Decadal Challenges for Predicting and Controlling Materials Performance in Extremes

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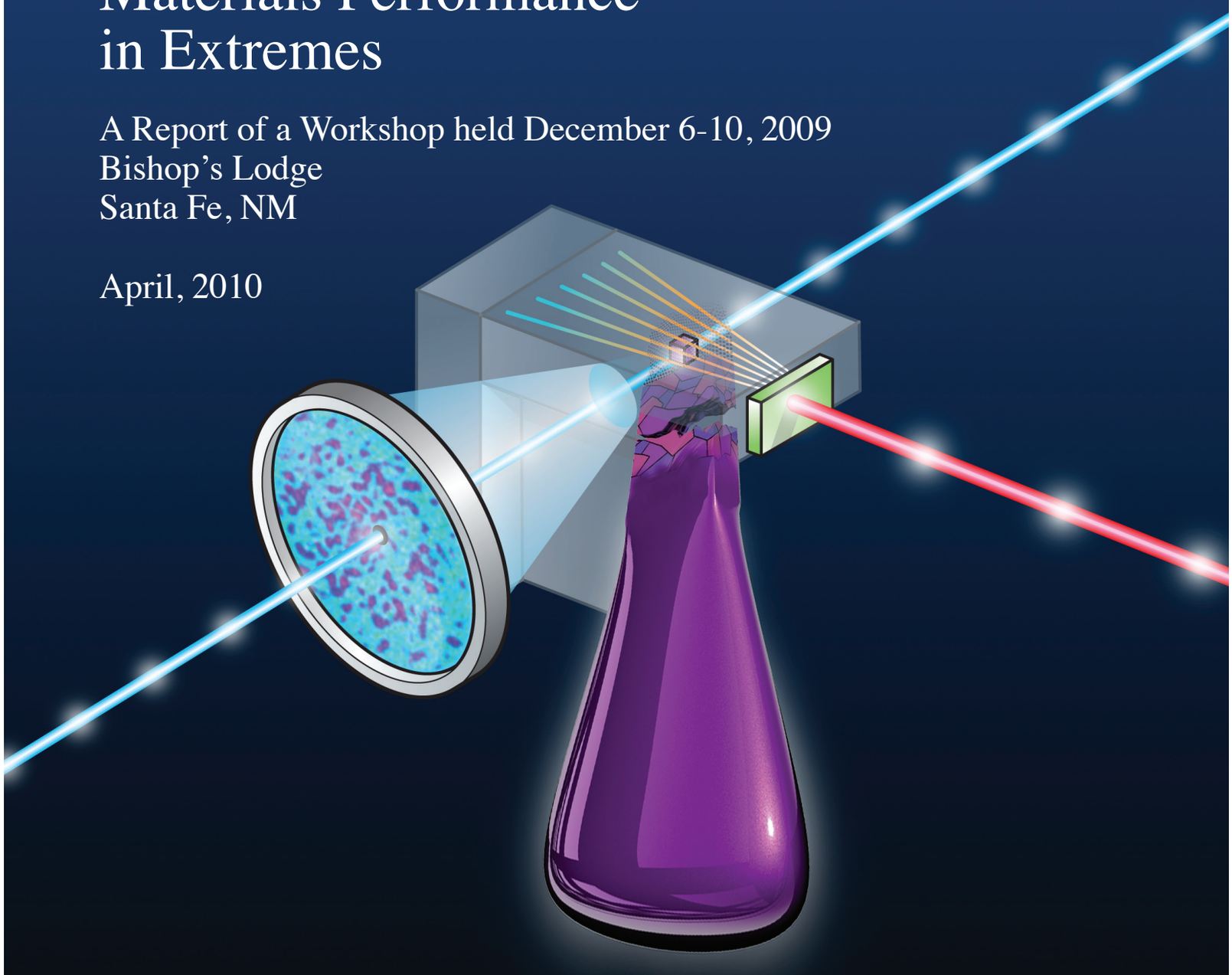

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Workshop Chair

John Sarrao, Los Alamos National Laboratory

Panel Leaders

Todd Allen, University of Wisconsin and Idaho National Laboratory

Robert Cauble, Lawrence Livermore National Laboratory

George Crabtree, Argonne National Laboratory

Tomas Diaz de la Rubia, Lawrence Livermore National Laboratory

Roger Falcone, Lawrence Berkeley National Laboratory

Paul Follansbee, St. Vincent's College

Rus Hemley, Carnegie Institution of Washington

Richard Lesar, Iowa State University

Malcolm McMahon, University of Edinburgh

Tony Rollett, Carnegie Mellon University

Steve Zinkle, Oak Ridge National Laboratory

LANL Workshop Steering Committee

Curt Bronkhorst

Micheline Devaurs

George T. "Rusty" Gray

Quanxi Jia

Jack Shlachter

Marius Stan

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Executive Summary

The performance of materials in extreme environments is central to a number of national security challenges, including especially the need for sustainable energy solutions. From fission & fusion energy to nuclear weapons to a broad suite of renewable challenges, a science-based approach to certifying materials performance for extended lifetimes is needed. The need to develop materials that perform in new and more extreme environments is also acute. Put simply, we lack sufficient confidence in the materials we have to reliably predict or extend their lifetime. Materials often fail at one tenth or less of their intrinsic limit and we do not know why.

There is great potential to change this reality. Materials research is on the brink of a new era of science in which the traditional approach of observation and validation of materials performance is replaced by prediction and control of materials functionality. Progress in this endeavor will enable a new generation of materials solutions from a more reliable nuclear stockpile to paths to higher efficiency clean energy technologies. The urgency of the challenge extends beyond the benefits from the envisioned end uses: the next generation of materials qualification facilities is presently being contemplated and designed with known materials. Near-term progress can yield smarter, more effective facility designs as well as higher performing materials.

Against this backdrop of urgent mission need and high scientific potential, a workshop of approximately 100 international leaders in materials research was convened in Santa Fe, New Mexico in December, 2009, to explore "Decadal Challenges in Predicting and Controlling Materials Performance in Extremes." While a number of recent workshops have recognized the challenge of materials in extremes, far fewer have focused on the means to meet this challenge. Therefore, the present workshop emphasized specifically needed capabilities and tools to seize the opportunity.

To achieve the vision of prediction and control of materials functionality, workshop participants recognized that a key grand challenge is the ability to predictively manipulate microstructures to achieve desired macroscopic performance. Central to this challenge is the potency of defects, either to be exploited intentionally for enhanced performance or to suffer their deleterious effects. The role of defects is a microcosm of the broader impact of rare events and fluctuations that are a key stumbling block in achieving prediction and control: the extremes of heterogeneity in a material dominate performance at the expense of the homogenous bulk. Considering only the time- and space-averaged properties of an "ideal" material is inadequate; the complexity of "real" materials must be embraced.

Further, while the era of 'cook and look' Edisonian materials discovery is largely behind us and 'directed serendipity' is a potent engine of materials discovery, there is a key difference between 'prediction and control' and 'more cooking' and 'more looking' or even 'looking while cooking.' The seamless integration of theory, observation, and synthesis is required to achieve desired functionality and accelerate materials discovery by design.

The vision of prediction and control will only be achieved through the development of in-situ, real-time, multi-probe “tools” (including advanced theories and information science and technology methods, high performance computing, advanced measurement capabilities, and controlled environments) to enable dynamic, in-situ measurements of real materials in real environments.

A final element of the challenge relates to the workforce required to achieve success. Predictive control of materials functionality lies at the boundary between ‘science’ and ‘engineering’ and requires the integration of multi-disciplinary teams that span traditional ‘chemists’, ‘materials scientists’, ‘physicists’, etc. This approach necessitates broader education and training for materials researchers in which the focus is not structure→ property relationships, but rather property→ structure relationships.

In the end, workshop attendees enthusiastically concluded that achieving the grand challenge of prediction and control of materials performance in extremes was within our reach. The workshop helped to identify a roadmap of capability gaps that need to be addressed. This report documents the fruits of those efforts.

Introduction

The performance of materials in extreme environments is central to a number of national security challenges, including especially the need for sustainable energy solutions. From fission & fusion energy to nuclear weapons to a broad suite of renewable challenges, a science-based approach to certifying materials performance for extended lifetimes is needed. The need to develop materials that perform in new and more extreme environments is also acute. Put simply, we lack sufficient confidence in the materials we have to reliably predict or extend their lifetime. Materials often fail at one tenth or less of their intrinsic limit and we do not know why.

There is great potential to change this reality. Materials research is on the brink of a new era of science in which the traditional approach of observation and validation of materials performance is replaced by prediction and control of materials functionality. Progress in this endeavor will enable a new generation of materials solutions from a more reliable nuclear stockpile to paths to higher efficiency clean energy technologies. The urgency of the challenge extends beyond the benefits from the envisioned end uses: the next generation of materials qualification facilities is presently being contemplated and designed with known materials. Near-term progress can yield smarter, more effective facility designs as well as higher performing materials.

At present we lack a sufficient multi-scale understanding of component performance and failure to enable process-aware control of materials functionality. Central to this challenge is bridging the gap from first-principles, atomic-scale understanding to integrated bulk phenomenology; the manipulation and control of defects and interfaces on intermediate spatial and temporal scales is a key opportunity. The role of theory, modeling, and computation plays a central role. Recent advances in computational power enable multi-scale modeling and "co-design," the simultaneous interplay and optimization of theory, experiment, and computation. For materials research, the frontier of co-design is a material's microstructure – to be measured, modeled, and simulated at common spatial and temporal resolution.

The purpose of this report, and the workshop from which it is derived, is to identify the scientific challenges and research directions to achieve predictive materials performance in extreme environments, focusing specifically on needed capabilities and tools. Approximately 100 researchers from across the international materials community, spanning domestic and international universities, national laboratories, and industry gathered in Santa Fe, New Mexico in December, 2009, to address this challenge. Specifically, the workshop emphasized research needs in the areas of radiation-matter interactions for fission and fusion, radiation-matter interactions for energy conversion, and matter interactions in extremes. Building on previous studies by e.g., DOE's Office of Science, Office of Nuclear Energy, and National Nuclear Security Administration (NNSA) (see e.g., **Basic Research Needs for Materials under Extreme Environments**, http://www.science.doe.gov/bes/reports/files/MUEE_rpt.pdf**)**, workshop participants identified a series of priority research directions and the capabilities required to achieve success.

The workshop began with a series of plenary talks framing the mission challenge. George Crabtree from Argonne National Laboratory, Stuart Maloy from Los Alamos National Laboratory, Steve Zinkle from Oak Ridge National Laboratory, and Robert Hanrahan from NNSA discussed materials challenges for renewable energy, fission energy, fusion energy, and nuclear weapons, respectively. While the breadth of the challenges presented was exceptional, the common need to predict and control materials in extremes was clear and universal.

The work of translating this common vision to actionable priority research directions (PRDs) was done in four pairs of breakout panels. The charge for each panel (the titles of which are italicized) is given below:

Radiation Matter Interactions for Fission and Fusion

Extreme-environment tolerant materials by design: The need for higher performing materials in the extreme environments of advanced fission and fusion reactors is well documented. Approaches that accelerate the transition from the observation and validation of performance to the prediction and control of functionality through materials discovery and science-based certification remain grand challenges.

*"Watching damage happen:"*A particular challenge is the ability to make (and model/interpret) real time, in situ measurements of relevant phenomena in irradiation environments of interests and thereby advance fundamental understanding and predictability beyond 'cook and look' approaches.

Radiation Matter Interactions for Energy Conversion

Materials discovery and processing for advanced functionality: The need for predictive design, discovery, and growth of new materials, especially single crystals, to achieve advanced functionality is a grand challenge. Further, exploiting the full suite of synthesis, fabrication, and processing capabilities is essential if we are to discover by design next generation materials and enable the transition from observation to control.

"Making every photon count:" Translating quantum phenomena that arise uniquely on the nanoscale to bulk performance requires a predictive understanding of interface and microstructre effects that limit integrated efficiency and system lifetime that are central to achieving the full potential of advanced functional materials.

Matter Interactions in Extremes

Process aware material certification in extremes: In recent years it has become increasingly clear that how an extreme material is formed (not only the fabrication/processing techniques that created an initial structure and microstructure but also the path through phase space the material traversed to reach a given extreme condition) directly affects performance. Key challenges include rate dependence and path dependence of irreversible and kinetic processes.

"When solids stop being solids:" At sufficiently high temperature and/or energy density, solids become plasmas. In particular, warm dense matter is an important crossover regime characterized by inhomogeneities that derive from the consequences of materials failure, plasma-solid interactions, and associated turbulent phenomena.

Cross-cutting Challenges

Enabling the transition from observation to control: A true predictive understanding of materials performance would allow us to faithfully extrapolate performance beyond regions of experimental validation and would reveal the design principles that accelerate the discovery of higher performing materials in these extremes. Such a realization of 'materials by design' is presently beyond our reach, but key insights are being made. The means to accelerate this progress are an important focus area.

Bridging multiple scales in space and time: Current petascale computers and advanced algorithms are enabling the largest simulations ever performed. However, the frontier of multi-scale modeling remains achieving an experimentally validated predictive understanding that spans spatial and temporal scales in an integrated framework, moving beyond the passing of parameters between distinct models.

The panel topics described above were deliberately overlapping, and as a result, much cross-fertilization of ideas and workshop participants occurred. In particular, the 15 priority research directions (PRDs) that emerged from the worskhop do not necessarily derive from a specific panel.

As one specific example, the panel on *Materials discovery and processing for advanced functionality* initially identified four priority research directions:

1. Materials design and lifetime prediction (focus on materials design)
2. Rapid materials design and synthesis (focus on synthesis)
3. Corrosion science under extreme environments (fundamentals of corrosion)
4. Controlling nucleation phenomena (nucleation as a key barrier to materials design)

The first two represented high-level research direction assessments, while the second two represented more specific topics that have not received the same attention as the first two but which were considered to be critical shortcomings of the current state of "predictive design, discovery, and growth of new materials."

Nucleation, for instance, is a fundamental process step contributing to – if not in some cases controlling – many microstructural development and failure processes. Fatigue fracture and phase transformations are largely controlled by nucleation. Yet, the theory of nucleation, in the case of phase transformations or solidification, has advanced little beyond that contained within

the Johnson–Mehl–Avrami–Kolmogrov equation of the 1940s. Innovative measurements of nucleation events – particularly using transmission electron microscopy and small-angle neutron scattering – are emerging but presently lack both the spatial and temporal scales necessary to understand the fundamentals of nucleation. Higher resolution measurements are required both to validate theories and to spawn new theoretical studies.

Corrosion science also has achieved somewhat of a plateau in advancement. Yet materials performance in extreme, corrosive environments is of paramount importance to many energy applications. Panelists questioned whether this plateau was defined by the limitations of available characterization tools. Advances in spatially and temporally resolved measurements and in coupled models could move the field beyond this plateau, especially for understanding corrosion in extreme environmental conditions.

Comparison of initial PRDs among the eight panels showed many common themes. The panel on *Extreme-environment tolerant materials by design:* also identified a corrosion-related PRD, entitled "materials design for resistance to corrosion under irradiation" with obvious overlap with PRD #3 above. What resulted was an integrated PRD on "Materials design for resistance to corrosion and surface damage in extreme environments." Similarly, "rapid materials design and synthesis" is synergistic with "accelerating materials discovery". On the one hand, there was a focus on reigniting the capability to synthesize materials – particularly test specimens – for new materials discovery, while on the other is a need for enhanced design and combinatorial tools to accelerate materials discovery.

In what follows, brief summaries of each of the four focus areas (radiation-matter interactions for fission and fusion, radiation-matter interactions for energy conversion, matter interactions in extremes, and cross-cutting challenges) are presented. As illustrated above, the breadth and diversity of these deliberations ultimately gave rise to a set of 15 priority research directions, spanning the full range of the workshop. The report ends with a conclusion that summarizes the main messages of the workshop. Workshop participants agreed unanimously that focused effort on these priority research directions, including the development of capabilities needed to achieve success, would significantly advance our ability to predict and control materials performance in extremes.

Panel Summary: Radiation Matter Interactions for Fission and Fusion

The reliable performance of structural and fuel materials is central to extending the life of the current fleet of light water reactors and enabling the next generation of fission and fusion reactors. Experimentally-validated, multi-scale models are a key ingredient to realizing this potential. Capabilities are needed to expose materials to well characterized and controlled, extreme environments and simultaneously probe, measure, and manipulate interfacial reaction kinetics, transformations, and mechanisms associated with their performance.

The Importance of Material Performance to Nuclear System Performance

Adequate response to the significant demands on fuel and structural materials is critical to the performance of any nuclear system, either fission or fusion based. Improvements in materials science and technology will support the continued safe performance and extended lifetimes of existing light water reactors, enable building of new extended life light water reactors, advanced fission concepts, or fusion-based systems, and support a sustainable full recycle fuel cycle [1-3].

Currently, 432 light water reactors (LWR) generate 382 GWe, or about 16% of worldwide electricity demand. Doubling worldwide nuclear electricity production to 32% by 2100 will require generating about 5000 GWe, or about 4000 reactors worldwide. To take advantage of the existing LWR infrastructure in the United States, many reactor operators plan on extending the life of existing light water reactors to 60 and possibly 80 years. Operations to these extended times present challenges to materials, specifically degradation of thermo-mechanical properties and extended corrosion attack, requiring an accurate forecast of material properties beyond the current understanding. The ability to accurately forecast behavior is integrally linked to the scientific underpinnings of both radiation and corrosion material science.

In current LWR technology, <12% of the initial natural uranium is used in a reactor. The rest of the material and its associated potential nuclear energy content are relegated to nuclear waste. Existing spent nuclear fuel from LWRs could supply 75 TWe-yrs, which represents the entire U.S. electricity demand from now through 2100. A goal and a challenge are to more fully extract the energy content of nuclear fuel, thus minimizing both nuclear waste and proliferation concerns. The barrier is, to a large extent, directly related to the materials used to contain the fuel—the cladding and its robustness to the higher neutron dose concomitant with higher fuel burn-up in the fast reactor systems envisioned as the heart of a full recycle fuel cycle. To enable increasing burnup of fuels from 20 to 40% in a fast spectrum requires the development of new cladding materials. These new materials must withstand many degradation mechanisms including irradiation creep, low temperature embrittlement, void swelling, and fuel clad chemical interaction to doses up to 400 displacements per atom (dpa). Longer-lasting fuel and structural materials will make it possible to extract more energy from the fuel, reduce nuclear waste, advance the nation's nonproliferation goals, and improve our confidence in the long term safety of the nation's reactor fleet.

The Challenge of Predicting Material Performance in Nuclear Systems

The combined irradiation field and high temperatures under which nuclear systems operate can lead to changes in toughness, strength, ductility, fatigue, and creep resistance that shrink the allowed temperature and stress in which materials performance is adequate (Figure 1). Additionally, in a corrosive environment, materials can be attacked, leading to cracking and mass loss. The specific effects depend on the exact combination of temperature, stress, irradiation flux, and environment (corroding media), Figure 2. It is not possible to do experiments that simulate 80-years of irradiation damage and corrosion in a practical time frame. Approaches that accelerate the transition from the observation and validation of performance to the prediction and control of functionality through materials discovery and science-based certification remain grand challenges. A particular challenge is the ability to make (and model/interpret) measurements of relevant phenomena in irradiation environments of interest and thereby advance fundamental understanding and predictability beyond traditional approaches. Therefore, materials scientists will need to rely on theory, simulation, and modeling, validated by well-posed experiments to predict material behavior. As presented in Figure 3, this theory, simulation, and modeling must

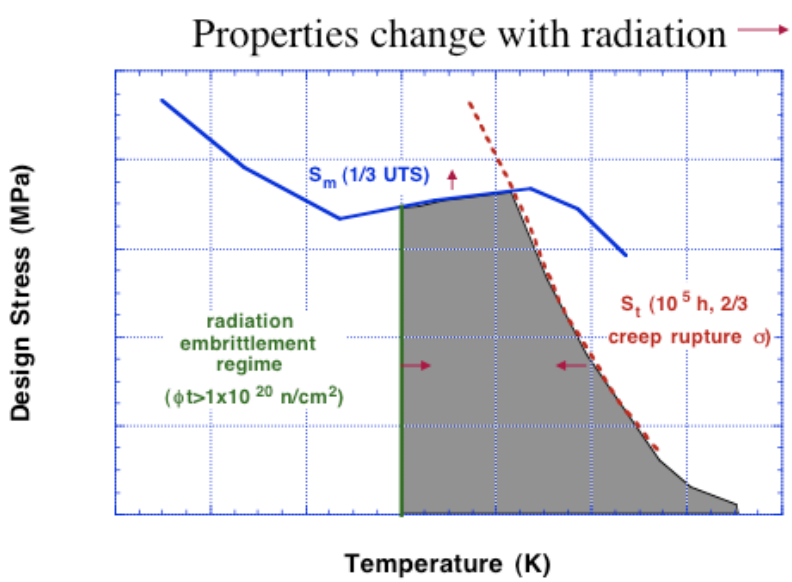

Figure 1. Each material has properties that allow it to be used in certain temperature and stress ranges and these are changed by irradiation. (Adapted from [4])

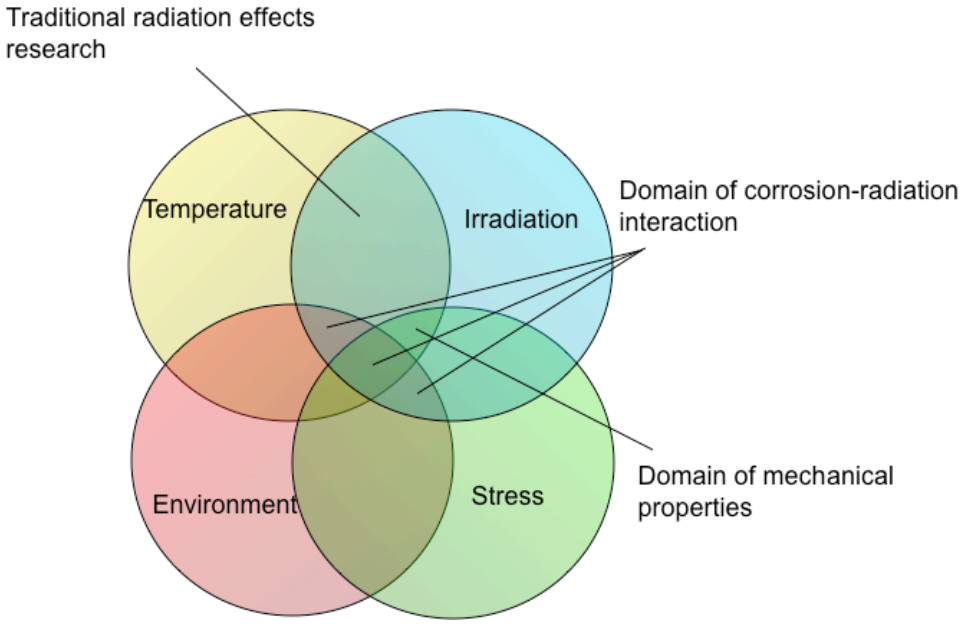

Figure 2. Radiation effects are a unique combination of temperature, stress, irradiation, and environment.

be developed on three general scales: 1) bulk material properties (strength, corrosion resistance, thermal conductivity, dimensional stability), 2) microstructure, and 3) atomic-scale unit processes. Information from the atomic-scale processes is required to understand the development of microstructures and the specifics of the microstructures determine the bulk properties. Developing the ability to predict and control the material response at each level would allow for the extrapolation of material properties beyond the existing database and control of materials properties through informed design.

As an example, void swelling is a dimensional change that occurs under radiation at intermediate temperatures (roughly 30-50% of the melting temperature of a material) -- Figure 4, left image-- and must be managed either through material replacement or material improvements. The amount of swelling is controlled by microstructural developments, specifically the nucleation and growth of voids and dislocation loops, at the mesoscale, (Figure 4, right image). Accurate prediction of the microstructural development requires a knowledge of many key processes that occur at the atomic level including the creation of radiation-produced point defects, transport of defects and atoms through the material, nucleation and growth of mesoscale defects, and interactions with sinks, as shown schematically in Figure 5 for the phenomena of radiation embrittlement and stress corrosion cracking. Understanding many of the phenomena shown in

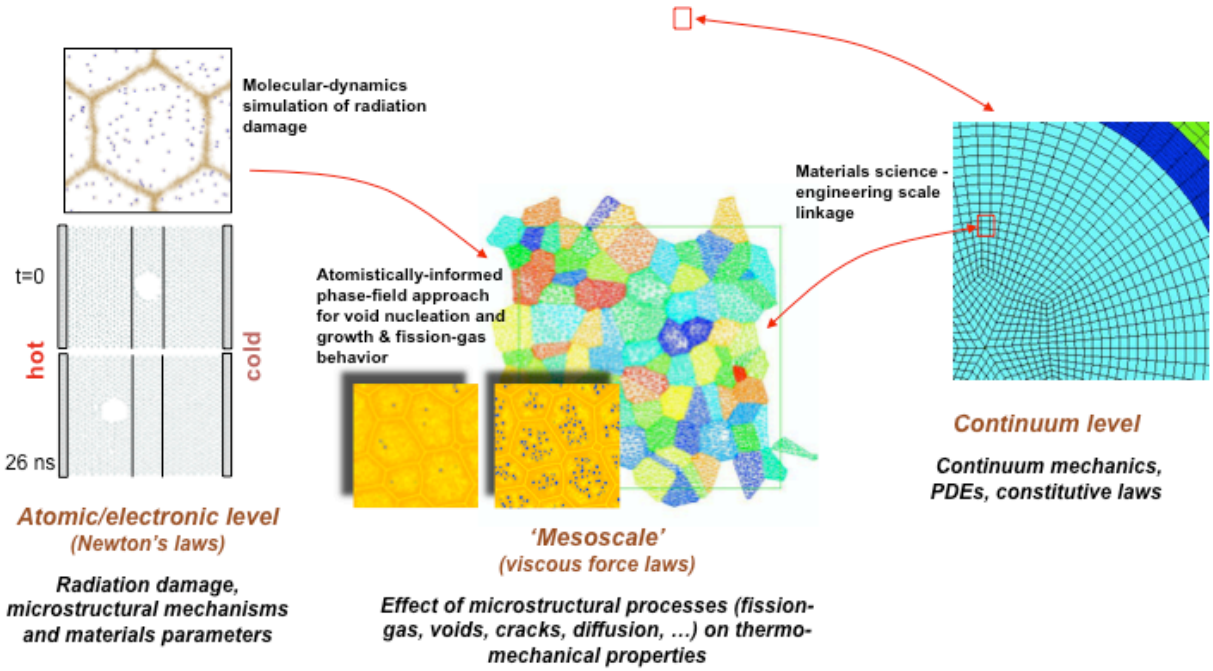

Figure 3. Material properties (continuum level) are determined by microstructural features (mesoscale), which form due to interactions at the atomic and electronic level.

Figure 5, such as point defect and atomic transport and radiation-induced segregation, is also critical in predicting other radiation-induced effects such as creep or void swelling.

For example, experiment and modeling have shown that void growth can be changed by radiation-induced segregation to the void surface and that radiation-induced segregation in austenitic iron-base materials is a strong function of bulk composition [5,6]. Therefore, to properly model radiation-effects requires understanding how structure, composition, and strain affect activation barriers in non-dilute, multi-component, crystalline solids. This is necessary to determine the complex interplay between structure and composition. Critically, all these atomic-scale effects (unit processes) occur concurrently, so establishing methods for understanding the concurrent development of many unit processes is critical to understanding the microstructure and thus bulk properties. Material solutions need to be designed to control deleterious radiation response.

One possible design to control radiation response is the use of selected interfaces to mitigate radiation damage [7-10]. Interfaces with low formation energy of vacancies and interstitials, high excess atomic volume and high density of misfit dislocation intersections are expected to be good sinks for radiation-induced defects. Thus, it should be possible to design materials with a high density of special "super-sink" interfaces to have a tailored response in extreme conditions of irradiation, stress and temperature.

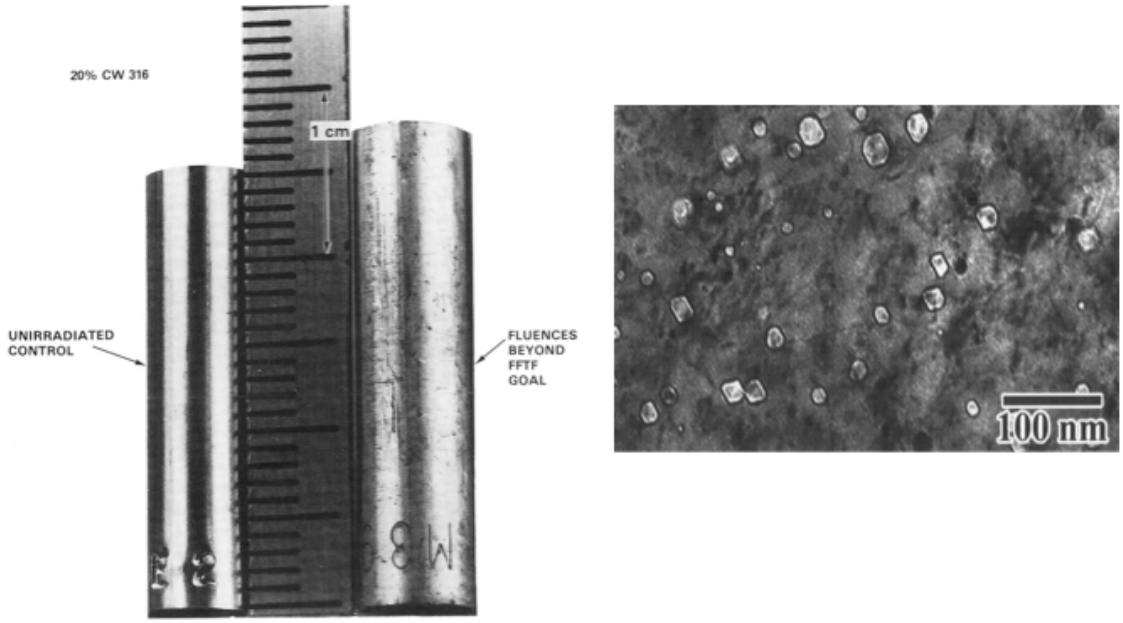

Figure 4. Swelling of an irradiated material (left image) and the underlying microstructure, a collection of voids (right image), which lead to the swelling. (After [11].)

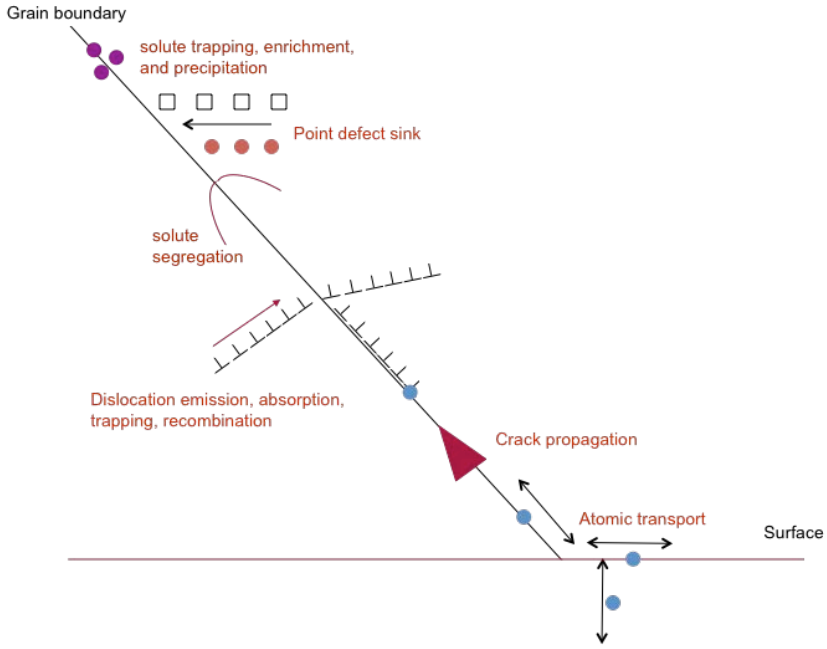

Figure 5. Many atomic scale interactions occur that lead to changes in microstructure [1].

Tools for Studying Radiation Matter Interactions for Fission and Fusion

Capabilities are needed to expose materials to well characterized and controlled, extreme environments and simultaneously probe, measure, and manipulate interfacial reaction kinetics, transformations, and mechanisms associated with their performance. These data and tools are essential to replacing empirical and database driven predictive models with knowledge-based models for design, prediction and control of performance, and prognostic health monitoring of materials targeted for use in extreme environments.

Unit processes, such as defect-interface interactions, strongly influence the material properties and irradiation stability of materials. For example, interfaces block slip and lead to unusually high strengths in materials with nanometer-scale spacing of interfaces. Interfaces also act as sinks for radiation-induced point defects and impurity atoms such as helium. The atomic structure of the interface is crucial in determining the number density of sites that are traps for defects and the formation energy of point defects at interfaces.

Understanding either a unit process or collective effect requires the proper tools to interrogate the proper length and time scale. Observation in-situ could significantly improve the ability to observe effects like defect production, diffusion, and nucleation. Recent advances in capability are greatly improving the ability to provide quantitative information on smaller length and time scales [12].

While many radiation effects of concern are initiated by collision between lattice atoms and high-energy neutrons, a significant amount of radiation damage in solids occurs between charged particles. Atom-atom collisions in damage cascades or interactions with fission products are two examples. Additionally, radiation interactions in liquid media can also be initiated from high-energy photons (gamma particles). Therefore, an understanding of radiation effects requires multiple tools, including test reactors, ion and electron beam facilities, and photon sources.

Typical neutron irradiation experiments in test reactors require 1-2 years of exposure in core. However, this is accompanied by additional time for capsule design and preparation as well as disassembly and cooling. Analysis takes additional time because of the precautions and special facilities and instrumentation required for handling radioactive samples. The result is that a single cycle from irradiation through microanalysis and property testing may take between 1 and 6 years. Such a long cycle length does not permit for rapid iteration on irradiation or material conditions that is a critical element in any experimental research program. Neutron irradiation is a necessity but scientific understanding can be accelerated through the complimentary use of ion beam, electron beam, and photon techniques.

In contrast to neutron irradiation, ion (heavy ions, light ions or electrons) irradiation frequently enjoys considerable advantages in both cycle length and cost. Ion irradiations of any type rarely require more than a few tens of hours to reach 1-5 dpa levels. Irradiation produces little or no residual radioactivity allowing handling of samples without the need for special precautions.

These features translate into significantly reduced cycle length. Ion irradiations can often be performed at a much lower cost per sample and in a much faster irradiation and analysis time The single energy beam energy is also suitable for controlled experiments to determine an understanding of unit effects.

The capabilities of ion irradiation, including in-situ techniques such as transmission electron microscopy, sliced pulses from synchrotron light sources, or optical techniques such as luminescence, are currently attractive in research on nuclear materials including advanced structural alloys (model and engineering), waste storage ceramics and glasses, and model fuel alloys. A strength of in situ work is the discovery and illumination of fundamental dynamic processes such as point defect clustering, dislocation loop formation, loop motion, coalescence and interactions with existing surfaces, interfaces, and microstructure, all processes that need to be understood in moving toward predictive capability of radiation stability. Additionally, ion beam techniques can be credibly adapted to include the study of synergistic interactions between radiation and environment (corrosive media in a light water reactor or plasma in a fusion system).

Additionally, there are certain cases where the phenomena of interest are the ion-matter interactions directly. For example, nuclear fuel is exposed to damage from fission fragments. These heavy projectiles with typical energy of 100 MeV produce radiation damage (tracks) that has significantly different characteristics compared with defects produced by neutrons or low-energy ions in the elastic collision regime. The interaction is based on pure electronic excitation processes. Tracks formed predominantly in insulators (and only in a few selected metals) consist of amorphized or otherwise modified extended damage structures. Heavy-ion irradiations could help to overcome the existing challenge of limited dose accumulation data. However, a better understanding of common effects and differences in resulting defect phenomena of swift heavy ions compared to neutron and low-energy ions is mandatory.

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Panel Summary: Radiation Matter Interactions for Energy Conversion

The success of future energy technologies demands materials with significantly higher performance and functionality. The limits of today's materials are not imposed by intrinsic constraints: performance is often a factor of ten below theoretically possible levels. Instead, materials are limited by our knowledge and control of the structural and electronic features that govern their behavior.

The multi-scale challenge

Although performance and functionality are manifested at macroscopic length scales, their roots reach down to the microscopic and nanoscopic domains. Macroscopic behavior is the visible outcome of a hierarchical network of structure and dynamics that spans multiple length and time scales. Our ability to understand macroscopic behavior, therefore, is ultimately dependent on our ability to observe and connect the links in the hierarchical chain of structure and dynamics starting with atoms and femtoseconds and ending with macroscopic properties like mechanical elasticity, electrical conductivity, and optical transparency.

The past decade has seen remarkable advances in the resolution and sensitivity of experimental probes of structure and dynamics, to the point that we can now imagine observing the key links in the hierarchical chain relating macroscopic behavior to its micro- and nano-scopic origins. Such observations of the development of electronic and structural behavior at each length and time scale would mark an enormous leap toward understanding macroscopic performance and functionality.

There are, however, vital elements that remain to be implemented. Much of our observational information comes from "before and after" measurements, where we must infer a dynamic process from snapshots capturing static structure at isolated times. Often the snapshots must be taken under prescribed laboratory conditions that do not reflect the actual temperature or other environmental conditions that are central to the process. We need instead in situ measurements that watch the dynamics of the process in real time (i.e., “during” measurements), revealing the evolutionary pathways and the causal relationships that mediate them.

A second vital element is bridging the gap between length scales. For example, the propagation of light as a surface plasmon at a metal-dielectric interface is governed by interfacial structure on the scale of the wavelength, where the atomic composition and structure are invisible. Similarly, a new macroscopic phase develops from a few microscopic nucleation sites, whose structure and dynamics are lost quickly as the new phase emerges. To be comprehensive, the output of theoretical descriptions and experimental probes for each of the relevant length scales must be interpreted within an intellectual framework connecting behavior at each scale to the neighboring scales above and below.

Dramatic advances in in situ observational tools and theoretical models linking length and time scales bring within reach a full understanding of the hierarchical chain linking macroscopic performance and functionality with micro- and nano-scopic structure and dynamics. Observation and understanding are not enough, however. To create new materials with superior performance and functionality we must make the transition from observation and understanding to prediction and control. This transition is achievable, using the advances in nanoscale fabrication of the last decade. Molecular beam epitaxy, atomic layer deposition, high-resolution lithography and directed self-assembly allow exquisite control of atomic and nanoscale architectures. Extreme environments such as high pressure, high flux irradiation with photons or particles, and high chemical corrosivity offer new levels of control over bulk synthesis of crystalline and disordered materials. Linking prediction based on in situ observation and understanding with control based on nanoscale fabrication and synthesis sets the stage for pursuing and achieving the decadal challenge of creating new materials with significantly higher performance and functionality.

Accelerating Materials Discovery and Control of Nucleation

The vision of "materials by design" is now three decades old and many important advances have been made toward realizing this vision. However, these have generally been materials "designs" with limited stretch beyond an existing, proven example. The grand vision of starting with a blank sheet and ending with a functioning material remains elusive. In addition to the broader elements of this vision of materials design and lifetime prediction, and rapid materials design and synthesis, two specific challenges, corrosion science and controlling nucleation phenomena, were identified as critical shortcomings of the current state of "predictive design, discovery, and growth of new materials."

Nucleation, for instance, is a fundamental process step contributing to – if not in some cases controlling – many microstructural development and failure processes. Fatigue fracture and phase transformations are largely controlled by nucleation. Yet, the theory of nucleation, in the case of phase transformations or solidification, has advanced little beyond that contained within the Johnson–Mehl–Avrami–Kolmogrov equation of the 1940s. Innovative measurements of nucleation events – particularly using transmission electron microscopy and small-angle neutron scattering – are emerging but presently lack both the spatial and temporal scales necessary to understand the fundamentals of nucleation. Higher resolution measurements are required both to validate theories and to spawn new theoretical studies.

Corrosion science also has achieved somewhat of a plateau in advancement. Yet materials performance in extreme, corrosive environments is of paramount importance to many energy applications. This plateau is defined, at least partially, by the limitations of available characterization tools; advances in spatially and temporally resolved measurements and in coupled models could move the field beyond this plateau.

Light-matter interactions

The interaction of light with matter is a promising two-way street for concentrating and shaping light through photonic crystals, plasmonic interfaces and metamaterials, and for controlling matter with light pulses that direct the course of chemical reactions and trigger phase transitions or other material responses. Both directions of light-matter interactions are in their infancy, with remarkable new phenomena like perfect absorption, perfect imaging, and quantum control of chemical reactions illustrating enormous promise for opening qualitatively new horizons.

The explosion of interest since 2001 in the classical behavior of light described by Maxwell's equations with negative permittivity and permeability has revealed a host of previously unexplored phenomena including total absorption of light, imaging below the diffraction limit of conventional lenses, and bending light along prescribed pathways in materials with a graded index of refraction. These new phenomena enable an equally remarkable array of applications, such as high efficiency solar energy absorbers, imaging with sub-wavelength resolution, cloaking of objects by bending light around them, high resolution optical lithography, high gain antennas, and high sensitivity sensors. The principles and techniques of metamaterials are now being applied beyond light to acoustic waves, opening rich opportunities in high-resolution ultrasound imaging, non-destructive structural testing, and novel underwater stealth technology [1]. The successes of metamaterials have been achieved with two-dimensional arrays of nano- and micro-scale split ring resonators, which introduce negative permittivity and permeability near resonant frequencies related to their physical size and configurational pattern. A primary challenge (Figure 6) is to reduce the size of the resonators to access the visible light regime. This requires new techniques for lithography at smaller length scales, and development of new materials and nanostructures with high frequency magnetic response that can be configured by self-assembly. A second challenge is to broaden the bandwidth of negative index of refraction response and to reduce its dependence on angle of incidence. This requires extending the two dimensional arrays to three-dimensional architectures and introducing controlled variation in the response and arrangement of the resonant elements.

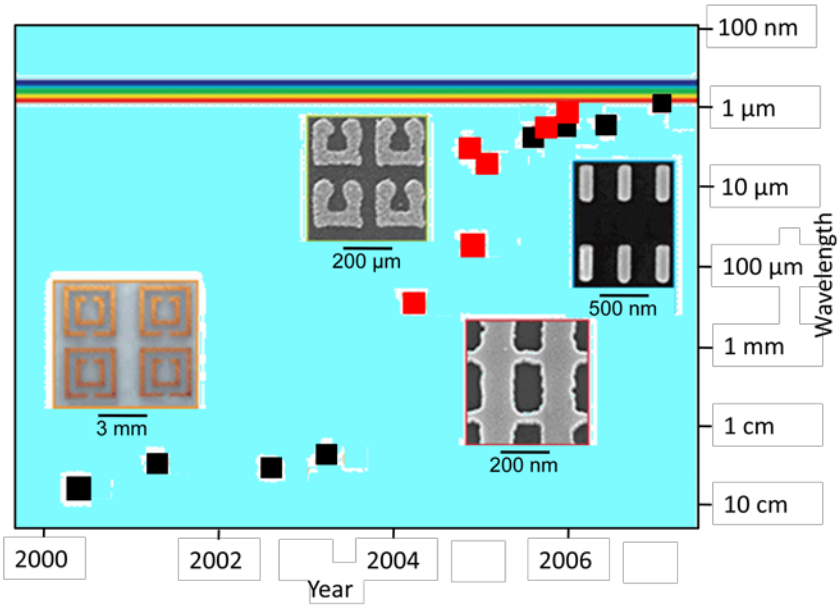

Figure 6. Advances in metamaterials. Black symbols denote negative index of refraction, red symbols denote negative permeability. Images indicate the sub-wavelength resonant structures used to control the electromagnetic response of the metamaterial. After [2].

Photonic crystals and interfacial plasmonic phenomena offer similar opportunities to manipulate light using diffraction and interference from wavelength-sized objects rather than the negative index of refraction of an effective medium composed of much smaller resonant elements [3-5]. The ability to guide, trap, reflect and intensify light from designed two- and three-dimensional structures enables applications for manipulating light with the richness and impact normally associated with semiconductor electronics. Examples include significant improvement in fiber optics for communications, high speed, low dissipation optical switching, computing with light instead of electrons, and optical data storage. Concentrating light of selected frequencies at fixed locations offers a host of opportunities for high efficiency solar photovoltaics and photochemistry. Enhanced electric fields at plasmon interfaces, up to a factor of 10^5, promise chemical and biological sensing with single molecule sensitivity and intriguing opportunities for the electrochemical promotion of chemical reactions. The challenges are experimental exploration and understanding of the fundamental phenomena of light propagation in structured materials, and the fabrication of two and three-dimensional designed architectures to produce targeted manipulation of light.

Metamaterials, photonic crystals and surface plasmonics use Maxwell's equations and intricate materials designs to manipulate light. In contrast, coherent control uses the quantum nature of light to manipulate the behavior of matter. In the quantum regime, the state of matter is described by ground and excited state energy landscapes. Photons of the right energy can drive the system into excited vibrational, structural and electronic energy landscapes that ultimately decay into a variety of final states. For example, acetophenone, $C_6H_5C(O)CH_3$, may photodissociate into $C_6H_5CO + CH_3$ or into $C_6H_5CH_3 + CO$. Initial excitation and subsequent nudging by specially designed photon pulses can control which outcome is achieved. Depending on the pulse sequence, a targeted mixture of dissociation outcomes can be produced.

The concept of quantum control is illustrated in Figure 7, showing an excited state potential energy surface for a chemical or condensed matter system [6]. The reaction coordinate can be manipulated by injecting energy through tailored pulses at key points on the trajectory, driving the system to targeted locations where it will decay into desired reaction products or ground states. The new ground state could have, for example, a new crystal, magnetic or electronic structure. Coherent control has been demonstrated for over 50 systems including the dissociation of complex molecules, energy transfer in artificial photosynthesis, ultrafast optical switching, molecular rearrangement and chirality, electronic states in quantum dots, and the metabolism of biological molecules and cells. Because the effect of the external pulse on the potential energy surface cannot in general be calculated, successful pulse sequences are determined experimentally by learning algorithms based on systematic variation of pulse parameters. The success rate is impressive - of order 100 iterations of pulse parameters is enough to produce ±15% or more change in the mixture of dissociation products.

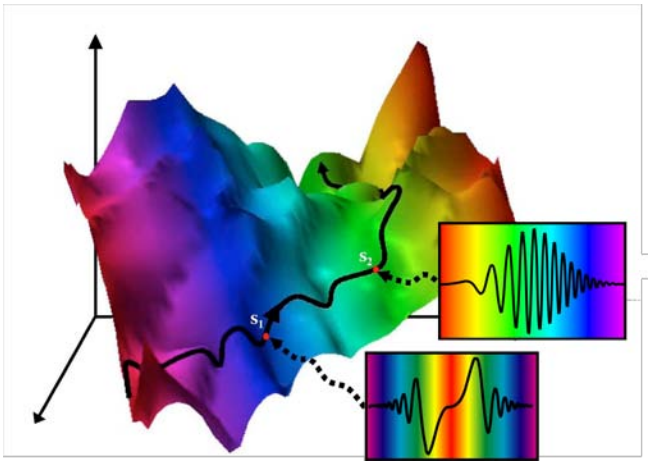

Figure 7. The potential energy landscape of a chemical reaction as a function of reaction coordinates such as atomic position and orientation. Injection of tailored light pulses at critical points along the reaction trajectory selects targeted outcomes.

Despite its early successes, coherent control of chemical and condensed matter systems is in its infancy. Each situation presents its own special challenges, which often must be addressed without the benefit of experience. The iterative learning algorithms for shaping control pulses favor specific outcomes, but there is no standard for judging their success relative to a theoretical "best case scenario". As light pulses become faster and more flexible in frequency and phase control, the limits of coherent control will expand. The pulse shape and sequence that works, however, is still an empirical discovery. Often the successful pulse shapes and sequences are impossible to interpret in terms of excited state potential energy landscapes and reaction coordinates, the first step toward being able to *design* a pulse sequence for a targeted outcome. The potential for coherent control is enormous, including eliminating expensive or rare catalysts like platinum in sustainable energy conversion reactions, controlling the synthesis of new high performance functional materials, and directing the solar splitting of water or carbon dioxide and its recycling to chemical fuel. Controlling the outcomes of chemical reactions, the properties of condensed matter systems, and the functionality of complex materials is a decadal challenge with high potential payoff for science and technology.

Electronic functionality from complexity.

The development of semiconductor electronics based on silicon is one of the primary scientific and technological triumphs of the 20th century, with game-changing impact at low cost on nearly every aspect of our personal, commercial, social and political lives. The foundation of this triumph, however, is the simplicity of silicon as an electronic material. It has two robust states, conducting and insulating, that can be switched reliably with a simple voltage. The functionality of silicon electronics comes from the complexity of large, intricately connected networks of transistors contained on tiny integrated circuit chips that transform the simple on or off states of millions of silicon transistors to sophisticated computational and decision making information machines.

For electronic functionality beyond information processing, a qualitatively different kind of electronic material is needed. Energy conversion among photons, electrons and chemical bonds requires electrons to be available in the energy states needed for excitation by a photon, for electron transfer between atomic orbitals in a chemical reaction, or for carrying electric current without loss in a superconductor. These electronic functionalities depend on strong interactions of electrons in a given system across the system boundary with states of nearly the same energy in an adjacent system. Various couplings among spin, charge, and lattice degrees of freedom are often key ingredients.

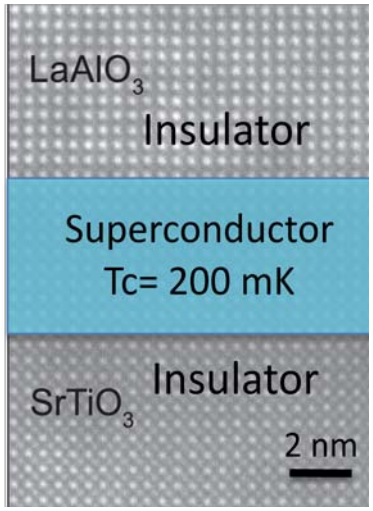

Figure 8. Superconductivity at the interface of two insulators. After [7].

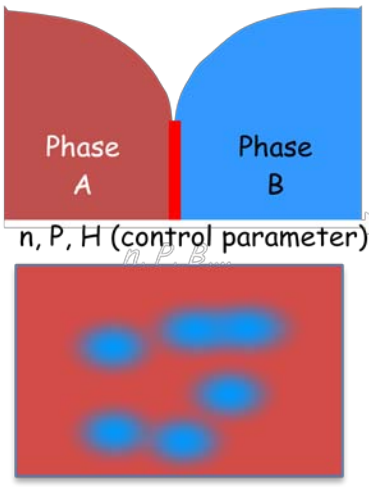

Figure 9. The competition between two phases (upper panel) can trigger fluctuating or static nanoscale phase separation (lower panel), or the emergence of an entirely new phase unlike either of its parent phases as in Figure 8.

An iconic example of surprising functionality arising from the interaction of closely spaced electronic states is illustrated in Figure 8: a superconducting phase appears at the interface of two insulators, $LaAlO_3$ and $SrTiO_3$. The superconductor has nothing in common with the insulators: it is neither a variation on nor an average of the two adjacent insulating states. In spite of its dramatic difference from its neighbors, the superconductivity is completely dependent on them, appearing only in the narrow interfacial region where the energy levels of the two insulating states interact.

This emergent interfacial state is an example of the rich variety of electronic behavior arising from competing phases, illustrated

in Figure 9. At the phase boundary between A and B, at least three distinct behaviors can occur. There could be a conventional phase transition, with A transforming to B sharply. If the system is inhomogeneous in the control parameter (e.g., composition) parts of it will transform before the rest, creating a mixture of two phases. Even if the system is perfectly homogeneous, however, two phases with equal energy can spontaneously phase separate, with the scale of the phase separation depending on the surface energy of A in B and B in A. A third possibility exists as well, that an entirely new phase will emerge at and near the boundary, unlike either of the parent phases.

Guided by these examples, we propose a new paradigm for electronic functionality emerging from electronic complexity. The necessary ingredients are closely spaced energy levels allowing the system to sample many levels under the influence of thermal or other environmental energies such as electric or magnetic fields or reaction with environmental reagents. The system is therefore energetically "soft." A second ingredient is interaction with closely spaced levels in a phase with different order, for example phase A might be a metal and B a magnet or insulator. The interaction of closely spaced levels from different ordered states provides the variety needed to break the symmetry of the ordered phases. A third ingredient is correlation, making the energy level structure dependent on the occupation of the levels. Correlation swings large energies with small changes in occupation; this provides a driving force for emergent phases with very different hybridized energy level structures to have decisively lower total energies.

These ingredients allow a diverse variety of emergent responses. The system can have a hierarchy of long and short range interactions, the former providing structural robustness and the latter "hot spots" of local functionality. The system can acquire a dominant physical response, such as superconductivity or a large susceptibility, or it can break into "chambers" with distinct functions that pass energy or charge from one to the other in sequential operation like an assembly line. Sequential operation is a signature phenomenon of biological systems, where the division of cells, the replication of DNA, or the folding of proteins is elaborately choreographed by subtle changes in energy levels. Other features of biological systems, such as self-healing, ageing, and learning, might be introduced through repetitive cycling through closely spaced energy states with feedback to subtly alter the states.

The paradigm of closely spaced electronic energy levels interacting across competing ordered phases with significant correlation energy offers a host of opportunities for emergent functionality born of electronic complexity, in close analogy to biological functionality born of structural and chemical complexity. The decadal challenges are to develop integrated capability, including theory, modeling, synthesis, and characterization, to create prescribed electronic energy landscapes by assembling multiscale hierarchical atomic and molecular patterns, to identify the relevant degrees of freedom and length scales for controlling macroscopic functionality, and to develop a quantitative framework to relate nanoscale complexity to robust macroscale functionality.

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Panel Summary: Matter Interactions in Extremes

The scope of matter interactions in extremes spans the frontiers of compression science, including new chemistry enabled in extremes and the regime of warm dense matter. In all cases the ability to reliably and precisely access the extreme environment and to then be able to perform in-situ measurements at appropriate spatial and temporal scales remains a grand challenge.

Frontiers of Compression Science

The influence that compression science has had on national security science and its manifestation through discovery and application cannot be overstated. In addition to supporting the certification of our nuclear stockpile in the absence of underground testing and a broad spectrum of engineering and defense applications, compression science has altered our view of the material world around us. The discovery of unexpected physical and chemical phenomena and new materials through the application of compression science techniques has led to a new and refined understanding of the nature of chemical bonding in extreme environments. However, it is clear that many important aspects regarding the response of materials to compressive loading are still not understood, let alone modeled in a predictive mode. As a result, we have not derived the many benefits that a predictive understanding would bring. The scientific needs that are required to achieve full understanding and that ultimately support our ultimate goal of moving from *"observation to control"* have been documented in a recent report [see Appendix].

Making progress on these challenges will require a suite of new experimental tools and diagnostics as well as a suite of conceptual frameworks and theoretical constructs. The suite of experimental tools must include the development of diagnostic capabilities, such as next generation light sources, for peering into and achieving time-resolved measurements in compressed materials at the smallest relative length scales while simultaneously characterizing them at higher length scales. The theoretical suite must include new frameworks of computation that will allow the incorporation of the stochastic nature of matter, as well as the ability to accurately describe the essential physics without the invocation of phenomenological models, while linking the atomistic to the continuum response. Progress on these challenges will not only allow us to develop a full understanding of compression science, it will create an environment in which we can train the next generation of scientists and provide them with the tools needed to move from studying "ideal" to "real" materials.

New Chemistry in Extremes

The electronic structure, bonding and chemical reactivity of atoms is challenging under ambient conditions. However, the rearrangement of atomic levels induced by compression can result in entirely new reactivity, bonding and structure. For instance a metal such as sodium can become a transparent insulator; simple molecular systems such as O_2 become metallic superconductors; and a greenhouse gas such as CO_2 can become a solid with novel optical properties. Such results

point to the existence of a "new" density-dependent periodic table, whose control and exploitation still require a deeper fundamental understanding of the effects of density on atomic and chemical bonding. Key scientific challenges include the prediction and creation of novel chemical states at extreme PT while understanding the effects of P and T on atomic structure, bonding, and reactivity; utilizing Gbar pressures to induce core-electron "kilovolt" chemistry; and using matter/radiation coupling in concert with P and T to control chemistry and reactivity.

Such challenges will require new computational tools for describing electronic structure and thus enable a predictive capability of chemical reactivity and bonding, over wide ranges of P and T. These challenges will also require the continued development of ultrafast *in situ* diagnostics in order to observe bond breaking/formation, local energy populations and their redistribution, stoichiometry, kinetics, and to observe the production and effects of short-lived transient states. However, our current ability to control thermodynamic states with the necessary precision over a large range of T, P, and strain rate is limited, and we do not currently have the time-dependent spectroscopic diagnostics capable of *in situ* (sub-surface) probing of extreme conditions at high spatial resolution. We must continue to develop time-domain diagnostics for extreme chemistry, and to move beyond existing theories to overcome the theory/experiment timescale gap.

Warm Dense Matter

Under extreme conditions the order parameters that define condensed matter change, fail, or disappear, and no longer apply to describe materials and their dynamic behavior. These conditions have relevance to inertial fusion, stockpile stewardship, or stellar explosions, and have significant uncertainty because of these complex dynamics. Creating the extreme conditions of matter, while simultaneously measuring its state variables with sufficient spatial and temporal resolution to determine gradients and fluxes is a scientific frontier challenge. Developing theory that can explain the material behavior in these new conditions where the usual order parameters fail is the other major research need.

Recent advances in intense, pulsed light sources provide revolutionary capabilities to subject matter to extreme conditions of pressure and temperature, creating novel conditions that span all the way from solid state to weakly coupled plasmas. Those sources also provide new powerful tools to diagnose those novel conditions. The state of matter between the solid state and weakly-coupled plasmas is known as warm dense matter (WDM). Understanding the nature of WDM is one of the fundamental goals of the physical sciences associated with laboratory astrophysics, planetary dynamics, evolution of stars, and energy technologies. WDM is extremely challenging to model, because the typical approximations (e.g., expansion parameters) used in either solid state or weakly-coupled plasmas are not applicable. Creating and diagnosing WDM is very difficult for several reasons, such as its transient nature, the need for dynamic measurements, and the difficulty in creating sufficiently large and homogeneous samples. Understanding WDM is important in basic science (e.g., to understand the nature of giant planets) as well as in applied

science (e.g., in understanding material behavior and equation of state in shocks and explosions, laser-matter interactions and non-linear optics, inertial fusion energy, etc.).

Panel Summary: Cross Cutting Challenges

Although a few examples exist of quantitative approaches to transitioning from (empirical) observation to (quantitative) control, generalizing this will require substantial developments in characterization, analysis, modeling, computation and design of (critical) experiments. The magnitude of task has the potential to be a challenge on a decadal timescale and, in particular, suggests the need for multi-scale modeling. Successful development of the required models will likely be achieved by creating an experimentally-validated framework that spans spatial and temporal scales through an integrated approach that moves beyond the passing of parameters between distinct models at distinct scales.

Decadal Challenges in Materials Development

Materials science and engineering is at a crossroads, moving from the traditional trial-and-error methods of materials development to a new era in which materials will be increasingly designed at multiple length scales simultaneously. This change is enabled by two equally important sets of developments – the remarkable increase in our ability to experimentally probe materials at a wide range of time and length scales, and the concurrent, and equally remarkable, advances in computational capabilities and algorithms that enable modeling and simulation to describe and predict materials properties and response with unparalleled fidelity. Materials science is clearly moving from its current state as an observational science with empirical development of materials, to one in which we can design and control materials behavior. Accordingly, we need to re-think our approach to both hypothesis-driven research and goal-oriented development.

Four main areas were identified that challenge both experiment and simulation:

- Heterogeneous materials
- Bridging length and time scales
- Developing closer integration of modeling and experiment
- Developing materials design tools to manage complexity

There is a flow of these topics, from developing experimental and simulation probes of complex structures, to adding variations of length and time, to developing truly integrated experiment/simulation, and finally to the primary goal of the "observation to control" theme of this workshop, the creation of the ability to design materials across scales of length and time.

Heterogeneous Materials

<u>Heterogeneities Driving Tails in Distributions</u>

Materials in technological use have always been heterogeneous, with ranges of disorder in composition and structure. These heterogeneities occur across scales, from local atomic disorder at the nanometer level to microstructural features at the many micron level. They may involve many phases or just one, but with many orientations. What is changing is our ability to design

heterogeneities at all scales, through a range of processing paths, with desired functionalities. Many challenges remain, however, in our understanding of the role that heterogeneities play in determining materials response, especially under conditions outside the norm. To control those functionalities will require an understanding of the relations between the global properties of a heterogeneous material and the local properties of its homogenous phases. A critical gap in the current approach is it is often not recognized that obtaining the global properties is not simply a matter of computing a suitable average but may, in fact, depend on the upper tail of a distribution. This is particularly true of materials properties such as corrosion resistance, fatigue resistance, spall resistance and almost any property related to damage evolution. Moreover, we will need to predict the evolution of structure and response of these complex materials in dynamic environments.

Defect-driven variability in material response:

When materials are exposed to extreme environments (radiation, high temperature) or pushed under extreme mechanical conditions (long term fatigue, shock), the statistical variation in material failure response among seemingly identical specimens increases substantially. In these cases, the variability in response is so significant that the usual Gaussian statistical analyses that calculate mean and standard deviations are not adequate descriptors. When material response exhibits so much uncertainty, reliability in material performance in extreme environments and conditions (no matter how strong or tough the material may be in less challenging circumstances) is compromised. Approaches to reducing the uncertainty begins by first understanding how it originates, followed by the ability to predict it, and ultimately to control it.

Experimental probes

Diffraction methods are increasingly important to both 2- and 3-D characterization of heterogeneous microstructure. Innovations in x-ray and electron diffraction methods have largely driven this area through advanced user facilities such as the Advanced Photon Source for high energy x-rays and electron microscopes for high resolution orientation scanning. In addition the Vulcan facility at the Spallation Neutron Source is likely to offer new capability for neutron diffraction in the coming decade. Combining different techniques both within each area and between the two main methods may offer substantial synergistic advantages. *Comparisons of computed fields with measured ones are likely to provide valuable feedback on the importance of the intrinsic elastic properties of grain boundaries, perhaps unaccounted for in the computer simulations. And other comparisons can be envisioned that would strengthen both experimental and computational results.*

Quantifying material complexity using n-point statistics:

A rigorous framework defining the spatial correlations of local states in the microstructure already exists in the form of *n*-point correlations or *n*-point statistics. These correlations provide a hierarchy of statistical measures of the microstructure that are essentially moments of the

structure function. They preclude the need to select, either intuitively or in an ad-hoc manner, the microstructure metrics of importance in a given application. A great advantage of the use of these correlations is that they can be computed very efficiently using fast Fourier transform (FFT) algorithms. *Ultimately, our goal is to develop a science-based understanding of the properties and performance of heterogeneous materials, especially by considering variations in composition and structures to move from the "ideal" materials of the laboratory to the "real" materials in actual use.*

Bridging length and time scales

<u>The impact of extreme values on modeling & simulation</u>

The greatest challenges of materials modeling and simulation arise from the wide range of length and time scales of importance in determining materials properties. Consider first length scales, fundamental to all material structure and response is the bonding between atoms, which is quantum in nature and is typically localized to a few tens of nanometers – that metals are different from ceramics, for example, arises from this bonding. However, the properties at a larger scale, say centimeters, may also depend on structures intermediate in scale, often referred to as the mesoscale. These structures are generally distributions of defects (e.g., dislocations, grain boundaries, …) or phases. The challenge is that predicting properties at any given scale (e.g., the mesoscale) implies understanding phenomena at lower scales (e.g., electronic/atomic). Moreover, for application to many engineered structures, it is critical to create mesoscale modeling with atomistic-level accuracy yet also connected to continuum. As discussed above, often the critical issues are not well described by averages – it is the tails of the distribution that dominate some response (e.g., failure). Again, incorporation of new theories and models of the statistics of extremes is essential.

<u>Scale Bridging:</u>

Accurate, computationally efficient, physics-based scale-bridging relationships are critical to integrating the microstructure features from distinct time and length scales into a cohesive multi-scale modeling framework.

To successfully predict and control, it is imperative to build the following features into scale bridging: (i) the scale bridging has to transmit information accurately in both directions between the length scales. (ii) the scale bridging has to be formulated in such a way that it allows inverse solutions that are central to successful materials design.

<u>Extending the ability of atomistic-level simulations to long times:</u>

Capability in atomistic simulations that can reach time scales of order seconds and beyond is currently lacking. This widely recognized challenge has remained unresolved since the early days of multiscale simulations. Closing the gap requires the demonstration of an atomistic

method (using interatomic potential as an input) that can elucidate behavior such as glassy relaxation and creep deformation response, which are widely acknowledged bottlenecks in the computational materials community.

Corrosion is a ubiquitous phenomenon underlying many scientific and technological challenges. It could be the oxidation of a high-temperature ceramic component in an aircraft engine, or the hydrolytic weakening of quartz in the earth mantle. Regardless of the specificity of the phenomenon one can identify a fundamental process vital to understanding the chemo-mechanics of materials. Suppose the problem for discussion is that of corrosion initiation. The relevant process is then the formation of a passive ultrathin oxide film and its evolution to the onset of structural breakdown. At the molecular level one needs to consider charged defect transport and the role of electron transfer in the aggregation of cation vacancies that eventually lead to film-substrate decoherence and pit nucleation. This is an example of combining unit process (charged transport) to study system-level behavior (film growth). *The decadal challenge is to identify and implement extensive and intelligent combinations of TMS in order to achieve predictive insights into transgranular versus intergranular corrosion cracking in structural materials.*

Developing closer integration of modeling and experiment

Integrated Computational Materials Engineering

As discussed in detail in a recent National Academy Report, *Integrated Computational Materials Engineering*, much progress can be made in materials understanding and design by more thoroughly integrating experiment and modeling/simulation. From a modeling and simulation perspective, experimental data serves as part of the validation process, testing the basic physics included in the models upon which the simulations are based. More importantly, experiments serve to help define models, which may then be incorporated into large scale simulations.

As a minimum requirement for their integration, simulations and experiments must yield some of the same quantities (parameters) and access the same length and time scales. Better still, both simulations and experiments should be reasonably efficient to allow multiple (better numerous) measurements to enable active feedback and cross-validation for improved accuracy. Given that properties and performance are defined by material microstructure and its evolution on appropriate scales, future development should be focused on *the microscale frontier*.

Linking Experiments with Theory, Modeling and Simulations (TMS) across scales:

The validity of microstructural level (and lower length scale) theory, modeling and simulation is limited by a lack of close coupling with experimental observations at the same scale. This is particularly true for processes (ranging from very long time aging to high rate dynamical loading) in which the microscopic structure of the material changes with time. Recently, it has become possible to non-destructively measure the grain-scale microstructure in materials used 3D x-ray diffraction (3DXRD).

New tools for analyses of large datasets at multiple spatial and temporal scales.

One of the greatest challenges in materials research is how to best capture the wide range of disparate, yet connected, information that results from modeling and experiment. A new field, materials informatics, is the application of the ideas of informatics to materials science and engineering. Informatics is a field of research in which information science, processing, and systems combine to examine the structure and behavior of information, enabling new ways to access and explore that information. In materials, information comes in many forms, as does the possible use of that information. It should not be surprising that the potential applications of informatics are equally diverse. While progress has been made in applying informatics to materials, many key challenges remain. On the strictly experimental side, our ability to represent complex three-dimensional microstructures is limited [1,2]. How to include more detailed information of structures is unclear. Yet developing correlations between these structures and materials response is critical. Another frontier is to incorporate results from modeling and simulation at one set of scales along with experiment at another scale to yield a richer, more inherently multiscale, description of materials response. These are just two examples of the challenges and opportunities for materials informatics.

Developing materials design tools to manage complexity

Uncertainty quantification (UQ)

Usefulness of simulations to material development, insertion and certification is greatly enhanced if simulation errors and uncertainties are quantified. Agreement or disagreement between experimental data and simulations can be firmly established only if errors and uncertainties of both are known. Simulation error and model uncertainty should not be confused. Simulation error is the difference between (the usually) approximate and (asymptotically) exact simulations of the same model. Model uncertainty, on the other hand, reflects insufficient accuracy of model parameters, model incompleteness (e.g. missing mechanisms) or inadequacy of the model itself, irrespective of the quality of numerical simulation. Quantification of simulation errors (verification) may require significant computational effort but otherwise is often relatively straightforward. What it means to quantify the model uncertainty is, however, not well understood. Recent debate on the quantitative significance of Representative Volume Elements and which properties can be demonstrated to remain invariant under repeated instantiations has sharpened the focus of the discussion [3]. Thus, UQ is important not only for enabling more meaningful interaction between simulations and experiments but also for the development of the theory itself. *UQ is a wide open area of applied and computational mathematics where much progress is expected in the near future. Tight integration of theory and experiment is likely to be a major benefactor of the emerging UQ methodology*.

Inverting information flow from performance to structure to processing

Materials design has tended to proceed from the empirically possible to the discovery of plausible applications. Inverting the materials design paradigm so that materials are designed to suit known applications is a first order challenge for materials design methodology in the coming decade. Green's function approaches [1], for example, are inherently highly invertible in terms of moving from homogenized properties or localization, back to the fields of microstructure. *One much needed advance in the study of localization related phenomena in heterogeneous materials would be approaches to develop analytical Green's functions for complex geometries and complex boundary conditions*.

IS&T for Multiscale Materials Modeling and Prediction

The development of a predictive capability for materials performance with a realistic assessment of model and prediction uncertainties is one of the key challenges. Bridging the "micron gap" of material properties is essential to addressing this challenge. At length-scales significantly larger than one micron, there are a number of techniques to characterize material response, albeit with averaging over material inhomogeneities and resultant fluctuations in thermo-mechanical response. Models, although nominally based on sub-scale physical processes, still rely on empirical adjustments that prevent extension beyond the range of calibration. At shorter length scales (~10 nm), the static properties of materials can be characterized or modeled with atomic precision. Unfortunately, due to limitations on size and simulation times accessible to current methods, we lack the capability to characterize the fundamental constitutive behavior that underlies the observed larger-scale phenomenology. *Bridging this micron gap is the critical roadblock to developing reliable multiscale understanding of materials that would enable truly predictive capability*.

The Grand Challenge in Materials Modeling & Design

A Grand Challenge is to simulate and predict materials properties and integrate the methods with those of Information Science and Technology to maximize our understanding of materials science, including aspects of: motivating, designing and analyzing experiments; achieving fully integrated multiscale modeling; data fusion of experimental and modeling results; techniques for dynamically analyzing massive data sets; and quantified measures of uncertainty applied to data extracted from both experiments and models. Based on advances in computational hardware and algorithm development, our expectation is that modeling capabilities in ~5-10 years will demonstrate closure of the "micron" gap within multiscale strategies. That is, we expect that we will be able to bridge the intermediate (or mesoscale) scales in which the approximations of fast/slow or small/ large no longer apply, which will enable us to directly link electronic/atomistic and continuum scales. Success is essential to enabling a capability of "*intentionally controlled functionality*".

This quantitative connection between atomistic simulations and continuum response models will have a significant impact on a broad variety of materials systems and issues. This capability will be critical for integrating experimental results into true materials understanding. The coupling of Materials Science and Information Science and Technology will demonstrate an integrated, innovative path with the following goals:

- Goal 1: Develop capability to achieve optimal use of data and design of experiments for prediction
- Goal 2: Establish the technical underpinnings of data-driven analysis and quantified predictive capability for materials performance

This strategy must focus on integrating expertise in materials modeling and condensed matter theory, existing experimental data and modern data analysis techniques to understand and predict materials behavior.

The potential impact of the challenges outlined above is manifold. Often overlooked is the crucial importance of effective frameworks for the pursuit of scientific and technological research. A serious effort to implement the integration of theory, modeling and experiment outlined above will transform the scientific environment for the next generation of scientists. More specific impacts include the development of quantitative understanding of the potency of the wide range of defects present in materials; a quantitative understanding of how populations of defects with their variable potency affect materials properties especially those with a strong sensitivity to history such as fracture and corrosion. These sorts of quantitative frameworks for materials properties in turn will enable substantially more sophisticated approaches to materials design at both the atomistic level (e.g. for catalytic activity) and at the microstructural level (e.g. toughness of artificial bone) where the performance requirements will drive the microstructure design. At the systems integration level, Integrated Computational Materials Engineering has the potential to transform materials development and refinement on the industrial scale if the right tools are provided. All these represent decadal challenges of the first order.

