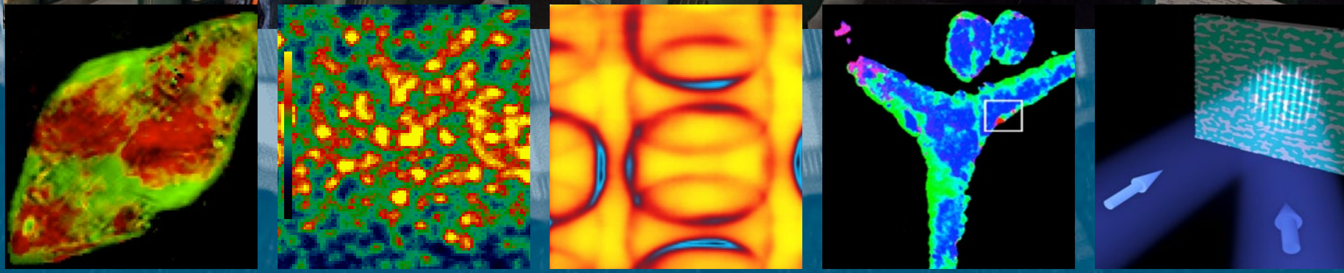
ALS-U:

Solving Scientific Challenges with Coherent Soft X-Rays

Workshop report on early science enabled by the Advanced Light Source Upgrade

January 18–20, 2017



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U.S. DEPARTMENT OF ENERGY
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ALS-U

Cover images: Primary image—Workshop participants attend the plenary session in the Building 50 auditorium. (Credit: Marilyn Chung/Berkeley Lab) Below (L to R)—1) In situ ptychographic image of $FePO_4$ during electrochemical intercalation with lithium (see Section 2.2); 2) Magnetic fluctuations in holmium (see Section 3.1.4); 3) Constant energy ARPES map showing the Brillouin zone of the undistorted Cu(I) plane of $LiCu_2O_2$ (see Section 3.1.6); 4) an x-ray photoelectron emission microscope (X-PEEM) component map of three mineral phases illustrating the growth pathway (see Section 3.2.7); 5) Schematic of interference between two coherent lasers or soft x-ray beams to create a charge-carrier grating inside a thin organic photovoltaic material (see Section 3.3.1).

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Table of Contents

Executive Summary

A revolution in x-ray science is underway that will take advantage of new technologies to enable the study of nanometer-scale features and interactions and the real-time observation of evolving chemical processes and functioning materials. The resulting information will pave the way to new scientific discoveries by enabling the understanding, prediction, rational design, and assembly of structures that exhibit emergent functionalities needed to address the world's most pressing technological problems.

So-called "third-generation" synchrotron light sources, like the Advanced Light Source (ALS), offer stable, nearly continuous x-ray beams that are ideal for studying homogeneous and simply organized systems. The vast majority of real-world systems, on the other hand, are heterogeneous and hierarchical. Today's soft x-ray storage-ring-based light sources lack the high transverse coherent flux that is necessary to effectively study these systems. A planned upgrade of the ALS, dubbed "ALS-U," will leverage recent advancements in accelerator technology to transform the ALS into a fourth-generation light source that can produce x-ray beams with 100–1000 times more coherent soft and tender x-ray flux than today's ALS—well beyond any storage-ring-based light source in operation, under construction, or planned.

ALS-U's capabilities will unlock the potential to image the locations of molecules, ions, and electrons and to measure how they migrate and interact. This information will lead to scientific advances in areas like ultralow-power information storage and processing, efficient chemical synthesis, highly selective ion transport and water purification, and artificial photosynthesis.

A workshop entitled "ALS-U: Solving Scientific Challenges with Coherent Soft X-Rays" was held at Lawrence Berkeley National Laboratory on January 18–20, 2017 to identify scientific challenges that ALS-U will address early on and to determine the instruments and tools essential for taking full advantage of ALS-U's capabilities. This report delineates the findings of the workshop.

ALS-U Techniques

The high coherent flux of ALS-U will offer the opportunity to perform ***3D nanoscale imaging*** with ***high spectral sensitivity*** over ***broad space and time scales***. Three interrelated classes of techniques, and the simultaneous application of combinations of them, are required to take full advantage of these capabilities:

1. **Nanoprobe spectroscopies** performed at ALS-U will allow many conventional soft and tender x-ray techniques to be performed with nanoscale spatial resolution.
2. **Coherent scattering and imaging** at ALS-U will encode information from inhomogeneous materials into scattered wave fronts, which can then be deciphered from speckle-diffraction patterns.
3. **Interferometry,** widely used in laser-based techniques, will become possible with ALS-U, allowing access to chemical and material properties with nanoscale resolution and very high spectral sensitivity.

ALS-U Early Science Opportunities

Equipped with the high coherent flux of ALS-U and the techniques above, new science opportunities will arise. Workshop participants discussed early science that will be made possible by ALS-U in three topical areas:

Spin, quantum, and topological materials: With applications in computing, information storage, transportation, and many more, numerous technologies will be revolutionized if we can learn to understand, predict, and control the properties of this class of materials at length scales from atomic to mesoscopic. Workshop participants identified key examples of early ALS-U science in this area, ranging from probing electronic states, imaging spin currents and magnetic moments, and characterizing response to external stimuli such as applied fields, strain, or changes in temperature.

Multiscale chemical processes: A wide range of processes, from catalysis and energy conversion to environmental transformation, occur over broad length and time scales. The ability to observe and model how these processes work together across scales is essential to determine system function. Workshop participants identified a number of applications of ALS-U capabilities towards this goal, including designing nanoparticle catalysts, imaging natural nanoparticle phenomena, and following biological and electrochemical transformations.

Soft and biological matter: Many soft and biological systems exhibit unusual properties and phenomena that we do not yet understand, including efficient thermally driven kinetics, self-assembly, and adaptation to environmental changes. We, therefore, are unable to predict these behaviors and design such systems from first principles. Workshop participants identified important early contributions that ALS-U's dynamic spatial and temporal range will make in this area, ranging from probing charge dynamics in organic materials and predicting rare events in soft condensed matter to examining the dynamics of soft-material interfaces and interactions between biological molecules.

Stemming from the early science opportunities, ***five crosscutting challenges*** were identified that ALS-U will address using its advanced capabilities:

1. **Spectral mapping of nanostructures and nano-objects:** ALS-U will offer a combination of few-nanometer resolution and soft x-ray electronic, magnetic, and chemical contrast that will complement scanning probe and electron microscopy to transform our understanding of and ability to control these systems.

2. **Designing functional interfaces:** ALS-U's photon-based microscopies, with few-nanometer resolution in 3D, will enable revolutionary probes of heterogeneous interfaces in diverse environments, taking advantage of a core expertise of ALS scientists and users who have led efforts to deploy these powerful chemical and material spectroscopies.

3. **Harnessing entropy as a material and chemical design tool:** ALS-U will enable the ability to measure, with chemical and material contrast, the thermally excited nanoscale fluctuations that store entropy.

4. **Manipulating nanoscale flows:** ALS-U will integrate highly sensitive interferometric detection with soft x-ray spectromicroscopy and dynamical measurements to detect nanoscale flows in diverse environments.

5. **Controlling materials chemistry and physics in confined spaces:** Powerful ALS-U spectromicroscopy tools will allow researchers to probe networks of confined chemical and material systems to optimize diverse functionalities.

These overarching, crosscutting challenges align closely with recent Department of Energy strategic reports, further cementing the case for upgrading the ALS to establish the world's leading fourth-generation soft x-ray synchrotron light source.

1 Introduction

Chemical and material products are crucial to our nation's security, economy, and standard of living. Advances in these products, including the technologies that power machines and devices, drive industries, and protect our health and physical well-being, increasingly depend on our ability to understand and control underlying chemical and material processes, particularly at the nanoscale, where many macroscopic properties emerge.

The scientific case for improved capabilities in material and chemical analysis has been building for more than a decade within the Basic Energy Sciences program of the U.S. Department of Energy Office of Science (DOE-BES). Numerous Basic Energy Sciences Advisory Committee (BESAC) studies and basic research needs (BRN) and roundtable discussion (RTD) reports point to a future in which hierarchical chemical and material structures support interacting processes across broad length and time scales to provide the functionality needed to revolutionize a diverse array of energy systems.

Soft x-rays are critical to effecting this revolution since they can reveal chemical, electronic, and magnetic properties. Optimizing chemical and material processes—for instance, how various nanostructures are positioned and interconnected and how their collective operation is regulated—will require the ability to image the locations of molecules, ions, and electrons and to measure how they migrate and interact to support efficient function. Although the Advanced Light Source (ALS) has a strong track record of leadership in soft x-ray science over the last 24 years, it, like other storage-ring-based x-ray light sources, lacks the combination of nanometer spatial resolution, diverse spectroscopic contrast, and broad temporal sensitivity that is required to design and synthesize organized nanoscale structures and to optimize the nano- and larger-scale chemical and material processes that lead to useful functionality.

The Advanced Light Source Upgrade (ALS-U) project will leverage cutting-edge accelerator technologies to offer up to a 1000-fold increase in coherent flux compared to today's ALS across the soft x-ray energy regime. This will enable transformational improvements in spatial, temporal, and spectral resolution, as well as the required sensitivities for a broad range of experiments in material, chemical, biological, and earth systems—precisely the capabilities required to optimize chemical and material processes as described above (Figure 1.1).

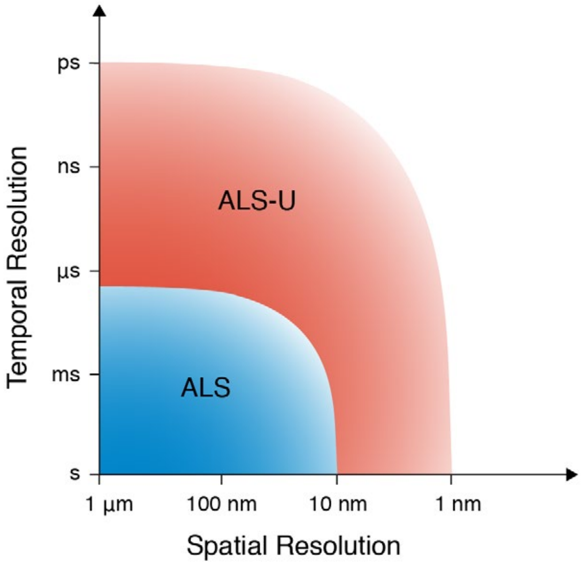

Figure 1.1. Compared to the capabilities of the current ALS, the upgraded facility, ALS-U, will offer access to a much broader range of space and time scales, enabling imaging of the locations of molecules, ions, and electrons and measurement of how they migrate and interact to support efficient function.

In September 2016, DOE initiated the ALS-U project by approving its "mission need" and assigning it critical decision (CD)-0 status, the first milestone in making ALS-U a reality. To delineate scientific opportunities enabled by ALS-U and identify tools and techniques required to take full advantage of ALS-U capabilities, a workshop entitled "ALS-U: Solving Scientific Challenges with Coherent Soft X-Rays" was held at Lawrence Berkeley National Laboratory on January 18–20, 2017. The 170 workshop participants from 45 institutions engaged in vigorous, future-oriented discussions, the outcomes of which are detailed in this report.

The workshop participants' primary charge was to identify scientific challenges that ALS-U would help solve early on in three topical areas—(1) spin, quantum, and topological materials; (2) multiscale chemical processes; and (3) soft and biological matter—and determine the instruments and tools that are essential for taking full advantage of ALS-U's capabilities. Stemming from the early science opportunities they identified were five multidisciplinary challenges spanning the three topical areas, which ALS-U will address:

1. Spectral mapping of nanostructures and nano-objects
2. Designing functional interfaces
3. Harnessing entropy as a material and chemical design tool
4. Manipulating nanoscale flows
5. Controlling materials chemistry and physics in confined spaces

These overarching and crosscutting challenges, described in more detail below, align closely with critical needs identified in BES reports, further cementing the case for upgrading the ALS to establish the world's leading fourth-generation soft x-ray synchrotron light source.

1.1 REVOLUTIONARY CAPABILITIES PROVIDED BY THE ALS UPGRADE

A revolution in x-ray science and technology is underway in which the high phase coherence enabled by next-generation x-ray sources, coupled to powerful x-ray techniques developed over the last several decades, will be leveraged to probe heterogeneous chemical and material systems and processes. Third-generation storage-ring-based light sources, like the ALS, offer stable, nearly continuous x-ray beams that are ideal for studying the properties of homogenous and simply organized systems. The vast majority of functional materials and chemical synthesis platforms, on the other hand, are heterogeneous and hierarchical, exhibiting multiple phases and key structural features at the nanoscale. Today's soft x-ray storage-ring-based light sources lack the high transverse coherent flux that is necessary to effectively study these systems.

ALS-U will combine state-of-the-art multibend achromat (MBA) lattice accelerator technology, recently demonstrated successfully at MAX IV in Sweden, with a new injection system based on a concentric accumulator ring. The upgrade will also capitalize on modern undulator technology and other components of the existing ALS infrastructure (Figure 1.1.1). With these advanced tools, ALS-U will produce 100–1000 times more coherent soft and tender x-ray flux than today's ALS—well beyond any storage-ring-based light source in operation, under construction, or planned (Figure 1.1.2).

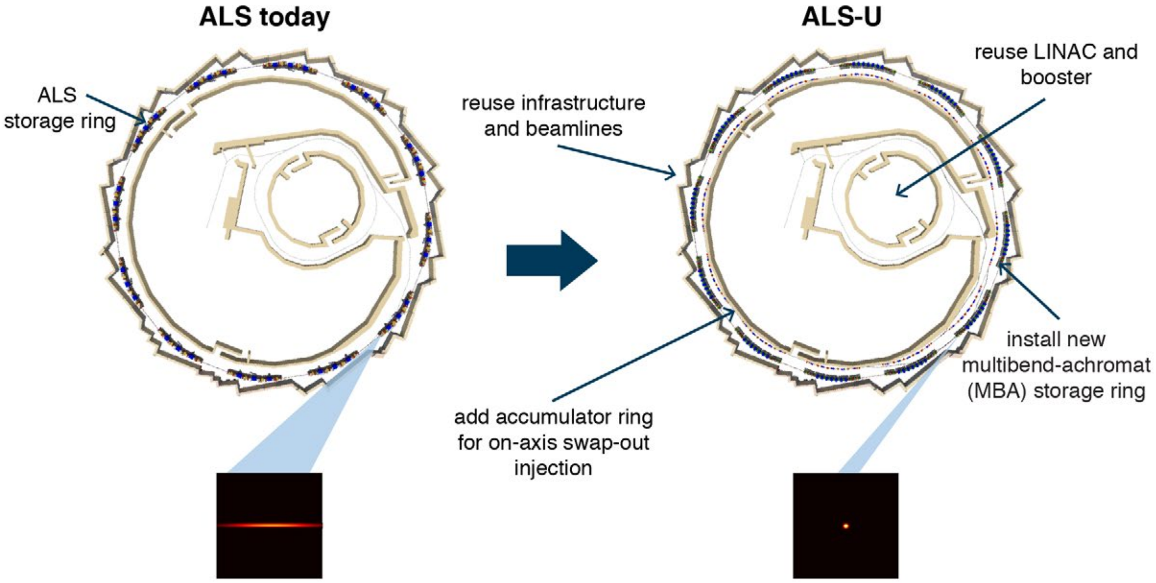

Figure 1.1.1. The planned ALS upgrade will involve removal of the existing accelerator lattice and installation of a multibend achromat lattice and an accumulator ring for swap-in, swap-out injection. The electron beam cross section will change from wide horizontally (left) to approximately circular (right) and small enough that the resulting x-ray beams will be transversely coherent (i.e., diffraction limited) through the entire soft x-ray regime.

An x-ray source that is small and sufficiently collimated (i.e., bright enough) will be diffraction limited, with a fixed phase relationship between any two locations on a wave front. The direct consequence is that all of the intensity of the beam can be focused into the smallest possible size, as defined by the wavelength. As a result, coherence-based experiments that are now done routinely with longer-wavelength lasers will become possible with x-rays with up to 1000-fold shorter wavelengths that are therefore sensitive to nanoscale phenomena.

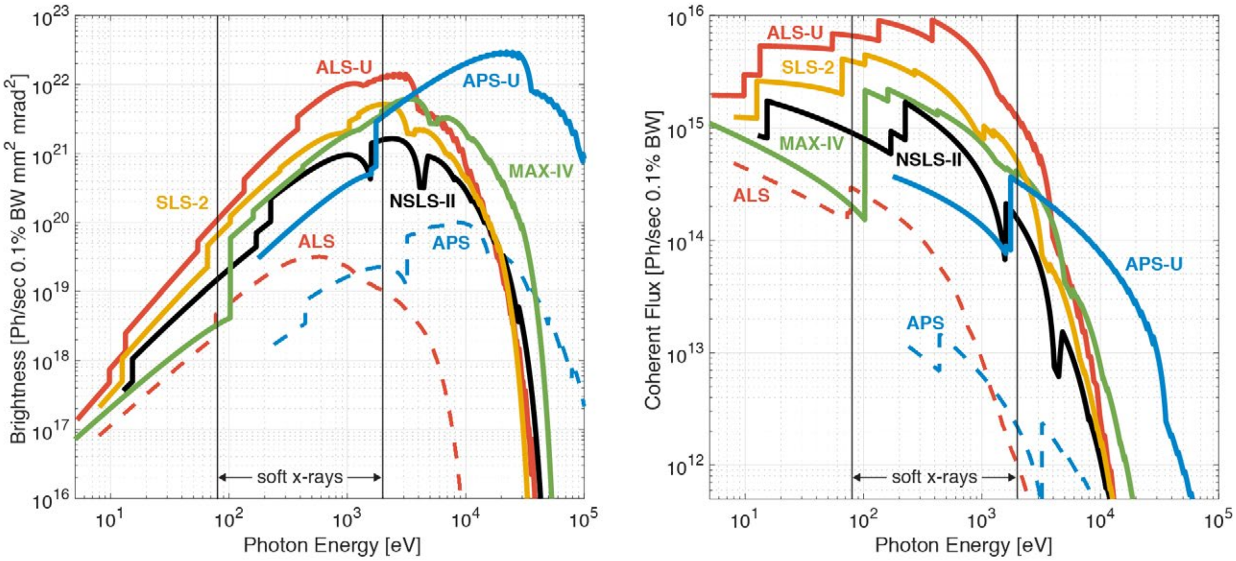

Figure 1.1.2. Envelopes of brightness (left) and coherent flux (right) for undulator sources at ALS, ALS-U, and several other operating and planned x-ray facilities. Coherent flux is the metric that determines the time required to accomplish an experiment with a given spatial, spectral, and temporal resolution, and is proportional to brightness divided by the square of the photon energy.

Previous generational advances in storage-ring-based x-ray facilities have provided similar degrees of increase in brightness and coherent flux, enabling new and powerful capabilities that have revolutionized our ability to understand chemical, biological, and material systems. The planned upgrade will transform the ALS into a world-leading fourth-generation facility characteristic of future synchrotron science. More specifically, the sensitivity of soft and tender x-rays to chemical and material processes will be dramatically enhanced when the x-ray wave fronts become smooth and transversely coherent.

Coherent soft x-ray beams can resolve nanometer-scale features and interactions while following real-time kinetics with high spectral sensitivity, revealing how chemical processes evolve and materials function. More specifically, the high coherent flux of ALS-U will enable a suite of tools that encompass ***3D nanoscale imaging*** with ***high spectral sensitivity*** over ***broad space and time scales,*** dramatically amplifying the already high impact of ALS soft x-ray spectroscopies. For example, chemical imaging experiments at the ALS have recently achieved few-nanometer spatial resolution in 2D on a model material, but on a more typical, realistic object can provide only 15-nanometer resolution with limited spectral coverage, resolution, and temporal sensitivity. ALS-U, on the other hand, would allow spectroscopies like angle-resolved photoemission spectroscopy to be applied to functional systems as nanoprobe techniques with natural or designed spatial or temporal heterogeneity. The suite of coherence-enabled tools is described in more detail in Chapter 2 and summarized by Table 2.1.

ALS-U's combination of capabilities, and their simultaneous application, will enable the understanding, rational design, and assembly of structures that exhibit emergent functionalities needed to address the world's most pressing technological challenges. These include materials and structures that can store and process classical and quantum information with ultralow power dissipation; microbial cells engineered to produce commodity and specialty chemicals from abundant starting materials; chemical microreactors designed to achieve efficient and selective multistep chemical syntheses; photoelectrochemical cells that enable artificial photosynthesis; and nanoporous membranes optimized for ion transport and water purification with high selectivity and efficiency.

1.2 FIVE CHALLENGES ADDRESSED WITH COHERENT SOFT X-RAYS

The science case for an improved source of coherent soft x-rays is supported by a host of BES documents. BRN reports elaborate the content of a broad-reaching series of BESAC-sponsored documents including *Directing Matter and Energy: Five Challenges for Science and the Imagination* (2008), *From Quanta to the Continuum: Opportunities for Mesoscale Science* (2012), and *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities in Discovery Science* (2015). The output from several recent BES RTDs is also relevant, including *Controlling Subsurface Fractures and Fluid Flow* (2015), *Neuromorphic Computing* (2015), and *Sustainable Ammonia Systems* (2016), each of which is loosely related to the subject of one of the BRN reports. The recent BRN and RTD reports also provide updated advice on the tools needed to connect basic research needs to trends in translational energy research for many years to come.

Analysis of the multidisciplinary science opportunities delineated by this workshop revealed five overarching challenges spanning multiple disciplines that ALS-U will address. These crosscutting challenges align well with the research priorities discussed in BES reports, providing strong validation of the output of the workshop and illustrating the breadth and expected impact of the facility's next 20–30 years. In addition to being described in detail below, the challenges are presented in Table 1.1 along with several relevant BRN and RTD reports[1] and science opportunities identified by this workshop that link the two together.

Challenge 1: Spectral Mapping of Nanostructures and Nano-Objects

Nano-objects

Scanning probe and electron microscopies are currently some of our most powerful tools for studying nanomaterials, from synthetic carbon nanostructures to biological nano-objects like protein molecules and complexes. These tools can produce a dazzling array of micrographs, yet they often lack the contrast to map the data contained in those images onto the elemental, chemical, and magnetic information that would help us better understand how macroscopic function emerges from nanoscale properties. ALS-U will offer a combination of few-nanometer resolution and soft x-ray electronic, magnetic, and chemical contrast that will complement scanning probe and electron microscopy to transform our understanding of and ability to control these systems.

Challenge 2: Designing Functional Interfaces

Interfaces

Soft x-ray photoelectron spectroscopy has contributed significantly to our understanding of homogeneous surfaces and thin films. Yet our inability to adequately carry out nanoscale probes has limited our understanding of material and chemical systems with natural or designed heterogeneity. These systems—and the interfaces between them—are poised to enable many future energy-related technologies like artificial photosynthesis. ALS-U's photon-based microscopies, with few-nanometer resolution in 3D, will enable revolutionary probes of heterogeneous interfaces in diverse environments, taking advantage of a core expertise of ALS scientists who have led efforts to deploy these powerful chemical and material spectroscopies.

Challenge 3: Harnessing Entropy as a Material and Chemical Design Tool

Entropy

Thermal motion and the entropy it produces play crucial roles in our ability to synthesize novel material and chemical phases and understand new phenomena. Our knowledge of the entropic contributions to

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[1] When this report was written, the BESAC and RTD reports noted above were all complete, and new BRN reports on Synthesis Science, Quantum Materials, Environmental Management, and Carbon Sequestration were also available. A BRN report on Water and Energy was in progress and is included here based on participation of workshop leads and attendees. An update of a BRN on Electrical Energy Storage is also in progress. Our discussion in these areas is based in part on RTD and BESAC documents and on previous BRN reports on similar subjects.

a system's free energy often relies on theoretical simulations that lack detailed experimental validation, and is not nearly as sophisticated as our understanding of the energetic contributions. This situation limits our capacity to design, create, and optimize targeted phases and structures. ALS-U will enable the ability, using quasielastic and inelastic soft x-ray scattering, to measure the thermally excited nanoscale fluctuations that store entropy. These measurements will be done with chemical and material contrast, so that, for example, the entropic contributions of spin, charge, and lattice degrees of freedom to the total entropy of a quantum material can be probed independently.

Challenge 4: Manipulating Nanoscale Flows

Flows

Nanoscale currents of molecules, charges, spins, and elementary excitations are poised to regulate the designed hierarchical structures of next-generation functional material and chemical systems. As in biological systems, the overall efficiency and selectivity of material and chemical systems will be determined largely by the degree to which we can localize and control these flows. Understanding currents in confined spaces, where chemical and material processes can be controlled and optimized, is particularly important. ALS-U will integrate highly sensitive interferometric detection with soft x-ray spectromicroscopy and dynamical measurements to detect nanoscale flows in diverse environments.

Challenge 5: Controlling Materials Chemistry and Physics in Confined Spaces

Confined Spaces

Biological systems are based on confined but connected spaces (e.g., subcellular components). This structure facilitates individual processes and allows overall cellular function to be regulated. The next generation of functioning chemical and material structures will be bio-inspired, with individual processes optimized in separate confined spaces. These processes will be connected by internally regulated nanoscale flows, and the overall network will be configured for specific applications like multistep catalysis and neuromorphic or quantum processing. Powerful ALS-U spectromicroscopy tools will allow researchers to achieve a precise measure of the internal workings of such systems, which will be crucial to their design and optimization.

Table 1.1. Close alignment of ALS-U crosscutting challenges and BES research priorities. Crosscutting challenges are listed in the lefthand column, and BES BRN and RTD reports are listed across the top row. Science opportunities identified by this workshop, and which link the challenges and reports together, are listed with the corresponding section of this report in which they are discussed in more detail.

ALS-U CROSSCUTTING CHALLENGES	**BES REPORTS**			
	Quantum Materials (2017)	**Synthesis Science (2017)**	**Electrical Energy Storage (2007, update in progress)**	**Energy and Water (2017), Environ. Mgmt. (2015), Carbon Capture (2010)**
Spectral Mapping of Nanostructures and Nano-Objects	Interferometric microscopy (3.1.5)	Multistep nanoparticle catalysts (3.2.3)	Granular electrodes (3.2.2)	Macromolecular machinery (3.3.6)
Designing Functional Interfaces	Antiferromagnetic spintronics (3.1.3)	Imaging electrocatalysis (3.2.2)	Soft material interfaces (3.3.4)	Environmental interfaces (3.2.6, 3.3.4)
Harnessing Entropy as a Material and Chemical Design Tool	Fluctuating spin phases (3.1.4)	Kinetic control of chemical processes (3.2.1)	Transport in soft matter (3.3.5)	Nucleating environmental and biological nanoparticles (3.2.4, 3.2.7)
Manipulating Nanoscale Flows	Imaging spin currents (3.1.1)	Imaging catalysis (3.2.2, 3.2.3)	Charge motion in photovoltaics (3.3.1)	Multiphase flows in nanoscale cracks (3.2.5)
Controlling Materials Chemistry and Physics in Confined Spaces	Imaging functionalized nanotubes (3.1.7)	Designing and controlling chemical kinetics (3.2.1)	Designing biosystems for biofuels (3.3.7)	Nanoscale environmental chemical kinetics (3.2.6)

1.3 REPORT OUTLINE

The remainder of this report describes in detail the opportunities and recommendations resulting from the charge to the workshop participants, which was to delineate the frontiers of soft- and tender-energy x-ray science enabled by ALS-U with the following goals:

- Identify and highlight some of the first transformative spectroscopy, scattering, and microscopy experiments that will be enabled by fully coherent and/or intense nanofocused soft x-ray beams provided by ALS-U;
- Determine essential ALS beamline and endstation developments and upgrades needed to execute these proposed experiments; and
- Explore complementary tools and techniques that are needed to take full advantage of the new capabilities of ALS-U, e.g., data processing, analysis, and interpretation tools; in situ sample preparation facilities; multimodal characterization techniques such as optical, electron, and scanned probe microscopies; and hard x-ray and infrared tools.

Chapter 2 discusses the research techniques of primary interest for coherent soft and tender x-rays at ALS-U, including: required upgrades to existing tools and the development of new tools as part of the ALS-U project to produce a suite of capabilities that will enable those opportunities, and ancillary tools that will be required to take full advantage of ALS-U capabilities.

Chapter 3 summarizes each of the three topical areas discussed in the workshop—spin, quantum, and topological materials; multiscale chemical processes; and soft and biological matter—and presents a number of specific early science opportunities that ALS-U will address. Each subsection describes the scientific importance, the essential role of ALS-U, and the broader impact of one of the opportunities. Labels in the header of each subsection identify the crosscutting challenges the opportunity addresses and the most applicable ALS-U techniques.

A related workshop on *Soft X-Ray Science Opportunities Using Diffraction-Limited Storage Rings*[2] was held in October 2014 at the ALS. The goal of that workshop was to evaluate how high phase coherence and stability could be leveraged more generally, whereas the current workshop and report concentrates on ALS-U science opportunities and the instruments needed to enable them. This workshop constituted an early step in ensuring that the upgrade will support a broad-based, vibrant, and world-leading scientific program. We look forward to continuing interaction with the ALS user and broader science community and to other, more focused workshops in the coming years.

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[2] The corresponding workshop report is available at **https://als.lbl.gov/wp-content/uploads/2016/09/sxr_workshop_report.pdf**.

2 ALS-U Techniques

When first invented, the usefulness of the laser was met with some skepticism and called “a solution looking for a problem.” With perfect hindsight we now know how wrong that opinion was. The coherent properties of x-ray beams produced by emerging ultrahigh-brightness free-electron lasers (FELs) and diffraction-limited storage rings (DLSRs) create a similar situation, and opportunity. As is evident in the optical domain, techniques enabled by both ultrafast-pulsed FEL and nearly-continuous-wave DLSR sources will play important roles in the coming revolution in coherent x-ray science.

In this chapter we extrapolate from soft x-ray techniques commonly used at third-generation storage-ring sources, which have coherence properties comparable to a mercury arc lamp, to those that will be enabled by the ALS-U undulators, which will provide full transverse coherence through much of the soft and tender x-ray regimes. In particular, ALS-U will enable a powerful suite of interrelated techniques for probing heterogeneous and hierarchical material and chemical systems. These techniques can be grouped in three classes.

