

# Proceedings of the Advanced Photon Source Renewal Workshop



Hickory Ridge Marriott Conference Hotel  
Lisle, IL.

October 20-21, 2008

February 2009

The Advanced Photon Source at Argonne National Laboratory is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

#### **About Argonne National Laboratory**

Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see [www.anl.gov](http://www.anl.gov).

#### **Availability of This Report**

This report is available, at no cost, at <http://www.osti.gov/bridge>. It is also available on paper to the U.S. Department of Energy and its contractors, for a processing fee, from:  
U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
phone (865) 576-8401  
fax (865) 576-5728  
[reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

#### **Disclaimer**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

# Proceedings of the Advanced Photon Source Renewal Workshop

Hickory Ridge Marriott Conference Hotel  
Lisle, IL.  
October 20-21, 2008

## Workshop Organizing Committee

Robert F. Fischetti	<i>Argonne National Laboratory, Biosciences Division; APS Life Sciences Council representative</i>
Paul H. Fuoss	<i>Argonne National Laboratory, Materials Science Division; APS Users Organization representative</i>
Rodney E. Gerig	<i>Argonne National Laboratory, Photon Sciences</i>
Denis T. Keane	<i>Northwestern University; DuPont-Northwestern-Dow Collaborative Access Team; APS Partner User Council representative</i>
John F. Maclean	<i>Argonne National Laboratory, APS Engineering Division</i>
Dennis M. Mills, Chair	<i>Argonne National Laboratory, Photon Sciences</i>
Dan A. Neumann	<i>National Institute of Standards and Technology; APS Scientific Advisory Committee representative</i>
George Srajer	<i>Argonne National Laboratory, X-ray Science Division</i>

# Table of Contents

Introduction	ii
Renewal of the Advanced Photon Source — White Paper	v
The Advanced Photon Source Renewal Workshop	1
Chemical Science & Engineering	5
Condensed Matter & Materials Physics	29
Engineering Applications & Applied Research	43
Fundamental Interactions in Chemical, Atomic, & Molecular Physics	70
Geological, Environmental, & Planetary Sciences	94
Interfacial Science	115
Life Sciences	134
Macromolecular Crystallography	149
Materials Science & Technology	168
Polymers & Soft Materials	188
Scope of the Advanced Photon Source Renewal Proposal	204
Appendices	
A. Advanced Photon Source Renewal Workshop Agenda	214
B. Advanced Photon Source Renewal Workshop Attendees	216
C. Beamline Mid-Term Proposals	220

## Introduction

Our nation's scientists and engineers, who are solving key problems in energy, the environment, and human health require access to the best research tools available. The U.S. Department of Energy's (DOE's) Advanced Photon Source (APS) is one such tool. Now in its 12th year of operation, the APS is the largest federally funded user facility in the U.S. as gauged by several important metrics, including number of visiting scientists per year, number of experiments performed per year, and the number of peer-reviewed journal articles published per year. This third-generation, hard x-ray synchrotron radiation research facility is the only one of its kind in the U.S. and one of three worldwide, the others being the European Synchrotron Radiation Facility at Grenoble, France, and SPring-8 at Harima, Japan.

But the new challenges in energy and the environment need sharpened tools. The problems that must be addressed in the future by APS users require a major renewal that will, within a decade, bring the APS to the state of the art in synchrotron x-ray science and maintain the facility's ability to provide the best hard x-ray capabilities to the U.S.

Since March of 2008, our user community has been engaged in a process to move forward on an APS renewal plan. From the beginning, the importance of user involvement in the development of this plan was recognized and an APS Renewal Steering Committee was formed with membership from the user community, the APS, and the APS Scientific Advisory Committee (SAC).

An open workshop held on October 20-21, 2008, was organized by the APS Renewal Steering Committee to stimulate the development of the scientific drivers for a substantial renewal of the APS. A primary goal of the workshop was to engage the SAC in identifying overarching scientific themes that would guide the technical aspects of the renewal. Two exciting themes emerged: *mastering hierarchical structures through x-ray imaging*, and *real materials in real conditions in real time*.

These two themes formed the focus for a white paper that was sent to the DOE's Office of Basic Energy Science in November 2008. This white paper outlines a proposed APS renewal that promises maximum scientific impact and high return on investment.

This document contains the proceedings of that workshop, the white paper, and the description of the proposed scope of the APS renewal.

*APS Renewal Steering Committee  
February 2, 2009*

**The APS Renewal Steering Committee:**

Robert F. Fischetti     *Argonne National Laboratory, Biosciences Division;  
APS Life Sciences Council representative*

Paul H. Fuoss            *Argonne National Laboratory, Materials Science Division;  
APS Users Organization representative*

Rodney E. Gerig        *Argonne National Laboratory, Photon Sciences*

Denis T. Keane         *Northwestern University;  
APS Partner User Council representative*

John F. Maclean        *Argonne National Laboratory, APS Engineering Division*

Dennis M. Mills, Chair *Argonne National Laboratory, Photon Sciences*

Dan A. Neumann        *National Institute of Standards and Technology;  
APS Scientific Advisory Committee representative*

George Srajer          *Argonne National Laboratory, X-ray Science Division*

# Renewal of the Advanced Photon Source — White Paper

## Executive Summary

To ensure that state-of-the-art hard x-ray tools are available for U.S. scientists and engineers who are solving key problems in energy, environment, technology development and human health, the nation's unique high-energy x-ray source needs a major renewal of its capabilities. The Advanced Photon Source (APS) renewal program responds to key scientific needs driven by our user community. The renewal encompasses many innovations in beamlines and accelerator capabilities, each of which will transform our tools and allow new problems to be solved. In particular the APS renewal dramatically expands two compelling avenues for research. Through x-ray imaging, we can illuminate complex hierarchical structures from the molecular level to the macroscopic level, and study how they change in time and in response to stimuli. Images will facilitate our understanding of how proteins fit together to make living organisms, contribute to development of lighter, higher-strength alloys for fuel-efficient transportation and advance the use of biomass for alternative fuels. Hard x-rays are also especially suited to the study of real materials under realistic conditions and in real time. The advances proposed in this area would help develop more efficient catalysts, enhance green manufacturing, point the way to artificial light-harvesting inspired by biology, and help us develop more efficient lighting. The scope of the renewal of our ~\$1.5 B facility is estimated to be ~\$350 M over five years. It is vital that the investment begin as soon as possible. The renewed APS would complement other national investments such as the National Synchrotron Light Source-II and would keep the U.S. internationally competitive.



The Advanced Photon Source at Argonne National Laboratory.

## Introduction

Supported by the U.S. Department of Energy’s Office of Science, Office of Basic Energy Sciences (DOE-BES), the Advanced Photon Source (APS) serves the nation’s largest scientific user community. Located at the Argonne National Laboratory near Chicago, Illinois, the facility provides brilliant high-energy (or “hard”) x-ray beams to 3500 users each year, who annually publish more than 1000 papers contributing to knowledge and innovation in the energy, health, environment, physical, and life sciences. At the core of the APS is a high-energy, 7-GeV electron accelerator that feeds a 1.1-km-circumference storage ring whose undulators and bending magnets deliver x-rays to almost 60 independently operating beamlines. There are only two other high-energy, third-generation storage ring x-ray sources operating around the world - the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, and the SPring-8 facility in Harima, Japan. Both facilities are planning major upgrades.

The APS began operations in 1996. To address the future needs of users and provide the best hard x-ray capabilities to the U.S., the APS requires a major renewal that would bring it to the state-of-the-art within a decade. Innovations in many instruments and beam sources would generate orders of magnitude improvements in sensi-

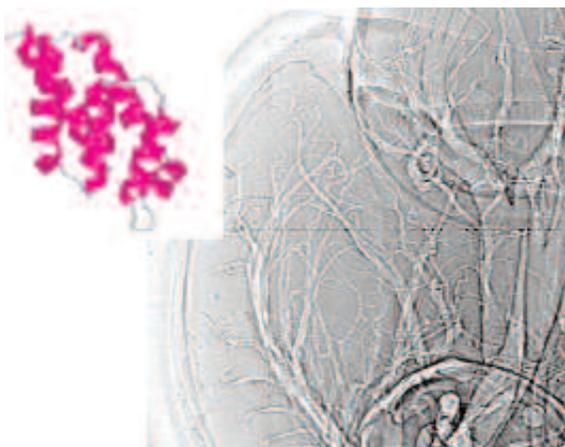
tivity and precision, deliver new capabilities that were not envisioned when the machine was built, and enable important experiments that cannot be accomplished today. The renewal plan was developed in an open process with our user community. The investments would take full advantage of our outstanding accelerator complex and skilled user base. Support for the APS renewal would complement other developments in the U.S. by offering the best source of hard x-rays.

## Scientific Vision for a Renewed APS

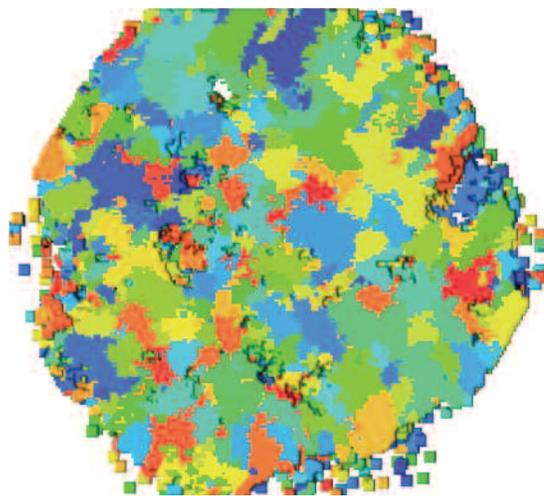
We invited input from our existing and potential user community to identify the innovations that would have revolutionary impact and address important scientific questions unanswerable with the capabilities available at the APS today. Among the spectacular potential impacts on science and engineering research that were presented, we identified two overarching themes that will guide our investments for the APS renewal: ***Mastering hierarchical structures through x-ray imaging***, and ***Real materials in real conditions in real time***. For each theme we have singled out some high-impact problems whose solution will be aided by the APS renewal.

### Mastering hierarchical structures through x-ray imaging

Hierarchical structures are pervasive—from machines to organisms. Because of their penetrating power, hard x-rays uniquely offer the ability to examine non-destructively the interior of hierarchical systems and characterize structure, composition and dynamics on length scales from nanometer to centimeter. Developments in optics, beam stability, detectors, and software are enabling revolutions in rapid imaging with



Images from proteins and living organisms will help connect the dots in understanding how genetics controls health and disease. (Courtesy W.K. Lee, ANL; © 2007 Socha et al.; licensee BioMed Central Ltd.)



Three-dimensional distribution of grains in a 1-mm cube of aluminum. (Courtesy R. Suter et al., Carnegie Mellon University)

hard x-rays inside large objects down to the nanometer length scale.

With new imaging tools we will be able to address one of the most important problems in biology—*How do proteins fit together to make organisms?* Every organism is the outward physical manifestation (phenotype) of internally-coded inheritable information (genotype).

An overarching challenge is to link genotype and phenotype, connecting the avalanche of data on genetics to

fundamental questions about biological diversity, and to medical concerns such as why one individual but not another becomes ill in response to the same stress. Resolving these questions requires techniques that bridge the scale of molecular biology to that of entire organisms. The APS is today the most productive source in the world for solving complex protein structures. Leveraging this capability at the molecular level with multiscale imaging on length scales from nanometer to centimeter will be transformative.

More than 8% of U.S. imported foreign oil could be saved if we reduce the weight of trucks and cars by only 10%, through the use of high-strength steel or aluminum alloys. Although the materials exist, we cannot yet use them because we do not understand the “springback” in these complex materials associated with stamping of automobile body parts. Springback is just one example of an engineering problem that could be solved by *better quantitative understanding and modeling of deformation in polycrystalline materials* enabled by advanced hard x-ray imaging at the APS. The techniques can also be applied to innovative new nanocomposites that offer ultimate control of properties by imitating biological materials.

***Transport of environmental contaminants*** remains inadequately understood. Advanced x-ray fluorescence imaging can address contamination problems ranging from safe storage of nuclear waste to cleaned-up manufacturing. Hard x-ray fluorescence is most appropriate to spatially resolve trace concentrations of contaminants, and promises to give important insight into the ***health and disease effects of metals in biology*** through sub-cellular imaging at the organelle level.

One of the most promising alternatives for petroleum-based fuel is ethanol obtained from biomass. Invaluable to understanding biomass conversion is ***imaging the molecular architecture of ligno-cellulose*** in plants and during processing into glucose, ethanol, and other chemical products. More generally, complex tissue is a fruitful area of study for advanced x-ray imaging, where not only structure but mechanics can be revealed by imaging of stress distribution, addressing important medical problems such as prostheses. Other major x-ray imaging challenges include ***sequestration of carbon in rock***, and ***fluid jets and sprays***. The latter example, with application to improved engine efficiency, demands not only high spatial resolution, but also ultrafast imaging.

To address these and a myriad of other important questions will require development of new, dedicated, high-performance imaging capabilities. Needs include one or more long beamlines to provide larger fields-of-view, higher spatial coherence to enhance phase contrast imaging of low-atomic number materials, new x-ray optics for nanoscale focusing, and faster detectors to take advantage of the high average brilliance of the APS and allow fast time-dependent imaging. Better software for image analysis and real-time modeling is equally important. Better electron and photon beam stability and nanopositioning of samples will be enabling goals of the renewal project. Complementary scattering and spectroscopy techniques will be developed to bridge to the molecular scale. We also plan to develop a unique, pulse-slicing source for hard x-rays that would be complementary to the new Linac Coherent Light Source (LCLS), offering tunable hard x-rays and time resolutions from 1 ps up to seconds or longer to use with imaging, diffraction, and spectroscopy. These coupled developments will lead to the orders-of-

magnitude improvement in time resolution and sensitivity that will be needed to solve the scientific challenges.

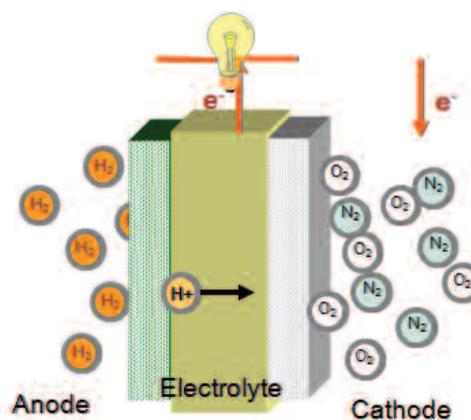
### Real materials in real conditions and real time

Hard x-rays above 20 keV are uniquely suited to penetrating complex environments and revealing atomic level structure. For example, APS researchers have studied combustion, materials under conditions of the Earth's core, surfaces buried under liquids, operating fuel cells, and catalytic reactors. To enable the dreams of scientists and engineers, and extend these experiments into new regimes, we must provide multiple techniques in one experiment to supplement the information from x-rays, and develop the ability to study in real time and provide images. With optimized beamlines, including access to complementary measurements during *in situ* experiments, improved detectors and optics, and enhanced data analysis capabilities, many important new experiments will become possible through the APS renewal. We also expect to attract a larger fraction of industrial users who are very interested in examining conditions used in manufacturing.

#### *Developing catalysts with the specificity and activity of enzymes.*

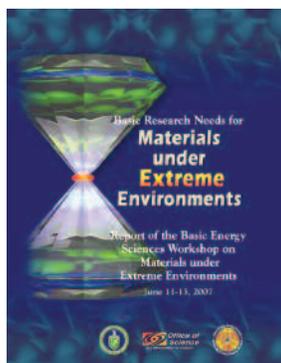
Catalysts are key to the modern world, but greatly improved catalysts are essential for development of sustainable energy. As an example, because we have been unable to develop catalysts with sufficiently high activity, fuel cells today contain very large loadings of precious metals. Yet we know that nature can produce catalysts (enzymes) that operate at low temperatures with very high activity and specificity, use readily available metals, and are resistant to degradation even in “dirty” environments.

Further development of catalysts requires understanding and perfecting their struc-



Schematic of an H<sub>2</sub> fuel cell. (Courtesy D. Myers, Argonne National Laboratory)

ture and dynamics under operating conditions. Hard x-rays are uniquely able to **penetrate high-temperature, high-pressure gas or liquid environments to reveal the molecular structure and dynamics of heterogeneous catalysts**. The added ability to image such structures and identify the active sites would be invaluable. High-speed acquisition of data is necessary to explore reaction dynamics.



The cover of this BESAC report shows a diamond anvil cell. APS is a world-leader in high-pressure research.

The APS today is the most prolific source of high-impact papers in the area of high-pressure science. These studies can be extended to more extreme conditions and shorter timescales. With new facilities for ultrafast compression and recording, we plan to enable new insights into dynamic shock compression physics. This would open the way to new regimes of extreme pressures and temperatures that cannot be sustained for long, but reveal energetic materials behavior important in weaponry.

About 20% of energy consumption in the U.S. goes to lighting, yet most lighting is very inefficient. Solid-state lighting represents a major improvement, and the development of **high-quality, inexpensive fabrication techniques will be favored by in situ studies of materials growth**.

Vast amounts of energy in sunlight are ripe for collecting if we can replicate nature's efficient mechanisms for photon-electron transfer. One key to artificial light-harvesting is understanding the complex chemical excited states involved in photosynthesis. Progress will be aided by the tunable, high-average-brilliance, 1-ps source that would be developed at the APS as a part of the renewal, accessing the large dynamic range of electron transfer after photoexcitation.

Nucleation is one of the most important phenomena controlling the structure, properties and failure mechanisms in materials, yet it is poorly understood. For example nucleation in liquids determines the structure and function of chemically synthesized

precipitates, from film emulsion to food. A major reason for our lack of knowledge of nucleation is that it is often a rare event. With a combination of high-speed imaging detectors and realistic large samples, we believe that the ***nature of nucleation can be exposed by the “triggering” of detectors*** in analogy with methods developed by high-energy physicists.

Similar approaches should shorten the cycle of development of new materials through efficient exploration of parameter space. Energy and other high-priority societal needs demand new materials with better functionality, including thermoelectrics, solid-state battery electrolytes, superconductors, and magnets.

Common to the themes described in our scientific vision – hierarchical imaging and real materials – is extending into real time and going beyond structure to examine the dynamics of materials. The APS is ideally suited for such studies over time scales from picoseconds to hours, and is complementary to the ultrafast single-pulse studies possible at the free-electron laser LCLS. Dynamical experiments will use diffraction, imaging, and spectroscopy.

Our two overarching scientific themes do not encompass all the innovations that would be implemented in the renewal, but they are ubiquitous and the improvements they would spawn will pay off in other important areas of x-ray science at the APS. For example, improved mechanical and beam stability will permit use of micron-sized crystals for protein structure determination, extending the method to a much larger number and wider range of proteins and assemblies than can currently be studied.

By developing capabilities with radically new scope addressing the two themes, together with complementary technique developments, we believe that the investment in the APS renewal will be enormously rewarded by benefits to environmentally responsible energy production and use, making the Earth a healthier planet, a stronger and more sustainable economy, human health, and scientific knowledge. Highlights have been included in this white paper, but a much

Table 1. Major light sources in the U.S.

Source Name	Location	Type	1st Year Operation	Characteristic Energy	Beam-lines	Users (2007)
Advanced Light Source	California	Third-generation storage ring	1993 (12-keV super-bend)	3.2 keV	43	1784
Advanced Photon Source	Illinois	Third-generation storage ring	1996	19.5 keV	60	3420
Linac Coherent Light Source	California	Free-electron laser	2009	N/A	4 (instruments)	N/A
National Synchrotron Light Source	New York	Second-generation storage ring	1982	7.1 keV	65	2219
National Synchrotron Light Source II	New York	Third-generation storage ring	2015	2.5 keV	~58 possible	N/A
Stanford Synchrotron Radiation Laboratory	California	Second- to third-generation storage ring	1973	7.5 keV	34	1151

fuller account is found in this proceedings, and can be seen at our Web site: <http://www.aps.anl.gov/Renewal/>.

## National Context

Table 1 lists the suite of major third-generation light sources in the U.S., and two major light sources under construction. The second-generation National Synchrotron Light Source (NSLS) in New York, which will be replaced by NSLS-II, is included for comparison.

Of these productive and complementary sources, the APS is unique with its high characteristic x-ray energy and very large user community. The APS will remain the only major hard x-ray source in the U.S. for a decade or more. Renewal of the APS will strengthen this role by providing world-class hard x-ray capabilities in the U.S. for decades to come. The APS would complement the new NSLS-II, which will deliver brilliant beams at intermediate x-ray energies, and the LCLS in California, which will deliver exceptionally bright single pulses at intermediate energies. Hard x-rays (>20 keV) are unique in penetrating complex environments and thick objects, and of-

Table 2. Major light sources worldwide.

Source Name	Location	Type	1st Year Operation	Characteristic Energy	Beam-lines	User Visits (06)
Advanced Photon Source	U.S.	Third-generation storage ring	1996	19.5 keV	60	3420
European Synchrotron Radiation Facility	France	Third-generation storage ring	1994	20.3 keV	49	6,090
PETRA III Light Source	Germany	Third-generation storage ring	2009	20.8 keV	14 (up to 20)	N/A
SPring-8	Japan	Third-generation storage ring	1997	28.9 keV	48	N/A

fering very high Q-space resolution. The application of these characteristics to important scientific problems forms the basis of our renewal proposal. Complementary developments in soft x-ray science will be facilitated at the Advanced Light Source in California, at NSLS-II, and at possible future light sources. In addition to synchrotron sources there are other facilities in the U.S., such as the Spallation Neutron Source in Tennessee, that use other types of radiation and probe matter in complementary ways.

## International Context

Table 2 lists the only high-energy, third-generation synchrotron sources operating or under construction in the world. The newest source, PETRA-III, will have lower emittance than the other three sources and will provide strong competition, although it will have relatively few beamlines.

SPring-8 and the ESRF are engaged in renewal and upgrade. At SPring-8, an x-ray free-electron laser is under construction that will provide a stand-alone new capability and allow injection of single bunches into the storage ring. SPring-8 is also engaged in beamline renovation and building, and planning for a new storage ring lattice upgrade in the next few years. The ESRF is in the advanced stages of securing ~ 170-MEuros capital investment for major beamline renovations, conceptually similar to the approach we are proposing for the APS renewal. We have benefitted from close involvement with these facilities. For instance, a recent Three-Way Meeting be-

tween SPring-8, ESRF, and APS management on the subject of upgrade and renewal was held in the spring of 2008 at the APS. Our renewal will help us define the state of the art in the key areas we have identified. Especially in imaging, we need to develop new capabilities to compete internationally. Without a major renewal we would slip behind in most areas.

Table 3. APS workshops: 2006-2008.

Title	Date
APS Renewal Workshop	Oct. 20-21, 2008
Small-Angle Scattering Short Course: Beyond $R_g$	June 28-July 2, 2008
Understanding Condensed Matter Dynamics at the Microscopic Level	June 23, July 2, 2008
Workshop to Introduce High-Resolution Inelastic X-ray Scattering on Earth Materials Using Synchrotron Radiation	May 31-June 1, 2008
Short-Pulse X-rays at the APS	May 9, 2008
APS Upgrade/ERL Optics Workshop	April 23, 2007
New Applied Materials Research from Improved High-Energy X-ray Sources	July 28, 2006
Detectors	July 21, 2006
Sub-meV Energy Resolution	July 20, 2006
Microscopy	July 17, 2006
Biology and Life Sciences	July 14, 2006
New Structural Science from Improved High-Energy X-ray Sources	July 13, 2006
Picosecond Science	June 29, 2006
Novel Science with Polarized X-rays	June 29, 2006
Interfacial and Surface Science	June 29, 2006
Coherence/Imaging	June 15 & July 11, 2006
Workshop on Intermediate-Energy X-rays	June 13, 2006
Science Opportunities Using X-rays and Split-Gap High-Field Magnets	June 8-9, 2006
Ultrafast SAXS	June 6, 2006
Fourth CW and High Average Power RF Workshop	May 1-4, 2006

## Development Process for the Renewal Plan

For the last five years the APS has been planning with its users for new high-priority scientific capabilities. Table 3 shows those workshops that have been held in just the last two years.

The DOE held a major peer review of the APS in December of 2007 that strongly recommended development of a renewal plan. Building on previous strategic planning, we solicited specific proposals associated with the renewal and began discussion of these at the May 2008 User Meeting, attended by over 600 users. Each beamline at the APS, whether operated by the facility, or independently by a collaborative access team, was encouraged to submit a science-based proposal on the investments needed to achieve world leadership. Forty-two beamline proposals were received. These were

Table 4. The APS Scientific Advisory Committee.

Name	Research Field
Prof. Jens Als-Nielsen <i>Neils Bohr Institut, Copenhagen</i>	X-ray physics
Dr. Michelle V. Buchanan <i>Associate Laboratory Director, Oak Ridge National Laboratory</i>	Molecular analysis, protein interactions
Dr. Howard Einspahr <i>Research fellow, Bristol-Myers-Squibb (retired)</i>	Protein crystallography, drug design
Prof. Janos Kirz <i>Scientific Director, Advanced Light Source</i>	X-ray microscopy
Prof. Miles V. Klein <i>University of Illinois (retired)</i>	Experimental condensed-matter physics
Dr. Dan Neumann <i>National Institute of Standards and Technology Center for Neutron Research</i>	Structure and dynamics in molecular materials
Prof. Piero A. Pianetta <i>Deputy Director, Stanford Synchrotron Research Laboratory</i>	X-ray microanalysis, especially surfaces and interfaces
Dr. William Stirling <i>Director General, European Synchrotron Research Facility</i>	Magnetic scattering
Dr. Soichi Wakatsuki <i>Director, Photon Factory</i>	Protein crystallography
Dr. Glenn Waychunas <i>Molecular Geochemistry Leader, Lawrence Berkeley National Laboratory</i>	Synchrotron radiation applied to geochemistry and environmental science
Prof. Donald J. Weidner <i>Department of Earth and Space Sciences, Stony Brook University</i>	Geophysics
Dr. Wei Yang <i>Chief, Structural Biology and Cell Signaling Section, National Institutes of Health</i>	Molecular biology and protein crystallography
Prof. Larry Lurio ( <i>ex-officio</i> ) <i>Northern Illinois University; Chair, APS Users Organization</i>	Coherent x-ray scattering and physics of soft materials
Dr. Denis Keane ( <i>ex-officio</i> ) <i>Director, DuPont-Northwestern-Dow Collaborative Access Team; Chair, APS Partner User Council</i>	Surface x-ray scattering and reflectivity

developed in close association with the user beamline advisory committees. Seven proposals for brand new beamlines were also submitted from the community and have received initial review from the APS Scientific Advisory Committee. Several of these could be accommodated at the three undeveloped insertion device beamlines that remain at the APS, whereas others could be incorporated in redeveloped sectors. All these proposals and more information can be found on our Web site: <http://www.aps.anl.gov/Renewal/>. Through a Renewal Steering Committee comprising facility and user representatives<sup>1</sup>, we appointed 10 science teams to identify the

<sup>1</sup> Dennis Mills (APS), Rod Gerig (APS), George Srajer (APS), John Maclean (APS), Denis Keane (APS Partner User Council Chair), Paul Fuoss (APS User Organization representative), Bob Fischetti (Life Sciences Council Chair), Dan Neumann (APS Scientific Advisory Committee Member)

science drivers for future users of the APS, and a number of technique coordinators to look at the instrumentation and expertise that would be needed to satisfy the science challenges. We also benefited from the recent decadal study of condensed matter and materials physics by the National Research Council (*Condensed-Matter and Materials Physics: The Science of the World Around Us: An Interim Report*, Committee on CMMP 2010, Solid State Sciences Committee, National Research Council, The National Academies Press [2006]; [http://www.nap.edu/catalog.php?record\\_id=11730](http://www.nap.edu/catalog.php?record_id=11730)) and the “Grand Science Challenges” report of the Basic Energy Sciences Advisory Committee (BESAC), which identified key scientific problems and the vital role of current and future light sources (*Directing Matter and Energy: Five Challenges for Science and the Imagination*, U.S. DOE-BES [2007]; <http://www.sc.doe.gov/bes/reports/list.html>). At the APS renewal planning workshop in October 2008, we brought together ~200 key users and staff to present these scientific visions to members of the APS Scientific Advisory Committee (Table 4), which provided the recommendations summarized in this document. The recommendations allow us to select and develop the highest priority proposals to include in the renewal project.

As we proceed with renewal planning, we will be holding a major set of workshops at the 2009 APS Users Meeting in May, and will continue our preconceptual design planning. With DOE approval of Critical Decision 0, we would develop a Conceptual Design Report (CDR), holding workshops and a SAC-based review process to prioritize and select the detailed projects that would comprise the renewal. We expect that we could be ready with a CDR by the end of 2009.

## Estimated Cost and Schedule

From our preliminary planning we estimate that the project will cost between \$300 M and \$400M, and take from 5 to 7 years to complete. There will be little major civil construction involved, although some extensions to beamlines that require small out-buildings and additional laboratory space are desired. We have simultaneously developed a plan to deal with infrastructure and obsolescence issues at the APS, which are becoming severe. This plan would be accomplished in parallel with the renewal, using our routine capital and accelerator improvement funds.

## **Beyond the Renewal – The Opportunity for a Major Machine Upgrade**

Once the renewal is complete, the APS will be in an excellent state for the next decade. In order to provide the best possible source of hard x-rays within the U.S. for the longer term, we are simultaneously exploring options for major upgrades to the accelerator that would build on the APS renewal investment. For example, next-generation sources would offer greater coherence and shorter pulses that would build directly on the themes that we have developed for the renewal. Options we have considered range from third-generation lattice improvements, to fourth-generation concepts such as the energy-recovery linac and the x-ray free-electron laser oscillator. While the lattice upgrades could be accomplished without significant further R&D, they offer less dramatic improvements. We anticipate being involved in R&D on the fourth-generation options in the next few years, and working with the DOE as they plan for next generation capabilities in the U.S. The BESAC is currently carrying out a national study of the need for fourth-generation light sources to address grand scientific and technological challenges. Our goal is to continue to lead the development of hard x-ray science in the U.S. and position the community for whatever next-generation investments may be made for hard x-ray sources in the decades to come.

## The Advanced Photon Source Renewal Workshop

*October 20-21, 2008  
Hickory Ridge Marriott Conference Hotel  
1195 Summer Hill Drive  
Lisle, Illinois*

Beginning in March 2008, Advanced Photon Source (APS) management engaged users, facility staff, the distinguished members of the APS Scientific Advisory Committee (SAC), and other outside experts in crafting a renewal plan for this premier synchrotron x-ray research facility. The scope of renewal for this ~\$1.5B facility is estimated to be about \$350M over 5 to 7 years. The only two comparable high-energy x-ray sources, the European Synchrotron Radiation Facility in Grenoble, France, and the SPring-8 facility in Harima, Japan, are both well along in planning for major upgrades. It is vital that the investment in the APS renewal begin as soon as possible in order to keep this important U.S. facility internationally competitive.

The APS renewal plan encompasses innovations in the beamlines and the x-ray source that are needed for major advances in science—advances that promise to further extend the impact of x-ray science on energy research, technology development, materials innovation, economic competitiveness, health, and far-reaching fundamental knowledge.

A planning milestone was the APS Renewal Workshop held on October 20-21, 2008. Organized by the APS Renewal Steering Committee, the purpose of the workshop was to provide a forum where leading researchers could present the broad outlines of forward-looking plans for science at the APS in all major disciplines serviced by x-ray techniques. To facilitate these dialogues, these 10 Science Teams were formed to develop draft reports that provided the basis for discussion at the workshop:

*Continued on next page*

**Science Field**

Chemical Science & Engineering  
Condensed Matter and Materials Physics  
Engineering Applications & Applied Research  
Fundamental Interactions in Chemical,  
Atomic, & Molecular Physics  
Geological, Environmental, & Planetary Sciences  
Interfacial Science  
Life Sciences (excluding MX)  
Macromolecular Crystallography (MX)  
Materials Science & Technology  
Polymers and Soft Materials

**Team Leader**

Jeffrey T. Miller  
*Argonne National Laboratory*  
Samuel D. Bader  
*Argonne National Laboratory*  
Gene E. Ice  
*Oak Ridge National Laboratory*  
  
Stuart A. Rice  
*The University of Chicago*  
Neil C. Sturchio  
*University of Illinois at Chicago*  
Paul A. Fenter  
*Argonne National Laboratory*  
Lee Makowski  
*Argonne National Laboratory*  
Anthony A. Kossiakoff  
*The University of Chicago*  
Paul G. Evans  
*University of Wisconsin-Madison*  
Kenneth R. Shull  
*Northwestern University*

The Charter provided to the Science Teams is given below:

“Members of the Science Teams are charged with developing the scientific case (for their respective areas) that will be the basis for a 5-year APS renewal proposal to the U.S. Department of Energy. The scientific case should clearly define how upgrades to beamlines (optics, detectors, insertion devices, end-station instrumentation, and software) and the facility will enable the science to progress and how that progression will impact the field. Management of the APS has already called for renewal proposals from beamline scientists describing how those renewals will enhance the capabilities of various beamlines and/or techniques. The Science Teams should select, consolidate, and optimize those proposals (and/or develop/call for new proposals if necessary) that support their scientific cases and outline how the renewal will position the APS to enable high-impact science.

“Technique Coordinators (experts in relevant techniques or instruments) will facilitate the identification of specific techniques that are important to each scientific dis-

cipline and, in particular, across disciplines. The Technique Coordinators will work with the Science Teams to develop a strategy for instruments that are required to enable high-impact science.

“The Chairs of the Science Teams will organize and lead the development of the scientific case. Members of the Science Teams have accepted responsibility for gathering information from the community and preparing the reports. The Science Teams will consult with other experts in the field and with the Technique Coordinators.

“Although the goal of the Medium-Term Renewal is to develop the case for a medium-term (5-year) renewal of the beamlines, the Teams should also keep in mind what sort of larger, longer-term upgrade of the entire APS facility would further enhance their area of science.”

Two days of scientific presentations, discussions, and dialogue (see Appendix A for the agenda) involved 188 scientists representing 41 institutions (see Appendix B for list). The scientific talks and breakout/discussion sessions provided a forum for Science Team leaders to present the outlines of forward-looking plans for experimentation in all the major scientific disciplines covered by photon science. These proceedings comprise the reports from the Science Teams that were commissioned by the APS Renewal Steering Committee, having been edited by the Science Teams after discussion at the workshop.

Among the spectacular impacts on science and engineering research that were offered, two overarching themes were identified that will guide the U.S. Department of Energy, Office of Basic Energy Science (DOE-BES) investments for the APS renewal: **Mastering hierarchical structures through x-ray imaging**, and **real materials in real conditions in real time**. These two themes formed the scientific foundation for a white paper outlining the proposed APS renewal, which promises maximum scientific impact and high return on investment. This white paper has been written and was sent to DOE-BES in November 2008. It can be found beginning on page v. of this volume.

## Renewal of the Advanced Photon Source: Chemical Science & Engineering

**Jeffrey T. Miller** (Chair) *Argonne National Laboratory*  
**Simon R. Bare** *UOP*  
**Peter J. Chupas** *Argonne National Laboratory*  
**James E. Penner-Hahn** *University of Michigan*  
**Deborah J. Myers** *Argonne National Laboratory*  
**Lynda Soderholm** *Argonne National Laboratory*  
**Nenad M. Markovic** *Argonne National Laboratory*

### Executive Summary

X-ray-based synchrotron techniques can provide the unrivaled, multilevel information necessary to explore structural correlations over a broad range of length scales to answer high-impact scientific questions such as:

- What determines the structural details of complex catalytic nanoparticles and how do these change under differing reaction conditions?
- How do structure, morphology, size, support, and promoters, etc., affect performance including catalysts capable of new chemistry and with selectivities approaching that of biological systems?
- What is the atomic-level spatiotemporal structure of a working catalyst in a catalytic reactor?
- How does the structure of a solution-electrode interface impact the chemistry, efficiency, and stable delivery of reactions, including those important to electrical power in fuel cells?

- What novel, non-noble metal nanoparticle compositions and synthesis methods are needed to produce high-efficiency fuel cells?
- How does solution chemistry of metal-ion speciation, including coordination, ligation Chemical Science & oligomerization, affect chemical reactivity, electrode and electronic response, and solubility?

In the near future, the characterization of solutions, interfaces, and nanoparticle samples will play a central role in both fundamental and applied chemical science and engineering. Challenges will include the provision of new, abundant, and environmentally safe energy for the nation. Solution and nanomaterial sciences offer great potential to create novel materials with tailored properties that strongly depend on the specific hierarchy of chemical or physical components, organized at different length scales. The function and behavior of these new materials can only be understood if their microscopic structure and dynamics are known over all length scales down to the molecular and atomic levels. Synchrotron x-ray techniques provide an unprecedented level of structural detail, even on materials lacking long-range order typical of those in chemical science and engineering. The primary techniques will be diffraction, scattering, and absorption spectroscopies, in both static and time-resolved modes. For systems and materials of importance to chemical sciences and engineering, measurements under *in situ* conditions, such as elevated temperatures, pressures, and applied potentials, as well as in reactive and corrosive solutions, will be necessary.

New capabilities are necessary that will help scientists to understand and find answers to these questions by providing unique information on the quantification and chemical state of complex structures of nanoparticles; solution complexes; the interfacial boundary of solid-solid, solid-gas, solid-liquid, and liquid-liquid; as well as trace elements at unprecedented sensitivity and spatial resolution, and ultimately, with time dependence. Hard x-rays provide the added benefit of enabling specific sample environments so that real systems in their near native environments can be studied.

## Expected User Communities

Chemical sciences and engineering addresses scientific questions over a broad range of disciplines. Research groups in industry, academia, and national laboratories have extensive research programs in these areas. The unique information provided by the techniques at the APS affords the greatest level of detail and understanding for many problems. While most scientists perform their analyses with laboratory methods, it is not always possible to analyze samples under *in situ* conditions. Improved capabilities will attract new users, but wider availability of beamlines with gas handling and other equipment needed to make *in situ* measurements will greatly increase the number of users in the chemical sciences and engineering field.

## Introduction

Catalytic technology is essential for economic prosperity, energy security, and environmental preservation in the twenty-first century. Catalytic science and technology has an extraordinary impact on the U.S. economy and quality of life, with applications to the fields of agriculture, transportation, petroleum refining, chemicals, batteries, fuel cells, electronics, health care, and environmental stewardship. The U.S. Department of Commerce estimates that about 90% of chemical manufacturing processes and nearly 30% of all manufactured goods in the U.S. are dependent upon a catalytic process to achieve the desired combination of economics and functional performance.

The importance of catalysis research to meet the energy needs of the nation and the central role of U.S. Department of Energy (DOE) facilities in advancing catalytic sciences has been specifically identified in the Energy Policy Act of 2005. The world demand for energy is expected to double by the year 2050. Compounding this challenge is the growing need to protect our environment by increasing energy efficiency and developing clean, safe, renewable energy sources. The solution to these challenges is vital to our future energy security, to address global climate change, and for continued economic prosperity. A U.S. Department of Energy, Office of Basic Energy Sci-

ences (DOE-BES) report on *Basic Research Needs to Assure a Secure Energy Future* [1] has recognized that solutions will require scientific breakthroughs and revolutionary developments. Within this context, nanoscience and nanotechnology present exciting and requisite approaches to addressing these challenges. Moreover, from the DOE-BES reports entitled *Basic Research Needs: Catalysis for Energy* [2], *Basic Research Needs for Solar Energy Utilization* [3], *Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels* [4], and *Basic Research Needs for the Hydrogen Economy* [5] it is clear that catalysis will play a major role in advancing the research and technology needs for the nation. As part of the reports on specific research needs, DOE also identified five Grand Challenges for Science and the Imagination. Mastery of catalysis and catalytic systems will require advances in all five of these challenges. The development of future technology will result from the synthesis of new catalytic materials, with the properties of unprecedented activity, selectivity, and stability.

Within the overall context of the critical role catalysis plays in energy-related technologies is the electrocatalytic conversion of chemical energy to electrical energy within a fuel cell. Due to its ability to efficiently convert fuels to electrical energy at low temperatures, and its high efficiency and power density, the polymer electrolyte fuel cell has the greatest potential to replace the internal combustion engine in vehicles, eliminate or greatly reduce greenhouse gas emissions, and decrease world dependence on petroleum-based fuels.

The successful deployment of advanced fuel cells depends on the development of new materials that can meet the demanding performance requirements under extreme conditions of high voltage, high temperatures, and corrosive electrochemical environments. The two most significant challenges to the widespread implementation of this promising technology are the high cost and limited durability of the platinum and platinum alloy nanoparticle cathode electrocatalyst.

The strategic goal is to acquire fundamental understanding of atomic/molecular-level interactions that occur at electrified solid-liquid interfaces. This fundamental knowl-

edge will eventually lead to the design and synthesis of selective, robust, impurity-tolerant, low-cost, and highly efficient, tailored, nanoscale electrocatalysts for fuel cell electrodes, thereby assisting in achieving one of DOE's mission goals for "revolutionary advancement in electrocatalysts and dramatically enhanced energy transfer in fuel cell systems."

Aqueous solutions containing dissolved metal ions have historically been viewed as homogeneous systems in which a solute (a metal ion, for example) is evenly distributed in a solvent (water). There is mounting evidence that this description is often inadequate and that significant solute organization can occur [1] with a measurable impact on a wide range of behaviors ranging from metal solubilities and reactivities to chemical separations. Dissolved metal-ion speciation, including coordination, ligation, and oligomerization, plays a central role in chemical reactivity, electronic response, and solubility. This chemistry also plays a critical role in a wide variety of energy-related technologies, including catalysis, the environmental fate and transport of heavy metal ions, and the separation of metal ions for purification and use. A necessary first step to a predictive understanding of metal-ion solution chemistry is a comprehensive picture of metal-ion speciation. This picture is currently in its infancy and needs to be developed to adequately assist theorists and modelers in a wide variety of technology areas.

## Key Science Drivers

### Catalysis by nanoscale materials

Catalysis controls the rates at which chemical bonds are formed and broken, thereby controlling the yields of desired products over undesirable ones in chemical reactions. Catalysis is, therefore, central to energy conversion and environmental protection, as well as contributing to a healthy economy. Achieving a high degree of selectivity in catalysis is recognized as a crucial challenge for the coming decades. While nature attains near 100% selectivity with enzyme catalysts, such selectivity in synthetic systems is rarely obtained. Nanoparticles and nanostructured (single-site) materials

offer new avenues of controlling catalytic function. The geometrical structure and electronic properties of nanoscale catalyst particles play a major role in selectivity; therefore, highly controlled particle-size distribution, composition, and morphology is essential. Furthermore, at the nanoscale, the catalytic rate and selectivity of metallic, alloy, and oxide nanoparticles cannot presently be predicted from the properties of the bulk materials.

It has long been known that the oxide surface and promoters also have a strong influence on the performance of nanoparticles, but how these alter that performance is largely not understood. The most significant research challenge needed to address these issues is to create and characterize interfaces and nanostructures that are tailored to optimize catalyst performance. The possibilities include fabricating interfaces using a wide variety of materials and chemical combinations, along with interface shapes patterned at the nanometer length scale. To accomplish this, a diverse array of synthesis methods ranging from top-down lithography through self-assembling materials growth, wet-chemical processing, and biological assembly must be combined to create novel structures. In parallel, experimental techniques for nanoscale characterization must be developed and used to relate structure and function. Finally, during reaction, the operating environment (e.g., gas composition, temperature, pressure, etc.) alters the surface composition. Few methods provide the structural and electronic details that allow for a fundamental understanding of how these properties affect performance.

The research challenge for catalysis is learning to tune the nanoparticle properties to control the chemical reactivity. Future catalysts will not only enable new reaction pathways, but will control the product selectivity with unprecedented selectivity. For example, catalysts with very high selectivity would eliminate the need for additional catalytic process steps or separations, thus significantly improving energy efficiency and reducing cost. Drawing from the lessons of biology, nanostructured materials must be designed to match both the structure and conformation of the reactants to control the reaction pathway to the desired product. To accomplish this, new and efficient methods of *in situ* characterization, combined with rapid high-throughput test-

ing of catalytic properties will be required. The choice of materials, structural parameters, and the experimental design must be guided by a continually improving fundamental understanding of the structure-function relationships of nanostructured catalysts.

## Electrochemical fuel cells

The major challenges for the development of a new generation of materials required for efficient energy conversion in fuel cells is to develop a fundamental understanding of metal-electrolyte interfaces. The activity depends on their atomic-level properties [7]. These properties include oxidation state, particle size, local atomic environment of the reactive site, electronic structure, inter-atomic bond lengths, and short-range order [8]. Characterization of these properties, especially while the catalyst is in the reactive environment, allows a correlation of these properties with activity, identification of the active catalyst site, an understanding of degradation mechanisms, and ultimately, improvement of the catalytic activity and durability. For example, identification of the active site allows synthetic methods to be tailored to maximize the density of these sites, leading to higher catalyst-specific and volumetric activities. Characterization of oxidation state and particle size in the reactive environment also provides critical knowledge regarding degradation mechanisms and the link between operating conditions and degradation, which allows tuning of catalyst composition and operating conditions to extend lifetimes. In addition, determination of the catalyst atomic structure during synthesis—such as during the heat-treatment step for converting the precursors to metals and alloys—provides critical knowledge on the temperature necessary to form the desired phase, but limits nanoparticle growth.

It is also of paramount importance to determine the mechanisms that control the microstructure, activity, and stability of nanostructured materials that are certain to find application in the next generation of fuel cell systems. To reach this goal, we need to resolve relationships between the structure, chemical nature, and composition of the electrochemical interface, and its activity and stability. To address these challenges, we have to learn how to: A) create novel states of catalytic materials by manipulating their surface electronic and crystal structure; B) characterize, at the

nanoscale, atomic and electronic properties of nanostructured interfaces by developing and using *ex situ* and *in situ* surface characterization techniques and state-of-the-art theoretical methods to explore structure/function relationships; C) understand, at the atomic/molecular level, the fundamental principles that govern efficient bond making and bond breaking at electrochemical interfaces; and D) optimize the active sites by an iterative process, guided by a fundamental understanding of structure function relationships at multimetallic electrochemical interfaces.

### Solution chemistry

One of the Chemistry Grand Challenges is to understand, predict, and control the behavior of dissolved metal ions in solution. The basic first step in realizing this challenge is a comprehensive picture of speciation, specifically the structure of ligands surrounding the ion of interest. Unfortunately, x-ray and neutron diffraction, two of the most powerful analytical tools for structure determination, require long-range correlations for their application and thus are not useful for solution work. Recently, single-ion probes such as nuclear magnetic resonance and extended x-ray absorption fine structure (EXAFS) have broadened our knowledge of solute environments, even in dilute solutions. Extended x-ray absorption fine structure has emerged as the tool of choice for probing metal-ion speciation in solution because this tunable, single-ion spectroscopy can be used to directly determine oxidation state, coordination number, and in selected cases coordination symmetry [9]. An emerging frontier for EXAFS is the routine application of time-resolved EXAFS to characterize solution reactivity. Over the last decade, the development of relatively inexpensive, easy-to-use, stopped-flow, ultraviolet-visible spectrometers has revolutionized the study of inorganic chemistry, allowing inorganic chemists to ask much more sophisticated questions about the kinetic (and ultimately, the mechanistic) properties of their materials. It is now becoming possible to extend these techniques to EXAFS, and this promises a similar advance in the detailed understanding of chemical kinetics (particularly if ultraviolet-visible and EXAFS stopped-flow can be combined on the same system).

Although EXAFS is broadly applied to many solution-based problems, it is not able, except in unusual situations, to give statistically reliable coordination information beyond the first coordination sphere, so that any ion-ion correlations at distances

longer than about 0.4 nm to 0.5 nm are not consistently revealed by EXAFS studies, as demonstrated in Fig. 1 (left). This information is critical for characterizing solute-solvent interactions. Consequently, the characterization of solute-solute and solute-solvent correlations has largely been limited to indirect techniques including colligative properties measurements, such as vapor pressure osmometry and spectroscopic techniques such as ultraviolet/visible, Raman, and infrared spectroscopies.

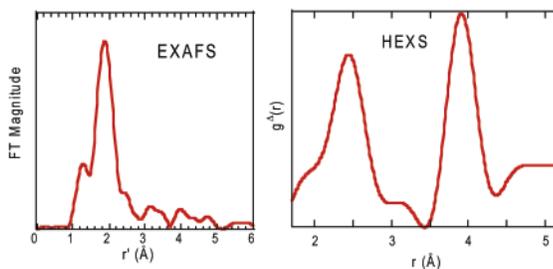


Fig. 1. A comparison of Fourier transformed EXAFS (left) and high-energy x-ray scattering (HEXS, right) data taken on the same Th solution. The peak at 4 Å in the HEXS data is attributable to Th-Th interactions, which are not observable in the EXAFS data. Not explicitly shown is the higher resolution available in the EXAFS data, which allows the observation of splitting within the first coordination sphere [10].

Understanding these correlations is particularly important when studying oligomerization, aggregation, and precipitation reactions, which require information at distances longer than those of the first-coordination sphere. Secondly, coordination numbers are usually significant only to about  $\pm 10\%$ , an error too large for many applications. For example, information about the coordination number of a lanthanide ion in solution often requires discerning whether the ion is 8 or 9 coordinate, a question that is not unequivocally resolved with EXAFS spectroscopy.

The research challenge for solution chemistry is to extend our understanding of self-assembly and correlations that occur in amorphous systems and at their interfaces with either a solid or another solution. This understanding needs to include an accurate means of assessing first-coordination sphere ligation of a solute ion, oligomeric interactions, ion pairing, and second and more distant coordination spheres. The data needs to include distances, and the nature and number of ligating ions. Within solutions themselves, self-assembly and ordering of ions or molecules at interfaces is important in many biotic and abiotic processes. Phase-transfer catalysis, pharmaceutical drug delivery, many electrochemical processes, nanoparticle synthe-

sis, and numerous chemical reactions take place at the interface between two immiscible liquids. Important environmental processes that rely upon interactions at interfaces include tertiary oil recovery, solvent extraction of radionuclides from nuclear waste, and permeation liquid membranes used for the cleanup of ions in the environment. For example, biological membranes at aqueous-aqueous boundaries are fundamental to cell chemistry and processes. In the area of separations science—a cornerstone of the chemical industry—solvent extraction and other metals separations technologies rely heavily on the transfer of metal ions across an interface.

## Significance of the APS

Understanding solution and materials chemistry requires knowledge of structure at the atomic level. Most of the standard structural characterization tools provide high-quality information on bulk, periodic, or crystalline materials. Equally high-quality characterization is needed for amorphous materials, solutions, and complex nanostructures. Synchrotron-based techniques can now be used to characterize samples irrespective of their state of crystallinity via different scattering and spectroscopic methods. X-rays are providing structural details at length scales that encompass local structure from about an ion to the long-range ordering present in well-formed crystalline materials, and have found applications in solutions, glasses, liquids, poor-quality crystals, powders (which can be multiphase), assemblies of micro-crystals, adsorbed surface layers, etc. Moreover, the evolution of structure under reaction conditions is also an important feature of a catalytic system that needs to be investigated and understood. Techniques most often used for analysis of catalytic materials include x-ray diffraction and scattering, pair distribution function (PDF), small-angle scattering (SAXS) and x-ray absorption spectroscopy (EXAFS and x-ray absorption near-edge fine structure, XANES).

## Current APS techniques and potential upgrades in capabilities

Synchrotron x-ray powder diffraction (SXRPD) is a core competency for structural analysis of catalytic nanoparticles. The major application of SXRPD is structural analysis of new catalytic materials using Rietveld refinement (e.g., zeolites and

mixed oxides). In recent years, there has also been much interest in *in situ* catalyst research. Having a beamline with capabilities for *in situ* measurements would be highly advantageous to the catalysis community, as many metallic nanoparticles are highly oxidized in ambient air.

There is also an urgent need for x-ray diffraction analysis on nanoparticles smaller than ~5 nm. For example, precise identification of the alloy phase in nanoparticles is often not possible. In addition, bimetallic catalysts may contain several structurally distinct phases and determination of the fraction of each is also currently not possible. Therefore, the determination of the fraction and structure of each phase in multi-component nanoparticle catalysts is crucial for identification of the catalytically active phase. Also, nanoparticles in bimetallic catalysts often form alloy phases, which are not known in bulk compositions. Similarly, new structures may occur in bimetallic catalysts (e.g., core-shell nanoparticles), which do not occur in bulk phase. Development of *in situ* SXRPD for determination of the structure and composition of 1-nm to 5-nm oxide and metallic nanoparticles would provide an unprecedented level of detail and lead to a new degree of understanding about the structure and function of catalytic surfaces.

The PDF is the real-space representation of the scattered intensity. The PDF directly recovers structural parameters in the form of a distribution of atom-atom correlations (i.e., interatomic distances) with a spatial resolution considerably finer than the length scale of a chemical bond (~0.1 Å) and extending out to distances as far as several nanometers [11,12]. Measurements up to high values of  $Q$  are needed to obtain high-resolution PDFs, which necessitates the high flux of high-energy x-rays (>60 keV) available at the APS. Recent work performed at the APS using area detectors has demonstrated PDF measurements as fast as 30 ms, orders of magnitude shorter than conventional experiments [13]. With this time resolution, and by measuring PDF differences between loaded and unloaded supports, meaningful *in situ* PDF studies on nanoparticles are now possible, which allow both the local and intermediate-range (1-nm to 4-nm) structure of supported clusters to be probed directly and simultaneously. A specialized application of PDF, the differential PDF (D-PDF)

approach, is ideally suited to directly probing nanoscale catalysts, as it allows the selective recovery of only the atom-atom correlations arising exclusively from the catalyst particle (i.e., only those involving the atoms of the catalytic clusters deposited on the support). It can be obtained by direct subtraction of a reference PDF for the bare support from that of the cluster/support complex. Differential PDF measurements can be used to monitor the structural changes of supported particles that occur under realistic reaction conditions. *In situ* measurements are possible under realistic catalytic conditions using specially designed flow cells that enable gas flow across samples with heating up to temperatures of 1000° C [14]. Pair distribution function is complimentary to other scattering techniques and can be combined with simultaneous SAXS measurements to yield information not just regarding local structural changes, but also particle shape.

Applied to high-surface-area and flat-model catalytic materials, SAXS and grazing-incidence SAXS (GISAXS), respectively, can provide both *ex situ* and *in situ* information on cluster size, shape, and interparticle distance. The ability to compare the two classes of materials will validate the formation of identical structures on the two support morphologies. Grazing-incidence SAXS can also give depth profile information, and the aspect ratio (height/diameter) of a cluster can be calculated from the GISAXS data to obtain the interfacial energy using the Wulff-Kaishew construction [15]. The GISAXS experiments are performed in a reaction chamber equipped with a heated sample holder and gas introduction system mounted on a goniometer. Products can be monitored by mass spectrometry and gas chromatography. During heat treatment, scattering data can be collected as a function of time and temperature.

Anomalous SAXS, or ASAXS, offers an extension to standard SAXS experiments in which the energy of the probing x-rays is tuned near the absorption edge of an element in the sample. By performing SAXS experiments near the characteristic absorption edge of any given atom, it is possible to vary the contrast for scattering by that particular element. This method overcomes the problem of separating the scattering of clusters from that of the support, or a second metal center. For the first time, anomalous GISAXS data have been obtained on Au metal clusters on surfaces

[16]. This approach has also been used also for Pt (L-edge) and is possible for both Pd and Cu (*K*-edges) [17-19].

X-ray absorption fine structure and XANES have become the workhorse techniques for catalyst characterization over the last 30 years. The popularity of these techniques is primarily the result of their power to provide *in situ*, element-specific, atomic-level chemical and geometric information on the structure of real working catalysts (both heterogeneous and homogeneous). While, in general, the structure of homogeneous and supported single-site catalysts is too complex to determine by EXAFS, by analysis of the difference spectra (between the starting structure and that under reaction conditions, for example) one can follow the changes in structure during pre-treatment or under reaction. The difference spectrum indicates which ligands were lost and by comparison with the initial structure, allows for determination of the active species. Likewise, the difference spectrum can allow for determination of small changes in the structure of nanoparticles that occur under reaction conditions. Structural details in the difference spectrum, however, require significantly improved signal-to-noise up to high-*k* values. For determination of subtle structural features, significantly improved signal quality is required. Finally, accurate determination of the catalyst structure simultaneously with measurement of the reaction kinetics will allow for identification of the active nanophase when several structures are present. Thus, it is not only necessary to obtain the analysis under reaction conditions, but also be able to simultaneously make high-quality kinetics measurements.

From the XANES spectra, the oxidation state and geometry of the metal atoms may be determined. During pre-treatment, for example, from the time-dependent XANES spectra, the kinetics of reduction (or oxidation) can be determined. The kinetics of changes in structure under different reaction conditions can similarly be determined. Changes in the occupancy and energy of the d-orbitals affect the chemical reactivity and small changes are important. Changes in XANES intensity of the  $L_{III}$  and  $L_{II}$  edges are proportional to the number of d electrons. A significant improvement in the resolution of the XANES spectra can be obtained by high-energy-resolution fluores-

cence (HERF) XANES measurements and represents an important new capability in catalysis research. Figure 2 shows significantly enhanced intensity and energy resolution of the HERF spectra compared to the transmission XANES for Au foil [20]. This method is especially important for determination of the small differences, which occur during reaction conditions.

