Synchrotron Scattering Techniques For Solid State Chemistry And Materials Science

Matthew Suchomel

Advanced Photon Source (APS)

Argonne National Laboratory

The Advanced Photon Source is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Argonne National Laboratory

What is a synchrotron?

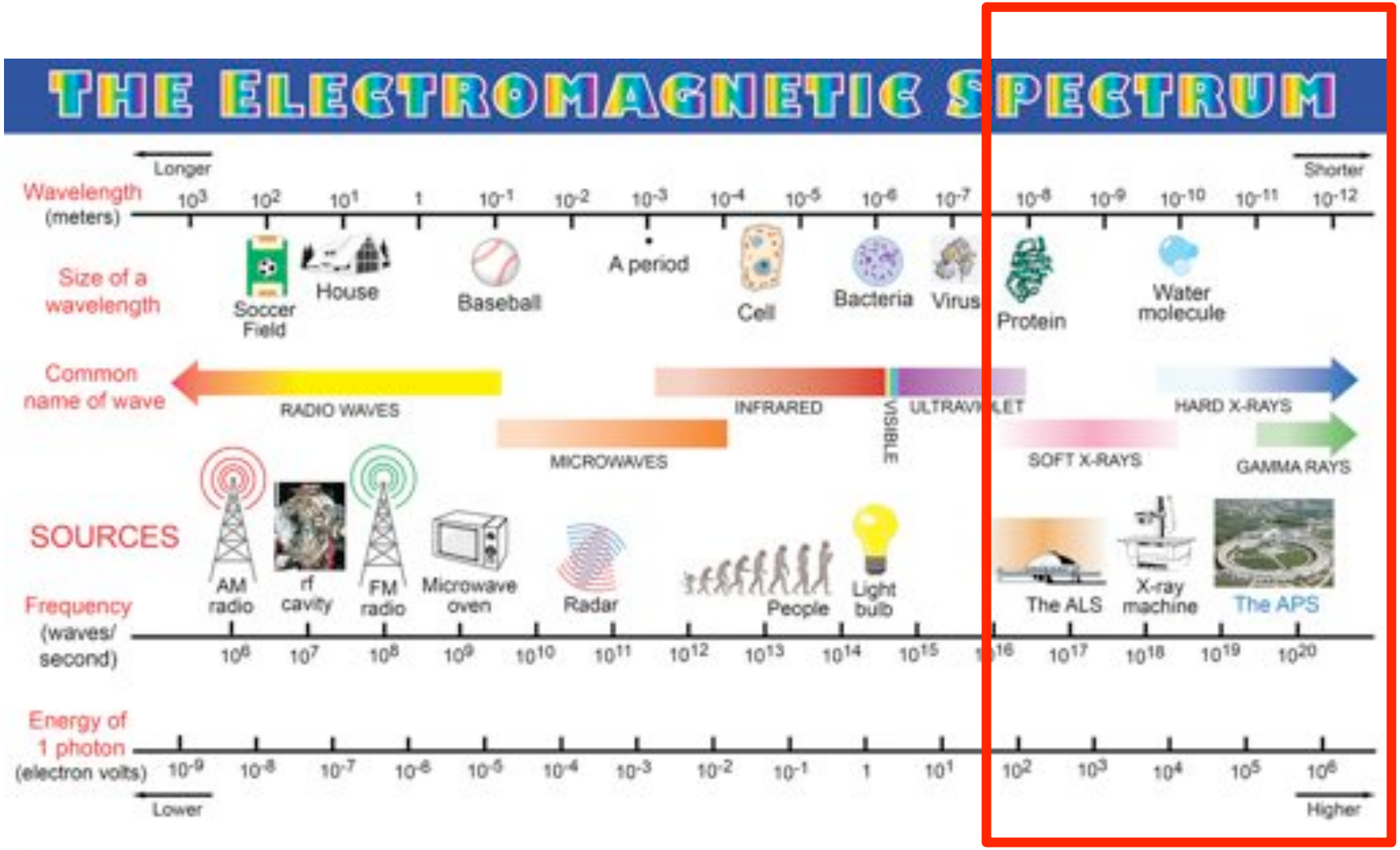
What is a synchrotron?

- Answer 1: (*from wikipedia.org*)

  *A **synchrotron light source** is a source of electromagnetic radiation produced by a synchrotron, which is artificially produced for scientific and technical purposes by specialized particle accelerators, typically accelerating electrons. Once the high-energy electron beam has been generated, it is directed into auxiliary components such as bending magnets and insertion devices (undulators or wigglers) in storage rings and free electron lasers. These supply the strong magnetic fields perpendicular to the beam which are needed to convert the high-energy electron energy into light or some other form of EM radiation…..*

- Answer 2:
  - A synchrotron is a source of very powerful x-ray beams
  - It works by some form of physics magic
  - It provides x-rays with **high flux**, **tunable energy**, **intense brightness,** and other advantages
  - Can be a very useful tool for solid state chemistry and materials science research

X-rays: a high-energy form of electromagnetic radiation (light)



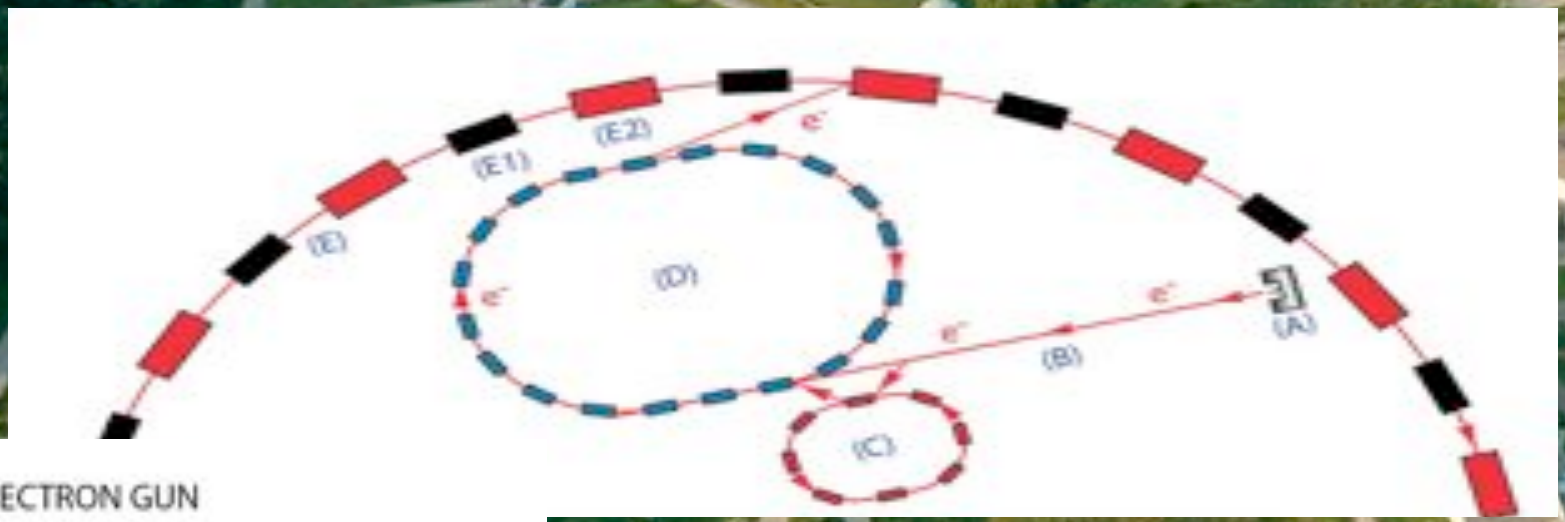
Synchrotrons Around the World

http://www.diamond.ac.uk/Home/About/Synchrotrons/World/largemap.html

Synchrotrons in Western Europe

lightsources.org

Parts of a “Synchrotron” Light Source



A. ELECTRON GUN

B. ELECTRON LINEAR ACCELERATOR
325 MeV-450 MeV

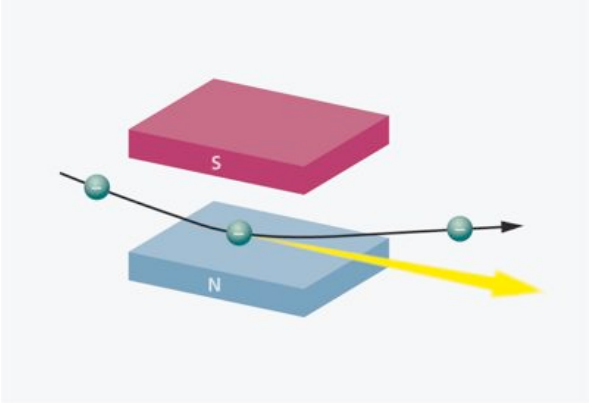
C. PARTICLE ACCUMULATOR RING
325 MeV-450 MeV

D. BOOSTER SYNCHROTRON
7 GeV nominal energy

E. STORAGE RING
7 GeV nominal energy
E1 INSERTION DEVICE
E2 BENDING MAGNET

How does a synchrotron make light (x-rays)?

When a charged particle is accelerated (its momentum is changed), light is produced (ref: Maxwell's equations). Deflecting an electron beam to make it go round in a circle produces light.

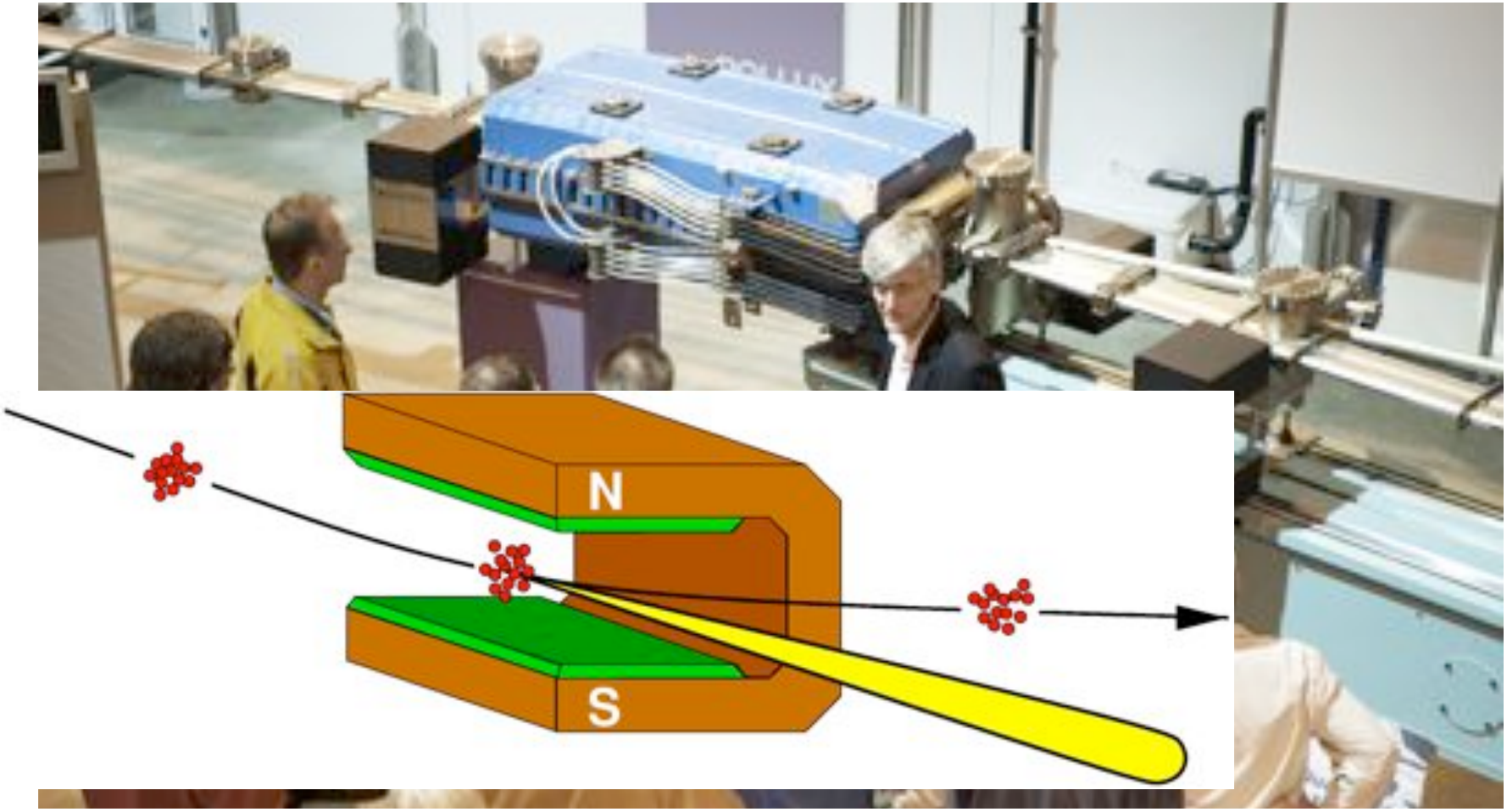


- Synchrotrons use very high energy electrons (typically 3-7 GeV) to produce x-rays with minimal deflection of the electrons.
- When synchrotrons were first invented, the light they produced was initially considered a nuisance. First "2nd generation" source opened 1980 (Daresbury UK)
- Where does the energy in the light come from?
  - The electrons lose a little bit of their energy and slow down a bit. RF fields in the storage ring pump in energy to keep the electrons at constant energy.
- Modern synchrotrons use two types of components to produce x-rays: bending magnets and insertion devices (wiggler or undulator)

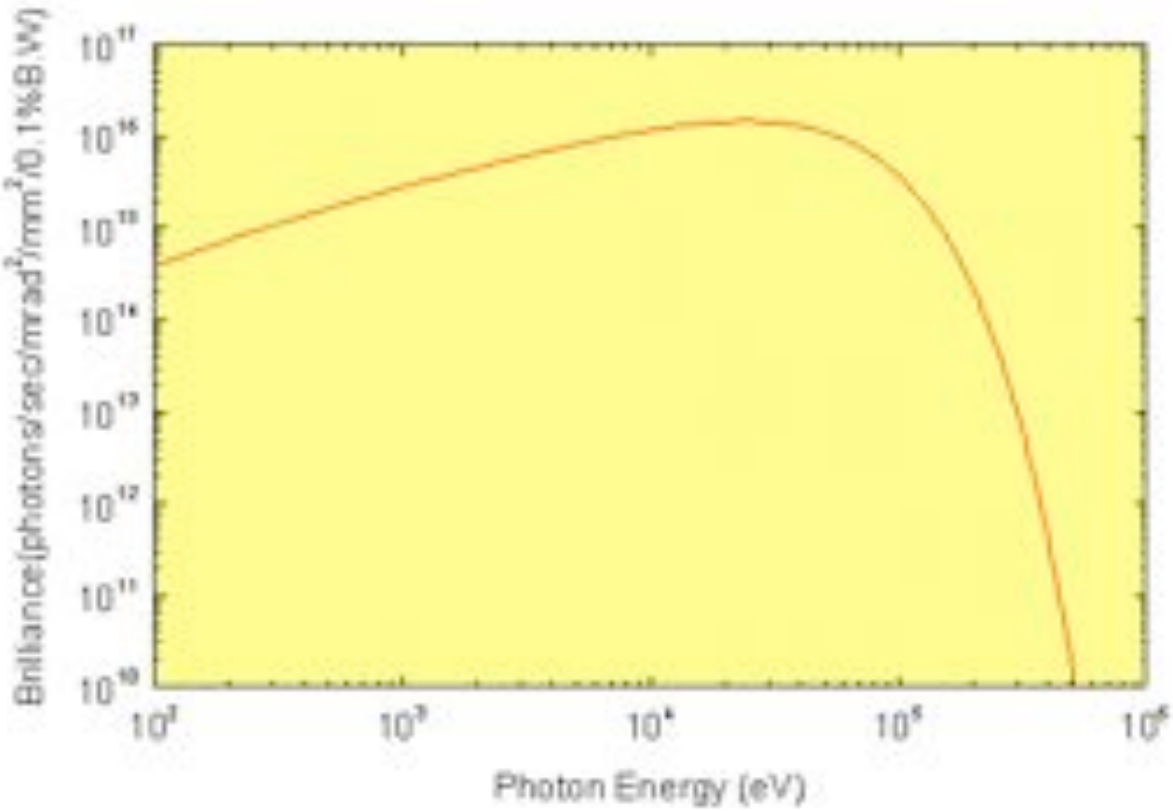
Interior view of APS booster synchrotron

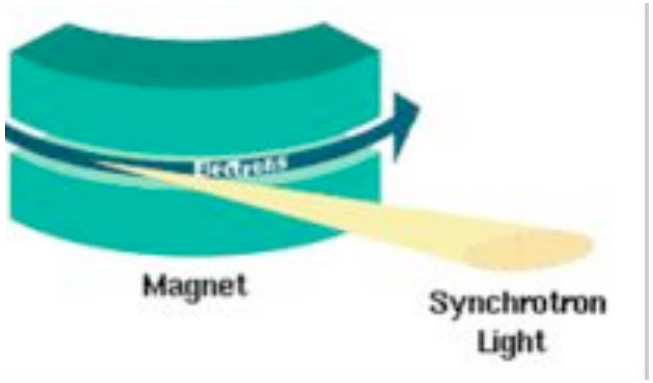
Bending Magnet

Required to make the “circle” – but also used for experiments



Bending magnets produce a broad spectrum
with horizontally diverging (spreading) beam

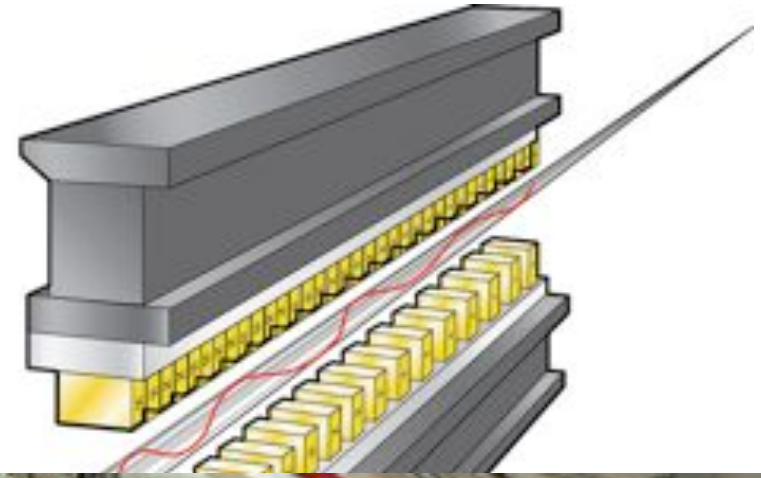




Insertion Devices Produce Intense X-rays

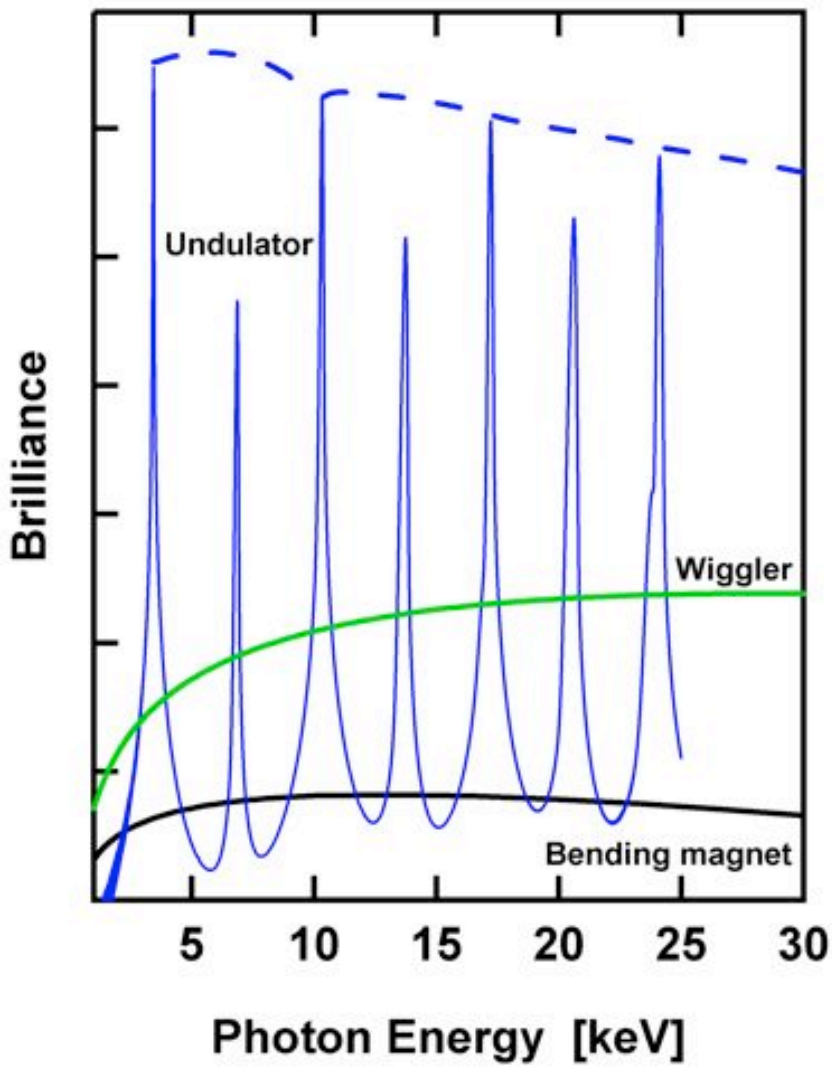
where the path of electrons is straight

- A undulator has more magnets than a wiggler
- Both set up a resonance condition that favors certain x-ray wavelengths



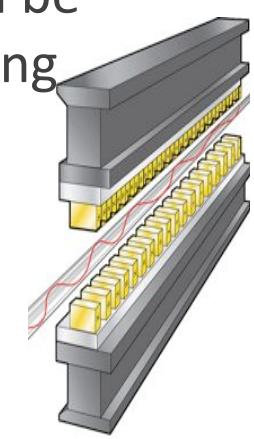
Spectra Comparison

Undulator, Wiggler and Bending Magnet



Undulator spectrum is dictated by design (number and strength of magnets) but also the size of the gap between the magnets.

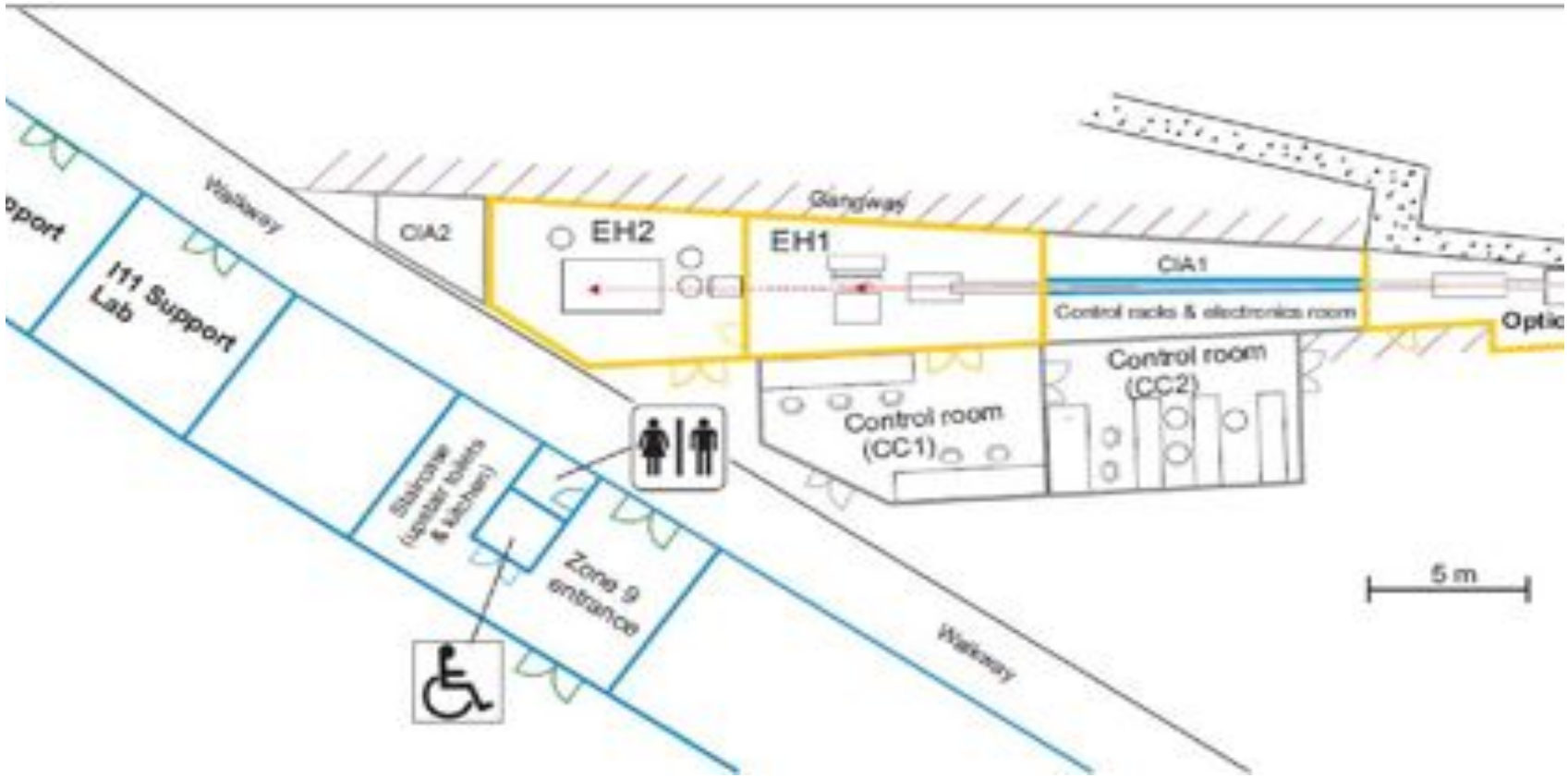
The gap is usually adjustable so that the spectrum can be changed so that a peak can be located where data are being collected.



