New Scientific Opportunities with soft x-ray SR

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Advanced Light Source

Lawrence Berkeley National Laboratory

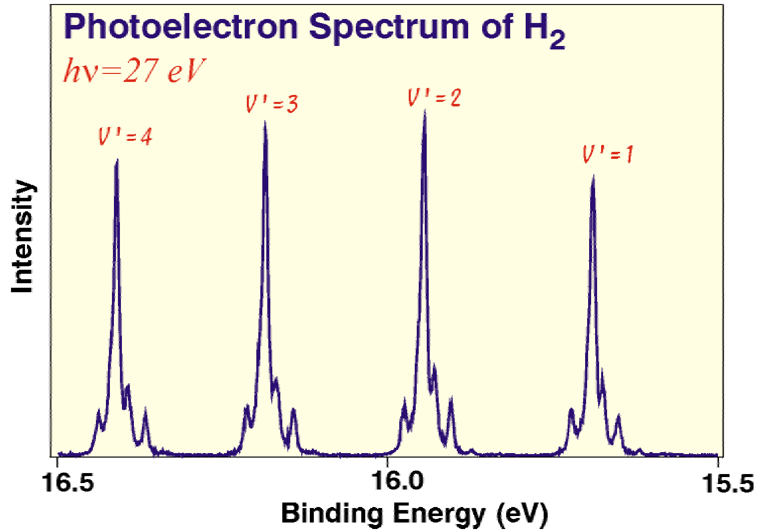
THE ADVANCED LIGHT SOURCE

The mission of the ALS is to

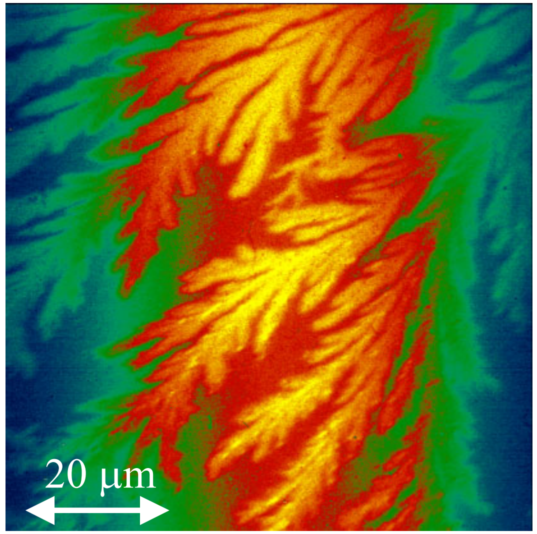
Support Users in doing Outstanding Science

(From 2002 BES review of the ALS)

WHAT DOES SR BRIGHTNESS BUY YOU?

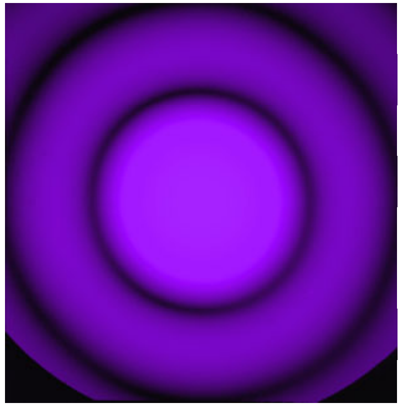


Very High Energy Resolution



Magnetic structure of $LaFeO_3$ layer on surface oxide.

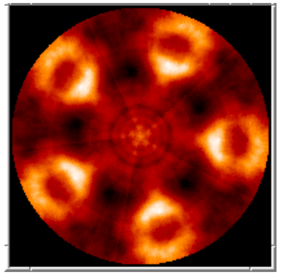
Submicron Spatial Resolution



Coherence

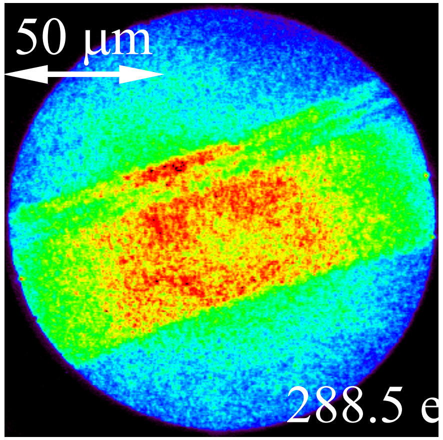
UNDERSTANDING PRPERTIES OF MATTER

Ultimately, the

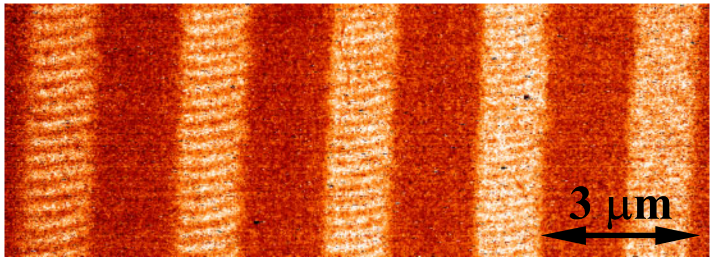


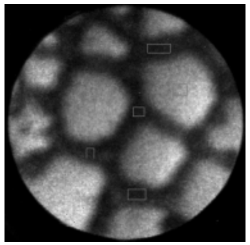
electronic,

magnetic,



chemical,





mechanical,

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

New Scientific Opportunities

- What are some of the important areas of science where soft x-ray SR could make big impact ?
- Where do we stand now ?
- How could we get there ?

Big Science (large facilities,~5-10 yrs effort$10'sM)

VS.

Small Science (modest experimental effort, big payoff)

- "Science is in the sample",

Daniel Chemla, ALS

New Scientific Opportunities, Summary

- **Ambient Pressure Photoemission** (in situ measurements, catalysis/corrosion, environmental science, biological systems)
- **Ultra-high Momentum and Energy Resolution ARPES** (Scienta electron energy analyzers, strongly correlated electron systems (high temperature superconductors, CMR)
- **Coherent Scattering** (magnetic imaging, dynamics)
- **Momentum-Resolved Inelastic Scattering** (optically forbidden transition, bulk sensitivity)
- **Spectromicroscopy** (SMART/PEEMIII, X-Ray Imaging, STXM)
- **Ion Spectroscopy** (study of positive and negative ions by measurements of ion fragmentation and/or electron spectroscopy)

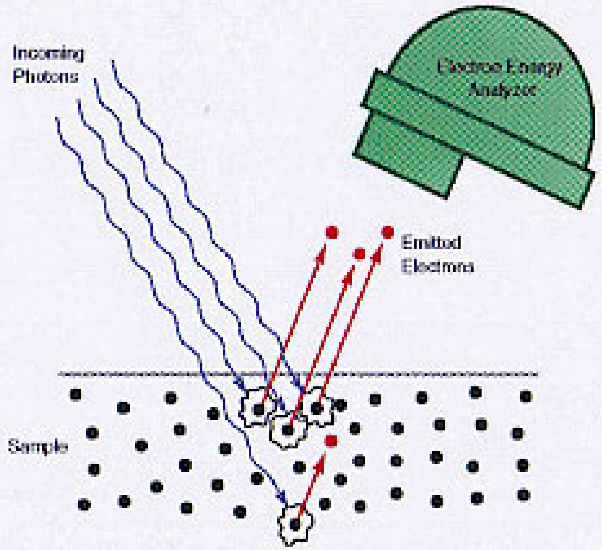
Time-resolved spectroscopy (f-sec research)

X Rays Are An Important Probe of Matter

- **Spectroscopy**

  Interact with electrons in atoms

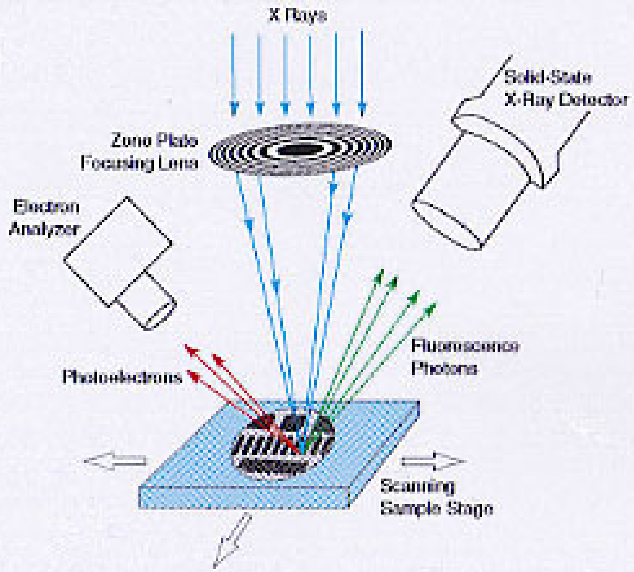
  Element and chemical state sensitivity



- **Microscopy**

  Short wavelength/Small focal spot

  Image small objects



- **Absorption coefficient appropriate**

  Penetrate matter
- **Can be polarized (linear, circular)**
- **Variable (tunable) energy**
- **Short-pulse time structure**
- **Partially coherent**

X-ray Spectroscopy of Condensed Matter

Quantum Number Selectivity:

- ✓ Absorption

$$\omega\ \varepsilon_2 \Rightarrow \Delta E = E_f - E_\iota$$

- ✓ Angle-integrated photoemission

$$N(E, \hbar\omega) \Rightarrow E_{f,} E_{i}$$

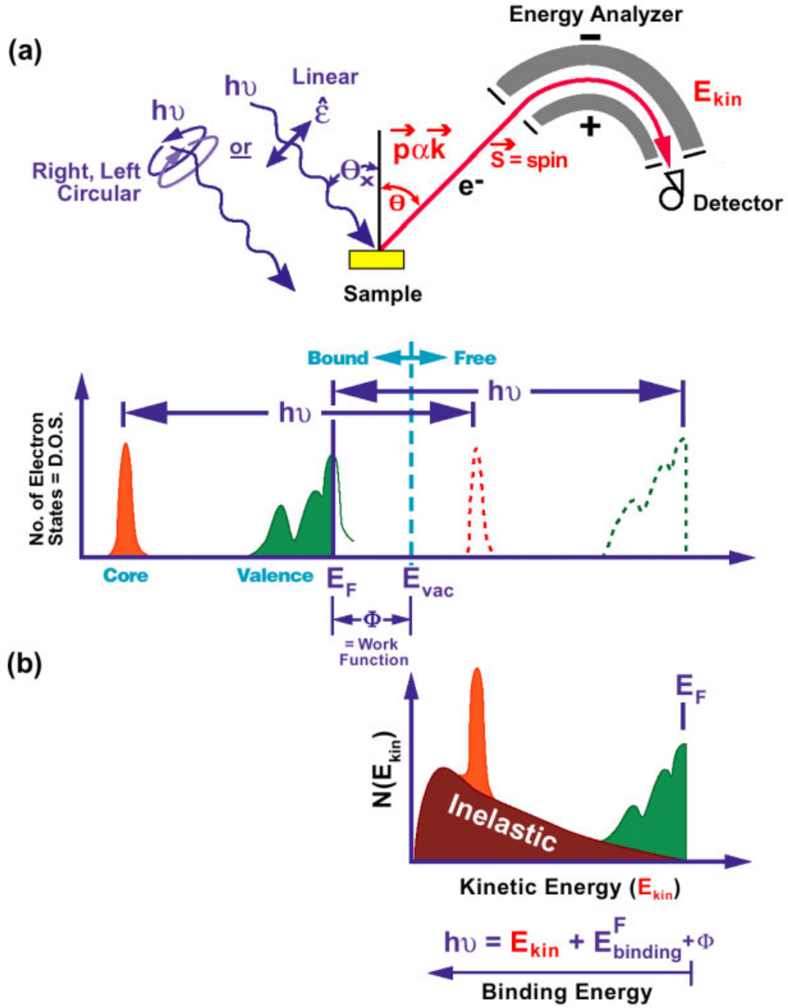
- ✓ Angle-resolved photoemission

$$N(E, \hbar\omega, \theta, \varphi) \Rightarrow E_{f,} E_{i,} \vec{\kappa}$$

- ✓ Spin-polarized photoemission

$$(N_\uparrow - N_\downarrow) / (N_\uparrow + N_\downarrow) \Rightarrow E_{f,} E_{i,} \vec{\kappa}, \vec{\sigma}$$

