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This workshop was the first in this series to concentrate largely on high-temperature superconductors. Its objectives were to identify the barriers limiting progress in high-temperature materials and to assess research areas that are ripe for important advances. The workshop was organized in four sessions, with Robert C.Dynes and Victor J.Emery leading the session on Fundamentals, Charles M.Falco and Donald U.Gubser leading the session on Materials, David K.Christen and Harry Kroger leading the session on Thin Films and Devices, and Sungho Jin and David T.Shaw leading the session on Bulk Materials and Large-Scale Applications. The organizational committee for the workshop consisted of David K.Christen, Alan F.Clark, Robert C. Dynes, Donald H. Liebenberg, David L.Nelson, and David T.Shaw (chair).

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June 26, 1992

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Dear Dr. Liebenberg:

Enclosed please find a copy of the Final Report on our ONR Grant No. N00014-91-J-4036 entitled "Workshop on Research Needs & Opportunities in High Temperature Superconductivity". I hope it meets with your approval. If you have any questions please call me.

Sincerely yours,

A handwritten signature in cursive script that reads "D. T. Shaw/jg".

David T. Shaw  
Principal Investigator

jg  
encl.

cc: Grant Administrator, ONR, Resident Representative N62927, 33 Third Ave., NY, NY  
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***NEW RESEARCH  
OPPORTUNITIES  
IN SUPERCONDUCTIVITY III***

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***August 1991***

**92-18219**



## **New Research Opportunities in Superconductivity III**

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**August 1991**

**A report on the Workshop on  
New Research Opportunities in Superconductivity**

**Copper Mountain, Colorado  
August 19 - 20, 1991**



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## **PREFACE**

This is the report of the Workshop on New Research Opportunities in Superconductivity held at Copper Mountain, Colorado on August 19 - 20, 1991. The workshop is a follow-up to two previous meetings to evaluate progress in superconductivity. The first, held at Copper Mountain, Colorado in 1983, focused on low-temperature superconductors (LTS), while the second in 1988 examined the progress of low-temperature materials and the potential of the then recently-discovered high-temperature superconductors (HTS). The summaries of these two superconductivity workshops were published in *Cryogenics* (July 1984, p. 378; and November 1988, p. 711).

This workshop was the first in this series to concentrate largely on high-temperature superconductors. Its objectives were to identify the barriers limiting progress in high-temperature materials and to assess research areas that are ripe for important advances. The workshop was organized in four sessions, with Robert C. Dynes and Victor J. Emery leading the session on Fundamentals, Charles M. Falco and Donald U. Gubser leading the session on Materials, David K. Christen and Harry Kroger leading the session on Thin Films and Devices, and Sungho Jin and David T. Shaw leading the session on Bulk Materials and Large-Scale Applications. The organizational committee for the workshop consisted of David K. Christen, Alan F. Clark, Robert C. Dynes, Donald H. Liebenberg, David L. Nelson, and David T. Shaw (chair).

## TABLE OF CONTENTS

|                                                      |            |
|------------------------------------------------------|------------|
| PREFACE                                              | <i>iii</i> |
| I. WORKSHOP SUMMARY                                  | 1          |
| II. FUNDAMENTALS                                     | 3          |
| A. Progress                                          | 3          |
| Normal State                                         | 3          |
| Superconducting State                                | 4          |
| Unconventional Superconductors                       | 4          |
| B. Research Opportunities                            | 5          |
| C. Role of Graduate Education                        | 6          |
| III. MATERIALS                                       | 7          |
| A. Progress                                          | 8          |
| B. Research Opportunities                            | 9          |
| Mechanisms of Superconductivity                      | 9          |
| Synthesis                                            | 10         |
| Phase Relations                                      | 10         |
| Properties and Techniques                            | 11         |
| Special Programs                                     | 11         |
| IV. THIN FILMS AND DEVICES                           | 12         |
| A. Progress                                          | 12         |
| Thin Film Growth                                     | 12         |
| Processing Techniques for Devices                    | 13         |
| Device Fabrication                                   | 13         |
| Fundamental Studies                                  | 14         |
| B. Research Opportunities                            | 14         |
| Improved Understanding of Film Growth and Properties | 14         |
| Circuit and Device Fabrication                       | 15         |
| Superconducting Device Physics                       | 17         |
| Supporting Technology                                | 18         |

**- New Research Opportunities in Superconductivity -**

|                                                            |           |
|------------------------------------------------------------|-----------|
| <b>V. BULK MATERIALS AND LARGE-SCALE APPLICATIONS</b>      | <b>20</b> |
| <b>A. Progress</b>                                         | <b>20</b> |
| Critical Current Densities                                 | 20        |
| Conductor Fabrication and Prototype Solenoid Demonstration | 21        |
| <b>B. Research Opportunities</b>                           | <b>22</b> |
| Fundamental Opportunities                                  | 22        |
| Applications                                               | 24        |
| <b>ACKNOWLEDGEMENTS</b>                                    | <b>27</b> |
| <b>LIST OF ATTENDEES</b>                                   | <b>28</b> |

## I. WORKSHOP SUMMARY

Superconductivity has evolved during the five years since the discovery of high-temperature superconductors as a science rich with fundamental questions, including those associated with the behavior of correlated electrons and vortex dynamics, as well as technological potential, which spans the spectrum from superconducting magnets to thin film sensors and electronic devices. This workshop report will address research opportunities in the areas of fundamentals of superconductivity, materials, thin films and devices, and bulk materials and large-scale applications. Since the previous report in 1988, there has been noteworthy progress in these areas; and pre-commercial developments are on the horizon in each of these areas. This progress will be identified and will point toward the current opportunities.

Fundamental issues in high-temperature superconductivity concern not only the superconducting state but also the normal state. Significant progress in understanding normal state properties, such as antiferromagnetism, transport behavior and the Fermi surface, has been reported. In the superconducting state much has been learned about pairing, energy gaps, and flux states. Opportunities include detailed study of the transition between the normal metal and insulator state, a region where rich new physics is likely to be found; further identification of energy gaps and excitations that may be in or near the gaps; and development of vortex dynamics and flux states theory and experiment.

Materials progress has included the discovery of over seventy new oxide superconductors, electron-doped oxides, non-copper oxides, and organic superconductors and recently the discovery of C<sub>60</sub> fullerene superconductivity. The availability of improved quality crystals has enabled more precise fundamental studies and provided an underpinning for the technology of films and bulk materials. Opportunities were emphasized in the areas of phase stability, phase kinetics, and phase equilibria. Additional opportunities were noted for the synthesis of new materials, novel processing, and a systematic approach to multi-component systems. Low-temperature and composite processing presented opportunities; and, in the low-temperature superconductors, the development of multilayers and arrays also opened up areas for fundamental studies. The development of screening techniques for low fraction superconductivity in samples and studies with atomic level of resolution are needed, in the latter case for relating structure to properties.

In the area of thin films and devices, there has been excellent progress in both passive and active device development through the routine fabrication of high critical current films by several techniques, including sputtering and laser ablation. Epitaxial multilayer structures have also been made; the crystal orientation during growth has been controlled. Josephson junctions (JJ's) have been made by a variety of techniques and high-sensitivity SQUID's have been demonstrated at 77 K.

Bolometric sensors and novel electric field devices have been fabricated; and a wide variety of processing techniques including patterning have been adapted to these materials. Opportunities abound especially since both near- and long-term device and system insertion studies are being actively pursued. There are immediate opportunities for work on lower temperature thin film processing, larger area coverage, lower dielectric constant substrates

and non-epitaxial growth. Understanding surfaces and interfaces at unit cell resolution is important for tunnel junction development as is a better understanding of grain boundaries and their weak link and noise properties. The availability of higher quality films has also opened up opportunities to study flux dynamics, optical properties, and the behavior of SNS sandwiches. Low carrier density, flux flow, and hybrid devices need further understanding and development. There is a need for integration of reliable refrigeration development with thin film devices. The time for circuit designers to develop and analyze systems has arrived.

Bulk and large-scale device development has proceeded well in the past several years, raising the critical current density,  $J_c$ , from near zero to  $10^4$ - $10^5$  A/cm<sup>2</sup>. Pinning enhancement by irradiation is noted and fabrication of 1 m lengths of Y/Ba/Cu/O (YBCO) with  $J_c = 10^3$ - $10^4$  A/cm<sup>2</sup> at 77 K and 1 T as well as of Bi/Sr/Ca/Cu/O (BSCCO) wires of 100 m length and  $10^5$  A/cm<sup>2</sup> at 77 K and 0 T show great promise. Better understanding of the phase diagrams, determination of mechanical properties, and processing of melt-textured wire has yielded improved properties, but important opportunities and challenges still remain in this area. Better understanding of the factors controlling the critical current and critical current density, the correlations with structure, nucleation and growth related to texturing, the control of the material within the phase diagram (especially as to whether congruent conditions rather than peritectic relations can be obtained) and the understanding of flux pinning and anisotropy in  $J_c$  and  $H_{c2}$  is needed. Improved fabrication processes are needed for wires, multifilament wires, and ribbons. Enhanced mechanical properties are needed, both macro-properties such as silver jacketing and micro-properties such as silver doping in BSCCO or 211 phase into YBCO to improve strength or flux pinning. Applications for both wire and bulk material that can trap in a field above 1 T exist. These include bearings (both passive and active), shielding, and specialized applications such as electromagnetic metal forming. Transmission lines for replacement of aging underground lines may be near application using currently available critical current and mechanical properties. Refrigeration development, both for improved reliability and integration with equipment designs, provides an opportunity for further progress.

