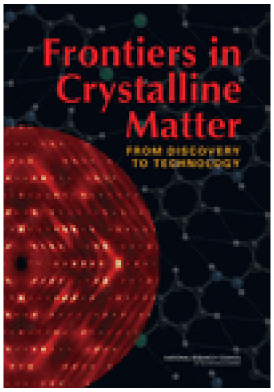

Frontiers in Crystalline Matter: From Discovery to Technology

Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth; National Research Council

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THE NATIONAL ACADEMIES
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Frontiers in Crystalline Matter

FROM DISCOVERY TO TECHNOLOGY

Committee for an Assessment of and Outlook for
New Materials Synthesis and Crystal Growth

Board on Physics and Astronomy

Division on Engineering and Physical Sciences

NATIONAL RESEARCH COUNCIL
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Cover: The technique of x-ray diffraction has long been one of the primary tools used to determine the atomic and molecular structures of crystalline materials and films. The diffraction pattern shown on the left is of the molecular compound N-(*p*-chlorobenzylidene)-*p*-chloroaniline, and the crystal structure associated with that pattern is shown in the background. Data for figures courtesy of Richard Welberry, Eric Chan, and Aidan Heerdegen (Australian National University) and Peter Chupas (Argonne National Laboratory); work performed at the Advanced Photon Source, Argonne National Laboratory.

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Preface

The National Research Council of the National Academies convened the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth to assess current work and new opportunities in the United States in the field of the discovery and growth of crystalline materials. The Solid State Sciences Committee of the Board on Physics and Astronomy developed the charge for this study in consultation with the study's sponsors at the Department of Energy and the National Science Foundation. The committee was charged to define the research areas in this field, to determine the health of activities in the United States in those areas, to identify future opportunities, and then to suggest strategies to best meet those opportunities. The complete charge is reproduced in Appendix A.

The committee that prepared this report is composed of experts from the many academic disciplines falling within this field and includes members from the different types of institutions—academic, government, and industrial research laboratories—involved with this research (see Appendix B for biographical sketches of the committee members). The full committee met in person three times (see Appendix C) to address its charge. The committee formed subgroups to study specific areas in further detail and to develop the text of the final report. At its meetings, the committee heard from experts in the field and from the federal agencies that support research in this field. Conference calls and e-mail correspondence were used to coordinate the work of the committee between meetings. This final report reflects not only the committee's concerns regarding the current level of activity in the United States in this field but also its enthusiasm and excitement for research opportunities presented now and in the foreseeable future in these areas.

As committee chair, I am grateful to the committee members for their wisdom, cooperation, and commitment to ensuring the development of a comprehensive report.

Paul S. Peercy, *Chair*
Committee for an Assessment of and Outlook for
New Materials Synthesis and Crystal Growth

Acknowledgment of Reviewers

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Meigan Aronson, Stony Brook University/Brookhaven National Laboratory,
Gregory S. Boebinger, National High Magnetic Field Laboratory,
Ian Fisher, Stanford University,
Patrick A. Lee, Massachusetts Institute of Technology,
Allan MacDonald, University of Texas at Austin,
Cherry A. Murray, Lawrence Livermore National Laboratory,
Mark R. Pinto, Applied Materials, Inc.,
Nicola Spaldin, University of California at Santa Barbara, and
Yoshinori Tokura, University of Tokyo.

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by Paul Fleury, Yale University. Appointed by the National Research Council, he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.

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Summary

A CHANGED LANDSCAPE: CHALLENGES AND OPPORTUNITIES

For much of the past 60 years, the U.S. research community dominated the discovery of new crystalline materials and the growth of large single crystals, placing the country at the forefront of fundamental advances in condensed-matter sciences and fueling the development of many of the new technologies at the core of U.S. economic growth. The opportunities offered by future developments in this field remain as promising as the achievements of the past. However, the past 20 years have seen a substantial deterioration in the United States' capability to pursue those opportunities at a time when several European and Asian countries have significantly increased investments in developing their own capacities in these areas. This report seeks both to set out the challenges and opportunities facing those who discover new crystalline materials and grow large crystals and to chart a way for the United States to reinvigorate its efforts and thereby return to a position of leadership in this field.

The two activities in this field—discovering new crystalline materials and growing large crystals of these materials—have long been intertwined. Here, "crystalline material" refers to materials in which long-range periodicity of atomic positions is critical for the material's functionality. It is noted that such materials form a class distinct from nanomaterials, the functionality of which is defined by attributes governed by one or more nanometer-sized dimensions of the sample specimen, whether crystalline or amorphous. Once a new crystalline material is found to be either sufficiently interesting scientifically or relevant for an application—

or as often happens, both—large single crystals of that material are needed for detailed study. Because of common heritage, shared resources, and strong educational bonds, it is natural to combine these related activities—the discovery and growth of crystalline materials (DGCM)—in a single study. The growth of thin, two-dimensional crystalline films also is included in this study because it shares many common scientific and technological goals with the growth of bulk, three-dimensional materials.

The research activities falling under the DGCM umbrella are broad, spreading over traditional academic disciplines such as chemistry, materials science, and physics and undertaken in institutions such as university, government, and industrial research laboratories. Research in DGCM covers subject matter such as electronic, magnetic, optical, and structural phenomena. This diversity notwithstanding, there is a clear identity associated with researchers involved in DGCM. As can be seen from the attendance at scientific conferences in this area, it is a fairly small community, with exacting and specific technical needs and educational requirements.

While academia, the national laboratories, and private industry all have important roles in this field, industrial research laboratories historically have provided a particularly critical environment for the flourishing of DGCM activities. There, technological advancement in sectors such as the semiconductor industry, optical communications, and displays has required not only applied research to improve the performance of materials such as silicon, glass, and liquid crystals but also basic research into their fundamental properties. Advances made in DGCM in these laboratories were the consequence of a continual interplay between device development and basic research in physics and chemistry as well as close contact among the relevant technical communities—the material scientists, the crystal growers, and the developers of technical devices. This environment also served as a critical training ground, where the specialized techniques needed for success were passed on to new generations of crystal growers.

Almost a century after the discovery of Bragg's law, by which x-rays scattered from crystalline matter were used to establish its periodic structure, DGCM research not only has a strong legacy of foundational discovery but also retains great intellectual vitality, high technological relevance, and seemingly unending promise for discovery. The demand for crystals and new materials remains strong. The past 20 years have witnessed great advances in measurement capabilities in the United States across the whole range of facilities. At small and medium-size facilities, factors such as computer-assisted automation, new spectroscopies such as scanning probes, and the commercialization of diagnostic techniques have played a large role in driving demand for new materials. At the large national laboratories, several new U.S. synchrotron x-ray sources have been built, and new capabilities in neutron scattering have been installed at the National Institute of

Standards and Technology (NIST) and at the Oak Ridge National Laboratory. In addition, the National High Magnetic Field Laboratory, which opened in 1994, represents new capabilities in high magnetic field research, including a unique capability for studying the energy states of electrons in crystalline metals. These facilities represent some of the best characterization facilities in the world, creating opportunities to study, in great detail, novel magnetic, electrical, and structural properties of materials for which large single crystals are available. However, balance is needed between supporting the development of world-class characterization facilities and supporting the best materials growth; simply put, using the best neutron scattering facility in the world with suboptimal samples will engender suboptimal results.

The excitement and the promise of DGCM-based research already have been reflected in major initiatives abroad. For example, through projects such as Exploratory Research for Advanced Technology (ERATO), Japan now leads in the growth of strongly correlated oxides and organics both in bulk and thin-film form. China has significantly increased its commitment to develop expertise in crystal growth and basic materials research. And in certain areas such as ferroelectric crystals for information storage and actuator applications, China has developed the capability to produce large single crystals not currently available in the United States. The importance of international competition extends beyond national pride, however. Historically, those institutions that develop new materials are the ones with the best chance to exploit the resulting science and technology opportunities, the latter through intellectual ownership.

Despite the promises offered in this field, DGCM research in the United States today is substantially weaker than it was 20 years ago. The large industrial laboratories that historically led the nation in discovering new materials and in developing techniques for growing pure crystals no longer engage in these activities to a significant degree. DGCM research also has not found a “natural” home in the academic world in the United States. The nature of the work is inherently multidisciplinary and does not readily fit into the traditional, departmental structure of U.S. universities. Further, the start-up and operating costs of a DGCM researcher can be significantly higher than those of the typical university single investigator. Consequently, despite fundamental discoveries by DGCM researchers that have led to the establishment of entirely new subfields in condensed-matter physics, materials science, and chemistry, the presence of these researchers in U.S. universities is low. The net result of industrial laboratories’ no longer engaging in DGCM research and the low level of research in the academic sector is that scientists and engineers in the United States face significant constraints because of inadequate access to crystals for scientific research and technology development, which frequently puts them, and the United States in general, at a competitive disadvantage.

RECOMMENDATIONS

This report was commissioned in the context of the deteriorating DGCM capacity in the United States. The National Research Council's Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth was charged with assessing this research area, identifying future opportunities, and recommending strategies to enhance opportunities in the United States (see Appendix A). In response to that charge, the committee concludes that DGCM remains a critically important area in condensed-matter research, and because of a change in the landscape in the United States, the continued competitiveness of the United States in this field requires that concrete and substantive steps be taken. The steps recommended by this committee are presented in the following paragraphs and are discussed more fully in Chapter 4 of the report.

Recommendation 1. Develop a focused, multiagency initiative to strengthen U.S. efforts to discover and grow new crystalline materials.

Crystalline materials research impacts a broad set of technologies encompassing energy, defense, information, communications, and industrial standards, and it straddles a number of traditional academic disciplines such as chemistry, materials science, and physics. Thus, an initiative for establishing and sustaining programs specifically directed toward driving the discovery and synthesis of new crystalline materials should be coordinated among agencies that fund research in these areas, including the National Science Foundation, the Department of Energy, the Department of Defense, and the Department of Commerce (NIST). The broad goals of such an initiative should be to establish crosscutting synthesis capabilities, educational thrusts, and openly available cyber resources that will enable broad research efforts. Programs funded through such an initiative would range from small-scale equipment run by single investigators to large-scale, centralized facilities for the discovery, growth, and characterization of crystalline materials, a range necessary to address the spectrum of research needs of this field.

Recommendation 2. Develop discovery and growth of crystalline materials "centers of expertise."

Funding should be provided for one or more "centers of expertise" that are capable of addressing the broadscale issues arising in the DGCM area. Centers have a role that cannot be filled by small programs. In contrast to small programs, centers can provide the infrastructure needed to house specialized facilities and the robust multidisciplinary environment needed for cutting-edge materials development. The purpose of these centers would be to address a range of problems, including those requiring large-scale facilities, facilities for using toxic chemicals, and facilities requiring significant technical support. In addition, the mission of one or more centers should be to address problems of crystal growth of immediate interest to U.S. industry. Working on a cost-recovery basis, these industry-oriented centers would be responsible for forming strong industrial partnerships, engaging in technology development with their industrial partners, and maintaining the expertise and infrastructure needed for industrial crystal growth. These centers also should support a small number of education and training programs that explicitly address the discovery and growth of crystalline materials and should complement the university-based education in DGCM addressed below in Recommendation 3.

Recommendation 3. Develop and sustain programs specifically designed to strengthen and sustain education and training in the field of the discovery and growth of crystalline materials.

In order for the United States to have a strong and sustainable effort in the discovery and growth of crystalline materials, federal agencies should develop programs and policies that focus on providing the specific and often unique education and training needed for those engaged in discovering new crystalline materials and synthesizing large crystals. Special attention should be given to developing federally funded programs that encourage academic organizations to prepare cross-disciplinary curricula and opportunities for educating the United States' next generation of DGCM scientists.

Recommendation 4. Promote cultural changes to develop and solidify academic programs in the field of the discovery and growth of crystalline materials.

The culture of U.S. science, as currently promulgated in the departmental or discipline-centric environment of universities, frequently does not reward DGCM synthesis research as much as it rewards measurement science. In order for the United States to have a strong and sustainable effort in the discovery and growth of crystalline materials, federal agencies should develop programs and policies that make it attractive for universities in the United States to hire crystal growers and promote robust research programs in this area by providing ample funding specifically for such work. The committee specifically urges that more crystal growers be hired into tenure-track positions at universities.

Recommendation 5. Develop a network approach for research-enhancing collaborative efforts in the discovery and growth of crystalline materials while preserving intellectual ownership.

New approaches to communication are needed to advance the field of discovery and growth of crystalline materials. The internal collaboration common in industrial laboratories formerly engaged in DGCM activities greatly aided the development of materials by providing rapid responses to synthesis needs as well as rapid feedback from measurement to synthesis. A similar approach to communication among researchers should be promoted through programmatic means by the federal agencies. The committee envisions a "DGCM network" as a novel approach to scientific collaboration that would both fulfill conventional needs for greater communication and enable the new modes of collaboration afforded by cyber infrastructure. The envisioned DGCM network would provide a virtual forum for organizing synthesis efforts, crystal growers would be able to announce the availability of new compounds, and a measurer would be able to request collaboration with a crystal grower to meet the measurer's need for a specific sample. The envisioned DGCM network would also provide access to information in the physical archive of already-synthesized samples stored in individual laboratories throughout the country, further enabling collaborations. At the same time, policies and procedures for participating in the network would be designed to enhance collaborative work while protecting the intellectual contributions of researchers who discover or develop novel crystalline materials.

1

Introduction

FOCUS AND SCOPE OF THIS REPORT

Improvement in materials has been a hallmark of the advance of civilization. Prehistoric and historic periods, such as the bronze and copper eras, indeed often carry labels in which a development in materials technology is seen as a defining feature. This also holds true in archaeological classifications. That is not to say that advances in materials technology are determinant; rather they provide a background against which events have occurred.

Scientific advances of the 20th century completely redefined the interplay between experiment and theory in the understanding of materials, providing the modern basis for the formulation and solution of scientific and technological problems. The advent of x-ray diffraction studies of the atomic architecture of materials was central to these advances. In many cases of great importance, the availability of crystalline samples, either natural or synthetic, was the crucial factor in enabling such studies.

The world is now entering a new age in which modern experimental capabilities allow manipulation at the level of the single atom and molecule, as well as interrogation and control of properties of solids at this scale. Taking full advantage of such capabilities for tailoring the properties of new functional materials requires the sophisticated control over materials preparation protocols that lies at the forefront of the development of single-crystal growth technology. Advancing the forefront of crystal growth is central to the strength of technology-based industries and to the scientific enterprise on which the technologies rest. Sensitive equipment now essential in medical and national security areas depends on high-quality single-crystal detectors. The search for ever better radiation detector materials is an important part of the new materials work that goes hand in hand with single-crystal growth. This is just a part of the broad search for functional new materials and the research and development that follow, which are vital to the competitive health of this nation's high-technology industries.

The intent of the present study by the National Research Council's Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth is to investigate whether an articulated agenda on the growth of crystalline materials would serve the national interest scientifically and technologically. The formal charge to the committee is presented in Appendix A.

The discovery and growth of crystalline materials (DGCM) encompass a broad range of activities involving both theory and experiment. One very substantial activity is the growth of large boules (synthetically grown single-crystal ingots), most notably defect-free silicon for the semiconductor industry. Silicon technology designed for flat-panel displays is now being adapted to produce large-area multicrystalline solar panels. Another significant activity is the development of laser materials, using both known and new materials, for novel communications applications. Various gamma-ray detection arrays in high-energy physics experiments depend on discovering new, or employing known, single-crystal materials. Single crystals are increasingly used in metallurgical settings, for example, as turbine blades in jet engines. Two-dimensional films of single crystals are increasingly used in the semiconductor industry, and the long-term projection is for even more use of such material. Diamond films are one example of an emerging technology with many applications, including wear-resistant coatings on cutting tools as well as high-power transistors. Crystalline material also promises to play an integral role in meeting homeland security needs, with semiconductors offering significant advantages in efforts to develop more-sensitive radiation detectors. Finally, crystallization of organic materials, highly important in biological and biochemical sciences, is receiving attention for its potential in application-based uses such as photovoltaics and electronics. All of the applications mentioned above are based on a physical functionality imbued by a material's crystalline structure.

Crystal growth is a diverse field. Crystals can be grown using a remarkable variety of techniques. Many people are familiar with the growth of rock candy sugar crystals from aqueous solution. This method is a prototype for the growth of intermetallic compounds from molten metal solvents, hydrothermal growth of quartz crystals, and flux growth of oxides, for example.

In preparing this report the committee necessarily had to delineate the scope of the study, and in doing so it left out activities and research fields that arguably could have been included. The committee focused on crystalline materials, both bulk and thin-film, with unique physical properties. It did not seek to describe comprehensively either the marvels of crystal growth or its successes, but rather to assess U.S. national strengths and weaknesses in these activities and to address what responses appear appropriate based on this assessment. The committee did not consider protein crystallography or crystals for the pharmaceutical industry. While these areas are extremely important, they lie outside the scope of the committee's charge. The committee also did not consider nano-sized material to be within the scope of this report. While there are many overlaps in applications between nano-sized material and the crystalline material discussed here, there is much less overlap in the scientific realm. Further, the historical and current levels of programmatic support for these two research areas differ significantly. U.S. agency leaders in the physical sciences and engineering have recognized the importance of nanoscience and engineering (nanomaterials), and they have established strong national initiatives to address those opportunities. The enduring importance of the discovery and growth of crystalline materials has not received the same recognition and support. Therefore, the committee limited its assessment to the current health and future support needs for research in bulk and thin-film crystalline material.

Basic research in solid-state chemistry and condensed-matter physics uses crystal growth as a technique in the search for new materials. After creating a new material, much effort is often required to produce the large crystals needed for physical measurements of new, interesting properties (Box 1.1). Many materials of interest are significantly anisotropic and in many cases exhibit two-dimensional or even one-dimensional mechanical or electrical properties. A compelling rationale for producing single crystals of such materials clearly extends to application. The ability to grow crystals of a known material is generally not straightforward, and continuing advances are being made in growth techniques coupled with theoretical insight. For applications, the goal is often low-defect-density or defect-free crystals; achieving such perfection requires detailed understanding of the system under investigation, coupled with in-depth knowledge of crystal growth techniques.

Crystal growth includes a variety of activities that have been profoundly important from both basic science and technological standpoints. Such activities are often driven by individual researchers in close symbiotic alliance with measurement and theory colleagues. Many questions arise naturally in the context of seeking to strengthen support for crystal growth: What kind or kinds of facilities provide the best approach to the science? How should the search for new materials fit with crystal growth production activities? How can it be ensured that there will be an adequate workforce with high competence in crystal growth science and technology and the new paradigms needed for conducting research in this new age of material control? These important issues are addressed later in this report (Chapter 3). It is clear that crystalline perfection is a route to new functional possibilities for materials. Experimental and theoretical investigations on new as well as known materials will have important payoffs for both science and technology.

BOX 1.1
Growth of Large Crystals for the National Ignition Facility

In order to meet the needs of the National Ignition Facility at the Lawrence Livermore National Laboratory (LLNL) for hundreds of half-meter-scale, high-quality single-crystal plates of potassium dihydrogen phosphate, KH_2PO_4 (KDP) (see Figure 1.1.1) and deuterated potassium dihydrogen phosphate, KD_2PO_4 (DKDP), the Laser Program at LLNL undertook a major effort to develop a method for growing these crystals at high production rates. This effort resulted in a production technology capable of producing half-meter boules at 5 to 10 times the rates previously possible. In addition, this effort led to a mechanistic understanding of the physics of KDP growth as well as the connection between growth defects and optical performance.

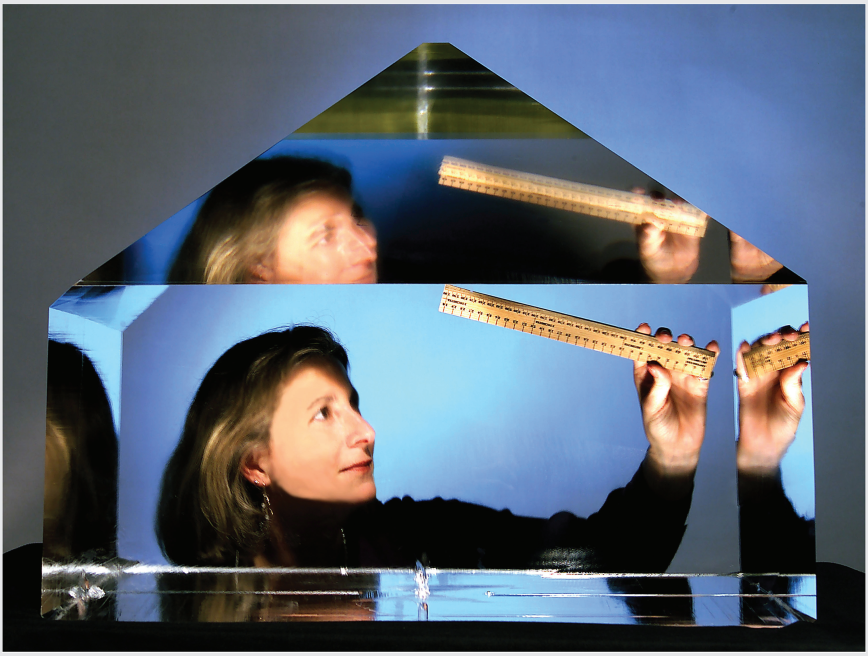

FIGURE 1.1.1 This potassium dihydrogen phosphate (KDP) crystal, weighing 701 pounds and measuring approximately 26 inches by 21 inches by 23 inches high, was produced in a record 52 days through a rapid-growth process perfected at the Lawrence Livermore National Laboratory (LLNL). A crystal of this size would have taken 2 years to grow using conventional methods. The enormous crystal was sliced into plates for use in the National Ignition Facility (NIF), a giant laser under construction at LLNL. The crystal plates (½ inch thick and 16½ inches square) are used to convert the laser's infrared light beams to ultraviolet light just before the beams strike the laser target. About 500 of these plates are needed for NIF. SOURCE: Courtesy of Lawrence Livermore National Security, LLC, Lawrence Livermore National Laboratory, and the Department of Energy under whose auspices the work was performed.

ORGANIZATION OF THE REPORT

The balance of this introductory chapter uses four examples from history to illustrate how the discovery and growth of crystalline materials have played a leading role in a range of scientific and technological advancements. Chapter 2 turns from history to the future, setting out three grand challenges facing those engaged in the discovery and growth of crystalline materials. These include meeting the needs of information and communications systems with new crystalline materials, developing materials for the next generation of energy sources, and bringing to fulfillment the long-sought capability of designing, from first principles, materials that meet specific technological requirements.

Chapter 3 examines the current health of DGCM activities, including efforts to educate those entering this field, and the levels of financial support being provided by industry and federal agencies. It also discusses efforts other countries are undertaking to support these activities. The final chapter contains strategies for addressing some of the shortfalls currently facing those engaged or wanting to engage in this field, and for developing the structures that will increase opportunities in this field.

The appendixes provide background information about the committee and those activities engaged in by the committee in preparing this report as well as discussions on synthesis techniques for crystalline growth, the classifications of materials, and a more detailed development of some of the structural recommendations made in the concluding chapter.

HISTORICAL EXAMPLES OF CRYSTAL GROWTH AND TECHNOLOGY

Following introductory remarks, this section examines four examples from the history of crystal growth that illustrate the remarkable intertwining of fundamental and applied science common to this field. These examples—from metallurgy, semiconductors, thin films, and high transition temperature (T_c) superconductivity—represent leading-edge activities in which the ability to control the growth of crystals not only led to the advancement of science but also made a direct and significant contribution to society in general.

Naturally occurring crystals have always attracted attention. A natural quartz crystal is seen in an ancient medicine bag displayed at Mesa Verde National Park in Colorado. The double refraction of Iceland spar (calcite) and its investigation opened the door to optical polarization. Pasteur's identification of the handedness of crystals and its connection with the rotation of plane-polarized light is another remarkable observation (see Box 1.2). Such scattered findings were paralleled by a disjoint mathematical development resulting ultimately in the theory of space groups, which was complete before the discovery of x-rays and the ability to verify

BOX 1.2
Pasteur and the Discovery of the Relationship Between Natural Optical Activity and Crystal Morphology

The French 5-franc note honoring Louis Pasteur contained mirror images of faceted crystals (Figure 1.2.1). Pasteur, in his studies of wine fermentation, noted that tartaric acid crystallized in two mirror-image habits, only one of which occurred in grapes. He was able to separate crystals of these two morphologies under the microscope and show that one rotated plane polarized light counterclockwise, the other clockwise, reflecting a preferred handedness in the naturally occurring variant.

The finicky nature of crystal growth is also demonstrated by this example, because above 27°C only one morphology forms. Thus, had Pasteur worked in a warmer climate or on a warmer day, this discovery would have been postponed.

FIGURE 1.2.1 French 5-franc note honoring Louis Pasteur, containing mirror images of faceted crystals inside the vertices of the braided ellipse. SOURCE: Courtesy of Z. Fisk, University of California, Irvine.

atomic crystalline order experimentally. The tensor description of material properties also predates x-ray diffraction studies of solids.

It is no exaggeration to state that developing the ability to analyze crystals using x-rays was key to ushering in the modern scientific and technological era. With that ability, the nature of crystalline structures began to reveal itself to researchers. Such phenomena as the double refraction of calcite and piezoelectric and ferroelectric behavior could now be understood on an atomic scale. In turn, the deeper understanding of materials from such studies opened new avenues to industrial use in, for example, the advancing technological requirements of the telephone industry. As early as the 1930s, Bell Laboratories began investing in materials research, leading not only to a better understanding of many fundamental constructs of crystalline materials, but also ways to use that understanding in a wide range of applications. For example, it was discovered that the piezoelectric properties of quartz are highly dependent on crystallographic direction. As a result, the so-called ZT-cut was adopted for use when temperature insensitivity is desired. In the late 1930s, Bell Laboratories assembled a significant fraction of the nascent solid-state physics expertise in semiconductor material. Research on that material led swiftly to the realization of the dominant deleterious effect of grain boundaries on electronic properties. It also led to the discovery of the technique of zone—and later floating zone—refining: a technique that opened completely new vistas in semiconductor research and applications.

The strong coupling within the semiconductor research activities that led to these discoveries spread to other areas of research at Bell Laboratories. For example, the study of the magnetic properties of oxide garnet crystals was based on the technique of flux growth of single crystals, pioneered by J.P. Remeika and L.G. Van Uitert. These single crystals allowed Bell Laboratories researchers to exploit a hunch with respect to interesting properties of the crystals that had been suggested by E.F. Bertaut of the Laboratoire de Crystallographie in Grenoble, a hunch Bertaut had not been able to explore because he had lacked a source for the single crystals.

The story of crystalline thin films leading to quantum-well structures paralleled the developments in bulk crystals. Starting with the work of F. Fang and colleagues at the IBM Thomas J. Watson Research Center on silicon-based field-effect transistors, the artificial construction of tailored layer structures was seen as a route to create two-dimensional electron systems. Development of molecular-beam epitaxy (MBE) by A. Cho and J. Arthur at Bell Laboratories allowed unprecedented control of crystallinity in multilayer structures. The deep interplay between basic physics and application was enabled by the remarkable and continuously improving ability of the film growers to increase charge carrier mobilities through increasing crystalline perfection. The basic physics that came from this effort proved a complete surprise, and the surprises continue.

A startling development in engineering materials was the discovery that intermetallic compounds can be used as structural materials. Conventional wisdom had held that chemically ordered intermetallic compounds were much too brittle for most usual metallurgical methods of use and handling. That intermetallic single crystals are now used as turbine blades in jet engines is remarkable both in light of that conventional wisdom and in that scientists and engineers had the courage to undertake the extensive research necessary to determine otherwise.

Many materials whose properties depend on highly anisotropic crystal structures find important use in polycrystalline form. The ferroelectric barium titanate, whose useful properties derive from its non-centrosymmetric structure, is used in a wide range of applications, from the dielectric material in capacitors to piezoelectric material in transducers such as microphones. The active material in Polaroid film is herapathite, a crystal originally discovered growing in a container of urine from a dog fed quinine by a doctor. Under a microscope, superimposed crystals showed reduced or no light transmission. Edwin Land, founder of the Polaroid Corporation, used this observation in an unusual way, grinding synthetic herapathite into small crystalline needles that could be aligned by stretching them in a plastic sheet. In this case the properties were only known from single-crystal observations, but their extremely anisotropic character was exploited by clever processing.

Academia, the national laboratories, and private industry have all been important components of the crystal growth community. In the past decade the industrial research laboratories have downsized to the point that this traditional balance has been dramatically altered. Industry clearly has needs that require close focus and tightly controlled communication to the outside. This seems particularly to be the case for both the semiconductor and pharmaceutical industries. The academic and national laboratory efforts are more parallel, with national laboratories tending to cut across disciplinary divides in basic research areas more easily than do universities. Materials science departments have development efforts directed toward improving the size and quality of crystals, while chemistry and physics studies of single crystal focus on new materials: new structures tend to be of interest to chemists and new functionalities of interest to physicists. The area of crystal growth has considerable commonality of purpose between the universities and national laboratories. National laboratories have the ability to assemble teams in a way not always available to universities. This raises the question of whether a more natural setting for what might be called crystal-driven research would be at national laboratories, or whether an equally effective research program can be built from a distributed effort across university–national laboratory boundaries.

The metallurgist R.W. Cahn, in *The Coming of Materials Science,* has discussed the study of crystals as a *parepisteme:* an inquiry at the boundary between disciplines, not generally a freestanding study in and of itself, but one that is ancillary and important to other investigations.[1] Of the many interesting paths that one can follow into the history of the subject, four that have important contemporary relevance are presented below.

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[1] R.W. Cahn, *The Coming of Materials Science,* Oxford, United Kingdom: Elsevier Science, 2003.

Example from Metallurgy: Single-Crystal Superalloys for Jet Engine Turbine Blades

A remarkable and successful example of the commercialization of single crystals involves single-crystal superalloys (alloys able to perform in extreme environments) for jet engine turbine blades. This example was chosen to illustrate the unexpected way in which control of crystal growth can be utilized for tailoring commercially important products.

In turbine blade applications, the general goal is to increase the operating temperature of the engine. Higher temperatures provide greater fuel efficiencies, ultimately leading to greater thrust-to-weight ratio, as shown in Figure 1.1. However, at elevated temperatures (typically above 50 percent of the melting temperature of the engineering material), creep deformation—a slow plastic strain developing below normal yield strength—occurs. Deformed components in a rotating environment such as a spinning turbine can lead to catastrophic failures. In a polycrystalline sample, the primary mechanism for creep involves atomic movement along boundaries of given crystals. Because these boundaries are eliminated in single crystals, such turbine blades deform less at elevated temperatures.

Before the 1970s, industrial-scale production requirements for single-crystal turbine blades were considered too expensive to be a viable technology. In the early 1970s, however, improvements to casting methods, developments in cooling schemes, and advances in solidification modeling using multicomponent thermodynamics significantly improved the manufacturing of superalloys. Single-crystal turbine blades now operate in environments at 85 percent of their melting temperatures.

Further improvements were achieved in the metallurgical development of the material used for the blades. The workability of metals usually depends on a plasticity coming from the ability of like atoms to slide past one another in the metallic lattice. In contrast, intermetallics with their crystallographically ordered arrays of unlike metal atoms generally show brittle fracture arising from the lack of interchangeability of unlike atoms under shear. This brittle fracture limits strength, albeit at a large value in certain cases. Superalloys for jet turbines were developed that gained the rigidity associated with intermetallics but had sufficiently elevated brittle limits at operating temperatures that they could be incorporated safely into jet turbines.

The effect of this improvement in material and increased operating temperature is captured for selected engines in Figure 1.1. The increased temperature capability of single crystal (compared to polycrystalline) alloys is conservatively 50°C to 100°C for the base metal, which translates to an increased efficiency of roughly 25 percent and a resulting significant savings in fuel consumption.

Although fundamental research in single crystals and their properties has a long history, the turbine blade example is unusual, as it represents an incremental

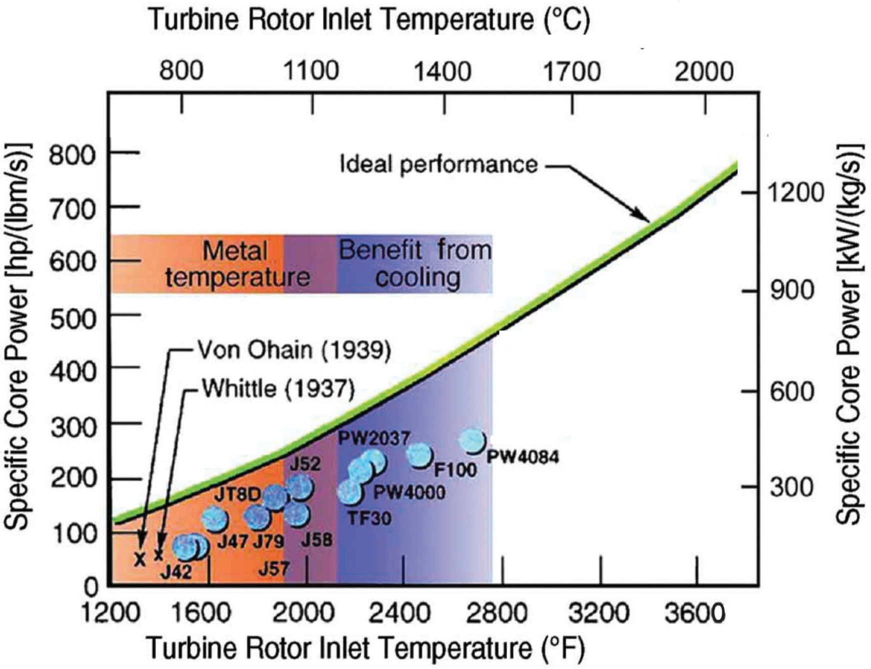

FIGURE 1.1 Specific core power as a function of inlet temperature in the turbine section of selected jet engines. The data for specific engines span about 70 years and are compared to the theoretical limit. The red section shows increased operating temperatures through turbine material development (including single-crystal development), and the blue section reflects advances in cooling schemes in the jet engine materials. The increase in metal temperatures incorporated many advances, including both alloy and manufacturing advances. Most notable, the development of single-crystal turbine blades increased the operating temperature roughly 50°C to 100°C. From the figure it is apparent that this increase in operating temperature translates to an approximately 25 percent increase in engine efficiency, providing large energy savings. SOURCE: Adapted by permission of the *MRS Bulletin* from Dennis M. Dimiduk and John H. Perepezko, "Mo-Si-B Alloys: Developing a Revolutionary Turbine-Engine Material," *MRS Bulletin,* **28,** No. 9 (2003), p. 639, Figure 1.

but significant improvement of an existing material. The optimized creep resistance in single crystals compared to that in polycrystalline solids was fundamentally defined and known. The incremental step to advance the industry involved methods to translate the laboratory-scale understanding to a commercial process. This is in contrast to the silicon industry, where the true properties (compared to the optimized) were only available in single crystals, whose history is considered below.

Example from Information Technology: Single-Crystal Silicon for Microelectronics

A second example of the leading role that crystal growth has had in advancing science and technology is that played by highly perfect single-crystal silicon (Si) in microelectronics. This example was chosen not only to demonstrate its absolutely central importance to modern information technology (IT) but also to illustrate how such an achievement can both make a collateral impact technologically and foster fundamental advances in the study of other single-crystalline materials.

Silicon is perhaps the most important technological material of the past half-century. It is the workhorse of the semiconductor, integrated circuit, and electronics industries. The Si integrated circuit underlies the $270 billion per year semiconductor industry and the $1.5 trillion per year electronics industry.[2] It also underpins the IT and communications industries. Recent estimates[3] attribute 25 percent of the economic growth in the United States to IT-producing industries, even though these industries contribute only 3 percent of the gross domestic product. As a group, the four IT industries (semiconductors, computers, communications equipment, and software) contribute more to economy-wide productivity growth than do all other industries combined. The importance of single-crystal silicon to IT and thus to the worldwide efficiency of labor suggests a label analogous to that of prehistoric eras: Humankind lives at present in the silicon age. Unlike the prehistoric and historic eras, however, the development of silicon relied on quantitative science both in crystal growth and materials characterization. And an essential element in that development was the recognition that previously unattained high purity and crystalline perfection would be needed for reliable and reproducible transistor action.

The need for crystal perfection in semiconductors was unprecedented in the history of materials development. Understanding why this is so requires visiting some of that history. Early in the study of solids, materials were divided into classes according to how readily they conducted electricity. Good electrical conductors, such as copper (Cu), were called metals; materials that did not conduct electricity, such as quartz, were labeled insulators. Other materials exhibited widely varying electrical conductivity, ranging from relatively high conductivity to very low conductivity, often in the same material system. These materials, with conductivity between that of metals and insulators, were given the disparaging label of semiconductors because of their irreproducible properties. The earliest semiconductors discovered were oxides and sulfides. Eventually, as the elements in the periodic

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[2] iSuppli Corporation. Available at http://www.isuppli.com/news/default.asp?id=8718. Last accessed September 3, 2008.

[3] Dale W. Jorgenson, *Moore's Law and the Emergence of the New Economy,* SIA 2005 Report, Semiconductor Industry Association, San Jose, California (2005), pp. 17-20.

table were identified, it was recognized that the group IV elemental materials silicon and germanium (Ge) were semiconductors. However, while it was discovered that different classes of solids exhibited different behavior, why these different classes existed and why they exhibited such properties were not known. In order to understand the origin of the differences among classes of solids and to be able to control their properties, two major scientific and technological advances had to take place: the development of quantum mechanics and the ability to grow high-purity single crystals.

Quantum mechanics, as it was developed and then applied to explain atomic structure and the dual wave-particle nature of electrons, provided the theoretical tools needed to understand the lattice and electronic properties of solids. The quantum mechanical description of how electrons reside in solids shows that the energy levels available for occupancy occur in bands, separated by energy gaps (forbidden regions, energetically, where electrons cannot reside). A fundamental principle of quantum mechanics is that no two electrons can occupy the same state, so the electronic states are filled up progressively in energy. In the case of semiconductors, exactly enough electrons are present to fill a band and no more. This means that the material cannot conduct electricity because, in order to move, the electrons must go into unoccupied states, and these are only available at significantly higher energies, across the band gap, in the next set of band states. However, if the gap is not too large, temperature can supply energy to electrons to get them across the band gap. The size of the energy gap in silicon is approximately 1.12 electronvolts (eV)—that is, the energy that an electron acquires when it is accelerated through a potential difference of 1.12 volts. This seems small perhaps, but the thermal energy of an electron moving at room temperature is 1/40 eV, while the typical energy of light from the Sun is on the order of 2.5 eV. Consequently, while at low temperatures there are virtually no electrons able to be excited into empty states, at elevated temperatures thermal excitation will cause some electrons to be excited across the band gap, and therefore able to serve as mobile charge carriers. Note that this band structure is in contrast to that of metals, which do not possess a band gap in the relevant energy range and thus have large electron densities in partially filled conduction bands able to serve as charge carriers.

However, in order to compare the results predicted by quantum mechanics to the behavior of actual crystals, high-purity crystals were required, especially in the case of semiconductors. The above-mentioned variability of conductivity in the same semiconducting material can be restated: in semiconductors, very low levels of impurities or lattice defects can have very large effects on the electrical conductivity. Indeed, impurities, such as boron (for hole conduction) or phosphorus (for electron conduction), are introduced in selective regions of group IV semiconductors such as Ge or Si to engineer the electronic properties of the semiconductor for device applications. These "dopants" create localized states with energy lying in the "forbidden" energy gap and quite close in energy to either the bottom or top of the energy gap; *n*-type dopants with electrons in energy states near the bottom of the conduction band donate electrons to the conduction band that conduct electricity, while *p*-type dopants with unfilled energy levels near the top of the valence band trap electrons from the valence band to leave "holes" (absence of electrons) that conduct electricity.

The simple picture is that solid Si has four valence electrons that exactly fill up the so-called valence energy bands, with an energy gap much larger than the room-temperature thermal energy to the next empty states (in the conduction band). Boron has three valence electrons and phosphorus has five, so one of these atoms replacing Si in the solid leaves a hole (boron) in the set of filled levels or adds an electron (phosphorus) into the empty state. The detailed physics shows that either of these states is weakly localized owing to the different nuclear charge on the substituted atom from silicon, and this translates into this "impurity" state being either just above the top of the valence band (boron) or just below the bottom of the empty conduction band (phosphorus). The "just" in the above description means that thermal excitation of carriers happens at room temperature. It also means that almost any "dirt" (that is, unintended impurities) that inadvertently gets into Si will produce carriers, and the exquisite control of "dirt" becomes a highest priority. Thus, the early observations of variability were transformed, with the advent of high-purity single crystals, into a materials property that could be engineered usefully.

The invention of the transistor in 1947 was aided by the availability to Bell Laboratories scientists of high-quality single crystals of germanium, grown for use in microwave rectifiers. Subsequent attempts to improve semiconductor crystal quality at Bell Laboratories led to the development of many of the modern techniques of crystal growth, among the most important of which are the Czochralski method of G.K. Teal and J.B. Little and the float-zone technique developed by W. Pfann to perfect Si single crystals. This work was driven by the realization that the first transistor used a point-contact geometry, which was difficult to produce and quite fragile. Although the theory for *p*-*n* junctions and bipolar transistors had been developed, and the field-effect transistor had been patented as early as 1926, neither functional bipolar nor field-effect transistors could be built because of the lack of high-purity single crystals. Thus, one of the major impacts of the transistor-related research was the success in materials understanding achieved by application of the scientific approach to crystal growth.

While purity in the bulk crystal sets the stage for device performance, device functionality is determined at the interface between the semiconductor and the other materials that comprise a modern integrated circuit (IC)—insulators, metals, and dissimilar semiconductors. Because of Ge's lower melting temperature and weak affinity for oxygen compared with Si, the first generation of transistors used Ge. However, under modest temperature increases the small band gap of Ge (0.66 eV) led to thermally generated charge carriers that overwhelmed the charge carriers introduced by doping. Thus it was clear that Si, with an energy band gap of 1.12 eV, was a better material than Ge, but Si single crystals had to be grown without defects or undesirable impurities, especially oxygen. Although removing oxygen impurities was a challenge, synthesizing fully oxygenated Si, amorphous SiO_2, is straightforward. Indeed silicon oxide was to be nature's gift to the semiconductor and IC industry, as it forms an almost perfect insulator with which to electrically separate semiconducting Si from a gate electrode. While most of the early transistors and ICs, such as those in early mainframe computers, used bipolar transistor structures, metal oxide semiconductor (MOS) field-effect transistors became the workhorse of the IC industry. The MOS transistor is illustrated schematically in Figure 1.2.

The Si-based IC is expected to be the dominant microelectronics technology for the foreseeable future because of the expected continued improvement in its performance; the enormous existing research, development, and manufacturing infrastructure for Si ICs; and the large application base for them in information and communications electronics that already exists worldwide.

The state of the art of the silicon IC in 2007 was 35 nanometer (nm) feature size and more than 1 billion transistors in a given IC. The incorporation of high-

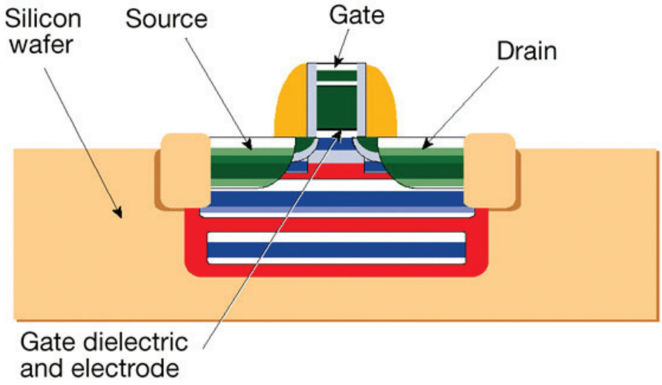

FIGURE 1.2 Schematic illustration of a metal oxide semiconductor (MOS) field-effect transistor. In a field-effect transistor, the electron or hole carriers flow from the source to the drain along the channel in the crystalline silicon (Si) near the interface between Si and the SiO_2 gate oxide. The number of electrons or holes that flow in the channel is controlled by the voltage on a metal gate. It is easy to imagine, in view of the earlier discussion in this chapter of electron energetics in doped Si, how a small voltage, on the order of 1 volt, on the gate can influence carriers in its vicinity. SOURCE: Reprinted by permission from Macmillan Publishers Ltd., *Nature*, P.S. Peercy, "The Drive to Miniaturization," *Nature,* **406,** 1023-1026. Copyright 2000.

dielectric-constant (κ) materials needed to reach this feature size illustrates the complexity of materials considerations in future IC development. As the transistor gate length is decreased to increase the switching speed, the thickness of the gate dielectric must also be decreased to maintain the appropriate electric field levels for high-performance operation. When the dielectric (oxide) thickness approached a few atomic layers en route to the 35 nm node, high leakage currents resulting from charge carrier tunneling through the dielectric layer forced industry to introduce high-κ material, such as hafnium oxide, for use as the gate dielectric. These new gate dielectric materials required replacing the polycrystalline Si gate electrode with metal electrodes. In addition, the width of the metal interconnect needed to be decreased as the entire circuit was scaled to accommodate the shorter transistor gate length. As the cross-sectional area of the metal interconnects decreased, interconnect resistivity increased, which increased the resistance-capacitance (RC) time constant that controls signal propagation speed and delay time, degrading the overall speed of the IC. To reduce the RC time constant, polycrystalline aluminum (Al) was replaced with Cu in the metal conductors to reduce the interconnect resistance, requiring that new low-κ dielectrics be developed for insulators between the metal interconnects. Thus, a change in one component can lead to a cascade of materials challenges.

Further improvements in transistor performance and the resulting improvements in IC performance were achieved by controlling the band gap and charge carrier mobility of Si using strain generated by epitaxial growth of SiGe alloys on selected regions of the transistors. Other approaches to band-gap engineering for higher transistor performance and continued scaling to smaller feature size include new generations of selective SiGe epitaxial crystals on Si and new Si-based single-crystal alloys for increased carrier mobility and interface control. Improvement in device and circuit performance is expected to continue; the semiconductor industry has developed a technology roadmap for semiconductors that follows Moore's law for steadily decreasing feature size for the next several years.[4]

As important as it is, the Si-SiO_2 interface is far from perfect (Figure 1.3). The chemical bonds from the crystalline Si do not all join to atoms in the amorphous oxide. The unmatched chemical bonds can become charged interface states that can trap the conduction electrons as they migrate along the interface. The Si-insulator interface must be well ordered for high-performance devices. Both Si and compound semiconductor systems with atomically engineered single-crystal interfaces (made by MBE) offer extremely high charge carrier mobility that not only enabled the development of very high performance devices but also led to

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[4] The International Technology Roadmap for Semiconductors is regularly updated and can be found at http://www.itrs.net/. Last accessed on June 2, 2009.

