Scientific Opportunities with Synchrotron Radiation for Nano-Science

Zahid Hussain

Scientific Support Group, Leader

Advanced Light Source

Lawrence Berkeley National Laboratory

Outline

- Why and How?
  - *What we need to learn about nano systems ?*
  - *What kind of tools are necessary ?*
  - *What facilities are available at the synchrotron (ALS) ?*
  - *What facilities need to be developed ?*

- **Understanding complex nano-phenomena require advanced tools**
- **Close proximity essential for efficiency and timely results**

Opportunities for nanoscience with soft x-rays @ ALS

1. Spectroscopy (In-Situ, real time)

Absorption/Emission Spectroscopy (photon-in photon-out, bulk sensitivity, mag/elctric field)

Photoemission Spectroscopy (photon-in electron-out, surface sensitivity, upto 10 torr)

2. Microscopy (sometime combined with spectroscopy)

Scanning Transmission Microscope (STXM; Res ~25nm)

Transmission Imaging Microscope (XM1/2; Res ~15 nm)

Photoemission electron microscope (PEEMII/III; Res ~5-50nm)

Lensless diffractive imaging (3D images, Res ~5-10nm)

3. Scattering

Resonant Scattering (~100-1000 times higher cross section)

Resonant Inelastic Scattering (res ~3-4meV @ Mn/Cu 3p edges)

Coherent (dynamic) Scattering (time resolution msec to nanosec)

Small and Wide Angle Scattering (SAXS/WAXS, soft x-rays provide unique capabilities)

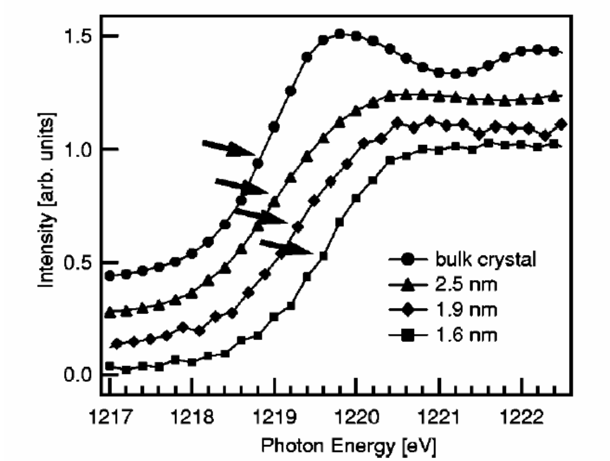
Spectroscopy

- Quantum confinement (properties different than constituents)
- Chemical Bonding (chemical reactivity)
- Electronic Structure (understanding complexity)

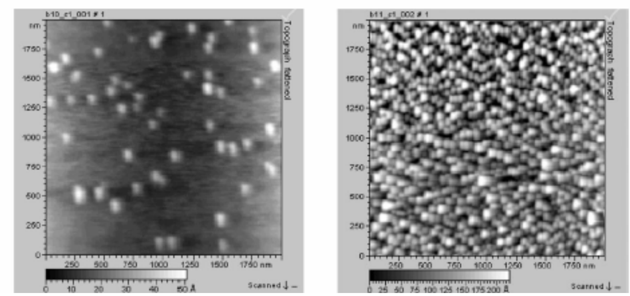
Crystal size determines color (quantum confinement)

Quantum-confinement effects and particle-particle interactions in Ge & Si nanocrystals

Absorption Spectra

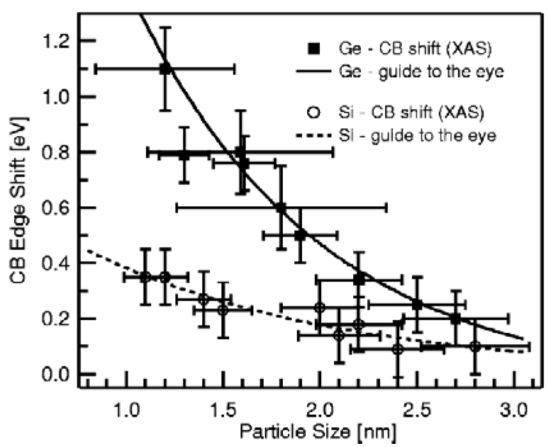


Atomic force microscope



sub-ML multilayer

- Ge nanoparticles condensed out of the gas-phase
- Particle-size determined post-situ by AFM
- Blue-shift of Ge L-edge correlated with decreasing cluster size
- Stronger CB confinement effects observed in Ge than in Si nanoparticles.

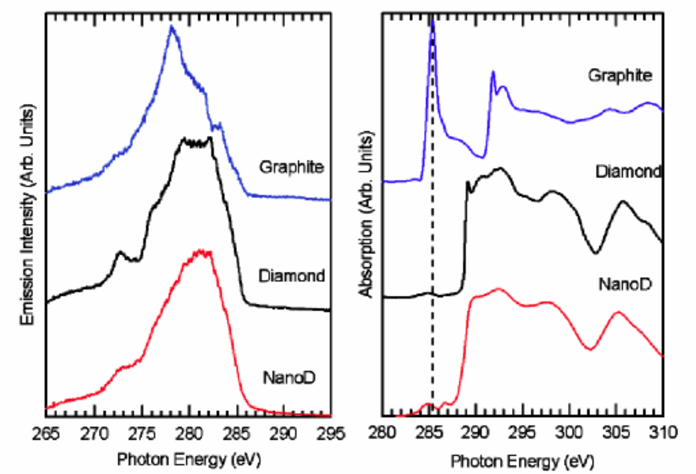


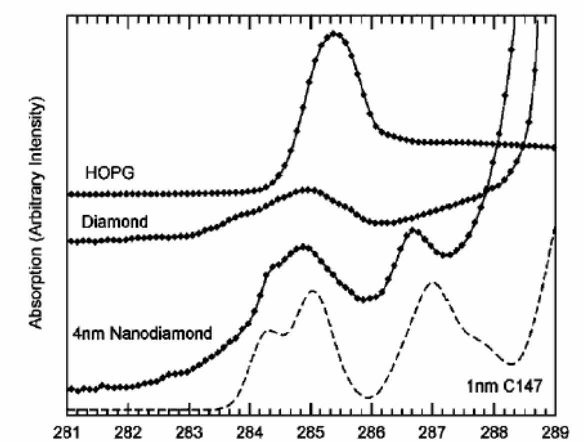
Conduction band shift vs particle size

C. Bostedt et al. APL 84, 4056 (2004) — LLNL PRT
C. Bostedt et al. APL 85, 5334 (2004)

Surface Reconstructions in Nanodiamonds

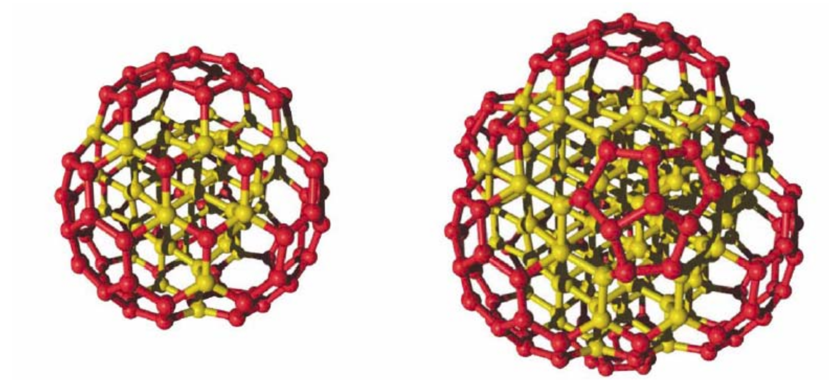
Emission **Absorption**





Need of theory

Core – Diamond; Surface – buckyballs

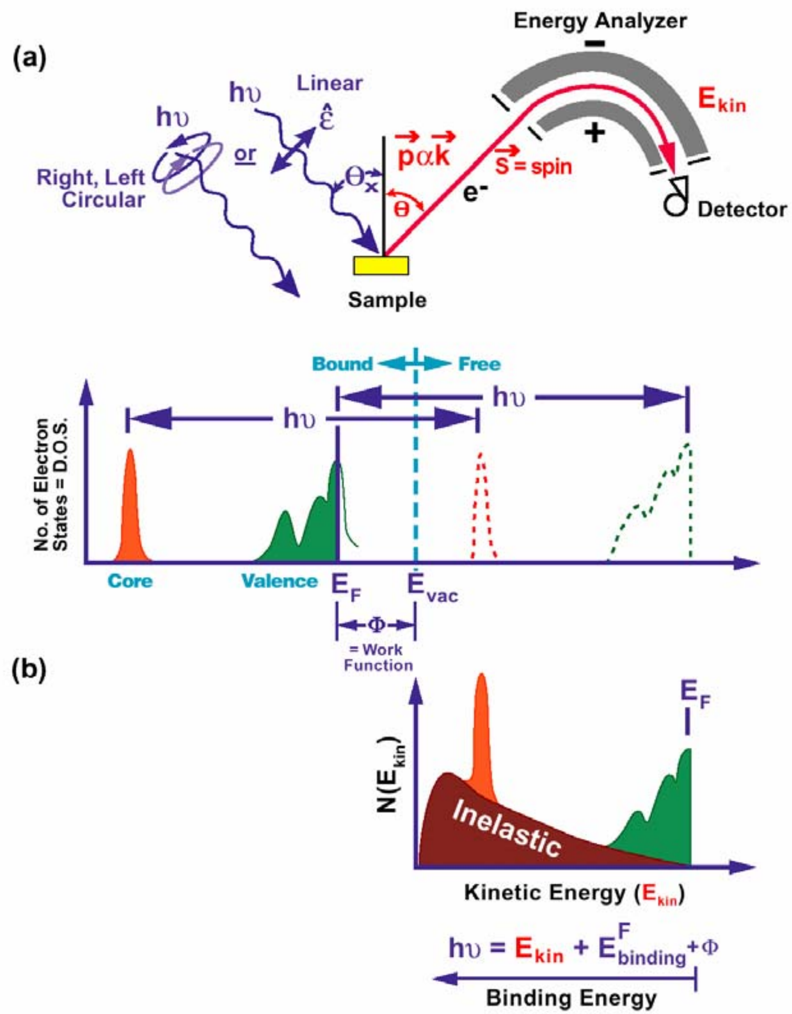


C_{147} (≈1.2 nm) C_{275} (≈1.4 nm)

- **Pre-edge Carbon K-edge structures observed in diamond clusters different from bulk diamond.**
- **Fullerene-like reconstructions determined at surfaces of diamond clusters by *ab initio* calculations compatible with pre-edge XAS**

J.-Y. Raty, G. Galli, C. Bostedt, T.W. Buuren & L.J. Terminello, PRL 90, 4056 (2003) — LLNL PRT