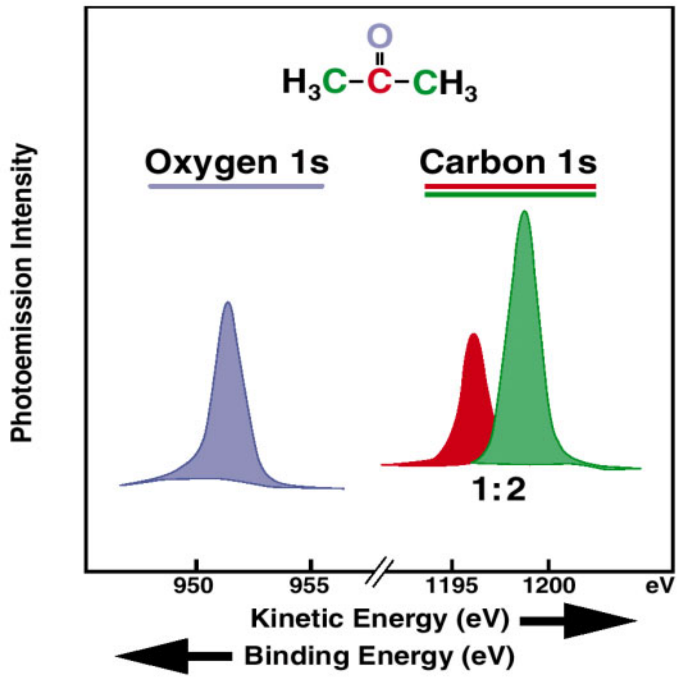
Photoelectron Spectroscopy



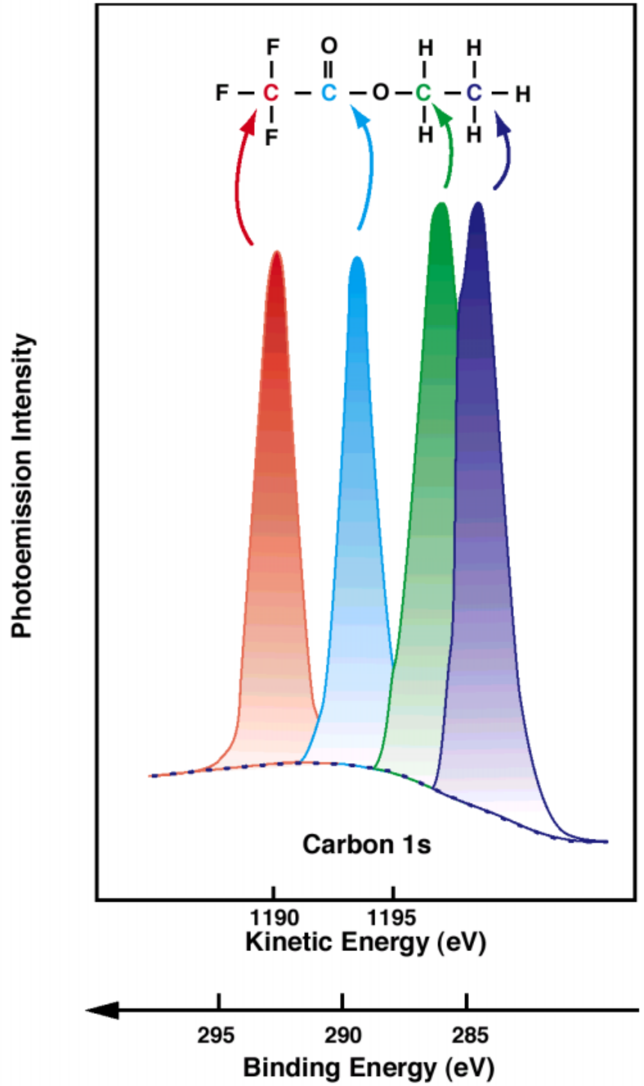
Photoelectron Spectroscopy

Provides information about

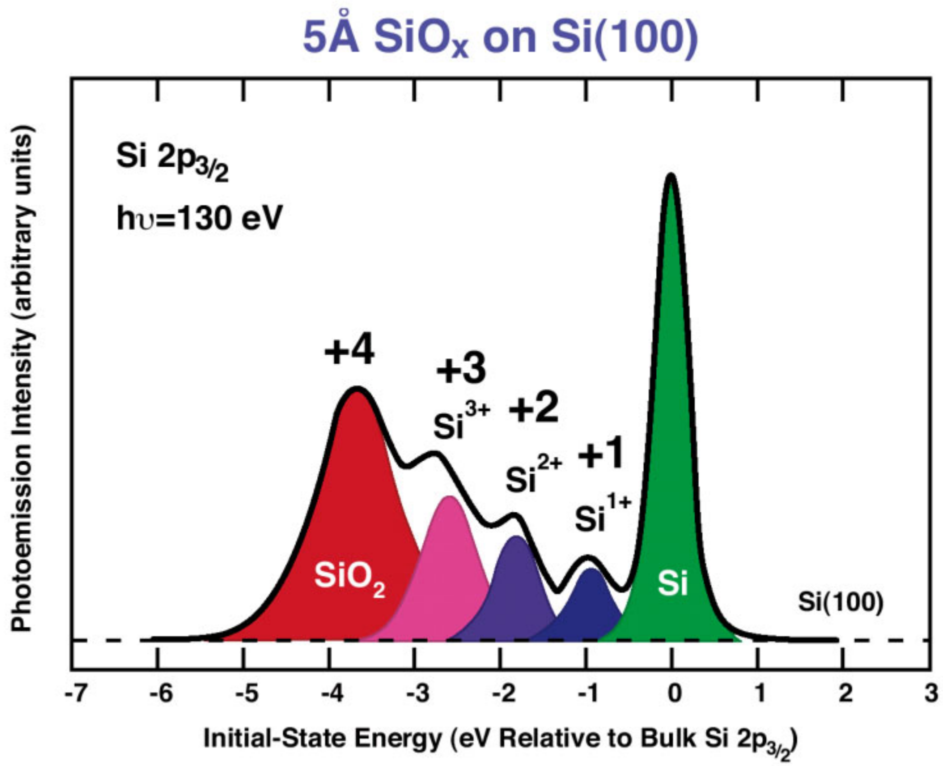
- Kind of atom
- Number of atoms
- Chemical shift



Chemical Shift



Chemical Shift



Ambient pressure (in-situ) soft x-ray spectroscopy

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•Ambient Pressure Photoemission:

Pressure ~ (up to 17 torr,vapour Pressure of H_2O @RT)

30 years of surface science knowledge for understanding of electronic structure of surfaces/interfaces in UHV (model systems)

➔ Now it is possible to apply under real conditions ….

•Absorption/emission spectroscopy

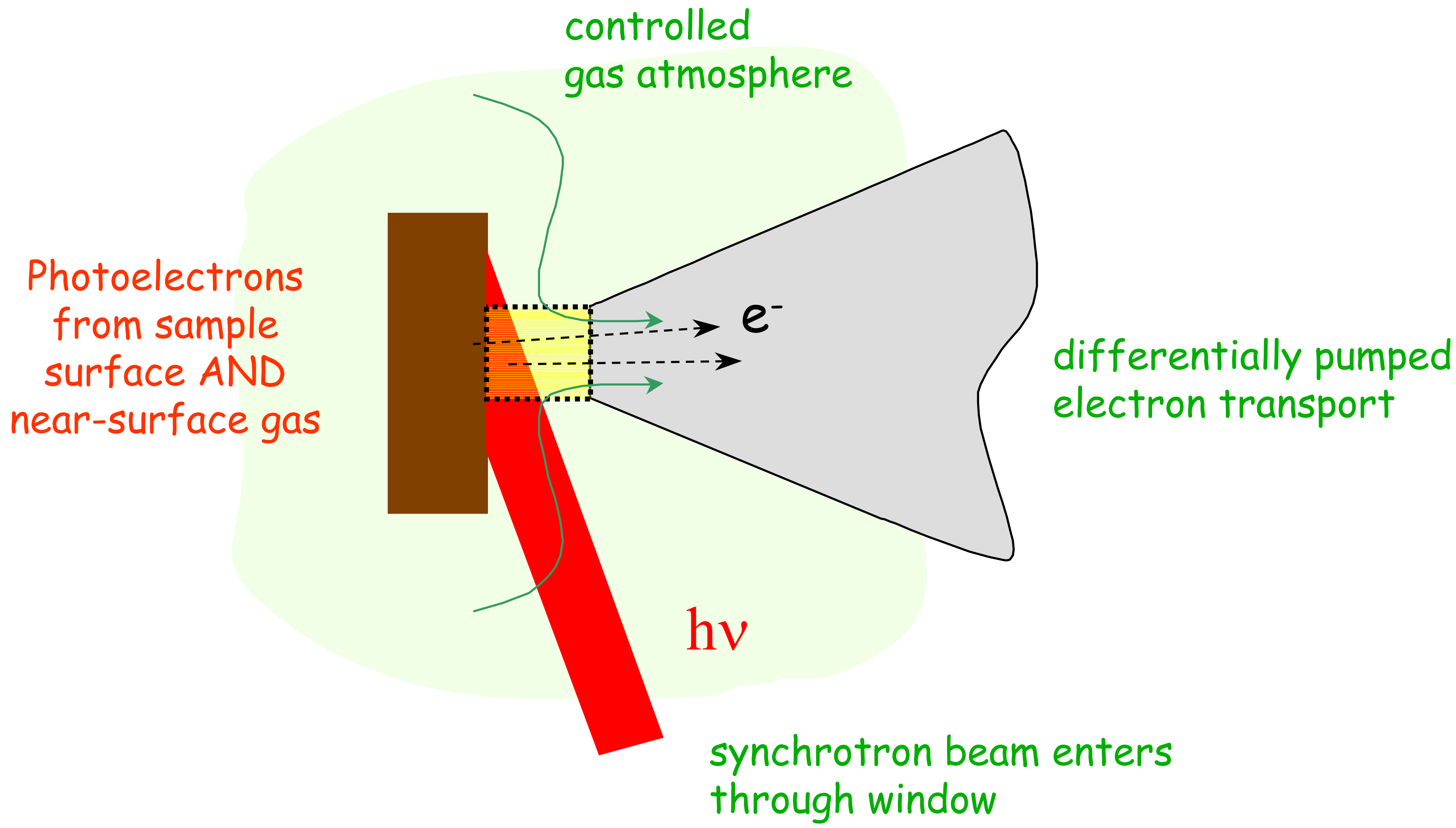
(photon in/photon out): study of unoccupied and occupied valence bands

Pressure ~ (up to 1-20 atmospheric pressure

theoretical analysis a must, (example)

Totally new science !!

Ambient pressure soft x-ray spectroscopy: Concept



Ambient pressure soft x-ray spectroscopy: Basic Concept

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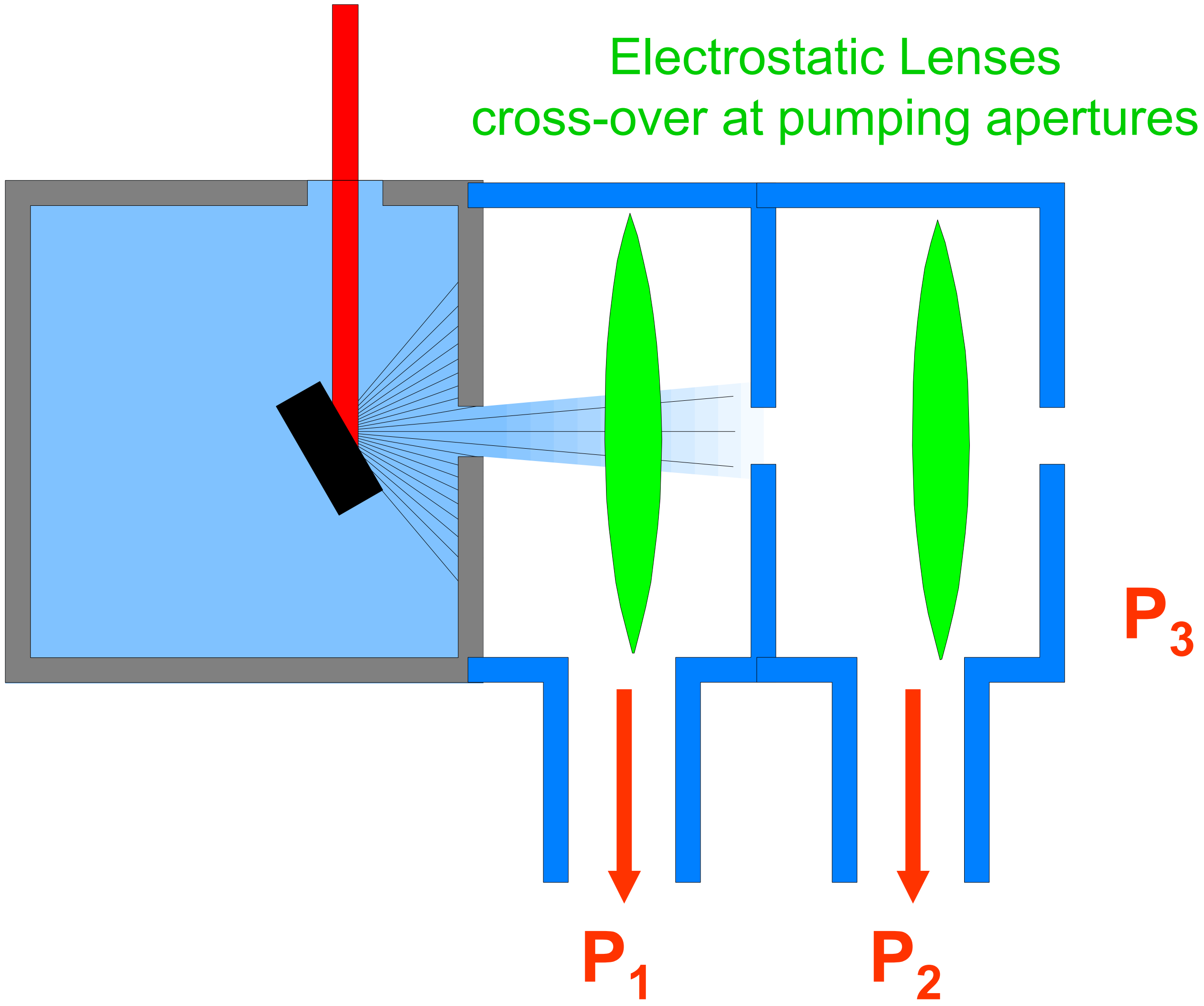


Ambient pressure soft x-ray spectroscopy: History

- Several groups have used differentially-pumped XPS
  - — K. Siegbahn, H. Siegbahn *et al.*
    - Gas phase photoemission
    - Surfaces of low vapor-pressure liquids

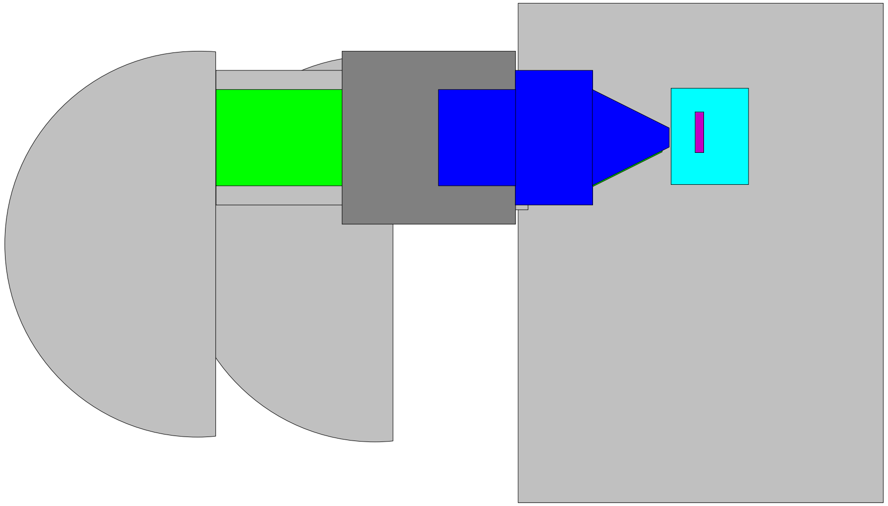
    H. Siegbahn, K. Siegbahn, J. Elec. Spectrosc. Rel. Phen. 2 (1973) 319
  - — Modified XPS sample holder
    - Moveable differentially-pumped sample cell

    R. W. Joyner, M. W. Roberts, K. Yates, Surf. Sci. 87 (1979) 501
  - — M. Grunze *et al.*
    - Surface reactions and catalysis

    H.J. Ruppender, M. Grunze, C.W. Kong, M. Wilmers, Surf. Interface Anal. 15 (1990) 245
- What's new?
  - – Differentially-pumped electron optics for higher signals
  - – Synchrotron light-source allows smaller apertures
  - – Pressure range extended 1-2 orders of magnitude