In summary, these technical opportunities depend on some issues of broad concern. Sustained support for the basic studies that enable a broad range of potential product developments is deemed critical. The anticipated growth of products is also tied to the development of trained personnel, especially graduate students. Graduate education in this field provides opportunities for in-depth exposure to sample fabrication, characterization with various techniques, measurement of physical properties, and analysis and comparison with theory as well as the development of new theory. Prototype development of electronic systems for real comparison of performance with alternate systems is needed and will help to verify the computer simulations being developed for superconducting devices and circuits. Prototype development in large-scale applications is critical to evaluating performance and reliability; the lack of such information currently limits the potential for applications to a few areas such as transmission line power buses, intermediate scale motors (3,000 - 10,000 HP), bearings, and small superconducting magnetic energy storage (SMES) systems (1 - 50 MJ). SQUID sensors, IR detectors, and the potential for non-hysteretic electronics provide challenging opportunities for scientists and engineers.

The workshop viewed a very wide spectrum of devices and equipment that can be expected to emerge on the marketplace given adequate support by government, universities, and industry. The world competition, which has developed in superconductivity and especially in high-temperature superconductivity is a challenge, which this community is positioned to accept and successfully meet provided that the base research is maintained and the appropriate inducement for specific products is provided.

## II. FUNDAMENTALS

The understanding of high-temperature superconductors has advanced to a remarkable extent since the last HTS workshop, although it is still far from complete. While conventional superconductors are well understood as the low-temperature phase of a Fermi-liquid normal-metallic state, the HTS cuprates and bismuthates are doped insulators, obtained by chemically adding charge carriers to highly correlated insulating states. They do not appear to be simple Fermi liquids. It is important to compare and contrast these two extreme situations to enhance our understanding of both.

Progress in high-temperature superconductivity is a consequence of improvements in the synthesis and characterization of materials, and the application of an exceptionally wide variety of experimental techniques. The interaction between theorists and experimentalists has been of great importance both in establishing the overall behavior of oxide superconductors and in sharpening the questions to be addressed. At this level, the relevant theory is not necessarily technically sophisticated, but the entire field is the major stimulus for the development of the many-body theory of strongly correlated electron systems. It has already led to a detailed understanding of the properties of two-dimensional Heisenberg antiferromagnets. Further progress will surely lead to a deeper understanding of doped metallic systems.

### A. Progress

Five years ago cuprate metals were virtually unknown. Today we have several dozen different superconducting compounds with transition temperatures as high as 125 K. The normal state ( $T > T_c$ ) of these materials is peculiar, and explaining it is almost certainly a prerequisite to understanding their superconductivity. The following key characteristics, none of them known five years ago, are now established and widely accepted.

#### Normal State

The common structural aspects of the cuprate superconductors are stacks of  $\text{CuO}_2$  layers, separated by charge reservoir building blocks that modify the carrier concentration in the electronically active  $\text{CuO}_2$  layers. The Cu-O bond is strongly covalent; and the relevant orbitals at the Fermi energy are derived from oxygen  $2p_x$  and copper  $3d_{x^2-y^2}$  orbitals. Cuprate superconductors evolve from highly correlated antiferromagnetic insulators as charge is introduced into the  $\text{CuO}_2$  layers through chemical modification of the reservoir layers. In a similar way, superconductors based on  $\text{BaBiO}_3$  evolve from a correlated insulating state as carriers are added by heterovalent substitution.

Charge response measurements, such as frequency- and temperature-dependent electrical conductivity, Hall effect, and Raman spectroscopy, strongly suggest that the normal state is not described by the simple Fermi-liquid model and that only the added carriers contribute to transport properties. In view of the highly correlated parentage, the normal state peculiarities, and the low carrier concentration, the observation in the metallic state of a

"Fermi surface" by angle-resolved photoelectron spectroscopy has been highly significant. Its shape and size, also probed by positron annihilation studies, appear to be fairly well given by Local Density Approximation (LDA) calculations. Theories have begun to reconcile these observations.

Consistent nuclear magnetic resonance (NMR) results obtained by different groups provide detailed insight into the spin dynamics of cuprates. Neutron scattering spectroscopy has begun to add information on spin excitations at higher energies.

Physical properties are very sensitive to sample quality. Most progress in crystal growth has been made for YBCO, achieving even untwinned samples, and thus the main body of quantitative results has come from studies of YBCO and La/Sr/Cu/O. Extending measurements to other families is certainly of importance, but it requires high-quality samples.

### **Superconducting State**

The superconducting state consists of pairs of electrons. The experimental evidence is consistent with the pairs having singlet spin state, total momentum zero and forming at  $T_c$ .

The coherence length  $\xi$  and penetration depth  $\lambda$ , the characteristic length scales of the superconducting state, have been determined accurately for YBCO and are reasonably well known for other oxide superconductors. In the cuprates, these quantities are anisotropic and extreme:  $\xi$  is very short and  $\lambda$  rather long. The bismuthates are isotropic. Their coherence lengths are somewhat larger than those of the cuprates.

The bismuthates have an energy gap whose value and temperature dependence is consistent with simple BCS theory. The situation in the cuprates is more complicated. There are certainly clear indications of gap-like structures that appear in many measurements; yet there are still unresolved issues about excitations at lower energies and some lingering questions about the symmetry of the order parameter.

There is a strong correlation between  $T_c$  and carrier concentration in both the cuprates and the bismuthates. This appears to be a characteristic of superconductivity in doped insulators. The progression from insulator to superconductor to metal as the carrier concentration increases is a common feature of the cuprates, although more work is required to obtain an understanding of the underlying physics.

The properties of the cuprates in a magnetic field have been widely studied. As in conventional superconductors, the field penetrates in the form of vortices, each containing a single flux quantum. At low fields, the vortices form a triangular lattice, distorted by the anisotropy of the penetration depth. At high fields and in the presence of an imposed current, there is a very rich phase diagram. In fact, some features first discovered in the cuprates, such as an irreversibility line, were subsequently found to occur in conventional superconductors, but in much more limited regions of the phase diagram. Much progress has been made in understanding the various magnetic phases and the associated flux dynamics.

### **Unconventional Superconductors**

There has been significant progress in the synthesis of unconventional superconducting materials -- that is, materials that may not be explained by the conventional electron-phonon mechanism. The most dramatic example is the observation of superconductivity in doped

C<sub>60</sub>.  $T_c$  for these materials has already reached 42 K, which places them firmly in the category of high-temperature superconductors. Detailed investigation of new dopants and of the superconducting properties of existing materials is in progress. The transition temperature in the (BEDT-TTF)<sub>2</sub>X class of organic superconductors has now been raised to about 13 K, which is comparable to that of oxide superconductors before 1986. Several new classes of organic superconductors have been discovered, although  $T_c$  is typically less than 5 K. A significant improvement in crystal size for some of the heavy fermion superconductors has been made. This has led both to an increase in the precision of experimentally measured properties and to a demonstration that, in contrast to conventional superconductors, the order parameter has nodes. These developments demonstrate once again the importance of supporting the search for new and improved superconducting materials.

## B. Research Opportunities

Our increased knowledge of both the superconducting and normal states has led to the identification of the following areas as particularly crucial for continued progress or especially ripe for important advances.

There is a need for further progress in the growth and characterization of HTS single crystal materials. Only in the case of YBCO are the samples sufficiently well characterized, with a reliable set of parameters for  $\lambda$ ,  $\xi$ , resistivity, etc. Similar data on well-characterized single crystal samples of the other cuprates will allow studies of trends both within a family of compounds and between families. This will help to solidify the present understanding of the anomalous properties of the normal state and further identify trends of out-of-plane versus in-plane properties.

For the above studies on other cuprates (and for further work on YBCO), homogeneous single crystals are essential. They must be sufficiently large for the specific experiments to be performed, e.g., length scales on the order of centimeters for neutron scattering and millimeters for transport, thermodynamic and most optical experiments. The crystals must also be subjected to complete microstructural micro-chemical analysis to assure reproducibility. Where the samples are orthorhombic, techniques are needed to prepare untwinned samples, as has been successfully accomplished with YBCO. Otherwise, averaging of in-plane properties will confuse fundamental analyses of experiments as will effects associated with twin boundaries. We can not over-emphasize the need for well-characterized single crystals of appropriate size and doping for a wide variety of studies.

