



# Scientific Opportunities with Synchrotron Radiation

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**Scientific Support Group, Leader  
Advanced Light Source  
Lawrence Berkeley National Laboratory**

# Science with Synchrotron Radiation



- **Techniques ?**

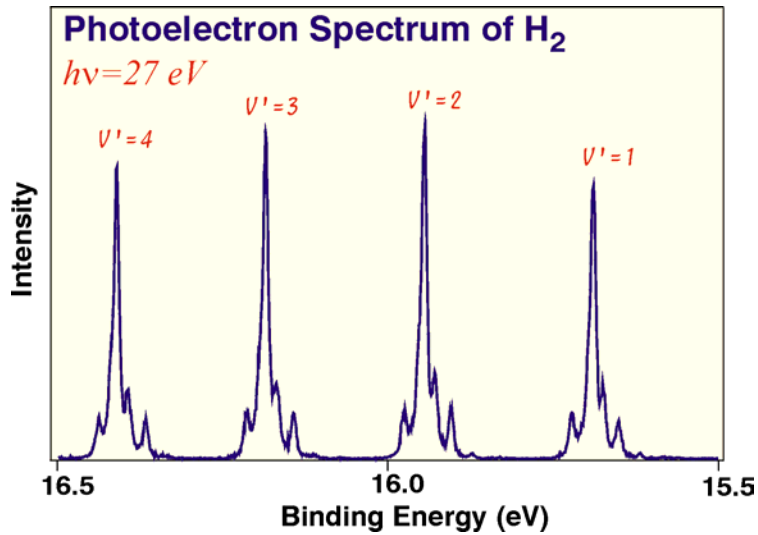
100 years of Physics :

Story of Einsteins' Photoelectric effect

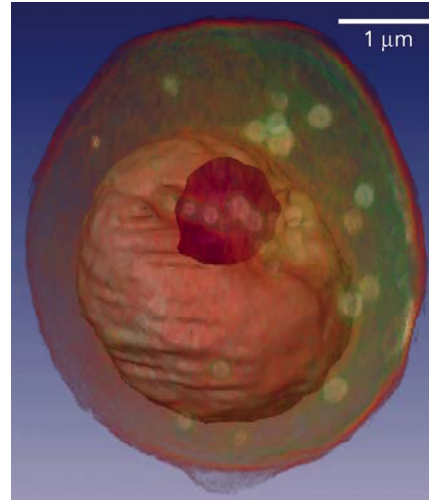
- **Applications in the field of:**

- Nano science (quantum confinement, dynamics of self assembly, in-situ studies)
- Strongly correlated systems (high T<sub>c</sub> superconductor, CMR)
- Magnetism (magnetic circular dichroism, exchange bias)
- Energy (**solar energy**, combustion dynamics, electrochemical cell, Hydrogen storage)
- Environment (in-situ elemental/chemical identification of contaminants, imaging)
- Catalysis (tailoring of catalysts, surface characterization)
- Medical Science (in-situ imaging, macromolecular crystallography)

# WHAT DOES SR BRIGHTNESS BUY YOU?

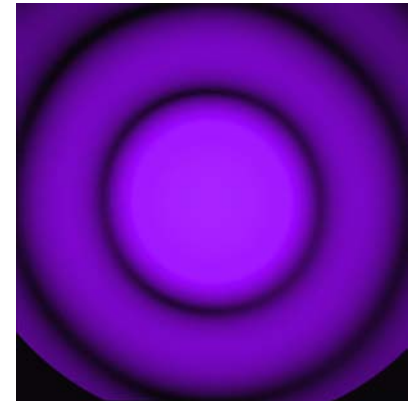


Very High Energy Resolution



Tomographic reconstruction of *Saccharomyces cerevisiae* (yeast).

Submicron Spatial Resolution



Coherence

# IMPORTANCE FOR MATERIALS AND CHEMICAL SCIENCES



Ultimately, the

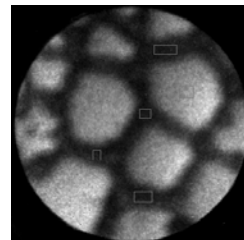
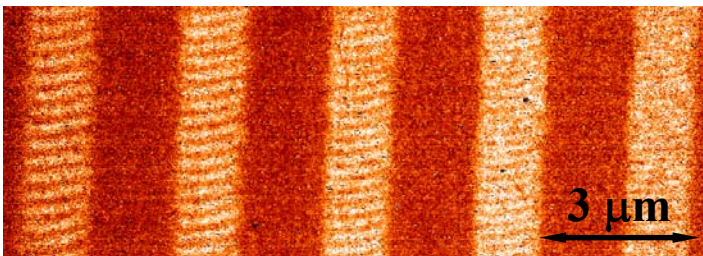
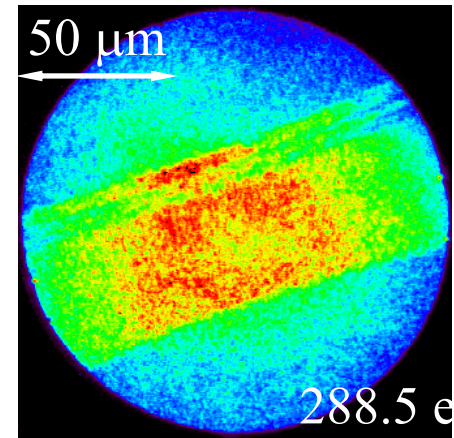
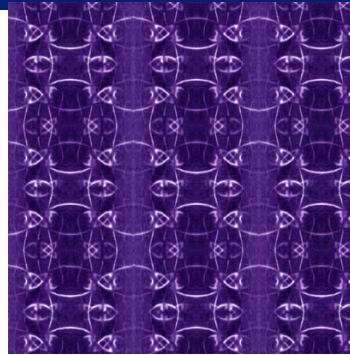
**electronic,**

**magnetic,**

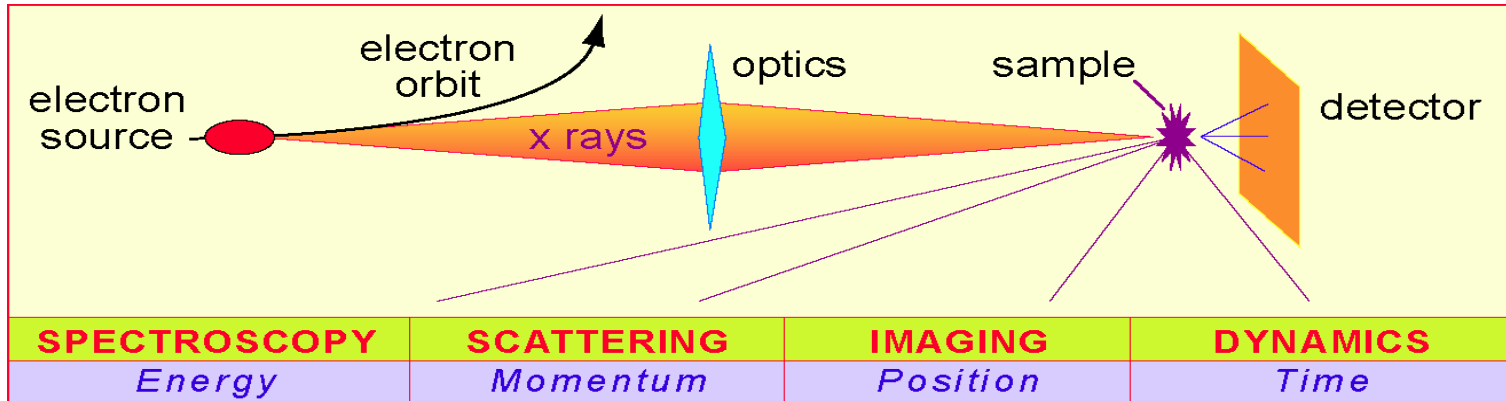
**chemical,**

**mechanical,**

**optical, thermal, and structural properties of matter depend on the behavior of electrons.**



# Techniques of SR



The fundamental parameters necessary for perception of physical world:

- Energy (spectroscopy, state of matter)
- Momentum (scattering)
- Position (imaging, spatial distribution)
- Time (dynamics)



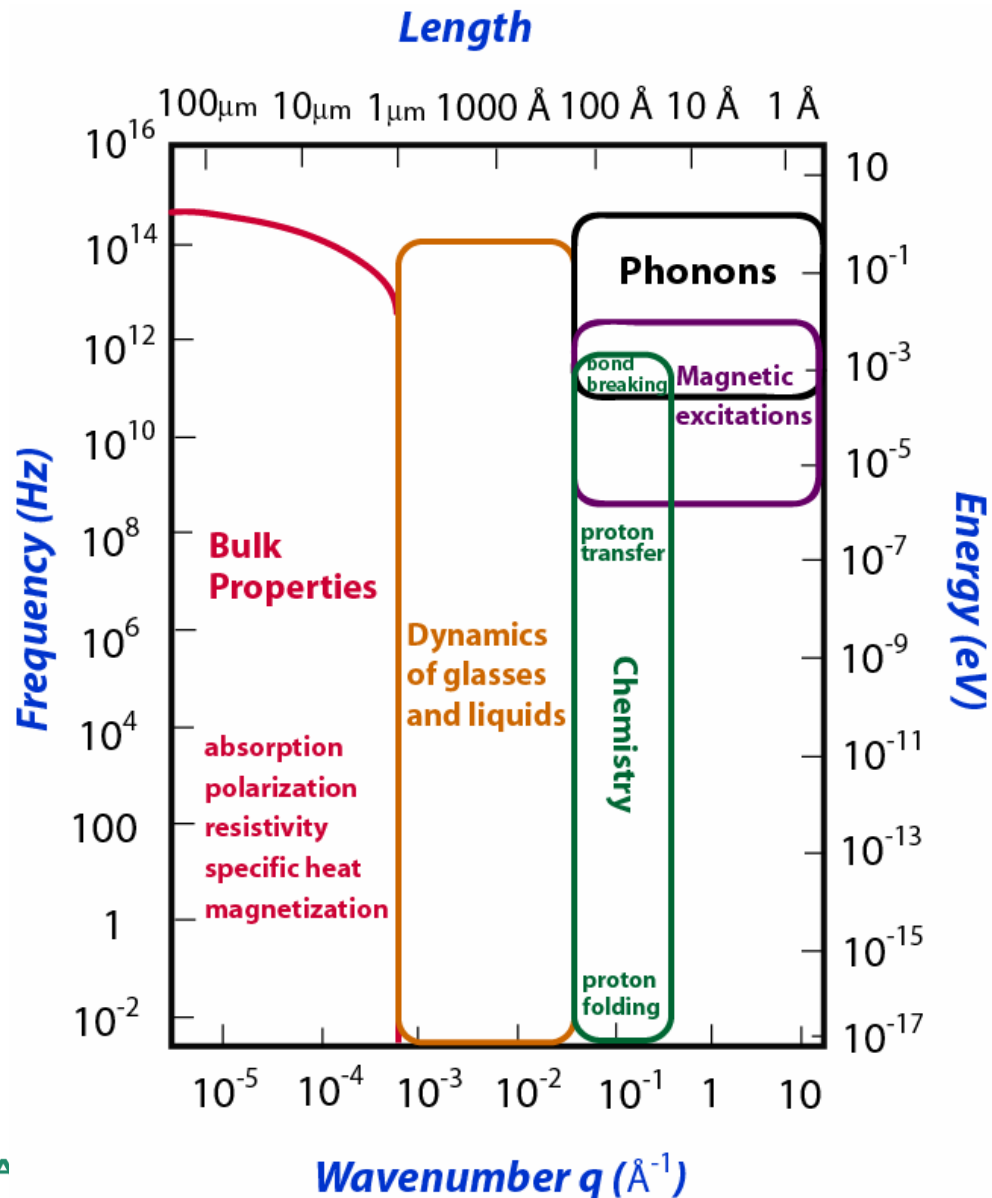
numerous techniques of SR

<b>Spectroscopy</b>
01 Low-Energy Spectroscopy
02 Soft X-Ray Spectroscopy
03 Hard X-Ray Spectroscopy
04 Optics/Calibration/Metrology

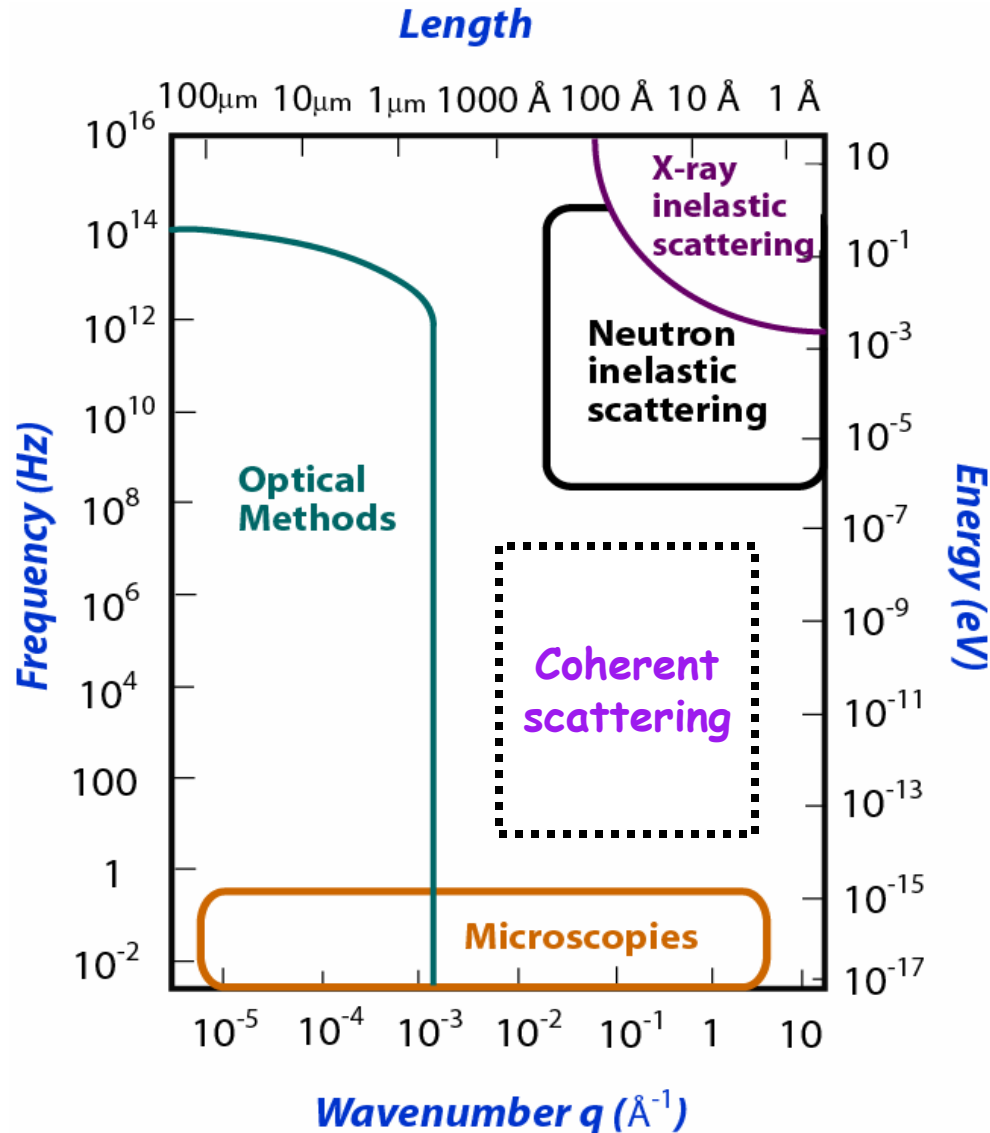
<b>Scattering</b>
05 Hard X-Ray Diffraction
06 Macromolecular Crystallography
07 Hard X-Ray Scattering
08 Soft X-Ray Scattering

<b>Imaging</b>
09 Hard X-Ray Imaging
10 Soft X-Ray Imaging
11 Infrared Imaging
12 Lithography

# Relevant spatial and temporal frequency scales for various physical phenomena



# Spatial and temporal frequency sensitivities of various techniques





# Modern Photoelectron Spectroscopy

## - 100 Years Since Einstein's Photon

# 100 Years of Photoemission



**World Year of Physics 2005**  
Einstein in the 21st Century

$KE_{\max} = h\nu - \phi$

$h\nu$

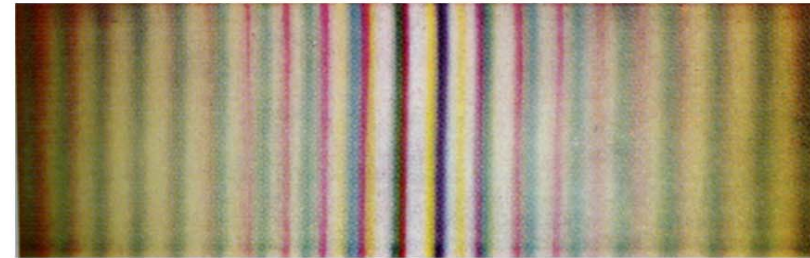
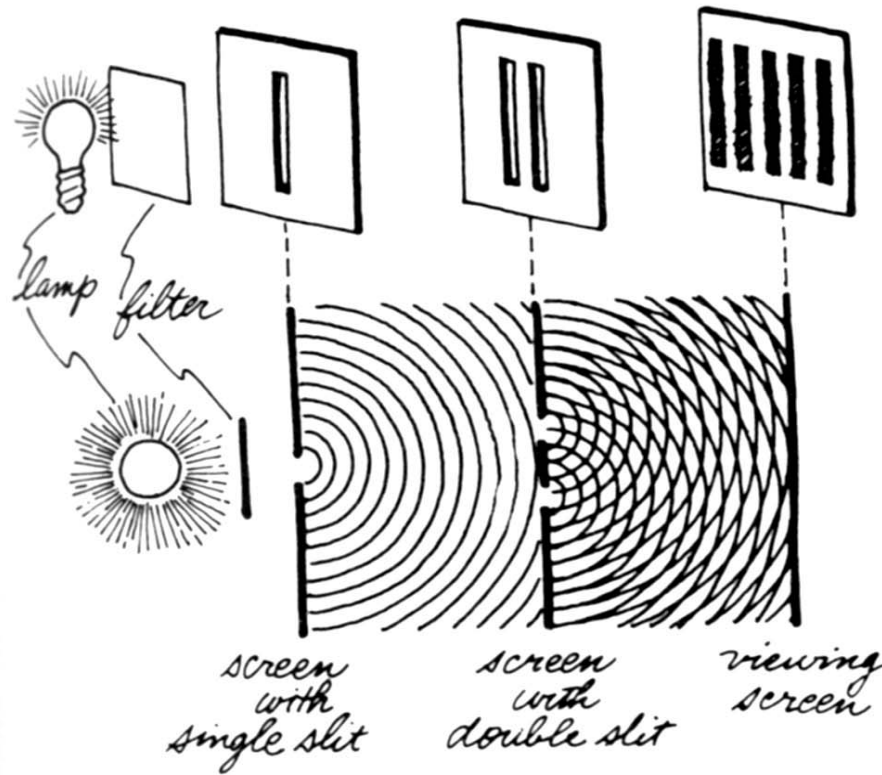
Help make 2005 Physics Year!

Timed to coincide with the 2005 Centennial Celebration of Albert Einstein's Miraculous Year, the World Year of Physics 2005 will bring the excitement of physics to the public and inspire a new generation of scientists. Visit [www.physics2005.org](http://www.physics2005.org) to find out how you can get involved.

[www.physics2005.org](http://www.physics2005.org)

The poster features a portrait of Albert Einstein, a diagram of a photoelectric cell with incident light  $h\nu$  and emitted electrons, and a vertical bar with four colored segments (blue, green, yellow, red). The equation  $KE_{\max} = h\nu - \phi$  is prominently displayed.

# Light as a Wave - Thomas Young 1803



Interference pattern produced by white light through two narrow slits.



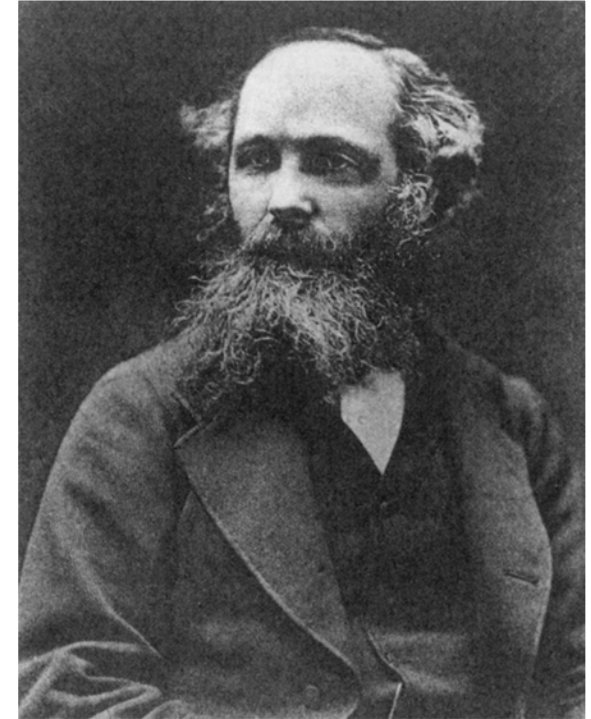
Thomas Young  
Light as a wave, 1803

Young's interference experiment; holes replaced by slits.  
(After K.R. Atkins, *Physics*, Wiley, New York, 1965)

# Maxwell's Eqs - Describe the propagation of Electromagnetic radiation



James Clerk Maxwell  
Electromagnetism, 1865



$$E_x = E_{x0} \cos \left[ \omega \left( t - \frac{z}{c} \right) + \theta \right],$$

$$c = \frac{1}{(\epsilon_0 \mu_0)^{1/2}}$$

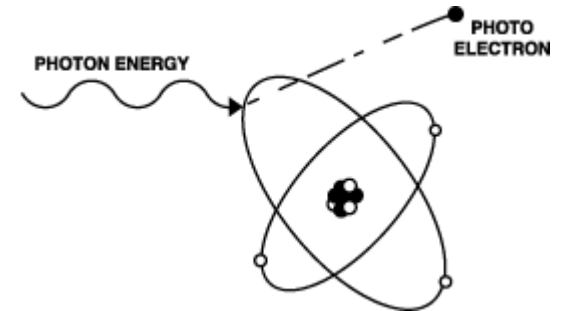
# 100 Years of Photoemission



Hertz  
(1887)



von Lenard  
(1902)

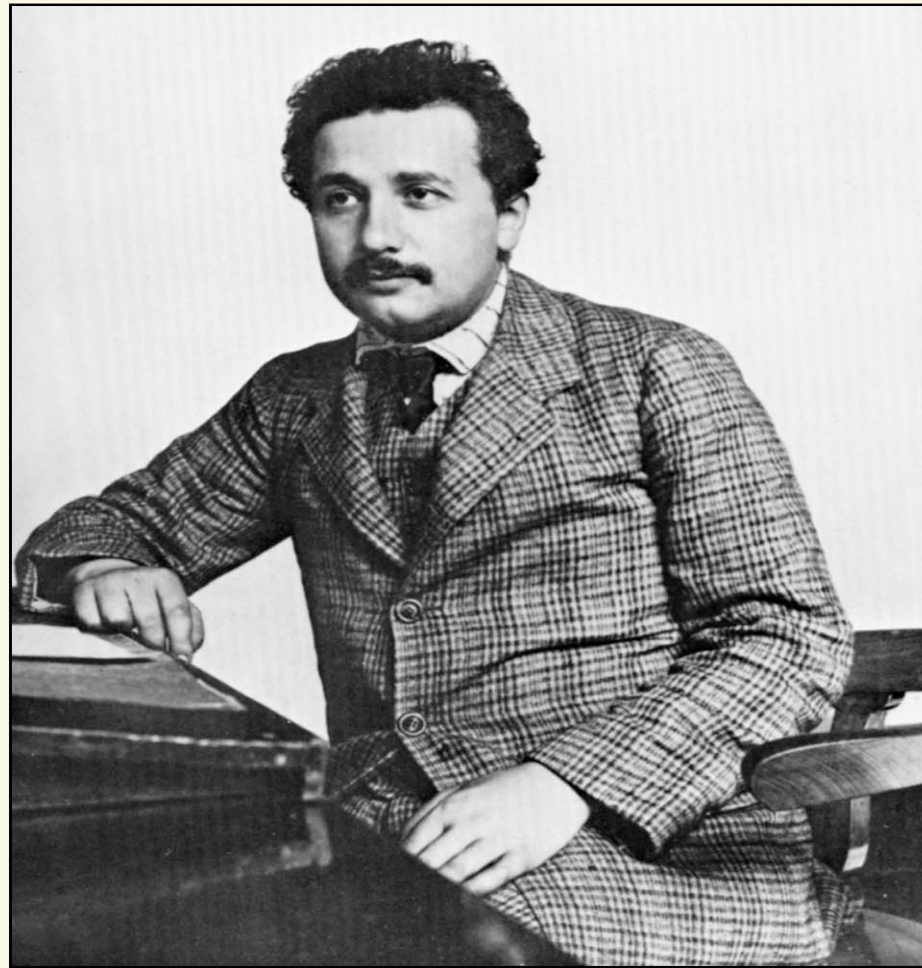


## Einstein's Photoelectric Equation

The electron leaves  
the body with energy

$$\frac{1}{2}mv^2 = h\nu - P,$$

where  $h$  is Planck's constant,  
 $\nu$  is the light frequency and  
 $P$  is the work the electron  
has to do in leaving the body.



Albert Einstein, 1905



*In his 1913 letter nominating Einstein for the membership of Prussian Academy, Max Planck wrote:*

- *"In sum, one can say there is hardly one among the great problems in which modern physics is so rich to which Einstein has not made a remarkable contribution. That he may sometimes has missed the target in his speculations, as, for example, in his hypothesis of light quanta, cannot really be held too much against him, for it is not possible to introduce really new ideas even in the most exact sciences without sometimes taking a risk."*

***“I would like to tell you how pleased I am that you  
have given up your light-quantum theory”***

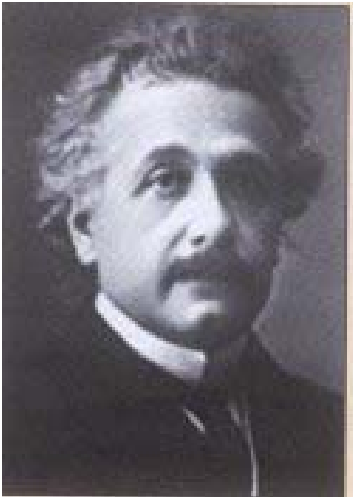
*von Laue to Einstein, 1907 letter*

# Photoelectric Effect - A legacy of Physics

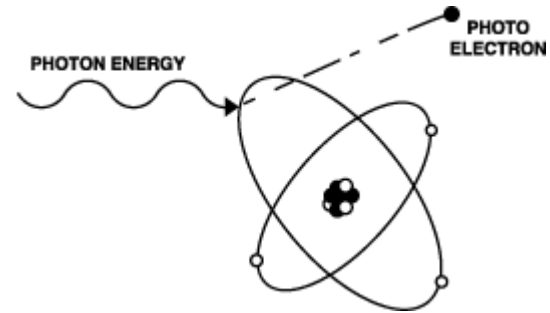


1887: HENRICH HERTZ

1905: ALBERT EINSTEIN



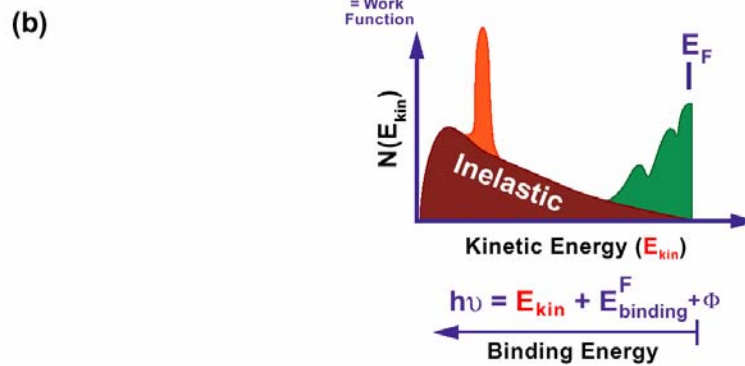
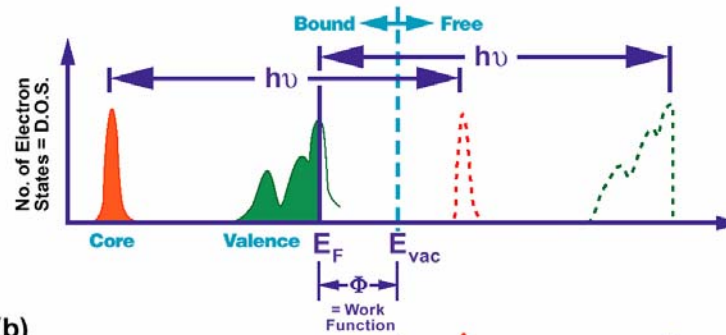
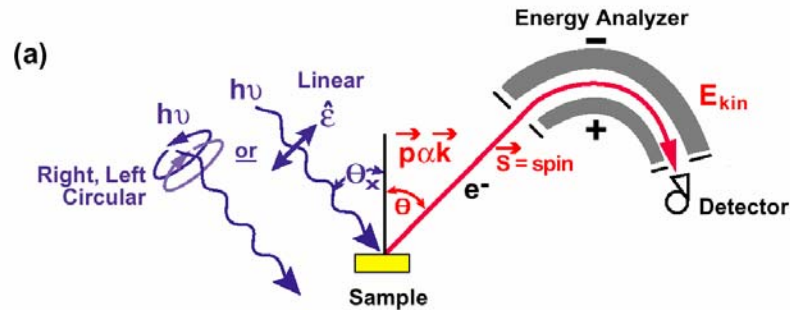
$$E_{\text{Kin}} = h\nu - E_B$$



## Impact:

- Development of modern physics.
- Solar cell.
- Photoelectron spectroscopy as a powerful tool.

