IXS Capabilities of NSLS-II and Opportunities for Materials Research under Extremes

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Workshop: Exploring the Pivotal Role of Next Generation X-rays in Bridging the Scale-Gaps in Next Generation Energy Materials Under Extremes, NSLS/CFN Users' Meeting, May 19, 2014

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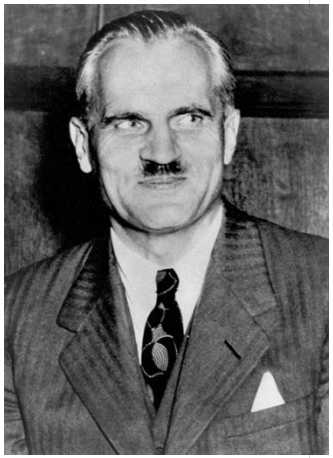
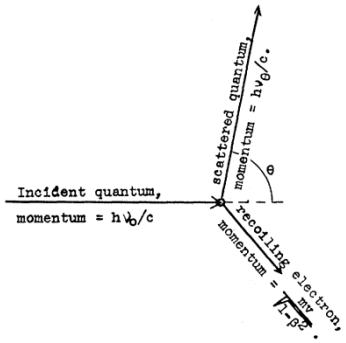
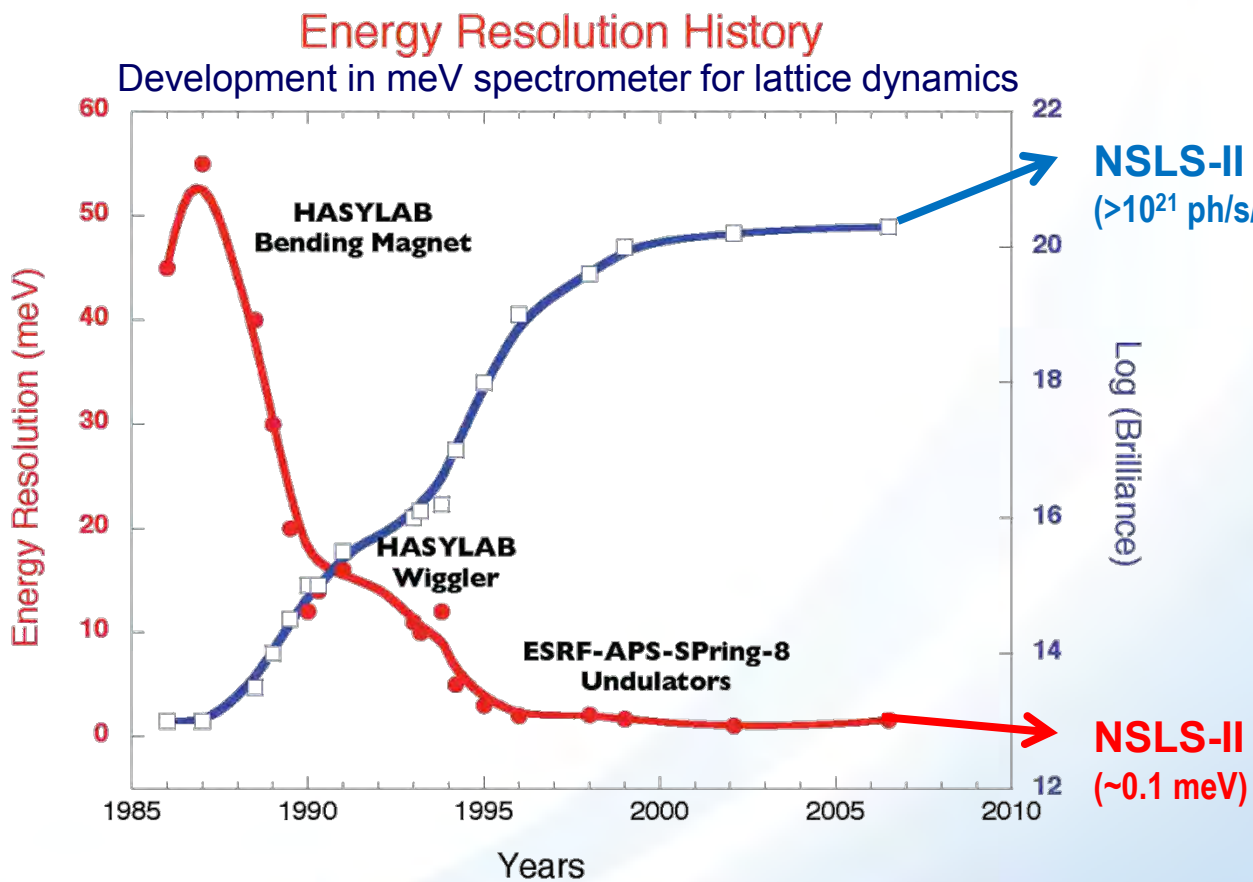
Office of Science

Inelastic X-ray Scattering in the Synchrotron Era

Despite a long history, practical applications became possible only with the advent of highly brilliant and intense synchrotron sources, and the advancement of X-ray optics







Compton, Phys.Rev. 1923

Courtesy of Ercan Alp (APS, ANL)
Source: E. Burkel, Rep. Prog. Phys. 63, 171 (2000)

Outline

- A Brief Introduction
- Science and Applications under Extremes
  - Some recent examples of study under extreme P
- IXS Capabilities of NSLS-II
  - Scientific opportunities at the IXS beamline
- Summary

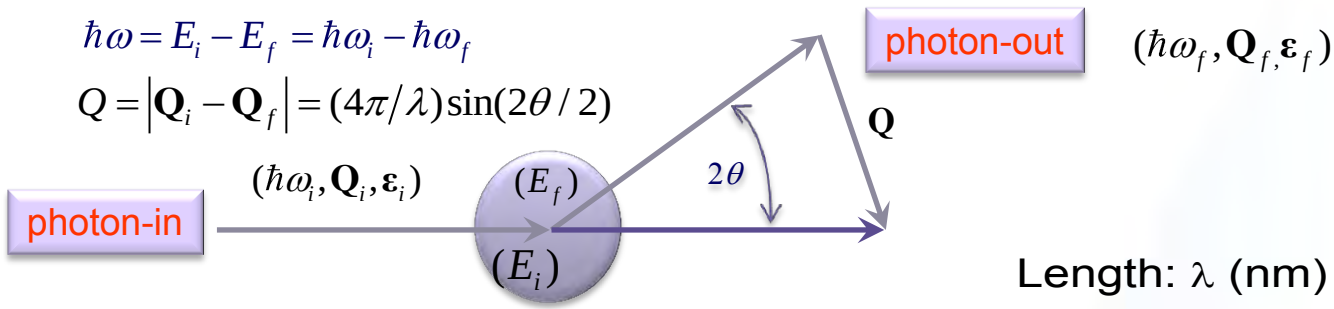
Inelastic X-ray Scattering

- A photon-in photon-out probe with a rather weak scattering cross section

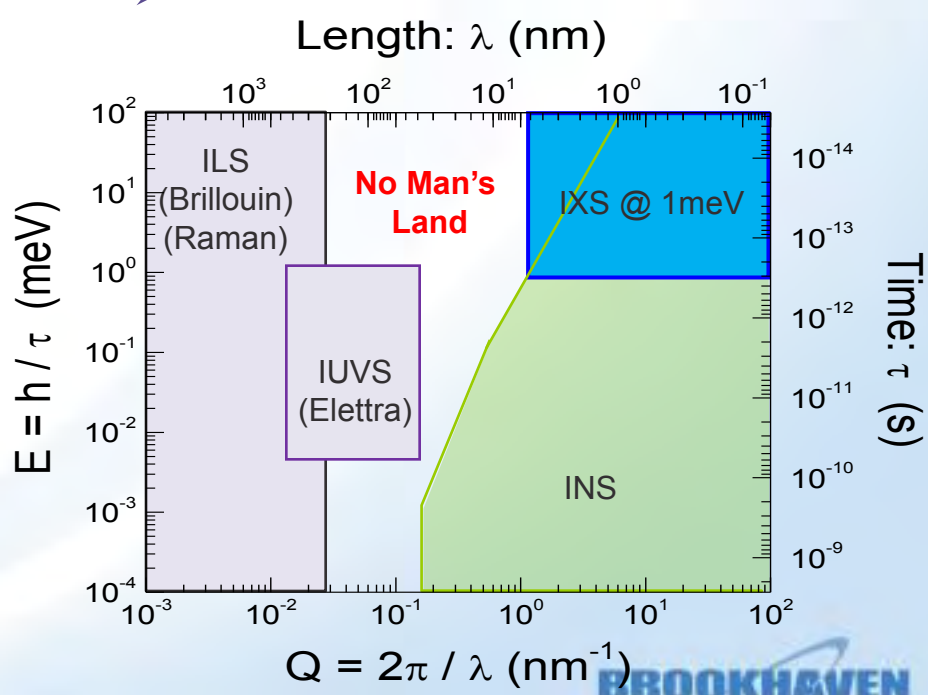
$$\frac{d^2\sigma}{d\Omega d\omega}(\mathbf{Q},\omega) = Nr_e^2(\boldsymbol{\varepsilon}_i\cdot\boldsymbol{\varepsilon}_j)^2\frac{E_f}{E_i}\left[f^2(Q)S_{ion}^{coh}(\mathbf{Q},\omega)+zS_{val}^{inc}(\mathbf{Q},\omega)+(Z-z)S_{ion}^{inc}(\mathbf{Q},\omega)\right]$$

$$\hbar\omega = E_i - E_f = \hbar\omega_i - \hbar\omega_f$$

$$Q = \left|\mathbf{Q}_i - \mathbf{Q}_f\right| = (4\pi/\lambda)\sin(2\theta/2)$$



- Coupling to matter
  - Coupled directly to the electronic charge
  - Lattice excitations via coherent scattering (equivalent to INS)
  - High penetration, truly bulk-sensitive
  - Element, charge and spin specific
  - Applicable to systems under extreme environments, and systems that are not compatible with vacuum (e.g., liquids)
- Kinematics Strengths
  - ħω and Q are effectively decoupled
  - (ħω, Q) covers the full range of dielectric response, limited only by achievable resolutions



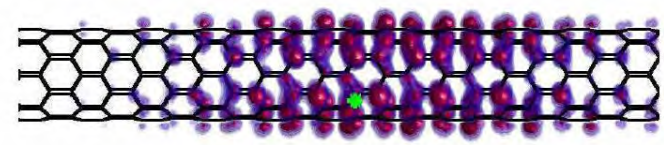
The Relevant Energy Scales

- Given the appropriate energy resolution, IXS can be utilized to study dynamic behaviors of materials in the relevant time scale (picoseconds ~ femtoseconds)

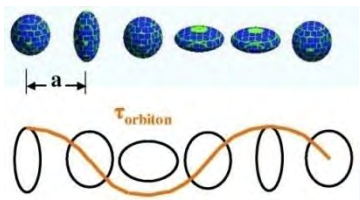
Energy

❑ 1-1000 eV:
Plasmon
Exciton
Valence & core excitations

Exciton in carbon nanotube
(S. Louie, Berkeley)

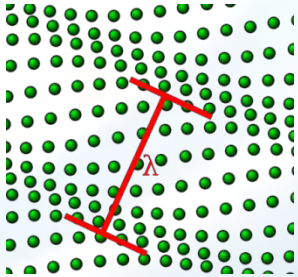


❑ 0.1-1 eV:
Magnon
Orbiton



Orbital excitation
(M. Rotter, U. Wien)

