Spectroscopy/Inelastic Scattering with MBA Lattice

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- **Peter Abbamonte** *University of Illinois*
- **Dario Arena** *Brookhaven National Laboratory*
- **Simon Bare** *UOP LLC, a Honeywell Company*
- **Thomas Gog** *Argonne National Laboratory*
- **Daniel Haskel** *Argonne National Laboratory*
- **John Hill** *Brookhaven National Laboratory*
- **Gerald Seidler** *University of Washington*
- **Thomas Toellner** *Argonne National Laboratory*

- And thanks to many others who contributed

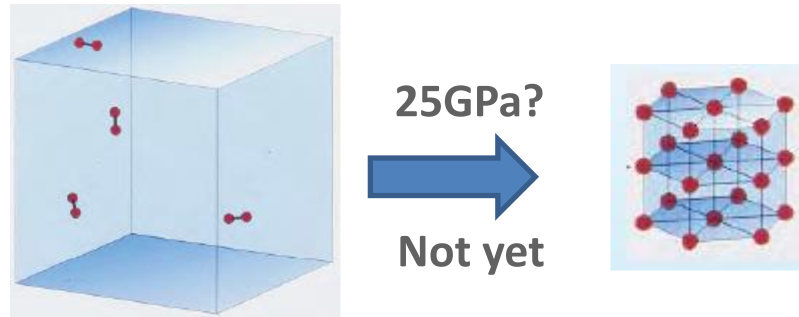
Spectroscopy/Inelastic Scattering at APS

- Broad collection of techniques
  - From industrial users to fundamental science
  - ~1/3 beamlines with spectroscopic programs
- MBA lattice impacts areas differently
  - All techniques will benefit
  - Full benefit requires substantial optics/detector upgrades

Some Major Impacts

- High pressure studies gain ~1000 from flux and brilliance
  - Metallic hydrogen
- Fast spectroscopy for batteries and catalysis
  - Gains in spatial (50 x) and temporal resolution (60 x)
- Understanding correlated electron systems
- Understanding nature of disordered systems
- New undulators allow novel spectroscopic studies
  - New opportunities with fast polarization and energy switching
- Many experiments flux starved – gain factor of 3-6

Metallic Hydrogen
the holy grail of high pressure science



Reports

77k, 250 GPa nearly opaque

Optical Studies of Hydrogen Above 200 Gigapascals: Evidence for Metallization by Band Overlap

H. K. Mao and R. J. Hemley

Direct optical observations of solid hydrogen to pressures in the 250-gigapascal (2.5-megabar) range at 77 K are reported. Hydrogen samples appear nearly opaque at the maximum pressures. Measurements of absorption and Raman spectra provide evidence that electronic excitations in the visible region begin at ~200 gigapascals. The optical data are consistent with a band-overlap mechanism of metallization.

Solid hydrogen at 342 GPa: no evidence for an alkali metal

Chandrabhas Narayana*, Huan Luo*†, Jon Orloff‡ & Arthur L. Ruoff*

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Optical studies of solid hydrogen to 320 GPa and evidence for black hydrogen

Paul Loubeyre*, Florent Occelli* & René LeToullec*†

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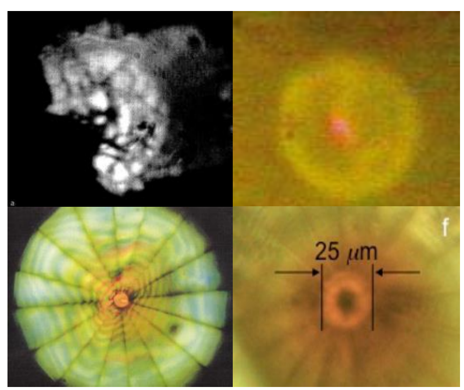


5402 (2012) PHYSICAL REVIEW LETTERS week ending 6 APRIL 2012

Synchrotron Infrared Measurements of Dense Hydrogen to 360 GPa

Chang-Sheng Zha, Zhenxian Liu, and Russell J. Hemley
al Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington D.C. 20015, USA

(Received 26 December 2011; published 3 April 2012)

Diamond-anvil-cell techniques have been developed to confine and measure hydrogen samples under static conditions to pressures above 300 GPa from 12 to 300 K using synchrotron infrared and optical absorption techniques. A decreasing absorption threshold in the visible spectrum is observed, but the material remains transparent at photon energies down to 0.1 eV at pressures to 360 GPa over a broad temperature range. The persistence of the strong infrared absorption of the vibron characteristic of phase III indicates the stability of the paired state of hydrogen. There is no evidence for the predicted metallic state over these conditions, in contrast to recent reports, but electronic properties consistent with semimetallic behavior are observed.

Metallization at 450 GPa? Electronic structures?

