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Frontiers of Materials Research: A Decadal Survey

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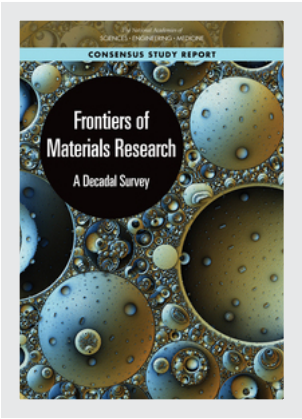

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Frontiers of Materials Research: A Decadal Survey

Committee on Frontiers of Materials Research: A Decadal Survey

National Materials and Manufacturing Board

Board on Physics and Astronomy

Division on Engineering and Physical Sciences

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Cover: Materials research is a never-ending quest. A snapshot in time of the frontiers of yesterday, today, and tomorrow is explored in this decadal survey. As each sphere of understanding is scaled back and understood, a universe of spheres still remains to be explored. Graphic Artist: Erik Svedberg.

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Preface

The National Science Foundation (NSF) and the Department of Energy (DOE) requested that the National Academies of Sciences, Engineering, and Medicine perform an in-depth and broad study that will articulate the status and promising future directions of materials research (MR) in the United States in the context of similar efforts worldwide. This is the third decadal survey in MR; the first was published in 1990 (*Materials Science and Engineering for the 1990s: Maintaining Competitiveness in the Age of Materials*) and the second in 2010 (*Condensed-Matter and Materials Physics: The Science of the World Around Us*).

Included in the statement of task for this assessment is that MR will be considered broadly in terms of material type, forms/structure, property, and phenomenon, as well as the full breadth of approaches to MR (e.g., experiment, theory, computation, modeling and simulation, instrument/technique development, synthesis, characterization, etc.). In particular, the report will

- Assess the progress and achievements in MR over the past decade;
- Identify the principal changes in the research and development landscape for MR in the United States and internationally over the past decade, and how those changes have impacted MR;
- Identify MR areas that offer promising investment opportunities and new directions for the period 2020-2030 or have major scientific gaps;
- Identify fields in MR that may be good candidates for transition to support by other disciplines, applied research and development (R&D) sponsors, or industry;
- Identify the broad impacts that MR has had and is expected to have on emerging technologies, national needs, and science;
- Identify challenges that MR may face over the next decade and offer guidance to the materials research community for addressing those challenges; and
- Evaluate recent trends in investments in MR in the United States relative to similar research that is taking place internationally by using a limited number of case studies of representative areas of MR that either have experienced significant recent growth or are anticipated to see significant near-term growth, and based on those trends, recommend steps that the United States might take either to secure leadership or to enhance collaboration and coordination of such research support, where appropriate, for identified subfields of MR.

In addition to the five full committee meetings, the committee will engage in extensive data gathering. Data gathering for the project will consist of

1. A review of relevant published literature;
2. Invited presenters at the committee's public meetings;
3. Sustained engagement with the materials research communities; and
4. If the committee decides, commissioned papers.

The project will conduct a review of the literature related to aspects of the issues to be addressed by the project, which will include previous work (such as seminal reports) done in the last decade by other not-for-profits, societies, and foreign entities.

The project will engage in sustained efforts to solicit broad input from relevant communities. These outreach efforts will include sessions at geographically dispersed locations across the United States, and may include town halls, professional meetings, solicitation of white papers, and aggressive use of electronic communications and networks

The committee closely followed the statement of task, with the following small deviations:

- In the fourth list item, it was interpreted that "transition" cannot simply be a handoff, as even if a fundamental discovery appears ready for other disciplines or applications, communication back to the bench is required for successful implementation—especially as processes become more complex.
- Workforce empowerment is not in the statement task, but research by the committee and a great deal of input from the community indicated that it must be mentioned.
- MR and economics are, by nature, intertwined. The committee decided that addressing economic policy is beyond its scope, and so the topic is not addressed here.

During the course of the study, the committee came into agreement that MR in the United States is at a precipice—there have been extraordinary advances in materials growth, measurement, and computation, both separately and in coordinated collaborations at universities, in national laboratories, and in industry, across nearly all fields of MR. Many breakthroughs are reported here, many are directly predicted, and many are as yet unforeseen, which will have tremendous effect on our understanding, and significant impact on our daily lives, globally. If the United States does not maintain its position as a world leader in MR, it risks not being a significant player.

Finally, a disclaimer: The statement of task was extremely broad, and the committee could not cover every aspect of MR, from the most fundamental to the most disruptive manufacturing, without leaving important and even crucial areas of MR out of the report, or providing only brief mention. This does not indicate that the committee felt these areas were less important or crucial.

Acknowledgment of Reviewers

This Consensus Study Report was reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise. The purpose of this independent review is to provide candid and critical comments that will assist the National Academies of Sciences, Engineering, and Medicine in making each published report as sound as possible and to ensure that it meets the institutional standards for quality, 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 thank the following individuals for their review of this report:

Ewa A. Bardasz, NAE, Zual Associates in Lubrication LLC,
Malcolm R. Beasley, NAS, Stanford University,
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Angus Rockett, Colorado School of Mines,
David J. Srolovitz, NAE, University of Pennsylvania,
George W. Sutton, NAE, Analysis and Applications, Inc., and
Michael J. Yaszemski, NAM, Mayo Clinic.

Although the reviewers listed above provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations of this report nor did they see the final draft before its release. The review of this report was overseen by David W. Johnson, Jr., Bell Laboratories, Lucent Technologies, and Celia I. Merzbacher, Office of Institutional Planning, Oak Ridge National Laboratory. They were responsible for making certain that an independent examination of this report was carried out in accordance with the standards of the National Academies and that all review comments were carefully considered. Responsibility for the final content rests entirely with the authoring committee and the National Academies.

The committee also thanks the following guest speakers and panelists at its meetings, who added to the members' understanding of the frontiers of materials research:

Paul Alivisatos, University of California, Berkeley,
Frank Anderson, CoorsTek,
David Awschalom, University of Chicago,
Greg Boebinger, National High Magnetic Field Laboratory,
Geoff Brennecka, Colorado School of Mines,
Craig Brice, Lockheed Martin,

Timothy Bunning, Air Force Research Laboratory,
Tzahi Cath, Colorado School of Mines,
Noel Clark, University of Colorado, Boulder,
Amy Clarke, Colorado School of Mines,
George Crabtree, University of Illinois, Chicago, and Argonne National Laboratory,
Arrelaine Dameron, ForgeNano,
Rod Eggert, Colorado School of Mines,
Jim Fekete, National Institute of Standards and Technology,
Mike Gazarik, Ball Aerospace,
Judah Goldwasser, Office of Naval Research,
Nancy Haegel, National Renewable Energy Laboratory,
Heinrich Jaeger, University of Chicago,
Sylvia Johnson, National Aeronautics and Space Administration,
Mercouri Kanatzidis, Northwestern University,
Alexander King, Critical Materials Institute,
Melissa Krebs, Colorado School of Mines,
Cristina Marchetti, Syracuse University,
David Marshall, University of Colorado, Boulder,
Jerry Martin, Synthio Chemicals, LLC,
Seth Miller, Heron Scientific,
Margaret Murnane, University of Colorado, Boulder,
Corinne Packard, Colorado School of Mines and National Renewable Energy Laboratory,
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Nicole Smith, Colorado School of Mines,
John Speer, Colorado School of Mines,
Reginald Stilwell, Allosource,
Stein Sture, University of Colorado, Boulder,
Mark VanLandingham, U.S. Army Research Laboratory,
Andriy Zakutayev, National Renewable Energy Laboratory,
Alex Zunger, University of Colorado, Boulder, and
All members of the University Materials Council.

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Ryan Baumbach, National MagLab,
Thomas N. Theis, IBM, and
Lucas Wagner, University of Illinois, Urbana-Champaign.

Every member of the committee made heroic efforts to complete this daunting task. Erik Svedberg provided guidance and management, and we also appreciate such from Jim Lancaster. We thank the outside speakers listed and are grateful for the input from the entire community.

Contents

Summary

Modern materials science builds on knowledge from physics, chemistry, biology, mathematics, computer and data science, and engineering sciences to enable us to understand, control, and expand the material world. Although it is anchored in inquiry-based fundamental science, materials research (MR) is strongly focused on discovering and producing reliable and economically viable materials, from super alloys to polymer composites, that are used in a vast array of products essential to today's societies and economies.

This report is the result of an in-depth consensus study requested and supported by the National Science Foundation (NSF) and the Department of Energy (DOE), aimed at documenting the status and promising future directions of materials research in the United States in the context of similar efforts worldwide. This is the third decadal survey in materials research. The first was published in 1990 (*Materials Science and Engineering for the 1990s: Maintaining Competitiveness in the Age of Materials*, National Academies Press, Washington, D.C.) and the second in 2010 (*Condensed-Matter and Materials Physics: The Science of the World Around Us*, National Academies Press, Washington, D.C.). The current report reviews the progress and achievements in materials research and changes in the materials research landscape over the last decade; research opportunities for investment for the period 2020-2030; impacts that materials research has had and is expected to have on emerging technologies, national needs, and science; and challenges the enterprise may face over the next decade.

A remarkable number of paradigm-changing advances have been made in materials research over the past decade, and the pace of discovery is accelerating. Moreover, the tools that support that research—including capabilities for materials characterization, synthesis and processing, and computational modeling—have advanced considerably, enabling previously unachievable insights. The science and engineering are exciting, the prospects for creating and controlling new materials are high, and the pathway to important applications is very encouraging. This positive view is tempered somewhat by the prospect that many of the advances that can now be foreseen require resources that are by no means guaranteed, and by the reality that international competition, particularly from China and from Asia more generally, is threatening U.S. leadership in materials research.

Certain areas of materials research emerge from this survey as particularly important. Computational materials science and engineering is just one such area. Integrating computational methods (including data science, machine learning, and informatics) with materials characterization and synthesis and processing methods is accelerating the discovery of designer materials and their use in products. This momentum extends into digital manufacturing, wherein additive manufacturing and other processes connect materials synthesis directly with fabrication. Materials for quantum information science (QIS) have emerged as another very high priority direction for the next decade. QIS comprises not only quantum computing but also storage, quantum sensing, and communication technologies, and draws on advances in superconductors, semiconductors, magnets, and two-dimensional (2D) and topological materials.

Materials science and technology from across the entire spectrum of materials has enormous potential for impacting the quality and sustainability of Earth's environment. One such area that has seen recent progress is in designing new materials to catalyze a range of important chemical reactions. For example, researchers have learned a lot about the role of surface conditions on efficient catalysis, such as in plasma-assisted hot electron catalysis. Future research could certainly improve sustainable

manufacturing of materials—for example, choice of raw materials, energy-efficient manufacturing methods, and recyclability. This opportunity calls especially for cooperation between universities, national laboratories, and industry, a need that appears multiple times in this report.

Continued investment in research infrastructure at all levels is essential for the health of the U.S. materials science enterprise. This includes assets ranging from instrumentation at university laboratories to the largest facilities in our national laboratories. This infrastructure constitutes a treasure for U.S. materials research, and it must be sustained at world leadership levels for the health and productivity of the field.

ILLUSTRATIVE ADVANCES FROM THE PAST DECADE

The past decade has seen extraordinary advances in materials research, and these advances cut across the full range of materials classes. For example, graphene—which received only modest attention in the last decadal survey of the discipline—has since spawned an exciting field of other 2D materials. Perhaps more importantly, graphene inspired work on new physical phenomena, with potential utility in many electronics applications such as solar cells, transistors, camera sensors, digital screens, and semiconductors. Another surprise of the last decade has been the evolution of additive manufacturing (AM), which while available for decades, has now emerged as an important process that can be used for both mass production as well as for one-off fabrication on demand. A few other major materials advances from the last decade include affordable light-emitting diode (LED) lighting, flat panel displays, and improved batteries.

Some important developments were the product of pure discovery-driven science (e.g., topological insulators), while others arose through concerted technological efforts (e.g., Gorilla Glass), and still others represent some combination of the two (e.g., additive manufacturing and vitrimers). Two major government initiatives—the Materials Genome Initiative (MGI), and the National Nanotechnology Initiative (NNI)—played important roles in stimulating materials research in the United States.

Exciting advances were achieved over the past decade in metals, bulk metallic glasses, high-performance alloys, ceramics and glasses, among other classes. Composite and hybrid materials have found high-value applications owing to their abilities to withstand harsh environments; as bulk, composite, and coating materials; and for their functionality in devices. Advances in coating technologies have led to increased reliability and their use in thermal and environmental protection systems. Layered material systems are replacing advanced monolithic materials in a growing number of applications where the unique properties and functionality of each layer provides dramatically increased performance and life. Great advances have been seen in polymers and in biomaterials of many kinds, and in soft matter such as colloids and liquid crystals.

Superconductivity has remained a fertile field, while the area of quantum materials more generally—including materials such as quantum-spin liquids, strongly correlated thin films and heterostructures, novel magnets, graphene and other very thin materials, and topological materials—is advancing rapidly.

ILLUSTRATIVE RESEARCH OPPORTUNITIES

Building on these recent advances, the study also found many examples of compelling materials research opportunities anticipated to arise in the coming decade. These exciting opportunities span the full range of materials classes and hold the promise of many valuable applications.

Our fundamental understanding of metals and alloys will continue to advance through increasingly coupled experimental and computational modeling, with real-time characterization of materials as their conditions and behavior change. New directions will also come from innovations in the design, composition, processing, and fabrication methods that take advantage of advanced capabilities in

materials manufacturing. High-entropy alloys (which have five or more elements present at comparable concentrations) will continue to offer considerable promise in the next decade. Such materials offer the possibility of overcoming dilemmas and barriers associated with traditional alloys, such as strength-ductility trade-offs. A second nontraditional area of metals that seems poised for advances is that of nanostructured metallic alloys, whose morphology and intricate structure is controlled at the nanoscale (e.g., nanotwinned metals).

Much of the research in semiconductors and other electronic materials will continue to be driven by the information and computation technology industries, moving toward increasingly complex monolithic integration devices, more highly functional microprocessors, and chips that take full advantage of three-dimensional (3D) layouts. Included will be materials for new devices that combine the functions of memory and logic, and other devices with energy-efficient architectures capable of executing machine learning and other algorithms that significantly differ from traditional computer logic and architectures. Research that will enable more efficient power management, at many scales of power and voltage, will also continue to be a major focus.

Two-dimensional materials, including graphene, offer opportunities for exploring the nature of surface electronic states. By layering such materials, the weak interplay between layers and the presence of designed defects presents a rich area for discovery, with potential opportunities for electronic and optical applications. Topological materials, whose properties are determined by topological properties of their excitation spectra, will continue to offer a wide range of areas for exploration, with the potential for a host of applications.

Some of the opportunity areas identified for ceramics are energy-efficient processes for their creation, which will enable the production of denser and ultra-high-temperature ceramics. Increased capabilities for characterization and processing are opening new opportunities in glass research, leading perhaps to their service as solid electrolytes for energy storage and for nonlinear optical devices.

Composite materials will become increasingly tailored for more advanced applications, extending well beyond the structural roles they traditionally have performed. Areas of promise include incorporating biomaterials as constituents and developing materials with properties that can change in a desirable and predictable manner over time. In the area of hybrid materials, perovskites will continue to draw significant interest, largely because of their potential advantages for single-junction solar cells. Hybrid nanocomposites, because of their constituent particles' good optical and high carrier-mobility properties, offer promise for applications in optoelectronics and photovoltaic conversion technologies.

Architected and metamaterials are of interest principally because of their designed structures, typically at the micro- or nanoscale levels, which offer a wide range of enhanced functionality to the devices in which they are incorporated. Lightweighting, through the designed distribution of a material's composite cells, offers opportunities for a host of technologies in aerospace, transportation, and energy generation, among others. Multifunctional materials, such as those that provide both structure and also thermal management, enhanced communication, or sensing capabilities, are an increasingly important segment of this materials class. Metamaterials are another important class, whose structure provides specific functional responses, and they offer tremendous opportunities in many different technologies such as energy-efficient light sources, sensing applications, thermal engineering, and microwave technology. This discussion of promising research opportunities is only illustrative. The full report provides further detail about these directions, plus additional ones.

> **Key Finding:** Research into metals, alloys, and ceramics continues to provide fundamental understanding of atomic-scale processes that govern synthesis-microstructure-property relations in many classes of materials. Armed with this understanding and state-of-the-art synthesis, characterization, and computational tools, novel alloys and micro/nanostructures with extraordinary properties are being realized. Traditional areas of materials research can have surprising new developments, for example, in multicomponent, high-entropy alloys and inorganic glasses.

Key Recommendation: Federal funding agencies (NSF, DOE, DOD) should maintain robust programs to support, and in some cases expand, fundamental research in long-established areas such as metals, alloys, and ceramics.

Key Finding: Quantum materials science and engineering, which can include superconductors, semiconductors, magnets, and two-dimensional and topological materials, represents a vibrant area of fundamental research. New understanding and advances in materials science hold the promise of enabling transformational future applications, in computing, data storage, communications, sensing, and other emerging areas of technology. This includes new computing directions outside Moore's law, such as quantum computing and neuromorphic computing, critical for low-energy alternatives to traditional processors. Two of the National Science Foundation (NSF)'s "10 big ideas" specifically identify support of quantum materials (see *The Quantum Leap: Leading the Next Quantum Revolution* and *Midscale Research Infrastructure*).

Key Recommendation: Significant investments by, and partnerships among, NSF, DOE, NIST, DOD, and IARPA will accelerate progress in quantum materials science and engineering, so crucial to the future economy and homeland security. U.S. agencies with a stake in advanced computing, under the possible leadership of DOE's Office of Science and NNSA laboratories and the DOD research laboratories (ARL, NRL, AFRL), should undertake to support new initiatives to study the basic materials science of new computing paradigms during the next decade. To remain internationally competitive, the U.S. materials research community must continue to grow and expand in these areas.

DEMAND FROM THE ULTIMATE APPLICATIONS

Fundamental connections exist between the broad field of materials research and the needs and interests of the industrial sector. Looking just at national security as an example, materials research has led to new materials that provide better armor that weighs less, to batteries that deliver more power to the warfighter in the field, and to materials better able to withstand extreme conditions, such as ultra-high-temperature materials for hypersonic flight and propulsion systems operating above 2000°C.

In energy-related industries there is growing demand for high-performance materials that are able to perform under a variety of extreme operating environments. Two examples of demanding applications are lightweight, high-strength, high-toughness materials for aerospace and terrestrial transportation applications and structural materials and fuel systems for advanced fission or fusion energy systems capable of extraordinary resistance to high radiation doses. More generally, energy challenges span production, distribution, transduction, and utilization. Materials such as improved photovoltaics and advanced batteries contribute fundamentally. Energy utilization can be improved through materials development such as better catalytic materials.

Another wide-ranging demand is for materials needed to move, store, pump, and manage heat. Over 90 percent of the energy used by humans for electricity, for heating and cooling applications, and for transportation originates from thermal processes. Consequently, even small efficiency improvements in the ability to control and convert thermal energy has a significant impact on the world's energy use.

Throughout the materials research community there is a broadly voiced desire for greater interactions among universities, private enterprise, and national laboratories. Efforts to streamline cooperation and flow of information among these major engines of creativity and innovation in materials science and technology will pay dividends. The continuous and desirable interplay of basic science stimulating practical advances and technological challenges stimulating new fundamental research should be reinforced at every opportunity. The United States needs to ensure that it is translating basic discoveries into practical technologies. These considerations lead to a recommendation for a new sort of

funding mechanism designed to stimulate faculty, students, industrial scientists, and engineers to engage in intimate teamwork.

> **Key Finding:** Many of the real-world challenges and opportunities in materials research occur at the intersections among traditional disciplines, and at the interfaces between fundamental and applied research. Pure science often benefits from proximity to applied research. Collaboration and information transfer among different disciplines and among academia, industry, and government laboratories greatly increases the likelihood of successfully meeting these challenges and capitalizing on these opportunities.
>
> **Key Recommendation: Government agencies, led by the Office of Science and Technology Policy (OSTP), should work with high priority to foster communication among materials research stakeholders through the support of interdisciplinary research and the development of modalities for freer flowing interactions among universities, private enterprise (including start-up ventures), and national laboratories.**
>
> **Key Recommendation: The White House Office of Science and Technology Policy (OSTP) should provide leadership in the development of awards that enable diverse funding agencies to work together when needed to facilitate collaboration among university and industry researchers.**
>
> **Key Recommendation: The National Science Foundation (NSF) should develop a new type of center that will enable, and indeed stimulate, students, faculty, and industrial scientists and engineers to work side by side. Such a Discovery to Translation Materials Research Center (DTMRC) would create a unique learning and research environment. The effort should be supported by several NSF directorates and should continue for a minimum of a decade.**

The concept of a DTMRC would complement NSF's existing Materials Research Science and Engineering Centers, which promote fundamental research, and its Engineering Research Centers, which promote technology development, by bringing both into functional synergy in an unprecedented manner. The desire to connect basic materials research more cooperatively with technology should in no way be taken as lack of support for high-risk, fundamental research, which continues to be of critical importance.

> **Key Finding:** Materials science and technology has an enormous impact on the quality and sustainability of Earth's environment across the entire spectrum of materials types. This is another important opportunity for university, national laboratory, and industry cooperation.
>
> **Key Recommendation: Research in numerous directions that improve sustainable manufacturing of materials, including choices of feedstocks, energy efficiency, recyclability, and more, is urgently needed. Creative approaches for funding materials research toward sustainability goals should be developed by NSF, DOE, and other agencies.**

INFRASTRUCTURE NEEDS

Many of the advances in materials research over the last decade are a consequence of continued investments and improvements in the tools used to conduct this research. However, to unlock the promise of the many emerging opportunities, the study identified a number of structural steps that are necessary to facilitate the greatest effectiveness of materials research in the United States.

The past decade has seen significant advances in the characterization, synthesis and processing, and computational capabilities available to materials researchers, enabling previously unachievable materials insights. Characterization has been advanced especially through tools such as transmission

electron microscopy, atom probe tomography (APT), scanning probe microscopy, ultrafast probes, and 3D- and 4D-characterization capabilities (where 3D is our common three-dimensional space with length, width, and depth, and 4D adds the dimension of time). Precision synthesis promises to transform materials science in a revolutionary way. A number of methods and tools are enabling new capabilities in precision synthesis. The state of the art now allows researchers to control, with fidelity and exactness, the placement and arrangement of atoms, molecules, and defects—with the latter being of importance because they often control material properties.

In the area of computational capabilities, researchers have seen significant improvements in modeling materials on multiple length scales, enabling (for example) the calculation of material properties with high fidelity. These computationally derived results are being used to predict structure-property relationships for many material types, discover new structures, and enhance the interpretation of experimental data. In addition to physics-based models, data-driven machine learning has been used to explore materials compositional space, identify new structures, discover quantum phases, and identify phases and phase transitions.

Another major enabling advance has been through the confluence of computational design of material properties, fabrication processes with nanometer to micrometer control, and experimental characterization methods with equally fine resolution. The integration of these capabilities has made it possible to create novel bulk materials with radically superior properties via architectural control at the appropriate scales. In much the same way that arches, columns, beams, and buttresses revolutionized the construction of buildings, towers, and bridges in past centuries, the materials community is now exploiting material architecture to expand the material design space in multiple dimensions, independently manipulate material properties that are currently coupled, and develop materials with vastly superior properties than can be achieved with solid objects. The large amounts of data generated at some of the major U.S. materials facilities has led to a strong interest in coupling these experiments with modeling and simulation capabilities. Several agencies have developed advanced computational facilities that play major roles in predictive modeling of functional materials and also in coherently understanding materials across many length scales.

Capabilities for assessing and characterizing materials, processing and synthesizing those materials, and modeling and simulating their properties are at the heart of materials research. The network of instruments and facilities that provide researchers the ability to carry out these investigations—from the individual investigator, through midscale instrumentation facilities and science research centers, to national facilities—is the infrastructure that supports the entire materials research enterprise.

Enormous demand on research infrastructure exists in all subfields of materials research, and over the past 10 years the ever-rising costs of acquiring and maintaining state-of-the-art research infrastructure, combined with a lack of adequate funding avenues for instrumentation, have culminated in a critical situation for all of materials science and engineering in the United States.

For the most part, the federal agencies, private foundations, and industry that fund most university research do not provide funding for the instrumentation that is needed to carry out that work. The NSF is the major exception, sponsoring research instrumentation through its Major Research Instrumentation (MRI) program. But that program is not large enough to address the current needs across materials research and engineering. The Department of Defense (DOD)'s Defense University Research Instrumentation Program (DURIP) can help in principle, but the level of its typical grant is too low for a large portion of the instruments used in materials science and engineering. The Department of Energy (DOE) operates impressive scattering facilities that are integral to several fields of materials research, just as the National Institute of Standards and Technology (NIST) Center for Neutron Research and the National Aeronautics and Space Administration (NASA)'s portion of the International Space Station (ISS) support some key materials research. However, those sorts of national facilities, while essential for our continued progress in materials research, cannot satisfy the need for research infrastructure *at universities*, where much of the nation's forefront research in materials is carried out. In many cases, it is critical to have instrumentation on campus—for example, a research project that involves synthesis of new materials typically requires a constant and immediate feedback loop between synthesis, structure,

and property measurements that may go through many cycles within a short period of time. It is not feasible to carry out this research by relying on remote facilities. This is true for most materials research.

As a result of the lack of funding options, the burden to support research instrumentation has been shifted largely to the universities. The typical result is that universities support new research instrumentation as part of a package to attract young experimentalists. But the consequence of that model is a lack of funding to sustain and upgrade the instrumentation over time. The model also leads to downward pressure on hiring of young people.

Key Finding: Infrastructure at all levels, from midscale instrumentation for materials characterization, synthesis, and processing with purchase costs of $4 million to $100 million in universities and national laboratories to large-scale research centers like synchrotron light sources, free electron lasers, neutron scattering sources, high field magnets, and superconductors is essential for the health of the U.S. materials science enterprise. Midscale infrastructure, in particular, has been sorely neglected in recent years, and the cost of maintenance and dedicated technical staff has increased enormously.

Key Recommendation: All U.S. government agencies with interests in materials research should implement a national strategy to ensure that university research groups and national laboratories have local access to develop, and continuing support for use of, state-of-the-art midscale instruments and laboratory infrastructure essential for the advancement of materials research. This infrastructure includes materials growth and synthesis facilities, helium liquefiers and recovery systems, cryogen-free cooling systems, and advanced measurement instruments. The agencies should also continue support of large facilities such as those at Oak Ridge National Laboratory, Lawrence Berkeley National Laboratory, Argonne National Laboratory, SLAC National Accelerator Laboratory, National Synchrotron Light Source II (Brookhaven National Laboratory), and National Institute of Standards and Technology—and engage and invest in long-range planning for upgrades and replacements for existing facilities.

Key Finding: Progress in three-dimensional (3D) characterization, computational materials science, and advanced manufacturing and processing have enabled an increasing digitization across disciplines of materials research and has in some cases dramatically accelerated and compressed the time from discovery to inclusion in new products.

Key Recommendation: Federal agencies (including NSF and DOE) with missions aligned with the advancement of additive manufacturing and other modes of digitally controlled manufacturing should by 2020 expand investments in materials research for automated materials manufacturing. The increased investments should be across the multiple disciplines that support automated materials synthesis and manufacturing. These range from the most fundamental research to product realization, including experimental and modeling capabilities enabled by advances in computing, to achieve the aim that by 2030 the United States is the leader in the field.

Key Finding: The Materials Genome Initiative, and the earlier Integrated Computational Materials Engineering approach, recognized the potential of integrating and coordinating computational methods, informatics, materials characterization, and synthesis and processing methods to accelerate the discovery and deployment of designer materials in products. The translation of these methodologies to specific industries has resulted in numerous successful applications that have reduced the development time with corresponding cost savings.

Key Recommendation: The U.S. government, with NSF, DOD, and DOE coordinating, should support the quest to develop new computational and advanced data-analytic methods, invent new experimental tools to probe the properties of materials, and design

novel synthesis and processing methods. The effort should be accelerated from today's levels through judicious agency investments and continue over the next decade in order to sustain U.S. competitiveness.

NATIONAL COMPETITIVENESS OF U.S. MATERIALS RESEARCH

The importance of materials research to a country's economic well-being and security is now a given, and countries the world over pursue national programs to support materials research and to facilitate the transition of that research to the marketplace. As part of this study of progress in materials research, an examination was made of the contribution of materials research to the world economy and materials programs and investment in a select number of countries. One salient result of that examination is that many countries' programs are more focused and more directly tied to economic development than the program of the United States. Asian countries, most notably China and South Korea, now invest a greater fraction of their gross domestic (GDP) in materials research than do the United States and European countries.

Key Finding: Intense competition among developed and developing nations for leadership in the modern economic drivers, including smart manufacturing and materials science, will grow over the coming decade.

Key Recommendation: The U.S. government, with input from all agencies supporting materials research, should take coordinated steps beginning in 2020 to fully assess the threat of increased worldwide competition to its leadership in materials science and in advanced and smart manufacturing. The assessment program, which should be established on a permanent basis, should also define a strategy by 2022 to combat this threat.

Materials research is a critical underpinning to economic growth as well as national competitiveness, wealth and trade, health and well-being, and national defense. The impact that materials research has had on emerging technologies, national needs, and science has been important to date, and it is expected to become even more so as the United States moves through the digital and information age and faces current and future global challenges. Many of the world's larger nations and economies have recognized this relationship, and recent trends show that today many nations have developed and articulated national investment strategies to ensure robust progress in materials research for national competitiveness in a global economy. The impact that materials research has had on emerging technologies, national needs, and science has been important to date, and as the United States moves through the digital and information age and faces current and future global challenges, this impact is expected to become even more important.

1

Brief Survey of Developments over the Decade

Producing a survey for the next decade of a field as immense and significant as materials science—and a report that contributes to advancing the field—is a complex and engaging responsibility. As in most areas of science, the pace of change in materials research (MR) is accelerating owing to new tools and insights. By studying earlier decades and reading the reports that were produced, researchers know to expect the unexpected, which is precisely the allure of science.

There have been surprises, to be sure, in the last decade. It is useful to examine a few examples of important developments that were not foreseen. For example, although graphene was first reported in 2004, it was given scant mention in the previous decadal survey in 2010. Since then, graphene has spawned an exciting field of other two-dimensional (2D) materials, and perhaps more importantly, it has instigated work on new physical phenomena, with potential utility in many electronics applications such as solar cells, transistors, camera sensors, digital screens, and semiconductors. Soon after the discovery of graphene, theorists predicted what are now called *topological insulators*, materials that are insulators in the interior, owing to a Fermi level that falls within the bulk bandgap, but whose surface contains conducting states. As a result, electrons move along only the surface of such materials. (See Figure 1.1.)

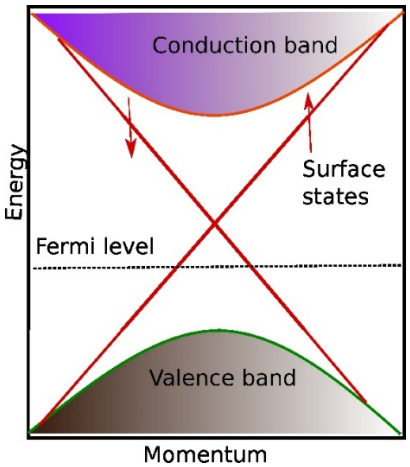


FIGURE 1.1 Energy versus momentum for topological insulators, showing surface states that traverse the bulk bandgap. SOURCE: Azimatu, "Band Structure of a Topological Insulator," image, July 27, 2018, https://en.wikipedia.org/wiki/File:Topology_azeema.jpg, Creative Commons Attribution-Share Alike 4.0 International License, https://creativecommons.org/licenses/by-sa/4.0/deed.en.

Moreover, the electrons flowing over the surface of a topological insulator are all aligned in a specific way: their spins are locked at right angles to their direction of motion. The original theoretical proposal pointed to graphene as an example, but the spin-orbit interaction in graphene is too weak for practical realizations. In 2008, materials exhibiting the predicted properties were synthesized with crystalline structures based on bismuth antimonide and related materials. Symmetry-protected topological order has now been shown to occur in three-dimensional (3D) materials as well. These recent discoveries

contributed to recognition in the 2016 Nobel Prize in physics of earlier work by Thouless, Kosterlitz, and Haldane on phase transitions and transport, where topology plays a crucial role. This was a gratifying capstone to a body of work in the last decade that was not anticipated 10 years ago. Subsequent chapters of this report discuss these discoveries and the opportunities based on them in more detail.

Another surprise of the last decade has been the evolution of additive manufacturing (AM), which has existed for decades and was initially known as stereolithography or rapid prototyping. Within the last decade, AM has emerged as an important process, which can be used not only for mass production but also for one-off fabrication on demand.[1] This general methodology was not mentioned in the last decadal report, perhaps for understandable reasons. Early AM was really 2D printing, over and over again, albeit interfaced with computer-aided design (CAD), which was very useful for producing realistic prototype models of objects ranging from medical devices to parts of complex shape.

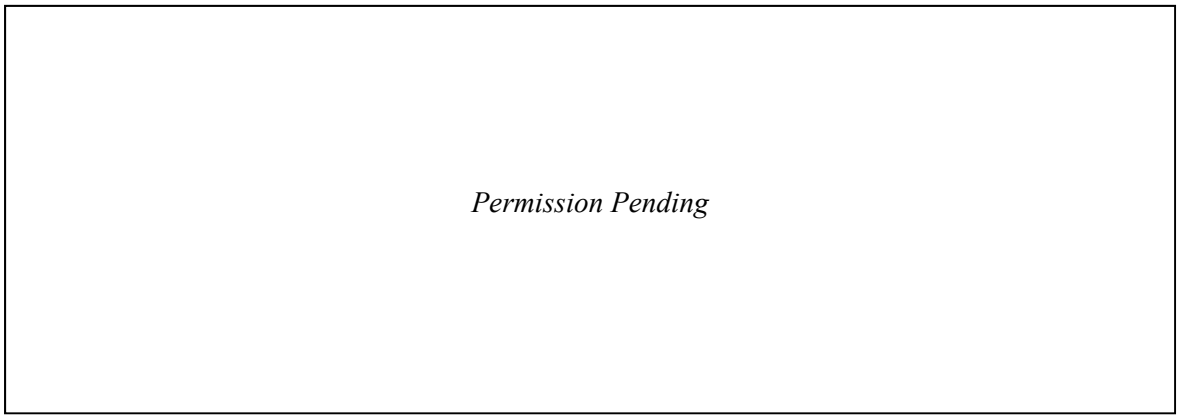


FIGURE 1.2 Engineers from General Electric are building a new turboprop engine using an advanced additive manufacturing technique called *direct metal laser melting*. This additive manufacturing method is producing a growing list of parts for numerous industries, making stronger components with less material waste that are impossible to create using traditional machining techniques. For the GE Catalyst Advanced turboprop engine example shown here, the design reduced 855 separate parts to just 12. As a result, more than a third of the engine is additively manufactured. SOURCE: GE Aviation, "GE93 Rendering," image, https://en.wikipedia.org/wiki/General_Electric_Catalyst#/media/File:General_Electric_GE93.jpg.

Early additive manufacturing was almost exclusively with polymeric materials. The 2010s were the decade in which parts made of metals like aluminum and titanium were first produced. They are now significant in many industries—aerospace in particular. (See Figure 1.2 and Case 2 in Section 5.3.) With the application of light and other fields to change the material during the process, additive manufacturing is no longer actually printing in 3D at all but instead is using spatially controlled polymerization (polymers) or fusion (metals and ceramics). With the advantages of CAD for AM, it is clear that much more is coming, as discussed in subsequent sections.

While some developments in the last decade were near-total surprises, others were the product of diligent work directed at a previously unrealized but desired scientific or technological objective. Self-healing polymers fall into this latter category, as they have been a recurring scientific goal for many years. Soft organic materials often have mechanical properties roughly similar to human tissue, so it is natural to explore self-healing in that domain of soft, noncovalently bonded materials produced, for example, by hierarchical self-assembly. Such materials have various uses, but they are not usually physically robust. Welding of polymers by diffusive interpenetration, induced by heating or solvents, is

[1] See, for example, https://3dprint.com/168461/us-navy-3d-print-a-thon/, accessed June 14, 2018.

possible but of limited use. Other major materials advances from the last decade include light-emitting diode (LED) lighting, flat panel displays, and improved batteries. In this survey, there is room to mention only a few examples, but all of them do have an effect on society.

Self-healing of polymers realized a new paradigm with the development of polymers with dynamically reconfigurable covalent bonds. One example, a remarkable new class of plastics now known as *vitrimers* (a term for glass-like polymers), was unanticipated 10 years ago. Vitrimers exhibit properties similar to silica glasses but in which the covalent bond network topology can be rearranged by exchange reactions without depolymerization. They remain insoluble and yet processable as bulk materials. The development of vitrimers, and other polymers with dynamic covalent bonds, has spawned new synthesis and processing research, discussed in Chapter 2.

Smartphone touch screen technology, which made its appearance at the beginning of the last decade, created entirely new roles for glass. This glass serves three functions: it enables user input, protects the display beneath it, and transmits the information on the display to the user even after years of use, in addition to resisting breakage owing to accidental drops. The material has to be mechanically durable, scratch resistant, thin, stiff, dimensionally stable, flat, smooth, impermeable to water, and transparent to both visible light and radio waves. Corning was able to surmount all of these challenges in a very short time through application of deep understanding of glass composition and manufacturing technology. The short time scale dictated older, familiar glass technology and existing manufacturing facilities as the starting point. Successive matters of processing conditions, bubble formation, and color formation were solved to yield Gorilla Glass,[2] which was not mentioned in the last decadal survey but is now nearly a $400 million annual market for Corning.

This set of prefatory examples has been selected to make several points. The first has already been expressed—namely, that none of these interesting developments was foreseen clearly as recently as 10 years ago—and so the committee introduces this decadal survey with humility. On the other hand, there were previous accomplishments on which these particularly striking advances in the last decade were built. Graphene set the stage for topological insulators. Repetitive 2D printing of polymers gave rise to a much broader field of additive manufacturing. A search for robustly self-healing materials led to the unique chemistry and properties of vitrimers and other polymers with dynamically reconfigurable covalent bonds. Motivation supplied by emerging smartphone technology spurred the development of Gorilla Glass.

A second point is that some important developments were the product of pure discovery-driven science (topological insulators), while others were concerted technological efforts (Gorilla Glass), and still others some combination of the two (AM and vitrimers). This is a strong argument for supporting materials research across a span of technology readiness levels, and for creating environments in which basic and applied research, as well as academic and industrial research, interact intimately.

A third point from these examples is that two are from industry and two are from academic institutions (one U.S., one international), providing evidence of the broad range of institutions generating modern, advanced materials science.

1.1 INDUSTRIAL PERSPECTIVES

The current decadal survey paid particular attention to understanding the industrial point of view, as the translation from basic research in universities and national laboratories into industry is the most effective path for deriving societal benefit in the form of useful products from basic materials research.

[2] See M.S. Pambiachi, M. Dejneka, T. Gross, A. Ellison, S. Gomez, J. Price, Y. Fang, P. Tandon, D. Bookbinder, and M.-J. Li, 2016, "Corning Incorporated: Designing a New Future with Glass and Optics," pp. 1-38, in *Materials Research for Manufacturing: An Industrial Perspective of Turning Materials into New Products* (L.D. Madsen and E.B. Svedberg, eds.), Springer.

To assess how industries viewed the impact of materials science and materials engineering as enabling technologies, a selection of companies from different sectors were asked to provide their input by responding to four requests and questions:

1. Identify scientific achievements in materials research, including materials synthesis and processing, made in the last decade that have enabled your industry to make major breakthroughs in product development.
2. Identify scientific materials roadblocks or new materials that must be addressed for your industry to make the next major advance in technology or product development.
3. Are there enabling technologies and tools (e.g., advanced characterization, computation, synthesis and processing) needed to make these advances happen?
4. In terms of materials research and development within your organization, is it conducted in-house in the United States or globally, with U.S. universities or with universities outside the United States? If you work internationally, why?

Sixteen companies, spanning a range of sizes and technology sectors, responded to these four requests. The high-level challenges and opportunities common across the different industry sectors are summarized below. The committee believes that this input from industry is important to assess the overall societal benefit of materials research.

The combined responses to the first inquiry highlighted the importance of advances in properties of materials, development of new materials and coatings, increased durability of materials, and weight reduction. Advances in materials synthesis and processing, deposition processing methods, robotics, and high-throughput discovery, in addition to the growth in additive manufacturing for low-volume components, were seen as enabling technology developments. Sustained by efforts such as Integrated Computational Materials Engineering (ICME)[3] and the Materials Genome Initiative (MGI), computational approaches, statistical analysis, and data analytics have been used to reduce the cost of developing a new material for a specific application. Incorporation of these approaches were seen as impacting not only how materials were developed but also the in silico testing of components to determine their functionality and durability.

The second inquiry was designed to identify the improvement on material properties or performance of new models or computational methods, or of experimental tools, needed to address the specific roadblocks preventing the next major technology advance within their own spheres. Industries identified several areas in which advances would have impact. Accelerated discovery of new materials or the optimum structure and composition of a material and moving beyond the advances enabled by the ICME approach to "materials by design" was seen as enabling breakthroughs in the future.

For example, the need for new materials to go "beyond silicon" for increased power, frequency, or improved energy efficiency in information technologies; to extend performance of materials through novel coatings or clean energy-storage technologies; and to create materials in which the sensors are an embedded and integrated component of the material were all seen as areas of opportunities that would be accelerated by utilizing an integrated computational materials science and engineering approach.[4] Others saw the potential impact on their industry of adopting an integrated computational science and engineering methodology, as this approach had yet to be implemented within their sector. Enhancements in synthesis and processing, deposition techniques, and joining technologies, especially between dissimilar materials, were identified as areas in which advances were needed to enable use of new

[3] Committee on Integrated Computational Materials Engineering, National Materials Advisory Board, Division on Engineering and Physical Sciences, National Research Council, 2008, *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security*. The National Academies Press, Washington, D.C., p. 132.

[4] Defined as ICME.

materials and to improve product design. It also was noted that there was a need to be able to scale the synthesis and processing methods used for small batches in university research laboratories to industrial-scale manufacturability. Scalability science was seen as an area of opportunity to realize significant gains when producing new materials at larger volumes. For the potential of additive manufacturing to be realized, it was pointed out that there was a pressing need to understand the process itself, to control the process at all length scales to optimize the functionality and properties, to determine the properties of materials produced by additive manufacturing, and to accelerate component certification. Last, it was recognized that there was a pressing need for a shift in the education of students to create a workforce skilled in the use of data analytics, materials informatics, and computational methods to increase the rate of innovation in materials research.

For the third inquiry, several technologies were identified that would enable the breakthroughs discussed in response to item 2. In the area of theory, modeling, and simulation, advances were identified that included computer modeling and simulation of processes that occur during synthesis and processing—particularly in the area of additive manufacturing. There is an ongoing need to advance the realization of the vision of accelerated materials discovery and development enabled by computer simulations and to actually produce new materials faster. New computational chemistry tools are needed to improve the predictions around chemical reactions and their resulting products. Advances are required for predictive models that describe the evolution of material properties for materials exposed to harsh environments, where the environment is defined by the material and application. The models and simulations must predict the long-term properties of materials in specific environments as new materials are being deployed in applications with a design life of 50 years and beyond. Last, there is a need to develop tools to enable the rapid exploration of materials and processing space to discover new materials and compositions and to optimize the synthesis and processing routes to make them with the desired properties.

With advances in synthesis and processing methods, there is a need for new in situ diagnostic capabilities to understand the physical and chemical reactions. To have meaningful impact, these diagnostic tools need to be coupled with computational tools to analyze and interrogate the data and to make decisions. It was noted that the introduction of machine learning algorithms and data analytics had the potential to accelerate insight and advances in this area. Coupled with the use of theory, modeling, and simulations to identify potential new properties, structures, and compositions of materials was the need for the development of high-throughput screening and testing methods.

The fourth and final inquiry was designed to assess how and where U.S. industries conduct research and how they interact specifically with U.S. universities. The responses varied depending on the nature of the industry, with some conducting all of their research in-house because of the proprietary nature of their products, the need to protect prior intellectual property, and the complexity often associated with negotiating intellectual property agreements with U.S. universities. Other companies conduct research in their facilities but have collaborations with other industries and universities globally. The reason for conducting the research with entities across the world varied and included access to a diverse talent pool, geolocation in relation to their global business, specific research expertise that might not be available in the United States, and gaining access to unique facilities and capabilities. This latter interaction was especially significant in cases of specialized experimental tools or tools that were too expensive for a single company to own and operate. Here, the major scientific facilities operated by the Department of Energy (DOE) and the National Science Foundation (NSF) are noteworthy. It was noted that in some areas, the United States had ceded leadership in materials research in a specific area, requiring that companies must conduct research outside the United States. The responses from industry raised some concerns about the state of industrially relevant or industrially sponsored research being conducted at U.S. universities. Some responses implied that industrial research being conducted at universities outside the United States is increasing, owing to difficulties in reaching intellectual property (IP) agreements and the cost of conducting research at U.S. universities.

1.2 DEFENSE AND NATIONAL SECURITY PERSPECTIVES

This entrée into the current decadal survey concludes with some observations concerning defense and national security. Materials research plays an important role in U.S. national defense. It is easy to see how new materials with improved properties can produce, for example, better armor that also weighs less, systems that can deliver more power to the warfighter in the field, and materials that can withstand extreme conditions for more efficient aerospace components, allowing for faster flight while using less fuel. Not only are new materials for new systems important for U.S. national defense, today there are also many legacy systems where spare parts are increasingly harder to get. There are also many situations where materials used in the past are no longer desired. One such recent example is in corrosion-protective hexavalent chromium coatings that are effective but toxic. It is clear that advanced materials are key to many of the Department of Defense (DOD) funding and operational initiatives. The major mission agencies, including the Air Force, Navy, and Army, gave presentations to the committee during the November 2017 committee meeting. One of the key aspects discussed was the importance of better understanding how and why materials fail when used under extreme conditions, and by extension how to avoid such failures. Materials research issues focusing on failures will always benefit from more data, and thus better characterization techniques would be beneficial, especially in situ methods that would work at extreme conditions; today, many failure processes are often not fully understood, thus preventing the design of mathematical models for use in predicting the material behavior. Clearly, there are opportunities for materials research to make inroads not only in modeling at multiple length scales, but also for in situ characterization. Although motivated by differing objectives, there is strong convergence in the priorities of both the commercial and the defense sectors on the need for strong emphasis on advancing computational and data science, and for investment in increasingly powerful characterization tools, including those that can work under challenging conditions such as extreme pressure and under real-time process conditions.

National security considerations also play a significant role in developing best steps forward in the area of international collaboration. Sections in this report that discuss collaborations at facilities such as the International Space Station (ISS), European Organization for Nuclear Research (CERN), Synchrotron-Light for Experimental Science and Applications in the Middle East (SESAME), and Laser Interferometer Gravitational-Wave Observatory (LIGO), and also Section 5.4, emphasize the value of engaging on the international level, but impediments are appearing and increasing. Although the concerns leading to these impediments are serious and must be respected, U.S. materials research will be held back if sensible ways to collaborate and to exchange personnel and basic science information are not only allowed but are also encouraged. Cooperation, even in the face of competition and political conflicts, is a long-standing U.S. tradition dating back to the Cold War and before.

1.3 CONCLUSION

Three prominent conclusions can be derived from the information presented in this chapter. The first is that surprises occur because of both fundamental exploratory research and persistent pursuit of challenging goals with no precise roadmap for their attainment. The second is that the investigation of industry perspectives revealed many pieces of useful information, but none more prominent than the increasingly essential role of integrated computational materials science, data science, and machine learning. This is reinforced in subsequent chapters based on capabilities in universities, industry, and national laboratories. The third conclusion is that industrial-university research relationships should be further optimized to make them more fruitful and rewarding to all participants.

Some other aspects of this survey of materials research that have been less prominent in previous reports are more extensive and penetrating insights into the role of materials research in international

economic competitiveness and of national security. Chapter 5 develops the case, based in part on the 2016 book *Advanced Materials Innovation, Managing Global Technology in the 21st Century*,[5] that over three-quarters of all economic growth in coming decades will be attributable to the development and application of advanced materials, and that investments in materials research are tied directly to national competitiveness and economic prosperity. This is an important new lens through which researchers must evaluate the importance of materials research. Materials research exerts its influence demonstrably in many sectors of the economy, including computer and information technology, energy, biotechnology and healthcare, transportation, construction, and manufacturing. One way to look at where materials research can have an important societal impact in the coming decade is to consider what materials research can do in advancing the 14 Engineering Grand Challenges set up by the National Academy of Engineering[6]—these span the gamut from improving health to preventing climate change. The committee encourages the reader of this survey to consider the many opportunities available in providing access to clean water, improving the urban infrastructure, engineering better medicines, reverse-engineering the brain, and making solar energy economical, to mention just a few of many more challenges. On the international front, the committee is cognizant of the fact that several economies—China's in particular—have significantly increased research and development (R&D) spending. In 2010, China, with the second largest science base in the world, spent about $212 billion gross (Government and Industry) on R&D, less than the United States ($408 billion). By 2015, China's expenditures had nearly doubled, to $409 billion, while those of the United States increased to only $496.6 billion.[7] Viewed in light of the influence of materials research on the economy, this is a significant fact.

1.4 KEY FINDINGS AND RECOMMENDATIONS

Key Finding: Advanced materials are increasingly central to everyday life and well-being. New developments are products of the broad and interdisciplinary field of materials science, drawing on all the traditional fields of science, engineering, and more recently, computer and data science (algorithms, big data, artificial intelligence, machine learning), with the special perspective that comes from a focus on materials. The health and future growth of materials research, and its capability to serve society, depend critically on the flow of information among its stakeholders, from university researchers to industrial engineers to government labs.

Key Recommendation: Government agencies, led by the Office of Science and Technology Policy (OSTP), should work with high priority to foster communication among materials research stakeholders through the support of interdisciplinary research and the development of modalities for freer flowing interactions among universities, private enterprise (including start-up ventures), and national laboratories.

Key Finding: Many of the real-world challenges and opportunities in materials research occur at the intersections among traditional disciplines, and at the interfaces between fundamental and applied research. Pure science is stimulated by proximity to applied research. Collaboration and information transfer among different disciplines and among academia, industry, and government laboratories greatly increases the likelihood of successfully meeting these challenges and capitalizing on these opportunities.

Key Recommendation: Government agencies, led by the Office of Science and Technology Policy (OSTP), should work with high priority to foster communication among materials

[5] S.L. Moskowitz, 2016, *Advanced Materials Innovation: Managing Global Technology in the 21st Century*, Wiley, Hoboken, N.J.

[6] See http://www.engineeringchallenges.org/, accessed August 8, 2018.

[7] NSF Science and Engineering Indicators, January 2018.

research stakeholders through the support of interdisciplinary research and the development of modalities for freer flowing interactions among universities, private enterprise (including start-up ventures), and national laboratories.

Key Recommendation: The White House Office of Science and Technology Policy (OSTP) should provide leadership in the development of awards that enable diverse funding agencies to work together when needed to facilitate collaboration among university and industry researchers.

Key Recommendation: The National Science Foundation (NSF) should develop a new type of center that will enable, and indeed stimulate, students, faculty, and industrial scientists and engineers to work side by side. Such a Discovery to Translation Materials Research Center (DTMRC) would create a unique learning and research environment. The effort should be supported by several NSF directorates and should continue for a minimum of a decade.

Key Finding: The integrated computational materials science and materials engineering methodology has had a significant impact on product development in specific industries, as the committee has learned through industrial input. There is potential for further impact through the inclusion of integrated data sciences into the materials research for all length scales and material types.

Key Recommendation: All government agencies funding materials research should encourage the use, when appropriate, of computational methods, data analytics, machine learning, and deep learning in the research they fund. They should also encourage universities to provide students of science and engineering exposure to these new methods by 2022.

Key Finding: Basic research in fundamental science directions, meaning work that neither anticipates nor seeks a specific outcome, is the deep well that both satisfies our need to understand our universe and feeds the technological advances that drive the modern world. It lays the groundwork for future advances in materials science as in other fields of science and technology. Discoveries without immediate obvious application often represent great technical challenges for further development (e.g., high-Tc superconductivity, carbon nanotubes) but can also lead to very important advances, often years in the future.

Key Recommendation: It is critically important that fundamental research remains a central component of the funding portfolio of government agencies that support materials research. Paradigm-changing advances often come from unexpected lines of work.

2

Progress and Achievements in Materials Research over the Past Decade

This chapter highlights select examples of the advances that have been made since 2008 in the broad field of materials science and materials engineering. It is impossible to document all of the progress that has been made, so this chapter emphasizes a selection of achievements in fundamental understanding and enhancements of the properties of materials, and the acceleration of materials development and optimization of the properties through use of computational methods. What is not covered in this chapter are advances that have been made in computational methods, the developments in experimental tools and capabilities as well as in synthesis, and processing methods that are applied by the materials community. These enabling methodologies have undergone significant advances in the last decade sufficient to warrant a separate chapter.

A significant development in this period was the announcement in 2011 by President Barack Obama of the Materials Genome Initiative (MGI). The ultimate goal of the MGI was "to discover, manufacture, and deploy advanced materials twice as fast, at a fraction of the cost."[1] The key to the initiative was the Materials Innovation Infrastructure (MII), which realized that progress would be accelerated by working at the intersection of computational materials science and engineering, materials informatics, and synthesis and processing, as well as material characterization and property assessment. This framework of combining the three areas was intended to operate synergistically across all seven components of the materials development continuum—discovery, development, property optimization, systems design and integration, certification, manufacturing, and deployment (including sustainability and recovery). Reduction in the time from discovery to deployment and in the overall development cost was envisioned to be achieved by replacing the current linear approach to the materials development continuum with one in which each area was in constant communication with all other areas. These different design concepts are captured schematically in Figure 2.1. For the envisioned change to become effective, the different sectors engaged in materials engineering need to be educated about the efficiencies to be gained by this approach and become willing to use materials developed through this approach. An example, selected from many possibilities, of how this methodology has been applied in industry is given in Box 2.1. This initiative impacted the federal funding agencies, with the result that material databases have proliferated and teams of experimentalists and computational materials scientists and engineers have been formed to address scientific challenges. This has impacted the discipline, with more multidisciplinary teams forming to tackle key material challenges.

[1] *Materials Genome Initiative for Global Competitiveness*, https://www.mgi.gov/sites/default/files/documents/materials_genome_initiative-final.pdf.

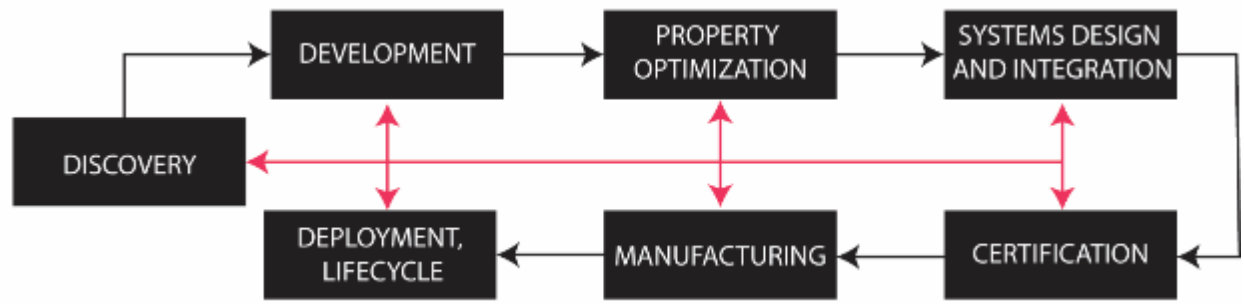


FIGURE 2.1 Linear versus continuous feedback materials continuum development. The traditional linear approach leads to longer and more expensive discovery to deployment cycles, whereas within the continuous feedback method each sector is in continual discussion with each and every other sector. The latter approach was seen as one in which the time from discovery to deployment of a new material would be reduced significantly from the typical 20 years for many industries.

2.1 METALS

2.1.1 Accelerated Development

Powered in part by widespread efforts such as the Integrated Computational Materials Engineering (ICME)[2] approach to materials development, the National Nanotechnology Initiative (NNI), and the Materials Genome Initiative (MGI),[3] metals research during the past decade has achieved numerous advances. (Although this section focuses on metals, it is clear that the aforementioned programs cover all materials, and that progress has been made on all fronts.) For example, bulk structural alloys designed with self-organized nanoscale dispersoids with strengths exceeding 1.5 to 2 GPa while still retaining acceptable ductility and fracture toughness have been developed. This is a remarkable advance compared to historical practical strength limits of <1 GPa for 20th century structural materials, one that can enable significant lightweighting and cost reduction in key structural components for transportation and energy applications. Similar improvements in high-strength structural alloys with adequate ductility or other targeted performance criteria have been discovered by efficient utilization of ICME approaches, leading to several examples of accelerated transition from material invention/discovery to practical industrial implementation. An example of this acceleration and the impact on industries is provided in Box 2.2.

[2] National Research Council, 2008, *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security*, The National Academies Press, Washington, D.C., https://doi.org/10.17226/12199.

[3] See https://www.mgi.gov/sites/default/files/documents/materials_genome_initiative-final.pdf.

High-entropy alloys (HEAs), multiprincipal element alloys, or complex concentrated alloys are composed of nearly equimolar concentrations of five or more metals that form extended solid solutions.[4] Since the first reported study on high-entropy alloys in 2004, research has dramatically expanded to approximately 1,000 journal publications per year. These alloys can be fabricated using conventional metal fabrication techniques as single- or multiphase materials with a variety of crystal structures.

BOX 2.1
Accelerating Product Development Through Computational Modeling of Manufacturing Processes

Advanced computational models are being used in manufacturing to accelerate the development and introduction of new materials into marketable products. The computational models capture manufacturing-history-sensitive materials information with manufacturing simulation and allow engineering product performance analysis to be conducted in silico. The impact is a significant acceleration of the product development cycle time. For example, Brunswick Corporation, and particularly its Mercury Marine division, used this approach for new aluminum and stainless-steel alloy development as well as castings to improve the performance of existing materials and products, and ultimately, to reduce production cost.

Figure 2.1.1 compares the deformation behavior of two types of rivets for use on boats produced by the Lund boat division and Mercury Marine. By using this approach, the companies compared different geometries and selected the one that met performance requirements in silico. This manufacturing deformation of each rivet was combined into an overall structural model of a boat and loaded with appropriate forces "in the computer" to assess boat durability. Therefore, they avoided the need to make and test different geometries, shortened product development time by approximately 35 percent, reduced the risk associated with interaction between the manufacturing process and the loading on the boat in service. This improved the end product and reduced development costs.

Permission Pending

FIGURE 2.1.1 Calculation of the maximum principal stress distributions for two rivet configurations. Stress concentrations are evident at the upper corners of the left rivet as tiny red areas, suggesting that these might become failure sites. SOURCE: Courtesy of Mercury Marine.

[4] There is no universally agreed-upon definition of a *high-entropy alloy*. Some researchers describe them as having at least five elements, while others have described four-component alloys.

BOX 2.2
Accelerating the Process of Alloy Development Through Computation

Ferrium S53 is an ultra-high-strength and corrosion-resistant steel that eliminates toxic cadmium plating, and Ferrium M54 is an upgrade from legacy alloys. Figure 2.2.1 demonstrates the time from development to deployment from eight years for Ferrium S53 and four years for Ferrium M54 steels. Ferrium S53 is flying as safety-critical landing gear on USAF A-10, T038, C-5, and KC-135 and on numerous SpaceX rocket flight-critical components. Ferrium M54 steel has been deployed on the U.S. Navy's T-45 safety-critical hook shank component, offering more than twice the life of the incumbent steel while saving $3 million in overall program costs.

Technology readiness levels are as follows: TRL 1 is basic principles observed; TRL 2 is technology concept formulated; TRL 3 is characteristic proof of concept; TRL 4 is validation in laboratory; TRL 5 is component validation in relevant environment; TRL 6 is system demonstration in relevant environment; and TRL 7 is prototype demonstration in operational environment. MMPDS refers to metallic materials properties development and standardization.

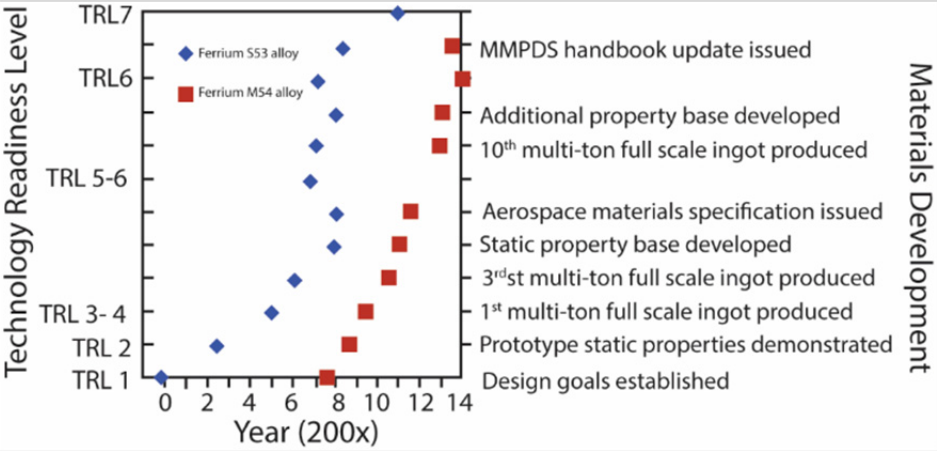


FIGURE 2.2.1 The timeline (from 2000 to 2014) for the development of two alloys, Ferrium S53 steel (8 years) and Ferrium M54 steel (4 years), licensing them to a U.S. steel producer and deploying into demanding applications. The accelerated timeline in the improvement of these alloys and their deployment in applications was enabled by applying computational methods to optimize the composition and structure to achieve the desired properties. The left vertical axis indicates the different technology readiness levels (TRLs), and the right vertical axis indicates some of the important milestones. SOURCE: W. Xiong and G. Olson, 2015, Integrated computational materials design for high-performance alloys, *MRS Bulletin* 40:1035-1044, doi:10.1557/mrs.2015.273, reproduced with permission.

The properties of these alloys are determined by a combination of the entropy (thermodynamics), sluggish diffusion (kinetics), structural distortion associated with the variation in the atomic size, and effects that are derived from the dependence of the properties on the composition. Several high-entropy alloys based on face-centered cubic and body-centered cubic crystal structures have been recently fabricated with mechanical properties superior to conventional alloys such as austenitic stainless steel. As an example, Figure 2.2 compares the fatigue properties of different classes of metals in a plot of the fracture toughness, a measure of the ability of a material to tolerate an existing flaw such as a crack, K_c, against the yield strength of the material, σ_y, a measure of the stress at which a material will start to

deform plastically.[5] From this figure, it can be seen that high-entropy alloys exhibit some of the highest fracture toughness values of metals. The dashed lines in the figure represent the size of the crack tip plastic zone ($=(1/\pi)(K_c/\sigma_y)^2$); this is a measure of the resistance of the material to the driving force behind propagation of a crack. A large plastic zone radius would indicate a higher resistance to crack propagation.

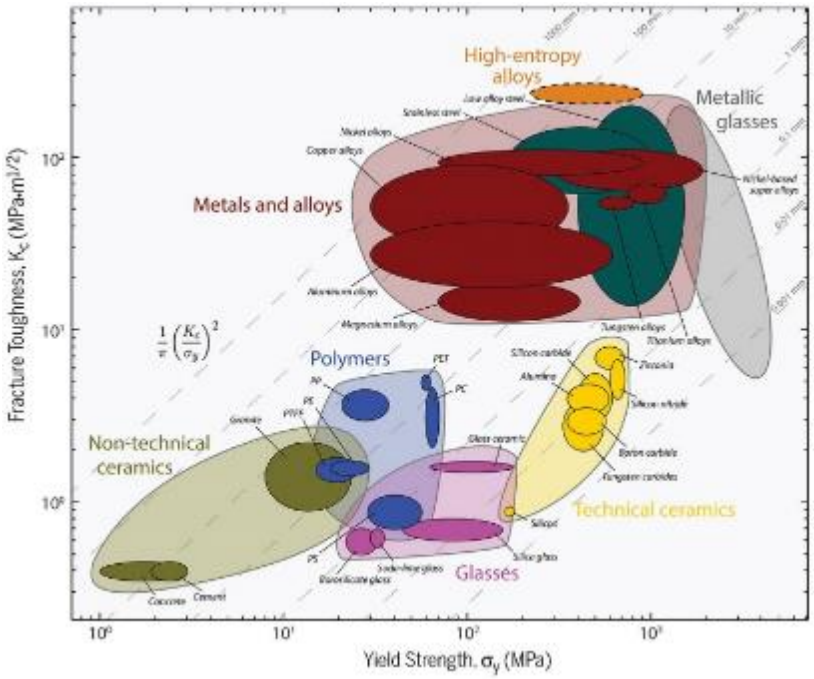


FIGURE 2.2 Comparison of the fracture toughness and yield strength of different materials showing the improvement in properties of high-entropy alloys. The dashed lines represent the radius of the crack tip plastic zone, which is equal to$(1/\pi)(K_c/\sigma_y)^2$. This parameter gives a measure of the resistance of the material against the forces driving the advance of a crack. The larger the plastic zone size, the higher the resistance to crack advance. In other words, more energy will need to be provided to advance the crack, as some is dissipated by plastic deformation. SOURCE: From B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, R.O. Ritchie, 2014, A fracture-resistant high-entropy alloy for cryogenic applications, *Science* 345:1153-1158, reprinted with permission from AAAS.

2.1.2 Bulk Metallic Glasses

Similarly, evolutionary advances achieved with bulk metallic glasses during the past decade have fostered their progression from a scientific curiosity into a variety of specialized commercial products. Bulk metallic glasses offer near net shape[6] formability, potential improvements in corrosion resistance, and useful strength and fracture toughness. The key scientific advance enabling the fabrication of commercial bulk metallic glasses is associated with improved understanding of the atomic compositions that suppress crystallization during cooling (while also providing attractive mechanical properties). Since the maximum sample size varies inversely with the critical cooling rate for crystallization, identification of atomic compositions with slow cooling rates for crystallization allow relatively large amorphous

[5] B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, R.O. Ritchie, 2014, A fracture-resistant high-entropy alloy for cryogenic applications, *Science* 345:1153-1158.

[6] *Near net shape* is an industrial manufacturing technique. The name implies that the initial production of the item is very close to the final (net) shape, reducing the need for surface finishing.

structures to be fabricated. Of the numerous metallic alloys that can be fabricated with an amorphous (glassy) structure by rapid quenching from the molten state, over one thousand have been identified that can quench in the amorphous structure even for relatively slow cooling rates, thereby enabling bulk (>1 to 10 cm thick) amorphous structures to be fabricated from a variety of alloy compositions.

2.1.3 High-Performance Alloys

A suite of specialized high-performance alloys with demonstrated significantly improved resistance to property degradation during exposure to extreme environments such as nuclear reactor irradiation, high temperatures, high applied stresses, and high strain rates have emerged during the past decade. For example, improvements in the processing conditions of oxide-dispersion-strengthened ferritic steels (enabled by atomistic modeling and nanoscale structural and chemical characterization) has led to the creation of several families of new alloys with ultrahigh densities ($\sim 10^{24}/m^3$) of nanoscale dispersoids. These new self-organized nanostructured alloys have room-temperature tensile strengths exceeding 1 to 2 GPa (over 50 percent stronger than conventional oxide-dispersion-strengthened or precipitation-strengthened steels), 10,000 hour thermal creep strengths exceeding 100 MPa for temperatures as high as 800°C (a nearly 200°C increase in upper use temperature compared to conventional ferritic steels), and unprecedented resistance to void swelling associated with neutron damage up to damage levels exceeding 500 displacements per atom (more than double the maximum allowable radiation damage level in conventional ferritic steels). These advances in high-performance, radiation-resistant structural materials provide the scientific basis for deploying new "Generation IV" nuclear reactors that offer significant potential improvements in fuel utilization, safety, electricity-generation economics, and reduced radioactive waste compared to current reactors.

Controlling the size of the grain is a traditional approach to enhancing the properties of metallic alloys, with impressive improvements in room-temperature properties achieved for nanocrystalline grain sizes. Since most nanocrystalline grains are susceptible to dramatic coarsening during prolonged operation at room temperature or higher, research during the past decade has been instrumental in identifying the roles of composition and structure, such as grain boundary junctions, on modifying grain growth and accompanying mechanical properties. The complexity of the structure of the grain boundary was shown to be dependent on the presence of impurities, temperature, pressure, and chemical potential. The interfacial phases formed have been termed *complexions* to distinguish them from bulk phases. It has been found that the impurities on the grain boundaries reside in specific sites, lower the interfacial energy, and, depending on the boundary character, can be periodically distributed along it.

In the last decade, alloys designed with stabilized interfaces and married with processing paradigms to produce nanostructured material at scale were transitioned to successful commercialization applications. For example, electrodeposited Ni alloys stabilized with W have been qualified for a variety of functional coating applications, including as a finish component in high-performance electrical connectors, where the alloy has been fielded on billions of components. Recent efforts at combining these nanostructure stabilization concepts in the domain of powder metallurgy have led to bulk sintered nanocrystalline components for use in construction tools and lightweighting applications.

The shift in materials used in construction to lightweight alloys such as aluminum and magnesium, development of high-strength low-alloy steels,[7] implementation of composite structural materials, and combinations thereof have introduced new concerns regarding corrosion. Environmental concerns over the use of toxic corrosion inhibitors, such as hexavalent chromium and cadmium, have necessitated the development of alternative coating materials and processes to prevent corrosion. Existing low-cost aqueous-based deposition processes such as immersion coatings and electrodeposition have led to new processes, such as zirconium-based conversion coatings and zinc-based alloys, to replace

[7] High-strength, low-alloy (HSLA) steel is a type of alloy steel that provides better mechanical properties or greater resistance to corrosion than carbon steel.

hexavalent chromium and cadmium, respectively. High- and low-temperature solid-particle spraying technologies have been developed and implemented that provide a means to create compounds and alloys with chemistry tailored to the specific corrosion environments. Development of rare-earth oxide corrosion inhibitors, such as cerium oxide or praseodymium oxide,[8] for paints and primers has found application for military aircraft as environmentally benign replacements for carcinogenic compounds. Improvements in protective coatings for oil and gas pipelines, as well as bridges and buildings, have reduced the impact of corrosion under widely varying climatic conditions.

2.2 CERAMICS, GLASSES, COMPOSITES, AND HYBRID MATERIALS

2.2.1 Ceramics

Ceramics and glasses have found high-value applications owing to their abilities to withstand harsh environments; as bulk, composite, and coating materials; and for their functionality in devices. Nonoxide ceramics, in particular, have properties that are amenable to applications in harsh environments, ranging from high temperatures to tribological conditions to high impacts. These materials have been used as diesel filters, thermal barrier coatings, armor, turbine engine components, and refractories. Significant advances in the last decade have provided insights into the structure of these materials, improvements in processing, and ability to tailor the chemistries to achieve new properties. In addition, the last decade has seen the development of novel processes that achieve materials with increased durability by creating silica-rich layers that protect the material from oxidation. These approaches allow the material to be used in new applications. This approach yielded a material with improved oxidation resistance. ZrB_2/SiC could be considered as a matrix resin for composites, oxidation protection coatings, or possibly raw materials for additive manufacturing approaches

Nonoxide ceramic materials also found application as oxidation reduction reaction cathodes in polymer electrolyte fuel cells or Li-air, Zn-air, and Al-air battery chemistries. Over the past decade, several materials have demonstrated improved fuel cell performance, including titanium nitride (TiN), titanium carbide (TiC), and titanium diboride (TiB_2) Further work to better understand how these materials achieve these improvements is ongoing, and the exact mechanism remains unclear.

Extension of single-phase nonoxide materials to biphase materials has recently been pushed to the limit with the fabrication and characterization of high-entropy metal diborides such as $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2$. These materials offer promise as ultra-high-temperature ceramics, and the hardness and oxidation resistance of these materials appear to be greater than any of the single diborides. However, manufacturing of such five-component metal diborides may be difficult even though they consist of predominantly one solid-solution AlB_2 type structure.

Nonoxide ceramics have also found important uses as piezoelectrics for high-temperature sensors in automobiles, aircraft, and furnace and reactor monitoring systems, and as bulk acoustic resonators (necessary for filters in every cell phone). A typical high-temperature piezoelectric is aluminum nitride (AlN), which is both stiff and compatible with complementary metal-oxide semiconductor (CMOS) technology. However, its piezoelectric coefficient, d_{33}, is exceedingly low, as is the low intrinsic electromechanical coupling factor. Scandium doping of AlN, motivated by the identification of metastable ScN structures from first-principle calculations, demonstrates increases in d_{33} by a factor of 4,[9] and coupling factors up to 12 percent.[10] This significant advancement has now made its way to the corporate sector, to Murata, Taiyo Yuden, Qualcomm, Broadcom, and so on.

[8] The rare-earth corrosion inhibitors are preferred over chromate-based inhibitors. The use of the latter is subject to regulation. Neither cerium nor praseodymium are listed as critical rare earths.

[9] M. Akiyama et al.,2009, *Advanced Materials* 21:593-596.

[10] M. Schneider et al., 2017, *Proceedings* 1:305, doi:10.3390/proceedings1040305.

2.2.2 Glasses

Advances in glasses over the last decade include a combination of expanded compositional options with next-generation wafer processing. Refractive indices and dispersion curves are customized by composition choices (e.g., Ge additions). Rare earths incorporated into chalcogenide glasses result in increased photoluminescence for optical amplifiers at 1300 and 1500 nm telecommunications windows.[11] Fibers made from these materials—for example, $Ga_{17}Ge_{25}As_{8.3}S_{65}$ + 0.05% Pr^{3+} or Nd^{3+}—have resonance excitation from the rare earth, but also from the light absorption in the host glass that is then transferred to the rare earth.

Wafer scale processing of these materials to make devices is now possible. Binary volumetric diffractive optical elements (VDOEs) are synthesized on a fused silica substrate with antireflective coatings below and above the $Ge_{33}As_{12}Se_{55}$ (AMTIR-1) layer. Photopatterning has been improved to yield very fine feature control in beam shapers,[12] beam splitters, or high-pass dichroic filters with adjustable parameters. Cut-off frequencies can be tuned from a few tens of picometers up to 10 or more nanometers.

There is interest in fabricating photonic devices on stretchable substrates for applications such as epidermal sensing, strain-optical tuning, or aberration-free imaging. Depositing fairly low thermal expansion chalcogenide glasses on higher thermal expansion stretchable substrates, such as polydimethylsiloxane (PDMS) elastomers, generally produces high strain rectified by depositing the photonic device in a meandering or serpentine layout such that it can expand without fracturing (Figure 2.3).