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Priority Research Direction: Predictive understanding of atomistic and collective fundamental mechanisms of radiation effects in materials

Problem Statement

Radiation effects encompass a broad range of multi-scale phenomena, ranging from atomic scale unit mechanisms to collective effects occurring at the mesoscale. In order to develop a firm predictive understanding of radiation effects in materials for advanced fission and fusion energy systems, improved understanding of these atomistic unit mechanisms and collective phenomena are needed.

Executive Summary

Key fundamental unit processes involving solute atoms and point radiation defects, and phenomena that control their collective microstructural evolution, are poorly understood. These represent source terms for long-term development of persistent microstructures and accompanying physical and mechanical property changes due to radiation. Atomistic unit processes of atomistic and electronic defect production, their interactions, energy release pathways to materials in a radiation environment, as well as the collective impact to material properties are critical to controlling and engineering materials performance. A comprehensive research effort is needed to understand the interaction between point defects and solutes and the sinks such that quantitative predictions of sink strengths can be made. In order to access the relevant spatio-temporal scales of such processes, new measurement tools capable of simultaneous spatial and temporal resolution approaching 1 Å and <1ps are needed. These research tools include emerging enhanced capabilities in leadership-class experimental facilities utilizing X-rays, neutrons, electrons, and ion beams. Of particular importance is development of in-situ test capabilities (both during irradiation and post irradiation during heating and mechanical stressing). Acquisition of an improved understanding of these atomistic and collective radiation effects processes will enable bottom-up design of materials with unprecedented tolerance to extreme environments.

Scientific Challenges

The understanding of fundamental unit mechanisms responsible for processes such as Frenkel pair recombination, defect clustering and precipitate nucleation, point defect interactions with interfaces, and dislocation core spreading are critical to the prediction and control needed for the bottom-up design of materials with unprecedented tolerance to extreme irradiation environments [1]. Similarly, atomistic and mesoscale phenomena that involve collective or coordinated processes may ultimately determine the overall radiation resistance of materials. Examples of poorly-understood collective phenomena include defect production via non-ballistic mechanisms such as fission fragment ionization tracks [2], dislocation annihilation of defect clusters (important for understanding dislocation channeling, radiation embrittlement and fatigue) [3,4], grain boundary sliding and pinning mechanisms at thermal creep conditions [5-7], stress-assisted

helium bubble formation at grain boundaries (basis for high temperature helium embrittlement of grain boundaries) [8,9], and quantification of the efficacy of various precipitate and grain boundary interfaces in facilitating point defect recombination and trapping of transmutant helium atoms [8-11].

The importance of interface structure in influencing these unit mechanisms cannot be over emphasized. Early work studying the interaction between point defects and grain boundaries (homophase interfaces) [12, 13] confirm qualitatively that the response of different grain boundaries to irradiation and impurity concentrations depends on interface structure [14,15] and the presence or absence of coherency. However, because experimental and modeling methods were limited, the connections between modeling and experiments were necessarily qualitative in nature. The dependence of interface response to atomistic and collective processes occurring at extreme doses, dose rates, stress and temperatures were not investigated and remain poorly understood. Improvements in computational resources and the advent of accurate inter atomic potentials have allowed atomistic modeling to provide greater insight to the connection between interface structure and response to irradiation. Modeling has shown that different atomic structures of interfaces can lead to the operation of different unit mechanisms responsible for processes such as point defect absorption, emission and diffusion at interfaces. The efficacy with which the various unit mechanisms intrinsic to a given interface operate *collectively* to mediate radiation damage can strongly affect the radiation tolerance of a material. For any interface, there exist irradiation conditions that are sufficiently severe to overwhelm that interface's ability to heal radiation damage leading to morphological and/or chemical instabilities and degradation in mechanical properties. If, however, the dependence of those limits on the collective behavior of the unit mechanisms intrinsic to that interface is well understood, then the interface structure can be tailored to obtain the kind of unit mechanisms that lead to greatest survivability of a material under a given set of irradiation conditions. Therefore, the discovery of previously unanticipated unit mechanisms, determined through atomistic modeling and validated with new measurement tools, will be important in defining the source terms for long-term development of persistent microstructures and accompanying physical and mechanical property changes due to radiation

Research Directions

Research is needed to acquire improved understanding of radiation effects phenomena at multiple scales, ranging from atomistic processes of defect production in displacement cascades to atomistic and collective phenomena that determine the fate of migrating point defects.

Improved understanding of electronic defect production in nonmetals, point defect interactions with extended defects in materials, energy release pathways to materials in a radiation environment, as well as the collective impact to material properties are critical to controlling and engineering materials performance. While progress has been made in modeling the dynamics of collision cascades in materials, dynamic charge effects and collective processes are much less

understood. Defect production research topics of high priority include time-resolved experiments to validate displacement cascade models, quantification of localized charge effects at defects and interfaces, rupture or changes in nature of covalent and ionic bonds, enhanced defect and atomic diffusion, and changes in phase transformation dynamics.

It is well known that dislocations and grain and interphase boundaries act as sinks for radiation-induced point defects. Also, foreign elements such as helium can migrate to microstructural sinks whereas substitutional solutes (e.g., Cr in steels) can either enrich or deplete from boundaries. A comprehensive research effort is needed to understand the interaction between point defects and solutes and the sinks such that quantitative predictions of sink strengths can be made. For example, what is the role of boundary structure and energetics on the sink behavior? This requires a coupled modeling and experimental approach. Atomistic modeling can explore the structure of sinks and interaction of point defects with sinks, both at the level of unit processes (e.g., interaction energies of *individual* vacancies and interstitials with sinks) and collective phenomena (e.g., interaction of cascades with sinks). The solubility of foreign elements such as helium at sinks can also be estimated from the atomic structure of the sink via atomistic modeling. Experimentally, the interaction can be measured in terms of defect accumulation in bulk vs. at sinks for the same irradiation condition. New *in situ* studies (e.g., ion irradiation in dynamic TEM and ultrafast x-ray diffraction analysis of cascades) are needed to elucidate the interaction of radiation-induced point defects with microstructural sinks of different atomic structure and geometry to understand which sink types interact most strongly with defects and solutes.

Improved experimental tools [16] are needed to directly observe and understand fundamental defect and solute agglomeration processes. These phenomena are the driving force for establishing the life cycle of microstructural features and their impact on material properties.

Capability Gaps

In order to access all relevant spatio-temporal scales of such processes, new measurement tools capable of simultaneous spatial and temporal resolution approaching 1 Å and <1ps are needed. A variety of materials characterization probes offer attractive features. X-ray sources offer the potential of ultrafast spectroscopy on a wide variety of materials. Neutron scattering provides complementary characterization of solutes, precipitates and lattice strains in bulk materials. Electron microscopy offers high spatial resolution of defect structures and solute segregation and precipitation at moderate time resolution. Ion beam analysis can be utilized to examine solute segregation and lattice locations of atoms, along with a variety of ultrafast optical spectroscopy tests. Currently only very limited in-situ test capabilities exist for examining irradiated materials in leadership-class materials characterization facilities (both during irradiation and post irradiation). The problem is particularly acute for examination of neutron irradiated materials, where daunting logistical barriers exist for the introduction of radiological materials [17].

On a decadal horizon, hard X-ray sources are very promising sources for this purpose: the short wavelength (on the order of≈1 Å) allows for atomic spatial resolution; the high penetration into matter permits to study buried structures and bulk samples; and with the upcoming generation of hard X-ray free-electron lasers the achievable time resolution will reach the femtosecond regime. The high peak brightness of such sources will allow for single-shot imaging of non-repeatable events and for the investigation of non-periodic structures by means of coherent scattering techniques. While hard X-ray facilities are currently being developed around the world (LCLS in the US, XFEL in Germany, SCSS in Japan), their application to the study of radiation effects in materials presents special challenges. First, enabling the introduction of irradiated radioactive materials into a coherent hard X-ray facility will be crucial. Furthermore, appropriate pump-probe schemes need to be devised in order to image fast dynamic processes. Here, a capability gap exists in the technology for initiating radiation-induced dynamics with sub-picosecond precision. It will be essential to develop pulsed ion, photon, and neutron sources that can be combined and synchronized with an ultrafast X-ray source.

The combined utilization of in situ TEM and ion irradiation is a powerful technique in research on nuclear materials including advanced structural alloys, waste storage ceramics and glasses, and model fuel alloys. A strength of in situ work is the discovery and illumination of fundamental dynamic processes such as point defect clustering, dislocation loop formation, loop motion, coalescence and interactions with existing surfaces, interfaces, and microstructure. Although TEM has been used extensively in the study of radiation damage in materials, it is currently limited with regard to spatial and temporal resolution to elucidate point defect evolution in real time. *In situ* studies of ion irradiation in a TEM typically capture dynamics at rates of 30 frames/second but the defect evolution starts at sub-ps time scales. Also, sub-Å resolution is needed to resolve point defects, as opposed to defect clusters on the scale of 1 nm that is achieved currently. This represents a significant gap between experiments and modeling. Molecular dynamics simulations can reveal radiation-induced point defect interactions with interfaces at sub-pico to nano-second time scales, but experiments only resolve defect clusters (≈ 1 nm diameter) at time scales on the order of 1/30 second. Improvements in both experimental and modeling capabilities are needed to bridge this substantial difference in time scales.

A significant development is appearing which can have great impact on experimental work in irradiation effects at the 0.1 nm scale. This is the coming development of doubly aberration corrected (spherical and chromatic aberrations) electron microscopes with expanded accessible volume for *in situ* ion irradiation (1,2 or 3 beams) combined with well controlled specimen environment (temperature, stress, gas or liquid) and space for additional measurement techniques (laser based, x-ray, physical properties) beyond just the electron beam techniques (which will be quite powerful in itself: energy filtering, analytical probes, tomography, etc). Accommodation of this expanded space for *in situ* experiments will compromise the ultimate spatial resolution, but resolution limits of 0.1 nm may still be achievable. Useful temporal resolution for the study of dynamic processes should also be extended down to millisecond or shorter timescales over the

next decade. Future directions should include measurements of local chemistry changes (electron energy filtering), tomography, enhanced spatial and temporal resolutions, and the expanded experimental space afforded by aberration corrected microscopes. Capability is needed for simultaneous measurement by multiple probes (in-situ or ex-situ) in order to firmly establish links between microstructure and properties

Over the last few decades, ion beam analysis (IBA) to characterize atomic profiles and nanometer structure has developed into a mature field, and today comprises numerous techniques, including Rutherford backscattering spectrometry (RBS), elastic recoil detection analysis (ERDA), nuclear reaction analysis (NRA), and ion-beam-induced luminescence (IBIL). Perhaps the most conventional IBA technique is RBS, in which light probing ions scattered from heavy target nuclei yield information on the mass and depth of the target atoms. A powerful relative of RBS is ERDA, where recoiled target atoms are detected with near-monolayer depth resolution and good elemental, and even isotopic, identification. NRA can detect and quantify most of the light elements and their isotopes. IBIL signals are highly sensitive to defect formation, bonding changes, transient unstable states and phase transformation, as well as precipitate and nanoparticle formation. Ion beams along low-index crystallographic directions are sensitive to atomic displacements from the crystalline lattice sites, such as interstitials within channels, unaligned atoms in amorphous domains or due to local strain from dislocations. RBS, NRA and IBIL combined with ion channeling technique can provide critical information on ongoing changes of defect evolution, damage accumulation, thermal- and radiation enhanced solute diffusion, and structural transformations in a radiation environment to validate predictive models.

There is a performance gap in utilizing and advancing the ion beam tools to address relevant phenomena in radiation environments of interests for fission and fusion. Additional beamlines to deliver multiple probe ions will be needed in new multiple-beam test facilities. The *in-situ* or on-line IBA characterization capabilities, together with other spectroscopy and microscopy techniques, can effectively monitor the evolution of radiation damage (atomic migration/nucleation, interface degradation, structural stress, nano/microstructure evolution, helium and solute agglomeration, etc), therefore, are powerful diagnostic tools to understand material behavior and response to various physical and chemical processes.

Potential Impact

An improved understanding of the atomistic and collective processes that define the persistent microstructures in irradiated materials is essential for the development of improved high performance materials. This understanding would enable the development of validated physics-based multiscale models, which will allow accurate extrapolation beyond the current knowledge base. It would also facilitate an improved understanding of irradiation flux effects (including pulsing and accelerated testing), as well as provide the basis for understanding how to use

accelerated test techniques to more rapidly design, develop and qualify high performance materials for future advanced nuclear energy systems. Ultimately, this knowledge will enable bottom-up design of materials with unprecedented tolerance to extreme environments.

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Priority Research Direction: Controlling thermo-mechanical properties and dimensional stability during irradiation

Problem Statement

The service life of reactor components is frequently limited by dimensional changes and degradation of mechanical properties during irradiation. Dimensional changes, specifically swelling and irradiation-induced or enhanced creep, result from the disposition of radiation generated defects at sinks (dislocations, dislocation loops, boundaries, voids). Degradation of mechanical properties results from irradiation induced microstructural changes including evolution of dislocation loops, voids and bubbles, and from microchemical and phase changes. In ceramic materials such as nuclear fuel, these same microstructural changes can degrade phonon and electron transport and thus decrease thermal conductivity. Though there is a good understanding of irradiation effects on thermal-mechanical properties and dimensional stability of nuclear reactor materials, the ability to predict materials performance beyond the regime of experimental experience, e.g., to higher temperatures, higher accumulated radiation damage, and higher stresses, is still lacking. The current approach in establishing high temperature design rules of nuclear structural components is practically empirical. Such an engineering approach often proves to be successful only when it is supported by a robust database and involves no data extrapolation, but can be overly conservative or problematic when the time-dependent processes such as creep and creep-fatigue are involved, and irradiation adds to a new dimension to these complex problems. A more fundamental approach based on a thorough mechanistic understanding is therefore needed to achieve the required predictive capabilities. The understanding of the origins and processes of deformation and fracture under irradiation is also critical to the design and development of advanced materials with radiation tolerance, while maintaining good thermal-mechanical properties and dimensional stability.

Executive Summary

The performance of nuclear fuels and structural components during reactor operation is dictated by their thermal-mechanical behavior. A predictive understanding of irradiation effects on thermo-mechanical properties of multi-component, multiphase materials is essential for rational design of advanced materials for structural, fuels and waste-form applications and for development of new reactor technologies. The understanding of the complex thermal-mechanical responses of irradiated materials requires a combination of integrated theoretical, experimental, and modeling techniques from the atomic scale to the meso- and macro-scales. New experimental capabilities are required to provide insight into thermo-mechanical behavior under nuclear reactor environments at all relevant time and length scales.

Over the past twenty years in-situ mechanical testing combined with lattice strain measurements in either neutron or (more recently) synchrotron x-ray spectrometers has allowed researchers to develop a good understanding of how metals deform at the single crystal level in polycrystals.

This allows the prediction of plasticity under multi-axial, or highly constrained stress conditions like those ahead of a crack. This helps designers to understand the conditions that cause initiation and propagation of fracture, fatigue cracks, and other slow crack growth mechanisms such as delayed hydride cracking in Zr or Ti alloys. These techniques could readily be extended to the understanding of irradiated materials, if facilities were available for preparation, shipping and handling of radioactive specimens at neutron and synchrotron x-ray facilities. This capability would help the understanding of both fracture and dimensional stability of materials under irradiation.

Scientific Challenges

A fundamental understanding of the mechanical responses of a material to complex loading under extreme temperature and radiation environments is essential to the structural integrity and lifetime prediction of nuclear components and to the design and development of advanced materials for next-generation fission and fusion energy systems. The mechanical response of a material is a result of many competing deformation and damage processes (e.g. dislocation interactions, grain boundary motion, segregation, and diffusion, etc) that originate at atomic and microscopic scales with macroscopic consequences. A key challenge for the accurate assessment and prediction of mechanical properties in extreme environments is to integrate a number of coupled processes involving a broad range of time and length scales to capture the complex nature of real materials in real environments. In nuclear reactor environments, irradiation changes the active deformation systems (slip, twinning, climb, grain boundary sliding), causes dimensional changes including creep and swelling, and leads to the loss of fracture resistance. Many outstanding questions remain regarding mechanical properties of materials during irradiation. The physical mechanisms responsible for flow localization during plastic deformation, low-temperature irradiation embrittlement and the increase in the ductile-brittle transition temperature (DBTT) in irradiated body-centered-cubic (bcc) metals and alloys, high temperature grain boundary and helium embrittlement, irradiation-assisted stress corrosion cracking, material response under fatigue and creep-fatigue loading and irradiation are still unclear. A microstructural basis for fracture mechanisms is lacking for irradiated materials.

Understanding the fundamental mechanisms of deformation and fracture will allow prediction of materials response under static or dynamic loading in nuclear reactor environments. The prediction of mechanical properties of materials, at the current stage, is still limited to a few simple cases and model configurations. The modeling of the relationship between the state of the microstructure and the deformation and damage mechanisms has remained largely phenomenological. Though there has been substantial development in understanding the deformation and fracture behavior in nuclear reactor materials, lack of understanding of contributions from structural heterogeneity is a primary limitation in the development of predictive capabilities, especially for crack initiation. The scientific challenge is to model real materials with complex microstructure and their response to complex thermal, mechanical, and irradiation conditions. Quantitative modeling is needed to incorporate individual deformation

and damage micro-processes into mesoscopic computer modeling to accurately describe the evolution and interactions of microstructural elements such as dislocations, second-phase particles, grain boundaries, radiation defects, and to produce the required macroscopic mechanical response under any external conditions (temperature, strain rate, stress and stress state) in complex material systems. An ultimate challenge is to develop a reliable computational tool that can be used for structural design of nuclear components and be accepted for qualification and licensing of nuclear materials.

In addition to understanding the changes in mechanical properties due to irradiation, changes in thermal transport and the underlying microstructural changes, are critical to understanding the performance of ceramic materials under radiation. Degradation of thermal properties resulting from microstructural and microchemical evolutions has become a limiting factor of the performance of nuclear reactor fuels. To achieve a higher burn-up, quantitatively correct modeling is critical for the development of nuclear fuel. New experimental capabilities are needed to characterize the evolution of physical and mechanical properties under the bombardments by energetic particles.

Research Directions

Research is required to further the fundamental understanding of nuclear materials and to develop technology required to extend the life of existing reactors and design more efficient fission and fusion energy systems. The research must address the thermo-mechanical aspects of materials performance under irradiation, including dimensional stability (growth, swelling), creep, fatigue, creep-fatigue, plasticity, crack initiation and propagation, thermal transport, and the microstructural and microchemical/phase changes that influence these phenomena.

Despite many years of research and development of materials for advanced nuclear energy applications, fundamental knowledge is still lacking in areas that are vital to the integrity and safety of nuclear reactor systems. For instance, a fundamental understanding of time-dependent deformation, dynamic microstructural evolution under thermal-mechanical loading, fatigue and creep-fatigue crack initiation and propagation, and synergistic interactions between static and dynamic loading and irradiation is still largely unknown. The current elevated-temperature structural design rules were developed in 1970s-80s, and have no fundamental physical basis. The design methodology cannot provide an adequate foundation for component designs in complex stress states and for long-term service in harsh reactor environments. The qualification and licensing of any new material still requires a large experimental campaign to establish an extensive database. It is critically important, therefore, to have a basic understanding of dynamic deformation processes and material aging behavior under long-term creep-fatigue loading and irradiation to develop predictive capabilities for modeling the mechanical performance of materials exposed to high temperature, high radiation damage and complex stress states.

At present there are no models for predicting the full range of mechanical behavior of irradiated materials needed to design and operate reactors under all operating conditions. Many existing deformation mechanism models (e.g. thermal creep) and radiation effect models are semi-empirical. These models do not truly capture the fundamental physical processes of the interactions of dislocations with barriers (e.g. second-phase particles, radiation defects, grain boundaries, etc.) and do not necessarily provide a good description of material behavior beyond the testing conditions. Models, such as the phase-field model that can describe the microstructure for multiple concurrent defect processes, are presently not available but are in development. Such models provide averaged physical properties, such as elastic modulus, density, thermal conductivity etc. as modified by irradiation effects, for finite element models of the macroscopic behavior. Thus they span the length scales between μm and m and are informed by processes down to the atomic length scale. Fracture mechanics models need to incorporate more physics to allow the transfer of small volume test results to complex structures involving different constrain conditions. Ultimately, a first-principle understanding of the relationship between microstructure and mechanical properties during irradiation must be developed and used for the design of components and the development of complex materials with tailored properties.

Evidently, multiscale computational modeling must be closely coupled with in-situ experiments of nano- and micro-scale structural evolution and mechanical behavior of materials. Characterization of irradiated materials requires a variety of techniques, including ex-situ and in-situ mechanical testing, metrology, neutron and x-ray diffraction and small angle scattering, strain mapping, electron microscopy, atom probe, tomography, etc. Advances in characterization techniques using electrons, neutrons, x-ray and ions provide unprecedented opportunities for investigating mechanical properties over a wide range of time and length scales. New and sophisticated capabilities are available to probe mechanical response over small material volumes. Materials can also be characterized nondestructively in-situ, during service and within actual components where material response is fundamentally different from the behavior in near-surface regions or in thin foils. Spatially-resolved characterization of stress distribution, texture, and dislocation evolution in single grains and particle distribution at structural inhomogeneities are also possible. These emerging characterization capabilities are powerful tools for validating and guiding models and for improved performance of structural components.

Capability Gaps

One of the key requirements for such research is long term irradiation, at the appropriate temperatures, of bulk specimens to lifetime exposures, of thermal, fast and fusion reactors, in the latter two cases to 200-400 dpa, as well as ion beam technology to allow for focused understanding of microstructural development and the relationship to deformation and thermal transport. At present there are no facilities available in the United States to expose materials up to 100-400 dpa for full scale mechanical testing. There are currently no ion-irradiation facilities combined with in-situ mechanical testing on small samples that can be irradiated through the volume. Likewise no facilities are available to irradiate materials to high dpa with fast neutrons

to simulate processes occurring in a reactor. What is needed is a copious source of fast neutrons, such as the BOR-60 source in Russia, the JOYO facility in Japan, a fusion source such as the proposed IFMIF, or a spallation source such as the Materials Test Station (MTS) at LANSCE. Full-scale mechanical testing includes tensile, fracture toughness, fatigue and creep-fatigue testing to cover present and future high temperature reactors. The additional presence of H and He ions is required to simulate the irradiation conditions in fusion reactors since these have a strong effect on embrittlement.

Studies of the dynamic effects of irradiation will require in-situ testing, i.e, simultaneous irradiation and observation using analytical techniques. This will allow the study of transient effects such as microstructure evolution and dislocation interactions with defects and irradiation-induced, or-modified precipitates and their correlation with the mechanical response under different irradiation conditions (dose, dose rate, temperature or stress, etc). Ion beam irradiation is promising for such in-situ irradiations, and facilities combing ion irradiation with transmission electron microscopy with heating and straining capabilities already exist (e.g. the IVEM-Tandem facility at the Argonne National Laboratory). Triple beam facilities combining heavy ion irradiation with light element implantation (H, He) will allow the simulation of thermal fission, fast fission and fusion conditions for mechanistic studies and rapid statistical sorting of potential new materials. However, the observations in such experiments are often affected by the specimen surfaces, and may not be fully representative of the bulk. Efforts are underway to model the surface effects in thin foils during in-situ ion irradiations with experimental validation and verification [1]. The success of such computational and experimental efforts not only allow bulk irradiation effects to be modeled, but also provides a valuable interpretation tool for small volume in-situ experiments.

One potentially useful technique is the combination of proton irradiation of “bulk” specimens (50-250mm thick), combined with synchrotron x-ray or neutron sources for diffraction, scattering, spectroscopy or imaging characterization. An ideal situation would be to have a load frame mounted on a synchrotron x-ray diffractometer so that the intergranular or type-2 strain response could be captured as well as the macroscopic strain response to applied stress while the sample is being irradiated with ions. Recent progress has shown great promise of synchrotron x-ray techniques for characterization of materials for nuclear energy applications. The third-generation hard x-ray beams allow measurements with high-spatial resolution and fast in-situ measurements of dynamic processes. Evolution of internal stresses for different phases or crystal families by in-situ diffraction measurements during tensile, compressive, cyclic loading provides unique experimental information about deformation mechanisms in polycrystalline materials [2]. Strain and texture mapping around a crack tip by in-situ synchrotron XRD provided a better understanding of deformation and crack propagation mechanisms under static and fatigue loading [3]. A recent work on grain structure mapping by diffraction contrast tomography and in-situ observation of stress corrosion cracking by synchrotron x-ray micro-tomography has provided insight into the dynamic interaction of a growing crack with crystal structure and the

contribution of different boundary types to cracking resistance [4]. Synchrotron radiation techniques also allow visualization of internal cracks in a material in three dimensions and to characterize stress/strain condition, grain orientation and local chemistry that provide more details critical to the understanding of the fundamental mechanisms of stress corrosion cracking. Information of spatially inhomogeneous residual stress distribution in materials and components with complex geometries can be directly applied for validating finite element modeling for stress prediction in large-scale components. These new directions in understanding deformation and fracture mechanisms in unirradiated materials are critical areas that need to be explored to understand the mechanical performance of materials in nuclear reactor environments.

Some synchrotron radiation tests can now be carried out on archived materials with low activities [5]. However, for materials irradiated to high doses, shielded facilities and remote handling will be required. Many technical questions remain to be addressed such as the set-up and shielding of the beam facilities, signal to noise issues for highly radioactive samples that may mask the diffracted signal, and affect the survival of x-ray detectors in a high γ-ray flux. New instrument technologies such as new detector and signal processing technologies may be necessary. The ability to transfer highly active material between the irradiation source and the x-ray and neutron equipment or the microscopes in which the samples will be examined, is a difficult task that must be addressed. This is easier if all the facilities are on the same site. As yet an ion accelerator to provide sample irradiation has not been set up at a synchrotron x-ray station although this has been proposed. The easiest irradiation plus observation process to implement would be on small pillars of materials milled from bulk material that can be irradiated through the whole volume by suitable ion irradiation. These can readily be examined by electron microscopy and x-ray diffraction during in-situ mechanical testing. However the question arises whether results on sub-micron size coupons are characteristic of the macroscopic response required for engineering design. Models are required to superpose the results from the two sample scales.

Potential Impact

A complete bridging of the capability gap discussed above will lead to substantial improvement in understanding the thermal and mechanical behavior of materials under irradiation. The development of facilities for high dosage, full-scale and in-situ thermomechanical testing could provide great benefit for the validation of advanced nuclear energy materials. This facility would also provide the best simulation to the environment that would be present in advanced nuclear reactors. A facility developed for rapid and efficient synchrotron or neutron diffraction of highly radioactive materials would be of great benefit in understanding the microstructural evolution of reactor fuels. This understanding could then be used to develop an efficient fuel with known microstructure throughout the cradle-to-grave life cycle. Furthermore, the development of a synchrotron facility that could also provide *in situ* irradiation capabilities would provide real time details of the microstructural evolution. Quantified microscale thermomechanical testing within an electron beam during helium and ion irradiation would provide a method to directly observe the defect structure development as an effect of both

irradiation and various thermal, mechanical, or other applied loads. The directly observed mechanisms would provide significant input for the development of microstructural and mechanical models. The development of correlations relating thermomechanical properties reported from various testing techniques over multiple length scales would provide great benefit in the transfer, accumulation, and access materials property description. This would drastically increase the efficiency of materials selection for a wide range of applications.

The combined impact of these new facilities, methodology, and theories will result in significant benefit to the nuclear energy industry. A thorough understanding of the life limiting effects on the thermomechanical properties may result in the suggestion of advanced materials. These materials will be better suited for the high temperature, high radiation dosage, and corrosive environment that will be present in the next generation of nuclear reactors. Advanced thermomechanical testing of new materials will be expedited and provide greater assurance during the validation process. Finally, a better understanding of thermomechanical properties in corrosive and irradiation environments will permit better maintenance practices and life prediction of current nuclear reactor facilities. A complete understanding of dimensional degradation and altered mechanical properties may permit a life extension of existing nuclear plants resulting in the savings of billions of dollars in rebuilding costs.

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Priority Research Direction: Defining the frontiers of microstructure science under irradiation

Problem Statement

The goal is to develop a computationally-predictive, experimentally-validated multi-scale understanding of nuclear materials (fuel and cladding) that incorporates the effects of irradiation and temperature on microstructure formation and evolution and enables prediction of how these processes affect thermo-mechanical properties.

Executive Summary

The cumulative effect from fission-damage processes, high temperatures, high stresses, and high thermal gradients is to cause severe degradation in the thermo-mechanical properties of a nuclear-fuel assembly (fuel plus cladding), limiting its lifetime and strongly affecting operational cost [1]. Similar effects occur in reactor core structural materials due to damage initiated by high-energy neutrons [2]. Elucidation of the microstructural causes and mechanisms controlling this degradation behavior requires development of a comprehensive program of spatially-resolved, multi-scale computation and complementary experimentation, on commensurate length scales [3-4]. The ultimate goal is the development of computationally-predictive, experimentally-validated multi-scale understanding of nuclear materials that fully incorporates all the various, concurrently occurring and highly coupled microstructural process within a unified computational and conceptual framework. The experimental limitations in the non-destructive characterization of evolving microstructures and irradiation effects provide major challenges for the community. Also, current experimental techniques, both in-situ (ion and neutron) [5] and ex-situ [6], do not characterize evolving microstructures in irradiated materials with sufficient statistical detail, making the analysis of unit mechanisms very difficult.

Scientific Challenges

A comprehensive understanding of microstructural processes is a critical component of the development of a predictive, materials-physics-based nuclear materials modeling capability. In spite of considerable experience in studying microstructural processes in nuclear materials, such as void swelling [7-8], fission-gas release [9] and crack development [10], a comprehensive understanding of how microstructural processes control the thermo-mechanical properties and performance of nuclear materials remains to be developed.

Apart from large empirical databases [11], fundamental information that connects “structure” across the relevant length- and time-scales with fuel and cladding behavior does not currently exist. What is particularly lacking is a comprehensive multi-scale model that captures how microstructure development during irradiation (including defect generation and evolution), leads to the degradation of the fuel and cladding.

Another challenge is correlating thermo-mechanical properties to the neutron flux in the reactor [12]. Since a certain flux can be associated with a variety of changes in the properties of the materials, depending on the history and damage mechanisms involved, solving for the irradiation level may lead to mathematically ill-posed inverse problems. On the bright side, the direct problems (change in properties versus irradiation level) can be solved using simulations [13].

Research Directions

What is needed is an experimentally validated, hierarchical multi-scale modeling approach for microstructure evolution under irradiation that combines spatially-resolved, multi-scale computation with complementary experimentation, on commensurate length scales. This unique combination will enable capturing the interplay between the material microstructure, fission products, and lattice defects and their effects on -mechanical properties. The centerpiece of the multi-scale strategy (Figure 1) is a *unified* meso-scale approach that combines phase field with heat and chemical-species transport theory to predict *concurrent* formation and evolution of microstructure under irradiation, high-temperature, environment and stress. Four critical elements of this approach are:

- Development of a comprehensive theoretical and computational mesoscale approach that considers all the various, concurrently occurring and highly coupled microstructural process within a unified framework;
- Capturing irradiation effects within the mesoscale modeling framework;
- Coupling the neutron transport with the heat and chemical species transport via complex models of thermo-mechanical and chemical properties of the fuel and clad.
- Linking the microstructural simulations with continuum fuels-performance simulations via a scale-bridging approach.

The mesoscale approach receives input from the lower length scales (the atomic and electronic-structure levels (see Figure 1) and/or from experiments in the form of bulk and interfacial mechanisms and materials parameters (see also the Priority Research Direction on Predictive Understanding of atomistic and collective fundamental mechanisms of radiation effects in materials). The output from the mesoscale simulations, in the form of homogenized properties such as the elastic moduli or the thermal conductivity for a given microstructure, provide the input to the continuum level (or engineering-scale; see Figure 1).

The experimental validation of microstructural predictions requires in-situ characterization tools such as of in-situ TEM and ion irradiation, electrons, x-ray, and neutron scattering. A strength of in-situ work is the discovery and illumination of fundamental dynamic processes such as point-

defect clustering, dislocation-loop formation, loop motion, coalescence and interactions with existing surfaces, interfaces, and microstructure.

Future directions should include measurements of local chemistry changes (electron-energy filtering), tomography, enhanced spatial and temporal resolutions, and the expanded experimental space afforded by aberration-corrected microscopes.

Capability Gaps

• Current experimental techniques, both in-situ (ion and neutron) and ex-situ, do not characterize evolving microstructures in irradiated materials with sufficient statistical detail, making the analysis of unit mechanisms very difficult.

• Due to the very long neutron irradiation times necessary to achieve doses relevant to reactor operation regimes, ion beam (light or heavy) irradiations are used for accelerated studies. The equivalence or complementarily of the two methods requires careful consideration in the differences in damage rate and damage structure.

• The understanding of heat and chemical species transport, defect formation and evolution, and phase behavior in complex, heterogeneous materials is currently mostly based on observation and empirical correlations that involve (linear) combinations of the properties of the homogenous

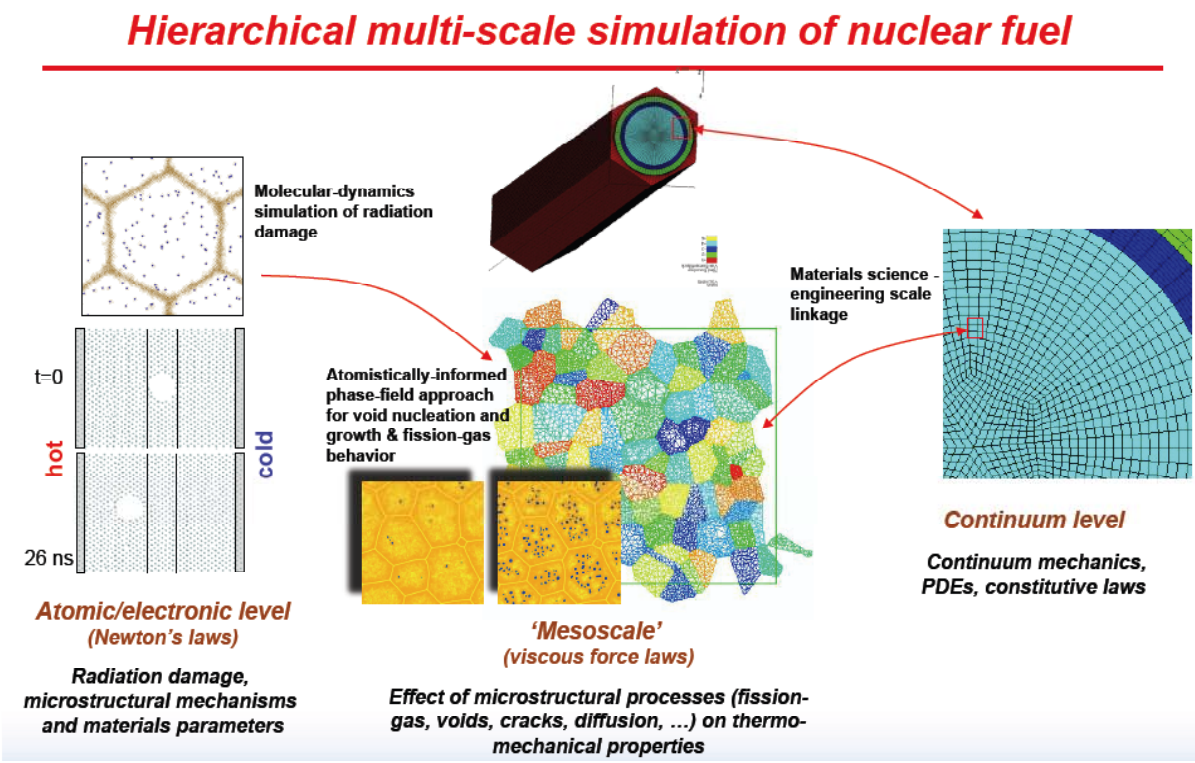

Figure 1. Hierarchical multi-scale simulation approach for materials-physics based prediction of the performance, degradation and lifetime of nuclear materials (see text).

phases. A more sophisticated theoretical and computational framework is necessary.

• Current reactor simulation tools perform calculations of criticality, temperature profiles and heat transport that ignore the detailed radiation-induced changes in materials properties. Although computationally intensive, the coupling is necessary for accurate predictions of both materials and reactor performance.

• Although good results are available at specific scales (atomistic, meso-scale, and continuum), there is a shortage of robust scale-bridging algorithms able to capture critical properties driving microstructural changes under irradiation.

Potential Impact

Understanding the relations between microstructure and continuum thermal, mechanical, and chemical properties of irradiated materials will positively impact:

- The development of fuels- and materials-performance tools capable of predicting the behavior of nuclear-fuel elements in normal and ab-normal (transients, accidents) reactor regimes.

- The design of new, innovative, fuels and structural materials with optimal functionality and performance.

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Priority Research Direction: Co-design of experiments and models of time & space dependent radiation damage

Problem Statement

Twenty-five years ago experimentalists and theorists in radiation damage effects worked quite separately, and on very different length and time scales. Today, experiments and theory working at similar length scales are being realized. In order to take full advantage of the advances in theory, simulation, and modeling it is essential that experiments are intimately coupled at each length scale and time scale. Efforts to achieve this vision of co-design need to be accelerated and substantially enhanced.

Executive Summary

Experiments coupled with theory, simulation, and modeling will play an important role in accelerating materials development for advanced reactors, improving safety, and increasing performance in nuclear energy systems. It is imperative that in the development of multi-scale theory, simulation, and modeling (TSM) that the research plan emphasizes the intimate contact between experiments, and the TSM itself. Community experience suggests that a positive impact on the safety, reliability, and performance of nuclear reactors can be expected in 5 to 10 years as the methodologies described here become acceptable to the nuclear energy practitioners.

Science Challenges

Experiments coupled with theory simulation and modeling will play an important role in accelerating materials (both fuels and structural) development for advanced reactors, improving safety, and increasing performance in nuclear energy systems (both fission and fusion). During the R&D phase of development such models can reduce development costs by helping to down-select the best materials choices for further development. It is generally agreed that for those situations where materials age slowly while in service it is desirable to have simulations and models that predict performance degradation long before failures or deficiencies become evident in operation. However, there is a conundrum which is this; the development of robust models requires that there be available a large amount of experimental data covering not only the engineering space, but also the materials physics space. This data must be such that specific mechanisms of the aging process of the material can be isolated and studied in a way that it informs the models of the fundamental physics—the so called unit mechanisms. *(Side bar 1 describes the importance of unit mechanisms in more detail.)*

Research Directions

It is imperative that in the development of multiscale theory, simulation, and modeling (TSM) that the research plan emphasizes the intimate contact between experiments, and the TSM itself. Recently, high performance computing at the petascale and exascale for nuclear energy materials was reviewed in "Science Based Nuclear Energy Systems Enabled by Advanced Modeling and Simulation at the Extreme Scale"

(http://www.science.doe.gov/ascr/ProgramDocuments/Docs/SC-NEWorkshopReport.pdf). Useful references focused on the materials challenges for nuclear energy can be found in this report. A central question of the report was how high performance computing might accelerate the deployment of advanced nuclear energy systems. It is noted; "(*in the past*) scientists could not credibly utilize the results of accelerated out-of-pile materials experiments to develop reliable forecasts of in-pile performance." This problem is a challenge facing TSM that must be met and resolved if validated models and simulations are to emerge from this enterprise.

Twenty-five years ago experimentalists and theorists in radiation damage effects worked quite separately, and on very different length and time scales, today experiments and theory working at similar length scales are being realized. In order to take full advantage of the advances in TSM to date it is essential that experiments are inter-digitated with physics models at each length and time scale. How this is done is an expansive topic worthy of a workshop in its own right.

What the separable elements are for both TSM and for the unit mechanistic experimental effort can be listed. In so doing, we will generate thoughtful consideration of the challenge of designing experiments that truly "inform" TSM of the underlying physics of radiation effects in materials. Such an experimental strategy might be considered, in parallel with multiscale TSM, as multi-scale experiments, experiments that are, in terms of the underlying physics, *substantially equivalent* to the multi-scale TSM.

The TSM picture reflecting time and length scales has been outlined in numerous articles. One particularly graphic representation often shown is in Figure 1. Here, simulation techniques addressing separable events at differing length and time scales are indicated. The inference is that the models at lower length scales can provide analytical models to inform longer length or time scale models about relevant properties.

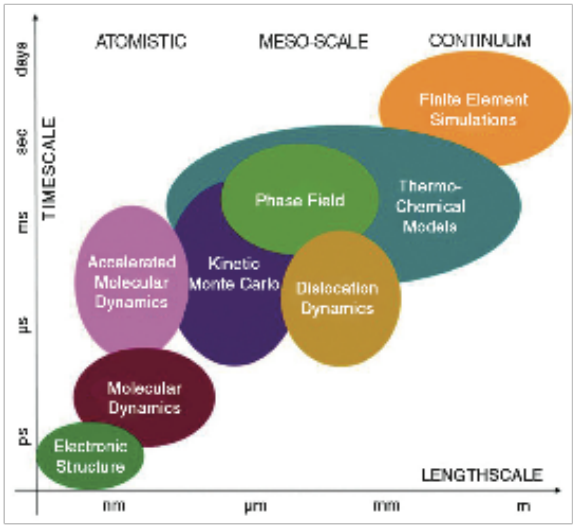

Figure 3: Multi-length and time scale modeling after M. Stan, Materials Today 12 (2009) 20-28

These computational elements map on to numerous materials effects; hardening and embrittlement including helium embrittlement, phase instabilities, irradiation creep, and volumetric swelling that connect to critical nuclear reactor continuum code simulations such as TRACE, TRAC, RELAP and SASSYS. Examples of the underlying unit mechanisms are; He generation (in some cases hydrogen generation), primary defect production, short-term annealing, defect recombination,

clustering & migration, gas diffusion and trapping, cascade aging, local solute re-distribution, long-range defect transport & annihilation, radiation enhanced diffusion and induced segregation of solutes, nano/microstructure & local chemistry changes, and nucleation and growth of extended defects and precipitates. These physical mechanisms are examples of the experimental glue that can inform the models of the underlying physics.

If one considers, as one should, the employment of ion-beams to accelerate the research to develop a fundamental understanding of unit mechanisms, we immediately realize that while damage (dpas) can be produced 1000 times faster with ions than with reactor neutrons, we are also faced with a very intricate issue of a change in the time scale for the post cascade or displacement events. If one is not cautious, this change in rates could lead to misinterpretation of the experimental results. This point is illuminated in more detail in side bar 2.

In summary we suggest the following research direction to integrate experiments and TSM:

Design and execute the critical ion-beam experiments that will "inform" the TSM in the following areas:

1) Develop the formalisms to follow micro-structural evolution of materials at the rate of nuclear reactors and to predict macroscopic properties.
2) Identify the relevant length scales applicable to the physics mechanisms in the evolving microstructure
3) Predict the evolution of complex interfaces: corrosion, abrasion, and fuel-cladding interface

Capability Gaps

The discussion above brings into focus four gaps in our capability to perform multiscale modeling for nuclear energy materials.

1) Discovering, via closely coupled experiment and theory, the key factors of materials performance and including them in models
2) Bridging the time and length scales for materials evolution in the extremes of the nuclear environment
3) Dealing with the complexity of multi-component materials and their evolution due to nuclear reactions
4) Transcending ideal materials systems to engineering materials (*ideal to real*)

Closing these capability gaps will be daunting and challenging. However, we can say with some confidence, that it is essential for TSM of nuclear energy materials to establish a close, even intimate relationship with if at the end of the day the goal is predictive capabilities necessary to achieve acceptance within the engineering community. Today, multiscale-modeling links to experiments through an almost quixotic dependence on serendipitous experimental discovery. While motivation for TSM often comes from the results of integral experiments, carried out over many years in reactor environments, the problems having been reduced to their component elements within the modeling community, are never passed to the experimental community so

that specific, focused experiments are designed, executed and then serve as the basis for validation and verification of the elements of the multiscale approach. Tightening this linkage of experiment and TSM would open a new approach not currently extant in the nuclear energy area.

Indeed the goals for advanced fission systems and for fusion energy are beyond current empirical experience. Only through modeling can we hope to explore this space in reasonable time scales and at reasonable costs. Experiments are the key to assure that models developed for this exploration are physical accurate and predictive in their results.

Potential Impact

Experiments coupled with theory simulation and modeling will play an important role in accelerating materials development, improving safety, and increasing performance in nuclear energy systems (fission and fusion). It is generally agreed that for those situations where materials age slowly while in service it is desirable to have simulations and models that predict performance long before serious failures or deficiencies become evident in operation. Indeed during the R&D phase of development such models can reduce development costs by helping to down-select the best materials choices for further development. Separable variable and/or unit mechanism experiments coupled with time and length transcending TSM will lead to higher levels of materials reliability and faster R&D associated with application specific materials development. Positive impact on the safety, reliability, and performance of nuclear reactors can be expected in 5 to 10 years as the methodologies described here become acceptable to the nuclear energy practitioners.

Side Bar 1: Isolating Unit Mechanisms

Why are unit mechanisms such an important concept? This point has been illuminated in a paper titled "Mixed Atomistic-Continuum Models of Material Behavior: The Art of Transcending Atomistics and Informing Continua" by M. Ortiz et. al, *MRS Bulletin*, **26** (3) 216-221, March 2001. In this paper the connection between the atomistic world and the continuum is defined in terms of unit mechanisms. We quote from this paper:

"It is clear, therefore, that atomistic and continuum theories need and reinforce each other. This atomistic/continuum handshake is most effectively achieved within the framework of multiscale modeling. Multiscale modeling is a 'divide and conquer' modeling paradigm. Firstly, the entire range of material behaviors is divided into a hierarchy of length scales (as well as time scales author note). Secondly, the relevant 'unit processes' are identified at each length scale. The unit processes at one scale represent averages of unit processes operating at the immediately lower length scale. This relation introduces a partial ordering of processes. In addition, the unit processes should operate roughly independently: two processes which are tightly coupled should be considered as a single unit process (author note for example the role of helium in void growth).

For systems for which these relations are well defined, the modeling effort reduces to the analysis of each unit mechanism in turn and the computation of averages, eventually leading to a full description of the macroscopic behavior of the material. This is an inductive process which must be given appropriate initial conditions. In many cases, such initial conditions take the form of unit mechanisms operating at the atomic scale and which are, therefore, accessible to atomistic modeling. In this manner, atomistics informs material modeling at higher continuum length scales and transcends its own size strictures.

Unfortunately, the multiscale paradigm is more easily stated than carried out in practice. At present, the analysis of the unit mechanisms and the characterization of effective behavior relies either on numerical schemes or a motley assortment of analytical tools. Examples of the latter are mean-field theories, statistical mechanics, transition-state theory, direct methods of the calculus of variations, and homogenization. Because of the broad scope of the field and its present state of development, multiscale modeling in general, and mixed atomistic-continuum modeling in particular, cannot be readily reduced to a self- contained and unified formal theory and remains an art as well as a science."

So, with this definition the critical role for experiments is to inform theory simulation and modeling at every step of the multiscale process by designing experiments that capture the essential physics of the models. Moreover, it is incumbent to not only explore the engineering phase space of the application but also a wider phase space bounded by failure mechanisms or materials instabilities such as phase transformations changes in mechanical properties or the termination of mechanisms or the onset of new mechanisms. In this manner the models can more adequately inform engineering codes based on scientifically defendable methodologies.

Side Bar 2: It is not Acceleration

The execution of experiments that isolate unit mechanisms with the purpose of informing multiscale models of the essential physics at each step of the modeling process is not accelerated aging. While experiments that isolate unit mechanisms can and do benefit from an experimental platform where the processes are much faster than the in-service conditions they are not accelerated aging!

What then is accelerated aging or testing?. All definitions of this engineering approach to materials failure have one thing in common; they are integral experiments, where as experiments that isolate unit mechanisms are by their very definition not integral experiments. Examples of simple definitions of accelerated aging or testing are given here:

- Accelerated aging is a testing method used to estimate the useful lifespan of a product when actual lifespan data is unavailable. ...
- A test that simulates long time environmental conditions in a relatively short time.
- A set of laboratory conditions designed to produce in a short time the results of normal aging. Usual factors included are temperature, light, oxygen and water.
- A test in which voltage, temperature, etc. are increased above normal operating values to obtain observable deterioration in a relatively short period of time. The plotted results give expected life service under normal conditions.
- Procedures for subjecting pressure sensitive label material to special environmental conditions in order to predict the course of natural aging.

Accelerated aging plays an important role in product environments and in identifying weaknesses prior to their catastrophic consequences. However, it is generally believed that the acceleration rates must be modest. This arises because of a lack of understanding of the fundamentals of the underlying failure mechanism(s) – the unit mechanisms. The point to remember is that high-speed experiments designed to reveal and understand unit mechanisms are not accelerated aging experiments.

Priority Research Direction: Materials Design for Resistance to Corrosion and Surface Damage in Extreme Environments

Problem Statement

Corrosion and other surface degradation processes, such as oxidation, vaporization, and hydriding, are major limiting factors in the application and lifetime of materials used in extreme environments. In fact, the integrity of materials in fission and fusion systems is challenged as much by chemical aggressiveness of the environment as by radiation as most problems in LWRs and many GenIV concepts are driven by chemical interaction. The inclusion of irradiation adds a significant and new dimension to the challenge of developing materials to withstand the extreme environments of these systems, as very little is known about how radiation alters chemical processes such as corrosion and oxidation at surfaces. The problem then is one of understanding the fundamental processes of materials degradation in extreme environments consisting of high temperature, stress, irradiation and chemically aggressive species, and to use that understanding to design a new generation of resistant materials.

Executive Summary

A scientific understanding of the corrosion process has been hindered by the complex interactions of many simultaneously occurring phenomena that cover wide ranges in length and time. Critical phenomena include transport mechanisms, reaction thermodynamics and kinetics, galvanic effects, and environmental interactions in extreme environments consisting of radiation, temperature, pressure and aggressive chemical environments. Even where the overall environment may be benign in terms of general attack, localized conditions may result in aggressive attack over very restricted regions such as in the cases of pitting and stress corrosion cracking. A schematic of the various processes acting during corrosion in such an extreme environment is presented in Figure 1.

Although the details of corrosion phenomena vary widely for a given material and environment, the types of information required to construct a sound scientific model for any particular problem share a common thread. Detailed knowledge of the mechanisms of transport of point defects, electrical charge, and chemical species along with pertinent chemical reactions and phase equilibria and the effects of applied stress states are required for a complete description of any corrosion process. The development of such a knowledge base is complicated by the fact that many processes occur simultaneously and, thus, interact in unknown ways.

To elevate corrosion science to a level where confident predictions of the corrosion performance of existing and new materials can be applied to the design of components for extreme environments, several advances in capability are required. Test stations that contain the chemical environment of interest while providing the ability to apply appropriate conditions of stress, temperature and irradiation do not exist today. In addition to being able to apply appropriate environments, probes to allow for the simultaneous measurement of critical

phenomena at appropriate length and time scales are required. In addition to experimental capabilities, models for the various phenomena of interest that allow for integrated predictions of performance have yet to be established.

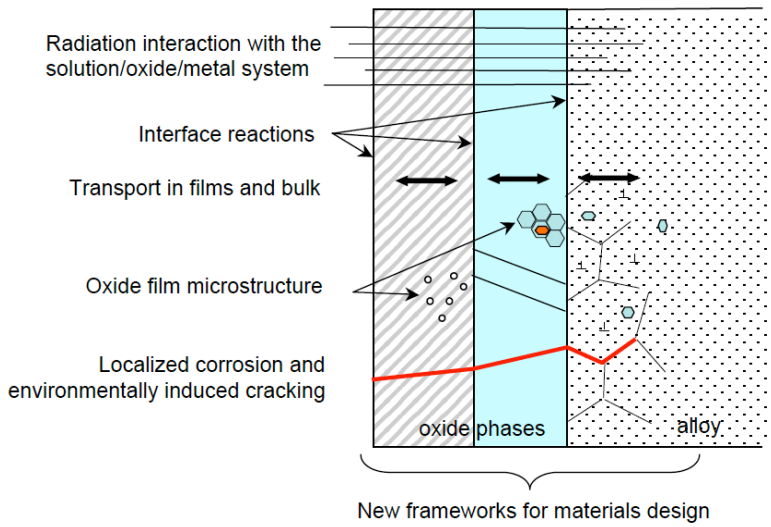

Figure 1. Schematic representation of key microstructural processes affecting corrosion in extreme environments characterized by high temperature, stress, radiation and an aggressive environment.

The general efforts described above represent a significant challenge for any given material and environmental condition. However, significant progress can be expected over a decadal time frame for a small subset of problems. An additional benefit of such an effort would be the establishment of generalized experimental and computational approaches for studying corrosion that could be applied to any particular problem in corrosion science. Examples of potential problems to focus on first include the effects of irradiation on corrosion of materials used in nuclear reactors for power generation, the pitting of landing gear alloys for fighter aircraft, and the stress-corrosion cracking of reactor components in high temperature water.

Scientific Challenges

Advancements are needed to simultaneously observe and measure materials structures and reaction kinetics, as well as local environmental conditions at and near interfaces through a range of length and time scales under extreme conditions. These measurements and observations are must be achieved *in situ* (combined with ex situ measurements) and must probe surface chemical reaction kinetics, transport processes, phase and defect nucleation, local stresses and strain anisotropy, and heterogeneous processes such as void and crack formation. It is critical that we measure dynamic processes over time scales from picoseconds (e.g., radiolysis time scale) to years (e.g., crack propagation time scale). The initial focus of these studies should be on

relatively simple systems to successfully model unit processes, and subsequently more complex processes.

New fundamental, atomistic and physics-based models should be developed to replace or enhance existing modeling approaches to predict materials behavior in extreme environments. Models must combine the physical properties of materials with environment. A goal of the proposed research should be to have the ability to predict materials corrosion and near-surface phenomena under complex conditions, for example, where variables such as temperature, pressure, irradiation conditions, and environment chemistry vary with time. Modeling and experiment should be done with an effort toward continuous validation and refinement predictive and design capabilities.

There is a great need for experimental and theoretical capabilities that will enable measuring and characterizing material-environment reactions under extreme conditions with the spatial and temporal resolution described in many sections of this report. Through fundamental understanding, more rapid and effective design of materials can be achieved enabling the identification of materials compositions, structures, and operating parameters with enhanced resistance to corrosion and surface damage in extreme environments.

Research Directions

Corrosion and interfacial reaction processes are complex, involving the need for understanding dynamic and multi-variable environmental processes and their effects on materials processes which can be extraordinarily challenging to observe directly through the length and time scales that we required to design to and understand materials performance. In particular, the following processes are areas in which a significant research effort is needed to better elucidate the mechanisms and to establish more fundamental models:

- point defect and chemical transport
- interfacial reactions, film formation and phase stability
- localized oxidation and environmentally assisted cracking
- radiation-induced corrosion

Corrosion and oxidation are still described by models that were developed decades ago. Their verification and accuracy is limited by the lack of understanding of point defect behavior and chemical transport in metal-oxide systems. Corrosion is an electrochemical process that relies on charge creation and transport. The understanding of charge transport in the corrosion process is still unclear and more robust models are required to address this important process that is often believed to be the rate limiting step in surface degradation. This is particularly true under extreme conditions. We require a far more fundamental understanding of how extreme environments, including irradiation, temperature, pressure, and a variety of chemical potential gradients, affect material-environment interfaces and processes– including chemical reactions,

charged species transport, and plasma-surface interactions. For example, a more robust treatment of point defects and the transport of chemical species via an electrochemical potential gradient in oxides is required in order to understand the growth of films.

Environmental interaction involves the formation and evolution of oxide layers, which can either protect or consume the structural material. Reactions at the interfaces are critical to the understanding of the evolution of the fluid-oxide-metal system. This involves the determination and modeling of the chemistry of molecules near interfaces, of bound interfacial species and of the near-surface solid material. It also includes the processes of oxide film nucleation and early growth. The stability of oxide phases formed far from equilibrium is important to understand for applications in extreme environments.

Localized oxidation and environment-induced cracking present unique challenges in complexity with controlling processes occurring in constrained environments influenced by local chemistry, structure, temperature, stress, deformation and radiation. Stress plays a strong role in the environmental integrity of materials by destabilizing surface films, altering oxide nucleation and growth and inducing localized cracking through films. High resolution, in-situ techniques are needed to understand the reactions that drive localized processes such as pitting, selective oxidation and stress corrosion cracking.

In the few experiments conducted to measure its effect, radiation has been observed to induce large increases in corrosion of as much as 10x that in its absence. However, as stated in the report on basic energy needs to assure a secure energy future [1], "there is insufficient fundamental understanding of radiation effects on the chemical behavior of nuclear reactor components to reliably predict component properties and thus mitigate service failures." Radiation can accelerate corrosion by a number of processes including radiolysis of the coolant, generation of surface excitons, increased diffusion through the metal-oxide couple, nucleation of oxide particles, etc. However, since radiation-induced corrosion requires that corrosion occur under irradiation, few experiments have been conducted that directly interrogate the system to elucidate the most important processes. This is a key research direction that is vital to the development of corrosion resistant materials for nuclear systems.

Capability Gaps

There is a great need for capabilities that that allow us to manipulate extreme environments and *simultaneously* observe, accelerate, control and mitigate kinetics, phase transformations and mechanisms. Experimental stations are, therefore, needed for in situ measurements in extreme environments that would allow us to control radiation levels, temperature, pressure, and environmental chemistry. In kinetics, proof of a mechanism is very much like a proof in a court of law and, therefore, no single method is adequate for resolving specific rate limiting mechanisms and governing processes. Therefore, these experimental stations must have a range

of diagnostic capabilities that can acquire information in parallel. Examples of the types of in-situ diagnostics required are:

- Researchers at Los Alamos demonstrated the ability to measure corrosion rates by electrochemical techniques under extreme irradiation conditions as part of the Accelerator Production of Tritium (APT) program [2].

- Oxide growth on nickel metal and stainless steel samples was measured in-situ in a microreactor cell using x-ray diffraction at APS with samples at high temperature (400°C) and high pressure (25 MPa) [3].

- Interfacing of a particle accelerator and the TEM provides for real-time imaging of defect cluster formation, evolution and destruction, that provides unique information on the fundamental processes involved as well as the time scale for their occurrence [4].

It is expected that new diagnostic tools and detectors will require development to probe and possibly survive under extreme conditions. These systems must probe the environment as well as a range of materials processes. Examples of techniques for probing materials surfaces include: synchrotron x-ray and neutron diffraction, glancing angle and bulk diffraction, XANES, XAFS, X-ray tomography, Raman spectrometry, etc.

A range of irradiation capabilities, including high flux sources (neutrons, ions, gammas, plasmas) and diagnostic tools will be required. While reactors are ideal for the study of radiation effects in relevant conditions, instrumented target chambers interfaced with particle accelerators provide accessibility that is difficult to achieve in reactors. As such, the development of a range of irradiation sources will be required to make significant progress on this objective. In particular, particle accelerators are required that are capable of producing radiation damage in targets subjected to other components of the extreme environment. Interfacing of multiple beam lines to capture additional elements of the radiation environment (e.g. formation of He) and to visualize damage as it occurs (TEM-accelerator interfaces) are also important to the problem.

In addition to the gaps in experimental sciences, computational modeling tools that simultaneously treat multiple processes in multiple phases must be developed. Chemistry effects due to radiolysis of the environment, material and point defect transport through a growing corrosion film, stress effects such as mechanical breakdown of the growing film due to volume changes between the growing film and parent material, the nucleation and evolution of irradiation damage in the underlying metal, hydrogen transport and the precipitation of hydrides under stress and temperature gradients, and the localization of chemical and mechanical effects are just some of the processes that need to be accounted for. Each of the these processes can have significant impact on material performance and need to be treated on their individual length and time scales. A complete model for macroscopically observed behavior must knit those models together in a meaningful way. As an example, phase field models for evolution of microstructural damage need to be fed information on defect interaction energies and cascade

dynamics from molecular dynamics simulations and coupled with finite-element calculations of the stress-state. The ultimate goal is a predictive tool for film growth that is based on the appropriate underlying physics that can be simplified for use in design of corrosion resistant materials. A similar model structure can be defined for more local phenomena such as stress-corrosion cracking.

Potential Impact

Robust materials have not been designed to survive in these extreme environments for extended periods of time because the underpinning degradation mechanisms are not sufficiently understood in the complex, high temperature environment consisting of radiation, a corrosive coolant and mechanical stress. Replacing empirical and data-based approaches to prediction of corrosion and other surface degradation processes with physics-based, experimentally-verified models will provide the capability to treat corrosion as an integral part of materials development and performance. It will also provide the capability to model the full response of materials to all components of an extreme environment and to use this knowledge to develop new, corrosion resistant materials.

The knowledge and capability will provide predictive models to support a range of national needs including plant life extension of nuclear power plants that employ existing materials as guidance for the more rapid development and validation of new materials for advanced fission and fusion reactor concepts, and predictive models will be developed that can be applied to nuclear weapons stockpile stewardship. Corrosion is estimated to cost the U.S. on the order of 3.1% of GDP [5]. Consequently, improved predictive and design capabilities will improve sustainability practices, reduce infrastructure costs and broaden the operating window for many materials applications in corrosive and extreme environments.

Many parallels exist between the performance of materials in extreme and environments and functional materials such as energy storage materials and gas separation membranes. Corrosion is likely to be a key issue in solar cell lifetime and wind turbine performance and will become more important in large-scale central power plants. Strategies for scrubbing emissions and capturing carbon will likely be limited by corrosion. Similarly, high efficiencies of central station plants are achieved through very high temperature of the working fluid, which means a much higher cost of corrosion than we see today. The storage and (eventual) disposal of nuclear waste are largely an issue of containment vessel corrosion rates and possible failure modes. Virtually all energy sources will see an increasing cost of corrosion and the manifestation of new forms of corrosion. Therefore, developments in corrosion technology are key to improved efficiency in energy production.

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Priority Research Direction: Creating and Exploiting the Chemistry of a New Periodic Table Through Extreme Pressure-Temperature (P-T)

Problem Statement

Compression of matter results in reordering of the shell structure of electronic levels in atoms, effectively creating a "new" periodic table with the promise of creating wholly new materials. When combined with the ability of using temperature to rearrange populations of states, the chemistry observed at extreme P-T conditions is radically different than that observed at ambient pressure and temperature. We seek to exploit the resulting novel chemistry to create new, stable materials with new functionality; understand the chemistry of planetary interiors; and facilitate the development of new theories with enhanced predictive powers.

Executive Summary

The electronic structure, bonding and chemical reactivity of atoms is challenging under ambient conditions. However, the rearrangement of atomic levels induced by compression can result in entirely new reactivity, bonding and structure. For instance a metal such as sodium can become a transparent insulator; simple molecular systems such as O_2 become a metallic superconductor; and a greenhouse gas such as CO_2 can become a solid with novel optical properties. Such results point to the existence of a "new" density-dependent periodic table, whose control and exploitation still require a deeper fundamental understanding of the effects of density on atomic and chemical bonding. Key scientific challenges include the prediction and creation novel chemical states at extreme P-T while understanding the effects of P and T on atomic structure, bonding, and reactivity; utilizing Gbar pressures to induce core-electron "kilovolt" chemistry; and to use matter/radiation coupling in concert with P and T to control chemistry and reactivity.

Such challenges will require new computational tools for describing electronic structure and thus enable a predictive capability of chemical reactivity and bonding, over wide ranges of P and T. These challenges will also require the continued development of ultrafast *in situ* diagnostics in order to observe bond breaking/formation, local energy populations and their redistribution, stoichiometry, kinetics, and to observe the production and effects of short-lived transient states. However, our current ability to control thermodynamic states with the necessary precision over a large range of T, P, and strain rate is limited, and we do not currently have the time-dependent spectroscopic diagnostics capable of *in situ* (sub-surface) probing of extreme conditions at high spatial resolution. We must continue to develop time-domain diagnostics for extreme chemistry, and to move beyond existing theories to overcome the theory/experiment timescale gap.

However, should such capability gaps be overcome, the scientific impacts will be revolutionary. Control of the new periodic table will enable the creation of wholly new, stable materials with exotic new properties, which we imagine will be replicable at "normal" conditions. In addition, closure of these gaps will lead to the understanding of reactivity, mechanisms and chemical processes in planetary interiors. Such knowledge is needed to understand matter where reactive

energy – the energy released from chemical reactions or burn – is significant relative to other sources. We also imagine the ability to design and control the energy release in energetic materials: this could lead to safer nuclear weapons (use of on/off explosives), enhanced defeat of Improvised Explosive and Nuclear Devices (IEDs and INDs) and modern munitions with increased performance for a given mass.

Scientific Challenges

The key to exploiting a high-density periodic table is first to determine the effect of extreme density and temperature on the electronic structure, bonding and reactivity of matter, and then to develop new theoretical and computational tools to enable predictive capability. Accordingly, this PRD addresses the following critical scientific questions:

- How can we predict and create novel chemical states at extreme PT that potentially alter our view of the periodic table under these conditions?

- What are the effects of high pressure and temperature on atomic structure, bonding, and reactivity?

- Is chemistry and structure different at Gbar pressures, where the energy of compression is of the order of a keV, and thus high enough to promote core electrons to participate in bonding and reactivity?

- Can we control chemistry and reactivity by coupling matter and radiation in concert with extreme P and T?

Research Directions

The goal of this PRD is to develop a detailed understanding of how electronic structure and atomic and molecular mechanisms are changed by extremes of P, T and strain rate, and to predict and control the creation of new materials formed under such conditions. Developing such an ability will have wide ranging consequences across wide ranges of materials science, defence needs, and geo and planetary science. Three key research directions are identified.

Developing computational tools to enable prediction of chemical reactivity, bonding, over a range T, P, ρ states

The success of modern DFT and other computational methods has resulted in an ever-increasing number of non-specialists using these techniques to support and direct experimental studies of materials. Such techniques can accurately describe the properties of “normal” metals at ambient conditions, and are expected to become a still better computational tool for understanding highly-dense matter where materials might be expected to become more free-electron like. However, such techniques cannot accurately describe atomic bonding, particularly van der Waals bonding,

chemical reactivity, or the energy released from chemical reactions. Furthermore, the use of established and widely-used simulation techniques such as traditional molecular dynamics needs to be carefully examined for extreme conditions, where the ambient-pressure interatomic interaction potentials are no longer appropriate.

In order to fully exploit a density-dependent periodic table it will be essential that we develop specialized computational tools that correctly describe the exotic electronic structures and interatomic interaction potentials occurring at high density over the necessary length- and time-scales, and thereby enable a predictive capability of chemical reactivity, bonding, over a wide range of T, P, and strain states.

Developing ultrafast diagnostics to observe bond breaking/formation, local energy creation, stoichiometry, kinetics

In order to understand the new chemistry, reactivity and reaction kinetics that will arise at extreme densities and temperatures, it will be essential to develop a new generation of *in situ* diagnostics in order to observe bond breaking/formation, local energy populations and their redistribution, changes in structure and stoichiometry, and phase separation and kinetics over the complete range of time and length-scales. While such techniques (TEM, AFM, femto-second spectroscopy, ultra-fast electron diffraction, tomography) are well established at ambient pressures, the experimental constraints imposed by the methods required to produce high-density matter (either statically in a diamond anvil cell or via dynamic compression) impose serious constraints on experimental techniques (either geometrically or temporally) and/or the interpretability of data.

The suite of new advanced probes must include a combination of x-ray and neutron diffraction, spectroscopy, scattering, other electron and proton probes, pump-probe experiments that combine both optical and x-ray probes (or other particle probes), and advanced imaging techniques that span length-scales from angstroms to millimeters. The ultimate goal is the femtosecond imaging of chemical reactions on material surfaces, interfaces, or buried within a compressed sample with atomic-scale spatial resolution. This effort will be complemented with the development of 3D tomographic studies at relevant length- and time-scales of chemically reacting solids in extremes.

Observing the production and effects of transient states

While static compression techniques have had some success in determining the physical properties of final, stable states and reaction products at high density, there is little detailed information on either the existence of, of properties of, transient states that exist before the final stable state. Of particular importance are the many transient states created during dynamic compression experiments, where the reaction pathways (the many different possible routes in P, T, strain and composition space through which the reaction can take place) which may result in very different materials.

Capability Gaps

While the exploitation of a new high-density periodic table has possibility to offer revolutionary breakthroughs in the understanding of matter and reactions at high density, and the creation of wholly new materials, there are a number of critical capability gaps that need to be addressed.

For example, we do not currently have the ability to control state conditions with necessary precisely over a large range of T, P, ρ. The necessary time-dependent spectroscopic diagnostics capable of *in situ* (sub-surface) probing of bonding, structure and reactions over all relevant length-scales have not yet been adapted to the study of reactions of solids and in extreme environments. Similarly, the development of time-domain diagnostics for extreme chemistry is still in its infancy. Finally, concerted effort is required to move beyond existing theories to overcome the orders-of-magnitude timescale gap that currently exists between theoretical and experiment studies of high-density matter.

Potential Impact

The discovery of new forms of chemical reactivity and behavior that are promised by establishing and exploiting a new periodic table would be transformative.

We can envisage the controlled creation of new stable materials, with properties unlike those yet observed under "normal" conditions. Our understanding of high-density chemistry will enable us to understand chemical reactions within the Earth – essential to the understanding of CO_2 sequestration in the Earth's crust – and also at the very much higher pressure found in other planets, which will enable an ability to determine the chemical makeup of extra solar planets

The detonation and deflagration of energetic materials is still understood at a rudimentary level. Present theories lump most of the chemistry into overall reaction rates or energy release rates. The overall goal is to develop a complete time-dependent description of detonation and the evolution of the products equation of state for military purposes as well as to facilitate the introduction of new energetic materials for military, counter-terrorism, surety and industrial applications. This will lead to the design and control the energy release in energetic materials, which will lead to safer nuclear weapons (use of on/off explosives), enhanced defeat of Improvised Explosive and Nuclear Devices (IEDs and INDs) and modern munitions with increased performance for a given mass.

Finally, when reactions occur they can put or take away energy from the system. This will affect the hydrodynamics and thermodynamics of the system in new ways. Understanding how systems that are "burning" (introducing additional significant energy terms into the system) behave and the nonlinear interactions caused by the burning will have major impact on understanding and control of applications from turbulent chemical flows to inertial fusion.

Priority Research Direction: Predicting, characterizing, and controlling the performance of matter between solids and plasmas

Problem Statement

Recent advancements in intense, pulsed light sources provide revolutionary capabilities to subject matter to extreme conditions of pressure and temperature, creating novel conditions that span all the way from the solid state to weakly coupled plasmas. Those sources also provide new powerful tools to diagnose those novel conditions. The state of matter between the solid state and weakly-coupled plasmas is known as warm dense matter (WDM). Understanding the nature of WDM is one of the fundamental goals of the physical sciences associated with laboratory astrophysics, planetary dynamics, evolution of stars, and energy technologies. WDM is extremely challenging to model, because the typical approximations (e.g., expansion parameters) used in either solid state or weakly-coupled plasmas are not applicable. Creating and diagnosing WDM is very difficult for several reasons, such as its transient nature, the need for dynamic measurements, and the difficulty in creating sufficiently large and homogeneous samples. Understanding WDM is important in basic science (e.g., to understand the nature of giant planets) as well as in applied science (e.g., in understanding material behavior and equation of state in shocks and explosions, laser-matter interactions and non-linear optics, inertial fusion energy, etc.).

Executive Summary

The area of WDM where the conventional theories of condensed matter physics and plasma statistical physics are invalid is found in the regime above the solid with high temperature and pressure in the temperature-pressure phase space. Model calculations in this regime predicts exotic states including new atomic and electronic band structure, phase transitions, anomalous transport and scattering properties and changes of opacity . However, due to the lack of the appropriate light source and robust diagnostics, experimental investigation has been limited. The study of WDM offers the possibility of exploring new material science and physics in diverse areas including solids in extreme conditions, extreme chemistry, planetary physics, and inertial fusion. In summary, we expect that the understanding WDM will have a far-reaching impact in the research of materials in extreme conditions, the overarching opportunity for a new interdisciplinary research frontier.

Scientific Challenges

The applications of these new theoretical and experimental tools will enable an increasing understanding of WDM and an exploration of matter in extreme density and temperature conditions. Advanced scientific challenges include:

1) What is the nature of the extreme behavior of matter (compression, shear strength, flow, structure, "solidity") at extreme conditions?

2) Can we predict the behavior of matter as we traverse pathways through the phase space described by extreme pressures and temperatures.