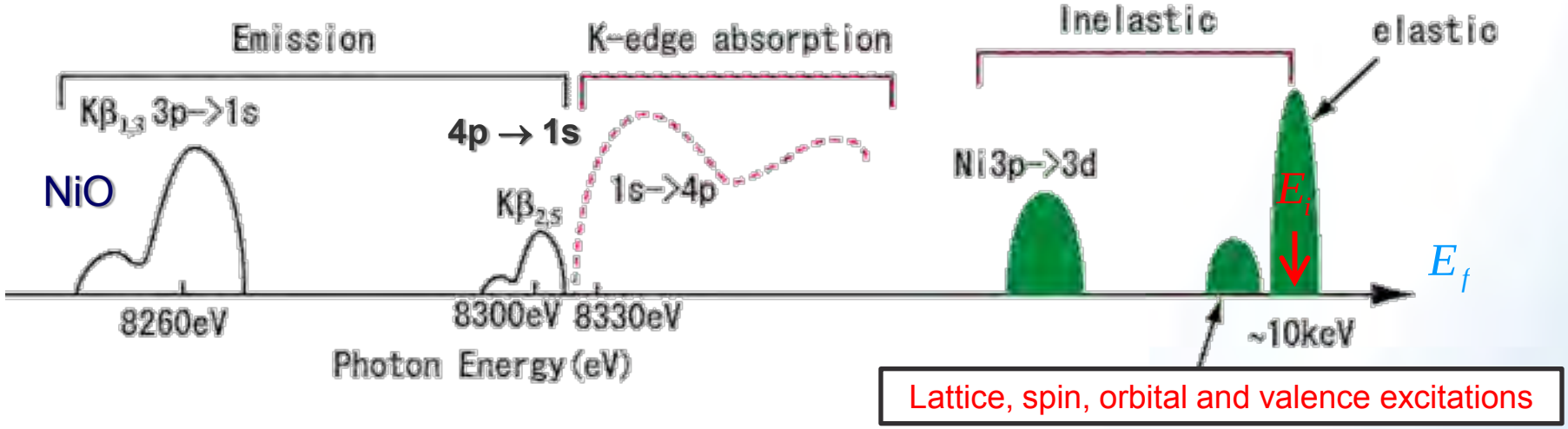
❑ 0.1-100 meV:
Phonon
Collective mode



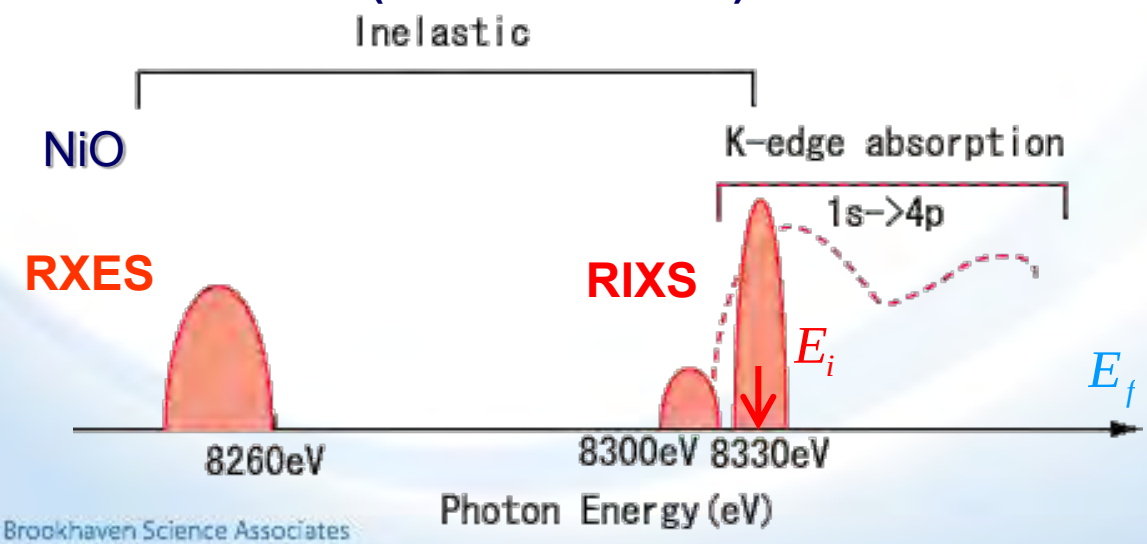
Phonon mode
(Wikipedia)

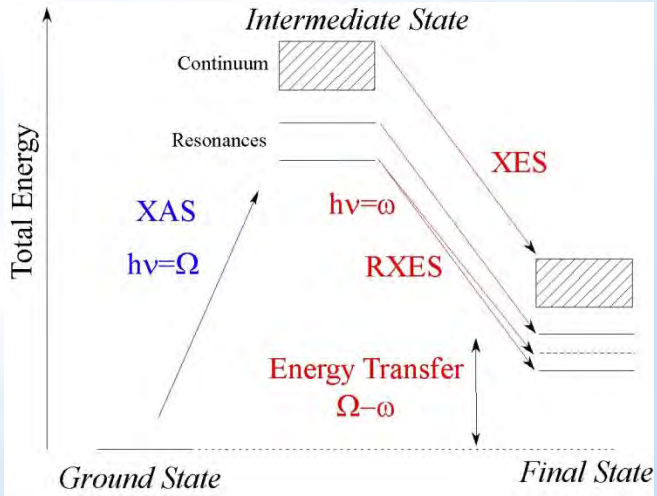
IXS Spectroscopic Information

- **Non-resonant IXS (XRS/XES/PFY-XAS)**



- **Resonant IXS (RXES/PFY-XAS)**

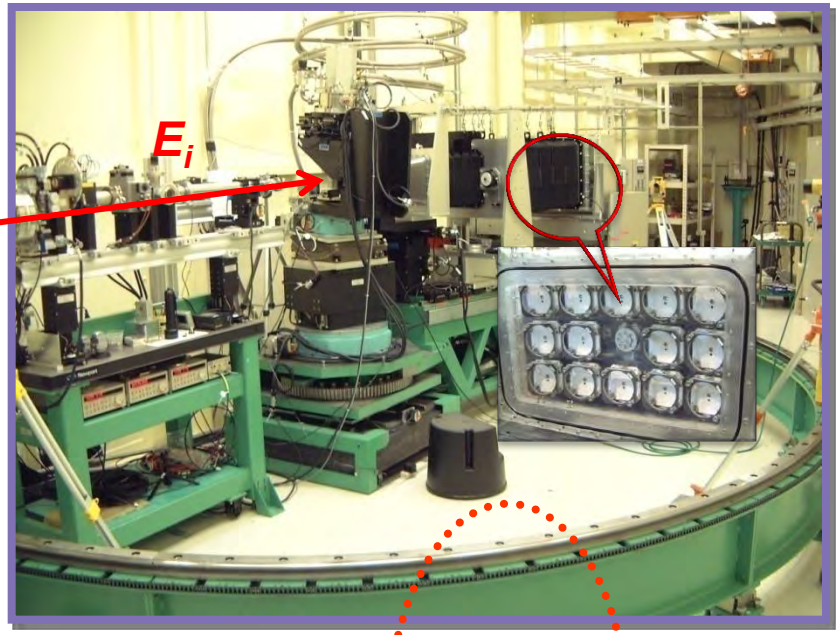


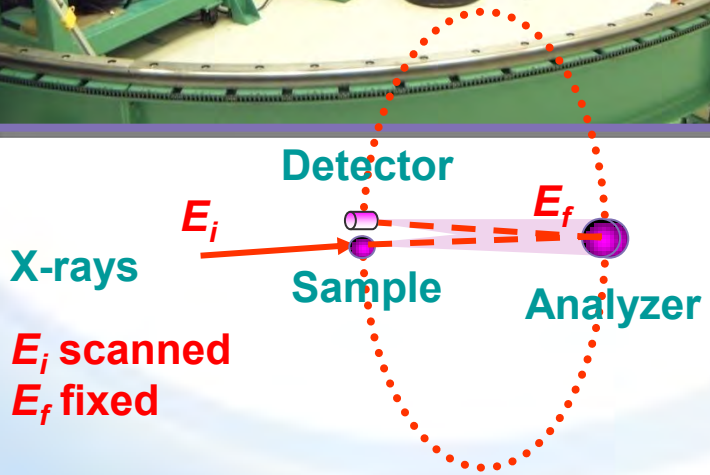


Conventional Instrumentation for IXS

- Spectrometer at BL12XU, SPring-8

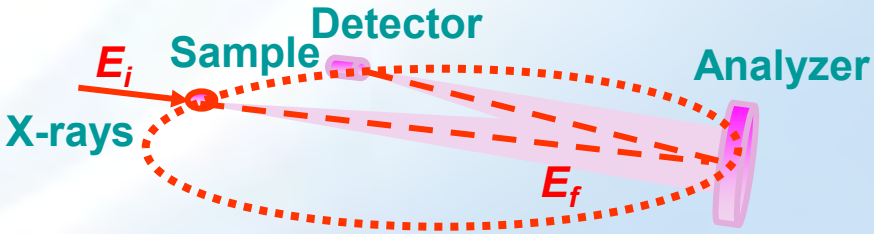
- NIXS Setup





E_i scanned
E_f fixed

- RIXS Setup



E_i fixed but stepped thru edge, E_f scanned
CFS: E_i & E_f scanned together

XES: Probing high-spin-low-spin transition in Fe compounds

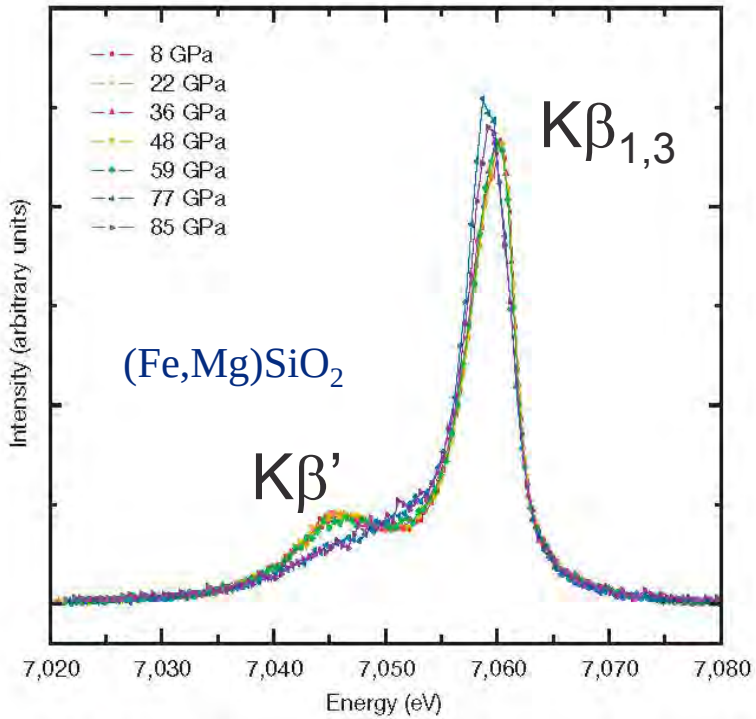
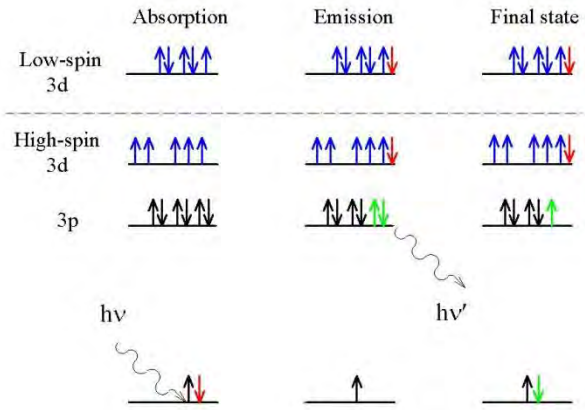
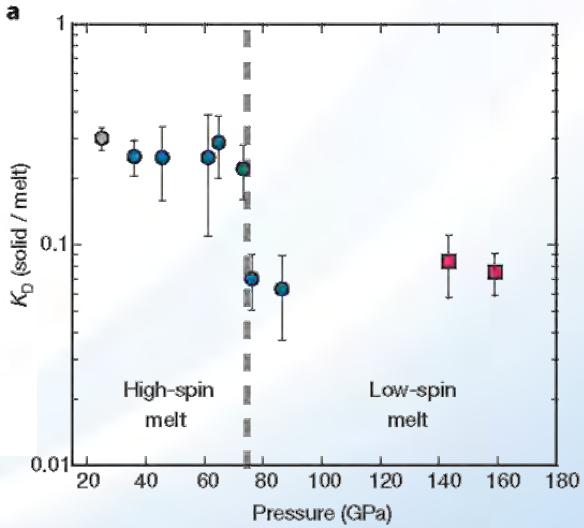
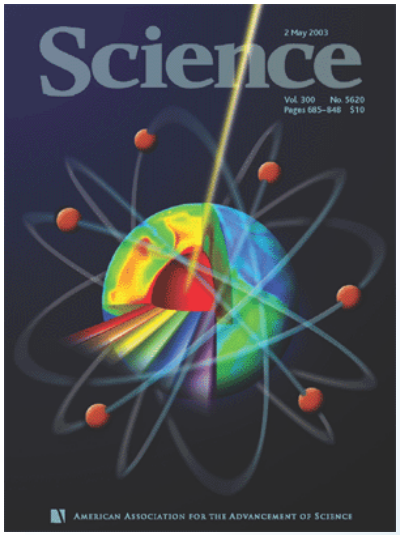


Figure 3 | Evolution of X-ray emission spectra of $(Mg_{0.95}Fe_{0.05})SiO_3$ glass with increasing pressure. Measurements were conducted at 300 K. All spectra are normalized to transmitted intensity, and shifted so that the weighted average of main (Kβ) plus satellite (Kβ′) emission lines is set to 7,058 eV. The satellite peak decreased slightly at 59 GPa and completely disappeared at 77 GPa, indicating the spin crossover of iron.







