Structural and High Energy Scattering, Small Angle X-ray Scattering

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Robert Suter	*Carnegie Mellon University*
Randall Winans	*Argonne National Laboratory*

Schedule

Structural and High Energy Scattering, SAXS Location - 431/C010

13:00	13:15	0:15	Introduction	Jan Ilavsky
13:15	13:40	0:25	Nanoscale X-ray Diffraction for Ultralight Elements in Ultrahigh Pressures	David Mao
13:40	14:05	0:25	Scientific Opportunities for High Energy X-ray Diffraction with an MBA Lattice	Robert Suter
14:05	14:30	0:25	In-Situ Study of Dumbbell Nucleation	Elena Shevchenko
14:30	14:55	0:25	New Opportunities for Solar Fuels and Electrochemical Energy Conversion Analysis Using In-Situ Hard X-ray Scattering	Dave Tiede
14:55	15:10	0:15	***Break***	
15:10	15:35	0:25	In-Situ Diffraction and Imaging Studies of Transient and Irreversible Phenomena in Materials	Todd Hufnagel
15:35	16:00	0:25	Prediction and Accelerated Laboratory Discovery of Heterogeneous Catalysts	Kenneth Poeppelmeier
16:00	17:00	1:00	Discussion and Report Writing	

Plan for this group

- Monday October 21 plan:
  - Talks for everyone to get acquainted with the issues, input collection
  - Discussion in small groups for specific subset areas
- Tuesday October 22
  - Work in smaller groups on subset documents
- Wednesday – Thursday (October 23-24)
  - Ilavsky/Levine combine into one document
  - Make available to group in Dropbox
- Friday October 25 – Tuesday October 29
  - Input by committee members, editing
- October 30 – 31
  - Ilavsky/Levine combine into draft
  - Deliver draft to APS
- November 1-4
  - Feedback from committee
- November 5
  - Deliver final report to APS

Want to contribute?
Request invitation to Drobox
(send ilavsky@aps.anl.gov e-mail)
and contribute in your area…

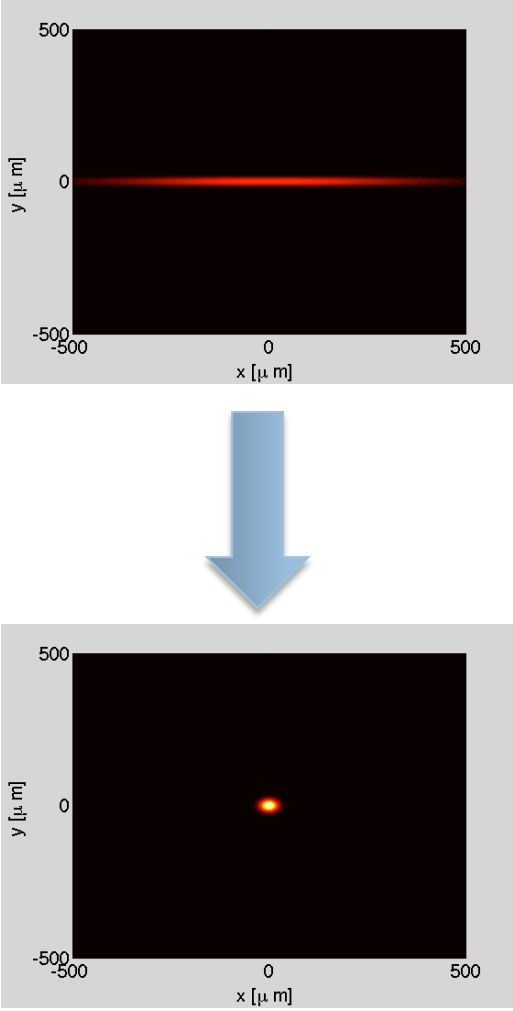
Note: need input on enabling technologies
That seems to be limited at this time.

Recent Advances Enable Ultra-Bright Rings

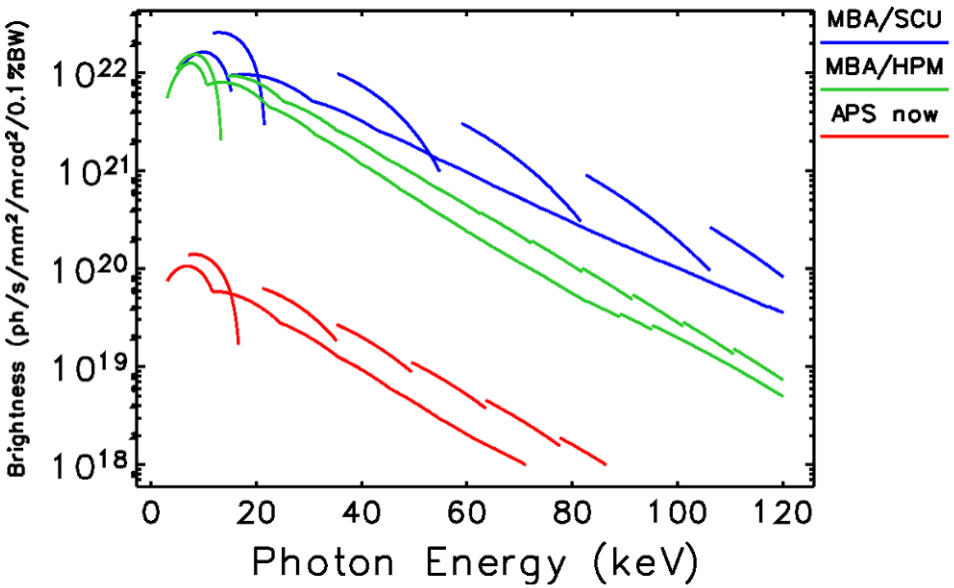
- Storage ring light sources have not reached their practical limits of brightness and coherence.
- Dramatic improvements are on the horizon due to transformational advances in accelerator design.

- **What's Changed:**
  - Tightly-packed multi-bend achromat lattices via new magnet and vacuum technology.
  - Success of top-up, better understanding of storage ring scaling, advances in simulation, optimization, and alignment.

- **Outcome:**
  - High confidence that diffraction-limited rings are feasible.
  - International community is now upgrading existing facilities and building new facilities with diffraction limited capability that will enable new science.

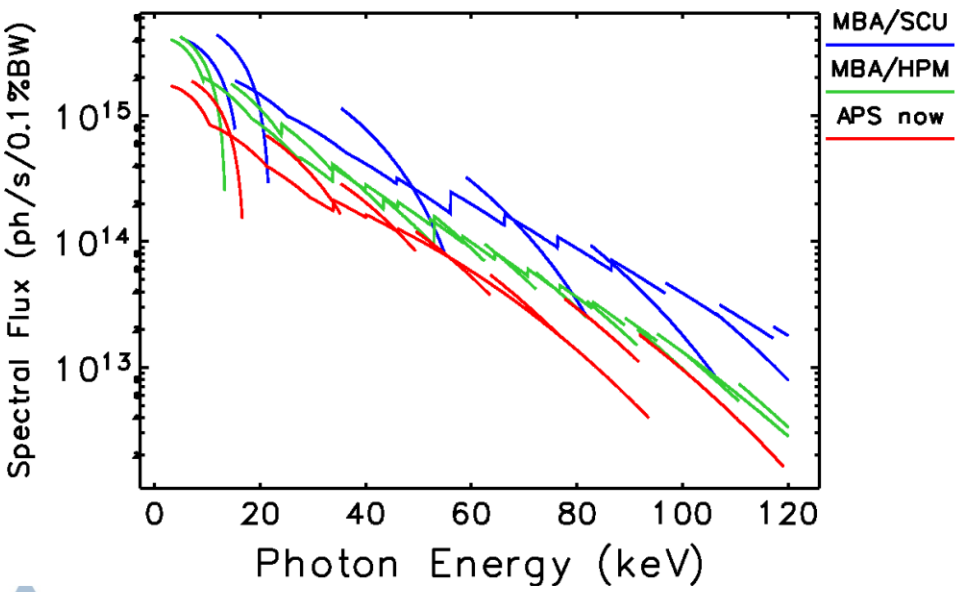


Examples of Preliminary Expected Performance



Brightness increases of 100x or more compared to the brightest devices in APS today

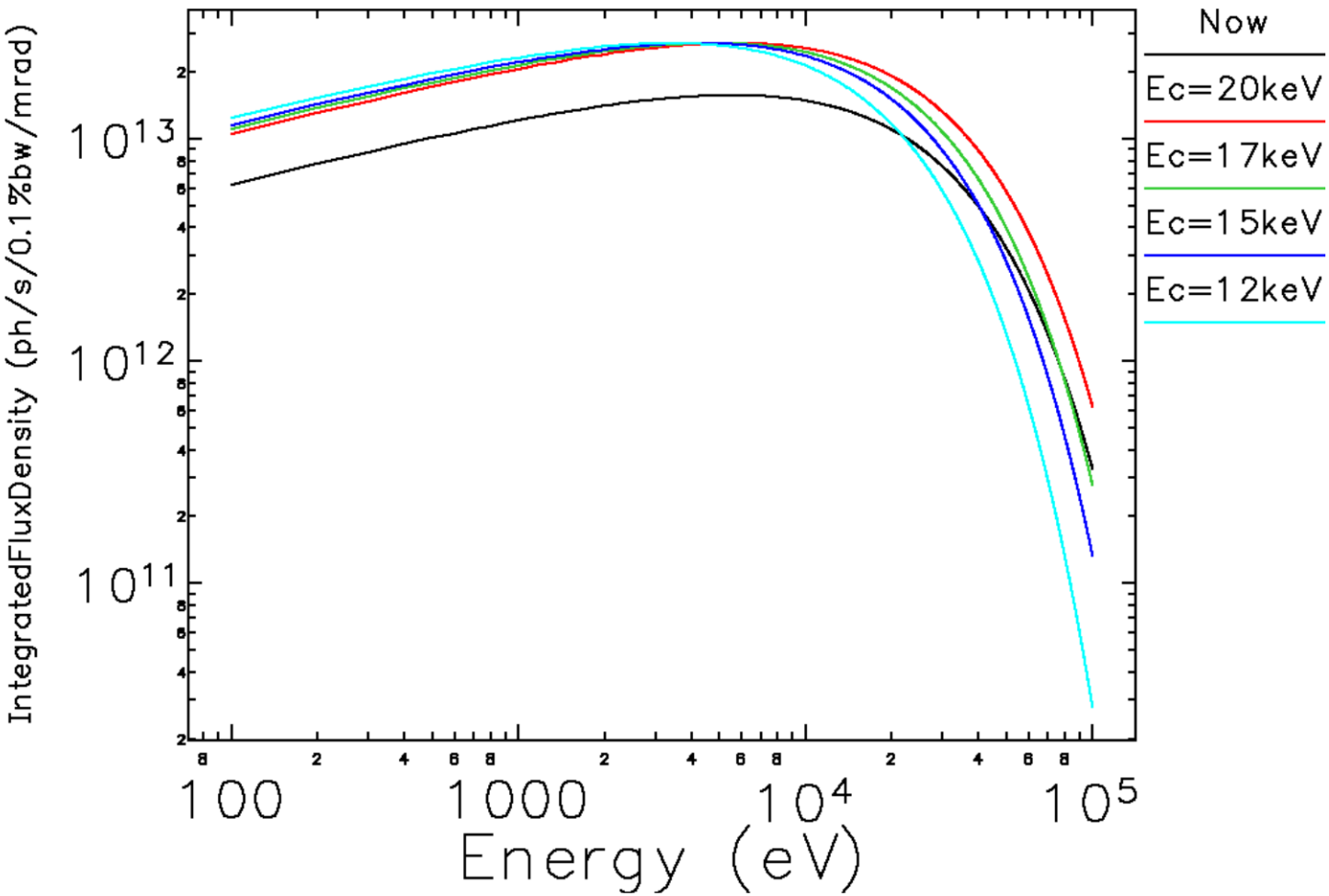
Biggest increases for hard x-rays



Flux increases of about a factor of two or more

APS now: existing 4.8-m U27 and U33 at 100 mA
MBA curves based on latest 80-pm lattice, 200 mA
MBA/HPM: 8.5-mm-gap,4.8-m-long HPMs.
MBA/SCU: 8.5-mm-gap, 3.7-m-long NbTi SCUs.