3) Can we control and utilize matter under extreme conditions?

Research Directions

To accomplish the goal for the understanding of this new area, we outline the research direction in two key issues.

Measure EOS, atomic and electronic structure, opacity of WDM

Experimentally, the study of WDM has been severely limited because the creation of WDM and its diagnosis is extremely challenging.. Characterization of WDM is the first step on the road to understanding its properties. The equation of state (EOS) is a thermodynamic expression that relates pressure, density, and temperature, describing how WDM responds to the change of those three variables. There is no general, validated EOS model for WDM. Measurement of

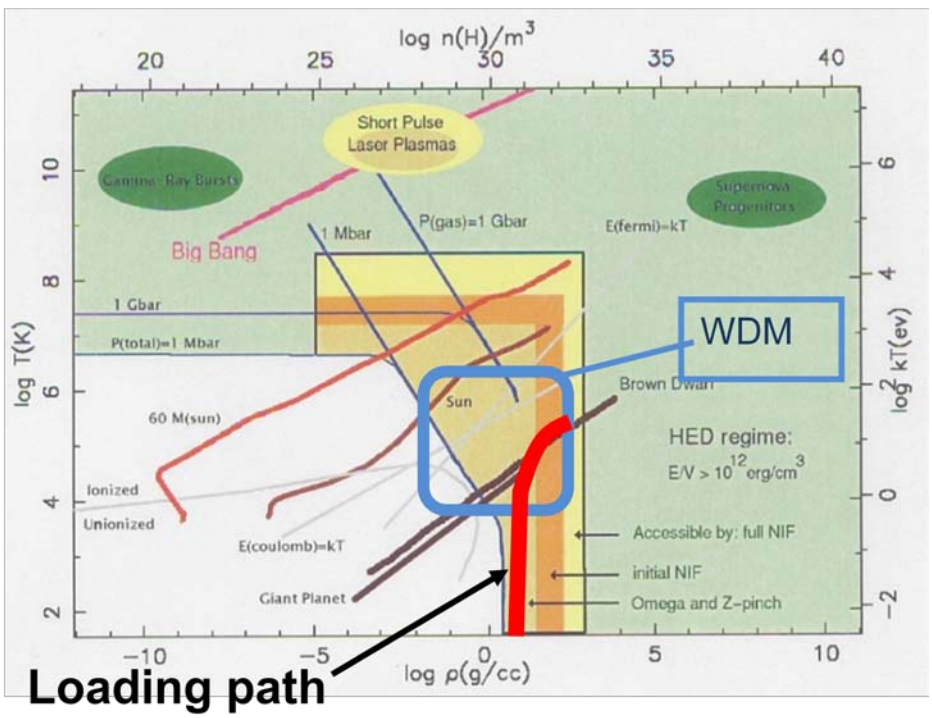


Figure 1. Schematic phase diagram of hydrogen.

populations of bound/free electrons will provide the information of atomic and electronic structure of WDM. Diagnosis of the opacity, conductivity and other transport coefficients, as well as compressibility also will provide fundamental information needed to characterize a given WDM system. The ability to provide different loading pathways, besides the traditional shock Hugoniots, is necessary to access and study the parameter range of interest.

For example, an illustrative experiment on hydrogen in Figure 1 shows an arbitrary loading pathway. The red line notes isochoric heating to a few eV with a proton beam and isentropic compression to a few g/cc. To characterize this WDM area, proton radiography diagnosis of ρr, keV X-rays & heavy ion-beam probe, X-ray Thomson scattering, dE_b / dx, and opacity diagnostics are required.

Develop self-consistent theory that permits prediction of WDM properties

The ability to calculate EOS is critical to predict WDM properties. Since no obvious ordering parameters exist and the theoretical uncertainties in existing models are huge, standard theoretical approaches in the WDM regime are neither validated nor reliable. The key will be in integrating the diverse, reduced models describing different phenomena at different spatial and temporal scales into a framework and tools with predictive capability. The development and validation of a more general WDM theoretical framework will have a profound impact on the study of WDM per se, as well as other disciplines where WDM plays a role. There are many systems in applied and basic science that either live in, or traverse the WDM phase space. There is also astrophysical interest in WDM modeling. A theoretical description of WDM at Mbar pressure will pin down theories of formation of astrophysical entities such as planets, brown dwarfs or neutron stars, some of which are very difficult to observe.

Capability Gaps

Using time- or spectrally- resolved techniques in scattering and spectroscopic diagnostic tools, we may be currently able to probe the WDM within limited conditions. However, conventional visible-light probes cannot penetrate dense matter to measure transient WDM properties volumetrically, limiting their use to surface measurements. For the successful achievement of WDM study, the following issues must be addressed.

- *Creation of homogeneous WDM using arbitrary pathways*
- *Theoretical ability to treat degeneracy, strong coupling, and quantum effects simultaneously*
- *Multi-beam sources for WDM sample and probes for simultaneous measurements of multiple state variables*
- *Develop time-dependent Thomson scattering (theory with experiment) and diffractive imaging*
- *In situ diagnostics for atomic-to-macroscopic structure higher fluence, higher energy light sources*

Potential Impact

The area of WDM which occurs in extreme condition of high pressure and temperature is strongly related to the other research areas, including strongly coupled plasma physics, high-temperature and pressure condensed matter physics, extreme chemistry, planetary dynamics, astrophysics, and energy technologies. When a comprehensive understanding of the nature of WDM comes, it will provide quantification of load-path-dependency of physical properties of WDM, prediction, manipulation, and control of high pressure matter. Further it will also motivate advances use-inspired research such as inertial fusion, material damage, and manufacturing materials under extreme conditions.

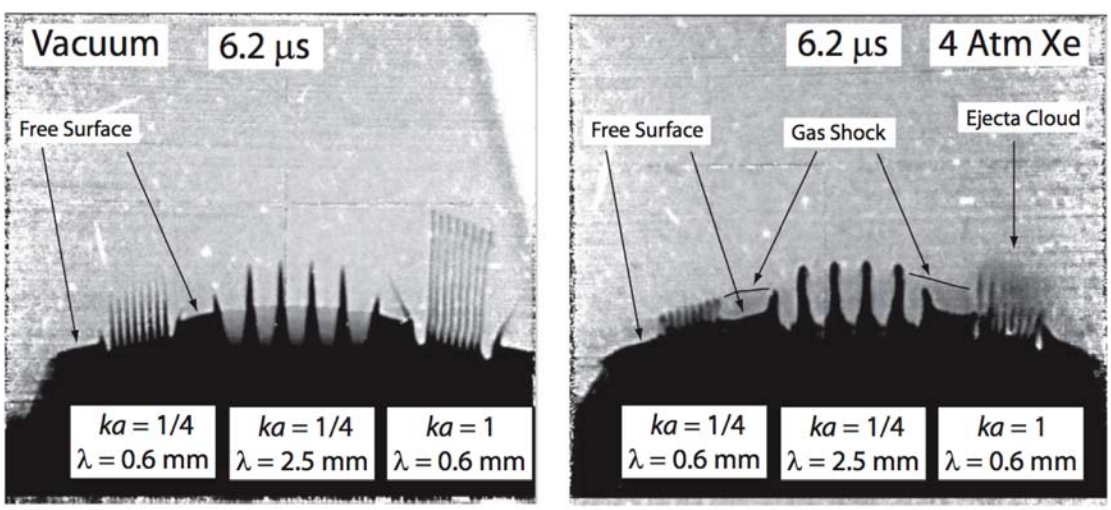
Priority Research Direction: Determining the transport of energy, momentum and mass under extreme density and temperature

Problem Statement

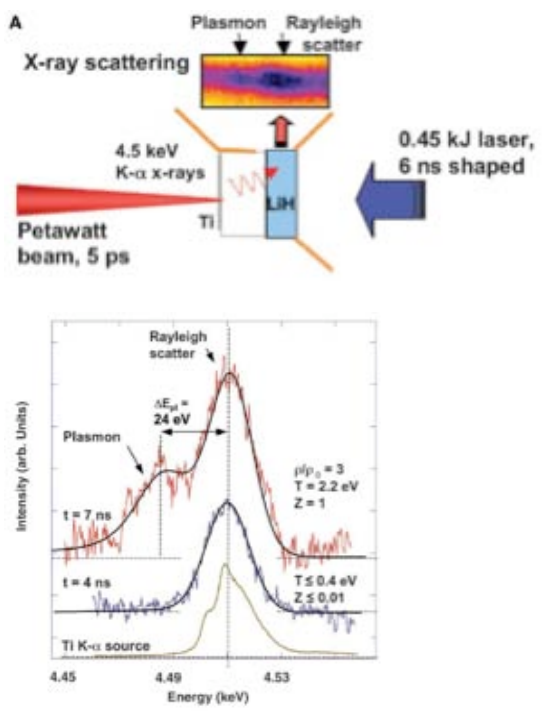
Once warm dense matter is made and characterized (matter at extremes of density and temperature where the usual order parameters fail), the next problem is determining its dynamic behavior: what are the fluxes of mass, momentum and energy in conditions where materials may lose strength, may melt and re-freeze, are in transition regimes in fluid parameters, and may introduce quantum or coupling effects that are new.

Executive Summary

The dynamic behavior of materials depends on transport coefficients that relate fluxes of state variables (energy, momentum, and mass) to their gradients. Under extreme conditions the order parameters that define condensed matter change, fail, or disappear, and no longer apply to describe materials and their dynamics behavior. These conditions, have relevance to inertial fusion, stockpile stewardship, or stellar explosions, and have significant uncertainty because of these complex dynamics. Creating the extreme conditions of matter, while simultaneously measuring its state variables with sufficient spatial and temporal resolution to determine gradients and fluxes is a scientific frontier challenge. Developing theory that can explain the material behavior in these new conditions where the usual order parameters fail is the other major research need.



The transition of solid material to spikes, ejecta, and eventually particulate matter. These are proton radiographs of perturbed surfaces under shocked conditions. Data courtesy of William Buttler, LANL.



Example of transient measurements needed for transport measurements in extreme conditions. This example shows x-ray scattering. spectrum from shocked LiH. From Kritcher et al., Science 322 (2008) pg. 69

Scientific Challenges

Making the matter in these extreme conditions of density and temperature in ways that allow *in-situ* measurements before hydrodynamic disassembly, as well as making the multiple simultaneous measurements to properly quantitatively diagnose the overall state are challenges to this field. Measurement of transport coefficients requires not just the values of the state variables, but also spatial resolution to provide measurement of the gradients or time resolution to measure time derivatives. The usual order parameters that can be used to theoretically describe the topology and behavior of the material begin to fail in these extremes; quantum effects change as pressure puts additional effects into the system.

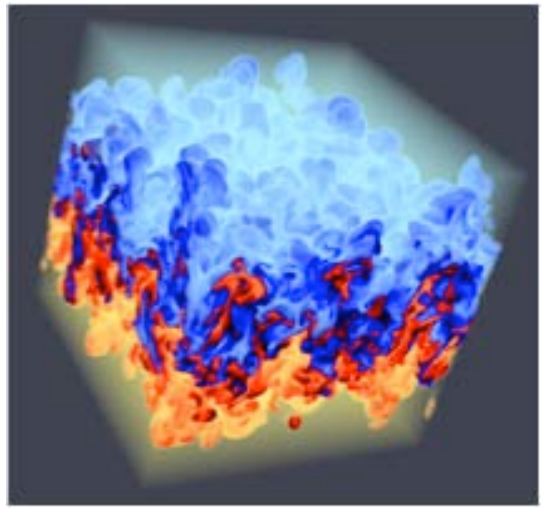
Key questions that need to be addressed include:

- What is the relationship between strength of solid materials, viscosity of fluids, and in general resistance to states of shear stress? Understanding such relationships help connect flow to constitutive properties of materials, and are vital for predictive capability of hydrodynamic behavior.
- How can accurate simulations be done in the absence of easy asymptotic parameters (parameters large or small that theories can be expanded around), and what experiments are needed to validate the underlying theories? These extreme conditions are difficult to create in a controlled manner, but vital for many applications, and so limited data will be available to develop critical theories.

Research Directions

In general we see two thrusts: 1) advances in theory, and 2) advances in experiments. In these conditions of extreme matter where usual order parameters fail, a self-consistent methodology needs to be developed for calculating viscosity for momentum diffusivity (similarly mass, temperature, and electrical diffusivities), thermal capacity, charged particle stopping power, and electron-ion equilibration. Based upon sound physical reasoning, new materials theories applicable to these regimes must be discovered, developed, and validated to allow accurate and efficient predictive capability.

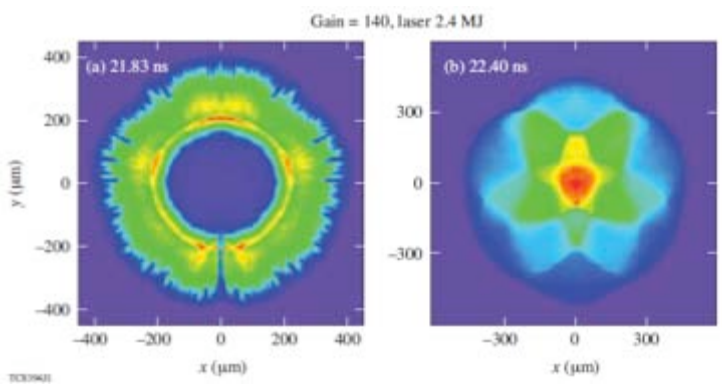
In experiments, these extreme pressure and temperature create strong gradients and therefore very rapid transport conditions. Because of these strong spatial gradients, development of experimental techniques to simultaneously create the necessary material states and measure strong gradient conditions in adequate spatial resolution the for short times are needed.



An example where turbulence meets reactive chemistry. It is proposed that for the case of this slow reaction the turbulent flame is of single-fractal character, and the distribution of temperature is strongly intermittent. Simulation from Michael Chertkov, LANL.

Capability Gaps

The capability gaps for determining transport behaviors and properties are even more challenging than measurement of local state variable properties because of the need for higher time and space resolution (gradients are non-local quantities). Homogeneous warm dense matter must be created using arbitrary pathways, which requires significant energy density to be applied. Multiple state variables (density, temperature, etc.) must be simultaneously (space and time) measured, which requires multiple-beam sources for making the WDM sample and then probing it. The current revolutionary tool in this field is the x-ray free-electron laser (XFEL), which provide high brilliance at sufficient photon energy to probe these states of extreme matter. They can provide *in-situ* diagnostics for atomic-to-macroscopic structure; however, gaps remain in our ability to make the matter in relevant states. A key diagnostic is x-ray Thomson scattering; the technique must be develop to include time-dependent Thomson scattering (theory with experiment) and its coupling with coherent diffractive imaging. Finally, there are significant gaps in theory and its ability to treat degeneracy, strong coupling, and quantum effects simultaneously.



An example of inertial fusion energy target implosion calculations from a two-dimensional simulation, illustrating the impact of hydrodynamic instabilities on fusion burn. Calculation courtesy A. J. Schmitt, NRL.

Potential Impact

Material flow is central to important energy applications, and becomes a significant uncertainty for matter in extremes. In particular, better understanding of variable density flow in rapidly transforming objects and is critical to such applications as inertial fusion energy, stockpile stewardship, stellar explosions, nuclear reactors, cooling devices, and casting.

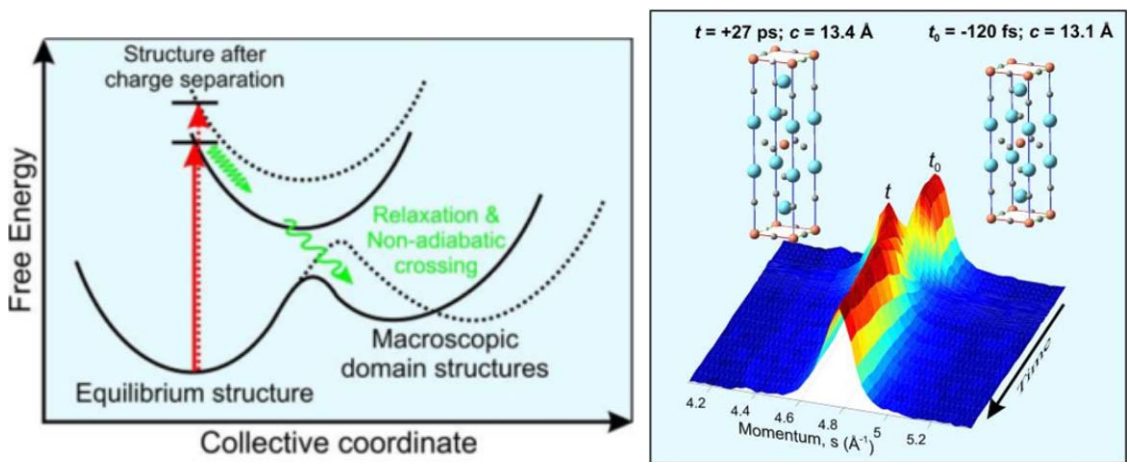
Priority Research Direction: Controlling photon-matter interactions: making every photon count

Problem Statement

Applications ranging from renewable energy to advanced computation require significant advances in the scientific basis for controlling photon-materials interactions, as well as the conversion of the resultant excitations into usable energy. Classically, this concept of 'making every photon count' involves the creation of tunable photonic materials with multifunctional, broadband electromagnetic response. In the quantum regime, we aspire towards a predictive capability for the design of materials and/or pulse sequences to coherently control the outcome of the interaction, either electronically or structurally.

Executive Summary

The goal of this priority research direction is to develop the science and accompanying technology to enable exquisite control of photon-matter interactions over a wide range of conditions for multiple applications. To achieve this goal, we will need to understand, control and optimize photon-material interactions, spanning the classical regime of electromagnetic interactions, currently enabled through plasmonics, photonic crystals and metamaterials, to the quantum regime of coherent excitations, and materials design to control functionalities such as



(a) **(b)**

Figure 1: (a) New metastable photo-induced state in $La_2CuO_{4+\delta}$ that is not thermally accessible. (b) Characterization of metastable state using ultrafast electron diffraction reveals that a structural phase transition has occurred. Excitation to this state via coherent control with optimally shaped pulses should enhance access (lower threshold fluence, etc.) [From: Gedik et al, Science 2007]

charge and energy transfer and transport, charge separation, and the conversion of electronic excitations into optical signals or electrical energy. Such control will be essential for next generation renewable energy technologies, the design of catalytic materials and multifunctional materials for sensing, advanced computing and communications, the understanding of reaction mechanisms, and new directions such as the nanomechanics of Casimir force control.

Scientific Challenges

In the area of classical control of light, currently comprising metamaterials, plasmonic structures, and photonic crystals, we must address the following scientific challenges:

- Controlling loss or introducing gain in photonic structures in order to enable their use beyond visible frequencies.
- Developing new approaches to enable broadband electromagnetic response, rather than narrow resonances.
- Understanding and controlling bianisotropy in order to achieve magneto-electric functionality.
- Design and fabrication of 3D structures with isotropic functionality
- Understanding of the effects of inhomogeneity beyond the effective medium approximation.
- Understanding, designing and optimizing nonlinear response in novel photonic

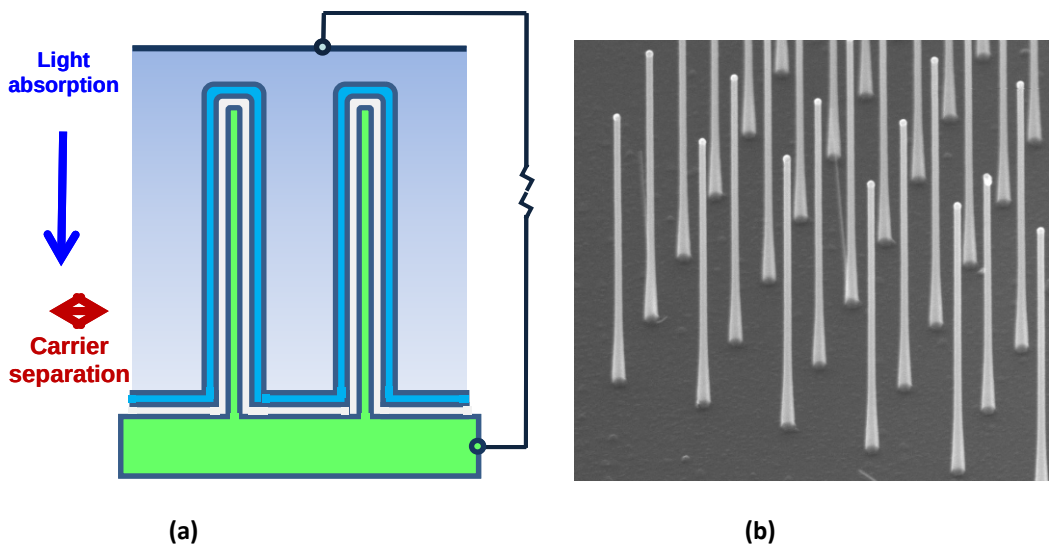


Figure 2: Semiconducting nanowires provide geometrically separate mechanisms for controlling light absorption and carrier separation, essential for third generation solar energy harvesting. (a) Schematic of radial p-i-n nanowire photodetector showing the separate processes. (b) SEM image of ordered array of nanowires. [Picraux et al, unpublished]

structures which would enable further functionality from these materials, including dynamic control of functionality.

- Manipulation of higher frequencies of photons (beyond visible), using smaller and smaller nanostructures, ultimately requiring manipulation on the atomic scale (and therefore merging with quantum control.

In the area of quantum control of photon-matter interactions, we must address the following scientific challenges:

- The discovery of non-thermally accessible states (Figure 1) with unusual properties and an understanding of their properties.
- Development of a predictive capability to design and implement pulse sequences to coherently control the interaction of photons with electronic (femtosecond to attosecond timescales) or structural degrees of freedom (picosecond timescales) in order to control material functionality or chemical reactions.
- Design, synthesis and fabrication, characterization and optimization of materials to control functionalities essential for photon conversion processes, such as charge and energy transfer and transport, charge separation, and the conversion of electronic excitations into optical signals or electrical energy. (See Figure 2 for an example of this challenge.)
- The combination of materials developed for specific photon-matter interactions with coherent control to optimize or provide further control for a specific functionality.
- Development of pulse shaping techniques, analogous to multidimensional NMR spectroscopy to control multiple degrees of freedom.
- Integration of classical quantum control to ultimately ‘make every photon count.’

Research Directions

Research directions here encompass the two sides of the light-matter interaction: using light to quantum mechanically control matter through its interaction with electronic or structural degrees of freedom (Figure 3) and matter to classically control light through plasmonics, photonic crystals and metamaterials (Figure 4). The first promises new functionality for matter in controlling its chemistry and bulk response (including synthesis of new materials), the second new functionality for light in controlling its intensity and propagation for communication, imaging, cloaking, switching, sensing and interacting with matter. The two are synergistic, in that plasmonics and metamaterials can be used to shape light pulses classically that are then used to quantum mechanically control matter.

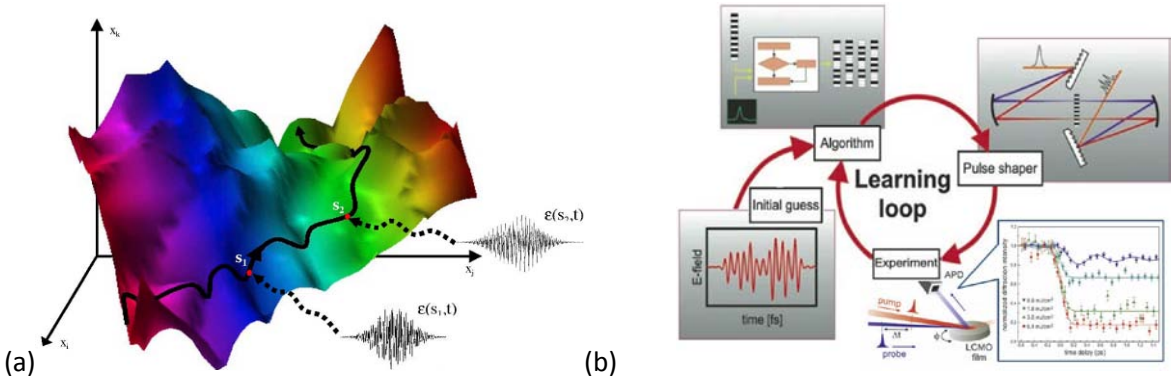
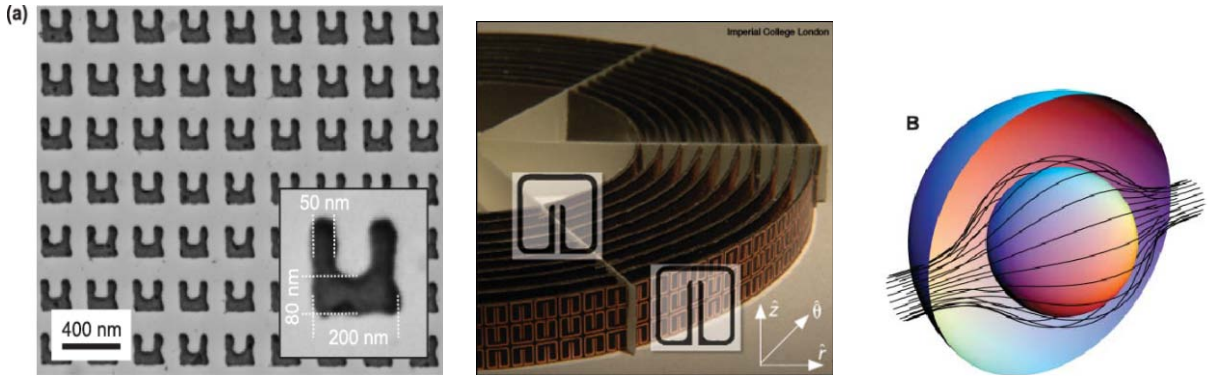


Figure 3: Quantum coherent control is a quantum mechanical process that exploits the fact that the evolution of a quantum system is a result of constructive interference between multiple available routes connecting initial and final system states. If the laser pulse has a broad enough spectrum to overlap with several paths (states), it will impose its spectral phase and amplitude distribution on the corresponding path probabilities. (a) Proper selection of the laser pulse phase and amplitude profiles provides a way to guide a system along a particular path through destructive interference of all alternate routes. (b) In general, the tremendous complexity in modeling sizable quantum systems precludes *a priori* identification of optimal pulse shapes; instead, an adaptive coherent control method is used to extract the desired pulse shape from the analysis of pulse-system interactions. Diagram of an adaptive coherent control experiment is shown where a randomly chosen initial pulse shape is iteratively optimized to eventually provide the desired experimental outcome.



(a) **(b)**

Figure 4: Metamaterial based structures enabling classical control of electromagnetic radiation. (a) Negative index metamaterial, optimized for infrared frequencies. (b) Structure enabling electromagnetic cloaking at microwave frequencies and simulation of cloaking based on the concept of transformational optics.

To date, the fields of plasmonics and metamaterials have allowed rudimentary control over classical interactions of light with matter, while a combination of materials design and coherent control has enabled optimization of quantum mechanisms and/or wavefunctions for specific functionality such as control of reaction products, phase transformation or energy conversion. In the classical regime, research directions required 'to make every photon count' include developing new approaches to next generation photonic materials to address issues of bandwidth, loss, isotropy, dispersion, inhomogeneity, bianisotropy, active control, and nonlinearity. In the quantum regime, research should be directed towards the development of a predictive capability to design materials and/or pulse sequences to coherently control the interaction of photons with electronic or structural degrees of freedom.

Capability Gaps

Specific capability gaps required to achieve control of photon-matter interactions include:

- A predictive theory of nanoscale electromagnetic interactions beyond effective medium theory, ultimately incorporated into simulation tools for design of functional electromagnetic structures
- A predictive theory of coherent photon-matter interactions.
- Fabrication of complex 3D nanoscale architectures
- Integration of diverse nanoscale materials to achieve the desired functionality
- Nanoscale materials' characterization with ultrafast temporal resolution.
- Coherent spectroscopic techniques with ultrafast temporal and nanoscale spatial resolution, as well as specificity to functionality (electronic, magnetic, structural, photonic, chemical, etc.).

- Design/implementation of ultrafast pulses (attosecond to picosecond) to control structural and/or electronic excitations.

Potential Impact

'Making every photon count' will impact multiple application areas from renewable energy to global security to discovery science. The development of a predictive capability to control photon-matter interactions, spanning classical to quantum regimes will impact the following areas:

- Renewable energy and environmental security: the creation of materials tailored for unique photon conversion applications efficient catalysis.
- Global threat reduction: design and development of sensors and detectors involving photons, quantum and classical, optimized for specific applications and materials for advanced communication systems.
- Nuclear deterrent: next generation materials for advanced computation.
- Discovery science: novel materials and phenomena and detailed understanding reaction mechanisms.

These research directions, coupling advanced synthesis, characterization and theory, are poised to provide answers to the five Grand Challenges posed in the BES report "Directing Matter and Energy: Five Challenges for Science and the Imagination."

- How do we control materials processes at the level of electrons?
- How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?
- How do the remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and how can we control these properties?
- How can we master energy and information on the nanoscale to create new technologies with the capabilities rivaling those of living things?
- How do we characterize and control matter away--especially very far away--from equilibrium?

The proposed research directions will apply the methods and tools of control science to advanced photonic materials with the goal of controlling functionality, an explicit requirement for next generation materials research, as described in the BES report, "New Science for a Secure and Sustainable Energy Future." This capability is required to attain the goal of controlled functionality in materials that will enable a secure future for our Nation.

Priority Research Direction: Control Functionality from Electronic Complexity

Problem statement

To develop a science-based framework for the design and fabrication of high performance functional materials based on multiscale electronic complexity in classes of inorganic, organic and hybrid materials through understanding the origins, consequences and control of complexity. Bringing together recent advances in theory, modeling, multiscale probes and synthesis will enable the required prediction, characterization, control and design .

Executive Summary

The last three decades have seen remarkable advances in the discovery of complex inorganic, organic, biological, and electronic materials with unexpected function and performance. Examples include superconducting oxides, pnictides and borides, giant and colossal magnetoresistance materials, plastic conductors and superconductors, carbon nanotubes, and graphene. The last decade has seen a similarly remarkable explosion of new and improved experimental probes of structure and function for multiple spatial and temporal scales, including scanning probe microscopies, focused x-rays, angle resolved photoemission, a variety of pump probes, time resolved crystallography, EXAFS, and diffuse scattering. There have also been remarkable enabling advances in synthesis including, for example, atomic layer control and directed self-assembly. These materials and probes increasingly reveal novel electronic functionalities that exist at several distinct scales organized into robust hierarchical, self-consistently supported systems. Creating new high performance materials with designed functionality requires understanding and controlling the link between complexity and functionality.

Harnessing electronic complexity for new levels of functionality will mark a qualitatively new era beyond the familiar Bloch theory applicable to periodic systems and small deviations therefrom. The Bloch framework has been remarkably successful for describing and controlling many simpler scientific and technologically important materials such as silicon. However, creating materials with higher levels of performance and functionality requires creating and controlling higher levels of complexity. Achieving this goal for the next decade is now feasible because of major advances in:

- Synthesis
- Multiscale space and time probes
- Simultaneous probes of multiple properties
- Theory of nonlinear, nonadiabatic, far from equilibrium phenomena, including systems with coupled spin, charge, and lattice degrees of freedom
- Modeling and simulation, including a new generation of high performance computing and visualization tools

In short, we can now build the "science of electronic complexity" – understanding its origins, measures, and consequences - and exploit this new knowledge to create radically new forms of electronic materials with greatly enhanced multifunctionalities, tunability, control and performance.

Scientific Challenges

The principal scientific challenges are

- Develop integrated capability, including theory, modeling, synthesis, and characterization, to create prescribed electronic energy landscapes by assembling multiscale hierarchical atomic and molecular patterns.
- Identify the relevant degrees of freedom and length/time scales for controlling macroscopic functionality.
- Relate nanoscale complexity to robust macroscale functionality

Research Directions

The functionality of electronic materials is linked to specific ingredients of their electronic complexity: closely spaced energy levels (e.g., electronic, phononic, magnetic) belonging to two or more competing and interacting phases. These ingredients can lead to ordinary phase transitions, nanoscale phase separation, emergent phases, or spontaneously generated hierarchical spatiotemporal patterns. The research direction is to control the outcome of these competitions and to design their functionality.

The major achievements of the research direction are

- Creating and understanding design principles for controlling the energy landscapes of interacting, competing states and the new phases they produce
- Identifying model systems with sufficiently rich energy landscapes to enable the above emergent features, particularly those arising from various couplings among spin, charge, and lattice degrees of freedom. Examples include relaxor ferroelectrics, heavy fermions, emergent phenomena near quantum critical points and at interfaces in multilayer systems.
- Developing experimental tools to correlate the local structural, spectroscopic and functional behavior of electronically complex systems. These must include a range of

time and length scales, using, for example, ultrafast spectroscopic techniques, fluctuation spectroscopy, and multi-color excitations such as multidimensional NMR.

- Developing appropriate theory and modeling tools for describing landscapes of closely spaced energy levels and interpreting the experimental probes.

The conceptual framework linking electronic complexity to functionality integrates the following challenging elements:

- Near degenerate energy states
- Far from equilibrium theory
- Time resolved dynamics, beyond simple relaxation time and effective temperature approaches
- Competing phases and the emergence of novel states
- Charge transfer driving structurally embedded electronic phases, e.g. Zintl phenomena
- Hieracrchical long and short range interactions
- Self-consistently organized local "hot spots" which collectively mediate functionality.

Capability Gaps

- Diffraction, imaging and spectroscopy tools for characterizing closely spaced energy landscapes with resolution approaching nanometer length and femtosecond time scales.

- Description of materials beyond Bloch theory (“thinking outside the Bloch”!): electronic structure techniques including nonadiabatic techniques for closely spaced electronic energy landscapes with nanoscale spatial inhomogeneity.

- Tools for working "outside the Boltzmann box": computational techniques to address far from equilibrium electronic, lattice and spin states using, for example, nonequilibrium Green’s functions and quantum Monte Carlo methods.

- Understanding and achieving robust functionality, learning, self-healing, and ultimately sequential functionality via feedback from nonlinearity.

Potential Impact

- Creation of a new paradigm for the design of functional materials, starting with a targeted functionality, choosing the constituent competing ordered phases and designing the closely spaced energy landscape, wave function symmetry and competing interactions,

followed by iteration of the energy landscape inputs to converge the desired functional outcome.

- Creation of radically new forms of electronic materials with greatly enhanced mutifunctionalities, tunability, control and performance.

- Designing new materials with unprecedented performance for solar, fission, fusion and biofuel energy applications.

- Next generation multifunctional materials for sensing, communication and computation.

Priority Research Direction: Controlling nucleation phenomena

Problem Statement

Nucleation is a fundamental process step contributing to – if not in some cases controlling – many microstructural development and failure processes. Fatigue fracture and phase transformations are largely controlled by nucleation. Yet, theory of nucleation, in the case of phase transformations or solidification, has advanced little beyond that contained within the Johnson–Mehl–Avrami–Kolmogrov equation. Innovative measurements of nucleation events – particularly using TEM and SANS – have been published but measurements are lacking at both the spatial and temporal scales necessary to understand the fundamentals of nucleation. New measurements are required both to validate theories and to spawn new theoretical studies.

Executive Summary

Too little is known about the "form", i.e., the structure, composition, dimensions, etc., of a pre-embryo, nucleant, and nuclei. New time-resolved measurements with the required spatial and temporal resolution could provide information that would feed theoretical developments and compare to numerical simulations. A formidable challenge in nucleation is heterogeneous nucleation, in which interfaces, defects, stress concentrations, etc., can provide a site for nucleation before a homogeneous event would occur. This introduces a stochastic aspect and an uncertainty in where to look for the event. Ultimately, a predictive capability, requires representation of heterogeneous and unlikely events in models, which remains a grand scientific challenge in general and a critical challenge to the understanding of nucleation.

A predictive capability in nucleation would remove one of the key barriers to predictive design. Such a capability would need to be followed with theories and models for growth and, ultimately, coalescence to enable predictive design of microstructure or growth of dominant cracks leading to failure. Of all the material processes that contribute to development of microstructure and properties, nucleation is one of the most important and least understood.

Scientific Challenges

Nucleation phenomena play a key role in fatigue fracture and phase transformations as well as many other processes. To motivate the broader challenge, we discuss in detail the specific role of nucleation phenomena in initiating phase transformations.

Nucleation Phenomena Controlling Phase Transformations

Because of its atomic-scale origins and attendant difficulties in making direct observations, nucleation — the formation of the smallest amount of a new phase that is kinetically resistant to dissociation — remains one of the least-understood phenomena in phase transformations. The atomic rearrangements needed for nucleation pose an energetic barrier, except in special instances such as spinodal decomposition. The reaction path needed to surmount this barrier and

achieve nucleation and subsequent growth has yet to be directly observed. Hence, existing quantitative nucleation theories and models must rely on a set of unverifiable assumptions, some of which are likely to be vast oversimplifications of the actual underlying physical processes.

Diffusional nucleation theory is premised on the spatio-temporal evolution of clusters, a generic term for any localized region of the system that differs from the matrix phase in terms of crystal structure, composition and/or degree of order. Prospective nuclei, termed embryos, are initially unstable n-atom clusters that must climb up an energetic hill if they are to grow, since the creation of a new matrix-embryo interface requires more energy, at small sizes, than is liberated by the chemical driving force. Cluster evolution is therefore biased in favor of dissolution, not growth. Given time, a favorably-growing embryo will eventually reach the peak of the energetic hill once it attains a critical number of atoms, n*, at which point it is called the critical nucleus. Adding one more atom to the critical nucleus is considered to render the cluster safe against dissolution. All such clusters having >n* atoms are considered to be stable precipitates that then proceed into the growth stage, for which there is always a net energy release, as the chemical driving force now outweighs the energy sinks of interfacial (and strain) energy.

To date, quantitative studies of nucleation have been done through ex-situ nucleation rate measurements using the indirect methods of electrical resistivity and small angle scattering, and the less indirect methods of electron microscopy and atom probe. The generalized steady-state nucleation rate J_{ss}* of second-phase precipitate from a supersaturated matrix (in units of nuclei per unit volume per unit time) is as follows [1]:

$$J_{ss}^{*} = \beta^{*} C_{n^{*},ss} = \beta^{*} NZ \exp\left[-\Delta G^{*} / kT\right] \qquad [1]$$

where:

- β^* = frequency factor, the rate at which atoms attach to critical nuclei
- C_{n^*ss} = steady state concentration of critical nuclei
- N = number of available nucleation sites per unit volume
- Z = Zeldovich non-equilibrium factor
- ΔG^* = free energy required to form a critical nucleus
- k = Boltzmann's constant
- T = absolute temperature

The concentration of critical nuclei is expanded into its three major components in the right side of this equation. The most important of these is the height of the energetic barrier, ΔG* (Figure 1), which depends on the nucleus configuration (to be described later) and the driving force.

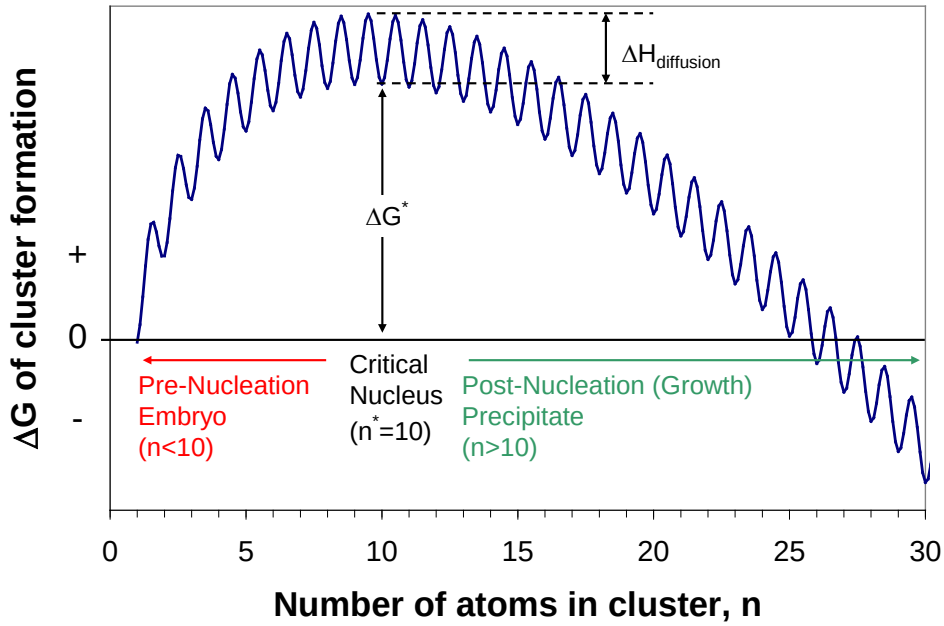


Figure 1. Schematic energy landscape for a cluster expanding/shrinking via diffusional jumps of atoms to/from any given n-atom cluster, one atom at a time. The cluster initially travels up the free energy hill, since for $n<n^*$ the surface energy sink (scaling as $n^{2/3}$) outweighs the negative volumetric energy source (=chemical driving force less strain energy, and scaling as n^1). The cluster is considered nucleated when it expands to $n>n^*$, crossing the top of the energy hill, ΔG^*.

The energy landscape depicted in Figure 1 is specific to a cluster having a particular configuration — defined by its crystal structure, shape, matrix-embryo interfacial energy (or energies, in the non-isotropic case), composition, and degree of order. One would suppose that any given supersaturated matrix could try out an enormous number of prospective nuclei (via trial combinations of crystal structures, shapes, interfaces, compositions, and degrees of order), with the likely result that only one such combination will win out (the others being kinetically uncompetitive owing to higher ΔG^* values). Furthermore, the kinetic winner is not necessarily the equilibrium phase, as embryos of metastable phases may be able to assemble faster.

The most ambitious experimental goal would be time-resolved observations of all cluster configurations. For example, there may be patterns as to how the fluctuations in these different attributes are coupled to one another, for example, interfacial energy and composition. At a minimum, it would be desirable to sort out the fluctuations attributable to phonons from those attributable to electronic interactions. Detailed experimental information on the complex sequence of atomic rearrangements by which an embryo evolves to critical size would spark a renaissance in nucleation theory, modeling, and ultimately prediction.

Lacking any observations of this kind of pre-nucleation activity — the system "trying out" different clusters configurations through random, statistical fluctuations — nucleation theory and modeling has resorted to making the following key assumptions:

1. the critical nucleus is the equilibrium crystal shape, determined by simultaneous, independent minimizations of the total interfacial and strain energies

2. clusters grow or shrink by one atom at a time; mutual interactions among multi-atom clusters are considered negligible.

The time evolution of n-atom clusters (of a specified configuration) for $2 \leq n \leq n^*$ in a supersaturated matrix is schematically depicted in Figure 2. The one-atom-at-a-time rule severely constrains the actual shapes of the C_n curves. *The acquisition of in-situ experimental data on cluster populations, which could be plotted as in Figure 2, is a key goal of future experimental efforts to understand nucleation.* Even if all the details of the cluster configuration were not known, if there was certitude that a given population had the same configuration (whatever it might be), such data would be of tremendous use in refining existing atomic potentials and cluster-evolution models and prompt the development of improved ones.

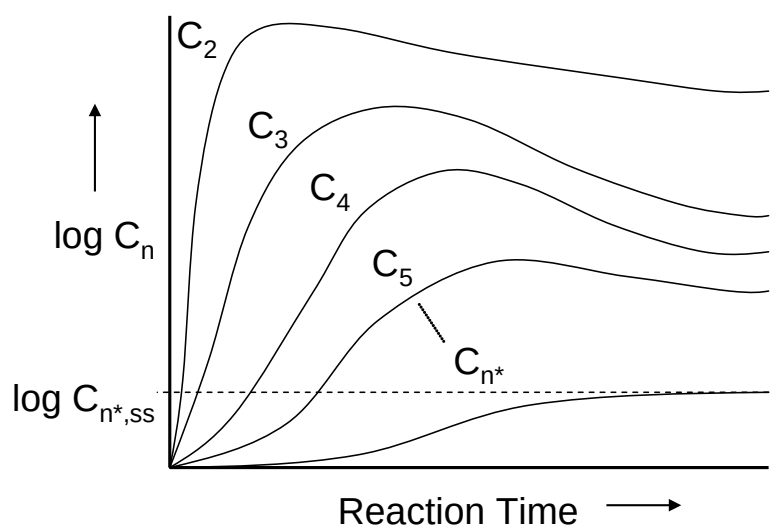


Figure 2. Schematic of the concentration C_n of n-atom clusters as they evolve with reaction time in a supersaturated solution. The concentration of critical nuclei is given by C_{n*}, for which there is an initial transient prior to the achievement of a steady-state population $C_{n*,ss}$. (cf. Equation 1)

The lack of accurate ancillary experimental data has precluded closure between nucleation theory and experiment, and new spatially and temporally resolved experiments would be instrumental in closing this gap. The simplest case of homogeneous nucleation of a spherical precipitates with an isotropic interfacial energy will be used to motivate this discussion. For this simplest case, Eq. 1 reduces to:

$$J_{ss}^{*} = \frac{2Dx\gamma^{1/2}}{a^4 (kT)^{1/2}} \exp\left[-\frac{16\pi\gamma^3}{3(\Delta G_V + W)^2 kT} \right] \qquad [2]$$

where:

- D = applicable diffusivity in the matrix phase
- x = atom fraction of solute in the matrix
- γ = specific interfacial energy between the matrix and the embryo/nucleus/precipitate
- a = averaged lattice parameter of the matrix and precipitate phases
- ΔG_V = chemical volumetric free energy change per unit volume of precipitate formed (negative quantity; the more negative, the higher the driving force)
- W = elastic strain energy work per unit volume of precipitate (positive quantity)

Lacking any better information, nucleation studies have had to make do with continuum measurements and models of D, γ, ΔG_V, and W, even though their applicability to clusters containing only tens to thousands of atoms should be immediately suspect. Realistic measurements under the actual conditions of interest to nucleation and growth problems would be valuable in driving the next generation of theory. Opportunities for improving two of these parameters will be highlighted.

The most important parameter in Eq. 2 is the nucleus-matrix interfacial energy γ [2]. Unfortunately, this suffers from the greatest error in its measurement, on the order of factors of 2-10, which is greatly compounded by the cube power in the exponential term of Eq. 2. Such is the case that most experimental studies of nucleation conclude by back-calculating the value of γ and considering of whether this is a reasonable value. Improved back-calculation of γ through highly accurate J^* measurements, or better yet, some alternate means of measuring γ more directly at more realistic temperatures and alloy compositions would enable true closure.

The second most important parameter is the applicable diffusivity D. Classically, D is extrapolated down from higher-temperature measurements, creating uncertainty as to whether such extrapolation is legitimate, given the likelihood of short-circuit diffusion paths at the lower temperatures of interest to nucleation (and perhaps more importantly, to growth). Time-resolved

and/or high-throughput measurements of atomic motion would constrain the value of D needed in nucleation and growth equations, and in all likelihood would result in the upsetting of conventional wisdom about diffusion and prompt the development of better models.

A brief consideration of the issues surrounding heterogeneous (defect-mediated) nucleation is in order before closing this section. Heterogeneous nucleation occurs at/near structural defects (dislocations, grain/twin boundaries, other interfaces) whose local interfaces, strain fields, and compositions differ from the perfect matrix in such a way that reductions in ΔG^* and n^* (vs homogeneous) are realized. Given the ubiquity of defects such as dislocations, grain boundaries, and free surfaces (e.g., in powders) and the kinetic benefits of such defect mediation, heterogeneous nucleation is assumed in experimental studies unless proven otherwise. Unfortunately, since nucleation events cannot be directly observed with current capabilities, the defect and its local character (or "sweet spot", e.g., local grain boundary structure or local dislocation line direction) that are actually responsible for heterogeneous nucleation cannot be identified. Observations made of actual precipitates typically take place ex-situ, long after nucleation, and with only a narrow 2D view of a 3D microstructure. Given these experimental limitations, the correlation of the nucleation event with specific defects touching the precipitate can often be misleading. A nucleation model cannot possibly succeed if the nucleating defect is mis-identified. In-situ experiments would be in a position to correctly identify these defects as they interact with growing embryos, and help generate relevant maps of the energy landscape containing such features. Such data would refine and update atomic potentials and cluster evolution models, in addition to having the immediate benefit of constraining N in Eq. 1.

Research Directions

In order to realize the vision articulated in the previous section, the following research directions should be pursued:

- Determine the form of the pre-embryo, nucleant and nuclei and interrelationships (structure, composition, strain).
- Determine methods to characterize these various forms.
- Develop theories for heterogeneous nucleation that account for multiply distributed nucleant potency.
- Experimentally characterize and quantify distributed heterogeneous nucleation behavior.
- Explore methods for seeding the structure with defect controlling nucleation
- Use undercooling techniques to watch embryo development at time scales that we can measure.

Capability Gaps

Current state of the art theoretical and experimental methods are inadequate to address the research directions listed above. Success would require the following advances in capability:

- Development of experimental probes and models that can probe nuclei at small length scales (10 nm) and time scales (~ps-ns) but sampling large volumes (microns – mm) over time scales (secs to days).
- 3D X-ray diffraction measuring lattice strain (~10 nm res.) to detect onset of nuclei (current state 2D, 20 nm).
- Compositional and structural fluctuations can be measured via TEM down to nm scale, but not at time scales needed. How do we improve temporal resolution?
- Connection of theoretical models with real heterogeneous fluctuations.
- Develop theoretical models, models and experimental probes aimed at understanding interfacial mechanisms: nucleant interface and nucleus interface.

Potential Impact

Nucleation is a fundamental process step contributing to many microstructural development and failure processes. A first-principles, experimentally validated theory of nucleation would remove a key barrier to predictive capability for microstructural control across numerous application areas. Success would enable control of novel distribution of phases for improved functionality.

References

1. H.I. Aaronson and J.K. Lee, "The Kinetic Equations of Solid-Solid Nucleation Theory and Comparisons with Experimental Observations," in "Lectures on the Theory of Phase Transformations," H. I. Aaronson, ed. (TMS, Warrendale, PA, 1999), p. 165.

2. R.K. Trivedi, "Theory of Capillarity," in "Lectures on the Theory of Phase Transformations," H. I. Aaronson, ed. (TMS, Warrendale, PA, 1999), p. 135.

Priority Research Direction: Accelerating Materials Discovery

Problem Statement

The discovery of new materials is essential for the discovery of new science. The 1986 discovery of high temperature superconductivity in the cuprates changed the face of condensed matter science. More recently, the development of electrodes based on lithium iron phosphate has transformed battery technology. Impressive as these discoveries are, they occur far too rarely to sustain the steady advance of the frontier of science and technology innovation. A new paradigm for accelerating materials discovery is needed: a tight integration of theory, synthesis and physical property measurement. The advantage of this closed loop is strong feedback that guides synthesis towards interesting and useful materials. The feedback is enabled by developments over the last decade in characterization of materials and first principles based theory. Theory is now capable of quickly providing detailed information about properties and their origins in increasingly complex materials, thus enabling a marriage of experiment with theory that is reshaping how new materials research can and is being done. The challenge is to leverage these developments to establish materials discovery teams that effectively integrate these modern capabilities. The promise is an accelerated pace of discovery, enabling new technologies that will underpin our future competitiveness and energy independence.

Executive Summary

The striking technical progress in materials characterization capabilities and computation of materials properties calls for their effective incorporation into a tight synthesis-characterization-computation loop to transform the nature of new materials discovery. Achieving this will require a steep learning curve to integrate the advanced tools into a new materials loop free from bottlenecks. We have the ability to not only learn more in microscopic detail about real materials now than ever before but also at a rate which is fast enough to influence a typical synthesis protocol. The integration of theory, computation and characterization with synthesis will give new focus to the search for new materials and can be expected to lead to qualitatively new ways to think about structure-property relations, the overarching agenda of new materials research.

Scientific Challenges

The next generation of energy technologies is dependent on the discovery of new materials that will enable revolutionary and transformative advances in how we generate, use and store energy. The process of materials discovery requires a new paradigm, from an expert-based intuition-driven process to a more comprehensive approach that closely integrates theory, synthesis and characterization.

Research Directions

Discover guiding principles for materials functionality. Traditionally, solid state chemists have used empirical guiding principles to find new materials, such as crystal structures that harbor interesting functionality, exemplified by ferroelectricity in perovskite-related structures. Another example is Zintl-based ideas of charge transfer triggering covalent reorganization of polyatomic anions guiding the discovery of interesting new intermetallic compounds. The interplay of modern theory and experiment enables guided searches for new materials by developing detailed microscopic understanding of trends connecting structure with properties. This guided approach should be exploited in focused searches for materials with specific properties needed for energy technology, including, for example, high performance magnetic materials, superconductors and thermoelectrics.

Synthesis and process modeling of novel phases from extreme conditions. The systematics of materials properties often suggest new materials with enhanced properties which do not form under normal preparation conditions. As example, there is a trend towards higher superconducting critical temperatures in less stable phases and there is a strong association between phases that form under high pressure and super-hard materials. Further, the recent advances in high pressure research find quite unexpected structures and properties in elements and compounds. Materials synthesis under extreme conditions expands greatly the phase space available for the deeper understanding of structure/property relations. These methods include high pressure, intense radiation fields and large electric potential gradients that occur in electrolytic processes. Effective exploitation of methods for synthesis under extreme conditions is needed.

Exploration of unstable and metastable phases. The properties of unstable and metastable phases vastly expand the phase space of interesting materials. Glass is an ancient example with extensive continuing interest. Diamond, which is now finding multiple applications in thin film form, is another example. Metastable materials usually require special synthetic routes which process modeling can address. Furthermore, they often support anomalous atomic valence states and these in turn can lead to novel properties. Finally, these materials show functional possibilities that can be designed into new stable but as yet unknown materials via appropriate functional units. For example, discovery of novel properties in unstable high pressure phases may lead to realization of these properties in metastable or stable phases. Exploitation of modern techniques for the discovery of new metastable phases is needed.

*Identification of Synthesis Routes for Promising Materials***.** Methods, both theoretical and experimental, that inform the synthesis process must be developed and integrated into the materials discovery process. These advances include computational methods based on first principles theory and the development of experimental screening probes for thin films as in combinatorial searches. For instance, studies of thin films with compositional spreads using a combination of appropriate probes, such as laser melting coupled with x-ray diffraction, can

rapidly elaborate solid-liquid phase relations and the resultant microstructural development leading to a more complete realization of multi-component phase diagrams. These experimental methods coupled with computational prediction of multi-component thermodynamics and kinetic pathways will lead to rapid identification of synthesis routes.

Morphological control of crystal growth. Proper characterization of complex materials depends to a large extent on measurements on suitable single crystals. An example is provided by materials for radiation detection, where it is essential to perform experiments on large single crystals to determine the performance of a given material. Producing single crystals, especially with high perfection, remains a significant challenge. Generally imperfections such as point and line defects, compositional gradients and second phases, are generated at the advancing solid-liquid interface and depend on the morphology and stability of this interface. Greater understanding of the growth conditions, such as growth temperature, velocity and supersaturation levels, will lead to stable growth morphologies and allow greater manipulation of the growth process which can significantly speed progress in the study of new materials.

Capability Gaps

Advances in the past decade in characterization tools, in particular in intense sources of photons and neutrons for scattering experiments, now allow sample analysis of a sort never before possible and promise a new era of materials discovery. Realizing this promise requires not only utilizing the tools fully but also coupling their output into the synthesis-characterization-theory loop in an immediate way that does not bottleneck the flow of ideas and results.

Scientific approaches that integrate the ground breaking scattering capabilities of user facilities with modern capabilities in theory and synthesis, and harness them to accelerate the pace of materials discovery are needed.

The tremendous extent of the space of materials that can be made and the tiny fraction of these materials that are known underscores both the challenge and the promise of materials discovery. This is exemplified by the many recent unanticipated discoveries in superconductivity, such as two-band superconductivity in MgB_2 and iron-based superconductivity in pnictides and chalcogenides, which continue to occur even after decades of research in the field. Methods for effectively exploring the materials space are needed. Promising approaches include guided materials synthesis in which theory, characterization and synthesis are tightly integrated to discover trends and guiding principles and use them to find useful materials, and combinatorial synthesis where large numbers of materials are synthesized and rapidly screened for interesting properties. Theory and computation can also be used in a combinatorial fashion to suggest interesting materials for experimental synthesis and characterization.

Within the past decade, advances in combinatorial thin film methods and reliable detailed theoretical descriptions of materials functionality have lead to a rapid identification of many potential new useful materials. Trends identified from experimental and theoretical studies

suggest regions of materials space that should be explored for advanced materials. However, synthesis of bulk samples is often challenging and in many cases is the limiting factor of such approaches. The low capacity of materials synthesis capabilities in the US further limits the pace at which materials discovery can advance. Rapid methods for assessing synthetic routes and process modeling to optimize synthesis are needed. At this time, development of synthesis routes remains iterative and serial, requiring multiple syntheses and time-intensive characterization to identify and optimize synthesis. Combinatorial approaches generally stop short of providing sufficient information to assess appropriate bulk synthesis routes and similar considerations apply to computational searches for new materials. For example, most solidification based synthesis methods require a set of material parameters that inform the growth conditions needed to stabilize the morphology of the solid-liquid interface and allow full control of microstructural and compositional development.

A new generation of in situ probes to monitor and control synthesis is needed, allowing real-time feedback as growth occurs to manipulate defect structure formation and/or impurity level and distribution, and to control long range homogeneity, and/or local inhomogeneity.

Combinatorial approaches either through experimental thin film methods and/or by computational approaches are beginning to demonstrate success in guiding searches for new materials discovery by refining the limits of phase space. Thin film methods that utilize chemistry spreads to sample a portion of a phase diagram essentially provide an infinite number of samples limited only by the spatial resolution of the characterization probes. This powerful approach can be developed further by minimizing the unwanted stress during growth that leads to crystallographic textures that can hide intrinsic behavior. New high-resolution characterization probes of materials functionality that are applicable to thin films need to be developed. Similarly, tools to characterize very small bulk samples will be very helpful for materials discovery in general but are lacking for many key properties.

Potential Impact

The continuing surprises in new materials discovery sends the resounding message that we are far from even remotely knowing the full range of nature's possibilities. One has only to look at the small sub-field of superconducting materials to realize just how unexpected the findings are. Superconductivity in the high transition temperature cuprates, MgB_2 and now the iron pnictides are the prominent tip of a much larger iceberg. The fact that elemental Li at one million atmospheres pressure is a 20K superconductor is a finding that defies conventional understanding. The focused search for new superconductors, as for many other materials classes, is in need of guiding principles. Establishing a paradigm for new materials research based on full utilization of the state-of-the-art characterization tools, advanced computational capability, modern theory and a complete suite of synthesis techniques has the potential to define entirely new perspectives for materials discovery. An important collateral impact is a vastly enhanced set

of skills, competencies and promising new horizons for the next generation of materials synthesizers.

The accelerated identification of new materials with novel properties will result in the rapid introduction of new materials into the basic research and technology streams that define and enable scientific and economic competitiveness. Capitalizing on discoveries of new materials is very much a matter of timing, both in basic research and in technological application. The element of immediacy should not be underestimated in its relation to maintaining scientific health, both for the enterprise and for attracting the finest students to the field to maintain future capabilities.

Priority Research Direction: Realizing materials design and performance: lifetime prediction

Problem Statement

Empirical discovery techniques can achieve incremental advances. Steel-making for example dates back over thirty centuries, but the strengths of most present-day empirically-developed commercial steels are less than a factor of two higher than that used in swords during the medieval-era. While this empirical description has some success in describing the simple tests in which the response was sampled, their applicability outside this regime is based on extrapolation to fits not to observed behavior. As new manufacturing techniques are developed, processes are better understood and new mechanisms are accessed. Equally probing and accessing new extreme loading paths takes matter through a suite of new mechanisms. These are different in each phase, in each class and each component of a material system, and until they are mapped and analytically described there is no possibility of accurately describing behavior nor controlling fabrication and design of new materials.

Executive Summary

The only means of achieving the ambitious goal of realizing materials design and lifetime prediction is to evolve a suite of tools and a knowledge base that is built upon the physical mechanisms that operate both in the formation and processing of the materials at their inception, but also in the means by which the microstructure responds to loads delivered in the environment in which the material must operate. At present mathematical descriptions are derived from a limited suite of tests in a small part of loading phase space and fitted to the responses observed. Thus a vital, science-based challenge is to engineer materials based upon a cadre of knowledge founded on scientific mechanisms as opposed to empirical relationships fitted to testing.

Scientific Challenge

Understanding of the relationships between processing, structure and properties will give rise to the integrated performance of the material in the range of applications and environments that the twenty-first century will require and which the new environments man accesses will impose. This interrelation of structure to processing and its connection to the response achieved in use, must be understood to exploit materials for the extreme but also to design new processing routes for the modern world. These paradigms offer an exciting forefront for the future advance of materials and structures constructed from them through the next century.

To advance on these fronts requires accelerated qualification and testing for the use of these optimized materials to acquire performance through life. To do so safely and reliably requires a new means of qualification and testing to be developed to allow rapid assessment and licensing of the materials. Such schemes and structures already exist (e.g. Accelerated Insertion of Materials; AIM) to ensure assurance for performance through life. But full development of these

will allow more rapid use of materials from the drawing board through to a safe and productive life in a particular application.

Research directions

Materials Design

Materials Design focuses on the development of *inverse* solution methodologies geared to identifying new materials and microstructures that are theoretically predicted to meet a set of designer specified performance criteria. Broadly, the tasks involved in materials design can be broken into two main components: (i) Identify the complete set of microstructures that are theoretically predicted to meet or exceed a combination of desired material properties or performance characteristics. (ii) Identify processing routes that are theoretically predicted to physically realize elements of set of the desired (presumably optimized) microstructures. Developing a rigorous mathematical framework that facilitates these inverse solutions constitutes an important decadal challenge that can transform the current practice in the field of materials science and engineering and provide a clear pathway forward for the rational design and processing of high performance materials.

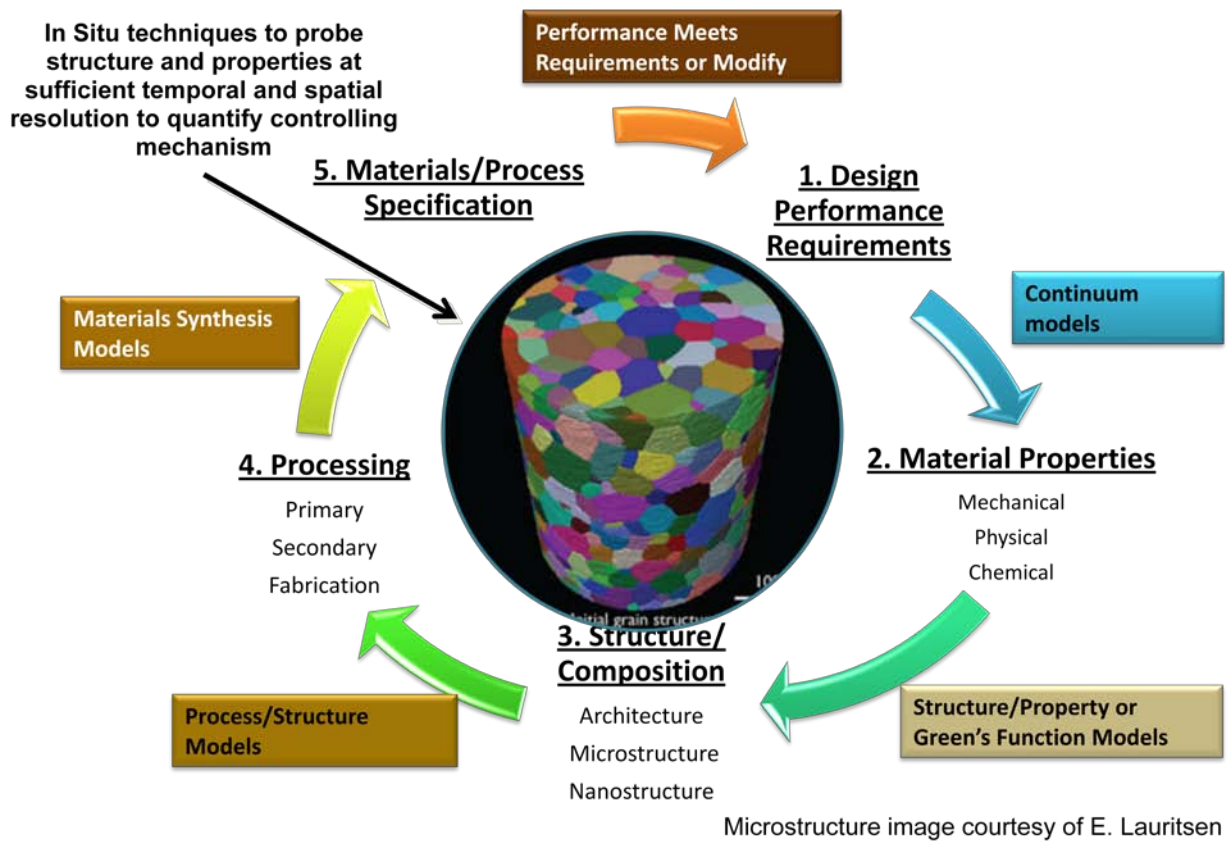
A critical element for success in materials design is the availability of validated forward models that predict the structure-property-processing relationships in the material systems of interest to desired accuracy. Given that the materials phenomena of interest often span distinct time and length scales, it is imperative to develop a cohesive multi-scale modeling framework that is also critically validated with direct experimental observations. Additionally, to facilitate materials design, it is critical that the scale-bridging in the multi-scale modeling framework is designed to transmit information accurately in *both directions* between the constituent spatial and temporal scales. It should be noted that the focus in most of the current multi-scale approaches is homogenization (going up in scales). For success in materials design, it is imperative that we focus equally on localization, i.e. passing information to the lower length scales.

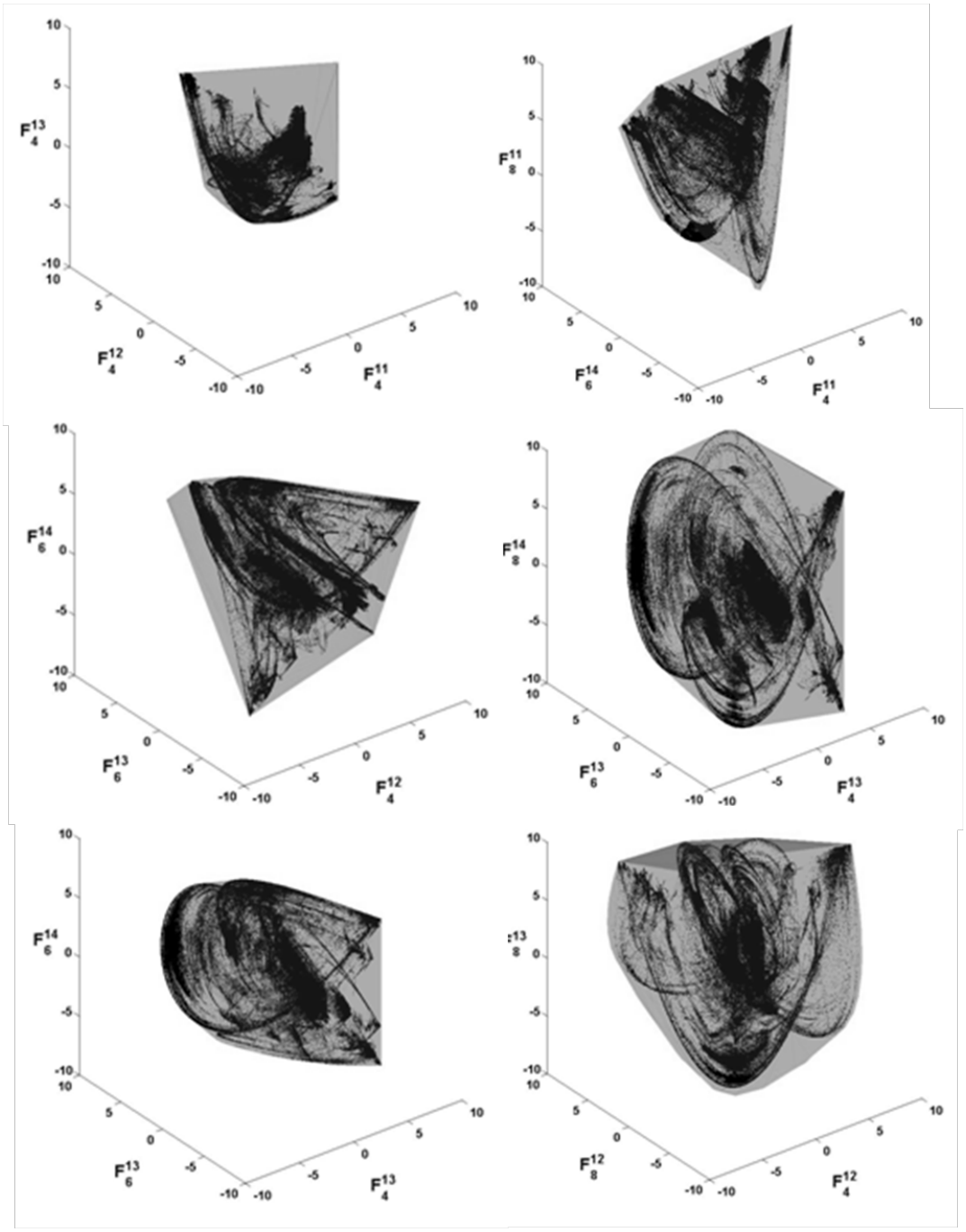
There could be tremendous benefits from employing established concepts in Digital Signal Processing and Systems Engineering in developing a mathematical framework that can address the challenges described above. Using these ideas can lead to FFT-based computationally efficient procedures for (i) fast retrieval of important microstructure statistics (e.g. defined in terms of *n*-point statistics), (ii) rigorous extraction of representative volume elements, (iii) automatic objective classification/cataloguing of microstructures, (iv) real-time searchable and shareable microstructure databases that can lead to improved collaborations among materials researchers and scientists worldwide, (v) computationally efficient data-mining tools that can extract the underlying knowledge in the large experimental and numerical datasets being assembled by materials scientists and produce a new class of modern *Materials Knowledge Systems*.

On the processing side, combining known manufacturing options into hybrid processing routes to develop targeted new materials is a particularly promising approach that deserves focused attention. However, the very large number of available manufacturing options, combined with the huge space of possible microstructures on which they operate, precludes process design by a purely combinatorial experimental approach. Once again a database approach that captures important details of microstructure evolution in a broad range of processing options can help deliver process design solutions much more efficiently than the brute-force methods.

Throughout the design process, it is vital that the system of theoretical prediction is tightly coupled to an efficient experimental system of model calibration and validation to define accuracy through the quantification of model uncertainty. This is especially important for the application of modern probabilistic design methods to achieve reliability and safety with reduced reliance on macroscopic empirical statistics.

The following figures provide some examples of possible materials design research directions described above.





Texture evolution networks of deformation processing showing a database of process networks projected in selected three-dimensional subspaces. The pathlines depict the various options available to transform a given initial texture in a sample into a desired texture. Every point in this space denotes a distinct texture. Therefore, process design reduces to finding a pathline in this network that starts at a selected initial point and gets to a selected final point, much like how a GPS system plots a route between any two selected destinations.

Materials Lifetime Prediction

The DARPA-AIM initiative of 2001-2003 represents an important milestone in demonstrating the power of deterministic modeling of complex multiscale microstructural evolution during processing, using statistically defined process variation to accurately predict probabilistic material property variation arising from multistage manufacturing [1]. The modeling approach and supporting tools were driven in this case by the need to accelerate process optimization of a new material at the component level and to forecast minimum property "design allowables" with greatly reduced reliance on empirical data. A recent NMAB study of best computational materials engineering practices [2] identified the AIM demonstration as the highest achievement in acceleration of materials technology transition. The example opens the way to a broader predictive probabilistic science of materials with emphasis on behaviors controlled by distributed heterogeneous nucleation, such as high-cycle fatigue (HCF) life. A firm foundation for such an approach lies in the well developed theory of heterogeneous nucleation of first-order phase transformations, particularly the cases of martensitic transformations and solidification. Here quantitative nucleation theory has defined deterministic multi-parameter structure/property relations at the level of a single nucleant, and thorough fundamental experiments have quantified the statistics of nucleant potency distributions from which probabilistic properties can be predicted. Ongoing efforts to apply the approach to HCF life modeling incorporate path dependent behaviors both in terms of the role of processing history on nucleant damage state and the role of load path history on properties emerging from anisotropic microstructural distributions. While significant research investment will be required to fully develop this new probabilistic materials science, the ability to predict low probability behaviors from fundamental mechanistic knowledge with minimal calibration from empirical data offers a major technological breakthrough in the life-based robust design, qualification and accelerated certification of safe reliable engineering systems.