Other related works:

Badro *et al*, *PRL* 1999
Badro *et al*, *PRL* 2002
Li *et al*, *PNAS* 2004
Badro *et al*, *Science* 2003
Badro *et al*, *Science* 2004
Lin *et al*, *Science 2005*

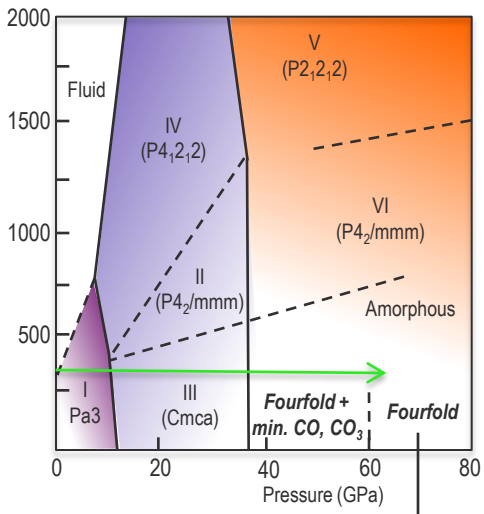
- Changes in Fe-Mg distribution coefficient as a function of pressure.
- Implications for the lower mantle

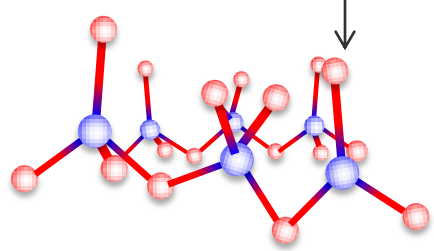
Nomura et al, Nature (2011)

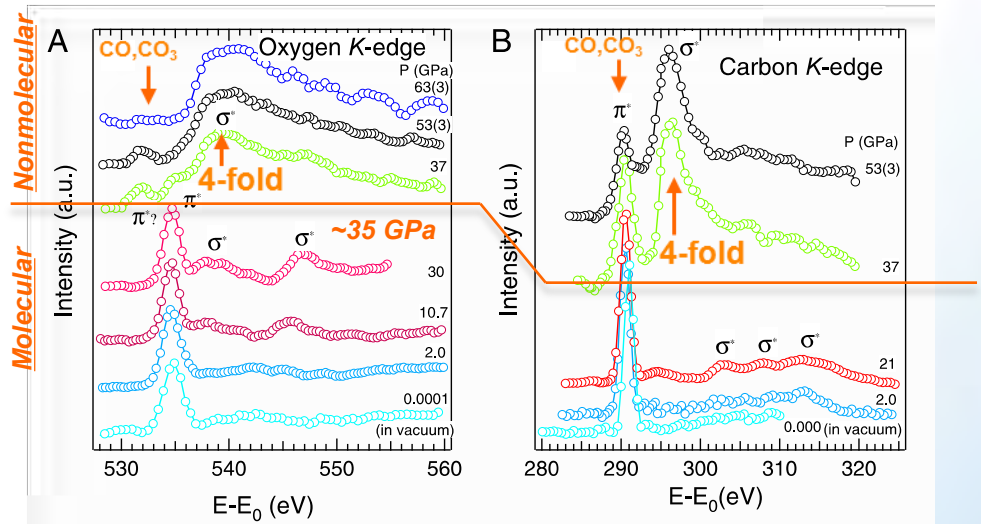
SPring-8 BL12XU

XRS: Molecular to Nonmolecular Transition in high-P CO_2

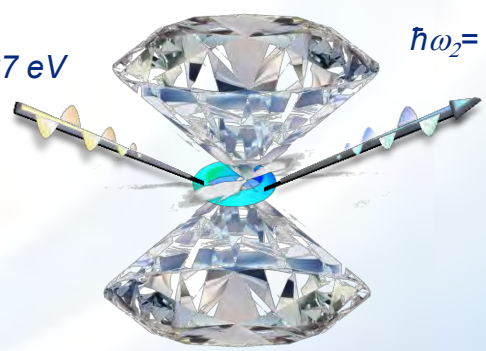
- Performing soft XAS with hard x-rays







$\hbar\omega_1$= 9887 eV

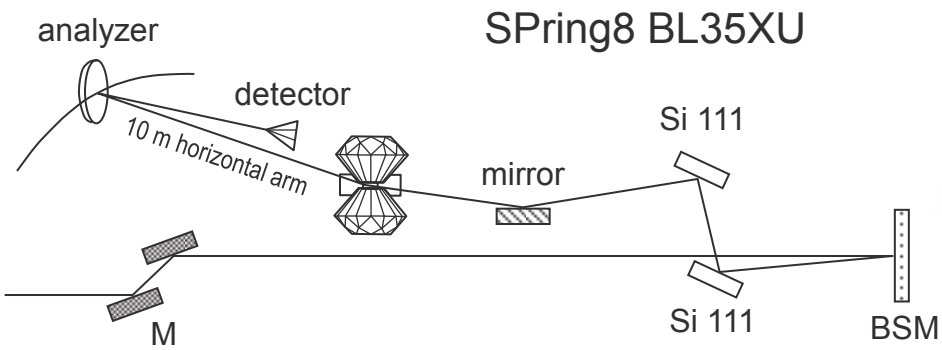


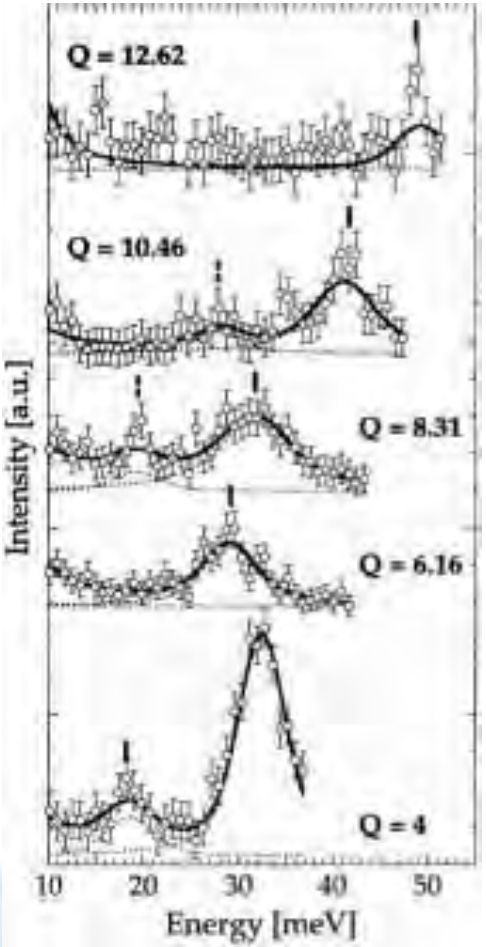
$\hbar\omega_2$= (9887-535) eV : O-K edge
(9887-290) eV : C-K edge

- Phase diagram of CO_2 better understood in the nonmolecular region
- XRS sensitive to bonding changes under pressure, and to coordination number in amorphous material.

S. Shieh, I. Jarrige, Y. Cai, et al, PNAS 2013

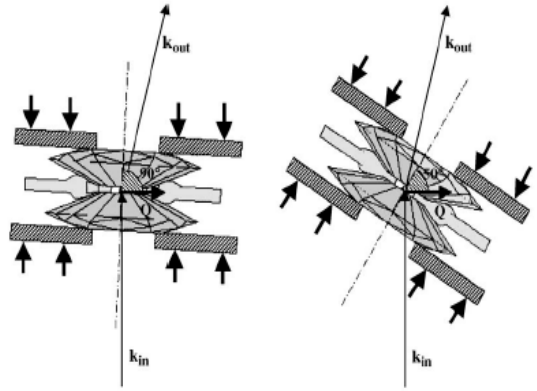
Phonon Dispersion in hcp-Fe over 100 GPa

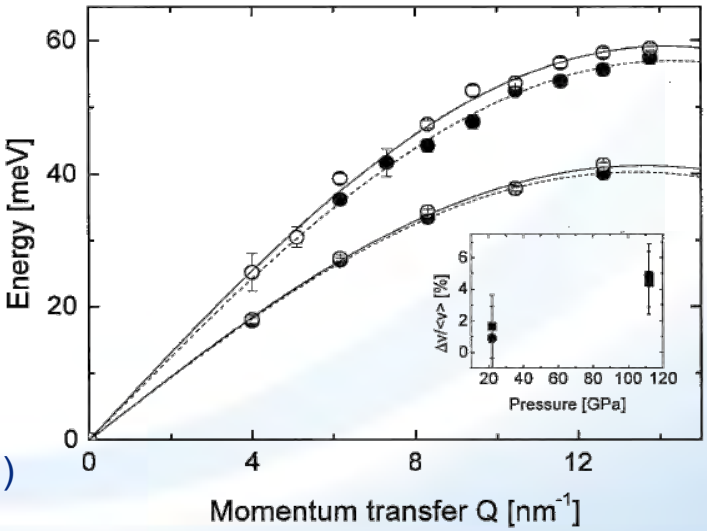




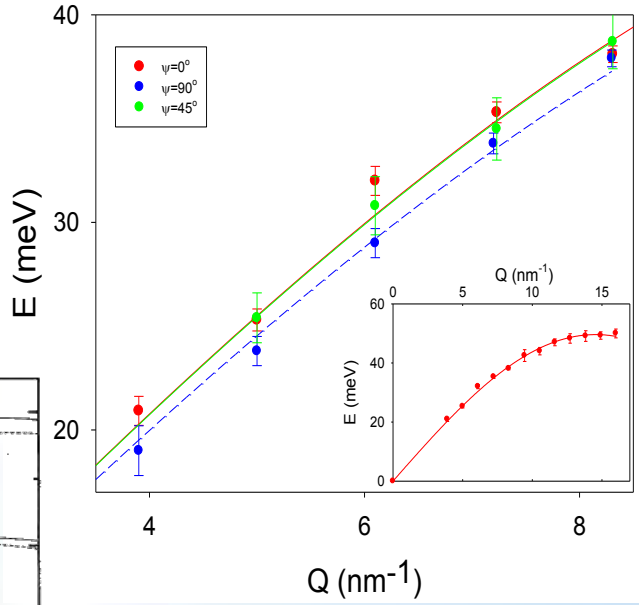
ESRF

Fiquet *et al.*, *Science* (2001)





Antonangeli *et al.*, EPSL (2004)



W. Mao *et al.*, JGR (2008)

Courtesy of Dave Mao

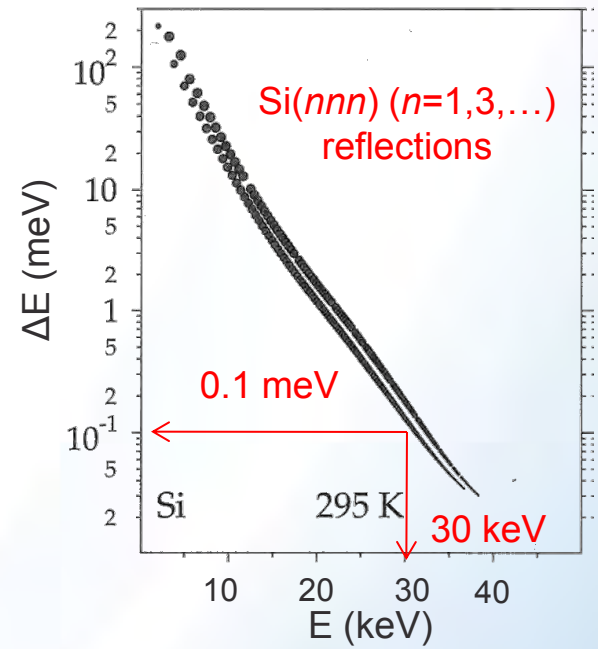
Limitations of Current IXS Instruments

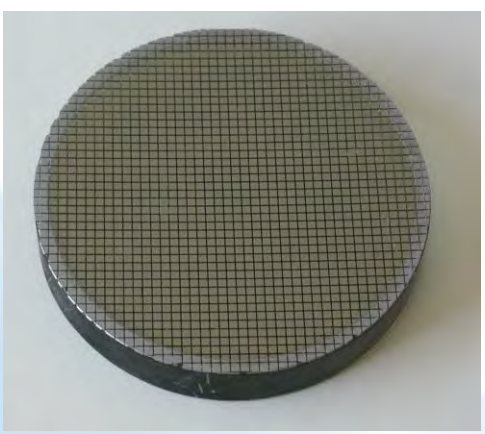
- E,Q resolutions dominated by spherical diced analyzers:

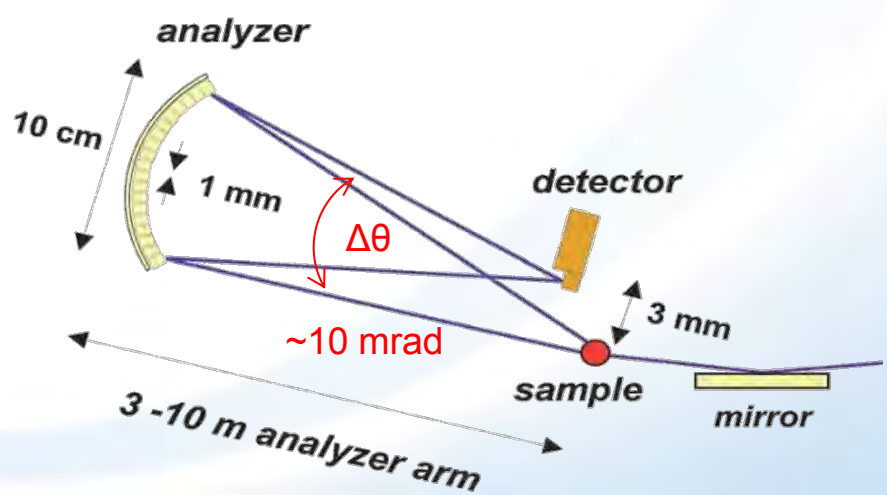
$$\left(\frac{\Delta E}{E}\right)_A = \left[\left(\frac{\Delta E}{E}\right)_h^2 + \left(\frac{\Delta E}{E}\right)_g^2 + \left(\frac{\Delta E}{E}\right)_S^2\right]^{1/2}, \quad \Delta Q_A = \frac{2\pi}{\lambda}\cos(\theta)\Delta\theta$$