Synchrotron Experiments

are performed in a Beamline "Hutch"
Beamline can have a name or number

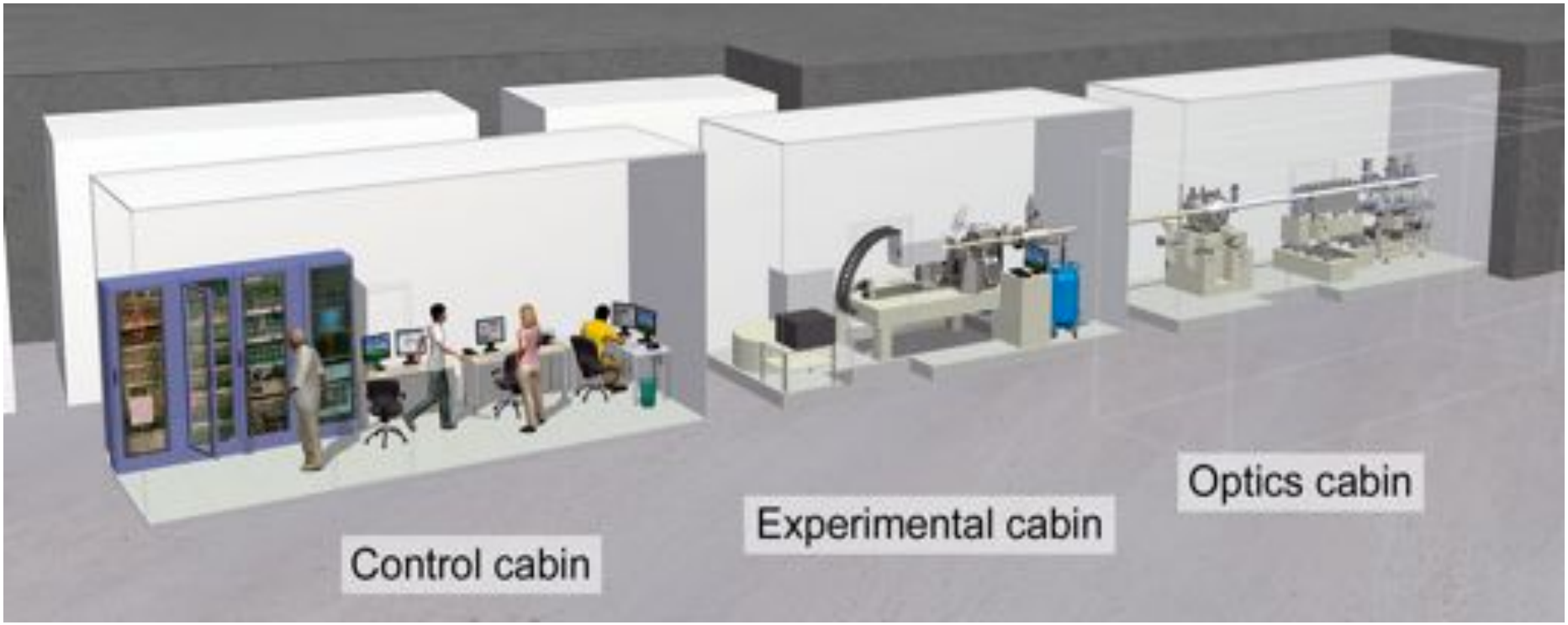
Plan of beamline "I-11" at Diamond (UK)

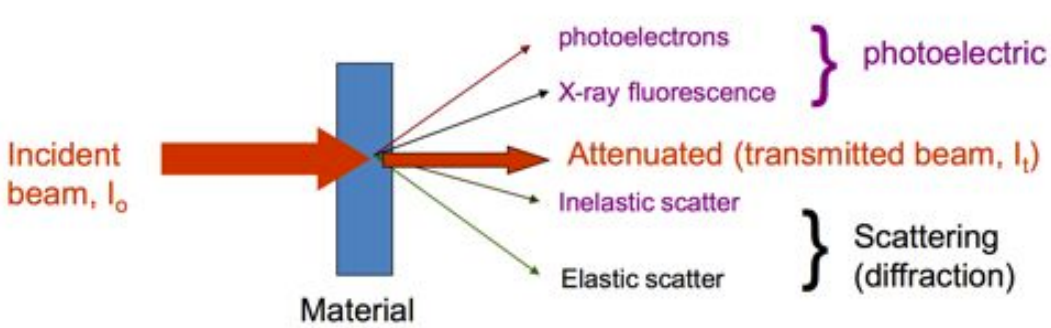


Typical Synchrotron Beamline Layout

Optics – Experiment Hutch – Controls Area

ESRF website





Detector

ence by Argonne National Laboratory

Detectors are equally important at Synchrotrons

Remember: Many types of x-ray detectors for many types of x-ray science!

Electronics:

- Recognize and process x-ray signal
- Pass data to acquisition system
- Key parameter: Signal-to-noise ratio

High-speed data link

Data acquisition system

- Runs detector control software for user
- Writes data to permanent storage
- Some quick data processing

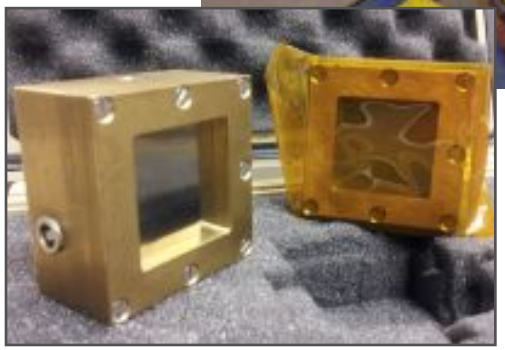
Sensor:

- Converts x-rays to a use-able electrical signal
- Semi-conductor, scintillator, etc
- Key parameter: Efficiency (Probability x-ray will convert in media)

Bradford Robert <rbradford@aps.anl.gov>

Counting Detectors

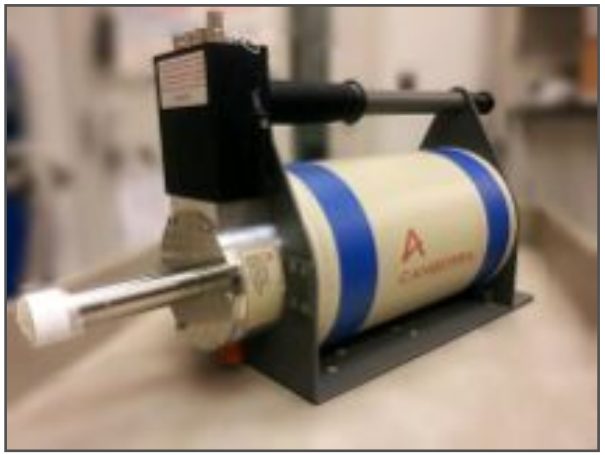
- Counts # of x-rays striking face of detector
  - Intensity at one point in space
- Example: Diodes, scintillation counters
- To think about:
  - Detector has an upper limit on rate at which it can count
  - Ex: Scintillation counters usually limited to <500 kHz, but limit depends on speed of amplifier.

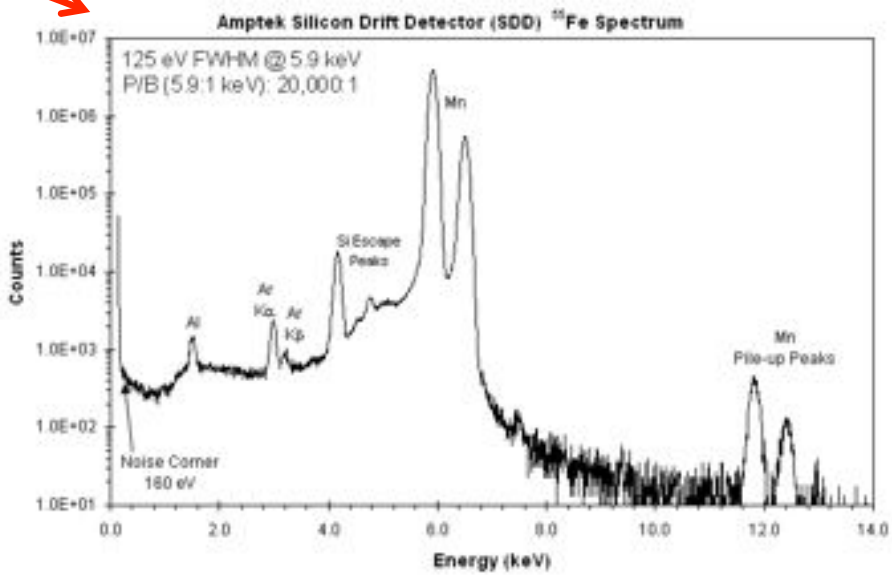


Bradford Robert <rbradford@aps.anl.gov>

Energy Dispersive Detectors

- Counting-like detector capable of measuring x-ray energies
- Examples: Silicon drift detectors, germanium detectors
- When combined with MCA, provides an energy spectrum
- To think about:
  - Count rate limitation: ~100 kHz
  - Energy resolution:
    - 120 eV for Si
    - 200 eV for GeGe more efficient than Si above 15 keV, but requires use of LN2





http://www.amptek.com/drift.html

Bradford Robert <rbradford@aps.anl.gov>

Area Detectors

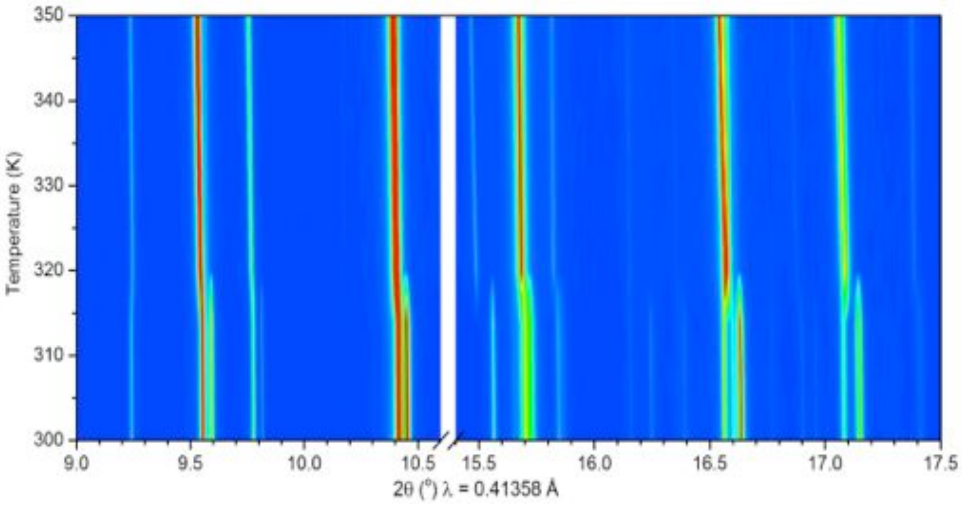
- 2D array of detectors record both position and intensity in single exposure

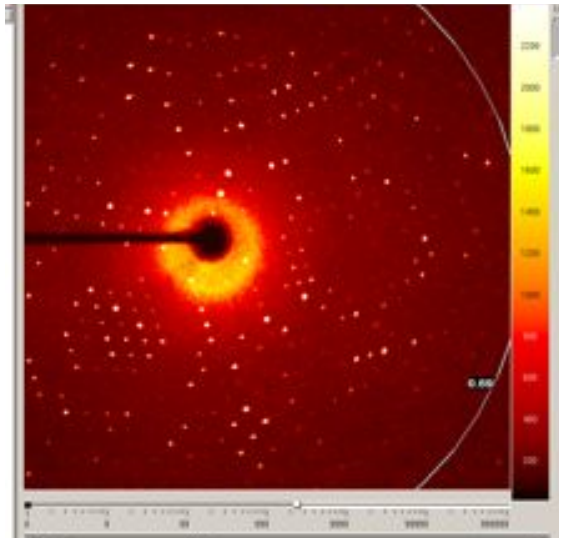
- Lots of different kinds
  - Film
  - Image Plates
  - CCDs
  - Hybrid Pixel Detectors (Pilatus)
  - Amorphous silicon flat panels
  - CMOS detectors

- To think about:
  - spatial resolution / pixel size
  - Frame rate, dynamic range, and field of view vary widely for area detectors, and need to be chosen carefully.

Bradford Robert <rbradford@aps.anl.gov>

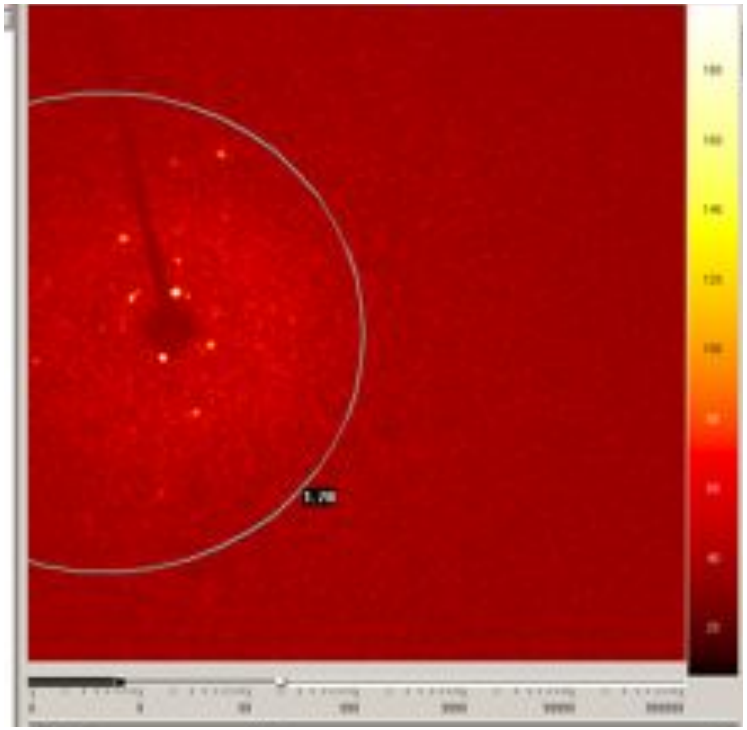
Synchrotron Scattering Crystalline and Amorphous Materials





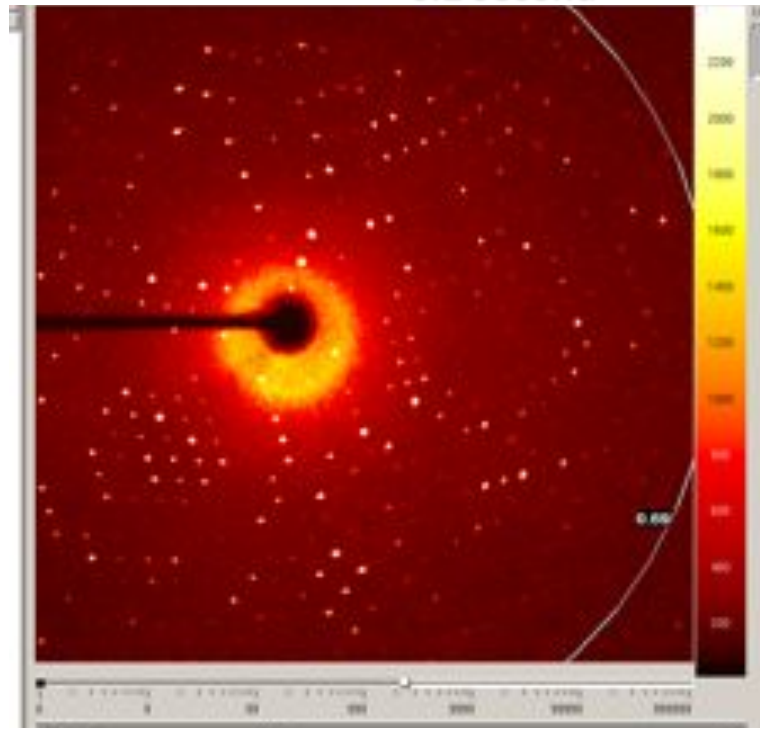
Synchrotron for Single Crystal Diffraction

In-house exposure time 120 second



No structure determined

Synchrotron exposure time 0.2 second



Synchrotron data:

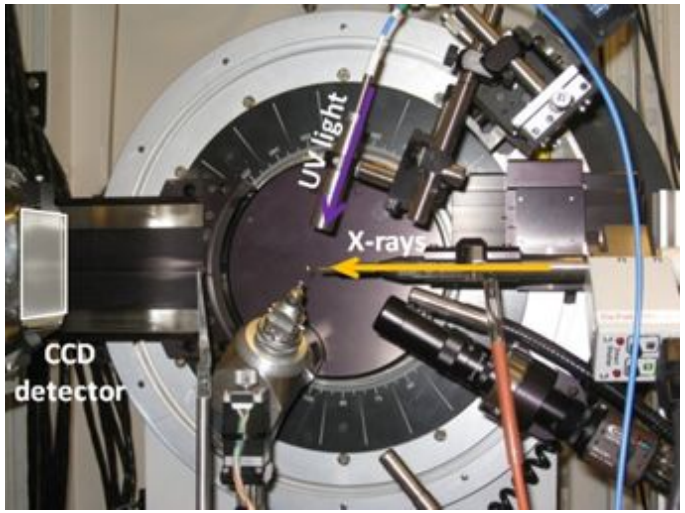
- Much less exposure time
- Strong data in 9.00- 1.78 Å region
- Still significant intensity out to 0.69 Å

Chen Yu-Sheng <yschen@cars.uchicago.edu> at ChemMatCARS, APS Station 15-ID-B

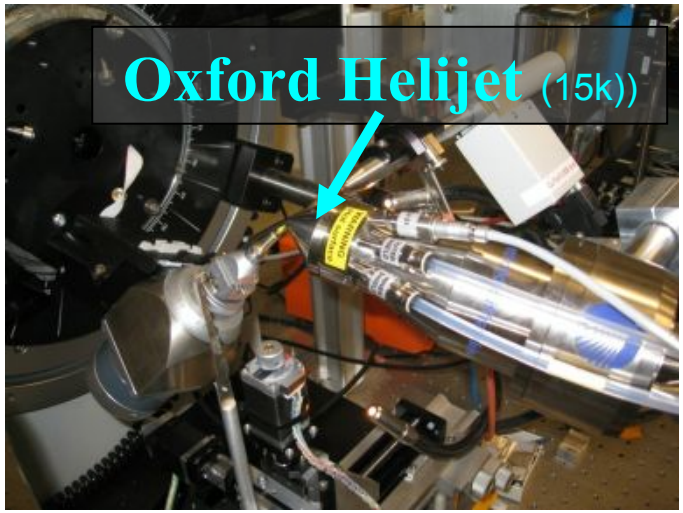
The Advanced Photon Source is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Argonne National Laboratory

Advanced (single) Crystallography at APS

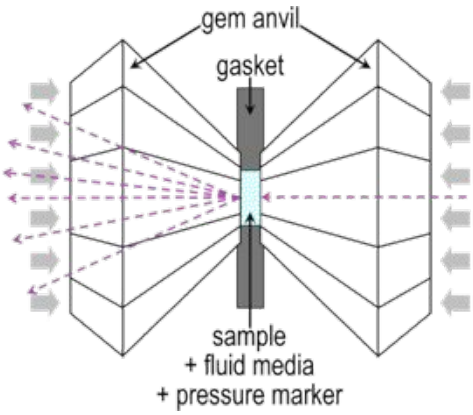
Photo-crystallography



Low temperature crystallography



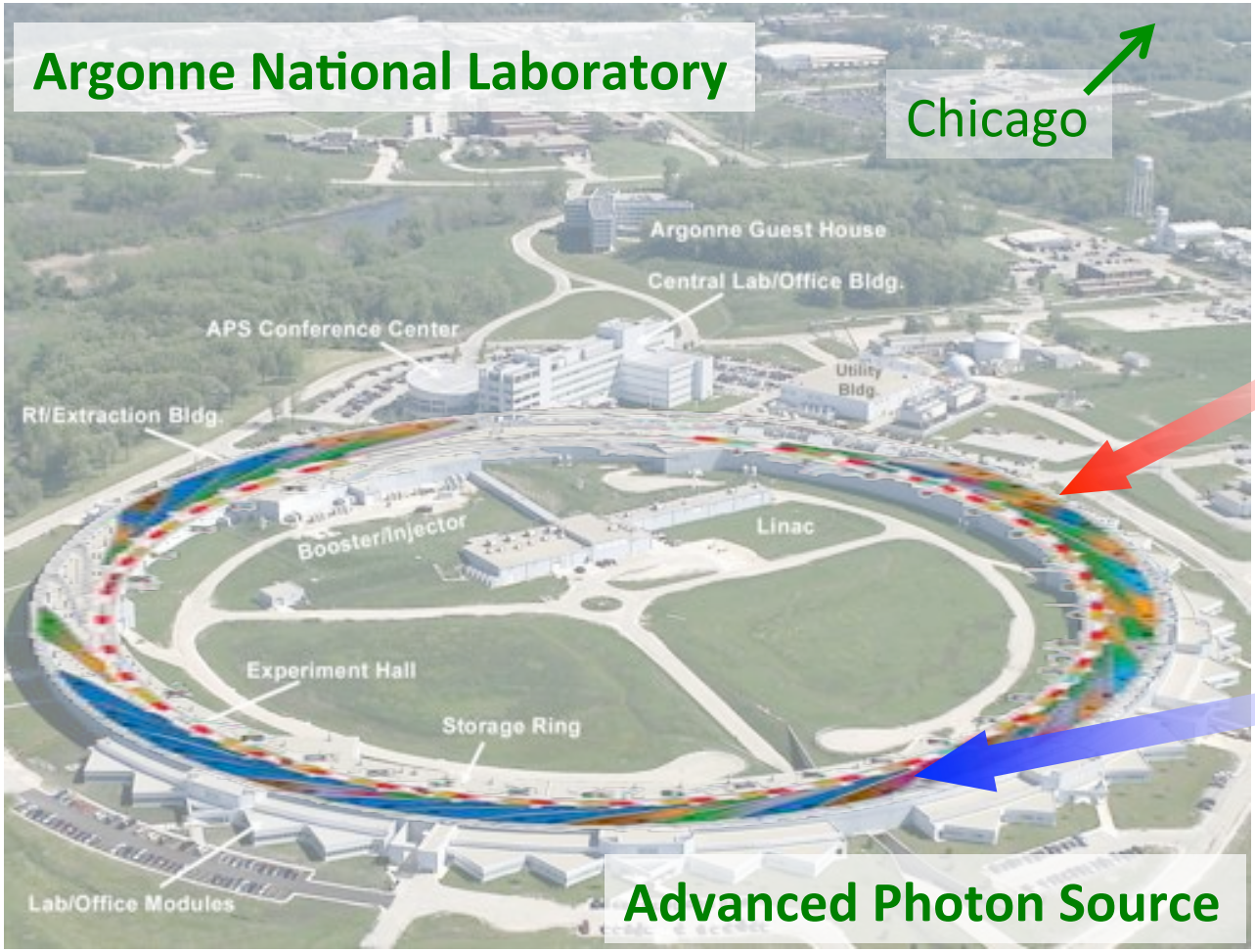
High pressure (GPa) -crystallography



Chen Yu-Sheng
<yschen@cars.uchicago.edu>

Powder Diffraction at the APS

powder XRD is performed at multiple instruments (often called beamlines)



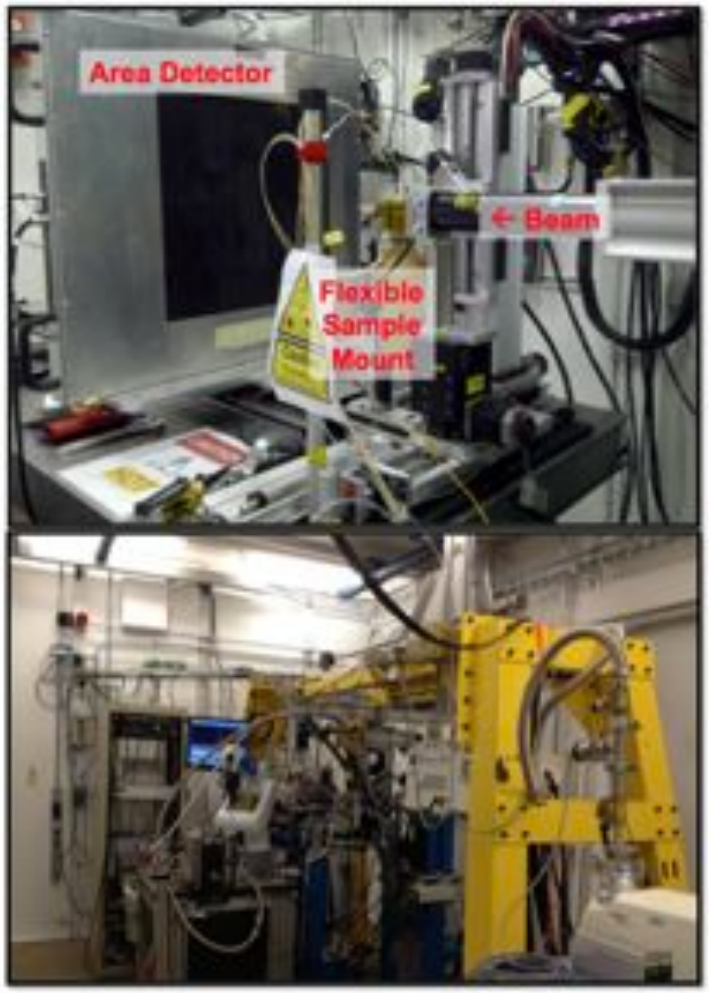
11-BM

- Highest 2θ Resolution
- Superb Sensitivity
- **RA Mail-In Program**

17-BM

- In-situ Studies
- Flexible Set-Up
- Rapid Scans

APS Powder Diffraction Beamlines



Fast Area Detector (17-BM)

17-BM is a powder diffraction instrument at the APS optimized for in-situ experiments under non-ambient conditions. A state-of–the-art area detector enables fast data acquisition, and on-site users benefit from a wide variety of flexible sample environments.

Instrument Specifications

- Energy Range: 7 – 20 keV
- Resolution: $\Delta d/d \approx 1\times10^{-3}$
- Scan Time: 0.1 - 60 seconds

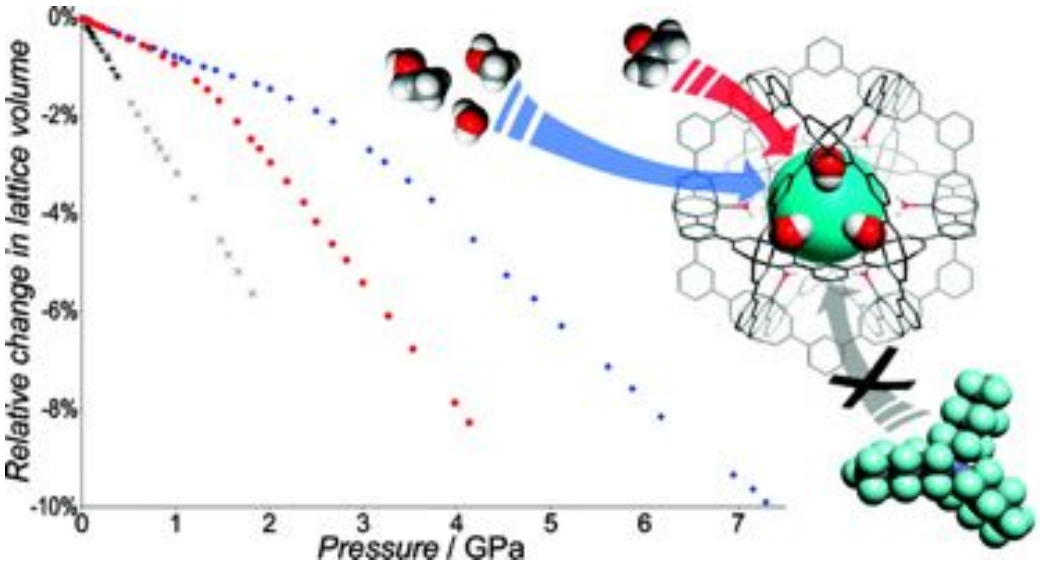
Sample Environments

- Flowcell Reaction Furnace (<900 ^{o}C) [4]
- Oxford Cryostream (100 - 450 K)
- In-Situ Controlled Atmospheres
- Diamond Anvil Cells (<10 GPa)

Greg Halder <halder@aps.anl.gov>

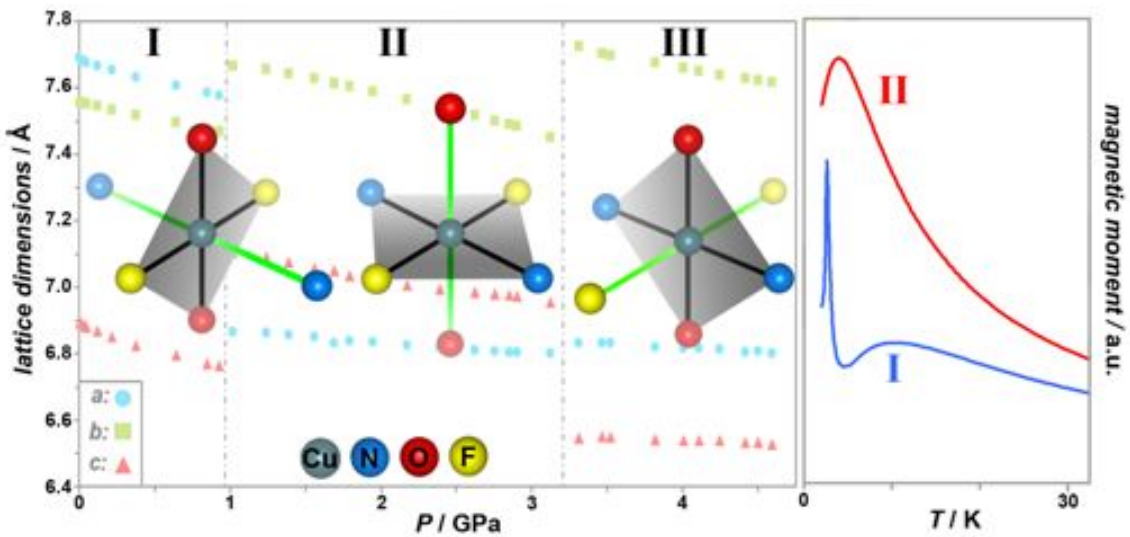
APS Powder Diffraction Beamlines

Greg Halder <halder@aps.anl.gov>



Guest-dependent high pressure behavior in a MOF

Jahn-Teller switching in a molecular magnet



APS Powder Diffraction Beamlines

High-Resolution (11-BM)

11-BM is a dedicated high resolution powder diffraction instrument at the APS. It affords powder diffraction data with world-class resolution and outstanding sensitivity. The beamline supports both on-site and rapid access mail-in user programs.