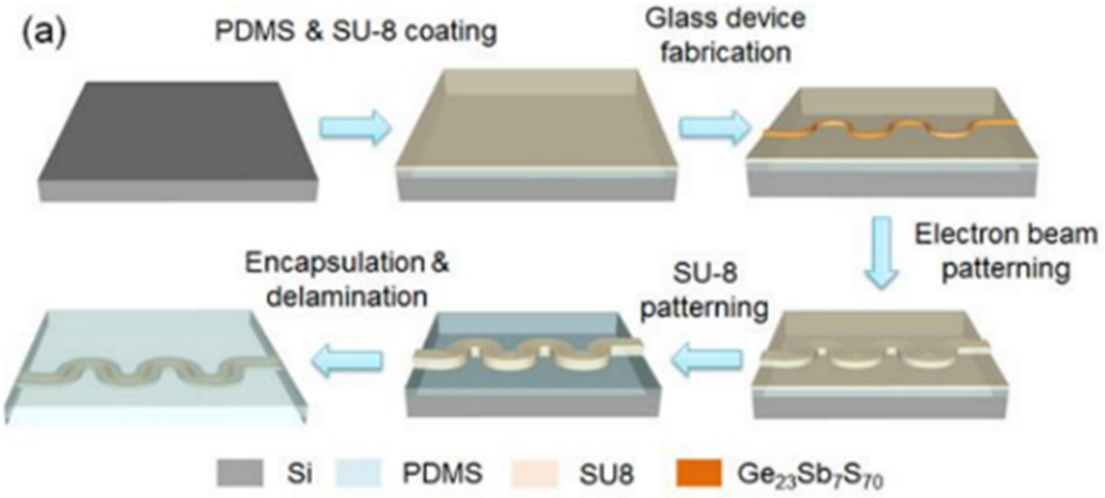


FIGURE 2.3 Fabrication process of the stretchable photonic devices. The steps are initial coating with PDMS and the epoxy-based photo resist (SU-8), fabrication of the glass device using serpentine layout, E-beam patterning, SU-8 patterning, removal of excess material, and delamination so that the stretchable PDMS layer becomes the substrate for the device. SOURCE: H. Lin, L. Li, Y. Huang, J. Li, C. Ramos, L. Vivien, J. Lonergan, K.A. Richardson, and J. Hu, 2016, "Monolithic High-Index-Contrast Stretchable Photonics," Paper FF5F.2 in *Frontiers in Optics 2016*, OSA Technical Digest (online); used with permission.

[11] ZBLAN glass fibers are also important for their transparency in the mid-IR and potential uses in optical transport, doped-fiber amplifiers and lasers, and nonlinear optics. See http://madeinspace.us/mis-fiber/, accessed July 5, 2018.

[12] From a few tens of picometers up to 10 or more nanometers.

Integration of graphene into wafer-scale device manufacturing is achieved by keeping the graphene-coated Si at room temperature during thermal deposition of the chalcogenide glass films.[13] Patterning is achieved through fluorine plasma etching or liftoff. Microresonator devices in both near- and midwave IR wave bands have been demonstrated without optical loss from the graphene layer. Integration of other 2D layers (WS_2, $MoTe_2$) has been demonstrated, potentially leading to photonic integration on 2D transparent conductor materials.

Newer applications for chalcogenide glasses include natural gas sensing and superionic conduction for lithium- or silver-conducting solid electrolytes.

2.2.3 Composites and Hybrids

Composite and hybrid materials have seen increased applications over the past decade, building on the foundation that investments in polymer matrix composite have achieved in broader understanding of these highly engineered materials. Monolithic materials can be easily shaped into engineering components via casting, forging, injection molding, machining, and a myriad of manufacturing processes, and historically the use of monolithic materials has far outpaced the use of hybrid materials in man-made engineering systems. That is changing with ever-increasing demands for performance and design freedoms. Fiber- and particulate-based composites that offer a unique balance of properties have gained increased utility in the last half century, and the past decade in particular has seen maturation of composite technologies into the wholescale production of numerous products, including but not limited to bulletproof vests, massive wind turbines, and commercial airliners. Recent advances in the development and use of multicomponent hybrid material systems are well-documented. For example, during the last decade, the increase of carbon-fiber composites for structural components in aircraft increased from less than 25 percent in 2010 to around 50 percent at the time this report was prepared. The timeline for incorporation of carbon-fiber composites in commercial aircraft is shown in Figure 2.4, and the development and impact of ceramic matrix composites for application in aircraft engines and gas turbines is highlighted in Box 2.3. Much of this advance was the result of sustained support of fundamental and applied research in this area, along with a close cooperation between researchers and gas turbine manufacturers.

Although the concept of composite and hybrid materials has a long legacy, the era of this class of materials took off with the investment in carbon-fiber polymeric composites for aerospace applications. The ability to reduce weight through the material's high specific strength and modulus, the ability to form previously challenging complex shapes via the buildup of layers versus the hogging out of ingots, and the ability to place the structural properties where needed through the design of the built-up composite—a crude form of additive manufacturing—ushered in significant investments that rapidly matured this class of materials from concept to military applications in recent decades, and today it is the basis of the Boeing 787, enabling a lower fuel burn and more comfortable passenger experience airplane, and the BMW i3 and i8, enabling battery-powered engines.

[13] U.S. Patent US20150206748A1, "Graphene layer formation at low substrate temperature on a metal and carbon-based substrate," Current Assignee University of Chicago Argonne, LLC.

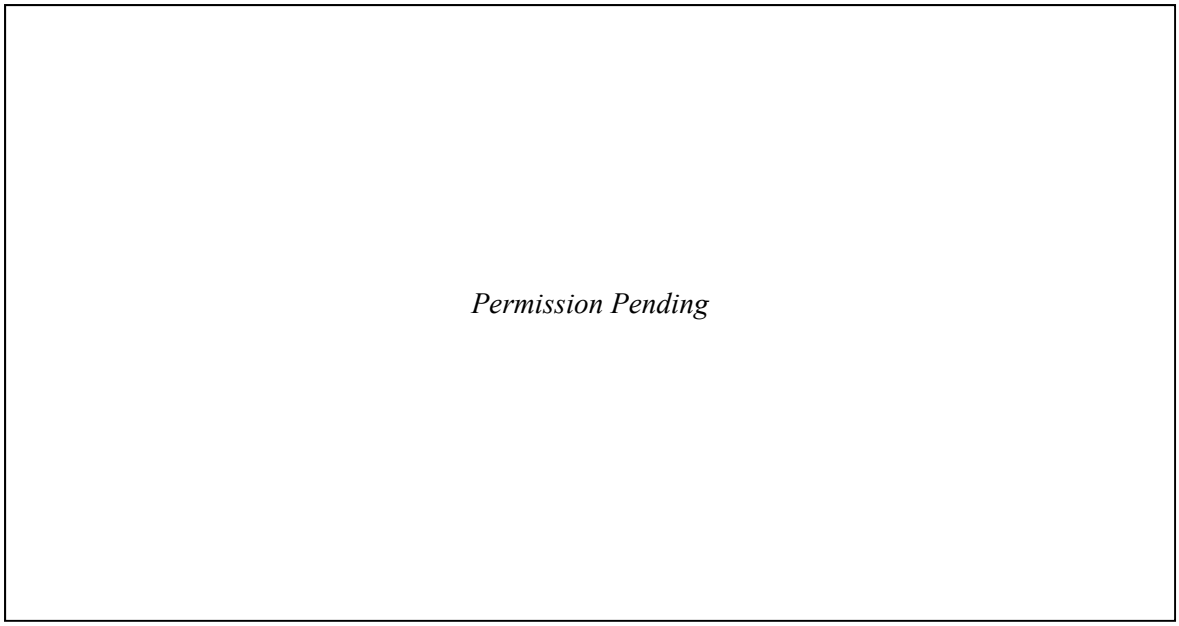


FIGURE 2.4 Increasing carbon-fiber composite content in commercial aircraft. SOURCE: http://webfiles.wichita.edu/cedbr/WIRED_comp_ov_5_14_08.pdf. Data from Teal report, Boeing, Airbus, Composite Market Reports.

Today, there is a strong industrial base that provides carbon fiber and carbon-fiber composites globally for a rapidly diversifying market. The commercial success of this specific class of composite materials has provided a foundation of new design, analysis, modeling, and manufacturing technology for the United States, and it has generated growth across the globe. Oil and gas and deep-sea structures see increasing use of composite pipes and structures; lightweight infrastructure and shelter applications have emerged; and transportation modes of all types are investing in use of these tailorable materials. Technical advances over the past decade in processing science and manufacturing have enabled new fabrication approaches.[14] Novel multidirectional weaving of reinforcements has been demonstrated, as have nanotailored composites. Improved fibers, polymers, and additives have been demonstrated in various fields of use. Processing science models that can simulate the creation of the material in its final component form have been developed in the past decade and show great promise in enabling the simulation of processing routes before investing in laboratory or industrial fabrication. These advances must continue and be extended to capture a greater subset of the composites and hybrids that are being developed. In recognition of the critical need to be able to quickly model and downselect promising microstructures from among the multiple possible combinations of numerous constituents, multiscale modeling efforts have emerged, with some success in capturing the complex formations of composites and in particular the thermosetting composites that include chemical reactions. Early applications of the ICME in composites and hybrids have occurred in the past decade,[15] with, for example, the development of a hybrid-disk concept for jet engine applications that would benefit from increased compressor exit temperature or increased time at elevated temperature for both the compressor and the high-pressure turbine.[16]

[14] R.M. Jones, 2014, *Mechanics of Composite Materials*, CRC Press.

[15] Cowles et al, 2012, *Integrating Materials and Manufacturing Innovation* 1:2, http://www.immijournal.com/content/1/1/2, accessed August 8, 2018.

[16] See http://www.dtic.mil/dtic/tr/fulltext/u2/a529049.pdf, accessed August 8, 2018.

BOX 2.3
Development of Ceramic-Matrix Composites (CMCs) for Aircraft and Stationary Gas Turbines

Increasing the operating temperatures by 100°C to 200°C and reducing the component weight results in an increase upward of 2 percent in efficiency, and consequently, fuel saving. The weight reduction arises because the density of CMCs is one-third that of the superalloys used in current turbine engines. Achieving these goals required development of CMCs through advances in both materials and their processing. The composite requires a high-strength, refractory fiber that can sustain thermal excursions. High-strength, creep-resistant, oxygen-free SiC fibers such as Hi-Nicalon Type S from NGS Advanced Fiber, provide these properties. Unlike the load transfer from matrix to fiber that is characteristic of polymer-matrix and metal-matrix composites, CMCs require a weak, low-toughness, fiber-matrix interface, which ensures that matrix cracks do not propagate through the fibers, thus ensuring their load-carrying function. This issue was addressed through the development of a multilayer, boron nitride-based coating that provides the adequate low toughness and, equally important, sustains the melt-infiltration.

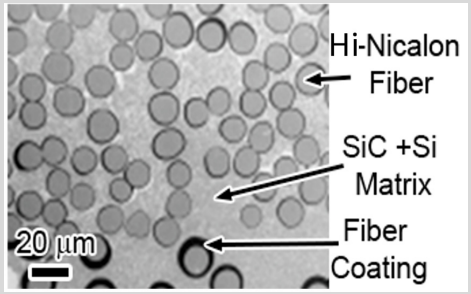


FIGURE 2.3.1 Left: Microstructure showing the ceramic matrix, the silicon carbide (SiC) fibers with a boron nitride (BN-)based coating. Right: CMC Stage 1 shrouds for the LEAP engine. There are 18 of these components per LEAP engine. SOURCE: Reprinted from G.S. Corman and K.L. Luthra, 2017, Development history of GE's prepreg melt infiltrated ceramic matrix composites material and applications, in *Comprehensive Composite Materials II*, Elsevier, New York, with permission from Elsevier.

Also equally important, the coating sustains the melt-infiltration composite-fabrication process without damage. Another essential development was the chemical-vapor deposition coating technique that was scaled to continuous fiber lengths. This ensured that the fiber coatings would remain independent. Last, the composite was produced by a melt-infiltration process, in which a coated fiber array is impregnated with a slurry of SiC and carbon (C) and melt-infiltrated with silicon to produce a dense SiC matrix reinforced with SiC fibers.

The development of a CMC suitable for aviation took more than 25 years of development, which highlights the challenge of translating materials development at the laboratory scale to product development. However, through federal agency support from the Department of Energy (DOE) and other agencies, and companies such as General Electric, a new generation of jet engines employing CMCs was developed. The impact is that when CMCs are fully implemented in jet engines, fuel consumption will be reduced by 1.5 percent, which translates into a savings of over $1 million per aircraft over a 10-year period.

Unlike the composite strategies used for stiffening and strengthening in carbon-fiber composites, advances in ceramic fiber-reinforced ceramics provide a solution to the traditional brittleness associated

with ceramics coupled with greater refractoriness and reduced weight compared to superalloys. CMCs were successfully employed, for the first time, in General Electric's leading-edge aviation propulsion (LEAP) engine in 2017 (see Box 2.3). Driving the development and implementation for both aviation and stationary gas turbines is the scaling of engine efficiency with gas temperature in the engine. The major increase in material temperature afforded by CMCs compared to nickel (Ni)-based superalloys was achievable, not only through material selection, but by fundamentally new design and analysis approaches, as well as by innovative processing methods. Figure 2.5 shows the increase in the operating temperature with the development of Ni-based superalloys, and the increase in operating temperature achieved through the introduction of thermal barrier coatings (TBCs), without and with cooling.[17] Over the period from 2010 to 2015, the increase in operating temperature achieved by alloy development was small and increased from 1120°C to 1140°C; with thermal barrier coatings, it increased from 1323°C to 1365°C; and with thermal barrier coatings with cooling, it increased from 1481°C to 1527°C. With thermal and environmental barriers with cooling, the temperature of CMCs will increase the operating temperature to over 1620°C, increasing the operating temperature by about 100 degrees.

Thermal protection systems are enabling space exploration. An example is the Solar Probe Plus satellite, which will venture closer to the Sun than any man-made object has ever gone (see Box 2.4).

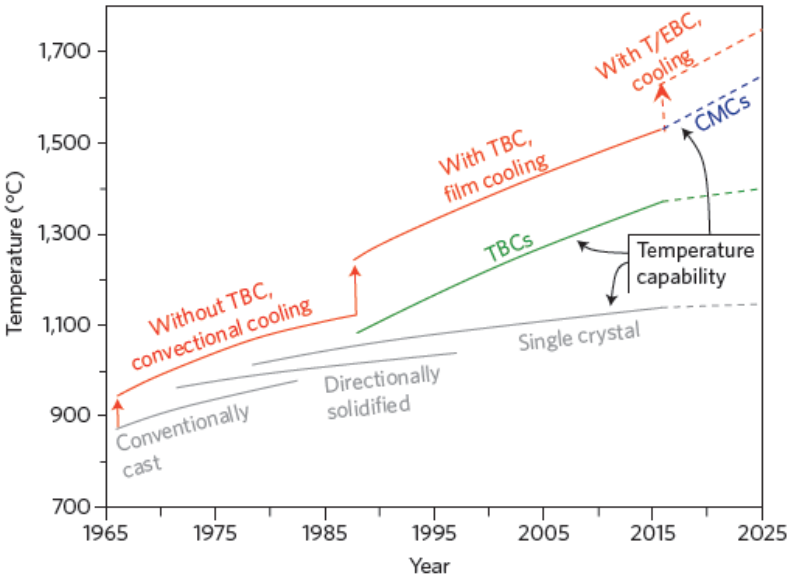


FIGURE 2.5 The progression and projection of temperature capabilities of nickel (Ni)-based superalloy (gray) with thermal barrier coatings (TBCs; green), ceramic-matrix composites (CMCs; blue), and maximum allowable gas temperatures with cooling (red). SOURCE: Reprinted by permission from Springer Nature: N.P. Padture, 2016, Advanced structural ceramics in aerospace propulsion, *Nature Materials* 15:804-809, © 2016.

[17] N.P. Padture, 2016, Advanced structural ceramics in aerospace propulsion, *Nature Materials* 15:804-809.

BOX 2.4
Thermal Protection System

The Parker Solar Probe will fly within 10 solar radii of the Sun, closer to the Sun than any other man-made spacecraft, in order to study the origins of the solar wind. The mission is enabled by development of a thermal protection system (TPS) that allows the spacecraft bus to function at about 30°C, while the shield takes the brunt of the Sun and withstands 1300°C on the front surface. The TPS is a multimaterial sandwich panel that optimizes the optical performance, mechanical integrity, and thermal insulation performance. The development of the TPS by the Johns Hopkins Applied Physics Laboratory (APL) required a successful teaming approach with Johns Hopkins University, NASA, government test facilities, and industry partners across the country. Consisting of a carbon-carbon and carbon-foam sandwich panel with a specially designed alumina coating, the 2 m diameter, 70 kg heat shield utilizes structurally integrated insulation to withstand launch loads and the extreme temperatures of the mission. This novel hybrid technology required development of new materials, utilization of high-temperature materials in new ways, and the elaboration of new testing approaches and methods. Owing to the novelty of the approach, extensive materials testing, manufacturing process development, structural analysis, thermal analysis, and testing were required to bring about a successful TPS in a little over four years.

FIGURE 2.4.1 Hybrid thermal protection system (TPS) for Parker Solar Probe Plus. SOURCE: Courtesy Johns Hopkins University Applied Physics Laboratory.

Advances in coating technologies have also engendered significant advances and increased reliability and use of multilayered wear, thermal, and environmental protection systems. Layered material systems are replacing advanced monolithic materials in a growing number of applications where the unique properties and functionality of each layer provides dramatically increased performance and life. Thermal barrier coatings (TBCs) for metallic Ni-base superalloys and environmental barrier coatings (EBCs) for ceramic-matrix composites are two examples of layered material systems that have been developed for extreme environments, consisting of high stresses and oxidizing and corrosive gases at temperatures on the order of 1500°C. These chemically, mechanically, and physically diverse layers interact and evolve throughout the lifetime of the coating, and important phenomena affecting performance and durability occur in each layer and particularly at the interfaces between disparate materials. The successful implementation of strain tolerance and low conductivity coatings have dramatically increased coating lifetimes. The use of layered materials extends across material class.

The use of polymeric coatings for environmental protection has expanded in the past decade. For example, the development of high-surface-tension polymeric films with highly controlled chemistry and nanoscale features has fueled the use of tunable superhydrophobic and ice-phobic coatings that now protect microelectronics, solar cells, wind turbines, and airplane wings.

2.3 SEMICONDUCTORS AND OTHER ELECTRONIC MATERIALS

Semiconductors are the workhorse materials for electronic and photonic device applications—making up integrated circuits, circuit boards, and light emitters, and incorporated into packaging materials, displays, and any number of controlling and monitoring devices.[18] This section discusses some of the principal developments in semiconductors and other electronic materials that have allowed continued, significant advances in modern electronics and photonics. Like many of the materials discussed in other sections of this chapter, the discovery paths followed in electronic materials have, in many cases, been influenced or even been directed by the industrial environment in which these materials discoveries participate. This section will begin by describing some of those impacts, and then discuss how materials research has responded to these far-reaching factors. The final subsections of Section 2.3 will discuss the significant impacts that semiconductor research has made in optoelectronics and some of the developments in organic and flexible electronics.

2.3.1 Materials and Devices for Information Technology

Integrated circuits have transformed information and computational technologies. This revolution was enabled by five decades of improvements in the performance of silicon field-effect transistors (FETs) and has been characterized by exponentially compounded progress in the miniaturization of electronic devices and circuits. However, the last 20 years have encountered limits that have affected efforts at further miniaturization. The 1990s saw devices reach sizes where gate insulator thickness and operating voltage became less effective avenues for further device scaling. In the early 2000s, heat removal and power density considerations contributed to the plateauing of microprocessor clock frequencies. In the last decade, relevant feature sizes have reached the single digits of nanometers, where fundamental physics is imposing increasingly rigorous constraints.

The responses by those in research and development (R&D) communities have been several-fold. Continued efforts to miniaturize have provided incremental gains. Parallel with those efforts have been concerted attempts to find alternative approaches to satisfy the needs of traditional information and computational technology needs. These efforts have been seeded by a number of efforts jointly funded and directed by the public and private sectors (see Box 2.5). Last, another major push in electronic materials over the past 10 years, heavily entwined, at times, with the other efforts, has been to develop new materials that will be potentially useful for totally new computation and information capabilities and needs.

The importance of the interplay between device and materials research exists in all of the examples discussed in this section. In some cases, materials research is focused on material properties critical to the performance of an established device concept. In other cases, adventurous materials research is inspiring new device concepts and making the impossible suddenly possible. In all cases, much more remains to be done.

[18] The committee thanks Thomas Theis, Columbia University, for his insightful thoughts and ideas in developing this portion of the report.

BOX 2.5
Industrial/Government/Academic Joint Pursuits of New Solutions for Information Technologies

Our ongoing information technology revolution has been enabled by six decades of exponentially compounding progress in the miniaturization of electronic devices and circuits. Of course, all exponential trends must eventually end, and there is mounting evidence that progress in miniaturization is slowing.[1] Nevertheless, ongoing research supports an optimistic outlook for further advances in the hardware that enables information technology. The often-predicted, long-delayed, and gradual "end of Moore's law" is setting the stage for exciting new developments in information technology as the focus of research and development shifts from miniaturization of long-established devices to the coordinated introduction of new devices, new integration technologies, and new architectures for computing.[2]

The impetus for this shift in research investment goes back to the period 2003-2005, when microprocessor clock frequencies, constrained by considerations of heat removal and power density, suddenly plateaued.[3] Aware that these constraints could not be fully addressed by continued incremental advancement of established technologies, representatives of several microelectronics manufacturers began to discuss a research program with longer-term goals. As a result, the Nanoelectronics Research Initiative (NRI) was chartered in 2005 by a group of Semiconductor Research Corporation (SRC) member companies to develop and administer a university-based research program aimed at entirely new devices and circuits for computing. In partnership with the National Science Foundation (NSF), NRI would fund university research to "demonstrate novel computing devices capable of replacing the CMOS FET as a logic switch in the 2020 time frame." In 2007, the National Institute of Standards and Technology (NIST) joined the private-public partnership, resulting in the creation of four multiuniversity, multidisciplinary research centers. NRI's bold and clearly articulated research goals caught the attention of funding agencies in Europe and Asia and helped to spark new initiatives in those geographies. In 2013, the Defense Advanced Research Projects Agency (DARPA) joined with industry to fund STARnet, expanding the program and focusing U.S. university researchers on the exploration of post-CMOS devices. As the NRI and STARnet programs evolved, the interest of the industrial sponsors shifted from exploration of isolated devices toward co-development of new devices, circuits, and architectures. This was made explicit with new programs announced by SRC and NSF in 2016 and by SRC and DARPA in 2017.

[1] T.N. Theis and H.-S.P. Wong, 2017, The end of Moore's law: a new beginning for information technology, *Computing in Science and Engineering* 19:41.

[2] See https://eps.ieee.org/images/files/Roadmap/SIA-SRC-Vision-Report-3.30.17.pdf.

[3] T.N. Theis and P.M. Solomon, 2010, in "Quest of the 'Next Switch': Prospects for Greatly Reduced Power Dissipation in a Successor to the Silicon Field-Effect Transistor, *Proceedings of the IEEE* 98:2005.

SOURCE: Courtesy of Tom Theis, Columbia University.

2.3.2 Continued Miniaturization of Silicon-Based Field-Effect Devices

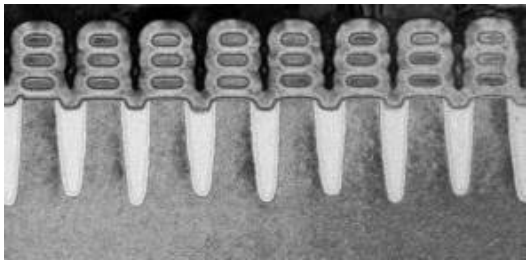
Over the past decade, materials and process innovation made significant contributions to efforts to further miniaturize silicon-based field-effect devices. Selected materials research highlights include the following:

- New low-k dielectric films based on chemical vapor deposition (CVD, or similar) of "SiOC" precursors. Initial advances were made by lowering the integrated dielectric of the film based on precursor design, then by introducing engineered porosity or air gaps into the integrated film. UV-curing has been a critical ally to the successful integration of such fragile, low-k strategies. New capping or sealing layers protected the fragile dielectrics (especially films with porosity) from damage during subsequent processing steps or device operation.
- A wide array of new liners, barrier stacks, and capping agents have improved metallization, resistive-capacitive (RC) delay, and electromigration, especially as feature sizes have been reduced. These include but are not limited to Cu, Ta, TaN, TiN, CuMn, MnN, Ru, W, and Co.
- A metal-insulator-metal (MIM) capacitor, introduced to improve the voltage linearity properties across a chip.
- Industry's migration to new gate dielectric materials with higher dielectric permittivity, primarily based on hafnium oxide, that greatly improved gate leakage at the ≤45 nm node. New metal gate electrodes for n- and p-type metal-on-semiconductor (NMOS, PMOS), atomic layer deposition (ALD), and chemical mechanical polishing (CMP) were all instrumental to realizing this transformative advance.

Last, in one of the most publicized innovations seen in the last decade, the semiconductor industry has moved to 3D field-effect transistors called FinFETs (Figure 2.6). The 3D FinFET improved transistor performance by forming a conducting channel on all three sides of the vertical fin structure, improving power when compared to a traditional planar transistor at the same nominal dimension.

Miniaturization performance gains over the past 10 years have also come through scaling driven by optical and extreme ultraviolet (EUV) lithography. Early in the last decade, traditional gains were provided by advances in optical lithography. For example, the industry moved from 193 nm dry to 193 nm immersion lithography by introducing water as an immersion fluid between the final lens element of the exposure tool and the photoresist.[19] While providing a significant resolution enhancement (~40 percent), the immersion fluid caused leaching of photoresist components and defects arising from complex fluid dynamics of the high-speed exposure tool. In most cases, these problems were addressed by developing materials for use as a spin-on topcoat to physically separate the photoresist and immersion media.

Permission Pending



(a) Intel 22 nm node, 3D FinFET

(b) IBM proposed 5 nm node, nanosheet

FIGURE 2.6 To sustain the silicon revolution, devices have pushed to 3D over the last decade. (a) Initially, the push was to the 3D FinFET. (b) More recently, devices such as IBM's 5 nm node nanosheet transistor have achieved the highest layout efficiency. SOURCE: (b) A. Tilley, 2017, "IBM Shows the

[19] Early this decade, a consensus formed that for 193 nm immersion lithography (193i), water would be the most likely candidate for 65 nm and 45 nm device nodes, bridging the gap between "dry" or conventional 193 nm lithography and EUV lithography. See, for example, *Optical Microlithography XVIII*, 2005, edited by B.W. Smith, *Proceedings of SPIE*, vol. 5754, SPIE, Bellingham, Wash., doi: 10.1117/12.600025.

World How to Build a Super Dense 5-Nanometer Chip," *Forbes*, June 5, https://www.forbes.com/sites/aarontilley/2017/06/05/ibm-5nm-chips/#3ae8462d3c56; courtesy of IBM.

As 193 nm lithography faced ultimate resolution issues (<90 nm pitch), industry turned to multipass patterning. Initially straightforward, "litho-etch-litho-etch" (LELE) cycles generated the desired pattern by stitching together separate passes. The cost and complexity of this approach quickly exploded (mask design and count, feature variation, etc.), especially as it was applied to more complex situations. These included strategies such as self-aligned double patterning or other variants based on CVD[20] or ALD, providing tight layer-to-layer alignment, and simplifying integrated fabrication flows. ALD also allowed for the integration of new high-k dielectrics and metal gates. New CVD and ALD precursors, thin films of various oxides and nitrides, and processes that took a "bottom-up approach" were critical for these efforts toward the continued miniaturization of electronics.

Industry's ultimate "top-down" 2D scaling strategy is extreme ultraviolet lithography, or EUVL,[21] which was introduced in the last decade. With a wavelength of 13.5 nm (or 91.8 eV), this lithographic technique is a radical departure from previous optical approaches. As all matter absorbs radiation at this wavelength, EUVL exposures occur in a vacuum chamber using reflective rather than transmissive optics. Photoresist outgassing during EUVL exposure serves as an additional performance constraint that the patterning film must consider, as resist by-products will damage the costly lens elements. Second, unlike UV-based photoresists designed in an energy space well understood by chemists, EUV photons create a complex cascade of photoelectrons and secondary electrons that transact the exposed material in poorly understood ways. As such, stochastic EUVL simulations have been important for understanding the process margin and design rules for features patterned via this high-energy technique.

All of these EUVL advances have benefited and will continue to benefit tremendously from the synchrotron research and light sources discussed in Chapter 4. For example, a Lawrence Berkeley National Laboratory (LBNL) EUV patterning tool was used to characterize and study more than 12,000 material systems, an EUV photomask microscope was used to prove the existence of defects visible to only EUV light, and an EUV scatterometer was instrumental in the development of sub-nm wavefronts needed for further development of novel photomask architectures and materials.

2.3.3 Alternative Solutions to Address the Bottlenecks in Field-Effect Transistors

Low-Voltage, Low-Power Devices

Ongoing research continues to provide possibilities for profound advances in the capability of information technologies, beyond continued miniaturization. One (of many) such examples is the negative capacitance field-effect transistor (NCFET), sometimes also called the ferroelectric field-effect transistor (FEFET). The promising 2008 theoretical proposal was directly motivated and funded by the SRC's NRI program described in Box 2.5. It showed a new way to break the existing constraints on power and performance, but building the proposed device with known ferroelectric materials at the nm-scale dimensions required for cost-competitive digital circuits appeared impractical. The subsequent discovery of new materials exhibiting ferroelectric behavior in films as thin as a few nm ignited significant R&D activity. It is still too soon to predict when the NCFET will be commercialized and how important it will

[20] CVD is chemical vapor deposition and is all types of depositions relying on chemical reactions. ALD is atomic layer deposition, a subset of CVD that used alternatively pulsed gas sources to progress growth layer by layer. MBE is molecular beam epitaxy, which takes place in high vacuum with no carrier gas.

[21] T. Haga, 2018, The early days of R&D on EUV lithography and future expectations, *Journal of Photopolymer Science and Technology* 31:193.

become for information technology, but a recent demonstration of a superior power-performance trade-off relative to closely comparable conventional FET circuits is very encouraging.[22]

The NCFET is just one example of an emerging class of transistor-like devices that switch by physical principles that are fundamentally different from the operating principle of the conventional field-effect transistor (FET), and can thus transcend some of the FET's fundamental limits.[23] The tunneling field-effect transistor (TFET) is another exemplar device that has improved rapidly in recent years, enabled by materials advances such as the controlled growth of compositionally graded semiconductor nanowires. Other compelling low-voltage, low-power device concepts are less developed. None of these will advance without further advances in materials.

New Materials Yielding New Classes of Memories

The last decades have seen a rapid maturation of emerging memory technologies based on novel materials and new cell architectures. These include spin-, phase change-, resistive- (or memristors), and ferroelectric-based memories—all now commercially available. Emerging random-access memory (RAM) devices include spin-transfer torque magnetic RAM (STT-MRAM), ferroelectric RAM (FERAM), conductive bridge RAM (CBRAM), resistive RAM (RRAM), and phase-change memory (PCM).[24] These are very distinct devices, each based on a different class of materials, but all share some highly desirable attributes. In particular, they can all be fabricated at relatively low process temperatures, enabling integration of memory devices directly above blocks of logic. This fine-grained integration of memory and logic is seen as a key to the implementation of energy-efficient logic-in-memory and memory-in-logic architectures. At the same time, each of these devices offers advantages and disadvantages compared to the others. Each will advance only with advances in the properties of its requisite materials. The opportunity for STT-MRAM in the embedded memory market as an alternative or replacement to NOR flash is significant, as it is projected to be a good solution for harsh environments, such as the growing automotive market.

Nanophotonics and Nonlinear Optical Materials

Sophisticated nanophotonic communication networks based on passive waveguides and electro-optic phase and amplitude modulators have been demonstrated in recent years and are approaching large-scale commercialization. Frontier research in nanophotonics is focused on demonstration and development of tiny nonlinear optical devices based on the large nonlinear optical coefficients obtainable with 2D materials integrated in nm-scale optical resonators.[25] This research relates to plasmonics, metamaterials, and coherent optics, and is enabling new technological opportunities in optical communications including energy-efficient all-optical gates and 100 THz all-optical modulators. Such devices may allow computational functions to be distributed in optical networks for smart routing and management of data flow.

[22] Z. Krivokapic, U. Rana, R. Galatage, A. Razavieh, et al., 2017, "14 nm Ferroelectric FinFET Technology with Steep Subthreshold Slope for Ultra-Low-Power Applications," 2017 IEEE International Electron Devices Meeting, San Francisco, p. 15.1.1.

[23] T.N. Theis and P.M. Solomon, 2010, In quest of the "next switch": prospects for greatly reduced power dissipation in a successor to the silicon field-effect transistor, *Proceedings of the IEEE* 98:2005.

[24] T.N. Theis and H.-S.P. Wong, 2017, The end of Moore's law: a new beginning for information technology, *Computing in Science and Engineering* 19:41.

[25] A. Autere, H. Jussila, Y. Dai, Y. Wang, H. Lipsanen, and Z. Sun, 2018, Nonlinear optics with 2D layered materials, *Advanced Materials* 30:1705963.

From Two to Three Dimensions

The last decade has seen a number of efforts to expand two-dimensional circuitry into three dimensions. This includes the FinFET discussed above. More generally, 3D chips are becoming the de facto standard in the market, with most major suppliers creating 3D negative-AND gate (NAND) parts having 32 or more layers.[26] Those manufacturers are pushing to 128 or more layers by the year 2020 and will soon sell more 3D NAND than traditional 2D NAND. While many of the basic fabrication materials are similar to those found in 2D NAND, the high aspect ratios (30:1 or more) in 3D NAND pose significant challenges for deposition, patterning, high-aspect-ratio etching, and metallization. Overcoming these challenges required the introduction of paired deposition layers of customized oxide-nitride films, the use of an amorphous carbon hardmask, and novel plasma reactors that could yield smooth, vertical profiles. Atomic layer deposition (ALD) techniques have become more prominent in 3D NAND, as ALD processes can deliver good uniformity and coverage, even for high-aspect-ratio features. While the price per 3D NAND wafer is higher than a 2D NAND wafer, the added performance per chip arising from 3D integration retains the promise of Moore's law economics, as the estimated cost per GB for the 3D NAND is lower than that for the 2D NAND part. The move to 3D design and layout plays an increasingly prominent part in the roadmap for semiconductors and electronics.

Another example of materials research contributing to the development of 3D designs is in the area of radio frequency (RF) transformers. The ubiquitous wireless connectivity of devices has required the development of new on-chip components, and one such type of component, an RF transformer, has been developed using rolled-up membrane technology. These devices have large turn ratios, large coupling coefficients, and high maximum working frequencies. Such 3D structures, essentially nano- and microscale tubes, have been produced by fabricating semiconductor scrolls through the application of a strain-induced self-rolling process. Control of the inner diameter of the tube is essential for application in some devices. By employing finite element modeling, researchers have studied the process by which the film is released, thereby guiding the engineering of the strained layer to obtain different rolled-up structures and predicting the diameters of the final product. Scrolls of Si/SiGe, strained SiN_x, and GaAs/AlGaAs have been fabricated. The tubular SiN_x structures, along with accompanying prepatterned metal layers, have been used to produce a novel on-chip tube inductor design platform to produce inductors for application in radio frequency integrated circuits. Control of the size of two-layer metal InGaAs scrolls, in which the metal is used as the stressor, has been achieved through lithographic patterning, as seen in Figure 2.7.

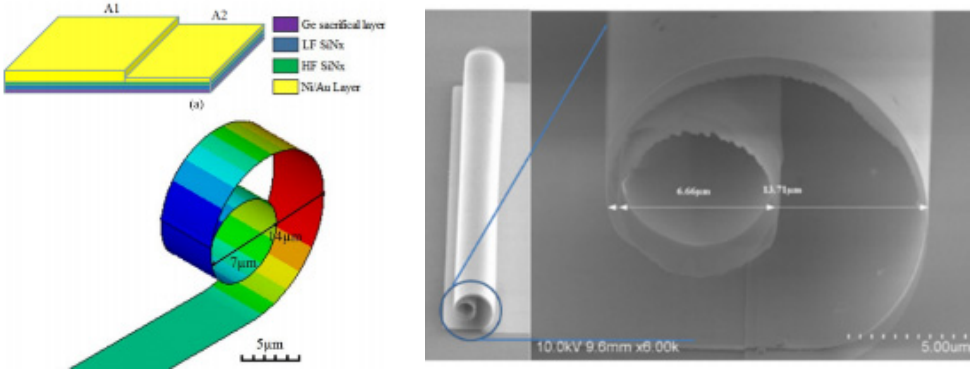


FIGURE 2.7 *Left:* Simulation of a coaxial structure. *Right:* Coaxial structure rolled up by local stress. SOURCE: Reprinted with permission from W. Huang, S. Koric, X. Yu, K.J. Hsia, and X. Li, 2014, Precision structural engineering of self-rolled-up 3D nanomembranes guided by transient quasi-static

[26] 3D NAND is driven by interconnect layers, which is a subset of the technological requirements for 3D logic.

FEM modeling, *Nano Letters* 14(11):6293-6297, doi:10.1021/nl5026369. Copyright 2014 American Chemical Society.

Combination Devices/MEMS

The integration of mechanical and electronic components within a single microfabricated package is a technology known as a *microelectromechanical system* (MEMS). Optimized and innovative technology, in combination with the economics of high volume/low unit cost production, has expanded the application of MEMS to include devices such as sensors, actuators, micropower generators, chemical reactors, and biomedical devices. Diversification of this portfolio will continue, but the extent will be predicated on the development of appropriate materials and fabrication technologies.

The complexity of MEMS devices is increasing rapidly. Inkjet print heads, one of the original silicon-based MEMS devices, transformed document printing with a heating element and an orifice. Then silicon-based devices with moving parts enabled the development and commercialization of miniature pressure sensors, accelerometers, and gyros. Further miniaturization, bulk high-volume fabrication, and improved sensor design have enabled the integration of MEMS-based sensors with numerous consumer products, where they are primarily used for monitoring and control.

2.3.4 Semiconductors for Optoelectronics

The last decade saw widespread commercial adaption of lighting using light-emitting diodes (LEDs) based on IIII-nitride semiconductors, developed through sustained materials and device research efforts over the previous few decades. Further research in this area over the past decade has led to continued improvements in the materials required for this important application. Gallium nitride (GaN) on either sapphire or silicon carbide (SiC) is commonly used for LEDs. With efficiency gains reaching a maximum for LEDs grown on sapphire, the efficiency drop, the cost of sapphire wafers, and the challenges associated with large-scale fabrication have led to an interest in growing GaN on substrates such as GaN, silicon (Si), and metals. In the last decade, progress has been made in developing methods to produce bulk GaN substrates. The availability of such substrates has resulted in the production of GaN-on GaN LEDs with an equivalent light output to conventional LEDs but on a much smaller chip. In addition, green lasers have been produced on semipolar GaN substrates. GaN-based LEDs have been fabricated on Si substrates. This is a challenge because of the large difference in lattice parameter and thermal expansion coefficient. The issue of cracking owing to the thermal stresses has been addressed by growing multilayers of AlGaN/GaN on a prepatterned substrate. This technology offers the advantage that large-diameter Si wafers are available at low cost and are processed routinely in the electronics industry.

Semiconductor quantum dots have applications in lighting technologies, display resolution, drug delivery, and imaging at the molecular level. In the last decade, progress has been made in several areas including but not limited to tuning the emission spectrum in ultrasmall cadmium selenide (CdSe) quantum dots through post-synthesis treatments; correlating the optical properties of the dots to the atomic structure on an individual quantum dot; indium nitride (InN) quantum dots on Si substrate; and ordering of indium arsenide (InAs)-based quantum dots on gallium arsenide (GaAs).

2.3.5 Organic Semiconductors

Conjugated semiconducting polymer/organic materials offer in some cases opportunities for a low-cost, additive, environmentally benign, printable electronics manufacturing ecosystem built on materials designed to be lightweight, flexible, and solution processable over large areas. These materials offer opportunities for functional electronic devices for applications including organic field-effect

transistors (OFETs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), batteries, biomedical devices, and sensors,[27] many of which form the case studies in Section 5.3.

While it is fair to say that the synthesis of novel molecules has led to significant improvements in charge carrier mobility, which is the key metric that defines electrical performance, the solution processing and thin film deposition of conjugated polymers must also be properly controlled to obtain high-performance devices with the requisite crystallinity, intergrain connectivity, and alignment. Precise control of the electrical performance of a material depends critically on its solid-state thin film microstructure and on the intramolecular- to the device-length scales.

The organic semiconductor technology that has become a marketplace reality in the past decade is the display technology based on OLEDs.[28] Significant efforts went into the design of the materials and processes that enable today's displays—see, for example, Case 1 in Section 5.3. Lighter in weight and less likely to shatter than their LCD counterparts, vivid color OLED displays are now a mainstay of smartphones. And through efforts with OLED, TVs are beginning to appear.

OLED display technology is also simpler than that of LCDs: the organic displays are composed of pixels that individually emit red, green, and blue light to create an image. The conjugated organic molecules are positioned between two electrodes, and when current flows from the cathode to the anode, electrons and holes combine to emit light. Since black is simply created by leaving the requisite pixels off, the "black" is often called "true black" and is perhaps one reason that OLED displays exhibit much sharper and brighter images. OLED technology is also more energy efficient—to achieve the color black, no energy is consumed.

While challenges surrounding materials and process costs continue, as does research to identify more stable materials for longer life displays, with the demonstration of a viable technology, other active organic materials technologies are likely to follow. One particularly promising area for OLEDs is the use of data informatics approaches to help identify promising target molecules, coupled with the development of new, more sustainable approaches to materials synthesis.

2.3.6 Flexible Electronics

In the last decade, flexible electronics[29] have developed beyond earlier applications in curved and flexible displays and panels to new advances in foldable, stretchable, conformable devices that are being increasingly widely applied as even softer, portable, wearable sensors (Figure 2.8), especially for continuous monitoring of physiological signals but also in devices to enhance human physiology, as in controlling motion or haptic and tactile senses, and in internal devices such as prostheses or interventional devices, as illustrated in Figure 2.8.

There are different strategies for creating flexibility while retaining electronic properties, including strain minimization via nanoscale processing of established materials and synthesis of new functional nanomaterials. The nanoscale dimensions of the materials dramatically decrease flexural rigidity of devices while acting as electrodes, transport channels, and light-emitting/photon-absorption materials. Flexible designs with locally rigid materials have been created by shaping or patterning the material architecture to allow larger scale global deformability. This is a rapidly evolving area of materials research.

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[27] N.E. Persson, P.-H. Chu, M. McBride, M. Grover, and E. Reichmanis, 2017, Nucleation, growth, and alignment of poly(3-hexylthiophene) nanofibers for high-performance OFETs, *Accounts of Chemical Research* 50(4):932-942.

[28] The rise of OLED displays, *Chemical & Engineering News*, July 11, 2016, vol. 94, issue 28.

[29] J.A. Rogers, M.G. Lagally, and R.G. Nuzzo, 2011, Synthesis, assembly, and applications of semiconductor nanomembranes, *Nature* 477:45.

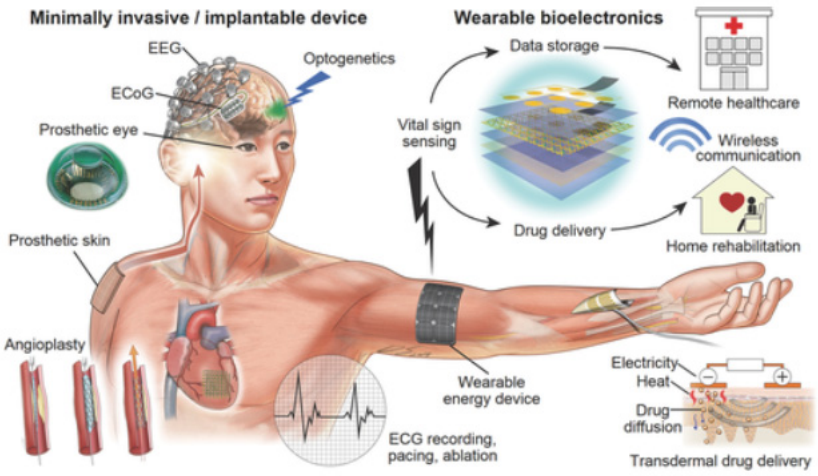

FIGURE 2.8 Illustrations of uses of flexible electronics under development in physiological monitoring and medicine. SOURCE: Reprinted with permission from Y. Liu, M. Pharr, and G.A. Salvatore, 2017, Lab-on-skin: A review of flexible and stretchable electronics for wearable health monitoring, *ACS Nano* 11(10):9614-9635, doi: 10.1021/acsnano.7b04898. Copyright 2017 American Chemical Society.

2.4 QUANTUM MATERIALS AND STRONGLY CORRELATED SYSTEMS

2.4.1 Superconductors and Strongly Correlated Electrons

Superconductivity[30] was serendipitously discovered in 1911, and the microscopic theory (Cooper pairing of electrons in BCS theory) was articulated in 1957. Applications for superconductors arise in their unique transport and quantum-mechanical properties: production of large magnetic fields (e.g., high-field research, MRI, supercolliders); detection of small magnetic fields (e.g., superconducting quantum interference devices, or SQUIDs), high-frequency detection (e.g., radio astronomy); and energy transmission and production (e.g., power grid and turbines). Further, dozens of families of unconventional superconductors have been discovered; see Figure 2.9 for results, including the high-critical-temperature (Tc) cuprates and iron-based superconductors. These discoveries have not only advanced the field of superconductivity but have also foreshadowed quantum materials more broadly.

In the past decade, superconductivity has remained a fertile field, with the discovery of both Fe-based superconductor families[31] and hydrogen-rich superconductors at extremes of pressure.[32] In addition, the pursuit of novel superconductors has enabled the development of new tools such as scanned probe microscopes. The enhanced integration of theory, experiment, and synthesis is accelerating progress toward understanding the origins of superconductivity in new materials discovered by the community. Nevertheless, there is still much that researchers do not understand. A predictive theory of superconductivity in the cuprates remains elusive.

[30] J.L. Sarrao, W.-K. Kwok, et al., 2006, "Basic Research Needs in Superconductivity," Basic Energy Sciences, U.S. Department of Energy, Office of Science, http://www.sc.doe.gov/bes/reports.lists.html, accessed February 11, 2018.

[31] Charles Q. Choi, 2008, A new iron age: new class of superconductor may help pin down mysterious physics, *Scientific American*, June 1, 2008.

[32] W. Hui, L. Xue, G. Guoying, L. Yinwei, and M. Yanming, 2018, Hydrogen-rich superconductors at high pressures, *WIREs Comput Mol Sci*, 8, doi:10.1002/wcms.1330.

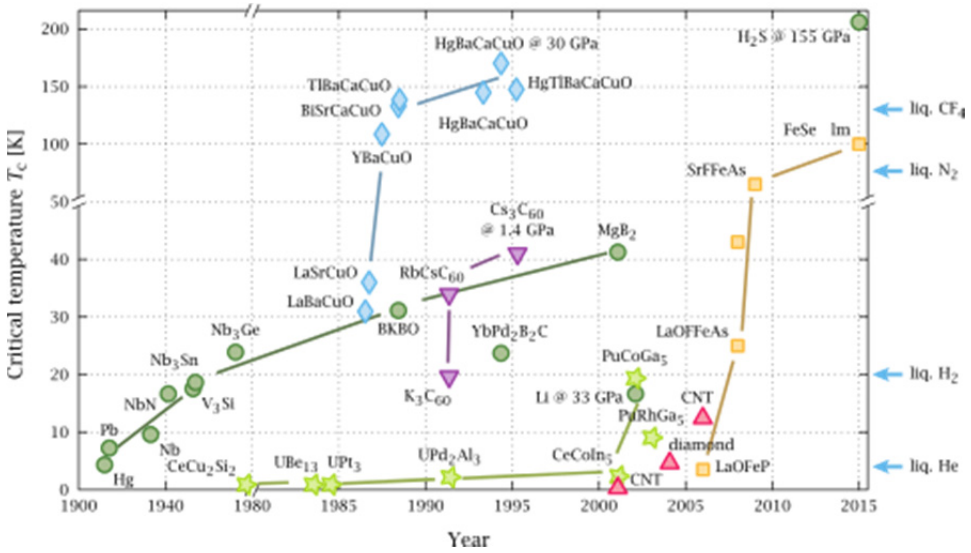

FIGURE 2.9 The observed superconducting transition temperature (Tc) of a variety of classes of superconductors is plotted as a function of time. Recent discoveries have increased the highest-observed Tc in a number of materials to unprecedented levels. BCS superconductors are displayed as green circles, cuprates as blue diamonds, carbon-based superconductors as purple and red triangles, heavy-fermion compounds as green stars, and iron-based superconductors as yellow squares. SOURCE: Figure 2.4 from Pia Jensen Ray, 2015, "Structural Investigation of La(2-x)Sr(x)CuO(4+y)—Following Staging as a Function of Temperature," master's thesis, Niels Bohr Institute, Faculty of Science, University of Copenhagen, doi:10.6084/m9.figshare.2075680.v2, Creative Commons Attribution-Share Alike 4.0 International license.

Strongly Correlated Electrons

Strong electron correlations play an important role in the physical properties and quantum states of materials in two very different regimes: low-density semiconductors for which *long-range* Coulomb interactions remain unscreened, and high-carrier-density, narrow-band metallic systems, whose properties are influenced by *short-range* (on-site) Coulomb interactions. During the past decade, as in prior decades, advancing the understanding of the wide range of unique phenomena that can be attributed to electron correlations has remained a major activity in materials physics. In the arena of Coulomb interactions in low-density systems, graphene has provided new ways of studying interactions in high magnetic fields, where unusual excitations, such as "composite Fermions," can exist in the fractional quantum Hall regime.

In strongly correlated metallic systems, which are often transition metal oxides, understanding the nature of unusual ordered states, such as spin-density waves, charge-density waves, nematic order, and superconductivity, has remained a major focus of investigation, as have associated phenomena, properties, and pathways between phases, such as metal-insulator transitions.[33]

A major focus over the past decade has been on quantum spin liquids.[34] These can have an impact on data storage and memories in addition to furthering the understanding of high-temperature superconductivity. In these materials, fluctuating spins do not order down to the lowest temperature but

[33] H. Yang, S.W. Kim, M. Chhowalla, and Y.H. Lee, 2017, Structural and quantum-state phase transitions in van der Waals layered materials, *Nature Physics* 13:931-937.

[34] S. Lucile and B. Leon, 2017, Quantum spin liquids: a review, *Rep. Prog. Phys.* 80(1):016502.

rather form a highly entangled state. Several different approaches to realizing these quantum spin liquids were pursued, exploiting avenues to obtain frustrated magnetic interactions. Significant experimental and theoretical work was motivated by the "Kitaev model" of $S = 1/2$ Fermion on a honeycomb lattice. Experimentally, several possible candidate systems were discovered, but a definitive proof that these materials are indeed quantum spin liquids is still outstanding. The search for quantum spin liquids was also one major motivation for extensive studies of the iridate family of materials over the past decade. These materials combine strong correlation physics and spin-orbit coupling. A second major motivation for the studies of iridates and related materials is the idea that exotic superconducting pairing symmetry might be realized in doped spin-orbit Mott insulators. In general, strong spin-orbit coupling emerged as a major theme motivating new materials design and synthesis over the past decade, including in materials as diverse as correlated materials,[35] topological insulators, and magnetic skyrmion systems.

Thin Films

The past decade also saw major progress in strongly correlated thin films and heterostructures. These studies are motivated by the ability to design novel quantum states using approaches such as quantum confinement or electric field gating that are not available in the corresponding bulk materials. For example, significant research activities over the past decade in rare-earth nickelate thin films were motivated by theoretical predictions of a cuprate-like Fermi surfaces in heterostructures. Thin film studies—in particular, strain and interface engineering—led to new insights into the role of lattice coupling in strongly correlated phenomena such as metal-insulator transitions. Major advances were also made in thin film synthesis—in particular, molecular beam epitaxy (MBE)—of correlated materials. Examples include very high mobility complex oxide thin films grown by MBE and the demonstration of superconducting Sr_2RuO_4 films.

Developments in the areas of computation, growth, and measurement, and their coordination[36,37] have led to substantial advances in the field of quantum materials. The utilization of these techniques have led to the discovery of new superconductors, with Tc over 200 K in the hydrogen-sulfides at extremely high pressure, and to a deeper understanding of novel quantum phases owing to enormous advances in the measurement of electronic properties (e.g., tunneling, point contact, photoemission, and terahertz spectroscopies; some of these challenging measurements are done with surface tools in order to measure bulk properties), quantum oscillations, resonant inelastic X-ray scattering, and neutron scattering—all possible because of the substantial improvement in materials quality, crucial to this field. The Cooper pairing mechanism for the various families of unconventional superconductors is also being clarified—phonons, spin-excitations, and orbital fluctuations all seem to have a role to play. Last, researchers have discovered, identified, and gained understanding and control of newer forms of quantum matter, including topological insulators, and van der Waals semiconductors where the roles of strong electron correlations, broken symmetries, topology, and dimensionality are being explored. Researchers have learned to control and manipulate their quantum phases with a variety of experimental techniques, including those at extreme conditions, such as high pressure, high photon flux, and high magnetic field. An example is the recent observation of the Higgs mode in a disordered superconductor[38] and in NbN using time-resolved terahertz spectroscopy.

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[35] J. Mannhart and D.G. Schlom, 2010, Oxide interfaces—an opportunity for electronics, *Science* 26:1607-1611.

[36] C. Broholm, et al. "Basic Research Needs in Quantum Materials," Basic Energy Sciences, U.S. Department of Energy, Office of Science, http://www.sc.doe.gov/bes/reports.lists.html, accessed February 11, 2018.

[37] D.N. Basov, R.D. Averitt, and D. Hsieh, 2017, Towards properties on demand in quantum materials, *Nature Materials* 16, 1077-1088, doi:10.1038/nmat5017.

[38] D. Sherman, U.S. Pracht, B. Gorshunov, S. Poran, J. Jesudasan, M. Chand, P. Raychaudhuri, et al., 2015, *Nature Physics* 11:188-192.

2.4.2 Magnetic Materials

Magnetic materials principally are used in two major types of applications—electromagnetic devices and magnetic information storage and logic. In electromechanical applications, motors, and actuators, the quest for new materials focuses on hard magnets—that is, materials that develop strong external magnetic fields that, in turn, produce strong forces. These are particularly relevant today, as electric propulsion is becoming prevalent, and the performance of hard magnets enables the design of ever more powerful, compact, and lightweight motors; see, for example, Case 3 in Section 5.3.

The second class of applications is in computers, and particularly magnetic memories and readouts. In the near future, distributed sensing and computing will require greatly reduced power consumption and the integration of multifunctionality into single-chip devices that will require new materials and architectures. Magnetism has an important role to play in this multidimensionality. Almost the entire industry of nonvolatile memories (those that retain the information when the power is switched off) are based on magnetic random-access memory (MRAM). So are magnetic recording devices such as hard drives. These devices are largely based on the physics of *spin dynamics*. Progress in this field has been driven by the discovery of the giant magnetoresistance, for which the 2007 Nobel Prize in physics was awarded jointly to Albert Fert and Peter Grünberg.

Over the course of the last three to four decades, progress has been made in developing new rare-earth-based hard magnets (neodymium-iron-boron or samarium-cobalt). These materials have enabled the development of compact high-power motors for electric transportation. The core of the work consisted in developing materials with a high remanent magnetization (the magnetic field that a magnet can produce by itself), a high coercive field (the amount of external magnetic field that a magnet can take without losing its own magnetization), and a high operating temperature. One drawback of the current materials is that they rely on rare-earth elements, which are costly to extract and purify. Nanotechnology has been of substantive help in this work, as nanometer-size grains of magnetic material tend to pin down the magnetic alignments in the grains and increase the coercivity. Progress in manufacturing of these materials includes the development of printable magnets (see Box 2.6).

The last decade has seen considerable progress in *spin dynamics and spin transport*, typically in linear spin transport. Recent developments include the discovery of the spin-dependent Seebeck effects (thermoelectric effects of spin-polarized conduction electrons); the characterization of the out-of-equilibrium magnon system not only by its classical dispersion relation but also by the new theoretical concepts such as the magnon chemical potential. In magnonic systems, linear transport is described in terms of a spin conductance and a spin-Seebeck effect in either metallic ferromagnets like Permalloy, magnetic semiconductors like GaMnAs, or, most recently, in ferromagnetic insulators like yttrium-iron-garnet (YIG).

Spin transport across interfaces enriches the number of possible effects because the interface breaks the symmetry present in uniform materials. In the last decade, the bilayer system consisting of a ferromagnet and a metal with strong spin-orbit interactions, most notably Pt/YIG, has become the paradigm for new discoveries and for new explanations developed for older discoveries, such as the anomalous Hall, spin-Hall, inverse spin-Hall, and spin-Nernst effects.[39] These effects have led to a completely new way of measuring local magnetizations and spin currents: a new tool that will lead to future important discoveries in magnetic materials and widen the possibility of designing new spin-electronic devices, such as logic elements, amplifiers, and oscillators. Topological insulator materials, which are also based on strong spin-orbit interactions, have been coupled in this way to ferromagnetic solids, typically Bi_2Se_3/YIG.

[39] S. Meyer, Y.T. Chen, S. Wimmer, M. Althammer, T. Wimmer , R. Schlitz, S. Geprägs, et al., 2017, Observation of the spin Nernst effect, *Nat Materials* 16(10):977-981, doi: 10.1038/nmat4964.

BOX 2.6
Printable Magnets

The Critical Materials Institute (CMI), which is part of the Department of Energy's Ames Laboratory, has developed a process to print high-strength bonded magnets that outperform conventionally processed magnets in some applications. This allows for devices like generators and electric motors to be made with reduced demand for critical materials such as neodymium and dysprosium.

The process was recognized with an R&D 100 Award in 2017 and offers electric machine designers some distinct advantages, as follows:

- Net shape or near-net shape production reduces machining losses of valuable magnet materials.
- The ability to print complex shapes allows for improved use of magnetic flux.
- Comparable motor performance can be achieved with less magnet material, or improved performance can be achieved with the same amount used in a design based on conventionally manufactured magnets.

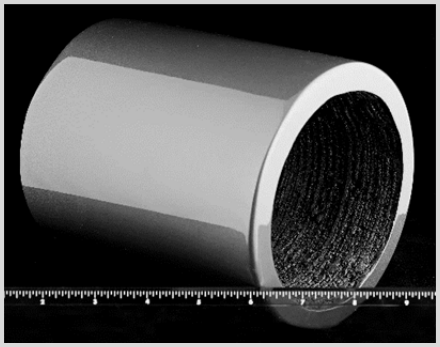
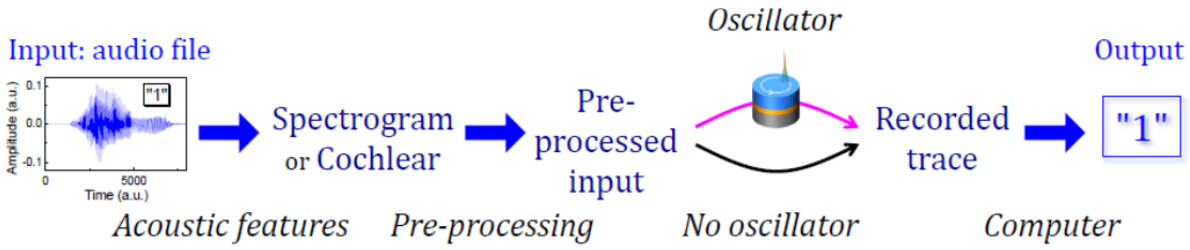


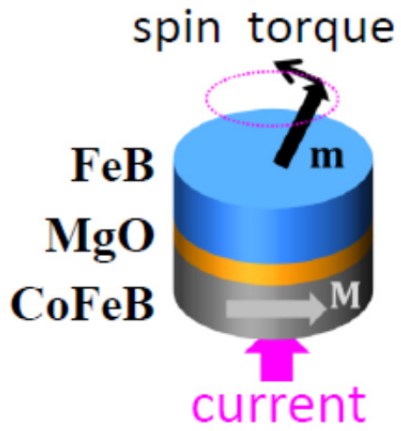
FIGURE 2.6.1 Isotropic, neodymium-iron-boron bonded permanent magnet, 3D-printed at the Department of Energy's Manufacturing Demonstration Facility at Oak Ridge National Laboratory. NOTE: See L. Li, A. Tirado, I.C. Niebedim, O. Rios, B. Post, V. Kunc, R.R. Lowden, et al., 2016, Big area additive manufacturing of high performance bonded NdFeB magnets, *Scientific Reports* 6:36212, doi: 10.1038/srep36212. SOURCE: Courtesy of Oak Ridge National Laboratory.

Spin-Torque Oscillators

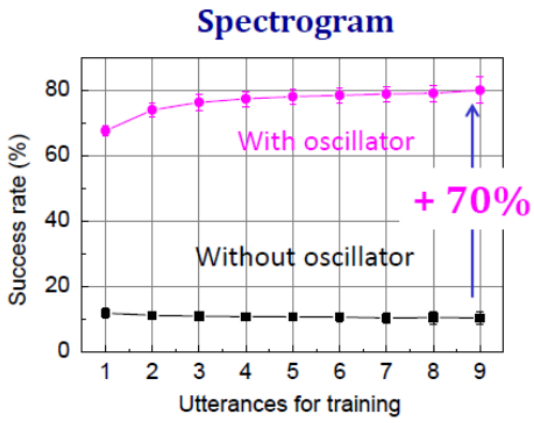
Spin-torque oscillators such as FeB/MgO/CoFeB trilayers in 100 nm diameter pillars predate the last decade. However, it was suggested in 2017 that they could provide an extraordinary hardware platform on which to perform neuromorphic computations. Neuromorphic computers are analog computers inspired by the logical architecture of the brain. The architecture requires highly stable oscillators (the source of "brain waves") that give an output function that is nonlinear with respect to the input signal yet do not dissipate too much power. Spin-torque oscillators have all the desired characteristics, while being solid-state devices that operate at GHz frequencies. They have been demonstrated to provide a significant boost to speech-recognition algorithms (see Figure 2.10).



(a)



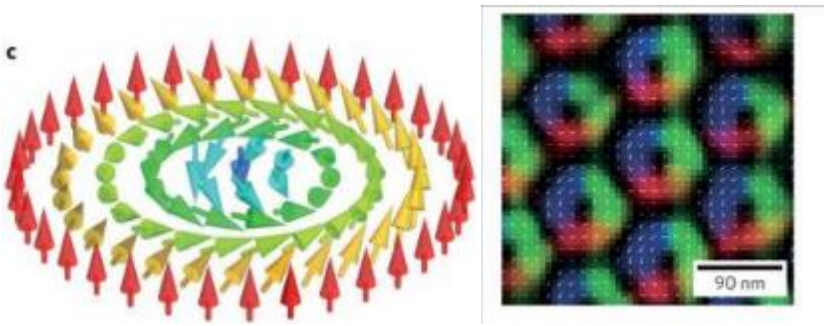
(b)



(c)

FIGURE 2.10 (a) FeB/MgO/CoFeB trilayer spin-torque oscillators improve speech recognition by 70 percent. Spoken numbers (1 to 10), input as an audio file, are preprocessed by a conventional computer and then fed to a highly stable but nonlinear spin-torque oscillator driven by a current. The output waveform in the current is analyzed for word recognition by a classical digital computer. (b) Trilayer spin-torque oscillators of a multilayer stack consisting of FeB/MgO/CoFeB as a current is passed through the stack. (c) The success rate during training with and without the spin-torque oscillator: adding the spin-torque oscillator increases the success rate of the word recognition by 70 percent. SOURCE: Panels (a) and (c) were committee generated. Panel (b) is from J. Torrejon, M. Riou, F.A. Araujo, P. Bortolotti, V. Cros, and J. Grollier, 2017, Neuromorphic computing with nanoscale spintronic oscillators, *Nature* 547:428-431.

Antisymmetric exchange interactions—for example, the Dzyaloshinskii-Moriya interaction—favor orthogonal spin alignment, which leads to a number of new skew effects such as a possible magnon Hall effect. This introduces chirality in the magnetization—for example, in *skyrmions*. Skyrmions are localized reversals of magnetization in an otherwise uniform ferromagnet (see Figure 2.11a). Their spatial extent is generally greater than a lattice spacing but still small (down to a few nanometers), and they move with little energy cost (several orders of magnitude lower than that needed to move magnetic domain walls). These properties project the possibility that skyrmions can be used to create magnetic memory elements with extremely high information density and low power consumption.



(a) (b)

FIGURE 2.11 (a) The smallest possible perturbation of the otherwise uniform magnetization (up-arrows) of a ferromagnet is a skyrmion. Its core (down-arrow) is a single atom surrounded by a twisting of atomic magnetic moments that returns the spin texture to the background direction. (b) A triangular lattice of skyrmions has been observed in FeGe. SOURCE: (a) Reprinted with permission from Springer Nature: C. Pfleiderer, 2011, Magnetic order: surfaces get hairy, *Nature Physics* 7:673-674, copyright 2011. (b) Reprinted with permission from Springer Nature: A. Fert, V. Cros, and J. Sampiao, 2013, Skyrmions on the track, *Nature Nanotechnology* 8:152-156, copyright 2013.

The integration of magnetic effects on single-chip devices will be further enhanced by the development of multiferroic materials, which combine magnetic effects with electrical ones.

Multiferroic materials involve simultaneously two or more "ferroic" orders—for example, ferromagnetism and ferroelectricity. Thus, when ferroelectric solids (those that are spontaneously polarized with reversible electric polarization) also display ferromagnetic or ferrimagnetic order (spontaneous magnetic polarization), the materials are known as multiferroic. Two possibilities have come to the fore in the last 10 years. $BiFeO_3$ is the sole single-phase multiferroic that demonstrates ambient temperature magnetoelectric coupling. Used in concert with $CoO_{0.9}Fe_{0.1}$ to amplify magnetization, $BiFeO_3$ is the closest switching multiferroic to production. The second successful room-temperature multiferroic for switching is a lutetium-based superlattice consisting of hexagonal $LuFeO_3$, a ferroelectric, with $LuFe_2O_4$, a ferrimagnet. In constructing the superlattice, a monolayer of $LuFe_2O_4$ is added once every 10 layers of the $LuFeO_3$ through the addition of FeO during the molecular beam epitaxial growth to produce the multiferroic response. Switching is a significant hurdle in the development of devices. Optical control, to afford picosecond control, is likely required, so long as the switching is perfectly reversible down to the level of the magnetic domains.

Multiferroic studies also have inspired new research and technology development in other material-related areas. For example, more general studies of possible mechanisms that promote spontaneous order in ferroelectrics are under way. Significant progress in the growth of oxide heterostructures has advanced to enable joining of multiferroics with circuitry. Nonlinear laser spectroscopy has advanced to allow imaging of magnetic and ferroelectric domains and their interaction.

2.4.3 Two-Dimensional Quantum Materials

Graphene

The modern ascension of 2D materials began with the isolation and electrical measurement of single-atomic-layer graphite, or graphene, by Geim and Novoselov in 2004, which garnered a Nobel Prize in 2010.[40] Although the band-structure of graphene had been calculated in 1947, and individual flakes had

[40] See https://www.nobelprize.org/nobel_prizes/physics/laureates/2010/press.html, accessed August 6, 2018.

been imaged with electron microscopy, Geim and Novoselov demonstrated that one-atom-thick membranes could be simply created and easily fabricated into electronic devices. While the first graphene devices were created by mechanical exfoliation of graphite using adhesive tape, large-area growth can now be achieved via chemical vapor deposition, liquid-phase exfoliation, and synthesis on SiC.[41] Graphene is a zero-gap semiconductor having properties such as high electron mobility (>15,000 $cm^2V^{-1}s^{-1}$), large thermal conductivity, mechanical strength and elasticity, optical transparency, impermeability, and high electrical sensitivity to adsorbates.

Experiments on graphene have demonstrated novel and potentially useful electronic, photonic, mechanical, and thermal behavior. For example, it has been shown that charge carriers in graphene display relativistic effects such as tunneling through large barriers and can also display collective hydrodynamic flow, while the unique properties of graphene's optical absorption make it highly opaque. However, to enable graphene to be used in electronic and optoelectronic devices it is necessary to determine how to create a tunable bandgap. Different approaches have been developed including confinement, defect introduction, mismatch strain from a substrate, adsorption, and strain.

Mechanically, graphene is similar to paper: it is hard to stretch but easy to bend. This property was predicted and later shown to be attributed to ripples in the graphene membrane. The high tensile strength of graphene means that it breaks at low strains. However, large deformation strains have been shown to be possible in graphene through the use of kiragami-like cuts, with reversible elongations of 240 percent having been achieved. A remarkable finding was that the electrical and thermal conductivity was insensitive to strain—a property achieved by the lack of deformation of the graphene itself. This use of strain engineering to graphene sheets opens avenues to using them for stretchable electronics, hinges, springs, and thermal management.

Further remarkable properties have been demonstrated in multilayer and encapsulated graphene. For example, the application of a gate voltage can induce a gap in bilayer graphene, leading to an ultrathin but mechanically robust semiconducting material. Adding layers ("few-layer graphene") yields metallic material that maintains useful properties such as thinness, mechanical and thermal stability, transparency, and sensitivity to functionalization. It has been shown that the properties of graphene can be optimized by encapsulation in an inert material, particularly hexagonal boron nitride, which is itself a monolayer insulator that is lattice-matched to graphene.

There has been tremendous effort toward creating graphene-based applications, with a few commercial products already at market, including security tags using graphene ink (Siren Technology), graphene-enhanced diaphragms for earphones (FiiO Electronics), graphene-composite tennis rackets (Head) and helmets (Catlike), graphene supercapacitors (Skeleton Technologies), and graphene-based molecular sensors (Nanomedical Diagnostics).

Transition Metal Dichalcogenides

Since the isolation of graphene, there has been a revolution in the discoveries of monolayer and few-layer materials that can be mechanically or chemically exfoliated. The observation in 2010 of the dramatic increase in the photoluminescence in a monolayer of molybdenum disulphide (MoS_2) over that in the bulk material or even in bilayer MoS_2 has led to an explosion in activities in the genre of materials known as *transition metal dichalcogenides*, MX_2, in which M is a transition metal and X is sulfur, selenium, or tellurium. These materials span the full range of electronic behavior from metallic to wide-bandgap insulators. These materials have diverse electronic, quantum, thermal, optical, chemical, and mechanical properties, ranging from MoS_2 or phosphorene as n- and p-type semiconductors to $NbSe_2$ as a superconductor and WTe_2 as a Weyl semimetal (see Box 2.6 for an explanation of Weyl semimetal).

[41] E.O. Polat, O. Balci, N. Kakenov, H.B. Uzlu, C. Kocabas, and R. Dahiya, 2015, Synthesis of large area graphene for high performance in flexible optoelectronic devices, *Scientific Reports* 5:16744.

They are also known as *van der Waals materials* because in the crystal the monolayers are held together by weak van der Waals interactions. The monolayer itself consists of an atomic layer of hexagonally packed metal atoms sandwiched between two layers of chalcogen atoms. This sandwich structure results in valence-satisfied atoms, making the basal plane inactive. As with graphene, monolayer transition metal dichalcogenides exhibit quantum confinement leading to enhancements in the electronic, optical, thermal, and mechanical properties that are significantly different from those of the bulk material—for example, the semimetallic to semiconducting transition observed in ultrathin TiS_2, the metallic-to-insulating transition of TaS_2, and the indirect-to-direct bandgap transition together with the widening of the bandgap for Mo and W dichalcogenides. Some of these 2D materials also exhibit interesting strongly correlated electron phenomena, such as charge density waves and superconductivity. Another very promising property of semiconducting monolayer transition metal dichalcogenides is the remarkably strong light-exciton interactions and greatly enhanced electron-electron interactions. Exciton binding energies in these materials can be hundreds of meV, two orders of magnitude larger than what is seen in typical bulk semiconductors. Similar is the trend in the binding energies of trions (charged excitons), about tens of meV, much larger than that in ordinary semiconductors, owing to reduced electron screening resulting from their 2D nature. Moreover, there is the possibility of full control of the valley and spin occupation by optical pumping with circularly polarized light. Monolayer MoS_2 has already also been shown to yield field-effect transistors with very high current on-off ratios and to function within a vertical graphene-MoS_2-graphene tunneling transistor structure. These properties, in combination with the promise of synthesis of large-area high-quality samples (notably by recently developed CVD methods), suggest interesting possibilities for applications of this and related materials in electronics and optoelectronics.[42]

Naturally, the structural and chemical terminations of the edge of the 2D transition metal dichalcogenides play a role in determining the local physical and chemical properties of these systems. Furthermore, vacancies in the basal plane and dopant can also change the local electronic structure. First principles calculations have predicted that diverse edge passivation in metal dichalcogenides could produce different spins states that modify the edge electronic and magnetic properties. In addition, high spin density could be localized surrounding metal vacancies. Calculations also predict that electronic structural changes brought about by vacancies could lead to chemical reactivity. While experimental exploration is still at an early stage, preliminary results already point to promising chemical activity of this otherwise inactive basal plane when pristine. Adsorbed metallic nanoparticles could also facilitate chemical reactions of 2D MoS_2. Given the bandgap of about 1.8 eV, monolayer MoS_2 is also a promising candidate for water splitting. Although monolayer MoS_2 became popular as a possible opto-electronic material, its catalytic activities seem to have been realized at a faster pace.

Looking Beyond Graphene and Transition Metal Dichalcogenides

There are many layered materials that go beyond the transition metal dichalcogenides (TMDs), including monochalcogenides (GaSe, etc.), monoelemental 2D semiconductors (silicene, phosphorene, germanene), black phosphorus, and MXenes (see Figure 2.12). The great ability to tune the bandgap, band offset, carrier density, carrier polarity, and switching characteristics in 2D materials provides unparalleled control over device properties and possibly new physical phenomena. Devices based on atomically thin monolayers are the extreme scenario for the future lightweight, low-power consumption, and wearable electronics. Moreover, the true potential of these layered materials may emerge from the ability to stack them, layer by layer in any desired sequence, to create novel 3D architectures with entirely new functions.

[42] See https://pubs.acs.org/doi/full/10.1021/nn400280c, accessed March 3, 2018.

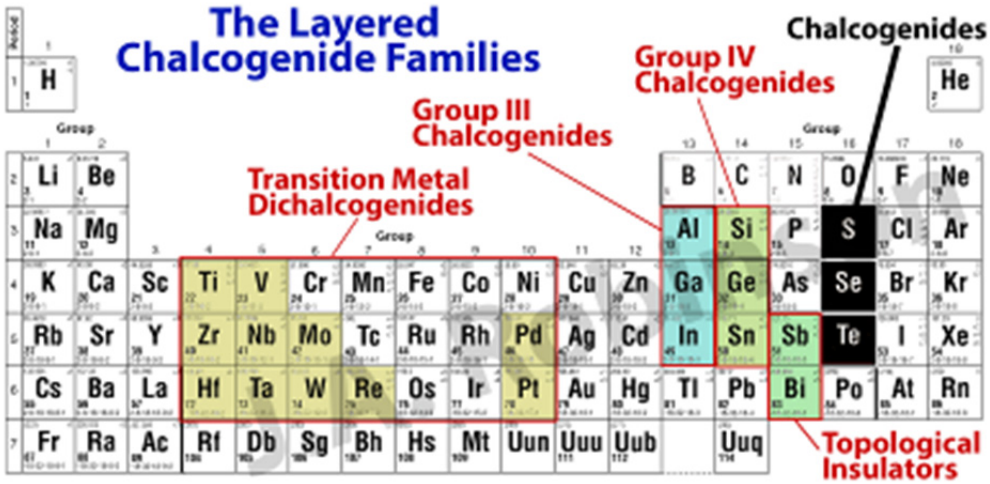


FIGURE 2.12 The Chalcogenide families. SOURCE: Courtesy of Joshua Robinson, Penn State, https://news.psu.edu/story/466016/2017/05/01/research/stenciling-atoms-two-dimensional-materials-possible.