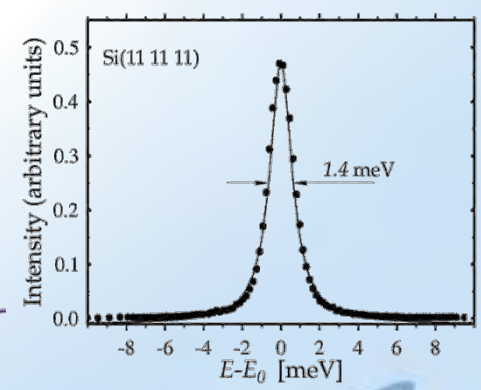
$(\Delta E/E)_g \propto (c/R)$; $(\Delta E/E)_S \propto s/R$
Resolution function tails: Lorentzian

- Practical E,Q resolutions are flux limited to ~1.5 meV and ~0.5 nm^{-1} [5 mrad acceptance @ 21.7 keV – Si(11,11,11)]
- Higher energy resolution requires higher incident energy
  - ➢ Incompatible with undulator performance



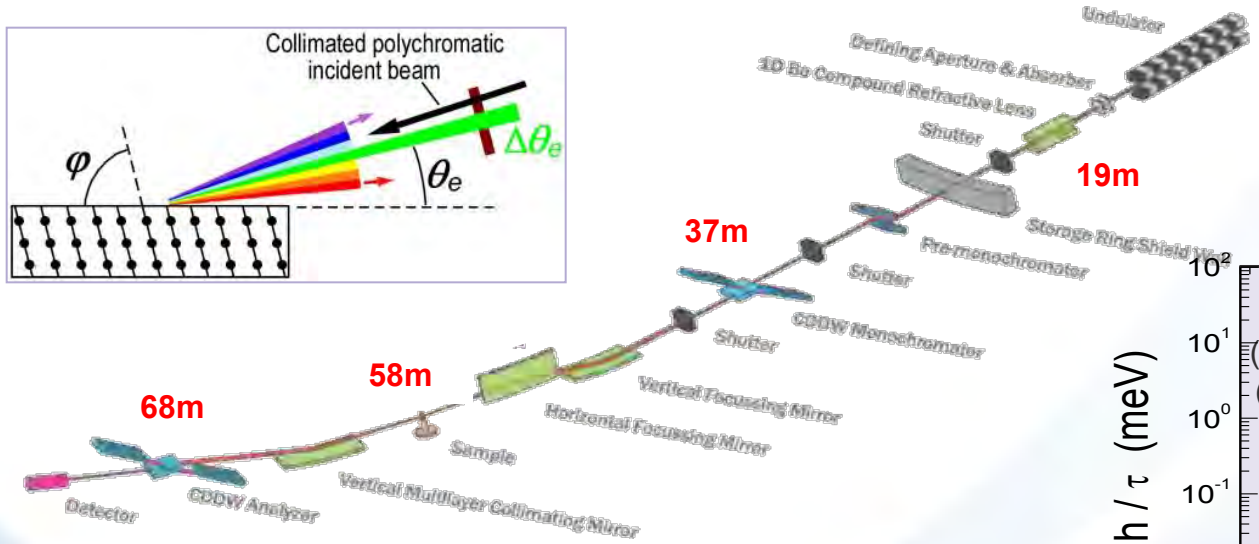




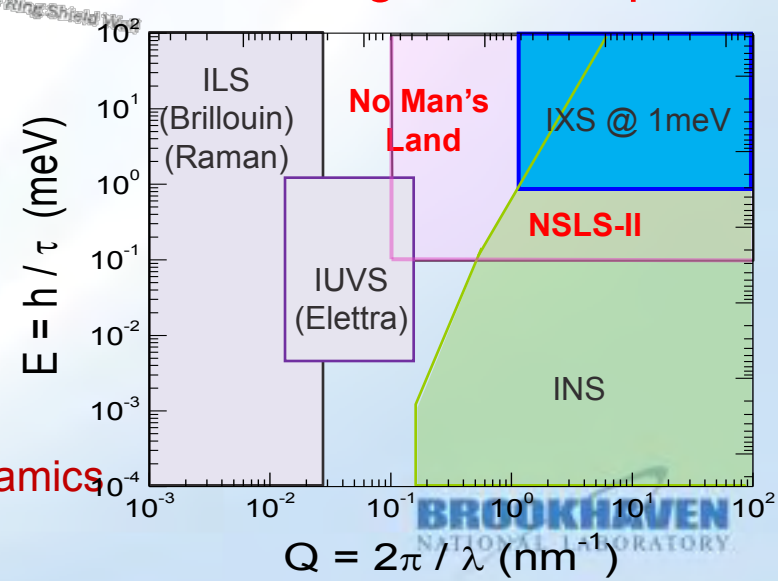


IXS Beamline Overview

- Designed to Achieve Best-in-Class Performance for IXS :
  - Angular dispersive crystal optics for cutting-edge resolution (**0.1 ~ 1 meV**) with **sharper tails** in resolution function and high Q resolution (**0.1 nm^{-1}**).
  - Medium operation energy (**9.1 keV**) capitalizing on NSLS-II's strengths in flux and brightness
- Scientific Interests
  - Ultrafast dynamics in liquids, soft matter, and biological systems
  - Phonons in single crystals, surfaces, interfaces and systems under extreme conditions



"Filling in the Gap"



Ultimate Goal:

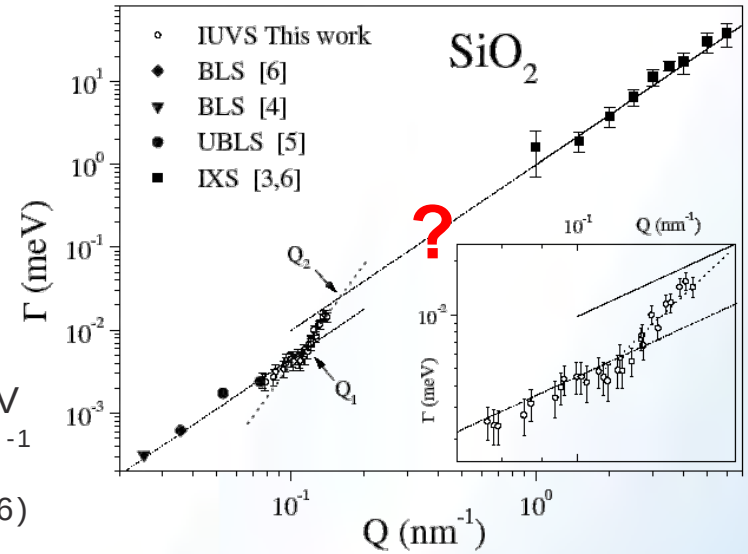
World-leading 0.1 meV energy resolution for studying dynamics

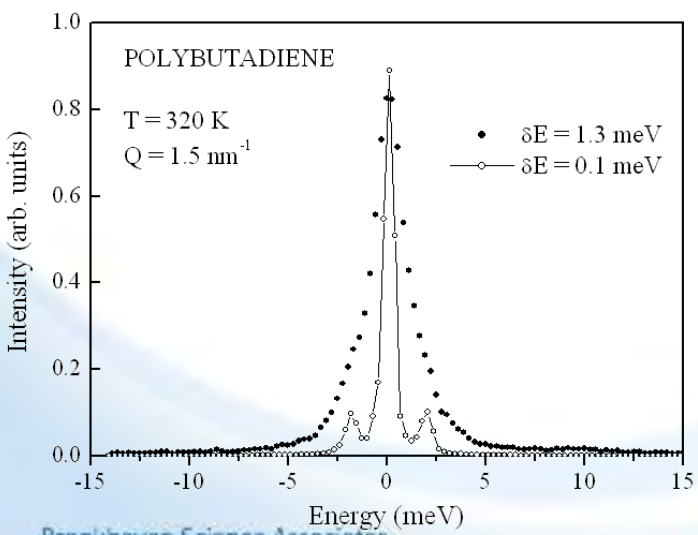
What do we gain with higher resolution in E and Q?

- Better defined energy position
  - Viscoelastic transitions in liquids/glasses
  - Phonon dispersion curves in crystals
- Better defined line width
  - Dynamical heterogeneities in glasses
  - Phonon lifetime

SiO_2: Change in acoustic damping @ 0.01meV < E < 1meV
0.1nm^{-1}< Q < 1nm^{-1}

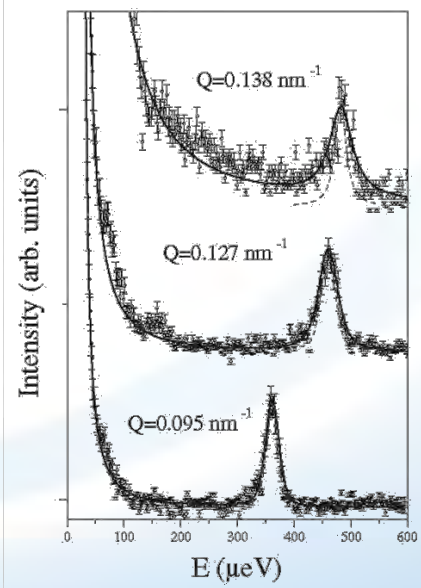
Masciovecchio et al., Phys. Rev. Lett. 97, 035501 (2006)





Fioretto et al., Phys. Rev. E (1999)

IUVS: ΔE~ 0.014 meV



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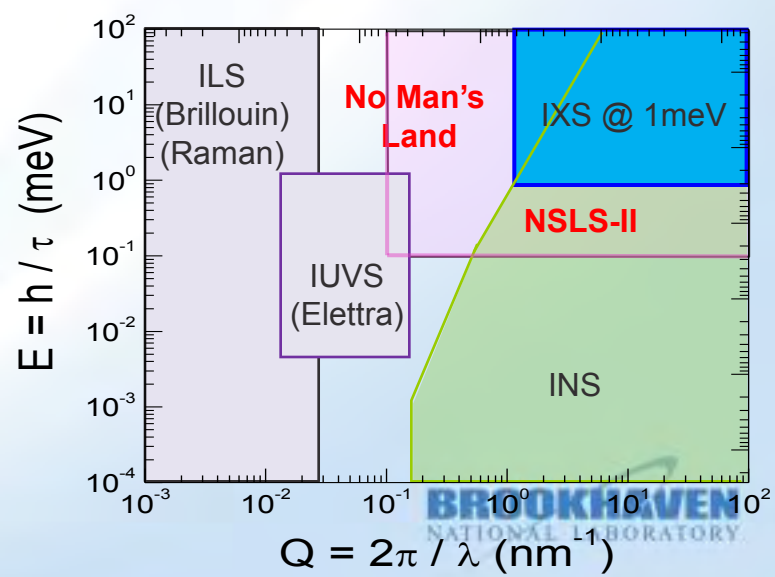

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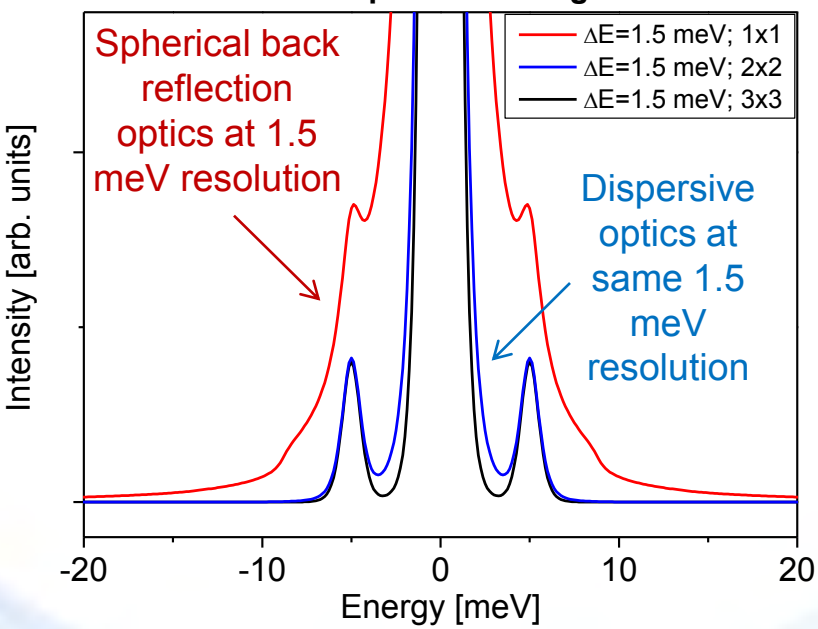
Spectral Contrast Matters

- Better defined line shape
  - Transverse mode
  - ➢ Biological systems (lipid membranes)