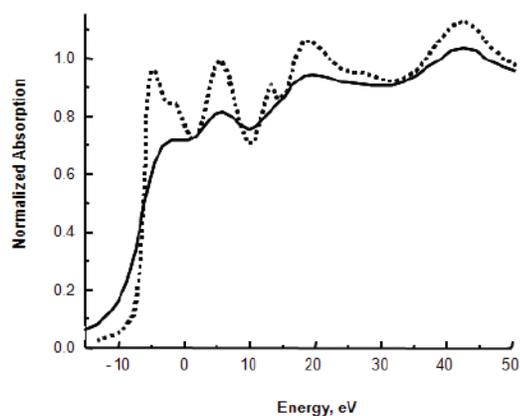


Fig. 2. Comparison of the high-energy-resolution fluorescence XANES (dotted) to the transmission XANES (solid) for Au foil [15]. © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

In many catalysts, the catalytically active element of interest is present in a mixture of forms. In synchrotron-based investigations as they are currently performed, the signal (spectroscopic or otherwise) is an average characterizing the various species that contain that particular element. For a fundamental understanding of active catalytic species, it is necessary to be able to separate the signal characterizing the element in each of the structures and configurations. Emerging techniques such as high-energy-resolution x-ray fluorescence (HERF) spectroscopy, x-ray emission spectroscopy (XES) [21], and resonant inelastic x-ray scattering (RIXS) [22,23] are showing potential for determining the local electronic and geometric arrangement of an element in such complex, non-uniform samples as typical solid catalysts. The grand challenge is to conduct such investigations of catalysts as they function in a time-resolved manner.

When a reactant adsorbs or interacts with the catalyst surface, it changes the electronic structure of the catalyst, primarily in the valence band. With a probe that can interrogate these electronic changes, the fundamentals for surface bonding can be determined. Changes to the electronic structure have been demonstrated to be measurable by careful analysis of the x-ray fluorescence spectrum emitted from the sample. In particular, the  $K\beta$  lines exhibit a wealth of fine structure, and therefore, information about the sample's valence states. For example, the energy of one of the  $K\beta$

satellite peaks has been shown to be directly related to whether a transition metal is coordinated to N, O, or F [21].

The power of the high-energy-resolution x-ray spectroscopy technique is that it may be combined with x-ray absorption spectroscopy (XAS) to become RIXS. By measuring the x-ray fluorescence intensity as a function of both incident energy and emitted energy (or energy loss) around a particular fluorescence line, additional electronic structure can be resolved compared to the standard XAS measurement, where the fluorescence is not energy analyzed. This additional structure can be related to the electron density of states.

This combination has the potential to isolate the x-ray absorption spectrum due only to the atoms interacting with the reactants (i.e., surface sensitive), and then provide data on the oxidation state and near-neighbor environment (neighboring elements and distances) of only the active atoms in the catalyst particle. The specificity of this technique already has been demonstrated for spin state, site occupation, and valence states

The integral nature in the way that EXAFS data have traditionally been collected also means that no spatial information is obtained. In many cases in catalysis there is spatial variation in the catalyst structure. What is required is spatially-resolved molecular structure information, preferably under reaction conditions. Two different approaches have recently been applied to bring spatial information to EXAFS: full-field transmission microtomography, and scanning x-ray microtomography. Each of these methods has specific advantages and disadvantages, but each has been demonstrated to reveal spatial information under reaction conditions for several different catalytic reactions. There is an urgent need to implement these techniques at the APS. A natural extension of this work is in the temporal domain in order to obtain spatiotemporal structural detail of the working catalyst.

Electrochemical interfaces play a crucial role in many aspects of analytical, synthetic, and materials chemistry, as well as in chemical and photochemical energy conver-

sion. In the past, these interfaces have been treated empirically with limited understanding of the fundamental, molecular-level processes associated with bond-making and bond-breaking events at an inherently complex multi component environment. This has motivated the development of *in situ* surface-sensitive probes, most notably synchrotron-based surface x-ray scattering (SXS) and scanning tunneling microscopy (STM). Since the early 1990s, these techniques have enabled the transformation of electrochemistry from a largely phenomenological subject into a discipline that addresses atomic/molecular-level issues at a degree of detail that is equivalent to what has been accomplished in ultra-high-vacuum-based surface science.

The SXS method takes advantage of the ability of x-rays to penetrate a thin solution layer, along with the simple theory of backscattering, allowing the collection of very detailed spatial information. Of particular interest has been the exploration of potential-driven phenomena at ambient temperatures, ranging from ordering, phase transitions, and mobility in metal surface atoms and adsorbed layers [24,25] to the surface compositions and segregation profiles of bimetallic systems [26,27]. Although such potential-dependent interfacial transformations are important, the successful deployment of advanced electrochemical systems depends critically on the development of *in situ* methods capable of providing information on temperature-dependent surface structures at a level of sophistication that is equivalent to that obtained in potential-dependent studies. To overcome the existing “temperature gap,” electrochemical SXS cells now operate over the range of 275K to 325K. With a new temperature-controlled SXS cell, it will be possible to study *in situ* temperature-induced reconstruction and relaxation of surface atoms, stability of active sites and the nature of active sites, and the structure and nature of adsorbates and reactive intermediates.

In addition to surface x-ray diffraction, *in situ* x-ray fluorescence spectroscopy (EXAFS and XANES) and wide-angle diffraction techniques are used to characterize the electronic and structural properties of multimetallic nanoparticle catalysts during (half)-cell operation. One of the main advantages of x-ray techniques is its versatility to various forms of nanoparticle catalysts.

Until the recent application of high-energy (>30-keV) x-ray photons to the problem of metal-ion speciation in solution [28,29], x-ray scattering was essentially limited to crystalline and amorphous solids. Some early work using in-house x-ray sources and Mo K radiation showed the potential of the technique, but the lack of both flux and  $Q$  range significantly limited the systems for study and the information obtainable [30]. The availability of a high flux of high-energy photons at selected third-generation synchrotrons, including the APS, brings an opportunity to enhance and further develop HEXS as a tool for studying correlations in solution.

There are three specific advantages to the use of high-energy photons. The first advantage involves the minimal absorption by aqueous solutions, which permits data acquisition in the transmission mode, thereby limiting the need for geometric corrections. As a result, absorption effects, which can be a significant source of error in scattering or diffraction experiments conducted at more conventional energies (8 keV to 20 keV), are typically small enough to be neglected for higher-energy data. The second advantage, also related to the low absorption cross section, is the increased stability of redox-active metal ions in the beam. Lower-energy photons have a propensity to influence the oxidation state of ions in solution and thus vitiate the data. The third significant advantage gained from using high-energy x-rays comes from the extended  $Q$ -range generally available, since  $Q = 4\pi(\sin\theta)/\lambda$ , where  $\theta$  is the scattering angle and  $\lambda$  is the x-ray wavelength. Thus, higher energies, or shorter wavelengths, result in higher  $Q$ s for the same scattering angle. Higher  $Q$ -range data are necessary for accurate background subtraction and resolution in the Fourier-transformed data. Background correlations arising from solvent-solvent interactions are the main limiting factor to the use of x-ray scattering for probing solute correlations and can be accurately removed only with the information on self-scattering that is available at higher  $Q$ . These advantages are demonstrated in Fig. 1 (left).

There are two different x-ray scattering experiments of particular use in studying solutions and their interfaces. The first experiment involves the Fourier transform of background-subtracted HEXS data to provide a direct picture of solute correlations in solution. This technique has been recently used to study the solution environment of

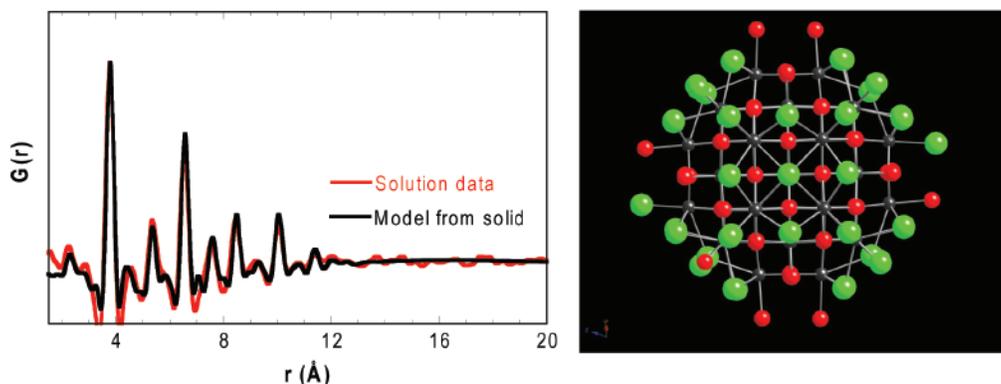


Fig. 3. The FT of HEXS data obtained from a  $[\text{Pu}_{38}\text{O}_{56}\text{Cl}_{54}]^{14-}$  cluster in solution is compared with a model obtained using atomic positions obtained from a single-crystal structure of the same cluster. The data were obtained on the mother liquor from which crystals were harvested, indicating that the clusters were pre-organized in solution [34].

a dissolved metal ion [10,28,31-34] and provides evidence of remarkable organization about the solute ions. Of particular interest is the detailed information about nano-cluster formation, structure, and surface ligation, as shown in Fig. 3. The second use is for probing liquid-liquid interfaces [35]. Recent x-ray surface scattering studies have determined the distribution of ions at these interfaces. These experiments are sensitive to the different chemical environments of an ion in the bulk and at the interface. High-energy scattering from interfacial ions, analogous to those just described in the bulk solution, may provide information on the local ionic structure near the interface. Such experiments can also probe the interaction of ions with molecular assemblies at the interface. This provides an opportunity to observe the effects of different solvation structures on ionic interactions.

Initial x-ray studies also demonstrated that surfactants at liquid-liquid interfaces behave very differently than at the liquid-vapor interface, though in a manner that is unexpected. The presence of an aqueous and an organic phase leads to strong interactions with both the polar and non-polar parts of surfactants. Depending upon the surfactant, this may lead to solvent mixing into surfactant monolayers and a re-ordering of the monolayer. X-ray studies have demonstrated the role of surfactant tail-group flexibility, surfactant head-group interactions, and solvent chain length on interfacial ordering at both the liquid-liquid and liquid-vapor interfaces. Control of the interfa-

cial electric field at a liquid-liquid interface allows for the investigation of electrostatic effects on surfactant organization. Additionally, chemical reactions occur between molecules solvated in the two phases that meet only at the interface.

The development of x-ray scattering from liquid interfaces has been closely tied to advances in synchrotron sources and instrumentation. These experiments usually require a

very brilliant x-ray beam. The study of buried interfaces, such as liquid-liquid interfaces, can benefit from higher x-ray energies. Focusing techniques that are optimized for the study of liquid interfaces are needed to study heterogeneous interfaces, small biological interfaces, and highly curved interfaces. Also, new time-resolved instruments are required to meet the need for studying kinetic and dynamic interfacial processes at interfaces.

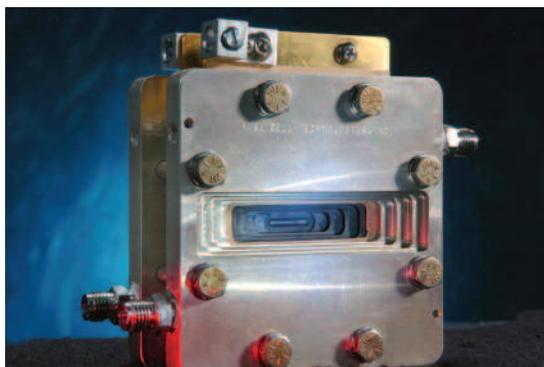


Fig. 4. Cell for *in situ* x-ray absorption studies of fuel cell catalysts. Standard Fuel Cell Technologies cell hardware was machined to allow x-ray fluorescence studies of cathode electrocatalysts in an operating membrane-electrode assembly (fuel cell). (Argonne National Laboratory photograph)

## Scientific Community

An enhanced catalyst research beamline with capabilities for *in situ* XAFS, powder diffraction, and kinetics measurements would benefit the entire catalysis community, i.e., government research laboratories, academia, and industry. The beamline and its staff would also serve as a focal point for expanding catalyst research to other APS beamlines using advanced techniques not routinely applied to catalyst systems, e.g., SAXS, XES, RIXS, and HERF spectroscopy. Development of these latter methods would position the APS as a leader in this area and attract leading scientists from all over the world. It is expected that new users would initially characterize their materials and identify appropriate systems for specialized techniques.

Throughout the U.S. and the world, there are countless research groups working to develop the enabling material in fuel cell catalysis: an oxygen reduction electrocatalyst that is less expensive and more durable than platinum [36-38]. A few of these groups utilize synchrotron-based x-ray techniques to characterize their electrocatalysts; however, these studies are almost exclusively in environments mimicking the reactive environment or are *ex situ*. A notable exception is the catalyst development effort being led by Los Alamos National Laboratory, which encompasses many approaches and involves many university and national laboratories. As part of this project, Argonne researchers have developed the capability to characterize catalysts containing low-atomic-number elements in an operating fuel cell using XAFS at the APS. Utilizing this cell (Fig. 4), Argonne scientists have determined the active site in a cobalt-containing catalyst. This capability would be extremely useful to other catalyst development teams around the country and the world, and it is envisioned that a dedicated APS electrocatalysis beamline could be designed and made available to these teams. The neutron source at the National Institute of Standards and Technology (NIST) has a beamline dedicated to studies of water transport in fuel cells, which has provided invaluable information for fuel cell materials design. The APS beamline would be the catalyst counterpart to the NIST beamline.

A molecular-level understanding of the interactions and correlations that occur in solution and between solution phases is essential to building a predictive capability of a metal ion's solubility, reactivity, kinetics, and energetics. Until the recent availability of tunable, high-energy x-rays this understanding has been significantly limited by the absence of structural probes. The APS, with its high flux of high-energy x-rays, is the ideal synchrotron source to provide this new information, which is critical to the advancement of solution chemistry. The utility of high-energy x-rays is currently being demonstrated as part of an APS Partner User Proposal (PUP-52), and has received high visibility, including an *Inorganic Chemistry* feature cover [34]. This effort is interesting a cadre of solution chemists that, to date, have not been part of the user base at synchrotron facilities. The extension of high-energy capabilities from simple PDF experiments to more complex liquid-liquid interfaces is expected to significantly broaden this new interest group into areas including soft-matter studies.

## References

- [1] *Basic Research Needs to Assure a Secure Energy Future*, A Report from the Basic Energy Sciences Advisory Committee (U.S. Department of Energy, February 2003). <http://www.sc.doe.gov/bes/reports/abstracts.html#SC>
- [2] *Basic Research Needs: Catalysis for Energy*, Report from the U.S. Department of Energy Basic Energy Sciences Workshop, August 6-8, 2007 (Office of Basic Energy Sciences, U.S. Department of Energy). [http://www.sc.doe.gov/bes/reports/files/CAT\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/CAT_rpt.pdf)
- [3] *Basic Research Needs for Solar Energy Utilization*, Report on the Basic Energy Sciences Workshop on Solar Energy Utilization, April 18-21, 2005 (Office of Basic Energy Sciences, U.S. Department of Energy). [http://www.sc.doe.gov/bes/reports/files/SEU\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf)
- [4] *Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels*, Report of the Basic Energy Sciences Workshop on Clean and Efficient Combustion of 21st Century Transportation Fuels (Office of Basic Energy Sciences, U.S. Department of Energy). [http://www.sc.doe.gov/bes/reports/files/CTF\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/CTF_rpt.pdf)
- [5] *Basic Research Needs for the Hydrogen Economy*, Report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage, and Use, May 13-15, 2003 (Office of Basic Energy Sciences, U.S. Department of Energy). <http://www.sc.doe.gov/bes/hydrogen.pdf>
- [6] M.R. Antonio and L. Soderholm, "X-ray absorption spectroscopy of the actinides," *Chemistry of the Actinide and Transactinide Elements*, third edition; L.R. Morss, J. Fuger, and N. Edelstein, eds. (Springer: Dordrecht, 2006) p. 3086.
- [7] *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, A. Wieckowski, E.R. Savinova, and C.G. Vayenas, eds. (Marcel Dekker, Inc., New York, NY, 2003).
- [8] S. Mukerjee, "In-Situ X-ray Absorption Spectroscopy of Carbon-Supported Pt and Pt-Alloy Electrocatalysts: Correlation of Electrocatalytic Activity with Particle Size and Alloying," *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, A. Wieckowski, E.R. Savinova, and C.G. Vayenas, eds. (Marcel Dekker, Inc., New York, NY, 2003) p 501.
- [9] B.K. Teo, *EXAFS: Basic Principles and Data Analysis* (Springer-Verlag: Berlin, 1986) p. 349.
- [10] P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey, and S.J.L. Billinge, "Rapid-acquisition pair distribution function (RA-PDF) analysis," *J. Appl. Cryst.* **36**, 1342 (2003).
- [11] T.E. Egami and S.J.L. Billinge, *Underneath the Bragg Peaks, Volume 7: Structural Analysis of Complex Materials*, R.W. Cahn, series ed. (Pergamon, October 16, 2003).

- [12] V.M. Niels and D.A. Keen, *Diffuse Neutron Scattering From Crystalline Materials*, 2001
- [13] P.J. Chupas, K.W. Chapman, and P.L. Lee, "Applications of an amorphous silicon-based area detector for high-resolution, high-sensitivity and fast time-resolved pair distribution function measurements," *J. Appl. Cryst.* **40**, 463 (2007).
- [14] P.J. Chupas, M.F. Cirraolo, J.C. Hanson, and C.P. Grey, "In Situ X-ray Diffraction and Solid-State NMR Study of the Fluorination of  $\gamma$ - $\text{Al}_2\text{O}_3$  with  $\text{HCF}_2\text{Cl}$ ," *J. Am. Chem. Soc.* **123**, 1694 (2001).
- [15] C. Revenant, F. Leroy, R. Lazzari, G. Renaud, and C.R. Henry, "Quantitative analysis of grazing incidence small-angle x-ray scattering: Pd/MgO(001) growth," *Phys. Rev. B* **69**, 035411-1 (2004).
- [16] B. Lee, S. Seifert, S.J. Riley, G. Tikhonov, N.A. Tomczyk, S. Vajda, and R.E. Winans, "Anomalous grazing incidence small-angle x-ray scattering studies of platinum nanoparticles formed by cluster deposition," *J. Chem. Phys.* **123**, 074701-1 (2005).
- [17] S. Vajda, G.P. Wiederrecht, A. Bouhelier, G.Y. Tikhonov, N. Tomczyk, B. Lee, S. Seifert, and R.E. Winans, "Optical Properties of Gold Nanoparticles Produced by the Assembly of Size-Selected Clusters: Covering the Full Visible Wavelength Range in the Smallest Particle Size Regime," *Collect. Czech. Chem. C* **72**, 121 (2007).
- [18] S. Vajda, R.E. Winans, J.W. Elam, B. Lee, M.J. Pellin, S. Seifert, G.Y. Tikhonov, and N.A. Tomczyk, *Top. Catal.* **39**, 161 (2006).
- [19] R.E. Winans, S. Vajda, G.E. Ballentine, J.W. Elam, B. Lee, M.J. Pellin, S. Seifert, G.Y. Tikhonov, and N.A. Tomczyk, "Supported Gold Clusters and Cluster-Based Nanomaterials: Characterization, Stability and Growth Studies by In Situ GISAXS under Vacuum Conditions and in the Presence of Hydrogen", *Top. Catal.* **39**, 145 (2006).
- [20] J.A. van Bokhoven, C. Louis, J.T. Miller, M. Tromp, O.V. Safonova, and P. Glatzel, "Activation of Oxygen on Gold/Alumina Catalysts: In Situ High-Energy-Resolution Fluorescence and Time-Resolved X-ray Spectroscopy," *Angew. Chem. Int. Ed.* **45**, 4651 (2006).
- [21] G. Luo, S. Malkova, J. Yoon, D.G. Schultz, B. Lin, M. Meron, I. Benjamin, P. Vanysek, and M. Schlossman, "Ion Distributions near a Liquid-Liquid Interface," *Science* **311**, 216 (2006).
- [22] U. Bergmann, C.R. Horne, T.J. Collins, J.M. Workman, and S.P. Cramer, "Chemical dependence of interatomic X-ray transition energies and intensities – a study of Mn  $K\beta$ ' and  $K\beta_{2,5}$  spectra," *Chem. Phys. Lett.* **302**, 119 (1999).
- [23] P. Glatzel, L. Jacquamet, U. Bergmann, F.M.F. de Groot, and S.P. Cramer, "Site-Selective

EXAFS in Mixed-Valence Compounds Using High-Resolution Fluorescence Detection: A Study of Iron in Prussian Blue,” *Inorg. Chem.* **41**, 3121 (2002).

[24] N.M. Markovic and P.N. Ross, “Surface science studies of model fuel cell electrocatalysts,” *Surf. Sci. Rep.* **45**, 117 (2002).

[25] N.M. Markovic and P.N. Ross, Jr., “New electrocatalysts for fuel cells: from model surfaces to commercial catalysts,” *Cat. Tech.* **4**, 110 (2000).

[26] V.R. Stamenkovic, B. Fowler, B.S. Mun, G. Wang, P.N. Ross, C.A. Lucas, and N.M. Markovic, “Improved Oxygen Reduction Activity on Pt<sub>3</sub>Ni(111) via Increased Surface Site Availability,” *Science* **315** 493 (2007).

[27] V. Stamenkovic et al., “Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces,” *Nat. Mater.* **6**, 241 (2007).

[28] L. Soderholm, S. Skanthakumar, and J. Neufeind, “Determination of actinide speciation in solution using high-energy X-ray scattering,” *Anal. Bioanal. Chem.* **383**(1), 48 (2005).

[29] S. Skanthakumar and L. Soderholm, *Mater. Res. Soc. Symp. Proc. 2006*, **893**, (Actinides 2005-Basic Science, Applications and Technology) p. 411.

[30] M. Magini, G. Licheri, G. Paschina, G. Piccaluga, and G. Pinna, *X-ray diffraction of ions in aqueous solutions: hydration and complex formation*, (CRC Press Inc., Boca Raton, Florida, 1988) p. 267.

[31] S. Skanthakumar, M.R. Antonio, R.E. Wilson, and L. Soderholm, “The Curium Aqua Ion,” *Inorg. Chem.* **46**, 3485 (2007).

[32] J. Neufeind, L. Soderholm, and S.J. Skanthakumar, “Experimental Coordination Environment of Uranyl(VI) in Aqueous Solution,” *J. Phys. Chem. A* **108**, 2733 (2004).

[33] R.E. Wilson, S. Skanthakumar, P.C. Burns, and L. Soderholm, L., *Angew. Chem. Int. Ed.* **46**, 8043 (2007).

[34] R.E. Wilson, S. Skanthakumar, G. Sigmon, P.C. Burns, and L. Soderholm, *Inorg. Chem.* **46**, 2368 (2007).

[35] L. Soderholm, P.M. Almond, S. Skanthakumar, R.E. Wilson, and P.C. Burns, “Structure of the Homoleptic Thorium(IV) Aqua Ion [Th(H<sub>2</sub>O)<sub>10</sub>]Br<sub>4</sub>,” *Angew. Chem. Int. Ed.* **47**, 493 (2008).

[36] P. Glatzel and U. Bergmann, “High resolution 1s core hole X-ray spectroscopy in 3d transition metal complexes—electronic and structural information,” *Coord. Chem. Rev.* **249**, 65 (2005).

[37] R. Borup et al., “Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation,” *Chem. Rev.* **107** 3904 (2007).

[38] H.A. Gasteiger, S.S. Kocha, B. Sompalli, and F.T. Wagner, “Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs,” *Appl. Catal. B: Environmental* **56**, 9 (2005).

## Renewal of the Advanced Photon Source: Condensed Matter & Materials Physics

<b>Samuel D. Bader</b> (Chair)	<i>Argonne National Laboratory</i>
<b>Susan N. Coppersmith</b>	<i>University of Wisconsin-Madison</i>
<b>John W. Freeland</b>	<i>Argonne National Laboratory</i>
<b>Patricia Mooney</b>	<i>Simon Fraser University</i>
<b>Julia M. Phillips</b>	<i>Sandia National Laboratories</i>
<b>Ivan K. Schuller</b>	<i>University of California, San Diego</i>
<b>Gopal K. Shenoy</b>	<i>Argonne National Laboratory</i>
<b>G. Brian Stephenson</b>	<i>Argonne National Laboratory</i>

### Executive Summary

The twenty-first century has ushered in many new societal challenges, the greatest being to develop alternative energy technologies. This is an area where condensed matter and materials physics (CMMP) can play—and is playing—a major role. Condensed matter and materials physics is an engine for innovation emanating from its quest for new materials, new properties, and a new understanding of the world around us. Condensed matter and materials physics also provides new instrumentation to enable many diverse fields of endeavor: from information technology to healthcare to tools for exploring the cosmos. However, the U.S. is at a turning point where its leadership in the field of CMMP is not to be taken for granted. New strategic investments are necessary. U.S. Department of Energy (DOE) major facilities, including the Advanced Photon Source (APS), need to continue to play a central role in making progress toward significant national scientific and technological goals. The charge is to identify where major breakthroughs are likely to occur in the coming decade, and to utilize this perspective in order to outline upgrade investments needed to enable the APS to perform optimally in uncovering, exploring, and understanding the new science in CMMP.

This report presents an examination of the grand scientific challenges in CMMP in order to provide sets of hot questions that can be addressed in the future within a laboratory setting. These questions are then generalized to provide a clear indication of where it is most worthwhile to invest in APS upgrades in order to support the science of the next decade or so. From the six grand challenges considered, dozens of hot questions are posed within this report. These questions provide a roadmap for a fundamental set of APS upgrades. The challenges include the interdisciplinary scientific and applications realms of emergence, energy, biophysics, non-equilibrium phenomena, nanoscience, and information technology (IT). The hot questions focus on opportunities to create new materials, new structures and morphologies, new properties and functionalities, and new theoretical and computational understandings that have an advanced level of predictive ability spanning multiscale spatio-temporal regimes.

Transformational scientific advances require a new look at the ways synchrotrons are equipped and organized. There is a need for new operational philosophies, new end-station configurations, sharply focused x-ray optics, and novel source properties in order to provide the following, which will have to be prioritized in independent studies:

- Multiple extreme environments, such as high fields and/or pressures, extreme temperatures, and facilities for reactive or radioactive samples
- The presence of multiple, complementary probes in order to determine structure and properties simultaneously
- Sample preparation and processing *in situ* needed to study growth mechanisms and the onset of new properties
- Small spatial resolution in imaging and spectroscopy to complement structural investigations
- Short time resolution to probe rapid dynamics and non-equilibrium phenomena

In addition, a paradigm change is needed in the way synchrotrons are utilized in order to actively drive new science within the user community rather than merely

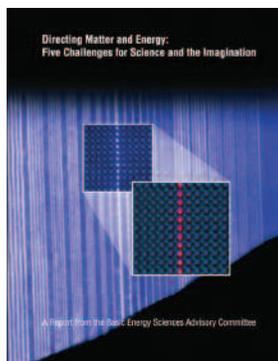
satisfying the needs of disparate user groups. This would be the first stage of a concerted effort to address the scientific needs of a world facing global instabilities. *Rising Above the Gathering Storm: Energizing and Employing America for a Brighter Economic Future*, a report from the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine [1], has captured the nature of the challenge. This new approach to synchrotron utilization requires surveys to determine which twentieth-century beamlines and programs should be cleared away to accommodate the science of the twenty-first century. This report is the beginning of a dialogue of deep introspection that will bring about sweeping changes to advance a critical scientific agenda of renewal to ensure U.S. leadership in scientific and technological goals that are shared globally. More detailed recommendations will require workshops to further examine the ideas set forth herein.

## Introduction

Condensed matter and materials physics is an engine of innovation for society at large, leading to industrial applications, especially in areas of high technology, and thus stimulating the economy, helping to ensure our defense and homeland security, and, most importantly, improving our energy independence. Condensed matter and materials physics helped to initiate the information technology revolution that is changing our world in so many ways, from the Internet to the iPod<sup>®</sup>. Condensed matter and materials physics is also an enabler of scientific ventures outside of its own domain because of the materials and instruments that it creates and perfects (such as solid-state lasers, transistors, fiber optics, magnetic resonance imaging, and scanning probe techniques) that energize fields from healthcare to space exploration and particle accelerators. Thus, CMMP is among the most exciting areas of science: discovering and investigating the emergence of new materials and phenomena.

Condensed matter and materials physics embraces “the science of the world around us” [2]. It involves the creation of advanced materials, the exploration of their properties, and an understanding in terms of both the theoretical underpinnings of the phenomena of interest, and the structure-properties relationships exhibited. Condensed

matter and materials physics is a broad field that encompasses mission-oriented research, such as for advanced solar cells, and largely curiosity-driven research, such as in the fractional quantum Hall effect. It encompasses bench-top science as well as major facility research; independent investigator research as well as team research; experimental physics, theoretical physics, and computational physics. It can involve hard materials—such as superconductors—or soft matter such as polymers, organics and biomaterials. It can involve different forms of these, such as solids, liquids, and glasses; and crystalline, amorphous, nanostructured, and/or composite systems. The structure and properties can be intriguing in their equilibrium states, or in metastable or dynamically driven environments as a function of state variables and/or spatio-temporal constraints. Thus, there is a richness and diversity to the field that makes for a lively internal culture characterized by a mix of virtuosity, inquisitiveness, and unpredictability—a culture shared by many scientific disciplines.



Cover of the BESAC report, “Directing Matter and Energy: Five Grand Challenges for Science and the Imagination.”

There have been many efforts to encapsulate what the twenty-first century will represent scientifically. The U.S. Department of Energy Office of Basic Energy Sciences (BESAC) Grand Challenges Committee coined the new century as the “Age of Control” [3]. Physics Nobelist Robert Laughlin dubbed it the “Age of Emergence” [4], where we delight in the study of the complex organizational structure that grows out of simple rules. The journalist Thomas Friedman alluded to an “Era of Energy and Technology” [5]. These are all apt descriptions predicting exciting possibilities that lie within our grasp.

## Key Science Drivers

The scientific case for the APS renewal can begin with the grand challenges in CMMP. These were already identified in the CMMP 2010 report [2]. (The Basic Energy Sciences Grand Challenges report [6] emphasizes similar themes, encompassing additional scientific areas.) Thus, our focal point is the six challenges identified in the

CMMP 2010 Report: How do complex phenomena emerge from simple ingredients? How will the energy demands of future generations be met? What is the physics of life? What happens far from equilibrium and why? What new discoveries await us in the nanoworld? How will the IT revolution be extended?

These six overlapping challenges point to where we anticipate finding the most exciting breakthroughs over the next decade and beyond: emergence, energy, biophysics, non-equilibrium, nano, and information technology. The committee fleshed out these challenges with lists of hot questions that make the challenges more tangible in a laboratory setting. We outline below examples of these questions, which reveal patterns indicating that similar approaches are needed to address the different challenges. This allows us to identify fundamental types of experiments that are needed to advance the field. Many of them could benefit from the hard x-rays that the APS provides, if there were suitable upgrades, as will be outlined elsewhere in this report.

In summary, we will see that the following hot questions have a healthy amount of redundancy to them, and lend themselves to experiments that require:

- Multiple extreme environments, such as high fields and/or pressures, extreme temperatures, and facilities for reactive or radioactive samples, and
- The presence of multiple, complementary probes in order to determine structure and properties simultaneously
- Sample preparation and processing *in situ* in order to study growth mechanisms and the onset of new properties (in, for example, single crystals, films, foams, glasses, proteins, polymers, heterostructures, and/or nanostructures)
- Small spatial resolution in imaging and spectroscopy to complement structural investigations
- Short time resolution to probe rapid dynamics and non-equilibrium phenomena

### **How do complex phenomena emerge from simple ingredients?**

Is it possible to develop multi-scale spatio-temporal methods to theoretically or computationally predict desired properties, structures, dynamics of transitions between

structures, and synthetic pathways? Theorists have developed powerful codes to simulate materials properties at the atomic scale, at the mesoscale, and in the continuum limit. One challenge is to tackle the weak-coupling limit where such codes can be meaningfully integrated into a hierarchy so that the properties of macroscopic systems can be simulated from elementary constituents, including organic, molecular and biological building blocks, as one traverses vastly different time scales. This involves confronting the challenging issues associated with the interface at each hierarchical step, in order to reconcile assumptions, pass meaningful parameters, and retain physically significant and accurate results and insights. The strong-coupling limit will require entirely new theories and approaches.

How does one describe materials whose electrons/atoms are neither perfectly localized nor fully itinerant (i.e., correlated electron/atom systems)? Fermi liquid theory has enjoyed great utility, but there are important classes of materials that defy description and require going beyond present-day theoretical understanding of complex matter. Traditionally, the high-temperature superconductors and narrow-band metals, such as the heavy fermion systems, fall into the category where understanding is a major challenge. The  $5f$ -electron systems are relatively unexplored, but might hold the key to understanding because their  $f$ -bands and bands are more itinerant than are the  $4f$ 's, but tend to be more localized than  $3d$ -states. Can we identify and understand materials with quantum critical points? Today another important facet of the problem is to understand correlated atom behavior in ultra-low temperature Bose-Einstein condensates, such as have recently been discovered and explored using laser cooling methods.

Can we integrate materials whose properties tend to be mutually exclusive, such as ferromagnetic and superconducting, or transparent and conducting? There is always the challenge of searching for elusive single materials that embrace diverse properties, such as novel multiferroics. This quest to create hybrids has more recently captured the imagination of the scientific community. For example, combining soft and hard matter could bring the physics community closer to understanding intriguing issues associated with the life sciences. What is the origin of such contra-indicated

properties? What are the limits of their performance, and why are there limits?

### **How will the energy demands of future generations be met?**

Fundamental advances in CMMP are central to all technologies currently being eyed as contributors to meeting future energy demands, from renewable energy such as solar energy or biofuels, to carbon-neutral energy sources such as nuclear energy, to energy efficient technologies such as solid-state lighting. The diverse roles of materials in these technologies raise an equally diverse set of scientific questions.

Can we create high-efficiency, low-cost photovoltaic devices? Is there a self-assembly strategy that can produce highly efficient solar energy conversion? Can we solve the doping and other materials problems in wide-bandgap semiconductors (Group III-Nitrides and ZnO) for green, blue, and ultraviolet light emitters? Can we improve wide bandgap materials/devices (GaN, SiC, etc.) for high-power and high-temperature applications (e.g., electric transmission, electronics for improved efficiency of automobile and aircraft engines)?

A key to progress might be a new understanding of materials that enable rapid searches of phase space to gain a wide variety of information. In developing thermoelectrics, which convert heat into electricity, the need is to balance the properties of phonons vs. electrons. How can we advance the search? For nuclear technologies we need to study fundamental properties of transuranic systems, fuel rod designs, environmental remediation, and stewardship of materials. In summary, we need to discover new classes of materials and combinations with outstanding properties such as efficient light emission, photovoltaic conversion, superconductivity, catalytic efficiency, electrodes for fuel cells, etc.

What is the source of the uniqueness of catalytic sites on a surface? What is their structure? How can we distinguish “spectator” sites from “player” sites? Are there new catalytic properties of nanostructured elemental or composite materials that are not the canonical ones in use today? Are there classes of energy conversion reactions that share similarities in their transition state? Can we identify the structures and

similarities and use them to create new insights and sets of design rules, and to tune chemical intuition?

### **What is the physics of life?**

How does one distinguish, characterize, and differentiate living materials from inert materials? What is the chemical language by which cells communicate? What are the differences between right- and left-handed DNA and what is the basis for chiral asymmetry in life? Does this question relate to the chemistry and physics of how molecules form in extreme environments? Can we observe and record the structural changes in arbitrary biomolecules when they interact with each other or with external stimuli? How does protein folding influence the properties of active sites? What can we learn from biosystems in order to culture and harvest the materials we need, from biofuels to self-repairing materials, to computer subsystems?

What are the “design rules” governing the three-dimensional architecture and properties of soft materials in specific environments (temperature, radiation, chemical, etc.)? What is the origin of “mistakes” in structure during synthesis? Can we avoid these mistakes to get compositionally and structurally pure material? What governs the limits of charge transfer in organic/polymer materials? How can we optimize this property for particular needs?

### **What happens far from equilibrium and why?**

Is there a general way in which collective behavior emerges or disappears? Phenomena such as magnetism, superconductivity and ferroelectricity can be created out of non-equilibrium states, i.e., by pumping with light to a higher excited state, or by pumping an ordered state into the disordered phase. Can the glassy state be described theoretically?

Is there a universal description of quantum transport that can embrace electrons, spins, molecules, and fluids? Non-equilibrium quantum transport equations must be examined within the broadest perspective to encompass phenomena as diverse as, for example, superfluid systems, organic spintronics, single electron transistors, and

ultra-fast dynamics of optically excited semiconductors. Can all ranges of frequency, mobility and spatial scale be meaningfully covered? Is there a universal origin to  $1/f$  noise? Can we witness the birth of an elementary excitation in CMMP systems?

### **What new discoveries await us in the nanoworld?**

Nanomaterials offer the promise to enable us to continue to develop technologically as we face the fact that present-day materials and processes are reaching their limits. The questions concern what lies beyond silicon? Can we transcend microlithography with bottom-up approaches? Can we harness spintronics, near-field photonics, and other advanced concepts and approaches to meet the needs of tomorrow? Will quantum computing become a reality? Will we learn to utilize bio-inspired approaches to address our many societal concerns?

As objects shrink in size, are new methods are needed to measure what we make, thus enabling the study of the new physics that emerges? Can we achieve the level of control needed to fabricate integrated nanosystems with the same level of reproducibility as found in today's integrated circuits? What are the limits to controlled fabrication of integrated nanosystems with reproducible properties? And what governs these limits? Can one control and manipulate organic-infrared and to find new detectors that extend farther into the infrared?

What are the rules that govern phase separation? What are the rules that govern self-organization in general? Self-assembly, defined as the autonomous organization of components into patterns or structures, is rapidly emerging as a topic of major interest. Self-assembly occurs on length scales that extend from the molecular to the cosmic. Self-assembly provides pathways to create new nanoscale materials from the bottom up that transcend the spatial limits of lithographic patterning, and it is implicated as a universal feature in the physics of many complex systems. The thermodynamic and kinetic rules that govern self assembly, and the underlying structural and electronic properties, need to be understood in order to harness self assembly to create a new generation of advanced materials and hierarchically organized systems, as well as to get a better physical understanding of living systems. For example, how

does surface topology influence morphology? Can porous membrane materials provide a new platform to catalyze heterogeneous chemical reactions while separating reactants and products?

### **How will the information technology revolution be extended?**

As we reach the end of Moore's Law in silicon technology, advances in CMMP will have a crucial role in extending the IT revolution. Can we solve the materials issues related to the convergence of III-V semiconductors with silicon: integration of light emitters/detectors with silicon integrated circuits? Can we engineer new substrates for semiconductors that are not lattice matched to bulk materials and thereby exploit strain to tailor properties? Can we heterogeneously integrate different materials on one integrated circuit chip, with multiple layers of devices (three-dimensional integration), overcoming problems of differential thermal expansion and stress? Can we tackle the problems of advanced packaging/heat extraction from circuits? What lies beyond the semiconductor roadmap? Can we understand and develop alternatives to silicon electronics, i.e., determine the limits of optoelectronics, photonics, plasmonics, or spintronics? Can we utilize the wide range of functionalities of complex oxides, together with their high susceptibility to external perturbations, to develop wholly new types of (Mottronic) technologies?

Modern semiconductor-based electronics utilize the charge of the electron, but ignore its spin. Harnessing the spin can add value and functionality, such as in non-volatile electronics that retain stored information when the power is off, and in the creation of ultra-low-heat dissipation circuits that communicate via pure spin currents without the flow of charge. Can we image a pure spin current? Can we find materials for spintronics devices (for injection of spin-polarized electrons into semiconductors)? Can one find nearly 100% spin polarized electron sources and retain interfacial control of the polarization? Can one create a spin transistor with gain to enable spintronic applications? Can one find magnetic semiconductors that operate well above room temperature? A corollary challenge is to integrate new spintronic materials with conventional electronic materials and processes in order to add value and evolve the technologies in a continuous fashion.

How does one store and address information with light? As interest in optical materials and phenomena migrates to the sub-wavelength and near-field realms, new challenges arise. Exploring and understanding the relevant issues will advance the emerging areas of photonics and plasmonics. The key requirement of addressability—the ability to direct the movement of energy or signals within a useful architecture—is a difficult challenge. Future developments in photochemical energy transduction, optoelectronics, and optical computing might hinge on such breakthroughs. A corollary challenge is to address the question of what materials parameters drive the coupling and diffusion of thermal energy on length scales shorter than a phonon wavelength.

Can we create solid-state devices that operate at 80K or higher for quantum computing? What are the ramifications of quantum entanglement and coherency in computation? The goal ahead is to explore new paradigms to enable computations that cannot otherwise be achieved. A challenge is to develop arrays of quantum coherent objects that would form the quantum bits (qubits) and the logic gates of a quantum computer. What materials systems and configurations permit sufficiently long quantum coherence times for computation?

## Significance of the APS

The APS is one of the world's premier hard x-ray facilities, offering a crucial set of tools to attack these forefront scientific areas. These powerful hard x-ray synchrotron techniques, such as high-resolution scattering, imaging, and spectroscopy, offer a unique ability to penetrate materials and provide an element-resolved picture to address the scientific grand challenges and associated hot questions outlined above. However, a new paradigm must be embraced in order for the APS to realize its full potential to keep our nation at the leading edge of the scientific frontier. Presently, the APS is largely organized to serve independent user communities. In the future the APS will provide greater value by leading and focusing the user community in order to make sure that a critical mass of talent is focused on grand-challenge goals. This means that the APS will have to reorganize to act as a single organic entity to

address a hierarchy of scientific questions in a coherent manner. The APS will need to make room for new twenty-first century science, expanding some of its lab modules into full-service laboratories, of which the Center for Nanoscale Materials can be considered as a first model. End-stations on rolling platforms may be moved in place or x-ray beams may be brought to semi-permanent installations through collaborations from contiguous institutes where the hot questions are pursued 24/7. User agreements will span over periods of years, rather than days, in order to get serious work accomplished, as outlined below.

## Scientific Community

The CMMP scientific community will benefit, as well as our country and the planet as a whole.

## Requirements and Capabilities

This proposal encompasses a transformational change in the way experiments are undertaken at major synchrotron facilities. Rather than having the x-ray studies conducted separately, a complete suite of experiments would be performed *in situ* on the beamline in real time by combining a variety of probes and processing tools. The evolution of static and dynamic properties can directly connect with information provided by the x-rays. We outline several types of experiments and capabilities. Key to this approach will be a strengthening of ties to existing external users as well as generating new users who would partner to perform long-term (1-3 years) dedicated scientific programs. The new types of combined experiments fall into general categories:

- Expansion in facilities to bring widely applicable, powerful hard x-ray synchrotron techniques such as high-resolution scattering and spectroscopy to bear on a greater variety of materials and processes.
- An appropriate balance of facilities for specialized, high-performance, niche techniques (e.g., inelastic scattering, magnetic scattering, ultra-fast or coherent x-ray techniques).

- The presence of multiple, ancillary, and complementary probes. The ability to follow material properties in real time is crucial in order to correlate the x-ray measurements with changes due to transitions between allowed phases. This will be accomplished by enabling beamlines to directly integrate laboratory-based measurements of electrical, magnetic, and optical properties. This also encompasses the ability to externally perturb systems away from equilibrium with electrical and optical stimulation, which is crucial to the study of phase transitions and systems both near and far from equilibrium.
- Combinations of extreme environments ( to alter temperatures, pressures, and fields, and to accommodate reactive chemistry, radioactive samples, and ultra-short electromagnetic pulses and shock waves.) Such measurements are suited to x-ray probes that can handle small sample volumes because high pressures and pulsed magnetic fields are more readily created over confined spaces. While today such experiments can be undertaken in environments with one extreme condition, in the future multiple extreme conditions imposed simultaneously will be used to track the behavior across a multidimensional phase space.
- *In situ* processing and synthesis. Understanding, for example, catalytic phenomena requires the ability to alter reaction conditions in real time. Obtaining rate laws and transition state information, and being able to extract general insights depends on following reactions dynamically. Similarly, *in situ* studies of film growth processes provide a unique opportunity to understand the formation of materials in real time. Via such studies much of the art of materials growth can be transformed into a science, where intuition will succumb to sets of rules to guide discovery. It is envisioned that major efforts can be launched to provide a synthesis institute with an initial array of grow environments that include, for example, different types of growth chambers, such as molecular beam epitaxy, as determined by workshops that identify the optimal goals in synthesis and processing.
- Where possible, portable systems offering the above capabilities to the user community can be transported to multiple beamlines, optimized for different x-ray studies. With an integrated laboratory space, such systems could then be harnessed when off-line in preparation for experiments.
- Where needed for complex, non-portable apparatus, facilities and peer-reviewed ac-

cess will allow building and operating experiments for extended periods (two years) in multiplexed hutches where an x-ray beam can service multiple experiments.

- A range of spatial resolutions extending to  $\sim 1$  nm for imaging and probing with various x-ray contrast mechanisms (absorption, phase contrast, diffraction, fluorescence, spectroscopy, polarization).
- A range of temporal resolutions extending to  $\sim 1$  ps to probe rapid dynamics and non-equilibrium phenomena.

The above can be considered as a first generation of recommendations to be discussed, altered, and/or refined via a process that is open to stakeholders in the community.

## References

- [1] *Rising Above the Gathering Storm: Energizing and Employing America for a Brighter Economic Future, Committee on Prospering in the Global Economy of the 21st Century: An Agenda for American Science and Technology*, National Academy of Sciences, National Academy of Engineering, Institute of Medicine (The National Academies Press, Washington, D.C., 2007).
- [2] *Condensed-Matter and Materials Physics: The Science of the World Around Us*, Report of the Committee on CMMP 2010, Solid State Sciences Committee, Board on Physics and Astronomy, Division on Engineering and Physical Sciences, National Research Council of the National Academies (The National Academies Press, Washington, D.C., 2007).
- [3] Graham R. Fleming and Mark. A. Ratner, "Grand challenges in basic energy sciences," *Physics Today*, 20 (July 2008).
- [4] Robert B. Laughlin, *A Different Universe*, (Basic Books, New York, 2005)
- [5] *The New York Times*, July 30, 2008
- [6] *Directing Matter and Energy: Five Challenges for Science and the Imagination. A Report from the Basic Energy Sciences Advisory Committee* (U.S. Department of Energy, December 20, 2007).

## Renewal of the Advanced Photon Source: Engineering Applications & Applied Research

<b>Jonathan D. Almer</b>	<i>Argonne National Laboratory</i>
<b>Mark R. Daymond</b>	<i>Queen's University</i>
<b>George R. Fenske</b>	<i>Argonne National Laboratory</i>
<b>Gene E. Ice (Chair)</b>	<i>Oak Ridge National Laboratory</i>
<b>Lyle E. Levine</b>	<i>National Institute of Standards and Technology</i>
<b>Robert M. Suter</b>	<i>Carnegie Mellon University</i>
<b>Angus P. Wilkinson</b>	<i>Georgia Institute of Technology</i>

### Executive Summary

A fundamental multiscale understanding of the origin of materials behavior is vital to the design and development of new and improved materials for structural, energy, and other engineering applications. Similarly, applied studies of fuel-spray turbulence, dendritic growth, bubble formation, chemical segregation/transport, and other processes are essential to optimize and guide the development of important systems such as gas engines, electrodeposition systems, fuel cells, toxic barriers, and batteries. These kinds of studies can be classified as engineering applications and applied research, and represent an area where the Advanced Photon Source (APS) can significantly impact technologies of critical national interest.

We propose a strategy to make the APS the leading synchrotron institution in the world for engineering applications and applied research. This proposal includes hardware and software upgrades that will make the APS accessible to a wider range of engineering and applied research scientists and will provide unprecedented experimental capabilities. These upgrades exploit unique capabilities of the APS that enable fundamentally new characterization tools and offer a huge return on investment

that will stimulate American competitiveness and create new opportunities in areas of critical national interest including energy independence and national defense.

This proposal leverages off special properties of the APS that make it the key x-ray source in the United States for engineering applications and applied research. In particular, the high brightness of APS x-rays at short wavelengths creates unprecedented opportunities to study real materials in real environments and in real time; with ultra-bright hard x-ray beams, materials can be characterized nondestructively *in situ*, during service, and deep within actual parts where materials behavior is fundamentally distinct from the behavior in near-surface regions. For example, spatially-resolved measurements with high-energy x-rays are a transformational class of synchrotron science with the potential to revolutionize engineering and the applied sciences. Spatially-resolved characterization of stress distributions, texture, and particle size distributions that evolve near structural inhomogeneities can test and guide models and dramatically improve the performance of manufactured parts. Nondestructive, spatially-resolved measurements will also allow for characterization of process-driven grain growth and phase evolution, including the driving forces of anisotropic or transient stress states. Other approaches will allow for ultra-high-resolution characterization of engineering materials at the mesoscale level of defects—such as grain boundaries, dislocation walls, and phase boundaries—to test emerging mesoscale and multiscale theories of materials behavior. In short, the emerging potential to image scalar and tensor distributions of chemistry, structure, orientation, and defects in three dimensions will transform our understanding of the hierarchical structures that control materials behavior.

An area of almost unexplored potential is the detection and characterization of minor phases that emerge at interfaces of real materials, including complex phases at cladding interfaces in nuclear fuel rods, phases at the fiber/matrix interface in composite materials, and in-service measurements of corrosion including elastic stresses and studies of stress corrosion cracking. In addition to spatially-resolved measurements, time-resolved measurements—made possible by high source brightness and efficient x-ray sensitive area detectors—will allow for the discovery of transient

phases that evolve during welding, heat treatment, concrete solidification, amorphization, and other phase-evolving processes.

Finally, high-brightness, high-energy beams offer unique advantages for nondestructive imaging. For example, phase-contrast high-energy radiography and tomography can resolve structures in low- $Z$  or low-density materials that would otherwise be invisible to x-rays. Phase contrast imaging can also resolve internal structures in specimens comprised of mixed  $Z$  components or inside environmental chambers, and can characterize sprays and jet distributions that are difficult to study by alternative methods. With advanced instrumentation, imaging can also be used to follow the evolution of cracks, voids, precipitates, and other phenomena in near real time.

To realize the immense scientific potential of the APS for engineering and applied research, dedicated instrumentation is essential, including sophisticated hardware, software, and high-performance computational facilities. To address urgent near-term needs and emerging scientific opportunities we propose the following steps that will significantly increase user access and experimental capabilities at the APS:

- Dedicate an additional beamline to high-energy x-ray measurements of aggregate stress/strain/texture from materials.
- Complete the Phase II upgrade of the X-ray Operations and Research (XOR) 1-ID beamline.
- Build a dedicated polychromatic nanoprobe hutch and install canted undulators on XOR beamline 34-ID to allow for simultaneous and independent use of polychromatic mesoscale and nanoscale probes.
- Optimize at least one bend-magnet beamline for high-energy energy-dispersive diffraction.
- Develop a dedicated high-energy tomography station with phase-contrast sensitivity.
- Develop a range of environmental chambers for powder diffraction and small-angle x-ray scattering (SAXS) targeted to catalysis and other applied studies.

- Develop user-friendly “expert” software for all engineering stations that insures users walk away from experiments with data sufficiently processed for analysis at their home institution.
- Coordinate combined techniques/characterizations to follow materials evolution.
- Develop user-friendly mail-in capabilities in anticipation of the growing difficulty of travel, given the likelihood of high energy costs and in the interest of energy conservation.

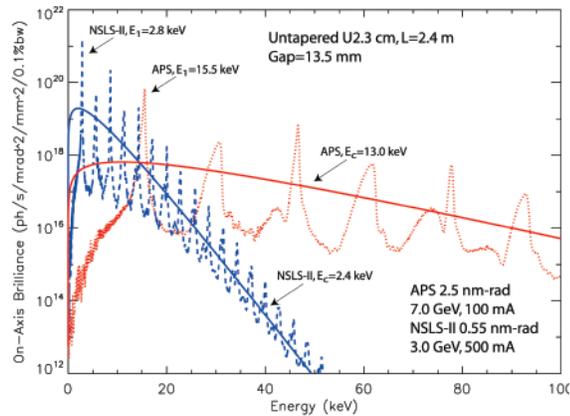


Fig. 1. On-axis brilliance for the untapered undulator U2.3 cm (APS23#1) installed on the APS and the NSLS-II storage rings. The undulator is 2.4-m long and the undulator gap is 13.5 mm. The first harmonics and the critical energies for two cases are labeled. The solid lines show the wiggler approximation using the corresponding critical energies. (Courtesy R. Dejus, Argonne National Laboratory)

## Introduction

The unique properties of APS x-ray beams should be augmented by upgrades to undulators, beamlines, techniques, and supporting infrastructure. Indeed, much of the science proposed here and discussed in APS mid-term upgrade proposals ([http://www.aps.anl.gov/Renewal/mt\\_beamlines.html](http://www.aps.anl.gov/Renewal/mt_beamlines.html)) simply cannot be done at other synchrotrons in the Americas. Even the ultra-low emittance projected for the new National Synchrotron Light Source (NSLS) II at Brookhaven National Laboratory cannot produce high-energy beams with the brightness possible from those at the APS (Fig. 1).

The importance of the APS for engineering applications and applied research is clear from the recent growth in the number of users and facility oversubscription in these areas. For example, polychromatic microdiffraction developed at the APS [1-3] is now being instrumented on beamlines around the world. But the infrastructure and capabilities of the XOR 34-ID-E beamline remain unmatched, with a >400% oversubscrip-

tion for available beam time and with outstanding proposals unable to secure beam time. Similarly, the development of high-energy diffraction microscopy [4,5] programs and high-energy powder, small-angle-scattering, and other diffraction methods [6-8] have led to the development of large user communities, so available beam time is highly oversubscribed for these powerful probes of engineering materials. Other techniques, such as high-energy imaging, have been demonstrated but have not been properly instrumented for routine user operations. The explosive growth of these research areas is driven by the high-energy brightness of the APS x-ray beams, which allow for nondestructive imaging of systems during processing or in service. The combined ability to nondestructively probe volumes deep inside complex environments with spatial resolution, time resolution and density, and crystal and chemical sensitivity requires ultra-bright high-energy x-rays. There is simply no source in the Americas with the high-energy brightness of the APS.

Although there are no comparable sources in the Americas, the European Synchrotron Radiation Facility (ESRF) in France, the SPring-8 light source in Japan, and the new PETRA III facility in Germany are international competition with similar potential to the APS, and with strong engineering and applied programs. Synchrotron research for engineering materials is particularly active in Europe, with strong ties to major European industries like Airbus and Volkswagen, and with close university collaborations [9]. Nevertheless, the proposed upgrades will provide scientists in the U.S. with a suite of tools for engineering applications and applied research that is unmatched anywhere else in the world. Beyond these upgrades, there is a need to develop closer collaborations with industrial and university researchers to best exploit the capability of synchrotron research in transforming engineering and applied research, and make the U.S. more efficient and competitive. In order to realize a meaningful collaboration with university and industrial scientists, non-specialist control and data-analysis software for engineering and applied research must reach a new level of sophistication that makes experiments at the APS more user friendly. This is a realistic goal, which together with a suite of sample environmental chambers, will make efficient use of precious engineering and applied research capabilities.

## Key Science Drivers

The ability to nondestructively image inhomogeneous materials with unprecedented spatial, chemical, crystallographic, and defect sensitivity opens fundamentally new opportunities for engineering and applied research. Similarly, the ability to detect and characterize ultra-small sample volumes and transient phases will transform our understanding of materials behavior during processing and in service, and will bring clarity to nonlinear phenomena where average properties are insufficient to understand materials behavior. Below we briefly touch on a few of the many long-standing engineering and applied research issues where new instrumentation and software can have a major impact.

### Fracture

Fracture is a long-standing issue with broad implications for engineering materials. Lack of control and understanding of fracture necessitates over-design of parts that adds cost and weight and lowers performance. Fracture is inherently a spatially inhomogeneous phenomenon with atomic level interactions near the crack tip and with mesoscale strain fields both near the crack tip and in the post-crack region. For this reason, nondestructive, spatially-resolved measurements can provide essential new information to further our understanding of crack behavior. Of course, beautiful transmission electron microscopy (TEM) experiments can image crack propagation in real time, but dislocation motion is influenced by the thin sample size required for TEM. X-ray studies are essential for the study of cracks in samples with true bulk behavior.

Fracture is an area where research has already begun, but where improved instrumentation and software can have a huge impact. For example, energy dispersive studies of fine-grained materials have detected unexpectedly large plastic deformation “wake fields” behind propagating cracks [10]. In addition, studies of Ni-Ti alloys have revealed the extents of both plastic and shape-memory zones around stress concentrations [11]. The APS has the brightness to push the spatial resolution of these measurements by orders of magnitude and with time resolution. This will require

high-performance achromatic focusing optics to achieve small beams and banks of ultra-fast energy-resolving detectors to characterize the local plastic and elastic strains. In addition, special techniques implemented at the APS — such as polychromatic microdiffraction and high-energy diffraction microscopy— allow for sub-grain-resolved studies in samples with typical grain sizes of 0.5 to 20  $\mu\text{m}$ . Ultimately, an improved understanding of fracture physics will have a direct and wide-spread impact on part design and materials.

Related areas of research include fatigue cracking [12] and stress corrosion cracking [13] that impact industry, transportation, and energy production. An example is thermo-mechanical studies of alloys used for nuclear reactor applications. Recent high-energy scattering studies have provided strain and texture evolution of non-irradiated, Zr-based alloys used as cladding materials for current and future reactors [14]. Future studies on radiated and composite materials, under realistic conditions of thermomechanical deformation, are expected to provide unique spatially-resolved microstructural information and improve life-cycle predictions.