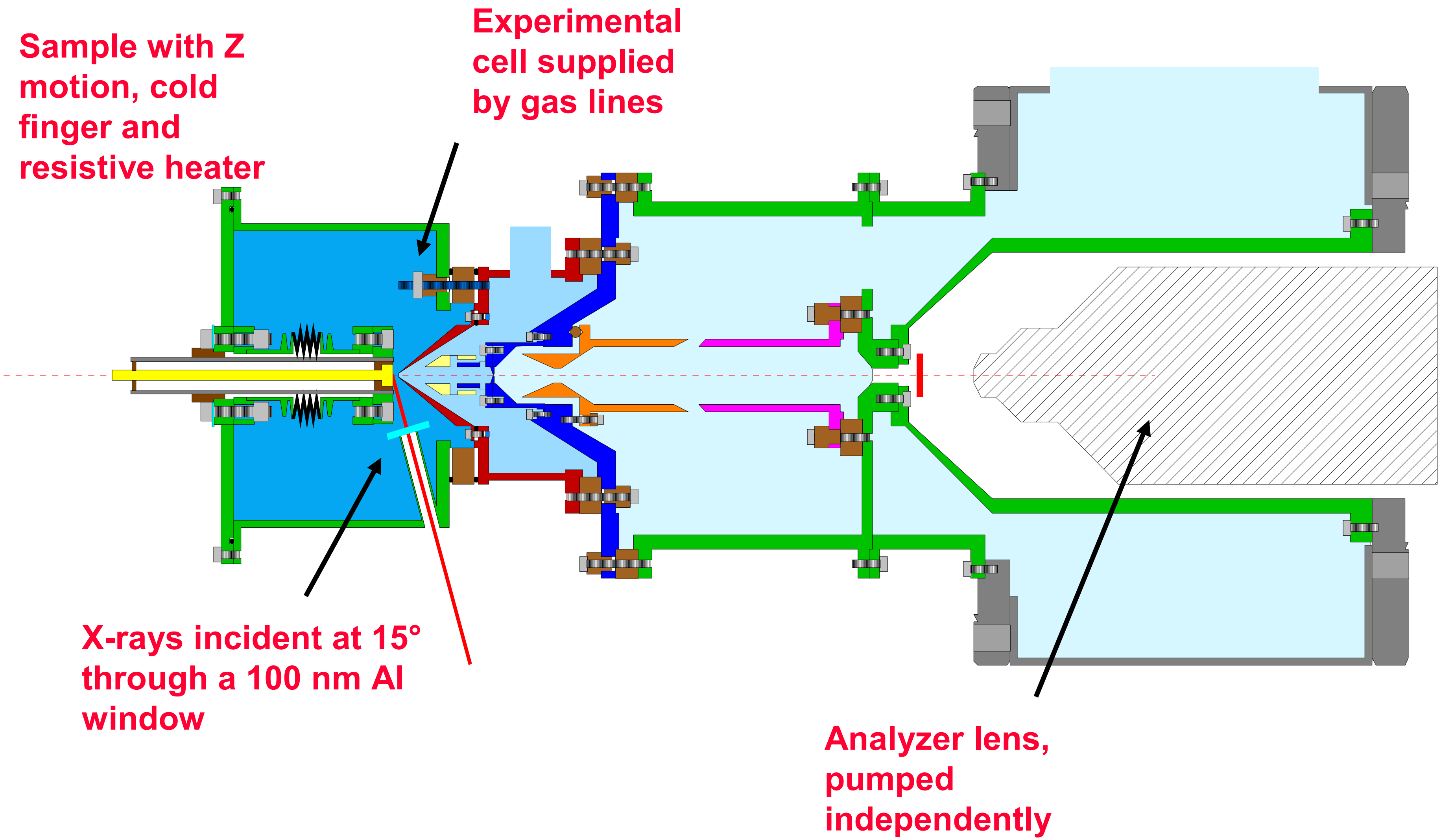
Prototype Ambient Pressure Photo-Emission System

HP-PES Differentially Pumped Optics



Modify conventional surface science vacuum system

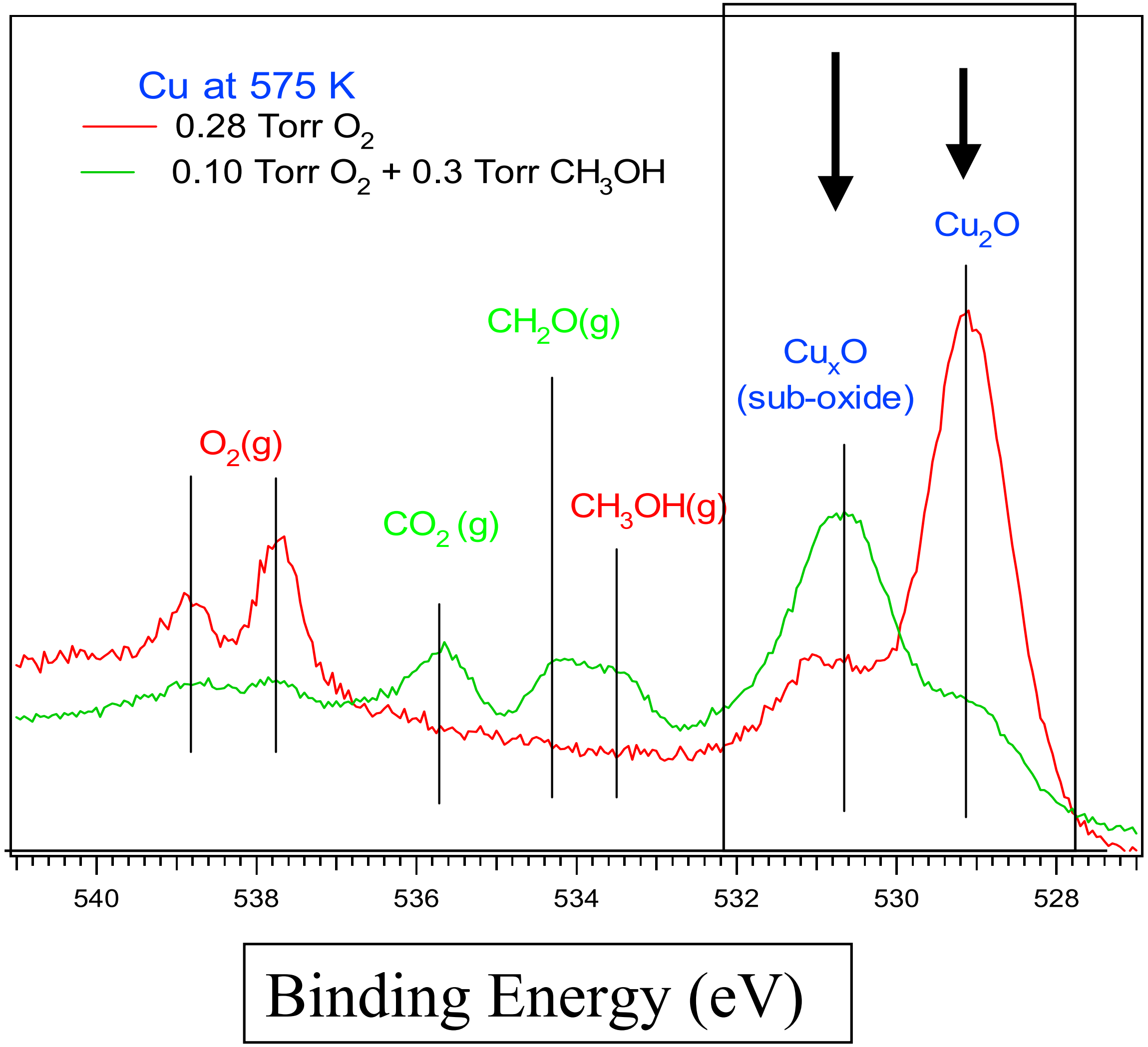
Ambient Pressure Photoemission: Schematic



Ambient pressure soft x-ray spectroscopy: Possible Applications

- *In situ* studies of surface reactions
  - closing the catalysis "pressure gap"
- Surface science of liquids
  - Segregation at solution liquid-vapor interfaces
  - Fundamental Electrochemistry
- Environmental Chemistry
  - Surfaces exposed to water vapor near ambient conditions
  - Solvation and ion-transport
  - Corrosion
- Biological Science
  - Study in the presence of water (in situ)

In Situ Catalysis



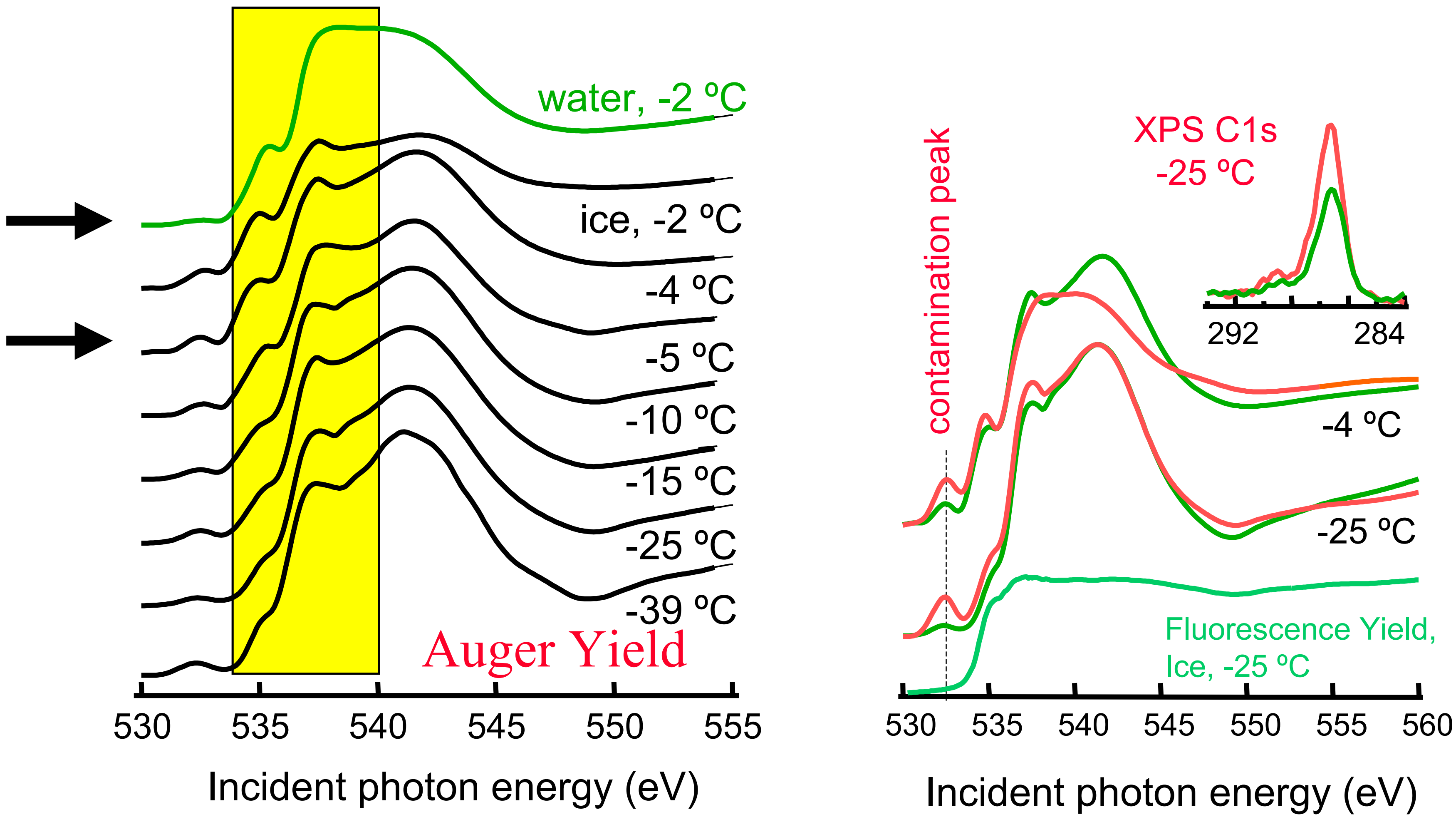
Partial oxidation of methanol to formaldehyde over copper

$CH_3OH + O_2 \rightarrow CH_2O$

Active site exists under reaction conditions

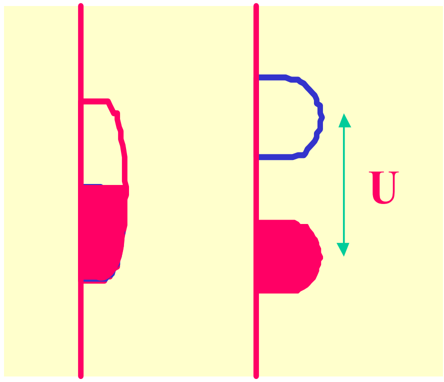
Hendrick Bluhm *et al.*

NEXAFS of Ice Premelting



Highly Correlated Electron Systems

Mott Insulator



One-electron Band Theory

Mott Insulators

An unsolved problem in Many-body physics

Doped Mott Insulators

High-T_c Superconductivity
Cuprates

Colossal Magnetoresistance
Manganites

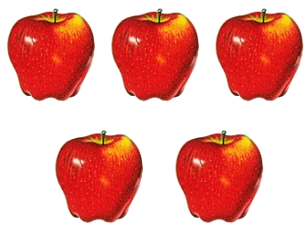
Stripes & Orbital Order
(many Oxides)

Anomalous Transport & Spectroscopic properties

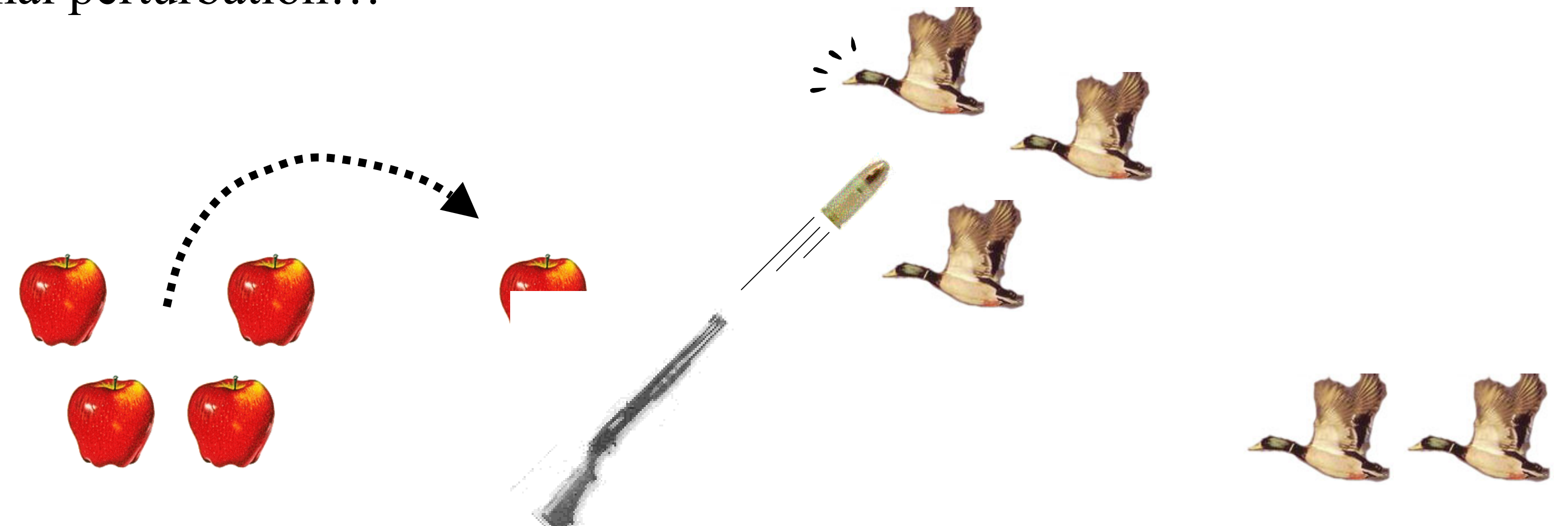
Highly Correlated Electron System

uncorrelated system — correlated system

ground state



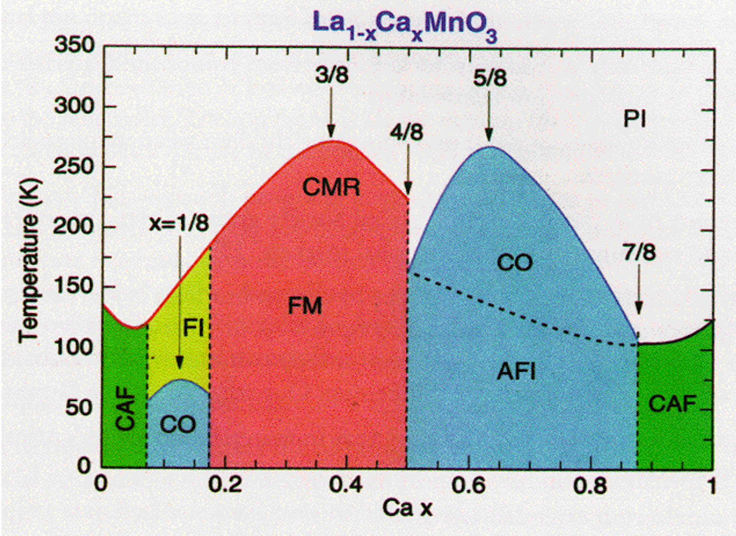
with external perturbation…



The responses are different due to **correlation effect**!