Nanoprobe spectroscopies

Nanoprobes

ALS-U will be the ideal source for efficient, diffraction-limited focusing, allowing many conventional soft and tender x-ray techniques to be performed with nanoscale spatial resolution. A transversely coherent wave diffracts perfectly from a grating or a Fresnel zone plate, while a partially coherent wave will only be partially diffracted, and the incoherent fraction will be lost. Fourier optics, such as zone plates, require transverse coherence and will become 100–1000x more efficient at ALS-U.

Coherent scattering and imaging

Coherent Scattering **Coherent Imaging**

When a coherent wave front scatters from an inhomogeneous medium, the inhomogeneity is encoded into the scattered wave fronts to produce a speckle-diffraction pattern. The strength of the encoding is determined by the optical constants of the medium, so the speckle patterns can be used to probe many kinds of chemical and material inhomogeneity with spatial, spectral, and temporal resolution.

Interferometry

Interferometry

Interference effects and standing wave fields, which are widely used in laser-based techniques for understanding microscale phenomena with very high sensitivity, will become viable with ALS-U, allowing access to chemical and electronic properties with nanoscale resolution and very high spectral sensitivity.

Table 2.1 summarizes soft and tender x-ray tools that will benefit markedly from the high brightness and coherent flux provided by ALS-U. These tools are classified by the above experimental modalities and are elaborated in more detail in the balance of this chapter. For convenience, a list of acronyms is provided in Appendix D.

It is important to note that the total flux from ALS-U will not be very much larger than that from ALS. The primary difference is that the flux from ALS-U will be nearly transversely coherent throughout the soft x-ray regime. Most other existing ALS tools will benefit from the smaller, circular source of ALS-U, though less so than those that require coherent wave fronts.

Table 2.1. Summary of techniques that will benefit from ALS-U, classified by nanoprobe, coherent scattering/imaging, and interferometry modalities.

Modality	Technique	Application	Highlighted ALS-U Capabilities	Improvement over ALS
Nanoprobe Spectroscopies	soft- and tender-energy STXM, nanoXAS	map material heterogeneity with chemical, electronic, and magnetic contrast	<10-nm resolution, 3D possible with XAS contrast	100–1000x improved signal on undulator; 5–10x on bend magnets
	nanoXMCD, nanoXMLD, nanoXFMR	map orbital/magnetic/spin heterogeneity in spin and quantum materials and structures	<10-nm resolution, XMCD vector contrast, high sensitivity with XFMR	100–1000x improved signal on undulator; 5–10x on bend magnets
	nanoARPES, nanoRIXS, nanoAPXPS	probe nanoscale electronic structure and excitations in spin and quantum materials	<10 nm ARPES, XPS, tender fluorescence, 100-nm RIXS; ptychography enabled	100–1000x improved signal on undulator
Coherent Scattering	XPCS	probe nanoscale thermal motion in chemical and material systems	ns time resolution with few nm scattering sensitivity	up to 10^6x improved time resolution
Coherent Imaging	coherent diffractive imaging, ptychography	map chemical phenomena with few-nm resolution and perform cryo-imaging to ~10 nm with soft and tender energy	2–3 nm resolution in 3D, XAS, XMCD contrast; diverse sample environments	100–1000x improved acquisition speed
	FXS	image 3D structure of biopolymer complexes in solution using tender-energy x-rays	target ~1-nm resolution at tender x-ray energy	1000x improved signal/throughput at tender energy
Interferometry	differential interferometric SXM	perform differential, phase-sensitive nanoscale x-ray imaging	<20-nm resolution; ultrahigh chemical and magnetic/spin sensitivity	shot noise-limited measurement of weak signals
	x-ray standing wave techniques	form soft/tender x-ray standing wave in free space to allow 3D imaging with full-field microscopy	<20-nm resolution in 3D; XMCD or XAS contrast	cannot be performed at ALS; requires a fully coherent source
	FT-RIXS	Fourier-transform spectroscopy for high throughput or high resolution	target 1-meV energy resolution at 1 keV in a compact spectrograph	new technique

2.1 NANOPROBE SPECTROSCOPIES

The scientific community applies spectroscopies in the existing ALS toolbox to probe diverse material, chemical, and biological problems. These techniques include x-ray absorption spectroscopy (XAS) and magnetic variants like x-ray magnetic circular dichroism (XMCD); x-ray photoelectron spectroscopy including angle-resolved photoemission (ARPES) and ambient-pressure photoemission spectroscopy (APPES); and resonant elastic and inelastic scattering (REXS, RIXS). In the soft x-ray spectral regime, these spectroscopies provide particularly useful information about chemical bonding, magnetism, superconductivity, and a wealth of other electronic states, phases, and interactions.

A primary outcome of the workshop was understanding that deploying these as nanoprobe spectroscopies at ALS-U will dramatically expand those sensitivities by simultaneously providing associated nanoscale spatial information. For example, nanoXAS (more commonly called scanning transmission x-ray microscopy, or STXM) maps chemical oxidation states and functionalities, nanoXMCD and nanoREXS image magnetic, orbital, and spin structures, and nanoARPES and nanoRIXS can probe the electronic structure, excitations, and phase behaviors of quantum materials—all with nanoscale resolution. Moreover, all of these techniques can be performed in confined and functioning structures. These nanoprobe techniques rely on diffraction-limited focusing, meaning that performing them at ALS today requires spatially filtering the incident beam (with a pinhole) to produce smooth, coherent wave fronts, resulting in a loss of more than 99% of the total soft x-ray flux.

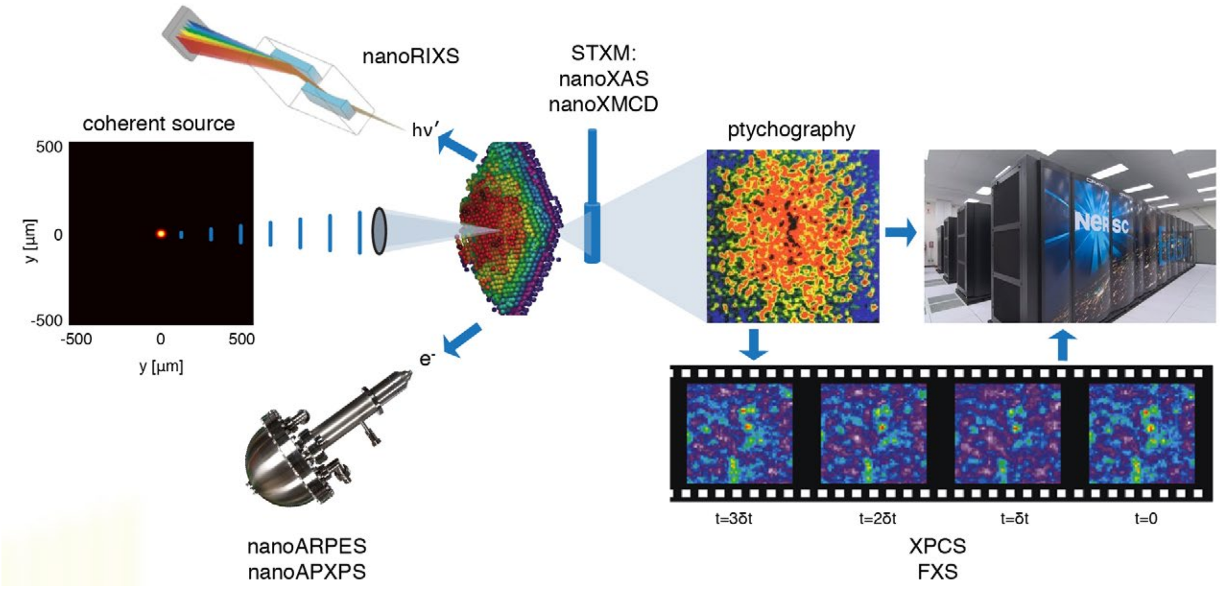

Figure 2.1.1. ALS-U will accelerate the transformation of soft x-ray spectroscopy and scattering tools into powerful nanoprobe and coherent scattering techniques, respectively. The ALS-U source (left) will be small and collimated enough that the soft x-ray wave fronts produced will be smooth and coherent. In the nanoprobe modality, these are focused with high efficiency into a diffraction-limited spot, which in turn can be scanned across the sample to apply soft x-ray spectroscopies with nanoscale resolution, e.g., STXM, nanoXMCD, nanoRIXS, nanoARPES, or nanoAPXPS. Alternatively, the coherent soft x-ray beam can be scattered in transmission through or reflection off a heterogeneous sample to produce a speckle/diffraction pattern with chemical or magnetic contrast that can be set by tuning the x-ray energy near absorption resonances. New computational approaches like ptychography or fluctuation x-ray scattering (FXS) can transform these speckle patterns into 2D or, with tomography, 3D images. As another option, temporal sample fluctuations can be mapped onto fluctuations in the speckle pattern, and these can be analyzed to probe motion over broad spatial and temporal scales.

Figure 2.1.1 illustrates how the small size and divergence of the ALS-U electron beam will produce soft x-ray beams with smooth and coherent wave fronts, intrinsically and without filtration. This will increase the signal/throughput of ALS nanoprobe spectroscopies by a factor of 100–1000. For example, at today's ALS, nanoARPES is capable of producing correlated spatial and electronic maps, but the technique is currently very slow and applicable only under static conditions. At ALS-U, all of these nanoprobe spectroscopies will be possible with data acquisition rates two to three orders of magnitude faster, enabling measurements over larger areas, with higher resolution, and with the ability to observe the samples as they evolve under such conditions as varying temperature, molecular exposure, applied voltage, or other directed influences.

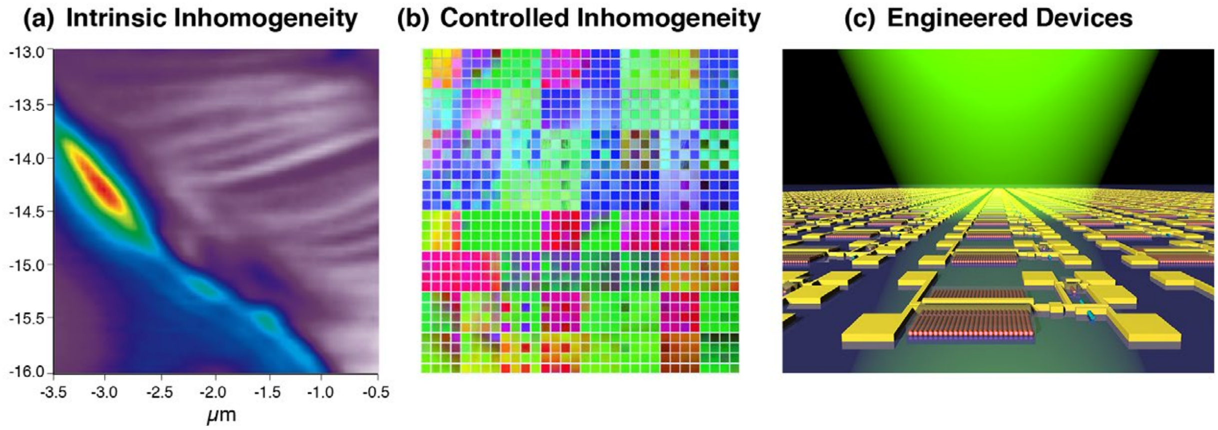

Figure 2.1.2. Examples of experimental modalities that probe heterogeneity. a) Map of intensity of intrinsic nanoscale inhomogeneity, in this case of ARPES intensity from a graphene film grown on a SiC substrate, can be obtained under varying experimental parameters (current, field, temperatures, stress) (Courtesy: R. Koch); b) Controlled inhomogeneity in "3D-printed" microarrays of samples synthesized using combinatorial approaches, i.e. fabricating hundreds of samples with slightly varying parameters (J. Wang et al., *Science* **279,** 1712 (1998)); c) Combination of locally applied fields on engineered arrays of samples with varying compositions and structures (Courtesy: A. Javey).

ALS-U will not only allow naturally inhomogeneous samples to be probed (Figure 2.1.2a), but also deliberately designed arrays of varying composition or structure (Figure 2.1.2b), enabling the systematic investigation of the correlation between structure, composition, electronic/magnetic properties, and functionality. For this purpose, nanoARPES, nanoRIXS, nanoXAS, and nanoXMCD are ideal because they directly probe essential quantum mechanical properties such as momentum, wave-function symmetry, valence-band spin polarization, and transition-matrix elements, which can be directly associated with desired functionality such as superconducting gaps, metal–insulator transitions, and magnetism. In addition, ancillary probes, including visible luminescence, microprobe transport, scanning probe microscopies, in the same or (with accurate sample registry) adjoining stations can be applied to the same sample arrays to determine further correlations such as atomic arrangement or photonic properties.

The ultimate probe of heterogeneity will be a combination of external field control of sample arrays (Figure 2.1.2c). These can be tailored not only to understand the evolution of electronic properties with external fields but also to directly probe transport properties using x-rays. For example, XFMR (x-ray ferromagnetic resonance), a variant of XMCD, has recently been used to detect pure ac spin currents at ALS. At ALS-U this will become nanoXFMR and will allow mapping spin currents in device geometries with ~20-nm spatial resolution.

2.2 COHERENT SCATTERING AND IMAGING

Tools based on the scattering of coherent soft x-rays at ALS-U will further facilitate the combination of spectroscopic, structural, and dynamical sensitivities already featured in many ALS tools. “Coherence” is the characteristic of waves that allows interference and diffraction patterns of extended objects to be formed with time-integrating detectors, which in turn enables spatial and temporal correlations in complex, interacting, and functioning systems to be measured. For example, removing the point detector for STXM measurements will enable a coherent scattering modality in which a transversely coherent beam is scattered in transmission through (or, in some cases, in reflection off) a sample (Figure 2.1.1). Any heterogeneity in the illuminated spot is projected into a diffraction pattern onto a pixelated area detector. The resulting diffraction pattern provides a fingerprint of the sample under study with chemical, electronic, and/or magnetic contrast and which can be analyzed to yield detailed spatial, spectral, and temporal information. Moreover, any nanoscale motion will also be encoded in sequences of such diffraction patterns and can be studied, either by inversion into real-space movies or statistically in Fourier space.

Using emerging phase retrieval algorithms, the diffraction patterns can be inverted to provide real-space phase and amplitude images with few-nanometer spatial resolution. Ptychography, a robust coherent imaging approach, is already a valuable ALS technique and it is being applied to increasingly complex systems and sample environments (Figure 2.2.1). ALS-U will increase the signal/throughput by a factor of 100–1000x and will moreover enable 3D, wavelength-resolution images of complex media.

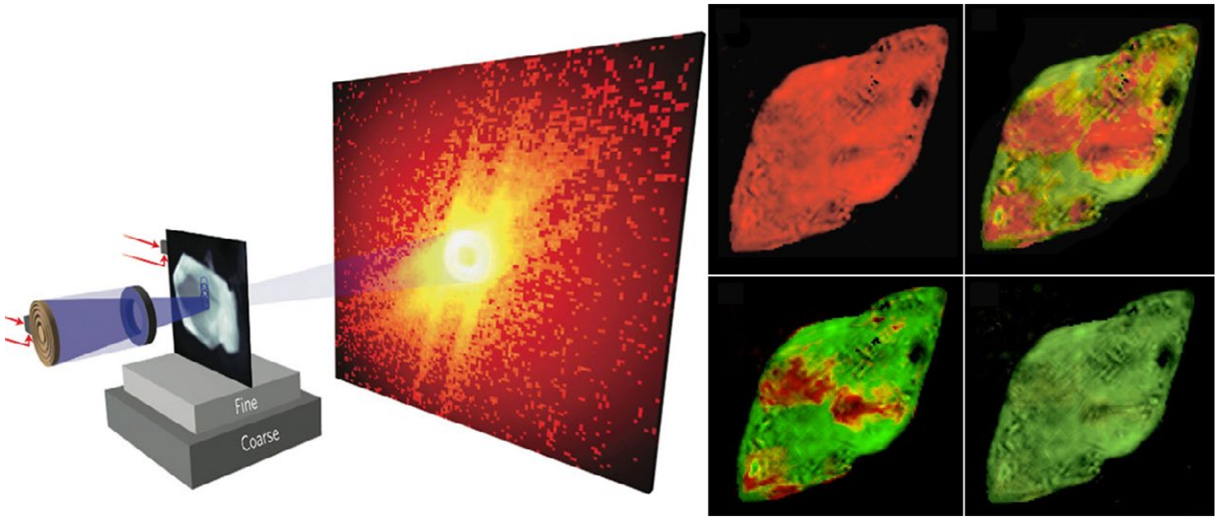

Figure 2.2.1. In situ ptychographic images of a ~1-micron grain of FePO$_4$ during electrochemical intercalation with lithium. Oxidation state contrast is provided by choosing photon energies near the Fe L$_3$ absorption edge. (Courtesy: D. Shapiro)

A related, but still emerging, coherent imaging technique is called fluctuation x-ray scattering (FXS, Figure 2.2.2). This method is being developed at free-electron laser sources to image biomolecules and their complexes in solution. In its simplest form, an FXS experiment stitches together many diffraction patterns from randomly oriented identical structures to produce a full 3D Fourier image, which can be phased to produce a real-space image. Alternatively, an FXS study of an extended material with short-range order measures the space-averaged Patterson function and provides a much more robust test of structural models than small-angle x-ray scattering (SAXS). The high coherent flux from ALS-U and the larger x-ray scattering cross sections at longer wavelength will enable FXS measurements with the added benefits of high stability, repetition rate, and capacity.

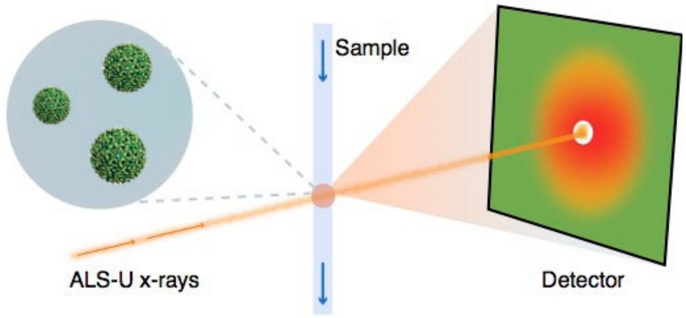

Figure 2.2.2. FXS is a hybrid of SAXS, which uses limited coherence, and coherent diffractive imaging, which is being developed to determine the structure of biopolymer molecules and complexes. (Courtesy: P. Zwart)

Static images like those in Figure 2.2.1 normally average over thermal fluctuations that must exist in all materials. These fluctuations are fundamentally important, both because they carry entropy and therefore contribute to phase stability, and because they are directly related to dissipative processes through the fluctuation–dissipation theorem. They also drive material and chemical kinetics and so are important to a very a diverse array of processes.

In addition to coherent imaging techniques, Figures 2.2.1 and 2.2.2 represent the experimental modality for a third coherent scattering technique, called x-ray photon correlation spectroscopy (XPCS). XPCS using ALS-U will provide a robust statistical measure of these fluctuations at nanosecond time and nanometer length scales. In a simple representation, fluctuations in a sample are mapped onto fluctuations in the diffraction patterns, then collected into a movie using a fast area detector. Each speckle corresponds to a different scattering wave vector and spatial length scale, and temporal correlations in the sample at that length scale are mapped onto intensity correlations in the corresponding speckle. These correlations might involve material diffusion, a chemical kinetic process, or nanoscale motion of a magnetic, spin, or orbital texture. Formally, XPCS results measure intermediate scattering function $S(q,t)$, which is a common output of theoretical simulations of many classes of complex hard and soft materials where thermal fluctuations play an important role in phase stability.

An important characteristic of XPCS is that the timescale that can be probed scales as the inverse square of the differential scattering rate. Whereas ALS can provide enough coherent flux to measure sub-millisecond kinetic processes, the ultrahigh coherent flux of ALS-U will enable study of nanosecond timescales, spontaneous processes with soft x-ray contrast, and, with some tricks and substantial detector development, this might be extended to tens of picoseconds.

2.3 INTERFEROMETRY

The field of interferometry was invented over a century ago by Albert Michelson to perform precision measurements based on the interference of two mutually coherent beams. It has been broadly applied since the invention of the laser to detect weak signals, probe dilute systems, achieve high spectral resolution, and support diverse optical technologies. However, the low coherence of most x-ray sources has limited the development of x-ray interferometric techniques. At ALS-U, full transverse coherence through the entire soft x-ray regime will enable new interferometric techniques that are very difficult or impossible at the ALS today, and this will lead to entirely new, highly sensitive soft x-ray tools.

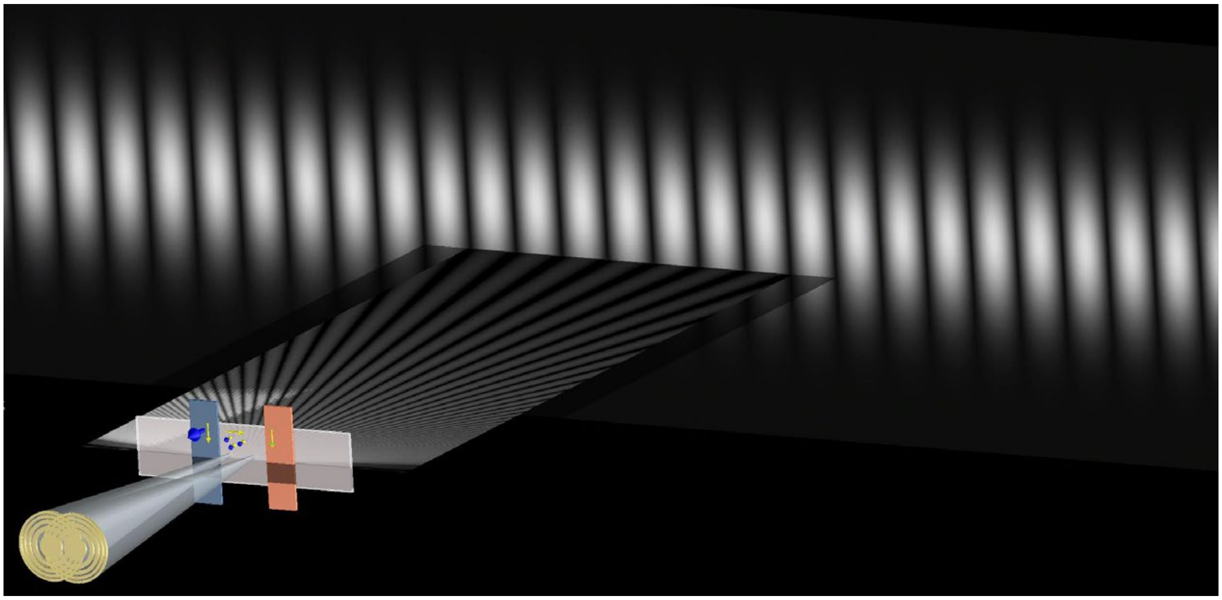

Figure 2.3.1. A "differential STXM," which is proposed to detect and image very weak x-ray absorption signals like dilute systems and spin currents. (Courtesy: A. Scholl)

Many x-ray experiments today measure the intensity and/or energy of photons or electrons. In the optical regime, interferometry is a well-developed approach based on measuring phase instead of wave amplitude, which can provide high precision, high sensitivity, and high spectral resolution. ALS users have successfully adapted some of these approaches, for example, to test optics in the extreme ultraviolet (EUV) regime for lithography applications. One proposal is to extend the capability of STXMs to enable phase-sensitive detection as described in Figure 2.3.1. Two coherently illuminated Fresnel zone-plate lenses produce two closely separated foci. The transmitted direct beams will be differentially absorbed and phase-shifted by sample heterogeneity and then will interfere on a detector. Small changes in phase between the two beams, which arise from traversing different parts of the sample, can be detected with high precision by measuring shifts in the interference pattern. This approach is expected to exceed our current ability to monitor differences in x-ray absorption with 10^{-5} precision.

Another application based on simple interference is to create x-ray standing waves for x-ray sectioning measurements. X-ray standing waves were first developed over 30 years ago based on the interference of incident and lattice-Bragg-reflected waves. The advantage of the technique is that the lattice planes, in conjunction with the angular offset from the Bragg angle, set the phase of the standing wave; there is no requirement for transverse coherence in the photon beam. A more flexible approach would be to form the standing wave by splitting and recombining a transversely coherent x-ray beam, as suggested in Figure 2.3.2. The position and orientation of the standing wave would then be fixed in space, and a sample could be "sectioned" in one dimension simply by moving it through the standing wave. This concept can be further developed in the intermediate-energy regime using crystal Bragg reflectors and beam splitters, in a configuration used for many years in neutron interferometry. An attractive application would be to apply this standing-wave technique in combination with a full-field imaging, soft x-ray spectroscopy like photoelectron microscopy or full-field x-ray microscopy. The combination would make it possible to do a tomographic reconstruction of a sample like an interphase layer in an electrochemical cell.

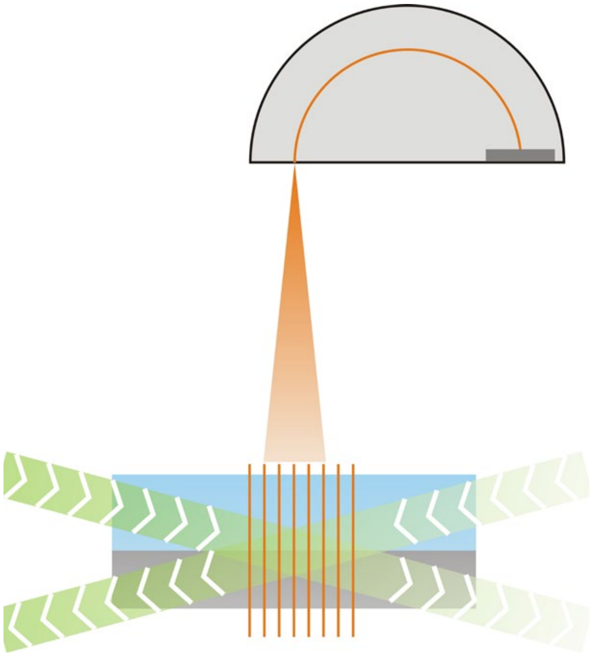

Figure 2.3.2. A standing wave is formed when two spatially and longitudinally coherent waves overlap in space. When combined with an x-ray full-field spectroscopy, this standing wave would allow tomographic reconstructions with spectroscopic contrast. (Courtesy: E.J. Crumlin)

The differential phase-contrast microscopy described above is intriguing in its simplicity: it is accomplished with no moving optical elements. It can be directly adapted to existing STXM technology and would benefit in direct proportion to source brightness. The soft x-ray standing wave experiment is one step more complicated in that, ultimately, one would like to vary the period of the standing wave by changing the included angle between the two beams. This will require a more elaborate optical system, though the longitudinal path-length difference between the two beams would remain small and constant. The most general interferometry concept would involve also varying this path-length difference, as is done in Fourier-transform spectroscopy. The coherence requirement for this technique depends on details of the design, but in general, full coherence will lead to a simpler and more easily optimized design.

In principle, applying these ideas to Fourier-transform RIXS could achieve dramatic improvements in spectral resolution beyond the practical limits set by spectrograph size, since the resolving power is set simply by the maximum path-length displacement divided by the wavelength. Fourier-transform spectroscopy with a resolving power of 10^6 has recently been achieved in the vacuum ultraviolet regime at Synchrotron Soleil, and an aspirational goal for ALS-U would achieve similar performance through the soft x-ray regime.

3 ALS-U Early Science Opportunities

The three sections of this chapter describe ALS-U science opportunities in specific contexts while also representing broader classes of science. These opportunities are by no means intended to be an exhaustive list, but they are a compelling set that speaks to the crosscutting challenges described in Section 1.2. The opportunities are divided into three topical areas as described below. Each opportunity is accompanied by labels that identify the crosscutting challenges the opportunity addresses and the most applicable ALS-U techniques.

Spin, quantum, and topological materials present a unique blend of emergent optical, electronic, and magnetic properties that promise an immense range of useful functionality. Although soft x-ray tools have already provided crucial and unique understanding in this area, progress has been hampered by spatial resolution that is inadequate to probe the intrinsic heterogeneity of the materials and to monitor functioning submicron structures with adequate sensitivity. ALS-U imaging tools will revolutionize our ability to design, understand, and optimize this fascinating class of materials.

Achieving feedback and control of thermally driven ***multiscale chemical processes*** will lead, for example, to improved synthetic efficiency and selectivity, to optimized energy storage and conversion systems, and to more robust predictive models for subsurface carbon sequestration and energy production systems. Enabling that feedback and control will require understanding the interplay between atomic-scale dynamic and nanoscale kinetic processes in designed structures ranging from nanoparticle catalysts to nanoscale cracks in rocks. High-resolution and high-sensitivity soft x-ray coherent imaging and scattering tools will probe the chemical structure and motion of these complex landscapes.

A defining feature of ***soft and biological matter*** is a high density of strongly interacting modes at an energy comparable to k_BT. In soft condensed matter, for example, this leads to the many unusual phase behaviors observed (though not always understood) in complex fluids. Biological systems based on thermally driven kinetics have evolved to function with very high fidelity and efficiency despite being immersed in a thermal bath fluctuating at k_BT energy. The high brightness and coherent flux of x-ray beams from ALS-U will provide broad dynamic range in both space and time, which promises to significantly enhance our understanding of key structural and functional properties of soft and biological systems, including self-assembly, emergent behavior, and adaptation to environmental changes.

3.1 SPIN, QUANTUM, AND TOPOLOGICAL MATERIALS

Soft x-ray tools have become indispensable for understanding the diverse and potentially useful properties of spin, quantum, and topological materials, including oxide and pnictide superconductors, manganites exhibiting colossal magnetoresistance, graphene and other 2D materials, topological insulators and Weyl semimetals, multiferroics, and many others (Figure 3.1.1). This broad class of materials often exhibits competing emergent phases that can be externally controlled with light, electrical current, or applied fields and therefore are ideal candidates for developing new multifunctional materials. Numerous electronic, spintronic, and photonic technologies will be revolutionized if we can learn to understand, predict, and control the emergent properties of spin, quantum, and topological materials at length scales from atomic to mesoscopic.