# Photoelectron Spectroscopy

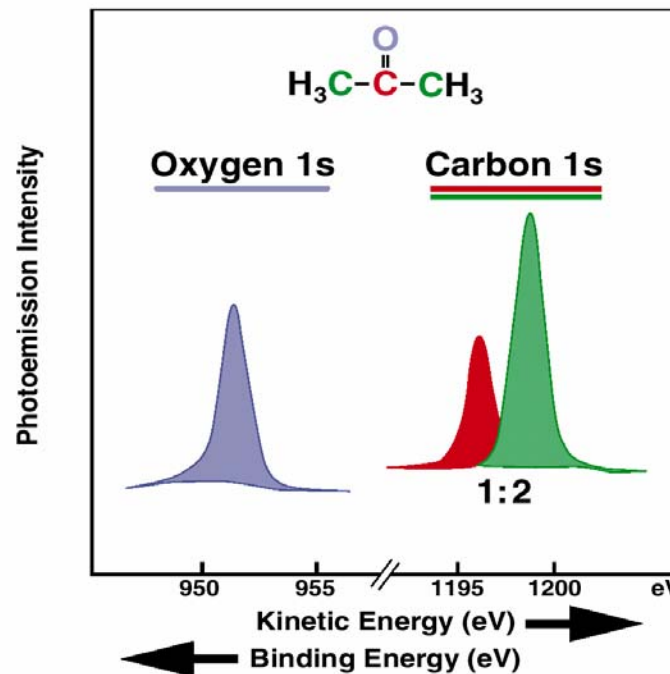


# Photoemission Core Level Spectroscopy



Provides information about

- Kind of atom
- Number of atoms
- Chemical State – simple analysis

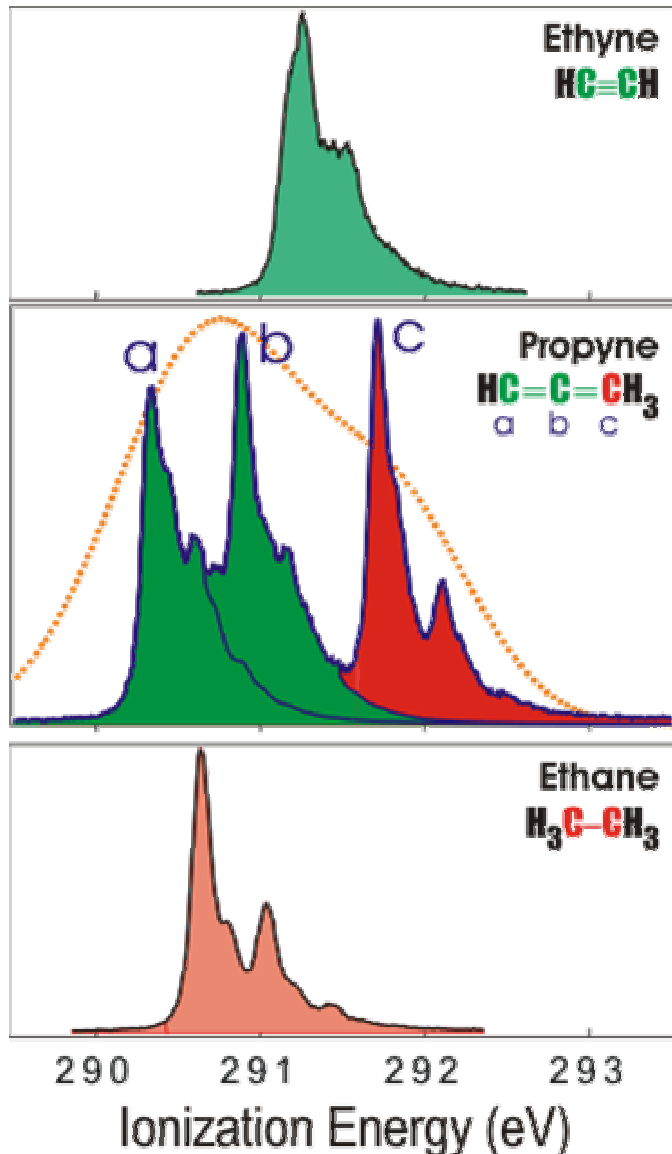


**Sensitivity to Hydrogen Bonding**

(Siegbahn et al)

**Lab x-ray source: Resolution = ~ 0.5 eV (mono)**

# High resolution C 1s 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.

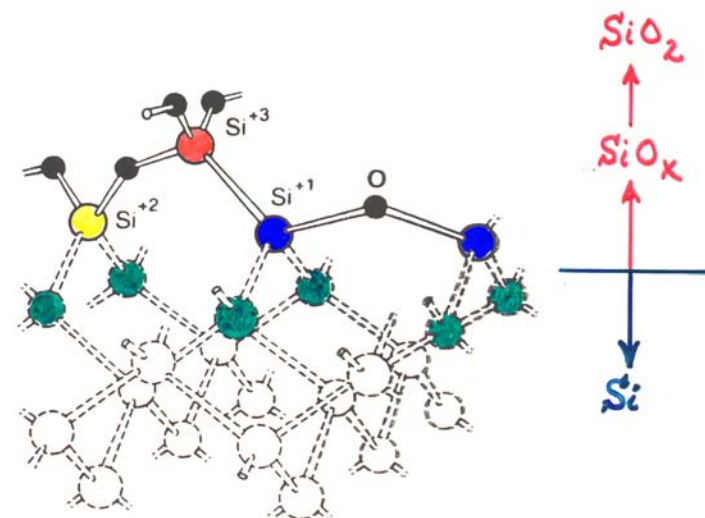
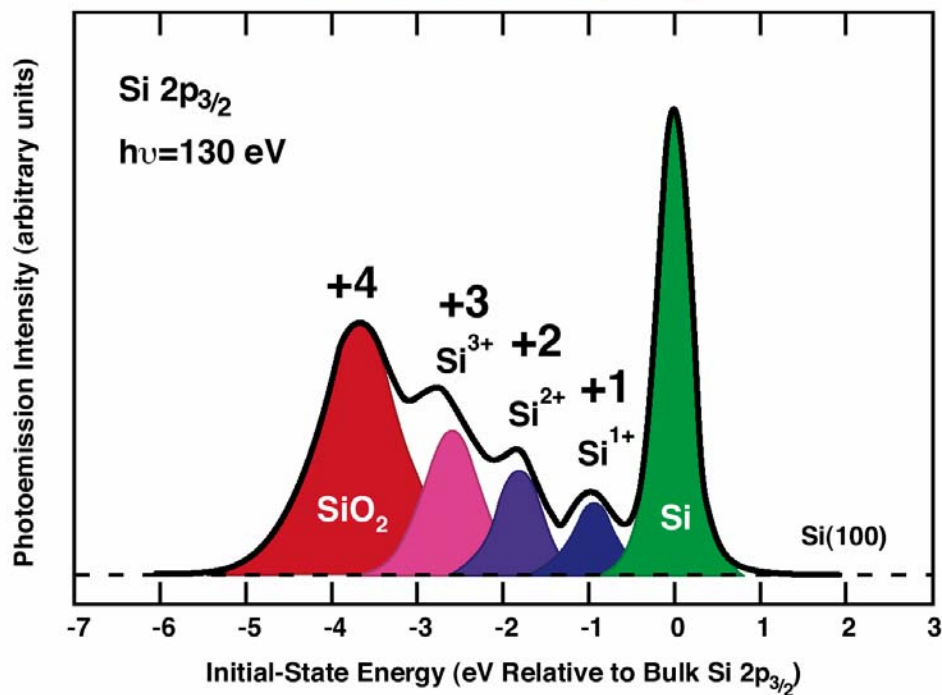
Shift of the methyl (CH<sub>3</sub>) peak in propyne relative to ethane is due to the electronegativity of the ethyne (HC<sup>°</sup>C) group.

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

# Chemical Shift

5Å SiO<sub>x</sub> on Si(100)



(Himpsel et al, NSLS)

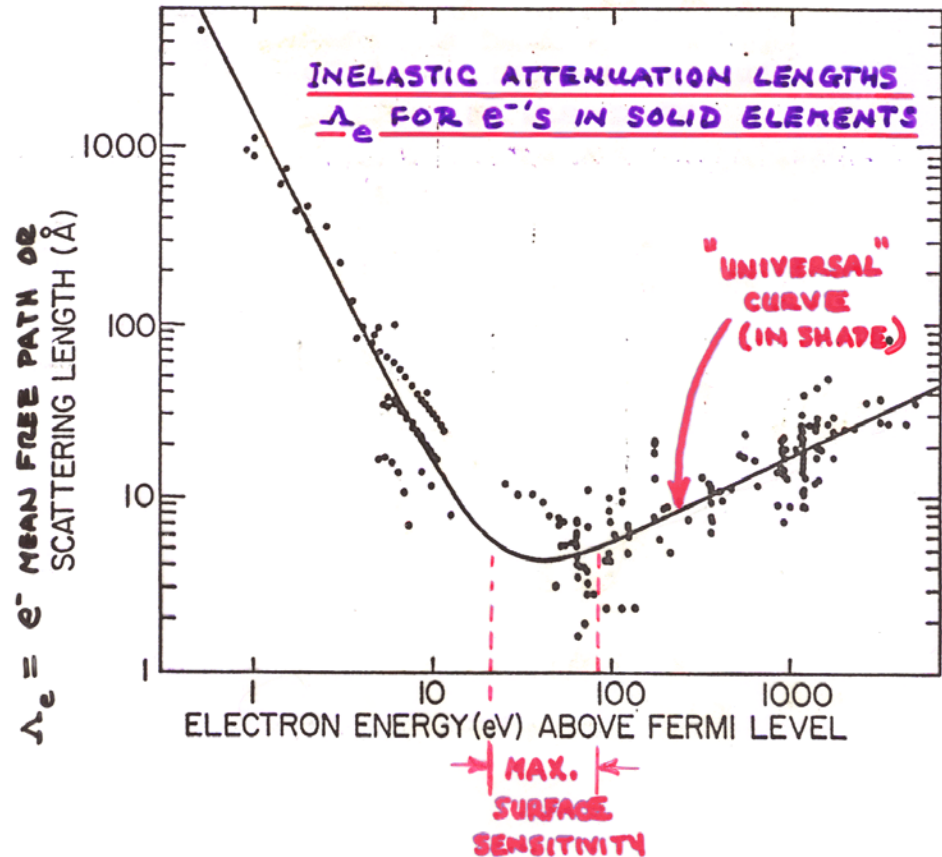
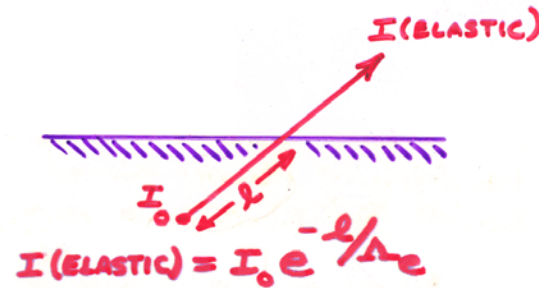
# Electron Escape Depth : Surface Sensitivity



Why are electrons  
so useful as probes  
of surfaces?

Or

Not so useful for  
studying bulk  
properties !!

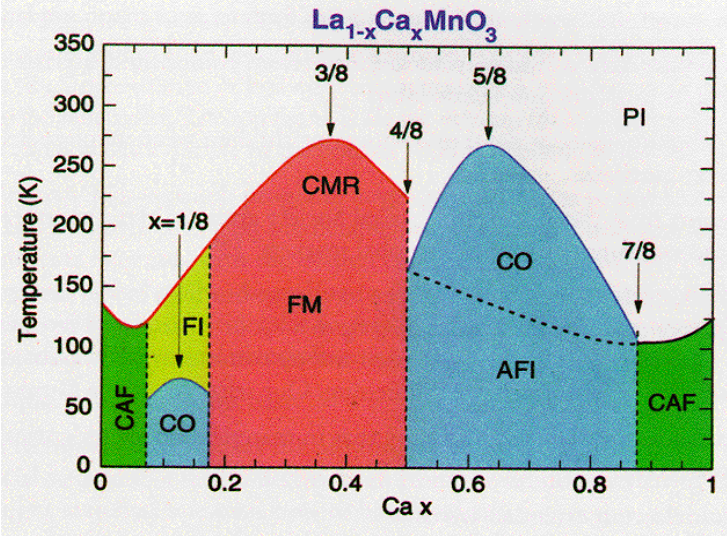


COMPILATIONS: Seah & Dench, *Surf. Int. Anal.* 1, 2 (1979)  
Tanuma, Powell, & Penn, *Surf. Int. Anal.* 17, 911 & 927 (1991); 21, 165 (1994)  
Powell & Jablonski, *J. Phys. Chem. Ref. Data* 28, 19 (1999); *Surf. Int. Anal.* 29, 108 (2000)

# Colossal Magnetoresistance (CMR) Effect

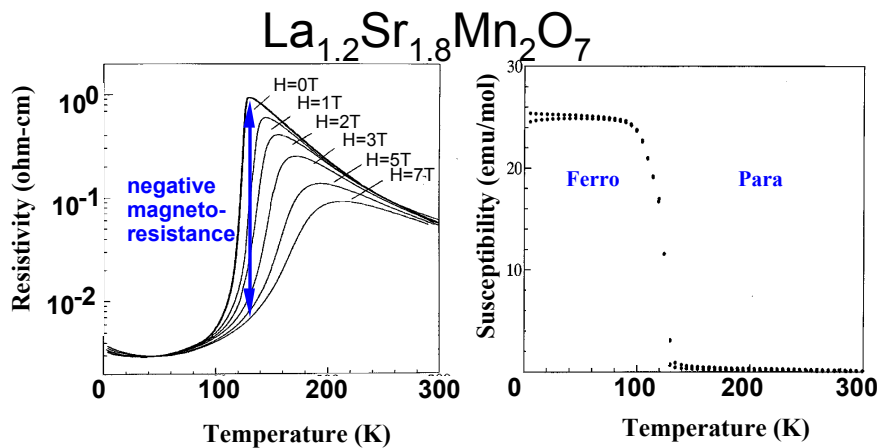


## Novel Electronic Phases



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

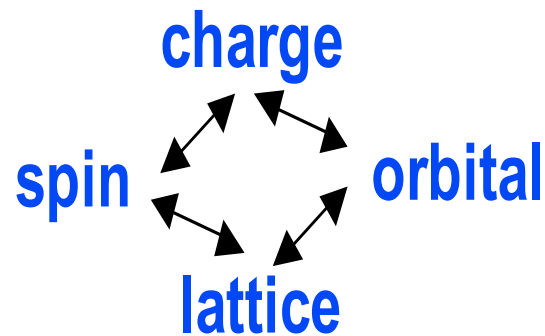
- Large drop of resistivity upon relatively small magnetic fields
- Para → Ferromagnetism
- Most dramatic on the insulating phase (short range orbital order)



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



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

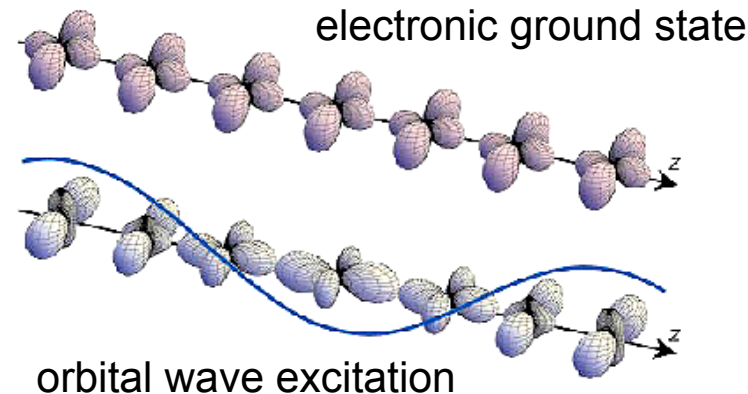


Competition among many **Energy** and **Length** scales  
Determine the physics of these systems

An unexplored degree of freedom in transition metal oxides:

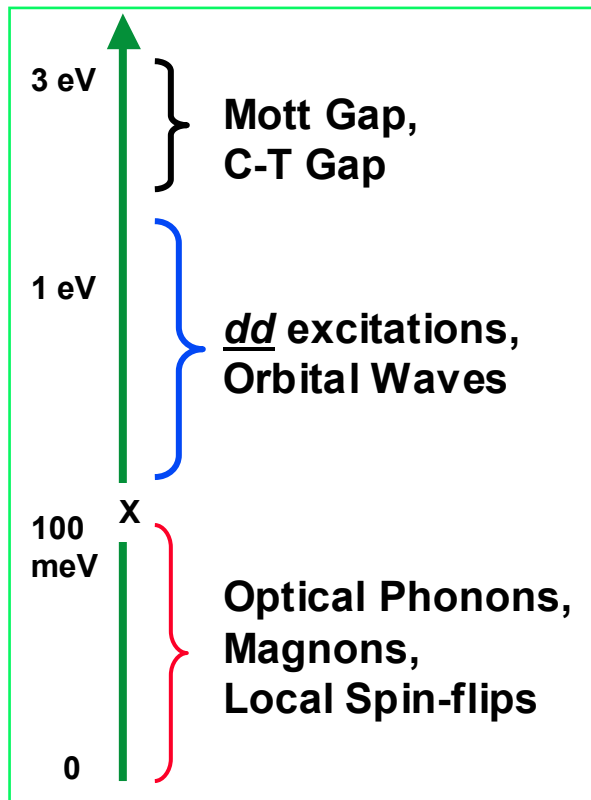
## Orbital Density Waves

Ordering of orbitals produce long-range orbital density waves - a new type of collective excitation in crystals



*E. Saitoh et al. Nature 410, 180 (2001)*

# Energy scales of various excitations



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

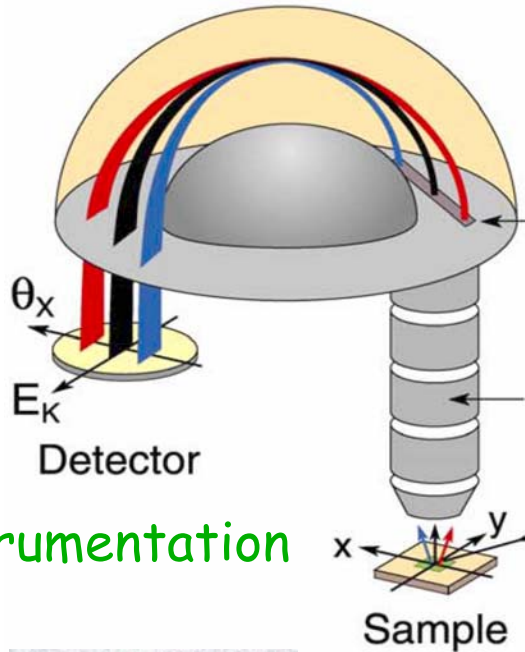
*Requires study of energy losses with energy resolution better than 10meV*

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

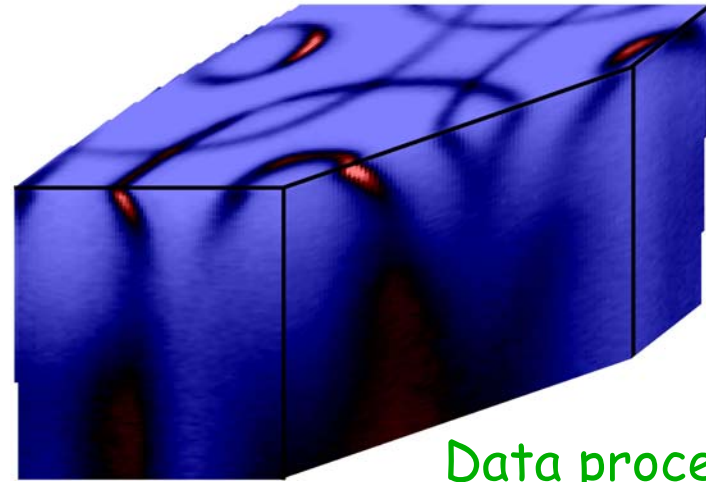
## Techniques of choice:

1. Angle resolved photoemission (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

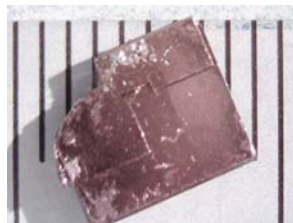
# Angle-resolved Photoemission Spectroscopy



Instrumentation



Data processing



Materials

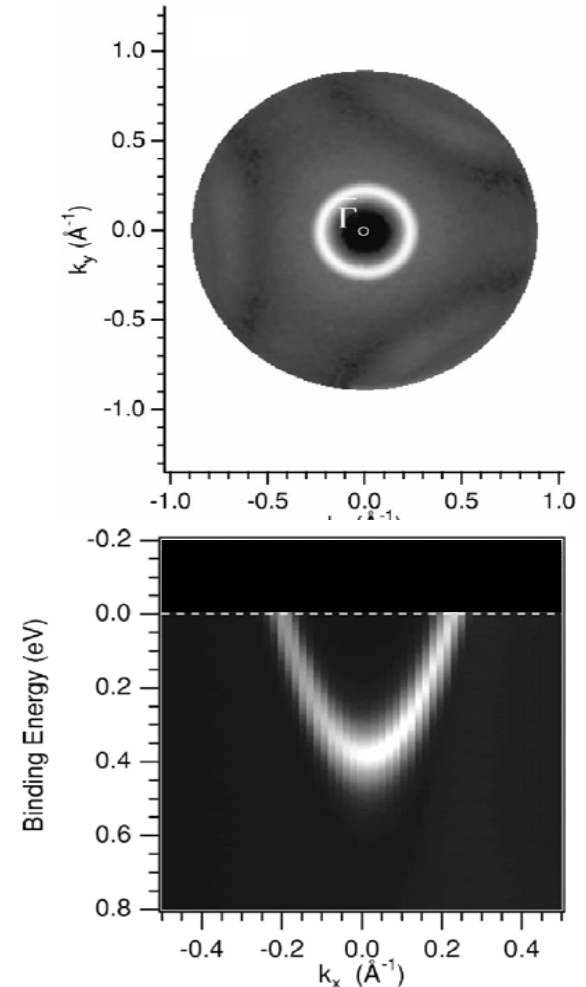
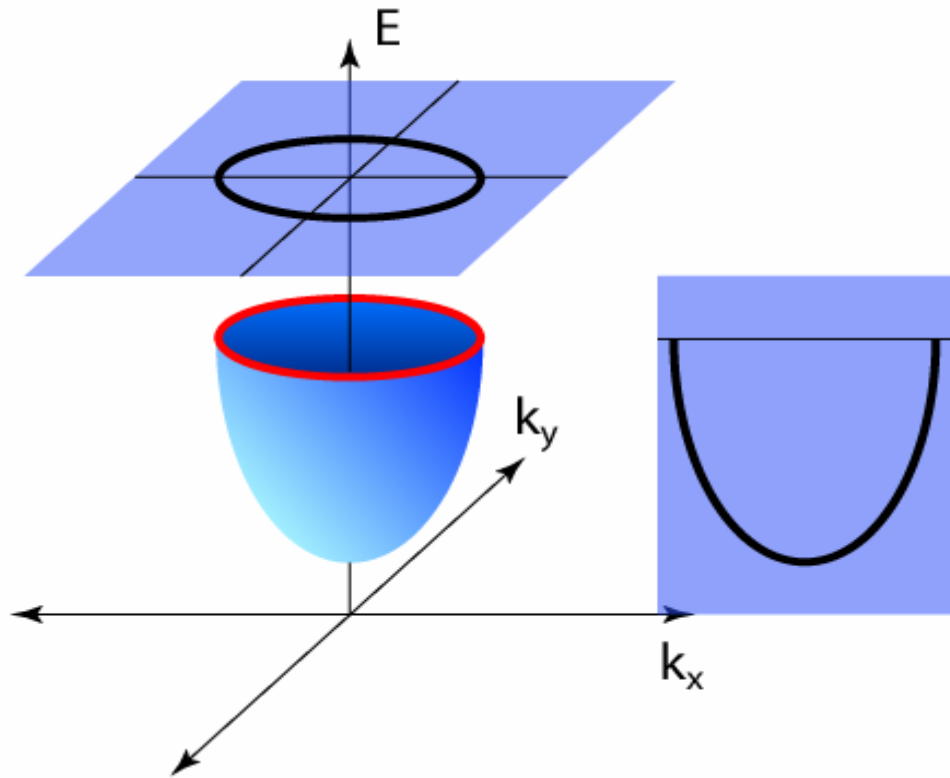
Scientific issues



# A Simple Example : Cu (111) Surface State



## Copper

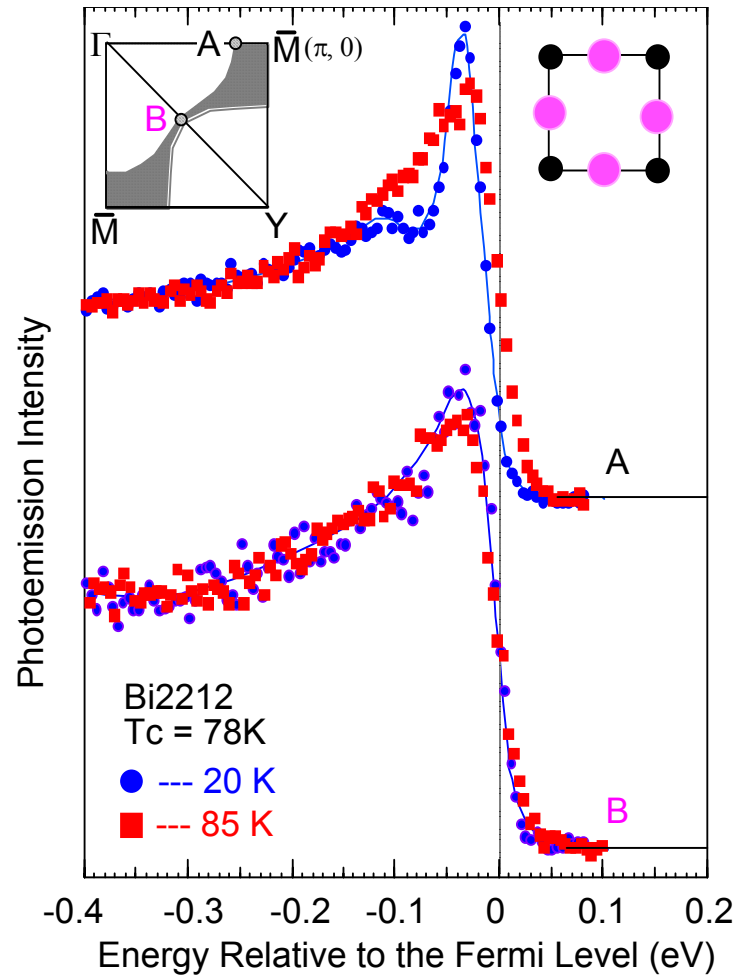
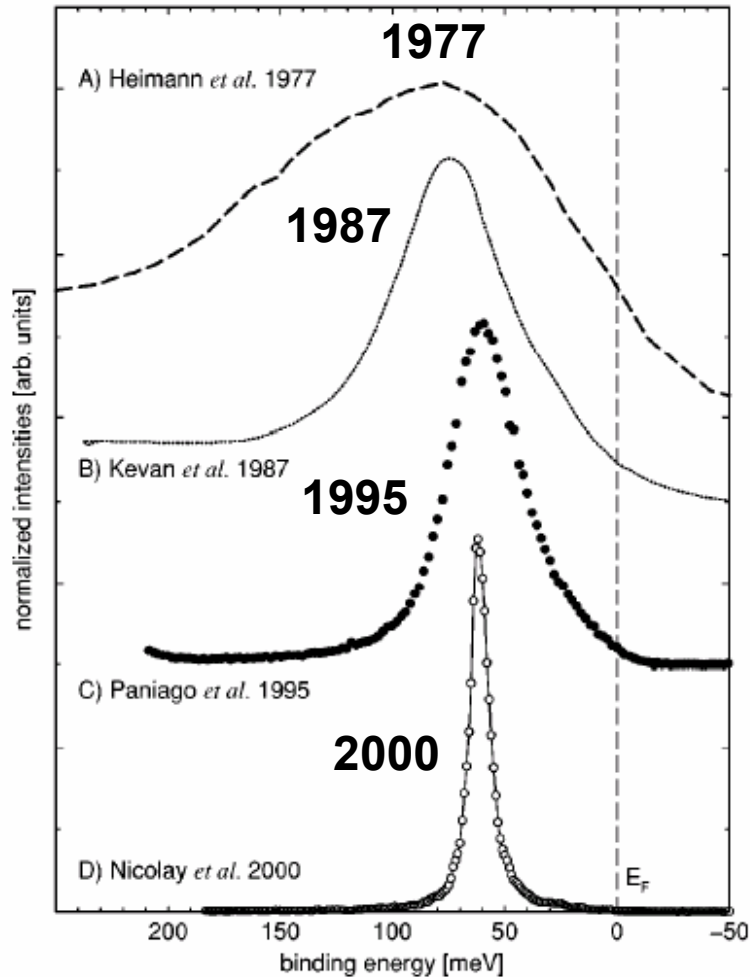


F. Baumberger et al., PRB 64, 195411 (2001)

# Improvement in Energy Resolution



Ag(111) L-Gap Surface State by PES



F. Reinert *et al.*, PRB 63 (2001)

Shen *et al.*, PRL 70, 1553 (1993)

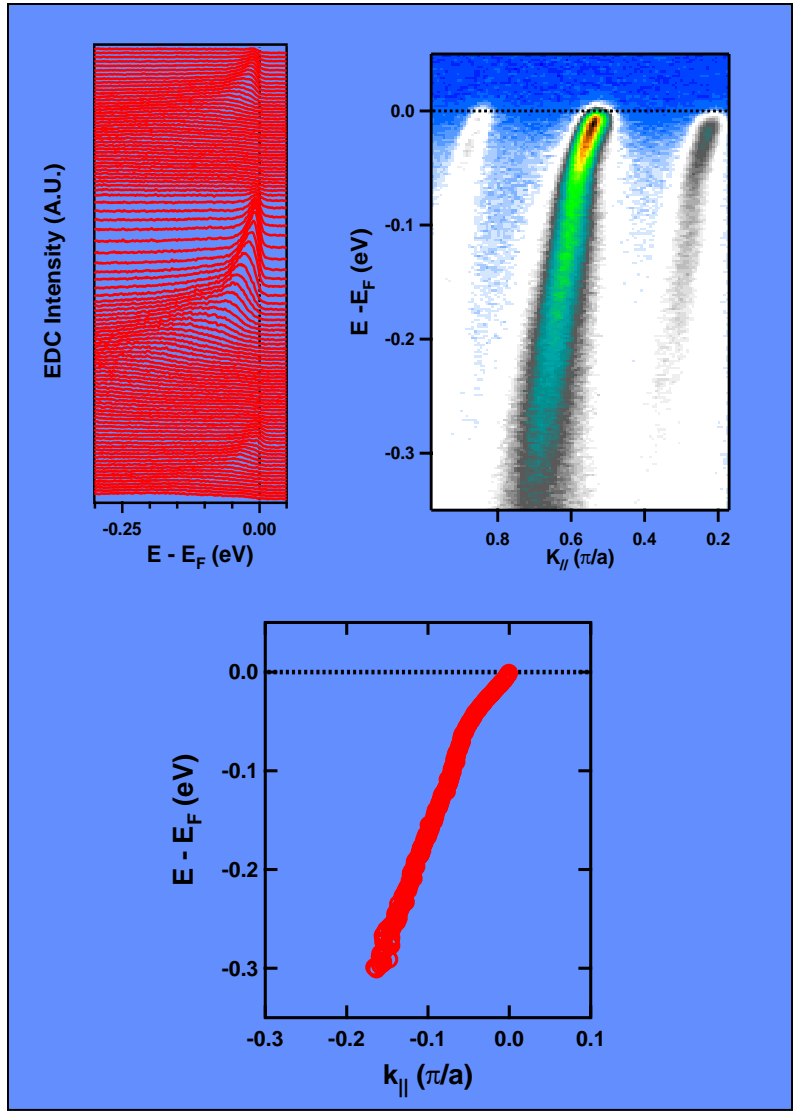
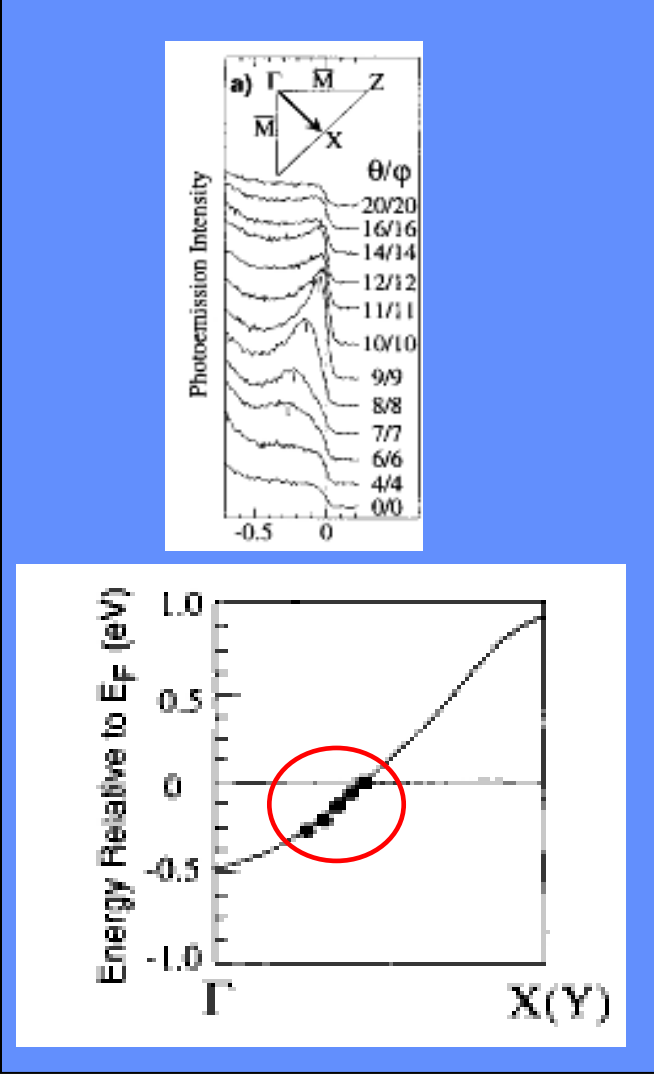
LAWRENCE BERKELEY NATIONAL LABORATORY