Elemental examples of 2D materials include the X-enes: graphene, phosphorene, stanene, and germanene, to name a few. Two-dimensional allotropes and compounds are rapidly growing in number with 2D nitrides, such as hexagonal boron nitride (h-BN), and TMDs, such as molybdenite (MoS_2), receiving the greatest attention. Other TMDs having the form of MX_2 (where M = Mo, W, Ti, Nb, etc., and X = S, Se, or Te) have started to gain significant interest. More complex compounds such as fluoro-X-enes, chloro-X-enes, X-anes, and MX-enes have also been theorized and demonstrated. Potential applications include energy harvesting and storage, sensing, pharmaceuticals, electronics and photonics, and bioengineering.

Another 2D material that was discovered in the wake of graphene is 2D hexagonal boron nitride (h-BN), which was theoretically predicted to induce a bandgap in graphene when serving as its substrate. The flurry of activity in h-BN because of its role as a stable substrate, and as a gate dielectric or deep ultraviolet emitter, however, has promoted it as an interesting material in its own right. While being a wide-bandgap semiconductor, it has recently been shown to be an excellent hydrogenation catalyst, when laden with defects. As one of the few metal-free catalysts, it has emerged as a promising 2D material. In summary, there are now over 600 different 2D materials recognized, most of which had 2D stability predicted only in the last decade, and some of which have not yet been synthesized.

2.4.4 Topological Materials

It is rare that unexpected states of matter appear; however, in 2005-2006 it was predicted that a new quantum state, a *topological insulator* (TI), should exist in materials where spin-orbit coupling causes electrons to develop an excitation spectrum with a nontrivial topology and wavefunctions characterized by an invariant (e.g., a Chern number) that remains unchanged under adiabatic deformations of the system. Unlike conventional atomic insulators, TIs exhibit gapless, conducting edge states in addition to a full insulating gap in the bulk so that the material behaves as an insulator in its interior, but the surface contains conducting states, meaning that electrons can move only along the surface of the material.

The past decade saw the prediction and characterization of topological insulator properties in many materials, including InAs/GaSb heterojunctions, $Bi_{1-x}Sb_x$ alloys, Bi_2Te_3, $GeBi_2Te_4$, and SmB_6. Additional progress in theoretical techniques include band structure analysis under spin-orbit interactions and systematic analysis of crystal symmetries, which have been developed to determine a multitude of topological properties and predict bulk and edge properties. In 2016, the efforts resulted in the Nobel

Prize in physics being awarded "for theoretical discoveries of topological phase transitions and topological phases of matter."[43] Beyond the basic recognition of topological properties, there has been significant progress in fabricating topological materials that clearly express the topological properties, which are needed for fundamental research or to enable device applications.

Most materials, such as the Bi-based ones, were grown as bulk crystals. Thin films were directly exfoliated from crystals or grown by molecular-beam epitaxy, while nanowires of Bi_2Se_3 were grown by the vapor-liquid-solid mechanism. Doping Bi_2Se_3 with Cu or Nb can induce superconductivity, while doping with Mn induces ferromagnetism. However, for many materials, it remains a challenge to tune the Fermi energy to within the bandgap, where topological states should dominate. For example, Bi_2Se_3 and related compounds suffer from strong n-doping owing to Se vacancies; this was alleviated by adding bulk dopants such as Sb, or by utilizing undoped compounds such as SmB_6.

Soon after the initial predictions, transport measurements of 2D HgTe/CaTe quantum wells provided evidence of quantized edge states and angle-resolved photoemission spectroscopy (ARPES) of protected surfaces states with single Dirac cones (see Figure 2.13). Since then, many other experiments have determined unusual properties of TIs: helical spin polarization was shown via spin-polarized ARPES on 3D TIs, while quantized edge states have been found in other 2D TIs such as $ZrTe_5$ and InAs/GaSb. Scanning tunneling microscopy on 3D TIs near defects showed evidence of suppressed backscattering, while measurements of quantized polarization switching in light reflected off TIs is consistent with predicted additional cross-terms for magnetization and polarization in Maxwell's equations (the quantized magneto-electric effect). Magnetically doped TIs exhibited a quantum anomalous Hall effect, where ferromagnetism and spin-orbit coupling combine to create a quantum Hall effect at zero external magnetic field. Other predicted behavior in TIs, such as of fractional edge charges and bulk spin-charge separation, remain to be demonstrated.

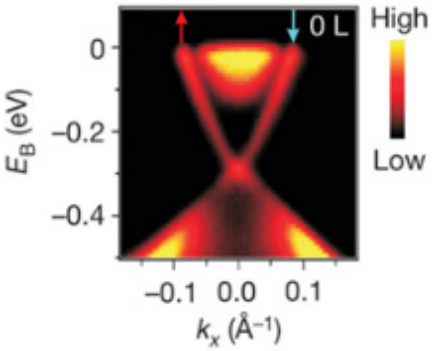


FIGURE 2.13 High-resolution ARPES surface band dispersion through of Bi2-δCaδSe3 (111). The arrows denote the topological spin polarization of the bands. The separation between surface and bulk states, as well as Dirac-like dispersion can be seen. SOURCE: Reprinted with permission from Springer Nature: D. Hsieh, Y. Xia, D. Qian, L. Wray, J.H. Dil, F. Meier, J. Osterwalder, et al., 2009, A tunable topological insulator in the spin helical Dirac transport regime, *Nature* 460:1101-1105, doi: 10.1038/nature08234, copyright 2009.

A topological superconductor is predicted to have a gapped bulk and gapless surface states, with excitations that are Majorana zero modes. Although many experiments to date have studied superconducting proximity effects in topological surface states, clear evidence of Majorana modes in these systems has not yet been demonstrated. Topological superconductivity was proposed to exist in semiconducting nanowires with strong spin-orbit coupling, proximity-coupled to s-wave superconductors,

[43] The 2016 Nobel Prize in physics was awarded to David Thouless, Duncan Haldane, and Michael Kosterlitz. See, for example, https://www.nature.com/collections/fwsytynlwg, accessed May 6, 2018.

and placed in magnetic fields, so that spin-triplet superconductivity is induced. The predicted Majorana excitations have been demonstrated in InSb wires coupled to s-wave superconductors, as well as in a related system of atomic-scale Fe nanowires on Pb substrates. However, coherence, braiding and other qubit properties remain to be demonstrated.

The last decade has identified a wealth of materials, beyond 2D and 3D topological insulators, with interesting and potentially useful topological properties, opening a new materials area of "topological quantum matter." Among these are Weyl semimetals (see Box 2.7), conducting materials whose excitations are highly mobile fermions (a chiral half of a Dirac fermion); after theoretical predictions, Weyl properties were discovered in TaAs via ARPES spectroscopy.

Weyl semimetals are a specific example of the broader category of "topological metals" whose excitations are topologically protected fermionic quasiparticles. Topological crystalline insulators, such as SnTe, and $Pb_{1-x}Sn_xSe$ are topological phases of matter that are protected by crystal symmetries, including rotation and reflection; the Dirac cones and surface-state properties of these materials have been explored via ARPES and STM. New research has demonstrated that disorder and interactions may further tune the properties and phase transitions of topological materials. Last, a large variety of topological materials formed from 2D membranes has been proposed.

The great advances in the topological physics of electron waves have naturally led to an explosion of research on topological properties of photons, phonons, plasmons, and other waves. Initial research in this arena focused on replicating electronic behavior in microwave photonics in easily constructed centimeter-scale systems. The earliest demonstration of such a system was a materials system consisting of a square array of gyromagnetic ferrite rods (providing coupling between electric and magnetic fields) in an external magnetic field (to break time-reversals invariance) that exhibited the optical analog of the quantum Hall effect with a single topologically protected, unidirectional edge mode that propagated around arbitrary disorder without reflection. This and related systems enable novel device designs for a variety of optical applications. Optical systems involving a double-gyroid lattice in a magnetic field[44] exhibit Weyl points and line nodes, and coupled infrared optical resonator waveguides with degenerate oppositely moving modes mimic the quantum spin Hall effect of topological insulators with edge states that have effective topological protection. Similarly inspired topological mechanical and fluid mechanical models exhibiting protected edge modes have also been constructed. For example, Vitelli and Irvine et al.[45] have built a new type of mechanical metamaterial: a "gyroscopic metamaterial" composed of rapidly spinning objects that are coupled to each other. At the edges of these materials, they find that sound waves are topologically protected so that they cannot be scattered back into the bulk.

[44] J.A. Dolan, B.D. Wilts, S. Vignolini, J.J. Baumberg, U. Steiner, and T.D. Wilkinson, 2014, Optical properties of gyroid structured materials: From photonic crystals to metamaterials, *Advanced Optical Materials* 3:12-32, https://doi.org/10.1002/adom.201400333.

[45] L.M. Nash, D. Kleckner, A. Read, V. Vitelli, A.M. Turner, and W.T.M. Irvine, 2015, Topological mechanics of gyroscopic metamaterials, *Proceedings of the National Academy of Sciences U.S.A.* 112(47):14495-14500.

BOX 2.7
Weyl Semimetals

The topological insulator (TI) and Weyl semimetal (WSM) or Dirac semimetal (DSM) are shown in Figure 2.7.1. The topology of both a TI and a WSM/DSM originates from a similar inverted band structure.

Permission Pending

FIGURE 2.7.1 (a) The spin-orbit coupling (SOC) opens a full gap after the band inversion in a TI, giving rise to metallic surface states on the surface. (b) In a WSM/DSM, the bulk bands are gapped by SOC in the 3D momentum space except at some isolating linearly crossing points—namely, Weyl points/Dirac points—as a 3D analog of graphene. Owing to the topology of the bulk bands, topological surface states appear on the surface and form exotic Fermi arcs. In a DSM all bands are doubly degenerate, while in a WSM the degeneracy is lifted owing to the breaking of the inversion symmetry or time-reversal symmetry, or both. The net Berry phase accumulated in the 2D k plane between a pair of Weyl points induces a nonzero Chern number $C = 1$ with a quantized anomalous Hall effect (AHE), while the Berry phase is zero in other planes with $C = 0$. (c) The type-I WSM. The Fermi surface (FS) shrinks to zero at the Weyl points when the Fermi energy is sufficiently close to the Weyl points. (d) The type-II WSM. Owing to the strong tilting of the Weyl cone, the Weyl point acts as the touching point between electron and hole pockets in the FS. SOURCE: B. Yan and C. Felser, 2017, Topological materials: Weyl semimetals, *Annual Review of Condensed Matter Physics* 8:1-19.

2.4.5 Qubits—The Building Blocks for Quantum Computers

Quantum computers hold the promise of being able to solve some problems efficiently that are believed to be intractable for classical computers. They are challenging to construct because one must have a way of specifying and controlling the quantum operations while avoiding decoherence arising from unintended interactions with the environment. A summary of the goals and comparative

achievements of quantum computing is summarized in the report "Technical Roadmap for Fault-Tolerant Quantum Computing,"[46] Tremendous progress toward the development of quantum computers has been made in the past decade, and progress in materials has been critical to these achievements.

The qubit types that have emerged in the last decade along with the pros and cons of each are summarized in Box 2.8. Of these qubit types, the two leading ones are superconducting qubits and ion-trap qubits. This section focuses on those qubits with materials challenges.

BOX 2.8
Qubit Types

In quantum computers, materials and physical processes are optimized to form qubits, a localized system that can take the values of not only one or zero but also any superposition of these. When two or more qubits interact, quantum entanglement can occur, enabling operations on many qubits simultaneously, and inspiring visions of calculations that are beyond the reach of classical computers. Entangled states are still fragile, and rates of decoherence affect not only accuracy but also gate depth (number of consecutive operations). The leading qubit platforms are described in Figure 2.8.1.

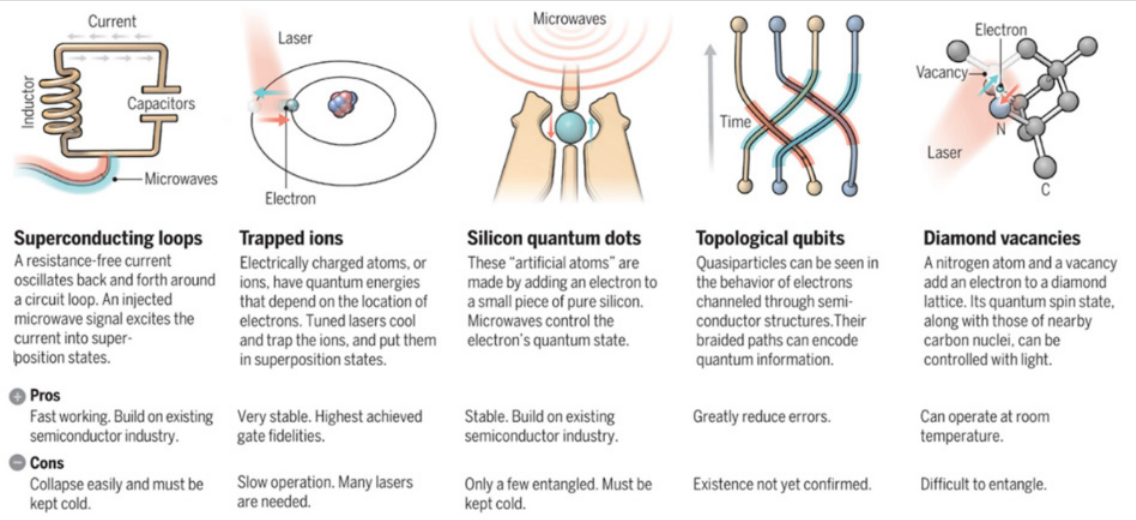


FIGURE 2.8.1 The leading qubit platforms. SOURCE: Figure adapted from G. Popkin, 2016, Quest for qubits, *Science* 354:1090-1093. Copyright © 2016, American Association for the Advancement of Science.

The most commonly used superconducting qubit is the transmon, an anharmonic oscillator where nonlinear inductance is provided by a Josephson junction shunted by a capacitance provided by large superconducting pads in proximity. The typical transmon utilizes the most mature and simply fabricated superconducting junction, Al-AlO_x-Al, where the AlO_x is grown inside the evaporation chamber without breaking vacuum. Nonetheless, amorphous AlOx has been measured with a two-level-system defect density of not less than 0.5 $(mm^2\text{-}GHz)^{-1}$. To put this in perspective, current transmons are tenths of a mm in size, and since the microwaves used to communicate with the transmons are in the GHz range, even this minimized defect density will result in roughly one defect every 10 GHz per qubit. In order to advance this technology, a greater understanding and control of defects in these materials is necessary.

[46] See https://nqit.ox.ac.uk/sites/www.nqit.ox.ac.uk/files/2016-11/NQIT%20Technical%20Roadmap.pdf.

Current promising directions toward removing defect sources include growing an epitaxial insulating layer, such as epitaxial Al_2O_3 by creating Re-Al_2O_3-Re or Re-Al_2O_3-Al junctions, epitaxial MgO as in Re/MgO/Al, epitaxial Nb-Al-Al_2O_3-Nb, or semiconducting nanowires sandwiched between Al leads.

To protect transmons from the environment, an architecture called *circuit quantum electrodynamics* (cQED) is employed whereby the qubit is coupled to a microwave resonator, and that readout resonator is coupled to the external environment. For the cQED component, microwave resonators are usually patterned by a subtractive process from sputtered or expitaxial films, requiring materials that are simple to etch through a photomask (e.g., Al, Nb, Re, TiN). A low-power Q for these resonators is also sought. One style of transmon couples the qubit on a sapphire substrate to the microwave field in a 3D cavity. Since qubits measured in this way have the highest lifetimes, this technique has been used for studies of surface participation on qubits, thereby informing qubit design. These cavities are typically made from high-purity Al, but other materials and coatings/processes have been considered. There have even been reports of high-Q 3D-printed cavities.

Quantum annealing has been used to find the lowest energy state of a single challenging Hamiltonian, which is relevant for many optimization problems. In this computer, which uses a different type of transmon, switches are formed from Josephson junctions of two Nb layers separated by a thin layer of insulator such as AlO_x. Variability in junction thickness is a challenge, ameliorated with additional circuitry and fields. The question of the amount of quantum speedup for this type of machine is an area of active scientific discussion.

Topological qubits, which have emerged only in the past decade, have attracted much excitement because they can be inherently fault tolerant. These qubits are quasiparticle excitations of hybrid topological systems (e.g., superconducting proximity-coupled topological insulators, or proximity-coupled semiconducting nanowires in magnetic field). The excitations are characterized as nonabelian anyons, which have superimposed quantum states that can be encoded in braided quasiparticle trajectories. These braided paths are "topologically protected," meaning that they require less error correction than other types of qubits (e.g., transmons). Finding clear evidence of nonabelian anyons—specifically, Majorana excitation—has been a challenge. Promising results have been achieved in InSb wires coupled to s-wave superconductors, as well as in a related system of atomic-scale Fe nanowires on Pb substrates. However, coherence, braiding, and other qubit properties remain to be demonstrated, and it remains unclear which systems, materials, and measurements will be optimal.

Semiconductor quantum dots, which act as "artificial atoms" with addressable spin and charge states, have the advantage of building on existing semiconductor technology infrastructure. Early quantum dots were made in heterostructures of gallium arsenide and aluminum gallium arsenide, but it is now much more common to use devices made in silicon (Si) or in silicon/silicon-germanium (Si/SiGe) heterostructures, with the electrons confined and manipulated using voltages applied to lithographically defined metallic gates. Charge and nuclear spin noise are the dominant sources of decoherence and gate errors. To counteract spin noise, isotopically purified Si is often used, while the effects of charge noise are mitigated by changes in qubit design including dopants. Recent work has demonstrated that other materials systems could be suitable for hosting quantum dot qubits. For example, an artificial double quantum dot molecule in a gated MoS_2 van der Waals heterostructure, has promising controllability, properties, as well as manufacturable reproducibility. The use of 2D chacolgenides gives promise for spin-valley qubits. Also, it has been proposed that donor atoms of "deep" chalcogen donors, such as sulfur, selenium, tellurium, and particularly $^{77}Se^{+}$ is possible. The unique optical properties of 2D and heterostructured materials open possibilities of accessing the strong coupling limit of cavity quantum electrodynamics using silicon photonic resonator technology and integrated silicon photonics.

Qubits have been demonstrated by manipulation of optically active crystal defects—for example, Nitrogen-vacancy (NV) centers in diamond. This has a negative charge, which creates an optically active, paramagnetic spin-1 complex. NV-centers are initialized by optical pumping and can be read out using optical (spin-dependent photoluminescence) or electronic methods. Entanglement and quantum logic operations have both been demonstrated. Another defect that acts like an artificial atom, with a paramagnetic spin that has, like a nitrogen vacancy in diamond, relatively few decoherence interactions,

is the divacancy in silicon carbide. Scaling of spin systems to larger regular arrays is difficult because magnetic dipole interactions are detectable only up to around 30 nm, and placing vacancies to that density in diamond is a challenge.

Another application of quantum information is to sensing and metrology, where entangled states are used as robust, sensitive, nanoscale sensors. Leading qubits for this application are nuclear and electronic spins in semiconductors, and nitrogen vacancies in diamond.

Quantum computing is an emerging technology that has appropriately attracted much attention. Given the current state of the art, materials research can accelerate progress by focusing on challenges such as the role of defects and noise in device performance.

2.5 POLYMERS, BIOMATERIALS, AND OTHER SOFT MATTER

2.5.1 Polymers

The last decade has seen a powerful acceleration of capabilities in the precision synthesis of polymers, consistent with a drive in every area of materials science to control, with fidelity and exactness, the placement and arrangement, not only of atoms and molecules, but also of defects, which often control material properties. This takes specific form in polymer synthesis in the control of polymer primary structure including programmed degrees of chain uniformity, monomer sequence, and placement of short and long branches, which has advanced greatly owing to the progress in controlled, living polymerization (CLP). CLP continues to expand capabilities beyond living anionic polymerization, especially in the realm of controlled free-radical polymerization (CFRP) including water-based ones, for which increasingly potent reagent and catalyst systems have been introduced. CFRP has been shown to be much less sensitive to environmental conditions than other CLP, which leads to increased versatility.

Synthetic biology has also produced some intriguing advances in precision macromolecular synthesis of relevance to materials science. Biology, and all of its functionality, is controlled by the sequences formed from combinations of monomers inscribed in linear polymers. No such level of control is even remotely possible yet in chemically synthesized copolymers. Biological synthesis, however, can be commandeered to produce unnatural amino acid polymers, which can be further diversified by post-translational, or even post-polymerization, chemical modification. Techniques that enable biological polymerization of a wide diversity of chemical types of monomers are currently very limited, but some progress has been made in polymerizing α-hydroxy acids and dipeptides. Work on reengineering the ribosome and the development of cell-free synthetic biology are enabling these accomplishments.

The functionality and properties of polymeric materials, of course, depend on structures at length scales between molecular and macroscopic. Areas of polymer materials science in which very important advances have been made in the last decade have been in self-assembly, yielding supramolecular, noncovalent structures and the solidification processes of crystallization and vitrification. Self-assembly, broadly construed here, is the set of mechanisms via which information-encoding structures at shorter length scales direct structure formation at larger length scales. The size of a polymer chain depends on the molecular weight and ranges from ~5 nm to ~50 nm for large molar mass chains. In semicrystalline polymers and in block copolymers, which undergo self-assembly by microphase separation, there is structure on the length scale of tens of nm, owing to the crystalline lamellar thickness in the former case, and the self-assembled nanostructures in the latter. There is mesoscale structure in the form of chain-folded lamellae in semicrystalline spherulites, in grains of ordered block copolymers, and in component domains in phase-separated polymer blends. Understanding of structure evolution on all of these length scales, and its impact on bulk properties, have seen enormous advances in the last decade.

Polymerization-induced self-assembly and phase separation, hybrid covalent-noncovalent polymerizations, and the introduction of selective intrachain interactions have all been demonstrated effectively to generate tertiary and quaternary structures, leading to useful functional properties in synthetic polymers. Self-assembled building blocks have been shown to assemble further into higher-

order structures to create new hierarchically structured materials. Self-assembly has come to be viewed as a chemical reaction-like process, moving with some kinetics from reactants to products. Nucleic acid self-assembly, which brings programmability and addressability not possible with hydrophobic or van der Waals forces, is evolving from initial concepts to practical possibilities in information and biomedical technologies. Likewise, peptide (and peptoid) nanotechnology has exploited self-assembly of amino acid polymers for practical applications in tissue engineering and biomedical nanoparticles. Directed self-assembly (DSA), through the use of chemical or topological templates, has advanced notably in the last decade from scientific exploration to a viable industrial technique for microprocessor and storage-device fabrication. Spatial control of patterns on the nanoscale in a scalable, parallel, and robust fashion now seems within reach. This evolution of DSA from experimentation to concrete invention in nanolithography was steered and accelerated enormously by a closely connected program in computational materials science, an indication of much more to come.

Progress in the last decade in the solidification processes of crystallization and vitrification has included: (1) computer simulations that enable visualization of the early stages of these processes; (2) quantitative determination of how structural relaxation is slowed, and glass-transition temperatures suppressed, within 100 nm of free and solid surfaces; (3) recent engineering advances with ultra-high-molecular-weight polyethylene (UHMWPE) that have led to state-of-the-art artificial hip replacements; and (4) time-resolved structural characterizations using X-ray scattering at synchrotron sources in combination with rheology or processing.

Perhaps the most striking accomplishment in the area of glassy polymers has been the development of vitrimers, a remarkable new class of plastics that exhibit properties similar to silica glasses. Permanently cross-linked materials have outstanding mechanical properties and solvent resistance, but they cannot be processed and reshaped once synthesized. Non-cross-linked polymers and those with reversible cross-links are processable, but they are soluble. Vitrimers are networks that can rearrange their topology by exchange reactions without depolymerization and remain insoluble and processable. They are self-healing and can be shaped, welded, and repaired by techniques that would be familiar to glassblowers. They derive from and have many of the same properties as thermosetting plastics widely used in manufacturing and especially in the automotive and aircraft industries. Their discovery and development relate directly to a fundamental understanding of the differences between the glass transition in polymers and in conventional inorganic glasses. The fluidity results from bond exchange. A new bond is formed only at the expense and at the position of an existing bond. Figure 2.14 illustrates the chemical process schematically and explains some of the characteristics of vitrimeric materials.

In silica glass, the bond exchange is catalyzed by the presence of boron or other elemental impurities. Vitrimers mimic this basic bond exchange mechanism by a judicious choice of functional ligands and catalysts. A compelling demonstration of this mechanism is the dependence of the viscosity and melting temperature on catalyst concentration. Originally, the bonds were ester linkages in which exchange was catalyzed by zinc catalysts. Chemistries producing vitrimer-type exchange have now been expanded to include polybutadiene rubbers (linkages based on alkene metathesis) and catalyst-free polyurethane systems. The glass-like properties mean that plastics can be blown, twisted and shaped while cooling much as their inorganic cousins. Two separate vitrimer rods can be welded together, or a break healed simply by holding the pieces together and heating. Bond exchange at the interface welds the two pieces together. At low temperature, the rate of bond exchange slows considerably, making the material a solid with essentially no flow and thus recovering the attractive properties of the thermosetting plastic.

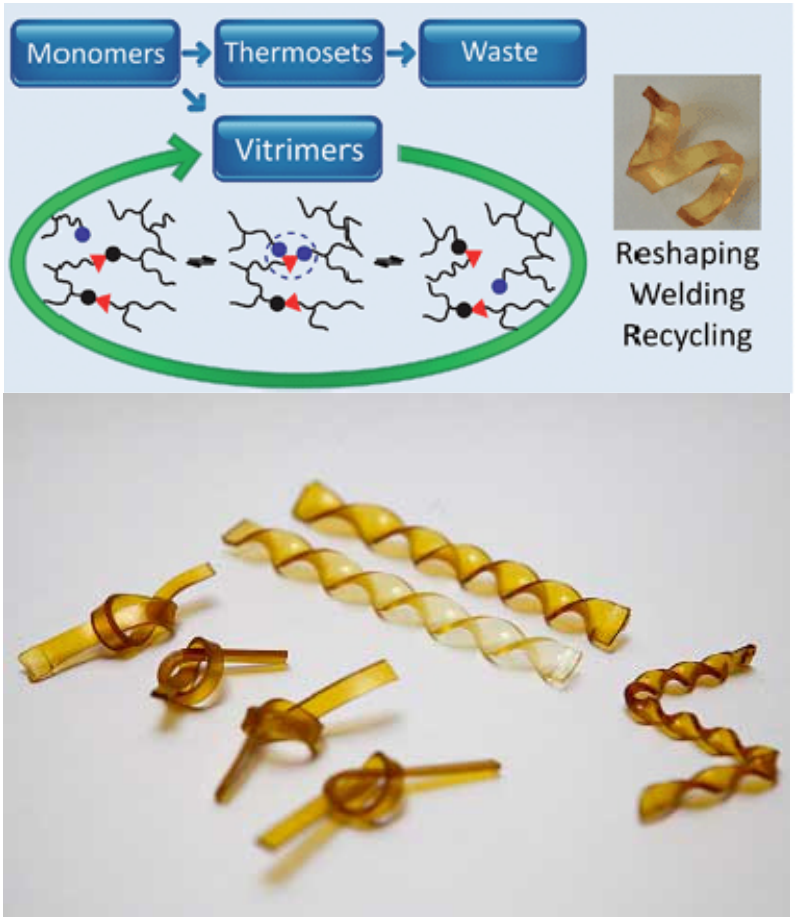


FIGURE 2.14 *Top:* In a vitrimer, the number of interpolymer bonds are kept fixed. Bonds are formed at the expense of other bonds being opened using catalyzed bond-exchange reactions. Although the material is, at all times, a 3D, covalently cross-linked network, heating allows malleability through the bond exchange process illustrated. Therefore, unlike cross-linked networks without bond exchange, vitrimers can be processed similarly to non-cross-linked glassy polymers, can be welded, can enable self-healing, and can be recycled. *Bottom:* Over a large temperature range, the material behaves as a viscoelastic melt before becoming a rigid glass on cooling. This malleability allows processing/shaping of polymers in much the same way as conventional silica glass, or as non-cross-linked glassy polymers. The creation of the shapes shown here, as a means of illustrating the high level of fluidity that can be induced in vitrimers, is demonstrated. Once formed, these objects become rigid, glassy objects on cooling. SOURCE: *Top:* Adapted from W. Denissen, J.M. Winne, and F.E. Du Prez, 2016, Vitrimers: permanent organic networks with glass-like fluidity, *Chemical Science* 7:30-38. *Bottom:* D. Montarnal, M. Capelot, F. Tournilhac, and L. Leibler, 2011, Silica-like malleable materials from permanent organic networks, *Science* 334:965-968, © CNRS Photothèque/ESPCI/Cyril FRÉSILLON.

Vitrimers could be viewed as a particular class of self-healing materials, which repair and restore their functionality without external intervention after a damage event. Self-assembly implies a thermodynamic tendency to self-healing, although being thermodynamically spontaneous by no means implies kinetically instantaneous. Self-assembled block copolymers and hydrogels have demonstrated self-healing. Closely related are olymeric materials with dynamic covalent bonds. This class of polymers combines intrinsic reversibility with the robustness of covalent bonds, thus enabling formation of mechanically stable, polymer-based materials that are responsive to external stimuli. External stimuli can

trigger self-healing including changes in pH, UV light, electrical potential, and mechanical strain—for example, the central C–C bond in diarylbibenzofuranone, which is known to reversibly cleave and reform under mild conditions of physical stress. In the emerging field of mechanochemistry, a new concept in self-healing, mechanical deformation events trigger changes in optical and mechanical properties before a critical damage event occurs through mechanically triggered chemical events. Yet another category of self-healing materials consists of those that contain an encapsulated healing agent, and in some cases a microvasculature to distribute it, creating polymer self-healing somewhat analogous to wound healing in humans. An example of this latter type of self-healing is highlighted in Box 2.9 in the form of a coating that is currently transitioning to a commercial product. Today, self-healing has been demonstrated in thermoplastics and thermosets, electronics, and batteries, and a variety of self-healing materials are entering the marketplace—for example, self-healing technology based on dynamic bonds is currently being commercialized by the chemical company Arkema. Self-healing polymers have the potential to reduce plastic waste both by prolonging the useful life of plastic-based products and by facilitating their recyclability.[47]

Catalytic chemistry in polymer materials science has been progressing enormously in the last 10 years. New catalysts for carbon-fiber reinforced polymer, for metathesis polymerization, and for controlled olefin polymerization have led to many useful, new polymeric materials. Catalysts for new electroactive conjugated polymers, with applications from solar energy to nonlinear optics, have been introduced. New catalysts have also been central to a growing body of work aimed at green polymer science. Important recent work in this arena includes the catalytic conversion of sugars to lactic acid using zeolites; using carbon dioxide for polymer synthesis, attractive given its prevalence and the new developments in the catalytic conversion of carbon dioxide to polymers with interesting and attractive properties; and the use of nontoxic metals for the catalytic conversion of monomers to polymers. Chemical recycling, catalytically activated, back to the original monomers or to new products that have value has emerged as an area of research with outstanding potential.

All of materials science, polymer science included, is founded on the interrelationships among composition-structure-processing-properties. Bringing processing into the science considerations means understanding what is happening at high stresses, strains, and speeds, leading material scientists to give increasing attention in recent years to nonlinear and nonequilibrium phenomena. In this realm in polymer science, the last decade has seen transformational advances in the nonlinear mechanical response of polymer hydrogels. They are rooted in improved chemical strategies for engineering toughness into networks from a molecular level. These advances open the door to new life-altering advances in artificial tissues. In the understanding of polymer melt rheology, especially its nonlinear aspects, the last 10 years have seen some convergence among bead-spring, tube, and slip-link models, both in their physical interpretations and in predictions of behavior. Progress has also been made on the theoretical and computational front through the development and use of coarse-grained and field-theoretic approaches, which rely on the well-established fact that many polymer properties do not depend on the detailed atomic, or even segmental, structures of the chains. As in other areas of materials science and engineering, the advances in computational power and computational methods has had a significant impact on polymer science. The introduction of deep learning[48] methods to polymer science is in its infancy but is expected to have a significant impact in the coming decade. Advances in computational methods are discussed in detail in Chapter 4.

[47] See https://engineering.stanford.edu/magazine/article/super-stretchy-self-healing-material-could-lead-artificial-muscle.

[48] "Deep learning," inspired by information processing and communications patterns in biological systems, is a machine learning method based on analysis of data representations, as opposed to task-specific algorithms.

BOX 2.9
Basic Science to Commercial Product: Self-Healing Coatings

The basic science behind the self-healing material shown in Figure 2.9.1 was conducted at the University of Illinois, Urbana-Champaign, and the researchers launched the company Autonomic Materials, with the first product appearing in 2017.

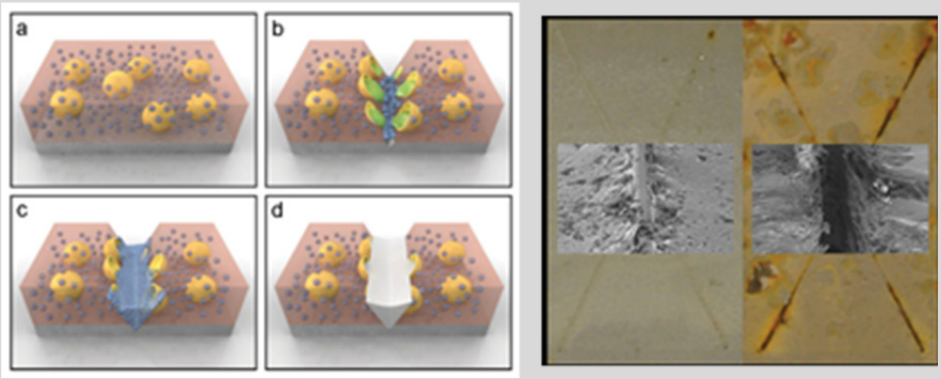


FIGURE 2.9.1 The left figure shows schematically the concept of a self-healing polymer coating on a metal substrate. The yellow spheres contain the catalyst; the blue spheres are the self-healing phase-separated agent droplets and the orange is the polymer coating. A scratch on the coating breaks the yellow spheres, releasing the catalyst and the self-healing agent. The scratch fills with a polydimethylsiloxane filler, which protects the base metal from exposure to the environment. The right figure shows the protection of the self-healing polymer coating (left panel) over a conventional coating (right panel) on a steel plate following 5 days of exposure of the scratched plate in a 5 percent NaCl solution. The background images are optical micrographs showing the scratch, and the enlarged images in the center are scanning electron microscope image showing details of the scratch. The polydimethylsiloxane has filled the scratch. SOURCE: S.H. Cho, S.R. White, and P.V. Braun, 2009, Self-healing polymer coatings, *Advanced Materials* 21:645-649, ©2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In addition to mechanical and rheological properties, transport properties of ions, protons, electrons, and phonons in polymers have come to the fore in this decade, owing in part to increasing interest in applied technologies such as membranes for separations, energy-related technologies such as batteries, fuel cells, organic energy conversion devices, and sound-dampening materials. Molecular dynamics simulations have played a role in the design of new materials for polymeric electrolytes in batteries.

Related to ion transport in polymers is the broad topic of polyelectrolytes, which de Gennes once termed the "least understood form of condensed matter." Owing to progress in the last decade, that statement is probably no longer apt. Not only have many aspects of the solution structure of individual polyelectrolyte chains been clarified, again with the help of advanced theory and computation, but interactions with other ions in solution—particularly, multivalent metal ions and oppositely charged polyions—have come to the fore. Polyelectrolyte brushes[49] have been shown to create extremely slick surfaces in low concentrations of monovalent salt but become much less slippery in the presence of multivalent ions. Twenty years ago, the technique of layer-by-layer (LBL) growth of alternating

[49] Polyelectrolyte brushes are long polyelectrolyte chains densely affixed to a surface.

polyanions and polycations was introduced by Decher in a *Science* paper that has now been cited over 10,000 times.[50] Consistent with observations about self-assembly and rheology above, LBL leads to interesting and useful but inherently nonequilibrium structures. Not only has LBL been the subject of considerable follow-on work itself, but it has also led to the deeper exploration of polyelectrolyte complexes in the past decade. The long-standing, ad hoc Voorn-Overbeek theory of polyelectrolyte complexation has been shown to be conceptually inadequate and quantitatively inaccurate. Polyelectrolyte complexation is also a new driving force for block copolymer self-assembly, with the need for caveats about possible nonequilibrium structures still applicable.

Nanocomposite materials have come to the fore in the last 10 years—for example, carbon nanotube and graphene composites with various polymers added—as they decrease small molecule transport and simultaneously increase electrical conductivity relative to the pure polymer. Cellulose nanocrystals can introduce hydrophilic channels in otherwise hydrophobic polymers. With respect to mechanical properties, orders of magnitude in strength, with a concomitant increase in electrical conductivity, have been reported. Novel electric, magnetic, optical, and transport properties have also been demonstrated. Achievement of many of these gains have been enabled by enhanced ability to manipulate interfacial physics and chemistry in polymeric materials.

Hybrid-bonding polymers are an important emerging class of macromolecular soft materials in which the bonding among monomeric units is covalent or noncovalent in different nanoscale domains of their structure. These materials are therefore composed of covalent and supramolecular polymers and can be synthesized through various pathways, which includes the methodology in which covalent and supramolecular polymerizations occur simultaneously. This approach demonstrated the possibility to "catalyze" covalent polymerization using noncovalent interactions of a forming supramolecular polymer with growing covalent chains. In this context, research in this area could reveal the principles behind ribosomal synthesis of proteins, which is definitely aided by noncovalent interactions in the environment of the growing chain. Earlier efforts had often focused on the covalent capture of ordered supramolecular polymers to create covalent polymers, or post-polymerization modifications via noncovalent bonding of small molecules without formation in either case of an actual supramolecular polymer within the structure. The dual nature of bonding among structural units introduces the potential for highly dynamic properties in polymeric soft matter that originate in the noncovalent bonding of supramolecular polymers, integrated with the mechanical robustness of covalent polymers. Examples of dynamic properties include fast self-healing of defects, rapid response to external stimuli, enhanced rates of biodegradation, and new opportunities in recycling, toughening mechanisms, and electrical actuation.

2.5.2 Biomolecular and Bio-Inspired Materials

Research on soft matter outside conventional covalent polymers over the past decade has been dominated by the area of self-assembling materials, most commonly supramolecular polymers, organogels, DNA and peptide nanotechnology, supramolecular nanostructures, 2D materials, as well as metal-organic and covalent organic frameworks. Research on self-assembling materials has been motivated by great interest in bio-inspired systems as a rich source of ideas for novel functions in soft matter. This trend has come to define the field of "biomolecular materials," in which chemical structures found in biological systems are integrated into synthetic systems, or biological structures at all scales and their functions are emulated with abiotic chemistry. In this context, the broad field of biomolecular materials has been an important direction in soft materials research over the past 10 years.

Advances in this field over the past decade have benefited enormously from novel synthetic strategies to create organic materials and characterization tools for soft matter, which include high-resolution microscopies, measurements on molecular dynamics, and scattering techniques. It has also

[50] G. Decher, 1997, Fuzzy nanoassemblies: Toward layered polymeric multicomposites, *Science* 277(5330):1232-1237, doi:10.1126/science.277.5330.1232.

become obvious that computational techniques, either coarse-grained or atomistic, are being established as an integral part of this research area. A common element in biomolecular materials research over the past decade has been the search for the functional power of ordered structures obtained through self-assembly strategies. Another nascent objective has been the exploration of dynamic behavior in soft matter. This last goal connects to the objective of discovering materials with autonomous capacity for self-healing of defects, or the capacity to actuate or move in response to stimuli, thus emulating living organisms. Thermal energy and light have been used as common stimuli to develop this behavior in soft matter. Systems exhibiting dimensional and shape changes in response to an energy input are currently perceived as important for integration into smart systems useful in medicine, manufacturing, wearables, and robotics, among others.

2.5.3 Biomaterials

The global market of medical implants presently exceeds $100 billion, and the optimal performance of materials in this space has never been more critical given the demographic changes that have occurred worldwide. The most significant changes have been the great increase in aging populations, and the strong cultural aspiration to achieve the highest possible quality of life throughout life spans approaching three-digit numbers. There is therefore great awareness that permanent implants used in orthopedic surgery, stents, and dental implants must perform optimally for longer periods of time. At another extreme, the field of regenerative medicine, seeking to rebuild tissues and organs lost to trauma, disease, aging, and congenital defects, has established itself over the past decade as an exciting global grand challenge and offers an avenue for addressing organ donor shortages. The 2014 book by D. Williams, *Essential Biomaterials Science,* reinforces these statements and nicely summarizes progress to that point. Advances in metallic, ceramic, and soft biomaterials over the past decade have significantly advanced efforts to address these needs.

Metallic Biomaterials

In the field of metallic biomaterials, there have been a number of active research areas that focus on improving implants. One direction has been the integration of secondary functions in metals beyond the load-bearing structural role of the parts. Examples include the modification of surfaces to render them antimicrobial, since preventing infection at tissue-implant interfaces remains an important challenge, and also improving methods to create porosity in order to promote bone ingrowth in orthopedic implants. For this particular purpose, development of effective methodologies to create metallic foams have been of interest recently. In the case of antimicrobial surfaces, for reasons that are not yet clear, silver nanostructures have been found effective at preventing bacterial infections. Attempts to understand the origin of antimicrobial properties of silver nanostructures have focused on the dissolution of silver ions from the nanostructures and the interactions of these metal ions with peptides, which are of course present in bacterial membranes. However, the specific mechanism behind this very important function of metallic nanostructures remains unknown. A different approach to promote bone ingrowth in metallic implants for fixation to the tissue has been the use of "osteoinductive" coatings on metals. The use of calcium phosphate ceramics such as apatites has been a common approach, but other efforts have contemplated the functionalization of metallic surfaces with biological macromolecules such as growth factors. In the case of cardiovascular biomaterials, there has been interest over the past decade and even earlier in improving methods to coat drug-eluting polymeric coatings on surfaces of metallic stents with the purpose of avoiding restenosis of blood vessels.

A different area of interest in metallic biomaterials over the past decade has been "biodegradable" biometals. Examples of such metals include magnesium, iron, and zinc, since these metals are part of natural processes in mammalian biology. Zinc, for example, is found in hundreds of enzymes, and its presence is critical to their catalytic functions. There is also evidence that metals such as magnesium can have beneficial effects on the regeneration of bone. The use of iron alloys for stents have faced some

challenges in animal models related to poor control of degradation rate, but at the same time their magnetic nature could help to stimulate cells positively through particulate displacement with external fields. The use of biocompatible biodegradable metals has remained an attractive objective over the past decade that will require moving forward a significant amount of basic science research. Access to fully biodegradable metallic parts would be particularly attractive in the context of bone regenerative medicine applications where the structural support of a metallic scaffold would be fully replaced by new tissue formation. Advances of the past decade have also shown that implantable electronic devices could in principle be developed using biodegradable metals. The area could have impact in other technologies outside biomaterials—for example, in strategies to create degradable and more easily recyclable electronic devices. Last, a major area of development in metallic biomaterials over the past decade is that of additive manufacturing of implants. Techniques such as selective laser sintering of metallic powders, cryo-milling, and printing to create designed implants with tailored micro- and nanostructure are of great interest in personalized medicine.

Ceramic Biomaterials

Over the past decade, a major area of research in ceramic biomaterials involves the use of calcium-phosphate-based materials with applications in the area of bone implants. Many compositions have been explored and methodologies developed to coat metallic implants. These ceramic materials have the capability to be osteoconductive, creating stable interfaces with living bone, and are also broadly biocompatible. Mirroring activity in metallic biomaterials, there has been great interest in developing strategies to create implants using additive manufacturing techniques. As is the case for metals, additive manufacturing offers the opportunity to customize implants to patients and, most importantly, to design macroscale and microscale architectures to optimize biological functionality.

Soft Biomaterials

Advances in polymer science of the past decade have impacted the field of soft biomaterials by providing novel approaches to improved physical properties and integration of function. In terms of physical properties, the field of soft biomaterials has benefited from progress in the area of hydrogel networks that are of interest in tissue engineering. Specifically, new chemical and processing approaches to the mechanical reinforcement of hydrated macromolecular networks, via interpenetrating networks or the preparation of hybrid nanocomposites with internal reinforcement, offer the possibility to use them not just as transient scaffolds to template the growth of tissues but also as permanent artificial tissues in areas where regeneration is still distant. One example would be the replacement of intervertebral discs, which is a great societal need given the high incidence of degenerative disc disease. Related to this area, fundamental advances in the understanding of polyelectrolytes and coacervate phases offer the possibility to develop lubricious surfaces that may be useful in the development of artificial joints and catheters. In terms of function integration in soft biomaterials, the popular area of layer-by-layer materials has been used to integrate within individual layers different types of bioactivity as well as drug delivery functions. The last decade has seen an enormous advance in our ability to use and control self-assembly processes to create such new biomaterials.

The most significant development in soft biomaterials over the past decade occurred in the area of "supramolecular biomaterials." Covalent polymers, nonbiodegradable or biodegradable, have been the materials of choice for soft biomaterials (see Figure 2.15). An important research shift of the past decade in this field is the exploration of supramolecular polymers as biomaterials. In supramolecular polymers, bonding among monomeric units involves weak noncovalent interactions, thus creating many exciting new directions in soft materials. For example, the binding energies among monomers become tunable over a broad range, and the end result is a broad platform of soft materials in which the bond lifetimes can vary significantly. With bond lifetimes among monomers spanning microseconds to seconds, there is great potential for control of dynamic properties and new processing opportunities. Responsiveness to

complex and interacting stimuli and reconfigurability are now being enabled by some of the advances in polymer science.

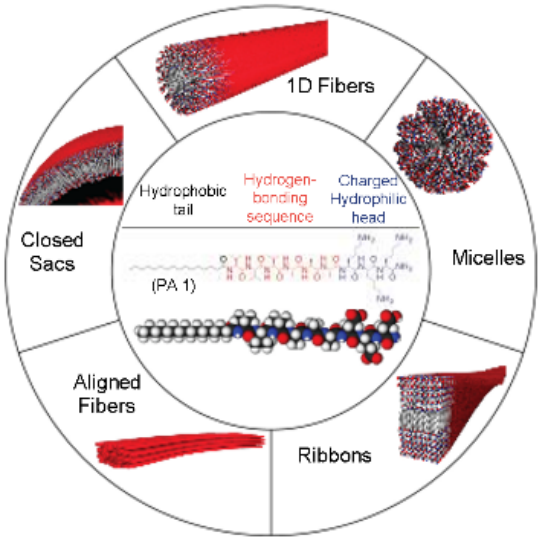


FIGURE 2.15 General structure of a peptide amphiphile (PA, center) surrounded by many of the supramolecular nanostructures that have been formed from these molecules to create supramolecular biomaterials. These were the first examples of supramolecular biomaterials exhibiting high levels of bioactivity in cell signaling for regenerative medicine, biocompatibility, and rapid biodegradation in vivo. SOURCE: M.P. Hendricks, K. Sato, L.C. Palmer, and S.I. Stupp, 2017, Supramolecular assembly of peptide amphiphiles, *Accounts of Chemical Research*, 50(10):2440-2448, https://pubs.acs.org/doi/10.1021/acs.accounts.7b00297, © 2017 American Chemical Society.

By far, the most popular chemistry in supramolecular biomaterials over the past decade has been the use of peptides and modified peptides such as peptide amphiphiles as the building blocks. Peptide supramolecular assemblies can compete with designed proteins to offer useful biological functions and a high diversity of structures. From a structural perspective, peptide assemblies can generate filaments, 2D materials, cross-linked networks, spheres, tubes, helical structures, and materials with higher structural complexity as researchers learn to master chemical morphogenesis. Thus, the motivation for materials designed through peptide nanotechnology has been to create biomaterials that could be potentially bioactive, designed rationally to signal cells for tissue regeneration, and also with controlled structures for mechanics and delivery of therapeutic components.

Peptide-based materials can also be programmed for self-assembly in water to create biomimetic extracellular matrices. The approach has been extremely successful in demonstrating the ability of these new bioactive and biodegradable materials to trigger regeneration of a wide variety of tissues. The exciting functional capacity of these supramolecular biomaterials seems to be partly based on their ability to form biomimetic nanofibers while accommodating a large diversity of signals that are displayed to cells. Furthermore, the supramolecular nature of this new type of biomaterial as opposed to conventional polymers has introduced the capability of rapid and full biodegradation after a “productive” short-lived bioactive interaction with cells.

Another important new area in soft biomaterials over the past decade has been the use of DNA to utilize the great fidelity of Watson-Crick pairing among nucleotides in order to generate designed structures across the scales. This is an emerging field, and many advances can be expected in the future with this approach to develop novel biomaterials. Soft biomaterials are also beginning to be impacted by the development of additive manufacturing techniques in order to control macroscopic form and

microscopic architecture. Printing also brings the possibility of creating constructs that are hybrids of soft biomaterials and cells, allowing the localization of cells in specific compartments of a 3D structure.[51]

It is worth mentioning that there has been a recent trend to the formation of Current Good Laboratory Practice (cGLP)[52] and Current Good Manufacturing Practice (cGMP)[53] facilities in several academic medical centers and universities. By and large, these facilities manufacture novel cellular, biomaterial, viral, and molecular materials for first-in-human use, general use (especially for cellular therapeutics), and treatments for rare diseases. As work progresses in the materials research area, and particularly in fields using DNA and similar biological materials, it will become increasingly important to be aware of the cGLP and cGMP efforts.

2.5.4 Soft Matter

Colloids

Soft matter[54] is best described as matter with a small or vanishing elastic modulus that governs a material's ability to withstand deformation. In addition to many forms of polymers, it includes colloids, foams, emulsions, and granular and active matter composed of entities much larger than atoms but still much smaller than the sample size and arranged on a mesoscopic scale. Energy scales are often of the same order of magnitude as the thermal energy, but certainly no larger than those of atomic solids. Their large length scales thus require small elastic moduli, which scale as energy divided by volume. Soft matter is often strongly dissipative, disordered, entropy dominated, far from equilibrium, and characterized by strong nonlinear and slow dynamical responses. Although these properties have been extensively studied over the last several decades, our understanding of them is still incomplete. This section will review representative advances in nonbiological soft matter (other than polymers).

Colloidal science has undergone a revolution over the past decade or so. Whereas in the past, colloids were mostly restricted to micron-scale spherical particles suspended in an isotropic fluid and interacting through a few elementary forces—steric repulsion, electrostatic, attractive van der Waals, and depletion—it is now routine to create particles of essentially any shape (e.g., the letters of the alphabet) with specific directional, reversible, and irreversible interactions dispersed in anisotropic liquid crystals in addition to isotropic fluids. Among these are Janus particles with inhomogeneous surface properties that control self-assembly of colloidal molecules and even open structures like kagome and diamond-like lattices, lock-and-key particles, and rod-like biopolymers like actin or microtubules, with controlled chirality, that mimic the idealized rods of the Onsager theory of liquid crystal order. The latter system forms large unilamellar membranes in the presence of depletants. These advances open new ways to probe and control phenomena like defect production in liquid crystals,[55] self-assembly, and jamming.

Clever synthesis and technologies adapted from other emerging areas such as DNA nanotechnology have contributed to the growth of colloidal science. For example, colloids with valence and directional bonding have been created[56] by attaching single-stranded DNA to patches on patchy

[51] Another example is virus templating; see K.M. Bromley, A.J. Patil, A.W. Perriman, G. Stubbs, and S. Mann, 2008, Preparation of high quality nanowires by tobacco mosaic virus templating of gold nanoparticles, *Journal of Materials Chemistry* 18(40):4796-4801.

[52] Food and Drug Administration, 1981, *Guidance for Industry: Good Laboratory Practices, Questions and Answers* (revised December 1999 and July 2007), U.S. Department of Health and Human Services, https://www.fda.gov/downloads/ICECI/EnforcementActions/BioresearchMonitoring/UCM133748.pdf.

[53] Food and Drug Administration, "Facts About the Current Good Manufacturing Practices (CGMPs)," updated June 25, 2018, https://www.fda.gov/drugs/developmentapprovalprocess/manufacturing/ucm169105.htm.

[54] S.R. Nagel, 2017, Experimental soft-matter science*, Reviews of Modern Physics*, 89(2):025002.

[55] I.I. Smalyukh, 2018, Liquid crystal colloids, *Annual Review of Condensed Matter Physics* 9:207-226.

[56] Y.F. Wang, Y. Wang, D.R. Breed, V.N. Manoharan, L. Feng, A.D. Hollingsworth, M. Weck, and D.J. Pine, 2012, Colloids with valence and specific directional bonding, *Nature* 491(7422):51-U61.

colloids. Hybridization with similar particles with complementary DNA single strands on their patches allows specific association and a new type of directional colloidal interaction mediated by the DNA. When densely packed finite clusters of spherical particles are swollen with an appropriate solvent and then polymerized, they form the aforementioned patch colloids, as shown in Figure 2.16. The specificity and design facility of DNA hybridization is a useful new tool even for spherical particles.

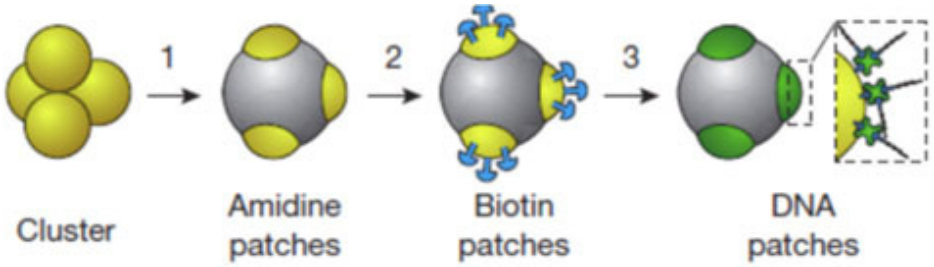


FIGURE 2.16 Schematic of the formation of DNA-stranded patchy colloids. SOURCE: Reprinted by permission from Springer Nature: Y.F. Wang, Y. Wang, D.R. Breed, V.N. Manoharan, L. Feng, A.D. Hollingsworth, M. Weck, and D.J. Pine, 2012, Colloids with valence and specific directional bonding, *Nature* 491(7422):51-U61, copyright 2012.

Liquid Crystals

The most common liquid crystals are formed by molecules with oily tails that avoid water. There are, however, hydrophilic molecules that form a liquid crystal phase when dissolved in water at sufficiently high concentration. Among these are chromonic liquid crystals[57] formed from flat molecules, which include an asthma drug, dies, and DNA nucleotides, with aromatic cores that aggregate in stacks that align to form nematic or columnar phases. Only recently have the viscosities and Frank elastic constants of chromonics been measured.[58] Somewhat surprisingly, the twist constant is of order 6 to 11 times smaller than the bend constant, and it appears the elusive saddle-splay constant, whose contribution to the energy integrates to the boundary, is of order 50 times larger than the twist constant.[59] The result is that chromonics in confined geometries (as in a spherical micelle or a cylindrical capillary) develop unusual conformations.[60] Oriented dried thin films of chromonics exhibit semiconducting properties. Applications involving chromonics include polarizing films, biosensors, and controlled self-assembly of nanorods.

The ferronematic liquid crystal phase, the only known liquid that exhibits true long-range ferromagnetic order coexisting with nematic order, was discovered in the last decade.[61] The original version of this phase was created by dispersing ferromagnetic nanodiscs with magnetic moments normal to their flat planes into a standard nematic. The nanodiscs aligned with their magnetic axes parallel to each other and parallel to the nematic anisotropy axis. An alternative version of the ferronematic was created by dispersing the magnetic nanoparticles in a nonpolar solvent that did not appreciably screen the

[57] H.S. Park, and O.D., Lavrentovich, 2012, Lyotropic chromonic liquid crystals: emerging applications, pp. 449-484 inLiquid Crystals Beyond Displays: Chemistry, Physics, and Applications (Q. Li, ed.), John Wiley & Sons, Hoboken, N.J.

[58] S. Zhou et al., 2014, Elasticity, viscosity, and orientational fluctuations of a lyotropic chromonic nematic liquid crystal disodium cromoglycate, *Soft Matter* 10(34):6571-6581.

[59] Z.S. Davidson et al., 2015, Chiral structures and defects of lyotropic chromonic liquid crystals induced by saddle-splay elasticity. *Physical Review E*92(1):019905.

[60] J. Jeong et al., 2015, Chiral structures from achiral liquid crystals in cylindrical capillaries, *Proceedings of the National Academy of Sciences of the United States of America*112(15):E1837-E1844.

[61] A. Mertelj et al., 2013, Ferromagnetism in suspensions of magnetic platelets in liquid crystal, *Nature*, 504(7479).

Coulomb interaction between them.[62] Last, a biaxial ferronematic[63] in which a surface treatment of the nanomagnets forced the magnetic moments to align at an angle to the nematic director specifying the direction of uniaxial anisotropy. Because of the strong coupling to the director, their magnetic excitations are overdamped and do not exhibit the traditional dispersion with frequency proportional to wave-number squared.

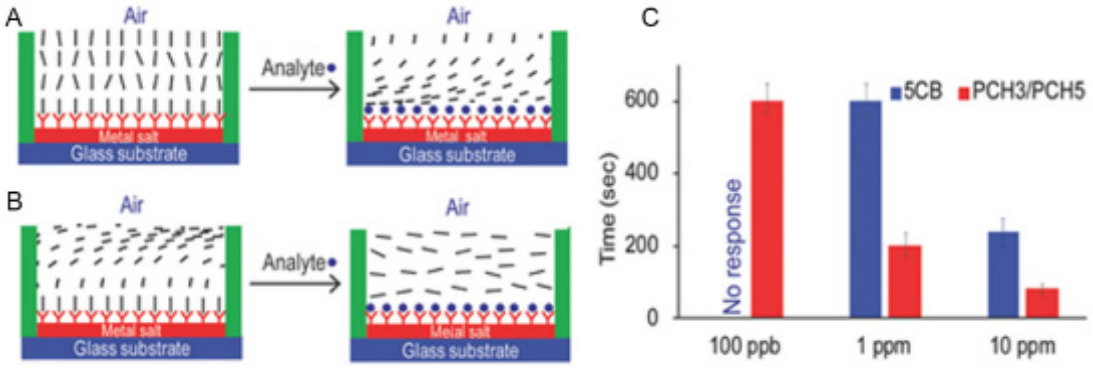


FIGURE 2.17 Schematic comparison of the response of 4-cyano-4′-pentylbiphenyl (5CB) and a mixture of 4-(trans-4-pentylcyclohexyl)benzonitrile (PCH5) and the homologue 4-(trans-4-propylcyclohexyl)benzonitrile (PCH3) to exposure to an analyte such as dimethyl methylphosphonate, a nerve agent stimulant. (A) Director profile of the liquid crystal, 5CB, with homeotropic anchoring at the free surface, prior to and after exposure to the analyte. (B) Director profile of PCH5/PCH3 with coordination interaction with metal-salt-decorated surface and a planar anchoring at the free interface, prior to and after exposure to the analyte. (C) The response time of the two sensors to different concentrations of the analyte. The PCH5/PCH3 liquid crystal sensor shows improved sensitivity and faster response time than 5CB. SOURCE: K. Nayani, P. Rai, N. Bao, H. Yu, M. Mavrikakis, R.J. Tweig, and N.L. Abbott, 2018, Liquid crystals with interfacial ordering that enhances responsiveness to chemical targets, *Advanced Materials* 30(27):1706707, © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In the last decade, there have been advances in the use of liquid crystals for chemical and gas sensors. This is based on the disruption of the orientations of liquid crystal at either the liquid crystal/solid or the liquid crystal/air interface, caused by the analyte. Advances in the atomic/molecular scale design of chemoresponsive systems that resulted in the improvement in the sensor performance (selectivity and sensitivity to a given analyte and system response time) was shown to occur by tailoring the properties of the liquid crystal such that they were oriented parallel rather than perpendicular to that the free surface while anchored in a perpendicular orientation at a surface decorated with metal cations. An example of this advance in sensor performance is shown in Figure 2.17.[64]

Also, modern computational chemistry methods have demonstrated great potential toward designing efficient chemoresponsive systems at the molecular scale and in a time frame much smaller than the traditional trial and error approach based on experiments alone.

[62] M. Shuai et al., 2016, Spontaneous liquid crystal and ferromagnetic ordering of colloidal magnetic nanoplates, *Nature Communications* 7.

[63] Liu, Q.K., et al., 2016, Biaxial ferromagnetic liquid crystal colloids, *Proceedings of the National Academy of Sciences of the United States of America* 113(38):10479-10484.

[64] N. Karthik, R. Prabin, B. Nanqi, Y. Huaizhe, M. Manos, T.R. J., A.N. L., 2018, Liquid crystals with interfacial ordering that enhances responsiveness to chemical targets, *Adv. Mater.*30(27):1706707.

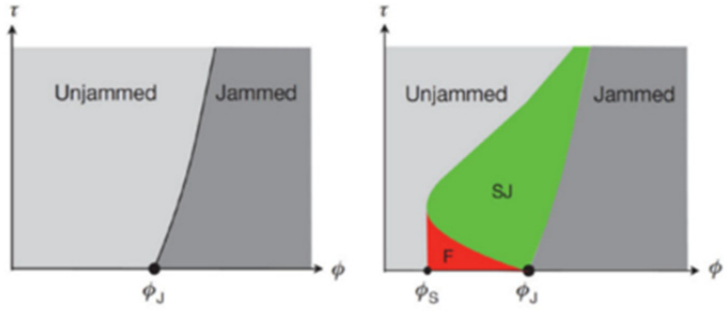
Granular Materials

Granular materials are aggregates of individually solid grains that interact with their neighbors via contact forces. Their properties do not depend significantly on temperature, and they do not explore the many internal configurations that thermal equilibrium systems do (they are nonergodic). Granular materials are everywhere—on sandy beaches, in loose dirt on mountain faces, in coal hoppers, in grain elevators, and in medicine bottles. They are important to industrial processing, and they are finding new applications in fields like robotics. Yet, in spite of their ubiquity and importance, they continue to be poorly understood. Research over the last 10 years, however, has improved our ability to control and utilize granular materials.

One of the most remarkable properties of granular materials is their ability to transform from a fluid to a solid state merely by the application of pressure, or equivalently by increasing the volume fraction of constituent particles. A bag of unjammed granular particles can easily spread around and engulf objects of the appropriate size. When air is sucked out of the bag, the density of particles increases until the jamming transition is reached. An object, now strongly clamped, can be displaced at will. The result is a universal gripper,[65] a prototype material with tunable adaptive compliance that can grab and move objects of any shape with obvious uses in robotics.

Grains in granular materials can be of any size from the submicron (e.g., colloidal particles) to the meter scale and more (e.g., boulders). An application at the micron scale is to force vesicles, which prefer to be spherical, to adopt nonequilibrium shapes by absorbing particles on their surface at sufficient density that they jam, and thereby develop a nonvanishing shear modulus.[66]

Much of the work on granular materials has focused on jamming of spherical frictionless particles, but recent studies have emphasized the importance of friction. The phase diagram of dry frictionless spheres as a function of external shear stress and granular volume fraction shows unjammed and isotropically jammed phases (Figure 2.18a), whereas that of particles with friction shows two other phases (Figure 2.18b): a fragile phase that resists forces along one dimension (in 2D) but not the other and a shear-jammed phase that resists stresses along both directions but with greater strength along one direction than the other.[67] Work such as this on granular materials and jamming has had a significant impact on understanding of the mechanical and flow properties of dense suspensions.



(a) (b)

FIGURE 2.18 Phase diagrams for granular matter as a function of particle volume fractions φ and shear stress, τ. Left: Spherical frictionless particles showing jammed and unjammed regions and the zero-stress jamming point at φJ. Right: Spherical particles with friction showing the unjammed, jammed, fragile (F) and shear-jammed (SJ) regions. SOURCE: Reprinted by permission from Springer Nature: D. Bi, J. Zhang, B. Chakraborty, and R.P. Behringer, 2011, Jamming by shear, *Nature* 480:355-358. © 2011.

[65] E. Brown et al., 2010, Universal robotic gripper based on the jamming of granular material, *PNAS* 107:18809-18814.

[66] M.M.Cui, T. Emrick, and T.P. Russell, 2013, Stabilizing liquid drops in nonequilibrium shapes by the interfacial jamming of nanoparticles, *Science* 342:460-463.

[67] D.P. Bi et al., 2011, Jamming by shear, *Nature* 480:355-358.

Packing of Hard Objects

The structure of liquids, solids, and glasses is intimately related to the volume fraction of ordered and disordered (random) hard-sphere packings. Simulations have shown that hard tetrahedra form a columnar quasicrystal with 12-fold symmetry with a packing fraction of 0.85 compared to 0.74 for spheres packed in a face-centered cubic crystal structure (FCC) lattice. This tetrahedral packing fraction is noticeably higher than initial analytic estimates. A version of this lattice composed of nanoparticle square and triangular elements with targeted attractive interactions has been created.[68] There is now an exhaustive "periodic table" of the phases produced by different-shaped hard particles based on directional entropic forces. There are of course an infinite variety of shapes, and there has been some effort to identify the shape that produces the highest random-packing density. An exploration of packing of particles consisting of overlapping spheres yielded a triangular particle with a random packing fraction of 0.73,[69] almost as high as that of spheres on an FCC lattice (see Figure 2.19).

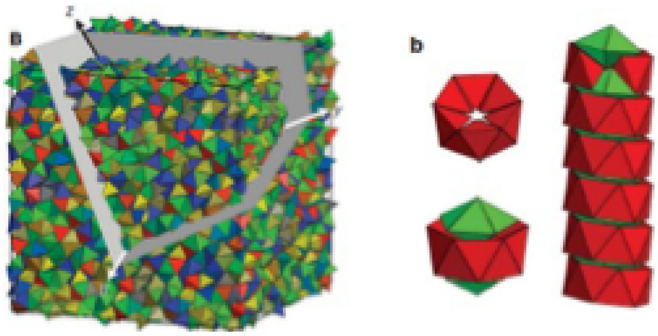


FIGURE 2.19 Left: Configuration of tetrahedra in the 12-fold quasicrystal. Right: Local configuration of tetrahedral and the columnar structure they form. SOURCE: Reprinted by permission from Springer Nature: A. Haji-Akbari, M. Engel, A.S. Keys, X. Zheng, R.G. Petschek, P. Palffy-Muhoray, and S.C. Glotzer, 2009. Disordered, quasicrystalline and crystalline phases of densely packed tetrahedra, *Nature* 462:773-777, doi: 10.1038/nature08641. © 2009.

Particles with more exotic shapes, like that of the letter Z (or Y, as discussed earlier), have interesting properties. They jam under their own weight, and as a result, they have entered the imagination of architects, who have built stable structures like an arch. Alternatively, string tethers can provide sufficient targeted compression to stabilize granular packing of architectural-size particles. This new field now goes under the heading of *aleatory architecture*.

Properties of materials often result from the different forms of order, or broken symmetry, that they exhibit. Examples are the rigidity of crystals arising from their periodic structure and the optical properties of liquid crystals arising from molecular alignment in a particular direction.[70] A more subtle form of order, called *hyperuniformity*,[71] is characterized by reduced density fluctuations. If particles are randomly distributed in a space of *d*-dimensions, the mean-square fluctuation in the number of particles in

[68] X. Ye et al., 2017, Quasicrystalline nanocrystal superlattices with partial matching, *Nature Materials* 16:214.

[69] L.K. Roth and H.M. Jaeger, 2016, Optimizing packing fraction in granular media composed of overlapping spheres, *Soft Matter* 12:1107-1115.

[70] P. Chaikin and T. Lubensky, 1995, *Principles of Condensed Matter Physics,* Cambridge University Press, Cambridge, UK.

[71] S. Torquato and F.H. Stillinger, 2003, Local density fluctuations, hyperuniformity, and order metrics, *Physical Review E* 68(4, Pt. 1):041113.

a sphere of radius R scales as the average number of points in a sphere or as $N \sim R^d$. In hyperuniform systems, these fluctuations grow as R^s, where s lies between d and $d-1$. Hyperuniformity can be achieved in disordered systems. Calculations and experiments show that hyperuniform structures have photonic bandgaps.[72] While it is not yet clear whether hyperuniformity is required for the existence of bandgaps, it is now clear that complete bandgaps are possible without periodicity. This opens a fundamental question as to what properties are necessary for making bandgap materials. Hyperuniform disordered structures do not exist in equilibrium materials with short-range interactions. They have been produced out of equilibrium—for example, in jammed systems at the jamming point and in driven systems such as periodically sheared-random organization dynamics, at their critical point. Hyperuniform patterns can be generated on a computer and additively manufactured.

Soft 2D Materials

Two-dimensional sheets are an interesting form of soft matter because of their ability to deform into the third dimension with very little energy cost. Atomically thick monolayer graphene is probably nature's most perfect 2D material. It is best known for its intriguing electronic properties, but it also has very interesting elastic properties that were measured for the first time in the last decade.[73] At zero temperature, these properties are controlled by the 2D Young's modulus measuring resistance to in-plane strain and the bending stiffness measuring resistance to out-of-plane bending; the former yielding a 3D Young's modulus for a stack of sheets three orders of magnitude greater than that of steel. Graphene is much like paper: it is hard to stretch but easy to bend. A quantitative measure of the relative strength of stretch to bend is the Foppl-von-Karman number νK. A large νK implies easy folds. A 20 cm square piece of paper has $\nu K \sim 10^7$, whereas the same square made of graphene at zero temperature has $\nu K \sim 10^{11}$. For graphene, unlike paper, thermal fluctuations are important. Thermally excited bending modes lead to substantial length-scale-dependent renormalization of both the bending and Young's moduli. It is easy to see how these modes affect the bending modulus: corrugations in a flat sheet make it harder to bend the sheet. Measurements of the effective bending stiffness of a strip of graphene in a water shows a 4000-fold enhancement relative to its bare zero-temperature value, in very good qualitative agreement with the thermal enhancement theory, but they do not rule out the possibility that quenched-in height fluctuations or other mechanisms might contribute to this enhancement.

A second class of 2D sheets that deform into the third dimension are rubbery materials that have a much smaller Foppl-von-Karman number than graphene but can nonetheless fold easily. What is interesting about these sheets is that 2D patterning on them can produce controlled shape change upon change of external condition like temperature, chemical potential, or light intensity. In one version, a flat circular sheet of an N-isopropylacrylamide (NIPA) gel is prepared with a radial gradient of cross-link density. When heated, NIPA gels undergo a sharp reversible transition at a temperature $Tc = 33°C$, characterized by a volume reduction dependent on the density of cross-links. Thus, upon heating, an inhomogeneously cross-linked sheet will undergo differential shrinking that causes it to bend out of plane. The final 3D shape can be calculated with good accuracy from knowledge of the initial inhomogeneous cross-link density. An alternative version of this procedure is a halftone process (like that used in newspaper photos) in which circular dots of higher rigidity are introduced on a lower-rigidity background sheet to produce inhomogeneous swelling factors controlled by the dot density.

The uniaxial anisotropy of nematic elastomers and glasses (basically cross-linked nematic polymers) provide a different avenue for printing metric tensors on a flat sheet. Upon heating (cooling) these materials shrink (expand) in directions along the local director and expand (shrink) along the opposite direction. Heating thus causes initial flat sheets to deform into the third dimension imposed by

[72] M. Florescu, P.J. Steinhardt, and S. Torquato, 2013, Optical cavities and waveguides in hyperuniform disordered photonic solids, *Physical Review B* 87:165116.

[73] M. K. Blees, et al., 2015, *Nature* 524(7564):204.

their original imprinted director configuration. For example, a sheet with an implanted +1 disclination, in which the director follows contours that encircle the defect core, as shown in Figure 2.20, will stretch along its circumference but expand along its radii and deform to a cone. Extended versions of the periodic structure shown in Figures 2.20 (c) and (d) can lift up to 100 times their own weight without buckling. As in the case of kirigami, algorithms,[74] which have been experimentally verified, have been developed that specify two-dimensional director configurations that will yield any 3D shape, including, for example, a face.[75]

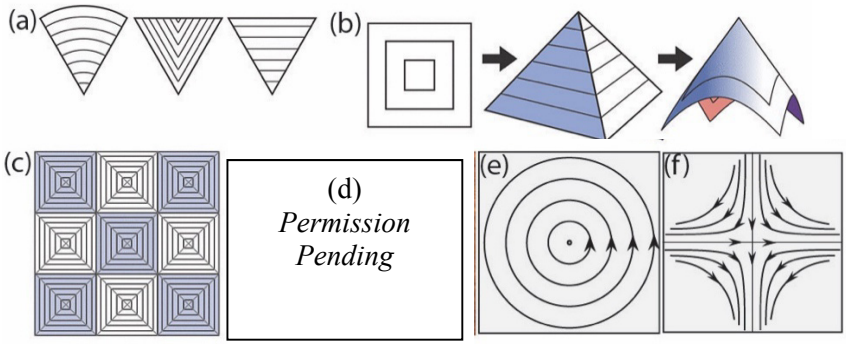


FIGURE 2.20 Kirigami example using nematic elastomers and glasses**.** (a) Patterns with director tangent to lines. (b) Closed pattern—a configuration topologically equivalent to the +1 defect shown in (d). Upon heating, this pattern shrinks parallel to the director and expands in the perpendicular direction to form the pyramid in which sharp corners eventually relax. (c) A more complex director pattern, and (d) the resultant experimental 3D structure, which can support more than 100 times its own weight. (e) and (f) +1 and –1 topological defects, respectively. SOURCE: Panels (a-c), (e), and (f) are reproduced with permission from C. Modes and M. Warner, 2016, Shape-programmable materials, *Physics Today* 69(1):32-38, © 2016 American Institute of Physics, https://doi.org/10.1063/PT.3.3051. Panel (d) is from T.H. Ware, M.E. McConney, J.J. Wie, V.P. Tondiglia, and T.J. White, 2015, Voxelated liquid crystal elastomers, *Science* 347(6225):982-984.

Active Matter

Active-matter materials are composed of homogeneously distributed self-driven units capable of converting stored or ambient free energy to systematic movement. The interaction of active particles with each other, and with the medium they live in, gives rise to highly correlated collective motion and mechanical stress.[76] These systems are fundamentally out of equilibrium, and there is no thermodynamic maximum entropy principle to control their properties. As a result, even their steady-state behavior is often exotic. Biological cells are the quintessential form of active matter, but a variety of other forms, such as schools of fish, bacterial baths, shaken 2D granular gasses, various adenosine diphosphate (ADP)-driven artificial systems, are currently being studied.

Active matter is characterized by the symmetry of its active constituents (polar or apolar for filamentous particles or simply disc-shaped or spherical particles) and by the medium in which they move (e.g., on a dry substrate, or in a liquid host, possibly a viscoelastic, fluid). Hydrodynamic theories for

[74] C. Modes and M. Warner, 2016, *Physics Today* 69(1):32-38.

[75] Aharoni et al., 2018, Universal inverse design of surfaces with thin nematic elastomer sheets, *PNAS* 115, 7206.

[76] See https://research-information.bristol.ac.uk/en/activities/bger--visits-to-research-groups-in-the-departments-of-chemical-engineering-evolutionary-biology-and-mechanical-engineering-at-princeton%283ad890cb-55f1-4664-8695-ff49e6f21246%29.html, accessed March 16, 2018.

polar and apolar media have been developed and applied to both model "in vitro" systems and to living cells. They have predicted various properties of active matter such as spontaneous flow, rheological response, and the formation and annihilation of topological defects. More microscopic models with specific interactions between self-propelled particles or that include molecular motors like myosin as the source of active motion have also proven to be very useful especially for numerical simulation (see Figure 2.21).

