Opportunities for New X-Ray Sources to Shed Light on Mesoscale Functional Materials

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Santa Fe, New Mexico
The development of new femtosecond x-ray free electron lasers (XFEL)—such as Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory, SACLA in Japan, and the European XFEL—has enabled groundbreaking discoveries in biology, chemistry, materials science, and physics.

At Los Alamos National Laboratory, the first very hard (42-keV) XFEL, part of the MaRIE (Matter-Radiation Interactions in Extremes) facility, is being developed to study the dynamic properties of materials under extreme conditions for national security science missions.

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1. Executive Summary

In a seminal 2000 paper, Nobel prize-winning Professor Robert Laughlin put forth the idea and importance of the mesoscale: the bridge between the nanometer scale (dominated by quantum mechanics) and the macroscale (the realm of emergent phenomena, bulk behavior, and continuum effects) [1]. Similarly, several recent reports from the White House and the Department of Energy specifically emphasize the importance of understanding and controlling how nanometer scale quantum mechanical effects, such as the atomic structure, electronic state, and spin ordering of a material, determine the microscopic behavior of properties such as its magnetism, conductivity, and strength [2–5]. Being able to understand and subsequently control the functionality of these materials at the mesoscale will therefore be critical to future information and energy technologies.

Recent revolutions in accelerator-based light sources are enabling unprecedented increases in coherent X-ray flux that are poised to have a profound impact on how we probe materials not only at the mesoscale, but also at the smallest and fastest

Figure 1: Plot of peak X-ray brilliance versus photon energy for current synchrotron (3rd generation) sources and numerous existing or planned XFELs. (Modified from ref. [10]).
length and time scales. These novel light sources include a new generation of synchrotron sources known as diffraction limited storage rings (DLSR), enabled by new multi-bend achromat technologies, as well as X-ray free electron lasers (XFELs) [6,7]. DLSRs promise to increase coherent hard X-ray flux by 2-3 orders of magnitude compared to current 3rd generation storage rings [8]. Similarly, XFELs, like the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory, have increased peak coherent X-ray brilliance by nearly 10 orders of magnitude (Figure 1). The world’s first hard X-ray FEL, the LCLS, began operations in 2009, and a recent summary of the first five years of operation highlights the numerous discoveries enabled by such sources that have fundamentally changed our understanding of materials behavior at the femtosecond and nanometer scale [9]. The success of the LCLS has spawned numerous other XFELs that are operation, or are soon to achieve first light in the near future, including SACLA at Spring-8 in Japan (operational in 2011), PAL-XFEL in South Korea (first light in 2016), the European XFEL in Germany (first light due in 2017), the Swiss FEL, and many other planned facilities. Los Alamos National Laboratory is also proposing a very hard XFEL, known as the Matter-Radiation Interactions in Extremes (MaRIE) facility (marie.lanl.gov). MaRIE will feature very hard femtosecond (fs) X-ray pulses (40-70 keV), with a unique timing structure of >30 micro-pulses per 1 ns macro-pulse and ~10^{11} coherent photons/micro-pulse. One of the stated goals of MaRIE is to produce ‘mesoscale movies’ of materials dynamics, particularly under extreme conditions.

On July 21-22, 2016, the MaRIE leadership at Los Alamos National Laboratory held a workshop entitled “Opportunities for New X-ray Sources to Shed Light on Mesoscale Functional Materials” in Santa Fe, New Mexico. The workshop was co-sponsored by the LANL Institute for Materials Science (ims.lanl.gov). The goal of this workshop was to explore the scientific opportunities that would open up in fundamental materials science from the unique photon energy range and time structure of the MaRIE XFEL.

Some questions explored at the workshop were:

- How does one link micro-to-macro under dynamic loading? (the multiscale problem, related to the U.S. DOE BESAC Mesoscale Challenge [5])
- How do we design and synthesize materials that enhance our control of dynamic processes? (the co-design problem, related to the Materials Genome Initiative [2])
• What are the transformative new diagnostics, drivers, and predictive models needing development? (*transformative technology*)

These issues were discussed in the context of several different classes of materials, including strongly correlated electron systems (e.g., superconductors, magnetic materials, multiferroics, and actinides), structural materials (including semiconductors, metals, and ceramics), and nanomaterials (e.g., nanowires, quantum dots, two-dimensional materials, and organics), with an emphasis on controlled functionality. Novel techniques for using X-rays to shed light on dynamic material properties were also discussed. This report summarizes the discussions and insights gained from the workshop and will guide the future development of not only the MaRIE facility and potential first experiments for this novel light source, but also other light sources as they continue to revolutionize the way we probe materials at the mesoscale. In the following, we will describe the outcome of the presentations and discussions for each topical area, as well as cross-cutting directions between different topical areas.