Capability Gaps

Accelerated Discovery of Controlling Mechanisms

Addressing deficits in materials understanding that pace our predictive design capability requires the means to more quickly find the operating physical mechanisms that occur in a loaded microstructure. When these fundamental processes are understood, exciting opportunities to use extreme thermo-mechanical conditions to design and manufacture new classes of materials open up. Such advances may allow extremes such as the theoretical strength to be achieved through confinement effects on dislocations. Thus a shift in perception and boundary conditions is necessary to bridge the gap between materials today and the theoretically achievable. Further, these processes differ across material classes. Metals respond differently to polymers and they in

turn behave differently to brittle solids. The response is driven not by pure compression of atoms but by shear between agglomerations of atoms, that slide on planes as dislocations in metals or flow like spaghetti formed from polymer chains. In brittle solids inelastic response is preceded by fracture where cracking must first fragment the solid before compression can follow. In all of these cases it is flaws and defects that determine the nature of the behavior. Thus each of these varying behaviors must be probed with suitable sensors that are optimized to deliver the required data to understand the operating mechanisms. A series of deformation mechanisms are triggered by extreme loading, each having different operating kinetics. The various operating regimes for the devices limit the relevant mechanisms that can be accessed. This means that new loading devices and facilities need to be designed and operated to allow the accelerated discovery of controlling mechanisms.

Ability to quantify the full spectrum of the Dynamic Statistical Distribution of the Structure and Properties with the Required Spatial and Temporal Resolution

Diffraction methods are increasingly important to 2- and 3-D characterization of heterogeneous microstructure. These remarks pertain primarily to x-ray and electron diffraction methods. A case can be made for combining the two methods to take advantage of both.

Probes based upon electron diffraction are capable of resolving lattice orientation differences down to 0.005^0 and elastic strain/rotation to ~0.0003. It is expected that order-of-magnitude improvements in these current resolution limits can be achieved with appropriate emphasis (funding) with improved hardware and calibration of the electron optical systems within ~ 5 years. Spatial resolution of these techniques is approximately 20nm for the semi-infinite samples examined by SEM-based systems, and sub-nm in the thin sections prepared for TEM-based observations. Thus, the electron diffraction methods are essentially 2-D in nature.

X-ray probes, based upon the synchrotron light sources such as APS, offer 3-D imaging capability typically over cubic millimeters of volume. Current spatial resolution is ~ 1 micron. These systems have not yet been fully developed for resolution of the elastic fields, and at this point it is difficult to speculate on achievable angular resolution.

Both x-ray and electron diffraction methods require substantial experimental time frames to characterize extensive microstructure and response fields. EBSD-based electron diffraction can currently occur at rates of up to 1000 points per second for lattice orientation determination. High-resolution methods are currently implemented off-line, and the EBSD patterns are stored for subsequent analysis of the elastic and defect fields. It can reasonably be expected that with sufficient emphasis the high-resolution methods could be made real-time, so that ~ 1000 patterns per second could be fully analyzed for lattice orientation, elastic strain/rotation and their derivative – continuum dislocation density.

X-ray campaigns also require substantial time frames for extensive characterization of the microstructure fields. Thus experimental campaigns in excess of 24 hours are typical for a full

3-D characterization of volumes containing several thousand grains. The main recovery at this point is lattice phase and orientation, although one can reasonably expect that resolution of local first-order elastic properties (i.e., elastic strain and rotation) may be possible in the future. One large advantage of the x-ray probes is the ability to apply temperature and mechanical loads more readily than can be accomplished within the chamber of an SEM or TEM.

Temporal resolution is currently a serious issue for both x-ray and electron-diffraction systems. Strategies for rapidly noticing changes in the fields during in-situ experiments, and then focusing the probe in to the nearby region where the change is occurring are contemplated, and limited experience has been achieved. But this is an area where much work needs to be undertaken, if these instruments are to be optimally efficient for the study of localization-related events (e.g., nucleation events).

It is interesting to contemplate a hybrid instrument that would couple electron diffraction capabilities with x-ray diffraction, and with computer simulations. One can imagine, for example, an EBSD-based SEM introduced into a beam line at APS. Simultaneous probing with the x-ray and electron beams seems quite possible. The 3-D x-ray capability, with resolution on the order of 1 micron, could provide required information for simulation of the mechanical fields, identifying where "hot spots" should occur near the surface. Samples could be placed under thermal and mechanical loads. After these determinations the electron beam could be trained in the neighborhood of predicted surface hot spots, and these could be characterized at much higher resolution by SEM-EBSD methods. Comparisons of computed fields with measured ones would provide valuable feedback on the importance of the intrinsic elastic properties of grain boundaries, perhaps unaccounted for in the computer simulations. And other comparisons can be envisioned that would strengthen both experimental and computational results. Finally, for selected areas it would be possible to use FIB methods to cut TEM samples for further, even higher-resolution characterization.

Predictive capability for inverting information flow from performance to structure to processing:

There is a strong case for using Green's Function (GF) methods as much as possible for predicting the response fields in heterogeneous microstructure. The GF methods result in localization relations that are integrations over space (and time) of the product of GF operators acting on the microstructure fields. These microstructure fields include elastic polarizations that can be computed from knowing the elastic constants of the phases present in the material, and the local lattice orientation. But they also include the fields of dislocation density at grain interiors and at grain boundaries.

This basic *separable* character of the influence functions and the microstructure fields is of great advantage to inverse problems, because it enables the investigator to consider how the analytical form of the microstructure influences the tensorial nature of the response field. And since the integral equations are essentially sums, the effects of various components of the microstructure

can be summed up. Even non-linear constitutive behaviors can be treated in this way by considering perturbations away from an average response that can be conveniently selected from averages.

The GFs themselves are solutions to the equilibrium equations (for example), and they are of simplest form for infinite media under uniform boundary conditions. However, some progress has been made in terms of generalizing the approach to BCs, to make things more realistic.

Invertibility of the materials design paradigm is an important attribute of design methodology GF approaches are inherently highly invertible in terms of moving from homogenized properties or localization, back to the fields of microstructure. One much needed advance in the study of localization related phenomena in heterogeneous materials would be approaches to develop analytical Green's functions for complex geometries and complex boundary conditions.

Required changes in education

While the power of computational materials design has now been well demonstrated [3], the principal barrier to further materials design technology development is the relative lack of a design tradition in the materials research community. This fundamental cultural barrier is best addressed by significant educational reform at both the undergraduate and graduate levels. As examples of progress, we discuss recent educational initiatives at Northwestern University and Brigham Young University (BYU).

An upper undergraduate course in Computational Materials Design has been underway at Northwestern since 1989 [4]. Building on the systems view of materials proposed by the late Cyril Smith, the course develops the application of general practices of systems engineering to materials as multiscale interactive hierarchical systems. With projects drawn from funded graduate research, materials majors incorporate research findings from allied disciplines of applied mechanics and quantum physics applying a microstructure-based parametric design approach to the specification of materials composition and processing, employing computational thermodynamics as the principal integrative tool. Since 1993, national undergraduate design competitions of the TMS and ASM materials societies have fostered design curriculum development, and showcased best practices of winning teams, for which Northwestern has been a leading contributor. The program at Northwestern has been further strengthened by the development of an engineering school-wide Freshman Design and Communication course sequence that has built a common design practice foundation across disciplines. Taught jointly with writing faculty, this "techmanities" education initiative integrates communication skills to enhance both client/user interactions and team creativity [5]. With this foundation, the upper-level Materials Design course can focus more on technical design principles. Further technical depth in design projects is fostered by a hierarchical coaching system in which graduate students engaged in doctoral design research serve as mentors to the undergraduate design teams [6]. The course employs 5 computer laboratory sessions to develop basic proficiency in the computational

tools employed in the design projects. Greater comfort with the tools is fostered by an ongoing initiative to introduce the tools in core courses where the associated scientific principles are taught. Under auspices of an engineering school-wide Design Institute, a sequence of upper-level Interdisciplinary Design project courses brings together undergraduate students from multiple departments to engage in systems engineering projects, including the concurrent design of materials and structures [7].

For approximately 3 years activities at BYU have also fostered undergraduate and graduate level education in materials design. The approach has been to integrate materials design into the larger design enterprise. Engineering designers have little difficulty in understanding that materials design could increase their design space, affording greater flexibility in design and allowing novel and unusual designs. However, there exist significant barriers to be overcome. The investment of mechanical designers in ordinary strength of materials concepts (which nearly always invoke unwanted assumptions about material, such as homogeneity and isotropy) is considerable, and it is difficult to get them to move away from these ideas. Anisotropy is difficult to teach, because it requires the use of tensors – and the concept and manipulation of tensors is not usually taught at the undergraduate level. Introducing tensorial concepts at the undergraduate level is widely viewed as difficult. Materials design can be introduced without anisotropy, but this limits the potential benefits that can accrue from materials design.

One of the more effective educational tools is to form design teams surrounding an interesting design problem. Some examples taken on by BYU undergraduates include the design of a flywheel for energy storage, combined geometry and heterogeneous microstructure design for an electrostatic MEMS switch, and the design of an orthopedic implant for the femur, with the aim of minimizing the elastic mismatch between bone and implant. These teams were typically about 6 students + 1 faculty member. BYU's experience is that these experiences need to be at least 2 semesters in length, given that the concepts and methods of microstructure design must be introduced before students can work with them.

It is interesting to contemplate an alliance with the national labs in this educational process. High end, highly-constrained design problems are typical within the DOE labs, and there will be an ongoing need for materials design. The institute program, with alliances to selected universities emphasizing materials design, could be a useful vehicle for promoting materials design as an important discipline.

Potential impact

These benefits are the applied consequences conceived now without all of the advances in new physical science and engineering gained from understanding the new behaviors occurring and modeling the controlling mechanisms. The range of conditions that can be addressed apply to loading that comes from a specific environment but also stimuli that can be used to engineer new designer microstructures. The stimuli under this umbrella span high energetic fluxes, intense

electromagnetic- and extreme mechanical loading. If these can be adequately controlled then materials can be created with tailored performance and further accelerated transition into application will result.

When such knowledge has been assembled, one will be able to apply the designed materials or use existing stock outside of the existing design envelopes accepted in modern engineering. This will allow extension of the abilities of materials both in service life for existing components but also to access new operating conditions for use in the field. The future will see faster, better structures capable of lasting longer times in safety to address the challenges of the modern world.

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Priority Research Direction: Bridging Length and Time Scales

Problem Statement

One of the most challenging problems facing the integration of modeling and simulation with experiment to advance materials development is that of scale. The physical phenomena that govern materials response range over many orders of magnitude in both length and time. The current approach, in which we develop methods that are applicable over small ranges of length and time, and then attempt to link those together, is often inadequate. New approaches that take advantage of advances in material theory, computational resources and information science, are needed. Strategies for attacking such problems are proposed. Linkage with experiment will be critical, both for validation of the physical models as well as to provide information not available from calculation.

Executive Summary

One of the basic challenges in multiscale materials design is the wide range of length and time scales that govern the properties of materials. The standard modeling approach is to identify the various phenomena that govern a specified property at given ranges of length and time, and to identify the fundamental "unit" whose behavior dominates the materials response at that scale.[1] For example, at the smallest scale, the bonding between atoms dominates, which arises from the underlying electronic structure, with the electron as the fundamental unit. To describe this bonding requires the use of a specified set of computational tools geared to solve that problem. At larger scales, where the behavior of multitudes of atoms dominates the response, simulation methods based on those atoms (e.g., molecular dynamics) may be most appropriate. At still larger scales there are too many atoms for us to consider, so we must find new approaches that focus on the dominant "units." These units often may be dislocations, grain boundaries, or some other defect, and the simulations would use these defects as their fundamental entities.

Thus, each scale is generally dominated by a different set of fundamental microvariables, which typically describe some sort of collective behavior of sets of microvariables from smaller scales. To model each scale generally requires unique methods and is usually done by different research groups. While much progress has been made in modeling at many of the individual scales, especially with respect to length, bridging from one scale to another is still a major challenge.

Modeling of multiscale materials systems encompasses a broad range of increasingly challenging phenomena and physics. While there are currently many efforts focused on developing techniques for multiscale modeling, there are no proven methodologies to creatively *design* multiscale materials and processes and there are few research efforts to develop these needed design techniques. The design of multiscale materials is unique in several ways - by working across scales, additional degrees of freedom are introduced into the design space and small changes at one scale can have a significant impact on other scales relevant to the intended purpose of the design. The methodologies and tools to do this type creative engineering design do not, however, currently exist. Here we describe a research direction that would help create these tools.

More progress has been made in bridging length scales than in bridging time scales. Too many of the physical processes governing materials behavior are not easily separable in time. Thus, a

great deal of effort has gone into developing new approaches that extend the time scale of existing methods. While these efforts are essential, new theoretical approaches are also needed. It is these two primary tasks that are the focus of this PRD.

Scientific Challenges

Development of accurate, computationally efficient, and physics-based approaches to bridging scales in length and time are critical to integrating the microstructure features from distinct time and length scales into a cohesive multiscale modeling framework. While there are specific challenges to be met for distinct classes of methods, there are general requirements. To successfully predict and control, it is imperative to build the following features into scale bridging: (i) scale bridging has to transmit information accurately in both directions between the length scales. (ii) scale bridging has to be formulated in such a way that it allows inverse solutions that are central to successful materials design.

It is an especially important challenge to **extend** atomistic calculations to long times that capture rare events. The most-used approach, molecular dynamics, is limited by the requirement that it resolve the fastest motion, which limits the time scale of a simulation to the nanosecond regime. While advances have been made for systems dominated by infrequent, and activated, events (e.g., hyderdynamics [2], etc.), new approaches are needed that can elucidate behavior such as glassy relaxation and creep deformation response which are widely acknowledged bottlenecks in the computational materials community.

Ultimately, however, the key challenge is to develop new ways to integrate whatever information is needed for a given problem, at a given moment and at whatever scale, to describe materials behavior and response. That information could be from experiment, modeling, and/or simulation. What information is needed to describe one region of a structure may be different than that needed for another; the structure could be under complex stress states or in varying chemical environments. One approach is to take a broad view of information across scales and to employ new approaches to describe and use that information. Thus, new methods to catalog and characterize such information, from a variety of sources and at a variety of scales, are essential

Research Directions

Research activities needed to meet the scientific challenges can be loosely grouped into three categories: theory, simulation, and computation. These are not entirely separate categories, however, and the ultimate goal is to incorporate this broad range of activities into a unified package, creation of which will require a fourth category of research: information science.

First and foremost, there must be a strong effort in the theory of multiscale materials behavior, especially with respect to the bridging of scales. For materials, perhaps the most critical area is at the microstructural scale (i.e., the mesoscale), i.e., at the scale of the ensembles of defects that often dominate materials response. With the advent of high-resolution structural probes, for example, a central challenge is the development of theories or models that describe the self-organization or collective behavior that emerges in evolving microstructure. Theories need to be

based on identifying the important driving modes or "order parameters" for a given phenomenon, and then to relate those order parameters to the appropriate energy terms. The merit of such an approach is that questions may be answered by the methods of statistical physics. More importantly, one can add disorder to these theories and study transitions to more complex behavior. To date, there are very few examples where this approach has been demonstrated. However, developing such theories is crucial if we are to understand and predict the complexity of materials issues.

Coupled with new theory is a need for advances in the fundamental models and simulation methods applied to materials. There are many important areas of research in this area, many that are underway in various places around the world and others that have not yet been identified. One of the most important would be the development and characterization of infrequent-event sampling algorithms for extending scales, especially in time. Many events are stochastic, involving activated processes and occurring only rarely. Better methods for handling such events are essential. As an example, a primary research direction would be to perform benchmark simulations to determine the viability of existing atomistic methods (e.g., hyperdynamics [2], first-passage Monte Carlo [3], and metadynamics [4-5]). Appropriate problems to be considered include calculating the viscosity of supercooled liquids, for which experimental are available for comparison, and the stress relaxation of a solid under fixed strain deformation. A metadynamics method in the form of a series of activation-relaxation involving the use of an energy penalty function has been demonstrated to close the capability gap in predicting the temperature of glassy liquids [4]. This approach, in which the system is able to climb out of any potential well, shows promise as a sampling method for the potential energy surface of a material system in a study of deformation response at strain rates from 10^4 s^{-1} to 10^{-11} s^{-1}, a range that is beyond the capability of MD simulations [5].

It is also necessary to create an increased ability to link methods across scales. Given the stochastic nature of many processes, and their importance in determining materials behavior (e.g., fracture, failure, materials aging), this will require the development of statistically reliable accelerated algorithms for cross-scale simulations, by which we mean that the probability of rare-events is appropriately incorporated at all scales. Many methods to address this challenge have been proposed (e.g., Bayesian statistics [6], etc.), but much development remains. Another critical need is to be able to track uncertainties across scales, i.e., how inaccuracies at one scale affect the prediction of materials behavior at larger scales. Usefulness of simulations to material development, insertion and certification is greatly enhanced if simulation errors and uncertainties are quantified. Agreement or disagreement between experimental data and simulations can be firmly established only if errors and uncertainties of both are known. Simulation error and model uncertainty should not be confused. Simulation error is the difference between (the usually) approximate and (asymptotically) exact simulations of the same model. Model uncertainty, on the other hand, reflects insufficient accuracy of model parameters, model incompleteness (e.g. missing mechanisms) or inadequacy of the model itself, irrespective of the quality of numerical

simulation. Quantification of simulation errors (verification) may require significant computational effort but otherwise is often relatively straightforward. What it means to quantify the model uncertainty is not as well understood. Few robust methods exist to date, yet it is a critical need for predicting materials behavior.

All of these methods and algorithms must take advantage of new computational architectures. As of now few methods are well optimized for current architectures with massive numbers of processors, especially for some of the more innovative computers (e.g., the Roadrunner). As we move to exascale computing, optimizing computations is likely to be even more challenging. It is critical that we start now to develop new approaches to take advantage of these machines.

To link these disparate activities together in a unified package for materials prediction and design will require new and innovative ways to organize information across scales. These needs arise in computational algorithms, e.g., optimal multiscaling via adaptive model refinement and self-learning algorithms, as well as in flowing information from one scale to another, e.g., incorporating microstructure-based simulations into engineering modeling systems. The recent focus on semantic ways to handle information may offer a productive way to think about information flow in materials in that it does not prescribe linkages, but rather enables the information to self-identify and self-organize, eliminating redundancies and optimizing the ability to have the needed information at the desired fidelity at the right time. Given the complexities of the information flow needed to describe the multiscale nature of materials, this feature of the data flow may be essential.

Capability Gaps

The reach program described above will be made more difficult by gaps in our knowledge and capabilities. These include:

A lack of theoretical and computational approaches needed to bridge length and time scales. One approach has been to average properties at one scale (either from experiment or modeling) and to use those averages to develop models for behavior at larger scales. There are a number of limitations to this approach. The averaged models tend to be limited in range and applicability, they are often time-consuming to produce, they typically are limited in the quality of physics they can represent, and they cannot represent “abnormal” or rare events, which are stochastic in nature and not generally amenable to an averaged description. For example, we cannot couple properties at the mesoscale with the underlying dynamic electronic structure, as needed for multiscale predictions. This “message passing” approach is, however, the most common way people attempt to link simulations from one scale to another. An alternative is to embed one simulation method within another, i.e., different methods are employed to model different regions of the material. The most common example in materials is the incorporation of atomistic simulations within finite-element calculations, which has been accomplished by a number of groups. What has been done to date has, however, been limited. Moreover, the design is static, with fixed interfaces between the simulations. Thus, they do not provide flexibility to handle the

information inherent in a multiscale description of material properties nor to describe the range of physical states different parts of a material might have in use. Thus, they cannot be the basis of the systematic approach needed for full multiscale design.

The ability of atomistic simulations to reach time scales of order seconds and beyond is currently lacking. This widely recognized challenge has remained unresolved since the early days of multiscale simulations. Closing the gap requires the demonstration of an atomistic method (using interatomic potential as an input) that can elucidate behavior, such as glassy relaxation and creep deformation response, which are widely acknowledged bottlenecks in the computational materials community.

We currently lack methods to perform inverse mapping from larger to smaller scales, largely because the problems are underdetermined, i.e., many representative microstructures, for example, could yield the same average response at a higher scale.

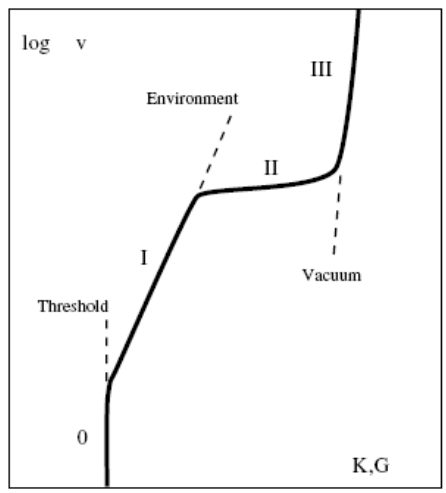

Figure 1. Schematic view of stress corrosion cracking, plotting the log of the crack velocity versus load.[7]

Many materials system exhibit behavior in which their properties show a marked change in character over a very small range of applied conditions, e.g., a large change in stress strain behavior over a small range of applied stress. This is an example of a threshold phenomenon, which generally arises when there is a competition between nonlinear physical processes. There are other threshold phenomena that are more catastrophic, for example a sudden change in behavior in radiation damaged materials. In Figure 1 we show an example of a threshold in a schematic view of stress corrosion cracking. We lack a general theoretical understanding of such behavior and, because of limitations in modeling/simulation capabilities, can rarely predict such behavior computationally.

We lack a set of robust algorithms required to make the best use of petascale and exascale computing. Methods developed when the computation employed a few thousand processors are unlikely to be most efficient when used in a platform in which there are tens of thousands of processors that may or may not behave similarly. How data is stored and transferred between processors, how loads are balanced, etc, are all questions yet to be answered

Potential Impact

The potential impact of successful completion of the research thrusts in this PRD is enormous. Currently, we rely mostly on experiment to observe material behavior, especially when that

behavior is stochastic and rare. With the multiscale modeling and simulation methods suggested here, it will allow robust extraction of underlying physical principles across scales, with an emphasis on physics at the mesoscale, which often dominates materials behavior. Indeed by bringing a mathematically grounded approach to materials science and engineering, we will create capabilities that will allow the transformation from observation to prediction and control of materials properties.

Perhaps the greatest impact will be on the creation of a new ability for integrated computational materials design. Engineered designs are generally based on the use of a constrained, and fixed, set of materials. However as multiscale materials behavior is understood, and new computationally-based predictive tools are developed, we will be able to design the material properties of each part, providing enormous freedom in the design of new processes and products. The need for such capabilities are outlined in detail in a recent National Academy study entitled *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security*.[8]

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Priority Research Direction: Exploiting materials complexity

Problem Statement

Materials exhibit considerable complexity and especially those used in engineered applications. The natural tendency in hypothesis-driven research is to identify one aspect at one length or time scale and investigate it or engineer with it. In reality, however, many of the important properties of materials are sensitive to the full complexity of the microstructure. As examples, consider the properties of corrosion resistance, radiation damage resistance and fatigue resistance. All these depend on synergistic interactions between such features as grain structure and chemical heterogeneity and responses to loading such as mechanical response. These sorts of properties reveal another important subtlety, which is that all the features and responses are populations with varying strengths and that the members of these distributions that concern us are often not the mean values but rather the extremes. Strategies for attacking such problems are proposed. Advances in instrumentation, simulation and analysis will all play a crucial role in allowing such issues to be addressed.

Executive Summary

If all that is required in a given situation is the average response of a material then microstructure often plays a minor role. For the more complex but important materials properties such as fatigue, corrosion, and spall resistance, however, safety often dictates that minimum values must be used. This means that one must understand the variability in materials response at least and in some cases the extremes values ("tails") of distributions. With this mind, careful examination of materials response under extreme conditions reveals some important characteristics.

- Heterogeneity-dependent variability in material response, more so under extremes of loading.

- Size dependence (microstructure, sample size) based on weakest link statistics.

- Time (or strain) dependence: scatter is most apparent at either end of life (e.g. in creep, fatigue or shock) and this scatter is linked to microstructural variability.

- Where multiple processes are concurrent, such as in materials subjected to irradiation and mechanical load, the interactions of defect production, defect loss to sinks and defect-mediated deformation, coupled with anisotropy, can result in counterintuitive behaviors.

The sources of such variability in materials response are manifold. Whatever the nominal composition of a material, it is rarely the same from one point to another because of the segregation that commonly occurs in thermomechanical processes (or analogous variability in other synthesis routes). Consequently the population of second phase particles can be highly variable. Most metals and ceramics are polycrystalline (along with the semicrystalline polymers), which means that a grain boundary network exists in the material. Thus there is

variability associated with crystal orientation (texture), grain shape, grain boundary character (nearest neighbor correlations in orientation) as well as potentially higher order correlations.

Scientific Challenges

We currently lack methods that can accurately model dynamic situations in which the electrons and the ions are not in equilibrium, e.g. ion bombardment in radiation damage. The scientific question is, therefore, to postulate that there are computational methods that address such problems in reasonable times. The opportunity is to be able to go beyond, say, hard sphere models for calculating radiation damage plumes.

We currently also lack probabilistic theories of material failure that relate the 3D statistical distribution of defects to the statistical distribution in material performance. Although there are a number of statistically based models available (e.g. peridynamics) we do not have theories that take microstructure directly as an input and make predictions. The scientific question is to devise experiments, both physical and numerical that can provide the necessary links.

We lack efficient computational schemes for evaluating the impact of microstructure on material response, especially in 3D. This also brings up the issue of a Representative Volume Element (RVE) versus a Statistical Volume Element (SVE). The scientific question is therefore how best to bound the distributions of properties, especially where it is the upper (or lower) tail of a distribution that controls the material property.

We lack ability to accurately model multi-component systems, e.g. phase relationships and diffusion. The scientific question, at least at present, is how best to combine *ab initio* calculations with computational thermodynamics (Calphad) and produce arbitrarily complicated phase diagrams. Even more challenging is the need to be able to predict diffusion in multi-component systems since this is a non-equilibrium property that requires long simulation times, relative to atomic vibration frequencies.

We lack robust approaches to quantify the uncertainties (and/or distributions) of materials properties, e.g. thermal properties, voiding, cracking. In some cases, such gaps can be addressed by numerical experiments, keeping in mind the need to analyze the variations from successive instantiations and the need to understand at a scientific level where that variability arises in the microstructure. There is an opportunity to establish a methodology for predicting not just the mean value of a (microstructure-dependent) property but also its distribution.

Research Directions

Heterogeneities Driving Tails in Distributions

Materials in technological use have always been heterogeneous, with ranges of disorder in composition and structure. These heterogeneities occur across scales, from local atomic disorder

at the nanometer level to microstructural features at the many micron level. They may involve many phases or just one, but with many orientations. What is changing is our ability to design heterogeneities at all scales, through a range of processing paths, with desired functionalities. Many challenges remain, however, in our understanding of the role that heterogeneities play in determining materials response, especially under conditions outside the norm. To control those functionalities will require an understanding of the relations between the global properties of a heterogeneous material and the local properties of its homogenous phases. A critical gap in the current approach is it is often not recognized that obtaining the global properties is not simply a matter of computing a suitable average but may, in fact, depend on the upper tail of a distribution. This is particularly true of materials properties such as corrosion resistance, fatigue resistance, spall resistance and almost any property related to damage evolution. Moreover, we will need to predict the evolution of structure and response of these complex materials in dynamic environments.

Defect-driven variability in material response

When materials are exposed to extreme environments (radiation, high temperature) or pushed under extreme mechanical conditions (long term fatigue, shock), the statistical variation in material failure response among seemingly identical specimens increases substantially. In these cases, the variability in response is so significant that the usual Gaussian statistical analyses that calculate mean and standard deviations are not adequate descriptors. When material response exhibits so much uncertainty, reliability in material performance in extreme environments and conditions (no matter how strong or tough the material may be in less challenging circumstances) is compromised. Approaches to reducing the uncertainty begins by first understanding how it originates, followed by the ability to predict it, and ultimately to control it.

Non-negligible variability in material response in extremes is the result of a combination of enhanced sensitivity in two components: distributions of defects, inherently linked with 'microstructure' (including atomic structure, nano-structure) and variability in the forcing component (stress, radiation, temperature). When and where defects nucleate and how slow or how fast they coalesce depend on a combination of these two components: material and mechanical. As a simple illustration of how these two components interact, consider the two illustrations in Figure 1 (first cartoon with all 'red' defects) and Figure 2 (second cartoon with red and blue defects).

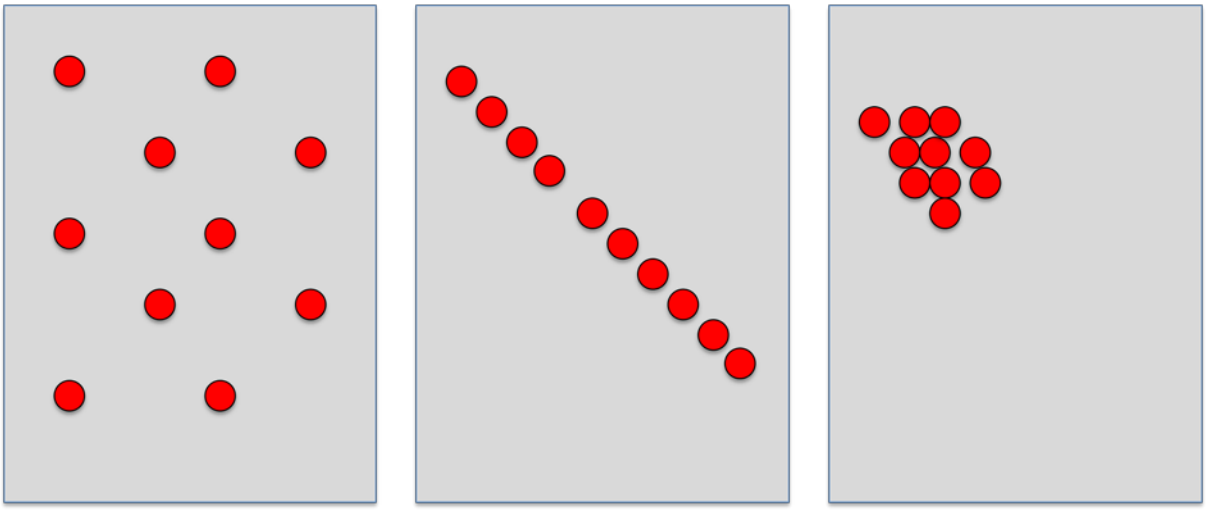

Figure. 1. Illustration of the effect of variable spatial distributions of defects at constant volume fraction.

In Figure 1, the stress state is uniform across the sample and the same for all three samples. The only difference is the spatial distribution of these defects. Although the mean volume fraction is the same for all three, the distribution in the first picture is uniform (no correlation-class A), the distribution in the second picture is highly correlated in 1D (class B), and in the third it is highly correlated in 2D (class C). The response among many samples of class A would exhibit very little variation and little size effect. The responses of many samples of class C, however, would vary significantly. The macroscale response of material C would be highly sensitive to the likelihood of activating several 'potent' defects in close proximity as shown. The chance this cluster appears increases as the size of the sample C increases. As a result the response (its mean, variation, and lower tail) would change as the sample size became larger. Last, samples of class B would likely exhibit even more variation than samples of class C. We can imagine that the 1D defect distribution in class B is far worse than the defect distribution in either A or C, yet the chance of such a well aligned defect configuration being present is smaller. Moreover, the chance it exists increases rapidly as the sample size increases and hence the size effect for samples of class B will be the most pronounced.

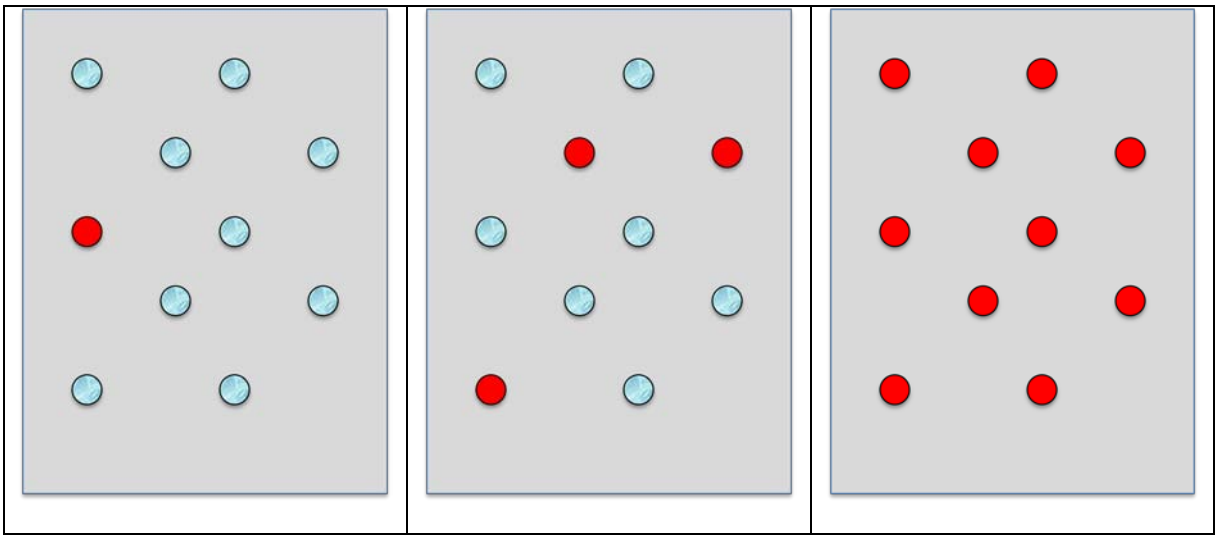

Figure. 2. Illustration of the effect of variable potency for the same population of defects; The loading increases going from left to right thereby increasing the fraction of defects that originate damage, leading to variation in outcomes in finite size samples.

In Figure 2, the defect distribution is the same; however, the stress level is different. In (a), the stress level is low (creep, high cycle fatigue) and hence failure processes and ultimate failure would occur over large time scales. In (c), the stress level is high (shock, low cycle fatigue) and failure processes and ultimate failure would occur in relative short times. Case (b) represents an intermediate level, in which, uncertainty in failure time and stress is perhaps the greatest. In all three cases, variations and size effects would manifest. However, the mechanisms and sequences of events leading to failure are different between (a), (b), and (c). Thus, the distribution in the response of many samples exposed to stress condition (a) cannot be expected to be the same as that for many samples exposed to stress condition (c).

Such variations have been observed in, for example, tests of thin films by Rupert *et al*. [1]. They inserted two holes into free-standing nanocrystalline thin films of aluminum and performed tensile tests. Two different arrangements of the holes were made, one with the holes in line with the tensile axis, and one with the two holes at 45° to the axis, somewhat akin to the variations in Figure 1. Not only were the response in terms of damage very different between the two arrangements but they also detected stress-driven grain growth. For the latter, the different stress patterns induced by the two different arrangements were crucial in permitting the deduction to be made about the driving force for grain growth.

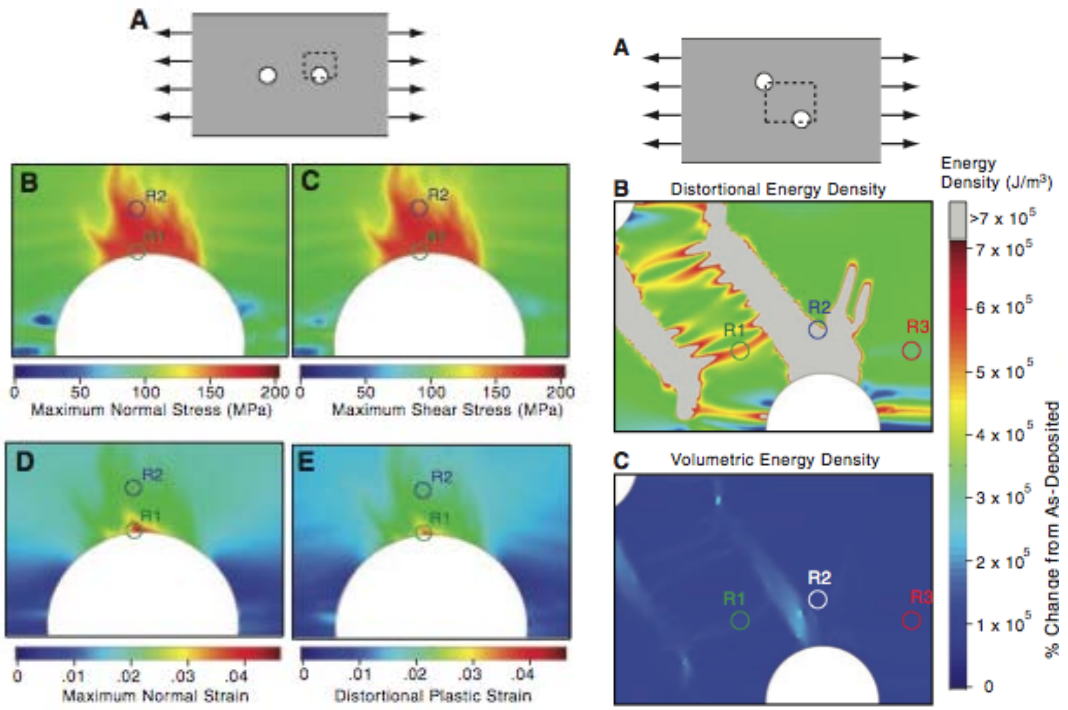

Figure 3. Diagrams showing two different arrangements of holes inserted into nanocrystalline thin films of aluminum, with finite element calculations of the stress and strain fields, showing significant variations between the in-line (left) and diagonal (right) arrangement of holes. [1] These different hole arrangements resulted in different localizations of (stress-driven) grain growth in the material.

Capability Gaps

Experimental probes

Diffraction methods are increasingly important to both 2- and 3-D characterization of heterogeneous microstructure. Innovations in x-ray and electron diffraction methods have largely driven this area through advanced user facilities such as the Advanced Photon Source for high energy x-rays and high resolution orientation scanning in the electron microscope. The Vulcan facility at the Spallation Neutron Source is likely to offer new capability for neutron diffraction in the coming decade. Combining different techniques both within each area and between the two main methods may offer substantial synergistic advantages. *Comparisons of computed fields with measured ones are likely to provide valuable feedback on the importance of the intrinsic elastic properties of grain boundaries, perhaps unaccounted for in the computer simulations. And other comparisons can be envisioned that would strengthen both experimental and computational results.*

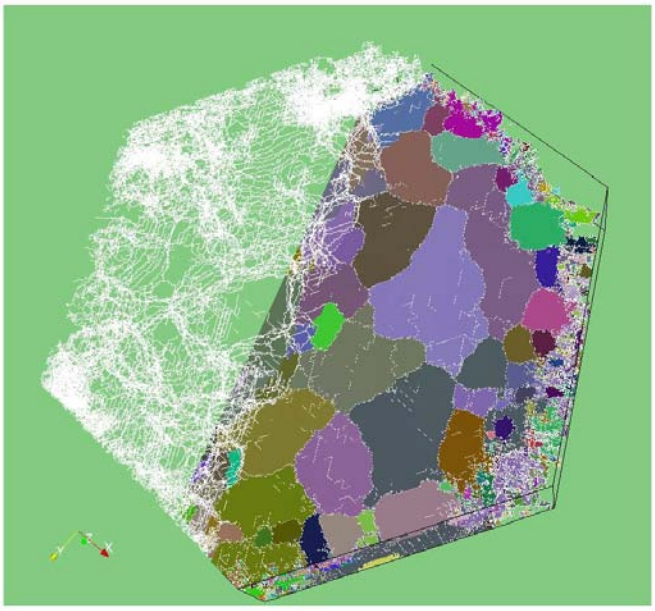

Figure 4. Combined 3D orientation color map and grain boundary outline (lines on successive layers) in a commercial purity aluminum measured by high energy x-ray diffraction at the Advanced Photon Source (APS). Image courtesy of R. Suter, CMU.

Quantifying and predicting material complexity using n-point statistics

A rigorous framework defining the spatial correlations of local states in the microstructure already exists in the form of *n*-point correlations or *n*-point statistics. These correlations provide a hierarchy of statistical measures of the microstructure that are essentially moments of the structure function. They preclude the need to select, either intuitively or in an ad-hoc manner, the microstructure metrics of importance in a given application. A great advantage of the use of these correlations is that they can be computed very efficiently using fast Fourier transform (FFT) algorithms. Given the strong contrast in properties among the various components of materials microstructure, there is also a need for more efficient methods of computing the response of materials to various types of loading. To complement the established finite element methods, there is increasing interest in image-based methods and these are likely to be increasingly useful as 3D characterization of materials produces ever larger datasets. To concretize this remark, we note that recent reports on 3D microstructure characterization have shown (individual) images of order 300^3 (as a number of points or voxels), whereas it is clear that we will soon be working with images of order 1000^3. As acquisition speeds increase and resolution increases, the image sizes may soon reach $10{,}000^3$. These image-based methods also exploit FFT algorithms for computational efficiency.

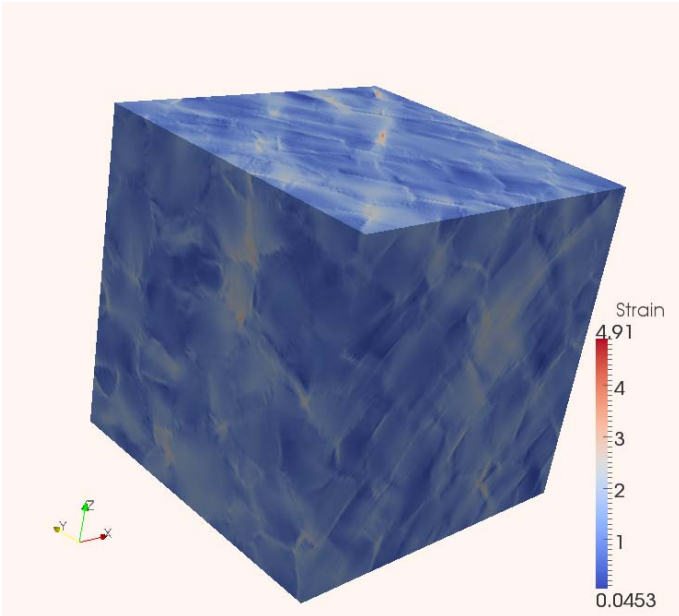

Figure 5 Image of the strain rate field from a full-field solution using the FFT viscoplastic method for unaxial tensile deformation of a randomly oriented polycrystal. [Rollett, unpublished work 2009]

Ultimately, our goal is to develop a science-based understanding of the properties and performance of heterogeneous materials, especially by considering variations in composition and structures to move from the "ideal" materials of the laboratory to the "real" materials in actual use.

Potential Impact

The potential impact of success in quantifying materials complexity includes the following:

• We will be able to quantify the reliability of engineering components based on validated theoretical models that fully capture the heterogeneous character of materials and handle realistic boundary conditions and gradients.

• We will have statistically-based definition of properties and performance characterized in terms of distributions that are based on materials history. Where appropriate to the material property of interest, these distributions will include quantified tails.

• Size & Time Scaling Laws will have been developed quantitatively. For example, we will be able to describe quantitatively how fast 'strength' decreases as sample size increases, or as microstructural length scales (grain size) increase. In terms of component performance, this should permit failure times in the laboratory to be correlated to failure times in service.

References

1. Rupert TJ, Gianola DS, Gan Y, Hemker KJ. Science 2009;326:1686.

Conclusion

Materials are central to every national need, and future technologies will place increasing demands on performance in a range of extremes: stress, strain, temperature, pressure, chemical reactivity, photon or radiation flux, and electric or magnetic fields. To lower fuel consumption in transportation, future vehicles will demand lighter-weight components with increased strength and damage tolerance. Next-generation nuclear fission reactors require materials capable of withstanding higher temperatures and higher radiation flux in extremely corrosive environments and for longer service lifetimes without failure. To counter security threats, defense agencies require the means to field protection for the populace against terrorist attack and to protect critical facilities and buildings against human or atmospheric extremes. Finally, nuclear weapons represent among the most extreme environments that can be achieved.

Empirical discovery techniques can achieve incremental advances. Steel-making for example dates back over thirty centuries, but the strengths of most present-day empirically-developed commercial steels are less than a factor of two higher than that used in swords during the medieval-era. However, 21st century challenges demand the ability to move beyond empiricism to predictive control.

A key grand challenge to achieve this vision is the ability to predictively manipulate microstructures to achieve desired macroscopic performance. Central to this challenge is the potency of defects, either to be exploited intentionally for enhanced performance or to suffer their deleterious effects. The role of defects is a microcosm of the broader impact of rare events and fluctuations that are a key stumbling block in achieving prediction and control: the extremes of heterogeneity in a material dominate performance at the expense of the homogenous bulk. Considering only the time- and space-averaged properties of an “ideal” material is inadequate; the complexity of “real” materials must be embraced.

The workshop on which this report is based identified fifteen priority research directions as key to realizing this vision:

> Predictive understanding of atomistic and collective fundamental mechanisms of radiation effects in materials
>
> Controlling thermo-mechanical properties and dimensional stability during irradiation
>
> Defining the frontiers of microstructure science under irradiation
>
> Co-design of experiments and models of time & space dependent radiation damage
>
> Materials design for resistance to corrosion and surface damage in extreme environments
>
> Creating and exploiting the chemistry of a new periodic table through extreme Pressure-Temperature (P-T)

Predicting, characterizing & controlling the performance of matter between solids and plasmas

Determining the transport of energy, momentum and mass under extreme density and temperature

Controlling photon-matter interactions: making every photon count

Controlling functionality from electronic complexity

Controlling nucleation phenomena

Accelerating materials discovery

Realizing materials design and performance: lifetime prediction

Bridging Length & Time Scales

Exploiting materials complexity

The vision of prediction and control articulated in detail in these priority research directions will only be achieved through the development of in-situ, real-time, multi-probe "tools" (including advanced theories and information science and technology methods, high performance computing, advanced measurement capabilities, controlled environments) to enable dynamic, in-situ measurements of real materials in real environments with the spatial and temporal resolution of microstructures, interfaces, and defects.

Workshop participants concluded that the grand challenge of prediction and control of materials performance in extremes was within reach. Success requires the pursuit of the priority research directions defined in this report and the development of needed capabilities required to achieve success.

Appendix: Workshop Agenda

Decadal Challenges for Predicting and Controlling Materials Performance in Extremes

FINAL

December 6-10, 2009
Bishop's Lodge, Santa Fe NM

Sunday, December 6, 2009

5:30-7:00 PM	Registration and Reception @ Tesuque Pavillion Portal)	
(5:30 PM	Panel Chairs Working Dinner @ Las Fuentas Alcove Room)	

Evening Plenary Session – MaRIE Introduction
Tesuque A and B

7:00-7:10PM	Welcome	John Sarrao
7:10-8:00PM	MaRIE overview	John Sarrao
8:00-9:00 PM	Reports from prior MaRIE workshops (4 x 10 minutes each)	
	" Research Frontiers and Capability Gaps for Controlling and Designing Functional Materials January 20-22, 2009"	Mark McCleskey
	"Structural Materials Under Extreme Conditions July 29-31, 2009"	Dave Teter
	"Opportunities for Examination of Activated Materials by Synchrotron X-Rays and Neutrons September 20-22, 2009"	Mark Bourke
	"21st Century Needs and Challenges of Compression Science September 22-24, 2009"	Dave Funk

Monday December 7, 2009
Tesuque A and B

7:45 AM	Continental Breakfast **@Tesuque Pavillion Portal**	
8:15 AM	Welcome	Terry Wallace
8:20 AM	Workshop Charge and Overview	John Sarrao

Plenary Session – Mission Needs for Extreme Materials
Tesuque A and B

8:50 AM	Materials challenges for renewable energy	George Crabtree, ANL
9:30 AM	Materials challenges for fission energy	Stuart Maloy, LANL

10:10 AM Break **@Tesuque Pavillion Portal**

10:30 AM Materials challenges for fusion energy Steve Zinkle, ORNL

11:10 AM Materials challenges for nuclear weapons Robert Hanrahan, NNSA

11:50 AM Overview of Panel Structure/Vision Panel Leads (in pairs)

Radiation Matter interactions for Fission and Fusion	Steve Zinkle, Todd Allen
Radiation Matter Interactions for Energy Conversion	George Crabtree, Paul Follansbee
Matter Interactions in Extremes	Roger Falcone, Malcolm McMahon
Cross-Cutting Themes	Tony Rollett, Richard LeSar

12:15 Lunch **@ Las Fuentas Main Room**

Breakout Session #1 (8 parallel rooms)- Initial Discussions

1:45 PM Initial Panel Breakout Discussions
Presentation of each participant's materials (5 min per participant)

Extreme Environment Tolerant Materials by Design	Thunderbird 1
Watching Damage Happen	Thunderbird 2&3
Materials Discovery and Processing for Advanced Functionality	El Charro
Making Every Photon Count	Tesuque Pavillion C
Process Aware Material Certification in Extremes	Las Fuentas Fiesta
When Solids Stop Being Solids	Las Fuentas Alcove
Enabling the Transition from Observation to Control	Skylight North Lodge
Bridging Multiple Scales in Space and Time	Room 173

3:30 PM Break **@Tesuque Pavillion Portal**

4:00PM Continue breakout discussions and generate first round of synthesis

5:30PM End of Day One Discussions
(5:30 pm Panel Chairs meeting – status/issues **@ Thunderbird 1**)

Tuesday, December 8, 2009

8:00 AM Continental Breakfast **@Tesuque Pavillion Portal**

Breakout Session #2 (8 parallel rooms)- Distillation of Panel Input

8:30 AM Continue Breakout Discussions in 8 panel rooms
Same rooms as Monday afternoon breakout session #1

10:00 AM Break **@Tesuque Pavillion Portal**

10:15 AM Continue Breakout Discussions

11:30AM Lunch **@ Las Fuentas Main Room**

Plenary Session – Initial Panel Reports
Tesuque A and B

12:30 – 2:00PM Initial panel output highlighting draft priority research directions and capability gaps (10 minutes each)

	Panel Leads
Extreme Environment Tolerant Materials by Design	Todd Allen
Watching Damage Happen	Steve Zinkle
Materials Discovery and Processing for Advanced Functionality	Paul Follansbee
Making Every Photon Count	George Crabtree
Process Aware Material Certification in Extremes	Malcolm McMahon
When Solids Stop Being Solids	Roger Falcone
Enabling the Transition from Observation to Control	Tony Rollett
Bridging Multiple Scales in Space and Time	Richard LeSar

2:00 PM Break **@Tesuque Pavillion Portal**

Breakout Session #3 (4 parallel rooms)- Integration of Panel Input

2:30-5:00 PM Combine panels into 4 breakouts
(collapsing two panels in each major topical area)

Radiation Matter interactions for Fission and Fusion (Panels 1&2)	Thunderbird &3
Radiation Matter Interactions for Energy Conversion (Panels 3&4)	Tesuque Pavillion C
Matter Interactions in Extremes (Panels 5&6)	Fiesta & Alcove
Cross-Cutting Themes (Panels 7&8)	Thunderbird 1

(5:30 PM Panel Chairs meeting – status/issues **@ Thunderbird 1**)

6:30 PM Informal Discussion / Reception **@ Thunderbird and El Charro**

7:30 PM Banquet Dinner **@ Thunderbird and El Charro**

"Prospects for a Comprehensive Test Ban Treaty and National Security Implications, ", Terry Wallace , Principal Associate Director for Science, Technology and Engineering, Los Alamos National Laboratory

Wednesday December 9, 2009

8:00 AM Continental Breakfast **@Tesuque Pavillion Portal**

Breakout Session #4 (4 parallel rooms)- Final Report Preparation

8:30AM Combined 4-panel breakouts prepare outbrief presentations/dry runs
Same rooms as Tuesday afternoon breakout session #3

12:00 PM Lunch **@ Las Fuentas Main Room**

Plenary Session – Final Panel Reports & Crosscutting Considerations
Tesuque A and B

1:00 -3:00 PM 30 min presentations by each of 4 combined panels

Radiation Matter interactions for Fission and Fusion	Steve Zinkle, Todd Allen
Radiation Matter Interactions for Energy Conversion	George Crabtree, Paul Follansbee
Matter Interactions in Extremes	Roger Falcone, Malcolm McMahon
Cross-Cutting Themes	Tony Rollett, Richard LeSar

3:00 PM Break **@Tesuque Pavillion Portal**

3:30PM Wrap Up: Crosscutting Themes/Emergent Issues John Sarrao

5:00 PM **Workshop adjourns**

Thursday, December 10, 2009
Las Fuentas Fiesta Room

Executive Session: Report Writing (Core Writing Team Only)

8:00AM Continental Breakfast
8:30 AM Panel Chairs and Core writing team draft reports (5-7 pages from each)
12:00 PM Core Writing Team Adjourns

Decadal Challenges for Predicting and Controlling Materials Performance in Extremes
Attendee List
Bishops Lodge, Santa Fe
December 6-10, 2009

Brent Adams
Brigham Young University
(801) 422-7124
b_l_adams@byu.edu

Todd Allen
University of Wisconsin
(608) 265-4083
allen@engr.wisc.edu

Malcolm Andrews
Los Alamos National Laboratory
(505) 606-1430
mandrews@lanl.gov

Charlie Baker
Sandia National Laboratory

baker505@comcast.net

Sasha Balatsky
Los Alamos National Laboratory
(505) 665-0077
avb@lanl.gov

Cris Barnes
Los Alamos National Laboratory
(505) 665-5687
cbarnes@lanl.gov

James Belak
LLNL
(925) 422-6061
belak1@llnl.gov

John Benage
Los Alamos National Laboratory
(505) 667-7483
benage@lanl.gov

Irene Beyerlein
Los Alamos National Laboratory
(505) 665-2231
irene@lanl.gov

Alan Bishop
Los Alamos National Laboratory
(505) 667-6645
arb@lanl.gov

Jonathan Boettger
Los Alamos National Laboratory
(505) 667-7483
jn@lanl.gov

Mark Bourke
Los Alamos National Laboratory
(505) 665-4735
bourke@lanl.gov

Neil Bourne
Atomic Weapons Establishment (AWE)
+44 1793 790296
neil.bourne@mac.com

Curt Bronkhorst
Los Alamos National Laboratory
(505) 665-0122
cabronk@lanl.gov

Don Brown
Los Alamos National Laboratory
(505) 667-7904
dbrown@lanl.gov

Eric Brown
Los Alamos National Laboratory
(505) 664-0090
en_brown@lanl.gov

Kimberly Budil
DOE, Ofc of the Under Sec for Science
(202) 586-1448
Kimberly.Budil@science.doe.gov

Vasily Bulatov
LLNL
(925) 423-0124
bulatov@llnl.gov

Mike Burke
Westinghouse Electric Company
(412) 256-1788
burkema@westinghouse.com

Darryl Butt
Boise State University
(208) 426-1054
DarrylButt@boisestate.edu

Alfredo Caro
LLNL
(925) 422-1711
caro2@llnl.gov

Robert Cauble
LLNL
(925) 422-4724
cauble@llnl.gov

Wendy Cieslak
Los Alamos National Laboratory
(505) 664-0916
wcieslak@lanl.gov

Gilbert W. Collins
LLNL
(925) 422-2571
collins7@llnl.gov

George Crabtree
Argonne National Laboratory
(630) 252-5509
Crabtree@anl.gov

Micheline Devaurs
Los Alamos National Laboratory
(505) 667-1519
devaurs_micheline@lanl.gov

Michael Di Rosa
Los Alamos National Laboratory
(505) 667-0095
mdd@lanl.gov

Barney Doyle
Sandia National Laboratory
(505) 844-7568
bldoyle@sandia.gov

Roger Falcone
LBNL
(510) 486-6692
rwf@berkeley.edu

Juan Fernandez
Los Alamos National Laboratory
(505) 667-6575
juanc@lanl.gov

Alp Findikoglu
Los Alamos National Laboratory
(505) 663-5560
findik@lanl.gov

Zachary Fisk
University of California - Irvine
(505) 670-6707
hutzpa@gmail.com

Michael Fluss
LLNL
(925) 922-8808
fluss1@llnl.gov

Paul Follansbee
Saint Vincent College
(724) 805-2448
paul.follansbee@email.stvincent.edu

David Funk
Los Alamos National Laboratory
(505) 667-9659
djf@lanl.gov

Tim Germann
Los Alamos National Laboratory
(505) 665-9772
tcg@lanl.gov

Jim Glownia
DOE Office of Science
(301) 903-2411
James.Glownia@science.doe.gov

Robert Goldston
Princeton Plasma Physics Laboratory
(609) 243-3550
goldston@pppl.gov

Alexander Goncharov
Carnegie Institution of Washington
(202) 478-8947
agoncharov@gl.ciw.edu

Rusty Gray
Los Alamos National Laboratory
(505) 667-5452
rusty@lanl.gov

John Hack
Bechtel Marine Propulsion Corp
(412) 476-6930
jehack@aol.com

Robert Hanrahan
NNSA
(202) 586-4606
Robert.Hanrahan@nnsa.doe.gov

Khalid Hattar
Sandia National Laboratory
(505) 845-9859
khattar@sandia.gov

Donald Hickmott
Los Alamos National Laboratory
(505) 667-8753
dhickmott@lanl.gov

Tom Holden
Northern Stress Technologies
(613) 584-2819
holdent@magma.ca

Rick Holt
Queens University
(613) 533-6831
holt@me.queensu.ca

Daniel Hooks
Los Alamos National Laboratory
(505) 667-6407
dhooks@lanl.gov

Scott Hsu
Los Alamos National Laboratory
(505) 667-3386
scotthsu@lanl.gov

Alan Hurd
Los Alamos National Laboratory
(505) 665-0630
ajhurd@lanl.gov

Quanxi Jia
Los Alamos National Laboratory
(505) 667-2716
qxjia@lanl.gov

Surya Kalidindi
Drexel University
(267) 235-4208
skalidin@coe.drexel.edu

Arthur Kerman
Massachusetts Institute of Technology
(617) 253-7072
kerman@Ins.mit.edu

Wayne King
LLNL
(925) 435-6547
weking@llnl.gov

Marquis Kirk
Argonne National Laboratory
(630) 252-4998
kirk@anl.gov

Edward Kober
Los Alamos National Laboratory
(505) 663-5623
emk@lanl.gov

Alex Lacerda
Los Alamos National Laboratory
(505) 665-6504
lacerda@lanl.gov

Hae Ja Lee
SLAC/LCLS
(650) 926-2049
haelee@slac.stanford.edu

Richard LeSar
Iowa State University
(515) 294-1841
lesar@iastate.edu

Meimei Li
Argonne National Laboratory
(630) 252-5111
mli@anl.gov

Thomas Lograsso
Ames Laboratory
(515) 294-8425
lograsso@ameslab.gov

Turab Lookman
Los Alamos National Laboratory
(505) 665-0419
txl@lanl.gov

Stuart Maloy
Los Alamos National Laboratory
(505) 667-9784
maloy@lanl.gov

Joe Mang
Los Alamos National Laboratory
(505) 665-6856
jtmang@lanl.gov

T. Mark McCleskey
Los Alamos National Laboratory
(505) 667-5636
tmark@lanl.gov

Malcolm McMahon
The University of Edinburgh
+44 131 650 5956
mim@ph.ed.ac.uk

Amit Misra
Los Alamos National Laboratory
(505) 667-9860
amisra@lanl.gov

Michael Nastasi
Los Alamos National Laboratory
(505) 667-7007
nasty@lanl.gov

Greg Olson
Northwestern University
(847) 491-2847
g-olson@northwestern.edu

Richard (Alan) Patterson
Los Alamos National Laboratory
(505-665-1535
rapatterson@lanl.gov

Antonio Redondo
Los Alamos National Laboratory
(505) 667-4401
redondo@lanl.gov

Donald Rej
Los Alamos National Laboratory
(505) 665-1883
drej@lanl.gov

Matteo Rini
ITU-European Commission
+49(0)7247-951-823
Matteo.RINI@ec.europa.eu

Ian Robertson
University of Illinois
(217) 333-1440
ianr@illinois.edu

A.D. (Tony) Rollett
Carnegie Mellon University
(412) 268-3177
rollett@andrew.cmu.edu

John Sarrao
Los Alamos National Laboratory
(505) 665-0481
sarrao@lanl.gov

Kurt Schoenberg
Los Alamos National Laboratory
(505) 667-5051
kurts@lanl.gov

Susan J. Seestrom
Los Alamos National Laboratory
(505) 665-4454
seestrom@lanl.gov

Guoyin Shen
HPCAT-Carnegie Institution of
Washington at Sector 16
(630) 252-0429
gshen@ciw.edu

Jack Shlachter
Los Alamos National Laboratory
(505) 665-1888
shlachter@lanl.gov

David Singh
Oak Ridge National Laboratory
(865) 241-1944
singhdj@ornl.gov

Darryl Smith
Los Alamos National Laboratory
(505) 667-2056
dsmith@lanl.gov

Marius Stan
Los Alamos National Laboratory
(505) 667-8726
mastan@lanl.gov

Antoinette Taylor (Toni)
Los Alamos National Laboratory
(505) 665-0030
ttaylor@lanl.gov

David F. Teter
Los Alamos National Laboratory
(505) 665-0160
teter@lanl.gov

Carlos Tome
Los Alamos National Laboratory
(505) 665-0892
tome@lanl.gov

Christina Trautmann
GSI Helmholtz Centre

C.Trautmann@gsi.de

Gary Was
University of Michigan
(734) 763-4675
gsw@umich.edu

Dieter Wolf
Idaho National Laboratory
(208) 526-8394
dieter.wolf@inl.gov

Sidney Yip
Massachusetts Institute of Technology
(617) 253-3809
syip@mit.edu

Choong-Shik Yoo
Washington State University
(509) 335-5345
csyoo@wsu.edu

Yanwen Zhang
Pacific Northwest National Laboratory
(509) 371-6516
yanwen.zhang@pnl.gov

Steven Zinkle
Oak Ridge National Laboratory
(865) 574-4065
zinklesj@ornl.gov

Research Frontiers and Capability Gaps for Controlling and Designing Functional Materials

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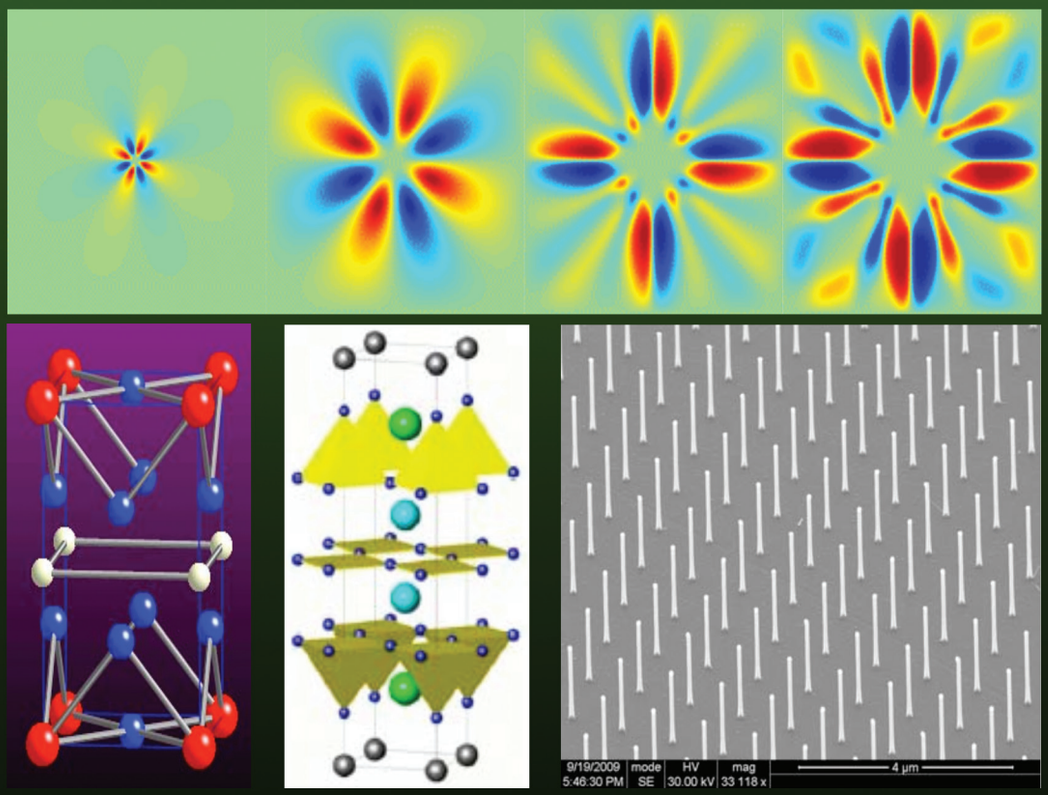

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Research Frontiers and Capability Gaps for Controlling and Designing Functional Materials

Executive Summary:

Scientific Challenge - Control Science.

Most advances in materials have focused on an observation approach that involves detailed characterization of a new material followed by integration of the material into applications based on the material properties. These properties are further tuned by changes in the processing conditions via a trial and error effort. The notion of predicting the properties of a material and systematically controlling the composition, defects and interfaces is typically viewed as something far off in the future. One exception that stands out is in the computer industry where the systematic characterization, and controlled manipulation of both purity and interfaces at ever increasingly finer resolution has lead to material advances and performance capabilities that not long ago would have been viewed by most people as impossible.

Areas with future scientific challenges requiring the same control approach to realize solutions include:

- Sustainable energy future
  - efficient electrical grid -superconductivity
  - energy conversion - photovolatics
  - energy storage - batteries, capacitors and electrosynthesis
  - solid state lighting
- Information storage and processing
- Advanced optical materials

At the heart of all of the areas is the grand challenge of predictive design of materials to control emergent behavior. To design new materials with predicted properties we must transition away from the historical observational approach to a controlled approach where theory, synthesis and characterization are effectively integrated. The desired property may arise from a variety of interactions involving spin, phonons or electrons. The ability to predict properties in such advanced functional materials requires a detailed theoretical understanding of the correlated interactions between electrons, phonons, spin and charge that lead to the remarkable properties such as colossal magnetoresistance, superconductivity, multiferroicity, and electronic phase separation, and ferroelectricity. Advances in theory will rely on the combination of a synthetic ability to systematically control composition, defects and interfaces and characterization tools to watch how defects and interfaces evolve. Integrating these activities will provide the framework for control science to test and verify new theoretical codes designed to tackle the challenges of highly correlated systems. The focus on interfaces and defects is especially crucial in the area of emergent phenomenon where interfaces between materials with dissimilar properties can lead to the emergence of entirely new properties. The transition from observation to control science will allow for the accelerated design and discovery of new materials with predicted properties.

Currently we rely on an Edisonian approach to materials discovery by serendipity or intuition. Great advances have been made by this approach, but most materials still have a performance or lifetime that falls far short of theoretical limits. There are so many potential combinations of materials that a continued Edisonian approach is unlikely to lead to dramatic improvements rapidly. Synthetic efforts need to be guided by predictive theory. Improved theoretical approaches are needed with an emphasis on first principle theories designed to predict material properties without requiring material measurements as parameters. Synthesis must be

flexible enough to make a wide range of possible theoretical materials and have the capability to control composition, defects and interfaces systematically. Characterization techniques must address the challenges of 3-D non-destructive imaging and dynamic characterization of solid state materials with sub grain size resolution on the time scale of electron-electron and electron-phonon interactions.

Prediction of emergent properties will not happen overnight. This is a multi decadal challenge that will be significantly accelerated by effective integration between theory, synthesis and characterization. Initial advances in theory will rely on databases of materials properties in which parameters such as composition and architecture are systematically varied. Such databases will provide the statistical basis set for new theoretical directions in material property predictions and allow new theoretical codes to be effectively benchmarked for validity. Rapid synthesis that can explore a large suite of possible materials combined with characterization techniques that can effectively probe both structure and material properties will play an essential role to develop such databases. To be effective the material databases must be designed such that the compositional changes and the materials properties to be measured match well with the input and outputs of the theoretical codes. The ability to predict material properties fundamentally means that we must connect theoretical codes across scales as one starts with the atomic composition and adds defects and interfaces to ultimately predict the bulk properties of interest such as superconductivity, band gaps, magnetism, and electron transport. Likewise, synthetic techniques must bridge scales from small well defined single crystals to bulk materials that incorporate defects and interfaces and characterization tools must be able to determine both long range structure and local atomic in homogeneities.

The future promises to grow increasing complex as nanoarchitectures, become integrated into composite structures. These new composite materials offer the promise of multi functional capabilities not possible with in single component material, but bring with them a tremendous challenge to manipulate and control interfaces and defects. Simultaneously accelerating materials discovery and advancing 'interface engineering' hold great promise for controlling and designing next-generation functional materials.

Decadal Challenges in Theory, Synthesis and Characterization

The primary goal of the workshop was to identify decadal type challenges in each of the sessions. These challenges clustered into thematic areas of theory/ modeling/ visualization, synthesis, and characterization. Decadal challenges identified for accelerating materials discovery include:

Theory/Modeling/Visualization

- Theories that treat strong correlation dynamically
- Modeling and theory that includes full electronic, ionic relaxation for large systems with interfaces
- Theories that can describe defect interactions at an interface and predict property changes – issue of multiple scales and boundaries
- Visualization -- a large data visualization capability for 3-D tomography data
- Predicting materials properties via learning from database of models/experiments

Synthesis

- Rapid synthetic exploration of new materials coupled to rapid characterization
- Synthetic control and characterization of defects, phases and atomic composition to 1ppm

- Synthetic control and characterization of interfaces to 10's of nm in plane and 1 nm perpendicular
- High quality crystals and crystalline composites to benchmark theories
- Control of strain and phase to generate metastable states
- Design of bulk materials with nano – micron inhomogeneities

Characterization

- In situ characterization during nucleation and growth of materials
- Characterization of buried interfaces to study electron- electron, electron-phonon and phonon-phonon interactions
- Non destructive 3-D characterization
- Characterization in extreme environments including magnetic fields to 20 T, temperatures of 10 mK to 300K, and pressures to 20 GPa to tune spin charge interactions
- Characterization of the evolution of defects and interfaces during synthesis, in response to extreme environments and during function of integrated devices

These challenges must be attacked in a concerted manner. A modern materials discovery center must integrate capabilities in each of these areas in order to have the ability to control composition, defects and interfaces in a systematic manner over a variety of length scales. Control of composition, defects and interfaces requires a theory component able to integrate many length scales, a highly flexible synthetic capability that can both rapidly explore a set of new materials and make selected materials with extremely high purity and near monolayer interfacial control, characterization facilities with both the resolution to observe defects and interfaces and the temporal capability to watch them evolve in time in response to different environments, and a close coupling of characterization and synthesis during the critical nucleation and growth process.

Key crosscutting topics

Across all three areas of theory, synthesis and characterization there are crosscutting topics that emerge as key areas that must be addressed to solve the decadal challenges:

- **Interfaces and defects**
- **Control over multiple length scales from nano to micron**
- **In situ techniques to characterize how properties emerge and evolve**

<u>Interfaces and defects</u>

The fascinating properties that emerge in solid state materials begin based on elemental composition that can lead to magnetism or superconductivity but these properties are dramatically altered by defects/interfaces that can lead to quenching of excited states or vortex pinning in superconductivity or entirely new physics as competing order parameters come together at interfaces with different materials in intimate contact such as colossal magnetoresistance. The functionality often comes from controlling or tailoring the large response of a material to a small perturbation as a result of competition between nearly degenerate ground states involving coupled charge, spin, and lattice degrees of freedom. Critical to understanding the emergent phenomena is the ability to make single crystal materials with controlled interfaces and as part of composite materials. The US currently lacks a crystal growth resource either in industry or academics and most US researchers buy crystals from other

countries such as Japan. A national crystal growth facility is needed for the US to maintain its leadership in materials discovery and subsequent technical advances. High quality single crystals are critical to the understanding of emergent properties that enable many fields of science such superconductivity, ferroics, colossal magneto resistance, and potential future materials base on orbitronics for faster processing. Traditional material discovery centers of the past such as Bell Labs and IBM have completely disappeared or down sized tremendously. This change has the potential to put the US at a disadvantage technologically in the future. The US has always been at the forefront of materials discovery in the past with strong leadership in previous society changing technological advances such as the discovery and technology developments in polymers, semiconductors, and superconductors. Today the landscape is changing as many other developed countries are beginning to devote national resources to extensive research in materials. Workshop participants unanimously concluded that there was a consensus need across all of the areas for national materials facilities in the United States.