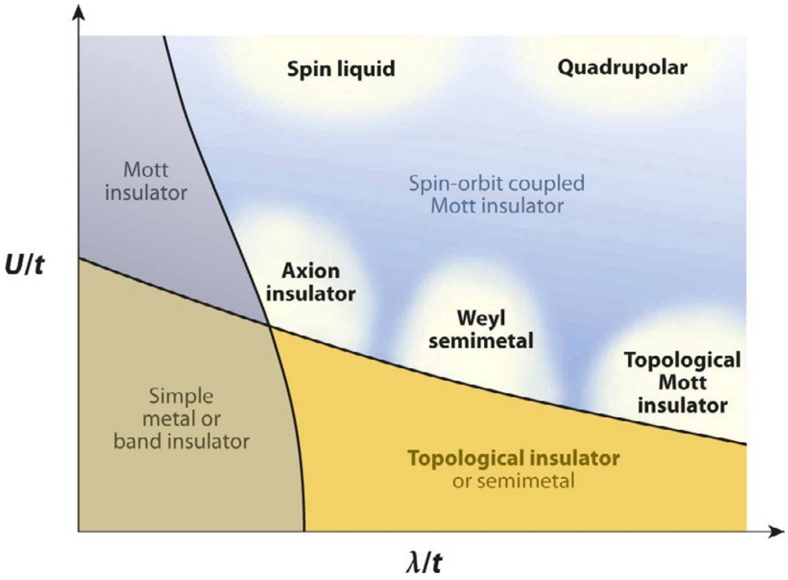

Figure 3.1.1. Schematic of a generic electronic phase diagram in terms of the single site correlation energy *U* and the spin-orbit energy λ, both normalized to the one-electron bandwidth determined by the intersite hopping integral *t*. ALS users have already had a large impact in confirming the existence of topological insulators and in the discovery of Weyl semimetals, and ALS-U will continue this record of innovation as materials like this are deployed, for example, in heterostructures, nanostructures, and gated devices. Moreover, as rich as this phase diagram is, it includes only two (normalized) interactions. Consideration of other interactions, such as scalar and vector exchange, spin anisotropies, and orbital and lattice energetics, will lead to many additional exotic spin and quantum materials that exhibit topologically protected electronic phases. (W. Witczak-Krempa et al., *Annu. Rev. Condens. Matter Phys.* **5**, 57 (2014))

Although the energy of electrons as a function of their spin and momentum is derived from quantum mechanics at the atomic scale, “quantum materials” depend on quantum mechanical phenomena at much longer scales. For example, the competition among many collective modes can lead to purely quantum mechanical ground states like high-temperature superconductivity.

Spin materials and magnetic phenomena bridge the quantum and classical worlds. Spin is a fundamental quantum number of the electron, and spins interact at the atomic scale through quantum-mechanical exchange forces. Since charge currents generate macroscopic magnetic phenomena, models have been developed to treat mesoscopic spin systems in semiclassical, micromagnetic models. Magnetic domain walls, bubbles, and skyrmions have quantum mechanical building blocks that are complex clusters of spins at short scales but can be understood at long range within parameterized ad hoc continuum models.

Spin interactions play an important role in determining the functionality of well-known phenomena such as ferromagnetism. Moreover, an issue of significant current interest is how spins are connected to materials that have topologically protected electron states. A defining characteristic of such topological materials is the locking of spin direction with electron motion, which also ties electron wave functions to mesoscopic behaviors like spin currents and quantum entanglement. There are many proposed applications of topological materials in spintronic and quantum information technologies.

Soft x-ray techniques applied to these materials can be classified into those that probe ground and excited electronic states, their symmetries, transition probabilities, as well as atomic spin and orbital magnetic moments, and those that characterize their functionality in terms of response to external stimuli such as applied magnetic and electric fields, optical excitation, strain, as well as changes in temperature. More recently, resonant x-ray scattering and microscopy have been developed to probe spatial correlations. Because both intrinsic and designed nanoscale heterogeneity dramatically impact the connection between fundamental interactions and the resulting functionality, applying all these techniques ***with nanometer spatial and broad temporal resolution*** is essential to learn how to design new materials and material structures with targeted emergent functionality. These capabilities will be enabled by ALS-U.

The de novo design of new and useful spin, quantum, and topological materials is challenging because of the large number of coupled degrees of freedom responsible for their functionality. In correlated materials, these include spin, charge, orbital, and lattice interactions. Other interactions in magnetic and topological materials include magnetocrystalline anisotropy, dipolar interactions, the Dzyaloshinskii-Moriya antisymmetric spin coupling, and the atomic and Rashba spin–orbit interaction. These interactions need to be examined to understand complex, ordered, topologically protected electronic states, particularly in thin films and nanostructures. Soft x-ray techniques, from angle-resolved photoemission spectroscopy (ARPES) and resonant inelastic x-ray scattering (RIXS) to spectroscopy and resonant scattering with x-ray absorption spectroscopy (XAS), x-ray magnetic circular dichroism (XMCD), or x-ray magnetic linear dichroism (XMLD) contrast, directly probe all of these interactions. Moreover, characteristic electronic and spin length scales lead to fascinating emergent phase behaviors when these materials are strained or embedded in heterostructures and nanostructures (e.g., the emergent metallic interfacial phase in $LaAlO_3/SrTiO_3$ heterostructures). Variants of all the above techniques, using nanoprobe and coherent diffraction imaging, have either been deployed at the ALS or are planned for development, even before ALS-U is commissioned.

The science opportunities in this section strongly relate to the crosscutting opportunities discussed in Section 1.2. The need for functional and controllable interfaces, the role of fluctuations in phase stability and device function, and the desire to measure and control nanoscale spin and ion currents all play prominent roles. And, of course, a dominant motivation for developing emergent spin, quantum, and topologically protected phases is to provide new electronic, spintronic, and sensor functionalities. These will often be manifested in gated nanoscale structures, which is the hard-matter version of the emphasis on confined spaces discussed in Section 1.2.

3.1.1 Imaging Spin Currents

Challenges:	Nano-objects	Interfaces	Flows
Techniques:	Nanoprobes	Coherent Imaging	Interferometry

Scientific Opportunity

The digital revolution and information age are built on our ability to control and direct minute electrical currents on the nanometer scale. Modern microelectronics is based on the capability to store and process information in the form of electric charges by shaping semiconducting materials through doping and lithography. Spintronics, which uses an electron's spin instead of its charge to encode information, promises to outperform today's technology, offering faster memory and logic operations and significantly reduced energy consumption while simultaneously increasing information density and durability (Figure 3.1.2).

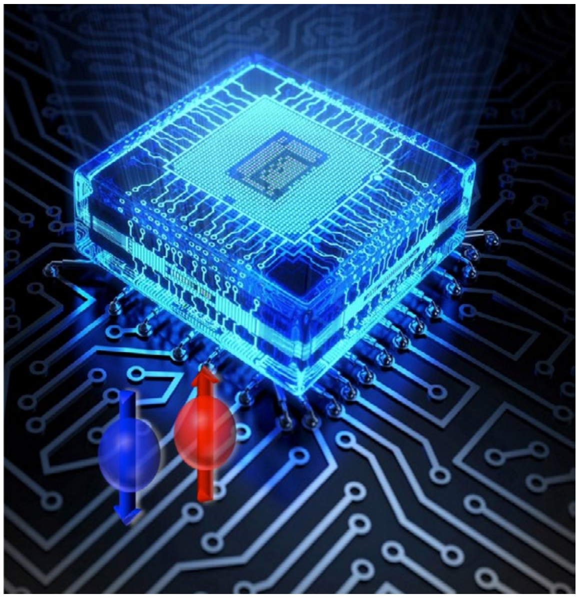

Figure 3.1.2. Spin-based electronics are poised to outperform today's charge-based microelectronics. Realizing their potential depends on advancing our understanding of spin transport on the nanoscale through 3D imaging of spin currents.

Characterizing and understanding the generation and transmission of spin currents on the nanoscale are critical to enabling this new paradigm. The detection of spin currents to date has remained mostly indirect, achieved through measurement of secondary effects such as spin-torque-driven magnetization precession, induced second-harmonic optical effects, and the inverse spin-Hall effect. XMCD measures the imbalance in occupation of the spin-split states near the Fermi level, enabling spin currents to be detected directly as tiny XMCD effects. The very high coherence and brightness of ALS-U will allow researchers to monitor spin currents with the nanoscale spatial resolution and nanosecond time scales required to gain in-depth fundamental understanding of spin transport and to develop the next generation of information technologies.

Importance of ALS-U

Spin currents in the form of spin-polarized charge currents can be generated by transmitting an electrical current through a ferromagnetic material to an adjacent non-magnetic layer (Figure 3.1.3) [1]. A first proof-of-principle experiment [2] demonstrated that it was possible to detect a transient magnetic moment of 3×10^{-5} μ_B per Cu atom associated with a spin current in a 27-nm-thin Cu layer using XMCD. For comparison, ferromagnetic Co has a moment of 1.7 μ_B per atom. Pure spin currents, which have angular momentum without moving charges, can be created by the precession of spins in a ferromagnet that is excited by an alternating external field or pulsed charge current and transferred into an adjacent non-magnetic layer. This "pumping" of spins has recently been detected as an alternating XMCD signal in a NiFe/Cu/CuMn/Cu/Co multilayer using soft x-rays [3]. In both cases, the XMCD effects are very small—10^{-4} to 10^{-5} μ_B per atom—and at the limit of what can be detected today in experiments that take days to weeks of beam time.

Despite these successes, we are approaching the limit of what can be inferred without improved spatial resolution. Future work will need to study spin transfer not only in simple metallic multilayers but also in more complex exchange springs and antiferromagnetic systems, where significant variation can take place within layers—that is, as a function of distance from the interface, not just between layers. Measuring spin transfer in these systems will require studying a series of devices with varying material properties to enable engineering interfaces that allow for the most effective spin transfer. The ability to efficiently and routinely image spin accumulation at interfaces will also deepen our understanding of spin-Hall effects and related spin-orbit phenomena crucial for spintronics. A lateral spatial resolution of 2–10 nm will be essential for identifying the impact of confinement and edge effects in microstructures and devices on spin currents and spin transport.

ALS-U will be the ideal source for efficient, diffraction-limited focusing, increasing the throughput of soft x-ray nanoprobe spectroscopies by a factor of 100–1000. This will allow us for the first time to detect spin currents with ~10-nm spatial resolution in an optimized scanning x-ray microscope. Ptychography techniques in transmission or reflection geometries will further enhance the spatial resolution of these experiments down to 2–5 nm. Moreover, employing highly interface-sensitive x-ray resonant magnetic reflectivity will allow us to directly measure the depth profile of the induced spin current within the individual layers of a multilayered nanostructure. Also, new detection modes relying on the phase of the x-ray beam, such as differential scanning transmission x-ray microscopy, or "differential STXM," proposed for ALS-U, are expected to be able to image very weak differences in x-ray absorption signals associated with spin currents.

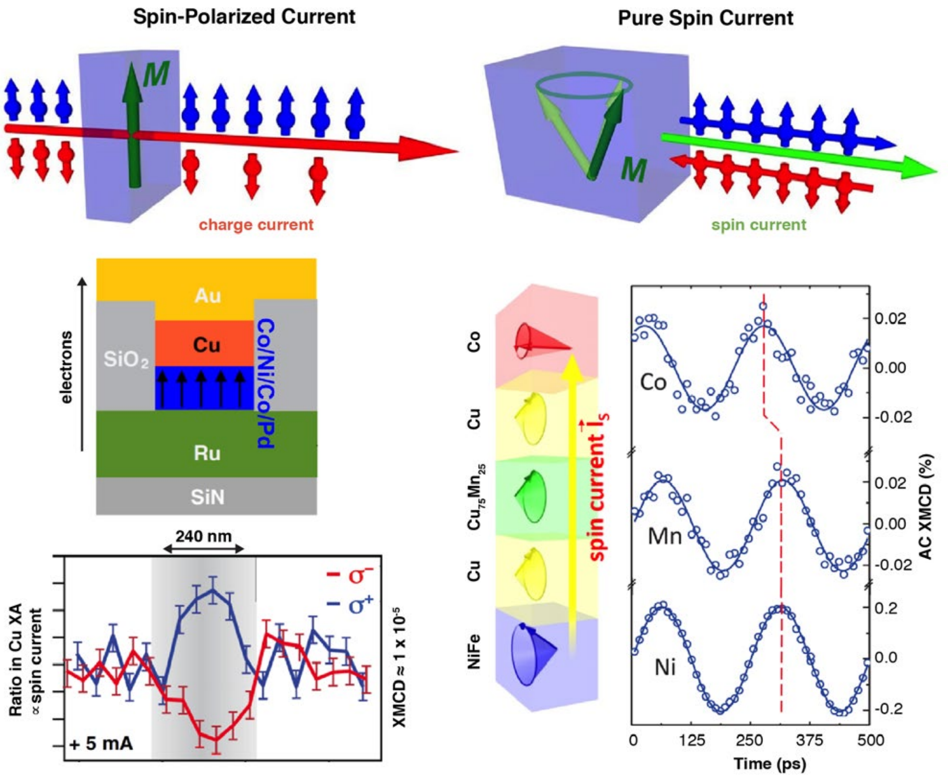

Figure 3.1.3. Left: Spin-polarized currents are generated by transmitting an electrical charge current through a ferromagnetic material (top) to an adjacent non-magnetic layer [1]. In a first proof-of-principle experiment using a specially designed sample (middle), a transient moment of $3 \times 10^{-5}\ \mu_B$ per Cu atom was detected using XMCD with left- (σ^-) and right- (σ^+) circularly polarized x-rays (bottom) [2]. Right: Pure spin currents are created by the precession of spins in a ferromagnet and transferred into adjacent non-magnetic metal layer (top). This "pumping" of spins has been detected using XMCD in a NiFe/Cu/CuMn/Cu/Co multilayer as an alternating XMCD signal (bottom) [3].

Broader Scientific Impact

ALS-U's ability to directly detect spin currents across interfaces in multilayered structures and at edges of nanoscale devices will provide the detailed understanding of a broad range of spin transport phenomena lacking today and crucial for the development of powerful spintronic applications. In the future, it will be critical to study spin injection efficiencies over a broad range of materials under widely different conditions. This will allow researchers at ALS-U to successfully bridge the gap between fundamental proof-of-principle research and solutions to challenges in applied research on the nanoscale.

References

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[2] R. Kukreja et al., *Phys. Rev. Lett.* **115**, 096601 (2015).
[3] J. Li et al., *Phys. Rev. Lett.* **117**, 076602 (2016).

3.1.2 Ionic Control of Functional Properties

Challenges:	Nano-objects	Interfaces	Flows
Techniques:	Nanoprobes	Coherent Imaging	

Scientific Opportunity

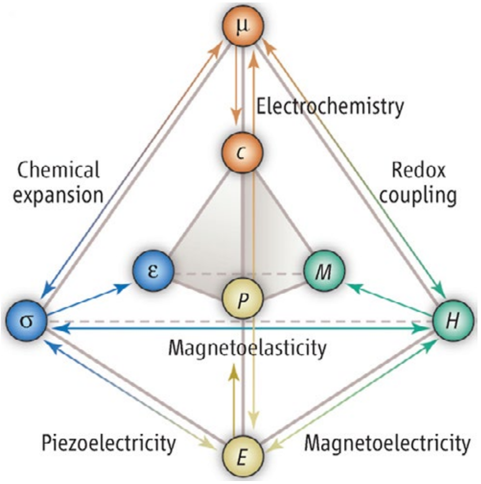

Figure 3.1.4. The usual control parameters for tuning functionality are electric field, E, which controls the polarization, P; magnetic field, H, which controls the magnetization, M; and stress, σ, which controls strain, ε. The chemical potential, μ, captures functionalities driven by mobile ions and defects described by the concentration of the mobile species, c [1].

The particular sensitivity of the electronic, magnetic, and optical properties of transition metal oxides to composition, doping, and structuring makes them prime candidates for diverse applications in sensor and electronic technologies. In some cases, functionality may be actively controlled through external parameters such as magnetic and electric fields (Figure 3.1.4). Very recently, induced ionic motion has emerged as an exciting new opportunity for tuning material properties such as magnetization [2], conductivity [3], and even crystal structure [4]. In particular, devices based on chemically or electrically induced oxygen migration have the potential to provide nanoscale control of nearly every aspect of a material. The ultralow power requirements, stability, and reversibility of oxygen-based ionic devices suggest they will be the basis of many novel architectures in the coming decades.

Nanoscale structure and heterogeneity play a critical role in device performance, determining reversibility and switching speeds. By understanding the elementary, nanoscale mechanisms of solid-state electrochemical processes, we can pave the way for knowledge-driven design and optimization of materials. This goal in turn necessitates capturing local electronic, magnetic, and structural parameters, i.e., element-specific information about valence state, orbital occupation, and magnetic moment and their interplay with lattice distortions. A “dream experiment” would be to perform plan-view and cross-sectional soft x-ray spectromicroscopy on these materials to understand and control oxygen-migration-induced heterogeneity at the nanometer length scale under the application of the gate bias.

Importance of ALS-U

Doped perovskite oxides, $ABO_{3-\delta}$, provide ideal material systems for exploiting electric-field-induced oxidation and reduction as a means to control functional properties since their electronic, magnetic, and optical properties are all strongly dependent on δ. Devices using ionic conductors (e.g., Gd or GdO_x) as “ionic gates” are now being tested to demonstrate oxygen insertion/removal from perovskite channel materials. However, definitive measurements of changes in the oxygen concentration, electronic state of the *B*-site cation, and magnetic/orbital behavior within the perovskite layer all require a local spectroscopic probe with nanometer spatial resolution. In particular, oxygen-deficient perovskites are highly susceptible to magnetoelectronic phase separation, which is expected to play a critical role in device performance. This nanoscale heterogeneity is almost impossible to characterize in sufficient detail with today’s technology. ALS-U will make Fresnel zone-plate focusing dramatically more efficient and allow us to image heterogeneity associated with small changes in x-ray absorption due to ion migration, leading, for instance, to different local structures such as perovskite and Brownmillerite (Figure 3.1.5). Ptychography will provide even higher spatial resolution.

Another opportunity for nanoprobe spectroscopy is to measure the evolution of composition and electronic behavior in oxide heterostructures as they undergo topotactic reactions. Two examples of recently explored post-growth reactions are fluorination to convert $ABO_{2.5}$ to ABO_2F [3] and extreme reduction to convert ABO_3 to $ABO_{2.5}$ [5]. While the feasibility of both of these reactions has been demonstrated, there is limited understanding of the reaction mechanisms and diffusion behavior throughout the process. Scanning nanoprobe x-ray spectroscopy, reflectivity/diffraction, and ptychography during reactions will probe the depth dependence of elemental composition and *B*-site valence of a sample as a function of time. This will elucidate reaction processes, providing quantitative information on the insertion and removal of different atomic species and their impact on material properties.

So far, electric-field control of phase transformations has made use of the mobility of a single ionic species (e.g., O^{2-}, H^+, F^-, etc.). Ultimately, we can imagine the electric-field control of dual-ion phase transformations, e.g., with insertion and extraction of two ion species, such as O^{2-} and H^+, enabling reversible phase transformation among ***three*** or more phases with distinct functionalities.

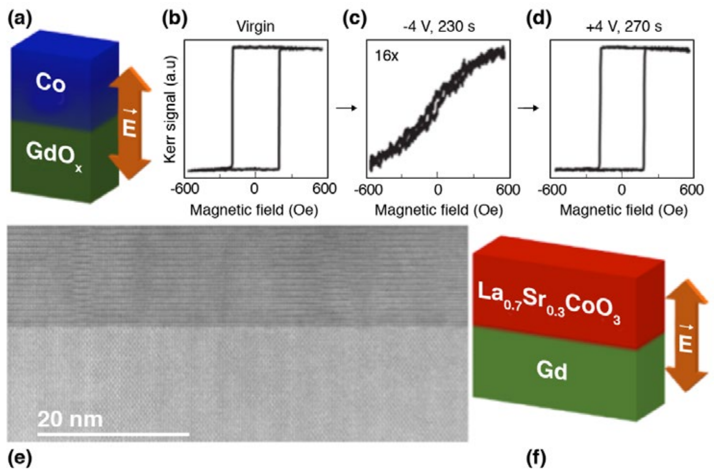

Figure 3.1.5. Top: Device schematics and voltage control of magnetic anisotropy in a Co/GdO_x layered structure [2]. Hysteresis loops showing the device in its original state (left), after applying a voltage V_g=−4 V for 230 s (middle), and after applying V_g=+4 V for 270 s (right), returning the system to its original state. Bottom: STEM image of Gd-reduced $La_{0.7}Sr_{0.3}CoO_3$ showing heterogeneity on the 5-nm scale with both perovskite and induced Brownmillerite structures [4]. Magnetic and electronic properties are expected to be similarly heterogeneous.

Broader Scientific Impact

Soft x-ray nanoprobe spectroscopy enabled by ALS-U is unique in its ability to probe electronic, magnetic, and orbital information with element specificity in a non-destructive manner and in the presence of external fields (in situ measurements). The ability to gather high-quality 2D and 3D maps of spectroscopic information with 1–10 nm resolution at ALS-U will have tremendous impact on our understanding of phase transitions and separations, topotactic reactions, and ionic motion. Spectroscopic studies on this length scale provide the information needed to “close the feedback loop” in creating designed materials with switchable functionality.

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3.1.3 Enabling Antiferromagnetic Spintronics

Challenges:	Nano-objects	Interfaces	Flows
Techniques:	Nanoprobes	Coherent Imaging	Interferometry

Scientific Opportunity

Antiferromagnetic (AFM) materials are critical to emerging spintronic applications, enabling information storage with much higher density and faster speed. In AFM materials, the direction of the magnetic moment of each atom alternates between adjacent atomic sites (Figure 3.1.6). The resulting zero net magnetization means there is no stray field, which makes their magnetism invisible on the outside. Still, AFM materials form domains with spin axes aligned along equivalent crystallographic directions. The main driving force for this domain formation is lowering the system energy due to magnetostriction and lattice distortions, i.e., the interplay between magnetic and structural degrees of freedom. As in ferromagnets, information could be stored in AFM domains. However, since the domains have no stray field, information stored in an AFM “bit” will not magnetically affect its neighbors no matter how densely the elements are arranged, and information stored in AFM domains is insensitive to external magnetic fields. The intrinsic high frequencies of AFM

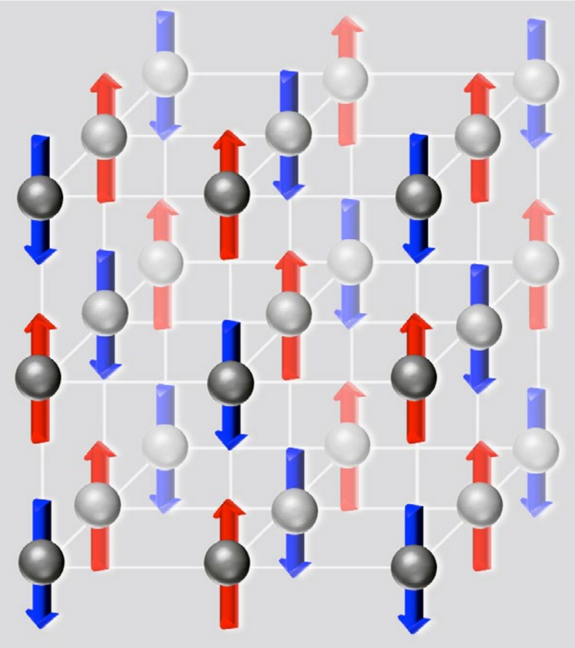

Figure 3.1.6. Developing antiferromagnetic materials for spintronic applications will enable information storage with much higher density, faster speed, and inerasable by high magnetic fields.

dynamics are another property that makes antiferromagnets distinct from ferromagnets and attractive for new spintronic devices. The recent observation of room-temperature electrical switching between stable spin configurations in AFM CuMnAs thin films [1] and electrical read-out based on AFM anisotropic magnetoresistance allow storage in AFM spintronic devices. Remarkably, antiferromagnetism, unlike ferromagnetism, can coexist with Dirac quasiparticles in the electronic structure. An entirely new research front has arisen based on the intertwined fields of antiferromagnetism (Nobel Prize 1970), spintronics (Nobel Prize 2007), Dirac quasiparticles (Nobel Prize 2010), and topology in condensed matter physics (Nobel Prize 2016).

A fundamental understanding of AFM domain behavior will be vital to delivering the promise of AFM spintronics. This is directly analogous to the situation over the past decades for nanoscale ferromagnetism, which has kept it one of the most active and intriguing areas of fundamental and applied research. Soft x-ray microscopy is the only imaging tool that provides AFM contrast with nanometer spatial resolution that is well matched to the heterogeneity of AFM spin textures. The dramatically enhanced nanoscale imaging and nanoprobe spectroscopy capabilities enabled by ALS-U will allow characterizing, understanding, and ultimately controlling intriguing properties of AFM nano-heterostructures.

Importance of ALS-U

Today, images of AFM domain structures are typically obtained using photoemission electron microscopy (PEEM) with XMLD contrast. This combination monitors the spatial distribution of photoelectrons emitted from a sample surface illuminated with variable linearly polarized soft x-rays (Figure 3.1.7). However, PEEM is incompatible with external magnetic fields, has a probing depth limited to the top few nanometers of the sample, has a fixed angle of x-ray incidence to the sample, and provides a spatial resolution of typically only 30 nm.

The very high brightness provided by ALS-U will revolutionize AFM domain imaging. Until now, systems studied with scanning x-ray microscopy (SXM) have predominantly been thin films that are not epitaxial but rather are free standing or supported by thin membranes that are transparent to soft x-rays. For AFM materials, the interplay between atomic and spin structure determines the magnetic domain configuration, and therefore the study of epitaxial systems is crucial. Epitaxially grown AFM thin films and multilayers, however, are generally deposited on single crystalline substrates such as MgO, $LaAlO_3$, and $SrTiO_3$, which serve as templates for the film and ensure well-defined atomic arrangements. Although these substrates are impenetrable by soft x-rays, a team at ALS recently demonstrated that such substrates are in fact efficient converters of soft x-rays to visible light. Detecting visible luminescence from the substrate as a function of position of the x-ray nanoprobe turns a SXM into a universal tool for characterizing AFM epitaxial thin film systems with nanometer spatial resolution. The probe depth in this detection mode is limited only by the soft x-ray absorption length and allows the study of AFM domains, domain walls, and complex spin textures in thin films, at their interfaces and in multilayered nano-heterostructures not accessible today. Since photons (and not electrons) are employed, in situ operation in applied fields is possible. The new luminescence detection mode combined with applied magnetic and electric fields, variable temperature capabilities, and flexible experimental geometries will provide a uniquely powerful SXM for the study of AFM domains at ALS-U.

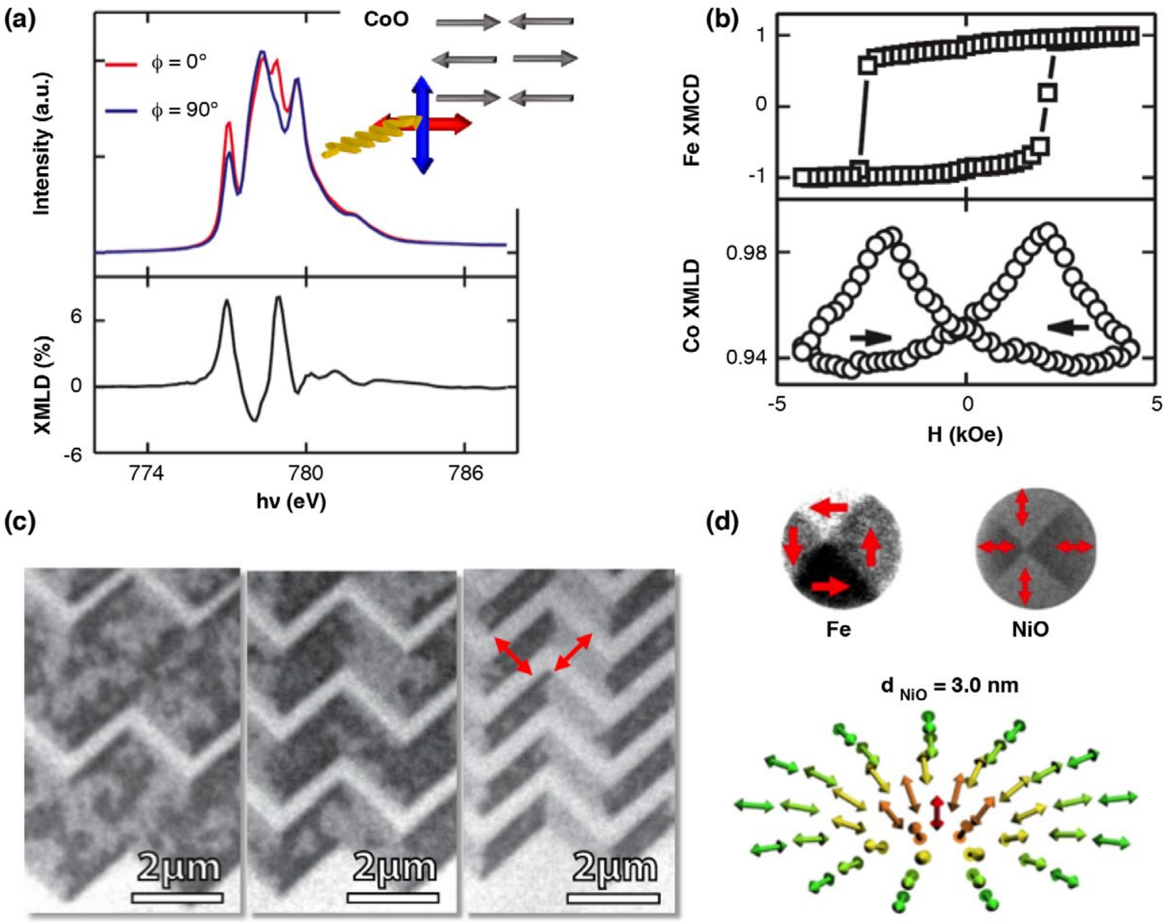

Figure 3.1.7. Examples of AFM phenomena characterized with soft x-ray spectroscopy and microscopy. a) X-ray absorption spectra of Co L_3-edge in CoO taken at two orthogonal linear polarizations (ϕ= 0° and 90°) relative to the AFM spin axis. The XMLD signal, i.e., the normalized difference (below) can be employed to image AFM domains [2]. b) Hysteresis loops of FM Fe and AFM CoO, respectively, for a Fe/CoO bilayer measured by monitoring the Fe XMCD and Co XMLD as a function of applied field [3]. An external magnetic field reorients the FM moments and then through interfacial coupling reorients the AFM moments. c) XMLD-PEEM images of AFM domains in zigzag patterns defined in $LaFeO_3$, indicating the impact of nanoscale pattering on the AFM domain structure [4]. d) Divergent vortices in a Fe/NiO bilayer imaged using Fe XMCD and Ni XMLD, respectively [2].