References:


2. Background and Discussion Questions:

The primary goal of the breakout sessions was to explore whether the MaRIE XFEL could be a unique tool for addressing outstanding scientific questions in each class of materials. As input to these sessions, three unique properties of the proposed XFEL were given. 1) The peak photon energy will be centered at 42 keV. 2) The timing structure will consist of multiple micro-pulses nested in a microsecond macro-pulse operating at 10 Hz. Within each macropulse, 10-100 fs long pulses can be separated by as little as 2.3 nanoseconds (ns) with up to 100’s of micropulses in a macropulse. 3) Simultaneous measurements with complementary proton and electron beams will be made possible. A list of questions to guide the discussions was formulated:

1) What are key current and future (10-15 years) science challenges in your field?
2) Which of these problems can be addressed using XFEL (5-150 keV) and similar probing techniques?
3) What are the corresponding basic functional requirements for the XFEL (e.g., energy tunability, pulse sequence)?
4) What are the requirements for supporting facilities (e.g., other experimental facilities, theoretical/modeling support)?
5) What would be interesting first experiments?
6) Are there possible collaborations that can be started now using existing facilities to transition to MaRIE when it is available?

These and other questions were discussed during the breakout sessions, with specific outcomes for each topic area discussed below.
3. Opportunities for Studying Correlated Electron Systems Using the MaRIE XFEL:

High intensity coherent X-ray beams with time-resolved capabilities offer many possibilities for the study of strongly correlated electron systems [1]. Plenary talks from Peter Littlewood, Bob Schoenlein, and Gabe Aeppli discussed some of these opportunities. Peter Littlewood emphasized the role correlated electrons might play in energy-relevant applications; for example, improving battery storage will drive electrons closer together, which has the consequence of increasing electronic correlations. Bob Schoenlein discussed the relevance of strong correlations, fluctuations, non-equilibrium states, and nanoscale heterogeneity in quantum materials and, hence, how a high intensity coherent light source can bring new information to these systems. The opportunity to go beyond transient absorption or X-ray scattering and use X-ray photon correlation spectroscopy to directly probe the fluctuations of correlated electrons was one of many exciting potential developments he presented. With respect to correlated electrons, Gabe Aeppli echoed the sentiments of previous speakers and gave the specific example of using time-resolved probes to study transient superconductivity, as well as exploring the phase diagrams of complex matter in strong pulsed magnetic fields and high-pressure environments (relevant, e.g., in the recent discovery of record high-$T_c$ superconductivity in $\text{H}_2\text{S}$ [2]).

This breakout session concluded that the main opportunity for research on correlated electron materials presented by the proposed facility is LANL’s unique position to study systems in challenging sample environments, which could not be easily undertaken at other XFEL facilities. One of the most striking opportunities is in the study of radioactive materials. As emphasized by invited speakers Gabi Kotliar and Jim Tobin, the physics of plutonium is an outstanding problem in strongly correlated electron physics. The impact of correlations goes beyond simply the electronic structure, since chemical bonding and physical structure are also dictated by electronic correlations. For example, if electronic correlations are ignored, first principles calculations underestimate the volume of plutonium by 20%. To understand correlated matter, such as plutonium, thus requires probing the intertwined spin, charge and lattice degrees of freedom with greater precision. Neutron scattering measurements have revealed dynamic spin fluctuations in plutonium (Figure 2). However, the $f$-electrons of plutonium will also have a response in the charge degrees of freedom, which could be probed by (inverse) photoemission
and resonant inelastic X-ray scattering experiments, for instance. Moreover, as Jim Tobin pointed out, MaRIE’s hard X-rays at 42 keV may be well suited for photoelectron holography as a bulk sensitive probe of the phase transformations. Dynamic probes are also required to study the physics of plutonium. For other materials such measurements can be done elsewhere, possibly with better resolution, but given the strict handling conditions for plutonium, MaRIE may be the only such facility where these measurements could be possible. In addition to studying hazardous and/or radioactive materials that are difficult to handle at other facilities, MaRIE could also take advantage of its ability to study materials in dynamic environments that could access phase space under extremes of pressure, temperature and magnetic field, which exist for only fractions of a second. Using an XFEL could supply the requisite number of photons – and a rapid sequence of short pulses for stroboscopic measurements – to study materials under extreme conditions that survive for less than a millisecond.