Electronic IXS of Light Elements at High Pressures

Opportunity

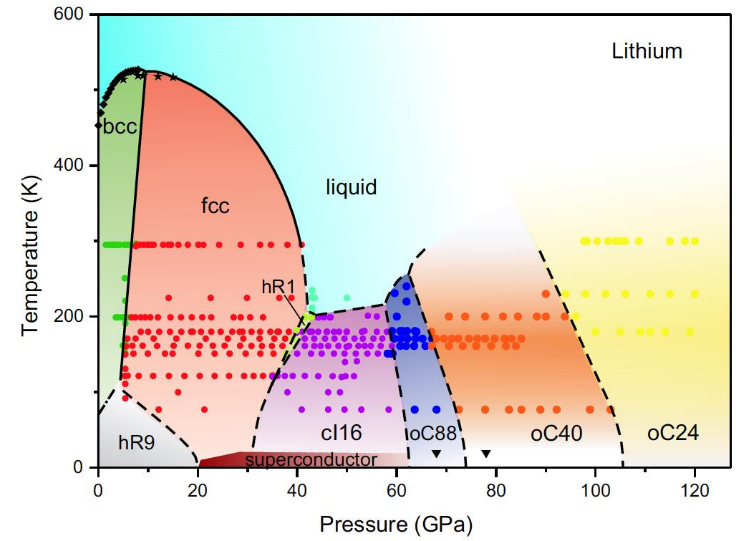
- Plasmons of high-*P* insulating Li and Na.
- Pressure-induced π to σ bonding transitions in B, C, and N.
- Oxygen bonding change in high-*P* symmetric ice and superconducting oxygen.

Challenge

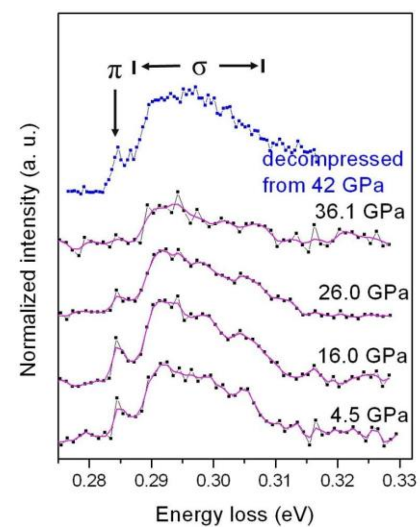
- Weak IXS signals from µm-size samples at multimegabar pressures.
- High background in DAC.

MBA Strength:

- The two of magnitude higher brilliance at MBA APS will be essential for improving the signal. The submicron focusing capability allows probing the sample while avoiding the DAC backgrounds.



Phase diagram of Li. *Guilaume et al. Nature Physics 2011*



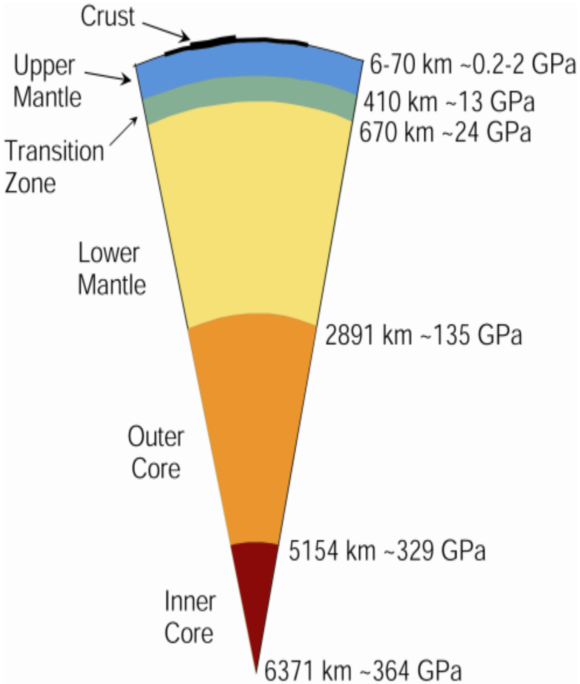
Carbon K-edge X-ray Raman spectra

Long-range ordered with amorphous carbon building blocks.

