which will be discussed in a later section. The MAMMA response of superconducting oxides is described in the following section.

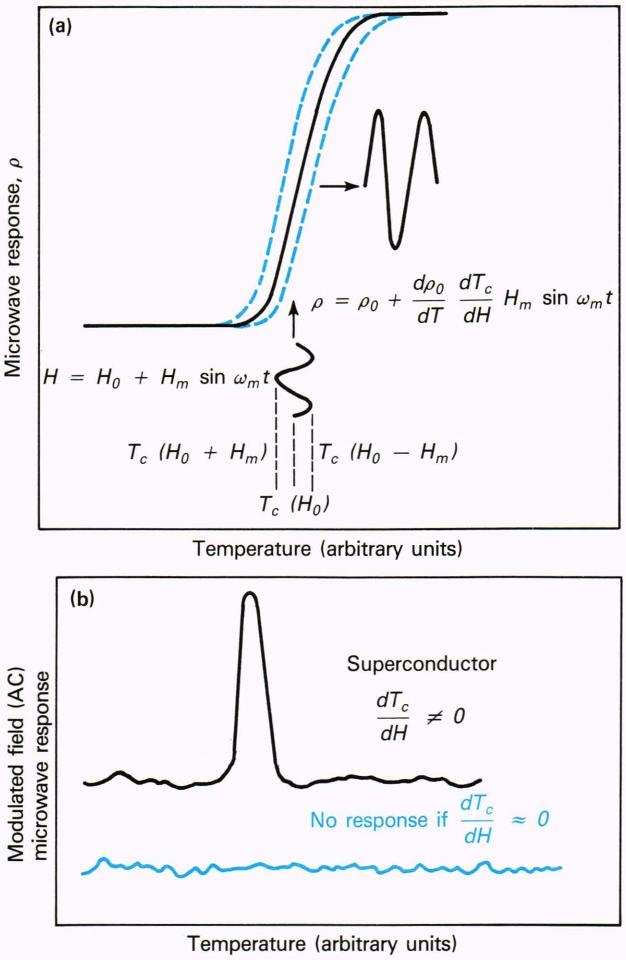


Figure 4—Schematic description of MAMMA (a) in a superconductor $dT_c/dH \neq 0$, and (b) for a metal-insulator transition $dT_c/dH \approx 0$.

BULK SUPERCONDUCTING OXIDES

The temperature dependence of DC resistance for a bulk sample of $YBa_2Cu_3O_7$ was shown in Fig. 3. A sharp transition at $T_c = 94$ K is observed that has been confirmed in other measurements, such as the Meissner effect and MAMMA response, as shown later (Fig. 8a) for that material. An example of the latter measurement

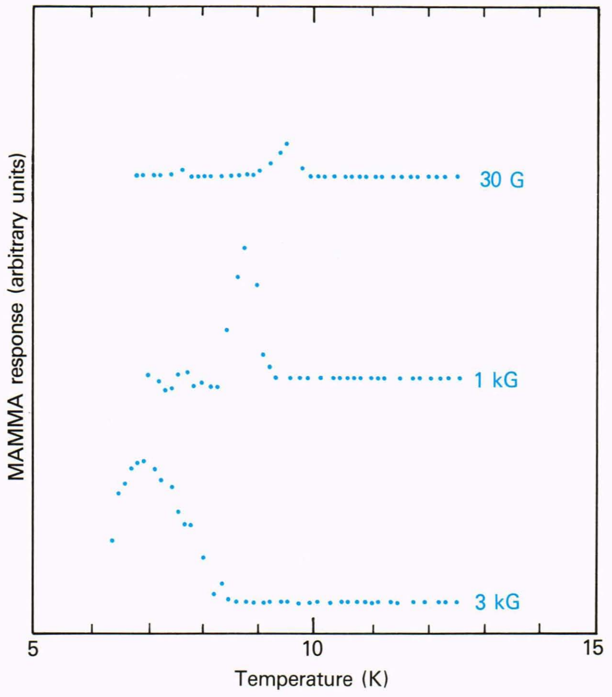


Figure 5—Temperature dependence of MAMMA in niobium at different values of the static magnetic field. (Reproduced by permission, Mater. Res. Soc.)

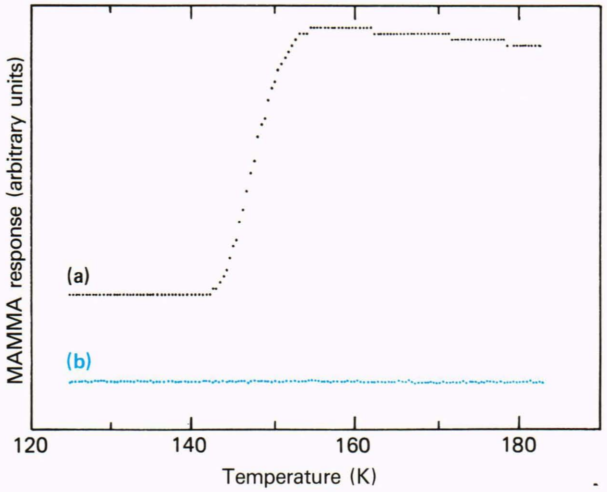


Figure 6—Microwave absorption in V_2O_3 versus temperature: (a) conventional microwave absorption, and (b) magnetically modulated microwave absorption. (Reproduced by permission, Mater. Res. Soc.)

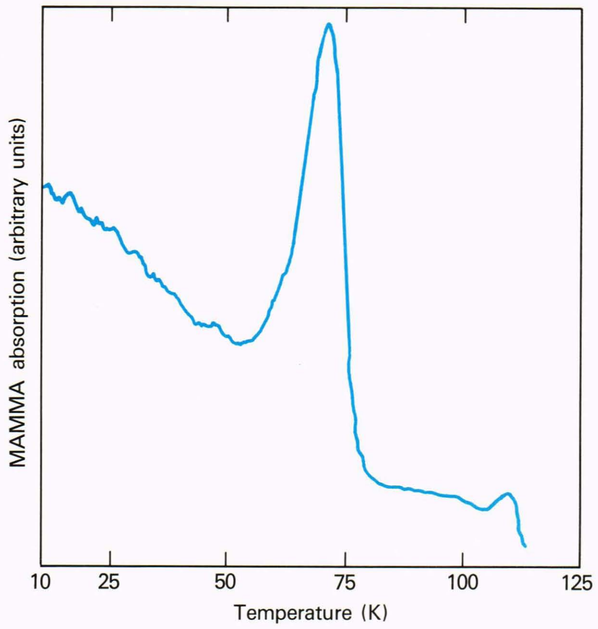


Figure 7—MAMMA of $BiSrCaCu_2O_x$ as a function of temperature.

on a bulk sample of nominal composition $BiSrCaCu_2O_x$ is shown in Fig. 7. A number of superconducting phases are revealed.[16] The one with the highest T_c lies at 110 K, followed by a broad peak centered at approximately 100 K, and finally a prominent peak at 72 K. The figure vividly illustrates the ability of the MAMMA technique to separate superconducting transitions in a multiphase material. The method also allows quantitative estimates of the fraction of the superconducting phases associated with each value of T_c. Approximately 95% of the sample has $T_c = 72$ K, while the rest is associated with superconducting phases at higher values of T_c. Those samples, further characterized by other techniques,[10-13] were used as targets in the laser-ablation-processing cell to obtain thin films whose properties are discussed in the next section.