Photoelectron Spectroscopy

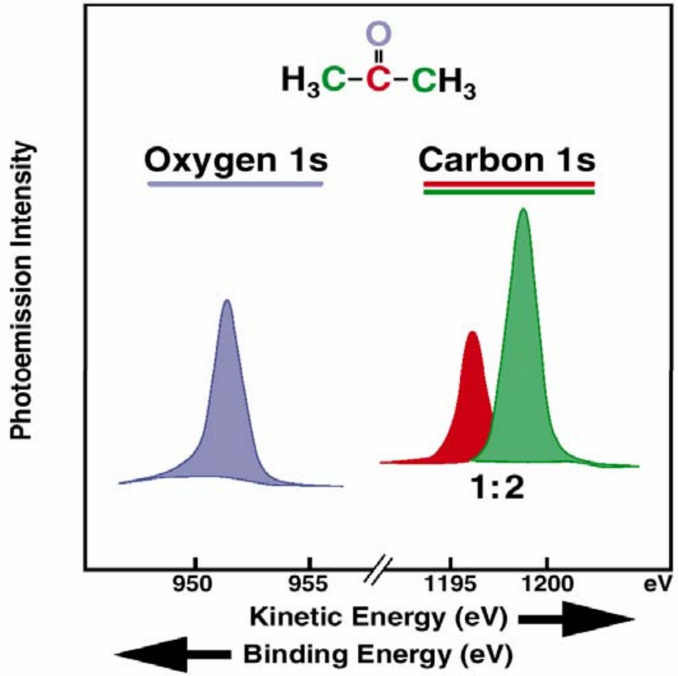


ag.zh/photospectros1/7-97

Photoelectron Spectroscopy

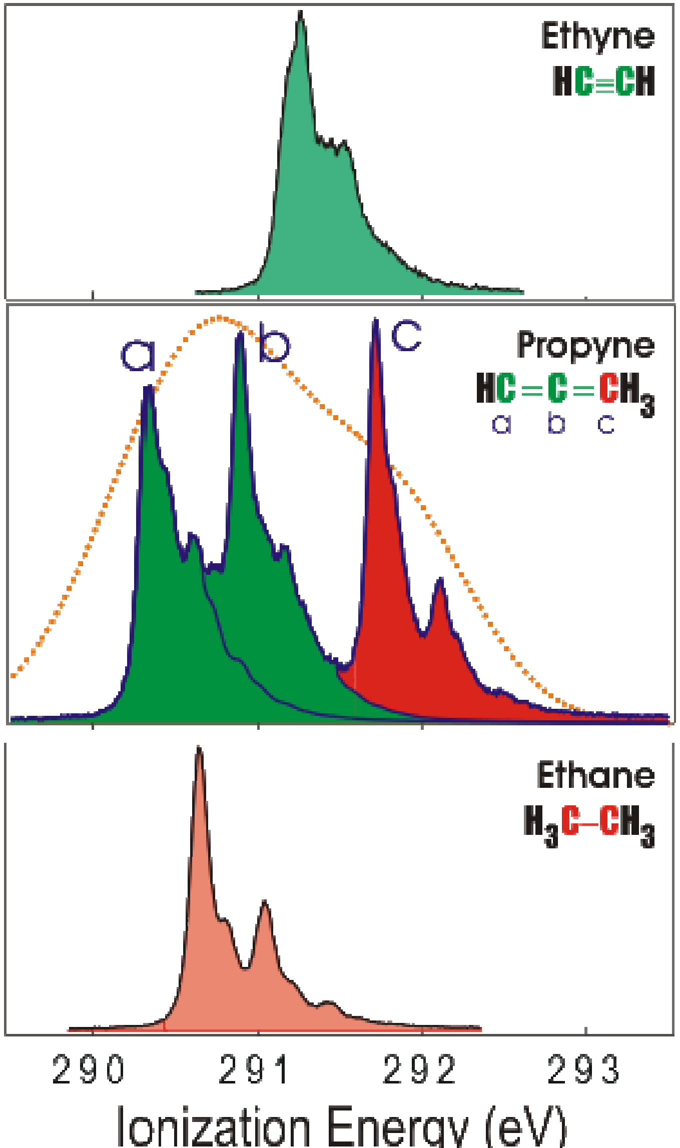
Provides information about

- Kind of atom
- Number of atoms
- Chemical shift



ag.zh/photospectros2/7-97

High resolution C1s Photoelectron Spectra of hydrocarbon



C 1s photoelectron spectra of propyne and two model compounds ethyne and ethane measured.

Unambiguous assignment of peaks in propyne spectrum is made possible by characteristic vibrational structure and ab initio theory.

Shift of the methyl (CH3) peak in propyne relative to ethane is due to the electronegativity of the ethyne (HC°C) group.

Previous C 1s spectrum of propyne measured with a lab source is indicated by the dashed line

From BL 10.0 (AMO, ALS)
Thomas et al, PRL

Ambient pressure photoemissiom

Microscopy

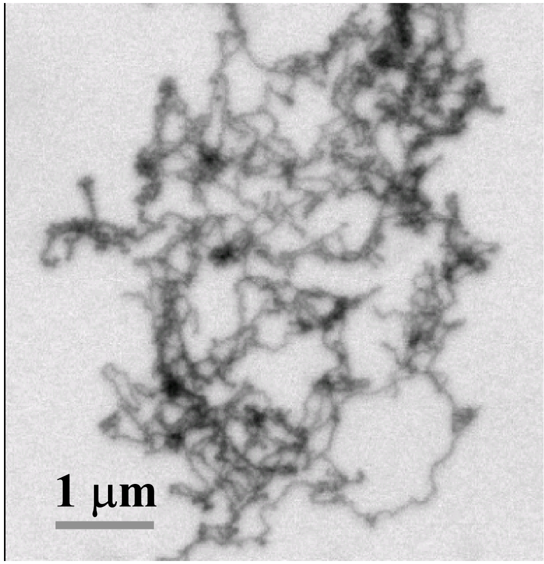
STXM: Microbial Polymer Templates for Iron Oxyhydroxides

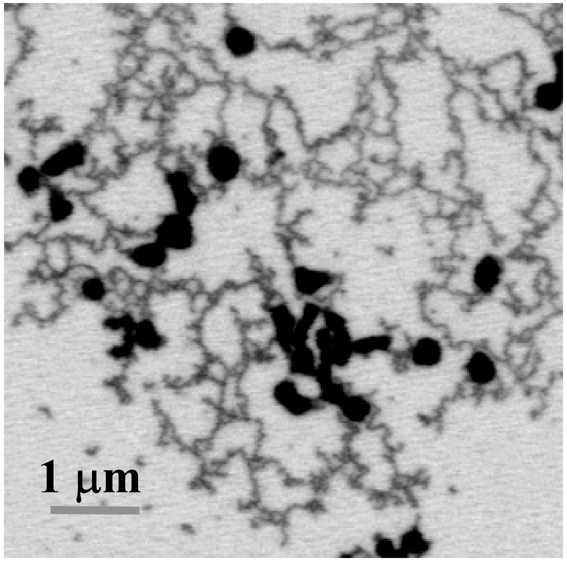
Natural filaments

Fe (~ 25 nm) with a polymer as core (~5nm)

Synthetic filaments (Fe-Alginate)

Spectra taken above C K edge



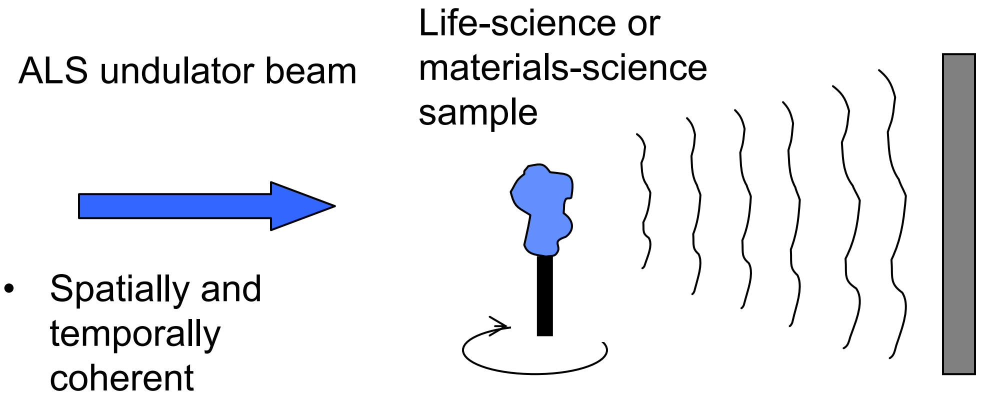


Look like natural filaments!

STXM confirmed that the natural polymers are mostly polysaccharides with some proteins (by doing spectroscopy)

C.S. Chan, G. De Stasio, S.A. Welch, M. Girasole, B.H. Frazer, M.V. Nesterova, S. Fakra, J.F. Banfield, "Microbial Polysaccharides Template Assembly of Nanocrystal Fibers", Science 303, 1656-1658 (2004). LBNL-55375

WHAT IS COHERENT X-RAY DIFFRACTION IMAGING (CXDI) OR LENSLESS IMAGING ?



- Spatially and temporally coherent
- Monochromatic
- 0.5-5 keV energy

- Alignment
- Viewing
- Rotation
- Cryoprotection

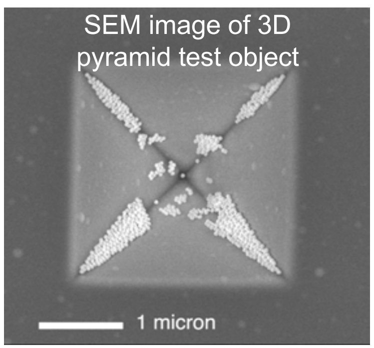
- CCD detector
- Directly records diffraction pattern

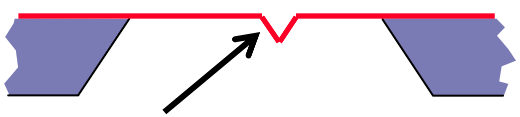
- **To get a 3D image:**
  - **record a tilt series of diffraction patterns**
  - **insert the resulting Fourier amplitudes into a 3D Fourier space**
  - **use a 3D phase retrieval algorithm to get their phases**
  - **get an image by Fourier inversion ("true" 3D imaging)**

Lensless Imaging:

TEST IMAGES IN 3D AND 2D

Pyramid 3D test object

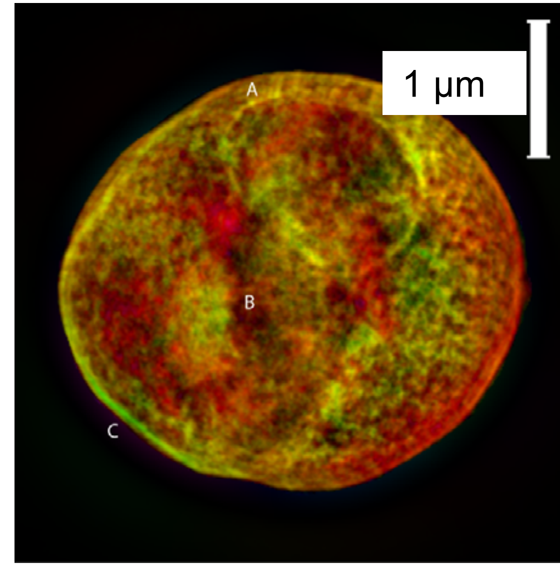




Object mounting on silicon nitride membrane

- Test object of 50 nm gold balls
- Individual gold balls resolved
- Estimated resolution 20 nm
- 130 views -65 to +65°
- Exposure time 10 hours
- X-ray energy = 750 eV
- Object width: about 2μm
- Reconstruction on a Macintosh G5 in about 10 hours

Chapman/Howells/Spence et al - ALS



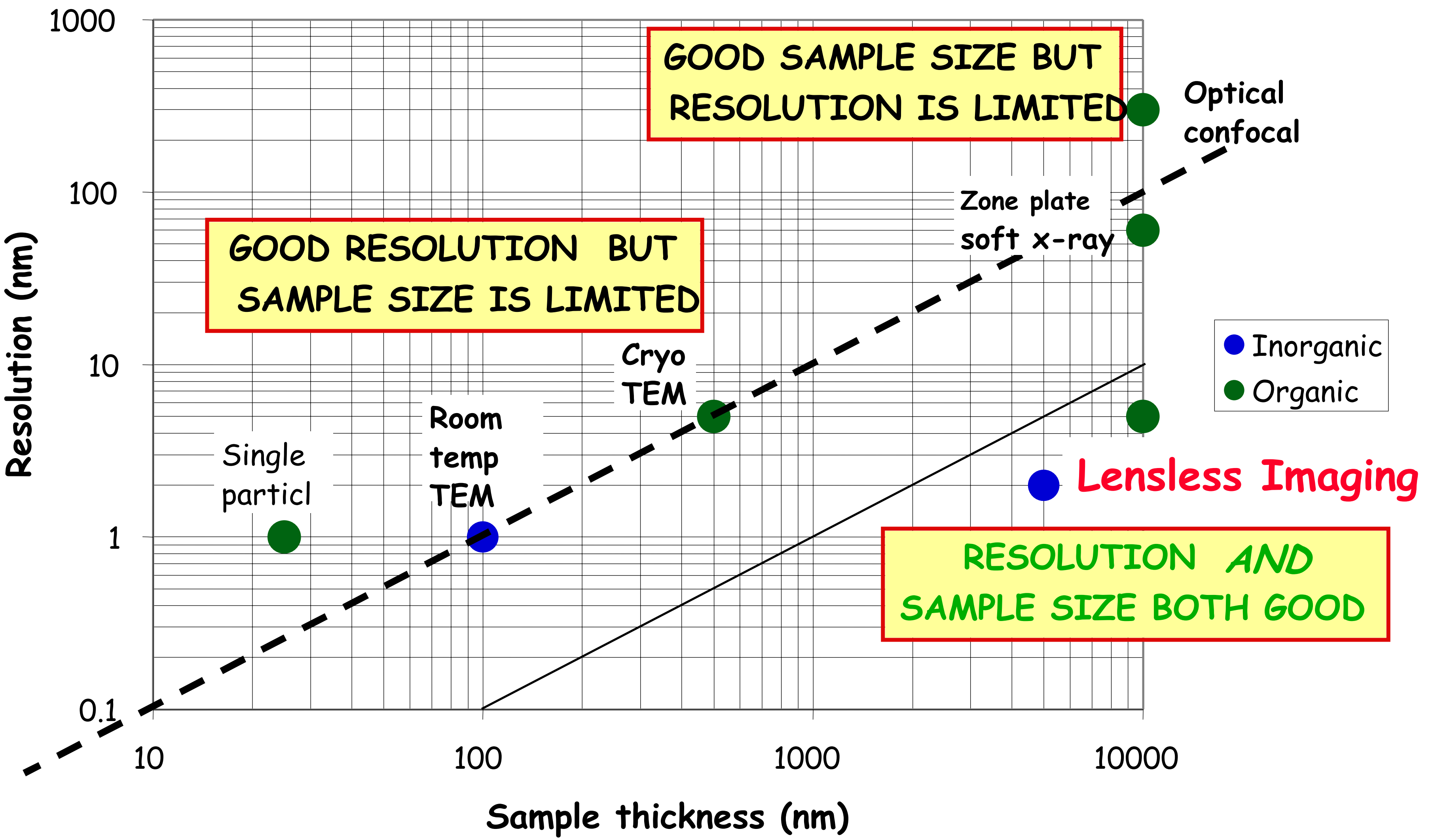
- Reconstructed image of freeze-dried dwarf yeast

  A = nucleus; B = vacuole; C = cell wall
- X-ray energy = 520 eV
- Estimated resolution

  30 nm
- Exposure = 45 sec

Kirz/Jacobsen/Elser/Sayre et al -ALS

3D MICROSCOPES: RESOLUTION AND SAMPLE-THICKNESS LIMITS



Unique features of scattering in the soft x-ray region.