### Stress, residual stress, and deformation

Understanding mesoscale structural evolution in materials is one of the great challenges for engineering materials research. Recent work at the APS has begun to characterize defect self-organization in systems where the starting conditions and processing conditions are sufficiently well defined to allow for direct comparison to

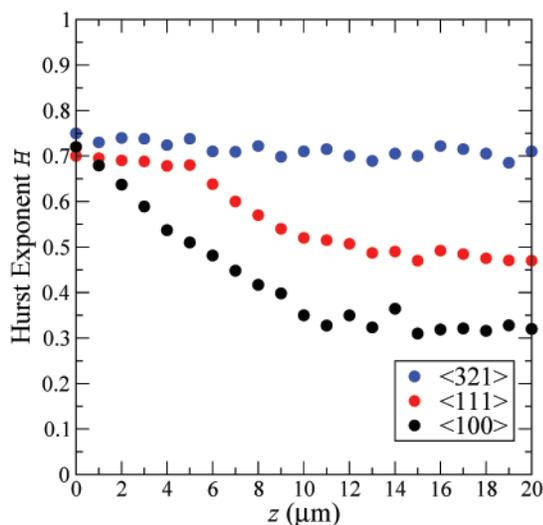


Fig. 2. Hurst coefficient for correlated lattice rotations in a deformed single crystal shows crystallographic and depth-dependence. In the 321 crystal only a single slip system is activated and the near surface behavior extends deep into the crystal. In the 111 and 100 orientations, multiple slip systems are activated and the near-surface behavior is confined to a few micron region. (Courtesy J. Pang, Oak Ridge National Laboratory)

models. This is an area of enormous importance, where better spatial resolution, faster detectors, and brighter x-ray sources can move experiments from demonstration and proof-of-principle to transformative. Measurements on single crystals [15,16, bicrystals [17], and polycrystals [18] are beginning to provide guidance about the ways dislocation behavior near surfaces and interfaces differs from the behavior within a grain (Fig. 2). This information is essential for multiscale models of engineering and other materials. The ability to nondestructively study local crystal rotations with submicron spatial resolution and with good angular sensitivity now allows for the first nondestructive measurements of the Nye, or dislocation, tensor and has stimulated the development of a formalism to cleanly separate plastic from elastic deformation in complex stress states [19]. This will enable critical tests of plasticity models that invoke the Nye tensor to explain evolving materials behavior.

Residual stress measurements (lattice strains) are another important application where high-energy x-rays can transform studies of engineering materials. This area is essential for industrial research and has long been the domain of neutron scattering due to the deep penetration of neutron beams into real parts. High-energy x-rays offer the potential for good sample penetration with much faster measurement speeds than neutrons and with much better spatial resolution [20]. Because residual lattice strains ultimately arise from defect distributions in materials, the improved resolution and faster time scale offered by a dedicated high-energy beamline will both guide designers and resolve specific issues with engineered structures, and will tie directly to model simulations of defect evolution in materials. The need for such improved structural assessments is anticipated to grow, for example, in the nuclear industry where planned plant lifetime extensions will place emphasis on limiting damage to critical components such as welds.

### **Deformation in novel materials**

The APS renewal also provides opportunities for transformational studies of novel structural materials including nanomaterials and amorphous materials. Recent *in situ* high-energy pair distribution function (PDF) studies have demonstrated the abil-

ity to characterize strain in amorphous bulk metallic glasses [21,22]. These first experiments show a surprisingly strong dependence on local chemically-specific atomic correlations. Extensions of this technique will provide unique insights into the role of local structure and stress in amorphous materials. Similarly, the unique deformation properties of nanoscale materials has begun to be understood with the aid of high-energy scattering studies [23]. Finally, high-energy studies of biomaterials have revealed important information about the micromechanics of bone deformation, and extensions of these studies toward biomaterials constructs such as implants in bone and teeth are anticipated.

### Dynamic deformation

Materials behave fundamentally differently under dynamic deformation, defined at time scales on the order of hundreds of nsec and below. Applications here are primarily defense/national security related, and post-deformation analysis can provide information about activated slip systems and other deformation mechanisms [24,25]. Ultimately however, real-time measurements are desirable. Possible studies include high-energy x-ray scattering with large detectors capable of region-of-interest read-outs (nanoseconds fast), and high-speed radiography. The APS recently hosted a workshop on dynamic compression, which advocated a separate collaborative access team sector based on the special needs of the dynamic deformation community; information can be found at [http://www.aps.anl.gov/News/Conferences/2008/DC\\_Workshop/](http://www.aps.anl.gov/News/Conferences/2008/DC_Workshop/).

### Imaging

Elemental maps and three-dimensional (3-D) tomographic visualization are often useful in support of emerging diffraction research. For example, 3-D density maps can help identify positions of greatest interest in crack samples and can be used to guide diffraction studies. Similarly, in some materials minor elements are known to drastically influence intra-granular cracking. For example, boron and other elements are known to ductilize by segregation to grain boundaries in NiAl superalloys and Ti [26,27], and hydrogen is believed to embrittle these same alloys. If surrogate elements with higher  $Z$  can be found for these behaviors, then 3-D fluorescence tomog-

raphy can provide nondestructive analysis of elemental segregation before, during, and after fracture.

### **Nucleation, grain growth, and texture evolution**

Another research arena where the APS can transform engineering research is in providing new insights into nucleation, grain growth, and texture evolution. Much of materials processing is related to attempts at controlling grain size, competing phases, and texture in materials. Heat treating, rolling, extruding, and other processing steps affect grain size, phase fractions, and texture. Yet the basic driving forces for grain nucleation, growth, and texture evolution remain controversial and largely untested. Recent synchrotron-based research has begun to address this area and suggests a path forward toward a greatly enhanced understanding of these critical phenomena. For example, Budai et al. [28] used polychromatic microdiffraction to study 3-D grain growth with submicron spatial resolution and sensitivity to small-angle grain boundaries that would be difficult to detect by other means. Their results support a key role of defect density in grain boundary evolution (grain refinement).

Similarly, Poulson et al. [29,30] have studied texture evolution and grain growth using a high-energy diffraction microscope that is functionally equivalent to the microscope on XOR beamline 1-ID. They find rough agreement between the simple Sachs and Taylor models for texture evolution, with discrepancies occurring near crystallographic symmetry lines. These discrepancies may arise from near-neighbor effects, but further research is needed. In addition, they find highly discontinuous growth of grains that is not explained by current models. Work at beamline 1-ID will systematically study grain growth in a series of samples starting with high purity and progressing toward higher alloying element concentrations. This work should shed light on recent theory as well as the role of grain boundary segregation in determining the nature of boundary motions.

These pioneering studies will become even more useful with improved spatial resolution and with larger sample volumes. These competing needs demand fast, x-ray-sen-

sitive area detectors, powerful data-analysis software, and high-performance computational facilities, as well as advanced x-ray optics.

### Transient and evolving phases

Transient and evolving phases are everywhere and play a major role in engineering materials. For example, surfaces exposed to  $O_2$  develop oxides that can either be tenacious or fragile. *In situ* measurements at the APS have recently revolutionized our understanding of oxide coatings on high-temperature steels (Fig. 3).

This is only one small example of the general corrosion issue, which represents a huge cost to our developed infrastructure: about 3% of the gross domestic product per year

[31,32]. High-temperature oxidation is a particular issue in energy-generating parts for coal, gas, and nuclear power plants [33]. Stress corrosion cracking is also an important problem in the nuclear and oil industries.

Similarly, thermal processing is essential to the development of the multiphase materials microstructure needed to combine strength and ductility. Yet the evolution of phase fractions is only now being investigated by real-time measurements [34,35]. Recent measurements of steel components during heat treating can follow the evolution and dissolution of phases during processing. This new information can test theories and help clarify paths toward ideal microstructures.

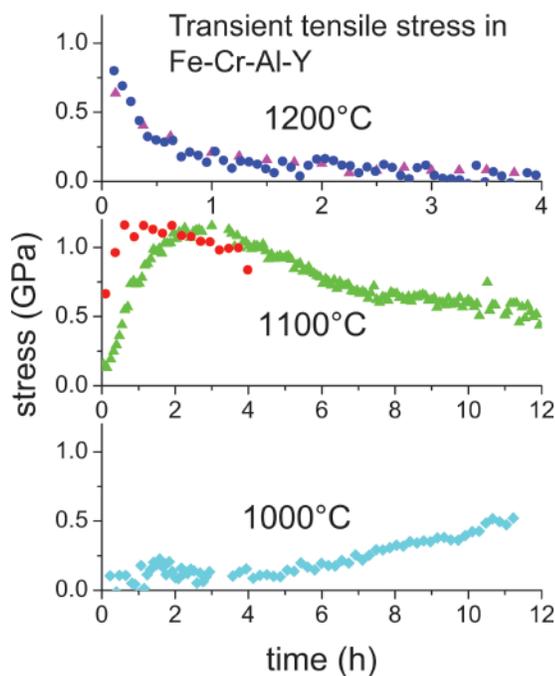


Fig. 3. Oxide stresses in a high-temperature steel at temperature. Because the lattice expands during oxidation, the oxide coating was assumed to be under compressive load. *In situ* experiments at the APS found that the coating is actually in tension, which is critical for cracking and failure of the protective oxide coating. (Courtesy E. Specht, Oak Ridge National Laboratory)

## Boundary layer phases and buried interfaces

One area of essentially unexplored potential is the study of minor phases that develop at the boundary layer of engineering materials. In nuclear clad fuels, a rich progression of phases can exist at the fuel/cladding boundary. In fiber-reinforced composites, minor phases at the fiber-matrix boundary can significantly enhance or degrade performance. Finally, knowledge of phase stability at the electrode-electrolyte interfaces in fuel cell stacks is crucial for assessing the performance and durability of these systems. The high brightness of APS x-ray beams can be used to perform powder and single-crystal diffraction on very small volumes with no need to section the sample. Improved spatial resolution and new *in situ* capabilities that simulate realistic operating conditions can target key issues including oxide layer evolution in thermal-barrier coatings [36]; deformation and thermal evolution during tribological contact of low-friction coatings; and depth-resolved measurements throughout the anode, electrolyte, and cathode layers of operating fuel cells [37]. New instrumentation is needed to make such measurements practical.

Two specific examples are lightweight materials and cement.

***Lightweight materials*** The development of lightweight materials for automotive applications is a topic of critical national importance that can greatly benefit from new capabilities at the APS. The Energy Independence and Security Act of 2007, SEC. 651. LIGHTWEIGHT MATERIALS RESEARCH AND DEVELOPMENT, calls upon the U.S. Department of Energy (DOE) to conduct research “to determine ways in which the weight of motor vehicles could be reduced to improve fuel efficiency” and specifically mentions the introduction of new aluminum alloys and high-strength steels.

Transportation consumes 69% of the petroleum used in the U.S. and is responsible for 33% of all U.S. CO<sub>2</sub> emissions. Reducing this dependence upon non-domestic oil is the most critical factor in achieving U.S. energy independence and energy security. Attention has largely focused on alternative fuels and power systems. But regardless of which engine technology ultimately prevails, the weight of a vehicle plays a major

role in its energy efficiency. A recent study by the National Research Council [38] identified weight as the most critical factor in automobile fuel efficiency and showed that reducing the weight of automobiles and light trucks by just 10% would reduce U.S. oil imports by approximately 8.5%. Lessening vehicle body weight by substituting lighter-weight materials such as aluminum alloys and high-strength steels is particularly effective because a lighter automobile body requires a less-massive suspension, transmission, engine, etc., thus multiplying the weight reduction without compromising vehicle safety.

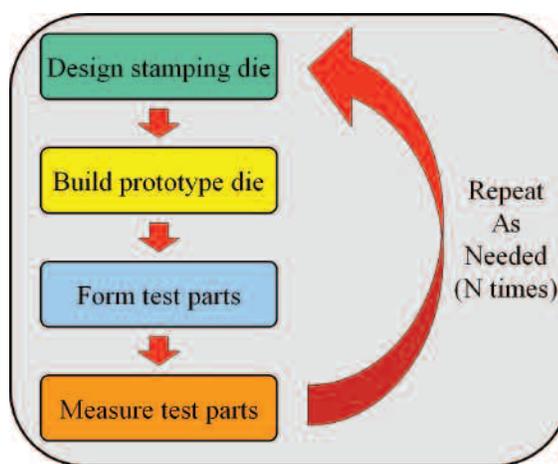


Fig. 4. Because deformation "spring-back" cannot be predicted, dies must be iterated until they form the correct shaped part. Although this process is manageable with soft steels, the iteration process is unacceptably long for the high-strength steels and low-density alloys that could drastically reduce the vehicle weight. (Courtesy L. Levine, National Institute of Standards and Technology)

Large-scale introduction of advanced lightweight alloys is limited by their complex behavior during production. The central technical issue is the inherent multiscale nature of materials behavior, where small-length-scale processes govern the behavior at the macroscopic level. The most intractable problems reside at the mesoscopic length scale where long- and short-range interactions between millions of mobile and immobile dislocations produce complex dislocation structures that are responsible for the observed macroscopic behavior (Fig. 4). As shown in Fig. 7, synchrotron x-rays are uniquely suited to studies of dislocation structure evolution because they can penetrate deep into macroscopic samples and provide quantitative measurements from sample volumes smaller than the size of typical dislocation structures. The APS is already at the forefront of research in this field, with published groundbreaking studies resulting from depth-resolved microbeams on beamline 34-ID and high-energy, high-angular resolution diffraction on beamline 1-ID. If the APS is to retain a leading posi-

tion in this field and continue producing research results that drive engineering advances, investments are required in facility upgrades such as new high-performance focusing optics, area-detector arrays, and real-time data analysis using parallel processing software and hardware. These upgrades would provide higher spatial resolution, faster data acquisition, and real-time access to data, allowing researchers to make informed decisions during their experiments, all critical factors for successful research in this field.

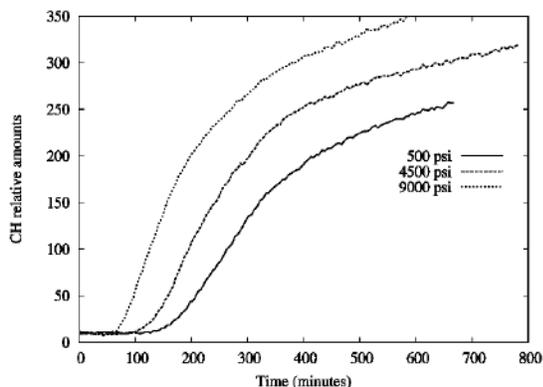


Fig. 5. Kinetics for the formation of  $\text{Ca}(\text{OH})_2$ , the major crystalline hydration products of Portland cement at low temperature, as slurries are hydrated at different pressures. Pressure dramatically reduces the observed induction time. (Courtesy A. Wilkinson, Georgia Institute of Technology)

**Cement** Studies of cement are another example of the critical importance of the APS. Cement has a global environmental impact through the large amounts of carbon dioxide released during production. Nevertheless, cement finds wide-spread use in concretes, mortars, and grouts. More Portland cement is produced than any other man-made material. Synchrotron x-ray techniques, including diffraction, small-angle scattering, and imaging are essential for studies that examine the early hydration of cements in order to gain an understanding of how mechanical property development relates to the mix chemistry, and how the long-term degradation of cement-based materials can be better controlled. Access to high-energy x-rays is essential for studies of cement samples that are large enough to represent “bulk” material and to make use of special sample environments.

Studies of cement grouts (slurries) illustrate the importance of sample environment. Cement grouts are used to seal the space between the bore holes in oil and gas wells and the steel pipe that is placed in the bore hole. Because oil wells can penetrate to great depths, these cement slurries can experience extreme pressures (>1 kbar in

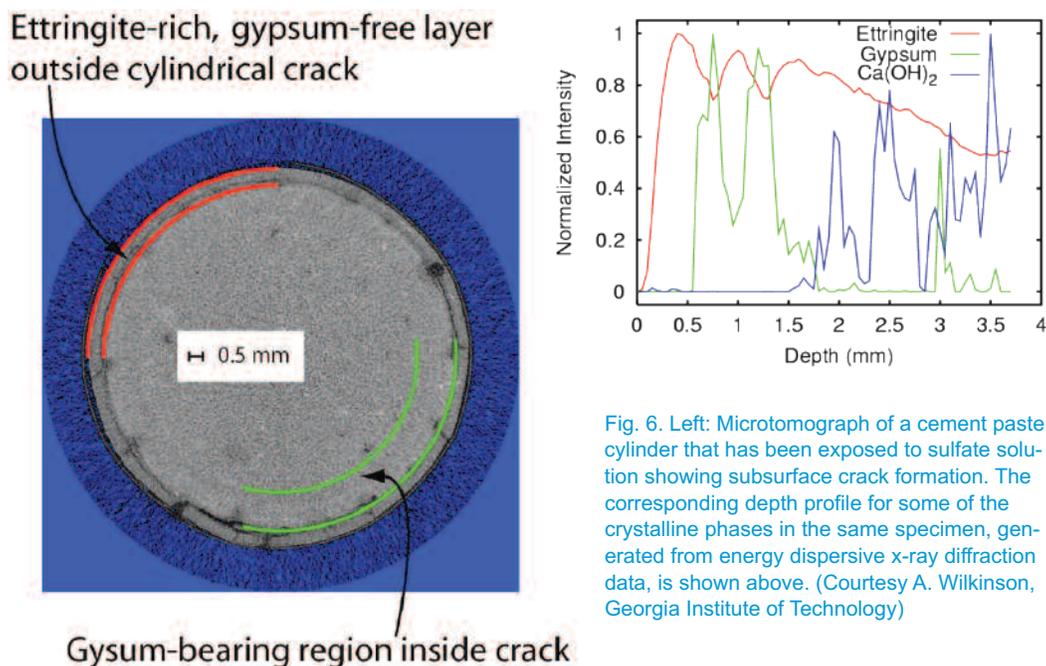


Fig. 6. Left: Microtomograph of a cement paste cylinder that has been exposed to sulfate solution showing subsurface crack formation. The corresponding depth profile for some of the crystalline phases in the same specimen, generated from energy dispersive x-ray diffraction data, is shown above. (Courtesy A. Wilkinson, Georgia Institute of Technology)

some cases) and temperatures during their hydration. The hydration process and final properties of the cement are controlled by the use of a wide variety of additives in the cement slurry. High-energy synchrotron scattering offers a powerful window for examining the crucial early hydration stage of these slurries under realistic oil well conditions. Radiation of 30 keV to 60 keV from APS bending magnets has already been used for studies at pressures up to 600 bar and show the dramatic effects of pressure on cement chemistry (Fig. 5).

Environmental degradation of cement-based materials is another area where APS capabilities can clarify the underlying science. Cement-based materials are subjected to a wide variety of chemical agents that accelerate degradation and reduce service lifetime. This is a significant economic and environmental issue. Synchrotron radiation can be used to both image microstructural changes in specimens and generate corresponding maps or depth profiles of how crystalline phases are distributed within the specimens leading to a better understanding of damage mechanisms (Fig. 6). High-

energy synchrotron methods complement more traditional analytical tools, as experiments can, in many cases, be done nondestructively and without concern over artifacts arising from specimen preparation. Early phase-mapping experiments at the APS made use of energy dispersive diffraction capabilities at beamline 1-ID, which are presently not available but would be with the proposed high-energy bending magnet beamline. Furthermore, higher spatial resolution studies could be conducted on these materials using high-energy diffraction microscopy.

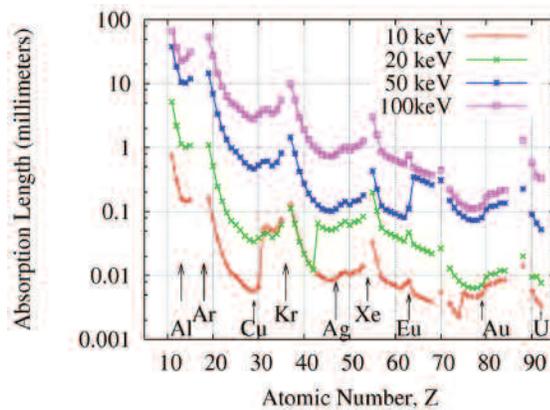


Fig. 7. Absorption length in millimeters as a function of atomic number,  $Z$ , for 10-, 20-, 50-, and 100- keV x-rays. (Courtesy R. Suter, Carnegie-Mellon University)

## Significance of the APS

Among x-ray sources in the Americas, the APS is uniquely suited for engineering applications and applied research. The penetration depth of x-rays scales roughly as  $\lambda^{-3}$ , and only hard x-rays (i.e., those with short wavelengths) can travel millimeters to centimeters through samples for studies of bulk properties and processes (Fig. 7). In addition, a minimum wavelength is required for access to a reasonable volume of reciprocal space and hard x-rays have low absorption but modest real-scattering factors for phase contrast imaging applications on low  $Z$ , mixed  $Z$ , or for samples inside environmental chambers. These factors make hard x-rays essential for engineering applications and applied research.

With this understanding, high-energy x-ray brightness is the figure of merit for virtually all engineering and applied experiments. The APS is uniquely bright at hard x-ray energies and will remain the premier U.S. source for high-energy x-rays for the

foreseeable future. For example, the deflection parameter  $K = 0.934B_0(T)\lambda_u$  of an undulator is a unitless constant that depends on the undulator period,  $\lambda_u$ , and on the maximum magnetic field strength,  $B_0$ , but is independent of the electron energy. To compare the performance of a state-of-the-art undulator on two rings, it can be assumed that the minimum period and maximum field strength are about the same. With this assumption, the maximum  $K$  and minimum undulator period are fixed by technology. As shown in Fig. 1, at high energies, brightness for a comparable undulator on the APS is significantly above even that of the ultrabright NSLS II. One figure-of-merit exception is for high-energy, full-field imaging (radiograph, tomography) and energy-dispersive measurements, where a high flux and large beam size are often desired. Due to the high APS storage ring energy, bending magnet beamlines provide a unique, nationwide source for such studies.

## Scientific Community

The scientific community that will use these facilities is immense.

Leading academic institutions include the University of Michigan, Northwestern University, Carnegie-Mellon University, Cornell University, the University of Tennessee, the University of Illinois at Urbana-Champaign, Vanderbilt University, M.I.T, Stanford University, the Georgia Institute of Technology, and Stony Brook University.

Industrial laboratories include Alcoa, Ford, Chevrolet, Dodge, Boeing, General Electric, John Deere, Martin-Marietta, and Pratt & Whitney.

Government laboratories include those belonging to the DOE, the Department of Defense, the Nuclear Regulatory Commission, the National Aeronautics and Space Administration, the National Institute of Standards and Technology, the Defense Advanced Research Projects Agency, the Navy, the Air Force, and the Army.

## Requirements and Capabilities

### X-ray optics

As described above, spatial resolution is a key driving force for engineering applications. Applied research and the ability to study increasingly small sample volumes will revolutionize engineering and applied research into the foreseeable future. In order to lead in this area, the APS beamlines must have access to the world's best focusing and imaging optics. Past progress at the APS has resulted in promising x-ray optics with demonstrations of record smallest one-dimensional hard x-ray focusing (a Laue zone plate lens with 16-nm full width half maximum [39]) and demonstration of the world's smallest polychromatic probe, a Kirkpatrick-Baez total-external-reflection mirror system with 80-nm-diameter probe size [40]. But these optics are not widely available at the APS and a major effort is needed to approach these performance numbers routinely and for x-rays above 40 keV. Stable optical environments require new levels of engineering to achieve the promise of emerging optics. Major efforts at the ESRF have produced sub-50-nm achromatic optics, and a tremendous program at Osaka/SPring-8 has recently set a new record for the smallest hard (20-keV) x-ray beam at 15 nm. Refractive-based optics provide efficient, source-size-limited focusing of monochromatic high-energy x-rays to the  $\mu\text{m}$ -level, with relatively low divergence as required for high- $q$ -resolution studies of (e.g.) strain.

### Detectors

There is no question that advanced x-ray-sensitive area detectors can revolutionize synchrotron science in general, and engineering applications and applied research specifically. This is an area that is rapidly developing, with dedicated synchrotron-driven area detectors under development around the world, and with the continued evolution of more-powerful area detectors driven by electron science and visible-light cameras. In the near term, ultrafast detectors with readout times of 100 to 10,000 frames-per-second will efficiently use intense x-ray beams and extend 3-D microscopy methods. These cameras will also allow for monitoring of increasingly short-lived transient phases, and stresses.

Over the next five years, x-ray cameras will become available with  $\sim 1\%$  energy resolution per pixel. These cameras will greatly improve signal-to-noise in virtually all classes of diffraction experiments, will resolve diffraction orders, and will revolutionize fluorescence spectroscopy, including the development of differential aperture methods to accelerate fluorescence spectroscopy. X-ray-sensitive area detectors with crystal-spectrometer-class energy resolution (0.01%) will further revolutionize synchrotron science in a number of ways that will directly impact engineering applications and applied research. Two clear examples—out of the numerous possibilities—are for polychromatic microdiffraction and for grain-average-challenged powder diffraction.

In polychromatic microdiffraction, a broad bandpass beam intercepts a small crystal volume and generates a characteristic Laue pattern. The angles between the Laue reflections determine the average crystallographic orientation of the sample volume and the deviatoric strain (distortion of the unit cell shape). This information is incredibly useful, but even more information can be recovered if the energy spectra of each pixel in the area-detector pattern can be analyzed. For example, the average energy spectra of even one Laue spot will determine the unit cell volume and therefore the hydrostatic strain of the unit cell. More practically, in virtually all engineering materials, Laue spots are streaked by dislocations and strain gradients. With energy-resolved area-detector patterns, the signal-to-noise of the pattern is vastly improved and a detailed map of plastic and elastic strain is possible, including diffuse scattering (sensitive to defects) that would be difficult to resolve with an energy-integrated map.

In powder diffraction, as the sample volume decreases, particle statistics become insufficient for high-precision measurements of lattice parameters and strains. In particular, reflections are nearly specular with respect to the lattice planes, and a grain even off the ideal Bragg angle will scatter through the Lorentzian tail of the reflection. Because sample volumes with low particle statistics often do not include grains oriented near the ideal Bragg condition, a false peak position can be observed. If however, a white beam is used to probe the small sample volume, there are  $\sim 10^2$  to  $10^4$

more chances for grains to satisfy the Bragg condition. The particle statistics problem is therefore vastly improved and the overlapping Debye rings from the different energies can be separated according to the encoded energy at the detector.

Finally, high-spatial-resolution cameras will improve resolution for tomography and remove some of the burden on point-probe techniques that are inherently slow compared to full-field imaging of samples. For example, with more-efficient cameras and more-optimized insertion devices, 100-ps exposures are possible at the APS for radiography and tomography on “few-millimeter”-thick steel samples. With very high frame rate cameras (1 Mhz) this opens the potential to track the evolution of a crack propagating in excess of 1 km/s.

With APS renewal funding, the spatial resolution available with transmission x-ray microscopy can also be greatly improved and the technique can be pushed to much higher energies. This is an area that will require combining advanced x-ray optics and special small-pixel detectors to push resolutions with hard x-rays. Existing developments have achieved ~40-nm resolution, but only for long wavelengths.

### **Software and experimental control**

Although instrumentation builds experimental capabilities, beamline-control and data-analysis software are the keys to widening the experimental community and are deciding factors in facility productivity. Some techniques lend themselves to user-friendly operations. For example, absorption tomography, powder diffraction, extended x-ray absorption fine structure, and SAXS are comparatively easy to automate and users can be efficiently trained. Other experiments are more difficult to automate and may require data analysis that is still evolving. For example, high-energy diffraction microscopy and polychromatic microdiffraction are emerging methods with no history of data acquisition or analysis software. It is essential that high-performance computations are accessible during data collection so that users see microscope output in time to guide further processing steps. The enormous potential of these methods is challenged by the need to develop user-friendly data acquisition and analysis packages.

## Undulators

The 7-GeV electron energy of the APS makes possible ultra-bright, high-energy undulators that are simply not possible at any other source in the Western Hemisphere. Indeed, specially optimized undulators can vastly improve beamline brightness and flexibility at high energies. Canted undulators offer the prospect of individual undulator control on stations that would otherwise be forced to work with compromised, shared spectral qualities. Consider, for example, the energy spectra above  $\sim 20$  keV. Figure 1 compares the theoretical performance of an undulator on the APS to the calculated performance of a similar device on the NSLS II. As can be seen, an optimized undulator on the APS can deliver about an order of magnitude more bright x-rays above 20 keV, and roughly 3 orders of magnitude greater brightness greater than 40 keV.

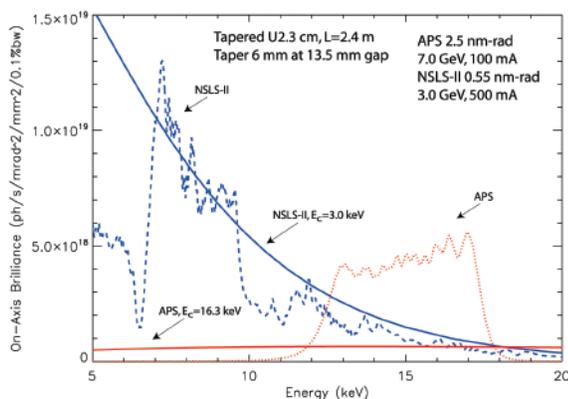


Fig. 8. On-axis brilliance for the tapered undulator U2.3 cm (APS23#1) installed on the APS and the NSLS-II storage rings. The average undulator gap is about 13.5 mm and the gap taper is about 6 mm over the full length of the device (2.4 m). The critical energies for two cases are labeled. The solid lines show the wiggler approximation using the corresponding critical energies. Note the much higher brilliance over the range of 12–18 keV on the APS. (Courtesy R. Dejus, Argonne National Laboratory)

For polychromatic microdiffraction, there are also important opportunities to optimize the source properties. Polychromatic microdiffraction utilizes broad-bandpass radiation and studies materials behavior with submicron to nanometer resolution. The geometry pioneered at the APS has the detector at  $90^\circ$  to the incident beam path, which allows for good spatial resolution in all three dimensions. X-ray beams of around 12 keV to 18 keV are favored by this geometry; this energy range allows for many Laue spots, with reasonable integrated reflectivity in the high-energy reflections. At lower energy and narrower bandpass, there are too few reflections for general purpose characterization of materials. At higher energy, the integrated reflectivity falls rapidly and a transmission geometry is favored, which reduces spa-

tial resolution along the beam. There are interesting possibilities of moving to more-penetrating high-energy beams for polychromatic microdiffraction, but even in the 12-keV to 18-keV regime, the APS offers major advantages for polychromatic microdiffraction. As illustrated in Fig. 8, even in the 12-keV to 18-keV range, the bandpass-integrated brightness (photons/sec/mm<sup>2</sup>/mrad<sup>2</sup>) is about five times higher for an undulator on the APS than for a similar device on NSLS II. Indeed, tapering an undulator, working on- or off-axis, can broaden the undulator spectra and allow for spectra with approximately 2 to 3 orders of magnitude more brightness than from second-generation sources, but with wide bandpass.

## Specific Recommendations

- Dedicate an additional beamline to high-energy x-ray measurements of aggregate stress/strain/texture from materials. This should include state-of-the-art ancillary equipment for sample environments and mechanical testing. Complementary x-ray imaging and small-angle scattering capabilities should be integrated into the beamline for simultaneous measurements. The current aggregate materials program on XOR beamline 1-ID will be moved to this new beamline. For more information, see [www.aps.anl.gov/Renewal/Proposals/1-ID\\_upgrade.pdf](http://www.aps.anl.gov/Renewal/Proposals/1-ID_upgrade.pdf).
- Complete the 1-ID Phase II upgrade. With the completion of number 1 above, this upgraded beamline will have a dedicated high-energy diffraction microscope (HEDM) station and a dedicated station for high-energy microfocused PDF and powder diffraction experiments. The HEDM station will include tomography capability. For more information, see [www.aps.anl.gov/Renewal/Proposals/1-ID\\_upgrade2.pdf](http://www.aps.anl.gov/Renewal/Proposals/1-ID_upgrade2.pdf).
- Build a dedicated polychromatic nanoprobe hutch and install a canted undulator pair to allow for simultaneous and independent use of polychromatic mesoscale and nanoscale probes. Station 34-ID-E at the APS is instrumented for the only 3-D diffraction microscope in the world with submicron spatial resolution. To meet the already overwhelming and growing demand for beam time, the coherent-diffraction station should be relocated to a long beamline where it can benefit from larger sample-to-source distances and the polychromatic microprobe should be given a dedicated

canted undulator. The canted undulators will be optimized as described above to produce ultra-high brightness beams between 12 and 18 keV. A second canted undulator would be dedicated to a nanoprobe station that can be located beyond the current microprobe station. This nanoprobe would have an initial polychromatic focal spot of ~40 nm, and with further development, beams of ~15 to 20 nm should be achievable in the near future.

- Optimize at least one bending magnet beamline for high-energy, energy-dispersive diffraction. As noted throughout the document, the APS is well suited to produce high-energy x-rays. Compared to insertion device beamlines, bending magnet beamlines have received little attention for high-energy development despite their strong potential. More information can be found at [http://www.aps.anl.gov/Renewal/Proposals/HE\\_BM\\_midterm.pdf](http://www.aps.anl.gov/Renewal/Proposals/HE_BM_midterm.pdf).
- Develop a dedicated high-energy tomography station with phase-contrast sensitivity. This station could be developed in addition to, or integrated with, the above beamline.
- Develop a range of environmental chambers for powder diffraction and SAXS targeted for catalysis, *in situ* thermomechanical loading, and other applied studies.
- Develop user friendly “expert” software for all engineering stations that insures users walk away from experiments with data sufficiently processed for analysis at their home institution. This will require an investment in computational infrastructure, both in the form of personnel and hardware. Data need to be automatically pipelined to appropriate machines for analysis during data collection. In some cases, this may require getting data through firewalls to TeraGrid machines or other off-site systems.
- Coordinate combined techniques/characterizations to follow materials evolution.
- Develop user-friendly mail-in capabilities in anticipation of the growing difficulty of travel given anticipated high fuel costs.

## References

- [1] J. S. Chung and G.E. Ice, "Automated Indexing for Texture and Strain Measurements with Broad-Bandpass X-ray Microbeams," *J. Appl. Phys.* **86**, 5249 (1999).
- [2] G.E. Ice, "3D Micron-Resolution Laue Diffraction" *Neutrons and Synchrotron Radiation in Engineering Materials Science*, W. Reimers, A.R. Pyzalla, A. Schreyer, H. Clemens eds., (Wiley-VCH, Weinheim, Germany 2008) p. 353.
- [3] B.C. Larson, W. Yang, G.E. Ice, J.D. Budai, and J.Z. Tischler, "Three-Dimensional X-Ray Structural Microscopy with Submicrometre Resolution," *Nature* **415**, 887 (2002).
- [4] H.F. Poulsen, Wolfgang Ludwig, and S. Schmidt, "3D X-ray Diffraction Microscope," *Neutrons and Synchrotron Radiation in Engineering Materials Science*, W. Reimers, A.R. Pyzalla, A. Schreyer and, H. Clemens, eds. (Wiley-VCH, Weinheim, Germany 2008) p. 335.
- [5] B. Jackobsen, H.F. Poulsen, U. Lienert, J. Almer, S.D. Shastri, H.O. Sorensen, C. Gudlach, H.F. Poulsen, W. Pantleon, "Formation and subdivision of deformation structures during plastic deformation," *Science* **312**, 889 (2006).
- [6] A. Wanner and D.C. Dunand, "Synchrotron X-ray Study of Bulk Lattice Strains in Externally-Loaded Cu-Mo Composites," *Metall. Mater. Trans. A* **31**, 2949 (2000).
- [7] A.A. Kulkarni, H. Herman, J. Almer, U. Lienert, and D. Haeffner, "Depth-resolved porosity investigation of EB-PVD thermal barrier coatings using high-energy X-rays," *J. Am. Ceram. Soc.* **87** 268 (2004).
- [8] J.-S. Park, P. Revesz, A. Kazimirov, and M.P. Miller, "A methodology for measuring *in situ* lattice strain of bulk polycrystalline material under cyclic load," *Rev. Sci. Instrum.* **78** 023910 (2007).
- [9] *Neutrons and Synchrotron Radiation in Engineering Materials Science*, W. Reimers, A.R. Pyzalla, A. Schreyer, and H. Clemens, eds. (Wiley-VCH, Weinheim, Germany 2008).
- [10] M. Croft, N. Jisrawi, Z. Zhong, K. Horvath, R.L. Holtz, M. Shepard, M. Lahshmiathy, K. Sadananda, J. Skaritka, V. Shukla, R.K. Sadangi, and T. Tsakalakos, "Stress gradient induced strain localization in metals: High resolution strain cross sectioning via synchrotron x-ray diffraction," *J. Eng. Mater-T. ASME* **130**, 021005 (2008).
- [11] M.R. Daymond, M.L. Young, J.D. Almer, and D.C. Dunand, "Strain and texture evolution during mechanical loading of a crack tip in martensitic shape-memory NiTi," *Acta. Mater.* **55**, 3929 (2007).
- [12] R.I. Barabash, Y. Gao, Y. Sun, S.Y. Lee, H. Choo, P. Liaw, D. Brown, and G. Ice, "Neutron

and X-ray diffraction studies and cohesive interface model of the fatigue crack deformation behavior” *Phil. Mag. Lett.* **8**(8), 553 (2008).

- [13] P.M. Scott, “F.N. Speller Award Lecture: SCC in PWRs interpretation modelling and remedies,” *Corrosion* **56**, 771 (2000) and <http://www.esrf.eu/news/spotlight/spotlight66>.
- [14] M. Kerr, M.R. Daymond, R.A. Holt, and J.D. Almer, “Strain evolution of zirconium hydride embedded in a Zircaloy-2 matrix”. *J. Nucl. Mater.* **380**(1-3), 70 (2008).
- [15] L.E. Levine, B.C. Larson, W. Yang, M.E. Kassner, J.Z. Tischler, M.A. Delos-Reyes, R.J. Fields, and W.J. Liu, “X-ray microbeam measurements of individual dislocation cell elastic strains in deformed single-crystal copper,” *Nat. Mater.* **5** 619 (2006).
- [16] J.W.L. Pang, G.E. Ice, and W. Liu, “The role of crystal orientation and surface proximity in the self-similar behavior of deformed Cu single crystals,” submitted to *Ultramicroscopy* (2008).
- [17] T. Ohashi, R.I. Barabash, J.W.L. Pang, G.E. Ice, and O.M. Barabash, “X-ray Microdiffraction and Strain Gradient Crystal Plasticity Studies of Geometrically Necessary Dislocations Near a Ni Bicrystal Grain Boundary,” *Int. J. Plasticity*, in press (2008) DOI:10.1016/j.ijplas.2008.04.009 .
- [18] J.W.L. Pang, R. Barabash, W. Liu, and G.E. Ice, “Determination of Deformation Inhomogeneity in Polycrystalline Ni under Uniaxial Tension with 3D X-ray Microscope,” *TMS Lett.* **1**, 5 (2004).
- [19] B.C. Larson, A. El-Azab, W. Yang, J.Z. Tischler, W. Liu, and G.E. Ice, “Experimental Characterization of The Mesoscale Dislocation Density Tensor,” *Philos. Mag.* **87**, 1327 (2007).
- [20] D.R. Haeffner, J.D. Almer, and U. Lienert, “The use of high-energy X-rays from the Advanced Photon Source to study stresses in materials,” *Mat. Sci. Eng. A* **399**, 120 (2005).
- [21] H.F. Poulsen, J.A. Wert, J. Neufeind, V. Honkimaki, and M. Daymond, “Measuring strain distributions in amorphous materials,” *Nat. Mater.* **4** 33 (2005).
- [22] T.C. Hufnagel, R.T. Ott, and J. Almer, “Structural aspects of elastic deformation of a metallic glass,” *Phys. Rev. B* **73**(6), 64204 (2006).
- [23] R. Wang, H.W. Chen, Z.L. Lu, S.H. Qiu, and T. Ko, “Structural transitions during aluminum leaching of NiAl<sub>3</sub> phase in a Raney Ni-Al alloy,” *J. Mater. Sci.* **43**, 5712 (2008).
- [24] J.M. McNaney, M.J. Edwards, R. Becker, K.T. Lorenz, and B.A. Remington, “High-Pressure, Laser-Driven Deformation of an Aluminum Alloy,” *Mettal. Trans. A* **35**, 2625 (2004).

- [25] B.A. Remington, P. Allen, E.M. Bringa, J. Hawreliak, D. Ho, K.T. Lorenz, H. Lorenzana, J.M. McNaney, M.A. Meyers, S.W. Pollaine, K. Rosolankova, B. Sadik, M.S. Schneider, D. Swift, J. Wark, and B. Yaakobi, "Materials Science under Extreme Conditions of Pressure and Strain Rate," *Mettal. Trans. A* **35**, 2587 (2004).
- [26] E.P. George, R.L. Kennedy, and D.P. Pope, "Review of element effects on high-temperature fracture of FeO and Ni-base alloys," *Phys. St. Solidi A-Applied Res.* **167**, 313 (1998).
- [27] E.P. George, C.G. McKamey, E.K. Ohriner, and E.H. Lee, "Deformation and fracture of iridium: microalloying effects," *Mat. Sci. Eng. A* **319**, 466 (2001).
- [28] J.D. Budai, W. Yang, B.C. Larson, J.Z. Tischler, W. Liu, H. Weiland, and G.E. Ice, "Three-Dimensional Micron-Resolution X-Ray Laue Diffraction Measurement of Thermal Grain-Evolution in Aluminum," *Mat. Sci. Forum* **467**, 1373 (2004).
- [29] L. Margulies, G. Winther, and H.F. Poulsen, "In situ measurement of grain rotation during deformation of polycrystals," *Science* **291**, 2392 (2001).
- [30] H.F. Poulsen, L. Margulies, S. Schmidt, and G. Winther, "Lattice rotations of individual bulk grains-art I: 3D X-ray characterization," *Acta Mater.* **51**, 3821 (2003).
- [31] <http://www.nace.org/content.cfm?parentid=1011&currentID=1045>
- [32] *Materials and Coatings to Resist High Temperature Corrosion*, D.R. Holmes and A. Rahmel, eds. (Applied Science Publishers, London, 1978).
- [33] S.M. Bruemmer and G.S. Was, "Microstructural and microchemical mechanisms controlling intergranular stress corrosion cracking in light-water-reactor systems," *J. Nucl. Mater.* **216**, 348 (1994).
- [34] S.S. Babu, E.D. Specht, M.L. Santella, G.E. Ice, and S.A. David, "In-Situ Observations of Oxidation and Phase Stability in Cast Nickel-Based Intermetallic Alloys," *Metall. Mater. Trans. A* **37A**, 195 (2006).
- [35] H.J. Stone, M.J. Peet, H.K.D.H. Bhadeshia, P.J. Withers, S.S. Babu, and E.D. Specht, "Synchrotron X-ray Studies of Austenite and Bainitic Ferrite," *Proc. R. Soc. London, Ser. A* **464**, 1009 (2008).
- [36] J. Almer, E. Ustundag, G.A. Swift, J.A. Nycha, C.C. Aydiner, and D.R. Clarke, "In situ synchrotron measurements of oxide growth strains," *Mater. Sci. Forum* **490**, 287 (2005).
- [37] J.D. Almer, D.J. Liu, B. Harder, and C. Weyant, "High-energy X-ray measurements of layered systems," *Proceedings of the 29th Risø International Symposium on Materials Science: Energy Materials - Advances in Characterization, Modelling and Application* (Risø National Laboratory for Sustainable Energy, Roskilde, Denmark, September 2008) p. 207.

[38] National Research Council

[39] H.C. Kang, J. Maser, G.B. Stephenson, C. Liu, R. Conley, A.T. Macrander, and S. Vogt, "Nanometer Linear Focusing of Hard X Rays by a Multilayer Laue Lens," *Phys. Rev. Lett.* **96**, 127401 (2006).

[40] W.J. Liu, G.E. Ice, J.Z. Tischler, A. Khounsary, L. Assoufid, and A.T. Macrander, "Short focal length Kirkpatrick-Baez mirrors for a hard x-ray nanoprobe," *Rev. Sci. Inst.* **76** 113701 (2005).

## Renewal of the Advanced Photon Source: Fundamental Interactions in Chemical, Atomic, & Molecular Physics

<b>Lin X. Chen</b>	<i>Argonne National Laboratory</i>
<b>Peter J. Chupas</b>	<i>Argonne National Laboratory</i>
<b>Paul G. Evans</b>	<i>University of Wisconsin-Madison</i>
<b>Stephen T. Pratt</b>	<i>Argonne National Laboratory</i>
<b>Stuart A. Rice</b> (Chair)	<i>The University of Chicago</i>
<b>Robin Santra</b>	<i>Argonne National Laboratory</i>
<b>David M. Tiede</b>	<i>Argonne National Laboratory</i>
<b>Linda Young</b> (Co-chair)	<i>Argonne National Laboratory</i>

### Executive Summary

Tracking the response to controlled excitation of a system initially at equilibrium yields deep insight and is a step toward the fundamental understanding required to control function at the molecular level. A modern scientific challenge has been to observe, understand, and control the relationship between structure and function in complex systems on the intrinsic time and length scales associated with electrons, atoms, and molecules. Due to technical limitations, experiments seeking structural information on the atomic length scale have emphasized time-independent or slowly varying properties. For the past century x-ray diffraction has been the cornerstone of structural science. Newly emerging time-resolved x-ray methods permit tracking atomic and electronic motions on the ~100-ps time scale at synchrotron light source facilities and, in the near future, on the ~100-fs time scale at hard x-ray free-electron lasers (FELs). The proposed Short-Pulse X-ray (SPX) source at the Advanced Photon Source (APS) based upon the radio-frequency cavity chirping proposal by Zholents [1] will extend time-resolved capabilities to the im-

portant 1-ps time scale while retaining the powerful characteristics of synchrotron radiation: user-controlled, continuous tunability of energy, polarization, and bandwidth combined with exquisite x-ray energy and pulse-length stability over a wide energy range. The 1-ps stroboscopic images can freeze molecular rotations and capture photoexcited molecular transition states, stress/strain wave propagation, magnetic domain wall dynamics, phase transitions, energy relaxation, and the coupling between electron, phonon, and spin degrees of freedom in condensed matter systems. The very high average flux ( $\sim 10^{13}/\text{s}$ ) of the proposed SPX, combined with high-repetition-rate excitation methods and year-round operation, will enable time-resolved studies with unprecedented precision, yielding joint resolution of picoseconds and picometers for a variety of atomic, molecular, chemical, and materials systems. These enhanced capabilities provide a compelling reason to locate at Argonne a proposed Energy Frontier Research Center.

## Introduction

The first half of the twentieth century witnessed explosive growth in understanding of the atomic and molecular basis for what we observe in the world around us. Because of technical limitations, the overwhelming emphasis in those developments was on time-independent or slowly varying properties of physical and biological systems. The latter half of the twentieth century witnessed the development of tools that permitted extension of our understanding to include many aspects of the time dependences of atomic and molecular processes of all kinds. The time resolution available to investigators shrank from milliseconds in the 1950s, to microseconds and nanoseconds by the end of the 1970s, to picoseconds and femtoseconds by the year 2000, and now to attoseconds in the first decade of the twenty-first century. In fact, studies on all of these time scales are needed to understand real-world processes.

Again because of technical limitations, comparable time resolution was not available across the spectrum of experimental methodologies, particularly not for structural studies by x-ray or electron diffraction. Yet it is arguable that we have learned more about the structure of matter from diffraction measurements than

from any other single method, and the creation of technology that permits the time evolution of structure to be studied is likely to yield similar advances in understanding, since it will permit unraveling of the relationships between physical processes and function.

It is possible to generate short x-ray pulses with either femtosecond or picosecond duration; the former will be generated at the Linac Coherent Light Source (LCLS) as  $\sim 100$ -fs-duration self-amplified spontaneous emission pulses, and the latter can be generated as  $\sim 1$ -ps-duration synchrotron pulses by the SPX at the APS. Atomic and molecular processes occur over such a wide range of time scales that both facilities are needed for the proper study of matter and its transformations, and for both the physical and biological sciences.

Indeed, a very important subset of those processes takes place on the few-picoseconds to few-nanoseconds time scale and are optimally studied with a source that generates picosecond x-ray pulses with high repetition rate, stable pulse shape, and high average intensity. Moreover, time-resolved x-ray spectroscopy in all its variants requires that the x-ray source be tunable. The proposed SPX facility at the APS satisfies both of these requirements, while an FEL source, although generating shorter x-ray pulses with very high intensity, has a relatively low repeti-

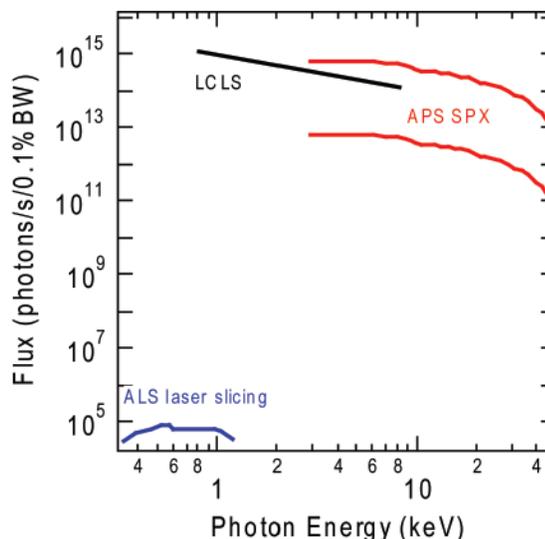


Fig 1. Photon flux for various accelerator-based, short-pulse x-ray sources. The LCLS has a projected pulse duration of  $\sim 230$  fs, the Advanced Light Source (ALS) laser slicing source has a pulse duration of  $\sim 200$  fs, and the APS SPX has a projected pulse duration of  $\sim 1$  ps. The LCLS photon energy is discretely specified under accelerator operator control, whereas both synchrotron-based sources (APS, SPX, and ALS laser slicing) are continuously tunable under local user control, thus enabling time-resolved spectroscopy. The high average flux of the APS SPX enables all x-ray techniques currently in use: spectroscopy, scattering, diffraction, microscopy, and imaging. The extension of the APS SPX to higher x-ray photon energies allows higher spatial resolution. (The APS SPX curves are based upon Undulator A, 3.3-m period.) Two other synchrotron-based laser slicing sources at the Swiss Light Source and BESSY have performance similar to the ALS laser slicing source. (Courtesy L. Young, Argonne National Laboratory)

Table 1. Operating parameters for SPX and LCLS.

Property	SPX	LCLS
Pulse duration (FWHM)	1 ps <sup>1,2</sup>	230 fs
Repetition rate	6.5 MHz	120 Hz
Photons/pulse @ 8 keV	10 <sup>6</sup>	10 <sup>12</sup>
Energy range	500-100000 eV	800-8000 eV
Tunability	Local-user control continuous	Accelerator-operator control discrete points
Average flux @ 8 keV	6.5 x 10 <sup>12</sup> photons/s	1.2 x 10 <sup>14</sup> photons/s
Pulse-to-pulse stability	Excellent	Limited by SASE

<sup>1</sup>SPX can be operated with variable pulse length from 1 ps to 100 ps. The flux values in the table should be increased 100 × for 100-ps operation.

<sup>2</sup>SPX pulse duration is a monotonically decreasing function of the x-ray energy (see Fig. 6). At 500-eV photon energy, the pulse duration full width half maximum (FWHM) is ~5 ps.

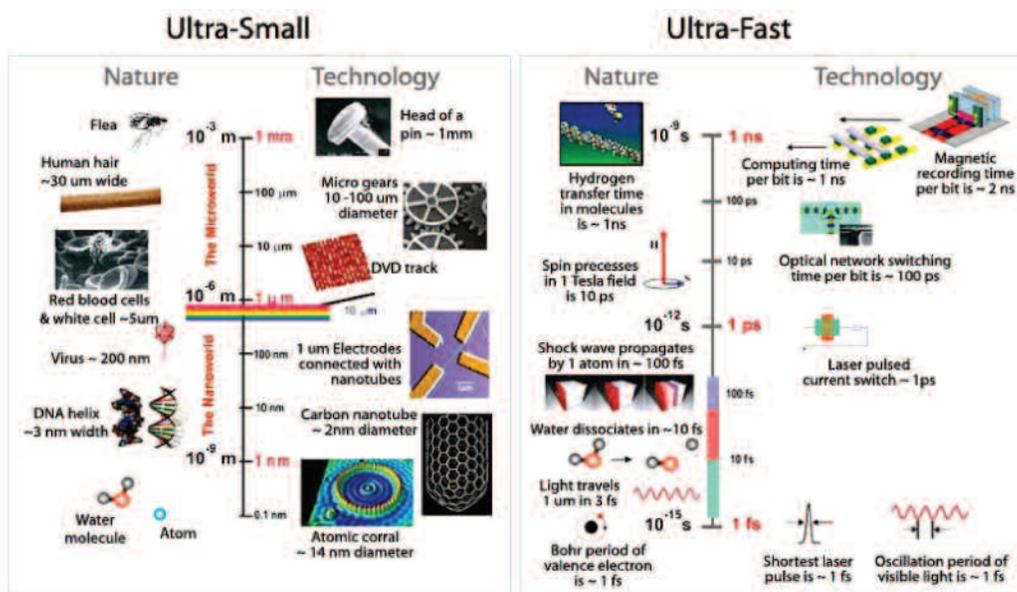


Fig. 2. The ultra-small and the ultra-fast. (Courtesy SLAC National Accelerator Laboratory)

tion rate, does not have a stable pulse shape, and is not conveniently tunable by the user. Thus, the two sources serve complementary purposes. A comparison between the SPX and the LCLS is shown in Fig. 1 and Table 1.

## Key Science Drivers

The frontier of the ultrafast and ultras-small world (Fig. 2) can be explored with the SPX, which provides joint resolution on the picosecond and picometer scales. Both natural and technological phenomena can be explored *in situ* and in real time using hard x-rays with the sub-Å wavelength, high penetrating power, and short pulse duration that provide ultrafast stroboscopic snapshots, as shown in Fig. 2. Understanding photoabsorption and subsequent energy transfer and dissipation in complex systems is a key scientific goal, one which will lead to a richer understanding of, for instance, the structure-function relationship in molecules relevant for efficient solar-energy conversion. Molecular-scale electronics represent the technological future; device time scales fall in the terahertz domain and become accessible by the SPX. A few specific examples of scientific opportunities in fundamental atomic and molecular, chemical, and materials physics follow.

### Control of atomic/molecular dynamics

A fundamental and enduring challenge in science is achieving control, at the atomic/molecular level, of dynamical processes, specifically control of electron and atomic motion. Quantum control is enabled by recent advances in laser technology that tailor phase and amplitude of electromagnetic pulses from the visible to infrared. This is the subject of the 2006 National Academy report *Controlling the Quantum World, The Science of Atoms, Molecules, and Photons* [2], and was issued as a Grand Challenge by the National Research Council. With this technology, we can attempt to realize the dreams that has existed since the inception of the laser. Can one steer molecular processes to a desired outcome? Can one control electron flow in semiconductors? Can one control non-radiative processes in semiconductors to enhance solar conversion efficiency? Combining this “photonic reagent” technology with short-pulse x-rays will allow us to view laser-controlled phenomena on ultrafast time scales with atomic-scale resolution.

Strong electromagnetic fields ( $\sim 0.1$  to  $1\text{V}/\text{\AA}$ ) are commonly employed in exercising control over molecular and electron motion. The non-resonant interaction of a laser

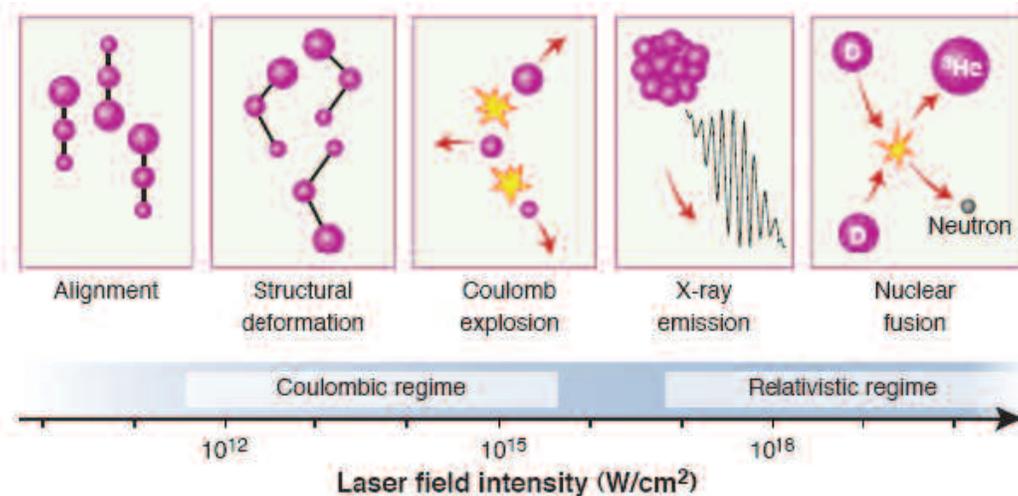


Fig. 3. Strong optical laser field interactions with matter. (K. Yamanouchi, *Science* **295**, 1659 [2002], © 2002 American Association for the Advancement of Science)

field with a molecule's polarizability can be used to reversibly modify potential energy barriers and thus control the outcome of photochemical reactions, and strong fields have been used to induce phenomena such as transient bond hardening or softening. The use of strong non-resonant laser fields to align and orient molecules has permitted forefront applications, examples of which are tomographic imaging of molecular orbitals, enhanced generation of high harmonic radiation, and serial crystallography of large molecules in the gas phase. X-rays allow one to probe the response of the molecular framework to the laser-aligning fields and through experimental/theoretical collaborations achieve a predictive theoretical understanding of molecular behavior in well-controlled, extreme environments. Strong electromagnetic fields can be used to modify x-ray absorption of atoms in a reversible manner via electromagnetically induced transparency (EIT), which may lead to an x-ray pulse shaper enabling femtosecond laser pulse shapes to be imprinted onto x-ray pulses. Photonic control methods such as STIRAP (stimulated Raman adiabatic passage) can effect population transfer from the ground state into target states with almost unit efficiency and thus markedly enhance x-ray measurements of excited state structures. In general, the use of x-rays to probe phenomena created by strong-field laser interactions with matter is in its infancy and poised for discovery (Fig. 3).