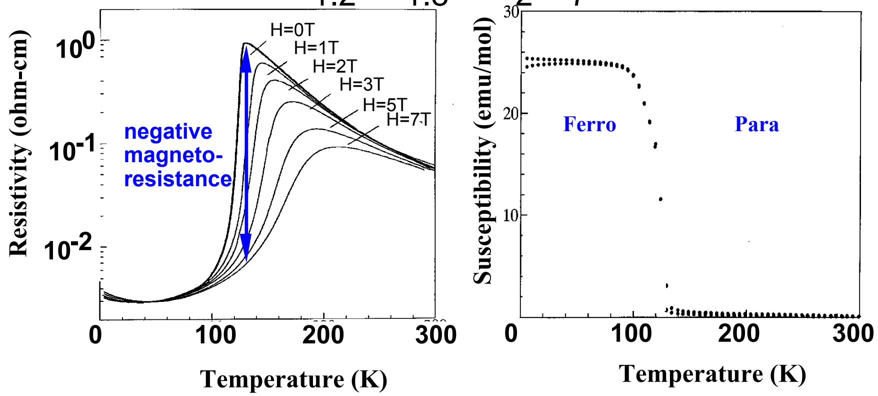
Colossal Magnetoresistance (CMR) Effect

Novel Electronic Phases



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

$La_{1.2}Sr_{1.8}Mn_2O_7$



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

Study of Highly Correlated Electron Systems

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High Momentum and Energy Resolution Photoemission:
A technique of choice for the study of electronic structure of correlated systems

- Confirming breakdown of one electron band theory
  - Splitting of band in NiO due to e-e interaction
- Determination of the Fermi Surface (example)
- D-wave anisotropy of the super-conducting gap
- Static and dynamics stripes in LSCO (example)
- Observation of strong e-phonon coupling (example),

Continue photoemission development to achieve:
Ultra high momentum resolution ~ 1% of BZ
energy resolution ~ 1 meV

The need for ultra-high energy and momentum resolution angle-resolved photoemission (ARPES)

Goal -

- Making connections to transport, thermodynamics, and other low-energy scale properties of solids, especially those where these properties are exotic or poorly understood.

- In particular, where these properties are k-dependent, anisotropic, and/or low dimensional.

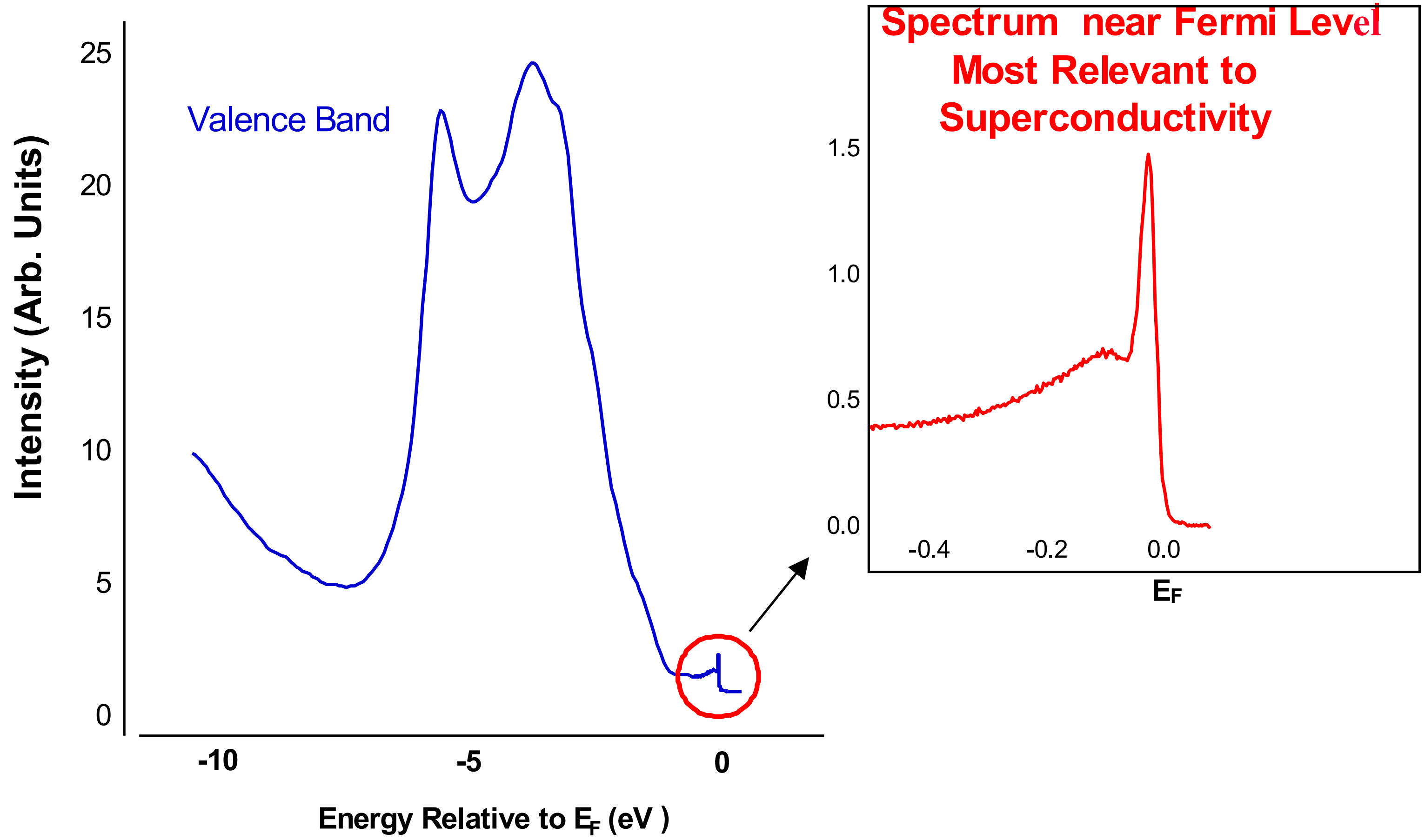
ultra-high energy resolution ARPES-Capabilities

Key physical properties measurable in ARPES:

- Energy vs. wave vector(k)
- Fermi Surface
- Mean Free Paths
- Effective carrier masses
- Scattering rates
- Electron Self energies
- Scattering or nesting vectors
- Number of carriers
- Pseudogaps and superconducting gaps

The only technique that can get all these in a single self consistent way.
Usually the only way to measure these in a k-resolved way.
Only worthwhile if done with energy resolution comparable or better than other key energy scales, temperatures.

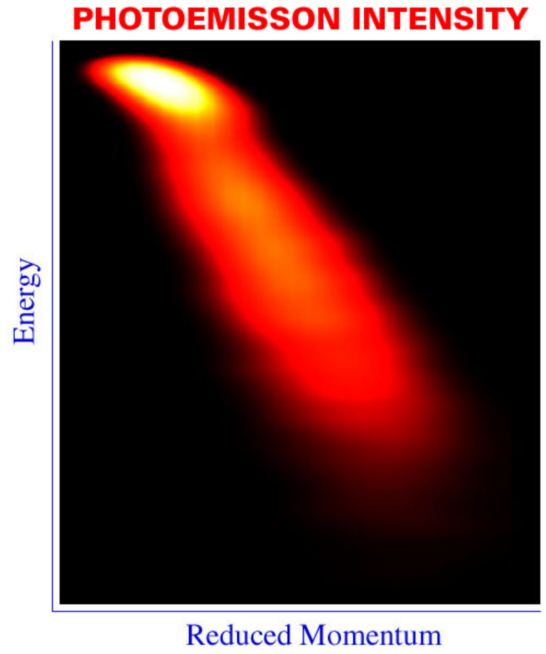
Typical Valence Band Photoemission Spectrum from a High Temperature Superconductor



Intrinsically weak signal experiments

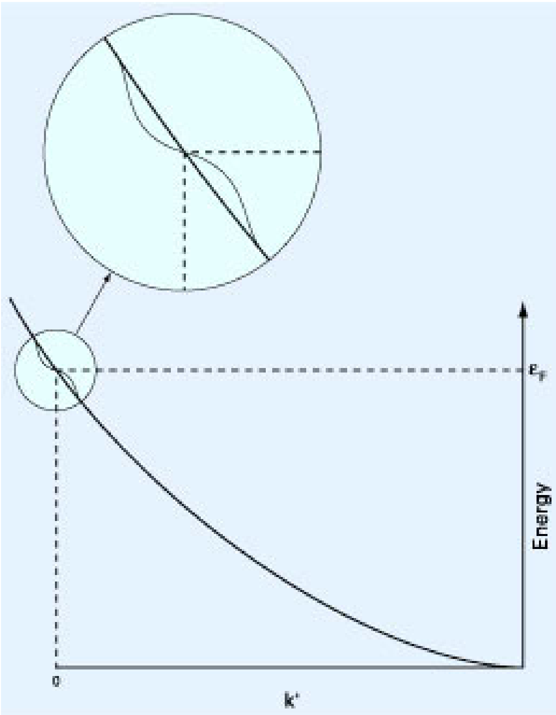
Observation of electron phonon coupling in high Tc superconductors

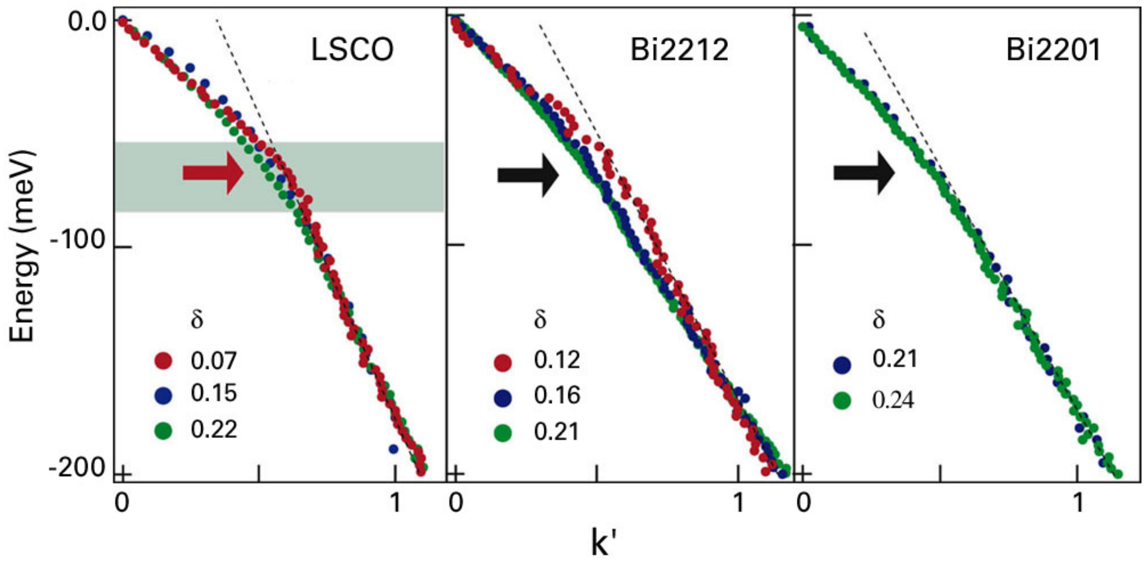
- **Mechanism of high-temperature superconductors (HTSCs) unexplained**
  - —Electron-phonon interaction underlines conventional superconductors
  - —Previous experiment and theory suggest a different mechanism is operative in HTSCs
- **Angle-resolved photoemission (ARPES)**
  - —High angular resolution at the ALS probes electron dynamical parameters
  - —Feature at characteristic energies give insight into operative physical processes



- **New APRES evidence from three families of HTSCs**
  - •Kink in electron-momentum (dispersion) cureves ubiquitous in all three different classes of samples
  - •Common kink energy and other evidence suggests electron-phonon coupling
  - •Revives question of role of phonons in driving superconductivity in HTSCs

Strong electron phonon coupling in High Tc Superconductors

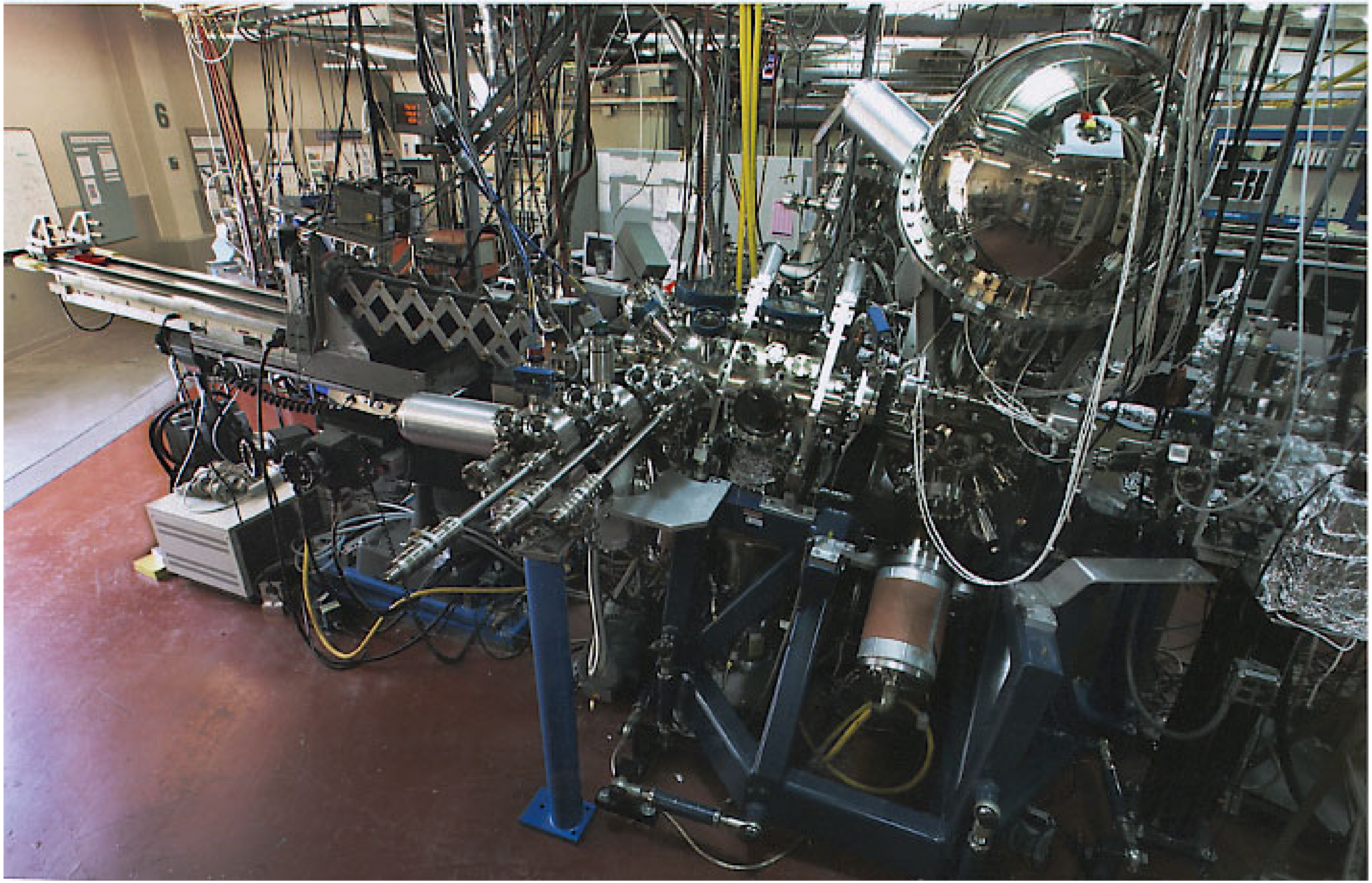




(left) Electro-phonon coupling modifies the electron-momentum dispersion curve near the Fermi energy. (right) Dispersion curves for three families of high-temperature superconductors show a common kink at an energy (arrow) that matches an oxygen lattice vibration. The parameter δ is the doping concentration that determines the transition temperatures in the materials. k' is the reduced momentum (momentum at the Fermi energy k_f minus the actual momentum k).