Studies of chemical and structural order on the atomic scale are needed in the cuprates. With only a few superconducting pairs within a coherence volume, the local chemistry and structure influence the superconductivity profoundly. Local probes such as NMR and NQR, as well as defect-sensitive optical techniques, have taught us much, but development of still other analytical techniques with very high spatial resolution is needed (scanning tunneling microscopy (STM), high-resolution EDX and EELS, selected area diffraction, etc.). Combining such techniques is recommended. Analysis of the effects of selected structural transitions on superconducting properties can be extremely useful in sorting out the relationships between superconductivity and other types of order at both the macroscopic and microscopic level.

In the doped cuprates, it is generally understood that there is a strong correlation between  $T_c$  and carrier density, but quantitative details require further clarification. Different techniques to measure carrier concentration (optical, chemical, transport) yield different values; and this discrepancy has yet to be resolved. The apparent dependence of the carrier

concentration on temperature also remains unresolved. These discrepancies must be clarified; only then can the subtle changes in  $T_c$  with doping be fully understood.

With increased doping, the progression from antiferromagnetic insulator to superconductor to normal metal offers a richness uncommon in systems other than the cuprates. While the data are well documented, fundamental questions associated with whether chemical or electron-driven phase separation are responsible for these transitions remain unanswered. These questions are both profound materials questions as well as deep theoretical puzzles.

The relationships among the cuprates, the bismuthates, and other "exotic" superconductors remain unclear. Do the latter exhibit normal state anomalies like those in the cuprates? More specifically, what properties of conducting bismuthates derive from correlations remaining from the CDW insulating parent state? If the normal state is indeed a highly correlated one, why does the superconducting state appear to be so ordinary?

It is important to identify the properties of a single or isolated  $\text{CuO}_2$  plane. Determination of whether such a layer is superconducting, and of the influence of fluctuations on the single layer will impact theoretical understanding. Comparison of results for superlattices or heterostructures, such as YBCO and PrBCO, with those for ultra-thin films of conventional superconductors will be very instructive.

A more complete investigation of spin and charge dynamics and the relationship between them is essential for our understanding of the nature of exotic superconductors. Charge dynamics should be explored up to about 1 eV. The essential energy scale of spin dynamics in superconducting materials has yet to be fully established.

Several features of the statics and dynamics of the flux line lattice need to be understood at a much deeper level if we are to increase the strength of flux pinning for practical devices and to obtain a broader understanding of this state of the superconductor. Specifically, more work is needed on:

- The magnetic field dependence of the energy gap or the superfluid density;
- Time-resolved measurements on a broad time scale; and
- Space-resolved information about the superfluid density near possible pinning sites.

Model systems that isolate individual effects contributing to pinning and the organization of the flux lattice, glass, or liquid should be studied. Such systems might include isotropic and anisotropic HTS materials, LTS materials, and superlattices.

### **C. Role of Graduate Education**

Graduate education plays an important role in the development of research opportunities in superconductivity. Research in superconductivity requires interaction with synthesis and fabrication of samples, extensive characterization using a variety of instrumentation and facilities, measurement of important physical properties, and careful analysis of results and interpretation with theory. Such in-depth exposure in each aspect of research in superconductivity is essential to provide a broad understanding of the important concepts of condensed matter sciences. Graduate students who have received a strong foundation in all of these areas are most likely to provide the professional condensed matter scientists of the future. The richness of research activities in superconductivity is similar to that in other materials research areas, and is consistent with rigorous academic standards.

### III. MATERIALS

The synthesis of new superconducting materials and the proper characterization of their properties, composition, and structure are necessary for progress in the field. To date, empirical studies have been responsible for most of the progress in the synthesis of new materials; and this is likely to remain true in the future. With regard to characterization, there has been an evolution to smaller scales that has paralleled instrumentation development. The development of high-resolution electron microscopes and synchrotron high photon flux has enabled researchers to examine small samples.

Also emphasized is the importance of research opportunities in studies of the nucleation and growth of materials, particularly with respect to the possibility of producing metastable materials. Such studies include the use of sophisticated instrumentation for growth (e.g., high pressures, physical vapor deposition) and for characterization (e.g., electron probe microscopes, high-frequency electromagnetic probes). Important research opportunities also exist for studies of surfaces, interfaces, and tunneling barriers. In this context, the role of dimensionality is very important.

The need for interdisciplinary research involving solid state chemists, physicists, metallurgists, and electrical engineers is becoming increasingly important to superconductivity as well as to most scientific disciplines. The importance of materials processing studies and the development of appropriate phase diagrams and phase kinetics to guide the processing studies is recognized. These studies are essential to the growth of quality single crystals, thin films, and materials with controlled microstructure. Without these materials, progress toward the development of fundamental understanding or the development of a viable technology will be almost impossible.

Tremendous research challenges and technology needs exist for the discovery and synthesis of new materials. The synthesis of materials must be coupled with the processing and characterization of the materials. The crystalline and microstructural details must be carefully determined; and these results must be correlated with physical property characterization. Only by this close synergism between processing, and structural and property investigations will meaningful progress be made. It is also essential to develop processing procedures to optimize the quality of the material for specific purposes, whether it be single crystals for pure research, textured polycrystalline materials for wire, or thin films for electronics.

Closely associated with the general themes of materials research has been the increasing use of innovative and/or sophisticated instrumentation. In many cases, innovative ideas such as rapid screening techniques for measuring critical temperatures, critical currents, or surface losses have led both to rapid progress in the field and to new commercial products. In other cases, the use of sophisticated techniques, such as STM or high-resolution transmission electron microscopy (HRTEM), has led to significant progress in understanding flux pinning issues and grain boundary defects, respectively. Materials research has a great need for continued instrumentation and technique development and many opportunities for further work exist.

## A. Progress

Progress in materials development has been so prolific that a detailed account would be impossible in the short length of this report. Therefore, only a few of the notable results of the past four years are recounted in this section. The majority of materials research in superconductivity has centered on the oxide materials. From a scientific point of view, the improvement of material quality has been enormous. The growth of large single crystals is essential for rapid progress. Progress in this area has been due primarily to improvements in processing procedures and to better understanding of the material phase diagrams.

Superconducting bismuth and thallium oxides [BSCCO and Tl/Ba/Ca/Cu/O (TBCCO)] exist in many closely related phases, which has complicated research on these materials. Thallates have the additional complication of being toxic. Consequently great care must be taken in synthesizing and processing these compounds. Nearly phase-pure materials are now being formed; and controlled texturing (crystallite alignment) is permitting formation of film and bulk specimens for scientific and technological studies.

In non-cuprate oxide materials, such as in the Ba/K/Bi/O (BKBO) system, single crystals having critical temperatures up to 32 K have been grown by electrodeposition from a KOH melt. Studies of non-cuprate oxides will have important consequences with regard to the understanding of the fundamental mechanism(s) of superconductivity.

Most of the highest transition temperature cuprates have hole- or p-type carriers. Electron or n-type carriers have been found in some materials, which now have critical temperatures up to about 40 K. These materials form a very important subclass of the cuprates since they may help in the understanding of a number of fundamental and practical questions. For instance, do these materials have a different pairing mechanism for the carriers? They are potentially important from a practical standpoint as well because they are stable under high vacuum conditions where the p-type cuprates are unstable.

New single layer thallium compounds have recently been discovered that appear to have strong pinning sites and stronger coupling across individual grain boundaries. These and related materials may have important implications in applications involving high magnetic fields.

Another important area of progress has been in the metalization of oxide superconductors for the purpose of making ohmic, low-resistance electrical contacts. Initially, the inability to make low-resistance electrical contacts to the HTS materials placed severe limitations on characterization as well as commercial development. This difficulty contributed to the problem of reproducibility of experimental results. Today, techniques for preparing the surface of HTS materials with subsequent metalization procedures have led to electrical contacts with resistances of the order of  $10^{-10}$  ohm/cm<sup>2</sup>.

An understanding of the important role that oxygen stoichiometry and ordering plays in superconductivity has been one of the major areas of progress in the last few years. Novel techniques for the determination of oxygen stoichiometry, such as gas evolution, or of the connection between oxygen stoichiometry and certain Raman lines have been exploited for non-destructive determination in thin films and bulk materials. Iodometric titration analysis, coupled with bulk x-ray diffraction data, is now routinely used for characterization of the oxygen content of bulk YBCO samples.

Progress in the conventional or LTS materials has also been made. Improvements in materials processing and characterization have led to remarkable progress effecting technology in the LTS composite conductor NbTi. Commercial wire is now available with significantly enhanced performance characteristics due to the combined efforts of university-based research and industrial-based processing studies. Studies are now concentrating on new composite materials, such as Nb<sub>3</sub>Sn and the HTS oxides.

## **B. Research Opportunities**

### **Mechanisms of Superconductivity**

While significant research opportunities exist for these exciting new superconducting materials, the mechanism of superconductivity is by no means clear. High quality materials and accurate measurements are needed to resolve many issues. Electron tunneling has proven to be an important probe for superconductivity. Such studies require improvements in surface quality and development of the ability to make quality tunnel junctions. Research needs here closely parallel those discussed in the thin films and devices section, which demonstrates the efficacy of interdisciplinary collaborations.