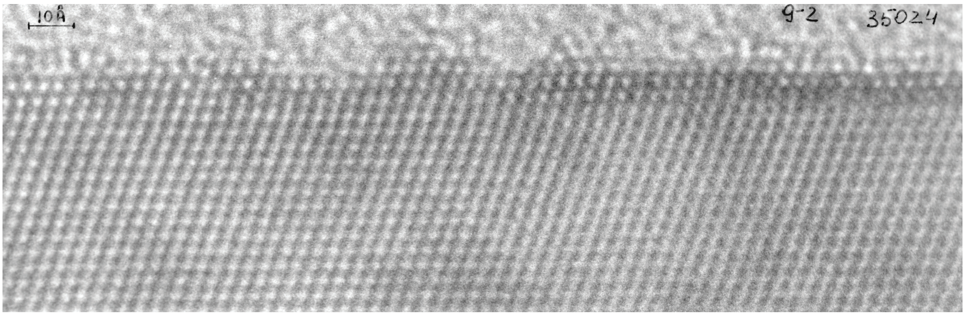

FIGURE 1.3 Transmission electron micrograph of a silicon-silicon dioxide (Si-SiO_2) interface. With advances in electron microscopy, the interfaces in a modern integrated circuit can be imaged, as seen here in an atomic resolution micrograph of an interface between electrically conductive crystalline Si (bottom) and its nonconductive amorphous thermal oxide, SiO_2 (top). This interface is the basis of the Si field-effect transistor, which is used in all modern electronics and computers. SOURCE: Courtesy of Stephen Goodnick, Arizona State University.

the discovery of elegant new fundamental physics. These advances are illustrated for the gallium arsenide (GaAs) system in the following subsection.

Example in the Area of Thin Films: Gallium Arsenide-Based Heterostructures

A third example of crystallography leading to major discoveries in both science and technology is the development of gallium arsenide-based heterostructures. These single-crystal GaAs films are a natural extension of the deep experience of the scientific community with single-crystal Si. This work was chosen to illustrate the essential coupling between high-quality crystal growth and the discovery of completely new and unexpected physical phenomena. It also illustrates how the ability to produce single-crystal films of ever higher quality is the determining factor in making progress in this field of physics.

A search by physicists for a more perfect semiconductor-insulator interface than Si-SiO_2 led to the development of the GaAs-aluminum arsenide (AlAs) system, in which both the conducting GaAs and the insulating AlAs are incorporated in the *same* single crystal. Interestingly, these crystallize in the same tetrahedrally bonded diamond structure as that of Si, having the same average valence electron count. Using advances made in techniques to epitaxially grow single-crystal films, near-perfect crystal interfaces can be produced. Figure 1.4 is an atomic-scale micrograph showing 12 atomic layers of semiconducting GaAs (darker layer) sandwiched between layers of semi-insulating AlAs (lighter layers). Notice that in this figure the atomic layers of GaAs cleanly link up to the adjacent atomic layers of AlAs,

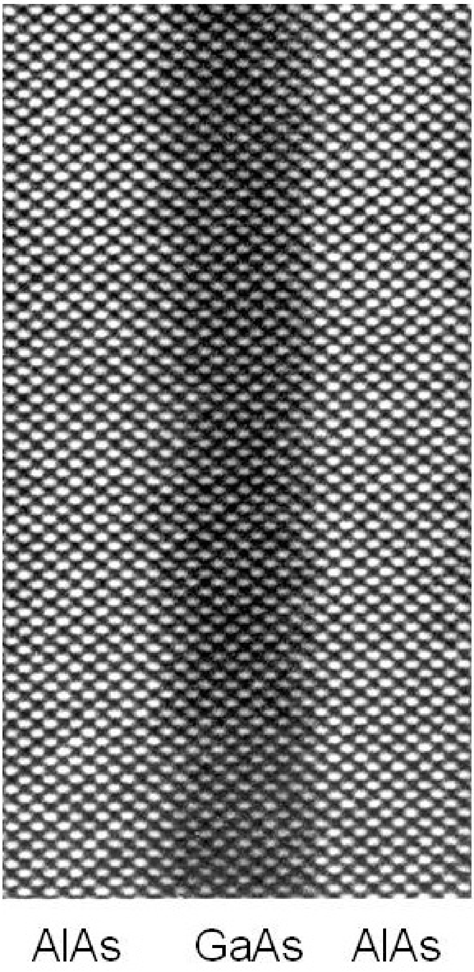

FIGURE 1.4 Cross-section transmission electron micrograph at atomic resolution of a crystal, grown by molecular-beam epitaxy, containing 12 molecular layers of aluminum arsenide (AlAs), then 12 layers of gallium arsenide (GaAs) and 12 layers of AlAs. SOURCE: Courtesy of Loren Pfeiffer, Bell Laboratories, Alcatel-Lucent.

in marked contrast to the Si-SiO_2 micrograph in Figure 1.3. Thus, the GaAs-AlAs system has the potential for *no* dangling chemical bonds at the electronic interfaces, and thus no interface traps.

The absence of a disordered electronic interface gives the freedom to reduce the conducting channel thickness to about 10^{-6} cm, which is about the quantum size of the conduction electrons in GaAs. The motion of the electrons then becomes two-dimensional. The electrons can move in the plane of the GaAs channel but not out of the GaAs layer because of the AlAs insulating barriers. The nature of the two-dimensional electrons can be probed in the experiment shown in Figure 1.5. In the sketch, the two-dimensional conducting GaAs channel just below the sample surface is placed in a perpendicular B-field, and a current, I_{xx}, is caused to flow in the long direction. The sample is characterized by a longitudinal resistance R_{xx} and a transverse Hall resistance, R_{xy}, named for E. Hall, who first observed it in 1878.

For metal samples such as the gold leaf foil used by Hall, R_{xy} grows smoothly and linearly with increases in the magnetic field B. For high-purity semiconducting systems at low temperatures, however, the Hall resistance shows a series of discrete plateau steps that cannot be understood without considering the *quantum* properties of the conducting electrons. An example of these remarkable quantum steps in the Hall resistance is shown in Figure 1.6(a) for a GaAs-AlGaAs sample. Even more striking is that the *numerical values* of the various resistance plateaus are given by *exact* ratios of fundamental physical constants,

$$R_{xy} = \frac{1}{\nu}\frac{h}{e^2},$$

where h is Planck's constant, e is the electron charge, and ν is a quantum number having integer values 1, 2, 3 . . . .

This quantum Hall experiment was first performed by von Klitzing, Dorda, and Pepper in 1980 using a high-quality version of the Si-SiO$_2$ interface shown in Figure 1.3.[5] The theoretical picture of the quantum Hall effect is that the resistance plateaus are due to electrons making cyclotron orbits around the magnetic flux lines of the B-field. A natural interpretation of the experiment has the magnetic B-field quantized from the point of view of the conduction electrons, in units of $h/e = 4.1 \times 10^{-7}$ gauss cm^2. Thus the integer quantum number, ν, becomes the number of electrons, 1, 2, 3 . . . in cyclotron orbits around each magnetic flux quantum. The plateau resistivity values are the same for an Si-SiO$_2$ interface as for a GaAs-AlAs interface. Indeed, this universal material-independent behavior, along with extreme accuracy of the h/e^2 determination, has led to the adoption of these Hall resistance plateaus as the international standard for resistance, thereby *defining* the ohm in terms of h and e. The effect has become known as the *quantum* Hall effect, and its discoverer, Klaus von Klitzing, was awarded the Nobel Prize in physics in 1985. The discovery was not anticipated in the earlier quantum mechanical treatments of two-dimensional electrons, but instead was the direct result of the new availability of high-quality crystalline samples.

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[5] K. von Klitzing, G. Dorda, and M. Pepper, "New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance, *Physical Review Letters,* **45,** 494 (1980).

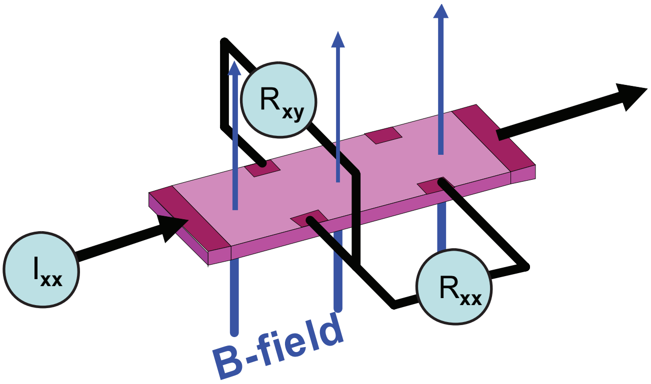

FIGURE 1.5 Experimental setup for a Hall-effect measurement. The two-dimensional electron system lies in the plane of the sample; electrical contacts are indicated by dark patches. The magnetic B-field is perpendicular to the two-dimensional electron system. SOURCE: Adapted from E.H. Hall, *American Journal of Mathematics,* **2**, 287 (1879).

The realization that increasing the crystalline quality in the two-dimensional region could lead to a more robust quantum Hall effect led to experiments similar to that of von Klitzing, but with the potentially higher-quality GaAs-AlGaAs interface. In 1982, H.L. Stormer, D.C. Tsui, and A.C. Gossard published a truly shocking experimental result shown in Figures 1.6(a) and 1.6(b). Not only did they see the integer von Klitzing effect, but they also saw a clear R_{xy} plateau at $\nu = 1/3$, and in the longitudinal R_{xx} signal a hint of something also at $\nu = 2/3$. They had discovered the *fractional* quantum Hall effect (FQHE). Since the physical interpretation of the *integer* quantum Hall theory relied on ν being the number of electrons in a cyclotron orbit around each B-flux quantum, the existence of fractional values of ν seems to suggest a state whereby the electron itself is breaking up into fractional charges. However, particle physics tells us that an electron cannot be broken apart. Instead the FQHE experiments reveal a new state of matter, one in which new, particle-like excitations emerge owing to particle-field interactions that are qualitatively different from the interactions of elementary particles in free space. But this was only the first sighting of new families of emergent excitations in these two-dimensional electron systems.

The discovery of the fractional quantum Hall effect in GaAs launched a worldwide effort to further improve the quality of the GaAs crystal samples. Figure 1.6 shows the increasing richness of observed fractional states as the sample quality (measured by the electron mobility μ) has improved. In the Figure 1.6(c) trace, for a sample of mobility 500,000 cm^2/Vsec, one sees that the states at 1/3 and 2/3 are joined by states at 2/5 and 3/5, and in the Figure 1.6(d) trace, these states are

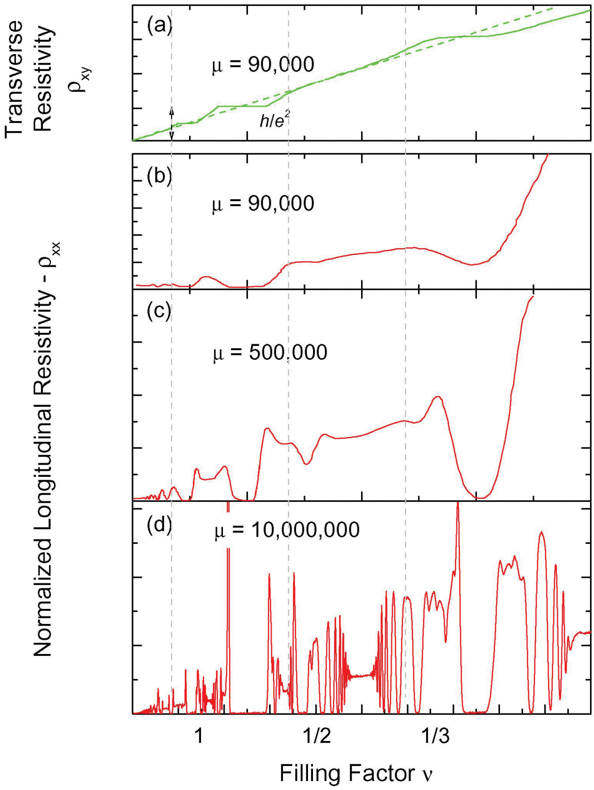

FIGURE 1.6 Improvement in mobility through improvement in crystal quality of two-dimensional electron gas samples leading to new states of quantum matter: (a) The quantum Hall effect R_{xy} in a gallium arsenide (GaAs)/aluminum gallium arsenide (AlGaAs) heterojunction at $T = 0.48$ K, as a function of magnetic field, or equivalently as the filling factor or number of electrons per magnetic flux line. The dashed line is the classical Hall effect as it would be seen at room temperature (D.C. Tsui, H.L. Stormer, and A.C. Gossard, "Two-Dimensional Magnetotransport in the Extreme Quantum Limit," *Physical Review Letters,* **48,** 1559 [1982]). Panels (b), (c), and (d) show longitudinal resistance R_{xx} for three different GaAs/AlGaAs two-dimensional electron gas samples indicating the appearance of new quantum states with increased purity as represented by mobility, μ, in units of cm^2/Vsec. (b) The first observation of fractional filling at $\nu = 1/3$ and $T = 0.48$ K in the same sample as panel (a) (D.C. Tsui, H.L. Stormer, and A.C. Gossard, "Two-Dimensional Magnetotransport in the Extreme Quantum Limit," *Physical Review Letters,* **48,** 1559 [1982]). (c) New states at $\nu = 1/3$, 2/5, 2/3 achieved in a higher-mobility sample at $T = 0.55$ K (H.L. Stormer, A. Chang, D.C. Tsui, J.C.M. Hwang, A.C. Gossard, W. Wiegmann, "Fractional Quantization of the Hall-Effect," *Physical Review Letters,* **50,** 1953 [1983]). (d) Data from a typical modern high-mobility sample at $T = 0.035$ K (W. Pan, H.L. Stormer, D.C. Tsui, L.N. Pfeiffer, K.W. Baldwin, K.W. West, "Fractional Quantum Hall Effect of Composite Fermions," *Physical Review Letters,* **90,** 16801 [2003]). This sample exhibits self similarity between the $\nu = 0$ and $\nu = ½$ states that is the basis for the "composite fermion" description of electronic states, which are described in Chapter 2 of this report.

joined by a hierarchy of many more states at 3/7 and 4/7 and so on, all having odd denominators and all organized around an absent state at $\nu = ½$. The full story of how the new states are organized around ½, and the dramatic evidence for a series of new emergent particles called composite fermions, will be continued in Chapter 2 of this report.

The Stormer-Tsui-Gossard FQHE experiment uncovered deep new physics emerging from a system that is simple to describe, namely, electrons interacting through the Coulomb potential but confined to two dimensions. As the crystalline quality of the samples improved, these electron-electron interactions became important over larger and larger distances, revealing electronic states that previously were hidden by disorder. In 1998, Stormer, Tsui, and theorist Robert Laughlin were awarded the Nobel Prize for their work on the fractional quantum Hall effect;[6] as the perfection of the samples was further improved, new hierarchies of states whose full explanations are beyond the Laughlin theory were uncovered. At present, the progress in uncovering new quantum states through ever-purer samples continues unabated. The recent increase in GaAs sample mobility to 31,000,000 cm^2/Vsec revealed new surprises, such as striped regions of alternating-integer filling factor, non-Laughlin-even-denominator states, and the formation of re-entrant insulating states.

For GaAs heterostructures of the highest crystal perfection, the magnetotransport data now contain enough information to make a compelling argument for the existence of a new fundamental particle called the composite fermion. The blue trace of Figure 1.7 (bottom panel) reproduces the data in Figure 1.6(d) showing the FQHE in a 15,000,000 cm^2/Vsec mobility GaAs-AlGaAs sample grown recently at Bell Laboratories. The data are plotted versus magnetic B-field up to 18 tesla, and the principal filling factors previously discussed are labeled. The raw data show that, in addition to the fractional organizational state at $\nu = ½$, there is another such organizational state at $\nu = ¼$. Around each of these organizational states, a complete array of quantum Hall fractions is seen with the usual odd denominators given by the empirical formulas $\nu = j/(2j \pm 1)$ near $\nu = ½$, and $\nu = j/(4j \pm 1)$ near $\nu = ¼$, where j is an integer, $j = 0, 1, 2, \ldots$.

If two identical copies of this spectrum (arbitrarily colored blue and red) are arranged so that $\nu = ½$ at 8.3 tesla in the red copy is placed exactly above the zero tesla starting point of the blue copy, as shown in the figure, *all* of the fractional quantum Hall states to the right of $\nu = ½$ in the red copy of the data *line up perfectly, state for state,* with the original integer quantum Hall states in the lower, blue copy. It is as if the 8.3 tesla magnetic field at $\nu = ½$ was somehow reset to zero, and the data started over with the pattern of the integer quantum Hall effect. Further, this

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[6] It is worth noting that Arthur C. Gossard, the person who grew the samples that enabled this groundbreaking experiment, was not included among the Nobel Prize winners.

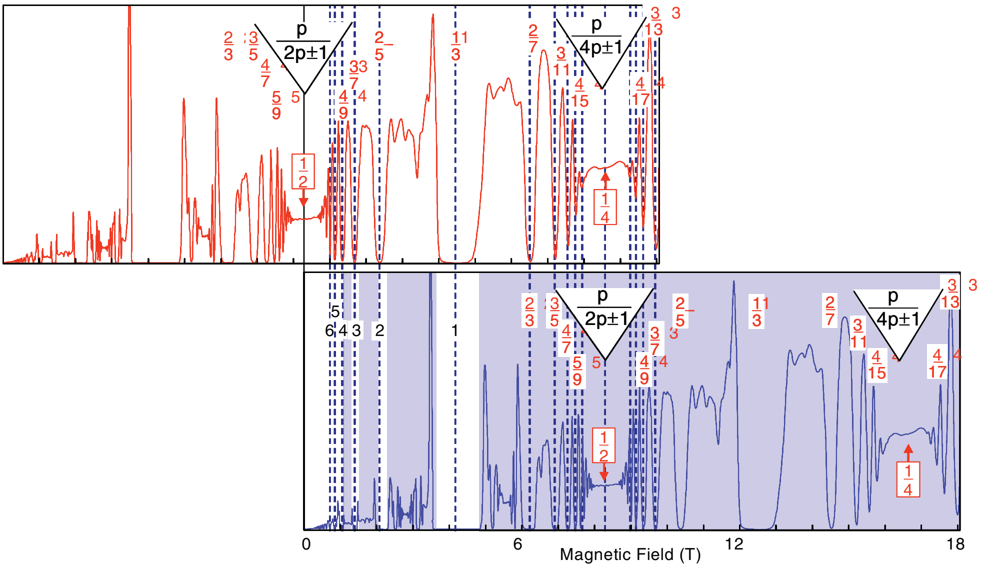

FIGURE 1.7 Longitudinal resistance R_{xx} data taken on a modern GaAs/AlGaAs high-mobility two-dimensional electron system exhibiting the fractional quantum Hall effect and composite fermion fractions. The red (top) and blue (bottom) traces are identical copies of the same data set. SOURCE: W. Pan, H.L. Stormer, D.C. Tsui, L.N. Pfeiffer, K.W. Baldwin, and K.W. West, “Fractional Quantum Hall Effect of Composite Fermions,” *Physical Review Letters,* **90,** 16801 (2003).

resetting of the B-field happens again at $\nu = ¼$. Now all the states around $\nu = ¼$ in the red data line up state for state with the $\nu = ½$ states in the blue data, and if the red data are slid *farther* to the left until $\nu = ¼$ at 16.6 tesla is lined up to zero tesla on the blue trace, the fractional states in the red trace would *again* line up state for state with the integer states of the blue trace.

Theorists have accommodated this apparent resetting to zero of the 8.3 tesla and 16.6 tesla magnetic fields by proposing the existence of two new particles that *incorporate* the flux quanta of the B-field in their creation. The new particles are called *composite fermions*. The composite fermion associated with $\nu = ½$ is made up of an electron and two magnetic flux quanta. The composite fermion associated with $\nu = ¼$ is an electron and four magnetic flux quanta. The magnetic flux quanta incorporated in these new particles are no longer available, and the magnetic field is naturally reset to zero at $\nu = ½$ and again at $\nu = ¼$. With this new theoretical picture, the fractional quantum Hall effect becomes much easier to understand. It is just the *integral* quantum Hall effect *of these new composite fermion particles!* The beauty in this hierarchy of structure suggests further levels and more exotic particles.

Shortly after the discovery of composite fermions, new theoretical work suggested a new chapter in the story of emergent particles in two-dimensional electron systems: the possible existence of emergent non-abelian quasi-particles. Non-abelian quantum particles can only exist in a two-dimensional environment, such as the one under discussion at the heterointerface in GaAs-AlGaAs. The known quantum particles occupy three-dimensional space and thus are all abelian. Non-abelian quasi-particles would have bizarre properties. In a two-dimensional sheet of quasi-particles, if a quasi-particle is caused to make an encircling path around one of its nearest neighbors and then comes back to where it started, for abelian particles nothing would change, but for non-abelian particles such an encirclement would cause quantum entanglement. Moreover, the quantum entanglement would not be affected by the usual processes that cause quantum decoherence of abelian particles. The *only* way that the entanglement of non-abelian particles could be undone is by reversing the original topological path or making topologically complicated additional loops. Thus, if non-abelian quasi-particles can be found in these two-dimensional systems, they could in principle be used as a topological lock against quantum decoherence. Such a topological lock may be just what is needed to make quantum computing a future reality.

The story of the continuing interaction between GaAs MBE and the search for new semiconductor physics nicely demonstrates how the improvements in the perfection of the crystal interface between a semiconductor and its surroundings have led to profound insights in low-dimensional semiconductor physics, and how, in turn, this success has led to an ongoing effort to make still more perfect semiconductor interfaces.

Example of High-Temperature Superconductivity

The final example illustrating the historical role played by crystal growth in advancing both applied and basic science is in the field of high-T_c superconductivity. This example was chosen for several reasons. First, because of the complex structure of the metallic oxide materials involved, it demonstrates the absolute necessity of being able to control the growth of the materials precisely in order to gain a fundamental understanding of their nature. Second, it is a highly active area of research with much promise, not only for expanding current knowledge of solid-state physics but also for the technological opportunities that it presents.

Superconductivity, discovered in 1911 by K. Onnes shortly after his achievement of liquefying helium, resisted understanding until the Bardeen-Cooper-Schrieffer theoretical breakthrough in 1957. Superconductivity was long thought to be a rare occurrence; the highest known superconducting transition temperature was 23.2 kelvin (K) until Bednorz and Müller stunned the science community in 1986 with their discovery of 28 K superconductivity in barium-doped La_2CuO_4, followed quickly by 90 K in $YBa_2Cu_3O_7$ (see Figure 1.8). This discovery was made in polyphase ceramic powders, and determination of the actual superconducting crystal structure and its composition involved intense competition within the materials community. A succession of related materials with still higher transition temperatures (T_c) was discovered, with T_c reaching the remarkable level of 156 K under pressure in a mercury-based cuprate material. This T_c is well beyond that thought possible based on existing theory. Exceeding a T_c of 77 K is a major technological triumph, since superconductivity could now be attained by cooling with liquid nitrogen rather than the more expensive and much less abundant liquid helium.

While holding the promise of important industrial use, these new superconducting materials also were intriguing from a fundamental science perspective, having electrical and magnetic characteristics quite different from those of more familiar materials such as copper. Before it could understand and explain the physics of such materials though, the research community first had to determine their physical properties precisely. This, in turn, required a high level of control in growing the materials to remove effects of impurities and defects. The cuprate

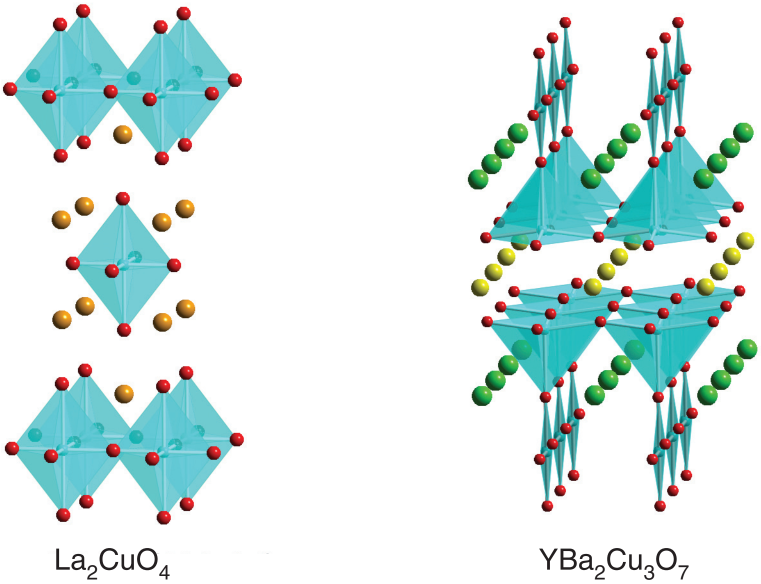

FIGURE 1.8 Crystalline structures of two superconductors: (left) La_2CuO_4, consisting of a sublattice of copper-oxygen pyramids (blue, with oxygen atoms shown in red) and the larger lanthanum atoms (yellow); and (right) $YBa_2Cu_3O_7$, consisting of a sublattice of the copper-oxygen pyramids (blue) and the larger yttrium (yellow) and barium (green) atoms. SOURCE: Courtesy of M.A. Subramanian, Oregon State University.

superconductors and their relatives have layered crystal structures with large anisotropy between in-plane and out-of-plane properties; single crystals are essential to deeply probing the physics of these materials. Perfecting this crystal growth has proven to be difficult. In the 20 years since their discovery, only recently have crystals of sufficient quality been grown to allow "classical" types of experiments common in single-crystal metal physics to be conducted—namely, measurement of de Haas-van Alphen oscillations. These experiments determine aspects of the electronic structure, which appears to lie at the heart of understanding the high-T_c phenomena. Single-crystal growth of these high-melting-point oxides is performed in an optical furnace, where a hot floating zone is achieved by focusing light from high-power lamps, the optical offspring of the much older radio-frequency and electron-beam floating zone crystal growth of semiconductors. This technological development was perfected in Japan, and recent advances in the still-incomplete understanding of high T_c are coming from continued improvement of crystal quality resulting from this technology.

After more than 20,000 publications, experimental research in high-T_c superconductivity is finally making reasonable progress, although a consensus microscopic theory is still sought. Crystal growth played an essential role, not only for this field but also for progeny fields such as quantum criticality, orbital-ordered magnets, colossal magnetoresistance, and geometrical frustration. Understanding high-T_c superconductivity has served as a major motivation for increased development of experimental probes such as angle-resolved photoemission spectroscopy, scanning probe microscopy, tricrystal tunneling, pulsed laser deposition, high field magnets, and neutron scattering. Starting as a small-scale discovery of a new compound by two researchers, this topic spawned a great multitude of new scientific discoveries and extensive fundamental questioning of how well we understand solids. Such is the ongoing promise of growth of crystalline matter. The search for new materials with even higher transition temperatures continues, there being no reason to suppose that the cuprates represent any limit as to what is possible.

CONCLUDING COMMENTS

The return on investment to the public that ultimately pays for research such as that exemplified above comes in several forms: new technologies are enabled that simply would not exist without the continuing advances in single-crystal growth. It is not an exaggeration to say that these new technologies have transformed modern life. The transistor is based on single-crystal technology, and in a very real sense the computer would not be possible in any useful way without the transistor. One has only to look at a wristwatch to appreciate a remarkable and inexpensive result of very sophisticated single-crystal technology based on synthetic quartz crystal oscillators as a highly stable frequency device.

The ways in which crystal growth is intertwined with technology are many and varied, as seen by the contrast between the example of Si technology and that of the commercialization of single-crystal turbine blades. In the case of Si, pure material was required to lead to the understanding of the science and technology needed to develop commercial applications. In contrast, crystalline turbine blade commercialization was based on improvements in existing industrial processes. Commercial processes can and do benefit from the use of single crystals with significant economic consequence.

Beyond this, single-crystal research has been and continues to be the path to new science. Maintaining scientific leadership in the world demands ready access to the advanced materials from single-crystal synthesis. Advances in the science of crystal growth yield ever-increasing control over materials and their uses, as well as new uses enabled by such control.

These and many other examples illustrate a return on investment that can be economic or scientific, and often is both.

The world is entering a new age of materials and is gaining the ability to investigate, interrogate, and potentially control materials at a level approaching that of individual atoms. Single crystals are the stage on which the new capabilities play, and the ability to create these single crystals and then to produce them well is of primary scientific and technical concern. Not all materials are equal: some can be perfected much more effectively than others. The importance of a strong continuing search in the wide materials phase-space for ever-better functional materials cannot be overstated.

2

Science and Technology of Crystalline Systems

The importance of symmetry in nature has been recognized since the time of the Greek philosophers. Today, new applications of symmetry continue to influence scientific thought in many fields, ranging from biology to astrophysics. In particular, the description of how symmetry in condensed matter is lowered or "broken," such as when a liquid becomes a crystal, forms a mathematical connection with other disparate phenomena, such as the handedness of an oligomeric protein to the evolution of matter after the big bang. Indeed, the remarkable properties of graphene (see Box 2.1) originate from the unique way in which a single sheet of carbon atoms breaks spatial symmetry.

Symmetry is described mathematically through the theory of space groups, which are the set of spatial translations and rotations that leave a crystal structure unchanged. The structural symmetry is defined at high temperatures, when the crystal forms. At lower temperatures, interactions of lower energy than that of the interatomic bonds yield states such as superconductivity, ferromagnetism, and ferroelectricity, which then lower the symmetry of the interacting particles and fields even farther.

Crystal lattices can also serve as a laboratory for studying broken symmetries that arise in a much different context: for example, the generation of elementary particles. Elementary particle theorists often impose the symmetry of a lattice to calculate the consequences of subnuclear interactions such as the Higgs mechanism, at present being sought at the European Organization for Nuclear Research's (CERN's) Large Hadron Collider. Such theoretical concepts can also be realized in crystalline solids. For instance, certain magnetic systems on chain-like crystal

BOX 2.1
Graphene

Elemental carbon adopts a variety of crystalline forms—three-dimensional diamond, layered graphite, carbon nanotubes, and C_{60} fullerite. In 2005, a new form of carbon, graphene, was discovered. Graphene is a single sheet of hexagonally ordered carbon atoms.

The purely two-dimensional nature of graphene sheets gives rise to an astounding array of new phenomena, among which are the following:

- Behavior that mimics the relativistic motion of particles in high-energy accelerators,
- New states of matter in the quantum Hall regime (in Chapter 1 of this report, see the subsection entitled “Example in the Area of Thin Films: Gallium Arsenide-Based Heterostructures”),
- Electronic conductivity at zero electron density, and
- Extremely fast “ballistic” motion of electrons and holes even at room temperature.

The latter property suggests a new class of electronic devices with switching speeds much greater than those achievable in silicon complementary metal oxide semiconductors, perhaps reaching terahertz frequencies.

These properties and more result from an unusual electronic momentum-energy relationship. Electrons in the hexagonal crystal structure of graphene behave like massless relativistic electrons in a world with only two dimensions. Many materials possess a quasi-two-dimensional hexagonal structure in which the sheets interact slightly with neighboring sheets, such as in graphite itself, thus breaking the special momentum-energy relationship of electrons in graphene. What makes graphene special is that the sheets are only one atom or a few atoms thick.

The technical breakthrough that led to an explosion of research into graphene (now more than 1,000 papers per year; see Figure 2.1.1) was the discovery that crystals with a thickness of only a nanometer can be seen under an optical microscope when the crystals are placed on a Si wafer coated with a layer of silicon dioxide (SiO_2) (see Figure 2.1.2). The SiO_2 layer thickness must be precisely engineered—300 nm will not work, whereas 315 nm will—to produce interference contrast with the graphene crystal.

Thus, the discovery of graphene is an instance of the combining of a novel measurement approach with a prosaic “synthesis” technique. A large part of the future challenge for creating graphene-based devices will be that of replacing these techniques with a scalable manufacturing process that does not sacrifice the unique properties of this remarkable form of crystalline matter.

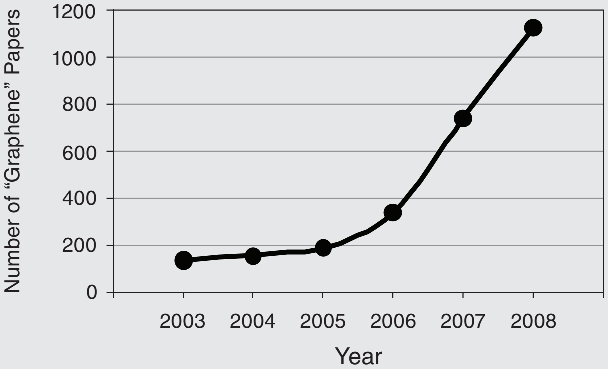

FIGURE 2.1.1 The number of papers published on an annual basis from 2003 through 2008 that relate to graphene, revealed by a citation search for "graphene" on the Web of Science.

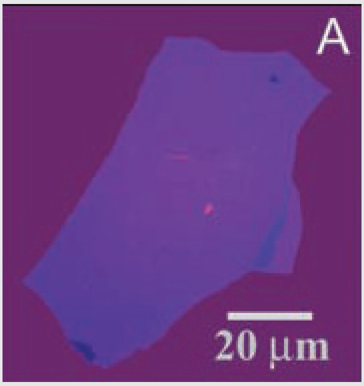

FIGURE 2.1.2 Photograph of an approximately 3-nanometer-thick graphene flake on top of an oxidized silicon wafer. SOURCE: From K.S. Novoselov, A.K. Geim, S.V. Morozov et al., "Electric Field Effect in Atomically Thin Carbon Films," *Science,* **306,** 666 (2004); reprinted with permission from the American Association for the Advancement of Science.

lattices are described by the same mathematics used to model elementary particle mass generation. Thus, crystalline symmetry provides an intellectual connection spanning 15 decades in energy!

Crystalline systems are exemplars of condensed matter. The usual image of a crystal is one of clarity, which originates from the perfect ordering of atoms. In the laboratory, symmetry is manifested in regular x-ray scattering patterns, a phenomenon discovered by Sir William Lawrence Bragg and his father, Sir William Henry Bragg, for which they shared the 1915 Nobel Prize in physics. The microscopic crystal images shown in various figures in this report are constructed mathematically from such x-ray diffraction patterns; the produced images have a type of beauty appreciated especially by the scientists studying them.

An additional measure of perfection comes in the physical properties of crystals. Examples abound in which "fragile" states are able to form only in crystals possessing a very low density of defects. One example is the set of fractional quantum Hall states discussed in Chapter 1, which are not seen in samples with crystalline disorder.

Advances in measurement technology enable the probing of ever-higher degrees of crystalline perfection, allowing scientists to better match theories with experiments on exotic properties of matter. Currently, no general theoretical prescription exists for many of the new states of matter that emerge with increasing crystalline perfection. Discovering and understanding such states demand continual and close collaboration among synthesis, experiment, *and* theory.

Controlling and minimizing defects in crystalline materials also constitute an important path to device innovation. Many next-generation devices for applications such as solar energy, solid-state lighting, and novel sensors require crystalline order among nontraditional atomic, molecular, or nanoscale building blocks. Controlling such ordering will be key to creating devices that will form the foundation of these future technologies, just as controlling covalently bonded semiconductors enabled today's microelectronics industry.

Innovation involving crystalline materials has historically benefited from a fruitful interplay between basic research and device development, as described in Chapter 1. This interplay was guided by large industrial laboratories that operated significant basic research divisions whose scientific agenda was to address technology goals of the corporation to which they belonged. Research scientists and engineers outside these corporations thus had a window onto technology roadmaps through interactions with fellow basic researchers in industry. Each of these laboratories often employed 100 or more discovery and growth of crystalline materials (DGCM) scientists, including many crystal and film growers. They provided generally stable and substantial operating funds for DGCM activities and had the ability to respond rapidly to new materials opportunities without the need to pursue new funding to do so.

In the current business climate, U.S. corporations no longer sustain such basic research divisions, with the result that an important mechanism for communicating technology needs has been greatly diminished. The impact of this loss is evidenced by the reduction in industrial publications in physics from 998 in 1988 to 312 in 2005 (see also the discussion in the section entitled "The Role of Industry in Crystal Growth" in Chapter 3). The impact of this loss on crystalline materials could also be high, considering that most modern crystal growth techniques as well as a significant amount of materials discovery in the past 50 years were achieved in the integrated corporate laboratory environment. Achieving the scientific vision expressed in this chapter while addressing an increased need to innovate will carry with it the challenge that future research activities be organized to emulate the modalities of interaction in former industrial DGCM research environments. The recommendations of the committee presented in Chapter 4 include suggestions for new approaches that go beyond the industrial research model to accommodate the changing needs of DGCM researchers in academia, national laboratories, and industry.

In the major sections immediately following, the committee presents a vision for the future of both bulk and thin-film crystalline systems in the form of three grand challenges. This chapter then concludes by discussing the needs for applied crystal growth in technology development and the role that characterization will continue to have in new crystalline materials discovery.

GRAND CHALLENGES IN THE SCIENCE AND TECHNOLOGY OF CRYSTALLINE MATERIALS

Advances in the science and technology of condensed matter will continue both to challenge and to enable society's understanding of the physical world for the foreseeable future. Crystalline matter is at the heart of many of the most exciting areas of research, as shown by three grand challenges:

- *Grand Challenge 1. The Development of Next-Generation Crystalline Materials—New States of Matter and New Materials—for Future Information and Communications Technologies*

The ability to tailor both the symmetry and dimensionality of a crystalline lattice allows for the creation of a delicate balance between dissimilar ground states, especially in crystals supporting strongly correlated or quantum-mechanical interactions among the electrons. Such appropriately tailored crystals can exhibit completely new behavior: quantum phenomena such as superconductivity or quantum coherence at room temperature, the ability to switch and store multiple types of signals (electric, magnetic, and structural), or the attributes of physical states not anticipated by present theory. With respect to this grand challenge, the ensuing physics will be so unexpected that scientists possess a priori, besides a few general design guides such as effective dimensionality, little understanding of how atoms should be assembled. Thus, this challenge is tantamount to creating a research ecosystem for discovery-based inquiry in crystalline matter.

- *Grand Challenge 2. The Creation of New Crystalline Materials for Energy Production and Conversion*

Future energy technologies will require dramatic advances in crystalline materials, including thermoelectric materials for heat-to-electricity conversion, solar photovoltaic materials for sunlight-to-electricity conversion, novel materials for hydrogen production and storage, new electrode and membrane materials for fuel cells, and affordable catalysts for feedstock-to-fuel conversion. Many such energy applications will require crystalline phases with low parasitic energy loss, such as low-cost solar cells with 50 percent power efficiency. Each individual topic in the area of crystalline materials for energy production and conversion requires a stretch goal for materials performance involving an unprecedented degree of atom-level control. Collectively these topics constitute a grand challenge for increasing energy availability and self-sufficiency in the United States.

- *Grand Challenge 3. Evolution in the Capacity to Create Crystalline Materials by Design*

In the next 10 years, advances in theory and modeling, coupled with dramatic increases in computational power, will enable the creation of completely new materials incorporating either thin-film or molecular subunits. More than ever before, these new materials will possess specific device functionalities. Realizing a materials-by-design approach would enable industry to move beyond current device limitations to provide cheaper and more efficient solar cells, high-power electronics, and devices with functionality not yet imagined.

GRAND CHALLENGE 1: DEVELOPMENT OF NEXT-GENERATION CRYSTALLINE MATERIALS—NEW STATES OF MATTER AND NEW MATERIALS—FOR FUTURE INFORMATION AND COMMUNICATIONS TECHNOLOGIES

In analogy to the traditional states of matter—solid, liquid, and gas—researchers have discovered a multitude of fascinating states in crystalline materials. These states depend on the effective spatial relationships between atoms within the crystal. Of particular importance is effective dimensionality and connectivity of substructures within the crystal; for example, materials based on lamellar sheets of atoms can be considered two-dimensional for electronic or magnetic excitations. These excitations interact among themselves to create patterns, or states of matter, that are highly dependent on the effective dimensionality and connectivity. Such states of matter include modified traditional states of ferromagnetism, ferroelectricity, and superconductivity. Other, more exotic states such as vortex matter, spin ice, and quantum states with no classical interpretation can occur in such sublattices. It is the ability of crystalline solids to emulate spaces of different dimensionality and connectivity that allows the realization of exotic new states of matter with novel properties. A few examples of future directions of new crystalline materials with novel properties are presented below.

Scaffold Structures

The challenge of creating novel states is that of using unusual and innovative combinations of elements to create an electronic structure in which there is competition among possible states or forces, and then of fine-tuning the balance with chemistry. One approach uses an atomic sublattice to serve as the scaffolding for another sublattice. Examples are shown in Figures 2.1 and 2.2. In the first example, the high-transition-temperature (T_c) superconductor $YBa_2Cu_3O_7$, the superconducting phase is formed from the sublattice of copper-oxygen (Cu-O) pyramids, with the Cu-O chains and larger yttrium and barium atoms providing the necessary spacing to create a two-dimensional electronic structure (Figure 2.1). In addition, the Cu-O chains form a spatially distinct subsystem that acts as a charge reservoir for the two-dimensional subsystem.

Another example of atomic scaffolding is in the skutterudites. Skutterudites have the general formula RM_4X_{12}, where R is a rare-earth ion; M is iron (Fe), ruthenium (Ru), or osmium (Os); and X is phosphorus (P), arsenic (As), or antimony (Sb). A structure is shown in Figure 2.2. Characterized by an open structure and large numbers of synthetic combinations, the skutterudites exhibit a wide array of physical properties, including metal-insulator transitions, heavy-fermion superconductivity, and large thermoelectric power figure of merit. The latter property is aided by large voids in the crystal structure that allow large thermal vibrations for the atoms that reside in them—the atoms rattle around. This rattling is responsible for unusually large phonon scattering, which reduces thermal shorting in a thermoelectric cooling application.

Another example of scaffolding is found in the molecular compound [BEDT-TTF]Mn[$Crox_3$] (BEDT-TTF is bis(ethylenedithiolo)tetrathiafulvalene and ox is oxalate). Here, the coexistence of magnetic ordering and metallic-like electrical conductivity occurs due to alternating electrically conducting layers composed of $[\text{BEDT-TTF}]^+$ and ferromagnetically ordered layers composed of $\{\text{Mn}[\text{Crox}_3]\}^-$.

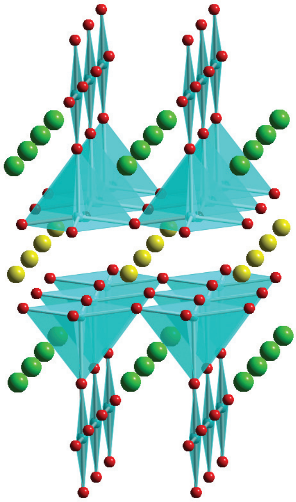

FIGURE 2.1 Crystal structure of $YBa_2Cu_3O_7$ showing the sublattice of the copper-oxygen pyramids (blue) and the larger yttrium (yellow) and barium (green) atoms providing the spacing for a two-dimensional electronic structure. SOURCE: Courtesy of M.A. Subramanian, Oregon State University.

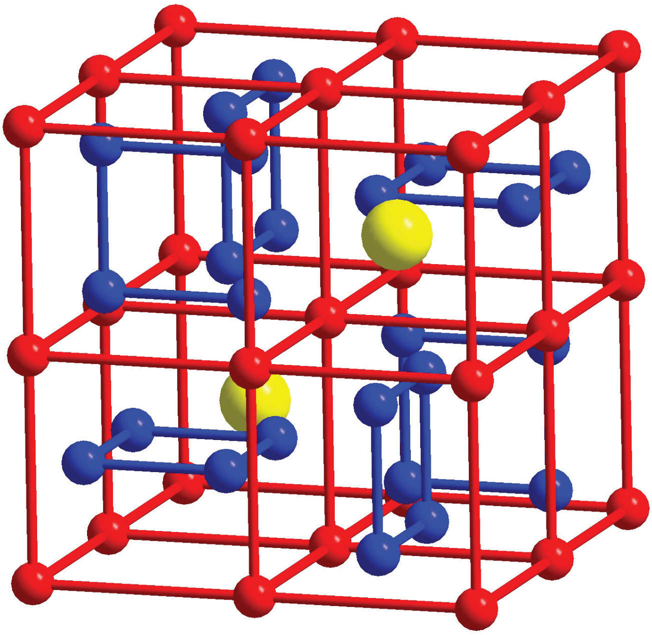

FIGURE 2.2 Filled skutterudite $LaFe_3CoSb_{12}$ showing the large open spaces where the lanthanum ions (yellow) rattle to scatter phonons. Iron (Fe) and cobalt (Co) (red) and antimony (Sb) (blue) are also shown. SOURCE: Courtesy of D. Mandrus, Oak Ridge National Laboratory.

The final example is the newly discovered magnetic material of Figure 2.3, in which the presence of the second interpenetrating lattice led to anomalous magnetic switching behavior not observed before.