Broader Scientific Impact

SXM optimized for imaging AFM systems will elucidate the interplay between magnetic, electronic, and atomic structure in AFM materials ranging from simple transition metal oxides (e.g., NiO, CoO), complex oxides (e.g., $BiFeO_3$), semiconductors (e.g., MnTe), as well as metals (e.g., MnIr). By also utilizing circular dichroism that is sensitive to FM ordering, we can study the relationship between FM and AFM order, which is important for exchange coupling, colossal magnetoresistance, and FM domain walls in AFM materials.

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3.1.4 Understanding Fluctuations in Spin Materials

Challenges:	Entropy	Flows
Techniques:	Coherent Scattering	

Scientific Opportunity

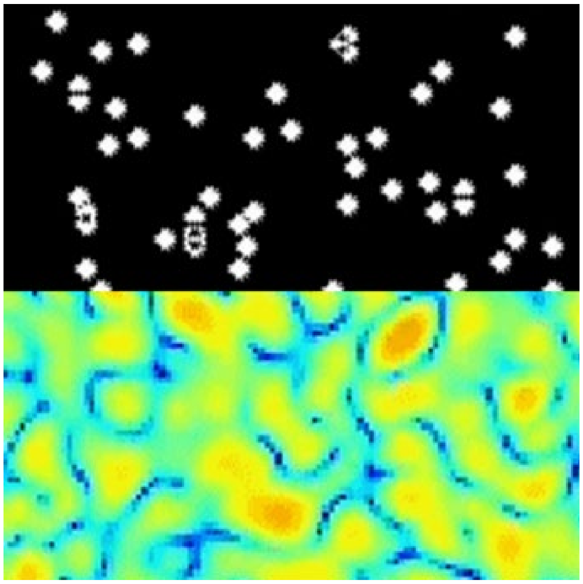

Figure 3.1.8. Any arrangement of scatterers, such as particles (top) or domains, produces a characteristic "speckle" pattern (bottom) when it scatters coherent x-rays [1]. If the arrangement of scatterers changes due to thermal fluctuations, applied fields, or external excitations, the speckle pattern changes. Comparing speckle patterns using suitable correlation techniques provides a quantitative measure of the underlying dynamics and heterogeneity. ALS-U will allow using this technique for the study of processes on nanosecond time scales and nanometer length scales.

Nanoscale heterogeneity associated with ordered phases is crucial for material and device functionality. Within compositionally homogeneous materials, nanoscale heterogeneity can result from the spontaneous formation of regions with distinct atomic, electronic, and/or magnetic order, and indicates the coexistence of energetically degenerate, competing phases. Domains with spin axes pointing along equivalent crystallographic directions in ferromagnetic and antiferromagnetic materials are well-known examples. Coexisting conducting and insulating phases can occur near metal–insulator transitions; colossal magnetoresistance can emerge where ferromagnetic and antiferromagnetic domains compete; and charge-ordered and superconducting regions are present simultaneously in materials exhibiting high-temperature superconductivity.

Nanoscale heterogeneity is connected to important spontaneous dynamics such as domain fluctuations, domain-wall motion, sliding, and avalanche dynamics. Domain-wall dynamics play a crucial role in magnetization reversal processes, as thermally activated domain-wall motions determine the lifetime of magnetically stored information. Skyrmion topology and domain-wall chirality are especially intriguing properties to improve stability against fluctuations. Moreover, the energy landscape connected with intermittent dynamics of domains and heterogeneity is closely related to local defects and pinning centers, adding further intricacy to the science [2].

Although nanoscale heterogeneity has been studied in detail for decades in quasi-static configurations using microscopy and scattering techniques, our understanding of its spontaneous dynamics and fluctuations is in the very early stages. The very high coherent flux provided by ALS-U will allow x-ray photon correlation spectroscopy (XPCS) to be employed in the study of nanoscale fluctuations with time resolutions down to nanoseconds, boosting our insights into equilibrium dynamics and the impact of intermittent dynamics on magnetic/spin technologies.

Importance of ALS-U

XPCS is a coherent x-ray scattering technique that probes collective dynamics based on the observation of fluctuating speckle patterns (Figure 3.1.8). The measured intensity correlations in reciprocal space are directly related to the fluctuations of the relevant order parameters in real space. X-rays provide elemental, electronic, orbital, and magnetic contrast through resonant excitations in the soft x-ray range, allowing independent access to relevant charge, orbital, and spin order parameters with element specificity. Speckle at different distances from the diffraction peak center are related to real-space domains on different length scales. Therefore, XPCS offers the possibility to access a wide range of length scales down to nanometer resolution (Figure 3.1.9). Speckle fluctuations may be tracked as a function of time (XPCS [3]) and as a function of external parameters such as temperature, electric/magnetic fields, or strain (speckle metrology). XPCS characterizes the entire volume determined by the x-ray spot size and x-ray penetration depth, ensuring sufficient ensemble averaging. The information of charge, orbital, and spin order across the wide range of length and time scales can then be correlated and provides a detailed picture of the energy landscape and interactions in the materials.

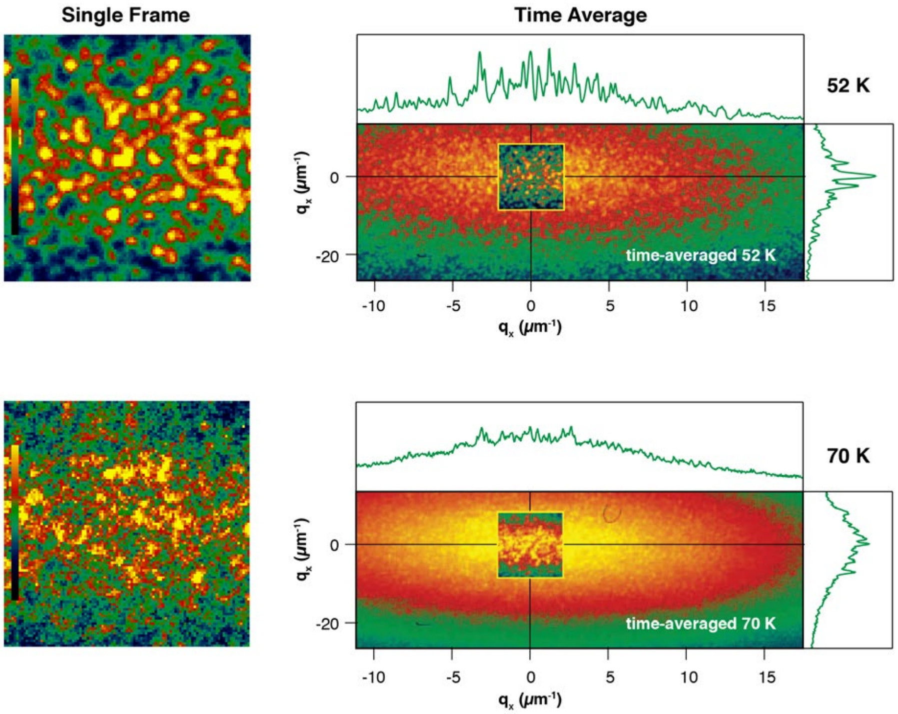

Figure 3.1.9. Magnetic fluctuations in holmium. Scattering of coherent radiation causes a speckle pattern reflecting the magnetic domain structure of the illuminated spot. At T = 52 K (top) the average pattern is equal to that of a single frame, indicating that no fluctuations occur. At T = 70 K (bottom) the average pattern is smoother than individual frames, i.e., domain walls fluctuate and remaining static speckles indicate non-fluctuating parts in the domain pattern. This behavior is prototypical for systems in which domain walls are pinned in the potential landscape formed by disorder [3].

The key figure-of-merit for XPCS experiments is the shortest timescale accessible, which scales with the inverse square of the average coherent flux. At present XPCS is suited for probing slow (10^{-2}–10^{4} s), spontaneous nanoscale dynamics not accessible by other techniques (e.g., dynamic light scattering or inelastic x-ray scattering). XPCS has provided insight into glassy, collective, and jamming behaviors [4]. With the increase in coherence at ALS-U, we will have access to timescales a factor of up to 10^{6} faster than currently available, meaning we can routinely measure dynamics with timescales in the range of 10–100 ns or even less. Advanced detectors may allow the time window to be further extended down to tens of picoseconds.

Broader Scientific Impact

Studying fluctuations and other collective phenomena over a wide range of length and timescales with XPCS at ALS-U will enhance our understanding of the energetics involved in formation of complex spin and quantum phases in correlated matter. This information will allow us to manipulate order parameters, engineer domain structures, and control fluctuations to obtain desired functionality.

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3.1.5 Imaging the Dynamics of Topological Spin Structures

Challenges:	Nano-objects	Flows	Confined Spaces
Techniques:	Nanoprobes	Interferometry	

Scientific Opportunity

Currently, the most powerful neuromorphic complementary metal–oxide–semiconductor (CMOS) element requires 10,000 times more power than its biological equivalent, as highlighted in a recent DOE BES report on neuromorphic computing [1]. Spintronic materials are candidates for future ultralow-power devices [2] and combine the non-volatility of magnetic storage with the speed and direct access of silicon electronics. Recent research has discovered efficient methods to generate and transport spin patterns and currents. Spin-transfer torque and the spin-orbit torque rely on the injection of spin currents across an interface from either a ferromagnet or a material with a large spin–orbit interaction [3,4]. Both mechanisms have been used successfully to manipulate nanoscale magnetism, but techniques that are capable of rapidly detecting and imaging spin currents and spin accumulation are scarce. Lossless lateral transport of spin information is possible via ballistic or diffusive spin currents, for example, in materials with low spin scattering, such as graphene, or by using spin solitons, like magnetic skyrmions, which are exceptionally stable topological magnetic structures (Figure 3.1.10). Material properties, pattern geometries, and manipulation techniques that are conducive to the creation and preservation of skyrmions are very actively researched [5,6].

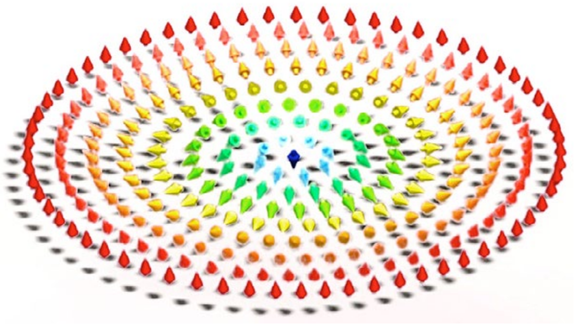

Figure 3.1.10. Micromagnetic model of a ~10-nm-sized skyrmion spin spiral.

To determine skyrmion topology, creation, and interactions will require contactless 3D metrology with a temporal resolution that allows us to determine morphological changes in real time. We will also need to detect spin currents and watch how they are generated at interfaces, travel and decay within a channel, and interact with a target skyrmion. Together, these parameters define the boundaries in space, time, and sensitivity that next-generation magnetic imaging techniques need to reach: 5 nm in spatial resolution (the size of a skyrmion core), down to milliseconds, microseconds, or even nanoseconds in temporal resolution, and 0.001% in magnetic sensitivity (the magnitude of the polarization of a spin current).

Importance of ALS-U

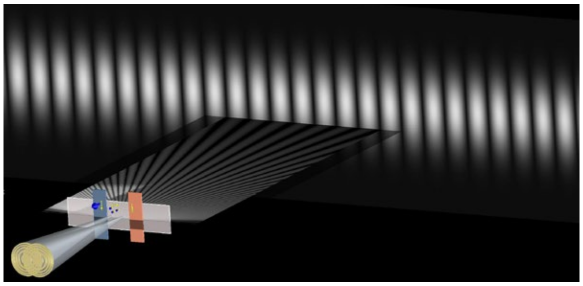

Figure 3.1.11. Simulation of the interferometric detection of spin currents in a nanoscale spin channel using a twin zone-plate x-ray interferometer. (Courtesy: A. Scholl)

Soft x-rays are a particularly useful magnetic probe because of their spatial, spin, and temporal sensitivity. The full coherence of soft x-rays from ALS-U will be used to: 1) detect the minute spin polarization near an interface resulting from spin injection or spin-orbit torque and 2) image the 3D structure of skyrmions and skyrmion lattices in real time. These could be achieved using an interferometric nanoprobe setup (Figure 3.1.11). Two coherent nanofocused beams interact with the sample and a reference material, and differential changes in spin polarization are detected with extreme sensitivity by recording the resulting fringe pattern on a 2D detector. Simulations show that the required sensitivity to detect spin accumulation can be readily achieved using the coherent x-ray flux of ALS-U.

High-speed, real-space images of 2D and 3D topological structures could be acquired using Fourier-transform holography [7]. Here, a coherent wave front scattered from a sample creates an interference pattern. One part of the wave front interacts with the sample, for example, a skyrmion lattice, and the sample properties and morphology are encoded in the interference with a reference beam (Figure 3.1.12). The high coherent flux of ALS-U will allow recording of full-frame patterns at speeds high enough to study dynamics. As a full-field lensless imaging method, this technique will be ideal for rapid imaging of extended structures with down to diffraction-limited spatial resolution.

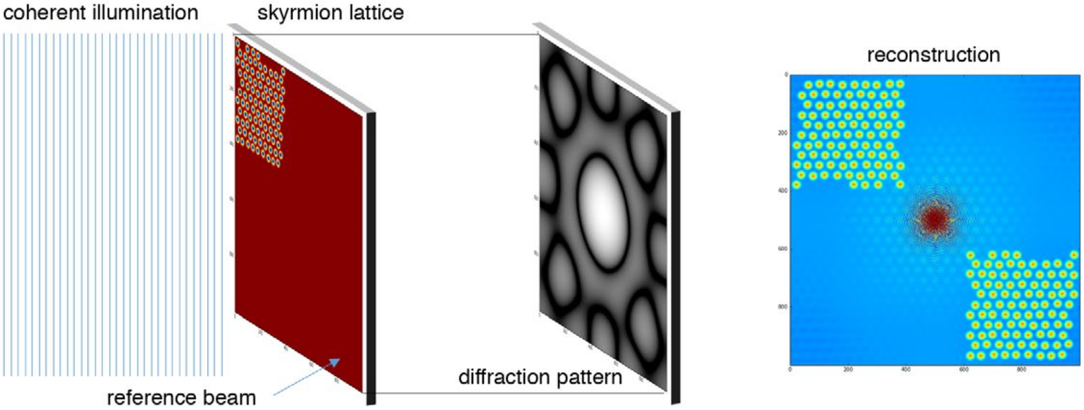

Figure 3.1.12. Simulated Fourier-transform holography reconstruction of a magnetic skyrmion lattice using a fully coherent x-ray source. (Courtesy: A. Scholl)

Broader Scientific Impact

The combination of ALS-U imaging with interferometric detection presents opportunities to probe weak magnetic signals (e.g., spin currents and accumulation, antiferromagnetic structures, and diamagnetic currents in superconductors) as well dilute systems (e.g., ion currents in shales and frozen neurons). This new class of science will be enabled and revolutionized by ALS-U.

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3.1.6 Deciphering the Cuprate Zoo

Challenges: Nano-objects Interfaces
Techniques: Nanoprobes

Scientific Opportunity

The observance of high-temperature superconductivity (HTS) in the cuprate family will likely still be an unsolved mystery at the onset of ALS-U experiments. HTS emerges from the interplay of many degrees of freedom—for instance, charge, lattice, and spin—resulting in inhomogeneous properties on a length scale (5–15 nm) that is terribly difficult to handle theoretically, and furthermore makes integrative probes like transport, magnetotransport, optical response, and (conventional) ARPES difficult to interpret. Numerous phases, such as antiferromagnetic, charge-ordered, pseudo-gapped, and "strange metal," have been observed, but the relationship between these phenomena, HTS, and this inhomogeneity remains unclear.

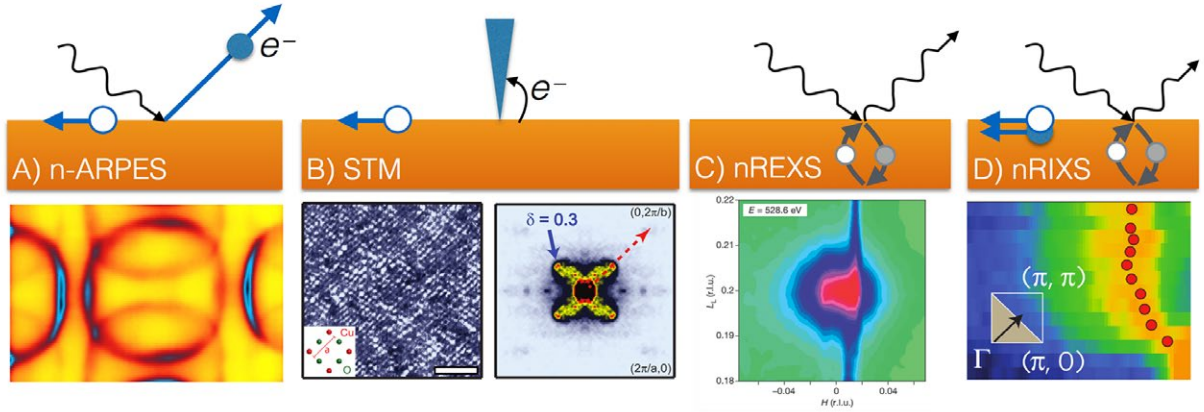

Figure 3.1.13. The nano-toolbox for deciphering cuprate physics. At ALS-U, we will study inhomogeneous cuprate high-temperature superconductors with a combination of: a) nanoARPES for studying momentum-resolved charged excitations [2]; b) STM, for atomic structure (left) and momentum-transfer imaging (right) [3]; c) nanoREXS, for chemically resolved symmetry of states [4]; and d) nanoRIXS, for studying momentum-resolved neutral excitation [5].

Of the entire HTS cuprate family (36 members were known already in 1995 [1]), only a few have been studied with powerful soft x-ray tools, even though some of them, such as $(EuCe)_2(BaEu)_2Cu_3O_{10}$, have respectable critical temperatures (e.g., T_c = 43 K). Some exist in fine granular form, presently inaccessible to bulk and surface probes, while others do not yield large facets upon cleaving. Of the hole-doped families of HTS cuprates studied most often, bismuth strontium calcium copper oxide (BSCCO) is most cleavable, with accessible, flat CuO_2 planes, and is therefore most commonly examined with ARPES/scanning tunneling microscopy (STM), while the others are more suitable for magnetotransport and neutron scattering. Meanwhile, electron-doped materials have both similarities to and differences from hole-doped materials. When results are compared from these diverse combinations of methods and materials, it is difficult to isolate properties that are intrinsic to all HTS from those that are unique to a particular compound.

Importance of ALS-U

ALS-U will provide the capability to probe the smallest crystals and facets, so that a survey of the entire cuprate family can be conducted at multiple length and energy scales. A soft-to-tender x-ray beamline with 5–15 nm spatial resolution will offer four complementary techniques (Figure 3.1.13): nanoARPES, which probes the spectral function $A(\mathbf{k},\omega)$ of charged excitations; STM, which measures the real-space spectral function $A(\mathbf{r},\omega)$; nano-resonant elastic x-ray scattering (nanoREXS), which measures the chemically resolved weight of unoccupied states in momentum space; and nanoRIXS, which measures the spectral function of neutral excitations such as spinons, excitons, and orbitons. NanoREXS will exploit the coherent properties of ALS-U by collecting “speckle” patterns with spatial distribution of symmetry- and energy-related states at a maximum resolution limited by the x-ray wavelength, or a few unit cells of the cuprate lattice. To truly correlate structure and electronic properties, the techniques should probe the same spot on the same samples, meaning the soft x-ray endstations for these techniques should be connected through ultrahigh vacuum (UHV) sample transfer to the STM and sample growth/characterization facilities, with nanoscale sample registry between the various tools.

Broader Scientific Impact

Many material classes are initially discovered in polycrystalline or power form, for example, using a probe of bulk magnetization. As with the cuprates, a fairly small number of these new materials can be screened with powerful soft x-ray techniques, which to date have generally played a major role in understanding reasonably well-developed material classes. Even without deploying a formal mechanism for combinatoric analysis, the pace of discovering materials with interesting spin, quantum, and topological properties can be significantly accelerated with ALS-U tools.

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3.1.7 ARPES of Individual Nano-Objects

Challenges: Nano-objects | Flows | Confined Spaces
Techniques: Nanoprobes | Coherent Imaging

Scientific Opportunity

The many-body interactions that determine emergent material properties are strongly wavelength dependent, suggesting that they can be manipulated by engineering the morphology of sample structures on the nano- to mesoscale. By doing so, we can hope to tune the interactions and control the ground-state properties of materials. Example studies are the optimization of thermoelectrics by tuning the coupling of electrons to vibrations in materials at phononic length scales; tuning the optical properties of laterally structured 2D chalcogenides; patterning materials to control chemical reactivity; and probing the electronic structure in individual domains of "twisted" bilayer materials such as bilayer graphene or arbitrary combinations of 2D chalcogenides.

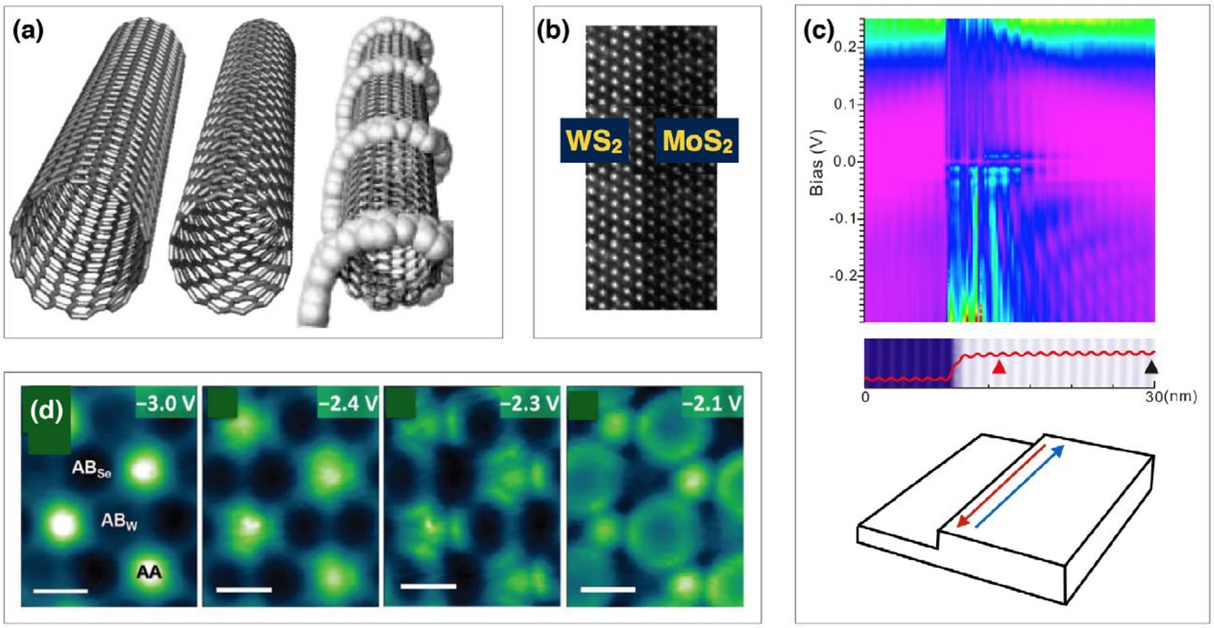

Figure 3.1.14. Examples of nano-objects that can be studied at <10-nm resolution with nanoARPES at ALS-U: a) Conductive carbon nanotubes of various helicities or functionalizations [1]; b) Grain boundaries in 2D materials such as metal chalcogenides (figure adapted from [2]); c) Confined states at the edges of 2D topological insulators such as $ZrTe_5$ [3]; d) Individual AA, AB aligned regions in moiré lattices of twisted materials [4].

Importance of ALS-U

Probing such nano-objects requires the smallest possible spot size, but the zone-plate optics used to focus the light are heavily constrained by the requirement that the sample surface must have free line of sight to the electron detector in the near-normal direction. Thus, nanoARPES is constrained to spatial resolutions on the order of a few times the x-ray wavelength. To reach a resolution of a few nanometers, one strategy is to increase the photon energy, which can only be done reasonably at ALS-U because of the greatly increased coherent flux (100–1000x) at shorter wavelengths. At a few hundred electron volts, we can reach probe beams on the order of 10 nm or smaller without compromising the ability to collect nanoARPES with sensitivity to electrons near normal emission. A second strategy is to use sufficiently thin samples and supports, in a transmission geometry with a downstream electron analyzer, so that the maximal numerical aperture of x-ray optics can be employed. This would allow <10 nm direct focusing at ~100 eV photon energy, which is nearly optimal for ARPES.

Broader Scientific Impact

A prototypical experiment is the measurement of the ARPES spectral function of an isolated, 1D object of molecular width. Examples include single metallic nanotubes, which are expected to have Luttinger liquid (spin-charge-separation) ground state; edge states of 2D topological insulators; and states at the boundaries between terraces at surfaces. Studying such 1D objects is feasible with spot sizes much larger than the wire width, provided that the wires are perfectly straight and span the entire probe beam, and if there is a sufficiently high signal-to-background noise ratio (typically >5000, which is possible only if there is a lack of stray electrons from nearby surfaces). This condition can be met at ALS for special cases, such as free-hanging, single-wall carbon nanotubes but is not realistic for most 1D objects on solid supports (Figure 3.1.14a). But at ALS-U, the spot size can be reduced to a few wire widths, and therefore embedded 1D materials, such as grain boundaries, confined states at edges of 2D topological insulators (Figures 3.1.14b and c), superconducting interfaces between oxides (in side-on geometry), and individual nanotubes in upright "forests" or layered "spaghetti" will become accessible. Even more difficult experiments, such as directly measuring the properties of embedded "zero-dimensional" structures, such as domains of moiré lattices in twisted bilayers (Figure 3.1.14d) or heterogeneous electronic structures in high-T_c cuprates, also become possible.

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3.1.8 Coherent NanoARPES

Challenges:	Nano-objects	Flows	Confined Spaces
Techniques:	Nanoprobes	Coherent Imaging	

Scientific Opportunity

The combination of fully transversely coherent soft x-rays at ALS-U and focused beams with special tailored properties can enable novel probes of electronic matter. With nano-diffractive optics, the amplitude and phase of soft x-ray wave fronts can be tailored with great flexibility, and this flexibility can be leveraged to measure the coherence and topology of the electron and spin wave functions being probed with nanoARPES and other soft x-ray nanoprobe spectroscopies.

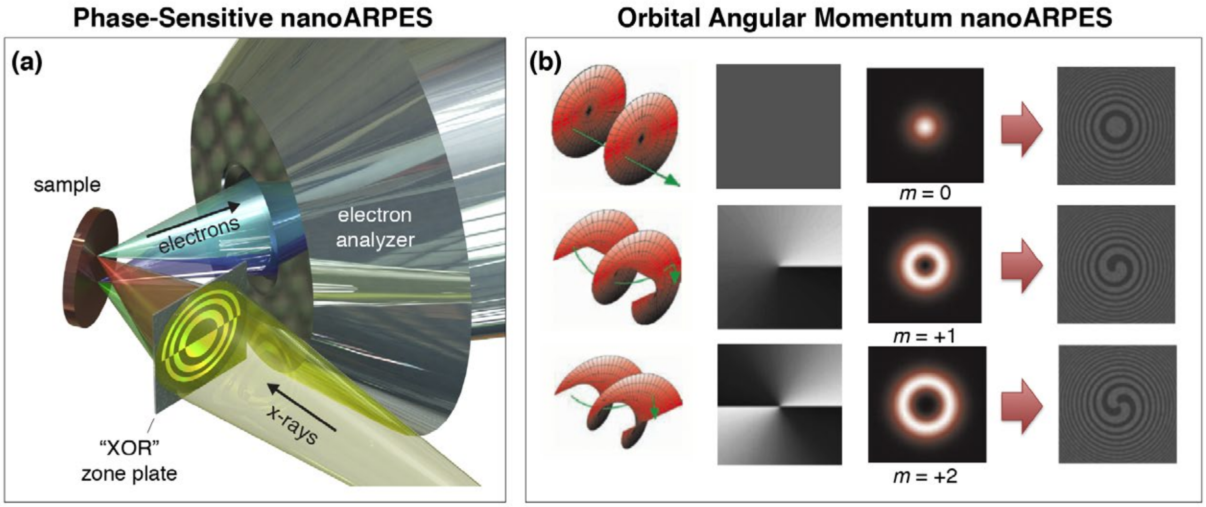

Figure 3.1.15. Sculpted focused photon beams can be used as nanoprobes for specialized nanoARPES or other nanoprobe experiments. a) dual-focused beams generated by XOR zone plates can be used as a probe of local electronic phase changes; b) spiral zone plates can induce a helical photon wave front in the x-ray beam, which corresponds to orbital angular momentum with helicities ±1, ±2, … for novel dichroic measurements. (Courtesy: C. Jozwiak)

Importance of ALS-U

Figure 3.1.15a shows an experimental arrangement that is sensitive to nanoscale changes in the phase of electronic wave functions. A special "XOR"-patterned Fresnel zone plate can be produced that creates two focal spots separated by a distance *d*, chosen to be less than the relevant electronic coherence length of the sample. This coherence length depends strongly on the material and its heterogeneity. The experiment requires that the electronic phase coherence length exceed the spot separation of tens of nanometers—a requirement that is met by many metals, high-T_c superconductors, and 2D materials. This length can be estimated by the inverse width of ARPES momentum distribution curves. The operating principle is readily calculated: If the coherent beams simultaneously land on regions of identical phase, there is no difference in the nanoARPES signal compared to a single-spot probe. But when the beams straddle a boundary or imperfection, such as a step edge between terraces that induces a phase change in the electronic wave function, the signal from the terraces can interfere, and it can be shown that this will cause oscillations in the ARPES yield as the boundary is scanned through the beams.