The question has arisen whether all existing layered cuprates are mere modifications of the known phases. All superconductors discovered to date that operate above 77 K are hole-type conductors in the normal state. Electron-doped superconductors have been synthesized and studied, but their critical temperatures remain lower than 45 K. Is the mechanism responsible for Cooper pairing and condensation the same as for the hole-type superconductors, which currently have critical temperatures ranging up to 127 K? Similarly, with regard to the bismuthate superconductors, BaKBO or Ba/Rb/Bi/O (BRBO), is the mechanism for their superconductivity the same as for the Cu-based hole- or electron-doped superconductors? These are open (and difficult) questions that need to be addressed. In this area, synthesis of new materials and use of innovative techniques will prove vital. Use of new types of synthesis techniques, such as high pressure synthesis or various thin film synthesis techniques, will be extremely valuable methods for the preparation of new, possibly metastable, superconducting materials. New techniques for rapidly screening the properties of these materials will also be needed, as the quantity of material is often very small and is frequently mixed with other phases.

Several empirical superconductivity-structure correlations are observed for the cuprates, including correlation of  $T_c$  with carrier concentrations, the Cu-O distance within the CuO<sub>2</sub> sheets, and the number of CuO<sub>2</sub> sheets stacked directly on top of each other. The complexity of the compositions and structures has impeded development and utilization of these correlations. Determination of the structure of superconducting systems that give highest critical temperatures, e.g., BSCCO and TBCCO, need particular attention, especially regarding the effect of temperature and composition on their superstructure.

An important aspect of comparison between theory and experiment is the use of low-temperature superconductors as model systems. Although the focus is on high-temperature superconductors, this should not be viewed as diminishing the need for continuing efforts in conventional (low-temperature) superconductivity. In some respects, low-temperature superconductors, with their relative freedom from materials complications, may be preferable for studying fundamental superconducting properties. Opportunities include investigations of the role of dimensionality, interactions between competing mechanisms (superconductivity-magnetism, superconductivity-localization, etc.), the flux lattice, H-T phase diagrams (including irreversibility), Josephson effect, proximity effect, fundamental quantum behavior, and granular superconductivity. The primary point is that superconductivity is a field with an underlying conceptual unity; the material-dependent

variation in characteristic lengths, temperatures, energies, and other parameters provides an opportunity for understanding this complex phenomenon, which can be helped considerably by a synergistic approach using HTS and LTS materials.

## Synthesis

Historically, the best approach to the discovery of new HTS materials has been the so-called "enlightened empirical" approach, which builds on a vast knowledge of known materials. This approach is likely to remain preeminent in the future. Opportunities range from synthesis of new classes of borides, nitrides, halides, non-copper-based oxides, and organics to compounds with cage-like  $C_{60}$  molecules susceptible to a broad range of intercalation procedures. Development of new preparation methods should be pursued, including those involving high pressures, high temperatures, epitaxial growth, solid state diffusion reactions, etc.

In addition to the obvious search for materials with higher transition temperatures, it must be remembered that other important properties may eventually dictate the material of choice for specific applications. There is a need for superconductors with improved mechanical properties (more malleable), with higher, stronger flux pinning sites, with lower processing temperatures, and with less reactivity to substrates and interfaces, etc.

Continued strong synthesis programs involving thin film preparation methods must be maintained. Deposition of phase spread thin films is one technique for rapidly exploring a wide variety of compositions. Different techniques should be developed as they may have features that would make them preferable for specific applications. Included in these studies should be work on substrate interaction and/or coating used for tunneling barriers or protection.

An important issue is the difficulty in obtaining the same structural and superconducting properties in thin films and bulk materials. The high critical temperatures of the TBCCO and BKBO systems have not been obtained yet in thin films. Conversely, the high  $J_c$ 's obtained in thin films of YBCO have not been obtained in bulk materials. A better understanding of structure-property relationships and the use of quantitative structural and chemical tools should lead the way to both better thin films and better bulk materials.

Many of the superconductors also have large levels of point defects of all varieties: antisite disorder, vacancies, and interstitials. Techniques are available to define these complex structures, although they are very time consuming and require specialized facilities. Obstacles to further progress and to commercialization of these materials do exist. Many of these new compounds are chemically unstable in air. Procedures for synthesis and characterization must allow for this difficulty. Encapsulation or *in situ* techniques may be required for future development.

## Phase Relations

Much more information is needed on phase equilibria, phase diagrams, and phase kinetics. The synthetic chemistry of known HTS systems needs to be improved so that high-quality, well-characterized samples (crystals, bulk materials, and films) are reproducibly available for meaningful studies of physical properties. Improvement will result from detailed systematic studies of chemistry-structure-property relationships. The details of sample preparation conditions, including atmosphere, heating/cooling rates, and reactant and container material, need to be correlated with the structures, chemical compositions, and properties of products.

Phase diagram studies, including those of variable oxygen partial pressure, should be expanded in order to provide a working basis for crystal growers. Such studies will also provide basic information for much-needed investigations of the kinetic aspects of solid state reactions in bulk, surfaces, and interfaces. Improved synthetic control of the known HTS phases requires such kinetic studies due to the thermodynamically unstable nature of the materials. As a result, the HTS phases are intrinsically defective, and typically display non-stoichiometric, local structures that differ from the "average" structures as determined by x-ray diffraction and microstructural/chemical inhomogeneities. The development of improved characterization methods for these types of "microlevel" features is needed in order to elucidate variations with synthetic conditions as well as the resulting HTS properties.

### **Properties and Techniques**

Development of new techniques, apparatus, and/or methods to synthesize and characterize existing materials as well as searching for new materials is vital to research in general and superconductivity in particular. Researchers should be encouraged to propose such development efforts; and the funding agencies and proposal reviewers should be receptive to quality proposals for techniques, apparatus, and/or methodology developments.

Improvements in techniques are needed in a variety of areas. At present, the materials synthesis scientist frequently has difficulty in detecting new superconducting compounds in trace quantities. In view of the processing problems associated with producing new pure-phase superconductors, it would be extremely helpful for new techniques to be developed for their detection. At present, SQUID susceptometry gives the more reliable indication of the presence of superconducting phases. It would be useful for new, high-sensitivity, non-contacting techniques, such as microwave conductivity measurements, to be developed. This development could lead to the commercialization of such apparatus, which would be readily available to the synthesis scientist.

Technique development for property determination would also be helpful in the area of rapid screening techniques, which are needed to survey a large number of samples. It is vitally important to provide rapid feedback on property measurements to the scientist who is synthesizing or processing the material. Often precise measurements are not needed, but speed to guide the development of the materials is important.

Once the material is developed to a suitable quality, accurate and reproducible measurements must be made. These will include structural investigations and a variety of property investigations. Here collaborations with different research groups can be extremely beneficial as this type of exchange provides a variety of techniques, increases the veracity of the measurements, and speeds information flow.

### **Special Programs**

Semi-empirical searches for new materials and phase equilibrium studies have traditionally had difficulty obtaining funding. Such work should be evaluated by considering whether substantial rationale is presented for investigating the proposed systems (including chemical and structural arguments). The "track record" of the principal investigator also needs to be considered, except in the case of young investigators. In parallel with proposed work purely in search of new compounds, there should be some level of research effort in the chemistry-structure-property relations of known superconductors. This assures payoff of research effort for the investigating team, the sponsor(s), and the superconductivity community, while permitting exciting (but high risk) efforts in exploratory synthesis to continue.

#### IV. THIN FILMS AND DEVICES

Perhaps the most exciting and potentially diverse applications of high-temperature superconductors will be achieved through development of thin film materials. LTS thin film device technology, already well established, provides a strong foundation from which to guide and expand capabilities into the HTS regime. Not only will operation of a variety of known sensitive and useful devices be extended to higher temperatures, but the unique and complex nature of these materials likely will lead to the development of novel, currently unforeseen devices. Key elements to realizing this potential are the development both of highly controlled, reproducible deposition processes and of techniques to fabricate complex, multi-component structures. A thorough understanding and characterization of the component materials and device structures are also needed. The beginnings of a HTS electronics technology has rapidly been established. Useful HTS SQUID sensors, passive microwave devices, and IR transition edge bolometers have been fabricated. A novel amplifier device, which is only practical using HTS materials, has also been demonstrated.

##### A. Progress

###### Thin Film Growth

Rapid progress has been made in the fabrication, characterization, and utilization of HTS thin films. Thin films with reproducible and technologically-useful superconducting properties are now being routinely fabricated by a variety of deposition techniques. These techniques include pulsed laser ablation from single or multiple targets, single- or multi-target sputtering, coevaporation, molecular beam epitaxy, and metallo-organic chemical vapor deposition.

High quality films have been grown on a variety of single crystal substrate materials, some with close lattice matching for direct epitaxy and others providing highly oriented films by near-coincident site epitaxy. Good films have been produced on chemically incompatible substrates through the deposition of appropriate buffer layer materials. Control of film orientation, surface morphology, and grain boundary orientation has been demonstrated. Grain boundary work has resulted in control of both in-plane grain boundaries for potential planar junction devices and substrate normal orientations, such as a-axis oriented film for trilayer sandwich junctions.