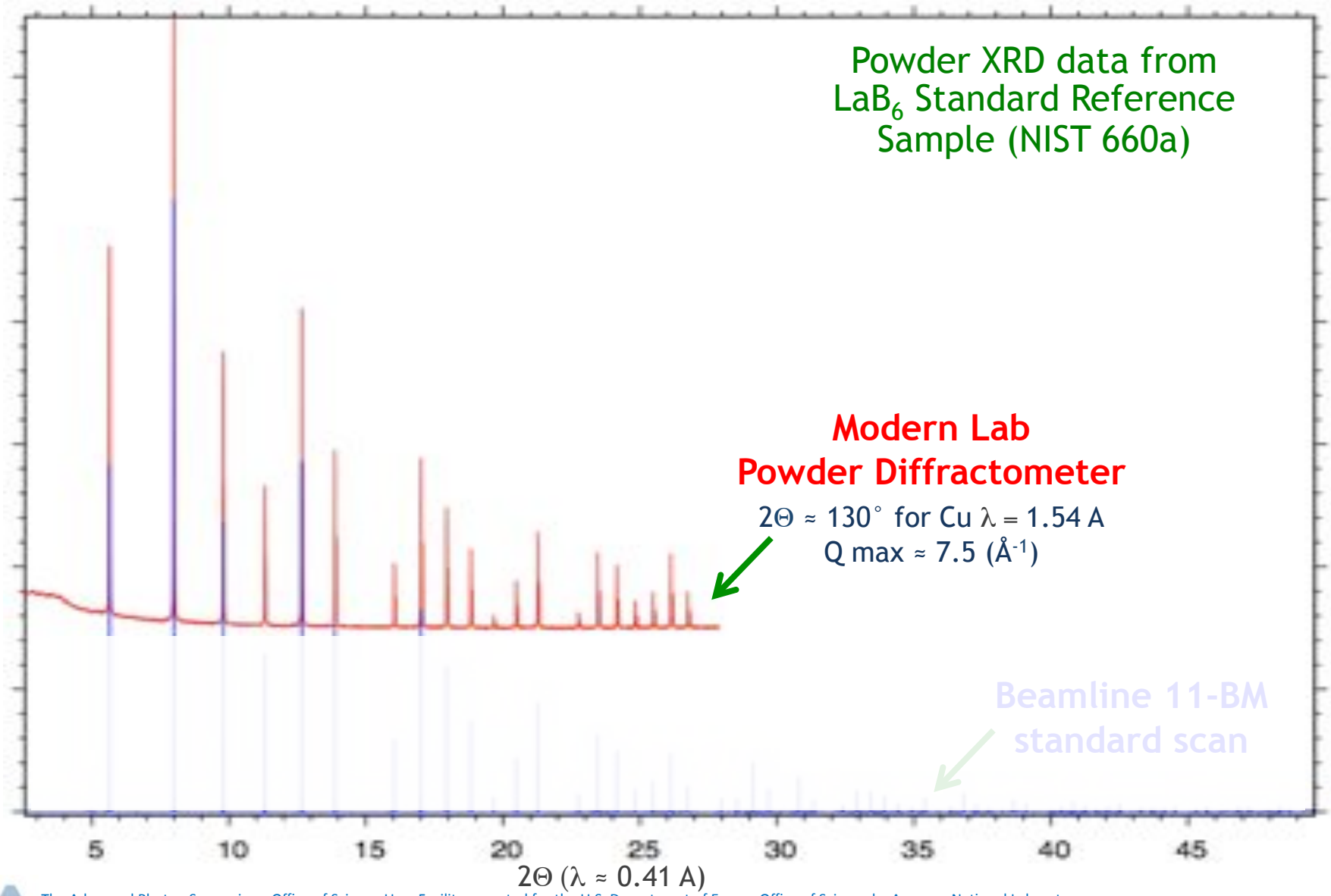
Instrument Specifications

- Energy Range: 20 – 35 keV
- Resolution: $\Delta d/d \approx 2\times10^{-4}$
- Scan Time: 10 - 60 minutes

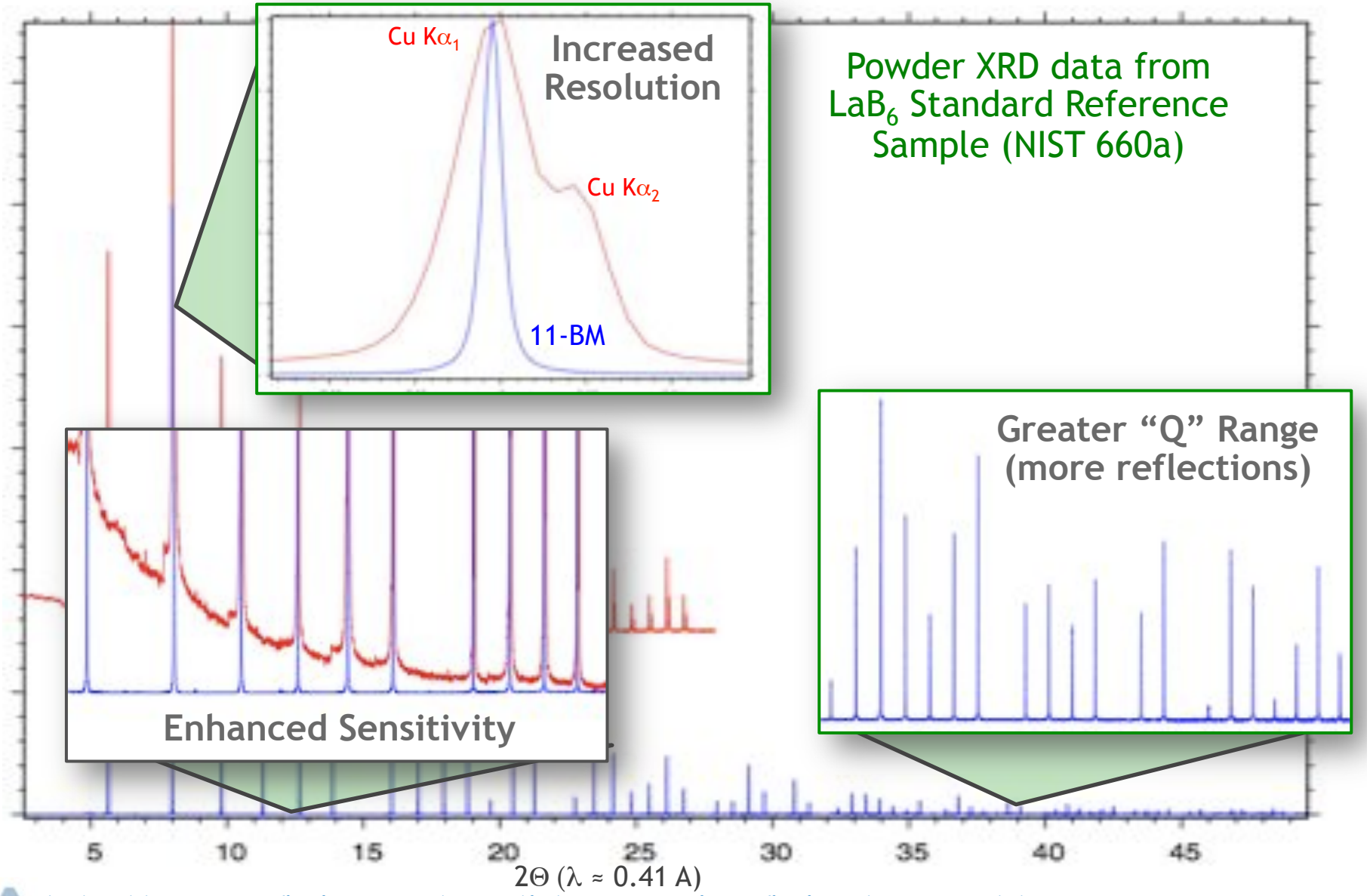
Sample Environments

- Oxford Cryostream (100 - 450 K)
- Cyberstar Hot Gas Blower (25 - 900 °C)
- Helium Flow Cryostat (5 - 150 K)
- Gas Reaction/ Flow Cells
- High Temp (>1000 °C) furnace (underway)

Why Use a Synchrotron for Powder Diffraction?



Why Use a Synchrotron for Powder Diffraction?



Rapid Access Mail-In Measurements @ 11-BM

- Short Proposal, Fast Review
- Open to US & International Users
- Limited to 8 Hours per Proposal
- **Free** (no cost!) for Non-Proprietary Work
- Sample Mounting Kits Provided
- Scans at Ambient or 100-450 K
- Fixed Energy 30 keV (0.41 Å)
- Download Data in ~ 4 weeks

more information

http://11bm.xor.aps.anl.gov

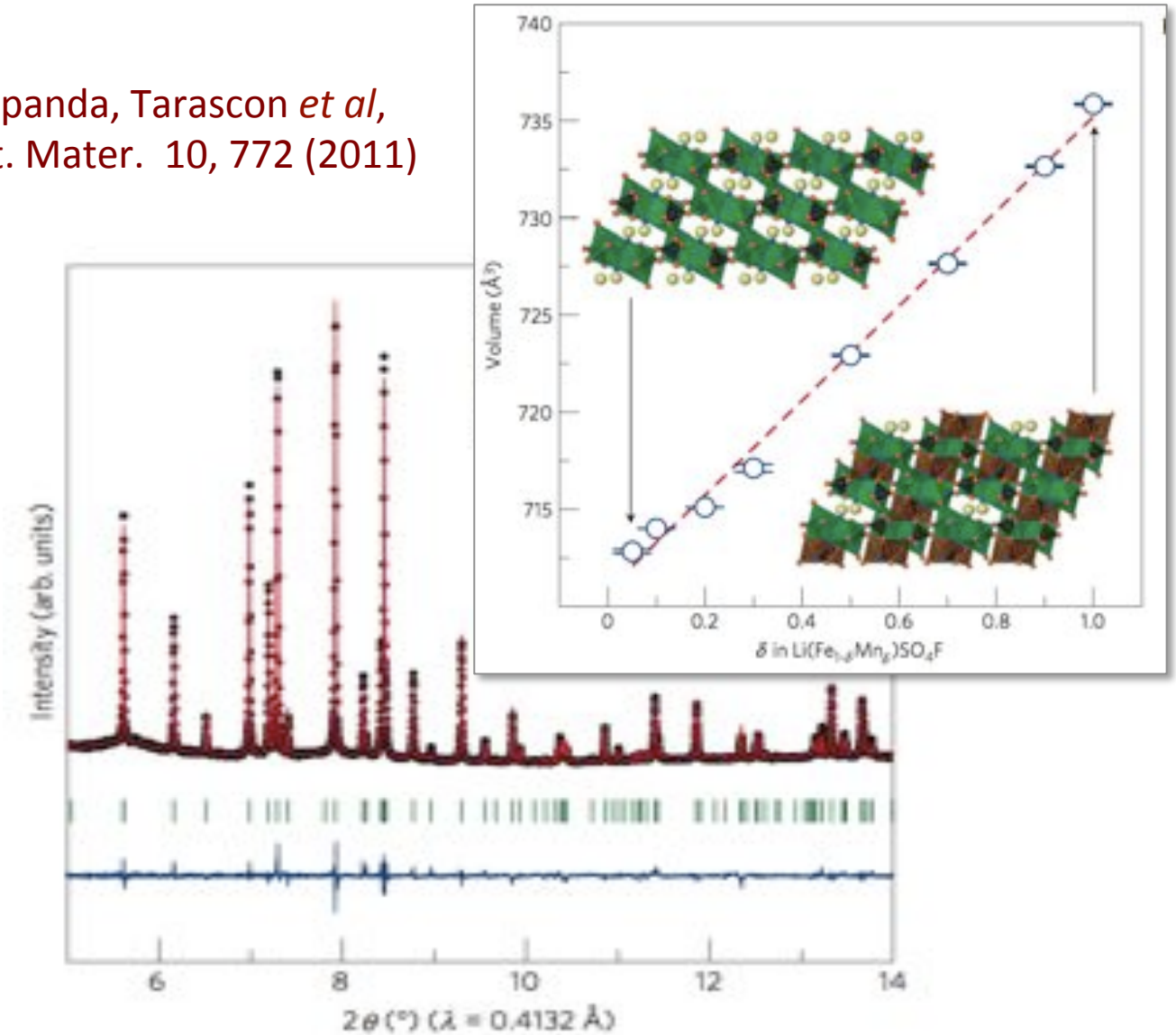
email: 11bm@aps.anl.gov

11-BM Mail-In = High Impact Science

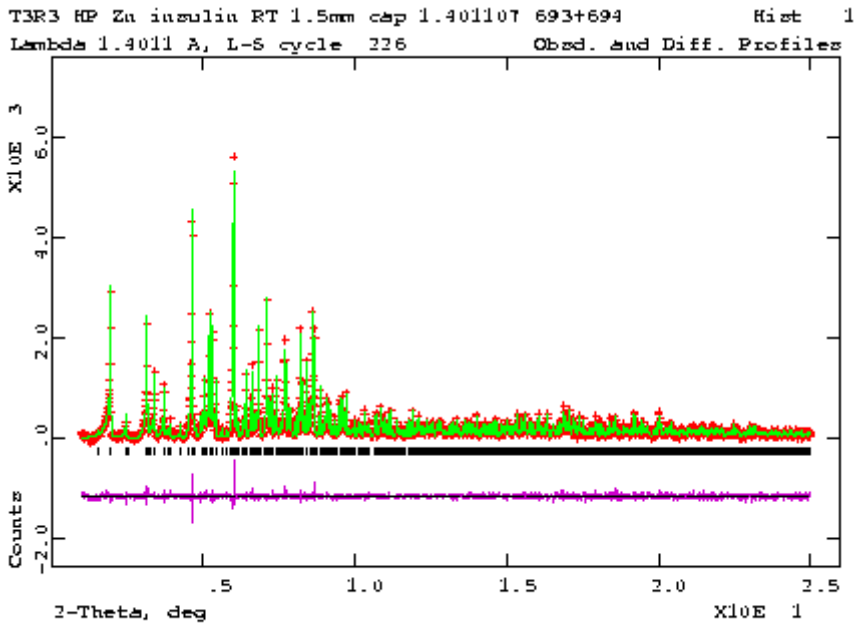
nature materials

Barpanda, Tarascon *et al*,
Nat. Mater. 10, 772 (2011)

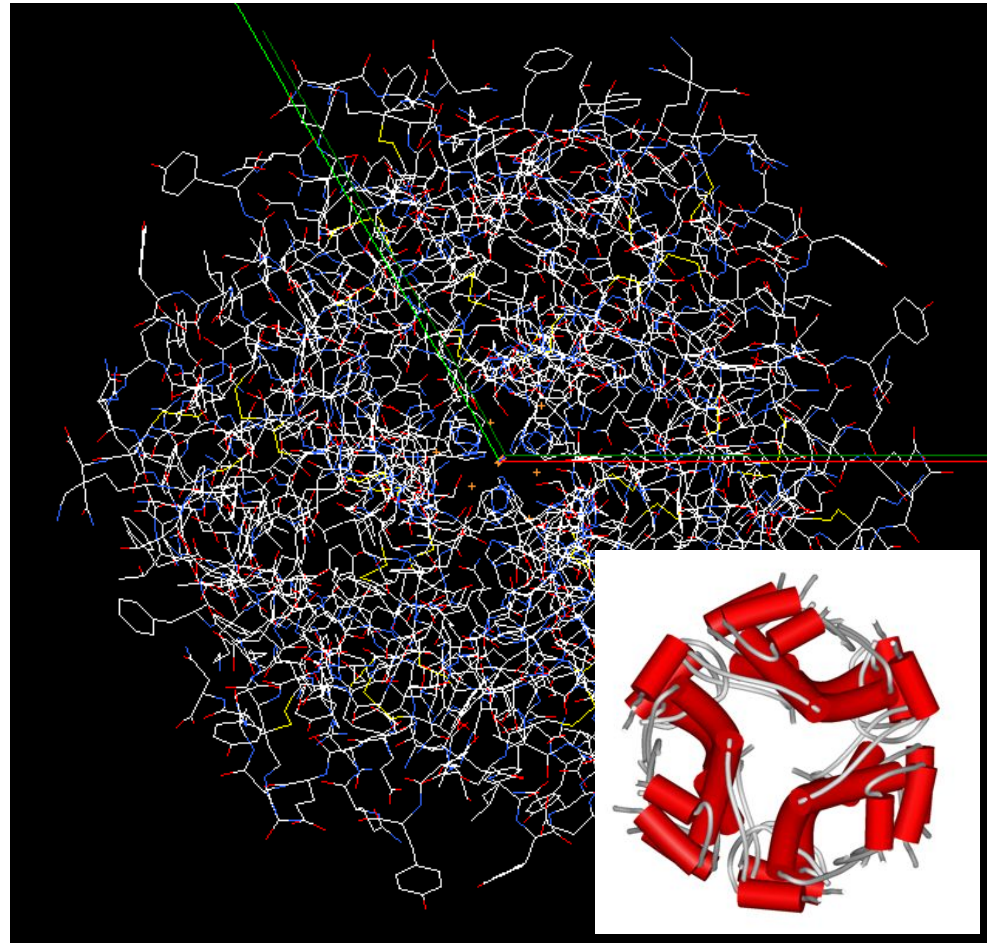
- Li-ion fluorosulphate electrode materials
- Track structural trends in $Li(Fe_{1-x}Mn_x)SO_4F$
- Quantify 0.6% volume change with Li -insertion



High Resolution X-ray Powder Diffraction on Proteins



1st Molecular replacement solution!!
3 parameter problem



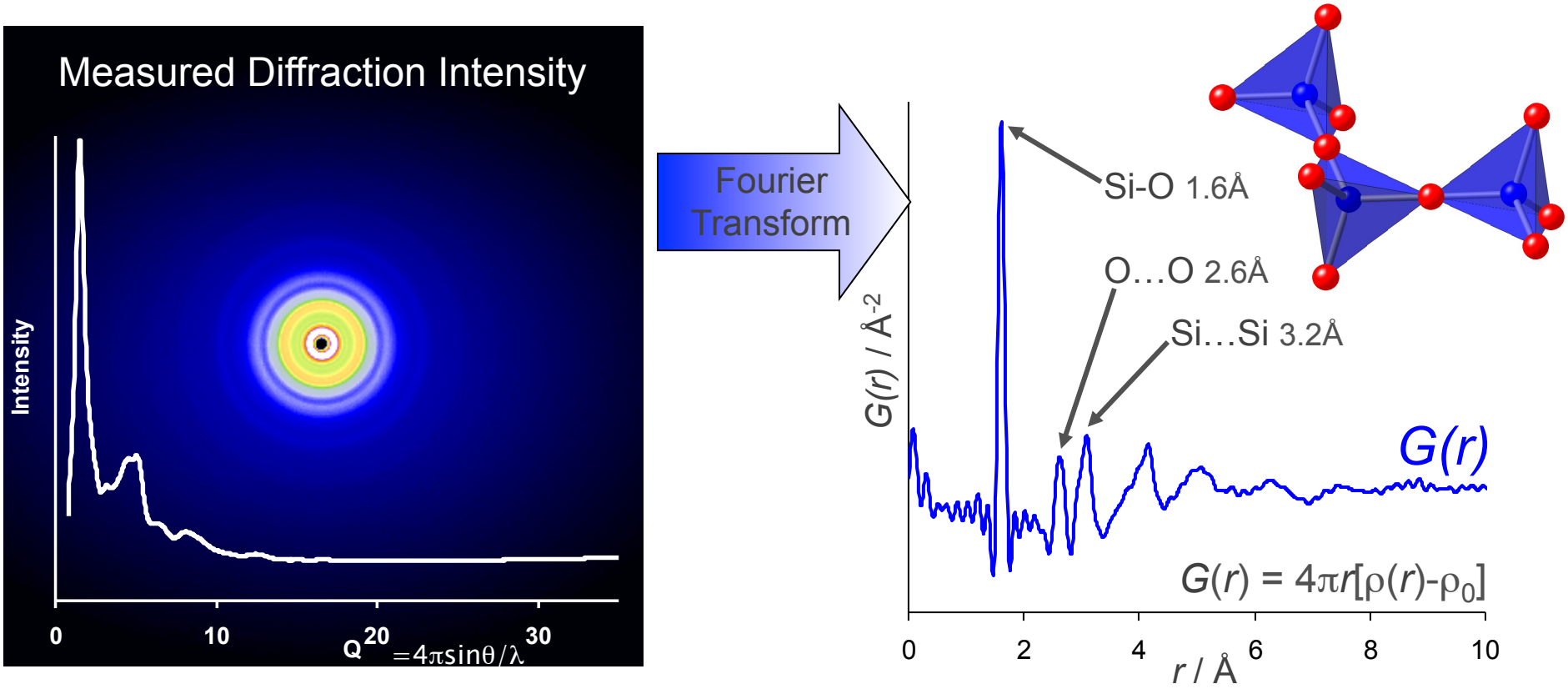
Zn insulin structure determined from powder diffraction data

- R3 unit cell a=81.276Å,c=73.037Å
- Indexed from pattern
- V=418,000Å^3!!
- >1600 atoms!!
- Rietveld refinement (GSAS)
- R_{wp}=3.74%

R.B. Von Dreele, Advanced Photon Source

Pair-Distribution Function (PDF) measurements:
Area detectors + High Energy X-rays

- The structure factor S(Q) measured as a function of diffraction angle using monochromatic X-rays
- Area detectors collect all data simultaneously to yield more rapid measurement



Karena Chapman <chapmank@aps.anl.gov>

The Advanced Photon Source is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Argonne National Laboratory