Bending Magnet Performance



A critical energy of 17 keV matches or beats present performance over a wide range of photon energies

Sector 1 - HEXD Gains with MBA

- APS now:
  - σ_x , σ_y , $\sigma_{x'}$, $\sigma_{y'}$ = 270 µm, 11 µm, 11.4 µrad, 3.5 µrad
  - 1-ID source: PMU, 2.4m long, 2.3 - 2.5 cm period
  - Full beam size at 70 m: 2.0 x 0.7 mm FWHM (H x V)
- MBA lattice:
  - σ_x , σ_y , $\sigma_{x'}$, $\sigma_{y'}$ = 9 µm, 4 µm, 7 µrad, 1.5 µrad (216 bunch-mode, 68 pm emittance, 11 % coupling)
  - 1-ID source: SCU, 2 m long, 1.7 cm period

Technique(s)	Beam type used	Current: Beam size at sample (HxV), µm*	MBA: Beam size at sample (HxV), µm*	Flux(-density) gain on sample: MBA/now (at 70keV)	Comments
Near-field diffraction (nf-HEDM)	1d v-focused@ short-f	2000 x 0.8	1200 x 0.2	3.6 (9.7)	Desire mm's -wide beam
Far-field diffraction, PDF, SAXS	2d focused @ long-f	635 x 26	21 x 9	6.0 (473)	Fully brilliance driven
Far-field diffraction, PDF, SAXS	2d focused @ short-f	19 x 0.8	0.6 x 0.2	6.0 (473)	Fully brilliance driven
Far-field diffraction, PDF, flourescence	Slit, unfocused	Variable (100x100 typ)	Variable (100x100 typ)	6.0 (6.0)	Flux density driven
Direct beam tomography	Full, unfocused	2000 x 700	1200 x 400	2.3 (6.0)	Total flux driven

- Focused #s are source-size limited values (assume perfect optic)

Short-f: 68m source-optic, 2m optic-sample
Long-f: 35m source-optic, 35m optic-sample

11ID MBA Impact on our beamlines/instruments

- 11-ID technical specs (cf 11-ID-B/11-ID-C: PDF, high energy diffraction)
  - 2.3cm Undulator (shared device) -> Superconducting or Helical undulator
  - Monochromator: Brilliance preserving bent Si Laue (fixed E e.g. 59, 86, 107KeV)
    - Lower ring energy will reduce flux at high energy
  - Focusing at high E is challenging: CRLs provide horizontal+vertical focusing
    - Reduced divergence will Improve acceptance/efficiency

- Summary:
  - Reduced relative flux at high X-ray energies (>50keV) is most significant concern
  - x higher flux, smaller beam size
    - Improved diffraction resolution
    - Improved sensitivity of PDF at intermediate length scales
    - Improved time resolution for signal-to-noise limited in-situ measurements
  - Higher coherent fraction
    - ENABLES coherent PDF technique (3-body correlation information) a new paradigm for amorphous materials
  - Smaller horizontal divergence / improved focusing:
    - ENABLES high resolution PDF tomography: e.g. for 3D PDF mapping of complex multicomponent devices such as batteries

Technical Impact on 12ID SAXS

- 12-ID technical specs (cf 12-ID-B/12-ID-C: SAXS and GISAXS)
  - Canted undulators: 3.3 (12IDC) and 2.7 (12IDB) Undulator -> Heat load is not an issue up to 150mA operation.
  - B: Two flat mirrors for focusing/harmonic rejection and Side bounce Monochromator
  - C: Pink mirror and vertical focusing/harmonic rejection mirror.
  - CRLs focusing is in consideration to make pseudo-parallel beam.

- Summary:
  - higher flux due to reduced H beam size/divergence
    - 2~3 times increase at B for the side bounce mono
    - Less fraction of beam will be cut away by slits, which may increase flux at sample by a factor ~2.
    - Improved collimation and thereby SAXS resolution in both minimum q and delta q. Significant improvement for self-assembly or superlattice studies.
    - Should be coupled with a smaller pixel detector and longer sample-to-detector distance.
  - Higher coherent fraction
    - <u>ENABLES</u> coherent small angle scattering imaging and tomography.
    - <u>ENABLES</u> to resolve much sharper peaks and larger domain size due to the longer coherent length (4um→ 100um in H).

15ID USAXS/SAXS/WAXS Technical Impact

- 15ID technical issues (as related to 15ID-D : USAXS, SAXS, WAXS)
  - Undulator A (3.3cm) -> Undulator 2.7mm
  - Si 111 & Si 311 monochromator – no major impact
  - Bimorph mirrors, vertically focusing – used by SAXS only, should be OK
  - Upgrades planned: CRLs – can be customized as needed

- Summary:
  - no major detrimental problems foreseen for any 15ID-D technique
  - 2-3x higher flux, smaller beam size
    - Improves USAXS
    - Improves SAXS
  - Higher coherent fraction
    - ENABLES USAXS-XPCS
  - Smaller divergence horizontal :
    - ENABLES USAXS-Imaging & USAXS-tomography
    - Improves absorption/coherent Imaging
    - Improves 2D-collimated USAXS

BM beamline Powder Diffraction Technical Impact

- Dedicated Powder Diffraction instruments on APS BM beamlines
  - 11-BM (high-resolution), 17-BM (fast area detector)
  - 11-BM and 17-BM share similar source and optics
    - 20 – 35 keV operating energies
    - BM critical energy of 19.5 keV at 7 GeV, with acceptance of 2-3 mrad
    - Collimating and focusing mirrors, with 2 bounce sagittal focusing monochromator
- Impact
    - **Lower ring energy reduces BM flux at X-ray energies most demanded by users**
    - Higher ring current may partially offset flux loss (?)
    - **Important to preserve 3 mrad source to maintain focused flux**
    - Smaller horizontal divergence may (?) simplify sagittal focusing
    - No expected heat load change from new BM sources.
- Opportunities
  - High-resolution experiments
    - Flux limited - significant benefit by relocation to high energy (~ 60 keV) ID source
    - Would facilitate higher throughput, new sample environments, resonant studies
  - Fast area detector experiments
    - Smaller MBA beam size enables diffraction mapping, rastering scans of radiation sensitive samples
    - Reduced horizontal divergence improves integrated resolution of area detector

Division of parts?

- **What is being probed:**
  - Average atomic structure i.e. Crystallography/diffraction (includes high resolution, high energy diffraction)
    - **Matthew Suchomel, Jonathan Almer**
  - Local atomic structure i.e. PDF (includes amorphous materials, nanomaterials, disordered systems, molecular-binding interactions)
    - **Karena Chapman, Todd Hufnagel**
  - Meso-scale structure i.e. SAXS (includes nanomaterials, ...)
    - **Randall Winans, Jan Ilavsky**
  - Micro-scale structure i.e. Engineering Materials/HEDM (includes)
    - **Jan Ilavsky, Lyle Levine, Wenjun Liu, Bob Suter, Jay Schuren**
- **Under what conditions**:
  - Extreme conditions (includes high pressure, magnetic fields, thermo-mechanical deformation, post-irradiation)
    - **Mark Rivers, Guoyin Shen, Stas Sinogeikin, Jay Schuren, Jonathan Almer, Zahir Islam**
  - Reactions and transformations (includes catalysis, batteries, synthesis studies, time-resolved)
    - **Karena Chapman, John Okasinski, Chris Benmore**

Diffraction & Crystallography

Drug formulation screening and characterization

Opportunity

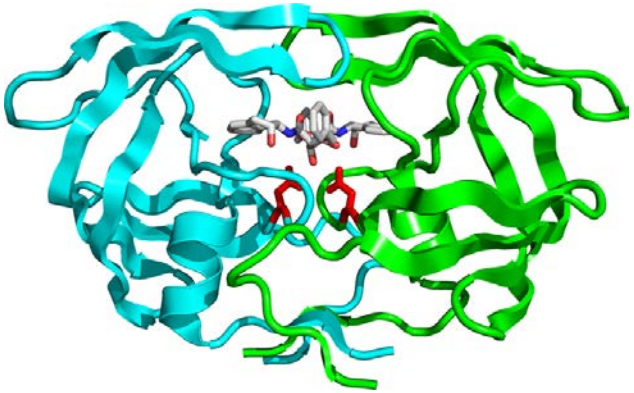
- Development of faster acting and more effective amorphous drug formulations.
- Perform *in-situ* experiments that mimic the spray drying process.
- Probe drug-binder interaction to predict shelf life of amorphous pharmaceuticals.

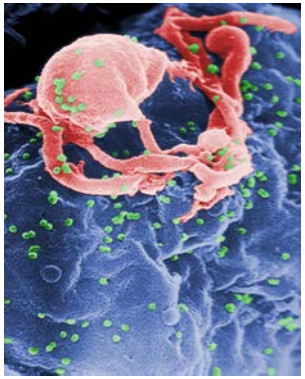
Challenge

- Particle sizes in pharmaceutical spray drying process ~100 microns. Current *in-situ* scattered x-ray intensity on x5 larger levitated droplets too weak to identify amorphous content.