Low-Dimensional Structures

As mentioned above, crystalline materials can possess internal scaffolding structures with effective dimensionality lower than three dimensions. Such crystalline structures possessing either chains or planes of interacting atoms modify the flow of energy for magnetic and electronic excitations, creating platforms for useful devices. This lower effective dimensionality can also lead to entirely new ground states. For instance, when local degrees of freedom are continuously variable, an atomic spin can point in any direction, and fluctuations suppress a long-range ordered state in one or two dimensions. In some cases, excitations in such systems can be "topological," like knots in a string. Solitons, which are localized waves whose shape is unaffected by usual dispersive effects, are an

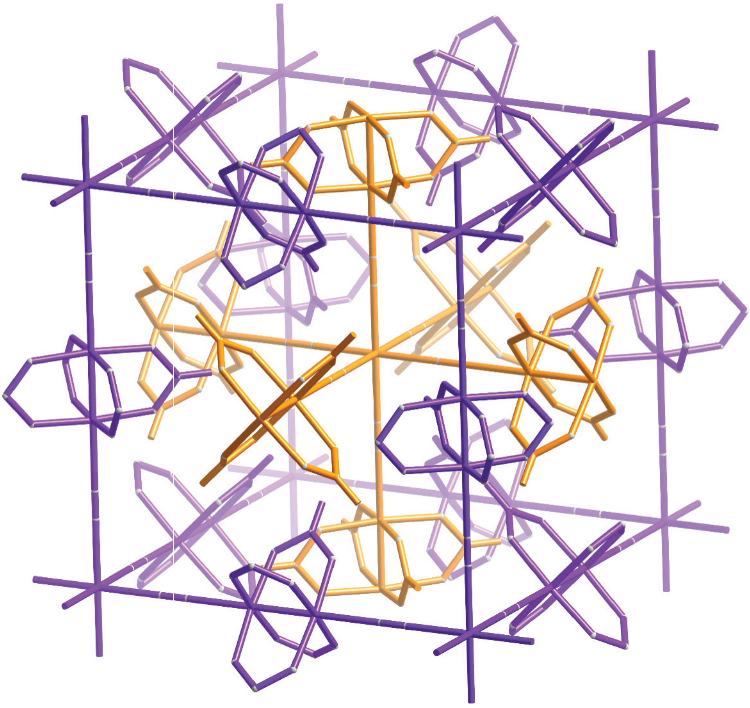

FIGURE 2.3 Interpenetrating $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ lattices are depicted in orange and purple. SOURCE: Courtesy of J.S. Miller, University of Utah.

example of topological magnetic excitations in one dimension. In two dimensions a common topological excitation is the vortex, which resembles a swirling pattern of spins. Topological character implies insensitivity to localized defects and dispersive effects that commonly destroy the coherence of harmonic, or wave-like, excitations. Such features are important for future information technologies; for instance, topological excitations in a two-dimensional electron gas have been discussed as possible stable bits of information in a quantum computer. Magnetic topological excitations are also potential "qubit" candidates, but the understanding required to design a material supporting such excitations is in the very early stages of development.

Low-Dimensional High-T_c Cuprates

Several central themes come together in the cuprate materials that exhibit high-T_c superconductivity, with $YBa_2Cu_3O_7$ (Figure 2.1) being the best-studied example. These materials have copper oxide sheets that are doped and effectively two-dimensional by means of a superlattice spatially distinct from the sheets. Absent a widely accepted microscopic theory, most contending theories feature the hybridized copper oxygen band as a key component of the superconducting as well as the normal state. The formation of patterns indicative of density variations in a high-T_c compound is shown in the scanning tunneling microscopy data of Figure 2.4.

Low-Dimensional High-Thermopower Cobaltates

The concepts of low dimensionality, geometric frustration of spin ordering, structural and orbital degrees of freedom, correlated electron physics, and quantum fluctuations converge to yield the unexpected physical properties of the layered oxide cobaltates. In a structural family based on hexagonal CoO_2 layers, these metallically conducting compounds display thermoelectric coefficients two orders of magnitude larger than those observed in conventional metals. Furthermore, superconductivity is observed in the hydrate $Na_xCoO_2 \cdot yH_2O$. The origin of these phenomena is not understood but could be due to a combination of low dimensionality and strong correlations unique to the combination of cobalt and oxygen.

Structures Leading to Strong Competition of Internal Forces

Patterns among low-energy degrees of freedom in a solid (such as those shown in Figure 2.4) can be thought of as distinct phases of matter. New phases are often found when competing forces are finely balanced at the microscopic

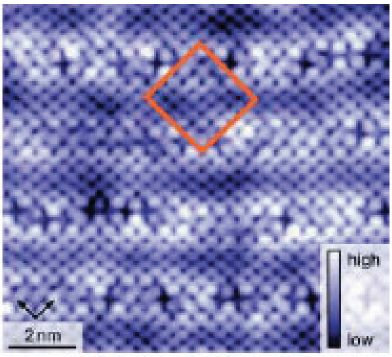

FIGURE 2.4 An example of anisotropic superconductivity in a cuprate material is seen in this scanning electronic micrograph in which the dark and light regions represent differing electron density. SOURCE: Courtesy of J.C. Seamus Davis, Cornell University.

level, either chemically by means of a novel combination of elements, or physically, for example by means of magnetic fields. The following are examples of competing states: localized versus itinerant electrons, spin alignment versus spin antialignment, or classical versus quantum fluctuations. When systems with finely balanced forces pass from one state to another, their physical response can become very large. An example is colossal magnetoresistance in manganite perovskites. Another example is the very large thermal resistance effect in vanadium oxide, used as the sensor in commercial infrared imaging systems. Physicists describe such behavior as "emerging" from the collective behavior of the large number of atoms ($\sim 10^{22}$) that comprise a solid. The synthesis scientist approaches the challenge of creating such new emergent behavior by using different paradigmatic approaches to crystal growth.

Geometrically Frustrated Structures

One route to optimizing competing interactions is through geometrical frustration of magnetic interactions. In geometrically frustrated materials, the spins that constitute magnetic matter interact antiferromagnetically: interactions favor antiparallel alignment of neighboring spins, as shown in Figure 2.5. Such interactions cannot be simultaneously satisfied when the spins occupy a triangular lattice, as also shown in Figure 2.5. The inability to achieve a state that minimizes the energy of all two-body interactions, and the resulting low-energy entropy, are called *geometrical frustration*. This simple paradigm has deep consequences. When spins in anisotropic pyrochlore magnets are allowed to point only up or down, in a manner similar to that shown in Figure 2.5 for a triangle, the spin system

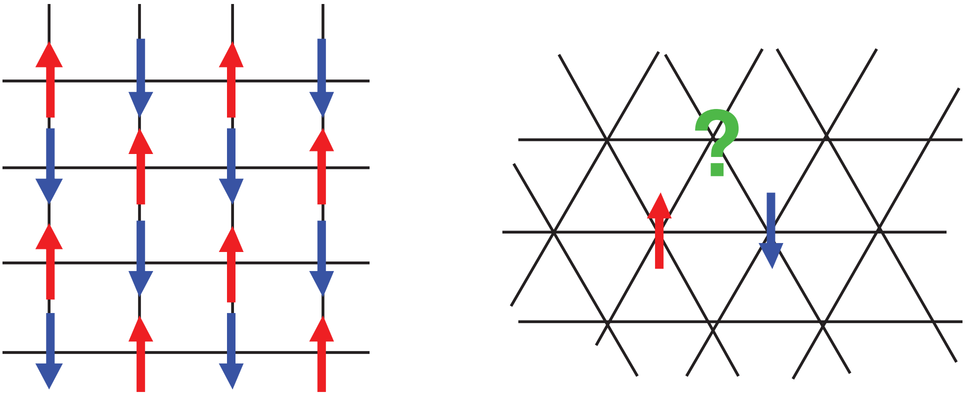

FIGURE 2.5 (Left) An example of a two-dimensional antiferromagnetic spin arrangement. (Right) The quandary posed for antiferromagnetically interacting spins on a triangular lattice.

is formally identical to the hydrogen atoms in water ice; hence the distinct state of magnetic matter in which long-range order is frustrated at low temperature is called *spin ice*. When the spins are allowed to point in a continuously variable set of directions, like the needle of a compass, other magnetic states, called *spin liquids*, can arise. In the spinel antiferromagnet $ZnCr_2O_4$, geometrical frustration produces novel low-energy degrees of freedom. The near cancellation of the strong interactions between neighboring spins produces new, weakly interacting low-energy excitations described by a theory of topological excitations with long-range interactions—a loose analogue of liquid crystals, but one in which the excitations retain their quantum character.

Experimental studies of quantum spin liquids in frustrated magnets are in their infancy. Exciting issues include the possibility of making new topological quantum spin states, the use of these states for quantum computation, and the novel couplings between lattice and orbital fluctuations. Especially exciting are the largely unexplored regimes of chlorides, fluorides, and chalcogenides; most exotic spin systems studied to date are oxides. Indeed, the recent discovery of a spin-½ kagome lattice in the hydroxychloride compound $ZnCu_3(OH_6)Cl_2$ has excited physicists for its indications of a quantum spin liquid and illustrates the potential of searching beyond oxides. Because many of the qualitatively new phases anticipated theoretically are extremely sensitive to defects, experimental progress is often entirely controlled by progress in materials synthesis techniques and in identifying new materials that realize specific lattice symmetries and/or that can be produced in a particularly pure form.

Orbital Degeneracy and Frustration

Magnetism in a solid results from both the spin and angular momenta of electrons orbiting the nucleus. When different orbital states have the same energy, quantum fluctuations are increased and classical long-range order is suppressed. This orbital degeneracy is similar to geometrical frustration-induced spin degeneracy in its close connection to the crystal lattice symmetry, and recent work has provided evidence for both orbital liquid and orbital glass phases in compounds with the spinel crystal structure.

Phase-Change Materials

When two different structural states are similar in energy, they compete with each other for the right to exist at a given temperature. Such a situation exists in the so-called *phase-change materials*. These are typically germanium-antimony-tellurium (Ge-Sb-Te) alloys that have, at room temperature, two different stable states, crystalline and amorphous. Either state can be locked in by using one of two different heating and cooling procedures. These procedures use a laser or a current pulse to produce a confined area (a bit) with elevated temperature. To create an amorphous bit, the material is heated well above the melting temperature for a very short time. To create the crystalline phase, a lower temperature, just above the melting temperature, is induced for a longer period of time. The resulting state, crystalline with higher conductivity or amorphous with lower conductivity, is then read either optically or electrically. Phase-change materials are already used in commercial products such as Blu-ray discs and High-Definition/Density Digital Versatile Disc (HD-DVD) storage and are expected soon in products such as random access memory disks for personal computers (PC-RAM) and super-resolution near-field structure discs. As an information-storage medium, phase-change materials are faster than flash memory and are more readily scalable to smaller bit sizes and therefore higher information density. Despite their advanced state of application, important aspects of the phase-change process, such as the dynamics of melting and recrystallization, are not completely understood. A better understanding of such dynamic, nanoscale crystallization processes will be needed to realize the full benefit of scaling to smaller bit sizes.

Heavy-Fermion Metals

In certain intermetallic systems, the conducting electrons can interact so strongly with coexisting magnetic atoms that the magnetically ordered state is suppressed and the magnetic character of the atoms is "dragged" along, or hybridized, with the conducting electrons. With respect to the magnetic atoms, there is strong competition between magnetic long-range order and full itineracy of the electrons on the magnetic atom. In the itinerant limit, these electrons become "heavy" in the sense that specific heat and resistivity behave as though the mass of an otherwise free electron was increased. In some materials this increase is three orders of magnitude over the mass of an electron in free space. Examples of such materials include uranium- and cerium-based intermetallics such as UPt_3 and $CeCu_2Si_2$. Several of these systems undergo a transition to a superconducting state as the temperature is lowered. Since the electron is carrying the vector character of the magnetic atoms, unusual types of superconductivity can occur. For instance, the macroscopic quantum state that constitutes superconductivity can become imbued with an anisotropy that normally characterizes atomic orbitals—for example, the *s*-, *p*-, and *d*-wave (and perhaps higher angular momentum) states.

Despite the large amount of phenomenology developed for heavy fermions, there are major gaps in the scientific understanding of these systems. In certain heavy-fermion materials the temperature-dependent properties do not behave like free electrons within the so-called Landau Fermi-liquid description. Strange fractional exponents characterize thermodynamic properties at low temperatures, indicating a critical state that is qualitatively different from that of the well-known Landau Fermi-liquid. This leads to important questions: What other conducting states are possible beyond the Landau Fermi-liquid? Are there distinct universal states of which the Landau Fermi-liquid is but one, or are some of the phases part of an extended critical phase with nonuniversal and continuously varying exponents? Answers to these questions would represent major progress in the understanding of strongly correlated quantum systems. Other important questions from the experiments include these: Why are heavy-electron states so sensitive to crystal quality? Why are there so few heavy-electron superconductors? How does a nascent heavy-electron material with very few magnetic atoms (a so-called Kondo system) develop into a heavy-electron material?

Extreme Conditions

Another route to controlling competing interactions and creating new states is through the introduction of extreme environments. In many strongly correlated materials, energetically similar ground states compete for space in the crystal, which can lead to the coexistence of multiple ground states, such as superconductivity and charge order. Applying pressure, high magnetic or electric fields, or extreme temperatures can suppress one of these states while enhancing the other. For basic science, extreme environments offer the possibility of continuously tuning properties to access unique critical parts of phase space that may be inaccessible through materials synthesis without introducing disorder. A practical outcome could be dramatically enhanced properties, such as stronger structural alloys or a higher-performance superconductor stabilized at ambient conditions following synthesis under multiple extreme conditions.

Multifunctional Structures

Materials are often grouped into classes according to their functionality (see Appendix E). Metals, ferromagnets, and nonlinear optical materials, for example, are all defined by their response to external fields and resulting functionality when incorporated into a device. New classes of multifunctionality can be created by combining two (or more) distinct properties in one material such that there is coupling between these states. Alternatively, for materials where such coupling is small, multifunctionality can be thought of as the superposition of two desired responses in a single material. While the physics of such systems might not be new, they offer the possibility of reducing weight, power, and cost for device applications. Materials with anomalously large coupling to multiple stimuli such as magnetic and electric fields might, for example, lead to new information-storage systems. Since the functionality of a material often derives from a specific atomic element, creating a multifunctional material often involves creating compounds with specific types of atoms situated in the crystal structure so as to maximize their interaction. The advent of molecule-based magnets has heightened opportunities for magnetic materials with multiple properties. For example, light control and electrochemical control of magnetic behavior have already been demonstrated. (For a discussion of the thin-film approach to multifunctionality, see the subsection on “Thin Films,” under Grand Challenge 3). Much of the recent research in multifunctional materials has focused on magnetoelectric response, discussed below. There are, however, many other generic types of multifunctionality, such as electrochromic, magnetostrictive, magnetooptic, and electrooptic that are comprised by this field.

An example of a magnetoelectric multifunctional material is shown in Figure 2.6. The number of specific atoms known to induce a single functionality is usually small. For instance, ferromagnets usually possess cobalt, iron, nickel, or manganese. The number of combinations allowed between atoms from different classes is large, however, particularly when different crystal structures are taken into account. In the above example of magnetoelectric multifunctional materials, the search for new compounds also requires synthesis and characterization of single crystals, given the need for the intrinsic response of the dielectric as well as the need to access anisotropic structures. Other examples of multifunctional properties are magnetooptic, magnetostrictive, and magnetic semiconducting responses. A material displaying any of these responses, especially at or above room temperature, with adequate sensitivity is all but guaranteed to have a major technological impact.

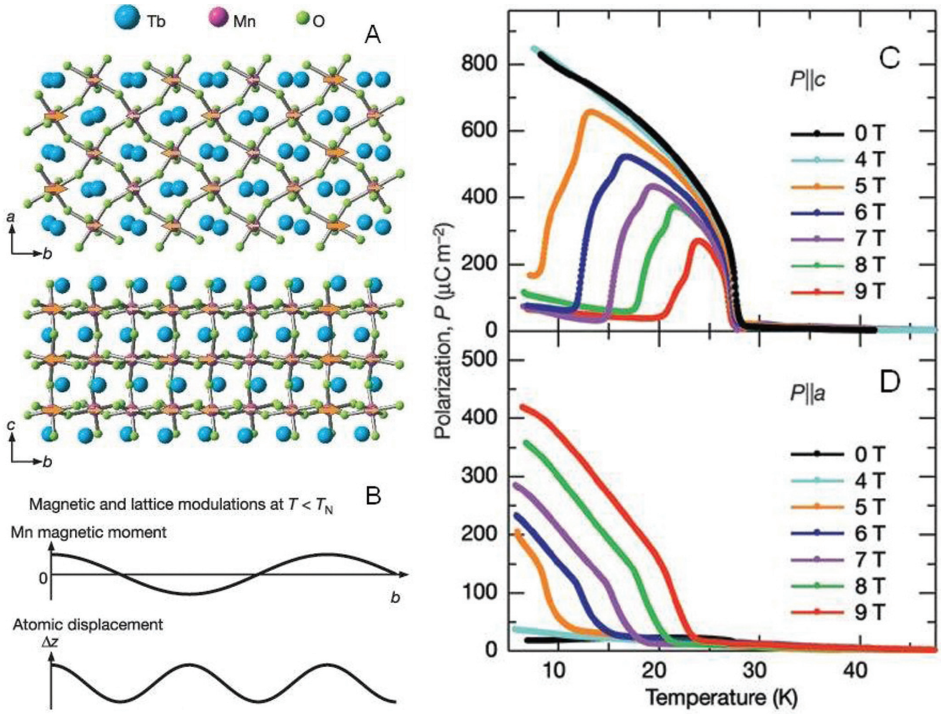

FIGURE 2.6 Crystal structure for $TbMnO_3$ showing atomic positions at room temperature (upper panel [a]) and the spatial variation and local spin direction along a given direction (lower panel [a]). (b) At low temperatures the spins develop an oscillating component along the c-axis so as to form an inversion symmetry-breaking spiral. This state is accompanied by inversion symmetry-breaking atomic displacements, hence ferroelectricity. Panels (c) and (d) show the electric polarization of $TbMnO_3$ in two different crystallographic directions as a function of temperature for different values of applied magnetic field. SOURCE: Reprinted by permission from Macmillan Publishers Ltd: *Nature*, T. Kimura, T. Goto, H. Shintani et al., *Nature,* **426,** 55 copyright (2003).

Electric Field Control of Magnetism, Magnetoelectrics, and Multiferroics

The previous subsection describes an approach to magnetoelectric multiferroics that relies on novel combinations of atoms in a bulk crystal. New approaches to control and alter magnetism with an electric field, or, conversely, altering a ferroelectric state with a magnetic field, suggest novel thin-film multiplayer structures. In the schematic example shown in Figure 2.7, control of magnetism with an electric field requires a coupling mechanism at the interface that inherently breaks time reversal symmetry, which is required to switch the state of magnetization. In contrast, strain coupling can be used to modulate magnetism, for example, in heterostructures.

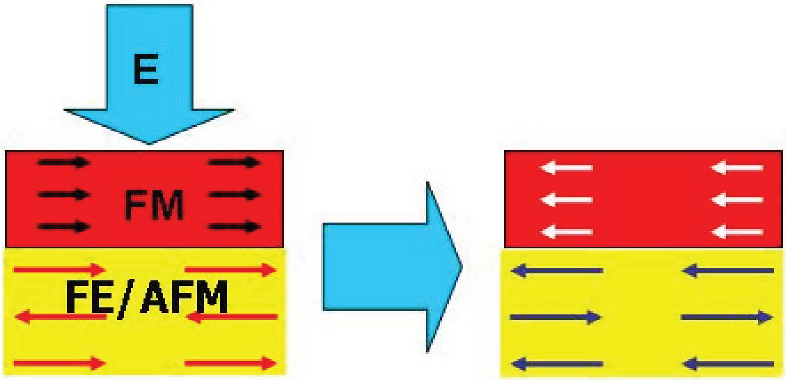

FIGURE 2.7 Schematic illustration of a ferromagnet-multiferroic (FM) (ferroelectric [FE]/ antiferromagnetic [AFM]) heterostructure that can be used to control and switch ferromagnetism with an electric field (E). The arrows in both layers depict the direction of the magnetic moments.

Electrically Tunable Exchange Bias in Magnetic Heterostructures

Exchange bias coupling is well known in magnetism and is exploited extensively in magnetic sensing and storage applications. Exchange bias typically occurs between an antiferromagnet and a ferromagnet; strong exchange interactions at the interface "pins" the spins in the ferromagnetic layer. The antiferromagnet in conventional exchange bias structures is typically a metal (manganese, iridium manganese) or a semiconductor (nickel oxide). Ferroelectric antiferromagnets (such as the multiferroic perovskites) present a new and exciting opportunity to attempt to modulate or control the magnetic structure by the application of an electric field. Such effects do not necessarily require a multiferroic material; the presence of a large magnetoelectric effect in the crystal would be sufficient.

The presence of ferroelectricity in the crystal provides the opportunity to control antiferromagnetism in a permanent (nonvolatile) way. The next step is to couple the antiferromagnet to a ferromagnet and attempt to switch the ferromagnetism through the application of an electric field. Indeed, this area of research promises to be exciting and has the potential for new device technologies. One such emerging technology is *spintronics,* which seeks to use the spin of the electron instead of its charge as the fundamental bit of information, which would lower the power consumption in a microprocessor. The use of magnetoelectric coupling in multiferroic spintronics would enable the manipulation of spin magnetism not by slow and weak-coupling magnetic fields but by fast and strong-coupling electric fields.

Search for New Multiferroic Crystalline Compounds

Will there be a ferromagnetic-ferroelectric in future information systems? To answer this question, researchers must explore the frontier of materials design at the atomic level to create materials that simultaneously exhibit ferromagnetic and ferroelectric behavior. In many oxide systems, exchange interactions are mediated by the oxygen ions and lead to antiferromagnetic coupling (a key exception is the manganite system that exhibits so-called colossal magnetoresistance). This conundrum appears to present an ideal opportunity for innovative materials and device design. Even if device designers cannot capitalize on an idealized ferromagnetic-ferroelectric at room temperature, it may be possible to create a canted magnetic structure, intermediate between antiferromagnetism and ferromagnetism, that breaks inversion symmetry. Is it possible to tune canted magnetism such that macroscopically useful magnetic moments can be realized in a ferroelectric canted magnet?

New Behavior in Artificial Structures and Interfaces

The interface between two dissimilar crystalline materials provides a powerful platform for exploring novel properties and controlling device functionality. As Herbert Kroemer, recipient of the Nobel Prize in physics in 2000, noted in his Nobel Lecture, "The interface is the device."[1] Starting with the notion of interface states crucial to the operation of the original transistor, the ability to engineer and control interfaces has progressed to present-day deposition techniques whereby atom-level control is a reality. Indeed the ability to control atomic deposition allows materials scientists to create completely artificial materials that have no analogue in bulk crystals. The excitement surrounding interface physics stems from the nascent capability of pushing device design down to the atomic level, where engineering, physics, and computational modeling come together.

Conventional Semiconductor Heterostructures

Three decades of research and development yielded practical devices such as the field-effect transistor, the quantum-well laser, and the quantum-cascade laser. They also provided insights into fundamental science from unusual quantum states such as the quantum Hall effects and exciton Bose-Einstein condensates. Developing these types of structures in other materials is a priority: new interface behavior could include, for example, the formation of new electronic phases leading to

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[1] See http://nobelprize.org/nobel_prizes/physics/laureates/2000/kroemer-lecture.pdf. Last accessed June 3, 2009.

phenomena such as superconductivity, spin-polarized correlated electron gases, spin-transistor devices, new optoelectronic devices, and novel sensors. The ability to create chemically and structurally perfect interfaces is a prerequisite for the study of these electronic phenomena. Advances in deposition tools and instrumentation, discussed below, are needed to enable the control of such interfacial phenomena. The power of heterostructure interface design and engineering is illustrated with a few examples, spanning a spectrum of physical phenomena.

Phonons, Phonon Confinement, and the Phonon Laser

Tailoring acoustic phonon properties is important for terahertz-frequency phonon devices, including the generation and amplification of coherent phonons. Recently, terahertz acoustic cavities have been demonstrated with enormously amplified acoustic phonon/photon interaction, leading to the possibility of modifying the lifetime of optical phonons through tailored anharmonic processes. Acoustic cavities could also provide the required feedback mechanism for a phonon laser (see Figure 2.8). Important developments in terahertz acoustics are based primarily on compound semiconductors using mature epitaxial growth techniques, such as molecular-beam epitaxy (MBE), that enable the construction of heterostructures with atomically flat interfaces by design. Heterostructures of oxide materials such as $BaTiO_3$ and $SrTiO_3$ with strong coupling between sound, charge, and light offer an almost completely unexplored, but rich, terrain of versatile compounds with superior acoustic properties. They provide a range of acoustic impedances that can exceed the acoustic impedance mismatches in semiconductor heterostructures. In addition, they can be strongly piezoelectric, providing additional mechanisms that can significantly enhance sound-and-light coupling and allow electrical tuning of acoustic cavity wavelengths.

Coupled Phenomena at Interfaces: Interconversion and Coupling Between Electrons, Phonons, and Photons

Multiferroics provide a good example of coupling between two types of order parameters. An alternative way to approach materials design and synthesis is to explore the possibility of converting and/or coupling/decoupling interactions between electronic and thermal properties of matter. An obvious example is in thermoelectric materials, in which it is desirable to decouple electronic and thermal transport. The example of the phonon laser described above would be a natural consequence of the ability to confine phonons. Another key area of materials development is in the conversion of light energy to free-electric charge, as in photovoltaic solar cells. Artificially engineered nanostructures and heterostructures are the most obvious approach for exploring ways to overcome the exciton mean free path, for

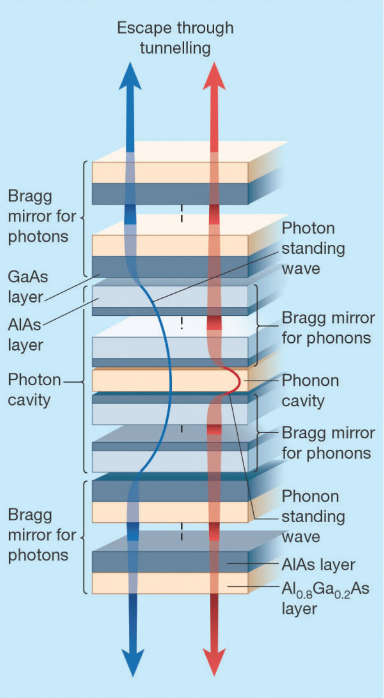

FIGURE 2.8 Schematic illustration of a device incorporating a resonant cavity for acoustic phonons inside an optical cavity, thereby enhancing interaction between sound and light. SOURCE: Reprinted by permission from Macmillan Publishers Ltd: *Nature,* Adapted from J.M. Worlock and M. Roukes, "Applied Physics: Son et Lumière," *Nature,* **421,** 802 (2003).

example. Considerable success has been achieved in developing photovoltaic systems with a mixture of materials on the nanoscale (see Figure 2.9). One approach to the optimization of such materials would involve incorporating crystalline molecular structures to replace the present disordered structures.

Polariton Bose Condensates

Strong coupling between photons and electron-hole pairs in semiconductors is the basis for the conventional semiconductor laser. Using a high-quality Bragg mirror to confine the light, it is now possible to develop a new state of matter in which the photon and the electron-hole pair are coherent (forming a new particle called a *polariton*). Macroscopic condensation of these excitations leads to a new Bose-Einstein condensate formed at relatively warm temperatures of tens of degrees kelvin (Figure 2.10). With improved device fabrication and more strongly bound

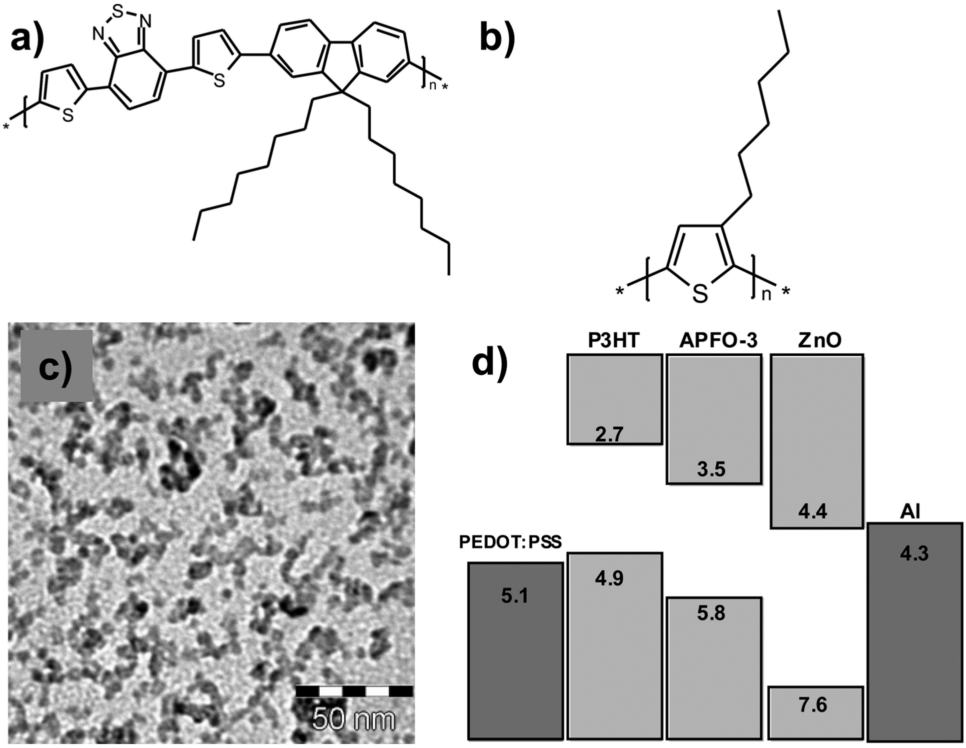

FIGURE 2.9 Composite structure of two polymer materials—(a) APFO-3 and (b) P3HT—to provide electron and hole transport, combined in a nanoscale composite with zinc oxide (ZnO) nanoparticles; (c) transmission electron microscope image of ZnO nanoparticles; (d) highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) levels (in electronvolts) of APFO-3, P3HT, and ZnO nanoparticles with respect to common metal electrodes. SOURCE: Reprinted, with permission, from H.M.P. Wong, P. Wang, A. Abrusci et al., "Donor and Acceptor Behaviour in a Polyfluorene for Photovoltaics," *Journal of Physical Chemistry C,* **111,** 5244-5249 (2007). Copyright American Chemical Society.

electron-hole pairs, it might be possible to obtain Bose-Einstein condensation temperatures that approach room temperature.

Bulk Crystalline Matter Discovery Challenges

Crystalline matter discovery can be broadly divided into two categories: growth of bulk crystals and growth of crystalline thin films. Thin-film growth is most closely associated with a level of control not attainable with bulk-crystal growth techniques. Challenges in thin-film growth are addressed in the section below

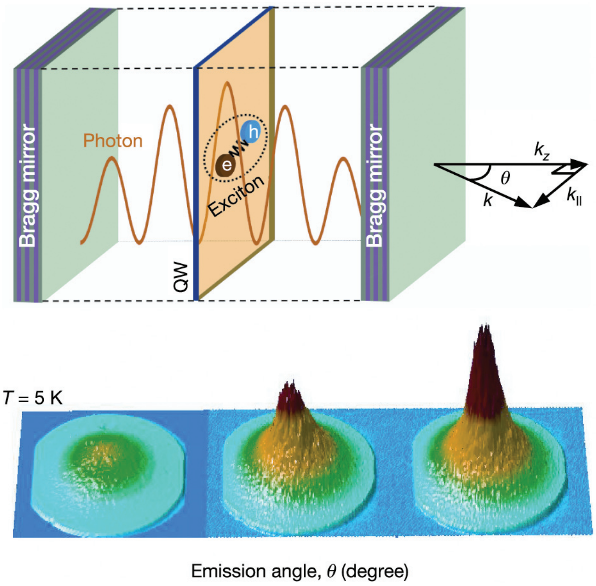

FIGURE 2.10 (Top) A schematic view of quantum-well (QW) excitons coupled to microcavity photons. (Bottom) The momentum distribution of exciton-polaritons in a cadmium tellurium (CdTe) microcavity, showing the emergence of a coherent Bose-Einstein condensation peak of low momentum states as the density is increased. **SOURCE: Reprinted by permission from Macmillan Publishers Ltd.**, *Nature*, J. Kasprzak, M. Richard, S. Kundermann et al., **“Bose-Einstein Condensation of Exciton Polaritons,”** *Nature,* **443**, 409 (2006).

entitled “Grand Challenge 3: Evolution in the Capacity to Create Crystalline Materials by Design.” In this subsection, challenges are discussed for the growth of bulk-crystalline material, both in the highly exploratory phase of new materials development and in the growth of large single crystals.

New materials synthesis using solid-state chemistry primarily yields polycrystalline specimens composed of single crystals with dimensions on the order of 100 to 1,000 nanometers (nm). These crystallites are large enough to support phenomena such as ferromagnetism or superconductivity; however, many of the phenomena of current interest are either anisotropic or extremely sensitive to grain boundaries, which dictates the need for crystal growth even in the discovery phase. After the initial discovery of a novel phenomenon, single crystals are always required, regardless of the nature of the effect, in order to probe direction-dependence or defect-sensitive properties.

Combinatorial chemistry was developed in the 1990s to accelerate the rate of discovery of new functional compounds. This technique proved to be successful in the search for new pharmaceuticals. In the materials arena, combinatorial chemistry is typically based on polycrystalline films with an inherent chemical phase and compositional distribution. While combinatorial chemistry has been successful in a small number of materials searches, the overall impact on materials science has been limited.

Flux growth remains an important route to the growth of single crystals with novel functionalities. Recent examples include ZrW_2O_8 (pictured in Figure 2.22), a cubic material that contracts on heating from 0 to 1050 K, and the 115 family of strongly correlated metals such as $CeCoIn_5$. The importance of these discoveries is reflected by the fact that more than 400 papers referencing one or both of these compounds were published in the year 2007.[2] These compounds were discovered as a result of the ingenuity of individual scientists using little more than a crucible, a high-temperature furnace, and high-purity starting materials.

The physical tasks required to crystallize a novel material are time-consuming and have not benefited substantially from automation. A polycrystalline ingot is prepared by mixing component powders in the solid state and performing multiple sinterings for every desired composition. Zone refining is required to grow a crystal from such a polycrystalline ingot, which can take from hours to days. For the synthesis of oxides, the installation of several dozen optical float zone furnaces that employ focused high-intensity light as the heat source (see Appendix D) in Japan in the 1990s expanded capabilities for oxide crystal growth to larger crystals, lower defect densities, and more complex stoichiometries. However, as is the case for most other advances in crystal growth technology, this development did not increase the ability to leverage human resources as have advances in measurement techniques. Direct human involvement requiring trained and highly skilled scientists remains an essential aspect of growing new crystalline materials.

GRAND CHALLENGE 2: CREATION OF NEW CRYSTALLINE MATERIALS FOR ENERGY PRODUCTION AND CONVERSION

Crystalline materials will play an important role in future energy systems. Examples abound of the relevance of crystalline materials in a broad array of energy applications that impact all facets of the energy cycle, from energy generation and transportation to storage. For photodiodes and photovoltaic (PV) conversion, single crystals provide a means for reaching ultimate performance limits for energy generation and control. For thermal energy scavenging, thermoelectric devices use monoliths containing small single-crystalline grains. Rechargeable batteries such as those used in portable electronics are based on the mobility of lithium ions between two crystalline electrodes. Crystalline materials also appear in the energy

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[2] ISI Web of Knowledge search, http://apps.isiknowledge.com/——“CeCoIn5” OR “ZrW2O8” in Topic AND “2007” in Year Published.

cycle in less obvious manifestations, such as in the energy savings associated with the high-strength crystalline turbine blades discussed in Chapter 1. The importance of energy in every aspect of people's lives and the potentially large impact of crystalline materials for energy production, storage, and efficiency demand a focused effort.

Not only are crystalline materials currently in widespread use, but they will also continue to play a critical role in developing solutions to energy needs in the future. Described below are three representative areas of energy research that rely critically on the ability to control the growth of crystalline materials and that exemplify great opportunities for energy generation and conservation. These areas are solar energy and solid-state lighting (luminaries); superconductivity for electricity delivery, motors, and generators; and catalysts for fuel conversion and hydrogen storage.

Band-Gap Engineering for Solar Energy and Solid-State Lighting

Solid-state lighting relies on light produced by de-excitation of free charges injected into a junction between dissimilar semiconductors. The converse of this process arises in PV devices (solar cells), in which light absorbed at a junction induces the production of free charges (Figure 2.11). Discovery and growth of crystalline materials activities play a central role in advancing capabilities in these areas. At the basic science level, these two functionalities benefit from many of the same advances in fundamental understanding of energy and charge transport

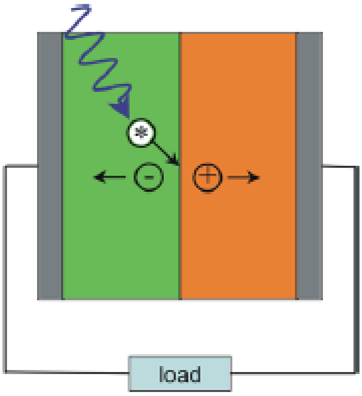

FIGURE 2.11 Simple schematic of a solar cell. The energy from incident light leads to the creation of an electron-hole pair, which separates to create electrical energy. SOURCE: Reprinted from U.S. Department of Energy, Office of Science, Report of the Basic Energy Sciences Workshop on Solar Energy Utilization, April 18-21, 2005, *Basic Research Needs for Solar Energy Utilization,* Figure 30, available at http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf.

across interfaces in heterogeneous thin-film systems. At the applied level, much of the development in these areas centers on creating new organic and inorganic materials with greater efficiencies but whose large-scale fabrication costs render their use economically viable. While both technologies at present have small markets, they are viewed by the Department of Energy (DOE) and an increasing number of private-sector companies as fertile areas for further product development.

The vast majority of today's PV production is Si-based, single band-gap material, based on either single-crystal or multicrystalline ingots or on multicrystalline ribbons. The crystallinity of the material plays an important role in both the efficiency and the cost of the device. At present, Si PV devices cost less than $3 per watt of peak power, with the price decreasing roughly as the cube root of cumulative production. The record efficiency for single-crystal Si PV devices with a single *p*-*n* junction is currently about 25 percent, and further advances are expected through materials processing research. While the economics of Si PVs are subject to the demand for high-purity material for use in integrated circuits and energy costs for producing high-purity crystalline Si, much research is devoted to improving the trade-off between the efficiency and cost of growth and the purity and crystallinity of ingots grown by the traditional Czochralski process. Most of the innovation in crystal growth is in non-ingot-based technologies such as Si ribbon growth, which circumvents the cost of slicing ingots to produce wafers. Semiconductors such as II-VI systems CdS, CdSe, and CdTe have band gaps larger than Si and thus increase the PV efficiency through increasing the open-circuit voltage. These materials are readily processed using scalable thin-film techniques such as spraying, solution growth, or electrodeposition combined with postdeposition processes to promote crystallinity and purity.

The best performance comes from the highest-quality single-crystal-based PV devices, which approach the Shockley-Queisser efficiency limit for single band-gap PVs of 32 percent (Figure 2.12). Grain boundary recombination and related losses associated with noncrystallinity reduce the quantum yield of light-to-electricity energy conversion. Consequently, amorphous Si cells have half the efficiency of the highest-quality single crystals. This gain in efficiency is accompanied, however, by significant increases in energy usage and cost associated with producing high-quality single-crystal material. The search for alternative, higher-efficiency materials has focused on compound semiconductor heterojunction cells made from III-V compounds that circumvent the Shockley-Queisser limit by incorporating multiple band gaps in a heterojunction device. Power efficiencies on the order of 40 percent are currently achieved in three-junction devices. However, the cost of their complex fabrication processes and high-purity raw materials makes them impractical to manufacture at present on a large scale. Further progress will rely on solving the complex materials challenges that arise in fabricating multilayer junctions with high crystallinity, yet at low cost.

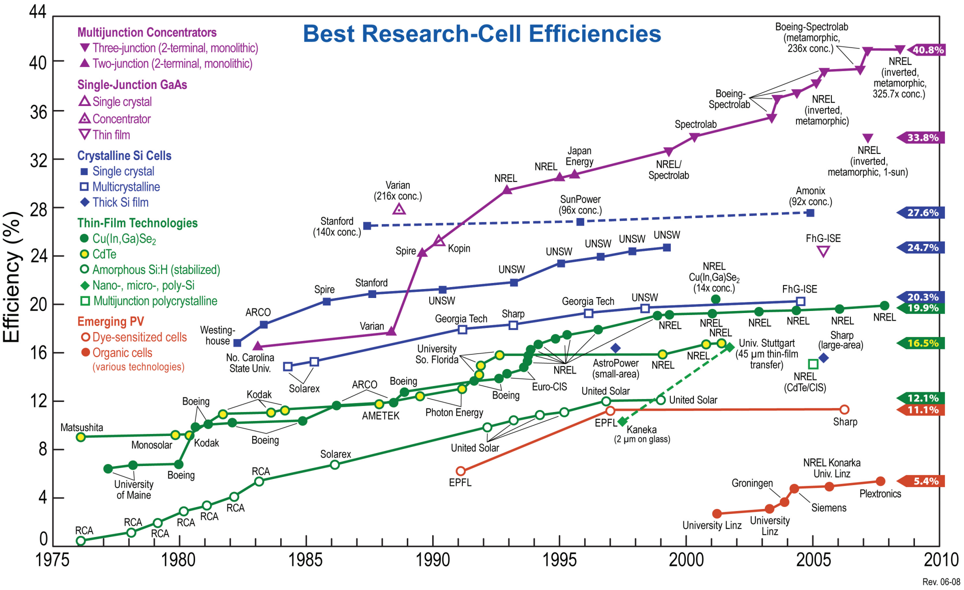

FIGURE 2.12 Improvements in solar cell efficiency, by system, from 1976 to 2008. NOTE: NREL, National Renewable Energy Laboratory; FhG-ISE, Fraunhofer Institute for Solar Energy Systems; UNSW, University of New South Wales; EPFL, Ecole Polytechnique Federale de Lausanne; AMETEK, Ametek, Inc.; ARCO, ARCO Solar, a division of ARCO; Euro-CIS, European Consortium in $CuInSe_2$. SOURCE: This figure was developed by the National Renewable Energy Laboratory for the U.S. Department of Energy.

Organic-based materials are potentially attractive candidates for PV applications because of their low formation energies and associated low fabrication cost. Typical fabrication processes involve evaporation or spin deposition from a solution of organic molecules; in contrast, most Si PVs are fabricated from zone-refined single crystals. Perhaps not surprisingly, the best efficiency reported for organic-based cells is approximately 6 percent. Improvements to this figure of merit will come from enhancing both charge injection and extraction and quantum photoconversion efficiency. The performance of organic-based PVs is at present dominated by the existence of large densities of charge-trapping impurities that impede free charge transport as exciton transport. Research is required to improve the understanding of these fundamental charge and energy transport mechanisms in bulk materials and at interfaces and to assess achievable gains through the development of improved materials. One approach is to develop a level of materials control comparable to that of Si and other mature semiconductor technologies. There is no known intrinsic reason that the efficiencies of either inorganic or organic PV devices cannot be substantially improved to produce electricity at a competitive price.

Indoor lighting accounts for 20 percent of total electricity use in the United States, and light-emitting diodes (LEDs) have the potential to reduce electricity use for indoor lighting by 50 percent, making this area a very important focus for energy reduction. Compound semiconductors that emit light are generally single-crystal materials grown as thin films at very high purity using layer-by-layer growth processes such as MBE or metal-organic chemical vapor deposition. For reasons discussed above for PV applications, organic light-emitting diodes (OLEDs) are viewed as a potential improvement in solid-state lighting technology. However, despite progress in recent years, the purity of organic materials relevant to solid-state lighting remains more than three orders of magnitude below that for common inorganic semiconductors. Again, the goal is to develop a level of materials control comparable to that of mature semiconductor technologies such that the efficiencies of organic materials can be sufficiently improved to meet this need. Reviews of the science and technology of solar energy and solid-state lighting are available from DOE.[3]

Superconductivity for Electricity Delivery

Electrification was identified as “the greatest engineering achievement of the 20th century” by the National Academy of Engineering.[4] As the U.S. use of electrical energy increases, more efficient means for transporting electricity over the nation’s power grid are required (see Figure 2.13). A report by DOE’s Office of Basic Energy Sciences entitled *Basic Research Needs in Superconductivity to Secure our Energy Future* specifies the importance of discovery and growth of crystalline materials in the form of superconducting materials in impacting the grid. Through this grid, electricity provides clean energy from a wide variety of sources to a wide variety of end users. However, in the 21st century, the growing demand in the United States for energy is already challenging the existing grid (e.g., when brownouts occur). At present, the annual world electrical energy consumption of approximately 2 terawatts (TW) is predicted to double and triple by 2050 and 2100, respectively, surpassing present grid capability. Today, over 60 percent of transported energy is lost in production and delivery, with 8 to10 percent being lost in the grid.

Transporting energy across time zones may also become more important

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[3] See http://www.science.doe.gov/bes/reports/files/SEU_rpt.pdf and http://www1.eere.energy.gov/buildings/ssl/. Last accessed March 3, 2009.

[4] W.A. Wulf, “Great Achievements and Grand Challenges,” *The Bridge—Report of the National Academy of Engineering*, **30,** No. 3/4 (Fall/Winter 2000). Available at http://www.nae.edu/nae/bridgecom.nsf/weblinks/NAEW-4STLP8?OpenDocument. Last accessed March 3, 2009.

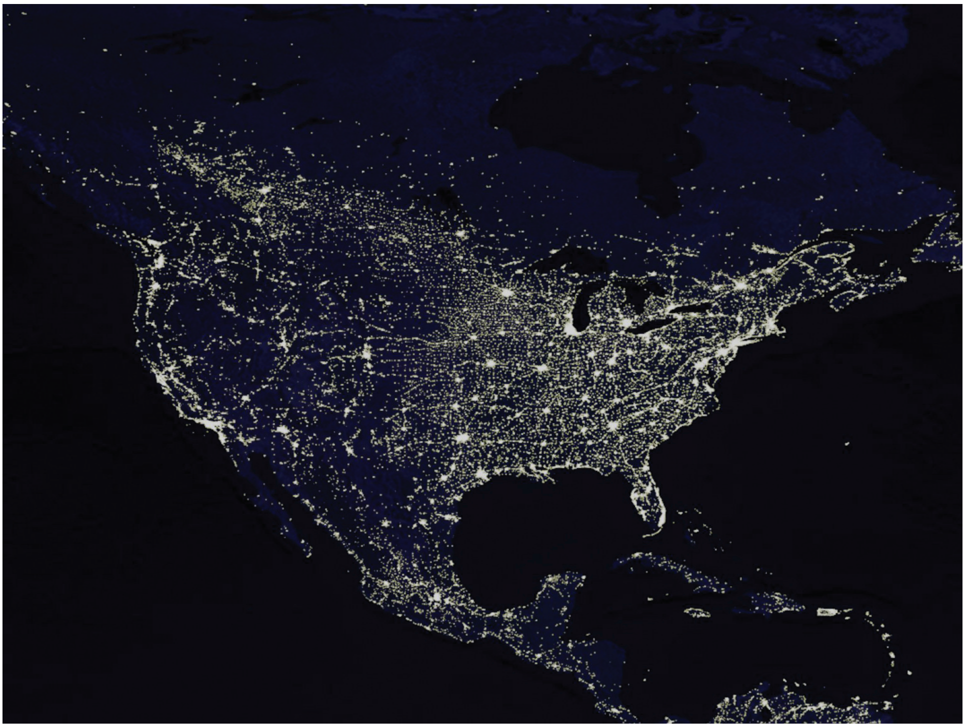

FIGURE 2.13 North American electric grid as viewed from space at night. SOURCE: Courtesy of Goddard Space Flight Center. Available at http://svs.gsfc.nasa.gov/goto?2276.

with increased reliance on solar energy. Superconducting cables providing lossless energy transport offer the ultimate solution. Superconducting wires can carry currents up to five times the currents that copper wires with the same cross section can carry. Replacing sections of the grid with superconductors, particularly in the regions where the voltage is stepped down and resistive loss becomes more significant, would have a dramatic effect on grid efficiency.