Figure 3.1.15b shows another application of wave-front shaping, whereby the light properties can be sculpted by using spiral zone plates. These can impart helical phase fronts that carry orbital angular momentum with values $\pm\hbar$, $\pm2\hbar$, …) to the beam. This is in contrast to ordinary circular polarization, which is a spin-like helicity restricted to angular momentum values of $\pm\frac{1}{2}\hbar$. Therefore, the control of orbital angular momentum offers new possibilities for experiments with non-dipole transitions (e.g., s → d levels) that are not possible with normal dipole selection rules, with applications to resonant photoemission, valence band dichroism, RIXS/REXS, and absorption. Twisted beams are also expected to couple to mesoscopic structures such as persistent currents, which occur in both normal and superconducting materials from the micro- to the nanoscale; chiral currents at the edges of 2D topological insulators; and topological spin structures such as skyrmions [1].

Broader Scientific Impact

Wave-front control is hardly a new concept in the optical domain, where coherent laser sources have been available for half a century, but in the x-ray regime it is a new and exciting prospect. It is enabled by the full transverse coherence of ALS-U coupled to the flexibility developed in producing nano-diffractive optics over the past decades, and benefits significantly from the spatial and spectral sensitivities of soft x-ray spectroscopies. The above ideas are placed in the context of nanoARPES, but related approaches will be possible with other soft x-ray techniques like STXM, nanoXMCD, and nanoREXS. Also, ptychography remains a fairly new imaging technique, and the notion of wave-front shaping—to change sensitivities or to enhance the phase retrieval algorithms—is just starting.

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3.1.9 Spatial "Pump–Probe" Measurements

Challenges:	Nano-objects	Interfaces	Flows
Techniques:	Nanoprobes	Coherent Imaging	

Scientific Opportunity

Pump–probe measurements are a mainstay of many areas of optical science, but in most cases spatial information is not available or is only inferred by detailed analysis. Figure 3.1.16 shows a generalization of pump–probe experiments, incorporating spatial probing at ALS-U. By pumping with a laser or other source, thermal energy, carriers, or excitations generated at the pump site will be transported to a second region of interest, which is probed using a soft x-ray nanoprobe for the detection of photoelectrons or scattered phonons. This experiment will provide a statistical measure of externally driven motion at the nanoscale.

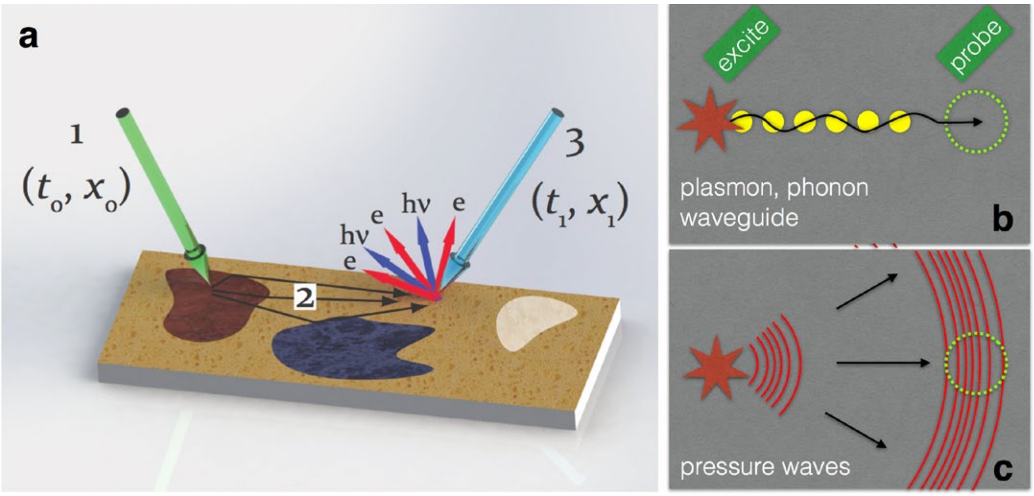

Figure 3.1.16. a) A generalization of the conventional "pump–probe" to consider both spatial and temporal separation of pump and probe beams. Green arrow = excitation at space-time (x_0, t_0), blue arrow = ALS-U focused beam at (x_1, t_1); b) A novel experiment in which a steady-state beam of plasmons or phonons is guided into an otherwise pristine sample region, which can be probed by nanoARPES or other nanoprobes. The waveguide properties and excitation wavelength are chosen to tune the plasmon/phonon wavelength to take apart the many-body interactions wavelength by wavelength; c) A novel experiment in which short pulse pumps may be used to excite pressure waves for studies of electronic matter at GPa pressure ranges [1]. (Courtesy: E. Rotenberg)

Importance of ALS-U

The high coherent power of ALS-U combined with advanced soft x-ray spectroscopies will make these novel spatial pump–probe experiments possible. Two practical examples are shown in Figure 3.1.16b and c. In panel b, which is performed in steady state, an optical or infrared laser is used to generate a coherent beam of plasmons, phonons, or other quasiparticles. A waveguide, which can be designed to select the wavelength of the excitation, conducts the beam to a region of interest, which is interrogated by nanoARPES, for example. In this way, we can unfold the electron–quasiparticle interaction in the probe region, wavelength by wavelength. At the same time, we can move the probe region to map the propagation of energetic excitations through the sample's morphological features. Figure 3.1.16c shows how a powerful laser pulse is used to generate a pressure wave. Remarkably, pressure waves up to 15 GPa have been generated in graphene in this way. Using this technique, the band structure as a function of pressure will be obtainable for the first time.

Broader Scientific Impact

These experiments are similar in spirit to transient grating and related measurements, which are pump–probe measurements that provide simultaneous spatial and temporal information. Like transient grating measurements, the experiment shown schematically in Figure 3.1.16 will measure space–time correlations, though with the addition of incisive soft x-ray spectroscopies, which can probe specific states and excitations. For this reason, such experiments are applicable to a very broad range of systems, e.g., exciton motion in semiconductors and photovoltaics, pair formation and breaking in superconductors, and measuring the response of skyrmions to spin currents.

The ideas in this section are presented primarily in the context of nanoARPES, but clearly other soft x-ray nanoprobe techniques could be performed in this spatially resolving pump–probe approach including STXM, nanoXMCD, and nanoRIXS.

Reference

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3.1.10 Beyond Combinatorics

Challenges:	Nano-objects	Interfaces	Entropy
Techniques:	Nanoprobes	Coherent Imaging	

Scientific Opportunity

High-throughput discovery paradigms are aimed at the fast determination and optimization of materials families through the adjustment of typically a small number of material parameters. For example, the Joint Center for Artificial Photosynthesis (JCAP) measures the photocatalytic properties of quaternary Ce-based alloys (Figure 3.1.17). Both sample growth and initial screening and characterization are obtained in a few seconds per sample. When a promising candidate is discovered, the sample can be analyzed in more depth, using such techniques as scanning tunneling microscopy, transmission electron microscopy, or today's ALS nanoprobes, to develop insight into the structure or fundamental causes of the functionality. Although these analytical techniques are 10^4 times slower than the original screening

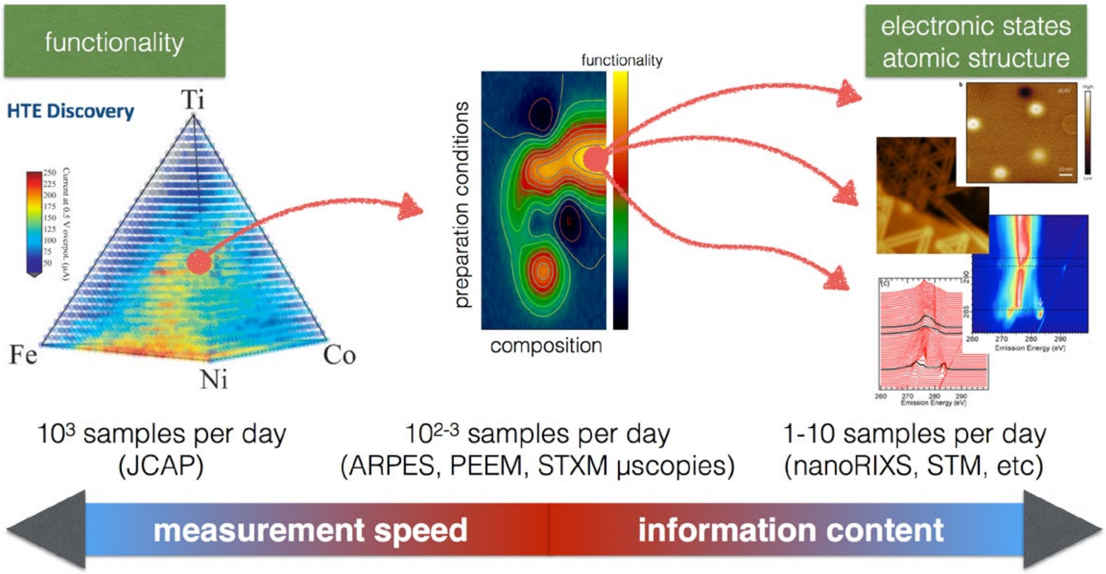

Figure 3.1.17. Phase-space microscopy as a tool for materials discovery and optimization. On the left, high throughput discovery programs such as at JCAP screen tens of thousands of samples in a day, grown by "3D printing" and quickly screened for functionality using integrative probes [1]. On the opposite extreme (right), much slower but information-rich spatially resolved techniques at ALS and elsewhere can be used to answer why a particular functionality arises [2-4]. ALS-U will offer an important "medium-throughput" technique for further optimizing and investigating the role of nanoscale phases (Courtesy: E. Rotenberg). For highest efficiency, and for clean surfaces, the sample growth should be integrated into a nanoprobe beamline.

technique, they yield far more information per sample and address why a particular functionality is strong by interpreting observed correlations between heterogeneity and function.

Importance of ALS-U

ALS-U will allow not only the nanoscale chemical and electronic characterization of these materials, but crucially the efficiency of these probes will be greatly increased, so that ALS-U nanoprobes can play a new, intermediate role in the discovery/automation process. In this role, the optimal sample stoichiometry can then be examined over a narrower range by growing macroscopic gradient samples, and, in addition, morphological variations can be examined by varying the preparation conditions in an orthogonal-gradient geometry (Figure 3.1.17b). At ALS-U, microARPES will be able to examine such samples at the rate of hundreds to thousands of probed spots per day (100–1000x faster than at present), producing maps of composition correlated to the quantum-mechanical properties tied to functionality. When the most promising regions are found, we can zoom in to each sample using nanoARPES and nanoRIXS to probe the nanoscale heterogeneity and its role in the functionality.

For the highest efficiency, a beamline outfitted for this technique will require a high degree of robotic automation, integrated sample preparation, and sufficient floor space for modular sample preparation elements so that the sample growth and functional characterizations can be configured for different projects.

Broader Scientific Impact

Practitioners of combinatoric synthesis understand that their success depends on the fidelity of information provided by their screening techniques coupled to the time it takes for those techniques to be applied and the results understood. ALS-U micro- and nanoprobe spectroscopies, combined with the ongoing process of vastly streamlining the data and analysis path, will make ideas like this a reality. Twenty years ago it took hours, at least, to calculate a simple x-ray absorption spectrum; today is takes less than a minute. The concepts expressed in this opportunity can be broadly applied, using many techniques and to a very broad range of systems.

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3.2 MULTISCALE CHEMICAL PROCESSES

Much of our understanding of diverse chemical processes, from catalysis and energy conversion to environmental transformation, is built on models deliberately designed to capture a limited number of aspects of the full system. This simplification is, in part, due to the need to first build an understanding of underlying fundamental phenomena. However, it is also a direct consequence of the inability of existing experimental tools to probe the relevant chemical processes within intrinsically heterogeneous, multiscale systems at the relevant length and time scales.

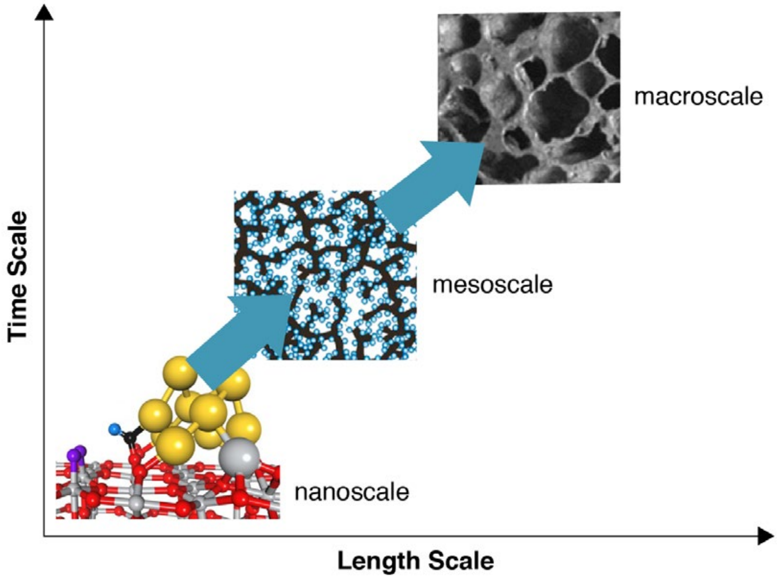

Figure 3.2.1. Schematic showing the broad range of length and time scales relevant in heterogeneous chemical catalysis. Bond breaking and forming processes occurring at the atomic length and ultrafast time scales are commonly linked to a mesoscale organization of catalytic centers controlling diffusion at longer length and time scales, which in turn are packaged into macroscopic porous material structures. The entire assembly is optimized, often by trial and error, for high efficiency and selectivity. ALS-U will provide several complementary experimental tools needed to probe chemical processes at scales that determine fundamental properties of diverse chemical systems.

Chemical and materials scientists increasingly realize that observing and modeling how processes work together across scales is essential to determine system function. Figure 3.2.1 could describe equally well batteries, fuel cells, hydrogen-storage materials, catalytic reactors, atmospheric aerosols, subsurface soil particles, or many other heterogeneous, functional chemical systems that are the subject of this section. This commonality is particularly apparent from nanometer to micron length scales and from nanosecond to second time scales, where chemical structure–function relationships determine, for example, the efficiency of a catalyst, the lifetime of a battery, and the capacity of a shale formation to sequester actinide waste or CO_2. Research communities focused on these problems all seek tools that probe these length and time scales with high chemical contrast and sensitivity.

The emerging synergy between the experimental and theoretical tools that probe the regions covered in Figure 3.2.1 will revolutionize how we think about complex, multistep chemical processes. These processes all occur across multidimensional free-energy landscapes that govern correlated atomic and molecular motion over multiple length and time scales. Controlling spontaneous, incoherently driven thermal processes across such landscapes presents a difficult inverse problem: How do we tailor a nanoscale structure of a reacting system and its temporal evolution to produce a desired free-energy landscape that supports a targeted chemical behavior? Achieving this feat requires a detailed understanding of structure–function relationships, with feedback and regulation over all of the relevant length and time scales.

Our vision is that a decade from now such extremely complex, though realistic, processes will be susceptible to in-situ, in-operando probing using new soft x-ray techniques enabled by ALS-U and described in Chapter 2. These techniques will reveal spatially resolved local chemistry, bonding, composition, and microstructure across a range of length scales in real time, allowing imaging of electronic and geometrical structure and probing of chemical kinetic processes. The ALS-U science opportunities described in this section provide only a small subset of the exciting possibilities that exist if this vision is realized.

The prominence of the ALS-U crosscutting challenges and the need for experimental tools summarized in Tables 1.1 and 2.1, respectively, are evident in this section. Many systems described in this section involve chemical reaction–diffusion processes in mesoscale, confined spaces: ion transport in nanoporous membranes, adsorption/absorption/reaction processes within aerosol droplets, precipitation/dissolution in mineral fractures, and catalysis on a functionalized nanoporous support material. Poorly defined interfacial regions determine the functional properties of all of these: the solid–electrolyte interface, the chemically active interface between an aerosol and its environment, and the region between a nucleated nanomaterial and its environment. Finally, these systems often involve complex correlations that operate over broad spatial and temporal scales, where evaluating entropic contributions to the free energy will be essential to developing predictive power.

3.2.1 Kinetic Control of Chemical Transformations

Challenges:	Entropy	Confined Spaces
Techniques:	Coherent Scattering	Interferometry

Scientific Opportunity

The ability to guide chemical transformations is a goal in diverse contexts, including electro-, photo-, and enzymatic catalysis, molecular self-assembly, and heterogeneous processes in aerosols, in confined spaces, and on nanoparticles. These transformations are governed by complex free-energy landscapes that determine correlated atomic and molecular motions over multiple length and time scales. For example, supramolecular chemistry is governed by a subtle interplay of non-covalent interactions between molecules, which gives rise to the formation of intricate self-organized chemical structures [1]. These processes were thought to be mostly driven by thermodynamics, but we now know that kinetics can be a determining factor, as the selectivity and yield are dictated by the reaction pathway instead of the free energy of the product. Another important class of chemical transformations is those where the system is initially driven far from equilibrium through a sudden change in chemical potential, illumination, pressure, or temperature. Non-equilibrium transformations can result in emergent spatiotemporal behaviors; for example, adaptive chemical networks formed in an evaporating droplet; the transient assembly of material structures; and oscillatory enzyme catalysis in a supramolecular nanovessel. Active kinetic control of emergent behavior in chemical transformations promises revolutionary approaches to targeted synthesis but will require detailed understanding of reaction–diffusion kinetics on system-relevant length and time scales, which both span many orders of magnitude. To date, very few experimental methods offer these capabilities with the requisite chemical sensitivity. Methods utilizing fully coherent soft x-rays from ALS-U will vastly expand the experimental capabilities in this area, as described below.

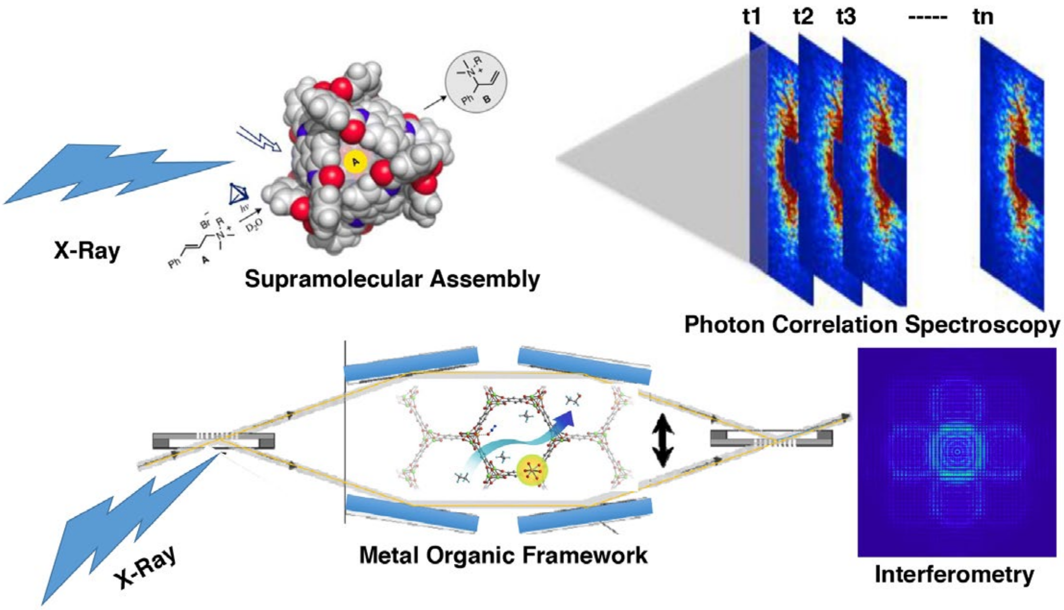

Figure 3.2.2. Top: Schematic of a chemical XPCS experiment on a supramolecular assembly, where coherent x-rays from ALS-U will map spatiotemporal chemical kinetics into a stream of speckle-diffraction patterns with nanosecond sensitivity. Bottom: Measurement of kinetic and dynamical changes in a metal–organic framework catalyzing a chemical transformation using Fourier-transform RIXS. Together these two approaches will probe an extraordinary spatiotemporal range of kinetic processes with high chemical contrast. (Courtesy: M. Ahmed, figure elements from [2].)

Importance of ALS-U

X-ray photon correlation spectroscopy (XPCS) and resonant inelastic x-ray scattering (RIXS) performed with soft x-ray chemical contrast will enable the measurement of structural and chemical fluctuations from seconds to picoseconds and from microns to nanometers [3]. The top panel of Figure 3.2.2 illustrates this experiment for a supramolecular assembly. The high coherent flux of ALS-U will enable XPCS experiments to track the structural and chemical kinetics of the assembly process with high time resolution. These types of XPCS measurements can be coupled with many different reaction platforms, including trapped and merged droplets, nanoparticle beams, liquid jets, and windowless reactors, to probe the chemical reactions of interest. Another complementary approach (Figure 3.2.2, bottom panel) would be to use Fourier-transform x-ray interferometry to perform very high energy resolution RIXS, which provides information that is the time Fourier transform of XPCS, to track the dynamics of interest [4].

The fully coherent x-rays from ALS-U will also revolutionize the investigation of catalytic reactions using scanning transmission x-ray microscopy (STXM) and ptychography [5]. ALS-U's two to three order-of-magnitude gain in coherent flux translates directly into faster data acquisition, higher spatial resolution, greater sensitivity, and a larger field of view. Taken together, these advances enable exploration of chemical transformations at the device level down to the nanoscale. Dispersive detectors for scanning microscopy have the potential for simultaneous measurement of entire absorption spectra given the increased flux into each detector pixel. The vastly increased brightness of ALS-U also allows x-ray fluorescence microscopy, which is currently extremely slow due to the weak fluorescence yield of low-Z materials. Fluorescence microscopy is a powerful technique that enables quantitative measurement of the concentration of many elemental species simultaneously.

Broader Scientific Impact

Measurements of chemical changes with high spatial and temporal resolution across multiple length and time scales are relevant for a much broader range of scientific areas than just catalytic reactions, including porous materials and liquids in confined spaces; metal–organic frameworks and their applications in gas capture and storage; nanofluidic devices for fast mixing of liquids; and measurement of short-lived reaction intermediates and nucleation phenomena.

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3.2.2 Imaging Electrochemical Processes

Challenges:	Nano-objects	Interfaces	Flows
Techniques:	Nanoprobes	Coherent Imaging	

Scientific Opportunity

Electrochemical devices are pervasive in modern applications ranging from electrocatalysis to diverse energy technologies. A rapidly emerging field involves electrochemically controlled material modification, targeting resistive memory ("memristors"), selective catalysts, sensors, and beyond. A working electrochemical device is a heterogeneous, dynamic system in which many structural, electronic, and chemical processes are intimately coupled; consequently, operational mechanisms and reasons for failure often remain elusive with today's characterization tools. Understanding and improving the electrochemical materials and interfaces remains one of the grand challenges for today's sustainable energy applications.

Importance of ALS-U

Chemical transformations and charge transfer at solid–liquid or solid–solid interfaces, which are now readily accessible via powerful soft- and tender-energy spectroscopies, determine functionality in electrochemical devices. Transforming these spectroscopies with ALS-U into a suite of x-ray imaging modalities with sub-10-nm resolution and spectroscopic contrast (Figure 3.2.3) will dramatically improve our ability to optimize the efficiency, selectivity, and stability of electrochemical processes. An important goal is to probe these systems with depth as well as lateral resolution, which can be accomplished by combining nanoprobe and other imaging modalities with x-ray standing wave techniques, particularly in the tender energy regime (see Section 2.3). The high coherent flux from ALS-U will vastly expand the temporal dynamic range of these techniques, so that buried interfaces can be probed during operation.

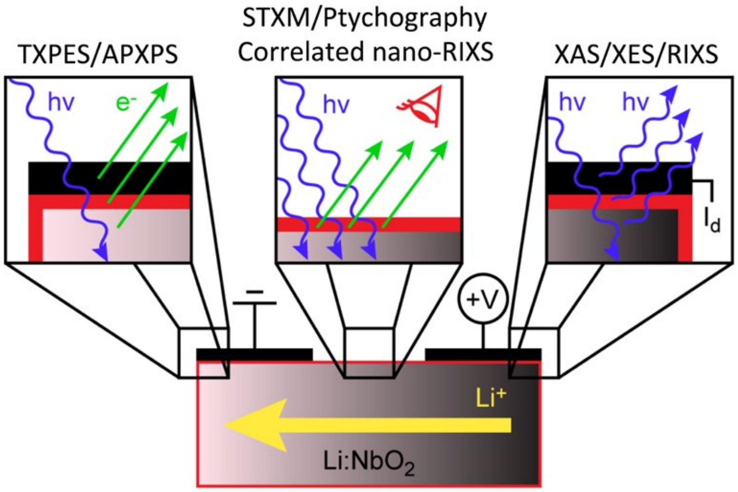

Figure 3.2.3. Schematic of a solid-state device based on electrochemical modification of a Li:NbO$_2$ film. The structure and chemical composition of complex, heterogeneous interfaces control the operation. To understand and optimize these interfaces will require a combination of several techniques with high spatial resolution and spectral sensitivity. (Courtesy: L. Piper)

Broader Scientific Impact

Optimization of buried electrochemical interfaces is a key problem in many contexts.

Electrochemical materials modification: Electrochemical modification of oxide thin films to produce useful functionality is largely accomplished today by trial and error. ALS-U will allow spatial profiling, for example, of the metal/Li$_{1-x}$NbO$_2$ in Figure 3.2.3, to examine both the development and operation of the memristor material junction [1,2]. In this way it will be possible to tune and exploit new modeling and theoretical developments in this area.

Anionic redox: Many conventional electrochemical devices are based on transition-metal (TM) reaction centers. Recent reports have suggested that novel redox reactions involving, for example, both TM cations and ligand anions could lead to dramatic improvement in electrochemical performance. Anion redox reactions are often hard to probe because they typically do not display the sharp atomic multiplet of TMs, but the high sensitivity of ALS-U will solve this problem.

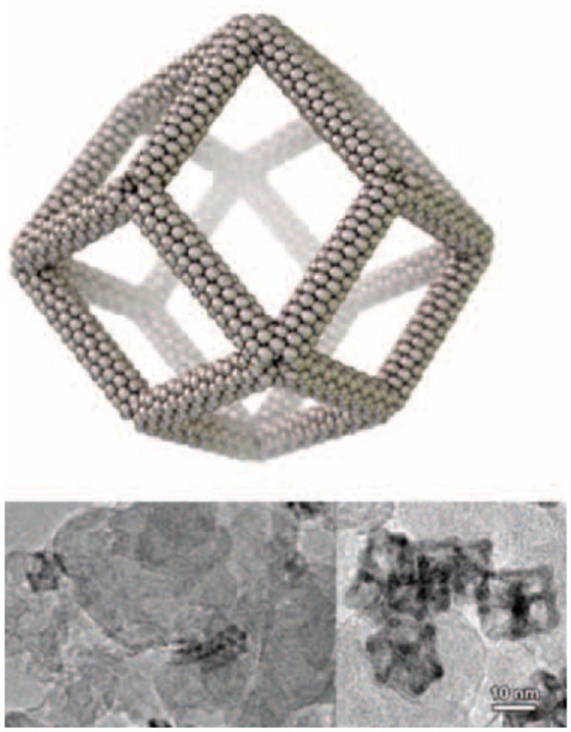

Figure 3.2.4. Platinum nanoframes offering enhanced electrocatalytic efficiency for the oxygen reduction reaction [3].

Optimized electocatalysts: The nanostructure of electrocatalysts can be tuned to significantly improve the efficiency and selectivity of various catalytic reactions, including the oxygen reduction reaction (Figure 3.2.4) [3]. To understand those improvements, and ultimately to design truly optimized electrocatalyst platforms, will require new soft x-ray spectroscopy and microscopy tools, coupled to multiscale theory and modeling efforts, to probe electrochemical interfaces during operation.

Electrochemical additives: The solvation and desolvation of ions plays the key role in determining the stability and performance of electrochemical systems. Proper control of the solvation shell is typically accomplished through empirical approaches based on a large number of additives [4], and optimizing these is one of the crucial developments needed to revolutionize the performance of electrochemical devices. The high spectral and spatial sensitivity of ALS-U in-situ probes will illuminate the crucial role of these additives.

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3.2.3 Designing Multistep Nanoparticle Catalysts

Challenges:	Nano-objects	Interfaces	Flows
Techniques:	Nanoprobes	Coherent Imaging	

Scientific Opportunity

The chemical industry worldwide consumes about 40 exajoules (10^{18} joules) of energy per year, about 90% of which is for commodity chemicals that are produced using supported metal catalysts. Learning how to design better catalysts will dramatically reduce energy usage. Metal nanocrystals with well-controlled shapes and sizes are attractive materials for catalyst design since their tunable electronic and geometric structures offer control of catalytic activity, selectivity, and durability [1].

One approach to improving catalytic processes is to combine two or more catalytic sites or interfaces, optimized for different reaction steps, onto a single nanostructure, producing high activity and selectivity for multistep reactions. To accomplish this, new catalyst synthesis approaches are required that can measure and control catalyst structure and composition on an atomic scale.

Importance of ALS-U

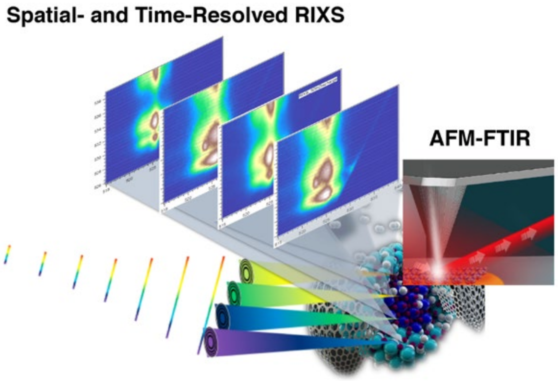

Figure 3.2.5. Coherent x-ray beams from ALS-U will give access to several important probes of chemical and electronic states of matter through nanoRIXS and nanoFTIR and transmission geometry for STXM and ptychography [2]. (Courtesy W. Yang and J. Guo)

Combining scanned-probe, electron, and soft x-ray microscopies will enable the structure and activity of designed nanoparticle catalysts to be mapped. In-depth understanding under realistic reaction conditions requires nanosecond–second temporal resolution and soft x-ray spectroscopy with nanometer spatial resolution, which will become possible with ALS-U. A particularly attractive capability is to correlate soft x-ray spectral imaging tools with near-field FTIR microscopy (Figure 3.2.5) [2]—recently developed at ALS and offering ~20-nm spatial resolution—to probe chemically active layers within nanoscale catalytic reactors. ALS-U will enable the multimodal characterization capabilities necessary to simultaneously probe reaction activity, product selectivity, and correlations at the sequential and tandem catalytic reaction sites.