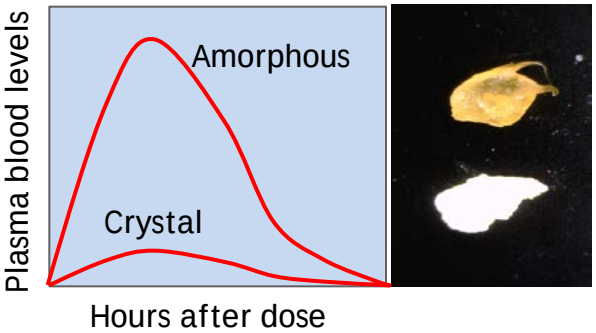
4GSR Strength

- Higher brilliance will allow us to map out optimum drug-binder formulation *in-situ* and determine best spray drying conditions.
- Perform PDF measurements to isolate degree of binding between drug and polymer.





Protease Inhibitors for treatment of HIV



Amorphization of drugs by mixing with binder increases solubility and bioavailability

C.J. Benmore, S.R Byrn et al. J. Pharm. Sci. 102(4) (2013) 1290.

Drug formulation screening and characterization

The important points are :

1) Glassy or amorphous drugs have a much higher solubility (typically anywhere between x2 to x100) and bioavailability than their crystalline forms i.e. you need less of it to have the same effect. There are a handful of glassy drugs on the market e.g. HIV protease inhibitor Ritonavir, cholesterol drug Crestor.
2) Stability (shelf-life) is the biggest problem, so polymer binders are added to keep the drug amorphous longer. Pharmaceutical companies are interested in screening their drug-polymer binder combinations to see which are amorphous and also investigating how the drug is bound to the polymer.
3) Most glassy drugs are made by a spray drying process. The spray dried particles are ~100 microns - too small to be measured currently in-situ. The advantage is being able to probe the structure of the drugs during processing with a more brilliant beam.
4) Currently we use an acoustic levitator to look at the structure of drugs being amorphized which holds much larger particles. Argonne has applied to patent this process. A company Improved Pharma will soon be offering this proprietary characterization service to drug formulation companies.

pdf

PDF single fiber diffraction

Opportunity

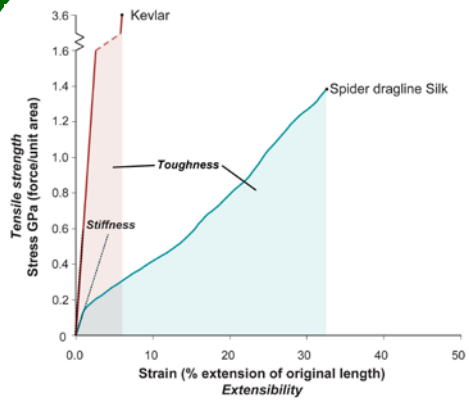
- High energy x-ray PDF studies able to probe nanoscale order on structurally orientated single fibers and heterogeneous materials.
- Characterize spider silk spinning process *in-situ* to enable better synthetic synthesis methods.

Challenge

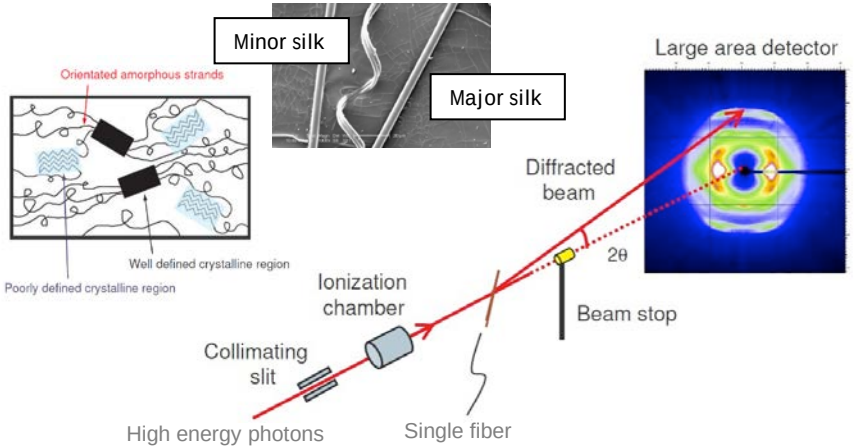
- Total scattering measurements from single fibers of silk are difficult as only 3-4 microns diameter.
- Spiders produce very small amounts of minor silks.

4GSR Strength

- Intense, focused high energy x-ray beams will enable single fiber studies.
- Rubberization of single protein fibers on contact with air, with little or no sample degradation.
- Heterogeneity of disordered materials can be probed.



Silk protein is tougher than steel or kevlar



Spiders produce seven types of silk for different uses
Synthetic silks need to reproduce spinning process

F. Teulé, R. Lewis *et al*. Biopolymers 97(6) (2012) 418. C.J. Benmore, J.L Yarger *et al*. Phys. Rev. Lett, 108, 178102 (2012).

PDF single fiber diffraction

The important points are :

1) Fiber diffraction was used to solve the helical structure of DNA by Watson & Crick and is commonly used to characterize crystalline reflections in reciprocal space.
2) Spider silks are protein fibers which are largely (~90%) amorphous and are tougher than kevlar or steel. Toughness is a combination of tensile strength and extensibility. These silks offer probably the best route towards artificial ligament or tendon replacement.
3) In order to make synthetic silks we need to understand the structural changes that occur during the spinning process, as the protein liquid rubberizes on contact with air (see Teule et al, Biopolymers). This means being able to study the structure of a single, amorphous, low-Z thread of 3-4 microns in diameter with methods like PDF which is not currently possible.
4) By measuring silks with a more brilliant beam out to higher Q-values, PDF measurements as a function of azimuthal angle could be used to characterize the diffuse amorphous structure in real space (See Benmore et al PRL).

Many body correlations in disordered materials

Opportunity

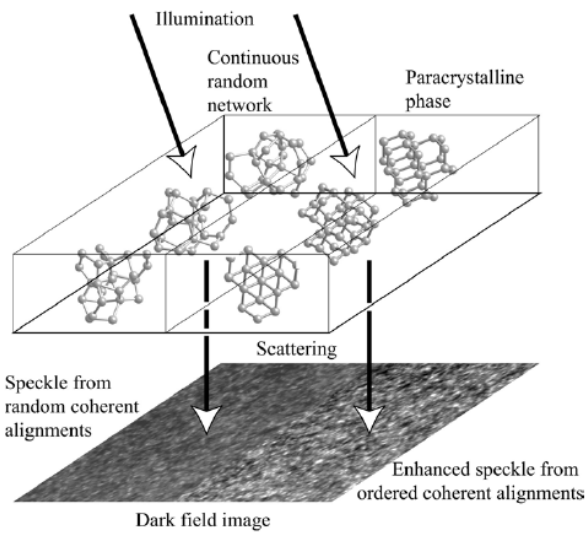
- Currently we probe pair distribution functions (PDF).
- However many body (3-, 4-, 5-body) interactions can be probed using coherently scattered radiation e.g. as a supercooled liquid vitrifies many body correlations become stronger and could provide new information on the glass transition.

Challenge

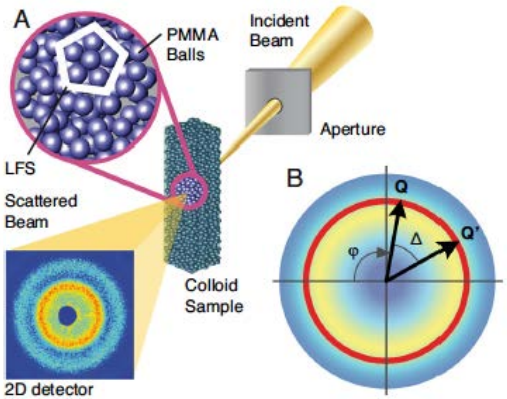
- The degree of coherence in the incident beam needed to observe these correlations needs to be determined.
- New methods of data interpretation will be needed to explain these additional (weak ?) features in the coherently scattered intensity.

4GSR Strength

- The coherent part of the incident x-ray beam will provide additional information on the arrangement of structural entities relative to each other on a the length scale of a few nanometers.



M.M.J. Treacy et al. Rep. Prog. Phys. 2005.



P. Wochner et al. PNAS 2009.

Many body correlations in glasses

The important points are :

1)Little is known about many body correlations in disordered materials because such information is difficult to access and interpret using conventional methods. For example, changes in intermediate range order (on the length scale of 1-2nm) become important during the glass transition as the “ergodic” liquid state crosses over into a “non-ergodic” glassy state.

2)A brilliant coherent x-ray beam has the potential to measure higher order correlations, beyond the well established Pair Distribution Function Method. These higher order correlations are related to intermediate range ordering and dynamic heterogeneities in glasses and amorphous materials.

3)Besides a few previous experiments e.g. Treacy et al. looking at fluctuations in the speckle pattern of glasses and Wochner et al. observing local symmetries in colloidal glasses, the technique has been largely unexplored.

Mesoscales (SAXS & GISAXS)

BIOMOLECULES IN 2D CRYSTALS AND ARRAYS

Opportunity

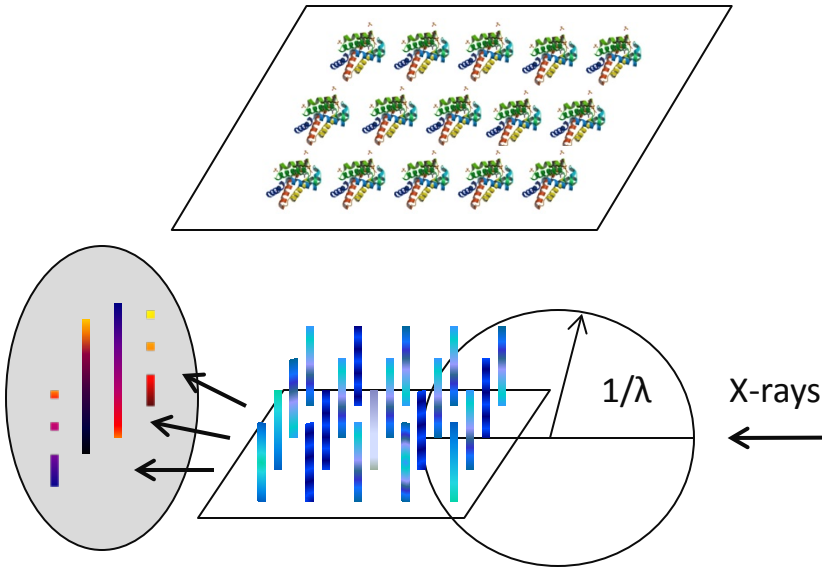
- The upgrade will enable high-resolution structure determination of bio-molecules in 2D crystals and arrays via grazing incidence X-ray scattering and diffraction (GISAXS, GIWAXS, GIXD).
- Grazing incidence permits use of a wide range of supporting materials for engineering order in arrays via the growing field of nanotechnology.