Wang et al. Science 2012

Hokwang Mao/Carnegie Institution

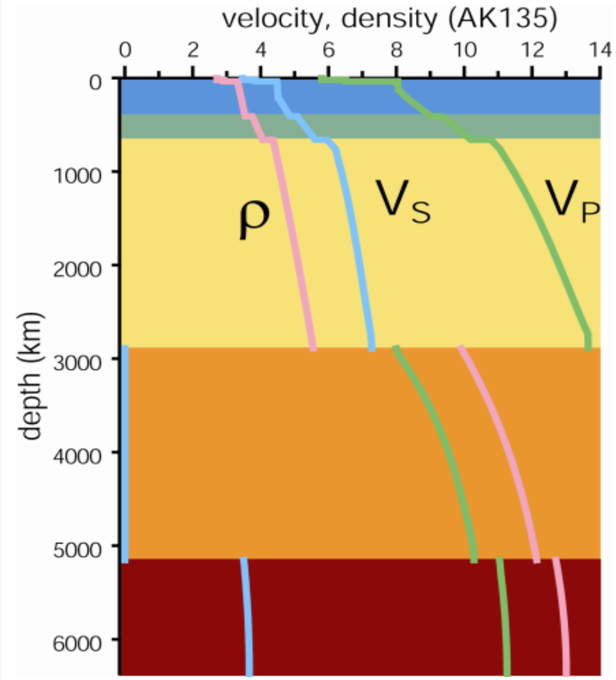
Understanding Interior of Planets



Measuring sound velocity of candidate materials is very important in geophysics for constraining possible models of Earth's interior.

HERIX can be used to determine the compressional and shear sound velocity (V_p , V_s) directly.

Together with in-situ diffraction measurement, V_p –density (r) at elevated P-T provides reliable constrains on the properties of the core.

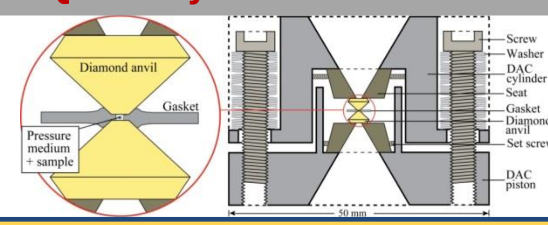


Pressure Tool: Diamond Anvil Cell (DAC) & Sample Size for Quasi-Hydrostatic Environment

Culet size (µm)	Max. pressure (GPa)	* Max. sample diameter (µm)	& Practical sample diameter (µm)
500	30	150	≤ 100
300	70	100	≤ 60
250	100	80	≤ 40
100	200	30	≤ 20
50	300	10	≤ 10

* Max. sample diameter – size allowed by the sample chamber

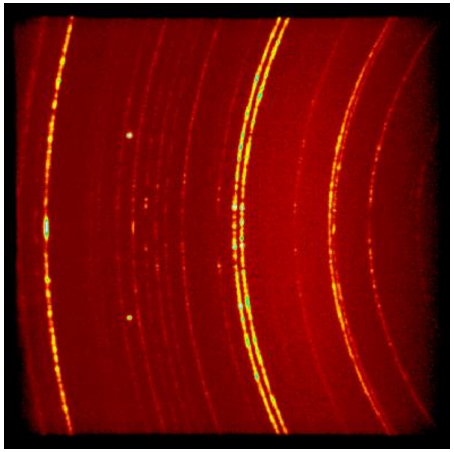
& Practical sample diameter – for a quasi-hydrostatic environment



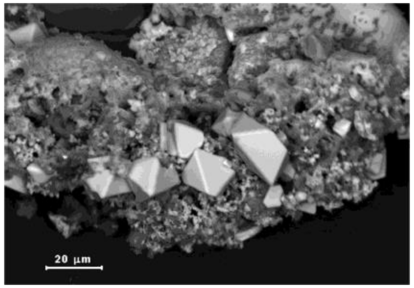
Current limit (~100-150GPa; with sample size 40µm)

Expected limit(~300-360GPa; with sample size 10µm)

Sub-micron Samples



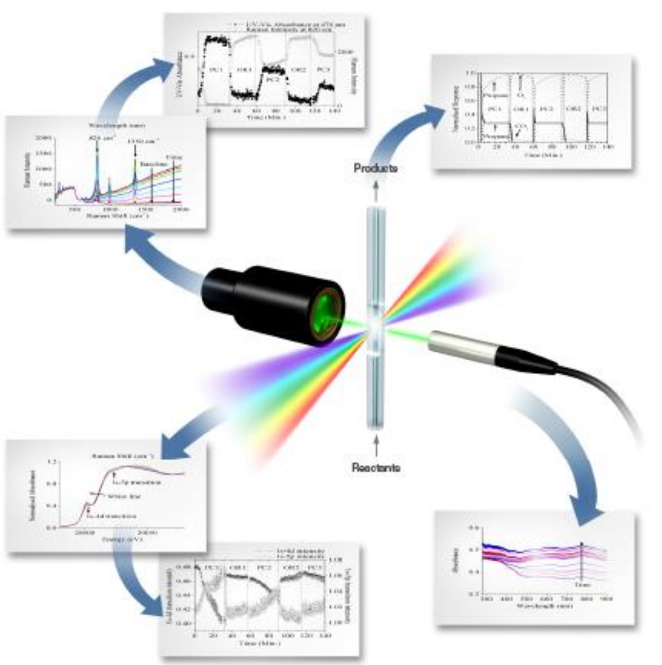
- Can study POWDERS
  - Excellent powder is 1 micron particles
    - Have to grind powders to get this small
  - Ideal probe for new materials
    - $La_{2-x}Ba_xCuO_4$ at x=1/8 took 15 years to grow single crystal
    - Doped samples especially difficult
  – Volumes 10^9 times smaller than neutrons can be studied