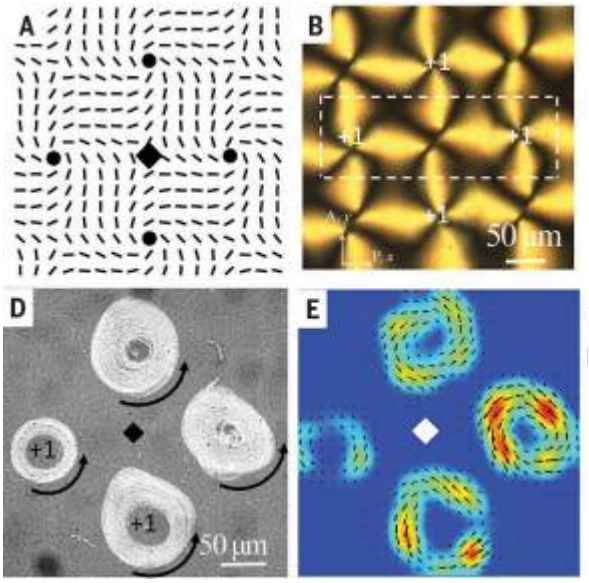


FIGURE 2.21 Experiments with bacterial colonies in biocompatible chromonic nematics on above patterned surfaces. (A) Externally imposed director pattern with a single –1 defect (diamond at the center surrounded by 4 +1 defects. (B) Polarizing optical microscopy texture of the pattern. (D) Counterclockwise trajectories around the four +1 vortices. (E) Map of corresponding velocities. SOURCE: From C. Peng, T. Turiv, Y. Guo, Q.-H. Wei, and O.D. Lavrentovich, 2016, Command of active matter by topological defects and patterns, *Science* 354:882-885, doi: 10.1126/science.aah6936, reprinted with permission from AAAS.

Experiments have investigated various types of self-propelling units, including bacteria and particles on vibrating substrates. Of particular interest are those using molecular motors. In one version,[77] a planar substrate is covered with immobilized molecular motors, which are fueled by ATP, that propel the actin filaments in the fluid above. Above a critical filament density, this system self-organizes into coherently moving structures with persistent density modulations. In another version, bundled microtubules are set in motion by molecular motors.[78] The result at sufficient density is a system with local nematic order with disclination defects that form, distort, and eventually annihilate in pairs.

2.6 ARCHITECTED MATERIALS

In the past decade, the confluence of computational design of material properties, fabrication processes with nanometer to micrometer control (origami- and kirigami-inspired fabrication, lithography, self-propagating photopolymers, additive manufacturing, etc.; see Chapter 4), and experimental

[77] V. Schaller et al., 2010, Polar patterns of driven filaments, *Nature*, 467(7311):73-77.
[78] F.C. Keber et al., 2014, Topology and dynamics of active nematic vesicles, *Science* 345(6201):1135-1139.

characterization methods with equally fine resolution has made it possible to use material shape, or architecture, to create novel bulk materials with radically superior properties via architectural control at the appropriate scales. In much the same way that arches, columns, beams, and buttresses revolutionized the construction of buildings, towers, and bridges in past centuries, the materials community is now exploiting material architecture to expand the material design space in multiple dimensions, independently manipulate material properties that are currently coupled, and develop materials with vastly superior properties than can be achieved with solid objects. Stochastic metallic foams have given way to metamaterials and microlattices with ever finer features and ever broader material classes and functionalities.[79] Breakthrough improvements in specific strength and stiffness, energy absorptivity, negative Poisson ratio, zero thermal expansion, thermal conductivity, as well as electromagnetic sensing, filtering, cloaking, and communications have all been reported for laboratory quantities of materials in the past decade. Figure 2.22 shows how this approach can fill property gaps such as in the strength to density of materials.

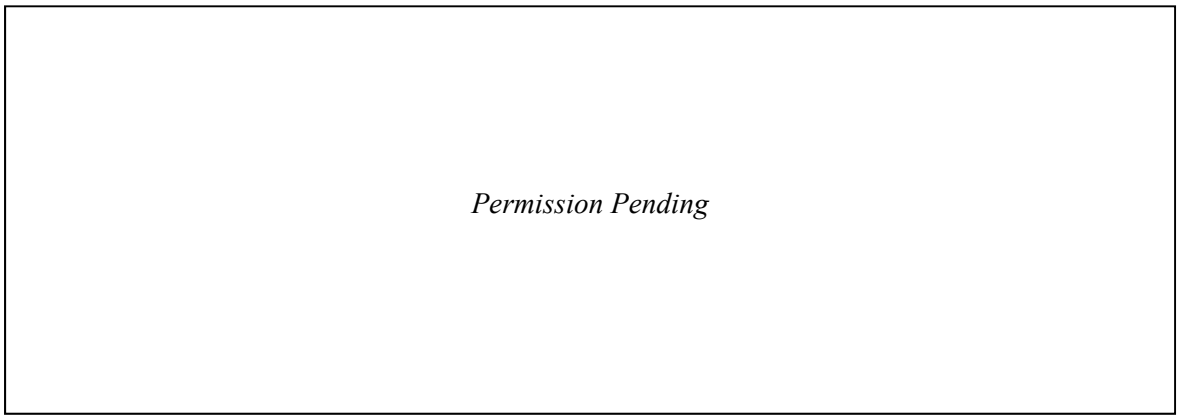


FIGURE 2.22 Architected structures can be used to fill the void in producing lightweight materials with high yield strength. The figure shows the property space occupied by nickel-based and diamond-based lattices in comparison to conventional bulk materials. SOURCE: G.V. Franks, C. Tallon, A.R. Studart, M.L. Sesso, and S. Leo, 2017, Colloidal processing: enabling complex shaped ceramics with unique multiscale structures, *Journal of the American Ceramic Society* 100:458-490.

2.7 MATERIALS FOR CATALYSIS

Catalysts are materials that facilitate the chemical conversion of reactants to desired products. Their global importance can be gleaned from the simple fact that in 2018, they constitute a $20 billion industry. The majority of catalysts, approximately 80 percent, are heterogeneous (made up of solid catalysts in a liquid reaction mixture); while some others (17 percent) are homogeneous (where the catalyst is in the same phase—gas or liquid—as the reactants); and a small number (approximately 3 percent) are based on enzymes. Enzyme catalysts include a protein with an active site that increases the rate of a chemical reaction.

Continued advances in synthesis, characterization, and predictive modeling, as described in more detail in Chapter 4, have led to the birth of several new classes of materials for catalysis that may transcend the division among the three types mentioned above. Much progress has been made through controlled synthesis routes, such as atomic layer deposition, and in situ techniques that work under reaction conditions. Characterization techniques include a number of spectroscopies, microscopies, and

[79] G.V. FranksC. Tallon, A.R. Studart, M. L. Sesso, and S. Leo, 2017, Colloidal processing: enabling complex shaped ceramics with unique multiscale structures, *Journal of the American Ceramics Society* 100:458-490.

chromatographies that are now capable of quantifying the adsorption, desorption, diffusion, and reaction characteristics, as well as the structural changes in the catalyst, in real time. In tandem, high-throughput computational screening, armed with data-enabled methods, are helping to identify descriptors and material design principles that accelerate the discovery of cost-effective catalysts. As a result of these efforts, hybrid forms of catalysts have been developed that exhibit enhanced reactivity and product selectivity.

The nature of the *active site* heterogeneous catalysis determines both its *activity* and *selectivity* for specific chemical reactions. The ideal active site for a given reaction will turn over reactants to products at the highest possible rate and at the lowest reaction temperature, leading to substantial energy savings. Second, the ideal active site will produce only the desired set of products, with no by-products, which would save the energy required from subsequent costly product-separation processes. The third major consideration for the active site is its long-term *stability* in reactive environments. The ideal catalyst would not need regeneration or replacement for a period of several years.

The last decade has seen a great deal of progress in terms of new materials, which could catalyze a range of important chemical reactions, but also the role of surface conditions such as in plasma-assisted hot electron catalysis.[80] One class of such materials relies on shape-controlled wet synthesis of late transition metal nanoparticles. Figure 2.23 shows octahedral and cubic nanocages of Pt with a nanocage thickness of only a few atomic layers.[81] These hollow structures with well-defined facets maximize atom efficiency by eliminating the need for core materials, meanwhile exposing both inner and outer faces of the shell to maximize the active catalytic surface area. First-principles theory has guided experiments toward the optimal thickness of each facet, as well as the most active type of facet exposed for structure-sensitive reactions. The hollow structures show oxygen reduction activity, a key reaction for low-temperature fuel cells, that has five times higher mass activity and substantially enhanced durability in comparison to commercial Pt/C.

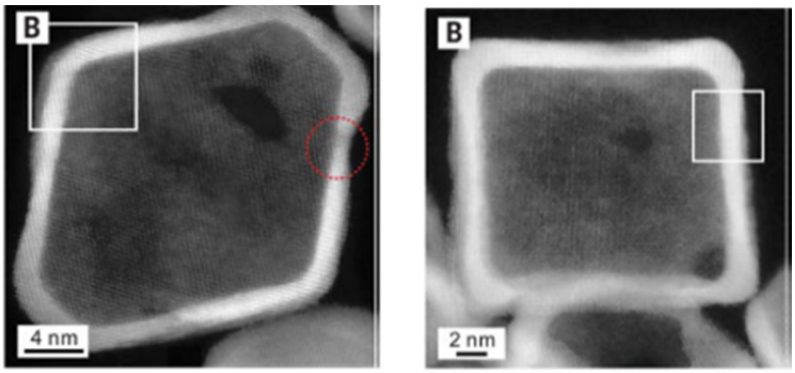


FIGURE 2.23 Platinum hollow nanocages for stable and efficient low temperature catalysis. SOURCE: From L. Zhang, L.T. Roling, X. Wang, M. Vara, M. Chi, J. Liu, S.-I. Choi, et al., 2015, Platinum-based nanocages with subnanometer-thick walls and well-defined, controllable facets, *Science* 349:412-416, reprinted with permission from AAAS.

The ultimate size limit for nanoparticles is single-atom or subnanometer clusters. These atoms are typically supported on a substrate, and the catalytic activity can be associated with the metal atom as well as the surrounding support structure. Molecular dynamics computer simulations have been used to

[80] J.Y. Park, L.R. Baker, and G.A. Somorjai, 2015, Role of hot electrons and metal-oxide interfaces in surface chemistry and catalytic reactions, *Chemical Reviews* 115(8):2781-2817.

[81] L. Zhang, L.T. Roling, X. Wang, M. Vara, M. Chi, J. Liu, S.-I. Choi, et al., 2015, *Science* 349:412.

understand the interaction and found that a single atom may be released from the nanocluster to become the active site for the reaction, the atom returning to the cluster on completion of the reaction.

Advances in characterization capabilities, not only in the spatial, temporal, and energy resolution but also in the ability to conduct experiments in situ under operando conditions, have accelerated understanding of the dynamic structural and compositional changes that occur during the catalytic cycle.[82] Multimode experimental tools now allow the structural and compositional modifications to be probed in a single experiment in real time and operando conditions. Tomographic methods now provide three-dimensional insight of porous substrates and the dispersion of the nanoparticles, and of oxides on and in substrates to identify active sites, and information on the elemental distribution.

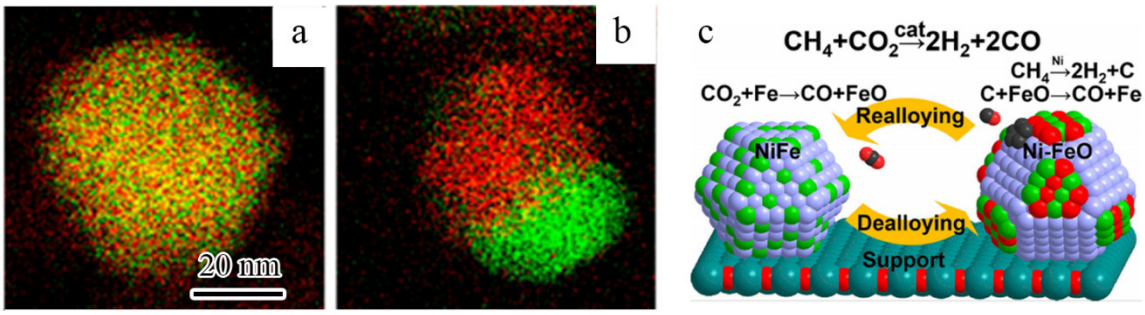


FIGURE 2.24 Energy dispersive X-ray spectroscopy maps of the change in composition of a Ni-Fe particle. (a) Composition after reduction in hydrogen gas. (b) Composition after oxidation in CO_2. (c) Schematic of the dealloying and realloying reactions and the interaction of carbon with iron oxide. In the compositional maps, red corresponds to Fe and green to Ni. SOURCE: S.A. Theofanidis, V.V. Galvita, H. Poelman, and G.B. Marin, 2015, Enhanced carbon-resistant dry reforming Fe-Ni catalyst: role of Fe, *ACS Catalysis* 5(5):3028-3039, © 2015 American Chemical Society.

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These in situ and operando capabilities have provided new insights as to the dynamic structural and compositional processes taking place during catalysis. For example, Ni-Fe nanoparticles realloy following reduction in H_2 gas and dealloy after CO_2 oxidation. This compositional change is highlighted in Figure 2.24, which shows energy dispersive X-ray spectroscopy maps of the change in the composition of a Ni-Fe nanoparticle on oxidation. In the maps, Fe is red and Ni is green.[83] The redistribution of Ni and Fe from the homogeneous distribution to a nonhomogeneous distribution on oxidation is evident. Fe, but not Ni, has been oxidized, and it is the iron oxide on the surface that reacts with carbon. This schematic of the dealloying and realloying, as shown in Figure 2.24(c),[84] shows how the oxidation of Fe and the elemental redistribution leads to a decrease in the accumulation of carbon, which is known to decrease the efficiency of catalysts in the dry reforming of methane.

Driven by the need to increase catalyst surface area, decrease the use of precious metals, and improve the stability of nanoparticles, considerable progress has been made in confining nanoparticles within open structured systems, such as metal organic frameworks, novel zeolites, zeolitic imidazolate frameworks, porous organic polymers, materials, carbon nanotubes, and so on. A consequence of

[82] F. Tao and P.A. Crozier, 2016, Atomic-scale observations of catalyst structures under reaction conditions and during catalysis, *Chemical Reviews* 116(6):3487-3539.

[83] S.A. Theofanidis, V.V. Galvita, H. Poelman, and G.B. Marin, 2015, Enhanced carbon-resistant dry reforming Fe-Ni catalyst: role of Fe, *ACS Catalysis* 5(5):3028-3039.

[84] B. Zhoufeng, D. Sonali, W.M. Hui, H. Plaifa, and K. Sibudjing, 2017, A review on bimetallic nickel-based catalysts for CO2 reforming of methane, *ChemPhysChem* 18(22):3117-3134.

introducing a confinement cage is that it creates a local environment that is different from that encountered in the bulk form. This has led to enhancements in the selectivity and reactivity as well as opened new reaction pathways with faster reaction rates.

First-principles computational methods have been used extensively to interpret spectroscopic data, calculate binding energies and activation energy barriers, and provide electronic structure information as well as reaction energetics of elementary reaction steps, leading to an unprecedented understanding of structure-activity and structure-selectivity correlations in catalysis. Further, ab initio thermodynamics has been shown to provide essential insights as to the nature of the catalytic phase under reaction conditions. For example, DFT calculations coupled with ultrahigh vacuum surface science studies have revealed the different forms particles can take on a surface as a function of pressure, temperature, and chemical potential of the environment to which the catalytic particles and their support are exposed to. Importantly, modern electronic structure theoretical methods, in conjunction with detailed microkinetic modeling, have enabled the prediction of catalytic materials with unique structure and composition, which possess improved catalytic properties compared to materials found by trial and error.

Another area of active research is the controlled deposition of oxophilic metal promoters (e.g., Fe, Mo, Re, Zr, Mn, Sn) onto the surface of reducible metal nanoparticles (e.g., Pt, Rh, Cu) to produce catalysts containing interfacial sites that show high activity for important reactions, such as water-gas shift, methane conversion to ethylene, synthesis gas conversion to alcohols and alkenes, and hydrogenolysis of cyclic ethers.

Driven by the need to increase catalyst surface area and decrease the use of precious metals, attention has turned to novel geometries such as those afforded by metal organic frameworks (MOFs), novel zeolites, zeolitic imidazolate frameworks, mesoporous materials, 2D materials, and single-site catalysts. The challenge is to synthesize these materials with controlled, reproducible, and stable properties. In this regard, carbon-based materials have attracted a great deal of attention because of their simple architecture, which facilitates heat- and mass-transport phenomena, thermodynamic stability, and the promise of a metal-free catalyst. Their high chemical inertness allows them to withstand operations in aggressive media. Surface functionalization or matrix doping with N and O species allows further tuning of their surface reactivity. Application of carbon-based catalysts can be found in hydrogen oxidation, desulfurization, and liquid-phase transesterification reactions.

2.8 CONCLUSION

The past decade has seen significant advances across all areas of materials science and engineering, much of this enabled by the teaming of experimentalists with computational materials scientists and the emerging importance of material informatics. Materials synthesis and processing to produce new materials as well as high-quality materials for fundamental investigations remains an ongoing challenge. The pace of fundamental discovery accelerated and many new materials and processes, some unanticipated, moved into commerce and society during the last decade.

3

Materials Research Opportunities

Materials research spans the spectrum from end-use application in manufactured components to fundamental studies of complex many-body phenomena. A classical approach to evaluating materials research (MR) opportunities is organized along specific types or classes of materials, such as metallic alloys, semiconductors, superconductors, and ceramics; such a discipline-specific research focus strongly leverages current state-of-the-art knowledge and has a proven track record of successful materials research advances as documented in part in Chapter 2. Alternatively, use-inspired research applications such as energy or data science can motivate broad crosscutting materials research and development (R&D) that lead to beneficial societal applications. Furthermore, fundamental discovery science endeavors can catalyze new scientific advances that reach beyond the current materials knowledge base and may launch entirely new material functionalities. These three approaches to materials research are not mutually exclusive, and in general each approach benefits from knowledge gained from the other approaches. This chapter will outline examples of compelling materials research opportunities anticipated to arise in the coming decade. These research opportunities are categorized according to classical material type at the start of this chapter (Sections 3.1 to 3.6), followed by several sections of use-inspired cross-disciplinary materials research opportunities (Sections 3.7 to 3.9). Discovery science is not explicitly discussed in this chapter since by its nature it involves unfettered exploratory research.

3.1 METALS

This section describes in the first part fundamental studies of metals and alloys including high-entropy alloys (HEAs). Further discussions relate to nanostructured metallic alloys.

3.1.1 Fundamental Studies of Classical Metals and Alloys

Fundamental studies of metals and alloys underpin basic materials research by illuminating with unprecedented clarity and fidelity the atomic and mesoscale processes associated with phase transformations and the formation and evolution of defects and interfaces, which govern the synthesis and performance of not only metals and alloys but materials in general. Studies of metals have provided the basis for understanding the structure-dependent properties and processing of not only metals but also ceramics, semiconductors, composites, and hybrid materials across ever-broadening length and time scales.[1] Buoyed by robust thermodynamic and structural databases, foundational advances in computational materials science and engineering coupled with in situ, in operando, and post-mortem three-dimensional (3D) and time-dependent four-dimensional (4D) characterization of metals and alloys are ushering in a digital age of materials development. During the next decade, fundamental research in metals and alloys is anticipated to continue to enable revolutionary new science and deeper understanding

[1] C.A. Handwerker and T.M. Pollock, 2014, Emerging science and research opportunities for metals and metallic nanostructures, *JOM* 66:1321-1341.

of material behavior, which will lead to new material devices and systems. Metals are ubiquitous, from steel, aluminum, and nickel-base superalloys for energy production, infrastructure, and transportation, to titanium and shape memory alloy biomedical implants, to metallic thin films and integrated circuit vias for thermal and electrical functionality, and nanoparticles for catalysts and cancer treatment. Promising research areas for the coming decade include coupled experimental and computational modeling studies performed at the same length and time scale (heretofore not possible owing to experimental and computational limitations), real-time analysis of in situ/in operando experimental characterization data (rather than conventional post-measurement detailed analyses), processing and compositional innovations to enable next-generation high-performance lightweight alloys, ultra-high-strength steels and refractory alloys, and design and fabrication of multifunctional highly architected materials systems. Emerging opportunities for advanced manufacturing of metals and other materials are discussed in Chapter 5. Two examples of metals research that have recently garnered significant attention and hold considerable promise are summarized below; to highlight continuing advances in our understanding of processing-structure-property-performance relations. The choice of these topics is inherently subjective, and it is essential to maintain broad support for the field so as not to overlook the surprises that turn out to be strikingly important.

3.1.2 High-Entropy Alloys

High-entropy alloys (HEAs), also known as compositionally complex or multiprincipal element alloys (MPEAs), inhabit a vast compositional space, and the advances attained in the past decade likely represent only the tip of the iceberg in the development of this promising class of alloys.[2] HEAs differ from conventional alloys (where there is typically one predominant element known as the solvent and one or more minor concentration elements) in that five or more elements are present at comparable concentrations. It was originally believed that this might increase the configurational entropy, but the role of entropy is no longer thought to be important. Nevertheless, it is clear that other concentrated alloying effects not present in conventional alloys are at play. It appears that synergistic effects of multiple elements acting in parallel or in sequence produce results that are difficult to achieve in conventional alloys. For example, when it comes to mechanical behavior, one might be able to overcome the strength-ductility trade-off that is a long-standing dilemma in structural materials. With proper scientific understanding, one could envision tailoring the stacking fault energies, twin energies, phase instabilities, and so on to trigger multiple transformation toughening mechanisms. At ambient temperatures, this would result in high toughness and energy absorption, which could in turn be employed in crumple zones in automobiles, increased blast resistance, or reducing cyclic fatigue. To predict how different alloying elements contribute to strength and toughness, researchers need to understand how each element affects its local environment. Simply using Goldschmidt radii to calculate volume misfits is not applicable in concentrated alloys. The local "chemistry" and atomic interactions are important. At the other extreme, doing a full-blown density functional theory (DFT) calculation for each case is out of the question. It would help to have simple "correlations" for how different elements affect strength using physical parameters that are relatively easy to measure. At elevated temperatures, one might be able to utilize "sluggish" diffusion to kinetically limit phenomena that would otherwise be thermodynamically possible. While single-phase MPEAs are not likely to be useful as high-temperature materials, the development of multiphase MPEAs, similar to Ni-base superalloys, hold significant promise. A better understanding of solid solution effects in MPEAs could help researchers to realize better multicomponent phases. Additionally, certain phases, and reaction pathways between phases, may exist only in higher-order systems. By accessing these, one might be able to create microstructures that are not possible in simpler (conventional) alloys. Doing this efficiently and cost effectively will require development of reliable

[2] D.B. Miracle and O.N. Senkov, 2017, A critical review of high-entropy alloys and related concepts, *Acta Materialia* 122:448-511.

experimental and computational thermodynamic databases that are currently very limited in both scope and breadth.

3.1.3 Nanostructured Metallic Alloys

Transformational advances in nanoscale materials synthesis, characterization, and modeling have spawned a plethora of nanoscience activities to exploit processing-structure-properties relations and create nanostructured materials that exhibit ultrahigh strength and other unusual properties.[3] Nanoscale disturbance of dislocation-based plasticity underpins the improved strength, but may reduce overall ductility. The strength-ductility trade-off is evidenced by the fact that nanocrystalline metals typically have higher hardness and strength than conventional microcrystalline counterparts but generally exhibit much lower tensile ductility. Nanocrystalline metals are also susceptible to thermal and mechanical microstructural instabilities and have lower electrical conductivity. By comparison, nanotwinned metals provide strength enhancements similar to those for nanocrystalline materials while also maintaining a more beneficial balance of properties—for example, high ductility, improved microstructural stability, and low electrical resistivity.[4,5] Numerous studies have demonstrated these enhancements in low stacking-fault-energy metals and alloys and related them to the activation of hard and soft slip systems, interactions of dislocations with coherent twin boundaries, and detwinning. Recent reports of nanotwinned NiMoW alloys with strength several times greater than high-strength steel, enhanced microstructural stability, tailorable ductility, and electrical conductivities comparable to bulk alloys, extends the synthesis of nanotwinned materials to high-stacking-fault-energy, high-temperature alloys.[6] Building on the extensive insights on nanoscale materials synthesis, characterization, and modeling performed during the past decade, there are several important concepts still to be resolved. In particular, experiments and modeling to identify deformation mechanisms in nanotwinned materials, and the role of resolved stresses, and better understanding of microstructural evolution are still needed. Armed with this knowledge, an understanding of the influence of alloy chemistry and deposition parameters would allow for tailoring of nanotwins and properties in a wide variety of materials. In the coming decade, it may be possible to achieve tailored design and fabrication of nanostructured materials containing multiple hardening approaches (e.g., finely dispersed matrix nanoparticles in nanotwinned material) that would enable a dramatic improvement in high-strength, high-toughness materials.

3.2 CERAMICS, GLASSES, COMPOSITES, AND HYBRID MATERIALS

This section begins with a discussion of ceramics and inorganic glasses, the ubiquitous defect structures that determine their properties, and processing opportunities for greater energy efficiency. Also introduced are composites and hybrid materials, including hybrid nanocomposites and soft machines, a rich area of opportunity for materials research demanding expertise in diverse materials types, and the interactions that occur at the interfaces between them.

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[3] *The National Nanotechnology Initiative: Supplement to the President's 2018 Budget*, https://www.nano.gov/sites/default/files/NNI-FY18-Budget-Supplement.pdf, accessed January 18, 2018.

[4] L. Lu, Y. Shen, X. Chen, L. Qian, and K. Lu, 2004, Ultrahigh strength and high electrical conductivity in copper, *Science* 304(5669): 422-426.

[5] I.J. Beyerlein, X. Zhang, and A. Misra, 2014, Growth twins and deformation twins in metals, *Annual Review of Materials Research* 44:329-363.

[6] G.-D. Sim, J.A. Krogstad, K.M. Reddy, K.Y. Xie, G.M. Valentino, T.P. Weihs, and K.J. Hemker, 2017, Nanotwinned metal MEMS films with unprecedented strength and stability, *Science Advances* 3(6):e1700685.

3.2.1 Ceramics and Glasses

Emerging opportunities in ceramics and glass research were identified in a National Science Foundation (NSF)-sponsored workshop held in September 2016.[7] In addition to the topics highlighted below are ceramic- and glass-related content in the section on materials for extreme environments (see Section 3.7.3), thermal barrier coatings (see Section 3.9.4), and additive manufacturing (see Section 4.2.4).

Energy-Efficient Ceramic Processing

Historically, the densification of ceramic bodies is conducted using high-temperature sintering, which often requires hours for completion. Over the past decade, field-assisted processes, either by current flow or by noncontacting applied fields, have resulted in enhanced densification at significantly lower temperatures and shorter times. For conducting ceramics, the current assistance depends, at least in part, upon Joule heating, while field effects on the densification of insulating ceramics remain an area of debate. An understanding of point-defect formation and migration in a noncontacting electric field, and alteration of space charge zones at grain boundaries and free surfaces, is ultimately required to allow microstructural tailoring for given applications.

A significant advantage of these methods, beyond their greater energy efficiency, is their ability to produce dense solids that cannot be made by other methods. These include nanocrystalline solids, which tend to coarsen during traditional high-temperature sintering, and ultra-high-temperature ceramics (see Section 3.7.3) whose melting points exceed 3000°C. In the latter, Joule heating by internal currents reduces the required temperature for densification. Further, the high heating rates and short processing times coupled, in some cases, with pressure can generate some intriguing nonequilibrium microstructures.

A second shift in ceramic processing adapted from classical hydrothermal techniques, known as *cold sintering*, is also gaining attention. Ceramic bodies have been shown to densify at temperatures as low as 25°C to 300°C via a transient liquid phase water coupled with high pressures.[8] Ceramic-metal and ceramic-polymer composites are particularly attractive candidates for cold sintering, since the method provides a pathway to fabrication that precludes reaction between constituents or melting or decomposition of the second phase. Little is known, however, about the fundamental mechanisms of densification in the presence of the fugitive liquid phase at and near ambient temperatures.

The Defect Genome

Defects over multiple length scales have long played a role (and in many cases, a desirable role) in the performance of ceramic materials—point defects for transport properties; line defects for deformation; planar defects for ferroelastic, piezoelectric, and ferroelectric response; and volume defects for mechanical properties. Likewise, defect concentrations and their interactions over time and length scales are known to influence functionality. A "Defect Genome" initiative,[9] whereby defects in ceramics over multiple length scales are characterized and their response under thermal gradients, stress, and electric or magnetic fields are understood and defect-defect interactions are made computationally and experimentally tractable, will add a new dimension to materials design. Ultimately, precise defect placement, coupled to atomic placement, would be the target.

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[7] K.T. Faber et al., 2017, The role of ceramic and glass science research in meeting societal challenges: report from an NSF-sponsored workshop," *Journal of the American Ceramics Society*100(3):1777-1803.

[8] J. Guo, H. Guo, A.L. Baker, M.T. Lanagan, E.R. Kupp, G.L. Messing, and C.A. Randall, 2016, Cold sintering: a paradigm shift for processing and integration of ceramics, *Angew. Chem.* 128:11629.

[9] *J. Phys. Chem. C* 121(48):26637-26647 for a discussion of a defect genome of cubic perovskites.

As one example, in the continuing understanding of planar defects in polycrystalline materials, grain boundaries have a profound significance. The concept of grain-boundary "complexions" was proposed in 2014. Grain boundaries behave as their own phase with discontinuous changes in mobility, diffusivity, and cohesion behavior, and are therefore differentiable from stand-alone materials. The changes lead to opportunities to tailor properties via processing routes or composition. Time-temperature-transformation diagrams specific to the grain-boundary complexions[10] have already added new insight to phenomena such as abnormal grain growth.[11] Understanding grain boundary phase evolution with respect to grain phase evolution will help design composition and processing to achieve the goals of the Materials Genome Initiative (MGI).

A second timely example that would benefit from the Defect Genome is the family of oxide perovskites, structurally ABO_3, oxide perovskites are being investigated as catalysts in solar-to-fuel conversion reactions through solar-driven redox cycles,[12] as well as for oxygen transporting membranes. Perovskites can incorporate multiple A-site and B-site cations into their $ABO_{3-\delta}$ lattice to form $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ structures. Because of the variety of the substitutional cations, a range of electronic, ionic, or magnetic properties can be attained. Moreover, oxygen activity and reactivity can be controlled via the stoichiometry of the final structure. Typically, three types of point defects can exist in the perovskites: electronic defects (in either undoped or doped structures), oxygen vacancies, and cation vacancies. Multiple cation types coupled with mixed defects create an immense phase and defect space, for pathways to exceptional properties and stability. For example, it has been demonstrated that bandgaps can be tailored by acceptor-doping in a variety of families: manganites, ferrites, cobaltates, chromates, and aluminates. By coupling the Materials Genome with the Defect Genome, a fundamental understanding of this class of oxides can be achieved along with pathways for the design of new perovskites.

Glasses

A paper from 2013 lays out several areas of glass research important to the glass industry, including, among others, structure-property relations, densification, and strength in glass.[13] Two new application areas mentioned in those studies are energy storage[14] and quantum communications. Solid-state batteries can solve both an energy density and fire-safety concerns compared to conventional Li-ion batteries (see, for example, Case 5 in Section 5.3). Both glassy and crystalline solid electrolyte materials are under study at multiple institutions that are designed to meet those needs and concerns.[15] Early generations of solid electrolyte were based on LAMP chemistries (LAMP is lithium aluminum metal phosphate; the metal can be Ge, Al, etc.), but those materials were unable to stop dendritic growth leading to early failures of the batteries. Recent lithium-stable chemistries include crystalline lithium lanthanum zirconium oxide (LLZO) and amorphous sulfide-based materials. LLZO stabilized in the cubic phase has high enough conductivity ($\sim 10^{-4}$ S/cm^{-1}) to be practical, if point contact can be eliminated to prevent dendritic growth.

Another example where glasses are rapidly making inroads is in quantum communication, even though there are still needs such as improved single-photon generation and detection and low-loss optical

[10] Cantwell, Tang, Dillon, Luo, Rohrer, Harmer, 2014, Grain boundary complexions, *Acta Materialia* 62.

[11] P.R. Cantwell et al., 2016, Expanding time-temperature-transformation (TTT) diagrams to interfaces: a new approach to grain boundary engineering, *Acta Materialia* 106:78-86.

[12] M. Kubicek, A.H. Bork, and J.L.M. Rupp, 2017, Perovskite oxides—a review on a versatile material class for solar-to-fuel conversion processes, (review article), *J. Mater. Chem. A*, 5:11983-12000, doi: 10.1039/C7TA00987A.

[13] J.C. Mauro and E.D. Zanotto, 2014, Two centuries of glass research: historical trends, current status, and grand challenges for the future, *Int J Appl Glass Sci.* 5:313-327.

[14] J.W. Fergus, 2010, Ceramic and polymeric solid electrolytes for lithium-ion batteries, *J of Power Sources*, 195(15):4554-4569.

[15] B.V. Lotschand J. Maier, 2017, Relevance of solid electrolytes for lithium-based batteries: a realistic view, *Journal of Electroceramics* 38(2-4):128-141.

transmission. Quantum communications will benefit from the wafer processing of optical components.[16] Areas of active research include silicon on insulator-type structures, III-V materials, silica wafers with femtosecond laser written features, and nonlinear optical materials such as lithium niobates. Each type of material will need advanced processing, characterization, and modeling to achieve the desired performance goals.

3.2.2 Composites and Hybrid Materials

Composites

The introduction of advanced polymer resin matrix materials and high-performance fiber reinforcements will naturally provide increased structural performance (stiffness, strength, toughness), but future applications will require exploitation of improved tailorability of properties and multifunctional performance. Multidimensional fiber reinforcements that follow natural load paths across 3D space and have spatially optimized properties will enable increased structural efficiency over today's 2D laminates. The joining of composite components organically, without fasteners, offers manufacturing and performance benefits and requires analysis tools and in situ process control for the necessary confidence of bondline qualities. Innovations in composite materials constituents are needed to provide tailorable functionalities such as increased electrical and thermal conductivity, and acoustic performance. Early demonstrations of nanoscale tailorability and of integration with biomaterials opens up new horizons for composite behavior. And the development of composite materials that have adaptive properties, properties that can change in a desirable and predictable manner over time, will provide new levels of component performance across many fields. Whereas historically composites have been largely optimized for structural performance, development and exploitation of the many innovative processing and fabrication approaches for composite materials can transform production systems and factories and fabrication costs. A variety of polymers beyond epoxies are mature enough to incorporate, including thermoplastic polymers. Multiple processing approaches to transform the polymer to a cured or consolidated state, other than autoclave or thermal processes, have promise and feasibility. Analysis and predictive tools that enable rapid evaluation and accurate prediction of complex behaviors of composites that have been tailored across multiple scales, dimensions, and constituents will be required to open up the true performance of this class of engineered materials.

To bring these materials to their full potential as described, a more robust and richer suite of multiscale modeling tools must be developed, tools that model the processing, capturing the kinetics and stresses as the material is processed into its final structure as well as tools the can predict the material behavior under its ultimate intended use environment and loading. Significant advances in specialized fields have been noteworthy, but the integration of modeling and simulation tools as well as their extension to a broader range of constituents is needed. Hybrids that bring together hard materials such as metal and ceramics with polymeric composite materials have been shown to withstand quite extreme environments. The properties that can be achieved by integrating and blending their extremely different properties (still such that the resulting hybrid material can be fabricated) is an emerging area that requires broader exploration to determine the limitations of these concepts. Exploration and maturation of multidimensional reinforcements and gradient morphologies will require not only advances in process simulation and multiscale modeling but also parallel and integrated manufacturing science research to explore the limitations of building such innovative engineered materials. The opportunity for computation as well as data analytics for this class of materials is great. Fundamental research in these complex engineered materials may provide foundations for other complex engineered materials such as

[16] A. Orieux and E. Diamanti, 2016, Recent advances on integrated quantum communications, *Journal of Optics* 18(8).

metamaterials and biomaterials; collectively driving the cross-discipline training necessary for successful development of engineered and composite/hybrid materials.

Despite the commercialization of ceramic matrix composites (CMCs) in the leading-edge aviation propulsion (LEAP) engine introduced in 2017 (see Box 2.4 and Case 2 in Section 5.3), state-of-the-art materials are limited to use temperatures of 1250-1300°C.[17] Residual silicon, a remnant of the reactive melt-infiltration process of the SiC matrix, precludes its use at higher temperatures. Achieving operating temperatures greater than 1400°C for SiC-based systems is likely to require vapor deposition processes or preceramic polymers for silicon-free composites. Future strategies might include self-healing compositions or new melt-infiltration systems for more refractory systems. In the long term, new systems will require materials and microstructural architecture design to allow for use temperatures greater than 1540°C.

As operating temperatures increase, any airborne dust, such as sand or volcanic ash, is likely to deposit, melt, and react with CMC engine components. Although efforts to address this issue have been taken, no proven solutions are at hand. Recent efforts have had an emphasis on multilayer solutions—specifically, thermal barriers to reduce temperature and environmental barriers to prevent reactions. The problem is particularly troublesome because the reaction product with molten dust and the current environmental barriers is poorly matched with the underlying CMC, and hence, results in cracking and spallation. Resolutions to this will require new coating chemistries that will either preclude reaction with molten dusts or react quickly with them to form stable and adherent phases.

Hybrid Materials and Nanocomposites

In the last decade, single-junction solar cells made of organo-metal-trihalide perovskites[18] have gone from 3.8 percent conversion efficiency in 2009 to a record 22 percent in 2016.[19] The perovskites take the structure AMX_3, where A is an organic cation, commonly methylammonium (MA) or formamidinium (FA), M is a metal such as lead (Pb), and X is a halide anion such as bromine (Br) or iodine (I). The first structures used were in the form of $MAPbI_3$. However, the smaller bandgap of $FAPbI_3$ has led to its use by some researchers. This level of dramatic improvement was achieved through modifying the layers adjacent to the methylammonium lead halide, improving the chemistries of the perovskite itself and employing novel structures. A separate layer for hole transport has been eliminated, as the perovskite can transport both electrons and holes. Improvements in thin film deposition techniques and architecture structures, such as bicontinuous pillared structures, have also been employed. Both materials and process are fairly inexpensive in that wet chemistry and not high-temperature vacuum deposition, as in silicon solar cells, is used in manufacturing.

Perovskites transport both electrons and holes, which can be inadvertently recombined, decreasing efficiency or lifetime. If a single crystal-like structure, using inexpensive wet chemistry or other processing techniques, can be achieved, then defect interactions, especially at grain boundaries, can be reduced or eliminated. Stability of methylammonium-based perovskite solar cells remains an issue, as they degrade near 85°C; improvements are expected from encapsulation, structural, thermal, and atmospheric stability. Mixing MA and FA together can achieve both low- and high-temperature stability, but problems remain upon exposure to heat and humidity, as the compounds can be attacked by other

[17] C.S. Corman, R. Upadhyay, S. Sinha, S. Sweeny, S. Wang, et al., "General Electric Company: Selected Applications of Ceramics and Composite Materials," in *Materials Research for Manufacturing*, L. D. Madsen and E. B. Svedberg, eds., Springer Series in Materials Science 224 (2016).

[18] The Rise of Highly Efficient and Stable Perovskite Solar Cells, Michael Grätzel, Acc. Chem. Res., 2017, 50 (3), pp 487-491, DOI: 10.1021/acs.accounts.6b00492.

[19] Rational Strategies for Efficient Perovskite Solar Cells, J. Seo, J.H. Noh, and S.I. Seok, *Acc. Chem. Res.*, 2016, 49 (3), pp 562-572, doi: 10.1021/acs.accounts.5b00444.

chemistries in the stack. Eliminating the need for toxic elements is also a potential focus for future work. Some researchers are investigating A2BB′X6 halide double perovskites with Ag and In as the two cations.

One of the primary barriers inhibiting the full practical realization of hybrid nanocomposites is an insufficient ability to control the structure and dispersion state of polymer-nanoparticle mixtures.[20] This stems from the fact that most inorganic nanoparticles are hydrophilic, while most polymers are hydrophobic, which inherently hinders polymer-nanoparticle miscibility, leading to poor nanoparticle dispersions. Increased miscibility can be achieved either by adding functional groups to polymer chains or by functionalizing the nanoparticles with small ligand molecules or large polymeric grafts. The latter strategy has led, in some instances, to the development of a new class of amphiphiles capable of self-assembling into a variety of superstructures reflecting their unique hydrophilic/hydrophobic balance. Additional routes for improving dispersion are to alter the processing parameters (e.g., use of extrusion to promote directional nanoparticle flow, selection of casting solvents exhibiting a preference for nanoparticle surfaces, etc.) to drive the systems into metastable states exhibiting favorable properties and long lives or to push them into equilibrium states that are far from quiescent using electric or magnetic fields.

With respect to polymer-nanoparticle hybrid materials and nanocomposites, setting out the behaviors of the phases in carefully outlined superstructures, as well as assembling the nanoparticles, has seen much advancement. Unfortunately, there remains perplexity around hard nanoparticles combined with thread-like polymers spanning comprehensive parameter space. Further, issues remain when creating functionalized nanoparticles. Despite thorough attempts, poor understanding of the system dynamics, such as the various components' mobilities, also persists. It is imperative that future work emphasize how external fields (electric, magnetic) affect active nanoparticle assembly. The definitive obstacle currently preventing practical applications of these hybrid materials involves understanding and controlling how the assembly states affect engineering properties that arise, and how to tune them.

Hydrogels swell in response to changes in humidity, temperature, pH, and salt concentration. To date, researchers have only scratched the surface of how geometry, chemistry, and electrostatics that generate large deformation can be used to stimulate intriguing and useful advances in hybrid materials. Another area that is receiving considerable attention is that of "soft robotics," where the goal is to replace hard and stiff linkages and pneumatic actuators with softer, more compliant and active materials. The materials paradigm is that hard materials offer great structural capacity but very small displacements, while soft materials provide a much greater range of displacement but very low load-carrying capacity. Hybrids of hard and soft materials with distributed actuation appear to be one of the most promising solutions for multimaterials robots.

3.3 SEMICONDUCTORS AND OTHER ELECTRONIC MATERIALS

The directions for semiconductors and other electronic materials described in Chapter 2 provide much of the guidance for where opportunities will lie in this field for the next 5 to 10 years.[21] Materials must enable electronics to tackle increasingly complex monolithic integration schemes and bring new functionality onto microprocessors, must allow for the construction of chips that take full advantage of 3D layouts and design, and must utilize advanced packaging solutions that improve the performance and form factor of heterogeneous electronics.

Many of the new and emerging devices promise dramatic advances in information technology in the post-Moore's law era, but their success will depend on the properties of materials that are new to

[20] S.K. Kumar, V. Ganesan, and R.A. Riggleman, "Perspective: Outstanding theoretical questions in polymer-nanoparticle hybrids," *Journal of Chemical Physics*, 147 (2017) 020901.

[21] The committee thanks Thomas Theis, Columbia University, for his insightful thoughts and ideas in developing this portion of the report.

electronics and photonics, and the ability to integrate these materials into nm-scale device structures. To achieve this, one must consider not only the materials, but also the system in which they will be working. Furthermore, no one can predict what new possibilities for information technology will result from blue-sky research in areas such as topologically protected and quantum-coherent materials.

3.3.1 Device Miniaturization and Advances Beyond Miniaturization

Many of the device miniaturization efforts discussed in Chapter 2, such as continued efforts to develop extreme ultraviolet lithography (EUVL) fabrication capabilities and pursuit of advances in thin film ferroelectrics, will be a focus over the next few years. Research needed to advance information and communication technologies, in addition to continued miniaturization, are discussed in the following sections.

New Devices Combining the Functions of Memory and Logic

Magnetism has long been the basis for information storage devices such as the hard-disk drive and spin transfer torque magnetic random-access memory (STT-MRAM) discussed in Chapter 2, but recent materials discoveries have raised the possibility of magnetic devices for digital logic. With the digital state of each device represented by a persistent magnetic polarization, there would be no need to save the state of a computation before the power is turned off. This capability could be of immediate value in power-starved systems dependent on intermittent power sources, and in the longer term, it could profoundly change computer architecture. First, however, the energy efficiency of magnetic polarization switching must be made competitive with that of electronic switching. One exciting research frontier is the study and demonstration of mechanisms for voltage-controlled magnetism in ferromagnetic and antiferromagnetic materials.[22]

Neuromorphic Devices

Artificial neural networks (ANNs) are being aggressively explored as energy-efficient architectures for execution of machine learning algorithms. With the explosive growth in applications of machine learning, ANNs could become the most profound development in computer architecture in many decades. However, attaining their full potential may require the introduction of new devices that more compactly and efficiently implement key network functions. For example, much effort has gone into the development and demonstration of analog memory devices to store the weights of synaptic connections, but the material properties and resulting device characteristics are still far from ideal for this application.

3.3.2 Multifunctional Devices and the "Internet of Things"

The concept of the "Internet of Things" (IOT), a network of devices, machines, appliances, and other items embedded with sensors, actuators, other electronics, and software that continually communicate and interact, has been around for some time. The next 10 years will see IOT extend to more and more spaces and applications, triggering demands for commensurate technologies and the materials required to meet those needs.

Mines, industrial plants, and power facilities will be monitored for process controls; residential and commercial spaces for safety and convenience; farms for crop and other agricultural management; and hospitals for overall connectivity and patient service. Sensors will be needed to monitor patients'

[22] S. Fusil, V. Garcia, A. Barthelemy, and M. Bibes, 2014. Magnetoelectric Devices for Spintronics. Annual Review of Materials Research. 44:91. C. Song, B. Cui, F. Li, X. Zhou, F. Pan. 2017. Recent progress in voltage control of magnetism: Materials, mechanisms, and performance. *Progress in Materials Science* 87:33.

conditions and symptoms; to test the air for pollution and the presence of odors and toxic gases; to test soils for the presence of nutrients, pollutants, and water; to monitor traffic control and security in cities; and to track water usage for canal management. Most of these sensors will need to be inexpensive and off-the-shelf, detecting light, motion, or pressure, but much more advanced sensors will also be needed and will have to be built at the frontiers of physics, chemistry, engineering, and biology, utilizing cutting-edge materials. As just one example, sensors for harsh environments, where temperatures remain higher than 200°C, will require new materials. STT-MRAM (discussed in Chapter 2) offers opportunities in the area of embedded memory as an alternative or replacement to NOR flash, as it is projected to work well in such harsh environments.

Many of the electronic devices that will meet these needs will be multifunctional, including microelectromechanical systems (MEMS) discussed in Chapter 2, and there will be materials challenges associated with supplying increasingly complex and capable devices. Materials selection for the structural elements of current MEMS devices is limited to a small subset of materials that are compatible with conventional very-large-scale integration (VLSI) fabrication technologies, with silicon (Si) being the dominant structural material. Suspended single-crystalline silicon or polysilicon elements, like those found in accelerometers, are easily fabricated with deep reactive ion etching and are dimensionally stable at room temperature. They cannot, however, be used at elevated temperatures because Si creeps at elevated temperatures and junction leakage occurs at temperatures as low as 120ºC.[23] Ceramics such as silicon dioxide, silicon nitride, silicon carbide, and silicon-carbo-nitride have been incorporated into MEMS devices that can operate at higher temperatures, but wide application of these materials has been limited by low tensile strengths, high residual stresses, and complex fabrication processes. Moreover, many forward-looking MEMS applications will require materials that combine high electrical conductivity with mechanical integrity. Advanced metallic alloys possess an attractive balance of properties (stiffness, strength, density, conductivity, etc.), but deposition and micromachining techniques for the formation of complex MEMS components from these alloys is still in its infancy. Thermoplastic forming of bulk metallic glass is intriguing as a fabrication method for low- to moderate-temperature MEMS devices. Electrodeposition and physical vapor deposition provide alternative routes to depositing metallic alloys, but these films are often deposited far from equilibrium and with microstructures that are much finer and often less stable than for bulk alloys. Once these issues are understood scientifically, the development of technologies for the deposition and shaping of metal MEMS alloys holds great promise and will enable realization of the IOT.

Development of tomorrow's IOT sensors will also require materials with enhanced functional properties. Take, for example, sensors that serve as electronic "noses." Such sensors must detect trace amounts of gases, inorganic or organic, but will probably need a different material and functionality or physical process for every category of gas to be detected. This is, and will continue to be, an area of active, forefront research. Likewise, medical sensors will need to be able to go into the human body, and either disintegrate, be naturally expelled, or be surgically extracted. Their design presents significant demands. They will need to detect extremely weak signals that combine electronic, rheological, chemical, and biological properties and must be designed with certain critical tolerances.

Other areas under active research and development are developing capabilities in the inspection and optimization of defects, parts, and processes in the manufacturing environment.

3.3.3 Next-Generation Semiconductors for RF and Power Electronics

Next-generation information and energy systems will require a new class of electronic materials and devices that can provide higher power density, higher efficiency, and smaller footprint than that possible with conventional semiconductors such as Si. Electronic materials such as wide-bandgap

[23] P.G. Neudeck, R.S. Okojie, and L.-Y. Chen, High-temperature electronics—A role for wide bandgap semiconductors?, *Proceedings of the IEEE* 90(6), 2002, doi: 10.1109/JPROC.2002.1021571.

semiconductors GaN, AlN, Ga2O3, and diamond have a higher breakdown field that can enable higher power density and gain at significantly higher frequencies, leading to disruptive advances in mm-wave and THz frequency communication and radar technologies. Research toward realization of high breakdown strength and synthesis of low-defect density layers could also enable highly efficient solid-state power electronics at voltages ranging from a few hundred volts to tens of kilovolts. Last, explorative studies on the integration of materials that exhibit new phenomena such as Mott-insulator transitions and ferroelectricity into semiconductor device platforms could enable a range of unconventional new architectures for logic, communication, sensing, and energy conversion.

3.3.4 Interconnects and Packaging

The changes in integration and packaging, and the emergence of new devices such as field-effect-transistors, spintronic devices, and photonic devices, will also impose new restrictions on interconnects that will require materials solutions. The transition from 2D to 3D monolithic integrated circuits requires stacked layers of transistors, which poses challenges for interconnect routing and thermal budget control. For spintronics and photonics, signal conversion and density in interconnect hierarchy must be considered. Spin-based propagation heavily depends on relaxation length and time, which results in restrictive specifications for signal volatility and integrity. Optoelectronic device performance scales nonmonotonically with device length owing to design restrictions, which causes trade-offs of signal quality with density scaling. Last, integrating interconnects with new devices will require thermal budget matching, resistive-capacitive (RC) management, and electrical contact with new materials.

The increasing diversity and complexity of products, from small embedded sensors to heterogeneous "systems on a chip" also pose growing technical challenges for packaging. Today's heterogeneous systems integrate elements that were formerly relegated to board-level integration, such as passive components (capacitors, inductors, etc.) and active components (antennas and communication devices such as tunable filters), as well as memory and logic. While this allows more function per unit volume, it also accentuates challenges such as the management of within-package power density, thermal density, and the maintenance of signal integrity. It also increases assembly complexity and costs.

3.4 QUANTUM MATERIALS

Quantum materials were previously defined as materials whose properties cannot be explained by simple Fermi liquid theory, or those with strong electronic correlations. In the past decade, this definition has been broadened to include 2D and topological materials—materials whose electronic functionality reaches beyond simple 3D metals, semiconductors, and insulators. There exist many families of quantum materials, even dozens in the subset of unconventional superconductor, whose fundamental properties remain to be solved. The two solved families are the electron-phonon coupling of Cooper pairs within the BCS theory of conventional superconductivity, and the quantum and fractionalized quantum Hall effects (the discovery of both of these phenomena led to Nobel prizes). The fundamental nature of these materials is astounding—including how the electrons "group" into novel phases such as stripes and nematic states, and how conducting surface states can be "topologically isolated" from an insulating bulk. That there are so many unsolved quantum materials means that researchers must enable a suite of coordinated computation, growth, and measurement techniques to elucidate these natures. The technological payoffs for energy, and quantum information sciences (QIS) are enormous. And for the latter, researchers stress that the material or materials that are finally used for QIS (qubits, sensors, etc.) have not yet been determined, making this a crucial materials research area for the United States, especially in light of international competition. This is well described in the 2017 Department of Energy

(DOE) Report *Opportunities for Basic Research for Next Generation Quantum Systems* and in the 2018 National Science Foundation (NSF) Report *Midscale Instrumentation for Quantum Materials*.[24]

3.4.1 Superconductors

Superconductivity continues to be a fertile field of discovery with the ultimate grand challenge being the discovery of room-temperature superconductivity. The move of high-Tc superconductivity from being a "phenomenon" to a useful physical effect in a variety of copper oxide materials in the late 1980s and early 1990s has been transformational in extending superconductivity from a low-temperature physics phenomenon to a potentially useful applied technology.[25] Superconductors with sufficiently high transition temperatures and sufficiently large current-carrying capacity are being used in the form of coated conductors in the electricity grid, for superconducting magnetic energy storage, as turbine/motor components for enhanced energy efficiency, as transformers with less than half the weight of traditional transformers,[26] and as quantum sensors as well as spintronics device elements in a number of emerging technologies. Nevertheless, a predictive understanding of high-Tc superconductivity currently remains beyond our grasp as a scientific grand challenge, something that will put computational efforts to the forefront in order to solve.

Over the past decade, superconductivity has been found in unexpected regimes, from a growing number of families of iron-based superconductors to reports of remarkably high Tc in hydrogen-rich superconductors at the extremes of high pressure. These "surprise" discoveries serve to reinforce how little researchers actually know about the origins of superconductivity. Further, superconductivity is just one of a variety of quantum matter phenomena in which novel ground states give rise to surprisingly useful materials. The enhanced integration of theory, experiment, and synthesis is accelerating progress toward understanding superconducting phenomena. Additionally, the development of new capabilities to understand novel superconductors is impacting a variety of related fields. Nevertheless, a predictive understanding of cuprate superconductivity remains elusive, and the means by which low-energy tuning of coupled and competing interactions yields new states of matter is at best only partially understood.

U.S. researchers are making discoveries more quickly than in the past,[27] and a general theme of new physics through new materials remains robust. However, international colleagues are being more effective at sustained investment at scale (see Chapter 5), especially when it comes to synthesis science,[28] and this is creating a discovery imbalance (e.g., as measured by the number of new superconductors being discovered domestically versus internationally). As researchers look to the future, the opportunity is beyond "just" new materials discovery/single crystal growth and includes hierarchical structures/functional assemblies that eventually can be economically scaled to kilometer lengths. To seize this opportunity in a timely way, focus could be on coupled theoretical, computational, and experimental tools to predict novel materials and functional architectures, which is a path forward not only for superconductivity but also for all areas of materials research. Further, the role of coherence and topological protection is displacing low-energy tuning as a central focus of understanding quantum matter. Quantum matter, especially as it relates to quantum information science more broadly, has the opportunity to be a key research area for the next decade, and the discovery and understanding of novel superconductivity has the possibility to continue to drive this field.

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[24] 2017 DOE report available for download at https://science.energy.gov/~/media/bes/pdf/reports/2018/Quantum_systems.pdf, accessed December 5, 2018.

[25] See http://www.sc.doe.gov/bes/reports/files/SC_rpt.pdf, accessed May 23, 2018.

[26] See http://www.die.ing.unibo.it/pers/morandi/didattica/Temporary-ESAS-summer-school-Bologna-2016/Noe.pdf, accessed June 6, 2018.

[27] Michael Kremer, 1993, Population growth and technological change: one million B.C. to 1990, *Quarterly Journal of Economics* 108(3):681-716, https://doi.org/10.2307/2118405.

[28] See http://ec.europa.eu/research/era/pdf/key-figures-report2008-2009_en.pdf, accessed May 23, 2018.

3.4.2 Magnetic Materials

Classical studies of magnetism will always have a place in materials characterization. It is inherently part of the study of the properties of any newly synthesized compounds that contains atoms with unfilled d- or f-shells. It is therefore reasonable to expect progress in the discovery of new types of magnetic alignments, of magnetic exchange (the energy involved in the magnetic exchange between neighboring atoms), of ordering temperatures (Curie or Neel) that are out of the ordinary range, and of low-dimensional effects (recent developments here include Cu-salts with spin-ladder and spin-chain structures). By combining electronic structure calculations and other numerical models with advanced materials synthesis methods, novel magnetic materials have been designed and demonstrated. Sustained efforts using these techniques in synergy will yield additional advances as other materials and structures are explored. This is the type of progress that the Materials Genome Initiative (MGI) has yielded and will continue to yield. Research directions that will receive new emphasis could be the following.

Antiferromagnets

It is worth pointing out that *antiferromagnets* generally are more prone than ferromagnets to developing complex and rich ordered structures. Triangular lattices can result in magnetic frustration, which in turn can lead to dynamical effects (see below). Many more antiferromagnets than ferromagnets are electrically insulating, which makes it possible to study the ordering in the absence of itinerant electrons. The large variety of possible antiferromagnetic ordering schemes also increases the likelihood that unexpected phenomena will be discovered and identified in the future, with the potential to develop applications that cannot be anticipated today. The antiferromagnetic resonant frequency lies in the 100 GHz range or above, an order of magnitude higher than the ferromagnetic resonance, offering the possibility of developing much faster spintronic switches and memories. The drawback is that, because they have little or no net moment, external magnetic fields do not couple very readily to the magnetic sublattices of antiferromagnets. This complicates the experimental side of research on antiferromagnets and requires investment in instrumentation beyond magnetometers (such as spin-sensitive optical methods and neutron diffraction).

Spin-Dynamic Effects

The research emphasis on magnetism shifted some 20 years ago toward spin-dynamic effects; the last decade focused on linear spin transport. It is reasonable to extrapolate these developments into future discoveries in the field of *nonlinear transport.* Under strong-enough driving forces, new collective spin modes are predicted to develop, some of them labeled “magnon Bose-Einstein condensates.” While nanopillar spin-based oscillators are nonlinear devices, it is likely that the condensates can give rise to new mechanisms for auto-oscillations. Another promising possibility is that of *magnonic logic and memory*, where classical electronic functions will be realized in magnonic spin transport in ferromagnetic or antiferromagnetic insulators. While magnon transport is not dissipation-less, one can hope that this approach can reduce the Joule losses associated with charge-based electronics. These fields will expand to include antiferromagnets. Because there are many more antiferromagnets, particularly among nonmetals, than ferromagnets, and because of the diversity in possible ordering structures, they promise to be a particularly fertile area for future discoveries in spin dynamics. While the field of spin dynamics is very much theory-driven, ultrafast optical probes of spin dynamics, alongside the spin-Hall and inverse spin-Hall effects, are new tools that will result in experimental progress in this field.

Antisymmetric Exchange Interactions

It is likely that the field of *antisymmetric exchange interactions* will expand beyond the concept of skyrmions. Because of the similarity with chiral electronic structures (such as topological insulators and Weyl semimetals), it is reasonable to expect important new physics and applications to arise from research on *noncollinear spin textures* in both real space and reciprocal space in general.

Multiferroics

The large response of many complex materials to electromagnetic radiation raises the possibility of ultrafast control of those materials properties through the application of short, intense photon pulses. This new field of materials research is showing promise in a number of areas including especially strongly correlated electron materials. One example of this is multiferroic materials, which show promising potential applications in which magnetic order is controlled by electric fields. However, the underlying physics and ultimate speed of magnetoelectric coupling remains largely unexplored. As shown in Figure 3.1, using ultrafast resonant X-ray diffraction revealed the spin dynamics in multiferroic $TbMnO_3$ coherently driven by an intense few-cycle THz light pulse tuned to resonance with an electromagnon mode.[29] The results show that atomic-scale magnetic structures can be directly manipulated with an electric field of light on a subpicosecond time scale.

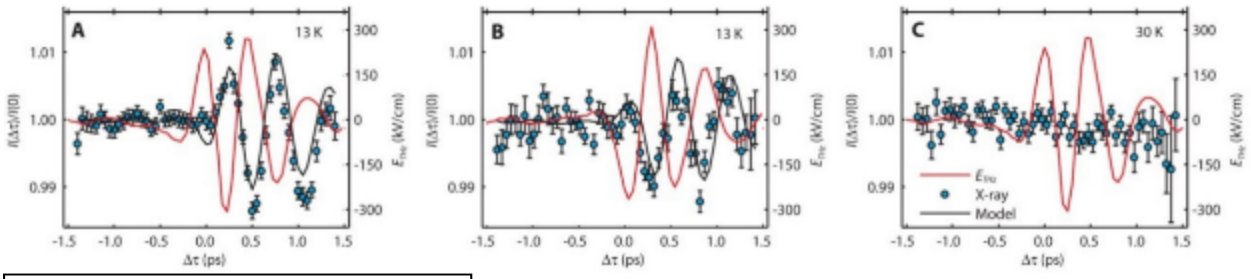

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FIGURE 3.1 *Top:* (a) X-ray scattering signal from magnetic spiral excited state follows the THz pulse field distribution with half-cycle delay. (b) Inverting the THz polarization inverts the effect, implying that the E-field drives the spiral alignment. (c) Effect is observed in the low-temperature, multiferroic phase but not in the paraelectric/spin-density wave phase. *Bottom:* Motion of the magnetic moments in $TbMnO_3$ (red arrows) is excited by a few-cycle THz pulse (red beam) and probed by an ultrafast X-ray pulse (blue beam). SOURCE: *Top:* From T. Kubacka, J. A. Johnson, M. C. Hoffmann, C. Vicario, S. de Jong, P. Beaud, S. Grübel, et al., 2014, Large-amplitude spin dynamics driven by a THz pulse in resonance with an electromagnon, *Science* 21:1333-1336, reprinted with permission from AAAS. *Bottom:* Teresa Kubacka.

3.4.3 Two-Dimensional Materials

The isolation of graphene in 2004 from graphite was a defining moment that gave "birth" to the modern field of two-dimensional (2D) materials. There continues to be intense activity in the study and

[29] T. Kubacka, J. A. Johnson, M. C. Hoffmann, et al., *Science* 343, 1333 (2014).

commercialization of graphene. However, challenges persist in achieving commercial graphene devices. Materials limitations include the inability to consistently achieve large-scale growth and processing of uniform materials, as well as the difficulty to achieve good electrical, thermal, and mechanical contact with other materials. While chemical exfoliation can be inexpensive, it is difficult to minimize defects and control layer number; on the other hand, the cleaner chemical vapor deposition (CVD) growth using metal catalysts is relatively expensive. It has also been difficult to make small devices that maintain the properties of larger areas, because of issues such as edge scattering. Intrinsic properties such as lack of a bandgap and poor out-of-plane thermal conductivity limit some applications.

In 2011, a high-performance single-layer MoS_2 transistor created excitement over the use of transition metal dichalcogenides (TMDs) in beyond complementary metal-oxide semiconductor (CMOS) - devices, as graphene had lacked a natural bandgap. In a short time span since then, the field has gone "beyond graphene." Opportunities abound, as well as needs from the capability of creating large-scale defect-free materials to enhancing researchers' ability to probe the properties and defects of a variety of single-layer materials. Researchers often acquire these 2D materials via inorganic approaches such as the formation of molydenite via the direct sulfidation of elemental molybdenum. While synthetic approaches like these have allowed researchers to make great progress in understanding the fundamental physics of 2D materials and confirm theoretical predictions, there must be a shift in emphasis in order to realize many of the promised applications. This next decade must incentivize chemists, material scientists, and chemical engineers to develop robust, low-temperature synthetic approaches that create high-quality "beyond graphene" 2D materials. Without practical deposition techniques that provide high-quality 2D materials at controlled film thicknesses and of comparable quality to their bulk inorganic films, many of these materials will remain a lab curiosity into the foreseeable future. Center(s) of excellence, such as the NSF-funded Center for Two-Dimensional and Layered Materials (2DLM)[30] are starting to make inroads into this formidable challenge.

Push to Understand Heterostructures and Interfacial Behavior

Two-dimensional materials and layered combinations of different 2D materials (or van der Waals heterostructures) can possess unique properties that make them highly attractive for electronic and optical applications. The design and development of low-dimensional material platforms based on the controlled assembly of atomically thin structures will allow researchers to explore novel physical phenomena induced by quantum coherent electronic states. Once again, the controlled growth of high-quality 2D materials and their multilayered heterostructures remains a significant challenge. Pursuing additional development of chemical vapor deposition and atomic layer deposition processes such as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) to synthesize these 2D material combinations is critical.

Some 2D materials are sensitive to oxidation and must be sealed to preserve their structure and unique properties. Understanding how the interfaces of these van der Waals materials interact in heterostructures and surroundings and with impurities of varying type is important for understanding how to encapsulate them (if required), reliably make electrical contact and measure accurate bandgaps, and, finally, how to unlock their full potential. Computation has a special role in this regard, as there is a rapidly growing body of simulations about 2D materials, their fundamental properties, and anticipated heterostructure properties.

Energy Storage, Electrical Interconnects, and Mechanical Devices

Devices such as super capacitors, fuel cells, and rechargeable batteries are seeing an increased usage of 2D materials and should witness significant growth in the next decade. R&D to lower the manufacturing cost and time would accelerate their implementation.

[30] See https://www.mri.psu.edu/mri/facilities-and-centers/2dlm.

2D or 2D-metal hybrid interconnect structures have seen some initial exploration. Advantages include high mobility and thermal conductivity. Roadblocks include the lack of large-area deposition techniques suitable for their application to high-volume manufacturing, a high out-of-plane contact resistance, and difficulties in controlling multilayer films with suitable electrical properties (mobility, carrier density, resistivity, etc.). While novel approaches have been proposed to address these challenges, many of the concepts are still in their infancy.[31]

Two-dimensional materials are leading candidates for next-generation nanomechanical devices. The in-plane covalent bonds and lack of dangling bonds on the van der Waals surfaces leads to high Young's modulus and breaking strains, chemically inert surfaces, and low friction between layers. Like mechanically robust molecular analogs of plastic wrap or pieces of paper, monolayers of 2D materials can be manipulated, transferred, and stretched to form heterostructures, 3D architecture, or suspended membranes. In addition, the coupling between the mechanical and other physical properties (thermal, electronic, optical) is of great interest in exploring novel applications. Areas of fundamental mechanical interactions still need to be explored, including the mechanics of interfaces (adhesion and friction) for heterostructured and integrated devices.

3.4.4 Topological Materials

The development of materials whose electronic, optical, magnetic, and even structural properties are controlled by topology has changed our understanding of fundamental materials physics, and will guide the search of new physical phenomena for the next several decades. For example, semiconductor, semimetal, and superconductor heterostructures with signatures of topologically protected transport of electrons, Cooper pairs, and a host of new emergent quasiparticles are being discovered as the electronic properties of these materials are probed.

Utilizing topological properties may lead to a host of applications. For example, the lack of backscattering may offer new opportunities for dissipation-free nanoelectronic devices, while the helical spin properties provide an opportunity for spintronics devices. Further devices, such as ultrafast inductors and fault-tolerant quantum computing elements, become possible when the topological materials are coupled to systems such as ferromagnets or superconductors. It should be noted that topological effects typically occur without requiring extreme conditions such as low temperatures or high magnetic fields. Mechanical metamaterials are also a new possibly important direction of research; these are engineered materials whose structures give them novel mechanical properties, including negative Poisson's ratios, negative compressibilities, and phononic bandgaps. Of particular interest are systems near the point of mechanical instability, which recently have been shown to distribute force and motion in robust ways determined by a nontrivial topological state.[32] The field of topological materials has been unique in that is has been largely theory driven, with experiments following; however, it could still benefit from more realistic modeling of spectral and transport properties.

3.5 POLYMERS, BIOMATERIALS, AND OTHER SOFT MATTER

This section addresses materials that are predominantly, although not exclusively, organic in nature. It is a huge swath of the materials domain, rich in both fundamental science questions and in important applications for commerce and society. The three elements of the title of this section are strongly overlapping, in that polymers are the largest and most economically significant class of soft

[31] Semiconductor Research Opportunities An Industry Vision and Guide, March 2017. https://eps.ieee.org/images/files/Roadmap/SIA-SRC-Vision-Report-3.30.17.pdf?, accessed January 10, 2018.

[32] D. Zeb Rocklin, Shangnan Zhou, Kai Sun & Xiaoming Mao, "Transformable topological mechanical metamaterials," Nature Communications volume 8, Article number: 14201 (2017).

materials and are also dominant in the field of biomaterials. Therefore, it is reasonable and valuable to discuss these elements in concert.

3.5.1 Polymers

Polymer materials are ubiquitous in our daily lives. The past century has seen significant growth in the large-scale production of polymers such as nylons, polyesters, polyolefins, and others. The products that were enabled by and rely on these materials range from commodity textiles to biomedical devices and implants. These materials play a significant role in meeting the grand challenges facing global society.

Polymer science and engineering research and the plastics industry are intimately connected. From biomedical technology, to electronics and communications, to structural materials, to commodity products, polymers (plastics) are everywhere. As researchers look to the future and think about significant societal needs, they need to think about the challenges and opportunities for polymer science and engineering. Application areas of importance to society where polymers are expected to have a significant role include environmental impact, energy and natural resource applications, communications and information, health. Several promising specific lines of work can be identified in each of these application areas.

- *Environmental impact:* The objectives in this area should be to use both feedstocks and finished polymer products in an efficient and sustainable way. Some specific directions of particular interest or promise are as follows: (1) exploitation of neglected raw materials (such as waste products from agricultural, industrial or human waste, or other carbon- or silicon-containing substances such as carbon dioxide and limestone sand) to form useful polymeric materials; (2) capitalization on the last decade's progress in self-healing materials to enhance lifetime, durability, and recycling (currently 14 percent for plastic packaging versus 70-90 percent for iron and steel); and (3) separation or other physical processes to enable recycling of mixed plastics.
- *Energy and natural resource applications:* Polymers are a notable player in renewable energy processes such as wind, solar, and fuel cells. Advances in polymer technology can improve the efficiency of these processes, reduce their cost, and increase capacity. Some specific directions of particular interest or promise are as follows: (1) improved safety and efficiency of energy storage systems, including solid electrolytes, all-organic batteries, and redox polymers for flow batteries; (2) polymers for energy conversion applications, including organic photovoltaics and LEDs, thin film transistors, thermoelectrics, leading to flexible and wearable systems; (3) polymers for the energy-water nexus, such as membranes and antibiofouling materials; (4) smart construction materials that improve energy efficiency and transport clean water; and (5) implementation and integration of the principles of *green chemistry and engineering* and *life cycle/sustainability thinking* into the design and development of commodity and advanced polymer technologies.
- *Communications and information:* Communications and information technology is a key area where polymers play a critical role. In addition to providing the foundation for packaging of communications and electronics technologies and the protective coatings for fiber optics cabling, polymers also play a significant role as active materials. Some specific directions of particular interest or promise are as follows: (1) in polymer and organic semiconductors, issues that remain to be addressed include relatively low charge carrier mobility, which limits charge transport in devices; weak oxidation stability and short working lifetime owing to destabilized HOMO and LUMO energy levels; and a fairly high bandgap that limits absorption of available sunlight; (2) design and development of semiconducting organic and polymer materials for optoelectronic applications requires consideration of *structure-property-process relationships*; (3) development and implementation of *data repositories* to facilitate researcher access to raw data that can be mined and analyzed to advance the field.
- *Health:* Biomedical materials are playing a significant role in the health enterprise, and many of the advances that researchers have seen in recent years have been enabled by polymers. Polymers

will continue to be critical to improving human health. Researchers need cost-effective, innovative materials to control, treat, and diagnose infectious diseases. Further, as implant technologies continue to be developed, along with drug-delivery systems and multifunctional biosensors, researchers need a better understanding of how polymers react in dynamic and in some ways harsh environments in the body. These fundamental insights will open the door to new biomedical polymer-based technologies. Some specific directions of particular interest or promise are as follows: (1) expanding the design of polymer-based nanomaterials from tissue regeneration and drug delivery into new applications such as immuno-engineering; (2) additive manufacturing of devices and scaffolds leading to better control of nano- and microstructure as well as the possibility for made-to-order, one-off, on-the-spot construction of devices and implants; and (3) development of polymer-based tissue engineering to minimize the use of animal models in drug and materials testing.

An August 2016 National Science Foundation Workshop, "Frontiers in Polymer Science and Engineering" (co-sponsored by AFRL/AFOSR, ARO, DOE/BES, FDA, NIST, and ONR), "focused on the most promising directions for research associated with macromolecular materials," and it affirmed many of these application directions. In addition to applications, the opportunities for fundamental advances in basic polymer science are enormous. Overarching opportunities include the following:

1. Connecting research in synthesis, structural control, property characterization and dynamic response across many length scales. This opportunity touches instrumentation, theory, and computation with feedback into polymer synthesis. The most exciting opportunities will connect subdisciplines and length scales.
2. Creating and aggregating advanced instrumentation so that facilities and capabilities that may be out of reach of individual institutions, from synchrotron and neutron scattering down to electron microscopy, nuclear magnetic resonance (NMR), and rheology, are readily accessible.
3. Ubiquitous theory and computation should break down barriers between theoretically focused and experimentally rooted investigators through investment in collaborative initiatives that exploit both sets of skills. This is the application of the Materials Genome Initiative to polymer science.
4. A key opportunity is the development of accessible, scalable polymers that match or exceed the property matrix of existing materials while having a greener life cycle.

Macromolecular science starts with synthesis. As in other areas of materials research, there is a focus in polymer science on opportunities in precision synthesis. Better control over sequence, composition, tacticity, branching, architecture, topology, dimensionality, functionality, and dispersity is needed. Techniques that are leading to near-biological precision in sequence control represent exciting opportunities in a basic science sense, although an equally exciting opportunity is to demonstrate what new properties can be achieved with this level of precision synthesis. Synthesis is also where considerations of other opportunities start. Green polymer chemistry can create strategies that improve recyclability, reduce environmental effects, and control the durability of polymers.

Polymer materials synthesis includes higher-order structure formation and supramolecular assembly for in situ access to complex nano-objects and polymerize preorganized monomers to create programmed architectures. Noncovalent bonding, including mechanical interlocking via catenanes and rotaxanes, is as yet underexploited in creating higher-order structures. Not only should higher-order assembly processes be explored for the distinctive structures that they can form, but also it should be recognized that self-assembly, and other higher-order assembly processes, while thermodynamically spontaneous, are not instantaneous, and therefore, study of the kinetics of these assembly processes is needed. To quote the NSF Workshop Report, "We must begin to think of assembly not as a process with fixed thermodynamic states defined by equilibrium but rather as a pathway with useful intermediates that yields a richer and more complex phase space. Assembly can be designed in a manner similar to a

chemical reaction path, where many unit operations simultaneously take advantage of the kinetics and thermodynamics of assembly."

Like many areas of materials science, polymer materials science is now fueled significantly by data science. There is a need for accessible and well-managed cyberinfrastructure that facilitates and encourages the storage, organization, curation, retrieval, and effective use of experimental and computational data on polymer properties. First-principles prediction is the ultimate opportunity. Real-time acquisition, and, more importantly, interpretation, is an opportunity to accelerate integration of experiment with analysis. This opportunity is pronounced when the arena is more in the realm of polymer processing than is polymer equilibrium structure. Polymer processing frequently employs far-from-equilibrium conditions and nonlinear deformations such that the design of processing methods to control polymer properties is often accomplished by good intuition and empirical findings. Although equilibrium and linearity have long been useful bases, the future opportunities are in understanding dynamic states. Polymer materials have unique problems in these areas, especially in correlating processing conditions to polymer structure, most notably in semicrystalline polymers. A particular example is that the physics of failure in polymeric materials is poorly understood.

3.5.2 Biomaterials and Bio-Inspired Materials

Future directions for the broader objective of deepening our mastery of biomolecular materials science will require integration of advanced synthesis, novel characterization tools, and computation. Advances in polymer science will be critical in developing this frontier given the essential role of covalent macromolecules in cell components as well as plant and animal extracellular matrices.

There are many possible directions for the next decade ranging from autonomous behavior in soft matter to mastering the creation of synthetic materials with comparable properties and functions to those of musculoskeletal tissues. In the latter objective, it is critical to learn how to encode in molecules the formation of hierarchical structures using multiple components over a broad range of molecular weights. The opportunities in autonomous behavior could focus on rapid time scales in actuation and motion that are molecularly encoded in soft materials. Related objectives could search for materials with dynamic mechanical properties that originate in materials with capacity to reconfigure their bonding configurations or undergo the type of reversible self-assembly that operates in the cytoskeleton.