# Better Resolution Reveals Electron Kinkiness in High-Tc Materials



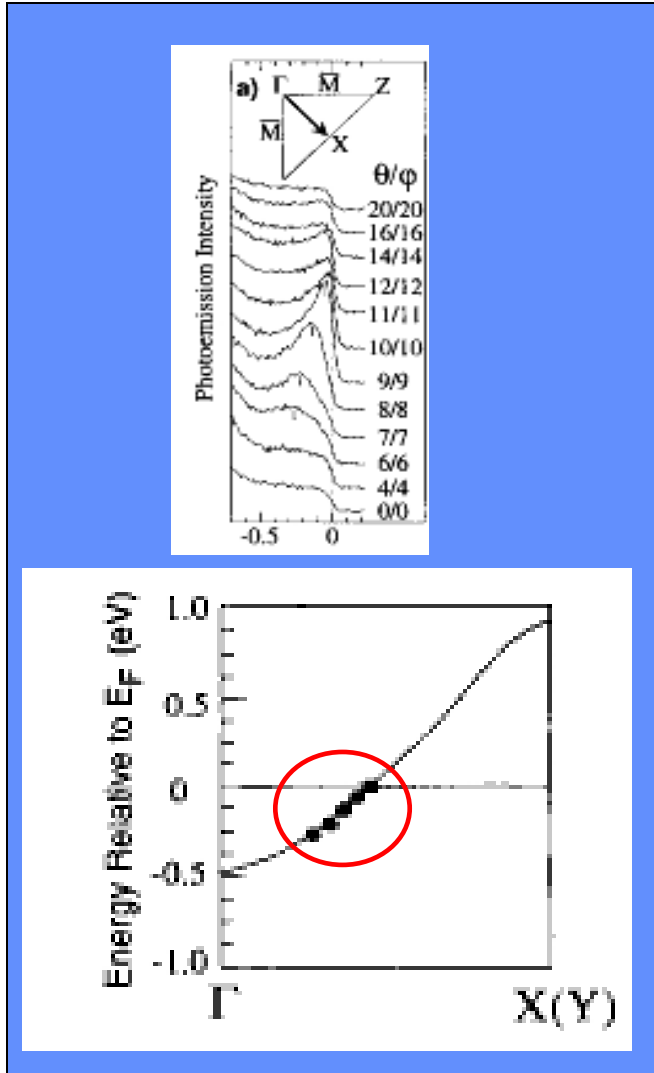
Angular Resolution: 0.3 degree

Angular Resolution: 2 degrees

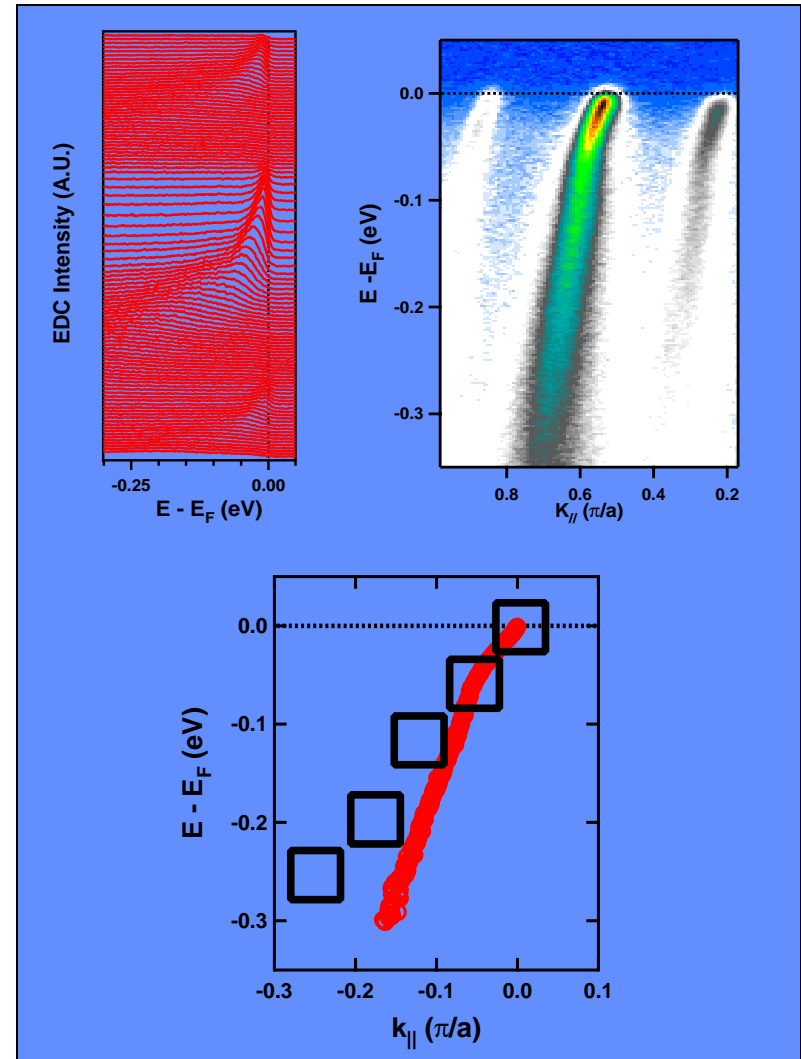


# Better Resolution Reveals Electron Kinkiness in High-Tc Materials

Angular Resolution: 2 degrees



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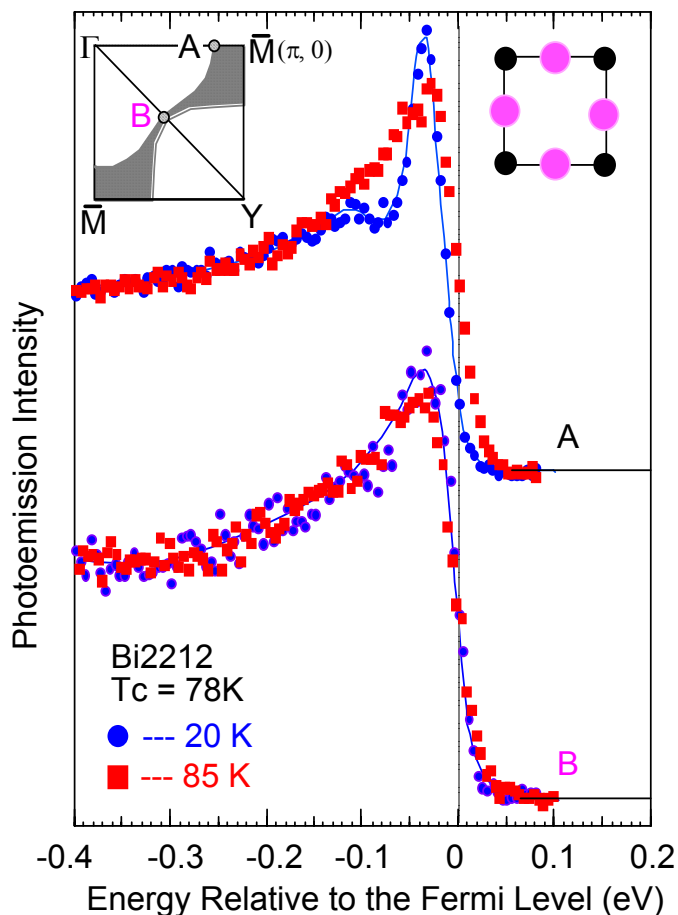


# ARPES : Then and Now

## Data Throughput & Efficiency



1993 : Detection of an anisotropic d-wave gap



One EDC with 30 meV &  $\pm 1^\circ$  resolution :

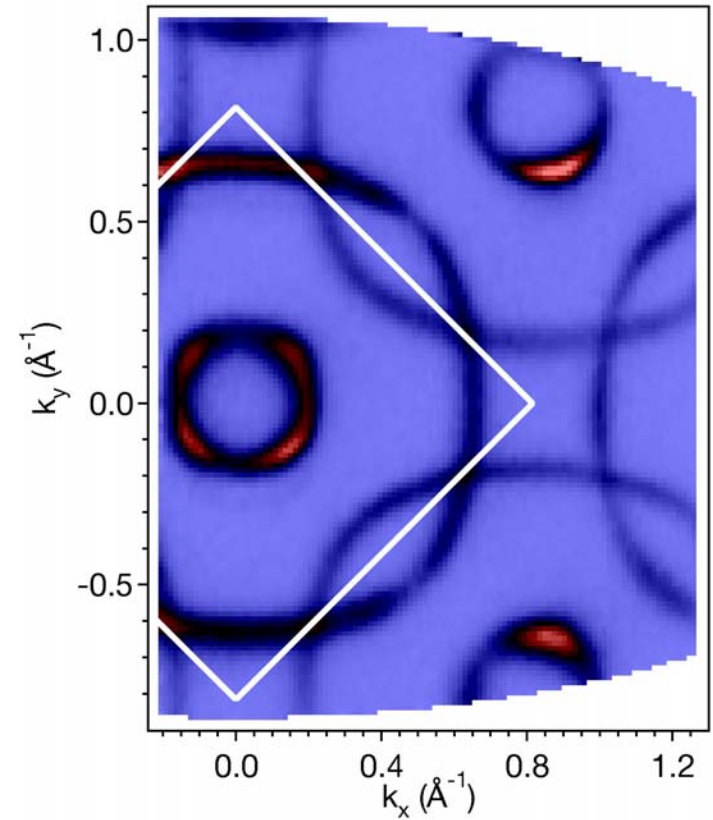
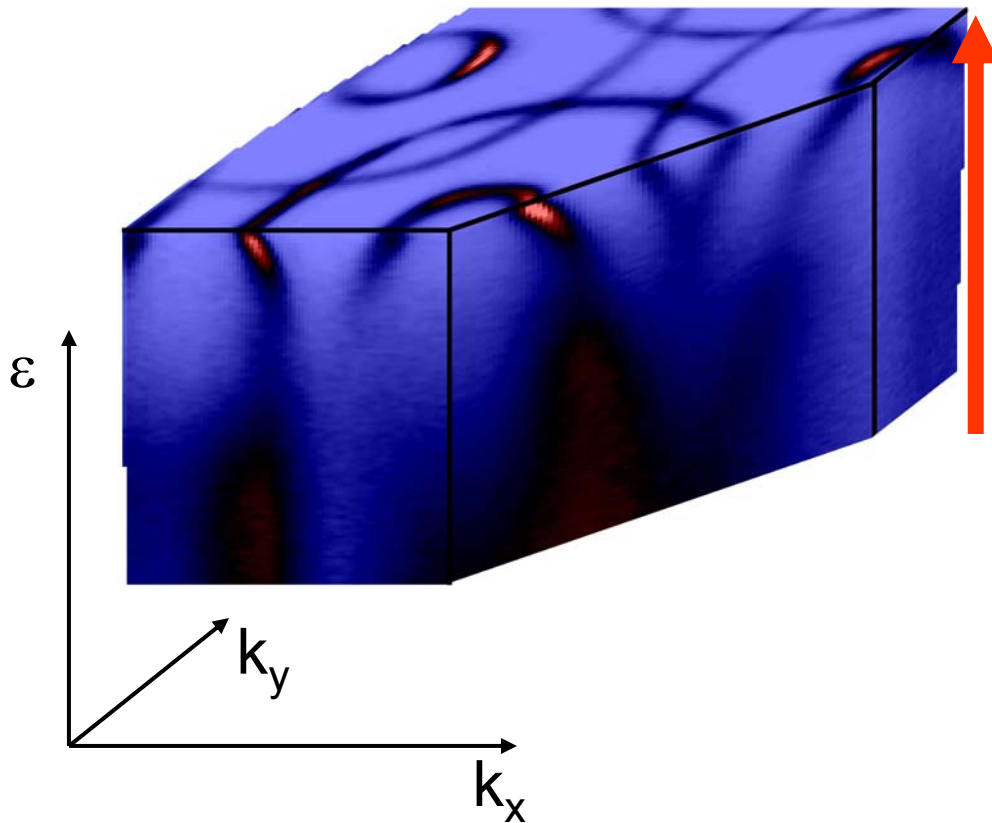
**3 hours per spectrum**

Shen *et al.*, PRL **70**, 1553 (1993)

# Last Decade Saw Great Improvements in ARPES (Band mapping: $\text{Sr}_2\text{RhO}_4$ )



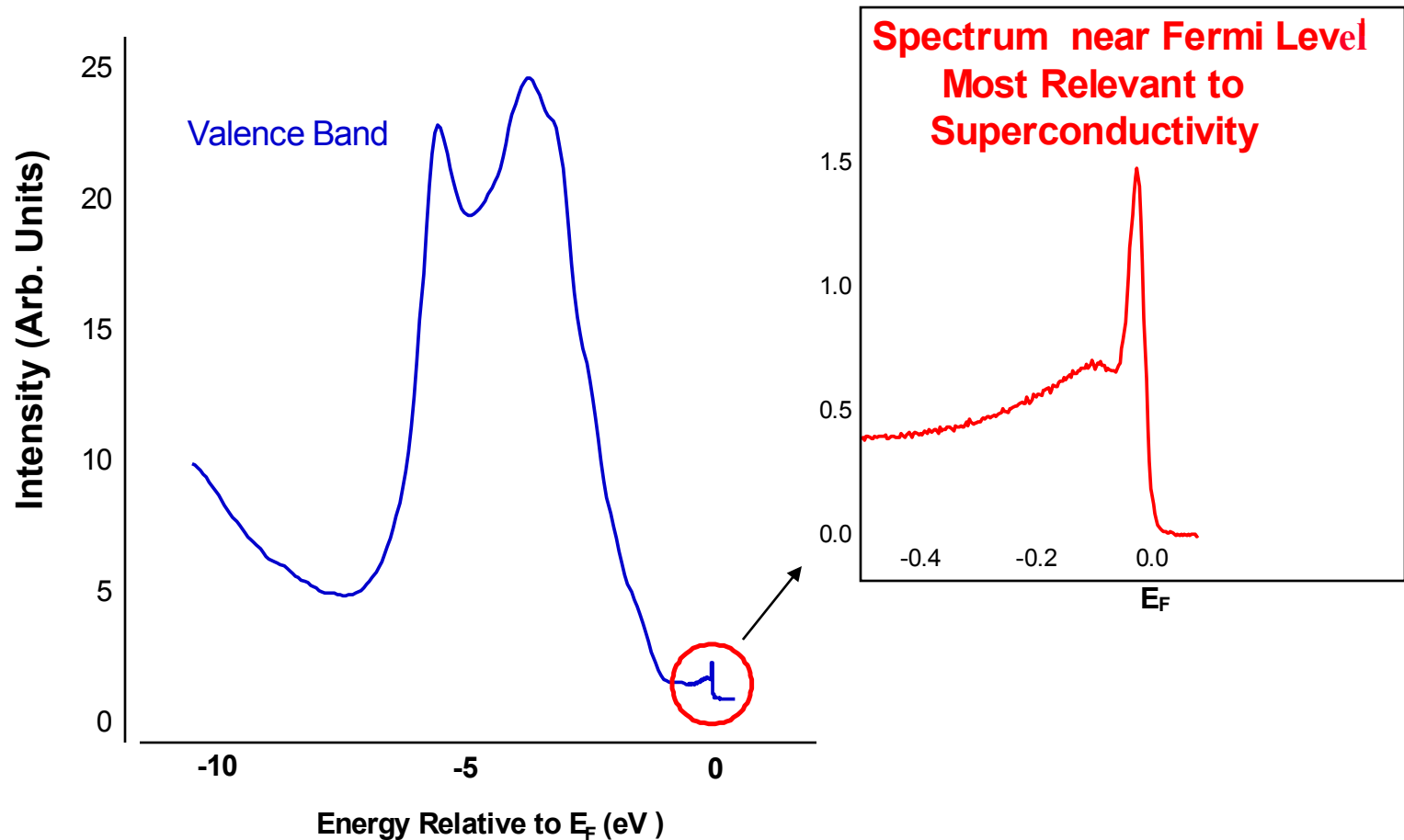
$> 10^4$  spectra in 9 h (3.1 s / spectrum)



F. Baumberger et al, *in preparation*

# How data is collected ?

# Typical Valence Band Photoemission Spectrum from a High Temperature Superconductor

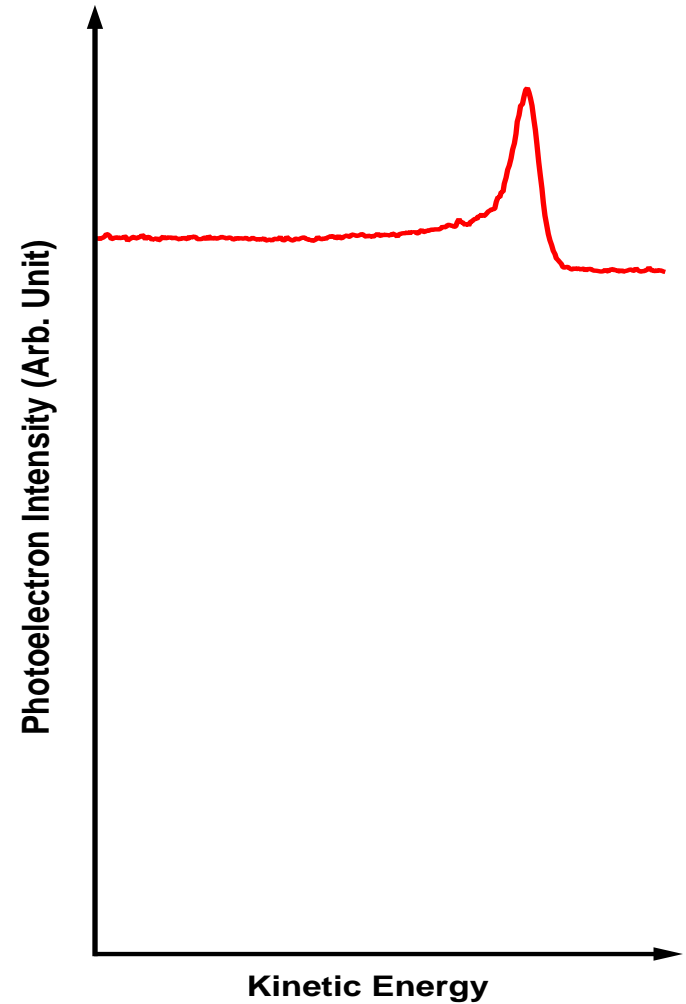
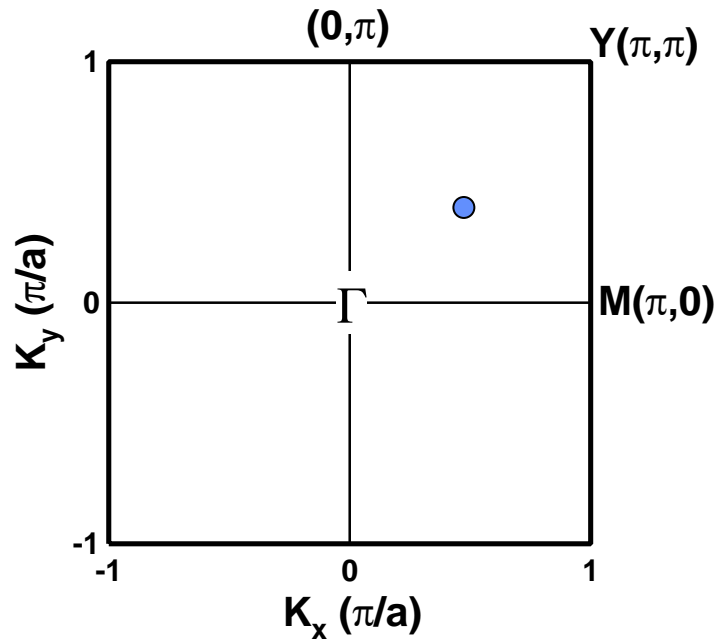


**Intrinsically weak signal experiments**

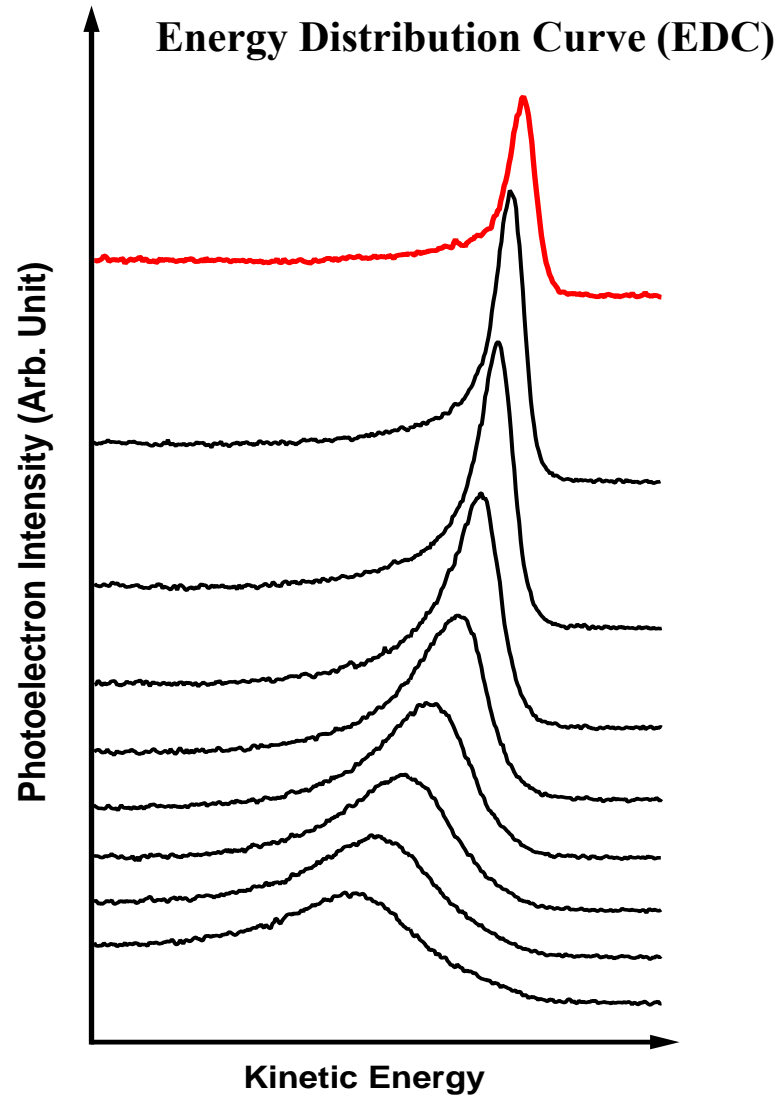
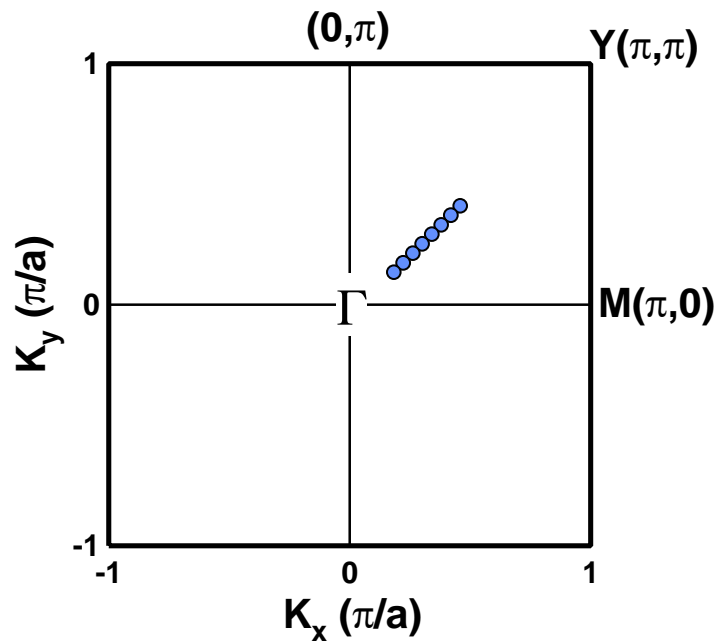
# ARPES -Band Mapping and Fermi Surface (prior to ~1998)



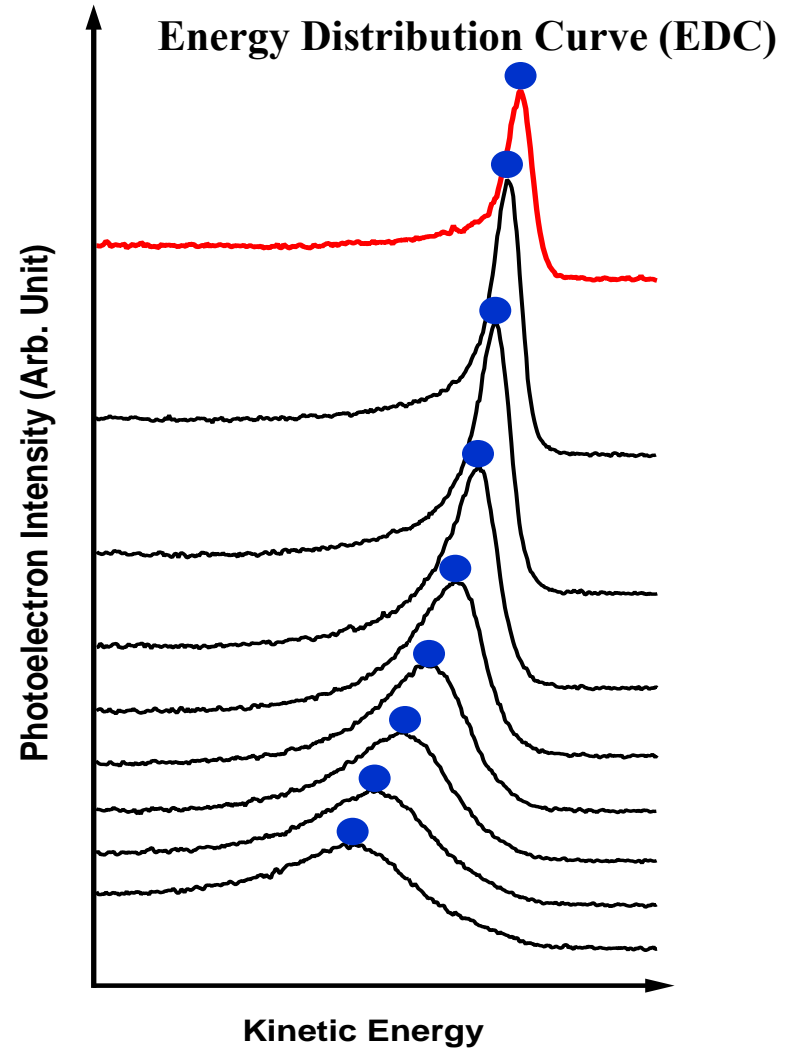
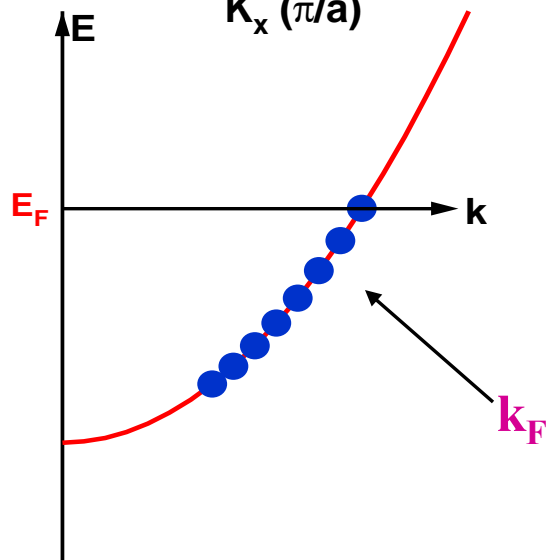
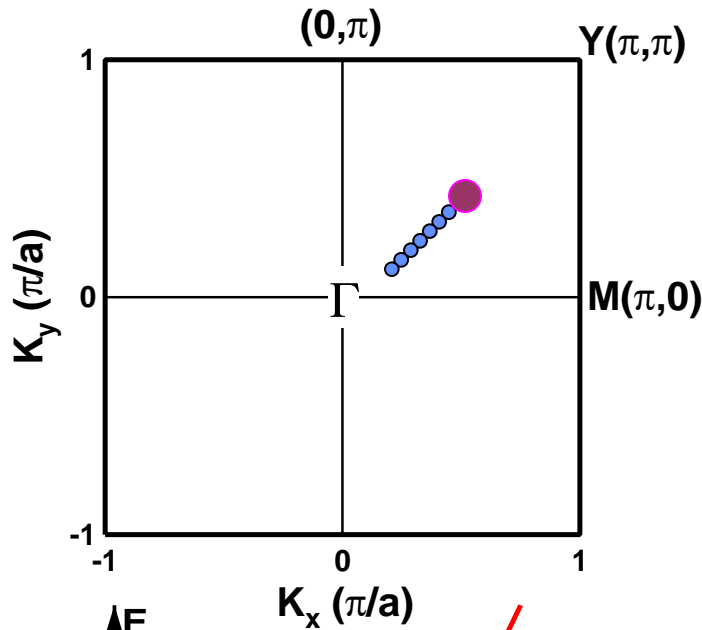
## Energy Distribution Curve (EDC)



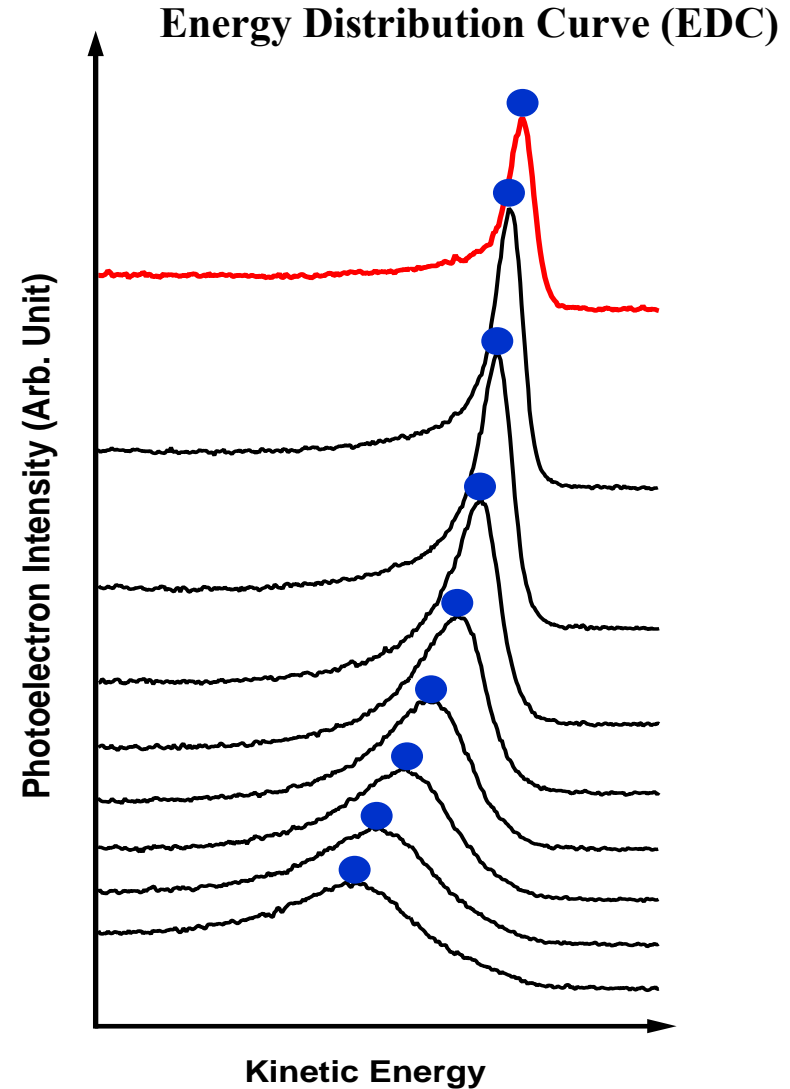
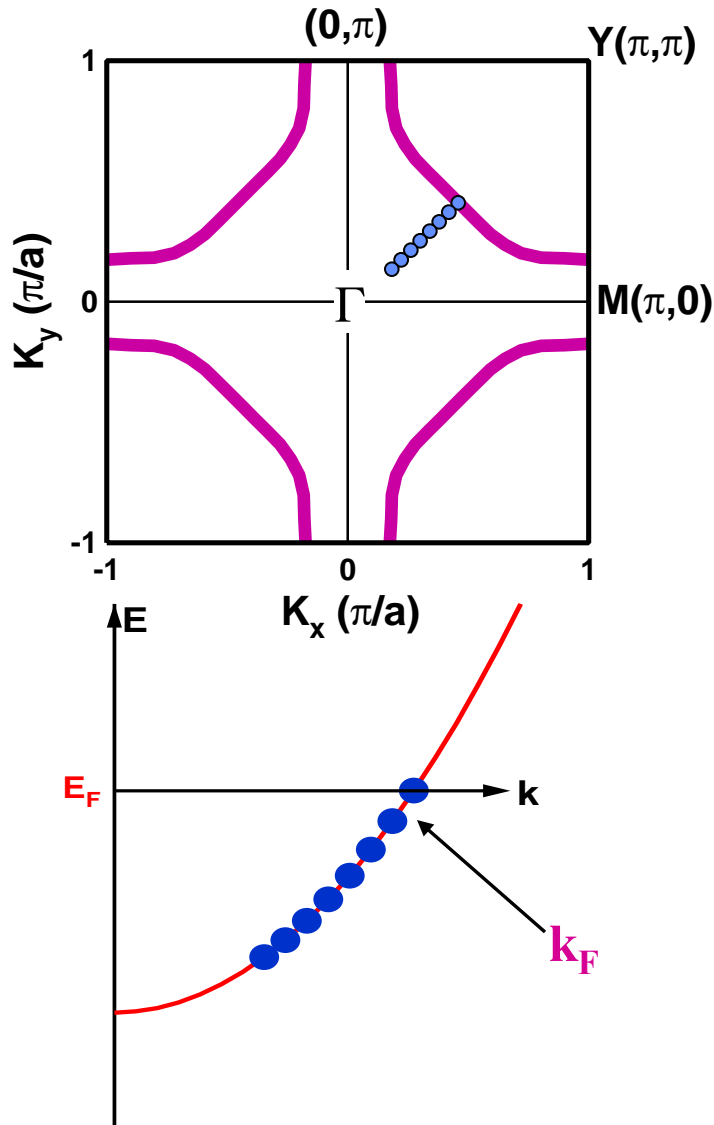
# ARPES -Band Mapping and Fermi Surface (prior to ~1998)



# ARPES - Band Mapping and Fermi Surface (prior to ~1998)



# ARPES - Band Mapping and Fermi Surface



# Real Physics Is Deeper



- Not enough resolution!