Lanzara, Hussain, Shen et al. Nature **412**,510 (2001)

High Energy Resolution Spectroscopy (HERS) Endstation at BL 10.0.1, Advanced Light Source



Limitations of photoemission - need of new spectroscopy

However Photoemission:

Measures single particle spectral function of occupied states

It is highly surface sensitive

Spectra could become complicated for 3-D systems

Example: YBCO, difficulty due to surface state

Look for additional tools !!

Resonant Inelastic soft x-ray scattering

Momentum-resolved provides information about the unoccupied band and anisotropic (direct/indirect) nature of energy gaps in solids.

Great for study of fast Correlated motion of electrons in CMR magnites and HTc cuprate

Spectroscopy's of Correlated Electrons

Techniques of choice:

•Angle resolved photoemission (ARPES) :
Single-particle spectrum $A(k,\omega)$

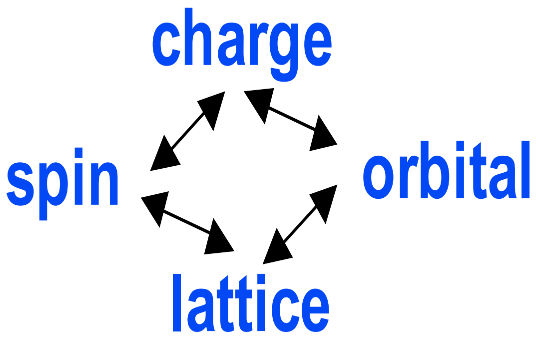
•Inelastic Neutron Scattering (INS) :
Spin fluctuation spectrum $S(q,\omega)$

•Inelastic x-ray scattering (IXS) :
New info on the Charge Channel : $N(q,\omega)$

This extra experimental info can help understand correlated systems

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

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

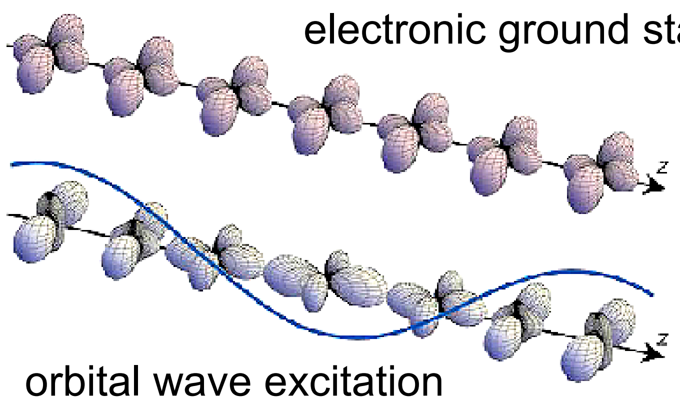


Competition among many *Energy* and *Length* scales Determine the physics of these systems

An unexplored degree of freedom in transition metal oxides:

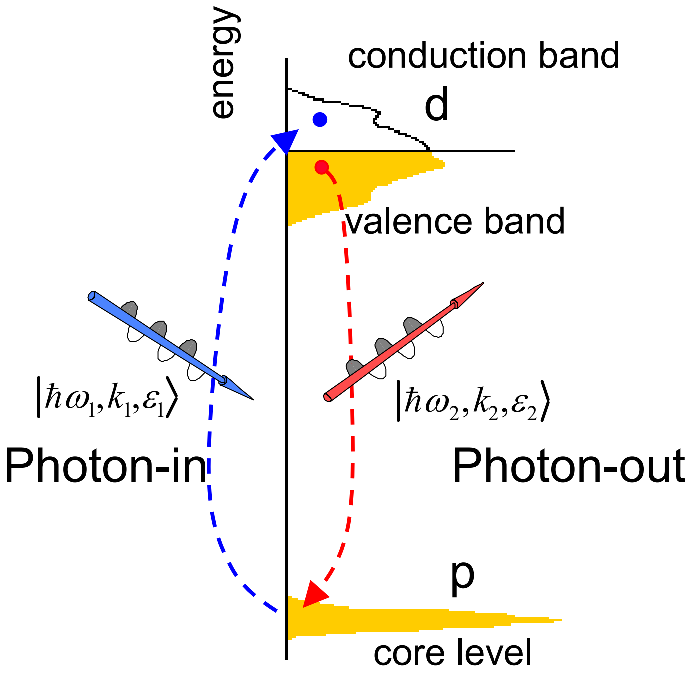
Orbital Density Waves

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)*

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

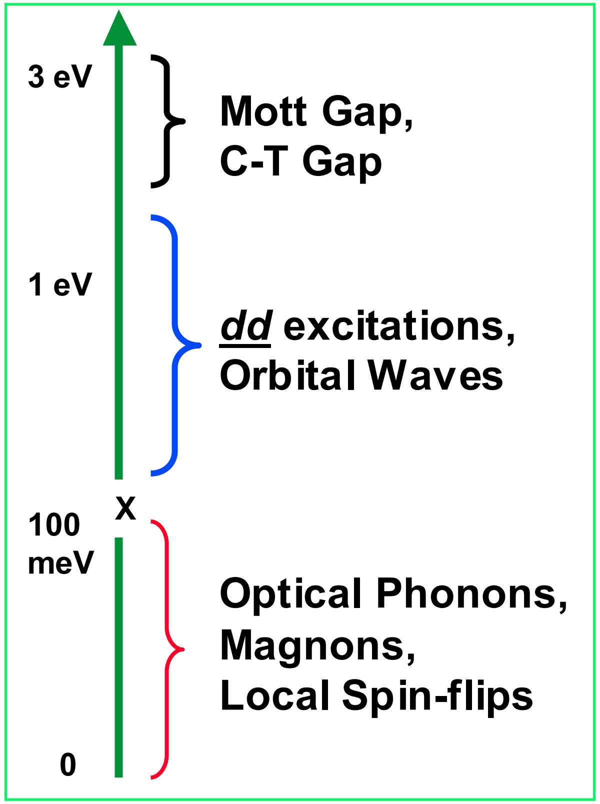


Energy loss: $\omega=\omega_2-\omega_1$
Momentum transfer: $q=k_2-k_1$
Resonance: $\omega_1 \sim \omega_{edge}$

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_BT resolution

Energy scales of various excitations



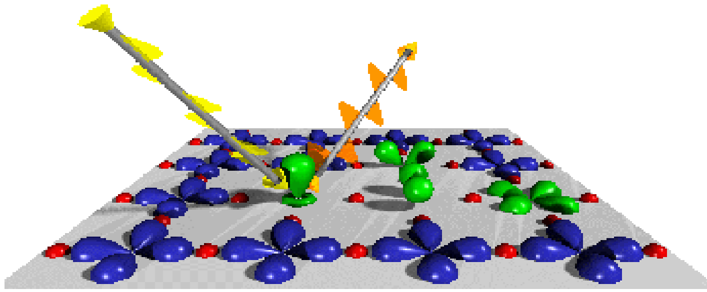
- Optical Phonons: ~ 40 - 70 meV
- Magnons: ~ 10 meV - 40 meV
- Orbital fluctuations (originated from optically forbidden d-d excitations): ~ 100 meV - 1.5 eV

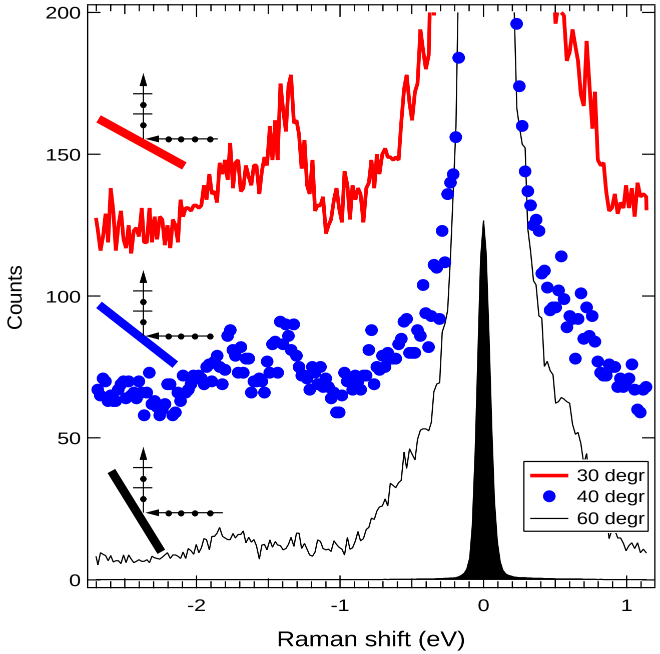
Requires study of energy losses with energy resolution better than 10meV

Soft x-ray resonances (3p -> 3d) provide the most sensitive channels of excitations to study orbital wave excitations

Current State-of-the-Art
Study of d-d Excitations in Cuprates

Cu d-d excitation at 74eV





➢ **Previous experiments (@ ALS):**

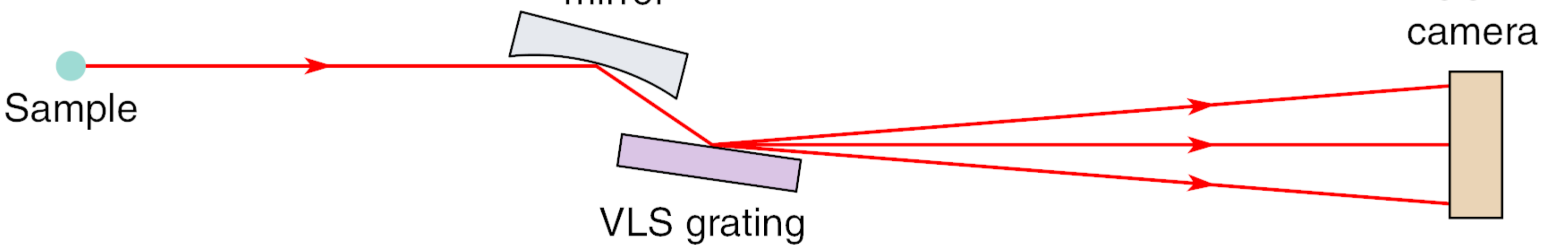
Energy resolution = 200 meV
Throughput = low

Need better energy resolutions (<10 meV) and higher throughput

Kuiper, Nordgren, Sawatzky et al., Phys. Rev. Lett. 80, 5204 (1998)
Expt carried out @ ALS

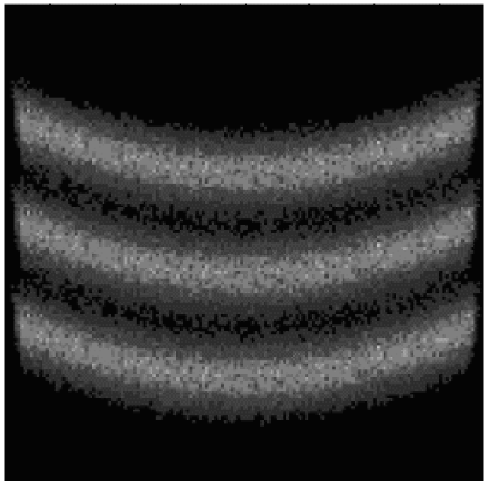
meV Resolution VLS Spectrograph

Optical Design



Ray Traces

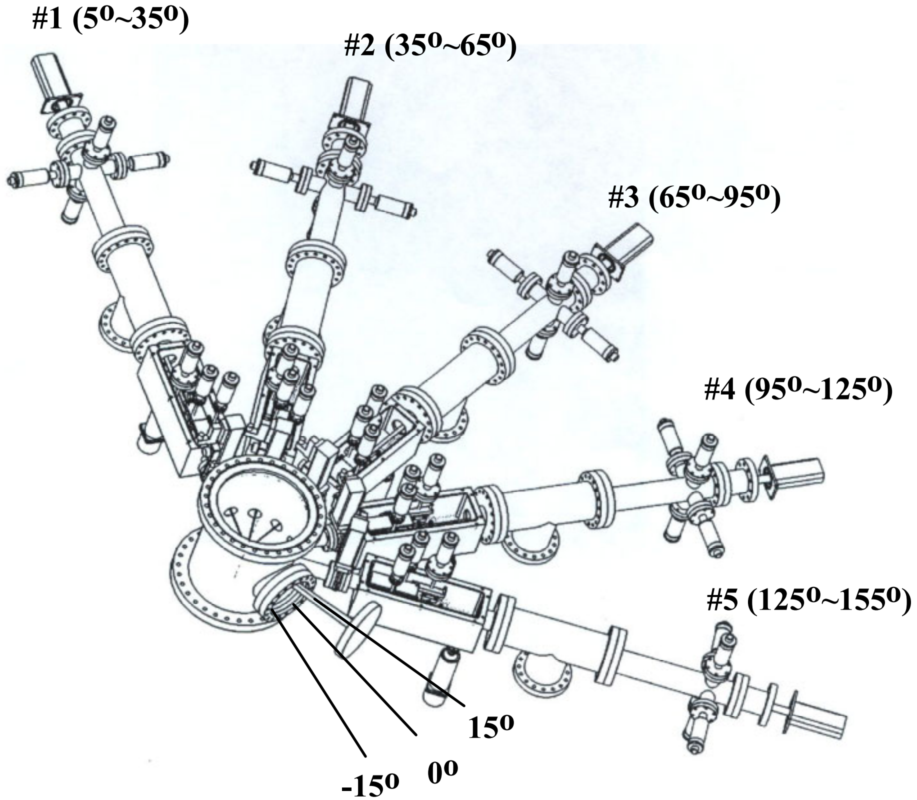
- **Resolution approaching 1 meV.**
- Overall length = 2 meters.
- Designed for Mn 3p (47 eV)
- Source size = 4 microns.