### ***Laser-dressed potential energy***

***surfaces*** The laser field couples the potential energy surfaces of the field-free molecule. In this way, new potential energy minima and, hence, molecular structures emerge. The laser intensity necessary for studying laser-dressed potential energy surfaces is most easily obtained by employing a pulse duration below 100 ps. Most useful is structural information measured at an essentially constant intensity within the temporal and spatial profile of the laser pulse. The 100-ps x-ray pulses currently available at the APS are too long. Using a 10-ps laser pulse with energy of 2 mJ focused to a focal diameter of 40  $\mu\text{m}$ , one can reach a peak intensity of about  $10^{12}$  W/cm<sup>2</sup>. This is about an order of magnitude below the intensity needed to saturate multi-photon ionization, and it is more intense by a factor of 10 than the intensity needed to align molecules. In this intermediate regime, one expects to see a pronounced laser-dressing effect on the molecular structure. Using 1-ps x-ray pulses, it will be possible to perform *in situ* measurements of the resulting molecular structures.

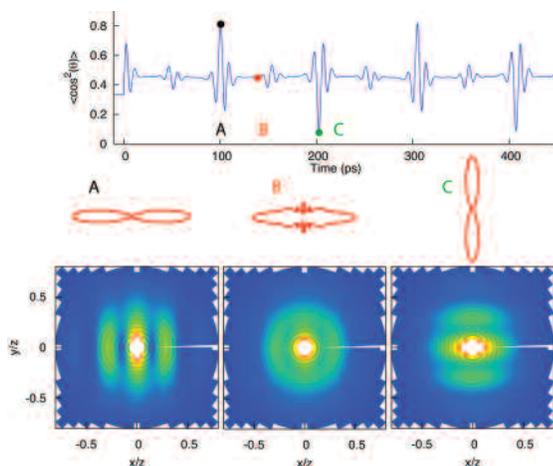


Fig. 4. Ultrafast x-ray diffraction imaging of rotational wave-packet dynamics of bromine molecules (1K) kicked by a horizontally polarized 50-fs laser pulse, centered at  $t = 0$ , with a peak intensity of  $10^{13}$ W/cm<sup>2</sup>. The top panel shows the time evolution of the ensemble average of the cosine squared of theta, where theta is the angle between the molecule's principal axis and the laser polarization axis. The probability to observe a given theta is shown in the middle panel as a polar plot. At time delay A, the molecules are highly aligned along the laser polarization axis. At time B, there is partial alignment; at time C, the molecules are anti-aligned with respect to the laser polarization axis. The x-ray diffraction patterns (20-keV photon energy, 1-ps pulse duration) reflect the molecular alignment at the three different time delays A, B, and C. (Courtesy R. Santra, Argonne National Laboratory)

### ***Field-free molecular alignment***

If the laser pulse duration is short in comparison to the characteristic rotational time scale of the molecule, then the laser-molecule interaction launches a rotational wave packet that undergoes periodic alignment and de-alignment, as shown in Fig. 4, where calculations are shown for bromine mole-

cules at 1K exposed to a horizontally polarized 50-fs laser pulse, centered at  $t = 0$ , with a peak intensity of  $10^{13}\text{W}/\text{cm}^2$ . Theta is the angle between the molecule's principal axis and the laser polarization axis. The expectation value of the cosine squared of theta is thus a measure of the degree of alignment of the molecular ensemble. As may be seen in the figure, the molecules are highly aligned at the time delay A. This is about 100 ps after the laser pulse is off, when the molecules are no longer perturbed by the laser field. In order to exploit this phenomenon of field-free alignment, one has to be able to probe the molecules in the extremely short time interval during which the alignment persists. This is not possible using 100-ps x-ray pulses. However, 1-ps x-ray pulses are ideal for this purpose, as is shown in the three bottom panels of the figure. X-ray diffraction patterns, calculated assuming a 1-ps, 20-keV x-ray pulse probing the molecular ensemble at three different time delays after the laser pulse, clearly reflect the dynamics of the rotational wave packet.

An important potential application of such impulsively aligned molecules is the measurement of x-ray-induced electron angular distributions with respect to the molecular frame. Photoelectron and Auger electron emission patterns normally detected are rotationally averaged, resulting in a loss of information about the electronic structure of the target molecule. Recent applications of molecular-frame electron angular distributions include the identification of the excitation mechanism of the satellite accompanying the C 1s photo-line of the  $\text{CO}_2$  molecule and ultrafast probing of core hole localization in  $\text{N}_2$ . So far, the measurement of molecular-frame electron angular distributions requires the complete fragmentation of the target molecule. In principle, each fragment must be an atomic ion. These ions are then collected on a position-sensitive detector and, assuming that fragmentation is fast in comparison to a rotational period of the molecule (axial recoil approximation), it is possible to reconstruct the spatial alignment of a given molecule from the fragmentation pattern.

Evidently, for this technique to work, not only must ultrafast and complete atomic ionization and fragmentation take place upon x-ray absorption, which is not generally the case in polyatomic molecules, but the measurement must be done effectively with only one molecule at a time. The beauty of laser-induced alignment is

that A) it is not limited by the axial recoil approximation, B) it may be applied to polyatomic molecules, and C) it may be applied to a large number of target molecules, thus enabling more rapid data accumulation. A recent measurement of photoelectrons generated via strong-field ionization of impulsively aligned molecules found the first experimental evidence of the dependence of the electron angular distributions on the relative orientation between the molecule and the polarization of the ionizing laser field.

***Molecular alignment in the liquid phase*** One frontier research area is the extension of studies of isolated molecule rotational alignment to the liquid phase, to investigate whether strong-field alignment survives in dense environments and the degree to which decay and decoherence can be photonically controlled. Although the theoretical work is just beginning, one can expect laser alignment to become a versatile tool in chemistry once the effects of dissipative media are properly understood. Obvious applications of three-dimensional (3-D) molecular alignment in liquids range from control of chemical reactions to means of controlled assembly at the molecular level. The unique coherence properties of intense laser alignment should allow the disentanglement of decoherence from population relaxation. Laser alignment and trapping of nanoscale objects in solution has already been achieved.

***Controlling and probing vibrational and electronic motion*** Although the rotational motion and alignment of molecules can be controlled and probed on the picosecond time scale, the vibrational and electronic motions of molecules typically take place much faster. Although direct time-domain studies of such motions are beyond the reach of even 1-ps x-ray pulses, these motions can still be studied by using alternative approaches. For example, the stimulated Raman scattering and STIRAP techniques with shaped femtosecond laser pulses can be used to transfer a large fraction of the sample to selected, highly excited vibrational levels. Such levels often sample very different portions of the potential energy surface than the ground vibrational state, and probing these selectively prepared molecules by using x-rays could provide direct information on how molecular geometry and structure change for different vibrational modes of the molecule. Even if the experiments were not time-resolved, this

approach would be interesting if existing control techniques were used to drive molecules along the reaction coordinate for decomposition or isomerization.

Similarly, while electronic rearrangement takes place on a time scale much shorter than 1-ps, excited-state lifetimes are typically much longer. Thus, short-pulse lasers can be used to prepare selected electronic states and monitor the structural and spectroscopic changes that occur. While some work along these lines is being pursued in the condensed phase (see, for example, the work of Chen and Moffat), essentially no work has been done in the gas phase, and the untapped potential for this approach is enormous. The situation becomes even more interesting when the excited state undergoes a radiationless transition by internal conversion or intersystem crossing. Note that, in many such cases, 1-ps resolution may not be sufficient to resolve the radiationless transition rate; however, x-ray probes of the structure of the triplet states or high vibrational levels of the ground state would be of considerable interest. In such a case, it should be possible to pump a significant fraction—i.e., more than half—of the molecules into the triplet state. X-rays have the potential to provide unique structural information on high vibrational levels of both low-lying triplet states and the electronic ground states. The acetylene molecule provides an interesting example. Excitation in the near ultraviolet pumps the molecule from the linear ground electronic state to the trans-bent  $A^-$  state, thus inducing large structural changes in the molecule. Perhaps even more interesting, it is thought that some levels of the  $A^-$  state couple with highly excited cis-bent levels, and that this coupling drives the isomerization from the acetylene structure to the vinylidene structure. X-ray probes of levels exhibiting such large-amplitude motion can provide tremendous insight into the isomerization process.

### **Chemical reaction dynamics: structure of the transition state**

A chemical reaction almost always generates a change in the structures of the molecules involved. Although we know a great deal about the initial structures of reactants, and the final structures of products there is no direct experimental information about the atomic pathways that are involved in these structural changes, excepting a few gas-phase electron diffraction results. Some reactions (for

example, direct fragmentation following absorption of a photon) occur on the femtosecond time scale. Other reactions (such as photo-fragmentation via a metastable state, photoisomerization and ring closure) can be many orders of magnitude slower, especially when large-scale atomic motion is involved in the formation of the product. And the time scale of a reaction is usually different in the gas phase and in solution. The availability of high-repetition-rate, stable-pulse-shape, intense, picosecond-duration hard x-ray pulses will permit the study of the evolution of molecular geometry in a substantial class of chemical reactions, including determination of the transition state between reactants and products. Only a short-pulse x-ray source can be used to study structural changes accompanying chemical reaction in both the vapor and solution phases. It is clear that determination of the structures of transition states in chemical reactions will transform our understanding of molecular dynamics by providing information about the displacement pathways of all of the atoms involved, thereby replacing the simplistic descriptions now employed.

Studies of the evolution of structure along the pathway from reactant to product are restricted, for technical reasons, to either unimolecular reactions or reactions initiated in a preformed bimolecular complex. Despite this restriction, there are so many important chemical reactions that choice of systems for study will be targets of opportunity. Isomerization reactions, both in the gas phase and in solution, are prime targets for study, as they involve large atomic displacements and are involved in the first stages of photosynthesis and of vision. Despite decades of study using spectroscopic probes, the mechanism of isomerization about a carbon-carbon double bond, and/or multiple double bonds, remains uncertain. There is new theoretical evidence that such reactions are determined by so-called conical intersections of potential energy surfaces, which occur in polyatomic molecules with multiple electronic states. Calculations of the change of electronic structure as a molecule undergoes the geometric changes that characterize the isomerization suggest that x-ray structural studies can provide crucial information about the reaction mechanism and dynamics.

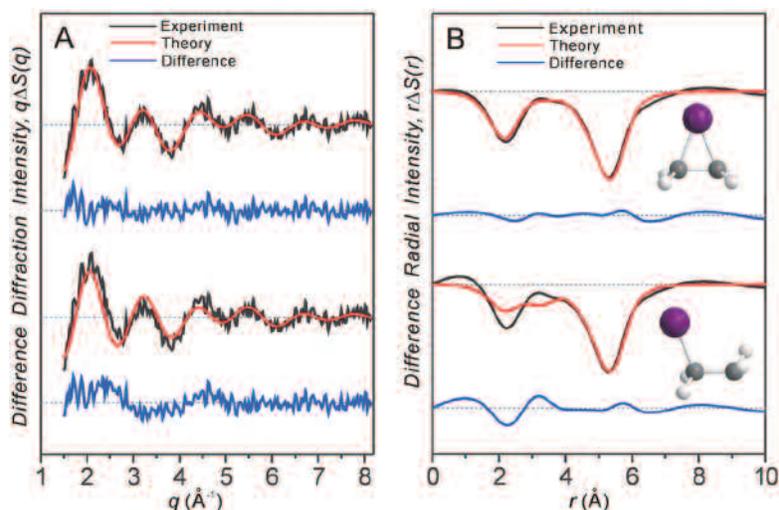


Fig. 5. Structure determination of the C<sub>2</sub>H<sub>4</sub>I radical in methanol at t = 100 ps. The contribution from C<sub>2</sub>H<sub>4</sub>I alone is isolated by subtracting other contributions from the raw data, allowing comparison with the gas-phase model of the anti and bridged structures. (a) Theoretical (red) and experimental (black) difference intensities for two possible reaction channels. The difference between the theory and experiment is also shown in blue. The upper curves are for the formation of the bridged C<sub>2</sub>H<sub>4</sub>I radical and the lower ones are for the classical anti structure. (b) Corresponding radial density functions for the two possible reaction channels, and molecular structure (iodine, purple, carbon, gray). (Courtesy H. Ihee et al.)

That time-resolved x-ray diffraction measurements can be carried out on a reacting molecule in solution, on the 100-ps time scale, has been demonstrated at the European Synchrotron Radiation Facility (ESRF; see Fig. 5). The proposed SPX source will generate shorter x-ray pulses with greater flux than was available for those experiments. Indeed, there should be ample intensity available for studies of the unimolecular reactions of isolated molecules in the vapor phase because the density need only be low enough that the time between collisions is much greater than the pulse length and much greater than the characteristic reaction time. The x-ray diffraction experiments can be carried out on freely rotating molecules, in which case the structure is determined by fitting to model structures, as is conventional in electron diffraction experiments. Alternatively (see previous section), the x-ray diffraction experiments can be carried out on aligned molecules to greatly increase the information content of the diffraction pattern and reduce uncertainty in the structure determination. The effect of inert gas (solvent) collisions on the evolution of the structure can be determined from measurements in, for instance, an He envi-

ronment. The determination of the time dependence of the molecular structure in solution is complex because of the need to account for scattering from the solvent and the influence of the evolving reactant on the solvent, but it also offers the opportunity to learn how solvent structure influences the reactant molecule structure and its evolution. Methods for separating the contributions to the scattering from reactant molecule and solvent have been developed. We expect that determination of, say, the transition state structure in the isomerization of gaseous stilbene and related molecules in an He atmosphere, and then in solution, will test our understanding and challenge our conceptual description of these and other isomerization reactions such as the ring expansion of toluene to heptatriene, and of reactions that occur in the refining of oil.

There are many photochemical reactions of metal complexes that are relevant to solar energy conversion. For example, multiple-metal-center complexes are involved in photo-induced water splitting reactions, where single photon events are coupled with multiple electron redox reactions. It is challenging and ultimately important to visualize how and how fast the reaction coordinates correlated with electronic configuration changes induced by photons lead to the transformation from the Franck-Condon state to products. Such information will help us to design molecules and learn how to control structural factors correlating with electronic transitions and to direct chemical reactions to desirable directions via photonic excitation. The concepts developed in these experiments can be applied to capturing the transition state during photochemical reactions, such as substrate binding to metal complex photocatalysts.

Franck-Condon states have not been directly observed in condensed phase photochemical reactions, where the nuclear geometry relaxation, both internal vibrational relaxation and solvent cooling, are on a time scale of <1 ps to 10 ps. By coupling a laser-pump pulse with a picosecond x-ray pulse, it becomes possible to directly observe electronic and nuclear structural changes simultaneously with x-ray absorption spectroscopy and solution x-ray diffraction.

We believe that the first determinations of transition-state structures in isomerization reactions will be paradigm changers. Continuation of such measurements in a thematic program to determine transition state structures in many reactions will yield a database that can be used to suggest new concepts and to test old concepts *vis a vis* the relationships between structure and reaction mechanism; the results of such data mining are likely to greatly advance our understanding of chemical reaction pathways. The need for information concerning transient structures in chemical reaction pathways is so great, and the diversity of chemical reactions is so great, that we anticipate widespread demand from the community for time for such studies.

### **Fundamental responses of materials to applied fields**

A unifying theme in condensed matter and materials science is the development of an understanding of materials' response to applied fields, including mechanical stresses and magnetic and electric fields. Materials respond to applied fields by developing internal strains, electrical or magnetic polarizations, or with dramatic phase changes. The dynamics of the relationships among structure, magnetism, polarization, and applied fields in solids extends from very long times to times as short as 1 ps or less.

The relationships between applied fields and responses are the keys to the phenomena underpinning nanomagnetism, nonlinear optical materials, ferroelectric devices, and metamaterials. The responses to applied fields are also the key to understanding correlated electron systems such as sliding charge density wave conductors and colossal magnetoresistive oxides. The fundamental problem is that although quantitative tools for probing the magnetism and structure of the ground states of materials are highly advanced, there are few probes capable of looking at structures driven into transient states far from equilibrium. The SPX facility can address these questions by providing the opportunity to perform time-resolved x-ray diffraction and scattering studies with samples driven into short-lived transient states. Many materials exhibit a slowing down (and concomitant growth in the spatial scale) of phenomena near phase transitions. The soft-mode dynamics of ferroelectrics are an excellent example of this.

The magnetic multiferroic oxides provide an important example of the opportunities involved in manipulating these responses, as shown in a diagram developed by Spaldin and Fiebig (Fig. 6). The applied magnetic and electric fields  $\mathbf{H}$  and  $\mathbf{E}$ , and the mechanical stress  $\sigma$  lead to responses in magnetization  $\mathbf{M}$ , electric polarization  $\mathbf{P}$ , and strain  $\epsilon$ . The coupling among these degrees of freedom is only beginning to be understood and very little is known about the dynamics of the relationships between the magnetism and the applied fields in these materials.

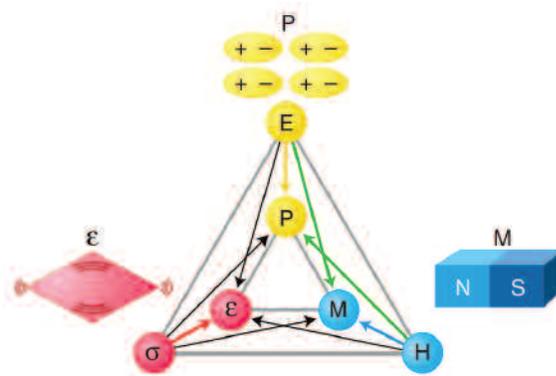


Fig. 6. The response of materials to applied fields. (Spaldin and Fiebig, *Science* **309**, 391 [2005], © 2005 American Association for the Advancement of Science)

These phenomena have a fundamental structural and magnetic basis that can be probed directly and quantitatively using x-ray scattering and spectroscopy. X-rays are unique in this sense because they are largely non-perturbative, penetrate complex sample environments, and can provide information across a wide range of time and length scales. The fundamental scales of the responses of materials vary, but the large-scale responses have times corresponding to tens to hundreds of picoseconds. Phenomena associated with domain dynamics and the conventional linear constitutive relations such as elasticity or polarizability all have characteristic time and length scales.

The time resolution of structural measurements at the proposed SPX facility will be comparable to the fundamental time scales associated with these phenomena. Electronic and magnetic phenomena can be driven at the high repetition rates available at the SPX and benefit from the inherent flexibility of the high-repetition rate approach. X-rays couple to these phenomena via a wide range of quantitative scattering mechanisms including resonant- and non-resonant magnetic scattering, diffuse scat-

tering, and coherent scattering. The 100-ps resolution presently available is too long in duration to match the fundamental times associated with these responses.

The following present several areas in which the few-ps time resolution of the proposed SPX will be essential.

***Dynamics in nanomagnetism*** Nanomagnetism is the field that arises from the intersection of the physics of magnetic materials and the capability to fabricate and understand nanostructures. The long-length scale dynamics of magnetism involves the control of magnetic domains and domain walls and has resulted in devices such as giant magnetoresistive sensors, and device concepts such as magnetic racetrack memories. In addition, nanomagnetic structures provide the means for discovering new phenomena in magnetism, such as spin-transfer torques.

Magnetic domains are linked to a small magnetostrictive distortion of the magnetic solid, so domain wall velocities are typically limited to be approximately the same as the speed of sound, kilometers per second, or nanometers per picosecond. A picosecond source of x-rays has fundamentally the appropriate time resolution for the study of magnetic domain dynamics and the phenomena linked to them.

The magnetism of thin-film structures can be manipulated using spin-polarized currents of electrons. The coupling of the spins carried by the spin-polarized current to the remnant magnetism of the layers results in magnetic forces that can cause the magnetization of ferromagnetic layers to precess, nucleate magnetic vortices, and ultimately switch the magnetization. In addition to the potential to switch the stored magnetization in devices electrically, the resonance itself is interesting because resonance frequencies can exceed 10 GHz, even in relatively large devices, and because these frequencies can be electrically tuned. These devices are beginning to incorporate more complex materials, including the magnetic multiferroics. These materials can be reconfigured using applied fields, and require structural and magnetic characterization tools with sufficient time resolution.

***Metamaterials and materials at THz frequencies*** Lithographic structures with sizes smaller than or comparable to optical wavelengths can have surprising and useful optical properties, including effectively negative indices of refraction. These structures are rapidly evolving to incorporate materials with properties that can be manipulated with external fields. Laser-pumped optical switches with single-cycle THz pulses can drive these materials. The potential to probe the structure of the metamaterials during their operation can be extremely valuable. The pulse duration of the SPX facility will be an excellent match to the time scale of the optical pulses in non-linear metamaterials systems, and for the THz radiation and THz optical properties of materials.

***High-frequency microelectromechanical systems and nanoelectromechanical systems*** The range of frequencies at which nanomechanical systems can operate is already above 1 GHz and will reach higher frequencies. At present, these systems are studied using lumped parameters such as the resonance frequency, and understood using simulations. The potential to examine the structural distortion locally in operating devices will dramatically improve the potential to design these structures.

***Ferroelectrics and multiferroics*** Ferroelectric materials have a remnant electrical polarization that can be manipulated with applied electric fields. As in magnetic materials, the response of ferroelectrics to applied fields includes domain wall motion, which typically involves times of many nanoseconds. Shorter times effectively freeze the domain walls, allowing the intrinsic local response of materials to be studied at high fields, large strains, and highly unstable polarization-electric fields states. It has recently become possible to begin development and testing of predictions for the response of ferroelectric oxides to very high electric fields. The physics of ferroelectrics in this regime is fascinating because it is far outside the range of validity of conventional descriptions based on free-energy models.

## **Frontier research in photosynthesis and molecular solar fuels catalysis**

Critical scientific challenges in solar energy and solar fuels generation, as outlined in

the U.S. Department of Energy workshop on “Basic Research Needs for Solar Energy Utilization,” derive from the need to couple ultrafast, single-electron, excited-state photochemistry in molecular photosensitizers to multiple-electron, proton-coupled, chemical fuels catalyses on transition metal complexes in a manner that avoids excited-state free-energy loss, quenching, and chemical back reactions, and ultimately to accomplish all of this using renewable, naturally abundant materials. Biology has achieved the ideal of efficient solar initiated water-splitting coupled to reductive chemical energy storage using abundant, renewable, self-assembling “soft” materials. Emerging work is suggesting synthetic pathways for achieving comparable solar fuels catalysis in organometallic and inorganic systems. However, progress in the development of solar-energy-converting materials is currently restricted by the lack of information on time-dependent, photoexcited-state electronic and coordinate structure changes, and resolution of how these structural dynamics are linked to energy-conserving chemistry.

Development of SPX capabilities at the APS will create opportunities for groundbreaking discoveries in electronic and atomic coordinate structural dynamics that underlie solar energy conversion across the full range of biological, organometallic, and inorganic photocatalytic materials, and provide a strategy for accelerating solar-fuels catalyst development by adding to synthetic design information on structure-dependent excited-state energy conversion processes. Particularly significant will be development of SPX-related facilities with capabilities for photoexcited structure mapping using short-pulsed x-rays across a broad x-ray energy range, including tunable hard x-ray energies for combined high-resolution spectroscopy and anomalous scattering experiments, high-energy pulsed x-rays for high-resolution time-resolved pair distribution function (PDF) analysis, and low-energy x-rays for time-resolved electronic structure analysis of the complete first-row transition metals and sulfur ligands.

The critical role that SPX-related facilities will play in frontier research in solar energy can be illustrated by considering the photoexcited-state reaction cycles for organometallic solar fuels catalysts. Significant recent synthetic work is directed at the challenge of synthesizing first-of-a-kind supramolecular ensembles composed of

photosensitizers connected by electron conducting linkers to transition metal catalysts, with the goal of producing supramolecular ensembles that couple ultrafast, single-electron, excited states to multiple-electron, water-splitting, and hydrogen-evolving reactions. Comparable approaches are also being investigated using biological and inorganic light-harvesting materials. One example is illustrated in Fig. 7,

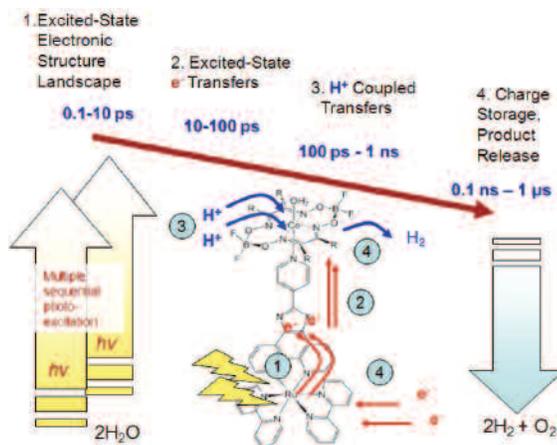


Fig. 7. Excited-state reaction cycle for a photosensitizer linked to a hydrogen-evolving catalyst. Prototype photocatalyst adapted from Fontcave et al., *Angew. Chem. Int. Ed.* **47**, 564 (2008). (Courtesy D. Tiede, Argonne National Laboratory)

showing a molecular device composed of a cobaloxime-based hydrogen-evolving catalyst coupled to a ruthenium tris(diimine) photosensitizer moiety. This construct is the most efficient supramolecular photocatalytic system produced to date, although it operates with only about a 5% efficiency. Sources for the low yield have not been resolved, but even the “simple” two-electron reduction of  $2\text{H}^+$  to produce  $\text{H}_2$  requires the repetitive passage through two complex photochemical cycles that include the following dynamics: A) Initial photo-excitation and subsequent ultrafast electronic structure relaxation involving vibronic (F-C) transitions and, depending upon the photosensitizer, electronic reorganization such as intramolecule charge transfer (for example, metal-to-ligand charge-transfer, MLCT), intersystem crossing (S-T transitions), Jahn-Teller distortions, and photo-isomerization processes. These ultrafast electronic structure and coordinate structure dynamics are crucial for establishing the precursor state energies and reactivities for subsequent chemistry. B) Excited-state electron transfer from the excited-state photosensitizer to catalyst that theory has shown to be coupled to rate-determining inner sphere and outer sphere atomic reorganization, but have yet to be directly observed. C) Proton-coupled transfers that are similarly coupled to rate-controlling inner- and outer-sphere reorganization events. D) Bond changes and product release. Breakthroughs in solar catalyst design would be realized by resolving excited-state electronic structures throughout the photon-initiated reaction cycle,

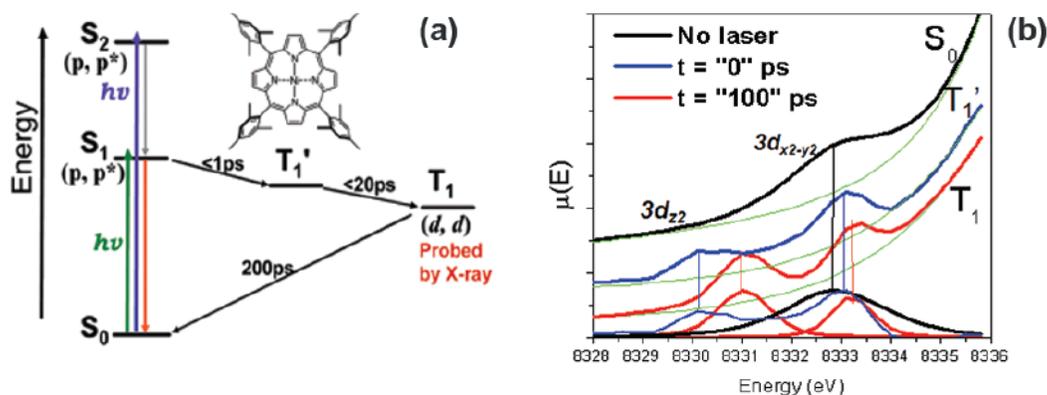


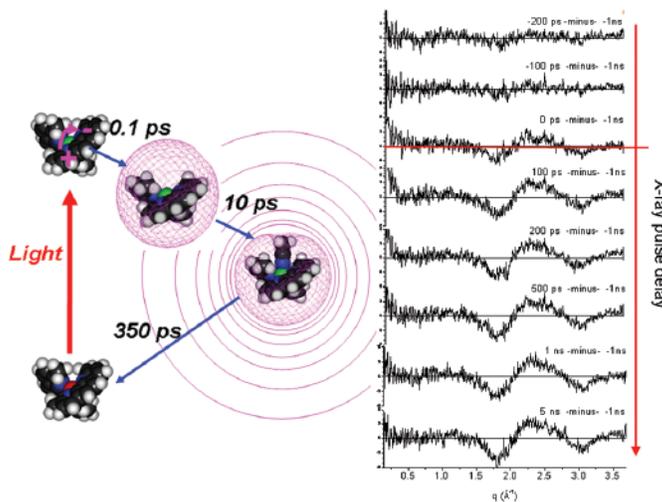
Fig. 8. Time-dependent electronic configuration changes for a photo-excited Ni-porphyrin measured by pump-probe time-resolved x-ray absorption (TR-XAS). The ground  $S_0$  state is characterized by a  $1s \rightarrow 3d_{x^2-y^2}$  transition with a 2.2-eV bandwidth (290K) and 1.8 eV at 15K, showing evidence of structural diversity. The excited  $T_1$  state: the singly occupied  $3d_{z^2}$  and  $3d_{x^2-y^2}$  MO in the XAS final state with a d-d splitting of 2.2 ( $\pm 0.2$ ) eV and widths of the peaks are  $< 1$  eV. The MO energies shift with probe delay time corresponding to an E-shift of  $d_{x^2-y^2}$  MO by 0.3 eV from the GS. (Part (a): Chen et al., J. Am. Chem. Soc. **129**, 9616 [2007], © 2008 American Chemical Society. Part (b): Courtesy L. Chen, Argonne National Laboratory)

and correlating these structural dynamics to chemistry in organometallic, inorganic, and biological solar catalysis. Key questions include resolving possible electronic interactions between the photosensitizer and transition metal catalysts in light-excited states, roles for microenvironments and second-sphere ligand environments for tuning excited-state chemistry, and atomic-scale resolution of reaction mechanisms.

Milestone experiments have demonstrated the unique capabilities offered by time-resolved x-ray measurements. Excited-state electronic configuration changes (process A above) have not been directly observed in condensed-phase photochemical reactions, where the nuclear geometry relaxation, both internal vibrational relaxation and solvent cooling, are on a time scale of  $< 1$  ps to 10 ps. By coupling a laser pump pulse with a picosecond x-ray pulse, it becomes possible to directly observe electronic and nuclear structural changes simultaneously with x-ray absorption spectroscopy and solution x-ray diffraction (Fig. 8). For example, the  $S_1$  excited state of nickel porphyrin undergoes an electronic  $\pi-\pi^*$  transition, followed by internal energy transfer to generate a transient d-d excited state that relaxes to an expanded porphyrin macrocycle geometry. Although the resulting electronic configuration and nuclear geometry have been observed with 100-ps x-ray pulses, the correlation of the elec-

Fig. 9. Reaction scheme (left) and time-resolved difference x-ray scattering patterns measured using single, 100-ps, 12-keV x-ray pulses set at variable time-delays following laser excitation. (Courtesy D. Tiede, Argonne National Laboratory)

tronic transition with the ensuing nuclear geometry change could not be resolved. With 1-ps x-ray pulses, the time scale at which one can investigate excited-state electronic and configurational changes can be significantly shortened to allow a direct monitor of the reorganization processes most critically coupled to energy converting events.



Similarly, time-resolved solution x-ray scattering (TR-SXS) provides the new opportunity to directly observe nuclear geometry changes in the excited state. For example, Fig. 9 shows single 100-ps x-ray pulse scattering pattern changes measured with variable time delays following a laser pulse for a Cu(I)[dimethylphenanthroline] complex (CuDMP). Upon photon absorption, the CuDMP complex undergoes instantaneous MLCT followed by an excited-state Jahn-Teller distortion and coordination change that is complete within 20 ps. The reconfigured MLCT state decays back to ground state in 350 ps in water. The “0 ps” TR-SXS transient measured with 100-ps pulses shows a fully developed set of changes that includes small-angle changes indicative of the coordination state change, and changes at higher angle that reflect outer sphere reorganization that includes change due to both the ligand structure and solvation layer. The outer sphere changes are seen to continue to evolve during the MLCT state lifetime. The current TR-SXS measurements are limited by the 100-ps pulse duration that cannot resolve the early conformational changes in the excited state, and low experimental repetition frequency (1 kHz) that prevents the acquisition of high-signal-to-noise data.

The development of a multiple-energy SPX facility at the APS will provide dramatically new opportunities for breakthrough discoveries in solar energy research. Critical new capabilities will include: A) The use of tunable, hard x-ray energies for combined high-resolution spectroscopy and anomalous scattering measurements that will enable precise resolution of ultrafast electronic structure changes and inner and outer sphere nuclear geometry changes with 1-ps time resolution, and B) the development of high-energy SPX capabilities that will create an entirely new opportunity for high-resolution PDF excited-structure mapping, allowing the global scattering measurements to achieve a spatial resolution comparable to that obtained by metal-centered x-ray absorption fine structure measurements. Finally, the development of low-energy SPX capabilities will enable electronic and metal-centered coordinate structure to be measured for the entire first-row transition metals and sulfur ligand that are high-priority synthetic targets for solar catalyst development.

## Significance of the APS

The APS is poised to become the leading synchrotron x-ray facility in the world for time-resolved studies at the 1-ps and longer time scales. There are only two hard x-ray synchrotron facilities in the world that can incorporate the Zholents radio-frequency (rf)-deflection cavity scheme to produce short-pulse x-rays, the APS and SPring-8 in Japan. (The PETRA-III synchrotron, due to begin operation in 2009, may be able to incorporate this scheme. The ESRF, a 6-GeV machine with a smaller circumference than the APS, has no available real estate for superconducting rf cavities.) Researchers at the APS have performed extensive engineering studies for implementation of the superconducting rf-deflection cavities, and at this point in time are ahead of the SPring-8 group in planning. The relatively long, 150-ns period between x-ray pulses in the standard 24-bunch operating mode of the APS storage ring facilitates recovery of samples and the gating of detectors for time-resolved studies.

Importantly, the APS has a strong community of world-leading researchers in time-resolved x-ray science spanning many fields: atomic and molecular physics, photo-

chemistry, materials science, condensed matter, and biology. To serve the biology community, a Laue diffraction beamline has recently been commissioned (BioCARS) that produces 100-ps pulses with  $10^{10}$  x-ray photons/pulse at a 1-kHz repetition rate within a 3% bandwidth. This is suitable for time-resolved diffraction of crystalline materials with long recovery times at an incident energy of  $\sim 12$  keV. The SPX serves a complementary purpose by enabling studies of both non-crystalline and crystalline materials at higher temporal and spatial resolution, higher repetition rate, and with widely variable photon energy, thus allowing the use of all x-ray spectroscopic, scattering, diffraction, and imaging methods.

## Scientific Community

We argue that the scientific community will benefit from the SPX at the APS in three complementary ways:

- The opportunity to carry out a small set of “must do” experiments that address what are widely accepted premium problems in specific subject areas, the results of which are likely transformational. The experiments suggested are matched to the unique capabilities of the proposed SPX facility.
- At the other extreme, a facility that can be used to study many systems and solve many problems, providing information not now obtainable by other means. The notion is that adding the capability for picosecond and longer time-resolved x-ray measurements of all types will assist the solution of problems across almost all fields of the physical and biological sciences, and that the provision of high-throughput beamlines and stations available to the scientific public is a matter of national interest. The emphasis here is on the added value of an interwoven net of scientific measurements. Although very few experiments are of type (1), even type (1) experiments benefit from the web of knowledge gained from other, less spectacular studies.
- Between categories (1) and (2) falls the definition of a few thematic problems the solution of which will benefit from a coordinated generation of data from studies of many systems, from which new concepts and transformational developments will be

gleaned. The notion is that selecting systems for study with reference to a central theme will draw complementary experiments on many systems, and the collection of data obtained can be used to test old theories, develop new theories and concepts, etc. Two models for this category are the Sloan Digital Sky Survey (<http://www.sdss.org/>), which has radically altered cosmology and astrophysics by generating a database that has been used to ask and answer entirely new questions; and the Protein Data Bank (<http://www.rcsb.org/pdb/home/home.do>), which has performed a similar function in advancing understanding of protein folding.

A partial listing of non-Argonne researchers interested in ultrafast x-ray science spanning many scientific disciplines is shown below.

Yves Acremann (SLAC)	Jonathan S. Lindsey (N. Carolina State Univ.)
Nicola Armaroli (ISOF—CNR, Italy)	Hector Lorenza (LLNL)
Jim Belak (LLNL)	Braja K. Mandal (IIT)
Phil Bucksbaum (Stanford Univ.)	Roberto Merlin (Univ. of Michigan)
David Cahill (Univ. of Illinois)	Gerald J. Meyer (Johns Hopkins Univ.)
Felix Castellano (Bowling Green State Univ.)	Martin Newcomb (Univ. of Illinois at Chicago)
Roy Clarke (Univ. of Michigan)	Martin Nielsen (Copenhagen Univ.)
Phillip Coppens (Univ. at Buffalo)	Daniel Nocera (MIT)
David Ederer (Tulane Univ.)	Hendrik Ohldag (SLAC)
Paul Evans (Univ. of Wisconsin)	Stanislas Pommeret
Peter Fischer (LBNL)	(Commissariat à l'énergie atomique)
Eric Fullerton (Hitachi)	David Reis (Univ. of Michigan)
Chuan He (The Univ. of Chicago)	Kirk S. Schanze (Univ. of Florida)
Michael Hopkins (The Univ. of Chicago)	Russell Schmehl (Tulane Univ.)
Joseph Hupp (Northwestern Univ.)	Michael Schmittel (Univ. Siegen, Germany)
Himansu Jain (Lehigh Univ.)	Ed Stern (Univ. of Washington)
Jacob Jones (Univ. of Florida)	Michael R. Wasielewski (Northwestern Univ.)
Jorgen Larsson (Univ. of Lund)	Glenn A Waychunas (LBNL)
Soo-Heyung Lee (KRISS, Korea)	Luping Yu (The Univ. of Chicago)
Frederick D. Lewis (Northwestern Univ.)	Ling Zhang (Southern Illinois Univ.)
Aaron Lindenberg (SLAC)	Jeffery Zink (Univ. California, Los Angeles)

## References

- [1] A. Zholents, P. Heimann, M. Zolotarev, and J. Byrd, *NIM A* **425**(1-2), 385 (1999).
- [2] *Controlling the Quantum World: The Science of Atoms, Molecules, and Photons*, Committee on AMO 2010, National Research Council of the National Academies (The National Academies Press, Washington, D.C., 2007).

## Renewal of the Advanced Photon Source: Geological, Environmental, & Planetary Sciences

<b>Steve M. Heald</b>	<i>Argonne National Laboratory</i>
<b>Russell J. Hemley</b>	<i>Carnegie Institution of Washington</i>
<b>Ken M. Kemner</b>	<i>Argonne National Laboratory</i>
<b>Robert C. Liebermann</b>	<i>Stony Brook University</i>
<b>Kathryn L. Nagy</b>	<i>University of Illinois at Chicago</i>
<b>Neil C. Sturchio (Chair)</b>	<i>University of Illinois at Chicago</i>
<b>Stephen R. Sutton</b>	<i>The University of Chicago</i>

### Executive Summary

Mankind's continued inhabitation of planet Earth will depend increasingly on strategic stewardship of our natural resources. Sustainable use of energy and raw materials, with minimal environmental damage, is imperative to ensure a viable quality of life for Earth's inhabitants. Only with an adequate understanding of the structure, composition, and function of natural systems, at scales ranging from atomic to global, can we accurately predict and control the environmental consequences of our actions. The requisite levels of understanding for this have not yet been achieved in the geological, environmental, and planetary (GEP) sciences. There are many new opportunities for planetary science driven by direct sampling missions of other bodies and observational discoveries that include planets far beyond our solar system. The use of synchrotron radiation for third-generation sources such as the Advanced Photon Source (APS) has enabled noteworthy progress across a wide spectrum of problems in the GEP sciences. Geological, environmental, and planetary science at the APS makes up about 15% of the user base, and has significant growth potential. But it is also highly interdisciplinary, and experiments in physics, chemistry, and materials science (e.g., in extreme conditions) are often carried out to address problems in GEP science. One key characteristic

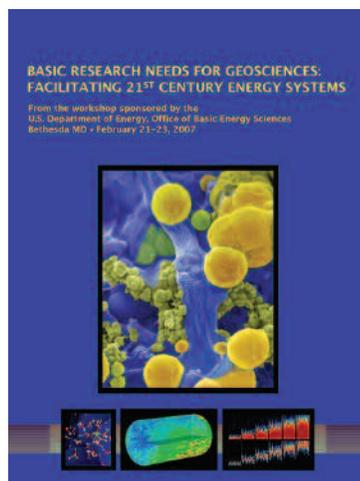
shared by the GEP sciences is the complex nature of the materials involved, which occur over extremely broad ranges of length scales, time scales, and temperature and pressure. At the foundation of GEP science are the molecular-scale structure, composition, and reactivity of the constituent phases. These phases behave differently, depending on the systems in question, to produce a rich palette of large-scale properties that are difficult to understand without knowledge of the molecular-scale fundamentals. Thus, it is crucial to have access to state-of-the-art facilities such as a renewed APS to be able to continue advancing scientific progress in GEP science. Some of the factors that limit this progress are as simple as the number of available beamlines, but in other cases it is a lack of sufficient flux and brilliance at the available beamlines, and the quality of available x-ray optics and x-ray detectors. Also, full use of the APS by GEP scientists requires more beamline personnel who could contribute to designing and running experiments, and more ancillary experimental hardware, including sophisticated sample chambers capable of maintaining controlled conditions of pressure, temperature, and fluid composition. Additional laboratory space for staging the increasingly complex experimental preparations should also be available.

## Introduction

Further progress in GEP is limited by the availability of scientific tools capable of measuring the atomic- to macro-scale properties and behavior of natural materials *in situ*, in real time, and under a wide range of conditions. An exceptionally powerful set of tools for such investigations is provided by high-brilliance synchrotron radiation facilities such as the APS. Experiments performed at these facilities have led to new findings and conceptual advances of fundamental importance. Improvements in the spatial and temporal resolution of synchrotron x-ray measurements, as well as increases in sample throughput, will be enabled by new x-ray optics and detectors. These improvements will lead to wider use and ever more powerful applications of synchrotron radiation to make new discoveries and develop new theories in the GEP sciences.

## Key Science Drivers

The GEP sciences encompass a wide range of multi-faceted topics that frequently cross conventional disciplinary boundaries. Much of the forefront research in these fields has a clear relevance to applications in energy-related activities, as described in the workshop reports produced by U.S. Department of Energy's Office of Basic Energy Sciences (DOE-BES): *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems* [1] and *Basic Research Needs for Materials under Extreme Environments* [2]. Because of their strengths in characterizing complex materials over a range of length scales and x-ray energies, synchrotron radiation techniques have become essential tools in such research. Classic scientific questions of geology and planetary science are also being addressed using synchrotron radiation. High-priority science targets under investigation at the DOE synchrotron radiation facilities include mineral-water interface complexity and dynamics, nanoparticle reactivity and transport, trace-element mobility and distribution, biogeochemistry in the subsurface, high-pressure mineral physics and structure of the Earth's and other planet's interiors; cosmochemistry and planetary geochemistry; and life in extreme environments and the origin of life. Brief descriptions follow of the driving questions and methods employed in each of these areas, with reference to the limitations imposed upon such research by the available hardware at the synchrotron radiation facilities.



Cover of the BES workshop report on "21st Century Energy Systems."

### Mineral-fluid interface complexity and dynamics

The mineral-fluid interface is the principal site of geochemical reactions at or near the Earth's surface. Mineral-fluid interface processes exert a powerful influence on the natural geochemical and biogeochemical cycles in our environment. These processes are crucial in the diagenesis of sediments and weathering of rocks, in the formation of ore deposits and petroleum reservoirs, and in soil formation and plant nutrition. Mineral-fluid interface processes effectively control the compositions of

groundwaters, surface waters, the oceans, and to a large extent, the Earth's atmosphere. These processes are integral to vital aspects of the dynamic natural world in which we live; in many practical ways, our lives depend on them. Minerals also have critical applications in technical fields such as construction, manufacturing, ceramic synthesis, catalysis, gas and liquid separations, water and wastewater treatment, waste disposal, agriculture, and horticulture. For these reasons, we must improve our fundamental understanding of mineral-fluid interface processes to make efficient and intelligent use of our natural resources and to protect the quality of our environment. Only by quantifying these processes at the molecular scale will we be able to predict behaviors in a wide range of geological and environmental systems. Examples of such complex systems include contaminant transport in groundwater aquifers, interaction of complex crustal fluids with rocks, the consequences of deep injection of CO<sub>2</sub> into depleted oil and gas reservoirs, the extraction of geothermal energy from hot rock, and the long-term isolation of high-level nuclear waste.

Much of the recent work on mineral-fluid interfaces and mineral surfaces began by applying experimental and theoretical techniques first used by scientists studying interfaces of other materials such as catalysts and semiconductors. Despite significant experimental and theoretical efforts in the past decades, our understanding of the actual molecular-scale geochemical processes (including adsorption, dissolution, growth, and precipitation) remains, in most cases, poorly constrained by direct observations. The current state of knowledge is limited by the intrinsically complex nature of geochemical interfaces and the great difficulty of probing mineral-water interfaces *in situ* at the molecular scale. The advent of the atomic force microscope and the development of non-linear optical and synchrotron x-ray techniques have initiated new classes of *in situ* nanoscale and atomic-scale studies of mineral-fluid interfaces in the past two decades [3-9]. Meanwhile, computational advances have enabled more sophisticated theoretical understanding of mineral surface properties [10]. Now that these experimental and computational approaches have matured to a point where they can be applied to a common and representative system size, they have begun to be used synergistically to test our understanding of mineral-fluid interfacial systems (e.g., Cheng et al. [11] vs. Park and Sposito [12]; Geissbühler et al. [13] vs. Kerisit et

al. [14]; [15]). Quantitative agreement between experimental observations and theoretical predictions provides a non-trivial confirmation of our understanding, while contradictions, in turn, suggest that our understanding is inadequate.

The over-arching goal of future research is to develop a fundamental comprehension of mineral-fluid interfacial processes through direct observation of interfacial structures and dynamic processes at the molecular scale. New conceptual understanding will provide answers to questions such as: What controls the reactivity of a mineral surface? What is the actual structure of the mineral-fluid interface? How do ions and organic macromolecules adsorb to charged mineral-water interfaces? How do minerals dissolve and grow? Ultimately, the ability to improve the predictive capability of geochemical transport models, and to relate fundamental molecular-scale processes to field-scale behavior, relies on the development of appropriate theories that are validated through direct, *in situ* observations. Improvements in the flux and brilliance of synchrotron radiation sources, along with improved x-ray optics and detectors, are essential for making progress in this area.

### **Nanoparticle reactivity and transport**

Natural nanoparticles are ubiquitous at and below the Earth's surface, and have specific importance in certain GEP-science processes. Nanoparticles can form in geomicrobiological reactions, at mixing fronts of highly supersaturated contaminant plumes with ground water, during rock weathering, in the rhizosphere, in smokestacks from coal-burning, in subsurface sedimentary rocks, and in the cosmos. At the Earth's surface their formation, disappearance, and mobility affect the quality of our water, air, and soil, and hence the viability of life. Natural nanoparticles can be purely inorganic, organic, or a mixture of both. They may be relatively impure in contrast to engineered nanoparticles and have proteinaceous [16] or dissolved organic matter coatings. Their suspension in flowing air or in surface and ground water can rapidly mobilize contaminants that either compose the nanoparticles or are adsorbed on other nanoparticle substrates, a problem designated as a priority research direction in the geosciences in the aforementioned DOE-BES report on basic research needs in geosciences [1]. Deep in the Earth, nanoparticles may form

at and subsequently control rock motion along faults, which generates earthquakes at the surface [17,18]. New, engineered nanoparticles synthesized for technology developments ultimately may contact and interact with Earth surface environments (water, air, biogeosystems) in unpredictable ways. Given this burgeoning attention to nanoparticles, we must rapidly expand our knowledge of how they form; their compositions and structures; how their surfaces react chemically in bulk fluids and when coated with thin fluid films; how they move in bulk fluids, in fluids confined by grain boundaries or pore throats, or gaseous atmospheres; and how they aggregate and/or grow to larger size. Observations must pertain to the chemically and structurally complex range of natural environments in which nanoparticles exist.

Recent advances in characterization approaches—e.g., the use of high-energy x-ray scattering to extract nanoparticle structures at correlation length-scales beyond the range of x-ray absorption spectroscopy—are providing new insights on the formation and transformation processes relevant to geoscience questions [19,20]. Such data will allow development of a thermodynamic description for particles that bridge the size gap between aqueous complexes and micrometer-scale crystallites [21]. At this range of molecular scale the lack of a general theory is severely stalling advances in our understanding of the phase chemistry and kinetic behavior of natural nanoparticles. Information that is only accessible with the use of high-energy x-rays is essential for theoretical progress. Synchrotron microprobe analyses of complex natural materials such as soils and sediments have proven remarkably valuable in identifying associations between contaminants and particular compositional and structural components that lead to a new understanding of processes involving nanoparticles [22-24] despite the micrometer-scale spatial resolution that is currently attainable. However, these advances in multicomponent analyses must be extended to the nanoscale and to trace concentrations in order to have an impact on our fundamental understanding of how nanoparticles influence the fate and transport of environmental contaminants. Both structural and compositional measurements of experimental and *in situ* natural nanoparticles must also be accomplished at other than ambient conditions to reflect the range of geological and planetary en-

vironments in which they occur. For these purposes, x-rays will have to penetrate different containment materials.

New knowledge of nanoparticle behavior in the environment is also critical for addressing the important issue of human sustainability. For example, if we can understand natural nanoparticle formation and stability under stress conditions, we can make progress in understanding when and where earthquakes occur. If we can characterize nanoparticles and their transport in porous media, we will have a significant but currently missing component for models of contaminant groundwater flow. If we could characterize small numbers of target atoms on the surfaces of a few nanoparticles, we would better understand the processes that control the environmental distribution of contaminants at the low concentrations considered toxic to human health. Greater access to high-energy x-ray scattering facilities, dedicated micro- and nanoprobes, and improved detectors and optics are essential to make the needed advances.

### **Trace element speciation and incorporation**

Trace elements are often the targeted concern in environmental studies. They are commonly risk-drivers at remediation sites or rate-limiting factors in biogeochemical systems. They can have important health consequences when they enter the food chain. For example, Fe in seawater is present at trace levels and is considered an important limiting factor for biological uptake of CO<sub>2</sub> by the oceans. Mercury in aquatic systems can be methylated by bacteria, and then consumed in succession by phytoplankton, fish, and mammals including humans. A major barrier to furthering our understanding of the effects of trace elements is that they are present in concentrations that are difficult to study by most techniques. This is especially true when samples must be studied under natural conditions, such as in anaerobic or aqueous environments. Synchrotron radiation analyses are capable of being used to determine key properties of trace elements such as their chemical form and location in complex heterogeneous systems, but only at concentrations typically much higher than their critical levels. Improved capabilities are sorely needed to attain lower detection limits and for time-resolved studies of mineral-water interface reactions, three-dimensional

transport in porous media, and biogeochemical processes.

Many of society's most pressing environmental challenges require detailed knowledge of trace element behavior. At DOE sites the relevant trace elements are fission products, actinides, and hazardous metals such as Cr and Hg. Elsewhere, hazardous trace elements range from As and Sb in mine tailings to heavy metals at industrial sites. Knowledge of trace element speciation and incorporation in field samples is needed to predict future transport and bioavailability, information critical to making intelligent remediation choices. Predictions often require detailed measurements in the laboratory of surface reactions, biofilms, and inter- and intragranular microenvironments. Researchers are often faced with the technically challenging requirements of measuring very low concentrations in very small regions.

For example, arsenic can enter the environment through natural processes, mining activities, and pesticide use. Disastrous consequences ensue once arsenic enters water supplies or the food chain, as observed in Bangladesh and West Bengal. Arsenic's many chemical forms [organic or inorganic, As(V) or As(III)] have varying degrees of toxicity, mobility, and bioavailability. Traditional chemical extractions may not retrieve all of the As and can change speciation. *In situ* speciation techniques using synchrotron radiation have become essential in establishing the human health risks in many studies.

At the APS, trace elements are analyzed using techniques such as bulk x-ray absorption fine structure (XAFS), microprobe-based fluorescence mapping and tomography, micro-XAFS, and surface diffraction on model systems. Diffraction and micro-diffraction can be used to identify the host materials. The microprobe-based methods are most widely used because samples are usually heterogeneous and full-field imaging methods lack the needed sensitivity to parts-per-million levels. With the APS renewal, there is the opportunity to improve current microprobes with upgraded optics and detectors, which will provide smaller, more intense beams. New, large arrays of spectroscopy-caliber detectors will be needed to take full advantage of these beams. The net result could be more than an order of magnitude increase in data collection

efficiency. More dilute trace element concentrations will become measurable, and the study of larger numbers of samples will be possible. Currently, long data acquisition times restrict investigations to, at most, a few imaged areas in a few samples. The critical question is, how representative are these regions of the whole complex environmental system?

### **Biogeochemistry in subsurface environments**

Microorganisms can control the redox state of major and minor constituents in soils and subsurface environments, and biogeochemical reactions can affect the mobility and bioavailability (i.e., cycling) of most elements in the Periodic Table. Understanding biogeochemical cycling of elements requires information about the relationships between the metabolic processes and cellular microenvironments of microbial species and the reactivity of solid and liquid geochemical phases. Biogeochemical cycling affects element sequestration, release, precipitation, and solubility; organic complexation and degradation; and other chemical modifications of contaminants and mineral surfaces. A deeper understanding of the complex reactions that control biogeochemical cycling from atomic to global spatial scales will enable scientists to address areas of concern as diverse as global warming, production of alternative energy feed stocks and their conversion to fuels via biological processes, optimization of chemical sequestration technologies, development of new environmental remediation strategies based on biostimulation approaches, and even the origin of life.

The microenvironment in the few cubic microns at and adjacent to actively metabolizing cell surfaces can be significantly different from the bulk environment. Microbial polymers (polysaccharides, DNA, RNA, and proteins), whether attached to or released from the cell, contribute to the development of steep chemical gradients over very short distances. It is currently difficult to understand the behavior of contaminant radionuclides and metals in such microenvironments. Thus, information about biotransformations and biogeochemical interactions at the microbe-mineral interface is crucial for predicting the fates of contaminants and for designing effective bioremediation approaches.

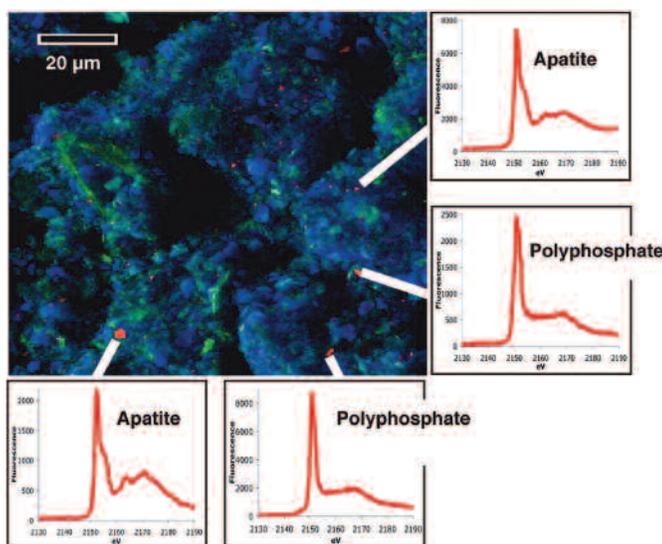


Fig. 1. X-ray fluorescence micrograph and fluorescence spectra of phosphorus-rich regions in Effingham Inlet sediment. Sedimentary phosphorus (red) appears as distinct, heterogeneously distributed submicrometer-sized particles against a comparatively uniform background of sedimentary aluminum (blue) and magnesium (green). On the basis of high-resolution x-ray spectroscopic characterization, about half of the 147 phosphorus-rich regions examined were found to be polyphosphate, whereas the other half were classified as apatite. (© 2008 American Association for the Advancement of Science) See: J. Diaz et al., "Marine Polyphosphate: A Key Player in Geologic Phosphorus Sequestration," *Science* **320**, 652 (2 May 2008)

There are numerous examples of the use of hard x-ray synchrotron radiation to investigate transformations of minerals, contaminant metals, and radionuclides, but only a small number of synchrotron-based microprobe studies have been performed to directly probe the microenvironment at or near the mineral-microbe interface. For example, x-ray microspectroscopy at the APS was recently used to describe a mechanism by which diatom-derived polyphosphates play a critical role in the formation of calcium phosphate minerals in marine sediments (Fig. 1) [25]. These results show how biogeochemical cycling of phosphorous is tied to that of carbon. Similarly, microspectroscopy has been applied to delineate the role of biofilms in chemically transforming carcinogenic heavy metals such as chromium [26].

Submicron x-ray microprobes have also been used to investigate the biological components of biogeochemical cycling. For instance, x-ray microprobe studies at the APS have identified mineral assemblages within microorganisms thought to facilitate respiration in the absence of an external oxidant [27], and biochemical mechanisms used by other microorganisms to scavenge reactive oxygen species [28].

Application of synchrotron technologies will enable the understanding of coupled bi-

otic and abiotic processes under ambient and extreme environmental conditions, and will provide practical opportunities for scientific discoveries in environments contaminated with metals, radionuclides, and organics; agricultural sites to be used for the sustained production of biofuel feed stocks; degradation of cellulosic biofuel feedstocks; and systems affecting atmospheric CO<sub>2</sub> concentrations.