A Pair Distribution Function

- a weighted histogram of ALL atom-atom distances

Peak Position ⟷ **Atomic distances**

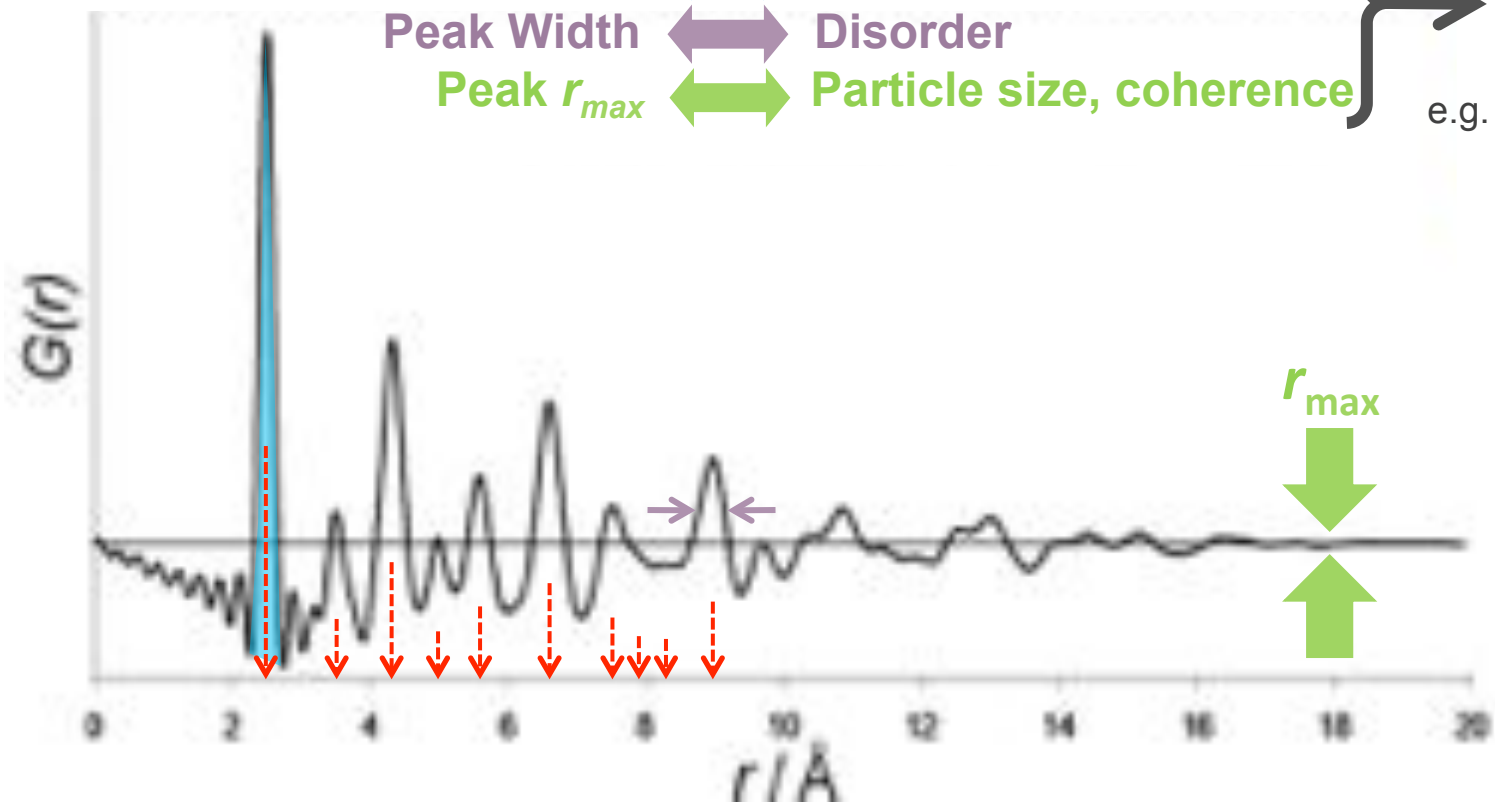
Peak Area ⟷ **Coordination number**

Peak Width ⟷ **Disorder**

Peak r_{max} ⟷ **Particle size, coherence**

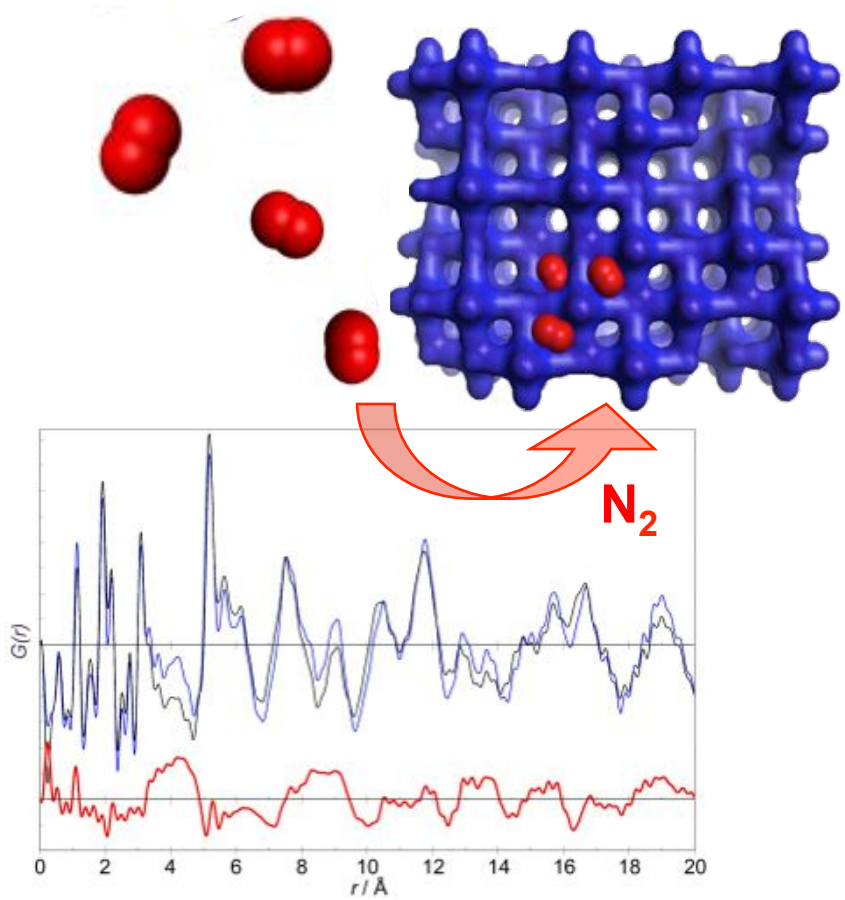
→ **Structure Modeling**

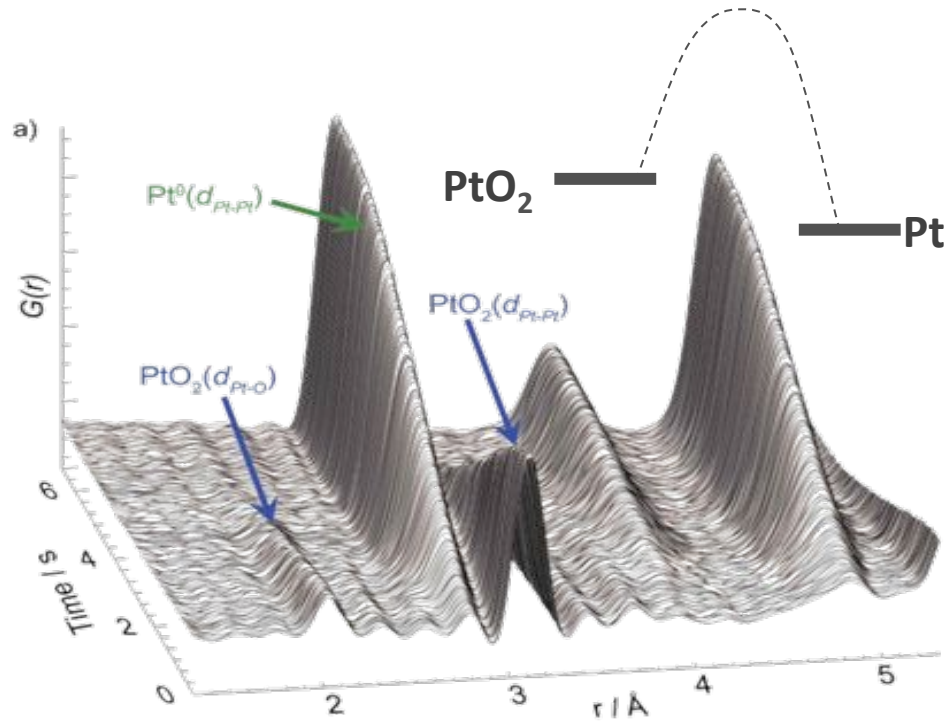
e.g. "real-space Rietveld"



Karena Chapman <chapmank@aps.anl.gov>

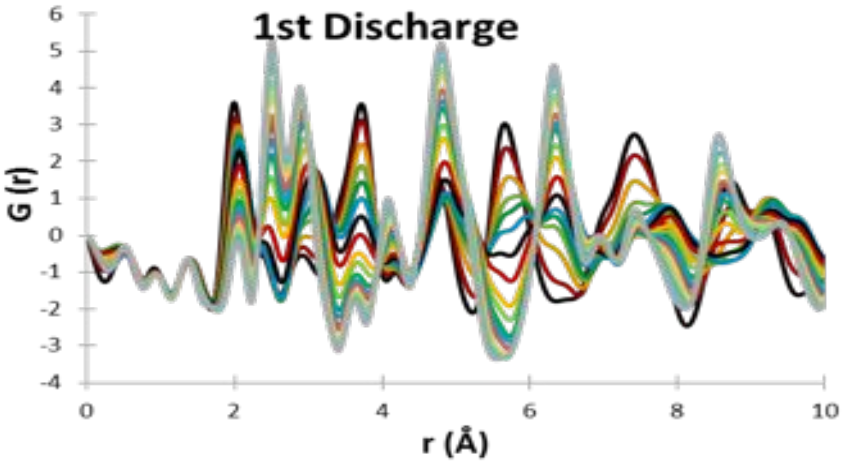
PDF as a function of temperature, reaction progress and guest-loading now relatively routine

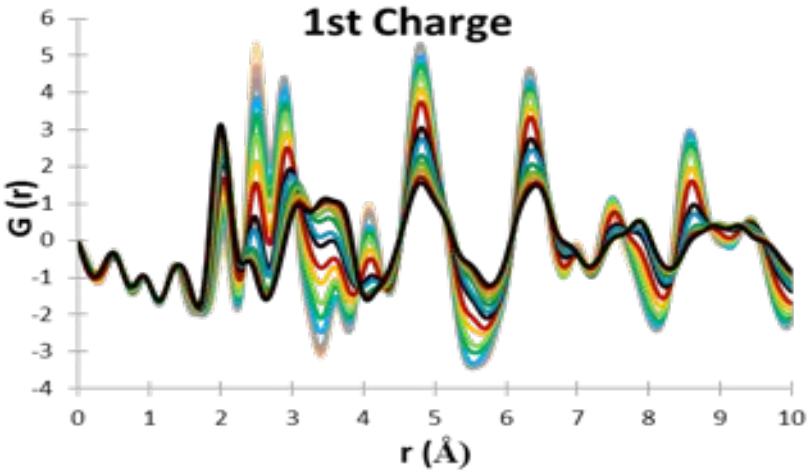


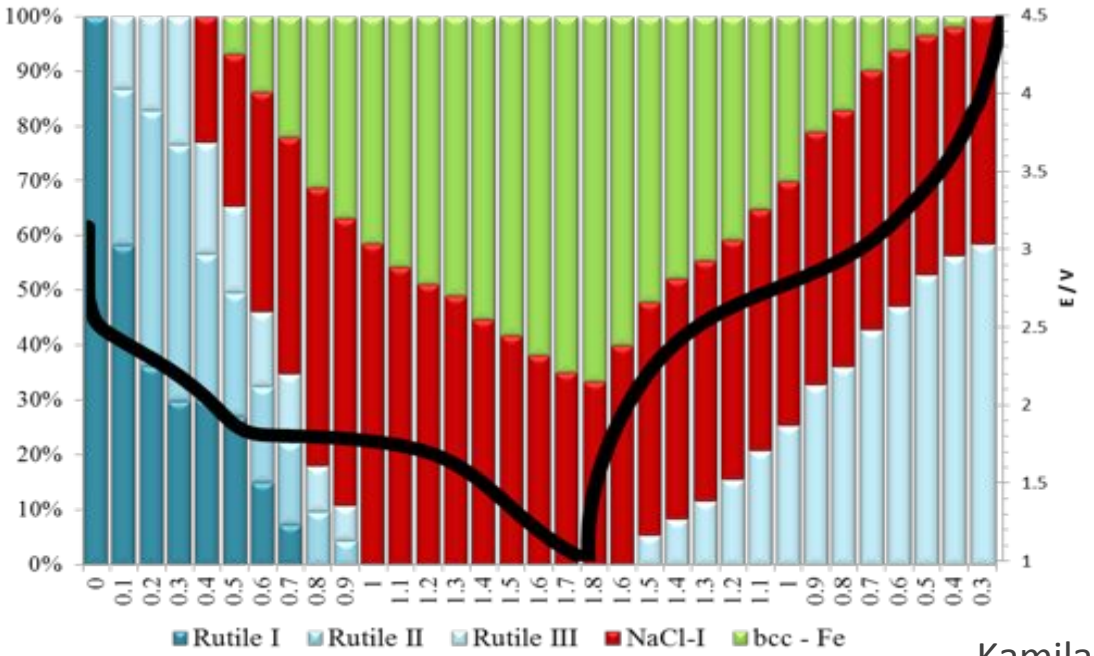


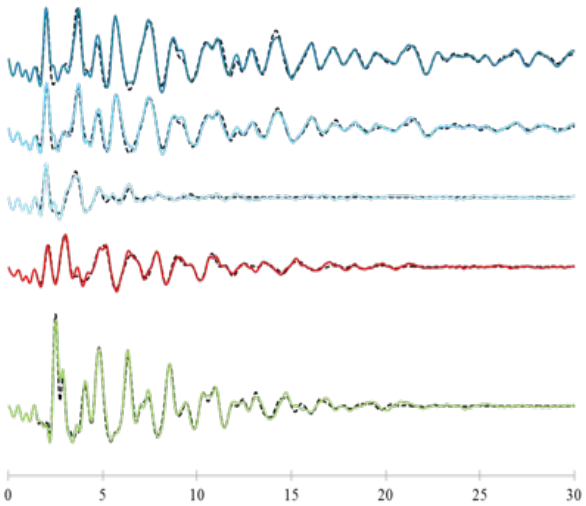
Karena Chapman <chapmank@aps.anl.gov>

FeOF *in situ* PDFs: First Electrochemical Cycle



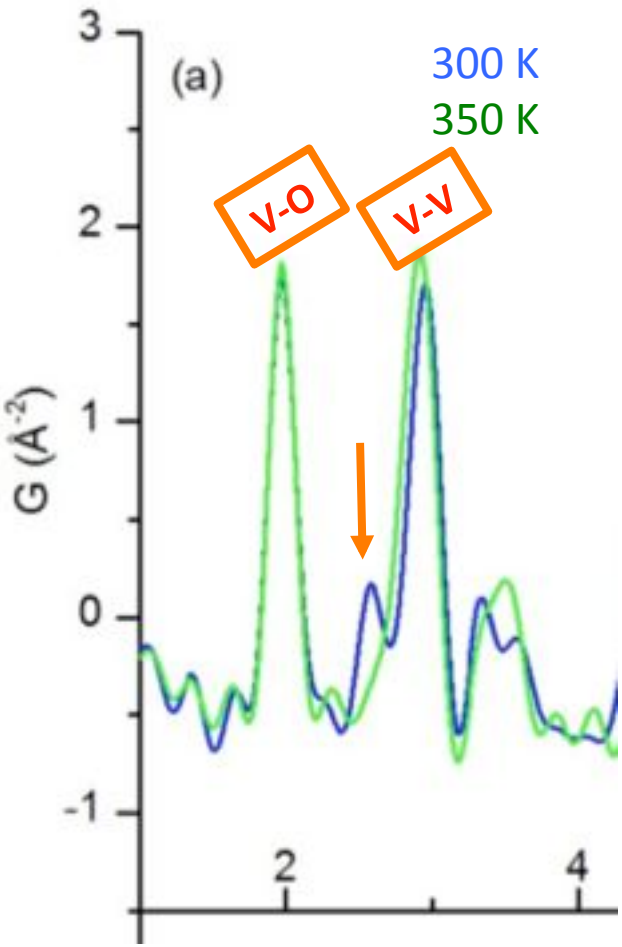


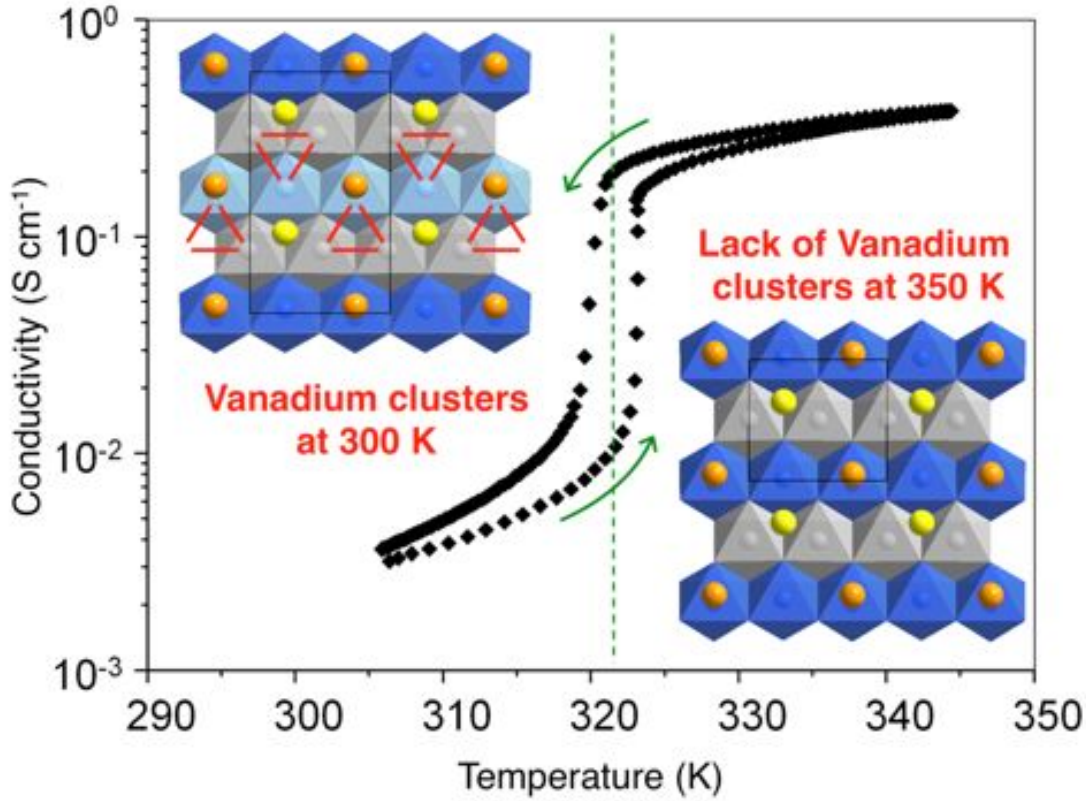




Kamila Wiaderek <kwiaderek@aps.anl.gov>

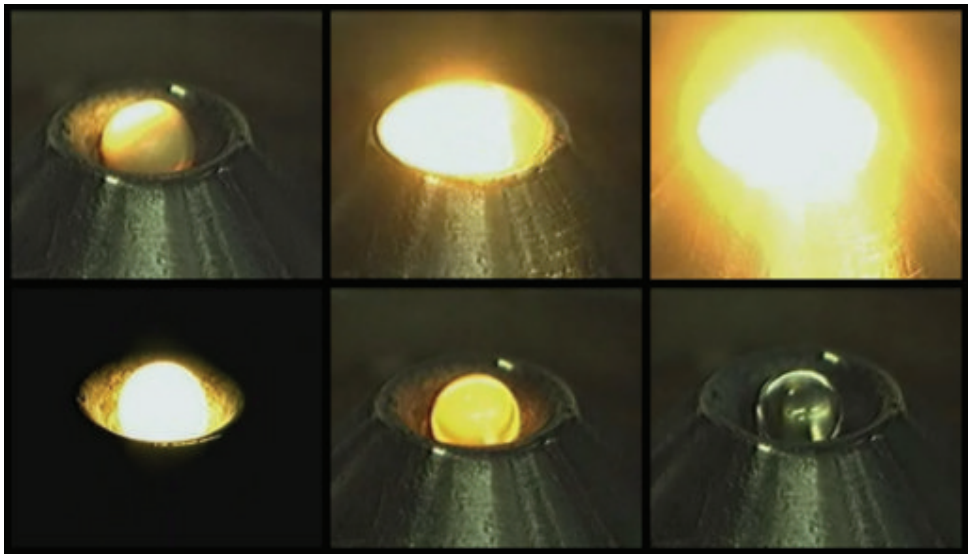
PDF Studies of Vanadium Clustering in $Na_{1/2}VO_2$

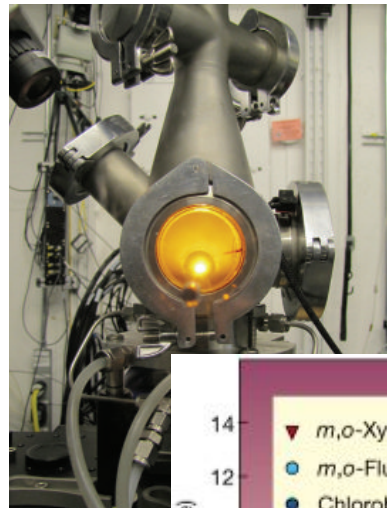


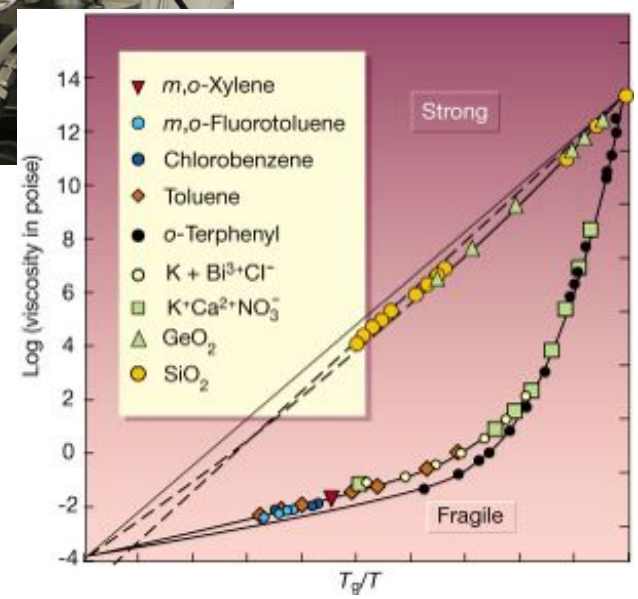


Guignard et al, 2103 submitted

Aerodynamic levitation with laser heating
studying meta-stable structures in liquids/glasses





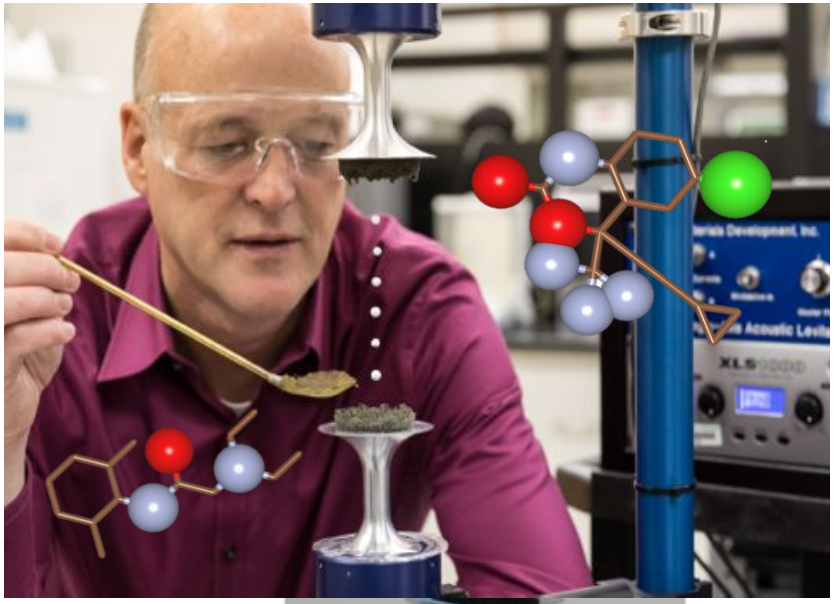


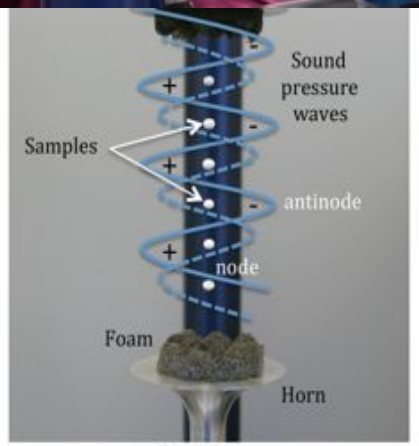
- 400W CO_2 laser
- Temperature range 1500 to >3300°C
- Fast measurements (every 200ms) possible on "fragile" liquids & glasses
- G.N. Greaves *et al*. Science, 322 (2008) 566.

Chris Benmore <benmore@anl.gov>

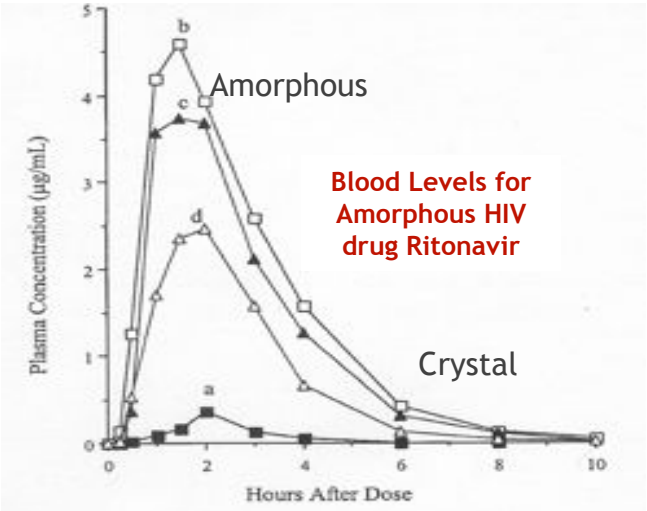
Acoustic Levitation

Synthesis and characterization of amorphous Pharmaceuticals





- Amorphous drugs have enhanced solubility and faster dissolution rates.
- Enhanced amorphization from saturated solutions or by laser heating in acoustic levitator.
- 10W CO_2 laser heating system needed for *in-situ* measurements.
- C.J. Benmore *et al*. J. Pharma. Sci. 102 (2013) 1290.