Soft x-ray resonances bring new contrast mechanisms:
- molecular bond sensitivity
- elemental sensitivity

Extremely sensitive to small sample volumes
- cross section $\propto \lambda^3$
- ideal for nanoscience
- coherent power $\propto \lambda^2$

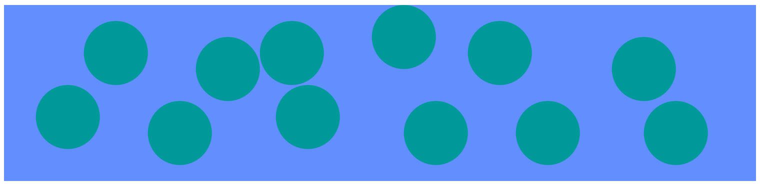
Low *q* scattering at higher angles:
- wide range structure in 3*mm* – 1*nm*
- "incoherent" & "coherent"

Unique capabilities for
spectroscopy
microscopy
time-resolved dynamic studies

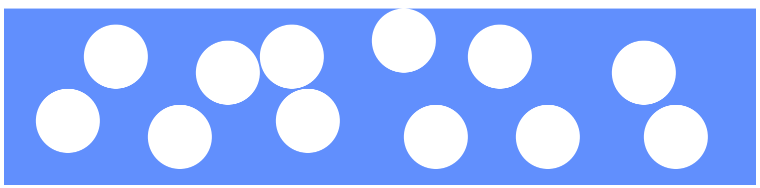
- Spectro-microscopy of nano materials
- Inhomogenities of correlated systems (charge/orbital order)

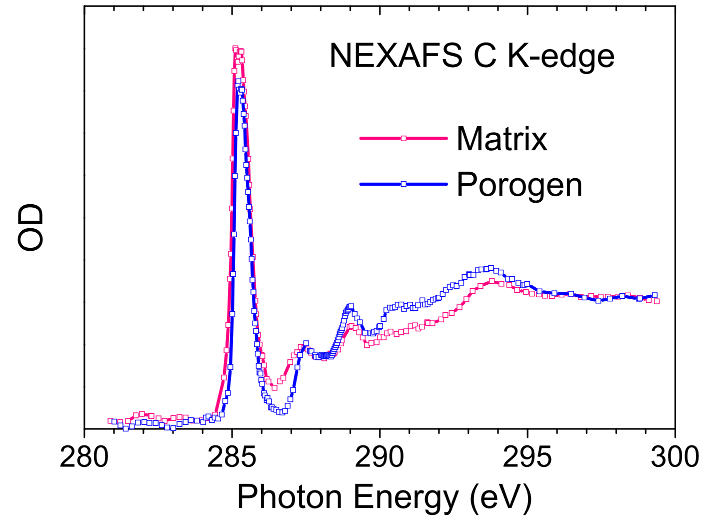
Porous low-K dielectric films via templating process

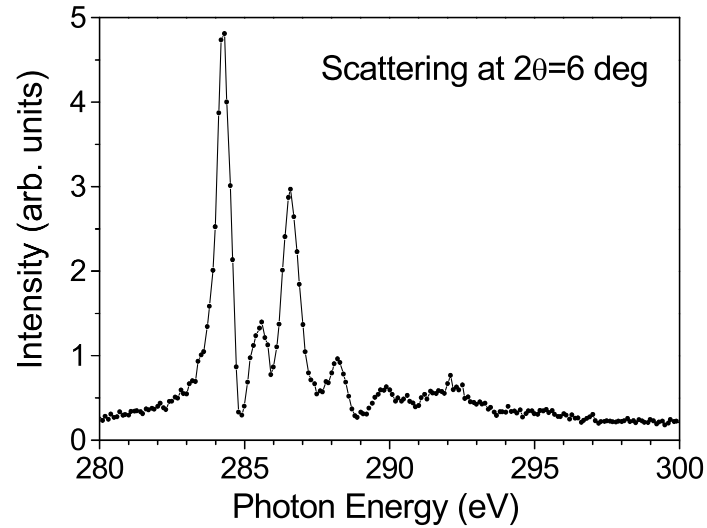
porogen in matrix



after porogen removal





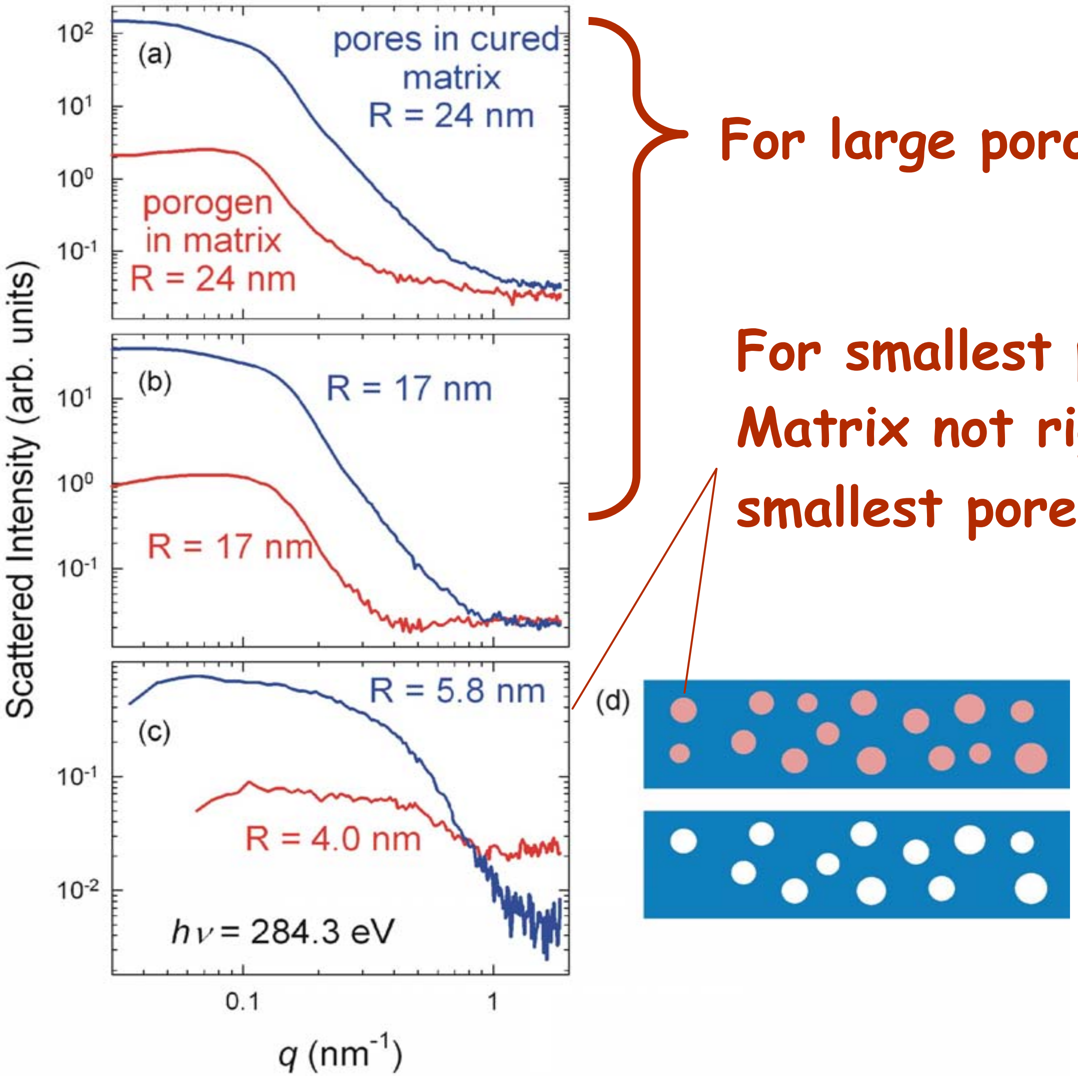


Lower limit to pore size?

Processing effects?

Mitchel, Kortright et al (unpublished)

Scattering pre- and post-processing to remove porogen phase particles.

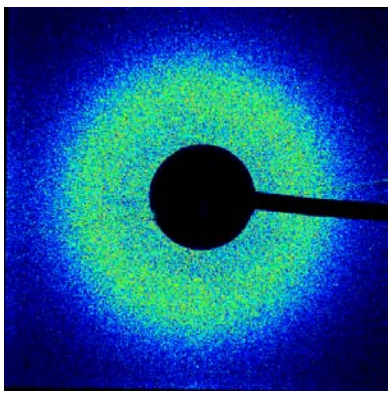


For large porogens, $R_{pore} = R_{porogen}$.

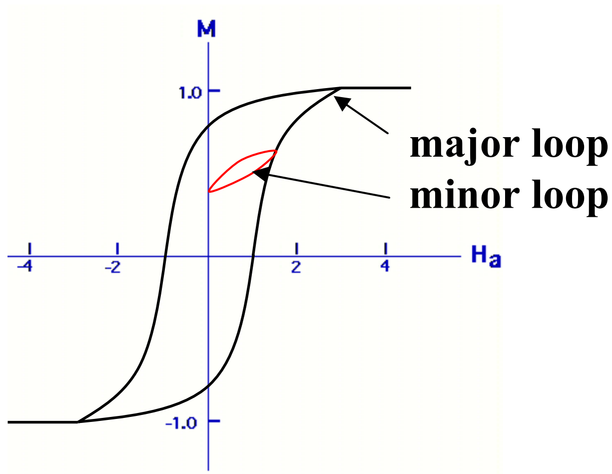
For smallest porogen, $R_{pore} > R_{porogen}$. Matrix not rigid enough to sustain smallest pores.

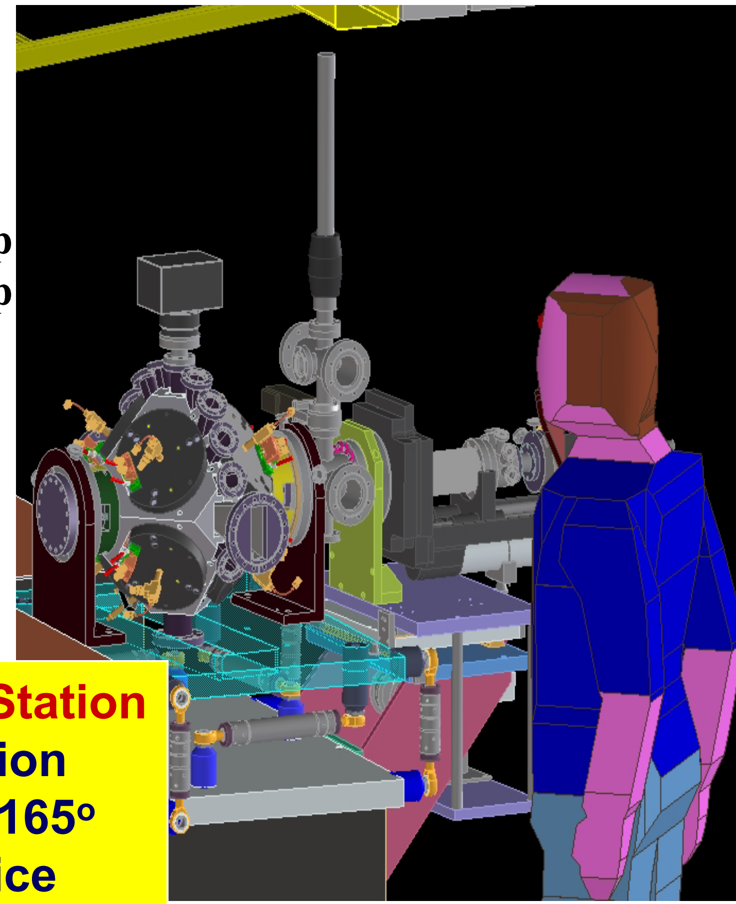
Coherent soft-Xray Scattering – Dynamical Studies !!