The enabling strategies for critical advances in biomolecular soft matter are many, and some of them may not be easily envisioned at the time this report was published. However, some of them are suggested based on initial work that has been recently reported. One such strategy described earlier as an emerging area just barely initiated in this past decade is the rational integration of supramolecular phases with covalent polymers. These systems were described earlier in this report as *hybrid-bonding polymers*—materials that could generate properties not previously observed when covalent polymers and supramolecular polymers are rationally integrated. In the past 10 years, there are examples of ordered membranes formed through self-assembly composed of such hybrid structures. In another example, simultaneous covalent and supramolecular polymerizations have yielded materials encoded for chemical regeneration. Given advances over the past decade on DNA nanotechnology, it will be important to explore whether robust and scalable chemistries with the interactive fidelity of nucleic acids can be developed in fully synthetic systems. A key objective in this area would also be a practical protein synthesis technique. While DNA is easily produced to order, proteins are not. A true "made to order" protein synthesis method would be a breakthrough in the ability to produce bio-inspired and biomolecular materials and devices. It would also make an enormous impact on the ability to develop devices based on synthetic proteins including any based on nonbiological amino acids. Last, an important enabling strategy is to understand energy landscapes in biomolecular soft materials, a field that was just barely started at the end of the past decade.

Research in the next decade in the area of biomaterials is important not only because of its direct impact on biomedical technologies but also because basic and translational research in this area will lead us to materials innovation through bio-inspired materials. The biomedical side is critical given the growth

of aging populations and society's strong interest in high quality of life. The great opportunities in bio-inspired materials will be catalyzed by advances in biomaterials, since the latter will be designed to interact directly with living organisms and this will require emulating the materials of life. Historically, the field of biomaterials for nearly three-quarters of a century has borrowed for its needs materials developed for technology at large. Excellent examples include metals with high corrosion resistance and polymers developed for textiles and consumer goods. As researchers begin the next decade, this process is inverting, and the "new biomaterials" may in turn inspire development of materials with capabilities observed in "living matter" and produced for use outside the body. This could involve highly dynamic materials that adapt to environments by changing their properties, materials that self-repair, or materials with "robotic" character that actuate or move to perform useful tasks. Other efforts such as the National Institutes of Health (NIH)-led Tissue Chip Initiative[33] is developing human tissue chips that accurately model the structure and function of human organs for improved drug screening, pushing the frontier between semiconductor technology and soft matter.

One important opportunity in inorganic biomaterials is further work on metallic materials composed of biometals that could not only resorb after implantation but also deliver metal ions for a bioactive function. Work has already been pursued on the use of magnesium, but other metals such as zinc and iron-based alloys should be explored further. This work could also have impact on discoveries relevant to biodegradable electronics to be implanted in living tissues or designed for other applications. A direction of value would be to create biomaterials or materials for other functions in which biometals are integrated with soft materials in the form of composites. Similar opportunities exist with ceramic biomaterials. In the case of biomaterials, this would offer more options to match mechanical properties of implants with those of tissues while retaining capacity for full resorption and even bioactivity. For materials at large, such combinations would lead to better options for recycling or nontoxic biosensors and wearable components. The expansion of capabilities for additive manufacturing with metallic materials also greatly expands the possibilities for on-the-spot fabrication of metallic biomedical parts.

A different opportunity with metals or ceramics that would integrate functions in biomaterials or other materials is the development of strategies to create nanoscale topographies on hard materials. In this area, there are possibilities with inspiration from topographies observed in living organisms that would impact on interfacial friction and adhesion among other properties. In ceramic biomaterials, there is also the possibility to create biocompatible piezoelectric apatite-based compositions, possibly through computationally guided design, that could electrically stimulate regeneration of tissues. Again, any developments along these lines are likely to find applications in areas outside of biomaterials.

The use of additive manufacturing methodologies involving sintering, melting, or soft-hard hybrid inks should continue to expand the functionality of metals and ceramics as biomaterials and other applications as well. Precision in the internal structure of implants could be used to rationally guide blood vessel and tissue ingrowth, and perhaps even antimicrobial functionality as the resolution begins to improve in additive manufacturing and more is understood about bacterial colonization of implants. Additive manufacturing using inorganic powders could have great impact in many technologies, but in the context of biomaterials it would be particularly important in the expanding areas of orthopedics, cardiovascular medicine, dental implants, and generally on fabrication of biomedical devices.

Soft biomaterials are the materials of choice to promote regeneration, partly because they can emulate the structures and mechanical properties of soft tissues and, when combined with inorganic components, those of hard tissues such as bones and teeth. Furthermore, they can be designed through self-assembly strategies with the biomolecular structures present in cell components and their extracellular matrices. Soft biomaterials have traditionally been composed of polymers, and opportunities in this area will continue to develop with advances in polymer science that are described elsewhere in this report. However, the past decade established the many opportunities available in supramolecular soft

[33] See https://ncats.nih.gov/tissuechip/projects, accessed July 21, 2018.

biomaterials in which self-assembling "bioactive" molecules are used as components in order to signal cells directly and trigger biological events.

In this context, an important scientific investment for the next decade is to contemplate the development of biomolecular materials with ability to signal cells dynamically and autonomously. This implies ability to turn off signaling when no longer needed, or change signals to guide sequential steps of a biological process. This capability would be important in the use of biomaterials to manage expansion and transformations of stem cells for regenerative therapies. Equally important would be the use of biomaterials to drive dedifferentiation of a given type of cell, followed by differentiation into a different lineage, as is done in induced pluripotency stem cells. An important type of dynamic behavior researchers do not currently know how to design for is the continuous assembly and disassembly of components for temporal changes in physical properties. Recent breakthroughs have shown that incorporation of DNA chemistry in soft biomaterials (see Figure 3.2) could help craft these behaviors using molecular displacements in double helices.[34] Related mechanisms could also be developed to trigger changes in mechanical properties in biomaterials in order to mediate the surprising phenomena uncovered by the field of mechanobiology. Also, an important research direction in the field of bioactive biomaterials for the next decade is glycochemistry, since great challenges are still faced in our ability to produce synthetic glycans.

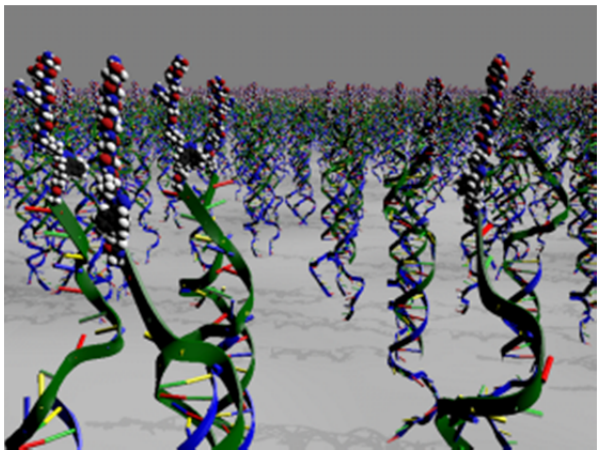

FIGURE 3.2 Biomolecular structures covalently conjugated to surfaces of biomaterials in order to trigger dynamic signaling to cells in the presence of specific molecules in the environment. The pictorial representation shows biomolecular structures containing peptide signals covalently attached to double-stranded DNA. Each signal is encoded with a specific DNA sequence, and the presence of its complimentary strand in an aqueous environment removes the signal, which can be reactivated with soluble DNA-peptide conjugates. SOURCE: See K. Samuelson, 2017, "New Technology to Manipulate Cells Could One Day Help Treat Parkinson's, Arthritis, Other Diseases," *Northwestern Now*, July 10, https://news.northwestern.edu/stories/2017/july/manipulate-cells-treat-diseases. Courtesy of Mark Seniw, Northwestern University.

In the next decade, effective development of soft biomaterials will require advances in our ability to achieve higher levels of structural precision not currently possible. Both chemical and physical strategies are needed to control nanoscale features in supramolecular assemblies and at the other extreme hierarchical structures across the scales. In this regard, it will be important to learn more about the energy landscapes of assemblies used to create soft biomaterials in order to select the right pathways for their synthesis. Possibly the most important opportunities lie in structural control in supramolecular assemblies

[34] Freeman, R., Stephanopoulos, N., Alavarez Z., Lewis, J.A, Sur, S., Serrano, C.M, Boekhoven, J., Lee, S., and Stupp, S.I., Nature Communications, 8, article number 15982, DOI: 10.1038/ncomms15982, 2017.

on scales that are much smaller than their overall dimensions—for example, the details of molecular self-sorting at the scale of nanometers in micron-long one-dimensional assemblies such as nanofibers. Another important component will be the merger of opportunities offered by advances in polymer science, described elsewhere in this report, with supramolecular materials that rely on self-assembly processes among molecules without formation of covalent bonds. An important opportunity from polymer science in this context will be to establish if meaningful functions can arise from the long-sought objective of achieving molecular precision in synthetic polymers.

The combination of structural control and dynamic behavior in soft biomaterials is important not only in the use of biomaterials for regeneration and drug delivery that dominated the past decade but also to take advantage of new materials in important applications such as development of organoids for biological research, gene editing, microbiome control, modification of decellularized organs for transplantation, and development of organs on a chip to understand disease and create new therapies, among others. Since soft biomaterials commonly take the form of hydrogels, further advances will also require research on the organization and dynamics of water in these materials as an essential feature of their physical properties and ability to signal cells.

Expanding the potential of supramolecular biomaterials for biomedical functions will benefit from advances in our understanding and control of supramolecular dynamics. This would be important in their ability to react to biological environments, causing structural reconfigurations that change or optimize their function. Another important direction is to learn how to master precise spatial positioning of multiple biological signals within nanostructures. This area will advance as better imaging techniques are developed, and a deeper understanding of intermolecular interactions is achieved. A third needed direction is research to advance synthetic chemistry in order to integrate potent biological signals using not only peptides, which have been more common so far, but also nucleic acids and glycans.

3.5.3 Soft Matter and Granular Materials

Colloidal self-assembly will become ever more sophisticated, holding out the hope, for example, that it will eventually lead to self-replication, more efficient manufacturing processes, and evolvable materials. DNA will continue to be used to construct building blocks that will enable self-assembly of more complicated and more useful materials. It will also be used to build model systems that will enhance our understanding of natural systems. For example, nanometer-scale cross-linkers with three or more arms designed to connect to different types of linear polymers and with controlled angular stiffness for different pairs of arms could give lead to the creation of new types of polymer networks with tailored mechanical or chemical properties. Protein nanotechnology with natural and artificially designed polypeptides is a growing area that will complement and compete with the more well-established DNA nanotechnology. Foldable and deformable emulsion and colloidal constructs will bring some of this technology to the micrometer scale. All of these developments provide opportunities for breakthrough advances.

The near future offers continued opportunities to create new colloidal particles with bespoke shape, size, and surface structure and chemistry to control local interparticle interactions and to react to and report chemical or physical changes in their host fluid or in other particles. These made-to-order particles will open new opportunities to control self-assembly, possibly leading to more efficient manufacturing or to evolvable materials. They will improve and broaden our understanding of the general phenomenon of jamming. The increased library of particle shapes and interaction offers opportunities to explore the self-assembly of possibly large particle clusters that respond only if the clusters are in a particular configuration or that exhibit the controlled allosteric response, in which forces between specified particles induce displacements between pairs of other specified, sometimes distant particles, that has already been demonstrated in random frames.[35] There is much to be learned about colloidal systems

[35] J. W. Rocks, et al., PNAS 114 (10), 2520-2525 (2017).

(and the systems they model) that are driven into nonlinear regimes or at faster time scales. Investigation of these and related phenomena will benefit from the development of new techniques that provide simultaneous, high-speed, 3D measurements of particle positions and local stresses.

In a trend that is already well under way, research can be expected at the boundaries between different traditional fields, running the gamut from the most fundamental to the most applied. There are opportunities for further advances in the manipulation of liquid crystalline elastomers with various external agents—light, pH, heat—with applications like artificial cilia or movable parts in soft robots. Research will open the door to increased use of liquid crystals in architectural settings such as glass walls with changeable color and opacity[36] and for digital optical applications like digital eyeglasses, switchable contact lenses, and virtual reality glasses, and even to the prevention of counterfeiting.[37]

There are many opportunities for research on nanometer-scale inclusions in liquid crystals. For example, surfactant-coated nanoparticles segregate on the surface of chiral, cholesteric liquid crystals vesicles and can form patterns following those of the underlying cholesteric,[38] and gold nanorods segregate in nanometer-scale cores of disclination lines in nematics liquid crystals, giving rise to surface plasmon resonances tuned by the nanorod concentration.[39] These represent a developing trend in liquid crystals to obtain better control over 3D conformations of their anisotropy, layering, and defect structure, often through various surface patternings. Ferronematics, which currently are based on alignment of ferronematic nanoplatelets, are in their infancy. Their magnetism provides opportunities for new responses to magnetic fields that could be used in applications. Better control of surface chemistry will allow templating of surface boundary conditions at shorter length scales.

Opportunities in active matter are almost unlimited. They start with the creation of new micro- and nanoscale particles preprogrammed with specific properties like the ability to move, manipulate flows of matter and energy, or transform one form of energy to another, and then continue to the design of new functional media to host the new particles such that the combined system presents new collective behavior. The long-term goals will be to further understand the statistical mechanics of these active systems and, with that understanding, to engineer them to perform useful functions like facilitating self-assembly or enabling soft microrobots that manipulate matter and the flow of energy. This is a highly interdisciplinary field that will require collaborative efforts of materials scientists, physicists, engineers, chemists, applied mathematicians, computer experts, and biologists.

Although it has been under intense study for almost two decades now, there are still many aspects of jamming that researchers do not understand and that open opportunities for future research. There is a long list of questions that can be posed but cannot yet be answered. How do microstructure (i.e., particle shape, roughness, and friction) and intermediate-scale structure (i.e., the geometric arrangement of particles) affect the dynamics of flow and force transmission within a static dry pile? This is still not understood. Will a more detailed understanding of the linear elasticity of piles inform us about catastrophic failure modes such as avalanches? How can the buildup of static electricity in flowing dry grains be controlled?

Soft matter experiments now collect staggering amounts of data—for example, from high-speed videos. Identifying physically relevant features in even one of these videos presents a daunting challenge. In addition, soft matter systems are often so complex that it is often difficult to know what parameters encode the most important physical properties. New techniques like machine learning, evolutionary algorithms, and network methods are making their appearance, but more needs to be done. Simulations

[36] https://www.emdgroup.com/en/news/liquid-crystals-leeds-cooperation-18-05-2017.html.

[37] https://www.technologynetworks.com/informatics/news/from-tv-to-tactile-robots-the-future-of-liquid-crystals-304510.

[38] Tran et al., Shaping of nanoparticle fingerprints at the interface of cholesteric droplets, arXiv:1804.04278 [cond-mat.soft].

[39] Lee et al., Fine Golden Rings: Tunable Surface Plasmon Resonance from Assembled Nanorods in Topological Defects of Liquid Crystals, Advanced Materials, 28, 2731 (2016).

and modeling play an ever-increasing role in soft matter. As in other disciplines in materials science, there are readily available codes, like large-scale atomic/molecular massively parallel simulators (LAMMPS) for running molecular dynamics simulations, but new codes will be needed to deal with new methods of data analysis. The soft matter community does not have access to large databases of experimental results and N-body simulations that can shorten the time and cost of materials development, and demand for such access in increasing.

3.6 ARCHITECTED AND METAMATERIALS

Artificially structured materials offer tailored materials properties and responses, even beyond those found in nature. They may enable key advances in areas including lightweighting, energy efficiency, optical/thermal/acoustic devices, and imaging. Challenges and opportunities exist in the development of new designs via computation, as well as new techniques to efficiently fabricate at large scales.

3.6.1 Architected Materials

The use of shape in the design of architected materials and mechanical metamaterials has only begun to scratch the surface of what could be done. Lightweighting with architected materials—that is, materials having a designed topological distribution of composite cells—offers increased energy efficiency, payload capability, and life cycle performance as well as increased quality of life via less invasive implants, high-performance prosthetics, and functional exoskeletons. Lightweighting through the design and manufacturing of architected structural materials thus holds great promise for numerous technologies including aerospace, transportation, energy generation, and industries that employ large rotating components. Developing robust methodologies for decoupling and independently optimizing properties would usher in a new wave of multifunctional architected materials—for example, structural materials or skins that provide thermal management, environmental protection, and enhanced communications, sensing, or invisibility. Creation of architected multimaterial systems would open the property space even further and could be used to impart enhanced functionality. Going beyond origami- and kirigami-inspired shape transformations, unidirectional wave guiding, electromagnetic sensing, programmable stiffness, and tailored energy absorption are all possible.

Computer-based topology optimization codes provide a very promising avenue for decoupling and independently optimizing material properties and functionality. Moreover, coupling this numerical approach with digital additive manufacturing threatens to disrupt current engineering design and manufacturing practices. Full realization of this potential will require developing topology optimization methods to model highly complex and nonlinear phenomena, incorporating manufacturing constraints into the optimization codes, digital transfer of optimized designs, and cost-efficient additive manufacturing of the desired architectures with requisite precision and accuracy. Challenges remain in then realizing these designs, particularly in a cost-effective way. Further, manufacturing challenges related to surface roughness, dimensional acuity, property anisotropy and property homogeneity must be addressed and overcome. Qualification and validation of additively manufactured materials and components is receiving considerable attention and this problem must be solved to realize both the development of exciting new applications and advancement of the fundamental science to anchor this disruption.

3.6.2 Metamaterials for Photonics, Phononics, and Plasmonics

Metamaterials are a class of structurally architected materials designed to have specific functional (e.g., magnetic, electrical, vibrational, or mechanical) responses that are often not found in nature. These materials offer tremendous opportunity for new photonic, phononic, plasmonic, and electromechanical

devices that can be used, for example, for microwave technology, integrated photonic circuits, energy-efficient light sources, lithography, sensing applications, catalysis, thermal engineering, and imaging techniques beyond the diffraction limit. Early work on metamaterials involved 3D arrays of metallic circuits, which produced properties such as negative optical refraction index (useful for subwavelength imaging), cloaking, and superlensing. Future growth potential incudes making nanometer-scale structures for photonic applications, as well as nonlinear designs that control electromagnetic phase-matching conditions, and also designs to produce negative refraction index in nonelectronic materials (e.g., for manipulating elastic and acoustic response). Implementing devices will require the development of technologies such as 3D nanofabrication at large scales. Another challenge with metallic metamaterials is the intrinsic losses from electronic transitions. New opportunities exist in metamaterials made from nonmetals, such as dielectrics, as well as in designing metallic or hybrid systems that minimize the impact of losses. There are also opportunities in designing metamaterials having multifunctional properties—for example, thermal and electrical conductivity for energy efficiency.

3.7 MATERIALS FOR ENERGY, CATALYSIS, AND EXTREME ENVIRONMENTS

3.7.1 Materials for Energy

Energy expenditures correspond to approximately 10 percent of the world's economic output; annual energy expenditures in the United States have routinely exceeded $1 trillion/year since 2003 and have varied between 6 and 9 percent of the U.S. gross domestic product (GDP) over the past 15 years. While energy represents a significant economic activity in its own right, even greater value is associated with its role as the crucial enabler for nearly all transportation, industry, and consumer activities. Therefore, providing reliable and cost-effective energy solutions is a societal and scientific grand challenge. Materials discovery and exploitation will continue to be a central element of any effective energy strategy.

Opportunities for significant advances in research on materials for energy fall into several large categories, including energy conversion, energy storage, energy efficiency, materials for energy, and resource sustainability. Some specific exciting examples of future opportunities have been described earlier in this section. Materials for solar energy conversion to electricity should continue to pay dividends from long-standing work on amorphous silicon and organic photovoltaics, to newer work on perovskites. A plentiful and large-scale solar energy supply will be possible only if an inexpensive storage mechanism is developed. Conversion of solar energy to hydrogen that can be stored and used in fuel cells merits substantial further effort, building on the type of work led by the Harvard "artificial leaf" project. Penetration of solar energy is limited at least as much by needs for energy storage materials as it is by energy conversion materials. The sluggish pace in the development of energy storage materials should be attacked on all fronts from basic electrochemistry to new battery materials to flow batteries and new battery designs.

The opposite direction of energy conversion—namely, electricity to light, in the form of light-emitting diodes (LEDs), both inorganic and organic, and solid-state lighting—also presents opportunities for enormous improvements in energy efficiency. For solid-state lighting to fully realize its enormous potential, the current use of phosphors to produce white light with desirable spectral qualities must eventually give way to mixing multicolor semiconductor electroluminescence in the blue, green, and red. This requires the development of new light emitting materials.

Energy efficiency is another important area to focus on. There are opportunities to increase energy efficiency by better thermoelectric materials, in which inorganic and organic embodiments are being explored. Although the needed performance characteristics to be effective in, for example, capture and use of waste heat are not there yet, it seems possible that hybrid materials may provide some progress. Extending the use of certain high-performance structural materials to high temperatures can enable better thermodynamic efficiency of processes in some cases. Low-power electronics is another

important area for future materials development related to energy efficiency. Power consumption and the resultant heat dissipation is a major obstacle confronting advanced high-performance computing. Neuromorphic computing is a concept developed in the late 1980s, describing the use of very-large-scale integration (VLSI) systems containing electronic analog circuits to mimic neurobiological architectures present in the nervous system, which obviously operate with much greater efficiency. New materials development, particularly materials for resistive switching in contrast to charge-based switching, is key to the development of neuromorphic computing. Energy efficiency in transportation may be enabled by appropriately architected metamaterials leading to lighter weight while retaining high strength.

The inter-relationships between energy and water have recently been recognized by NSF, DOE, and other agencies. For example, the report from the 2017 DOE BES Basic Research Needs Workshop begins, "Cooling in power plants, refining petroleum, producing fuel, and extracting energy resources from the earth make up a significant fraction of water use. Conversely, water treatment, distribution, and use represent significant energy demands."[40] Materials research problems and needs abound in this space. Reverse osmosis membrane desalination of seawater operates near maximum possible efficiency, but there are numerous other performance characteristics of membrane separations that could be significantly enhanced such as solute selectivity and resistance to biofouling. Improvements in biofouling resistance could also yield energy efficiency in marine transportation. A 2011 study estimated that biofouling increases the frictional drag on ships so much that it costs the U.S. Navy between $180 and $260 million per year in added fuel use.[41] (*WHOI Magazine*, 2011) These are just a few of the important opportunities in materials research related to energy and water, contributing further to the richness of work on materials for energy.

3.7.2 Materials for Catalysis

Theoretical predictions for improved catalytic materials have started leading the way toward the design of improved catalysts for specific reactions. Often, composition and architecture of predicted catalysts point toward the synthesis of bimetallic and multicomponent alloys, exposing the preferred crystallographic orientations on their surface. Core-shell nanoparticles with specified number of atomic layers for the shell metal is one such example (see Figure 3.3). These are promising metastable states of matter, capable of performing highly selective catalysis at low temperatures, where stability of the catalyst is not an issue. However, the synthesis of, for instance, shape-selected core-shell nanoparticles as prescribed by quantum mechanics still poses a challenge to inorganic materials synthesis. Furthermore, scalability of the synthetic protocols remains a challenge that needs to be addressed for industrial application of these highly efficient catalysts.

Another challenge for materials synthesis is to achieve the selective deposition of promoter moieties onto the active sites of the catalytic reaction to produce a narrow distribution of site architectures, thereby optimizing catalyst performance. Moreover, the synthesis of these materials containing well-defined active sites allows the results from experimental studies to be compared with predictions from theoretical calculations.

[40] See https://science.energy.gov/~/media/bes/pdf/reports/2017/BRN_Energy_Water_rpt.pdf, accessed December 12, 2018.

[41] See https://www.whoi.edu/oceanus/feature/barnacles-and-biofilms, accessed December 12, 2018.

Permission Pending

FIGURE 3.3 Ru-core/Pt-shell nanoparticle for low-temperature preferential oxidation of CO in the presence of hydrogen. SOURCE: Eichhorn Research Group, University of Maryland, "Bimetallic Nanoparticles, http://www2.chem.umd.edu/groups/beichhorn/Eichhorn_Research_Group/Bimetallic_Nanoparticles.html.

The recent interest in 2D materials has rekindled efforts to understand and manipulate the catalytic activity of molybdenum disulfide, a common lubricant, a layered material like graphite with an inert basal plane that has already been exploited in its 3D form as a hydrodesulfurization catalyst. The ability to induce and control reactivity in its 2D form would open many doors for catalyzing new reactions, given the incredibly large surface-to-volume ratio that allows a high density of surface-active sites. These 2D materials also have excellent mechanical properties, high stability, and durability. Their high thermal conductivity could facilitate the conduction and diffusion of heat generated during exothermic reactions, while their high electric conductivity makes them good candidates for electrocatalysis or as electrocatalyst support. Furthermore, the electronic structures of the 2D materials are markedly different from their bulk forms. Given their shape and geometry, multiple ways may be found to further manipulate their electronic structure, with one example being nanoparticles coated with single-layer molybdenum disulfide.

Defects, dopants, hybrid formations, and layered heterostructures are thus among the strategies being pursued to produce not only 2D molybdenum disulfide, but also other 2D transition metal dichalcogenides, such as graphitic carbon nitride, hexagonal boron nitride, as well as graphene. They offer the potential for catalyzing important reactions, such as higher alcohol formation from synthetic gas (formed by a combination of carbon monoxide and hydrogen), oxygen reduction reactions, and hydrogen evolution reactions. Recent work has observed high activity of defect-laden hexagonal boron nitride toward hydrogenation of alkenes to alkanes (see Figure 3.4).

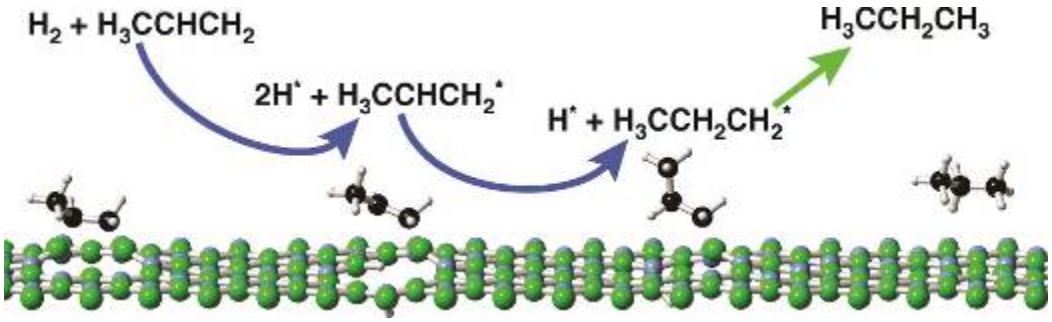

FIGURE 3.4 Hydrogenation of alkenes to alkanes catalyzed by defect-laden hexagonal boron nitride. SOURCE: D.J. Nash, D.T. Restrepo, N.S. Parra, K.E. Giesler, R.A. Penabade, M. Aminpour, D. Le, et al., 2016, Heterogeneous metal-free hydrogenation over defect-laden hexagonal boron nitride, *ACS Omega* 1:1343, © 2016 American Chemical Society.

3.7.3 Materials for Extreme Environments

There is growing demand for high-performance materials capable of satisfactory operation under a variety of extreme operating environments.[42] These demanding applications include lightweight, high-strength, high-toughness materials for aerospace and terrestrial transportation applications; ultra-high-temperature materials for hypersonic flight and propulsion systems operating above 2000°C; structural materials and fuel systems for advanced fission or fusion energy systems capable of extraordinary resistance to high-dose neutron irradiation-induced property degradation while being subjected to high heat fluxes, corrosive coolants, and high mechanical stress; and high-temperature corrosion-resistant materials to enable ultrasupercritical fossil energy power systems. Additional important niche applications include structural materials with superior resistance to ultra-high-cycle mechanical fatigue, materials for ultrahigh field magnets, semiconductors, and other electronic materials for high-temperature environments, high electric field insulators that are resistant to dielectric breakdown, cryogenic materials with high strength and high toughness, and materials for ultrahigh strain rate (shock wave) environments. In many cases, the known menu of candidate materials is sparse and highlights the critical need for the discovery/design of new materials, the strategies for their processing, and the determination of their foundational thermodynamic properties in extreme conditions. The timely discovery, design, and development of a new generation of high-performance materials would impact multiple advanced technology platforms.

Building upon research advances achieved in the prior 10 to 15 years, a solid mechanistic understanding is now generally available that allows science-based designs to be proposed for next-generation high-performance materials tailored for optimal performance in specific extreme environments. In particular, growing confidence in the proven value of computational thermodynamic tools to guide identification of the appropriate composition and processing specifications of new materials, paired with improved fundamental understanding of the unit processes that control property degradation in materials, offers the prospect of dramatically shortening the time period to design (see, for example, Section 4.3.1 and the discussion of MGI and ICME), fabricate, and validate the performance behavior of tailored materials. Consequently, there is a good scientific basis to be optimistic regarding the prospects for accelerating the rate of improvement in key metrics such as tensile strength (while retaining adequate ductility and toughness) or resistance to neutron displacement damage property degradation. For example, although there have been steady evolutionary enhancements in the tensile strength of alloys (while retaining adequate ductility), the current best-performing materials are still more than one order of magnitude below the ideal shear strength limit. Leveraging recent improvements in the understanding of temperature-dependent nanoscale deformation mechanisms in materials, it is now conceivable that a new family of alloys could be designed and tested in the coming decade with bulk strengths at the desired operating temperature over a factor of two higher than the current best high strength commercial materials. Whereas computational modeling of ceramic materials for ultra-high-temperature applications is generally more challenging than in metals, methods based on DFT are now able to calculate mechanical, electronic, and thermophysical properties of some ceramics over a wide range of temperatures, and theory has recently provided a fundamental explanation for the reported maximum in melting point for rock-salt solutions of TaC-HfC. Similarly, improved understanding of the unit radiation defect recombination ("self-healing") processes in irradiated materials offers realistic optimism that materials resistant to radiation-induced property degradation at energy-relevant elevated temperatures up to displacement damage levels more than twice the current best-performing structural materials (i.e., >500 displacements per atom) are conceivable to be successfully developed during the coming decade. Analogous improvements in scientific understanding of corrosion mechanisms can be leveraged in the

[42] Faber KT et al., "The Role of Ceramic and Glass Science Research in Meeting Societal Challenges: Report from and NSF-Sponsored Workshop," J. Am. Ceram. Soc. 100 [3] 1777-1803 (2017).

coming decade to design new corrosion resistant materials capable of performance lifetimes up to ten times longer than current materials.

Recently developed research tools can enable important insight on the behavior of materials at extreme conditions. Laser techniques now permit characterization of melting at temperatures approaching 4000°C (e.g., $HfC_{0.98}$, at 3959 ± 84°C). New approaches also can reveal a material's strength, heat capacity, thermal expansion, thermal diffusivity, and electrical conductivity at extreme temperatures. One example is the development of superconducting power cables and how losses are measured by calorimetric methods.[43] Measurement of thermodynamic properties at extreme temperatures can be performed using recently developed novel calorimetric techniques (e.g., aerodynamic levitation with laser melting), where containment of materials at these temperatures without introducing contamination or measurement artifacts had been a major practical issue. Phase transformations can be interrogated using X-rays coupled with noncontact methods of heating (e.g., quadrupole lamp furnaces), although these are still limited to temperatures below about 2000°C. Oxidation studies up to 2000°C are possible for high-temperature ceramics such as refractory borides by leveraging their metallic conductivity for resistive heating. The combination of diamond anvil cells and high-luminosity synchrotron sources allows high-temperature, high-pressure in situ measurements of structural, thermal, transport, chemical, and even magnetic properties. Collectively, the emergence of these new advanced tools offers significant opportunities to dramatically improve understanding of performance limits and fundamental degradation mechanisms in materials under extreme operating conditions.

Extreme operating conditions represent a crosscutting materials opportunity both in terms of R&D to develop new materials capable of satisfactory performance under extreme conditions and harnessing extreme or nonequilibrium test conditions to obtain new insight on material properties and degradation mechanisms (e.g., phase stability of materials under extreme pressures). This forefront research offers opportunities to couple unique experimental facility research with theory and computational modeling to explore fundamental materials behavior under extreme conditions, validate model predictions and thereby simultaneously improve understanding of materials and develop new generations of high-performance materials.

3.8 MATERIALS RESEARCH IN WATER, SUSTAINABILITY, AND CLEAN TECHNOLOGIES

Researchers face the task of developing new, integrated materials and smart technology that will satisfy the next generation's needs, without further jeopardizing Earth. These materials must be durable, aesthetically pleasing, lightweight, modular, and inexpensive, while also being produced in an environmentally conscious manner. The breadth of the range of demands for these materials is considerable. They must encompass construction, infrastructure, and transportation sectors, in order to replace current aging buildings, fundamental facilities, and the other systems required to meet the needs of a rising global population. Sustainable infrastructure also includes the availability and provision of sufficiently abundant clean water, a stable electrical grid with reduced dependence on fossil fuels that can then fuel more sustainable modes of transportation, and a robust system for recycle and reuse of materials.

CO_2 is the highest volume contributor to greenhouse gas (GHG) production, and while it mostly comes from burning fossil fuels, materials research has a major role to play in reducing CO_2 emissions.[44]

[43] M. Kalsia, R.S. Dondapati, and P.R. Usurumarti, AC losses and dielectric losses in high temperature superconducting (HTS) power cables for smart grid applications: A comprehensive review, *International Journal of Control Theory and Applications* 9(41) (2016): 309-317.

[44] IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland.

The most common building material, concrete, is one of the largest CO_2 producers, creating up to 5 percent worldwide of human-made emissions. A 10 percent weight reduction of a fossil-fuel vehicle produces about a 6 percent improvement in fuel economy, which in turn produces about a 3 percent reduction in GHG emission averaged over the standard vehicle population of cars and trucks. Electric cars powered by renewable solar power will have a much lower CO_2 footprint, compared to gas- or diesel-powered cars. Between 5 and 7 percent of the energy in a vehicle's fuel is lost to rolling resistance between the tires and road surface. Innovative materials and devices to reduce or scavenge this dissipated energy could yield important reductions in GHG, comparable to lightweighting. Materials research for carbon capture[45] and storage holds many research opportunities, including the following: solvent, sorbent, and membrane-based carbon capture; new carbon capture materials, such as metal organic frameworks; electrochemical capture; and sequestration with geological materials.

BOX 3.1
Oleo Sponge: Argonne Invents Reusable Sponge That Soaks Up Oil, Could Revolutionize Oil Spill and Diesel Cleanup

When the Deepwater Horizon drilling pipe blew out seven years ago, beginning the worst oil spill in U.S. history, those in charge of the recovery discovered a new wrinkle: the millions of gallons of oil bubbling from the sea floor weren't all collecting on the surface where it could be skimmed or burned. Some of it was forming a plume and drifting through the ocean under the surface. Now, scientists at the U.S. Department of Energy's (DOE) Argonne National Laboratory have invented a new foam, called Oleo Sponge, that addresses this problem. The material not only easily absorbs oil from water, but is also reusable and can pull dispersed oil from the entire water column—not just the surface. "The Oleo Sponge offers a set of possibilities that, as far as we know, are unprecedented," said co-inventor Seth Darling, a scientist with Argonne's Center for Nanoscale Materials and a fellow of the University of Chicago's Institute for Molecular Engineering. The scientists started out with common polyurethane foam, used in everything from furniture cushions to home insulation. This foam has lots of nooks and crannies, which could provide ample surface area to grab oil; but they needed to give the foam a new surface chemistry in order to firmly attach the oil-loving molecules. Previously, Darling and fellow Argonne chemist Jeff Elam had developed a technique called sequential infiltration synthesis, or SIS, which can be used to infuse hard metal oxide atoms within complicated nanostructures. After some trial and error, they found a way to adapt the technique to grow an extremely thin layer of metal oxide "primer" near the foam's interior surfaces. This serves as the perfect glue for attaching the oil-loving molecules, which are deposited in a second step; they hold onto the metal oxide layer with one end and reach out to grab oil molecules with the other. The result is Oleo Sponge, a block of foam that easily adsorbs oil from the water. The material, which looks a bit like an outdoor seat cushion, can be wrung out to be reused—and the oil itself recovered.

SOURCE: L. Lerner, March 6, 2017, https://www.anl.gov/articles/argonne-invents-reusable-sponge-soaks-oil-could-revolutionize-oil-spill-and-diesel-cleanup.

There are many materials problems associated with abundant clean water; a very large fraction of them relate to interfacial materials science phenomena in membranes, sorbents, catalysts, and subsurface

[45] Materials and Processes for CO2 Capture, Conversion and Sequestration, L. Li, W. Wong-Ng, K. Huang and L.P. Cook, editors, Wiley, February 2018; and D. Nocera, Solar fuels and solar chemicals industry, *Acc. Chem. Res*. (2017) 50:616-619, doi:10.1021/acs.accounts.6b00615.

geological formations. New materials, new characterization methods, and deployment of new interfacial chemistries are needed. The scientific issues differ between large-scale purification, which might include desalination or waste water reclamation, and remediation, which might include cleaning up contaminated groundwater or oil spills. Box 3.1 describes one such effort, the development of the Oleo Sponge by scientists at DOE's Argonne National Laboratory (ANL). While it is difficult to improve the purification efficiency and operating expenses of current desalination processes simply by creating new membranes, as they operate near thermodynamic limits, it is possible to extend the lifetimes of membranes and reduce the capital expenses of desalination by surface treatments that reduce biofouling, such as grafting layers of zwitterionic polymers. More generally, there is a need and some promising directions for "omniphobic" surfaces.[46] Catalytic remediation is also a promising direction, especially for cleaning up industrial contamination of water. The interdependence of water and energy means that science to improve efficiency in providing clean water also has a GHG impact.

Solar and wind energy need to be stored because they are intermittent and diurnal. There are enormous materials research opportunities in the pursuit of economically feasible storage of renewable energy. Lithium-ion batteries have improved in energy density only slowly in their 30-year history. A transformational jump in energy density may come from multivalent ion conductors or new battery material chemistries, and must also be achieved with improvements in cycle life, fast charging, and safety; many of the needed materials simply do not yet exist. Batteries are not the only conceivable answer for large-scale solar energy storage. The conversion of water to H_2 and O_2 is one of the most practical carbon-neutral schemes to store solar energy on a global scale,[47] requiring new, efficient catalytic materials. The solar energy stored by water splitting may be released in the useful form of electricity by a fuel cell. The infrastructure does not currently exist to accommodate a water splitting/fuel cell energy system. The discovery of new materials to store hydrogen at high energy density will greatly accelerate the development of such an infrastructure.

Polymeric materials offer unique opportunities and challenges in the realm of sustainable, clean technologies. Clearly, they contribute powerful assets in diverse areas such as packaging for food preservations, membranes for water purification, and lightweight materials for transportation and infrastructure. But there is much more to do, including the development of new plastics derived from sustainable sources, designed to decompose harmlessly on demand, or to be recycled and repurposed. Life cycle analysis is especially relevant in the case of recyclable materials such as many polymers.[48] Such analyses take into account all aspects of polymer development, production, implementation, and destruction, creating a comprehensive assessment of the effect a polymer has on the environment. In this vein, progress is being made, but much more needs to be done in using highly naturally abundant polymers, such as cellulose, which are difficult to process in useful ways.

Over the past decade, a clear theme of sustainability has emerged in materials research. This includes, for example, a reliance on naturally abundant materials in seeking energy solutions as a design constraint. Further, a focus on materials recycling and reuse spanning the entire life cycle of relevant materials has also been recognized, thereby resulting in reduced usage of scarce or critical materials. Last, there is an appreciation that, for example, materials for energy are directly coupled to water utilization and that a systems approach to energy sustainability is essential, including the need for energy- and water-efficient processing strategies for materials utilization. This requires considering materials requirements in a broader context.

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[46] Wong, Tak-Sing, Sung Hoon Kang, Sindy K. Y. Tang, Elizabeth J. Smythe, Benjamin D. Hatton, Alison Grinthal, and Joanna Aizenberg. 2011. Bioinspired Self-Repairing Slippery Surfaces with Pressure-Stable Omniphobicity. Nature 477, no. 7365: 443-447. doi:10.1038/nature10447.

[47] The conversion is not only needed on a global scale but for space travel too; see http://theconversation.com/method-of-making-oxygen-from-water-in-zero-gravity-raises-hope-for-long-distance-space-travel-99554, accessed July 16, 2018.

[48] See https://onlinelibrary.wiley.com/doi/pdf/10.1111/jiec.12069.

Consistent with recent progress in developing materials solutions for energy needs, a number of materials research directions have embraced the challenge of materials availability and supply chain considerations. In this paradigm, it is not enough to simply discover a new higher-performing material, but rather one includes as a materials design/selection criteria the availability of sufficient quantities of a given material via a reliable supply chain as an important element of desired functionality. The recent focus on rare-earth materials as "critical materials" with limited domestic supply is an exemplar of this challenge. Mitigation strategies include not only more efficient use of rare earths in such systems but also the search for higher-performing non-rare-earth alternatives and a focus on materials recycle/recovery after utilization (see Box 3.2). Similarly, research on advanced fuel cells should continue to emphasize seeking nonplatinum catalysts to reduce cost and improve sustainability.

BOX 3.2
Aluminum-Cerium Alloys

The Critical Materials Institute (CMI), which is part of the Ames Laboratory, conceived Al-Ce alloys as a means of using up excess cerium produced by rare-earth mines, to improve the economics of extracting critical elements such as neodymium and dysprosium. The alloy develops strength from a eutectic microstructure, direct from the melt, and does not require the solution treatment and aging typical of aluminum alloys, although additional strengthening can be provided by age-hardening. Al-Ce alloys exhibit

- Superior castability;
- Superior strength, and strength retention, at high temperature;
- Superior corrosion resistance;
- Reduced processing energy requirements; and
- Freedom from warpage induced by heat treatment.

The alloy was recognized with an R&D 100 award in 2017.

Permission Pending

FIGURE 3.2.1 *Left:* SEM image of alloy as cast. *Right:* Ternary diagram showing the composition space. SOURCE: Z.C. Sims, O.R. Rios, D. Weiss, P.E.A. Turchi, A. Perron, J.R.I. Lee, T.T. Li, et al., 2017, High-performance aluminum-cerium alloys for high-temperature applications, *Materials Horizons* 4:1070-1078, doi: 10.1039/c7mh00391a. © The Royal Society of Chemistry 2017

Materials life cycle considerations are a broader example of the recent focus on materials recycling and reuse. To enhance sustainability, a number of manufacturing processes are exploring materials recovery and recycling as a source term for needed materials input. This focus impacts

manufacturing methods due both to varied forms of materials input as well as an explicit focus on materials recovery after intended use. Thus, the efficient and effective use of a material during its full system life cycle, rather than achieving a singular functional response, becomes the overall objective. Done well, this engineering approach dramatically enhances both systems performance and full life cycle costs.

Last, a central element of sustainability strategies is the recognition of the intimate coupling of energy and water utilization. From a materials research perspective, this has dual implications. A focus on energy-water sustainability emphasizes efficient materials processing and manufacturing strategies that are not energy or water intensive, with recent advances in additive manufacturing being a prime example. Further materials discoveries in advanced catalysts and separation science enhance the efficient use of energy and clean water, thereby advancing energy and water sustainability.

The emergence of sustainability as a key theme in materials research has both necessitated a broader focus on integrated materials solutions and enhanced the utility of these advances. By including sustainability as well as reliability as "design parameters" in seeking advanced materials functionality, materials discoveries are more readily incorporated in systems solutions. This focus on sustainability accelerates the adoption of these breakthroughs, further emphasizing the impact of materials discovery for societal needs.

3.9 MATERIALS TO MOVE, STORE, PUMP, AND MANAGE HEAT

Heat management has become one of the most crucial aspects of many technologies, ranging from batteries to hypersonic aircraft. For example, continued downward scaling of integrated circuits is limited significantly by heat management from electron devices (see the discussion in Section 3.3 for further details). Heat management also limits the performance and reliability of high-frequency and high-power amplifiers and switches.[49] Furthermore, over 90 percent of all energy used by humanity as electrical power in heating and cooling applications or for transportation originates from thermal processes. Consequently, even small efficiency improvements in our ability to control and convert thermal energy has a significant impact on the world's energy equation. Last, as the world population increases in warmer regions of the planet with concomitant increases in wealth, there reasonably will be an increased demand for climate control. This must occur with sustainable cooling technologies that have minimal impact on climate change.

Because small efficiency increases can have a significant impact on energy use in high-demand devices and applications, increased effort in developing materials that can store, convert, pump, and otherwise manage energy in its thermal form is required. Such materials could be developed to a sophistication that rivals electronic and structural materials. The potential for significant technological impact from fundamental studies of thermal processes is assessed in Shi et al. (2015).[50]

In general, heat is the energy stored in the form of random thermal fluctuations of particles, typically atoms and electrons. First-order phase transitions and their accompanying enthalpy changes likely are the most widely used form of heat storage and conversion, the most ubiquitous example being the three-centuries-old and still widely used steam power systems that enabled the Industrial Revolution.

[49] S.V. Garimella, A.S. Fleischer, et al., Thermal challenges in next-generation electronic systems, IEEE Trans. Compon. Packag. Technol. 3, 801-815 (2008).

[50] L. Shi, C. Dames, et al., "Evaluating Broader Impacts of Nanoscale Thermal Transport Research," Nanoscale Microscale Thermophys. Eng. 19, 127-165 (2015).

3.9.1 Thermal Energy Storage

Solar-thermal electricity generation presently is in large-scale use.[51] The technology today is more costly than photovoltaic electricity without storage, but it has one major advantage in that the heat from the sun can be stored during daytime hours, then used during high-electric-demand evening hours. The energy storage in solar-thermal today uses molten salts. The thermal efficiency of electricity production improves as operating temperatures increase. Improvements in efficiency thus require the development of more stable and corrosion-resistant materials. Research into new phase-change materials with larger changes in heat of melting[52] would also have significant impact as well as raising the efficiency of the conversion.

3.9.2 Solid-State Thermal Energy Conversion

Thermoelectrics and thermophotovoltaic effects are heat conversion engines with no moving parts; therefore, in principle, they do not wear, require no maintenance, and promise a near-infinite lifetime. They can be used as heat pumps for refrigeration and cooling or as electricity generators. Thermoelectric cooling has a very high specific power and uses no greenhouse gases, and thermoelectric power generation has been studied for waste heat recovery. Both technologies work over very large temperature ranges because they do not rely on phase changes. The last decades have seen the efficiency of thermoelectric materials double (measured by the figure of merit ZT). It is unlikely that further reducing the lattice thermal conductivity, the main contribution to the doubling of ZT achieved in the last 20 years,[53] will result in significant future progress because the lattice thermal conductivity of modern thermoelectric materials is close to the amorphous limit. Totally new approaches are needed. Note that the best thermoelectric used in cooling applications belongs to the same class of materials as the best topological insulators.[54] Promising approaches involve solids with energy dispersion relations that depart significantly from those of conventional bands, such as correlated electron systems, systems with topological or chiral features, or spin-based thermoelectric effects.[55]

Magnetocaloric (adiabatic demagnetization) effects rely on the heat that accompanies the ferromagnetic/paramagnetic phase change. Electrocaloric effects rely on the heat accompanying the ferroelectric-paraelectric phase change, but these are much smaller than magnetocaloric effects and may not be as promising. Both latter technologies rely on phase changes, thus operating only at a fixed temperature (unlike thermoelectric conversion), and also require heat switches (see later). Promising materials should be developed that have particularly large enthalpies of magnetization of polarization, but also have minimal hysteresis, which leads to cycle losses.

3.9.3 Active Thermal Devices, Rectifiers, and Switches

All the above technologies stand to gain from the discovery and development of new materials in which heat conduction is nonlinear (i.e., the heat flux is not proportional to the temperature difference) or is controlled externally. There is a technological need for efficient thermal rectifiers, amplifiers, and

[51] See for example, http://www.ivanpahsolar.com/. accessed June 6, 2018.

[52] I. Gur, K. Sawyer, and R. Prasher, "Searching for a better thermal battery," Science 335, 1454 (2012).

[53] K. Biswas, et al., "High-performance bulk thermoelectrics with all-scale hierarchical architectures," Nature 489, 414 (2012).

[54] J. P. Heremans, R. J. Cava, and N. Samarth, "Tetradymites as thermoelectrics and topological insulators," Nat. Rev. Mater. 2, 17049 (2017).

[55] Vandaele, K., Watzman, S. J., Flebus, B., Prakash, A., Zheng, Y., Boona, S. R., and Heremans, J. P., "Thermal Spin Transport and Energy Conversion," Mater. Today Phys.1 39-49 (2017).

switches. Just like modern electronics is based on nonlinear electrical circuit elements like diodes and transistors, such active thermal devices would be particularly relevant if implemented in solid-state form.

The technological impact of active nonlinear thermal materials would reveal itself in applications in which one needs to keep materials at a constant temperature, such as batteries, or where one has to keep things cool intermittently, such as spot-cooling on an integrated circuit. In another example, solid-state thermal switches could eliminate the moving parts in magnetocaloric and electrocaloric cycles. The most intriguing possible application for active thermal circuits would be in increasing the thermodynamic efficiency of heat engines operating under time-dependent loads. Indeed, by combining a pair of heat switches with a pair of heat reservoirs (thermal energy storage devices), one can increase the temperature difference across which a heat engine operates (see Figure 3.5), but only if that heat engine operates with a cyclical heat source (e.g., the sun in a solar-thermal system).[56] This in turn increases the Carnot thermal efficiency of such an engine.

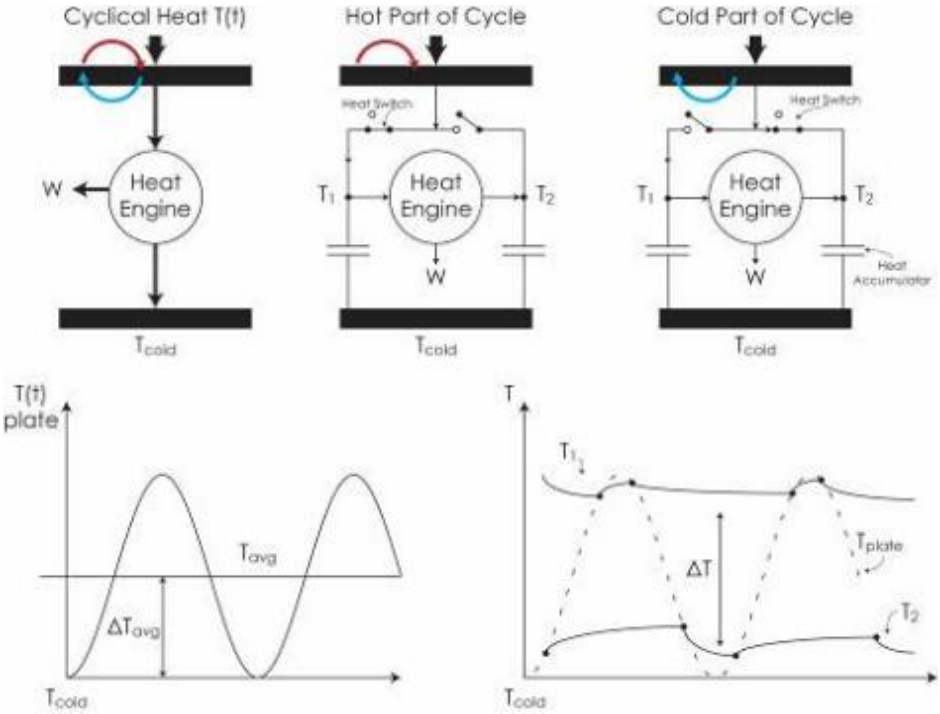

FIGURE 3.5 Materials to move heat: If practical solid-state heat switches existed, they could be used in combination with heat accumulators to enhance the thermodynamic efficiency of heat engines that operate on cyclical heat load, such as the day/night cycle in solar-thermal installations. By the second principle of thermodynamics (Carnot), heat engines are more efficient when they operate over larger temperature differences. At left is a conventional thermodynamic cycle that generates work W from such cyclical heat: the heat engine operates over an average temperature difference ΔT_{avg}. In contrast, if the heat could be switched to the left heat accumulator while the top plate is hot (middle frame), but to the right accumulator when it is cold (right frame), the heat engine can operate between temperatures T_1 and T_2, a much larger difference than ΔT_{avg}, thereby increasing its efficiency. SOURCE: Reprinted frm G. Wehmeyer, T. Yabuki, C. Monachon, J. Wu, and C. Dames, 2017, Thermal diodes, regulators, and switches: physical mechanisms and potential applications, *Applied Physics Review* 4:041304, with permission from AIP Publishing.

[56] G. Wehmeyer, T. Yabuki, C. Monachon, J. Wu, and C. Dames, "Thermal diodes, regulators, and switches: physical mechanisms and potential applications," Appl. Phys. Rev. 4, 041304 (2017).

A number of ideas for materials that could act as thermal switches or rectifiers are reviewed in the recent literature.[57] One direction for the research in active thermal materials will involve connecting thermal properties to external forces, such as strain, electric, or magnetic field. Another direction is the exploration of phase transitions, driven either by temperature itself or by the same external forces as above. New ideas are constantly being developed, including the use of topologically protected surface states.[58]

3.9.4 Thermal Barrier Coatings

Advances in coating technologies have also engendered significant advances and increased reliability and use of multilayered wear, thermal and environmental protection systems. Layered material systems are replacing advanced monolithic materials in a growing number of applications where the unique properties and functionality of each layer provides dramatically increased performance and life. Thermal barrier coatings (TBCs) for metallic Ni-base superalloys and environmental barrier coatings (EBCs) for ceramic matrix composites are two examples of layered material systems that have been developed for extreme environments, consisting of high stresses and oxidizing and corrosive gases at temperatures on the order of 1500^{o}C. These chemically, mechanically, and physically diverse layers interact and evolve throughout the lifetime of the coating, and important phenomena affecting performance and durability occur in each layer and particularly at the interfaces between disparate materials. The successful implementation of strain tolerance and low-conductivity coatings have dramatically increased coating lifetimes. As is the case for most materials designed specifically for thermal application, materials capable of operating at higher temperature and better able to withstand wear and corrosion would significantly extend the range of applications in which they can be deployed.

3.10 FINDINGS AND RECOMMENDATIONS

Key Finding: The Materials Genome Initiative, and the earlier Integrated Computational Materials Engineering approach, recognized the potential of integrating and coordinating computational methods, informatics, materials characterization, and synthesis and processing methods to accelerate the discovery and deployment of designer materials in products. The translation of these methodologies to specific industries has resulted in numerous successful applications that have reduced the development time with corresponding cost savings.

Key Recommendation: The U.S. government, with NSF, DOD, and DOE coordinating, should support the quest to develop new computational and advanced data-analytic methods, invent new experimental tools to probe the properties of materials, and design novel synthesis and processing methods. The effort should be accelerated from today's levels through judicious agency investments and continue over the next decade in order to sustain U.S. competitiveness.

Key Finding: Research into metals, alloys, and ceramics continues to provide fundamental understanding of atomic-scale processes that govern synthesis-microstructure-property relations in many classes of materials. Armed with this understanding and state-of-the-art synthesis, characterization, and computational tools, novel alloys and micro/nanostructures with extraordinary properties are being realized. Traditional areas of materials research can have

[57] G. Wehmeyer, T. Yabuki, C. Monachon, J. Wu, and C. Dames, 2017, Thermal diodes, regulators, and switches: physical mechanisms and potential applications, *Applied Physics Review* 4:041304.

[58] T. M. McCormick, S. J. Watzman, J. P. Heremans, and N. Trivedi, "Fermi arc mediated entropy transport in topological semimetals," arXiv:1703.04606 (2017).

surprising new developments, for example, in multicomponent, high-entropy alloys and inorganic glasses.

Key Recommendation: Federal funding agencies (NSF, DOE, DOD) should maintain robust programs to support, and in some cases expand, fundamental research in long-established areas such as metals, alloys and, ceramics.

Key Finding: Quantum materials science and engineering, which can include superconductors, semiconductors, magnets, and two-dimensional and topological materials, represents a vibrant area of fundamental research. New understanding and advances in materials science hold the promise of enabling transformational future applications, in computing, data storage, communications, sensing, and other emerging areas of technology. This includes new computing directions outside Moore's law, such as quantum computing and neuromorphic computing, critical for low-energy alternatives to traditional processors. Two of the National Science Foundation (NSF)'s "10 big ideas" specifically identify support of quantum materials (see *The Quantum Leap: Leading the Next Quantum Revolution* and *Midscale Research Infrastructure*).

Key Recommendation: Significant investments by, and partnerships among, NSF, DOE, NIST, DOD, and IARPA will accelerate progress in quantum materials science and engineering, so crucial to our future economy and homeland security. U.S. agencies with a stake in advanced computing, under the possible leadership of DOE's Office of Science and NNSA laboratories and the DOD research laboratories (ARL, NRL, AFRL), should undertake to support new initiatives to study the basic materials science of new computing paradigms during the next decade. To remain internationally competitive, the U.S. materials research community must continue to grow and expand in these areas.

Key Finding: Materials science and technology has an enormous impact on the quality and sustainability of Earth's environment across the entire spectrum of materials types. This is another important opportunity for university, national laboratory, and industry cooperation.

Key Recommendation: Research in numerous directions that improve sustainable manufacturing of materials, including choices of feedstocks, energy efficiency, recyclability, and more, is urgently needed. Creative approaches for funding materials research toward sustainability goals should be developed by NSF, DOE, and other agencies.

Finding: Sustainability and environmental impact have special import in the domain of polymer materials research owing to the dual factors of the massive accumulation of discarded polymeric materials in the environment and the unique challenges to polymer recyclability.

Recommendation: The massive accumulation of discarded polymeric materials points to several needed actions, namely, stimulating and executing further research on environmental degradability of polymers, better methods of separating incompatible polymers out of waste streams, research toward recycling without separation, and fundamental research in green chemistry possibilities within polymer research.

Finding: Over the past decade, it has become increasingly clear that the modern materials enterprise, from mining of raw materials to processing to disposal, often affects the environment and ecosystems and consumes considerable energy.

Recommendation: All government agencies funding materials research should explore ways of including sustainability, reliability, and life cycle analysis in appropriate grants dealing with new materials, particularly those that are close to industrial usage. The EPA and other agencies able to influence sustainability should immediately begin to support fundamental research, from the molecular to the systems level, at a rate that can advance materials sustainability within the next decade.

Finding: The real and potential importance of composite and hybrid materials is enormous, encompassing a diversity spanning organo-metal hydride perovskites for photovoltaics, to polymers reinforced with micro- or nanoscale inorganic particles to yield unique properties, to natural biohybrid materials with steep spatial gradients in their properties. The important zone in composite or hybrid materials is very frequently at the interfaces between materials types.

Recommendation: NSF and DOE, as well as other agencies with a stake in the composite and hybrid materials field, should support modalities such as biannual or quarterly workshops and also centers (akin to Fraunhofer Institutes) to foster fundamental research on composite and hybrid materials across all relevant disciplinary boundaries. Both efforts should, at the latest, start by 2022 and be supported for a minimum of a decade.

Finding: The fields exemplified by metamaterials for photonics, phononics, and plasmonics have impressive growth potential, and could have significant impact on the next generation of tailored functional materials having properties beyond what is found in nature. New opportunities exist in the creation of multimaterial, multiscale, and multifunctional structures.

Recommendation: To advance the fields represented by metamaterials for photonics, phononics, and plasmonics, new computational techniques, as well as a focus on addressing manufacturing challenges are needed. This need for new computational techniques and addressing manufacturing challenges is especially true when related to the quality and control of additively manufactured materials, and the development of new technologies such as 3D nanofabrication.

Finding: The benefits of using shape and geometry to define material response have been clearly identified for a variety of metamaterials and their attendant properties, but the design, fabrication, and use of metamaterials is still in its infancy, while contributions are seen in many fields.

Recommendation: NSF and DOE should create ecosystems that support interdisciplinary efforts to merge topology optimization and other computer-based design tools with cost-effective manufacturing processes that will advance the production of multifunctional metamaterials with requisite internal shapes and architectures.

Finding: Advances in polymer science across the board, from polymer physics to new, applied, functional, organic materials, are often driven by powerful polymer synthesis capabilities.

Recommendation: Examples of directions in polymer materials synthesis that should be pursued vigorously by the community include precision synthesis (synthetic methods aimed at biological levels of control of macromolecular structure); self-assembly and noncovalent synthesis (including advancing our understanding of hydrophobic, electrostatic, hydrogen-bonding, π–π and cation–π electronic interactions); and dynamic covalent bonding and self-healing. This recommendation is aimed first at the polymer synthesis research community to continue to generate new ideas along these lines, but then action is needed at the funding agencies that support polymer synthesis research.

Finding: Soft matter deals with a wide variety of materials, including polymers, colloids, foams, emulsions, liquid crystals, and even the flowing mixture of dirt and water that is a mudslide. It has provided liquid crystal displays, microfluidics, and insights to such fundamental concepts as topological defects and maximum packing of odd-shaped objects. It is poised to provide smart materials that change shape in response to environmental cues and parts for soft robots. It is leading research into self-assembly and the exciting new field of active matter, and its impact on related fields like biomaterials and bio-inspired materials will continue to grow. It is crucial for soft matter to be a part of the nation's research portfolio.

Recommendation: Given the diversity of directions in soft matter research, federal agencies that fund materials research, particularly NSF and DOE, should keep abreast of advances in soft matter through focused workshops and provide support for research on subjects such as self-assembly and active matter that show great promise.

Finding: The crossroads of materials research for use in biological environments (biomaterials) and the derivation of insight into new materials science through the understanding of biology (bio-inspired materials) is very rich and continues to generate new materials science.

Recommendation: Agencies such as NIH, NSF, DOE, and DOD should work together to provide interagency support for research in biomaterials and bio-inspired materials because of the fundamental interdisciplinarity of such research.

Finding: Extreme operating conditions (ultrahigh temperatures, pressures, strain rates, high-dose irradiation, or corrosive environments) pose challenges in materials discovery, synthesis, processing, and verification. Recent advances in computational modeling and innovative extreme testing methods are providing new insight into material structure and behavior, such as those for nonoxide ceramic systems that melt at temperatures near 4000°C.

Recommendation: To enhance materials understanding under extreme conditions, federal agencies (NSF, DOE, NASA, DOD) should work in concert to provide support for computational modeling and for the development and operation of shared experimental facilities for extreme conditions.

Finding: Heat management is an integral part of the design of many systems and for batteries, electronic circuits, engines, turbine blades, and materials for extreme environments. Heat management, storage, conversion to electricity, and active control of heat flow promise improvements in energy efficiency and size and cost reductions in a wide variety of technologies. Materials are needed that enable these technologies.

Recommendation: Fundamental research on the thermal properties of materials should be integrated into the material design process, and not be limited to a mere material selection process. In many cases, research on the thermal properties of a material should be considered on an equal footing with that on the electronic or mechanical properties. Predictive tools should be developed for thermal conductivity, heat capacity, and other thermal properties in the design of new materials. Research on new approaches beyond the classical band structure and crystal lattice properties should be encouraged. Steps should be taken by NSF and DOE, possibly in cooperation with other government agencies such as NIST and DOD, to encourage research proposals related to solid-state devices for thermal energy conversion, rectification, and switching.

Finding: Metals and semiconductors have long been among the most important of drivers of the U.S. economy, providing everything from skyscrapers to computer chips. Yet they continue to provide interesting and important opportunities for further development such as the possibility of bespoke materials through high-entropy alloys or atomic-scale precision in the manufacture of semiconductor materials.

Recommendation: Government funding agencies should pay careful attention to exciting advances and opportunities in fields such as metals and semiconductors without neglecting these and other more established but nonetheless important projects in traditional fields where incremental advances can still have a big impact.

Finding: The physical limits of scaling, or miniaturization, of silicon-based technology in computer chips are expected to be reached in the next decade. Given the multiyear timeline for

bringing new materials for computing to manufacture, materials research to support new computing methodologies is essential.

Recommendation: DOE, DOD, NSF, NIST, NIH, and other agencies with a stake in advanced computing should, for the next decade, place a high priority on materials research that advances new modalities of information technology.

Finding: Increasingly, biomaterials designed to regenerate tissues require functional properties other than mechanical, such as molecularly based bioactivity for signal transduction or safe and rapid biodegradation, that are challenging fundamental research capacity. These define a broad new direction in materials research that will create the knowledge necessary to bring synthetic materials, and devices made from them, into more intimate functional contact with human physiology, both internally, for medical purposes, and externally, for a wide range of potentially wearable devices.

Recommendation: All agencies, particularly NIH, which has a very specific interest in biomaterials, should participate in supporting fundamental science of these materials at a level relevant for their mission during the next decade. DOD should expand its research funding in this area as part of its interest in human-machine interaction and warfighter performance augmentation.

Finding: The proliferation of waste products that pollute the environment and threaten Earth's ecosystems is an international problem that demands international cooperation.

Recommendation: All government agencies, particularly those funding materials research that includes life cycle studies, should seek to establish communication links among similar agencies in other countries by 2020 to bring the best of world research to bear on the problem of the proliferation of waste products that pollute the environment and threaten Earth's ecosystems.

4

Research Tools, Methods, Infrastructure, and Facilities

In the past decade, significant advances have been made in the characterization (Section 4.1), synthesis and processing (Section 4.2), and computational (Section 4.3) capabilities available to materials researchers. These new tools have enabled previously unachievable materials insights, and this is especially true when used in combination—for example, in situ measurement and control of novel synthetic strategies or advanced data analytics techniques utilized simultaneously with advanced imaging diagnostics (Section 4.4). Development of these tools is a research frontier in its own right meriting further investment. This chapter highlights a number of methodological advances and the impact they have had on the materials community. One consequence of continually improving tools is the need for infrastructure reinvestment to ensure the availability of state-of-the-art tools (Section 4.5). Novel modalities for such investment are discussed. Last, the current and emerging capabilities available at intermediate-scale facilities as well as national user facilities are highlighted (Section 4.5).

4.1 CHARACTERIZATION TOOLS

4.1.1 Electron Microscopy

Transmission electron microscopy (TEM) is a key technique in all areas of materials science because it helps reveal how a material's internal structure is determined by synthesis and processing and how it correlates with its physical properties and performance. Imaging, diffraction, and spectroscopy can all be carried out across length scales ranging from interatomic distances to micrometers, often within a single transmission electron microscope and on the same sample.

The past decade has seen tremendous advances in instrumentation—in particular, spherical and chromatic aberration correctors, monochromators, and new detectors (see Figure 4.1). One example is the continued evolution of the aberration-corrected microscopes. Advanced aberration-corrected scanning transmission electron microscopes (STEMs) can now achieve 0.5 Å resolution in TEM and STEM modes along with 0.1 eV energy resolution.[1,2] Other examples of advances afforded by spherical aberration correction include picometer-precision in determining atom column positions, and tremendous improvements in the quality of atomic-scale electron energy-loss and energy-dispersive X-ray spectroscopic images, the latter in combination with new large solid-angle detectors. Understanding what sets the ultimate limit in the quest of further improving instruments to achieve even higher spatial resolution is a topic of ongoing research in the field. Advances in monochromators now allow for energy resolution of 30 meV (or better) in electron energy loss spectroscopy, sufficient to study phonons. Faster cameras and new types of sample holders developed over the past decade provide new opportunities for in

[1] Pennycook SJ, "The impact of STEM aberration correction on materials science," Ultramicroscopy, 180 [1] 22-33 (2017).

[2] Ramasse QM, "Twenty years after: How "Aberation correction in the STEM" truly placed a "A Synchrotron in a Microscope," Ultramicroscopy, 180 [1] 41-51 (2017).

situ studies of a wide range of processes in materials. Important ongoing developments include high-speed pixel array detectors that allow for detecting scattered electrons as a function of position in the detector plane. These new detectors allow for utilizing new imaging modes (e.g., differential phase contrast to image electric polarization) and, more generally, improve visibility of features and interpretability of electron microscope images.

In parallel with instrumentation, electron microscopy techniques have also made substantial advances. One of the main advantages of electrons for imaging—namely, their strong interaction with matter—was long thought to pose a challenge in the quantitative interpretation of image intensities. Truly quantitative interpretation of image intensities was demonstrated in the past decade, opening up quantitative analysis of atomic resolution images not just in terms of the position, but also the content, of atomic columns in a sample. Another highly active research area is three-dimensional (3D) imaging (electron tomography)[3] of crystalline samples. A number of different approaches are actively being developed in the field. Such approaches have been applied to analyze the 3D positions of atoms in nanoparticles. Tomography has also been used in diffraction contrast imaging of crystal defects and, in combination with in situ straining, has allowed for dynamic visualization of the interactions of dislocations with grain boundaries.[4]

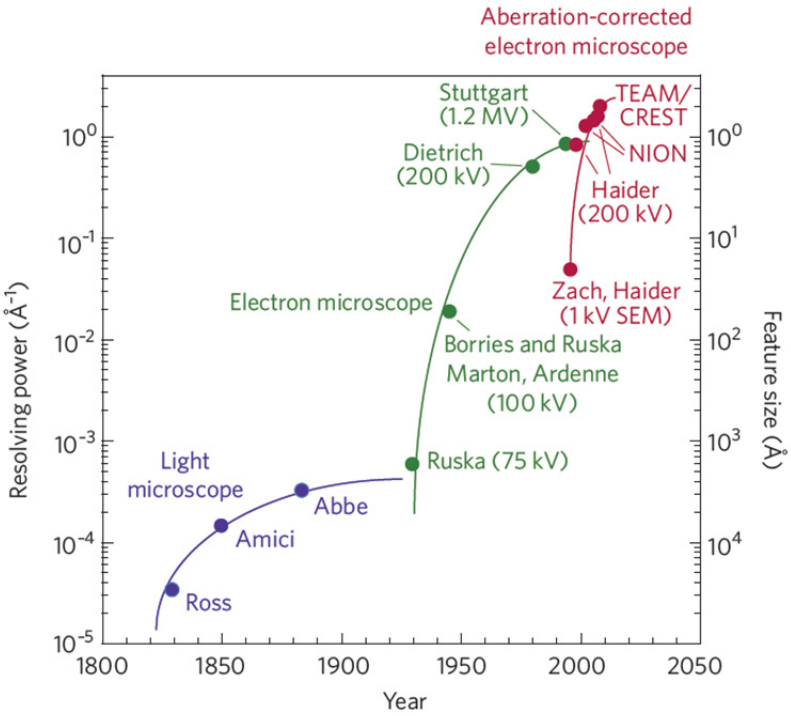

FIGURE 4.1 Improvements in the spatial resolution in light and electron microscopy. SOURCE: Reprinted by permission from Springer Nature: D.A. Muller, 2009, Structure and bonding at the atomic scale by scanning transmission electron microscopy, *Nature Materials* 8:263, © 2009.

[3] Maire E, Withers PJ, "Quantitative X-ray tomography," International Materials Reviews, 59 [1] 1-43 (2014).

[4] A. King, P. Reischig, Simon Martin, Joao F. B. D. Fonseca, M. Preuss, et al., grain mapping by diffraction contrast tomography: extending the technique to subgrain information. Risø International Symposium on Materials Science: Challenges in materials science and possibilities in 3D and 4D characterization techniques, Sep 2010, Denmark. <hal-00531696>.

4.1.2 Atom Probe Tomography

Current and emerging research areas in the physical and life sciences increasingly require the capacity to quantitatively measure the structure and chemistry of materials at the atomic scale. This atomic scale information enables nanoscience research across a wide range of disciplines including materials science and engineering, fundamental physics, chemical catalysis, nanoelectronics, and structural biology.

Atom probe tomography (APT) is the only currently available material analysis technique offering extensive capabilities for simultaneous 3D imaging and chemical composition measurements at the atomic scale. It provides 3D "maps" that show the position and elemental species of tens of millions of atoms from a given volume within a material, with a spatial resolution comparable to advanced electron microscopes (around 0.1-0.3 nm resolution in depth and 0.3-0.5 nm laterally) but with higher analytical sensitivity (<10 appm). The development of commercially available pulsed-laser atom probe systems now allows for the 3D analysis of composition and structure at atomic resolution in nonconductive systems such as ceramics, semiconductors, organics, glasses, oxide layers, and even biological materials in addition to metals and alloys. New focused ion beam (FIB) methods enable the fabrication of tailored site-specific samples for atomic scale microscopy with much higher throughput than was previously possible.

The latest generation of atom probe instruments now offer increased detection efficiency across a wide variety of metals, semiconductors, and insulators, increasing the fraction of atoms detected from approximately 60 percent to approximately 80 percent, and increasing the sensitivity. Faster and variable repetition rate dramatically increases the speed of data acquisition, and advanced laser control algorithms provide measurably improved sample yields. Atom probe experiments are inherently low throughput. The rate at which experiments can be conducted limits the outcomes that can be achieved, so improvements in the speed of acquisition and the yield of successful data sets promises an enormous step forward. This allows greater sensitivity per unit volume, which is extremely useful for the measurement of trace quantities of materials. This is a great help with geosciences applications such as mineral dating or measurement of nanoparticles or quantum devices.

One opportunity includes the development of new detectors or detector technologies that could push atom detection limits closer to 100 percent and raise the possibility of achieving kinetic energy discrimination, which would permit deconvolution of overlapping isotopes. Another significant opportunity lies in the development of multimodal instruments incorporating either a TEM or an SEM column directly into an APT system or vice versa, to provide real-time or intermittent imaging or diffraction data. This could allow assessment of specimen shape and crystallography during APT analysis, which could significantly increase reconstruction accuracy for complex heterogeneous materials. Additional opportunities include automation of procedures such as specimen alignment and application-specific control, which could free the user from monitoring the acquisition and encourage optimized analysis conditions as different material types or interfaces are exposed during analysis.

Currently, there is significant ongoing discussion about the development of APT standards. Such developments could help in establishing unified protocols for APT sample preparation, data collection processes, data reconstruction and analysis, and reporting of results worldwide. All these developments could lay the foundation for a bright future for APT as a characterization capability that can take not only materials scientists but also researchers from a variety of disciplines, including geology, biology, and solid-state materials, closer to the goal of achieving the 3D composition, structure, and chemical state of a material atom by atom. Sophisticated data analysis tools are required to extend the reach of the technique beyond visualization, and extract the type of meaningful, quantitative information that is required for the purpose of materials design (e.g., for thermodynamic calculations or grain boundary engineering).

Intensive research in this area promises to improve the potential to open up to the application of this powerful technique to a wide range of scientific research areas.[5]

4.1.3 Scanning Probe Microscopies

Scanning probe microscopy (SPM) fundamentally relies on atomic interactions between a tip and a surface. In the two decades following its invention, advances focused on increasing spatial resolution, developing quantitative theory of sample-tip interactions and improving the robustness of signals. The first wave of SPM, extending the range of properties beyond surface structure, resulted in EFM (electric force microscopy), SKFM (scanning kelvin force microscopy), PFM (piezoresponse force microscopy), SCM (scanning capacitance microscopy), and so on.

The last decade witnessed a dramatic expansion of the properties that could be probed by exploiting the frequency dependence of imposed and detected signals, achieving low detection limits, increasing scan and detection speed, and managing spatially and temporally resolved functional data sets. These advances allowed access to property functions rather than just constants at nm resolution, driving advances including the following:

- Not only capacitance and charge, but the real and imaginary components of dielectric function in organic, inorganics, and biological systems from impedance probes;
- Spatially resolved quantum efficiency of photo-generated charge in solar cell materials;
- Ultrasonic force detection for subsurface imaging;
- Electrochemical strain and ionic diffusion in battery materials;
- Dynamic processes including surface diffusion and real-time nucleation and growth in phase transformations;
- Ferroelectric switching and domain wall dynamics;
- Flexoelectricity in water or ambient of organic or inorganic materials;
- Force modulation quantifying elastic moduli and energy dissipation locally;
- Nuclear magnetic resonance, spin-resolved STM, and spectroscopy of magnetic atomic particles;
- Multi-tip STM quantifying transport and electronic structure of nanotubes, graphene, and two-dimensional (2D) materials; and
- Switching of polaritons in 2D materials and others with near field IR spectroscopy.