SUPERCONDUCTING THIN FILMS

Figure 8 shows the MAMMA response for a thin film deposited from bulk $YBa_2Cu_3O_7$ by the laser-ablation-processing technique. The film was deposited on an unheated fused-quartz substrate and no post-deposition annealing was done. The resulting film was not electrically continuous, but contained superconducting regions, as clearly demonstrated in Fig. 8b. While the parent bulk material (see Fig. 8a) exhibits a broad response with a peak located at 94 K, the film shows three sharp peaks located at 93, 90, and 86 K. The broad response of the bulk sample is thought to result from slight variations in composition or structure that cannot be revealed in resistivity measurements. The sharp responses in the thin film, given the processing conditions, suggest that part of the material is being ablated off the target, with its structure and composition essentially intact, and these parts then act as seeds for the growth of proper superconducting structures.

To investigate the dependence of atomic structure on the substrate, films were deposited on a (100)-oriented single-crystal strontium–titanate substrate that has lattice constants closely matched to the planar lattice constants of $YBa_2Cu_3O_7$. Indeed, structurally superior films are obtained on heated substrates (heated to approximately 300°C) and after post-deposition annealing

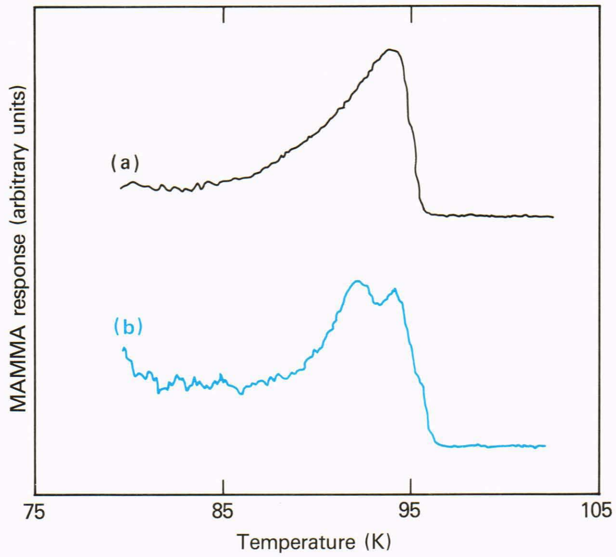


Figure 8—MAMMA versus temperature for $YBa_2Cu_3O_{7-\delta}$: (a) bulk sample with one superconducting phase, and (b) superconducting thin-film sample deposited on unheated fused-silica substrate, without post-deposition annealing. (Reproduced by permission, Mater. Res. Soc.)

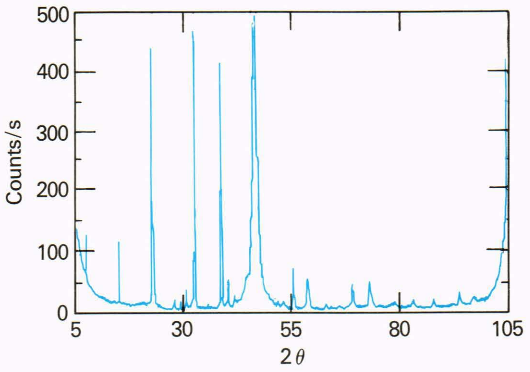


Figure 9—X-ray diffraction pattern of a $YBa_2Cu_3O_7$ thin-film sample deposited on a strontium-titanate substrate at 300°C and annealed at 950°C after deposition.

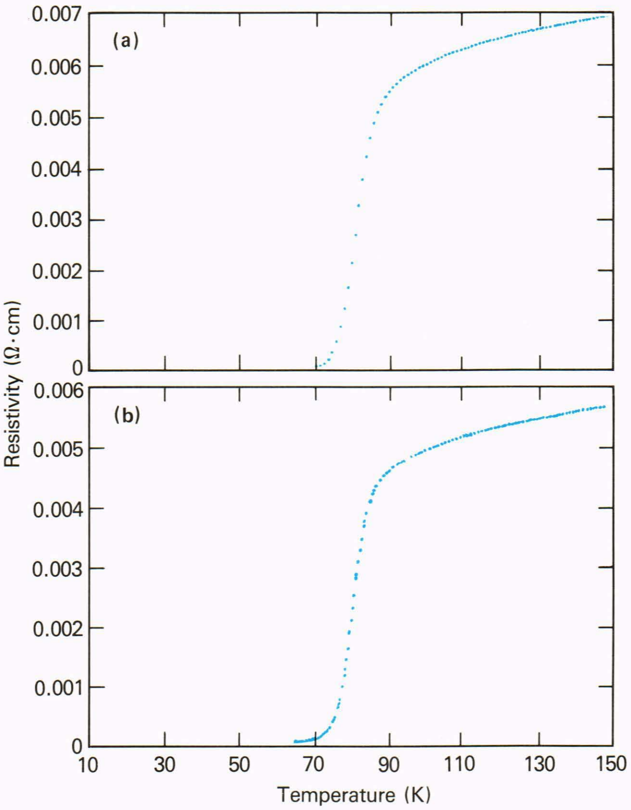


Figure 10—Resistance versus temperature of $BiSrCaCu_2O_x$ films deposited on a (100)-oriented zirconia substrate and annealed for 10 min at 950°C after deposition: (a) unheated substrate, and (b) substrate heated to 300°C. (From B. F. Kim, J. Bohandy, T. E. Phillips, W. J. Green, E. Agostinelli, F. J. Adrian, and K. Moorjani, "Superconducting Thin Films of Bi-Sr-Ca-Cu-O Obtained by Laser Ablation Processing," *Appl. Phys. Lett.* **53**, 321 (1988). Reproduced by permission, Am. Inst. Phys.)

at high (approximately 950°C) temperatures. That is clearly seen by the X-ray diffraction pattern of one of the films (Fig. 9), where many lines can be identified as arising from the orthorhombically distorted perovskite structure of the $YBa_2Cu_3O_7$ material.[17] The pattern shows that they are excellent crystalline films. Similar results have been obtained for $BiSrCaCu_2O_x$ thin films deposited on oriented-zirconia substrates, and for both materials excellent compositional homogeneity is observed in thin films.[17]