**PAST**

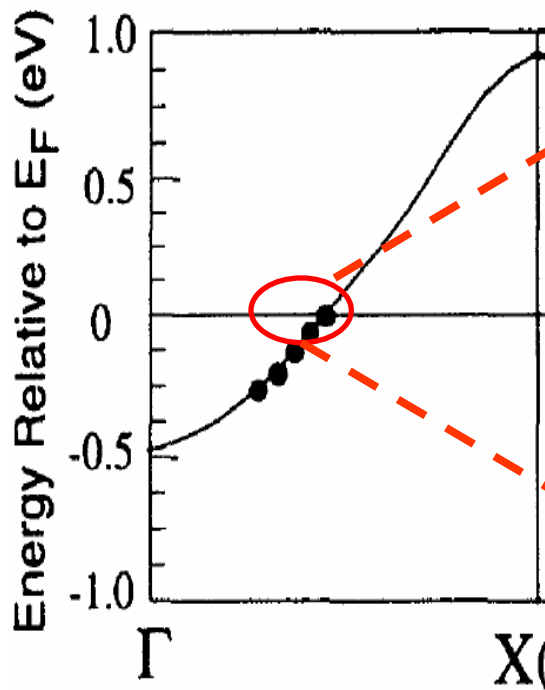
$\Delta E: 100\text{meV}$

$\Delta\theta: 2^\circ$

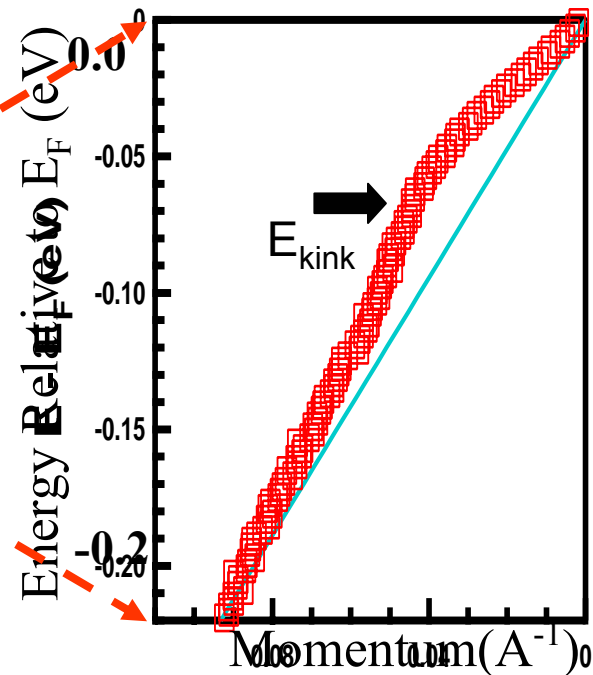
**TODAY**

$\Delta E: 1 - 10\text{meV}$

$\Delta\theta = 0.05 - 0.3 \text{ deg}$

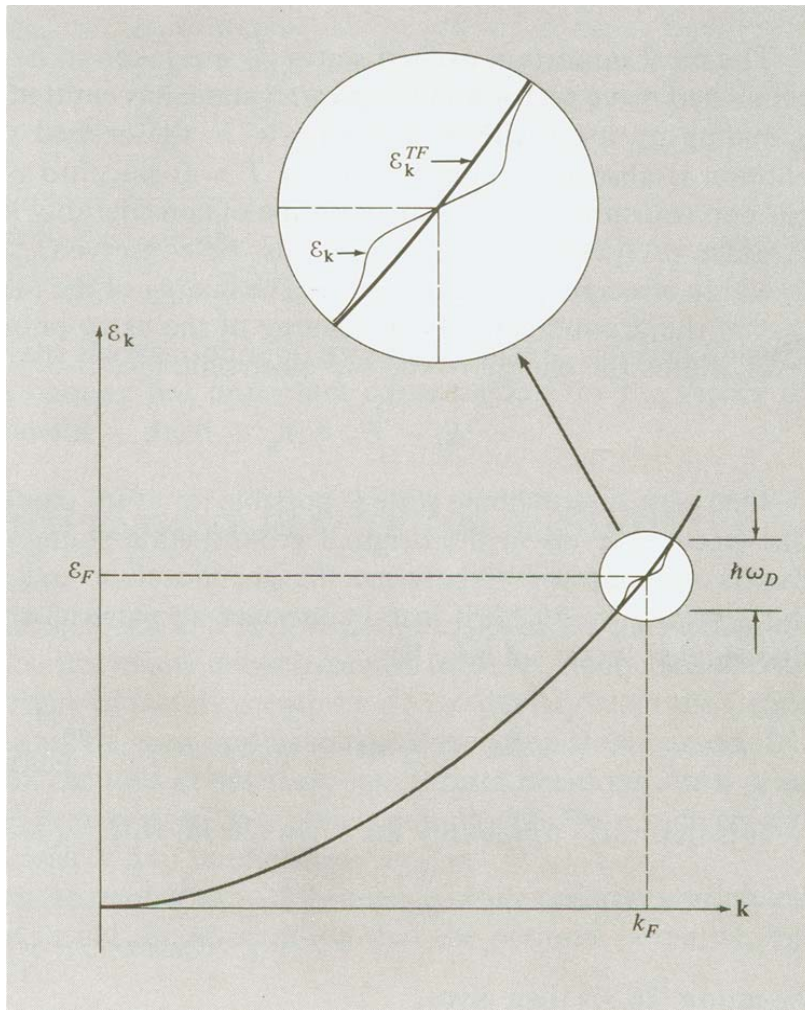


D. Dessau *et al.*, PRL 71, 2781 (1993)



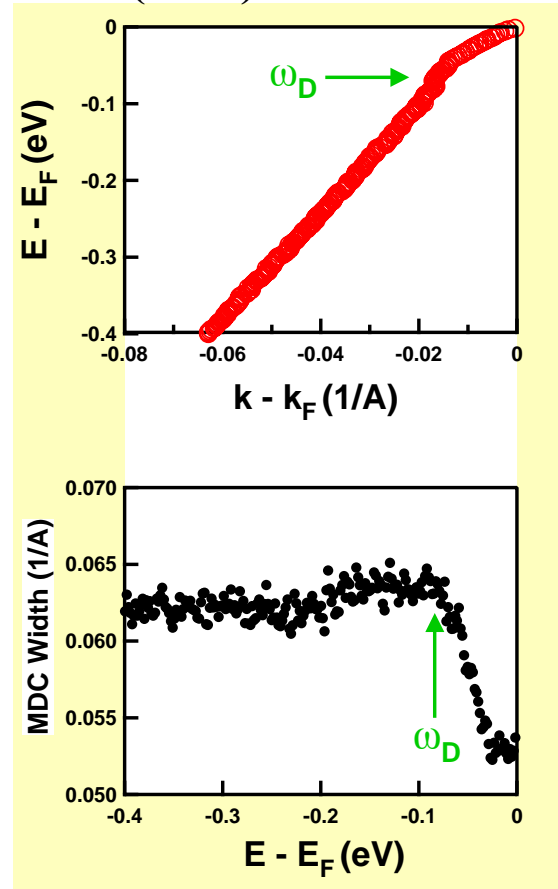
P. V. Bogdanov *et al.*, PRL(2000)

# Manifestation of Many-Body Effects: Band Renormalization



Ashcroft-Mermin, Solid State Physics

## Be(0001) Surface State



Hengsberger et al., PRL 83(1999)592.

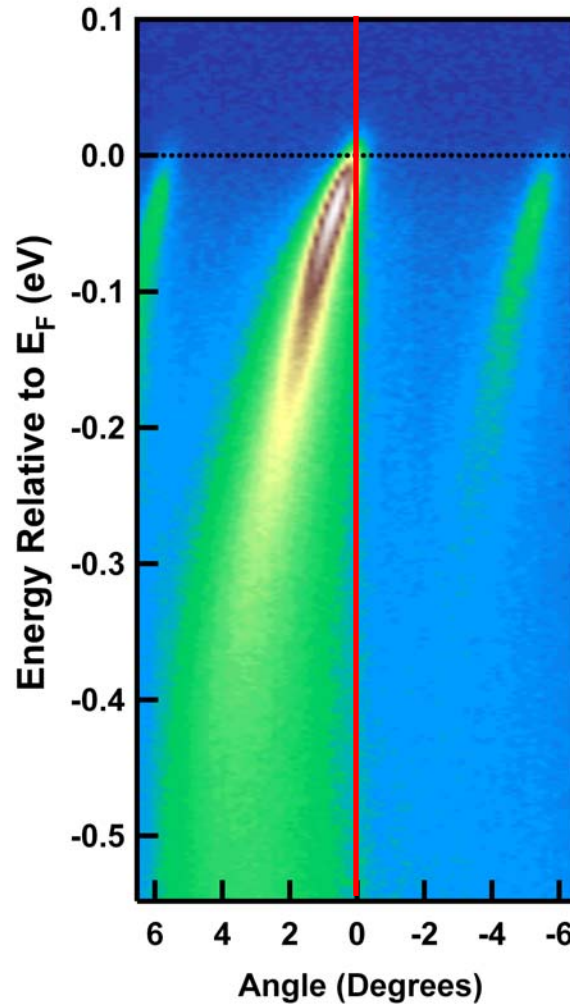
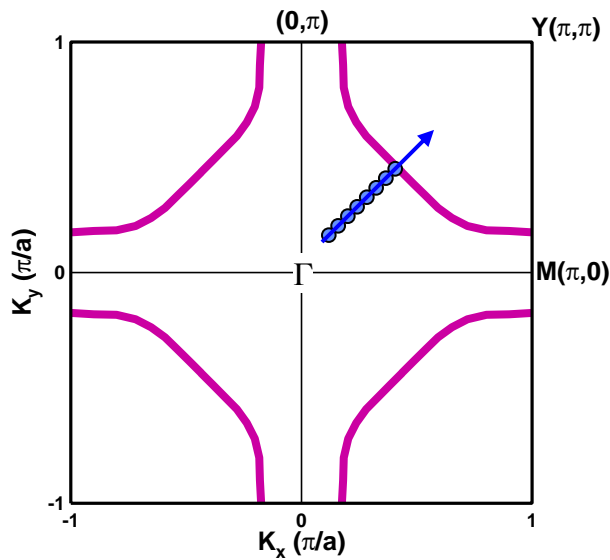
S. Lashell et al., PRB 61(2000)2371.

S. J. Tang et al., Phys. Stat. Solidi.

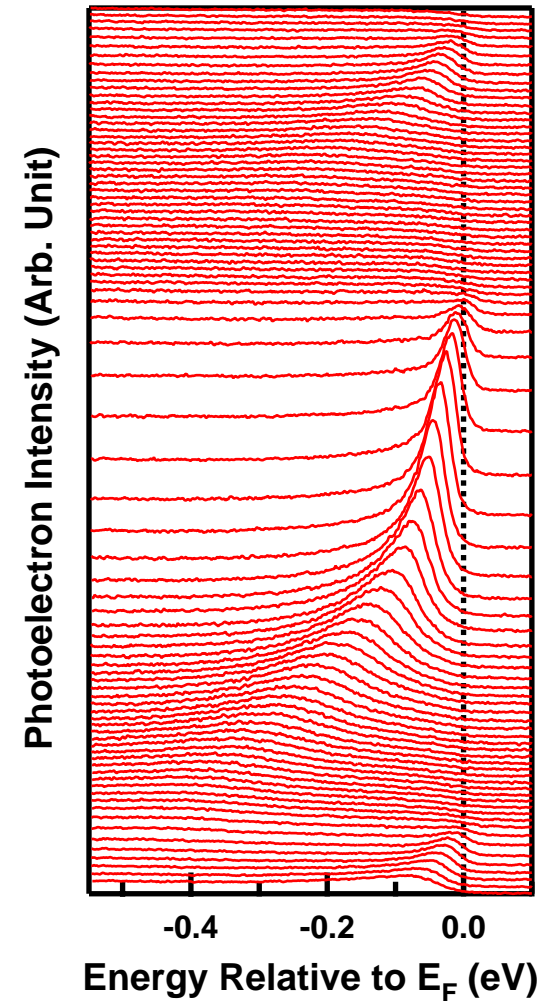
# State-of-the-Art ARPES - Multiple Angle Collection



@ Detector Plane



EDCs



What kind of information could be extracted ?

# ARPES - A Tool for Many-Body Effect



Under the sudden approximation, photoemission measures  
*single-particle spectral function*

$$A(k, \omega) = \frac{1}{\pi} \frac{\text{Im} \Sigma}{[\hbar\omega - E_k^0 - \text{Re} \Sigma]^2 + [\text{Im} \Sigma]^2}$$

Electron self-energy:  $\Sigma = \text{Re} \Sigma + i \text{Im} \Sigma$

*Dispersion: E-k Relation (Velocity;  
Effective mass etc.)*

Scattering rate  
(Lifetime)

# ultra-high energy resolution ARPES- Capabilities



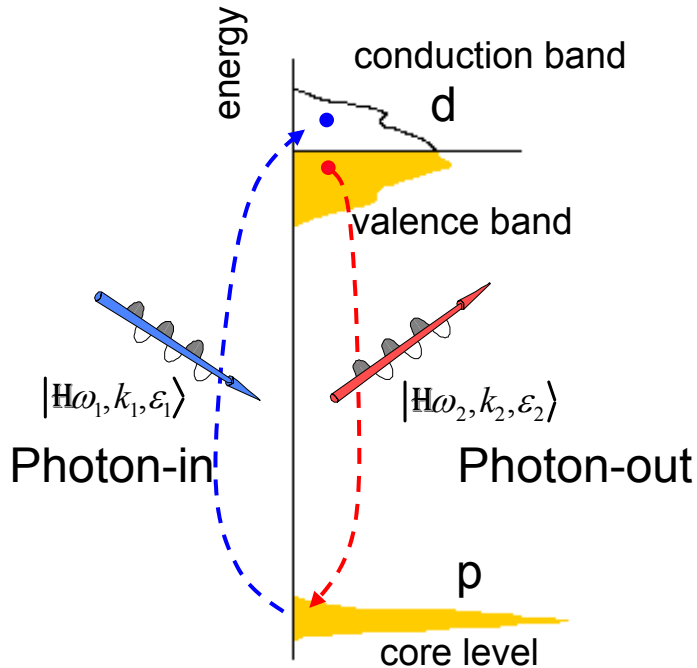
## Key physical properties measurable in ARPES:

- Energy vs. wave vector( $k$ ) (Band Structure)
  - Fermi Surface
  - Mean Free Paths
  - Effective carrier masses
  - Scattering rates
  - Electron Self energies
  - Scattering or nesting vectors
  - Pseudogaps and superconducting gaps
  - Number of carriers
- ✓ ARPES is the technique of choice to measure these properties with momentum ( $k$ ) resolution.
- ✓ The only technique that can measure all in a self consistent way.

## Techniques of choice:

1. Angle resolved photoemission (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:  $\mathbf{q} = \mathbf{k}_2 - \mathbf{k}_1$   
Resonance:  $\omega_1 \sim \omega_{\text{edge}}$

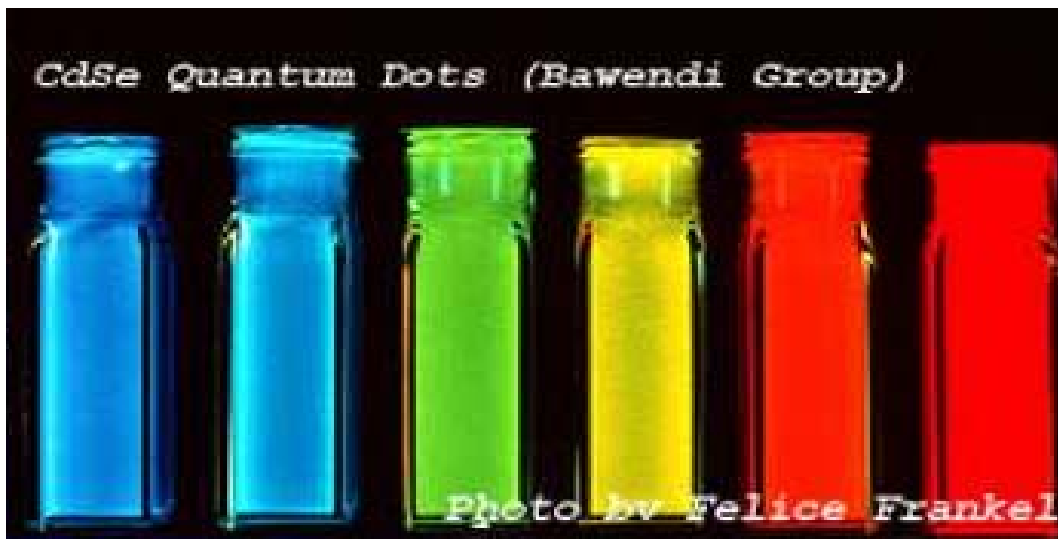
## Why???

- 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

# Nanoscience with Synchrotron Radiation



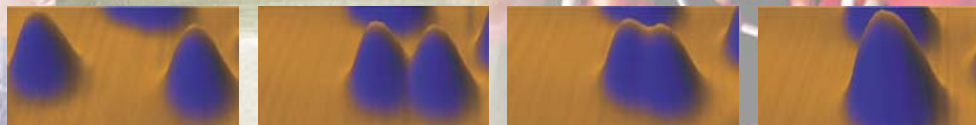
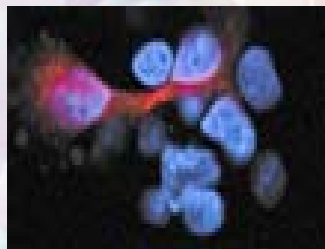
## Why and How ?



**Crystal size determines color (quantum confinement)**

# THE MOLECULAR FOUNDRY

**A Nanostructures User  
Laboratory at Lawrence Be  
National Laboratory**



# Goals - Molecular Foundry



- Provide scientists and engineers from all disciplines and institutions with the capability to design and develop advanced **new materials based on nanoscale patterning and control**
- **Educate** and train the first generation of nanoscale scientists
- Push the state-of-the-art in **nanoscale materials synthesis**
- Provide the means to **solve important problems in energy science**

## 1. Spectroscopy (In-Situ)

Photoemission Spectroscopy (upto 10 torr)

Absorption Spectroscopy (also with EPU & mag field  $\sim 1$  T; any dir.)

Emission Spectroscopy - (nano science characterization chamber)

## 2. Microscopy

Scanning Transmission Microscope (STXM; Res $\sim 30$ nm)

Transmission Imaging Microscope (XM1/2; Res  $\sim 15$  nm)

Photoemission microscope (PEEMII/PEEMIII : Res  $\sim 10$ -50nm)

lensless (diffractive) imaging (goal : single molecule imaging?)

## 3. Scattering

Resonant Scattering

Resonant Inelastic Scattering (res  $\sim 3$ -4meV @ Mn/Cu 3p edges;  
MERLIN beamline)

Coherent (dynamic) Scattering; presence of filed

Small angle scattering (SAXS, time-resolved; s to ms)

# Nanoscience: Electronic Structure Determination - Techniques of choice



*Need, in situ, investigation of:*

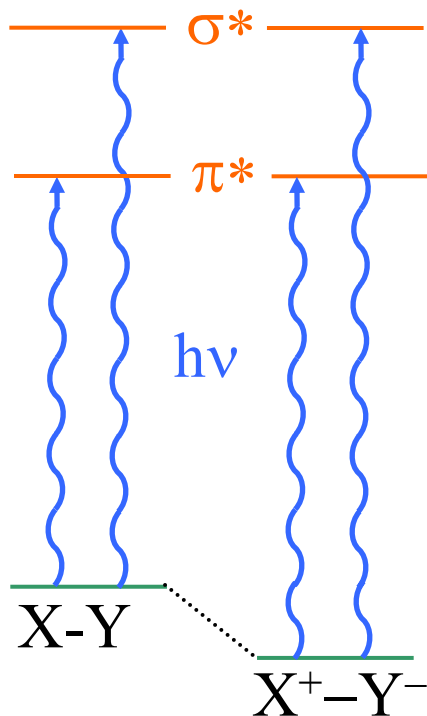
- **Valence orbital** (bonding, energy gap)
- **Core level** (charge transfer, elemental/chemical specificity)

**How?**

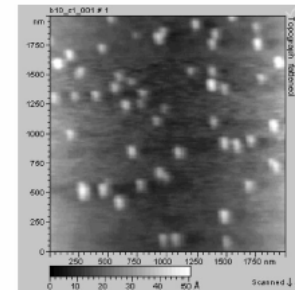
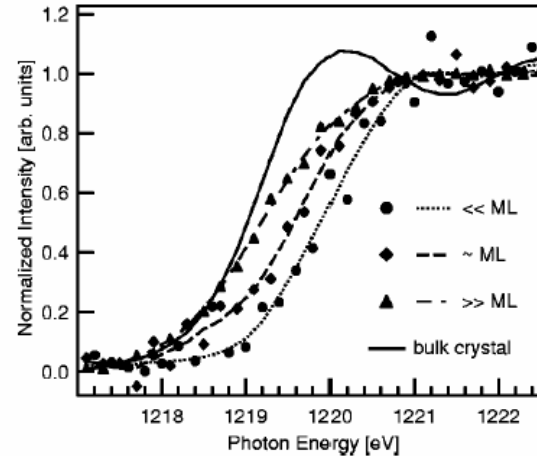
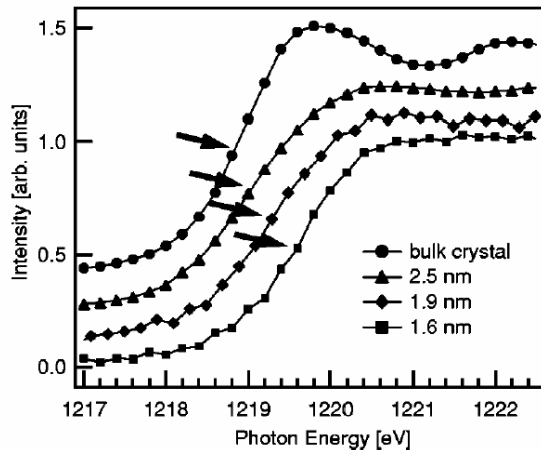
- Unoccupied bands are studied by **Absorption Spectroscopy**
- Occupied bands are studied by **Emission Spectroscopy and Photoelectron Spectroscopy**

- Use of polarizations allows to probe the orientation of molecules on surfaces

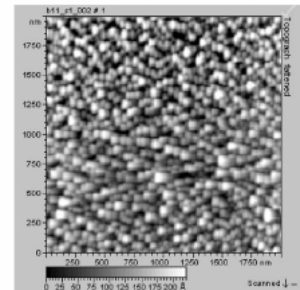
**Requires close coupling between theory and experiment**



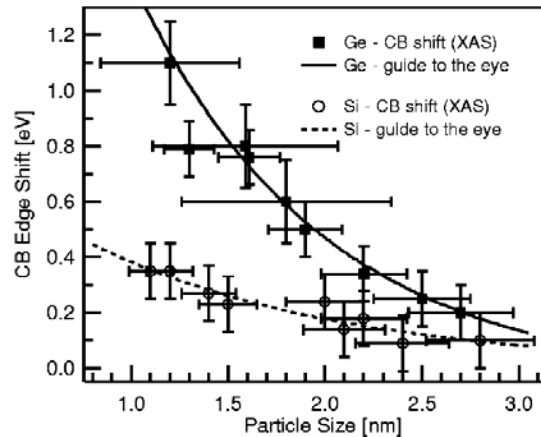
# Quantum-confinement effects and particle-particle interactions in Ge nanocrystals



sub-ML



multilayer

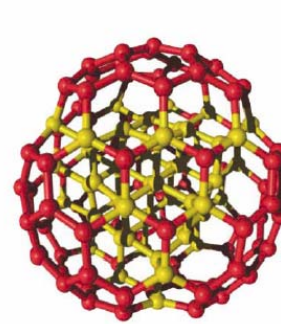
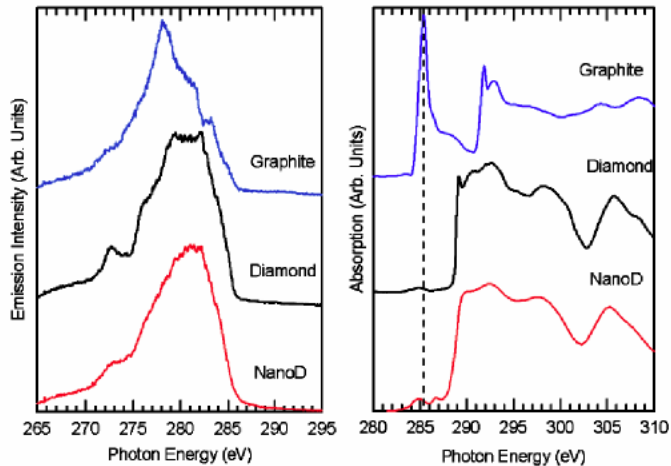


- Ge nanoparticles condensed out of the gas-phase and in situ characterized by Ge L-edge XAS
- Particle-size determined post-situ by AFM
- Blue-shift of Ge L-edge correlated with decreasing cluster size and decreasing particle-particle interaction (subML to multilayer coverage)
- Stronger CB confinement effects observed in Ge than in Si nanoparticles.

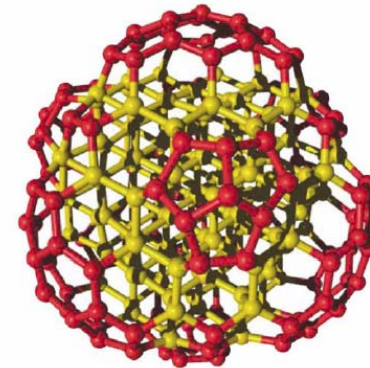
C. Bostedt et al. *APL* **84**, 4056 (2004) — LLNL PRT

C. Bostedt et al. *APL* **85**, 5334 (2004)

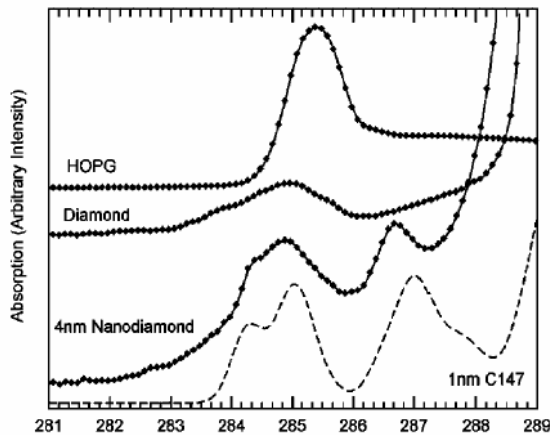
# Surface Reconstructions in Nanodiamonds



C<sub>147</sub> (≈1.2 nm)



C<sub>275</sub> (≈1.4 nm)



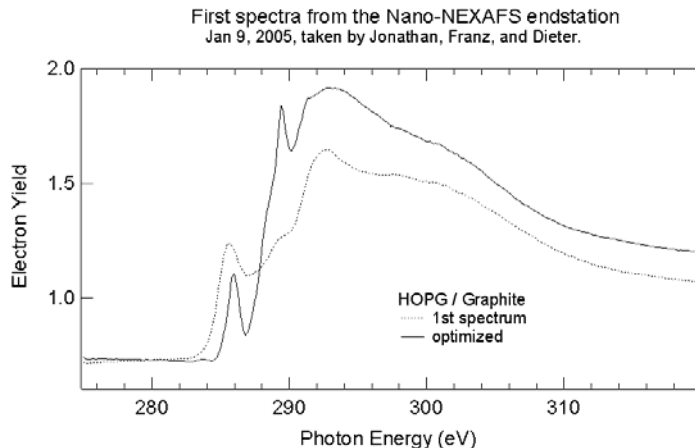
- Pre-edge Carbon K-edge structures observed in diamond clusters different from bulk diamond.
- Fullerene-like reconstructions determined at surfaces of diamond clusters by *ab initio* calculations compatible with pre-edge XAS

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

# Nanoscience Characterization Facility

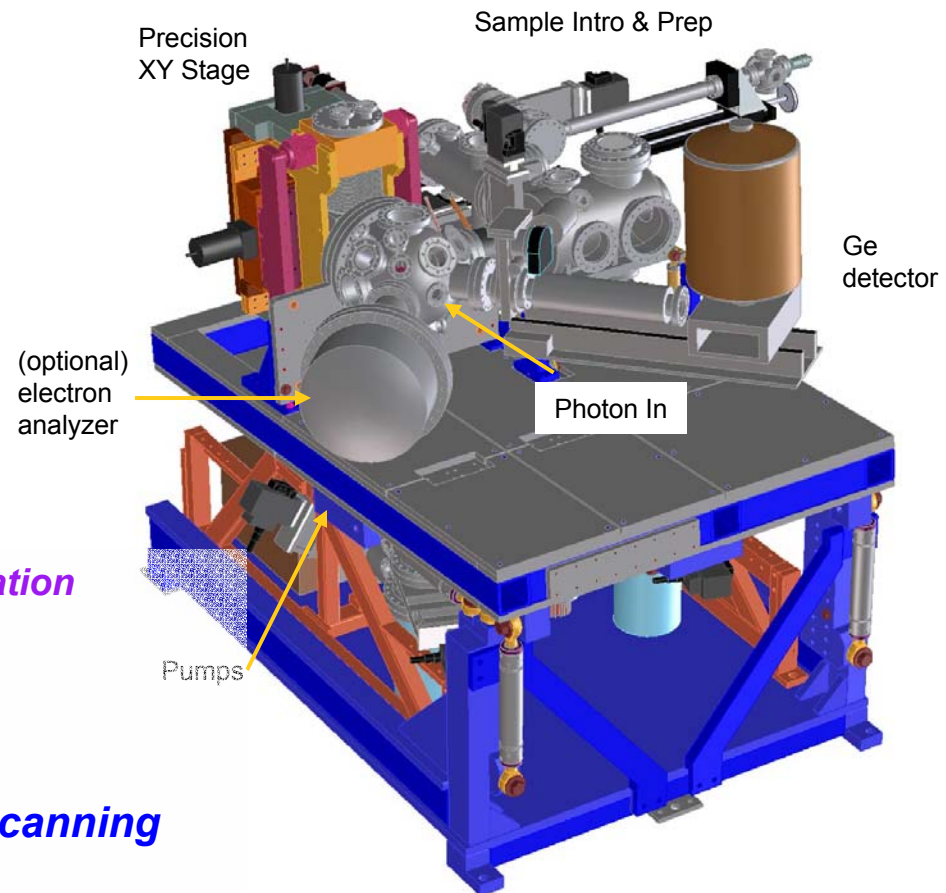


System is being commissioned



*“User-friendly for nanostructure characterization endstation” proposal funded by DOE (U. Wisconsin-Madison, F. Himpsel)*

- (1) Micro-focus (~10  $\mu\text{m}$ ) beam spot**
- (2) 2 inch travel micron-precision XY-scanning stage**
- (3) Efficient fluorescence yield detectors for XAS**
- (4) Emission Spectrograph (VLS)**
- (5) Photoemission (Scienta 100)**

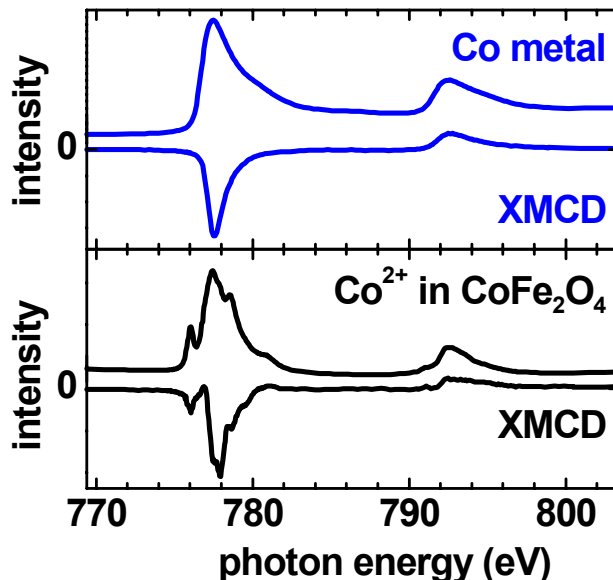
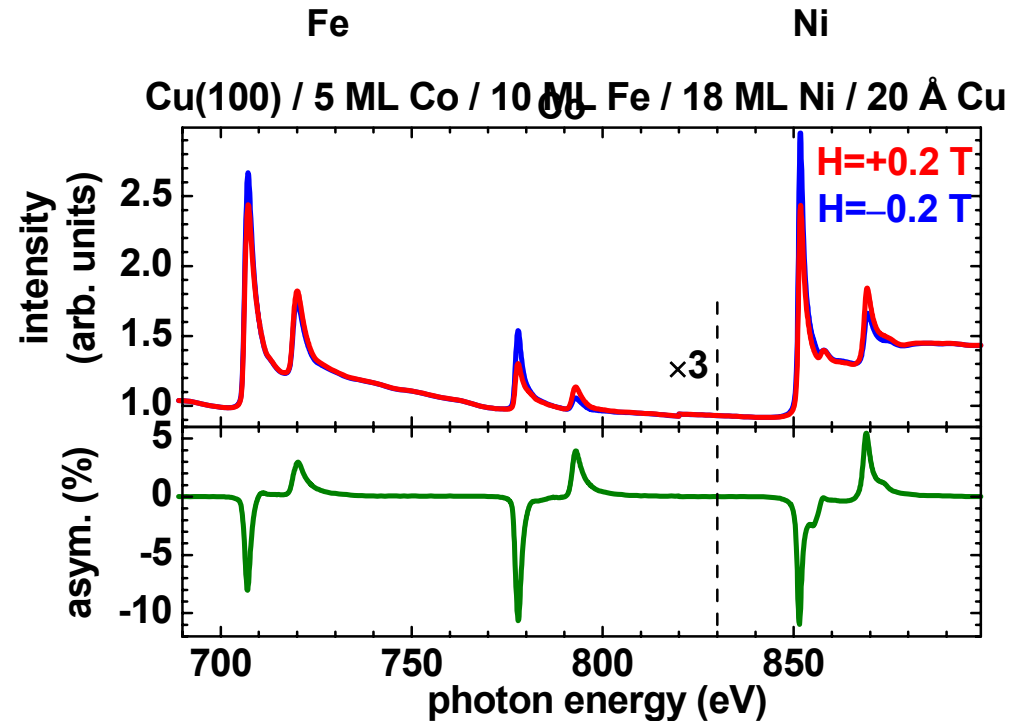