### Mineral physics and Earth and planetary interiors

Processes occurring within the interiors of the Earth and other planets are controlled by the physical and chemical properties of the materials that compose these bodies.

Most of what geologists and planetary scientists know about planetary interiors is based on seismic and gravity data, along with inferences from bulk composition and moment of inertia. Additional constraints on the structure, phase relations, and mechanical behavior of planetary interiors can be obtained directly from experimental studies of appropriate compositions performed at extreme conditions of pressure and temperature. These experiments can now be performed using pressurized devices such as the diamond-anvil cell (Fig. 2 and the multi-anvil apparatus, in which samples can be laser-heated under pressure and measurements can be made *in situ* using ultrasonic methods, light scattering, and synchrotron radiation techniques including x-ray diffraction, x-ray inelastic scattering, and x-ray absorption spectroscopy.

High-pressure experimentation in a laser-heated diamond anvil cell using high-brilliance, hard x-ray synchrotron radiation for *in situ* structure determination by x-ray diffraction resulted in the recent discovery of a post-perovskite phase of MgSiO<sub>3</sub> at conditions approximating those of the Earth's core-mantle boundary



Fig. 2. Diamonds in a diamond anvil cell. The sample is confined between the two diamond single crystals. See: S. Merkel et al., "Deformation of (Mg,Fe)SiO<sub>3</sub> Post-Perovskite and D" Anisotropy," *Science* **316**, 1729 (22 June 2007)

[29]. This discovery has major implications for the interpretation of the D'' seismic discontinuity [30], which has been a controversial geophysical topic for decades. This example illustrates how such experimental data can constrain interpretations for seismic observations of density stratification in the Earth and other planets. The composition and properties of the Earth's core have fundamental implications for its geochemical evolution and dynamics, including the origin of the Earth's magnetic field. Studies of the melting of candidate materials for the core (e.g., Fe and Ni, alloyed with light elements such as Si or S), as well as the physical properties of these molten fluids, are needed to unravel the current composition and history of the core. Such studies should also be conducted with both static and dynamic compression techniques to achieve the extreme pressures of the extra-solar planets and provide time-resolved data. Finally, the advanced microanalytical methods developed for high-pressure techniques can be used to study natural samples [31,32].

Some of the outstanding questions in geological and planetary science that can be addressed using synchrotron radiation are outlined in the workshop reports *Current and Future Research Directions in High-Pressure Mineral Physics* [33] and "Role of User Facilities in Earth Sciences Research" [34]: How much potassium and other radioactive elements can be present in the core? What light elements are present in the core? What is the energy source that drives the geomagnetic dynamo? How does the core melting temperature vary with composition? What is the nature of the D'' layer at the base of the mantle? Is the mantle partially molten at the core-mantle boundary? What is the crystal structure of the inner core, and is it partly molten? How do small amounts of water affect the properties of minerals at mantle conditions? What is the structure and behavior of hydrogen-rich compositions at temperatures and pressures characteristic of the outer planets and their icy satellites?

Over the past decade, special facilities have been developed and installed on beamlines at the APS to enable next-generation, state-of-the-art experiments in high-pressure Earth and planetary science mineral physics. These include the diamond-anvil and multi-anvil apparatus at the GSECARS beamlines 13-BM and 13-ID, the high-pressure diamond-anvil facilities at the High Pressure Collaborative Access Team

(HP-CAT) sector, and the nuclear resonant inelastic x-ray scattering facilities at the X-ray Operations and Research 3-ID beamline. HPSynC is a consortium that supports the integration and development of high-pressure activities of some dozen beamlines at the APS involved in this area of research, including high-pressure geoscience (Fig. 3s). At each of these beamlines, new techniques are being added to this arsenal of tools to study the structure and behavior of materials at extreme conditions. Of critical importance is the need to integrate and exploit multiple techniques that take advantage of the unique features of different beamlines to understand high-pressure phenomena (e.g., Ding et al. [35]).

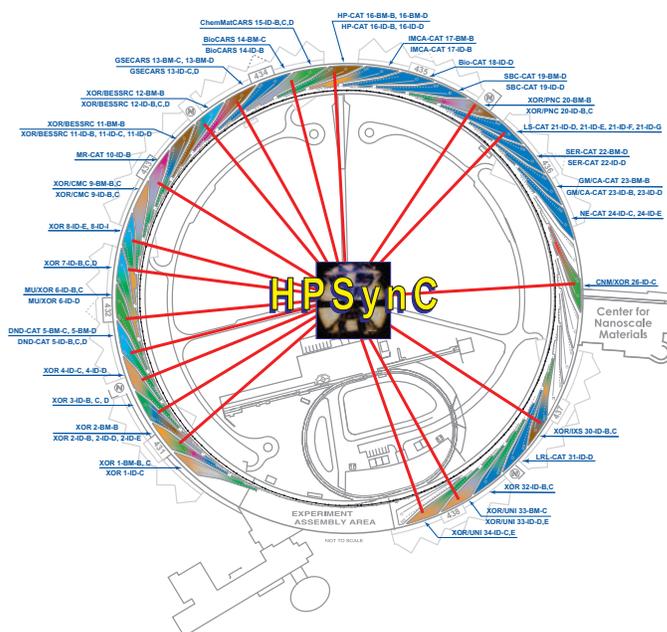


Fig. 3. The APS sectors served by HPSynC.

Ever-brighter sources from 1 keV to 100 keV are essential for this work because photons remain the key probe of the crystallographic, electronic, and defect structures of minerals and mineral assemblages under the most extreme conditions. There are important opportunities for exploring the nanophase materials described above to extreme conditions using <10-nm beams. New microfocusing/imaging techniques developed at the APS are opening new fields for imaging complex natural assemblages, textured materials, and buried interfaces under extreme conditions [36,37]. Current single-phase diffraction/scattering techniques need to be extended to tomographic diffraction/spectroscopic (e.g., x-ray Raman; see, for instance, Hemley et al. [38]) imaging of bulk materials under extreme conditions using these

nanometer-scale x-ray beams. In addition, there are proposals for dedicated facilities at the APS for direct measurements of materials on dynamic compression, based on successful shock-wave, single-crystal x-ray measurements carried out at HP-CAT in 2007 [39]. As mentioned above, this new class of experiments, including combined static and dynamic compression measurements at synchrotron sources, hold the promise of accessing and probing entirely new  $P$ - $T$  regimes within the Earth and other planets. The scientific questions listed above, and many others, can be addressed more effectively by improvements in the flux, brilliance, x-ray optics and detectors at the APS.

### Cosmochemistry and planetary geochemistry

Clues to the origin and evolution of our Solar System and other cosmological bodies are locked within extraterrestrial materials available for laboratory study, including



A promotional poster for the Stardust mission. (Courtesy of NASA)

lunar samples returned by the Apollo program; meteorites from the Moon, Mars, and asteroids collected from Earth's surface, notably Antarctica; interplanetary dust particles collected in the stratosphere; comet particles collected by the Stardust spacecraft; and solar wind collected by the Genesis spacecraft. The science drivers involve fundamental questions: How did the universe begin and what is its ultimate fate? How did the Sun's family of planets and minor bodies originate and evolve to their present state? How did life begin on Earth and are conditions right for life on other celestial bodies? What are the fundamental physical and chemical processes at work in the space environment from the Sun to Earth, to other planets, and beyond to the interstellar medium?

Synchrotron-based techniques are playing an important role in defining the states of these samples and obtaining insight into the properties of their parent bodies and the

processes that formed them. Organics derived from individual (~10- $\mu$ m) stratospheric interplanetary dust particles, cometary dust, and meteorites are being studied by scanning transmission x-ray microscopy and Fourier transform infrared spectroscopy to test formation hypotheses such as catalytic reactions on mineral surfaces and provide insight into the likelihood of seeding of the Earth by extraterrestrial material at the onset of terrestrial life [40-43]. New classes of extraterrestrial organic matter can also be discovered in this way [44]. Evidence for a close relationship between the dust in comets and carbonaceous meteorites is being provided by x-ray microprobe (XRM) compositional analyses [45,46]. The evolutionary relationships between primitive components of carbonaceous meteorites, such as chondrules and refractory inclusions, are being uncovered by microXAFS analyses [47,48]. Formational environments of presolar SiC grains from meteorites are being revealed by XRM analyses [49-52], and coupled resonance ionization mass spectrometry analyses will eventually yield insight into the associated stellar types. Oxidation states of Martian siliceous melts are being determined by XRM analyses of Martian meteorites [53,54] as well as the evolution of Martian fluids in its early history [55,56]. Synchrotron-based x-ray standing-wave methods offer one of the few opportunities to extract compositional data from the compromised Genesis solar wind collectors [57,58]. Synchrotron x-ray microdiffraction revealed new minerals and the origin of weathering on airless bodies such as the moon [59], as well as the effects of shock metamorphism on planetary surfaces [32]. Instrumentation at the APS is playing a vital role in the high-energy components of this research.

This cutting edge, synchrotron-based, cosmochemical research is currently limited by spatial resolution and sensitivity capabilities. Extraterrestrial materials are exceedingly fine-grained (nanometer-scale) and synchrotron instrumentation is just beginning to be able to probe these materials at spatial scales where individual phases dominate. In addition, high elemental sensitivity in these sub-micrometer regions is essential. Elements of interest tend to be in trace concentrations, indicating that analytical capabilities in the attogram range are required. Technical improvements that will drive these advances include higher brightness sources, improved optics (especially those capable of high efficiency and sub-micrometer beam production), im-

proved detectors (primarily in terms of higher throughput, but high-energy resolution is also essential), and sample manipulation systems with higher spatial resolution and stability.

Accessibility is also a critical issue. The APS instruments currently used for this research are highly oversubscribed, making it challenging to obtain comprehensive data sets in reasonable time periods. This accessibility shortfall can be addressed with the addition of new instruments, an increase in the amount of beam time available on existing instruments, or a combination of these two approaches. Canted undulator upgrades (as pioneered at the APS) are effective means for dramatically increasing instrument availability.

These technical advances will maximize our ability to extract information not only from currently available extraterrestrial materials collections, but also samples from future return missions, such as those likely to sample the Moon, Mars, asteroids, and comets. The relatively non-destructive nature of the synchrotron x-ray analyses is extremely advantageous for characterization of these precious returned extraterrestrial materials that often are in exceedingly small quantities. The total comet dust collection returned by the Stardust spacecraft has an estimated mass of ~1 mg. The total mass of the Genesis solar wind collection is estimated to be ~400 µg. Importantly, x-ray analyses can be done without sample alteration, often while within the collection substrates and containers, leaving the materials available for further destructive analyses that require extraction, such as isotopic composition by mass spectrometry. Such consortium-style analytical approaches maximize the science return from individual samples.

## References

[1] *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems*. Report from the workshop sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Bethesda, MD, February 21-23, 2007 (Office of Basic Energy Sciences, Department of Energy, June 2007). [http://www.sc.doe.gov/bes/reports/files/GEO\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/GEO_rpt.pdf)

[2] *Basic Research Needs for Materials under Extreme Environments*. Report of the Basic En-

ergy Sciences Workshop on Materials under Extreme Environments, June 11-13, 2007 (Office of Basic Energy Sciences, Department of Energy, February 2008). [http://www.sc.doe.gov/bes/reports/files/MUEE\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/MUEE_rpt.pdf)

[3] G. Binnig, C.F. Quate, and C. Gerber, "Atomic force microscope," *Phys. Rev. Lett.* **56**, 930 (1986).

[4] F. Ohnesorge and G. Binnig, "True atomic-resolution by atomic force microscopy through repulsive and attractive forces," *Science* **260**, 1451 (1993).

[5] Y.R. Shen, "Surfaces probed by nonlinear optics," *Surf. Sci.* **300**, 551 (1994).

[6] M.F. Hochella and J.F. Banfield, "Chemical weathering of silicates in nature: A microscopic perspective with theoretical considerations," *Rev. Mineral.* **31**, 353 (1995).

[7] G.E. Brown, Jr., and N.C. Sturchio, "An overview of synchrotron radiation applications in low-temperature geochemistry and environmental science," *Rev. Mineral. Geochem.* **49**, 1 (2002).

[8] P.A. Fenter, "X-ray reflectivity as a probe of mineral-fluid interfaces: A user guide," *Rev. Mineral. Geochem.* **49**, 149 (2002).

[9] M.J. Bedzyk and L. Cheng, "X-ray standing wave studies of minerals and mineral surfaces: Principles and applications," *Rev. Mineral. Geo.* **49**, 221 (2002).

[10] R.T. Cygan and J.D. Kubicki, eds. "Molecular Modeling Theory: Applications in the Geosciences," *Rev. Mineral. Geochem.* **42**, 531 (2001).

[11] L. Cheng, P. Fenter, K.L. Nagy, M.L. Schlegel, and N.C. Sturchio, "Molecular-scale density oscillations in water adjacent to a mica surface," *Phys. Rev. Lett.* **87**, 156103 (2001).

[12] S.H. Park and G. Sposito, "Structure of water adsorbed on a mica surface," *Phys. Rev. Lett.* **89**, 085501 (2002).

[13] P. Geissbühler, P. Fenter, E. DiMasi, G. Srajer, L.B. Sorensen, and N.C. Sturchio, "Three-dimensional structure of the calcite-water interface," *Surf. Sci.* **573**, 191 (2004).

[14] S. Kerisit and S.C. Parker, "Free energy of adsorption of water and calcium on the  $\{10\bar{1}4\}$  calcite surface," *Chem. Commun.* **1**, 52 (2004).

[15] T.P. Trainor, A.C. Chaka, P.J. Eng, M. Newville, J. Catalano, G.A. Waychunas, and G.E. Brown, Jr., "Structure and reactivity of the hydrated hematite (0001) surface," *Surf. Sci.* **573**, 204 (2004).

[16] J.W. Moreau, P.K. Weber, M.C. Martin, B. Gilbert, I.D. Hutcheon, and J.F. Banfield, "Extracellular proteins limit the dispersal of biogenic nanoparticles," *Science* **316**, 1600 (2007).

- [17] H.W. Green, II, and P.C. Burnley, "A new self-organizing mechanism for deep-focus earthquakes," *Nature* **341**, 733 (1989).
- [18] B. Wilson, T. Dewers, Z. Reches, and J. Brune, "Particle size and energetics of gouge from earthquake rupture zones," *Nature* **434**, 749 (2005).
- [19] L. Soderholm, S. Skanthakumar, D. Gorman-Lewis, M.P. Jensen, and K.L. Nagy, "Characterizing solution and solid-phase amorphous uranyl silicates," *Geochim. Cosmochim. Acta* **72**, 140 (2008).
- [20] F.M. Michel, L. Ehm, S.M. Antao, P.L. Lee, P.J. Chupas, G. Liu, D.R. Strongin, M.A.A. Schoonen, B.L. Phillips, and J.B. Parise, "The structure of ferrihydrite, a nanocrystalline material," *Science* **316**, 1726 (2007).
- [21] A. Navrotsky, L. Mazeina, and J. Majzlan, "Size-driven structural and thermodynamic complexity in iron oxides," *Science* **319**, 1635 (2008).
- [22] A. Manceau, M.A. Marcus, and N. Tamura, "Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques," in *Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science*, P. Fenter and N.C. Sturchio, eds., *Reviews in Mineralogy and Geochemistry*, Vol. **49**, (Mineralogical Society of America, Washington, DC., 2002) p. 341.
- [23] A. Manceau, K.L. Nagy, M.A. Marcus, M. Lanson, N. Geoffroy, T. Jacquet, and T. Kirpichtchikova, "Formation of metallic copper nanoparticles at the soil-root interface," *Enviro. Sci. Tech.* **42**, 1766 (2008).
- [24] J.G. Catalano, S.M. Heald, J.M. Zachara, and G.E. Brown, Jr., "Spectroscopic and diffraction study of uranium speciation in contaminated vadose zone sediments from the Hanford site, Washington State," *Enviro. Sci. Tech.* **38**, 2822 (2004).
- [25] J. Diaz, E. Ingall, C. Benitez-Nelson, D. Paterson, M.D. de Jonge, I. McNulty, and J.A. Brandes, "Marine Polyphosphate: A Key Player in Geologic Phosphorus Sequestration," *Science* **320**, 652 (2008).
- [26] K.M. Kemner, S.D. Kelly, B. Lai, J. Maser, E.J. O'Loughlin, D. Sholto-Douglas, Z. Cai, M.A. Schneegurt, C.F. Kulpa, Jr., and K.H. Nealson, "Elemental and redox analysis of single bacterial cells by X-ray microbeam analysis," *Science* **306**, 686 (2004).
- [27] S. Glasauer, S. Langley, M. Boyanov, B. Lai, K.M. Kemner, and T.J. Beveridge, "Mixed valence cytoplasmic iron granules are linked to anaerobic respiration," *Appl. Enviro. Microb.* **73**, 993, (2007).
- [28] M.J. Daly, E.K. Gaidamakova, V.Y. Matrosova, A. Vasilenko, M. Zhai, K.M. Kemner, B. Lai, B. Ravel, L.P. Wackett, S.W. Li, and J.K. Fredrickson, "Protein Oxidation Implicated as the Primary Determinant of Bacterial Radioresistance," *PLoS Biology* **5**(4), e92 (2007).

- [29] M. Murakami, K. Hirose, K. Kawamura, N. Sata, and Y. Ohishi, "Post-perovskite phase transition in  $\text{MgSiO}_3$ ," *Science* **304**, 855 (2004).
- [30] K. Hirose, "Postperovskite phase transition and its geophysical implications," *Rev. Geophys.* **44**, RG3001, (2006).
- [31] N.V. Sobolev, B.A. Fursenko, S.V. Goryainov, J. Shu, R.J. Hemley, H.-k. Mao, and F.R. Boyd, "Fossilized high pressure from the Earth's deep interior: the coesite-in-diamond barometer," *Proc. Nat. Acad. Sci.* **97**, 11875 (2000).
- [32] M. Chen, J. Shu, H.-k. Mao, X. Xie, and R.J. Hemley, "Natural occurrence and synthesis of two new post-spinel polymorphs of chromite," *Proc. Nat. Acad. Sci.* **100**, 14651 (2003).
- [33] *Current and Future Research Directions in High-Pressure Mineral Physics*. Workshop report, Consortium for Materials Properties Research in the Earth Sciences, August 2004. J.D. Bass, ed. [http://www.compres.stonybrook.edu/Publications/BassReport/Bass\\_Report\\_8\\_31\\_04.pdf](http://www.compres.stonybrook.edu/Publications/BassReport/Bass_Report_8_31_04.pdf)
- [34] G.E. Brown, G. Calas, and R.J. Hemley, "Role of user facilities in Earth sciences research," *Elements* **2**, 23 (2006).
- [35] Y. Ding, D. Haskel, S.G. Ovchinnikov, Y.-C. Tseng, Y.S. Orlov, J.C. Lang, and H.-k. Mao, "Novel pressure-induced magnetic transition in magnetite ( $\text{Fe}_3\text{O}_4$ )," *Phys. Rev. Lett.* **100**, 045508 (2008).
- [36] R.J. Hemley, H.-k. Mao, and V.V. Struzhkin, "Synchrotron radiation and high pressure: new light on materials under extreme conditions," *J. Synchrotron. Rad.* **12**, 135 (2005).
- [37] G.P. Ice, W. Dera, W. Liu, and H.-k. Mao, "Adapting polychromatic x-ray microdiffraction techniques to high-pressure research: energy scan approach," *J. Synchrotron. Rad.* **12**, 6-9-617 (2005).
- [38] R.J. Hemley, V.V. Struzhkin, and R.E. Cohen, "Measuring high-pressure electronic and magnetic properties," *Treatise on Geophysics*, G. D. Price, ed., (Elsevier, Amsterdam, 2007), p. 293.
- [39] S.J. Turneure, Y.M. Gupta, K. Zimmerman, K. Perkins, C.S. Yoo, and G. Shen, "Real-time microstructure of shocked crystals using synchrotron x-rays," *Science*, submitted (2008).
- [40] G.J. Flynn, L.P. Keller, M. Feser, S. Wirick, and C. Jacobsen, "The Origin of Organic Matter in the Solar System: Evidence from the Interplanetary Dust Particles," *Geochim. Cosmochim. Acta* **67**, 4791 (2003).
- [41] G.J. Flynn, L.P. Keller, C. Jacobsen, and S. Wirick, "FTIR and Carbon-XANES Examination of Organic Carbon in Tagish Lake: Evidence for a Moderately Volatile Organic Component," *Lunar and Planetary Science XXXIII* (Lunar and Planetary Institute, Houston, TX, 2002) p. 1593.

- [42] S. Messenger, "Identification of molecular cloud material in interplanetary dust particles," *Nature* **404**, 968 (2000).
- [43] L.P. Keller, S. Messenger G.J. Flynn, S. Clemett, S. Wirick, and C. Jacobsen, "The nature of molecular cloud material in interplanetary dust," *Geochim. Cosmochim. Acta* **68**, 2577 (2004).
- [44] S. Sandford et al., "Organics captured from comet 81P/Wild 2 by the Stardust spacecraft," *Science* **314**, 1720 (2006).
- [45] G.J. Flynn et al., "Elemental compositions of comet 81P/Wild 2 samples collected by Stardust," *Science* **314**(5806), 1731 (2006).
- [46] A. Lanzirotti, S. R. Sutton, G.J. Flynn, M. Newville, and W. Rao, "Chemical composition and heterogeneity of Wild 2 cometary particles determined by synchrotron x-ray fluorescence," *Meteorit. Planet. Sci.* **43**, 187 (2008).
- [47] S.B. Simon, S.R. Sutton, and L. Grossman, "The Valence of Titanium in Refractory Forsterite," *Lunar and Planetary Science XXXVIII* (Lunar and Planetary Institute, Houston, TX, 2007a) 1892.
- [48] S. Simon, S.R. Sutton, and L. Grossman, "Valence of Titanium and Vanadium in Pyroxene in Refractory Inclusion Interiors and Rims," *Geochim. Cosmochim. Acta* **71**, 3098 (2007b).
- [49] Y. Kashiv, "Trace element abundances in single presolar SiC grains by synchrotron x-ray fluorescence," Ph.D., The University of Chicago (2004).
- [50] Y. Kashiv, Z. Cai, B. Lai, S.R. Sutton, R.S. Lewis, A.M. Davis, R.N. Clayton, and M.J. Pellin, "Condensation of trace elements into presolar SiC stardust grains," *Lunar and Planetary Science XXXIII* (Lunar and Planetary Institute, Houston, TX, 2002) p. 2056.
- [51] Y. Kashiv, A.M. Davis, Z. Cai, B. Lai, S.R. Sutton, R.S. Lewis, R. Gallino, and R.N. Clayton, "Extinct  $^{93}\text{Zr}$  in Single Presolar SiC Grains and Condensation from Zirconium Depleted Gas," *Lunar and Planetary Science XXXVII* (Lunar and Planetary Institute, Houston, TX, 2006) p. 2464.
- [52] K.B. Knight, S.R. Sutton, M. Newville, A.M. Davis, N. Dauphas, R.S. Lewis, S. Amari, I.M. Steele, M.R. Savina, and M.J. Pellin, "Trace Element Determinations in Presolar SiC Grains by Synchrotron X-Ray Fluorescence: Commencement of a Coordinated Multimethod Study," *Lunar and Planetary Science XXXIX*, LPI (Lunar and Planetary Institute, Houston, TX, 2008) p. 2135.
- [53] E.L. Walton, P. Jugo, and C.D.K. Herd, "The nature and origin of localized shock melts in Martian meteorites: Major and trace element composition, sulfur speciation and texture of EET 79001 shock melt veins and pockets," *Lunar and Planetary Science XXXIX* (Lunar and Planetary Institute, Houston, TX, 2008) 1880.

- [54] S.R. Sutton, M.N. Rao, and L.E. Nyquist, "Sulfur and Iron Speciation in Gas-Rich Impact-Melt Glasses from Basaltic Shergottites Determined by MicroXANES," *Lunar and Planetary Science XXXIX* (Lunar and Planetary Institute, Houston, TX, 2008) p. 1961.
- [55] M.N. Rao, , S.R. Sutton, D.S. McKay, and G. Dreibus, "Clues to Martian Brines based on Halogens in Salts from Nakhilites and MER Samples," *J. Geophys. Res.-Planet (Early Mars Special Issue)* **110**, (2005).
- [56] M.N. Rao, L.E. Nyquist, S.J. Wentworth, D.H. Garrison, J. Herrin, and S.R. Sutton, "The Nature of Martian Fluids based on Mobile Element Studies in Salt-assemblages from Martian Meteorites," *J. Geophys. Res.-Planet* **113**, E06002,(2008).
- [57] K. Kitts, Y. Choi, P. Eng, S. Sutton, S. Ghose, and D. Burnett, "Discrimination and Quantification of Implanted Solar Wind in Genesis Collector Shards Using Grazing Incidence Synchrotron X-Ray Techniques: New Detector Initial Results," *Lunar and Planetary Science XXXIX* (Lunar and Planetary Institute, Houston, TX, 2006) p. 1296.
- [58] K. Kitts, S. Sutton, P. Eng, S. Ghose, and D. Burnett, "Discrimination and Quantification of Contamination and Implanted Solar Wind in Genesis Collector Shards Using Grazing Incidence Synchrotron X-Ray Techniques: Initial Results," *Lunar and Planetary Science XXXVII*, (Lunar and Planetary Institute, Houston, TX, 2008) p. 1451.
- [59] M. Anand, L. A. Taylor, M. A. Nazarov, J. Shu, H. K. Mao, and R. J. Hemley, "Space weathering on airless planetary bodies: clues from the lunar mineral hapkeite," *Proc. Nat. Acad. Sci.* **101**, 6847 (2004).

## Renewal of the Advanced Photon Source: Interfacial Science

<b>Paul Fenter</b> (Chair)	<i>Argonne National Laboratory</i>
<b>Michael J. Bedzyk</b>	<i>Northwestern University and Argonne National Laboratory</i>
<b>Joel D. Brock</b>	<i>Cornell University</i>
<b>Roy Clarke</b>	<i>University of Michigan</i>
<b>Ronald S. Pindak</b>	<i>Brookhaven National Laboratory</i>
<b>Michael F. Toney</b>	<i>Stanford Synchrotron Radiation Laboratory</i>
<b>Hoydoo You</b>	<i>Argonne National Laboratory</i>
<b>Paul Zschack</b>	<i>Argonne National Laboratory</i>

### Executive Summary

Transformative opportunities in interfacial science can be created in the next decade through advances in instrumentation and software at the Advanced Photon Source (APS). These advances will enable the observation of interfacial processes in complex environments, in real time, and with micron-scale fields of view and Angstrom- to nanometer-scale sensitivity and resolution. These extraordinary capabilities will lead to a better understanding of relevant molecular-scale processes, control of interfacial composition and structure, and help create novel materials and devices. More generally, these capabilities will enable the study of “realistic” interfaces with inherent heterogeneity at a level previously attainable only for highly homogeneous “model” systems.

Interfaces are of critical importance for the next generation of energy-related technologies [1]. For example, the chemical, structural, and electronic nature of new materials and nanoscale-structured interfaces relates directly to the performance of multilayer solar cells and other energy harvesting media [2], catalysts [3], energy storage materials [4], thermoelectrics, and solid-state lighting [5]. Interfacial stabil-

ity under extreme chemical environments is critical to numerous energy technologies, including the operation of nuclear reactors [6] and the geological sequestration of energy by-products (carbon and nuclear material sequestration) [7]. Interfaces are also critical in the reprocessing of nuclear materials [8].

Central to achieving these scientific goals is our ability to understand the elementary processes that take place at the interface between distinct media—such as adsorption, chemical reactions, growth, and processing—within a diverse range of fields, disciplines, materials, and environments. Areas directly impacted by such processes range from the efficient use of energy resources to the creation of novel materials and maintenance of our natural environment. Interfacial science is invigorated by the many scientific and technological opportunities associated with matter at small dimensions—typically Angstroms to nanometers—and is challenged by the need to access interfaces through complex environments.

## Introduction

Interfaces are the boundaries between media such as solids, liquids, and gases with distinct physical and chemical properties. The presence of an interface typically leads to gradients in the chemical potential, perturbs the properties of the two media to a depth controlled by the properties of the individual medium, and introduces interfacial states, such as structural and electronic, that differ from that of either medium. Well-known examples include the formation of Schottky barriers at the metal-semiconductor interface, the electrical double layer at the interface of a charged solid in contact with an electrolyte solution, and the spontaneous symmetry breaking associated with surface reconstructions. Interfaces can also act as kinetic barriers between reactive media, effectively stabilizing materials that are thermodynamically unstable, such as passive oxide coatings on aluminum metal that inhibit corrosion.

Interfaces are central to many diverse fields of study (Fig. 1). These include materials science, where control of the composition and structure of an interface can lead to de-

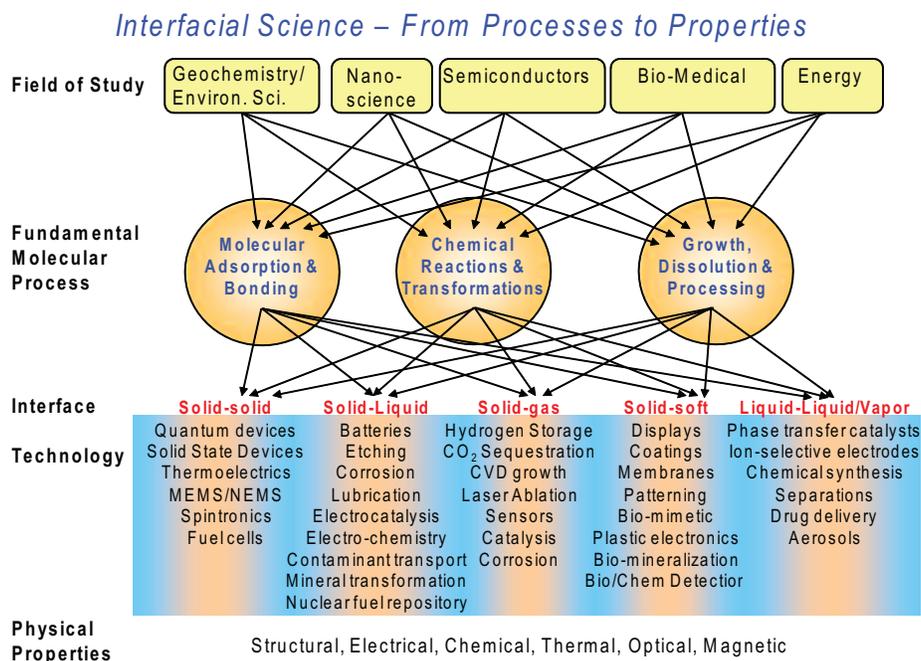


Fig. 1. The diversity and commonality of interfacial science.  
(Courtesy P. Fenter, Argonne National Laboratory)

sirable materials properties; geochemistry and environmental science, where the transport and sequestration of nutrients and contaminants is often controlled by their interactions with mineral surfaces; chemical science, where the heterogeneous reactivity of interfaces in “supported” catalysts creates facile pathways that promote chemical reactions; energy science, where robust energy-storage technologies currently rely on the passivating layers at solid-electrolyte interfaces to prevent catastrophic failure; nanoscience, where the nanomaterial properties are modified by their surfaces due to their large surface to volume ratios; and bioscience, where membrane proteins actively maintain chemical gradients necessary for sustaining life. Solid-solid, solid-fluid, or fluid-fluid interfaces are all relevant. The solids may be either “hard” (metals or semi-conductors) or “soft” (organic, molecular, or model membranes), and the fluid may range from an aqueous solution to liquid metals or supercritical fluids.

It is apparent from these examples that the understanding and control of interfacial

processes are central to modern life. A more robust understanding of these areas can therefore lead to significant advances in addressing critical societal needs such as renewable production of clean energy, greater energy storage capacity to make full use of renewable energy sources, efficient production of petroleum-based products, maintaining fresh-water supplies, and continued improvement in memory storage and other electronic devices. Yet the ability to understand interfaces, especially those in complex environments, remains both a scientific and technical challenge.

The apparent diversity of disciplines, phenomena, materials, and environments within this field masks deep underlying commonalities. Interfacial processes can be understood within the context of a few classes of molecular phenomena. These include molecular adsorption and bonding, in which the presence of the interface leads to the organization and concentration of species from the environment; chemical reactions and transformation, in which the constituents of the environment and/or substrate react and transform into new species; and growth, dissolution, and processing, in which materials are either deposited or consumed. It is at this level that the commonalities become clear. For example, the concepts of heterogeneous epitaxy—originally developed to understand the principles behind semiconductor and metal-film growth—provide the context to understand geochemical processes such as the anomalous inhibition of dolomite growth, a mineral that is often highly supersaturated in natural waters. Epitaxy is also closely related to the concept of wetting, which explains the morphology of liquid films and is responsible (through interactions between hydrophobic and hydrophilic regions) for the conformations of biological molecules such as proteins.

## Science Drivers

Given the broad impact and relevance of interfacial science to a wide range of fields of study, it is not possible to provide a complete description of the many science drivers in this community. However, it is evident that much of the activity in this area can be illustrated by a few representative examples.

## Interfacial reactivity in complex environments

Differences in the local coordination of interfacial species with respect to that found within the bulk media can substantially modify interfacial reactivity, either by decreasing thermodynamic barriers to enhance the reactions of surface-bound species (e.g., catalysis of chemical reactions) or through the development of kinetic barriers associated with compositionally or structurally modified interfacial layers that inhibit the transport of material through the layers, such as the formation of protective coatings. Reactive interfaces are found in a broad spectrum of technical fields ranging from energy storage (batteries), to electrocatalysis (fuel cells), geochemistry (transport of contaminants), hydrogen storage, catalysis, materials growth, and corrosion at liquid-solid and gas-solid interfaces.

Intrinsic to each of these areas are the divergent spatial and temporal scales describing interfacial reactivity. The fundamental step in these reactions involves the formation and breaking of chemical bonds between reactants and with the substrate. Insight into these reactions has normally been obtained by static views of the associated molecular ( $\sim$ Angstrom-scale) structures, before and after reactions. Individual defects (steps, adatoms, vacancies) typically have intrinsic reactivities that are substantially modified with respect to that of an ideally flat surface, leading to substantial lateral heterogeneity (from approximately nanometer to greater than micron) in the reactivity. The idealized concept of a molecularly-sharp interface that is normal to the interfacial plane is often unrealistic because gradients in the chemical potential across an interface can lead to extended structures normal to the interfacial plane (extended elemental distributions in an “electrical double layer,” or the development of compositionally modified layers) tens of nanometers to hundreds of nanometers thick. The relevant temporal scales at interfaces are similarly broad. Reorganization times of individual water molecules at an oxide interface vary from  $\sim 1$  ps to  $\sim 1000$  ps; the time for catalytic turnover ranges from  $\sim 1$   $\mu$ s to  $\sim 1$  s; and the growth or removal of individual layers ranges from approximately microseconds to hours.

The coupling of these disparate spatial and temporal scales can lead to unexpected

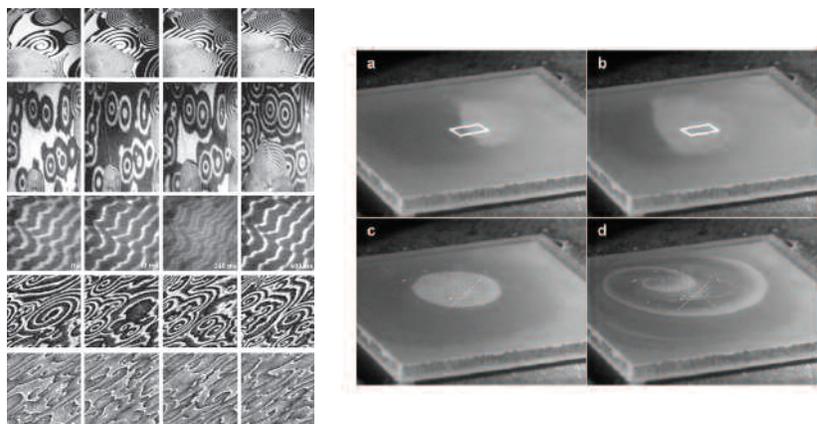


Fig. 2. Spatio-temporal oscillations at reacting interfaces. Left: Platinum surfaces imaged by photoemission electron microscopy during catalytic oxidation of CO where light and dark regions are associated with CO-covered and oxygen-covered regions of the surface. (From: <http://fizz.phys.dal.ca/~hrotermund/>) Right: Growth of InN films on GaN under metal-organic chemical vapor deposition growth conditions in which bright and dark regions are InN islands and In droplets, respectively. (Jiang et al., *Phys. Rev. Lett.* **101**, 086102 [2008], © 2008 The American Physical Society, all rights reserved)

complexities that have been largely unexplored (Fig. 2. A prime example is the observation of temporal oscillations during the catalytic oxidation of CO to CO<sub>2</sub> at platinum surfaces under nominally static conditions, which was a key element in the Chemistry Nobel Prize awarded to Gerhard Ertl in 2007. Ertl showed that this phenomenon was due to non-linear reaction dynamics associated with the formation of reaction waves, ultimately associated with the differential reactivity of metal surfaces between two distinct surface structures and the associated transport of material between these regions. This is part of a general class of Belousov-Zhabotinsky reactions that are known to exhibit an extremely rich range of behavior ranging from regular periodic switching to chaotic dynamics. Spatio-temporal reactions have recently been observed under chemical vapor deposition growth conditions (Fig. 2, right).

These considerations reveal that a robust and fundamental understanding of interfacial reactivity relies on our ability to observe interfacial reactions in real time, with high spatial resolution, and over large distances so that the complexities of transport, kinetics, and heterogeneities, etc., can be visualized directly. There re-

mains, in particular, a broad need to project this level of understanding to realistic systems in complex environments (such as those in contact with liquids, or high-pressure gases that are opaque to traditional surface-science tools) that are representative of the complex and often heterogeneous interfaces central to many technical and industrial activities. The ability to observe such reactions in real space (both within and across the interfacial plane) will require the development of robust “contrast” mechanisms that image individual components of a reaction, such as elemental specificity, or that differentiate chemically distinct regions like oxidation states, or that can differentiate between the reactivity of idealized terrace sites and spatially separated defect sites.

### Emergent materials properties at interfaces

Interfaces are not simply the place where two materials meet, with each of them retaining its own properties. There are abrupt changes in chemical and electrostatic potentials, as well as a lattice-mismatch that exerts significant stress on the material. Ionic and electronic reconstructions can occur at the heterointerface leading to the emergence of entirely new physical properties and phenomena.

An essential requirement for the study of heterostructure interfaces is the ability to image the laterally-averaged, three-dimensional structure of buried interfaces without sample thinning at atomic-scale resolution. This is a formidable problem because only the *intensity* is usually measured in conventional x-ray scattering experiments; the *phase* of the scattered x-ray is undetermined. This is the well-known phase problem. Significant progress has been made in finding a solution to this problem for epitaxial thin films and buried interfaces. The importance of these developments lies in the fact that nearly all current electronic and optoelectronic materials applications and devices rely on heteroepitaxial interfaces, including compound semiconductor heterostructures and oxides exhibiting correlated-electron behavior.

The  $\text{LaAlO}_3\text{-SrTiO}_3$  heteroepitaxial interface is a prime example in that it forms a quasi-two-dimensional electron gas at the interface between two nominally insulating materials. The class of perovskite oxides to which this system belongs is

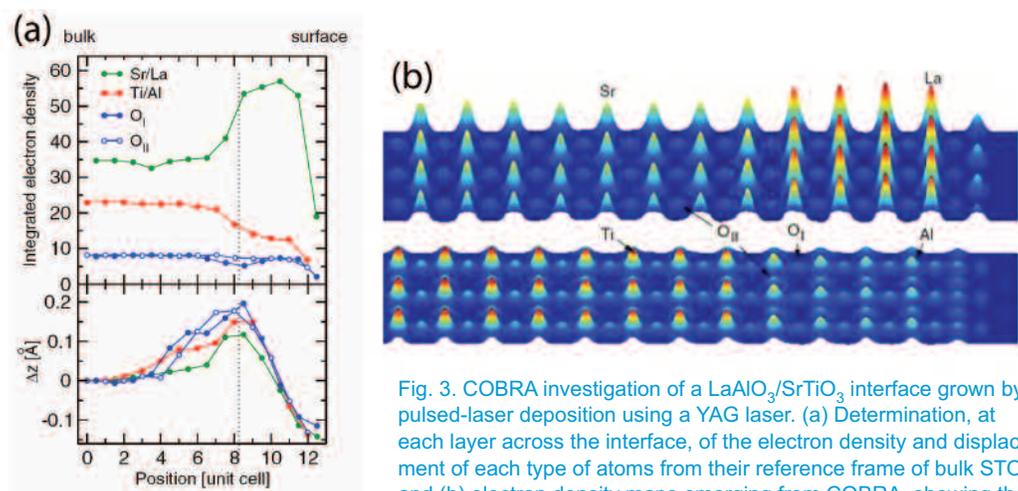


Fig. 3. COBRA investigation of a  $\text{LaAlO}_3/\text{SrTiO}_3$  interface grown by pulsed-laser deposition using a YAG laser. (a) Determination, at each layer across the interface, of the electron density and displacement of each type of atoms from their reference frame of bulk STO; and (b) electron density maps emerging from COBRA, showing the plane normal to the surface containing the La, Sr, and  $O_{II}$  atoms and the plane containing the Al, Ti,  $O_I$  and  $O_{II}$  atoms. (Wilmott et al., *Phys. Rev. Lett.* **99**, 155502 [2007], © 2007 The American Physical Society, all rights reserved)

broadly interesting because it exhibits various important emergent correlated electron phenomena such as novel metal insulator transitions, interface superconductivity, and colossal magnetoresistance. Surface x-ray scattering experiments (Fig. 3) have revealed the formation of a metallic  $\text{LaSrTiO}_3$  layer at the  $\text{LaAlO}_3$ - $\text{SrTiO}_3$  interface with an accumulation of trivalent Ti at the interface that is responsible for the observed lattice dilation (Fig. 3) and for minimizing the electrostatic energy at the  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrate surface. The net result of this combined ionic and electronic reconstruction is to lower the conduction band minimum below the Fermi level, as confirmed by density functional band structure calculations. These findings illustrate the importance of heterointerface structure as the basis for the emergence of an electrically conducting interface, as well as suggesting interesting directions for the design of epitaxial oxide multilayers with novel electronic properties.

### Soft-material interfaces

Soft materials include small organic molecules, macromolecules, polymers, polyelectrolytes, amphiphiles, block copolymers, colloids, liquid crystals, elastomers, and sur-

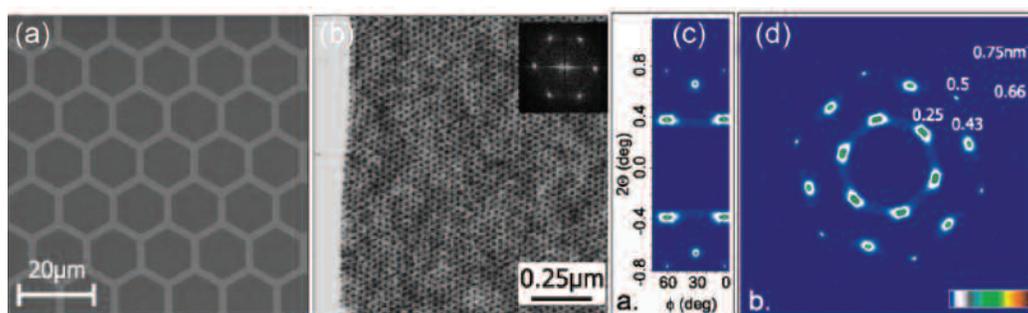


Fig. 4. (a) Scanning electron microscopy image of hexagonal wells photolithographically patterned on a silicon substrate. (b) Atomic force microscopy image of the in-plane structure of PS-PVP diblock copolymer spheres adjacent to and aligned by a well edge. (c)  $I(2\theta, \phi)$  data map constructed from GID measurements of the edge-aligned diblock copolymer sample where  $2\theta$  is the in-plane diffraction angle and  $\phi$  is the in-plane rotation angle. (d) Data from (c) shown as a radial plot. (Stein et al., Phys. Rev. Lett. **98**, 86101 [2007], © 2007 by The American Physical Society, all rights reserved)

factants. Novel synthetic strategies, some inspired by biological processes, can be used to engineer the properties of these materials to be photo or chemical reactive, conducting or semiconducting, or to have different chemical affinities and localized interaction sites. This ability to tailor functionality has resulted in a wide range of applications such as high-resolution displays, organic light-emitting diodes, field-effect transistors, and photovoltaics. Advantages of soft-materials-based devices include potentially low-cost production, environmentally friendly solution-processing, and roll-to-roll production methods on flexible substrates. Organic monolayers can also be used to modify surfaces for low friction, adhesion, and hydrophobicity, and may be functionalized to have selective recognition and be used as chemical or biological sensors. Soft materials can self-assemble into ordered structures as occurs with liquid crystals, block copolymers, and membranes. These self-assembled structures can be oriented by alignment surfaces and edge interactions (Fig. 4). Soft materials can alternatively be nano-patterned using imprint, dip-pen, electrochemical lithography, and ink-jet technology. Hybrid devices in which inorganic nanoparticles or nanorods are oriented in an organic matrix have potential applications as photovoltaic devices.

The use of soft materials in applications often requires a systematic exploration of their numerous processing parameters and molecular degrees of freedom. High-efficiency devices have yet to be achieved and progress is slowed by gaps in our funda-

mental understanding of the underlying interactions and electronic properties. A challenge for the next decade will be to understand what controls local and long-range orientational and positional order in soft materials, and the impact of bulk and interfacial structure on transport properties. A representative example is illustrated in Fig. 4, where grazing incidence x-ray diffraction (GID) was used to determine how the edge of a confining hexagonal well influenced a thin film of a spherical diblock copolymer as it self-assembled into a two-dimensional hexagonal crystal. Numerous scientific opportunities in this area include understanding how processing conditions such as thermal and solvent-annealing affect thin-film order; how the orientation of organic monolayers affects lubrication or charge mobility; how the local crystalline order and orientation of polymer films impact performance when fabricated into different devices; how mixtures of p-type and n-type semiconducting polymers phase separate into nanometer-size domains; and how the morphology of these domains and the molecular packing within the domains can be optimized. The concept of biomineralization offers additional synthetic approaches to materials design and fabrication inspired by the complex structural control displayed by nature. The use of an organic framework apparently is central, but the exact role of this framework is poorly understood. Time-resolved studies of crystallization under Langmuir monolayers will shed light on the fundamental processes at organic/inorganic interfaces.

Soft materials are also models for understanding biological systems, such as cell membranes. The chemical language of cells conveys information and ultimately has the potential to exert control over cellular processes. For example, voltage-gated cation channels (e.g., K, Na, and Ca) are integral membrane proteins that are responsible for the generation and propagation of the potentials that underlie nerve and cardiac action potentials. But an understanding of the structural changes within these membranes as a function of the applied transmembrane electrochemical potential is missing. Millisecond time-resolved studies of supported membranes can provide this missing information and make the connection with electrophysiological phenomena. Studies of model membranes at liquid-liquid interfaces offer the additional potential for understanding the structural and dynamic properties of model membranes associated with membrane elasticity and membrane-protein interactions.

## Significance of the APS

The development of synchrotron-based sources had a major impact on interfacial science. First, the routine (if challenging) application of x-ray-based techniques to interfaces was first enabled by the development of second-generation sources, a need arising from the intrinsically weak x-ray scattering cross-sections. This led to significant advances in our understanding of interfacial structures, with some of the first precise ( $<0.1\text{-\AA}$  precision) determinations of interfacial structures. Second, x-rays opened the possibility of *in situ* studies in complex environments such as the liquid-solid interface. The development of third-generation sources such as the APS has led to substantial quantitative improvements associated with its higher flux (measurements in hours instead of days), brilliance (high collimation, spatial coherence, and the ability to probe smaller samples) higher photon energy (greater penetration into complex environments), tunability (enabling routine application of element-specific approaches such as resonant anomalous x-ray reflectivity and x-ray standing waves), and stability (making it possible to obtain the high-quality data necessary for phase-recovery). These distinct advantages led to the evolution of a large and mature interfacial science community at the APS.

Of perhaps even greater significance to this community are the potential benefits of fully utilizing the current properties of the APS and the anticipated properties of a renewed APS. New and powerful advances in capabilities are available to this community by applying approaches that previously could be applied only to bulk materials. Many of these advances involve “imaging” interfaces, through traditional microscopy, the use of coherent diffraction, or phasing of data. Other advances include the application of ultra-fast techniques to this area in order to extend the temporal sensitivity to as low as  $\sim 1$  ps. Some proof-of-principle demonstration measurements have been performed, but substantial advances in instrumentation, as well as the development of new sources (for time-resolved measurements) will be needed to make the application of these capabilities routine. It is expected that these capabilities will transform this field, extend its reach to ever more complex and relevant interfaces, and allow many scientific and technical challenges to be met.

## Scientific Community

The interfacial-science community was one of the first to capitalize on the benefits of synchrotron radiation. Consequently, the community is both diverse and highly experienced. This community has been quite productive, in spite of the fact that these experiments are difficult, labor intensive, require extensive beam time, and often involve complex instrumentation. Until recently, the community was relatively fragmented in that the various technical advances were developed independently through efforts in individual laboratories. It is apparent that this community stands to benefit greatly from having a strong institutional connection with the APS, especially as the community moves forward to make use of advances in optics, sources, and software whose cost and required expertise extend beyond the reach of individual research groups. The establishment of XOR/UNI Sector 33 at the APS to emphasize interfacial science was an important first step that has substantial potential benefits for this community. The growth and development of this activity, as well as the development of a new x-ray interfacial science sector, is critical to enabling the various technical and scientific developments discussed in this document.

## Requirements and Capabilities

In the near term, substantial benefits can be obtained for interfacial science by relatively modest investments in instrumentation. The use of area detectors such as charge-coupled devices and the PILATUS has the ability to substantially improve the efficiency of measurements as well as the quality of the associated data. Improvements in the energy resolution and throughput of fluorescence detectors can similarly impact measurements. High-energy x-rays ( $E > 40$  keV), a strength of the APS, are generally recognized as being well-suited for *in situ* atomic-scale structural studies. Hard x-rays have two key properties: They readily penetrate through centimeters of material, enabling the study of deeply buried structures or surfaces in complex environments, and the scattering of high-energy x-rays is characterized by a very large Ewald sphere, so that the crystal truncation rods (CTRs) from each of the low-index surfaces of a nanoparticle can be characterized in a single image.

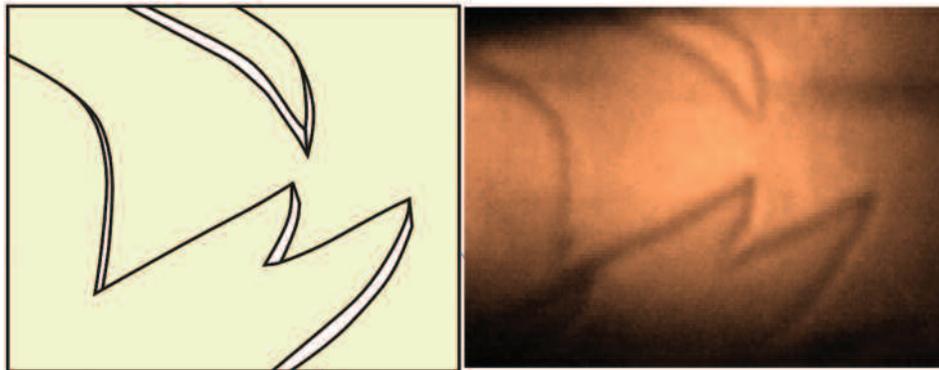


Fig. 5. The XRIM images elementary interfacial topography through intensity contrast. Left: Schematic interface topography. Right: An XRIM image where dark lines are 0.6-nm-high steps. (Fenter et al., Nat. Phys. 2, 700 [2006], © 2006 Nature Publishing Group, a division of Macmillan Publishers Limited, all rights reserved)

A fundamental understanding of interfacial structure and dynamics relies on our ability to observe the processes in real time and real space. Here, we describe a number of opportunities that, if implemented, will have an enormous impact by substantially expanding the spatial and temporal scales over which interfaces can be probed (from  $<1 \text{ \AA}$  to  $\gg 1 \text{ }\mu\text{m}$ , and from hours/days down to picoseconds). To be realized, such capabilities will require substantial investments in infrastructure and staffing.

### Interfacial x-ray microscopy

The ability to work in direct space is a broad need in this area. The conversion of reciprocal-space intensities to real-space structures has a significant limitation, namely probing those properties (average defect spacing, height-height correlation functions) that are statistically averaged over the sample; and this makes it difficult to investigate the behavior of isolated (aperiodic) structures and defects. Imaging elementary topography in real space demonstrates the ability to probe the behavior of individual structures. This capability has recently been demonstrated with x-ray reflection interface microscopy (XRIM; Fig. 5). X-ray reflection interface microscopy is similar to traditional full-field optical and x-ray microscopes, but uses the weak interface-reflected x-ray beam (with a reflectivity of  $<10^{-5}$ ) to create an image. Since the reflectivity signal is interface-specific, this leads to the ability to

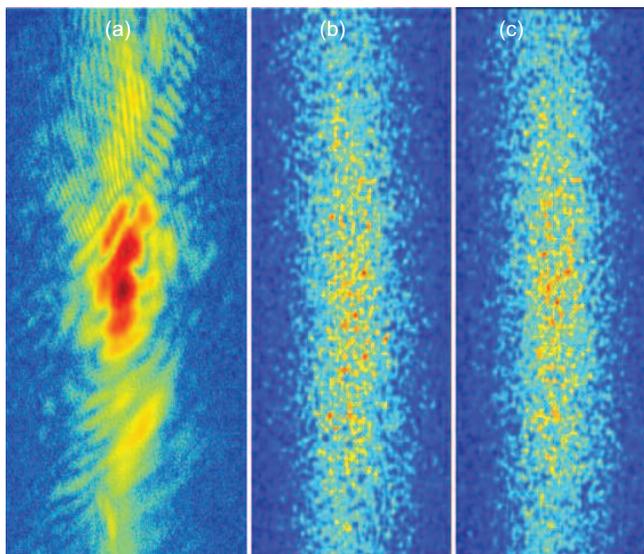
image interfacial topography. The differential reactivity of defects vs. ideal terrace areas can be assessed through direct observations. The primary challenge for this approach is that it is significantly photon-limited, especially given the weak reflectivity signal, the relatively low efficiency of the x-ray optics (~10%), and the need to measure statistically significant signals in  $\sim 10^5$  pixels. In the first generation, images can be obtained in a few minutes, but only over a relatively narrow reciprocal space range, for instance where the signals were strong. The spatial resolution is ultimately limited by the numerical aperture of the x-ray optics, and was observed to be  $\sim 170$  nm (compared to the expected 100 nm). Improvements in optics, instrumentation, and ultimately the x-ray source itself will lead to substantial improvements in spatial resolution ( $\sim 30$  nm) and temporal resolution (e.g., video rate imaging of interfacial processes).

Scanning x-ray probe microscopes are complementary to the full-field XRIM instrument. Such instruments have numerous contrast mechanisms available by probing various elastic (Bragg peaks) and inelastic (fluorescence) signals as a function of position on the sample. Of particular interest is the Argonne Center for Nanoscale Materials/APS nanoprobe, which is expected to attain a spatial resolution of  $\sim 10$  nm. This will result in an instrument with exceptionally high photon density that can be used to probe fast kinetics such as ferroelectric switching of individual nanoscale domains in a thin-film material.

### Surface-coherent x-ray scattering

The surface-coherent x-ray scattering (SCXS) technique is only now being explored due to the relatively low coherent flux of third-generation synchrotron light sources. Unlike phase-contrast microscopy, SCXS does not use an objective lens and is therefore limited only by the sample and beam characteristics, and the sampling of the diffraction images. The evolution of diffraction images can be analyzed to reveal temporal dynamics (e.g., relaxation times) and evolution using x-ray photon correlation spectroscopy (XPCS). Alternatively, direct inversion of the diffraction pattern using phase-retrieval algorithms allows lensless imaging, known as coherent diffractive imaging (CDI). The XPCS technique has been successfully applied to

Fig. 6. (a) Coherent x-ray diffraction pattern of the Au(001) hex-reconstruction peak (1.2 1.2 0.2) at 25° C. (b) and (c) time evolution of anti-Bragg speckles at 840° C; the two frames are separated by several minutes. (Pierce et al., unpublished results [2008])



probe the dynamics of bulk systems and polymer liquids. Coherent diffractive imaging has imaged the shape and strain field in micron-size lead crystals.

The brilliance of the APS and other third-generation light sources, along with advances in optics and detectors, are just now enabling *interfacial coherent* x-ray scattering measurements. The feasibility of coherent interfacial x-ray scattering applied to the study of high- $Z$  (e.g., gold or platinum) surfaces has been demonstrated recently at the optimized 8-ID beamline at the APS. Platinum and gold surfaces are interesting due to their importance as catalysts and the interplay of reactivity and structure that is known to exist on these surfaces, as seen in Fig. 2. Interfacial dynamics under catalytic conditions will lead to new insights into the factors that control catalytic activity, as well as becoming a test-bed for interfacial SCXS techniques.

Proof-of-principle interfacial SCXS images of a reconstructed Au(001) surface are shown in Fig. 6, including (a) the hexagonal peak, and in (b) and (c) the anti-Bragg reflection. While the hexagonal peak image was taken at room temperature (and is therefore static), the anti-Bragg reflections were measured at 840° C where both hex and  $(1 \times 1)$  surface phases coexist and evolve. Here, the speckle structure varies with

time providing sensitivity to the temporal evolution of domain distributions. Ultimately these interfacial XPCS and CDI measurements can be combined leading to a real-time *and* real-space surface x-ray imaging technique, providing quantitative measurements of micro- and nano-sized system evolution. Currently, the time scale over which this can be applied is in the range of  $>30$  s, with the ability to resolve objects at  $>500$  Å due to the Q-range of the diffraction images. Eventually, the development of nearly fully-coherent hard x-ray sources will allow this approach to be extended to substantially faster time scales ( $< 1$  s), to smaller spatial resolution, and to the interfaces of low- $Z$  materials.