The processing conditions for bismuth-based superconducting oxides do not seem to be as stringent as for the rare-earth-based materials. Figure 10 illustrates the temperature-dependence of resistivity for two films of $BiSrCaCu_2O_x$ obtained on (100)-oriented zirconia substrates.[11] One of the films was deposited on an unheated substrate, while the other was deposited on a substrate heated to 300°C during deposition. Both films were subsequently annealed at 850°C for 10 min. As seen in Fig. 10, the two films have essentially the same value of resistivity above the transition, exhibit deviations from linear resistivity at approximately 110 K, and show zero resistance at 69 K. However, the MAMMA responses for the two films (Fig. 11) are remarkably different. The film deposited on an unheated substrate shows a much broader peak and a lower average value of T_c, suggesting a larger variation in composition or structure. This example vividly illustrates the utility of the MAMMA technique, which globally probes the sample, in contrast to the DC resistance, which is determined by the minimum-resistance percolation path in an inhomogeneous sample.

MAGNETIC FIELD EFFECTS

The superconducting transition temperature decreases with the increase in the magnitude of an externally applied magnetic field (see the boxed insert) until, at the upper critical field H_{c2}, the material loses its superconductivity and reverts back to the normal state. One should therefore see field-dependent changes of the peak position in the MAMMA method and from the magni-

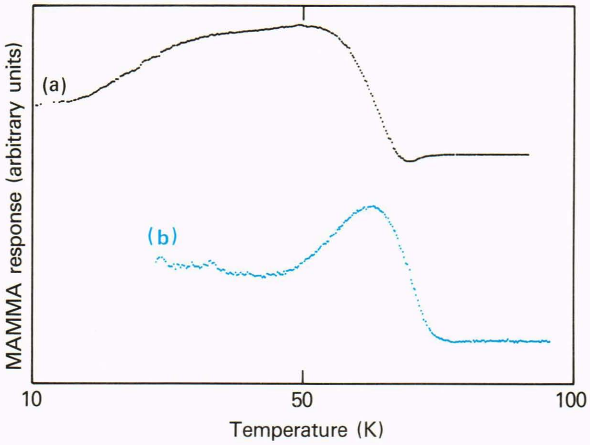


Figure 11—MAMMA of $BiSrCaCu_2O_x$ films deposited on a (100)-oriented zirconia substrate and annealed for 10 min at 950°C after deposition: (a) unheated substrate, and (b) substrate heated to 300°C. (From B. F. Kim, J. Bohandy, T. E. Phillips, W. J. Green, E. Agostinelli, F. J. Adrian, and K. Moorjani, "Superconducting Thin Films of Bi-Sr-Ca-Cu-O Obtained by Laser Ablation Processing," *Appl. Phys. Lett.* **53**, 321 (1988). Reproduced by permission, Am. Inst. Phys.)

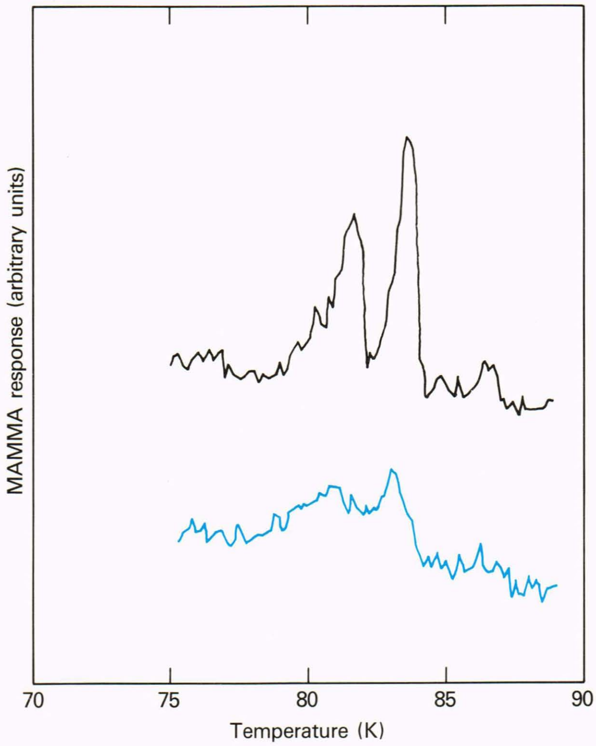


Figure 12—MAMMA versus temperature for a thin film of $YBa_2Cu_3O_7$ in different DC magnetic fields.

tude of the shift be able to estimate the value of H_{c2}. That is seen for niobium (Fig. 5), where, from the field-induced shifts in T_c, one obtains the known value (approximately 0.55 T) of H_{c2}. We have performed similar experiments on superconducting oxides that exhibit enormous values of H_{c2}. Results on a thin film of $YBa_2Cu_3O_7$ (Fig. 12) show the shift in T_c to be 1.2 K/T, indicating values of H_{c2} upward of 100 T.[18]

SAMPLE ORIENTATION EFFECTS

Since the superconducting oxides are structurally highly anisotropic, their magnetic properties would also be expected to be anisotropic. Thus, changing the orientation of the magnetic fields as well as the microwave electric field is of interest in samples that may contain oriented superconducting regions. Indeed, the position of the peaks for thin films varies with sample orientation (Fig. 13), showing that the superconducting regions in thin films are structurally oriented. However, to determine precisely the texture in thin films, one needs to calibrate the measurements by performing similar experiments on single crystals. Preliminary results on very small single crystals show that this can be achieved. One also needs to understand fully the orientation dependence by taking into account the effect associated with the orientation of various superconducting regions in the film with respect to the electric component of the microwave field.

RADIATION EFFECTS

If the new superconducting ceramics are ever to find uses in microelectronic circuitry, especially for applications in satellites and other systems operating in outer space, they will have to exhibit radiation hardness, particularly to ionizing radiation such as γ and X rays, since those will pass through protective shielding more readily than the particulate radiation. Therefore, the effects