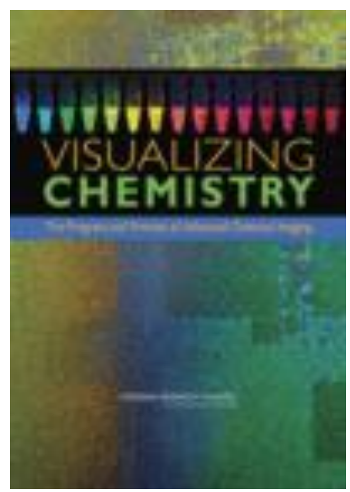


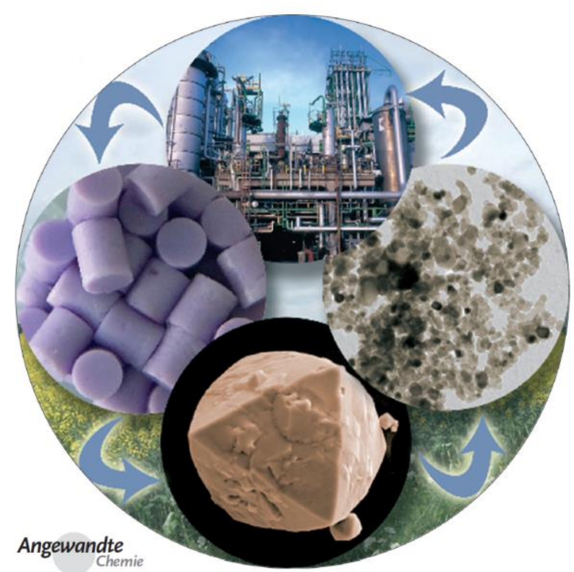
The Future: Spectroscopy & Microscopy

Honeywell

- Most current catalysis-related studies are static in time domain and averaged in spatial domain
- Future: *in situ* spatiotemporal imaging with spectroscopy for characterization of catalysts at work at previously unattainable resolution and sensitivity





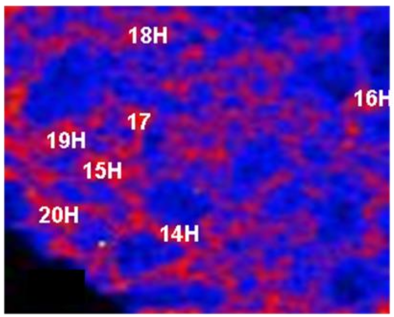


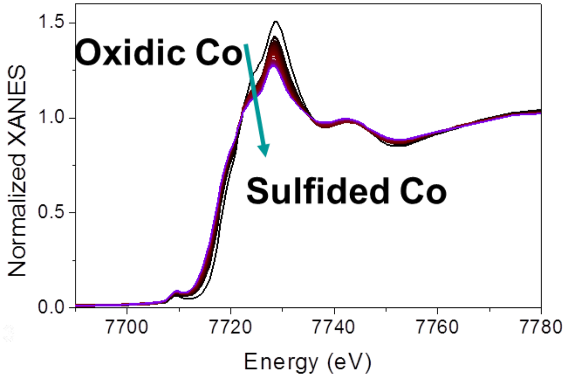
New Capability – XES mapping of Co-containing catalyst

- Sulfided Co-Mo catalysts produce ultra-low sulfur gasoline by removing sulfur while minimizing octane loss.
- In-situ monitoring of Co and Mo sulfidation desirable.

Now: ex-situ XRF mapping + XANES

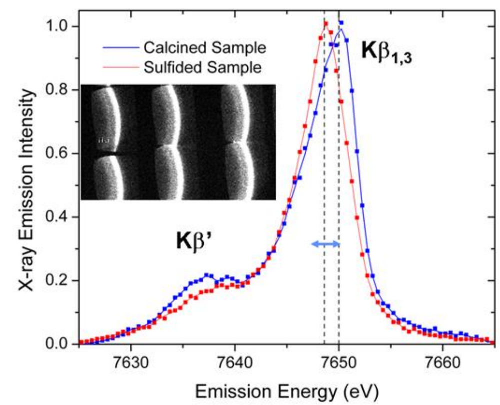
Co Fluorescence map





- Time-consuming (10's minutes for XANES)
- Need to select points for XANES (possible experimental bias)