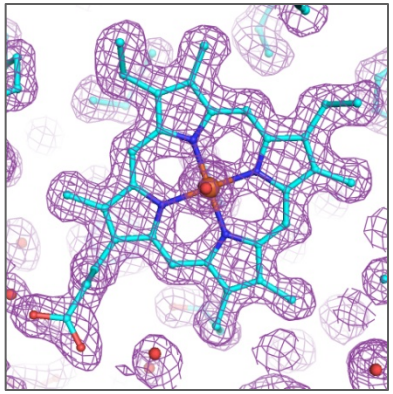
Challenge

- Crystallization is the main bottleneck for determining biological structures at atomic resolution, particularly for membrane proteins, which are attractive pharmaceutical targets.
- Small crystal sizes, disorder, low S/N, and X-ray damage severely challenge current capabilities for determining structures from 2D crystals.

4GSR Strength:

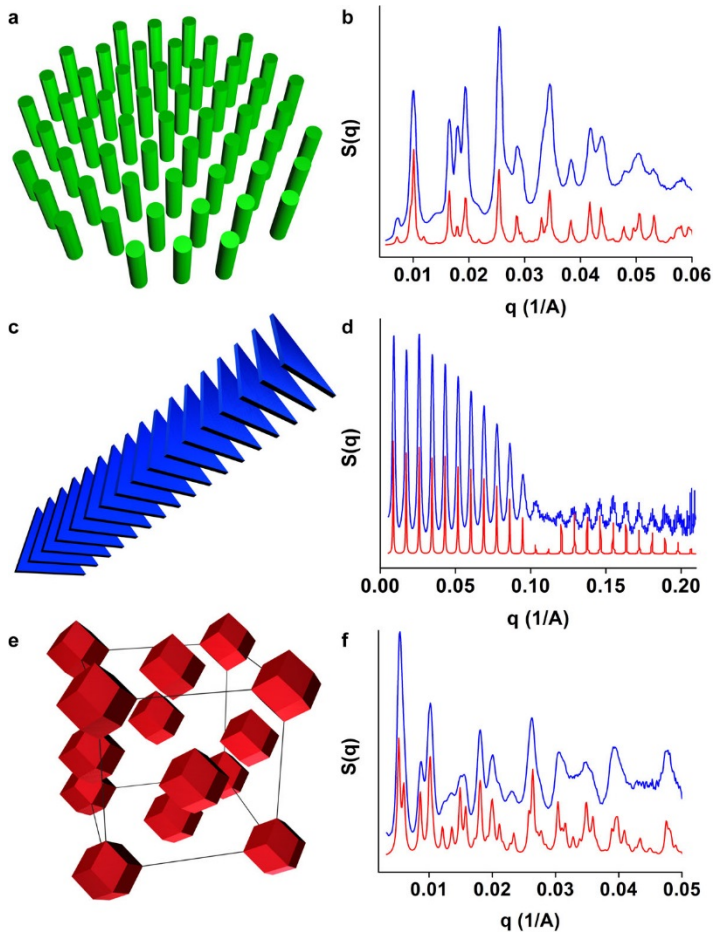
- The improved flux density will facilitate work with small crystals and arrays, which improves feasibility for engineering atomic order, and high beam stability allows smooth merging of data.
- Providing a line focus tuned to the size of small 2D samples, and options to orient undulators, will allow beamline configurations that maximize S/N and minimize X-ray damage.



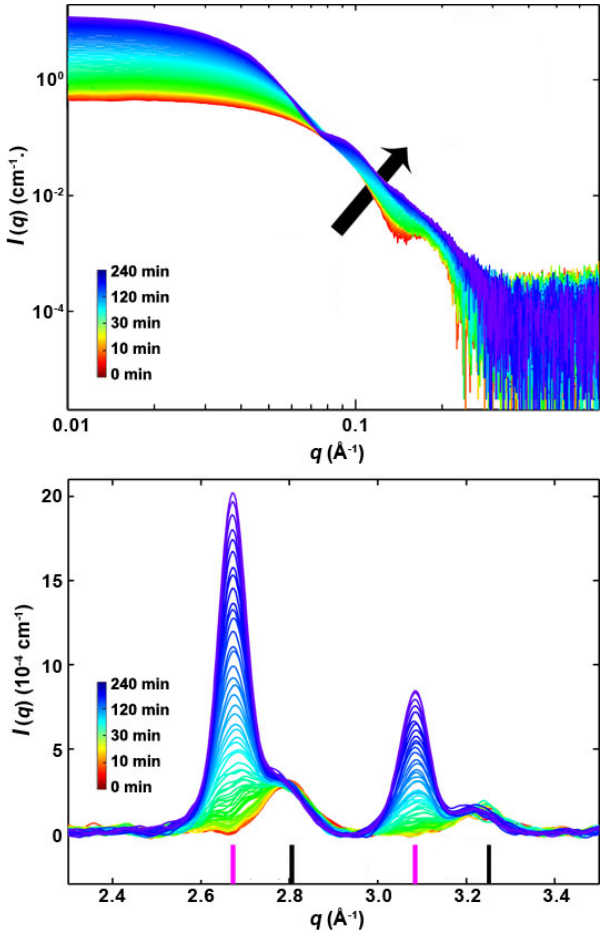


X-ray Scattering for Nanomaterials research

The APS upgrade will facilitate high-resolution structure determination of self-assemblies of nano-building blocks and in-situ synthesis of nanoparticles and their assemblies.



High resolution SAXS data/simulation



In-situ SAXS/WAXS study of nanoparticle growth

Longer coherent length, very good collimation, parallel small beam, and positional stability of x-ray beam are critical for SAXS/WAXS experiments for nanoscale materials.

Engineering materials, HEXD, USAXS

Diffraction Tomography

Opportunity

- Provides rich set of imaging information for any scattered signal; used in lieu of HEDM when spot overlap cannot be avoided:
- Nano-grains, high deformation, weakly ordered systems
- Energy materials and biological materials

Challenges

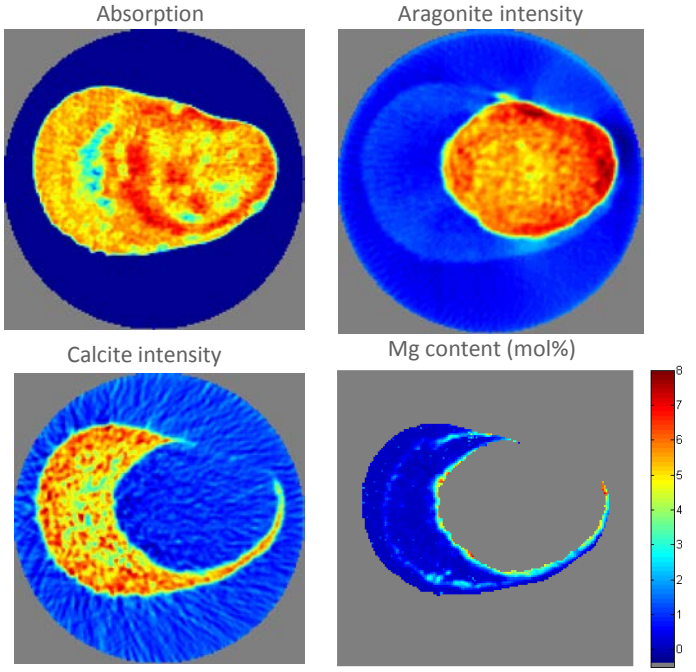
- Require reduced horizontal focal size ~1 um AND small divergence
- Data intense: Need for N^2 measurements for a single layer

4GSR Strength

- Ability to focus horizontally to ~1um will DIRECTLY benefit achievable resolution, currently set at ~10um
- Increased flux will permit rapid data collection
- This combination will allow voxel resolutions to micron level – enabling new methods to image material heterogeneity

Imaging with rich detail

Diffraction spectra from byssus sample are voxellized to produce detailed maps of phase distribution including intra-phase composition. Correlated data for any scattering signal (diffraction/pdf/saxs) can be reconstructed.

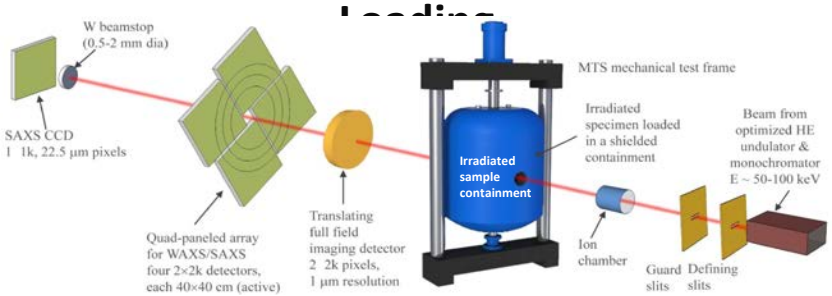


Leemreize, Almer, Stock & Birkedal. J. R. Soc. Interface 10 (2013)

DT technique: scan + rotate

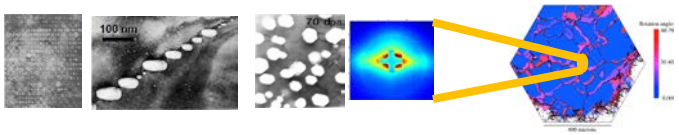
In situ Studies of Nuclear Materials in Extreme Environments

In situ Characterization of Irradiated Materials under Thermal-mechanical Loading



Combined techniques and penetrating hard x-rays visualize material evolution on relevant length scales:

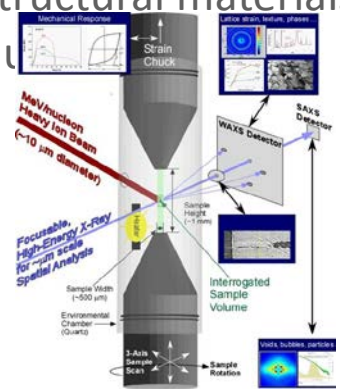
- Tomography = meso-scale structure
- **S**mall **A**ngle **X**-ray **S**cattering = nano-scale structure
- **W**ide **A**ngle **X**-ray **S**cattering = atomic scale structure (phase and lattice strain)

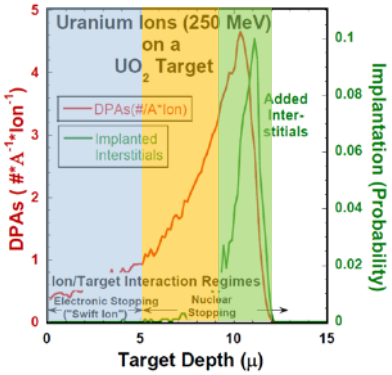


Information of spatial distributions of irradiation defects, e.g. voids and bubbles, and defect annihilation at microstructural sinks measured by combined WAXS/SAXS/tomography is critical to the design of high-performance materials and development of predictive models.

XMAT*:* eXtreme MATertials beamline for *in situ* studies of materials under irradiation

The proposed XMAT beamline will provide x-ray probes for *in-situ* study of materials in simulated nuclear reactor environments, enabling rapid evaluation of new materials performance under extreme service conditions including structural materials and for the first time nu





Focused X-ray beams allow studies of spatially-separated effects with well-controlled parameters in extreme radiation environments.