Given these opportunities, we also note that the energy scales of correlated electron phenomena range from several eV (e.g. the screened Coulomb interaction and bond energies) to below thermal energies \((k_B T = 25 \text{ meV at room temperature})\). Thus, while some studies will be possible with a 42 keV photon beam, even more insight will be gained by having lower energy photons available. Moreover, an option to generate lower photon energies (down to \(\sim 3 \text{ keV} \)) would also provide important capabilities to access M-edge absorption. In terms of energy (E) resolution, for instance, an impressive resolving power \((E/\Delta E) \) of \(10^5\) would be required using 10 keV photons with 100 meV resolution. This brings up the question (posed by Jim Tobin) of whether building such a facility such as MaRIE presents an opportunity to develop novel

Figure 2. Left panel: Dynamical spin fluctuations as a function of momentum transfer \(Q\) and energy transfer \(E\). Right panel: the calculated result from dynamical mean field theory (DMFT), which includes electronic correlations and well reproduces the data. Figure adapted from M. Janoschek et al., Sci. Adv. (2015) [3].
instrumentation. Time-of-flight spectrometers are used in neutron scattering to obtain extremely high energy and momentum resolution, and have been used for low-resolution charge spectroscopies. Despite the serious engineering challenge, an ultra-sensitive time-of-flight spectrometer for photoemitted electrons, coupled to the high photon energies and distinctive pulse structure of the MaRIE XFEL, would present a unique instrument to the condensed matter community. We expect the further development of MaRIE to lead to other novel approaches to measuring important phenomena in condensed matter.

References:


4. Opportunities for New Insight into Structural Materials using the MaRIE XFEL

The potential for improvements in the majority of our current technological capabilities is limited by material properties [1]. There is therefore a demand for intelligent design of materials with tailored properties across many industries and applications [1-3]. Examples include high strength steels for the automotive industry, damage resistant lightweight metals for military applications, and corrosion/temperature tolerant materials for the energy industry. However, in order to design these smart materials, we must understand the relationship between processing and performance.

To date, the development and application of new structural applied materials has been characterized by lengthy trial and error development and extensive laboratory testing. Even after this cycle, large engineering safety margins are required for critical components. This long development cycle (years or decades) significantly impedes progress in many sectors of the
economy, including energy, transportation, and defense. A significant contributor to the problem is the fact that computational models that attempt to mimic the responses, for example, to mechanically applied loads or thermal treatments, are not sufficiently accurate or predictive to take the place of or shorten the needed testing cycle [1-3]. Current models require test data to tune free parameters, and even then only qualitatively reproduce the properties and responses of existing materials. These models are based on qualitative observations of responses in broad classes of materials, but the underlying physics is unproven. For example, polycrystals under tension or compression respond through slip along preferred crystallographic planes [4-5] as seen in single crystals, but does this occur smoothly as stress is applied, as is assumed in models? Do these events occur in the same way in all the constituent crystals? If the material is modified in some way (processing route, composition, etc.), how will the response characteristics change? Today’s models cannot rigorously address such questions. Only when physics-based (in place of empirical parameter-based) models can reproduce variations in such measurements will these models become trusted engineering tools.

Progress in the direction of predictive modeling requires experimental probes that connect basic responses on the nanoscale to macroscopic material properties, which requires measurements that themselves span many length scales. It is also clear that a vast range of time scales is tied to these different length scales (femtoseconds for single dislocation formation to hours for accumulated damage and cracking). The range of phenomena that need to be understood was exemplified in the two breakout session presentations on structural materials. In one, Dr. Brad Boyce (Sandia National Laboratories) presented studies of fatigue response in a nickel-iron sample (Figure 3) [6]. Synchrotron based X-ray diffraction measurements revealed that, as the mechanical load was cycled, a few grains (mesoscale features) near the sample surface grew anomalously and that cracks tended to form in those large grains. This observation raises many questions: what is the driving force for the growth? What is the characteristic that picks out specific grains? How universal is this phenomenon? Only with answers to such questions can materials be modified to prevent or slow this failure mechanism.