MBA: in-situ simultaneous XRF and XES



- Co $K\beta$ lines sensitive to ligands (O or S)
- With upgrade sub-second XES spectra possible
- Current 30s with 5μm beam

New capability enabled by MBA lattice, multilayer monochromator, and improved beamline optics and detectors. In-situ studies possible with sub-s acquisition

High Energy Resolution X-ray Fluorescence: Nanoscale Spectroscopy

Challenge:

Determining chemical states at 30 to 100 nm scale is difficult.

needs energy scanning AND focusing optics

Opportunity:

- High resolution XRF (~1 eV at 6 keV) allows chemical/spin state determination without scanning incident energy. NO MOVING PARTS
- Developments with superconducting XRF detectors (MKIDs, TES) promise ~1 eV resolution at 10^5 Hz.
- high flux nano-probe beam from MBA APS, will allow chemical state determination for **multiple elements** simultaneously.

MBA Allows

Currently impossible nano-scale mapping of chemical states, and revolutionize scientific areas in biology, energy sciences, materials chemistry, and geo-sciences.

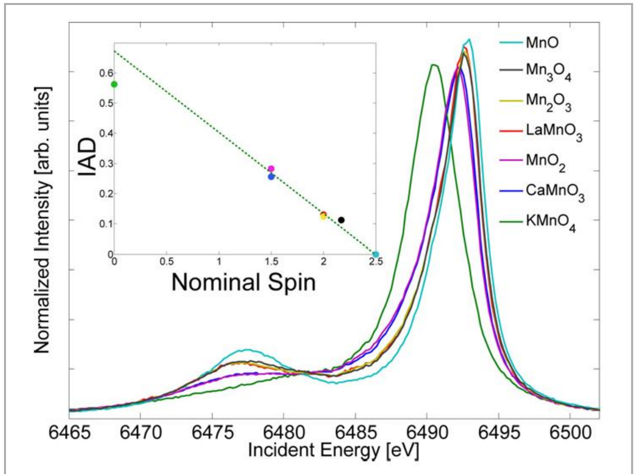
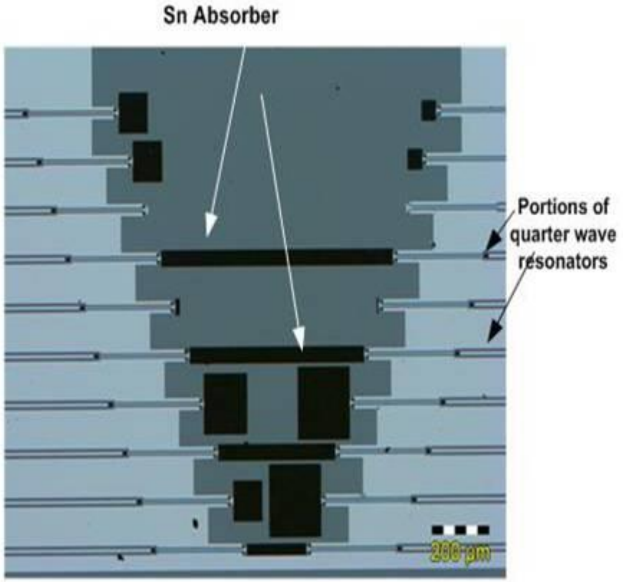


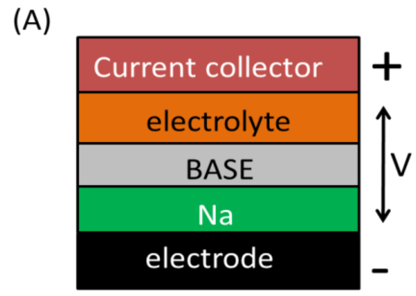
Fig. 6. Kβ main X-ray emission spectra normalized to the spectral area of manganese oxides, $K^{VII}MnO_4$ and perovskites $CaMn^{IV}O_3$ and $LaMn^{III}O_3$; (inset) IAD values with MnO as reference as a function of formal spin state with linear fit that considered MnO, MnO_2 and perovskites. The statistical error is smaller than the symbols.

Superconducting XRF Detectors in development at APS and NIST should achieve 1 eV resolution at 6 keV



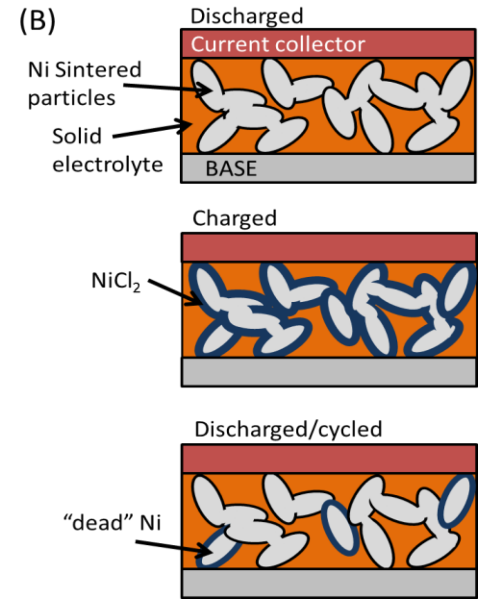
Example – Chemical mapping in a 'Zebra' battery