Soft x-rays: - More coherent flux - Scales like λ^2 X brigtness
- High sensitivity for 3d metals: Resonant 2p-3d transition-
- Dynamical studies: Time resolution: > ms - 5ns) limited by time correlator



Speckle-diffraction Pattern through a Co:Pt film.

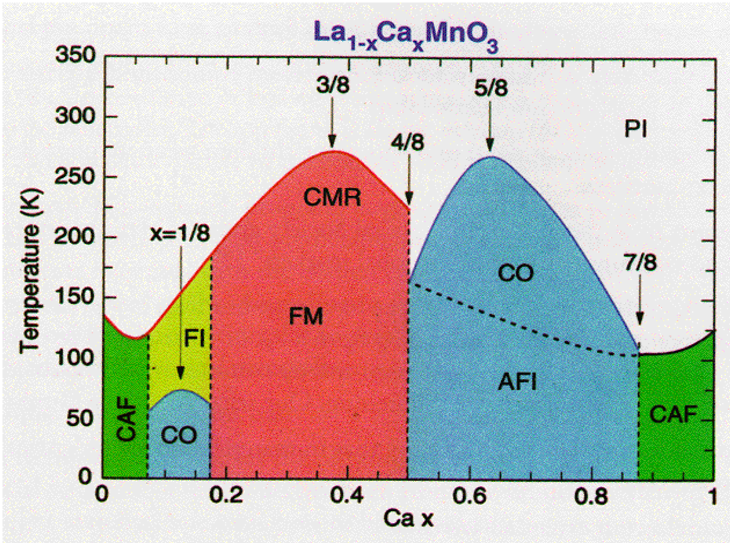




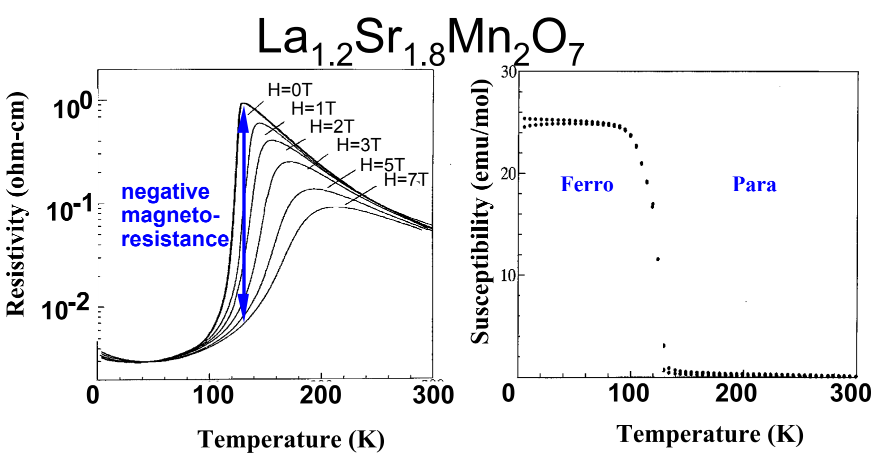
Coherent Soft X-ray Magnetic Scattering End Station
- **Applied field to 0.52 T of arbitrary orientation**
- **'Continuous' scattering angle from 0° to ~ 165°**
- **Functional prototype for higher field device**

Colossal Magnetoresistance (CMR) Effect

Novel Electronic Phases



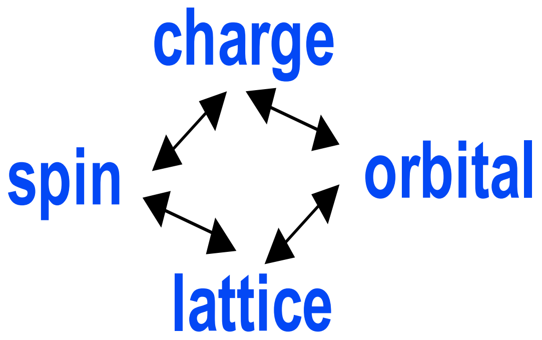
CO :	Charge Order (Stripes)
FI :	Ferromagnetic Insulator
AFI :	Antiferro. Insulator
CAF :	Canted AFM Insulator
CMR :	Colossal MagnetoResis.



- O **Large drop of resistivity upon relatively small magnetic fields**
- O **Para → Ferromagnetism**
- O **Most dramatic on the insulating phase (short range orbital order)**

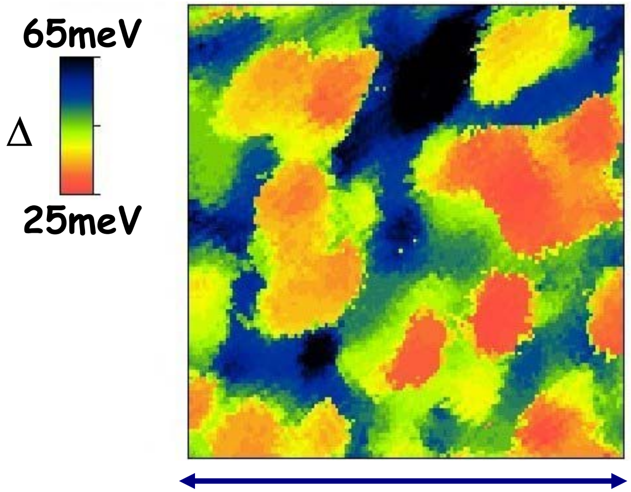
Manganites Exhibit Interplay of Charge, Spin, lattice and Orbital degrees of freedom

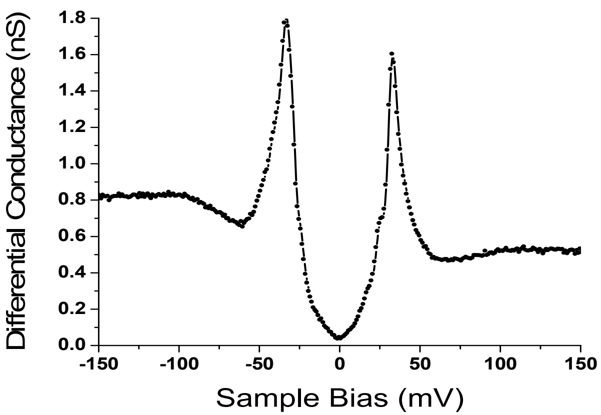
Interacting **degrees of freedom (complex electron systems)**



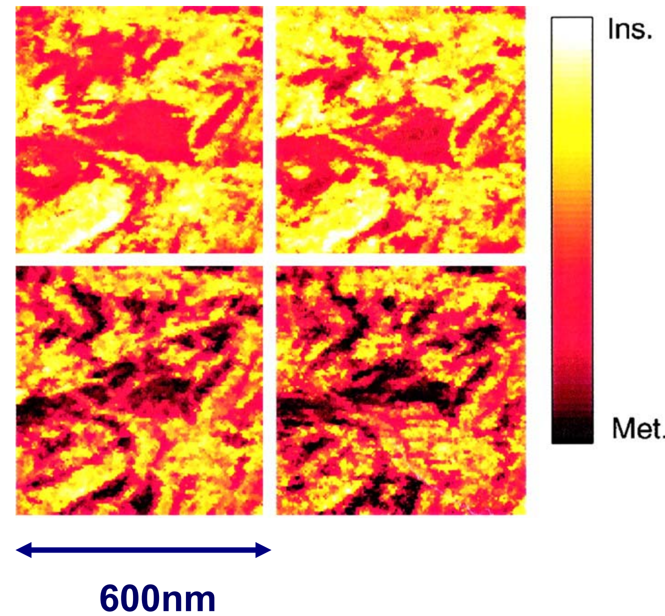
Competition among many *Energy* and *Length* scales
Determine the physics of these systems

Nanoscale electronic disorder in Correlated Systems (STM)





Spatial distribution of energy gap (Δ) in Bi2212 (High Tc materials)

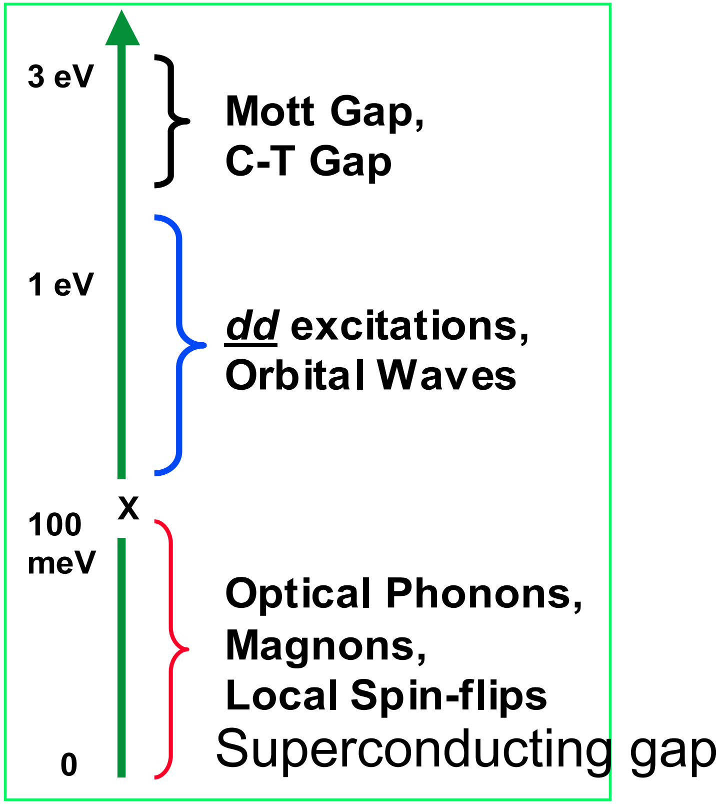


Metal-Insulator transitions in the CMR material La Ca MnO_3

Energy scale: ~10meV
Length scale: 2 - 1000nm

Ch. Renner et al, Nature, 416, 518 (2002)

Energy scales of various excitations



- Superconducting gap: ~ 1-10meV
- Optical Phonons: ~ 40 - 70 meV
- Magnons: ~ 10 meV - 40 meV
- Orbital fluctuations (originated from optically forbidden d-d excitations): ~ 100 meV- 1.5 eV

Soft x-ray resonances (3p -> 3d) provide a very sensitive channels of excitations
MERLIN (<1meV res. beamline: Spectrograph ~3 meV)

Spectroscopies of Correlated Electrons

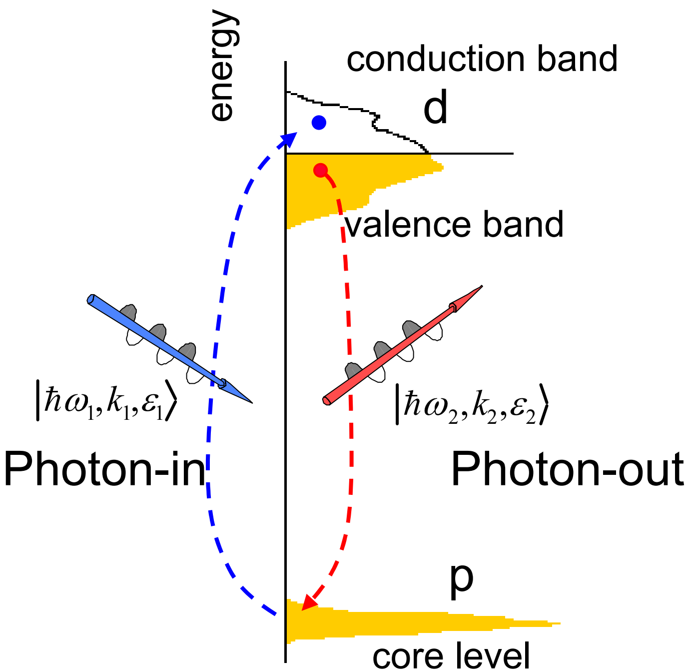
Techniques of choice:

1. Angle resolved phtotemission (ARPES) :
   Single-particle spectrum $A(k,\omega)$

2. Inelastic Neutron Scattering (INS) :
   (neutrons carry magnetic moment)
   Spin fluctuation spectrum $S(q,\omega)$

3. Inelastic x-ray scattering (IXS) :
   New info on the Charge Channel : $N(q,\omega)$
   This extra experimental info can help understand correlated systems

Resonant Inelastic soft X-ray Scattering (*Raman* Spectroscopy with finite q)



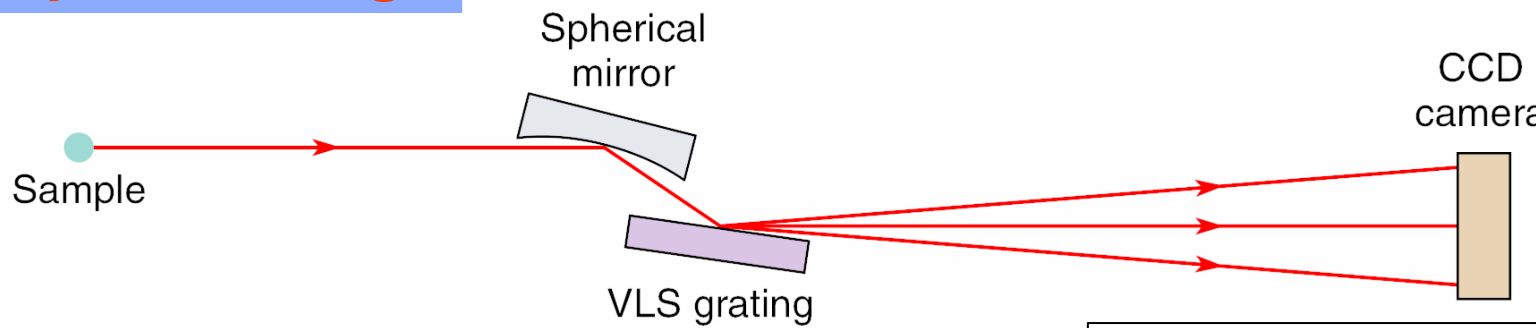
Energy loss: $\omega = \omega_2 - \omega_1$
Momentum transfer: $q = k_2 - k_1$
Resonance: $\omega_1 \sim \omega_{edge}$

Why???