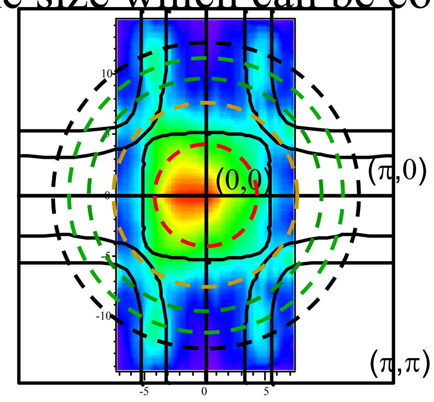
hν = 47 eV ± 5 meV

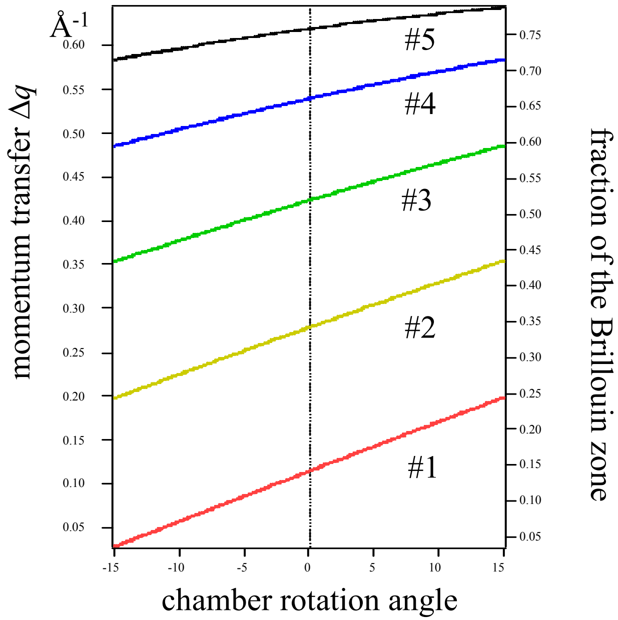
Resonant Inelastic soft X-ray Scattering

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



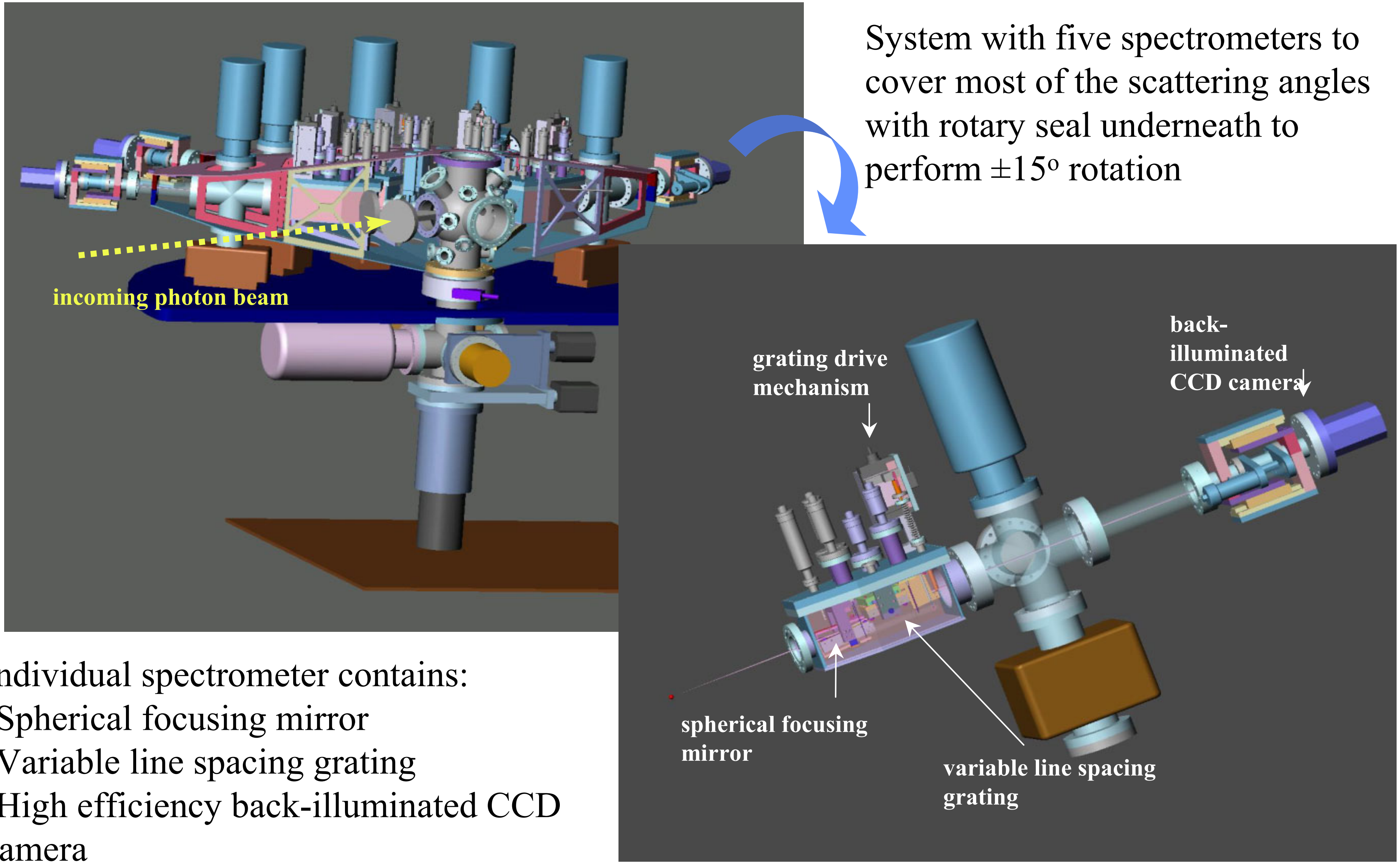
Brillouin zone size which can be covered by this spectrometer





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

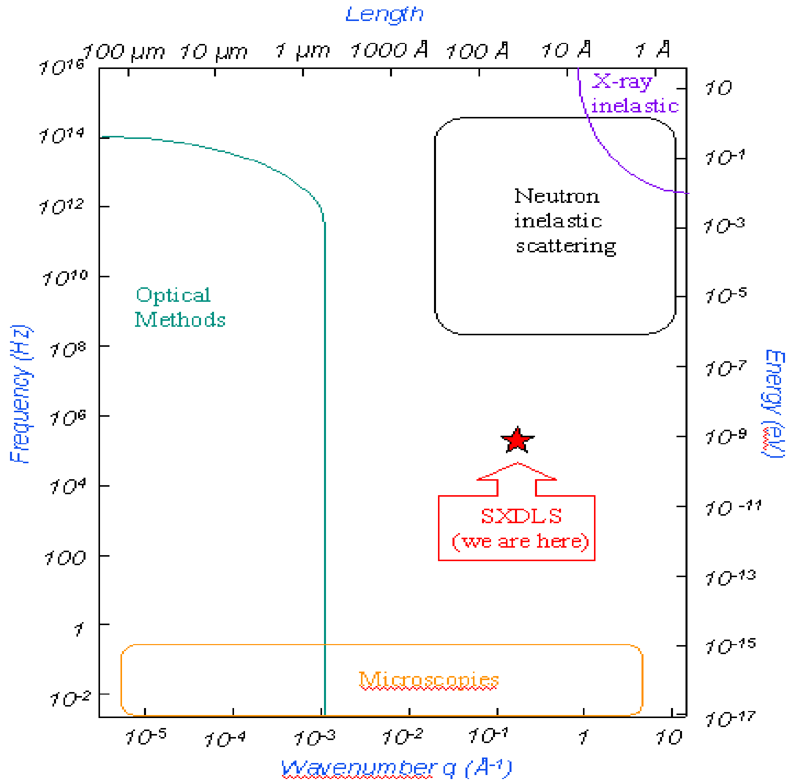
Resonant Inelastic soft X-ray Scattering



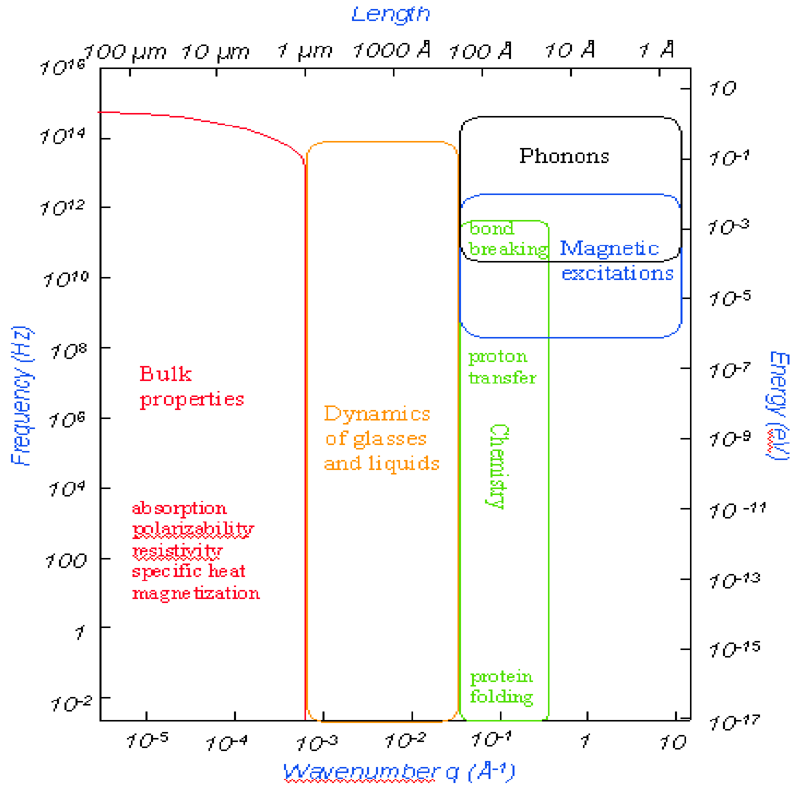
System with five spectrometers to cover most of the scattering angles with rotary seal underneath to perform ±15º rotation

Individual spectrometer contains:
- Spherical focusing mirror
- Variable line spacing grating
- High efficiency back-illuminated CCD camera

Combined Nanometer Spatial and Microsecond Temporal Resolution- Coherent Scattering



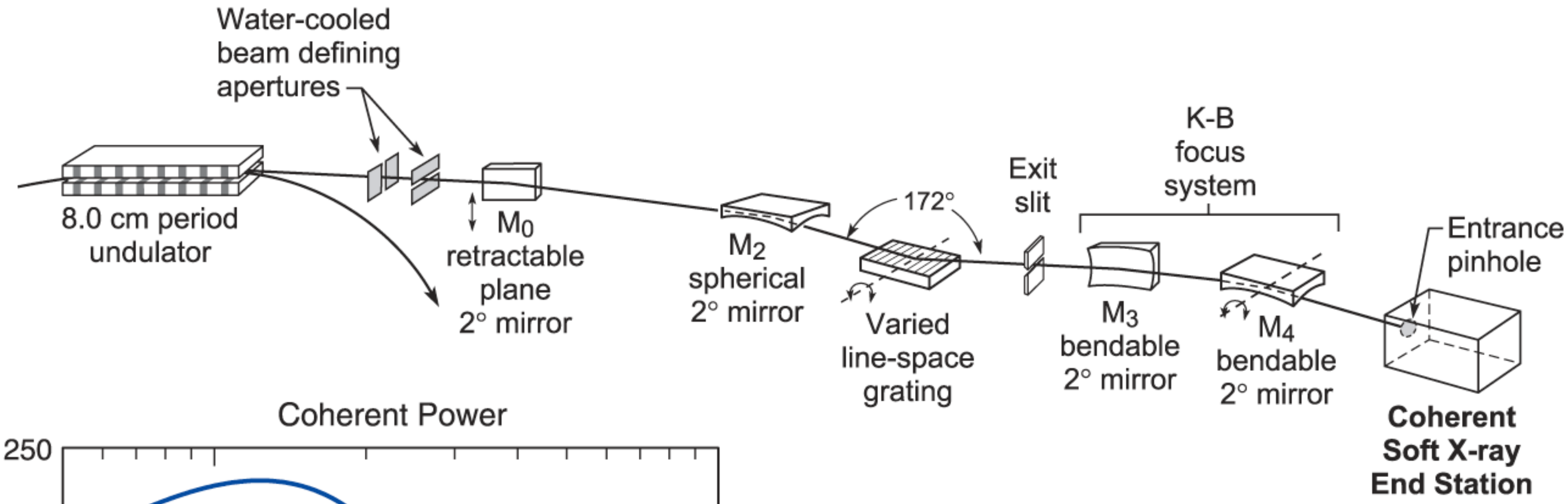
Spatial and temporal frequency sensitivities of various techniques

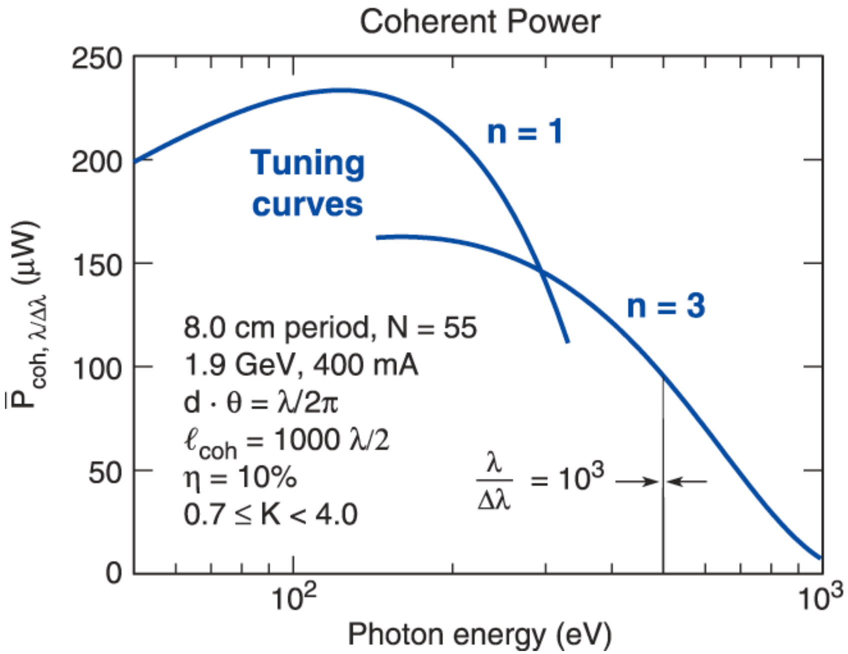


Relevant spatial & temporal frequency scales for various physical phenomena

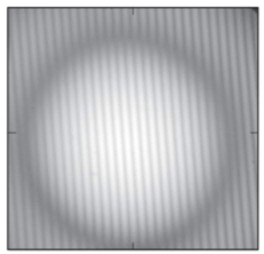
Intense, transversely coherent soft x-ray beams will allow extension of dynamic laser light scattering to probe temporal fluctuations on the scale of nanometers.