Control over multiple length scales from nano to micron

Nanotechnology has progressed tremendously over the last decade, in part, through the efforts of the BES nanocenters. These nanocenters combined with university and international efforts have lead to a greater understanding of nanoscale phenomena and an enhanced ability to synthesize nanowires, and nanoparticles that includes control over dimensions as well as core shell structures in which the composition of the layers is varied to tailor the properties or add multiple functionality. These nanoscale phenomena and materials will play an important role in devices of the future. The next grand challenge is to understand how nanoscale features in a material grow and evolve over micron scales to ultimately affect bulk performance in a material. For example, the nanoscale features that control vortex pinning are known to have significant effects on the meter long superconducting tape. Advanced solar cells are currently being designed with nanoscale architectures designed to efficiently move electrons and holes in opposite directions over micron length scales. Such future devices will involve the manipulation and placement of nanoscale features in an overall architecture with micron and greater length scales.

Hybrid nanostructured materials will provide the key to the future design of multifunctional materials with emergent properties “by design”. For example, areas of particular opportunity include energy harvesting and storage, including photovoltaic and photochemical energy conversion, thermoelectric conversion of heat to electricity and visa versa, piezoelectric conversion between strain and electric fields, rapid cycling of battery electrodes to high capacities, electrostatic capacitive charge storage to high energy densities, and electrochemical energy storage and conversion in fuel cells. The control of energy transfer is a key aspect to each of these areas. The ability to exploit the high local fields, large surface areas, enhanced chemical reactivity, short length scales, quantum confinement, local strains, enhanced strength, and the stability of nanoscale arrays in nanostructured materials is opening up new opportunities for advances. An improvement of a factor of 2 to 3 in any of these areas would have dramatic consequences. While incremental increases will almost certainly be achieved over the next few years, an ability to achieve such larger improvements and to do this “by design” in complete devices (rather than empirically) with new understanding of how to control energy transfer by nanoscale structuring is a 5 to 10 year goal requiring a control science approach. The key challenges are the controlled synthesis and fabrication of heterogeneous combinations of

materials at the nanoscale and the understanding, through characterization and modeling, of the design of materials performance.

In situ techniques to characterize how properties emerge and evolve

Properties in a material both emerge during the nucleation and growth of synthesis and evolve overtime in a real device as it is often subjected to extremes of cycling, temperature, pressure, electromagnetic fields, or chemical environment. In control science, effective synthesis relies on *in situ* characterization techniques to understand what processing parameters control a material microstructure. This can be clearly seen in the case of thin film deposition where RHEED coupled to high vacuum deposition techniques has allowed for the precise growth of thin films with real time feedback. The result in the case of molecular beam epitaxy (MBE) is a digital growth process that can precisely deposit multiple layers of different compositions. This type of synthetic control has helped to advance our understanding of properties such as colossal magnetoresistance (CMR). Fundamental characterization of the nucleation and growth of nanoclusters will also play an important role in furthering the understanding of how and when properties emerge. On the decadal scale, a grand challenge for emergent phenomena will be the integration of multiple synthetic techniques with the same type of *in situ* characterization to control and build up hybrid nano materials. These will include both layered materials and new materials with nanoscale features embedded into larger crystalline matrixes. Such materials will require non-destructive 3-D *in situ* imaging of microstructure and composition in order to obtain the necessary synthetic control.

Solving the future problems in energy and information technology will be greatly accelerated by designing functional materials based on advanced theoretical models of how interfaces and defects affect material performance across multiple length scales. For these new solutions to be successful the materials must also perform with long lifetimes compete effectively in the market place and to avoid future waste issues. In practice such functional materials are often exposed to some type of extreme condition during their use that eventually results in failure. To extend lifetimes and minimize failure or design self healing materials we will need to understand how these failure mechanisms begin at the atomic scale and eventual manifest themselves at the micron and bulk scale. Such understanding will be greatly accelerated by watching the defects and interfaces as they evolve in the extreme conditions and simultaneously measuring the material performance. In order to achieve this we must be able to non-destructively characterize microstructure and composition while the material is exposed to the extreme conditions. Multi-probe experiments in extreme environments, and the non-destructive 3-D characterization to enable multiple measurements on a single sample represent significant decadal challenges.

Workshop Goals

The initial charge for the workshop was to discuss the grand challenges in correlated materials and emergent properties. The sessions were organized to include issues in the areas of synthesis, characterization and theory. The intent was to evaluate the scientific grand challenges of the future and define the state-of-the art and future expectations of the capabilities, developments and innovation in the next 5-10 years with an emphasis how a new facility could be designed to facilitate and accelerate materials discovery. The areas of focus included (a) emergent functional behavior at nanoscale in condensed matter systems and (b) the collective, coherent functional response in single crystal and composite materials.

The workshop was organized into 8 sessions including strongly correlated electron materials, application of electronic materials and oxide interfaces, time resolved aspects of functionality, size dependence:quantum and nanoscale effects, ferroics, clusters and computational tools. Participants included both LANL and external speakers with 18 speakers outside LANL from a variety of academic facilities and national laboratories including Harvard, MIT, University of Minnesota, UCSB, UCD, ANL, LBL, MIT, Kyoto University, Rutgers, UCSD, University of Maryland, University of Michigan, Penn State, and Iowa State.

Detailed breakout results:

Applications of Electronic Materials and Oxide Interfaces

Chairs: Michael Fitzsimmons (LANL), Darryl Smith (LANL)
Speakers: Christopher Hammel (Ohio State), Paul Ruden (U. Minn.), Christopher Palmstrøm (UCSB), D. Basov (UCSD), A. Bhattacharya (ANL), E.D. Dahlberg (UMN), W. Pickett (UCD), I.K. Schuller (UCSD)

Composite materials have long been important constituents of commercial products; however, with improvements in the synthesis and characterization of materials enabling nanometer-control of length-scales, the importance of interfaces becomes preeminent. Materials with nanometer structures, or so called nanoscale materials, necessarily mean that interfaces play a decisive role in determining the response of composites to their environment. Many materials systems are composites of materials with dissimilar properties. The resultant behavior of the composite can be simple leverage sums of its constituents, e.g., hardness and toughness of ceramic-metal composites, or produce new behavior due to competing order parameters.[1] In comparison to interfaces in metals and semiconductors, the electronic (spin and orbital) and magnetic character of the cation and anions that comprise oxide interfaces lead to complex behavior. For example, in ferroelectrics, interfaces are sinks for defects that pin the motion of ferroelectric domains,[2] affect the anisotropy of ferroelectricity through interfacial strain, or, as sites for discontinuity in electric polarization, may lead to improper ferroelectricity through proximity effects. Oxide interfaces also exhibit some of the largest figures-of-merit for thermoelectric response,[3] which is believed to be a consequence of high charge conductivity and low thermal conductivity. The structural perfection of interfaces is believed to play a crucial role in the performance of acoustic cavities[4] and phonon lasers,[5] which provide new opportunities to couple photons, phonons and electrons. Some of the most promising applications of materials that couple electric fields and magnetism involve composites of materials that utilize exchange bias across an interface to amplify magnetoferroic response.[6] In all these examples, the novel behavior is often *attributed* to interfaces, but the actual role of interfaces is often not actually known, e.g., the phonon dispersion of an interface has never been measured.

Perhaps the most dramatic example of how the future might be influenced by oxide interfaces lies in the potential to use the orbital spin degree of freedom to convey (or manage) information. The unique opportunity of oxide electronics vis à vis semiconductor electronics is the degeneracy of orbital occupation that could be controlled using electric field, strain etc. with unprecedented speed. This arises from the fact that the orbiton frequency—between 10 and 100 THz—is much higher than the electron spin precession frequency of 1-100 GHz.[7] Presently, off-the-shelf computers have clock speeds around 3 GHz. If clock speeds increase at a rate that double every 18 months (Moore's law), then in ten years' time, clock speeds will approach ~300 GHz. The higher speeds might be realized using the concepts of spintronics that are presently

[1] R.E. Newnham et al., Mat. Res. Bull. **13** 525 (1978).
[2] M. Dawber et al., J. Phys. : Condens. Matter **20** 264015 (2008).
[3] H. Ohta et al., Nature Mater. **6** 129 (2007).
[4] J. Chen and J.B. Khurgin, Appl. Phys. Lett. **81** 4742 (2002).
[5] P.A. Fokker et al., Phys. Rev. B **55** 2925 (1997).
[6] N. Spaldin and R. Ramesh, MRS Bull. **33** 1047 (2008).
[7] E. Dagoot and Y. Tokura, Mat. Res. Bull. **33** 1037 (2008).

being developed (and indeed are in place for certain products). Yet, what about the time beyond 10 years—the time frame of MaRIE? To achieve clock speeds in the THz regime, orbital engineering or orbitronics, appears attractive. Thus our view is that rather than focusing on the transitional technology of spintronics, MaRIE should focus on the dramatically new technology of orbitronics—a field that would require a radical change from semiconductor to oxide electronic technology (since the orbital occupancy of semiconductors is much less easily manipulated compared to oxides).

Making, Measuring, Modeling Materials

New materials can be discovered in one of two ways—either through serendipity or through use of predictive methods. Regrettably, in practice, interesting materials have been discovered primarily through serendipity. This argues for new approaches that rely on "serendipity-by-design". Serendipity-by-design endeavors to discover interesting materials by synthesizing large numbers of samples using parallel synthesis methods (as opposed to serial methods of the past), and applying parallel characterization methods (discussed later) to discover the interesting ones. An example of the approach is to grow many chemically different interfaces using phase spread alloys[8]—an alloy obtained from co-deposition of materials from two or more sources. The composition of the deposited material—covering the entire phase diagram—varies in a controlled fashion across the substrate. Combining parallel synthesis and characterization approaches, uninteresting compositions can be rapidly discarded to discover those that are interesting. Once discovered, traditional serial growth techniques can be employed to optimize sample structures.

One such traditional approach is molecular beam epitaxy (MBE). Typically MBE yields compositionally disordered films (much like those grown using bulk techniques) with a minimum of defect structures. In many cases, compositional disorder also means strain disorder, since cations in oxide films are not necessarily the same size. However, a new form of MBE, called digital growth MBE (DG-MBE),[9] offers a dramatic new opportunity to grow compositionally ordered films (and interfaces) with the same average composition of traditional MBE without the variance in strain disorder. For example, in the case of $La_{0.5}Sr_{.0.5}MnO_3$, a digitally grown structure consists of alternating layers of $LaMnO_3$ and $SrMnO_3$. Since the thickness of each layer is less than the critical thickness for strain relaxation, the strain is uniform; thus, its variance is zero throughout the film.

The ability to synthesize an ordered film with zero strain variance can have dramatic consequences on materials properties. In the case of an LSMO film, an A-type antiferromagnet, the Néel temperature of the chemically ordered film is 65 K greater than the chemically disordered film.[10] It is no small wonder that modeling would have difficulty predicting the Néel temperature of a disordered film. In fact, synthesis and characterization of ordered films may reduce the complexity of modeling (discussed later). The ability to reduce strain and compositional variation to zero will enable us to push the average composition of samples to the extreme limits of the phase diagram.

Grand challenges in making:

(1) Intelligent approaches (e.g., parallel growth methods, information-science-guided methods) towards materials discovery that seek to enhance chances of serendipitous discovery. Having discovered an interesting system…

[8] I.K. Schuller, private communication.
[9] H. Luo et al., J. of Electronic Mater. **22** 467 (1993).
[10] A. Bhattacharya, private communication.

(2) Growth of the highest quality samples (e.g., using DG-MBE) with a minimum of defects, e.g., less than one part in 10^6 (dictated by the size of a wave function in an oxide),

(3) zero or alternatively well controlled variation (much less than 0.1%) of strain (0.1% strain can change anisotropy, etc.),

(4) control of rumpling (to length scales less than a dimension of the wave function of an electron) and reconstruction of interfaces, and

(5) zero or alternatively well controlled variation (much less than 0.2%) of composition (dictated by the desire to be as close as possible to the transition between different phases) that is comparable to what is obtained by the semiconductor industry.

(6) (2)-(5) need to be applied to grow samples with macroscopic dimensions that are inhomogeneous on length scales of tens of nanometers. In other words, we are not simply interested in thin films and planar interfaces, but arrays of stripes, dots, etc. in two-dimensions that may also be stacked in three-dimensions. To achieve this goal, improvements in the polydispersity (much less than 10%) of bottoms-up (self-assembly) approaches and the throughput (goal of $1cm^2$ samples) of top-down (lithography) approaches are required.

Making, Measuring, Modeling Materials

Strategies to characterize materials fall into two classes. The first "parallel characterization" aims to quickly discard samples that do not exhibit a property of interest. For example, measurements of temperature dependent microwave absorption from large samples (even ones that are inhomogeneous on nanometer length scales) can identify those that are not superconducting.[8] These are discarded. Specialized techniques—the 2nd of the two classes—are then brought to bear on the remaining samples.

One goal of MaRIE should be to develop tools to rapidly identify samples as interesting or not according to the property du jour, e.g., superconductivity, ferroelectricity, thermoelectricity, etc. A second goal should be to refine specialized characterization techniques aimed at determining atomic structures with sub nanometer precision and the static and dynamic (DC to 100+THz) properties (electronic, magnetic, acoustic etc.) of individual interfaces. This implies that specialized techniques must have the ability to distinguish the structure and properties of the interface from the adjoining material. In other words, the probes must be spatially discerning (to 1-nm length scales, or its equivalent in reciprocal space). In the time domain, electronic transitions (fs) are of interest. Measurements of the dispersion (wave vector) in the response of the system to excitations are needed. Indeed, many bulk structures (and presumably interface structures) are energetically equivalent (or nearly so) at 0 K, and it is primarily the entropy of the structure at higher temperature (introduced through phonons) that determines the most stable structure. To date, there are no experimental measurements of phonon dispersion for interfaces. Such measurements are crucial to understanding electron-phonon and photon-phonon coupling found for multiferroic, ferroelectric, thermoelectric and acoustic phenomena.

Many of the requirements for characterization we seek (imaging, spatial and dynamic specificity) can be fulfilled using the coherent and pulsed characteristics of a free electron laser. An outstanding challenge is to tailor the x-ray wavelength from the FEL to provide the element specificity presently obtained using x-ray resonance techniques as practiced today at synchrotrons.

Additional emphasis on (or thought aobut) computing is warranted. Some of the characterization techniques envisioned for MaRIE (e.g., reflectometry, resonance probes that are

highly non-linear, etc.) require computation of recursive algorithms. Recursive algorithms are not amenable to parallel computation. The speed of the Roadrunner is due to its massively parallel architecture.

Grand challenges in measuring:

(1) Develop tools to rapidly distinguish samples exhibiting interesting properties from the many that do not.
(2) Develop techniques to measure vacancy concentration (1 ppm) and stoichometry with tens of nanometer lateral resolution and 1 nm resolution perpendicular to an interface.
(3) Develop techniques to measure magnetization from ordering of 10's of orbitals or spins.
(4) Develop *in situ* characterization of samples during growth that include quantitative measurement of vacancy concentration, stoichometry and atomic structure of an interface.
(5) Develop techniques to measure the dispersion of phonons at interfaces in μg samples.
(6) Develop techniques to measure orbital occupancy with 10 nm lateral and 1 nm perpendicular resolution.
(7) All of the above techniques need to be performed in high (20 T) magnetic fields, low (10's mK) temperature and applied stress (producing ~1% strain) along prescribed directions preferably at the same time! (For thin films and interfaces, application of stress is the interesting control parameter as opposed to pressure for bulk materials.)

Making, Measuring, Modeling Materials

The modeling community can point to several successes where modeling has provided reasonably compelling explanations for interfacial phenomena, e.g., conductivity at the LAO/STO interface, collapse of magnetism as a driver of the Mott transition in MnO, and origin of the metal-insulator transition in VO_2. Beginning with the framework of interatomic potentials, modeling can predict lattice relaxations in response to electrostatic (i.e., polar) discontinuities that yield band structures from which the conductivity (though not yet magnetism?) of interfaces can be predicted. A specific example in hand is the case of the predicted shift of surface states towards the Fermi level in LAO/STO bilayers that increases with LAO thickness in response to an increasingly strengthening Coulombic potential. Eventually, the LAO layer becomes conducting.

Modeling will be a significant benefactor of improved sample growth proposed as a MaRIE goal. The ability to grow compositionally ordered films with little or no strain variance should greatly increase the relevance of model calculations (model assumptions of perfection in imperfect samples—to make modeling tractable—can be realized with better samples). Modeling will also benefit from faster computers; however, it should be noted that for some instances, particularly in highly correlated systems, the calculations may not benefit from highly parallel computing. For example, the landscape of magnetic and insulating texture—a consequence of competing order parameters—is highly correlated.[11] The very existence of a magnetic/conducting region in one part of the sample stabilizes non-magnetic/insulating regions in other parts. Thus, in these instances it is not yet clear that parallel computing is necessarily advantageous.

[11] K.H. Ahn et al., Nature **428** 401 (2004).

Grand challenges in modeling:

(1) Full electronic, ionic relaxation (including rumpling, rotating, reconstructing) for large systems modeling isolated interfaces, and for thin slabs where interfaces are still coupled to the surface.

(2) To treat isolated defects near interfaces realistically [including relaxation as in (1)] will require at least many hundred atoms, with codes that should include the developments mentioned below.

(3) Strong correlation treated dynamically, since *ab initio* calculations do not properly incorporate strong electron-electron interaction.

(4) Full charge self-consistency including correlations.

(5) Include atomic dynamics (phonon dispersion) in (1)-(4).

(6) Obtain and include entropic effects, especially spin entropy. Properly done, would require dynamic quantum spins; less precisely, statistical averages of classical spins.

(7) Calculate electron transport, thermodynamics. Key issues to understand include defect energetics and kinetics, many-body physics, transport in and about interfaces in systems that are spatially non-uniform.

(8) Predict critical temperatures, e.g., for superconductivity, magnetism, etc.

(9) Computational materials design particularly pertaining to interfaces. Develop physically based guidelines as well as computational algorithms.

(10) Predict occupancy of orbitals at interfaces. [This is implicit in (1), (3), and (4) above.]

(11) Include and/or refine models, incorporating experimental information on atomic structures and dynamical effects at interfaces.

Strongly Correlated Electron Materials

Chair: Eric Bauer (LANL)
Speakers: Sasha Balatsky (LANL), Eric Hudson (MIT), Takasada Shibauchi (Kyoto Univ.), Joe Thompson (LANL), Rich Martin (LANL)

Functionality comes from controlling or tailoring the large response of a material to a small perturbation. In strongly correlated *d*- and *f*-electron materials, new states of matter and phenomena emerge from the competition of nearly degenerate ground states involving coupled charge, spin, and lattice degrees of freedom. These new and often unexpected states and phenomena are the (large) response to competing interactions of the system. Control of these responses in correlated matter, which are inherently quantum mechanically derived, defines an important decadal challenge for the scientific community and MaRIE. Unconventional superconductivity formed from an antiferromagnetic state in cuprate, heavy fermion, and organic materials is a prototypical example of a (phase) coherent quantum mechanical response to the underlying nearly degenerate interactions, while charge stripes in LSCO and the (possible d-density wave) pseudogap in both electron- and hole-doped cuprates are examples of coupled quantum states out of which superconductivity emerges. The control of even one (or a select few) of these collective and emergent quantum phenomena is a promising route to new functionality and could lead to the development of room temperature superconductivity or a multi-functional (e.g., multiferroic—ferroelectric—superconducting) material that displays a large coherent response near room temperature in small magnetic/electric fields.

As history has shown with Bednorz and Muller who set out to make a better ferroelectric material and ended up discovering high temperature superconductivity, unexpected and potentially much more interesting phenomena in strongly correlated electron materials can be uncovered in a research effort with a well-defined scientific agenda. Once the scientific agenda has been defined, three focus areas (Fig. 1) applied to correlated electrons are necessary for progress towards control of their inherent response to competing states and subsequent functionality: 1) novel routes of complex electronic materials growth, 2) understanding the fundamental interactions and associated energy scales at the microscopic level that comprise the complex and competing phases through basic characterization, atomic-level imaging techniques, and specialized spectroscopies, and 3) new microscopic theories and theoretical/modeling techniques that provide a thorough understanding of the fundamental interactions and a predictive capability of materials properties.

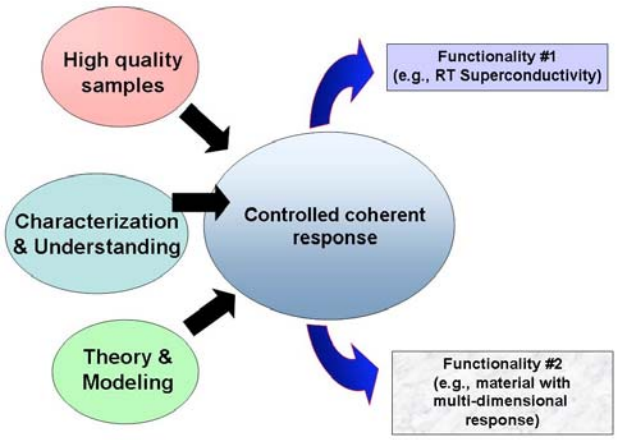

Figure 1 Schematic diagram of the approach to control of the quantum mechanical response of strongly correlated electron materials to competing interactions

A renewed emphasis on materials synthesis and crystal growth is essential for a solution to any aspect of the control of strongly correlated electron materials. Several BES/DOE (Ames 2003, CMMP 2010), NAS (2009), and popular (Physics Today 2007) reports lament the decline of crystal growth infrastructure and expertise, largely supported by industry (Bell, IBM, etc.) in the past, and all make strong recommendations to reestablish U.S. superiority in novel materials synthesis. The high-T_c cuprates illustrate the difficulty well. Nearly a decade passed from their initial discovery to a point where the samples were of sufficient quality (and quantity), primarily produced by the optical float-zone technique in Japan, that sophisticated measurements could obtain a deeper understanding (e.g., intrinsic inhomogeneity, Fermi surface), and that were generally consistent. Even today, almost a quarter-century later, most large-scale single crystals of cuprates still come from Japan. A U.S.-based crystal growth facility that included the following capabilities would address this national need and provide the means to achieve the chosen scientific mission in correlated electron materials: 1) synthesis of exceptionally high-quality single crystals to minimize extrinsic effects that obscure intrinsic behavior and to uncover emergent states only observed in ultra-clean samples, 2) production of large-scale single crystals suitable for neutron scattering and other spectroscopies to understand both the underlying competing interactions and the manifest coherent responses, 3) novel synthesis routes such as high-pressure synthesis to produce metastable phases, and 4) (intermetallic) molecular-beam-epitaxy (MBE) or other growth techniques for thin films for control of crystal growth at the atomic level, production of metastable phases, and multilayer arrangements to tune/control dimensionality and important energy scales.

The coupled of charge, spin, and lattice degrees of freedom in strongly correlated systems pose a significant challenge to understand the essential interactions responsible for their physical behavior. These interactions produce a delicate balance between competing states and give rise

to emergent phenomena (e.g., charge-ordered, magnetic, ferroelectric and superconducting states) with properties quite distinct from the original states. The necessary understanding of all of these complex states of matter will only come from the application of a suite of experimental techniques. We envision the following decadal-scale needs for this characterization and understanding: 1) measurements of the physical properties under the extremes (or a combination) of pressure (20 GPa), temperature (50 mK), and magnetic field (>20 T) to both access emergent states of matter and to tune relevant and competing interactions to elucidate their influence on the physical behavior; 2) the development of advanced spectroscopies, including spin-resolved atomic-scale imaging (e.g., STM, MRFM), spin-resolved, angle-resolved photoemission (ARPES) (<1 meV resolution) to probe charge and spin degrees of freedom; 3) inelastic neutron scattering and NMR capability development in a variety of extreme sample environments to provide the necessary probes to understand the intertwined fundamental interactions involving spin and charge. In some cases, competing interactions in correlated matter yield electronic, magnetic and structural inhomogeneities at the nano-to-micro scale that exhibit nontrivial spatial and temporal dynamics. The combination of atomic-scale imaging techniques and ultrafast spectroscopies, such as the proposed free-electron laser, would provide unique insight into the competing interactions between the correlated system's constituents (and associated inhomogeneites), such as electron-phonon, electron-electron, and spin-lattice interactions, which are necessary for a complete understanding of the emergent phenomena.

Strongly correlated electron materials also pose serious hurdles for theory and modeling. While Local-Density Approximation (LDA), Dynamical Mean Field Theory (DMFT), and hybrid Density Functional Theory (DFT) approaches show promise for accounting for strong correlations, the community still lacks a microscopic theory. Furthermore, many "effective" theories are not able to predict physical properties. Proposed theory/modeling advances to provide a theoretical underpinning of the mechanisms of strong correlations, a predictive capability of properties, and a guide for a directed search for new materials include: 1) band structure calculations on unknown materials, 2) a density functionals for hybrid DFT that allows calculation/prediction of relevant energy scales and physical properties with sufficient precision, 3) development of the Random Phase Approximation (RPA) for a DFT approach to correlated metals, 4) adequate modeling of competing interactions with spatially inhomogeneous states, and 5) a theory of time resolved probes and electronic, magnetic, and lattice states far from equilibrium.

Time Resolved Aspects of Functionality

Chair: Toni Taylor (LANL)
Speakers: Keith Nelson (MIT) Robert Schoenlein (LBL) Roberto Merlin (U. Mich.)

The study of non-equilibrium phenomena in condensed matter has become over the past decade a major field of research. Ultrafast techniques provide the means to investigate phenomena approaching the fundamental timescales of electronic and atomic motion, offering a unique snap-shot into the properties of cooperative condensed matter and material systems, complementing techniques such as time-integrated optical spectroscopy or inelastic neutron scattering. It is now possible to routinely generate and detect sub-100 femtosecond pulses across the electromagnetic spectrum enabling a broad portfolio of novel time-resolved spectroscopic investigations. For example, capabilities such as ultrafast x-ray diffraction and absorption

spectroscopy, electron diffraction, terahertz and photoelectron spectroscopy are currently being developed and applied providing complementary dynamical information to conventional ultrafast spectroscopy. A key characteristic of these dynamical techniques is that the system investigated is no longer in strict thermodynamic equilibrium (this deviation might be marginal or great). The material under study may be either in an excited state whose decay into other degrees of freedom is being probed, yielding information unavailable to conventional time-averaged frequency domain spectroscopies, or in a metastable state with fundamentally different physical properties. To fully exploit the promise of new materials, especially at the nanoscale, requires an integrated design, fabrication, measurement, modeling and theoretical effort to achieve a predictive understanding of complex materials. By developing the ability to better understand, predict and utilize the significant differences of energy states and transport, novel electromagnetic response, as well as the differing scaling laws due to surface to volume ratio effects, we will better guide materials development and discovery for emerging applications including superconductivity, sensors, transducers, microelectronic devices, photovoltaics, bandgap engineering and photonics and metamaterials.

1. Ultrafast dynamics in correlated materials:

- *Quasi-particle dynamics in superconductors, colossal magneto-resistance materials, low-dimensional charge and spin density wave compounds, insulators, Kondo systems and heavy fermion compounds*
- *Dynamics of structural, electronic, magnetic and orbital degrees of freedom*
- *Photon-induced phase transitions in complex materials*

From a materials science perspective, femtosecond temporal resolution combined with spectral selectivity enables detailed studies of electronic, spin, and lattice dynamics, and crucially, the coupling between these degrees of freedom. In complex materials there is no dominant energy scale with the implication that the charge, lattice, orbital, and spin degrees of freedom couple to determine their functional, and often emergent, properties. This exciting possibility enables, for example, nonequilibrium phenomena such as the selective photo-doped creation of a metastable state that would not, necessarily, be thermally accessible. A vast array of potential couplings leads to rich macroscopic and mesoscopic behavior including colossal magnetoresistance, superconductivity, multiferroicity, and electronic phase separation. Hence, there is a need, and opportunity, to explore and develop this approach to better understand the optical and electronic properties of complex material systems from the dual perspectives of fundamental phenomena and potential functionality.

2. Ultrafast materials science:

- *Electron-phonon interactions, non-equilibrium electronic structure, vibrational energy dissipation*
- *Structural dynamics during phase transformations, such as the atomistic mechanisms for grain boundary and interface changes*
- *Ultrafast magnetic and electronic phenomena*
- *Structural rearrangements in crystalline solids*
- *Ultrafast induced irreversible changes in materials in both perturbative and non-perturbative (extreme conditions) regimes*
- *Solid-liquid and solid-solid structural phase transitions*

- *Electron-phonon interactions, non-equilibrium electronic structure, vibrational energy dissipation*

Conventional diffraction techniques such as X-ray, neutron, and electron diffraction, are all powerful probes of the equilibrium atomic arrangement of material systems, but are unable to follow the evolution of transient nonequilibrium structural states. The promise of ultrafast techniques in materials dynamics is to elucidate the changes in the atomic and electronic configuration of materials along dynamical pathways while they are occurring. Relevant dynamic material behavior benefiting from study with high temporal resolution, especially high-fidelity single-shot approaches, include advanced diffraction and measurement techniques range from fundamental strain induced electronic and magnetic effects, to the identification of and phase transformations, plasticity, melting and solidification, deformation twinning, solid-state chemical reactions, radiation damage, and shock propagation processes. Such observations will allow the direct measurement of certain quantities used in models and would serve to validate materials simulations across varying length scales.

3. Ultrafast processes in nanoscale materials:

- *Excitation and relaxation processes in 0-, 1-, and 2-D materials*
- *Charge separation, charge transfer and transport, exciton transport, spin dynamics*
- *Phonon dynamics, thermal dissipation, and phase transitions*
- *Interactions and energy flow on the nanometer spatial scale*

Nanoscience, through materials synthesis, self-assembly, and advanced characterization, seeks to produce emergent functionality in materials systems, via design of their nanoscale structure. As might be expected when considering dynamics of nanoscale systems, ultra small dimensions equate to ultrafast phenomena such as energy and charge transport, energy relaxation, and excitation mechanisms. In fact, understanding and designing emergent phenomena in nanoscale materials requires an understanding of nanoscale interactions in materials that fundamentally occur on ultrafast timescales. As in the study of strongly correlated materials, as described above, understanding and manipulating the fundamental properties of nanoscale materials, along with the creation of emergent functionality in these materials, requires tools which enable detailed studies of spatial and temporal (or dynamic) correlations over a range of length and time scales. Ultrafast spectroscopic tools, which enable measurements at the fundamental timescales of electronic and nuclear motion, can therefore be expected to play an increasingly important role in the quest to understand and tune fundamental interactions in nanoscale materials. Recent activity in the topics outlined above is emphasized providing insight into important and fundamental processes in nanoscale materials occurring on ultrafast time scales.

4. Ultrafast materials chemistry:

- *Ultrafast dynamics of energy transfer*
- *Coherent control in condensed phase materials*
- *Production of new states of matter via ultrafast interactions*
- *Control of energy flow, charge separation, charge transfer and transport, exciton transport, spin dynamics*

A major theme in atomic and molecular science is if we now understand the basics of how atoms and molecules work; can we manipulate and control them in useful ways? Ultimately this often requires understanding the essence of energy transfer amongst various degrees of

freedom and is a multiscale problem. Ultrafast techniques provide a means to directly interrogate such processes. Here, the study and control of matter on the sub-nm, sub-fs, distance- and time-scales is exploited to explore the limits of fundamental atomic and molecular processes, as well as the limits of optical technology. In the realm of understanding and coherently controlling more complex material systems, a very recent result hinting at the promise that this area holds involves controlling a phase of matter by coherently manipulating specific vibrational modes. Complex solids with strongly correlated electrons, in which subtle crystallographic distortions result in colossal changes of the electronic and magnetic properties, are an ideal class of materials for exploiting this approach to achieve important new insight to the physics underlying these remarkable materials. Since atoms and molecules interact with their environment entirely by means of electromagnetic fields, the preceding question specifically asks: Is it possible to "design" a pulse of light that, when incident on an atom or molecule, can precisely control its evolution in any desired way?

During the past decade, as laser technology has progressed, light pulses can now be manipulated on a cycle-by-cycle basis, and the topic of "coherent control" of atoms and molecules has drawn increasing interest. Control of coherent behavior in condensed matter systems has been difficult primarily due to the fast dephasing times of electronic or excitonic states. With advances in ultrafast lasers it is now possible to contemplate extending coherent quantum control techniques, first applied to gas phase atoms and molecules, to condensed matter systems. From a fundamental scientific perspective, entirely new physics emerges when the quantum states of solids are coupled and manipulated by intense optical fields. Our understanding of tightly coupled light-matter systems is, however, hampered by our lack of in-situ microscopic probes. Recent and foreseeable advances in high-brightness x-ray sources create an unprecedented opportunity to micro-probe the primary event in how optical radiation manipulates matter. When we ask a light pulse to manipulate matter it accomplishes this task by driving atomic scale distortions in a material's valence charge density. These initial microscopic distortions then propagate out to drive subsequent material evolution. Numerous experiments have now demonstrated the concept of optimal control to emphasize certain quantum trajectories over others, selectively excite given vibrational modes, or drive dissociative reactions to a prescribed set of final products. However, to date, coherent control has been demonstrated in simple bulk samples, primarily in the gas phase, generally employing amplified and programmably shaped ultrafast coherent radiation pulses to control dynamics in matter. The objective in such schemes is to prescribe a new quantum state of the physical system, such as a new chemical, a special kind of light, or an excited state of a molecule with special properties. Perhaps the most exciting development in quantum control research is the learning control algorithm. In a learning algorithm, the quantum system under study actually runs the experiment itself. The apparatus interrogates the atom or molecule, which provides direct feedback to the laser. The laser system and the quantum system work together through an evolutionary optimization approach to find the optical field that can produce the desired dynamics. Recent breakthroughs helping to advance this field are identified and described.

<u>5. Novel experimental techniques and diagnostics for ultrafast materials science:</u>

- *Femtosecond x-ray techniques*
- *Ultrafast electron pulses and diagnostics*
- *Ultrafast terahertz science*
- *Towards the attosecond regime*

Our understanding of tightly coupled light-matter systems is, however, hampered by our lack of in-situ microscopic probes. Recent and foreseeable advances in high-brightness x-ray sources create an unprecedented opportunity to micro-probe the primary event in how optical radiation manipulates matter. When we ask a light pulse to manipulate matter it accomplishes this task by driving atomic scale distortions in a material's valence charge density. These initial microscopic distortions then propagate out to drive subsequent material evolution. Advanced, high-brightness x-ray sources offer new opportunities for direct probing of the lattice, as well as the valence charge density on ultrafast and ultrasmall scales. This new experimental capability provides fundamental insights important for learning how coherent quantum control techniques might be used to synthesis novel materials. We will review recent remarkable advances and will present a vision for a path an imaging capability at the frontier of ultrafast science, enabling measurements which begin to simultaneously approach the intrinsic length (Å) and time (10^{-18} s) scales of matter. The resultant detailed understanding of the properties of materials on an ultrafast time scale enables a robust rational basis for the design and development of new materials possessing desired properties and functionalities.

Size Dependence: Quantum and Nanoscale Effects

Chair: S. T. Picraux (LANL)
Speakers: E. Garfunkel (Rutgers U.), V. Klimov (LANL), E. Yu (UCSD), G. Rubloff (U. Maryland)

1. Nanoscale materials for multifunctional control

Nanoscale materials offer new opportunities to advance our fundamental understanding of the design and control of emergent properties of materials. The recent focus on nanomaterials research has revealed a wide variety of new approaches to achieving enhanced materials performance not previously imagined. These concepts are enabled by two things: 1) the new properties of materials that emerge at the nanoscale, and 2) the ability to integrate these properties into hybrid nanomaterials. These ideas point the way for a future of multifunctional designer materials where properties are combined and optimized to reach new levels of performance.

A key opportunity is to achieve new materials combinations that control and exploit the high structural quality (crystalline or amorphous), well defined interfaces, large strains, enhance fields, and quantum effects at the nanoscale. Quantum well heterostructures that localize coherent light generation and provide built-in strain to tailor valence and conduction band matching are design elements that provide increased efficiency of light output and are used in essentially all semiconductor lasers manufactured today. The above advances in electronics and photonics are based on the synthesis of hybrid nanoscale materials and the ability to control fabrication of ordered 3-dimensional nanoscale architectures.

The benefits of hybrid nanostructured materials are not limited to the above electronic and photonic examples. Rather this approach provides the key to the future design of multifunctional materials with emergent properties "by design". For example, areas of particular opportunity include energy harvesting and storage, including photovoltaic and photochemical energy conversion, thermoelectric conversion of heat to electricity and visa versa, piezoelectric conversion between strain and electric fields, rapid cycling of battery electrodes to high

capacities, electrostatic capacitive charge storage to high energy densities, and electrochemical energy storage and conversion in fuel cells. The control of energy transfer is a key aspect to each of these areas. The ability to exploit the high local fields, large surface areas, enhanced chemical reactivity, short length scales, quantum confinement, local strains, enhanced strength, and the stability of nanoscale arrays in nanostructured materials is opening up new opportunities for advances. An improvement of a factor of 2 to 3 in any of these areas would have dramatic consequences. While incremental increases will almost certainly be achieved over the next few years, an ability to achieve such larger improvements and to do this "by design" (rather than empirically) with new understanding of how to control energy transfer by nanoscale structuring is a 5 to 10 year goal requiring a MaRIE-level effort. The key challenges are the controlled synthesis and fabrication of heterogeneous combinations of materials at the nanoscale and the understanding, through characterization and modeling, of the design of materials performance this control makes possible.

2. Nanoscale Synthesis and Assembly

The controlled synthesis and assembly of materials and their heterogeneous combinations at the nanoscale is a key gap. Without control of materials fabrication little progress can be expected. The current state of the art enables relatively good control of 2-dimensional (3D) layered nanostructures for crystalline semiconductors, amorphous dielectrics, and polycrystalline metals. This control is achieved by top-down methods of layer deposition (MBE, CVD, ALD, vapor deposition, sputtering, PLD). However for other classes of materials such as crystalline oxides, ferroelectrics, organics, superconductors, even 2D control is limited. Further, to advance this area 3-dimensional (3D) structures need to be synthesized and hybrid nanostructures fabricated. This area of 3D heterogeneous fabrication is still greatly lacking at the nanoscale. Selected materials such as gold or II-VI nanoparticles by solution phase processes and semiconducting nanowires by vapor phase processes can now be synthesized with some degree of control, but formation of hybrid structures, even for the best studied cases, is very limited. Research needs to be extended across the range of semiconductors, complex metal oxides, metals, and organic materials where multifunctional nanostructured systems hold great promise.

Emerging bottom-up approaches to synthesis, in combination with top down processing, show much promise but improved experimental control and in situ methods to monitor and understand growth are essential. We must learn to exploit the nanoscale forces that lead to self-assembly of nanostructured materials and arrays, which provide self-limiting reactions for size control, and which can exploit natural templates for assembly of nanoscale architectures. To do this the role of surface and interface energies, growth catalysts, kinetics, and low temperature growth processes need to be much better understood. As examples, catalyst-controlled chemical vapor deposition is enabling the growth of electrical doped nanowires with 3D hybrid structure control, and atomic layer deposition is providing self-limiting growth of conformal films with single atomic layer control over 3D structures for aspect ratios exceeding10^3. Polymer-assisted synthesis and other mediated growth methods also offer new opportunities for low temperature growth of inorganic materials. The use of surfactants, catalysts, and differences in interfacial energies has made it possible to achieve liquid phase growth of hybrid materials with selective shapes and core-shell structures. Such new synthesis methods need to be greatly extended in terms of new materials, their combinations, doping, interface structure, and morphology control. Cluster chambers that allow sequential growth of different types of materials (semiconductors, metals, dielectrics, organics, etc.) as well as low temperature solution-based approaches need to

be exploited to explore nanoscale heterostructure properties. Hybrid materials assembly at the nanoscale is also essential and methods for the assembly of nanocomposite materials must be expanded. Examples motivating such assembly include high density nanowire arrays for Li ion battery storage, nanoparticles in a semiconducting matrix for efficient, tunable light emission, and nanowire-organic matrix structures for improved light harvesting. Advances in nanomaterials integration into micro and macro length scale structures is a crucial area to advance. Low temperature methods to self-assemble or fabricate such nanostructure composites are limited and poorly controlled at present. Focusing these hybrid nanoscale materials studies on energy detection, harvesting, transfer, and storage, and on radiation and chemical detection and sensing will provide many opportunities for advancing DOE mission areas as well as addressing a broader set of national needs.

3. Real-time Nanometrology

Dynamic observation, such as by optical scattering, electron microscopy, and x-ray scattering, can greatly accelerate progress in understanding nanomaterials synthesis and stability. High resolution/analytical electron microscopy and ultrafast optical spectroscopy are premier approaches to gain microscopic structural and electronic information about nanomaterials. Fast time-resolved electron and optical in situ characterization during growth can revolutionize progress in hybrid nanomaterials fabrication and assembly, as well as understanding of the response and stability of these materials during energy harvesting, conversion, and storage.

4. Nanoscale Properties and Modeling

An essential need for nanoscale multifunctional materials development is to establish the microscopic properties on a length scale comparable to the heterogeneous tailoring of the materials and to learn how interactions allow one to manipulate hybrid materials performance. For example, how do electronic, optical, structural, and magnetic interactions in nanostructures with their associated large field and strain gradients, and structural variation on length scales comparable to characteristic excitation wavelengths change the transport of electrons, photons, plasmons, phonons and other excitations? How can we manipulate and control surface and interface states, and carrier and energy flow across interfaces? How can we understand and predict the collective effects of regular nanostructured arrays in establishing the performance and emergent properties of nanosystems (for example in the control of energy flow by photonic lattices and metamaterials)? To address these questions we require probes with high spatial and time resolution. Electron and optical probes have continued to rapidly advance. A state of the art high resolution analytical electron microscopy facility must be established for structural characterization and ultra fast optical spectroscopy techniques continue to be exploited for electronic structure and energy transfer characterization. Scanning probes with high spatial resolution are the third area which needs to be pursued. Such probes include those based on optical excitation (absorption and excitation spectroscopies, Raman, local nanoprobe field enhancement), conducting, potential, electron tunneling, force, and thermal measurements. Additional new nanoprobe tools such as atom probe tomography, photoemission electron microscopy, and the full suite of scanning probes need to be considered. Establishing local structure, properties, and time response of energy transfer processes in combination with theoretical modeling will provide the basis for exploiting the new properties available with hybrid nanostructured materials and high density nanostructure arrays.

Theoretical techniques must be developed to treat the interactions and composite response of multi-domain systems. Due to the small dimensions, the high density of interfaces, and high field and strain gradients new approaches to deal with nonlinear responses are needed. Both materials growth kinetics and materials performance needs to be addressed. The small dimensions lead to quantum confinement, strong interactions between charges, reduced dielectric screening, and relaxation of conservation rules. For example, in nanowires it has been observed that thermal transport (phonon flow) can be greatly reduced relative to electrical transport (electron flow), and that the effects are not predicted by conventional theory. Such properties could provide large enhancements in thermoelectric performance by increasing the ZT parameter by up to a factor of 3, completely revolutionizing the harvesting of waste heat for electricity and refrigeration without moving parts. Other examples include the understanding of energy transfer effects in high fields, for example in field-enhanced energy absorption, carrier multiplication by multi-exciton formation, and plasmon flow and energy loss within nanostructures. Control of charge separation and radiative versus non radiative energy flow are at the heart of nature's approach to solar energy harvesting and fuel production. Methods to understand and optimize the relative flow of energy and minimize energy-loss channels, for example between radiative, Auger and charge transfer processes, could have far-ranging impacts, from new generation high efficiency solar cells, to ultra-efficient solid state lighting, to Si-based lasers. To exploit the opportunities afforded by nanoscale 'materials engineering' given the wide range of possible hybrid nanostructured systems, progress in microscopic characterization of energy transfer processes together with advances in theoretical modeling and simulation of these processes is essential.

Ferroics

Chair: Turab Lookman (LANL)
Speakers: Dan Dahlberg (U. Minn.) Wenwu Cao (Penn State) Cristian Batista (LANL)

The study of multiferroics (and in particular magnetoelectrics) and associated heterostructures is amongst the fastest growing and most cited research areas in condensed matter physics. The scientific challenge entails understanding the mechanisms of the coexistence of magnetism, polarization and strain on the one hand, and learning to increase and control the effect for applications. Although many classes of single phase magnetoelectrics have been discovered, the coupling is often too weak or at extreme temperatures (< 20K) or magnetic fields (>5T). The possibility of magnetoelectric memory, that could be realized in the next decade, will dramatically increase the speed and stability of read/write devices, compared to today's technology that depends on either ferromagnetic materials based on reversal of magnetic dipole or ferroelectric random access memory that depends on electric dipole direction.

The aim of this session was therefore to evaluate the current science and future developments in magnetism, ferroelectricity and magnetoelectricity.

1. Nanomagnetism frontier (Dahlberg):

It is clear that the next frontier in magnetism requires dealing with response in the presence of defects. The role of defects in both statics and dynamics of magnetic behavior is not really understood, yet they seem to dominate key properties in many technologies. Having a long exchange interaction length can help in overcoming this, but there is a need to have a fundamental understanding of how surfaces, and point defects affect magnetic properties,. As an example, the crescent feature seen in Ni dots was stable in the real experiments but micro-magnetic simulations

showvery slow transients. It is very likely that there is a defect effect which stops the slow evolution, leading to trapping in the crescent shape.

Characterization: With advanced probes the spatial resolution has been demonstrated to be on the order of 30 nm. With commercial tips the resolution is limited to between 100 and 200 nm and the moment sensitivity observations have lower limits of 3*10^6 Fe atoms, with a signal to noise of at least 10 to 1. It is likely that sensitivity could be reduced to somewhere on the order of 1*10^5 Fe atoms. Inherent difficulties are that the MFM tip can produce a magnetic field which can influence observations. This can make quantitative MFM measurements difficult but could also be used as a microscopic susceptibility probe by doing two scans with opposite tip magnetization and subtracting the images.
The MFM is sensitive to the field gradients at the tip. This means one is sensing ALL the fields from the specimen at the tip position. On the positive side it implies that the probe is is not merely limited to the surface magnetization. The technique of magnetic STM is only sensitive to magnetism for a specific atom, which can be good or bad. There is always the question of separating magnetism from possible artifacts. In many respects, the exchange length is comparable to the MFM resolution so the added resolution of Magnetic STM may not be needed.

Micromagnetic simulations: These have been extensively developed with open software widely available. This has become a standard tool for interpreting experimental results. Its based on solving the Landau-Lifshitz-Gilbert equations with various interaction energy terms, including exchange, anisotropy and magnetostatic. In most cases, there is excellent agreement between MFM images and micromagnetic simulations. This agreement implies that the micromagnetic simulation's much better resolution can be relied upon for atomic scale states. The real problem, however, is that the simulations are sensitive to the specific damping values used in the simulations. These damping values have to be obtained using other measurements. Other problems include that the coercive field calculated by the simulations is always greater than experiment. Moreover, the simulations do not reflect the effects of defects either in the bulk or at the surface. Although not generally accepted, energy minimization techniques provide an easy first step in determining the likely magnetic state. Developments in dealing with various magnetic hetergonetities represents an outstanding challenge in theory. Applications of pure magnetic systems include sensors, advanced memory elements, and fundamental magnetic research MFM. Simulations have also proven to be excellent tools.

2. Ferroelectrics (W, Cao):

Ferroelectric materials are by far the most studied over the last 50 years of any of the ferroics. Experimental measurements on well characterized samples, together with the use of a well parametrized Landau theory, and the need for sensors and fast memories are factors primarily responsible for the progress.

The emphasis will now be on finding Pb free ferroelectrics. Currently, the polarization susceptibility, d_33, of these lead free candidates is ~ 230 pC/N, about half of PZT (lead titanate) ceramics which are the most prevalent. Moreover, the ferroelectric phase transition temperatures are also lower than PZT, so significant issues related to temperature stability as well as limitations on not having high enough temperatures, remain. This is a central materials challenge in the field for next decade as there are environmental considerations that also come into play.

Domain engineering is a future strategy for designing ferroelectrics. Here the idea is to use appropriate polarization domain inclusions to provide access to regions in the field E vs temperature T phase diagram where d_33 can be maximized. Scattered studies have been conducted but this will be a dominant strategy in the future. In addition, there is a need for design tools to minimize search times and parameter space in the search for materials with desired specifications.

The science questions relate to understanding why Pb is so important to piezoelectric activity. These questions include: Can we find substitute elements that have this property and are non-toxic? Why do good piezoelectric materials have perovskite structures? Can we stabilize some meta-stable crystals structures that can have better piezoelectric effect using extreme processing methods? In addition, there is need for characterization methods that can directly probed the ferroelectric domain walls. These are funtional interfaces that control the microstructure and these can be hidden in bulk. Hence, a need for very refined structural work and polarization probing at nano-meter scale within domain walls.

The use of piezoelectric and pyro-electric materials as efficient energy harvesting materials is a future challenge Most piezoelectric electricity harvesting produce power on the order of mW, which is too small for system applications. However, this output may be enough for hand-held devices such as some commercially-available self-winding wristwatches, monitoring sensors and mobile phones. For better efficiency of energy harvesting there is a need for more intelligent designs. Finally, we require devices that will be robust enough to endure long-term exposure to hostile environments (in space and extremes of temperature, pressure) and have a broad range of dynamic sensitivity.

3. Magnetoelectric multiferroics (C. Batista)

The decadal and central challenge of the field is to design room temperature magnetoelectrics with small switching fields. Progress will depend on innovation in synthesis and characterization techniques coupled with an understanding of the mechanisms that couple polarization and magnetization. This understanding and associated theoretical developments are the key to optimizing and controlling the effect for applications.

Single phase magnetoelectrics, such as the family of Tb based (TbMnO_3, TbMn_2O_5) and hexagonal Ho based (HoMnO_3)perovskites, have been instrumental in the revival of interest in multiferroics. However, the size of the magnetoelectric coupling is two orders of magnitude less than what is desired for applications. Moreover, the energy scale is such that the temperature where the effect occurs is very low (< 25K). Soft organic systems are potentially candidates for larger effects and there are on-going efforts at NHFML, LANL in this direction. Charge density wave insulators potentially could have strong polarization and magnetoelectric effects as well. These are induced by competition between the super and double exchange and could be a route to applications. Low dimensional multiferroics, such as quasi one-dimensional chains and two dimensional sheets, also represent possible frontier candidates.

From an applications point of view, nanocomposites of ferroelectric (e.g. PZT) and ferromagnetic (e.g. BiFeO_3) epitaxial films offer the best prospects of room temperature multiferroics. One suggestion is to increase the magnetoelectric coupling by rotation of the polarization by the action of a magnetic field. The rotation would take place by the action of strain on the ferroelctric that results by applying a magnetic field. Developments in sputtering techniques, high resolution x-ray diffraction and piezoresponse force microscopy would accelerate the search for these composite layered magnetoelectrics.

Computational Tools
Chair: Frank Alexander (LANL)
Speakers: Krishna Rajan (Iowa State), Ivan Schuller (UCSD), James Ahrens (LANL), Christopher Stanek (LANL)

This session discussed the need for a new breed of computational tools, both software and algorithms, for materials science and condensed matter physics suited to work with petascale and exascale computational hardware. This set of tools must accelerate discovery and analysis processes via informatics approach and must maximize information acquisition from each experiment -- Make every photon count! There is a need to develop high-throughput screening for materials problems similar to what's been/being done for biological systems – namely a data-driven Materials Science -- like genomics, proteomics, metabolomics, etc. One area of focus discussed how statistical/combinatorial, learning methods can build in expert knowledge to improve performance.

Several topics were discussed in the session included:

1.) A Combinatorial Approach / Quasi Monte Carlo / Sampling Parameter Space Search/Coverage to experiment design and search
2.) The application of Statistical Learning / Machine Learning to predicting materials performance.
3.) Work flow management for collaborative efforts in large scale experiments.

A specific focus, important to MMMM is the understanding of defects.Defects often alter (inhibit or enable) performance of functional materials. Their role and importance for scintillator design and engineerig was discussed. In particular, the goal is to identify deleterious defects and subsequently remove or minimize those defects. A pathway to achieve this is to combine modeling and experiment for defect identification.

Grand Challenges in Making:

1.) Can one predicting materials properties via advaces in machine/statistical learning ?
2.) Can one design a superconductor or a material with other desired characteristics?
3.) Can one achieve optimal (or near optimal) Experiment Design?

Grand Challenges in Measuring:

One of the key challenges in measuring is the ability to absorb the information coming out of the experiments. Visualization is a key to this challenge and was discussed extensively. In particular,

1.) Visualization -- need a 3d large data visualization capability
Understanding the scientific results of MARIE simulations, experiments and theoretical models is at the heart of the MARIE endeavor. Key to MARIE's success will be using advanced visualization and analysis techniques to rapidly analyze and understand results. Real-time visualization of experimental results will also help steer the experimental process. The process envisioned for MARIE includes three phases:

1. An experiment planning/design phase
2. The running of the experiment phase and
3. A post-experiment analysis phase.

Requirements that direct our visualization effort include:

1. The size of data being generated during each phase
2. the speed at which the data needs to be processed
3. the type of data being generated (specifically detector results and large-scale simulation results) and
4. the type of visualization approaches (such as comparative visualizations and custom visualizations).

Additional requirements are driven by the locations the results are delivered to. On the LANL campus, these locations include:

1. offices and a theater in the new science complex building,
2. the M4 materials facility and
3. the MARIE four experimental halls located at LANSCE and
4. external collaborators around the world.

Modern science is team-based and results will be delivered to all these locations supporting collaborative science.

Given the multi-year time horizon for MARIE instantiation, it is critical to think about technology trends and what future technology will be available to meet these requirements. To address these requirements the following four efforts are required:

1. Real-time large data visualization algorithms - software and hardware will need to be developed to handle the massive data output from sensors during each MARIE experimental run.

2. Multi-disciplinary visualization and science teams – Based on our previous successes, we believe the best way to enable effective visualization is to deploy teams composed of both visualization scientists and materials scientists to address the visualization and analysis needs of each phase of the MARIE process.

3. State-of-the-art facilities – We can improve the way we do scientific work by creating state-of-the-art facilities (especially offices) as an integral part of the MARIE infrastructure. The facilities will effectively deliver visualization and analysis results. Collaborative support for multiple stakeholders to interactively explore, view and discuss their scientific results is a key part of our vision.

2.) Recording and following a workflow and collaborating
3.) Verification and Validation --comparing simulation with experiment
4.) Provide scientists tools which greatly reduce the need for human intervention
5.) High-speed networks
6.) Desktop supercomputers
7.) Software for fusion of disparate data to create knowledge
8.) Multidimensional Data analysis
9.) Data Provenance

Modeling can benefit greatly from enhanced experimental capabilities.

Grand Challenges in Modeling:

One of the significant challenges in modeling is to develop models which also come with prediction guarantees. This requires a rigorous and yet practical form of uncertainty quantification. Support Vector Machine classification for establishing phase diagrams was described as one such principled way to carry this out.

Clusters
Chair: Roland Schulze
Speakers: Joel Parks (Harvard), Bogdan Mihaila (LANL), Milan Sykora (LANL),

In the broader view of scientific knowledge and advancement, the scientific community believes it has a good understanding of the principles governing atomic and molecular behavior, and a good understanding of the principles governing much behavior in condensed matter. However, it is in the transition region between these two extremes that we are only beginning explore. This transition region, from the regime of stable molecules composed of a few to a few hundred atoms, to the regime of condensed matter composed of extended, ordered structures of tens of thousands atoms and larger, is largely unexplored except for the situation of special cases such as large biomolecules and perhaps soft matter systems of polymers. The initial foray into the transition regime has produced many new surprises regarding physical and chemical behavior of small ensembles of atoms in the regime where quantum effects couple with classical continuum properties, and materials (and ensemble sizes) with new properties are discovered almost every day. Examples here include quantum dots and quantum structures where new physics is manifest due to scaling effects and where quantum processes may dominate.

Current state of the art in the field of clusters is synthesis and fabrication of materials through synthetic chemical methods. In general, with some exceptions, these methods produce not a select composition and size of clusters, but rather produce a distribution. As such, the measured properties present an average, or at best a distribution, making analysis and interpretation difficult. Nonetheless, these methods can be very powerful for materials discovery in this transition, cluster regime of materials. Many of these discoveries are made in an Edisonian mode by trial and error coupled with more comprehensive study of significant results. What is required for a systematic study of new materials through this transition regime are new tools for rapid production of clusters of carefully controlled composition and carefully controlled size coupled with direct methods for measurement of physical and chemical properties of these assembled clusters. Furthermore, the experimental measurements indicated here have the real possibility of coupling directly to theory, as the phase space is limited in size, and so full theoretical models, as well as mean field theories, are computationally within reasonable grasp.

The goal of this discussion was to foster ideas regarding the role cluster science should have in defining or influencing activities and capabilities in future material facilities. In this context, cluster science is defined as the careful study of small elemental or alloy clusters ranging from a few atoms to a few 10-thousand atoms in size. Cluster creation, cluster characterization and properties measurement, and cluster theory are examined. The intention here is to determine how cluster science can contribute to the advancement of new functional materials. This discussion includes possible contributions to fundamental condensed matter science, the science of nano-scale materials, and clusters in non-equilibrium situations (non-ground state, metastable, and extremes), as well as providing ideas for methods for a foundry of materials discovery. It is clear

that success in this area will lead to new understanding of the assembly of matter through the nano-structural regime.

It is important to have the ability to create clusters rapidly, characterize and separate them on a real-time basis by composition and size or mass, and then interrogate them to measure their physical and chemical properties in an isolated state (gas phase or perhaps isolated in rare gas matrix) where there are no possibilities of correlations beyond the surface limits of the individual cluster. New methods must be defined and developed to produce clusters in rapid, combinatorial fashion, with the ability to select and filter these by exact size and composition. Gas phase molecular beam methods are an obvious choice, although there may be other viable approaches. The further modification of these mass and composition segregated clusters through gas phase surface reactions or perhaps annealing processes is also important. The important specific measurements to make on these clusters will include atomic structure, electronic structure, phononic structure, magnetism and spin momentum, correlation effects, surface effects including chemical reactivity, excited state properties, and others. The types of measurements are virtually unlimited and will be tailored to answer specific questions regarding the clusters, in addition to the basic fundamental set. The collection of these clusters on a surface with the intention of building condensed matter materials under specific and definable conditions then comes essentially free, and must also be considered as a fundamental mode of materials synthesis. The direct ability to attain both equilibrium and metastable energy states in these atomic clusters is possible through various modes of production. This can be done by thermal variation of the clusters during formation and afterwards through collisional cooling and/or annealing. This will allow modification of both atomic structure and symmetry of the cluster as well as concurrent modification of the specific electronic structure

Equally important, and vital to materials discovery and design, is the need to understanding the transition of properties from individual atoms and molecules to the solid-state in a theoretical framework. Coupling the measurement and calculation of clusters will foster this goal. For the first time, modern theoretical, computational, and experimental techniques are available to solve this problem in an accurate and efficient way. This is a tremendous opportunity and direct many-body theory is called upon to provide leadership and support. The development of a predictive many-body computational capability will transform the understanding of the fundamental properties of condensed-matter systems and materials. It will also provide the much necessary linking across length and temporal scales leading to successful extrapolations of existing models to regimes of temperature and pressure that are not currently accessible in the laboratory.

New methods to study the properties of finite-size many-body systems (e.g. clusters of atoms) are required. One example consists of using a new approach to solving the coupled-cluster expansion (CCE) of the many-body Schrödinger equation. The lofty goal of developing a predictive many-body theory can be achieved by taking advantage of the progress in the algorithm development surrounding the CCE and by exploiting the LANL high-performance computational capabilities. In particular, the hybrid architecture of Roadrunner is a perfect fit for addressing the problem of finite-size many-body systems.

The presentations by Joel Parks, Bogdan Mihaila, and Milan Sykora, which all discussed cluster science methods at the forefront of science, technology, and application, were aligned with themes of current and future general materials scientific needs and requirements to make MaRIE/M4 a "signature" concept. Joel Parks of the Rowland Institute at Harvard spoke of gas phase cluster production and structural analysis using electron diffraction methods, of size (mass) selected clusters. Key here was the ability to measure the cluster structure with size differences consisting of a single atom: the transition of a basic structural configuration (and properties) of these clusters took place in the span of adding a single atom, and can be basically thought of as a phase transition in the cluster with concurrent changes in physical properties. The ability to examine fundamental transformations at the energetic ground state of materials, such as a phase transition in a limited size cluster, is a powerful tool to understand the basics of condensed matter behavior. Dr. Parks also spoke of changes in the chemical reactivity of the cluster as a function of size, and it became clear that this methodology also is a powerful tool for discovery of new materials with tailored properties such as catalytic activity. Bogdan Mihaila from LANL spoke of the direct link between accessible theoretical methods in this size regime and the experimental tools now possible in cluster science – the calculation is *exactly* what is being measured in the experiment. The power and excitement of this area comes from the ability to calculate and predict exactly cluster structure and properties of the sizes of interest in this transition region using coupled cluster methods within many-body theory. It is fair to predict that the carefully controlled experimental cluster methods for making and measuring properties of clusters described and suggested here will become a test bed for new theoretical developments. Theoretical frameworks and understanding, and computational methods such as used in Roadrunner now make it possible to forgo mean field theories and calculation, and perform exact calculations in reasonable time frames for the cluster sizes or interest (a few 10s to a few 10000 atoms). It is imperative that the theoretical basis for exact computation and understanding in the material ground state be comprehensively complete in order to develop predictive theories for use in understanding the behavior of matter in extreme environments or far-from-equilibrium cases. This direct coupling between theory and computation and experimental measurements gives us the opportunity to do so. Milan Sykora of LANL spoke of more conventional chemical methods of producing larger clusters in the form of quantum dots and making measurements on them to discern their specific properties and characteristics. This highlighted the great advances in synthetic methods to producing narrow size and composition distributions of useful clusters, but also emphasized the importance of producing exact size and composition materials so that measurements are on isomorphous materials rather than an average over a distribution of composition and size. Furthermore, the control required to do this means finding methods of producing clusters where the interface – the outer surface of the cluster – is carefully controlled; either through a direct termination of the primary composition or tailored ligands or surface layers. This extreme degree of compositional control is necessary in order to insure specific measurement of known materials rather than averages over a distribution.

A variety of general and specific points were made in this discussion of clusters. These included concepts required to carefully study clusters and cluster properties:

1) ultra-careful synthesis and characterization/verification of cluster solids produced
2) parallel synthetic method across size and composition ranges – combinatorial approach
3) rapid, direct measurements of fundamental properties of clusters in situ

4) New theory method(s) including coupled cluster concepts to improve viability of performing exact calculations (in addition to mean field methods) with systems involving many particles, and to take advantage of new computational hardware and approaches (Roadrunner)
5) direct coupling of experimental and theoretical methods (requirement/desire that modeling is exactly what is measured)
6) aspects in line with "materials discovery" concepts
7) collection of clusters (having desired property) to enable building in a controlled manner, bulk solids/thin films with desired properties

Functional needs for future development of methods to achieve careful control of cluster size and composition as well as tools for promoting guided materials discovery include:

1) Stable super high-intensity gas phase cluster sources to produce mass selected cluster beam – production of highly controlled cluster materials
2) New synthetic routes to mass produce bulk amounts of high quality cluster materials in specified size and composition space
3) New methods and ideas to collect clusters in order to build materials
4) New tools (instruments) to relatively rapidly synthesize and examine properties (electronic structure and others) across broad size and composition scales – linking length scales across the nano-regime and covering broader compositional phase space
5) New theoretical methods to perform full computation and treat correlations exactly

Summary:

Prediction of material properties has been a lofty dream for some time. As computational tools have progressed to current supercomputer systems that can operate at petaflops, the theoretical codes that were at one time severely restricted to idealized systems with no boundaries can now perform atomistic modeling with cubic micron volumes. In the upcoming decades computational power will continue to expand and theory will be able to incorporate interfaces in composite systems. Such modeling progress offers great potential for realizing the goal of designing functional materials. Future materials must be designed with both composition and architecture in mind. Although composition can play a large role in discoveries such as the next high temperature superconductor, interfaces and defects within the material play an equally important role in properties and material performance. Defects and interfaces can control quenching of excited states in photovoltaics or vortex pinning in superconductivity or entirely new physics as competing order parameters come together at interfaces such as colossal magnetoresistance. The functionality often comes from controlling or tailoring the large response of a material to a small perturbation as a result of competition between nearly degenerate ground states involving coupled charge, spin, and lattice degrees of freedom. Critical to understanding the emergent phenomena is the ability to make single crystal materials with controlled interfaces and as part of composite materials. Composite materials can drive functionality both in terms of combining multiple known material properties and discovering new properties at interfaces. The role of these composite systems is rapidly growing and will impact materials solutions in areas including sustainable energy, information storage and processing and advanced optical materials.

There are so many possible combinations of material types and architectures that rapid advancement will require the ability to effectively design functional materials based on theoretical principles. Composition, interfaces, nanostructures and 3-D micron architecture will all have critical roles to play. Predictive design of functional materials is a grand challenge that will require an understanding of defects and interfaces across multiple length scales and decades of work. These defects and interfaces must be controlled synthetically and observed temporally to understand how they evolve in extreme conditions. Linked to this grand challenge is a transition from an observational approach to control science. In order to develop theoretical design principles it is first necessary to have the synthetic control to systematically change a material. This material synthesis capability must be closely coupled to detailed observations that are designed to test theoretical codes from atomistic molecular dynamics to
Control science relies on an integration of theory, synthesis and characterization.

There was a consensus that synthesis and characterization tools are required to systematically vary and measure both defects and interfaces over a variety of length scales from atoms to microns. *In situ* techniques play a key role in enabling synthetic control through understanding nucleation and growth process and in watching how functionality evolves in time and in extremes. Well defined samples with systematic variations combined with characterization measurements of both structure and properties will provide the material database to develop and validate new theoretical codes capable of predicting functional properties. There will be significant challenges in many areas including *Applications of Electronic Materials and Oxide Interfaces, Strongly Correlated Electron Materials, Time Resolved Aspects of Functionality, Quantum and Nanoscale Effects*, *Ferroics, Computational Tools and Clusters*. The greatest challenge will be the effective integration of people and the wide range of synthetic and characterization tools. New materials based discovery centers in which integration occurs at a single facility and focuses on a class of materials will play an important role in accelerating the path to materials by design.
The material discovery centers at Bell Labs and IBM were immensely successful and provided tremendous advances to the semiconductor industry working with only a handful of materials. Future large scale materials facilities are needed for the United States to maintain its leadership in materials discovery and subsequent technological advances. From the workshop it was concluded that for a large scale facility to be effective it will have to have

- *Integrated capabilities that include synthesis, characterization and theory*
- *Modeling and theory that includes full electronic, ionic relaxation for large systems with interfaces*
- *Ability to manipulate defects and interfaces by adapting FAB techniques where appropriate and developing new methods to control the architecture of novel materials.*
- *A crystal growth and thin film capability that goes beyond current state of the art to provide rapid materials exploration and incorporate nanostructures within the crystalline domain.*
- *Control of strain and phase to generate metastable states*
- *Theoretical codes that can cross length scales and effectively pass parameters back and forth*
- *In situ characterization tools to understand nucleation and growth of crystalline materials and defects within the materials*

- *Rapid, non-destructive 3-D characterization of microstructure and composition*
- *Theories that treat strong correlation dynamically*
- *Characterization of the evolution of defects and interfaces in response to extreme environments and during function of integrated devices*
- *Characterization of buried interfaces to study electron- electron, electron-phonon and phonon-phonon interactions*

Finally, the people will be a key ingredient as well. A state of the art facility will attract talented people, but there must be an effort to recruit a wide range of talent with a culture of integrated problem solving to ultimately be successful.

Appendix 1
RESEARCH FRONTIERS AND CAPABILITY GAPS FOR CONTROLLING AND DESIGNING FUNCTIONAL MATERIALS

Los Alamos Research Park
Rooms 203A and 203B

January 20-22, 2009

Tuesday, January 20

8:30 – 9:00 Welcome, MaRIE Initiative — John Sarrao (LANL)
M4 Concept — Mark McCleskey (LANL)

Applications of Electronic Materials — *Darryl Smith (LANL)*

9:00 – 9:30 — Christopher Hammel (Ohio State)
9:30 – 10:00 Modeling of Electron Devices Fabricated from Novel Materials — Paul Ruden (U. Minn.)
10:00 – 10:30 TBD — Christopher Palmstrøm (UCSB)
10:30 – 11:00 Breakout Session / Break

Oxide Interfaces — *Michael Fitzsimmons (LANL)*

11:15 – 11:45 New frontiers in infrared spectroscopy of complex materials: gated structures and nano-scale spatial resolution — Dimitri Basov (UCSD)
11:45 – 12:15 State-of-the-art Electronic Structure Calculations — Warren Pickett (UCD)
12:15 – 12:45 Superlattices, MBE — Anand Bhattacharya (ANL)
12:45 – 1:30 Breakout Session /Lunch
1:45 – 2:00 Emergent Behavior at Nanoscales — Sasha Balatsky (LANL)

High Tc Superconductivity/Heavy Fermion Physics — *Eric Bauer (LANL)*

2:00 – 2:30 — Eric Hudson (MIT)
2:30 – 3:00 Heavy Fermions in Flatland — Takasada Shibauchi (Kyoto)
3:00 – 3:30 Break/Snack
3:30 – 4:00 Superconductivity in Strongly Correlated Electron Materials — Joe Thompson (LANL)
4:00 – 4:30 Hybrid Dynamic Field Theory Approaches for Strong Correlations — Rich Martin (LANL)
4:30 – 5:15 Breakout Session / Close

Wednesday Jan 21, 2009

8:45 – 9:00	Controlled Coherence and Functionality	Toni Taylor (LANL)

Time Resolved Aspects of Functionality — *Toni Taylor (LANL)*

9:00 – 9:30	Coherent Control Over Interacting Dynamical Responses	Keith Nelson (MIT)
9:30 – 10:00	Advanced Ultrafast Techniques for Understanding and Controlling Complex Materials	Robert Schoenlein (LBL)
10:00 – 10:30	Optical Magnetism	Roberto Merlin (U. Mich.)
10:30 – 11:15	Breakout Session / Break	

Size Dependence: Quantum and Nanoscale effects — *Thomas Picraux (LANL)*

11:15 – 11:45	Nanoelectronics and Materials	Eric Garfunkel (Rutgers)
11:45 – 12:15	Electronic and Photonic Effects	Victor Klimov (LANL)
12:15 – 1:00	Lunch	
1:00 – 1:30	Exploiting Nanowires and Nanoparticles for PV	Edward Yu (UCSD)
1:30 – 2:00	Nanostructures for Energy Devices	Gary Rubloff (U. Maryland)
2:00 – 2:45	Breakout Session / Break	

Ferroics — *Turab Lookman (LANL)*

3:00 – 3:30	Nanomagnets: Imaging, Simulations, Magnetic Reversal	Dan Dahlberg (U. Minn)
3:30 – 4:00	Ferroelectric and multi-Ferroic Materials	Wenwu Cao (Penn State)
4:00 – 4:30	Magnetoelectrics	Cristian Batista (LANL)
4:30 – 5:15	Breakout Session / Close	

Thursday Jan 22, 2009

Computational Tools — *Frank Alexander (LANL)*

8:30 – 9:00	Combinatorial and Informatics Based Materials Design	Krishna Rajan (Iowa State)
9:00 – 9:30	Materials Design	Ivan Schuller (UCSD)
9:30 – 10:00	Visualization at the Nanoscale	James Ahrens (LANL)
10:00 – 10:30	Modeling Defects	Christopher Stanek (LANL)
10:30 – 11:00	Breakout Session / Coffee	

Clusters *Roland Schulze (LANL)*

11:15 – 11:45	The Evolution of Structural Order with Metal Cluster Size	Joel Parks (Harvard)
11:45 – 12:15	Quantum Many Body Theory for Atomic Clusters	Bogdan Mihaila (LANL)
12:15 – 12:45	Quantum Dot Synthesis and Characterization	Milan Sykora (LANL)
12:45 – 1:30	Final Breakout Session / Lunch / Close	

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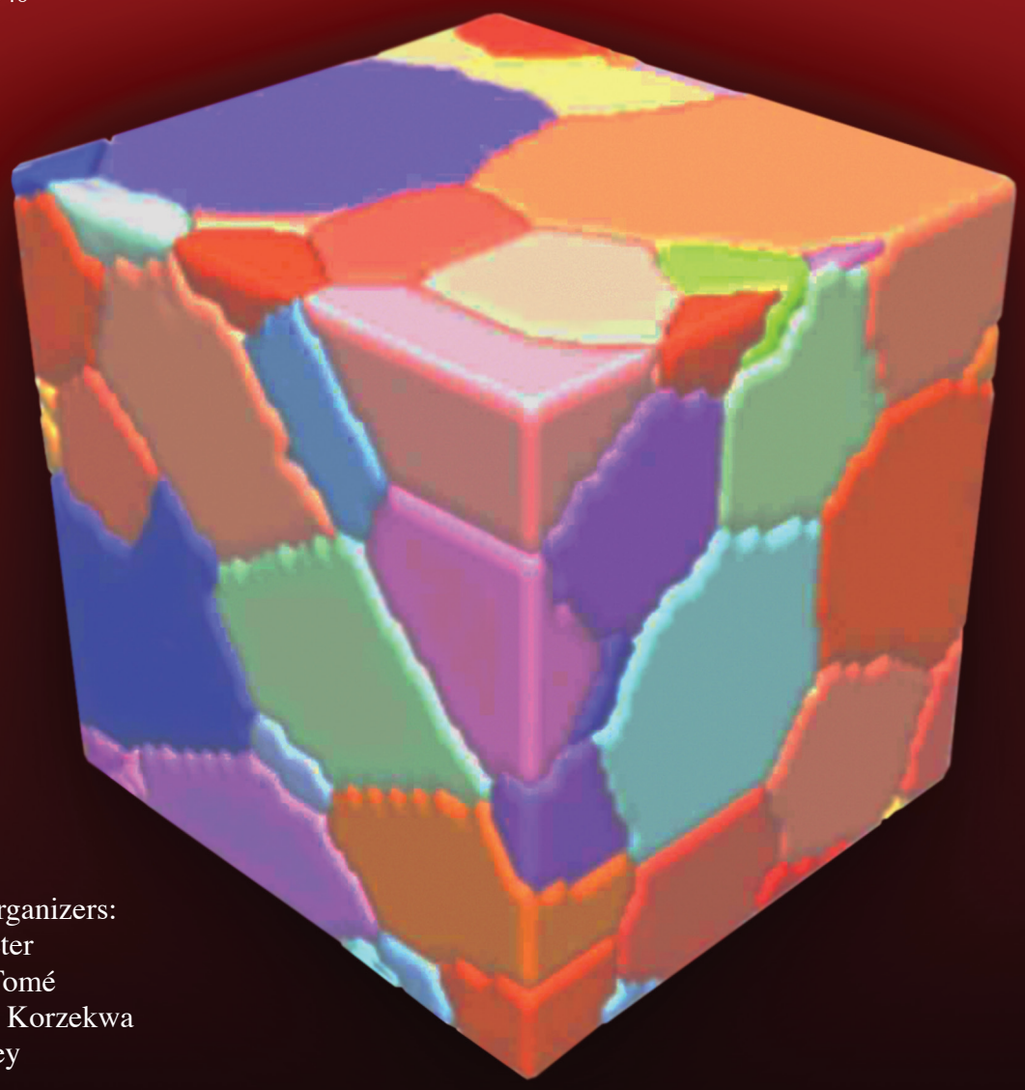
Structural Materials Under Extreme Conditions

A MaRIE Workshop
Los Alamos National Laboratory, July 29-31, 2009

Workshop Chairman: Bob Field

LA-UR-09-07540



Internal Organizers:
Dave Teter
Carlos Tomé
Deniece Korzekwa
Jim Foley

External Executive Committee:
Tresa Pollock (University of Michigan)
Ian Robertson (University of Illinois)
Darryl Butt (Boise State University)
Jim Williams (The Ohio State University)

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Executive Summary of MaRIE Workshop on Structural Materials

LANL is in the process of holding a series of focused workshops designed to engage the external scientific community and help define the facilities and capabilities to be incorporated into MaRIE. A three-day workshop focused on structural materials was held July 29-31, 2009 at LANL. The purpose of the workshop was to assess future needs in structural materials applications and supporting research, and to identify the developments and innovation necessary in the next ~10 years. Of particular interest was the development of in situ characterization techniques during processing, synthesis, and functioning of structural materials, along with supporting modeling to develop a predictive capability of materials performance.