- Can be applied in the presence of **magnetic/electric field**
- **Bulk sensitive** probe for studying unoccupied electronic states
- Optically forbidden **d-d** excitation
- Finite **q** transfer allows to study indirect Mott gap
- Couples to **charge density** directly (Neutrons couples to spin).
- Energy Resolution **not** limited by the **core hole lifetime**: achieve $k_B T$ resolution

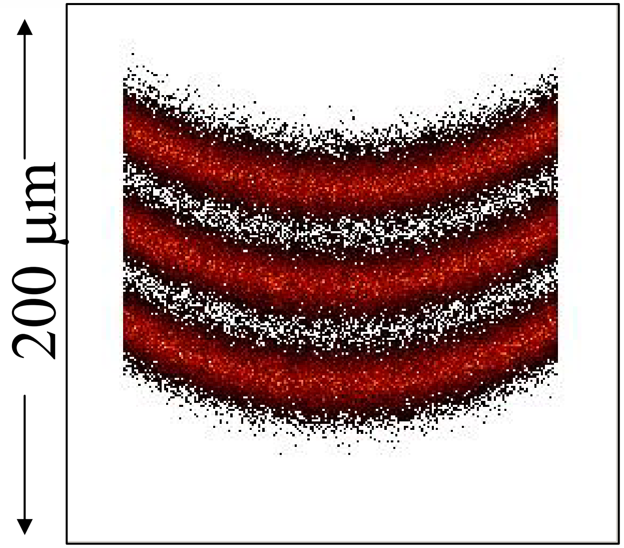
meV Resolution VLS Spectrograph

Optical Design



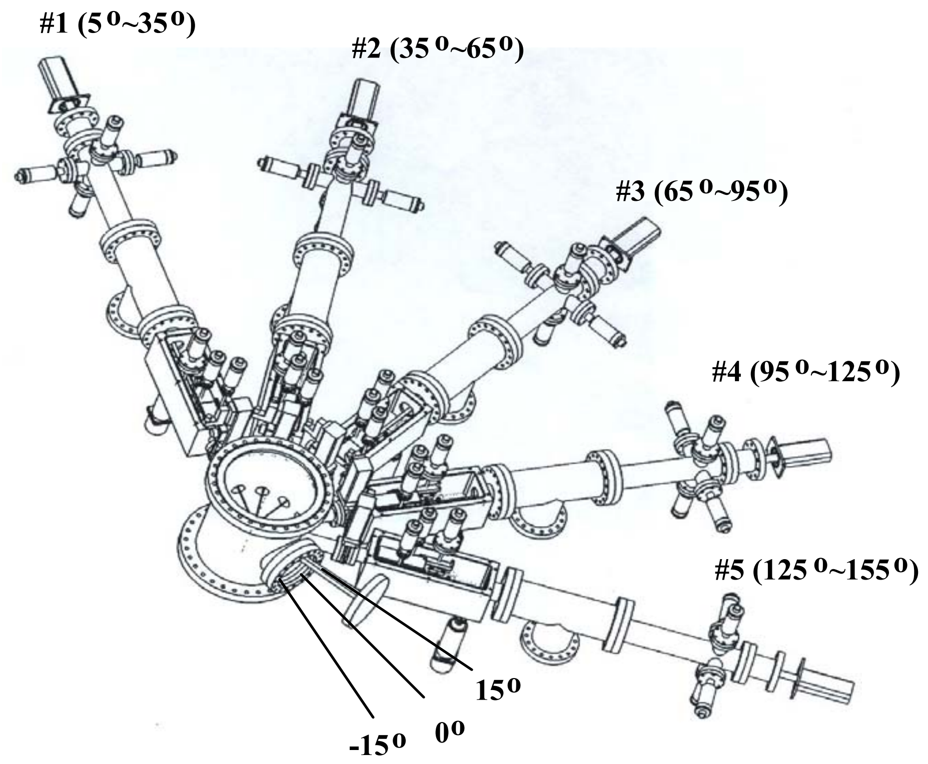
Ray Traces

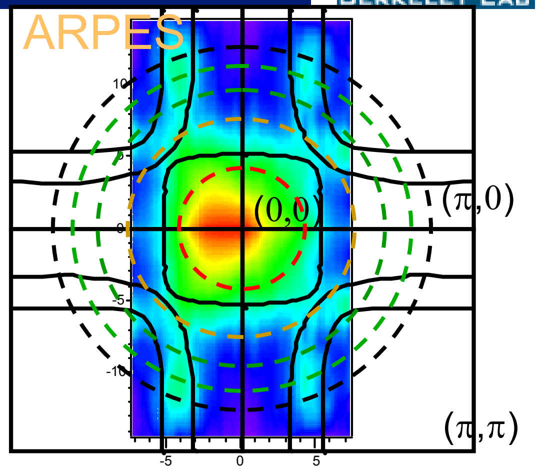
- Calculated/measured Resolution
  3 meV (high efficiency)
- Overall length = 2 meters.
- Spectrograph for Merlin beamline
  (completion end of 2006)
- Early experiments on bl 12
  (starting in July, 2005)

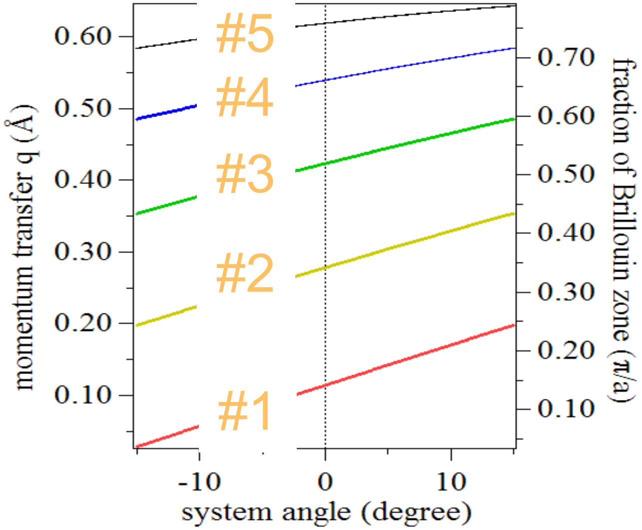


$h\nu = 49\ eV \pm 5meV$

Momentum-Resolved Soft X-ray Inelastic Scattering

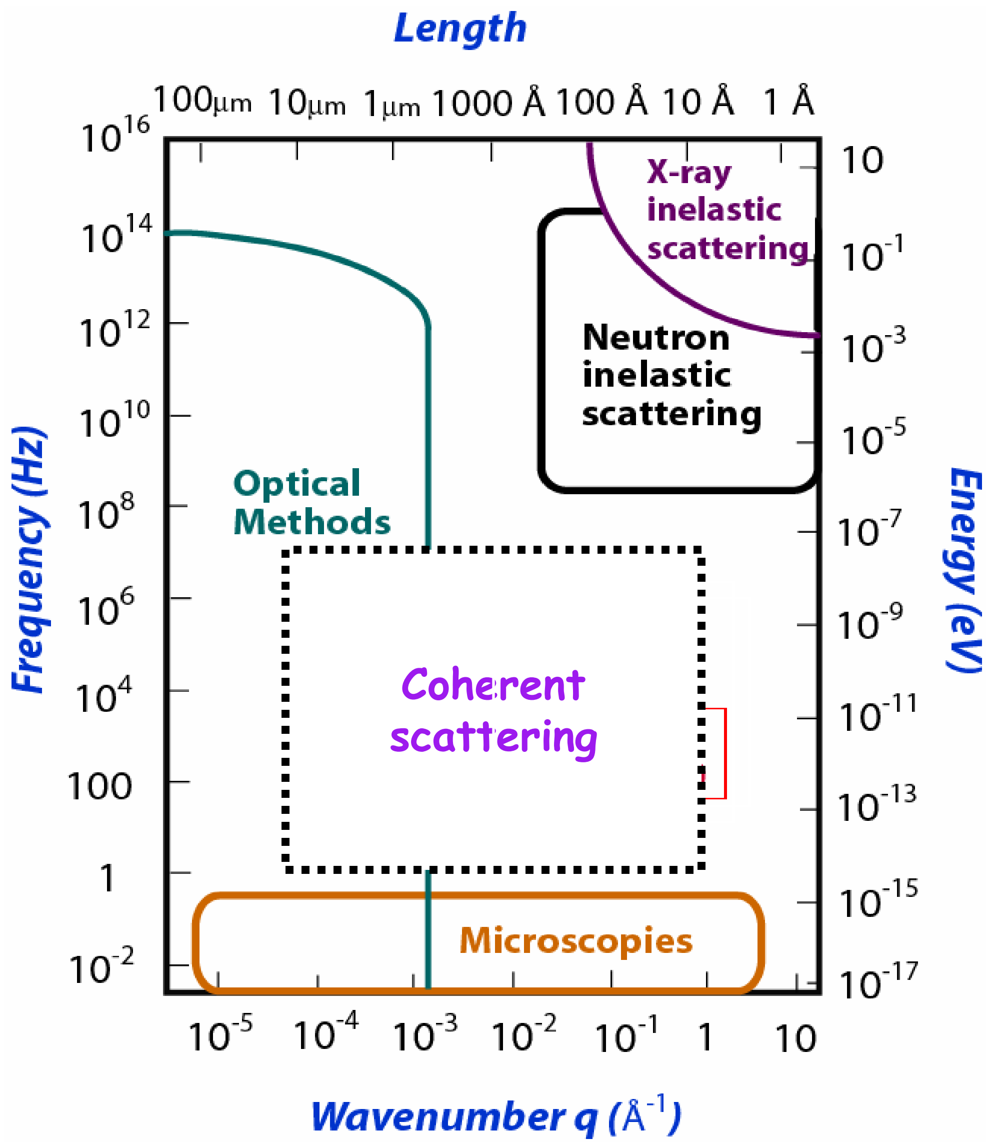






By combining the rotation of chamber and 5 mounting ports, one is able to perform momentum-resolved RIXS; need Resolving Power ~ 100,000 – QERLIN !!

Spatial and temporal frequency sensitivities of various techniques



Concluding remarks

- In situ (real conditions) studies. Photon-in photon-out studies, Ambient pressure photoemission.

- Single nanoparticle imaging and spectroscopy. STXM

- Lensless Imaging: Bulk 3D images, resolution ~ 2 λ (inorganic ~ 2nm, Organic ~ 5nm (radiation limit)
  think of combining with atomic resolution protein
  Crystallography.

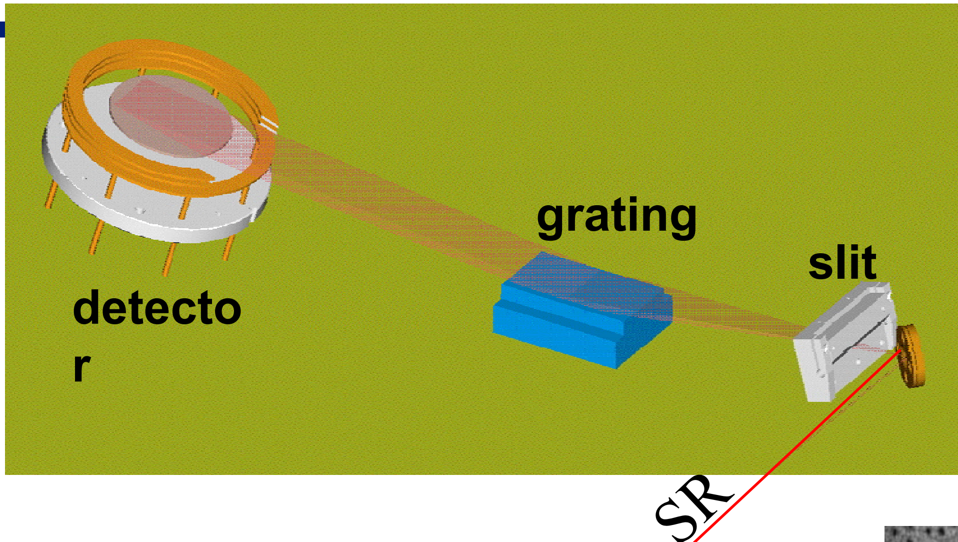
- Dynamic coherent scattering. (ms – 5 ns, limited by time correlator).