# SOFT X-RAY MAGNETIC DICHOISM



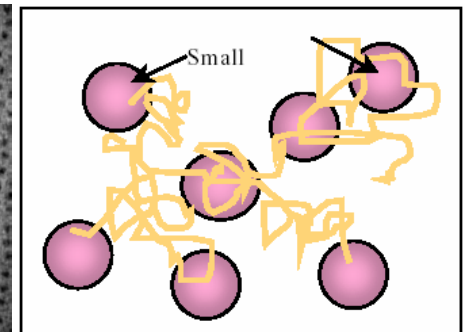
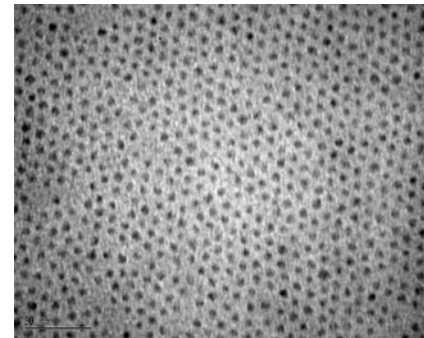
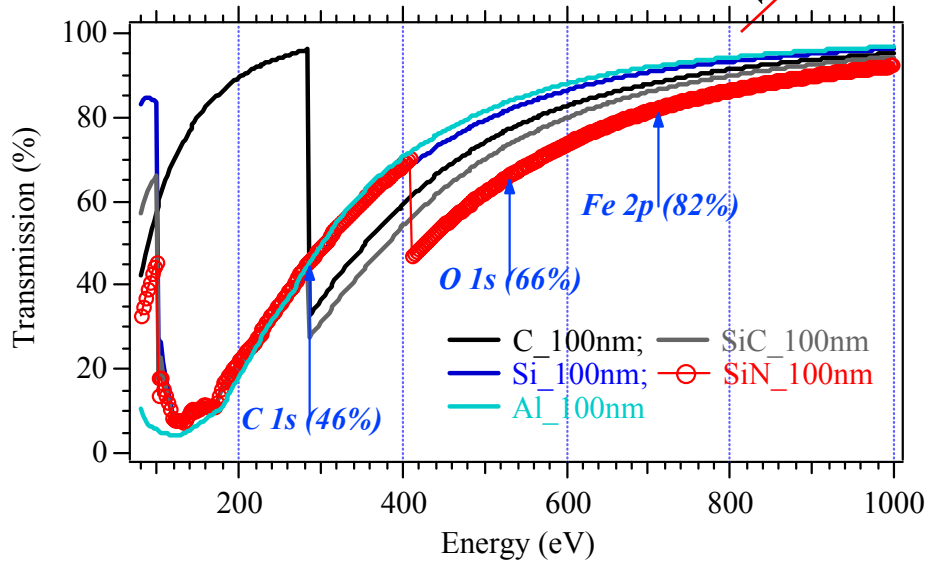
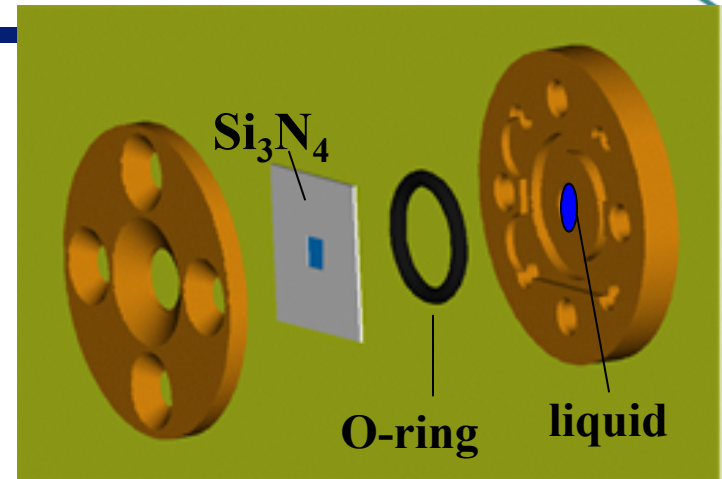
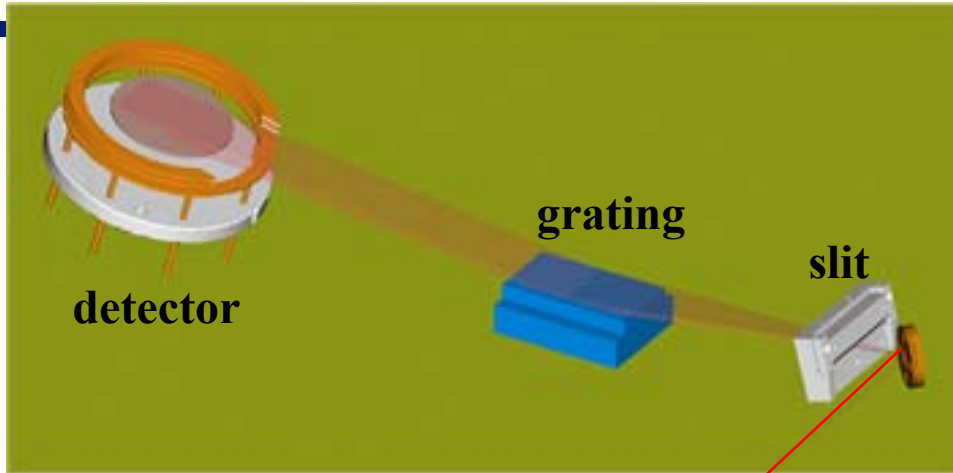
## Soft x ray magnetic dichroism

- **element-specific**
- **chemical site sensitive**
- **high sensitivity** to small moments
- **allows to determine quantitatively orbital and spin moments, anisotropy constants etc. using sum rules.**



- **X-ray magnetic circular dichroism XMCD**  $\propto \mathbf{k} \cdot \mathbf{M}$ , i.e. magnetic moment along photon momentum direction  $\mathbf{k}$
- **X-ray magnetic linear dichroism XMLD depends only on  $M^2$** , i.e. antiferromagnetic systems can be studied

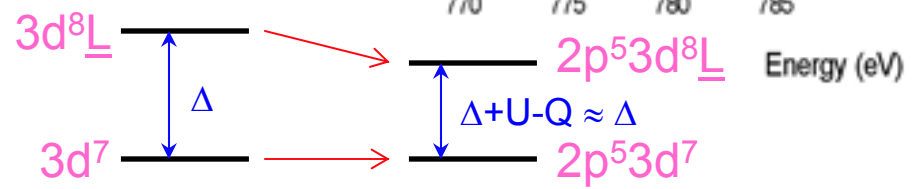
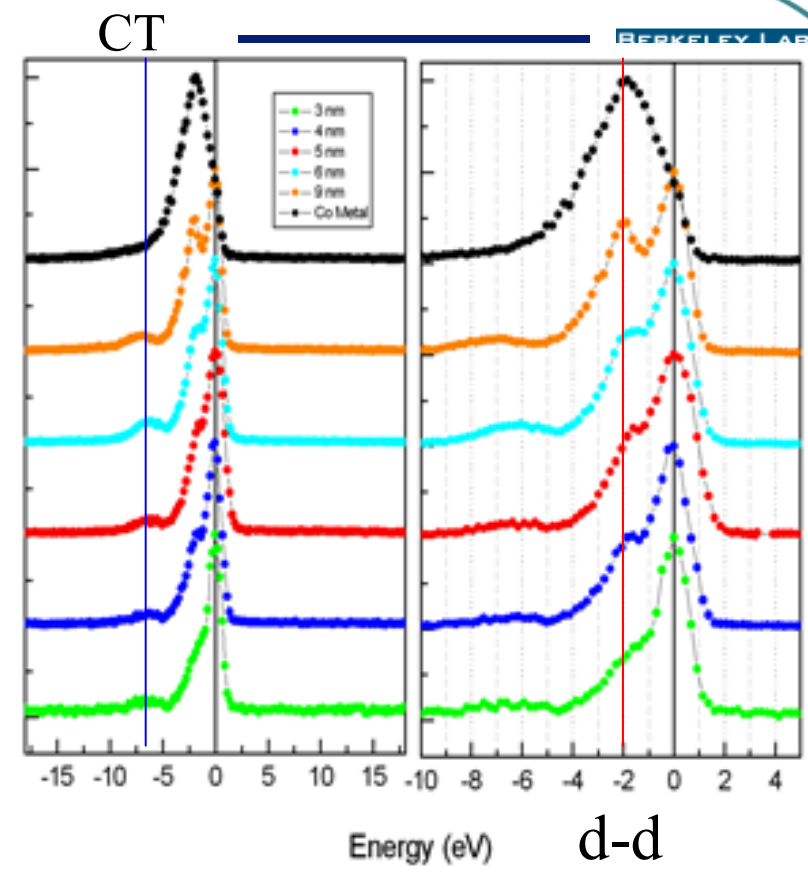
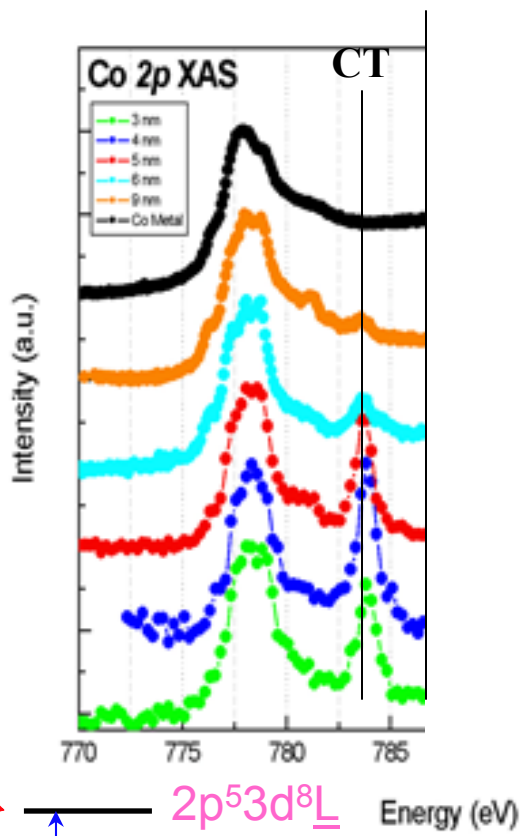
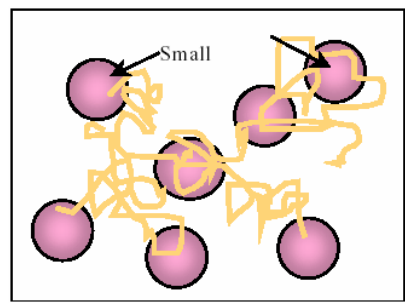
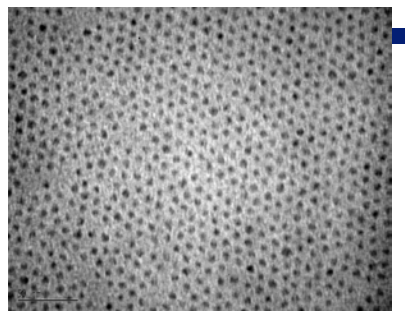
# Liquid Cell - Static



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

100nm  $Si_3N_4$ , ~4  $\mu l$  liquid volume, 66% transmission  
@O1s, vacuum pressure  $< 1 \times 10^{-9}$  Torr

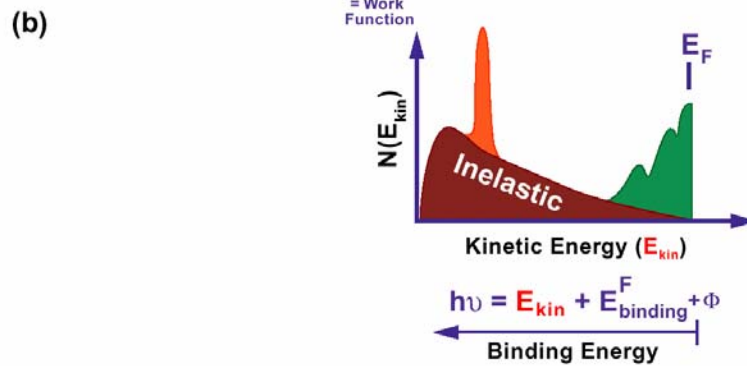
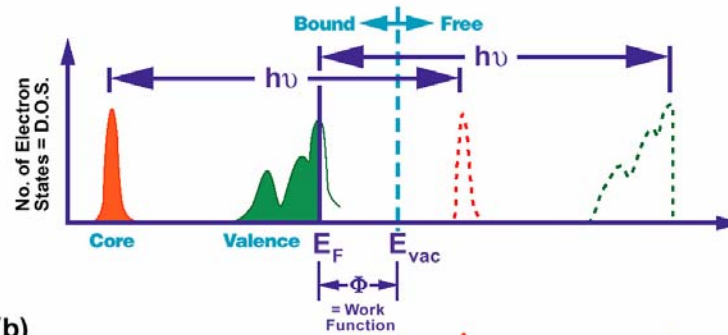
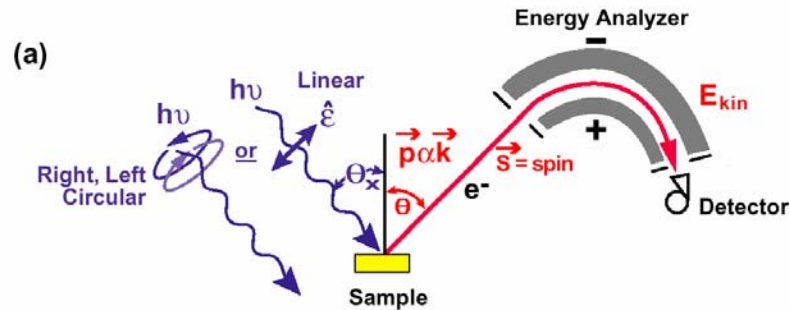
# In-situ analysis of Co nanoclusters in solution



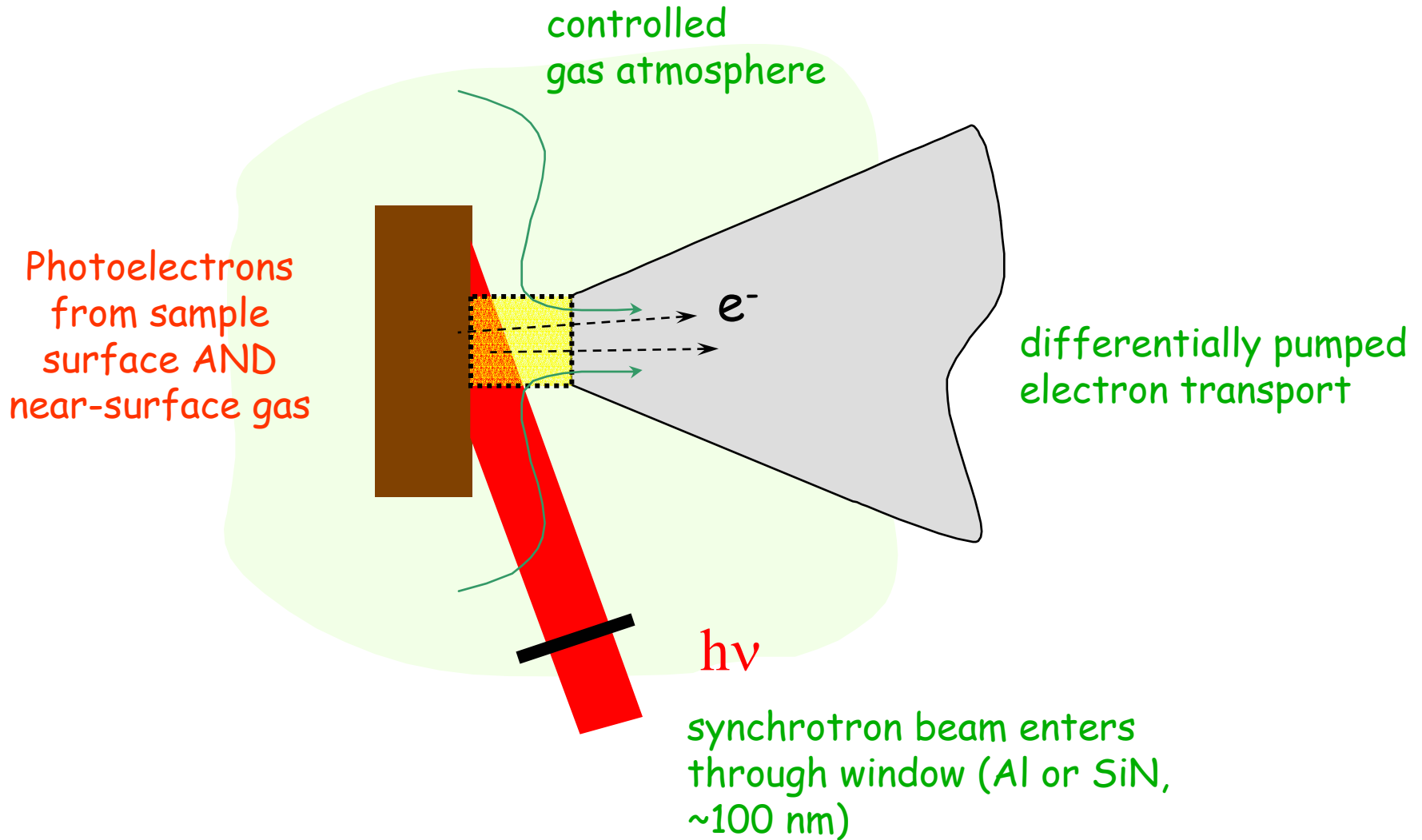
$$I_{d-d} \sim N_{\text{bulk}} / N_{\text{surface}}$$

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

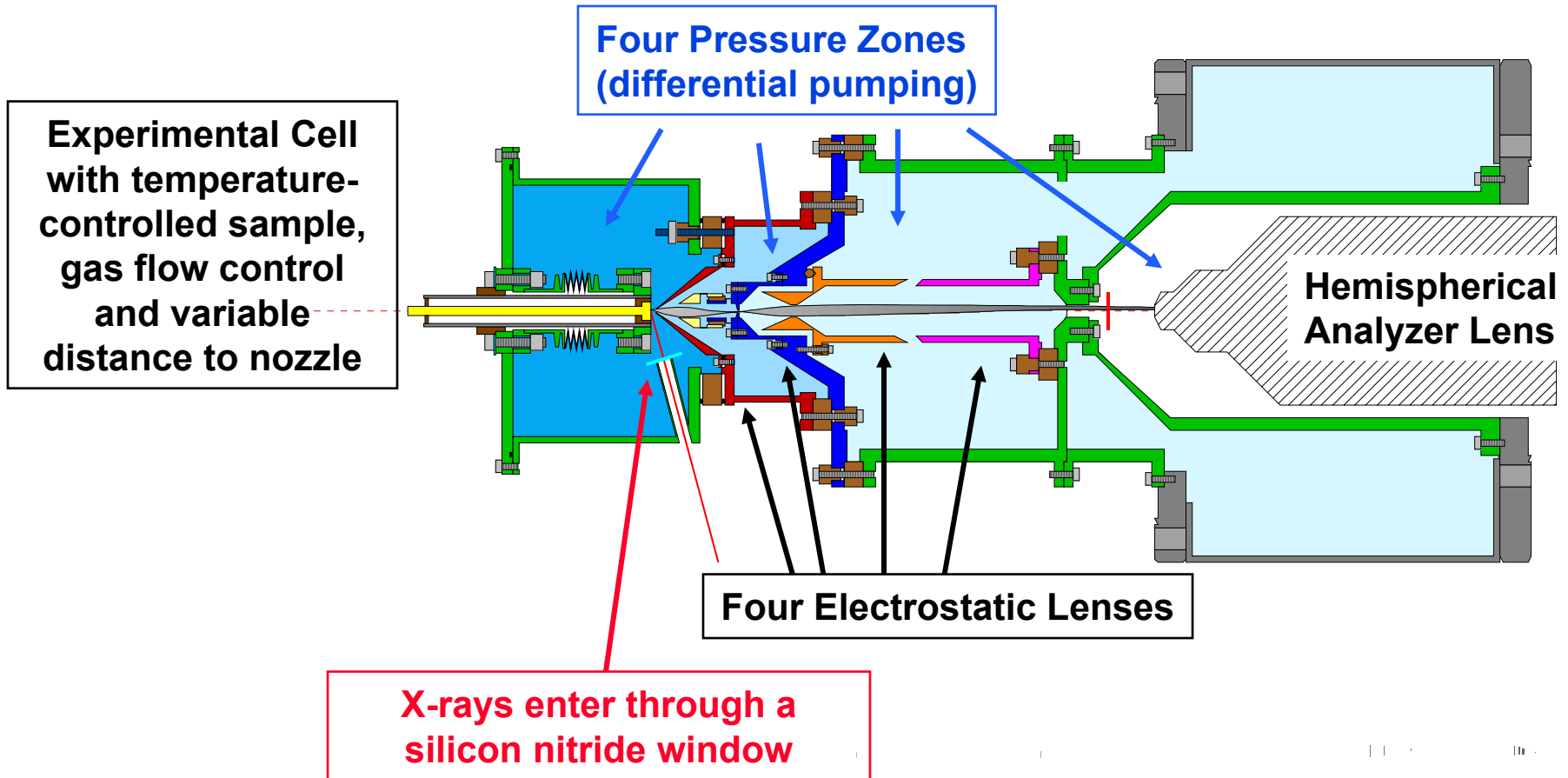
# Photoelectron Spectroscopy



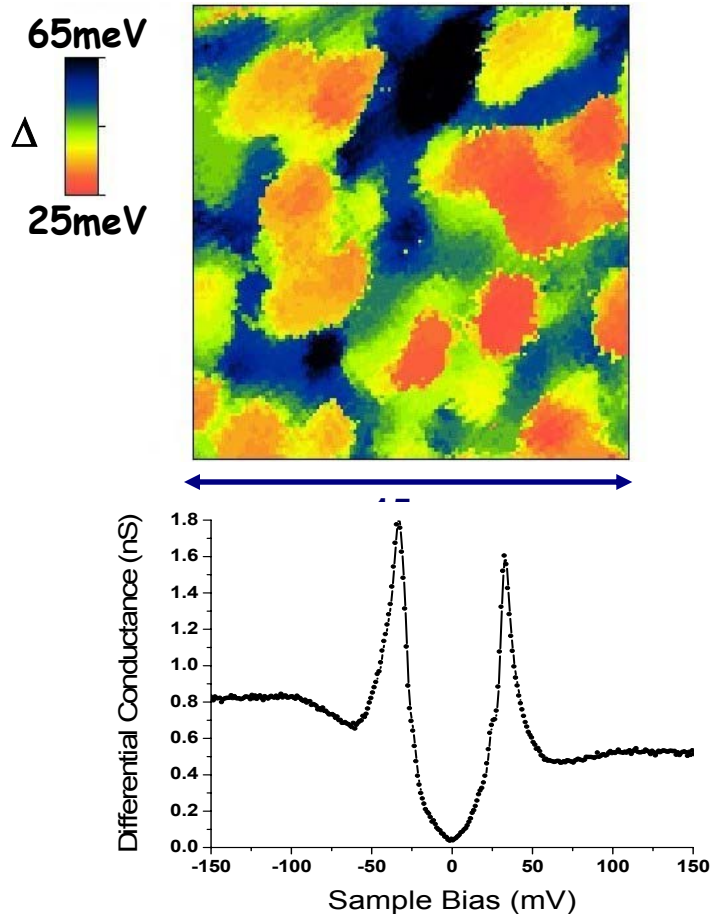
# Ambient pressure soft x-ray spectroscopy: Concept



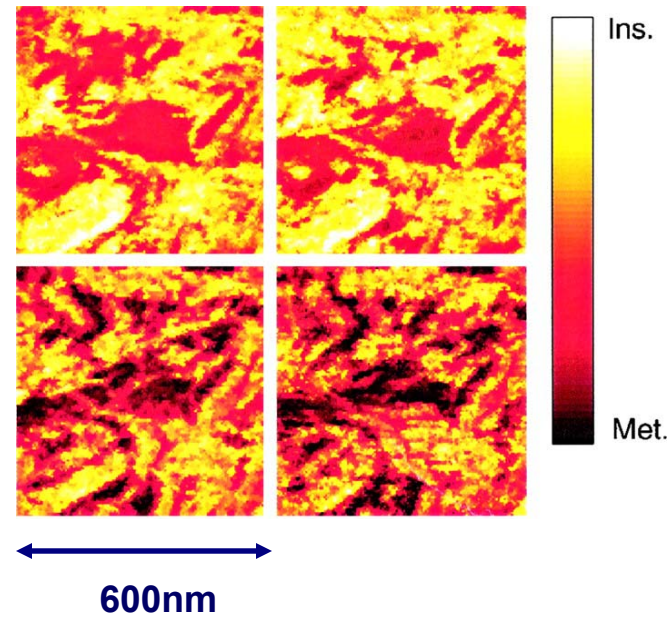
# High Pressure Transfer Lens - Schematic



# Nanoscale electronic disorder in Correlated Systems (STM)



Spatial distribution of energy gap ( $\Delta$ ) in Bi2212 (High Tc materials)

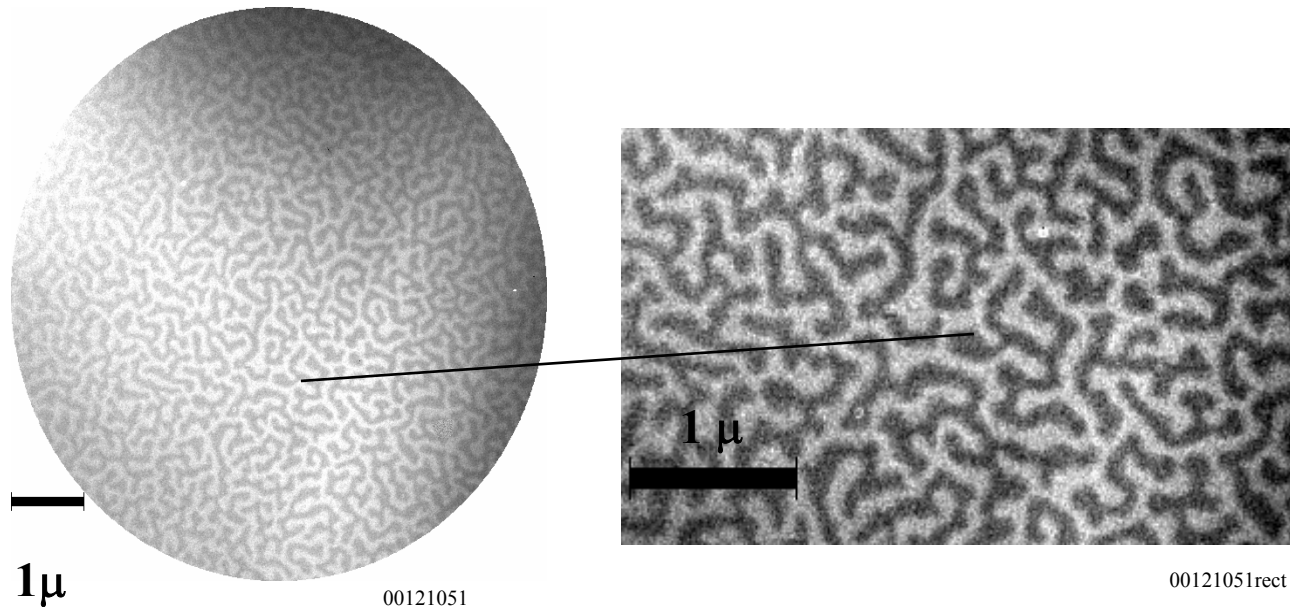


Metal-Insulator transitions in the CMR material La Ca MnO<sub>3</sub>

Energy scale:  $\sim 10$  meV  
Length scale: 2 - 100 nm

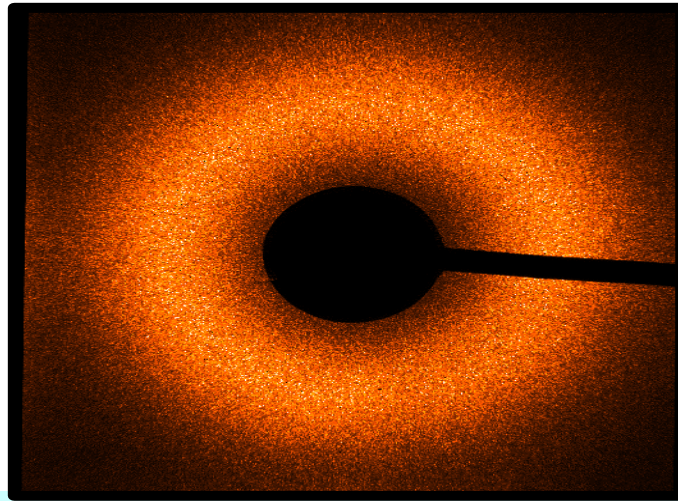
Ch. Renner et al, Nature, 416, 518 (2002)

# Imaging Magnetic Domains with a Soft X-ray Microscope



- Contrast provided by huge magnetic circular dichroism near the Co  $L_{23}$  absorption edge [ $2p_{3/2} - 3d$ ] at  $h\nu \sim 780$  eV
- Wavelength  $\lambda \sim 15.8$  Å allows good spatial resolution

# Soft X-ray Speckle Pattern of a Pt:Co Multilayer

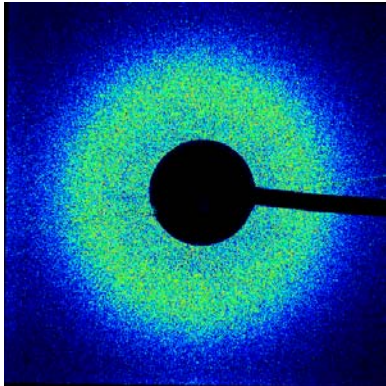


- Speckle pattern  $\equiv$  diffraction pattern of the magnetic domain structure;
- Domain sized inversely related to angular width of the 'doughnut';
- Contrast provided by x-ray magneto-optic effects near the specific atom L- absorption edge;
- New facilities will enable measurement of the individual Fourier components fluctuating at MHz time scales;

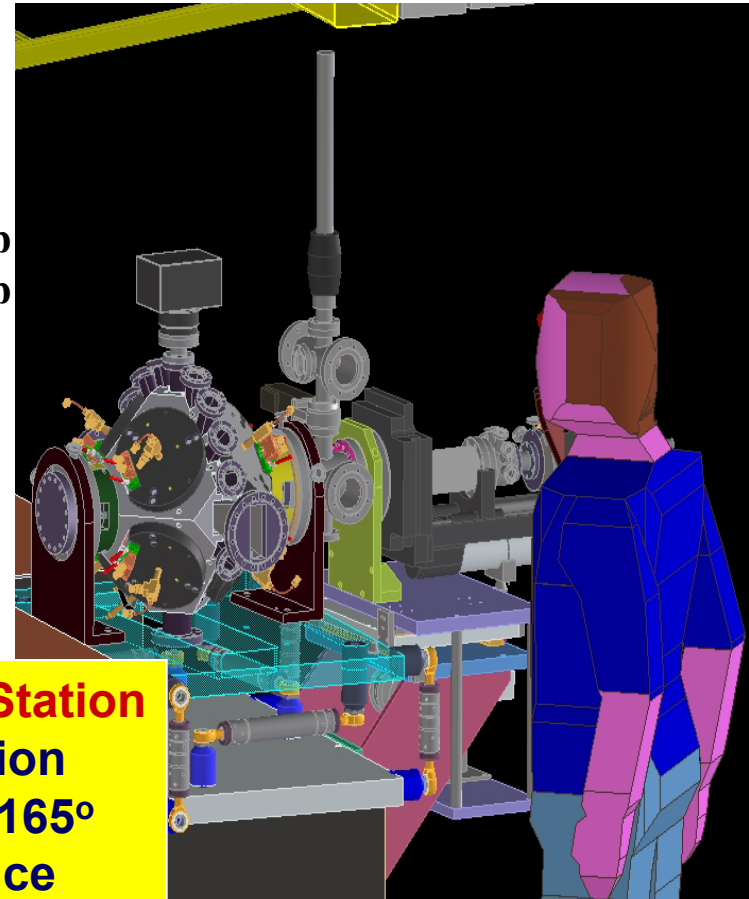
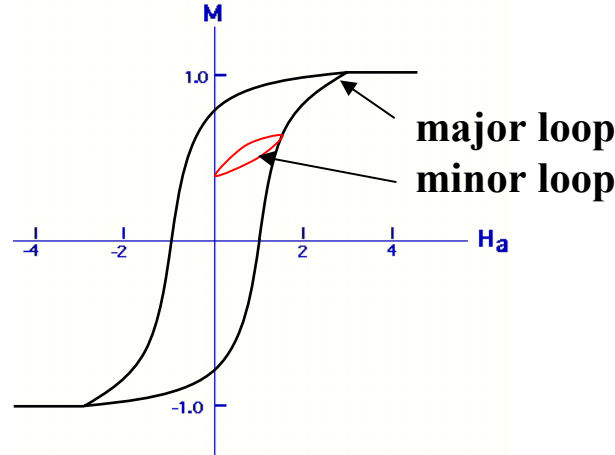
# Coherent soft-Xray Scattering – Dynamical Studies !!