The workshop was structured around a series of talks by both internal and external experts in structural materials development, production, application, and characterization. Speakers and attendees represented industry, academia and other National Laboratories. The talks and group discussions were asked to build upon current state-of-the-art work to define the experimental and modeling capabilities that will not only shape of the future of materials research at LANL and more broadly, but provide a new set of tools for the structural materials community at large. An external executive committee composed of Tresa Pollock (U. Michigan), Ian Robertson (U. Illinois), Darryl Butt (Boise State U), and Jim Williams (Ohio State U) played an important role in defining the overall structure of the workshop and the conclusions that emerged.

The workshop was organized into five sessions: (1) materials needs – specific applications, (2) materials modeling, (3), materials processing (4) materials characterization, and (5) specific properties/materials interactions. At the end of the talks we brought the speakers back to the front of the auditorium to facilitate a broader discussion based upon what was presented during the session and previous sessions. Recommendations were made in the following areas:

<u>Common Scientific Needs</u>

- Pressing technical problems
- Integrated Computational Materials Engineering (ICME)
- Broad range of environments for in situ experiments
- Multiscale capability
- Wide range of spatial and temporal resolution
- Multiple probes/detectors for simultaneous recording of disparate data
- New detector technology optimized for Materials Science
- 3D analysis
- Data management and analysis
- Data archiving and sharing

User Facility Considerations

- Flexible/modular design
- Shared experimental tools
- User support
- Educational component
- Hazardous/difficult materials
- Ancillary characterization facilities
- Computational capability

MaRIE Specific Technical Recommendations

- An integrated modeling/experimental approach is vital to the future of materials development. The approach for MaRIE in this area should be consistent with ICME.
- Multiple in situ extreme environments are needed to simulate real life conditions as closely as possible and investigate complex mechanisms of materials degradation and failure. This will require a flexible facility that can accommodate complex experimental apparatus.
- Major breakthroughs in the understanding of fundamental materials phenomena will require simultaneously active multiple probes and detectors to fully characterize the specimen during in situ experiments.
- Coordinated multiscale modeling and experiments are critical to success. The latter will require multiple probes with a range of spatial and temporal resolution and real time analysis of data in order to zero in on "hot spots" in the microstructure for more detailed analysis.
- In addition to the advanced probes proposed for MaRIE, advanced detector development could have significant impact on the community at relatively low cost.
- Advanced n-D microstructural characterization techniques and the tools to analyze the enormous data sets are needed. (n is 3D for spatial, plus time, grain orientation, strain, chemical signature, etc).
- There is a need for a large-scale facility dedicated to environmental/corrosion science. MaRIE could fulfill this need.
- There is a need for a facility that can routinely handle radioactive/hazardous material, with the ability to store samples for further analysis. MaRIE could fulfill this need.
- There is a need for a large-scale facility for in situ characterization of materials during processing (e.g. casting, thermomechanical processing, welding, etc.). MaRIE could fulfill this need.
- State-of-the-art characterization and modeling tools are needed in addition to the "beamline tool" for a more enhanced experience for visiting users. Example: having SEM, TEM, FIB, atom probe, spectroscopy available to further characterize the sample ex situ, with transfer capability between in situ experimental site and ancillary capabilities.
- MaRIE should have a strong educational component to develop personnel for interdisciplinary teams needed for the future success of this type of facility.

- Shared experimental tools, data, and models would strongly enhance the impact of a user facility. A NIH model could be implemented. NIH requires that models and data be available to all who are funded by NIH. "Superusers" with enhanced funding/access would have a greater opportunity/responsibility for developing sharable tools.
- Customer support in setting up experiments, and acquiring, storing, and processing huge amounts of information is vital for the user. General software and hardware should be maintained by the facility, with personnel allocated to this function.
- Effective data archiving and open dissemination is central to the future of collaborative materials research. This must be developed upfront at a high level, not in an ad hoc manner by individual researcher/groups.
- The mission of MaRIE should focus on only 2-3 major materials challenges and address them comprehensively and holistically. MaRIE would develop personnel, tools and integrated models that solve complex problems and lead to new materials solutions.

A1. Workshop Summary - Introduction

LANL is in the process of holding a series of focused workshops designed to engage the external scientific community and help define the facilities and capabilities to be incorporated into MaRIE. A three-day workshop focused on structural materials was held July 29-31, 2009 at LANL. The purpose of the workshop was to assess future needs in structural materials applications and supporting research, and to identify the developments and innovation necessary in the next ~10 years. Of particular interest was the development of in situ characterization techniques during processing, synthesis, and functioning of structural materials, along with supporting modeling to develop a predictive capability of materials performance.

The workshop was structured around a series of talks by both internal and external experts in structural materials development, production, application, and characterization. Speakers and attendees represented industry, academia and other National Laboratories. The talks and group discussions were intended to build upon current state-of-the-art work to define the experimental and modeling capabilities that will not only shape of the future of materials research at LANL and more broadly, but provide a new set of tools for the structural materials community at large. An external executive committee composed of Tresa Pollock (U. Michigan), Ian Robertson (U. Illinois), Darryl Butt (Boise State U), and Jim Williams (Ohio State U) played an important role in defining the overall structure of the workshop and the conclusions that emerged.

The workshop was organized into five sessions: (1) materials needs – specific applications, (2) materials modeling, (3), materials processing (4) materials characterization, and (5) specific properties/materials interactions. At the end of the talks we brought the speakers back to the front of the auditorium to facilitate a broader discussion based upon what was presented during the session and previous sessions. A summary of the individual talks and group discussions is provided below.

A2. Workshop Summary – Session/Presentation Summaries

Materials Needs - Specific Applications (Weds. 7/29 –AM) – Chair: Dave Teter

Integrated Computational Materials Engineering (ICME): A New and Essential Capability for Surviving Extreme Environments in the Automotive Industry, John Allison (Ford Motor Company)

This presentation outlined the challenges facing the auto industry, specifically Ford Motor Company. Dr. Allison presented the ICME concept promoted by the National Academy of Engineering (NAE) (see Figure 1) and an application of the ICME framework to the specific problem of Al alloy castings. The industry is driving materials design to provide faster turnaround, higher quality, lower costs, smaller and lighter components, and improved fuel economy and performance, all in an industry that has had to cut costs 50% in a year! Specific materials challenges noted

were (1) lightweight materials (AHSS, Al, Mg, CFRP); (2) high temperature and high strength materials for advanced power trains, and increased exhaust temperatures – primarily for improved fuel efficiency; (3) electrification (HEV/Plug-in/Full Electric): battery materials and manufacturing technology for zero fossil fuel use.

Ford implemented the ICME approach to casting modeling using a combination of continuum (OPTCAST), thermodynamic (ThermoCalc) and empirical (PanDat and Dictra) modeling in a serialized approach. Empirical models are costly, requiring significant amounts of materials testing to develop an accurate model, and cannot easily be extrapolated to other material systems or conditions. An opportunity exists in the area of microstructural modeling, currently not well implemented in the design models. Ford is exploring phase field modeling to develop accurate predictions of precipitate kinetics for modeling microstructural evolution.

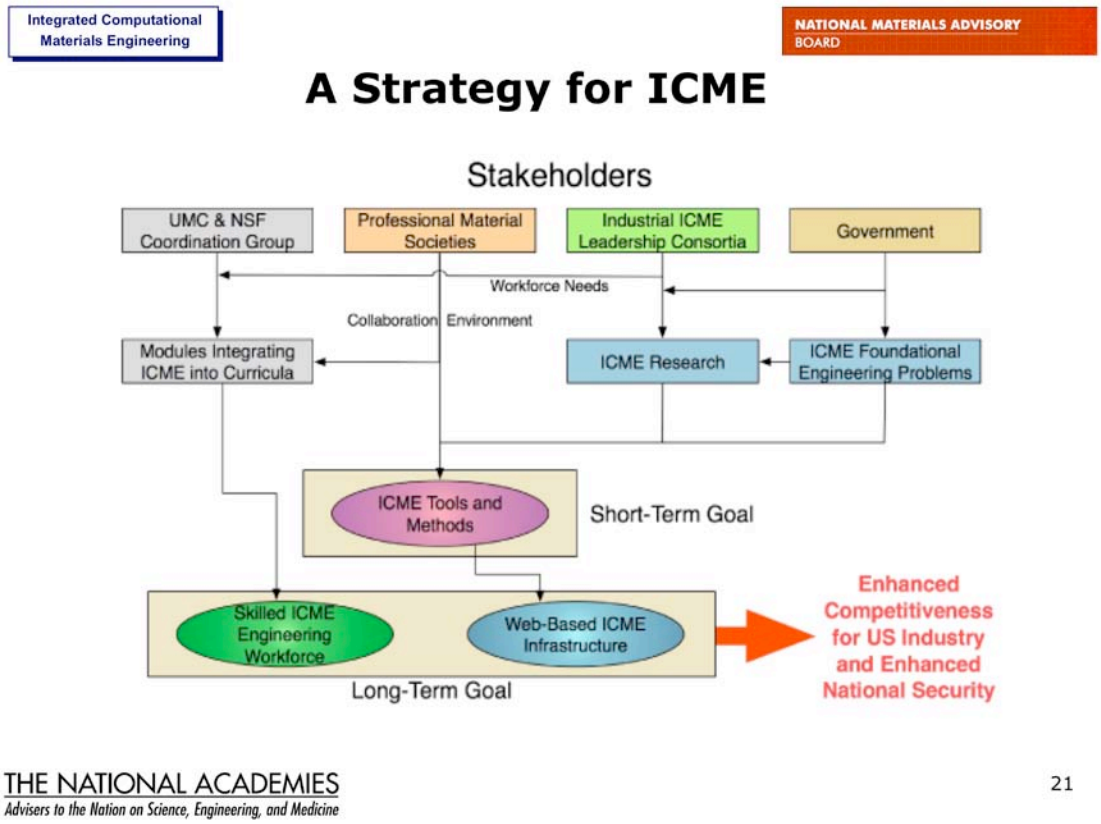

Figure 1. Integrated Computational Materials Engineering (ICME) strategy (J. Allison)

Structural Challenges in Nuclear Energy Systems, Steve Zinkle (Oak Ridge National Laboratory)

For advanced nuclear reactor designs and extension of current reactor lifetimes, a number of technological challenges must be addressed, including dose-temperature windows and burn-up limits, enhanced safety, minimized waste streams, and proliferation resistance. In the development of advanced materials for nuclear

reactor application, the economic impact must also be considered. Depending on the type of improvement, the net capital cost may be less or significantly greater than the current material design.

One of the goals of the nuclear energy industry is to have zero fuel failures by 2010, which requires being able to predict fuel life so maintenance can be planned. In order to achieve the goal of 100% failure-free performance, we need to address a wide range of physical mechanisms causing failure, including cladding-material corrosion, hydrogen content in cladding, oxide spallation (local blisters), radiation damage, and cracking. Radiation damage can cause large changes to structural materials, limiting their lifetimes. Phenomena which require a more quantitative understanding are: (1) radiation hardening and embrittlement (<0.4 T_M, >0.1 dpa), (2) phase instabilities from radiation-induced precipitation (0.3-0.6 T_M, >10 dpa), (3) irradiation creep (<0.45 T_M, >10 dpa), (4) volumetric swelling from void formation (0.3-0.6 T_M, >10 dpa), and high temperature He embrittlement (>0.5 T_M, >10 dpa).

Gen III and IV reactors require new materials with higher operating temperatures (>300˚C) and radiation damage limits (>50dpa). Thermodynamic and kinetic tools will be required to develop new alloys. Advanced characterization tools for highly radioactive materials are also needed; current facilities do not allow this, although some user facilities are becoming more open to the examination of radioactive samples.

Aerospace Materials, Jim Williams (The Ohio State University)

Materials problems in jet engines, rocket engines, and hypersonic aircraft were discussed in this presentation. The speaker stressed the importance of being able to develop new materials using a combined experimental/modeling approach to predict properties/performance in real applications, with a variety of environmental factors, including temperature, stress, pressure, time of exposure, rate of change of any of these, constant or cyclic exposure, and physical environments (e.g. air, vacuum, corrosive, H_2 gas, radiation). Large changes in any of these compared to previous experience represent an "extreme". Interpolation is possible if functional dependence is known, but extrapolation is risky. The difficulty is to accurately represent actual environments during experiments and properly define input parameters and interactions in modeling.

Major issues in jet engines are maximum operating temperature and time at temperature in hot sections. Rocket engines are more limited by large transients and gradients as well as H_2 and O_2 exposure. Hypersonic vehicles face extreme temperatures, requiring thermal protection, and ultraviolet exposure. Ni-base superalloys are currently operating at 80% of melting temperature, approaching their limits. Future advances are likely to come from hybrid materials (e.g. multi-materials systems with adaptive microstructures: MMSAM) with locally tailored properties. These can be made up of multiple classes of materials (e.g. metals/ceramics/polymers) or single classes with variations in composition and/or microstructure. These hybrid systems present new challenges in development and

property/performance prediction. Lastly, the speaker emphasized that materials are generally limited by minimum rather than average properties, so that understanding the weakest link in a microstructure is often most important (e.g. in fatigue). This concept was explored further in Prof. Jones' presentation on fatigue.

Materials Challenges in Oil and Gas Industry, Greg Kusinski and Jim Skogsberg (Chevron)

The two speakers addressed the two primary areas of concern for the industry: upstream (production, i.e. wells) and downstream (refining) processes. Similar issues arise in both cases, mostly revolving around corrosion/environmental properties. The vast scale of materials required also introduces large economic factors, pushing selection criteria in the direction of less expensive materials. Mechanistic understanding of degradation/failure mechanisms can go a long way to improving performance, lowering costs, increasing lifetimes (or inspection intervals), improving safety, and reducing environmental impact.

Corrosion environments vary widely, with concerns about chlorides (HCl), sulfur (H_2S), amines, high molecular weight carboxylic acids, naphthenic acid, and hydrogen effects at various temperatures (100-500˚C), with other complications including high fluid flows (erosion), high pressures, and thermal shock. Carbon steels are preferred for cost reasons, but Cr-Mo steels, stainless steels, and Ni-base alloys are also used. The ability to go to lower cost materials is highly desirable (e.g. higher strength/corrosion resistant low alloy steels or development of stainless steels to replace Ni-base alloys). There is a critical need for new materials or use of existing materials in new applications (e.g. Ti alloys or composites). The main interest with respect to facilities like MaRIE is the development of realistic in situ corrosion testing and modeling to predict performance of these materials. This requires proper definition of the environments (a significant challenge in itself, as pointed out by Prof. Williams) and testing under multiple, simultaneous environmental conditions, with multiple probes to assess complex mechanisms.

Group Discussion

Much of the discussion revolved around the role of modeling and supporting experimental work on reducing development time and cost and increasing the useful life of components by more accurately predicting failure. A systems (holistic) approach to modeling was advocated, along the lines of ICME. This would include integrated models of processing, performance, and failure, taking into account materials variability with the introduction of probabilistic distributions of defects. Experiments must more closely mirror actual application environments, so that critical failure mechanisms are not missed. This requires test cells to accommodate multiple environmental factors (e.g. temperature, stress/pressure, corrosive media, radiation, etc.) as well as multiple probes to evaluate material response.

The goal is not necessarily to eliminate the need for component/certification testing, but to better define the failure modes with increased confidence so that fewer, more targeted tests can be performed. Similarly, more robust models can be coupled with in-service diagnostics and NDE inspections to better predict failure, allowing

extended service of deployed components. This goal requires an integrated modeling approach, which does not necessarily capture all of the physics, but provides performance windows that can be used to drive development and guide in-service evaluation and repair/retirement decisions.

Materials Modeling (Weds. 7/29 –PM) – Chair: Carlos Tome

"Modeling and Experimental Characterization of Local Features (stress, strain, microstructure)", Carlos Tome (Los Alamos National Laboratory)

"Interrogating Grain Scale Deformation within a Polycrystalline Alloy using New Micromechanical Testing Techniques and Crystal-Based Elastic Plastic Material Models", Matthew Miller and Paul Dawson (Cornell University)

The presentations by Tomé and Miller tackled modeling of polycrystal aggregates and identified structural features relevant to the models and measurable using diffraction techniques. Both presenters have experience with neutron and X-ray synchrotron diffraction techniques. Both emphasized the need for 3D characterization of grain structures (morphology and orientation), plus capabilities for distinguishing size and shape of voids, twins or cracks. Both emphasized the need for measuring local strains as a conduit for calculating local stresses: resolution of local plastic effects at grain boundaries, near voids and twins, and intragranular stress-strain gradients. Typically 10μm features should be resolved for comparison to models. Depending on deformation regime (creep, quasi-static, high rate) full in-situ measurements of stress-strain evolution should be performed either instantly (as snapshots) and/or without interrupting deformation (in a continuous manner). In any case, full structure characterization times of the order of seconds are desired.

Numerically efficient mesoscopic models based on homogeneous deformation of grains embedded in an effective medium can be validated using Finite Element (FE) or Fast Fourier Transform (FFT) methods, which solve stress equilibrium and calculate local stresses and strains. Diffraction experiments will be used, in turn, to validate the FE or FFT results. At this scale, experiments and models co-validate, since neither is exactly assured. It is desired to measure hundreds of grains and to characterize their full stress tensors. Alternatively, it is also desired to focus on specific regions, such as in the vicinity of voids, cracks, twins, or grain boundaries, and measure localization effects in detail (~100nm). Once validated, the local numerical characterization will be used to benchmark Effective Field and Phase Field models, which are faster but based on homogenization assumptions.

"Multiscale Modeling of Deformation in Metals Under Extreme Conditions", Hussein Zbib (University of Washington)

"Phase Field Modeling of Coupled Displacive-Diffusional Processes", Yunzhi Wang (The Ohio State University)

The presentations by Zbib and Wang were more concerned with microscopic scales of materials. Dislocation cores, defect-dislocation interactions, irradiation cascade

dynamics and defect production, micro-cracking, transmissibility of dislocation across interfaces, radiation strengthening, nanolayer strength, mobility of dislocations, diffusivity, and precipitation.

Their models rely on Molecular Dynamics (MD) approaches coupled to Dislocation Dynamics (DD) or Phase Field methods (see Figure 2). The advantage of this approach is that very specific microscopic deformation mechanisms can be unraveled, especially at high rates, where experimental characterization is difficult. The spatial scale of the calculations is of the order nm's and time scale in μs's. The presentations focused well on modeling issues but did not necessarily address the connection with potential experimental characterization. The characterization of dislocations and cascades will require in-situ TEM and 3D characterization capabilities.

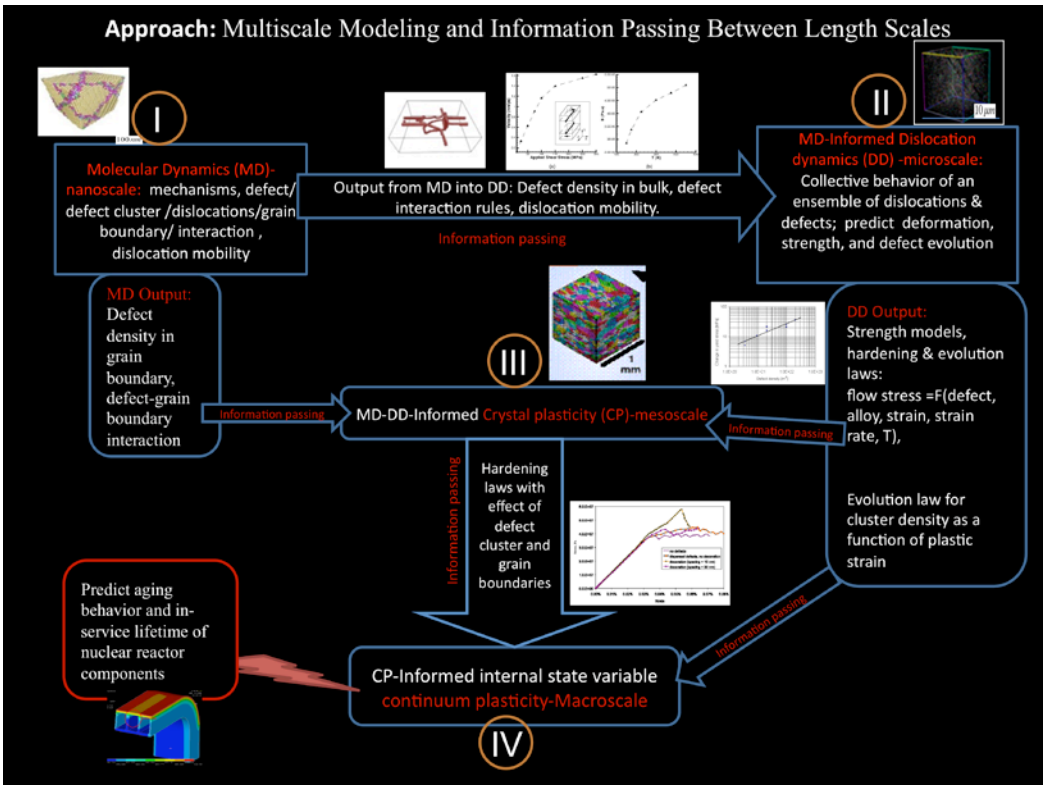

Figure 2. Multiscale plasticity modeling approach (H. Zbib)

Group Discussion:

Much of the discussion dealt with the experimental data needed to validate the models. The need for subgrain (100nm) resolution as well as sufficient temporal resolution to yield time resolved data without stress relaxation during the measurement was stressed. More details about dislocation core structure, intragrain dislocation structures, and transmission across boundaries are needed.

The subject of how to deal with stochastic processes was also discussed. Most models are deterministic, but material response exhibits a good deal of local variability. Phase field methods are well poised for dealing with complex

heterogeneities. Local variability sometimes determines the mechanical outcome. Capturing such variability with models and with experiments is high in the 'wish list' of materials scientists. New experimental and modeling approaches may be required for capturing the variability. An 'ensemble statistics' approach could be used, modeling several similar systems, taking averages, and comparing with experiments.

Materials Processing (Thurs. 7/30 A) – Chair: Deniece Korzekwa

"Solidification Modeling and Experiments – What we think we know and what we need", Deniece Korzekwa (Los Alamos National Laboratory)

Solidification modeling is valuable tool and saves a tremendous amount of time and money over a "trial and error" method of casting. The desire is for casting modeling to be more predictive, but to date the models still rely on a large amount of empirical data. There is a need for better understanding of underlying physics and kinetics as well as more precise data about interfaces and boundary conditions. Two examples of these needs are the undercooling and nucleation observed during phase change and the heat transfer coefficient between the metal and the mold wall (see Figure 3). There is also a need for more physical properties of alloys as a function of temperature, multi-component phase diagrams (equilibrium and metastable), and in situ observation of solidification processes. 3-D information is required to probe the intricacies of the solidification microstructure (see example in Prof. Pollock's presentation).

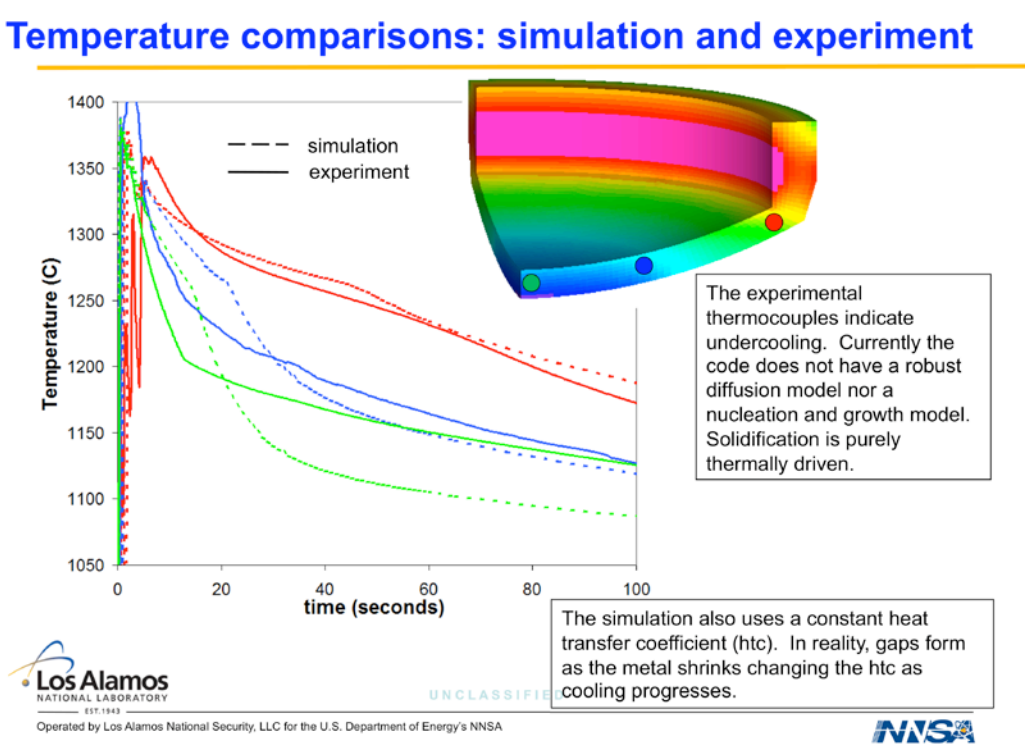

Figure 3. Comparison between casting model and experimental data (D. Korzekwa)

"Role of Joining Science in Developing Hybrid Structural Materials", Suresh Babu (The Ohio State University)

Joining is even more important as we move to hybrid materials. Prof. Babu posed three challenges: 1) fundamental understanding of joint formation, 2) mapping characterization into material models, and 3) optimization using integrated materials joining models. He also identified three needs: 1) more researchers to address materials joining problems, 2) infrastructure to measure thermo-mechanical transients at good spatial and temporal resolution, and 3**)** the industrial need for quick answers for rapid deployment with minimum experimentation.

How can we join materials without destroying the microstructure and properties? This is the scientific challenge. Extreme conditions are inherent to fusion processes, especially welding. The process is fast and variable. Thermal-physical material properties during rapid processing conditions are needed. Although integrated models are available to predict the performance of joints, a trial and error approach is still required to develop the correct properties and parameters. The mechanisms involved such high strain rates and high temperature gradients are not well understood. Traditional characterization methods such as EBSD can evaluate only the original and final materials. Thus, there is a need for in situ evaluation with high spatial and temporal resolution.

"Radiation Effects on Metal/Oxide Interfaces", Darryl Butt (Boise State University)

In nuclear power plants, water/metal interfacial corrosion plays a large part in the lifetime of the reactor. The ability to predict the service and maintenance requirements of all parts within the reactor will significantly reduce costs and failures. Radiolysis plays a large part at the corrosion interface. If the short-lived products at the surface react, we need to understand how the surface oxide and the underlying metal are affected. In most cases the interface structure is not well understood. Future needs include in situ probes to measure the corrosion reactions at the interfaces in radiation environments, remote diagnostics, electrochemical measurements, and multi-scale modeling, particularly of the radiation-corrosion-oxide-metal interface. The importance of education, outreach, long term commitment, collaboration, and collegiality was stressed.

"Exploiting the Power of Powder Synthesis Reactions for Advanced Structural Materials", Iver Anderson (Ames Laboratory)

Nuclear and coal power plants require a high temperature (900˚C), long lifetime, structural material. Oxide dispersion strengthened steels are one option that is being explored. The current processing pathway requires high energy, longtime ball milling for mechanical alloying and results in a product that is prone to contamination and hard to control. Gas atomization followed by hot isostatic pressing (HIP) would be a simplified process, but the atomization needs better characterization and control. The Gas Atomization Reaction Synthesis (GARS) process being developed uses controlled atmospheres during atomization to introduce oxide layers that can diffuse and react during HIP to form dispersoids.

However, the atomization/reaction process is not well understood. We need to understand the wave breakup and droplet formation and be able to image the surface of the droplets and the droplet temperatures. This requires in situ experimental capabilities for imaging two-phase flow with high spatial (10μm) and temporal (μs) resolution. In situ monitoring of oxygen diffusion and dispersoid formation during HIP is also needed. This needs to be coupled with modeling, with phase field modeling approaches of particular interest.

Group Discussion:

Much of the discussion concerned the nature of collaborative research, particularly with respect to large user facilities, and the mission of a facility like MaRIE. There was a consensus on the need for collaboration, as no single institution has the resources to address large technical problems. The consortium approach was discussed, with the Advanced Steel Processing & Products Research Center (ASPPRC) at Colorado School of Mines as an example. One challenge of this approach is handling intellectual property, particularly when specific technology is involved. It was suggested that a CRADA like model might be applicable. A specific question arose as to whether the atomization unit at LANL could be used in conjunction with MaRIE, as research capabilities in this technology are waning.

There was discussion as to the goals of MaRIE and many believed that it should be focused on one - or a few - large problems that can be taken from start to finish (e.g. processing to performance). This was thought to be good both for development and student education and training, but requires processing/production as well as characterization capabilities. MaRIE could be a showcase for this approach. Integration of modeling with experiment was again emphasized, with the need for computing facilities as well as programs on method development and data reduction. The topic of staging and experimental set up was discussed. This is time consuming and the need for assistance in this area was expressed. A modular design with separate staging/set up areas may address this issue.

Characterization (Thurs. 7/30 PM) – Chair: Bob Field

"In Situ Neutron Diffraction Techniques", Sven Vogel (Los Alamos National Laboratory)

The speaker presented an outline of LANSCE current capabilities, particularly SMARTS and HIPPO. He also summarized proposed and ongoing capability enhancements, including those that are part of the Enhanced Lujan Project. Improvements include a hot cell diffractometer, the LAPTRON instrument (diffraction, radiography, ultrasonic testing, deformation, and calorimetry in a single instrument), as well as improvements in detectors (to increase acceptance angles and time resolution as well as allow for smaller specimens), better beam focusing and collimation, and more user-friendly software to make advanced analysis techniques faster and more routine.

"Characterization of Phase Transformations in Structural Materials Under Extreme" Conditions", Mike Kaufman (Colorado School of Mines)

The talk emphasized the importance of combining multiple techniques in characterizing microstructures. Specific examples were provided in the use of high resolution (aberration corrected) S/TEM, focused ion beam (FIB), local electrode atom probe (LEAP), and modeling to solve problems of phase transformations, interfaces, and radiation damage. In-situ techniques were also discussed, particularly with regard to S/TEM, including dynamic TEM (DTEM), which has the potential to probe reactions in materials with high temporal and spatial resolution. The speaker also referred to the 2006 NSF Workshop Report: "Dynamic in-situ electron microscopy as a tool to meet the challenges of the nanoworld", which emphasized the need for centralized facilities and expertise with remote access and teaching capabilities and funding for development of new techniques.

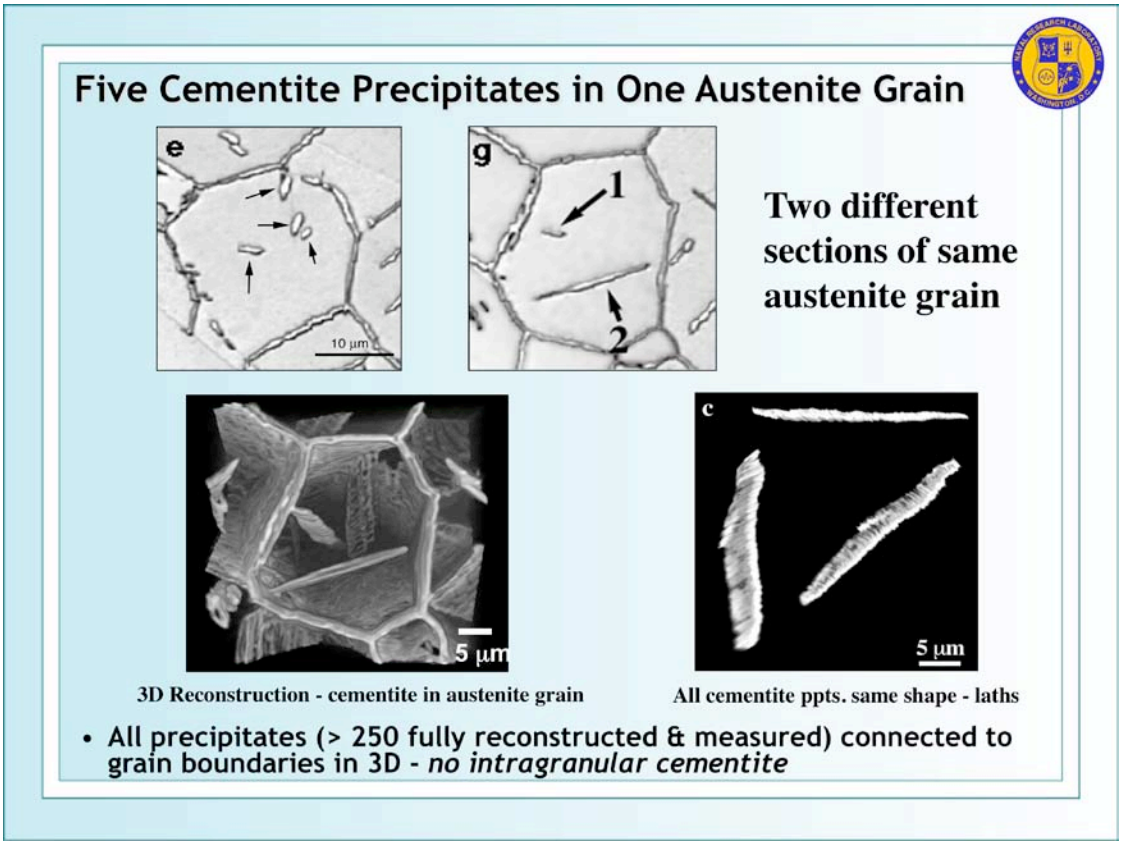

Figure 4. Example of the need for 3-D microstructural characterization techniques (A. Geltmacher: M. V. Kral and G. Spanos, *Acta Materialia*, **47,** 711-724 (1999))

"3D Microstructural Characterization and Analysis", Andy Geltmacher (Naval Research Laboratory)

A summary was presented of recent work at NRL in 3D data collection, analysis, and modeling. The need for 3D investigations of microstructures was emphasized with examples from real systems in which important aspects of the microstructure are missed in 2D characterization, e.g. "intragranular" cementite in steels is actually all

connected to the grain boundaries, generally to edges and corners (see Figure 4). Also 2D characterization tends to miss "outliers" (e.g. large grains) that can dictate properties. 3D also allows new types of data (e.g. crystallographic interface normal distribution – CINT) to be correlated with properties. Experiment/modeling links were also discussed, including incorporating experimental data into models and more efficient modeling through generating relevant volume elements (RVE) via multiple statistical volume elements (SVE) to generate representative properties. Future needs include higher resolution and larger volume characterization, both in situ and ex situ, better experimental/modeling approaches to achieve "materials by design" goals, and determining microstructure/property relationships from large data sets.

"High Energy X-Ray Diffraction Microscopy: Access to Volumetric Microstructural Responses", Robert Suter (Carnegie-Mellon University)

The talk summarized high energy x-ray diffraction microscopy (HEDM) techniques, near field measurements (e.g. grain mapping) and far field measurements (e.g. single grain strain distributions). Current spatial resolution is in the micron range for volumes of several mm^3; however, collection times are long (~12hrs.). This work generates large data sets; data sets will grow even larger if more details of the microstructure are analyzed, such as strain distributions in association with subgrain boundaries. These techniques can also be combined with microtomography (e.g. to map voids), but association of these features with the microstructure is problematic. Other future challenges include decreased collection times to allow better in situ experiments. This will require small, high flux, high energy beams; fast, efficient, large detectors; and human resources to develop hardware and software to analyze large data sets.

"In-Situ 3D X-Ray Techniques", Erick Lauridsen (RISO, Denmark)

This talk also involved 3D x-ray techniques, but addressed several different techniques, including several tomography techniques (absorption, phase contrast, diffraction contrast, holo-, and topo-tomography). The speaker emphasized the concept of 4D characterization (3 spatial dimensions and time) and the trade-off between spatial and temporal resolution. Several examples were presented in which simultaneous collection of data using a combination of techniques was used to address different problems. The need for better detectors to improve spatial and temporal resolution was stressed - today's detectors were developed for the medical imaging industry and are not optimized for materials science problems. The need for high beam quality (flux, brilliance, and stability), simultaneous use of multiple image modalities, and dedicated software development, with special focus on automation and user friendliness to handle large data sets, was also discussed. The need for data analysis was again stressed, as well as archiving. This must be addressed by the experts (many exist in the biological community).

Group Discussion:

The use of multiple, simultaneous characterization techniques is the best approach to solve complex scientific and technical problems, both during an in situ

experiment and before/after. The need for ex situ pre and post experiment characterization was discussed (this is part of the function of the M4 facility). There was a lively discussion of the need for better detectors and better definition of what detectors we need. This is a particularly challenging problem with a multiple probe facility, requiring multiple detectors. We must define what detectors are needed and develop them. Most of the detector technology comes from the medical imaging community and is not optimized for material science. Detector development would be a relatively inexpensive effort (compared to building large beam lines).

Data analysis and archiving at MaRIE will be critical to its success. This includes memory issues (these experiments create huge data files, e.g. in the terabyte range), data reduction, analysis and visualization, and the ability to archive and make widely available large amounts of data. This needs to be done by experts, not ad hoc by individual researchers or groups. The biological community is very good at this and is looking for other areas to apply their tools (Marc DeGraef at Carnegie-Mellon Univ. was given as an example of someone interacting with the biological community in this area). NIH also has requirements for open source of data generated by their funding that promotes collaborative research. The nature of multiscale experiments, vis-à-vis multiscale modeling was also discussed. Modelers start at the fine scale and work up to meso- and macro-scale. Experimenters often do this in reverse, looking at the overall system and then zeroing in on "hot spots". This requires real time data analysis to recognize areas of interest and focus in on them.

Specific Properties/Materials Interactions (Fri. 7/31 AM)– Chair: Jim Foley

"Challenges in Materials Degradation by Corrosion: Needs for Prognosis and Computational Materials Design", John R. Scully (University of Virginia)

Prof. Scully pointed out that most corrosion work is empirical with little predictive capability. Moreover, there is a need for a centralized location for corrosion work. This was cast into experimental/modeling approach of ICME (see John Allison's presentation), with the goal of not only predicting performance of new parts, but residual lifetimes based on inspection. Other needs are the ability to measure isolated electrochemical properties at finer length scales. The multiscale nature of corrosion problems was stressed in this context (see Figure 5). Similar to fatigue, corrosion failure is often driven by defects and local events (weakest element) as opposed to average behavior, making multiscale approaches even more important. Corrosion has some overlap with hydrogen embrittlement, because of the formation of hydrogen during the formation of some corrosion products.

Needs for a facility like MaRIE are: multiple simultaneous tools and probes to advance characterization of governing heterogeneities at sub-micrometer scale (electrochemical, chemical, mechanical, other); ability and create model analogs that can be tested with confidence, exploiting rescaling as necessary (both isolated and reassembled to model complex microstructures); development of models that can accept as inputs environmental stresses, physical, as well as metallurgical factors

and can output properties or attributes, some at the engineering level; and rational connection of length and times scales such that atomic scale information is of value to engineers.

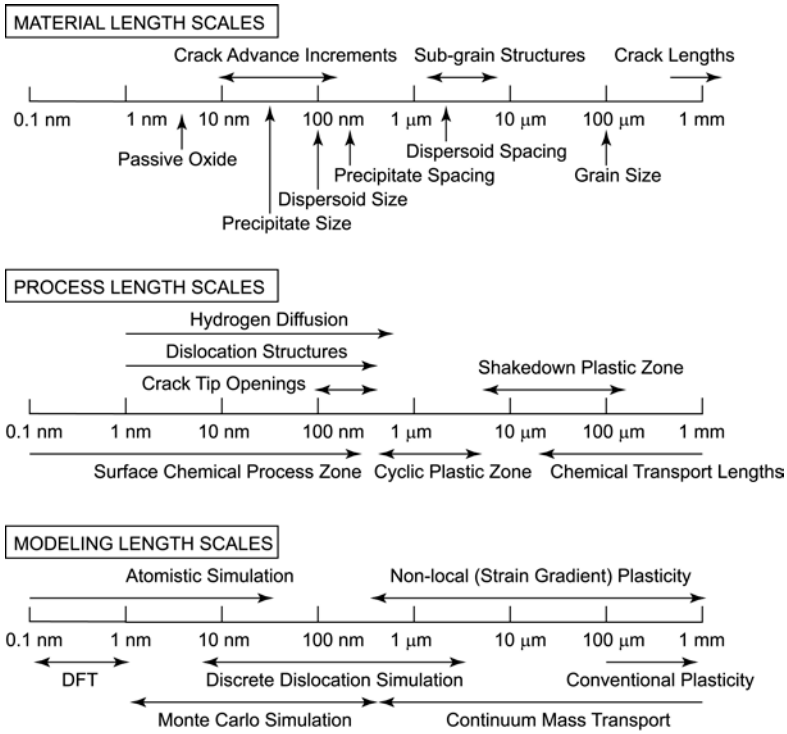

Figure 5. Length scales of corrosion processes and current modeling capabilities (J.R. Scully)

"Hydrogen Embrittlement – current status and future directions", Ian M. Robertson (University of Illinois)

There are several different mechanisms for hydrogen embrittlement; the principal mechanisms are decohesion (either of the general lattice or at defects such as grain boundaries and precipitates) and enhanced plasticity (especially near crack tips) as hydrogen segregates to dislocations. To distinguish between these and determine details of the mechanisms requires us to determine not only how hydrogen gets into a sample, but where the hydrogen is located in a given sample and how it moves. Hydrogen location has to be determined in 3D, dynamically and at the atomic level, in order to have the greatest impact on fundamental understanding.

In situ electron optical techniques have contributed greatly to our understanding of this phenomenon, but higher spatial and temporal resolution techniques will be needed. Hydrogen often acts in concert with other impurities and defects to cause embrittlement. Hydrogen embrittlement has some overlap with fatigue since fatigue resistance is reduced with the presence of hydrogen. Hydrogen embrittlement arises in a number of technological areas, as reflected in other presentations, and therefore represents a challenging problem with broad impact.

"Understanding the Role of Microstructure Variability on Fatigue Behavior", J. Wayne Jones (University of Michigan)

Prof. Jones presented results from research on very high cycle fatigue (VHCF, $>10^7$ cycles), where the variability of life is so large that the concept of a "fatigue limit" becomes unreliable. In this regime, microstructural variability becomes even more important and the need for multiscale/multiprobe experiments becomes critical. There is a need to identify the weakest volume element (WVE), rather than the representative volume element in modeling as well as experiments. This volume element is no longer necessarily a defect, but a microstructural feature, such as a large grain (or cluster of like oriented grains), carbide, or precipitate/dispersoid cluster. Experimentally, it may be necessary to identify this defect during the experiment and then focus in on it for more detailed analysis. He described in situ experiments conducted at APS to identify initiation sites and follow crack propagation.

In addition to his technical discussion, Prof. Jones commented on the philosophy of a large user center. He stated that such a facility should look for impact, not necessarily uniqueness. He also stressed the importance of building a user infrastructure that supports young faculty members to develop strong collaborations with lab scientists/engineers and other users.

"High Temperature Materials: What Next?", Tresa Pollock (University of Michigan)

Prof. Pollock pointed out that most extreme engineering systems are limited by the materials from which they are made. She stressed the need for an integrated suite of material models to design materials for multiple conditions, with models driving experimental work. Integration is often more important than complexity, with simple models, representing 80% of the physics, often sufficient if they are integrated to provide a useful design tool. Prof. Pollock presented many examples where an integrated model, based on the ICME approach, could be used to predict the best solution, including turbine discs and hybrid materials solutions for hypersonic vehicles. She stressed the need for 3D analysis, from the μm to cm range, to properly characterize microstructure, with examples of solidification structures using optical techniques and precipitate distributions in steel using a femtosecond laser ablation technique. Prof. Pollock also reiterated the important role of hybrid materials in addressing future materials challenges, with examples including thermal barrier coatings and zero expansion composite structures, consisting of geometrical arrangements of diverse materials that minimized differential expansion effects.

Prof. Pollock's thoughts on user facilities reflected her belief (widely held by the participants) that the future of materials research rests on large, collaborative projects requiring archival databases and models to promote interdisciplinary collaboration. She pointed to success stories from other communities, such as the genome project, in which specific, quantitative goals and a structure that promoted collaboration and data dissemination contributed to the success. This included "Support of research training of pre and postdoctoral fellows until a critical mass of

students with the right combination of computational and experimental skills is available".

Group Discussion:

Most of the discussion concerned how the facility should be set up and operated. The consensus was that the community is too fragmented and MaRIE could be a model for promoting open, collaborative research. This should include not only collaborators connected by funding (the traditional approach) but by a common scientific problem. The vision was a large collaborative team, both on and off site, working on any given experiment, requiring remote as well as local facility access. Remote access for experimenters would also be useful for training and preparation for experiments, maximizing the use of on-site time.

The importance of educational out reach was also emphasized. The need for local assistance for setting up experiments was discussed: from things as simple as having a machine shop for last minute modifications or repairs, to instrument specialists to assist users, ex situ characterization capabilities, and computational capabilities (hardware and software) – not just a "here's the beam" approach. Separate hutches, away from beam lines, that can be used for staging were recommended. The European concept of "superusers" (external and internal) that are funded to develop capabilities that can then be shared by other researchers was introduced. This could include software/modeling as well as complex experimental modules, designed for general use (i.e. user friendly but adaptable).

B. Common Scientific Needs

Pressing Technical Problems: Several specific materials problems that are considered to be vital to technological challenges were brought up during the workshop:

- Develop an understanding of microstructure variability and the relationship of that variability to material failure such as crack initiation in fatigue and corrosion pitting. This requires a multiscale experimental/modeling approach.
- There is a need for a large-scale facility dedicated to environmental/corrosion science. Hydrogen in materials is a particularly ubiquitous phenomenon that affects many different technological problems. The details of where the hydrogen resides in the materials microstructure as a function of time and environment and the mechanisms of hydrogen induced material degradation are of vital interest to the community. This will require spatial resolution from μm to the atomic regime and temporal resolution down to the μs level.
- Materials processing provides many opportunities for the development of new, novel materials. Models might tell us what optimum structure is, but how do we develop these processes? For example, many structural material applications rely upon casting as the processing route because it is relatively quick, cheap and efficient. Most codes today only predict the thermal history of a casting, and then use either inference or empirical tools to predict microstructure in a general

sense. In order to become more predictive with our casting modeling codes, we need a better understanding of the microstructural processes occurring during solidification, e.g. nucleation and growth phenomena, chemical partitioning, grain orientation, and phase changes after solidification. For most applications this would need to be done at the micron scale and in the time scale of seconds.

Integrated Computational Materials Engineering (ICME): Modeling is integral to design and optimization in the development of advanced materials. Therefore a strong modeling component (software and hardware) is vital to the success of a facility like MaRIE. The link between modeling and experiment must be made throughout the material lifecycle: from manufacturing through performance to final retirement, with covalidation between experiments and models. From the industry perspective, cost needs to be an integral part of the modeling and materials design framework. Note that cost is not part of the traditional materials tetrahedron and may need to be included. This concept has been considered in detail by the National Materials Advisory Board of the National Research Council of the National Academies in their report: "Integrated Computation Materials Engineering (ICME) [1]. ICME is the integration of materials information, captured in computational tools, with engineering product performance analysis and manufacturing-process simulation. In essence this is a design framework that integrates materials processing, microstructural, property, and performance models. Optimization via ICME reduces development time and costs and increases the confidence in fielding a new design.

Broad range of environments for in situ experiments: In situ experiments are particularly useful in understanding mechanisms in materials. There is a need to perform experiments under a broad range of environments, including stress, stress/strain rate, pressure, chemical environments, temperature, temperature rates/gradients, radiation, etc – and combinations of these. Defining and reproducing environments are both often difficult and will require multiple environmental factors imposed simultaneously on the specimen during the experiment. A flexible, modular design for experimental apparatus is particularly important to allow a wide range of environments to be explored.

Multiscale capability: Many materials problems require characterization of the sample on different length scales with varying resolution, even in the same experiment. Fatigue studies are a good example. Because of the stochastic nature of fatigue failure, the important life-limiting microstructural feature is not necessarily identified by monitoring a representative volume element (RVE), but the weakest volume element (WVE). A general survey of the sample, covering mm^3 or greater volumes with relatively low spatial resolution is required initially to identify the initiation site (i.e. WVE) and its relationship to the overall microstructure, followed by more detailed analysis of this element during subsequent crack growth. This requires the ability to analyze data in real time to identify pertinent features and focus in on these features during the remainder of the experiment. Many other

[1] NAE ICME Report, 2008

examples of the need for this capability can be identified. This capability is the experimental compliment to multiscale modeling. One suggestion was to combine multiple characterization tools and materials processing into a single connected instrument so that a material could be processed, exchanged in controlled environment to the characterization wing, transferred back to processing, and then transferred to further characterization of structure or properties.

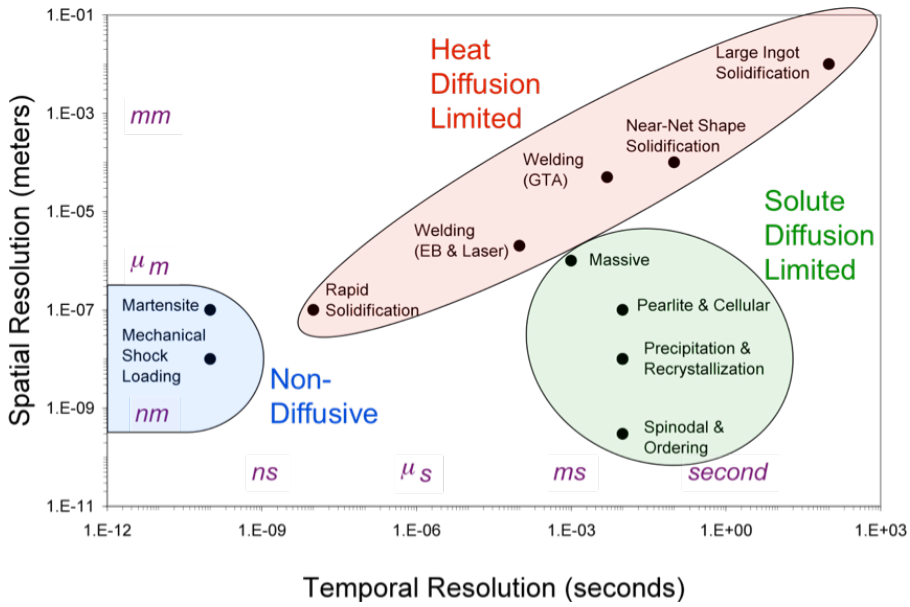

Figure 6. Resolution requirements for various phase transformation (R.E. Hackenberg, LANL)

Wide range of spatial and temporal resolution: The required spatial and temporal resolution is variable depending on the experiment and there are generally trade-offs between the two as well as the nature of the signal being collected. As stated above, different levels of resolution may be required within a single experiment. Temporal and spatial resolution are not as important for most structural materials as they are for functional materials, in which the operative mechanisms occur at atomic level in time intervals measured in picoseconds. Neither is temporal resolution as important here as it is for shock experiments (considered as separate issue for the sake of this report, since a separate workshop was conducted on this subject). However, the need for high spatial and temporal resolution is certainly present, particularly in cases where more detailed information is to be collected. For many of the structural materials applications of interest we would like timescales on the order of msec to sec. There are some applications that also require time resolution down to ns or μs for investigations of nucleation events, e.g. twin or martensite nucleation. The various regimes of temporal and spatial resolution required for a variety of phase transformation studies are summarized in Figure 6.

Multiple probes/detectors for simultaneous recording of disparate data: Once an experimental apparatus has been developed to produce a specific environment for in situ testing, the more information that can be collected during the experiment, the better the chance of obtaining a true understanding of the mechanisms being investigated. This requires multiple probes and detectors that can simultaneously gather data during the experiment. One example cited was the VULCAN diffractometer at the ORNL SNS facility, which combines small angle (SANS) and high angle detectors in the same instrument. One speaker stated that the ideal probe would have the "penetration of neutrons, detection speed of x-rays, and resolution of electrons". Obviously a single probe cannot achieve this, but strides toward this ideal can be achieved using multiple probes, as well as multiple detectors to gather different aspects of the signal.

New detector technology optimized for Materials Science: Many talks focused on the need for improved detector technology for neutrons and X-rays: increased sensitivity, spherical shapes, semi-transparent, etc. Most beam users today rely on commercial technology developed by the medical imaging industry. With current technology, it may take several days to collect the multiple data sets (e.g. as a function of time in the environment or strain) for a single experiment. Advanced detector development can address this issue and represents a potential opportunity for MaRIE to help the overall scientific community. This would be relatively inexpensive compared to the development and construction of large beam lines.

3D analysis: Advanced n-D microstructural characterization techniques and the tools to analyze the enormous data sets are needed (n is 3D for spatial, plus time, grain orientation, strain, chemical signature, etc). Several examples were presented in which 2D characterization provided a false or incomplete understanding of the microstructure. The need for 3D analysis increases the time necessary for data collection as well as the amount of data collected. Current experimental capabilities (serial sectioning and EBSD analysis) require approximately 2 weeks to setup and collect grain orientation data with 1μm resolution and analyzed volume of 200 x 500 by 1000μm.

Data management and analysis: Data sets from some of the experiments referred to above are currently in the 3-10 Tb range and data analysis can take months to years. The increasingly large and complex (e.g. n-D) data sets that will arise from the experiments anticipated in the future demand a much more sophisticated approach to data management and analysis. Customer support in acquiring, storing, and processing the huge amount of information generated is vital for the user. In the words of one participant, a goal of MaRIE should be to "go from heroic to routine effort for analyzing the data collected". There should be a parallel funding program to help with method development and data reduction. The goal should be to develop standardized data reduction and visualization algorithms, particularly for large 3D data sets, that are automated and user friendly (e.g. an interactive "gaming" interface).

Data archiving and sharing: Open sharing of data and analysis software is vital to the future development of new and novel materials. The need for curated, shared

databases, with standardized formats, was strongly emphasized. Several participants pointed to the medical and biological community as a model for the development and implementation of this concept. For example NIH requires that models and data developed using their funding be available to all who are funded by NIH.

C. User Facility Considerations

Flexible/modular design: One of the limiting factors at many large user facilities is the time that it takes to assemble the experimental apparatus on site. The more assembly that can be achieved before installation at the beam line site, the more efficient the facility becomes. A flexible design at the beam line that allows for modular experimental apparatus design, as well as staging areas for assembly, will greatly enhance the productivity of the user. Remote facility training will also allow users to take better advantage of their time on site.

Shared experimental tools: Once an apparatus has been built for a particular purpose, the ability for other users to take advantage of this equipment enhances its utility. The concept of the "Superuser" from European facilities was introduced. This class of user can be internal or external. He/she has more extensive access to the facility as well as development funds. In return, developments by this user must be available to others for their experiments.

User support: Customer support in setting up experiments, as well as acquiring, storing, and processing the huge amount of information generated is vital for the user. Coordinating communication/collaboration between experts in different fields is also necessary, as no individual has enough resources to develop these complex experiments alone.

Educational component: There is a need to develop the right kind of students and staff for a multi-disciplinary facility like MaRIE. Students have to be trained to work as a team and understand multiple disciplines as opposed to be narrowly focused on their specific research area. A summer school model similar to Lujan's would also be appropriate.

Hazardous/difficult materials: The need for the ability to handle a wide variety of hazardous/difficult materials was emphasized. Given the mission of LANL, the ability to deal with radioactive materials and store them for future analysis after experiment is essential.

Ancillary facilities: A complete and up to date characterization facility for post mortem analysis is needed. This facility should have the ability bring to bear a combination of complimentary techniques for analyzing the specimen, e.g. TEM, SEM with focused ion beam (FIB) capability, and 3-D atom probe (LEAP). The ability to perform in situ experiments at this facility, such as dynamic TEM (DTEM) is also essential for any modern materials facility, as well a 3-D characterization (e.g. TEM tomography). On-site facilities as common such as machine shops are also recommended.

Computational capability: Modeling is also a critical component of any modern materials facility. This aspect has been discussed in previous sections, but is reiterated here. Advanced computational capabilities are a vital component to the integrated experimental/modeling approach.

D. MaRIE Specific Technical Recommendations

- An integrated modeling/experimental approach is vital to the future of materials development. The approach for MaRIE in this area should be consistent with ICME.
- Multiple in situ extreme environments are needed to simulate real life conditions as closely as possible and investigate complex mechanisms of materials degradation and failure. This will require a flexible facility that can accommodate complex experimental apparatus.
- Major breakthroughs in the understanding of fundamental materials phenomena will require simultaneously active multiple probes and detectors to fully characterize the specimen during in situ experiments.
- Coordinated multiscale modeling and experiments are critical to success. The latter will require multiple probes with a range of spatial and temporal resolution and real time analysis of data in order to zero in on "hot spots" in the microstructure for more detailed analysis.
- In addition to the advanced probes proposed for MaRIE, advanced detector development could have significant impact on the community at relatively low cost.
- Advanced n-D microstructural characterization techniques and the tools to analyze the enormous data sets are needed. (n is 3D for spatial, plus time, grain orientation, strain, chemical signature, etc).
- There is a need for a large-scale facility dedicated to environmental/corrosion science. MaRIE could fulfill this need.
- There is a need for a facility that can routinely handle radioactive/hazardous material, with the ability to store samples for further analysis. MaRIE could fulfill this need.
- There is a need for a large-scale facility for in situ characterization of materials during processing (e.g. casting, thermomechanical processing, welding, etc.). MaRIE could fulfill this need.
- State-of-the-art characterization and modeling tools are needed in addition to the "beamline tool" for a more enhanced experience for visiting users. Example: having SEM, TEM, FIB, atom probe, spectroscopy available to further characterize the sample ex situ, with transfer capability between in situ experimental site and ancillary capabilities.

- MaRIE should have a strong educational component to develop personnel for interdisciplinary teams needed for the future success of this type of facility.
- Shared experimental tools, data, and models would strongly enhance the impact of a user facility. A NIH model could be implemented. NIH requires that models and data be available to all who are funded by NIH. "Superusers" with enhanced funding/access would have a greater opportunity/responsibility for developing sharable tools.
- Customer support in setting up experiments, and acquiring, storing, and processing huge amounts of information is vital for the user. General software and hardware should be maintained by the facility, with personnel allocated to this function.
- Effective data archiving and open dissemination is central to the future of collaborative materials research. This must be developed upfront at a high level, not in an ad hoc manner by individual researcher/groups.
- The mission of MaRIE should focus on only 2-3 major materials challenges and address them comprehensively and holistically. MaRIE would develop personnel, tools and integrated models that solve complex problems and lead to new materials solutions.

Agenda

"Structural Materials Under Extreme Conditions"
MaRIE Workshop

Materials Science Laboratory (MSL)
July 29 – July 31, 2009

Wednesday, July 29th

7:15 – 8:20	Badging, Badge Office, TA-3, Bldg. 0261	Sheila Girard

AM Session: Materials Needs - Specific Applications – Chair: Dave Teter

8:30 – 8:40	Welcome/Announcements	Dave Teter LANL
8:40 – 9:10	MaRIE Overview	John Sarrao LANL
9:10 – 9:40	"Integrated Computational Materials Engineering: A new and essential capability for surviving extreme environments in the automotive industry"	John Allison Ford
9:40 – 9:50	Break	
9:50 – 10:20	"Structural Materials Challenges in Nuclear Energy Systems"	Steve Zinkle ORNL
10:20 – 10:50	"Aerospace Materials"	Jim Williams Ohio State U
10:50 – 11:20	"Materials Challenges in Oil and Gas Industry"	Greg Kusinski Jim Skogsberg Chevron

11:20 – 12:00 Discussion

12:00 – 1:30 Lunch (on your own)

Agenda

PM Session: Materials Modeling – Chair: Carlos Tome

1:30 – 1:40	Session Introductions/Announcements	Carlos Tome LANL
1:40 – 2:15	"Modeling and Experimental Characterization of Local Features (stress, strain, microstructure)"	Carlos Tome LANL
2:15 – 2:50	"Interrogating Grain Scale Deformation within a Polycrystalline Alloy using New Micromechanical Testing Techniques and Crystal-Based Elastic Plastic Material Models"	Matthew Miller Paul Dawson Cornell U
2:50 – 3:05	Break	
3:05 – 3:40	"Multiscale Modeling of Deformation in Metals Under Extreme Conditions"	Hussein Zbib U Washington
3:40 – 4:15	"Phase Field Modeling of Coupled Displacive-Diffusional Processes"	Yunzhi Wang Ohio State U
4:15 – 5:15	Discussion	
5:15	Adjourn	
6:30	Informal Dinner	

Thursday, July 30th

AM Session: Materials Processing – Chair: Deniece Korzekwa

8:15 – 8:30	Session Introduction/Announcements	Deniece Korzekwa LANL
8:30 – 9:05	"Solidification Modeling and Experiments - What we think we know and what we need."	Deniece Korzekwa LANL
9:05 – 9:40	"Role of Joining Science in Developing Hybrid Structural Materials"	Suresh Babu Ohio State U

Agenda

9:40 – 9:55	Break	
9:55 – 10:30	"Radiation Effects on Metal/Oxide Interfaces"	Darryl Butt Boise State U
10:30 – 11:05	"Exploiting the Power of Powder Synthesis Reactions for Advanced Structural Materials"	Iver Anderson Ames Lab
11:05 – 12:00	Discussion	
12:00 – 1:30	Lunch (on your own)	

PM Session: Characterization – Chair: Bob Field

1:30 – 1:40	Session Introduction/Announcements	Bob Field LANL
1:40 – 2:10	"In Situ Neutron Diffraction Techniques"	Sven Vogel LANL
2:10 – 2:40	"Characterization of Phase Transformations in Structural Materials Under Extreme Conditions"	Mike Kaufman Colo. Sch. Of Mines
2:40 – 3:10	"3D Microstructural Characterization and Analysis"	Andy Geltmacher Naval Res. Lab.
3:10 – 3:25	Break	
3:25 – 3:55	"High Energy X-ray Diffraction Microscopy: Access to Volumetric Microstructure Responses"	Robert Suter Carnegie-Mellon U
3:55 – 4:25	"In-situ 3D X-ray Techniques"	Erik Lauridsen RISO
4:25 – 5:30	Discussion	
5:30	Adjourn	

Agenda

Friday, July 31st

AM Session: Specific Properties/Materials Interactions – Chair: Jim Foley

8:15 – 8:30	Session Introduction/Announcements	Jim Foley LANL
8:30 – 9:05	"Scientific Challenges Associated with Materials Degradation by Corrosion: Some Needs for Prognosis and Corrosion-Informed ICME"	John Scully U Virginia
9:05 – 9:40	"Hydrogen Embrittlement – Current Status and Future Directions"	Ian Robertson U Illinois
9:40 – 9:55	Break	
9:55 – 10:30	"Understanding the Role of Microstructure Variability on Fatigue Behavior"	Wayne Jones U Michigan
10:30 – 11:05	"High Temperature Materials: What Next?"	Tresa Pollock U Michigan
11:05 – 12:00	Discussion	
Noon	Adjournment	
PM:	Meeting of Organizers and Session Chairs	

Workshop Participants

Workshop Chairman: Bob Field, MST-6

Internal Organizers:

Dave Teter, MST-6
Carlos Tomé, MST-8
Deniece Korzekwa, MST-16
Jim Foley, MST-6

External Executive Committee:

Tresa Pollock (University of Michigan)
Ian Robertson (University of Illinois)
Darryl Butt (Boise State University)
Jim Williams (The Ohio State University)

Speakers:

John Allison (Ford Motor Company)
Steve Zinkle (Oak Ridge National Laboratory)
Jim Williams (The Ohio State University)
Greg Kusinski and Jim Skogsberg (Chevron)
Carlos Tome (Los Alamos National Laboratory)
Matthew Miller (Cornell University)
Hussein Zbib (University of Washington)
Yunzhi Wang (The Ohio State University)
Deniece Korzekwa (Los Alamos National Laboratory)
Suresh Babu (The Ohio State University)
Darryl Butt (Boise State University)
Iver Anderson (Ames Laboratory)
Sven Vogel (Los Alamos National Laboratory)
Mike Kaufman (Colorado School of Mines)
Andy Geltmacher (Naval Research Laboratory)
Robert Suter (Carnegie-Mellon University)
Erick Lauridsen (RISO, Denmark)
John R. Scully (University of Virginia)
Ian M. Robertson (University of Illinois)
J. Wayne Jones (University of Michigan)
Tresa Pollock (University of Michigan

Other Attendees:

Addessio, Frank	T-3
Alexander, David	MST-6
Bai, Xian-Ming	MST-8
Barnes, Chris	P-DO
Bingert, John	MST-8
Blake, Nolen	MST-6
Bourke, Mark	MST-8
Budiman, Arief	MPA-CINT
Cerreta, Ellen	MST-8
Chan, Shao-Ping	T-1
Cieslak, Wendy	MST-DO
Clark, Blythe	SNL
Clarke, Amy	MST-6
Clarke, Kester	MST-6
Da, B. C.	SNL
Devaurs, Micheline	SPO-SC
Devlin, David	MST-7
Di, Zengfeng	MPA-CINT
Dunn, Paul	MST-DO
Farrow, Adam	MST-16
Gibbs, John	MST-6
Hatter, Ghalid	SNL
Hill, Mary Ann	MST-6
Horfer, Khalid	T-8
Hosemann, Peter	MST-8
Knapp, Cameron	MST-6
Korzekwa, David	MST-6
Lookman, Turab	T-4
Maloy, Stuart	MST-8
McCluskey, Mark	MPA-MC
Nastasi, Mike	MPA-CINT
Necker, Carl	MST-6
Orler, Bruce	MST-7
Pena, Maria	MST-6
Sanders, Billy	UC-Davis
Shlachter, Jack	ADEPS
Sintay, Stephen	CCS-2
Stan, Marius	CCS-2
Thoma, Dan	MDI
Valone, Steve	MST-8
Van den Bosch, Joris	MST-8
Van, Igor	MST-8
Way, Zhiqiang	T-3
Wei, Qiangmin	MPA-CINT
Xu, Wei	MPA-CINT
Zocco, Adam	MST-6

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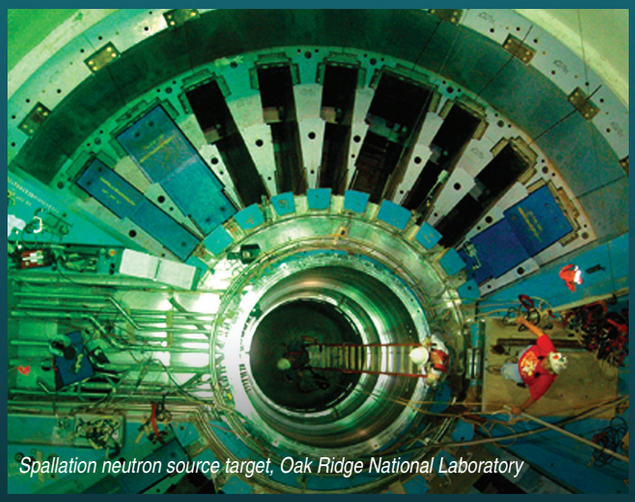
Research Needs and Opportunities for Characterization of Activated Samples at X-Ray and Neutron User Facilities

Bishops Lodge, Santa Fe, NM
September 20—22, 2009

Workshop Chairmen: Tom Holden, Mark Bourke, and Stuart Maloy



Spallation neutron source target, Oak Ridge National Laboratory

Shielded container, Chalk River Laboratories National Research Council

Advanced photon source target, Argonne National Laboratory

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Attendees at the workshop, Research Needs and Opportunities for Characterization of Activated Samples at X-Ray and Neutron User Facilities, held in Santa Fe, New Mexico.

Left to right: Thomas Proffen, Phil Withers, and Lyndon Edwards

Left to right :Tom Holden, Jack Shlachter, and Mark Bourke

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1. Executive Summary

On September 20-22, 2009, a workshop entitled Research Needs and Opportunities for Characterization of Activated Samples at X-Ray and Neutron User Facilities, sponsored by Los Alamos National Laboratory, was held in Santa Fe, New Mexico. The workshop was motivated by the potential that light and neutron sources have to proffer advances in our understanding of radiation damage and to validate new science-based materials performance models. The charge of the workshop addressed measurement needs, current activity, and opportunities that can be realized in the next five years and insights that could be realized by new diagnostics and experimental methods. This report outlines the content and discussion of the workshop.