Films having thicknesses ranging from unit cell dimensions to several microns have been successfully grown and tested. Post-annealing techniques have been optimized to yield films with properties comparable to those of *in situ* deposited films. The films deposited by this latter technique have been grown at high deposition rates (up to several 100 Å/s) over large areas (2" diameter).

Techniques have also been developed to deposit epitaxial, multilayer superlattices composed of high-temperature superconductors and other near-lattice-matched materials.

Structural control of these films has enabled their use in fundamental studies and in fabrication of device-like structures.

### **Processing Techniques for Devices**

The fabrication of technologically-useful HTS devices will require processing techniques as demanding as those currently employed in LTS and advanced semiconductor technologies. The direct adaptation of those procedures to HTS materials has been hindered by the high chemical reactivity of copper oxides and the intrinsic non-metallic nature of their free surfaces. Techniques have been successfully adapted to overcome many of these problems, allowing the development of HTS prototype device structures. Novel methods have permitted such advances as the controlled patterning of films down to submicron resolutions without degradation of superconducting properties; the development of both ohmic and superconducting electrical contacts; wire bonding to ohmic contacts; deposition of epitaxial insulating overlayers, including growth of good HTS films on patterned sublayers; and improvements in the chemical etching of YBCO.

### **Device Fabrication**

Mature junction fabrication technology using niobium is now available at a number of centers in the United States. This technology is important for the production of electronic devices, SQUID sensors, and detectors used in astronomy. It is essential for studies of quantum effects in small structures. Likewise, hybrid low-temperature superconductor-semiconductor FET-like structures have been fabricated and have revealed important information on the proximity effect. The development of HTS devices can both complement and augment the knowledge base gained through research on LTS devices.

Advances in HTS devices have occurred rapidly. Josephson effects have been observed in a variety of HTS device structures, including grain boundary junctions (naturally occurring and engineered), S-N-S trilayer sandwich structures and microbridges, and a variety of other weak link structures (edge junctions, damage structures, etc.). As a result of these developments, non-hysteretic Josephson junctions can now be made using techniques compatible with integrated circuit fabrication. Reproducibility of junctions and control of critical currents are approaching levels that are suitable for development of functional circuits.

Thin film SQUID's have been fabricated that exhibit performance suitable for a number of the proposed applications. The flux noise levels in these devices are low enough to detect many of the magnetic signals of interest. In addition, monolithic integrated SQUID magnetometers have been demonstrated based on multilayer epitaxial YBCO technology.

The first generation of passive RF (microwave and millimeter wave) devices have been demonstrated with performance far superior to normal conductors operated in a similar fashion. A variety of resonators, filters, delay lines, and other passive elements has performed well enough to attract the attention of systems designers and to encourage the development of more complex microwave systems and subsystems.

IR transition edge bolometers have been demonstrated that show promise for both commercial (photospectroscopy) and military (IR focal plane) applications. Novel designs and implementations are improving on some of the early limitations on speed and sensitivity in these devices.

Novel superconducting devices that are not possible with LTS materials have been demonstrated. These include superconducting flux-flow transistors (SSFT) made from

YBCO and TBCCO as well as electric field-effect devices. Some of these devices hold considerable promise for the eventual combining of low-voltage Josephson technology with high-voltage semiconductor technology.

### **Fundamental Studies**

Advances in the reproducible fabrication of high quality HTS films have enabled their use in the study of several basic physical phenomena. Epitaxial films have helped to elucidate the effects of large material anisotropy on both equilibrium and non-equilibrium electrical transport. In high current density studies, which are difficult to perform on single crystals, anisotropic effects on flux pinning and vortex motion have been quantified. The new phenomenon of "intrinsic" large flux pinning by the layered crystal structure of the copper oxide was first identified in YBCO films with the magnetic field aligned parallel to the  $\text{CuO}_2$  plane. Combined studies of particle irradiation effects on films, crystals, and bulk materials have clarified the limits to flux pinning and loss-free conduction. Likewise, the role of thermally-activated flux motion or vortex lattice melting in limiting critical currents at high temperature has been studied extensively in films.

The formation of epitaxial high-temperature superconductor-insulator superlattices has enabled systematic studies exploring the effects of interlayer spacing, coupling, and reduced dimensionality on the HTS state. In this context, it is necessary to recognize the importance of the insights provided by complementary studies on LTS films, multilayers, and structures. These systems have been models for studies of reduced dimensional and dimensional crossover effects, the superconducting-insulator transition, properties of quasi crystal and fractal geometries, squeezed quantum states, and macroscopic quantum tunneling.

Multi-source layer-by-layer deposition techniques have facilitated the formation and study of metastable phases and structures of HTS materials that can not be produced by conventional thermal processing. These studies have provided an improved understanding of the growth process in the complex crystal structures. They have led to the recognition of the subtle but significant differences that exist among the different classes of high-temperature superconductors and that are influenced by details of the deposition environment (e.g., oxygen partial pressure). Insights into the stability of the crystal structure and the interdiffusion processes have been advanced through microanalytical studies of superlattice heterostructures.

### **B. Research Opportunities**

#### **Improved Understanding of Film Growth and Properties**

There is not yet a complete understanding of the nucleation mechanisms on various kinds of substrates (crystalline, polycrystalline, and amorphous). Examination of the initial stages of grain and unit cell formation is needed. Much could be learned from such studies, including control of the wetting process.

Interfacial reactions during film growth and interdiffusion with substrate material have not been completely categorized, especially for ultra-thin layers and multilayers. The effect of these phenomena on the superconducting properties of the films should be more completely studied.

There are possible analogies to the epitaxial growth of semiconductors, which have not been fully exploited in the deposition of HTS films. These include strain-layer-superlattices akin to III-V semiconductors and the possible role of surface reconstruction

similar to silicon. In multilayer active device structures, such as S-N-S Josephson junctions, the normal layer deserves as careful a study as the superconductor layer. In all film growth research, it is important to realize that a description of the interfaces must be obtained on a scale of atomic and unit cell dimensions. Correlation of thin film and interface properties with film composition and structural perfection is also important.

To date there has not been an experimental demonstration of S-I-S Josephson junctions fabricated with HTS cuprate films. Possibly new composition and growth effects should be studied in order to present a successful demonstration with barriers free of pin holes and variable-range hopping conduction mechanisms. Such a demonstration could enable wider practical applications as well as improved fundamental understanding of the materials. It could even lead to HTS tunneling spectroscopy.

In order to understand the Josephson weak link properties of grain boundaries, a number of important questions need to be resolved. Why are clean and abrupt grain boundaries Josephson weak links? Can the properties of such weak links be controlled and further improved to meet the needs of high performance Josephson junction applications? There is a strong incentive to establish whether this weak link effect can be sufficiently reduced, or essentially eliminated, by some process or technique. This would allow textured HTS films to be used for demanding bulk transport applications (i.e., applications where low surface resistance,  $R_s$ , or  $J_c > 10^6$  A/cm<sup>2</sup> are required). Solutions to these grain boundary/weak link problems would have major impact on the course of HTS thin film technology development.

Another class of HTS Josephson devices is thin film sandwich structures, such as the interesting YBCO-PrBCO-YBCO devices. However, the conduction mechanism of these films is not understood. The PrBCO barriers do not obviously behave as either insulators or normal metals. Elucidating the conduction mechanism might provide clues to alternate structures or, conceivably, suggest new physics.

### **Circuit and Device Fabrication**

As HTS thin films and Josephson devices continue to advance and evolve, careful and detailed characterization of their normal and superconducting properties will be required to effectively evaluate their performance limits and to determine areas where further materials development is essential. Noise and transport properties in high magnetic fields are of particular importance because of both the impact of these properties on possible device applications and the insights such measurements can bring to the understanding of the basic materials properties.

Advances in HTS devices and circuits will also depend on obtaining improved dielectric substrate materials. Ideally, these should be twin-free and atomically flat surfaces. Improved preparation and/or the use of different materials are needed to obtain the desired material properties, including better lattice and thermal expansion coefficient matches to the superconducting film and lower loss tangents. Lower dielectric constant substrates are desirable for digital interchip interconnects and possibly for millimeter wave integrated circuits, where high dielectric constants might require superconducting films to be patterned on a size scale (and with acceptable tolerance) that is difficult to achieve.

Also needed are materials with these properties that can be deposited on 3 - 4" diameter substrates. Better mechanical strength is important as well. The research opportunities posed by substrate selection could have a major impact on future advances in HTS circuit

fabrication. It may also be fruitful to explore methods of more rapidly screening candidate substrate materials.

The basic device parameters used to describe film quality need to be improved -- at least for some applications. These are critical current density, surface resistance, and critical temperature. These properties should, of course, continue to be correlated with the structural properties of the films.

There are also research opportunities for depositing thicker films at higher deposition rates over non-planar surfaces. These films might find application in coating the interior of three-dimensional structures as cavities or waveguides.