Many of the recent SPM advances have been made routine and will continue to provide facile characterization to drive progress in materials research and application in the next decade.

Some challenges on the horizon require additional advances. The expansion of in situ/in operando measurements that approach realistic conditions in terms of chemical environment, temperature, and pressure would eliminate the need to extrapolate measured directly to applications. Opportunity space in this area includes battery materials, fuel cells, corrosion, catalysis, thin film growth, and nanoelectronics fabrication. Imaging rates are continuously increasing, but they are not routinely at video rates. As more scanning probes achieve this speed, the range of dynamic processes that can be quantified will increase.

While an optimal pathway is not yet clear, the potential implementation of quantum computation requires characterization of quantum mechanics-based behavior in a variety of settings: quantum optics at multiple frequencies, electronic transport in various materials configurations, and manipulation of matter at the atomic scale. The materials sets for this application range from graphene and other van der Waals materials, to topological insulators, to silicon qubits.

[5] A. Devaraj, D.E. Parea, J. Liu, L.M. Gordon, T.J. Prosa, P. Parikh, D.R. Diercks, S. Meher, R.P. Kolli, Y.S. Meng, and S. Thevuthasan, International Materials Reviews 63, 68 (2018).

SPMs that use mechanical interactions to acquire subsurface imaging can produce tomographic images, taking characterization to an additional dimension. Taking property tomography to the next level will advance understanding in thin film heterostructures, cells and biological materials, composites, and solar cells.

Many SPM techniques have evolved to probe structure and multiple property functions simultaneously, creating large data sets of interconnected information. Integrating the concepts of big data and machine learning could yield unexpected insight into complex behavior in functional materials.

4.1.4 Time-Resolved, Especially Ultrafast Methods

In the last decade, significant advances in time-resolved, ultrafast methods have been achieved with picosecond resolution routine, femtosecond common, and attosecond emerging. These methods enable the study of atomic-scale dynamics of materials. Ultrafast, atomic-scale, dynamical motions underlie the performance of all functional materials and devices, and the ability to resolve them opens previously untapped potential to enhance materials performance and create new functionality. Such methods are available through table-top systems owing to advances in laser technology as well as an emerging number of X-ray free electron laser user facilities, beginning with the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory (SLAC). Upgrades to LCLS are already under way to enhance its capabilities. More intense and coherent synchrotron sources are becoming available, which will also enable a variety of more time-resolved experiments.

Applications of ultrafast spectroscopy have been very useful when investigating ultrafast biological processes, such as photo-induced proton and electron transfer or excitation energy transfer. The demonstrations have shown how the time-resolved spectroscopic techniques were useful in providing the understanding of such processes. All the electron transfer steps, especially the initial ones, are ultrafast, and early femtosecond pump-probe experiments revealed the final details of this process.[6] Another more recent example of the impact of ultrafast methods is in atomic and ionic diffusion, which is fundamental for the functionality, synthesis, and stability of a wide range of materials. In particular, diffusion of electroactive ions in complex electrode materials is central to the function of fuel cells, batteries, and membranes used for desalination and separations. While much is known from first-principles modeling and simulation about how ions diffuse through a lattice,[7] little is known experimentally about the atomic-scale processes involved in ion diffusion. Individual ion-hopping events between adjacent interstitial sites may approach approximately 100 fs time scales and are associated with significant changes in the crystal strain field,[8] which in turn can influence the dynamics of neighboring ions.

The large response of many complex materials to electromagnetic radiation raises the possibility of ultrafast control of those materials properties through the application of short, intense photon pulses. This new field of materials research is showing promise in a number of areas, including especially strongly correlated electron materials. One example of this is multiferroic materials, which show promising potential applications in which magnetic order is controlled by electric fields. However, the underlying physics and ultimate speed of magnetoelectric coupling remains largely unexplored. Using ultrafast resonant X-ray diffraction revealed the spin dynamics in multiferroic $TbMnO_3$ coherently driven by an intense few-cycle THz light pulse tuned to resonance with an electromagnon mode.[9] The results show that atomic-scale magnetic structures can be directly manipulated with an electric field of light on a subpicosecond time scale.

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[6] Holzapfel, W., et al., Initial Electron-Transfer in the Reaction Center from Rhodobacter-Sphaeroides. Proceedings of the National Academy of Sciences of the United States of America, 1990. 87 (13): p. 5168-5172.

[7] G. S. Gautam, P. Canepa, A. Abdellahi, et al., Chem. Mater. 27, 3733 (2015).

[8] A. Van der Ven, J. Bhattacharya, and A. A. Belak, Acc. Chem. Res. 46, 1216 (2013).

[9] T. Kubacka, J. A. Johnson, M. C. Hoffmann, et al., Science 343, 1333 (2014).

Applications of X-rays to quantum materials research include ongoing efforts to understand high-temperature superconductivity, the recent detection and spatial mapping of spin currents using X-ray spectromicroscopy, and the direct demonstration and discovery of new electronic phases of topological quantum matter with angle-resolved photoelectron spectroscopy. Despite this important progress in understanding fundamental material physics, the direct impact of X-ray tools on quantum information technologies has been very low to date. This is because the X-ray tools presently lack the spatial resolution to probe quantum matter on the relevant length scales.

The combined spectral, spatial, and temporal sensitivity enabled by emerging high brightness X-ray sources will dramatically change this situation. X-ray beams are currently typically 10-100 μm in size. In most cases, this is much larger than underlying quantum coherence length and any quantum information is averaged out. The new sources will enable powerful spectroscopic nanoprobes with few-nanometer spatial resolution. These nanoprobes will be able to measure the decoherence of wavefunctions, the influence of device morphology on emergent quantum phenomena, and the motion of quantum information at the heart of emerging quantum technologies. These experiments will investigate not only the spatial and temporal fluctuations of idealized, pure materials but also their manifestation in real-world devices.

4.1.5 3D/4D Measurements, Including In Situ Methods

The last decade has seen tremendous growth in three-dimensional (3D) and four-dimensional (4D) characterization capabilities that are specifically geared toward quantifying mesoscale microstructure and response under stimuli. This growth was made possible by significant advances in computer-based control, sensing, and data acquisition, and has resulted in novel experimental toolsets and methodologies that were not possible a decade ago. These advances have enabled a move from qualitative observations to digital data sets that can be mined, filtered, searched, quantified, and stored with increased fidelity and operability.

Mesoscale 3D and 4D characterization of materials with X rays can be divided into two subfields, tomography[10] and diffraction-based microscopy. The former, commonly referred to as micro-CT, involves the collection of multiple radiographs with microscale resolution and computer-based reconstruction. Laboratory-based systems can readily produce 3D renderings of soft and lattice materials, but hard materials absorb X rays much more efficiently and require higher energy sources and in some cases synchrotron experiments. By comparison, diffraction-based 3D X-ray microscopy involves scanning a beam across a specimen and reconstructing the polycrystalline microstructure from reciprocal lattices. Variation in the placement of the detectors from near-field to far-field positions allows one to determine the orientation of individual voxels within the specimen, and close inspection of the far-field pattern facilitates the measurement of local elastic strains.

[10] S.R. Stock, Recent advances in X-ray tomography applied to materials, *International Materials Reviews* 53(3):129-181, 2010.

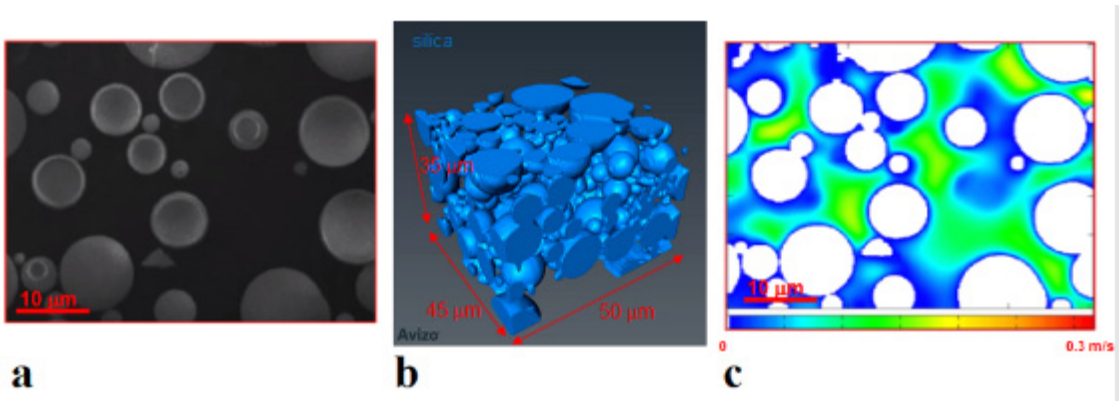

FIGURE 4.2 An experimental FIB/SEM tomography slice of a sample prepared by embedding silica beads in epoxy (a); the reconstructed 3D structure of the silica phase (b); air velocity field in a plane perpendicular to the inlet direction, computed for a 0.03 m/s inlet velocity and output atmospheric pressure boundary conditions (c). SOURCE: A. Rezikyan, 2016, FIB/SEM tomography of porous ceramics, *Microscopy and Microanalysis* 22(s3):1884-1885, reproduced with permission.

Serial sectioning combined with the acquisition of optical or electron micrographs and/or orientation and chemical maps has emerged as an alternative way of collecting and constructing 3D data sets. Focused ion beam-scanning electron microscopes (FIB-SEM) allow one to shape and extract materials with submicron precision (see, e.g., Figure 4.2), but the milling rates of conventional FIBs are prohibitive for mesoscale studies. Faster techniques have emerged and now allow for 3D characterization of volumes ranging from cubic microns to fractions of cubic millimeters. For hard materials, the emergent technologies have involved ultrashort (femtosecond) laser ablation, plasma-source focused ion beam (P-FIB), broad ion beam sectioning and mechanical polishing. The maturation of diamond-knife microtome sectioning systems that operate inside the SEM, has enabled the structural biology community to gather enormous 3D data sets from SEM imaging at the meso-scale, for example sectioning of the entire brain of a larval zebrafish.[11] Microtome sectioning is also emerging in the study of soft materials and metals.[12]

After data collection, a number of steps are needed to extract meaningful information from a 3D data set. The typical flow of data processing involves registration, reconstruction, classification, and analysis. The raw data is often misaligned and distorted, and *registration* of fiducials must be employed to remove these distortions and misalignments. *Reconstruction* involves moving from the abstraction of a series of 2D images or maps to a 3D volume of data. In the case of serial sections, whatever property was measured at the surface of the slice is generally assumed to be consistent through the entire thickness of that slice. As long as the slice thickness is small compared to the changes in the measured features, this is a reasonable assumption, but one that the practitioner should be mindful of when considering measurements within the data. *Classification* involves unambiguous identification of features of interest within the volume. This can be trivial—for example, precipitates with large density differences can easily be identified by backscatter imaging or tomography and grain boundaries can be highlighted by placing a threshold on the orientation gradient in an orientation map. But, in many cases, the contrast between two regions of interest are not easily differentiated. Human intelligence is extremely well optimized for pattern recognition and classification and can accept a very high level of anomalies within an image and through context and prior knowledge can easily infer and identify the features of interest within a set of images. However, the computer-based methods for determining regions of interest in most imaging modes do not have this context, and the segmentation of the volume is often much more difficult than expected.

[11] Hillebrand, Nature 2017.
[12] Hashimoto, Ultra, 2016.

The final step is that of *analysis* of the structures, which can be a wide variety of measurements including size, arrangement, shape metrics, crystallographic orientation textures and gradients. One of the greatest difficulties in 3D data processing and analysis is the lack of well-developed software packages and tools for 3D analysis. Materials researchers must develop custom codes and pipelines. While developing custom processing tools can have certain advantages, it is counterbalanced by the current massive duplication of effort across separate groups, which is further compounded by the lack of standards for data descriptions and file formats which would make interoperable tools easier to develop. As an example, the development of the DREAM.3D software package[13] has been extremely beneficial in reversing this trend. Initially developed for the analysis of 3D electron backscatter diffraction (EBSD) data, the platform continues to evolve to analyze multispectral data, providing a set of standards for data and processing formats and documentation.

As an example of the success of these methods, 3D data sets of polycrystalline microstructures have been obtained for a variety of aerospace aluminum, titanium, and nickel alloys, and recent in situ 4D synchrotron experiments have elucidated the importance of residual stress and the redistribution of stresses during plastic deformation.[14] A compact ultra-high-temperature tensile testing instrument, fabricated for in situ X-ray microtomography using synchrotron radiation, has been used to obtain real-time X-ray microtomographic imaging of the failure mechanisms of ceramic-matrix composites (CMCs) under mechanical load at temperatures up to 2300°C in controlled environments.[15] It should also be noted that X-ray diffraction studies of hard materials have historically been conducted in multiuser synchrotron facilities, but significantly enhanced laboratory-scale systems have emerged in recent years and hold the promise for much more widespread availability and use of this technique.

At the same time, improvements in experimental tools and accompanying modeling of mechanical properties at nanoscale to micron-scale dimensions have enabled mechanical properties to be quantified at a variety of length scales down to ~100 nm (see, e.g., Figure 4.3), enabling the quantitative study of micro- and mesoscale unit deformation processes with unprecedented spatial precision. Similarly, a variety of techniques have been reported that allow bulk physical properties such as thermal diffusivity to be accurately measured in micrometer-scale depths. This allows more comprehensive assessments to be made of the mechanical and physical properties of surface-modified materials treated by case hardening or ion implantation/plasma processing. In addition, these technique advances allow improved quantitative evaluations of the physical and mechanical properties of the near-surface regions of ion-irradiated materials as a proxy to neutron irradiation conditions that could be difficult, costly, and time-consuming (multiple-year experiments) to obtain. As an example, in situ measurements and 3D X-ray characterization of individual grains in polycrystalline bulk materials have paved the way to a better understanding of microstructural heterogeneity and localized deformation in irradiated materials. Such information is critical to the prediction of material aging and degradation in nuclear power plants and the design of new radiation-resistant materials for next-generation nuclear reactors. For instance, researchers have studied in situ heterogeneous deformation dynamics in neutron-irradiated bulk materials using high-energy synchrotron X rays to capture the micro- and mesoscale physics and link it with the macroscale mechanical behavior of neutron irradiated materials of relevance to reactor design.

[13] M. Groeber and M. Jackson, 2014, DREAM.3D: A Digital Representation Environment for the Analysis of Microstructure in 3D, *Integrating Materials and Manufacturing Innovation* 3:5. doi:10.1186/2193-9772-3-5.

[14] Various works of CMU, AFRL, Los Alamos, Riso, and Japanese groups.

[15] Ritchie et al. Review Scientific Instruments, 2014.

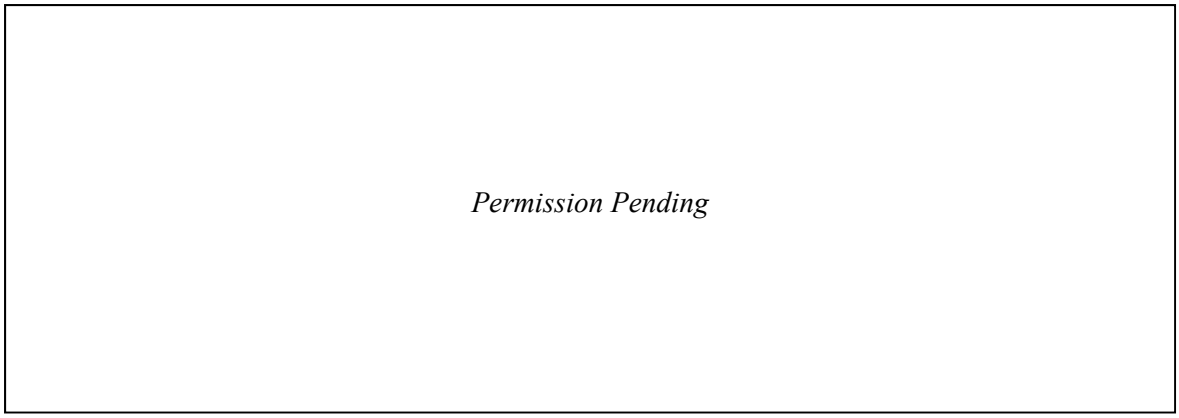

FIGURE 4.3 The wide range of length scales that affect a material's performance and properties, along with several models developed to capture each length scale. While this figure is specifically for aerospace materials, the ideas conveyed are valid for most material classes, including batteries, biomaterials, and nuclear materials. SOURCE: John Sarrao, Los Alamos National Laboratory.

It is clear that volumetric characterization at the meso- to macroscale via destructive and nondestructive experimental methods have matured tremendously in the past decade, enabling workflows that provide high-fidelity microstructural information across multiple length scales in a diverse range of material systems, but there are still many barriers that have limited its utilization within the materials community to first adopters and domain specialists. For both destructive and nondestructive workflows, a sorely needed advancement over the next decade is the in situ data analysis of the data collection procedure. The overwhelming majority of volumetric data collection is performed asynchronously and often independent of the analysis and ultimate utilization of the information. "Smart" data collection, where data is refined in key regions to provide additional resolution where required, or additional modalities to provide other attributes of materials state are needed. Dynamic sampling approaches, where data is collected efficiently and iteratively based on prior training using machine learning methods, has appeared in the literature for 2D data collection using a single modality,[16] and these methods will provide greater benefit in 3D because of the exponential growth in collection time.

Other examples include the ability to detect anomalies and other rare features in data collection using lookup tables and dictionary-based approaches, which may potentially allow for refining analysis dynamically for unknown features based on prior knowledge of the expected structure. Furthermore, truly incorporating and integrating multimodal "costly" information into 3D experiments—based on instrumentation price, acquisition time, or surface preparation requirements—can only realistically be achieved using such integrated approaches. Other needed advancements include utilization of machine learning (ML) in the classification of microstructure, the development of efficient collection methods that more directly measure properties of interest, the collection and use of more signals—ultrasound, contact methods (nano-indents), continuing to push the development of larger volumes to generate higher level statistics, and closed loop material removal for serial sectioning.

4.2 SYNTHESIS AND PROCESSING TOOLS

Given the increase in characterization tool capability and capacity over the past decade, there has been a corresponding need to advance synthesis and processing capabilities. These advanced tools not only facilitate accelerated materials discovery but also enable materials control with resolution consistent

[16] Bouman group, 2016.

with advanced measurements. Often these synthetic advances are facilitated by advanced computational methods for predicting new materials.

4.2.1 Precision Synthesis

Full realization of the promise of precision materials synthesis (size, shape, composition, architecture, etc.) across length scales will transform materials science in a revolutionary way. Specific examples emerging of the possibilities and power of precision synthesis include molecular engineering of catalytic materials for selective reactivity, control of electrochemical energy conversion with atomically precise materials, new biodegradable polymers with control of degradation rate via sequence control, precision placement of nitrogen vacancy (NV) center defects in diamond to create materials for quantum information, and self-assembly of peptide amphiphiles into fibrous and micellar structures with extraordinary bioactivity. These are the tip of an iceberg beginning to appear.

Realization of the full "iceberg" is a surpassingly ambitious objective but is an enormously promising direction to invest in. It means not only putting every atom in a material where you want it, but also knowing where you want to put the atoms, and why, and being able to determine whether you have really put them there. Therefore, what sounds at first hearing to be a "synthesis" challenge is actually a challenge for synthetic materials chemistry, theory, simulation, and instrumental characterization. The "across length scales" part of this challenge brings several new aspects into this synthesis challenge. Researchers need to gain the understanding necessary to predict how precision control structure at the atomic and molecular level plays out in macroscopic behavior and properties. They need to understand what level of precision is needed to achieve particular goals. Furthermore, as the Department of Energy (DOE) BES Basic Research Needs report on synthesis science points out, "The challenge of mastering hierarchy [meaning across length scales] crosscuts all classes of syntheses. In interfacial, supramolecular, biomolecular, and hybrid matter, hierarchy is the characteristic feature that leads to function."[17] This goal will require different synthesis techniques and chemical tools, all operating at different length scales. For example, covalent electronic chemistry would be used to make the building blocks, followed by noncovalent assembly of the building blocks into larger structures. Of course, this is research that is being done already, but without the kind of real-time instrumental monitoring and control needed to achieve optimum results. Atomic layer deposition (ALD) and molecular beam epitaxy (MBE) are atomic-level equivalents of additive manufacturing at the macroscale.

Hierarchical synthesis processes that have not traditionally been viewed as kinetic processes, such as self-assembly, *should be* considered as such; the fact that they are driven by thermodynamics does not mean they do not have kinetic trajectories (often sluggish ones). Kinetically stabilized and metastable phases may be the desired product. A wide variety of materials types will be incorporated into one finished product, necessitating wider understanding or, more likely, collaboration on the part of the synthesizers, in order to master the creation of these materials.

4.2.2 3D Structures from DNA Building Blocks

DNA origami is the folding of a long strand of DNA, the scaffold, into nanoscale objects through the use of short-chain DNA oligonucleotides, the so-called strands. The last decade has seen significant advances in the design toolbox to build 3D structures, and with each development the number of degrees of freedom increases and this enables construction of more intricate shapes. The first approach to 3D structures was achieved by bundling DNA helices in a honeycomb structure. Curved objects were achieved by adding or deleting the strands between the helical scaffold bundles. Another approach involved the use of curved rings to enable control of the shape. From the bundled helical structures came

[17] See report at https://science.energy.gov/~/media/bes/pdf/reports/2017/BRN_SS_Rpt_web.pdf, accessed June 19, 2018.

wire-frame designs in either a grid-iron pattern or triangular mesh. This advance has important implications for biomedical applications because structures created through these approaches offer higher resistance to cation depletion under physiological conditions. The advances in scaffold structures has been complemented by design platform software packages such as caDNano, DAEDALUS and vHelix.

DNA LEGO-like bricks (Figure 4.4) were developed in the last decade.[18] Each brick consists of four short single DNA strands; two head and two tail domains. Using a selection of bricks from a menu of preformed motifs, it is possible to self-assemble almost arbitrarily complex 3D structures without the need to use a scaffold structure.

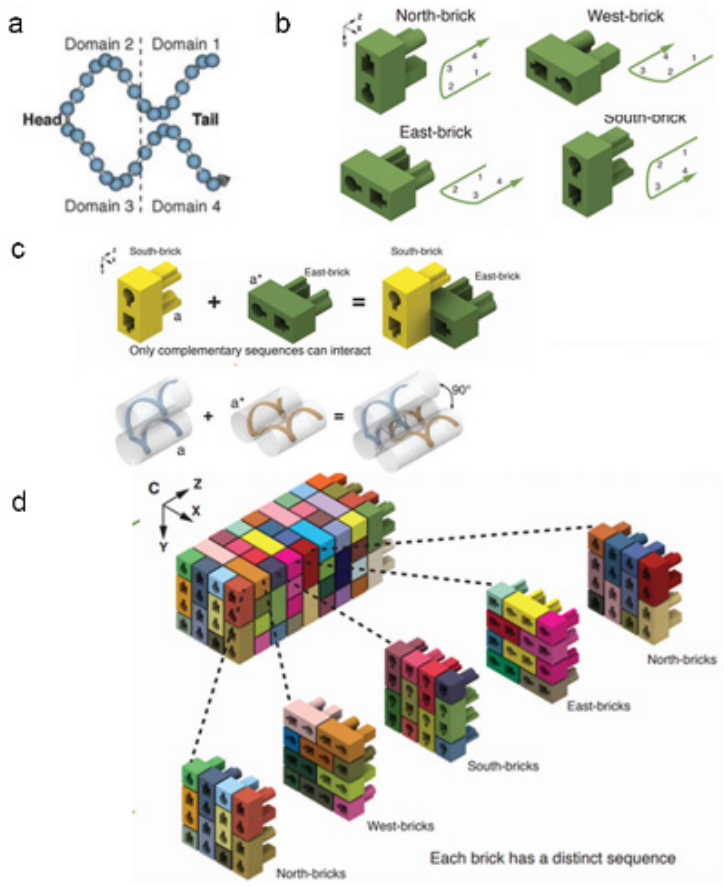

FIGURE 4.4 LEGO-like building blocks. (a) Four domains of single-stranded DNA brick. (b) Representation of the four possible different orientations as LEGO bricks. The tail domains (1 and 4) are represented by the protruding pins and the heads by the holes in the blocks. The possible connections are between blocks 1 and 3 and 2 and 4, and the shape of the protruding part must match the shape of the hole. (c) The connection of a south and east block to form the required 90-degree angle, and the joining of two complementary domains a and a*. (d) Connecting the blocks to form a structure. The first and fifth blocks are the same. SOURCE: From Y. Ke, L.L. Ong, W.M. Shih, and P. Yin, 2012, Three-dimensional structures self-assembled from DNA bricks, *Science* 338:1177-1183, doi: 10.1126/science.1227268, reprinted with permission from AAAS.

[18] Y. Ke, L. L. Ong, W. M. Shih, P. Yin, Three-dimensional structures self-assembled from DNA bricks. Science 338, 1177-1183 (2012). doi: 10.1126/science.1227268; pmid: 23197527.

The origami structures have been used as templates for producing Au nanoparticles, Au nanorods, and quantum dots; molds in which to synthesize nanoparticles; meshes for microlithography; biosensors; and for drug delivery. In addition, active systems, walkers, machines, and factories have already been demonstrated on origami platforms.[19] Perhaps an area that has not been given much attention is the possibility that when using DNA as a structural material, there might be unintended potential for DNA to behave in a signaling fashion.

Furthermore, it was demonstrated that origami was possible with long-chain RNA scaffolds. This was first demonstrated by using DNA staples and later using RNA staples.

4.2.3 2D Shape-Changing Materials

A class of reconfigurable metamaterials that has advanced considerably over the last decade is one based on two-dimensional (2D) films that fold or bend into predetermined three-dimensional (3D) structures. These materials have potential applications to biomedical devices (e.g., self-deployable stents), energy storage (e.g., stretchable Li-ion batteries), robotics, and architecture (smart window coverings to control light reflection). Advances in the ability to fabricate 3D structures at the micro- and nanolength scales were achieved.[20] This includes advances in additive manufacturing techniques and inks based on metals, metal oxides, biomaterials, and biocompatible polymers. Other approaches to develop 3D nanostructures exploit bending and folding of thin plates by the actions of residual stresses or capillarity effects and self-actuating materials. It is also possible to generate 3D structures that respond to an external stimulus such as heat or water. Origami (folding) and kirigami (cutting and folding)-inspired designs have expanded the structures that can be formed and increased the materials space to include important ones needed for future advanced technologies. An example of the processing of a mechanically guided scheme is shown schematically in Figure 4.5. The formation of robust 3D structures requires minimization of the overall strain as well as the formation of strain concentrations. The minimization of the strain has been achieved through the use of finite element modeling, which has shown that the length and width of the kirigami cut are important. It turns out that longer cuts are better than shorter ones, as stress concentrations are avoided, and wider cuts better than narrower ones, as the maximum strain is reduced. The minimization of the strain owing to the introduction of kirigami cuts is shown in Figure 4.6 for 2D square silicon membranes.[21] This illustration of finite element modeling is advancing the design of robust 3D structures.

One application of kirigami structures has been as window blinds to control the sunlight entering a room and thus creating an adaptive energy saving structure. To control the tilt of the louvres, a lattice of linear cuts on an elastomeric sheet is augmented by notches on one side or the other of the sheet, a technique referred to as kiri-kirigami to indicate cuts on cuts.[22] When stretched, the cuts open into diamond-shaped holes bounded by narrow segments that undergo out-of-plane buckling and twisting whose directions are controlled by the placement of the notches. Importantly, in this design the direction of the twist of the joints is independent of the loading direction. The reflectance of the stretched sheet depends on the direction of the twist. This can be controlled passively through mechanical stretching or having cuts on the front and back in the kiri-kirigami structure. Figure 4.7 (a) shows a schematic

[19] H. Gu, J. Chao, S.-J. Xiao, N. C. Seeman, A proximity-based programmable DNA nanoscale assembly line. Nature 465, 202-205 (2010). doi: 10.1038/nature09026; pmid: 20463734

[20] Y. Zhang, F. Zhang, Z. Yan, Q. Ma, X. Li, Y. Huang, J.A. Rogers, Printing, folding and assembly methods for forming 3d mesostructures in advanced materials, Nature Reviews Materials 2 (2017) 17019.

[21] Y. Zhang, Z. Yan, K. Nan, D. Xiao, Y. Liu, H. Luan, H. Fu, et al., A mechanically driven form of kirigami as a route to 3d mesostructures in micro/nanomembranes, Proceedings of the National Academy of Sciences 112(38) (2015) 11757-11764.

[22] Y. Tang, G. Lin, S. Yang, Y.K. Yi, and R. Kamien, 2017, Programmable kiri-kirigami metamaterials, *Advanced Materials* 29:1604262

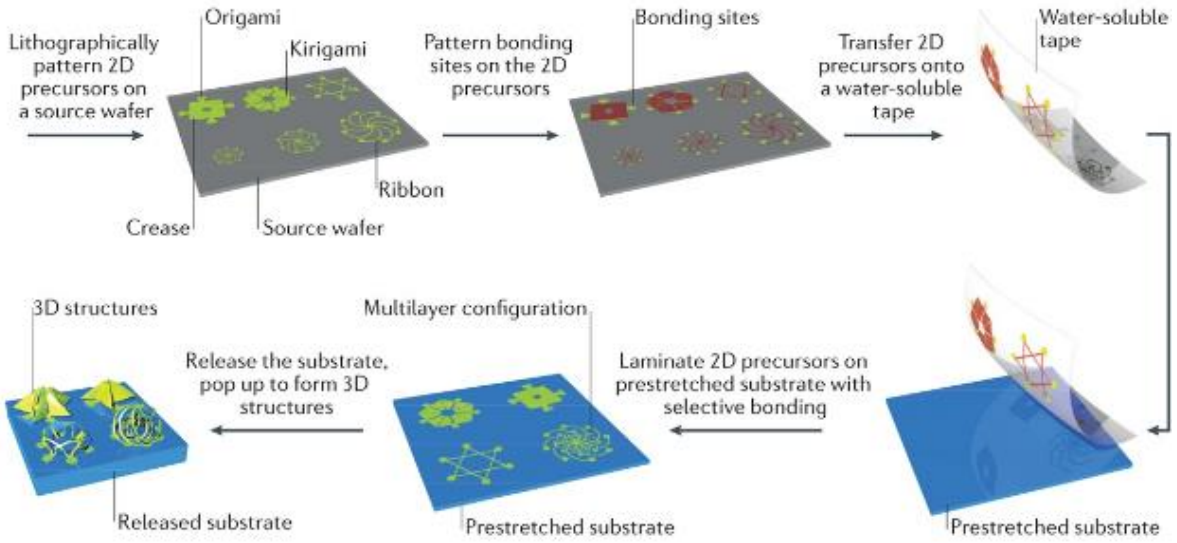

FIGURE 4.5 Schematic illustration of steps for fabricating 3D mesostructures by controlled mechanical buckling of 2D precursors formed using lithographic techniques. SOURCE: Reprinted by permission from Springer Nature: Y. Zhang, F. Zhang, Z. Yan, Q. Ma, X. Li, Y. Huang, and J.A. Rogers, 2017, Printing, folding and assembly methods for forming 3D mesostructures in advanced materials, *Nature Reviews Materials* 2:17019, © 2017.

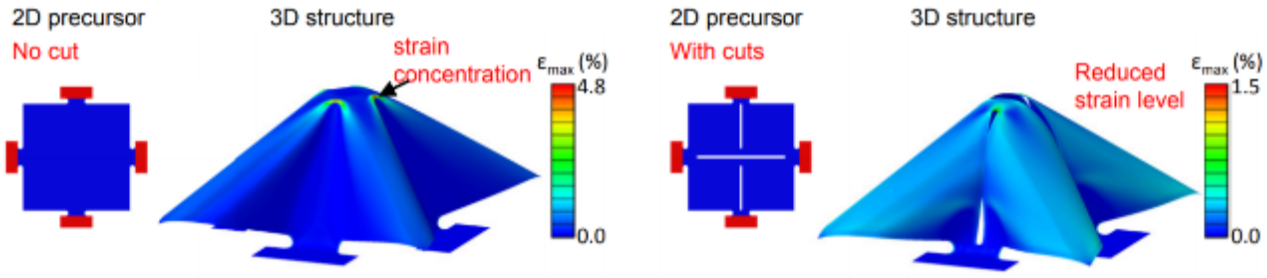

FIGURE 4.6 Finite element analysis of the strain developed on folding 2D square of silicon without and with kirigami cuts. Both structures included bilayers of silicon/polymer and the prestrain was 80 percent. The color represents the magnitude of the strain. SOURCE: Y. Zhang, Z. Yan, K. Nan, D. Xiao, Y. Liu, H. Luan, H. Fu, et al., 2015, A mechanically driven form of kirigami as a route to 3D mesostructures in micro/nanomembranes, *Proceedings of the National Academy of Sciences* 112(38):11757-11764.

illustration of the effect of loading in one and two directions on the distortion of the unit cell. Here it can be seen that the orientation of the twist is always the same, with images of light actually entering a room with windows without and with the kiri-kirigami louvres. Window treatments based on this design have been tested to determine the ability to use such structures to control light.

These experimental realizations of origami-kirigami structures have been accompanied by sophisticated theory, an example of which focuses on the special case in which kirigami cuts are constrained by the geometry of a honeycomb and are characterized by the disclinations and dislocations they create in that lattice.[23] An end product of this work is an algorithm[24] for arrangement of kirigami cuts

[23] See http://news.mit.edu/2017/algorithm-origami-patterns-any-3-D-structure-0622, accessed August 6, 2018.
[24] C. Modes and M. Warner, Physics Today 69 (1), 32-38 (2016).

that can produce any topographic shape. Similarly, an algorithm has been developed that successfully yields the folding pattern to produce any polyhedral shape in the least number of folds.

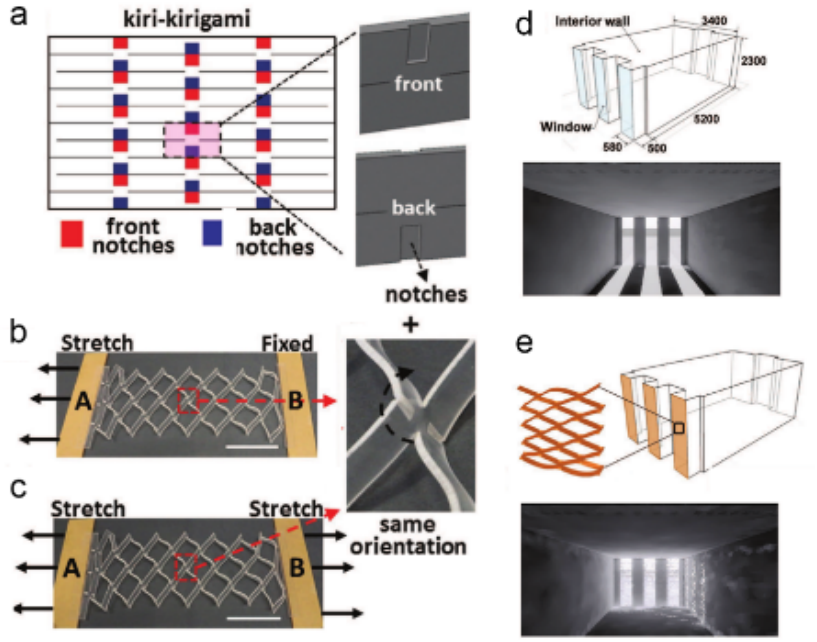

FIGURE 4.7 Kiri-kirigami structure. (a) Cutting and notch pattern. (b) and (c) When stretched in different ways, controllable and repeatable local tilting can be achieved. (d) A room with window wells where incoming light creates areas in shadow and areas cast in harsh light. (e) The same room but with windows covered by a carefully controlled kirigami structure that casts an even soft light in the room. SOURCE: Y. Tang, G. Lin, S. Yang, Y.K. Yi, and R. Kamien, 2017, Programmable kiri-kirigami metamaterials, *Advanced Materials* 29:1604262, © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.2.4 Additive Manufacturing

Several fabrication innovations have transformed the approach for producing complex components. During the past decade, additive manufacturing (AM) of metallic components has transformed from a fledgling research effort to a high-visibility commercial activity, with particularly high impact for aerospace and medical implant applications. AM is the ability to deposit materials layer by layer or point by point to fabricate complex components directly from computer-aided design models. An example is the Box 2.6. The materials palette for AM extends beyond metals to polymers, ceramics, composites, and biomaterials, employing a variety of different techniques for assembly. Even apartment buildings have now been additively manufactured in China.[25] As indicators of the increased interest in additive manufacturing, the current industrial growth rate is approximately 30 percent/year,[26] and the number of peer-reviewed publications per year more than quadrupled between 2006 and 2016.
In pursuit of AM for mainstream applications, four goals support more rapid and widespread usage of this technology:

[25] See http://www.3ders.org/articles/20150118-winsun-builds-world-first-3d-printed-villa-and-tallest-3d-printed-building-in-china.html, accessed July 14, 2018.
[26] D.L. Bourell, Perspectives on Additive Manufacturing, Annual Rev. of Mat. Res., Vol. 46:1-18, 2016.

1. Enhancing AM components performance through materials development;
2. Developing new methodologies for certifying additive components for use;
3. Developing integrated computational materials engineering capabilities together with high-throughput characterization techniques to accelerate the development to deployment cycle of AM; and
4. Developing new processes and machines with increased deposition rates, build volumes, and mechanical properties.

Materials development, certification, and integrated characterization and modeling (goals 1-3) represent an important investment opportunity because of the potential to enable disruptive change in manufacturing.

AM is still a very small market, at approximately $4 billion worldwide and growing at approximately 34 percent per year (compared to $11 trillion/year in worldwide manufacturing), but it is estimated to be valued at $33 billion by 2023.[27] AM systems are limited by the costs of materials, rates of fabrication, reliability of processes, integration with other processes, and limitations in layer-by-layer deposition. Historically, AM has been limited to small build envelopes at low deposition rates with limited materials that are sold by the equipment manufacturers. Next-generation systems explore controls, hardware, feedstock condition, and software to develop new machines with high deposition rates, large build volumes, and improved properties using the low-cost feedstocks available. As systems are enhanced, additional applications are possible, increasing the number of companies interested in the technology, and its potential impact. New control and robotic systems are driving advances in AM that have the potential to include out-of-plane deposition, resulting in true additive manufacturing and the ability to deposit multiple materials in the same machine. A wide range of feedstocks, including irregular particulate morphologies and other product forms, have the potential to lower overall cost of the materials involved. Development in smart or enhanced feed mechanisms will also increase reliability and the overall cost impact. All of these enhancements are directed at achieving transformation of AM from a 1- to 2-sigma process (30 to 70 percent success rate) to a 6-sigma process (3.4 failures per million). Achieving this goal will require specific focus on identification of design rules for new processes, development of robust tool paths via advanced slicing software to minimize residual stress and part defects, development of machine design, process monitoring and control to improve reliability and repeatability of the deposition process, and layer-by-layer inspection and adaptive process control to correct part defects during manufacturing. The improvements in AM processes and machines will proceed in parallel with the materials developments that expand the potential uses of the technology. One example of an improvement needed is better ability to control the surface finish.

4.2.5 Cold Gas Dynamic Spraying

Cold gas dynamic spraying, commonly referred to as "cold spray," is a solid-state material deposition process that uses powder particles sprayed at high velocity onto a substrate. The powder particles plastically deform upon impact, creating a metallurgical bond between the powder and the substrate. The process utilizes an accelerated gas stream (N_2, He, or air) to propel particles at speeds ranging from 300-1200 m/s toward a substrate, resulting in solid-state particle consolidation and rapid buildup of material. While cold spray is a fundamentally solid-state process, it is performed over a range of temperatures that can reach more than 50 percent of the melting point of the material. The advantages of cold spray are low thermal impact to the substrate, no combustion fuels/gases, no melting of the coating material, and a resultant coating with high density and moderate compressive residual stresses. More importantly, cold spray can be applied for additive repair in a field environment.

[27] See https://www.marketsandmarkets.com/Market-Reports/3d-printing-market-1276.html, accessed May 12, 2018.

As cold spray deposition technology rapidly advances, many critical and intriguing scientific questions are uncovered and remain to be answered. The actual physics present at a single-particle impact is still a very open question. New, fascinating, fundamental experiments using laser-shock acceleration combined with ultra-high-speed cameras are allowing for the imaging and measurements of single-particle impact dynamics. These new measurements are providing crucial experimental data to support, inform, and validate the many theoretical models that have been and are being developed to describe the cold spray deposition process. The sudden impact of metallic particles also causes the grain/crystallite structure to be reduced by an order of magnitude in size, but the mechanism by which this transformation takes place in less than 100 nanoseconds is still unknown. To this point, the community really needs more *quantitative* information about the micro- and nanostructures generated by the cold spray process.

4.2.6 Nonequilibrium Processing

Materials made either by nature or by manufacturing are seldom the result of equilibrium processes. Among the exceptions are crystals and alloys that are thermodynamically stable and formed by slow cooling. Living systems make their wide variety of functional materials from proteins. They continuously produce these proteins through an active process using ribosomes and genetic information to assemble specified amino acids. More than half of their metabolic energy is consumed in protein production. Manufacturing processes use energy to heat, cool, mix, stress, chemically change, and otherwise manipulate constituents into materials with desired properties that are not found in thermodynamically stable form. Material quenches and production techniques such as MBE produce metastable materials.

Although researchers are growing progressively more sophisticated in using far-from-equilibrium processing, from semiconductors to additive manufacturing (AM), the underlying science is missing. Thermodynamics and statistical mechanics provide rules for averaging the well-known dynamics of classical or quantum states to obtain the macroscopic properties of materials and many-particle systems in equilibrium. There is a solid foundation in laws that are universal, easily applied, and well tested over the past two centuries. The answers result from extremizing free energies and related state functions. There are no such universal governing principles or a set of free-energy-like functions to be extremized for nonequilibrium processes—for example, in some instances, dissipation is maximized; in others, it is minimized. The need for a deeper understanding of nonequilibrium phenomena is nowhere greater than in materials science.

Recent advances, such as additive manufacturing, present new challenges and opportunities for using and understanding nonequilibrium processes. “Laser-based AM processes generally have a complex nonequilibrium physical and chemical metallurgical nature, which is material and process dependent. The influence of material characteristics and processing conditions on metallurgical mechanisms and resultant microstructural and mechanical properties of AM processed components needs to be clarified.”[28] The extreme temperature, solvent, or stress gradients imposed by such processing will provide insight into far-from-equilibrium reactions and the properties of the metastable materials they produce.

Levitation is both a synthesis method and a characterization method because the influence of the container on the measurement is removed. Initial work in levitation was on metallic glasses, low-temperature melting materials to create high entropy, and nonequilibrium structures. Levitation methods have been expanded to include acoustic, aerodynamic, electromagnetic, and electrostatic, depending on the heating source and the sample size resulting. Both X-ray and neutron characterization can be applied to levitating materials. Samples fabricated from levitation are highly nonstable, and one must consider whether evaporation plays a role during characterization of said sample. These sets of techniques are helping to elucidate structure pathways of materials from high-temperature through a variety of cooling

[28] Gu, D.D., W. Meiners, K. Wissenbach, and R. Poprawe. "Laser additive manufacturing of metallic components: materials, processes and mechanisms." International materials reviews 57, no. 3 (2012): 133-164.

routes. Characterization of containerless synthesized materials is extremely helpful for understanding and design of novel materials.

4.2.7 Single Crystal Growth

Advances in fundamental and applied materials research have been driven by the development of numerous different families of crystalline materials with widely varied functionalities.[29] The two main paths involve synthesis of (1) high purity but chemically simple and abundant materials and (2) systems with complex stoichiometries/structures that feature multiple tunable characteristic energy scales. Examples in the first category include germanium, silicon, and gallium arsenide, while examples in the second category include strong rare-earth permanent magnets, high-temperature superconductors, and many other quantum materials. Despite the fundamental importance of crystal growth for many different scientific and commercial purposes, it remains the case that it is very often more of an art or technique than a science. Furthermore, many synthesis methods that are routinely used have made only marginal evolution during the past several decades. General categories include (1) solid-to-solid reactions, (2) liquid-to-solid reactions, and (3) vapor-to-solid reactions. Here, the focus is on methods to produce bulk crystals, but the arguments below lend themselves to thin films as well. For example, (1) includes solid-state reaction and spark plasma sintering; (2) includes molten flux growth, arc- and induction-furnace melting, Czochralski crystal pulling, and Bridgman crystal pulling; and (3) includes vapor transport (e.g., using iodine) and thin film techniques. For a detailed review of most such methods, see B. R. Pamplin's book first published in 1975.[30] Note that this and other detailed accounts of these synthesis methods were already presented at least four decades ago, and in many ways the same methods remain the state of the art. This emphasizes the difficulty in developing new strategies but also highlights that this is an area where there is significant opportunity for transformative advances.

Despite their usefulness, most crystal growth methods are limited by several practical problems that can now be addressed. First among them is that the progression of events during crystal formation is not often quantitatively understood. Instead, most processes are developed by trial and error, and even the philosophy of synthesis is guided by qualitative experience of individuals or isolated groups—that is, through colloquial methodology. In order to advance beyond these limitations, it is necessary to develop routine methods that provide detailed knowledge about processes that occur during a reaction as well as active modeling that allows modification of a growth in real time. There have been limited recent attempts to do this—for example, where a crystal growth process is observed through neutron scattering, but this field is wide open for advances. Also important is that most real materials harbor defects on all length scales that are difficult to characterize and even harder to correct. A simple example is seen for single crystals that are pulled from a melt (e.g., using the Czochralski technique), where chemical gradients along the growth axis are commonplace. For quantum materials, such variations often have a large impact on electronic and magnetic properties and a mastery of them is needed but undeveloped. An in-depth knowledge and control of the growth process would mitigate these problems and furthermore would open yet another tuning parameter to control a material's properties.

In order to accomplish these goals, a multifaceted and well-funded push to develop new intersections for crystal growth within the materials research community is needed. In this scenario, crystal growth would be treated as a research area of its own that is not strictly associated with specific classes of materials or topics. Two promising directions of research are (1) methods for rapid-throughput/rapid-characterization and (2) synthesis methods under extreme conditions (e.g., applied pressure, magnetic fields, electric field, etc.). This research requires suites of materials analysis (e.g., neutron, X-ray scattering, and microanalysis) and computation collaborations to facilitate progress, plus ways to broadly distribute information.

[29] See https://www.nap.edu/catalog/12640/frontiers-in-crystalline-matter-from-discovery-to-technology.
[30] See https://www.elsevier.com/books/crystal-growth/pamplin/978-0-08-025043-4.

4.3 SIMULATION AND COMPUTATION TOOLS

The nature and benefits of computation capabilities in materials research are extensive, but vary dramatically, depending on the material class or application. For example, the useful computational tools for the well-developed semiconductor and aerospace industries are very different from those needed for new materials, where there are still basic questions and no elaborate databases for mining or application of artificial intelligence. However, it is clear that computational capabilities, on both the large as well as the small scale, will continue to advance large expanses of the materials research landscape.

4.3.1 Integrated Computational Materials Engineering and Materials Genome Initiatives

Two initiatives began during the past decade that aimed to accelerate the timeline from development to deployment of a material, by highlighting the benefits of experiment and computation working together, and the need for materials computational design at all stages of the manufacturing process.

One initiative, the Integrated Computational Materials Engineering (ICME) approach, was detailed in a National Academies study of 2008.[31] The ICME approach seeks to integrate materials models across different length scales (multiscale) and computational methodologies to capture the relationships between synthesis and processing, structure, properties, and performance. The initial successes of ICME were enabled by the existence of a wealth of data on specific materials systems that had been generated over prior decades of research.[32]

The second initiative began in 2011, when President Barack Obama launched the Materials Genome Initiative (MGI) with the intent "to discover, manufacture, and deploy advanced materials twice as fast, at a fraction of the cost."[33] Central to this vision was the equal weighting of, and integrated nature of, computational tools, digital data, and experimental tools. The latter included synthesis and processing as well as material characterization and property assessment. It was recognized that in each area there was a need to develop new tools and capabilities to advance the field and to explore the intersection between each of the three. The initiative recognized the importance of data and the need to develop databases and the tools to interrogate and visualize it. This need is particularly important to the success of the initiative as extensive and accessible databases exist for only a few material systems. It was important that the integrated tools were to be one framework over the seven stages of the materials development continuum (the seven stages are discovery; development; property optimization; systems design and integration; certification; manufacturing; and deployment).[34]

Following the direction indicated by these two initiatives has led to some notable successes.[35] For example, Ford Motor Company used the ICME framework to obtain a 15-25 percent decrease in the product development time of cast aluminum power train products. For cast aluminum components, subtle changes in the manufacturing process or component design can lead to engine durability issues and program delays, but simulating the effect of manufacturing history on the engine durability allowed Ford to avoid these costly delays.

Computational methods integrated with material property databases have successfully been used to recently develop two forms of steel that were licensed to a U.S. steel producer (by QuesTek Innovation, LLC), and then deployed into demanding applications. The first alloy was for the U.S. Air Force: Ferrium

[31] National Research Council, 2008, *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security*The National Academies Press, Washington, D.C., https://doi.org/10.17226/12199.

[32] G.B. Olson / Acta Materialia 61 (2013) 771-781, http://dx.doi.org/10.1016/j.actamat.2012.10.045.

[33] See https://www.mgi.gov/sites/default/files/documents/materials_genome_initiative-final.pdf.

[34] Includes sustainability and recovery.

[35] See https://www.mgi.gov/sites/default/files/documents/mgi-accomplishments-at-5-years-august-2016.pdf.

S53, an ultra-high-strength and corrosion-resistant steel that eliminates toxic cadmium plating, and is now flying as safety-critical landing gear on USAF A-10, T038, C-5, KC-135, and on numerous SpaceX rocket flight critical components. The second alloy was for the U.S. Navy: Ferrium M54, an upgrade from legacy alloys, which offers more than twice the lifetime of the incumbent steel while saving $3 million in overall program costs and is now deployed on their T-45 safety-critical hook shank component. As seen in Box 2.2 in Chapter 2, the time from development to deployment was reduced from 8.5 years for Ferrium S53 (deployment in 2008) to 4 years for Ferrium M54 using only one design iteration (qualification in 2014). QuesTek has designed, also using integrated methods, a third steel: Ferrium C64, which is a best-in-class gear steel that allows for increased power density, fuel efficiency, and lift of military helicopters. This steel has been patented and is now available for purchase.

Other successful areas of integrated computation-experiment-data have been in new materials for batteries,[36] and many other companies, such as Boeing, use integrated approaches for advanced metals and other material discovery and deployment. An example of the acceleration of the discovery of materials through a combination of quantum mechanical calculations, synthesis, and experiments is the design and optimization of liquid crystal sensors.[37] These sensors work on the principle of the selective displacement of liquid crystal molecules by analytes that results in an optically detected transition of the liquid crystal. Liquid crystals are in general sensitive to UV light, poisons/pollutants, and strain. There are now many liquid crystal sensors. They hold promise as inexpensive, portable, and wearable sensors for key applications (e.g., poisonous gas detection).

One challenge regarding the MGI is that it has tended over time to become an interaction between materials modeling, computing, and data communications, leaving experiment behind. Vast databases have been created of purely computational results, without experimental validation of stability or accuracy. In addition, without experimental results, the materials cannot be easily tested or deployed for manufacture. Some of these issues are addressed further in Section 4.3.5 on databases. Another challenge is that it is difficult to maintain modeling continuity across the full range of seven stages from discovery to deployment unless the research group is immersed in a development environment. The MGI goal would be furthered by increased university-industry interactions, which have widespread benefits, as explained elsewhere in this report.

4.3.2 Computational Materials Science and Engineering

Over the past decade, there have significant improvements in modeling materials on multiple length scales, including quantum mechanical, atomic, mesoscale (course-grained or phase field), and continuum scales, in addition to statistical methods. This would also include, for example, the Landau-Lifshitz-Gilbert equation[38] for magnetic materials, and progress on understanding Gilbert damping.[39] These advances have been spurred on by the advances of physical science, such as the example just given, together with the vast increase in computing power over the last decade as well as the integration with experiment and data described in the last section. The area of quantum-level modeling has had perhaps the greatest advancement and opportunity for future improvements, and will be summarized first.

In a significant shift, electronic structure (i.e., density functional theory, DFT) computational software has become readily available in packages both commercial (CASTEP, VASP, WIEN2K) and

[36] For example, http://ceder.berkeley.edu/ and the many successes on that website.

[37] H. Hu, Z. Lu, and W. Yang, Fitting molecular electrostatic potentials from quantum mechanical calculations, J. Chem. Theory Comput., 2007, 3 (3), pp 1004-1013.

[38] For a recent review, see, e.g., M. Lakshmanan, The fascinating world of the Landau-Lifshitz-Gilbert equation: an overview, Phil. Trans. R. Soc. A 369, 1280 (2011).

[39] L. Chen et al., Emergence of anisotropic Gilbert damping in ultrathin Fe layers on GaAs(001) *Nature Physics* 14, 490 (2018).

open source (Quantum Espresso, Abinit).[40] These packages are well-documented online, and some (e.g., VASP) have well-developed user interfaces. The calculations of material properties enabled by these packages have high fidelity. They are used to predict structure-property relationships for many material types, discover new structures, enhance the interpretation of experimental data, and populate databases.

When magnetic material properties are calculated with DFT, the addition of a "Hubbard U" term can give very accurate properties of d-electron materials, and in the past decade there have been many developments in this area.[41] Modern DFT packages can handle full 3D spin dependence (not just spin up or down), and including relativistic effects and spin-orbit coupling is now a matter of setting parameters in the input file. DFT is challenged when there are multiple sources of magnetism, such as the f-electron materials, which often have unfilled d-electron orbitals as well (for which an additional parameter J is often added, and even then comparison with experiment is often needed), and whenever there are many-body interactions (superconductivity, metal-insulator transitions, Kondo effects, complex oxides, etc.) not describable by single-particle states, as DFT is, based on functions of the local density.

Many useful improvements of DFT have been developed in the past decade, including extensions of DFT to finite temperature, excited states, and time dependence. These often combine perturbation theory with standard methods (such as the GW method) or go beyond it.[42] These extensions add much calculation overhead. In addition, active work includes improvements to the exchange functional used in DFT codes, as well as to the pseudopotentials used to estimate the inner cores of atoms in programs such as quantum espresso and VASP.

Going beyond DFT to attempt to model many-body physics of complex materials such as the rare earths is dynamical mean field theory (DMFT), which maps the lattice problem to a local impurity model. This latter, even though it is a many-body problem, has a recognized set of solutions. The main approximation of this method is to assume that the lattice self-energy is independent of momentum, an approximation that becomes exact in the limit of infinite dimensions. This methodology, combined with DFT, has had some notable successes, including the phase diagram of plutonium,[43] and the metal-insulator phase transition in the Bose-Hubbard model.[44] By combining DMFT with time-dependent DFT (TDDFT), properties that depend on the time evolution of electronic states such as multielectron and hole bound states (excitons, trions, etc.) could be calculated. TDDFT has the advantage of being a theory of one time-argument function, the charge density.

Quantum Monte Carlo (QMC) is another technique for studying materials with many-body effects. In general, it is an accurate and reliable method that is trivially parallelizable and thus high-performance computing (HPC)-friendly. It is also computationally expensive, complex to apply, and thus challenging. Among the different flavors of QMC, Diffusion Monte Carlo (DMC) is the most popular. It is a stochastic method that allows direct access to system ground states and sometimes of the excited states of a many-body system as well. In principle, DMC is an exact method that maps the Schrödinger equation to a diffusion equation. However, approximations must be made for computational feasibility when modeling fermions (i.e., electrons). The most common approach is the fixed-node approximation—nodes of the wavefunctions are kept fixed to those of the original trial wavefunction during the search for ground-state wavefunctions.

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[40] For the five programs see https://www.castep.org; https://www.vasp.at; http://susi.theochem.tuwien.ac.at/; https://www.quantum-espresso.org; https://www.abinit.org, all accessed on 6/6/2018.

[41] Burak Himmetoglu et al., Hubbard-corrected DFT energy functionals: The LDA+U description of correlated systems, International Journal of Quantum Chemistry 114, 14 (2014).

[42] Shu Xia Tao, Accurate and efficient bandgap predictions of metal halide perovskites using the DFT-1/2 method: GW accuracy with DFT expense, Nature Scientific Reports, 7, 14386 (2017).

[43] N. Lanata et al., Phase Diagram and Electronic Structure of Praseodymium and Plutonium, Phys. Rev. X 5, 011008 (2015).

[44] Peter Anders et al., Dynamical Mean Field Solution of the Bose-Hubbard Model, Phys. Rev. Lett. **105**, 096402 (2010).

For molecular solids, quantum chemistry methods tend to be more accurate. These include configuration interaction (CI), coupled cluster (CC), and multireference methods. The trade-off for accuracy is that they are computationally formidable and not convenient for high-performance computing.

Moving from the subatomic scale of the quantum methods to those on the atomic scale, a technique widely used in chemistry for molecules but also useful for especially surfaces of materials is molecular dynamics (MD). This method uses force fields generated by DFT or other more approximate methods based on tables of vibrational analysis of bonds. MD can generate time dependence of atomic movements (for very short periods of time) at finite temperatures. A development to note of the past decade is the availability of highly modular, massively parallel shareware software to carry out large-scale atomic-scale simulations with high efficiency of dynamical properties of materials, including thermal conductivity, mechanical deformation, and irradiation, and many other properties. An example of an MD software package is LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator),[45] developed by Sandia National Laboratory. Such atomic-scale simulations have been further enabled by the availability of multiphysics (multiple interacting physical effects) reactive force fields or potentials that provide frameworks for the study of heterogeneous material systems. The cataloging of reactive potentials, through efforts at the National Institute of Standards and Technology (NIST) and the OpenKIM project,[46] are providing important ways to track performance and suitability of these empirical methods. Development of simple atomistic potentials with accuracies at the level of DFT and computational efficiency sufficient to undertake simulation of realistic (laboratory-level) large length- and time-scale simulations or for high-throughput calculations is necessary. Machine learning has helped develop such potentials, as described in Section 4.3.3.

Mesoscale modeling has also had significant advancements over the past decade. One example is the software CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry),[47] which enables the prediction of phase diagrams and thermodynamic behavior. Phase field modeling[48] simulates materials growth and mesoscale structure-property relationships, and as a third example on the mesoscale, coarse-grained simulation methods have much improved their usability for modeling molecular materials such as polymers.

Over the last decade, there has been an increasing translation of computational tools to industrial application: the boxes in Chapter 2 provide examples in alloy development and industrial processing. Continuum-state variable process models are used in manufacturing for casting, forging, rolling, vapor deposition, machining, and so on. Further, CALPHAD and the DICTRA diffusion code and method are ubiquitous and heavily supported by industry. The transition of other tools—for example, phase field, kinetic Monte Carlo, and so on—are in progress. Progress has been made in physics-based multiscale models for mechanical behavior prediction, but these have yet to be adopted by industry.

Intense effort has gone into developing and improving single- and multiscale methods that may be concurrent, hierarchical, or hybrid and that may be solved in parallel, sequentially, or in a coupled manner. These methods have enhanced both fundamental science studies of, for example, the mechanics of materials and the physics and chemistry associated with materials growth, and applied engineering efforts associated with, for example, the manufacture of material parts in industry. The ability of these methods to make full use of improvements in computer architecture varies with method type, length scales, and time scales. Time-dependent materials have made great strides over the last decade (e.g., modeling creep), but as is the case for classical molecular dynamics simulation, as system size increases,

[45] See Lammps.sandia.gov, accessed January 5, 2018.

[46] See https://www.ctcms.nist.gov/potentials/ and https://openkim.org, both accessed January 5, 2018.

[47] CALPHAD is a computational methodology. See, for example, www.thermocalc.com/products-services/databases/the-calphad-methodology/ or a free development at http://www.opencalphad.com/, both accessed January 5, 2018.

[48] L.Q. Chen, 2002, Phase-field models for microstructure evolution, *Annual Reviews of Materials Research* 32:113-140.

there are rapid increases of computational demands of time and memory. Consequently, redesigning software or using combinations of methods (e.g., molecular dynamics and Monte Carlo) are important.

Other advances have been achieved through co-design of experiment and computational infrastructure, which has come to the fore in the past decade. Examples include progress in image recognition for microstructure identification and the use of the parallel advances in brightness and power from scattering methods, such as X-ray and neutron scattering, and computational materials science that promise to advance the field of scattering science by elevating the interrogation of data from scattering experiments.

A grand challenge in computational materials science is to design the electronic structure of materials directly from first principles, to go from physical/mechanical properties to structure and atomic constituents, rather than the usual other way around. Technical roadblocks in the capabilities of computational methods are being addressed in federally supported research centers, as well as in selected academic centers and private companies, and much progress in the coming decade is expected toward this goal.

4.3.3 Machine Learning for Materials Discovery

Over the last decade, both supervised and unsupervised machine learning algorithms have been used to calculate materials properties, explore materials compositional space, identify new structures, discover quantum phases, and identify phases and phase transitions. Although training is usually necessary, once set up, these models are able to calculate a wide range of properties, with high accuracy, at large scale, and at speeds orders of magnitude faster than conventional computational methods. Supervised machine learning algorithms that have been applied to materials include random forests, kernel ridge regression, and multilayer perceptron artificial neural networks. These methods allow the mapping of a section of features—for example, atomic positions—to output values such as material properties and performance; their goal is to map output to input.

Machine learning methods have been used to efficiently and effectively explore materials space, considering all possible structures and combinations to identify new structures as well as ones with specific properties. For example, a machine learning model based on kernel ridge regression was used to calculate, with DFT accuracy, the formation energies of the 2 million possible elpasolites—an isometric-hexoctahedral quaternary (Al, F, K and Na) mineral. This method identified the most strongly bound elpasolites, proposed a new elpasolite order based on the energy, and identified 128 structures with 90 unique stoichiometries. This is one example from many in which machine learning was used to efficiently computationally screen many polomorphs to identify unique crystal properties (see Figure 4.8).

Normally, DFT is used to calculate the potential energy surfaces that are the necessary inputs to molecular dynamics or Monte Carlo simulations, and the time and memory demands of these programs significantly limit the length of time a large system can be simulated. By introducing the concept of a symmetry-function-value for each atom that reflects the local environment of that atom, a generalized neural net representation of DFT potential energy surfaces can be developed. This method provides the energy and forces as a function of all atomic positions for large system sizes and was several orders of magnitude faster than DFT.[49] The method can be used with nonperiodic systems and can be used to describe all types of bonding. There are now for MD, for example, artificial neural networks potentials and Gaussian approximation potentials. Support vector machines (SVMs) and the Spectral Neighbor Analysis Potential (SNAP) are extensively used. The most commonly used approach utilizes traditional fully connected, feed-forward, neural networks by mapping the arrangement of atoms as their input. The total potential energy of the system is broken into atomic energy contributions, whose local environment can be described using radical and angular Gaussian symmetry functions. These potentials, which are

[49] Jörg Behler and Michele Parrinello, 2007, Generalized neural-network representation of high-dimensional potential-energy surfaces, *Physical Review Letters* 98:146401.

analytical and easily integrated in broadly used molecular dynamics simulation codes such as LAMMPS, facilitate large-scale and long-time-scale simulations with affordable computational cost.

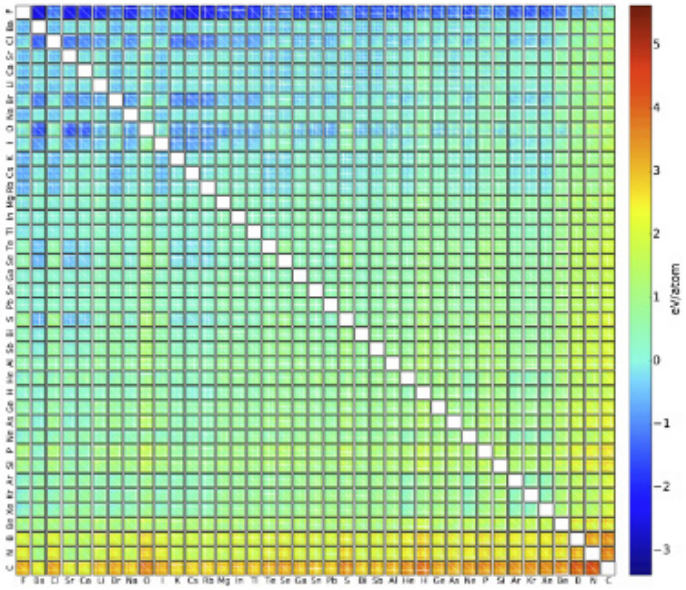

FIGURE 4.8 Elpasolite is $AlNaK_2F_6$ and its crystal structure is common among inorganic materials. Substituting other elements in the form ABC_2D_6 gives the large family of elpasolites. The authors have used their machine learning model to predict the formation energies for all 2×10^6 elpasolites made up of all main-group elements up to Bi. The figure shows a heat map of the energies, with the scale in eV/atom shown on the right. In the lower left half of the figure separated by the diagonal white line, the vertical and horizontal axes represent elements for D and C, respectively, and in the upper right half of the figure, the vertical and horizontal axes represent elements for B and A, respectively, with the other two constituents in each case running over all values, giving the two million materials. SOURCE: F.A. Faber, A. Lindmaa, O.A. von Lilienfeld, and R. Armiento, 2016, Machine learning energies of 2 million elpasolite (*ABC_2D_6*) crystals, *Physical Review Letters* 117:135502, https://doi.org/10.1103/PhysRevLett.117.135502, https://creativecommons.org/licenses/by/3.0/.

Unsupervised algorithms (such as principal-component analysis and deep-convolutional autoencoders) can be trained to categorize unlabeled data and can reveal patterns in high-dimensional material and chemical spaces that would otherwise be difficult to perceive.

Principal component analysis (PCA) is a statistical technique for data reduction in high-dimensional spaces. A linear rotation has been found that results in data with a smaller spread in the new space. A nonlinear form of PCA (via a deep convolutional autoencoder) has been used to explore phase transitions, such as a ferromagnetic Ising model of several thousand atoms.[50] Remarkably, it showed that fully connected and convolutional neural networks can identify phases and phase transitions, as well as unconventional low-order states, in a range of condensed-matter models.

Deep convolutional autoencoders belong to a relatively new class of "deep learning" algorithms based on multilayered artificial neural networks. Deep learning methods let the algorithm itself decide on the relevant features, operating directly on "raw" data. These techniques evolved from the field of computer vision. In traditional machine learning, manual feature selection is required prior to training. Deep learning techniques do not require this step (although they require a much larger training set). As an example, a deep convolutional neural network was used on the Ising model and obtained accurate

[50] J. Carrasquilla and R.G. Melko, 2017, Machine learning phases of matter, *Nature Physics* 13:431.

energies and magnetization for both a nearest-neighbor Hamiltonian and a long-range screened Hamiltonian. Training allowed the neural network to generalize to "never before seen examples," using observations from a limited number of configurations. Deep convolutional neural networks have been used for modeling large systems, with a method of domain decomposition into overlapping tiles for training and inference, and good results have been obtained for spin models and many-body quantum mechanical operators with DFT accuracy. Recently,[51] a deep convolutional neural network model, trained so that no manual feature selection was necessary, predicted ground-state energies of an electron in a random 2D potential to within chemical accuracies with no analytic form for either the potential or ground-state energy.

4.3.4 Quantum Computing as a Computational Materials Tool

Chapter 2 describes the materials research that has been under way for improved qubits. This section summarizes some of the research needed for quantum computing to become a functional, computational tool. Quantum computers use superposition and entanglement of quantum states to perform operations on many bits simultaneously. With the appropriate initial state preparation (in itself a research challenge to do optimally), N quantum bits could hold the information of 2^N classical bits. With enough error-corrected quantum bits (thought to be around 75-100), quantum computers could calculate properties of complex molecules well beyond the capabilities, both computational and memory, of foreseeable classical computers. This will impact many fields, including medicine and agriculture. Likewise, there is promise for being able to simulate excited states, and the time and temperature dependence of quantum materials, areas also beyond classical computational capabilities. Additional opportunities for quantum computing exist in the areas of optimization, cryptography, finance, and other fields.

In the present day, qubits still have a considerable rate of decoherence, which affects the accuracy and gate depth, limiting the number of consecutive operations. Error correction, routine in classical computation, is a significant challenge for quantum computation. With current qubit quality, estimates are that millions of qubits would be needed to do complete error correction for a single logical qubit. Even partial error correction could take dozens of qubits.

Nonetheless, significant progress is being made without fault-tolerant computing. There are operating quantum computers of up to around 30 qubits in superconducting (e.g., IBM, Google, Rigetti) systems, and of upward of 50 qubits in trapped ion systems (e.g., Professor C. Monroe, University of Maryland). IBM is notable for having put their quantum computer online,[52] the first quantum computer ever available in this way. There are also simulators of quantum computing online that run in the cloud on classical hardware, and these are limited by memory requirements to around 50 qubits. IBM was among the first to adopt this methodology; notable efforts, with large simulators, are also conducted by Microsoft. In addition, several quantum computing centers provide software kits and algorithms for using Python to submit jobs to the quantum computer.

With this infrastructure, researchers are performing calculations, and papers are appearing in top journals. Some landmark examples are as follows. Programming for a tour de force calculation[53] of three small molecules, the authors worked around the error, an indication of how computation on real quantum computers will need to be done in the foreseeable future. Using a one-dimensional (1D) chain of trapped alkali-metal atoms[54] as a 51-qubit quantum simulator, researchers observed a quantum phase transition. In

[51] K. Mills, M. Spanner, and I. Tamblyn, 2017, Deep learning and the Schrödinger equation, *Physics Review A* 96:042113.

[52] See https://www.research.ibm.com/ibm-q/, accessed December 3, 2018.

[53] A. Kandala et al., 2017, Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets, *Nature* 549:242.

[54] H. Berneien et al., 2017, Probing many-body dynamics on a 51-atom quantum simulator, *Nature* 551:579.

a system of 53 trapped ions,[55] researchers studied the nonequilibrium dynamics of the transverse-field Ising model with long-range interactions.

As quantum computing technologies mature, they hold the potential to impact many materials areas. There are extensive research opportunities in modeling and algorithm development, as well as in experimental implementation, for these and other related applications.

4.3.5 Materials Databases: Achievements, Promise, and Challenges

Materials databases have been available for decades, and they have been widely accessible on the Internet. Legacy efforts from the 1990s are largely characterized by the delivery of very high quality reference materials data that was hand-curated from the peer-reviewed literature, which gives some guarantee of quality. By contrast, more modern repositories are able to meet a number of additional demands, including ease of use for nonexperts, assignment of a persistent identifier, broad accessibility, and sophisticated searchability. Application programming interfaces allow machine-to-machine interactions with minimal human involvement, and the capacity to be federated across multiple instances in geographically disparate locations. Examples of general-purpose repositories include the NIST Materials Data Repository (https://materialsdata.nist.gov); the Materials Data Facility (https://materialsdatafacility.org) sponsored by the NIST center of excellence—the Center for Hierarchical Materials Design; the DOE-funded PRISMS Materials Commons (https://materialscommons.org); and numerous resources associated with the DOE Energy Materials Network (https://energy.gov/eere/energy-materials-network/energy-materials-network). There are also databases for specific materials types, such as catalysts, polymers, phase data, electronic properties, and more. NIST has a database of kinetic properties that are important for processing and material evolution. Additional databases that contain a digital representation of microstructure are being developed.

Some of the achievements of the past decade in using machine learning, a heavily data-driven technique, to advance materials understanding, were summarized in Section 4.3.3. Other uses of materials data, combined with data mining tools, are to search for new materials compositions. Such searches could include new thermoelectric compounds, and for additive manufacturing, new aluminum alloy compositions. Materials data combined with data mining can also be applied for microstructure development based on processing conditions. More recently, researchers have been combining these tools with robotics and in situ process monitoring and characterization to build autonomous research apparatuses like the Autonomous Research System (ARES) developed by Air Force Research Laboratory (AFRL) researchers to determine optimum growth conditions for carbon nanotubes.

A most telling example of the rising value of materials data is the emergence of for-profit institutions that provide data services. For example, Citrine Informatics provides free data repository services for those researchers willing to share their data with others as well as data analysis tools and services to commercial customers based on the vast wealth of materials data they are accumulating.

Another source of vast databases is databases created with density functional techniques of various materials and their properties. This leads to the question of the validity and verifiability of the data in databases.

As more calculations of known materials are performed and stored in databases, it is becoming possible to calculate the distribution of errors as well as the average error in calculations of certain physical properties. These known errors, together with enthalpy calculations of various competing phases, allow an estimation of how likely it is that a new material calculation will give a stable material at various temperatures. Databases include the Materials Project[56] of thermodynamic structure-property

[55] J. Zhang et al., 2017, Observation of a many-body dynamical phase transition with a 53-qubit quantum simulator, *Nature* 551:601.

[56] See https://materialsproject.org/.

relationships, which is being actively used for materials selection. An example of using such enthalpy calculations and data from the Materials Project is shown in Figure 4.9.

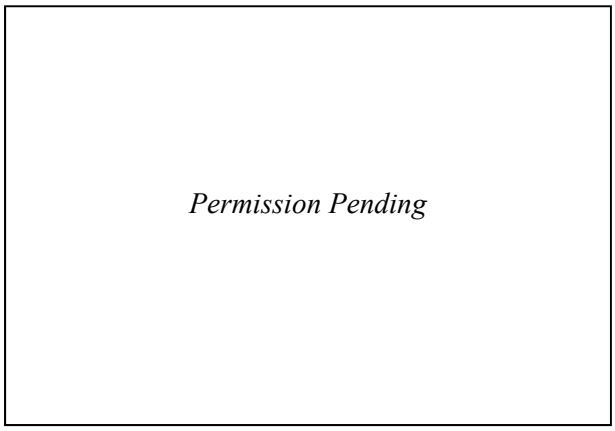

FIGURE 4.9 Over 2,000 compositions of perovskite materials, plotted as a function of their predicted catalytic ability and stability. Different symbol colors represent different perovskite structures. Red = ABO_3, blue = $AA*BO_3$ or $ABB*O_3$, and purple = $AA*BB*O_3$. An "x" symbol denotes an insulator and "o" a conductor. The catalytic ability estimates how well the material enhances surface exchange of oxygen in solid oxide fuel cell cathodes and is represented by the surface exchange coefficient k*, plotted on the *y*-axis, calculated using first-principles DFT techniques. For stability, solid fuel cell operating conditions (temperature, water vapor, etc.) were applied in a multicomponent phase stability analysis via the open source Pymatgen toolkit and Materials Project data, and an energy was calculated for each material, plotted on the *x*-axis, with lower energy indicating greater stability. Fifty-two promising candidates were found, ready for experimental testing for activity and stability, which in turn will improve the modeling tools. SOURCE: R. Jacobs, T. Mayeshiba, J. Booske, and D. Morgan, 2018, Material discovery and design principles for stable, high activity perovskite cathodes for solid oxide fuel cells, *Advanced Energy Material*s 8(11):1702708.