All superconductors need to be cooled to become superconducting, and the high-temperature superconductors, discovered in 1986, become superconducting at temperatures that are significantly easier to reach than those of conventional superconductors (Figure 2.14). They do not require expensive cryoliquids, such as liquid helium, and can easily be cooled with liquid air or mechanical refrigeration. At present, the best high-temperature superconducting cables—called 2G, for second-generation wires—contain the high-temperature superconductor $YBa_2Cu_3O_7$. DOE programs have successfully used these 2G wires in two pilot

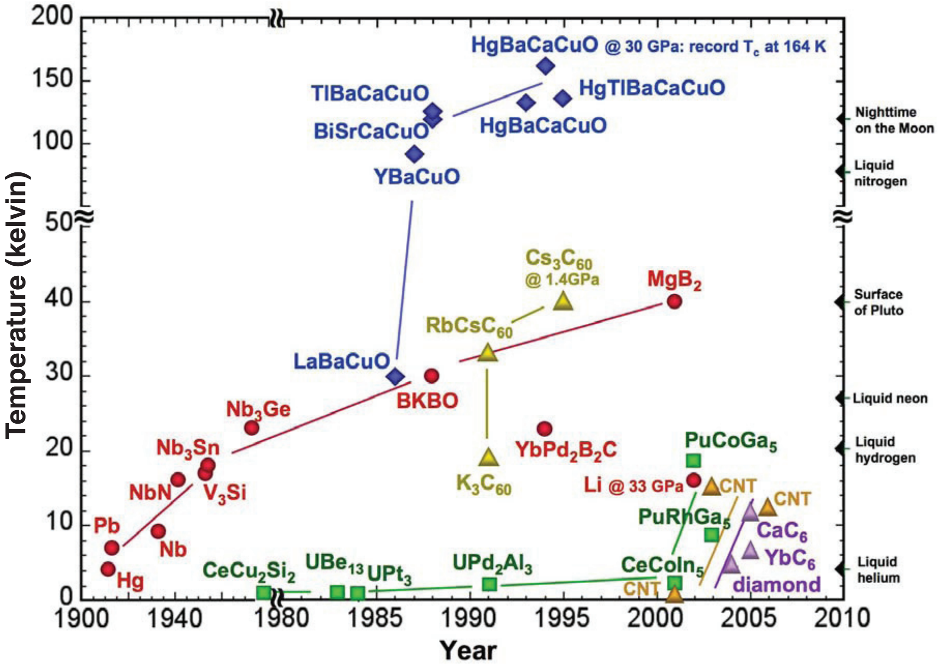

FIGURE 2.14 Time evolution of the superconducting transition temperature, T_c, of various superconducting materials. Note that certain classes exhibit dramatic increases and, as discussed in the text, these increases incorporated some degree of predictive discovery. SOURCE: Report of the Basic Energy Sciences Workshop on Superconductivity, May 8-11, 2006, *Basic Research Needs for Superconductivity,* Figure 24, p. 86, available at http://www.science.doe.gov/bes/reports/SC_rpt.pdf.

programs: power substations, with one near Columbus, Ohio, in operation since 2006, and transmission lines in New York State.

The 2G transmission lines have limited benefit to the grid, however, as the materials are extremely anisotropic and brittle and have limited reliability. Most important, they are expensive to produce, as they rely on a silver base and complex multilayer technology. The current capacity, J_c, and homogeneity of the 2G wires can be improved by engineering defects in the superconducting wires. These defects are needed because superconductors can experience loss due to motion of vortices, and defects can "pin" the vortices. Research is needed to optimize these defects and reduce loss.

Third-generation, 3G, wires, which are more reliable, isotropic, and have transition temperatures and J_c at least as high as those of the present high-temperature superconductors, are needed in order to have an impact on the grid. Over the past 30 years, research on strongly correlated electron materials, such as superconducting materials, has reached the point that scientists need not rely only on serendipitous discovery to identify the next material. Scientists have learned that emergent phases arise from phase boundaries between competing phases (such as between metallic and insulating phases). The universal phase diagram in Figure 2.15 is general to strongly correlated electron materials. That understanding has guided research from serendipitous discovery toward predictive discovery of materials. Figure 2.14 shows the dramatic increase achieved in the superconducting transition temperature, T_c, over the years. One of the more interesting systems is the "heavy-fermion 1-1-5" metals ($CeIrIn_5$, $PuCoGa_5$) in which T_c ranges from 0.4 K to almost 20 K. This extraordinary span of T_c in materials of the same crystal structure is thought to arise from an unexpected interplay between magnetism and superconductivity. Such unexpected trends were discussed in a recent article that noted a style of new materials development called "luck by design."[5] While it is not quite at the predicative discovery stage, scientists are approaching it with what they have learned from previous successes in materials design. As stated, "The more groups that search for interesting and potentially useful materials, the more diverse and viable the 'idea gene pool' becomes."[6]

Since a superconducting cable must be cooled below its transition temperature, there are dual challenges in applications: the efficiency of energy flow can be improved either by making the present materials more efficient or by discovering a new material that has a higher T_c, requiring less refrigeration. For both approaches, there are many materials hurdles, both basic and applied, to overcome, and almost all of them require single crystals.

At present there is not a homogeneous high-temperature superconductor with a high T_c and a high J_c that can be economically produced. However, over the past few years, it has become clear that significant progress can be achieved by pursuing research in three directions.

- The first of these is basic research aimed at the discovery of new materials. As stated above, this direction not only will lead to improved superconductors, but also to improved understanding of the mechanism of high-temperature superconductivity, which would in turn lead to improved materials in an exciting and fruitful cycle. Both the understanding of ultimate performance and the search for alternate materials require single crystals. For example, the highest-T_c materials contain light ions whose location and motion are difficult to ascertain using x-ray diffraction and require neutron scattering. Because neutrons interact weakly with matter, large crystals are necessary for accurate information on the structure and role of lattice vibrations and spin fluctuations in such systems.

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[5] P.C. Canfield, "Fishing the Fermi Sea," *Nature Physics,* **4,** 167-169 (2008).

[6] Ibid.

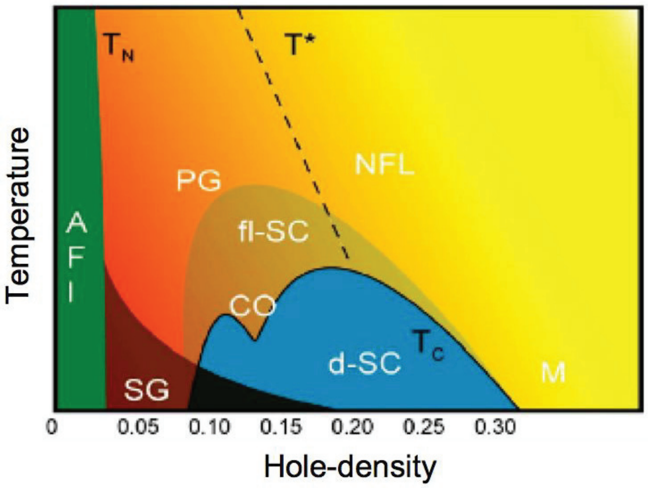

FIGURE 2.15 Canonical phase diagram to guide scientists in the pursuit of new superconducting materials. Note that new phases emerge from competing phases, and in this particular case, it is clear how high-temperature superconductivity emerges from competing phases of antiferromagnetism and “strange metal” (labeled NFL for “non Fermi liquid”). Such phase diagrams guide the researcher past serendipitous discovery toward predictive discovery and then toward “materials by design.” NOTE: AFI, antiferromagnetic insulator; SG, spin-glass; CO, charge-ordered state; d-SC, $d_{x^2y^2}$ symmetry; fl-SC, fluctuating superconductivity; M, metal; PG, pseudo-gap; T_N, Neel temperature; T^*, pseudo-gap temperature divider. SOURCE: **Report of the Basic Energy Sciences Workshop on Superconductivity,** May 8-11, 2006, *Basic Research Needs for Superconductivity*, Figure 21, p. 72, available at http://www.science.doe.gov/bes/reports/SC_rpt.pdf.

- The second research direction is to improve the current-carrying capability of the superconductors, typically with engineered defects, as stated above. The 2G wires are composed of anisotropic materials, and if the 3G wires remain anisotropic, at an applications level a power grid will require such a low level of grain boundaries and misorientation between grains that power lines will essentially contain single crystals by the mile. At an applied science level, since the optimum superconducting materials (layered cuprates) are highly anisotropic from a structural perspective, it is essential to understand the details of their crystal growth in order to optimize the manufacturing processes.
- The third research area involves the development of reliable and economical cables. Only a few laboratories in the United States address the second research direction (e.g., DOE’s Argonne National Laboratory and the National Science Foundation’s National High Magnetic Field Laboratory at Florida State University). Efforts to optimize the cables themselves,

including their current-carrying capability, are mostly confined to a few wire-manufacturing companies such as American Superconductor Corporation and Super Power, Inc. A review of the science and technology of superconductivity for energy delivery was recently prepared by DOE.[7]

Catalysts for Fuel and Hydrogen Storage

The process needed to convert raw feedstocks, such as oil and coal, into specific fuels, such as gasoline or diesel fuel, relies on catalysts. An important and contemporary research area is that of developing improved catalysts for hydrocarbon conversion reactions. By controlling the shape and size of pores in zeolite minerals, as well as other mesoporous materials, specific hydrocarbon interconversion reactions can be selectively favored with high efficiency. In addition, many other organic transformations occur on or are catalyzed by surfaces or edges of single crystals. The ability to grow large crystals, particularly with specific faces, is expected to lead to rapid progress in this area.

An additional application of crystalline materials is found in the separation and storage of fuel gases. Developing the capability to safely store, transport, and use hydrogen is critical for the success of a hydrogen-based economy. Porosity occurs for many crystalline materials because of the size and density of voids in the crystal structure, and many crystalline mesoporous materials can be used to store hydrogen and other hydrocarbon gases and to separate gases. Ongoing and future work in this area involves the development of "designer crystals" with porosity matched to a specific fuel gas.

Needed Crystal Growth Capability for Energy Conversion and Storage

Energy conversion and storage are representative areas in which both the development of new crystalline materials and the optimization of existing materials are needed in order to advance important technologies. U.S. research efforts have identified new opportunities, but in general these efforts are not sufficient in size or scope to change the technological landscape dramatically in the near term. Some areas of product development, such as large-area Si devices for solar energy, are progressing through private investment. In general, however, all progress in areas of technology development can be accelerated by focused efforts in the critical paths outlined below.

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[7] Report of the Basic Energy Sciences Workshop on Superconductivity, May 8-11, 2006, *Basic Research Needs for Superconductivity,* available at http://www.science.doe.gov/bes/reports/list.html. Last accessed March 3, 2009.

Capabilities for Solar Energy and Lighting

Both inorganic and organic solar cells are being pursued as potential commercial systems for solar energy production (see Figure 2.16). As discussed above, the highest efficiency is obtained with heterogenous-layered semiconductor materials in crystalline form. Thus, PV fabrication research should focus on the specific crystal growth problems of the following: (1) large area and thin layers of highly absorbing semiconductors; (2) high-mobility layered heterogeneous systems; (3) layered systems that use inexpensive materials to allow large-scale production—Si being one example, but organic materials offer an alternative route; and (4) materials that show potential for integration into heterostructures. Research projects to address these issues simultaneously, moving toward the goal of ubiquitous solar energy, are large scale and should mimic industrial processes. Such crystal growth research is also relevant to solid-state lighting applications.

Some of the requirements mentioned above for a path to large-scale production apply to organic-based semiconductors. The putative low fabrication costs make organic-based solar cells appealing, but efficiencies need to be enhanced from the present approximately 6 percent. Enhancement of the charge injection and extraction, as well as photoconversion efficiency, is essential. The performance of organic-based PVs is at present dominated by defects that trap charge and control exciton recombination rates; it is essential to develop higher-purity materials. At present, commercially available organic compounds contain several percent of impurity molecules that are incorporated into the crystal structure upon crystallization. It is expected that the feed material for crystallization will become more pure as production volume increases; partnering with chemical suppliers will be critical for

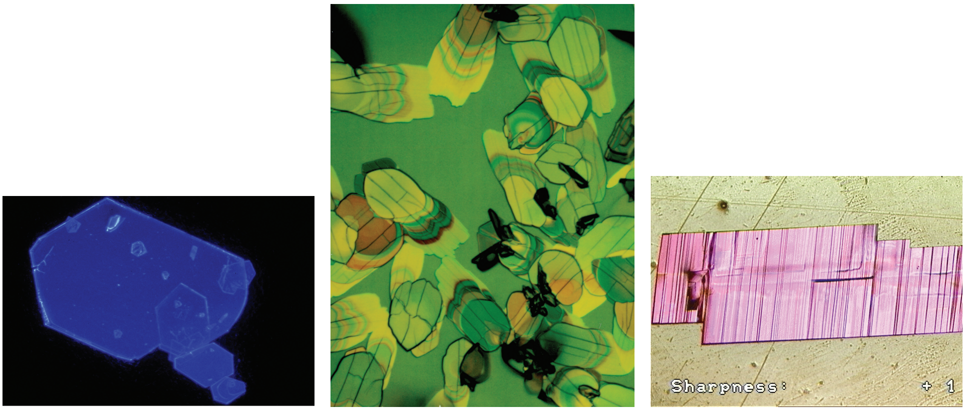

FIGURE 2.16 Examples of organic single crystals with possible use in solar cells. (Left) Anthracene seen in blue backlight, (middle) α-hexathiophene, and (right) fluorinated copper phthalocyanine showing growth steps. SOURCE: Courtesy of Christian Kloc, Nanyang Technological University.

this effort. One approach to understanding the role of impurities in organic PVs is to conduct research on single crystals such as those shown in Figure 2.16. These crystals are grown from vapor transport of sublimed molecules, and crystalline layers greater than 1 cm^2 are currently obtainable for several compounds.

Capabilities for Catalysts for Fuel and Hydrogen Storage

The discovery and development of new materials capable of efficiently and selectively converting raw oil, coal, and other feedstocks into fuels or petrochemicals, as well as the storage and separation of gases such as hydrogen, require the discovery and development of improved catalysts and porous materials. New and improved "designer crystals" are sought. Advances in computer modeling to identify the shape and size of the void spaces within the crystalline lattice are essential, as are ideas and paradigms for new families of materials.

GRAND CHALLENGE 3: EVOLUTION IN THE CAPACITY TO CREATE CRYSTALLINE MATERIALS BY DESIGN

This section presents Grand Challenge 3: that of developing the capability of designing new materials from first principles to meet specific technological needs. Long a dream of scientists and engineers, such "materials-by-design" approaches are becoming increasingly possible through rapid advances in theory and modeling, coupled with continuous increases in computational power. More than ever before, future devices will possess specific functionalities resulting from the design of the materials incorporated into the device. Realizing such an approach will free industry from current materials and device limitations, many of which are based on research carried out in academic and industrial research laboratories a generation ago. By combining materials by design with device science and engineering, new classes of devices will be created to provide lower-cost solar power, novel information and communications devices, and sensitive and multifunctional sensors.

The section begins with a discussion of representative theoretical and computational approaches to the design of materials, including some of the computational hurdles that must be overcome to fully implement those approaches. Examples of how the materials-by-design approach has already led to significant developments in the areas of structural alloys and sensors are then presented. Materials-by-design approaches that enable materials hitherto thought impossible to prepare are described next. These include the multiferroic materials previously discussed, as well as thermoelectric materials that are good electronic conductors but poor thermal conductors. The section ends with a discussion of selected specific technological challenges that must be addressed for further progress in the discipline of materials by design to be achieved.

Theoretical and Computational Approaches to Materials by Design

One of the most dramatic scientific achievements of the 20th century was the identification and development of the quantum-mechanical laws of matter. The quantum theory of solids that is built on those laws underpins our understanding of the physical nature of materials. It has proven remarkably successful in describing materials with electrons that can be represented as distinct particles engaging in generally weak interactions. However, such materials are few, and the limitations of this approach have been made obvious by its failure over the past two decades to lead to an understanding of many new classes of materials that display correlated electron behavior. Recently, though, with increases in computational speed and the development of new algorithms, some of these limitations are being overcome. The ability to simulate phenomena has now advanced to the point at which scientists are confident that, in the near future, simulation and modeling can be used routinely for materials discovery and development. The materials themselves, and the insight gained from them, will almost certainly contribute to next-generation technologies, including nanoelectronics, functional materials, and quantum information.

The flow diagram in Figure 2.17 illustrates how a typical computational design process takes place. The essential steps involve transcribing current theoretical understanding into a proposed trial compound. The properties of the compound can then be computed and compared to an experimental synthesis. The experimental and theoretical properties will agree in a successful design by computation. It may also be possible to use stochastic algorithms to predict new trial compounds. For example, evolutionary or genetic algorithms have recently been used to predict alloy properties and new crystal structures.

The promise of materials by design clearly exists. However, to fully realize the potential offered through materials by design, further advances must be made in a number of computational areas. Two such areas—the development of more-refined methods for predicting crystal structure and the simulation of crystal growth—are addressed here.

Methods for Predicting Crystal Structures

One of the most significant advances in the theory of materials occurred in the mid-1980s. At that time it was demonstrated that two ingredients could be combined to calculate the structural properties of crystals, with the exception of highly correlated systems. The first ingredient is the *pseudopotential.* This approximation replaced the electronic potential of all the electrons with a potential that replicated only the properties of the chemically active electrons, that is, those occupying valence states. The potential arising from the electrons in core states and the positively charged nucleus were combined to form a chemically inert "ion core" pseudopotential. This

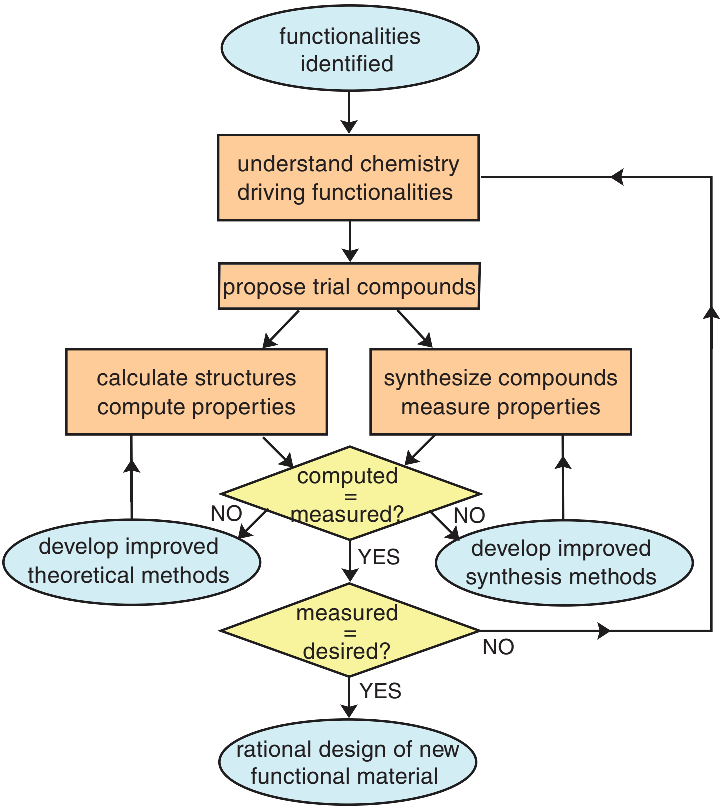

FIGURE 2.17 A schematic illustration of the methodology by which theoretical approaches can be used to carry out a rational design of new materials.

pseudopotential can be determined from an atomic structure calculation and does not change from one environment to another. The valence states now fix the energy and length scales of the electronic structure because the pseudopotential describes only these states. As a result, very simple basis functions, such as plane waves and Gaussian shapes, or simple grids can be used to describe the electronic states. This enormously simplifies the problem, especially for crystalline matter.

The second ingredient for calculating the structural properties of crystals is *density functional theory* implemented with the local density approximation or the generalized gradient approximation. Density functional theory allows the "many-electron" problem to be mapped onto a "one-electron" problem, resulting in the Kohn-Sham equation. This ingredient, coupled with pseudopotentials, enormously simplifies the problem and allows systems with hundreds, if not thousands, of atoms to be examined.

Using this approach, accurate structural energies can be calculated and used to make accurate predictions about crystalline materials and about more complex systems as well. Workers have demonstrated that in some cases—for example, crystals under high pressure—these methods often can be used to predict certain properties of crystals better than those properties can be measured.

In principle, this situation opens up the possibility for one to consider predicting accurately the properties of hypothetical materials on the computer. However, this endeavor is in its infancy, and notable issues must be addressed. Electronic structure methods usually are employed to compute thermodynamic properties as opposed to kinetic behavior. Thus, it might be possible to predict that a given crystal has a given property, but it might be a very different issue to know whether the structure can be synthesized. A standard example is graphite versus diamond. Electronic structure methods can predict that diamond is a stable form of carbon at high pressures, but these methods do not indicate the kinetics of the synthesis process such as the reaction rate or the optimal growth conditions.

Simulating Crystal Growth

The growth of bulk single crystals remains one of the most challenging and astonishing technical endeavors of materials processing. For example, electronic-grade Si grown by the Czochralski method is one of the purest and most perfect materials ever humanly produced. Current production technology routinely achieves impurity levels of less than parts per billion in single-crystal ingots of up to 400 mm in diameter and over 250 kg in mass, and these crystals are completely free of dislocations. Indeed, it is even possible today to control the distribution of microdefects, such as interstitials, vacancies, and voids, in bulk Si crystals.

Modeling has played an important role in clarifying the physical mechanisms governing crystal growth and the engineering principles that must be employed for successful crystal growth processes. In the classical processing-structure-properties triad of materials science, one goal of ab initio modeling is to define the structure-properties relationship for a crystalline material, while the goal of crystal growth process modeling is to clarify the processing-structure connection. In the engineering of bulk-crystal growth processes, the greatest purpose that modeling can serve is to directly connect processing conditions to the structure, and therefore the properties, of the grown crystal. In engineering measures, modeling is employed to enable the mantra of "faster, better, cheaper"—that is, the understanding enabled by modeling can increase the process yield, improve the product quality, and decrease the process cost.

Modeling of crystal growth must account for a host of physical mechanisms, representing both thermodynamic and kinetic phenomena and ranging over disparate length scales and timescales. The challenge is how to represent realistically the most pertinent of these phenomena, and modeling approaches have varied from the continuum to the atomistic. The extent to which modeling can realistically represent bulk-crystal growth is limited, owing mainly to these challenges and the limits of current computers and numerical algorithms. Nevertheless, advances in theory and modeling have led to and will continue to lead to important advances in crystal growth.

Bulk-crystal growth encompasses a wide variety of physical phenomena that occur over a vast range of length scales, making it among the most challenging of industrial processes to model. On a macroscopic scale, ranging from millimeters to meters, the transport of heat, mass, and momentum is always important. At a mesoscopic scale, ranging from tens of nanometers to tens of microns, the crystal interface can exhibit hillocks, steps, and other structures, even though it may appear macroscopically smooth. Mesoscale structure also occurs within the crystal in the form of grain boundaries or extended defects, and even within the melt, where structured complexes of molecular species sometimes appear. At a microscopic scale of nanometers or less, the fundamental mechanisms by which atoms or molecules are incorporated into the growing crystal and how they interact within the solid at high temperatures ultimately determine its final structure.

Bulk-crystal growth also encompasses a vast range of timescales. The longest of these is the time of growth, which can range from hours to months, depending on the type of crystal and the system used to grow it. Heat, mass, and momentum transport each have a characteristic timescale, depending on the dominant mechanism of transport and the physical properties of the system. If diffusion dominates transport, these timescales typically range from minutes to hours. Within the solution or melt, however, convective transport usually dominates, and the transport timescale is typically reduced to seconds or less. Phenomena occurring at mesoscopic length scales, such as morphological instabilities, typically evolve over timescales that are comparable to transport timescales.

Atomistic events important in bulk growth range from the rate of incorporation of atoms into a solidification of interface, occurring over timescales on the order of milliseconds or less, to much longer times associated with concerted action, such as nucleation events. A model that includes all these physical phenomena, spanning at least nine orders of magnitude of length scales and timescales, is far beyond the capability of today's computers. Therefore, a variety of modeling approaches have been employed to clarify phenomena on different scales. At a microscopic scale of tens of nanometers or less, ab initio molecular dynamics methods can be employed to study atomic behavior.

Unfortunately, while these methods are quite rigorous in their approach, even using today's fastest computers they are too computationally expensive to be applied to systems of more than a few thousand atoms or to be used to describe timescales of greater than hundreds of picoseconds. Molecular dynamics methods based on classical potentials can compute for much larger ensembles and longer timescales. To model atomistic behavior at even larger length scales and longer timescales, kinetic Monte Carlo methods have been developed. On a macroscopic scale, continuum methods are gainfully applied. Significantly, there are many important phenomena associated with crystal growth that occur on a "mesoscale," comprising hundreds of nanometers to tens of microns and occurring over long timescales (e.g., microseconds or longer). These phenomena are difficult to model by atomistic methods owing to the long timescales involved and are challenging for continuum methods owing to the very small length scales. Such phenomena require innovative, "multiscale" approaches, which, despite much fanfare, are still at nascent stages of development.

This challenge of scales motivates the need to formulate crystal growth models that include enough physics to make realistic, usable predictions that are simple enough to remain tractable with today's computational capabilities. Future challenges for modeling must lead to more realistic representation of the multiscale interactions important in crystal growth systems. Models must be capable of describing detailed system geometry and design (e.g., furnace heat transfer for melt growth systems), three-dimensional and transient continuum transport (flows, heat and mass transfer), phase-change phenomena (thermodynamics and kinetics), and atomistic events. Progress is being made on all of these fronts, but many challenges remain. The understanding gained from more realistic, multiscale models for crystal growth will ultimately lead to the ability to link crystal structure and properties with growth conditions and the macroscopic factors that influence them.

Areas of Success in Creating Materials by Design

Having discussed some of the theoretical and computational challenges that must be addressed in achieving future success in creating materials by design, the discussion now turns to some of the areas where success has already been reached.

Thin Films

The computational design of materials with novel functionalities, or combinations of functionalities, is becoming particularly valuable in the arena of thin-film heterostructures. In particular, the ability to combine different parent phases, to create new metastable phases, and to modify properties using epitaxial strain offers additional degrees of freedom in the design process, as described in Figure 2.17.

Accurate calculations of interfacial behavior are computationally demanding. While macroscopic properties based on bulk behaviors can often be described accurately within semiclassical theories, the atomic-level response of an interface is intimately related to the local details of chemistry, bonding, structure, and electronic properties, which often strongly depart from those of the constituent parent compounds. Therefore, detailed electronic structure methods are required for accurately reproducing the subtle balance of these competing factors. This issue is extraordinarily difficult to treat theoretically, given the absence of any periodicity in lattice mismatches.

A particularly important methodological development for modeling device behavior has been the rigorous framework for applying finite electric fields within density functional theory, and its extension to metal-insulator heterostructures and interfaces. These developments have enabled detailed theoretical studies of interfacial dielectric behavior, allowing the experimentally observed and technologically highly relevant suppression of the dielectric response of nanoscale capacitors to be understood and mitigated.

Defects in Materials

While the creation of defect-free, well-characterized crystalline matter is crucial for scientific study, most technologically relevant materials possess controlled densities of defects. Thus a quantitative understanding of defects in crystalline materials is required for the prediction of properties. A classic example is the controlled introduction of impurities in electronic materials, for example, the doping of semiconductors. Doping can dramatically alter the electronic properties of semiconductors; the introduction of 1 boron atom per 1,000 silicon atoms increases the conductivity of pure Si by three orders of magnitude at room temperature. Such profound changes are responsible for the functionality of almost all electronic devices, ranging from LEDs to integrated circuits. For electronic materials, the theoretical tools outlined above are capable of helping design materials with specific defect-induced properties.

For other systems, the issues of theoretical design are more problematic. Consider the example of the manganites. The parent phase of $LaMnO_3$, for example, is an uninteresting, antiferromagnetically ordered insulator. However, with the introduction of holes into this system through cationic substitution (for example, Ca, Sr, or Ba doping at the La site), the phase complexity of this system dramatically increases and the properties vary greatly: For example, the colossal magnetoresistive effect replaces the magnetic insulator. Furthermore, recent work has established the existence of an electronically inhomogeneous structure (the so-called electronically phase-separated structure) in which regions that are rich in electrons (conducting and ferromagnetic) are interspersed with regions that are deficient in electrons (insulating and antiferromagnetic), although the whole material appears to be chemically homogeneous. Another example is the case of relaxor ferroelectrics, which are described as an ensemble of nanoscale polar regions that are highly sensitive to their local chemical and electrical environment, thus leading to large dielectric and piezoelectric susceptibilities. The length scale of such processes in many of these materials is still under debate but is likely on the order of a few nanometers.

These examples set the stage for a rather interesting question: Is it possible to design the architecture of inhomogeneous systems such that the optimum in functional responses is obtained? For example, can one design the size of the polaron in such materials (one that is suspected to be the cause for the onset of ferromagnetism) through an atomic-scale "defective materials by design" algorithm? The types of theoretical tools that will be required to accomplish such tasks for these highly correlated systems are more complex than for the systems discussed above and are not as well understood.

Materials with High Strength and Toughness: The Next Generation of Steels

An area in which the materials-by-design philosophy has already paid handsome dividends is the field of structural alloys, particularly alloy steels. Several decades ago, DOE made a strategic commitment to the development of next-generation alloy steels having the desirable combination of ultrahigh strength and high fracture toughness, along with high corrosion resistance in chemically and thermally hostile environments. This was accomplished through a materials-by-design approach, involving careful studies of the atomic-scale microstructure of steels prepared under ultrapure conditions. At the next higher length scale, a considerable amount of effort went into "designing," through a combination of thermomechanical treatments, a microstructure that consisted of a fine distribution of lath martensite (in contrast to twinned martensite, which directly leads to brittle fracture behavior) at the boundaries of which is dispersed a thin layer (a few tens of nanometers) of ductile austenite (the original parent phase from which the martensite forms). Such a nanocomposite microstructure displays the desirable combination of tensile strength and toughness.

New Materials and Crystals for Sensors and Detectors

Another area in which the materials-by-design concept has been making inroads is that of sensors and detectors. Sensor networks are becoming common, and sensors with new capabilities are widely sought. New materials and functionalities are essential components of sensing and its converse functionality, actuation. In a broad sense, sensors can be categorized in four general classes, based on their primary mode of functionality: (1) chemical sensors, (2) field sensors (such as pressure, electric, magnetic), (3) radiation sensors, and (4) biological sensors. Markets for each of these classes are rapidly expanding, and new materials and functionalities are a major driver of this expansion. Many of the devices are built using thin-film-based approaches. The focus here is on radiation sensors, since the current worldwide political climate has necessitated the implementation of a wide range of radiation sensors for threat mitigation. Single crystals are likely to be of great value in this area.

Radiation Sensors

Illicit trade in nuclear materials on world markets poses a long-term international security threat and has created an urgent need for instrumentation that can rapidly, reliably, and inexpensively detect the x-ray and gamma-ray spectra of such materials. The core of such instrumentation is the *radiation detector*—a device that produces distinctive signals in the presence of radiation from nuclear material. Semiconductor materials have properties that make them exceptionally well suited for this task: in a single conversion step, semiconductor radiation detectors generate electrical pulses that are directly proportional to the energy of the x-rays and gamma rays of interest. This excellent linearity is one of the great assets of semiconductor detectors used in spectroscopy.

The fundamental physics of the interaction of energetic electromagnetic radiation (10 keV to 10 MeV) with matter provides clear guidance in the choice of materials parameters for optimized detectors. The linear absorption cross section for the photoelectric effect (the conversion of the energy of electromagnetic radiation into kinetic energy of an electron) is proportional to Z^n, where Z = atomic number and n = 4-5. Thus, the higher the Z of a detector material, the greater the stopping power for radiation and the more efficient a detector is for a given volume of material. The thinner detector layers needed with very high Z materials result in less stringent requirements for charge transport and collection. For gamma-ray energies between 100 keV and 1 MeV, the photoelectric absorption cross section of lead is more than 50 times larger than that of germanium (Ge), which, in turn, is 40 times larger than that of Si.

A second important requirement for inexpensive radiation detectors relates to the operating temperature. Room temperature is clearly desirable. This in turn requires a band-gap energy of 1.6 eV or higher because the thermal generation of charge carriers must be small compared to the charge carriers produced by the radiation to be measured. At the same time, too large a band gap is detrimental because the energy required to form an electron-hole pair is proportional to the band gap energy. This means that large-band-gap semiconductors produce small amounts of charge for a given radiation energy, a disadvantage for high energy resolution measurements. The optimal material requires a trade-off of competing factors, so band-gap tunability is a desired feature in future materials systems.

Finally, a third key parameter is related to the motion of radiation-induced charges through the semiconductor material. The typical planar radiation detector has two contacts on opposite faces of a cylindrical slice of material. In order to obtain identical signals, independent of the position of the incident radiation, the photon-generated holes and electrons need to travel all the way to their respective contacts. The larger the carrier mobility and carrier lifetime, the easier it is to fulfill this requirement. The mobility-lifetime product is perhaps the most critical quality measure for a semiconductor material used in radiation detectors. Si and Ge have products for hole and electrons exceeding 1 cm^2/V at 300 K and at 77 K, respectively, a value that allows the fabrication of large volume radiation detectors with excellent properties. All other radiation detector materials have significantly smaller products, especially for holes. This is why none of these existing materials can compete with Si or Ge detectors when energy resolution is most important.

The need for room-temperature operation precludes the use of Ge detectors (the 0.7 eV band gap is too small) and has led to a search for high-Z, wide-band-gap (WBG) materials. The most successful candidate to date has been $Zn_xCd_{1-x}Te$, with x in the few percentage range. Recent results with 1 cm^3-size crystals and a coplanar interdigitated contact structure have reached an energy resolution of approximately 1 percent for 662 keV ^{137}Cs radiation. These results were achieved using only the collection of radiation-generated electrons, since the mobility-lifetime product of holes is too small to produce a signal. The efforts spent discovering and improving CdTe-based detectors span the past 30 years and act as a reminder of the difficulties that lie ahead for identifying and developing new materials. A number of other materials have been investigated for suitability for room-temperature radiation detection. These include HgI_2, AlSb, and other materials. None of these materials has yet produced results comparable to those achieved with ZnCdTe. Requirements created by nuclear threats for very large numbers of radiation detectors with 1 percent energy resolution at 1 MeV operating at or above room temperature demand new approaches.

Potentially Successful Approach

A brief review of the development of ultrapure Ge for gamma-ray spectroscopy may offer some insight into a potentially successful approach. The discovery in the early 1960s of the lithium (Li) drifting process for the formation of wide-depletion-region *p-i-n* SiLi and GeLi detectors led to a new class of radiation detectors, vastly superior to the commonly used NaI(Tl) scintillation detectors. That GeLi detectors required cooling to achieve sufficiently small diode leakage currents was acceptable in view of the vast improvement in resolution. A serious problem was the unacceptable deterioration of device quality, related to only brief uncooled periods, which resulted in a loss of perfect Li compensation. Around 1970, Hall at the GE Research Laboratories suggested that it should be possible to develop ultrapure Ge for stable room-temperature radiation detectors. Goulding and coworkers at the

Lawrence Berkeley National Laboratory initiated a program for the development of the ultrapure Ge single crystals and detectors. The Czochralski melt-growth technique was selected, but many of the traditional crystal growth approaches had to be sacrificed for purity. New crucible materials were developed and a gas "blanket" of 1 atmosphere of flowing hydrogen was used to prevent residual impurities from reaching the melt. Dislocation-free crystals, naively expected to be the most perfect, showed poor charge trapping when made into detectors, and it was discovered that dislocations could play a key role in removing native defects. A large number of new defect centers were discovered and identified. In parallel to the crystal growth effort, radiation detector development and fabrication of gamma-ray spectrometer systems, including the detector, the cryostat, and all the associated electronics, were actively pursued. The entire operation was colocated in adjacent laboratories. New crystals were characterized with Hall-effect measurements and photothermal ionization spectroscopy within hours of crystal growth completion, and working detectors were fabricated within a few days. This extremely tight coupling between materials purification, crystal growth, and detector fabrication formed the recipe for success.

Decoupling Electron and Phonon Transport: The Search for High-Efficiency Thermoelectrics

Since the discovery of electricity, research on charge transport in materials has pushed the extremes of electrical conductivity, which now spans more than 20 orders of magnitude. Five decades ago, the invention of the transistor demonstrated external tuning of electrical conductivity, and this method of tuning formed the foundation for information processing that created the digital age. The societal impact of research in electrical conduction is clearly enormous. In contrast, heat transport in materials has received much less attention. The thermal conductivity of current solid materials spans only four orders of magnitude at room temperature, and its external tunability is limited. Yet the history of thermal transport goes back to primitive humans who combined empirical observations with applications (specific heat of stone for warmth, straw for insulation, wooden tools for manipulating fire, and so on). In modern times, research in thermal transport has enormous implications for the ability to efficiently convert, use, and store energy. Thermal barrier coatings in jet engines allow higher fuel efficiency, while thermal insulation in refrigeration systems has led to energy conservation. At present, the most serious issue in the miniaturization of electronic circuits is thermal management. The power density of microprocessors is expected to exceed that of a nuclear reactor before 2010 and to reach that of the surface of the Sun by 2015. In addition, power dissipation in organic and molecular electronics could be a key limitation. It is believed by many that if thermal transport could be externally tuned and its limits extended, the impact would be felt in areas whose diversity ranges from energy conversion (e.g., thermoelectricity) and storage to next-generation information processors (inorganic microprocessors, organic electronics, and qubit systems).

In contrast to magnetoelectrics, in which a large coupling between magnetic and electric order is desirable, in thermoelectrics one desires to decouple electron and phonon transport. The performance of a thermoelectric material is typically described by the figure of merit ZT, where $Z = S^2\sigma/\kappa$, σ is the electrical conductivity; S is the thermopower, or Seebeck, coefficient; and κ is the total thermal conductivity. S and σ are contraindicative, meaning that they change in opposite directions with the carrier concentration. Thus, much of the recent work has focused on nanostructuring as a means of reducing the phonon contribution to the thermal conductivity in order to increase ZT. However, to date the most attractive material (from a commercial perspective) has been Bi_2Te_3, which was discovered several decades ago. Despite a large amount of research devoted to surpassing Bi_2Te_3, there remains a pressing need for new materials with higher ZT values. There is the need to discover materials that can behave like a perfect thermal insulator (akin to an electrical insulator) as well as superthermal conductors (for heat dissipation applications).

Materials-by-Design Challenges

Notwithstanding the tremendous progress in creating novel materials (structural, electronic, functional, biological, and so on) over the past century, there are still huge challenges ahead for truly "designing" materials. The challenges remaining are (1) morphological length scales, (2) chemical stoichiometry control, and (3) matching energy scales.

Challenges at Morphological Length Scales

Today, various processes (bulk-crystal growth, thin-film growth) have enabled new materials with unprecedented properties to be made. In some cases (for example, MBE of GaAs-AlGaAs, discussed in Chapter 1 in the section entitled "Example in the Area of Thin Films: Gallium Arsenide-Based Heterostructures"), the deposition processes have evolved to an extent that atomic-scale control of structure and composition has become commonplace. For more complicated materials, however, such as the complex, correlated oxides, the situation is far less mature. MBE-like techniques are just beginning to be developed for the preparation of such materials in the form of epitaxial heterostructures. These heterostructures contain the desired phases, layered in the desired sequence with reasonable film-thickness control; however, the atomic-scale control of the interfaces between these phases, and stoichiometry control (described below) both within these phases and at their interfaces, present tremendous challenges to synthesis. Owing to their more complicated crystal structures and lower symmetries, far more options for different interfaces are possible among these complex systems than among III-V semiconductors. In the case of oxide growth in particular, tools to provide surface-specific chemical and structural information during heterostructure growth need to be developed.

The problems are equally challenging when considering crystals. In many cases, the complex phase equilibria in these systems (for example, lack of a congruent melting composition) mean that high-quality crystal growth processes, such as the Czochralski method, are not applicable. A good example is $SrTiO_3$, which is an important substrate material for oxide heterostructure growth. The lack of high-quality substrates (in terms of both chemical stoichiometry and low defect concentration) has become a critical limitation to progress in device development. The challenge in such cases is to create large-area (4- to 6-inch) wafers that approach the quality of state-of-the-art Si substrates.

Challenges also arise at mesoscopic length scales. Over the past 20 years, a fundamental insight that has emerged from studies of cuprate superconductors, relaxor ferroelectrics, and colossal magnetoresistive manganites is the importance of electronic charge inhomogeneity, as distinct from structural homogeneity. In the case of the cuprates and manganites, the parent compounds are both antiferromagnetic insulators. Doping them with holes (typically through cationic doping) leads to the onset of superconductivity in the cuprates and large magnetoresistance in the manganites. In both cases, these phenomena are correlated with an inhomogeneous electronic distribution, typically over a length scale of a few nanometers to 100 nm. This is generically similar to relaxor ferroelectrics, in which the large dielectric and piezoelectric susceptibilities have been correlated with nanopolar domains. Thus, key challenges on this front are (1) to determine the characteristic length scale over which such inhomogeneities should exist for optimum responses from the material, (2) to develop experimental methods of characterizing and controlling electronic inhomogeneity, and (3) to understand theoretically the role of electronic inhomogeneity from a structure-property perspective.

Chemical Stoichiometry Control

Controlling composition (both cationic and anionic) in complex oxides continues to be a key challenge. This challenge is illustrated through the example of oxygen content in perovskite oxides, aspects of which are common to strongly correlated oxide materials. It is widely accepted that oxygen vacancies form facilely in perovskite oxides. Furthermore, these vacancies are thought to be ionized, thus donating electrons to the conduction band. A 0.1 percent vacancy concentration, readily achieved, would likely lead to an electron concentration on the order of 10^{19}-10^{20} e/cm^3, a significant carrier concentration.

A specific implication of the presence of oxygen vacancies is the evolution of polarization fatigue and imprint in ferroelectric capacitors. A large body of evidence now directly points to the role of such defects in the fatigue process. With this background, the challenge becomes one of probing these defects in crystals or thin films with sufficient chemical resolution (1 part per million) and spatial resolution (1 nm). Of particular importance is the behavior of oxygen, since it is highly mobile and yet highly reactive and critical for electrical and magnetic behavior. Thus the electronic manifestation of the defect states that accompany the non-stoichiometry in single-phase samples can have huge effects on the properties of thin films and heterostructures of complex materials and can mask their intrinsic properties. A specific example of this could be the magnetoelectric perovskite heterostructures exemplified by the model system of $BiFeO_3$/$BiCrO_3$. In this heterostructure, it would be extremely desirable to be able to control the iron (Fe) or chromium (Cr) composition across the heterostructure with atomic precision. This, however, can be a daunting task owing to the chemical similarities of Fe and Cr and the interdiffusion that ensues. How does one create such precision-tailored heterostructures? How does one prevent interdiffusion?

APPLIED CRYSTAL GROWTH FOR TECHNOLOGY DEVELOPMENT

Grand Challenge 2, the Creation of New Crystalline Materials for Energy Production and Conversion, addresses a specific technology area. Crystalline materials are, however, crucially important in many other technologies. As was the case for basic research, the loss of industrial laboratories has had a large impact on crystal growth research focused toward technology development. In the past, such research was funded by corporate research and development (R&D) funds. Today research in applied crystal growth is modestly supported by programs such as the Small Business Innovation Research program through the Department of Energy, the National Science Foundation, and the Department of Defense. Such limited-term and application-focused funding, while useful for addressing some problems of importance, seems insufficient to support activities such as crystal growth, which by its nature relies on large infrastructure, a highly trained staff, and long-term institutional stability. It is also not clear that such a technology focus is well matched to the mission of any existing federally funded laboratory. Such a centralized laboratory that is industry oriented would have similarities to the centralized semiconductor R&D facility SEMATECH.

While research of industrial importance has diminished in the United States, in other countries such research remains vital. Germany, for example, shows how such applied research can form a critical link in the science-to-product chain. A mixture of activities, from the growth of novel superconductors to the growth of large boules of Si for microelectronics, is supported in several German institutes, the largest of which is the Institute for Crystal Growth in Berlin (see also the section entitled "International Activities" in Chapter 3). These institutes are funded by a variety of sources, including the German federal government and private corporations, and the institutes fulfill several needs not easily accomplished within either academia or modern corporations. First, they maintain a knowledge base for what might be termed large-scale or "industrial" growth techniques. These techniques are often applied to different materials classes (for example, floating-zone refinement is used both for semiconductors and for metals). It is critical for a country with a large industrial base in information, energy, and security technologies to maintain this expertise. Second, such expertise can be accessed by different companies, thereby increasing efficiency and speed to market. Finally, such activities provide an intellectual link between basic research and manufacturing. As basic researchers set strategic goals, their research should be informed by the range of possibilities and limitations in current manufacturing processes. The loss of such applied research in the United States is seen in many different areas.