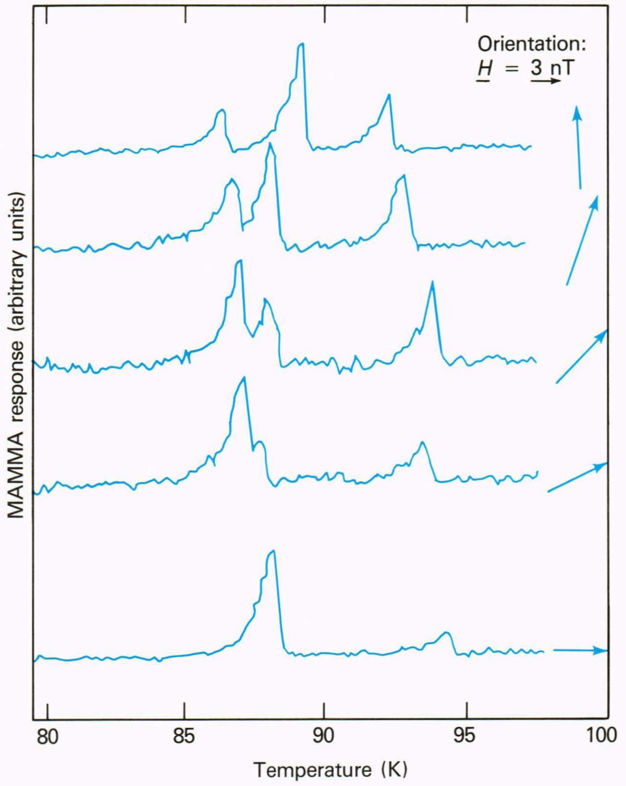


Figure 13—Orientation-dependence of MAMMA in a $YBa_2Cu_3O_{7-\delta}$ thin-film sample.

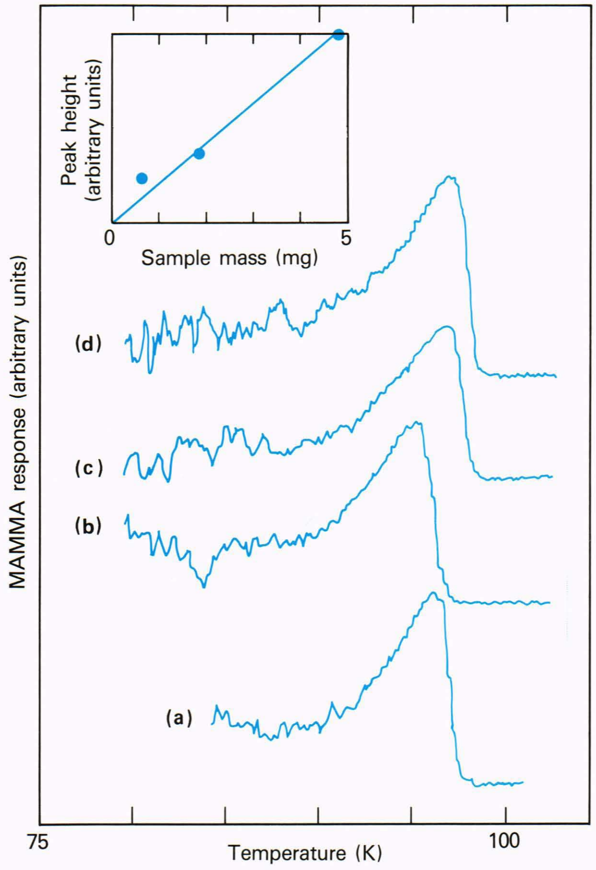


Figure 14—MAMMA versus temperature for a 1.7 mg $YBa_2Cu_3O_{7-\delta}$ sample as a function of ^{60}CO γ-irradiation dose: (a) not irradiated, (b) 2-krad irradiation, (c) 22-krad irradiation, and (d) 1.3-Mrad irradiation. Insert shows the peak height of the microwave response at T_c versus mass of a powdered $YBa_2Cu_3O_{7-\delta}$ sample. (From J. Bohandy, J. Suter, B. F. Kim, K. Moorjani, and F. J. Adrian, "Gamma Radiation Resistance of the High T_c Superconductor $YBa_2Cu_3O_{7-\delta}$," *Appl. Phys. Lett.* **51**, 2161 (1987). Reproduced by permission, Am. Inst. Phys.)

of γ-radiation on bulk samples of $YBa_2Cu_3O_7$ were investigated.[19] As seen in Fig. 14, the MAMMA response of samples exposed to ^{60}Co γ-irradiation up to a 1.3 Mrad dose shows no detrimental effects on the superconducting behavior. Those are very encouraging results and experiments are planned to obtain data on thin films of $YBa_2Cu_3O_7$ and $BiSrCaCu_2O_x$.

EFFECTS OF INTRINSIC JOSEPHSON JUNCTIONS

Many superconductors, particularly the new high-temperature superconducting ceramics, exhibit granularity in the sense that at temperatures below T_c, the material contains many small regions that are in the superconducting state, separated by regions in the normal conducting state. If a normal region separating two superconducting regions is sufficiently small, superconducting currents can tunnel through the normal region, giving rise to a Josephson junction (see the boxed insert). Clusters of interacting Josephson junctions, in the presence of a magnetic field, comprise a system similar to that of a spin glass, which has been termed the superconducting glassy state.[20,21] The superconducting glassy state is not detected by DC-resistance or magnetic-susceptibility measurements, but is readily detected by the MAMMA technique.[22] The superconducting glassy state is inferred in MAMMA measurements by noise caused by Josephson junction tunneling currents and a broad baseline shift caused by low-field nonresonant peaks attributed to intrinsic Josephson junctions.[20,23–26]

A Josephson junction is a region between two pieces of superconductor where the superconducting state is weakened. This can be achieved by establishing a thin tunneling barrier or narrow connection (or contact) between the two superconductors. When the current (I) through the junction is increased from zero, Cooper pairs (paired electrons) tunnel quantum-mechanically through the barrier or connection, which establishes a phase difference ($\Delta\phi$) between the phases of the superconducting state on each side. The resulting current is given by $I = I_c \sin \Delta\phi$, where I_c is the critical current. This is the so-called DC Josephson effect. When the current through the junction exceeds I_c, the phase difference evolves in time according to the relation $d\Delta\phi/dt = 2eV/\hbar$, where e is the electron charge, V is the voltage across the junction, and $2\pi\hbar = h$ is Planck's constant. This latter equation expresses the essence of the AC Josephson effect and can be used to show that the Josephson junction is a voltage-controlled oscillator. The varied applications of Josephson junctions stem from the basic DC and AC Josephson effects just described, as well as from suitable electronic circuits in which Josephson junctions reside. Josephson junctions can be used as sensitive detectors of millimeter waves and low-frequency magnetic fields, as well as oscillators, parametric amplifiers, and digital logic switches (to name only a few).

In recent experiments, Josephson junction effects in $YBa_2Cu_3O_{7-y}$ were studied as a function of sample particle size.[22] A sequence of powder samples was prepared by crushing bulk (1–2–3) material and subsequently separating the powder into sample groups of various particle sizes ranging from 10 to 425 μm. Figure 15 shows the MAMMA response for a bulk sample and the powder samples of various particle sizes in an external magnetic field of 0.1 T. The noise below T_c decreases with decreasing particle size. This is expected because the average number of Josephson junctions in a cluster must decrease owing to increased homogeneity of smaller particles. The baseline does not shift appreciably in these figures because the 0.1-T magnetic field is far removed from the region of the low field peak (approximately 3 mT) referred to previously. Figure 16, which shows the MAMMA response for powder samples of the three different particle sizes in an external magnetic field of 3 mT, illustrates the effect of the low field peak. The shift in the baseline at temperatures below T_c decreases with decreasing particle size because fewer Josephson junctions are contained in the smaller particles.