### Imaging with phase recovery and imaging elemental substructures

While the phase problem of crystallography is a substantial impediment for any structural determination—including traditional CTR measurements as well as surface coherent x-ray scattering—once the phase is recovered, the structural determination becomes essentially trivial. The seminal work of David Sayre showed that scattering phase can be retrieved solely from measured intensities under certain circumstances. Recent advances in phase-retrieval algorithms have made this possible for isolated nanostructures. Recently, similar algorithms have demonstrated the ability to recover *interfacial* structures, as illustrated in Fig. 3. Robust phase recovery formalisms would substantially benefit this community by transforming x-ray scattering data into real-space images. It is anticipated that such algorithms could be developed to provide rapid phase recovery, so that interfacial structures can be observed directly and in real time as the data is acquired.

Complementary to the phase-recovery techniques are approaches that can probe substructures (elemental, magnetic, etc.). Ideally, these measurements are designed to be explicitly phase sensitive so that one can view the scattering measurement as sampling the amplitude and phase of the substructure of interest (i.e., its complex structure factor). To date, this perspective has been applied to a few types of experiments, such as Bragg-x-ray standing wave and resonant anomalous x-ray reflectivity. It is expected that this general formalism can be applied to essentially any scattering technique, providing the ability to “image” substructures.

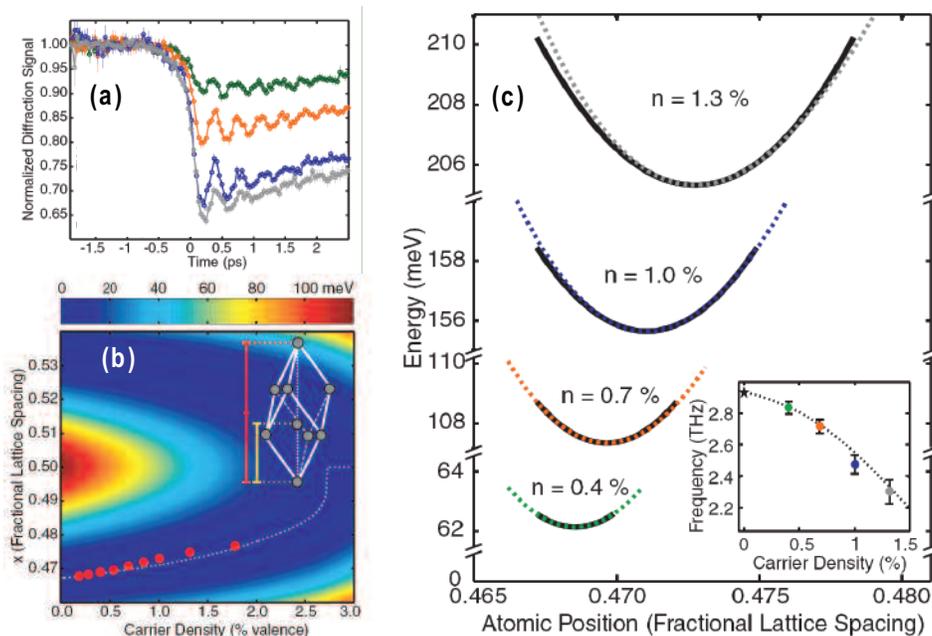


Fig. 7. Ultrafast measurement of lattice potentials. (a) Ultrafast x-ray diffraction efficiencies on (111) bismuth as a function of the time delay between pulses. (b) Experimental (red) and calculated (dotted line) interatomic quasi-equilibrium position as a function of the percentage of photoexcited electrons. (c) Reconstructed potential energy surfaces and phonon frequencies (inset) for different excitation levels. (Fritz et al., *Science* **315**, 633 [2007], © 2007 American Association for the Advancement of Science, all rights reserved)

## Time-resolved studies

Our fundamental understanding of interfacial and material structures has been advanced primarily by direct measurements of *time-averaged* structures using x-rays. But matter is not static. The characteristic time for atomic rearrangements is roughly the period of an optical phonon and is typically on the order of a picosecond. One can expect fundamentally new insights into the dynamics in chemical reactions, phase transitions, and in response to external stimuli if such measurements were to be performed at picosecond time scales. Only optical pulses are short enough to initiate such reactions precisely enough to follow the temporal response in real time. Thus, pump/probe measurements using ultra-fast laser pump beams and time-delayed probe beams have been the standard ultra-fast experimental technique for many years.

A substantial opportunity for interfacial sciences at the APS is the plan (spelled out elsewhere in this proceedings) to build a 2- to 3-ps x-ray source that operates at a high repetition rate (6.5 MHz) with  $\sim 5 \times 10^{12}$  ph/sec/1% bandpass. This source would have a time-averaged flux capable of allowing observation of fast (approximately picosecond) interfacial processes with  $< 1\text{-}\text{\AA}$  structural sensitivity and would substantially extend the temporal resolution available to interfacial processes at the APS. An example of the extraordinary science that can be accomplished by combining femtosecond laser excitation with ultrafast x-ray sources is illustrated in Fig. 7. Similar measurements could be performed to probe the perturbation of interfacial structures.

A major challenge to working at high repetition rates lies in dissipating the energy (usually in the form of heat) delivered by the pump laser. In solid samples, the time scale on which heat is dissipated is typically set by thermal diffusion. In principle, one can shorten the equilibration time by shrinking the volume illuminated by the pump beam. For example, the equilibration time for 10- $\mu\text{m}$  length scales in GaAs is on the order of 5  $\mu\text{s}$ , enabling the use of higher repetition rates. In practice, the decreasing depth of focus for the optical beam as the beam waist is decreased will set the practical limit for the minimum pump beam waist to be somewhere in the 1- $\mu\text{m}$  to 10- $\mu\text{m}$  range. In gas jets and liquid flow cells, the heating and radiation damage issues are handled by continually flowing in new sample.

## References

- [1] G.R. Fleming and M.A. Ratner, "Grand Challenges in Basic Energy Sciences," *Physics Today*, 28 (July 2008).
- [2] *Basic Research Needs for Solar Energy Utilization*, Report on the Basic Energy Sciences Workshop on Solar Energy Utilization, April 18-21, 2005, (Office of Basic Energy Sciences, U.S. Department of Energy). [http://www.sc.doe.gov/bes/reports/files/SEU\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf)
- [3] *Basic Research Needs: Catalysis for Energy*, Report from the U.S. Department of Energy Basic Energy Sciences Workshop, August 6-8, 2007 (Office of Basic Energy Sciences, U.S. Department of Energy). [http://www.sc.doe.gov/bes/reports/files/CAT\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/CAT_rpt.pdf).

- [4] *Basic Research Needs for Electrical Energy Storage*, Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, April 24, 2007 (Office of Basic Energy Sciences, Department of Energy, July 2007) [http://www.sc.doe.gov/bes/reports/files/EES\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/EES_rpt.pdf).
- [5] *Basic Research Needs for Solid-State Lighting*, Report of the Basic Energy Sciences Workshop on Solid-State Lighting, May 22-24, 2006. [http://www.sc.doe.gov/bes/reports/files/SSL\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/SSL_rpt.pdf).
- [6] *Basic Research Needs for Materials under Extreme Environments*, Report of the Basic Energy Sciences Workshop on Materials under Extreme Environments, June 11-13, 2007 (Office of Basic Energy Sciences, Department of Energy, February 2008). [http://www.sc.doe.gov/bes/reports/files/MUEE\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/MUEE_rpt.pdf).
- [7] *Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems*, from the Workshop sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Bethesda, Maryland, February 21-23 (Office of Basic Energy Sciences, U.S. Department of Energy, June 2007). [http://www.sc.doe.gov/bes/reports/files/GEO\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/GEO_rpt.pdf).
- [8] *Basic Research Needs for Advanced Nuclear Energy Systems*, Report of the Basic Energy Sciences Workshop on Basic Research Needs for Advanced Nuclear Energy Systems, July 31-August 3, 2006 (Office of Basic Energy Sciences, U.S. Department of Energy, October 2006). [http://www.sc.doe.gov/bes/reports/files/ANES\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/ANES_rpt.pdf).

## Renewal of the Advanced Photon Source: Life Sciences

<b>Jon F. Harrison</b>	<i>Arizona State University</i>
<b>Lee Makowski (Chair)</b>	<i>Argonne National Laboratory</i>
<b>Lisa M. Miller</b>	<i>Brookhaven National Laboratory</i>
<b>Joseph P.R. Orgel</b>	<i>Illinois Institute of Technology</i>
<b>Stuart R. Stock</b>	<i>Northwestern University</i>
<b>Stefan Vogt</b>	<i>Argonne National Laboratory</i>
<b>Gayle E. Woloschak</b>	<i>Northwestern University</i>

### Executive Summary

Utilization of synchrotron radiation by the life-science community has been growing rapidly in recent years, driven by advances in x-ray science and a need for new approaches to solving the multitude of questions arising from the explosion of biological information coming out of genomic, proteomic, and metabolomic projects. In many cases, life scientists have shared synchrotron facilities with materials scientists and chemists, utilizing multipurpose beamlines that represent, at best, a compromise between what physical scientists require for their experiments and the needs of the life-science community. This has limited the efficiency of experiments and the ultimate impact of the work. The community of biologists with compelling needs for synchrotron facilities has now grown to the point where the development of dedicated single-purpose beamlines at the Advanced Photon Source (APS) will be required for further progress. As we outline here, the impact of experiments enabled by this development will be substantial and widespread.

Every organism is the outward physical manifestation (phenotype) of internally-coded, inheritable information (genotype). An overarching challenge in biology and biomedicine is understanding the links between genotype and phenotype and predicting phenotypic effects of altered genotype. A major goal of modern biology is to reliably link the avalanche of data on genetic diversity and expression from molecular

biology to the major conceptual problems in biology. These range from basic research questions on biological diversity to applied concerns such as why one individual but not another becomes ill or injured in response to the same stress. Resolving these genotype-to-phenotype questions requires techniques that bridge the scales of molecular biology and those of organisms. New capabilities spanning length scales from nanometer to centimeter are essential and will lead to breakthrough results in basic and applied biology, and in biomedical science. Synchrotron-based imaging techniques provide unmatched and relatively unexplored methods for understanding the connection of molecular-based information in the phenotype to the hierarchy of structural scales relevant to organismal function.

The use of synchrotron radiation in life-science research is expanding dramatically as researchers realize the capabilities of novel scattering and imaging modalities. These techniques range from solution scattering and fiber diffraction to phase-contrast and scanning imaging. In many cases, the APS is the only synchrotron facility in the Western Hemisphere with the capabilities to support this research. Although much progress has been made in the life sciences using synchrotron radiation, this has often been done at multipurpose beamlines that require special adaptations to accommodate biological materials, slowing some experiments and precluding others. Progress will be greatest at beamlines dedicated to a single experimental technique and optimized for use on biological specimens. For example, the high sensitivity to radiation damage exhibited by many specimens requires cryo-preservation for measurement of relevant data. Studies of many variants under different conditions require the capability for high throughput of specimens at the beamline.

Many of the newly expanding life-science efforts involve biomedical applications that take advantage of all available imaging and scattering modes. These include studies in the development of contrast agents for biomedical imaging; the use of nanoparticles for image-guided therapeutics and diagnostics; fundamental studies of neurological diseases such as Alzheimer's disease and amyotrophic lateral sclerosis; and blood flow in capillaries during exercise, in the heart during infarctions, and in the brain during strokes. Other investigations being planned include the study of air flow in

lungs and among alveoli as regulated by chemicals or drugs, and studies to determine the changes in air flow induced by asthma. Investigators are exploring the use of x-ray imaging to approach questions about the effect of microbial infection or food allergies on the morphology and flow of the gastrointestinal tract. Finally, fundamental questions about osteoporosis and the mechanisms of bone and tooth fracture can be answered using the advanced imaging facilities currently being discussed. In many cases, the questions being asked require the penetrability and resolution available only at the APS.

The special requirements for preservation of molecular structure and handling of biological samples make the availability of dedicated beamlines a high priority for all of the relevant techniques. Beamlines for solution and fiber studies, scanning microscopy, coherent diffraction, phase contrast, and multi-length-scale tomographic imaging are very high priorities for the life-science community and will have significant impact on multiple fields in the biological sciences. The APS is one of the best places on Earth to stage these experiments and is well positioned to make a substantial impact on the biological sciences through their implementation and use.

## Introduction

The macromolecular crystallography x-ray technique has had a huge impact on the biological sciences, leading to many significant insights into the function of a myriad of biological systems. The impact of other x-ray techniques on biology is developing more slowly due to factors that include the limited availability of appropriate experimental facilities. The U.S. has been slow to develop facilities dedicated to scattering or imaging techniques for the study of biological specimens. Meanwhile, synchrotrons in Europe and Asia have a considerable advantage in these areas, placing U.S. basic scientists and engineers at a decided disadvantage in studying many fundamental biological questions.

A variety of factors contribute to making this an important time for the development of new x-ray facilities for the study of biological materials. First, development of novel x-ray optics is paving the way for development of the bionanoprobe. Second, convergence of computational and experimental techniques is greatly enhancing the amount of information that can be extracted from phase-contrast imaging and solution-scattering data. Third, development of bionanotechnology as an interface between inorganic and organic sciences is providing new tools for probing intracellular structures. Such technological advances have increased the sensitivities and temporal resolutions of x-ray imaging of biological structures by orders of magnitude.

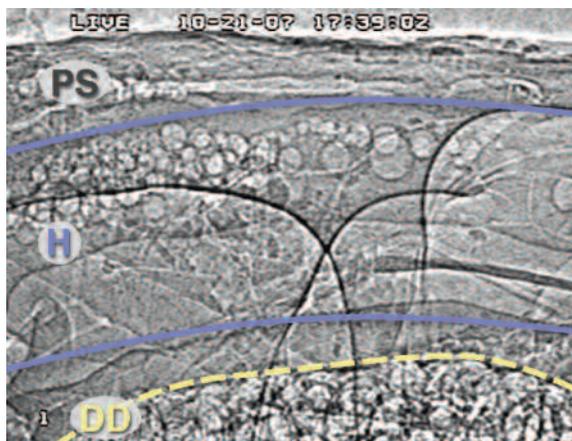


Fig. 1. From an x-ray video of flow visualization in the heart of a grasshopper (*Schistocerca americana*) obtained at the X-ray Operations and Research (XOR) beamline 32-ID at the APS using synchrotron x-ray phase-contrast imaging. This still image shows a region in the dorsal 3rd abdominal segment. Round structures are air bubbles used to visualize patterns of heartbeat and hemolymph flow. (Courtesy W.-K. Lee [Argonne National Laboratory] and J.J. Socha [Virginia Polytechnic and State University])

Enhanced capabilities for synchrotron-based imaging, scattering, and nanoprobe quantification of biological structures and elements will impact virtually every aspect of biology from biomedicine and pharmacology to evolutionary biology. A number of imaging tools can probe objects at nanometer spatial resolution, but few can image the internal structures of three-dimensional objects from nanometer to centimeter scales. Synchrotron x-ray imaging has become such a tool. It is uniquely suited for investigations of a broad range of objects in the biological and materials sciences with complex hierarchical internal or buried structures that cannot be properly preserved or studied by sectioning, and for carrying out dynamic and real-time studies of biological and materials processes intrinsic to physiological and biomechanical function.

## Key Science Drivers

The impact of proposed life-sciences facilities at the APS will span virtually all of biology, from biochemistry and molecular biology to ecology and evolution.

### Evolutionary biology

Understanding the evolution of life's diversity, and how our planet will respond to global climate change, requires detailed interrogation of diverse plant and animal systems. Among the questions that the new x-ray phase-contrast imaging methods will be essential to addressing are: How did the initial diversification of metazoans proceed, as represented by fossilized embryos from the late Neoproterozoic Era and earliest Phanerozoic Era? How did early angiosperms develop from even earlier forms? How did physiological systems develop their present characters (e.g., insect vs. mammalian respiration)? How did the two predominating biomineralization systems (calcium carbonate, calcium phosphate) develop—in particular, the apatite-collagen bio-nanocomposite system in bone? Not only do these (and other similar questions) have important intrinsic value, they also suggest directions for biomimetic materials design. For example, the many-spine architectures of the families of diadematoid sea urchins represent an evolutionary sampling of the “design space” for functional calcite structures such as cell-controlled, low-temperature ceramic processing pathways.

### Quantitative analysis of energy-supply systems (metabolism)

Many unanswered, fundamental questions exist in these areas that can be addressed with small animals of major agricultural, medical, and ecological importance. For example, how do birds and insects achieve one-way flow through their valveless respiratory systems? High temporal and spatial resolution of the volumes of the various regions of these systems is required to understand how these high-capacity respiratory systems function. A second fundamental question involves the scaling of metabolism. The energetics of cardio-respiratory flow are hypothesized to drive the well-known but poorly understood scaling of metabolic rate in organisms, whereby smaller organisms have higher mass-specific metabolic rates, tissue mito-

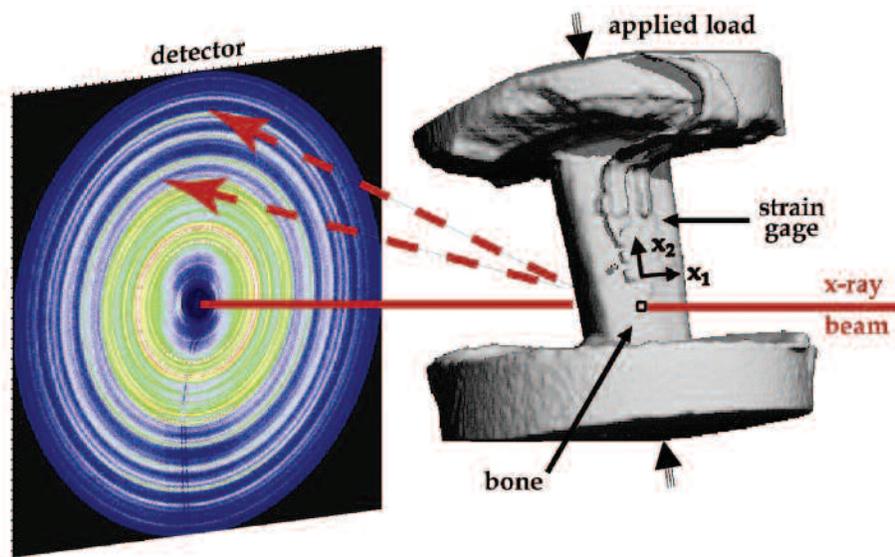


Fig. 2. Illustration of diffraction pattern collection for a bone sample. The x-ray beam (from right to left) shines through the specimen (right), and scattered x-rays produce rings on the area detector (left), with the higher intensities represented as brighter colors. (From "A Nanoscopic View of How Bone Handles Stress," *APS Science 2007*, ANL-07/25 [Argonne National Laboratory, May 2008] p. 60. Courtesy J.D. Almer and S.R. Stock. Studies carried out at XOR beamline 1-ID-C at the APS.)

chondrial contents, and heart rates. This fundamental scaling pattern drives much variation in life history ranging from heart rate to fecundity and life span, yet the mechanisms driving this pattern remain highly controversial. X-ray phase-contrast imaging of flow-through supply networks of animals (Fig. 1) promises the first technique for rigorously testing current supply-limitation theories of metabolic scaling.

### Environmental stress tolerance

Organisms vary dramatically in their tolerance to extreme environments, with some being able to survive freezing and others tolerating body temperatures exceeding 50° C. Extreme environmental stresses are always associated with major structural changes—such as ice crystal formation during freezing, vacuole formation during drying, and protein and lipid conformational changes during heat damage—that are extremely challenging to visualize with conventional methods. Synchrotron-based,

wide-field phase-contrast imaging is the only technique with the spatial and temporal resolution necessary to address these questions. How organismal structures (resistant vs. normal strains) respond to drying or temperature remains poorly understood, and understanding the role of specific phenotypic characters is key to developing a mechanistic understanding of environmental tolerance and the production of new plant, micro-organismal, and animal strains resistant to environmental stress. The structural hierarchies in soil are also extremely important for plant stress tolerance and remain poorly understood. A key policy goal for preventing food shortages associated with human population growth and global climate change is the development of new strains of drought, freeze, and heat-resistant plants; synchrotron-based imaging can provide critical tools in these efforts.

### **Tissue mechanics**

Nanocomposite-based biological support structures (bone, tendons, teeth, chitin, xylem, phloem, spider silk) exhibit combined strength and elasticity far exceeding engineered materials. Many important diseases including osteoporosis and joint injury result from the pathologies of bones and tendons. All of these support structures are complex nanocomposites possessing a hierarchy of structures of at least ten spatial scales. For example, bone is a nanocomposite of collagen and the mineral apatite. How the two very different phases function together to produce a tough, fracture-resistant material remains incompletely understood. Why certain aged patients suffer fractures due to osteoporosis remains incompletely predicted by current measures (bone mineral density, bone microarchitecture). This is a critical issue because osteoporosis-related hip replacements are estimated to cost the U.S. over \$16 B yearly. How loading-induced damage accumulates in bone remains to be quantitatively understood. The three-dimensional (3-D) network of the canaliculi-osteocyte system, thought to be the mechanical sensors controlling bone remodeling, remains largely unquantified. Numerical modeling of real networks of these submicron-diameter channels may help to explain how they function in this role. All of these areas require 3-D x-ray imaging beyond that presently available at the APS. In teeth, the mechanically tough interior dentin (another nanocomposite) and the hard and chemically resistant exterior enamel (very-high-density apatite) are

joined by the dentinoenamel junction. New APS imaging capabilities will greatly improve our understanding of how this natural graded interface functions and how it might be replicated in clad or coated engineering materials, including those for biomedical implants. Imaging coupled with *in situ* loading and x-ray scattering quantification of internal strain within the tissues is an example of instances of synergistic increases in understanding (Fig. 2).

### ***In vivo*, longitudinal biomedical imaging**

In modern medicine, it is important to quantify the development of key microstructural features in the natural history of a given disease and to understand (and eventually control) the molecular mechanisms and quantitative physiological responses of drugs for effectively treating the disease. Small-animal models are now preeminent in these studies. The use of each individual animal as its own control through repeated imaging over time has been an important advance, helping to minimize the effect of inter-individual variance. Although the first *in vivo* microcomputed tomography (micro-CT) imaging of small-animal models was done in the 1990s with synchrotron radiation, tube-based dedicated *in vivo* systems now dominate the field. However, *in vivo* synchrotron-based phase-contrast imaging remains very important for many diseases requiring imaging with higher contrast and higher spatial and temporal resolution. In particular, local tomographic reconstruction has opened new doors for studying details that are inaccessible to tube-based systems. For example, effects of asthma drugs on tracheal pathways and surrounding muscles in mouse models may be observed quantitatively, leading to better numerical models of these processes and to more effective treatment for asthma and other airway constrictive diseases. Study of heart valve and blood vessel calcification also require high-sensitivity imaging. Being able to apply high-resolution, high-speed phase-contrast imaging to the major biomedical models, including mice and rats, requires larger fields of view and a longer beamline than is currently available at the APS.

### **Metals in biology**

The biology of the past decades has significantly changed scope, and large compendia of data enabled us to study biological “meta units” such as the genome, proteome,

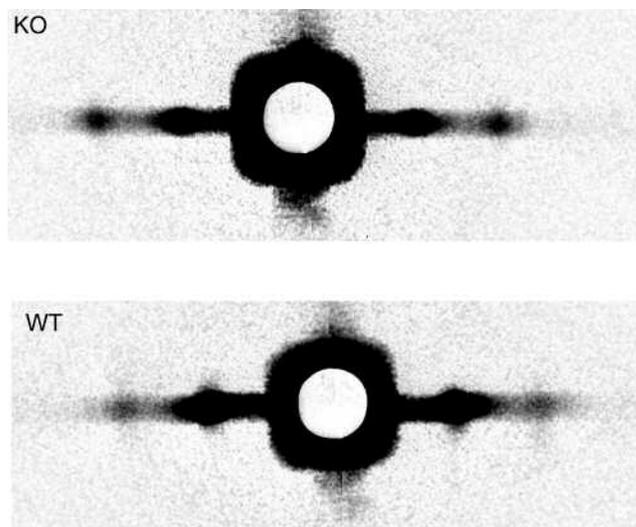


Fig. 3. X-ray diffraction patterns of normal mouse heart muscle (WT, bottom) and heart muscle from mice lacking cardiac myosin-binding protein-C (KO, top). Compared with WT muscle, the KO muscle matter is shifted toward its thin actin filaments (represented by the size of the outermost black dots in both images), as opposed to its thick myosin filaments (inner dots), implying that cardiac myosin-binding protein-C helps keep myosin filaments more tightly wound than they would be otherwise. (From: "Deconstructing Heart Muscle," *APS Science* 2007, ANL-07/25 [Argonne National Laboratory, May 2008] p. 66. Courtesy B. A. Colson, T. Bekyarova, D.P. Fitzsimons, T.C. Irving, and R.L. Moss. Imaged at Bio-CAT beamline 18-ID at the APS.)

metabolome, and transcriptome. At this time, the term “metalome” is still used only rarely, and yet it is estimated that one-third of all known proteins contain metal cofactors and function as metalloenzymes. With current developments in genomics and proteomics, our knowledge of the enormous number of pathways in which metals and trace elements are necessary for life is ever increasing. However, our knowledge about the redistribution of metals and trace elements accompanying the development of different degenerative diseases (such as Alzheimer’s disease, Lou Gehrig’s disease, and others) is limited even though metals and metal chelators represent an increasingly important class of drugs used to treat a diverse variety of diseases. At present, synchrotron radiation-based x-ray fluorescence microscopy (XFM) is the only available technique for quantitative elemental imaging of whole cells with submicrometer resolution. In the field of pathology, XFM and the bionanoprobe will enable studies of changes in metal and trace-element-abundance disease development in response to drugs. In the environment, many nonessential metals are toxic to cells even at extremely low concentrations (e.g., Cd, As, Pu, Cr, Hg, and Pb). In order to determine the mechanism of toxicity, it is important to identify the specific cell types and subcellular organelles that are targeted by these contaminants. To do so, an *in situ* probe with high spatial resolution and detection sensitivity is required.

## Bionanotechnology

Two areas that will particularly benefit from development of a bionanoprobe are bionanotechnology and pathology. In the field of bionanotechnology, the bionanoprobe will allow us to ascertain targeting specificity of nanovectors (hybrid organic-inorganic particles usually designed for diagnostics, imaging, or therapeutics), their intracellular stability and oxidation changes, and their capacity to create multi-particle assemblies *in vivo*. The penetrance of XFM will allow every aspect of these analyses to be done inside cells or tissues. Observing nanovectors “in action” at the site of their activity in cells—made possible by using flash-frozen samples treated with hybrid nanoparticles—will yield critical data that can be used to streamline and guide nanovector design. Many of these nanomaterials are being used as contrast agents for magnetic resonance, computed tomography (CT), and positron emission tomography imaging. Testing of these materials and their distribution in cellular systems prior to use in people is essential, and the XFM technique provides one of the few approaches for direct detection of these agents in cells. Coupling these studies with large-scale animal imaging, also proposed here, will provide synergistic links between subcellular and (organ) systematic scales.

## Fibrous biomaterials

A huge proportion of biomass is fibrous, from plant cell walls to connective tissues to muscle, and detailed analysis of much of this material is beyond the purview of crystallography, nuclear magnetic resonance, or electron microscopy alone. Fiber diffraction and ancillary techniques are making great strides toward a mechanistic understanding of the molecular mechanisms of cardiac and skeletal muscle contraction and regulation, and the construction of connective tissues and their metabolic processes in health and disease (Fig. 3). Fiber techniques have the potential for providing a greatly increased understanding of the molecular pathology of diseased aggregates in brain diseases of old age and from infectious particles. These techniques are finding applications in determining the structural changes that occur in plant structure designed for new food or fuel sources, and in the design of biomaterials for future sources of protective clothing and armor as well as food, fuel, and medical treatments. Because this technique utilizes the native crystallinity of samples, it is

able to offer molecular-resolution structural information free of artifacts and of direct relevance to the natural state of the system under study. Significant and focused efforts to develop better dedicated facilities that include the capability for relatively large-scale cryopreservation will contribute substantially to future progress.

### **Molecular structure and dynamics**

Solution scattering is poised to produce remarkable insight into the structure and dynamics of proteins and protein complexes. Although providing lower resolution information than crystallography, the ease with which data can be collected on very large complexes in multiple physiological and functional states makes it an important tool that is being used by an increasingly large community. The coordination of computational methods with solution scattering is enhancing the amount of information that can be extracted from solution-scattering patterns, and these data are increasingly being used as constraints or tests of the results of molecular dynamics or normal-mode analyses of protein structure and dynamics. High-impact studies will include those on membrane proteins, measurement of the amplitudes of normal modes of proteins in solution, the range of motion of enzymes undergoing catalysis, the measurement of domain motions during substrate binding, and the progression of structure formation during protein folding. Efficient utilization of these methods requires the development of dedicated beamlines that can readily accommodate high-throughput exchange of large numbers of specimens.

### **Significance of the APS**

The APS is the only source of high-energy x-rays in the Western Hemisphere where facilities for x-ray scattering from—and imaging of—biological specimens can be staged to adequately address these many scientific challenges. The APS provides sufficient flux of coherent x-rays photons to achieve the high sensitivity that the high-energy x-ray bionanoprobe and high-speed phase-contrast imaging require. The characteristics of undulator beamlines at the APS are close to ideal for solution scattering and fiber diffraction applications. The need for high-contrast, spatial, and temporal resolution for phase imaging and micro-CT make the APS the best place in the

hemisphere for most high-energy x-ray imaging techniques. In many cases, with development of appropriate instrumentation and facilities, the APS will continue to improve and add to its repertoire of important biological experiments that simply cannot be performed elsewhere.

## Scientific Community

The scientific community impacted will involve two cohorts: those biologists that actually use the facilities developed at the APS and those that benefit from the results of these studies. The first community is relatively small in this country, being limited by the low availability of appropriate x-ray facilities here. The second community is vast, and includes biological researchers involved in studies of systems with scales that range from molecules to ecosystems. The second community includes many researchers with little experience in the use of synchrotron radiation and substantial need to work either in collaboration with synchrotron scientists or with substantial guidance from these workers.

There is a large and growing community of users that will benefit from the development of the new beamlines and instrumentation discussed here. Most of the current beamlines used in whole or in part for biological research are over-subscribed by three-fold or more, making it nearly impossible to recruit new users into the program. There is clearly a need within those communities for the expansion of existing facilities and beamlines to accommodate the user base. It should also be noted that new users in biological areas usually require extensive support during the initial phases of their research, so extensive support from the APS will be needed to grow the community in a broader sense. Moreover, many of these new users will utilize synchrotron experiments as only a small fraction of their research programs, thus requiring continued collaboration with APS staff. In order to be successful, the APS will need to grow the life-sciences expertise on its staff by recruiting scientists in these areas. The development of capabilities that can benefit all users, including data analysis tools, sample preparation methods, animal holding facilities, and others, will be useful for all beamlines.

## Requirements and Capabilities

The APS is capable of supporting a vibrant life-science community engaged in a range of synchrotron-based studies with unique potential for study of biological systems across multiple length scales. The science drivers noted above require development of several beamlines in order to achieve the impact described here, including dedicated beamlines for the bionanoprobe, for coherent diffraction imaging, for phase imaging, and for small-angle scattering (SAXS)/wide-angle scattering (WAXS).

### Bionanoprobe

A hard x-ray bionanoprobe at the APS that will enable A) imaging of trace elements in samples as thick as 10  $\mu\text{m}$  with a spatial resolution of better than 20 nm, and B) detecting as few as five metal atoms in thin sections. The bionanoprobe will be applied in bi-nanotechnology studies and in biomedical research (e.g., studies in development and differentiation, neurobiology, molecular imaging, etc.). This instrument will be capable of microscopy, micro-spectroscopy and spectromicroscopy techniques ( $\mu$ -x-ray absorption near edge structure) and nano-CT, with an emphasis on x-ray fluorescence analysis of trace elemental content in biological samples. With the development of a complete toolbox of software utensils for data analysis and interpretation, the bionanoprobe will be well positioned to create a reference elemental database of living organisms for the entire scientific community, and will significantly increase our understanding of life and disease at an unprecedented level.

### Phase imaging capabilities

Advanced imaging capabilities, including wide-field x-ray phase imaging with high-definition phase sensitivity, can utilize any of a number of beamline configurations: addition of a long (200-m) beamline or shorter lines using advanced optics. This will enable fast, high-resolution imaging on the major biomedical research models (rodents). Such a capability will greatly expand the community of biological users of the APS, as biomedical researchers studying brain, heart, and bone function can use the APS to address important biomedical questions. X-ray phase (and absorption) imaging is now a standard tool at most synchrotron facilities and its user community is

among the most diverse, including as it does zoologists, entomologists, evolutionary biologists, and biomedical researchers. A dedicated bending magnet beamline can be configured optimally for phase and absorption micro-CT with capabilities for sub-micrometer voxel reconstructions. An insertion device beamline will be required for real-time phase radiography and micro-CT, with additional capabilities for nano-CT. Zoom-in capabilities are essential to allow moving from wide field-of-view to magnified observation.

### **Coherent diffraction imaging**

The potential of coherent diffraction methods for the study of biomolecular systems has been recognized only recently. Although its greatest potential may be realized at the Linac Coherent Light Source at the SLAC Accelerator Laboratory and hard x-ray free electron laser projects, the APS represents a source with characteristics adequate for a substantial range of important experiments. Existing capabilities, enhanced by advanced detector systems and sample handling hardware are well positioned to make a substantial impact.

### **SAXS/WAXS/fiber diffraction**

The rapidly growing community using SAXS/WAXS or fiber diffraction can easily support one or two dedicated beamlines, even if they were outfitted with robotic specimen handling equipment for rapid data collection. Hardware should be capable of a range of specimen-to-detector distances for measurement of scattering at spacings from 1000-Å out to 2-Å spacing at the very least. A very-high-speed two-dimensional detector with a minimum of  $2k \times 2k$  elements should be available and configured for sub-microsecond time-resolved studies.

### **Cryopreservation**

Samples preserved at cryogenic temperatures are substantially more resistant to radiation damage than those at room or physiological temperatures. Cryofreezing has had a substantial impact on macromolecular crystallography and is now almost universally used for crystallography at the APS. Non-crystalline samples are often much larger, requiring more elaborate techniques for freezing and more robust systems for

maintaining cryogenic temperatures during experiments. Routine methods for freezing these larger specimens (e.g., high-pressure freezing) will require access to specialized equipment.

## Detectors

While many solution or fibrous specimens give rise to diffraction pattern well served by conventional large-area charge-coupled device (CCD) detectors developed for macromolecular crystallography, other classes of experiments require specialized detectors optimized for this application. Diffraction patterns characterized by closely spaced, fine diffraction peaks superimposed on a high background require a detector with high dynamic range and very good spatial resolution. Detectors built using current large-format CCD technology with small demagnification fiber optic tapers and custom phosphors (providing relatively small point-spread functions and large active areas) are appropriate but expensive, and readout is slow. Existing detectors, however, are not yet up to the challenge of time-resolved experiments in which sub-millisecond readouts are required. Detectors using hybrid technologies with CCDs and massively parallel complementary metal–oxide–semiconductor readouts can potentially fill this void.

## The Advanced Protein Crystallization Facility

The planned Advanced Protein Crystallization Facility (APCF) building will place over 30,000 sq ft of biological laboratories and offices immediately adjacent to the APS. This facility has the potential to act as a central focus of biological research at the APS. Properly implemented and managed, this building can grow to be the centerpiece of greatly expanded life-science research at the APS, providing both staff and visitors with the shared laboratory space and facilities required for their work. The concept of a “biology village” is finding broad popularity at synchrotron facilities around the world. The APCF is poised to embody that concept for life-science researchers at the APS.

## Renewal of the Advanced Photon Source: Macromolecular Crystallography

<b>Keith E. Brister</b>	<i>Northwestern University</i>
<b>David Eisenberg</b>	<i>University of California, Los Angeles</i>
<b>Anthony A. Kossiakoff (Chair)</b>	<i>The University of Chicago</i>
<b>Keith Moffat</b>	<i>The University of Chicago</i>
<b>Janet L. Smith</b>	<i>University of Michigan</i>
<b>Ward W. Smith</b>	<i>National Institutes of Health (National Institute of General Medical Sciences)</i>

### Executive Summary

Structural biology has made a fundamental impact on our understanding of biological organization, function, and mechanism at the molecular level. Although techniques such as nuclear magnetic resonance (NMR) spectroscopy and microscopy have contributed significantly in transforming biology from a descriptive science into a molecular-based one, it is synchrotron radiation-based x-ray crystallography that has made by far the largest contributions. Its impact on biology can be traced directly to a set of technical advances made over the last decade. Notable among these are multi-wavelength anomalous diffraction phasing techniques, cryocrystallography, enhanced computing capabilities, and a broad range of new structure refinement techniques. Additionally, advances in molecular biology and biochemical techniques have been instrumental in the structure determination process by providing an ample supply of highly pure protein samples.

Nevertheless, the impact on structural biology of all these advances in aggregate pales in comparison to the impact of synchrotron radiation. Put bluntly, structural biology would still be a cottage industry without synchrotron x-ray sources. Approximately 50% of those using U.S. synchrotron facilities are life science researchers and the majority of those are macromolecular crystallographers. More than 80% of all

macromolecular crystal structures deposited to the Protein Data Bank (PDB) during 2007 were determined from diffraction data collected at a synchrotron source, a total of more than 5500 structures during that year alone (Fig. 1); researchers using the Advanced Photon Source (APS) have contributed more structures than users of any other synchrotron facility (Fig. 2). This is in part due to the low emittance, high brilliance, and high energy of the APS electron beam.

In some sense, the experimental infrastructure needed to perform high-level macromolecular x-ray crystallography at synchrotron sources (and at the APS in particular) is mature. Given the success record of this mature field, the question that might arise is, where do we go from here? Our subgroup identified two areas of research and development that would have a transformative effect on studies of complex structures and in elucidating relationships between structure dynamics and function. The first area is micro x-ray crystallography, where the objective is to develop methodologies that enable the study of microcrystalline samples. Because

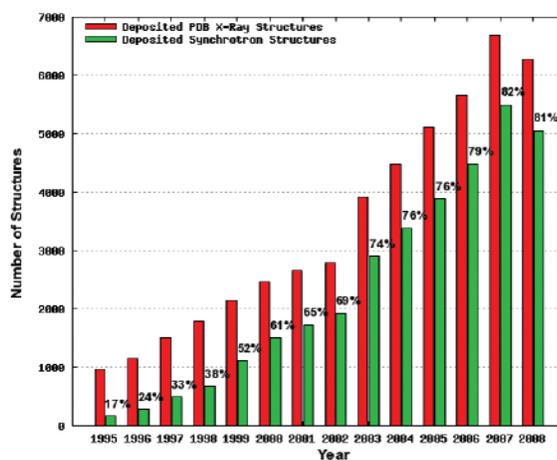


Fig. 1. Synchrotron structures deposited in the PDB vs. all PDB deposited structures. Note: The number of structures deposited in 2008 is incomplete because there is a lag time of up to one year between a structure being deposited and released to the public. (Source: <http://biosync.rcsb.org/BiosyncStat.html>; as of 2.24.09)

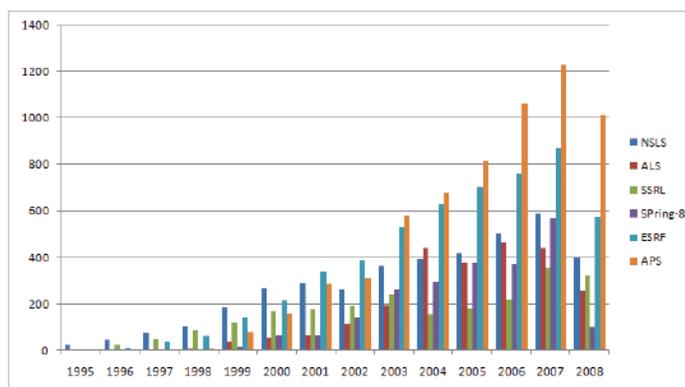


Fig. 2. Structures deposited in the PDB by APS researchers vs. other major light sources. (Source: <http://biosync.rcsb.org/BiosyncStat.html>; as of 2.24.09)

large, well-ordered crystals of proteins and macromolecular complexes remain hard to obtain, this would enormously increase both the number and types of systems that can be studied. Thus, we concur with the conclusion reached by a subcommittee of the Biological and Environmental Research Advisory Committee of the Department of Energy that addressed questions relating to synchrotron structural biology resources ([http://www.sc.doe.gov/ober/berac/SMB\\_Report.pdf](http://www.sc.doe.gov/ober/berac/SMB_Report.pdf)): “One area of special note for macromolecular crystallography is the need for beamlines/instrumentation optimized for microcrystal and microbeam studies.”

A second area of significant opportunity is high-resolution, time-resolved crystallography, which involves proteins that can perform chemical reactions in crystals. This is a very specialized field and requires sophisticated instrumentation and software that is tailored for time-resolved experiments. Nevertheless, it is uniquely powerful in its capability to produce high-resolution time slices of structural transitions along reaction pathways. These data provide a vital connection between structure/dynamics and their effects on function. This represents a major unmet need that has greatly limited our understanding of structure-function linkages in biological processes in general. Additionally, high-resolution time-resolved crystallography can provide an experimental framework to guide computational efforts to model conformational changes occurring during biological processes. We note that the ability to use microcrystals for these time-resolved experiments is also important. Because these experiments are initiated by introducing stimuli such as light, temperature, pH, etc. to commence the reaction cascade, it is important that as many molecules as possible undergo reaction in the crystal. The efficiency of reaction initiation is highly dependent on crystal shape and volume; typically, the smaller the crystal, the more rapidly and uniformly the reaction can be initiated. Thus, the two areas of microcrystals and time-resolved studies are in part linked.

To realize these objectives it will be essential to develop technologies on two fronts. First, microbeams on the order of a few micrometers will be needed. However, this is technically challenging because of the extreme demands on the stability of the source, x-ray optics, and endstation equipment. Beam stability is not an issue con-

fined to micro x-ray crystallography. Improving beam stability has important ramifications for a broad range of experiments; proposals that would improve beam stability have been put forth in the APS renewal plan. Second, a new generation of charge-coupled device (CCD) detectors and pixel-array detectors (PADs) with much faster readout times must be developed. Overlaid on these two major objectives is a set of complementary requirements. In order for micro x-ray crystallography to be practical, significant improvements in automation for crystal mounting and positioning must be realized. For time-resolved crystallography, ultra-fast x-ray pulses would have an impact by enhancing the time resolution that can be achieved.

## Micro X-ray Crystallography: Opportunities and Issues

A major misconception is that the principal bottleneck to solving high-profile structural biology problems is that crystals cannot be obtained. While this is certainly an on-going issue, the fact is that for many problems, microcrystals can be obtained, but they are not of a size adequate to acquire excellent data using current technology. The problem of small crystals is especially pronounced for cutting-edge problems in biology: large proteins, complexes of multiple proteins, complexes of proteins with nucleic acids and lipids, and partially ordered proteins. There is no hard data on the percentage of projects that are abandoned due to crystal-size limitations, but based on anecdotal data, it is not insignificant. Thus, it is widely recognized that developing new methodologies to deal with microcrystals would be transformative for structural biology. The facility that provides researchers with the effective capability to work in the microcrystal size domain will be the next Mecca for structural biologists and their research. Facilities for micro x-ray crystallography should be useful in all areas of chemical and geochemical crystallography, in which only small specimens are available.

From the standpoint of micro x-ray crystallography, “microcrystal” samples fall into two general categories: very small but highly ordered; and large and nonuniform, but with small areas of low mosaicity. These situations require different strategies that overcome particular sets of technical challenges to yield high-quality data. But if the

technical framework can be put into place to routinely facilitate collection of microcrystal data from both cases, the impact would be enormous. Below are described the issues and opportunities that each of these categories of microcrystals presents.

### Highly ordered microcrystals

Clearly, small crystals with typical dimensions in the 1- $\mu\text{m}$  to 5- $\mu\text{m}$  range with low mosaic spread represent the major class of microcrystal. If practical methods can be developed for manipulation, mounting, freezing, and taking data from these microcrystals, there are several potential attributes that can be utilized. Small crystals have the advantage of sometimes being better ordered than larger crystals. This means that structures can, in some cases, be determined to higher resolution using microcrystalline samples. Additionally, microcrystals may suffer less from radiation damage because the mean free path of outgoing photoelectrons exceeds the crystal dimensions [1,2]; the photoelectrons escape from the crystal before causing the full extent of radiation damage. Reduced radiation damage will—if confirmed—be extremely important. Otherwise, each microcrystal would yield only one or two diffraction patterns.

A pertinent example of the power of microcrystallography is the high-resolution analysis of amyloid-producing peptides by the Eisenberg group [3,4]. This class of peptides has been the subject of intense investigation because of their relevance to major classes of amyloid-related disease states such as Huntington's, Parkinson's, Alzheimer's, and amyotrophic lateral sclerosis among others. It had been known that these peptides formed  $\beta$ -sheet-like structures, but the atomic detail displayed by these structures was controversial.

By recording diffraction data from microcrystals on microfocus beamline ID13 at the European Synchrotron Research Facility (ESRF), Nelson et al. were able to determine structures for two polymorphs of the heptapeptide GNNQQNY (refined at 1.8- $\text{\AA}$  resolution) and of NNQQNY (refined at 1.3- $\text{\AA}$  resolution) [5]. These peptides are extended in conformation and are hydrogen-bonded to each other in standard Pauling-Corey parallel  $\beta$ -sheets. Because the strands are perpendicular to the long

axis of the microcrystals, hydrogen-bonded addition of GNNQQNY molecules to the growing  $\beta$ -sheet accounts for the elongated shape of the crystals as well as the fibrils. As previously suggested from x-ray powder diffraction of the microcrystals, the GNNQQNY  $\beta$ -strands within each sheet are parallel and exactly in register. A parallel, in-register arrangement is also seen for A  $\beta$  molecules in their fibrils. Each member of a pair of sheets is related to the other by a  $2_1$ -screw axis: the strands in one sheet are antiparallel to those in the neighboring sheet, and each sheet is shifted along the screw axis relative to its neighbor by one-half of the strand-strand separation of 4.87 Å. Thus, side-chains extending from a strand in one sheet nestle between side chains extending from two strands of the neighboring sheet.

More recently, Sawaya et al. have identified some 70 segments of fibril-forming proteins, which themselves form both fibrils and microcrystals [4]. To date, structures of 45 of these microcrystals have been determined, at resolutions between 0.8 Å and 2.0 Å. One result of these studies is that the fibrils associated with numerous disease states have similar structures at the atomic level.

### Large, non-uniform crystals

Although the application of small x-ray beams (1- $\mu\text{m}$  to 10- $\mu\text{m}$  diameter) to very small, but uniformly highly ordered crystals can bring excellent results, as illustrated above, the application of small x-ray beams to larger, less-ordered crystals is equally important. It has been generally observed that complex systems such as large protein assemblies, membrane proteins, and multidomain proteins are inherently susceptible to producing crystals with surface heterogeneities that impede crystal growth. A major frustration is that many times crystals grow preferentially along a single axis to produce long thin needles, or along two axes to produce very thin plates. In both cases, the crystals are fragile and prone to mechanical deformation and their volume is far too small to generate diffraction of sufficient signal-to-background with a conventional beam. In other cases, larger three-dimensional crystals can be grown, but they have significant non-uniformities. When probed with an x-ray beam that is matched to the crystal size, such crystals produce split, smeared, broad diffraction

maxima that extend only to limited resolution, which in many cases precludes measurement of useful data. However, within some of these crystals there exist diffraction “sweet spots,” small regions of lower mosaicity that can be the source of high-resolution data. But the sweet spots have to be identifiable and separable from the rest of the crystal by using an x-ray microbeam. Improved strategies for automatically scanning crystals to locate sweet spots are very important.

Another common practice is to systematically move the beam along the long axis of the crystal to access

fresh regions for collecting partial data that can be merged. This practice is made much more efficient by the use of microbeams. One striking example of a successful diffraction experiment is the structure determination of human  $\beta$ -2-adrenergic receptor from needle crystals using a beam of 5- $\mu\text{m}$  full width half maximum (FWHM) at the General Medicine and Cancer Institutes Collaborative Access Team (GM/CA-CAT) on Sector 23 of the APS [6,7]. The structure determination of this 7-transmembrane helix GPCR membrane receptor was one of the most anticipated structures in the last decade. It could not have been solved without using a very small beam and a search strategy to target the regions of the crystal that had maximal order. Using a conventional-size beam with dimensions of  $100 \times 30 \mu\text{m}$  (Fig. 3), the crystals did not diffract to a sufficiently high resolution due to the high background contributed from the surrounding mother liquor. A 5- $\mu\text{m}$  beam was used to optimize the signal-to-background, thereby extending the observable diffraction to high resolution. In addition, the small beam allowed the researchers to “walk” along the long axis of the

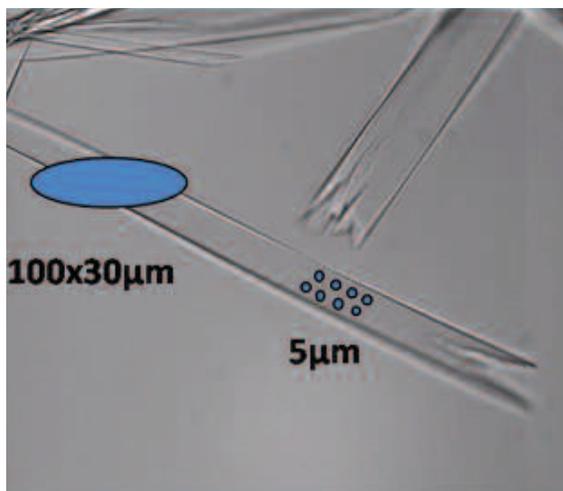


Fig. 3. Thin, needle-like crystals of  $\beta$ -2-adrenergic receptor. The investigators used a 5- $\mu\text{m}$ -diameter beam to target the best part of the crystal, maximized the diffraction/background by only hitting the crystal and not the surrounding mother liquor, and walked along the crystal collecting partial data sets, which were merged to solve the structure. Beam sizes are indicated in the crystal to provide a sense of scale. (Courtesy B. Kobilka and W. Weis, Stanford University)

crystal, collecting partial data sets that could be merged and thus mitigating the effects of radiation damage.

### **Present status of micro x-ray facilities**

Today, methods of structure determination from very small crystals (approaching 1  $\mu\text{m}$  in typical dimension) are being developed and implemented at third-generation synchrotron sources throughout the world, including beamlines at the APS [8,9]. Since the fall of 2007, microbeams of 5- $\mu\text{m}$  and 10- $\mu\text{m}$  diameter have been in routine use on both undulator beamlines (23-ID-B and 23-ID-D) at GM/CA-CAT. The microbeam capability was so successful in initial user tests that it was offered in automated form in February 2008. Users quickly learned the benefits of a 5- $\mu\text{m}$  or 10- $\mu\text{m}$  beam when it was made rapidly selectable at the click of a button without need for re-alignment. In the first two months of availability, 75% of GM/CA-CAT users took advantage of a microbeam for at least some of their crystals. Several reported that data were collected from crystals that would have been discarded if examined only with the large beam also available at these beamlines ( $\sim 30 \mu\text{m} \times 100 \mu\text{m}$ ). While 10- $\mu\text{m}$  microbeams have made an impact, even smaller beams will be needed to attack the types of cutting-edge problems that we envision in the future.

### **Detectors for microcrystallography**

The size of the diffraction spot on a detector depends on several factors, such as the beam size and divergence, crystal quality, and detector spatial resolution. For a microcrystallography experiment on a high-quality crystal, one might expect the width of the diffracted beam at the detector to be on the order of 30  $\mu\text{m}$  to 50  $\mu\text{m}$ . The resolution element of current CCD detectors is  $\sim 100 \mu\text{m}$ , so the diffracted intensity is spread over several pixels in two dimensions. This reduces the signal-to-noise ratio of the measured peaks and limits the maximum resolution to which data can be observed. To address this issue, vendors are offering new, thinner x-ray-sensitive phosphors to reduce the point-spread function and hence resolution element of their CCD detectors. However, there is a trade-off between phosphor efficiency and point-spread function, so the true benefits must be evaluated. The next generation of CCD detectors are currently being developed. In one implementation, only half of each CCD

chip is exposed to a branch of the fiber-optic taper. This allows the image to be rapidly frame-shifted to the other half of the chip, from which read-out occurs. The goal of this implementation is to achieve 10-Hz frame rates. This will be a significant improvement over current detectors with frame rates on the order of 1 Hz.

Another class of detectors has recently come to market. These PADs have very fast read-out times, allowing a data set to be collected 10 to 15 times faster than with current CCD detector technology. However, the only available large-format detector suitable for macromolecular crystallography, the PILATUS 6M, has a resolution element of 172  $\mu\text{m}$ . This is considered to be too large for microcrystallography experiments. It is anticipated that in the near future, large-format PAD detectors with smaller resolution elements will come to market. These will provide both increased data throughput and improved signal-to-noise.

### Stability requirements for microcrystallography

The APS is uniquely positioned among sources in the U.S.—and possibly the world—to develop microbeams for macromolecular crystallography. The low emittance and high brilliance of the source coupled with the large experimental hall have been exploited to provide beams with small cross sectional dimensions (typically much less than 100  $\mu\text{m}$ ) and low convergence (on the order of a few hundred  $\mu\text{rad}$ ). These properties allow diffraction data of high quality to be recorded from crystals of proteins, protein complexes, cellular machinery such as the ribosome, and viruses with unit cell dimensions that vary from less than 100  $\text{\AA}$  to greater than 1000  $\text{\AA}$ . The high-energy aspect of the source provides intense x-rays for multiple anomalous dispersion phasing experiments at the Se and Br  $K$  edges, as well as at the higher energies (20 keV) typically used for virus crystallography. These aspects have all contributed to making the APS the world leader in PDB depositions. To maintain this ranking in the macromolecular crystallography community, small beams on the order of 1  $\mu\text{m}$  must be routinely, rapidly, and robustly available. This will require improvements in the stability of the source, x-ray optics, and endstation hardware so that the intersection of x-ray beam and sample can be maintained to within 0.1  $\mu\text{m}$  while rotating the sample.

## Automation for sample changing and alignment

Sample manipulation presents another major technical challenge. Christian Riekell of ESRF has pioneered the development of several important aspects for microbeams for x-ray diffraction [10]. He and his collaborators have produced highly-focused x-ray beams (currently under 1- $\mu\text{m}$  diameter); have built a goniostat with a small sphere of confusion, suitable for orienting microcrystals; and have begun to develop methods for mounting and positioning small crystals. This set-up must be investigated to establish its strengths, weaknesses, and portability to the APS.

The importance of mounting and alignment cannot be over-emphasized. Methods for manipulation and mounting are still rather crude and need improvement to increase throughput. An essential future development will be the built-in capability for massive automatic sample changing. With current methods, a trained crystallographer can mount and center a microcrystal in 10 to 20 min. Because the small crystals are delicate, mounting and freezing them will also present numerous challenges. The experience and expectation is that, generally, many crystals must be screened prior to data collection to identify the best, from which suitable diffraction data can be collected. In the Eisenberg lab, experience suggests that about 20 to 40 crystals must be screened to find one that yields high-resolution data. For this reason, the lab routinely mounts 500 or more crystals before going to the synchrotron. At the beamline, most of the time goes into crystal screening. The whole process could be vastly speeded up by an automatic sample changer that would permit each crystal to be screened in seconds, rather than in tens of minutes. This is essential, because without a highly automated and efficient freezing and positioning capability, micro x-ray crystallography will never reach its full potential. Even if the unlikely circumstance holds (all crystals are excellent and no crystal screening is necessary), automation is essential because no microcrystals will yield more than a few diffraction patterns before radiation damage becomes too severe and the crystal must be discarded and replaced by a fresh crystal.

## Looking to the future

The immediate future of structural biology will be the examination of ever larger, more complicated macromolecules and complexes. Living systems depend on a vari-

ety of macromolecular machines to perform complex functions. The astonishing detail that has emerged from structures of a few of these machines—the ribosome, the RNA polymerase transcription complex, the fatty-acid synthesis complex, the nuclear pore complex—has whetted the appetite of biologists for greater detail on more systems. Tremendous effort is now being expended to extract important macromolecular complexes from cells. Both x-ray microcrystallography and electron microscopy will be critical tools for elucidating the structures of, for example, signaling cascades, transcription regulation complexes, and transport complexes. A second major area of growing importance is integral membrane proteins, which represent a large fraction of drug targets. These molecules, whether as individuals or in complexes, remain among the most challenging structural targets. The crystalline samples produced for both macromolecular complexes and membrane proteins are nearly always sub-optimal (small and poorly ordered) and present new technical challenges. Therefore, the most brilliant synchrotron sources, such as the APS, will be essential to obtaining useful diffraction data from crystals of macromolecular complexes and integral membrane proteins.