Crystalline Materials for Next-Generation Technologies

Crystalline materials lie at the heart of many modern technologies. Past examples are silicon for microelectronics, quartz in clocks and the Global Positioning System (GPS), gallium arsenide and indium phosphide in cellular phones, and ruby (aluminum oxide with chromium impurities) in lasers. In all of these examples, a nearly perfect crystal structure is needed for high performance. While research on existing technologies will need continuing improvement of known materials, developing technologies will require new materials as well as synthesis of known materials in high-purity single-crystal form. Examples are (1) gallium nitride (GaN) for energy-efficient lighting that some day could supplant incandescent lightbulbs, (2) new materials for use in detectors of weapons of mass destruction, (3) new semiconductors for infrared optics and space communications, and (4) new approaches to producing large-area semiconductors for solar energy applications. Several areas of opportunity for research in crystalline materials for next-generation technologies are reviewed in the following pages.

Next-Generation Crystalline Materials for Future Information Technology

The earlier section entitled "Grand Challenge 1: The Development of Next-Generation Crystalline Materials—New States of Matter and New Materials—for Future Information and Communications Technologies" discussed a wealth of phenomena with potential for integration into future information systems. While basic research on these materials provides technology directions, critical factors for eventual application will be determined farther down the development path where materials compatibility, materials cost and processing complexity, and compatibility with adjacent technologies are determining factors for the adoption of a particular technology. Part of the challenge of developing a new technology lies in the research that attempts to create prototype devices based on a new effect. The more focused projects necessary for this stage of development require dedication of specialized apparatuses for growth and fabrication. Many of the research activities already mentioned fall into this category, including the production of high-purity small-molecule organic semiconductor feedstock, the development of techniques for creating large crystals of GaN and other next-generation semiconductors, and the control of defects in oxides. Of particular interest is intensive recent research on graphene—single atomic sheets of graphite—that led to the discovery of remarkable and interesting electronic properties (see Box 2.1). Experiments performed on sheets one atomic layer in thickness peeled from single crystals of graphite suggest that graphene holds the possibility of becoming the electronic material of the future. This vision of a future featuring graphene-based electronics now drives the science and technology on very interactive parallel paths; a similar situation occurred in the study of carbon nanostructures.

Next-Generation Optical Devices for Security

Crystals are already used in a wide variety of optical device applications, including laser sources, frequency mixing through nonlinear response, and optical modulation. Laser materials include fluorides such as rare-earth doped $YLiF_4$ and CaF_2 and rare-earth doped oxides such as the garnets, $GdVO_4$, and $(Y,Gd)Ca_4B_3O_{10}$. Nonlinear crystals are typically oxides (for example, $LiIO_3$ in the 800 nm range, and $LiNbO_3$ in the 1,319 nm range). Optical modulation applications include amplitude and phase modulation using $LiTaO_3$ and $LiNbO_3$ crystals and Faraday rotation using the oxide garnet $Tb_3Ga_5O_{12}$.

Of great future interest is the use of nonlinear optical crystals for infrared-to-terahertz parametric sources. Here new materials are needed to provide higher efficiency and output power in the 2,000 to 8,000 nm (2- to 8-μm) wavelength range. Such materials require a highly nonlinear response with low absorption losses. Figure 2.18 shows some candidate materials envisioned for such purposes. Among these systems, crystalline $ZnGeP_2$ shows great promise for its low loss and large nonlinear coefficient, as demonstrated in the terahertz image shown in Figure 2.19. New crystalline systems are also needed for mid-infrared communications applications.

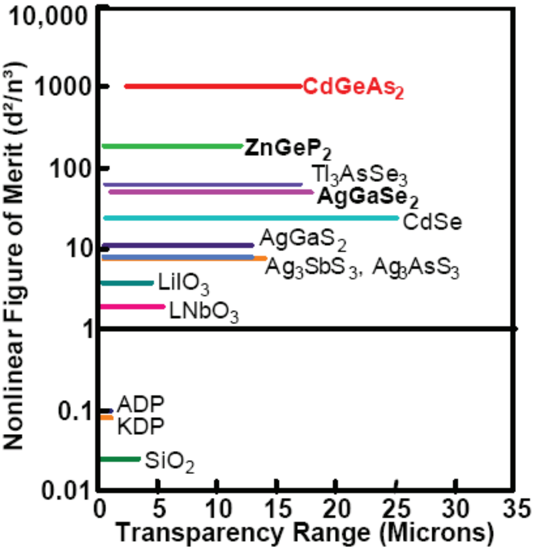

FIGURE 2.18 Nonlinear figure of merit for several crystalline materials used in infrared frequency conversion. SOURCE: Courtesy of Peter Schunemann, BAE Systems.

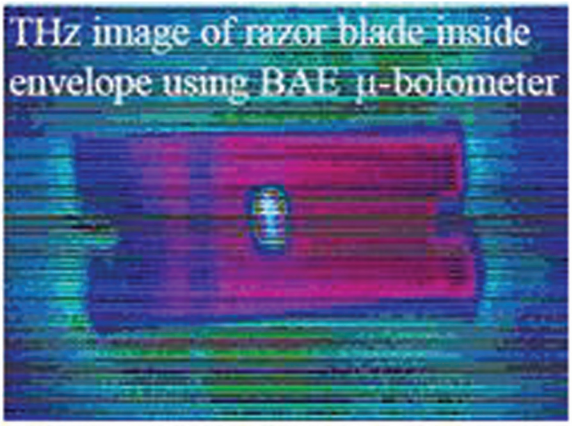

FIGURE 2.19 Image of a razor blade inside an envelope obtained using a crystalline $ZnGeP_2$ terahertz source. SOURCE: Courtesy of Peter Schunemann, BAE Systems.

Crystalline Materials for Electromechanical Actuation

A modern automobile contains more than 100 actuators. Future automotive design will use every opportunity to reduce weight and power consumption, and piezoelectric crystals and ceramics have been developed for actuating applications where speed and force are needed for a small displacement function. Such applications include fuel injection, positioning, and fast switching. Actuators take a variety of forms, including stacked piezoelectric elements, tubes, and disk actuators. For wider applicability, materials requirements such as high operating temperatures, durability, and internal electrode composition must be satisfied.

Substrates for Next-Generation Electronics

The growth of high-quality crystalline thin films requires crystalline substrates with atomic lattice sizes that match the width of the thin film. Thin films of interest are typically oxides for nonlinear optics, solid-state lighting, or strongly correlated electronic states; or a non-oxide for emitter/detector or high-power radio-frequency applications. As an example: for high-mobility $ZnO/Mg_xZn_{1-x}O$ films exhibiting the quantum Hall effect and *p*-ZnO/*n*-ZnO heterostructures exhibiting violet electroluminescence, $ScAlMgO_4$ was used as the substrate. For AlGaN/GaN heterostructures exhibiting mobility exceeding 1.6×10^5 $cm^2/Vsec$, sapphire-Al_2O_3 substrates were used. While WBG compounds such as zinc oxide (ZnO) and GaN have been grown on oxide substrates, there is much interest in growing oxides on WBG substrates to enhance the ability to tune charge density in a WBG compound through the gating of an oxide-induced dielectric or ferroelectric state. In addition to their use in substrates, single crystals have also been used as high-purity sources in epitaxial growth.

New Growth Techniques

The development of new crystal growth techniques requires a focused research effort, independent of efforts that use established techniques to vary chemical composition. New techniques usually strive to produce crystals that are purer, larger, or of a type that cannot be accessed using standard methods (e.g., growth at high pressure). Following are a few examples of promising techniques for advancing the science and technology of crystal growth.

- *The floating-zone (FZ) technique* has become common for the growth of large oxide and intermetallic single crystals (see Appendix D). The precise control of process conditions that characterizes FZ growth can be further enhanced by introducing laser heating in place of conventional halogen or xenon lamps. A high-pressure environment can also be combined with FZ growth, providing the unique opportunity to grow single crystals that are either unstable at ambient pressure or have very high oxidation states, such as those containing Cu^{3+}, Ni^{3+}, and/or Fe^{4+}. It is expected that further variations on the basic FZ process will be explored in the coming years.

- *Charge carrier doping* often plays a key role in producing novel electronic phases, including superconductivity. In many cases, carrier doping has been achieved by chemical substitution, which often suffers from structural disorder introduced by the mismatch of either atomic size or electronic structure of the substituent, or from the presence of a miscibility gap. *Electrostatic doping,* using a field-effect transistor (FET) structure fabricated on the surface of the crystal, is a nonchemical approach to modifying the carrier concentration while avoiding structural disorder. To date, however, the maximum number of charge carriers injected by such "FET chemistry" is limited up to $\sim 10^{-19}cm^{-3}$, due to the finite breakdown voltage of typical gate insulator materials. Recently, however, carrier injection using an electrolyte cell situated on the crystal surface, instead of a conventional FET structure, was reported. This electrochemical technique can inject carriers up to $\sim 10^{-20}cm^{-3}$ and has succeeded in "doping" the normally insulating $SrTiO_3$, to induce a superconducting phase. Thus, co-joined FET structures provide a novel route to altering the electronic properties of crystalline matter, and new FET methods will likely be developed in the future.
- Related to the interest in FET structures, *interfaces in crystalline heterostructures* are now seen as a well-established type of crystalline matter for studying new electronic states, not only in covalent semiconductors but also in ionic oxides and van der Waals bonded organics. The need for precise control of such interfaces requires characterization of local electronic states on the atomic level using state-of-the-art spectroscopies, including angle resolved photoemission (ARPES) and scanning tunneling microscope (STM). In order to conduct interface characterization in situ during layer-by-layer growth, the integration of the thin-film chamber (either MBE or pulsed laser deposition [PLD]) with ARPES or STM should be pursued. Indeed, efforts are now under way to perform PLD growth in a chamber connected directly to a synchrotron x-ray beam line for photoemission spectroscopy.
- In order to promote the search for new materials, a technique named *combinatorial chemistry* (CC) has been developed. This technique was first employed in the pharmaceutical industry to reduce the time and cost associated with producing effective and competitive new drugs. Efforts have been made to apply CC to oxide thin films in order to introduce dopants with a graded concentration (also called composition-spread films). This tech-

> nique has seen limited application; one example is the successful fabrication of correlated transition metal oxides such as the colossal magnetoresistance manganites. With these materials, researchers have investigated the phase diagram of the solid solution using a single film. Probes to characterize local lattice constant, resistivity, and magnetization of composition-spread film have been developed. In the future, CC is expected to be applied to an increasing number of materials problems in which compositions to optimize a particular property are desired.

Future directions in crystal growth techniques will depend strongly on the classes of materials that define the mainstream topics in condensed-matter science. New compounds are constantly being discovered, and novel approaches to producing large single crystals of these compounds are often required.

ROLE OF CHARACTERIZATION FOR NEW CRYSTALLINE MATERIALS DISCOVERY

The discovery of materials with novel, scientifically or technologically useful properties involves a wide range of scientific expertise, equipment, and processes in various institutions. Developments in the United States over the past 50 years have created an imbalance in this multifaceted process of new materials discovery and development. While facilities for materials characterization have increased capacity and expanded capabilities, the shrinking level of industrial basic research has led to a reduction in synthesis capabilities, as documented elsewhere in this report. This section focuses on opportunities to leverage the greater capacity for materials characterization to advance the scientific understanding and application of new crystalline materials.

Laboratory-Scale Materials Characterization Tools

In contrast to crystal growth, there has been extraordinary progress in laboratory-scale materials characterization tools. Mass production, automation, and information technology have greatly reduced the costs and increased the efficiency of such tools. Examples of improved materials characterization equipment in this category include x-ray diffraction instrumentation, Raman and infrared spectrometers, and cryogenic systems for specific heat, susceptibility, and transport measurements.

Consider, for example, a typical activity that would follow the development of a new material: a specific heat measurement. Twenty years ago, a measurement of the low-temperature heat capacity of a single crystal required expertise that could only be gained through dedication over a career, in conjunction with technical skills in cryogenics, vacuum technology, analogue temperature control, signal processing, and data analysis. Today a young researcher with a typical start-up package can purchase a commercial cryostat with fully automated cryogenics, vacuum, and electronics. Heat capacity is an affordable option, as are alternating-current susceptibility, magnetization, thermal conductivity, and electrical transport. In addition, data collection is fully automated and can be monitored remotely. All of these features greatly increase the individual investigator's measurement capacity.

There has also been dramatic progress in data analysis and presentation tools. Twenty years ago data analysis involved the use of unforgiving mainframe computers, and plotting was done by a graphic designer. These tasks are now completed faster and better by commercial software packages on desktop computers. As a result, experimentalists have the capacity to acquire, analyze, and publish comprehensive data for a much wider range of samples than was the case just 10 years ago. The capacity to probe bulk properties of new materials has increased, perhaps by as much as an order of magnitude per experimentalist.

National Facilities for Materials Characterization

While bulk experiments carried out in a single-investigator laboratory are typically completed first, full understanding of new materials often requires the use of national facilities that probe matter on the atomic scale. Table 2.1 provides an overview of major federally funded facilities for materials research. Experimental probes include neutrons, x-rays, and microscopy with photons and electrons. The role of facilities in the development of new materials and the sample synthesis requirements for each type of facility are discussed here.

TABLE 2.1 Overview of National User Facilities for Materials Science, with FY 2007 User Statistics and Number of Publications for CY 2006

Facility	Laboratory	Radiation	No. of Users in FY 2007[a]	No. of Papers in CY 2006[b]
NIST Center for Neutron Research	NIST	Neutrons, reactor	858	406
High Flux Isotope Reactor	ORNL	Neutrons, reactor	72	81
Spallation Neutron Source	ORNL	Neutrons, pulsed spallation	24	68
Los Alamos Neutron Science Center	LANL	Neutrons, pulsed spallation	272	170

TABLE 2.1 (Continued)

Facility	Laboratory	Radiation	No. of Users in FY 2007[a]	No. of Papers in CY 2006[b]
Intense Pulsed Neutron Source (IPNS)[c]	ANL	Neutrons, pulsed spallation	173	103
National Synchrotron Light Source	BNL	X-rays, synchrotron	2,219	612
Advanced Photon Source	ANL	X-rays, synchrotron	3,420	1,106
Advanced Light Source	LBNL	X-rays, synchrotron	1,748	593
Stanford Synchrotron Radiation Laboratory	Stanford University	X-rays, synchrotron	1,151	320
Center for Microanalysis of Materials[d]	University of Illinois at Urbana-Champaign	Electrons, microscopy	600 (approx.)	200 (approx.)
Electron Microscopy Center	ANL	Electrons, microscopy	199	89
National Center for Electron Microscopy	LBNL	Electrons, microscopy	183	150
National High Magnetic Field Laboratory[e]	NHMFL	High magnetic fields	1,144	404

NOTE: FY, fiscal year; CY, calendar year; NIST, National Institute of Standards and Technology; ORNL, Oak Ridge National Laboratory; LANL, Los Alamos National Laboratory; ANL, Argonne National Laboratory; BNL, Brookhaven National Laboratory; LBNL, Lawrence Berkeley National Laboratory; NHMFL, National High Magnetic Field Laboratory.

[a] Data from the Department of Energy, available at http://www.sc.doe.gov/bes/users.htm, except as otherwise noted below in footnote *e*. *Users* are defined generally as researchers who propose and conduct peer-reviewed experiments at a scientific facility. They include *remote users* (researchers granted authority to remotely produce data) and *offsite users (*researchers to whom the facility provides custom-manufactured materials, tools or devices). An individual is counted as one user no matter how often or how long the researcher conducts experiments at the facility during the fiscal year. User data for the NIST Center for Neutron Research were obtained from private correspondence with operators of the facility.

[b] Committee-collected data.

[c] IPNS closed in February 2008. Table shows the final number of users in FY 2007 and the number of publications for CY 2006.

[d] The Center for Microanalysis of Materials at the University of Illinois at Urbana-Champaign has not been designated a Basic Energy Sciences user facility since FY 2005; hence no current statistics are available.

[e] User information regarding the National High Magnetic Field Laboratory is from the *2007 Annual Report* for NHMFL, available at http://www.magnet.fsu.edu/mediacenter/publications/reports/annualreport-2007.pdf.

While a laboratory-based x-ray source is the traditional route to atomic-scale structural information, synchrotron x-ray sources provide unprecedented sensitivity, accuracy, and detail. The much higher source brightness makes it possible to determine the structure of minute crystals (with size on the order of cubic microns) typical of the early stages of materials discovery work. With the current generation of synchrotron x-ray sources, it has even become possible to probe dynamic properties of solids and liquids such as phonons in micron-sized samples. Such information is critical for understanding physical properties, from electronic transport to thermal conductivity. Thin films and nanosize crystalline materials will be incorporated into many future technologies, from quantum computers to medical therapies. The lack of long-range order in one or more dimensions and the very small quantities of materials involved preclude the use of conventional structural probes. Synchrotron x-ray sources provide unique capabilities for probing structure and dynamics under such conditions.

Electron microscopy can provide direct, real-space, structural, chemical, and electronic information, resolved at the atomic scale for crystals, buried interfaces, and point or line defects. Recent examples have included the imaging of oxygen vacancies near oxide grain boundaries and in artificially grown heterostructures. Lattice distortions and strain fields can be measured to a precision of a few picometers using the 0.1 nm or better resolution images acquired on aberration-corrected transmission electron microscopes. Scanning transmission electron microscopy (STEM) offers good chemical sensitivity at a comparable resolution and can be used to detect and image individual dopant atoms inside a crystal. Electron energy loss spectroscopy can be performed simultaneously with STEM, and it provides very similar information to that obtained with x-ray absorption spectroscopy, probing the local electronic structure, partitioned by chemical species and site at the atomic scale. Electron holography can measure real-time changes in the electric and magnetic fields in the thinned sample, with the sensitivity of a single fluxon.

Sample preparation techniques developed for semiconductor failure analysis have greatly improved the quality and speed of sample preparation, which had long been a bottleneck for rapid electron characterization. As this is a real-space imaging method, very small sample quantities are adequate, and the method is well suited for initial explorations of new materials systems. Secondary phases can be identified and studied or avoided as needed. This suggests that electron microscopy can be most effective when coupled closely to sample growth for timely feedback and insight. However, a modern electron microscope can be as sophisticated and complicated to operate as a synchrotron beam line. While most microscopists are well trained in general structural analysis for materials science, very few laboratories, whether in the United States or abroad, are producing users trained to quantitatively analyze and interpret the sophisticated spectra and images generated by modern instruments. As the complexity of the instrumentation increases, so must efforts to train graduate student and postdoctoral fellows in the use of the latest instrumentation for materials science.

Neutron scattering offers unique sensitivity to light atoms and magnetism, momentum-resolved spectroscopy spanning 10 orders of magnitude in energy (0.1 nanoelectronvolt to 1 eV), and the ability to penetrate thick samples, sample environment, and materials processing systems for in situ studies. For fundamental reasons that are directly tied to the utility of the technique, neutron interactions with matter are much weaker than for photons and electrons. In addition, because neutrons are tightly bound in nuclei, neutron sources provide orders-of-magnitude less flux on sample than photon flux at synchrotron facilities. While these factors have limited the use of neutrons for materials science in the past, the Spallation Neutron Source at the Oak Ridge National Laboratory and improved moderators and neutron optics at existing reactor facilities are leading to several orders-of-magnitude improvement in sensitivity and capacity. As a result, a substantial expansion in the use and impact of the neutron-scattering technique in research is occurring, which parallels the transition from rotating anodes to synchrotron sources for x-rays.

High magnetic fields continue to be an essential tool for discovering and understanding new materials functionality. An applied magnetic field will alter the course of an electron in a circular path called a cyclotron orbit. At fields greater than 1 tesla (T) (10,000 times Earth's field), the cyclotron orbit approaches interatomic dimensions. Measurements of electronic and thermal properties versus applied fields greater than a tesla can thus yield information on the electronic structure of a crystalline material. The National High Magnetic Field Laboratory in Tallahassee, Florida, is the primary U.S. facility with this focus; it routinely provides static magnetic fields in excess of 30 T and can reach 100 T in short (millisecond) pulses. As a rule of thumb, 1 T approximates 1 kelvin (K), and thus 100 T fields enable the probing of electronic interactions of 100 K in strength. The availability of such fields enables the study of novel electronic phenomena such as critical phases in the quantum regime, including new fractional quantum Hall states; characterization of high-temperature superconductors for both basic science and large-current-carrying applications; and novel phases in magnetic materials such as spin ice and low-effective-dimensionality materials. Science from this type of facility requires a steady stream of qualitatively new materials, preferably in single-crystalline form so that intrinsic anisotropies can be explored.

The growing capacity for facility-based materials characterization is illustrated by recent statistics for single-crystal experiments at the National Institute of Standards and Technology (NIST) Center for Neutron Research. Figure 2.20 shows the number of single-crystal neutron experiments over time, classified by instrument. While single-crystal experiments hold the potential for more detailed atomic-scale

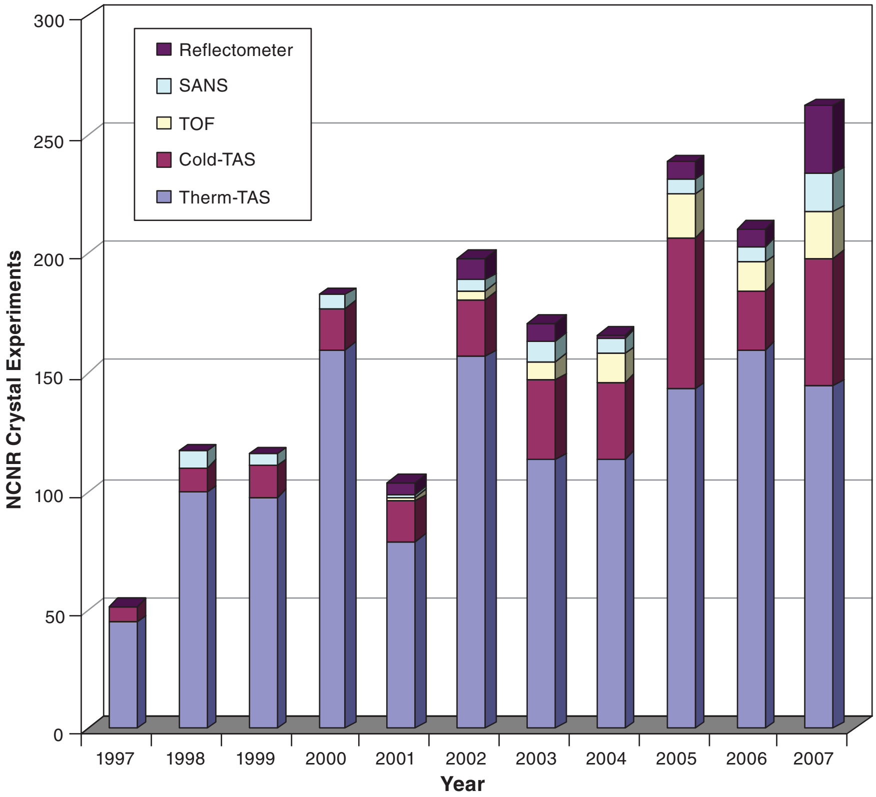

FIGURE 2.20 Number of single-crystal neutron-scattering experiments per year from 1997 through 2007 at the NIST Center for Neutron Research (NCNR). Color coding indicates the instrument types: reflectometry, small angle neutron scattering (SANS), time of flight (TOF) spectroscopy, and cold or thermal triple axis spectroscopy (TAS). SOURCE: Data provided by Peter Gehring, NIST Center for Neutron Research.

information, they also demand more of the instrumentation. The fivefold increase in the number of such experiments over the past decade is a result of progress in instrumentation and user access. With further improvements in these areas at both the NIST Center for Neutron Research and at the Oak Ridge National Laboratory, the capacity for single-crystal experiments will continue to grow dramatically in the coming decade.

While single-crystal neutron scattering is seldom the first experiment to be conducted on a new material, such experiments are often necessary in order to understand and control new materials properties. In the preceding decade the supply of novel crystalline materials apparently kept up with the demand, as indicated by the factor-of-two average instrumentation oversubscription at NIST. But as capacity grows, will there continue to be an adequate supply of exciting new materials for a strong scientific program?

To answer that question, the committee examined the origin of the materials discoveries underlying the rapidly expanding activity in single-crystal neutron scattering at NIST. Figure 2.21 shows crystal experiments over time, classified by the origin of the underlying materials discovery. Europe, the United States, and Japan are the dominant locations of origin. The strong European representation can largely be attributed to the continuing impact of Bednorz and Müller's discovery of high-temperature superconductivity in $La_{2-x}Ba_xCuO_4$. The large impact of Japan is associated with discoveries of novel correlated electron systems and magnetism in manganese (Mn)-doped gallium arsenide (GaAs). Materials classes underlying the U.S. impact include superconducting Y_2BaCuO_3, heavy-fermion intermetallics such as $CeCoIn_5$, and strongly correlated oxides such as $Sr_3Ru_2O_7$. However, a large fraction of the materials attributed to the United States could be called legacy materials with continuing scientific impact, such as $LaCoO_3$ and $LaMnO_3$. This indicates that Figure 2.21 is a lagging indicator of materials synthesis, not yet having picked up the decline in U.S. materials synthesis documented elsewhere in this report.

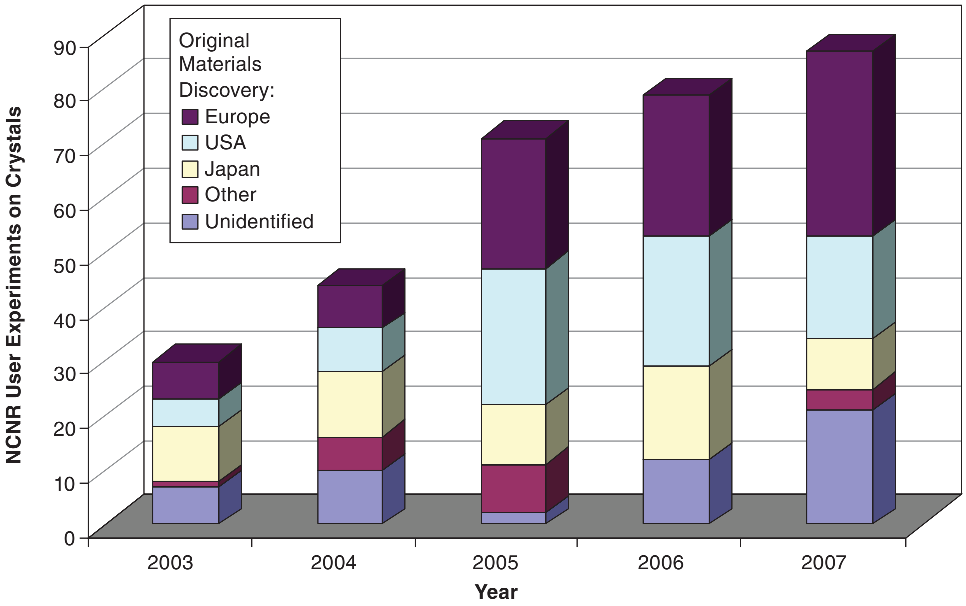

FIGURE 2.21 User experiments at the NIST Center for Neutron Research (NCNR) for the years 2003 through 2007, classified by the origin (country or region) of the materials discovery that initiated the research. SOURCE: Data provided by Peter Gehring, NIST Center for Neutron Research.

Opportunities Through Crystalline Matter Discovery

The expanded capabilities for materials characterization both in the laboratory and at national facilities create extraordinary opportunities for accelerated progress in materials science. However, investment in and coordination with crystalline matter discovery are essential for realizing this potential.

For nanoscale-structured materials, action has recently been taken in recognition of this need. By colocating nanophase synthesis centers with national facilities to probe materials, the Department of Energy has created extraordinary conditions for synergy between crystalline matter discovery and characterization for nanostructured materials. An example is the Center for Nanophase Materials Science colocated with the Spallation Neutron Source. Combining deuterium-labeled polymer synthesis capabilities with small angle neutron scattering and neutron reflectometry provides unprecedented capabilities for creating and probing self-assembled nanoscale structures for fundamental science and applications. Also, by combining the ability to create a thousand to a million copies of a given nanoscale structure with three-orders-of-magnitude-greater neutron brightness, it will be possible to probe phonons and magnons confined to the nanoscale. There are corresponding opportunities for extraordinary insight from x-ray diffraction and spectroscopy with microfocused synchrotron beams at the Advanced Photon Source, National Synchrotron Light Source, and Advanced Light Source on nanostructures created respectively at the colocated Center for Nanoscale Materials, Center for Functional Nanomaterials, and the Molecular Foundry.

The advances in materials characterization techniques also create new opportunities for understanding and controlling homogeneous crystalline materials. However, the utility and significance of the science produced depend critically on the resources devoted to discovering new materials and on producing them in sufficient quality and quantity for advanced characterization. For neutron-scattering experiments, the quality and depth of information produced are typically limited only by the sample's size and quality. Examples of samples used for recent experiments are shown in Figure 2.22. Two specific examples of crystal growth as the rate-limiting factor for scientific progress are provided below.

The first of these examples is that almost two decades ago, neutron scattering experiments uncovered a spectacular spin resonance in the superconducting state of $YBa_2Cu_3O_{6+\delta}$. It is a phenomenon that continues to be at the forefront of research in high-temperature superconductivity. To correlate the resonance energy with the superconducting gap amplitude, neutron and angle-resolved photoemission spectroscopy or scanning tunneling spectroscopy must be carried out on the same material. It took more than a decade to produce single crystals of cleavable $Bi_2Sr_2Ca_2CuO_{8+\delta}$ that were large enough for neutron-scattering experiments to accomplish this goal. At the time of the writing of this report, the correspond-

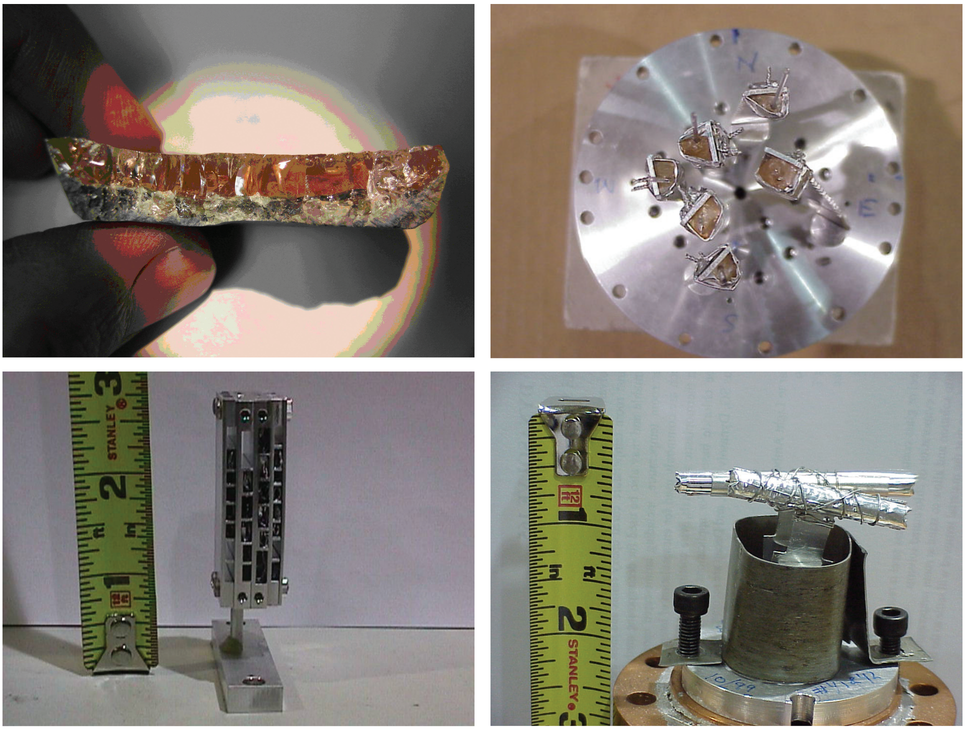

FIGURE 2.22 Images of crystals and sample holders for inelastic neutron scattering experiments. (Top left) ZrW_2O_8 grown using a flux technique by Glen Kowach, City College of New York. (Top right) Co-aligned ZrW_2O_8 single crystals used at the ISIS Facility to probe phonons in this negative thermal expansion material. (Bottom left) Co-aligned copper pyrazine dinitrate crystals used to probe an extended critical phase in a quasi-one-dimensional spin-1/2 antiferromagnet as a function of applied magnetic field at the NIST Center for Neutron Research. The crystals were grown in the group of Mark Turnbull and Christopher Landee at Clarke University. (Bottom right) Co-aligned Y_2BaNiO_5 single crystals grown by H. Takagi and used to probe the Haldane singlet phase in a quasi-one-dimensional spin-1 antiferromagnet. The chains extend approximately along the cylinder axis of the samples. SOURCES: Courtesy of (top left) Glen Kowach, City College of New York; (top right) Joost van Duijn, Universidad Complutense de Madrid, Spain; (bottom left and right) Collin Broholm, Johns Hopkins University.

ing letter to *Nature* reporting a spin resonance in the superconducting state of $Bi_2Sr_2Ca_2CuO_{8+\delta}$[8] had been cited 190 times since its publication in 1999.

A second example of research limited by crystal growth capabilities is the recent effort to understand charge and spin dynamics in $Na_xCoO_2{\cdot}yH_2O$. The fun-

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[8] H.F. Fong, P. Bourges, Y. Sidis et al., “Neutron Scattering from Magnetic Excitations in $Bi_2Sr_2CaCu_2O_{8+\delta}$,” *Nature,* **398,** 588 (1999). Number of citations obtained from the ISI Web of Science, http://apps.isiknowledge.com. Last accessed April 2, 2009.

damental importance of this material and of the exploratory materials synthesis that produced it is indicated by the more than 150 citations annually of the 2003 discovery paper by K. Takada et al.[9] While neutron scattering would provide key information for understanding electronic correlations in this material, adequate single crystals are at present not available. The central challenge for understanding $Na_xCoO_2{\cdot}yH_2O$ thus arguably lies in single-crystal synthesis.

In summary, there has been extraordinary progress in the ability to probe new materials through laboratory-scale instrumentation and national user facilities. The quality of the science produced is, however, critically dependent on (1) the discovery of new crystalline materials and (2) the production of high-quality samples with the appropriate morphology and dimensions for advanced characterization. Increased emphasis on the discovery and growth of novel crystalline materials is needed to realize the potential of facilities for new science and for materials-based applications in technologies ranging from information to energy.

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[9] K. Takada, H. Sakurai, E. Takayama-Muromachi et al., "Superconductivity in Two-Dimensional CoO_2 Layers," *Nature,* **422,** 53 (2003). Number of citations obtained from the ISI Web of Science, http://apps.isiknowledge.com. Last accessed April 2, 2009.

3

The Status of Activities in the Discovery and Growth of Crystalline Materials

To provide a complete picture of the status of activities in the discovery and growth of crystalline materials (DGCM) in the United States and internationally, the committee reviewed six areas that affect the field: education and training in DGCM; the role of industry; innovation and discovery; the breadth and depth of research; support for DGCM activities; and international activities. These areas are discussed further in this chapter.

EDUCATION AND TRAINING

The discovery and growth of crystalline materials and the scientific and technological enterprises dependent on them can only flourish if the field has a steady supply of young scientists educated in the cross-disciplinary science associated with the field and trained in the specialized techniques necessary for success in the field. To assess the state of education and training in the DGCM in the United States, the committee consulted with leaders in the field, including officers of the American Association for Crystal Growth and of the American Crystallographic Society. It also conducted surveys both of prominent crystal growers and of scientists who have only recently entered the field. Finally, it gathered information from public hearings and other sources. According to the information collected, the consensus of those in the crystal-growing community is that education in crystal growth and crystalline materials discovery is achieved through an apprenticeship model: graduate students are trained at universities by researchers in the field and then have postgraduate opportunities available to develop their skills further. However, the decrease in basic research at large industrial research laboratories, shifts in federal funding, and the organization of university research by discipline have all contributed to a marked decline in the availability of educational and training opportunities in the United States in this vital area; meanwhile, such opportunities elsewhere are increasingly available.

Before considering these causes and effects in more detail, it should be noted that the impact of DGCM extends well beyond the traditional fields of physics, chemistry, and materials science, influencing many diverse fields. In biology, for example, crystal growers seek to understand biomineralization and biological control of crystal growth, while in geochemistry researchers seek to understand molecular-scale processes as they relate to geological processes. However, this report focuses only on crystal growth and new materials discovery as they manifest in research in physics, chemistry, and materials science.

Impact of the Decline of Education and Training Opportunities in the Field

The extent of and reasons for the decrease in basic research at industrial laboratories are discussed later in this chapter. The impact of this decrease on the education and training of young researchers is significant. In the past, many graduates would spend a postdoctoral period at one of the large industrial research laboratories and receive intensive training in DGCM as part of an interdisciplinary team. For the most part, those opportunities are no longer available. Smaller companies that still grow crystals for the industrial or government markets typically do not have the capacity to provide such training. Selected national laboratories have significant efforts in the growth of specific materials, most notably the Ames Laboratory and the Lawrence Livermore National Laboratory (for very specialized materials needed for the National Ignition Facility [NIF]). However, few young people receive training in bulk-crystal growth at those facilities.

The lack of federal funding opportunities directed specifically to crystal growth has also taken its toll on efforts to educate and train future growers. As discussed in more detail later in this chapter, programs to investigate new electronic, magnetic, and optical properties of materials or to investigate crystal growth as it relates to challenging processes such as disease, biomineralization, or geochemistry do attract federal support, but support (and thus opportunities for graduate training) for the growth of the materials is much harder to obtain. In the past NASA provided significant support for crystal growth research through its Microgravity Research Program, but the program has been terminated, and many groups that depended on that source have disintegrated.

This lack of directed funding has limited the number of research groups in crystal growth. For a number of years, much attention was given in university laboratories to thin-film growth of silicon, germanium, gallium arsenide, and other semiconductors important for basic science and industrial applications. Many students were trained and a number of prizes in professional societies were awarded to researchers in this field during the 1980s and 1990s. More recently the synthesis and growth of nanostructures such as quantum dots and quantum wires have become a "hot" field that attracts students and has a strong presence in universities, supported by significant federal funding. Because of shifts in funding, many thin-film research groups have shifted their focus to creating such lateral nanostructures of known compounds while research into creating novel thin-film compounds and exploring their applications lags. While these nanostructures offer exciting possibilities for future technologies, research in thin-film and bulk-crystal growth continues to be of tremendous importance to creating new scientific knowledge as well as advancing existing technologies and enabling the development of new ones. The education provided by university research groups focused solely on nanostructures does not optimally equip young researchers to make contributions in the more established fields of thin-film and bulk-crystal growth.

Opportunities for education in bulk-crystal growth are more abundant in Europe and Asia (especially Japan) than in the United States. In regions outside the United States, it appears that the foundational role of DGCM for a wide range of vital technologies and for advances in fundamental science is more widely appreciated, and thus the support for research and education in crystal growth and materials synthesis is more abundant. The Europeans have traditionally had a strong focus on crystallography, with excellent programs in thin-film growth.

Recently such programs have undergone significant expansion in Asia. As a measure of the shift in crystal growth expertise from the United States to the rest of the world, one can note that many of the papers submitted to the *Journal of Crystal Growth* that focus strictly on the growth of materials now come from China. A comparison of the institutions of the authors of papers in that journal in 1992 and 2007 illustrates the point. Of the lead authors published in this journal in the period October–December 1992, 48 percent were at institutions in Europe or the United Kingdom, 23 percent were at Asian institutions, and 28 percent were at institutions in the United States or Canada. During the same months in 2007, the relative percentages of contributing authors had shifted significantly, with 29 percent of the authors at institutions in Europe or the United Kingdom, 58 percent at institutions in Asia, and only 9 percent at institutions in the United States or Canada. The membership of the editorial board and composition of the associate editor listing in the *Journal of Crystal Growth* show a similar shift, albeit less dramatic. In 1992, approximately 30 percent of the members of the editorial board and associate editors were in Europe or the United Kingdom, 15 percent were in Asia, and 55 percent were in the United States. By 2007 the percentage of members at Asian institutions had increased to 21 percent; the percentage in Europe and the United Kingdom had increased to 26 percent; and the percentage in the United States and

Canada had dropped to 50 percent (the remaining percentage is associated with a board member or associate editor not from these regions).

Expanding the scope of inquiry, a general search of the number of papers published in peer-reviewed journals that involve crystal materials or crystalline materials shows that the United States' dominant position in the percentage of papers published in this field has dropped considerably over the approximately past two decades. Table 3.1 lists the results of an ISI Web of Science query of papers published in peer-reviewed journals using the search term "crystal/crystalline and materials," ranked according to nationality of the lead author. In the early 1990s, over one-third of the published papers were from lead U.S. authors. By 2006-2007, that percentage had dropped to less than 20 percent. During that same span of time, authors from the People's Republic of China went from publishing only a small percentage of papers to publishing the highest percentage.

People trained in the United States in crystal growth (especially solution growth) often have difficulty finding jobs. Of the current employment in crystal growth in the United States, the committee estimates that approximately 25 percent are in bulk-crystal growth, with the remainder in epitaxial growth. Jobs in

TABLE 3.1 The Top 10 Sources of Papers on Crystal or Crystalline Materials Published in the Years 1990-1992, 1996-1997, and 2006-2007, by Nationality of Lead Author

	1990-1992		1996-1997		2006-2007	
Rank Among Top 10	Country of Lead Authors	% of 131 Papers	Country of Lead Authors	% of 252 Papers	Country of Lead Authors	% of 748 Papers
1	United States	33.6	United States	22.2	Peoples Republic of China (PRC)	20.4
2	Japan	11.6	Germany	14.8	United States	19.6
3	United Kingdom	11.0	Japan	12.2	Japan	11.6
4	Germany	9.4	United Kingdom	9.0	Germany	11.2
5	France	8.6	France	8.2	France	6.6
6	Italy	4.8	Peoples Republic of China (PRC)	7.8	Russia	5.4
7	USSR	3.6	Russia	7.6	India	5.2
8	Canada	3.4	Spain	4.8	United Kingdom	4.8
9	Peoples Republic of China (PRC)	3.2	Italy	3.8	Italy	4.4
10	India	2.8	India	3.4	Spain	4.2

NOTE: This survey was generated using the search topic "crystal/crystalline and materials" in the ISI Web of Science database, http://apps.isiknowledge.com/.

nanomaterials are abundant in academia, but universities typically will not hire a bulk-crystal grower (unless the grower can be described as an expert in an adjacent subject area, such as “novel magnetic materials”). National laboratories will occasionally hire such a person when there is a particular need (as at NIF), but this is rare. In the private sector, several small companies produce oxide crystals, but there is little to no U.S.-owned presence in the growth of silicon or compound semiconductor crystals—most of the U.S. manufacturing in this sector is by foreign-owned companies.

The varying expectations among relevant departments, combined with the lack of clear programmatic identity in the funding arena, create difficulties in the hiring and promotion of young faculty members. DGCM activities lie at the intersection of physics, chemistry, and materials science. This creates problems for a crystal grower, as the expectations vary considerably for such a person depending on whether his or her primary appointment is in a physics, chemistry, or materials science department, reflecting differences in the prevailing cultures. A member of a physics department would be expected to discover and measure novel properties of crystals grown in their laboratories, with the analysis of the properties of the crystal held in much higher esteem than the synthesis and growth of the crystal. In chemistry departments, significant emphasis would typically be placed on creativity associated with the growth of novel crystals of varying compositions and properties. In materials science departments, the discovery, growth, *and* characterization of crystals are valued with almost equal weight. The challenges continue even after an individual crystal grower is hired, because tenure still resides in traditional departments, and the scholarly work of young faculty members is typically judged against the traditional standards of research in that department. Although confidentiality factors make gathering detailed data on tenure outcomes extremely difficult, anecdotal evidence indicates that it is not uncommon for granting tenure to a scientist in this field to be made significantly more difficult because members of the tenure committee share but one or another of the views described above.

Another barrier to the hiring of young crystal growers is the start-up cost of equipping their laboratories. The committee solicited information from more than a dozen young DGCM scientists who had joined university departments or national laboratories in the past decade. At large research universities, the start-up packages included \$330,000 to \$870,000 for equipment, with the most expensive item typically costing from \$140,000 to \$350,000. In some cases the costs would have been even higher if shared equipment (for example, x-ray diffractometers, furnaces, transmission electron microscopes) had not already been available; creating a stand-alone fully equipped laboratory typically costs more than \$1 million. The scientists contacted also emphasized that the cost of consumables (such as chemicals, gases, containers, and cryogens) is a significant operating cost. While these start-up costs are feasible for some larger institutions, they are higher than is typical for many other areas of physics research, creating a disincentive for universities to invest in this field unless there is a strong expectation of a secure stream of future overhead revenue from the DGCM research program.

Findings on Education and Training

The Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth presents the following findings related to education and training in DCGM activities: A steady supply of expert DGCM scientists is vital to the continued health of a wide range of technologies and scientific endeavors, yet education and training opportunities for those going into the field have diminished in recent years. The loss of large industrial research laboratories has significantly reduced one of the principal advanced-training opportunities for scientists entering this field. Education and training in the United States for these scientists now occur almost exclusively in graduate programs, with students working in an apprentice mode with one or more professors. However, several factors have limited the increase in these types of programs. First, there exist very few federal funding programs specifically directed to crystal growth, which has limited the number of research groups concentrating in this field. Second, because DGCM activity lies at the intersection of physics, chemistry, and materials science, there is no natural academic home for this research in the discipline-based structure of most universities. Third, the high start-up and operating costs of such research create an additional barrier, especially if questions exist about whether the investment will be supported by a stable source of research funds. As a result, significant constraints exist in providing opportunities for educating and training the next generation of DGCM scientists.

ROLE OF INDUSTRY IN CRYSTAL GROWTH

Historical Leadership Shifts Since the Mid-1990s

Industrial laboratories in the United States and Europe were major drivers of DGCM throughout the 20th century. For example, during the mid-1980s, one of the preeminent industrial research facilities, Bell Laboratories, employed more than 110 full-time staff in DGCM research, at an annual budget in present-day dollars of approximately \$30 million.[1] Sometimes this role evolved in support of direct—though usually long-term—practicalities: for example, the development of zone refining for silicon crystal growth as a necessity for the semiconductor

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[1] Private correspondence between committee members and Bell Laboratories personnel—Cherry Murray, Frank DiSalvo, Leonard Feldman, and Walter Brown.

industry, or of yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) crystals for laser technology. But it was also true that industrial laboratories were often able to take a visionary stance on new technology. Perhaps nowhere is this clearer than in the development of epitaxial methods for crystal growth, including molecular-beam epitaxy (MBE). MBE and other epitaxial crystal growth methods are now routine and widely used in academia and industry, but they were pioneered in several major industrial laboratories in the 1970s.