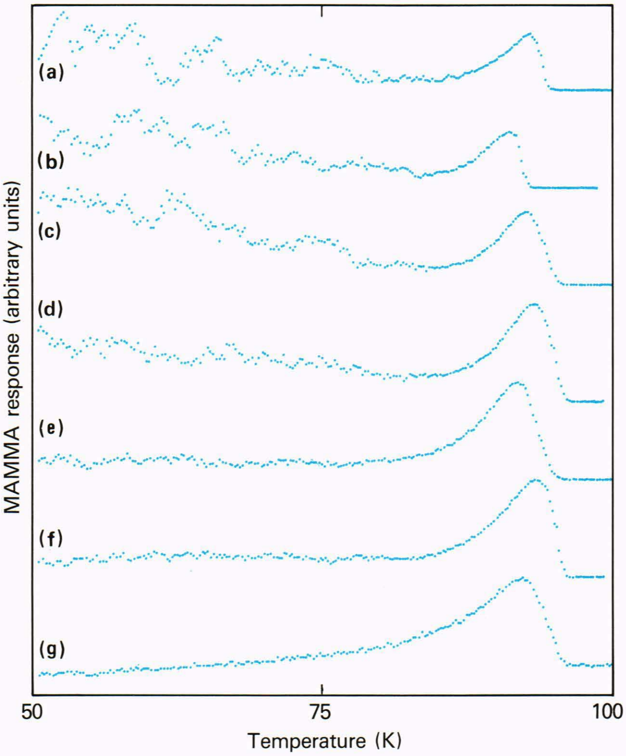


Figure 15—Particle-size dependence of MAMMA in $YBa_2Cu_3O_7$ in a 0.1-T DC magnetic field: (a) bulk sample, (b) 330 to 425 μm, (c) 90 to 125 μm, (d) less than 63 μm, (e) less than 38 μm, (f) less than 30 μm, and (g) less than 10 μm.

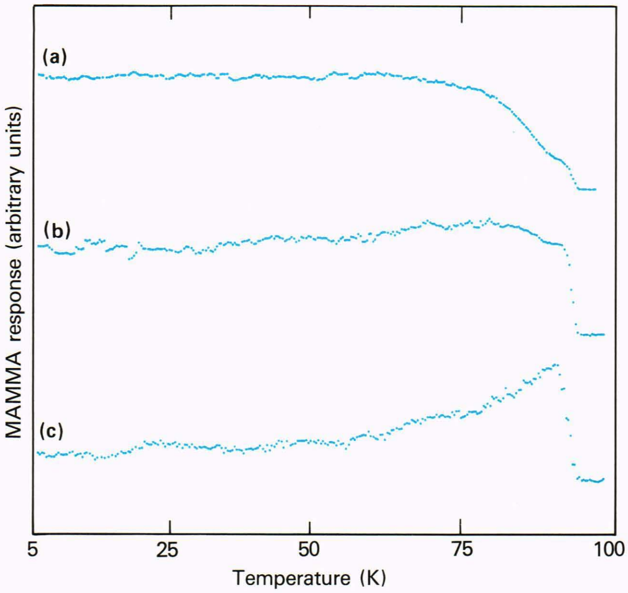
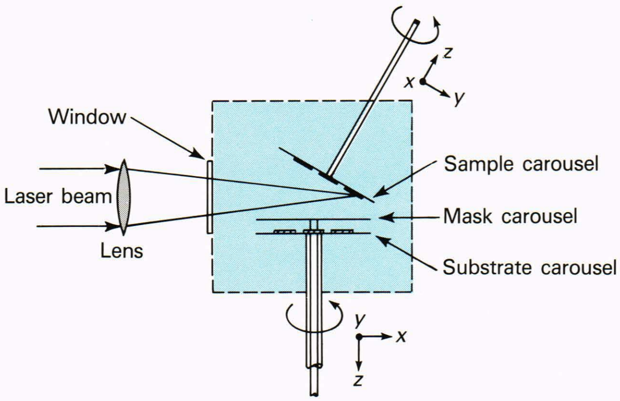


Figure 16—Particle-size dependence of MAMMA in $YBa_2Cu_3O_7$ in a low (3 mT) DC magnetic field: (a) less than 63 μm, (b) less than 38 μm, and (c) less than 10 μm.

From these results, the characteristic size of a Josephson junction cluster in bulk $YBa_2Cu_3O_7$ is estimated to be 400 μm (comparing Figs. 15a and 15b), and an estimate for the magnetic-field penetration depth into those superconductors, which determines the distance across a single Josephson junction, is 0.1 μm. The latter estimate is based on the value of an elementary flux quantum (2×10^{-15} T$\cdot$m^2) and the value for the Josephson junction critical field (approximately 1 mT), and the fact that the Josephson junction effects disappear for particle sizes of approximately 10 μm (Fig. 15g), which dimension multiplied by the field penetration depth determines the area of the junction. This estimate agrees with other values for the size of intrinsic Josephson junctions in $YBa_2Cu_3O_7$ that are based on other experimental methods.[27-29]



Notes: *x, y* motion is identical for mask and substrate carousels
z-axis motions for mask and substrate carousels are independent
Window is approximately 5 cm from laser focus

Figure 17—Schematic diagram of an improved cell for laser-assisted deposition and processing of materials.

APPLICATIONS IN MICROELECTRONICS

An unprecedented opportunity now exists to exploit high-temperature superconducting thin films in electronics. They offer the potential of a technological revolution analogous to that offered by transistors in the late 1940s. The application of those new materials in thin-film electronic devices is a major focus of the work at APL. To increase the throughput of available superconducting films, a sophisticated laser-ablation-processing cell has been designed that allows for upscaling and automatic operation. The cell consists of two independently manipulated carousels (Fig. 17) with each holding up to six targets, substrates, or masks. This will allow formation of films on various substrates with preplanned configurations, including the possibility of depositing buffer or passivation layers. The cell also incorporates facilities for heating the substrates up to 1000°C and carrying out *in situ* annealing in the absence or presence of various gases. The upscaled laser-ablation-processing cell is nearly complete and should be in place soon.

To develop a general impression of the potential applications, some examples will be described briefly. Very-high-speed integrated circuits could be built using superconducting interconnects. With proper care during fabrication, they should exhibit less heat dissipation and loss.