High-Energy Diffraction Microscopy

Opportunity

- Combined single-grain diffraction and radiographic contrast under in-situ deformation: revolutionary capabilities for basic and applied materials response
- Predictive capability for myriad applications including turbine blades, metal processing and battery operation – Central to materials genome initiative.
- Current development work (ex., AFRL-PUP) dovetails: immediate demand for upgraded capabilities

Challenges

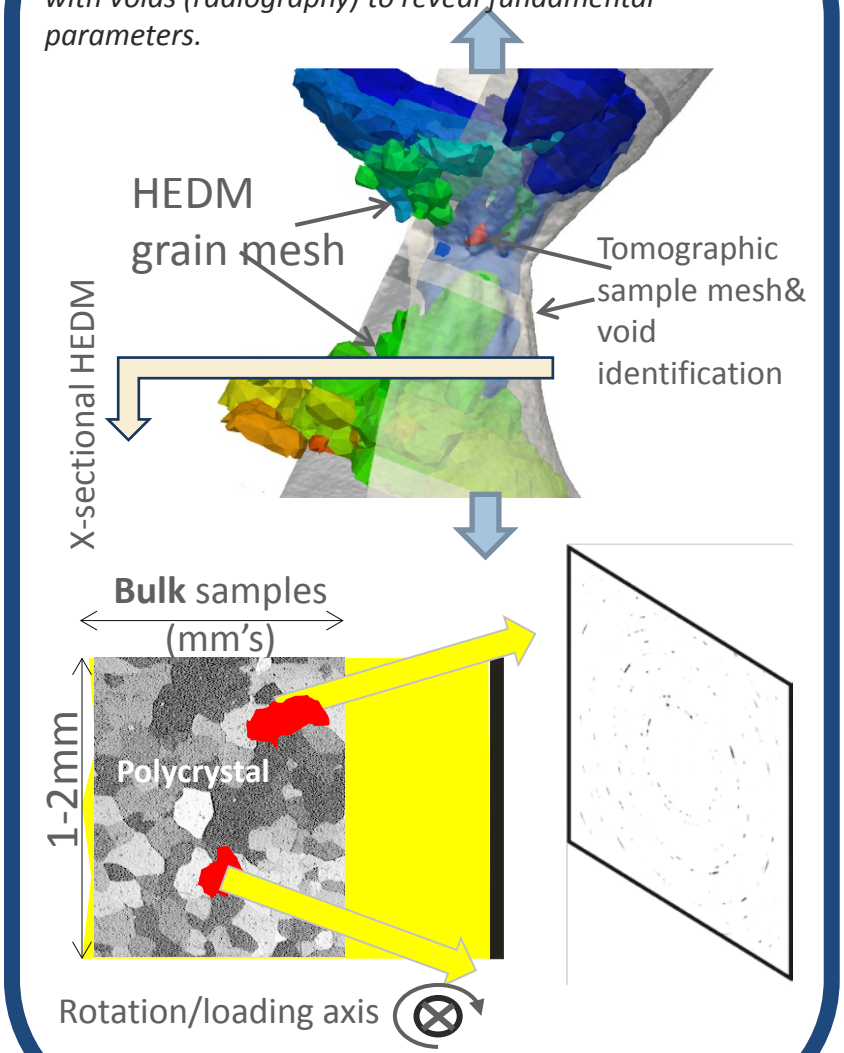
- Require reduced focal size <1 um AND small divergence
- Increased flux needed for high-energy resolution measurements; $\Delta E/E \sim 10^{-4}$ – cuts flux by ~20X from HEDM standard beam

4GSR Strength

- Gain of > 10X intensity at 70keV in focused beam
  - Voxel-by-voxel strain mapping becomes practical
- Submicron focusing
  - Reveal earliest stages of deformation, higher deformation states and more complex materials (e.g. composites)
- Higher flux shifts technique from physics novelty to engineering tool

In-situ deformation studies

Individual grain characteristics (HEDM) can be correlated with voids (radiography) to reveal fundamental parameters.



Images courtesy of B Suter et al.

In Situ Microstructure Imaging Using USAXS

Opportunity

- Macroscopic properties typically emerge from the underlying microstructure in the 10 μm to 100 nm length scale, which is ideal for high-energy USAXS imaging
- Understanding the intrinsic inhomogeneity of these materials holds the promise of optimizing and controlling their remarkable properties.
- Impacts range from improvements in next generation advanced steels, *in vivo* characterization of spinal cord regeneration in lampreys, and process optimization for controlling delamination in flexible electronics.

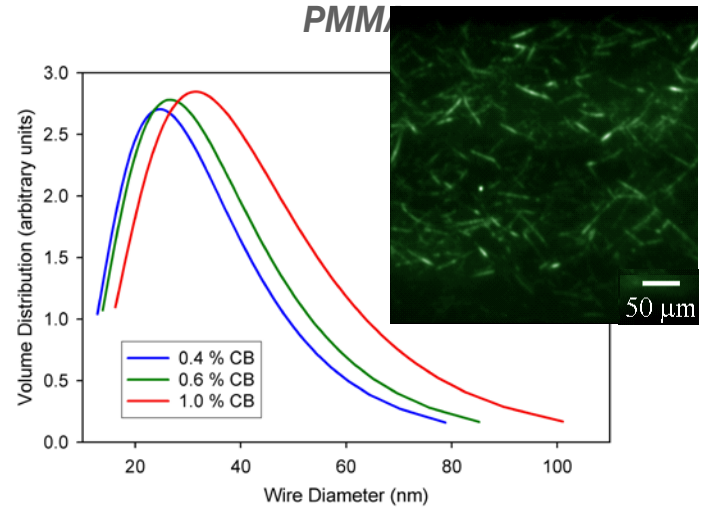
Challenge

- Multiscale characterization of a complex microstructure requires *in situ* microstructure configuration (USAXS imaging), microstructure statistics (USAXS+pin-SAXS), and structure (WAXS).
- Current sources and instrumentation do not allow *in situ* USAXS due to limited working distances.

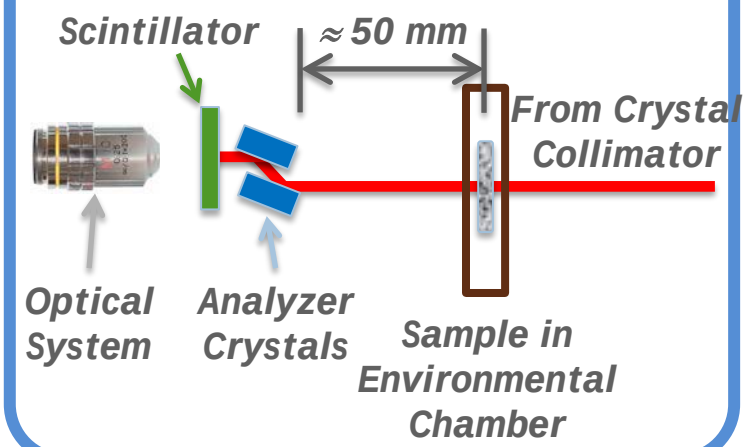
4GSR Strength

- Working distance increased from current 1-3 mm to 50 mm.
- Enables *in situ* sample stages / USAXS tomography

USAXS Image and USAXS Scan Analyses of Carbon Nanowires in PMMA



***In Situ* USAXS Imaging**



Ultimate Materials Characterization facility

Argonne NATIONAL LABORATORY

Opportunity

- Future materials – alloys, ceramics, polymers, and composites - are critical for future energy generation and utilization (e.g., turbines, cars, aircraft,…)
- These new materials exhibit complex, hierarchical, and multiscale microstructure which control their performance.
- Optimization of complex microstructures today needs multiple instruments with different samples, which makes efficient development challenging.

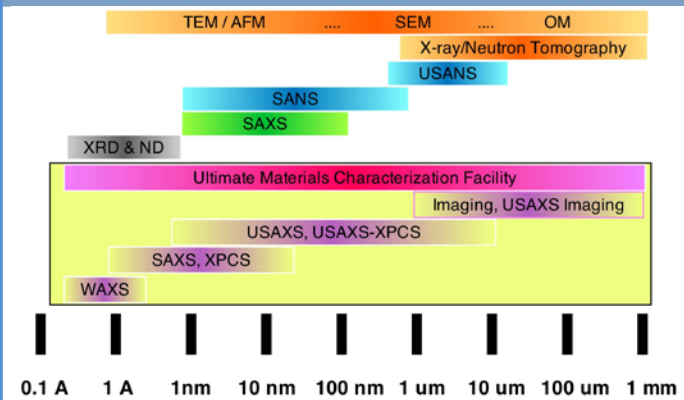
Challenge

- Develop one-stop characterization facility capable of static and dynamic measurement from millimeters to sub-A.
- Measurements at least in simulated (better in real) in-operando conditions (heat, pressure, stress,…).
- Current sources and instrumentation offer number of specialized techniques, which are not coordinated or combined.

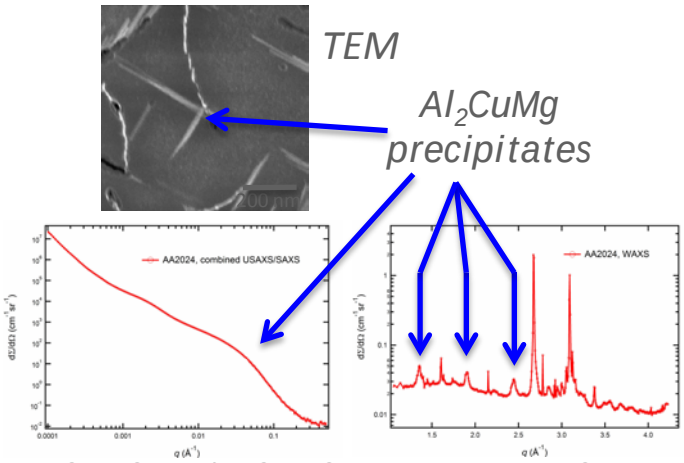
4GSR Strength

- Enables USAXS Imaging & tomography.
- Enables USAXS-XPCS
- Enhances Imaging, USAXS, SAXS and WAXS capabilities
- Enables combining these into unique dedicated materials characterization facility.