The deposition of good quality films at lower temperatures could open up important new opportunities for application of HTS circuits. For example, deposition under 500°C might permit the use of selected semiconductor films as contacts in novel devices. Another, more radical departure from conventional deposition techniques could be successful in depositing good quality films on amorphous substrates. If this could be achieved and could be coupled with extremely low-temperature depositions ( $< 400^{\circ}\text{C}$ ), then one could consider depositing HTS films on polyimides. Applications might include flexible, low thermal connection from the cryogenic side, using a low dielectric material in HTS digital interconnections and improved bolometers, providing unique geometries for SQUID circuits, and even perhaps for magnets and wires. The issue of whether high (or even "good") quality HTS films can be prepared without the requirement for epitaxy is still open and could have major practical implications.

The properties of HTS films and wires of very small (submicron and nanometer) dimensions are presently unknown. These properties should be explored for potential device applications.

The "medium-temperature superconductors" (MTS), BRBO and BKBO, offer extremely interesting device applications. Tunneling experiments have revealed that they have BCS-like isotropic energy gaps, although not in complete MTS thin film structures. It is reasonable to suppose that tunnel junction quality similar to that of low-temperature superconductors may be obtained. With a  $T_c$  of 30 K, one can expect excellent properties if operated  $\leq 18$  K. This is a significantly higher operating temperature than that of NbN, and completely avoids the more difficult cooling by immersion in liquid helium that Nb devices require. The ease of refrigeration coupled with possibly excellent tunnel junction characteristics invites consideration of these materials in digital, RF, and IR sensor circuits.

The invention of novel superconducting circuits and novel superconducting-semiconducting hybrid circuits also presents engineering research opportunities. For example, all HTS Josephson devices to date have non-hysteretic current-voltage characteristics. For this reason, they have been proposed as the active switching elements in Single-Flux Quantum (SFQ) logic, a collection of logic family that requires non-hysteretic junctions.

Since the use of HTS switching elements in SFQ could significantly increase performance, this area merits further research. However, full demonstrations of these circuits will require advances in testing technology of the circuits operating at clock frequencies of tens of gigahertz. Furthermore, their incorporation into useful systems will require architectural studies and optimization. This committee is not properly constituted to recommend research in this field other than to urge that similar criteria be applied as to novel device concepts. Careful and critical analysis of the impact of these circuits in system performance should precede extensive experimental development. Questions of margins, total chip

## **- New Research Opportunities in Superconductivity -**

power requirements, clocking, testing, and choice of memory (or evaluation of system performance without memory) need to be answered first. The committee does recognize, however, that research in circuit design in general is a valid means to uncover applications of superconductivity to digital systems. A generalization of this approach, which may prove fruitful, is to have a system architect who is knowledgeable in superconducting devices work with circuit designers in order to develop novel approaches to exploiting superconductivity.

Research opportunities exist for LTS circuits as well. The availability of niobium-based junction fabrication technology will facilitate the demonstration of unique device concepts with a controlled fabrication framework. These facilities will continue to be a source of detectors and sensors for other fields of science such as astronomy and geophysics. Junction arrays may be important for the detection and generation of electromagnetic radiation utilizing coherence properties of the array structure.

The use of superconducting devices and arrays of devices as model systems for problems in other areas of condensed matter physics presents continuing opportunities for study of statistical mechanics, chaos, macroscopic quantum tunneling, and squeezed quantum states. The availability of microSQUID's will provide important opportunities for biological research and research on mesoscopic phenomena.

LTS junctions, wire arrays, and multilayers will continue to serve as model systems for phenomena initially observed in HTS materials. They will offer advantages in more controllable material properties and more precisely known parameters. Ultra-thin superconducting films may provide input to the fundamental understanding of the role of a single  $\text{CuO}_2$  plane in high-temperature superconductors. Multilayers and bilayers may be systems in which exotic mechanisms for superconductivity, such as the excitonic mechanism, may be found. Additional work is needed in this area.

The combination of junction fabrication technology, either Nb or Al, together with nanometer-scale lithography will permit the study of the interplay of superconductivity with Coulomb effects, such as single electron tunneling in the mesoscopic regime. Work in this area may reveal theoretically predicted phenomena, which are the electrical dual of the Josephson effect.

Niobium nitride technology is developed to the level of niobium technology. If there was a need for the development of devices operating above 10 K, this technology could be developed further.

### **Superconducting Device Physics**

First generation HTS Josephson junction weak links are available, but more quality control and complete understanding of high-temperature superconductivity at the atomic interface level are needed. A clear goal is a reliable S-I-S process. While not essential for successful device technology, it would possibly give the level of control needed (as is the case for Nb) even if shunting is used for devices. Alternative controlled processes for high-quality weak link structure S-N-S and S-S'-S are needed. Good Josephson properties, RF step, magnetic modulation, high  $I_c R$  ( $> 1$  mV at 77 K), and high  $J_c$  (for device speed  $J_c > 10^4$  A/cm<sup>2</sup> is a reasonable goal) are also needed.

Many novel HTS device structures have been proposed. These include semiconductor-superconductor hybrid devices, the SFFT, "dielectric base" transistors, etc. Perhaps the most useful device is yet unknown. Research into novel devices is encouraged, but with

some caution. Not every device that exploits novel physics will be useful or practical. Research funds are finite so funding support should be concentrated on those devices that promise a real advantage for superconductivity. Comparison with alternate technologies, especially semiconductors, is vital. Device speed, while important, is only part of the complete issue. Power consumption (within the device itself and in on-chip current regulation), margins, alternate means to accomplish the same function with other circuits, and ease for testing in a realistic environment must also be considered.

Although it has not yet demonstrated that it can compete in an identified commercial niche, the SFFT deserves further study because of its uniqueness and promise of very high frequency operation ( $\sim 300$  GHz). Would slightly different properties from existing SFFT's invite their use in digital technology?

A number of physics questions persist. The low carrier density of high-temperature superconductors needs to be explored as do reports of observations of electric field effects in YBCO. The physics of this field effect is not understood. Questions regarding simple film structures also need to be resolved. Equilibrium and non-equilibrium electromagnetic properties in the visible and infrared should be further investigated. Are there small non-bolometric responses to optical excitation? Can the films be used for femtosecond response? Questions on transport properties, including magnetic behavior and noise properties, require additional investigation.

Further study is needed of the potential role of superconductors in conventional electronic and opto-electronic devices, where performance is limited by conductor losses. Other areas that appear promising, but require more study, include exploitation of unique properties of superconducting hybrid devices and small-scale demonstrations of HTS-compatible architectures and devices in a LTS format that is less expensive and can be more quickly fabricated and evaluated.

### **Supporting Technology**

Since superconductivity is inherently a low-temperature phenomena, at least at the present time, the successful utilization of this technology requires a cryogenic environment. In the research laboratory, the use of liquid cryogenics (helium and nitrogen) provides reliable maintenance-free operation. This technique will always be the preferred method for cooling superconducting devices and circuits as long as the logistics of supplying these cryogenics is not bothersome.

However, there are many circumstances where closed-cycle refrigeration systems will be preferred, especially in a variety of applications away from the research laboratory environment. Accordingly, there are research opportunities in cryogenic refrigeration systems, especially in the 40 - 80 K regime, but also in the helium temperature regime (4 - 12 K). These systems could be used with the established LTS device and circuit technology. In a large majority of such cases, cooling capacities from a fraction of a watt to several watts at the desired operating temperature will be required.

In order to employ cryogenic refrigerators, considerable research needs to be conducted to improve the reliability of the refrigerators while minimizing the weight, volume, and electrical input power. Presently available cryogenic coolers have Mean Time Before Failure (MTBF) of several thousand hours of operation. For widespread acceptance of superconducting technology, the cryogenics must be "transparent" and reliability of one or more years would be desirable. The goal is to achieve the same maintenance-free operations as the household refrigerator.

**- New Research Opportunities in Superconductivity -**

Support of basic and applied research is also needed to achieve efficient and economical integration of superconducting devices, circuits, and systems to appropriate cryogenic refrigerators. This thermal management issue will vary depending on whether a small single chip (such as a SQUID), a large chip (such as a microprocessor or analog signal processor), or a large number of chips (such as a general purpose computer) are to be cooled. In addition, depending on the superconducting component to be cooled, vibration electromagnetic interference (EMI) and temperature variation may be critical issues that ought to be considered.

Another research opportunity would be to develop techniques for processing high-quality HTS materials on the interior or exterior of irregularly shaped (either metallic or dielectric) surfaces for applications such as high-power circuitry for high-energy particle accelerators, wave guides, magnetic shields, etc. In some circumstances, cast or machined bulk material may be satisfactory, but in other cases thick film techniques (such as screen printing, painting, etc.) need to be perfected for suitable thick coating with parameters ( $J_c$ ,  $R_s$ , etc.) optimized for the particular end use.