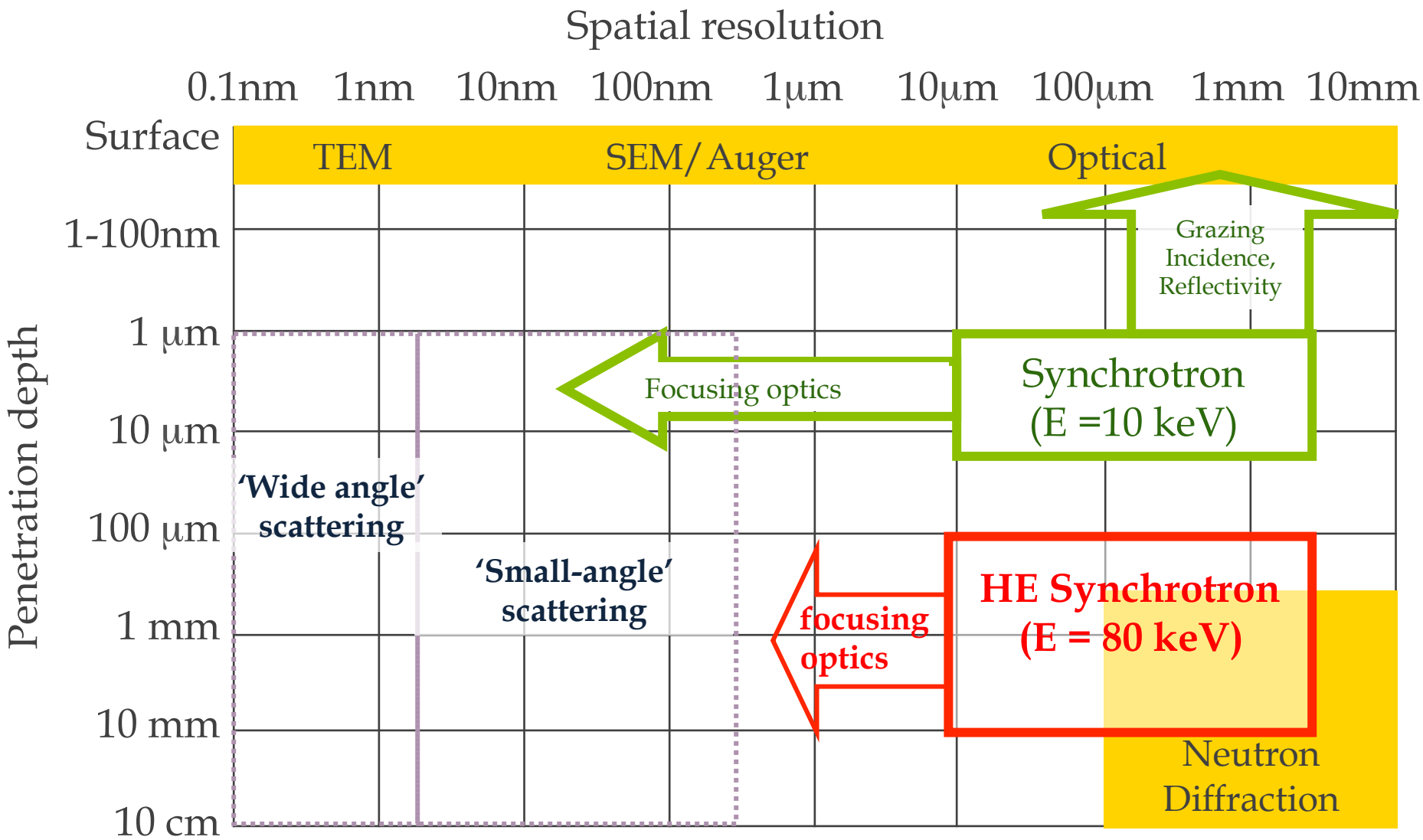
The Advanced Photon Source is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Argonne National Laboratory

Chris Benmore <benmore@anl.gov>

Acoustic Levitation Movie

http://www.youtube.com/watch?v=669AcEBpdsY

Resolution & penetration depth

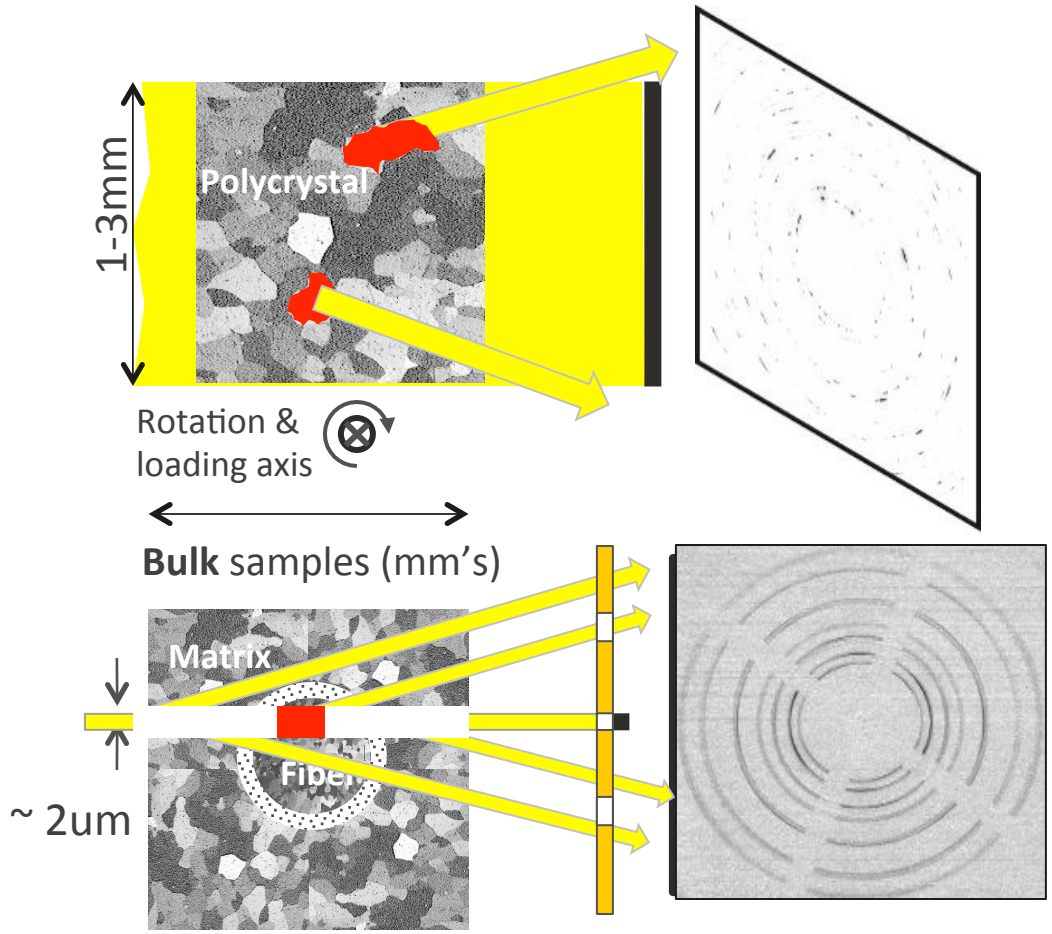


Jonathan Almer <almer@aps.anl.gov>

High-energy x-ray strain and microstructural mapping

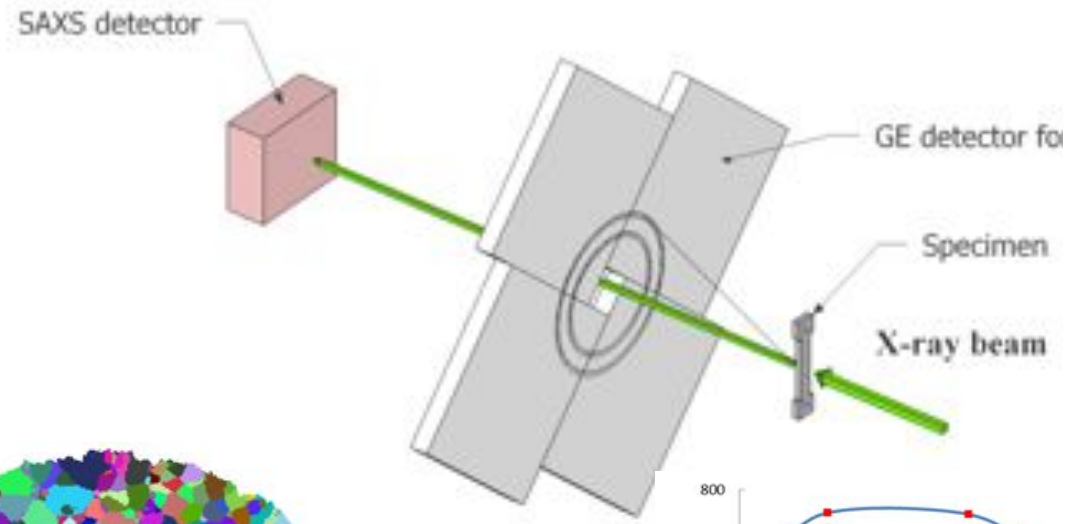
- Single-grain diffraction tomography (HEDM) + absorption tomography
- Grain-average scattering tomography + absorption tomography
- Conical slit diffraction

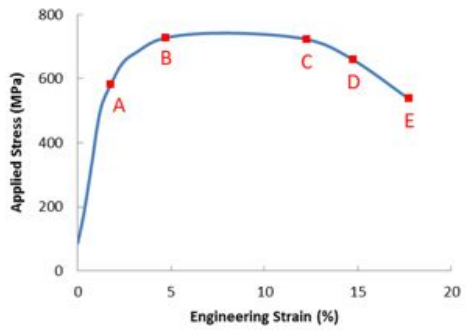
Incident beam E= 50-120 keV
Scattering angles <10 deg

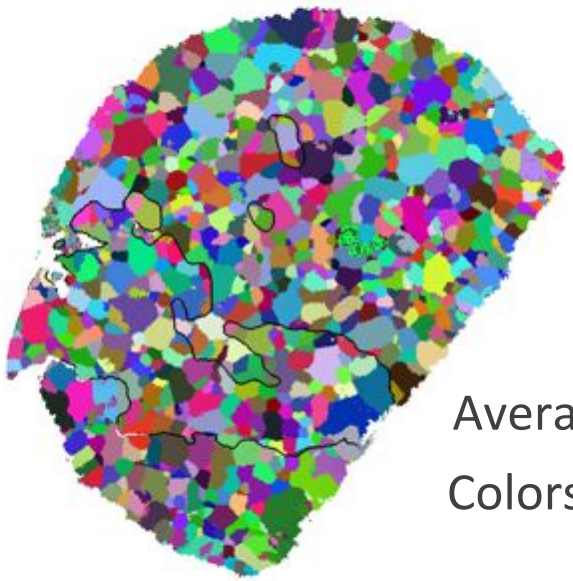


Jonathan Almer <almer@aps.anl.gov>

High-energy Experimental Setup





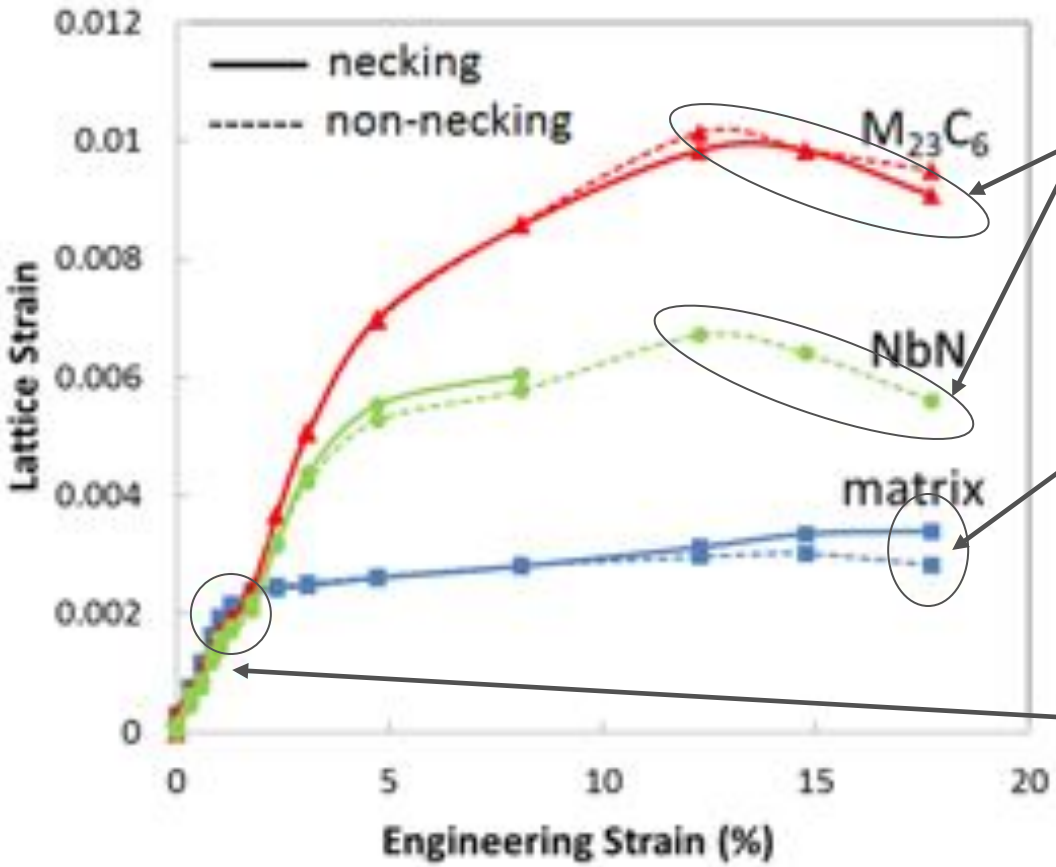


Average grain size ~ 20μm

Colors ~ grain orientation vector

Jonathan Almer <almer@aps.anl.gov>

In situ strain evolution in all phases of NF616 steel



After necking, particles started to detach from the matrix. Consequently, lattice strain in the particles dropped.

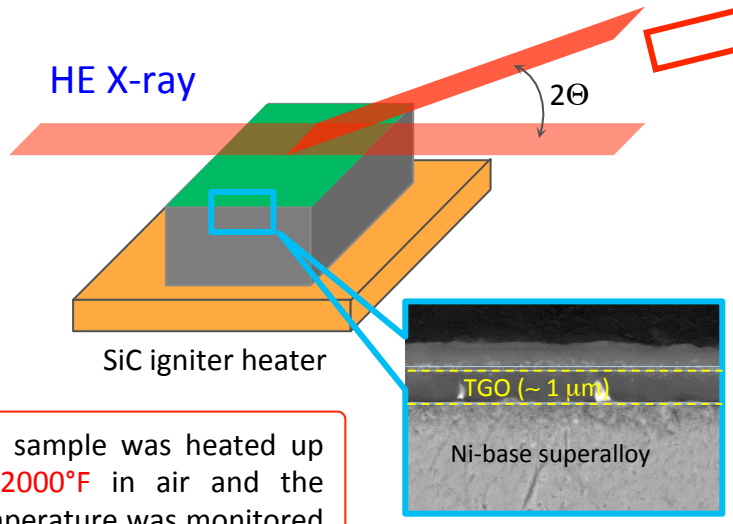
Lattice strain in the matrix became non-uniform after necking: the value was higher in the necking region than the non-necking region.

The BCC matrix yielded at 2% strain, while the particles were still under elastic deformation.

Jonathan Almer <almer@aps.anl.gov>

In-situ Strain Measurement of Thermally-Grown Oxide

TGO growth and creep strains are critical to engine's fatigue life

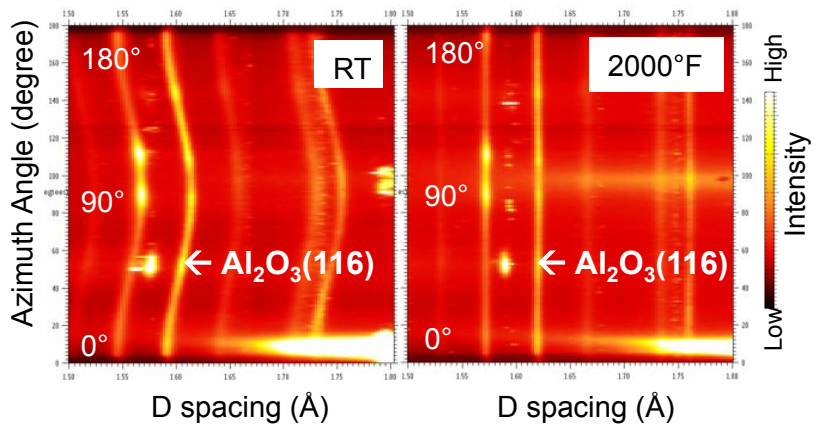


SEM micrograph

The sample was heated up to 2000°F in air and the temperature was monitored by Pt thermal expansion and pyrometer.

2D pattern of TGO (alumina) and spinel

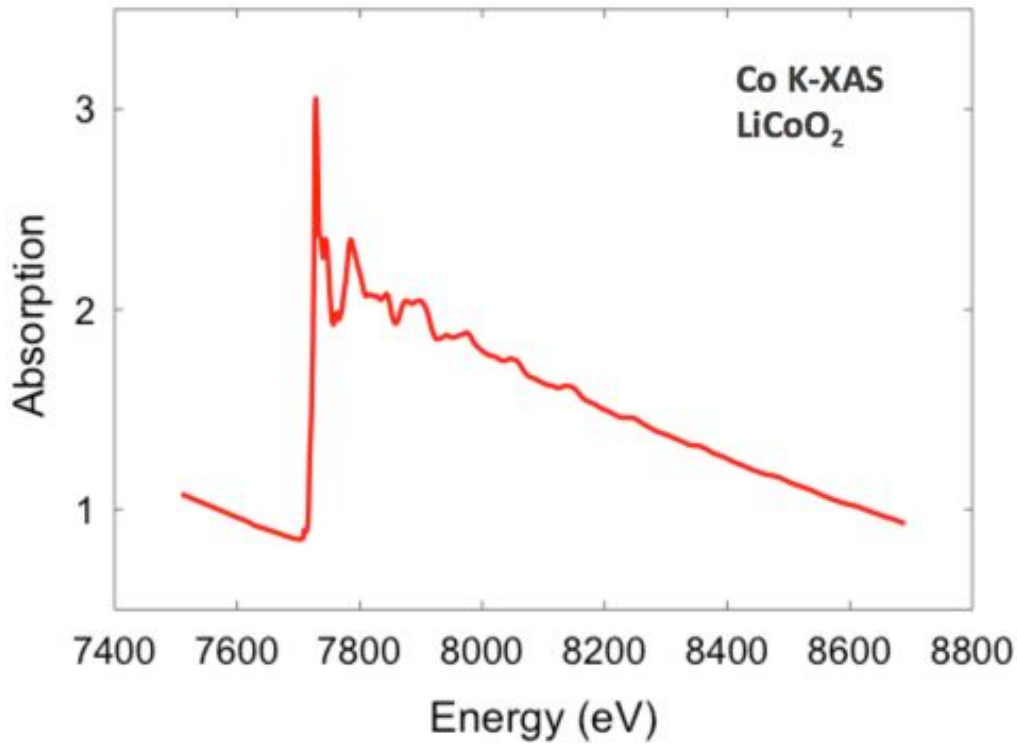
Strain distortion

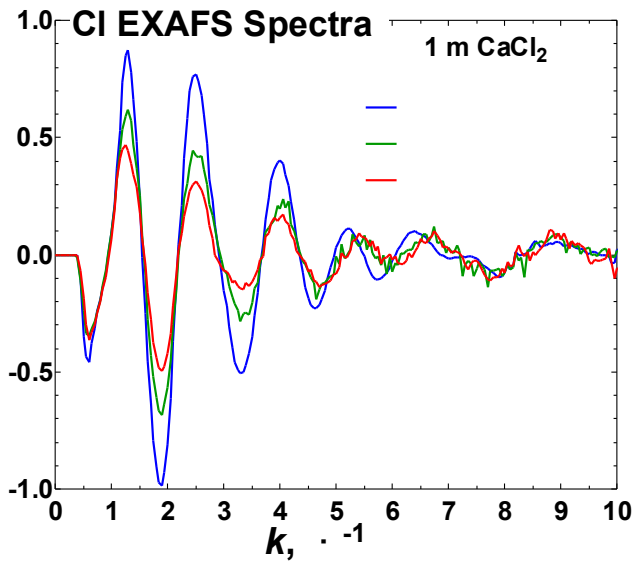


Suzuki, Gao, Lipkin, Singhal (GE), Almer (APS), Pollock (UCSB)

Jonathan Almer <almer@aps.anl.gov>

Synchrotron Spectroscopic Methods





Many Spectroscopic Abbreviations

- ***X-ray Absorption Spectroscopy (XAS)***
  - Extended X-Ray Absorption Fine Structure (EXAFS)
  - X-ray Absorption Near Edge Structure (XANES)
  - X-ray Absorption Fine Structure (XAFS)
  - Resonant and Non-resonant X-ray Emission (XES)
  - X-ray (Non-resonant) Raman Scattering (XRS)
  - …

Combine above methods with microbeams to obtain elemental-chemical-structural information with micron-scale spatial sensitivity

Coupled to the time structure of the synchrotron radiation provides access to processes in the ultrafast time domain.

Mali Balasubramanian <mali@aps.anl.gov>

Basic X-ray Absorption Spectroscopy

- ***X-ray Absorption Spectroscopy***

Element specific, sensitive to dilute constituents (sub-mono layer coverage), short-range order probe

❖ XANES is strongly sensitive to formal **oxidation state** and **site symmetry**

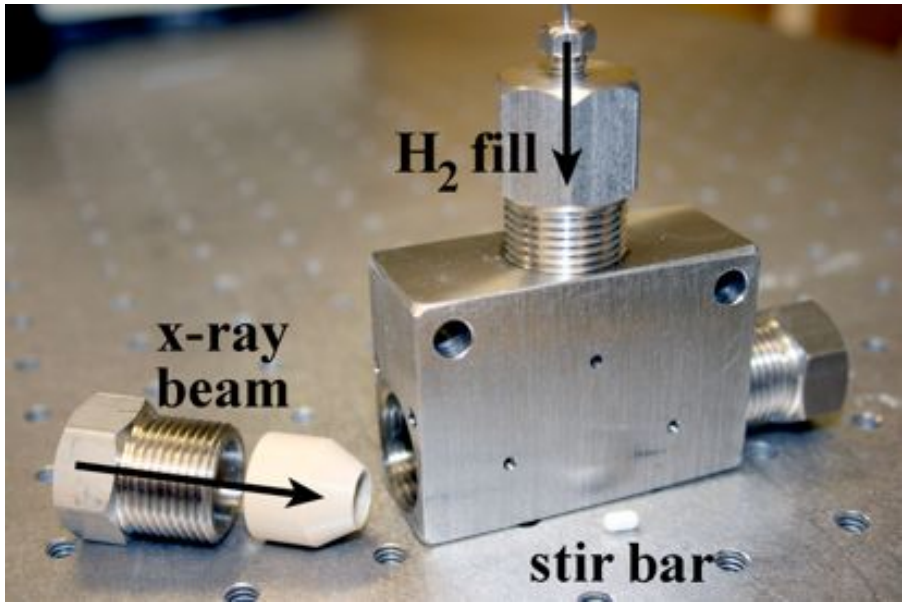
❖ EXAFS is used to determine the **distance, coordination number, disorder** and **type** of the neighbors in the local and medium-range (~ 6 Å)

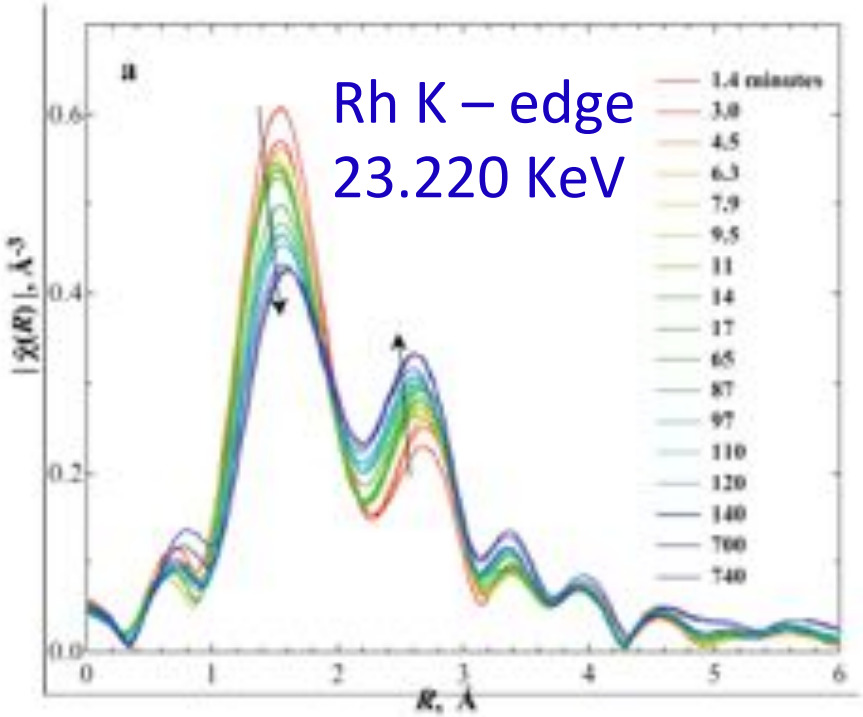
- ***Hard X-ray Non-resonant Raman***

Utilize in situ capability of hard x-rays with the power of soft x-rays, q-dependence provides additional information

- Uses High Flux Tunable Energy at Synchrotrons
- Chemical and structural information
- Short and medium range order probe
- Allows in situ/operando studies

Operando XAFS: Rhodium Catalyzed Hydrogenation of Benzene





A continuously stirred reactor for the *operando-XAFS :* $[RhCp^*Cl_2]_2$ at 100 °C and 50 atm initial H_2 pressure.

Mali Balasubramanian <mali@aps.anl.gov>

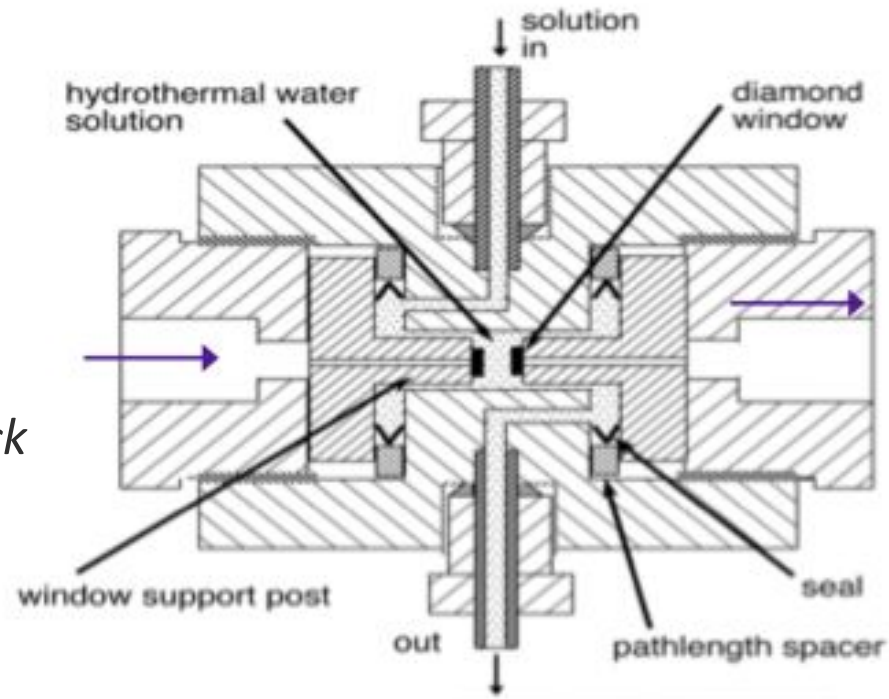
Linehan, Fulton et al. (PNNL), Finke (CSU)

Diamond-window transmission XAFS cell for low-Z Ions

Cell used to study low-Z ions:
Cl^-,K^+,Ca^{2+}

supercritical water cell design

- *500°C, 600 bar*
- *Beam size: 50-100 microns diameter,*
- *Window: [110] diamond 10 microns thick*
- *Lowest Energy: 2750 eV.*

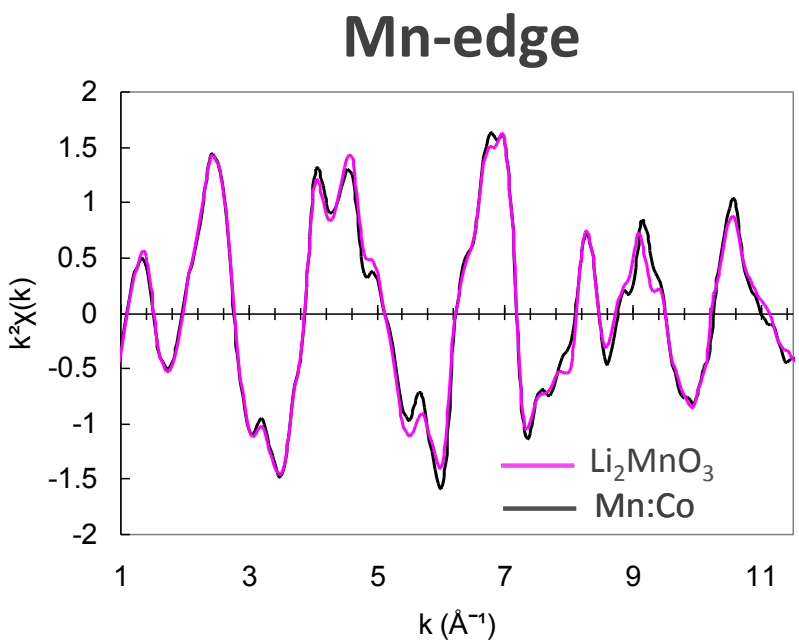


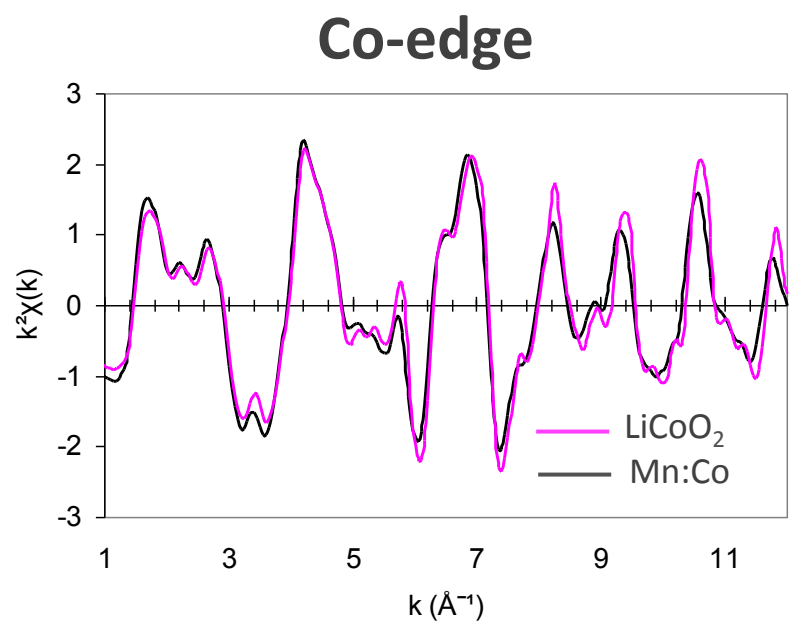
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

Fulton et al: Rev. Sci. Instrum.
75 (12), 5228-5231 (2004).