Discussions of the anticipated need covered fuels, structural applications, and materials discovery for fission and fusion reactors. For fuels priority, needs included characterization of defect distributions, voids, bubbles, cracks, precipitates, new chemical phases, alloy species redistribution, recrystallization, and grain growth. For structural components, priorities included the improved understanding of the changes in yield, ultimate tensile strength, embrittlement, and fracture toughness. Radiation-assisted stress corrosion cracking was also identified as very important. For new materials, an improved understanding of the interactions between strengthening features and radiation-induced defects was considered crucial.

When considering the opportunities available at existing facilities, the provision of three-dimensional spatial distributions of defect and chemical distributions with atomistic resolution were areas of opportunity, especially if they have temporal resolution consistent with the phenomena of interest. However, realizing the full potential of user facilities will, in many cases, require changes in the infrastructure and the requirements that are necessary for safe and efficient handling of activated material. Moreover, facilities need to provide sample preparation areas and bring to bear the full range of diffraction and spectroscopic techniques on increasingly small (and thus more radiologically manageable) samples.

Plausible priority research opportunities identified for the next five years included the following: 1. In situ crystallographic response to applied stress in archived irradiated materials; 2. Crack growth under fatigue conditions in irradiated alloys (e.g. zirconium) containing hydrides; and 3. Small angle scattering and diffraction of precipitates (e.g. M23C6 particles in Fe9%Cr steels) to explore the formation and strain fields around deformation-induced voids.

In workshop discussions concerning a decadal future facility, numerous opportunities were identified that coupled X-ray or neutron probes with an irradiation source: examination of individual grains in activated samples; handling and characterization of “large” components; in situ measurement of creep properties in conjunction with radiation and helium ingress; and defect kinetics measurements and characterization of spent fuel. No less important are handling facilities and hot cells. The requirement to have all the classical post-irradiation microscopy, such as electron microscopy and ion beam facilities, was integral to the vision. On the decadal time scale, the following areas of interest were identified of special import: 1. Materials for Generation 4 reactors; 2. In situ fatigue testing at temperatures that allow the quantification of fatigue-irradiation-creep interaction; and 3. Examination of individual particles to see how these interact under deformation with and without irradiation.

If the promise of the so-called nuclear renaissance is to be realized, especially in the United States, the breadth and depth of the nuclear science and engineering community must be enhanced substantially. In particular, there is a need to revitalize the materials science of radiation damage. It was clear to workshop participants that x-ray and neutron sources at national user facilities have an important role to play in this endeavor. Further, in addition to cultural changes that would allow the full exploitation of currently available tools and techniques, new capabilities need to be developed if science-based certification is to play a role in the resurgence of nuclear energy. Finally, given the magnitude and urgency of the need for carbon-neutral energy, approaches must be found to reduce the time and cost associated with licensing and certification.

2. Introduction

The current generation of nuclear power reactors was designed nearly 50 years ago and since then dramatic advances in tools for the pursuit of materials science have been realized. These include super-computers, X-ray and neutron user facilities. (See "Neutrons and Synchrotron Radiation in Engineering Materials Science" edited by W. Reimers, A.R. Pyzalla, A. Schreyer and H. Clemens, Wiley-VCH Verlag GmbH & Co. KGaA, Wertheim, 2008.) Using these tools, it seems likely that breakthrough insights will be possible in the next decade concerning the behavior of materials exposed to radiation damage.

The field of radiation damage research is heavily influenced by its relevance to the safety case of engineering applications in fission power generation. Much of the research and development is directed at this end-use. Current fission reactors present many managed but poorly understood problems, concerning the strength and practical life of materials. Material selection in fission power applications is far from a mature technology. As increased burn-up, fluence and temperatures are considered for fission and fusion applications, the need for improved understanding is compelling (see Figure 1). The potential societal implications are considerable. For example in the United States alone, the question of whether lifetime extensions are granted to the existing fleet of nuclear power stations has a fiscal import of billions of dollars.

The origin of radiation damage begins at the atomic scale but the accumulation and interaction of radiation-induced defects compromises macroscale properties. Ultimately, the engineering performance of fuels or structural materials in a reactor depends on these defects and, in particular, on their interaction with the microstructure. At the atomic level, the problems are as fundamental as any found in materials science. However, extrapolating from atomistic insights to macroscopic length scales requires a complex and difficult synthesis of science, metallurgy and engineering.

This workshop was motivated by the potential that new tools at light and neutron sources have to proffer unique advances in our understanding of radiation damage. These tools have the potential to inform and validate atomistic codes in ways

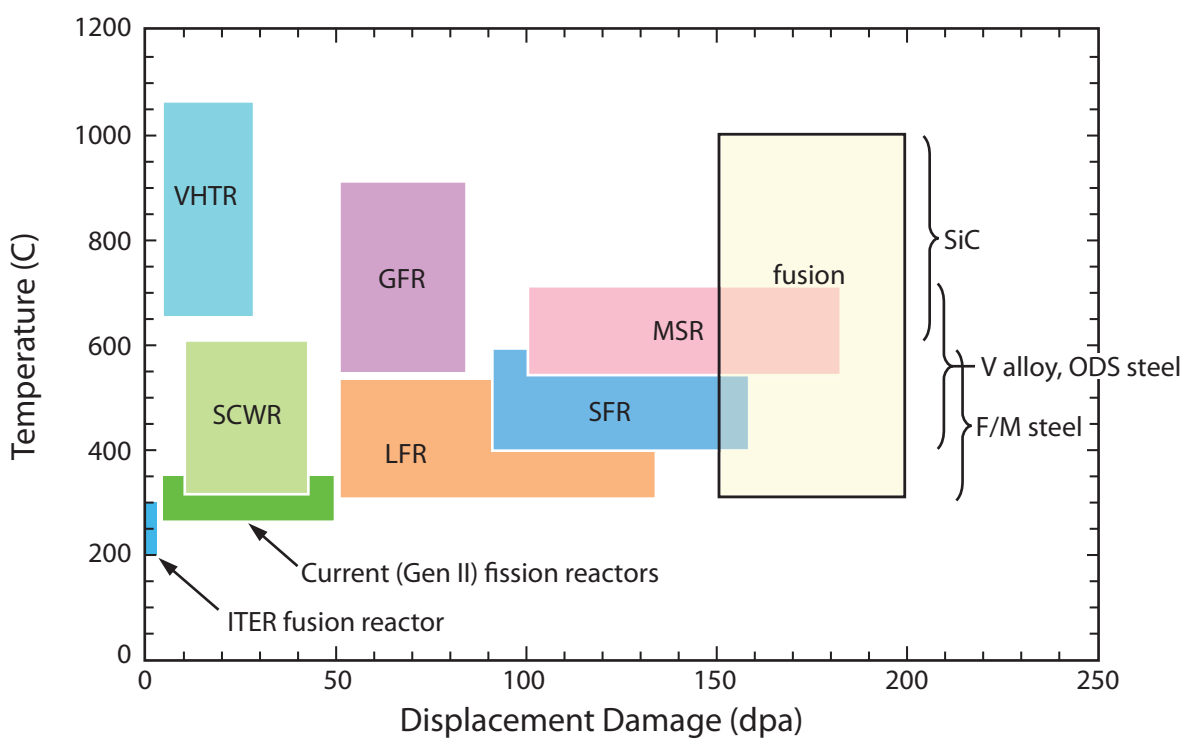


Figure 1. After S.J. Zinkle ,OECD NEA Workshop on Structural Materials for Innovative Nuclear Energy Systems, Karlsruhe, Germany, June 2007, in press

that have been hitherto impossible. With wider application, the resulting insights might accelerate our understanding and certification of materials used in nuclear applications. A subordinate motivation was a desire to explore opportunities that would complement Los Alamos National Laboratory's Matter-Radiation Interactions in Extremes (MaRIE) signature facility concept. The workshop was preceded by three Office of Science workshops: Basic Research Needs for Advanced Nuclear Energy Systems, Basic Research Needs for Materials Under Extreme Environments, and Next Generation Photon Sources.

The workshop was held Sept. 20-22, 2009, and focused on user facilities. The charge addressed the science and engineering challenges that warrant examination, current activity, opportunities that can be realized in the next few years and insights that could be realized by new diagnostics and experimental methods. Attendees came from many of the U.S. national laboratories, including Los Alamos, Lawrence Livermore, Argonne, Oak Ridge, Pacific Northwest and Idaho. U.S. industry was represented by two attendees from the Electric Power Research Institute and a representative from the Nuclear Regulatory Commission. There were six attendees from U.S. universities and six international attendees.

3. Measurement Needs

3.1 Introduction

The range of irradiated and activated samples that can benefit from examination at user facilities is considerable. Opportunities range from fundamental studies to practical studies. Fuels and structural materials were a common engineering theme over a wide range of dose, rate and temperature conditions. Some problems such as leaking fuel pool liners are of immediate import while others such as designs for a conceptual fusion reactor first wall have a much longer lead time. Noting the current advocacy for greater impact of modeling on certification and discovery, the workshop focused on tools that would contribute to the perennial desire to link models over multiple length and temporal scales.

In hot cells, characterization tools typically span the range of lab scale techniques such as electron microscopy, Auger Atom probe spectroscopy, positron annihilation spectroscopy, Raman, mechanical testing, etc. Often the studied materials are surveillance coupons, and the properties of interest are those most pertinent to engineering: hardness, tensile properties, toughness, residual stress, texture, yield strength, strain hardening, corrosion and oxidation rates, and materials compatibility. Handling irradiated samples in hot cells with remote handling is routine if not cheap. Whereas x-ray and neutron user facilities often provide opportunities to examine a wider range of phenomena non-destructively on smaller samples with greater precision, spatial, and temporal resolution, this capability is sparsely applied in no small part because of the reticence and lack of infrastructure at most user facilities to handle highly activated materials. Nevertheless, there are counter examples such as the Stanford Synchrotron Radiation Lightsource, which accepts samples up to 10 GBq (as indeed will the MARS soleil facility in France) or the Chalk River facility where shielded containers have been used to make neutron diffraction measurements on samples up to 20,000 R/hour.

Listed below are three problem areas that could strongly benefit from increased measurements: nuclear fuels, structural components, and new materials.

3.2 Nuclear Fuels

UO2 and mixed (uranium and plutonium) oxide are the primary candidates for fuels for new reactors over the next 25 years. The factors limiting fuel performance are the defect distributions, voids, bubbles, cracks, precipitates, new chemical phases, alloy species redistribution, recrystallization, and grain growth generated by radiation. Typically, information on these factors is needed as a function of radial position from the centerline to the fuel cladding and has been expensively obtained by classical microscopy techniques, but new methods may allow it to be determined non-destructively.

One of the potential advantages of fast-breeder fuels is their potential to offer higher burn-up when compared to current nuclear fuels (10% versus 3%). One candidate design is tristructural-isotropic (TRISO) fuel which comprises spheres (mm diameter) of (e.g.) Uranium carbide surrounded by moderating layers of carbon, contained within a stainless steel cladding. The result is a fuel that is inhomogeneous on the scale of the size of the spheres. Therefore, its behavior will be locally inhomogeneous on a similar length scale. Since it is expected to operate at higher temperatures, perhaps using liquid metal coolants, experimental capabilities are urgently needed to follow the inhomogeneous formation of defects, voids, crack, bubbles, and phase-changes that will form during irradiation. Fuel deterioration due to cracking of fuel within the cladding is one phenomenon that decreases the effective thermal conductivity and limits the rating of the fuel. Thus, a major advance in our understanding of the life limiting processes could be achieved if it were possible to follow fuel damage in situ. This is true for regular oxide fuels but will be even more important where the swelling will be exacerbated in fast reactor fuels.

There is also a need to monitor waste-form stability in which the evolution of new phases and damage accumulation contributes to the degradation of leachability barriers. For example the α-decay of irradiated UO2 causes radiolysis of water. The ensuing chemical reaction changes U4+ ions to U6+ ions, which are soluble in water, permitting uranium to be leached out of the waste. Adding H+ ions to the water produces a reducing environment that blocks the U4+ to U6+ pathway. How this occurs is not understood. With neutron reflectometry, it should be possible to examine the surface behavior of UO2 using D2O/H2O contrast matching to nullify the water scattering.

3.3 Structural Components

Understanding the degradation of the mechanical properties of the structural materials used within a reactor is vital to its operating safety case. In a radiation environment changes in yield and ultimate tensile strength, embrittlement, and loss of fracture toughness are all common. The fracture toughness, yield-point, and temperature determine what length a crack has to be before it grows rapidly is reasonably well understood in most cases. However less well understood is the effect of irradiation on fatigue (the response to cyclic loads provided by temperature cycling or vibrations caused by water flow), creep (the gradual growth of structures at high temperature and under stress), and their interaction.

Figure 2. A 7.5-inch diameter nuclear power plant pressurizer nozzle (after David Rudland)

Residual stresses associated, for example, with girth welds in nuclear pipe-work (such as nozzles close to the reactor pressure vessel) are important since a weld failure could result in a loss of coolant event (e.g., Radiation-induced stress relaxation of welded type 304 stainless steel," M. Obata, J.H. Root, Y. Ishiyama, K. Nakata, H. Sakamoto, H. Anzai, and K. Asano Proc 22nd Symp. on effects of radiation on Materials, ASTM STP1475, p. 15, Boston 2004). Since the magnitudes of the residual stresses generated by welding are often unknown, their assumed values often play a more important role in limiting lifetimes than the in-service stresses. In order to obtain a damage-tolerant estimate of remaining life, some assumption or knowledge about these residual stresses is needed to model crack propagation through welded material whose toughness has been reduced by radiation. Thus, radiation-assisted stress corrosion cracking is very important to both boiling water and pressurized water reactors. The Electric Power Research Institute (EPRI) has major national and international programs to investigate stress corrosion cracking particularly in the context of modern automated welding practices when compared to manual methods used in the past. The welds of interest are often complicated since they join body-centered cubic pressure vessel steels to corrosion resistant stainless steel and are sometimes thick, involving 3-6in. piping in which the welds are highly constrained by the pipe thickness (see fig 2).

Another important aspect of reactor safety is the integrity of the fuel cladding against breakage and the potential release of fuel and fission products resulting from cladding failure is of considerable importance. For zircaloy cladding, the issues are corrosion, hydride accumulation, growth driven by intergranular strains and crystallographic texture, and exacerbation by stress fields induced by manufacture or welding. Cladding integrity will be of even greater concern in future fast reactor systems for which potentially increased burn-up leads to greater swelling and hence pressure on the cladding.

3.4 New Materials

New materials of possible relevance for structural applications have recently been identified from research on so-called Generation 3 and 4 materials. These include oxide dispersion strengthened steels, ferrite/bainite (P91) alloys, and alloys of the form Ti3AlC2. In many cases, they appear to have good strength and radiation resistance but have little or no operational record in representative extreme radiation environments. Thus, a scientific understanding of the interactions between strengthening features and the radiation-induced defects is of paramount importance if they are to be certified for new applications. Segregation of alloying elements and the role of interfaces are two important areas of interest. Another need is the possibility of improving current materials within the envelope of their certification to avoid the drawn-out process of certifying anew.

Recent studies have shown some materials that have superior resistance to radiation, for instance the layered material CuNb, may attain this by virtue of the interfaces. Materials with strengthening features at the scale of nm often have superior mechanical properties. The reason for this improvement in properties may well be what happens in the interfaces rather than within the grains. Cladding material shows void denuding near the grain boundaries, suggesting that the interfaces are sinks for defects. If this proves to be the key phenomenon then diffraction (which originates in coherent effects in the grains), may be a less valuable probe than one which is sensitive to conditions in grain boundaries. Fortunately, the size of synchrotron beams is becoming smaller while still retaining intensity. Within the next decade, it may be possible to perform diffuse scattering from interfaces such as grain boundaries.

4. Near-Term Opportunities (One to Five Years)

4.1 Methods for Transformational Insights

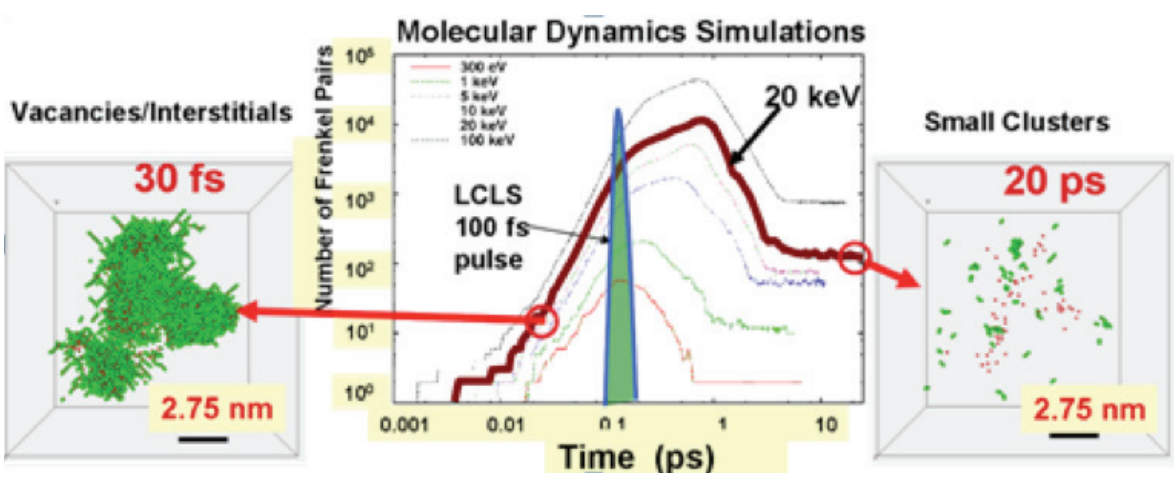
Much of what we think we know about primary damage formation comes from molecular dynamics (MD) simulations. However, much experimental effort misses the spatial and temporal regimes most pertinent to MD by focusing on long range or bulk average phenomena, such as resistivity, temperature, swelling, constitutive response and corrosion rates. Thus, new tools that provide three-dimensional spatial distributions of defect and chemical distributions with atomistic resolution could prove invaluable, especially if they have temporal resolution consistent with the phenomena of interest.

There is also a compelling need for engineering studies using new probes that can operate under extreme irradiation environments. For fuels, issues of interest include melt temperature as a function of actinide composition and chemistry; dimensional stability, thermal properties, and material diffusion as a function of chemistry, temperature and microstructure; heat generation from nuclear processes; fission product accumulation and gas release. Issues for cladding include strength and ductility as a function of microstructure, temperature, and chemistry; actinide and fission product diffusion; and chemical reactions at fuel-clad interface. In either case, the potential to make measurements during simulated failures such as loss-of-coolant accidents would allow failure margins to be explored.

Developments at third and fourth generation light sources as well as at new neutron sources such as the spallation neutron source at Oak ridge national laboratory hold the potential for unprecedented insights into fundamental processes that dictate radiation damage. Several specific areas of immediate opportunity were identified: diffraction measurements during loading of archival samples; residual stress measurements of structural welds; property determination of irradiated oxide dispersion strengthened/nano structured ferritic steels; inelastic neutron scattering on samples of atypical isotopic composition (e.g., Pu 242); resonant inelastic X-ray scattering fluorescence measurements (e.g., on Americium at high pressure) or elemental mapping on the sub-micron scale (0.03 μm resolution) with a sensitivity to chemical species of parts per billion; and development of advanced x-ray and neutron focusing optics (e.g., for studies of ion beam irradiated layers).

Opportunities implicit in the Linac Coherent Light Source (LCLS) were a frequent focus. The potential of LCLS to observe with pico-second resolution, defects, their interactions and dynamics may lead to better charting of damage pathways (see fig 3). The high intensity short photon pulses offer experimental potential that, for the first time, complements high performance computing atomistic models at the shortest relevant spatial and temporal scales. Realizing this potential will require the development of techniques that can use such radiation sources to measure nucleation of defect clusters, bubbles/voids, image dislocations, grain boundaries, and precipitates, and demonstrate the interaction of dislocations with defect clusters, bubbles, and voids.

Fig 3. Defect production during radiation (after Malcolm Stocks)



4.2 Radiography and Tomography

X-ray tomography can be pursued using laboratory or synchrotron sources that complement one another by investigating components over a range of length scales. Laboratory tomography can effectively cover the spatial range of 1-10 μm taking between a half hour and 10 hours for a scan. It has been applied to components of the order of a millimeter in maximum dimension such as crack growth in nuclear graphite, damage in LiTiO3 "pebbles" for fusion blankets and TRISO fuel elements. Defects in the SiC coating around a TRISO particle can readily be resolved. Conversely synchrotron tomography, carried out at major user facilities, and therefore requiring more organization, covers the size range 0.2-1.0 μm with scan times ranging between a few seconds and an hour. (High energy microtomography, with a resolution of 0.2 μm in a few seconds, has been applied to viewing crack growth in compact tension samples in real time.) Applications to visualizing defects in an irradiated microstructure are easy to envision.

Neutron tomography with a resolution of 200 μm continues to be limited by the availability of high resolution, two-dimensional detectors and by flux. Nevertheless new facilities are being built in Australia for examination of radioactive components, and new general user facilities are being built at the ISIS neutron source in the United Kingdom and at the Spallation Neutron Source at Oak Ridge National Laboratory. The continuous spallation source at the Paul Scherrer Institute in Switzerland, is used to examine large and highly radioactive samples. In situations where the user facility is at a licensed nuclear site the logistics of examining active components are greatly simplified because of pre-existing experience of transportation and handling issues.

Diffraction contrast tomography allows a map to be made of the grains and their boundaries by correlation of the grain image in the x-ray transmitted beam and the diffracted Laue spot image of the grain. This tool has been used to map grain growth, grain boundary modification, recrystallization, and phase changes. With micro-tomography on the same sample, one can superimpose the image of a propagating crack on the grain map to find out which grain boundaries are selected for crack growth. This is an immensely powerful tool for characterizing defect distributions, voids, and bubbles on the scale of the microstructure.

Phase contrast tomography is based on changes in refractive index and, therefore, phase at boundaries between regions of a sample with different densities. The technique often provides images in situations for which transmission based tomography is insensitive. The method has achieved successes in biology but has not yet been applied to activated materials.

4.3 Scattering

Small-angle scattering using x-rays and neutrons is a common approach for studies of inhomogeneities covering size ranges from Å up to 10 μm (using ultra small-angle techniques). Small-angle neutron scattering measurements (SANS) and ultra-small-angle scattering have measured the distribution of voids and defects in oxide dispersion strengthened steels by using the magnetic cross-section of the material to separate the non-magnetic defect scattering from other inhomogeneities in the steel in an unambiguous way. SANS has been also used to map creep cavitation (see Figure 4) in reactor pressure vessel steels close to the toe of a weld. (See "Quantification of creep cavitation damage around a crack in a stainless steel pressure vessel," P.J. Bouchard, P.J. Withers, S.A. McDonald and R.K. Heenan, Acta Mater, 52 2004 23–34.) There is now overlap (and agreement) between reciprocal space scattering methods of sizing particles and real space tomography in the 1–10 μm range.

Neutron diffraction measurements of residual stress have been made since the 1980s but the application to irradiated material is relatively new. Measurements of stresses in irradiated welds with 20,000 R/hr on contact have been carried out at the Chalk River Nuclear Laboratories of Atomic Energy of Canada by staff at the National Research Council of Canada. The welds were contained in specially designed containers such that the activity outside the container was less than 4 mr/hr and, therefore, safe to deploy on the reactor main floor. The results, interestingly, showed a systematic reduction of residual stress with damage. Diffraction measurements of irradiated low-enriched uranium molybdenum fuel (75 R/hr on contact) have also been made in shielded containers. The results showed that new phases appeared after irradiation plus an amorphous scattering component. A straightforward extension of the method would be to scan the fuel elements to find the distribution of phases as a function of position from the centre to the cladding generated by the temperature distribution from center to core.

Microdiffraction permits stress measurements to be made as a function of position within grains by the use of small x-ray beams generated by Baez-Kirkpatrick mirrors, with gauge volumes of order 0.4×0.6×0.7 μm3. This allows the stresses to be mapped out across grains, around defects and dislocations, and towards the grain boundaries. This is another powerful tool with good prospects of early application to understanding the stresses around bubbles and the genesis of cracks and crack fronts.

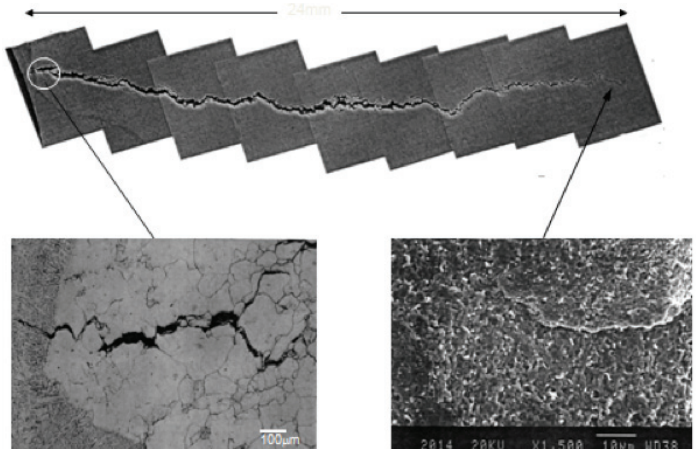


Figure 4. Cavities nucleate and join to form a life-limiting crack (after Phil Withers)

4.4 APS User Survey

In November 2008, a survey gathered input on the needs of scientists planning to use synchrotron x-rays for examining activated materials in connection with the MR-CAT project at the Advanced Photon Source. Figure 5 shows the technique requirements that were identified in the survey. Small-angle, ultra-small angle, and diffuse scattering were considered important for examining defects. (See Diffuse X-ray scattering measurements of point defects and clusters in iron," R.E. Stoller, F.J. Walker, E.D. Specht, D.M. Nicholson, R.I Barabash, P. Zscack, and G. Ice, J. Nucl. Mater, 367-370 2007 p. 209.) Both diffraction with mm size beams to measure phases and microdiffraction techniques to obtain stress distributions on the grain scale were identified. Surface diffraction and grazing incidence small angle scattering to examine near surface effects and corrosion were considered necessary. Tomography, radiography, phase contrast, and fluorescence imaging were all identified as highly important. XAFS, micro-EXAFS and x-ray photoemission were considered to be highly valuable spectroscopies.

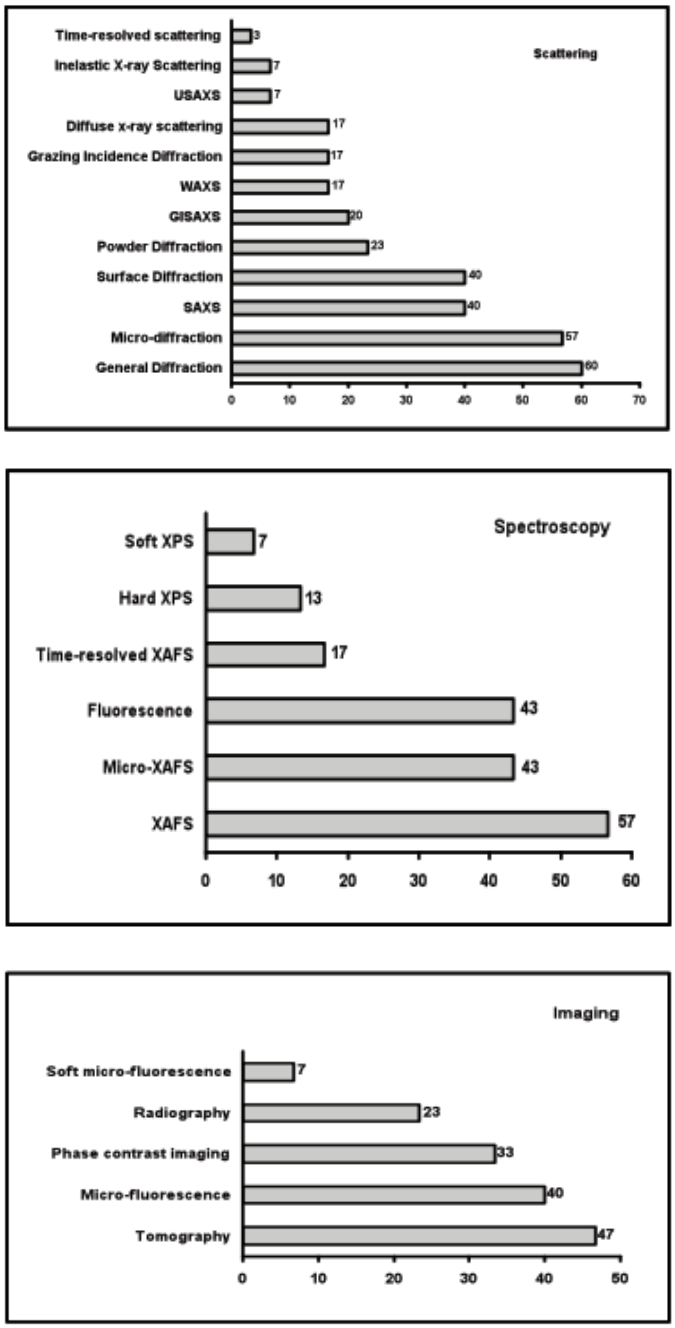


Figure 5. APS User Survey: Technique requirements (after MeiMei Li)

The beam size requirements were divided nearly equally between sizes less than 0.1 μm2, between 0.1 and 1.0μm2, and large beams for bulk measurements. Control over a wide range of temperatures was desired. 500–1000°C corresponds to high temperature reactors and fusion first walls. Temperatures between room temperature and 500°C correspond to thermal reactors; and cryogenic temperatures are sometimes used to minimize thermal phonon scattering when using diffuse scattering. Mechanical facilities included the ability to carry out in situ crack initiation and growth (stress and imaging) measurements, tension, compression and fatigue and internal pressurization. Structural alloys (30%) comprise the largest group of likely topics followed by nuclear fuels (20%), transmutation products and actinides (20%) and SiC, oxides, nitrides, and carbides (TRISO fuels) (30%). Requirements for specimen preparation, mounting, polishing, and cutting were also identified.

5. New Tools of Decadal Scope

5.1 Requirements in a Decadal Future Facility

The new x-ray facilities currently under development (e.g., the free-electron laser) exceed the brightness of current sources by a wide margin so the likelihood of being able to probe even smaller volumes over smaller time intervals than at present is inevitable.

On the second day of the workshop, the participants considered what capabilities might be required in a facility that could juxtapose irradiation capability with advanced probes a decade in the future. Although there was little consensus on what it would take for science-based certification to supersede the existing “cook and look” paradigm, there was nevertheless consensus that greater application of the neutron and x-ray sources for characterization would be valuable. The capability to irradiate under a variety of conditions (fission reactors, ion beams, spallation sources, etc.) was considered essential. Material test reactors, spallation sources, and ion beams were all discussed.

Regardless of the irradiation source, desirable functionality in a decadal future facility included in situ and ex situ measurements of a range of phenomena, e.g., diffraction during loading; examination of individual grains in activated samples; handling and characterization of "large" components; in situ creep properties with helium; defect kinetics measurements with resolution than overlap with models and characterization of spent fuel. Engineering requirements will likely be dominated by need for insight, particularly under high burn-up conditions, on new fuel types such as Triso, MOX, or Thoria, of which we have comparatively little experience.

5.2 Common Scientific Needs

Breakthroughs in understanding in the next 10 years are likely to come from the coupling between theory and modeling with experiment. At the experimental level, this might call for designing experiments over the whole range of length scales and time scales with input from the modelers. At the facilities level, this calls for complementary techniques, such as irradiation facilities, modern examination methods using high intensity x-rays and neutrons, the means to handle the active materials, mechanical testing and chemistry-related activities, and the input of theorists and modelers. The Materials research collaborative access team at the advanced photon source illustrates the value of complementary techniques brought to bear on a single sample and well supported by theory.

The major point here is that the new non-destructive methods of examination can establish the bulk behavior and the development of the accumulating damage over time. Previous methods provided a highly local view but not the statistical behavior nor the time development. From the point of view of developing models of the defect structure, the time development is vital. We have a theoretical picture of the formation of the initial cascade and the clustering that ensues over a short span of time based on kinetic Monte Carlo methods (See "Kinetic Monte Carlo modeling of cascade aging and damage accumulation in Fe-Cu alloys," P.R. Monasterio, B.D. Wirth, and G.R. Odette, J. Nucl. Mater, 361 2007 p. 12.) However, how the clustering leads to a distribution of voids in space and in time, and how these diffuse through the structure to develop a steady-state spatial distribution is not known. This covers a much longer timescale and needs to be followed. Since similar processes operate throughout the bulk, they may be followed with repeated x-ray and neutron diffuse scattering methods which sample the bulk in a statistical fashion.

For UO2 fuels, a thermal neutron environment is required since this is the situation in present day reactors. One can envisage making repeated ex situ measurements on the same fuel pin after intervals of irradiation to observe the development of the voids and bubbles with time. One can also envisage making repeated x-ray and neutron diffraction measurements of the phase content of the pin as a function of distance from the center of the pin and as a function of time. One may be able to make diffraction contrast tomography measurements to find the grain morphology and examine recrystallization as a function of radial position and time if the gamma background problem can be circumvented. The question of in situ examination of fuel by x-rays within the radiation source has been advocated. Since penetrations into a spallation irradiation source could be made following the development of new phases under irradiation with high energy x-ray diffraction is within the realm of possibility. Likewise, it may be possible to examine TRISO fuels, although this requires a neutron environment tailored to resemble a fast reactor. Repeated measurements taken in situ and ex situ of irradiated fuel would be feasible using tomography, diffraction to identify new phases and their distribution and grain configuration changes. These measurements would show the development over time of the voids and bubbles within the fuel and their distribution. Diffuse scattering would be difficult because of the inhomogeneous content of the element as well as its cylindrical shape.

It is desirable to do fatigue measurements within the radiation environment. Apart from the effect of embrittlement on crack growth, if the time scale for relaxation matches the time scale for fatigue, there will be a marked effect of one upon the other. Likewise, it is important for fast reactors, where the operating temperature is higher than thermal reactors, to determine whether high temperature

creep affects the fatigue properties of structural components. There is a remote possibility that the high temperature creep may anneal out the effect of fatigue. Fatigue measurements require penetrations into the radiation source to transmit the cyclic force to the sample, radiation insensitive strain gauges and a fair amount of space but are possible. It would be relatively easy to take the fatigued and irradiated samples from the neutron source and use new tools to look for void clustering and crack growth or make measurements of stress around the crack tip to enable the theory of crack growth. For new materials, the same considerations apply: the need to apply tensile and cyclic loads under irradiation and at a variety of temperatures to follow the creep-fatigue interaction. This would then be followed by examination by the new non-destructive tools.

5.3 User Facility Considerations

With the tools at hand, the easiest measurements to implement address length scales close to that of the microstructure (1–100 μm) where the time developments are slower. Many microstructural level measurements are of direct engineering relevance. The faster length scales having to do with the physics of cascade formation are far harder to access with neutron irradiation than ion bombardment.

Thus, the basic experimental building blocks are a neutron irradiation facility, and the possibility of in situ examination by high energy x-rays. No less important are handling facilities enabling tensile testing and fatigue testing of engineering samples in hot cells, the ability to employ all the methods using x-rays from an intense source on highly active samples, and easy access to neutron scattering tools also adapted for highly active samples. One also needs to have all the classical post-irradiation microscopy, such as electron microscopy. For example, interpreting diffuse scattering data can be problematic if there are several sources of scattering since the particular kind of defect cannot be identified without complementary examination.

An extensive program of irradiation at the Los Alamos Neutron Science Center (LANSCE) was carried out during the Accelerator Production of Tritium (APT) program. Irradiation with a spallation source adds a high energy tail to the neutron spectrum compared with a fission reactor. In addition the production of He4 from α-particles is a couple of hundred times higher than at a reactor. In this respect the spallation spectrum begins to approximate to a fusion spectrum. Many structural materials, steels and Al alloys were irradiated and archived. A pulsed fast neutron source, the Materials Test Station, MTS, could be incorporated in the LANSCE accelerator complex. This would have an average intensity that is twice as high as the ATR with intensity in the pulse 10000 times higher. On the other hand the neutron spectrum has a high energy component compared with a thermal reactor spectrum and the He4 content is about 100 times higher. Both the high energy tail and the He4 modify the response of materials.

One challenge for a new facility is rapid impact and one of the problems with neutron irradiation facilities is their relatively slow damage rate. Thus there is a need for accelerated testing. A very important part of the solution for accelerated testing is ion beam bombardment, which can simulate neutron damage. Ion beam irradiation sources provide damage rates that are typically several orders of magnitude faster than any conceivable neutron irradiation facility. Although they lack the penetration, fission fragments and helium production in prototypic neutron irradiations ion irradiation can serve as a powerful complement. By choosing the bombarding ion, one can simulate self-ion damage (say Fe and Cr in stainless steel) or fission gas accumulation. In a triple beam facility, material is bombarded with heavy ions, as well as H- ions and He4. Synergistic effects of the three beams on damage have been recognized. In the MR-CAT project at the Advanced Photon Source (APS) the intent is to bombard foil samples in a triple beam and examine the damage in situ with a synchrotron beam. Mechanical testing of foil samples is feasible although scaling up to engineering test samples and larger components is not assured.

For real space, spatial resolution neutron techniques cannot compete with x-rays, but because of the variability of elemental scattering lengths, neutrons do provide a way to distinguish elements close together in the periodic table or light elements in the presence of heavy elements. Moreover the magnetic cross-section provides another tool in some cases. The other major advantage of neutron diffraction and scattering is that it is not so difficult to shield against the gamma background from the irradiated materials as tests on fuels and welds have shown. (See Neutron powder diffraction of radioactive low enrichment uranium-molybdenum nuclear fuel," L.M. D. Cranswick, K.T. Conlon, R.L. Donaberger, J. Fox, L. McEwan, R. Rogge, D. Sears, D. Sediako, I.P. Swainson, and T. Whan, European Powder Diffraction Conference, Geneva 2006.) Residual stresses in irradiated components will continue to be relevant to the regulatory process. Dedicated spectrometers for neutron experiments, making use of SANS, diffraction, and stress measurements on irradiated samples will be an important part of a new facility.

6. Cross-Cutting Themes

6.1 Modeling

The needs of the modelers serve to define the requirements for experiments at each length scale. At the atomic level, what are the length and time scales for the fundamental cascades generating the damage? What are the length and time scales for these to come to equilibrium in the material? How are these entities situated in the microstructure and how do they interact with intrinsic defects, such as the grain boundaries, which arguably act as sinks. In turn, the microstructural information is needed to calculate the macroscopic properties of the fuel, such as thermal conductivity, temperature, and swelling.

From the current perspective of modeling, the mathematical description of the microstructure (length scale 1.0 to 100 μm) is recognized as the critical link between the behavior at the atomic level and the behavior of the material at the macroscopic level (see Figure 6). In fact, this is also true of the understanding of the mechanical properties of materials in general. At the atomic level, Kinetic Monte Carlo methods can describe the distributions

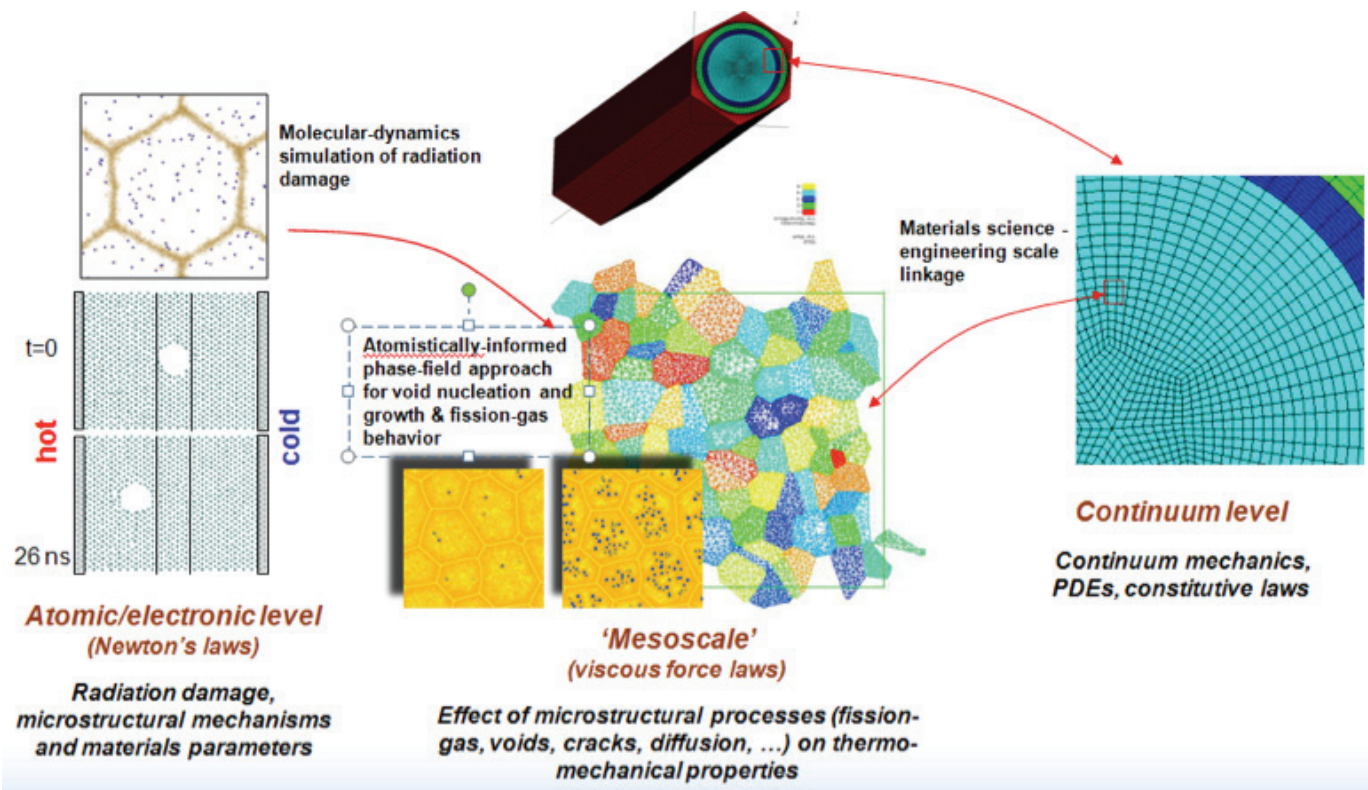


Figure 6. Hierarchical multi-scale approach to nuclear fuel simulation (after Dieter Wolf)

of vacancies and interstitials immediately after (30 fs) a fission product cascade has been initiated. In the following 20 ps, these vacancies and interstitials are thought to coalesce into small clusters over a spatial volume of diameter about 3 nm (0.003 μm). The outstanding fundamental proviso is that the interatomic potential for U and its 5f electrons remains unsatisfactory.

How voids and clusters populate the grains of fuel material is currently addressed by the "phase-field" model, which replaces every grain boundary by an order parameter varying continuously from 0 to 1. (See Phase field model calculation of grains and voids in fuel," S.Y. Hu et al., J. Nucl. Matter, 392 2009 292–300). The model can describe the genesis of gas bubbles and how they are distributed through the grains, in particular the experimentally observed denuded zones close to grain boundaries where there are fewer bubbles (see Figure 7). With this description of the inhomogeneities within the grains, a constitutive law for the local thermal conductivity can be derived. In turn, finite element models of behavior on the macroscopic length scale use this information to calculate the average thermal conductivity as a function of position and hence derive temperature distributions through the fuel. This is one example of the direction of in which models could be developed. While the modeling effort is close to connecting over the whole length scale, the field is not so much limited by computing power as by descriptive algorithms to describe behavior at the microstructure length scale. Another success has been the microstructural evolution of Fe0.9%Cu after irradiation. The initial vacancy-Cu clusters on a 10Å scale and their coalescence into a series of Cu precipitates have been predicted.

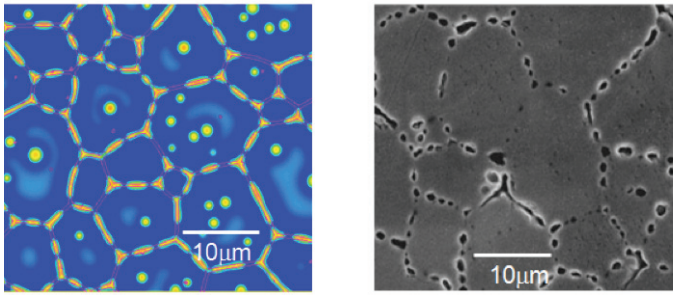


Figure 7. (Left) Phase field calculation using empirical free energy model (after SY Hu et al) & (Right) Irradiated UO2 in pressurized water reactor (after Zacharie et. al)

Currently, many models are not hardware-limited, but algorithm-limited in developing physically-validated methodologies for predicting, for example, microstructural evolution or tensile stress-strain behavior using mesoscale (dislocation dynamics) models. For this reason, much debate focused on measurements pertinent to atomistic and molecular dynamics calculations which were considered most in need of validation. A second theme in the workshop discussions pertained to the engagement of theorists. There was some belief that, even with new validation opportunities, the promise implicit in new generations of models would not be realized without complementary investment in what was called a "virtual computational end station." Essentially this theme advocated significant investment in developing the computational infrastructure necessary for the community to take advantage of insights that could be achieved by bringing light and neutron source characterizations to bear on activated materials.

6.2 Engagement with the Nuclear Power Industry

There was some discussion at the workshop concerning an assertion that the nuclear power utilities do not believe there are technical challenges for coping with irradiated material but that better allocation of funds is needed to support present examination methods. This suggests that there is currently a mismatch between what is seen as important within the nuclear industry with respect to post-irradiation examination and what researchers outside industry perceive. This mismatch should be explored. Another suggestion was the alignment of goals of research workers outside the industry with the research topics identified by EPRI in its interactions with the industry.

Three themes arose during the breakout discussions which merit attention in a discussion of advanced measurement capabilities. First, some difficulty in engaging nuclear in the advocacy of long term research was noted. The general assumption was that short-term commercial

imperatives focused industry attention on the immediacy of existing light water reactor re-certifications. The participants spent some time discussing this issue with solutions ranging from more aggressive participation of the research community at EPRI and NRC meetings; education of the user communities on the way safety case certification occurs now; definition of a DOE champion; efforts to bridge the gaps between the different modus operandi of the DOE offices of Science and Nuclear Energy; and addressing the issue of conflict of interest and intellectual property issues.

7. Conclusion

The overall impact of the workshop was captured in the final panel session. Panelists were asked to name experiments that could be done in the next five years with present resources that would advance the field significantly and those experiments that would have a major impact over the next decade. The panelists were also asked to identify the facilities needed. Two panelists represented academic research and their emphasis was on materials research with irradiated material. Others spoke from the point of view of re-licensing and regulation, requirements for fusion research, and the outlook for the modeling community. Each made suggestions that corresponded to a major program of work.

In materials science research, five priorities were identified for the next five years: 1. the in situ crystallographic response to applied stress in archived irradiated materials; 2. crack growth under fatigue conditions in irradiated zirconium alloys containing hydrides, since this is a major failure route for tubes and cladding; 3. SANS and SAXS measurements on Fe9%Cr steels to identify when deformation-induced voids begin to form around M23C6 particles within the steel and x-ray measurements of strain response to applied stress with microbeams around these precipitates; and 4. synchrotron x-ray measurements to find why materials subjected to hardening by irradiation fail at the same true stress.

On the decadal time scale the following program areas were identified: 1. examination of materials for Generation 4 reactors under irradiation including zirconium alloys and ceramics; 2. fatigue testing at high temperatures to quantify the fatigue-irradiation-creep interaction; and 3. examination of individual particles of M23C6 within the grains of Fe9%Cr steels to see how these interact under deformation with and without irradiation. In the 10-year timeframe, it would be desirable to have a materials irradiation source and associated handling facilities allowing active samples to be subjected to specialized x-ray and neutron tests all on the same site.

From the point of view of re-licensing reactors, the immediate emphasis is on the development of confidence in residual stress accuracy through a program of duplicating measurements at multiple laboratories with the available techniques, neutron and x-ray diffraction, deep hole drilling and the contour method. In the next 10 years, the major goals should be the following: 1. large section stress measurements on irradiated components to find the effect of fluence on weld residual stresses; 2. solution of emerging materials property issues such as the effect of irradiation on the thermal aging of cast stainless steel and austenitic stainless steels; 3. development of NDE techniques to measure radiation damage; and 4. high fluence toughness measurements, including crack growth and stress constraint change with crack growth. On the decadal timeframe, the new facility needs to be able to handle a variety of activated samples of different sizes and irradiated intensities and needs to be flexible enough to handle emerging issues. High temperature property development and characterization of irradiated materials should have a high priority.

For fusion reactors, an important task for the next five years is the analysis of oxide dispersion strengthened (ODS) steels with precipitates in the size range of 2–5 nm, which show promise for excellent creep strength and radiation resistance.

However, problems of the variability of the properties with batch need to be addressed. For the next decade, a major goal for fusion programs will be measurement of high temperature creep properties of ODS steels in a radiation environment in the presence of He^4.

From the perspective of modeling and simulation, in the next five years it should be possible to compute and measure the dynamics of cascade evolution on a picosecond time scale with the aid of synchrotron x-rays, and irradiation with ion beams. The calculation requires massive computing capability, viz. access to petaflop computers. It should be possible in this timeframe to include material specificity in modeling the behavior of cascades. On a 10-year time scale, there is an experimental requirement to match the spatial resolution of the computed cascade to verify the fluctuations within the cascade. An important goal for further benchmarking is obtaining real space and reciprocal space information on identical materials on the same length scale. Finally, since the theoretical effort needed is major, a community of scientists, not isolated groups, is needed to work on the problems.

Several general issues were addressed in the final wrap-up of the workshop's panel discussion. If the global renaissance of nuclear power is to become a reality, then low-cost, accessible, high intensity fast neutron sources must be built, since the availability of irradiation facilities is worse than ever before . The irradiation sources could be either reactor or accelerator based. At the radiation facility there should be access to all the current diffraction, spectroscopic and electron microscope techniques and flexibility to incorporate future developments. Modeling on the mesoscopic scale, with benchmarking by experiment, has enormous potential to connect with engineering behavior. There is no room for exclusive fields of endeavor such as engineering versus science, macroscopic versus mesoscopic, experiment versus modeling; these are all vital constituents of the final common goal.

At the workshop, the materials science requirements for activated materials were articulated. The tools developed over the past decade for examination of materials at the grain level were reviewed. An attempt was made to match the needs to the available tools, making note of the hurdles to be overcome. Finally a set of challenging experiments was suggested that will advance the field in the next five- and 10-year periods with the help of new facilities put in place over this time span.

If the promise of the so-called nuclear renaissance is to be realized, especially in the United States, the breadth and depth of the nuclear science and engineering community must be enhanced substantially. In particular, there is a need to revitalize the materials science of radiation damage. It was clear to workshop participants that x-ray and neutron sources at national user facilities have an important role to play in this endeavor. Further, in addition to cultural changes that would allow the full exploitation of currently available tools and techniques, new capabilities need to be developed if science-based certification is to play a role in the resurgence of nuclear energy. Finally, given the magnitude and urgency of the need for carbon-neutral energy, approaches must be found to reduce the time and cost associated with licensing and certification.

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[1]Fast-neutron sources in the United States. The Advanced Test Reactor (ATR) at Idaho National Laboratory is a user facility for neutron irradiation and subsequent examination. It offers a very high flux of fast neutrons (5×10^{14}n/cm^2/s), new post-irradiation and rabbit facilities, and a TRIGA reactor for neutron radiography. The ATR functions as the centerpiece of an academic and industrial group and is also associated with the MR-CAT facility at the APS. The high flux reactor (HFIR) at Oak Ridge offers two locations for fast-neutron irradiation. An extensive program of irradiation at LANSCE was carried out during the Accelerator Production of Tritium (APT) program. Irradiation with a spallation source adds a high energy tail to the neutron spectrum compared with a fission reactor. In addition, the production of He^4 from □-particles is a couple of hundred times higher than at a reactor. In this respect, the spallation spectrum begins to approximate to a fusion spectrum. Many structural materials, steels, and Al alloys were irradiated and archived.

Appendix A: Workshop Agenda

Workshop Title: Research Needs and Opportunities for Characterization of Activated Samples at X-Ray and Neutron User Facilities

Sunday 20 September 2009			
5:30 p.m.	Registration		Tesuque B, C
6:30 pm	Welcome	Tom Holden (NST)	Tesuque B, C
6:40 pm	Overview of DOE Workshops	Mike Fluss (LLNL)	Tesuque B, C
7:00 pm	MaRIE, a proposed signature facility	John Sarrao (LANL)	Tesuque B, C
7:30 pm	Free time		
Monday 21 September 2009			
7:30 am	Continental breakfast		Portal
8:00 am	Workshop goal	Tom Holden (NST)	Tesuque A,B
8:05 am	Workshop philosophy & Rationale	Mark Bourke (LANL)	Tesuque A,B
Session 1:- Measurement needs for activated samples – customer focus Chair/Scribe Rick Holt / Peter Hosemann			
8:30 am	Developing advanced nuclear structural materials for use in high radiation environments: An Australian perspective	Lyndon Edwards (ANSTO)	Tesuque A,B
8:55 am	Microstructure Modeling of Nuclear Fuel	Dieter Wolf (INL)	Tesuque A,B
9:20 am	Welding residual stress and material property measurements on irradiated materials	David Rudland (NRC)	Tesuque A,B
9:45 am	Breakout # 1 objectives	Jack Shlachter (LANL)	Tesuque A,B

10:00 am	Refreshments		Portal
Breakout # 1 -- In parallel			
Subgroup 1 Regulatory & Licensing *Chair / Scribe James Wall / Heather Volz*			
10:15 am	Seed Talk	Tiangan Lian (EPRI)	Tesuque A
10:25 am	Address breakout #1 charge	Subgroup	Tesuque A
Subgroup 2 Industry *Chair/Scribe Phil Withers / Don Brown*			
10:15 am	Seed Talk	Rick Holt (Queens University)	Tesuque B
10:25 am	Address breakout #1 charge	Subgroup	Tesuque B
Subgroup 3 Modeling *Chair/Scribe Brian Wirth / Turab Lookman*			
10:15 am	Seed Talk	Malcolm Stocks (ORNL)	Tesuque C
10:25 am	Address breakout #1 charge	Subgroup	Tesuque C
12:00	Lunch		
12:30 pm	Research on Transuranium Systems: Present Capabilities with Large Central Facilities (Lunchtime talk)	Gerry Lander (ITU retd.)	
1:30 pm	Breakout #1 chair summaries		Tesuque B,C
Session 2 Ongoing measurements on activated samples ***Chair/Scribe Angus Lawson / Heather Hawkins***			
2:00 pm	Neutron, Synchrotron & Laboratory X-ray imaging of Active Samples	Phillip Withers (UMIST)	Tesuque B,C
2:25 pm	Radiation Damage Effects in Structural Materials using Swiss Spallation Neutron Source and Light Source Facilities	Yong Dai (PSI)	Tesuque B,C
2:50 pm	Radiation Damage Studies at Los Alamos Neutron Science Center (LANSCE) ; What We Did and What we would Still Like to Do	Walt Sommer (LANL Retd.)	Tesuque B,C

3:15 pm	Breakout # 2 objectives	Jack Shlachter (LANL)	
3:20 pm	Refreshments		
Breakout # 2 --- In parallel			
Subgroup 1 Length scales - Nanometers (defects) *Chair / Scribe Mike Nastasi / Thomas Proffen*			
3:40 pm	Seed Talk	Jim Stubbins (UUC)	
3:50 pm	Address breakout #2 charge	Subgroup	
Subgroup 2 Length scale - Microns (Microstructure) *Chair / scribe Gene Ice / Steve Conradson*			
3:40 pm	Seed Talk	MeiMei Li (ANL)	
3:50 pm	Address breakout #2 charge	Subgroup	
Subgroup 3 Length scale – mm (components) *Chair / Scribe Jeff Terry / Don Brown*			
3:40 pm	Seed Talk	Ron Rogge (Chalk River Can.)	
3:50 pm	Address breakout #2 charge	Subgroup	
6:00 pm	Free Time		
7:00 pm	Dinner		
8:00 pm	Material & Fuel Testing for Advanced Nuclear Systems (After dinner talk)	Paul Lisowski (DOE Office of Nuclear Energy)	
Tuesday 22 September 2009			
7:30 am	Continental breakfast		
8:00 am	Breakout #2 chair summaries		

Session 3: New tools and new facilities decadal scope ***Chair/Scribe Mike Fluss/ Ming Tang***			
8:30 am	Materials By Design	Marius Stan (LANL)	Tesuque B,C
8:55 am	Light source opportunities	Gene Ice (ORNL)	Tesuque B,C
9:20 am	Facility needs	Rick Kurtz (PNNL)	
9:45 am	In situ measurements in a radiation environment	Mark Bourke (LANL)	Tesuque B,C
9:55 am	Breakout # 3 objectives	Jack Shlachter (LANL)	Tesuque B,C
10:00 am	Refreshments		
Breakout #3 in parallel			
Subgroup 1 structural components *Chair / Scribe Randy Nanstad / Tiangan Lian*			
10:20 am	Seed Talk	James Wall (EPRI)	Tesuque A
10:30 am	Address breakout #3 charge	Subgroup	Tesuque A
Subgroup 2 Fuels and Waste *Chair / Scribe Ken McClellan / Rex Hjelm*			
10:20 am	Seed Talk	Akos Horvath (HAS KFKI)	Tesuque B
10:30 am	Address breakout #3 charge	Subgroup	Tesuque B
Subgroup 3 Fundamental Materials *Chair/Scribe Alan Hurd / MeiMei Li*			
10:20 am	Seed Talk	Brian Wirth (UCB)	Tesuque C
10:30 am	Address breakout #3 charge	Subgroup	Tesuque C
12:00 pm	Lunch		
12:30 pm	Advanced Test Reactor national scientific user facility (Lunchtime talk)	Mitch Meyer (INL)	
1:30 pm	Breakout #3 chair summaries		

2:00 pm	Panel discussion	Rick Holt (Queen's Univ.) Jim Stubbins (UUC) David Rudland (NRC) Rick Kurtz (PNNL) Dieter Wolf (INL)	
3:00 pm	Open discussion	All	
4:00 pm	Refreshments		
Session 5: Synthesize Draft Conclusions ***Chair Mark Bourke***			
4:20	Draft Workshop Conclusions	Lyndon Edwards (ANSTO)	
5:00 pm	Written input	Tom Holden (NST)	
5:30 pm	Close		
7:00 pm	Dinner		
8:00 pm	Nonproliferation considerations for nuclear energy and nuclear weapons (after dinner talk)	DV Rao (LANL)	

Appendix B: Participants and Readers

Name	Organization	Email	Phone
Mark Bourke	Los Alamos National Laboratory (LANL)	bourke@lanl.gov	505-665-4735
Don Brown	LANL	dbrown@lanl.gov	505-667-7904
Carol Burns	LANL	cjb@lanl.gov	505-665-1765
Steve Conradson	LANL	conradson@lanl.gov	505-667-9584
Yong Dai	Paul Scherrer Institute	yong.dai@psi.ch	
Micheline Devaurs	LANL	devaurs_micheline@lanl.gov	505-667-1519
Lyndon Edwards	Australian Nuclear Science and Technology Organization (ANSTO)	led@ansto.gov.au	+61 (0) 297 173 652
Michael Fluss	Lawrence Livermore National Laboratory (LLNL)	Fluss1@llnl.gov	
Doug Fulton	LANL	fulton_robert_d@lanl.gov	505-667-4117
Patrick Griffin	Sandia National Laboratories (SNL)	pjgriff@sandia.gov	505-845-9121
Heather Hawkins	LANL	hawk14@lanl.gov	505-665-9020
Rex Hjelm	LANL	hjelm@lanl.gov	505-665-2372
Tom Holden	Northern Stress Technologies	holdent@magma.ca	613-584-2819
Rick Holt	Queens University	holt@me.queensu.ca	613-533-6831
Akos Horvath	HAS KFKI Atomic Energy Research Institute	akos.horvath@aeki.kfki.hu	+36 (1) 3922296
Peter Hosemann	LANL	peterh@lanl.gov	505-606-1437
Alan Hurd	LANL	ajhurd@lanl.gov	505-665-0630
Gene Ice	Oak Ridge National Laboratory (ORNL)	IceGE@ornl.gov	865-574-2744
Gordon Jarvinen	LANL	gjarvinen@lanl.gov	505-665-0822
Chi-Chang Kao	Brookhaven National Laboratory	kao@bnl.gov	631-344-4494
Jon Kapustinsky	LANL	jonk@lanl.gov	505-665-2800
Rick Kurtz	Pacific Northwest National Laboratory	rj.kurtz@pnl.gov	505-845-3300
Gerry Lander	Institute for Transuranium Elements (retd.)	LANDER@ILL.FR	33-476-216020
Angus Lawson	LANL (retd.)	aclawson@cybermesa.com	
MeiMei Li	Argonne National Laboratory	mli@anl.gov	
Tiangan Lian	Electric Power Research Institute (EPRI)	tlian@epri.com	650-855-2405
Paul Lisowski	DOE Office of Nuclear Energy	paul.lisowski@nuclear.energy.gov	301-903-7340
Turab Lookman	LANL	txl@lanl.gov	505-665-0419
Stuart Maloy	LANL	maloy@lanl.gov	505-667-9784
Ken McClellan	LANL	kmcclellan@lanl.gov	505-667-0423

Name	Organization	Email	Phone
Stuart Maloy	LANL	maloy@lanl.gov	505-667-9784
Ken McClellan	LANL	kmcclellan@lanl.gov	505-667-0423
Amit Misra	LANL	amisra@lanl.gov	505-667-9860
Mitch Meyer	INL	mitchell.meyer@inl.gov	208-523-9742
Randy Nanstad	ORNL	nanstadrk@ornl.gov	865-574-4471
Michael Nastasi	LANL	nasty@lanl.gov	505-667-7007
Robert Odette	University of California, Santa Barbara	Odette@engineering.ucsb.edu	805-893-3525
Thomas Proffen	LANL	tproffen@lanl.gov	505-665-6573
DV Rao	LANL	dvrao@lanl.gov	505-667-4567
Ron Rogge	National Research Council, Canada	Ron.Rogge@nrc.gc.ca	613-584-8811, x43989
Dave Rudland	Nuclear Regulatory Council	David.Rudland@nrc.gov	
John Sarrao	LANL	sarrao@lanl.gov	505-665-0481
Jack Shlachter	LANL	shlachter@lanl.gov	505-665-1888
Sara Scott	LANL	sscott@lanl.gov	505-665-8126
Kurt Sickafus	LANL	kurt@lanl.gov	505-665-8126
Walt Sommer	LANL (retd)	w_sommer@frontiernet.net	
Marius Stan	LANL	mastan@lanl.gov	505-667-8726
Malcolm Stocks	ORNL	stocksgm@ornl.gov	
Jim Stubbins	University of Illinois at Urbana-Champaign (UUC)	stocksgm@ornl.gov	
Min Tang	LANL	mtang@lanl.gov	505-665-1472
Jeff Terry	Illinois Institute ofTechnology	terryj@iit.edu	630-252-9708
Heather Volz	LANL	hvolz@lanl.gov	505-665-4370
James Wall	EPRI	jwall@epri.com	704-595-2659
Brian Wirth	UC, Berkeley	bdwirth@nuc.berkeley.edu	510-642-5341
Phil Withers	The University of Manchester	philip.withers@manchester.ac.uk	+44 161 306 8872
Dieter Wolf	INL	dieter.wolf@inl.gov	208-526-8394

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A Summary Report on the 21st Century Needs and Challenges of Compression Science Workshop

September 22-25, 2009
Bishop's Lodge, Santa Fe, NM

Organizers: Dave Funk, George T. (Rusty) Gray, Tim Germann, and Rick Martineau

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Image by NASA/JPL-CalTech

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Executive Summary

The influence that compression science has had on national security science and its manifestation through discovery and application cannot be overstated. In addition to supporting the certification of our nuclear stockpile in the absence of underground testing and a broad spectrum of engineering and defense applications, compression science has altered our view of the material world around us. The discovery of unexpected physical and chemical phenomena and new materials through the application of compression science techniques has led to a new and refined understanding of the nature of chemical bonding in extreme environments. However, it is clear that many important aspects regarding the response of materials to compressive loading are still not understood, let alone modeled in a predictive mode. As a result, we have not derived the many benefits that a predictive understanding would bring. As one product of the workshop we held, we identified five challenges that capture the scientific needs that are required to achieve full understanding and that ultimately support our ultimate goal of moving from *"observation to control."*

These five challenges are as follows:

- Acquire time and spatially resolved *in situ* measurements at all length scales (i.e., atomistic, micro -, meso-).
- Discover new physics and chemistry in extreme environments.
- Incorporate material complexity into multi-scale simulations to achieve predictive capability.
- Unify static and dynamic compression understanding across relevant length and time scales.
- Leverage scientific knowledge derived from theory and experiment to the design and control of real materials (i.e., chemistry, microstructure, defects, etc.)

Making progress on these challenges will require a suite of new experimental tools and diagnostics as well as a suite of conceptual frameworks and theoretical constructs. The suite of experimental tools must include the development of diagnostic capabilities, such as next generation light sources, for peering into and achieving time-resolved measurements in compressed materials at the lowest relative length scales while simultaneously characterizing them at higher length scales. The theoretical suite must include new frameworks of computation that will allow the incorporation of the stochastic nature of matter, as well as the ability to accurately describe the essential physics without the invocation of phenomenological models, while linking the atomistic to the continuum response.

Progress on these challenges will not only allow us to develop a full understanding of compression science, it will create an environment in which we can train the next generation of scientists and provide them with the tools needed to make progress and move from studying "Ideal" to "Real" materials.

1. Introduction

For applications in the future, the design, synthesis, and manufacture of new materials with increased performance and functionality require an increase in our fundamental understanding of matter over the broadest range of thermomechanical conditions. Furthermore, access to extreme states of matter results in a rich array of physical and chemical changes that requires a broad range of science—from quantum physics to the collective continuum response—to interpret. In fact, current research reiterates this need: "Compression induces changes in bonding properties, giving rise to altogether new compounds and causing otherwise inert atoms or molecules to combine. When coupled with changes in temperature, altogether new forms of matter may be produced. For example, it has recently become possible to use laboratory techniques to compress materials to the point where the interatomic spacings are reduced by up to a factor of two and densities increased by over an order of magnitude. At these densities, the changes in the electronic structure begin to influence our very notions of chemical interaction and atomic bonding."[1]

Thus, fully exploiting the possibilities of chemical bonding, as derived from the application of pressure and tuned with temperature, will require new tools to generate these extreme environments, but will also require an ability to diagnose and "calculate" them. The field of compression science has generated rich insight and made us aware of the fact that we do not fully understand the nature of the processes that we induce with pressure. Presently, pressures reached during static compression can exceed the 300 GPa (3 Mbar) range and can temporarily exceed temperatures greater than that of the surface of our sun (> 6,000 K), while those pressures reached during dynamic compression can exceed the TeraPascal (TPa or 10 Mbar) range. In addition, the dynamic processes of shock compression are so fast that the loading is usually adiabatic, the typical durations range from femtosecond to microsecond time scales, and temperatures reach greater than 10^4 K, depending on the rate of loading and the magnitude of the peak compression. Developing new capabilities for reaching further extremes and diagnosing these equilibrium states of matter with unprecedented spatial resolution will inform and advance our understanding, assisting in our goal of moving from "observation science" to "control science."

To quantify these needs and future directions, leaders in the static, dynamic, and theory of compression sciences participated in a workshop entitled, "21st Century Needs and Challenges in Compression Science," held September 22-25, 2009, in Santa Fe, New Mexico. A series of plenary talks were given (see Appendix I), followed by a day of breakout discussions in the areas of static compression science needs, dynamic compression science needs, and theoretical needs of compression science to define the decadal technical challenges and necessary developments to meet these challenges

[1] "Basic Research Needs for Materials Under Extreme Environments," a report of the Basic Energy Sciences Workshop on Materials Under Extreme Environments, June 11-13, 2007, Jeff Wadsworth, Chair, George Crabtree and Russel Hemley, co-Chairs.

At its highest level, the needs of compression science could be captured by the following five challenges:

- Acquire time and spatially resolved in situ measurements at all length scales (i. e., atomistic, meso-, micro-).
- Discover new physics and chemistry in extreme environments.
- Incorporate material complexity into multi-scale simulations to achieve predictive capability.
- Unify static and dynamic compression understanding across relevant length and time scales.
- Leverage scientific knowledge derived from theory and experiment to the design and control of real materials (i.e., chemistry, microstructure, defects, etc.).

The ability to address these challenges will require a new set of characterization tools, temporally and spatially enhanced diagnostics, and the development of new predictive models to characterize the behavior of matter under these extreme conditions. The information gathered in static compression science experiments, when combined with information acquired dynamically, offers the opportunity of understanding the fundamental mechanisms that drive the processes occurring in the matter observed throughout the universe, ultimately leading to an ability of controlling matter to meet our energy and national security needs.

2. Breakout Summaries: Static Compression Science

Static compression science is a burgeoning field that is undergoing unprecedented growth in addressing a broad range of materials problems that span the physical, engineering, and biological sciences. Methods that rely on static compression experiments have many advantages, including the availability of multiple simultaneous diagnostics. These diagnostics have the potential for full materials characterization with an accuracy, precision, and sensitivity that approaches measurements on materials at near ambient conditions. The field is turning its attention to addressing major grand challenges in materials science, including the DOE Grand Challenges of moving from observation to control science and harnessing materials far from equilibrium. There is a strong synergy between conventional static compression, dynamic compression method, and theory; indeed, many problems cannot be addressed without the combination of all three of these approaches. With the prospects for the creation of new facilities, including major radiation sources, many breakthroughs are on the horizon.

2.1 Scientific Discovery Challenges: Static Compression Science

2.1.1 Structure and bonding at high compression

Based on recent work, we currently have a limited understanding of structure and bonding in condensed matter at very high compressions. Making measurements with an accuracy and resolution equal to those attainable at ambient conditions over a broader range of P-T conditions, particularly at higher pressures, will allow the development of truly predictive theory: a new paradigm for understanding condensed matter. We will extend this knowledge across the periodic table over the full range of pressure and temperature, and extend chemistry from valence to core electrons, effectively to explore and develop "kilovolt" chemistry.

Our knowledge of materials is largely based on understanding obtained from systems at near-ambient conditions. Because of this, there are numerous examples of intriguing and poorly understood phenomena, nearly all of which were not predicted theoretically or were simply unexpected. Among the many examples are the recent observations of the novel $(O_2)_4$ cluster-based structure of dense oxygen; the unprecedented polymorphism of Na which exhibits some 11 different phases and melting below room temperature at megabar pressures; and the remarkable pressure-induced transformation of both Li and Na from metal to insulator. The origin of the behavior in all three previous examples at the level of truly predictive, general theory is lacking. Current static compression data observations are based on phenomena observed to pressures of 200–300 GPa. What happens at higher pressures, e.g., at 1 TPa and beyond? There are numerous possible other applications/fields for static higher-pressure compression, including materials science, and planetary science, astrophysics.

2.1.2 New physics in cold dense matter

Theory suggests the existence of new physics in materials at very high pressures (e.g., 0.5–1 TPa) and low temperatures. There are currently no experimental data in this regime; indeed, it is likely that experiments will reveal altogether new phenomena not predicted by theory. Achieving higher pressures together with variable temperatures and other extreme fields in combination with new diagnostics will lead to a deeper understanding of the nature of matter. The new physics that will be revealed, for example, will drive new theory into the mechanisms of magnetic and electronic order.

An excellent example is the predicted metallic superfluid; it is a proposed magnetic technique that would be a signature of the predicted new state of matter: a superfluid superconductor. The first challenge is reaching the combined pressures, temperatures, and fields needed and containing hydrogen to explore this. The diagnostics would involve imaging the vortex matter that would be created, as predicted by theory. Beyond fundamental physics, there are numerous potential implications for energy, planetary science, and astrophysics.

2.1.3 Fundamental thermodynamics

We currently have a limited understanding of the basic thermodynamic properties of many materials, including relatively simple elemental substances, in the currently accessible megabar pressure range. These properties include phase diagrams of many systems, where in some cases extremely large discrepancies in melting temperatures exist between static studies, shock compression, and theory. Since each of these approaches has its own limitations, and more important, may explore different phenomena or states of materials (e.g., stable versus metastable, relaxed versus unrelaxed), the existing putative discrepancies may provide evidence for new behavior in materials. Excellent examples include the melting curves of bcc transition metals, such as Ta. By bridging the current gaps that exist between these methods, we will find solutions to apparent discrepancies in phase stability, structures, transitions mechanisms, and dynamics, and thereby develop an understanding of the general phase behavior of materials at extreme P-T conditions. For this, accurate in situ probes of structures, dynamics, and equations of state are needed up to multimegabar pressures (e.g., 0.5 TPa) and temperatures from millikelvins to ~1 eV.