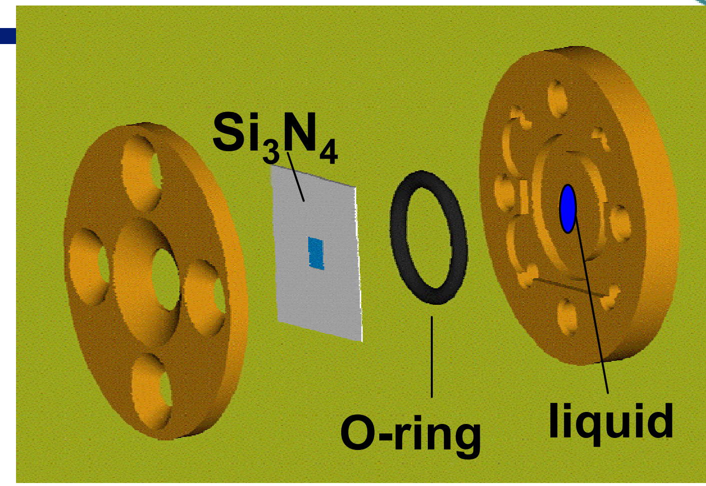
- Soft x-ray scattering: Provide new contrast mechanism for imaging. Imaging with spectroscopy.

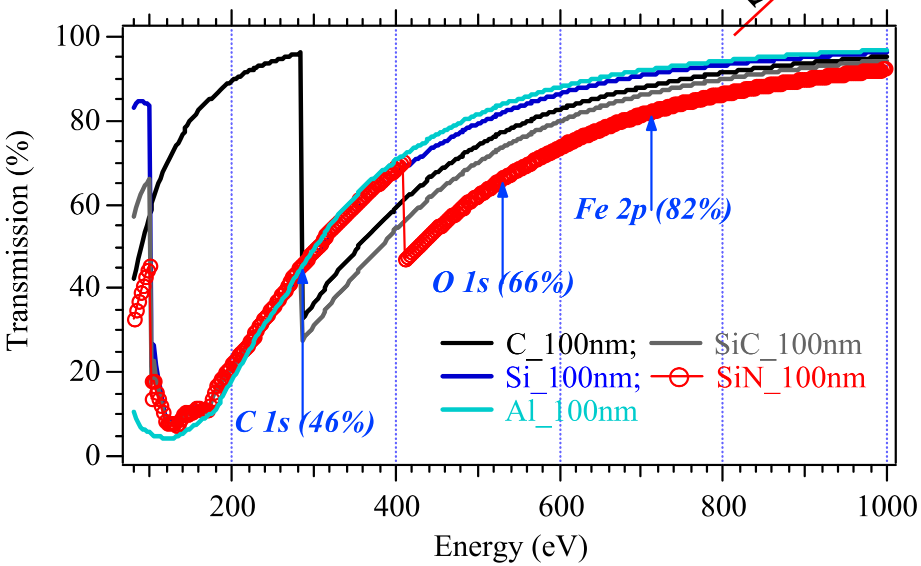
Acknowledgement

- o **Inelastic Scattering:** Yi-De Chuang, Jinghua Guo; Jonathan Denlinger, (LBNL, ALS), Eric Guillikson, Phil Batson (LBNL)
- o **Lensless Imaging:** Janos Kirtz, Malcolm Howells(LBNL, ALS)
- o **Nanoscience characterisation:** Franz Himpsel (univ of Wisconsin), Lou Terminello (LLNL)
- o **scattering:** Jeff Kortright (LBNL), Mitchel (Dow chemical), Ade (NCU)
- o **Coherent Scattering:** Steve Kevan (univ of Oregon)

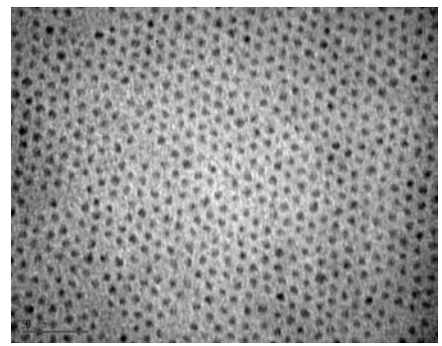
Liquid Cell - Static

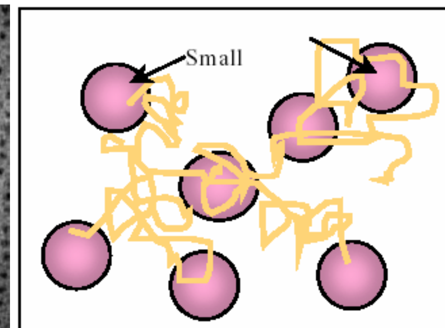






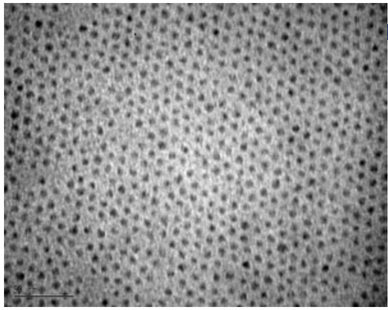
100nm Si_3N_4, ~4 μl liquid volume, 66% transmission @O1s, vacuum pressure < 1 x 10^{-9} Torr

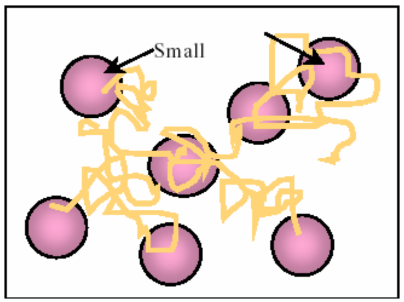


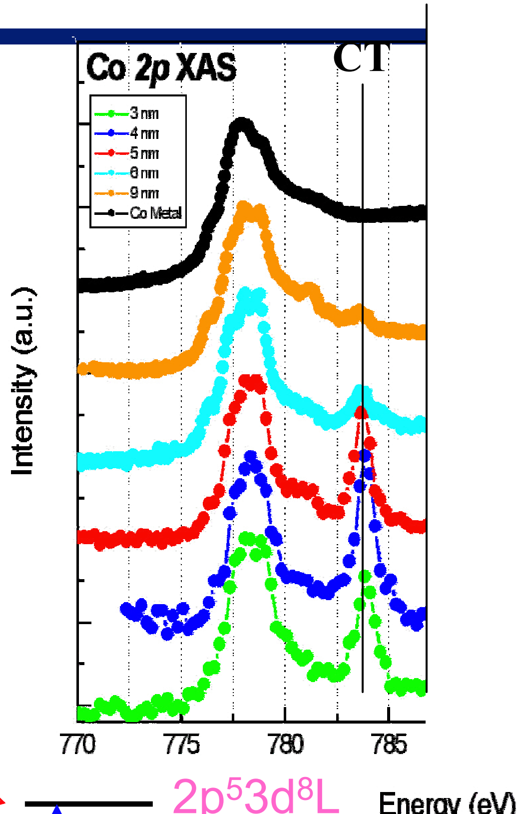


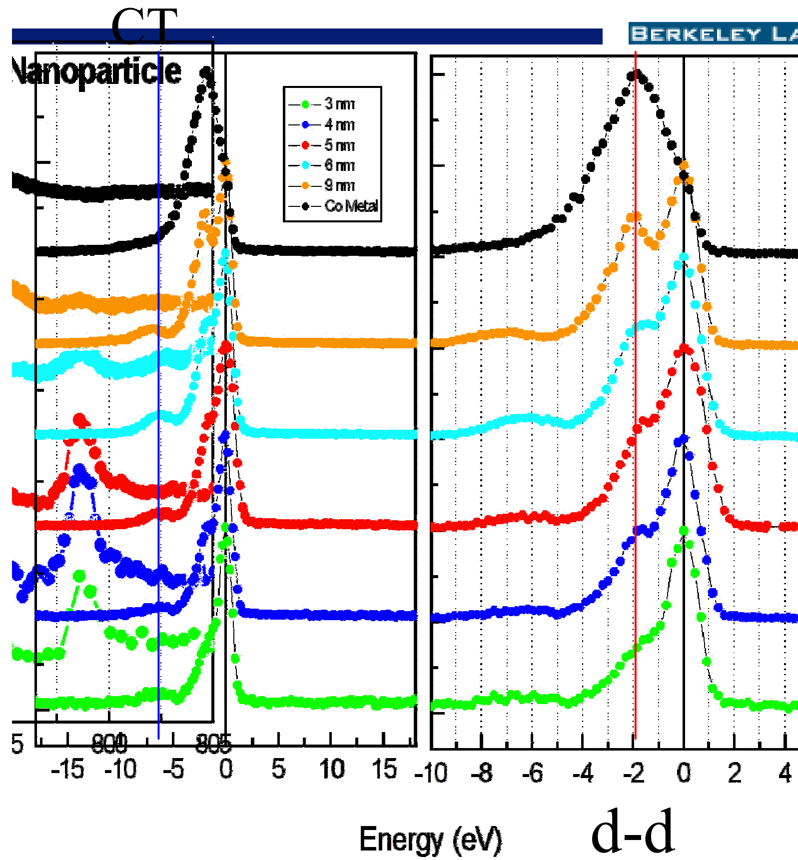
- **Ligand-stabilized Co nanoparticles**
- **Ligand material:** *Oleic Acid, $C_{18}H_{34}O_2[CH_3(CH_2)_7CH{:}CH(CH_2)_7CO_2H]$*
- **Solvent Solution:** *Dichlorobenzene, $C_6H_4Cl_2$*
- **Size (Measured using TEM):** *3, 4, 5, 6, 9 nm*

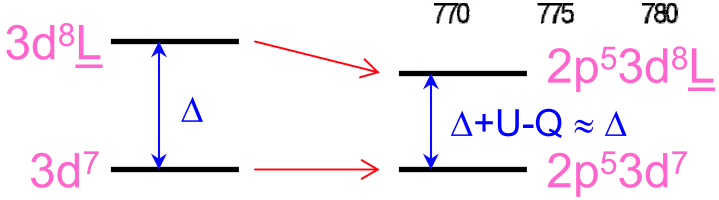
In-situ analysis of Co nanoclusters in solution









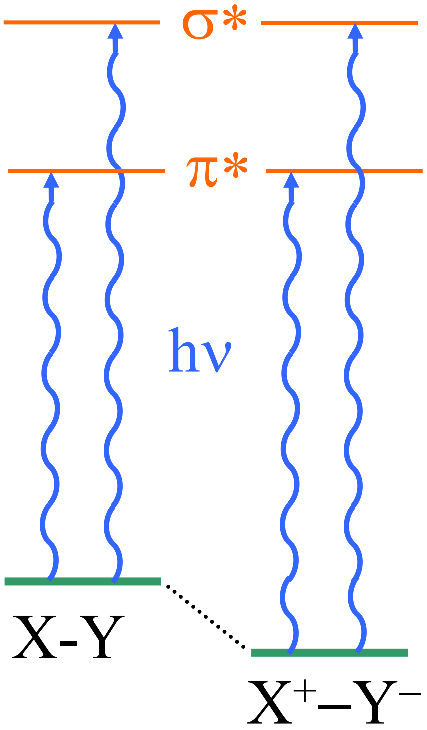


- **Ligand-stabilized Co nanoparticles**
- **Ligand material:** *Oleic Acid, $C_{18}H_{34}O_2$ [$CH_3(CH_2)_7CH{:}CH(CH_2)_7CO_2H$]*
- **Solvent Solution:** *Dichlorobenzene, $C_6H_4Cl_2$*
- **Size (Measured using TEM):** *3 nm, 4 nm, 5 nm, 6 nm, 9 nm*

$$I_{d\text{-}d} \sim N_{bulk}/N_{surface}$$

Molecular Foundry (P. Alivisatos & M. Salmeron) & ALS (J. Guo)

Nanoscience: Electronic Structure Determination - Techniques of choice



Requirements ?

"*in situ, real time*" studies of:

- Valence orbital (bonding, energy gap)
- Core level (charge transfer, elemental/chemical specificity)

How ?