Relevant measurements would, for example, probe lattice defect accumulation during cycling, by both tracking structure during individual cycles and spanning the large number of cycles required to initiate the cracks. Since the relevant number of cycles may exceed $10^4$, the measurement should sample many time scales, although it is presumably not feasible to continue
measurements over the entire process. Along with nanoscale lattice defect accumulation, the measurements should search for the point at which grain boundaries begin to move on the mesoscale and should follow the resultant changes in structure in order to elucidate the evolution of driving forces. Static measurements addressing some of these issues are possible today, but the idea of tracking structure changes at the rate of load cycling is challenging. This may be addressable with the flexible pulse structure being proposed for MaRIE.

The second presentation, by Prof. David Reis (Stanford University/SLAC), illustrated the capabilities of FEL sources for pump-probe measurements of ultrafast dynamics in solid-state systems. By varying the time delay between a fast optical laser pulse that deforms the sample and a FEL X-ray probe pulse, the relaxation of phonon modes could be mapped as a function of lattice momentum, $q$, and time, revealing their responses on a picosecond (ps) timescale. For structural and functional materials, this class of measurement provides the opportunity to track the fundamental dynamics which underlie many mesoscale and macroscale materials responses, from pressure waves in shock dynamics, to sudden slip events in plasticity, to the initiation of phase transformations induced by a variety of abrupt changes in fields. Such ultrafast measurements look at nanoscale collective responses of the sort that form or underlie the emergent behavior seen at the meso- and macro-scales.
Much insight into the properties of structural materials can be obtained using coherent diffractive imaging (CDI), a rapidly developing technology that yields 3D maps of structures up to a micron size (currently) with ~10 nm resolution of atomic displacement fields associated with defects, including dislocations [7-8]. The high coherence combined with high single pulse flux provided by XFEL sources should allow tracking of defect motions and their interactions with a variety of features, such as other defects and grain boundaries. This measurement technology will allow the coupling of nanoscale dynamics with meso- and macroscale properties if combined with concurrently developing high-energy microscopies. High-energy diffraction microscopies (HEDM) measure cubic millimeters of microstructure (lattice orientation fields and elastic strain states) with micron resolution, and new capabilities continue to be introduced in the U.S., Europe and Japan. Whether in-situ or ex-situ (for example, mesoscale measurements performed at a synchrotron source), the combination of “conventional” microscopy with coherent imaging has the potential to achieve the ideal of zooming over eight decades of length scales to yield information that documents the emergence of macroscopic behavior and explicitly connects it to defect properties. Quasi-static versions of such measurements will be done at, for example, the upgraded APS. However, watching the dynamics upon fast loading (e.g., mechanical or thermal) could be an interesting “first experiment” at either LCLS or MaRIE. Continuing development of pink beam (broad X-ray spectrum) techniques for rapidly obtaining 3D structure will enhance such pulsed measurements.

Challenges:

• **Getting 3D information on multiple length and time scales:** Structural materials contain anisotropic grains that interact fully in three dimensions. To aid in the development of models that accurately reflect material properties, measurements must articulate the full environment in which each grain exists. The fatigue-induced grain growth described above presumably involves more than just one grain that grows, and rather must be induced by a neighborhood of interacting grains. In this case, the intrinsic response lies at the nanoscale, whether it is through shuffling of atomic positions that allows grain boundary movement or dislocation motions in response to stress. At the same time, grain growth may be slow, occurring over many fatigue cycles, but atomic dynamics are clearly on much shorter time scales. Ideal measurements would therefore establish the mesoscale properties of an ensemble and then zoom in to observe the nanoscale response,
perhaps even zooming back out to see the resulting emergent behavior. Due to the vast separation of spatial and time scales, the zoomed out measurements could be carried out separately and ex situ, while fast responses are measured in identified local regions using XFEL pulsed observations, for example with CDI methods.