## V. BULK MATERIALS AND LARGE-SCALE APPLICATIONS

Superconducting wires and ribbons for large-scale applications require high critical current densities (e.g.  $>10^5$  A/cm<sup>2</sup>) at operating conditions and long lengths of the conductors with uniform properties and sufficient mechanical strength. Currently, none of the oxide conductors meet such requirements, although substantial progress has been made over the past three years in the fabrication of conductors utilizing HTS materials.

### A. Progress

#### Critical Current Densities

As illustrated in Figure 1, the critical current density has moved from about 10 A/cm<sup>2</sup> to the present  $6 \times 10^4$  A/cm<sup>2</sup> at 77 K and 1 T. This improvement in  $J_c$  of more than three orders of magnitude reflects the impressive progress made, since the last workshop in 1988, in the processing of short-length, HTS materials for future large-scale applications.

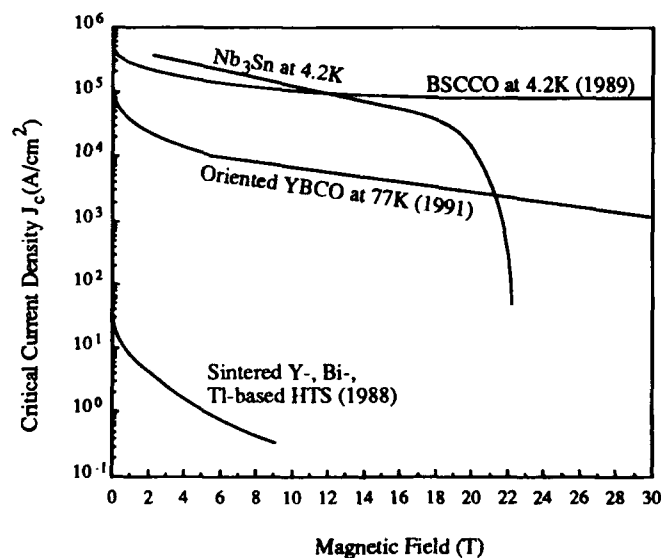


Figure 1. The dependence of critical current densities with respect to the magnetic field, indicating three orders of magnitude increase since 1988.

Among the best-known techniques developed to produce high critical current materials is melt-texture processing. First reported in 1988, this technique has been successfully used to process YBCO materials with a high  $J_c$  of  $10^4$  A/cm<sup>2</sup> at 77 K and 8 T. A major shortcoming of the technique is its extremely slow processing rate. The achievement of high texturing depends on maintaining a carefully controlled temperature gradient, which is typically achieved by moving the sample slowly in a heated oven at a rate less than 1 cm/hr.

There has been significant progress made in the processing of BSCCO superconductors in ribbon form using powder-in-tube or thin-foil coating techniques. Although the exact mechanisms for texture formation are not known, it is generally believed that directional growth is influenced by the silver sheath used in both techniques. Such silver-sheathed composite ribbons have extremely weak magnetic field dependence of  $J_c$  at 4.2 K. In fact, at fields larger than 20 T, their critical current densities are nearly constant ( $\sim 10^5$  A/cm<sup>2</sup>) and are higher than those of conventional superconducting wires based either on NbTi or Nb<sub>3</sub>Sn materials.

Since most large-scale applications require a critical current density near  $10^5$  A/cm<sup>2</sup> at 77 K and fields of 2 to 5 T, much attention has been given to techniques for flux pinning enhancement. Irradiation by either fast-neutrons or protons has been proven to be effective in this respect, with a 100-fold increase in  $J_c$  reported in some cases. However, these techniques may not be practical for industrial application because of the radioactivity generated by neutron irradiation, especially on silver-containing conductors. Significantly improved flux pinning has been achieved by phase decomposition (e.g., decomposing the YBa<sub>2</sub>Ca<sub>4</sub>O<sub>8</sub> precursor into YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> phase) or precipitation of second phases. Since the mechanisms of flux pinning in bulk or thin film samples are not understood, the task of artificially introducing flux-pinning centers in HTS wires is presently approached on an empirical basis.

### **Conductor Fabrication and Prototype Solenoid Demonstration**

The fabrication of wires is a highly sophisticated process, which will require a long, sustained research effort. At present, several techniques appear extremely promising. However, there are still many technical barriers to overcome, especially related to the ability to manufacture long-length conductors.

The Bi- and Tl-based high-temperature superconductors show appreciable capacity of alignment under cold deformation and thus are suitable for being processed into ribbons. So far, the majority of the long-length tapes are made of Bi-based materials (either in 2212 or 2223 phase), mostly because the toxicity of Tl-based materials makes their processing more demanding. Relatively long tapes (about 100 m long for BSCCO and 10 m for TBCCO) have been fabricated with critical currents larger than  $5 \times 10^3$  A/cm<sup>2</sup> at 77 K and 0 T. At fields exceeding 1 T, the values of  $J_c$  for these long tapes become impracticably low. At lower temperatures (< 20 K), these Bi-based wires have been used to fabricate wind-and-react coils, which can generate magnetic fields up to 1 T at 4.2 K. For TBCCO tapes, similar coils have been fabricated to produce magnetic fields in the order of few hundred gauss at 77 K.

The mechanical deformation properties of YBCO and its phase formation conditions make it very difficult to produce long-length, melt-textured samples. Continuous processing techniques have been developed to produce HTS melt-textured conductors in lengths of the order of one meter. To scale-up this production to much longer wires with uniform properties requires major modification of the YBCO phase diagram. It is very desirable to

facilitate high-speed processing by congruent melting rather than the peritectic reaction used at the present time.

In addition to being used as substrate/cladding materials, silver is also commonly used to form micro-composite structures in melt-textured YBCO for mechanical strength enhancement. Further advances in the area of micro-composites are needed for magnet applications of bulk high-temperature superconductors.

## B. Research Opportunities

Two main issues need to be resolved before improvements in bulk high-temperature superconductors can occur: critical current densities and fabrication of long conductors. These are discussed in detail in this section.

### Fundamental Opportunities

#### Critical Currents

*Weak Links:* Low transport critical current in bulk high-temperature superconductors is recognized as one of the major difficulties impeding their use in large-scale applications, and is related to the tendency of grain boundaries to inhibit transport current flow. During the last few years, it was shown that a part of this problem can be circumvented by using various grain alignment techniques to reduce or eliminate the areas of high angle grain boundaries. Both of these methods have provided very encouraging results. However, these do have serious limitations for producing conductors for large-scale applications (i.e., the zone refining melting techniques are too slow for fabrication of long lengths and the usefulness of the Bi-cuprates are currently limited to relatively low-temperatures (30 - 40 K) and to the plate-ribbon shaped conductors). Thus, it is important to find methods for improving the grain boundary transport behavior and/or to grow aligned grains with no restrictions in the shape of conductor cross section.

This problem may be approached in two ways. The first is to perform detailed structural characterization (misorientation, atomic position, oxygen stoichiometry, impurity segregation, etc.) of the grain boundaries and to relate this information to the transport properties of the boundaries. Such studies could elucidate the nature of the problems and might lead to possible remedies. Another approach, an empirical one, running parallel with the first, is to examine the influence of the doping elements on the transport properties of the grain boundaries. Both approaches face drawbacks. The first is extremely difficult to carry out, while the second lacks good guidelines for the selection of doping elements. However, the problem of the boundaries is so crucial to widespread applications of the high-temperature superconductors that every effort should be made to understand the properties of the boundaries and to resolve the problem.

*Flux Pinning:* One of the prominent properties of the oxides is the easy motion of magnetic flux lines under Lorentz force, particularly at temperatures near  $T_c$ . This indicates that the flux lines are not sufficiently pinned by the defects, which results in relatively low intragranular critical current densities in the high-temperature superconductors. This lack of strong pinning centers is generally associated with two fundamental properties of these oxides: strong anisotropies in the electronic effective masses along the  $a/b$  and the  $c$  crystallographic axes, and very short superconducting coherence lengths. In the very extreme case of the Bi-cuprates, loosely connected stacks of pancake-shape disk vortices on each  $\text{CuO}_2$  planes are envisioned. Because of the lack of rigidity in the flux line, the vortices remain highly mobile unless most pancakes can be pinned by defects. Also, the fact that the coherence lengths in oxides are so short implies that the most effective size for

the pinning centers is of the order of the atomic distances. The combined effect of the above suggests that very high densities of very small defects are required to reduce the easy motion of the flux lines and to improve the critical current densities in these oxides.

The above discussion raises a number of important questions regarding flux pinning. What is the best way to introduce fine and dense pinning centers, which do not deteriorate the properties of the oxide? Is it possible to minimize the effect of the anisotropy through the introduction of appropriate chemical dopants or pinning centers? For example, can the Bi-cuprates be made to be useful at 77 K and 5 T, particularly when the applied magnetic field is perpendicular to the conducting CuO planes? These are challenging questions. First of all, finding means to introduce atomic scale defects in materials that require high-temperature sintering or melt processing is very difficult. Also techniques for identifying such defects may need to be developed if the efficient pinning defects are oxygen atoms since current electron microscopy techniques are not suitable for observing individual oxygen defects. Furthermore, the flux line pinning mechanisms in these oxides are not yet fully understood. The development of a clear understanding of the pinning mechanisms requires careful characterization of the defects and the electromagnetic dynamics of the flux motion in these highly anisotropic oxides. Significant progress has been made towards this goal by the use of various irradiation techniques to introduce crystalline defects in the oxides. However, these are not practical methods for improving the critical currents in the superconductors for large-scale applications. Fabrication and processing techniques for the oxides are needed that will introduce defects similar to those formed by irradiation.