- Soft x-rays:**
- More coherent flux - Scales like  $\lambda^2$  X brightness
  - 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.

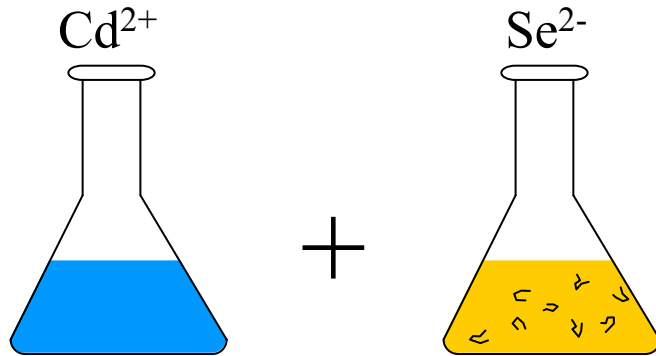


## Coherent Soft X-ray Magnetic Scattering End Station

- Applied field to 0.52 T of arbitrary orientation
- 'Continuous' scattering angle from 0° to ~ 165°
- Functional prototype for higher field device

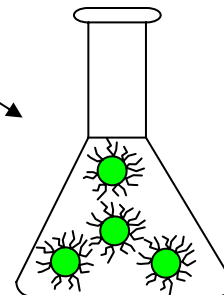
## Sample problem:

# self-assembly of CdSe nanoparticles



*Argument: Self-assembly is an important way to make macroscopic quantities of nano-materials. It is important to understand how it works.*

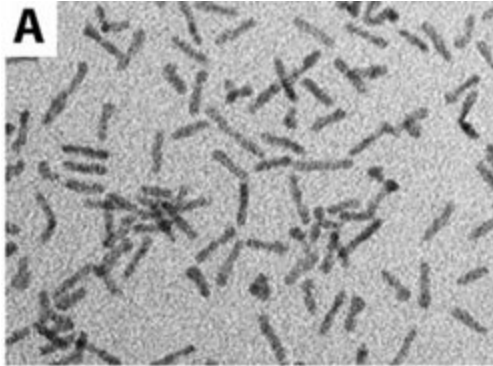
?



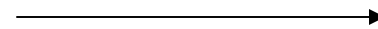
**What happened? How can it be controlled?**

# Other nanoparticle reactions of interest

CdSe

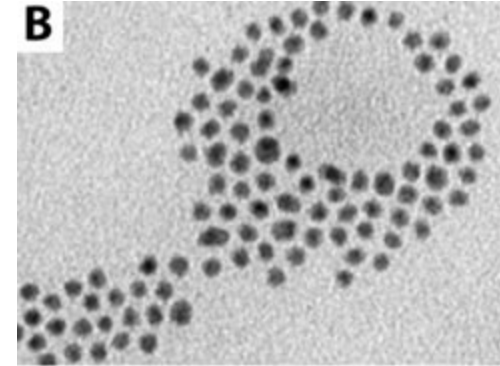


$\text{Ag}^+$ , millisecc.

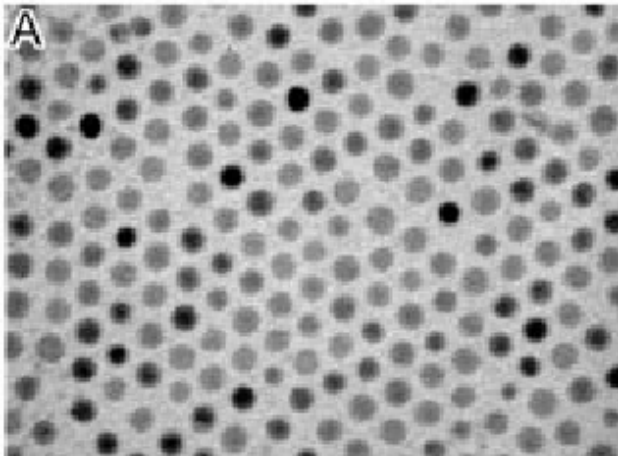


As seen in *Science Beat*

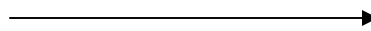
Ag<sub>2</sub>Se



Co

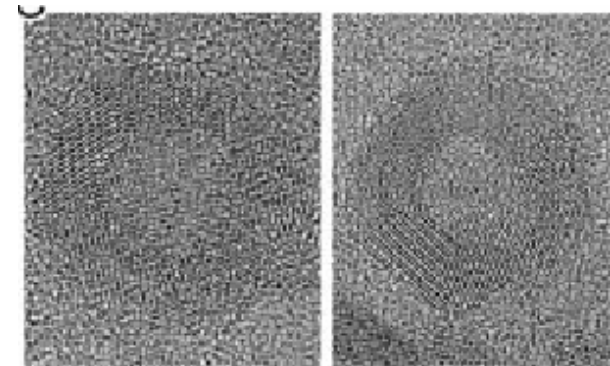


O<sub>2</sub>



As seen in *Science*

CoO<sub>x</sub>



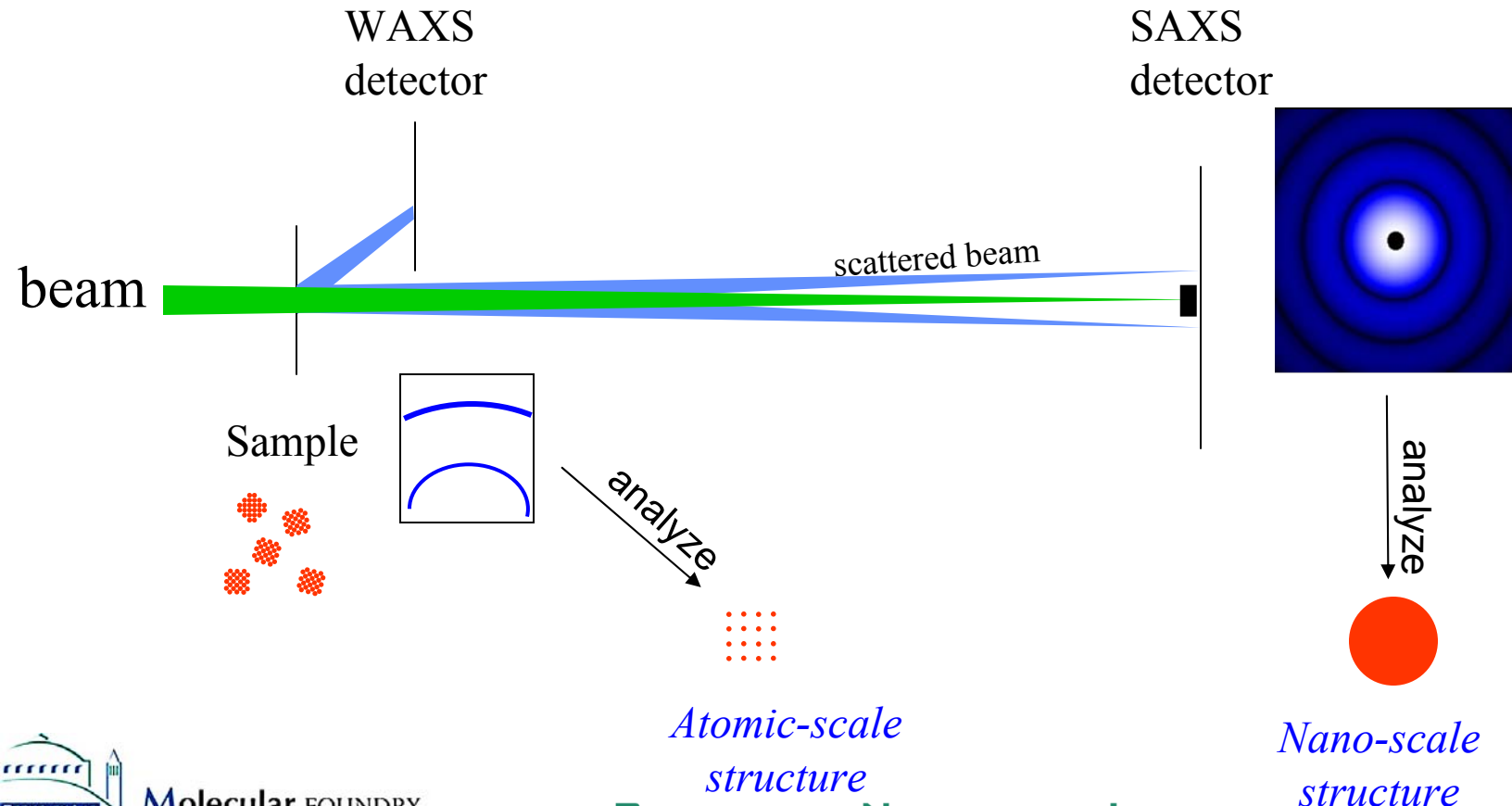
— 3 nm

# SAXS/WAXS - a quick review



SAXS = Small Angle X-ray Scattering ( $d > 1\text{nm}$ )

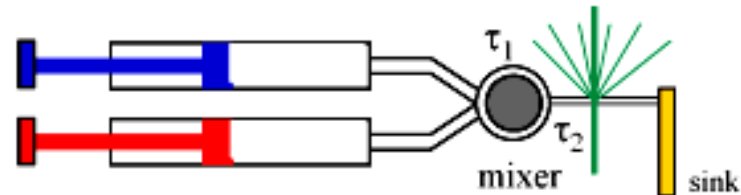
WAXS = Wide Angle X-ray Scattering ( $d < 1\text{nm}$ )



# Example of self-assembly

## *Self-assembly of micelles to vesicles*

Millisecond range SAXS & stopped-flow rapid mixing

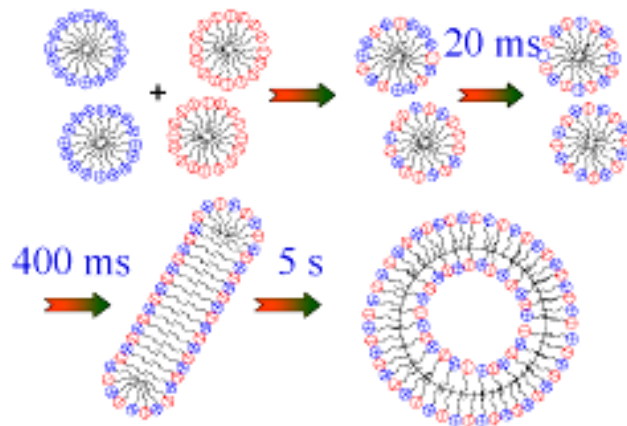


Structural intermediates

X-rays

spherical micelles

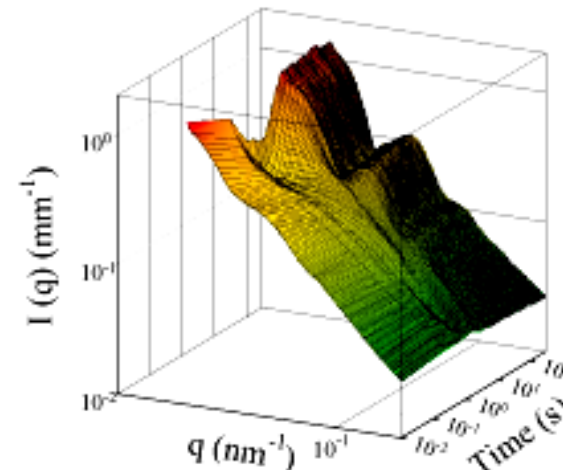
charge equilibration



elongated micelle

vesicle

Anionic TexaponN<sub>70</sub> H & cationic TTAOH micelles



Schmoelzer *et al.* *Phys.Rev.Lett.* **88**, 258301, (2002)

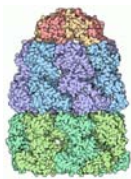
# Imaging of Biological Systems



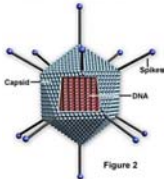
Size (m)  $10^{-8}$        $10^{-7}$        $10^{-6}$        $10^{-5}$        $10^{-4}$        $10^{-3}$        $10^{-2}$        $10^{-1}$       1



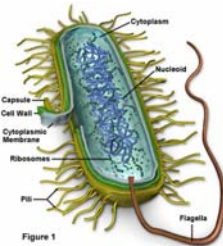
Molecules



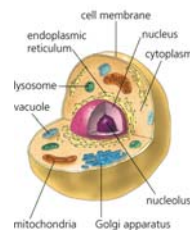
Complexes



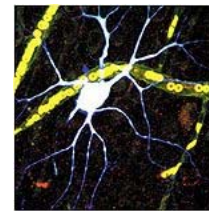
Viruses



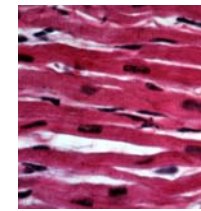
Bacteria



Cellular compartments



Cells



Tissues



Whole organisms

Cryo-electron microscopy

Light microscopy

MRI

**X-ray  
crystallography**

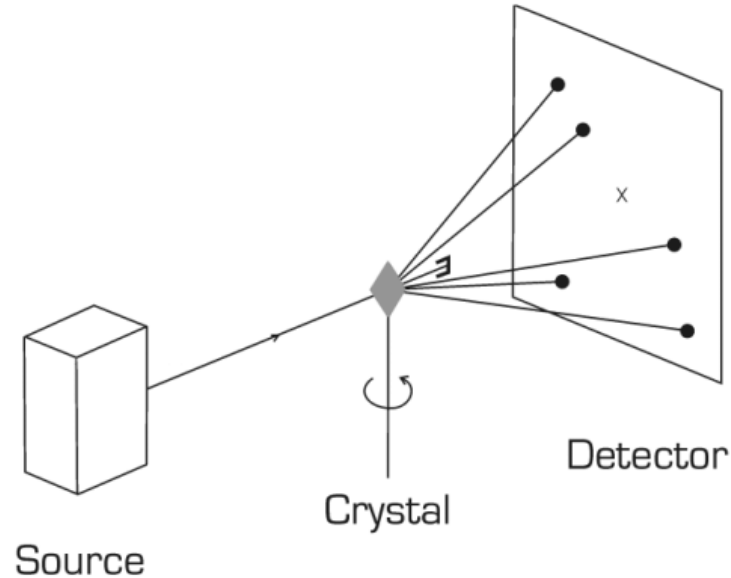
- atomic resolution
- needs protein crystals

**X-ray microscopy**

- 20 nm resolution
- thick objects (compared to EM)

# X-ray Crystallography

- Fixed energy beam
  - rotate crystal through small angle while recording data
  - repeat N times through large angle given by crystal symmetry

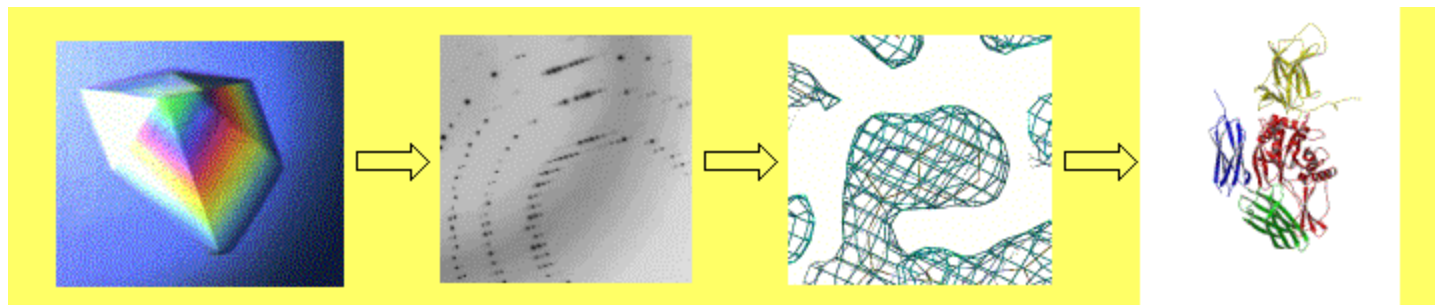


Crystal

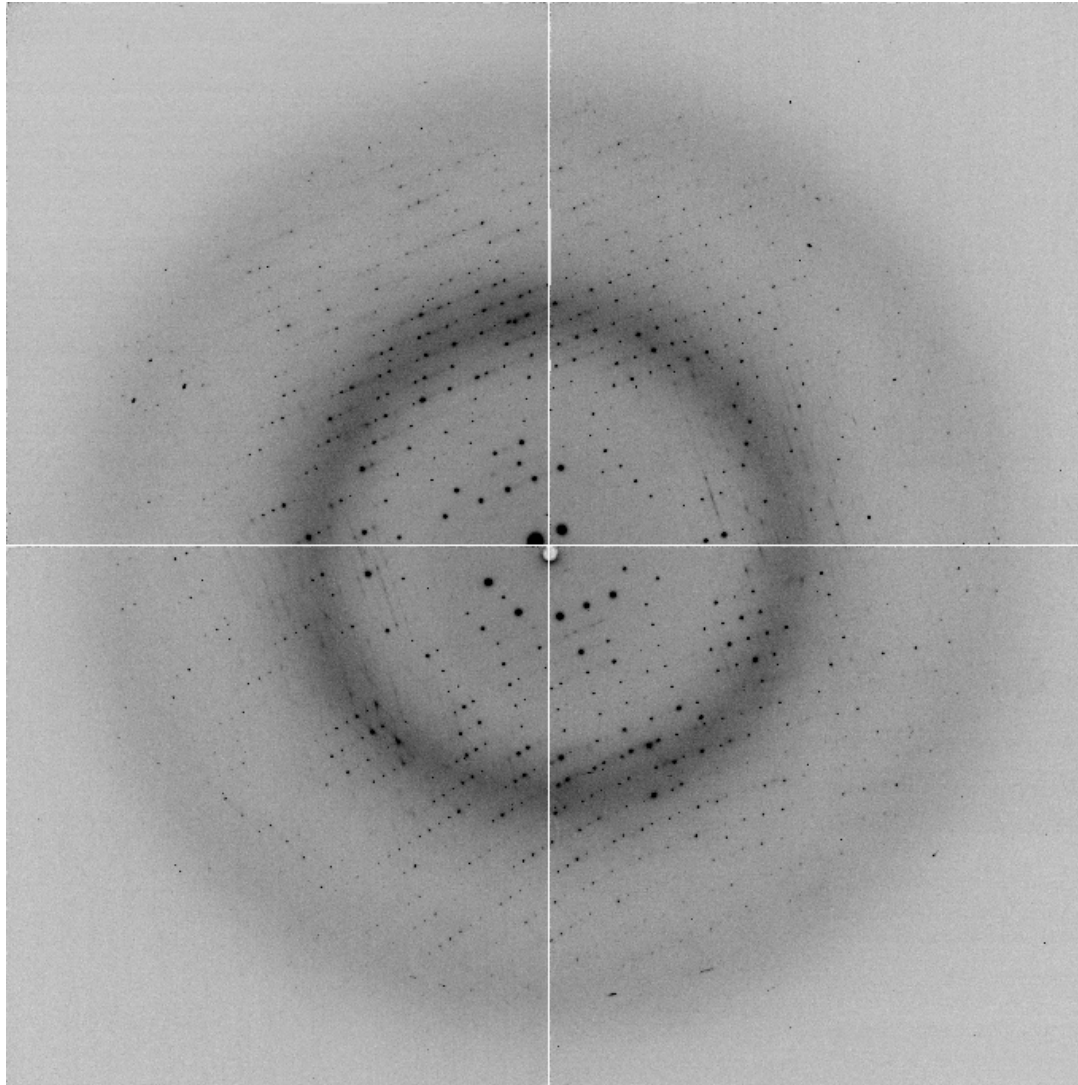
Diffraction data

Electron density

Model



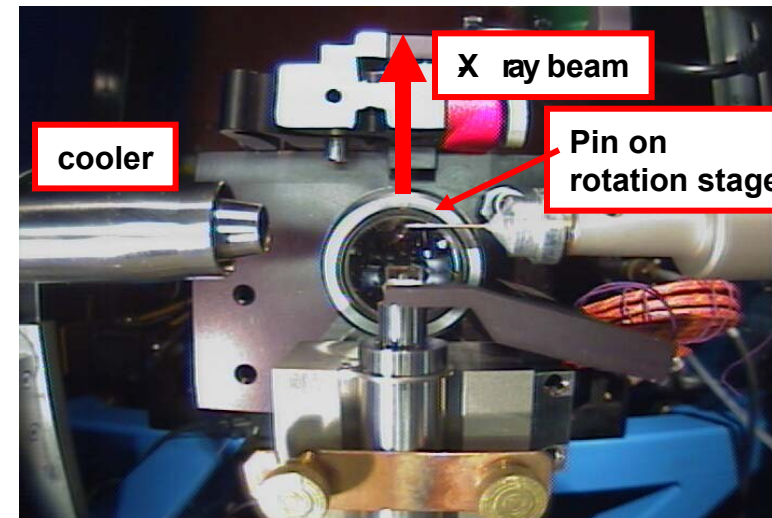
# X-ray Crystallography



Crystal in loop



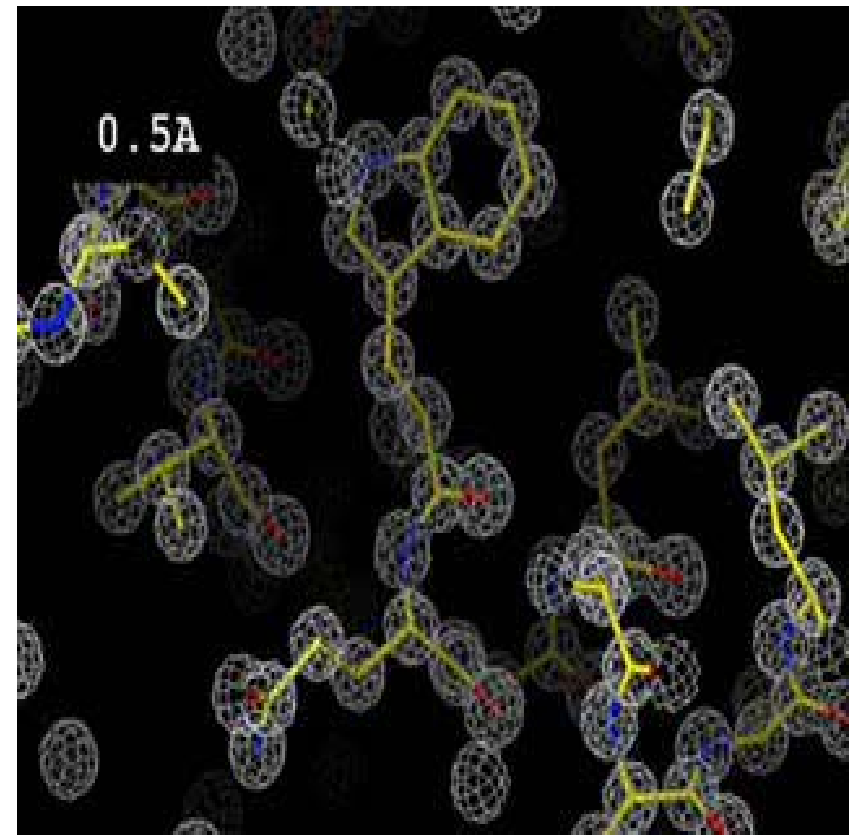
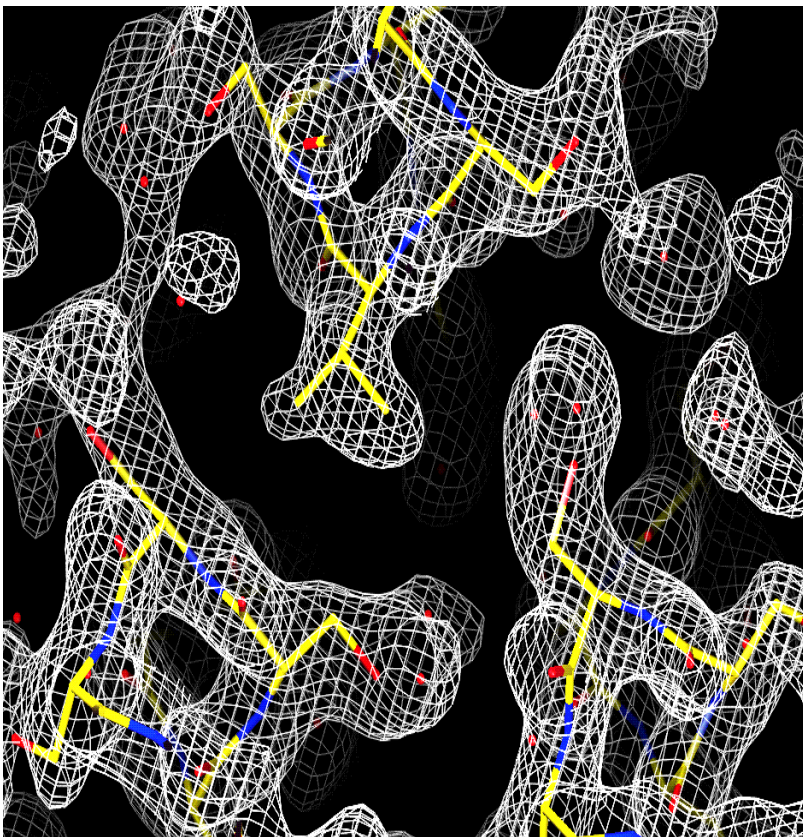
Loop on pin



# X-ray Crystallography

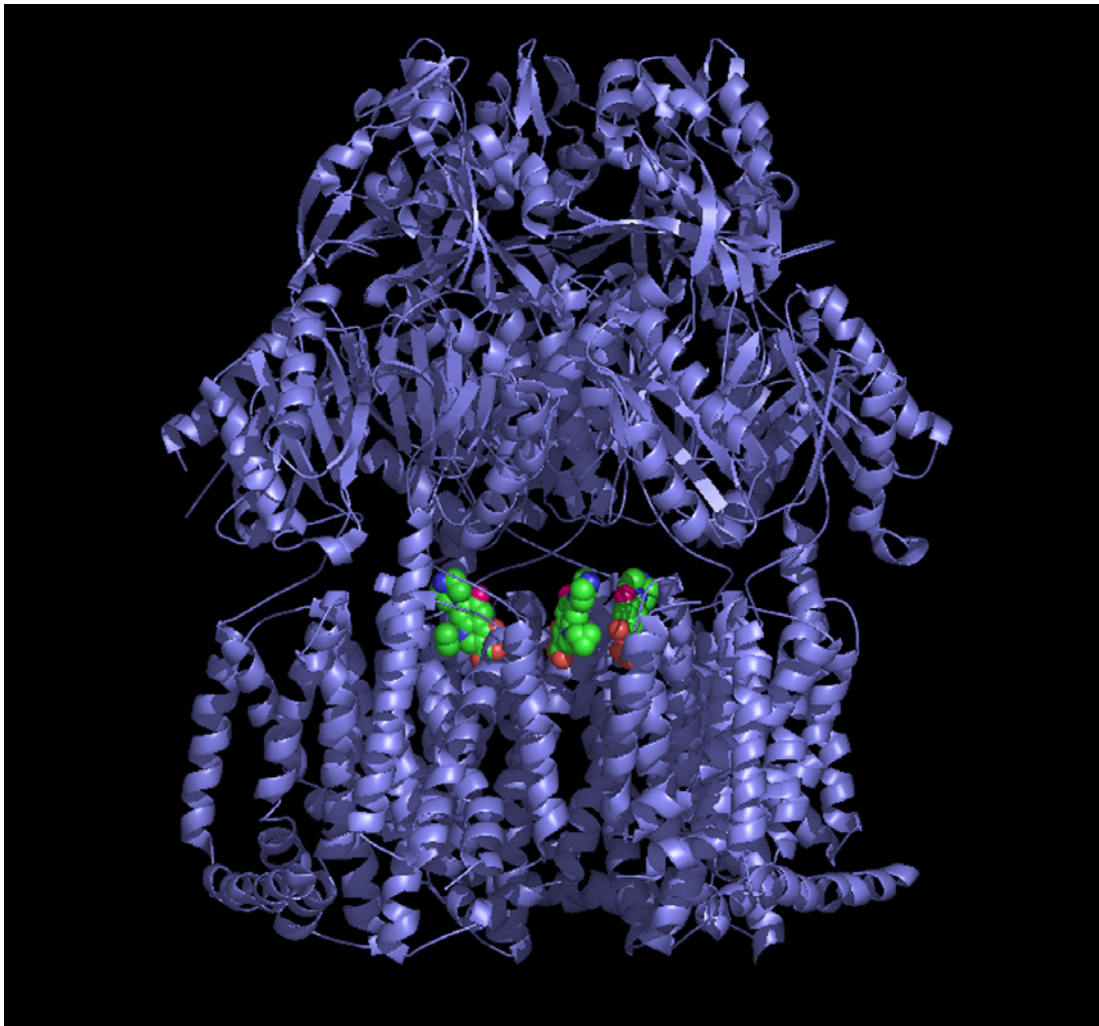


- determine electron density (i.e, recover phase information, MAD)
- fit known sequence information into electron density



# STRUCTURE OF THE AcrB PUMP

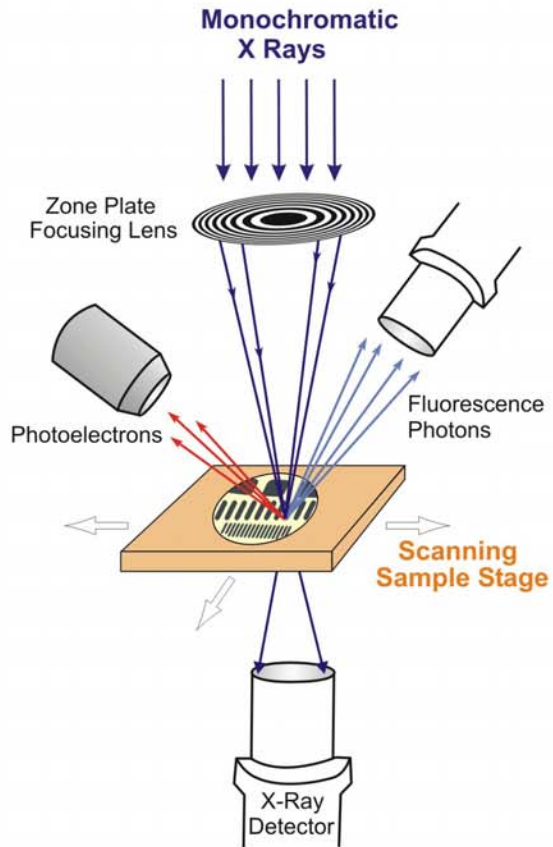
*Bacterial Drug Transporter Reveals Secrets of Drug Resistance*



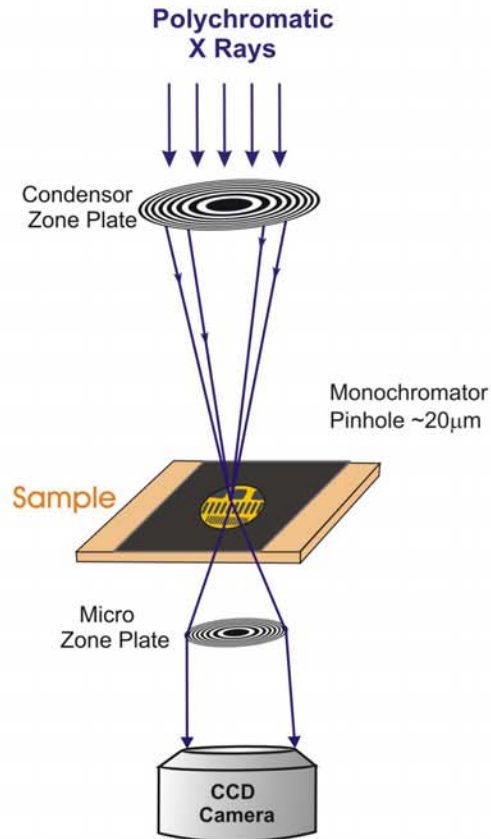
Even ciprofloxacin, an antibiotic used to treat a variety of bacterial infections including inhaled anthrax, is no match for AcrB. In this image, the green-colored drug is firmly ensnared in the protein's cavity.