Broader Scientific Impact

Tandem-interface catalysts: The concept of nanocrystal tandem catalysis represents a powerful approach towards designing high-performance, multifunctional, nanostructured catalysts for multiple-step chemical reactions, such as those proposed for artificial photosynthesis and electrolysis. Using lithographic techniques to integrate binary nanocrystals into ordered superlattices is a new way to form multiple interfaces with new functionalities (Figure 3.2.6) [3]. This new technique has pinpointed the areas on single ~100-nm metallic particles that are most active in chemical reactions [2]. The concept was tested using a CeO_2–Pt nanocube bilayer structure with well-defined surface structures on a silica substrate. Ethylene hydro-formylation with H_2 and CO formed in situ by methanol decomposition was demonstrated. Sequential chemical reactions at two different neighboring metal–metal oxide interfaces acted to produce propanol selectively. The ordered patterning of these nanoparticle tandem catalysts make them suitable for study with the standing-wave technique described in Section 2.3, which will provide 3D information. ALS-U will make it possible to study new kinds of structure–function relationships, including the oxidation and reduction activity of catalysts for oxygen reduction, hydrogen and oxygen evolution, and CO_2 reduction.

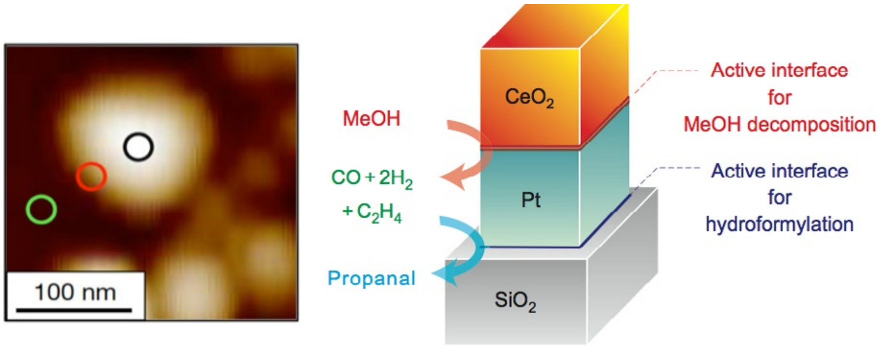

Figure 3.2.6. Left: Different chemistry occurs on different areas of individual nanoscale platinum particles [2]. Right: Illustration of the CeO_2–Pt–SiO_2 binary nanoparticle catalyst, formed lithographically on an oxidized silicon wafer [4].

Biomass conversion: Researchers are actively developing a technology to upgrade natural carbon materials using advanced C–C coupling chemistry to produce a broad range of fuels and chemicals with very high carbon efficiency. ALS-U will provide the capabilities to advance our fundamental understanding of the chemical nature of proximate active sites in a catalytic material needed for successful execution of the multistep catalysis process [5,6]. For example, the above combination of tools will allow understanding of multifunctional catalysis like the so-called Guerbet condensation reaction for conversion of bioethanol to high-value C_4 compounds such as butanol [7].

Solid-state hydrogen storage materials: One of the major scientific challenges for the development of viable solid-state hydrogen storage materials is to use nanostructuring to improve the kinetics and thermodynamics of H_2 desorption from metal hydrides. For example, small graphene-encapsulated nanocrystals, measuring only about 3–4 nm in diameter, are a key emerging concept to enable fast capture and release of hydrogen. Thin sheets of graphene oxide have natural, atomic-scale defects that allow H_2 molecules to diffuse through them and react with metal nanoparticles to form hydrides while simultaneously blocking larger molecules such as O_2 and H_2O that would decompose the hydride. The new tools at ALS-U will help in searching for different types of catalysts that can improve the fuel cell's conversion of electrical current, and in studying whether different types of materials can also improve the fuel cell's overall capacity.

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3.2.4 Imaging and Analyzing Natural Nanoparticles

Challenges:	Nano-objects	Interfaces	Entropy
Techniques:	Nanoprobes	Coherent Imaging	

Scientific Opportunity

In recent years, virtually all fields of earth and environmental sciences have recognized that natural and anthropogenic particulates play a major role in ocean, terrestrial, and atmospheric systems and can seriously impact human health. Natural nanoparticles transport and transform staggering quantities of nutrients and pollutants and seed cloud formation, and their impact is one of the largest sources of uncertainty in global climate modeling.

Importance of ALS-U

ALS-U tools will offer an unprecedented combination of imaging and chemical analysis of all solid and fluid phases of natural nanoparticles, including major and trace components, enabling system-level advances in understanding all regions of our planet. Soft and tender x-ray ptychography will enable tomographic imaging with spectroscopic contrast, at the damage-limited resolution of ~10 nm, and with enough throughput to measure a useful ensemble of materials under various conditions. Samples can also be studied by applying ALS-U tools to micron-sized liquid and droplet jets or droplets in an optical trap. For example, coherent diffractive imaging with a microsecond snapshot will provide a damage-free measurement of composition and structure with ~10-nm resolution under realistic environmental conditions. XPCS will probe the formation and evolution of ionic and chemical gradients. The use of droplet jets will enable fast mixing and study of kinetic processes.

Broader Scientific Impact

ALS-U tools will provide an ideal combination of chemical sensitivity and spatial and temporal resolution to study a broad range of particulates relevant to diverse earth processes.

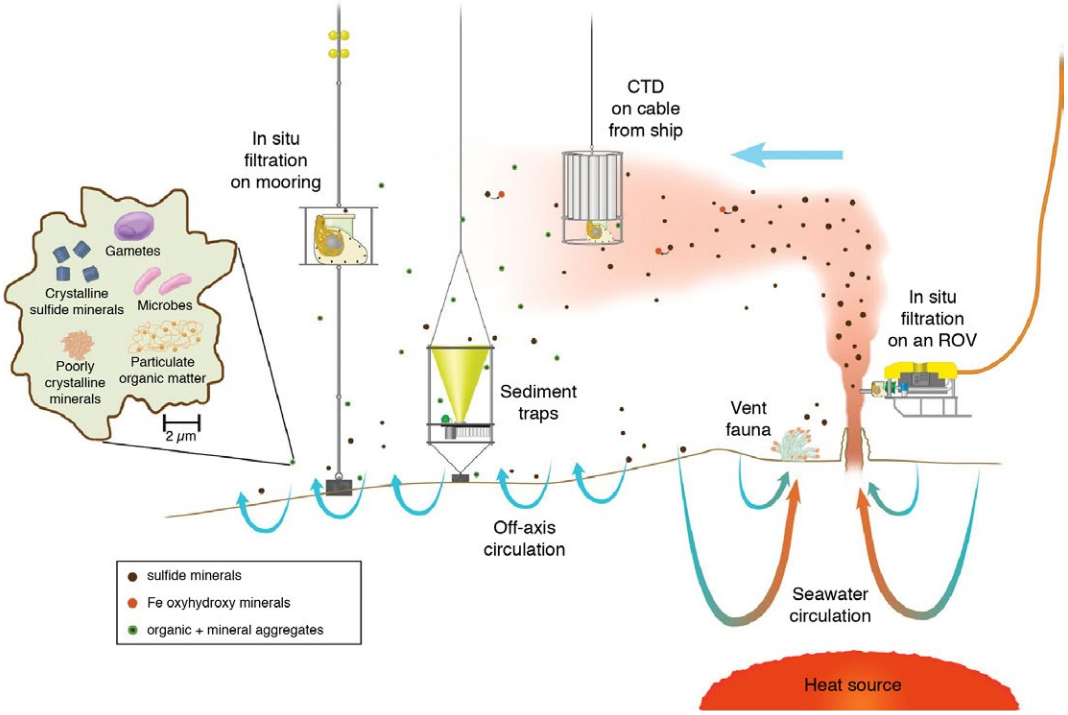

Figure 3.2.7. A scheme showing nanoparticle production in deep ocean vents, their interaction with the environment, and sampling apparatus for preservation and chemical analysis with x-ray and other methods [1].

Ocean nanoparticles: Mineral nanoparticle–water interfaces control key contaminant and nutrient speciation in a variety of environments (Figure 3.2.7). In the Southern Ocean—a critical region of carbon sequestration—biological productivity is limited by iron availability. Nanoparticulate iron sourced from West Antarctic Peninsula sediments, in the colloidal size fraction (0.2–0.02 μm), is a key iron input [1]. Multimodal soft and tender x-ray imaging instruments at ALS-U will reveal the structure and complex, heterogeneous interfacial chemistry of this and other colloidal fractions to describe mobility and bioavailability [2].

Atmospheric aerosols: Atmospheric aerosol particles play key roles in climate and human health. Their impacts depend on chemical composition, which undergoes continuous evolution via photolytic and free-radical oxidation. For example, recent results suggest that aerosols can fluctuate between liquid, semi-solid, and glassy states, and that these fluctuations are coupled to chemical reactions that change the diffusive properties of the interface [3]. This leads to complex nanoscale dynamics and nanoscale chemical gradients inside atmospheric aerosol particles. ALS-U tools will help develop a predictive understanding

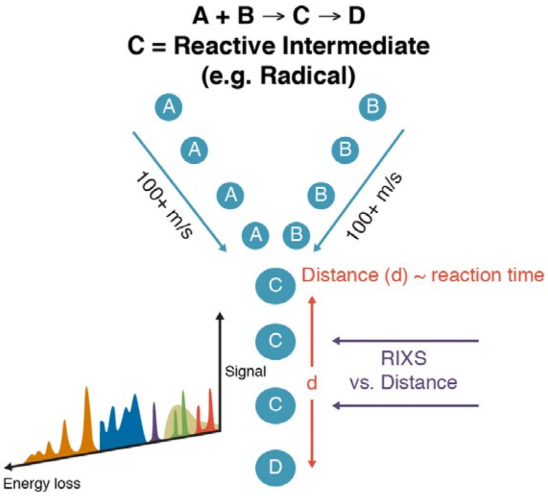

Figure 3.2.8. An approach to achieve fast mixing of submicron droplets and subsequent, time-delayed probing with ALS-U x-ray beams. (Courtesy: K. Wilson)

of the impact of aerosols by quantifying nanoscale chemical structure and the feedbacks between oxidation reactions and diffusion (Figure 3.2.8).

Electron transfer dynamics in natural nanoparticles: Metal redox reactions in natural environments frequently cause precipitation of metal-oxide nanoparticles. The reactivity of these precipitates exerts a strong influence on biogeochemical cycling of carbon and other nutrients. Redox-reactive natural nanoparticles can be highly dynamic, with spontaneous internal electron-transfer reactions coupled to surface proton or ion mobility. Recent studies show that different surface sites in δ-MnO_2 nanoparticles display a range of oxidative capacity (Figure 3.2.9). ALS-U tools will constrain the rates of electron transfer, the distribution of defects and charge density in nanoparticles, and the evolution of these features with different chemical triggers.

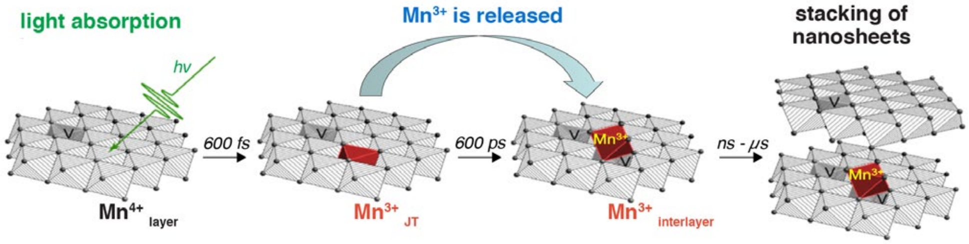

Figure 3.2.9. Pump–probe studies of the photochemistry of MnO_2 (birnessite) have revealed dramatic electronic and structural changes on a range of temporal and spatial scales [3]. We hypothesize that such coupled interactions take place close to equilibrium and during chemically (not photochemically) driven reactions [2].

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3.2.5 Controlling Chemistry, Wetting, and Immiscible Fluid Flow at the Nanoscale

Challenges:	Interfaces	Flows	Confined Spaces
Techniques:	Coherent Scattering	Interferometry	

Scientific Opportunity

The ability to predict and ultimately control the flow of immiscible fluids in microscopic and nanoscale pores, channels, and fractures is vital for many energy and environmental systems. For example, understanding the transport mechanisms of methane through brine-saturated shale will improve the recovery rate of natural gas from shale reservoirs, reducing drilling intensity [1]. Efficient geologic sequestration of CO_2 at the scale needed to limit climate change will require the use of diverse geologic formations, perhaps including depleted hydrocarbon reservoirs. Finally, subsurface storage of natural gas and hydrogen can provide seasonal storage of high-energy-density fuels produced by low- and zero-carbon processes, provided the sealing mechanisms of low-permeability cap rocks are fully understood.

We currently have a sound physical basis for predicting the flow of a single fluid phase through a porous medium, but, surprisingly, our theoretical and simulation tools have a limited ability to describe flow when two immiscible fluids compete for pore space [2]. This, in turn, reduces our ability to predict macroscopically important system parameters such as net fluid fluxes and the trapping of one fluid phase by a second immiscible phase. The experimental and theoretical challenges of describing multiphase flow are accentuated when the pore dimensions are sufficiently small that all fluid properties are influenced by physical and chemical interactions collectively referred to as confinement effects. Understanding the properties and flow of confined fluids, particularly chemically reactive fluids, will be an important challenge for years to come.

Importance of ALS-U

The spatial and spectroscopic sensitivity of ALS-U soft and tender x-ray tools will provide crucial insight into wetting, flow, and chemical reactions in confined geologic systems like nanopores, cracks, and grain boundaries. Cryo-imaging will achieve ~10-nm resolution and greater sensitivity to thin films through interferometry. For some systems, movies will probe nanoscale flows, though at lower resolution.

Broader Scientific Impact

ALS-U tools will find broad application in addressing mixed phase flows in diverse contexts, particularly in confined spaces that play important roles in many environmental systems.

Chemical reactions in nanopores and between grain boundaries: Chemical precipitation and dissolution in nanoporous rock and at grain boundaries is assumed to affect tensile strength and deformation, but tools to study and understand these mechanisms at the relevant length and time scales have not been available. Imaging and high-frame-rate movies using ALS-U tools will enable understanding of the impact of confinement on thermodynamic phase stability and phase separations in these reaction–diffusion systems under realistic static and flow conditions.

Multiphase flow through complex nanoscale geometries: X-ray microtomography is a valuable tool for observing the rates and pathways of multiphase flow within complex microscale geometries (Figure 3.2.10) [3]. By contrast, models to predict flow within nanoporous materials are in their infancy and require experimental validation. Soft x-ray imaging at ALS-U will have exceptional ability to differentiate between immiscible fluids based on their molecular properties and orientation, and to resolve static fluid–fluid and fluid–solid boundaries.

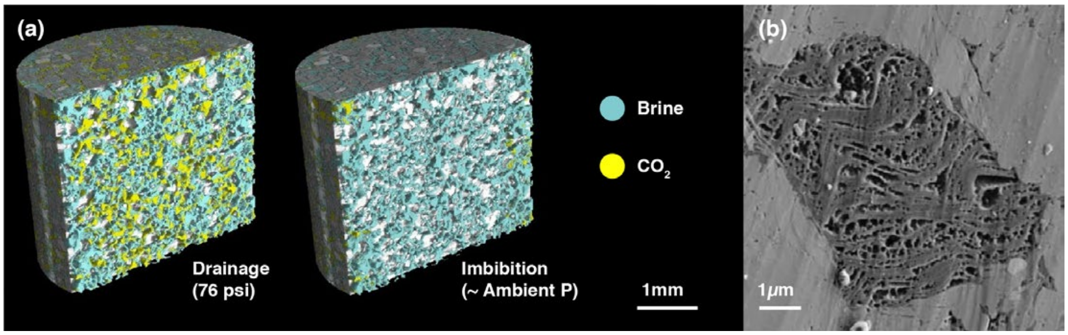

Figure 3.2.10. a) X-ray microtomography results show the replacement of brine by carbon dioxide in a 6-mm sandstone core followed by the reinjection of brine [3] (Courtesy: J. Ajo-Franklin). b) Determining the flow and distribution of fluids through nanoporous systems such as shale kerogen is an important frontier challenge in earth and materials sciences that will be revolutionized by ALS-U [4].

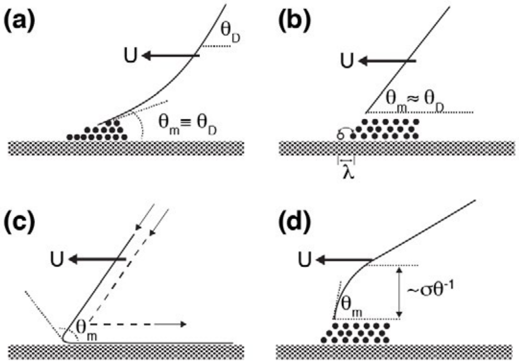

Figure 3.2.11. Hydrodynamic models predict singular forces at the fluid–fluid-surface vertex in mixed phase flow. Shown are several untested hybrid molecular/continuum models for contact-line structure and motion [5]. The spatial, temporal, and spectral sensitivity of ALS-U imaging tools can probe the structure and molecular orientation near the vertex to address this important multiscale system.

Understanding and controlling contact-line structure and dynamics: The replacement of one immiscible fluid phase by another is controlled by the displacement of the fluid–fluid interface along a solid surface. Even for ideally smooth surfaces, we lack a self-consistent molecular or continuum model for the fluids at this contact line [6]. Classical hydrodynamic models for flow near a moving contact line fail because the stresses on the fluid become unbounded at the vertex. Hybrid molecular–continuum models propose dissipation or mass exchange processes to avoid this singularity (Figure 3.2.11) [7], but these have not been experimentally validated at the relevant spatial and temporal scales. Ptychography available at ALS-U will be able to acquire chemical movies of contact-line motion at rates relevant to subsurface flow. The novel soft x-ray interference measurements such as differential STXM (Section 2.3) will provide ultrahigh sensitivity to nanoscale films that are out of the reach of direct optical or x-ray imaging methods.

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3.2.6 Elucidating Nanoscale Environmental Chemical Kinetics

Challenges:	Interfaces	Flows	Confined Spaces
Techniques:	Nanoprobes	Coherent Scattering	

Scientific Opportunity

Macroscopic properties of many natural systems are dictated by physical–chemical kinetics that occur at the nanoscale and over nanosecond time domains. Examples of these kinetic processes include the motion and ordering of micron-sized clusters of clay particles, the folding–unfolding and phase changes of natural organic matter macromolecules, the formation of aqueous ion clusters and mineral nuclei, and the movement and distribution of charge density within redox-active minerals and organic molecules. These processes control the structure and fertility of soils, the global cycling of carbon and other elements, the fate and transport of contaminants, including radionuclides, and the quality and safety of water resources and air.

Importance of ALS-U

The structural, spectroscopic, and temporal sensitivity of imaging tools and XPCS at ALS-U are well suited to study the structural and kinetic properties of environmental systems. Soft and tender x-ray ptychography will enable tomographic imaging with spectroscopic contrast, at the damage-limited resolution of ~10 nm, and with enough throughput to measure a useful ensemble of materials under various conditions. XPCS will probe chemical and structural fluctuations in these complex reaction–diffusion systems. A particularly important ALS-U capability is the sensitivity to probe the motion of individual molecular and ionic species as they are bound and unbound, for instance, in clay particles [1], in natural organic matter, and in other systems.

Broader Scientific Impact

Our ability to understand and model diverse environmental processes requires a sound understanding of nanoscale environmental structures and the kinetic processes they support. The combined chemical sensitivity and spatiotemporal resolution of ALS-U tools are ideally suited to provide this information.

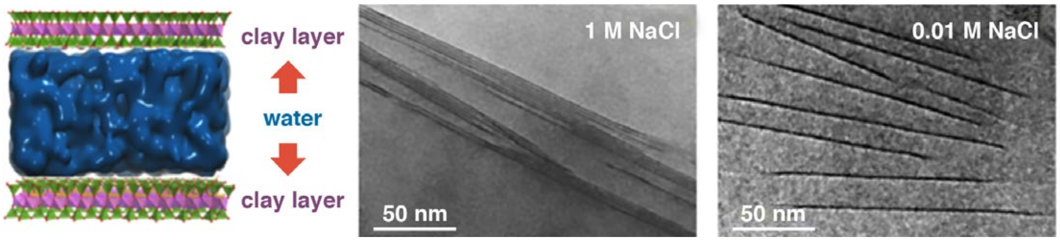

Figure 3.2.12. Swelling clays consist of negatively charged aluminosilicate layers that incorporate variable thicknesses of water and dissolved counterions. Cryogenic transmission electron microscopy (cryo-TEM) of flash-frozen suspensions reveals the significant differences in mean interlayer space controlled by salinity but cannot provide the timescales for swelling or interlayer Brownian motion [2].

Layer and chemical kinetics in clay particles: Clay particles play crucial roles in soil chemistry and in shales by storing water and hydrocarbons, controlling pH, and releasing or storing contaminant metals [3]. Swelling clays such as smectite are particularly important due to their ability to expand and incorporate water into their interlayers (Figure 3.2.12). The nanometer-scale chemical kinetics of clay swelling links water chemistry, soil or rock permeability, and the strength of clay-rich rocks and faults. Knowledge of the extent and timescales of the mobility of clay layers and the ions between them would provide important constraints on the rheology of clay suspensions and the transport of solutes through low-permeability clay-rich systems. Recent cryo-TEM provides unprecedented direct imaging of clays in a range of swelling states [2,4] but cannot probe layer and solute motions.

Structure and kinetics of natural organic matter: Natural organic matter (NOM) is a complex mixture of small and large organic molecules that control key features of natural systems including soil structure, water-holding capacity, and fertility (Figure 3.2.13) [5]. NOM also impacts the fate and transport of both organic and inorganic contaminants. Because of its complex nanoscale chemical structure, the role of NOM in many natural processes remains poorly understood. The 3D structure of the organic matter both in solution and on surfaces determines its key properties, including the decomposability of the organic matter, the development of micro-aggregates, the sorption and release of contaminants, and the structure and function of biofilms.

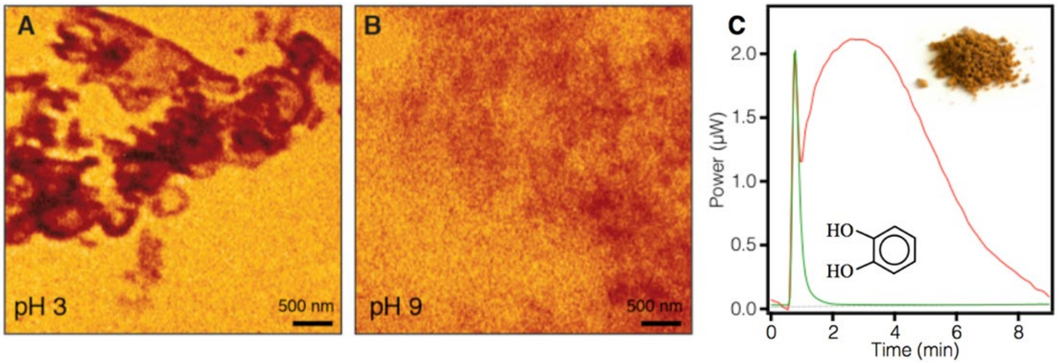

Figure 3.2.13. NOM is composed of diverse organic macromolecules that undergo conformational changes in solution that are correlated with their reactivity and transport. a) and b) Full-field soft x-ray microscopy at 543 eV to image fully hydrated fulvic acid macromolecules and to record the influence of pH, ionic strength, and complexing cations on the conformation [6]; c) Isothermal titration calorimetry reveals the enthalpies of complexation reactions of NOM and shows that introduction of molybdate ion causes reactions that take many minutes to complete—far longer than for a simple ligand such as catechol, *data from Thalhammer and Gilbert (unpublished).*

Chemical hysteresis presents a fundamental challenge in understanding multiple natural systems and is particularly prevalent in complex phases like NOM. The release of species, organic or inorganic, rarely follows the same time- or condition-dependent behavior as the uptake of those species. One potential explanation of this behavior is conformational and phase changes to organic host phases. This is particularly well established in the field of organic contaminant release but is potentially equally true for ion-based coagulation.

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3.2.7 Illuminating Intracellular Biomineralization

Challenges:	Nano-objects	Interfaces	Entropy
Techniques:	Nanoprobes	Coherent Imaging	Coherent Scattering

Scientific Opportunity

Biomineralization is a widespread natural phenomenon, forming our teeth, bones, and a variety of marine animal skeletons, most notably coral reefs. Coral reefs cover only 1% of ocean floors yet they host 25% of marine life. They have tremendous economic impact as they provide fishing, tourism, and coastline protection.

From scanning electron microscopy experiments we know that coral and other skeletons grow by attachment of nanoparticles ~100 nm in size [1]. Previous research has demonstrated that these particles are amorphous when they are deposited on the freshly formed biomineral surface of growing calcite sea urchin spicules [2], nacre-forming tablets in mollusk shells [3], growing coral skeletons [4], and forming bones [5] and teeth [6]. These particles must be formed intracellularly, presumably in vesicles, and can be distinguished spectroscopically and mapped as shown in Figure 3.2.14, but it has not yet been possible to observe them directly inside cells.

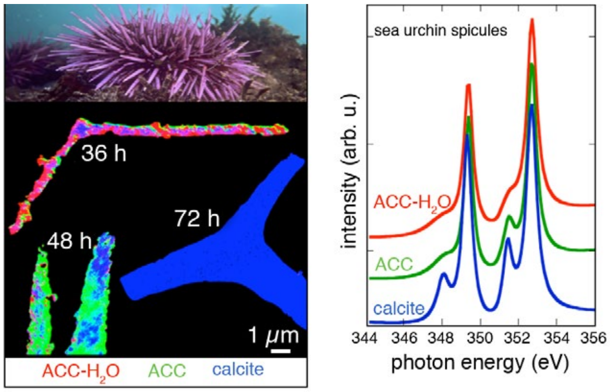

Figure 3.2.14. Preliminary data showing sea urchin spicules extracted from embryos harvested 36 h, 48 h, and 72 h after fertilization. Only the spicules, cleaned of any cells, can be analyzed at present. The color-coded particles in these component maps demonstrate that when the particles are first deposited they are hydrated amorphous calcium carbonate (ACC-H$_2$O, red), then they dehydrate to amorphous calcium carbonate (ACC, green), and finally crystallize to calcite (blue). These phases are distinguished by their spectra at the Ca L-edge, which are correspondingly colored. *PEEM data adapted from [2].* At ALS-U we must do similar mapping of phases but not in the extracted spicules, directly inside the cells forming them, to understand biomineralization processes at their early stages in sea urchins, mollusks, and corals.

Importance of ALS-U

Intracellular vesicles, and the amorphous calcium carbonate or phosphate particles being assembled therein, can only be imaged with the phase enhancement provided by coherent soft and tender x-ray ptychography. The relevant energies include the C, Mg, Ca, and P K-edges and the Ca, Mn, and Fe L-edges. As shown in Figure 3.2.15, biominerals can be studied now, but only after extraction and separation from the cells that formed them. By preparing samples with living cells forming a biomineral, as in Figure 3.2.14, we will be able to study biomineral particles as they are formed inside cells.

Photoemission electron microscopy (PEEM) will continue to be extremely important to discover new biomineral formation mechanisms via mineral component analysis [2] and polarization-dependent imaging contrast (PIC) mapping [8]. The longer bunch lengths at ALS-U compared to ALS will also reduce space charge in PEEM experiments. While not benefitting from ALS-U, the ALS nano-IR tools will provide valuable complementary information in these studies.

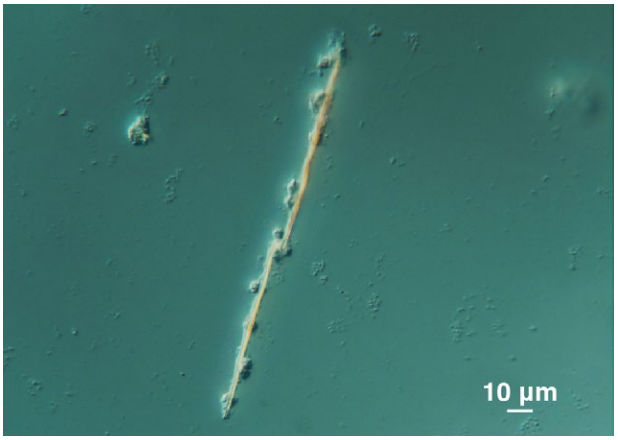

Figure 3.2.15. Phase-contrast visible light microscopy of sea urchin cells forming a calcite spicule in vitro [7]. This system, or its equivalent with coral cells forming an aragonite crystal, can be analyzed with ptychography to localize and spectroscopically identify the beginning of the biomineralization process, that is, amorphous nanoparticles in intracellular vesicles.

Broader Scientific Impact

The analysis and interpretation of macro- and micro-fossils of ancient biomineral deposits, in addition to modern systems, is critically relevant. Identification of the mineral phase and its stability in earth environments is essential for using mineral chemistry as a paleo-environmental indicator. After recent PEEM and micro-x-ray diffraction experiments at ALS [4,9], we anticipate that seashells and corals will play a major role in paleo-climate reconstructions. Such "discovery" experiments are harder to plan for the far future, but with PEEM and ptychography at ALS-U they will continue and improve.

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3.3 SOFT AND BIOLOGICAL MATTER

By far the largest impact to date of synchrotron radiation in bioscience and soft-matter physics has been structure determination. There are now over 100,000 entries in the protein structure databank, and most were determined with macromolecular crystallography at x-ray light sources. While spectroscopic studies of soft systems are common, they are most meaningful when the structural textures can be resolved with x-ray scattering or, increasingly, microscopy.

Soft x-rays are playing an expanding role in probing soft systems. For example, Figure 3.3.1 shows a schematic of an unusual chiral (helical) texture in smectic liquid crystals composed of achiral molecules that was recently observed at the ALS using the high chemical contrast of soft x-ray scattering near the carbon K-edge. Hard x-rays lack the necessary contrast to detect this structure, which had previously only been observed as a metallic replica imaged by cryo-fracture electron microscopy.