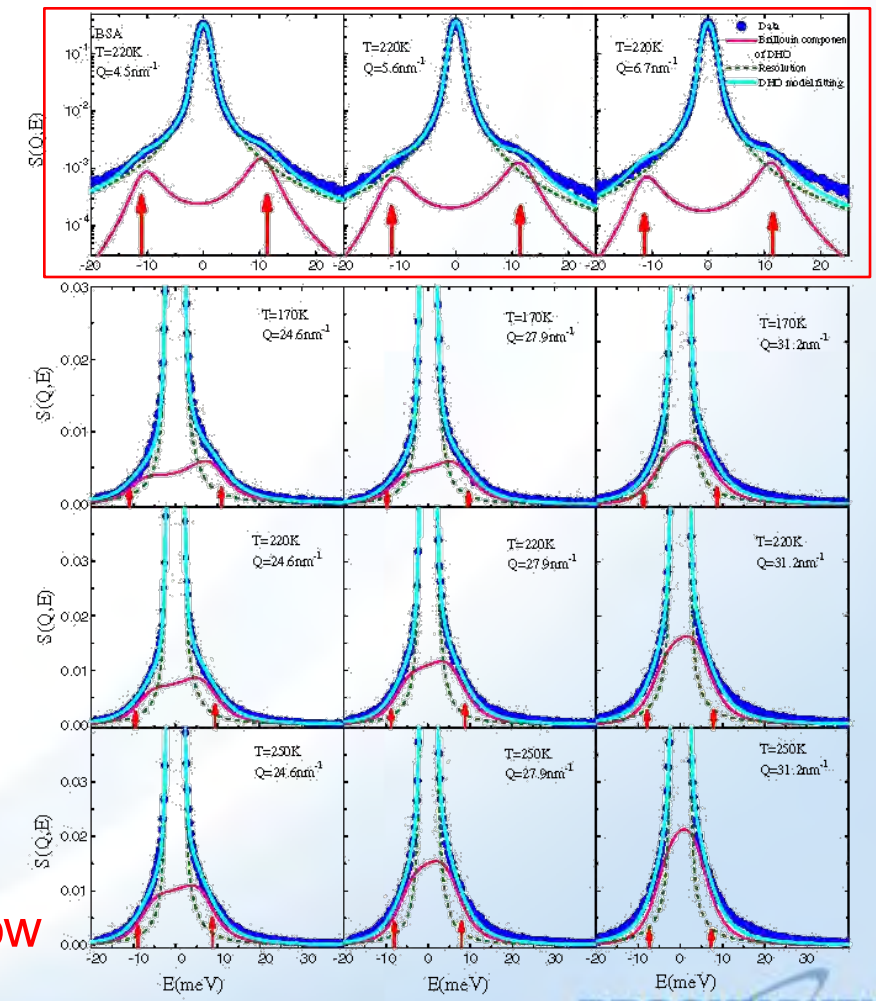
Phonon modes @ E ~ 10 meV
Q ~ 10 nm^{-1}

Generic spectrum of a glass



Phonon-like low-energy excitations

PRL **101**, 135501 (2008) *Liu and Chen, et al.*



- 0.1 meV gives access to ps time window
  - ➢ MD simulations to 100 ps
  - ➢ Tests of force field models

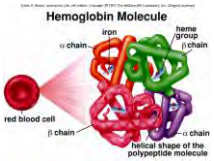
APS 30-ID, E = 23.724 keV, ΔE = 1.5 meV

The Relevant Length Scales

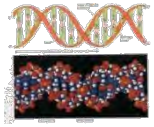
- Better Q resolution allows access to the mesoscopic length scale (5 ~ 50 nm, part of "no-man's land")
  - Fast dynamics of bio-molecular systems
  - Phonons in functional nanoparticle assemblies
  - Intermediate regime in disordered systems

Size (nm)

10^0 10^1 10^2

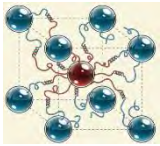


Hemoglobin

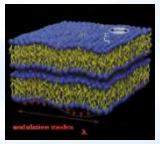


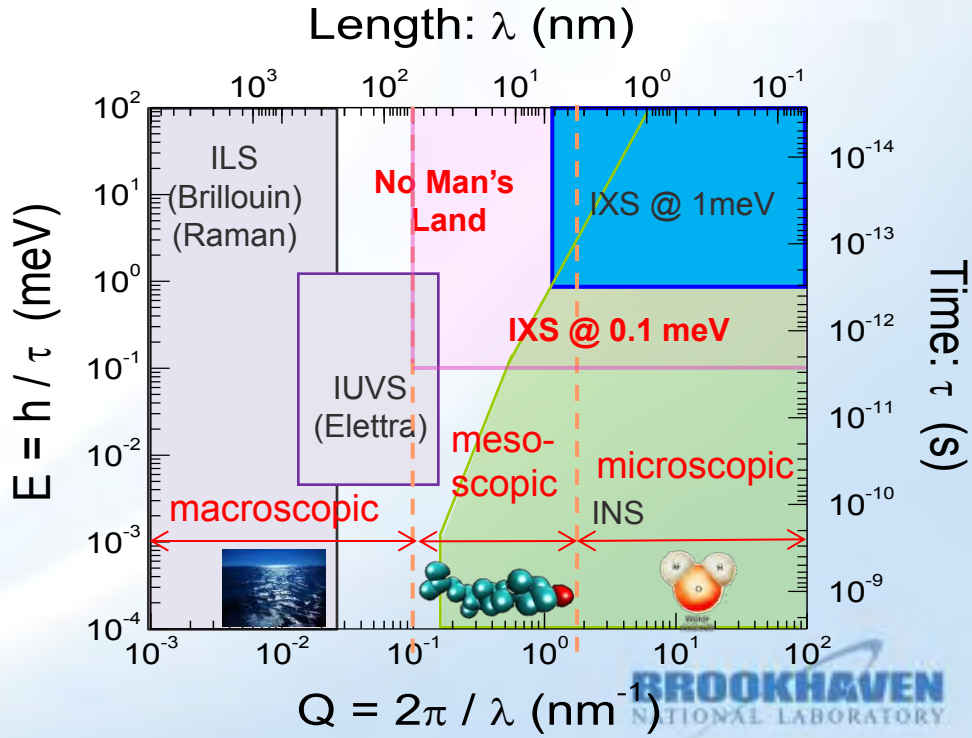
DNA

Super-lattices of nanoparticles



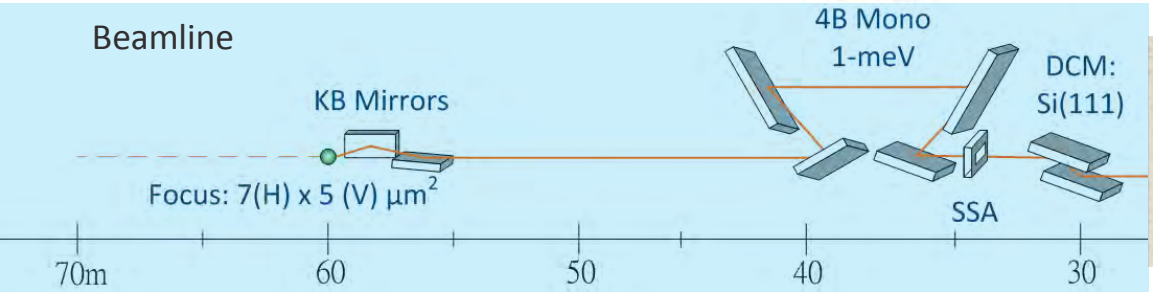
Lipid membrane

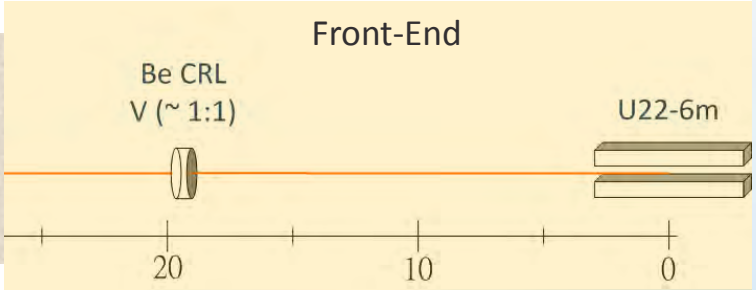


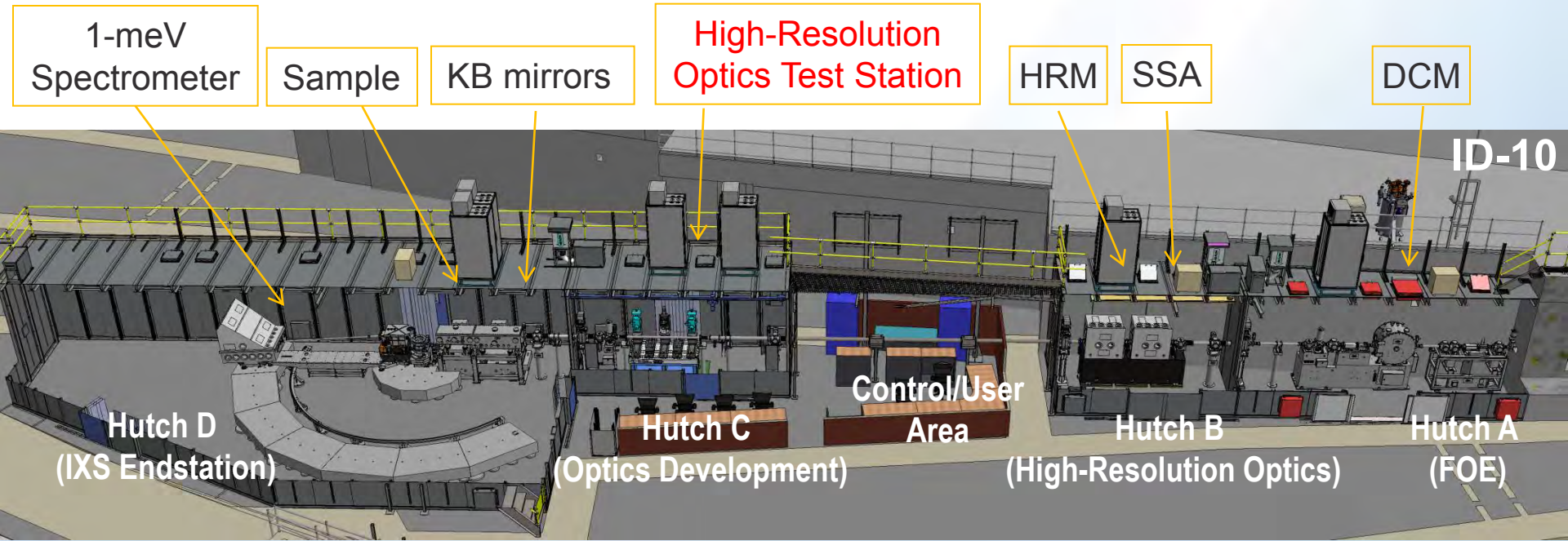


Beamline Design

- Be-CRLs for ~1:1 focusing at SSA (Vertical beam size ~30 μm FWHM, critical for 0.1 meV with CDDW scheme)
- HRM: inline 4B design (base line scope) for 1 meV, room for upgrade to 0.1 meV.
- KB Mirrors: large demagnification with bendable plane ellipse figure for fine focus on sample
- High-resolution optics test station: support continuing development towards 0.1 meV.





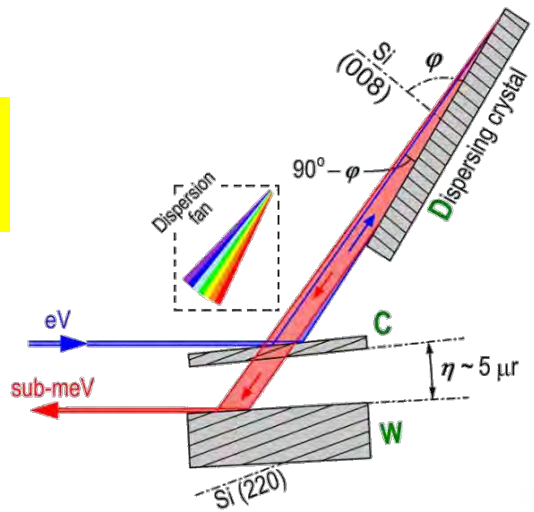


Asymmetric Back Scattering Optics

- Proposed by Shvyd'ko (2004, PRL 2006)
- Based on angular dispersion effect in asymmetric Bragg reflections.