- **Finding rare events in time and/or space.** Many nanoscopic and some mesoscopic events are expected to be intermittent and difficult to predict. Existing synchrotron-based methods should clarify and quantify this statistical behavior in the near future, but it is likely to remain challenging to know when and where to look for fast, local dynamical behaviors. Rare events like crack nucleation might occur in one out of $10^6$ to $10^9$ grains and might occur after $10^4$ loading cycles. A zoom-in and zoom-out capability using intermittent experimental time allocation needs to be considered.

- **Need capability to work in varied sample environments.** Chemical/environmental effects have been shown to affect crack formation and propagation. Tracking segregation of impurity/alloying elements to grain boundaries and defect sites has the potential to press “random, statistical” effects to a lower level, but these effects are temperature and composition dependent. In situ high temperature, varied loading conditions, and sample environments need to be available.

- **Making measurements and models relevant to engineering decisions.** Shock loading induces a variety of damage, including interacting voids and cracks. Can basic science measurements lead to models that are relevant to mitigating such damage? Similarly, additively manufactured metals include voids and, in as-deposited materials, strong residual stresses that have a serious impact on usefulness and the need for post-build processing. Can the results of basic science measurements guide build processing parameters, post-build processing, and reliability prediction to facilitate the tuning of engineered structures and process optimization modeling that is useful to engineers? Further, what is the time scale for transitioning from measurements that focus on fundamentals to relevant models? These are difficult and sometimes uncomfortable questions, but they are age old and reflect the evolution of progress in all technical fields. Perhaps these questions seem increasingly urgent because the scientific work in this field is performed on “applied materials,” so it seems the connection should be immediate.
However, after 15 years of development of synchrotron techniques for probing mesoscale microstructures and their evolution (HEDM, for example), breakthroughs directly relevant to plasticity modeling are just now emerging. XFEL work will build on both technology and knowledge gained from such earlier work. Progress will be made and measurements will probe relevant phenomena in deeper ways, but conversion to everyday relevance will continue to take time. Proposing and justifying a facility such as MaRIE should be based on recognition of such realities.

References:


5. Using MaRIE to Study Nanoscale Materials
MaRIE will offer tremendous opportunities for in-situ and operando studies of nanomaterials. The ultrafast pulse duration and high coherence and photon energy of the available X-ray beams will enable studies of growth, self-assembly and function of materials in their native environment. During this break out session, several decadal nanomaterial challenges were identified. For example, there are unknowns across every length scale in modern nanomaterial synthesis and application, so multi-scale data is critical. There are currently no individual techniques capable of interrogating modern functional materials at all relevant length scales (angstroms to micrometers) [1]. Similar to the description given above for structural materials, understanding this multi-scale structural behavior is critical to controlling performance. This will also make it possible to address the critical aspects of nanomaterial integration and hierarchy in functional materials. Another challenging area is understanding nanomaterial synthesis via in situ probing. Future X-ray facilities, including MaRIE, will provide such multi-scale, in situ capability, with dedicated instrumentation attached to a state of the art high energy, fully coherent, ultra-bright, X-ray source.

During the nanomaterials breakout session, two talks were presented, one by Oleg Gang on nanomaterial self-assembly and another by Edwin Fohtung on nanometer scale strain imaging with Bragg coherent diffraction imaging (BCDI). Oleg Shpyrko also discussed several relevant X-ray techniques for nanomaterial studies, including coherent diffractive imaging (CDI) and X-ray photon correlation spectroscopy (XPCS), during a separate session. Both CDI and XPCS would be techniques of choice for studies with MaRIE. CDI is entering a revolution in its capabilities, particularly when applied in the Bragg geometry to the study of crystalline samples [2], [3]. Recent efforts in advancing the required phase retrieval algorithms and instrumentation for Bragg coherent diffractive imaging are striving to achieve full 3D images utilizing broadband X-rays [4]. This could lead to full, high resolution, 3D images from single broadband ultrafast pulses at MaRIE. Coherent imaging will provide detailed local structural information on the nanoscale, potentially with sub-picosecond time resolution through pump-probe experiments [5], [6]. XPCS is used to study dynamics by comparing changes in coherent scattering from samples as a function of time [7], [8]. This method will be pushed to the limit of single X-ray pulse lengths by advances in X-ray split and delay technology [9]. In the following, we discuss two specific areas of opportunity for MaRIE studies of nanomaterials that were identified during this breakout session: nanomaterial growth and assembly.
Figure 4: In-situ hard X-ray diffraction from the silver nanocrystal growth chamber described in ref. [10]. Using MaRIE, the powder diffraction patterns shown in (B) and (C) will become coherent diffraction patterns from individual nanocrystals, which will be inverted to images of the crystals as they grow.