•Unoccupied bands:

Absorption Spectroscopy

•Occupied bands:

Emission Spectroscopy and
Photoelectron Spectroscopy

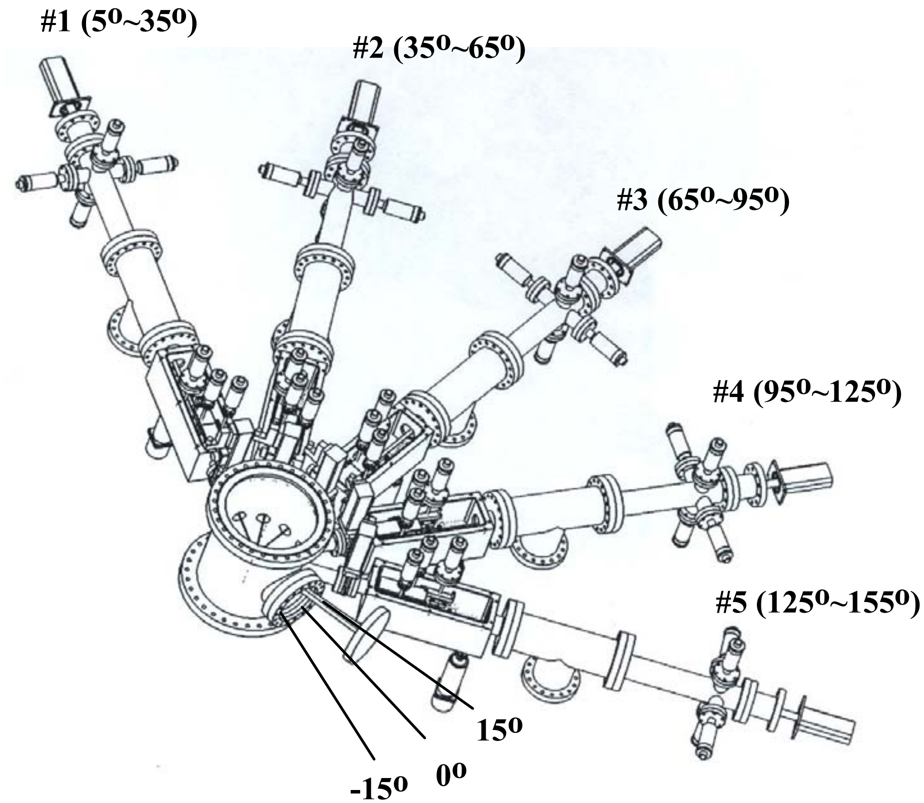
•Orientation of molecules on surfaces:

Polarization dependence studies

Requires close coupling between theory and experiment

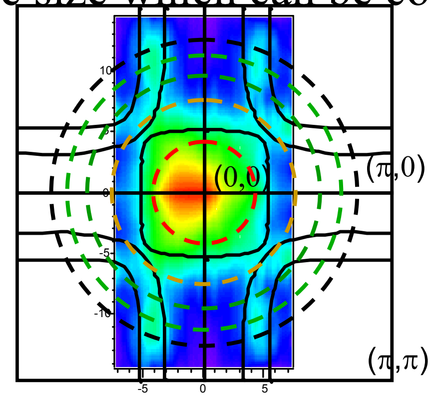
Resonant Inelastic soft X-ray Scattering

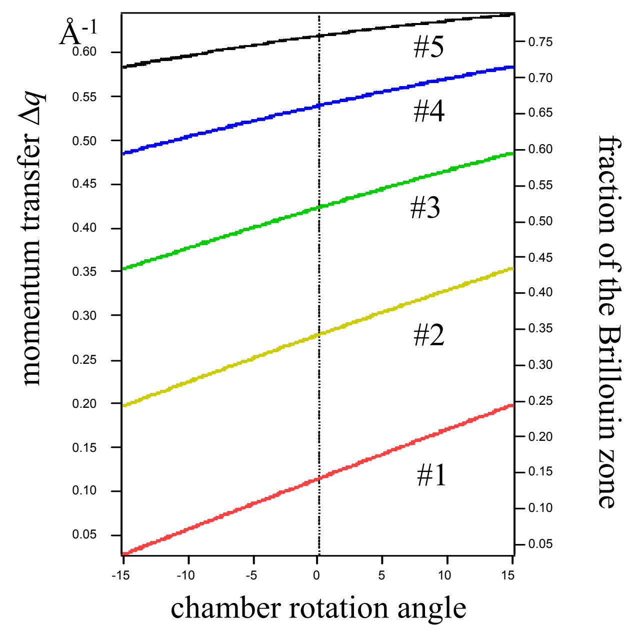
Calculation based on photon energy of 650eV and 3.85 Å lattice constant



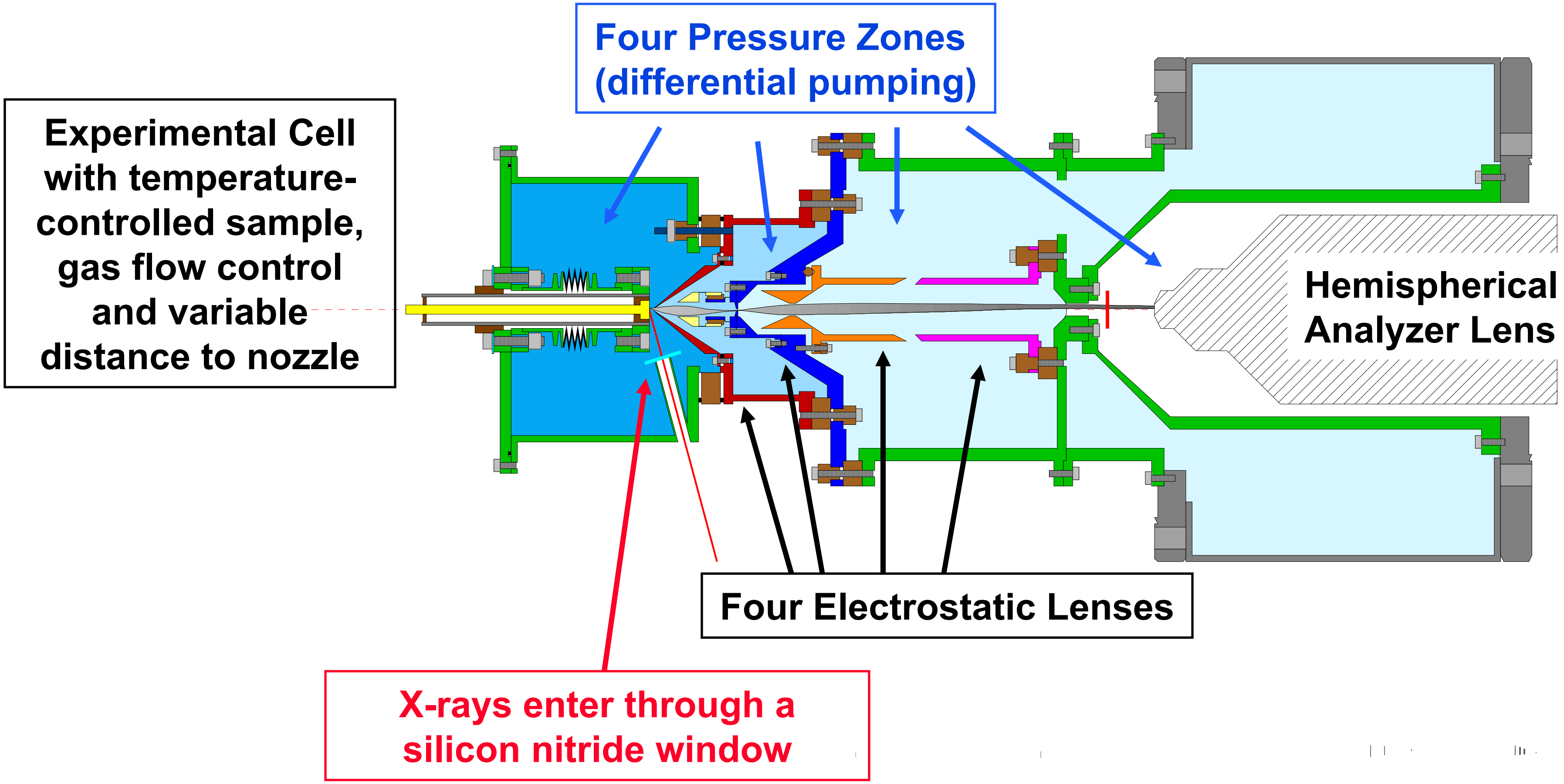
Five spectrometers with 30° rotations can cover most of the Brillouin zone

Brillouin zone size which can be covered by this spectrometer



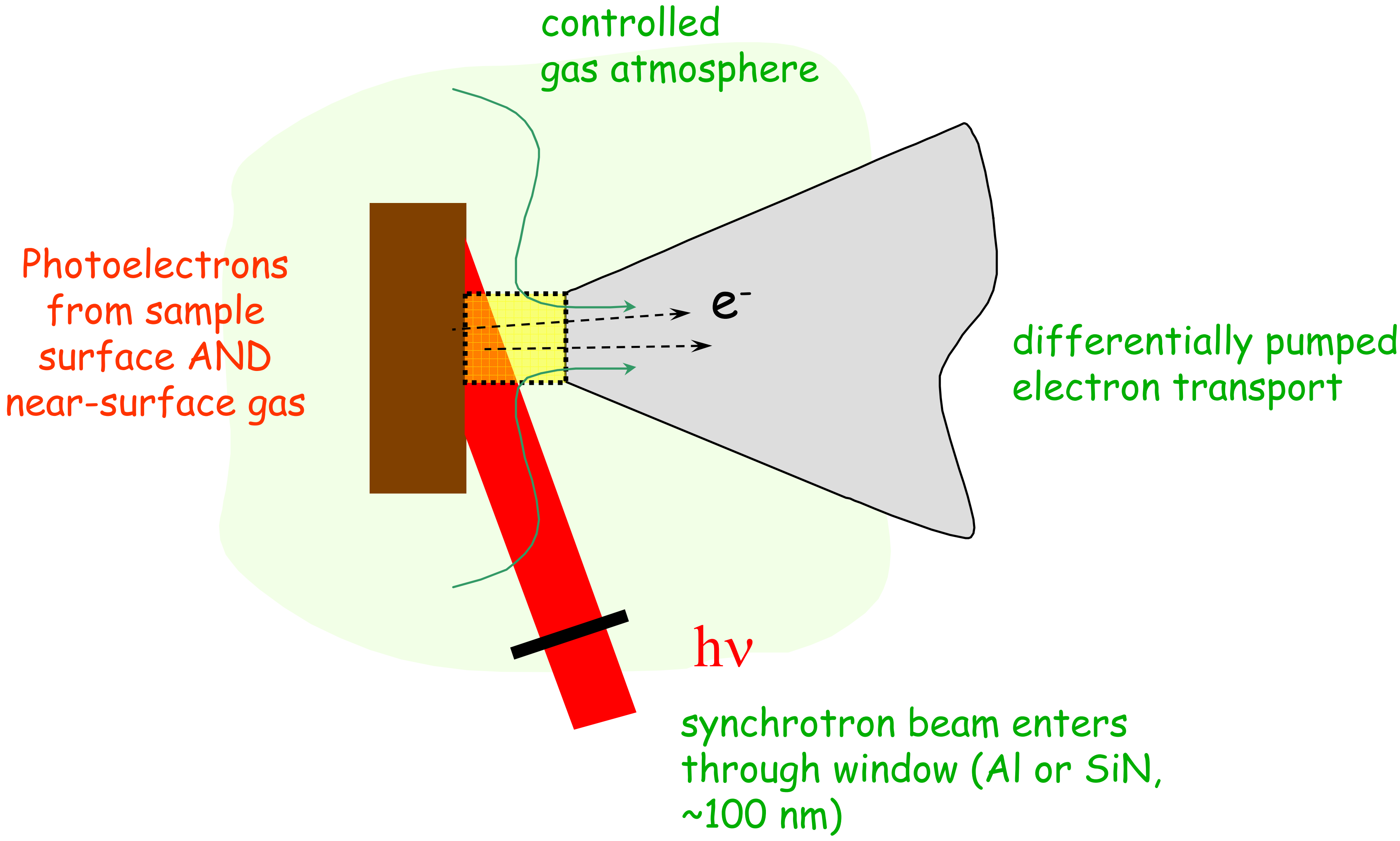


High Pressure Transfer Lens - Schematic



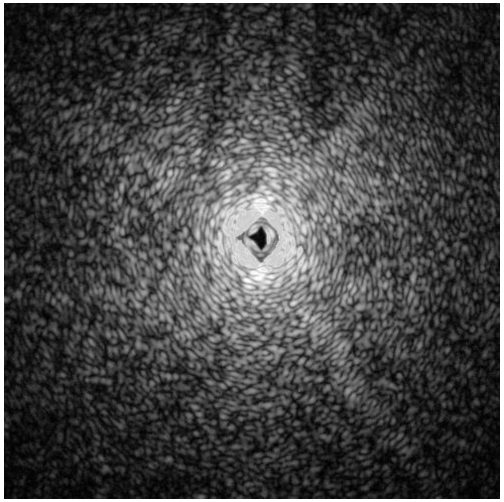
D.F. Ogletree, H. Bluhm, Ch. Fadley, Z. Hussain, M. Salmeron, Materials Sciences Division and Advanced Light Source, LBNL.