Figure 3.1 shows the committee's analysis of a search of the Web of Science using the search term "crystal AND epitax*." The top-10 cited papers over decadal and then annual periods[2] are reported, with the author affiliation for each paper assigned to industry, academia, or national laboratories in the United States, Europe, or Asia. Note that the database coverage of early years is patchy (for example, only titles are searchable), and raw numbers are not comparable from period to period. But the trends are unmistakable, with the early years of the field dominated by the industrial (and also national) laboratories and a substantial shift of leadership occurring in the mid-1990s. Figure 3.2 is a similar analysis of MBE in which the same pattern is clearly discernable. Note that much the same trend is visible for Europe as well.

Many reasons can be cited for the initial leadership by the industrial laboratories. First, the development of the needed tools was expensive and required a long-term effort—not easy prerequisites for a single university researcher to meet. Culturally, it seems to have been easier for such research to become established in an industrial environment that did not have concerns about boundaries between technology and branches of fundamental science. Nevertheless, there can be no doubt about impact: the five most-cited papers from a search using the key phrase "molecular beam epitaxy" (35,000 papers in total) describe fundamental emerging technologies from the 1990s that are now prominent. Three of these papers are from industrial laboratories; the other two are from Japan (academia). The five most-cited papers using "quantum well" as a search (39,000 papers in total) include the top two from the MBE list, plus three others. Three of these papers are from industrial laboratories; the other two are from academia (one from Japan and one from the United States).

The most-cited papers usually involve technological breakthroughs that had their genesis decades earlier in fundamental research, where again the fundamen-

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[2] Web of Science searches were conducted by the committee for the following periods: 1970-1980, 1981-1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, and 2005. There were not enough papers published annually in the first two decades for good statistics because prior to 1990, the Web of Science indexes only titles. After 1990, the Web of Science indexes both titles and abstracts.

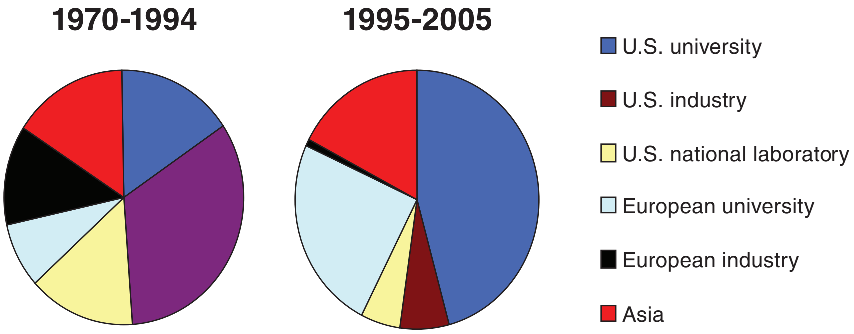

FIGURE 3.1 Origin of 10 most-cited papers revealed by a citation search of "crystal AND epitax*" on the Web of Science. The papers from Asia are a consolidated number from Asian universities, national laboratories, and industry. The total numbers of papers for the periods shown are 2,543 papers for 1970-1994 and 8,653 papers for 1995-2005.

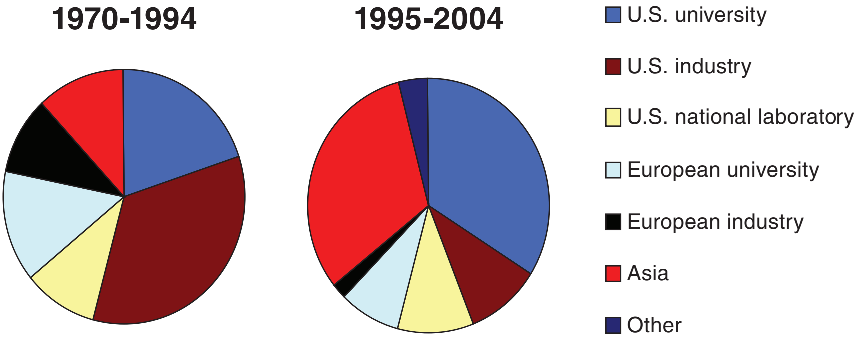

FIGURE 3.2 Origin of 10 most-cited papers revealed by a citation search of "molecular beam epitaxy" on the Web of Science. The papers from Asia are a consolidated number from Asian universities, national laboratories, and industry. The total numbers of papers for the periods shown are 9,955 papers for 1970-1994 and 19,684 papers for 1995-2004.

tal papers are widely known[3,4] but not always as frequently cited. Interestingly, the keyword searches did not identify two of the most fundamental discoveries in physics—the quantum Hall effects—presumably due to the small size of these fields of study. Nevertheless, it is clear that these discoveries would not have been possible without MBE technology.

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[3] A.Y. Cho, "Growth of Periodic Structures by Molecular-Beam Method," *Applied Physics Letters,* **19,** 467 (1971).

[4] L. Esaki and R. Tsu, "Superlattice and Negative Differential Conductivity in Semiconductors," *IBM Journal of Research and Development,* **14(1),** 61 (1970).

This decline of the involvement in industrial laboratories in basic research is part of a general pattern shown in the more general analysis made by the National Science Board (see Figure 3.3). The decline has been particularly marked in physics.

A sharper analysis of this trend is provided by looking at the career trajectories of a number of leading crystal growers, shown in Figure 3.4. By analyzing the careers of these researchers at different stages, it is clear that until the mid-1990s a common career path involved a first position at an industrial laboratory. That option has since largely disappeared. The transfer of major programs out of industrial laboratories into academia over the past decade and a half is also evident—and strikingly, the movement of staff in the reverse direction is almost absent. Lastly, the increasing role of the national laboratories can be discerned. Nevertheless, one notes that the United States has retained a preeminence in the area of crystal growth over four decades, which masks the transfer of activity (and quite often the staff) from industrial and national laboratories to universities.

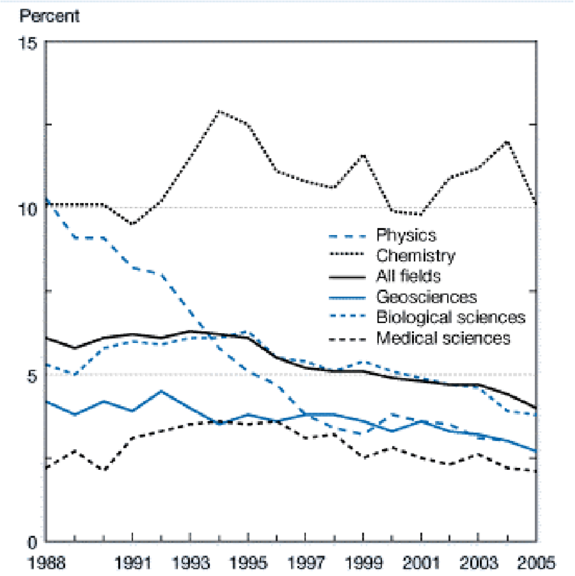
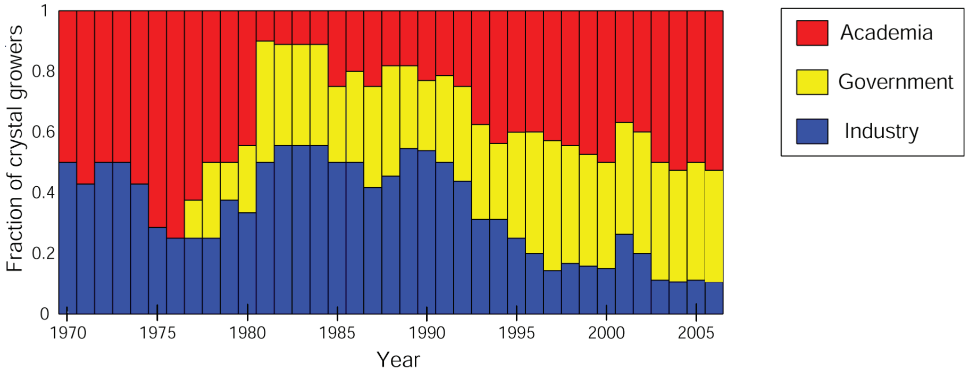


FIGURE 3.3 Articles on basic research in various fields published by scientists in private industry as a percentage of all U.S. basic research articles, 1988 through 2005. SOURCE: Reprinted from National Science Board, *Science and Engineering Indicators 2008,* Figure 6-27, Arlington, Va. National Science Foundation, 2008. Available at www.nsf.gov/statistics/seind08. Courtesy of the National Science Foundation.



Institutional Affiliation: Number of Selected Researchers Active in Crystal Growth: Data for Selected Years Shown in Figure 3.4

Institutional Affiliation	1970	1975	1980	1985	1990	1995	2000	2005
Academia	4	6	4	4	7	11	17	17
Government	0	0	2	3	4	9	9	10
Industry	3	2	3	5	6	4	3	2

FIGURE 3.4 Institutional affiliation of selected researchers active in crystal growth, starting with first position after receipt of Ph.D. through 2006. Out of the 29 researchers selected, 12 spent some portion of their career in laboratories operated by industrial companies: Bell Laboratories (7), DuPont Laboratories (2), International Business Machines Laboratories (2) and LTV Research Center (1). Out of 29 researchers, 16 spent some portion of their career in a government laboratory (some spent time at more than one laboratory): Los Alamos National Laboratory (5); Ames Laboratory (3); Oak Ridge National Laboratory (3); Argonne National Laboratory (2); Brookhaven National Laboratory (2); Sandia National Laboratories (1); National Institute of Standards and Technology (1); National High Magnetic Field Laboratory (1); CRISMAT, France (1); and ISTEC, Japan (1).

Findings on the Role of Industry in Crystal Growth

The Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth presents the following findings related to the role of industry in DCGM activities: The conclusions here are stark. The industrial laboratories historically provided leadership in both fundamental and applied materials research until the 1990s, and while the United States has kept preeminence in many areas, this position rides substantially on fundamental investment that was made more than two decades ago and which has not been maintained. Particular concern arises over the training and support of young researchers. While the data are slim, the paucity of career movements between academia, industry, and the national laboratories over the past decade is of concern.

INNOVATION AND DISCOVERY

The field of the discovery and growth of crystalline materials is invigorated periodically by discoveries of new materials, or by discoveries of new physical properties of existing materials. In a discipline such as condensed-matter materials, major discoveries often emerge unexpectedly in areas of research that might have seemed dormant or previously unexplored. Famous examples of this include the discovery of high-temperature superconductivity in the copper oxides and of exotic superconductivity in heavy-fermion compounds, the (re)discovery of enormous magnetoresistive properties of some rare-earth manganites, the emergence of carbon nanotechnologies (fullerenes, nanotubes, graphene), and the development of polymeric and organic compounds as light-emitting diodes, sensors, detectors, and photovoltaics. In these fields, single discoveries can lead to a profound reorientation of the discipline and the genesis of important technologies. It is clear that the future strategy of condensed-matter materials must include a vigorous component focused on such groundbreaking research.

The importance of materials discovery science is quantified in Figure 3.5, in which for three materials classes (the colossal magnetoresistance [CMR] manganites, the anomalous metallic ruthenates, and the heavy-fermion superconductor UBe_{13}) the committee reviewed citations to a single "discovery" paper (blue) and compared that to the total papers published on the topic. Note that a single paper can have a preponderant as well as a catalyzing effect. For example, as shown in Figure 3.5(c), a key paper has more citations than the total number of papers published subsequently referring to the same material (UBe_{13})—since the discovery (in this case of unconventional superconductivity) impacts a much broader field of science.

How good is the United States at engendering materials discovery science? The record is mixed and variable by subfield. To explore this topic in more detail, the committee looked at results in the subfields of superconductivity, magnetic materials, and intermetallic compounds. These subfields were selected because they are highly active areas of research and because advances typically made in these subfields are directly related to advances in crystal discovery and growth.

Superconducting Materials

The data in the top panel of Figure 3.6 show that for superconducting materials, the United States was a clear leader in measurement science in the mid-1990s, and the U.S. contribution to synthesis of samples, shown in the bottom panel of Figure 3.6, was comparable to that of Europe and Japan. Over the past decade, however, contributions from measurement science in the United States have waned, while the Japanese effort has increased and is now comparable to that of the United States. The impact of synthesis efforts in Japan has clearly exceeded that of the

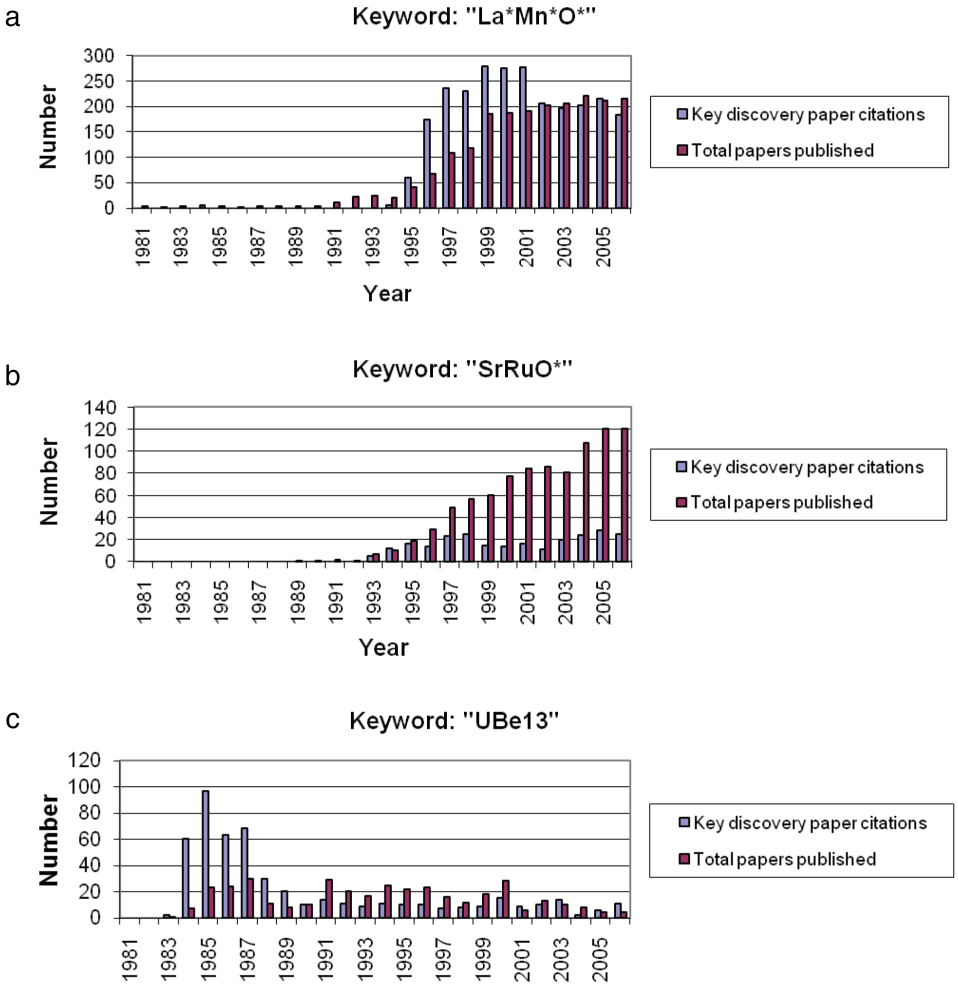


FIGURE 3.5 Key discovery paper citations measure the impact of the research discussed in those papers in future years. Here, the number of citations (annually) to a key discovery paper (blue) is compared to the total number of papers published annually on the same topic. Searches are from the Web of Science, using the following keywords: (a) “La*Mn*O*” (for colossal magnetoresistance manganites), (b) “SrRuO*” (for the anomalous ruthenates), and (c) “UBe13” (for the heavy-fermion superconductor).

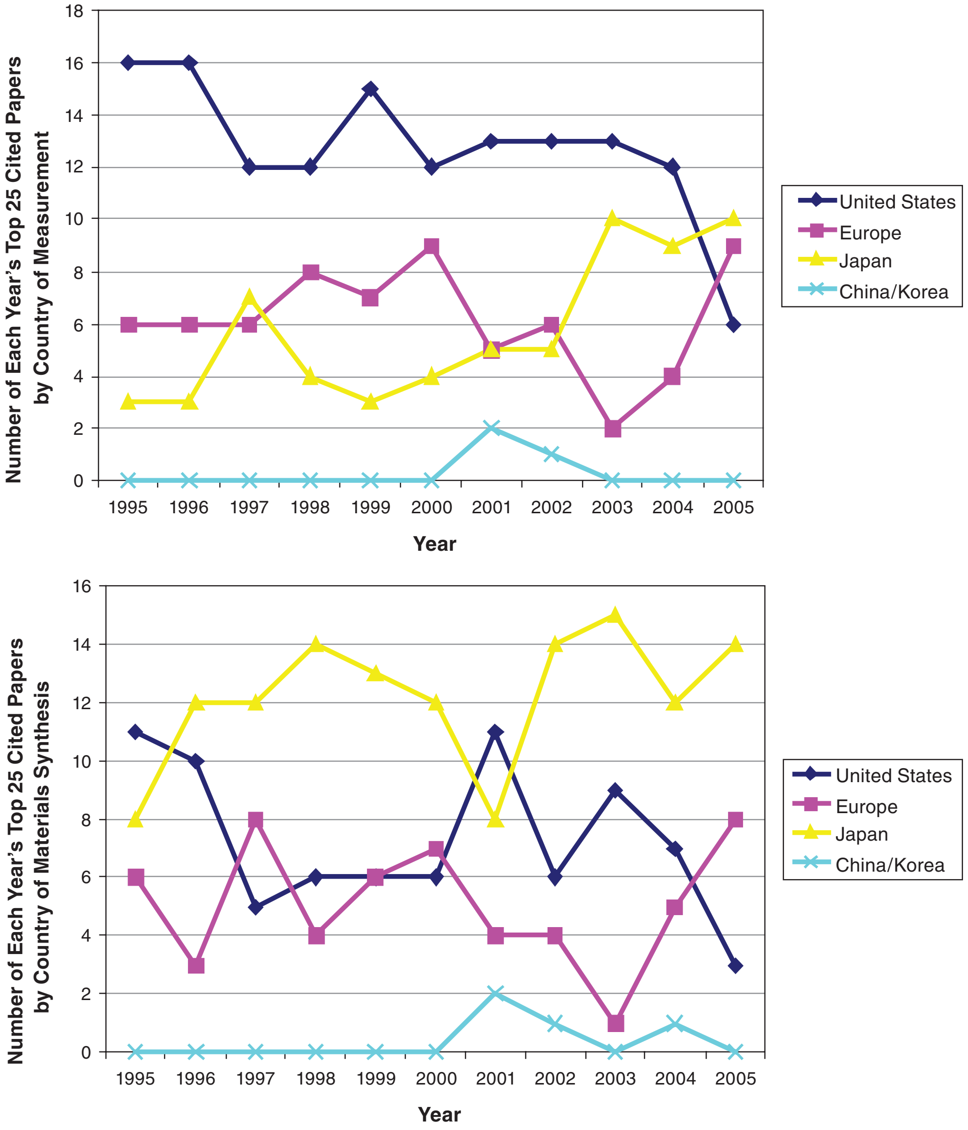


FIGURE 3.6 Country of origin of the 25 most highly cited papers in superconductivity by year, 1995 through 2005, distinguished by country of measurement (top) and country of materials synthesis (bottom).

United States and Europe. (See Box 3.1 on iron-based pnictide materials for a recent manifestation of this shift.)

However, this trend masks a more worrying decline in the U.S. production of key papers in this field. Over the past decade, the subjects of the most-cited superconductivity papers (each with more than 300 citations) together with the country of source material are as follows: MgB_2 (Japan), $CdPd_2Si_2$ (United Kingdom), UGe_2 (United Kingdom), $NaCo_2O_4$ (Japan), BiSrCaCuO (Japan), $LaSrCuO_4$ (Japan), MgB_2 (Korea), $LaSrCuO_4$ (Switzerland), $CeIrIn_5$ (United States), $CeCoIn_5$ (United States). Six of these papers had U.S. coauthors, and in four cases that person was the lead author. What is striking is that several different materials were featured in the top class (this is the single-paper discovery dominance noted above) and only a single class of materials was sourced in the United States.

BOX 3.1
Iron-Based Pnictide Materials: Important New Class of Materials Discovered Outside the United States

The New Discovery

The recent discovery of high-temperature superconductivity in the iron-based pnictide materials has led to a dramatic surge of worldwide research on these novel superconducting materials. These materials are the first new class of transition-metal-based high-transition-temperature (T_c) superconductors since the discovery of the copper oxide (cuprate) superconductors in 1987. The fact that they contain iron as the active electronic element was a great surprise to most superconductivity experts, since the magnetism of iron has traditionally been understood to be the complete antithesis of superconductivity. It is hoped that a complete understanding of this new, unexpected class of noncuprate materials will at last lead to the solution of the unsolved problem of the mechanism of high-T_c superconductivity. In addition, there is the hope of discovering even-higher-T_c materials with technological impact.

The work on these new materials is proceeding at a rate that is reminiscent of the explosion of research on the cuprates in 1987. Immediately after the discovery of high-temperature superconductivity in LaOFeAs, the number of papers related to the subject that were published between January and July 2008 exceeded 350, and their rate of publication since then has only been accelerating.

Discovery-Phase Work Done in Japan and China

The initial breakthrough work in Japan by Hosono and coworkers, published in March 2008,[1] reported a T_c of 26 kelvin (K) in fluorine-doped LaOFeAs. Since then the T_c has been increased to 55 K in a related compound made in China. In addition, two related classes of compounds (doped $BaFe_2As_2$ and LiFeAs) have been found to be superconducting, with a T_c as high as 38 K. *All of the discovery-phase work was done in Japan and China*. Shortly after the reported discovery of high-temperature superconductivity in this type of materials, Japan recognized the

Magnetic Materials

The data for magnetic materials broadly mirror the trends noted above for superconducting materials, although the rate of change is smaller. In the mid-1990s, research in both the United States and Europe exceeded the impact of Japanese research, both in measurement and in synthesis. Subsequently, however, top-cited Japanese papers have reached parity with those from the United States and Europe.

Several subtopics in magnetic crystalline materials were initiated in the United States during the past 15 years, including skutterudites, heavy-fermion magnets, and geometrically frustrated magnetism. Although important, these topics individually do not strongly impact the citation data. The subtopics highlighted below constitute the bulk of highly cited research in crystalline magnetic materials.

urgent need for funding and started a special program on iron-based pnictide superconductors through the Japan Science and Technology Agency. Twenty-four proposals (20,000 U.S. dollars per year are allocated for each program) have been accepted and are actively running. Similar special programs are also running or about to be run in China and Europe.

As for the United States, there was little widespread knowledge of this exciting discovery until about April 2008, when the first U.S. experimental paper reached the archives. Much of the delay in conducting work on this important material in the United States can be attributed to the traditional behavior of researchers in this field. It is common for materials growers to share their materials only with their colleagues, first at their own laboratory, then at their own institution, and then with their friends and previous collaborators in other laboratories. Typically these collaborators are in the country of origin of the growers, and in order for priority and credit to be established, it is typical to not advertise results or details until significant progress has been made.

The iron-based superconductors are yet another important class of materials discovered outside the United States. It is also important to note that these materials are extremely difficult to grow owing to safety concerns; only a few laboratories in the United States have the facilities and expertise to make them. As a result, U.S. researchers, including many eminent physicists with novel and important techniques of measurement, both in small laboratories and national facilities, are unable to obtain the crystals in the early stages. This lack of samples has led to widespread frustration among U.S. researchers and their exclusion from a major new field of study in its formative stages.

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[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, "Iron-Based Layered Superconductor La[$O_{1-x}F_x$]FeAs (x = 0.05-0.12) with T_c = 26 K," *Journal of the American Chemical Society,* **130,** 3296 (2008).

Colossal Magnetoresistance

One of the most active fields in magnetism in the 1990s was that of the colossal magnetoresistance materials. The ability to synthesize samples of CMR compounds in the form of polycrystals, single crystals, and thin films opened this field to a large number of researchers. Based on searches conducted by the committee using the Web of Science, the 10 most highly cited papers in this field were published from 1993 to 1996; each has more than 500 citations. Four of these papers are from the United States, four are from Japan, and two are from Europe.

Papers in CMR significantly outnumber papers in other topics on magnetism over the past 10 to 15 years. Nevertheless, the same time period witnessed a resurgence in non-CMR-related magnetism research.

Low-Dimensional Magnetism

Solids exist in three dimensions. However, the internal structure of a crystal allows the *effective* dimensionality to be one or two (for example, chains or planes of atoms). Some materials properties—for example, the quantum behavior discussed below—are exhibited *only* in lower dimensions. Such materials offer unique experimental opportunities to contribute to the understanding and control of matter.

It is therefore of interest in the present context to establish where this research is being conducted. Figure 3.7 shows, by country of origin, the percentage of papers published with mention of these materials in the title or abstract (abstract information was only available for papers indexed by the Web of Science after 1990). Japan emerges as the clear leader, with the United States a rather distant second.

Magnetic Semiconductors

A "holy grail" in device science is the utilization of spin—the electron's intrinsic magnetic moment—as an information bit for developing devices with high-speed switching, low energy consumption, and ultrafast memory access. This effort requires new measurement techniques as well as new classes of semiconductors that enable efficient transduction of magnetic information. The top 4 among the 25 most highly cited papers on this topic originated from Japan in the period between 1996 and 2001. At present, there is a more balanced international effort.

Multiferroics

Multiferroic materials exhibit a magnetic signature in response to an electrical input, or vice versa. This field recently emerged as a natural convergence of ferroelectric materials and CMR materials. According to the Web of Science, for

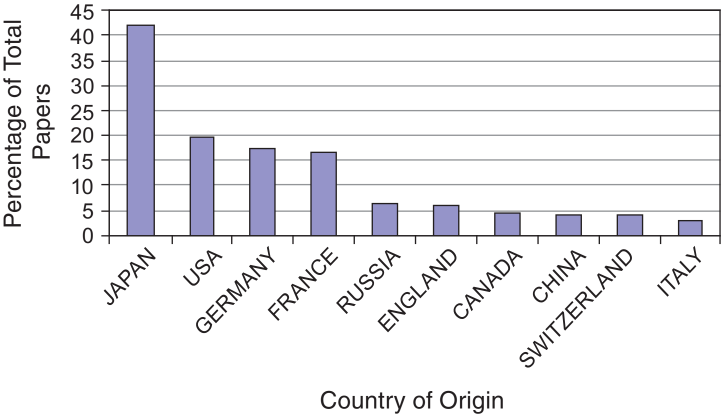


FIGURE 3.7 Percentage by country of origin for publications referencing prominent low-dimensional quantum magnets. SOURCE: Collin L. Broholm, The Johns Hopkins University, based on ISI Web of Science.

the years 2005 through 2008, 4 U.S.-based papers are in the top-10 cited papers in "multiferroics," with most of the remaining papers from Europe. However, essentially all of these papers involve crystals from Japan or Europe.

Intermetallics

The science and technology of structural intermetallic compounds are driven by the need to increase operating efficiencies of engines further, particularly of turbine engines. Higher melting temperatures, lighter alloys, lower-cost raw materials, increased strength at high temperatures, and low-temperature ductility and toughness (for manufacturing ease) are being pursued to meet these needs. The new intermetallics require inherent corrosion resistance. Most alloys are based on binary (two element) intermetallic alloys, and the structural usefulness of almost all of these systems was discovered in U.S.-based research. The discovery stage of most high-temperature, structural binary intermetallic research originated in the 1980s. Despite the advances, this research is on the decline in the United States.

The data in Figure 3.8 illustrate the trends in the top-cited papers over the past 8 years. Although binary structural intermetallics originated in the United States, Japan and the European Union now hold an edge in published research. The United States experienced a peak in the early 2000s as a result of research support by the U.S. Air Force.

Although it is useful to consider comparisons of discovery, measurements, and location of crystal fabrication, several additional issues can be noted upon read-

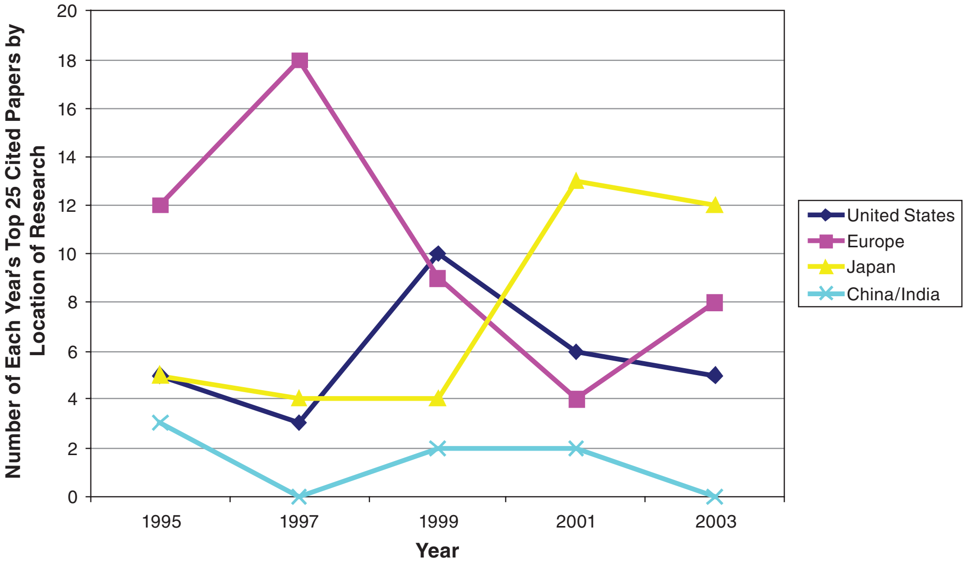
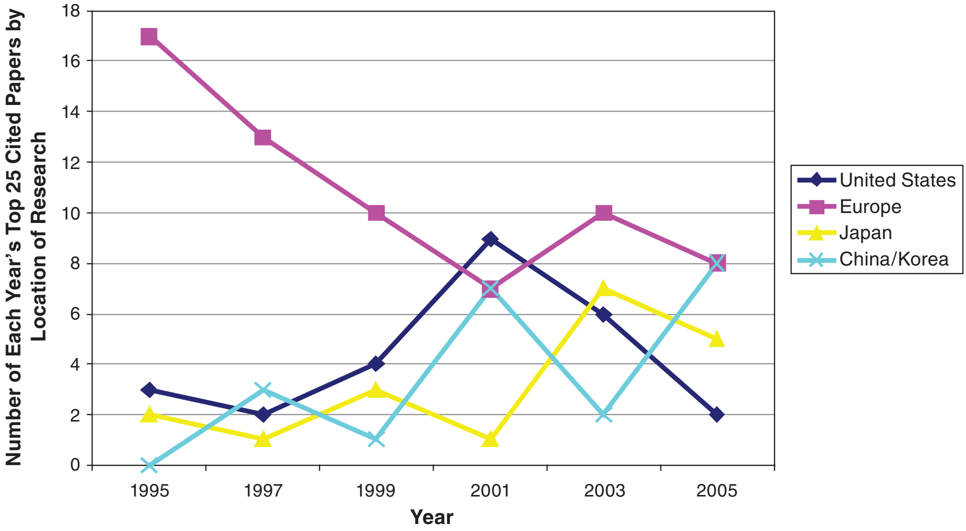


FIGURE 3.8 The number of top-cited papers, 1995 through 2003, on the topic of high-temperature structural intermetallic single crystals: the graph demonstrates the location of research (which closely matches that of the crystal fabrication).

ing the top-cited papers in high-temperature structural intermetallics. In most instances, measurement and production seem to take place in similar locations. In other words, the sharing of samples among researchers in different countries is not the norm, although it does occur in a few specific but not significantly relevant examples. Moreover, the details of the single-crystal synthesis discussed in the papers are limited to a brief mention of the technique used, and only rarely is the single-crystal grower acknowledged. In most instances, however, the name of the person growing the crystal is not even referenced.

The research history of a structural intermetallic can be compared with that of a functional intermetallic, shape-memory alloy. Shape-memory alloys originated with the discovery in AuCd, where a bent material, after heating, recovers its prebent shape. The most commercially viable shape-memory alloy, Nitinol (NiTi), was patented through the Naval Ordnance Laboratory in the 1960s.

As with structural intermetallics, functional shape-memory intermetallics were discovered in the United States; subsequently, many new classes of shape-memory alloys have been discovered in Japan, Ukraine, and other countries. The top-cited publications, as seen in Figure 3.9, illustrate that the European Union and Japan have very strong efforts. Similar to the situation with structural intermetallics, shape-memory alloys have closely matching synthesis and research locations. China



FGURE 3.9 Number of top-cited papers, 1995 through 2005, for shape-memory intermetallic single crystals: the graph demonstrates the location of research (which closely matches that of the crystal fabrication).

(including Hong Kong and Singapore) is clearly in a growth mode in this field and is competitive with the European Union and Japan.

Findings on Innovation and Discovery

The Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth presents the following findings related to the role of innovation and discovery in DCGM activities:

- The field of materials research is highly dependent on a few key discoveries that spawn much additional research; often a single paper sets a new trend.
- Overall the U.S. presence in the discovery and growth of crystalline materials remains solid in terms of gross activity, but this activity masks disturbing trends in declining support for the field and a loss of leadership in key areas.
- The worldwide leadership of the United States that existed up to the early 1990s in epitaxial growth and in superconducting and magnetic materials has significantly declined, particularly in terms of the most important discovery papers.

- Significant portions of the research pioneered in U.S. industrial laboratories in the 1970s and 1980s, along with many of the researchers who conducted it, left industry for universities or national laboratories. While this transition postponed a rapid decline in absolute materials research activity in the United States, the solution is temporary. It also removes what had been a productive training ground and career path for junior researchers.
- The lack of engagement by industry in innovation and discovery in the field of DGCM is of great concern, given the key role that new materials play in the technology base.
- The national laboratories have picked up some of industry's research activities, but there remains a large opportunity for government to engage in further efforts to bridge the gap between discovery science and applications.

BREADTH AND DEPTH OF RESEARCH IN THE DISCOVERY AND GROWTH OF CRYSTALLINE MATERIALS

Researchers who grow crystalline materials have an astonishingly broad impact on further research. To assess this impact, the committee compiled a list of 10 major senior researchers in this area and analyzed their publication records using a citation database. For comparison purposes, the committee used a similar list of 10 high-impact experimentalists in similar fields (for example, solid-state physics) compiled from ISI's list of highly cited researchers.[5] Researchers in both the crystalline materials grower group and the highly cited comparison group have outstanding publication and citation records. For the crystal growers, the average number of years of active research experience was 33 years, and for the experimentalists it was 43 years. A measure of the productivity and impact of these two groups is illustrated by the average *h* index for the two groups. The *h* index is a widely used measure of impact and productivity defined as the number of papers, *n*, with more than *n* citations.[6] While the *h* index depends on the field of research and other variables, a productive researcher in physics would have an *h* index comparable, roughly, to the number of years of active research experience. For the groups under comparison here, the average *h* index was 71 for the growers and 63 for the comparison group. These remarkably high numbers illustrate the enormous sustained productivity and impact of the researchers in these two groups.

The comparison between the two groups is shown in Table 3.2. A "frequent coauthor" was defined as an individual who had coauthored five or more times

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[5] See http://www.isihighlycited.com/. Last accessed April 1, 2008.

[6] For a further description of the *h* index, see J.E. Hirsch, "An Index to Quantify an Individual's Scientific Research Output," *Proceedings of the National Academy of Sciences*, **102(46),** 16569-16572 (2005).

TABLE 3.2 Comparison of the Productivity of Materials Grower Group and Highly Cited Comparison Group for 1996-2006

	Materials Grower Group (per researcher)	Highly Cited Comparison Group (per researcher)
Frequent coauthors	142.7	79.2
Total coauthors	836.2	454.7
Total papers	597.1	351.1
h index	70.9	62.9
Years of research experience	33.3	43.4

NOTE: Publication data were collected for 1996-2006. "Frequent coauthors" are individuals who have coauthored papers with a specific materials grower five or more times. "Total coauthors" is the total number of coauthors for the publication years for a member of one of the groups. All values are averages for the groups.

with the researcher on the list during the search years of 1996 to 2006. Since the comparison group has over 10 years more of average research experience, it is advantageous to compare rates of productivity by dividing by the number of years of experience. This comparison, shown in Figure 3.10, reveals several interesting features. First, the growers are remarkably prolific researchers, with publication rates and numbers of unique and frequent coauthors more than double that of the (also extremely productive) comparison group. This high productivity allows a relatively limited number of growers and synthesizers to have a substantial scientific impact: Their efforts are highly leveraged by the efforts of their many collaborators. Second, the materials grower group sustains a very high publication rate in absolute numbers: An average of nearly 18 publications per year per grower represents an astonishingly high demand (and workload) for this group of researchers.

U.S. FUNDING FOR DISCOVERY AND GROWTH OF CRYSTALLINE MATERIALS RESEARCH

Historically, support for basic research in DGCM was distributed from across many federal agencies and programs and was also supported by industry. There have not been specific federal programs that fund basic research in the discovery and growth of crystalline materials, and thus it is hard to quantify the total investment or trends in investment in DGCM activities. However, in an effort to quantify the present level of support and to determine the appropriate size of the U.S. effort in DGCM, 28 experts around the country in the discovery and growth of crystalline materials were surveyed by the committee. These experts were asked to provide information on the demand for synthesized materials and on their research support. The results of this inquiry are discussed below, followed by an overview analysis of the state of DGCM support by major federal agencies.

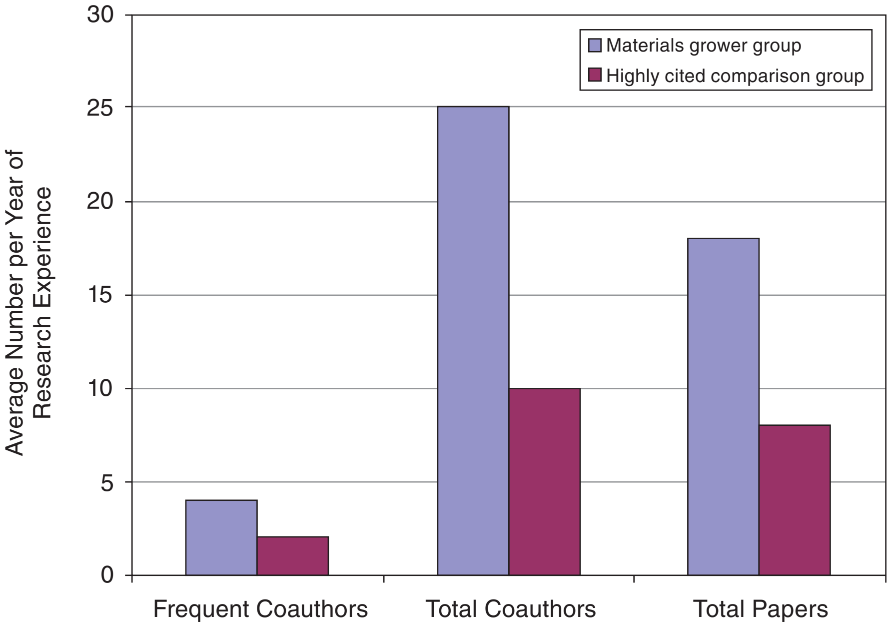

FIGURE 3.10 Comparison of the productivity of a group of 10 high-impact crystalline materials growers (selected by the committee) and a group of 10 solid-state experimental physicists (from ISI's Highly Cited list), normalized by the number of years of research experience. "Frequent coauthors" are individuals who have coauthored papers with a specific materials grower five or more times. "Total coauthors" is the total number of coauthors for the publication years for a member of one of the groups. All values shown are averages for the group. Publication data were collected for 1996 to 2006.

Survey of Experts in the Discovery and Growth of Crystalline Materials

To help estimate the need in the science community for high-quality crystalline samples, the survey conducted by the committee asked 28 experts in DGCM about the number of materials requests that these experts receive in a given year. By considering the results of the survey and engaging in follow-up discussions with experts, the committee determined that there is significant underfunding of the field of materials synthesis and crystal growth. Underfunding for the field is exacerbated by the small number of experts in DGCM and by the tendency of that small number to focus on materials of personal interest and of relevance to their own established collaborations, as described in the two points below.

1. The questions in the survey were constructed for "growers," not for "measurers." The classification of the scientists into these two groups by the

phrasing of the questions was considered to be inaccurate and offensive to those polled. Each grower is an outstanding scientist who understands the importance of control of novel materials for obtaining basic scientific information on intrinsic properties. None of them is simply a "supplier" of samples. According to the survey results, in many cases the growers and measurers are part of the same group, and in some cases the same person fills both roles. In all other cases, the growers and measurers work in a highly collaborative mode. This makes for better science, but it also limits external interactions: The grower plays an active part in every collaboration (so time is a limit) and only collaborates on measurements with materials of interest to the grower. Therefore, measurers with interests that do not overlap with those of particular growers may not be successful in procuring materials for their experiments.

2. According to the survey results, the ability to obtain crystalline samples for experiments depends on the researcher's status and familiarity with the expert grower. Requests for samples, even from respected researchers at research universities, often require multiple attempts. Furthermore, researchers from less prestigious institutions often do not even attempt to make materials requests, knowing that the requests will not be fulfilled. Therefore, the true number of samples that are needed and of laboratories that need materials must be larger than those reflected in the collected data.

As stated above, many requests for materials are made by measurers, but it is impossible for each request to be fulfilled. Over the past few years, on average each grower rejected requests from approximately 35 to 40 researchers per year and approximately 100 materials requests per year from those researchers. Coupled with the two points above, it is evident that hundreds of researchers are unable to get materials from growers at all, and on the order of thousands of materials requests remain unfulfilled.

The 28 experts surveyed were also asked about their present support and the level of support that they would need to fulfill all sample requests received. Those polled could not separate funding for the "growth" from the "materials research and measurement" part of their research. A significant fraction of their research funding supports discovery, characterization, and analysis for greater understanding of the novel materials, and the fraction of funding used to grow materials for outside collaboration is not clear. There was universal agreement among the 28 experts, however, that a factor-of-two increase in support would be needed to fulfill their sample requests. The increase is required both in supplies and in personnel; as stated clearly by one scientist: "My group would have a larger number of requests for samples if we could make faster progress on materials growth and characterization. We would be able to make faster and better progress and accommodate the larger number of requests for samples with more adequate funding."[7]

When they were asked what is needed for the United States to be a world leader in DGCM research, the most common answer given by this group of experts was the need for an increase in current levels of DGCM funding support by a factor of three to four. The committee finds this factor to be consistent with its observations, given that the factor-of-two increase for these experts to meet current demand does not take into account the needs of existing scientists who would like crystals but are not well connected and so do not ask for new crystalline materials, nor does it reflect the fact that there are other researchers who, because of a lack of access to state-of-the-art crystalline materials, forgo the opportunity to work in this field. Such additional support is needed not only for DGCM research and materials growth for collaborative experiments but also for training students in this area.

At present, there are five national laboratories funded by the Department of Energy—Ames Laboratory, Argonne National Laboratory, Brookhaven National Laboratory, Los Alamos National Laboratory, and Oak Ridge National Laboratory—that house significant materials growth efforts. These national laboratories interact strongly with a few key universities. One scientist, who called this the "hub and spoke" model, believed that it represents a reasonable way to support this field but that overall support is too low, both internally for the national laboratories and with respect to their ability to interact with the universities. The committee believes that increasing the DGCM support in national laboratory "hubs" would strengthen existing collaborations and also allow an increase in the number of "spokes" to include universities that historically do not have strong connections with national laboratories. However, the committee believes that a single approach of strengthening support for DGCM research at national laboratories will not be sufficient to advance science and technological industries dependent on discoveries in new materials and crystal growth. The spokes in such a model are equally important, and direct, concomitant support for research programs at universities would be essential.

Support for Discovery and Growth of Crystalline Materials Activities

Support for research in the discovery and growth of crystalline materials has historically come from federal programs and from industry. Some of the federal programs no longer support this research, and industry support has waned in recent years. This subsection describes the changing landscape of support for DGCM research.

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[7] Survey response.

Industry

The precipitous decline in DGCM research in industrial laboratories is described earlier in this chapter. While many industrial researchers have shifted to academia, the scale of the work has significantly changed, resulting in a net loss of funding for the field. The industrial laboratories were also a significant training ground for new scientists interested in the discovery and growth of crystalline materials. Declining research in DGCM activities thus also negatively impacts opportunities for the education of young researchers.

National Aeronautics and Space Administration

For more than 30 years, from the early 1970s until it was phased out in the early 2000s, NASA's Physical Sciences Division funded research into physical processes that are significantly affected by gravity. Materials science was one of the five broad areas included in the Microgravity Research Program. Crystal growth and defect control constituted one of the research themes within the materials science research program. During the mid-1990s, the Microgravity Research Program had a budget of approximately $100 million and funded approximately 400 projects. On average, 80 ground-based materials science projects were sponsored each year. A report published in 2003 by the National Research Council, *Assessment of Directions in Microgravity and Physical Sciences Research at NASA*, noted that the impact of NASA's materials research program was especially significant in the area of solidification and crystal growth.[8] The phasing out of this program in the early 2000s represents a significant loss of support for DGCM.

National Institute of Standards and Technology

The National Institute of Standards and Technology (NIST) also had a significant effort in the growth of bulk-scale single crystals and the modeling of growth processes in the 1990s. This emphasis has waned, and current research on single crystals at NIST has focused on the characterization of materials rather than the growth of new crystalline materials. Current research at NIST in DGCM activities is carried out in several cross-collaborative efforts, which makes separating out the staffing and budgeting for such activities impracticable.

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[8] National Research Council, *Assessment of Directions in Microgravity and Physical Sciences Research at NASA*, Washington, D.C.: The National Academies Press (2003).