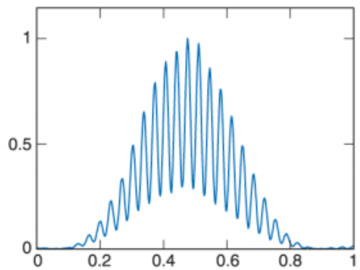
Coherent Soft X-Ray Science

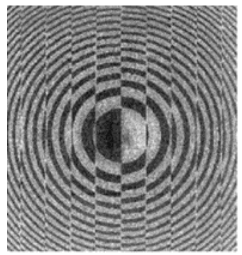




- Coherent scattering from dynamic systems
- Fourier optics at soft x-ray wavelengths

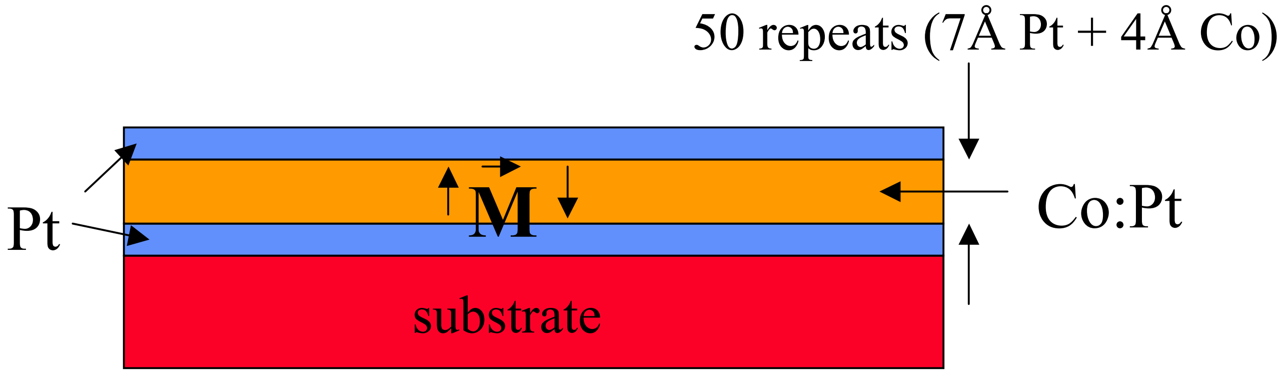






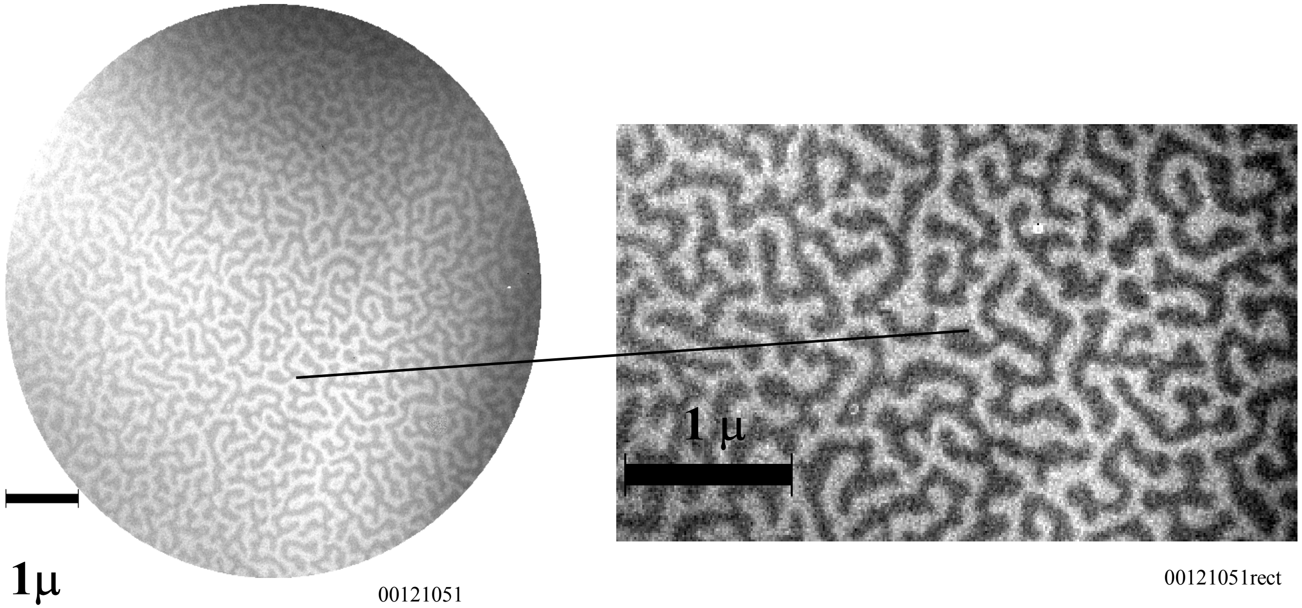
From Attwood

Magnetic Structure and Fluctuations in a Co:Pt Multilayer



- Candidate for future magnetic recording media
- Perpendicular magnetic anisotropy
- Magnetic domains ~ 100 nm
- ‘Tunable’ magnetization loop

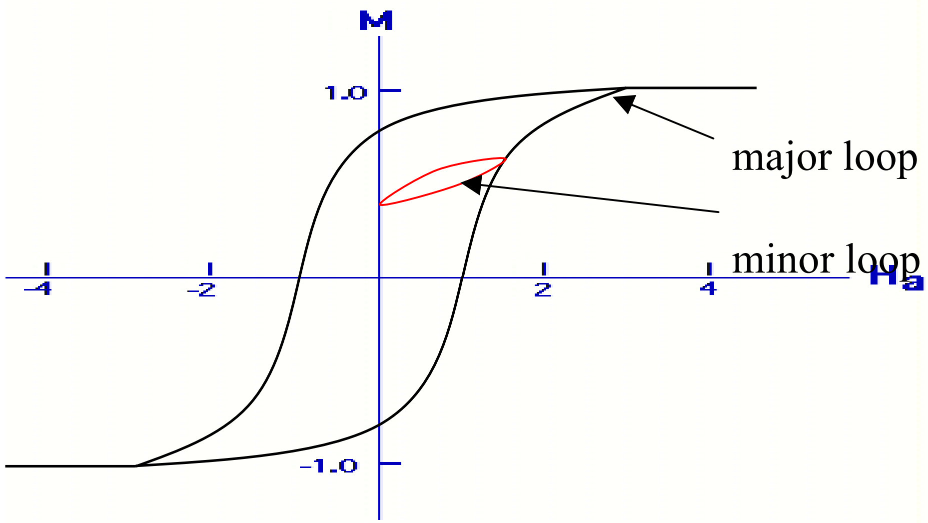
Imaging Magnetic Domains with a Soft X-ray Microscope



- Contrast provided by huge magnetic circular dichroism near the Co L_{23} absorption edge [$2p_{3/2}$ - 3d] at hν ~ 780 eV

- Wavelength λ ~ 15.8 Å allows good spatial resolution

Return Point Memory Effect



Macroscopic (Madelung, 1905):

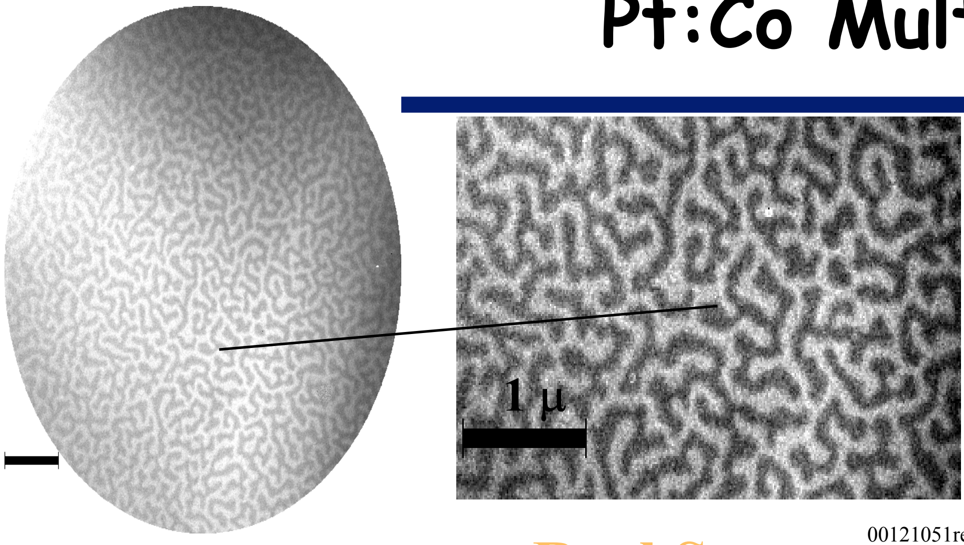
• The 'major magnetization loop' is well-defined - it reproduces after saturation;

• Excursion onto a 'minor magnetization loop' leaves from and reconnects to the major loop at a single point.

Microscopic:

• Is the magnetic domain structure reproducible around such major and minor loops?

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



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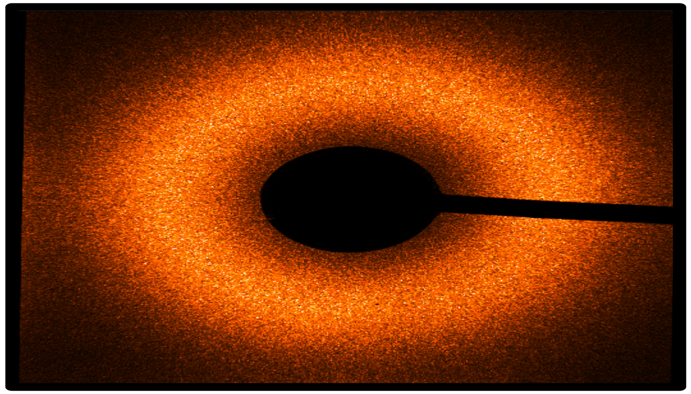
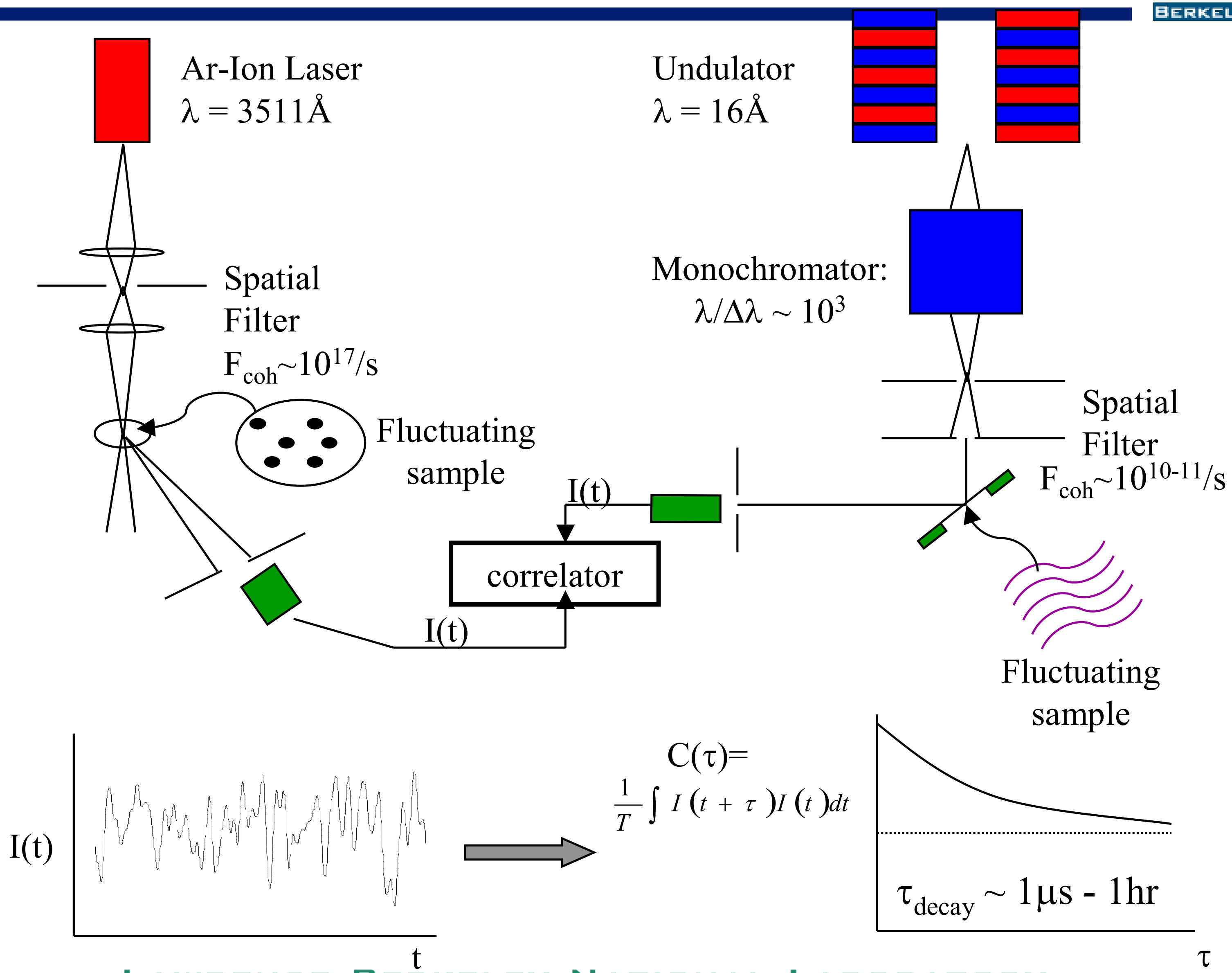
Real Space



Reciprocal Space

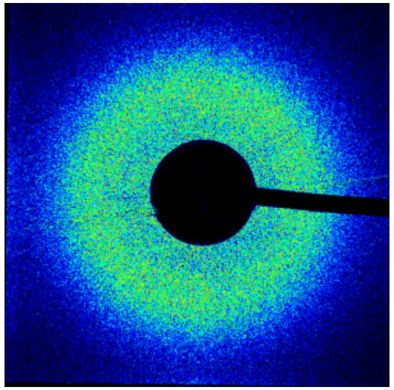
- Speckle pattern ≡ diffraction pattern of the magnetic domain structure;
- Domain sized inversely related to angular width of the ‘doughnut’;
- Contrast provided by x-ray magneto-optic effects near the Co L-edge.
- New apparatus will enable us to measure the individual Fourier components fluctuating at MHz time scales;
- We will measure domain flipping (Barkhausen noise) and domain wall motion with a combined spatial and temporal resolution not available with other techniques.

Dynamic Light Scattering

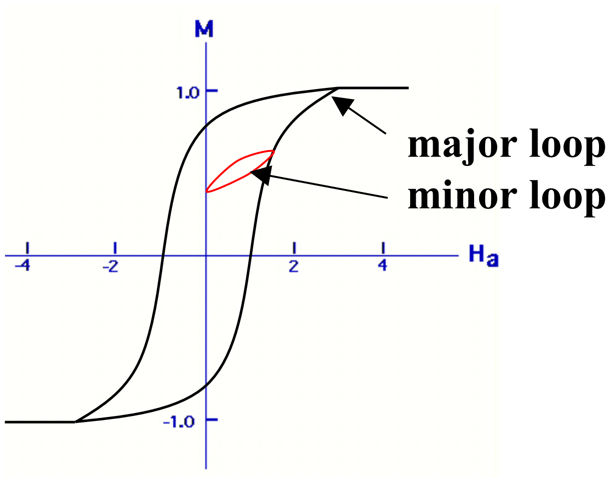


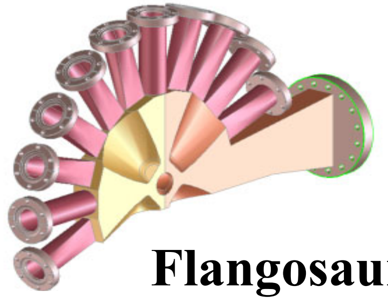
Coherent soft-X ray Scattering

The combination of the large soft x-ray magnetic contrast with high coherent flux of the new CSX beamline will enable many experiments that probe spatiotemporal magnetic fluctuations.

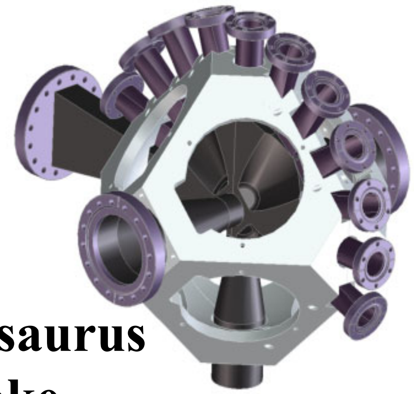


Speckle-diffraction Pattern through a Co:Pt film.