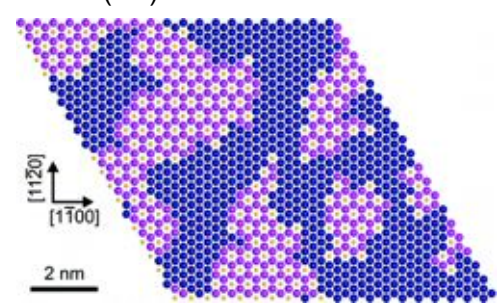
Mali Balasubramanian <mali@aps.anl.gov>

Element specific local structure: $Li(Li_{0.2}Co_{0.4}Mn_{0.4})O_2$





- **Mn XAFS very similar to Li_2MnO_3**
- **Co XAFS very similar to $LiCoO_2$**



Bareno et al., Chem. Mater. DOI: 10.1021/cm200250a

Mali Balasubramanian <mali@aps.anl.gov>

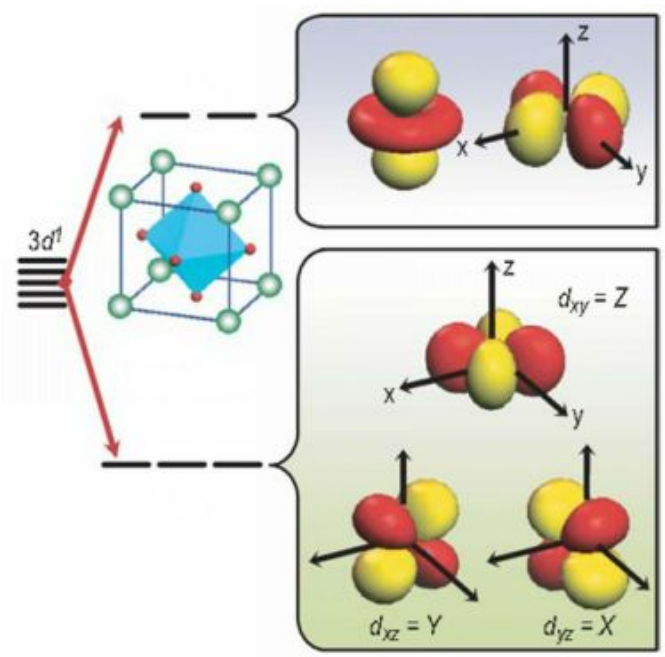
X-ray Raman Scattering (XRS)

XRS is an inelastic x-ray scattering process

TM redox chemistry can be studied using K-edge XAS

Current scientific interest :
understand the role played by oxygen in charge compensation and also role of the TM d-states

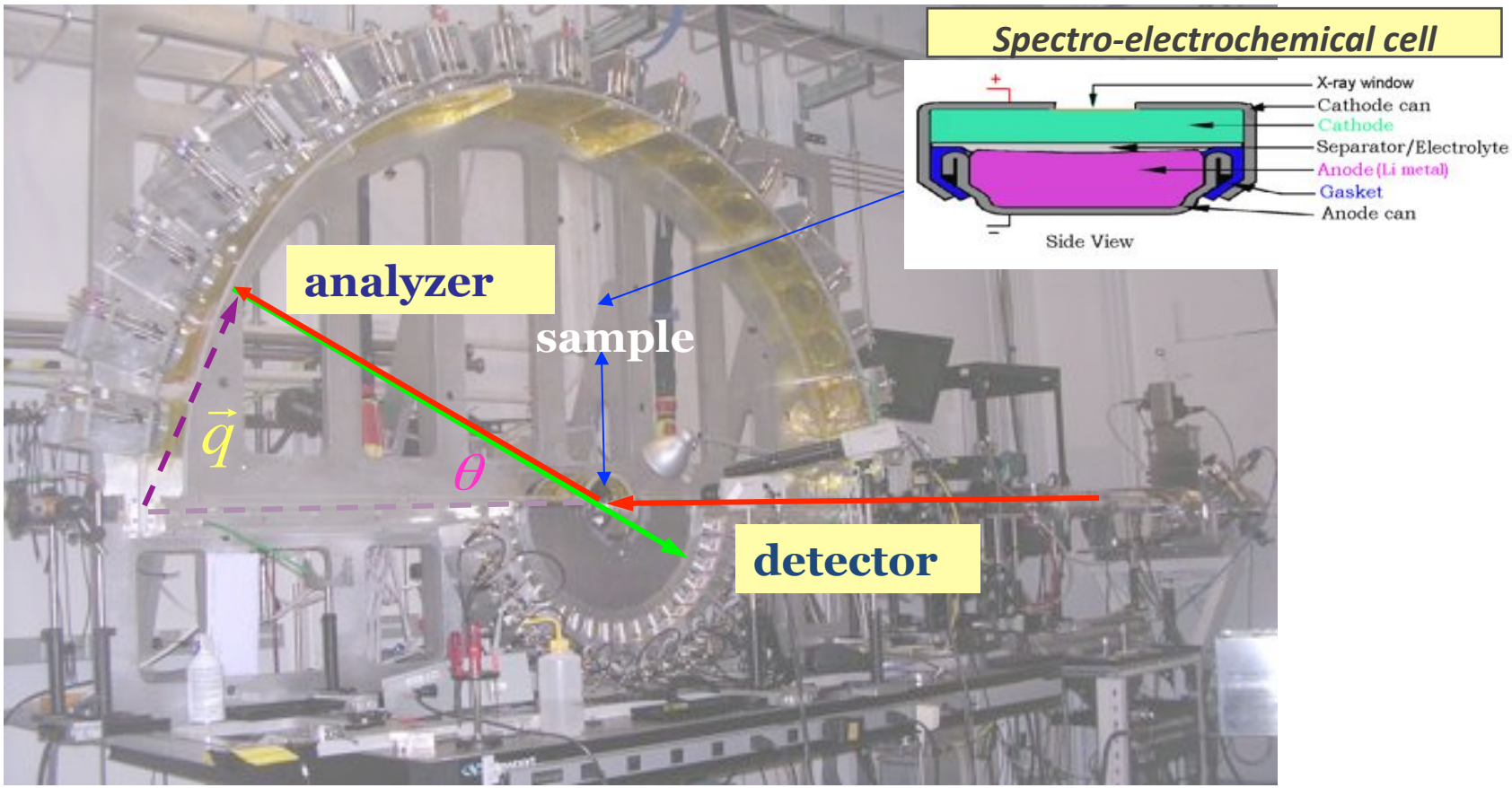
O K-edge and TM 2p and 3p edges traditionally studied using EELS or soft-XAS



XRS: In situ alternative to soft–XAS or EELS

Mali Balasubramanian <mali@aps.anl.gov>

How to measure XRS efficiently?

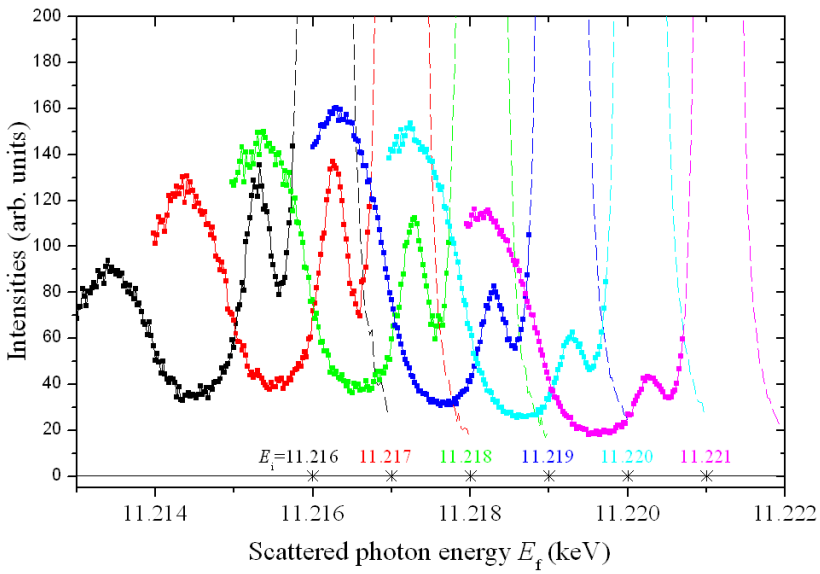


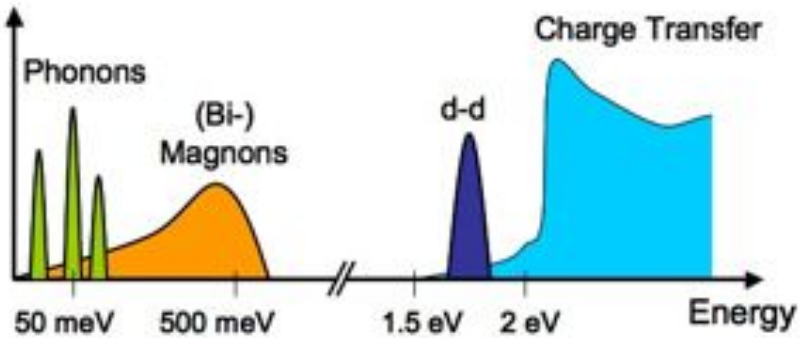
APS Beamline 20-ID Mali Balasubramanian <mali@aps.anl.gov>

Other Inelastic X-ray Scattering

Inelastic X-ray Scattering (IXS)
Resonant enhancement 100 times larger than non-resonant

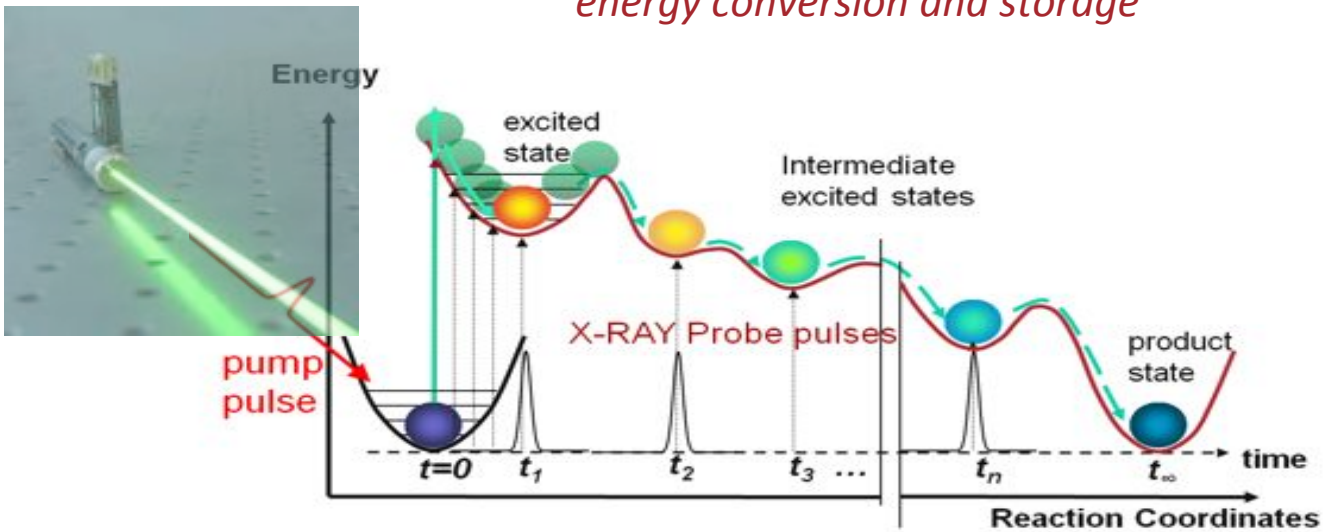
Resonant Inelastic X-ray Scattering (RIXS)
measures both the energy and momentum change of the scattered photon





Time-resolved X-ray spectroscopy and scattering

Studying electronic and structural dynamics of processes related to energy conversion and storage

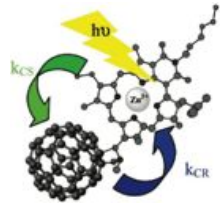


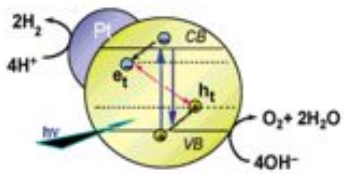
TR-XAFS or TR-WAXS

- *Electronic structure*
- *Local coordinate*
- *Global shape*
- *Oxidation state*
- *Distance to neighboring atom*
- *Number of neighbors*

Scientific Areas:

- *Photochemistry*
- *Pphotophysics of transition metal complexes*
- *Structural dynamics in photovoltaic solar cells*
- *Time-resolved x-ray science in geochemistry*
- *Catalysis and Fuel Cells*





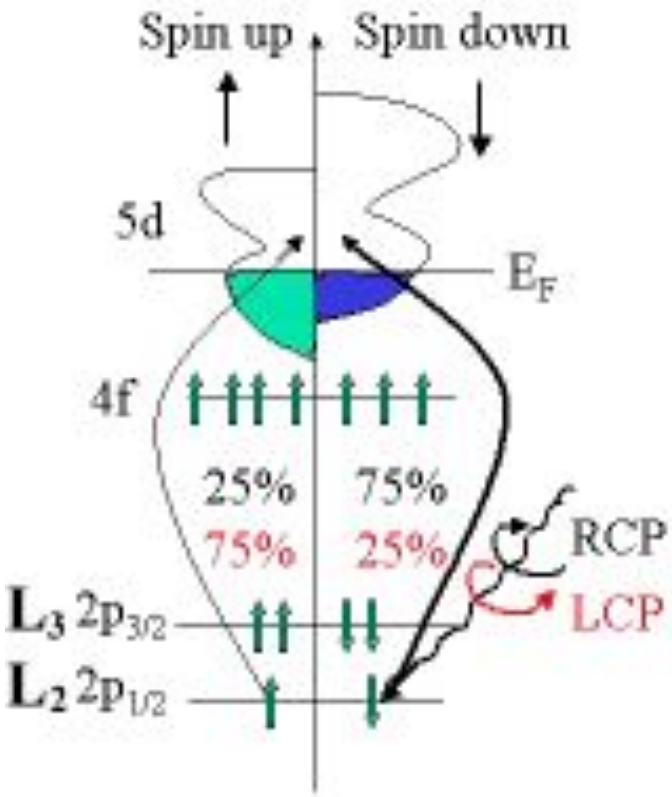
Multiple time scale: 80 ps - 1 ms

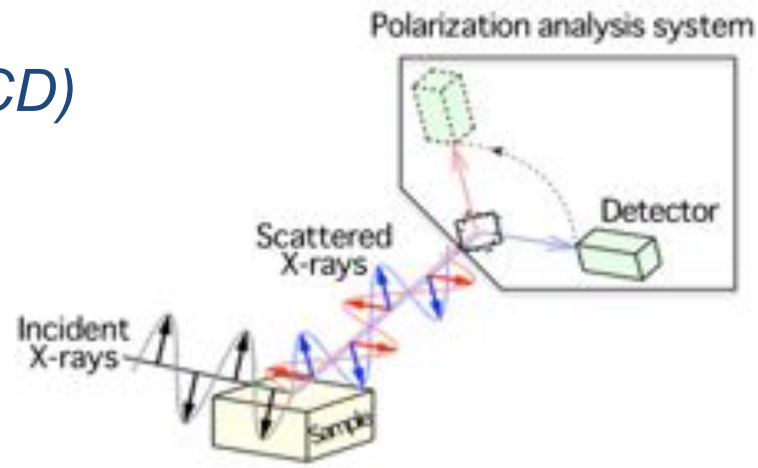
Multiple length scales: 1 Å to 1 mm!

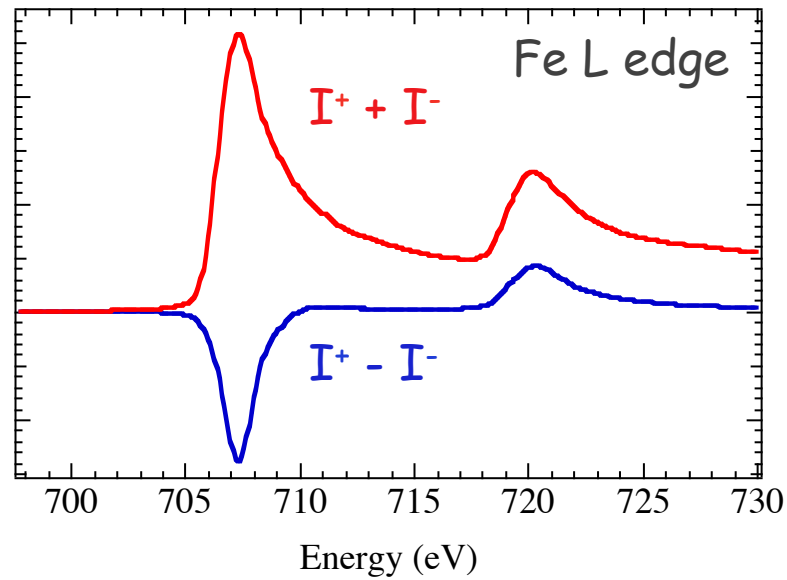
Xiaoyi Zhang <xyzhang@aps.anl.gov>

Magnetic X-ray Scattering

X-ray magnetic circular dichroism (XMCD)







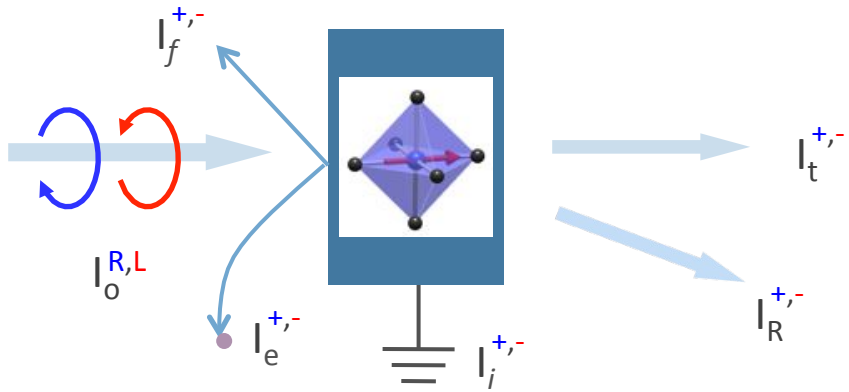
$I^+ + I^-$ → Chemical

$I^+ - I^-$ → Magnetic

Choi Yong <ychoi@aps.anl.gov>

XMCD Examples

X-ray Magnetic Circular Dichroism (XMCD)



Absorption difference when change chirality of x-ray beam

Spectroscopy (Vary Energy)

☞ Electronic configuration

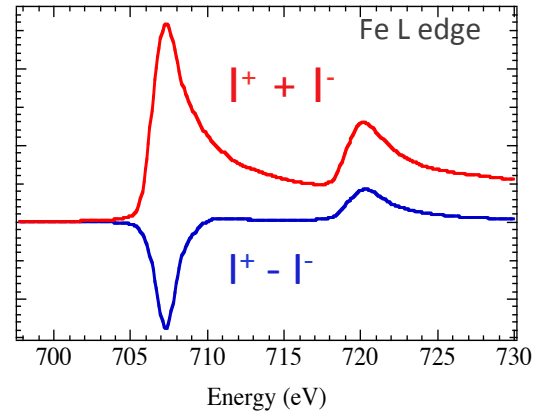
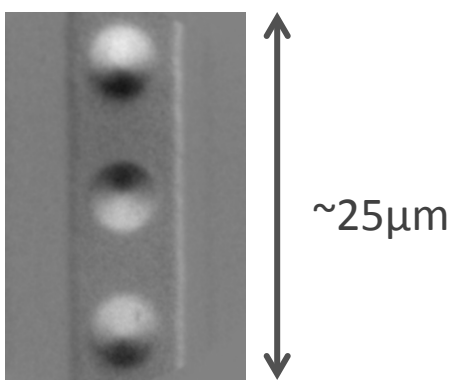
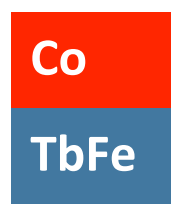


Photo-electron imaging (Timing)

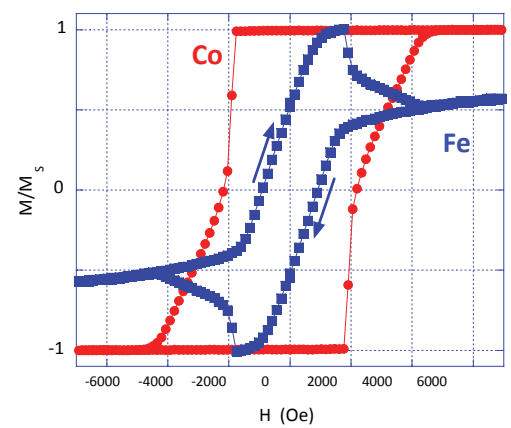
☞ Magnetic Domain Structure





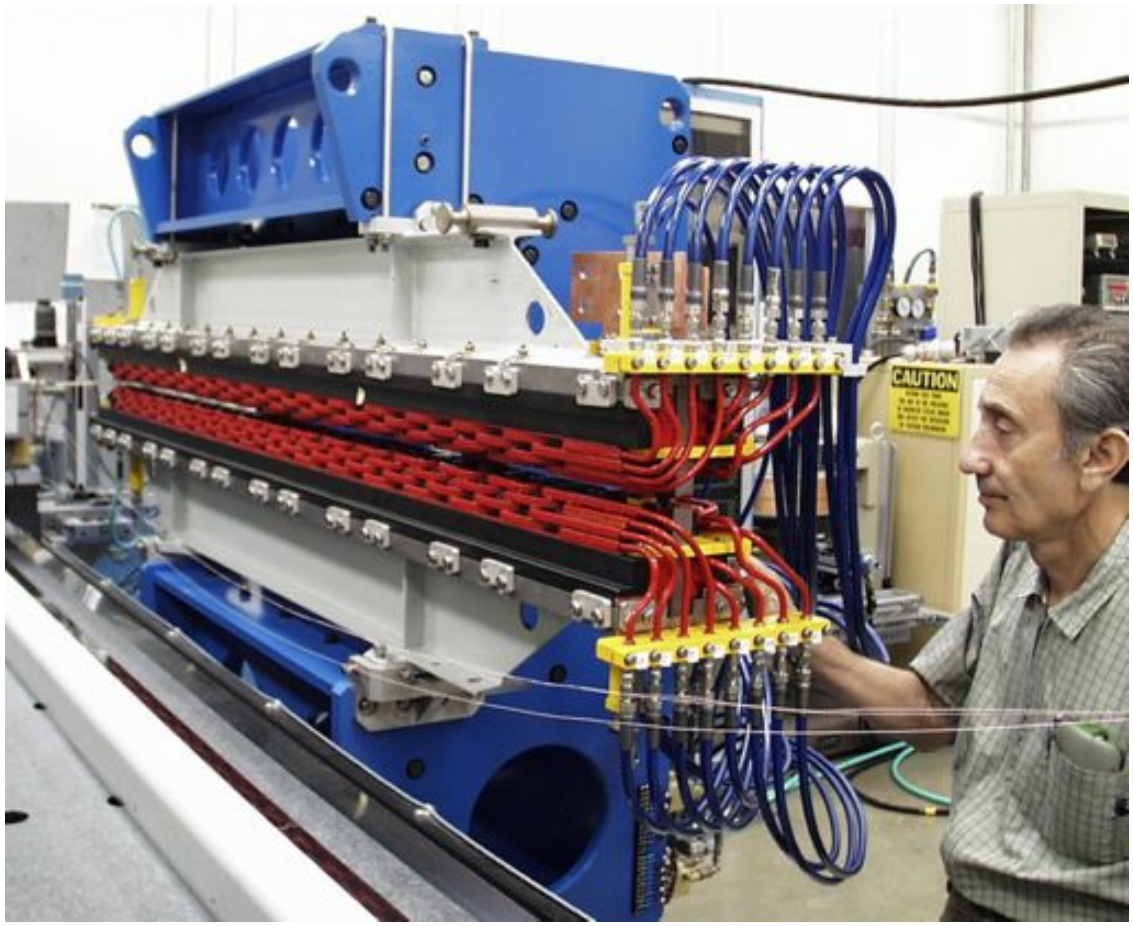
Elemental Hysteresis (Vary Field)

☞ Sample Magnetization



Choi Yong <ychoi@aps.anl.gov>

Circularly polarizing undulator



Normal planer undulators produce linearly polarized light even off-axis

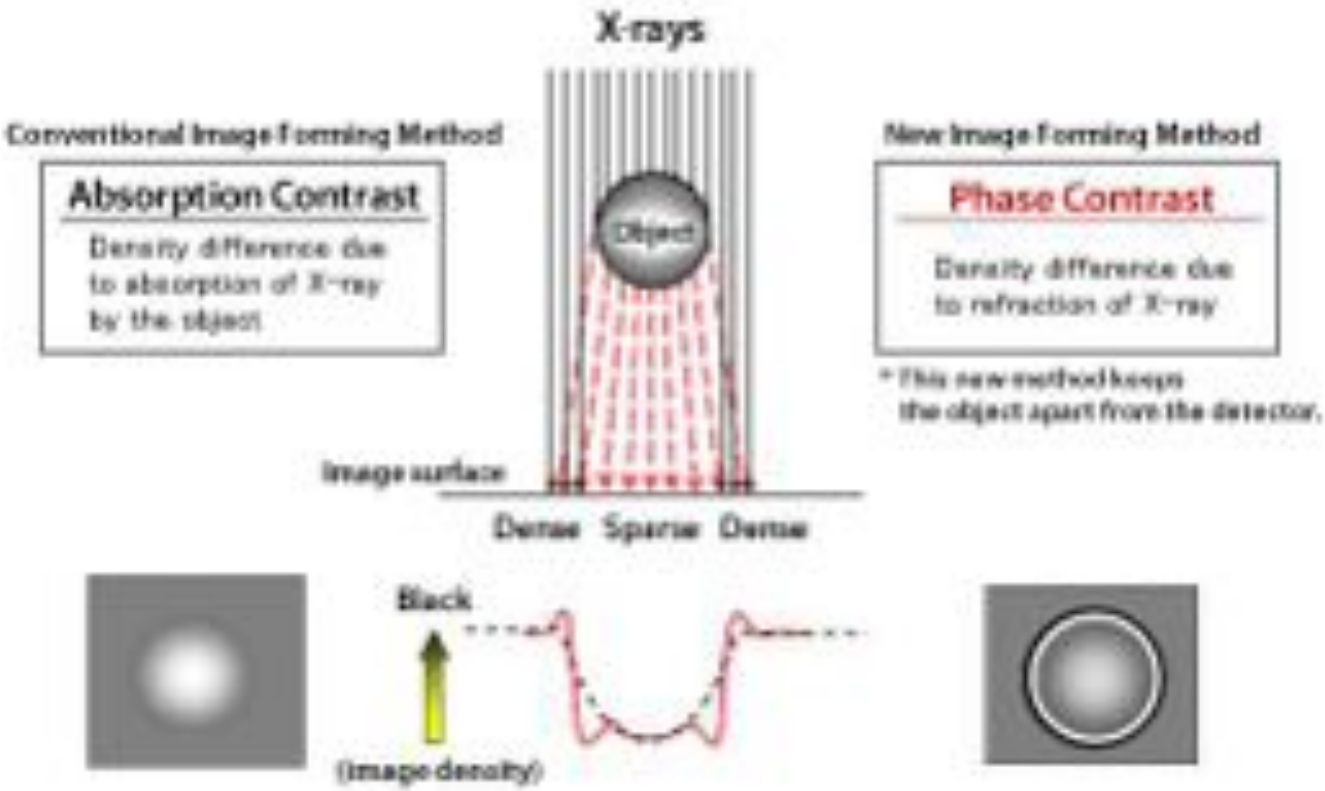
Particle beam moves in helical rather than planar orbit.