Capabilities comparison



In situ AA2024 precipitation hardening: simultaneous microstructure + structure (USAXS + pin-SAXS + WAXS)



Extreme conditions

Reaching Terapascal Pressures

Opportunity

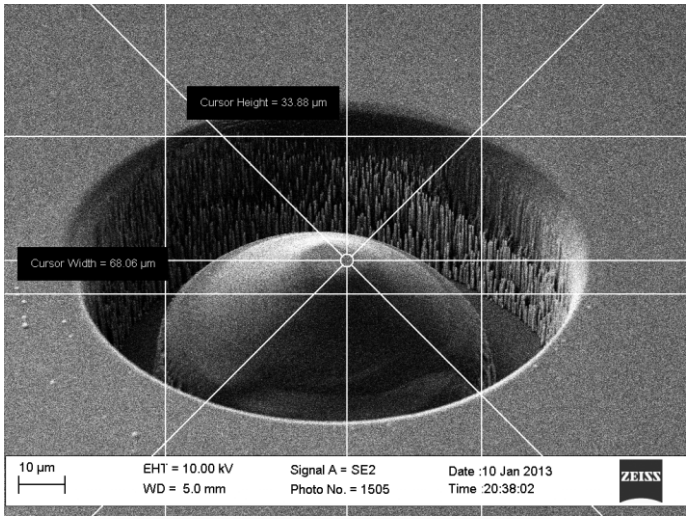
- High-pressure research opens fertile grounds for the observations of new phenomena and formations of new materials.
- The ultimate scope is defined by our capability to reach the highest pressures.

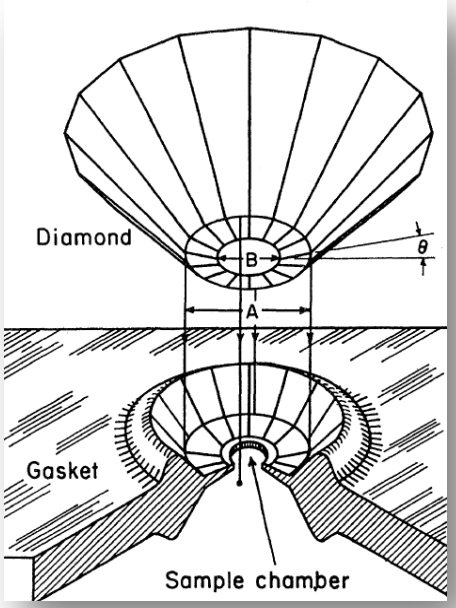
Challenge

- To exceed the present ceiling of 400 GPa, we need ever smaller anvil tips.
- New FIB machining can produce submicron size diamond anvil tips necessary for terapascal pressures.
- Submicron x-ray diffraction is required for determination of the pressures based on the sample equations of state

4GSR Strength:

- MBA APS provides the ideal probes for nanoscale x-ray diffraction at pressure.





Crystal Structures of Ultradense Hydrogen

Opportunity

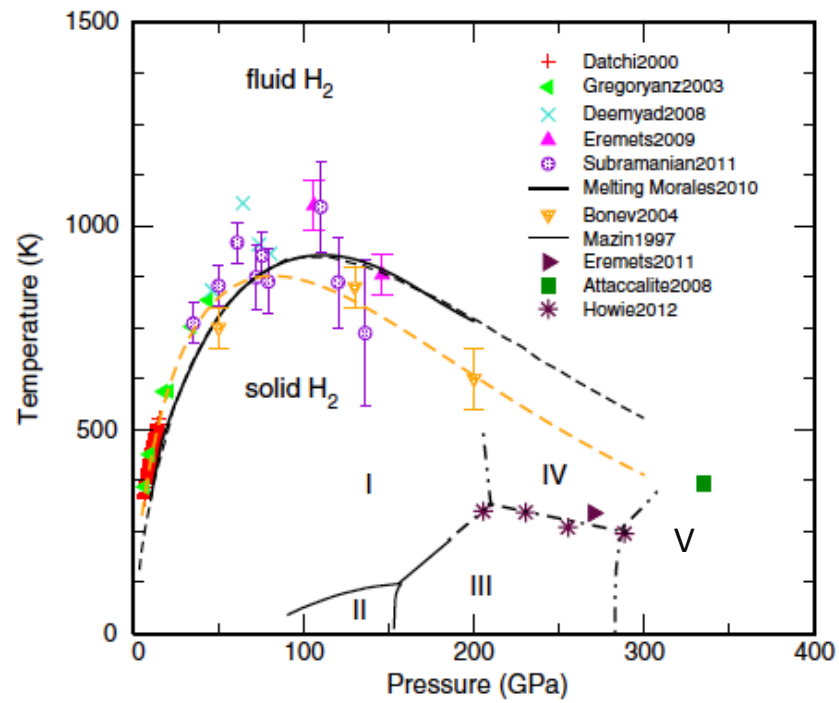
- As the most abundant element in the Universe, hydrogen under high pressures has been the focus of intense theoretical and experimental investigations.
- X-ray diffraction data are desperately needed to resolve the crystal structure of phase III, IV, and V.

Challenge

- Recently optical spectroscopy studies have revealed important new high-pressure phases of molecular hydrogen.
- As the lightest element, hydrogen yields very weak x-ray diffraction signal.

4GSR Strength:

- The submicron focusing capability and two of magnitude higher brilliance at MBA APS will be essential for meeting the challenge.



Ultrahigh pressures are achieved at the expense of smaller sample size. Only the structures of hydrogen I and II have been determined by x-ray with 10 µm sample up to 120 GPa. The maximum size of 1-3 µm for phases III, IV, and V would required the new capabilities of MBA APS.

Diffraction at high pressure and temperature

Opportunity

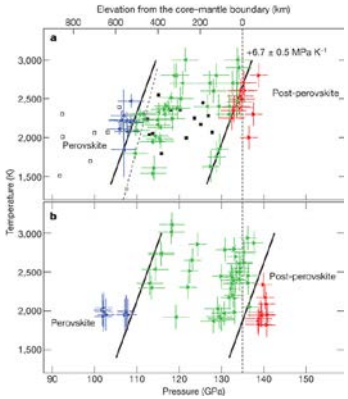
- Ultra high P/T diffraction. Simultaneously obtain pressures over 300 GPa (3 MBar) and temperatures over 4000K.
- High quality single-crystal structural information from sub-micron grains at high-pressure and high-temperature.
- Studying melting at extreme pressures and temperatures

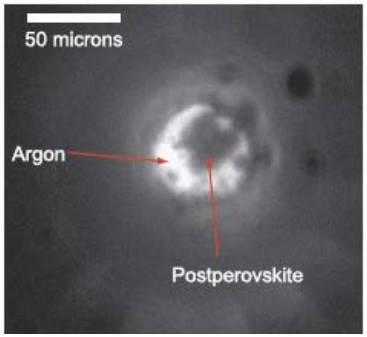
Challenge

- At extreme pressures the sample volume is very small, need more tightly focused beams.
- Counting times at ultra high pressures are limited, need high brightness, i.e. many photons in a small spot with small divergence.
- Scattering from melts is weak, need high flux on small sample

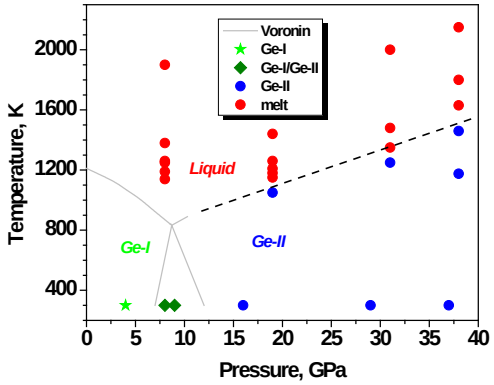
4GSR Strength

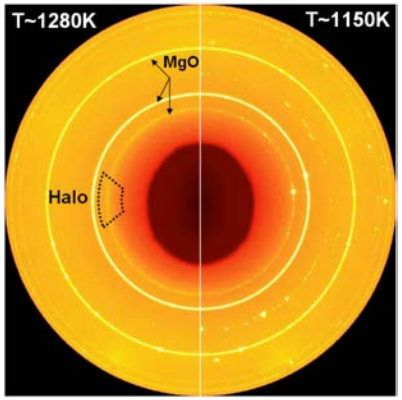
- A smaller, more intense beam allows more flux on part of sample which is at the highest pressure.
- Sub-micron beams and multi-crystal diffraction permit single crystal techniques on samples previously limited to powder diffraction.





Thickness and Clapeyron slope of the post-perovskite boundary
K. Catalli, S-H Shim & V. Prakapenka. Nature **462**, 782-785(2009)





High P-T phase diagram of Germanium
Prakapenka et al., High Pressure Research, **28** (2008)

Crystallography at ultra-high temperatures

Opportunity

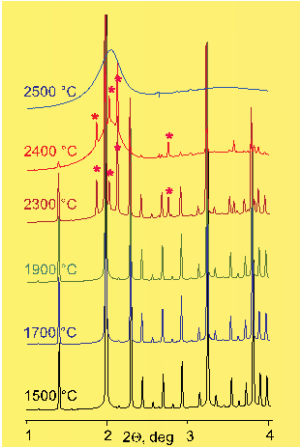
- Ultra high temperature crystallography of oxides from 1500 to 3500°C.
- The structure of most very high temperature phases are quenched and refined. The *in-situ* temperature dependence of **single phase** crystals could be determined.

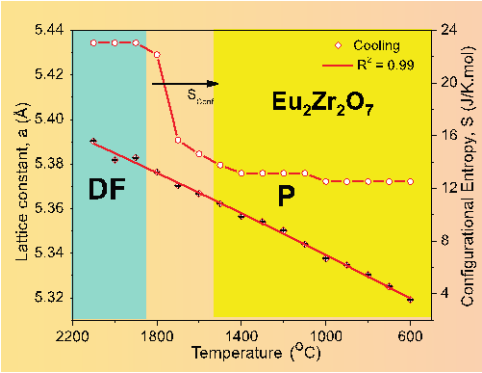
Challenge

- Temperature gradients of several hundred degrees in laser heated samples using aerodynamic levitation often lead to mixed phases.
- Counting times at ultra high temperatures are limited.

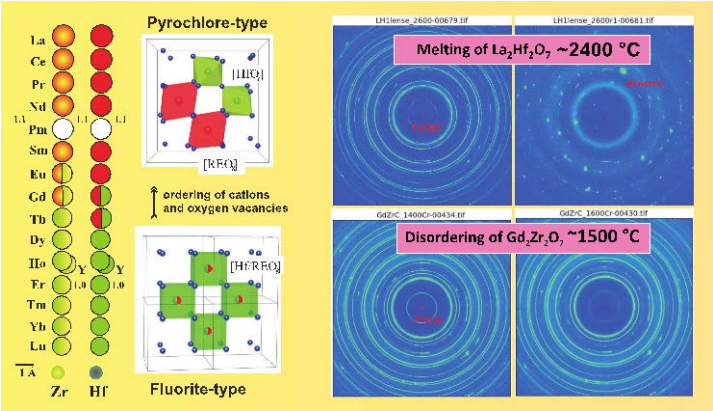
4GSR Strength

- A smaller, more intense beam allows more flux on part of sample which pyrometer accurately measures the temperature.
- Short lived or *meta-stable* states could be identified and refined.