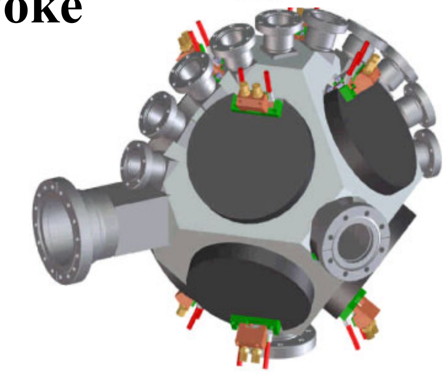




Flangosaurus



Flangosaurus with yoke



Octapolar Flangosaurus

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**

Why dynamic soft X-rays coherent scattering ?

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

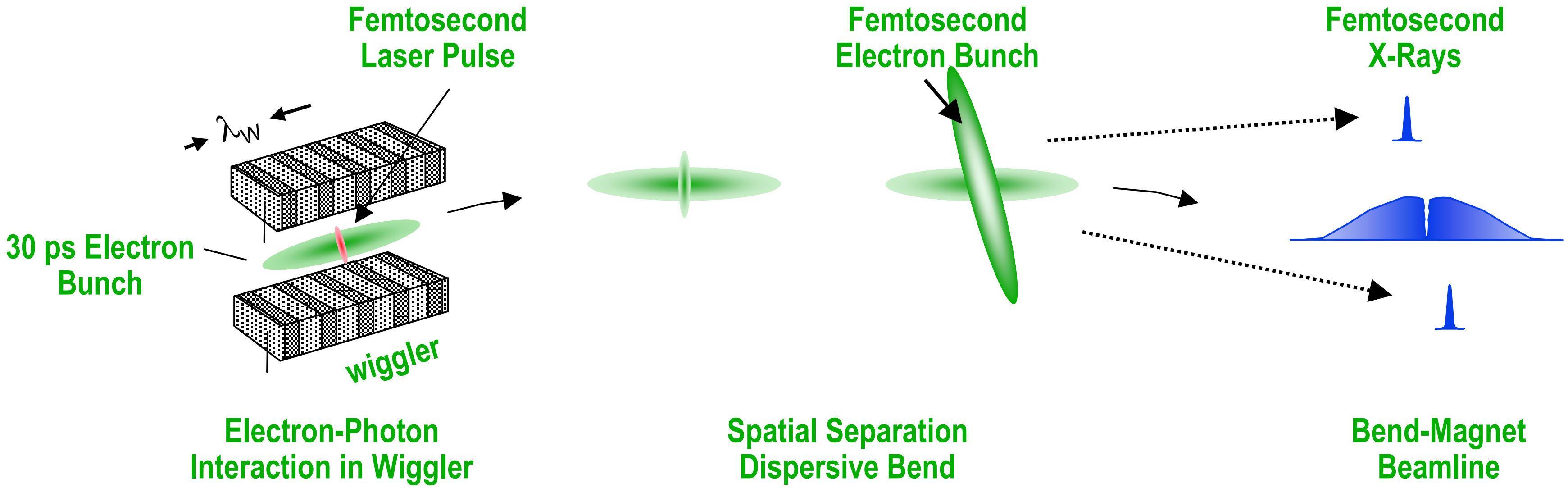
Time-Resolved X-Ray Spectroscopy

- Ultra-fast time regime: $\leqslant$ 200fs
  - Electron excitation/de-excitation (fs)
  - Bond breaking
  - Carrier-carrier scattering
  - Hole-optical phonon scattering
  - Charge density wave/charge transfer
- Time regime: $\leqslant$ 2ps
  - Carrier acoustic phonon scattering
  - Relaxation of biological system after light absorption (Rhodopsin); Phase transition (diamond $\longleftrightarrow$ graphite)
- Time regime: $\geqslant$ 1-100ps
  - Stripe fluctuation in High Temp Superconductor
  - Magnetic recording
  - Protein folding (ps-s)

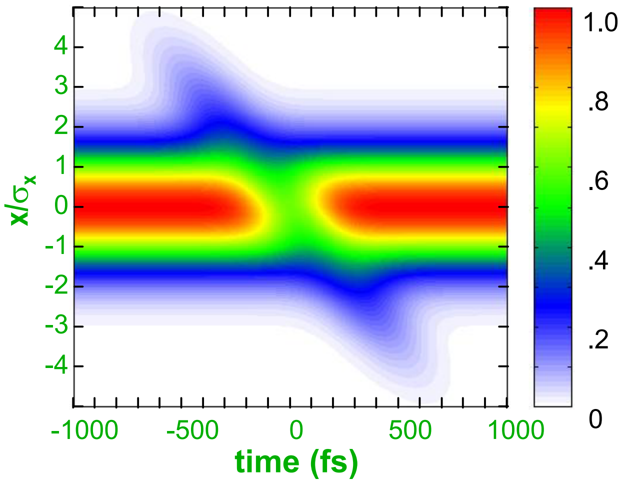
Time-Resolved X-Ray Spectroscopy Techniques

- Laser Time Slicing of SR, τ ~ 100 - 200fs
- Bending Magnet ~ 10^5 photons/s
  - Undulator ~ 10^8 photons/s
  - Phase transition
- Streak Camera; τ ~ 1-2 ps, limited by detector
  - Could use dispersive methods in time and energy
  - Ultrafast lattice dynamics (coherent phonons)
  - Polarons in condensed matter (magnites)
- Dynamics Coherent Soft X-Ray Scattering, τ > 1ns - μs
  - Stripe fluctuation in High Temp Superconductor (ns-μs)
  - Magnetic recording (ns)
  - Protein folding (ps-s)

GENERATION OF FEMTOSECOND X-RAYS FROM THE ALS



Calculated Electron Density Distribution



Zholents and Zolotorev, *Phys. Rev. Lett.*, **76**, 916,1996.

Schoenlein et al., *Science*, **287**, 2237, 2000

Science of Heterogeneous systems, Interfaces, heteromagnetism

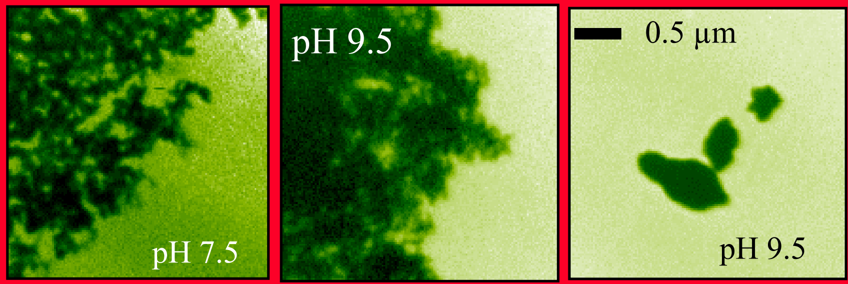
BERKELEY LAB

- Real Space Microscopy (transmission, scanning or imaging)
  - Biological systems (water window, in-situ conditions, resolution ~20-30 nm, → Tomography (Larabell et al)
  - Environmental Science
- Spectromicroscopy of interfaces down to nm resolution (PEEM III,SMART, abberation corrected optics)?
  - Exchange bias in magnetic layers (Co/$LaFeO_3$), (example)
- Reciprocal space Imaging with Coherent Soft x-ray Scattering; Spatial resolution ~ 1nm - 40μm
  - Magnetic domains (Co/Pt multilayer), (example)
  - Stripe fluctuation in High Temp Superconductor

Development of these techniques necessary for Nanotechnology; "shape the world atom by atom" Ronald Hoffmann

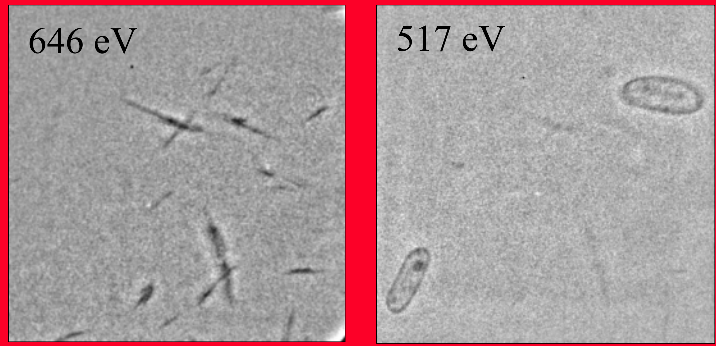
HIGH SPATIAL RESOLUTION MICROSCOPY OF HYDRATED MATERIALS

Reactions at Fe-oxides



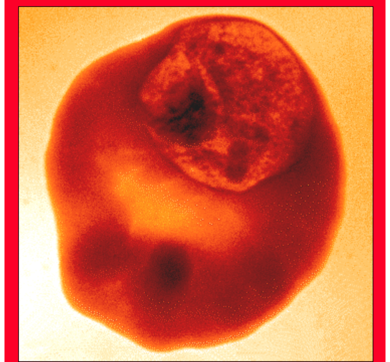
*S. Myneni et al., Science **278**, p.1107*

Manganese-Eating Bacteria



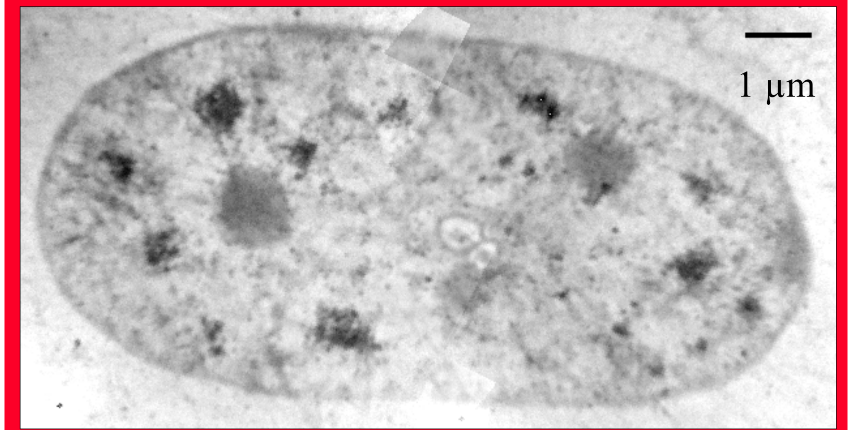
B. Tonner K. Nealson et al.

Malaria



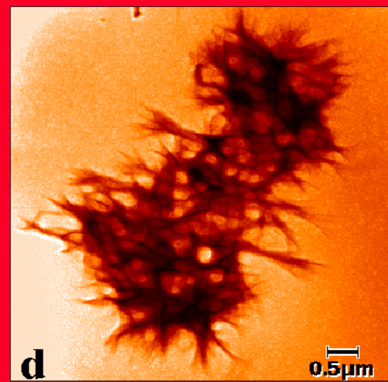
C. Magowan et al.
*PNAS **94**, 6222*

Cell Nucleus Labeled for Splicing Factor



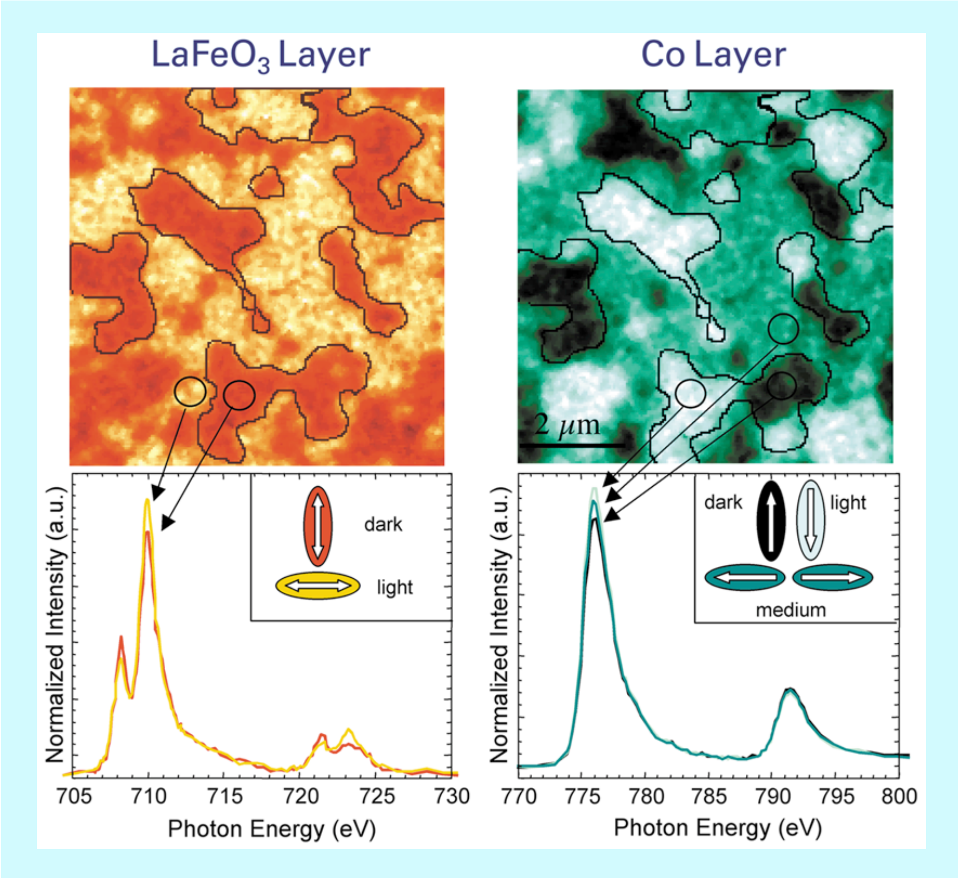
C. Larabell, S. Lelièvre, D. Hamamoto, M. Bissell

Alkali-Aggregate Reaction



K. Kurtis, P. Monteiro et al.
Cement & Concrete Research

Exchange bias in magnetic nanostructures



Linear dichroism at Fe L edge images AFM domains (left). Circular dichroism at Co L edge images FM domains (right). Comparison of images shows that the Co domains align with the AFM domains (light and dark regions inside outlined areas).

F. Nolting et al, Nature, 405, 767(2000)

Acknowledgements

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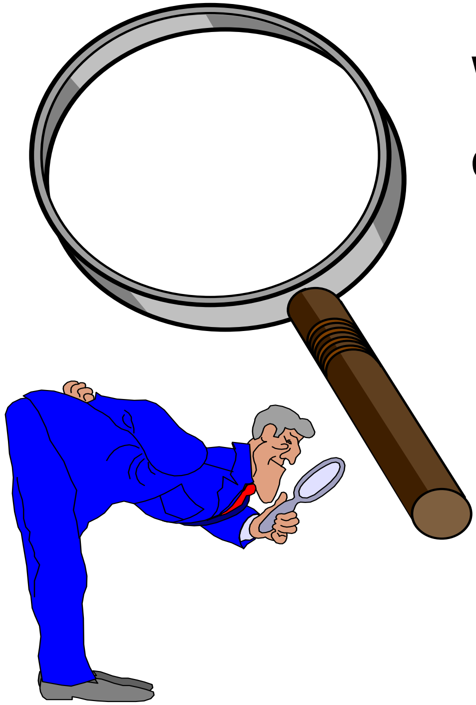
Conclusions



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