Synchrotron Imaging, Tomography and Elemental Mapping

Hand of his wife Anna Bertha Ludwig
wife of Wilhelm Röntgen ~ 1895

Imaging / Tomography / Elemental Mapping

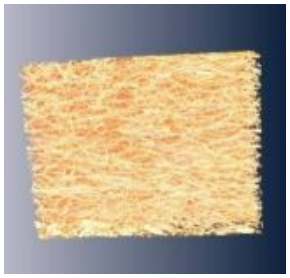
- 2D - Real Time (20Hz) and High Speed (>200 kHz)
- 2D - X-ray magnifying optics: 30 nm resolution
- 3D for micro **C**omputed **T**omography) CT (1 to 100 Hz)



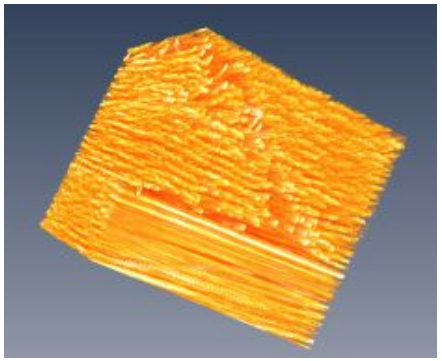
Francesco De Carlo <decarlo@aps.anl.gov>

Micro Tomography of Static Samples

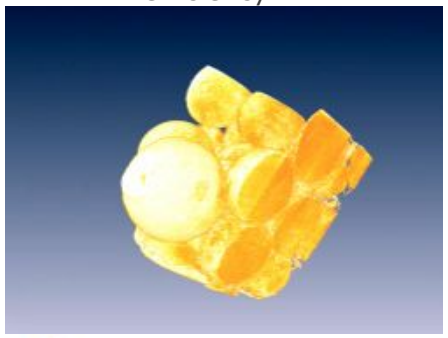
High throughput fully automated 1μm resolution tomography



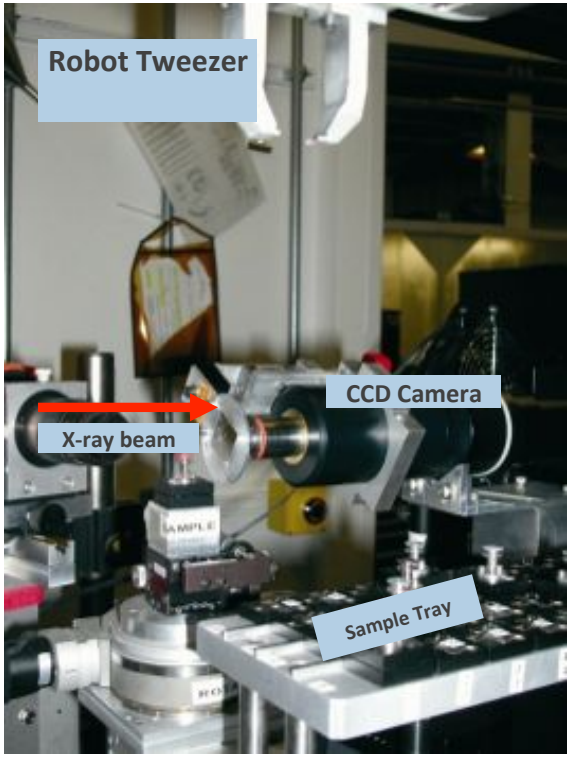
New Reusable Solid Rocket Motors Insulation



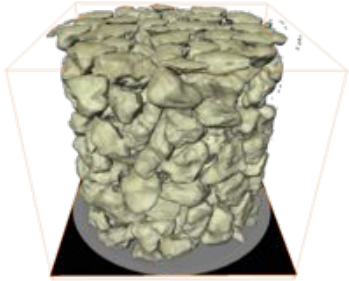
Self healing composite - healing efficiency



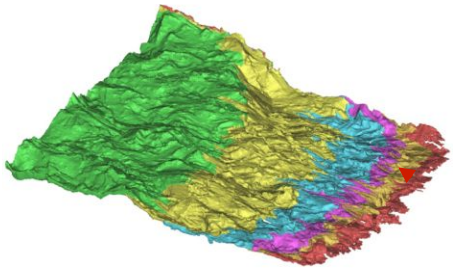
Ceramic coating layers



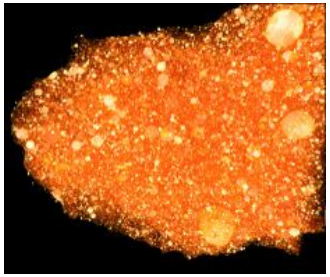
Much Data!! ~ 5 TB/day



Mechanical behavior of sand under compression



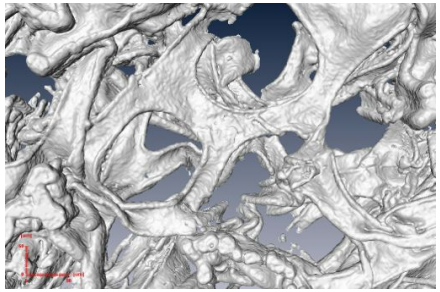
Fatigue cracking (N. Chawla)



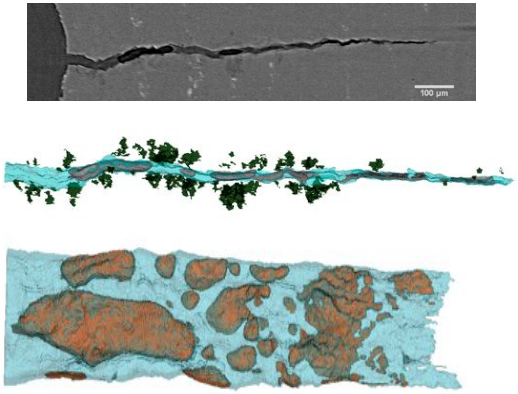
Geopolymers

Francesco De Carlo <decarlo@aps.anl.gov>

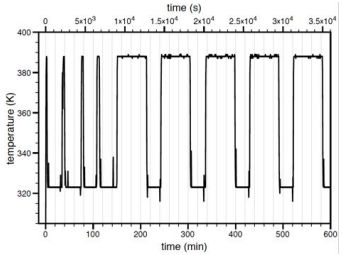
Micro Tomography of Dynamic Samples



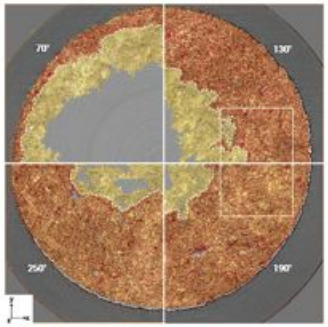
3D rendering of porous Cu:Sn electrode cycled vs. Li metal
Lynn Trahey et al., 221st ECS Meeting (2012)

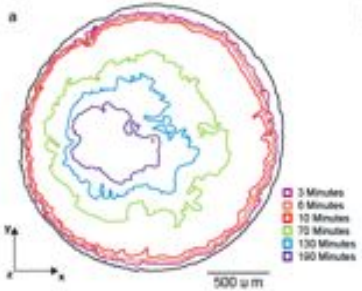


Dynamic metal corrosion studies to show a 3D cross section of a crack under corrosive and cyclic fatigue loading conditions.
N. Chawla et al.



Dehydration of Gypsum



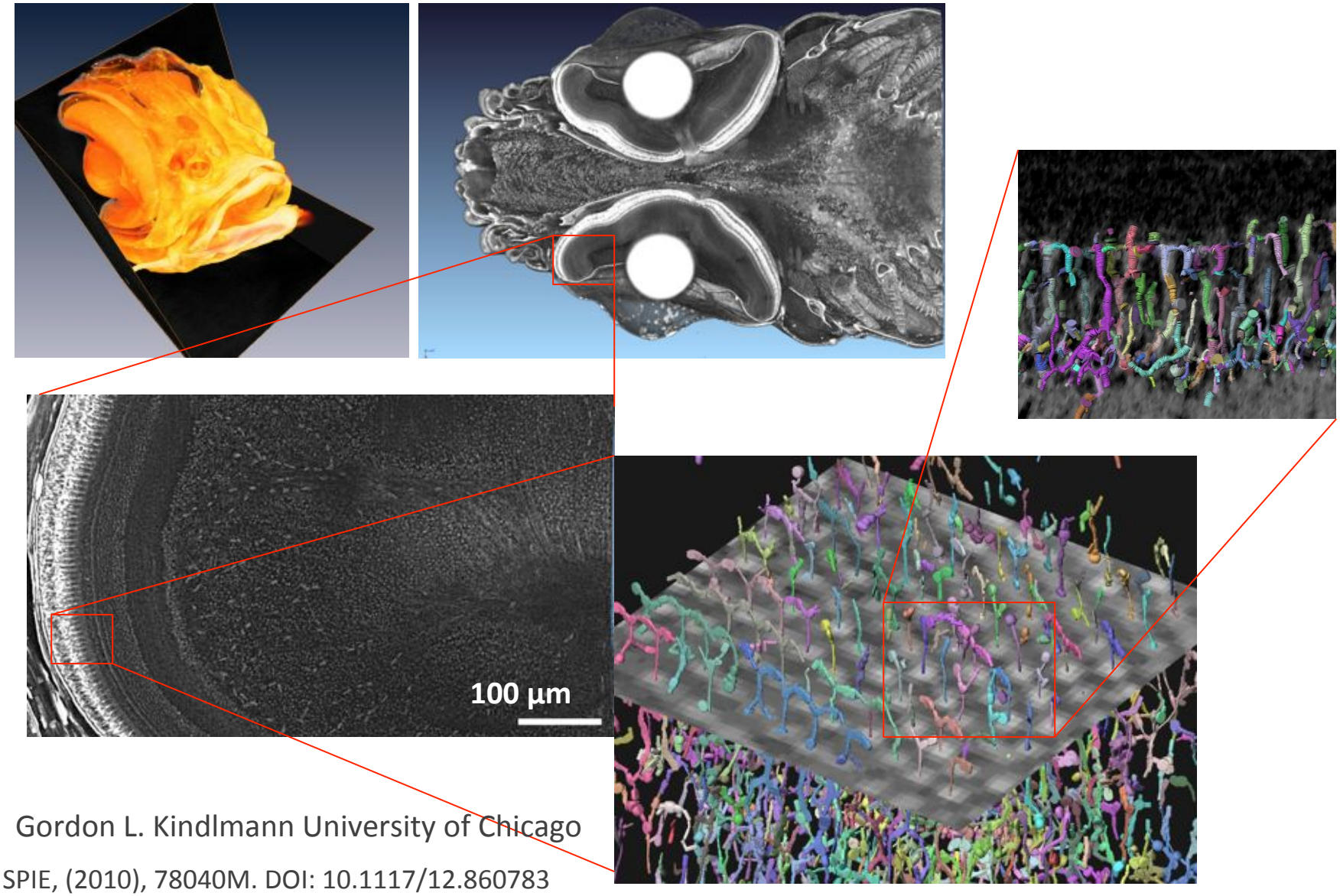


Even More Data!! ~ 125 TB/day

Francesco De Carlo <decarlo@aps.anl.gov>

Fusseis & Xiao et al, Sol Earth 2012

Data modeling
2D/3D of Juvenile Zebra Fish Retina



Gordon L. Kindlmann University of Chicago

SPIE, (2010), 78040M. DOI: 10.1117/12.860783

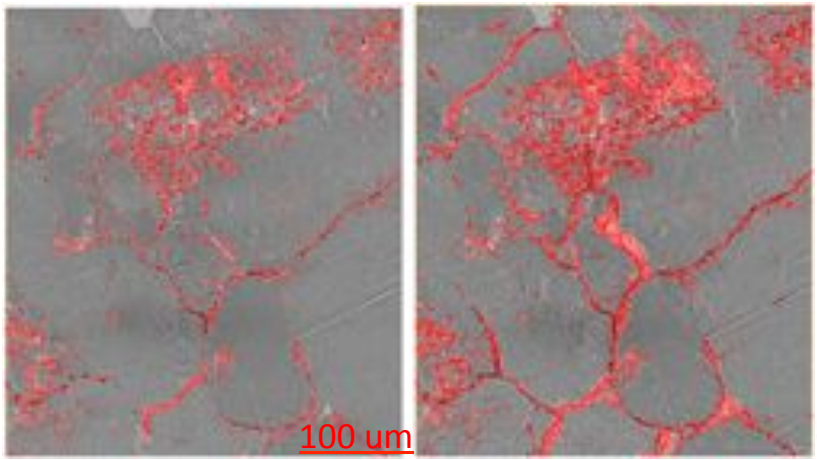
Francesco De Carlo <decarlo@aps.anl.gov>

Micro Tomography Science

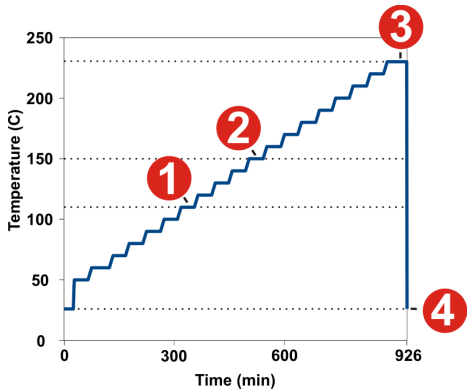
in-situ studies of real size samples

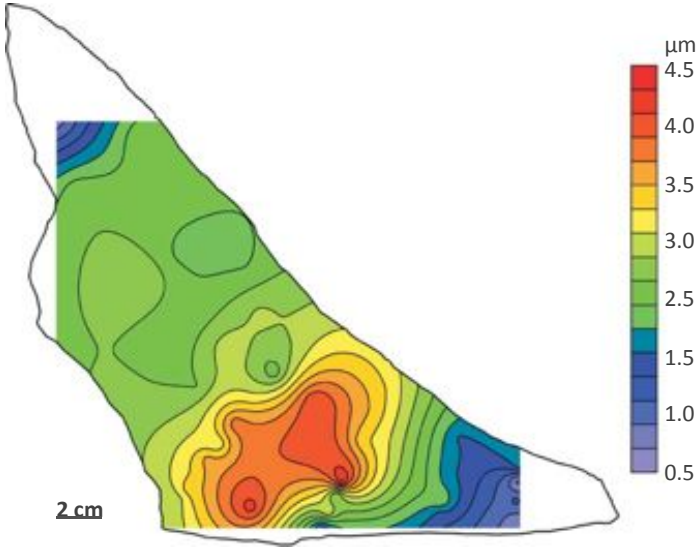
Thermal expansion cracking in rocks

Carbon sequestration, mine and oil exploration



200 °C 395 °C





pores distribution

Nature Vol. 459 18 June 2009 doi:10.1038/nature08051

Science **332**, 88-91 (2011). DOI: 10.1126/science.1202221

partment of Energy Office of Science by Argonne National Laboratory

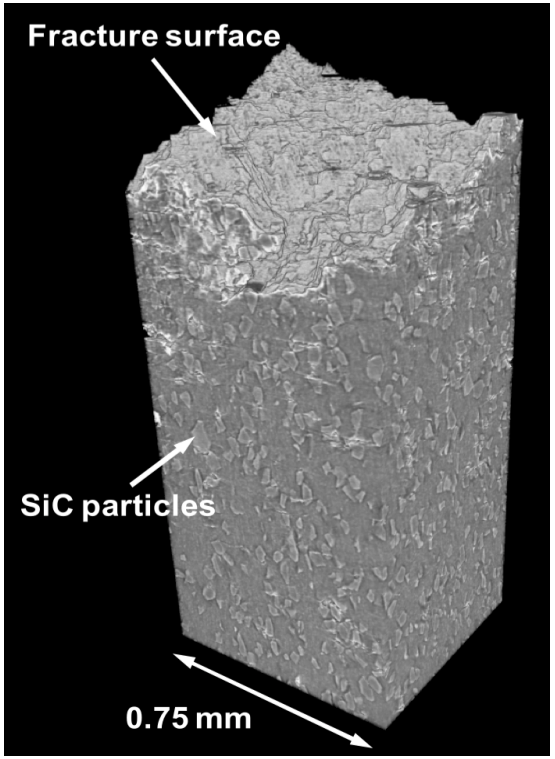
Francesco De Carlo <decarlo@aps.anl.gov>

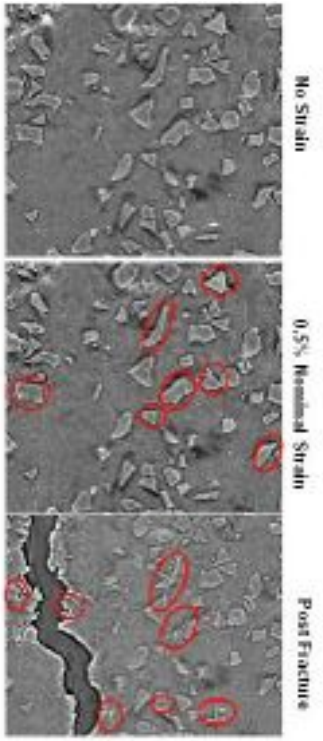
Micro Tomography Science

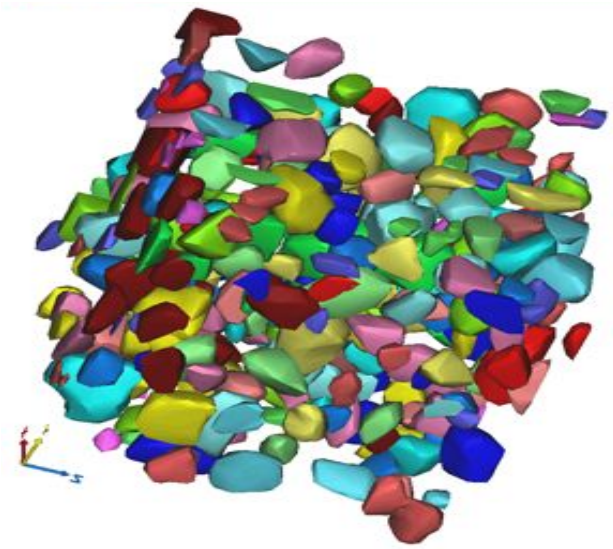
real size samples in real operational conditions

Mechanical Properties of Metal Matrix Composite Materials

transportation technology, new material, industrial applications







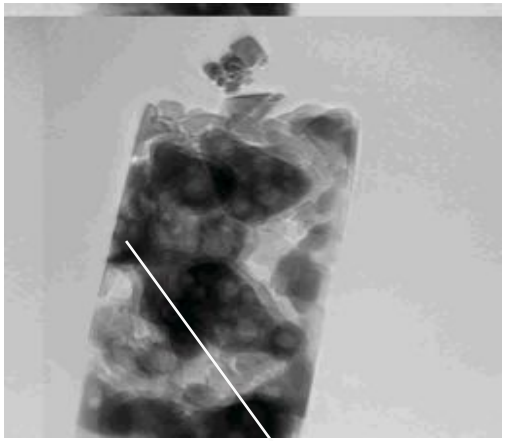
Metal Matrix Composite

N. Chawla J. Williams ASU

Francesco De Carlo <decarlo@aps.anl.gov>

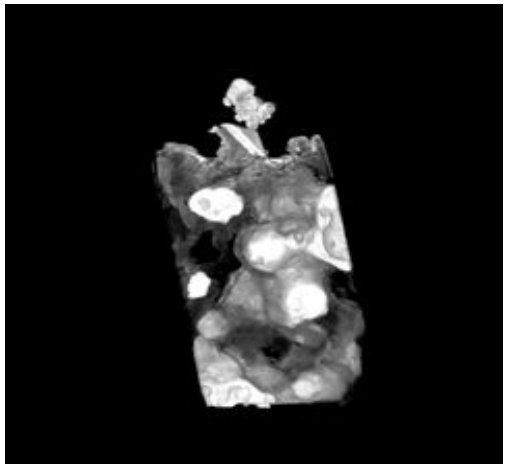
Nano-scale Imaging / Element Maps in 3D

Example: a study of Sulfur poisoning of solid oxide fuel cell (SOFC)



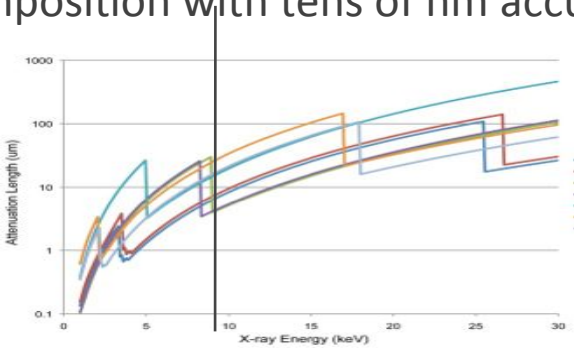
TXM images of SOFC sample throughout 180-degree rotation.
FOV ~ 25 um

Computed Tomography



Volume Rendering of reconstructed 3D volume data.

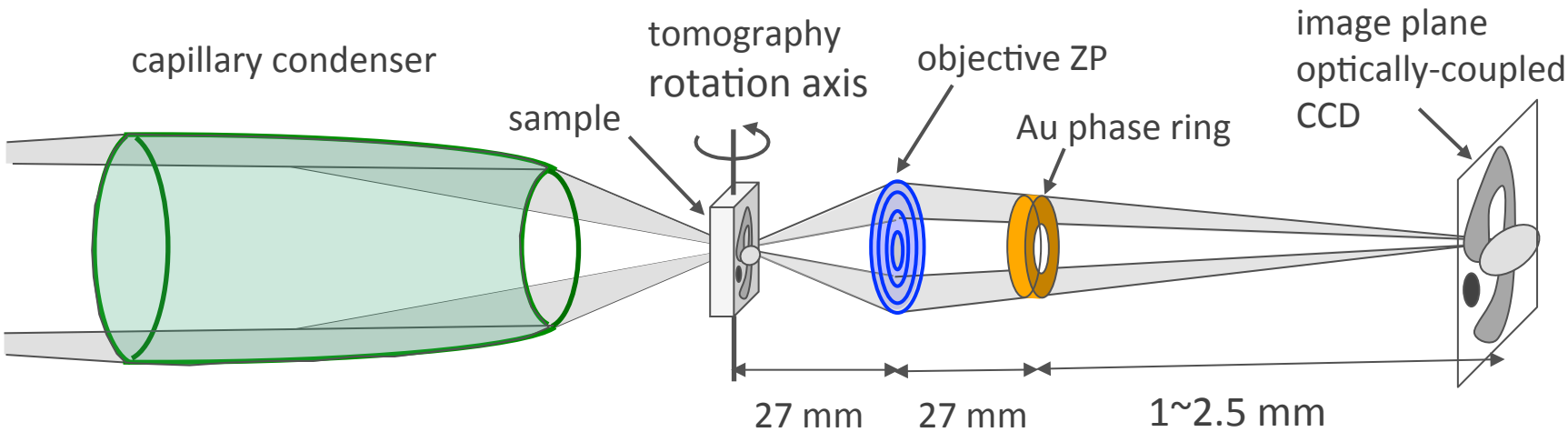
Map 3D elemental composition with tens of nm accuracy and ~1% sensitivity.