Pre-melting phase transitions in yttria
Order-disorder transitions in zironates and hafnates



High energy x-ray diffraction at ultra high temperatures

S. Ushakov, A. Navrotsky *et al.* Poster at a workshop on Scattering Techniques for Nuclear Materials 2012.

Conundrum of electronic phases in high-T_cs

Opportunity

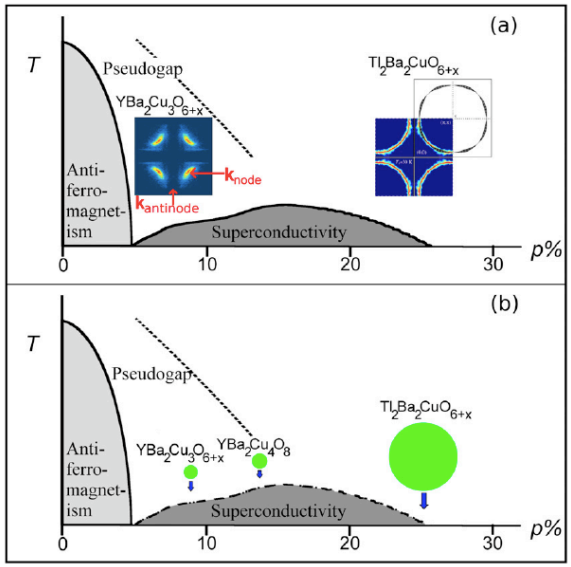
Detect very weak signature and exquisite details of phases that compete with the SC state in high-T_c cuprates using energy x-ray scattering

Challenge

Phase-pure, high-quality, single-crystal samples, which are tiny, needed to be studied with comprehensive bulk sensitivity w/ (to show competition w/ SC state) & w/out an external magnetic field

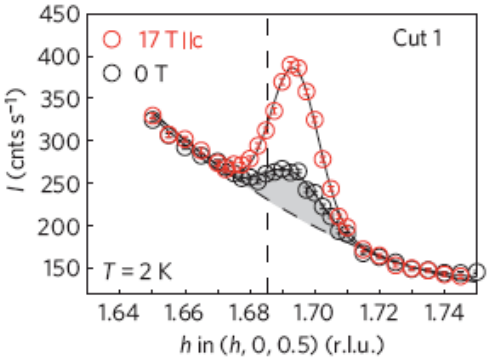
DLSR strength

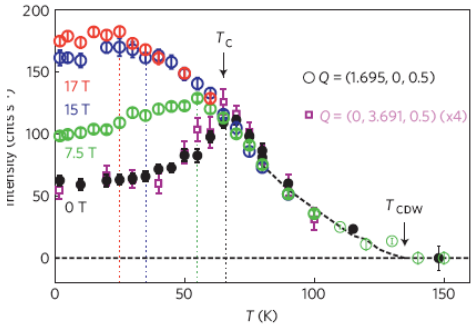
High brilliance high-energy beam easily available for high-resolution studies



Overdoped: a large normal-state FS (ARPES & QO); Underdoped: Fermi arcs (ARPES) & small FS (QO)

HEXS shows formation of CDWs that introduce gaps and compete w/ SC; however, CDW signatures are at the fringe of visibility; need comprehensive bulk-sensitive studies





Sebastian et al., Rep. Prog. Phys. **75**, 2012; Chang et al., Nature Physics (2012); Blackburn et al., PRL **110**, 137004 (2013)

Novel instrumentation: x-ray science at magnetic fields beyond 30 Tesla

Opportunity

- High magnetic field is a contact-free knob to vastly expand phase space to study novel electronic/magnetic order
- Implement NRC recommendation to deploy magnets at x-ray facilities to reduce knowledge gap in high field science
- Partnership of two laboratories

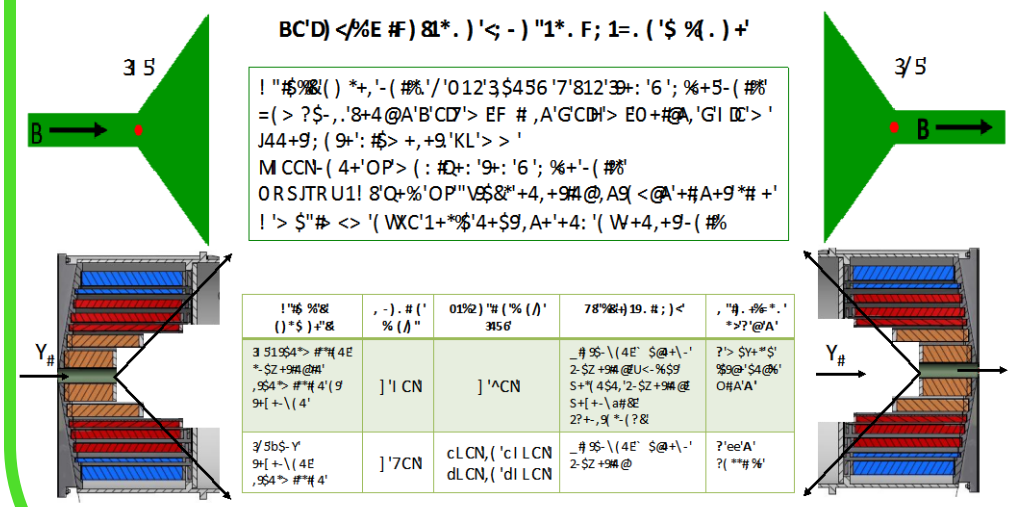
Challenge

Need high fields, a large optical access, a versatile geometry (e.g. **B||Q**, **B||k**$_i$, etc.) suitable for x-ray techniques at vaious beamlines. Allow combined stimuli *p* & **E**

DLSR Strength

Optical access and needed geometry possible by placing a sample in a field gradient; high brilliance makes such gradients irrelevant in a highly portable >30 Tesla all-superconducting magnet

A single magnet is shown in the two primary user configurations with a horizontal scattering plane; however, a vertical scattering plane is also possible. An axial translation provides a means to change the field strength on the sample without ramping the magnet.



X-ray diffraction on laser heated levitated samples: study of phase transitions and thermal expansion above 1500 °C

Sergey V. Ushakov, Saradhi P. Maram and Alexandra Navrotsky
Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, Davis CA

Richard J.K. Weber and Chris J. Benmore
Argonne National Laboratory, Argonne, IL 60439

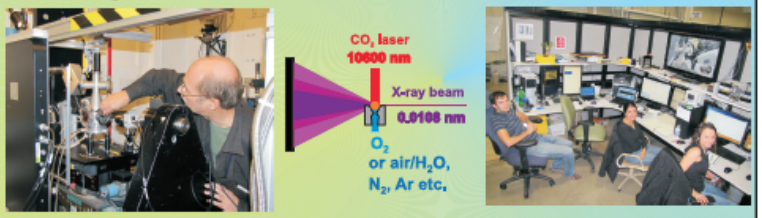
Background

The use of containerless approaches using levitation or self-container combined with laser heating is indispensable for high temperature studies in variable atmospheres.

Since the first X-ray study of levitated liquids pioneered in 1997,[1] levitation with laser heating was successfully used on neutron and synchrotron sources in the USA [2], Europe [3], and Japan [4] to study structure of high-temperature melts.

Aerodynamic levitation is only limited by surface tension and evaporation of the material, eliminates sample reaction with crucible container, and allows experiments in different environments (oxygen, inert gas, reducing gas mixtures, water vapor).

Aerodynamic levitator on a beamline 11-ID-C at APS



J.K.R. Weber, C.J. Benmore, G. Jennings, M.C. Wilding, and J.B. Parise, "Instrumentation for Fast In-Situ X-ray Structure Measurements on Non-Equilibrium Liquids," Nucl. Instrum. Methods Phys. Res., Sect. A, 624, 728–30 (2010).

Applications of aerodynamic levitation and laser heating for study of the structure of melts by X-ray and neutron scattering

1. S. Krishnan, J. J. Felten, J. E. Rix, J. K. R. Weber, P. C. Nordine, M. A. Beno, S. Ansell, and D. L. Price, "Levitation apparatus for structural studies of high temperature liquids using synchrotron radiation," Rev. Sci. Instrum., 68[9] 3512-18 (1997).
2. J. K. R. Weber, C. J. Benmore, G. Jennings, M. C. Wilding, and J. B. Parise, "Instrumentation for fast in-situ X-ray structure measurements on non-equilibrium liquids," Nucl. Instrum. Methods Phys. Res., Sect. A, 624 728-30 (2010).
3. L. Hennet, I. Pozdnyakova, A. Bytchkov, et. al, "Levitation apparatus for neutron diffraction investigations on high temperature liquids," Rev. Sci. Instrum., 77 053903/1-03/7 (2006).
4. A. Mizuno, S. Kohara, S. Matsumura, M. Watanabe, J. K. R. Weber, and M. Takata, "Structure of glass and liquid studied with a conical nozzle levitation and diffraction technique," Mater. Sci. Forum, 539-543 2012-17 (2007).

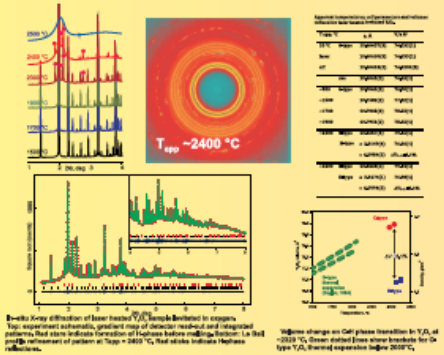
Conclusion

We demonstrated that X-ray diffraction experiments on laser heated aerodynamically levitated samples is not an exclusive domain of glass scientists and has untapped potential to provide data on thermal expansion and phase transitions in crystalline solids.

Experimental

Experiments were performed on levitating samples ~2 mm in diameter in argon and oxygen flow. An area detector was used at maximum possible sample to detector distance (~1.9 m). Image files were collected by summing 20 frames with 1s exposure time. X-ray beam (= 0.10798 Å) was collimated to 0.5 mm diameter. Samples were levitated in an aluminum nozzle with a 90° cone and a 1 mm orifice. Sample rotation was ensured by adjusting the gas flow in a 1.5 to 0.8 lpm range.
FIT2D, GSAS, ExpGUI and FULLPROF software were used for data processing

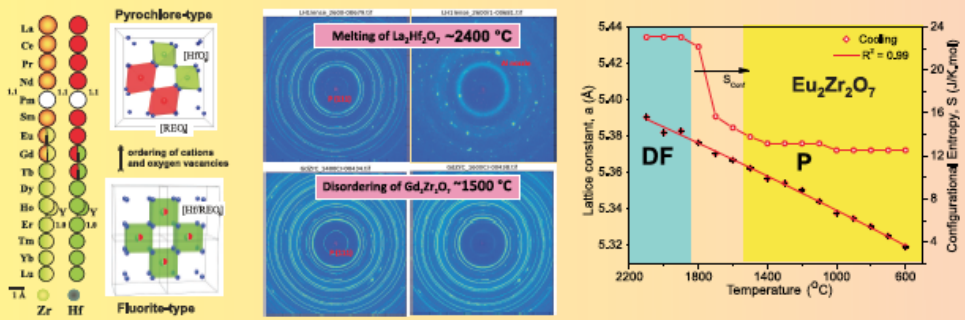
Y_2O_3 : the quest about pre-melting phase transition



The question "Does the cubic fluorite type structure represents the high temperature modification if Y_2O_3? Can the oxygen activity in the gaseous environment induce structural changes in yttria and other rare earth oxides at high temperatures?" was still open due perceived absence of *in situ* methods for structural characterization at high temperature and variable gaseous environments.