- Ni chemistry vital
- Need to examine internal structure of micron scale grains in entire layer
- Currently 60 sec/pt for 5 micron spot



Anode:
$2Na \leftrightarrow 2Na^{+} + 2e^{-}$

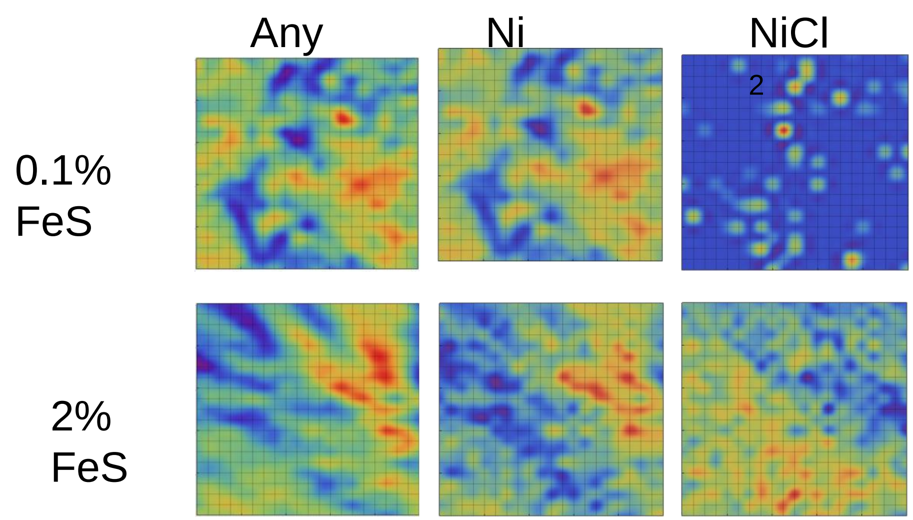
Cathode:
$NiCl_2 + 2Na^{+} + 2e^{-} \leftrightarrow Ni + 2NaCl$



MBA with advanced detectors:

100 nm in ~1 sec/pt

50x better spatial resolution
60x better time resolution



100 µm X 100 µm XES maps

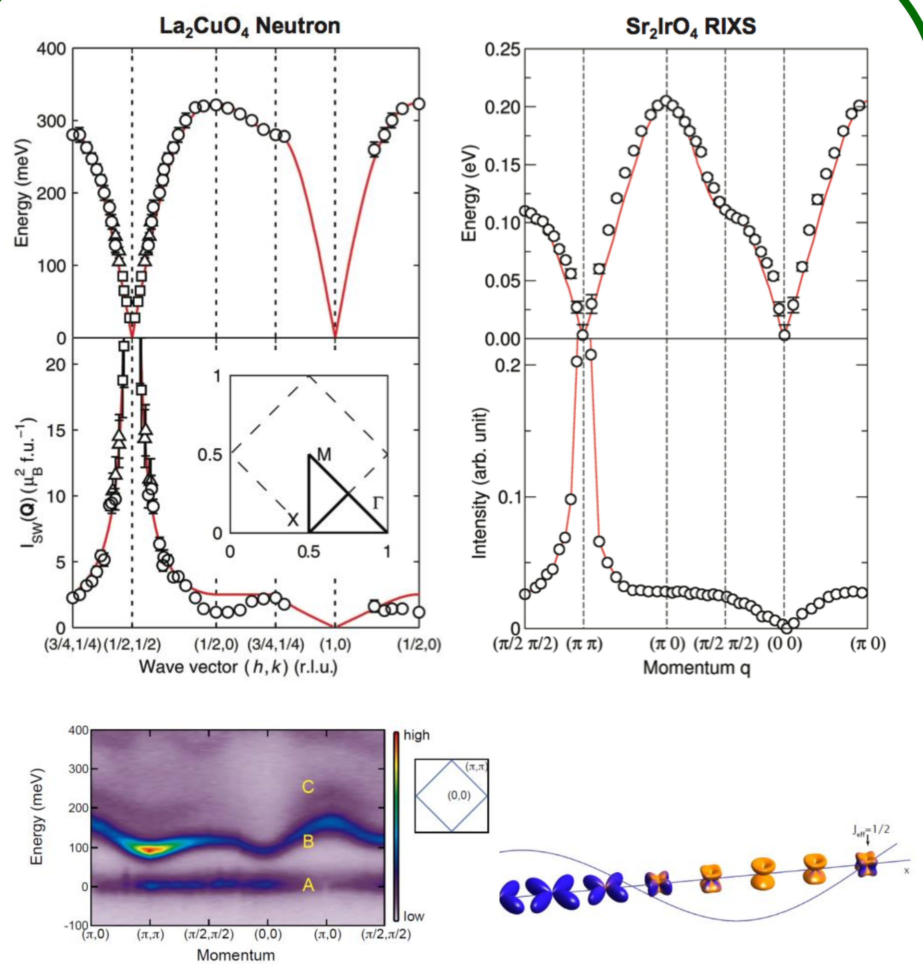
Correlated Electrons for Energy Sciences: Superconductivity