Department of Defense

Research in the discovery and growth of crystalline materials at the Department of Defense (DOD) is included in the basic research budget (6.1). Figure 3.11 shows that 6.1 funding at DOD has been approximately flat for the past 15 years. In addition, research supported by DOD must focus on mission applications. Although the amount of DOD's 6.1 spending for DGCM-related activities is not available, the combination of these factors suggests that support for DGCM activities at DOD agencies would likely be narrow in scope and approximately constant for the past 15 years.

Department of Energy and National Science Foundation

In the Department of Energy, Basic Energy Sciences supports DGCM research. At the National Science Foundation, DGCM research is supported by the Division of Materials Research in the Directorate for Mathematical and Physical Sciences. These two federal agencies support the majority of basic research in DGCM conducted at U.S. universities. Within each agency, the support is derived from many programs such as those for condensed-matter physics and solid-state and materials chemistry. For this reason, it is difficult to determine trends in DGCM support—essentially every grant awarded in these programs would have to be reviewed to determine whether DGCM research was involved. However, the overall funding for these programs has been approximately flat for the past decade.[9] Thus, it is reasonable to estimate that DGCM research activities have also been held constant in this time frame.

Findings on Support for Discovery and Growth of Crystalline Materials Activities

The Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth presents the following findings related to U.S. funding for basic research in the field of DGCM: Traditionally, industrial research laboratories conducted much of the basic research in the DGCM field in the United States. The decline in industrial efforts in this area leaves a large gap in overall support for DGCM activities in the United States. According to the committee's survey of and discussions with DGCM experts, federal funding for the DGCM field has not made up for this loss—hundreds of scientists go wanting for thousands of samples—and the United States will only be able to meet the demand of U.S. researchers for

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[9] National Research Council, *Condensed-Matter and Materials Physics: The Science of the World Around Us*, Washington, D.C.: The National Academies Press, 2007.

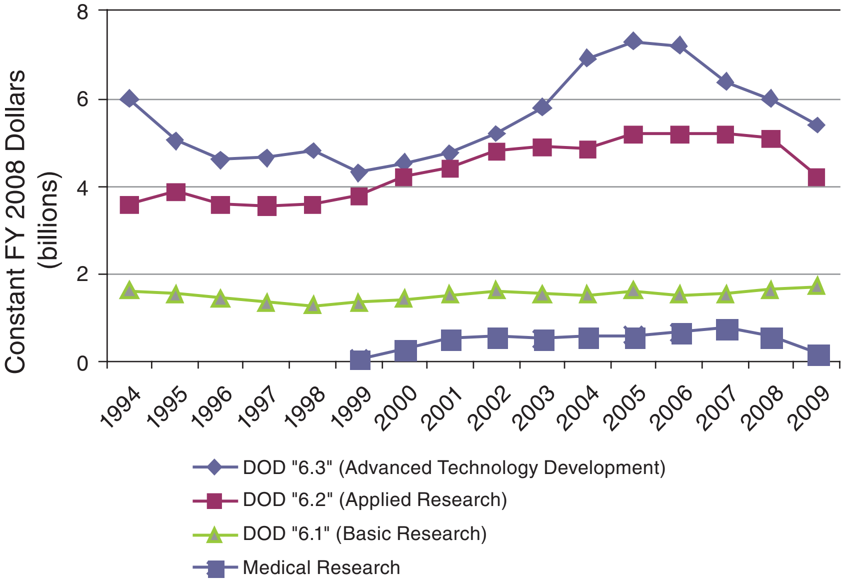

FIGURE 3.11 Support for basic research (6.1) at the Department of Defense has been approximately constant for the past 15 years. SOURCE: American Association for the Advancement of Science (AAAS), "Trends in DOD 'S&T'," FY 1994-2009 chart, February 2008, available at http://www.aaas.org/spp/rd/trdodst09pa.pdf. Data based on AAAS analyses of research and development (R&D) in annual AAAS R&D reports. The FY 2009 figures are the most recent AAAS estimates of the FY 2009 request. Medical research appropriated outside RDT&E [research, development, testing, and evaluation] funding; appropriated in "6.2" accounts before 1999.

crystals by doubling the amount of federal support for DGCM efforts. In order for the United States to achieve the rank of world leader in DGCM research, the experts surveyed by the committee believe that funding would need to increase by a factor of three to four times current funding levels. Because there are no current federal programs whose focus is funding basic research in the discovery and growth of crystalline materials, it is hard to quantify current total investment or historic trends in investment in DGCM activities. However, the few programs that were directed to DGCM efforts in the past have been phased out, while those programs indirectly funding DGCM efforts, for the most part, have seen their budgets remain flat.

INTERNATIONAL ACTIVITIES

The discovery and growth of crystalline materials have been an active area of research in Europe and Asia, especially in Japan, China, and Korea. As discussed below, three factors appear to be important in the promotion of DGCM activities in these countries.

Centers for the Discovery and Growth of Crystalline Materials Research

DGCM centers with concentrated human resources and significant budgets are undertaking initiatives to promote DGCM activities in Europe and Asia. These efforts appear to be quite effective when the research target is well defined and closely linked to industry. In Germany, for example, the Institute for Crystal Growth (IKZ) in Berlin and the Department of Crystal Growth in the Fraunhofer Institute for Integrated Systems in Erlangen employ staffs of 93 and 35 people, respectively. IKZ in particular has been very active in the growth of semiconductor crystals (such as silicon, gallium arsenide, gallium nitride, and zinc oxide) and optical crystals (such as fluorite), as well as in the development of growth and characterization techniques. A range of research expertise and crystal growth expertise is supported at these centers—computational modeling, analytical services, and technique development—to create an overall capability that does not exist in the United States.

These two German centers operate on a blend of funding from both industry and government sources. According to IKZ's latest annual report, its staff of 93—40 scientists, 42 technicians, 9 Ph.D. students, and 2 diploma students—is supported by an annual budget of 9.0 million euros (11.5 million U.S. dollars)—7.14 million euros (9.1 million U.S. dollars) from government funding and 1.87 million euros (2.4 million U.S. dollars) from projects and industrial grants.[10] While separate figures were not available for Fraunhofer's Department of Crystal Growth, the overall annual funding for Fraunhofer's staff of 140 people was 11.0 million euros (14 million U.S. dollars), with approximately 43 percent provided by industry, 18 percent provided by the German government, and the balance of funding from international sources, with the large majority from the European Union.[11]

Other examples of focused DGCM centers can be found in China. China has been playing a leading role in the growth of optical crystals, including borates such as lithium borate (LBO) and barium borate (BBO), and consequently dominates the market for these materials.[12] The Chinese Academy of Sciences has three crystal growth centers (in Fujian, Beijing, and Shanghai), each with a large number of

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[10] *IKZ Annual Repo*rt 2007/2008, p. 7. See http://www.ikz-berlin.de/publications_folder/report_folder/jbm0807/jb_08_02.pdf. Last accessed March 11, 2009.

[11] *Fraunhofer IISB Annual Report* 2007, p. 28. See http://www.iisb.fraunhofer.de/de/jber/Annual_Report_IISB_2007.pdf. Last accessed March 11, 2009.

[12] Recent articles describe the very real and negative consequences for those researchers not having access to such crystals. See David Cyronoski, "China's Crystal Cache," *Nature,* **457,** 953 (February 19, 2009).

scientists and technicians focused specifically on the growth of optical crystals. The success of China in optical crystal growth has been enabled by the presence of such focused and concentrated DGCM research efforts.

Research Support

In addition to the large centers for DGCM research, European and Asian countries have established programs that recognize the importance of and therefore provide funding for DGCM activities for individual researchers and smaller groups. In Japan, for example, DGCM activities are well supported as a part of group budgets. In addition to providing individual research grants (equivalent to National Science Foundation funding in the United States), the Japanese Ministry of Education, Sports, Science and Culture funds collaborative research activities as "Scientific Research of Priority Areas." At the time of this writing, five such programs were running in materials physics. Each program consists of about 20 principal investigators with a typical budget of a few million U.S. dollars (USD) per year. Within the program, crystal growth can be a priority in the budget. The Japan Science and Technology Cooperation has a program called Core Research for Evolutional Science and Technology, which is a strategic budget in the government that supports a few principal investigators with about 1 million USD per year. These budget sources, as well as the fact that students and staff are financially supported at the department level rather than at the principal-investigator or project level, allow considerable support and flexibility for DGCM activities in Japan.

In addition to the group budget systems mentioned above, a program in Japan providing single principal investigators with exceptionally-large-scale budgets (15 million to 20 million USD for 5 years) is noteworthy. The Exploratory Research for Advanced Technology (ERATO) program is operated by the Japan Science and Technology Agency and funds 5 to 10 projects on materials, running in parallel. Very strong DGCM activities often have been conducted as part of the ERATO program, and this funding played an important role in the recent Japanese discovery of iron pnictide superconductors (see Box 3.1).

Because of the programs described above and similar programs, in the past decade Japan has become the leader in DGCM for superconductors, strongly correlated oxides, organics, and quantum magnets. In fact, large single crystals of these systems grown in Japan are now often provided to researchers in the United States for subsequent study. Many new superconductors, including MgB_2, have been discovered in Japan recently and have stimulated research in the U.S. materials physics community.

The group funding approach also can be found in Europe, both at the individual country and at the European Union level. For example, the United Kingdom funds a program entitled "Portfolio Partnership" under the Engineering and Physical

Sciences Research Council. This program supports a group working on exotic quantum materials, which grows hundred-gram single crystals of high-temperature superconducting cuprate samples for neutron-scattering studies. Similar programs supporting DGCM research can be found in Germany, France, and Switzerland. Canada also supports programs for DGCM research, under the Canadian Institute for Advanced Research,[13] which funds research growing ultrahigh-purity single crystals of cuprates.

Small Cultural Gap Separating Disciplines

The third factor contributing to the success of DGCM activities in Europe and Asia is the smaller cultural gap, compared to that in the United States, separating research groups and disciplines and thus facilitating collaboration. For example, the cultural gap between physics and crystal growth is relatively minor in Japan, partly because students are encouraged to train for DGCM research. Educational opportunities presented in research groups merge materials and physics at the graduate level. Graduate students also have an opportunity to learn both crystalline matter synthesis and measurements early in their careers. This leads to the virtuous cycle of generating future principal investigators who have strong expertise and interest in both materials and physics.

It is also common in Japan for physicists working on specific crystals to grow their own crystals and then to make them readily available to others: a kind of “borderless” approach seen in the fields of oxides, heavy fermions, and organic conductors. Indeed, it is often the case that crystals supplied from Japan to the United States are grown by physicists actively working on specific probes rather than by professional growers. The size of the groups in Japan also facilitates developing expertise in growing crystals. Often more researchers work under one principal investigator in Japan than in the United States. At the top universities, 1 or 2 junior faculty members (between a postdoctoral associate and an assistant professor), a few postdoctoral associates, and 5 to 10 students work with a professor. This large group size enables a single research group to work on both materials synthesis and measurements.

Findings on International Activities

The Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth presents the following findings related to international activities in the field of DGCM: Efforts in Europe and Asia to develop their DGCM activities focus on three factors: (1) the development and sustained funding of

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[13] For more information, see http://www2.cifar.ca/. Last accessed April 1, 2008.

large centers, which are particularly effective when the research target is well defined; (2) the establishment of programs funding smaller groups and individual researchers that emphasize the importance of the discovery and growth of crystalline materials; and (3) cultural aspects of the education, training, and engagement in crystal growing and research, especially in Japan. These factors together have accounted for a large part of the success in DGCM research in these countries.

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Conclusions and Recommendations

The field of new materials research and crystal growth is in the midst of sweeping institutional and geographical change. Historically, central research laboratories of large U.S. corporations led the nation and the world in the work of discovering and synthesizing new crystals. In these facilities the vast majority of crystal growth techniques were developed and there, also, important postgraduate training was provided to successive generations of crystal growers. In the past few decades, several factors have caused these industrial capabilities in the United States to shrink to the point of near disappearance. This loss has become even more critical with the decrease in federal funding in support of the discovery and growth of crystalline materials (DGCM), as discussed in Chapter 3 of this report.

This deterioration in capacity occurred despite continued high demand for such materials and the value associated with their development. U.S. researchers could readily use more crystalline samples; as discussed earlier, U.S. scientists and technologists are frequently at a competitive disadvantage because of inadequate access to new crystalline materials and large, high-quality single crystals. As described in the discussion on gallium arsenide (GaAs) in Chapter 1 (see the section entitled "Example in the Area of Thin Films: Gallium Arsenide-Based Heterostructures"), ultrahigh-purity crystals exhibiting very high charge carrier mobility are qualitatively different from materials with low or moderate carrier mobility. Such high-purity crystals continue to lead to the discovery of new fundamental physical phenomena, not just in GaAs but in systems that produce novel states of condensed matter. Further, U.S. federal agencies have made significant investments in major materials characterization and analysis capabilities, such as synchrotron x-ray sources, neutron-scattering facilities, electron microscopes, and high magnetic field facilities. The availability of these leading-edge facilities offers U.S. scientists the opportunity to discover new science and to optimize crystalline materials for future technological applications, provided they have access to single-crystal samples of newly discovered material and large, high-quality single crystals for neutron scattering.

Discovery of new crystalline materials and growth of single crystals have been shown continually to be highly leveraged activities, yielding disproportionately large returns on investment while helping to address important national issues related to energy, information, transportation, national security, health, and other areas. As discussed in Chapter 1 (see the section entitled "Example of High-Temperature Superconductivity"), this leveraging recently was seen in the explosion of research following the discovery of high-transition temperature (T_c) superconductivity, which led to new metrologies and analysis capabilities that produce new fundamental science as well as to new modes for efficiently transporting energy. Similarly, this leveraging is illustrated historically by the growth of entire industries in the computer field, which were able to arise only after the DGCM community developed the capability to produce high-purity crystalline silicon and III-V compound semiconductors.

Today's scientists and engineers in the United States are severely constrained by a research environment in which crystal supply is limited at a time when governments in selected countries in Asia and Europe have recognized the foundational importance of new materials and high-purity single crystals, and in some cases will not make them available for political reasons. In contrast to the current state of affairs in the United States, these countries are becoming much stronger in the discovery of important new materials and phenomena through strategic investments. It must be emphasized that *if these trends continue, U.S. scientists, engineers, and industrial facilities either will become increasingly dependent on materials developed and grown outside the United States or will not have access to needed materials at all.*

COMPREHENSIVE SOLUTION TO ENHANCE COMPETITIVENESS

In this chapter, the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth recommends ways to address the issues and opportunities identified in this report. Concerted efforts will be required from those engaged in DGCM research, from the educational and research institutions in which those efforts take place, and from those agencies that provide funds and other support for scientific research. Specifically, the committee believes that a comprehensive solution to providing future opportunities in the discovery and growth of crystalline materials in the United States should include the following elements:

- *A focused, multiagency initiative* for establishing and sustaining programs specifically directed toward driving the discovery and growth of new crystalline materials;
- *Shared, large-scale facilities and small-scale equipment* for growth of new materials, large crystals of existing materials, and thin-film systems, and for advancing the state of the art of crystal growth;
- *Increased capability for hands-on training* in discovery and growth of crystalline materials for both new and established researchers;
- *Crystalline material synthesis performed in multidisciplinary research environments* complete with infrastructure and operational support (operations and technicians);
- *A crystal growth network* for the distribution of samples and information to amplify the impact of research support by helping to build new collaborations among the crystal growth, measurement, and theory communities; and
- *Technology transfer* to help address the needs of industry in areas of crystal growth methods and prototype crystalline material development, including codevelopment of technology.

Increasing Agency Engagement in Advancing the Discovery of New Crystalline Materials and New Methods of Crystal Growth

A significant gap has developed in this country between the demand for and the supply of both new crystalline materials and large, high-quality single crystals. The large industrial research laboratories that historically led the nation in discovering those new crystalline materials and in developing techniques for growing pure crystals no longer engage in these activities to a significant degree. Nevertheless, the need for basic research in materials for future technologies, especially for energy, information, and security, is greater than ever, thus imparting urgency to the remedial measures suggested in this report.

The natural entities to bridge this gap are those agencies already involved in funding basic and applied research. However, in part because of how the field of DGCM has historically developed and in part because of the inherently multidisciplinary nature of the field, the full breadth of DGCM research needs do not fit existing programs within any single funding agency. Further, because the DGCM field impacts a broad set of technologies encompassing energy, information, security, and industrial standards, the committee believes that a multiagency approach among relevant agencies should be undertaken to help bridge this gap. Therefore, the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth makes the following recommendation:

Recommendation 1. Develop a focused, multiagency initiative to strengthen U.S. efforts to discover and grow new crystalline materials.

Agencies that fund research involving discovery science, energy, information, and security that requires crystalline materials in some respect, such as the Department of Energy (DOE), the National Science Foundation (NSF), the Department of Commerce (DOC), and the Department of Defense (DOD), should develop a *coordinated initiative* designed to strengthen DGCM activities and to provide for their long-term, sustainable support. The broad goals of such an initiative should be to establish crosscutting synthesis capabilities, educational instruments, and openly available cyber resources that will enable broad research efforts.

The recommended initiative would consist of new programs focusing on the discovery and synthesis of new crystalline materials with novel properties, while placing high importance on establishing linkages between fundamental research and technology development, with the strong and ongoing participation of industry. Programs funded through such an initiative should provide the range of support necessary to address the spectrum of research needs of this field, from support for small-scale crystal growth laboratories run by single investigators to large-scale centralized facilities for crystalline materials discovery and the growth and characterization of single crystals (addressed in Recommendation 2). The costs of such programs will also vary, depending on their scope and scale. For comparison, the committee notes that in the discussion in Chapter 3, in the section entitled “International Activities,” it sets out the present costs for funding individuals and small groups of investigators in the Core Research for Evolutional Science and Technology and Ministry of Education, Sports, Science and Culture programs currently supported in Japan.

The precise forms of programs to be funded should be designed by the agencies and should be subject to competitive review. A number of individual investigators currently funded by DOE and NSF, in both national laboratories and universities, engage, as part of their overall research activities, in new materials discovery and single-crystal growth. These investigators provide a base of expertise on which to develop the detailed approaches needed to meet such an initiative’s goals for a competitive review process. It also makes sense to solicit guidance from present DGCM researchers on the structure of a future funding model for DGCM research and on the means of implementing the model. Finally, the proposal development process itself would generate visions for effectively realizing materials-driven science of the future, with the funding agencies choosing ways to implement the vision.

The process of competitive review should call for proposals to implement expanded new research activities in materials discovery and crystal growth and for proposals offering a range of educational initiatives, from workshops to on-site training to placement of agency-funded interns. The infrastructure to be funded through this review process should include support for the availability of technicians and specialists for crystallographic characterization and innovative growth techniques.

The committee urges DOE and NSF, the principal agencies that now fund the majority of such research, to establish as soon as is practicable a committee to evaluate the merits of this recommendation and a procedure for implementing it. The committee urges other agencies with programmatic interests in strengthened DGCM efforts, especially DOC and DOD, to participate actively in the initiative.

Advancing the State of the Art in the Discovery and Growth of Crystalline Materials

In previous decades, one important attribute of large central research laboratories in companies such as Bell Laboratories, IBM, General Electric, Westinghouse, and RCA was the presence of large, interdisciplinary teams whose members had the capability to address the "big problems" with a critical mass of researchers and facilities. Such teams were able to characterize a sample and provide rapid feedback to the crystal growers about the sample composition, crystalline nature, and related information. The immediate involvement of theorists at these large DGCM centers also played a vital role in achieving an understanding of physical properties that gave key feedback to the growers. That feedback, in turn, guided the crystal growers' efforts to improve the purity and crystalline quality of the desired material. These large central research laboratories not only developed and purified new crystalline materials, but they also trained the next generation of crystal growers and developed most of the crystal growth and purification techniques in common use today, such as techniques for single-crystal growth, float zone refining for purification of crystals, molecular-beam epitaxy for growth of films with atomic-layer control, and so forth. Such an environment is essential for the cost-effective and timely synthesis of new materials; for the growth of large, high-quality crystals needed for research and technological applications; and for sustaining DGCM research and education. Therefore, the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth makes the following recommendation:

> **Recommendation 2. Develop discovery and growth of crystalline materials "centers of expertise."**

Funding should be provided for one or more centers that are capable of addressing the broadscale issues arising in the DGCM area. Centers have a role that cannot be filled by small programs. In contrast to small programs, centers can provide the needed infrastructure to house specialized facilities and the robust multidisciplinary environment needed for cutting-edge materials development.

The purpose of these centers would be to address a range of problems including those requiring large-scale facilities, facilities for processing toxic chemicals, and facilities requiring significant technical support.

In addition to one or more centers addressing broadscale DGCM issues, there should be one or more centers whose main mission is to address problems of crystal growth of immediate interest to U.S. industry. Working on a cost-recovery basis, these industry-oriented centers would be responsible for forming strong industrial partnerships, engaging in technology development with their industrial partners, and maintaining the expertise and infrastructure needed for industrial crystal growth.

One or more of these large-scale centers might be focused on either a materials chemical class(es) or a materials synthesis technique(s). Several of these centers could be user facilities located at existing Federally Funded Research and Development Centers and would thus serve to enrich the user experience by offering access not only to synthesis facilities and expertise but also to existing advanced-measurement capabilities such as major x-ray and neutron facilities. Other centers could be on a smaller scale, residing at a university and formed around a particular expertise not requiring wide-ranging infrastructure support. In general, most if not all of these centers, whether large-scale, small-scale, or industry-oriented, should support a small number of education and training programs that explicitly address the discovery and growth of crystalline materials and complement the university-based research and education in DGCM addressed in Recommendation 3. While the costs of such centers will vary, depending upon the scope of their mission, the committee notes that in the discussion in Chapter 3, in the section entitled "International Activities," it sets out the present costs for funding comparable programs in Europe.

It is noted that the Physics Frontiers Centers program operated by NSF offers many of the funding and selection characteristics being considered by this committee. The NSF program might thus provide a good model for developing a program to support centers of expertise for DGCM activities.

Sustaining Expertise in the Discovery and Growth of Crystalline Materials

As noted earlier in this report, industrial research laboratories not only developed and purified new crystalline materials, they also trained future generations of crystal growers. While much of the expertise of those industrial laboratories has been retained in the migration of the industrial scientists to universities and national laboratories, the ability to train their successors—the new generation of materials developers and crystal synthesizers—has not been maintained. A focused effort to replace these valuable education and training capabilities must be undertaken. Therefore, the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth makes the following recommendation:

Recommendation 3. Develop and sustain programs specifically designed to strengthen and sustain education and training in the field of the discovery and growth of crystalline materials.

Federal agencies should develop programs and policies that focus on providing the specific and often unique education and training needed for those engaged in developing crystalline materials and synthesizing large crystals. Reflecting the wide variety of capabilities and skill sets required for crystalline matter discovery (and analysis) and crystal growth (and characterization), this field is inherently interdisciplinary. As a result, special attention must be given to developing federally funded programs that encourage academic facilities to prepare the cross-disciplinary curricula and opportunities for educating the next generation of U.S. DGCM scientists. Further, the centers of expertise proposed in Recommendation 2 should be charged with the responsibility of developing and implementing education and training programs that explicitly address discovery and growth of crystalline materials procedures as well as provide hands-on training opportunities for those entering the field. Larger-scale facilities, with their broad complement of technical staff, are particularly well suited to this hands-on training mission. (See Appendix G, "Educational Role of the Discovery and Growth of Crystalline Materials Centers of Expertise," for further information.)

Changing the Culture

The culture of U.S. science does not generally reward DGCM synthesis research as much as it rewards measurement science. This culture is promulgated in universities, where such solid-state synthesis research groups are more the exception than the rule. Given the departmental or discipline-centric nature of U.S. universities, coupled with the low level of federal funding for DGCM synthesis research, a strong natural academic "home" has not been established for this field in U.S. universities. However, new academic disciplines emerge as the needs of society change. It is time to address barriers caused by factors such as differences between the discipline-centric nature of U.S. universities and the inherent interdisciplinary nature of DGCM research and limited funding for the acquisition and operation of equipment. While recognizing the sentiment derived from industry that "culture eats strategy for breakfast,"[1] it remains incumbent on U.S. funding agencies to work with universities to ensure that DGCM activities, both the education/training treated in Recommendation 3 and the research treated in Recommendations 1 and 2, have a long-term academic home.

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[1] Headline on a *Wall Street Journal* article, January 23, 2006; the origin of the headline was reported to be a sign in Ford Motor Company's war room, reminding company planners of the limitations of developing strategies.

Therefore, the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth makes the following recommendation:

> **Recommendation 4. Promote cultural changes to develop and solidify academic programs in the field of the discovery and growth of crystalline materials.**

In order for the United States to have a strong and sustainable capability in the discovery and growth of crystalline materials, federal agencies should develop programs and policies that make it attractive for universities in the United States to hire crystal growers and promote robust research programs in this area by providing ample funding specifically for such work. The committee specifically urges that more crystal growers be hired into tenure-track positions at universities. Because of the multidisciplinary nature of this type of work, the department that would be most appropriate for such programs would vary, depending on the university. However, because materials science departments provide robust support for research that straddles physics, chemistry, and diverse engineering disciplines, they would be a potential academic home. The committee also notes that some progress has been made in academia in leveraging multidisciplinary activities in the broad area of nanoscience, where centers and research institutes bring together researchers from diverse fields such as biology, physics, chemistry, and engineering. Such efforts could provide a useful model for future success in the equally important area of DGCM.

Improving Interaction and Cooperation Within the Discovery and Growth of Crystalline Materials Community

The committee strongly believes that new approaches to communication are needed to advance the field of discovery and growth of crystalline materials. Specifically, the committee recognizes that the internal communication processes that defined fruitful directions for DGCM activities in industrial laboratories greatly aided the development of materials. Such processes provided rapid response to synthesis needs as well as rapid feedback from measurement to synthesis. Federal agencies should use a similar approach to promote communication among researchers through programmatic means. Obtaining the maximum benefit from the synthesis of crystalline materials requires the creation and support of a formally networked community that includes scientists and engineers who perform research on discovery and growth of crystalline materials, whether in large, shared facilities or as single investigators. These scientists need to interact strongly with one another and with scientists and engineers who perform research and develop technology based on these materials. Such communities developed naturally in large industrial research laboratories. While many of the scientists who engaged in DGCM activities in industrial research laboratories have migrated to universities and national laboratories and continue to be extremely productive, there has been a significant loss in the close collaboration with other members of the networked community that existed in industrial laboratories. U.S. industry cannot afford to rebuild these capabilities in today's highly competitive, high-technology global environment; thus a different approach is required to address national needs in this area.

The committee also notes that while this emphasis on collaboration requires significant transparency in certain aspects of research collaborations, fundamental aspects of intellectual ownership, which help to drive great discoveries, must be maintained. Greater transparency will require more formality and discipline among members of the DGCM community, including not only the scientists and engineers who grow the materials but also those who characterize the materials and those who rely on new materials and high-quality, high-purity single crystals for their scientific research. Such issues governing intellectual ownership in DGCM activities are not unlike those governing the research activities in national user facilities.

To address these issues, the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth makes the following recommendation:

> **Recommendation 5. Develop a network approach for research-enhancing collaborative efforts in the discovery and growth of crystalline materials while preserving intellectual ownership.**

The committee believes that the enterprise of new crystalline materials discovery would greatly benefit from the creation of a network that has as its primary missions both the communication of information related to synthesis and measurement capability across the United States and the coordination of DGCM programmatic activities. As a novel approach to scientific collaboration, the committee envisions a "crystalline materials network" that would both fulfill conventional needs for greater collaboration and enable the new modes of collaboration afforded by cyber infrastructure.

The envisioned crystalline materials network would provide a virtual forum for organizing synthesis and measurement activities. Crystal growers would be able to announce the availability of new compounds on a DGCM Web site. Conversely, measurers would be able to request collaboration with a crystal grower to meet a specific sample need. The crystalline materials network would provide information access to the physical archive of already-synthesized samples stored in individual laboratories throughout the country, further enabling collaborations. This network would also maintain a database constructed for the specific needs of researchers to facilitate information searches on physical property categories that change with time as a result of the discovery of new properties of materials. The crystalline materials network would stimulate and promote research in promising new areas by enhancing the ability of growers to work with the appropriate researchers performing characterization measurements and by promoting the effective dissemination of results. Outreach for the crystalline materials network, which would be critical, would be achieved through the organizing of professional meetings such as workshops, conferences, and summer schools devoted to the rapid development of DGCM science.

While a crystalline materials network is a new concept, every effort should be made to capitalize on the self-formed networks that are characteristic of single-investigator science. The proposed network would preserve all the strengths of extant U.S. DGCM activities while providing guidance for the use of greater funding resources to meet measurement demands (see Recommendation 1).

A key benefit of a crystalline materials network would be greater access to samples for scientists who work neither at DGCM centers nor at institutions with crystal growth efforts (see Recommendation 2). The committee envisions that this network would be administered from a center of expertise with sufficient size and depth of scientific expertise to address day-to-day oversight requirements.

Finally, to preserve intellectual property integrity, a common set of rules governing sample use would be needed to protect both the synthesizer and the characterizer of crystalline samples. The committee urges that policies be established that foster access to samples but also protect the intellectual contributions of the researchers who discover or develop novel crystalline materials. (See Appendix F, "Network Policies and Procedures," for a draft of such policies.)

Following on Recommendation 1, the committee urges DOE and NSF, the agencies that now fund the majority of such research, to establish as soon as is practicable a network to increase communication and enhance collaboration among DGCM researchers.

ONE POSSIBLE IMPLEMENTATION PLAN

Given the broad goals outlined above, the committee offers the following possible plan to illustrate a path forward to implement these goals. Such a path forward has the potential to achieve far more than the organization and communications structures previously found in industrial research laboratories. A new paradigm of DGCM discovery can be achieved by harnessing the full potential of modern and accessible DGCM synthesis facilities, educational and training opportunities, shared databases, and improved measurement capability. Through a crystalline materials network, all of these elements can be tightly coupled by cyber infrastructure in ways not possible even 10 years ago. The result should be the rapid acceleration of DGCM both to match the growth of measurement science and to accelerate the innovation process for new technologies.

Creation of a Crystalline Materials Network

The vision of a crystalline materials network is not simply to replace the networking system lost with the closing of the large industrial research laboratories, but to implement a cutting-edge program that takes full advantage of networking opportunities offered by cyber infrastructure. The model proposed seeks to amplify methods and procedures at present employed in successful DGCM research groups. The hallmark of such groups is the self-organization of social networks built around specific scientific problems. These problems are dynamically changing; in response, collaborations also change over time.

The overarching goal of the crystalline materials network would be to enhance the ability for research collaborations to change dynamically in the most productive manner by providing communications channels in both the synthesis and the measurement realms. The network could build and maintain a "materials development highway" that would enable researchers to collaborate more seamlessly. Thus, it would provide a forum where participants could share growth techniques and areas of expertise, provide information on available samples, disseminate information on results, and post sample access policies and procedures. Most importantly, the network could facilitate the distribution of samples and provide a searchable database of materials properties.

With the extra freedom of information available through a crystalline materials network, however, would come additional responsibilities. These responsibilities would be articulated through the forum of the network. Further, the network would not be directly responsible for administering programmatic funds but would operate in a spirit similar to the user committee of a beam-line sharing facility. While the committee does not intend to prescribe the exact nature of a crystalline materials network, a number of ideas were generated during the committee's deliberations that may be of interest. These are documented below in the form of specific possible elements of a crystalline materials network:

- *DGCM proposal modes:* Crystalline materials discovery is often motivated by synthesis experts seeking either a new crystal structure or a crystal comprising a new combination of elements or molecules. Motivation can also come from researchers seeking larger crystals, samples with elemental substitution, or samples with very high purity. It may also come from researchers seeking novel properties such as materials for energy-related applications. Both grower-motivated and measurer-motivated approaches should be accommodated in the organization of a future crystalline materials network.
  —*In the crystal grower-motivated proposal mode:* The originating idea for growing either a new compound or a high-purity single crystal of a

  known compound is developed by the synthesis scientist. This can be viewed as similar to research directed toward establishing new measurement capability by a resident scientist in a large user facility. For instance, a new spectroscopic tool developed by a resident neutron-scattering scientist would be made available to guest scientists. Similarly, when a new compound was synthesized or a higher-quality crystal of an existing compound was made, this would be made available, by proposal, to the external community.

  —*In the measurer-motivated proposal mode:* A measurement scientist would propose the synthesis of a novel compound, an existing compound, or a variation of an existing compound, such as a site-dilution series, to be grown by a particular expert in the network. The proposal would be handled in a manner similar to that for dealing with an external proposal for a user facility. The technical part of the proposal would consist of a short description of the desired compound and a description of the planned measurement and/or desired property. In order to manage the competitive nature of measurements, the samples would be disbursed with a stipulated understanding of exclusivity and confidentiality of measurement. Usually the measurer desires an exclusive right to a particular compound for a period of time that encompasses publication of the results in order to establish priority of discovery. This dormancy period might extend up to from 6 months to 1 year from publication. However, one can imagine rare circumstances when it is desirable for two researchers to perform, by consent of the grower, the same measurement on a given compound. The important point is that the grower would own the samples, subject to network policies and procedures, and would exert control over their distribution. As discussed above, coauthorship and acknowledgment of crystal growers and characterizers are essential and would be developed as part of the policies and procedures for access to the network.

- *Proposal mechanism:* A proposal to access or grow a particular sample would describe the type of measurement to be performed and indicate the principal investigators involved. Requesting a sample from the network would be tantamount to requesting research support funding; thus criteria usual for making such decisions would be applied. The main criteria for a successful proposal are the quality of the idea, the ability of the proposer to execute the research, the past performance of the proposer, and of course the capability of the network growers to fulfill the request. Proposals would be held in confidence by a proposal review board established by the network administration.

- *Oversight:* Oversight of the crystalline materials network would be carried out by two bodies: a scientific advisory board and an independent review panel. A scientific advisory board, appointed by the network director or head administrator, would provide advice on all elements of the network to the director, including the policies and procedures for access and for optimizing network impact. In addition, an independent review panel constituted of peers both within and external to the network would be assembled on a regular basis to review the impact of the network and its operating policies and procedures on access, proposal review, and so forth. A report containing the independent review panel's findings and recommendations would be submitted to the funding agencies.
- *Proposal review:* A proposal review board would review crystal growth proposals submitted to the crystalline materials network on the basis of criteria of the International Union of Pure and Applied Physics for excellence in research. Feasibility would be reviewed by the crystal grower(s) "requested" by the proposal and the proposal review board. The board would consist of scientists within and external to the network.
- *Reporting and oversight:* The crystalline materials network would issue an annual report of all published research conducted under its auspices. The reported research would include all collaborative activities involving one or more network-affiliated researchers. For collaborations, it is expected that the samples requested would undergo one or more measurements. The results of these measurements would likely be published. However, it is not uncommon for a measurement not to yield publishable results, and in this situation the network would request a brief summary of the measurement(s) attempted or performed and the reason for lack of publication.
- *Meetings:* The crystalline materials network would coordinate meetings to organize scientific activities, to review proposals, to hold workshops and summer schools, and to address administrative issues associated with archives and databases.
- *Crystal archive:* The crystalline materials network would create a virtual archive—a searchable database listing samples in storage at any location—that would consist of the significant collection of crystals that network synthesis scientists already possess in storage. Samples would be added to the database at the discretion of the grower. In addition, it is expected that crystals grown with network support would eventually be placed in the archive—say after the dormancy period discussed in the first item in this list. The archive would be accessible by means of downloadable spreadsheets that would be continually updated by the network. These spreadsheets would provide a brief description of the samples available from the archive. Archived samples would be available

by proposal directly from the grower. In addition, the network would maintain primary sample sources constituted from legacy collections.
- *Materials property database:* Databases have greatly enhanced the ability to access published information. The effectiveness of databases is no better, however, than the selection of key words by authors upon publication of scientific results. In addition to the present lack of standardization of key words, key word attributes only extend back in time a couple of decades, thus limiting accessibility to published data. Compendia such as the Landolt-Börnstein series attempt to address the need for information on collected materials properties. Such information is not, however, dynamically updated and is not easily cross-referenced. Thus, there is a need for a database that is searchable along crystalline materials properties lines, is dynamically updated as new papers are published, is searchable along arbitrary key word combinations, and is free to the DGCM community. It is envisioned that the crystalline materials network would administer this database. The committee believes that such a database would change the way that crystalline materials research is performed by enabling searches not now possible and by reducing unnecessary duplication of work that is essentially clerical.

Large Centers of Expertise

This subsection lists selected important characteristics of large DGCM centers of expertise and provides suggestions for their focus and potential contribution to an overall national effort. It also enumerates a few of the challenges and opportunities that large DGCM research centers could be expected to address.

- *State-of-the-art facilities:* Entire classes of important materials are not at present being explored in the United States owing to a general lack of large-scale facilities for synthesis. These include facilities for growth involving toxic materials, growth under extreme conditions, growth with in situ advanced characterization tools, and growth of very large, ultrapure crystals. Large DGCM centers could be established at national laboratories where the support staff, infrastructure, large-scale characterization facilities, and environmental, health, and safety procedures are well established.
- *Scope of centers:* Each center would be most productive if its research portfolio focused on several high-impact thematic areas of research, driven by selected classes of materials synthesis. Selection of these themes would be determined through extensive input from the scientific and industrial communities and would be subject to renewal by review on a regular basis to ensure continued optimal impact.

- *Scale of centers:* It would be critical that the large centers sustain a “critical mass” of researchers in each of the chosen thematic areas. Typically, a team of 5 to 10 staff would provide the full breadth of required skills, from synthesis to characterization and theory, for advancing the state of the art. Since a center might pursue three or four integrated themes, the committee envisions that any one center would incorporate up to 30 to 40 staff members, selected on the basis of their research area and demonstrated skill set.
- *Multidisciplinary environment:* While most laboratories can provide a modicum of measurement feedback, large centers have the capability to couple DGCM research to large-scale measurement capability for rapid information feedback. Large centers would also combine experimental activities with theory and computational efforts.
- *Addressing large-scale problems:* Many research challenges in DGCM cannot be addressed by small university research groups. Such challenges involve, for example, very long timescale growth runs, the growth of very large samples, or growth combined with complex diagnostic methods. These topics would be the natural domain of large DGCM centers.
- *Advancing the state of the art in DGCM:* Large centers would have as part of their mission the development of new DGCM techniques. Technique development normally involves a significant amount of engineering and infrastructure and long development timescales, none of which is feasible at small centers.
- *Promoting collaborative work with U.S. industry:* An important role of some DGCM centers would be to provide a link to industry. These centers would address basic research synthesis projects of importance to an industrial sector in order to augment applied research and development activities in specific companies. The centers would provide a vehicle for collaborative research between industrial and center-based researchers, for example through visitor programs, to grow desired materials. There are several existing models for such an industry-oriented center that can be evaluated and adapted. An example is the Crystal Growth Laboratory (CGL) affiliated with the Fraunhofer Institute for Integrated Systems and Device Technology in Erlangen, Germany. Started in 1996, CGL has maintained general crystal growth and assessment capabilities and has also developed several focal areas of expertise, including a specialization in the development of computer simulation. Its programs are regularly assessed and modified on the basis of its industrial partners’ needs. Given a similar funding model, namely, cost recovery, the industry-oriented center contemplated here would develop areas of expertise based on directions of interest to its industrial partners. As part of the crystalline materials network recom-

mended in this study, it also is expected that opportunities for industrial research would arise that would involve other centers in the network.

- *Growth of high-purity, known materials that have no commercial source of supply:* In new fields of study, commercial sources of raw materials are often not available in the necessary purity or crystal size for sensitive physical measurements. Large centers would have, as part of their distributed portfolio, the mission to perform noncommercial applied crystal growth for basic research needs.
- *Summer schools:* A critical part of a new DGCM initiative would be to create summer schools for the purpose of education and networking among members of the DGCM research community. In addition to formal instruction, such schools would provide hands-on training. The large DGCM centers are natural organizing centers for such schools. (See Appendix G, "Educational Role of the Discovery and Growth of Crystalline Materials Centers of Expertise," for more information.)

University-Based Programs or Centers

In addition to large centers devoted to DGCM, increased university-based efforts in DGCM are important to a comprehensive DGCM initiative. Geographically diverse university-based efforts provide a unique approach to DGCM activities. Some of the important operational characteristics for university-based programs are listed below, along with their contribution to the education and training of the next generation of DGCM experts.

- *Multidisciplinary research:* Advances in crystalline matter discovery are often initiated at the frontiers where disciplines meet. The university environment provides the ideal setting to encourage interdisciplinary efforts in chemistry, physics, and biology. The success of DGCM depends on university-based initiatives. Nevertheless, universities must find ways to lower the barriers to interdisciplinary activities and work to provide a natural home for synthesis researchers.
- *Multidisciplinary emphasis:* As mentioned above, efficient DGCM requires tight feedback with measurement. With modern capability for measurement of key properties such as crystal structure, electrical transport, and magnetic response, such rapid feedback would be readily achievable, even in smaller centers of expertise.
- *Shared equipment or facilities:* For DGCM centers to thrive in a university environment, access to both synthesis and measurement facilities should be treated as shared facilities rather than as captive capabilities of an individual faculty member or principal investigator.

- *Support for operations and technicians:* DGCM activities are extremely labor intensive, requiring high levels of support for operations, including infrastructure maintenance, raw materials, and technical support. This support is justified on the programmatic level because the materials synthesized by principal investigators associated with a university center should be made available to a larger scientific cohort than that of a single principal investigator.
- *Specific courses in DGCM:* For DGCM to be a bona fide intellectual endeavor—that is, embraced by university administrators and colleagues—it must support a curriculum by which future generations of DGCM researchers are trained.
- *Research programs as training grounds:* While informal or postgraduate training can occur in national laboratories, as it did in industry, the formal aspect of DGCM training should occur in a university setting where synthetic projects are developed in the course of graduate work.

SUMMARY

The discovery of new crystalline materials and the growth of single crystals with carefully tailored properties have very high scientific and technological impact. The convergence of technology streams and the rise of the global economy have resulted in major changes in the U.S. research landscape in this arena, leaving scientists and engineers in the United States severely constrained by inadequate supplies of crystals for scientific research and technology development. As a result, scientists and engineers in DGCM in the United States are at a competitive disadvantage compared to scientists and engineers in selected countries in Europe and Asia. Addressing this issue is important to U.S. economic competitiveness and national security. Based on an analysis of the needs, along with the characteristics of the most effective practices in DGCM, the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth has developed a series of recommendations to strengthen greatly the U.S. capability in the synthesis of new materials and crystal growth. The set of activities in the proposed approach would fit well within the mission of several agencies, including DOE, NSF, DOD, and DOC (National Institute of Standards and Technology) and is well matched to the anticipated growth in these programs under the authorized research funding increases to foster U.S. competitiveness.

Appendixes

Appendix A

Charge to the Committee

The purpose of this study is to:

1. Define the research area of the discovery and growth of crystalline materials, framing the activities in the broader context of the condensed-matter and materials sciences.
2. Assess the health of the collective U.S. research activities in new materials and crystal growth.
3. Articulate the relationship between synthesis of bulk and thin-film materials and measurement-based research; identify appropriate trends.
4. Identify future opportunities for new materials and crystal growth research and discuss the potential impact on other sciences and society in general.
5. Recommend strategies to address these opportunities, including discussion of the following issues:
    a. Existing efforts to improve accessibility to and distribution of samples
    b. Technology transfer from basic research to commercial processes
    c. Essential elements of nationally-coordinated crystalline matter discovery capabilities
    d. Comparisons to levels of effort in other countries

The study will place the need for new crystalline materials in a larger context of materials synthesis. The scope would include not only amorphous metals and nanoscale materials, but also glasses, plastics, composites, and granular media—all of which garner the attention of basic research.

Appendix B

Biographies of Committee Members

Paul S. Peercy (NAE), ***Chair,*** is dean of the College of Engineering at the University of Wisconsin at Madison. He received his B.A. in physics from Berea College and M.S. and Ph.D. in physics from the University of Wisconsin at Madison. Before moving to Madison, Dr. Peercy had been president of SEMI/SEMATECH, a nonprofit technical consortium of U.S.-owned and -operated companies that comprise the equipment and supplier infrastructure for the U.S. semiconductor industry. Prior to serving in that position he had been director of microelectronics and photonics at Sandia National Laboratories in Albuquerque, New Mexico. His research spanned several areas of solid-state and materials physics and engineering, including ferroelectricity, Raman and Brillouin scattering studies of solids, ion-solid interactions, laser-induced phase transformations, microelectronics and photonics, and solid-state devices. Dr. Peercy is a councilor of the American Association for the Advancement of Science (AAAS) and past councilor of the American Physical Society (APS) and the Materials Research Society, past vice president of the Materials Research Society, and past chair of the Division of Materials Physics of the APS. Dr. Peercy is a member of the National Academy of Engineering and a fellow of the IEEE, APS, and AAAS. He serves on the industrial advisory boards of various universities and national laboratories.

Collin L. Broholm is a professor in the Department of Physics and Astronomy at the Johns Hopkins University. He earned his Ph.D. from the University of Copenhagen in 1988. Dr. Broholm uses neutron scattering to explore anomalous quantum magnetism in low-dimensional, frustrated, and metallic systems. He has been a member of the Department of Energy's Basic Energy Sciences Advisory Committee and of various committees reviewing upgrade and instrumentation strategies for national and international neutron-scattering infrastructure. Dr. Broholm is directly involved with instrumentation design at the NIST (National Institute of Standards and Technology) Center for Neutron Research and the Spallation Neutron Source. He is a fellow of the American Physical Society.

Robert J. Cava is a professor of chemistry at Princeton University. He received his Ph.D. in ceramics from the Massachusetts Institute of Technology. His research expertise is in the area of solid-state chemistry, specifically focusing on the synthesis and characterization of transition metal oxide and intermetallic materials. He has directed the Princeton Materials Institute and was a distinguished member of the technical staff at Bell Laboratories. He has received the Wulff Award in Materials Science, the American Chemical Society Prize in the Chemistry of Materials, and the Matthias Prize. Dr. Cava is a member of the National Academy of Sciences and a fellow of the American Physical Society and the American Ceramic Society.