Ambient pressure soft x-ray spectroscopy: Concept



ALS BEAM LINE 9.0.1: Lensless Imaging

Diffraction station built by SUNY/BNL group

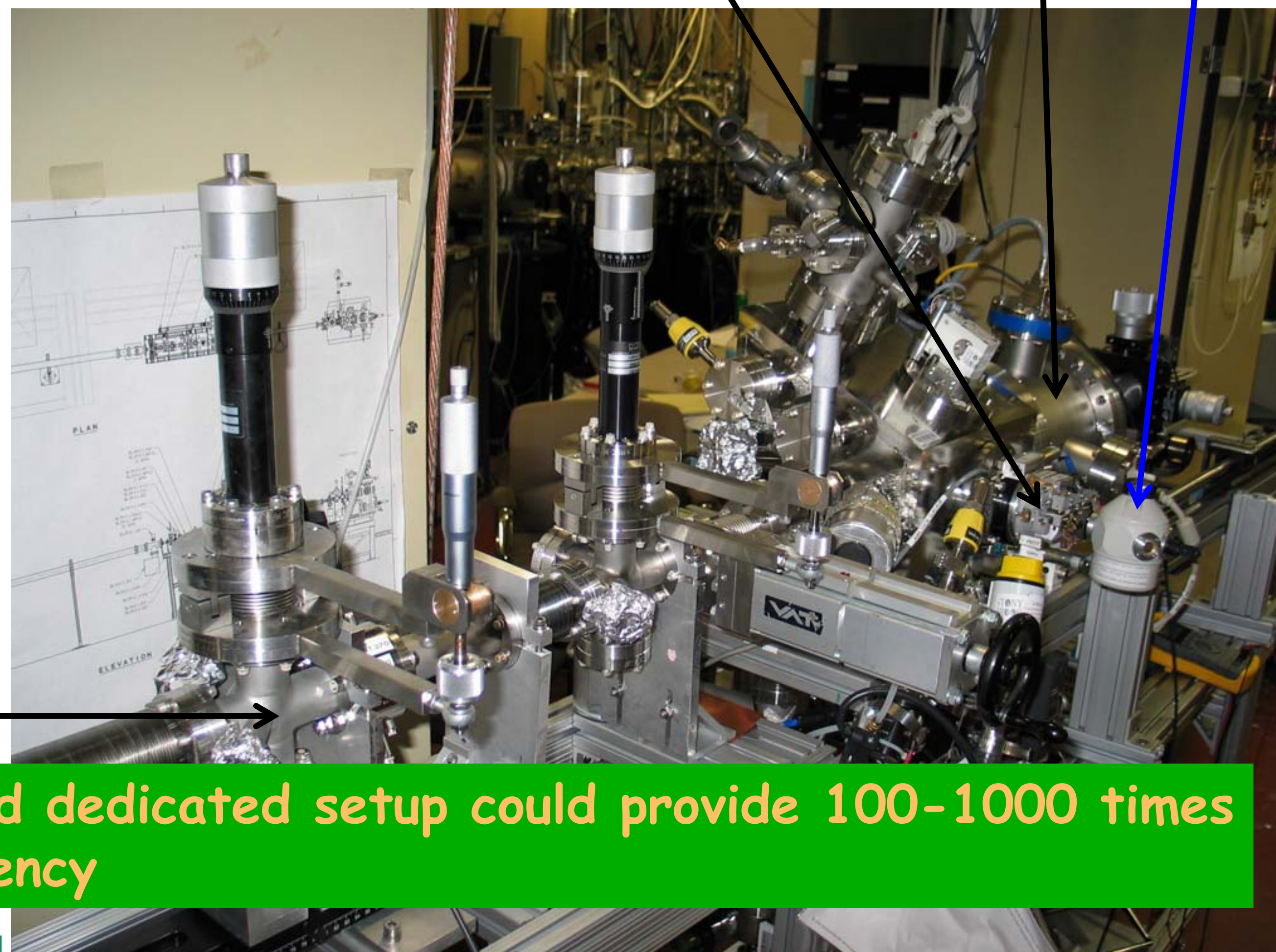


Diffraction pattern of freeze-dried yeast taken by SUNY gp

Cryo holder

CCD detector chamber

Sample manipulator

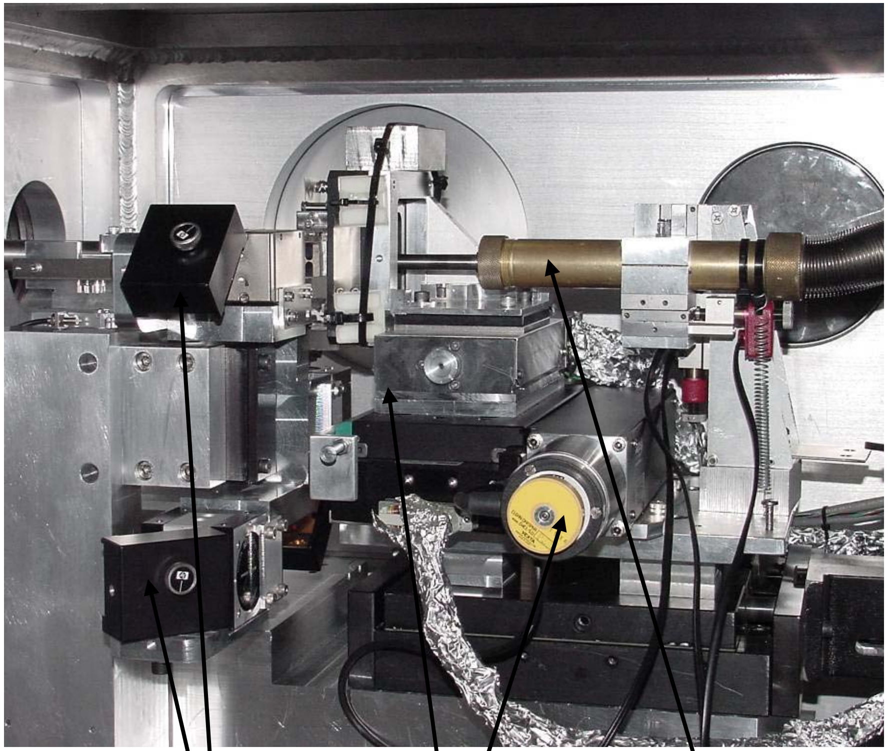


Monochromator zone plate

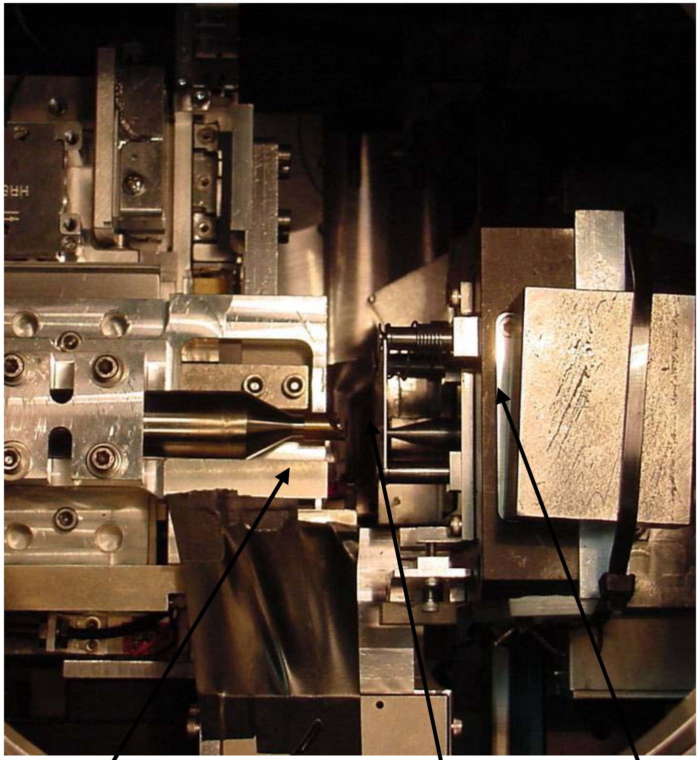
Optimized and dedicated setup could provide 100-1000 times better efficiency

Scanning Transmission X-ray Microscope (STXM) 11.0.2

Side view

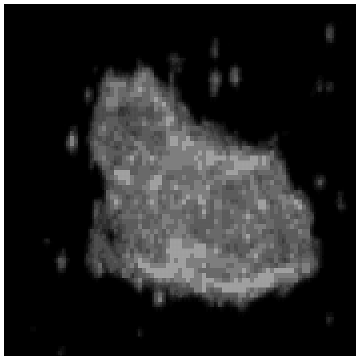


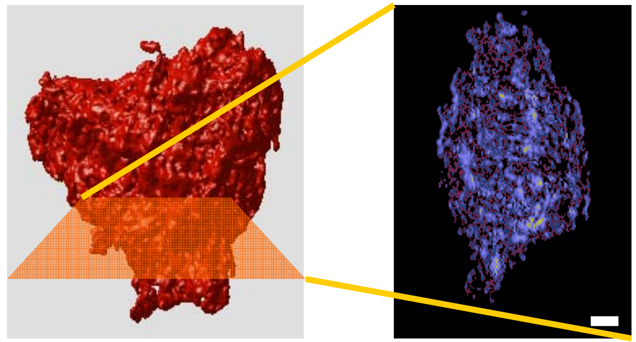
Top view



Imaging of tantalum oxide aerogel

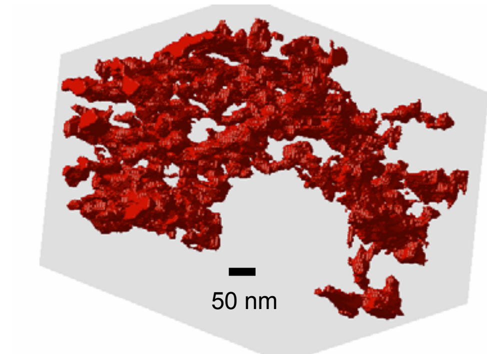
1 µm





3D isosurface

Cross-section (bar = 200nm)

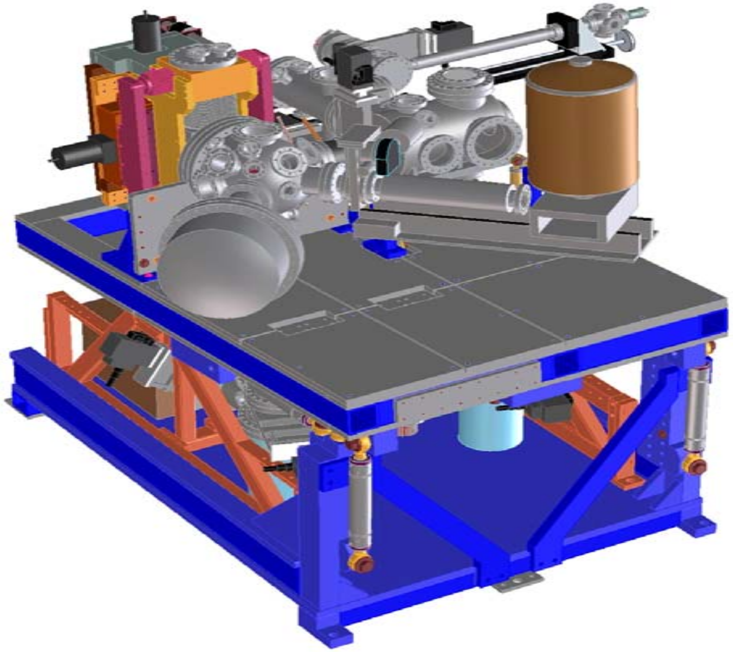


500 nm cube
res'n 20-30 nm

- 2-micron-wide particle of tantalum oxide aerogel
- Density about 0.1 gm/cm^3 which is about 1.2% of bulk density
- Applications for NIF target, hydrogen storage

Chapman/Howells/Spence et al - ALS

Nanoscience Characterization Facility @ ALS (bl 8.0)



System is being commissioned

"User-friendly for nanostructure characterization endstation" proposal funded by DOE (U. Wisconsin-Madison, F. Himpsel et al)

(1) Micro-focus (~10 μm) beam spot
(2) Efficient fluorecence yield detectors for XAS
(3) Emission Spectrograph (VLS)
(4) Photoemission (Scienta 100)