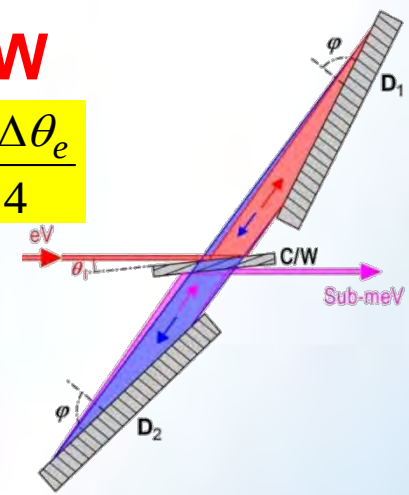
CDW

$$\frac{\Delta E}{E} \approx \frac{\Delta\theta_e}{2\tan\varphi} \approx \frac{\theta_e \Delta\theta_e}{2}$$



CDDW

$$\frac{\Delta E}{E} \approx \frac{\theta_e \Delta\theta_e}{4}$$



→ Angular acceptance ~100 μrad

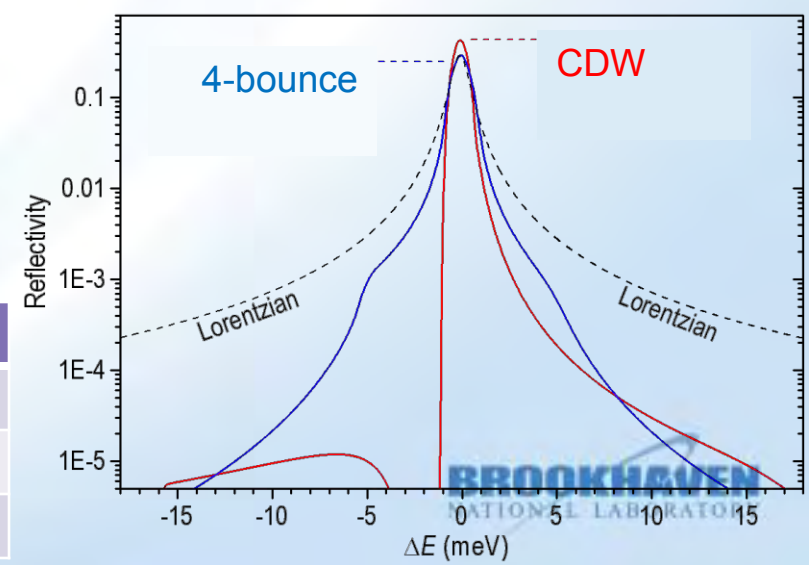
→ High peak reflectivity ~40%

→ Sharp tails (multiple reflections and anomalous transmission)

→ Sub-meV resolution at ~10 keV

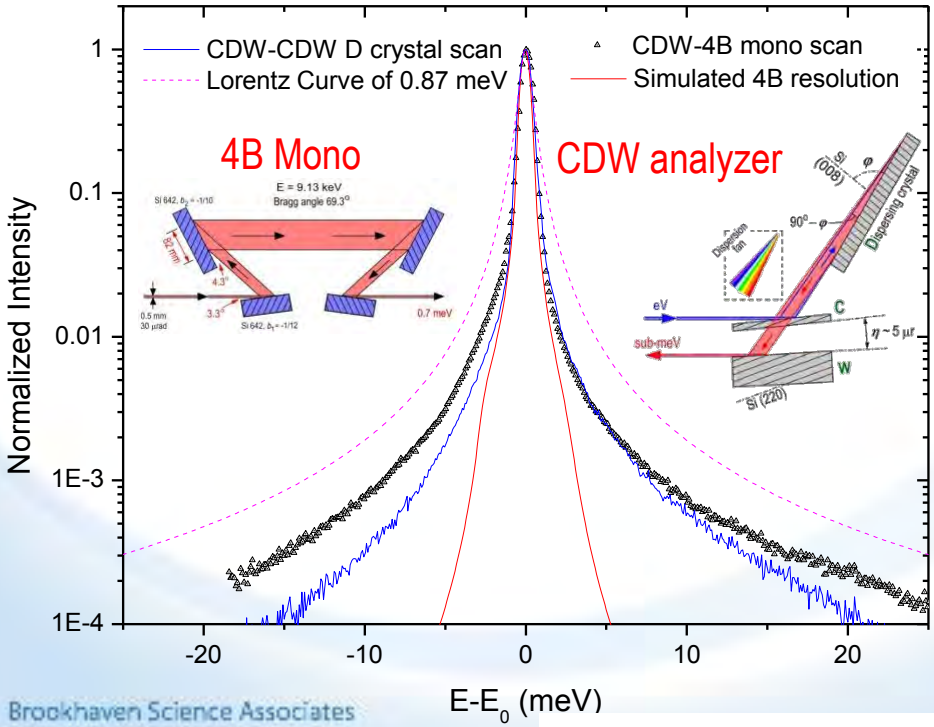
- Major parameters determined and verified for E = 9.13 keV, $\Delta\theta_e$ = 5 μrad, and h = 0.5 mm

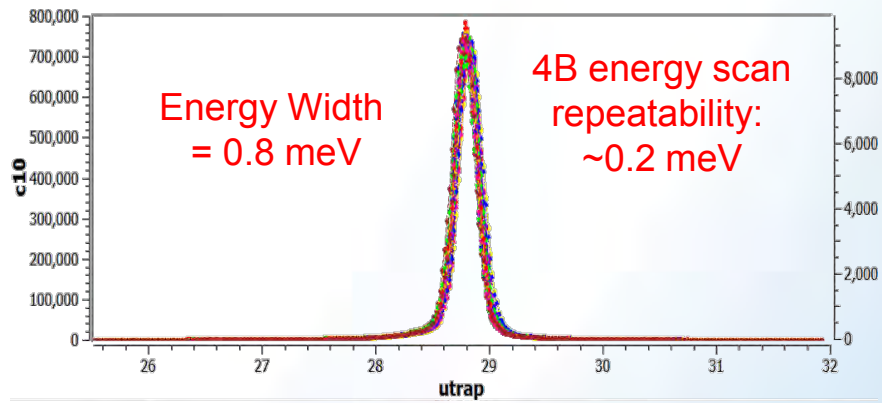
ΔE of CDW	ΔE of CDDW	Θ_e (= 90° – φ)	Length of D
2 meV	1 meV	4.5°	120 mm
0.7 meV	0.3 meV	1.5°	380 mm
0.2 meV	**0.1 meV**	**0.4°**	**1400 mm!**

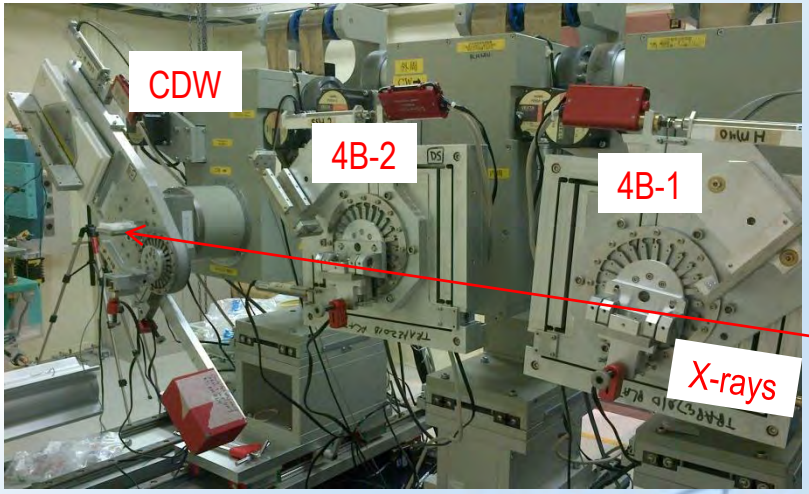


High-Resolution Crystal Optics R&D

- Achieved the initial goal of sub 1 meV resolution. Key performance parameters demonstrated include:
  - CDW analyzer (de-convoluted) resolution < 0.7 meV,
  - 4B-CDW combined resolution 0.8 meV,
  - 4B-HRM efficiency ~ 30%,
    CDW analyzer efficiency ~ 20%
  - Sharp Gaussian-like tails to ~2 orders of magnitude





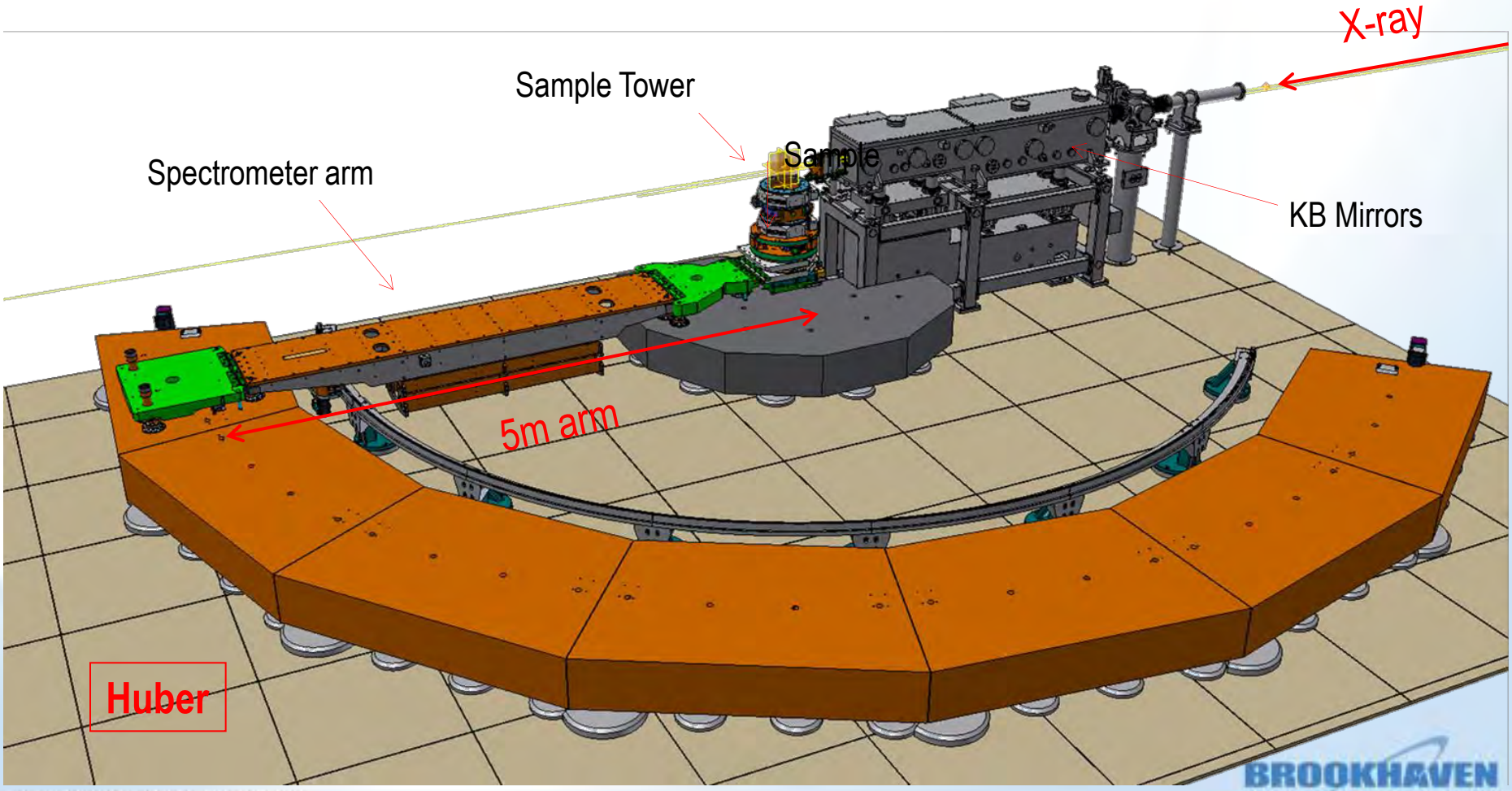


4B-CDW setup

(Cai et al, J. Phys.: Conf. Ser. 425, 202001; Keister et al, J. Phys.: Conf. Ser. 425, 052032)

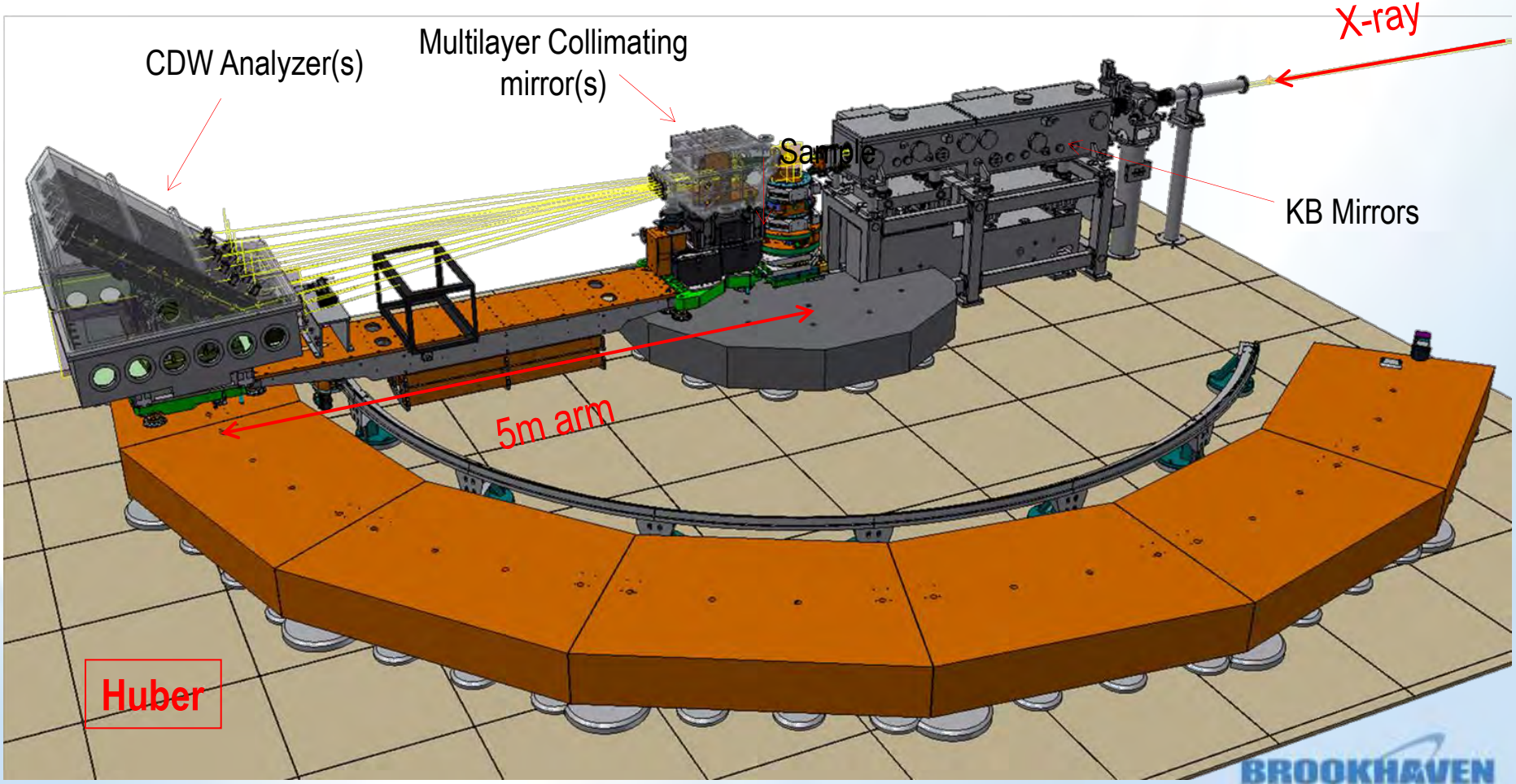
1-meV Spectrometer

- Spectrometer arm scattering angle range: -7 to ~130 deg (Q_{MAX} ~ 80 nm^{-1})