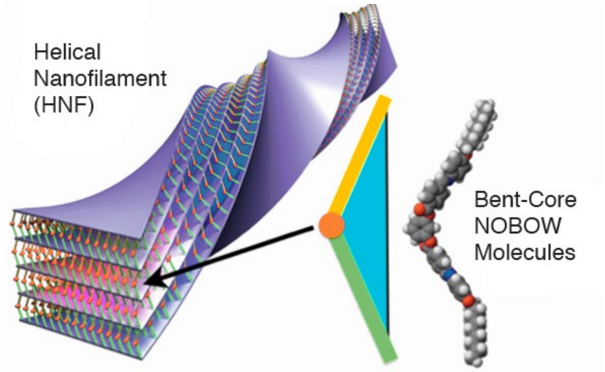

Figure 3.3.1. Schematic of a helical phase detected with resonant soft x-ray scattering. The phase had been predicted long ago and was first observed in the equilibrium phase using the chemical contrast provided by soft x-ray scattering near the near the carbon K-edge at the ALS (C. Zhu et al., *Phys. Rev. Lett.* **116**, 147803 (2016)).

The crosscutting challenges discussed in Section 1.2 demonstrate that ALS-U will significantly sharpen this focus on the structure of soft and biological systems but will also add important new capabilities. For example, a defining feature of soft materials is that they have many microscopic degenerate modes at energies comparable to k_BT, which lead to small bulk moduli and often to emergent behaviors. These modes can be manipulated easily with little energy input and, thus, are key to efficient function. For this reason, the truly transformational capability offered by intense, coherent x-ray beams will be a huge dynamic range for probing soft and biological matter in both space and time, in bulk and at interfaces. ALS-U will uniquely allow the unusual spectrum of microscopic modes in the above helical phase and in many other soft and model biological systems to be studied, leading to understanding how the properties of such systems emerge and how they function in active structures.

Quasielastic neutron scattering probes excitations down to ~1 μeV and has been broadly applied to soft systems. ALS-U will probe modes in soft systems over a broader time/energy domain by combining x-ray photon correlation spectroscopy (XPCS) with resonant inelastic x-ray scattering (RIXS), with much higher signal to noise, high chemical contrast, and tightly focused beams for straightforward application to thin films and nanostructures. The imaging resolution in these systems is expected to be limited by radiation damage to ~10 nm for frozen systems. For statistical techniques like XPCS, RIXS, and fluctuation x-ray scattering (FXS), sample delivery mechanisms will continuously provide fresh material, and broad spatial and temporal scales will be simultaneously measured.

3.3.1 Probing Charge Dynamics in Organic Materials

Challenges:	Interfaces	Flows
Techniques:	Coherent Scattering	Interferometry

Scientific Opportunity

Organic semiconducting materials, including small molecules, polymers, and organic frameworks, have applications in energy conversion (e.g., thermoelectrics, solar cells, light-emitting diodes), energy storage (e.g., batteries), and electrocatalysis. The design of new materials and the development of predictive transport models require knowledge of dynamic processes across multiple time and length scales.

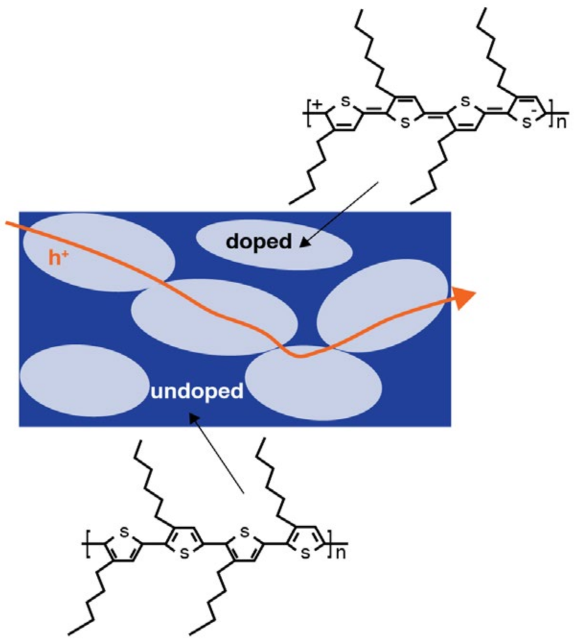

Figure 3.3.2. Schematic of the heterogeneous landscape experienced by excited electrons in an organic material.

A key advantage of organic materials is the ability to process them with scalable manufacturing methods such as printing or melt-processing at low temperatures. These processes lead to both electronic and structural disorder that makes charge motion difficult to measure and model. Structural disorder is known to exist on the ~10–100-nm length scale, and it is assumed that electronic disorder arises at the molecular and larger length scales (Figure 3.3.2). The ability to directly probe charge motion and decay at the nanoscale would provide a unique opportunity to understand how structural and charge disorder are coupled, impacting many emerging technologies.

Importance of ALS-U

ALS-U will enable charge transport in organic materials to be measured by combining near-edge soft x-ray absorption transitions—which are highly sensitive to the local electronic structure of organic materials (Figure 3.3.3)—with the spatial and temporal sensitivities provided by high coherent flux. This combination presents an opportunity to use soft x-ray methods to uncover critical features of electronic transport in soft materials. For example, diffusive motion of charge carriers under continuous-wave illumination related to charge hopping between domains could be revealed using XPCS. Probing the spontaneous motion of photoinduced charge density using XPCS might be very challenging, so an alternative, though more complicated, approach would be to develop a transient-grating measurement (Figure 3.3.4).

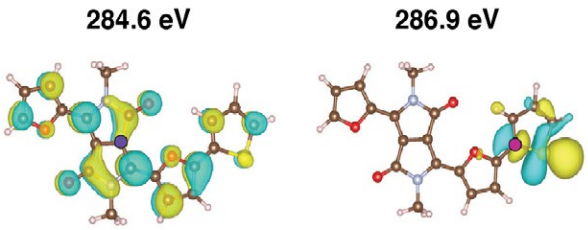

Figure 3.3.3. Calculated wave functions for C *1s* electrons excited into polaronic states at the two photon energies shown. Dramatic differences indicate the near-edge spectral contrast in these systems [1].

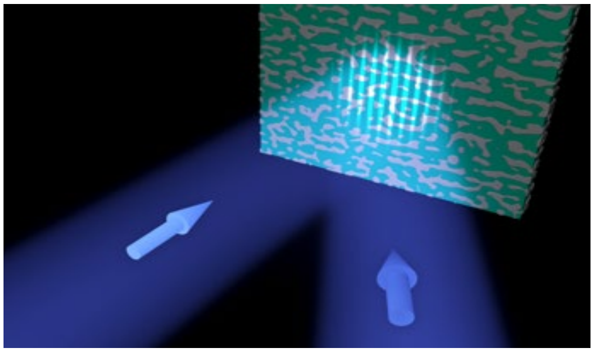

Figure 3.3.4. Schematic of interference between two coherent lasers or soft x-ray beams to create a charge-carrier grating inside a thin organic photovoltaic material, which can then be probed by resonant soft x-ray Bragg scattering. (Courtesy: A. Hexemer)

This would involve creating a standing-wave pattern in an organic photovoltaic film by overlapping two lasers or, with more difficulty, transversely coherent soft x-ray beams. This setup would excite a periodic density of carriers, which then could be detected by diffracting a separate soft x-ray beam off the induced carrier grating, tuning the photon energy of the probe beam to achieve simultaneous spectroscopic contrast.

To attain nanoscale sensitivity would require that the grating be produced with soft x-ray beams, by splitting a beam and recombining the split beams at a specific angle to create an interference pattern. Of course, the goal would also be to use this transient-grating approach to measure spatiotemporal dynamics by measuring the decay of the carrier grating in a pump–probe mode.

This challenging approach would require developing new optical modalities, probably based on nanodiffractive optics.

Broader Scientific Impact

Understanding charge-carrier motion and decay at the nanoscale will lead to control of electron motion in organic materials and therefore to optimized device performance. There are similar opportunities in emerging hybrid photovoltaic and photocatalytic systems. Organometal halide perovskites comprise inorganic layers with organic cations having significant molecular mobility due to vacancies in the lattice. These materials exhibit exceptional optoelectronic performance despite this property. Using next-generation sources, it may be possible to examine the motion of molecular species, including methyl ammonium in organometal halides, using soft x-ray energies specific to low-Z species.

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3.3.2 Studying Collective Dynamics and Dynamic Heterogeneities

Challenges:	Entropy	Flows	Confined Spaces
Techniques:	Coherent Scattering		

Scientific Opportunity

Thermally driven collective dynamics are the key to many macroscopic properties of soft materials. Yet our understanding of these dynamics, especially at the mesoscale, remains very limited. The main challenge arises from the cooperative and heterogeneous nature of the dynamics. Currently, there is no complete microscopic understanding of dynamic cooperativity and heterogeneities (Figure 3.3.5) [1,2], and the experimental methods available to study these dynamics, especially in confined systems, are lacking. Coherent x-ray scattering can enable studies of the collective dynamics over broad time and length scales not otherwise accessible, bridging our understanding from local (e.g., atomic-scale) dynamics to continuum-level descriptions of macroscopic properties of soft materials.

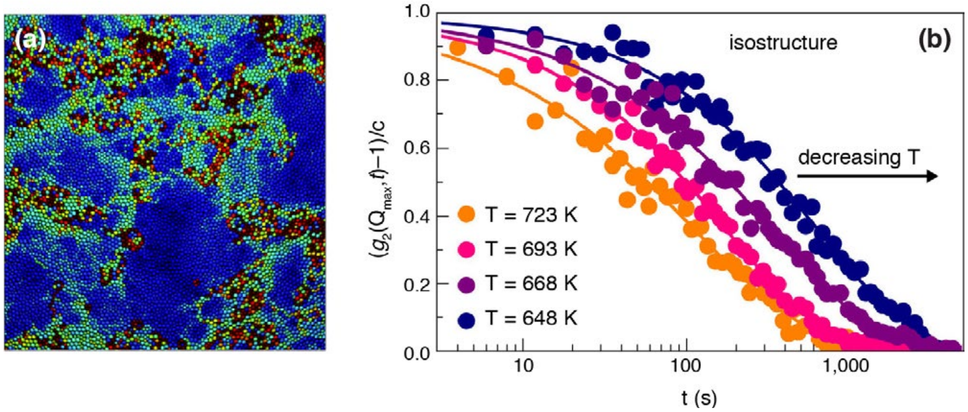

Figure 3.3.5. a) Simulation of dynamic heterogeneity in a glass-forming liquid. Color coding shows a snapshot of the simulated particles' speeds close to the glass transition [2]. b) XPCS results for relaxation dynamics of a network glass; note the very slow temporal range [3]. Stretched exponential behavior is taken as a signature of dynamic heterogeneity.

Importance of ALS-U

Currently, the accessible timescale of spontaneous nanoscale collective dynamics is restricted on the upper end to milliseconds using XPCS and, on the lower end, to faster than ~1 ns using neutron spin-echo scattering. ALS-U will allow the study of nano- to millisecond timescales and open up the most crucial time domain for collective dynamics. Additionally, soft x-ray spectroscopic contrast affords the opportunity to study dynamics of individual sub-components such as backbone and side groups in polymers and nanoparticles embedded in nanocomposites. The native contrast in resonant XPCS is a vast expansion over the hydrogen–deuterium contrast available for neutron spin echo. The polarized and resonant nature of the incident soft x-ray beam affords the opportunity to measure anisotropy in the dynamics [3,4], which is of particular interest for geometrically confined systems, motions at interfaces, or where there is directional flow.

An important issue in most soft-matter systems is the possibility of sample perturbation with the x-ray beam, either by heating or direct radiation damage. In XPCS experiments, the beam can often be moved across the sample, slowly on the timescale of the dynamics being measured, so as to average the dynamics from different points on the sample.

Broader Scientific Impact

The notion of dynamic heterogeneity refers to the existence of transient spatial fluctuations in the local dynamical behavior and is observed in virtually all disordered systems with glassy dynamics [1]. Dynamic heterogeneity is accompanied by a broad spectrum of temporal fluctuations, but this spectrum has not been studied at the short length scale where the behavior must break down. ALS-U will allow diverse systems exhibiting this behavior to be studied in this crucial spatiotemporal regime.

The structural and dynamical properties of materials must deviate from their bulk values as the system is confined below a characteristic length scale, for instance, a polymer radius of gyration or chain persistence length. Such changes can have dramatic consequences on the thermophysical properties of the system. For example, ion-conductive polymers are increasingly applied as nanometer-thick thin films and at interfaces with other materials to form multifunctional composite structures. Inorganic particles are also commonly incorporated in these hierarchically structured porous electrodes to facilitate reactions and provide additional functionalities, for example carbon/platinum in fuel-cell electrodes, or silicon in vapor-fed, solar-fuel devices. Surface interactions and confinement to thicknesses that approach the characteristic domain size of copolymers can cause an orientation of the domains and pose significant limitations to transport. Another good example is block copolymers, where the stochastic variations in composition and molecular weight can have profound impact on the self-assembly process in systems of finite size. Many other soft systems exist where confinement can have significant impact and where the attributes of ALS-U can be brought to bear.

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3.3.3 Predicting Rare Events in Soft Condensed Matter

Challenges:	Flows	Confined Spaces	
Techniques:	Nanoprobes	Coherent Imaging	Coherent Scattering

Scientific Opportunity

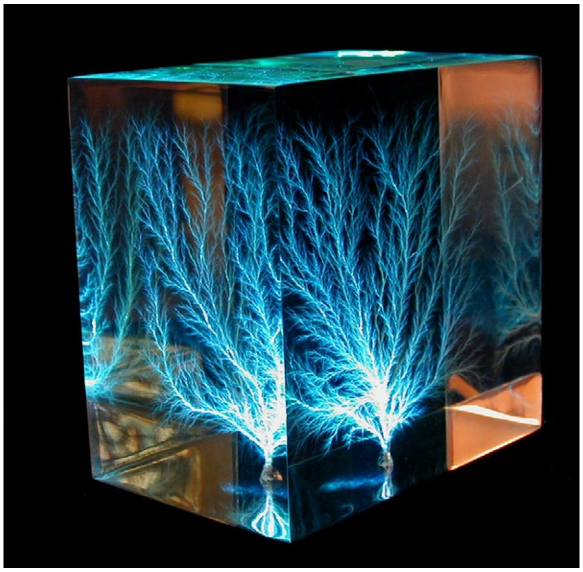

Figure 3.3.6. Corona discharge during dielectric breakdown in a polymer, a classic rare event, limits the suitability of a particular material in dielectric applications, from capacitors to fuel cells. (Courtesy: Bert Hickman, Wikimedia Commons)

As discussed in the introduction to this section, soft matter is defined by a degeneracy of interacting, thermally active modes. This leads to unusual and adaptable properties, but it also leads to jamming, where the system becomes stuck in a particular microscopic configuration. The lead-up to jamming involves rare events, which often trigger significant changes in materials and chemical morphology and are of vital importance in soft condensed-matter systems. Crystal nucleation, mechanical fracture, dielectric breakdown, and even certain modes of diffusion in glassy systems are typical examples.

Although we can easily measure the time-average structure and morphology of a soft material as well as steady-state microscopic modes that nominally determine its static properties, the point at which mechanical and electrical failure occurs is probabilistic in nature and involves very local chemical, mechanical, and structural changes. Understanding the origins of these rare events is critical to predicting the lifetimes of materials in applications. Being able to predict when these catastrophic events will occur or, at least, gaining insight into occurrences that lead up to these rare events, would allow us to predict when breakdown or failure will occur and to pre-condition materials to extend their lifetimes.

These events are often characterized post facto by structural and chemical changes in the materials (Figure 3.3.6). Consequently, by coupling the high brilliance and coherence of ALS-U with novel experimental designs to bias or confine the event to a specific location in the material, and by employing high-speed detection capabilities, we can enable the realtime monitoring of local chemical, structural, and configurational changes in the materials that would quantify events leading up to the spontaneous cascades that precede material failure. A quantitative understanding of rare events that can account for the location and time of event occurrence would enable the development of strategies for improving or more accurately determining polymer lifetimes.

Importance of ALS-U

ALS-U will provide several important improvements over existing sources for measuring rare events. Currently, most tools only render averages over large areas due to fairly large beams. However, to adequately probe the important areas, a small beam in the soft or tender x-ray range is needed to examine not only the morphology of the materials but also the chemical makeup. In particular, for electronic breakdown, the chemical change in the material will be revealed using resonant scattering techniques combined with XPCS to expose the dynamics of the process. This will allow us to study for the first time the chemical and morphological changes in polymers during fast events.

Broader Scientific Impact

Rare events play a key role in many processes that support soft manifolds in soft materials as well as in hard materials.

Dielectric breakdown (Figure 3.3.6) is a limiting factor in many technologies, from supercapacitors to batteries and fuels cells, for short- and long-term energy storage, respectively.

Barkhausen cascades in magnets occur when sudden local changes in domain structure lead to a larger magnetic cascade. Magnets themselves are usually hard materials, but the magnetic domain structures bear many similarities to soft matter. Superparamagnetism, which limits the storage density of magnetic media, involves rare events in which quasistatic fields and thermal stimulation contribute.

Nucleation is a rare event in which small regions of a new phase appear and grow in a majority phase. Classical nucleation theories are largely untested due to a lack of robust tools to study these rare events. Learning to control nucleation will be a key part of “materials by design.”

Diffusion in colloid and macromolecular systems near the glass transition involves many small motions punctuated by rare events in which a cascade is nucleated locally but manifests on a much broader scale. These events help determine viscoelastic properties.

3.3.4 Understanding Structure and Dynamics of Soft-Material Interfaces

Challenges:	Nano-objects	Interfaces
Techniques:	Interferometry	

Scientific Opportunity

Interface dynamics are of fundamental interest to the soft matter community. Chemical reactions, charge transport, and many device functions occur at interfaces between solids, liquids, and gasses. Both the chemistry and morphology of the interfaces, and how they change over the second to microsecond timescale, are critical to understanding and predicting the function of this important class of materials. Examples include the complex structure and dynamics of the solid – electrolyte interphase, electrical-double layers, photosynthesis, and catalyst surfaces.

Impediments to probing interfaces include the relatively low interfacial volume, the difficulty in accessing the interface (which requires a path through one of the materials), and the second to nanosecond timescale over which the dynamics of interest occur. These obstacles have limited existing probes in revealing either local or statistical information on the behavior of materials at interfaces.

Importance of ALS-U

ALS-U will enable: 1) x-ray absorption spectroscopy to probe the interfacial chemistry, 2) scattering to elucidate the statistical structure, and 3) coherent imaging to uncover the local structure to the damage limit, all with the potential for dynamics spanning nanoseconds to hours. In addition, polarization control of soft x-rays has the added ability to be sensitive to molecular alignment, potentially revealing a completely new measure of alignment dynamics of molecules at interfaces. In many cases, a spectroscopic signature in an upper layer can be exploited to find specific energies at which we can match the effective electron density close to vacuum and probe the interface as if it were a free interface.

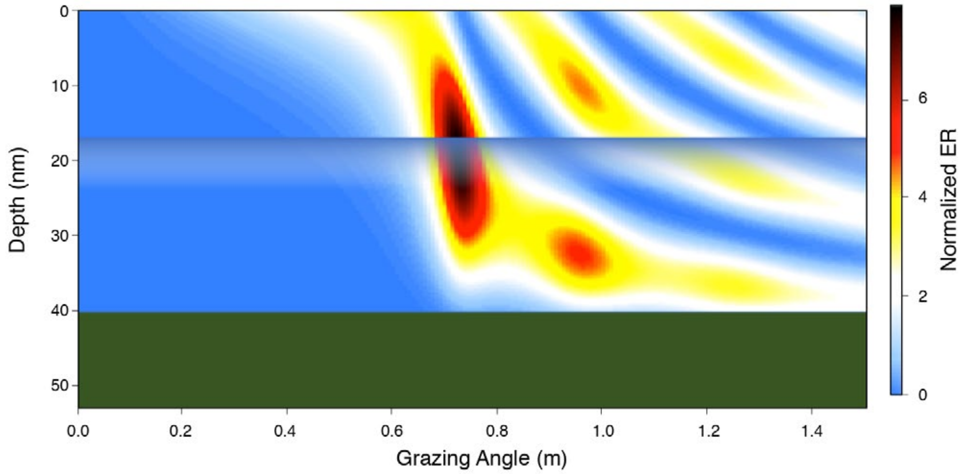

Figure 3.3.7. Standing waves formed in low-angle reflection off a thin film or heterostructure can enhance the amplitude of the x-ray wave field at the surface or buried interface with XPCS. The image is a simulation of wave-field amplitude (color scale) as a function of grazing angle (horizontal) and depth relative to the interface (vertical). Near the critical angle a large interface enhancement is observed. (Courtesy: A. Hexemer)

In more difficult cases, exploiting the energy, incidence angle, and polarization of soft x-rays will allow preferential sampling of the interfacial region and the ability to probe interface dynamics. The electric field intensity of a standing wave in the tender x-ray range is shown in Figure 3.3.7, where, near the critical angle, the incident and outgoing wave constructively interfere to generate maximum field intensity at the buried interface. This enhancement can be used to probe the chemistry and structures of interfaces and the dynamics at buried interfaces using XPCS (e.g., see Figure 3.3.8).

An alternative approach to “sectioning” soft-matter interfaces is to apply the standing-wave technique described in Section 2.3, but instead to form the standing wave in free space by splitting and recombining a soft or (more likely) tender x-ray beam. The soft-matter interface can then be translated through the standing wave rather than needing to tune the antinode of the standing wave through the interface by controlling the incidence angle near the critical angle.

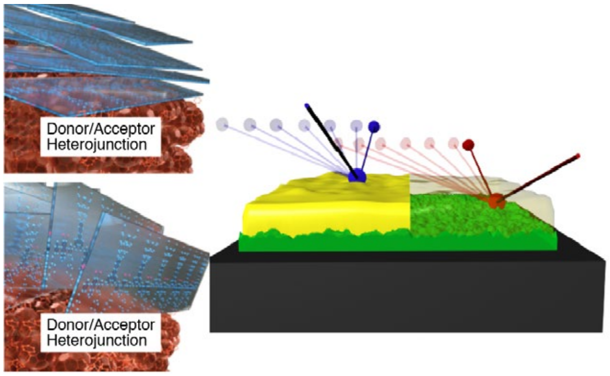

Figure 3.3.8. Left: Schematic diagrams of the buried interfaces between donor and acceptors in a bilayer organic photovoltaic device, where different orientations of the donor molecules are shown. Right: Schematic of polarized x-rays probing the surface and buried interface in the bilayer [1].

Broader Scientific Impact

With ALS-U, the coherent x-ray intensity will increase by two to three orders of magnitude. Since the fastest time accessible by XPCS scales as the inverse square of intensity, ALS-U will be transformative for correlation spectroscopy-based studies. The standing-wave geometry will allow access to interfacial dynamics down to the nanosecond time regime and thereby will enable a deeper understanding of diverse soft-material and soft/hard composite-material systems.

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3.3.5 Elucidating Transport in Soft Matter

Challenges:	Entropy	Flows	Confined Spaces
Techniques:	Coherent Scattering	Interferometry	

Scientific Opportunity

Ionomers are ion-containing polymers that facilitate ion transport through the ion-rich phase in their morphology. Ionomers are commonly used as the solid–electrolyte separator between the electrodes in many electrochemical-energy devices. These materials must conduct the ions in a mechanically robust matrix that inhibits the crossover of reactants and products. A class of ionomers well suited for this role is sulfonated ionomers—in particular, perfluorosulfonic-acid (PFSA) ionomers, which have been widely used and studied since the introduction of Nafion® in the 1960s, especially as the proton-exchange membrane for fuel cells.

Ionomers are more complex than many widely studied polymers and are always in quasi-equilibrium state due to the strong electrostatic interactions and their less well-defined chain structure. Self-assembly of ionomer pore structure is thought to be influenced by wetting interactions at both the substrate and free (vapor) interfaces as well as by confinement effects from the film structure (Figure 3.3.9). When the ionomer is in contact with water vapor, interfacial resistance limits the water transport into the membrane, leading to nanostructural changes that are four orders of magnitude slower than when the membrane contacts liquid water, in which equilibrium is reached in seconds. Such significant changes in water kinetics—from sub-seconds to hours—which are due to the wetting interactions at the surface, can be understood only by measuring the dynamics of water and ion transport through the ionomer's surface and underlayers with better time and spatial resolution than is presently possible. Advanced scattering techniques at ALS-U are capable of measuring the coupling between water mobility and dynamics of mesoscopically linked nanodomains in ionomers with responsive interfaces.

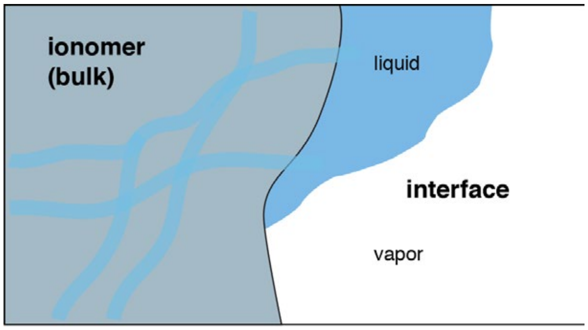

Figure 3.3.9. Schematic of the cross-section of the interfaces between an ionomer and liquid and vapor water. Ionic and water transport across the water/ionomer interfacial region is ~4 orders of magnitude more facile than across the ionomer/vapor interface, indicating a dominant correlation between wetting interaction, polymer motion, and ionic transport. (Courtesy: Z. Rostomian)

A robust debate continues over the exact nanostructure and connectivity of these domains and their interactive role in species transport, in part driven by the desire to improve and optimize material functionalities (e.g., conductivity vs. stability) by understanding the interrelation between transport mechanisms and behavior of mesoscopically connected water/ion channels. Moreover, their success in fuel cells as the electrolyte/separator has made them of interest for other solid-state energy-conversion and storage devices, such as flow batteries and solar-fuel generators, for which the ionomer behavior is expected to differ.

Importance of ALS-U

Techniques such as quasi-elastic neutron scattering have proven useful for probing the picosecond dynamic behavior of water in the polymers to explore confinement, characteristic residence time, and diffusion of water in clusters or ion channels, which could provide structural information complementary to that obtained by x-ray scattering techniques. However, most of these techniques have not been able to observe the chemical structure beyond the nanoscale, including the distribution, connectivity, and behavior of sulfonic-acid moieties and their dynamic interactions with the other species (e.g., counter-ions, solvents, etc.).

The high brightness, coherence, and spectroscopic sensitivity of ALS-U will have the potential to scan across critical time and length scales and provide an avenue to develop tools capable of: 1) probing the mobility of the ionomer's ionic moieties and the water behavior around them; 2) measuring the confinement and relaxation time of solvents; and 3) observing the mesoscale transport pathways and responsive interfaces as well as their sub-second response to environmental excitations. With such knowledge, the structure–transport–function relationship of ion-conductive polymers can be elucidated, leading the way to designing new materials by exploiting the solvent–polymer interactions, manipulating non-covalent interactions, and tuning mesoscale connectivity of domains, all of which can improve ionomer performance in devices.

Broader Scientific Impact

Probing fluctuations in ionomer nanostructures in the presence of multiple species would provide insight into optimal electrolytes and operating regimes for improving the performance of a variety of electrochemical technologies. Moreover, sulfonated ionomers have seen increased interest as water-treatment membranes, and understanding the transport mechanisms of anions and cations is key to the flux rejection tradeoff. When the water mobility increases in water-purification membranes, salt rejection decreases while the water flux increases, making water behavior in hydrated nanostructures an important aspect of the ion-exchange process. Thus, measuring water motion and probing water–polymer interactions at the necessary length and timescales would provide critical information for assessing the factors controlling the performance of these materials and for developing new polymer compositions for clean-water applications.

3.3.6 Probing Complex Cellular Machinery

Challenges:	Nano-objects	Flows	Confined Spaces
Techniques:	Coherent Imaging		

Scientific Opportunity

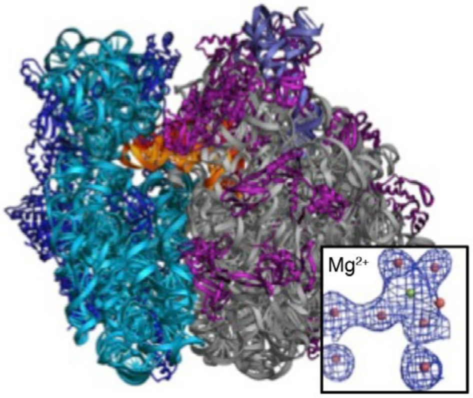

Figure 3.3.10. Mg and other ions are essential to ribosome function. These and other light elements can be located in these structures through native phasing. (Image from Protein Data Bank)

Dynamic interactions and structural hierarchies between biological molecules drive all processes in life, from translation of genetic information to gating of neurons. Delineating these interactions requires analysis on a wide length scale from the atomic level, as in the interaction between a salt ion and a protein surface, to structures on the order of microns, as in the assembly and disassembly of actin filaments used for cell mobility. The timescale for biological processes within the cell also varies widely, from the microsecond folding of small proteins to the minutes-long process of DNA replication. To gain fundamental knowledge about biological processes requires use of a wide range of methods including spectroscopy, microscopy, scattering, interferometry, and diffraction technologies—all tools that benefit from synchrotron light sources and that will be enhanced with the higher brightness enabled by ALS-U.

RNA translation: One example of large, complex cell machinery is the ribosome. The eukaryotic ribosome is a ~25-nm-sized protein–ribonucleic acid complex that resides outside the cell nucleus. Genetic information is carried from the nucleus to the ribosome in the form of RNA, and the ribosome reconstructs proteins from that information, building one amino acid residue at a time based on the original DNA sequence. While huge insights have been gained during the last decade into the structure and mechanism of the ribosome, many questions remain to be answered to fully understand and ultimately control this complex biological machine. For instance, what is the mechanism by which drugs bind to and alter ribosomal function? How are the events of nucleic acid binding and protein synthesis timed and coordinated? How does the ribosome recover from errors in protein production? New technical developments enabled by ALS-U will allow us to start answering some of these questions.