Another example of fundamental thermodynamics at extreme P-T conditions is the nature of equilibrium defects and grain boundaries under these extreme conditions in pure systems as well as interfacial phenomenon in alloys, composites, and complex materials. So far, there has been very little work on studying interfaces directly under any degree of compression. An interface at high pressure is a buried interface, so the most prevalent tools of surface science are useless. Interfaces currently may be studied using a monolayer of a material with a unique signature or using a surface-sensitive spectroscopic method such as sum-frequency generation. New interface sensitive *structural* probes are needed. The scientific challenges include understanding how interfaces and interfacial interactions between similar or dissimilar materials are affected by high pressure, how interfacial structure (e.g., interfaces with high surface free energy versus interfaces with lower surface free energies) changes with pressure, and how interfacial reactivity (e.g., the reactivity at the surface of a heterogeneous catalyst) responds to pressure. The applications include (1) lubrication resulting from the behavior of thin layers of lubricants between surfaces; (2) adhesion,

adhesion failure, and material aging, e.g., the interactions of adhesives with the surfaces of materials; (3) catalysis and electrocatalysis where the structures and, therefore, reactivities of the catalytic entities can be continuously varied by the application of high pressure; (4) control of the strength of materials by controlling the grain boundary structure; and (5) geoscience and planetary science in which this information is crucial for understanding the large-scale structure and physical properties of planets, including their evolution and dynamics of their deep interiors.

2.1.4 Time-dependent transformations

Equilibrium phase diagrams and stability relations are only a first step. In general, equilibrium properties do not adequately describe material behavior in dynamic processes. Compression-rate dependence of phase nucleation, growth, melt, and microstructure are vital to understanding and modeling dynamic events. By pioneering a broad range of time-resolved diagnostic probes (e.g., with x-rays, neutrons, or lasers), we need to selectively interrogate materials during pressure-induced transitions with the precision characteristic of static compression techniques. Such measurements will provide rate-dependent kinetic phase diagrams and establish an experimental basis for implementing predictive capability.

Development of a fundamental understanding of the influence of kinetics and compression-rate dependencies of phase transition will have a profound impact on high-pressure science and technology. Measurement and study of kinetic phase diagrams are crucial to understanding, modeling, and simulating dynamic processes. As a material is dynamically driven across a phase line, the nucleation and growth kinetics are the critical parameters determining the development of the new phase. Indeed, at exceedingly high-compression rates, the material may transform to altogether new (e.g., amorphous) phases rather than the thermodynamic equilibrium phase. Experimental data regarding kinetics at high pressures is very limited and credible predictive theoretical approaches do not exist. Pressure-drives with precise control and tunability across a broad range of pressures, temperatures, and compressions rates will provide crucial data for establishing insights into this challenging area of research.

This work will address the largely unexplored area of phase transition kinetics and dynamics and will be valuable in developing models of meteoritic impacts (geophysics) and other impact phenomena (DOE/NNSA and DoD). Control of phase transformation kinetics directly impacts the microstructure and associated constitutive properties of materials for technological applications. In addition, at high-compression rates, the possibility exists that the synthesis of materials with unique identification of novel metastable materials along reaction paths could have important technological and geoscience implications.

2.1.5 High-pressure strength, plasticity, and rheology

Material response under compression is a function of chemistry, phase content, microstructure, defects, impurities, as well as pressure and loading rate. By developing novel x-ray diffraction and nano-imaging techniques and pressure devices with the ability to apply controlled and characterized uniaxial or shear strain in well characterized environments, we will quantify the complete stress state in materials exposed to high pressure and the deformation mechanisms and flow stress as a function of strain rate and across grain boundaries.

The limited static (or quasi-static) high-pressure strength measurements performed to date rely on assumptions (e.g., magic angle analysis, peak broadening), and do not take advantage of new developments (e.g., emerging nanobeam probes and imaging methods). Required are new imaging techniques as a function of time, which will require in turn advances in anvil cell designs. These designs will permit pre-defined and controlled loading paths, direct nanoimaging of the stress state with nanometer resolution at nanosecond time scales, 3D tomographic mapping of strain of grains in composite materials, and full definition of the stress state as a function of material, pressure, and loading rate. Determination of stress tensors across material microstructures as a function of hydrostatic and deviatoric stresses provides critical input to theory, modeling, and simulation. The results would potential provide the basis for new physically based models for high P-T strength, including strain rate dependence. This information is of crucial importance for weapons physics, but there are also profound implications for geoscience, astrophysics, and planetary physics.

2.1.6 Synthetic chemistry frontier

Pressure can be used as a novel reactive variable in chemical synthesis. By interrogating intra- and intermolecular bond characteristics using novel x-ray and optical spectroscopies, by utilizing time-resolved probes following compression, and by using theory to develop recovery strategies and elucidating thermodynamic path dependencies, we will predict and control chemical reaction of novel materials and thereby develop a better understanding of the deeper intramolecular and intermolecular interactions under extreme conditions.

As one the largest ranges of any external variable, pressure can be used as a tool or "catalyst" for affecting new chemical reactions and bonding constructs not observed under atmospheric conditions, opening up intriguing possibilities for the discovery of new matter and novel methods of synthesis. Pressure increases local reactant concentrations, producing molecular (steric) configurations that have been shown to influence transition states or intermediates, and resultant product species along the reaction coordinate. The combination of controllable and well-defined high-pressure/temperature conditions offered by modern high-pressure cells devices, combined with advanced tools for probing these molecular states along the reaction coordinate, such as optical and vibrational spectroscopies, x-ray spectroscopies, and x-ray and neutron scattering methods offers exciting possibilities for controlling chemical reactions and discovering or designing new materials under these conditions.

The challenges to probing chemical reactions under high-pressure/high-temperature conditions include small sample volumes, the potentially low thresholds for material damage subjected to ionizing radiation, a lack of methods for temporally-controlled pressurization combined with transient probes of bond-breaking/making steps, and dearth of in-situ techniques typically used in the chemical synthesis laboratory within high-pressure devices in the absence of recovery and post-mortem analysis. Structural relationships for a wider variety of chemical functionalities under a range of high-pressure/temperature conditions and pathways are needed. This fundamental knowledge, combined with theoretical calculations of high-pressure reactant surfaces, could eventually lead to rational design of synthetic targets, much like the current status of the field of

organic chemistry. Here again, we must move from *observation* to *control*, an approach that so far is essentially lacking in high-pressure chemical synthesis at pressures above 1 GPa.

2.1.7 Optimized new materials

As indicated above, high compression has the possibility of creating new, quenchable materials with enhanced properties and functionality. By using the altered bonded states under such conditions, we will create new, useful materials that are recoverable to, and stable at, ambient conditions. Combined with developments in theory to predict material properties, suitable catalysts, and recovery pathways, we will develop new materials with enhanced superconducting, magnetic, thermoelectric, hydrogen storage, solar, and physical properties.

The highest temperature superconducting temperatures are found under pressure. For example, the Hg-Ba-Ca cuprate has the T_c of 164 K measured in 30 GPa; however, the high Tc does not persist when recovered to ambient pressure. Can these active mechanisms be understood and harnessed under ambient or moderately cool environments? Other possibilities, such as "green" hydrogen storage based on H_2O ices, and the prediction and creation of various ultra-hard materials, some with properties superior to diamond are expected to be possible in the future. It is known that double and triple bonds, for example, are particularly active under high-pressure conditions. Polymerization reactions, driven by electronic interactions, occur as "reactants" and are brought into closer contact with applied pressure. Small molecules, such as N_2, and its isoelectronic relative CO, have been predicted and shown to polymerize under moderate pressures. A polymeric form of CO has been recovered to ambient conditions and shown to be highly energetic, decomposing exothermically to gaseous CO, and offering the exciting possibility of new classes of explosive materials, prepared in the absence of catalysts and solvents. Still other examples include the recent creation of bulk metallic glasses under pressure and the prospect of making other types of glasses based on the observation of pressure-induced "polyamorphism." For these, the challenge is the recovery of these materials in large quantities for useful applications. There are obviously significant implications for materials science, energy science, and national security science.

2.1.8 Radiation-induced high-pressure chemistry

Ionizing radiation (e.g., x-rays, visible light, neutrons, and protons) can be used as a novel source of electronic rearrangement in chemical synthesis as well as an unwelcome mechanism of damage. By predicting bond ionization for the synthesis of desired products with a given functionality, and by investigating molecular bond breaking via time-resolved x-ray and optical spectroscopies, we will be able to design chemical reactions to target novel materials as well as calibrate and even control damage.

Understanding the behavior of materials under extreme conditions of high pressure and high radiation flux is vital for understanding and improving the performance and reliability of nuclear weapons and nuclear reactor components. In addition, as so many studies of materials are conducted using lasers, neutrons, and x-ray beams as part of current and next generation sources, it is vital to quantitatively calibrate and assess the damage caused by ionizing radiation. We have discovered that the rate of damage from x-ray beams has a strong and reproducible dependence upon the pressure (at least in the case of TATB,

slowing with pressure), which suggests that materials can be studied, despite radiation damage, by subjecting them to sufficient pressures or using time-resolved probes.

Techniques used to study radiation-induced chemistry to date include white beam energy-dispersive x-ray diffraction, x-ray Raman spectroscopy, and monochromatic angular dispersive x-ray diffraction. Samples are interrogated both before and after radiation bombardment to assess mechanisms and rates of damage. The challenge will be to develop additional probes and to use diagnostic in real time to determine atomic and electron level mechanisms with varying sources (light, neutrons, varying energy, varying x-ray flux). The benefits of this work would be twofold: (1) developing quantitative benchmarks for radiation-induced damage in materials *and* (2) using various kinds of radiation in combination with pressure, temperature, and other fields for the rational design of new materials with new properties and functionalities.

2.1.9 Earth science, planetary science and astrophysics

Static compression science is creating an ever-expanding picture window of increasing clarity and resolution on the interiors of our planet. Despite this advancing vision, many regions of the Earth remain poorly understood in terms of material properties. An excellent example is the Earth's core. This region of the planet is mainly composed of iron, but in a state that is far different from the element found near the surface of the planet. Iron has interesting, if not unusual polymorphism, elasticity, and strength; there are dramatic changes in chemical and magnetic properties, and iron is even a superconductor under pressure. We need to understand not only the high-density solid phases, but also the fluid states to pressures above 350 GPa. This information is crucial for modeling the Earth's magnetic field and determining the temperature distribution and heat flow from the interior.

Another rich area of study is the core-mantle boundary region, where oxide and silicate phases exist that are never seen on the Earth's surface and have completely different physical and chemical properties from near-surface rocks and minerals. Moreover, advances in observational planetary science and astronomy have led to materials questions about bodies throughout the cosmos. By reaching higher pressures and temperatures, and by making accurate determinations of the physical and chemical properties of planetary materials at such conditions, we will determine the structure, composition, dynamics, and evolution of the full range of planetary bodies and other astrophysical objects. This will have profound implications for our current understanding of the evolution of solar systems and the possibility of life elsewhere in the universe. Planets, stars, and other astrophysical bodies are natural high-pressure chambers, so interpreting the wealth of new geophysical and astronomical data in terms of their component materials will also add new understanding of information that is important for fundamental physics, chemistry, and materials science

2.1.10 Life in extreme environments

We do not currently know the limits of life in extreme environments. By developing new methods for making in situ measurements of structure-function of biological systems, from whole communities of organisms to component molecules, we will be able to define the habitable zone in the cosmos, the limits of life on Earth, the possible origin of life, new

methods for directed evolution, and thereby develop the new field of high-pressure genomics/proteomics.

2.2 Technical Grand Challenges in 'Static' Compression Science

2.2.1 Reaching 1 TPa and beyond

The recent dramatic improvements in high-pressure generation and extreme condition diagnostic capabilities are clearly leading to important scientific advances, but this is only the tip of the iceberg. Achieving pressures exceeding 1TPa, far beyond the current capability of ~400 GPa, will enable studies in entirely new regimes of physics. Novel high-pressure apparatus design and materials are needed to extend current pressures limits. New anvil materials, for example, could be based on CVD single crystal, nanocrystalline diamond, and new types of composites. Using a nano-focused x-ray beam to measure anvil nanostrains together with large synthetic diamond with enhanced physical properties, for example, we will optimize pressure cell design. Such breakthroughs will enable open extreme compression laboratory environments to myriad of diagnostic tools available in static compression studies and herald new understanding of matter under extreme conditions.

2.2.2 Developing multi-probe 'intelligent' devices

The next generation high-pressure designs that will extend pressures limits to 1 TPa and beyond will require tailored anvils that enable the measurement of a broad range of physical properties with high spatial resolution. Extension of tailored designer anvils can measure new physical properties, including electrical conductivity, thermal conductivity, and NMR. Nano-scale manipulation and sub-micron patterning and modification on anvils will result in a dramatic extension of measurements that will be enabled in extreme environments. The results could also lead to novel nanosensors with applications beyond extreme environments.

2.2.3 Stress-strain states and P-T calibration

Accurate characterization of the stress-strain state of materials is central to all aspects of high-pressure science; it also underlies the challenge of calibrating pressure as one reaches ever more extreme conditions. With the development of multi-diagnostic probes, "ab initio" calibrations of pressure can be developed (i.e., by measuring bulk modulus and density on the same loading state). However, we can now go much further and produce detailed maps of the micro-strains in samples from which the 3D stress distributions can be determined. The development of micro-focusing capabilities is crucial. Nano-focused x-ray beam will allow measurements of nanostrains in not only the anvils and gaskets but also the samples and pressure (stress) calibrants. Such high-spatial resolution probes can make detailed mapping of material properties. New theory and modeling of composite materials is needed to provide robust and reliable stress-strain inversions. Accurate calibration of temperature at very high pressure is also needed; this calibration needs to be carried out by combining static and dynamic compression and theory. Addressing these technical challenges is required in order to open extreme compression environments to the myriad of diagnostic tools available in static compression studies.

2.2.4 Advancing x-ray methods

Inelastic x-ray spectroscopies such as x-ray Raman Spectroscopy (XRS), x-ray absorption spectroscopy (XAS), x-ray emission spectroscopy (XES), extended x-ray absorption fine structure (EXAFS), nuclear forward scattering (NFS), and nuclear resonant inelastic x-ray scattering (NRIXS) will be harnessed to interrogate deep core-level bonding changes and phonon density of states (DOS) determinations under extreme conditions. Using techniques rooted in the phonon modulation of Mossbauer nuclear energies, the phonon density of states can be determined. In the XAS, XES, and EXAFS techniques, valence electronic states are probed by photoelectron absorption and emission. Temperature can be determined by appropriate fits of the phonon DOS, which can allow potential novel methods to ascertain sample temperature under extreme conditions. For experiments performed to date, Be gaskets are used to allow x-rays into and out of sample region. There is also likely to be sample decomposition with bombardment. XES is usually achievable for primarily heavier atoms. XRS reveals bonding changes (e.g., hybridization alteration) under extreme conditions. XAS and XES provide a measure of changes in valence and deeper electronic changes (cf., "kilovolt" chemistry). Though these are now established techniques, the measurements are, in general, photon limited.

NRIXS and NFS measurements are only possible with high flux sources due to their inherent low signals for conventional high-pressure-sized samples (nanoliters, cubic microns) and the requirement for highly filtered x-ray light using double monochromators to achieve meV energy resolution. Thus, long detection times are required due to low signal to noise; moreover, measurements at the highest pressures are impossible with current technology because the signal overwhelms the background. Only Mossbauer-sensitive nuclei can be used (NRIXS and NFS). Most measurements cannot be performed over the wide range of pressures needed (e.g., multi-megabar pressures) or with sufficient spatial resolution to address the above science challenges. Hence, higher brightness x-ray sources are required.

2.2.5 Real time x-ray imaging with nm resolution

The above dual advances in x-ray spectroscopies and time-resolved methods need to be combined ultimately for in situ time-resolved imaging. Such imaging methods are essential for understanding the time evolution of defects in materials, starting at the subpicosecond scale. Another example is the technological challenges for studying interfaces at high pressure, which stems from issues of sensitivity, i.e., detecting a small number of interfacial species, and selectivity and suppressing the background of the associated bulk media. For planar interfaces buried within opaque media, such as bimetallic interfaces in metal, grazing x-ray scattering could be useful. But for buried opaque complex interfaces, such as the grain boundaries inside a polycrystalline metal, good techniques do not yet exist. One suggested possibility, based on the paradigm of nonlinear optics, might be the use of nonlinear x-ray optics using intense short-duration coherent x-ray pulses, for example, imaging grain boundary structures using 2-photon x-ray microscopy.

2.2.6 Neutron scattering to multi-megabar pressures

Neutrons are complementary to x-rays, as they probe nuclei (not electron distributions), magnetic structure, are sensitive to hydrogen, and have high penetrating power. However, neutron scattering studies are currently limited to ~30 GPa by the need to use large sample volumes to overcome the inherent weakness of neutron sources. By using micro-focused

neutron beams, higher-intensity neutron sources, and larger sample volumes available using novel pressure cell technologies, neutron scattering measurements can be performed to above 100 GPa. The goal is accurate measurements to at least 300 GPa to address the scientific challenges described above. These measurements include both elastic scattering (e.g., diffraction) as well as the more difficult inelastic scattering (e.g., spectroscopy) measurements. Meeting these challenges requires advances in both high-pressure apparatus (e.g., larger sample volumes) and significant increases in neutron flux—not incrementally—but both by orders of magnitude. Such advances will enable the numerous strengths of neutron techniques to be extended to extreme compressions.

2.2.7 Challenge of liquids and amorphous materials

The inherent weakness of scattering from liquids and amorphous materials has long limited their study. Yet a wide range of novel extreme-conditions phenomena exists in such materials, including both polyamorphism and liquid-liquid phase transitions. We currently have a limited understanding of the nature of amorphous materials under high static and dynamic pressures. How are the atoms or molecules distributed spatially, and what is the range of local density variations? What new probes can bring insights into liquid-liquid transitions and melting phenomena at high-pressure conditions? How can melting be defined or determined (for metals, small molecules, etc.)? Likewise, second-order transitions between amorphous phases, such as glass transitions in polymers, are difficult to discern with current techniques. Methods such as neutron and x-ray scattering (SANS, SAXS, pair distribution function) currently give information about the distribution of atomic pairs in amorphous or liquid domains, but the scattering cross-sections are low, signals are often difficult to distinguish from diamond Compton scatter or other backgrounds, and analysis is difficult. Acoustic measurements used to derive bulk volumetric information are frequency dependent and do not offer atomic-level insights into compressive responses.

This area of study will require developing novel detector technologies to enable inelastic Compton scattering to be removed, extending neutron scattering techniques to higher pressures, and using nano-imaging techniques. For example, new methods are needed with enhanced signals (or enhanced detection) for interrogation of amorphous samples at high pressures in small sample volumes, coupled with high accuracy knowledge of local temperature and stress states. Potential improvements can be gained from back-drilling the diamond anvils along the incident x-ray axis, use of slits, or increased flux. Likewise, neutron scattering measurements with smaller focused beams in large volumes at even higher pressures, as discussed above, will open up a large number of potential measurements on amorphous phases. The measurements must be coupled with modeling efforts aimed at capturing and interpreting the stochastic nature of these forms of matter. Finally, extending these new tools to the time domain and combining them with transient measurements of transport properties, viscoelastic properties, and kinetics of liquid-liquid and liquid-solid phase transformations will be necessary for interpreting the dynamic aspects of phase diagrams, improving equations of state for amorphous or multiphase materials (including melt), and evaluating bonding in new forms of matter.

2.2.8 Filling the strain rate gap: Static to shock

Interesting and largely unexplored physics lies between the static and dynamic time-scales at high pressure. Mode transitions, as well as phase transformation kinetics, are known to

be strong functions of loading rate. By developing high-pressure cells with precisely controlled and calibrated loading rates capable of compression rates to 10^5, cycles at kHz, and single-shot rapid decompression, and by developing detectors and probes consistent with these new experimental capabilities (sub-micron spatially, sub nano-second temporally), we will elucidate the rate-dependent properties for the first time.

Systematic studies of phase transitions can be achieved using tunable precise pressure-drives in conjunction with time-resolved diagnostic probes (e.g., x-ray, neutron, and laser). The time-resolved probe can be synchronized and timed to selectively interrogate the sample as it is driven across the phase transition. The dynamic diamond anvil cell (dDAC) is one example of a tunable pressure-drive suitable for these types of studies. Pulse-selection hardware and high-speed detectors at high-performance sources are necessary technical components to perform these proposed studies.

2.2.9 Transport properties

There are few measurements of thermal and transport properties at high pressures/temperatures. Examples of desired measurements include thermal conductivity, diffusivity, and viscosity in small volumes at high-pressure/temperature conditions. The present state-of-the-art concerns the use of designer anvils for resistivity measurements, NMR and rolling-ball viscosity measurements at low pressures, and laser-based foil heating methods to estimate thermal conductivities. These challenges could be met with advances in pulse-probe NMR methods, development of non-magnetic diamond cells capable of high pressures, exploitation of confocal, ultrafast optical methods for both heating and detecting temperature changes spatially in high-pressure sample volumes, and design of new embedded-probe anvils for measuring heat flow.

2.2.10 Thermochemical measurements at multimegabar pressures

In addition to constituitive, transport, and dynamical measurements, there remain great challenges in measuring fundamental thermochemical data needed to address the science challenges discussed above. New techniques are needed, for example, to determine free energies, enthalpies, entropies, and heat capacities of pure, complex, and nanophase materials starting at even modest pressures. A combination of time-resolved optical methods combined with highly sensitive nanolithographic techniques need to be developed for measurements to be performed in concert with the in situ studies described above.

3. Breakout Summaries: Dynamic Compression Science

Dynamic compression science has historically been a field in which measurements have been made (primarily) at the bulk or continuum level. Details of the effects of phase transformations, defect generation, chemical composition, shock-induced chemistry, and the effect of grain boundaries and grain orientation on dynamic material response have only been inferred through wave profile analysis and/or post-experiment examination. That said, the level of detail gathered in the first decades of compression science was adequate for the simulation and modeling capabilities available at the time, and the weapons community was able to design modern weapon systems through a combination of "simple" simulation and experiment. This is no longer the case.

Today, we are on the verge of transforming dynamic compression science from science focused on developing understanding at the continuum level to a scientific discipline focused on developing understanding at the atomistic and mesoscopic scales, ultimately leading to the linking of scales and the ability to predict and control performance under dynamic loading conditions. Our current modeling and simulation capabilities have unprecedented temporal and spatial resolution: a result of modern platform development and better understanding of material response (though we have not yet reached simulation linking all scales), but we have not reached our goal of fully predicting and controlling material response. Reaching this goal will require a suite of new diagnostic tools and capabilities that can help answer the scientific challenges, described below, and provide validation data for next generation simulation capabilities. We will not succeed if we do not meet these challenging opportunities.

3.1 Scientific Discovery Challenges: Dynamic Compression Science

3.1.1 Kinetics and mechanisms of melting, freezing, and solid-solid phase transformations

A long-standing problem in compression science is the identification of the location (in Pressure-Volume-Temperature [P-V-T] space) and characterization of phase transformations, including melting, freezing, solid-solid transformations, and their associated kinetic rates. Of concern is the fact the static and dynamic measurements do not always yield the same location in phase space. This could be a result of differences associated with the transformation path dependence in P-V-T space, and/or the effect of strain rate (which can include both loading and release paths) on the transformation dynamics, or simply that the sample must be superheated during shock experiments to observe the transformation on the timescale of the experiment. Moreover, we have very few techniques for characterizing phase transformations, particularly dynamically. In principle, pyrometric techniques should yield characteristic signals associated with the temperature arrest that is indicative of a phase transformation, and transient X-ray techniques should provide structure information that ultimately could be quantified to yield fractional phases as a function of time. Neither technique has reached a maturity level that unambiguously meets our needs, and the data will be unimportant if our theoretical constructs regarding transformation are inadequate or at best phenomenological. Thus, in addition to advanced

diagnostic tools, we require the development of theories that accurately represent the physics of transformations and capture the path and rate dependence effects.

3.1.2 Warm dense matter (WDM): metallization, release around critical points

The metallization of matter when subjected to extremes of temperature and pressure has been considered and pursued since the development of band structure theory and the recognition that extreme pressure could cause a closure of such bands. That said, metals can also behave counter-intuitively. For example, lithium and sodium can become insulators under the extremes of pressure. Perhaps more importantly, the class of matter known as warm dense matter (WDM) lies in "no-man's land." It is not hot enough for direct application of Thomas-Fermi, yet too hot to accurately calculate the properties using classic cold-curve techniques. More important, we have very few methods for creating and characterizing such matter, both on initial compression and subsequent release. As an example, if one could reliably measure the conductivity under these unique conditions, while simultaneously measuring the temperature, pressure, and volume, the data set obtained would challenge and expand our current thinking regarding the equation of state (EOS) of matter in this regime. Furthermore, if we could create comparable conditions in a static setting, we could make a connection to between static and dynamic regimes that will improve our overall understanding. Thus, there is a significant need to develop capabilities for creating and diagnosing this state of matter, both to develop a fundamental understanding of such things as the nature of matter at the core of planets, but also to gain an understanding that can impact applications such as fusion, first-wall material studies for the International Thermonuclear Experimental Reactor (ITER), and enhance our understanding of nuclear weapon performance, including boost.

3.1.3 Evolution of microstructure under dynamic loading including defect distributions

Most metallic materials are polycrystalline in nature, such that they are an aggregate composite of metallic single crystals. As the polycrystal is deformed, the single crystals interact with each other so that the internal stress within the polycrystal is highly non-uniform. Simulations predict a factor of two or so difference between the minimum and maximum stress within the aggregate. If these materials are deformed a great deal, the temperature will certainly increase, and they begin to develop damaged regions and failure zones. The location of these damaged and failed regions is highly dependent upon microstructural characteristics (e.g., grain size distribution, impurity content, grain boundary strength) and the nature of the loading (e.g., time rate of loading, total strain, maximum stress). Figure 1 shows an image of tantalum deformed by plate impact loading. This image displays a snapshot of a material that has failed by the process of pore nucleation, growth, and coalescence (a ductile process). Note that the failed regions are spread out and indicate that the physical processes involved are stochastic in nature.

Predicting when and where material failure will occur with current theoretical and computational tools is still one of the biggest challenges facing the material modeling community. Failure is the final step in a complex physical process of microstructural evolution. The ability to understand and predict when and where failure will occur for any type of aggregate material (e.g., polycrystalline metals, high explosives, concrete, fibrous composites, etc.) requires that we not only understand the statistics of material initial

conditions such as grain size and morphology (for the case of polycrystalline metals), inclusion content and location, grain boundary shape, misorientation across grain boundaries, etc., but also how these quantities combine and evolve under service environments leading to failure. Deformation events that add to the initial heterogeneity are such things as inhomogeneous temperature change, dislocation cell formation, slip band formation, twinning, and phase transformation. Further microstructural evolution leads to discrete damage/failure processes, such as pore (ductile materials) or crack (brittle materials) nucleation, growth and coalescence, shear band formation and growth. These events also occur in three dimensions, of course, so we need to push our experimental and theoretical/computational capabilities to deliver this type of information in 3D. A two-dimensional characterization will never allow us to achieve success.

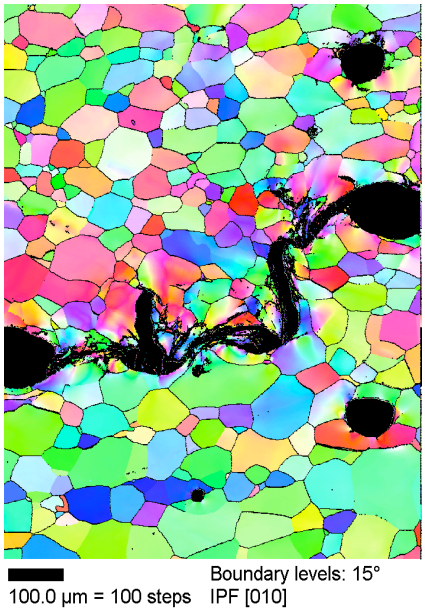

Fig. 1. Orientation Image Map of a deformed tantalum plate impact sample.

Thus, we have the need for a new experimental capability to track, in situ, the 3D microstructural (including defect distributions) and temperature field and their evolution. The information is needed to characterize and develop associated theories that incorporate the details of defect distributions leading to pore nucleation, pore growth and coalescence, dislocation cells, slip bands and twins, as well as shear bands.

3.1.4 Experiment/theory convergence: Developing the ability to reproduce simulations of 'real systems' for better understanding of experimental observations.

One of our greatest challenges is to be able to conduct experiments and perform associated simulations that are so precise in their initial conditions (such as the defect distribution and/or polycrystalline orientations and sizes) that we are modeling the "real" and not the "ideal" system. One approach would be develop experiments that directly evaluate the results of molecular dynamics (MD) simulations, such as an LINAC Coherent Light Source (LCLS) experiment with exactly the same number of atoms as an MD simulation, and validating at the appropriate length scale. Moreover, experiments might be designed to probe a particular physical regime to isolate and provide a means for better comparison with the simulations. Too often, we end up compromising on both the experiment and the simulation, with results that need interpretation or speculation to make the connection between the experiment and the simulation. Thus, the development of a series of experiments that are standards and/or the choice of simulations that we can properly diagnose in an experiment is critical to develop real understanding and to move from "observation to control."

3.1.5 Resolving the details of detonation and shock-induced chemistry

It has been the firm belief of many in the Energetic Materials (EM) community that the key to predicting explosives behavior for both performance and safety lies in the intimate understanding of the molecular-level processes. Energetics are complex systems that involve inter- and intramolecular bonding, numerous morphologies, different polymorphs, crystal defects, impurities, and component inhomogenities. EM can be made stable under ambient conditions, can be stimulated to energetic decomposition, will crystallize into a knowable structure with a given density, and can be fabricated into incredibly elegant shapes and strong mechanical structures. The crystal structure and intermolecular bonding strongly affect the density of the material and, thus, the energy delivered per unit volume of explosive. The molecular structure and the intermolecular bond energies will also affect the rate at which energy put into a molecule might escape to the bulk material, which in turn strongly affects the sensitivity and safety of the compound. Unfortunately, these molecular-level processes are not known even for systems that lack many of the complicating factors listed above. Without this detailed data, we cannot develop molecular-level predictive capabilities. Present theories can only lump most of the chemistry into overall reaction rates or energy release rates. The overall goal is to develop a complete time-dependent description of detonation and the evolution of the product's equation of state for military purposes as well as to facilitate the introduction of new energetic materials for military, counter-terrorism, surety, and industrial applications. These new energetic materials include explosives, rocket and gun propellants, and pyrotechnic devices. Various driving forces (which can be different for the wide variety of applications) include increased performance, increased safety margins, decreased cost, and decreased environmental impact. It is important to have optimal screening measures so that confident decisions can be made more rapidly on whether to proceed or not with a particular formulation. We need to develop the ability to screen, measure, and predict the performance of new or proposed materials for optimal use and/or unique applications.

3.1.6 Discovering new phases and forms of matter at ultra-high compression using tunable pathways and controlling reaction chemistry through pressure and temperature

As stated in the introduction, one of the key contributions of compression science has been through discovery, as generated by novel extremes of pressure and temperature. For example, the nature of the phase boundary in sodium and lithium was completely understood when the experiment elucidated its concave downward nature (in P-T space) and, in general, that the nature of bonding can significantly change with compression (imagine core electron participation in the extremes). Furthermore, chemical reactions that are forbidden on the ground state potential surface (e.g., Woodward-Hoffman forbidden) may be accessible under the extremes of pressure and temperature. Thus, the exploration of potential energy surfaces as a function of pressure may offer new routes for the synthesis and/or manufacture of materials that would otherwise be unachievable. The classic example of this is the conversion of graphite to diamond using pressure/temperature, but other examples such as the formation of polymeric nitrogen have demonstrated the utility of these concepts. Thus, using *ab initio* calculations as guides, and through the development of a robust experimental program (including the ability to tune pressure and temperature through the proper choice of wave profile, e.g., ramp, shock, etc.), we will be in a position to predict and/or discover new materials that may have functional behavior that meet our needs under extreme service conditions (e.g., armor, high neutron fluxes of reactors, etc.).

3.1.7 Discovering and understanding of the partitioning between dissipative and non-dissipative mechanisms

The concept of a shock is well defined. However, the underlying processes within the shock wave and the partitioning between dissipative and non-dissipative mechanisms are not well characterized nor well predicted. Predicting and measuring the Hugoniot Elastic Limit (HEL) and strength under loading is a must. We currently have little means for measuring and calculating transport properties, and therefore, our description of the loading process is incomplete and we cannot connect with theory. We must develop diagnostics at the appropriate scale (e.g., diffraction for atomic-level information) that allow the elucidation of mechanisms important in all rate processes, including transition from shockless loading to shock compression, and provide physical details that resolve phenomenological models of deformation such as the Swegle-Grady fourth power law. In addition to better experimental characterization, we have a need for the ability to predict transport properties, damage evolution, and localization phenomena.

3.1.8 Determine the role of shear in deformation processes

Shear can play a major role in initiating and controlling the physical and chemical processes that take place under dynamic loading, but needs to be quantified and better understood. We currently have little experiment and diagnostic capabilities for resolving shear so as to ascertain its role in dynamic material processes, including chemical reactions. For example, we would like to know the mechanisms that cause inelastic deformation, damage evolution, and failure and the extent to which shear contributes to these processes. Experiments designed to examine shear contributions would provide data that, in turn, would guide the development of a predictive capability by providing a mechanistic understanding of structural, chemical, inelastic deformation, fracture, and second-order phase transitions that can be driven by shear.

3.1.9 Develop understanding of the role of interfacial boundaries

There is a lack of understanding of the interaction of waves with boundaries (including spallation) and the stability of materials (or lack thereof) that result in the dynamic mixing of materials within local environments. Thus, we must conduct controlled experiments with high-resolution dynamic imaging to measure the velocity field evolution and dynamic mixing as a function of time, which would imply the need for measuring flow within opaque materials. Furthermore, this information is of little value without basic theories for prediction of the local geometries as well as thermodynamic states in the mixed phase regions. The mixed phase regions include heterogeneous interfaces of grain structure and their evolution. In addition, we need to understand the morphology, size of particulates, and their relation to global variables such as density evolution. Finally, we need the ability to determine material properties from observations of interfacial evolution under general loading conditions, which will allow us to predict and optimize material behavior to meet our functional requirements.

3.1.10 Develop an understanding of the transition in material plasticity and damage evolution across the 'thermally activated' to 'shock' to 'drag control' regimes

There is a lack of understanding of the operative mechanisms of defect generation and storage across the transitions from thermally activated plasticity under uniaxial stress to

uniaxial strain shock loading. Furthermore, as we increase strain rate, the transition to drag control occurs as relativistic effects become operative. To date, only surface diagnostic tools have been applied to studying these fascinating transitional regimes in plasticity with little insight. Accordingly, theory has not achieved physically based models to address these transitions owing to a lack of mechanistic understanding of the changes in defect generation, motion, and thereafter storage processes as a function of the applied strain rate.

3.2 Technical Grand Challenges in 'Dynamic' Compression Science

3.2.1 Characterization of melting, freezing, and solid-solid phase transformations

We need to develop a comprehensive definition of melt. We know that loss of shear modulus, loss of long-range structure, and loss of autocorrelation are indicators, and we need diagnostics that connect to this definition. (We also recognize that there is a distinction from amorphous solids.) Tools should include the following:

Phonon dispersion measurement—LCLS diffraction correlation instrument?

Measurement of shear modulus

Fully utilize advanced light sources

Coherent imaging and diffraction

Tomography (grain scale microstructure)

Time resolution (kinetics)

Diffuse scattering (statistical representation of defects)

Small angle scattering (nucleation and growth kinetics)

3.2.2 Real-time diagnostics for dynamic mapping of the thermo-mechanical field

We have a need to develop predictive capability that describes the generation and evolution of defects that control continuum material properties. We must develop and field multiple diagnostics for such experiments to achieve thermodynamic field measurements, in particular temperature measurements and specification of the full stress tensor. These diagnostics must include in situ temperature and stress diagnostics applicable to different compression regimes and time scales. This will allow the specification of time-resolved thermo-mechanical variables at different spatial locations. Thus, we need the following:

Accurate temperature and strain/stress field measurements

- Local environment temperature probes
- Multi-axial stress probes, e.g., single molecule spectroscopy
- Multi-axial strain probes, diffraction

Pre- and post-experiment characterization

- Tomography
- Diffraction Contrast Tomography

3.2.3 Ability to make experimental measurements to link length scales ranging from atomic to continuum dimensions

Continuum response depends on material behavior at lower length scales**.** A suite of in situ time-resolved measurements at different length scales is required to validate theoretical models as they transition from one length scale to the next. To reach this goal (need), we must develop new experimental capabilities that provide these linkages. The linkage of measurements at different length scales will lead to the first realistic models required for predictive capability.

3.2.4 Ability to make in situ spectroscopic measurements including those of electronic structure

Spectroscopic probes provide a characterization tool for measuring both the average and localized environmental effects of compression, depending on the probe and its practical implementation. Data regarding the effect of compression on molecular structure and/or chemical changes can be obtained through vibrational spectroscopies (e.g., Raman and IR absorption), while electronic spectroscopies provide a measure of the changes in conductivity (as manifested through changes in Fresnel coefficients) and changes in the potential surface. Nuclear spectroscopies (e.g., XANES/EXAFS) can also provide information regarding bonding and nearest neighbors. Thus, modern facilities must have capabilities for implementing the following spectroscopies in order to make stronger connection with theoretical models:

Reflectivity

Raman

X-ray spectroscopy

XANES and EXAFS

XEL

3.2.5 Complex loading path control

As discussed previously, the application of compression can provide routes to other forms of matter that would normally be symmetry disallowed or inaccessible on the noncompressed potential surface. Thus, the proper combination of ramp and shock can provide the mechanism for tuning the path and creating an environment conducive to generating new forms of matter or for “allowing” normally disallowed chemical reactions. In addition, the ability to quantify the partitioning of energy between dissipative and non-dissipative mechanisms requires techniques that allow for changing the relative contributions of these processes. Thus, ultimately achieving dynamical control of these processes will require the ability to carefully tune the loading profile, from isentropic to shock loading and anywhere in between, in order to vary the thermal content as well as access portions of the potential energy surface that can only be accessed under compression.

3.2.6 Develop first-order continuum analyses that produce better subscale models and capture defect evolution

Many of the current descriptions of dynamic loading are phenomenological in nature and cannot be connected in a "real" sense to the material world. As an example, to design optimal experiments for direct comparison, we have a need for realistic descriptions of inelastic deformation that incorporates material phenomena at lower length scales (microstructure, defects, texture, etc.). Often, experimentalists and theorists define experiments that are "ideal" in the sense that they are capable of being performed, even though the experiment or theory may not be modeled or tested. Thus, we need stronger experimental and theoretical collaboration to define optimal conditions and diagnostics from which to draw more accurate comparisons and, as a result, a better analysis and interpretation of experiments.

3.2.7 Learn how to conduct and diagnose experiments relevant to 3D applications

Real-world applications are inherently three-dimensional and will often involve phenomena that may not occur in one-dimensional experiments. Thus, we have a need to develop experimental methods and diagnostics that achieve and quantify controlled 3D loading conditions in such a manner as to allow interpretation. This work inherently includes the development of material models that are pertinent to 3D loading and devoid of knobs, if at all possible.

3.2.8 Design experiments that overlap different loading regimes and experimental platforms

We currently have at our disposal a large number of platforms for conducting dynamic experiments, with the Z machine and National Ignition Facility (NIF) as examples. However, we have not developed methods that guide the best use of these different experimental platforms and loading regimes. To achieve maximum effectiveness, we must learn how to coordinate and integrate experiments on different platforms and different time regimes. When coupled with a variety of volume- and time-scale probes (flexibility to span scales on facility), these types of experiments will aid in developing the understanding of the load path and strain rate dependence of material properties needed to achieve realistic and complete models.

3.2.9 Increase experimental throughput

We are often limited in dynamic compression science by the rate at which we can conduct experiments. We must work toward the development of new experimental methods that allow easier and faster measurements of dynamic properties while simultaneously developing new experimental paradigms for combining multiple diagnostics that yield increased efficiencies, decreased cost, and faster turnaround. These new experimental methods will allow for a more complete set of observations, which in turn, will increase development of realistic models, thereby advancing the field.

3.2.10 Develop improved materials and standards for uniform comparisons

Lastly, we have a need for the development of a set of standard materials that will allow us to connect measurements on a variety of platforms and using a diverse set of diagnostics. For example, loading a 50-micron thick tantalum sample on NIF may require the development and

production of an extremely fined-grained material to ensure that the data is not dominated by grain boundaries. To make a direct comparison of this data with that obtained on guns may not be an easy task. To start, we should make gun measurements with the fine-grained material, but our results may still be confused with loading rates that may influence the shock wave rise time. They may be further confounded by time-dependent changes in the wave profile. One example is the change in amplitude of the elastic precursor simply as a function of sample thickness. Thus, connecting these disparate temporal and spatial regimes will require careful thought and analysis. Furthermore, if we could develop better impedance matching materials that are transparent, we could begin to imagine (nearly) looking in at the processes that are taking place in bulk. These observations will be required if we truly expect to achieve control.

4. Breakout Summaries: Compression Science Theory and Modeling

An accurate material description involves the characterization of many variables that can only be captured in a statistical sense, e.g., chemical composition, defect density and distribution, texture, grain size, etc. Our premise is that these intrinsic properties and their linking across scales determine a material's properties (or functionality) and its performance. To develop control, we need to establish the correspondence between a 3D description of a material and its properties, from which we may develop a set of principles that provide an intelligent system for tailoring materials functionality. To make progress in linking behavior of materials to their processed characteristics, we must develop and maintain the intimate coupling of experiment with theory and simulation.

In other words, to develop "process-aware" models linking materials behavior with its 3D characteristics, we require tools that seek to couple and link the spectrum of materials length scales—from the electronic through the continuum and to the application or integrated system level. In fact, a long history of successful models punctuates the lineage of materials science in this quest. Some models, such as optical device theory, rely on fundamental physics; others, such as time-temperature heat-treating curves, arise from phenomenology; and most, such as phase diagrams, combine theory and empirical observation. Within the past three decades, the subspecialty of computational materials science has strived to provide additional modeling tools to the materials scientist, ranging from (i) fundamental (*ab initio* electronic structure and molecular dynamics) calculations at the atomic (usually single crystal) scale, to (ii) dislocation dynamics and phase field modeling at mesoscopic length scales, at which microstructural aspects such as texture and interfacial effects become important, to (iii) single crystal and polycrystal plasticity models that describe "bulk" materials behavior that can be encapsulated in (iv) Equation of State (EoS) and dynamic material strength models suitable for engineering-level simulations. Our computational materials science goals are to enable an integral and predictive capability, not postdictive, and to provide a link between materials, design, manufacturing, and functionality that will ultimately enable "control" of material functionality.

This panel attempted to envision this future research path and elucidate the advances in multi-scale modeling techniques and also the experimental capabilities needed to measure the required validation data that will be required to meet this goal. The heterogeneity of real materials and the non-equilibrium processes underlying dynamic compression phenomena are two key aspects absent from current models based upon a description of average

homogeneous, equilibrium behavior. A proper treatment of such aspects will enable predictions of a probabilistic bulk performance rather than just the ideal macroscopic behavior. The ultimate goal is to develop the scientific understanding that will enable a tailored "control" of the chemical and spatial structure of materials to be tolerant to extreme environments, replacing the conventional trial-and-error approach.

4.1 Scientific Discovery Challenges for Compression Science Theory and Modeling

4.1.1 Track dynamic microstructure evolution in situ

The response of materials to dynamic compression involves a wide range of length scales, ranging from individual point, line (i.e., dislocation), or surface defects at the nanometer length scale, to the nucleation and growth of voids, twins, or product phases at tens to hundreds of nm, collective dislocation microstructure at micron length scales, and finally the 10–100 m grain scale. Current computational materials science techniques have been developed for each of these length (and corresponding time) scales, but a corresponding set of direct in situ experimental probes has not yet been developed. This leads to two choices for design and parameterization of the higher length-scale models: either postdictive fitting of the end state of highly integrated experiments (e.g., Taylor cylinder impacts or recovered incipient spall samples) or an "upscaling" of dynamic material properties from one method to the next. The latter remains an extremely challenging task and introduces a typically un-quantified (but potentially quantifiable) error from one step to the next (*ab initio* electronic structure, to semi-empirical potentials for MD simulations, to mesoscale and finally continuum-scale models). Thus, there is an enormous benefit to direct in situ measurements of the dynamic microstructure evolution at the mesoscale, which lies in the gap between the microscale where theory is most reliable and the macroscale where experimental measurements are most readily made. Two of the most promising candidates in this regard are the following:

> X-ray scattering, which is sensitive to microscopic defects such as voids and dislocations. An outstanding challenge is the "inverse problem" of inferring such defect content from experiment.
>
> Microprobes on synchrotron light sources have reached a level of maturity where the 3D microstructure of a volume containing tens of grains can be mapped within an hour of beamtime. The grand challenge is to do such measurements in situ during static compression and ultimately during dynamic compression.

4.1.2 Discover new and unexpected high-pressure and temperature solid phases

The high-(P,T) equilibrium phase diagrams of elemental materials are in many cases still poorly mapped out, and the situation is even worse for alloys and compounds. The discovery of the hcp ε phase of iron by dynamic shock experiments, only subsequently confirmed by static experiments and theory, is a landmark achievement that greatly enhanced the stature of that community. The accuracy and predictive capability of *ab initio* and molecular dynamics has reached a state where that community should strive to seek such a discovery, by exploring the vast regions of phase space which lie between the principal Hugoniot, isentrope, and isotherms that dynamic and static experiments have

already accessed. The question of the structure of iron at Earth's core and related planetary science issues are being actively explored by these approaches, but otherwise this is a largely untapped area prime for discovery.

4.1.3 Design novel experiments to isolate key physics

To date, the vast majority of simulations has by necessity simplified the material description but, as a result, has neglected the material complexity that often dominates behavior under extreme conditions. The physics that are relevant for understanding the state of matter at extreme conditions include composition, phase, crystal structure and stability, elastic moduli, and local stress of the perfect crystal. In addition, real materials are composed of a collection of crystalline grains with various orientations, shapes, and internal defects that play a dominant role in determining the material behavior. Such material complexity includes internal vacancies, impurities, alloy elements, dislocations, inclusions, second phase particles, and grain boundary or other interfaces. As simulation and experimental scales are approaching each other, it is crucial that such complexity be incorporated in simulations.

To bridge this gap between the often idealized theory and simulations and the experiments using often insufficiently characterized engineering materials, there is a need for novel experiments involving samples with controlled (or at least adequately characterized) grain and defect structures. Simulations can thus be performed on identical samples (statistically if not exactly), and experiments can be performed with internal measurements of strain rate, temperature, and stress state that directly correlate to simulation observables.

4.1.4 Move beyond planar impact: Non-uniaxial strain experiments

Uniaxial and hydrostatic loading conditions have been most studied primarily because they are the most easily achieved in experiments, and modeled, but represent only a very limited subset of stress and strain tensor states that are accessed in complex integrated experiments. Experiments involving oblique impact, sweeping waves, bulge tests, etc., have been performed and modeled, but further work is needed to understand the dynamic material response to these more complex loading conditions and to enhance our confidence in dynamic material models and codes under the entire range of stress and strain states at which they are utilized.

4.1.5 Design novel simulations to isolate key physical mechanisms and observables

The behavior of material following a change in external conditions is determined by the defects inside the materials. By designing simulations that directly model these key unit processes, simulations will make a better connection to the experimental observables. Today's high-performance computing platforms enable the direct modeling, at an atomistic level, of materials starting from an experimentally characterized dislocation microstructure. A direct numerical simulation of the shock compression of material at the atomistic level reveals the deformation by dislocation mechanisms, which may be directly observed with experiment via diffuse X-ray scattering.

4.1.6 Develop ability to predict the kinetics of phase transitions (solid-solid, solid-liquid, and liquid-solid)

Materials exist in many states, and the kinetics of transformation between such states is poorly understood. To date, heuristic models have been fit to macroscopic experimental measurements, such as Velocity Interferometer System from Any Reflector (VISAR) wave profile records, but provide no insight into the transition mechanisms. Direct numerical simulation of transformations provides insight into the nucleation and growth of the product phase and can inform physically based models. For instance, the Kolmogorov continuum model requires nucleation rates, lag times, interface velocities, and other fundamental parameters that can be directly determined from simulations at lower length scales, including molecular dynamics and phase field simulations. However, these lower length scale models have never been validated at extreme conditions by experiment. In situ small-angle scattering experiments reveal the distribution of nuclei at a given point in time; such distributions at multiple times can provide information on the kinetics.

4.1.7 Understand relationship between microstructure and constitutive properties (e.g., strength) during dynamic processes

The dynamic behavior of a material depends upon its constitution, which includes phase, microstructure, and loading path and rate. The development of a predictive material model for that response requires the knowledge of the microstructure evolution along the loading path at the given loading rate. In particular, strength is primarily determined by dislocation unit mechanisms. The dislocation content changes during deformation, and the rate of change is largely unknown. Phenomenological strain hardening models account for this effect in a macroscopic way but do not represent the underlying microscopic physics. Mesoscale dislocation dynamics models can account for this microscopic physics; however these models need to be extended to include deformation, polycrystals, crystal rotation, and experimental information on dislocation mobilities under extreme conditions. Atomistic molecular dynamics simulations can also provide information on the mobility of dislocations at extreme conditions, including conditions in the presence of other defects such as vacancies, impurities, other dislocations, inclusions, or grain boundaries. This microscopic evolution of the dislocation microstructure must be captured in a continuum rate model. The validation of this microstructure evolution is essential and can only come from emerging in situ, real time, X-ray, neutron, and/or proton probes with high spatial and temporal resolution.

Nothing is known about the microscopic state of the material following a phase transition, for instance the dislocation density or grain (and subgrain) structure. The history dependence of a material element, following its evolution through phase transitions, can strongly affect its resulting strength and other dynamic properties in an as-yet poorly known manner, which needs further investigation.

4.1.8 Understand material failure

Material failure under shock compression may result from the localization of deformation and during release the nucleation, growth, and coalescence of microscopic voids or fractures may lead to ductile or brittle failure, respectively. Heuristic models omit such physics, for instance, by assuming that material failure occurs at a specified maximum compression (or tensile stress) η_{min} (or P_{min}). Nucleation and growth models have been developed for a

number of other physical situations but have not been widely applied to material failure to date. Direct numerical simulations of material failure under shock compression can reveal the evolving porous state of the material under load and the underlying physical processes. For example, mesoscale crystal plasticity models with an explicit representation of nucleation sites, informed by atomistic simulations of the nucleation and growth processes, can be developed. Dynamic in situ radiographic imaging, and eventually 3D tomography, can provide details of the void growth process needed to validate the models, overcoming the limitations of existing post-recovery analysis of incipiently spalled samples.

4.1.9 Resolve melting discrepancy in transition metals

Despite several recent attempts involving new theoretical calculations and static high-pressure experiments, the compression science community has failed to resolve a glaring discrepancy between the high-pressure melt curves in several body centered cubic (bcc) transition metals, most notably Mo and Ta. Whereas static high-pressure diamond anvil cell (DAC) experiments using laser heating reveal a very gradual rise in melting temperature (a few hundred degrees K) at high pressures, dynamic shock experiments and quantum molecular dynamics (QMD) simulations both predict a much steeper melt curve, rising thousands of degrees with remarkably good agreement between the dynamic experiments and theory. The fact that several groups in both the United States and Europe have demonstrated the reproducibility of many of these calculations and experiments makes this discrepancy even more intriguing and suggests an overlooked explanation that may potentially raise questions about a wider range of experiments or calculations. For instance, on the one hand, the assumption of a hydrostatic stress state and thermal equilibrium in DAC experiments, and neglect of electron temperature in virtually all QMD and MD calculations, even as temperatures approach 1 eV, could introduce significant errors. On the other hand, static and dynamic experiments are in excellent agreement with each other (and with theory) for non-transition metals, including Al, Fe, Mg, and Ni, which could suggest that an intermediate semi-ordered phase akin to a liquid crystal may be a precursor to melting for bcc transition metals, confounding the interpretation of what melting actually is.

4.1.10 Understand the behavior of the full anisotropic stress state at extreme pressures and temperatures, e.g., Poisson's ratio approaching melt

Related to the previous challenge, material properties such as Poisson's ratio and strength approaching melt are still poorly understood. The existence of new phases, or drastic changes in behavior of existing phases near melting, could affect the interpretation of experiments and provide insight into various theories of melting, from Born's proposed elastic instability to more modern theories of dislocation-mediated melting.

4.2 Technical Grand Challenges for Compression Science Theory and Modeling

4.2.1 Multiscale modeling free of ad hoc parameters: linking subscale processes to higher length/time scales

The field of multi-scale modeling today contains several theoretical and computational tools, which together span the time and length scale ranges of interest to static and dynamic compression science. Each modeling tool, in general, contains both physically based and

non-physical quantities (parameters) that allow the representation of material response. The non-physical quantities exist due to our lack of understanding about either the physical processes that occur in real materials or how to represent known physics into a theory or computational tool adequately. Our lack of experimental information about dynamic responses and structural evolution of materials at length scales of importance to the physical processes prevents us from developing the theoretical and computational tools to adequately achieve predictive models at the relevant length scales for our problems of interest.

The information deficit can be addressed through high-fidelity diagnostics applied to critical experiments. Eliminating non-physical parameters from today's models is the goal at all length scales.

4.2.2 Better theoretical tools in the mesoscale (1–10 mm) regime

The mechanics and physics community has over many years collectively produced theoretical tools that have started at the continuum level and worked down in length scale or at the atomic scale and worked up in length scale. Although these continuing efforts are critical, we do not have adequate theoretical tools that describe the complex ways in which dislocations interact and form substructures or how they interact with microstructural features such as inclusions, grain boundaries, point defects, precipitates, dislocation sources, etc. Present polycrystal plasticity models have demonstrated our deficiency in describing the development and evolution of subgrain heterogeneities and structure.

These theories must also represent real material length scales in their formulation in order to eliminate many of these deficiencies and provide microstructural size dependence, which is known to exist in all materials. At present, crude theories attempt to represent real material length scales, but these theories are very complex, less than physically based, and computationally expensive. We must drive our understanding to the point at which we can represent these length scale dependent behaviors with physically based models that are as simple as practically possible and include sufficient information to link across the length scales, which that particular model divides.

4.2.3 Transferable density functionals, pseudopotentials, and classical MD potentials valid at extreme conditions

Present day interatomic potentials are limited to the regimes of response within which they were calibrated. This limitation prevents translation to a wider set of physical regimes, which thus limits predictive capability. We must develop new computational frameworks that enable a wider range of known interatomic interactions to allow representation of the detailed complexities of real materials, which inherently contain defects and are exposed to extreme environmental conditions of loading. Particularly for dynamic compression experiments that access extreme pressure *and* temperature states, there is a need for further research into two techniques that promise to correct potentially fatal weaknesses in current density functional theory (DFT) and MD calculations: temperature-dependent density functionals and classical potentials for MD simulations that are electron temperature-dependent.

4.2.4 Equation of state treatment of materials beyond simply pressure and volume

Avoid reliance on simple separation into hydrostatic and deviatoric stresses

Two-temperature (electron and ion) EoS's

Present day theories are built upon the simplification of decoupling the effects on materials of the hydrostatic (pressure) and deviatoric (shear) partitions of stress. In reality, the equation of state for any crystal structure (except a cubic at reference configuration) compresses through application of hydrostatic pressure by changing both volume and shape. Theories used today do not account for the effect of the shear response during hydrostatic compression. Theories accounting for this coupling at present lack sufficient experimental information to enable their complete development and use. The lack of coupling between pressure and shear prevents an adequate treatment of pressure dependent plasticity and calculation of thermodynamics. Additional data from both experiments and simulations can be used to calibrate more complete EoS formulations.

Current EoS frameworks assume the Born-Oppenheimer approximation that electron contribution to the thermodynamics state variables is negligible. This forces the assumption of local thermodynamic equilibrium (LTE) at all conditions. It is currently believed that LTE does not exist under strong shock conditions and in warm dense matter. Extending formulations to two temperatures (electron and ion) is a first step toward providing a better treatment for non-LTE conditions.

4.2.5 Codes that preserve the integrity of material models

Current numerical frameworks do not handle steep gradients in loading and material state adequately. This diffuses fields, preventing the adequate treatment of surfaces (either material variables or interfaces). Many of these steep gradients are below the resolution of the computational grid. Numerical schemes are required to more adequately represent steep gradients and/or track material state without diffusion.

4.2.6 Quantitative dynamic x-ray probes (diffraction, XANES, EXAFS, etc.)

In situ determination of phase

Measure volume fraction of growing product phase

To acquire necessary experimental information at length scales that are not presently achievable, new diagnostic probes will be required. In general, diffraction techniques are used to distinguish material phase information in a volume averaged fashion. Diffuse scattering is impacted by the existence and evolution of disorder in which the materials can be both thermal and structural. Of particular interest is the spatial distribution of dislocations and the evolution of dislocation density with deformation, which is crucial in understanding the evolution of strength. Small-angle x-ray scattering is sensitive to the presence of density heterogeneity in the materials, and these materials include precipitates, voids, second phase particles, and phase nuclei. Both diffraction and small angle scattering can be used to determine the growing volume fraction of phase.

The XANES and EXAFS techniques probe the electronic state of the atom and are sensitive to the local environment surrounding the atom, including nearest neighbor spacing, stress, and temperature. These techniques or new techniques must be developed to enable the measurement of the nucleation of these phase changes events at very small time and length scales. In addition, new visualization and data processing tools will be necessary to deal with the large data sets produced from the three-dimensional measurements.

4.2.7 Develop local temperature and stress tensor gauges

Present temperature probes are limited to the surface of the sample or are invasive and have the potential to influence the results by their existence (e.g., thermocouples). Surface probes are based upon the emissivity of the sample, and theories describing emissivity as a function of temperature are inadequate for the basing measurement upon emissivity. Temperature is a fundamental quantity in determining the thermodynamic state of the material and in the influence that the thermal state has on the constitutive response of the material. We must develop the tools to enable the measurement of in situ temperature in a deforming body at length and time scales that are consistent with present modeling tools (e.g., 1 micron and 1 ns). Advancements of photonic crystals that could be embedded into a materials and images produced with a radiation source could hold potential for attaining a real three-dimensional temperature field.

As we have discussed earlier, we must begin to account for the complex three-dimensional stress state in both the treatment of EoS and strength theories. To do this, we must develop techniques to make in situ measurements of the full stress tensor field in materials as a function of position. This will allow us to more completely evaluate the local constitutive behavior of materials. Measurement of only the deformation field will still require us to estimate through modeling the kinetic response of the material. Manganin gauges are presently used and are limited to finite volumes and are used for traction only—no shear. The panel did not offer good suggestions for technologies that might show promise in making these measurements in situ and at a small length scale.

4.2.8 Local structural identification in static experiments, e.g., DAC, for amorphous materials and liquids

Static high-compression experimental techniques do well for crystalline solid materials – particularly diffraction techniques. The same diagnostic capabilities do not exist for other classes of materials such as amorphous solids and liquids, yet their behavior is not well characterized. We must develop the diagnostic techniques to enable the measurement of local scale strain, stress, structure for materials that lack crystallinity or are at least only partly crystalline.

4.2.9 3D orientation image mapping to dislocation length scales under dynamic conditions

The response of metallic materials to externally imposed loading is not simply a function of the types of elemental materials existing in the materials. Their response is also a function of the spatial position each of those elemental materials has in the bulk material. Imperfections and defects (e.g., grain boundaries, dislocations, impurity inclusions) also play a major role in determining the deformation behavior of metallic materials. The spatial arrangement of atoms and defects in the material comprise what is commonly termed as the material

microstructure. The microstructure also evolves substantially with deformation (distortion, dislocation movement/evolution/arrangement, heterogeneity evolution) and when conditions are extreme, this evolution leads to material damage and failure. These are unsolved problems from a theoretical perspective. We simply are not yet able to model these complex processes in a predictive manner. We need to be able to measure the evolution of the microstructure during dynamic loading conditions to enable us to make in situ observations of how microstructural heterogeneities evolve and lead to damage and failure. Orientation Image Mapping (OIM) is a well-known 2D technique, which is presently used to characterize the crystallographic orientation of polycrystalline metallic materials. Coupled with laborious mechanical serial sectioning, it can presently be used as a way to characterize the 3D microstructure of a material for a sample recovered from a mechanical deformation history. This 2D technique teaches us a great deal about the behavior of a material but only in 2D and after the fact. To get to the next level of understanding, we need have a tool which will tell us information like OIM is able to now but in 3D and during dynamic loading responses.

4.2.10 Extracting useful information from high-resolution 3D data (e.g., from 3D tomography or large-scale simulations)

As our ability to produce very large experimental or computational data sets becomes greater, so too is the need to be able to extract useful physics information from those large data sets. As we begin to think about how material microstructures evolve to produce an observed behavior or as we begin to be able to use new physics understanding to enable us to produce material microstructures that take advantage of inherent heterogeneities to our advantage, it will be increasingly important to make the linking between different physics events. For example, we may wish to derive an evolving 3D velocity, strain, or strain rate field, by performing image correlations for 100 time-sequenced 3D microstructural images to the level of resolution of the images. This will require characterizing each image (OIM type information) but also linking each image to the next image or next few images to be able to propose an evolving field. The same can be said for the analysis of large-scale MD calculations. Much information is produced during those simulations and the correlations of each atom with its nearest neighbors will define a lattice strain field but also may help to define a new solid phase depending upon the local structure. The analyses performed will generally have a basis in a particular physics question, which we may wish to address. Many of the processes we have discussed here have been around the concept of evolving statistics. We will also need higher order statistical models to be able to tractably capture the statistics of material behavior into something which we can use to help us link the evolution of heterogeneities to observed or designed properties. We can also use these statistical models to help define initial condition microstructures for MD, phase field, and polycrystal models that represent real materials of interest, which will always begin at an initial state of heterogeneity (defect structure).

5. Conclusions

The workshop offered an opportunity for open discussion of the problems and challenges in the field of compression science. These problems and challenges present opportunities for advancing our field and moving the field from that of discovery and observation to that of prediction and control. This transition requires that we diagnose and develop an understanding of materials, not in an ideal sense of theory alone, but also in a real-world sense of experiment and measurement. To make progress on these high-level goals requires the community to meet a set of challenges that include the following:

- Acquire time and spatially resolved in situ measurements at all length scales (i.e., atomistic, micro, meso).
- Discover new physics and chemistry in extreme environments.
- Incorporate material complexity into multi-scale simulations to achieve predictive capability.
- Unify static and dynamic compression understanding across relevant length and time scales.
- Leverage scientific knowledge derived from theory and experiment to the design and control of real materials (i.e., chemistry, microstructure, defects, etc.)

Furthermore, we have identified detailed challenges and opportunities within the framework of static, dynamic, and theoretical compression science that work toward attaining our end goal of control. Resolving all of these challenges is necessary for true predictive understanding, while partial resolution will lead to new paradigms regarding our thought processes on the material world around us. Compression science offers opportunities for discovery, yet challenges our ability to fully comprehend the controlling chemistry and physics. As scientists, we recognize the complexity and acknowledge the underlying beauty in the field of compression science, and we look forward to the surprises to come and the expected success of our predictive capability.

Appendix I Workshop Agenda

21st Century Needs and Challenges in Compression Science Workshop

Bishop's Lodge, Santa Fe NM
Tuesday, September 22, 2009

7:00 PM Dinner Tesuque A,B

If you are available, we are expecting a speaker on Tuesday, September 22, 2009

(unfortunately, not confirmed): 8:00 PM

Wednesday, September 23, 2009
Tesuque A, B

8:00 – 8:30 AM Continental Breakfast
Tesuque Pavilion

8:30 AM Welcome, Introduction and Workshop Kickoff……David Funk and Rusty Gray
Los Alamos National Laboratory

9:00 AM The Future of Static Compression Science……..……Malcolm McMahon
University of Edinburgh

10:00 AM Discussion

10:30 AM The Future of Dynamic Compression Science ……Yogi Gupta
Washington State University

11:30 AM Discussion

12:00 PM Lunch – Workshop Co-chair will lead discussion on the morning Plenary Talks
Tesuque Pavilion

Tesuque A, B

1:00 PM Experimental Needs for Material Phase, Strength, and Damage …….Neil Bourne
Atomic Weapons Establishment

James Asay
Sandia National Laboratories

2:00 PM Discussion

2:30 PM Break

3:00 PM Theory Needs for Material Phase, Strength, and Damage……. James Belak
Lawrence Livermore National Laboratory
Curt Bronkhorst
Los Alamos National Laboratory

4:00 PM Discussion

4:30-5:30 PM Summary Discussion

6:00 PM Reception / Informal Discussion
Tesuque Pavilion C

7:00 PM Dinner – Workshop Co-chair will lead discussion from breakout discussions (using key questions to stimulate discussion)
Tesuque Pavilion C

Thursday, September 24, 2009 - - Breakout Sessions
Las Fuentes Alcove Room—Future of Static Compression Science
Las Fuentes Fiesta Room—Future of Dynamic Compression Science
Tesuque Pavilion C—Theoretical Needs of Compression Science

8:00 – 8:30 AM Continental Breakfast
Tesuque Pavilion

8:30 AM Retire to side rooms for independent discussion and presentation of each participant's materials (ten minutes per participant)

12:00 PM Lunch – Panel Chairs will report back on the progress from the morning sessions; and that progress will be used by all in the afternoon breakout sessions
Tesuque Pavilion

2:00-4:00 PM Panels develop summary presentations (5 slides)

Tesuque Pavilion A
4:00 PM Panel Chairs present summaries (20 minutes each)

5:00-6:00 PM Summary Discussion

6:30 PM Informal Discussion / Reception
Tesuque A, B

7:30 PM Dinner – Panel Chair/Co-chair will lead discussion to refine workshop information presented in the afternoon session
Tesuque A, B

Friday, September 25, 2009 - - Report Writing

8:00 – 8:30 AM Continental Breakfast
Tesuque Pavilion Portal

Tesuque Pavilion C

8:30 AM Panel Chairs and Plenary Speakers draft reports (5-7 pages from each)

12:00 PM Workshop Adjourns

Appendix II Participants

21st Century Needs and Challenges in Compression Science Workshop

James Asay	Sandia National Laboratory E-mail: jrasay@sandia.gov
Cris Barnes	Los Alamos National Laboratory E-mail: cbarnes@lanl.gov
Richard Becker	Lawrence Livermore National Laboratory E-mail: becker@llnl.gov
James Belak	Lawrence Livermore National Laboratory E-mail: belak1@llnl.gov
Reinhard Boehler	Carnegie Institution of Washington E-mail: rboehler@ciw.edu
Neil Bourne	Atomic Weapons Establishment E-mail: neil.bourne@mac.com
Curt Bronkhorst	Los Alamos National Laboratory E-mail: cabronk@lanl.gov
Michael Desjarlais	Sandia National Laboratories E-Mail: mpdesja@sandia.gov
Micheline Devaurs	Los Alamos National Laboratory E-mail: devaurs_micheline@lanl.gov
Dana Dlott	University of Illinois Email: dlott@illinois.edu
Jon Eggert	Lawrence Livermore National Laboratory E-mail: eggert1@llnl.gov
William Evans	Lawrence Livermore National Laboratory E-mail: wjevans@llnl.gov
David Funk	Los Alamos National Laboratory E-mail: djf@lanl.gov
Timothy Germann	Los Alamos National Laboratory E-mail: tcg@lanl.gov

George "Rusty" Gray	Los Alamos National Laboratory E-mail: rusty@lanl.gov
Yogendra "Yogi" Gupta	Washington State University E-mail: ymgupta@wsu.edu
Russel Hemley	Carnegie Institution of Washington E-mail: larson@lanl.gov
John Klepis	Lawrence Livermore National Laboratory E-mail: klepeis1@llnl.gov
Marcus Knudson	Sandia National Laboratories E-mail: mdknuds@sandia.gov
Christian Mailhiot	Lawrence Livermore National Laboratory E-mail: mailhiot1@llnl.gov
H.K. Dave Mao	Carnegie Institution of Washington E-mail: Mao@gl.ciw.edu
Rick Martineau	Los Alamos National Laboratory E-mail: rickm@lanl.gov
Stephane Mazevet	Universite De Brtagne Occident E-mail : stephane.mazevet@cea.fr
Malcolm McMahon	University of Edinburgh E-mail: mim@ph.ed.ac.uk
John Moriarty	Lawrence Livermore National Laboratory E-mail: moriarty2@llnl.gov
Nigel Park	Atomic Weapons Establishment E-mail: nigel.park@awe.co.uk
Michael Pravica	University of Las Vegas E-mail: pravica@physics.unlv.edu
Paulo Rigg	Los Alamos National Laboratory E-mail: prigg@lanl.gov
Adam Schwartz	Lawrence Livermore National Laboratory E-mail: schwartz6@llnl.gov
D. Scott Stewart	University of Illinois E-mail: dss@illinois.edu
Sarah Stewart-Mukhopadhyay	Harvard University E-mail: sstewart@eps.harvard.edu

Justin Wark — Oxford University
E-mail: justin.wark@physics.ox.ac.uk

Phil Withers — University of Manchester
E-mail: philip.withers@manchester.ac.uk

Sasha Zivaljevic — Los Alamos National Laboratory
E-mail: sashaz@lanl.gov

Appendix III Cross-cutting issues identified during the workshop

Although materials under extreme environments of pressure, temperature, and strain rate are central to defense, energy, and other technologies, we know relatively little about how and why materials respond under these conditions. To understand the operative controlling mechanisms and learn to design and control the effects of extreme environments on materials, we must develop in situ experiments that see the dynamics in real time. Such experiments are coming within reach, as ever brighter sources of electrons, x-rays, and neutrons with ever higher spatial and temporal resolution allow sensitive measurements on ever smaller sections of materials.

A second reason for our limited knowledge of materials under extreme environments of static and dynamic compression is the enormous complexity of the effects such environments cause. Unraveling the emergent behavior of materials under extreme environments requires more than observing the response of the material in situ. We must understand and model this behavior to see how extreme environments damage, degrade, and ultimately disable materials. One of the most pervasive and difficult challenges blocking this understanding is the diverse range of time and length scales that govern compression behavior.

Discussion of the workshop attendees following the overview presentations led to the identification of a number of cross-cutting themes of relevance to static compression, dynamic compression, and theory as follows:

- How do we build confidence that classical MD provides representative and accurate physics in both atomic and polycrystalline simulations. Are the potentials accurate? That is, are the potentials accurate in both fully dense and defected materials? How do we develop a single simulation capability that can capture all of the relevant physical parameters (i.e., conductivity, phonon density of states, electronic structure, phase diagram, etc.)?

- How do we link static and dynamic results particularly in those situations in which large discrepancies exist? Are the issues kinetics/calibrations or misinterpretation of diagnostics, and how do we resolve this issue.

- Three-dimensional imaging of both single-crystal and polycrystalline materials is needed to drive our understanding of material response to compression.

- How do we elucidate linkage between microstructure, defects and other heterogeneities with constitutive properties under loading conditions; static or dynamic? Can we draw general inferences that will lead to predictive capability?

- When is local-thermodynamic equilibrium valid in dynamic systems (including static/laser coupling experiments)? How do we know when and if we have reached equilibrium?

- How do we build bridges between length and time scales that captures and hands off relevant physics? Can we look at multiple scales, both temporal and spatial, using multiple diagnostics in a single experiment and assess our multi-scale simulation capabilities?
- How do we create equilibrium conditions/states of pressure and temperature orders of magnitude greater than currently attainable in relevant sample sizes?
- How do we characterize and quantify the physical processes (viscosity, localization, instabilities/mixing, phase transitions, transport, defect generation and storage, damage) in an arbitrary loading event? [Geophysical to laser driven shock] How do we quantify the partitioning of energy between dissipative and non-dissipative processes?
- How do we characterize and potentially exploit chemical changes that occur either through static compression or material dependent changes induced by compression (polymer decomposition, detonation)?
- How do we formulate problems of study such that experiments look more like theory and theory looks more like experiments? What are the critical tests of theory that provide confidence in our predictive capability?
- How do we capture anisotropy in our constitutive and equation of state descriptions of real materials?
- How do we capture the stochastic nature of materials accurately with our simulation capabilities? Thereafter, how do we validate meso-scale simulations? What are the new numerical schemes that will capture subscale physics accurately; i.e., rare events?

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