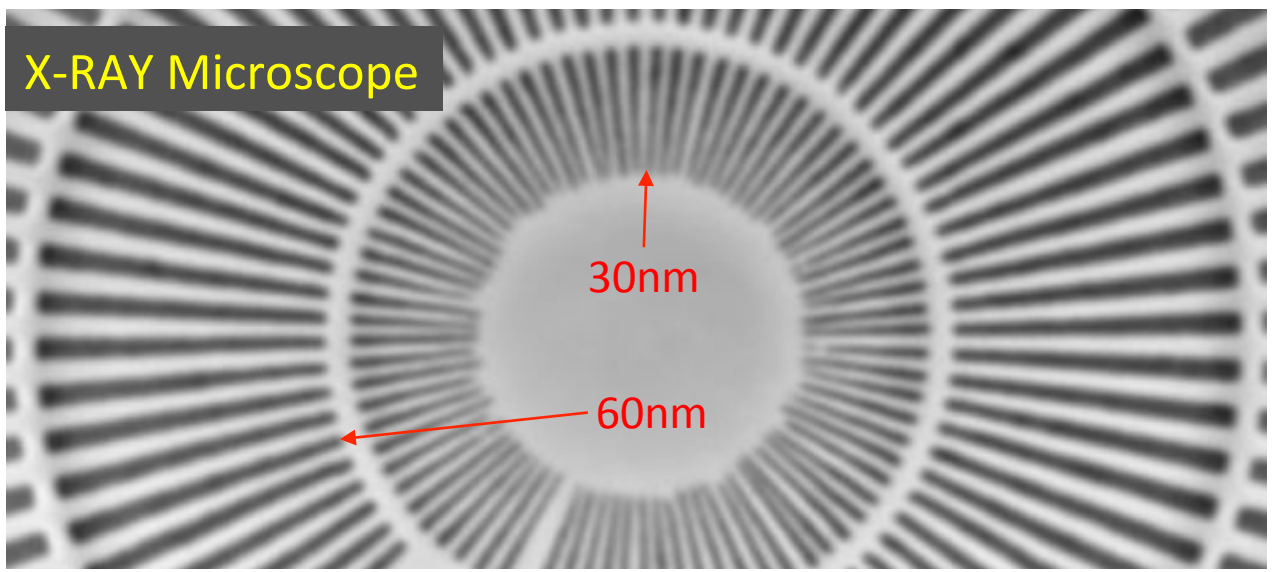


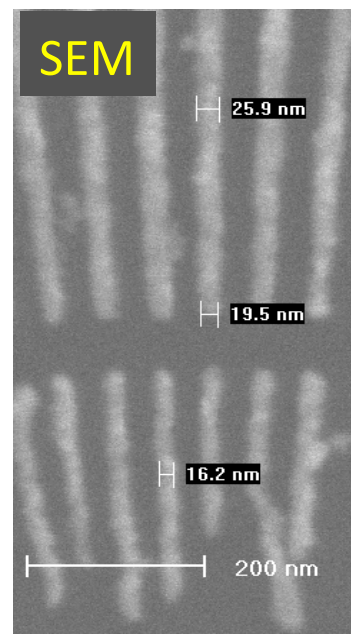
(unpublished data) Wilson Chiu, Uconn/HeteroFoaM EFRC

Francesco De Carlo <decarlo@aps.anl.gov>

Transmission X-ray Microscope

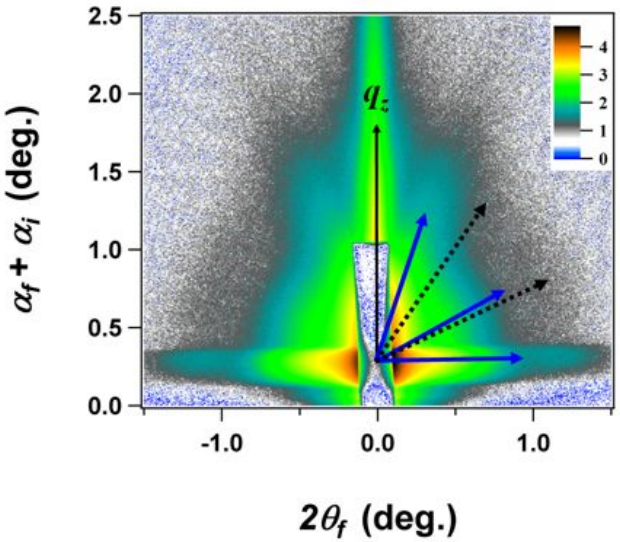


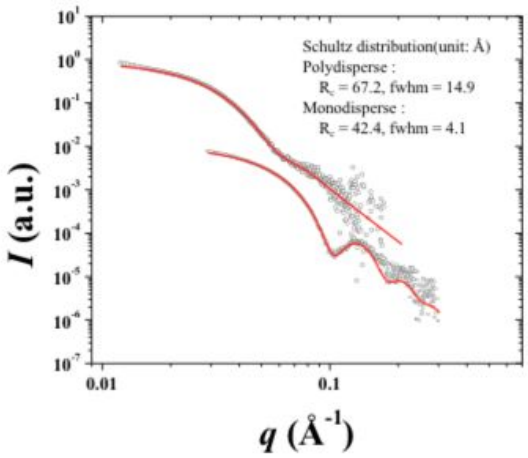




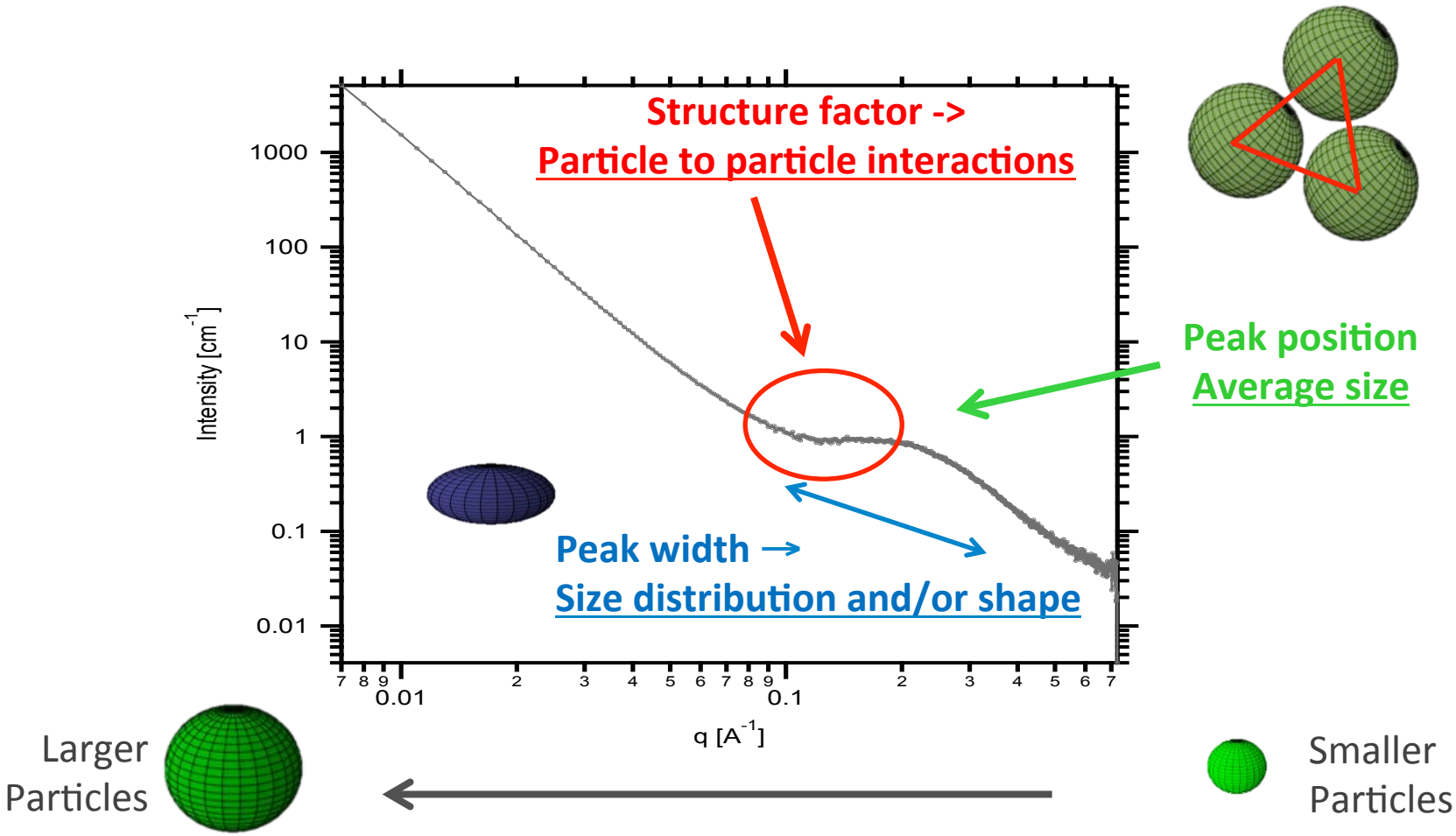
Francesco De Carlo <decarlo@aps.anl.gov>

Synchrotron
Small Angle & Surface Scattering
(SAXS, WAXS, GISAXS, USAXS)



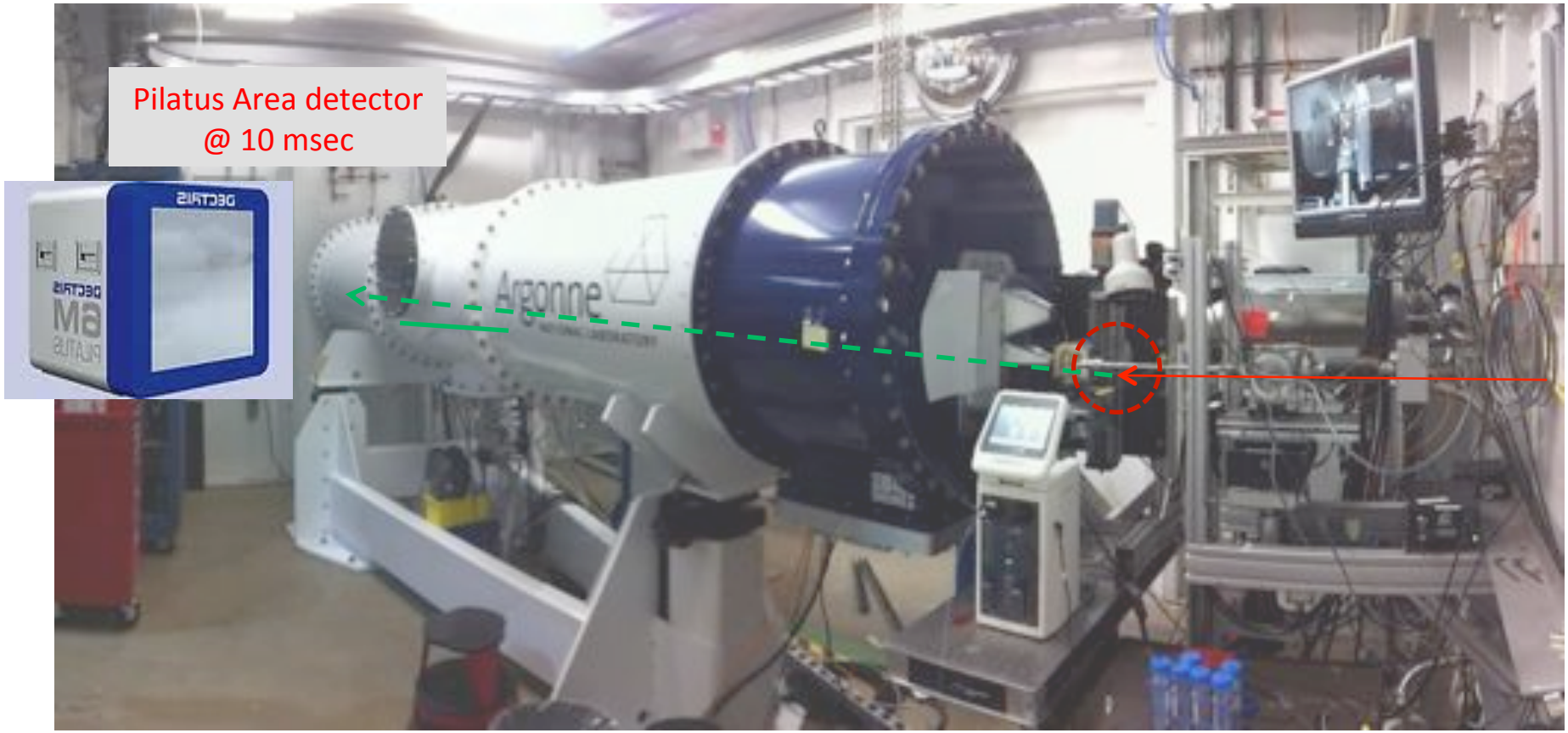


Insights from Small Angle X-ray Scattering (SAXS)



Kamila Wiaderek <kwiaderek@aps.anl.gov>

SAXS/WAXS Setup at Beamline 12ID-B (APS)

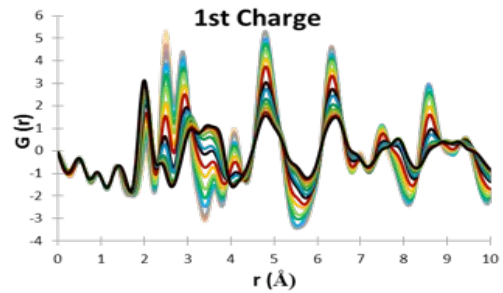


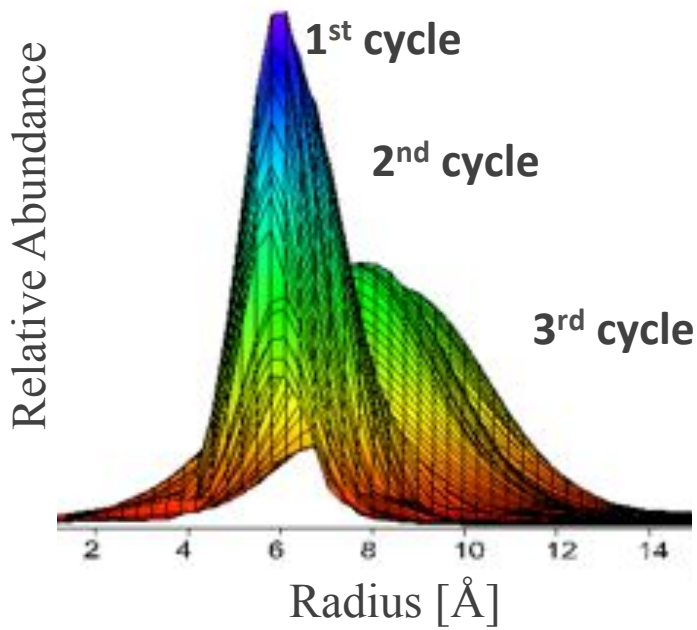
Byeongdu Lee <blee@anl.gov>

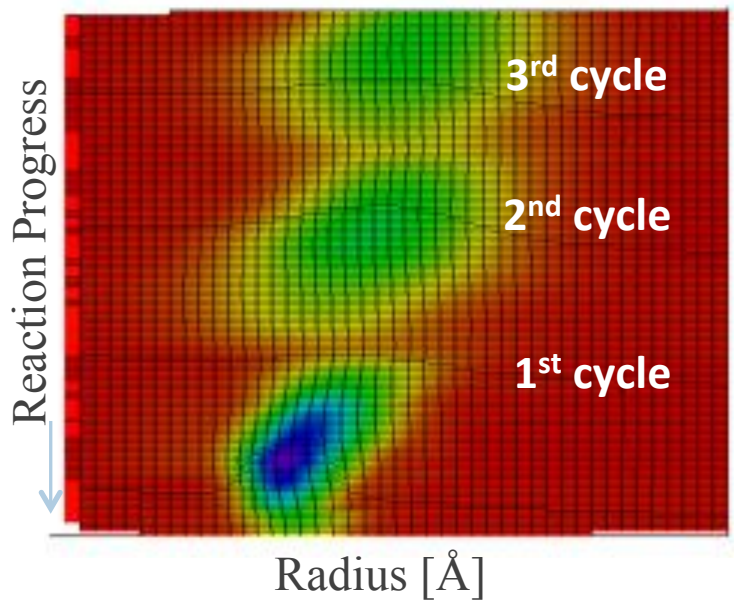
- SAXS & WAXS => 1 to 100 nm
- SAXS is from inhomogeneous e- density
- WAXS from longer range periodic variations of e- density (polymer p-XRD)
- USAXS (Ultra Small) => (10 micron) 10,000 nm - 10 nm

FeOF *in situ* PDFs: First Electrochemical Cycle

"Conversion" type battery material

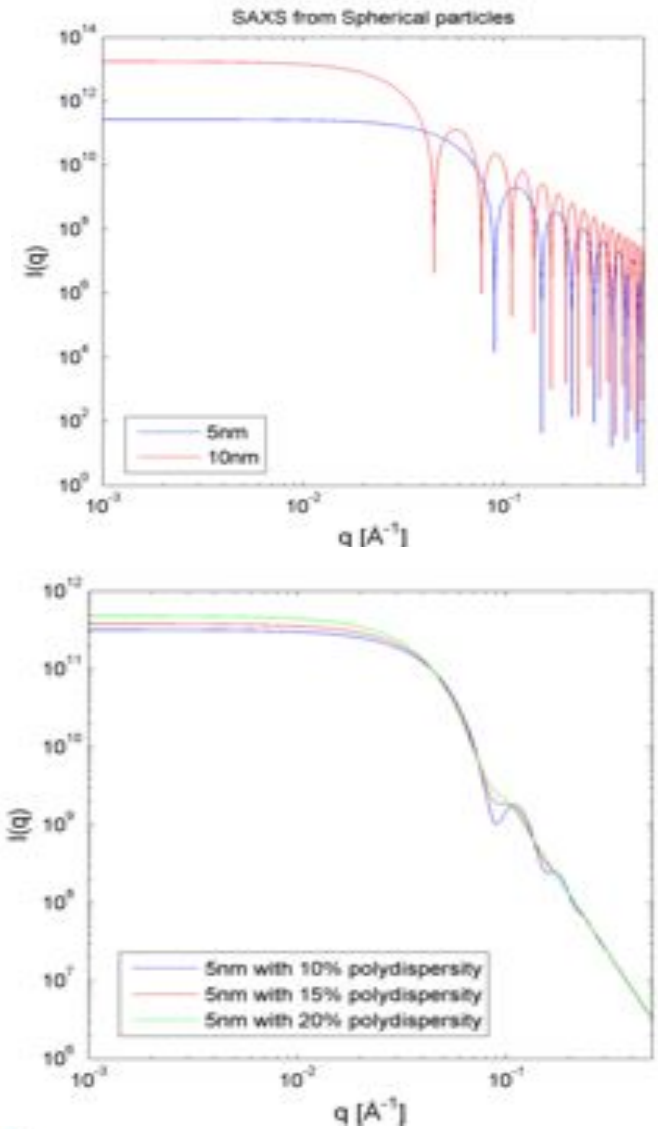




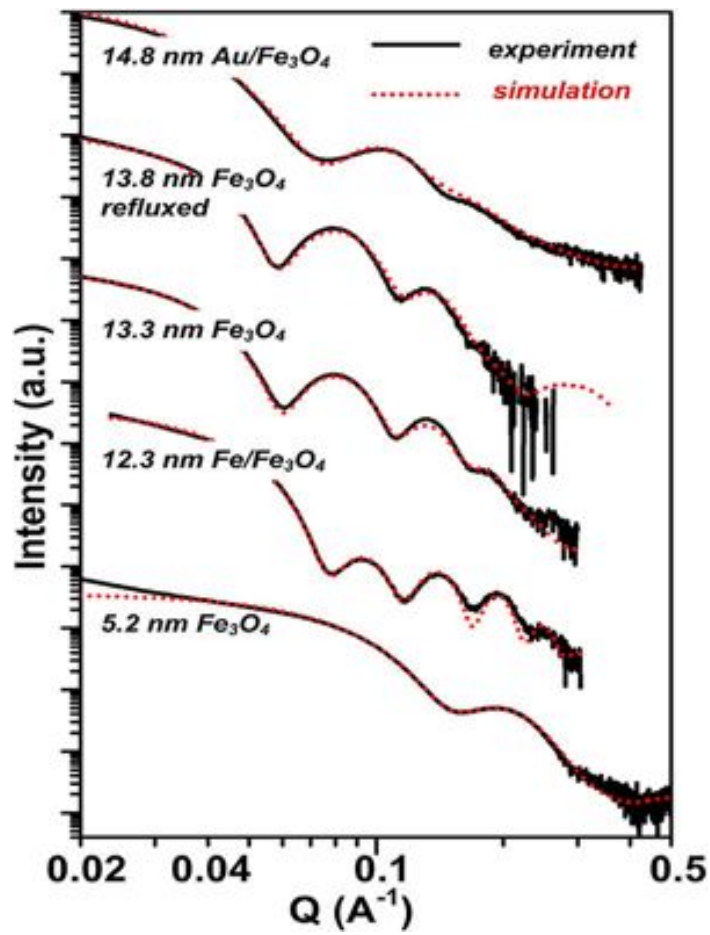


Kamila Wiaderek <kwiaderek@aps.anl.gov>

Small Angle Scattering Data Modeling



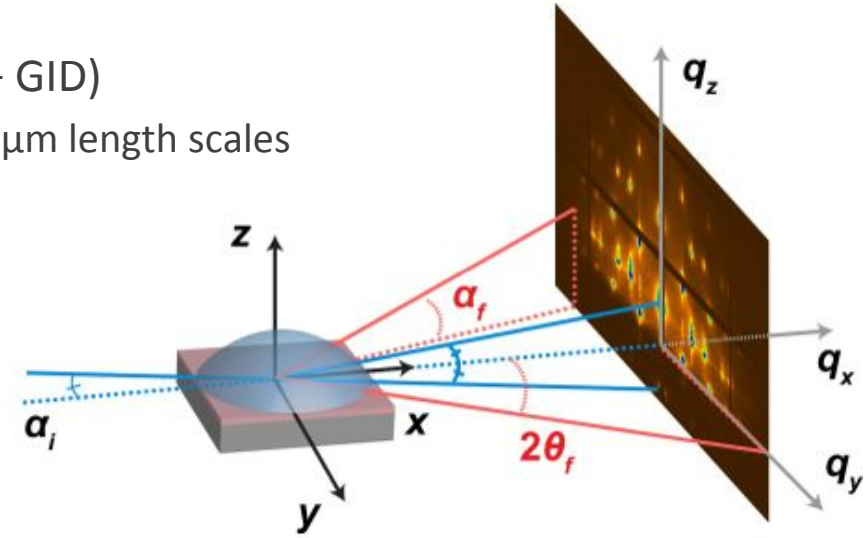
- Data can be fit and modeled



Byeongdu Lee <blee@anl.gov>

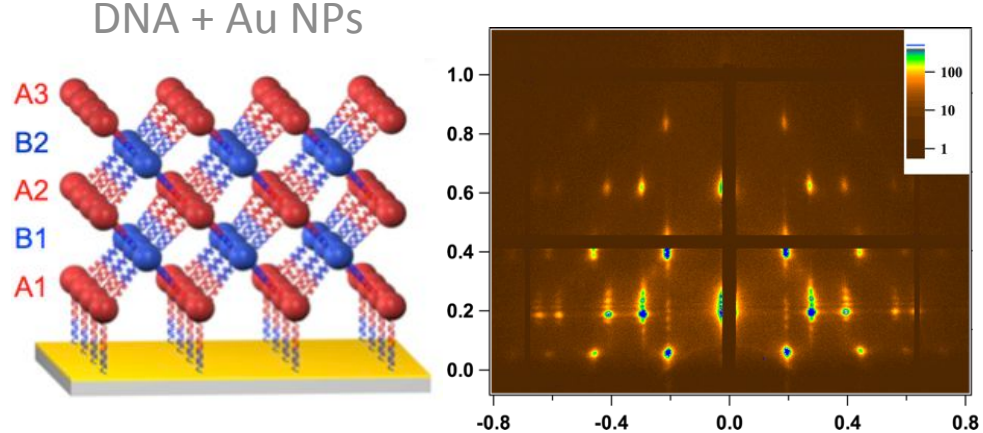
GISAXS Introduction

- SAXS for films and buried interfaces (SAXS + GID)
  - Structural characterization of films on nm to µm length scales
    - Self-assembled structures
    - Quantum dots
    - …
  - Depth sensitivity via incident angle variation and reflectivity
  - In-situ processing (kinetics) measurements
  - Non-ambient environments



- But…
  - Analysis complicated by strong/multiple scattering

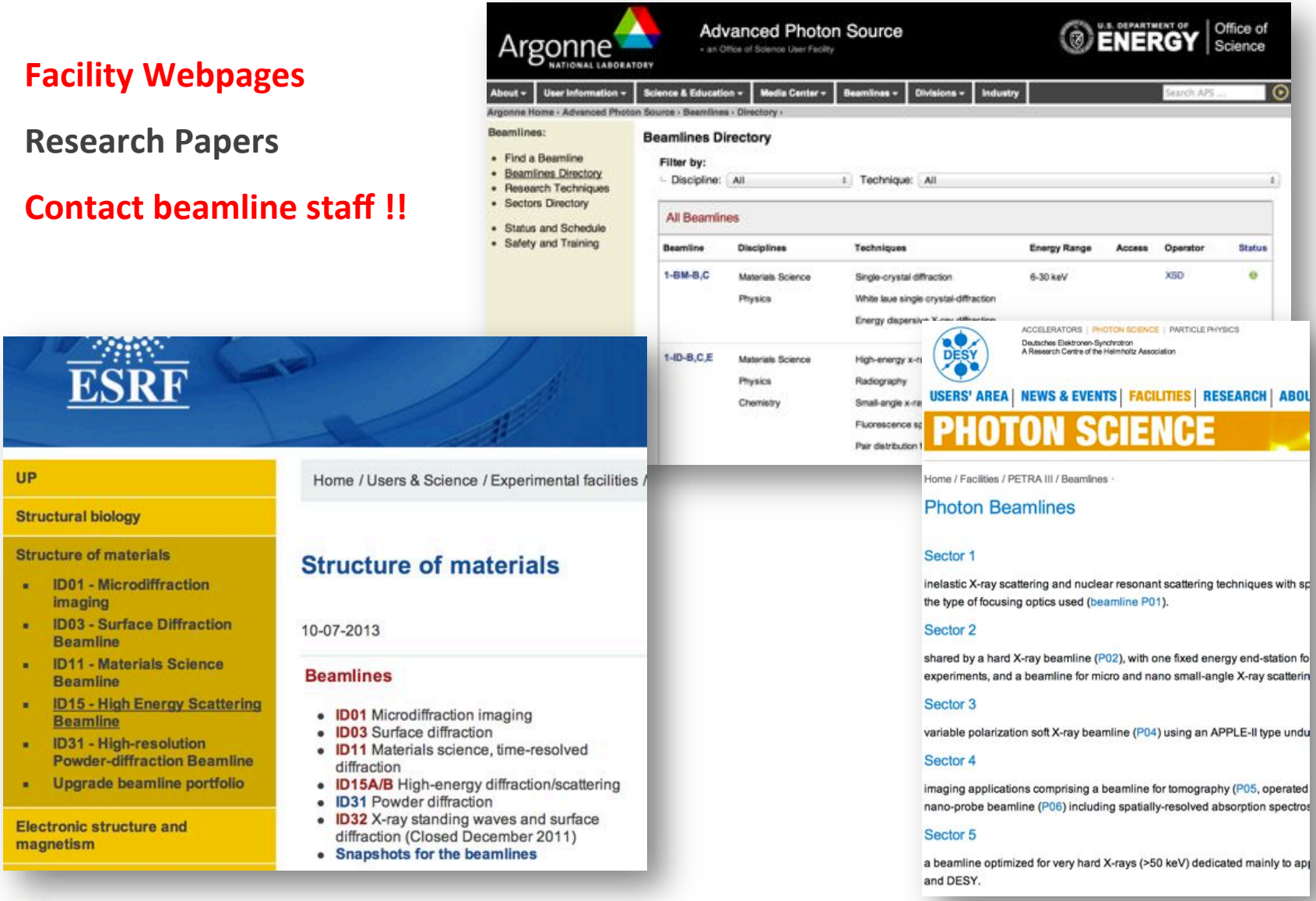
DNA + Au NPs



Joseph Strzalka <strzalka@aps.anl.gov>

How do I find a suitable beamline ?

- **Facility Webpages**
- Research Papers
- **Contact beamline staff !!**



How do I have a Successful Synchrotron Experiment ?

- Normally you write a proposal that explains why one needs it.
  - May need to register as a user in advance (Citizenship?)
  - Proposal include What, Why, How, Who ??
  - Note proposal deadlines
  - Proposals are reviewed and judged on science quality merit.
  - If new – good idea to contact beamline scientist(s) before submitting
  - Accepted proposals schedule some months later
  - Your team needs to travel to the facility
  - Experiments typically run for 24 hours per day
- Limited number of Mail-In Programs Options
- Experiment time is usually free
  - (exception is for proprietary commercial research)
- Be prepared and organized for the experiment (be nice to your contact)
- Publish! (This is the "output" of a user facility)

Contact Information and Acknowledgements

- **Matthew Suchomel suchomel@aps.anl.gov**
- Chen Yu-Sheng yschen@cars.uchicago.edu
- Greg Halder halder@aps.anl.gov
- Karena Chapman chapmank@aps.anl.gov
- Kamila Wiaderek kwiaderek@aps.anl.gov
- Chris Benmore benmore@anl.gov
- Jonathan Almer almer@aps.anl.gov
- Xiaoyi Zhang xyzhang@aps.anl.gov
- Mali Balasubramanian mali@aps.anl.gov
- Francesco De Carlo decarlo@aps.anl.gov
- Joseph Strzalka strzalka@aps.anl.gov
- Choi Yong ychoi@aps.anl.gov
- Byeongdu Lee blee@anl.gov

- Slides / Photos / Content / Thanks
  - Brian Toby, Wikipedia, APS, DIAMOND, ESRF webpages; Université Bordeaux 1, ICMCB colleagues and many others that I apologize for forgetting….