An active area of research, which has seen considerable growth over the last decade, is in the development of unambiguous, well-defined methods of verification, validation, and uncertainty quantification of computational results. In addition to collaborating with others who are disciplinary experts, materials scientists and engineers are ensuring that new methodology development takes place hand in hand with experimental work. The need for verification, validation, and uncertainty quantification increases in complexity when methods that span multiple length and time scales are combined, even as the need for robust assessment of these quantities increases as these scales approach those associated with processing and manufacturing. In other words, the closer researchers get to "materials by design," the more important it is not only to have predictions but also to have engineering-level understanding of their associated errors.

Data-driven approaches are poised to dramatically increase the productivity of materials research, but realizing the true potential is predicated on the development of a seamless Materials Data Infrastructure (MDI) that allows for the storing, sharing, searching, analysis, and learning from data spread over multiple sites. An underpinning goal of the MDI is to create a digital thread through the material life cycle, from discovery through recycling, where critical information is seamlessly passed digitally along the life cycle in order to reduce barriers of information transfer, thus reducing the relearning currently needed at each stage. One idea that has been suggested is to apply blockchain to data storage for security, timestamping, data version control, attribution, and so on, leading to more secure, reliable data bases.

FAIR data principles are important in making data findable, accessible, interoperable, and reproducible. To address issues around findability and accessibility, NIST has worked with the international community to create the Materials Resource Registry, allowing organizations to advertise metadata about organizations, data collections, application programming interfaces, informational sites and materials software, using set schema to describe their resources, similar to that used in the astronomy community to enable the Virtual Observatory.

In addition, several organizations have developed integrative or e-collaborative platforms that use web-based technologies to manage the materials data life cycle, implementing the FAIR principles. The goal of these platforms is to ease ingestion of data and metadata from experiments or simulation, and enable manual or automated data analysis, data search, and data publication.

NIST's lead in developing schemas will be very helpful in providing standards and criteria for describing and exchanging data. However, challenges remain. The prevalence of proprietary data formats used in scientific instrumentation works against this data being used by others, and in general the difficulty in extracting scientific data, and even more so the supporting metadata, from instrumentation makes data sharing a monumental and laborious challenge for individual investigators. The same lack of metadata holds for data produced by many computational programs as well.

Solutions at implementing the FAIR principles will vary by discipline and will evolve toward relatively stable metadata schemas only after a considerable shake-out period. For relatively simple systems, schemas already exist—for example, the Crystallographic Information File (CIF) format used by crystallography. For a general approach, NIST has developed a Materials Data Curation System, which requires each subdiscipline to define a schema that describes the type of data to be curated. Much effort still remains.

4.4 INTEGRATION OF SYNTHESIS, CHARACTERIZATION, AND MODELING

While alluded to in discussions throughout the report, the integration of the different types of tools used by materials researchers presents its own set of opportunities and challenges, some of which are discussed in this section.

4.4.1 High-Throughput Screening

High-throughput screening, in which thousands of experimental samples are subjected to simultaneous testing under given conditions, was first recognized as a tool in the 1980s at GEC Hirst Research Center. Over the next 30 years, high throughput was not highlighted as a tool for materials researchers. In the last decade, more and more materials researchers are using foundational high-throughput tools to further their own work.[57,58] High-throughput efforts can be separated into discovery and optimization, each with its own risks and rewards. Discovery (primary screening) is intended to sample broad and diverse areas. Optimization (secondary screening) accelerates development of new materials. The risk in the discovery arena is a higher number of false positives and false negatives than individual screening. In optimization, accuracy is usually sacrificed for speed, in that traditional characterization techniques do not always maintain pace with high-throughput synthesis.[59]

Over the past few years, screening has evolved from relatively simple materials and 1D and 2D synthesis (e.g., nanoparticles and thin films) to more and more complex materials and 3D synthesis (e.g.,

[57] E.B. Svedberg, chapter in, *Combinatorial and High-Throughput Discovery and Optimization of Catalysts and Materials* (R.A. Potyrailo and W. Maier, eds.), Critical Reviews in Combinatorial Chemistry, Vol. 1, CRC Press.

[58] E. Chunsheng, et al., 2006, Combinatorial synthesis of Co/Pd magnetic multilayers, *Journal of Applied Physics* 99:113901.

[59] Maier, Stowe, Sieg, 2007, *Angew Chem Int Ed*.

thick film, solution-based methods, additive manufacturing, etc.). Improvements in spectroscopic techniques and image analysis are the first characterization methods to maintain pace with materials synthesis. Characterization and data analytics can still be rate limiting.

A 2014 publication on high-throughput synthesis and characterization of bulk metallic glasses highlights the progress made in that area.[60] Over 3,000 alloy compositions were analyzed for both glass-forming ability and thermoplastic formability, an indication of their ability to respond to strain, through a creative methodology. Wells were made in a silicon wafer substrate, and then three confocal sputtering targets were used to deposit compositions in the Cu-Y-Mg family. Freestanding membranes were created by removing the silicon from the backside. These are low glass-transition temperature (T_g) glasses, and gases can generate enough pressure at 100ºC to elastically deflect the membrane in a short period of time. The height of the final membrane yields an indication of the thermoplastic formability and can be quantified (see Figure 4.10).

It is clear that high-throughput screening will be of increasing importance and that it will change how much of the materials research of the future is conducted.[61]

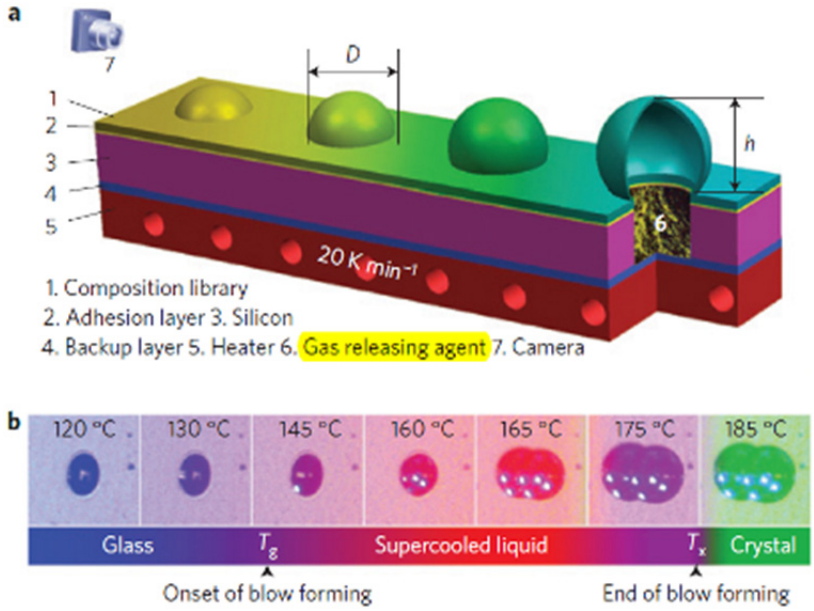

FIGURE 4.10 Image shows parallel blow-forming setup of compositional membranes and its realization. (a) Schematics of the parallel blow-forming setup. The relative thermoplastic formability is given by the final height of the membrane after deformation. SOURCE: Reprinted by permission from Springer Nature: S. Ding, Y. Liu, Y. Li, Z. Liu, S. Sohn, F.J. Walker, and J. Schroers, 2014, Combinatorial development of bulk metallic glasses, *Nature Materials* 13(5):494-500, © 2014.

4.4.2 Predictive Experimental Materials Design and Combined Experimental/Computational Analysis

Accompanied by advances in first-principles calculations, molecular-dynamics simulations, machine learning, and other data analytics tools, predictive material design is fast becoming the norm,

[60] S. Ding, Liu, Y., Liu, Z., Sohn, S., Walker, F.J., Schroers, J. 2014. *Nature Materials* 13: 494.

[61] See, for example, H. Shibata, et al., 2014, Chapter 4, pp. 173-196, Heterogeneous catalysis high throughput workflow: a case study involving propane oxidative dehydrogenation, in *Modern Applications of High Throughput R&D in Heterogenous Catalysis*.

accelerating materials discovery. There is, of course, necessary caution to be applied and further advances to be made before predictive modeling attains the kind of robustness necessary for industrial applications. For example, for the new generation of accurate but still approximate calculations, what are their errors? Standard and well-understood protocols have been developed to some extent, particularly in quantum chemistry, but many new techniques have spotty testing. It would be useful to have a clear suite of experimental properties that would serve as a test-bed. These large amounts of experimental data need to be collected in a coherent way. Among the many as-yet unanswered questions are: How do researchers encode all the differences in processing material samples? How do researchers extract what's relevant from what's not? Can researchers predict whether a substance can be doped (solubility), and what the effects of the doping will be? So far, multiple length scales and the need for high accuracy have made this an extremely challenging problem.

This is a challenge both in terms of theoretical and computational techniques and in interfacing those efforts with experiment, since out-of-equilibrium behavior is highly dependent on the initial conditions. Many materials being used are actually metastable, which raises a separate set of questions: How can researchers predict whether a metastable material can be formed and use that to design not just new materials but also experimental processes? Often what is computed from first principles is not quite what is measured experimentally. For example, while some techniques can compute angle-resolved photoemission spectroscopy (ARPES) spectra, they typically do so for systems under ideal conditions of temperature and pressure and for controlled geometry. In operando measurements, for example, confirm that materials undergo restructuring under ambient conditions. Can researchers develop computational techniques that bridge the pressure, temperature, and material gap?

Despite ever-increasing fidelity of and access to experimental facilities, opportunities still exist to fine-tune experimental conditions, accelerate analysis of the data, and move toward high-throughput screening of materials (see the preceding section) by coupling the instruments to computational facilities. Advancements in this area will not only improve the ability to fully interrogate the terabytes of data that can be acquired from a single experiment in a short time period but also change experimental conditions so as to maximize the utility and descriptiveness of the data that is collected. The idea would be to carry out real-time computational analysis of experimental data. For example, while in operando measurements are being taken of a chemical reaction on a nanocatalyst surface, digitized images of the catalyst under reaction conditions, the vibrational frequencies of the reaction intermediates and X-ray photoelectron spectroscopy data of the system could all be made available to a computational "beam line," which would calculate the same quantities for the "real" geometry and state of the catalyst. Real-time comparison of the two sets of data (experimental and computed) would allow both sides to tweak conditions (parameters) until the desired result is obtained. Such a scenario is achievable, given the advances made in the past decade, discussed earlier in this chapter, in tools that can interrogate materials with atomic-scale precision and computational techniques that aim to predict material structure and dynamics under laboratory conditions.

An early vision of conjugated experimental and computational analysis was proposed by the European Theoretical Spectroscopy Facility (ETSF),[62] which promotes standardization of computational codes, libraries, and tools to facilitate broad usage particularly by experimentalists. These ideas could be taken further by integrating such analysis-ready computational facilities to experimental beam lines. Given adequate resources, the United States could set the stage for real data analysis for accelerated materials discovery.

[62] See https://www.etsf.eu/.

4.5 INFRASTRUCTURE AND FACILITIES

Infrastructure for modeling and simulation, synthesis and processing, and property assessment and characterization is central to MR. This section outlines the need for such facilities within universities and for large-scale national facilities. Deficiencies in current funding modes for the operation of state-of-the-art characterization facilities at universities, and for the acquisition of instrumentation that falls in the well-known funding gap between $4 million and $100 million are highlighted.[63] The impact that national user facilities, stewarded primarily by DOE and to a lesser extent by the National Science Foundation (NSF), National Institutes of Health (NIH), and other agencies, have had and continue to have on MR is highlighted. The case for continued investment in developing new instrumentation and techniques for MR is made, both through university investment and at national user facilities.

4.5.1 Research Infrastructure

The field of materials research and engineering is a highly research-instrumentation-intensive discipline. Enormous demands on research infrastructure exist in all subfields, ranging from instrumentation to synthesize materials, characterize their structure and properties, to the fabrication devices, applications, and systems. Often, a single researcher uses highly complicated instrumentation in all three of these areas, often in the span of a few days. For example, a single researcher active in the area of electronic materials may use sophisticated instrumentation to synthesize thin films of a new electronic material, followed by characterization of the microstructure of the film by techniques such as X-ray diffraction or transmission electron microscopy (TEM), followed by measurements of physical properties, such as electrical resistance or magnetization, and then proceed to fabricating devices in a clean room and characterization of the devices using state-of-the-art measurement techniques. In the course of a typical project, instrumentation costing many millions of dollars is used by the student.

Over the past 10 years, the ever-rising costs of acquiring and maintaining state-of-the-art research infrastructure combined with the dire lack of funding avenues for instrumentation have culminated in a situation that can only be described as a crisis for all of materials science and engineering. Most extramural research at universities is funded by federal agencies, private foundations, and industry, *who do not provide funding for the instrumentation that is needed to carry out the research that they fund*. While the Department of Defense (DOD) has a mechanism to fund instruments through their Defense University Research Instrumentation Program (DURIP) program, the funding level of typical DURIP grants is much too small to pay the cost of many of the instruments used in materials science and engineering. This leaves the NSF as the main sponsor of research instrumentation (through their Major Research Instrumentation, or MRI, program). This program is extremely competitive, and the chances of getting funded are so low that it is inadequate to support the research instrumentation needed at major research universities.

As a result, the burden to support research instrumentation has been shifted largely to the universities. Today, the mechanism by which universities support research instrumentation is mainly through start-up funds of new faculty. As a result of the crisis in extramural funding for research instrumentation, start-up funds have risen enormously over the past decade, reaching levels of above a million dollars for beginning assistant professors in experimental hard matter sciences. These sharply rising start-up costs are affecting the number of faculty universities can hire—in particular, those universities that do not have large endowments. Furthermore, this mechanism of funding research infrastructure is completely inadequate in sustaining forefront research in the long term. Specifically, start-up funds are typically used to buy instrumentation within the first five years of a faculty member's

[63] See the findings and recommendations of Chapters 3 and 4 of the report National Academy of Sciences, National Academy of Engineering, and Institute of Medicine, 2006, *Advanced Research Instrumentation and Facilities*, The National Academies Press, Washington, D.C., https://doi.org/10.17226/11520.

career. If this remains the only the source for equipment funding, as the trend over the past decade suggests, instrumentation is bound to become out-of-date as academic researchers reach the years that are normally the peak productivity of their careers. Such a model is unsustainable if the United States is to remain at the forefront of materials science and engineering.

The Department of Energy is *the* major supporter of research facilities at the National Laboratories. These laboratories are excellently equipped with state-of-the-art instruments. The use of DOE supported scattering facilities (X-rays, neutrons) is an integral part of several fields of academic research in materials. Even the U.S. portion of the International Space Station (ISS) was in 2005 designated as a national lab, supported by NASA, conducting key materials research (see Box 4.1). However, these national facilities are no substitute and no practical means to address the crises in research infrastructure at universities, where much of the nation's forefront research in materials is carried out. In particular, most materials research requires the infrastructure to be located at a researcher's institution. To give an example, a typical materials project that involves synthesis of new materials requires a constant and immediate feedback loop between synthesis, structure, and property measurements that may go through many cycles within a short period of time—that is, a span of a few days. It is not feasible to carry out this research if it requires remote facilities, and this is true for most materials research.

Last, the dire situation of deteriorating research infrastructure at universities also has more direct consequences on the nation's economy. In particular, many large research universities operate open-access or shared user facilities, such as clean rooms and material characterization facilities, which are open to outside entities such as companies. In essence, the universities also function as incubators, resources, and technology transfer opportunities for small and large companies, including start-ups. To give an example showing that this has been an issue for quite some time, Figure 4.11 shows the breakdown of users of the nanofabrication facility at the University of California, Santa Barbara (UCSB) over 10 months in 2011 by type of users.

A large fraction of the 26 percent of users from small companies are from a vital start-up culture surrounding UCSB that relies on this facility. In other words, an up-to-date university research infrastructure can have many positive effects on the economy.

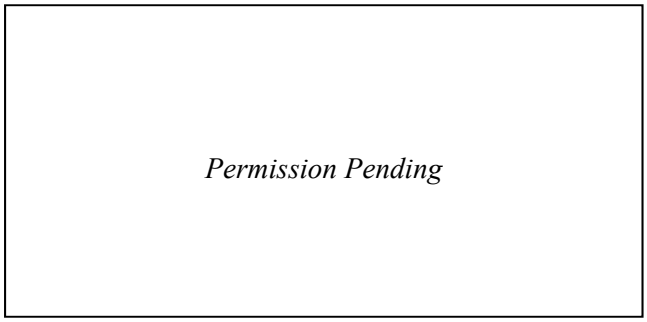

FIGURE 4.11 The breakdown of users of the nanofabrication facility at the University of California, Santa Barbara (UCSB), over 10 months in 2011 by type of users. SOURCE: National Nanotechnology Infrastructure Network, 2011, *NNIN Annual Report*: *March 2011-Dec 2011*, http://www.nnin.org/sites/default/files/NNIN_year_8.pdf, Image 139 e.

BOX 4.1
Materials Research Conducted on the International Space Station (ISS)

The International Space Station (Figure 4.1.1) is a multination facility that was assembled between 1998 and 2011 and has been continuously occupied since 2000. The ISS hosts a wide variety of laboratory facilities to enable discovery and innovation, with the U.S. portion being designated as a national lab in 2005.

FIGURE 4.1.1 NASA and CASIS (the Center for the Advancement of Science in Space is the managing entity of the ISS U.S. National Lab) support a materials science program on the Space Station. Investigators in the United States have access to this orbiting laboratory for conducting long-duration experiments in microgravity, where effects including convection, buoyancy-driven flow, and sedimentation are nearly negligible.[1] As an example, a project to develop better flame-retardant textiles compared combustion in Earth's gravity to that in microgravity, where diffusion-dominated flames result. The image on the right shows this difference between a candle flame on Earth and on the Space Station. The relative ease of access to the external space environment from the ISS also enables a variety of materials exposure experiments important to the space technology community. SOURCE: Courtesy of NASA.

Current ISS facilities for materials science research include: Low Gradient Furnace, Solidification and Quenching Furnace, Microgravity Science Glovebox, Pore Formation and Mobility Investigation Apparatus, Solidification Using a Baffle in Sealed Ampoules (modification to include CVD capabilities for 2D material growth is under study), Coarsening in Solid/Liquid Mixtures Apparatus, Transparent Alloys Experiment, Electromagnetic Levitator, Electrostatic Levitation Furnace, 3D Polymer Printer, and MISSE (Materials on ISS Experiment, which hosts external exposure experiments).

The following are recommended new materials research facilities as described in the MaterialsLab[2] Strategic Plan: Granular Materials Facility, Brazing and/or Welding Facility, Electrolysis of Molten Glasses, Diffusion Measurements, Float Zone Furnace, Biomaterials Facility, and 3D Bioprinting.

The primary selection criteria for proposals submitted to the ISS National Lab is that the research must require the persistent microgravity of the ISS or other unique property of the space environment and pass applicable feasibility and safety requirements. Investigators wanting to learn more about opportunities in materials research on the ISS may contact either NASA's ISS Program Office or CASIS.

[1] See http://www.spacestationresearch.com/, accessed March 6, 2018.
[2] See https://www.nasa.gov/feature/nasa-selects-16-proposals-for-materialslab-investigations-aboard-the-international-space, accessed March 6, 2018.

4.5.2 General Laboratory Infrastructure

The equipping of an experimental laboratory within a university is usually accomplished when the faculty member first joins the university. A similar dynamic occurs at a national laboratory or in industry, where more base infrastructure exists but the opportunities for equipment refresh are limited. Although there are opportunities at funding agencies for researchers to secure grants to acquire new equipment, the number of opportunities and the total level of funding available is limited. Similarly, at universities, there are limited resources available to replace or upgrade intermediate-scale equipment or to revitalize physical infrastructure (HVAC, lab modernization, etc.). A consequence of these limitations is that acquisition of everyday experimental capabilities, such as furnaces, tensile frames, lasers, and so on, is a challenge, which means these laboratories become obsolete over time. The difference is particularly striking when visiting universities laboratory facilities in other countries, in which a stronger commitment to infrastructure revitalization often is evident.

4.5.3 Midscale Instrumentation/Facilities

Midscale research facilities include many of the characterization, synthesis, and processing facilities discussed in earlier sections, and complement the national user facilities discussed below. Many research universities operate characterization and fabrication facilities,[64] and these are supported in part by the university or on a full-cost recovery mode from users. The acquisition cost of new instruments, while significant, has become just one component in meeting the escalating costs of operating a user facility.[65] The annual maintenance costs and the need for dedicated technical staff are becoming increasingly expensive. While the federal agency initiatives, such as the DOE Basic Energy Sciences (BES) nanoscience centers and the NSF Materials Innovation Platforms (MIP) are to be commended, the loss of such facilities at universities will limit progress especially in the area of instrument and technique development. There is a pressing need for a new national strategy on how to make available new instruments to a wide user base, meet the operational costs, and continue to stimulate creativity and development.[66]

Midscale funding for facilities,[67] in the range between a beam line or large magnet (tens of millions of dollars) and a full facility (in the billion-dollar range), has been a recognized challenge for some time.[68] The ability to study materials at extreme conditions—for example, in high magnetic fields while under extreme pressure, at very low or high temperature, with light or neutron scattering, or with scanning probes—has become an important direction of materials research on a global scale and is a prime example of the midscale funding gap. The capability to produce the desired environment is often beyond the scale of what a principal investigator (PI) can afford and also not within the budget of large-scale user facilities. For example, at MagLab, designing and building midscale projects such as the SC 32 Tesla and the series connected hybrid 41.5 Tesla magnet are in the several tens of millions of dollars

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[64] See, for example, *Science and Engineering Indicators 2018*, https://www.nsf.gov/statistics/2018/nsb20181/report/sections/academic-research-and-development/highlights#infrastructure-for-academic-r-d, accessed December 3, 2018.

[65] See Chapter 3, Instrumentation and universities outlines the various costs for facilities, in National Academy of Sciences, National Academy of Engineering, and Institute of Medicine, 2006, *Advanced Research Instrumentation and Facilities*, The National Academies Press, Washington, D.C., https://doi.org/10.17226/11520.

[66] Midsize facilities: *The Infrastructure for Materials Research*, 2006, https://www.nap.edu/catalog/11336/midsize-facilities-the-infrastructure-for-materials-research.

[67] *Workshop Report on Midscale Instrumentation to Accelerate Progress in Quantum Materials*. http://physics-astronomy.jhu.edu/miqm/.

[68] See, for example, National Science and Technology Council, 1995, *Final Report on Academic Research Infrastructure: A Federal Plan for Renewal*, National Science and Technology Council, Washington, D.C.

today, with running costs in the millions.[69] Another example is the challenge of developing next-generation high field magnets, the funding for which typically also falls in the $4 million to $100 million midscale range.

Novel growth ability also falls into this category, especially when addressing integration. For example, the control of interfaces of complex quantum heterostructures or devices becomes extremely critical; the interface often dictating the properties of the heterostructures. Control of the interface will also help us to understand the wavefunctions on either side of the interface, leading to our ability to design and synthesize functional quantum structures. This ability requires the integration, in a single system, of an advanced toolset for materials synthesis, interface and surface control, and in situ characterization.

4.5.4 Nanoscale Science Research Centers

In the last decade, a number of nanoscale science research centers have emerged whose scale is beyond those of midscale facilities at research universities. On a national scale, the DOE Office of Science's Scientific User Facilities Division operates five Nanoscale Science Research Centers (NSRCs) as user facilities that are located at National Laboratories, and the NSF operates the National Nanotechnology Coordinated Infrastructure at 16 universities. The National Cancer Institute's Nanotechnology Characterization Laboratory is another midscale facility, as is the National Institute of Standards and Technology's Center for Nanoscale Science and Technology. The five NSRCs are user centers for interdisciplinary research at the nanoscale. Each center has particular expertise and capabilities in selected areas, such as synthesis and characterization of nanomaterials; catalysis; theory, modeling, and simulation; electronic materials; nanoscale photonics; soft and biological materials; imaging and spectroscopy; and nanoscale integration.

This array of centers, sponsored by various agencies, have been very successful, as judged by the high oversubscription of their use and by the many important results that they have produced and reported. This leads to the conclusion that the expansion of this type of center would be a valuable asset to promote materials research in the United States. Such facilities not only empower U.S. researchers but also attract valuable international exchange and collaborations. Furthermore, organized collaboration and planning among existing and new centers as to the nature and types of facilities that they acquire and maintain would also be valuable.

4.5.5 X-Ray Light Sources

From the early days of synchrotron science, it was clear that light sources would have a large impact in the field of materials science. As is well documented, that early promise has been fulfilled many times over. Further, light sources have been improving at a rapid rate—the rate of increase in brightness of X-ray sources in the last 30 years exceeds that of Moore's law for transistors in the same period. The fulfillment of the promise, and the exciting future possibilities, of synchrotron light sources has been amply documented, for example, in these DOE reports: *Next Generation Photon Sources for Grand Challenges in Science and Energy*, *Report of the Workshop on Solving Science and Energy Grand Challenges with Next-Generation Photon Sources*,[70] and *Report of the BESAC Subcommittee on Future X-Ray Light Sources*.[71] This rapid improvement in brightness has driven ever more impactful uses of X rays to study the structure and function of materials. Most recently, the United States has seen the

[69] See https://nationalmaglab.org/magnet-development/magnet-science-technology, accessed December 3, 2018.
[70] See https://science.energy.gov/~/media/bes/besac/pdf/Ngps_rpt.pdf, accessed July 3, 2018.
[71] See https://science.energy.gov/~/media/bes/besac/pdf/Reports/Future_Light_Sources_report_BESAC_approved_72513.pdf, accessed July 3, 2018.

commissioning of the new National Synchrotron Light Source II (Brookhaven National Laboratory [BNL]), with brightness significantly higher than the other U.S. synchrotron light sources, and future upgrades are planned for two of the existing sources, the Advanced Photon Source Upgrade (APS-U) and the Advanced Light Source Upgrade (ALS-U), as shown in Figure 4.12. The accelerator lattice design for a diffraction-limited synchrotron pioneered at Max-IV in Sweden is being implemented as upgrades to existing synchrotrons or new facilities such as the Beijing high-energy synchrotron, which will be collocated with a major supercomputing and quantum materials effort.

A principal development of the last decade has been the emergence of X-ray free electron lasers as a complement to synchrotrons, notably the Linac Coherent Light Source (LCLS) and the future LCLS-II and its high-energy upgrade, LCLS-II-HE, at SLAC in the United States. New X-ray free electron lasers have been built or are under construction at DESY (Germany), PSI (Switzerland), CAS Shanghai (China), and elsewhere.

Collectively, these new ultrabright sources will drive further advances in the techniques, enabling transformative studies of materials with nanoscale resolution while under operating conditions and on ultrafast time scales. The United States had a significant fraction of all the world-leading capabilities 20 years ago, but that lead has eroded and today's landscape is one of intense competition from both Europe and Asia.

In addition to the increasing brightness of X-ray light sources, a second technological development has revolutionized the use of X-rays for materials science—the use of area detectors. This has facilitated the very rapid taking of data, allowing surveys of large swathes of reciprocal space to be undertaken and for new imaging modalities, such as coherent diffraction imaging, to be developed. The former has enabled, for example, tomographic studies of crystallographic grain orientation or studies of small distortions in crystal structures, while the latter has enabled, for example, studies of strain fields in nanoparticles and nanoscale semiconductors.

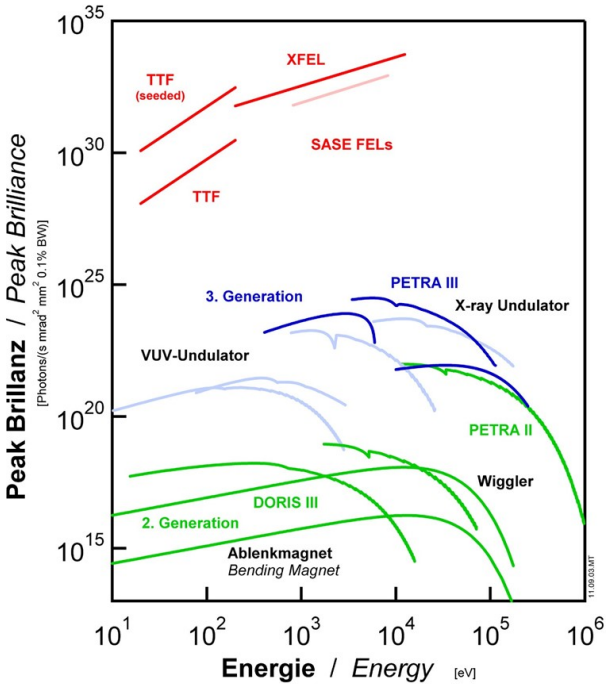

FIGURE 4.12 Time average brightness curves for selected existing (solid lines) and future (dashed curves) U.S. and international light sources. The plot illustrates the competitiveness of the international scene in both synchrotron and free electron laser light sources. SOURCE: Deutsches Elektronen-Synchrotron, Media Database, https://media.desy.de/DESYmediabank/ConvertAssets/Peak_Brillianz.jpg, © DESY.

The broad photon energy range available (from the far IR to hard X ray) and the intense brightness of the beams, which allows the photon beams to be tailored to specific experimental geometries and environments, makes X-ray light sources near-ideal probes of the structure and function of materials. The robust suite of experimental capabilities represented by APS, ALS, BNL, LCLS, and the Stanford Synchrotron Radiation Lightsource (SSRL) have enabled important contributions in quantum materials (superconductivity to graphene), energy storage (solid electrolyte interphase formation), self-assembly, advanced microelectronics (EUV lithography and strain engineering), as well as studies in extreme environments (high pressure and high magnetic fields) described elsewhere in this report. As the field moves toward the capability to fully integrate computational materials science, synthesis, and advanced manufacturing for real-world performance, the microscopic characterization of structure and dynamics enabled by the next generation of instruments and upgraded sources will provide the crucial link to enable materials by design.

4.5.6 Neutrons

The past decade has seen a revitalization of neutron sciences in the United States. A major stimulus has been the beginnings of operation of the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL), which now operates routinely at powers of over 1 MW and produces the world's highest peak flux neutron pulses for beam research on materials. The SNS first target station now operates with 19 specialized state-of-the-art instruments dedicated to materials research, spanning techniques aimed at structures at the meso-, nano-, or atomic-length scales, and dynamics on the micro- to picosecond time scales. At the same time, the continuous reactor sources of neutrons, including the NIST Center for Neutron Research (NCNR) and the HFIR at Oak Ridge, have seen significant improvements in the availability of cold neutron instrumentation. This has greatly increased the ability to perform unique investigations of "large-scale structures," such as those found in polymers, biomaterials, and solid-state nanoscale systems, as well as measurements of low-energy dynamics with excellent resolution and signal to noise.

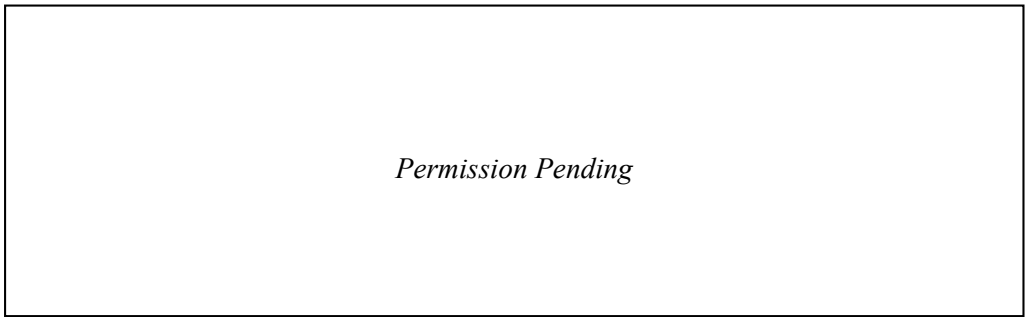

FIGURE 4.13 Map of peak brightness and average brightness that represent figures of merit for different classes of experiment for existing (solid) and planned (open) sources in the United States (blue), Asia (red), Australia (yellow), and Europe (green). SNS-FTS (Spallation Neutron Source—First Target Station, Oak Ridge National Laboratory, Tennessee), SNS-STS (Spallation Neutron Source—Second Target Station), ESS (European Spallation Source, Lund, Sweden), ISIS (ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Oxfordshire, UK), CSNS (China Spallation Neutron Source, Guangdon, China), HFIR (High Flux Isotop Reactor, Oak Ridge National Laboratory, Tennessee), ILL (Institut Laue-Langevin, Grenoble, France), FRM-II (Forschungs-Neutronenquelle Heinz Maier-Leibnitz -II, Garching, Germany), J-PARC (Japan Proton Accelerator Research Complex, Tokai, Japan), OPAL (Open-Pool Australian Lightwater Reactor, Sydney, Australia). SOURCE: Steve Nagler ORNL.

Figure 4.13 shows a comparison of selected neutron sources worldwide along the two axes of source performance, average brightness and peak brightness for a typical thermal neutron wavelength.

Depending on the nature of phenomena being studied and design of the instrumentation (fixed wavelength or time-of-flight), one or the other metric is more appropriate. Oak Ridge National Laboratories' High Flux Isotope Reactor (HFIR) and the NCNR are competitive in terms of average brightness, while SNS offers high performance in peak brightness (it should be noted the Japanese source J-PARC has not yet achieved its design power). Planned upgrades at SNS to increase the power to 2 MW and add a second, short-pulse, long-wavelength target station will preserve the competitive position even in the context of new facilities in Europe and China.

The large amount of data produced in modern neutron scattering instruments has in turn produced its own set of challenges, and at present researchers are starting to see early benefits of coupling high-performance computing and neutron scattering data analysis. This trend is also present for X-ray sources and microscopies, tools for integrating large volumes of data with modeling and simulation in real time to guide experiments is leading to closer coupling of experiment and theory.

The advances in neutron scattering sources and instrumentation discussed above have enabled substantial scientific advances spanning the range from fundamental discoveries about the nature of novel matter to new materials with specific technological applications.

Unconventional superconductivity has been a forefront materials problem for three decades, and within the past decade received a major impetus with the surprising discovery of iron-based superconductors. Almost immediately, neutron diffraction was used to elucidate the magnetic structure of parent compounds of several families of iron-based materials, showing that the ordering wave vector in most cases differed from the older cuprates. Detailed mapping of the phase diagrams uncovered regions of phase separation and evidence for stripe order. Inelastic neutron scattering showed the existence of a resonant magnetic excitation in the superconducting materials and found a striking relationship between the transition temperature and resonant frequency across many different types of unconventional superconductors.

The investigation of quantum materials is now a burgeoning forefront of research on solids. The field has been transformed by the developing understanding of the key role played by topology, and the possibility that topological materials or excitations might play an important future role in new technologies such as quantum computation. Neutron scattering has provided crucial information for much of this effort. The role of quantum fluctuations, and in particular fractionalized excitations, has been an overriding theme in the problem of quantum spin liquids. Inelastic neutron scattering has shown evidence for several different fractional excitations: spinons in Herbertsmithite,[72] which is possibly an example of a Heisenberg quantum spin liquid; magnetic Majorana fermions in α-RuCl3, which is believed to be proximate to a Kitaev quantum spin liquid; and excitations that are formally equivalent to the elusive magnetic monopoles in so-called spin-ice.

Evidence for topological structures in the form of magnetic skyrmion lattice was discovered by small-angle neutron scattering, and skyrmions now represent a promising new direction for spintronics applications. Neutron diffraction measurements of magnetic structures in various multiferroic materials have shown how chirality and frustration may play a role in multiferroic phenomena.

Polarized neutron reflectivity has been an especially valuable tool for studying buried interfaces, and it has shown how exchange bias in magnetic multilayers can lead to an interfacial region that is magnetically different from the bulk surroundings. In some cases, the interface can induce ferromagnetism in an interface layer one atom thick. Studies of interfaces between topological insulators and ferromagnetic insulators showed that shallow ferromagnetic regions can be induced in the topological insulator, and such structures might enable magnetic control via the electric field for new types of technologies.

Neutrons have had a large impact in the realm of functional materials, and particularly thermoelectrics, where careful measurements of phonon anharmonicities have revealed a path to producing greatly improved materials. Similarly, a deeper understanding of the requirements for

[72] Herbertsmithite is a mineral with chemical structure ZnCu3(OH)6Cl2.

improvement in energy storage materials has come about through a combination of conventional and operando diffraction studies of batteries and related materials. Neutron imaging has been particularly useful for understanding the inner workings of fuel cells.

The deep penetration of neutrons into most materials has enabled significant new insights into the microscopic origin of the properties of metal alloys, including deformation and plasticity of conventional alloys, and the phase transformation behavior of new high-entropy alloys. Neutrons have also been used to characterize the microstructure and consequent effects on mechanical properties of additively manufactured components.

The structure of porous materials has been investigated over a large range of length scales using both diffraction and small angle scattering. Particularly important work has been done on metal organic frameworks (MOFs), showing how the separation of light hydrocarbons might be greatly improved. Neutrons have also shed light on the possibility of both MOFs and shales for carbon sequestration and hydrogen storage.

Neutron scattering is ideally suited for studies of biological systems because it is a penetrating and nondestructive probe, providing structural and dynamical information across cellular scales of length and time, spanning from the position of an individual hydrogen atom in a protein to the nanomesoscale structure and dynamics of functional complexes and hierarchical assemblies within a cell. At the atomic level, neutrons provided insight into the role of critical H atoms in the catalytic mechanism of a peroxidase and binding of drug targets to proteins. Neutrons have been used in studies of proteins and their complexes because they can detect conformational changes and assembly/disassembly processes under near-physiological conditions. Nanoscale studies of protein-nucleic acid complexes have revealed how methylation events are used as a regulatory mechanism for rRNA folding and contributed to understanding into the regulatory function of cardiac myosin-binding protein C, a protein vital for maintaining regular heart function. Neutrons also reveal the organization and assembly of biological membranes and their interactions in the cell, providing insights into the structural and mechanical properties of lipid nanodomains and the mechanism of voltage gating, which can impact numerous neurological diseases as well as anesthetic action). The penetrating and nondestructive nature of neutrons has enabled studies investigating the architecture of the plant cell wall, providing new knowledge about structure of the cellulose microfibril, and its breakdown to release sugars for biofuel production. In the emerging thematic area of biological complexity, neutrons have been used to study cellular processes in living cells, a new area of application that has only recently become feasible. This has been achieved through targeted H/D isotope contrast to reveal the formation of nanodomains in plasma membranes and to study the dynamical processes of proteins in vivo.

4.5.7 High Magnetic Field Facilities

High magnetic fields represent a continuously tunable, reversible, and intrinsically quantum and topological probe of materials. Magnetic fields in the 10 to 100 T range compete with (and thereby effectively probe) the correlation energies of quantum matter and strong spin-orbit coupling of topological materials. Magnetic fields, by virtue of being both a thermodynamic variable and a vector quantity, can separate competing energy scales, as in quantum fluids and quantum spin liquids, and can induce new states of quantum matter (a quantum phase transition induced at absolute zero by varying for example the magnetic field), such as magnetic Bose-Einstein condensates and spin supersolids. Magnetic fields above 100 T will exceed the quantum limit of many low carrier density metals and sufficiently suppress the highest temperature superconductivity to reveal underlying quantum criticality.[73] Moreover, the technological impact of high magnetic field research is increasingly significant: whereas 10 to 20 T was sufficient to reveal fundamental electronic and optoelectronic properties (carrier mass, exciton binding energy, etc.) in silicon and GaAs, analogous studies of the new generation of atomically thin 2D

[73] Quantum criticality: a phase transition brought on by quantum fluctuations at absolute zero.

semiconductors (such as MoS_2, phosphorene, and the transition metal dichalcogenides) will require 100 to 200 T.

When magnetic fields interact with moving charges, they probe a characteristic length scale that decreases as the square root of the magnetic field. High magnetic fields of 20 T can probe spatial features comparable to a 6nm diameter quantum dot, while fields of 80 T are necessary to shrink this length by another factor of 2. As such, the study of electronic and magnetic phenomena down to atomic dimensions necessitates pushing the present limits of current magnet technology.

Three recent studies have looked into the current status and the potential for future developments of high field magnet research. For more detailed information and discussions of the various technical issues, the committee refers to these reports.[74] An important direction besides magnet development will be the integration of high fields with beam lines, as indicated by both COHMAG and MagSci. This would allow the investigation of the neutron and X-ray scattering properties of materials in high magnetic fields.[75] Currently, the highest field magnet on a beam line worldwide is a 26 T system at the Helmholtz Zentrum Berlin developed by the National High Magnetic Fields Laboratory (NHMFL).

4.5.8 Advanced Computational Facilities

Advanced Computational Facilities have played a major role in promoting and facilitating the leap forward in both predictive modeling of functional material and in developing the framework for understanding characteristics of materials at multiscales. These facilities, funded mostly by DOE and NSF, are home to the most sophisticated high-performance computers (HPCs), which enable computational material scientists to carry out detailed simulation of material properties from the microscopic to macroscopic length scales and ultrafast (subfemtoseconds) to standard time domains—regions not readily available in experiments.

Under the umbrella of its Advanced Scientific Computing Research (ASCR) program, DOE continues to maintain several world-class high-performance computing centers, enabling collaborative research in a number of fields including material science at the following: Argonne Leadership Computing Facility (ALCF), National Energy Research Scientific Computing Center (NERSC) at Lawrence Berkeley National Laboratory (LBNL), Oak Ridge Leadership Computing Facility (OLCF), and Energy Science Network (ESnet) at LBNL. These centers serve the high-performance computational needs of scientists from DOE labs, academia, and industry and maintain a high global profile in cutting-edge computer hardware. They were among the first to achieve the petascale (10^{15} machine operations per second) capability and are now gearing to break the exascale (10^{18} machine operations per second) barrier. These computer hardware advances coupled with a global effort in the development of refined computational codes suitable for application to challenging problems, at a variety of length and time scales, have enabled simulations of complex phenomena, which only a decade back were unimaginable. The material science community has been one of the biggest beneficiaries of these advances given the relevance of computational techniques used by researcher on collaborative projects that were initiated first under the Nanoscience and Nanotechnology Initiative (NNI) and more recently under the Materials Genome Initiative (MGI). Unsurprisingly, material science researchers are now one of the dominant users (comprising over 18 percent of all high-performance computing users). Fruitful interactions between experimentalist and computational scientists fostered by these two programs, among others, could not have been possible without the resources made available by the advanced computational facilities.

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[74] National Research Council, 2013, *High Magnetic Field Science and Its Applications in the United States: Current Status and Future Direction (MagSci)*, The National Academies Press, Washington, D.C.

[75] National Research Council, 2007, *Condensed-Matter and Materials Physics: The Science of the World Around Us (COHMAG)*, The National Academies Press, Washington, D.C., https://doi.org/10.17226/11967.

4.6 CONCLUSION, FINDINGS, AND RECOMMENDATIONS

No element of investment in materials research is more important than facilities, instrumentation, and infrastructure. With excellent facilities and instrumentation in place, a considerable amount of important research can be done with no further investment. These tools stimulate and unleash creativity and productivity. Several findings and recommendations aim to improve our national competitive status in this domain.

Key Finding: Progress in three-dimensional (3D) characterization, computational materials science, and advanced manufacturing and processing have enabled an increasing digitization across disciplines of materials research and has in some cases dramatically accelerated and compressed the time from discovery to inclusion in new products.

Key Recommendation: Federal agencies (including NSF and DOE) with missions aligned with the advancement of additive manufacturing, and other modes of digitally controlled manufacturing, should by 2020 expand investments in materials research for automated materials manufacturing. The increased investments should be across the multiple disciplines that support automated materials synthesis and manufacturing. These range from the most fundamental research to product realization, including experimental and modeling capabilities enabled by advances in computing, to achieve the aim that by 2030 the United States is the leader in the field.

Key Finding: Infrastructure at all levels, from midscale instrumentation for materials characterization, synthesis, and processing with purchase costs of $4 million to $100 million in universities and national laboratories to large-scale research centers like synchrotron light sources, free electron lasers, neutron scattering sources, high field magnets, and superconductors is essential for the health of the U.S. materials science enterprise. Midscale infrastructure, in particular, has been sorely neglected in recent years and the cost of maintenance and dedicated technical staff has increased enormously.

Key Recommendation: All U.S. government agencies with interests in materials research should implement a national strategy to ensure that university research groups and national laboratories have local access to develop, and continuing support for use of, state-of-the-art midscale instruments and laboratory infrastructure essential for the advancement of materials research. This infrastructure includes materials growth and synthesis facilities, helium liquefiers and recovery systems, cryogen-free cooling systems, and advanced measurement instruments. The agencies should also continue support of large facilities such as those at Oak Ridge National Laboratory, Lawrence Berkeley National Laboratory, Argonne National Laboratory, SLAC National Accelerator Laboratory, National Synchrotron Light Source II (Brookhaven National Laboratory), and National Institute of Standards and Technology—and engage and invest in long-range planning for upgrades and replacements for existing facilities.

Finding: There is a strong need for educated end users of software in order for the approximations, limitations, and full range of use cases to be appreciated and used toward significant impact on science and engineering. This includes in particular methods of machine learning as applied to materials.

Recommendation: Computational materials science training should be part of a core curriculum in undergraduate and graduate training in the subjects of physics, chemistry, materials science, and related fields, and this should include training in some of the larger computational software packages (and not just Matlab programming). More than one

section of this training is recommended to be in the area of machine learning applied to materials.

Finding: Researchers are close to a new world of precision synthesis in which the positions and species of individual atoms, molecules, and defects can be controlled to produce desired properties from the nano- to the macro scale, in both organic and inorganic materials, from sequence-controlled polymerization to molecular beam epitaxy with in situ characterization, scanning probe microscopies, spectroscopy, and angle-resolved photoemission.

Recommendation: All agencies that fund materials research, with NSF and DOE coordinating, should support research in the area of materials precision synthesis, particularly new methods that test the limits of what is fundamentally achievable and a new understanding of whether the levels of precision that can be achieved actually result in desired or interesting properties. The supported research should clarify when and how exquisitely precise synthesis is essential to achieving new functionality in materials. A multiagency workshop in 2020 or earlier could serve to initiate and propel this line of research into the next decade.

Finding: The integration of computational control and automation with advanced characterization techniques has made it possible to build 3D data sets that represent materials digitally with greater fidelity than previously imaginable. Methodologies for 3D characterization and analysis are currently developed locally; universally agreed upon process flows, tools, and analysis techniques are badly needed.

Recommendation: Federal agencies should invest significant resources into the creation and widespread use of autonomous experimental 3D characterization and the development of universal and widely shared computational methodologies for advanced registration, reconstruction, classification, and analysis of digital data sets.

Finding: The predictive design and fundamental understanding of the growth of crystalline materials promises enormous potential to impact our materials research and technologies. Crystalline materials play a fundamentally important role for modern society and commerce.

Recommendation: The establishment of materials growth hubs that are multiagency efforts (e.g., NSF, DOE, NIST, DOD) is recommended, where it is recognized that agencies with different but mutually beneficial priorities can share and fund knowledge while keeping proprietary information separate. Work at these facilities would not only seek to improve established methods but also would initiate new directions. These facilities would serve not only as foundries for synthesis of materials and development of new methods but also as homes to digital materials databases and real-world stockpiles of materials that would be available upon request.

Finding: Computer-intensive fields such as artificial intelligence, machine learning, and "big data" collection and analysis are now beginning to have a significant impact in materials science, the impact of which researchers are just beginning to see. To realize the full potential of this revolution, it is essential that researchers have access to the most advanced computer hardware and software.

Finding: In the future, as the scaling of microchips slows, emphasis on maximizing speed of floating-point operations might not be the best strategy for enabling increases in computing speed. Instead, advanced data analytics, fit-for purpose computers, and software interfaces (APIs and GUIs) might gain increased importance.

Recommendation: The DOE and NSF should begin in 2020 to support a broad computing program to develop "next-generation" and "fit-for-purpose" computers. These computers

should not only focus on speed but also include improved data analytics and other capabilities. The program should also include support to create and maintain new software and software interfaces (APIs and GUIs) and ensure that the broad materials research (MR) community has access to these tools. This support for code development should not go just to centers but also to single principal investigators (PIs) or small groups.

Finding: International collaboration plays an essential role in materials research, with engagements ranging from individual researchers to more formal institutional and facility partnerships. Examples include the International Space Station, CERN, SESAME, and LIGO. Advantages include pooling resources, promoting diversity in approaches for scientific progress, and scientific diplomacy.

Finding: Keeping in mind the importance of international collaboration, it is also important to note that there is a strong linkage between materials research, economic competitiveness, and national security. The U.S. leadership position has begun to erode, with major materials research initiatives and investments taking place outside the United States. Additionally, major state-of-the art facilities such as synchrotron light sources, free electron lasers, neutron scattering sources, high field magnets, and supercomputers are needed to attract and retain top researchers. Simply put, if the United States does not maintain leadership with major state-of-the art facilities, the erosion will only accelerate and hinder the U.S. ability to play major roles in international collaborations.

Recommendation: The U.S. government should aggressively enhance its support of large research facilities. Facility roadmaps for our funding agents (NSF, DOE, NIST, and DOD) should reflect a strategy for the coming decade of maintaining or increasing the current leadership role of the United States in major facilities for materials research while remaining abreast of developments in other countries and seeking cooperation when mutual benefit can be found.

5

National Competitiveness

There is now a clear understanding, particularly among countries in the Organization for Economic Cooperation and Development[1] (OECD) and the so-called developing countries, that science and technology buttressed by innovation (STI) are essential pillars of economic growth, and that advanced materials are a critical one of these pillars. Sanford L. Moskowitz, in his book *Advanced Materials Innovation, Managing Global Technology in the 21st Century*,[2] estimates that over three-quarters of all economic growth by 2030 to 2050 will be attributable to the development and application of advanced materials and that investments in materials research (MR) are tied directly to national competitiveness and economic prosperity. He also argues that never has the potential of MR seemed so important and crucial to human existence as it does for the 21st century, and he then explores the key questions that determine whether or not an MR invention becomes a robust market technology. Speed of innovation and commercialization are identified as key current issues facing MR, brought about by narrating stories of important 20th and 21st century innovations based on MR. In Table 5.1 below, he projects the impact of advanced material from 1980 to 2050 for information and computer technology, energy, biotechnology and health care, transportation, construction and infrastructure, and manufacturing.

As can be seen in Table 5.1 and in the sections that follow, MR is a critical underpinning to economic growth as well as national competitiveness, wealth and trade, health and well-being, and national defense. The impacts that MR has had on emerging technologies, national needs, and science have been important to date, and they are expected to become even more critical as researchers move through the digital and information age and face current and future global challenges. Many of the world's larger nations and economies have recognized this relationship, and recent trends show that today many nations have developed and articulated national investment strategies to ensure robust progress in MR for national competitiveness in a global economy. In some cases, these national strategies target specific national needs, and are internal to the nation; in others, collaborations have begun to be included in the investment tactics.

[1] An intergovernmental economic organization with 36 member countries, founded in 1961 to stimulate economic progress and world trade.

[2] See https://www.wiley.com/en-us/Advanced+Materials+Innovation%3A+Managing+Global+Technology+in+the+21st+century-p-9780470508923.

TABLE 5.1 Impact of Advanced Materials in Major Sectors of the U.S. Economy

Permission Pending

NOTE: The numbers are the percentages of total progress in performance in each industrial sector, attributable to advanced materials.
SOURCE: From S.L. Moskowitz, 2016, Table 1.2 in *Advanced Materials Innovation, Managing Global Technology in the 21st Century*, Wiley, Hoboken, N.J.

5.1 AMOUNTS AND DIRECTIONS

Given the economic importance of materials science, most advanced and developing nations have instituted national strategies for MR and for bringing its findings to the marketplace as rapidly as possible. Experience has taught us that fundamental research is an essential component of innovations that eventually spawn new industries and feed economic growth, so most national strategies seek to articulate and support research programs that run from fundamental to applied. Data about investments in materials science specifically are hard to obtain, but there are comprehensive sets of data about overall investments in science and technology, which MR should follow at least approximately. Figure 5.1 shows overall government budget appropriations and outlays for R&D for 2013 and 2015.

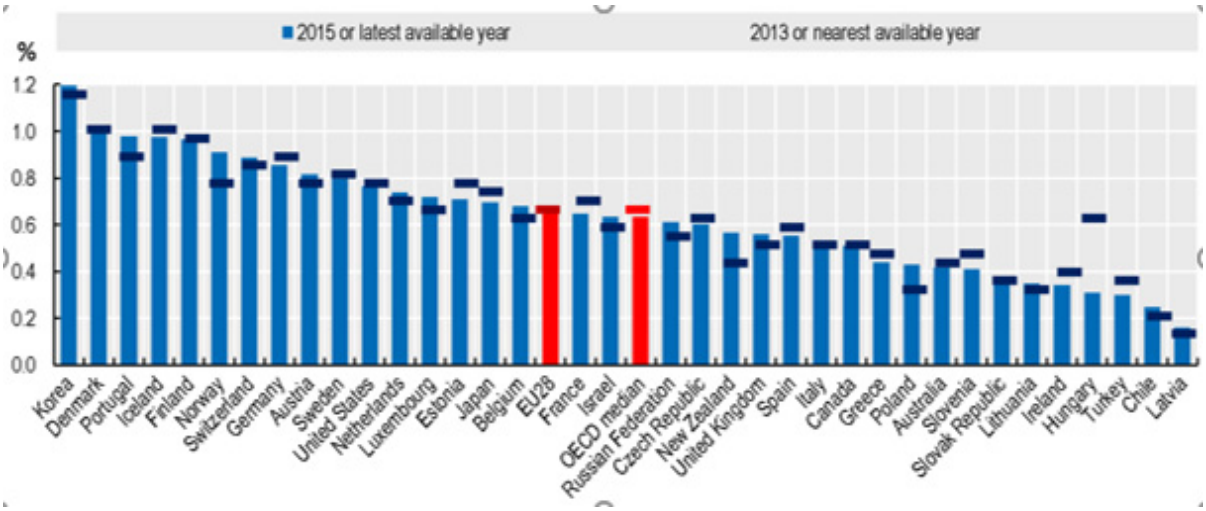

FIGURE 5.1 Government budget appropriations and outlays for R&D as a percentage of GDP, for selected countries, in 2013 and 2015. The height of the bar, compared to the line, reflects trends in funding for each country over this time period. See body of text for more detailed discussion. SOURCE: Organisation for Economic Co-operation and Development, *OECD Science, Technology, and Innovation Outlook 2016*, OECD Publishing, Paris, https://doi.org/10.1787/sti_in_outlook-2016-en.

Here are some general trends:[3]

1. Overall R&D capability (original wording in the OECD report is capacity, which in French is often translated as "capability") in the world has doubled in the last 15 years, with an increasing share of the growth attributable to increased business expenditures.
2. Several emerging economies, China's in particular, have significantly increased R&D spending.
3. Overall spending on publicly funded R&D (i.e., not including private and industrial R&D) shows a convergence toward 0.4 percent to 0.9 percent of GDP. Data in the report from OECD[4] shows Korea in the lead, with government R&D spending of 1.2 percent of GDP in 2013-2015, and the United States as number 11 at about 0.8 percent. It should be noted that over half of the U.S. government-supported R&D is defense related. U.S. spending is down from about 1 percent of GDP in 2008 and 2011. This decrease is, however, balanced by an increase in private investment. In 2015, the total R&D budget of the United States was $495 billion, about 67 percent provided by industry and 24 percent by the federal government (the rest by nonfederal government, higher education, and nonprofit organizations), and the total budget for basic research was $83 billion, about 44 percent provided by the federal government and 27 percent by industry.[5] In 2009, China, with the second largest science base in the world, spent about $154 billion gross (Government and Industry) on R&D, less than the EU ($298 billion) and the United States ($408 billion) and slightly more than Japan ($154 billion).[6] By 2015, China's expenditures expanded to $409 billion, while that of the United States increased to only $496.6 billion and those of the EU and Japan increased to $386 billion and $170 billion, respectively.[7]
4. There is a general shift in research policy agendas toward environmental and societal challenges (e.g., the EU Horizon 2020 framework program), in particular achieving sustainable growth. This shift, however, is unlikely to displace the long-standing emphasis on public science's contributions to national competitiveness. Nevertheless, the trend over the next 15 years is toward a greater emphasis on support for thematic, mission-oriented research, and it is likely that universities will play a greater role in this kind of research.
5. There is an increasing emphasis on interdisciplinary research, such as synthetic biology and neuroscience.
6. Strengthening of public research infrastructure, which has benefited most from international cooperation, is among the top STI priorities in the majority of countries.
7. Innovation has become a more significant imperative in policy development.
8. Many governments have shifted or plan to shift attention and support away from public research toward business innovation and entrepreneurship

5.2 A GLOBAL PERSPECTIVE

Materials research and innovation in materials science and engineering are now a worldwide enterprise that are essential to both the word economy and to that of individual regions and countries. In general, the world benefits from this globalization in which important new ideas come from small

[3] *OECD Science, Technology, and Innovation Outlook 2016.*
[4] *OECD Science, Technology, and Innovation Outlook 2016.*
[5] NSF Science and Engineering Indicators 2018.
[6] NSF Science and Engineering Indicators 2012.
[7] NSF Science and Engineering Indicators 2018.

countries (e.g., Skype from Estonia[8]) as well as larger ones. Aware that fostering innovation and technological advance in materials science and engineering increases the probability of thriving in this global environment, individual countries and the European Union have developed programs and institutions to support materials research and development. In planning U.S. support for materials research in the future, it is useful to know what other countries are doing to assess our relative strengths, weaknesses, and gaps, to identify possible areas for collaboration, and to learn from policy innovations of others. This section provides an overview of MR policies and planning in a representative group of countries and the EU.

There have been a number of assessments of future trends in science, technology, and innovation (STI) that identify transformative technologies. An OECD report synthesizes the reports from Canada,[9] the EU,[10] Germany,[11] the United Kingdom,[12] the Russian Federation,[13] and Finland.[14] The report lists 10 cutting-edge technologies; among them are the Internet of Things (IOT), artificial intelligence, neurotechnologies, nano/microsatellites, additive manufacturing, advanced energy storage, synthetic biology, and blockchain. At least six of these have substantial materials science component. The original country reports often featured materials science more explicitly (e.g., Canada—nanotechnology and materials science; EU—physical science and manufacturing enabling technologies; UK—advanced materials).

What follows provides more in-depth overviews of materials science and engineering in representative European (Finland, France, Germany, and the UK) and Asian (China, Japan, and Korea) countries and the European Union (which has agencies and resources separate from those of its member states). A broad and well-established trend emerges: the mature Western countries and Japan are seeing their share of the world's economies diminish and that of most Asian countries increase. This has caused the former to reassess their strategies for supporting materials science, tying those strategies more closely to economic development and stressing the importance of rapid conversion of knowledge into innovation. There is a clear realization that economic competition among nations will only increase in an extremely dynamic and unstable geopolitical climate. Although India is not included in this study, it is noteworthy that India's 2018 investment in materials has increased.[15]

Information that was readily available to the committee varied widely in content and format from country to country (the EU can be viewed as a "country" for the current purposes), and it proved, given the committee's time constraints, unrealistic to provide a common and uniform format for each of the country sections below. These sections do, however, strive to provide a reliable picture of national planning and priorities for MR in each of the selected countries.

European Union

The European Union provides support for individual researches, multimember consortia, and European science and engineering infrastructure. Its support is in general separate from that provided by individual European countries, whose programs are treated independently in this report. The EU prepares in-depth reports on science and technology around the world and on strategies for their development

[8] Skype was founded in 2003 by Niklas Zennström, from Sweden, and Janus Friis, from Denmark. The Skype software was created by Estonians Ahti Heinla, Priit Kasesalu, and Jaan Tallinn. The first public beta version was released on August 29, 2003.

[9] See horizons.gc.ca.

[10] Preparing the commission for future opportunities: *Foresight Network Fiches 2030* (2014).

[11] *Science and Technology Perspectives 2030*.

[12] *United Kingdom—Technology and Innovation Futures: UK Growth Opportunities for the 2020s*.

[13] *Russia 2030: Science and Technology Foresight* (2014).

[14] *100 Opportunities for Finland and the World: Radical Technology Inquirer (RTI) for Anticipation/ Evaluation of Technological Breakthroughs* (2014).

[15] See https://cen.acs.org/articles/96/web/2018/02/Indias-science-technology-funding-raised.html.

among its member nations. Advanced materials is one of the key enabling technologies identified by the European Commission. Together with advanced manufacturing, it underpins almost all other key enabling and industrial technologies.[16] The Materials Science and Engineering (MS&E) Expert Committee (MatSEEC) identified the need and value of knowledge and technology transfer in MS&E in Europe. In July 2017, the European Commission published a summary[17] of 11 recommendations based on results of the interim evaluation of Horizon 2020 and other documents and reports: "Our main message, and vision, is that investing in research and innovation is increasingly crucial for shaping a better European future in a rapidly globalizing world, where success depends ever more on the production and conversion of knowledge into innovation." Major initiatives include EuMaT—European Platform for Advanced Engineering Materials and Technologies—and ESF—the European Science Foundation. EuMat covers all elements of the life cycle of an industrial product, from design, development, raw materials, processing, qualification, and eventually decommissioning.

EuMaT's primary objective is to "produce the *Strategic Research Agenda* that, with appropriate involvement of industry and other main stakeholders, will provide bases" for identification of needs and establishment of priorities in the area of advanced materials and technologies.[18] The latest version of this report is the 2017 third edition.

- It seeks to promote the development of new materials technology that enables the design, production and use of innovative products with enhanced performance and new functions. Other targets are to protect the environment, to capture existing knowledge, to train future professionals, and to acquire capability and capacity to develop new generation of materials.
- It identifies eight critical focus areas, each with defined working groups: (1) modeling and multiscale; (2) materials for energy; (3) nanomaterials and nanostructured materials for functional and multifunctional applications; (4) knowledge-based structural and functional materials; (5) life cycle, impacts, and risks; (6) materials for information and communication technologies; (7) biomaterials; and (8) raw materials. Each has defined R&D priorities for 10- to 15-year horizons.
- Its overall policy is directed toward the achievement and maintenance of leadership and global competitiveness in advanced engineering materials. EuMaT works with other major organizations via collaboration and networking with the main European organization in this space such as the European Materials Research Society, the Federation of European Materials Societies, and the European Materials Forum. Involvement of industry is through participation in the governing boards. The Alliance for Materials (A4M) was created to ensure a value chain approach to improve speed of implementation of innovations in Europe that address grand societal challenges. It intends to be a single platform for all relevant initiatives, but not an overall structure to merge the R&D community; it is enabling versus controlling.

In ESF, the Materials Science and Engineering Expert Committee (MatSEEC) is an independent science-based committee of over 20 experts active in materials science and its applications, materials engineering and technologies, and related fields of science and research management. Committee members are nominated by their member institutions, and they maintain strong links with their nominating organizations and their respective scientific communities. The aim of MatSEEC is to enhance the visibility and value of materials science and engineering in Europe, to help define new strategic goals, and evaluate options and perspectives covering all aspects of the field.[19]

The EU's most recent centralized investment for future technology including MR is Horizon 2020, which is reported to be the largest EU program ever in research and innovation spanning nearly €80

[16] See http://ec.europa.eu/enterprise/sectors/ict/key_technologies/kets_high_level_group_en.htm.
[17] *Report LAB—FAB—APP: Investing in the European Future We Want*.
[18] Quote from EuMat website, www.eumat.eu.
[19] See www.esr.org.

billion over 7 years (2014 to 2020). The investment recognizes that additional private investment will be attracted by the program, which targets taking great ideas from the lab to the market. Economic growth and job creation is one of the key goals, and emphasis is on science excellence, industrial leadership, and tackling societal challenges. The program is structured to reduce red tape and response time to enable more rapid investments and results. Horizon 2020 is the financial instrument implementing the Innovation Union, a Europe 2020 flagship initiative aimed at securing Europe's global competitiveness.

Finland

Finland is a small country, but it strives to create a knowledge-based future, and its planning has some interesting twists. The Academy of Finland, part of the Finnish Ministry of Education, Science and Culture, is the primary agency for funding research. Its Strategic Research Council (SRC) funds research that has societal impact. Centers of excellence have been funded since 1995. TEKES is Finland's funding agency for innovation and it works directly with EU's Horizon 2020 program.

A focus of government funding is basic and applied research that has global impact, with an emphasis on science with societal impact. Overarching decisions guide national funding for research. The theme in 2017 was "Changing Society and Citizenship in a State of Global Flux" and for 2018 "Reform or Wither—Resources and Solutions." The cross-thematic focus areas for both years are information in decision making and execution, and sustainable growth in society.[20]

The Strategic Government Program of the Prime Minister, which was launched in 2015, is based on five strategic priorities: (1) employment and competitiveness; (2) knowledge and education; (3) well-being and healthcare; (4) bioeconomy and clean technologies; and (5) digitalization, experimentation, and deregulation. Specific focus areas in MR include adaptation and resilience for sustainable growth, keys to sustainable growth, nanoscience and nanotechnology, and energy-related science.

Of note are Finland's international interactions. The Academy of Finland engages in global cooperation with research funding agencies; it organized joint calls together with Brazil (Sao Paolo Research Foundation) on materials research and with India (Department of Science and Technology) on energy research, and it is active in the Joint Committees of the Nordic Research Councils. It also encourages submission of proposals from international scientists on competitive grants, as long as they have a Finnish host and collaborator.

France

The primary institution for the support of fundamental materials research in France is the CNRS (Centre National de la Recherche Scientifique), with a total budget of 3.30 billion euros in 2016, through its Chemistry, Engineering Sciences, and Physics divisions. The CEA (French Alternative Energies and Atomic Energy Commission) through its Renewable Energies sector also provides some support. The bulk of the CNRS support goes to university research departments, whereas that of CEA is concentrated in centralized research establishments like the Saclay Nuclear Research Center.

France's government promotes innovation for overall growth through its science, technology, and innovation (STI) policy. In 2013, France launched the Innovation 2030 Commission[21] to identify the major challenges the world will face in 2030 and key areas with significant implications for the French economy. The commission identified six pillars to put France on the road to long-term prosperity and employment: (1) energy storage, (2) recycling of metals, (3) development of marine resources, (4) plant proteins and plant chemistry, (5) personalized medicine, and (6) the silver economy—innovation in the service of longevity.

[20] See http://vnk.fi/en/article/-/asset_publisher/valtioneuvosto-paatti-teemat-strategiselle-tutkimukselle-vuosiksi-2017-2018, accessed March 8, 2018.

[21] See https://www.entreprises.gouv.fr/innovation-2030/the-innovation-2030-commission?language=en-gb.

France also leverages cluster strategies, and it established the European Cluster Collaboration Platform[22] in 2005 as an industrial cluster on advanced manufacturing that is motivated by investment in innovation as a key part of economic prosperity. Although the focus is manufacturing, materials and new materials are included, as is processing. A unique feature is an integration across market segments—aeronautics, naval, ground transportation, and energy—and a focus on creating synergies between members for research. EMC2 activities are enhanced by the IRT Jules Verne.[23] Funding is both public and private. EMC2 leads a network of small business enterprises and major industrial groups focusing on the key markets and technologies: aeronautics, automotive, energy, environment and green technologies, maritime, materials, metal processing and manufacturing, production technology, railway, and transport infrastructure. In 2016, its total budget for R&D was 1.4 billion euros, of which 523 million euros were public funds.[18]

Germany

Germany's investment in MR comes from two major programs: the German Ministry of Research (BMBF), "From Materials to Innovation," and the German Research Foundation (DFG), "Materials Science." In 2006, the German government created a plan called High-Tech Strategy[24] whose focus evolves over time; while initially attending to the market potential of specific technology areas, it later concentrated on society's need to develop and implement forward-looking approaches to policies (2010) and more recently on "civil society" alongside industry and research, and a number of new topics in which MR can be found (such as the digital economy and society, a sustainable economy and energy system, the innovative workplace and civil security). As part of this plan, Germany increased R&D expenditures from 8.5 billion euros in 2000 to 14 billion euros in 2013.

Federal investments employ a variety of strategies and initiatives aimed at ensuring Germany has the scientific, technological, and economical foundation to meet future challenges. A current focus is on new instruments to fund innovation; strengthen cooperation between enterprises, universities, and research institutions; and enhance society's active involvement in science, technology, and innovation.

Germany's foundation of unique funding models is well established and has benefited their country's MR. There is a high level of coordination of R&D across organizations and industry; academies play an active role. Continuous research support of academics is a part of faculty appointments, which enables strong research programs. Funding models address specific niches spanning basic through applied research. The Max Planck Society is world renowned, and its support complements research projects at universities. The Helmholtz Institutes focus on supporting large facilities (€3-6 million annually per institute with federal support). The Fraunhofer Institutes, the largest umbrella organization for applied research in Europe, conducts applied research for both private and public enterprises, as well as for the general benefit of the public. The Fraunhofer Institutes are unique in that they conduct research under contract for industry, the service sector, and public administration in addition to offering information and services. The MP3[25] is noted as one of the most famous inventions coming from the institutes. Their ability to bridge the so-called valley of death[26] by bringing industry needs to research projects has been recognized in key MR arenas such as manufacturing automation. The Leibniz Association connects independent research institutes that address issues of international societal importance, spanning the humanities and social sciences and economics through spatial and life sciences to mathematics, natural

[22] EMC2: https://www.clustercollaboration.eu/cluster-organisations/emc2.

[23] Institute of Shared Technology Research: https://www.irt-jules-verne.fr/.

[24] HTS: Hightech-Strategie.

[25] MP3 is an audio coding format for digital audio. Originally defined as the audio format of the MPEG-1 standard.

[26] "Valley of death" is a slang phrase used in venture capital to refer to the period of time from when a start-up firm receives an initial capital contribution to when it begins generating revenues.

sciences, engineering, and environmental research. The German Federation of Industrial Research Associations promotes R&D on behalf of small and medium-size enterprises (SMEs). The association, active at the national and the European level, is organized by industry and increases the competitive strength of SMEs by supporting the application of R&D. German states (Länder) and municipalities also fund and operate research institutes that support state research activities; advances in photovoltaics, renewable fuels, battery technology, and fuel cells are an example of MR benefiting from such an investment (Centre for Solar Energy and Hydrogen Research Baden-Württemberg).

Germany is responsible for introducing the concept of Industry 4.0,[27] often referred to as the Fourth Industrial Revolution, which follows the first steam-hydropower, the second electrical, and the third IT revolutions. Industry 4.0 envisions Cyber-Physical Systems (CPS) comprised of "smart machines, storage systems, and production facilities capable of autonomously exchanging information, triggering actions and controlling each other independently," designed to impart "a new level of organization and control of the entire value chain" to include custody over the full product life cycle.[28] This vision, related to the Internet of Things, although in its infancy is believed by many to be the future of manufacturing, and it is being promoted by the industrial world and, in particular, by China. It is not surprising that additive manufacturing is considered a part of the Fourth Industrial Revolution.

United Kingdom

The UK's centralized investment in MR has been shaped by its potential exit from the EU. The major government funding agencies for MR include the Engineering and Physical Sciences Research Council (EPSRC), Ministry of Defense: Materials and Structures Technology, and the recent Innovate UK: Manufacturing and Materials.

The UK's industrial strategy is based on four pillars: clean growth, AI and data economy, future of mobility, and aging society. A specific goal is to raise the R&D investment from 1.7 percent to 2.4 percent of GDP by 2027. A focus on MR is within the pillars, especially evident in clean growth—efficient new materials, "use of renewable biological resources to produce food, materials and energy." Noteworthy in the UK strategy is focus on regional research clusters, including materials-related themes: Manchester—advanced materials; Liverpool—materials chemistry. Unique factors for UK MR include a government-established Advanced Materials Leadership Council to advise on where investments have greatest impact. A Materials Exchange Research Forum operated by EPSCR is a platform for coordinating research.

In November 2015, the Knowledge Transfer Network (KTN) of the UK published a thorough review, "Survey of Market Needs and Growth Potential: Advanced Materials Study," that both identifies important materials areas for future growth and the resources and weakness of the UK in the areas in question. The five priority areas identified in the survey are (1) materials for transport, (2) materials for healthcare, (3) materials for energy, (4) materials for ICT, and (5) materials for demanding environments. For each of these areas, the survey discusses specific material needs, UK capacity to develop and exploit relevant technologies; immediate, medium-term, and longer-term trends and drivers; gaps in the UK industrial capacity; market growth opportunities; R&D/support infrastructure; international relationships; and global market trends.

China

China's "Made in China 2025" is an industrial master plan, based on the "Industry 4.0" concept introduced in Germany, to make China an industrial superpower in the coming decades. Among its goals

[27] See http://www.forschungsunion.de/pdf/industrie_4_0_final_report.pdf.

[28] *Material Data Space, An Initiative to Implementation of Industry 4.0 in Material Intensive Value Chains, Fraunhofer Verbund MatEriaLs*, 2016.

are a comprehensive upgrade of manufacturing in China to be innovation-driven, more efficient and integrated, emphasize quality over quantity, and raise the domestic content of core components of and materials to 40 percent by 2020 and to 70 percent by 2025. It highlights 10 priority sectors: (1) new information technology, (2) automated machine tools and robotics, (3) aerospace and aeronautical equipment, (4) maritime equipment and high-tech shipping, (5) modern rails transport equipment, (6) new-energy vehicles and equipment, (7) power equipment, (8) agricultural equipment, (9) new materials, and (10) biopharma and advanced products.[29]

Although "materials" appear explicitly only in item (9), materials will play an important role in many of the other items, especially if the stated goals of domestic content are reached. There is little doubt that this program has the potential to change the world landscape of industrial and thus materials production and substantially increase competition with current leaders in manufacturing.

Current plans, extending to 2020, call for China to pay more attention to the basic research in materials science, the exploration in the frontier areas, and to multidisciplinary research on national economic, social, and technological development and major needs. The Ministry of Science and Technology has allocated about 19 billion yuan ($3 billion) in 2016-2020 in areas of strategic electronic materials, key basic materials, biomedical materials and tissue replacement, nanometer science, additive manufacturing and laser manufacturing, and material genetic engineering. The National Natural Science Foundation of China plans to support about 4 billion yuan ($640 million) in this time period, across metal materials, inorganic nonmetallic materials, and organic polymer materials, including biomedical polymer materials. Much of the funding is aligned to investment in student programs.

China's centralized investment in MR focuses on projects that advance the economy and achieve independence from foreign suppliers. Specific areas of investment include aircraft engines, structural materials, electronic materials, energy materials, biomaterials, transportation, and quantum materials.

MR is strongly funded by the Ministry of Science and Technology, National Science Foundation of China, local and industrial sources, and sources focused on facilities for characterization and advanced manufacturing. The National Outline for Medium-and-Long-Term Scientific and Technological Development (2006-2020), released in 2006, identifies major special projects involving strategically important products, critical common technologies, and major engineering projects in line with national objectives. Projects are designed to enable scientific and technological progress, leapfrog developments in overall productivity and address China's strategic gaps.

Of note is the dramatic and effective return on centralized investment in China. Substantial government funding in MR has resulted in recruitment of talented researchers from around the world. Materials science papers from Chinese researchers tripled between 2006 and 2015. One in every ten papers in 2015 was in materials science.[30]

Over the last decade, China has built an impressive array of advanced state-of-the-art measurement facilities, including three synchrotrons (NSRL-Hefei, BSRF-Beijing, and SSRF-Shanghai), an advanced research neutron reactor (CARR-Beijing), and a spallation neutron source (CSNS-Dongwan, Guangdong). In addition, the Chinese government, through the National Development and Reform Commission and Ministry of Science and Technology, has approved the plan to establish three comprehensive National Science Centers. These "Science Cities" are the Beijing Huairo Center, the Shanghai International Science and Technology Innovation Center at Zhangjiang, and the Hefei Comprehensive National Science Center. It has just been announced that there will be a fourth Comprehensive National Science Center at Xi'an. The Beijing Center at Huairou ($1.5 billion) "will focus on areas of great advantages (to China), including materials science, space science, atmospheric environmental science, earth science, information and intelligence and life science." The new "Science City" is located on a 3,000-acre plot donated by the city government. There will be a new Beijing Advanced Photon Source, a Synergetic Extreme Condition User Facility, and the Earth System Simulator

[29] https://www.realclearworld.com/articles/2017/05/08/what_is_your_states_china_strategy.html.
[30] From https://www.nature.com/articles/545S54a.