## Malaria

About 2 million people die each year from malaria. *Plasmodium falciparum* is the parasite responsible for the deadliest form of the disease. During one stage of its complex life cycle, the parasite resides in a digestive vacuole inside human erythrocytes (red blood cells), where it catabolizes hemoglobin from the red cell. However, the parasite lacks a heme oxidase, so that the heme groups from hemoglobin cannot be catabolized. Because an excess of free heme groups is toxic to cells, the parasite survives by facilitating formation of an insoluble heme polymer, called hemozoin. Hemozoin accumulates inside the red cell, typically as sub-micron crystals, and it is thought that traditional anti-malaria drugs such as chloroquine exert their influence by preventing the formation of hemozoin [11]. An atomic model of hemozoin has been presented for beta-hematin, which is a synthetic polymer thought to be identical to hemozoin; the model was determined via powder diffraction, as the crystals were too small for standard x-ray crystallography (dimensions ranging from sub-micron to a few microns in the longest dimension) [12]. Resistance to traditional drugs is a major

problem in the fight against malaria. Efforts are under way to model binding of various drugs to hemozoin [13], so it is important to refine the structural model to a greater degree of accuracy than that provided by the powder-diffraction technique. The development of microcrystallography capabilities to study such small hemozoin crystals is fundamental to understanding the mechanism of action of current malaria fighting drugs and the development of more effective life-saving drugs.

## Probing Reaction Dynamics by Time-Resolved Crystallography

Structure determination by traditional x-ray crystallography or NMR techniques provides a view of molecules that is time-averaged over the duration of data acquisition. While this averaged view alone has proven to be remarkably powerful and provides crucial information, in reality all reactions in chemistry, biochemistry, and biology are highly dynamic processes involving structural transitions over a very wide time range from femtoseconds to kiloseconds. Critical information about the interplay between structure, dynamics, and function is lost when all the structural transitions are superimposed. Thus, a major area of investigation has been to develop new crystallographic approaches that exploit the high-resolution capabilities of diffraction, while also exploring the time scales that are relevant for biological phenomena.

### Snap-shots defining reaction pathways

In time-resolved crystallographic experiments, sequential snapshots of structural changes are taken in real time after the reaction is triggered by an appropriate stimulus [14]. (Note: These experiments differ from, and are complementary to, more widely used trapping strategies such as chemical trapping or freeze-trapping, which seek to prolong the lifetime of short-lived intermediates by chemical or physical means [14,15]). Time-resolved techniques could be described as “analytical trapping,” in which the intermediate structures are isolated and trapped, not during the data collection, but in the subsequent processes of data analysis. From the time-dependent electron density maps (or difference electron density maps relative to time zero) that are obtained, the goal is to identify and refine the time-independent structures of the

transient intermediates that comprise the overall chemical kinetic mechanism [14-19]. In practice, a stepwise reconstruction of the complete structural basis for the chemical process can be obtained. Unquestionably, this represents a major step forward in understanding the fundamental relationships between structure, function, and dynamics.

## Technical challenges

**Triggering the reaction** Initiating the reaction in an ultrafast and controlled way presents its own set of issues, in addition to the challenges of developing experimental setups for collecting diffraction data that faithfully represent time slices of a reaction pathway. In principle any extensive variable that influences protein structure can be used for reaction initiation, e.g., temperature jump, pressure jump, electric field jump, pH jump, or concentration jump via diffusion. The problem is that changes in almost all these variables can only take place very slowly, typically in the  $\mu\text{s}$  to hundreds of ms range, and such changes are therefore suitable only for exploring slow reactions. Even the more widely used photoactivation of caged compounds (for which caged adenosine triphosphate, ATP, is the classical example) proceeds with modest quantum yield and is slow, only liberating the desired ATP in the tens to hundreds of  $\mu\text{s}$  range. Further, photoactivation by rupture of a covalent bond is irreversible and proceeds via highly reactive chemical intermediates that often introduce unwanted side reactions. In contrast, in natural systems photoactivation by isomerization is ultrafast (on the femtosecond to picosecond time scale), devoid of side reactions, usually reversible, and proceeds with high quantum yield. But chemistry research and development is needed to devise suitable photoisomerizable substrates, cofactors, or inhibitors for this approach. For example, does a smoothly isomerizable, biochemically active analog of ATP or guanosine 5'-triphosphate exist?

Another approach offers promise: utilize domain fusion to confer light sensitivity on otherwise light-inert systems. This approach takes note of the fact that natural photosensors are modular, in which an input photosensor domain is coupled—usually covalently—to an output effector domain whose biological activity is thereby made light-sensitive. In nature there is a very wide variety of such output domains, e.g.,

histidine and serine/threonine kinases, phosphotransferases, and DNA binding proteins. We have successfully conferred sensitivity to blue light on the Trp repressor [20] and on a normally oxygen-sensitive histidine kinase [21], and we know of a successful application to a small GTPase [22]. In all three systems, a molecular biology-based approach was used to covalently link a blue light-sensitive, flavin mononucleotide-based, light-oxygen voltage sensor domain to the N-terminus of the desired output domain. It was not necessary to prepare a large library of fusions and screen them. This observation and the wide diversity of the three successful output domains suggest that this approach may be quite widely applicable. More research and development is necessary to establish whether this is indeed so, and whether the design principles derived from these three systems apply generally. The obvious requirement for time-resolved crystallography is that good crystals be obtained of the newly light-sensitive proteins, and that they retain both photochemical and light-dependent biochemical activity in the crystal.

***Detection of intermediates*** Because of limitations in current detector technology, all sub-second, time-resolved crystallographic experiments have been conducted in pump-probe mode, in which each pump or reaction initiation event is followed after a suitable, controllable time delay by a probe event [17,23-25]. A structural change in the molecules in the crystal is triggered by a short laser pulse or other means (e.g., temperature jump, pH jump, voltage jump, or diffusion of a key reactant) and probed by x-ray pulses of appropriate duration. The time resolution is dependent on the duration of the two pulses, pump or probe, and on jitter in the time delay between them. High-peak-power, femtosecond-pulsed lasers are readily available today for pumping or triggering reactions in photosensitive systems. The best time resolution is thus limited by the duration of the probe x-ray pulses: around 100-ps FWHM at all conventional synchrotron sources. Fast time-resolved experiments (100-ps to 100- $\mu$ s time resolution) require the Laue diffraction technique, in which a stationary crystal is illuminated by polychromatic x-rays. Conventional monochromatic, rotating-crystal techniques can be used when a time resolution of microseconds or longer will suffice. Reaction initiation is a critical step for the success of time-resolved experiments and has to be tailored to the particular biological system under investigation. Synchro-

nization electronics establish and vary the time delay between the pump and probe pulses. Individual x-ray probe pulses or longer multi-pulse trains must be selected by a fast x-ray shutter train from the continuous x-ray pulse sequence emitted by the synchrotron. The data sets in a time-resolved experiment are large because they span a four-dimensional space: the intensities over the unique volume in reciprocal space ( $hkl$ ) and the time range over which the reaction proceeds ( $t$ ). Typically, three or four complete data sets are acquired per decade of time, uniformly spaced in  $\log t$ ; a total of 30 to 50 time points is not unusual. Data are also acquired with high redundancy to permit the accurate determination of both the mean structure amplitudes  $|F(hkl,t)|$  and their variance  $\sigma^2(hkl,t)$ . The variance is essential to the implementation of data weighting schemes [18,26,27]. Indeed, because the time-dependent signal is small in magnitude and error prone, the entire experiment depends on the elimination of systematic error and the minimization of random error. Finally, analysis methods such as singular value decomposition [26] are needed that ultimately lead to the deduction of mechanism(s) that are compatible with the structural data and to the identification and refinement of structural intermediates.

### Current state of the art for producing time-resolved information

BioCARS at Sector 14 of the APS is the only facility in the U.S. equipped for studying the dynamics of biological macromolecular systems on time scales of 100 ps or longer, using the techniques of time-resolved crystallography that BioCARS scientists pioneered. The recently upgraded BioCARS 14-ID-B beamline surpasses all other such facilities in the world in both its x-ray and associated laser capabilities. Although the double, collinear undulator sources and x-ray optics were designed and optimized for both polychromatic (Laue) and monochromatic experiments on single crystals of biological interest, very recent data show that excellent small-angle and wide-angle x-ray scattering data can be obtained on protein solutions [28] and fibers [29].

Likewise, excellent data have been obtained that address problems in time-resolved chemical crystallography [30], and both static and time-resolved data arising from thermal diffuse scattering in silicon and gallium arsenide [31]. Thus, the BioCARS sector is well suited to time-resolved experiments, and the range of science conducted there may evolve more broadly.

## Technologies needed to reach the next frontier

One would like to be able to explore the structural course of ultrafast biochemical reactions such as those that occur in the earliest stages of photosynthesis, or in response to absorption of a photon of blue or red/far-red light in a signaling photoreceptor. Ultrafast spectroscopies suggest that such reactions extend into the femtosecond time range. There is a limited number of such reactions or systems, which all originate in the absorption of a photon, but they are critical to understanding photosynthesis and light-dependent signaling. Today's time resolution is set by the x-ray pulse duration at around 100 ps, which is in turn set by the radio-frequency characteristics and the long-term requirements on electron bunch stability in all circular storage rings. As a result, the structural bases of these ultrafast reactions are completely inaccessible at present.

Schemes have been advanced to generate much shorter x-ray pulses of a few ps duration via the introduction of "crab cavities" that would employ strong perturbation of individual electron bunches in the storage ring. These x-ray pulses would be highly suitable for exploring ultrafast reactions, provided there were sufficient x-ray photons in the shorter pulse to enable a good diffraction image to be obtained with one (or at most ~100) x-ray pulse(s). The figure of merit for recording a Laue diffraction pattern is photons/(pulse. mm<sup>2</sup> . 0.1% bandpass), and should comfortably exceed 10<sup>8</sup> to generate a good Laue pattern from a quite strongly-scattering crystal. We support research and development on the installation of crab cavities in the APS and on the means to achieve this figure of merit. Other schemes, such as laser-based pulse slicing of the synchrotron pulse, perturb only a small fraction of the electrons in the bunch and fall short of this figure of merit by orders of magnitude. But here too, research and development may suggest alternative approaches.

## Next-generation detectors

Most APS macromolecular crystallography beamlines currently use CCD detectors that impose a 1-s to 2-s readout time during which the x-ray shutter must be closed. We expect that over the next 5–10 years these detectors will be replaced with more advanced CCD detectors or PADs, as previously discussed, that allow the collection of

entire data sets without closing the shutter. This technology is currently available in a form factor well suited for macromolecular crystallography (PILATUS 6M) and will be evaluated for microcrystallography. When this detector is implemented on a beamline, the new bottlenecks will be the sample changer, crystal centering, and the ability to process data. Such a detector will replace the present “pump once/probe one time point” with a “pump once/probe many time points” approach.

Pixel-array detectors offer great promise because they are designed to record diffraction patterns at several time delays after a single reaction initiation event. However, a serious limitation of existing and proposed PADs is that they have a minimum interframe dead time of ~200 ns, just too long for recording rapid reactions. These require a minimum interframe time of 153.4 ns, the interbunch time in 24-bunch mode of operation of the APS storage ring. Another limitation with the current PAD detectors is that the photon-counting front end cannot handle the high instantaneous rates of a time-resolved experiment. Other so-called “mixed-mode” PADs are being developed that may overcome this limitation. Much research and development is required before such ideal, large-area, ultrafast PADs can be in routine use.

## References

- [1] C. Nave and E.F. Garman, “Towards an understanding of radiation damage in cryocooled macromolecular crystals,” *J. Synchrotron Radiat.* **12**(3), 257 (2005).
- [2] C. Nave and M.A. Hill, “Will reduced radiation damage occur with very small crystals?,” *J. Synchrotron Radiat.* **12**(3), 299 (2005).
- [3] Michael A. Hanson, Vadim Cherezov, Mark T. Griffith, Christopher B. Roth, Veli-Pekka Jaakola, Ellen Y.T. Chien, Jeffrey Velasquez, Peter Kuhn, and Raymond C. Stevens, “A specific cholesterol binding site is established by the 2.8 Å structure of the human  $\beta_2$ -adrenergic receptor,” *Structure* **16**(6), 897 (2008).
- [4] M.R. Sawaya, S. Sambashivan, R. Nelson, M.I. Ivanova, S.A. Sievers, M.I. Apostol, M.J. Thompson, M. Balbirnie, J.J.W. Wiltzius, H.T. McFarlane, A.Å. Madsen, C. Riek, and D. Eisenberg, “Atomic structures of amyloid cross-beta spines reveal varied steric zippers,” *Nature* **447**(7143), 453 (2007).
- [5] Rebecca Nelson, Michael R. Sawaya, Melinda Balbirnie, Anders Å. Madsen, Christian

Riekkel, Robert Grothe, and David Eisenberg, "Structure of the cross- $\beta$  spine of amyloid-like fibrils," *Nature* **435**(7043), 773 (2005).

[6] S.G.F. Rasmussen, H.-J. Choi, D.M. Rosenbaum, T.S. Kobilka, F.S. Thian, P.C. Edwards, M. Burghammer, V.R.P. Ratnala, R. Sanishvili, R.F. Fischetti, G.F.X. Schertler, W.I. Weis, and B.K. Kobilka, "Crystal structure of the human  $\beta_2$  adrenergic G-protein-coupled receptor," *Nature* **450**(7168), 383 (2007).

[7] Daniel M. Rosenbaum, Vadim Cherezov, Michael A. Hanson, Søren G.F. Rasmussen, Foon Sun Thian, Tong Sun Kobilka, Hee-Jung Choi, Xiao-Jie Yao, William I. Weis, Raymond C. Stevens, and Brian K. Kobilka, "GPCR engineering yields high-resolution structural insights into  $\beta_2$  adrenergic receptor function," *Science* **318**(5854), 1266 (2007).

[8] R. Sanishvili, V. Nagarajan, D. Yoder, M. Becker, S. Xu, S. Corcoran, D.L. Akey, J.L. Smith, and R.F. Fischetti, "A 7  $\mu\text{m}$  mini-beam improves diffraction data from small or imperfect crystals of macromolecules," *Acta Crystallogr. D* **64**, 425 (2008).

[9] R.F. Fischetti, S. Xu, D.W. Yoder, M. Becker, V. Nagarajan, R. Sanishvili, M.C. Hilgart, S. Stepanov, O. Makarov, and J.L. Smith, *J. Synchrotron Radiat.* **16**, 217 (2009).

[10] C. Riekkel, M. Burghammer, and G. Schertler, "Protein crystallography microdiffraction," *Curr. Opin. Struct. Biol.* **15**(5), 556 (2005).

[11] D.J. Sullivan, Jr., I.Y. Gluzman, D.G. Russell, and D.E. Goldberg, "On the molecular mechanism of chloroquine's antimalarial action," *Proc. Nat. Acad. Sci.* **93**, 11865 (1996).

[12] Silvina Pagola, Peter W. Stephens, D. Scott Bohle, Andrew D. Kosar, and Sara K. Madsen, "The structure of malaria pigment  $\beta$ -haematin," *Nature* **404**, 307 (2000).

[13] Inna Solomonov, Maria Osipova, Yishay Feldman, Carsten Baehtz, Kristian Kjaer, Ian K. Robinson, Grant T. Webster, Don McNaughton, Bayden R. Wood, Isabelle Weissbuch, and Leslie Leiserowitz, "Crystal Nucleation, Growth, and Morphology of the Synthetic Malaria Pigment  $\beta$ -Hematin and the Effect Thereon by Quinoline Additives: The Malaria Pigment as a Target of Various Antimalarial Drugs," *J. Am. Chem. Soc.* **129**, 2615 (2007).

[14] K. Moffat, "Time-resolved biochemical crystallography: a mechanistic perspective," *Chem. Rev.* **101**(6), 1569 (2001).

[15] D. Bourgeois and A. Royant, "Advances in kinetic protein crystallography," *Curr. Opin. Struct. Biol.* **15**(5), 538 (2005).

[16] K. Moffat and Z. Ren, "Synchrotron radiation applications to macromolecular crystallography," *Curr. Opin. Struct. Biol.* **7**(5), 689 (1997).

[17] Sudarshan Rajagopal, Spencer Anderson, Vukica Šrajter, Marius Schmidt, Reinhard Pahl, and Keith Moffat, "A structural pathway for signaling in the E46Q mutant of photoactive yellow protein," *Structure* **13**(1), 55 (2005).

- [18] Z. Ren, B. Perman, V. Šrajer, T.-Y. Teng, C. Pradervand, D. Bourgeois, F. Schotte, T. Ursby, R. Kort, M. Wulff, and K. Moffat, "A molecular movie at 1.8 Å resolution displays the photocycle of photoactive yellow protein, a eubacterial blue-light receptor, from nanoseconds to seconds," *Biochem.* **40**(46), 13788 (2001).
- [19] M. Schmidt, R. Pahl, V. Šrajer, S. Anderson, Z. Ren, H. Ihee, S. Rajagopal, and K. Moffat, "Protein kinetics: structures of intermediates and reaction mechanism from time-resolved x-ray data" *Proc. Natl. Acad. Sci. USA*, **101**(14), 4799 (2004).
- [20] D. Strickland, K. Moffat, and T.R. Sosnick, "Light-activated DNA binding in a designed allosteric protein," *Proc. Natl. Acad. Sci. USA* **105**(31), 10709 (2008).
- [21] Andreas Moeglich, Rebecca A. Ayers, and Keith Moffat, "Design and signaling mechanism of light-regulated histidine kinases," *J. Mol. Biol.* **385**, 1433 (2009).
- [22] Y. Wu (unpublished).
- [23] Hyotcherl Ihee, Sudarshan Rajagopal, Vukica Šrajer, Reinhard Pahl, Spencer Anderson, Marius Schmidt, Friedrich Schotte, Philip A. Anfinrud, Michael Wulff, and Keith Moffat, "Visualizing reaction pathways in photoactive yellow protein from nanoseconds to seconds," *Proc. Natl. Acad. Sci. USA* **102**(20), 7145 (2005).
- [24] Benjamin Perman, Vukica Šrajer, Zhong Ren, Tsu-yi Teng, Claude Pradervand, Thomas Ursby, Dominique Bourgeois, Friederich Schotte, Michael Wulff, Remco Kort, Klaas Hellingwerf, and Keith Moffat, "Energy transduction on the nanosecond time scale: early structural events in a xanthopsin photocycle," *Science* **279**(5358), 1946 (1998).
- [25] Z. Ren and K. Moffat, "Laue crystallography for studying rapid reactions," *J. Synchrotron Radiat.* **1**(1), 78 (1994).
- [26] Marius Schmidt, Sudarshan Rajagopal, Zhong Ren, and Keith Moffat, "Application of singular value decomposition to the analysis of time-resolved macromolecular x-ray data. *Biophys. J.* **84**(3), 2112 (2003).
- [27] T. Ursby, M. Weik, E. Fioravanti, M. Delarue, M. Goeldner, and D. Bourgeois, "Cryophotolysis of caged compounds: a technique for trapping intermediate states in protein crystals," *Acta Crystallogr. D* **58**(4), 607 (2002).
- [28] P. Anfinrud and colleagues (unpublished).
- [29] G. Stubbs, M. Reedy, T. Irving, and colleagues (unpublished).
- [30] P. Coppens and colleagues (unpublished).
- [31] D. Reis and colleagues (unpublished).

## Renewal of the Advanced Photon Source: Materials Science & Technology

<b>Paul G. Evans</b> (Chair)	<i>University of Wisconsin-Madison</i>
<b>Katherine T. Faber</b>	<i>Northwestern University</i>
<b>John F. Mitchell</b>	<i>Argonne National Laboratory</i>
<b>Ismail (Cev) C. Noyan</b>	<i>Columbia University</i>
<b>Carol Thompson</b>	<i>Northern Illinois University</i>
<b>Choong-Shik Yoo</b>	<i>Washington State University</i>

### Executive Summary

Developing new materials is both the ultimate practical goal of the research directions epitomized by the U.S. Department of Energy's (DOE's) five Grand Challenges [1] and a scientific challenge in itself. The x-ray techniques enabled by synchrotron sources are essential in developing new materials for applications in energy, information, health, transportation, and defense technologies. The fundamental challenges in each of these areas are defined by the capabilities of present materials. The greatest potential for future advances likewise comes from the development of new materials and new ways to process materials. In energy, for example, the development of materials for applications at high temperatures, in solar photovoltaics, and in light emission is the key to new technologies. Similarly, the potential to process existing materials with nanometer precision have driven information technology and will continue to do so. Structural materials with longer fatigue lives, higher strengths, and better wear characteristics likewise have great promise across a number of applications.

Advances in the way materials are processed have emerged as greater capabilities in theory, synthesis, and characterization have been developed. New directions in crystal growth, processing far from equilibrium, nanopatterning, and hierarchical self-as-

sembly present new opportunities in fabrication, characterization, and in the basic theoretical description of materials. The science of new materials depends on advanced characterization techniques at length scales ranging from the positions of single atoms, to structures and defects at nanometer scales, to the overall organization of materials at large scales. In addition, the creation and transformation of materials is inherently a dynamic process that is greatly influenced by rare events. The properties and structures of materials evolve during these events, leading to the need for a fundamentally new approach to studies of random processes.

Techniques using synchrotron radiation have a unique role in materials science and are rapidly evolving at the Advanced Photon Source (APS) and other light-source facilities in order to keep pace with developments in the way that materials are designed, studied, and produced. In addition to using these synchrotron radiation-based tools to characterize the end-products of materials processes, synchrotron light sources will, in the future, facilitate study of the outcomes of subtle changes in processing conditions that can have large effects on the properties of the end product. Crystal growth and the self-assembly of mesoscopic structures face similar challenges that will benefit tremendously from *in situ* instrumentation.

Renewed experimental facilities at the APS will enable a fundamental shift in the way that synchrotron radiation is used in materials science and technology. There are opportunities to develop new techniques, to use existing techniques more intelligently, and to combine scattering and imaging techniques with revolutionary advances in information technology.

## Introduction

Among the most important achievements of synchrotron x-ray research are new techniques that provide unparalleled insight into the atomic structure of bulk materials surface and interfaces, nanoparticles, and nanodomains. Within these structures, x-rays have unique sensitivity to atomic positions, correlation and order, defects, and

crystallographic distortion. Characterization techniques now allow the structure of individual nanostructures to be probed routinely. New facilities at the APS will allow diffraction, scattering, and spectroscopy techniques to be widely applied to samples and processes that have been out of the reach of the present generation of tools. Advances in detectors and sources promise to build on existing techniques by allowing them to be applied with great advances in speed and sensitivity, and with reduced radiation damage.

Recently developed x-ray scattering techniques are being applied to systems driven far from equilibrium. This is critical to materials science and technology from a fundamental perspective because the dynamic response of materials, the principles underlying the structure of materials and its evolution, and the dynamics of defects and domains are all driven by non-equilibrium phenomena. In this sense, the structural, dielectric, and magnetic response to applied fields provides fundamental insight into the physics of materials. The relevant time scales range from femtoseconds to microseconds, and there are now opportunities to probe materials dynamics at a renewed APS at times as short as 1 ps.

The processing of materials inherently occurs away from equilibrium, and the emerging capability to probe non-equilibrium systems will be a powerful addition in systems for which there is presently no detailed *in situ* characterization. The dominant phenomena in non-equilibrium systems are often irreversible and rare, as in nucleation, crack initiation, and hysteresis in magnetic or electrical response. These non-equilibrium phenomena often occur in magnetic, optical, and pressure conditions for which conventional microscopies and characterization tools are not available [2].

The transition from large-scale systems to nanoscience involves emergent phenomena that have no parallel in bulk systems. Electronic and magnetic phenomena are vastly different in confined systems, and emergent and critical phenomena take new forms at small scales, at surfaces, and at interfaces. Defining the electronic effects relevant to doping in nanocrystals, for example, involves different statistical assump-

tions and electronic boundary conditions than in bulk semiconductors [3]. These changes, and their dependence on size, composition, and how similar effects are manifested in nanoscale semiconductor devices are only beginning to be understood.

## Key areas

This report focuses on six specific scientific areas that serve as examples of the areas where the development of advanced experimental facilities at the APS will have a huge impact.

***Crystal growth.*** What phases and processes are relevant to crystal growth?

***Materials under transient pressure.*** What are the properties of materials under transient pressures far higher than those available in static experiments?

***Imaging random events.*** How can we understand the rare stochastic events behind nucleation, crack initiation, and other seemingly random incidents?

***Atomic positions in semiconductor devices, ultimate strain.*** What are the positions of atoms in devices with sizes on the order of tens of nanometers? How do the concepts of strain, composition, and concentration apply at this scale?

***Dynamics in applied fields.*** What is the structural response of materials to applied electric and magnetic fields?

***Interfaces in biomaterials.*** What types of interfaces can form between engineered materials and complex biological systems?

Progress in these areas must be accompanied by simultaneous advances in materials theory and in efforts that link theory to the results of new experiments. Advances in density functional theory, for example, now allow the prediction of the properties of insulators and semiconductors in high electric fields [4]. Similar advances in multi-scale techniques, in electronic properties predictions, and in models of materials growth are now required.

## Key Science Drivers

### Crystal growth

The design, discovery, and growth of new materials underpin the success of future materials-driven science and technologies. New energy-conversion and storage systems will require breakthroughs in materials design. The end of the silicon roadmap demands both new materials and processing paradigms to fuel the engine of information technology. The APS, by embracing a paradigm of “bringing the laboratory to the beamline” can advance the fundamental understanding of complex materials chemistry and physics, and in the process significantly advance our options for answering these and other materials-driven science and technology challenges.

Single crystals are extremely valuable as the gateway to intrinsic physical behaviors and anisotropies, be they electronic, mechanical, or thermal. The opportunity here is for the APS to provide a platform for elevating crystal growth from an art form to a science by harnessing the power of *in situ* growth characterization in ways not possible using laboratory-scale instrumentation. A strategic plan will be to energize both targeted synthesis of known materials and the discovery and exploratory synthesis of new materials. In keeping with the facility’s mission of providing unique capabilities, we identify several high-impact *in situ* approaches that will advance the state of the art in crystal growth, addressing the needs of a growing materials-chemistry and physics community.

### Floating-zone growth

Many of the highest-quality crystals of oxide superconductors and of heavy Fermion compounds derive from containerless floating-zone (FZ) crystal growth (Fig. 1). The quality of FZ crystals would be vastly improved through real-time knowledge of A) the melt composition in the zone, particularly at the solid-liquid interface where effects such as segregation, diffusion, and convection presently result in great uncertainty; and B) the microstructure of the growing crystal boule, i.e., how are crystallites nucleating and growing toward the single-crystal limit? These needs can be met by application of spatially-resolved element-specific probes using fluorescence,

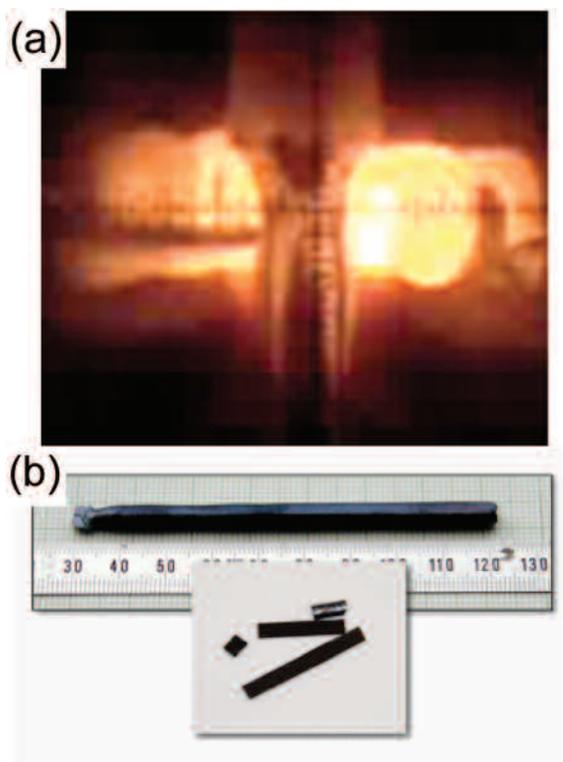


Fig. 1. (a) Floating-zone crystal growth. (b) FZ-grown oxide crystals. (Courtesy of John Mitchell [Argonne National Laboratory])

resonance scattering, and x-ray radiography techniques. The latter has been used to map dendritic growth in two dimensions at synchrotron facilities [5,6]; but a real three-dimensional (3-D) picture of the growing crystal is actually what is needed. For doped crystals, knowledge of the dopant profile (or equivalently, the effective distribution coefficient) could be addressed by spatial composition mapping during growth. However, the overall goal should be more than just characterization. A more powerful outcome will be to couple such information into a feedback mechanism for real-time adjustment of growth parameters, optimizing the growing crystal in response to the chemical and physical state during growth.

### High-pressure crystal growth

The frontier of new materials discovery and crystal growth lies at extreme conditions such as high pressure. New phases, extended solubility limits, metastable compositions, and crystals that cannot be grown at ambient conditions—with concomitant new properties—have been and will continue to be found at high pressure. Synchrotrons are not new to this arena, with several important single-crystal growth successes (e.g., GaN [7], oxide superconductors [8], low-dimensional magnets [9], and a number of other materials) depending on understanding solid-liquid phase relations at high pressure via *in situ* powder diffraction. A vision for the APS is to advance high-pressure crystal growth by going beyond phase diagrams toward *in situ* identi-

cation of nucleating crystallites. The crystallization pathway is essential information, particularly for incongruently melting compounds. Simultaneous advances in techniques for obtaining 3-D crystallographic data from samples in the pressure cell are also essential.

### Hydrothermal synthesis

Significant inroads have already been made in the area of crystallization kinetics using *in situ* techniques [10]. Rapid screening approaches, presumably by diffraction, would allow the grower to take either a combinatorial approach or to control products in real time.

### Flux growth

Molten fluxes (e.g., metals and salts) can be used to let equilibrium phase diagrams “compute” the stability of new phases. As in high-pressure synthesis, interrogation of the melt composition, knowledge of the stepwise crystallization products, and the ability to modify process parameters in real time would be distinct advantages for exploratory and targeted crystal growth. An opportunity for synchrotrons is identification of the first nucleating crystals using a highly focused, high-intensity beam rather than waiting hours or days to collect a specimen suitable for *ex situ* analysis.

### Biological/protein crystal growth and self-assembly

The opportunities and concepts associated with the precision of crystal growth can be extended to longer length scales using self-assembly techniques [11,12]. The repeating units of these materials are nanometers to hundreds of nanometers, but they pose a similar set of fundamental challenges in the control of the resulting structure. The larger scale of these materials presents a different set of characterization challenges in small-angle scattering and coherent scattering that should be addressed as part of a comprehensive effort in characterizing materials synthesis.

### Dynamic compression

Dynamic compression experiments (shock wave and shockless compression) subject

materials to extreme conditions (very large compressions, high temperatures, and large deformations) on very short time scales (picoseconds to microseconds) resulting in a rich array of physical and chemical changes. The most interesting regime for solid materials extends up to pressures of 500 GPa to 1000 GPa (5 to 10 Mbar) and temperatures up to 0.5 eV. The extreme conditions encountered under dynamic compression provide a unique opportunity to explore the delicate balance between mechanical ( $P\Delta V$ ) and thermal ( $T\Delta S$ ) energies by examining how this balance governs a wide variety of physical and chemical phenomena. The short times inherent in dynamic experiments result in the kinetics playing an important role in determining the governing mechanisms and the attainment of metastable states, beyond thermodynamic constraints. Dynamic compression can be used to examine fundamental scientific issues and questions related to condensed matter phenomena such as structural changes including electronic transitions, chemical reactions including bonding and energetics, and deformation and fracture.

Irrespective of the phenomena being examined, dynamic compression experiments are ideally suited to probe, in a time-resolved manner, physical and chemical changes as they occur. Such information is essential to a mechanistic understanding of condensed matter phenomena, and to providing knowledge with a broad impact on condensed matter sciences, well beyond dynamic loading. Dynamic compression experiments, because of the potential to probe physical and chemical changes as they occur on picosecond to microsecond time scales, are ideal for understanding condensed matter response at extreme conditions.

In recent years, there have been major experimental advances—mainly at the DOE-National Nuclear Security Administration (NNSA) laboratories—to vary the loading conditions of interest (compression, temperature, deformation, and loading times) in a controlled manner. These advances provide new opportunities for examining and understanding condensed matter phenomena. However, the experimental measurements to date are almost exclusively at the continuum scale. As such, the ability to address fundamental scientific issues related to mechanistic understanding at the microscopic level is limited.

Simultaneous with the major advances in dynamic compression technology, the extraordinary developments in computational capabilities (starting with the Accelerated Strategic Computing Initiative efforts) over the past 10 to 15 years have added a new dimension to scientific research. The pace in modeling and simulations will continue at this or an even higher rate for the foreseeable future. Despite the impressive advances in modeling and simulations of condensed matter phenomena, the following question continually arises: How valid are the predictions from these simulations? The third element of dynamic compression research, measurement capabilities, has lagged significantly behind in comparison to advances in dynamic loading technologies and computational developments. The principal need at the present time is for time-resolved, *in situ* microscopic measurements. Without comparable advances in measurement capabilities, the full scientific potential of investments and advances in dynamic loading and computational capabilities will not be achieved.

Time-resolved, *in situ* microscopic measurements constitute the most important need for achieving a fundamental understanding of condensed matter phenomena and processes under dynamic loading. Such measurements will lead to revolutionary scientific advances well beyond dynamic compression. Although the need for the above indicated measurements is clear, obtaining such data in single-event experiments is a formidable challenge and requires special measurement capabilities.

### Imaging random events

A number of problems in materials science and engineering derive from statistical origins. These include the initiation of fatigue cracks in metals [13]; brittle failure in ceramics, intermetallics and network polymers [14]; pitting by corrosion [15]; and grain-boundary environmental corrosion [16]. To gain a fundamental understanding of these processes, experiments are contrived in such a way as to eliminate their statistical nature. In fracture experiments, for example, pre-cracks or notches are placed in specimens to provide focus for the experiment. While affording useful information in assessing the steady-state phenomena of crack growth, these experiments risk the loss of crucial information regarding the nucleation or initiation event. Of even

greater concern, from a technological perspective, is that lifetime predictions-based continuum or fracture mechanics treatments for long, artificial cracks are not well suited for short or just-nucleated cracks [13]. Hence, *in situ* experiments with defect-free samples are particularly promising, not only for helping to elucidate fundamental mechanisms of nucleation events, but also for providing grist for lifetime models that more accurately simulate reality.

The random nature of these events poses serious challenges for observation. First, real-time imaging is essential. Dendritic growth during the solidification of aluminum alloys has been observed using real-time x-ray imaging [17]. However, the technique relies on a sharp difference in x-ray attenuation between separate phase domains; for example, a crack (void space) in a fatiguing metal or a corrosion product surrounded by non-corroded material. Secondly, observation volumes must be of the order of the sample size to “catch” the nucleation event. Large detector arrays would be required to afford sensing over the entire sampled volume in real time. Analogous screening has been done in the field of acoustics for seismic and biomedical imaging of random incidents [18] and in structural health monitoring [19], using time-reversal imaging. The technique affords both spatial and temporal focusing on regions of interest in inhomogeneous environment. Finally, environmental control must be uniform over the entire observation volume. This may require elevated temperatures, corrosive environments, applied loads, or some combination of these.

Once the locations of nucleation events are established, taking advantage of further capabilities of the synchrotron could enhance mechanistic understanding. For example, using near-field grain mapping, the evolution of the dislocation structure in individual grains could be followed and related to crack nucleation. Grain orientations could be monitored to assess corrosion prone orientations. Small-angle x-ray scattering techniques would be useful in tracking the statistics of void formation during elevated temperature fracture experiments.

Several kinetic processes in materials would benefit from these studies:

- Crack initiation and growth under monotonic loading in brittle materials. These

experiments would be limited to materials that demonstrate stable crack growth, such as that seen in ceramic-matrix composites.

- Fatigue crack initiation and growth in metals.
- Pitting during aqueous or gas-phase corrosion.
- Environmentally-assisted or embrittlement of grain boundaries. These experiments would highlight which grain boundaries are more susceptible to embrittlement than others.
- Vortices in superconductors and other nano-to-mesoscale phenomena in condensed matter systems.

Establishing the intrinsic or extrinsic causes for nucleation events would provide critical information for mechanistic models and life prediction strategies.

### **Atomic positions in semiconductor devices, ultimate strain**

The presence of strain distributions within semiconductor features influences many aspects of their behavior. For example, microelectronic technology that incorporates strained silicon improves device performance by increasing carrier mobility in the silicon channels. Because current semiconductor fabrication contains multiple levels of metallic and dielectric structures, an understanding of the mechanical response of the constituent elements is critical to the prediction of the overall device performance. In addition, the interaction of strain fields between adjacent structures becomes greater as feature sizes decrease and the corresponding feature density increases. Therefore, the mechanical response of the semiconductor and its environment is critical to assessing the true state of strain near these devices. The continuum mechanics concept of strain may be inapplicable when the linear dimensions of the semiconducting regions are less than 10 nm or so. The equilibrium spacing between the atoms on such a small length scale cannot be assumed to be constant; there is no rigorous definition of normalized displacement at a point. X-ray diffraction from these small structures includes coherent effects that cause dramatic effects (as in Fig. 2) that cannot be understood with the rules of thumb developed for larger structures [21]. As such, we need to measure the atomic coordi-

nates of the atoms within the channel region, since the local symmetry will determine the effective masses, and hence the mobilities of the charge carriers [22].

While modeling and verification of the electronic properties of regions on the nanometer length scale (e.g., the effect of size quantization through modified local density approximations) have been successful, corresponding analysis of the mechanical behavior at these dimensions is incomplete. There are significant theoretical and experi-

mental challenges to be addressed because the extension of continuum mechanics approaches to nanoscale volumes has not yet been verified. In addition to the intrinsic complexity associated with measurements at the relevant dimensions, the presence of local discontinuities (edges, free surfaces, interfaces, defects) can significantly modify the atomic positions within these domains. The presence of a single extended defect in these systems is already known to cause large deleterious electrical effects, and characterizing the nature of defects remains a challenge.

Emergent effects, including vastly different thermal properties, can appear at the small length scales being utilized in the latest integrated semiconductor devices. These emergent effects can be the key to using semiconductor technology in new thermoelectrics and in other applications taking advantage of the large-scale processing of silicon.

### Dynamics in applied fields

The structures and properties of materials can be dramatically changed by applied

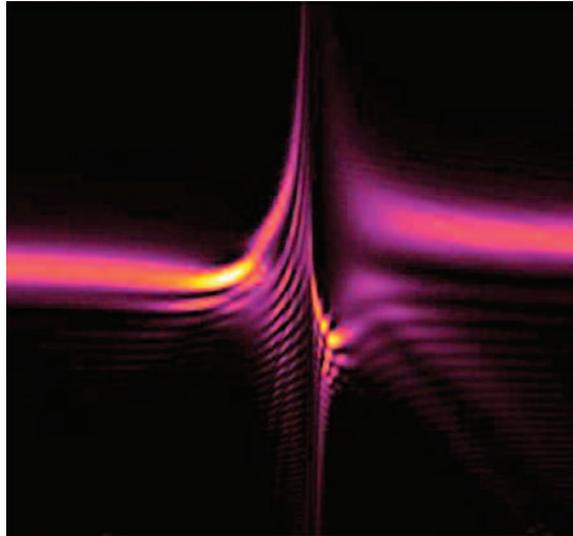


Fig. 2. Simulation of the nanodiffraction topograph arising from a highly strained silicon structure [21]. © 2008 American Institute of Physics

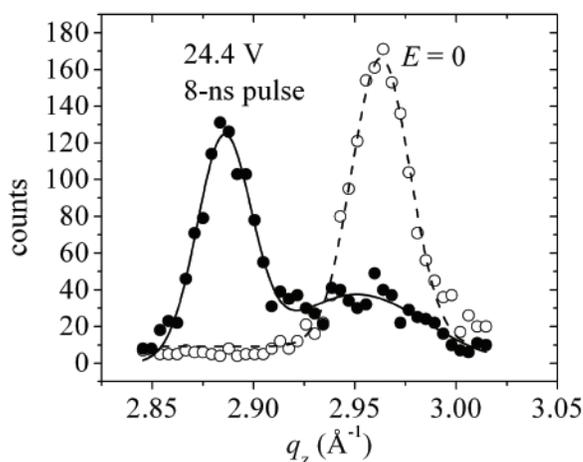


Fig. 3. Transient strain of 2.7% in a 40-nm-thick PZT film in response to an 8-ns electric-field pulse [26]. (© 2008 The American Physical Society)

principles calculations has recently been solved, making available a range of predictions of materials properties that have yet to be tested.

The time scales associated with the structural responses to applied electric fields range from seconds (as in the case of domain wall motion in ferroelectrics), to less than a picosecond (for the development of the ionic contribution to dielectric polarization). X-ray scattering is unique in providing structural information with essentially the same precision at these time scales as at any other. The transient strain developed in response to a short applied electric field pulse can be evaluated using diffraction and can reach several percent (Fig. 3) [26]. The opportunity to extend this approach to other, more subtle properties is exciting.

Strain and other properties result from modification of the interatomic potential in the applied electric field. Phonon dispersion provides a direct measure of the interatomic potentials and can be determined quantitatively using thermal diffuse scattering [27]. With specific technical advances, thermal diffuse scattering can be adapted to provide the equilibrium and non-equilibrium elastic properties of nanostructures.

electric fields. The effects associated with the response of materials include polarization, piezoelectric distortion, and—at high fields or strains—the stabilization of crystallographic phases that are structurally or electronically distinct from the ground state [24]. Transitions to these phases can be driven by piezoelectric strain or by charge carriers accumulated in the near-surface layer screening the applied field [25]. The problem of describing long-range polarization in first-

In multiferroic materials that are both ferroelectric and magnetic, applied electric fields can influence the magnetism of the material. X-rays are unique in providing a quantitative probe of magnetism that, unlike neutrons, can be focused to small sizes and used to study individual isolated devices and domains [28]. Magnetic scattering will provide a unique window into the coupling of the magnetic and electrical degrees of freedom in multiferroics. At interfaces, absorption spectroscopy and dichroism studies in applied fields will provide insight into the spin injection process in ferromagnetic semiconductor contacts.

More generally, the influence of applied fields on structural order has a wide influence in materials that are purely magnetic. Magnetic shape memory alloys such as  $\text{Ni}_2\text{MnGa}$  have a large structural response to applied magnetic fields. This response is influenced by structural, magnetic, and composition effects that are only beginning to be understood [29]. The physical fundamentals underlying the dynamics of this response are largely unknown, because there have been no structural probes available. It is now possible to rapidly traverse the thermal phase transitions relevant to similar materials using ultrafast laser techniques, and to create intense pulsed magnetic fields and spin polarized currents on a small scale [30,31]. Applying these approaches to understanding how structural phases coexist as a function of applied magnetic field and strain would be an important advance.

The time scales associated with the response to applied field can extend far below the times that can be resolved using the APS in its current form. Developing an ultrafast capability extending to the few-picosecond scale, and the capability to induce phase transitions and drive samples electrically and magnetically, would open a new range of possible experiments.

## Significance of the APS

The APS is uniquely suited to studies of materials using scattering and spectroscopy. Among U.S. light sources, only the APS has a large diameter and high electron energy. The large diameter of the APS allows it to be run in a mode in which the dis-

crete electron bunches are widely spaced in time, which greatly simplifies time-resolved experiments. This bunch spacing is an excellent match for the capabilities of new detectors suited to single-bunch time resolution .

The high electron energy of the APS allows insertion devices to produce intense beams at high photon energy. High photon energies with brilliant stable sources are essential for *in situ* scattering and imaging experiments in which the beam must penetrate into the environments of high pressure, high temperature, or high fields. High photon energies also allow x-rays to be used to study the liquid-solid interface in crystal growth, where absorption lengths at lower photon energies would penetrate only a few microns.

The APS has an inherently low emittance and an experiment hall floor layout that favors microscopy and imaging. Further developments in electron optics, insertion devices, and x-ray optics will solidify this advantage.

The APS is home to emerging technologies on which advances in the synchrotron radiation study of materials will be based. These include multilayer Laue lens optics for x-ray focusing [32], high-resolution primary beam monochromators and analyzers for inelastic scattering [33], high-pressure research [34], and a myriad of other areas. These efforts provide the APS with an important foundation for future developments.

## Scientific Community

There is a large community of researchers, scientists, and technologists who will find new ways of connecting to synchrotron radiation experiments using the developments described here. This scientific community will be strengthened by these developments through new opportunities for one-of-a-kind experiments at the cutting edge of synchrotron radiation technology. Such studies are the basis for future work with broad impact in the community. The challenges in these areas span all of the disciplines of materials science and involve communities of researchers in academia, industry, and government laboratories.

## Requirements and Capabilities

### Full-field microscopy and tomography

The development of full-field imaging and diffraction-enhanced imaging capabilities is essential to advancing areas of research that depend on surveying large areas of materials, including crystal growth and imaging random events. In studying 3-D phenomena, including crystal growth, real-time or near real-time tomographic reconstructions with high rates of data acquisition and analysis are essential. The proposed long beamline for imaging will provide for larger fields of view.

### Nanodiffraction

To address the questions associated with atomic positions in semiconductor devices, a state-of-the-art beamline with a beam size  $\sim 10$  nm or better and with energy resolution below 1 eV over the 5-keV to 30-keV range is needed. Large gradients in the strain distributions near the feature edges are convoluted by larger x-ray microbeam sizes. In order to capture the strain distributions in these critical regions, a smaller beam size is required. X-ray nanoprobe with improved spatial resolution in diffraction, imaging, and spectroscopy will allow us to measure these strain distributions at a much finer length scale that is commensurate with current silicon device sizes ( $< 65$  nm). Data analysis software that can be used to interpret the x-ray scattering from such small domains will be required for effective use of these new x-ray probes.

### Short-pulse sources

The Short-Pulse X-ray Source (SPX) will extend time-resolved capabilities to the important 1-ps time scale for the study of dynamic compression, dynamics in applied fields, and imaging random events while retaining the user-controlled continuous tunability of energy, polarization, and bandwidth combined with x-ray intensity and pulse-length stability over a wide energy range. The very high average flux ( $\sim 10^{13}/s$ ) of the proposed SPX, combined with high repetition rate excitation methods and year-round operation, will enable time-resolved studies with unprecedented precision, yielding joint resolution of picoseconds and picometers for a variety of atomic, molecular, chemical, and material systems.

## Environments

For dynamic compression experiments, the challenge is to combine the dynamic loading capabilities developed by groups at the DOE's NNSA laboratories with the microscopic measurement capabilities at the APS. The development in this sense could parallel the precedent of the High Pressure Collaborative Access Team at the APS, and result in the establishment of a first-of-a-kind user facility dedicated for dynamic compression experiments. For imaging random events, both elevated temperatures to 1500° C and controlled gaseous environments (e.g., water vapor or other corrosive species) coupled with dynamic loading are essential. Crystal growth requires a similar commitment to sample environments that can be integrated with imaging, scattering, and spectroscopy experiments.

## Facility-wide improvements and infrastructure

There are four facility-wide improvements that must accompany the critical upgrades in scientific capability.

**Information technology** Software to process the stream of data arising from these scattering and imaging tools. Advances in beamline control software are necessary to allow these experiments to take place routinely. This improvement in the information infrastructure will simplify use of the APS and allow its capabilities to reach wider groups of materials researchers.

**Beamlines** Better stability in beamline software and hardware must be achieved to allow experiments with *in situ* components. The accelerator side of the APS has developed metrics for the availability of the beam that enable the progress being made in optimizing the facility to be quantified, and a similar push needs to be made for the beamlines.

**Detectors** Improved point and area detectors for scattering and fluorescence will be required to allow the diffraction and imaging experiments to proceed.

**Infrastructure** Facility additions that enable the safe and usable installation of a variety of sample processing and synthesis environments will be needed, together

with access modes that permit long-term installation of both complex user-designed environments optimized for a particular material system, and general environmental chambers. Infrastructure needs include adequate ventilation and exhaust systems, and capability for gas and chemical handling, cleaning, and sensing.

## References

- [1] *Directing Matter and Energy: Five Challenges for Science and the Imagination*, A Report from the Basic Energy Sciences Advisory Committee (U.S. Department of Energy, December 20, 2007). [http://sc.doe.gov/bes/reports/files/GC\\_rpt.pdf](http://sc.doe.gov/bes/reports/files/GC_rpt.pdf)
- [2] *Basic Research Needs for Materials under Extreme Environments*, Report of the Basic Energy Sciences Workshop on Materials under Extreme Environments, June 11-13, 2007. (Office of Basic Energy Sciences, Department of Energy, February 2008). [http://www.sc.doe.gov/bes/reports/files/MUEE\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/MUEE_rpt.pdf)
- [3] D.J. Norris, A.L. Efros, and S.C. Erwin, "Doped Nanocrystals," *Science* **319**, 1776 (2008).
- [4] I. Souza, J. Iniguez, and D. Vanderbilt, "First-principles approach to insulators in finite electric fields," *Phys. Rev. Lett.* **89**, 11760 (2002).
- [5] H. Yasuda, I. Ohnaka, K. Kawasaki, A. Sugiyama, T. Ohmichi, J. Iwane, and K. Umetani, "Direct observation of stray crystal formation in unidirectional solidification of Sn-Bi alloy by X-ray imaging," *J. Cryst. Growth* **262**, 645 (2004).
- [6] L. Arnberg and R.H. Mathiesen, "The real-time, high-resolution x-ray, video microscopy of solidification in aluminum alloys," *JOM* **59**, 20 (2007).
- [7] W. Utsumi, H. Saitoh, H. Kaneko, T. Watanuki, K. Aoki, and O. Shimomura, "Congruent melting of gallium nitride at 6 GPa and its application to single-crystal growth," *Nat. Mater.* **2**, 735 (2003).
- [8] M. Azuma, T. Saito, S. Ishiwata, H. Yoshida, M. Takano, Y. Kohsaka, H. Takagi, and W. Utsumi, "Single-crystal growth of transition metal oxides at high pressures of several GPa," *J. Phys: Condens. Matt.* **14**, 11321 (2002).
- [9] T. Saito, T. Terashima, M. Azuma, M. Takano, T. Goto, H. Ohta, W. Utsumi, P. Bordet, and D.C. Johnston, "Single crystal growth of the high pressure phase of  $(VO)_2P_2O_7$  at 3 GPa," *J. Solid State Chem.* **153**, 124 (2000).
- [10] S. Mitchell, T. Biswick, W. Jones, G. Williams, and D. O'Hare, "A synchrotron radiation study of the hydrothermal synthesis of layered double hydroxides from MgO and  $Al_2O_3$  slurries," *Green Chem.* **9**, 373 (2007).

- [11] R. Ruiz, H.M. Kang, F.A. Detcheverry, E. Dobisz, D.S. Kercher, T.R. Albrecht, J.J. de Pablo, and P.F. Nealey, "Density multiplication and improved lithography by directed block copolymer assembly," *Science* **321**, 936 (2008).
- [12] L. Motiei, M. Altman, T. Gupta, F. Lupo, A. Gulino, G. Evmenenko, P. Dutta, and M.E. van der Boom, "Self-propagating assembly of a molecular-based multilayer," *J. Am. Chem. Soc.* **130**, 8913 (2008).
- [13] S. Suresh, *Fatigue of Materials* (Cambridge University Press, Cambridge, 1991).
- [14] B. Lawn, *Fracture of Brittle Solids* (Cambridge University Press, Cambridge, 1993).
- [15] T.T. Lunt, S.T. Pride, J.R. Scully, J.L. Hudson, and A.S. Mikhailov, "Cooperative stochastic behavior in localized corrosion. 2. Experiments," *J. Electrochem. Soc.* **144**, 1620 (1997).
- [16] V.Y. Gertsman and S.M. Bruemmer, "Study of grain boundary character along the intergranular stress corrosion crack paths in austenitic alloys," *Acta Mater.* **49**, 1589 (2001).
- [17] R.H. Mathiesen, L. Arnberg, K. Ramsoskar, T. Weitkamp, C. Rau, and A. Snigirev, "Time-resolved X-ray imaging of aluminum alloy solidification processes," *Metal. Mater. Trans. B* **33**, 613 (2002).
- [18] L. Borcea, G. Papanicalson, C. Tsogka, and J. Berryman, "Imaging and time reversal in random media," *Inverse Probl.* **18**, 1247 (2002).
- [19] C.H. Wang, J.T. Rose, F.K. Chang, "A synthetic time-reversal imaging method for structural health monitoring," *Smart Mater. Struct.* **13**, 415 (2004).
- [20] Y. Chu and W. Chiu, unpublished (2008).
- [21] H.F. Yan, O. Kalenci, I.C. Noyan, and J. Maser, "Coherency effects in nanobeam x-ray diffraction analysis," *J. Appl. Phys.* **104**, 023506 (2008).
- [22] M.L. Lee, E.A. Fitzgerald, M.T. Bulsara, M.T. Currie, and A. Lochtefeld, "Strained silicon, SiGe, and Ge channels for high-mobility metal-oxide-semiconductor field-effect transistors," *J. Appl. Phys.* **97**, 011101 (2005).
- [23] A.I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W.A. Goddard, and J.R. Heath, "Silicon nanowires as efficient thermoelectric materials," *Nature* **451**, 168 (2008).
- [24] S.-E. Park and T.R. Shrout, "Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals," *J. Appl. Phys.* **82**, 1804 (1997).
- [25] C.H. Ahn, A. Bhattacharya, M. Di Ventra, J.N. Eckstein, C.D. Frisbie, M.E. Gershenson, A.M. Goldman, I.H. Inoue, J. Mannhart, A.J. Millis, A.F. Morpurgo, D. Natelson, and J.-M. Triscone, "Electrostatic modification of novel materials," *Rev. Mod. Phys.* **78**, 1185 (2006).
- [26] A. Grigoriev, R. Sichel, H.N. Lee, E.C. Landahl, B. Adams, E.M. Dufresne, and P.G. Evans, "Nonlinear piezoelectricity in epitaxial ferroelectrics at high electric fields," *Phys. Rev. Lett.* **100**, 027604 (2008).

- [27] M. Holt, Z. Wu, Hawoong Hong, P. Zschack, P. Jemian, J. Tischler, Haydn Chen, and T.-C. Chiang, "Determination of Phonon Dispersions from X-Ray Transmission Scattering: The Example of Silicon," *Phys. Rev. Lett.* **83**, 3317 (1999).
- [28] P.G. Evans, E.D. Isaacs, G. Aepli, Z. Cai, and B. Lai, "X-ray Microdiffraction Images of Antiferromagnetic Domain Evolution in Chromium," *Science* **295**, 1042 (2002).
- [29] R. Tickle and R.D. James, "Magnetic and magnetomechanical properties of  $\text{Ni}_2\text{MnGa}$ ," *J. Magn. Magn. Mater.* **195**, 627 (1999).
- [30] Y. Acremann, J.P. Strachan, V. Chembrolu, S.D. Andrews, T. Tyliczszak, J.A. Katine, M.J. Carey, B.M. Clemens, H.C. Siegmann, and J. Stohr, "Time-resolved imaging of spin transfer switching: Beyond the macrospin concept," *Phys. Rev. Lett.* **96**, 217202 (2006).
- [31] Y.H. Matsuda, T. Inami, K. Ohwada, Y. Murata, H. Nojiri, Y. Murakami, H. Ohta, W. Zhang, and K. Yoshimura, "High-Magnetic-Field X-ray Absorption Spectroscopy of Field-Induced Valence Transition in  $\text{YbInCu}_4$ ," *J. Phys. Soc. Japan.* **76**, 034702 (2007).
- [32] H.C. Kang, J. Maser, G.B. Stephenson, C. Liu, R. Conley, A.T. Macrander, and S. Vogt, "Nanometer linear focusing of hard x rays by a multilayer Laue lens," *Phys. Rev. Lett.* **96**, 127401 (2006).
- [33] T.S. Toellner, M.Y. Hu, G. Bortel, W. Sturhahn, and D. Shu, "Four-reflection 'nested' meV-monochromators for 20-30 keV synchrotron radiation," *Nucl. Instrum. Meth. A* **557**, 670 (2006).
- [34] Y. Meng, G. Shen, and H.K. Mao, "Double-sided laser heating system at HPCAT for in situ x-ray diffraction at high pressures and high temperatures," *J. Phys. Condens. Matt.* **18**, S1097 (2006).

## Renewal of the Advanced Photon Source: Polymers & Soft Materials

<b>Kenneth R. Shull</b> (Chair)	<i>Northwestern University</i>
<b>Gila E. Stein</b>	<i>National Institute of Standards and Technology and University of Houston</i>
<b>Mark L. Schlossman</b>	<i>University of Illinois at Chicago</i>
<b>Jin Wang</b>	<i>Argonne National Laboratory</i>
<b>Brian G. Landes</b>	<i>The Dow Chemical Company</i>
<b>Simon G.J. Mochrie</b>	<i>Yale University</i>
<b>Derk Joester</b>	<i>Northwestern University</i>

### Executive Summary

The Advanced Photon Source (APS) has made a major impact on our understanding of polymers and soft materials. The high-energy x-rays available at the APS are ideally suited for soft materials applications where radiation damage must be minimized and penetration depths maximized. The APS has expanded the research forefront in these areas, with scientific impacts in a range of fields that include energy research, environmental science, and biomaterials development. For example, work at the APS has led to advances in our understanding of the next-generation surface patterning technologies needed by the microelectronics industry, interfacial interactions in liquid systems, and advanced materials processing methods. Progress in these fields has been enabled by the availability of state-of-the-art x-ray techniques, combined with an infrastructure that is particularly well suited to meet the specific needs of outside users. We believe that the APS will continue to be an indispensable tool in the future. For instance, a problem of vital importance is a fundamental understanding of combustion. With a renewed facility, we envision work on

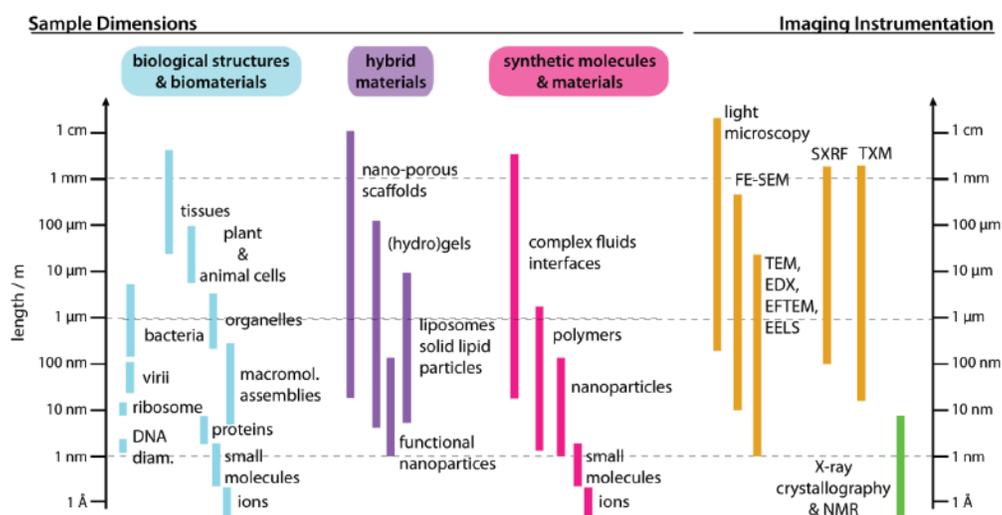


Fig. 1. Scheme of the relevant length scales in synthetic, biological, and hybrid soft-matter samples and available instrumentation for imaging at these different length scales. (Courtesy of Derk Joester, Northwestern University)

bitumen-based fuels to fully understand the fuel extraction and combustion processes. This report concludes with specific recommendations for facility enhancements that enhance the scientific impact of the APS in the field of polymers and soft materials.