For instance, conventional (low-temperature) superconducting (Josephson-junction) switches can operate with approximately 10^{-17} J dissipation per gate versus approximately the 10^{-14} J per gate that is characteristic of gallium–arsenide semiconductor technology. That will lead to smaller circuit dimensions, greater packing density, and smaller overall chip size. Superconducting lines can be as close as approximately 1 μm without incurring signal crosstalk, whereas metallic lines on semiconducting substrates must be approximately 400 μm apart. Hence, signal delay and clock skew during operation should be reduced. High-frequency, low-loss microwave and millimeter-wave integrated circuits should be possible, with better performance than that of similar devices using normal metals (such as copper or gold) by several orders of magnitude. Radiation-hardened detectors of electromagnetic waves with very broadband response could be achieved with the new ceramic superconductors. Even the "Holy Grail" of superconducting electronics—Josephson junctions—may eventually be realized in a practical form by clever fabrication techniques using high-temperature superconductors. Then it will be possible to exploit the higher gap frequency of those materials in high-frequency quantum detectors. Ultimately, supersensitive magnetic-sensing components, including superconducting quantum interference devices (SQUIDs), as well as their coupling coils may be devised.

Many of the applications cited above are of interest to investigators at APL. Plans call for the development of applications in radiation detectors and microwave integrated circuits. A crucial step in these endeavors is to devise patterning techniques that achieve the desired thin-film geometries. Following successful patterning tests, various configurations can be implemented and tested for ruggedness and performance. Examples of some configurations are shown in Fig. 18.

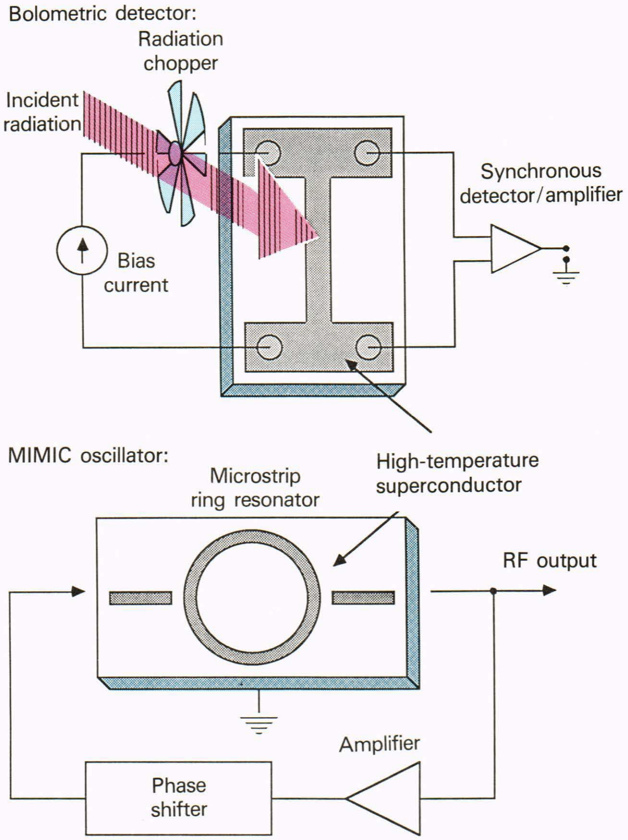


Figure 18—Examples of passive superconducting circuits and how they can be used in specific applications (radiation detection and microwave sources).

The simplest of these structures is a microbridge, which can be used initially as a bolometric detector element. In such a device, one takes advantage of the voltage induced in a detection circuit when a small portion of the bridge goes "normal" because incident radiation impinges on it.[30] This device takes advantage of the resistive transition of the superconductor that occurs at T_c (Fig. 3) of the superconductor. With such a device it may be possible to perform functions such as surveillance, acquisition, and tracking in an exoatmospheric environment. The utility of bolometers for such applications depends on an optimum tradeoff between sensitivity and response time, as expressed by the equation

$$NEP \cdot t^{1/2} = \text{constant} ,$$

where *NEP* is the noise equivalent power (the incident power required to achieve a signal-to-noise ratio of unity at the output in a specified bandwidth), and *t* is the response time of the detector. The smaller the value of *NEP* (that is, more sensitivity), the larger *t* must be (slower response). Low-temperature superconducting bolometers have been built with *NEP*s ranging from 10^{-15} to 10^{-8} W/Hz$^{1/2}$, with corresponding response times of 5×10^{-2} to 1×10^{-8} s. Recently, investigators at the Naval Research Laboratory[30] built a simple bolometer using a granular YBaCuO film and achieved an *NEP* of 10^{-6} W/Hz$^{1/2}$ and response time of 5×10^{-9} s. For laboratory and industrial settings, bolometers may be useful for infrared spectrometry and nondestructive testing, where radiation sources provide a good signal-to-noise ratio, and where simultaneous fast response is not crucial.

To overcome this tradeoff in bolometric (thermal) detectors, one must devise means of building quantum-limited detectors. This implies the use of Josephson junctions that operate on the basis of radiation-induced supercurrent states at finite voltage. The limiting factors to successfully making a Josephson junction are material and fabrication tolerances. Because the coherence length is so small in these new superconductors (approximately 2 nm at 0 K along the "benign" crystallographic axis), the hope of obtaining weak coupling by conventional means is slim. Novel means must be invented to achieve microscopic control of film-pattern dimensions, lattice stochiometry, or impurity profiles. One possibility that has been tried on conventional superconductors[31] and with the new superconductors for superconducting quantum interference devices[32] is ion implantation (Fig. 19). If ion-density profiles can be tailored accurately, there