Opportunity
- New high (room ?) temperature superconductors
- Novel materials (5d TM-oxides?)
- Energy grid

Challenge
- Pairing mechanism unknown
- Magnons, phonons, or both?
- Beyond cuprates and pnictides
- Lack of polarization tunability / Energy resolution

MBA lattice Strength

- Helical Undulator- Pol. dependence
- Brilliance translates into improved E-resolution
- Enables extreme conditions (P, H, …)
- Distinguishes magnons from phonons



Magnon Dispersion in Cuprates (neutrons) and Iridates (RIXS)

Correlated Electrons for Energy Science: Nuclear materials

Opportunity

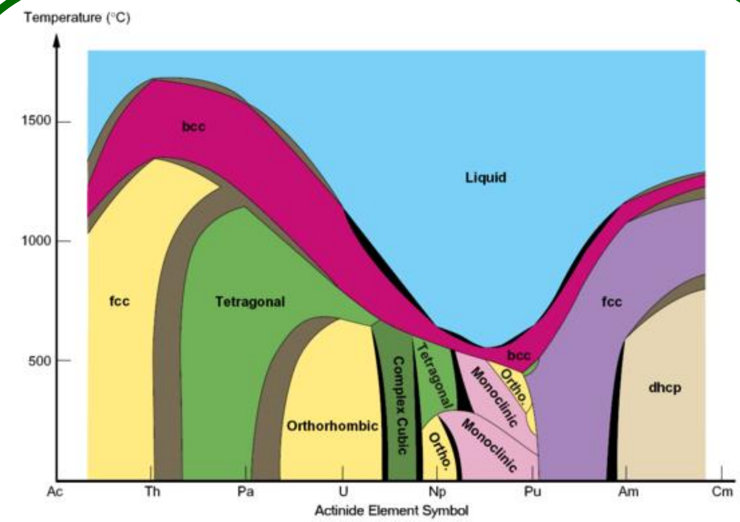
- Actinide materials
- 5f electrons and structural/phase stability
- Nuclear fuels

Challenge

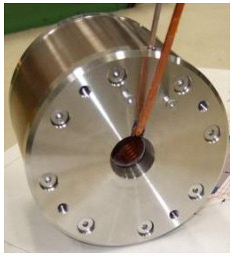
- Understand role of 5f electron localization, magnetism in phase stability
- Theories fail near localized/delocalized regime (Plutonium)
- Role of Spin-orbit interactions in stability of Pu phases.

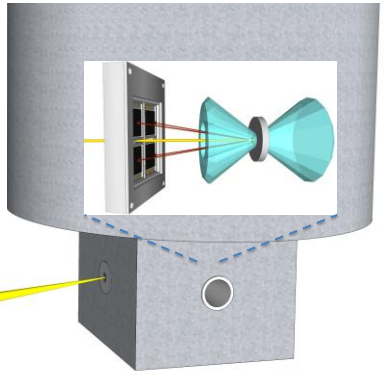
MBA Lattice Strength

- Brilliance enables ultra high-pressure probes of 5f electron interactions, localization, magnetism
- Small radioactive sample volumes
- Extreme magnetic fields (avoid field gradients)



Pseudo phase diagram of Actinides showing peak of odd behavior at Pu (Kmetko and Hill, 1976).