## Introduction

Applications of synchrotron-based x-ray probes to soft materials include investigations of traditional synthetic polymers, biological materials, and a wide range of hybrid materials. Uses include traditional reciprocal-space scattering techniques that probe length scales down to the Angstrom level, in addition to imaging modes able to probe length scales from tens of nanometers to millimeters. The spectrum of materials that fall into the soft materials class discussed in this report is illustrated in Fig. 1, which also includes a number of imaging techniques. Although nearly all

types of x-ray probes have been used for the suite of synchrotron-based x-ray techniques, those that are most relevant to soft materials are:

***Small-angle x-ray scattering (SAXS)*** Traditional x-ray Bragg diffraction is not included in this class of methods, since the materials of interest are often (but not always) non-crystalline, and are characterized by longer length scales (nanometers or greater as opposed to Angstroms).

***Grazing incidence x-ray scattering (GIXS)*** This version of x-ray scattering is particularly well suited for investigations of molecular assemblies at surfaces. Both wide-angle and small-angle versions are utilized, depending on the length scale of the surface features being investigated.

***X-ray standing waves (XSW)*** This technique is sensitive to the distributions of heavy atoms near interfaces.

***X-ray photon correlation spectroscopy (XPCS)*** This technique is able to probe the dynamics of electron density fluctuations at the wavelengths typically probed by scattering techniques, on time scales from  $\sim 10^{-3}$  s to  $\sim 10$  s [1].

***Synchrotron x-ray fluorescence (SXRF) microscopy*** Recent developments in this field enable the spectroscopic identification and localization of regions containing only tens of atoms [2].

***Transmission x-ray microscopy (TXM)*** This imaging technique has a resolution limit between those of light microscopy and electron microscopy, but is better suited than electron microscopy for the investigation of hydrated samples [3].

## Key Science Drivers

While a wide variety of examples can be included in order to demonstrate the appli-

cation of advanced x-ray techniques to problems of interest to the soft materials community, we have divided our examples into four general categories, each of which is discussed below in more detail.

## Surface patterning

***Molecular self-assembly at interfaces*** The structure of organic thin films is of interest to multiple scientific communities, including those working in soft-matter physics, applied microelectronics, and energy research. Traditional x-ray scattering methods reveal the structure at molecular and bulk length scales, providing essential information to help establish the origins of macroscopic function, but probing organic thin films is challenging due to weak contrast. As a result, the demand for GIXS at synchrotron sources has greatly expanded in recent years. By operating near the condition for total external reflection, the grazing-incidence geometry is sensitive only to the near-surface region of the sample. Grazing incidence x-ray scattering is perfectly suited to evaluation of silicon-supported samples and permits depth profiling (by varying the penetration depth of the x-rays) to distinguish between the structure at the interfaces and the bulk.

Block copolymer films are ideal model systems for studying interfacial self-assembly because the bulk phase behavior is very well understood, and the molecular parameters controlling structural and dynamic aspects of self-assembly can be exquisitely tuned. Thin block copolymer films self-assemble into periodic domains with size and periodicity on the order of 10 nm, offering a simple and inexpensive route for generating templates for nanolithography templates. X-ray scattering has been integral to advancing our understanding in this field. Some of the most demanding applications for block copolymer lithography require control over the positioning of domains with respect to features on or in the substrate, which is achieved with topographic or chemical registration features. An example of combined “top-down” and “bottom-up” self-assembly with topographic features is the lateral confinement of a single layer of block copolymer spheres in arrays of  $\sim 10\text{-}\mu\text{m}$ -wide wells. Grazing incidence small-angle x-ray scattering (GISAXS) measurements have demonstrated that a single crystal can be assembled in every well, but that the positional correlation function of

the domains decays algebraically, which is unacceptable for patterning addressable media [3]. These experiments offer general insight into the fundamental physics of ordering in low dimensions, as well as specific guidelines for the design of better systems for patterning.

***Structure-property correlations in organic electronics*** Conjugated polymers that are solution processable are being investigated for use in fabrication of low-cost, large-area devices such as thin-film transistors and photovoltaic devices. The efficiency of charge transport is determined by both the molecular and macroscopic structure, such as the packing modes of adjacent polymer chains, the structure of the interface between active components, and the orientation of the conductive pathways with respect to the device. Out-of-plane x-ray diffraction measurements, rocking curve measurements, and in-plane grazing incidence x-ray diffraction experiments have demonstrated the importance of regioregularity, molecular weight, and annealing conditions to achieve well-ordered crystallites of the conjugated polymers, which impacts the power conversion efficiency in photovoltaic materials and charge carrier mobility in thin-film transistors [4,5]. It has also been demonstrated that the substrate surface energy can be tuned to promote the desired crystal orientation, resulting in ten-fold performance enhancements [6].

***Critical dimensions of resist structures*** Resolution of lithographic processes that define integrated circuits is rapidly approaching sub-100-nm dimensions, so new metrology techniques are required to quantify the critical dimensions of these nanostructures. Transmission SAXS with high-energy x-rays has recently been proposed as a solution. The pitch, line width, height, and sidewall angle of resist lines are obtained with nanometer resolution by modeling the form factor oscillations [7], and the potential to measure line-edge/line-width roughness has been demonstrated [8]. Measuring the three-dimensional shape of nanostructures with transmission SAXS requires rotation of the sample with respect to the incident beam over a range of approximately  $50^\circ$ , which is time consuming in terms of executing the experiment and the analysis. Grazing incidence small-angle x-ray scattering is better suited to measuring depth-dependent structures, but the large beam footprint is not appropriate for

patterns that only span small areas ( $\sim 100 \mu\text{m}^2$ ). Constructing a GISAXS beamline with a micrometer-size beam is an attractive alternative, particularly if it were integrated with an atomic-force microscopy or optical microscope to facilitate alignment of the beam to the desired patterns on a chip. Resist relief structures scatter strongly and would not require additional flux to compensate for the reduced spot size.

## Liquid systems

***Assembly at liquid/liquid and liquid/vapor interfaces*** Self-assembly and ordering of ions and molecules at interfaces in soft materials underlies many processes of industrial and scientific importance. For example, biological membranes exist at aqueous-aqueous interfaces and provide a structural and dynamical platform for important cell processes. Phase transfer catalysis, pharmaceutical drug delivery, many electrochemical processes, nanoparticle synthesis, and numerous chemical reactions take place at the interface between two immiscible liquids. Important environmental processes that rely upon interactions at interfaces include tertiary oil recovery, solvent extraction of radionuclides from nuclear waste, and liquid membranes used for the cleanup of heavy metals in the environment. Industrial applications include the use of self-assembled surfactants in many domestic products, ion selective electrodes, and paints and coatings among many others.

Recent x-ray scattering studies of buried liquid/liquid interfaces have probed the distribution of ions at soft interfaces. These distributions underlie processes as diverse as electron and ion transfer at biomembranes and redox processes at mineral-solution interfaces, and also influence many practical applications in analytical chemistry and electrochemistry. The classic Gouy-Chapman theory of ion distributions ignores the liquid structure, i.e., it ignores the sizes and shapes of solvents and ions, as well as any correlations between them. Studies performed at the APS have addressed the limitations in the Gouy-Chapman theory by demonstrating that x-ray reflectivity data from the interface between two immiscible electrolyte solutions can be described by a Poisson-Boltzmann theory that includes a potential of mean force for the individual ions, as well as an electrostatic term [9]. Such studies lay the groundwork for the investigation of electrostatically controlled interfacial processes.

One important application that can take advantage of knowledge recently gained from x-ray scattering from liquid interfaces is extractant-mediated transfer of metal ions from an aqueous to an immiscible organic phase [10]. This process is complex and dynamic, depending on the diffusion of the ionic species in the two phases, the interfacial transport, and the chemical reactions taking place in the system. In spite of a large body of research on this solvent extraction process, no consensus exists on the fundamental mechanism that controls the kinetics. The most important component of any solvent extraction process is the extractant, i.e., a surfactant with a functional group capable of chemical interactions with the target ion. Permeation liquid membranes that contain long-chain azacrown ethers and fatty acid surfactants selectively extract transition metal ions such as Cu(II), Pb(II), and Cd(II), which are common environmental toxins [11]. Understanding these extraction processes requires further investigations of ionic distributions and surfactant ordering at liquid interfaces. X-ray interface scattering provides critical information about these processes that is unavailable from other techniques.

**Biological processes** Many biochemical processes and reactions occur at surfaces and interfaces. These include interactions between cells and the extracellular matrix, protein interactions at cell and organelle membranes, gas transfer at the lung tissue-air interface, and drug intake by cell membranes. Synchrotron x-ray surface scattering techniques are used to determine structure on the sub-nanometer length scale at soft, hydrated interfaces of biological interest. These studies are complementary to macromolecular crystallography because many biointerfacial processes rely upon the interaction of biomolecules within disordered interfacial structures that cannot be crystallized. Recent studies of lipid-protein and lipid-peptide interactions illustrate the power of these techniques. For example, studies of cytosolic phospholipase A<sub>2</sub>-C2 domain binding to a 1-stearoyl-2-oleoyl-sn-glycero-3-phosphocholine monolayer supported on water showed that analysis of x-ray reflectivity yields detailed information on the bound structure of this protein [12]. This structure indicated that the binding mechanism depends upon non-specific electrostatic calculations, hydrophobic interactions, and entropic effects due to water molecules that hydrate the lipid head groups. Future studies of bio-interfacial processes will explore the role of chemical hetero-

geneity in membrane processes and the structural basis for the kinetics of important cell processes such as cell signaling and trafficking.

**Structure and dynamics of emulsified heterogeneous fuels** One of the current grand challenges faced by the world is the depletion of nonrenewable fossil energy resources, including coal, oil, and natural gas. Efficient, environmentally friendly extraction of the remaining resources is of increasing importance. Bitumen-based fuels are an example where enhanced understanding of interfacial issues is needed. Bitumin is a stable, liquid, multiphase fuel made of very fine oil droplets dispersed in water, originating from heavy hydrocarbon feedstock such as refinery residue. Bitumen-based fuels represent a potentially important source of secured energy for the U.S. Extraction and utilization of these fuels in an economically viable way is very challenging. X-ray techniques can provide a better understanding of the extraction process and the structural and combustion properties of the fuel. Fundamental research on combustion of bitumen-based fuels to fully understand the fuel extraction and combustion processes is of vital importance.

**Behavior of high-speed liquid jets** High-speed liquid jets, with Weber number exceeding  $10^3$  and Reynolds number above  $10^5$ , are important in a range of applications

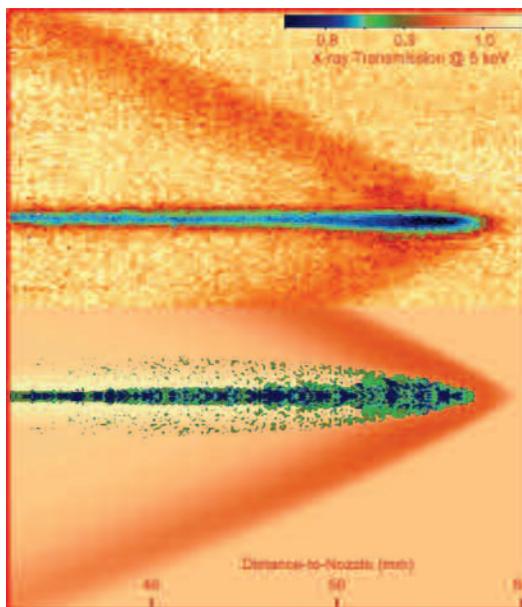


Fig. 2. Diesel jet and shockwave interaction: Microsecond synchrotron-based x-radiography (top) and multiphase computation fluid dynamics simulation (bottom) reveal the unique dynamical structure shock waves emanating from a high-pressure diesel jet. The diesel fuel was injected at 135 MPa into high-density sulfur hexafluoride. The color bar indicates the transmission of 6-keV x-rays, demonstrating the quantitative agreement between the ultrafast radiography and the time-resolved multiphase simulation. This combined approach should be effective for understanding fuel injection and combustion in modern diesel engines. (Im et al., Phys. Rev. Lett., in press [2009]. © 2009 by The American Physical Society)

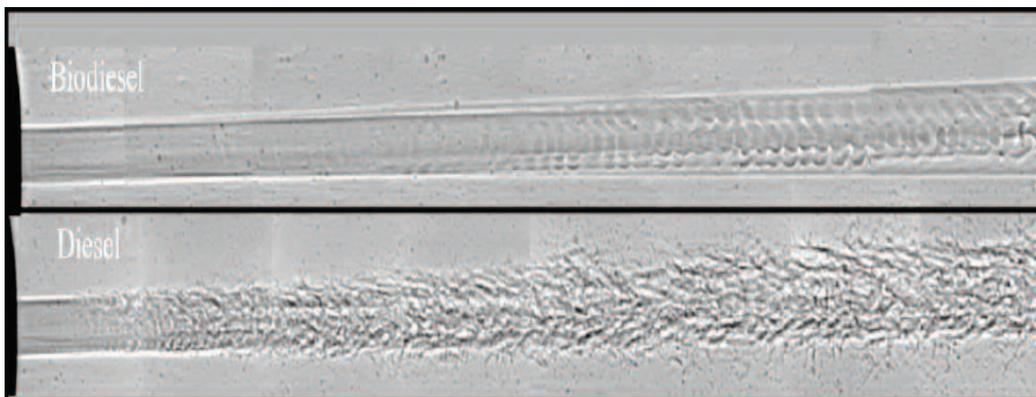


Fig. 3. Ultrafast x-ray images of biodiesel and diesel jets injected at 50 MPa with a common rail injector typically used for passenger car applications. The slight physical property difference between the two types of fuels introduced the great disparity of morphology and breakup properties between them. (Z. Liu et al., unpublished)

in agriculture, energy, medicine, materials processing, and combustion. These jets are poorly understood, largely because scattering prevents visualization of the internal structure by visible light. Techniques recently developed at the APS have enabled imaging of ultrafast phenomena with a time resolution of 100 ps, making it possible to image moving liquid jets traveling at velocities of 10,000 m/s with a motion blur of only 1  $\mu\text{m}$  (Figs. 2 and 3). With this capability we can now address long-standing and fundamental issues of droplet stability in high-speed liquid jets. Related processes of interest include droplet nucleation from a rapidly expanding supercritical fluid mixture.

***X-ray photon correlation spectroscopy studies of dynamics*** In XPCS, characterization of the time correlations in the coherent scattering intensity is used to obtain dynamical information about the sample under investigation. Access to dynamics at small length scales and long time scales makes XPCS valuable for studies of model glassy materials, such as colloidal gels and glasses, where microscopic dynamics become exceedingly slow as the materials approach structural arrest. The approach to glassy states is typically associated not only with a slowing of dynamics but more precisely with a growing separation of microscopic time scales. Certain localized motions, known as “beta” relaxations, remain relatively fast while the terminal structural relaxation becomes exceedingly slow. These beta processes, whose

nature is intimately associated with the approach to the glassy states, have eluded XPCS studies so far. However, the faster time scales accessible with a renewed APS will enable XPCS studies that capture this dynamic.

A wide variety of complex fluids show structures with characteristic length scales that are in the few-tens-of-nanometers range and characteristic dynamics in the microsecond to millisecond range. An enhanced capability to probe dynamics in this range of length and times will enable new opportunities to investigate such materials. Significant examples of such nanostructured complex fluids include nanocolloidal suspensions, mesophases of block copolymers, and membrane-based phases of oil and water mixtures that are stabilized by amphiphilic surfactants, such as the sponge and bicontinuous microemulsion phases. In recent years, these phases have been the subject of intense interest, including detailed theoretical work focusing on their dynamics. However, this dynamical behavior has largely eluded experimental investigation because the key length scales are too small for light scattering and the time scales are too long for neutron spin echo.

## Materials processing

The continual drive for faster integrated-circuit interconnects requires the development of new interlayer dielectric materials with dielectric constants less than 2.2. Porous, polymer-based semiconductor dielectric resins have been developed to achieve this low dielectric constant by introducing nanometer-sized pores into the polymer matrix. The development of metrology to characterize the pores in porous films was critical for the successful adoption of the material by industry, both to ensure that the film attains the desired dielectric properties and to monitor pore characteristics that may impact the integration process. Due to the complex nature of the porous structure, on-wafer characterization methods needed to be developed in order to quantify the porosity in porous films of SiLK™, a silicon-based, low-dielectric-constant material produced by The Dow Chemical Company. The use of SAXS to measure void fraction, pore size and size distribution, pore morphology, and their uniformity across porous dielectric films was made possible by technology developed at the APS and enabled a successful adoption of the material by the semiconductor

industry. In addition, the SAXS methodology developed at the APS was used as the basis for commercial metrology technology demanded by that same industry.

## Nanomaterials

The impact of nanotechnology on materials research is hard to overestimate. As applications, especially in imaging and bionanotechnology, are starting to be commercialized, fundamental research into making “smart” nanomaterials by sophisticated design strategies is becoming increasingly important. Very frequently, the resulting materials are hybrids of inorganic, organic, and/or biological molecules. Examples for such hybrids are oligonucleotide-functionalized  $\text{TiO}_2$  nanoparticles [12], peptide amphiphile carbon nanotube assemblies, and inorganic or Au/Si/Au multilayered nanoshells [13]. Nanoparticles are usually characterized by light-scattering techniques, by spectroscopy in case of fluorescent particles, by dry transmission electron microscopy/scanning electron microscopy, or dry/wet scanning probe microscopy (SPM). Especially in the case of complex assemblies, liposomes, and hybrid materials it is crucial that the particles remain pristine in their aqueous environment away from the distorting influence of overpowering interfacial forces that they are exposed to in conventional SPM imaging. APS instrumentation, specifically synchrotron x-ray fluorescence and transmission electron microscopy are ideally positioned to aid in the development of high-resolution imaging applications utilizing next-generation hybrid and transiently stabilized amorphous nanoparticles.

## Significance of the APS

The APS has already played a leading role in the development and use of many of the techniques described above. Notable examples include the imaging capabilities utilized for liquid jets and for heavy-metal atom distributions.

An additional factor of significance is the nature of the partnership between the users and staff scientists at the APS. The development of the nanoporous dielectric materials is a good example of this type of partnership. The scattering intensity

from these relatively thin, nanoporous films is quite low, and the background from parasitic scattering needed to be reduced considerably in order for these experiments to be successful. The resulting design, development, and application of ultra-low-background on-wafer transmission SAXS represented a true breakthrough technology and provided the semiconductor industry with a fast, quantitative screening tool for commercial-scale processes. This development was made possible only by the ability of the APS to optimize both a beamline and an experimental configuration for a specific application. Once a successful experimental protocol was fully defined, the key attributes were transferred for development on both laboratory- and commercial-scale devices. These advances led to development of commercial technology by equipment vendors for use in both laboratory and production environments. As a result, it is now possible to rapidly and accurately quantify the average pore size and pore size distributions for nanoporous SiLK™ coatings. This approach has been adopted by a variety of industrial partners, customers, and instrument vendors as the primary tool for porous media characterization. The technology has provided significant understanding of the effects of chemistry, formulation, and process on the development and retention of porous structures in SiLK™ films. In addition, this technology is now ready to provide information on the effects of the previously listed variables on both incipient pore formation and on the kinetics of pore development during cure. Future development is focusing on high-throughput methods for both data acquisition and data reduction/analysis.

## Scientific Community

The examples given in the previous sections illustrate ways in which the soft-materials community benefits from APS capabilities. Some of the broad thematic areas that the APS is able to address are further delineated below.

***Environmental research*** Metals, radionuclides, and (potentially) metal and semiconductor nanoparticles are major anthropogenic contaminants in a wide range of environmental settings. War and terror activities are increasingly adding

to already significant industrial pollution of this kind. In order to better understand the fate of these elements in natural systems, we must gather more information on the occurrence of these metals in amorphous and crystalline mineral phases, on colloidal particles, and on the mechanisms that control their release and migration in the surface environment (e.g., the sequestration of nanoparticles by agarose fibers). In order to probe their (radio)toxicity, we must understand how they interact with microbes on a cellular and organismic level. APS imaging capabilities play an important role in this work.

***Biomaterials research*** Examples include biologists who are interested in studying physiological processes, biophysicists interested in the underlying mechanisms of such processes, and materials scientists who are interested in using these processes to synthesize new materials. Imaging applications based on the use of functional nanoparticles as contrast agents are an additional area of relevance.

***Energy research*** Examples include processing issues related to polymer-based, affordable solar cells; fuel extraction from bitumen; and jet stability and droplet nucleation in fuel sprays.

## Requirements and Capabilities

The following capabilities are needed in order to build on existing work, and to accomplish some of the broader goals mentioned in previous sections.

### Extended energy range

Development of a liquid-interface instrument that is optimized for use at high energies (30 keV to 80 keV, or possibly higher) would be useful for the study of buried interfaces, including liquid-liquid, liquid-solid, and solid-solid interfaces. Use of higher energies would minimize absorption effects and valence changes in ions, and allow access to certain resonances in heavy metals.

## Detector resolution

As top-down/bottom-up assembly techniques move closer to perfection, the resolution limits of two-dimensional detectors will prevent analysis of the diffraction line shape. This is just one area where enhanced detector resolution would be helpful.

## Beam focusing, time resolution

The development of x-ray scattering from liquid interfaces has been closely tied to advances in synchrotron sources and instrumentation. These experiments usually require a very brilliant x-ray beam. Flat, buried interfaces, such as liquid/liquid interfaces or bilayer lipid membranes supported at the solid/water interface, can be studied with the high-energy x-rays currently available. Needed advances include focusing techniques that are optimized for the study of liquid interfaces that are heterogeneous, small in lateral extent, or highly curved. Also, new time-resolved instruments are required to meet the need for studying kinetic and dynamic interfacial processes at interfaces. Development of a time-resolved dispersive reflectometer will address the need for studying kinetic and dynamic interfacial processes, as well as the need for fast measurements of fragile biological materials.

## Cryogenic capabilities

With much-enhanced resolution in imaging, the demands on sample preparation have increased dramatically. Previously practiced “gold standard” procedures are now rapidly becoming obsolete: Random crosslinking by chemical fixation, structural distortions by drying, elemental contamination, and relocation and removal of mobile/soluble species by staining and washing can no longer be tolerated. Even more important is the realization that many soft-matter samples contain structural water or maintain their structure only in the presence of a solvent. This has led to a renaissance of cryogenic imaging in electron microscopy, and similar developments are needed in the x-ray community. It is thus imperative that synchrotron-based x-ray imaging instrumentation be adapted so that routine work at cryogenic temperatures becomes possible in the next five years.

## References

- [1] P. Falus, M.A. Borthwick, and S.G.J. Mochrie, "Fast CCD camera for x-ray photon correlation spectroscopy and time-resolved x-ray scattering and imaging," *Rev. Sci. Instrum.* **75**, 4383 (2004).
- [2] T. Paunesku, S. Vogt, J. Maser, B. Lai, and G. Woloschak, "X-ray fluorescence microprobe imaging in biology and medicine," *J. Cell. Biochem.* **99**, 1489 (2006).
- [3] G.E. Stein, E.J. Kramer, X. Li, and J. Wang, "Single-crystal diffraction from two-dimensional block copolymer arrays," *Phys. Rev. Lett.* **98**, 086101 (2007).
- [4] R.J. Kline, M.D. McGehee, E.N. Kadnikova, J.S. Liu, J.M.J. Frechet, and M.F. Toney, "Dependence of regioregular poly(3-hexylthiophene) film morphology and field-effect mobility on molecular weight," *Macromolecules* **38**, 3312 (2005).
- [5] Y. Kim, S. Cook, S.M. Tuladhar, S.A. Choulis, J. Nelson, J.R. Durrant, D.D.C. Bradley, M. Giles, I. McCulloch, C.S. Ha, and M. Ree, "A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene: fullerene solar cells," *Nat. Mater.* **5**, 197 (2006).
- [6] R.J. Kline, M.D. McGehee, and M.F. Toney, "Highly oriented crystals at the buried interface in polythiophene thin-film transistors," *Nat. Mater.* **5**, 222 (2006).
- [7] R.L. Jones, T. Hu, E.K. Lin, W.L. Wu, R. Kolb, D.M. Casa, P.J. Bolton, and G.G. Barclay, "Small angle x-ray scattering for sub-100 nm pattern characterization," *Appl. Phys. Lett.* **83**, 4059 (2003).
- [8] C.Q. Wang, R.L. Jones, E.K. Lin, W.L. Wu, B.J. Rice, K.W. Choi, G. Thompson, S.J. Weigand, and D.T. Keane, "Characterization of correlated line edge roughness of nanoscale line gratings using small angle x-ray scattering," *J. Apply. Phys.* **102**, 024901 (2007).
- [9] G. Luo, S. Malkova, J. Yoon, D.G. Schultz, B. Lin, M. Meron, I. Benjamin, P. Vanysek, and M.L. Schlossman, "Ion Distributions near a Liquid-Liquid Interface," *Science* **311**, 216 (2006).
- [10] J. Rydberg and C. Musikas, "Principles and Practices of Solvent Extraction," *Principles and Practices of Solvent Extraction*, G.R. Choppin, ed. (Marcel Dekker, New York, 1992) p. 1.
- [11] J. Buffle, N. Parthasarathy, N.K. Djane, and L. Mattheiasson, "Permeation liquid membranes for field analysis and speciation of trace compounds in waters," *In Situ Monitoring of Aquatic Systems: Chemical Analysis and Speciation*, J. Buffle and G. Horvai, eds. (John Wiley & Sons, Chichester, 2000) p. 407.

- [12] S. Malkova, F. Long, R.V. Stahelin, S.V. Pingali, D. Murray, W. Cho, and M.L. Schlossman, "X-Ray Reflectivity Studies of cPLA2 $\alpha$ -C2 Domains Adsorbed onto Langmuir Monolayers of SOPC," *Biophys. J.* **89**, 1861 (2005).
- [13] X.H. Xia, Y. Liu, V. Backman, and G.A. Ameer, "Engineering sub-100 nm multi-layer nanoshells," *Nanotechnology* **17**, 5435 (2006).
- [14] C. Wang, T. Araki, B. Watts, S. Harton, T. Koga, S. Basu, and H. Ade, "Resonant soft x-ray reflectivity of organic thin films," *J. Vac. Sci. Tech. A* **25**, 575 (2007).

# Scope of the Advanced Photon Source Renewal Proposal

## Introduction

The designs of the Advanced Photon Source (APS) storage ring (which began operations in 1996) and the associated beamlines date back to roughly 1990. In the intervening years, there have been significant advances (many developed at the APS) in accelerator technology, beamline optics, x-ray detectors, and scientific computing that enable entirely new x-ray capabilities. To address the future, and even current, needs of users and provide the best hard x-ray capabilities to the United States, the APS is in need of a major renewal that will systematically and comprehensively incorporate these advances into the fabric of the APS scientific infrastructure.

The focus of the APS renewal will be achieving this goal through enhancements of the x-ray beamlines (including the insertion devices and front ends). Major improvements are also being considered for the accelerator complex, including increasing the beam current to 200 mA, introducing a lattice with long straight sections, and improving beam stability. Beamline enhancements can range from the replacement of a few components for improved performance to the construction of an entirely new beamline from insertion device to station instrumentation. Equally important to new beamline hardware on the experiment hall floor are improvements to technical support capabilities. These include ancillary instrumentation for sample handling and preparation, state-of-the-art x-ray optics fabrication and metrology capabilities, upgrades to the computing infrastructure, and new or improved software for data acquisition and analysis. In addition to these enhance-

ments, we will develop a plan to deal with obsolescence issues at the APS, which are becoming severe. This will be complementary to the renewal proposal and we hope to support it through use of our normal capital and Accelerator Improvement Project funds freed up for this purpose during the renewal period.

We estimate that the renewal will take from 6 to 7 years and cost between \$300 M and \$400 M. Because there is not a large civil construction component to this proposal, and the renewal involves many aspects that can be developed concurrently, the renewal funding profile can be front loaded to accelerate the time scale.

## New and Upgraded Beamlines

At this point in time, the full scope of the beamline renewals has not been finalized. However, two things are already clear: (1) the three remaining straight sections will be completed and (2) several long beamlines (extending outside of the existing experiment hall) will be required. Unfortunately, the open straight sections are not all in the correct location for extending beamlines and so some beamlines will have to be “moved” (or more likely rebuilt) to free up sectors where extended beamlines will be compatible with existing buildings, real estate for the extended beamlines and stations, roads, wetlands, etc. In addition, some beamlines may need to be relocated to take advantage of long straight sections in a new lattice, which cannot be arbitrarily located in the storage ring.

We envision future beamlines as not just places to use x-rays to study a sample, but as laboratories where many experimental techniques can be applied to solve the problem at hand. As summarized in the report by the APS renewal Condensed Matter and Materials Physics (CMMP) science team, which appears elsewhere in this proceedings:

“This proposal encompasses a transformational change in the way experiments are undertaken at major synchrotron facilities. Rather than having the x-ray studies con-

ducted separately, a complete suite of experiments will be performed *in situ* on the beamline in real time by combining a variety of probes and processing tools. End-stations on rolling platforms may be moved in place or x-ray beams may be brought to semi-permanent installations, through collaborations from contiguous institutes where the hot questions are pursued 24/7.”

## Technical Support

Included under the heading “Technical Support” are a variety of items not necessarily associated with a particular beamline. These include improved detectors, detector fabrication capabilities and associated support, upgraded optical fabrication and metrology facilities, support labs, and ancillary equipment for the development of state-of-the-art sample environments that allow for multiple fields (pressure, temperature, electric fields, and magnetic fields) to be applied simultaneously.

Again from the CMMP 2010 report: “This means that the APS will have to reorganize to act as a single organic entity to address a hierarchy of scientific questions in a coherent manner. The APS will need to make room for new twenty-first century science, expanding some of its lab modules into full-service laboratories, of which the Center for Nanoscale Materials can be considered as a first model.”

## Detector development and procurement

Based on the proposals for beamline enhancements that we have received to date, many of the requests for improved detectors can be satisfied by detector systems that are commercially available today (or are expected to be on the market in the next five years or so). Nonetheless, not all requests can be met by simple procurements of off-the-shelf items and so other avenues will have to be pursued in order to meet these needs such as collaboration with groups that develop novel sensors and application-specific integrated circuits (ASICs), contracts with companies to build custom detectors based in existing technology, utilizing the Small Business Innovation Research Program/Small Business Technology Transfer Program process to develop new tech-

nologies, and getting increasingly involved with detector component R&D (i.e., research at the sensor and ASIC level).

## Optics

Although the APS has had a strong optics fabrication and metrology track record, much of our equipment is now showing its age and is no longer state-of-the-art. As part of the renewal, we are proposing an upgraded deposition system (new sputtering chamber) for multilayer Laue lens fabrication, and differential deposition for figuring Kirkpatrick-Baez mirrors. Our metrology instruments will be in need of upgrades as well, as it is “hard to make it when you can’t measure it.” We propose to procure a new Fizeau interferometer with a sample stage capable of measuring large mirrors, and a new atomic-force microscope. Finally, the Optics Fabrication and Metrology Group has proposed the development of a metrology and detector bending magnet beamline for at-wavelength metrology of mirrors. Such a beamline will also provide a stable set-up for tests of nanofocusing optics and detector testing and calibration, and can also be used to beta-test new software before it is installed on operating beamlines. Higher storage ring beam current will necessitate new front-end optics for many beamlines, so state-of-the-art high-power-load stable beam delivery optics will be developed and implemented as part of the renewal, to the benefit of all sectors.

## Sample environments

A more centralized support for specialized sample environments at the APS (expanding the HPSynC concept [[http://www.aps.anl.gov/Users/Scientific\\_Interest\\_Groups/HP-SynC/index.html](http://www.aps.anl.gov/Users/Scientific_Interest_Groups/HP-SynC/index.html)]) will be an important future step. A coherent and coordinated development of sample environments that support multiple fields (pressure, temperature, electrical, magnetic, etc.) will keep the facility on the cutting edge of science. Additionally, a key focus must be portable environmental systems because a single beamline does not have all the techniques required to solve complex scientific problems. Portable environment systems under consideration include sample levitation apparatus, *in situ* catalysis cells, and extreme chemical environments.

## Software

A common theme throughout many of the beamline renewal proposals was the need for better and more user-friendly data collection and data analysis packages. Data handling and analysis are increasingly a bottleneck for producing science from synchrotron experiments and are often a serious potential barrier to new and/or inexperienced users. Stated simply, we need to invest in this effort to both reduce the learning curve needed to use the facility and to improve the efficiency of the facility.

The capabilities offered by high-performance computing for near real-time optimization of experiments and for off-line data reduction are now attracting great interest in numerous areas of the community. This is an area that is ripe for investment.

Other areas that need attention are improved visualization of data and portable controls that can easily move between beamlines. We need to prepare for extensive remote access in the future, which implies fail-safe hardware, increased use of robotics, and secure methods of remote connection.

## Support laboratory instrumentation

Various support laboratories to be instrumented either near or adjacent to research stations in the experiment hall will dramatically enhance users' ability to prepare and characterize samples. Depending on the scientific area of a particular x-ray beamline, we envision laboratories equipped with specialized instruments, such as microscopes and lasers, to provide researchers with additional tools to better understand the system of interest. For example, laboratories with the capability to synthesize materials close to the x-ray facility will offer flexibility for the study of transient process. Support laboratories will clearly broaden many areas of research.

## Accelerator Systems

Portions of the science-based renewal strategy for the APS involve improvements to

the accelerator and facility infrastructure. In March 2008, APS management solicited proposals that addressed these areas. Over 80 proposals were received and were presented in an open forum in October 2008.

### **Increased current capabilities**

The existing stored beam current is 100 mA. By increasing the beam current to 200 mA, we can double the brilliance and flux, offering immediate improvements to many experiments such as inelastic scattering. At the same time, most beamlines will need improved optics, which can deliver potentially higher performance both in throughput and stability. The accelerator is designed to be ready for up to 300-mA operation, but some improvements will be needed to accommodate higher current. For example, improved higher-order mode damping systems will allow us to sustain the standard 24-bunch operating mode with higher current, and several older front ends will need replacement.

### **Long straights**

We have demonstrated that straight sections up to 8 m in length (compared with the existing 5 m) can be relatively easily incorporated into a new lattice provided they are introduced in a symmetrical pattern. Longer straights permit the use of longer undulators, which directly improve the x-ray source.

### **Improved electron and photon beam stability**

A program to improve photon beam stability from source to detector will be an integral part of the renewal. This program includes potential improvements in the storage ring tunnel temperature for better mechanical stability of the magnets and vacuum chambers, improvements in radio-frequency (rf) beam position monitoring and feedback for a more stable electron beam, and enhanced x-ray beam position and flux monitoring capabilities to pin down instabilities in beamline optical components. Early prototype work on the electron and photon beam position monitoring technology has demonstrated that substantial improvements will be achieved with a full deployment.

## Facility Infrastructure

The infrastructure category includes projects directed at both civil and computing infrastructure.

### Civil construction

Enhancements in this area include build-out of lab/office module (LOM) 437, expanding some existing LOMs to accommodate the increased staff that will be required to operate multiple beamlines from canted insertion devices, and satellite buildings for extended beamlines. A building adjacent to the storage ring that will serve as a staging and assembly area during project construction—and will later be used as an APS storage building—is also being evaluated. We will examine the need for any utility system expansion in order to support additional beamlines and buildings.

### Computing/networking

Computing infrastructure is the electronic backbone on which both beamlines and accelerator are totally dependent. Upgrades will be required to support the huge demands caused by the combination of additional beamlines and the amount of data generated by faster and larger detectors. These factors, coupled with the ever-advancing speed of computing hardware, will require investment in order to provide sufficient capacity for analysis, storage, and transfer of data.

## Short-Pulse Project

The science needs of the APS renewal anticipate the provision of very short x-ray pulses, on the order of 1 ps. In order to provide this to the user community, the APS staff is carrying out R&D toward implementation of a scheme developed by A. Zholents of Lawrence Berkeley National Laboratory. The scheme uses an rf deflecting cavity to impose a correlation (chirp) between the longitudinal position of the electron within the bunch and the vertical position/angle. A downstream cavity is needed to remove this chirp. Either bunch slicing or x-ray optics can then be used to produce a

short x-ray pulse. The project will include development of continuous-operation superconducting rf cavities, front ends, and beamline components. It is anticipated that the Short-Pulse X-ray Project will provide ultrafast x-ray pulses to several beamlines.

## Insertion Devices

As part of the APS renewal, users are considering ways in which insertion device(s) can be more precisely suited to their experimental programs. In some cases, the customization is as simple as a planar undulator with a new period length. Even seemingly small changes in period can result in a 2- or perhaps 3-fold increases in brilliance, depending on the photon energy and the tunability required. A few users are seeking increased brilliance at higher (>20-keV) photon energy, with a greater range of tunability than can be achieved with permanent magnets. An R&D project is under way to develop a short-period superconducting undulator to meet these requests. Short sections of superconducting magnetic structure have been successfully built and tested. The project is now extending into longer structures; cooling schemes are being developed for a full-size undulator that can be installed in the storage ring.

Users are also interested in photons with circular or variable polarization. An additional advantage of a circularly-polarizing undulator is that the on-axis radiation only includes the first harmonic, with no higher harmonic contamination. Also, most of the heat load in the beam from such a device is off-axis and can be masked off so that it never reaches sensitive beamline components further downstream.

An electromagnetic undulator with both horizontal and vertical field coils for producing linear polarization (either vertical or horizontal, or left- or right-handed circular polarization) is under development. In addition, users want to have the option of reducing higher-harmonic contamination even in linear polarization mode, so additional coils for introducing quasiperiodicity into the magnetic field are being incorporated.

Still other users are requesting an APPLE-style undulator that uses permanent-magnet arrays to produce variable (linear, circular, or elliptical) polarization. A project to bring such a device to the APS is in the early stages.

## Estimated Cost and Schedule

Table 1 provides an estimate of the budget allocations to various broad categories of the renewal.

Table 1. Estimate of APS renewal budget allocations.

<b>Project</b>	<b>Cost (\$M)</b>
New and upgraded beamlines	152.0
Technical support	67.0
Detector development and procurement	
Optics	
Sample environments	
Software	
Support laboratory instrumentation	
Accelerator systems	39.2
Increased current capabilities	
Long straights	
Improved electron and photon beam stability	
Facility infrastructure	20.0
Civil construction	
Computing/networking	
Short-Pulse Project	23.5
Insertion devices	12.8
<b>Total</b>	<b>314.5</b>
Contingency (25%)	78.6
<b>GRAND TOTAL</b>	<b>393.1</b>

# Appendices

## Appendix A. Advanced Photon Source Renewal Workshop Agenda

### Monday, October 20, 2008

7:30 a.m.	Registration	
8:15 a.m.	Welcome	Dennis Mills (Argonne National Lab.)
8:30 a.m.	Charge	J. Murray Gibson (Argonne National Lab.)
9:00 a.m.	Macromolecular Crystallography	K. Moffat for T. Kossiakoff (both Univ. of Chicago)
9:30 a.m.	Polymers and Soft Materials	K. Shull (Northwestern Univ.)
10:00 a.m.	Chemical Science & Engineering	J. Miller (Argonne National Lab.)
11:00 a.m.	Condensed Matter and Materials	J. Freeland for S. Bader (Argonne National Lab.)
11:30 a.m.	Engineering Applications / Applied Science	G. Ice (Oak Ridge National Lab.)
12:00 p.m.	Discussion of Presentations	All
12:30 p.m.	Working Lunch: Infrastructure Upgrades	J. Maclean (Argonne National Lab.)
1:30 p.m.	APS Upgrade Options	M. Borland (Argonne National Lab.)
2-5:00 p.m.	Breakout Sessions: <i>Macromolecular Crystallography</i> <i>Polymers/Soft Materials</i> <i>Condensed Matter and Materials</i> <i>Engineering Applications / Applied Science</i> <i>Chemical Science &amp; Engineering</i>	
5:00 p.m.	Summaries and Discussion	Team Chair or Designee

**Tuesday, October 21, 2008**

8:30 a.m.	Materials Science & Technology	P. Evans (Univ. of Wisconsin)
9:00 a.m.	Life Sciences	L. Makowski (Argonne National Lab.)
9:30 a.m.	Fundamental Interactions in Chemical, Atomic, and Molecular Physics	L. Young (Argonne National Lab.) for S. Rice (Univ. of Chicago)
10:00 a.m.	Geological, Environmental, and Planetary Science	N. Sturchio (Univ. of Illinois at Urbana-Champaign)
11:00 a.m.	Surfaces, Interfaces, and Thin Films	P. Fenter (Argonne National Lab.)
11:30 a.m.	Accelerator Opportunities	R. Gerig (Argonne National Lab.)
12:00 p.m.	Working Lunch: Medium Term Upgrade Proposal	Dennis Mills (Argonne National Lab.)
1-4:00 p.m.	Breakout Sessions:  <i>Materials Science &amp; Technology</i>  <i>Life Sciences</i>  <i>Fundamental Interactions in Chemical, Atomic, &amp; Molecular Physics</i>  <i>Geological, Environmental, &amp; Planetary Science</i>  <i>Surfaces, Interfaces, and Thin Films</i>	
4:00 p.m.	Summaries and Discussion	Team Chair or Designee
5:00 p.m.	Scientific Advisory Committee Perspective	Scientific Advisory Committee
5:30 p.m.	Wrap-Up	APS Renewal Committee

## Appendix B. Advanced Photon Source Renewal Workshop Attendees

Almer, Jonathan  
*Argonne National Laboratory*

Als-Nielsen, Jens  
*Københavns Universitet*

Alatas, Ahmet  
*Argonne National Laboratory*

Amer, Yeldez  
*Argonne National Laboratory*

Anderson, Wayne  
*Northwestern University*

Arnold, Ned  
*Argonne National Laboratory*

Baines, Stephen  
*Stony Brook University*

Bedzyk, Michael  
*Northwestern University*

Beno, Mark  
*Argonne National Laboratory*

Blasie, Kent  
*University of Pennsylvania*

Bolin, Trudy  
*Argonne National Laboratory*

Borland, Michael  
*Argonne National Laboratory*

Brister, Keith  
*Northwestern University*

Brody, Ryan  
*Argonne National Laboratory*

Bunker, Bruce  
*Notre Dame University*

Cai, Zhonghou  
*Argonne National Laboratory*

Chance, Mark  
*Brookhaven National Laboratory*

Chapman, Karena  
*Argonne National Laboratory*

Chen, Yu-Sheng  
*The University of Chicago*

Chiu, Wilson  
*University of Connecticut*

Chu, Yong  
*Argonne National Laboratory*

Chupas, Peter  
*Argonne National Laboratory*

Cyl, David  
*Argonne National Laboratory*

De Carlo, Francesco  
*Argonne National Laboratory*

Decker, Glenn  
*Argonne National Laboratory*

Den Hartog, Patric  
*Argonne National Laboratory*

Detlefs, Carsten  
*European Synchrotron Radiation Facility*

Dufresne, Eric  
*Argonne National Laboratory*

Einspahr, Howard  
*Bristol-Meyers Squibb (retired)*

Eng, Peter  
*The University of Chicago*

Evans, Gwyndaf  
*Diamond Light Source Ltd.*

Evans, Paul  
*University of Wisconsin-Madison*

Feng, Yejun  
*Argonne National Laboratory*

Fenner, Richard  
*Argonne National Laboratory*

Fenter, Paul  
*Argonne National Laboratory*

Fernandez, Patricia  
*Argonne National Laboratory*

Fezzaa, Kamel  
*Argonne National Laboratory*

Finney, Lydia  
*Argonne National Laboratory*

Fischetti, Robert  
*Argonne National Laboratory*

Freeland, John  
*Argonne National Laboratory*

Fuoss, Paul  
*Argonne National Laboratory*

Gerig, Rod  
*Argonne National Laboratory*

Gibson, J. Murray  
*Argonne National Laboratory*

Giometti, Carol  
*Argonne National Laboratory*

Gluskin, Efim  
*Argonne National Laboratory*

Gog, Thomas  
*Argonne National Laboratory*

Graber, Timothy  
*The University of Chicago*

Gray, Kenneth  
*Argonne National Laboratory*

Greenlee, Kendra  
*North Dakota State University*

Gupta, Yogendra  
*Washington State University*

Haeffner, Dean  
*Argonne National Laboratory*

Harkay, Katherine  
*Argonne National Laboratory*

Haskel, Daniel  
*Argonne National Laboratory*

Heald, Steve  
*Argonne National Laboratory*

Hong, Hawoong  
*Argonne National Laboratory*

Hwu, Yeukuang  
*Academia Sinica*

Ice, Gene  
*Oak Ridge National Laboratory*

Ilavsky, Jan  
*Argonne National Laboratory*

Islam, Zahirul  
*Argonne National Laboratory*

Jacobsen, Chris  
*Stony Brook University*

Jaski, Yifei  
*Argonne National Laboratory*

Jemian, Pete  
*Argonne National Laboratory*

Joachimiak, Andrzej  
*Argonne National Laboratory*

Joester, Derk  
*Northwestern University*

Karapetrova, Evgunia  
*Argonne National Laboratory*

Kaufmann, Elton  
*Argonne National Laboratory*

Keane, Denis  
*Northwestern University*

Keavney, David  
*Argonne National Laboratory*

Kelly, Shelly  
*UOP*

Kemner, Ken  
*Argonne National Laboratory*

Klein, Miles  
*University of Illinois at Urbana-Champaign*

Knowlton, J. Randy  
*National Institutes of Health*

Kropf, A. Jeremy  
*Argonne National Laboratory*

Kuzmenko, Ivan  
*Argonne National Laboratory*

Lai, Barry  
*Argonne National Laboratory*

Lal, Jyotsana  
*Argonne National Laboratory*

Landes, Brian  
*The Dow Chemical Company*

Lang, Jonathan  
*Argonne National Laboratory*

Lee, Byeongdu  
*Argonne National Laboratory*

Lee, Wah-Keat  
*Argonne National Laboratory*

Levine, Lyle  
*National Institute of Standards & Technology*

Li, Yuelin  
*Argonne National Laboratory*

Liebermann, Robert  
*Stony Brook University*

Lienert, Ulrich  
*Argonne National Laboratory*

Lin, Binhua  
*The University of Chicago*

Liu, Haozhe  
*Harbin Institute of Technology*

Liu, Di-Jia  
*Argonne National Laboratory*

Long, Gabrielle  
*Argonne National Laboratory*

Lurio, Laurence  
*Northern Illinois University*

Mao, Ho-kwang (David)  
*Carnegie Institution of Washington*

Maclean, John  
*Argonne National Laboratory*

Macrander, Albert  
*Argonne National Laboratory*

Makowski, Lee  
*Argonne National Laboratory*

Maser, Jorg  
*Argonne National Laboratory*

McNulty, Ian  
*Argonne National Laboratory*

Meron, Mati  
*The University of Chicago*

Miller, Jeff  
*Argonne National Laboratory*

Miller, Lisa  
*Brookhaven National Laboratory*

Miller, Matthew  
*Cornell University*

Mills, Dennis  
*Argonne National Laboratory*

Mitchell, Edward  
*European Synchrotron Radiation Facility*

Moffat, J. Keith  
*The University of Chicago*

Moog, Liz  
*Argonne National Laboratory*

Mooney, Patricia  
*Simon Fraser University*

Myers, Debbie  
*Argonne National Laboratory*

Narayanan, Suresh  
*Argonne National Laboratory*

Appendix B. Advanced Photon Source Renewal Workshop Attendees

Nassiri, Ali  
*Argonne National Laboratory*

Neumann, Dan  
*National Institute of Standards & Technology*

Newville, Matthew  
*The University of Chicago*

Nicol, Malcom  
*University of Nevada, Las Vegas*

Norman, Mike  
*Argonne National Laboratory*

Noyan, Cev  
*Columbia University*

Ogata, Craig  
*Argonne National Laboratory*

Ourmazd, Abbas  
*University of Wisconsin-Madison*

Pellin, Mike  
*Argonne National Laboratory*

Peters, Mark  
*Argonne National Laboratory*

Pianetta, Piero  
*SLAC National Accelerator Laboratory*

Pile, Geoff  
*Argonne National Laboratory*

Pindak, Ronald  
*Brookhaven National Laboratory*

Powell, Chris  
*Argonne National Laboratory*

Preissner, Curt  
*Argonne National Laboratory*

Quintana, John  
*Argonne National Laboratory*

Ramanathan, Mohan  
*Argonne National Laboratory*

Ren, Zhong  
*The University of Chicago*

Resnick, Andrew  
*Case Western Reserve University*

Rivers, Mark  
*The University of Chicago*

Rose, Volker  
*Argonne National Laboratory*

Rosenkranz, Stephan  
*Argonne National Laboratory*

Rosner, Robert  
*Argonne National Laboratory*

Ross, Steve  
*Argonne National Laboratory*

Rusthoven, Brian  
*Argonne National Laboratory*

Ruzicka, William  
*Argonne National Laboratory*

Ryan, Philip  
*Argonne National Laboratory*

Sajaev, Vadim  
*Argonne National Laboratory*

Sakurai, Yoshiharu  
*SPring-8*

Sandy, Alec  
*Argonne National Laboratory*

Schlom, Darryl  
*Pennsylvania State University*

Schlossman, Mark  
*University of Illinois at Chicago*

Schneider, Thomas  
*EMBL Hamburg*

Segre, Carlo  
*Illinois Institute of Technology*

Shastri, Sarvjit  
*Argonne National Laboratory*

Shen, Guoyin  
*Carnegie Institution of Washington*

Shenoy, Gopal  
*Argonne National Laboratory*

Shu, Deming  
*Argonne National Laboratory*

Shull, Kenneth  
*Northwestern University*

Shvyd'ko, Yuri  
*Argonne National Laboratory*

Sidorowicz, Ken  
*Argonne National Laboratory*

Smith, Matt  
*Argonne National Laboratory*

Soderholm, Lynda  
*Argonne National Laboratory*

Srajer, George  
*Argonne National Laboratory*

Stein, Gila  
*National Institute of Standards & Technology*

Stephenson, Brian  
*Argonne National Laboratory*

Stock, Stuart  
*Northwestern University*

Strasser, Susan  
*Argonne National Laboratory*

Streiffer, Steve  
*Argonne National Laboratory*

Strzalka, Joseph  
*University of Pennsylvania*

Sturchio, Neil  
*University of Illinois at Chicago*

Suter, Robert  
*Carnegie Mellon University*

Sutton, Stephen  
*The University of Chicago*

Terry, Jeff  
*Illinois Institute of Technology*

Thompson, Carol  
*Northern Illinois University*

Tiede, David  
*Argonne National Laboratory*

Tischler, Jon  
*Oak Ridge National Laboratory*

Toby, Brian  
*Argonne National Laboratory*

Toellner, Tom  
*Argonne National Laboratory*  
Turneure, Stefan  
*Washington State University*  
Ustundag, Ersan  
*Iowa State University*  
Vajda, Stefan  
*Argonne National Laboratory*  
van Veenendaal, Michel  
*Northern Illinois University*  
Vogt, Stefan  
*Argonne National Laboratory*  
Wagner, Al  
*Argonne National Laboratory*  
Wakatsuki, Soichi  
*KEK*  
Wang, Jin  
*Argonne National Laboratory*  
Waychunas, Glenn  
*Lawrence Berkeley National Laboratory*  
White, Marion  
*Argonne National Laboratory*  
Wilkinson, Diane  
*Argonne National Laboratory*

Winans, Randall  
*Argonne National Laboratory*  
Winarski, Robert  
*Argonne National Laboratory*  
Xiao, Xanghai  
*Argonne National Laboratory*  
Xiao, Yuming  
*Argonne National Laboratory*  
Yang, Wenge  
*Argonne National Laboratory*  
You, Hoydoo  
*Argonne National Laboratory*  
Young, Linda  
*Argonne National Laboratory*  
Zhang, Zhan  
*Argonne National Laboratory*  
Zitzka, Sue  
*Argonne National Laboratory*  
Zschack, Paul  
*Argonne National Laboratory*  
Zhang, Ke  
*HD Tech, Inc.*  
Zhao, Jinggzng  
*Harbin Institute of Technology*

## Appendix C.

### Beamline Mid-Term Proposals

Beamline/Sector	Title
1-ID	A Dedicated High-Energy X-ray Beamline for Studying the Mechanical Behavior of Materials
1-ID	Medium-Term (5-Year) Plan for the Development of High-Energy Diffraction Microscopy (HEDM)
1-BM & 11-BM	High-Resolution Powder Diffraction at the APS
2-BM	Mid-Term Plan for 2-BM Upgrade: Integration of Microtomography & Nanotomography Capabilities at 2-BM
2-ID	2-ID Mid-Term Upgrade Plan
3-ID	$\mu$ eV-resolution X-ray Spectroscopy
4-ID-C	Optics & Instrumentation Upgrades for Electronic & Magnetic Materials Research at Beamline 4-ID-C
4-ID-D	Optics & Instrumentation Upgrades for Hard X-ray Magnetic Spectroscopy Research at Beamline 4-ID-D
5	DND-CAT Medium-Term Upgrade Proposal
6-ID	Optics & Instrumentation Upgrades for Resonant Scattering & Diffraction Research at Beamline 6-ID
7-ID	Beamline 7-ID Mid-Term Upgrade Plan
8-ID	Extraordinary New Time-Resolved Capabilities for XPCS & GISAXS
9-BM	Catalyst Center at 9-BM
9-ID	Enhancement of Scientific Facilities for Medium-Energy-Resolution Inelastic Scattering & Liquid Surface Scattering at Beamline 9-ID
10-ID	Study of Complex Materials & Nanostructures Using Hard X-ray Photoemission Spectroscopy
11-ID-B	The Next-Generation Pair-Distribution-Function Beamline (NG-11IDB)
11-ID-D	Upgrade of Laser-Initiated Time-Resolved X-ray Facility for Photochemical Research
12-ID	Development of Dedicated SAXS Beamlines at 12-ID with Canted Undulators
13	Canted Undulator Upgrade for GeoSoilEnviroCARS Sector 13
14	Medium-Term Upgrades Enabling New Science at BioCARS
16-ID	Directing & Controlling Matter under Extreme Pressures & Temperatures: An integrated approach with at least one order of magnitude improvement in spatial, temporal, diffraction, & energy resolution at HP-CAT 16-ID
18-ID	Proposal to Upgrade the Bio-CAT Beamline 18-ID to a Dual-Inline Undulator A Configuration
20	Canted Undulator Upgrade at Sector 20 Providing a High-Throughput Dedicated Micro XAFS Station
26-ID	Nanoscale Phenomena Near Phase Transitions via Temperature-dependent Nanodiffraction
26-ID	Multilayer Laue Lens Microscope: Nanometer Imaging with Hard X-rays
30	Mid-Term Upgrade Proposal for 30-ID XOR/IXS Beamline
32-ID	Mid-Term Plan for 32-ID Upgrade
33	Surface & Interfacial Science at the APS
34-ID	Science Opportunities for 3-D X-ray Diffraction Microscopy - Sector 34
34-ID	Medium-Term Upgrade Proposal for Dedicated Coherent X-ray Diffraction Facility at 34-ID
	Frontier Science by Adding Pressure as a New Dimension at APS Beamlines: HPSynC Upgrade
	A High-Energy Bending Magnet Beamline
	High-Field Magnet Development for X-ray Scattering & Spectroscopy Studies
	A Microfocused, Multiprobe, High-Energy X-ray Beamline for Measurements at Extreme Conditions
	Microminiature XBPM & Flux Monitor for High-Flux Microfocused Hard X-ray Beams
	A New Ultra-High-Sensitivity Intermediate-Energy X-ray Magnetic Circular Dichroism Facility
	Strengthening X-ray Detector Development & Support Efforts at the APS
	Structural Science Using Tunable High-Energy Synchrotron X-ray Source
	Support Structure for Pixel Array Detectors
	Test-Bed for Nanopositioning Technique Enhancement
	Ultrafast-Detector Upgrades
	Understanding the Experiments of the Future
	X-ray BPM System Enhancement



Advanced Photon Source  
Argonne National Laboratory  
9700 S. Cass Ave.  
Argonne, IL 60439 USA

[www.anl.gov](http://www.anl.gov)  
[www.aps.anl.gov](http://www.aps.anl.gov)



A. U.S. Department of Energy laboratory managed by UChicago Argonne, LLC