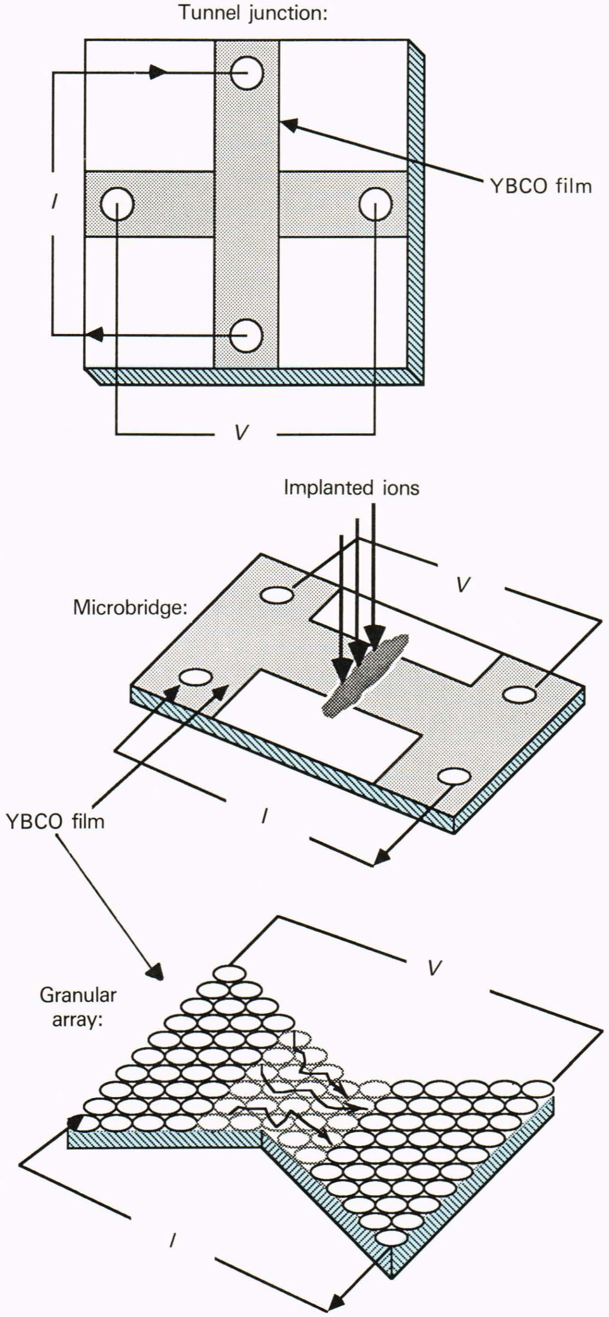


Figure 19—Some potential Josephson junction configurations using high-temperature superconducting thin films.

is a good chance that a Josephson junction can be made. Another possibility shown in Fig. 18 is to make a tunnel junction without an intercalated oxide layer, and to use the surface discontinuity between the overlapping layers as the tunneling barrier. This might work, despite the fact that the coherence length normal to the junction is very small (approximately 0.4 nm). Still another possibility is to control grain size to achieve a series or parallel array of junctions within a microbridge geometry. By varying the grain size and microbridge geometry, an initially large bolometric configuration might be made to asymptotically approach the behavior of a Josephson array in the weak-coupling limit.

In addition to radiation detectors, another application that also appears practical, simple, and ripe for enormous diversification is microwave integrated circuits. A simple example under investigation at APL is the superconducting microstrip resonator (Fig. 18). This device, as well as simple interconnects, take advantage of the lower RF surface resistance of superconductors, as compared with normal conductors. For resonators using conventional superconductors, this results in higher quality factors by several orders of magnitude. For superconductors with high transition temperatures, the expected performance gain may be only 2 orders of magnitude, but this may still be sufficient to warrant insertion of selected components or even entire subsystems into larger systems. (High-Q resonators are desirable for making sharply tunable filters and oscillators for stable frequency sources, as described below.) The biggest payoff, in fact, may come from all-superconducting subsystems, since with even the smallest component the investment in cryogenics is largely the same. Another straightforward application in microstrip circuits is high-speed interconnects between very-high-speed integrated circuits used for computing or signal processing. The attenuation should be 1 or 2 orders of magnitude smaller than for normal conductors at the required operating temperature. This will result in greater packing densities and smaller chip sizes by factors of 10 to 100, or even more. The extra cryogenic cost is also insignificant when comparing the technology with conventional supercomputing, since conventional systems already use liquid-nitrogen cooling. Again, this points to all-superconducting systems. The missing link here is once more the Josephson junction, since it could be used as an extremely fast switch in computing circuits.

Among the various monolithic microwave integrated circuits, high-Q resonators are attractive, since they could be used in highly stable frequency sources (for example, for geodetic positioning systems), and possibly in phase-locked loops for frequency-agile synthesizers for advanced radar systems. Other devices being contemplated include low-noise microwave amplifiers that use superconducting gate electrodes. Such devices could be used as post-detection amplifiers for superconducting radiation detectors. In the long term, dispersive delay lines for pulse-compression radar receivers and communication systems may be built from high-temperature superconductors. In such applications, substrate isotropy is as important as the required superconductor properties. The result would be signal processing at extremely high frequencies using electromagnetic delay lines, a development already achieved with conventional superconductors.[33]

KEY ISSUES

A number of key scientific and technological issues need to be addressed before the full potential of high-temperature superconducting thin films and multi-layered structures can be fully realized. All the applications require the integration of superconductors with one or more materials (insulators, semiconductors, and metals), so that interfacial effects are of crucial importance. The constraints imposed by mismatch of lattice constants between the superconducting material and the substrate, and the inevitable diffusion between the two materials, must be considered. It may be possible to reduce the lattice strains by matching lattice planes instead of lattice constants. The appropriate use of thin buffer layers to reduce strains as well as interdiffusion should be probed. Thin passivation layers may also be important to guard and enhance the physical and chemical stability of thin-film layered structures. Reducing the operating temperature for forming and processing multilayered structures will be highly beneficial in decreasing the interdiffusion and consequent degradation of superconducting films. The mechanical properties of thin-film structures are another important area that has received little attention until now. Extensive characterization of atomic structure, microstructure morphology, anisotropy parameters, chemical homogeniety, mechanical strength, and chemical degradation in multilayered structures is critically needed.

Critical currents upward of 10^6 A/cm^2 have already been achieved in thin films of superconducting oxides with high transition temperatures. Those highly desirable values are seen only in films deposited on oriented crystals of strontium titanate, zirconium oxide, and magnesium oxide. Whether equally high values can be achieved for layered structures incorporating technologically useful substrates, with or without buffer layers, remains to be seen. The low sensitivity of the critical current to externally applied magnetic fields is another essential feature that needs further exploration. The problem of critical currents in superconducting ceramics is further complicated by the inherent high anisotropy of those materials, and it would be necessary to determine if properly oriented superconducting films are going to be absolutely essential in exploiting the application of high-temperature superconductors. With the recent discovery of amorphous superconducting oxides,[34] it may be possible to overcome that problem.

The small values of the coherence length ξ (0.5 to 2 nm, depending on orientation)[35] undoubtedly pose challenges for fabrication of active devices based on Josephson junctions. However, the granular nature of superconducting oxides might allow the exploitation of intrinsic Josephson junctions that are prevalent in such materials because of separation of superconducting grains from the nonsuperconducting regions. That aspect may indeed lead to formation of entirely new devices that have not yet been conceived from studies of conventional superconducting materials.