# X-ray Microscopes

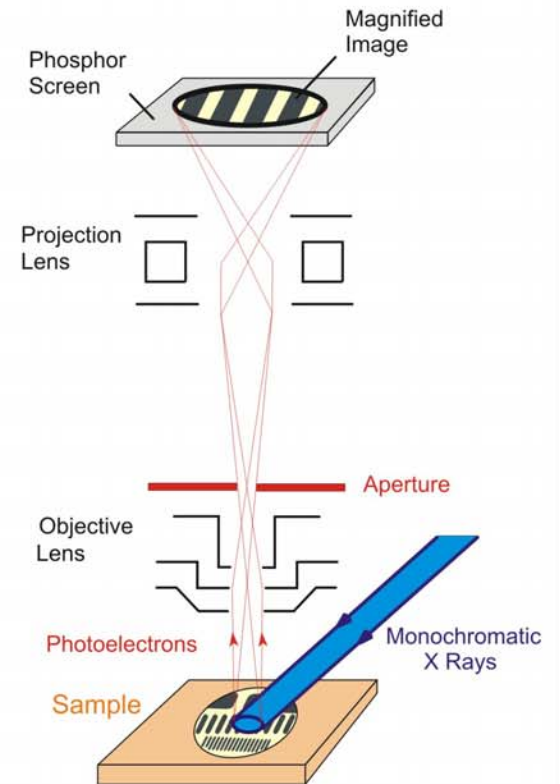
## Scanning Transmission X-ray Microscopy STXM

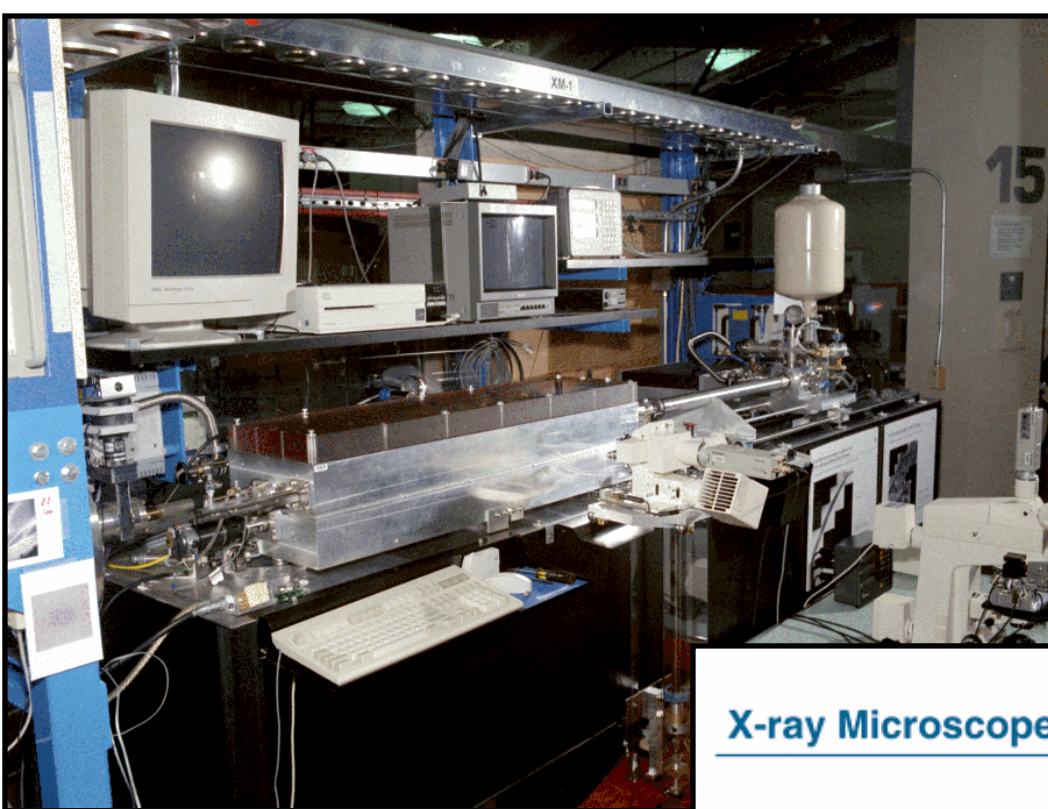


## Transmission X-ray Microscopy TXM



## X-ray Photoemission Electron Microscopy XPEEM





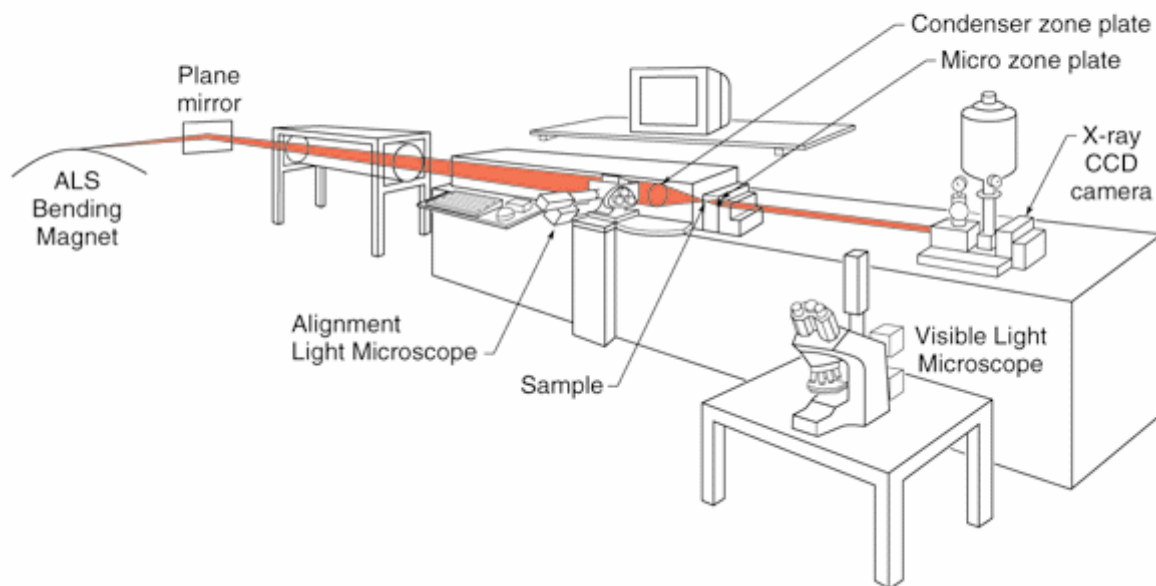
Beamline 6.1.2  
Full-field Transmission X-ray  
Microscope (XM-1)

Wavelength, 2.4 nm  
Photon energy, 517 eV

Center for X-ray Optics

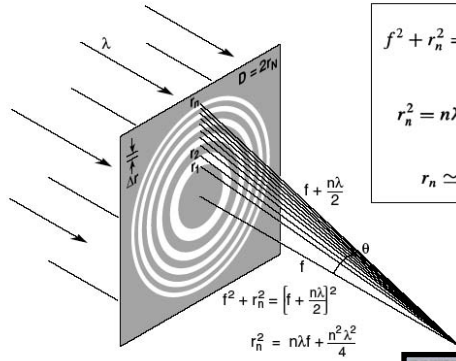
Erik Anderson  
David Attwood

X-ray Microscope XM-1





# Zone Plate Lenses 20 nm Resolution



$$f^2 + r_n^2 = \left(f + \frac{n\lambda}{2}\right)^2 \quad (9.8)$$

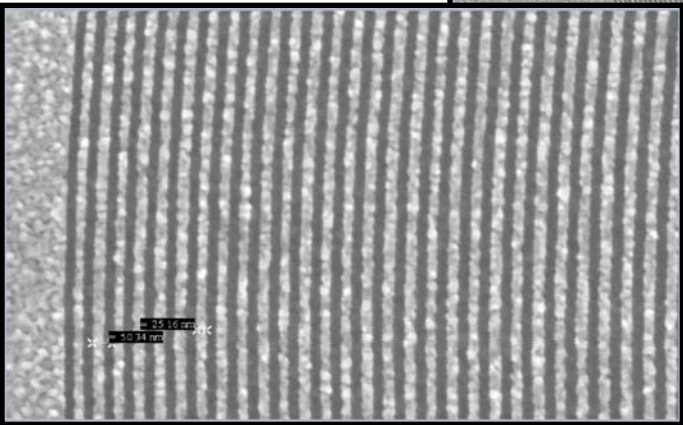
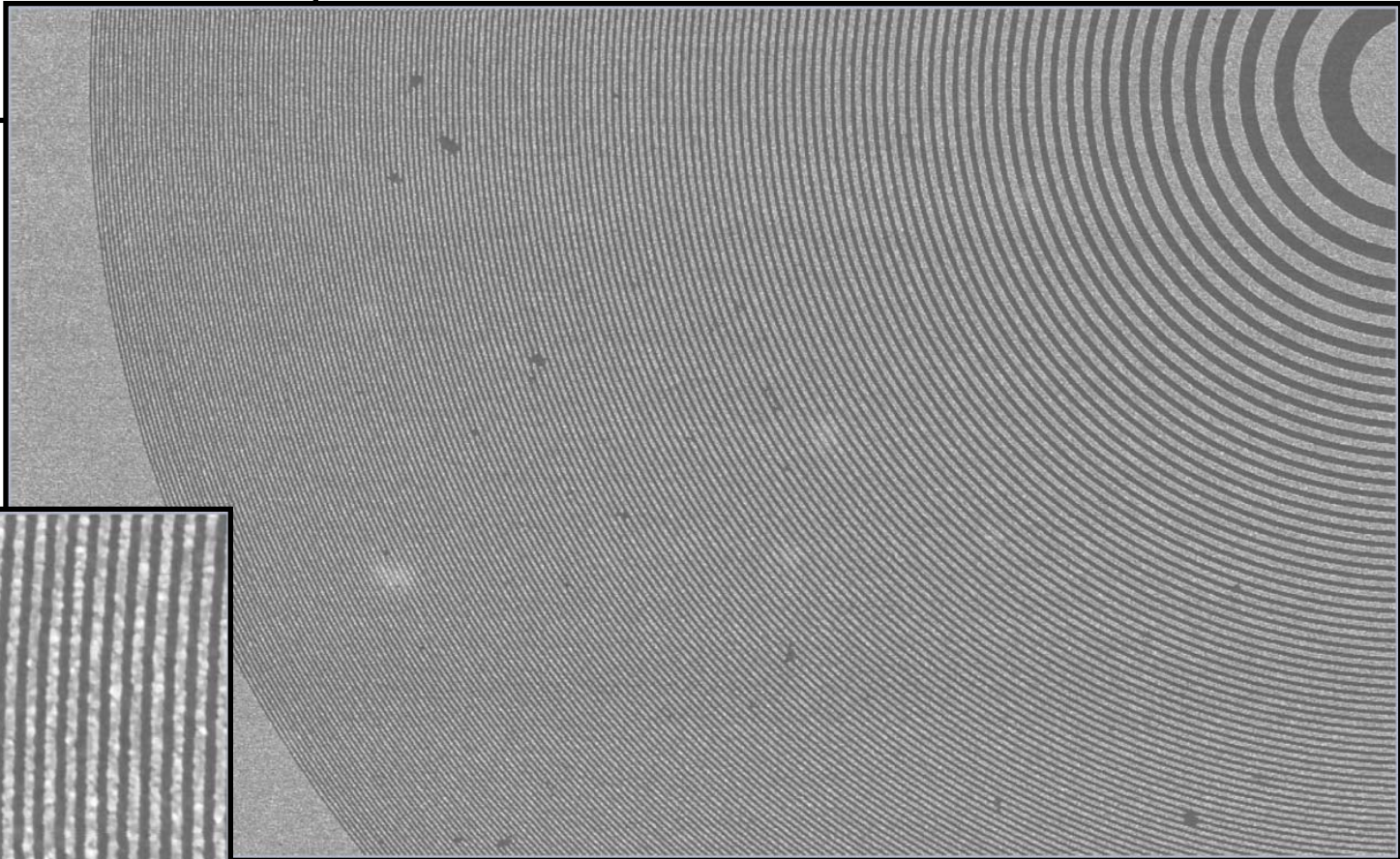
$$r_n^2 = n\lambda f + \frac{n^2\lambda^2}{4} \quad (9.9)$$

$$r_n \approx \sqrt{n\lambda f} \quad (9.10)$$

E. Anderson, D. Attwood, A. Liddle, D. Olynick, B. Harteneck, W. Chao; Center for X-ray Optics

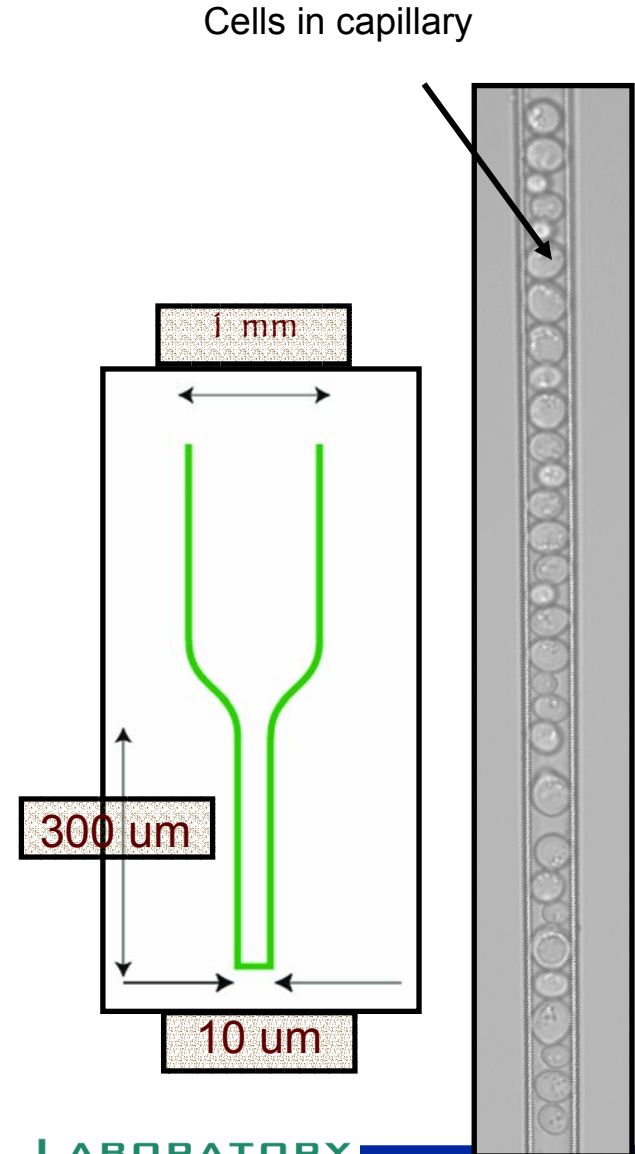
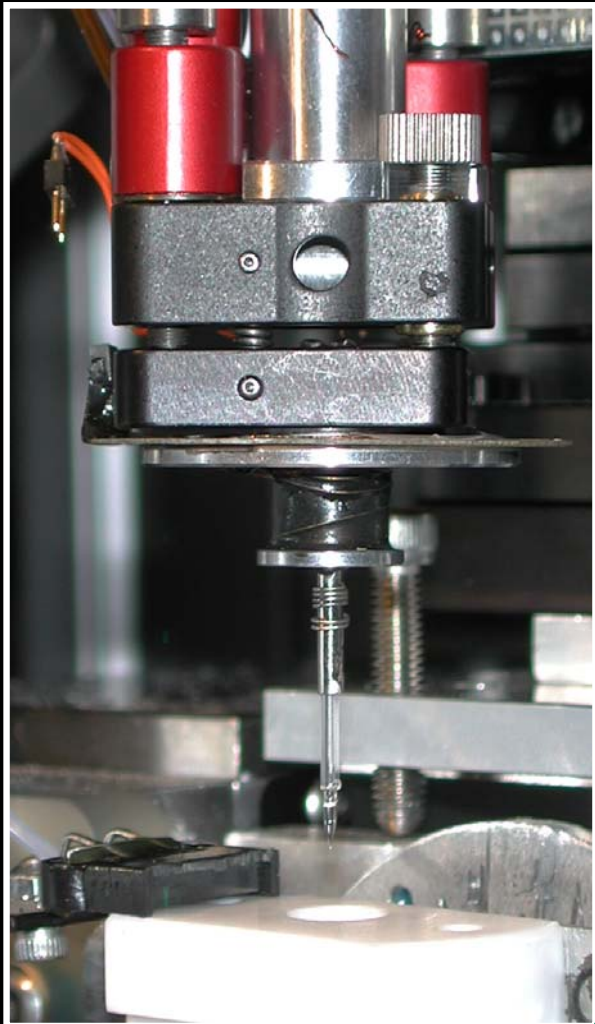
Professor David Attwood  
AST 210/ECS 213  
Univ. California, Berkeley

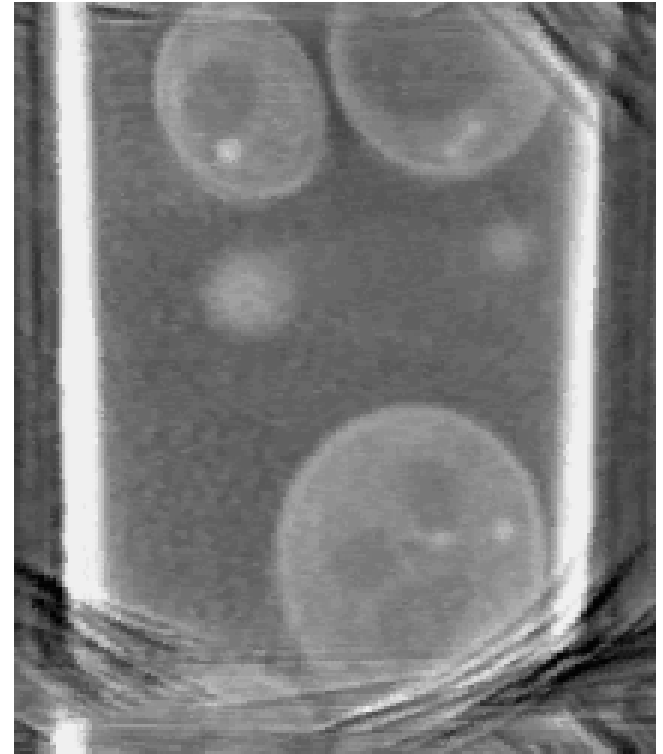
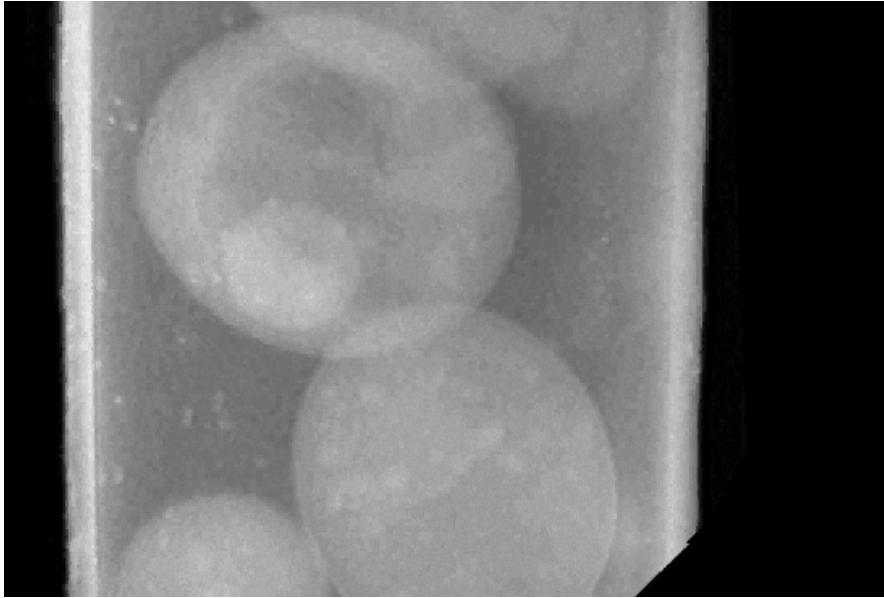
Dr = 25 nm  
 D = 63 μm  
 N = 618 zones  
 f = 650 μm  
 NA = 0.05  
 @ 2.4 nmλ



# Cryo X-ray Tomography

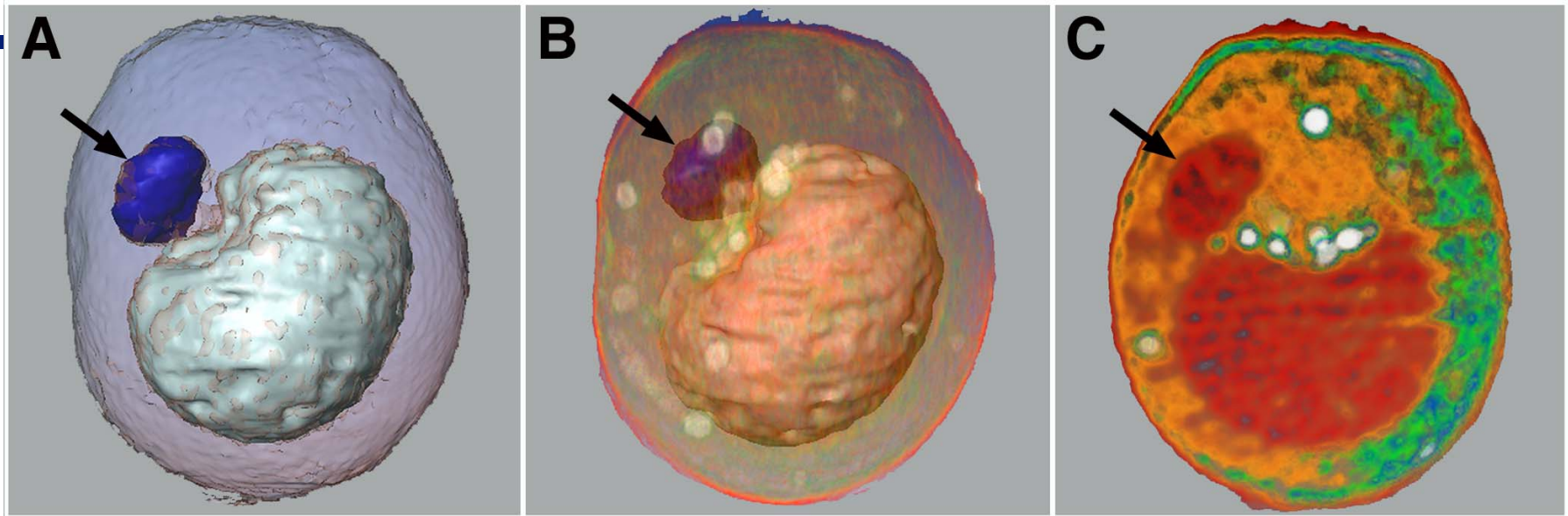
C.A. Larabell & M. A. Le Gros (2004).  
Molecular Biology of the Cell, 15(3), 956-962





C.A. Larabell & M. A. Le Gros (2004).  
Molecular Biology of the Cell, 15(3), 956-962

# *Saccharomyces cerevisiae*



Reconstructed data using different volume analysis algorithms.

- A) Combination of translucent outer surface & opaque surfaces highlight internal organelles; arrow points to nucleus that has been color-coded blue
- B) Surface views combined with volume rendering
- lipid droplets white
  - surface of large vacuole pink
- C) Computer section that was volume-rendered according to x-ray absorption
- lipid droplets white
  - internal structures of vacuole and nucleus red
  - other cytoplasmic structures appear green and orange.

C.A. Larabell & M. A. Le Gros (2004). *Molecular Biology of the Cell*, 15(3), 956-962

# Solar Energy



- Si solar cell efficiency ~ 15%
- Complex multilayer system ~ 35%
- Theoretical limit ~ 70%



**The Bell solar cell, 1954**  
**Pearson, Chapin and Fuller**

# Acknowledgement

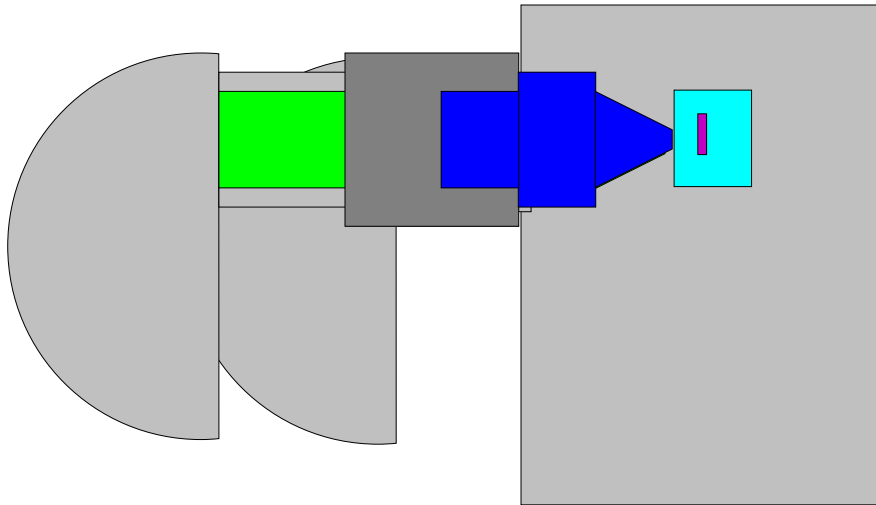


- o ZX Shen (Stanford University)
- o Yi-De Chuang, Jinghua Guo; Jonathan Denlinger, Eli Rotenberg, Simon Clark, Miguel Salmeron (LBNL, ALS)
- o Eric Guilikson, Phil Batson (LBNL)
- o Zahid Hasan (Princeton University)
- o Franz Himpsel (univ of Wisconsin)
- o Lou Terminello (LLNL)
- o Steve Kevan (univ of Oregon)

# Prototype Ambient Pressure Photo-Emission System



HP-PES Differentially Pumped Optics



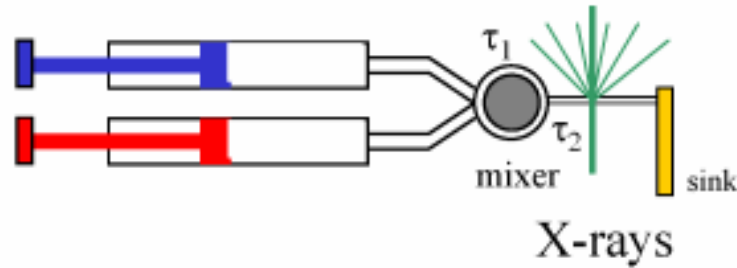
Modify conventional  
surface science vacuum  
system



# Watching system assemble

## *Self-assembly of micelles to vesicles*

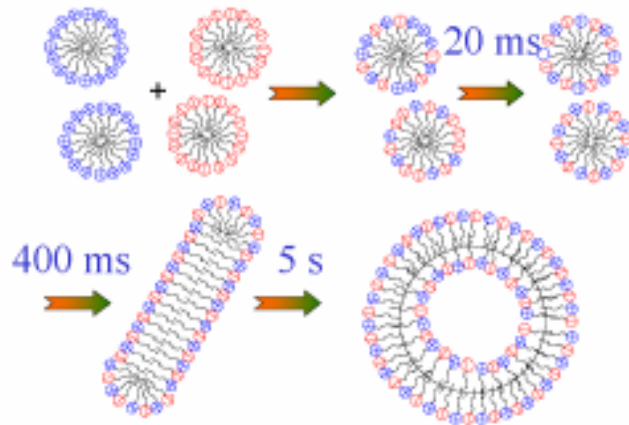
Millisecond range SAXS & stopped-flow rapid mixing



Structural intermediates

spherical micelles

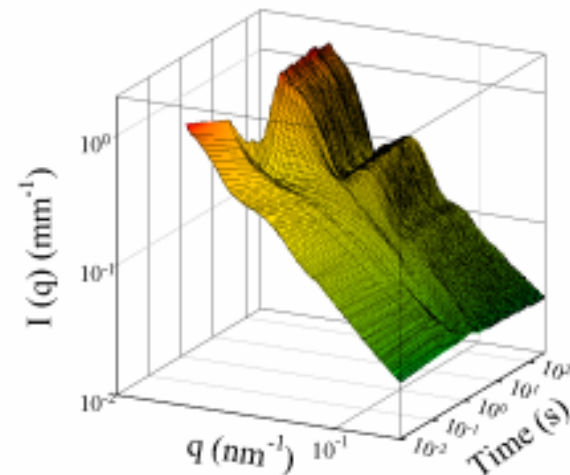
charge equilibration



elongated micelle

vesicle

Anionic TexaponN<sub>70</sub> H & cationic TTAOH micelles



Schmoelzer *et al.* *Phys.Rev.Lett.* **88**, 258301, (2002)

# The Foundry is a place with:

---



- **state-of-the-art instrumentation**
- **a leadership of senior investigators**
- **a technical support staff**
- **dedicated, collaborative, scientists, postdoctoral fellows**

# Associated Facilities

---



- **Advanced Light Source**
- **National Center for Electron Microscopy**
- **National Energy Research Scientific Computing Center**



# ORGANIZATION

# Outline



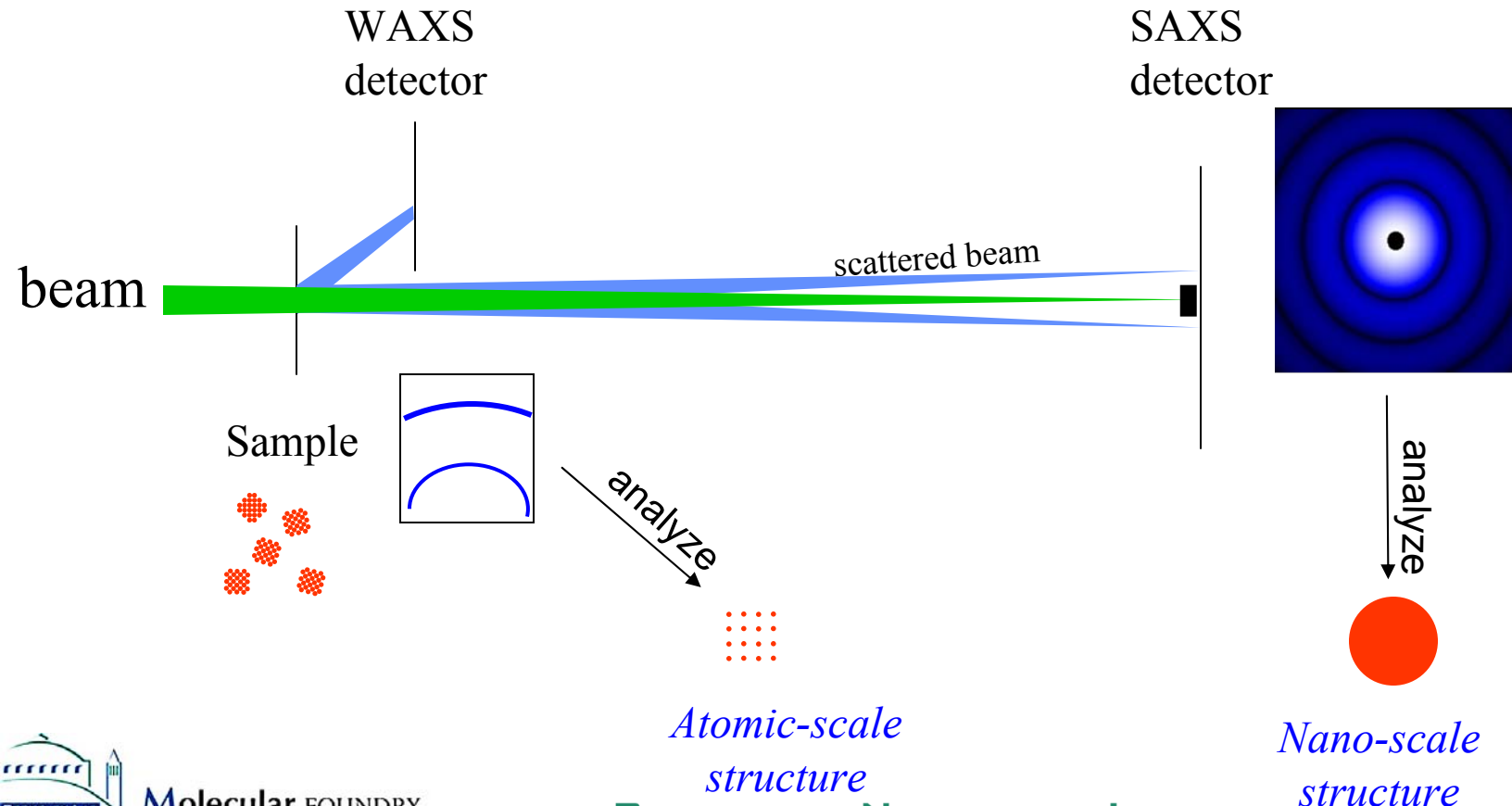
- ❖ **Photoemission Spectroscopy - some introduction**
  - **Ambient pressure photoemission**  
(pressure upto 20 torr (vapor pressure of water), catalysis/corrosion, environmental science, biological systems)
  - **Ultra-high Momentum and Energy Resolution Photoemission (ARPES)**  
(application to study of strongly correlated electron systems (high temperature superconductors, CMR materials))
- ❖ **Momentum-Resolved Inelastic Scattering**  
(optically forbidden transitions, bulk sensitivity)
- ❖ **Coherent Scattering** (magnetic imaging, dynamics)