Growth:

Growth kinetics of nanoparticles have recently been studied with in-situ high energy X-ray diffraction [10]. These processes are still not well understood on the local scale, where one may tune growth parameters to achieve desired nanoparticle shapes. The high energy X-rays of MaRIE will be capable of penetrating the chamber walls and chemical solutions in which these particles are grown, often with heating provided by microwave or radio frequencies. The ultrafast pulse duration will effectively freeze the motion of the particles in time and allow one to study the growth kinetics in femtosecond snapshots [11], [12].

Another example is shape control, a powerful way to tune function in nanoparticles. Catalytic activity has been shown to strictly depend on the shape of metallic nanoparticles [13]. MaRIE will enable nanoparticle shapes to be tuned during growth by altering surface capping components in-situ while being imaged in real-time through CDI. With the large, incoherent high energy X-ray beams available at current synchrotron storage ring sources, only powder diffraction patterns can be measured from the ensemble of particles, as shown in Figure 4. To literally design particles, one needs to image individual nanoparticles at all stages of growth with
high resolution. This capability should become a reality with next generation sources. Then, by observing stresses and strains induced in the nanoparticles during catalytic function, the active regions can be determined through imaging [14].

**Assembly:**

Assemblies of nanoparticles can offer unique optical, magnetic and physical properties that can be tuned through directed assembly [15]-[17]. One powerful mechanism to design nanoparticle structures is through linkages formed with DNA (Figure 5) [15], [18]. DNA can be programmed for specific bonding to precise sites on nanoparticles, given explicit control over heterogeneous assemblies. High-energy coherent diffractive imaging at MaRIE will enable understanding of the assembly process at all relevant length scales. Individual nanoparticles can be interrogated with BCDI for signs of DNA chemical bonding induced strains at specific sites [14], [19]. These strains can be watched as the assembly is functionalized during operando experiments for detailed understanding of the mechanical properties of the assembly.

![Figure 5. Example of NP assembly using DNA: Schematics (a) and AFM images (b) of gold nanoparticle structures tailored through DNA linkages to control bonding (scale bars are 200 nm). (c) Small angle X-ray scattering (SAXS) obtained structure factor S(q), with an inset showing a representative 2D SAXS pattern (from reference [15]).](image)

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CDI will also be used to study the assembly as a whole [20]. The reciprocal space of a nanoparticle assembly is highly compressed, owing to the relatively large spacing of nanoparticles as compared to hard X-ray wavelengths. This will enable imaging of nanoparticle assemblies, as shown in Figure 6, across tens to hundreds of micrometers of sample volume with single nanoparticle resolution. Defects and distortions in a periodic assembly will be readily visible [20]. Changes in the conformation of the assembly can be triggered by molecular replacement. The migration of these changes as a function of time can also be studied. Finally, XPCS will enable the study of fast dynamics within the resulting assemblies on picosecond to millisecond time scales.

![Figure 6: Coherent diffractive imaging of a photonic crystal formed by self-assembly of silica spheres, taken from reference [20]. Diffraction patterns obtained by aligning the photonic crystal along different axes are shown in (a) and (c). The corresponding images obtained via phase retrieval are shown in (b) and (d). A crystallographic defect is evident (arrows) in image (d).](image)

References:


6. Summary and Conclusion

The workshop on Opportunities for New X-Ray Sources to Shed Light on Mesoscale Functional Materials made clear that there are many scientific challenges in the field of X-ray materials studies that can be addressed using XFELs [1], [2], some of which are uniquely suited for the proposed MaRIE facility. In this final section, we summarize some of the cross cutting themes, suggested first experiments, and opportunities identified at the workshop.