James R. Chelikowsky is the W.A. "Tex" Moncrief, Jr., Chair of Computational Materials and professor in the Departments of Physics, Chemical Engineering, and Chemistry and Biochemistry at the University of Texas at Austin. He obtained a B.S. degree in physics from Kansas State University and a Ph.D. degree in physics from the University of California at Berkeley. His research interests are in the optical and dielectric properties of semiconductors, surface and interfacial phenomena in solids, point and extended defects in electronic materials, pressure-induced amorphization in silicates and disordered systems, clusters and nanoregime systems, diffusion and microstructure of liquids, and the development of high-performance algorithms to predict the properties of materials. Dr. Chelikowsky is the recipient of the 2001 David Turnbull Award from the Materials Research Society and the 2006 David Adler Award from the American Physical Society. He is also a fellow of the American Physical Society.

Zachary Fisk is Distinguished Professor of Physics at the University of California at Irvine. He received his Ph.D. in physics from the University of California at San Diego. He has held positions at the University of Chicago, the University of California at San Diego, the Los Alamos National Laboratory, Florida State University, and the Univeristy of California at Davis. Dr. Fisk's research examines the electronic properties of magnetic and superconducting materials. In this work, he has excelled at creating high-quality crystals of these superconducting materials. He has received many awards and honors in recognition of his work in condensed-matter physics, including the American Physical Society's International Prize for New Materials in 1990 and the E.O. Lawrence Award in 1992. He was elected a fellow of the American

Academy of Arts and Sciences in 1994, and in 1996 he was elected to the National Academy of Sciences for his work linking crystal chemistry with condensed-matter physics, which improved scientific insight into the transport and magnetic properties of a variety of magnetic and superconducting materials. Dr. Fisk is a fellow of the American Physical Society and the Los Alamos National Laboratory.

Patrick D. Gallagher is director of the National Institute of Standards and Technology (NIST) Center for Neutron Research. He received his Ph.D. in physics from the University of Pittsburgh. Dr. Gallagher's research interests include neutron-scattering instrumentation; diffraction of nanoscale structures, especially in soft condensed-matter systems such as liquids, polymers, and gels; and the experimental study of nonequilibrium structure and processes in complex condensed-matter systems. In 2000, Dr. Gallagher was a NIST agency representative at the National Science and Technology Council and the Office of Science and Technology Policy (OSTP), where he had responsibility in the areas of major science facilities, science funding, the government-university research partnership, radioactive waste management, radiation protection regulations, science and security at Department of Energy (DOE) national laboratories, and laboratory reform. He is currently chair of OSTP's Interagency Working Group on Neutron and Synchrotron Sources and a past member of the National Research Council's Solid State Sciences Committee. He has also been a member of numerous review and evaluation committees for DOE and the National Science Foundation and at major neutron and synchrotron facilities.

Laura H. Greene, Swanlund Professor of Physics at the University of Illinois at Urbana-Champaign, received her Ph.D. from Cornell University. She researches experimental condensed-matter physics focusing on strongly correlated electron systems, primarily investigating the mechanisms of unconventional superconductivity by planar tunneling and point-contact (Andreev reflection) electron spectroscopies. This research also involves growing novel materials and developing methods of materials microanalysis. Dr. Greene developed the course "How Things Work," designed as an outreach for nonscience majors. She has served on the International Union of Pure and Applied Physics, the Kavli Institute for Theoretical Physics, the Department of Energy's Basic Energy Sciences Advisory Committee, the Sloan Foundation Fellow Selection Committee, the Board of Trustees for Gordon Research Conferences, the Board on Physics and Astronomy, and on various committees for the American Physical Society (APS), the American Association for the Advancement of Science (AAAS), the National Science Foundation, and the National Research Council. Dr. Greene is a fellow of the APS, the AAAS, and the American Academy of Arts and Sciences, and she is a member of the National Academy of Sciences. She has received the Maria Goeppert-Mayer Award from the

APS and the E.O. Lawrence Award from the Department of Energy, and in 2007 was a visiting scholar for Phi Beta Kappa.

Eric D. Isaacs is director of the Center for Nanoscale Materials at the Argonne National Laboratory and professor of physics in the James Franck Institute at the University of Chicago. Previously he was director of the Semiconductor Physics Research Department and the Materials Physics Research Department at Bell Laboratories, Lucent Technologies. Dr. Isaacs received his Ph.D. in physics from the Massachusetts Institute of Technology. His current research centers on studies of novel electronic and magnetic materials, with a particular focus on creating images of new phenomena in reciprocal and real space at the nanoscale. Dr. Isaacs develops modern synchrotron-based x-ray-scattering techniques, including coherent x-ray scattering and hard x-ray nanoprobes. He is a member of the Department of Energy's Basic Energy Sciences Advisory Committee, a former councilor of the Division of Materials Physics of the American Physical Society, and a fellow of the American Physical Society.

Peter B. Littlewood is head of the Department of Physics and the Cavendish Laboratory at the University of Cambridge. He earned a B.A. in natural sciences from the University of Cambridge and a Ph.D. in physics at the Cavendish Laboratory, Cambridge, with a 1-year intermediate sojourn at the Massachusetts Institute of Technology as a Kennedy Scholar. He previously directed the Theory of Condensed Matter group at the Cavendish Laboratory and before that was head of the Theoretical Physics Research Department at Bell Laboratories. His research interests are in condensed-matter physics, including novel materials and superconductors, semiconductor optics, nonlinear dynamics, and statistical physics. He is a fellow of the Institute of Physics, the American Physical Society, and Trinity College Cambridge.

Laurie E. McNeil is a professor of physics and astronomy and of applied and materials sciences at the University of North Carolina (UNC) at Chapel Hill. She is also chair of the Physics and Astronomy Department. Her research interests are in condensed-matter and materials physics, specializing in optical spectroscopy of semiconductors and insulators. From 1996 through 1999, Dr. McNeil held a Bowman and Gordon Gray Professorship for "excellence in inspirational teaching of undergraduate students." During the fall of 2004, she held a Chapman Family Faculty Fellowship to produce a plan for the transformation of introductory physics teaching at UNC; the plan is now being implemented. She was the first recipient of the Tufts University Kathryn A. McCarthy Lecturer in Physics, which honors a pioneering female physicist who also served as provost of Tufts. Dr. McNeil was one of three people invited by the American Association for the Advancement of

Science (AAAS) to speak at a conference in Buenos Aires, Argentina, as part of the AAAS lecture series on Women in Science and Engineering. In March 2002, Dr. McNeil served as a member of the U.S. delegation to the International Union of Pure and Applied Physics Conference on Women in Physics. She is a fellow of the American Physical Society and a member of the University's Academy of Distinguished Teaching Scholars and of the Carolina Speakers program.

Joel S. Miller is a Distinguished Professor of Chemistry at the University of Utah. He received his B.S. from Wayne State University and Ph.D. from the University of California at Los Angeles. Dr. Miller held several positions in industry, including his work with the Xerox Corporation and DuPont before joining the faculty at the University of Utah. His research activities focus on new materials with fascinating magnetic, electrical, and optical properties. At the present time, his major effort is to prepare magnets based on molecular/organic/polymeric chemistry. Dr. Miller received the 2000 American Chemical Society Award for Chemistry of Materials, the 2007 American Physical Society McGroddy Prize, the 2004 Governor's Medal for Science and Technology, and the 2003 Utah Award. He was a Japan Society for the Promotion of Science Fellow in 2000 and is a member of the Inorganic Synthesis Corporation.

Loren Pfeiffer is a Distinguished Member of Technical Staff at Bell Laboratories, Alcatel-Lucent. He received his bachelor's degree in physics from the University of Michigan and his Ph.D. in physics from the Johns Hopkins University. Dr. Pfeiffer is an expert in molecular-beam epitaxy (MBE), producing uniquely clean materials in which new physics has been discovered. He has also created a variation of MBE called cleaved-edge overgrowth, which allows fabrication of quantum dots, quantum wires, and other quantum-scale structures of unprecedented quality. Dr. Pfeiffer received the 2004 McGroddy Prize of the American Physical Society. He is a fellow of the American Physical Society and of the Johns Hopkins Society of Scholars.

Ramamoorthy Ramesh is a professor of materials science and engineering and physics at the University of California at Berkeley. He graduated from the University of California at Berkeley with a Ph.D. in materials science in 1987. His current research activities encompass probing the physics of nanoscale phenomena in complex oxide heterostructures, multifunctional oxides, approaches to creating self-assembled functional nanostructures, integration of complex oxides with semiconductor technologies, and the use of nanoscale scanned probes to understand fundamental properties and dynamics in such materials. He was honored by the International Symposium on Integrated Ferroelectrics with an Outstanding Achievement Award in 2000. In 2001, he was awarded the Humboldt Senior Scientist Prize by the Alexander von Humboldt Foundation and fellowship in the American Physical Society. In 2005, he was awarded the American Physical Society's David Adler Lectureship.

Arthur P. Ramirez is dean of the Jack Baskin School of Engineering at the University of California at Santa Cruz. Prior to joining that university, Dr. Ramirez was leader of composites and device physics research at LGS, a subsidiary of Alcatel-Lucent, and also an adjunct professor of applied physics at Columbia University. He is also a former director of the Device Physics Research Department at Alcatel-Lucent's Bell Laboratories and a group leader at the Los Alamos National Laboratory. Dr. Ramirez received both his B.S. in physics and Ph.D. in physics from Yale University. He has pioneered the field of geometrical frustration in magnetism research. His other research interests include low-dimensional magnetism, heavy-fermion systems, thermoelectric materials, colossal magnetoresistive materials, high-dielectric-constant materials, molecular electronics, and superconductivity in various systems, including molecular compounds, intermetallics, and oxides. Dr. Ramirez is a fellow of the American Physical Society.

Hidenori Takagi has been a professor in the Department of Advanced Materials at the University of Tokyo since 1999 and chief scientist and director of the Magnetic Materials Laboratory, RIKEN (Institute of Physical and Chemical Research) since 2001. He received his B.S., M.S., and Ph.D. from the Department of Applied Physics at the University of Tokyo. His current research interests are in physics of correlated transition metal oxides, exotic superconductivity, quantum magnetism, and oxide electronics. He has been awarded the IBM Science Prize, the Nissan Science Prize, and the H.K. Onnes Prize.

Dan J. Thoma is a technical staff member at the Los Alamos National Laboratory and director of the newly formed Materials Design Institute, a collaborative educational research program with the College of Engineering at the University of California at Davis. He received his B.S. degree in metallurgical engineering from the University of Cincinnati and his M.S. and Ph.D. in metallurgical engineering from the University of Wisconsin at Madison. Dr. Thoma's research interests include physical metallurgy, with a particular focus on microstructural development during materials processing. Within this context, his efforts have been devoted to alloying theory, the thermodynamics and kinetics of phase transformations (both liquid/solid and solid/solid transitions), and property response as a function of microstructural evolution. Dr. Thoma has been active within the Minerals, Metals, and Materials Society (TMS), having served as its president in 2003, on the board of directors as programming director, and as chair and member of multiple committees. He is also active in ASM International and the American

Institute of Mining, Metallurgical, and Petroleum Engineers, of which he has been elected to the board of trustees and is currently president-elect. Dr. Thoma is also leading the Revitalization Task Force of the Federation of Materials Society. He received the 2007 Distinguished Service Award from TMS and is U.S. Chair for a Joint Working Group on Nuclear Materials with the United Kingdom.

Appendix C

Meeting Agendas

FIRST MEETING
WASHINGTON, D.C.
MARCH 3-4, 2007

Saturday, March 3, 2007

Open Session

8:00 a.m.	Welcome	
	Committee Introductions	Paul Peercy, *Chair*
8:45	Introduction to the National Research Council	Natalia Melcer
9:00	Perspectives from the Solid State Sciences Committee	Brian Maple
9:45	Department of Energy (DOE) Workshop: Design, Discovery and Growth of Novel Materials for Basic Research: An Urgent U.S. Need	Paul Canfield
10:30	Break	
10:45	Perspectives from DOE/Basic Energy Sciences	Harriet Kung
11:30	Perspectives from National Science Foundation/Division of Materials Research	Lance Haworth
12:15 p.m.	Working Lunch	

Closed Session

1:15	Committee Discussion: Statement of Task
2:15	Committee Discussion: Report Outline
3:15	Break
3:30	Committee Discussion: Report Outline
4:00	Discussion of Town Hall Meetings: Topics, Dates, Attendance
5:00	Break
6:00	Working Dinner
8:00	Adjourn

Sunday, March 4, 2007

Closed Session

7:30 a.m.	Reconvene
8:00	Committee Discussion: Report Outline
9:30	Committee Discussion: Writing Groups, Assignments
10:30	Break
10:45	Committee Discussion: What have we heard? What do we still need to hear? Review Timeline
Noon	Working Lunch
1:00 p.m.	Adjourn

SECOND MEETING
UNIVERSITY OF WISCONSIN AT MADISON
JULY 12-13, 2007

Thursday, July 12, 2007

Closed Session

8:00 a.m.	Welcome, Review of Agenda, Plans for the Meeting	Paul Peercy, *Chair*
8:30	Data Subgroup Report	Peter Littlewood (by teleconference)
9:30	Overview and History Subgroup Report	Zach Fisk (by teleconference)
10:30	Break	
10:45	Science and Technology Subgroup Report	Arthur Ramirez
Noon	Working Lunch	

Open Session

1:00 p.m.	Institute for Crystal Growth, Berlin	Roberto Fornari, Director (by teleconference)
2:00	Bulk Crystals: Urgent Needs and Opportunities	Eugene Haller
3:00	Break	
3:15	Disciplinary Boundaries in Academia	Thomas Rosenbaum
4:15	Discussion of Presentations	
5:30	Break	
6:30	Working Dinner	
8:00	Adjourn	

Friday, July 13, 2007

Open Session

7:30 a.m.	Reconvene	
8:00	Industrial Needs for New and Crystalline Materials	Mark Pinto, Applied Materials

Closed Session

9:00	Committee Discussion Review of First Day Review Charge to Committee Review Report Outline Review Writing Groups, Assignments	Paul Peercy, *Chair*
10:30	Break	
10:45	Committee Discussion: Review Timeline What do we still need to hear? Plans for moving forward	Paul Peercy, *Chair*
Noon	Working Lunch	
1:00 p.m.	Adjourn	

THIRD MEETING
WASHINGTON, D.C.
NOVEMBER 15-16, 2007

Thursday, November 15, 2007

Open Session

8:00 a.m.	Welcome	
8:30	Review of Agenda, Plans for the Meeting	Paul Peercy, *Chair*
8:45	Perspectives from the American Association for Crystal Growth	David Bliss, President
9:45	Crystal Growth Needs of the DOE Laboratories	Lynn Boatner, Oak Ridge National Laboratory
10:45	Break	

Closed Session

11:00 a.m.	Committee Discussions
8:00 p.m.	Adjourn

Friday, November 16, 2007

Closed Session

7:30 a.m.	Committee Discussions
1:00 p.m.	Adjourn

Appendix D

Synthesis Techniques

BULK CRYSTALS

A single crystal is called "bulk" when it can be physically separated from the growth medium and is large enough to be handled and measured independently from other crystals. Bulk crystals range in size from submillimeter to the two-foot-long crystal shown in Figure 1.1.1 in Box 1.1 in this report. Not surprisingly, a range of techniques are used to grow bulk crystals. In this appendix, the principal crystal growth techniques used in research and industry are reviewed.

Floating-Zone Growth of Oxide Crystals

Oxide crystals are grown by a wide spectrum of techniques, including crystal pulling by Czochralski (CZ) or Bridgman methods, flux growth, top-seeded solution growth, and others. Common to all of these techniques is the need for a crucible or other holder to contain the molten oxide. Ideally, this crucible will not react with the melt; in practice this is rarely true, as high-temperature oxide melts are typically quite aggressive. The optical-image floating-zone (FZ) technique offers a powerful alternative to these approaches, allowing the growth of congruently and incongruently melting materials that are both line compounds and solid solutions. FZ operates by focusing the images of halogen or xenon filaments to provide an infrared heat source that melts the feedstock polycrystalline oxide. FZ obviates the need for a container, as surface tension suspends the molten liquid between the feedstock rod and the growing crystal (see Figure D.1). Control of the processing

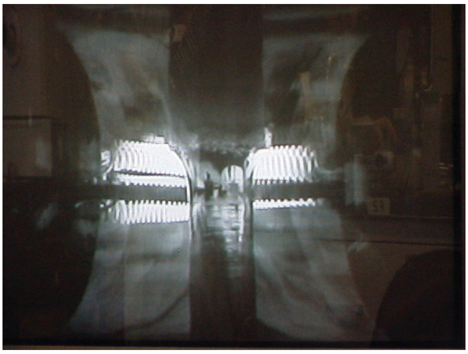

FIGURE D.1 Molten zone under stable growth conditions in a floating-zone furnace. From top to bottom: polycrystalline feed rod, molten zone, growing crystal. The image of the filament is clearly seen. SOURCE: Courtesy of Robert J. Cava, Princeton University.

atmosphere is straightforward. While flux methods are more efficient for exploring a complex compositional phase space, FZ crystal growth is the best and most generally applicable growth method when large, high-purity crystals of known materials are required. In many cases, crystals of cubic centimeter volumes can be routinely grown.

While such crystals impact the full spectrum of physical measurements, the greatest beneficiary of the FZ technique has been the neutron-scattering community. The relatively low flux of current-generation neutron sources demands large single-crystal samples, and the FZ approach has been able to deliver materials that meet this demand. Indeed, the increasing availability of large, high-quality specimens has led to breakthrough advances in fundamental neutron-scattering measurements in high-temperature superconductivity, colossal magnetoresistance and related magnetic oxide physics, ferroelectricity, multiferroics, geometric frustration, and many other areas. The success of future facilities, such as the Spallation Neutron Source, will be intimately tied to the broad availability of FZ-grown crystals. It is no wonder that Princeton University's Robert Cava has declared the FZ technique "arguably the best thing to happen to single-crystal growth in the past 25 years" and called for a 10-fold increase in the number of floating-zone crystal growth furnaces in the United States.

While the success of the optical-image FZ technique for the growth of oxide crystals speaks for itself, there are opportunities for improving this already powerful technique to further enhance its impact. These opportunities call for research and development on FZ furnace design and operation. The areas for continuing development are as follows:

- *Homogeneity control via feedback.* Owing to the extreme sensitivity of many electronic and magnetic states to composition, crystals of high compositional uniformity are becoming increasingly important for detailed physical measurements on complex systems. Recent work in colossal magnetoresistive oxides, with magnetic phases very closely spaced in composition, attests to the importance of even tighter control on compositional homogeneity than is at present available from commercial FZ furnaces. One potential solution is to adopt the image-processing-based feedback techniques used in the CZ growth of silicon. Sophisticated image processing of the zone shape can be used to generate an error function that feeds back to process variables. In this way, the zone volume and interface shape—two critical determinants of compositional uniformity—will be controlled with far greater precision and stability than can be done manually, which is the current state of the art. This is particularly critical in the case of incongruently melting compounds (which are the rule in complex oxides), where slow growth rates are essential and stability over long periods (days to weeks) may be necessary.
- *Controlled "composition spread."* The feedback approach could alternatively be used to deliberately stratify dopant ions in a controlled fashion along the length of the growing crystal. Proof of principle that feedback systems can be used in this mode to control dopant distribution effectively has already been demonstrated for laser-heated pedestal growth of Cr-doped $LaAlO_3$. Extension of this approach to more complex oxides utilizing the FZ technique will effectively allow for phase-diagram studies in a single growth experiment. As oxides become more widely used as active semiconductors, composition spread samples will aid in fundamental understanding of the doping mechanisms.
- *Extreme pressures.* Many important materials can only be synthesized at high pressure, and the accessibility of new phases is directly related to the range of available pressures. Currently available commercial FZ furnaces can attain total growth overpressures of only about 10 bar. This overpressure is commonly used to suppress component volatility or to promote oxidation. While this rather modest pressure has enabled growth of crystals that do not form at ambient pressure (e.g., $La_{2-x}Ba_xCuO_4$), much higher pressures would allow access to even more exotic low-dimensional and strongly correlated materials. The ultimate overpressures possible will be determined through the development of suitable transparent envelopes to contain the pressure while allowing transmission of the infrared light to the growing crystal.

Solution Growth of Crystals

Solution growth is perhaps the most versatile method for growing single crystals. It combines simplicity, versatility, high throughput, and economy. It allows for the growth of single crystals well below their melting points, or, in some cases, decomposition temperatures. This can be critically important for the production of crystals of materials that are either very refractory, or crystals that decompose before their melting points. Further, lower-temperature solution growth methods often offer a practical route to reducing the imperfections in crystals associated with the entropic disorder or loss of stoichiometry that accompany high crystal growth temperatures. In the same way, for example, that NaCl can be grown out of water below 100°C even though it melts near 800°C, CeSb, with a melting point near 1800°C, can be grown out of Sn at temperatures below 1000°C. The solution growth technique has been used to grow single crystals of virtually every class of materials, including elements, intermetallics, oxides, chalcogenides, and organic compounds (Figure D.2). In every case, the key to using this technique lies in discovering the appropriate solution from which to grow the crystals without introducing unwanted impurities, the temperature range for cooling to promote crystallization, and the optimal cooling rate. Determining each of these parameters can be time-consuming and is not always possible. Given its ease and power, together with difficulties that often are solved by a combination of experience and intuition, solution growth is considered by many to be a combination of a science and an art.

Solution growth of novel materials is currently practiced by numerous research groups in the United States and elsewhere. Established groups are teaching this method to a growing number of their students, and thus it is becoming even more commonly used as a research tool. Solution growth is not yet widely used in the materials physics community; owing to its increasing use, however, improvements

FIGURE D.2 (Left) Crystals of Ni_2SiO_4 olivine grown from an Na_2MoO_4-Li_2MoO_4-NaCl solution after cooling for a month. SOURCE: Courtesy of Robert J. Cava, Princeton University. (Right) Methyl pyridium tetracyanoethenide grown from acetonitrile after cooling for 4 days. SOURCE: From J.S. Miller, P.M.B. Piccoli, A.J. Schultz et al., *CrystEngComm,* **11,** 686-690 (2009). Reproduced by permission of the Royal Society of Chemistry.

and extensions of the technique will be leveraged by its expanding number of practitioners.

Advances in solution growth that are needed in the short term include broader and more practical control of crystal nucleation and of the initial growth process. This can be accomplished by the more general development and implementation of techniques that have been used for specialized crystal growth of highly optimized, technological materials such as silicon and quartz. Such techniques include the automated control of complex cooling profiles, control of thermal gradients, active mixing of the growth solution, and careful control of impurity content. Applying these techniques to the diverse range of novel and complex materials that can be grown from solution will be a substantial challenge.

Longer term, the new frontiers for solution growth will be the challenges of extremes: growth of extremely high temperature materials; growth of materials with extremely volatile, toxic, or reactive constituents; and growth of materials under extremes of pressure, for example. Another frontier of solution growth is the need to grow single crystals of complex, organic crystals for use in the determination of protein structure (and function). Many of the problems that exist for complex, inorganic compounds also are present for large organic molecules, over even narrower temperature and composition ranges.

With an expanded number of practitioners, with improved, simplified, and automated methods of growth and nucleation control, and with the availability of expanded chemical and physical phases, solution growth will be one of the frontline methods for growing crystals of new materials that will be the creative engines that drive basic and applied research for the next century.

Crystal Growth by Vapor Transport

For materials with volatile components, the growth of crystals from a vapor phase is often an important technique that is frequently employed to make crystals for fundamental property studies. In these methods, materials in polycrystalline form are either sublimed or placed in furnaces with thermal gradients. Molecules are transported or formed from the components at the hot end of the growth system. The molecules in the gas phase travel down the thermal gradient, where, at the cold end of the system, they then condense to form crystals (in some cases, the mass transport is up the thermal gradient rather than down the thermal gradient). The crystals typically grow over a period of days or weeks. Both closed (e.g., sealed, evacuated quartz tube) and open (e.g., open tube) growth systems can be employed.

The same technique can be employed to grow crystals with relatively low volatility components, if a "transport agent" is added to the crystal growth system. This transport agent, commonly a halogen such as Cl_2, Br_2, or I_2, reacts with the nonvolatile components, forming complex molecules that are stable in the gas phase at high temperatures. These molecules travel down the thermal gradient where they become unstable in the low-temperature part of the system, decomposing to deposit the normally nonvolatile components at the cold end, where the crystals grow. The vapor growth method has been particularly successful in growing crystals of transition-metal chalcogenides and some oxides as well as in purifying metals (see Figure D.3).

The volumes of crystals grown by this method are typically much smaller than those made in the solution, flux, CZ, or FZ methods. The crystals are, however, often sufficiently large for fundamental crystal structure, spectroscopic, magnetic, and transport characterization studies. This crystal growth method therefore is especially useful in solid-state chemistry research programs whose primary goal is the discovery of new materials with interesting magnetic and electrical properties, as fundamental property studies do not typically require large-volume crystals.

As in the flux methods, the optimization of vapor-phase crystal growth conditions requires substantial experience and skill on the part of the crystal grower. The magnitude of the thermal gradient, the type of transport agent employed, its concentration, the growth zone temperature, the transport gas flow rate in open systems, and the diameter of the growth tube are all variables that must be optimized.

Although establishing the basic parameters of the growth process and identifying the best transport agents have constituted a field of significant study in past years, the technique itself has not recently been subject to concentrated study. As with other crystal growth methods, further development of the vapor growth

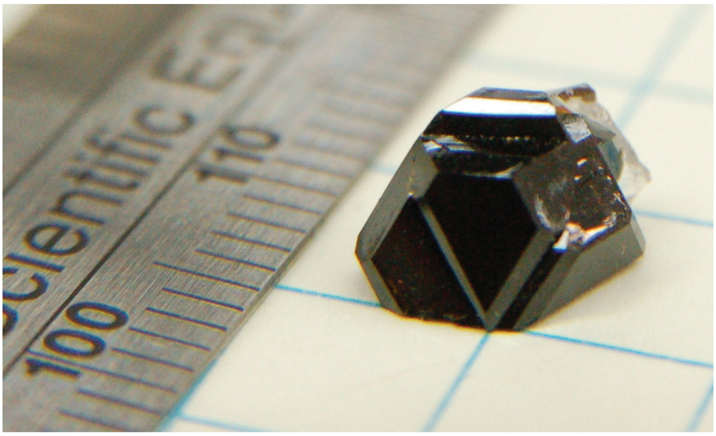

FIGURE D.3 A crystal of cobalt chloride boracite grown by vapor transport. SOURCE: Courtesy of Robert J. Cava, Princeton University.

technique might be made in the areas of extreme conditions of temperature and pressure. Further, for materials where vapor-phase growth is of particular interest from either a technological or a fundamental science perspective, further development of the understanding and functionality of the method could also involve increased spectroscopic analysis of the complex molecules formed in the gas phase during the transport process.

Hydrothermal and Solvothermal Crystal Growth

Hydrothermal growth methods have in large part been born from scientists' attempts to emulate geological crystal growth conditions in which crystals precipitate and grow from solutions based on high-temperature, high-pressure water. Temperatures of 400°C-700°C are often employed, at pressures up to a few thousand atmospheres, requiring high-strength steel autoclaves as containment vessels. There are relatively few practitioners of this growth technique in the fundamental materials science community at present, likely because of the specialized equipment and facilities (e.g., explosion-safe rooms) required for the growth. This method has, however, been an important part of industry-based crystal growth programs of both a fundamental and applied nature and has been exploited in very important, large-scale technological processes such as the growth of large single crystals of quartz from alkali-containing water (see Figure D.4). In the basic science arena, researchers at corporate research laboratories, particularly at the DuPont Company, have for many years employed the hydrothermal crystal growth of materials sealed in precious metal tubes such as gold and platinum as part of their exploratory new-materials programs. Small crystals of the "heavy fermion oxide" LiV_2O_4 have been grown hydrothermally in recent years in a Japanese academic research laboratory, but the use of this method to grow crystals for the study of basic condensed-matter physics in an academic setting is very rare.

Although the hydrothermal growth method has seen relatively limited use outside industrial science programs, a related method, called solvothermal growth, does see wide application in academic solid-state chemistry laboratories. This method grows crystals from aqueous and nonaqueous solvents at typically much more modest temperatures and pressures than those needed for hydrothermal methods. Inexpensive Teflon liners simply constrained by ordinary steel vessels with simple overpressure relief systems are very often employed. Many exploratory solid-state chemistry programs use this method to grow small crystals suitable for single-crystal structure determination, and in many cases the solvent molecules are part of the crystal structure of the new compounds obtained. Solvothermal growth is also widely used to grow semiconducting nanoparticles. There is no question that the extension of solvothermal and hydrothermal methods to the growth of larger-volume crystals of a broader range of materials whose study would address

FIGURE D.4 A single hydrothermally grown quartz crystal. SOURCE: Courtesy of Robert J. Cava, Princeton University.

forefront issues in condensed-matter physics would be both extremely challenging and very rewarding.

CRYSTALLINE THIN-FILM MATERIALS

Thin-film materials are ubiquitous in today's world. Key examples include the semiconductor laser, the high-electron-mobility transistors found in most cellular telephones, and magnetic multilayer materials that are of pivotal importance to the data storage industry. A large variety of techniques exist for growing crystalline thin films, including molecular-beam epitaxy (MBE), evaporation, sputtering, chemical vapor deposition, and laser ablation. Complex structures composed of stacked thin films with varying functionalities (electronic, optical, magnetic, and so on) are routinely synthesized. The enormous technological and economic importance of crystalline thin films has ensured that tremendous effort is applied to their growth, in the United States and around the world.

The discussion in Chapter 1 of the fascinating states of matter that emerge in two-dimensional electron systems when subjected to a magnetic field illustrates that crystalline thin-film materials also provide great opportunities for fundamental scientific research. The success of GaAs heterostructures for both science and technology provides a rationale for a similar program in MBE-grown transition metal oxide thin-film heterostructures. Because of the strong hybridization of oxygen *p* orbitals and transition metal *d* orbitals, oxides display a wider variety of strongly correlated behavior at room temperature than do covalently bonded semiconductors. The strongly coupled charge, spin, orbital, electronic, and lattice degrees of freedom offer the promise of novel functionality in thin-film devices, provided growth processes in oxides can be mastered. Recent work in Japan has shown that combining oxide functionality with the precision band-gap engineering commonly associated with covalent systems is feasible. Pursuing these goals is a national challenge of the highest order, both for science and for technology.

As with bulk-crystal growth, the growth of thin films should be tightly coupled with the measurement and characterization community. In contrast to bulk growth, however, in situ studies of growth processes are common. Ellipsometry, time-of-flight mass spectroscopy, synchrotron radiation, neutron reflectometry, and other related surface-sensitive probes are critical in enabling a fundamental understanding of how the surfaces and interfaces develop in such complex systems. The integration of state-of-the-art scanned probes (scanning tunneling microscopy, atomic force microscopy, magnetic force microscopy, and so on) with growth techniques to explore nanoscale phenomena in complex materials is in its early stages and severely limited by the availability of high-quality model materials systems. Today there are only a few thin-film crystal growers in the world capable of producing the kinds of heterostructure samples needed by condensed-matter experimentalists for cutting-edge research on collective behavior of two- and lower-dimensional electronic systems. The situation is made more difficult by the fact that the ultraclean samples of interest to the fundamental physics community cannot generally be grown in the same machines used for device fabrication. The high doping levels and multisource needs of the device developers lead to impurity incorporation and unacceptably low mobilities in the simpler structures needed for fundamental research. In addition, some experimental techniques such as neutron scattering require a large number of repetitions of a given multilayer structure to achieve sufficient sensitivity. Therefore, parallel tracks in growth efforts that push the limits of purity and overall sample size and those that explore new functionality are required. While the United States continues to lead in high-mobility GaAs, the situation today has grown perilously fragile, with a large number of experimental and theoretical condensed-matter physicists dependent on a very small number of growers. In the growing field of MBE oxide films, the United States will have to put forward a concerted effort to remain competitive owing to intense activity abroad.

Heterostructure Synthesis and Growth Diagnostics

Thin-film approaches to crystalline matter discovery constitute a rapidly evolving field. Future directions should continue to exploit the collective mastery of design, synthesis, and characterization of novel bulk and thin-film materials. Areas of continued emphasis should include both mature and emerging areas. The growth of semiconductor thin-film heterostructures, in which single-crystal material growth can be controlled at the atomic level, is at least a decade ahead of the complex oxide thin-film field in terms of the degree of sophistication (for example, materials purity resulting from the implementation of a host of in situ diagnostic tools, as well as the ability to scale to large wafer sizes). In correlated complex oxides, there has been dramatic progress in the development of thin-film deposition tools such as MBE and chemical vapor deposition. Past work on thin-film heterostructures (manganites, for example) has clearly demonstrated that interface chemistry, structure, and electronic structure are acutely sensitive to lattice mismatch and surface phenomena. Advances in the growth of heterostructures, especially the complex oxides, demands the immediate development of new approaches to in situ probes of the growth processes including the surface/interface structure, chemistry, and electronic structure. A deposition system that allows in situ probing of growth processes is in place at the Spring-8 beam line in Japan, where preliminary experiments have already been reported; some progress toward this has been made in the United States at the Advanced Photon Source (see Figure D.5), but it is clear that the U.S. researchers lag behind colleagues in Japan. Using the penetrating capabilities of x-rays along with their ability to determine surface/interface structure with very high precision provides an ideal way to understand the growth processes. Future deposition systems should be capable of reflection high energy electron diffraction (RHEED), ellipsometry, and surface chemical analyses

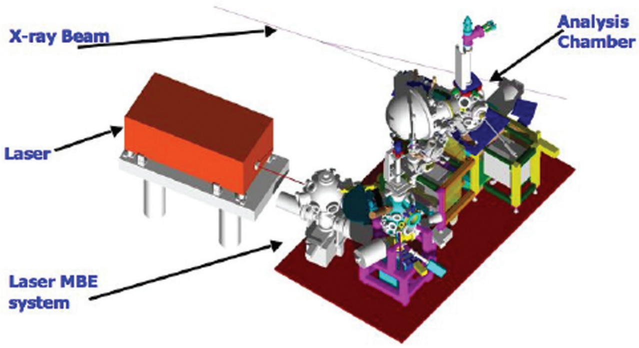

FIGURE D.5 In situ studies on a synchrotron beam line. SOURCE: Courtesy of Ramamoorthy Ramesh, University of California, Berkeley.

(Auger/x-ray photon spectroscopy [XPS], time-of-flight ion scattering and recoil spectroscopy [TOF-ISARS], and related techniques).

Atomic-Layer Deposition of Complex Materials

Atomic-scale control over the deposition process, namely, through an MBE-like deposition approach, has evolved considerably; however, a commercially manufacturable process could prove to be difficult, especially if conformal deposition over nonplanar surfaces is required, as is the case for memory devices. A chemical vapor deposition process that has within it the inherent ability for atomic-layer control (as manifested in an atomic-layer deposition process) is extremely desirable—such a process does not currently exist. It will require significantly better understanding of surface chemistry and the development of new precursors that can enable the atomic-level chemical selectivity and control characteristic of an atomic-layer deposition process. The development of such a tool would benefit greatly from the collaborative participation of scientists and engineers from academia, national laboratories, and industry.

Topological Control of Heteroepitaxial Interfaces

Figure D.6 illustrates two of the possible routes by which heteroepitaxy can be used to create novel interfaces. The first approach, which is more common, involves the layer-by-layer deposition of the relevant layer components (for example,

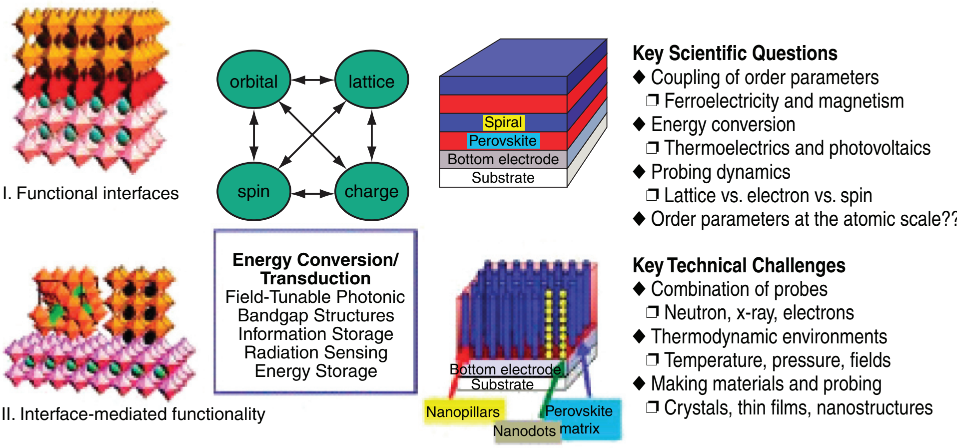

FIGURE D.6 Quantum materials design algorithms. SOURCE: Courtesy of Ramamoorthy Ramesh, University of California, Berkeley.

GaAs-AlGaAs, LAO/STO, and so on) to create a sandwich-like heterointerface. The second approach consists of using self-assembly as a tool to create vertically epitaxial nanostructures (for example, perovskite-spinel nanocomposites). Epitaxial constraints in three dimensions play a key role in the formation of such nanostructures, as well as enabling strong magnetoelectric coupling between the two phases. Understanding of the interface properties in such three-dimensional heterostructures is still in its infancy. From the point of view of the discovery of crystalline matter, it would be valuable to explore such topologies in greater detail: Can one control the architecture of these nanostructures at will? Can one create hierarchies of topologies and length scales at such interfaces?

Combinatorial approaches to new materials discovery have been used to great scientific and commercial advantage in the pharmaceutical industry as a rapid means to the discovery of new drugs. Since the mid-1990s, similar approaches have been explored for the discovery of inorganic materials, with limited success, mainly in the discovery of new phosphors and catalysts.

Appendix E

Classes of Materials

ORGANICS

Also called molecular crystals, organics are composed of carbon-based molecules. This group of materials also includes inorganic coordination compounds, which are sometimes referred to as metallo-organic or organometallic compounds. Organics exhibit many technologically important properties, such as magnetic ordering, high electrical conductivity, high- and low-dielectric constants, piezoelectricity, and superconductivity. Like atoms in inorganic materials, dissimilar molecules can be co-crystallized. Although generally thought of as being neutral species, when the electronegativities of co-crystallized molecules are sufficiently different, electron transfer occurs creating anions and cations, and examples can exhibit high direct current electrical conductivity or ferromagnetic ordering. When intermediate differences in the electronegativities occur, charge-transfer complexes form.

OXIDES

Oxides are materials containing oxygen as a primary anion—examples of current interest are $BaTiO_3$ (a ferroelectric), $YBa_2Cu_3O_7$ (a superconductor), and $La_{1-x}Sr_xMnO_3$ (a magnetoresistive material). The wide range of behavior found in metal oxides is due in part to the presence of strong interactions between metal d electrons and oxygen p electrons and a delicate balance between nearly energetically equivalent electronic configurations that involve coupling between electronic, magnetic, and structural degrees of freedom. The presence of oxygen is particularly critical to the creation of exotic properties—the orbital energies of the oxygen ion are well matched to transition metal orbital energies, yielding the added complexity of a balance between covalent and ionic bonding that differs from compound to compound. Finally, the relatively straightforward methods generally used in the synthesis of oxides and their chemical stability make them widely available to the condensed-matter and solid-state chemistry communities, resulting in vigorous worldwide research on many different compound systems. Examples of challenges that drive this field are the quest for room-temperature superconductivity and the production of a room-temperature ferromagnetic insulator. There is also a vigorous effort devoted to realizing qualitatively new magnetic phases such as two-dimensional critical spin liquids.

INTERMETALLICS

Intermetallics are materials made of combinations of two or more metallic elements. When one of the elements is a magnetic rare-earth or actinide metal (e.g., cerium and uranium), such crystalline systems embody the concentrated limit of the Kondo effect, in which the conduction electron forms a pair with the magnetic ion in a lattice periodic fashion. In this many-body limit, novel “heavy” electron states emerge. These materials constitute the frontier of exploration into the possibility of conducting states of matter that are qualitatively different from the conventional Landau Fermi-liquid, which describes metals such as copper and aluminum. Intermetallic compounds are widely used, though for different reasons, in today’s mechanical and electrical systems.

Appendix F

Working Draft of Policies and Procedures for a Crystalline Materials Network

The concept of a discovery and growth of crystalline materials (DGCM) network, described in Chapter 4 of this report, is new. It seeks to take the best operating procedures used by existing DGCM groups and imbue the entire DGCM community with greater freedom and commensurate resources. In order to protect the researchers who would participate in such a network from improper, dangerous, or even illegal use of crystalline samples, a set of clearly defined policies and procedures would be essential. Below, the Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth provides a "working draft" of such policies and procedures by describing the areas that they should cover.

The policies and procedures designed for a DGCM network should address the following:

1. *Transparency: open communication and full disclosure between growers and users.* The grower will provide to the measurer all information (e.g., stoichiometry) necessary to interpret measurement results. Conversely, the measurer will provide to the grower all data that result from the measurement.
2. *Roles and responsibilities of growers and users (e.g., "joint collaboration" relationship versus "supplier/user" relationship):*
   - *Roles and responsibilities of the measurement scientist.* The receipt of a sample from the network would include the acknowledgment of the specific roles of the measurement scientist, as well as responsibilities such as protecting the sample from undue damage and respecting

embargoes on the distribution of sample preparation knowledge not publicly reported. It is usual for the measurement scientist to perform only the measurements proposed formally to the network grower, and only within the measurement range formally specified or reasonably extended. Specifically, it will not be the role of the measurement scientist to ship network-grown samples to another measurer, that is, to act as a broker, without consent of the grower.

- *Roles and responsibilities of the grower.* The grower will not distribute samples of the same compound to different measurers for the same measurement without notifying the measurers. The grower will keep the measurement collaborator informed of all information obtained regarding materials of common, present interest that significantly impact the conduct or interpretation of measurements.

3. *Custodianship of samples (including physical protection and storage of samples).* Scientists responsible for the synthesis of new materials and the growth of crystals in the network would ultimately be responsible for the custodianship of the samples they create. Recognizing that samples are rarely sent back to the grower after a measurement is completed, it is expected that the measurer exercises reasonable care in storing samples.
4. *Intellectual ownership.* Whether research is motivated by the grower or the user, the grower creates the value of the crystal. For grower-motivated research, it is understood that all rights of priority normally accorded to federally funded synthesis research would be held by network-supported growers. These rights might include the selection of collaborators who would perform some of the first sample measurements, or it might require collaboration for the initial measurements. The goal is to ensure that the grower retains full intellectual ownership of materials discovery and initial properties. Simultaneously, the network would strive to increase access to network-grown samples. Achieving these two goals might require providing a dormancy period—perhaps 6 to 12 months after the first publication on a particular sample growth experiment—when the grower would possess right of first refusal for a sample measurement proposal. After this period, samples would become subject to the normal network proposal procedures.
5. *Intellectual property rights.* Details of intellectual property ownership and intellectual property rights would be developed by the network's external scientific advisory board in collaboration with the federal funding agencies and the network administrator.
6. *Attribution.* The guiding principle regarding the attribution of credit for research accomplishments would be that of collaboration. Specifically, sample provisioning by the network would be viewed as a collaborative activity, and the network scientists would be afforded credit and coauthorship

normally accorded to collaborators. Rules on collaboration are addressed in Section 02.2 of the "American Physical Society Guidelines for Professional Conduct," which includes the following statement: "Authorship should be limited to those who have made a significant contribution to the concept, design, execution or interpretation of the research study. All those who have made significant contributions should be offered the opportunity to be listed as authors."

7. *Reporting requirements.* The network would provide quarterly updates of its activities to the external scientific advisory board and issue an annual report of all published research conducted under its auspices. The research reported would involve internal as well as collaborative activities.

Appendix G

Educational Role of Centers of Expertise for Discovery and Growth of Crystalline Materials

As discussed in Recommendation 2 (see Chapter 4 in the report), a center of expertise for the discovery and growth of crystalline materials (DGCM) could have an educational program to help prepare the next generation of scientists engaged in materials discovery and development. Such a program should include both theoretical and practical (hands-on) training and should be geared toward giving young scientists adequate training to allow them to engage in independent research in DGCM either at their home institutions or at national or regional facilities. Ideally, the program would operate on several levels, meeting the needs both of undergraduate and graduate students and of postdoctoral researchers. For this reason, such a program would best be operated as a summer school so as not to interfere with academic calendars.

The program should include basic grounding in the important physics, chemistry, and materials science of crystal growth. The theoretical and experimental aspects of growth and characterization of semiconducting, oxide, metallic, organic, and perhaps biological crystals should form the basis for the tutorial portion of the school. Lectures should be included by leading researchers on crystal growth and epitaxial processes, nanocrystallization, in situ and ex situ characterization, properties, and applications; these lectures should be focused on fundamental discussions of the chemical and physical processes that control the assembly of atoms and molecules from the melt, solution, or vapor. A model for such a course of lectures is the periodic summer school on crystal growth operated by the American Association for Crystal Growth, most recently in August 2007. In order to meet the needs of students with a variety of backgrounds and educational levels, each set of lectures should begin at a level accessible to undergraduates and progress to more advanced discussions. Students would attend whatever portion of each set that they were able to benefit from.

This theoretical or classroom training should be augmented by practical, hands-on training using DGCM equipment. For pedagogical purposes the laboratory activities could involve the growth of well-known materials (rather than original research), but should use state-of-the-art equipment that the students can expect to use in their future research activities. Each student should have the opportunity to receive training on more than one growth technique as well as on a variety of characterization methods. The theoretical and practical portions of the course could be expected to span approximately 3 weeks, with lectures alternating with laboratory (and simulation) activities.

After completing the classroom course and practical exercises, students should, if possible, extend their stay to receive further training by engaging in research with scientists at the center of expertise. Undergraduates could participate in ongoing projects of the staff scientists throughout the summer under the aegis of a Research Experience for Undergraduates program funded by the National Science Foundation or the Department of Energy. Graduate students and postdoctoral researchers could pursue their own projects, under the guidance of the staff scientists, for variable periods of time depending on the nature of the projects. During this portion of the school their living expenses could be supported by grants held by their home institutions.

Support for such a program could be sought not only from the federal agencies but also from manufacturers of equipment that graduates of the school might be expected to purchase in the future. Companies that employ these trained crystal growers might also be expected to contribute. The center of expertise should have one or more staff members dedicated to the organization of the summer school and student recruitment.