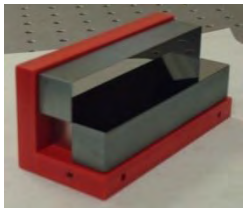
1-meV Spectrometer

- Support up to five analyzers, but only one analyzer will be built initially (base scope).
- Q range limited to ~40 nm^{-1} initially for scattering angle < 60 deg due to polarization effects (need phase plate – future scope, and improvement on CDW analyzer)

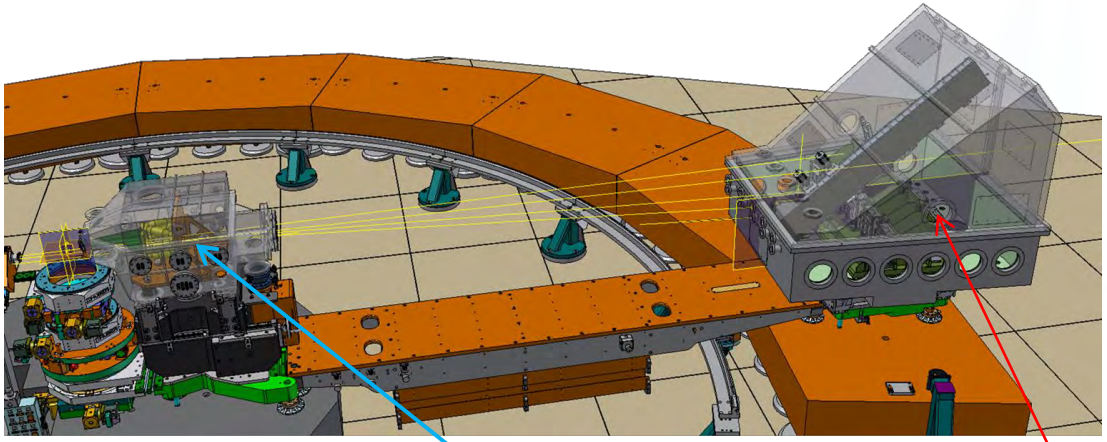


CDW–Montel Mirror Analyzer

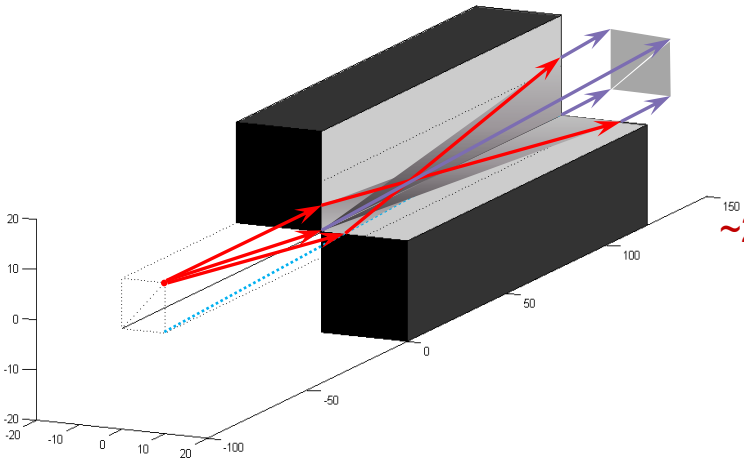
- The use of CDW optics for analyzer requires collimation: ≤ 0.1x0.1 mrad^2
- Montel mirror designed to achieve comparable acceptance to spherical diced analyzers: Angular acceptance @ full illumination: ≥ 10x10 mrad^2

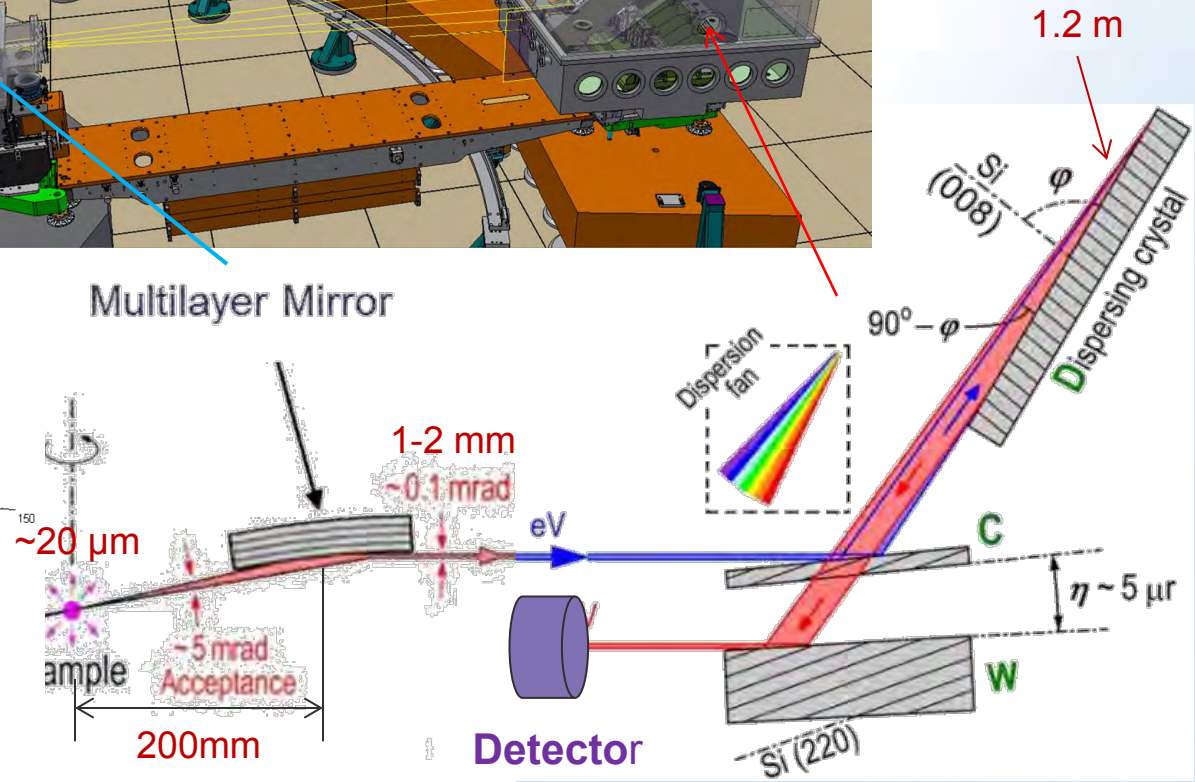


Montel mirror

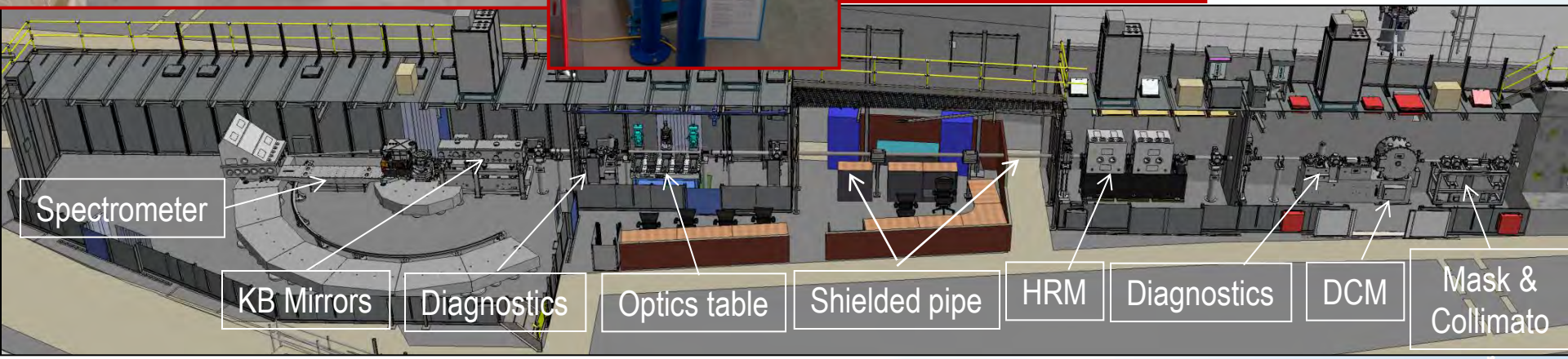


Multilayer Mirror

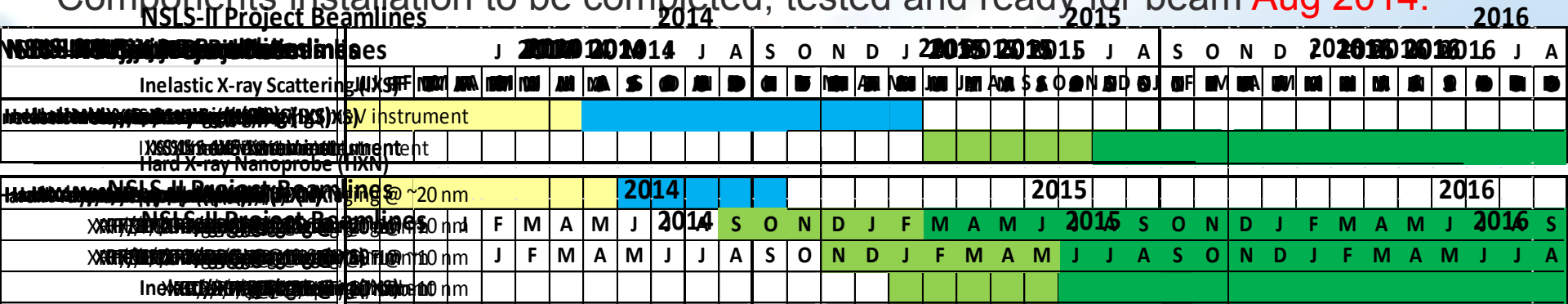




Beamline Development Status



- Components installation to be completed, tested and ready for beam Aug 2014.