(to be started in 2018 or 2019) and the extreme condition platform. The Chinese Academy is organizing several other platforms; among them, the Institute of Physics leads the construction of materials genome (40,000 m^2) and lithium-ion battery (80,000 m^2) platforms. Beijing City funds all the constructions and instruments for these two platforms, ~ CNY 0.9 billion (~130 million in USD), so these two platforms will be operational next year. The materials genome platform is composed of three parts: material computations and data analyses, high-throughput syntheses and fast characterizations, and instruments R&D and technical support. Fifty new appointments will be made to staff the materials genome platform. The new campus of the University of the Chinese Academy of Sciences is located in the "educational zone" of the Huairou Science City.

South Korea

South Korea's recent national investment in MR largely addresses commercialization. Its investment in scientific and technological R&D (government and private) for 2016 was sixth in the world (after the United States, China, Japan, Germany, and France) and one of the highest in the world in terms of percentage of GDP at 4.23 percent. In spite of its high investment in R&D, its return is low—with only a 20 percent rate of successful commercialization compared to about 70 percent for the United States and the UK and 54 percent for Japan. To address this gap, Korea has established a new "Government R&D Innovation Plan"[31] to reform their R&D ecosystem so that "investments will lead to profit and business achievements." Reorganization of R&D support systems to place greater emphasis on small and medium-size enterprises (SMEs) is part of the plan, as is the creation of a user-oriented optimal environment for research. MR will certainly benefit from this foundation.

Principal funding sources for science research in Korea include the National Research Council for Science and Technology (NST), which supports 25 Institutes, of which the following strongly support materials science: Korea Institute of Science and Technology (KIST), Korea Basic Science Institute (KBSI), Electronics and Telecommunications Research Institute (ETRI), Korea Institute of Machinery and Materials (KIMM), and Korea Institute of Materials Science (KIMS). Others government sources of MR funding may include the Ministries of Science, ICT and Future Planning; Trade, Industry, and Energy; National Defense; Environment; and Education.

Of note in the new plan is a clear division between the roles of the government and the private sector, with the government focusing on fundamental technologies and future growth drivers and the private sector focusing on commercialization. In addition, Korea plans to establish programs that will guarantee SMEs access to personnel and equipment in universities and government-backed research institutes (GBRIs) and will follow the effective German Fraunhofer model.

Japan

The Council for Science, Technology, and Innovation (CSTI) published Japan's Fifth Basic Plan for Science and Technology (S&T).[32] The ¥26 trillion (~230 billion USD), 5-year plan promotes a 10-year forward outlook focused on creating Society 5.0, also called the "Super Smart Society." This concept is that of "a human-centered society that balances economic advancement with the resolution of social problems by a system that highly integrates cyberspace and physical space." While the plan does not include research and development priorities at a detailed level, it outlines the ambition of the government

[31] See http://english.msit.go.kr/cms/english/pl/policies2/__icsFiles/afieldfile/2015/11/11/Government%20RnD%20Innovation%20Plan.pdf.

[32] See https://www.hrk.de/fileadmin/redaktion/hrk/02-Dokumente/02-07-Internationales/02-07-15-Asien/02-07-15-3-Japan/Iwamatsu_Cabinet_Office_Government_of_Japan_.pdf.

to identify important broad research areas that will spur system innovation, raise Japan's global position, and create enthusiasm among its aging citizenry.

A clear trend in the fifth plan, in relation to earlier plans, is the use of concepts such as "open science," "networked science," and "citizen science," displaying an ambition by Japan to open up the country's system for research and innovation. The plan recognizes that barriers for human resource mobility between universities and industry are hampering innovation and Japan's global position. While promoting collaboration between universities and corporate researchers, the government has also set some aggressive goals for 2020: they place added emphasis on strategic intellectual property management and standardization, look to double the number of license agreements on university patents, and want to increase the rate of initial public offering (IPO) cases regarding venture companies. A clearly stated goal of the plan is to have government, academia, and industry work together to transform Japan into "the most innovation-friendly country in the world."

Overall, the plan contains unusually sharp warnings that Japan is dropping in S&T competitiveness. This issue is addressed through improved political coordination between and within departments and research ministries, as well as a clearer focus on the basic components of the R&D-system that can drive Japan's open innovation model. The plan contains a number of numerical goals related to research for the coming five years and identifies several technology areas, such as bio- and nanotechnology, the Internet of Things (IOT), and artificial intelligence (AI) as important multidisciplinary enablers.

In alignment with the basic policies spelled out by CSTI's plan, 14 Japanese ministries set the policies, basic strategy, and budget allocations related to S&T. These include the well-known Ministry of Education, Culture, Sports, Science, and Technology (MEXT), as well as 12 others with a lower degree of immediate relevance to materials research and innovation. Investment areas that have been called out as priorities include energy, next-generation infrastructures, local resources, and health and medical.

In addition to the national S&T initiatives and what has already been discussed here, CSTI has selected two organizations (SIP and IMPACT) to promote and drive specific elements of this multidisciplinary open collaboration. They have estimated operating budgets of ¥50 billion/year and ¥55 billion/year, respectively.

- SIP, or the cross-ministerial Strategic Innovation Promotion program, promotes focused, end-to-end R&D, from basic research to practical application and commercialization. It also provides an intellectual property management system that will facilitate the strategic corporate use of research results from SIP programs. Program directors are selected by invitation from top-class leaders out of industry and academy and are asked to manage programs from a cross-ministerial perspective. Of the 12 S&T themes SIP manages, the two largest with a strong grounding in materials research and innovation are the Structural Materials for Innovation (SM4I) and Next-Generation Power Electronics programs. These programs are approximately ¥3.5 billion/year and ¥2.2 billion/year, respectively. SM4I looks to develop ultrastrong and ultralight heat-resistant materials for aviation, such as CFRPs, alloys, intermetallics, and ceramic-coatings, and accelerate their development and adoption through advanced computer science that correctly predicts complex material behavior. The Power Electronics program aims to use next-generation materials, such as silicon carbide and gallium nitride, to spread the adoption of improved electronics that result in a leap forward for energy management and efficiency.
- IMPACT, or Impulsing Paradigm Change Through Disruptive Technologies Program, looks to create disruptive innovations that revolutionize industries and society through high-risk/high-impact R&D. It is modeled after both the U.S. DARPA model and Japanese FIRST model. Armed with bold authority and budgets, IMPACT program managers (PMs) will set high targets for bringing about major changes to society and industry, will select research teams that provide optimum R&D capability, and will lead projects aimed at achieving disruptive innovation. IMPACTs "theme 1," a release from constraints on resources and innovation in "monozukuri (manufacturing)" capabilities, appears to have the tightest alignment to materials research and

innovation. It looks to achieve the low-cost production of high value-added materials and products through high-precision processing.

Drilling down to the next level of S&T impact and funding, Japan retains the globally renowned National Institute of Advanced Industrial Science and Technology (AIST), one of the largest public research organizations in Japan. AIST's Electronics and Manufacturing Department (~16 percent with 320 researchers) explores nanoelectronics, photonics, advanced manufacturing, spintronics, flexible electronics, and ubiquitous MEMS and microengineering. AIST's Materials and Chemistry Department (~20 percent with 415 researchers) studies nanomaterials, carbon nanotube applications, and the computational design of advanced functional materials.

To promote closer collaborations between universities and industry as called out by the fifth plan, AIST has created and is growing two new collaboration strategies. For materials and chemistry, these include the following:

- The concept of an open innovation laboratory (or OIL), with a collaborative research base located on a university campus. For now, there are two in service, OPERANDO-OIL and MathAM-OIL. Mathematics for Advanced Materials (MathAM-OIL) is applying advanced simulation and an inverse-problem analysis to material development to rapidly derive a material's structure based on its desired functions to expedite the material development cycle.
- Collaborative Research Laboratories (CRLs), bearing partner company names, to conduct research and development more closely related to the strategies of companies. For now, there are three in service related to materials, the Zeon-AIST Nanotube CRL, looking to accelerate the scaling of carbon nanotube (CNTs) production, the TEL—AIST CRL for advanced materials and processes for electronics and manufacturing, and the NGK Spark Plus-AIST CRL for healthcare materials.

Based on Japan's fifth Basic Plan for science and technology, AIST plans to establish more than ten OILs by FY 2020. It is reasonable to forecast that additional CRLs will be created as the new S&T strategy and funding from the fifth Basic Plan marry with the S&T interests of would-be Japanese industrial sponsors.

5.3 CASE STUDIES

A sense of the dynamical, international nature of MR can best be appreciated with the aid of case studies that show how important advances often begin with initial ideas being developed in one country, followed by necessary development in a second, and finally commercialized in a third. In the current state of rapid change with Industry 4.0 on the horizon, countries with relatively less developed MR experience can leapfrog past old techniques to world leadership in the new. This section will present brief case histories highlighting these trends.

Case 1—Flat Panel Liquid Crystal Displays

This is by now a fairly old story, played out over more than three decades, but it is illustrative of how the mélange of great creativity, unwillingness to abandon old ways, persistence, and missed opportunities determine the course of development of new products. Liquid crystals, which flow like a liquid yet exhibit anisotropy like a crystal, were first discovered by Fredrich Reintzer in 1888. Although E. Merck of Darmstadt sold liquid crystals for analytical purposes as early as 1907, they were far from the mainstream of scientific research, with only a few institutions studying them by 1960. In the early 1960s, RCA began a program to study liquid crystals with the eventual idea of developing a "hang-on-the-wall television." Although it did not succeed in that, it did produce the first LC display using a dynamical light

scattering mode to turn pixels on and off. RCA, with strong investment in CRTs and "silicon," abandoned any attempts to commercialize the technology and this effort was then taken up—and then also abandoned—by small U.S. start-ups. RCA was, however, inadvertently associated with the development of the twisted-nematic display that eventually led to today's flat-screen displays. It was invented by an RCA employee, Wolfgang Helfrich, who left RCA to work for Hoffmann-La Roche in 1970, and almost simultaneously by James Fergason, then at the Liquid Crystal Institute at Kent State University in Ohio. Europe, particularly the UK, would get involved with the technology by creating new types of liquid crystal materials, which were stable at room temperature, in its chemical laboratories but it was Japan that eventually succeeded.

Companies such as Sharp had sent its engineers to the United States to learn all it could from RCA and other U.S. companies about the LCD. Japan succeeded in eventually commercializing the technology, in part, because of its business culture—based on the importance of cooperation between firms (the "Keiretsu" system) in contrast to the individualistic, highly competitive nature of U.S. business. The scaling up of the LCD to flat panel displays for computers and large-screen TVs was a very complex and very expensive process. U.S. companies large and small shied away from spending so much on such a risky proposition (their perceived risk was high). In Japan, however, the government worked with different companies to create the flat panel display—this cooperative effort allowed capital and talent to be pooled in a way that could not be done in the United States. Moreover, companies in Japan tended to be large and diversified, and revenue streams from other commercial areas allowed these firms to work with other companies on this one project without having to worry about overall cash flow. Government aid also helped soften the blow (so here CEOs of Japanese companies had low perceived risk). By the first decade of the 21st century, Japan's government and the constellation of companies that it coordinated on this national effort were able to show the world it could do what the mighty United States could not, succeed in commercializing these displays. Other Asian countries—especially South Korea—followed Japan's lead, and together the region has become the world's hub for flat panel display technology. In this way, Asia took a largely American invention and found a way to tap the commercial potential in it.[33]

Lessons from this example include the following: (1) breakthrough applications often require advances and new ideas in many different fields, (2) persistence and vision are often the determining factor in actually bringing a product to market, and (3) such persistence and vision often rest on a few individuals. In addition, the sequence of necessary advances often occurs in different countries. In the liquid crystal case, the idea of a flat display and how it would work was the first essential step, but that idea could not come to realization without the advances in chemistry that provided room-temperature-stable liquid crystals. Advances in semiconductor technology were the final essential ingredient for the successful development of the amazing displays we now take for granted.

Case 2—Additive Manufacturing in Aerospace

In the last five years, additive manufacturing has in a sense come into its own in aerospace.[34] The four major jet engine manufacturers, Rolls-Royce, Pratt and Whitney, General Electric, and Safran Aircraft Engines, have begun to produce aircraft engines with additive-manufactured components that reduce weight, number of parts, and development time. NASA in collaboration with Space-X is developing additive-manufactured rocket engines, and companies around the world are using additive manufacturing to make reduced-weight plane seats, helicopter engines, and flying-car bodies. The manufacturers of aircraft engines had gained experience using additive manufacturing to prototype parts

[33] Based on communication with S.L. Moskowitz, author of *Advanced Materials Innovation: Managing Global Technology in the 21st Century*," Wiley, 2016. See Chapters 11 and 12 for the case study of LCDs and flat panel displays.

[34] National Research Council, 2014, *Limited Affordable Low-Volume Manufacturing: Summary of a Workshop*, The National Academies Press, Washington, D.C., https://doi.org/10.17226/18697.

as far back as the late 1980s. The story of development of the LEAP engine by CFM, the joint GE Aviation- Safran Aircraft Engine, is documented in an online GE report.[35] The CFM team designed a new engine that would dramatically reduce fuel consumption and emissions. Its design of fuel nozzles had an interior structure that was so complex that to make it would have required more than 20 parts that would have to be welded together, an almost impossible task. Mohammad Ehteshami, then head of engineering for GE Aviation, went to Morris Technologies, a local Cincinnati company that pioneered the use of metallic additive manufacturing and that made prototypes for GE projects, to investigate whether it could use additive manufacturing for mass production of a complex part. A nickel alloy prototype of the intricate nozzle tip exceeded all expectations: it combined all 20 parts into one and weighed 25 percent less than an ordinary nozzle and was more than five times as durable. GE Aviation acquired Morris Technologies in 2012, and in 2016 it spent more than $1 billion to buy controlling stakes in Sweden's Arcam AB and Germany's Concept Laser, two leading manufacturers of industrial 3D printers. In 2013, it also acquired the Italian firm Avio Aero, which now has one of the most advanced 3D manufacturing facilities in Europe, and it is already making parts for the TiAl turbine blades for the GE9X—the largest jet engine ever built. GE set up other additive manufacturing factories in Auburn, Alabama, and established the Additive Training Center near Cincinnati and the Center for Additive Technologies Advancement near Pittsburgh.

There are several lessons to be learned from the development of additive manufacturing as essential component of advanced manufacturing of complex parts: (1) At one level, this is a common story: a new idea often takes 30 or so years to mature, but when it does it can have a profound effect. (2) Access to advanced technology by large companies is more often than not obtained by the purchase of smaller and often more nimble companies. (3) Good ideas and international companies are not subject to national or geographic boundaries—a lesson that should be remembered as China works its way up the technological ladder.

Case 3—Permanent Magnets on the World Market

Permanent Neodymium-Iron ($Nd_2Fe_{14}B$) magnets are the strongest currently known, with extensive uses in motors, speakers, cell phones, wind turbines, hybrid cars—the list goes on. They were first discovered independently by different methods by General Motors in the United States and Sumitomo Special Metals (eventually acquired by Hitachi) in Japan in 1984 in response to increasing cost of Samarium in the then-standard SmCo magnet. The new material quickly became the industry standard, with dozens of firms engaged in its production. China has controlled production of rare-earth metals since at least the 1990s. By 2005 or so, because of strong demand and active enforcement of environmental policies, the price of rare earths increased considerably, putting pressure on both producers and purchasers of permanent magnets. The result was a shuttering of many producers and a flight of those who remained to Asia to be closer both to supplies and customers in the booming Asian economies. By 2008, there were no producers of Nd magnets in the United States. The situation was and continues to be complicated by litigation over patent violations (Hitachi, which holds most of the patents on Nd magnets, and Chinese firms) and imposition of unfair market barriers (Chinese firms against Hitachi) working through the U.S. court system.

The United States is, of course, aware of the magnet problem, and it would prefer not to have to rely so completely on a single technology or single material provider for something as increasingly important as permanent magnets. DOE has in fact funded research on alternatives materials for magnets through a DOE Advanced Research Projects Agency (ARPA)-E program, but no viable replacement has been found. On the other hand, DOE-supported research on additive manufacturing has developed a process that produces better magnet performance with less material (see Box 2.6).

[35] See https://www.ge.com/reports/epiphany-disruption-ge-additive-chief-explains-3d-printing-will-upend-manufacturing/.

The take-away from this case study is that forces beyond science and engineering often determine the fate of local commercialization of superior materials and their processing.

Case 4—Photovoltaics

Photovoltaics (PV) are semiconductor materials[36] that convert light (in particular from the sun) to electricity. They are becoming an increasingly important component of electric power grids around the world, with 302 gigawatts (GW—billion watts) of capacity in 2016 or about 1.3 percent to 1.8 percent of the world's electric power consumption, and an exponential rate of increase over the period 1992 to 2017. The first patent for a solar cell was awarded to (Russel Ohl) Bell Laboratories in 1946, and the first practical crystalline solar cell was realized in 1954, again at Bell Labs. Crystalline (c-Si) and polycrystalline silicon (poly-Si) remain the dominant material for photovoltaic cells, with 95 percent of the market in 2013. There are, however, two photovoltaic materials, CdTe discovered at RCA in 1954[37] and Cu(InG)Se (CIGS) studied at Boeing in the 1980s[38] have found commercial application and show some promise for the future. Unlike silicon, CdTe and CIGS are prepared as thin films on a substrate. These three materials all have peak efficiencies above 20 percent.

From 1946 through 1997, the United States dominated both research in and applications of photovoltaics. In 1977, President Jimmy Carter established what was to become the National Renewable Energy Laboratory (NREL) in Golden, Colorado, which, among other things, provides independent verification of efficiencies of solar cells. By the 1980s and through the 1990s, photovoltaics found applications in off-the-grid stand-alone power systems and in consumer products like watches and calculators. By 1996, the United States had 77 MW of solar PV capacity, and focus had begun to shift to grid-connected rooftop systems.

In 1995, the city of Kobe in Japan experienced an earthquake that led to severe power outages that paralyzed the entire neighboring electrical infrastructure. PV systems provided temporary replacement power. In the same year, the experimental Monje Nuclear Power Plant developed a sodium leak that forced a shutdown and that led to massive public outrage. These two events led to Japan's decision to invest heavily in PV power generation, and it quickly became a world leader, with 1.132 GW of PV capacity by 2004. Following its Renewable Energy Act of 2000, Germany displaced Japan as the world PV leader in 2005, a position it held until it was in turn displaced by China by 2015. China's five-year plan of 2015 set a goal of 100 GW of PV power by 2020, a goal that it exceeded in 2017, with a capacity of 131 GW.

Fluctuating national agendas and normal market fluctuations have created challenges for manufacturers of PV's, in many cases leaving them in bankruptcy. The 2000 decision of Germany to favor development of PV systems and the decision of China to begin investing in them and subsidizing their production led to an increase in demand for silicon by 75 percent. The result was a severe shortage in silicon and an increase in its price from $30/kg to $80/kg and even $400/kg for long-term contracts forcing the solar industry to idle about 25 percent of its cell and module manufacturing capacity. The polysilicon industry responded with technological improvements and investment in more capacity. The result was then overcapacity for silicon production and a drop in price to $15/kg, forcing some producers to suspend production or exit the sector. By 2013, the ratio of actual output of PV silicon to production capacity was still only at 63 percent. This overcapacity led to increasingly inexpensive exports from China to the United States, and then to U.S. allegations of Chinese dumping of solar products, followed by the imposition of tariffs in 2012 and to a similar move by the European Union a year later. China responded with antidumping tariffs of 57 percent on U.S. polysilicon producers.

[36] https://www.nrel.gov/research/re-photovoltaics.html
[37] J.A. Dietrich and R.A. Bube, PRB 96, 1190 (1954).
[38] See www.siat.cas.cn/xscbw/xsqk/201109/W020110913360381852247.pdf.

The story of thin film PVs provides a cautionary tale about commercialization of high-tech materials. Solyndra, a company founded in 2005, developed a technology for solar panels in which thin CIGS films were rolled and encapsulated in specially designed cylinders allowing, it was argued, for the panels to absorb energy in all directions. By 2009, following a near high point in the price of polysilicon (~$400/kg in 2008), Solyndra posted a revenue of $100 million and the future, with a $535 million government loan[39] under the American Recovery and Reinvestment Act, looked bright. But the future was planned without sufficient attention to increasing polysilicon production, which caused the price of polysilicon to fall to about $50/kg by the time the government loan was approved. Orders fell, and Solyndra declared bankruptcy in 2011, laying off 1,100 people.[40] The story of Nanosolar, a company started in 2002, is similar. It developed a CIGS PV ink that it spread on a flexible substrate whereupon nanoparticles in the ink aligned under a self-assembly process. In December 2007, it started solar cell production in its San Jose factory, and by February 2012, it had reached a production capacity of 115 MW per year, but in the end its total actual production was only 50 MW.[41] Like Solyndra, it went out of business (in 2013) because its product could not compete with cheaper silicon.

There are, of course, U.S. and U.S.-based international companies that have survived the feast-and-famine cycle of silicon availability and foreign competition. These include the following:

- SunPower (60 percent owned by Total S.A.)—crystalline Si technology and 2015 production capacity (mostly in the Philippines and Germany) of almost 400MW/yr;
- First Solar—CdTe technology, with total installation of over 17 GW of power worldwide and 2015 production capacity of 143 MW/year;
- Evergreen Solar—polycrystalline Si and 2015 production capacity of 103 MW/year; and
- Tesla Energy (merger SolarCity and Tesla), now a player with "Gigafactory 2" producing cells and panels in partnership with Panasonic in Buffalo.

The status of PV use and investment continues its state of competition and flux with the contested U.S. imposition in February 7, 2018, of 30 percent tariffs (to decrease to 15 percent by 2021) on c-Si PV cells and modules and the announcement by China of a 12 to 15 percent cut in the Feed-in Tariff[42] for projects installed after June 2018.

In spite of the complicated economics (and politics), PV electric power development will continue, and research will lead to improvements in efficiency and to new device structures. Research into CdTe and CIGS films continues; also, new perovskite and organic photovoltaic solar cells show considerable promise.

Case 5—Lithium-Ion Batteries

Lithium batteries were first proposed and realized by Stanley Whittingham while working for Exxon in the 1970s, although G.N. Lewis had initiated some explorations in the early 1900s. Lithium is the lightest of all metals, has the greatest electrochemical potential, and provides the largest specific energy per weight. With lithium metal as the anode, the safety issues owing to its reactivity and inherent instability were obvious, as were the problems associated with the formation of lithium dendrites, which grew with repeated cycling and short-circuited the batteries. Research shifted to nonmetallic materials using intercalated lithium ions. The final product, which is now called the Li-ion battery, has had a transformational impact on personal electronics and on personal mobility, affecting communication, computation, entertainment, information, transportation, and the fundamental ways in which people

[39] The loan was a political scandal for the Obama administration.
[40] *Washington Post*, Sept 13, 2011.
[41] E. Wesoff, 2013, Nanosolar, thin film solar hype firm, officially dead, greenmedia.com.
[42] A mechanism to accelerate investment in renewable energy through long-term contracts.

interact with one another and with information. The first successful Li-ion batteries were commercialized by Sony in 1991. Estimates in 2017 of the global market for Li-ion batteries are approximately $25 billion, with consumer electronics being the largest application, followed by automotive, industrial, and energy storage.[43] Growth of 12 percent per year has been forecast.

Since the initial inventions, the energy density of Li-ion batteries has improved and continues to improve at a rate of 5-10 percent per year due directly to progressive improvements achieved through advanced materials science research, carried out across a broad spectrum of university, major industry, start-up company, and government national laboratories. The trajectory of key innovations to date is a fascinating sequence of both discovery and design.

Sony used a soft carbon host structure (coke) in the first commercial battery containing lithium at the anode instead of metallic lithium, although the quest for Li-metal anodes continues today owing to the higher energy density attainable. Thus, the initial concept of the Li-metal anode was ultimately abandoned for a soft-carbon intercalation anode, which was itself abandoned for a hard-carbon anode and then a graphite anode, the evolution based primarily on the interaction that these carbon materials have with the organic liquid electrolyte that is the medium through which ions are transferred between electrodes during discharging and recharging. On the cathode side, much credit goes to Goodenough and co-workers for the development of a new class of cathode materials, layered transition-metal oxides, such as LixCoO2, first reported in 1980. In 1996, Goodenough and co-workers proposed lithium iron phosphate (LiFePO4) and other phospho-olivines (lithium metal phosphates with the same structure as mineral olivine) as positive electrode materials. In 2002, Yet-Ming Chiang and his group at the Massachusetts Institute of Technology showed a substantial improvement in the performance of lithium-ion batteries, boosting the material's conductivity by doping it with aluminum, niobium, and zirconium. In 2004, Chiang again increased performance by utilizing iron(III) phosphate particles of less than 100 nanometers in diameter. This decreased particle density almost 100-fold, increased the positive electrode's surface area and improved capacity and performance. Commercialization led to a rapid growth in the market for higher capacity Li-ion batteries. The Materials Genome Initiative has had a major impact in trying to develop ideas to go beyond Li-ion, such as the use of divalent ions that, all other things being equal (which they are not), would increase the energy density by a factor of 2. Likewise, silicon anodes are being actively explored for their greater Li binding capacity than graphite. Yet another important area of materials development is in the electrolytes, particularly in the development of solid electrolytes that both eliminate flammable organic liquid electrolytes and provide a physical barrier to dendrite short-circuiting.

Not only has this steady progress in materials research led to steady improvement in performance, but it has also led to as steady decrease in costs of manufacturing. In 1994, the cost to manufacture Li-ion in the standard 18650 rechargeable cylindrical cell was over $10 and the capacity was 1100 mA-h. In 2001, the price dropped to below $3, while the capacity rose to 1900 mA-h. Today, high-energy-density 18650 cells deliver over 3000 mA-h, and the costs are dropping further. Cost reduction, increased specific energy, and the absence of toxic material paved the road to make Li-ion the universally accepted battery for portable applications, heavy industries, electric power trains, and satellites.[44]

5.4 SCIENCE DIPLOMACY WITH INDUSTRIAL AND HOMELAND SECURITY

The findings in this decadal survey stress the need for continued international collaboration—especially as facilities become larger, more complex, and expensive. The findings also point out the need for the United States to not lose its strength in worldwide leadership in materials research, because access to international facilities and front-line research findings would then become more challenging. These two

[43] See https://www.gminsights.com/industry-analysis/lithium-ion-battery-market.

[44] Case 5, adapted in part from George Crabtree, Elizabeth Kocs and Lynn Trahey, MRS BULLETIN, Vol. 40, (2015), www.mrs.org/bulletin pg 1067.

findings are intimately related: The United States will lose its ability to be involved in front-line international collaborations if U.S. research erodes. The committee points out here that these international collaborations bring up an ever-rising challenge: How does the United States maintain international research while maintaining U.S. homeland and industrial security?

The committee has recently seen some of our governmental research laboratories prohibit its research employees from attending conferences in China and our U.S. Treasury department forbidding attendance of U.S. researchers to a conference abroad.[45] There are many additional examples of U.S. researchers being blocked from international travel, and it is also becoming increasingly challenging for foreign scientists to travel to the United States and for Chinese graduate students, in certain research areas, to obtain more than a one-year student visa.[46]

Note that in the early 1960s, U.S. physicists went to visit their counterparts in the Soviet Union—and that was during the heart of the Cold War, with both sides being heavily armed in nuclear weapons. These interactions played a formative role in substantially changing and growing theoretical condensed matter physics. During all of these interactions, continuing into the late 1980s, scientists were not only carefully watched but also remained vigilant in sharing only the most basic of their physics to move the fields forward, together.

Ceasing international collaborations will put the United States at a great disadvantage for materials research, from the most fundamental to the most applied industrial research. In the past, scientists knew how to write papers, discuss research, and present talks; sharing what needed to be shared, while keeping any sensitive materials confidential. But times have changed—and cyber security has raised new challenges. In this new age, using one's laptop or phone, or even checking e-mail, are possible security risks while traveling internationally; and there is a need to be mindful of international visitors to the United States. These new challenges also apply to industrial security within the United States.

5.5 A NATIONAL PERSPECTIVE

There was a time when R&D programs in the United States could be planned and carried out without regard to programs in other countries. That has not been the case for some time now, and today many of the MR programs in the rest of the world are already competitive with those of the United States or on their way to being so. This competition has been highlighted in the five case studies above that act as snapshots highlighting the issue. Most of the OECD and developing countries have specific plans to modify and upgrade their MR investments and planning, usually with an eye to economic competitiveness. China has the most aggressive program, Made in China 2025, which seeks to transform that country into a high-tech powerhouse that dominates industries like robotics, advanced information technology, aviation, and new energy vehicles. In this context, it can be argued that all MR in the United States should be viewed through the lens of the conflict between seeking mutual benefit through international sharing and cooperation on the one hand and maintaining or improving U.S. leadership positions on the other. Indeed, several findings of previous sections mention the need for action to maintain U.S. leadership.

Regarding cooperation, there is one area (in addition to climate change) for which there is a desperate need for international cooperation, and that is in problems related to the life cycle of materials. Most of the country reports in this section include some plans to study and confront these problems, and one might expect that international cooperation would be welcome. The problems of uncontrolled disposal of modern materials affect the whole planet. Plastic bottles and bags and the nanoscale particles

[45] See https://www.aps.org/publications/apsnews/201803/backpage.cfm, accessed July 5, 2018.

[46] See http://www.sciencemag.org/news/2018/06/more-restrictive-us-policy-chinese-graduate-student-visas-raises-alarm, accessed July 5, 2018.

that they break into, cover vast swaths of the oceans and are eaten by unsuspecting birds and fish, whose veins become clogged with nanoparticles.

5.6 FINDINGS AND RECOMMENDATIONS

Key Finding: Intense competition among developed and developing nations for leadership in the modern economic drivers, including smart manufacturing and materials science, will grow over the coming decade.

Key Recommendation: The U.S. government, with input from all agencies supporting materials research, should take coordinated steps beginning in 2020 to fully assess the threat of increased worldwide competition to its leadership in materials science and in advanced and smart manufacturing. The assessment program, which should be established on a permanent basis, should also define a strategy by 2022 to combat this threat.

Recommendation: Given that this competition is and will be a reality for the foreseeable future, the U.S. government, with input from all agencies supporting materials research, should take coordinated steps beginning in 2022 to define our priorities in materials science and engineering to continue high-quality research, facilitate economic development, and protect our intellectual property.

Finding: Countries across the globe have understood that materials science drives national economies, that competition to produce high-end products is ever increasing, and that only those countries that invest in materials research and development infrastructure will remain competitive in the world economy.

Recommendation: The U.S. government should fund and pursue a strategy-based permanent program of robust investment focused on materials science and smart manufacturing that will allow us to maintain our position as a world leader in materials science and not to fall behind our many competitors.

Finding: International scientific collaboration and science diplomacy is vital to U.S. success in fundamental and applied materials research. In some cases, scientists are forbidden to travel between countries. While many U.S. researchers understand how to protect sensitive material, with the increasing prevalence of cyber espionage, this understanding needs to be updated.

Recommendation: In order to maintain international collaborations, the United States must allocate funds to develop methods to educate our researchers on how to be vigilant in maintaining security both while traveling abroad and when welcoming international colleagues to the United States. Such education would also be crucial for maintaining industrial security within the United States.

Appendixes

A

Statement of Task

The Academies shall prepare a report that will articulate the status and promising future directions of materials research (MR) in the United States in the context of similar efforts worldwide. For this assessment, MR will be considered broadly in terms of material type, forms/structure, property, and phenomenon, as well as the full breadth of approaches to MR (e.g., experiment, theory, computation, modeling and simulation, instrument/technique development, synthesis, characterization, etc.). In particular, the report shall:

- Assess the progress and achievements in MR over the past decade;
- Identify the principal changes in the research and development landscape for MR in the United States and internationally over the past decade, and how those changes have impacted MR;
- Identify MR areas that offer promising investment opportunities and new directions for the period 2020-2030 or have major scientific gaps;
- Identify fields in MR that may be good candidates for transition to support by other disciplines, applied R&D sponsors, or industry;
- Identify the impacts that MR has had and is expected to have on emerging technologies, national needs, and science, broadly;
- Identify challenges that MR may face over the next decade in making the impacts identified in response to the previous bullet and offer guidance to the materials research community for addressing those challenges; and
- Evaluate recent trends in investments in MR in the United States relative to similar research that is taking place internationally by using a limited number of case studies of representative areas of MR that have either experienced significant recent growth or are anticipated to see significant near-term growth. Based on those trends, recommend steps the United States might take to either secure leadership or to enhance collaboration and coordination of such research support, where appropriate, for identified subfields of MR.

B

Town Halls

In addition to the questions to industry, and as a part of this decadal survey's connection with the different materials research communities, a set of nine town halls was conducted. These town halls were held in conjunction with some of the major societies associated with materials research and their main yearly meetings to enable a direct discussion with as many materials scientists in person as possible. During each town hall, anyone who attended the main event was also allowed to attend the town halls, which often were advertised not only in the meeting's main program but also with posters, postcards, flyers, and electronic media. A virtual town hall was also held in order to include the opinions of those scientists who were not available to travel to these events; this virtual opportunity was advertised by the National Academies Web pages. The function of these town halls was to gather additional input for the committee's discussions of the statement of task. The effect of the town halls has been to guarantee that many more voices could be heard than just the committee members' own. Each town hall consisted of an introduction to the survey and then continued with an item-by-item discussion of the statement of task among the attendees of what could be key considerations for the committee members to consider as they worked on the report. The town halls were led by National Academies staff together with available co-chairs and committee members who attend these specific society meetings regularly. The society meetings during which it was possible to hold town halls in 2017 were the Materials Research Society (spring and fall meetings); the American Chemical Society; the American Vacuum Society; the International Society for Optics and Photonics; the American Ceramic Society; the Optical Society; the American Physical Society; and the Minerals, Metals, and Materials Society. Each town hall lasted from an hour and a half to two hours. After the 10-minute introduction, the town halls were dominated by the discussion among the attendees—ranging from a handful to over 60 people—about key aspects that should not be forgotten as the committee considers the different facets of the statement of task. Each town hall was recorded and later transcribed, and the material was made available to the committee members who were not able to attend the specific town hall in person.

C

Committee and Staff Biographical Information

LAURA H. GREENE, *Co-Chair*, is the chief scientist at the National High Field Magnet Laboratory and the Francis Eppes Professor of Physics at Florida State University. Dr. Greene's research is in experimental condensed matter physics, investigating strongly correlated electron systems and focusing primarily on revealing the mechanisms of unconventional superconductivity by planar-tunneling and point-contact electron spectroscopies and growing and developing methods for predictive design of new superconductors. She is recognized for her work on superconductor/semiconductor proximity effects, elucidating the physical properties of pure and doped high-temperature superconductors (HTSs), the discovery of broken time-reversal symmetry in HTS, and spectroscopic studies of the electronic structure in heavy-fermion metals. Dr. Greene has been a visiting scientist at the National Center for Scientific Research (CNRS) in Orsay; University of California, Irvine; and Trinity College, Cambridge, and is a visiting distinguished professor at Seoul National University. Her various editorial positions include *Reports on the Progress in Physics* (editor-in-chief), *Philosophical Transactions A*, and *Current Opinions in Solid State and Materials Science*. Dr. Greene is a member of the National Academy of Sciences (NAS), and a fellow of the American Academy of Arts and Sciences, the Institute of Physics (UK), the American Association for the Advancement of Science (AAAS), and the American Physical Society (APS). She has been a Guggenheim fellow and has received the E.O. Lawrence Award for Materials Research from the U.S. Department of Energy (DOE), the Maria Goeppert-Mayer Award from the APS, and the Bellcore Award of Excellence. Dr. Greene has co-authored over 200 publications and has given approximately 500 invited talks.

TOM C. LUBENSKY, *Co-Chair*, is the Christopher H. Browne Distinguished Professor of Physics at the University of Pennsylvania. Dr. Lubensky is a theoretical condensed matter theorist with extensive research experience in phase transitions and critical phenomena, liquid crystals, soft matter physics (colloids, membranes, biological materials), and topological mechanics. He is a member of the NAS (Section 33 Chair, 2008-2011) and the American Academy of Arts and Sciences, a fellow of the APS and the AAAS, and an honored member of the International Liquid Crystal Society. He is a recipient of the 2004 Oliver E. Buckley Prize of the APS. Dr. Lubensky served as chair of the Department of Physics at the University of Pennsylvania from 2001 to 2009. He has served on numerous committees reviewing physics departments in the United States and in Korea; on the editorial boards of *Physical Review E*, *Annals of Physics*, and *Proceedings of the National Academy of Sciences*; as a member of the advisory board of the Kavli Institute for Theoretical Physics; and a member-at-large of the executive committee of the Divisions of Condensed Matter Physics of the APS. Dr. Lubensky is co-author with Paul Chaikin of a best-selling graduate textbook, *Principles of Condensed Matter Physics*.

MATTHEW V. TIRRELL is the founding Pritzker Director and Dean of the Institute for Molecular Engineering (IME), and the deputy laboratory director for science at Argonne National Laboratory (ANL). Before becoming founding director of the IME in 2011, Dr. Tirrell served as the Arnold and Barbara Silverman Professor and chair of the Department of Bioengineering at the University of California, Berkeley, and as professor of materials science and engineering and chemical engineering and

faculty scientist at Lawrence Berkeley National Laboratory. Prior to that, he was dean of engineering at the University of California, Santa Barbara. Dr. Tirrell began his academic career at the University of Minnesota as an assistant professor in the Department of Chemical and Materials Engineering and later became head of the department. He received his B.S. in chemical engineering from Northwestern University and his Ph.D. in polymer science and engineering from the University of Massachusetts. He specializes in the manipulation and measurement of the surface properties of polymers—materials that consist of long, flexible chain molecules—leading to new insight into polymer surface phenomena, such as adhesion, friction, and biocompatibility. Dr. Tirrell's honors include the Polymer Physics Prize of the APS; the Chevalier dans l'Ordre des Palmes Académiques (Ministry of Education of France); and the William H. Walker Award, the Charles M.A. Stine Award, and the Professional Progress Award, all from the American Institute of Chemical Engineers. Dr. Tirrell is a member of the National Academy of Engineering (NAE), the American Academy of Arts and Sciences, and the Indian National Academy of Engineering, and he is a fellow of the AAAS and the American Institute of Medical and Biological Engineering.

PAUL M. CHAIKIN is the Silver Professor of Physics at New York University (NYU). Prior to joining the faculty of NYU, Dr. Chaikin was a professor at the University of California, Los Angeles; University de Paris-Sud, Orsay; University of Pennsylvania; and Princeton University. He also worked as a research associate and consultant for Exxon Research and Engineering Company and the NEC Institute. His current research includes artificial systems that self-replicate and evolve, self-assembly and self-organization, active matter and driven systems, nanolithography with diblock copolymers, photonic noncrystals, and low-dimensional conductors and superconductors. Dr. Chaikin has published more than 300 articles in journals such as *Physics Review*, *Journal of Materials Science*, *Physical Review Letters*, *Journal of Physics*, *Nature*, and *Science*, and he co-authored the book *Principles of Condensed Matter Physics* with T.C. Lubensky (1995). Dr. Chaikin has served on the editorial boards of numerous refereed journals and has lectured at more than 200 meetings and at more than 200 universities and laboratories. He has also registered two patents. He received a Sloan Foundation fellowship and a John Simon Guggenheim Foundation fellowship. He is a member of the NAS and the American Academy of Arts and Sciences. He received his B.S. from Caltech in 1966 and his Ph.D. in physics from the University of Pennsylvania in 1971. Dr. Chaikin served as a member of several committees of the National Academies of Sciences, Engineering, and Medicine, including the Committee on Opportunities in High Magnetic Field Science (2003-2005); the Committee on an Assessment of and Outlook for the National Science Foundation (NSF) Materials research Laboratory Program (2005-2007); the Solid State Sciences Committee (2007-2010); and the Decadal Survey on Biological and Physical Sciences in Space: Fundamental Physics Panel (2009-2011).

HONG DING is a distinguished professor of the Institute of Physics (IOP), Chinese Academy of Sciences, and the managing director and chief scientist of Beijing National Laboratory for Condensed Matter Physics. Dr. Ding obtained his B.S. degree in physics from Shanghai Jiao Tong University in 1990 and his Ph.D. degree in physics from the University of Illinois, Chicago, in 1995. He was a postdoctoral fellow at ANL from 1996 to 1998. He joined the Department of Physics at Boston College as an assistant professor in 1998, became an associate professor in 2003, and became a full professor in 2007. He joined the IOP full time in 2008. Over the past 20 years, Dr. Ding has made important contributions to understanding high-temperature superconductors and topological materials using angle-resolved photoelectron spectroscopy. His major scientific achievements include the discovery of pseudogap in cuprate superconductors, first observation of s-wave superconducting gap in iron-based superconductors, and experimental discovery of Weyl fermions in solid-state materials. He has published more than 200 papers with a total citation number over 11,000 and H-index of 53, and he has given more than 90 invited talks in international scientific conferences. Dr. Ding received a Sloan Research Fellowship Award in 1999, was selected as one of the first "Thousand Talents Experts," and was elected an APS fellow in 2011.

KATHERINE T. FABER is the Simon Ramo Professor of Materials Science at the California Institute of Technology (Caltech). Dr. Faber's research interests include the fracture of brittle materials, toughening mechanisms, ceramic composites and coatings, porous ceramics, and cultural heritage science. Educated at Alfred University with a B.S. in ceramic engineering, she earned an M.S. in ceramic science at the Pennsylvania State University and a Ph.D. in materials science and engineering from the University of California, Berkeley. Prior to joining the faculty at Caltech in 2014, Dr. Faber was assistant and associate professor of ceramic engineering at the Ohio State University (OSU; 1982-1987) and associate professor, professor, and Walter P. Murphy Professor of Materials Science and Engineering in the McCormick School of Engineering at Northwestern University (1988-2014). Until 2016, she was co-director of the Northwestern University-Art Institute of Chicago Center for Scientific Studies in the Arts. Her administrative positions at Northwestern have included associate dean for graduate studies and research in the McCormick School and chair of the Department of Materials Science and Engineering. Among Dr. Faber's awards are the NSF Presidential Young Investigator Award, Distinguished Life Member of the American Ceramic Society (ACerS) and fellow of the American Society of Metals (ASM International), the Charles E. MacQuigg Award for Outstanding Teaching at OSU, the Society of Women Engineers Distinguished Educator Award, and the YWCA Achievement Award for Education. Dr. Faber is an ISI Highly Cited Author in Materials (2003), served as president of the ACerS (2006-2007), and was elected to the 2014 American Academy of Arts and Sciences class of fellows.

PAULA T. HAMMOND is the David H. Koch Professor in Engineering at the Massachusetts Institute of Technology (MIT). Dr. Hammond is a member of the MIT Koch Institute for Integrative Cancer Research, a member of the MIT Energy Initiative, and a founding member of the MIT Institute for Soldier Nanotechnology. She has recently been named the new head of the Department of Chemical Engineering. She is the first woman and the first person of color appointed to the post. She also served as the executive officer (associate chair) of the Chemical Engineering Department (2008-2011). Dr. Hammond was elected into the 2013 class of the American Academy of Arts and Sciences. She is also the recipient of the 2013 American Institute of Chemical Engineers Charles M.A. Stine Award, which is bestowed annually to a leading researcher in recognition of outstanding contributions to the field of materials science and engineering, and the 2014 Alpha Chi Sigma Award for Chemical Engineering Research. She received her B.S. in chemical engineering from MIT in 1984 and her M.S. from the Georgia Institute of Technology in 1988, and earned her Ph.D. in 1993 from MIT. Dr. Hammond has developed new biomaterials, including targeted nanoparticle drug carriers capable of delivering combinations of chemotherapy drugs, thin film coatings that release drugs from implant surfaces for tissue, and controlled release microneedle vaccines against infectious disease.

CHRISTINE E. HECKLE is the research director of the Inorganic Materials Research Division at Corning, Inc. Dr. Heckle is responsible for setting the materials research strategy and vision to deliver new materials to support next-generation products in glass and ceramics. She received her Ph.D. in glass science from Alfred University. Previously, she was research director, Crystalline Materials Research, where she led the development of new ceramic products to support the Environmental Technologies and Specialty Materials segments, as well as new business and exploratory arenas. Dr. Heckle joined Corning in 1997 in Corning specialty materials development. She then moved to environmental technologies to lead a variety of programs that introduced new products into the marketplace. Under her leadership, DuraTrap AT was expanded into the heavy-duty market, and two new product offerings were launched for the light-duty market. In 2012, Dr. Heckle won the inaugural R, D & E Leadership Award from National Organization for the Professional Advancement of Black Chemists and Chemical Engineers for her proven track record of producing results with an excellent use of emotional intelligence and people skills, as well as for being a key advocate and champion of diversity initiatives. Dr. Heckle is a member of SPECTRA, Corning's LGBT employee resource group, and ADAPT, Corning's employee resource

group for people with disabilities and those who care for people with disabilities. She mentors and coaches members of the Ethnically Diverse Group of Employees and the Society of Black Professionals.

KEVIN J. HEMKER is the Alonzo G. Decker Chair and Professor of Mechanical Engineering at Johns Hopkins University (JHU) and holds joint appointments in the Departments of Materials Science and Engineering and Earth and Planetary Sciences. Dr. Hemker joined the faculty at JHU in 1993, was an NSF National Young Investigator (1994) and an invited professor at the École polytechnique fédérale de Lausanne (EPFL, 1995) and the University of Paris XIII (2001), and received the ASM Materials Science Research Silver Medal in 2001. He served as chair of the Department of Mechanical Engineering (2007-2013), was editor of *Scripta Materialia* (2004-2011), and was a member and vice chair of the Defense Advanced Research Projects Agency (DARPA) Defense Science Research Council (2010-2015). He is currently a member of the Hughes Research Laboratories Technical Advisory Group and the SRI Technology Council, and is incoming vice president of The Minerals, Metals, Materials Society (TMS). Dr. Hemker has been named a fellow of the AAAS, the American Society of Mechanical Engineers (ASME), ASM International, and TMS. His group strives to elucidate the underlying atomic-level details that govern the mechanical response, performance, and reliability of disparate material systems including nanocrystalline materials, materials for microelectromechanical system, metallic microlattices, thermal barrier coatings, armor ceramics, extreme environments, and high-temperature structural materials in general. The results of this research have been disseminated in over 200 scientific articles, four co-edited books, and approximately 300 invited presentations and plenary lectures.

JOSEPH P. HEREMANS is an Ohio Eminent Scholar and a professor in the Department of Mechanical and Aerospace Engineering at the OSU. Dr. Heremans holds courtesy appointments in the Department of Materials Science and Engineering and in the Department of Physics of OSU. He joined OSU after a 21-year career at the General Motors and Delphi Research Laboratories, where his research resulted in three commercial products. His current research interests lie in materials for solid-state thermal-to-electric energy conversion technologies. This includes thermoelectric semiconductors and materials for thermal energy conversion based on thermally driven spin fluxes (spin-caloritronics). In thermoelectrics, Dr. Heremans pioneered the use of resonant levels in semiconductors to increase the figure of merit. In spin-caloritronics, the study of heat-driven spin currents that in turn drive electron currents, he is the lead author of a giant spin-Seebeck effect in InSb. His most current work aims at applying thermally driven spin fluxes in thermoelectrics to improve their ZT. Dr. Heremans holds 39 U.S. patents, three sets of which went into production. He is a member of the NAE and a fellow of the AAAS and the APS.

BARBARA A. JONES is a senior researcher who leads the theoretical and computational physics project at IBM's Almaden Research Center in San Jose, California. Dr. Jones received an A.B. degree in physics from Harvard University in 1982, followed by a year at Cambridge as a Churchill scholar. She earned M.S. and Ph.D. degrees in physics from Cornell University in 1985 and 1988, respectively. After postdoctoral research at Harvard University, she joined IBM at the Almaden Research Center in 1989. Dr. Jones has worked on a range of projects both fundamental and more applied, including managing experimentalists working on media and read heads, to theories of quantum wells and other effects in magnetic multilayers. Currently, she leads research to calculate the effects of magnetic atoms, in clusters or nanolattices, on metallic/insulating surfaces, as engineered and measured by scanning tunneling microscope. Among other distinctions, Dr. Jones was the 2001 recipient of a Tribute to Women in Industry Award and is currently the chair of the Division of Condensed Matter Physics of the APS, the chair and founder of the APS/IBM Research Internship for Undergraduate Women, past member and chair of the APS Committee on the Status of Women in Physics (1999-2002), and past chair of the IBM Almaden Diversity Council.

NADYA MASON is a professor of physics at the University of Illinois, Urbana-Champaign (UIUC). Dr. Mason received her bachelor's degree in physics from Harvard University and her Ph.D. in physics from

Stanford University. Before joining the Physics Department at the University of Illinois, Dr. Mason was a postdoctorate at Harvard, and then a junior fellow in the Harvard Society of Fellows. A condensed matter experimentalist, Dr. Mason's research focuses on how electrons behave in low-dimensional materials such as carbon nanotubes, graphene, and nanostructured superconductors. She is especially interested in the interplay between electron correlations and reduced dimensionality, as enhanced interactions in low dimensions are expected to create novel phenomena. Improved understanding of such systems is important for applications ranging from superconducting power lines to nanoscale electronic elements to quantum computers. Dr. Mason has received multiple awards for her work, including an NSF CAREER award and a Woodrow Wilson Career Enhancement Award, and she was honored as an "Emerging Scholar" by *Diverse Magazine* in 2008. In addition to her research and teaching, Dr. Mason is committed to increasing the numbers of under-represented people in the sciences.

THOMAS MASON is the senior vice president for laboratory operations at Battelle Memorial Institute. Previously, he was the director of Oak Ridge National Laboratory (ORNL). Dr. Mason graduated from Dalhousie University in Halifax, Nova Scotia, with a bachelor of science degree in physics, and completed his postgraduate study at McMaster University in Hamilton, Ontario, receiving a doctor of philosophy degree in experimental condensed matter physics. After completing his Ph.D., he held a postdoctoral fellowship at AT&T Bell Laboratories in Murray Hill, New Jersey, and then became a senior scientist at Risø National Laboratory in Denmark. In 1993, Dr. Mason joined the faculty of the Department of Physics at the University of Toronto. He joined ORNL in 1998 as scientific director for the DOE Spallation Neutron Source (SNS) project. In 2001, he was named associate laboratory director for SNS and vice president of UT Battelle, LLC, which manages ORNL for the department. In 2006, he became associate laboratory director for neutron sciences, leading a new organization charged with delivering safe and productive scientific facilities for studying of structure and dynamics of materials. In 2007, Dr. Mason was named director of ORNL, holding this post until his transition to Battelle. Dr. Mason has coauthored over 100 refereed publications describing experimental studies of novel magnetic materials and superconductors. As director of the largest science and energy laboratory in the DOE, he was focused on translating breakthroughs in fundamental science to applications relevant to energy technology and national security and the advantages to economic, environmental, and national security that will entail. Dr. Mason was named a fellow of the AAAS, the IOP, the APS, and the Neutron Scattering Society of America.

TALAT SHAHNAZ RAHMAN is a Pegasus Professor and Distinguished Professor of Physics at the University of Central Florida (UCF). Dr. Rahman's research interests focus in computational design of functional nanomaterials through microscopic understanding of their physical and chemical properties. A related interest is in multiscale modeling of chemical reactions and thin film growth processes. Apart from using density functional theory (DFT)-based methods as her workhorse, her group also works on techniques that go beyond DFT. Dr. Rahman's research is funded through grants from DOE and NSF. She is a fellow of the APS and the American Vacuum Society (AVS), and recipient of several professional awards including the Research Incentive Award from UCF, Alexander von Humboldt Research Prize, Higuchi Research Award from the University of Kansas, and the Distinguished Graduate Faculty Award, Kansas State University. She is engaged in establishing research initiatives in developing countries such as Pakistan. Dr. Rahman has published over 250 articles in high-impact journals and mentored over two dozen Ph.D. students. She has been engaged nationally and internationally in efforts to promote the participation of women and minorities (particularly through the Bridge Program of APS) in science, technology, engineering, and mathematics disciplines. She is also involved in pedagogical reforms in the teaching of physics and in the recruitment and training of students for careers in teaching through the APS PhysTEC program. Dr. Rahman is chair of the APS Topical Group on Energy Research and Applications (GERA) and member, executive committee, Surface Science Division, AVS. She also serves on the executive editorial board of the *Journal of Physics Condensed Matter and Progress in Surface Science*.

ELSA REICHMANIS is the Pete Silas Chair in Chemical and Biomolecular Engineering at the Georgia Institute of Technology. Prior to joining Georgia Tech, Dr. Reichmanis was Bell Laboratories Fellow and director of the Materials Research Department, Bell Labs, Murray Hill, New Jersey. She received her Ph.D. and B.S. degrees in chemistry from Syracuse University. She is a member of the NAE and the Latvian Academy of Sciences, and has received several awards for her work. Dr. Reichmanis has also been active in professional societies; she served as 2003 president of the American Chemical Society (ACS), and has participated in many National Academies activities. Her research, at the interface of chemical engineering, chemistry, materials science, optics, and electronics, spans fundamental concept to technology development and implementation. Her interests include the chemistry, properties, and application of photonic and electronic materials technologies. Dr. Reichmanis has contributed to the development of a molecular-level understanding of how chemical structure affects materials function, leading to new families of lithographic materials and processes for advanced very-large-scale integration (VLSI) manufacturing. Currently, her research relates to active, polymer, and hybrid organic/inorganic materials chemistries and processes for plastic electronics, photovoltaics, and photonic technologies.

JOHN L. SARRAO is the associate director for theory, simulation, and computation (AD-TSC) at Los Alamos National Laboratory (LANL). Dr. Sarrao received his Ph.D. in physics from the University of California, Los Angeles, based on thesis work performed at LANL. As AD-TSC, he leads the laboratory's efforts in applying science-based prediction to existing and emerging national security missions. TSC spans LANL's Theoretical; Computer, Computational, and Statistical Sciences; and High-Performance Computing organizations. Previously, Dr. Sarrao was the program director for the LANL Office of Science Programs, and for Matter-Radiation Interactions in Extremes (MaRIE), LANL's signature facility concept that will provide transformational materials solutions for national security challenges. Dr. Sarrao has held a number of leadership positions within LANL's materials community, including division leader of the Materials Physics and Applications Division and group leader of Condensed Matter and Thermal Physics. He has also served on a number of DOE Basic Energy Sciences Advisory Committee (BESAC) subcommittees, helping to set strategic directions for materials research. Dr. Sarrao's primary research interest is in the synthesis and characterization of correlated electron systems, especially actinide materials. He was the 2013 winner of the DOE E.O. Lawrence Award and the 2004 winner of the LANL Fellows Prize for Research, in part for his discovery of the first plutonium superconductor. He is a fellow of the AAAS, the APS, and LANL.

SUSAN B. SINNOTT is a professor and department head of materials science and engineering at Pennsylvania State University. Dr. Sinnott received her B.S. in chemistry from the University of Texas, Austin, and her Ph.D. in physical chemistry from Iowa State University. She was a National Research Council postdoctoral associate at the Naval Research Laboratory and was on the faculty at the University of Kentucky prior to joining the University of Florida in 2000. Dr. Sinnott's research is focused on the use of electronic structure calculations and atomistic simulations to optimize the processing and properties of materials. Her research interests include examining the chemical modification of polymer surfaces through mass-selected ion-beam deposition, exploring the dynamics associated with the growth of thin films, developing new methodologies for the atomistic simulation of materials, using atomic-scale simulations to study the catalytic behavior of metal clusters, investigating the molecular origin of friction and wear at interfaces, and combining electronic structure and thermodynamic calculations to predict defect formation in metal oxides. Dr. Sinnott is the author of over 160 technical publications, including over 140 journal publications and eight book chapters; she has also delivered over 120 invited presentations. She is a member of the AVS, the ACerS, the ACS, the APS, the Materials Research Society (MRS), and AAAS, and was named a fellow of AVS in 2005. She was named a fellow of ACerS in 2011 and a fellow of the AAAS in 2010.

SUSANNE STEMMER is a professor of materials at the University of California, Santa Barbara. Dr. Stemmer received her diploma in materials science from the Friedrich-Alexander University Erlangen-Nürnberg (Germany). She did her doctoral work at the Max Planck Institute for Metals Research in Stuttgart (Germany) and received her doctoral degree from the University of Stuttgart in 1995. Following postdoctoral positions, she held an assistant professor appointment in materials science at Rice University from 1999 to 2002. In 2002, she joined the University of California, Santa Barbara. Dr. Stemmer's current research interests include scanning transmission electron microscopy techniques, novel functional oxide thin films, molecular beam epitaxy, strong electron correlation phenomena, and topological materials. She has authored or co-authored more than 220 publications. Honors include election to fellow of the ACers, fellow of the APS, fellow of the MRS, fellow of the Microscopy Society of America, and a Vannevar Bush Faculty fellowship.

SAMUEL I. STUPP is Board of Trustees Professor of Chemistry, Materials Science and Engineering, Medicine, and Biomedical Engineering at Northwestern University. At Northwestern, Dr. Stupp directs the Simpson Querrey Institute for BioNanotechnology and the Energy Frontiers Research Center for Bio-Inspired Energy Science funded by DOE. Before coming to Northwestern in 1999, Dr. Stupp spent 18 years at UIUC, where in 1996 he became Swanlund Chaired Professor of Chemistry, Materials Science and Engineering, and Bioengineering. Dr. Stupp obtained his first degree in chemistry from the University of California, Los Angeles, in 1972, and his Ph.D. in materials science at Northwestern University in 1977. He was also assistant professor of biological materials at Northwestern from 1977 to 1980 before joining the faculty at UIUC. Dr. Stupp is a member of the NAE, the American Academy of Arts and Sciences, and the Spanish Royal Academy. He is a fellow of the APS, the Materials Research Society (MRS), and the Royal Society of Chemistry. His awards include the DOE Prize for Outstanding Achievement in Materials Chemistry, the MRS Medal Award, the ACS Award in Polymer Chemistry, the ACS Ronald Breslow Award for Achievement in Biomimetic Chemistry, the International Award from the Society of Polymer Science in Japan, and the Royal Society of Chemistry Award in Soft Matter and Biophysical Chemistry. He has received honoris causa doctorates from Eindhoven Technical University in the Netherlands, the University of Gothenburg in Sweden, and the National University of Costa Rica.

TIA BENSON TOLLE is the director of Advanced Materials, BCA Product Development. Prior to joining Boeing, Dr. Tolle held several technical and leadership positions at the Air Force Research Laboratory (AFRL) Materials and Manufacturing Directorate, and prior to that was a crew training instructor at NASA's Johnson Space Center. Dr. Tolle earned her B.S. in mechanical engineering from the University of Washington, and her M.S. and Ph.D. in materials engineering from the University of Dayton. She also holds a master's certificate in leadership and executive development from the University of Dayton and completed the Air Force Senior Leadership Development Course and Air War College Senior Leader Course from the Air University, Maxwell Air Force Base. Dr. Tolle is a fellow of the Society for the Advancement of Material and Process Engineering (SAMPE) and has been active in professional societies serving at several levels, including president of SAMPE, as well as president of the Materials Research Society (MRS). She is currently a member of the Condensed Matter and Materials Research Committee, a standing board of the National Academies; serves on Iowa State University's Aerospace Engineering and University of Washington's Materials Science and Engineering Industry Advisory Boards; and is a trustee for Edmonds Community College. Dr. Tolle is also Boeing's executive focal for SAMPE and for the University of Washington's Materials Science and Engineering Department, which enable her to help guide materials research and students toward future aerospace needs.

MARK L. WEAVER is a professor and interim department head at the University of Alabama in the Department of Metallurgical and Materials Engineering. Dr. Weaver has extensive experience in the characterization and development of materials for use in extreme environments. He holds Ph.D. and M.S. degrees in materials science and engineering from the University of Florida and a B.S. degree in metallurgical engineering from the University of Washington. He is an active member in several

professional societies, including TMS, where he is a member of the high-temperature alloys and mechanical behavior committees.

TODD YOUNKIN is the executive director of the Joint University Microelectronics Program (JUMP)—a $200 million, 5-year research initiative with support from DARPA and nine electronics companies representing both defense and commercial industries. Dr. Younkin received his Ph.D. in organometallic and polymer chemistry from the California Institute of Technology in 2001. His technical contributions have been in the areas of novel materials, integration, advanced lithography, and integrated photonics. With 16 years of research and development (R&D) experience spanning Intel's 0.18 µm-5 nm technology nodes, Dr. Younkin has held technical leadership roles in novel materials, integration, advanced lithography, and integrated photonics that have contributed to Intel's logic, memory, and networking products. Dr. Younkin has always looked to maximize the industrial relevance and impact of fundamental academic research. He spent 3 years (2010-2013) at IMEC to ensure that both extreme ultraviolet lithography (EUVL) and directed self-assembly (DSA) would graduate from "precompetitive, research" efforts into clearly defined internal development programs. More recently, Dr. Younkin has championed faster materials innovation following President Barack Obama's Materials Genome Initiative (MGI) by serving as a scientific advisor during the onset of the National Institute of Standards and Technology (NIST)-sponsored Center for Hierarchical Materials Design. In late 2015, he undertook an Intel Labs external assignment to the Semiconductor Research Corporation (SRC) to serve as the program manager for STARnet. STARnet is an approximately $40 million/year research effort focused on delivering novel beyond-complementary metal-oxide semiconductor (CMOS) hardware and architecture solutions. During that time frame, Dr. Younkin defined and created JUMP, a research program with DARPA, the defense industry, and commercial microelectronics sponsors. He is now the executive director of JUMP, a $200 million, 5-year research initiative. It will challenge and change the research paradigm to focus on heterogeneous electronic solutions for end-to-end sensing, signal and information processing, communication, computing, and storage to yield a smarter, autonomous future based on ubiquitous computing. Materials are a critical part of that future.

STEVEN J. ZINKLE is currently Governor's Chair Professor for Nuclear Materials at the University of Tennessee. Since 1985, Dr. Zinkle has held a series of research staff and management positions at ORNL. Dr. Zinkle received a B.S. degree in nuclear engineering, M.S. degrees in materials science and nuclear engineering, and a Ph.D. in nuclear engineering from the University of Wisconsin, Madison. Much of his research has utilized materials science to explore fundamental physical phenomena that are important for advanced nuclear energy applications. His research interests include deformation and fracture mechanisms in structural materials and investigation of radiation effects in ceramics, fuel systems, and metallic alloys for fusion and fission energy. Dr. Zinkle is a former recipient of the Robert Cahn Award and is a member of the NAE.

D

Acronyms

1D	one dimensional
2D	two dimensional
3D	three dimensional
4D	four dimensional
ABINIT	a computational software package
ACSR	Advanced Scientific Computing Research
ADAPT	Americans Disabled Attendant Programs Today
ADP	adenosine diphosphate
AFM	atomic force microscopy
AFOSR	Air Force Office of Scientific Research
AFRL	Air Force Research Laboratory
AHE	anomalous Hall effect
ALCF	Argonne Leadership Computing Facility
ALD	atomic layer deposition
ALS	amyotrophic lateral sclerosis
ALS-U	Advanced Light Source Upgrade
AM	additive manufacturing
AMTIR	a “glass-like” amorphous material that is able to transmit in the
ANL	Argonne National Laboratory
ANN	artificial neural network
APL	Applied Physics Laboratory
appm	atomics parts per million
APS-U	Advanced Photon Source Upgrade
APT	atom probe tomography
ARES	Autonomous Research System
ARO	Army Research Office
ARPA	Advanced Research Projects Agency
ARPES	angle-resolved photoemission spectroscopy
ASCR	Advanced Scientific Computing Research
BCS	Bardeen-Cooper-Schrieffer theory (named after John Bardeen, Leon Cooper, and John Robert Schrieffer)
BEPC II	Beijing Electron Positron Collider II
BES	Basic Energy Sciences (in DOE Office of Science)
BESAC	Basic Energy Sciences Advisory Committee
BMBF	German Ministry of Research
BMW	Bayerische Motoren Werke
BNL	Brookhaven National Laboratory (National Synchrotron Light Source II)
BRN	basic research needs

BSRF	Beijing Synchrotron Radiation Facility
CAD	computer-aided design
CALPHAD	Computer Coupling of Phase Diagrams and Thermochemistry
CARR	China Advanced Research Reactor
CAS	Chinese Academy of Science
CASTEP	Cambridge Serial Total Energy Package (a DFT software package)
CBRAM	conductive bridge RAM
CEA	French Alternative Energies and Atomic Energy Commission
CERN	European Organization for Nuclear Research
CFM	CFM International
CFRP	carbon-fiber reinforced polymer
CFRP	controlled free-radical polymerization
cGLP	Current Good Laboratory Practice
cGMP	Current Good Manufacturing Practice
CIF	Crystallographic Information File
CIGS	copper-indium-gallium-selenide
CLP	controlled, living polymerization
CMC	ceramic-matrix composite
CMI	Critical Materials Institute
CMOS	complementary metal-oxide semiconductor
CMP	chemical mechanical polishing
CNRS	Centre National de la Recherche Scientifique
CNY	China Renminbi
COHMAG	Committee on Opportunities in High Magnetic Field Science
CPS	Cyber-Physical Systems
cQED	circuit quantum electrodynamics
CRL	Collaborative Research Laboratory
CSM	Colorado School of Mines
CSNS	China Spallation Neutron Source
CSTI	Council for Science, Technology, and Innovation
CVD	chemical vapor deposition
DARPA	Defense Advanced Research Projects Agency
DCNS	Direction des Constructions et Armes Navales (now Naval Group)
DESY	Deutsches Elektronen-Synchrotron
DFG	German Research Foundation
DFT	density functional theory
DICTRA	diffusion module of computer code for Thermo-Calc
DMC	Diffusion Monte Carlo
DMFT	dynamical mean field theory
DNA	deoxyribonucleic acid
DOD	Department of Defense
DOE	Department of Energy
DOI	Department of Interior
DRAM	dynamic random-access memory
DREAM	software package for 3D data
DRIE	deep reactive ion etching
DSA	directed self-assembly
DSA	Digital Signature Algorithm
DSM	Dirac semimetal

DTMRC	Discovery to Translation Materials Research Center
DURIP	Defense University Research Instrumentation Program
EAGER	Early-Concept Grants for Exploratory Research
EBC	environmental barrier coating
EBSD	electron backscatter diffraction
EFM	electric force microscopy
EPA	Environmental Protection Agency
EPFL	École polytechnique fédérale de Lausanne
EPSRC	Engineering and Physical Sciences Research Council
ESF	European Science Foundation
ESnet	Energy Science Network
ESS	European Spallation Source
ETRI	Electronics and Telecommunications Research Institute
ETSF	European Theoretical Spectroscopy Facility
EuMaT	European Platform for Advanced Engineering Materials and Technologies
EUV	extreme ultraviolet
EUVL	extreme ultraviolet lithography
FA	formamidinium, a common component in some perovskites
FAIR	findable, accessible, interoperable, and reproducible
FCC	face-centered cubic crystal structure
FDA	Food and Drug Administration
FEFET	ferroelectric field-effect transistor
FERAM	ferroelectric RAM
FET	field-effect transistor
FIB	focused ion beam
FIRST	Funding Program for World-Leading Innovative R&D on Science and Technology (Japan)
FRM	Forschungs-Neutronenquelle Heinz Maier-Leibnitz-II, Garching, Germany
FRP	fiber-reinforced plastic
FS	Fermi surface
FTS	Spallation Neutron Source—First Target Station
GBRI	government-backed research institute
GDP	gross domestic product
GERA	Topical Group on Energy Research and Applications
GHG	greenhouse gas
GIWAXS	grazing-incidence wide-angle X-ray scattering
GPU	graphics processing unit
GRI	Global Reporting Initiative
GST	Goods and Services Tax
HEA	high-entropy alloy
HFIR	High Flux Isotope Reactor
HOMO	Highest Occupied Molecular Orbital
HPC	high-performance computing/computer
HSLA	high-strength, low-alloy
HTS	high-temperature superconductivity/superconductor
HVAC	heating, ventilation, and air conditioning

IARPA	Intelligence Advanced Research Projects Activity
IBM	International Business Machines Corporation
IBS	Institute for Basic Science
ICME	Integrated Computational Materials Engineering
ICME	International Council on Metals and the Environment
ICMSE	International Conference on Manufacturing Systems Engineering
ICT	information and communications technology
IEA	International Energy Agency
IEEE	Institute of Electrical and Electronics Engineers
IKTS	Fraunhofer Institute for Ceramic Technologies and Systems
IMPACT	Impulsing Paradigm Change Through Disruptive Technologies Program
IOT	Internet of Things
IP	intellectual property
IPCC	Intergovernmental Panel on Climate Change
IPO	initial public offering
IRT	infrared thermography
ISI	Institute of Scientific Information
ISIS	ISIS Neutron and Muon Source (a pulsed neutron and muon source; situated at the Rutherford Appleton Laboratory of the Science and Technology Facilities Council)
ISO	International Organization for Standardization
ISS	International Space Station
ITRS	International Technology Roadmap for Semiconductors
IVA	interactive visual analysis
JST	Japan Science and Technology
JUMP	Joint University Microelectronics Program
KAIST	Center for Catalytic Hydrocarbon Functionalizations
KBSI	Korean Basic Science Institute
KIMS	Korean Institute of Materials Science
KIST	Korean Institute of Science and Technology
KKR	Kernel Ridge Regression
KTN	Knowledge Transfer Network
LAMMPS	Large-Scale Atomic/Molecular Massively Parallel Simulator
LBL	layer by layer
LBNL	Lawrence Berkeley National Laboratory
LCA	life cycle analysis
LCD	liquid crystal display
LCLS	Linac Coherent Light Source
LEAP	leading-edge aviation propulsion
LED	light-emitting diode
LEGO	line of plastic construction toys manufactured by The Lego Group (the name LEGO is an abbreviation of the two Danish words *leg godt*, meaning "play well")
LELE	litho-etch-litho-etch
LGBT	lesbian gay bisexual transsexual
LIGO	Laser Interferometer Gravitational-Wave Observatory
LLZO	lithium lanthanum zirconium oxide
LUMO	Lowest Unoccupied Molecular Orbital
MA	methylammonium (a common component in some perovskites)

MaRIE	Matter-Radiation Interactions in Extremes
MatSEEC	Materials Science and Engineering Expert Committee
MAX IV	next-generation synchrotron radiation facility in Lund, Sweden
MBE	molecular beam epitaxy
MD	molecular dynamics
MDI	Materials Data Infrastructure
MEA	medium entropy alloys
MEMS	microelectromechanical system
METI	Ministry of Economy, Trade, and Industry
MEXT	Ministry of Education, Culture, Sports, Science, and Technology
MGI	Materials Genome Initiative
MII	Materials Innovation Infrastructure
MIM	metal-insulator-metal
MIP	Materials Innovation Platforms
ML	machine learning
MOF	metal organic framework
MOU	memorandum of understanding
MPEA	multiprincipal element alloy
MR	materials research
MRAM	magnetic random-access memory
MRI	Major Research Instrumentation
NAMII	National Additive Manufacturing Innovation Institute
NAND	negative-AND gate
NASA	National Aeronautics and Space Administration
NASEM	National Academies of Sciences, Engineering, and Medicine
NCFET	negative capacitance field-effect transistor
NCNR	NIST Center for Neutron Research
NEC	National English Center
NERSC	National Energy Research Scientific Computing Center
NGK	Nippon Tokushu Tōgyō Kabushiki-gaisha (a spark plug company in Japan)
NHMFL	National High Magnetic Fields Laboratory
NIH	National Institutes of Health
NIPA	N-isopropylacrylamide
NIST	National Institute of Standards and Technology
NMOS	n-channel metal-oxide semiconductor field-effect transistor
NMR	nuclear magnetic resonance
NNI	National Nanotechnology Initiative
NNSA	National Nuclear Security Administration
NOR	Boolean operator that gives the value one if and only if all operands have a value of zero and otherwise has a value of zero
NREL	National Renewable Energy Laboratory
NRI	Nanoelectronics Research Initiative
NSF	National Science Foundation
NSFC	National Science Foundation of China
NSRC	Nanoscale Science Research Centers
NSRL	National Software Reference Library
NST	National Research Council for Science and Technology
NTD	negative tone development
NV	nitrogen vacancy

OECD	Organization for Economic Cooperation and Development
OFET	organic field-effect transistor
OIL	open innovation laboratory
OLCF	Oak Ridge Leadership Computing Facility
OLED	organic light-emitting diode
ONR	Office of Naval Research
OPAL	Open-Pool Australian Lightwater Reactor
OPV	organic photovoltaic
OSTP	Office of Science and Technology Policy
PCA	principle component analysis
PCM	phase-change memory
PCRAM	phase-change random-access memory
PDMS	polydimethylsiloxane
PFM	piezoresponse force microscopy
PI	principal investigator
PLD	pulsed laser deposition
PMMA	poly(styrene-b-methyl methacrylate)
PMOS	p-channel metal-oxide semiconductor field-effect transistor
POSTECH	Center for Artificial Low-Dimensional Electronic Systems
PPU	Proton Power Upgrade
PRISMS	Predictive Integrated Structural Materials Science
PSI	Paul Scherrer Institute
PV	photovoltaics
QIS	quantum information science
QMC	Quantum Monte Carlo
R&D	research and development
RAM	random-access memory
RC	resistive-capacitive
RCA	root cause analysis
REACH	Registration, Evaluation, Authorization, and Restriction of Chemicals
RF	radio frequency
RNA	ribonucleic acid
ROI	return on investment
RRAM	resistive RAM
rRNA	ribosomal ribonucleic acid
RTI	Radical Technology Inquirer
SADP	self-aligned double patterning
SCI	Science Citation Index
SCM	scanning capacitance microscopy
SEM	scanning electron microscopy
SESAME	Synchrotron-Light for Experimental Science and Applications in the Middle East
SIP	Strategic Innovation Promotion Program
SKFM	scanning kelvin force microscopy
SLAC	SLAC National Accelerator Laboratory
SME	small and medium-size enterprise
SNAP	Spectral Neighbor Analysis Potential
SNS	Spallation Neutron Source

SOC	spin-orbit coupling
SPM	scanning probe microscopy
SQUID	superconducting quantum interference device
SRC	Semiconductor Research Corporation
SSRF	Shanghai Synchrotron Radiation Facility
SSRL	Stanford Synchrotron Radiation Lightsource
STEM	scanning transmission electron microscope
STEM	science, technology, engineering, and mathematics
STI	science, technology, and innovation
STM	scanning tunneling microscope
STS	Second Target Station
STT	spin-transfer torque
STT-MRAM	spin transfer torque magnetic random-access memory
SVM	support vector machine
TBC	thermal barrier coating
TCE	trichloroethylene
TDDFT	time-dependent density functional theory
TEKES	business, Finland
TEM	transmission electron microscope/microscopy
TFET	tunneling field-effect transistor
TI	topological insulator
TMD	transition metal dichalcogenide
TPS	thermal protection system
TRL	technology readiness level
TSC	theory, simulation, and computation
TSV	through-silicon vias
UCSB	University of California, Santa Barbara
UHMPWE	ultra-high-molecular-weight polyethylene
UNIST	Center for Multidimensional Carbon Materials
USAF	U.S. Air Force
USSR	Union of Soviet Socialist Republics
VAR	vacuum arc remelting
VASP	Vienna Ab Initio Simulation Package
VDOE	volumetric diffractive optical element
VIM	vacuum induction melting
VLSI	very-large-scale integration
WLP	wafer-level packaging
WOS	Web of Science
WSM	Weyl semimetal
YIG	yttrium-iron-garnet