EPILOGUE

This article has concentrated on the fabrication, properties, and some applications of high-temperature superconducting thin films. Further applications of such films in frequency standards and microwave technology are discussed in articles by Suter and Abita, respectively, elsewhere in this issue. In collaboration with J. C. Walker of the Department of Physics and Astronomy of The Johns Hopkins University, research on doped bulk superconducting oxides has been carried out.[13,36] Other activities at APL include the relationship of atomic structure and superconducting behavior[37] and the theoretical modeling of superconductors with high transition temperatures.[38]

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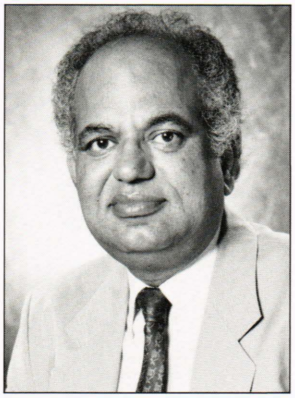
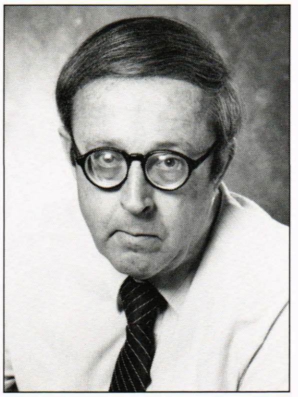
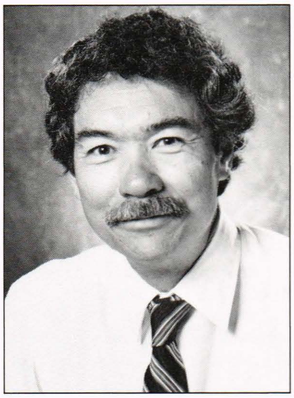


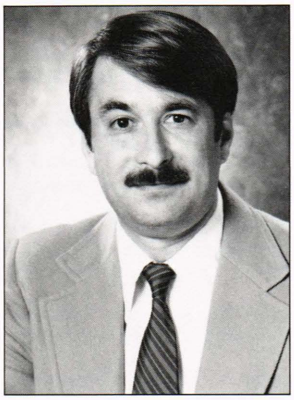
KISHIN MOORJANI is a physicist in the Materials Research Group of APL's Milton S. Eisenhower Research Center. He is engaged in problems related to high-temperature superconductors, photon-beam processing of materials, disordered structures, and nanocomposites. Born in India, he studied at the University of Delhi before receiving a Ph.D. in theoretical physics from The Catholic University of America in 1964. In 1967, Dr. Moorjani joined APL, where he is program manager of the microphysics project. He has coauthored a monograph, *Magnetic Glasses*, and has published extensively in the field of condensed matter science. He has held several visiting appointments at universities both in the United States and abroad. Dr. Moorjani teaches at The Johns Hopkins University G. W. C. Whiting School of Engineering and serves as chairman of the University's Applied Physics Program Committee.



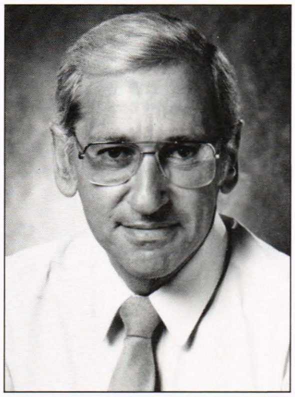
FRANK J. ADRIAN is a member of the Principal Professional Staff and is a senior scientist in APL's Milton S. Eisenhower Research Center. He joined the Research Center in 1955 after receiving an A.B. degree in chemistry from The Catholic University of America (1951) and a Ph.D. degree in physical chemistry from Cornell University (1955). His primary research interests are theoretical and experimental investigations of the structure of molecules and solids and the relationships between structure and chemical and physical properties. Many of these investigations, which have resulted in numerous publications, have involved the application and interpretation of magnetic resonance experiments. Dr. Adrian has been a Dunning visiting professor in the Chemistry Department of The Johns Hopkins University (1982–83) and is an adjunct professor in the Chemistry Department of Queen's Univeristy, Kingston, Ontario, Canada.



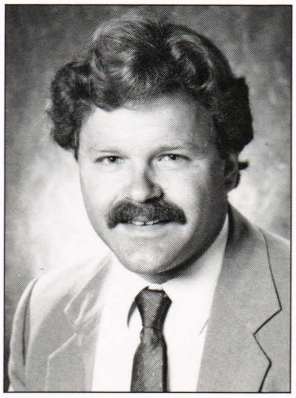
BORIS F. KIM was born in Ashland, Ga., in 1938. He received a B.E.S. degree in electrical engineering in 1960 and a Ph.D. in physics in 1967 from The Johns Hopkins University. Dr. Kim served as an officer in the U.S. Army during 1967–69, after which he joined APL. His research interests are in the fields of experimental atomic and molecular spectroscopy, computer vision, and superconductivity.



TERRY E. PHILLIPS is a senior staff chemist in the Materials Science Group of APL's Milton S. Eisenhower Research Center. Born in Sunbury, Pa., he received a B.A. degree from Susquehanna University, and M.S. and Ph.D. degrees in chemistry from The Johns Hopkins University in 1976. After completing postgraduate studies at Northwestern University in low-dimensional organic conductors, he joined APL in 1979. Dr. Phillips has been involved in problems in photoelectrochemical energy conversion, inorganic optical and electrical phase transition compounds, superconducting materials, and materials characterized with X rays, nuclear magnetic resonance, mass spectroscopy, and optical spectroscopic techniques.



JOSEPH BOHANDY, a native of Ohio, received B.S., M.S., and Ph.D. degrees from Ohio State University. He joined APL in 1965 as a member of the Microwave Physics Group of the Milton S. Eisenhower Research Center and worked on various problems in solid-state and chemical physics. In 1984, he became a member of the Materials Science Group of the Research Center, where he was involved in laser microchemical processing as applied to microcircuit fabrication. His recent principal professional efforts have been in the study and application of high-temperature superconductivity.



WILLIAM J. GREEN was born in Bethesda, Md., in 1957. He attended both Gettysburg College and the University of Maryland and plans to pursue a degree in applied physics at The Johns Hopkins University G. W. C. Whiting School of Engineering. Before joining the Microphysics Group of APL's Milton S. Eisenhower Research Center in 1985, he worked for Fusion Systems, Inc., of Rockville, Md., in quality assurance spectroscopy for ultraviolet curing systems. He also worked on a refractometer project for the Quantum Electronics Group at the University of Maryland.

ELISABETTA AGOSTINELLI was born in Gubbio, Italy, in 1956. She received the title of Doctor of Chemistry *cum laude* in 1982 from the University of Rome, where her thesis was on solid-state physics. She joined the Institute of the National Research Council of Italy in Rome on a fellowship, where she was involved in various problems of solid-state physical chemistry. In 1984, she became a researcher and started to study the magnetic properties of spin glasses and amorphous materials. In 1987, she was sponsored for a NATO fellowship by the Microphysics Group of APL's Milton S. Eisenhower Research Center and joined the program on the preparation and characterization of thin films of superconducting oxides.

BRADLEY G. BOONE's biography can be found on p. 275.