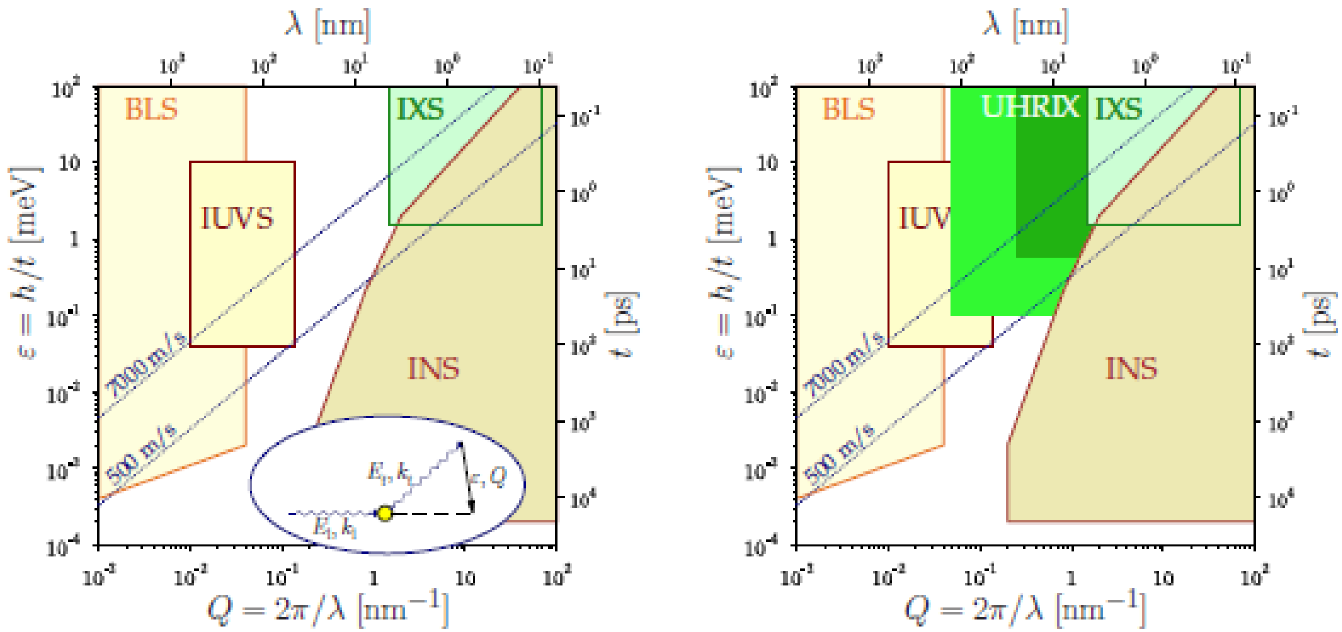


Small radioactive samples probed at extreme pressure and magnetic field

The nature of glass remains anything but clear

- "The deepest and most interesting unsolved problem in solid state theory is probably the nature of glass and the glass transition" /P.W. Anderson/.

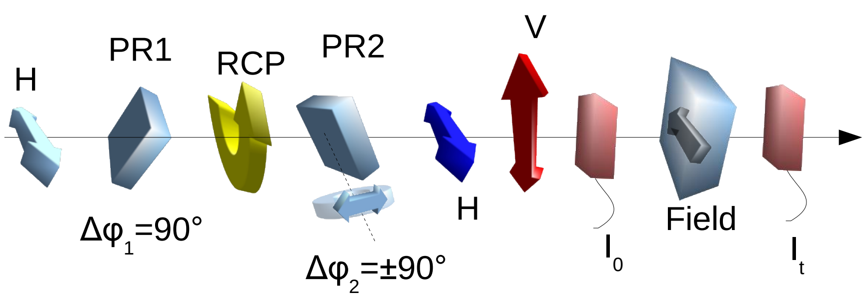
- Ultra-high-resolution IXS spectroscopy, enters the unexplored territories in the landscape of collective excitations in condensed matter, critical for understanding liquid-glass transitions.



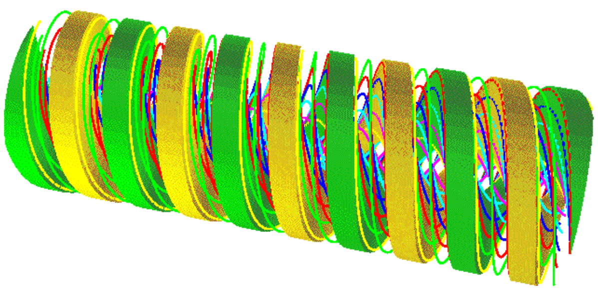
- Ultra-high-resolution IXS requires APS with the MBA lattice to achieve the 0.1-meV and 0.1 nm^{-1} resolution.

Novel polarizing insertion devices

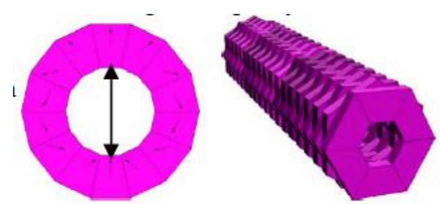
- A number of techniques will benefit from polarization tunability
  - IXS in the horizontal plane (polarization factor at large scat. angle)
  - Micro/Nano XANES on textured/single crystalline grains (pol. dependence)
  - Circumvent limitations of phase retarding optics in XMCD/XMLD measurements
- Round vacuum chamber (round electron beam) of MBA lattice enables novel devices for polarization control- with potential for fast switching capability



H→V eliminate phase plates – big signal gain



Superconducting-Helical



Permanent magnet-Helical