We demonstrated that Y_2O_3 transforms into the hexagonal phase before melting both in oxygen and argon environment.

Order-disorder transitions in rare earth zirconates and hafnates



Pyrochlore peaks observed in $La_2Hf_2O_7$ and $La_2Zr_2O_7$ prior to melting.
Pyrochlore to fluorite transition observed in $Gd_2Zr_2O_7$ and $Eu_2Zr_2O_7$.
Thermal expansion and anti-site occupancies have been refined for $Eu_2Zr_2O_7$.

This research supported by U.S. Department of Energy (DOE), Office of Basic Energy Sciences under Award DE-FG02-03ER46053 and by by Office of Naval Research under award N00014-12-1-0196.
Use of the Advanced Photon Source (APS), an Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory, was supported by the DOE under Contract No. DE-AC02-06CH11357.

Catalysis…

BIOMOLECULES IN 2D CRYSTALS AND ARRAYS

Opportunity

- The upgrade will enable high-resolution structure determination of bio-molecules in 2D crystals and arrays via grazing incidence X-ray scattering and diffraction (GISAXS, GIWAXS, GIXD).

- Grazing incidence permits use of a wide range of supporting materials for engineering order in arrays via the growing field of nanotechnology.

Challenge

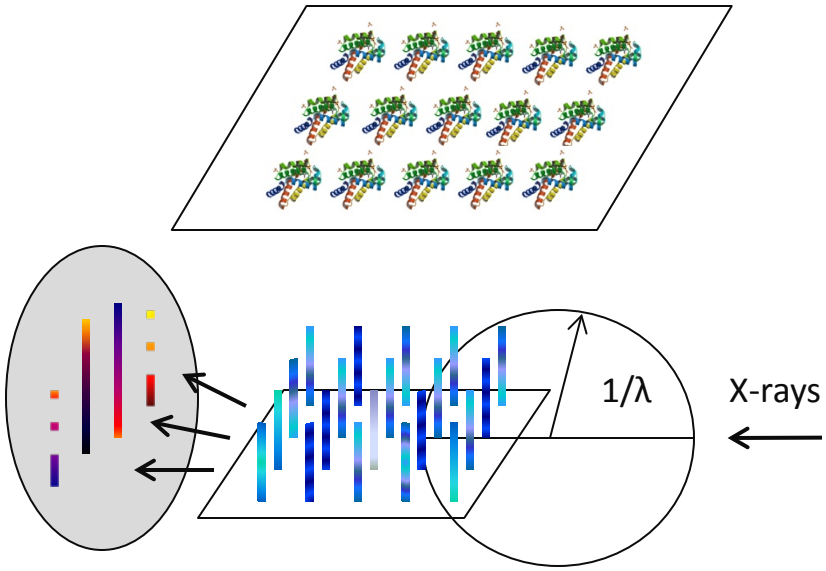
- Crystallization is the main bottleneck for determining biological structures at atomic resolution, particularly for membrane proteins, which are attractive pharmaceutical targets.

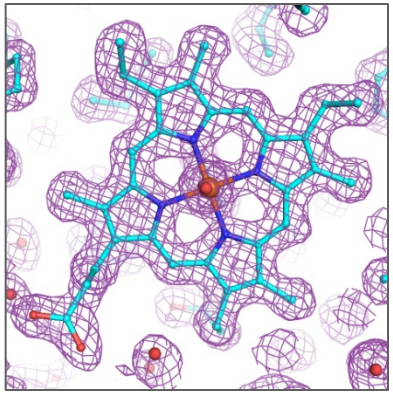
- Small crystal sizes, disorder, low S/N, and X-ray damage severely challenge current capabilities for determining structures from 2D crystals.

4GSR Strength:

- The improved flux density will facilitate work with small crystals and arrays, which improves feasibility for engineering atomic order, and high beam stability allows smooth merging of data.

- Providing a line focus tuned to the size of small 2D samples, and options to orient undulators, will allow beamline configurations that maximize S/N and minimize X-ray damage.





Capturing kinetics during materials synthesis & processing

Opportunity

- Synthesized and engineered materials offer new opportunities in energy production and storage.
- Creating materials requires *in situ*, multi-modal structural characterization techniques to understand and improve their processing and performance.

Challenge

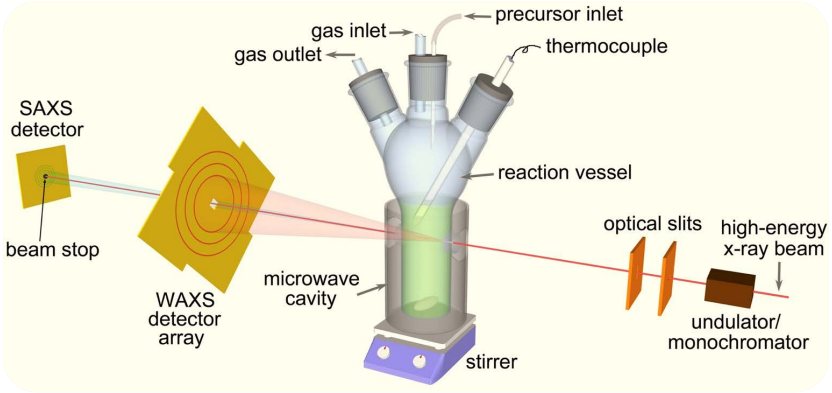
- Combine processing environments with high-energy x-rays to enable high-throughput screening of engineered and synthesized (nano)materials.
- Provide a generic platform to study structural transitions and defect evolution of (nano)materials in real time and under relevant conditions.

4GSR Strength

- HEXD with MBA will enhance brilliance-driven SAXS/WAXS, increase temporal resolution, enable lower Z-materials and sensitivity for dilute systems
- 10X improved q_{min} for SAXS -> probe larger particles
- impact a range of studies including:
  - nano-particle synthesis
  - dynamic deformation of structural materials
  - dynamics in welding metal structures

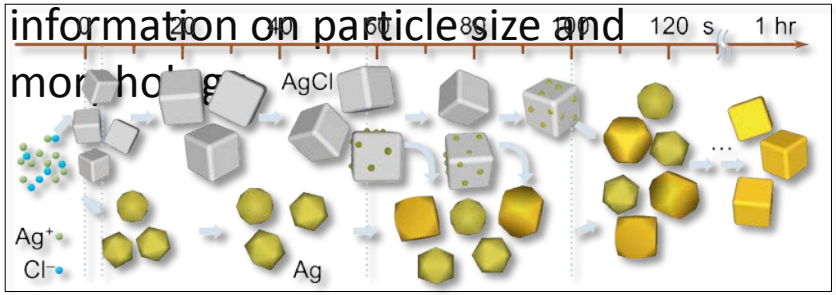
In situ nano particle synthesis

High-energy x-rays penetrate through complex chemical reactor vessels. Atomic- and nanoscale structures determined from multiple detector signals.



Wide **A**ngle **X**-ray **S**cattering yields atomic arrangement and chemical phases present.

Small **A**ngle **X**-ray **S**cattering produces information on particle size and morphology



Nanophase evolution involved in the synthesis of Ag nanocubes

Peng, Okasinski, Almer, Ren, Wang, Yang, and Sun, *J. Phys. Chem. C* **2012**, *116*, 11842.

In Situ X-ray Studies of Catalysis

Opportunity

- Surfaces designed for selectivity and nanometal particles are the trend in designer catalysts.
- The catalysts and reactants need to be studied under real reaction conditions.

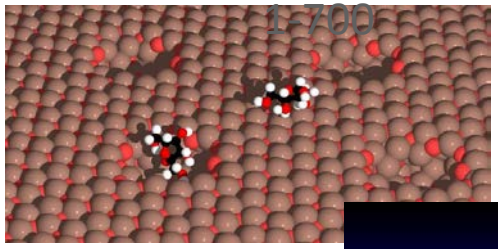
Challenge

- Need a small beam with enough X-rays to see very dilute, very small nano catalysts.
- Currently it is very difficult to see nanobowls in surfaces and the very reactive nano particles.

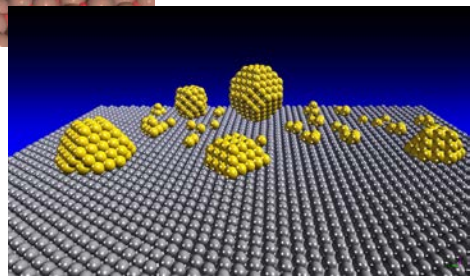
4GSR Strength:

- Small beams can be used to map out nano particles on the surface and how they change with temperature and pressure.
- GISAXS/WAXS can be combined with X-ray, Raman and FTIR spectroscopies.

Catalytic surfaces

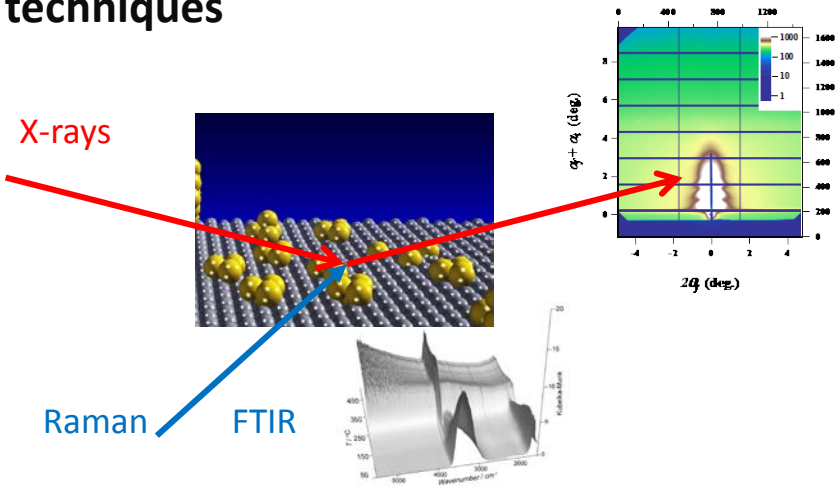


Bowls containing catalysts – size selective



Nano catalysts on surfaces

GISAXS combined with other techniques



Credentials (Winans, Marshall, Elam, Miller/ANL, Poeppelmeier, Stair, Notestein, NU)