# SAXS/WAXS - a quick review



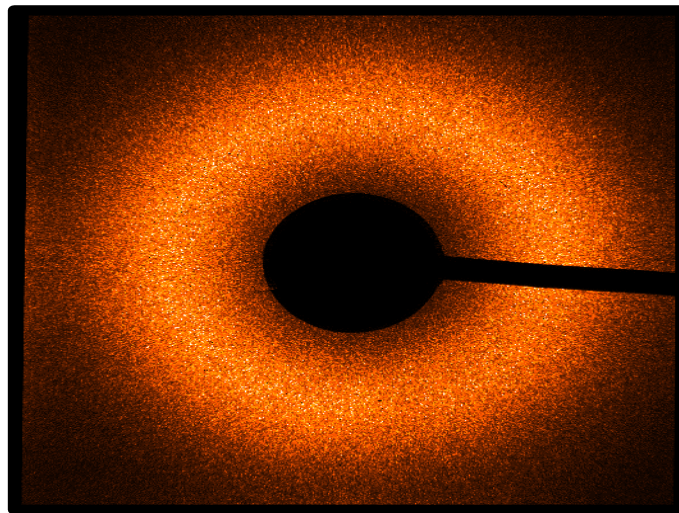
SAXS = Small Angle X-ray Scattering ( $d > 1\text{nm}$ )

WAXS = Wide Angle X-ray Scattering ( $d < 1\text{nm}$ )



## 3. Soft x-Ray Coherent Scattering

Static and dynamical study of magnetic domains and inhomogeneities in complex correlated systems

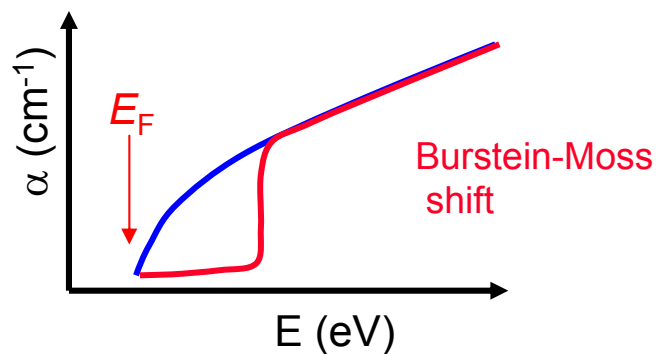
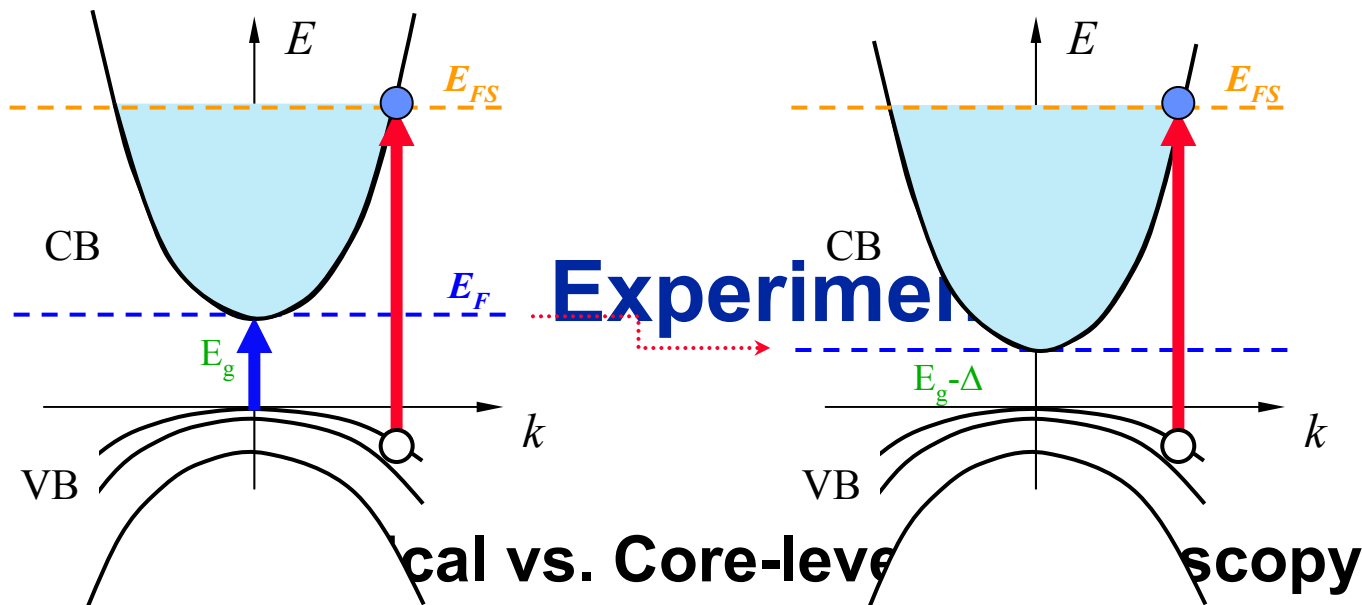


# Why dynamic soft X-rays coherent scattering ?

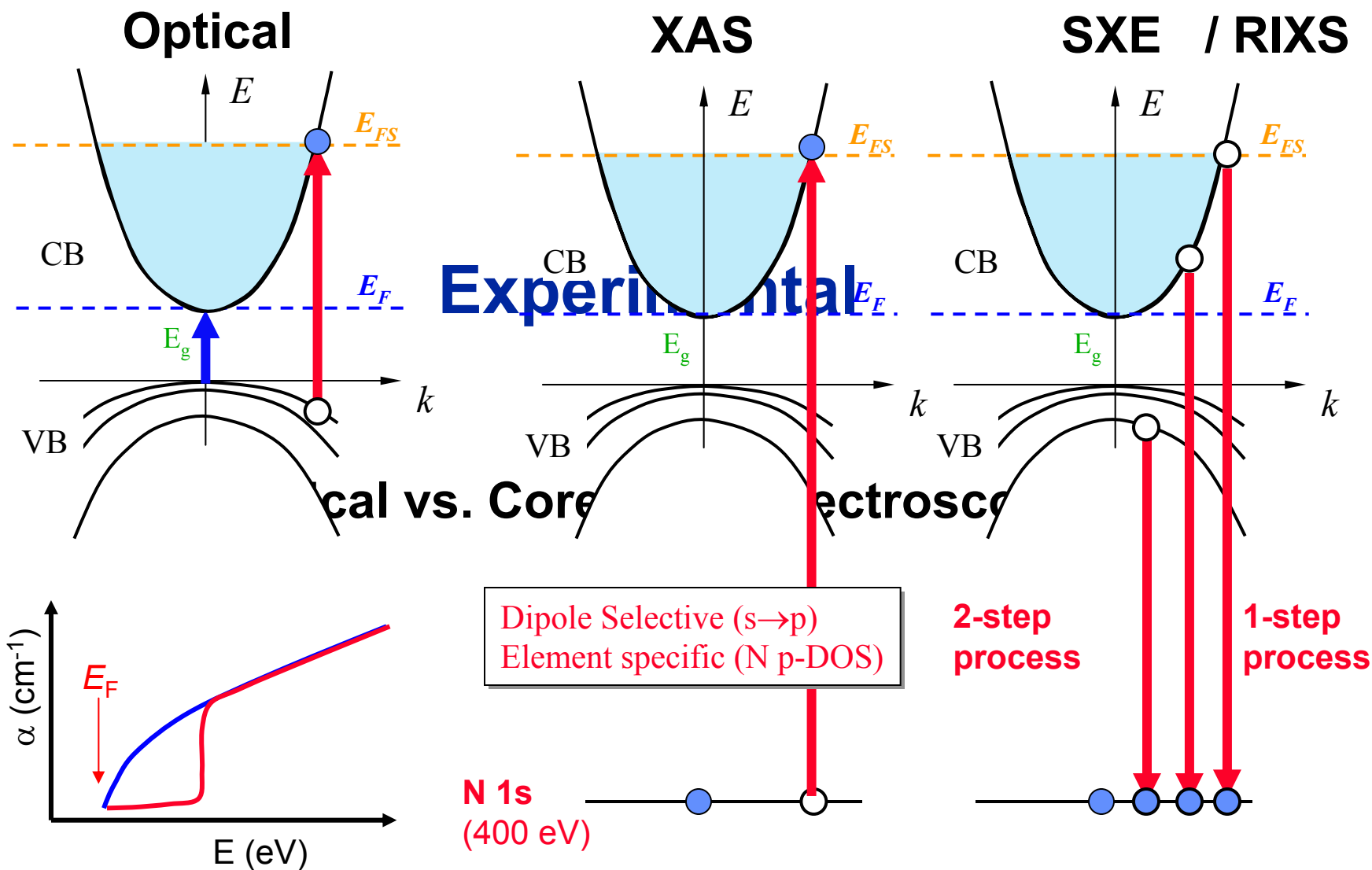


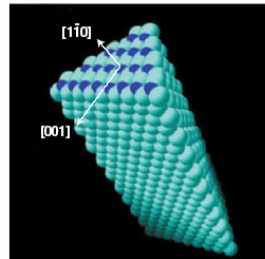
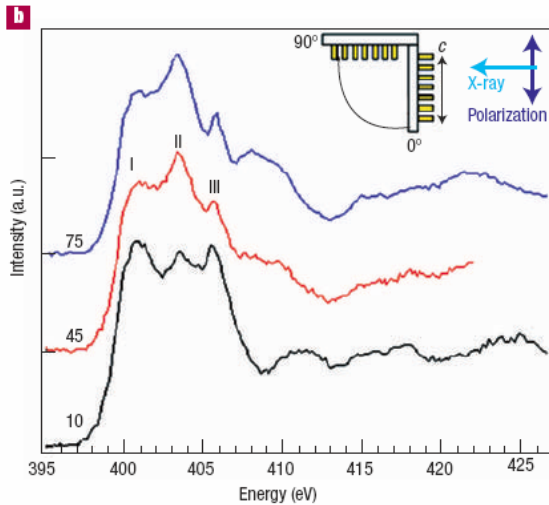
- o More coherent flux - Scales like  $\lambda^2$  x brightness  
(2000 times more coherent flux for  $\lambda = 4.4\text{nm}$  than for  $0.1\text{nm}$ )
- o High sensitivity for 3d metals: Resonant 2p-3d transitions  
(excited electrons into spin polarized empty 3d states)
- o Wide range of Spatial resolution:  
1 nm (wavelength of rad.) - 40  $\mu\text{m}$  (transverse coherence length)
- o Time resolution: >  $\mu\text{s}$  - 5ns) limited by time correlator
- o No multiple scattering complications (photons are weak scatters).
- o Bulk sensitivity
- o Can be applied in the presence of magnetic/electric field

# Optical

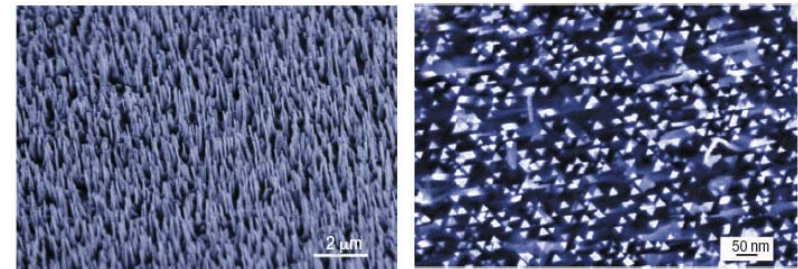


+ Band-gap narrowing

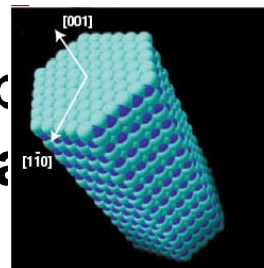
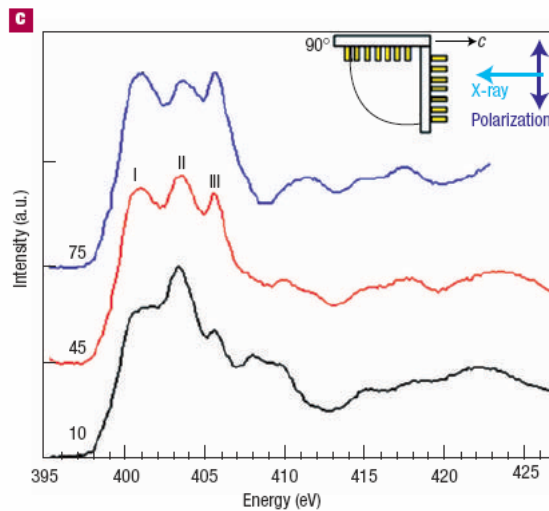




**[1-10] nanowires grown on  $\gamma$ -(001) LiAlO<sub>2</sub>**



**Figure 1** SEM images of the GaN nanowires.



**[001] nanowires grown on (111) MgO**

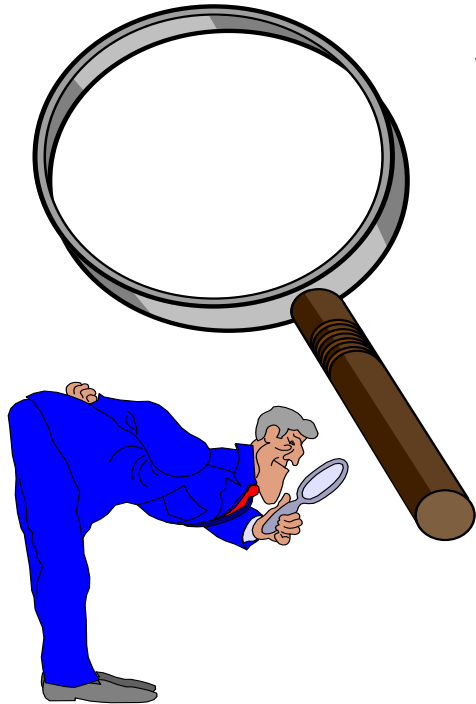
- Polarization-dependent N K-edge XAS anisotropy well known for bulk GaN (non-centrosymmetric wurtzite structure).

## Crystallographic alignment of high-density nanowire arrays

- XAS angular anisotropy confirms crystallographic alignment of GaN nanowires relative to each other, and to different substrates.



# Conclusions



We may need to look harder but  
**a lot of new physics still to come!!**



# Nanoscience



**Crystal size determines color (quantum dot)**

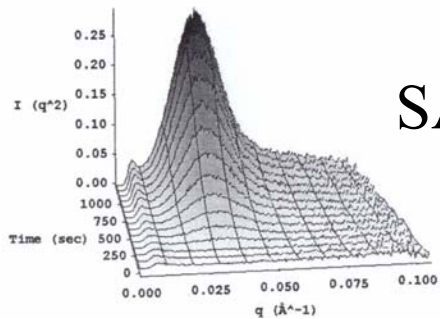
How the nanomaterials are prepared?

What we need to learn about these systems?

What kind of tools are necessary?

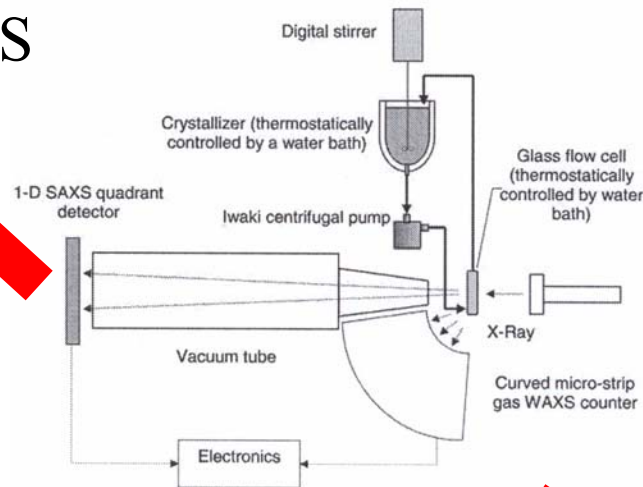
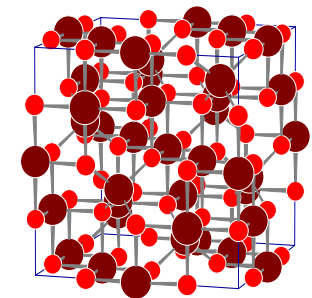
What facilities are available at the ALS?

# SAXS-WAXS basics



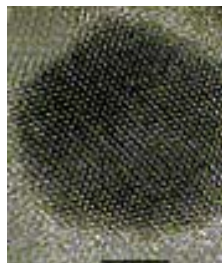
SAXS

Atomic structure

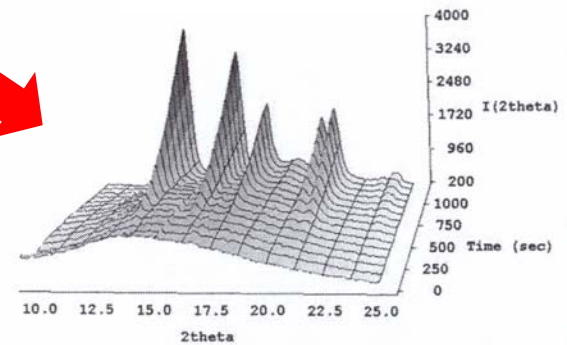


WAXS

Experimental layout on DUBBLE CRG at the ESRF



Nano-structure



Experimental layout and data taken from: Heeley et al. *Faraday Discuss.*, (2002) 122, 343-361.

LAWRENCE BERKELEY NATIONAL LABORATORY

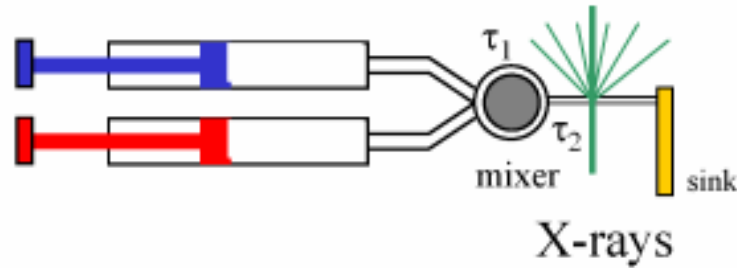
Electron micrograph courtesy of Paul Alivisatos group.

SESAME Worksp Pakistan, April, 2005

# Watching system assemble

## *Self-assembly of micelles to vesicles*

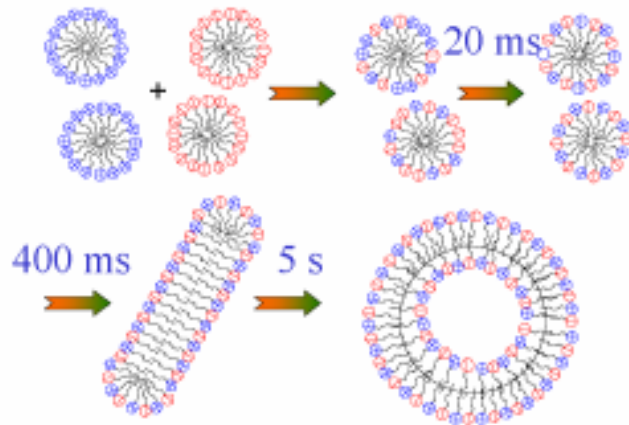
Millisecond range SAXS & stopped-flow rapid mixing



Structural intermediates

spherical micelles

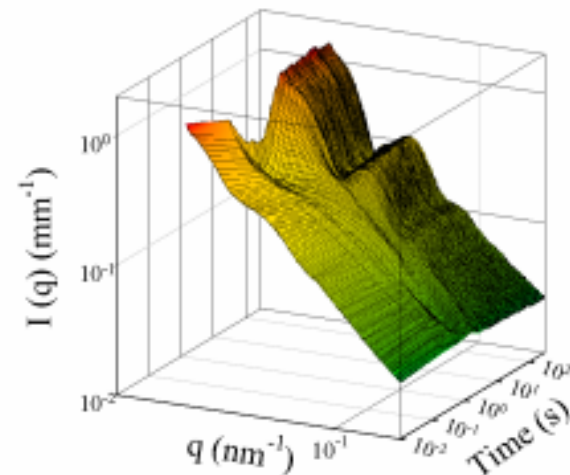
charge equilibration



elongated micelle

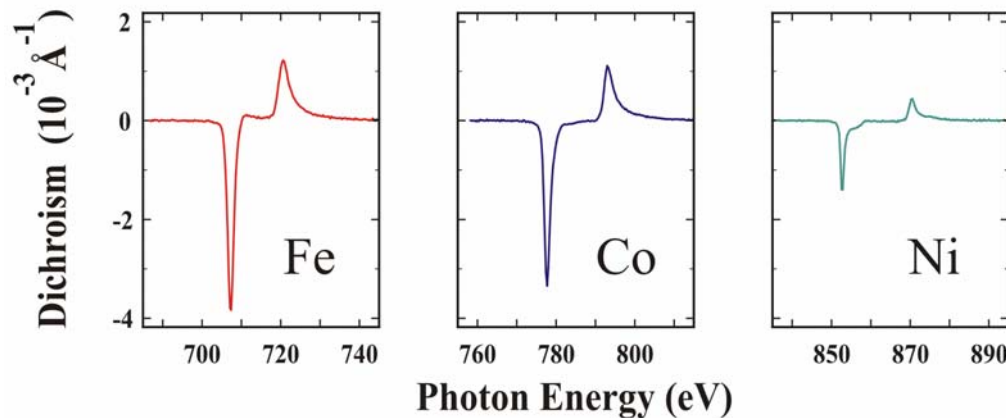
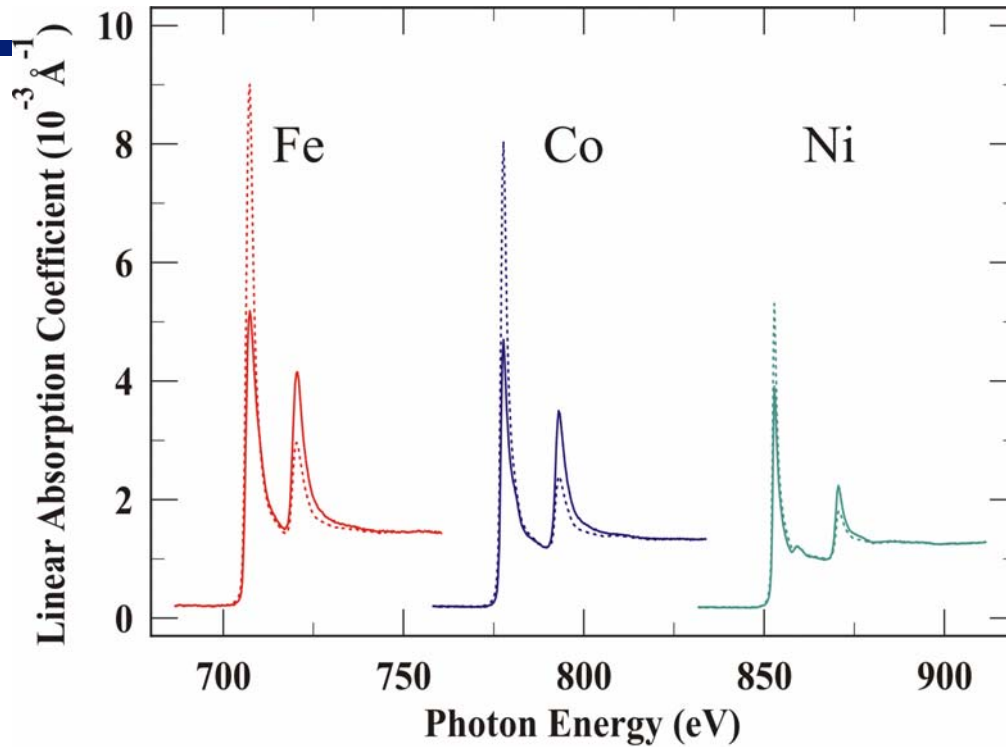
vesicle

Anionic TexaponN<sub>70</sub> H & cationic TTAOH micelles



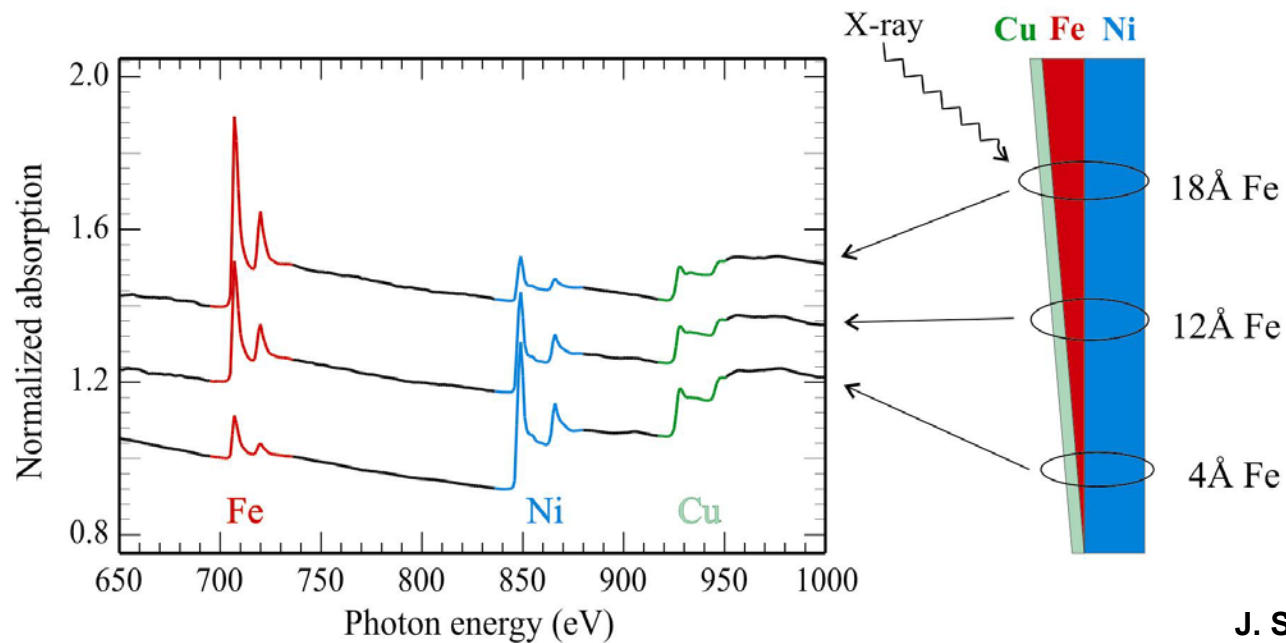
Schmoelzer *et al.* *Phys.Rev.Lett.* **88**, 258301, (2002)

# XMCD Spectra of the pure Metals

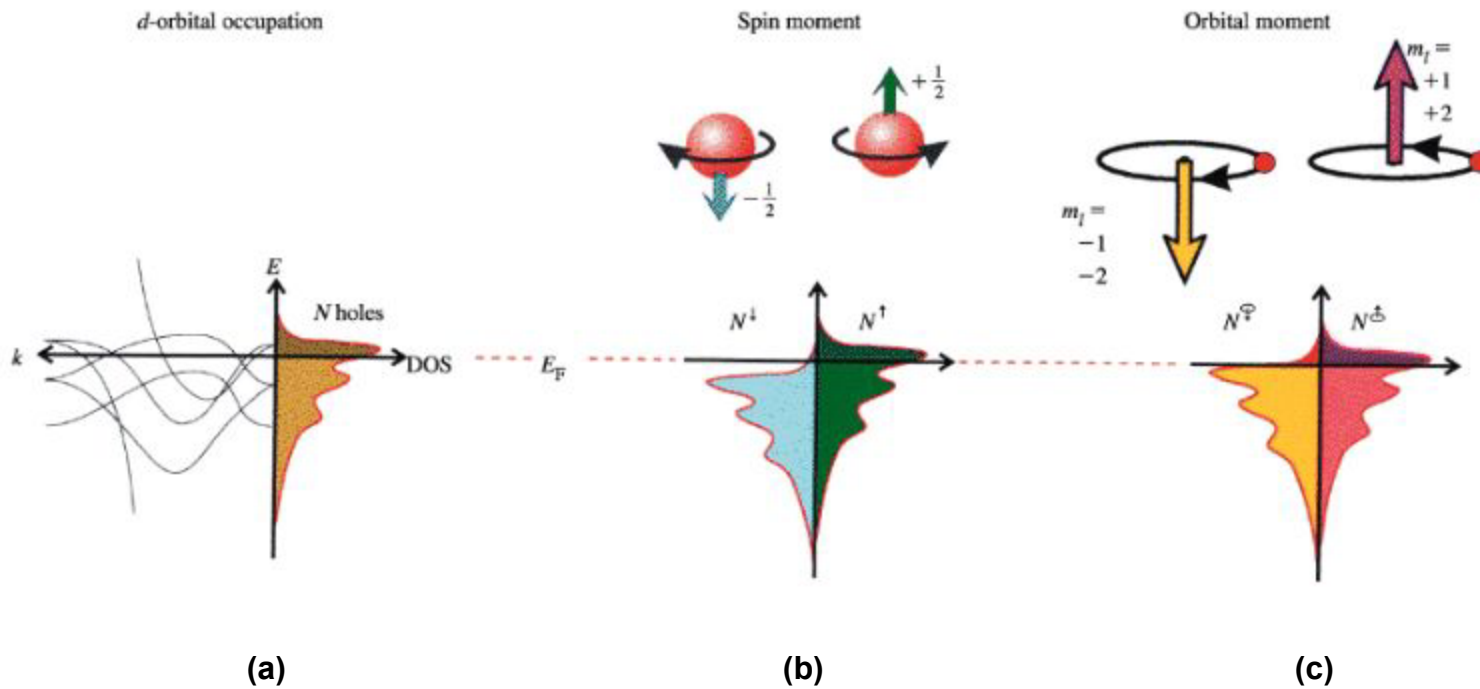


J. Stoehr, R. Nakajima  
IBM J. Res. Develop. 42, 73 (1998)

# X-rays can pick materials apart: layer-by-layer

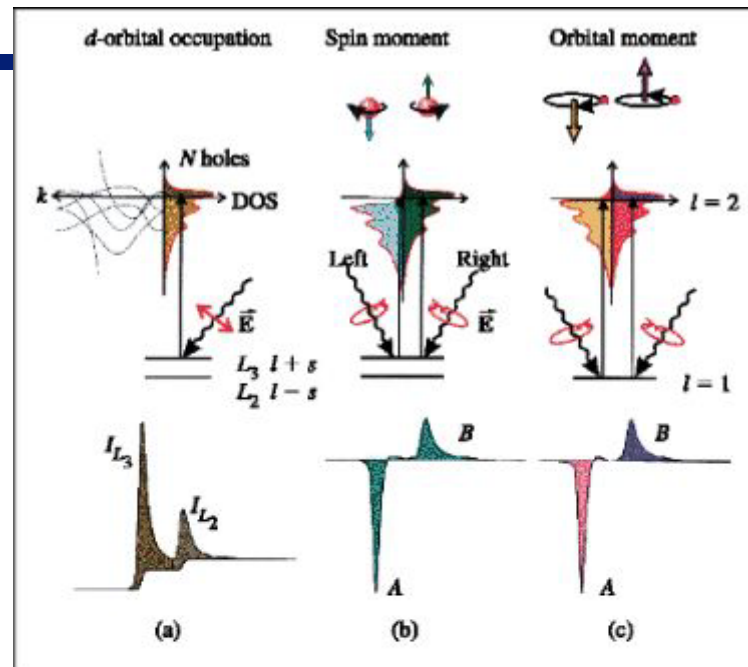


J. Stoehr



Electronic transitions in conventional L-edge X-ray absorption (a), and in X-ray magnetic circular dichroism (b, c), illustrated in a one-electron model. The transitions occur from the spin-orbit split  $2p$  core shell to empty conduction band states above the Fermi level  $E_F$ . In conventional X-ray absorption, the transition intensity measured as the white-line intensity  $I_{L3} + I_{L2}$  is proportional to the number of d holes,  $N$ . By use of circularly polarized X-rays, the spin moment (b) and orbital moment (c) can be determined from the dichroic difference intensities.

# NANO-MATERIALS STUDIES AT THE ALS



**Figure 3**

Electronic transitions in conventional  $L$ -edge X-ray absorption (a) (see Footnote 1), and in X-ray magnetic circular dichroism (b, c), illustrated in a one-electron model. The transitions occur from the spin-orbit split  $2p$  core shell to empty conduction band states above the Fermi level  $E_F$ . In conventional X-ray absorption, the transition intensity measured as the white-line intensity  $I_{L_3} + I_{L_2}$  is proportional to the number of  $d$  holes,  $N$ . By use of circularly polarized X-rays, the spin moment (b) and orbital moment (c) can be determined from the dichroic difference intensities  $A$  and  $B$ , as explained in the text.

# Other common methods



1. TEM  
*Great resolution, no in-situ*
2. Optical monitoring  
*Easy, fast, in-situ, indirect info*
3. Light scattering  
*Fast, in-situ, little direct nanoscale info*





The Bell solar cell, 1954  
Pearson, Chapin and Fuller