Although one of the Tl-cuprates has been found to have the highest  $T_c$  ( $\sim 125$  K), studies of this class of oxides are relatively few due to their toxicity. However, recent experimental results suggest that some of the Tl-cuprates have properties that are very desirable in regard to the weak link and the high anisotropy problems (i.e., under certain conditions, the grain boundary weak links appear to be less prominent in the Tl- than in the Y-cuprates and the anisotropy is significantly less in the Tl- than in the Bi-cuprates). For these reasons, in spite of their toxicity, studies of the Tl-cuprates deserve more extensive research efforts than are currently devoted to them.

#### Fabrication/Processing of Conductors

In general, conductors for large-scale applications will need to meet certain common properties, including minimum critical currents, strength for handling as well as for resisting deformation/fracture under Lorentz force, mechanical strain tolerance, stability against thermal disturbance, etc. To meet these requirements, conductors are necessarily composites. Some of the required components can be incorporated into the conductor after the superconductors are processed, but generally substrates are processed together to produce the necessary mechanical and thermo-electrical stabilities. Thus, detailed investigations of substrate-superconductor interactions are needed. In most cases, the interactions are deleterious to superconductors, but silver substrate is shown to be very beneficial to the growth of the aligned superconducting phases, particularly for the Bi-cuprates. Even though the effect of silver on the texture formation is well known, the mechanisms for this phenomena are not currently understood. This example indicates a need for basic studies of nucleation and growth of the superconducting oxides in relation to the formation of the textured structure. At present, very few such studies exist. For successful development of high-temperature superconductors for large-scale applications, these types of studies are indispensable.

In TBCCO, the recent report of improved flux pinning and  $J_c$  in one Tl-layered compound (such as in "1223") over those in "2223" is interesting; and this approach of reduced anisotropy for the purpose of minimizing the flux line movement is worth pursuing.

#### Mechanical Properties/Reliability

The high-temperature superconductors are mechanically brittle, ceramic materials. While thin wires/ribbons of ceramic materials can be elastically bent, the required handling of such wires, solenoid winding for magnet construction, and the magnet usage in the presence of Lorentz force necessitate the incorporation of mechanical reinforcement. Either macro-composite structure (such as Ag-cladding, Ag-core, or Ag-fiber, as well as the external jacketing of the superconductor wires/cables with high-strength materials) or micro-composite structure (such as fine Ag particles, "211" particles, embedded in the superconductor, especially YBCO) may be employed. One example of such micro-composites is the recent employment of melt-textured, silver-doped YBCO bulk magnets for levitation. These bulk magnets may be suitable for gyroscopes, energy-storage fly wheels, bearings, and transportation applications. Further advances in this area are needed to improve the performance of these devices to trap higher fields.

#### Applications

Previous reports of the Workshops on Problems in Superconductivity held at Copper Mountain, Colorado in 1983 and 1988 were optimistic about the impact of superconductivity on many large-scale applications. The enthusiasm expressed in these reports still prevails. The success of superconducting technologies in high-energy physics, the funding of the superconductor supercollider (SSC), the rebirth of interest in magnetically-levitated transportation in the United States, and the continued growth of magnetic resonance imaging (MRI) have catapulted superconductivity into a viable area for corporate and governmental investment. However, continued long-term federal support for thin film and bulk conductor development, as well as support for prototype development, is essential both to sustain this emerging industry and to open new frontiers for applications and commercialization.

Since the last workshop in 1988, significant progress in fundamental and device-fabrication has dispelled some of the earlier concerns about the viability of HTS for electronic and large-scale applications, and has encouraged researchers to re-examine possible near-term applications. However, monitors of this field should recall that the first reports of  $Nb_3Sn$  wire occurred in the late 1960's, and that it has taken in excess of twenty years to develop commercially viable material. Clearly, long-term commitments to research and development critical to applications will be needed.

#### Low-Temperature Superconductors

The discussion that follows primarily focuses on high-temperature superconductors and possible near- (1-3 years) and long-term applications. However, there are a number of reasons that strongly encourage maintaining reasonable levels of support for many LTS applications.

- Systems development issues often can be best addressed using LTS technologies and these LTS efforts will represent critical staging projects for future HTS developments and technologies.

**- New Research Opportunities in Superconductivity -**

- Many applications for high-temperature superconductors may not provide sufficient improvement in performance or savings, when compared to those available using low-temperature superconductors, to justify a refocusing of our attention to the integration of high-temperature superconductors into these areas.
- There are several issues that are more relevant to the development and support of effective applications of either kind of superconductor, but are not critical to other topical areas discussed in the report. Thus, there is a need for a balanced national program focused on both LTS and HTS development issues and technologies.

This last point is an important one because there have been numerous successful applications of low-temperature superconductivity, which have highlighted some of the common issues. These LTS applications have included:

- Magnetic resonance imaging;
- High-field nuclear magnetic resonance spectroscopy;
- High-energy physical accelerator development;
- Small superconducting magnetic energy storage systems;
- Magnetic levitation;
- Magnetic separation; and
- Custom research magnet systems.

**LTS - HTS Common Issues**

These LTS applications have led to the creation of numerous industrial efforts with total worldwide sales exceeding a billion dollars. In this development, several issues generic to superconductivity arose and still must be addressed if economic applications are to be achieved. Some of these issues are:

- An effective and responsive national program focused on applications should feature close collaborative efforts among industries, universities, and national research centers. Federal programs should encourage collaborative efforts that take advantage of the research expertise located at universities and national laboratories, but at the same time create an environment, which both promotes technology transfer to the industrial sector and strengthens educational and training programs within the universities.
- Efforts should be directed at enhancing interactions between the materials research and development communities and the communities primarily focused on applications. In particular, conductor development programs and magnet development efforts must be tightly coupled. Most of the magnet development companies within the United States do not have sufficient resources to sustain a competitive conductor development effort.
- Several subsystem problems must be addressed simultaneously with the development of HTS applications. In particular, attention should be given to refrigeration and heat transfer along with cryogen transport problems. In the past, there has been considerable investment in cryogenic engineering for helium refrigeration systems and technologies. These efforts have been critical to the development of many LTS applications. Similar concern should be focused on higher temperature cryogenic engineering to support the development of HTS systems operating well above 4.2 K.

## High Temperature Superconductors

### *Magnets*

The discovery of high-temperature superconductors led to early speculation that there would be significant growth in this industry, however it has become clear that immediate widespread commercialization is unlikely. A slow and sustained growth in applied superconductivity resulting from high-temperature superconductors is more likely, although there may be some more immediate benefits in selected areas. Recent successes in the development of HTS tape conductors point to a short-term beneficial impact on the development of magnet systems requiring fields exceeding 20 T. These systems would operate at or below 4.2 K and would integrate high- and low-temperature superconductors to extend access to magnetic fields greater than 20 T. Such systems are required for future advancements in high-field custom research magnets, improved resolution of high-field, high-homogeneity NMR spectrometers, and increased spatial resolution of *in-vivo* NMR spectrometers. Even though these applications respond primarily to the needs of the research communities, they represent a multimillion dollar commercial effort, in an area where the United States does not have a credible presence.

In addition to these areas for HTS applications, there are several lower field magnet systems that could benefit from improved efficiencies and simpler support subsystems due to operation at temperatures even moderately above 4.2 K. These include magnetic separation systems for ore concentration and pollution control, and improved high power microwave devices (e.g., gyrotrons for plasma heating applications in fusion development and possible military applications). For these applications, ac losses are not an issue, thus tape conductors are adequate. However, efforts must be directed at the development of processing methods leading to long lengths of strain-tolerant and fracture-tough composite tapes with overall conductor current densities in field of  $\sim 10^4 \text{ A/cm}^2$  or greater. Fabrication methods leading to reproducible, low-resistance and persistent junctions must also be developed.

### *Power*

Over the last ten to twenty years, there has been considerable attention focused on possible applications of low-temperature superconductivity to the power industry. These efforts have resulted in LTS demonstration projects for power transmission, SMES, and motors/generators. The information gained from these studies makes this area particularly attractive for possible HTS applications. However, ac losses will be a factor for many of these applications, making conductor configuration a more critical area for development. In addition, long-term reliability is one of the most critical issues to address in power-related applications. Most economic advantages are lost if one cannot produce operating reliabilities close to existing technologies. Even with these problems, there are growing needs that could be met with HTS technologies. Some of the most immediate successes of high-temperature superconductors in this area may result from innovative applications of these new materials to current limiting devices or current feedthroughs to low-temperature magnets.

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