Initial Performance & Capabilities

Performance Comparison :

Facility (Beamline)	ΔE (meV)	ΔQ** (nm^{-1})	E (keV)	$I_{inc.}$ @ ΔE (photons/sec)	Beam Size (V×H μm²)	Flux Density (photons/sec/μm²)	Sharp Res. Tails
ESRF (ID28)	1.6	0.5	21.7	6×10^{9}	7×12	7.1×10^{7}	--
APS (30-ID-C)	1.5	0.6	23.8	2×10^{9}	15×35	3.8×10^{6}	--
SPring-8 (43LXU)	1.5	0.5	21.7	$\sim5\times10^{10}$	20×35	$\sim7.1\times10^{7}$	--
NSLS-II (IXS)	1.0	0.2	9.1	$\sim1.6\times10^{10}$ (4B HRM)*	5×7	**$\sim5\times10^{8}$**	yes

* Performance for a IVU22-3m at 500 mA (flux 8×10^{14} phs/sec/0.1% bw) and 30% spectral efficiency for the 4B monochromator.
** Assuming 5 mrad acceptance angle.

$$\frac{I}{I_0} = \frac{r_e^2 \hbar^2 c^2 (\delta q)^2}{2eE_i^2} Z^2 \rho l_{abs} \frac{k_B T}{M \upsilon^2}$$

$$\frac{I}{I_0} \propto \left(\frac{\delta q}{E_i}\right)^2 l_{abs} = \left(\frac{2}{\hbar}\delta\vartheta\right)^2 l_{abs}$$

H. Sinn, J. Phys. Cond. Mat. (2001)

Count Rate Estimates (single analyzer):

Sample	Thickness (μm)	ESRF ID28 (cnts/sec)	NSLS-II IXS (cnts/sec)
v-SiO_2	2100/190	~0.2	**~0.2**
H_2O (HP)	1000/1000	~1.0	**~8**
La_2CuO_4	75.3/7.13	~0.5	~0.04
Solid O_2	10/10	~1.5	**~2**

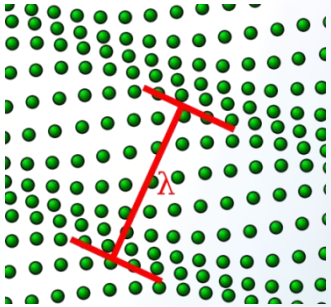
(ESRF data courtesy of M. Krisch)

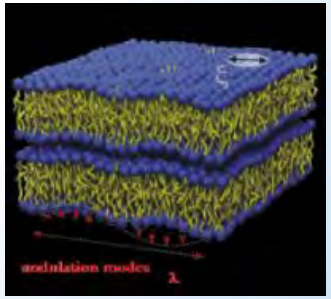
- Unique research strength for low-Z materials and high-pressure DAC systems (small beam size, highest flux density)

Scientific Opportunities

Areas that may benefit from the improved resolution tails and higher Q resolution :

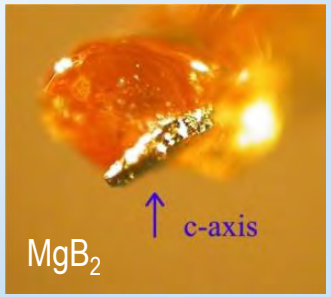
- Anomalies in thermal and elastic properties in liquids and disordered systems
  - Relaxation dynamics in liquids in the supercooled phase.
  - Acoustic properties and dynamical heterogeneities in glasses
- Dynamics of confined liquids
  - Material science, microfabrication, adhesion and lubricaton, biology, geology, nanoscience and nanotechnologies, including the development of hydrogen fuel cells
- Phonon-like excitations in bio-materials and soft matters
  - Important for understanding some biological functions (e.g., phonon-assisted transport of molecules across lipid bilayers)





Areas that may benefit from the excellent beam size and flux density:

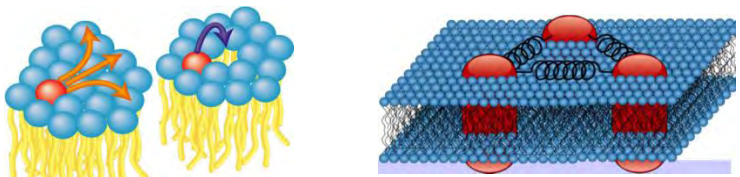
- Phonons in crystalline and polycrystalline materials
  - Single crystals of exotic new materials often available only in small size (10^{-4} ~ 10^{-6} mm^3)
- Phonon and vibration dynamics of surfaces and interfaces and systems under extreme pressure
  - Sample volume is limited in these cases.



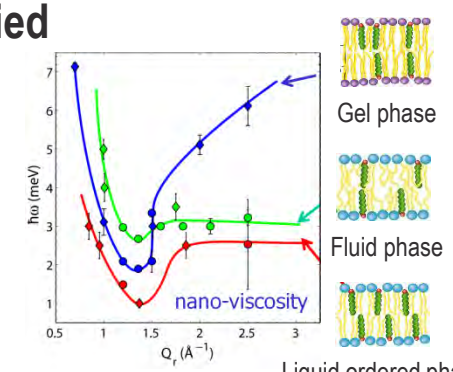
Size: ~ 400 x 400 x 40 μm^3

Lipid Membrane Dynamics

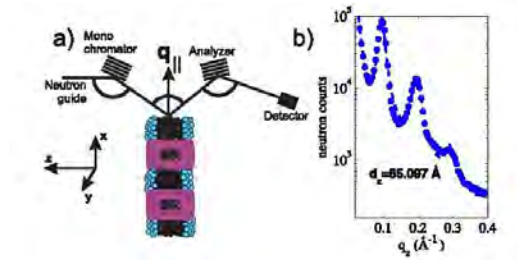
Key relevant biological processes to be studied



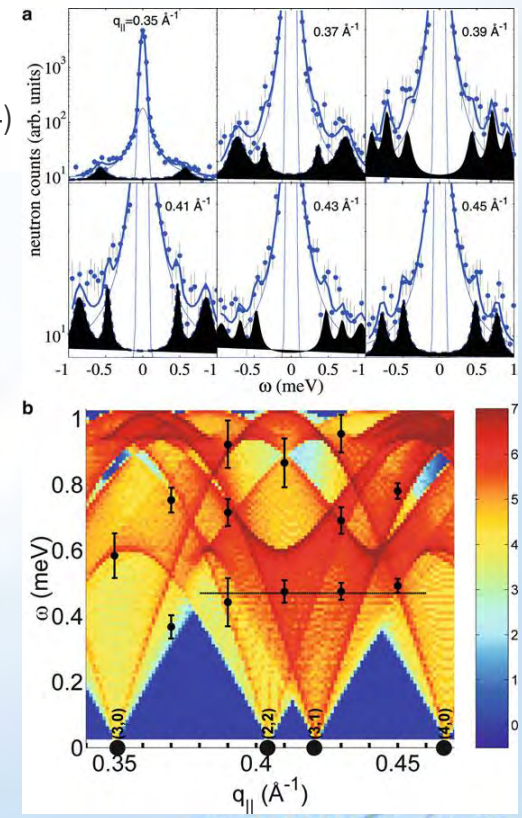
(Courtesy of M. Rheinstädter)



(Rheinstädter et al, Phys. Rev. Lett., 2004)



- Lipid and protein diffusion and transport;
- Protein-protein, protein-lipid interaction;
- Nanoscale dynamics in rafts



Protein-protein interaction in membranes
(Rheinstädter et al, 2009, Phys. Rev. Lett.)

- From the measured phonon dispersion with respect to membrane orientation, width of quasi-elastic peak and their temperature dependence, one derives detailed knowledge of elasticity, relaxation, viscosity, direction of diffusion and transportation, binding rigidity of the bi-layers, etc.
- Comparison with MD simulations: test of force field theories; prediction of functional behaviors; and design of engineered biomaterials.

Strengths of the IXS beamline

- Sub-meV resolution, sharp tails, high Q resolution comparable to INS.
- Coherent x-ray scattering on collective modes, no need to deuterate the samples.
- Low operation energy and small focus optimized for low-Z materials.

Light Elements under Extreme Environments

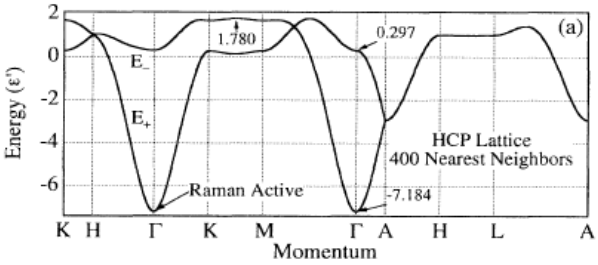
- Dave Mao (Carnegie)

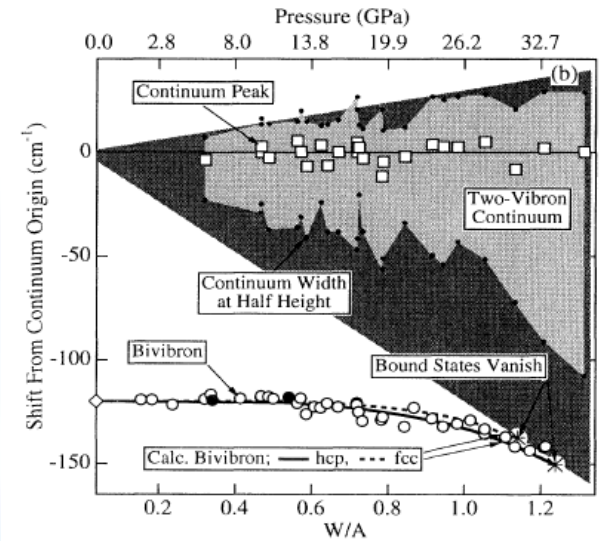
One of Holy Grails in high P-T research

- Vibrational and fluid dynamics of light elements (H, Li and Na)
- Intra- and intermolecular vibrations provides direct and sensitive information on the state of bonding and changes under extreme pressure and temperature.

Strengths of the IXS beamline

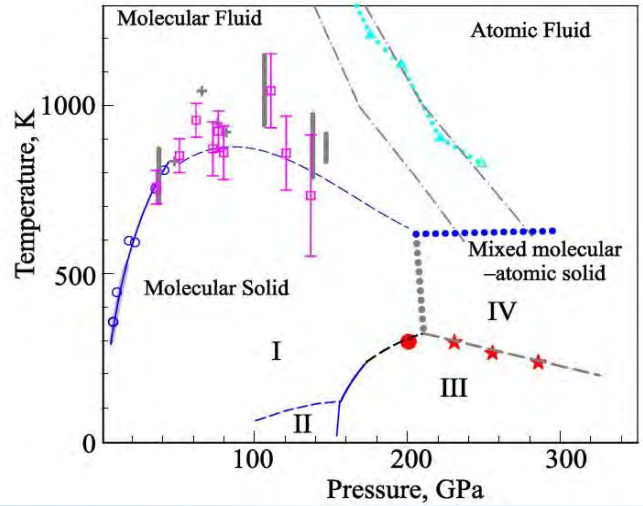
- IXS allows to map out the dispersion, whereas IR has access only to zone-center vibrons. The results will be a critical test of the pressure effect on vibron dispersion which has been deduced only from theories.
- The experiment is expected to shield new light on the many exotic properties of these systems, including the tantalizing I-M transition.

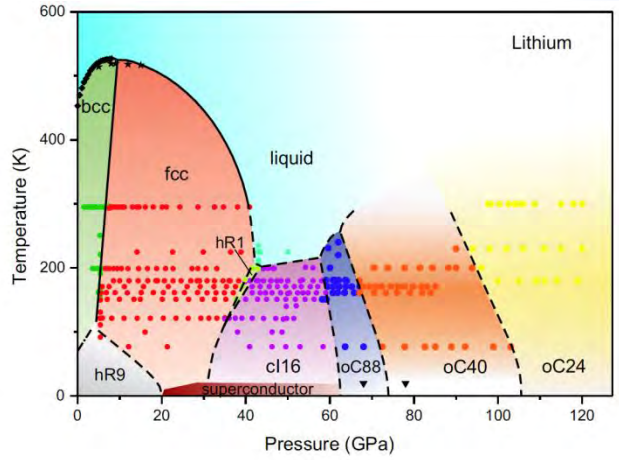




Vibron dispersion and bandwidth of hcp solid hydrogen as a function of pressure as determined by IR.

(Eggert, Mao, Hemley, PRL 1993)





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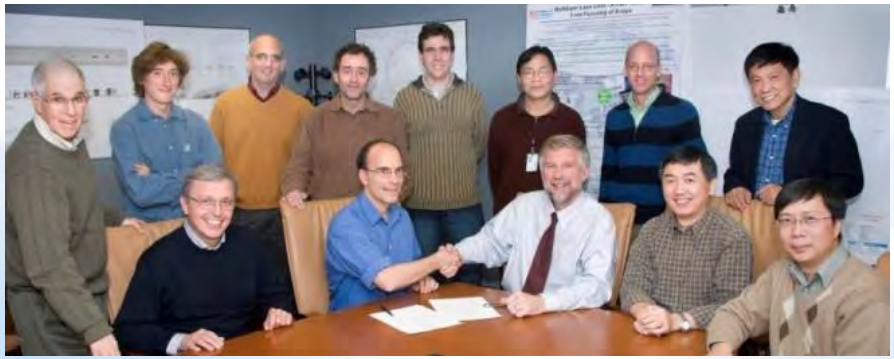
Summary

- Inelastic x-ray scattering can probe many of the important excitations in condensed matter over the relevant (ω, Q) space, and can be applied readily to studies under various extreme conditions.
- Count rate estimate for 1 meV resolution indicates better performance for low-Z materials in general, and for HP systems in particular, with substantial signal gain compared to state-of-the-art optics operating at 1 meV, and much enhanced contrast due to sharp resolution tails.
- Science programs should take advantage of the lower operating energy!

Acknowledgements

Thank you!

- **NSLS-II IXS Team Members**
  - Alessandro Cunsolo, *IXS Beamline Scientist*
  - Alexey Suvorov, *X-ray Optics Scientist*
  - Jeff Keister, *R&D Beamline Scientist*
  - Scott Coburn, *Senior Engineer*
  - Stephen Antonelli, *Engineer*
  - Leo Reffi, *Designer*
  - David Levy, *Technician (BL Support)*
  - Bill Struble, *Technician (Crystal Fabrication)*
  - Nalaka Kodituwakku, *Crystal Fabrication*
  - Yuriy Stetsko, *X-ray Optics*
  - Xianrong Huang, *X-ray Optics (APS)*
  - Marcelo Honnicke, *Multilayer Mirror (Goias, Jatai, Brazil)*
  - Zhong Zhong, *X-ray Optics*



- **Beamline Advisory Team (BAT)**
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  - Alfred Baron, *RIKEN/SPring-8*
  - Sow-Hsin Chen, *MIT*
  - John Hill, *BNL*
  - Michael Krisch, *ESRF*
  - Ho-kwang (David) Mao, *Carnegie*
  - Tullio Scopigno, *Univ. Roma*
  - Stephen Shapiro, *BNL*
  - Yuri Shvyd'ko, *APS*