Macromolecular crystallography with tender x-rays: Although macromolecular crystallography is one of the best-established synchrotron techniques, with experiments typically performed around 12 keV for highest-resolution diffraction, tender x-rays can offer complementary information. Obtaining anomalous diffraction data for native phasing experiments near the phosphorus or sulfur absorption edges in protein crystals is a very powerful method for determining protein structure. This method probes the sample in its “native” state, in the sense that no exogenous heavy elements or selenomethionine incorporation is required, and the anomalous signal for the lighter elements becomes stronger as the absorption edge is approached. Since most proteins contain sulfur and all nucleic acid contains phosphorous, the method is applicable to a very wide range of proteins and protein–nucleic acid complexes. The M edges of radionuclide-incorporated proteins can also be reached with a tender x-ray beamline. Currently, the protein database contains only a few structures of radionuclide-bound proteins, but interest is growing rapidly as researchers search for radionuclide–protein systems for bioremediation and for radiotherapy and radioimaging applications. With access to the absorption edges of light elements of significant biological importance, such as P, S, Cl, K and Ca, it is amenable to identify and locate these elements in protein structures. In the case of the ribosome structure, many questions about the role of metal ions are still open and could be answered [1,2]. However, diffraction experiments at the soft and tender x-ray energies are extremely challenging due to the strong absorption of most materials in these regions. Since the sample itself can effectively become a “beam stop,” only small crystals can be used, and thus a micron-sized, high-brightness beam is essential. Experiments must be performed in a helium or a vacuum environment, both of which present additional technical challenges. Radiation damage also becomes a significant issue, and often multiple samples must be screened and used to collect a successful complete dataset. Currently, there is only one tender x-ray beamline in the world dedicated to crystallography, located at Diamond Light Source [3].

Importance of ALS-U

ALS-U will provide a unique opportunity to combine native phasing with more standard hard x-ray diffraction because it will provide high brightness at both tender and hard x-ray energies. Co-located endstations, specializing in either end of the ALS-U x-ray spectrum, would allow samples to be efficiently screened, for example, on a hard x-ray beamline, and then immediately run on a native phasing beamline. In addition, high-resolution data obtained from a sample could be combined with low-resolution native data on the same crystal, precluding issues resulting from non-isomorphism.

Broader Scientific Impact

The ribosome is an example of an assembly of proteins and nucleic acid that functions as a cellular machine to translate genetic information into all the cellular components needed for survival. Many other complex "machines" exist in the cell. For example, the proteosome complex regulates concentrations of proteins by recycling misfolded or unnecessary proteins, while the nucleosome is a concentrated package of DNA and proteins which folds up into chromatin and carries epigenetic information that can be gained during an individual's life and then passed on to offspring. New tools and combinations of tools at ALS-U will enable the determination of the higher-order structures of these complex assemblies, as well as structures of the individual proteins within the assembly and precise information on locations of ions within those individual proteins. Together, this information will enable unprecedented insight into the fundamental workings of these complex cellular machines.

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3.3.7 Designing Biosystems for Biofuels

Challenges:	Nano-objects	Confined Spaces
Techniques:	Coherent Imaging	

Scientific Opportunity

Designer microbes and plants are the key to producing affordable biofuels and bioproducts as well as to developing new medicines and vaccines. The use of plant biomass as feedstock for biomanufacturing is a multistep process. It requires the production of plants amendable to deconstruction by engineering cell-wall biosynthesis, developing enzymes to break down the biomass into monomers, and designing microbes to transform the released sugars and aromatics into fuel.

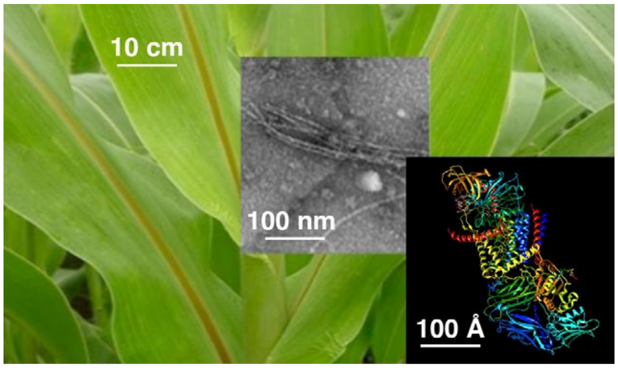

Figure 3.3.11. Sorghum plant (background) with inset of microfibrils synthesized by cellulose synthase (middle, picture from [1]), and crystal structure of bacterial cellulose synthase with cellulose analogue substrate (right).

Plant cell wall architecture: The process of biofuel production starts with and requires a fundamental understanding of plant cell-wall architecture (Figure 3.3.11). Cellulose, the main component of plant cell walls, is arranged in a matrix of proteins and other polysaccharides, which can be further coated with lignin, a complex polyphenolic network. Both the structure of these components individually on the molecular level, and the imaging of larger structures formed of these components, give vital information on the architecture of plant cell walls. Delineating the chemical interactions and bonding characteristics between cell-wall components is necessary for their control, both for deconstruction for biofuel synthesis and for the bioengineering of materials to make them stronger. Recently, it has been shown that cellulose synthase-8 is sufficient for cellulose biosynthesis in vitro [1]. The synchrotron techniques of soft x-ray tomography, spectromicroscopy, and high-resolution FTIR have allowed a view into subcellular structures, and these techniques stand to benefit from higher brightness sources. ALS-U will enable high-throughput tomographic diffractive imaging at the expected damage-limited resolution of ~10 nm in just 10–20 seconds, thereby allowing subcellular positioning of macromolecular assemblies to be a design parameter in bioengineering.

Ptychographic imaging with chemical contrast: Soft x-rays with wavelengths from 5–50 Å typically have attenuation lengths of several microns in matter. This makes them well suited for studying biological structures on the mesoscale that have features that are inaccessible to optical microscopy and have sample volumes too thick for electron microscopy. In addition, the interaction of soft x-rays with core-shell electrons provides chemical contrast at the K-edges for light elements and the L-edges of the transition metals. Soft x-ray tomography has proved a very powerful technique that has been pioneered by the National Center for X-Ray Tomography at the ALS. However, the resolution of x-ray microscopes is limited to the finest features that can be fabricated by electron-beam lithography in the diffractive x-ray optics. A complementary approach is x-ray ptychography, which can achieve high-resolution imaging without high-resolution optics. Novel x-ray optics, the high coherent flux provided by the ALS-U source, and advanced reconstruction algorithms will enable high-throughput cryogenic microscopy with the goal of enabling damage-limited spatial resolution of ~10 nm for cryogenic biological samples with full spectral contrast.

Importance of ALS-U

Spatial organization in biological systems is critical for normal function, from the localization of specific proteins in cell division and motility, to the xylan “glue” that binds cellulose into the plant wall structure [2], to carboxysomes, which are microbial organelles for CO_2 fixation [3]. The development of methods to label proteins with metals or other molecules detectable by soft x-rays will enable x-ray-based assays for subcellular biological self-assembly, catalysis, and the visualization of cellular responses to environmental perturbations. Likewise, imaging inclusions with naturally containing sulfur or phosphorous may potentially serve as a sensitive readout of cellular metabolic status. For FTIR, ALS-U provides the opportunity to redesign front-end optics for improved performance, which could lead to better focusing and a two- to three-fold increase in brightness, as well as the potential for improved stability of the source and some increased flux in the far-IR ($<500\ \mathrm{cm}^{-1}$). More broadly, there are exciting new findings relating phosphate status and cellular homeostasis/stress responses that suggest a previously blacked-out perspective on cellular metabolism could be visualized with soft x-ray methodologies.

Broader Scientific Impact

The ability to visualize the organization and chemical composition of subcellular structures will play a transformative role in engineering for biofuels and green chemicals. This will provide an entirely new means of phenotyping engineered biological systems.

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3.3.8 Advancing the Development of New Therapeutics

Challenges: Nano-objects Confined Spaces

Techniques: Coherent Imaging

Scientific Opportunity

What if synchrotrons became the screening tool of choice for identifying new therapeutics? Soft x-ray sources of high brightness could play a new role in drug discovery and metabolomics with major contributions to human health and manipulation of microbial communities. The simplicity of solution-scattering sample preparation (no crystals) and capability of collecting in nearly any solution environment make scattering a natural screening technique. The primary challenges of transforming x-ray scattering into a screening platform to identify important metabolites are three-fold: sensitivity, quantity of material, and radiation damage. These challenges can only be overcome at a synchrotron with a high-brightness source.

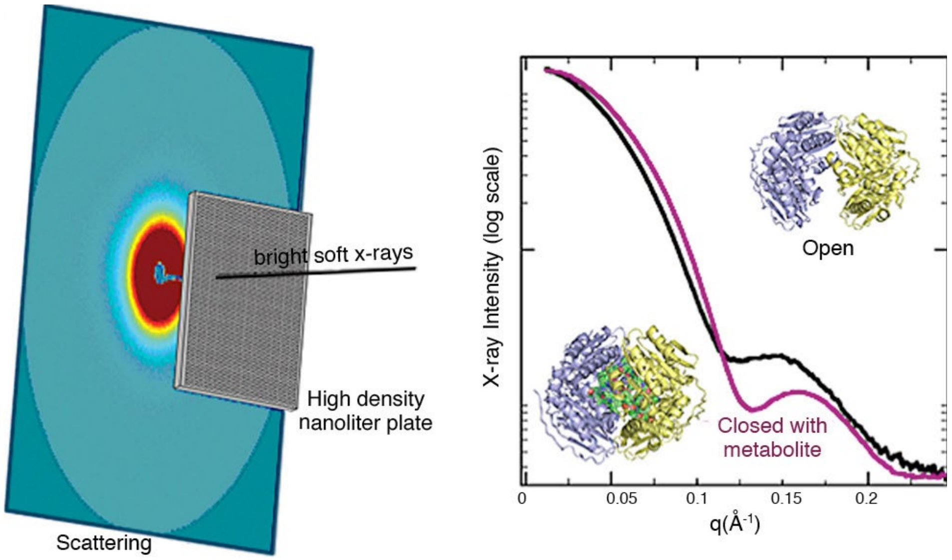

Figure 3.3.12. High-density, nanoliter screening of conformation to identify important drugs and metabolites with high-brightness soft x-rays. Scattering from solutions of macromolecules is sensitive to conformation and can be used as an assay competitive with current fluorescence-based screening techniques [2].

A powerful combination of solution methods: The combination of small-angle scattering, fluctuation scattering, and x-ray footprinting provides a unique platform on which to advance drug development. These three techniques all benefit from a high-brightness soft x-ray source. X-ray scattering senses conformation comprehensively, from the sub-nanometer [1] to the micrometer length scale [2]. The structure of biological macromolecules often changes when small molecules bind to active sites or when molecules interact to form assemblies (Figure 3.3.12). Macromolecules at the nanoscale are shaped by electrostatic interactions and are subject to thermal fluctuations. In some cases, a macromolecule's function within an organism is to bind and chemically modify metabolites for use in biological pathways. In other cases, binding changes activity by stabilizing a conformation that otherwise is transient due to thermal fluctuations. Binding events can shield a metabolite from solvent environments, avoiding wasteful side products and enabling remarkable chemistry. Solution x-ray scattering is sensitive to these changes. Typical drug-screening paradigms use fluorescent labels and libraries of thousands of compounds on nanoliter-sized samples. They identify binding but not changes in conformation. Contrasting the conformation induced by members of these libraries as probed by x-ray scattering provides a thus-far unexploited alternative approach if nanoliter volumes of fluorescent screens can be probed. Fluctuation x-ray scattering (FXS) is a natural extension of standard small-angle x-ray scattering, as it provides experimental access to the information describing the full variation of the scattered x-rays beyond the angular mean [3]. This additional information can be used to strengthen structure determination. By performing the solution scattering experiment with an ultrabright source, probing small volumes of samples while using x-ray snapshots below rotational diffusion times, the information content of the data can be significantly enhanced. An FXS experiment on biological materials is performed either in solution, requiring exposures at the nanosecond timescale, or with particles frozen in ice, similar to a setup used in cryo-electron microscopy.

The ultrabright x-ray beams in the tender and soft x-ray regime will allow rapid acquisition of FXS data of biological systems. The effect of the additional data will result in structural models with tighter confidence intervals, thus allowing for an improved understanding of conformational changes in biology. Highly complementary to solution scattering, x-ray footprinting reveals specific interaction points between molecules in solution, as well as location and dynamics of bound waters [4]. Bound or structural waters are required for folding, stability, enzyme activity and protein–protein interactions. It is known that grooves on the protein surface and cavities inside the transmembrane protein channels are formed by the interaction between bound water and amino-acid residues. In addition, it has been shown that water can help proteins achieve an “optimum association” and that water is critical in the design of protein–protein and protein–molecule interfaces in drug design. Combining the detailed interaction information resulting from radiolytic footprinting with the overall structural conformation obtained from solution scattering, all of which can be carried out in buffers representing physiologically relevant environments, will vastly accelerate drug-design efforts and will significantly advance our fundamental understanding of biological processes.

Importance of ALS-U

To increase sensitivity and reduce the quantity of sample required, soft x-rays have a ten-fold-higher scattering cross-section relative to the hard x-rays in common use. Biological small-angle x-ray scattering has relied on hard x-rays and is increasingly used for measuring macromolecular shape and shape variation. The preference for hard x-rays is in part historical: most new users are crystallographers with experience and access to hard x-ray sources. For screening with solution scattering, detecting conformational change is the primary goal rather than defining the structure. Sampling Bragg spacings of 0.1 nm is rare and only possible with hard x-rays. By using soft x-rays, the information is conveniently further from the primary beam, where background can be high, plus the amount of sample required for equivalent signal is at least ten-fold smaller.

Maximizing brightness will be critical for several reasons. First, small target samples are most desirable to increase the size of the screening library with limited quantities of macromolecules. Second, to overcome radiation damage on small sample volumes, sufficient signal must be generated before macromolecules diffuse and interact with one another. The scattering analogy to experiments conducted at free-electron lasers, where samples must diffract before they are destroyed, is ***scatter before they diffuse***. At ALS-U, a single pulse is estimated to have 10^9 photons in as small as a 1 μm spot, which should be sufficient for a complete experiment with currently used concentrations. FXS experimental requirements, in particular, dictate the use of ultrabright beams as delivered by ALS-U. The total signal in an FXS experiment is mainly determined by the brilliance of the beam and the number of snapshots taken. By reducing the exposed area, it becomes easier to measure small intensity fluctuations that lie at the foundation of FXS. An increase in flux and an increase in scattering cross-section by performing the experiment with soft and tender x-rays will strengthen the signal as well. The x-ray footprinting experiment makes use of absorbed energy to create hydroxyl radicals in solution, and uses the resulting covalent modification of macromolecules to determine conformation and dynamics of biological systems. The absorption of x-rays in the experiment is primarily in the range of 1–4 keV photons, and the higher the brightness, the better the signal to noise, the smaller the sample volumes required, and the shorter the timescale that can be probed. Because of this, ALS-U will enable microsecond kinetic investigations of biological molecules in solution.

Scientific Impact

Proteins are the protagonists of life, and understanding their structure and function is critical to understanding nearly every fundamental biological process, from translation of genetic information through the entire life cycle of the cell. Through tremendous effort over the last decade, huge progress has been made in delineating protein structure. But it is also increasingly clear that protein structure alone is not sufficient to form a complete understanding of biological processes or to effectively produce drugs to combat disease. Solution-scattering methods combined with radiolytic modification methods together give the level of structural and interaction detail necessary for understanding fundamental biological processes and to effectively design drugs to combat disease.

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Appendices

APPENDIX A. CONTRIBUTORS TO THIS REPORT

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Allendorf	Mark	SNL
Aloni	Shaul	LBNL - Molecular Foundry
Arenholz	Elke	LBNL - Advanced Light Source
Ashby	Paul	LBNL - Molecular Foundry
Bailey	Susan	LBNL - Advanced Light Source
Baker	Alex	LLNL
Bare	Simon	SLAC - SSRL
Belkacem	Ali	LBNL - Chemical Sciences Division
Bluhm	Hendrik	LBNL - Advanced Light Source
Bostwick	Aaron	LBNL - Advanced Light Source
Bras	Wim	ORNL - SNS
Brewster	Aaron	LBNL - Molecular Biophysics & Integrated Bioimaging Division
Brodie	Eoin	LBNL - Climate & Ecosystems Sciences Division
Bryant	Diane	LBNL - Advanced Light Source
Chabinyc	Michael	University of California, Santa Barbara
Chakhalian	Jak	Rutgers University
Chen	Gong	LBNL - Molecular Foundry
Chen	Xiaoqian	LBNL - Advanced Light Source
Chow	Ken	LBNL - Advanced Light Source / Engineering Division
Chuang	Yi-De	LBNL - Advanced Light Source
Comin	Riccardo	MIT
Cooper	Jason	LBNL - Chemical Sciences Division
Cordova	Isvar	LBNL - Advanced Light Source
Coric	Mihael	LBNL - Advanced Light Source
Crommie	Mike	University of California, Berkeley / LBNL - Materials Sciences Division
Crumlin	Ethan	LBNL - Advanced Light Source
Cuk	Tanja	LBNL - Chemical Sciences Division
da Silva Neto	Eduardo	University of California, Davis
Denlinger	Jonathan	LBNL - Advanced Light Source
Devaraj	Arun	PNNL
Drisdell	Walter	LBNL – Chemical Sciences Division / JCAP
Eichhorn	Bryan	University of Maryland
El Gabaly	Farid	SNL
Emori	Satoru	Stanford University
Fadley	Charles	UC Davis / LBNL - Materials Sciences Division
Falcone	Roger	LBNL - Advanced Light Source
Farhan	Alan	LBNL - Advanced Light Source
Fedorov	Alexei	LBNL - Advanced Light Source
Feng	Xuefei	LBNL - Advanced Light Source
Fischer	Peter	LBNL - Materials Sciences Division
Freychet	Guillaume	LBNL - Advanced Light Source
Gann	Eliot	NIST
Gessner	Oliver	LBNL - Chemical Sciences Division
Ghiringhelli	Giacomo	Politecnico di Milano
Gilbert	Benjamin	LBNL - Energy Geosciences Division
Gilbert	Dustin	NIST

Last Name	First Name	Organization
Gilbert	Ian	NIST
Gilbert	Pupa	University of Wisconsin - Madison
Glans	Anders	LBNL - Advanced Light Source
Glover	Ernie	Gordon and Betty Moore Foundation
Goldberg	Kenneth	LBNL - Advanced Light Source
Grutter	Alexander	NIST
Guo	Jinghua	LBNL - Advanced Light Source
Heinz	Tony	Stanford University / SLAC
Helms	Brett	LBNL - Molecular Foundry
Heske	Clemens	University of Nevada, Las Vegas
Hexemer	Alexander	LBNL - Advanced Light Source
Holman	Hoi-Ying	LBNL - Climate & Ecosystem Sciences Division
Houle	Frances	LBNL - Chemical Sciences Division / JCAP
Hussain	Zahid	LBNL - Advanced Light Source
Idzerda	Yves	Montana State University
Johnson	Peter	BNL
Jozwiak	Chris	LBNL - Advanced Light Source
Jungwirth	Thomas	Academy of Sciences of the Czech Republic
Kalinin	Sergei	ORNL
Kaminski	Adam	Iowa State University
Kao	Li Cheng	LBNL - Advanced Light Source
Kavner	Abby	University of California, Los Angeles
Kevan	Steve	LBNL - Advanced Light Source
Klewe	Christoph	LBNL - Advanced Light Source
Kumar	Dinesh	LBNL - Advanced Light Source
Kunz	Martin	LBNL - Advanced Light Source
Lanzara	Alessandra	University of California, Berkeley / LBNL - Materials Sciences Division
Lee	James	LBNL - Advanced Light Source
Lee	Jonathan	LLNL
Liebi	Marianne	MAX IV Laboratory / Lund University
Liu	Yi	LBNL - Molecular Foundry
Liu	Yi-Sheng	LBNL - Advanced Light Source
Liu	Yun	University of Delaware / NIST
Ma	Eric Yue	Stanford University
MacDowell	Alastair	LBNL - Advanced Light Source
Martin	Michael	LBNL - Advanced Light Source
May	Steven	Drexel University
Mo	Sung-Kwan	LBNL - Advanced Light Source
Moore	Rob	SLAC
Moreschini	Luca	LBNL - Advanced Light Source
Mortimer	Jenny	LBNL - Joint BioEnergy Institute
Morton	Simon	LBNL - Berkeley Center for Structural Biology
Moser	Simon	LBNL - Advanced Light Source
Myneni	Satish	Princeton University
N'Diaye	Alpha	LBNL - Advanced Light Source
Nico	Peter	LBNL - Energy Geosciences Division
Nix	Jay	Molecular Biology Consortium
Noad	Hilary	Stanford University / SLAC
Nordlund	Dennis	SLAC / Stanford
Ogasawara	Hirohito	SLAC
Ogletree	Frank	LBNL - Molecular Foundry
Ohldag	Hendrik	SLAC - SSRL
Osuji	Chinedum	Yale University
Padmore	Howard	LBNL - Advanced Light Source
Pandolfi	Ronald	LBNL - Advanced Light Source
Parkinson	Dula	LBNL - Advanced Light Source
Pejakovic	Dusan	Gordon and Betty Moore Foundation
Pena	Jasquelin	University of Lausanne
Piper	Louis	Binghamton University
Prasher	Ravi	LBNL - Energy Storage and Distributed Resources Division
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Qiao	Ruimin	LBNL - Advanced Light Source

Last Name	First Name	Organization
Qiu	Zi Q.	University of California, Berkeley
Ralston	Corie	LBNL - Molecular Biophysics & Integrated Bioimaging Division
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Robin	David	LBNL - Advanced Light Source / ATAP
Rotenberg	Eli	LBNL - Advanced Light Source
Roy	Sujoy	LBNL - Advanced Light Source
Russell	Thomas	University of Massachusetts Amherst
Sallis	Shawn	Binghamton University
Salmeron	Miquel	LBNL - Materials Sciences Division
Sannibale	Fernando	LBNL - Advanced Light Source / ATAP
Schmid	Andreas	LBNL - Molecular Foundry
Scholl	Andreas	LBNL - Advanced Light Source
Schwartzberg	Adam	LBNL - Molecular Foundry
Senanayake	Sanjaya	BNL
Shafer	Padraic	LBNL - Advanced Light Source
Shapiro	David	LBNL - Advanced Light Source
Shih	Chih-Kang	University of Texas
Shuh	David	LBNL - Chemical Sciences Division
Sloetjes	Sam	Norwegian University of Science and Technology
Sokol	Paul	National Science Foundation
Sokolov	Alexei	University of Tennessee / ORNL
Soles	Christopher	NIST
Srinivasan	Kumar	Western Digital
Stacchiola	Dario	BNL
Stan	Camelia	LBNL - Advanced Light Source
Steier	Christoph	LBNL - Advanced Light Source / ATAP
Stoerzinger	Kelsey	PNNL
Streubel	Robert	LBNL - Materials Sciences Division
Stubbs	Joanne	University of Chicago, GSECARS
Su	Gregory	LBNL - Advanced Light Source
Summers	Melissa	LBNL - Energy Sciences Area
Suzuki	Yuri	Stanford University
Takamura	Yayoi	University of California, Davis
Tamura	Nobumichi	LBNL - Advanced Light Source
Terminello	Louis	PNNL
Thevuthasan	Suntharampillai	PNNL
Thorne	Jim	Boston College
Toma	Francesca Maria	LBNL - Chemical Sciences Division
Toner	Brandy	University of Minnesota, Twin Cities
Urban	Jeff	LBNL - Molecular Foundry
van Buuren	Tony	LLNL
Vine	David	LBNL - Advanced Light Source
Vishik	Inna	University of California, Davis
Wadley	Peter	University of Nottingham
Wang	Cheng	LBNL - Advanced Light Source
Wang	Dunwei	Boston College
Wang	Feng	University of California, Berkeley / LBNL - Materials Science Division
Weber-Bargioni	Alexander	LBNL - Molecular Foundry
White	Ashley	LBNL - Advanced Light Source
Wilson	Kevin	LBNL - Chemical Sciences Division
Wojdyla	Antoine	LBNL - Advanced Light Source
Wray	L. Andrew	New York University
Yang	Peidong	University of California, Berkeley / LBNL - Materials Sciences Division
Yang	Wanli	LBNL - Advanced Light Source
Yano	Junko	LBNL - Molecular Biophysics & Integrated Bioimaging Division
Ye	Yifan	LBNL - Advanced Light Source
Yoshikuni	Yasuo	DOE Joint Genome Institute
Yu	Pengfei	LBNL - Advanced Light Source
Zaera	Francisco	University of California, Riverside
Zhang	Liang	LBNL - Advanced Light Source
Zhu	Chenhui	LBNL - Advanced Light Source
Zwart	Petrus	LBNL - Molecular Biophysics & Integrated Bioimaging Division

APPENDIX B. WORKSHOP CHARGE

Since its original commissioning 23 years ago, the ALS has been regularly upgraded to maintain world-class performance to enable outstanding soft x-ray science, while also supporting complementary infrared and hard x-ray tools. The scope of the planned upgrade of ALS to a diffraction-limited storage ring, a project called ALS-U, includes replacing storage-ring components, installing new undulator sources, and upgrading beamlines to dramatically increase the brightness and transverse coherence of the photon beam in the soft- and tender-energy x-ray ranges. This performance improvement means that all photons are useful in experiments that require focusing the x-ray beam into a nanosized spot or utilizing the phase of the x-ray beam for coherent scattering and diffraction.

This workshop will explore the frontiers of soft- and tender-energy x-ray science at ALS-U with the following goals:

- Identify and highlight some of the first transformative spectroscopy, diffraction, and microscopy experiments that will be enabled by fully coherent and/or intense nanofocused soft x-ray beams provided by ALS-U;
- Determine essential ALS beamline and endstation developments and upgrades needed to execute these proposed experiments; and
- Explore tools and techniques that complement coherent soft x-ray techniques and experiments and that are essential to taking full advantage of the new capabilities of ALS-U; for example, data processing analysis and interpretation tools, as well as in situ sample-preparation facilities, and multimodal characterization techniques such as optical, electron, and scanned probe microscopies, hard x-ray, and infrared tools, etc.

APPENDIX C. WORKSHOP AGENDA AND BREAKOUTS

WEDNESDAY, JANUARY 18	
8:00am–12:30pm, Plenary Session, Chair: Roger Falcone (ALS Division Director), 50 Auditorium	
8:00–8:10	**Welcome** Mike Witherell (LBNL Director)
8:10–8:25	**ALS-U Project** David Robin (ALS-U Project Director)
8:25–8:40	**ALS-U Science Opportunities** Steve Kevan (ALS/ALS-U Science Deputy)
8:40–9:00	**Additional Experimental Opportunities for New ALS-U Beamlines** Howard Padmore (ALS Division Deputy, Experimental Systems)
9:00–9:30	**Strongly Correlated Systems and the Role of Nanoscale Inhomogeneities** Peter Johnson (Brookhaven National Laboratory)
9:30–10:00	**Spin Materials** Elke Arenholz (ALS)
10:00–10:30	*Break*
10:30–11:00	**Soft X-Ray Tools for In Situ Characterization of Chemistry/Catalysis Process and Energy Materials** Peidong Yang (UC Berkeley)
11:00–11:30	**Earth and Environmental Science at ALS-U** Pupa Gilbert (Univ. of Wisconsin)
11:30–12:00	**Resonant Soft X-Ray Scattering of Liquid Crystals** Noel Clark (CU Boulder)
12:00–12:30	**Small-Angle Scattering Tensor Tomography: Nanostructure Mapping in Microscopic Samples** Marianne Liebi (MAX IV, Lund Univ.)
12:30–1:30	*Lunch*
1:30–3:00	Breakouts *(see locations below)*
3:00–3:30	*Break*
3:30–5:30	Breakouts *(see locations below)*
6:30–8:00	Catered dinner *(Building 54 Cafeteria)*

THURSDAY, JANUARY 19	
8:00–10:00	Breakouts
10:00–10:30	*Break*
10:30–12:30	Breakouts
12:30–1:30	*Lunch*
1:30–3:00	Breakouts
3:00–3:30	*Break*
3:30–5:30	Breakouts

FRIDAY, JANUARY 20	
8:00–12:00	Discussion/Report (Conference Room 15-253)
12:00	Adjourn

BREAKOUT GROUPS			
Conference Room	**Breakouts**	**Local Leads**	**Techniques**
33-306	Quantum Materials	Rotenberg (ALS), Weber-Bargioni (Foundry)	ARPES, RIXS, imaging
33-106	Spin Materials	Arenholz, Scholl (ALS)	Scattering/XPCS, imaging
80-234	Bioscience	Ralston, Zwart, Adams (MBIB)	Tender PX, Imaging, FXS
2-400F	Soft Matter	Hexemer (ALS), Russell (MSD), Liu (Foundry)	Scattering/XPCS
6-2202	Chemistry & Catalysis	Bluhm, Guo (ALS)	Chemical imaging, RIXS, XPCS
15-253	Energy Materials	Guo (ALS)	
15-300	Environmental Chemistry	B. Gilbert, Nico (EG), P. Gilbert (U Wisc.)	

APPENDIX D. LIST OF ABBREVIATIONS, ACRONYMS, AND INITIALISMS

AFM	antiferromagnetic
ALS	Advanced Light Source
ALS-U	Advanced Light Source Upgrade
APPES	ambient-pressure photoemission spectroscopy
ARPES	angle-resolved photoelectron spectroscopy
BES	Basic Energy Sciences (program within DOE Office of Science)
BESAC	Basic Energy Sciences Advisory Committee
BRN	basic research needs
CD	critical decision
CMOS	complementary metal–oxide–semiconductor
DLSR	diffraction-limited storage ring
DOE	U.S. Department of Energy
EUV	extreme ultraviolet
FEL	free-electron laser
FM	ferromagnetic
FTIR	Fourier-transform infrared
FXS	fluctuation x-ray scattering
HTS	high-temperature superconductivity
JCAP	Joint Center for Artificial Photosynthesis
MBA	multibend achromat
NOM	natural organic matter
PEEM	photoemission electron microscopy
REXS	resonant elastic x-ray scattering
RIXS	resonant inelastic x-ray scattering
RTD	roundtable discussion
SAXS	small-angle x-ray scattering
STEM	scanning transmission electron microscopy
STM	scanning tunneling microscopy
STXM	scanning transmission x-ray microscopy
SXM	scanning x-ray microscopy
TEM	transmission electron microscopy
TM	transition metal
UHV	ultrahigh vacuum
XAS	x-ray absorption spectroscopy
XFMR	x-ray ferromagnetic resonance
XMCD	x-ray magnetic circular dichroism
XMLD	x-ray magnetic linear dichroism
XPCS	x-ray photon correlation spectroscopy