**Cross Cutting Themes:** A common theme during the workshop was that the rapid expansion of available XFEL light sources will enable probing of dynamic materials behavior at the atomic/femtosecond scale (i.e. LCLS, SACLA, European XFEL, etc.). However, due to the
softer and less penetrating photon energies available at these sources, it is yet to be seen whether they will truly be able to probe mesoscale dynamics in ‘bulk’ materials. An important direction discussed throughout the workshop will be incorporating the emerging technology of coherent diffractive imaging, which has already had a significant impact in both physical and biological sciences using existing X-ray sources [3]. The challenge with MaRIE will be to extend these techniques to larger samples and higher photon energies. Coupling CDI with XFEL sources offers the advantages of high coherence and photon flux, making it possible to generate 3D images with atomic resolution. This can be used to track defect motion in structural materials, and the ability of high energy X-rays to penetrate vessel or chamber walls will make it possible for MaRIE to monitor nanoparticle shapes and assemblies during growth. One exciting avenue would be to combine conventional X-ray microscopy with CDI; this “zoom” capability would enable researchers to connect material behavior at the mesoscale to its nanoscale properties.

Furthermore, every session of the workshop identified that one of the primary advantages of MaRIE over other XFEL and synchrotron facilities will be the ability to study materials in extreme and/or hazardous environments, due to the harder X-ray photon energy and unique time structure. The harder, more penetrating X-ray flux will enable penetration of sample chambers enabling unique sample environments (radioactive, high pressure, chemically harsh environments). These considerations make it clear that coupling the MaRIE XFEL to a variety of sample environments and experimental systems will enhance its ability to provide new insight into the properties of mesoscale materials. Additionally, there are several opportunities to develop novel instrumentation, such as a time-of-flight photoelectron spectrometer, that could benefit from the unique pulse structure and high photon energies of MaRIE.

Finally, a recurring discussion was that while many other XFEL light sources will provide copious softer X-ray radiation (1-25 keV), there are unique opportunities that would be afforded by also having access to softer X-rays at MaRIE (down to 3 keV). For example, there are several applications in radioactive materials, such as plutonium-based heavy fermion materials, where access to M-edge resonant scattering would provide interesting and unique capabilities. Additionally, softer energies would open many opportunities for nanomaterials at MaRIE, where currently the hard X-ray energies may make signal levels from low average density nanoparticle samples vanishingly small.
**Suggested First Experiments:** Several first experiments were envisioned at MaRIE in the area of controlled functionality. The unique time structure of the MaRIE XFEL and ability to track materials in situ will enable unprecedented detail of materials synthesis and assembly. Especially in the areas of structural and nanomaterials synthesis, monitoring processes in situ will have a revolutionary benefit for technology, especially when done at pressure, temperature, and chemical extremes and with varied loading conditions and sample environments (e.g., to track nanoparticle growth or crack formation and propagation).

A rich and exciting area of research that MaRIE could open is in situ examination of radioactive materials such as plutonium, as described in Section 3. MaRIE’s hard X-rays at 42 keV may also be well suited for photoelectron holography as a bulk-sensitive probe of the numerous and little understood phase transformations of numerous actinides. Furthermore, also as discussed in Section 3, a high resolution \((E/\Delta E >10^5)\) time of flight photoelectron spectrometer coupled with the high photon energy provided by MaRIE would present a unique instrument to the condensed matter community in many areas, even beyond radioactive materials.

A final avenue where MaRIE should boost characterization capabilities is in the time domain, where the unique pulse structure of the MaRIE XFEL could be used to track structural dynamics while cycling mechanical or thermal loads on a material (a possible “first experiment”). This would also augment the capability to study materials that may only survive for a short timescale when subjected to extreme conditions (e.g., temperature, pressure, and/or magnetic field). XPCS can also be used to track dynamics on picosecond to millisecond timescales, with X-ray pump-probe techniques used to resolve shorter timescales of femtoseconds and possibly even attoseconds (limited by the X-ray pulse duration).

**Conclusion:** Overall, combining the unique aspects of the MaRIE XFEL with the ability to perform in situ measurements and subject materials to extreme and/or hazardous dynamic environments will enable a host of novel studies, particularly on materials such as plutonium that are difficult or impossible to study elsewhere. Incorporating the ability to tune MaRIE to lower photon energies would make this a more flexible source, capable of going beyond existing capabilities at other light sources worldwide. Nevertheless, we believe that MaRIE will be an important step towards achieving the ultimate goal of 3D imaging with femtosecond temporal
and nanometer spatial resolution, which will shed new light on the properties of mesoscale functional materials.

References:

