An Introduction to X-ray Methods

Sakura Pascarelli

sakura.pascarelli@xfel.eu

XVIII School on Synchrotron Radiation “Gilberto Vlaic”

Muggia (Trieste), Italy

21 September – 1 October 2026

Outline

- Radiation – matter interaction
- Experimental Techniques
  - Based on Scattering
    - ► Elastic Scattering
    - ► Inelastic Scattering
  - Based on Photoelectric Absorption
    - ► Core-hole Spectroscopies
      - X-ray Absorption Spectroscopy
      - X-ray Emission Spectroscopy, RIXS, X-ray Raman
      - X-ray Polarization Dependent Spectroscopies
      - X-ray Photoemission Spectroscopy
  - Imaging Methods

Pause : 11h40-11h50

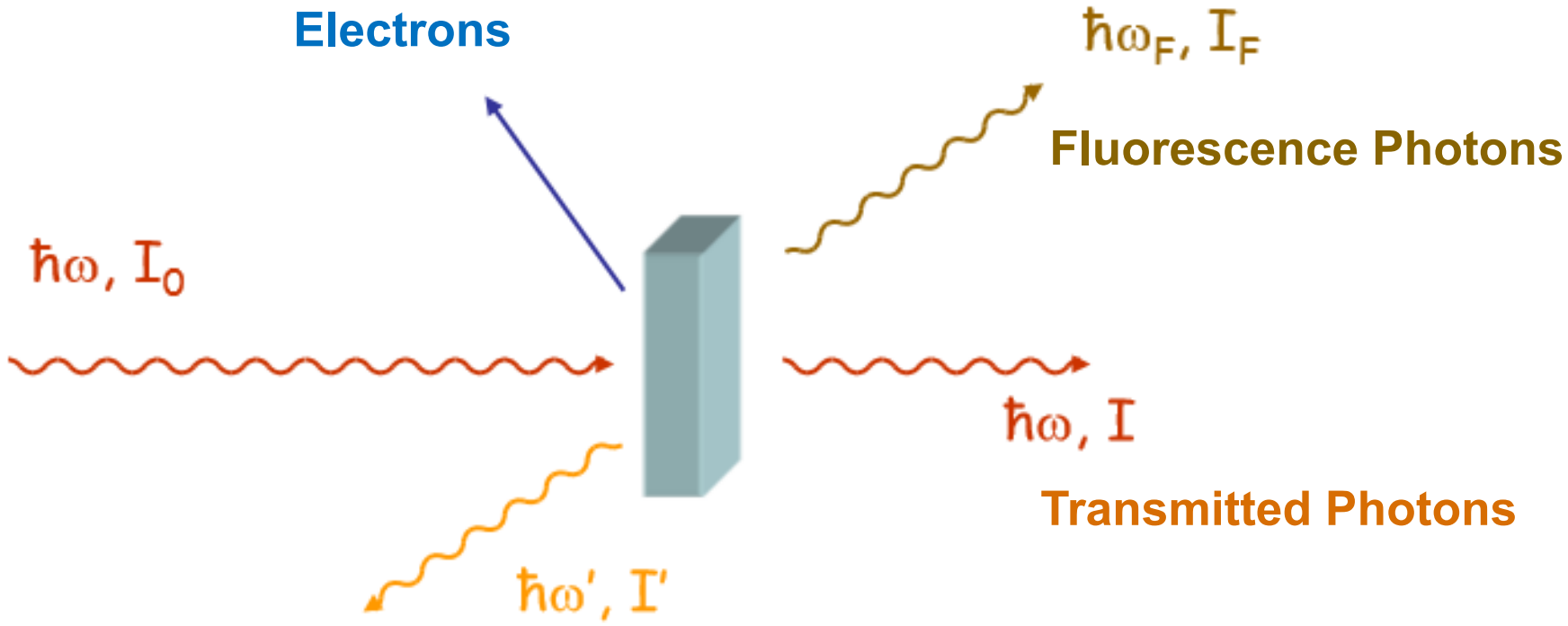
Outline

- Radiation – matter interaction
- Experimental Techniques
  - Based on Scattering
    - ► Elastic Scattering
    - ► Inelastic Scattering
  - Based on Photoelectric Absorption
    - ► Core-hole Spectroscopies
      - X-ray Absorption Spectroscopy
      - X-ray Emission Spectroscopy, RIXS, X-ray Raman
      - X-ray Polarization Dependent Spectroscopies
      - X-ray Photoemission Spectroscopy
  - Imaging Methods

Pause : 11h40-11h50

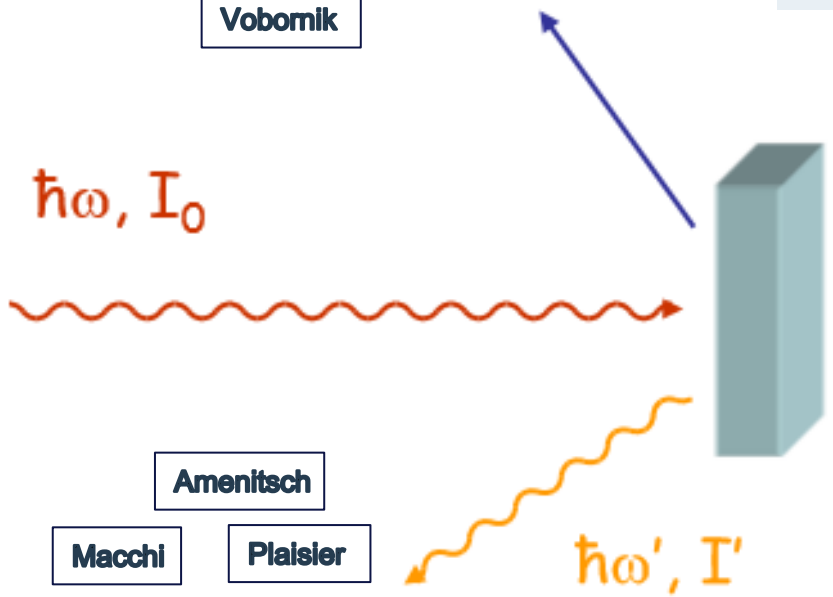
X-rays-matter interaction

X-rays-matter interaction



Boscherini 22 September

Main X-ray methods



Photoelectron Spectroscopy

Mariani
Baraldi
Vobornik

Electrons

+ imaging

X-ray Emission Spectroscopy

+ imaging

Wernet

Fluorescence Photons

Pascarelli
Di Cicco
Meneghini

X-ray Absorption Spectroscopy

+ imaging

Transmitted Photons

Amenitsch
Macchi
Plaisier

Elastic Scattering

Scattered Photons (elastically or inelastically)

Inelastic Scattering

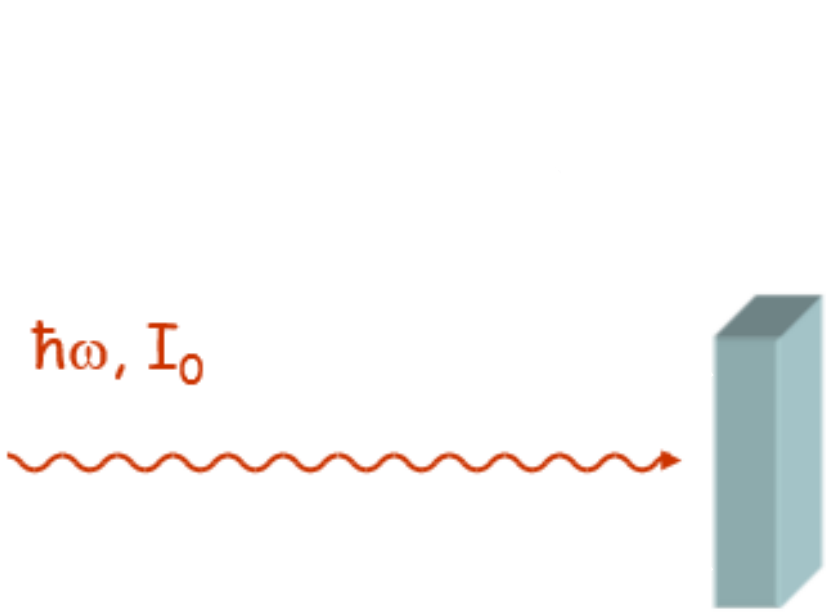
Thibault
Tromba
Gianoncelli

+ imaging

Moretti

+ imaging

Two fundamental X-ray matter interactions



Photoelectric absorption

X-ray scattering

Two fundamental X-ray matter interactions

Photoelectric absorption

Elastic scattering

Inelastic scattering

Two families of experimental techniques

Elastic Scattering

Elastic scattering

Photoelectric absorption

Spectroscopy

Inelastic scattering

Two families of experimental techniques

Elastic Scattering

no exchange of energy

microscopic geometric structure

- diffraction: crystals (XRD, GIXRD, ...)
- scattering: amorphous, liquids (XRS, WAXS, SAXS)

Spectroscopy

exchange of energy

electronic structure

local structure

dynamics

- absorption (XAS, EXAFS, XANES, ..)
- emission (XES, HERFD, ..)
- photoelectron (PES, XPEEM, ARPES)

- inel scattering (IXS, RIXS, X-Raman)

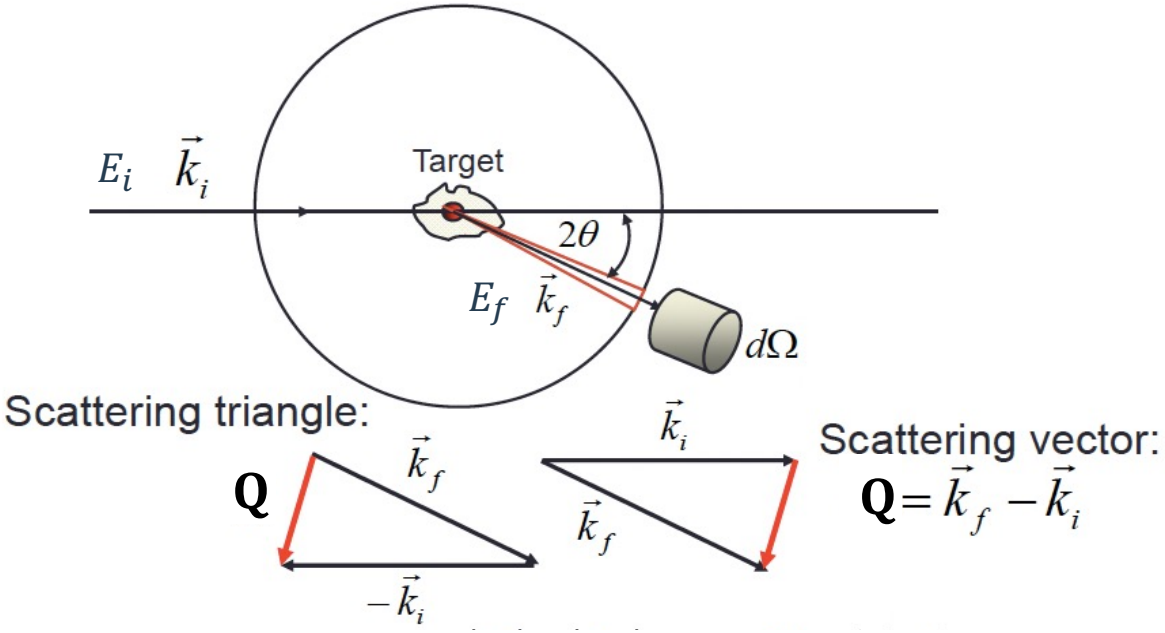
Outline

- Radiation – matter interaction
- Experimental Techniques
  - Based on Scattering
    - ► Elastic Scattering
    - ► Inelastic Scattering
  - Based on Photoelectric Absorption
    - ► Core-hole Spectroscopies
      - X-ray Absorption Spectroscopy
      - X-ray Emission Spectroscopy, RIXS, X-ray Raman
      - X-ray Photoemission Spectroscopy
      - X-ray Polarization Dependent Spectroscopies
  - Imaging Methods

Pause : 11h40-11h50

X-ray Scattering: Momentum and Energy Transfer

- X-rays interact primarily with the **electron density**
- Scattering is described by conservation of **momentum** and **energy**
- X-ray scattering measures the system response as a function of **momentum transfer Q** and **energy transfer $\hbar\omega$.**



Incident wavevector: $\mathbf{k_i} = \frac{2\pi}{\lambda}\hat{\mathbf{k}}_i$

Scattered wavevector: $\mathbf{k_f} = \frac{2\pi}{\lambda}\hat{\mathbf{k}}_f$

Momentum transfer $\boxed{\mathbf{Q} = \mathbf{k_f} - \mathbf{k_i}}$

Energy transfer $\boxed{\hbar\omega = E_i - E_f}$

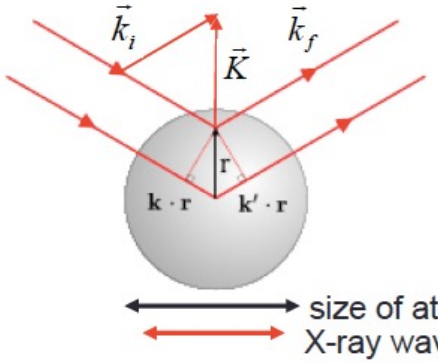
Elastic X-ray Scattering: basics

- The photon changes direction but **not energy** $E_i = E_f$, thus $\left|\vec{k}_i\right| = \left|\vec{k}_f\right| = k = {}^{2\pi}/_{\lambda}, \left|\boldsymbol{Q}\right| = 2k\sin\theta$
- Only momentum is transferred
- Elastic scattering probes the **static electron density**
- The quantity measured: $I(\boldsymbol{Q}) \propto |\, F(\boldsymbol{Q})\,|^2$ where

- $F(\boldsymbol{Q}) = \sum_j f_j\,(\boldsymbol{Q}) e^{i\mathbf{Q}\cdot\mathbf{r}_j}$ is the **crystal structure factor**
- $f_j\,(\boldsymbol{Q})$ is the **atomic form factor**

↑

Reciprocal Space

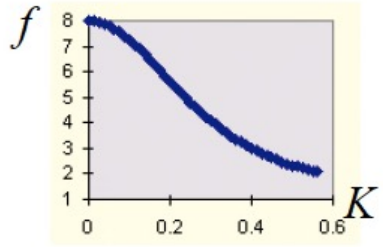


Atomic form factor is the Fourier transform of the electron density distribution in an atom ρ(r):

$$f(\boldsymbol{Q}) = \int \rho_e(\vec{r}) e^{i\boldsymbol{Q}\boldsymbol{r}}\, d\vec{r}$$

For spherical symmetric charge distribution follows:

$$f(Q) = \int \rho_e(r)\; e^{iQr\cos\varphi}\, 2\pi r^2 dr \sin\varphi\, d\varphi$$



$$= 4\pi \int_0^{\infty} \rho_e(r) r^2\; \frac{\sin Qr}{Qr}\, dr$$

$$f(Q=0) = Z$$

Elastic X-ray Scattering from a perfect crystal: the Bragg condition

- **Sharp peaks appear at θ that fulfill the Bragg condition**
- The path difference between wavefront1 and 2: **$\Delta r = 2d\sin\theta$**
- The condition for constructive interference: **$\Delta r = n\lambda$**

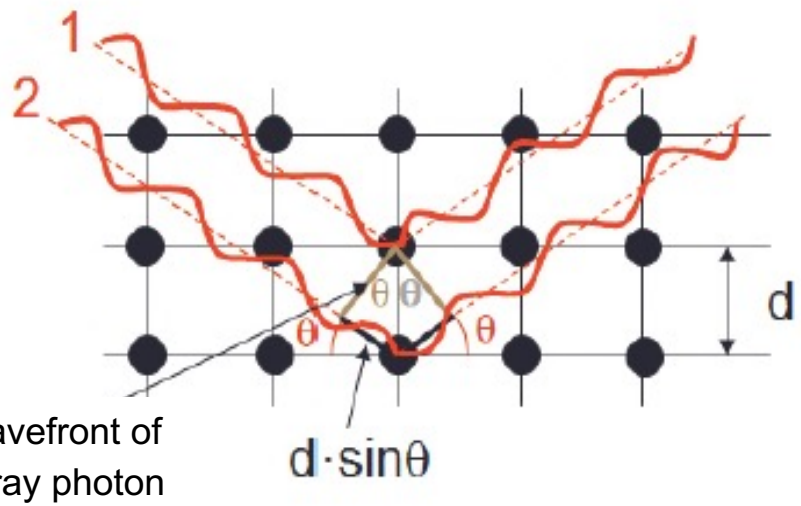
$$2d\sin\theta = n\lambda$$

Bragg condition for interference maxima

- Different crystal planes **d** diffract to different angles θ

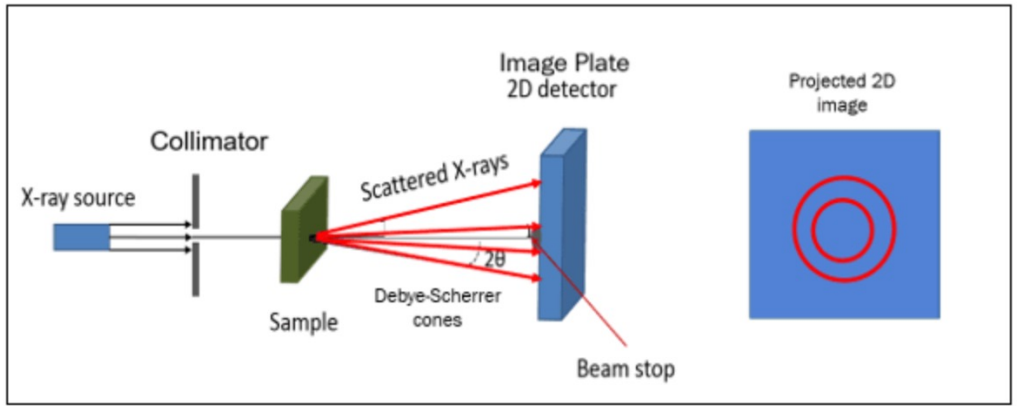
$$\boldsymbol{Q} = \mathbf{G}_{hkl}$$

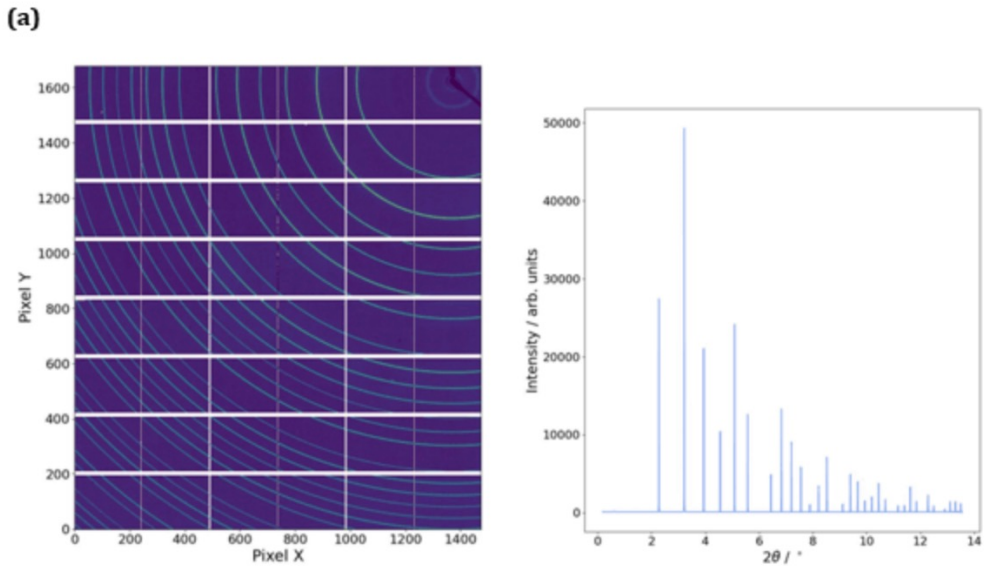
G_{hkl} = Reciprocal lattice vector



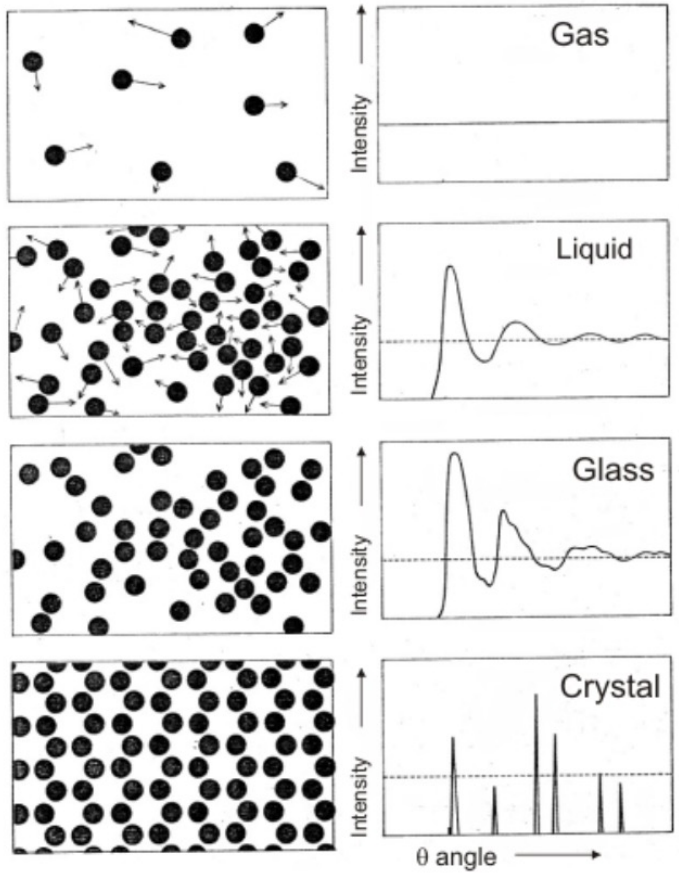
Wavefront of X-ray photon

Elastic X-ray Scattering: measuring structure





lcdd.com



Reveals

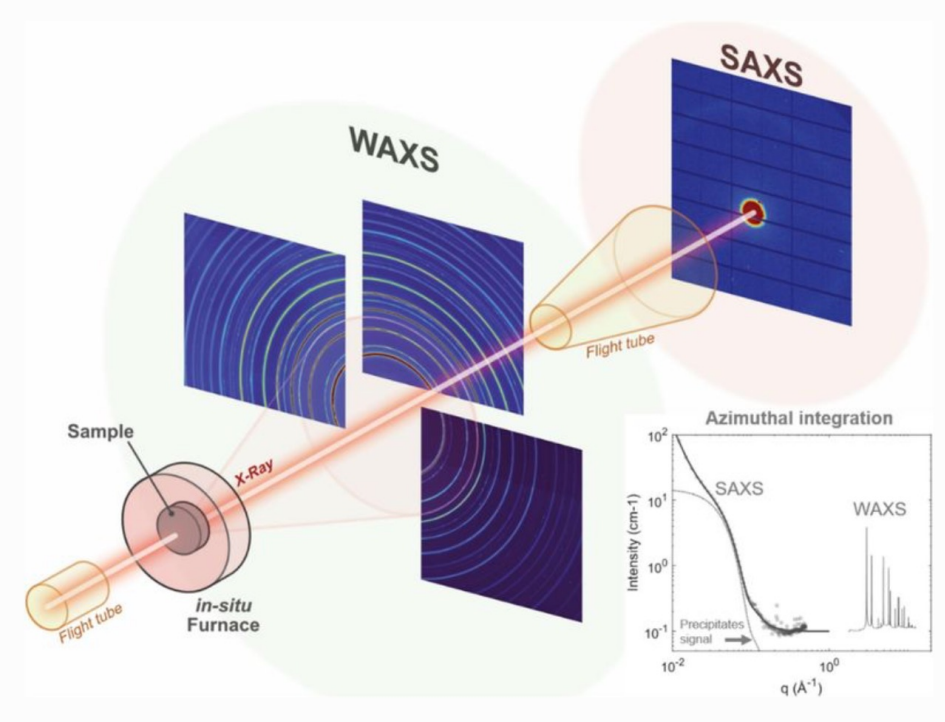
- Crystal structure
- Lattice parameters
- Long-range order
- Defects
- Nanostructure

Typical techniques

- X-ray diffraction (XRD)
- Small-angle X-ray scattering (SAXS)
- Wide-angle X-ray scattering (WAXS)
- Coherent diffraction imaging (CDI)

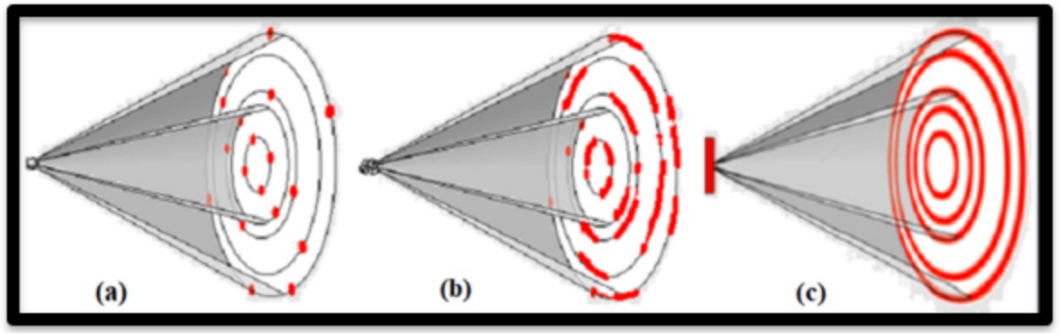
Small Angle vs Wide Angle X-ray Scattering: Reciprocal Space and Length Scale

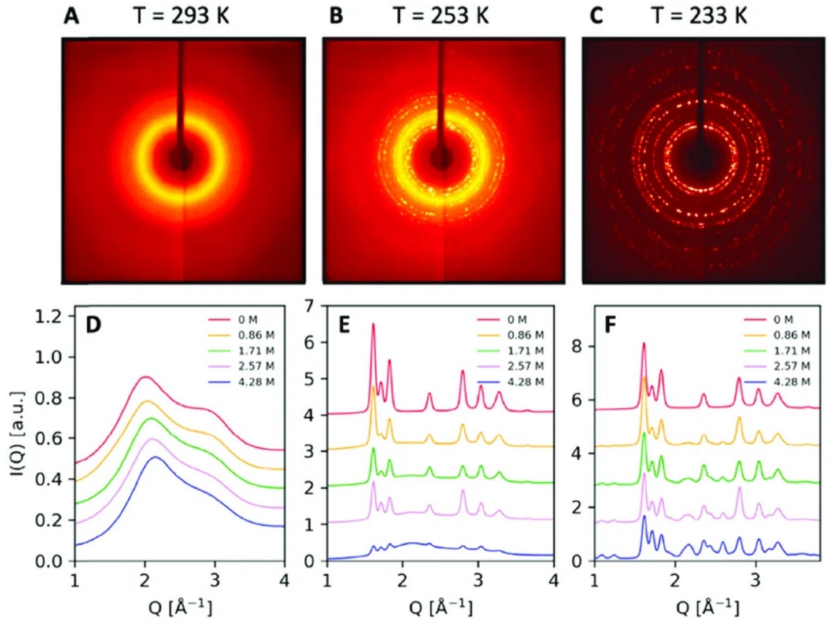
- Relationship between scattering angle and length scale
  - Momentum transfer: $q = \frac{4\pi}{\lambda}\sin\theta$
  - Characteristic length scale: $d \approx \frac{2\pi}{q}$
- SAXS and WAXS probe different regions of reciprocal space, corresponding to different real-space length scales.
  - **SAXS:long-range electron density fluctuations**
  - **WAXS: atomic correlations and crystal lattice order**



Schematic of the in situ simultaneous SAXS/WAXS measurement setup using a furnace sample environment at beamline P21.2, PETRA III.

Elastic X-ray Scattering: what do the patterns look like ?





Crystalline Materials (Long-Range Order)

- **Atomic Structure**: Highly ordered, repeating 3D lattice geometry.
- **Scattering Pattern**: Sharp, well-defined spots or sharp concentric rings (Bragg peaks).

Amorphous Materials & Liquids (Short-Range Order)

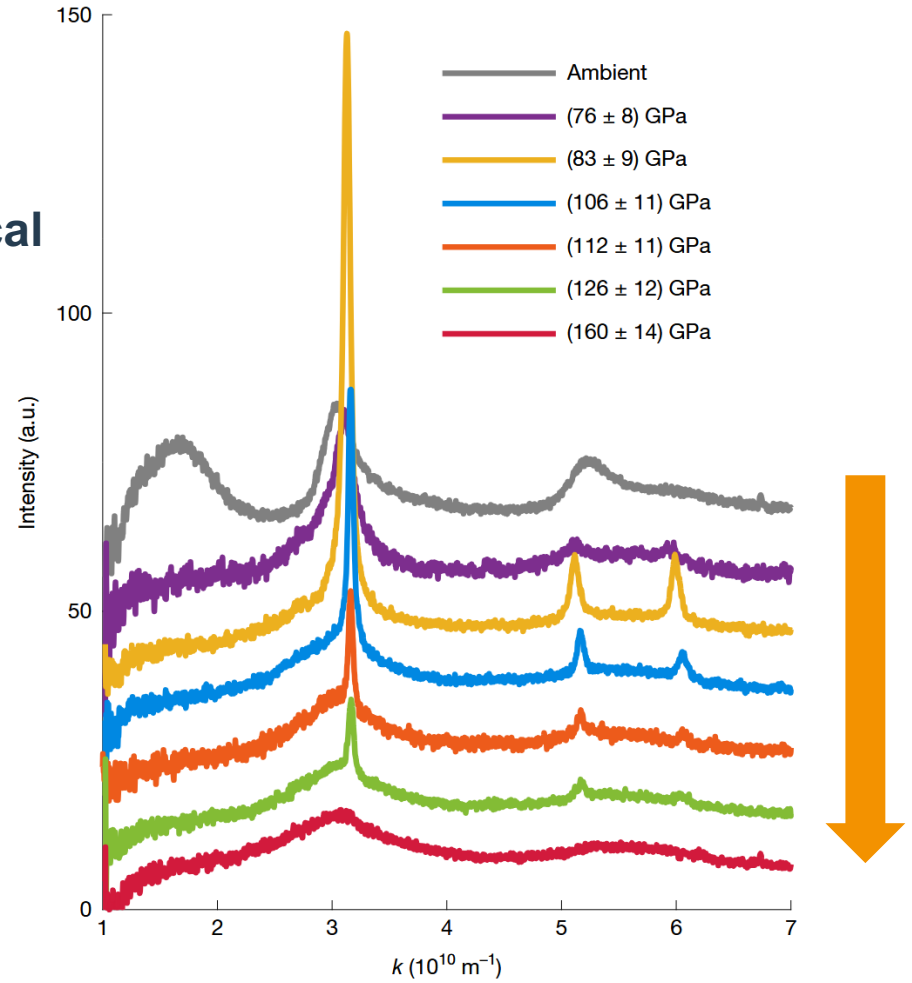
- **Atomic Structure**: Disordered, random arrangement with only nearest-neighbor consistency.
- **Scattering Pattern**: Broad, diffuse halos or a singular wide amorphous hump.

lcdd.com

Local structure in liquid carbon

Towards better control of the synthesis of novel carbon-based materials

- First experimental S(k) of liquid C
- Confirms tetrahedral coordination (N ~ 4)
- **First experimental determination of local structure in low Z matter at extreme conditions**



- glassy carbon: broad amorphous structures
- peaks appear: diamond formation
- complete disappearance of diamond, only melt visible

D. Kraus et al., Nature 642, 351 (2025)

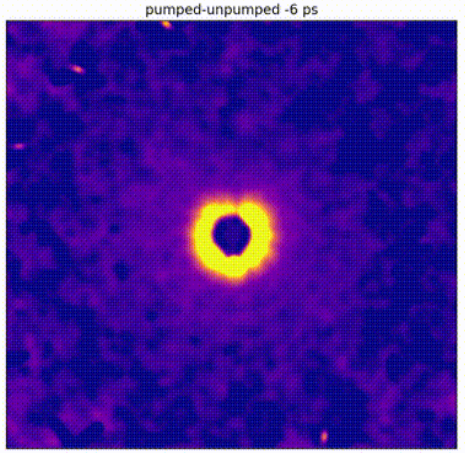
- HED@EuXFEL X-ray scattering on ns-laser shocked targets

Magnetic fluctuations in ferromagnetic multilayers by ps-resolved-SAXS

Towards fast energy-efficient memory applications

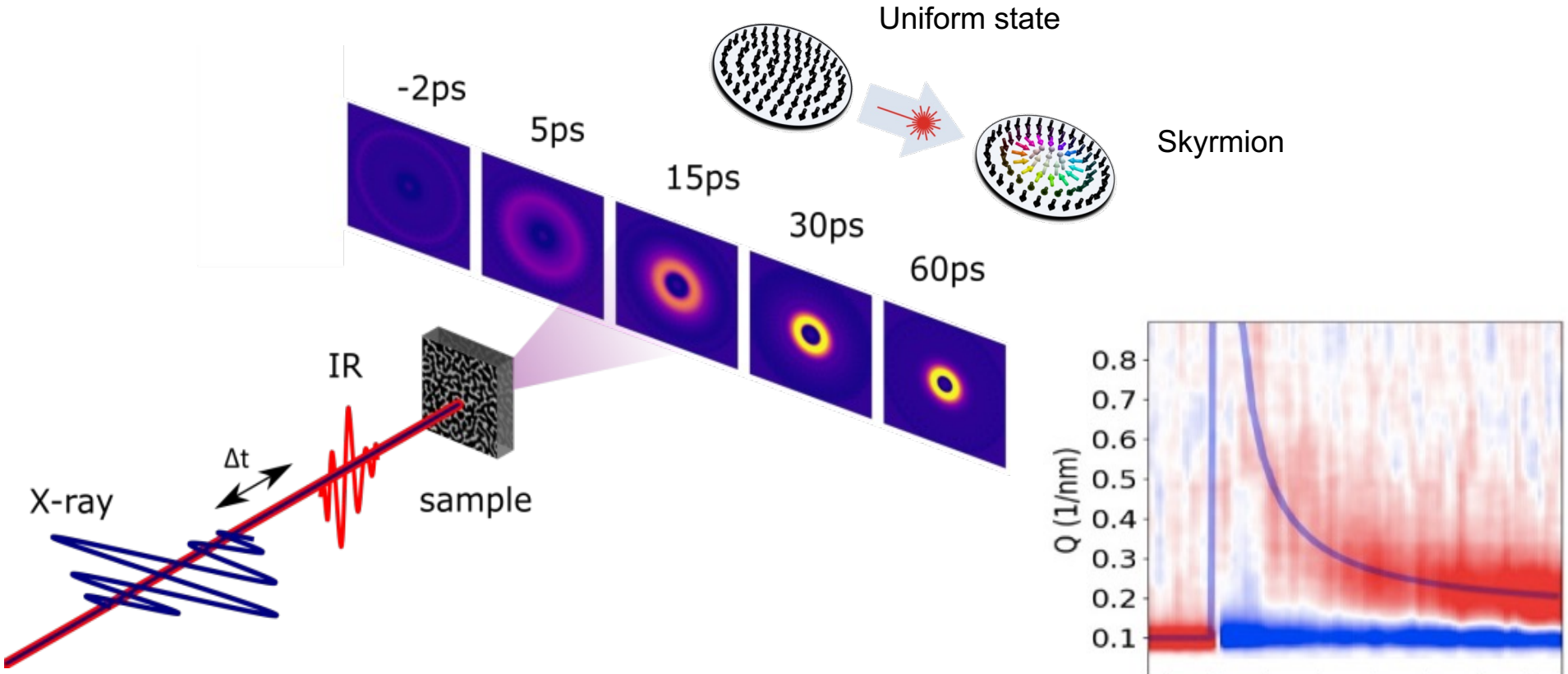
- Nanosize Co/Pt multilayers with perpendicular magnetization
- Probe **ultrafast nucleation and subsequent coalescence of magnetic fluctuations (skyrmions)**

SAXS vs delay time



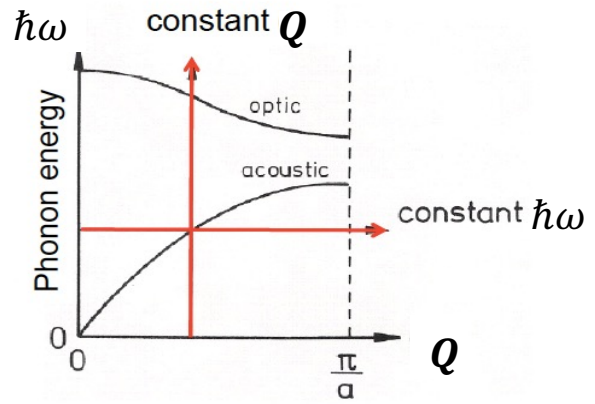
- SCS@XFEL ps-resolved resonant magnetic SAXS at Co L_3

European XFEL



Sergey M. Suturin et al. PRB **108**, 174444 (2023)

Inelastic X-ray Scattering: basics



- The photon exchanges energy with elementary excitations $E_i \neq E_f$.
  - Energy transfer : $\hbar\omega = E_i - E_f$
  - Momentum transfer : $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$
- This energy exchange reveals collective excitations and dynamical correlations
- The quantity measured is proportional to the **dynamic structure factor** $S(\boldsymbol{Q}, \omega)$ which contains information on the density correlations.

Elastic	**Inelastic**
$\Delta E = 0$	$\Delta E \neq 0$
Static structure	Dynamics
Electron density	Elementary excitations
Structure factor $F(\boldsymbol{Q})$	Dynamic structure factor $S(\boldsymbol{Q}, \omega)$

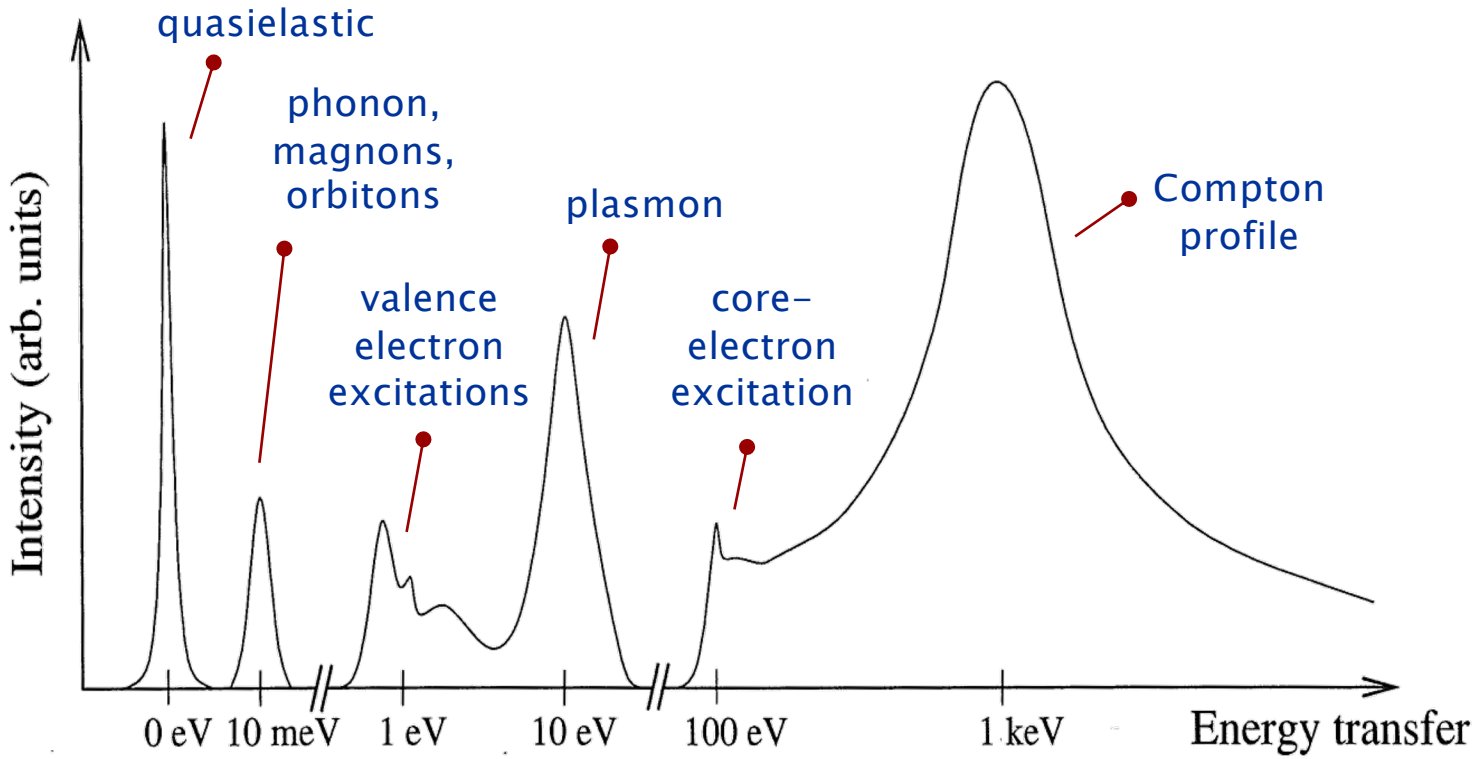
Inelastic X-ray Scattering: measuring excitations

Excitations observed

- Phonons
- Magnons
- Plasmons
- Crystal-field excitations
- Charge-transfer excitations
- Electronic band excitations

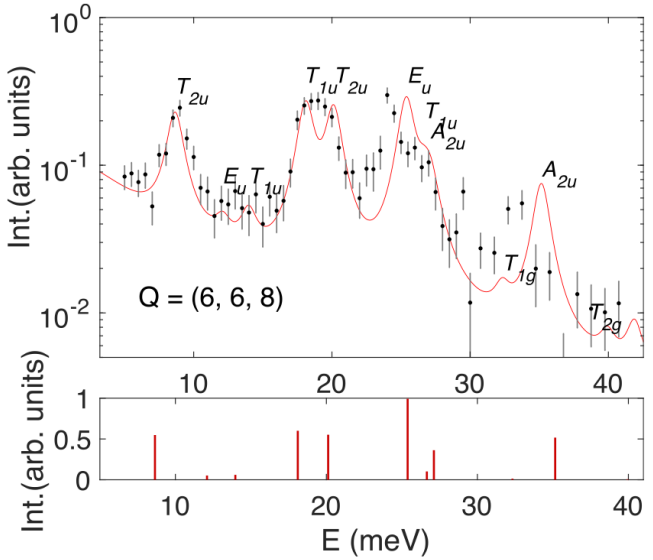
Experimental techniques

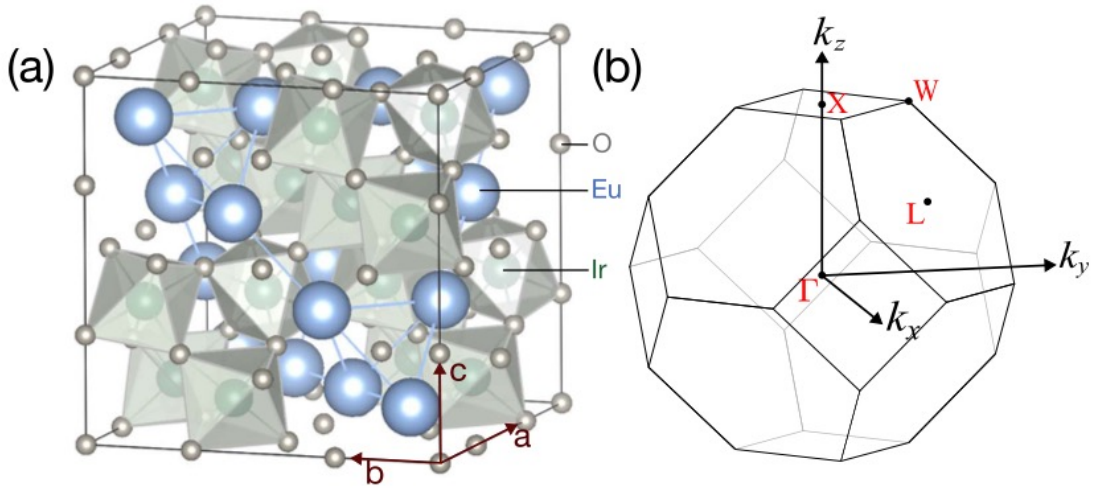
- Inelastic X-ray Scattering (IXS)
- Resonant Inelastic X-ray Scattering (RIXS)
- X-ray Raman Scattering (X-ray Raman)

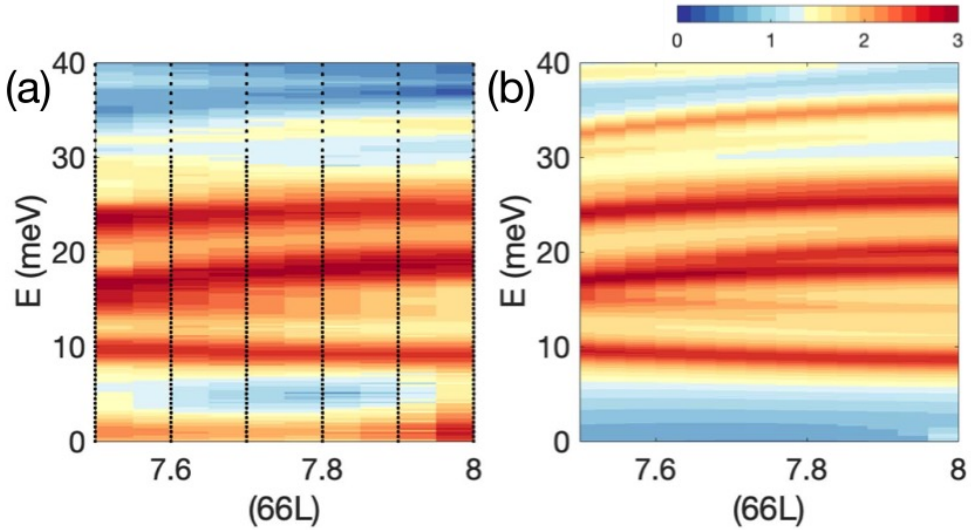


Phonon excitations in $Eu_2Ir_2O_7$ probed by inelastic x-ray scattering

- Phonon dynamics and its interplay with magnetic ordering is crucial for understanding the unique quantum phases in the pyrochlore iridates.
- 4d and 5d heavy transitional metal electronic systems → cutting-edge research domain in condensed matter physics.
- Unique amalgamation of extended 5d/4d orbitals, strong spin–orbit coupling and geometrically frustrated lattices, → rich platform to search for exotic correlated states.



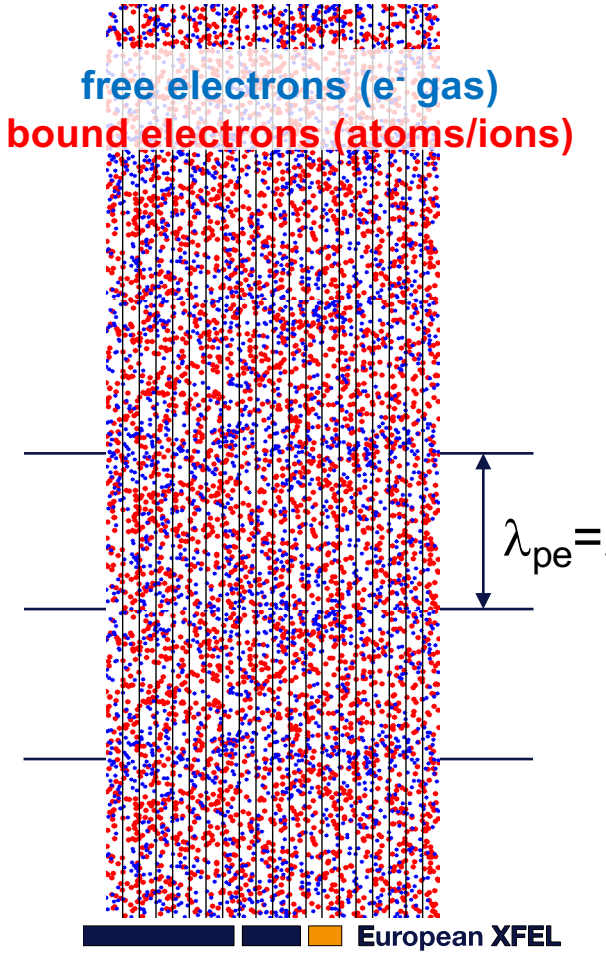


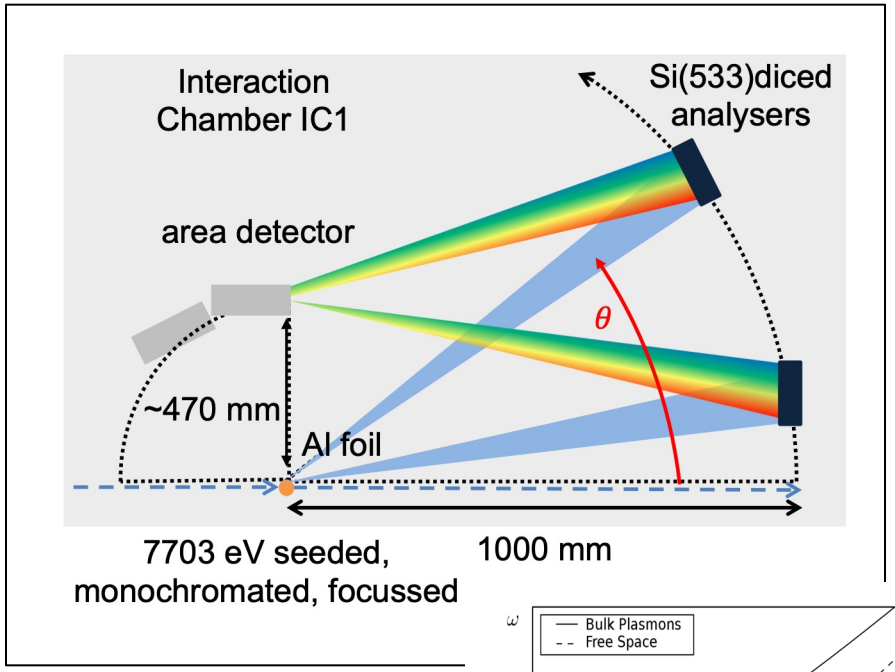


Wang et al. J. Phys.: Condens. Matter 36 (2024) 425705

Plasmon dispersion in shocked Aluminium

Achieving precision required to benchmark theoretical models

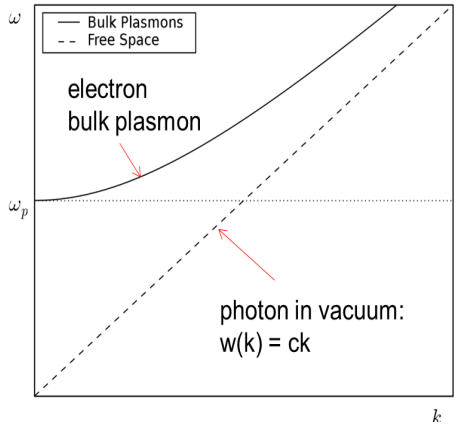




plasmon dispersion:

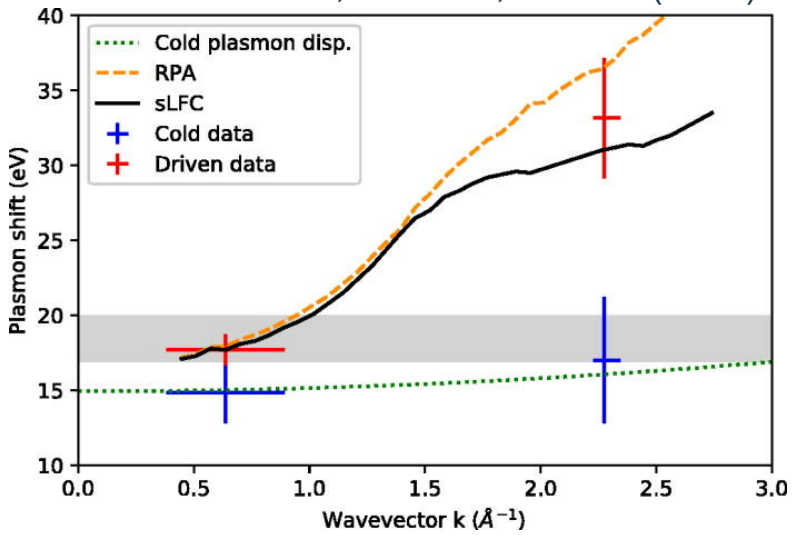
$$\omega^2_{plasmon} = \omega_{pe}^2 + c^2k^2$$

$$\omega_{pe} = \sqrt{\frac{e^2 n_e}{\varepsilon_0 m_e}}$$

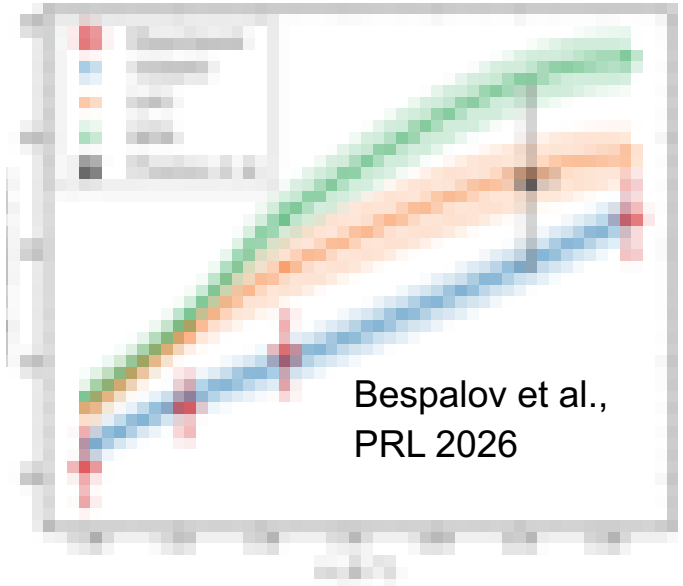


First measured (LCLS MEC, 2017)

Preston et al., *APL* 114, 014101 (2019)



Repetition (EuXFEL, HED-HIBEF, 2024)

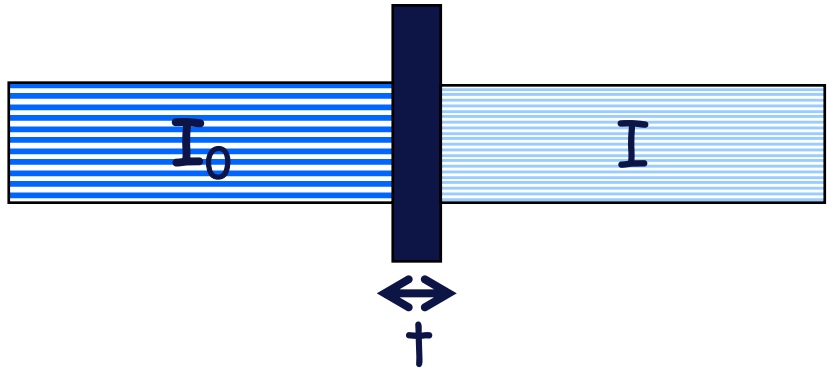


Outline

- Radiation – matter interaction
- Experimental Techniques
  - Based on Scattering
    - ► Elastic Scattering
    - ► Inelastic Scattering
  - Based on Photoelectric Absorption
    - ► Core-hole Spectroscopies
      - X-ray Absorption Spectroscopy
      - X-ray Emission Spectroscopy, RIXS, X-ray Raman
      - X-ray Polarization Dependent Spectroscopies
      - X-ray Photoemission Spectroscopy
  - Imaging Methods

Pause : 11h40-11h50

The Absorption Coefficient μ

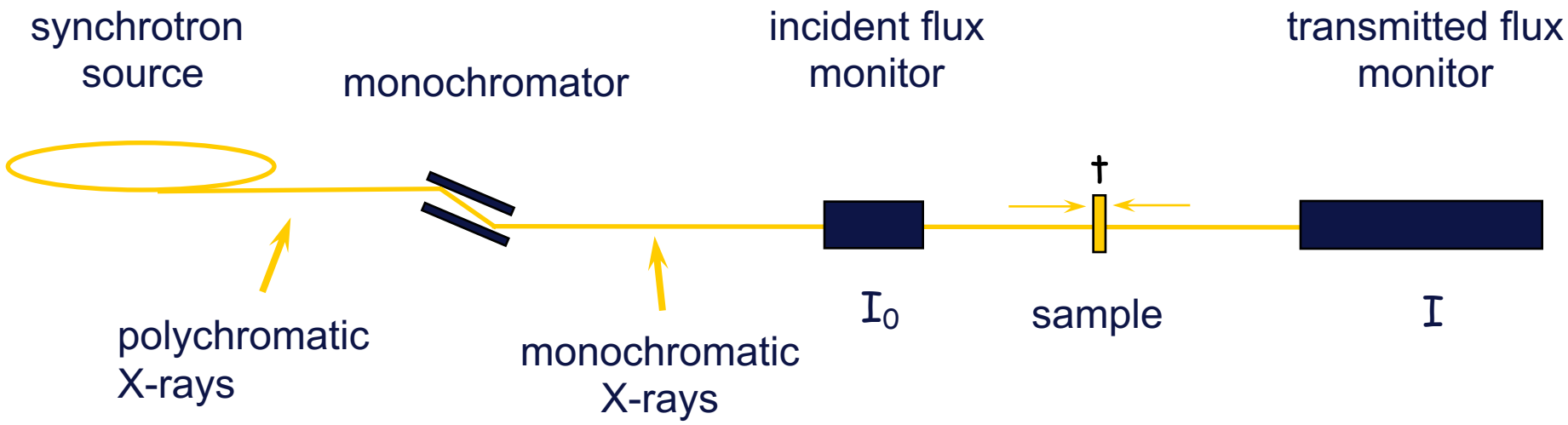


$$I = I_0 \exp[-\mu t]$$

linear absorption coefficient

$$\mu t = \ln [I_0 / I]$$

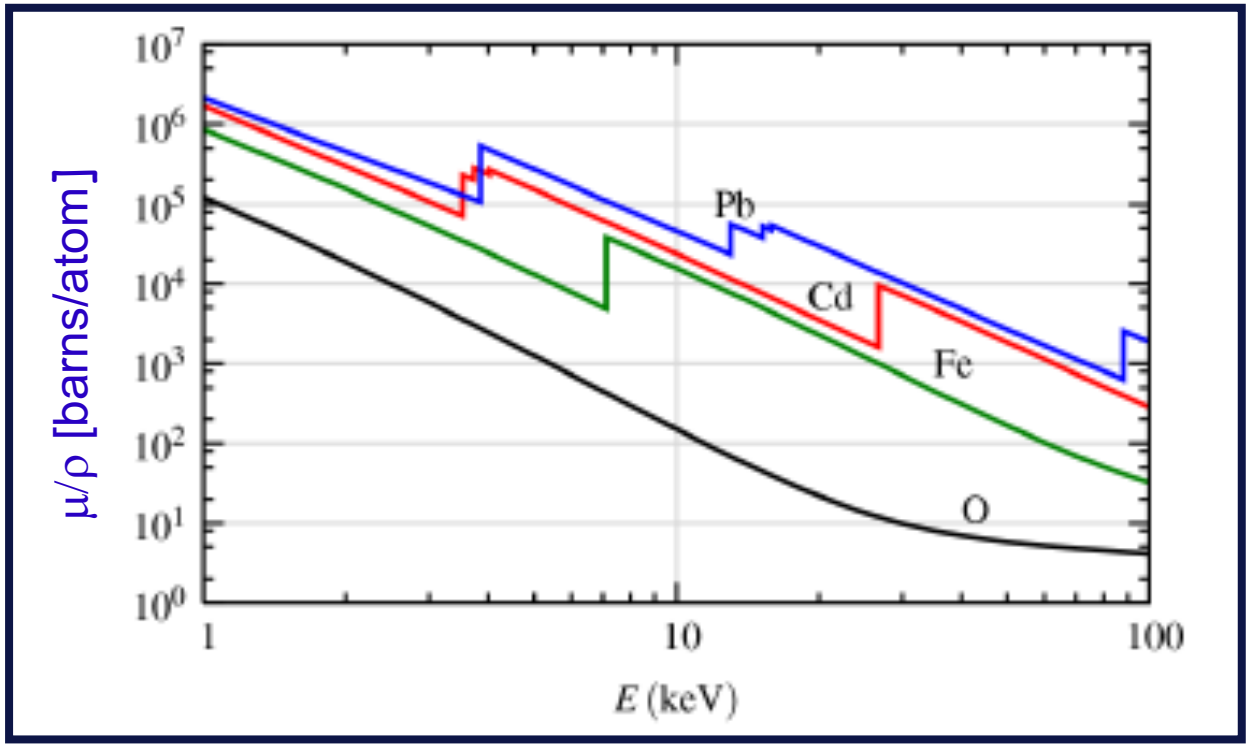
The Absorption Coefficient μ



1. Measure I_0 and I as a function of E_X

2. Calculate: $\mu t = \ln [I_0/I]$

The Absorption Coefficient μ

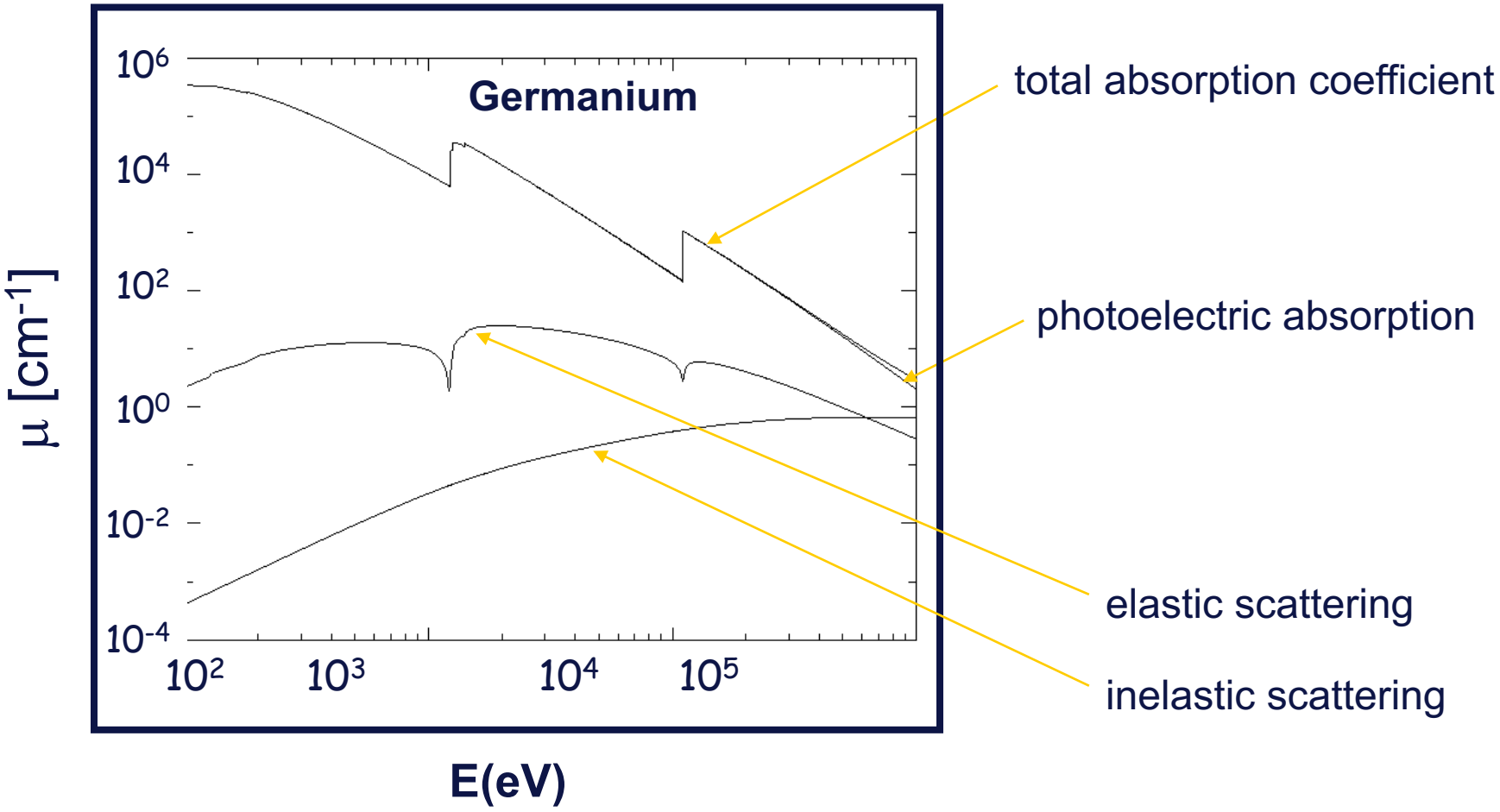


- μ depends strongly on X-ray energy **E** and atomic number **Z**, the density ρ and atomic mass **A**

$$\mu \approx \frac{\rho Z^4}{A E^3}$$

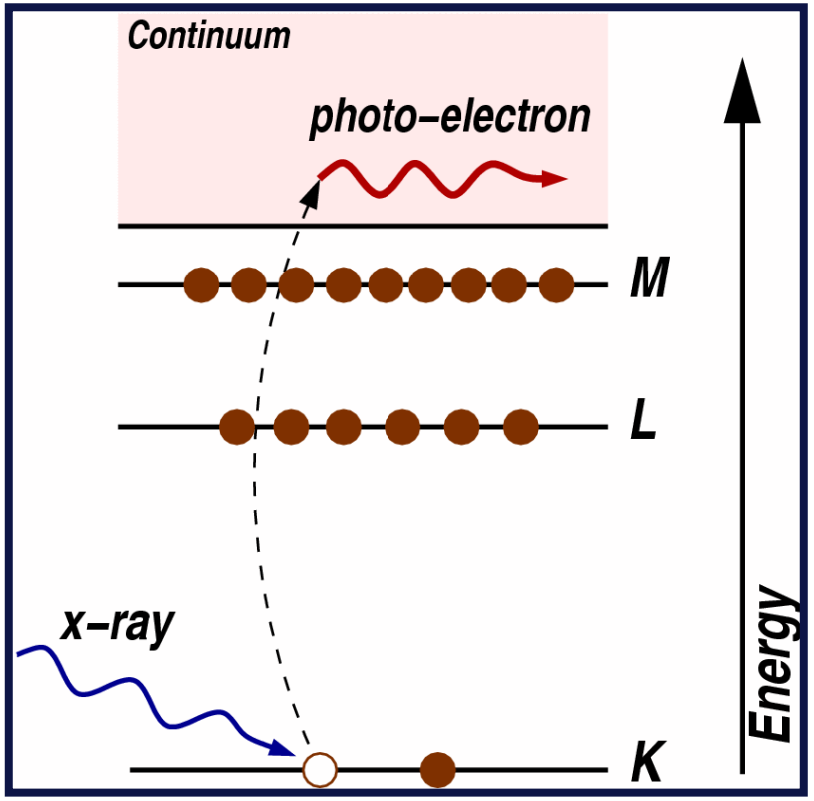
- μ has sudden jumps (absorption edges) which occur at energies characteristic of the element.

The Absorption Coefficient μ



Photoelectric Absorption: basics

- X-rays are absorbed by all matter through the photoelectric effect
- An X-ray is absorbed by an atom when the energy of the X-ray is transferred to a core-level electron (*K*, *L*, or *M* shell) which is ejected from the atom.
- The atom is left in an excited state with an empty electronic level (a core hole). Any excess energy from the X-ray is given to the ejected photoelectron.
- **Depending on its energy, and its position in the sample, the photoelectron can:**
  - Wander around the absorber, scatter from other electrons ie. neighbor atoms (XAFS)
  - Leave the surface of the sample (core – level photoemission spectroscopy)

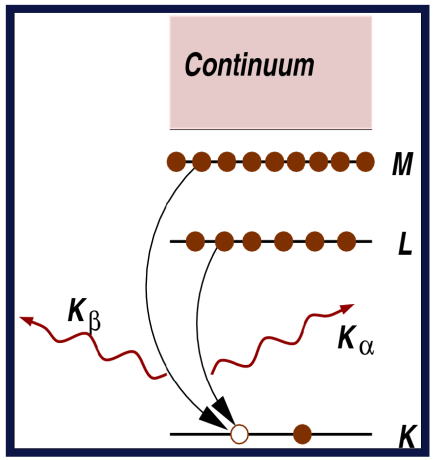


De-excitation: Fluorescence and Auger Effect

- When X-rays are absorbed by the photoelectric effect, the excited core-hole will relax back to a “ground state” of the atom.
- A higher-level core electron drops into the core hole, and a fluorescent X-ray or Auger electron is emitted.
- X-ray fluorescence and Auger emission occur at discrete energies characteristic of the absorbing atom, and can be used to identify the absorbing atom.

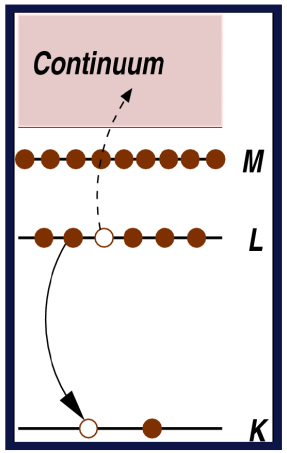
X-ray Fluorescence

An X-ray with energy = the difference of the core-levels is emitted.



Auger Effect

An electron is promoted to the continuum from another core-level.

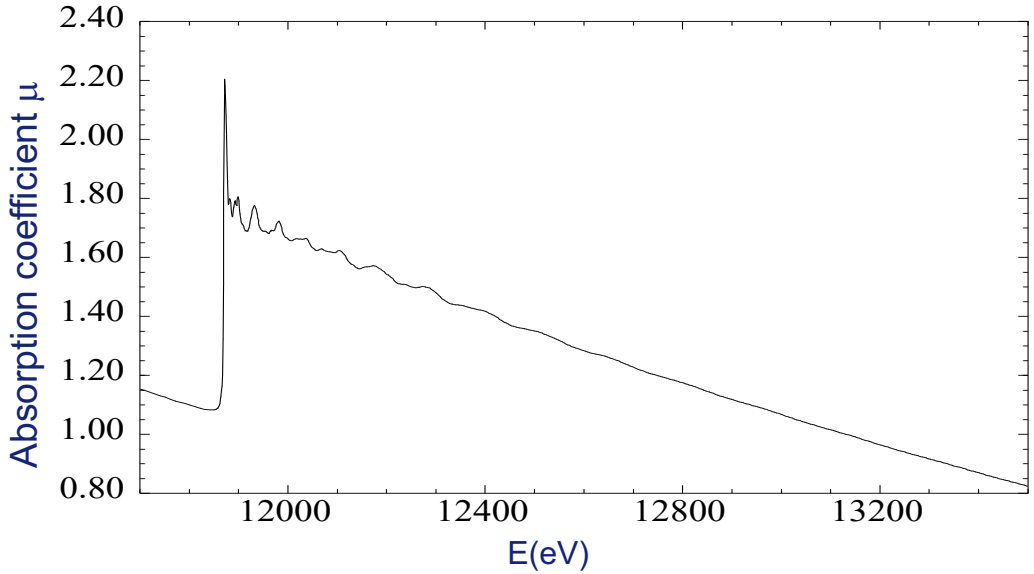


The “zoo” of core - hole spectroscopies

	X-ray Absorption Spectroscopy (XAS)	X-ray Emission Spectroscopy (XES)	Inelastic X-ray Scattering (IXS)
Incident photon energy far from core-electron binding energy	Extended X-ray Absorption Fine Structure (EXAFS)	Non resonant XES K_β spectroscopy	Non resonant IXS of core-electrons X-ray Raman Scattering (XRS)
Incident photon energy around core-electron binding energy	X-ray Absorption Near Edge Structure (XANES)	Resonant XES (RXES)	Resonant IXS (RIXS) High Energy Resolved Fluorescence Detected XAS (HERFD)
Dichroism	X-ray Linear Dichroism (XLD) X-ray Magnetic Linear Dichroism (XMLD) X-ray Magnetic Circular Dichroism (XMCD)	RXES – MCD	RIXS – MCD

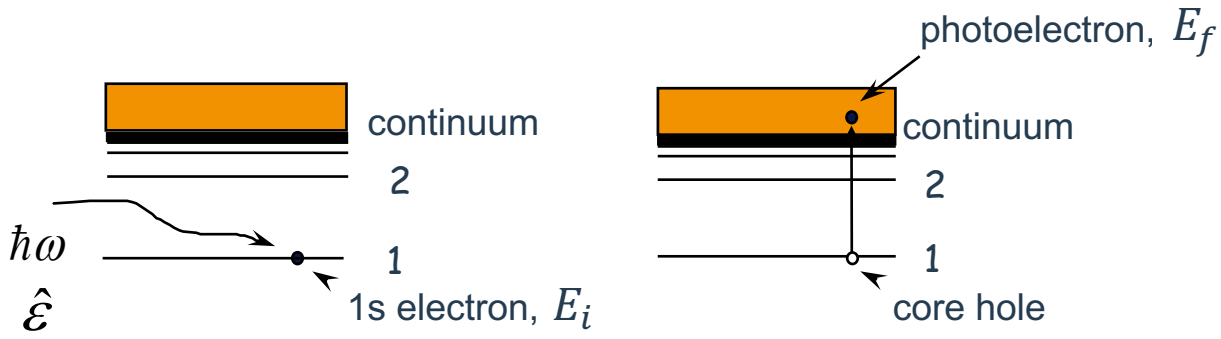
Transition Probability

1. The absorption coefficient μ(E) reflects the probability of absorption of a photon



$|i\rangle$ photon ($\hbar\omega$, $\hat{\varepsilon}$) + core electron

$\langle f|$ photoelectron + core hole



2. From a quantum mechanics perspective, the absorption coefficient μ(E) reflects the **transition probability** from **initial state i** to **final state f**

Transition Probability

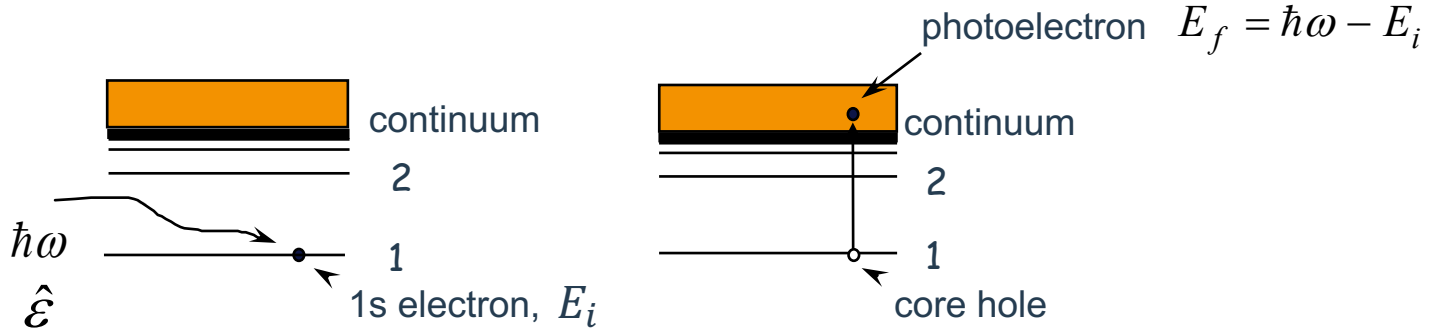
$$\mu(E) = \mu(\omega) \approx \sum_f W_{if} \qquad W_{if} \approx \left|\langle f|\hat{H}_I|i\rangle\right|^2 \rho(E_f)$$

transition probability from $|i\rangle$ to $|f\rangle$

$\rho(E_f)$ density of final states, compatible with energy conservation: $\delta(E_f - E_i - \hbar\omega)$

$\left|\langle f|\hat{H}_I|i\rangle\right|$ matrix element of $\mathrm{H_I}$ between initial and final state

$\hat{H}_I$ “electromagnetic field ↔ atom” interaction hamiltonian operator



Wavefunctions and probability density

- In quantum mechanics, we use the concept of wavefunction to describe the probability of finding a particle at position $\vec{r}$ and time t : $\psi(\vec{r},t)$
- This function represents a “probability amplitude” and is a complex number:

Initial state: $|i\rangle$ or $\psi_i(\vec{r})$ $\langle i|$ or $\psi_i^*(\vec{r})$ final state: $|f\rangle$ or $\psi_f(\vec{r})$ $\langle f|$ or $\psi_f^*(\vec{r})$

- The modulus squared of this quantity represents a probability or probability density: $\left|\psi_i(\vec{r})\psi_i^*(\vec{r})\right| = \left|\psi_i(\vec{r})\right|^2$ where : $\left|\int d\vec{r}\ \psi_i(\vec{r})\psi_i^*(\vec{r})\right|^2 = 1$
- The notation $\left|\langle f|\hat{H}_I|i\rangle\right|^2$ stands for : $\left|\int d\vec{r}\ \psi_f^*(\vec{r})\,\hat{H}_I\,\psi_i(\vec{r})\right|^2$
- So, if $\hat{H}_I|i\rangle = |f\rangle$ then the transition probability from $|i\rangle$ to $|f\rangle$ is equal to 1.

Transition Probability

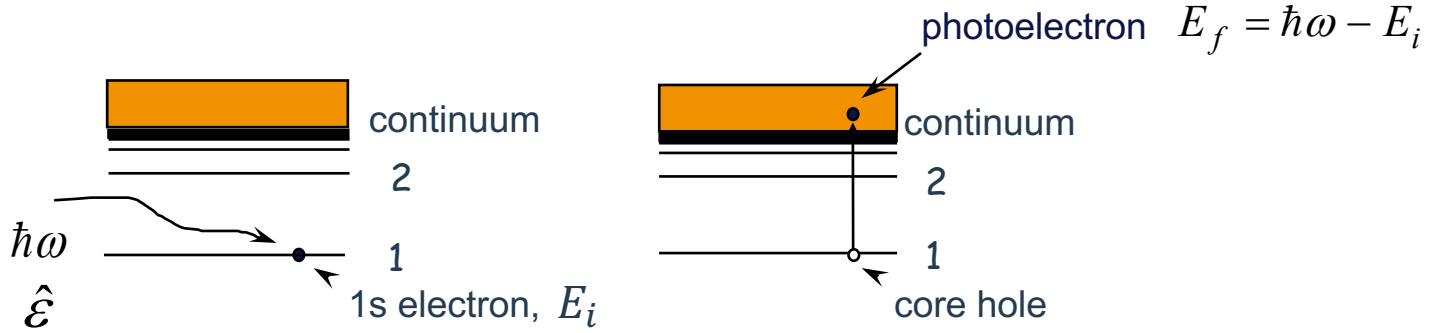
$$\mu(E) = \mu(\omega) \approx \sum_f W_{if} \qquad W_{if} \approx \left|\langle f|\hat{H}_I|i\rangle\right|^2 \rho(E_f)$$

transition probability from $|i\rangle$ to $|f\rangle$

$\rho(E_f)$ density of final states, compatible with energy conservation: $\delta(E_f - E_i - \hbar\omega)$

$\left|\langle f|\hat{H}_I|i\rangle\right|$ matrix element of $\mathrm{H_I}$ between initial and final state

$\hat{H}_I$ “electromagnetic field ↔ atom” interaction hamiltonian operator

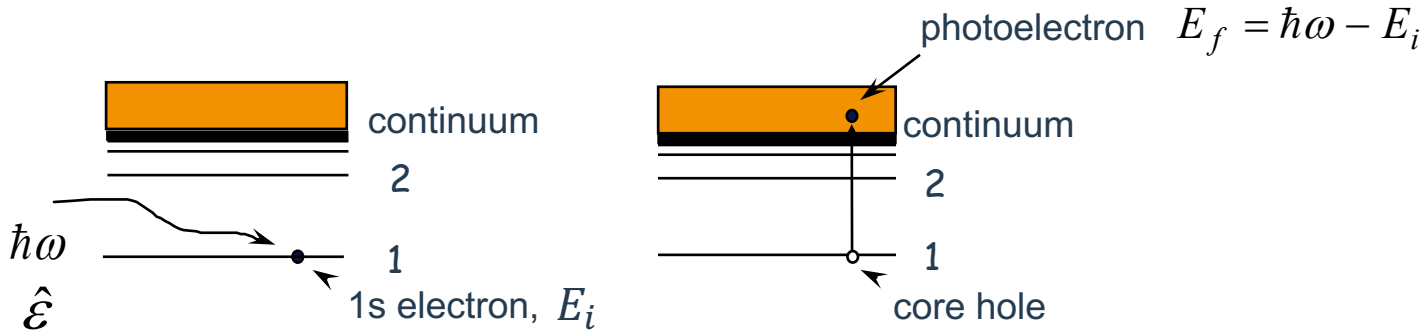


Consequence 1: “Core-hole broadening”

$\rho(E_f)$ density of final states, compatible with energy conservation: $\delta(E_f - E_i - \hbar\omega)$

Uncertainty in final state energy due to finite corehole lifetime δE_{ch} : $\delta E_f = \delta E_{ch} \sim \frac{\hbar}{\delta t_{ch}}$

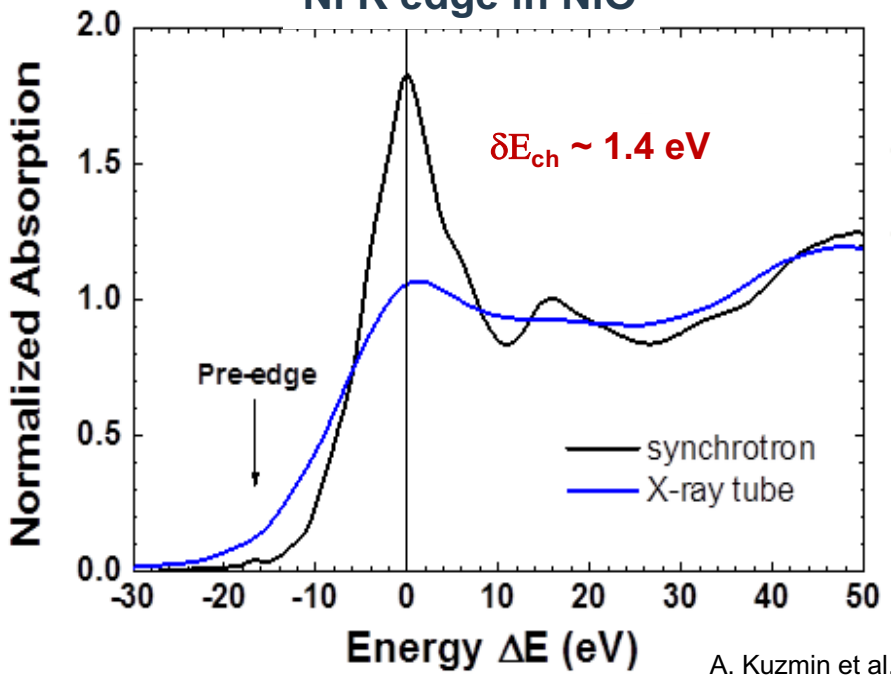
Cu K ~ 1.4 eV; Cu L ~ 0.5 eV
Ag K ~ 7 eV
Au K ~ 50 eV



Spectral broadening: two contributions

- Intrinsic (core-hole): $\frac{\delta E_{ch}}{E}$ ~ inversely proportional to core-hole lifetime
- Instrumental: $\frac{\delta E_{instr}}{E}$ ~ divergence of incoming beam & intrinsic resolution of monochromator

Ni K edge in NiO

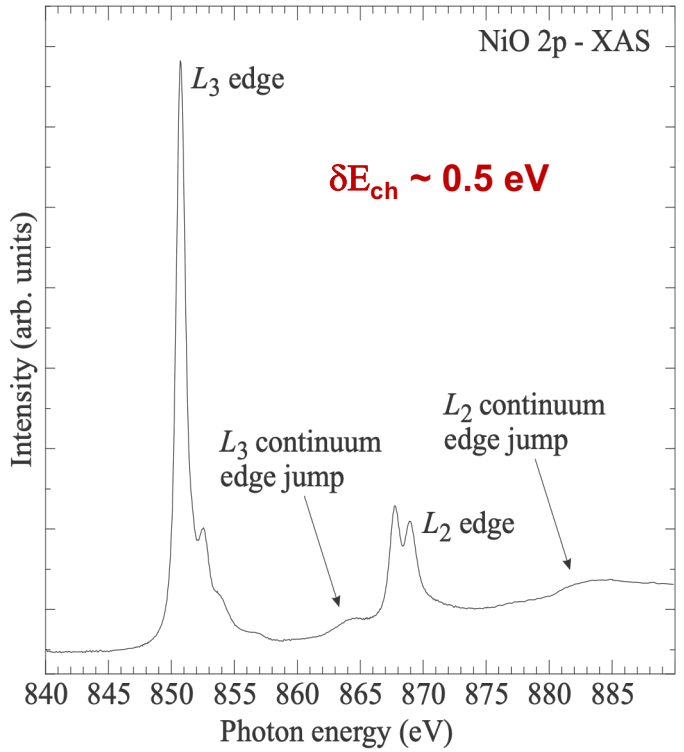


$\frac{\delta E_{instr}}{E} \sim 10^{-4}$

$\frac{\delta E_{instr}}{E} \sim 10^{-3}$

A. Kuzmin et al. Phys. Stat. Sol. (a) 135 (1993) 133-141

Ni $L_{2,3}$ edges in NiO



L. H. Tjeng et al.

Transition Probability

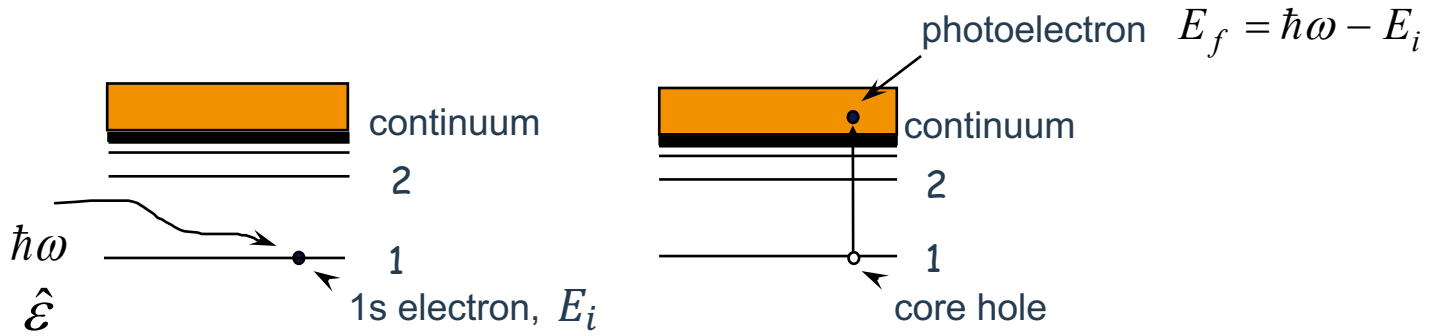
$$\mu(E) = \mu(\omega) \approx \sum_f W_{if} \qquad W_{if} \approx \left|\langle f|\hat{H}_I|i\rangle\right|^2 \rho(E_f)$$

transition probability from $|i\rangle$ to $|f\rangle$

$\rho(E_f)$ density of final states, compatible with energy conservation: $\delta(E_f - E_i - \hbar\omega)$

$\left|\langle f|\hat{H}_I|i\rangle\right|$ matrix element of $\mathrm{H_I}$ between initial and final state

$\hat{H}_I$ “electromagnetic field ↔ atom” interaction hamiltonian operator



Consequences 2 & 3: "Dipole Selection Rules & Dichroism"

$\hat{H}_I$ "electromagnetic field ↔ atom" interaction hamiltonian operator

$$\hat{H}_I \approx \hat{\varepsilon} \cdot \vec{r}$$ ("The Dipole Approximation")

$\hat{\varepsilon}$: polarization vector of photon

$\vec{r}$: position vector of core electron

$$\mu(\omega) \approx \sum_f |\langle f| \hat{\varepsilon} \cdot \vec{r} |i\rangle|^2$$

Many matrix elements cancel out
→ not all transitions are possible (Dipole Selection Rules)

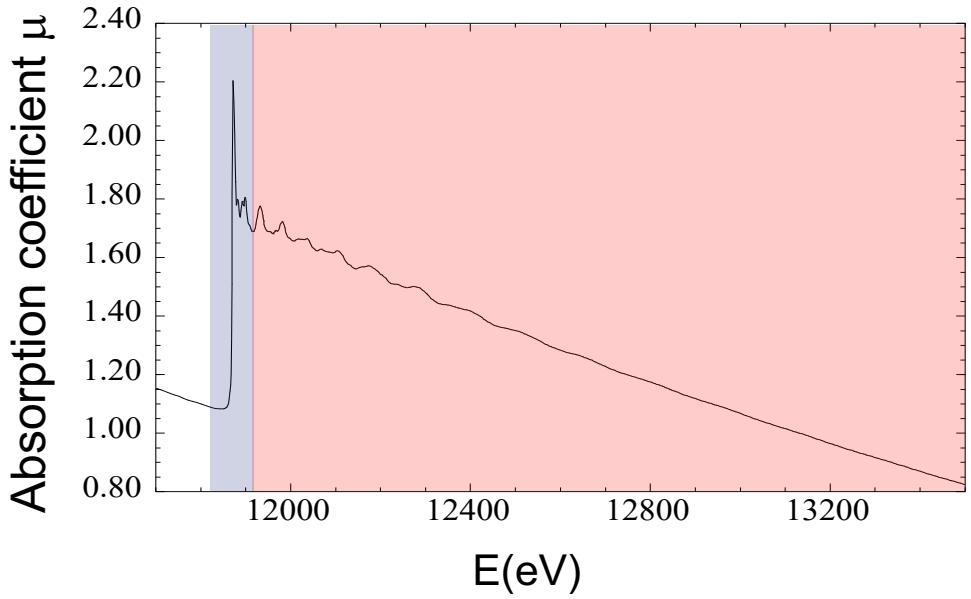
Absorption coefficient depends on $\hat{\varepsilon}$
→ polarization effects (i.e. X-ray dichroism)

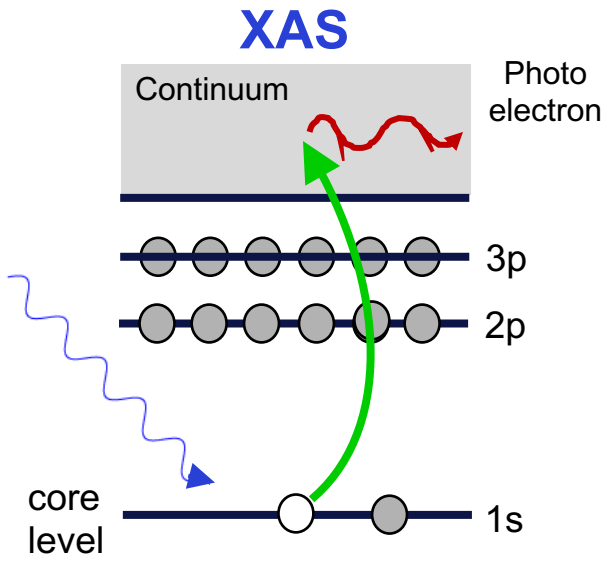
i.e $\Delta\ell = \pm 1$

K-edge: 1s ($\ell = 0$) → p ($\ell = 1$)

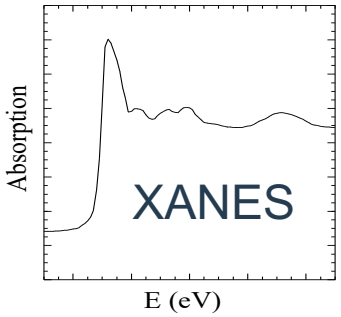
L-edge: 2p ($\ell = 1$) → s ($\ell = 0$) , d ($\ell = 2$)

X-ray Absorption (Fine Structure) Spectroscopy

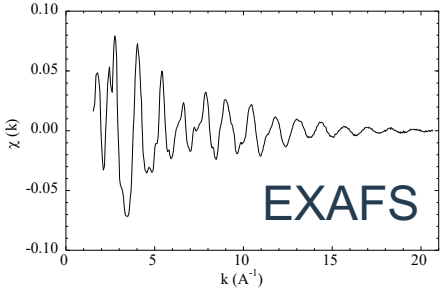




- **Electronic structure**
  - valence, oxidation state
  - site symmetry, coordination chemistry
  - orbital hybridization, occupancy

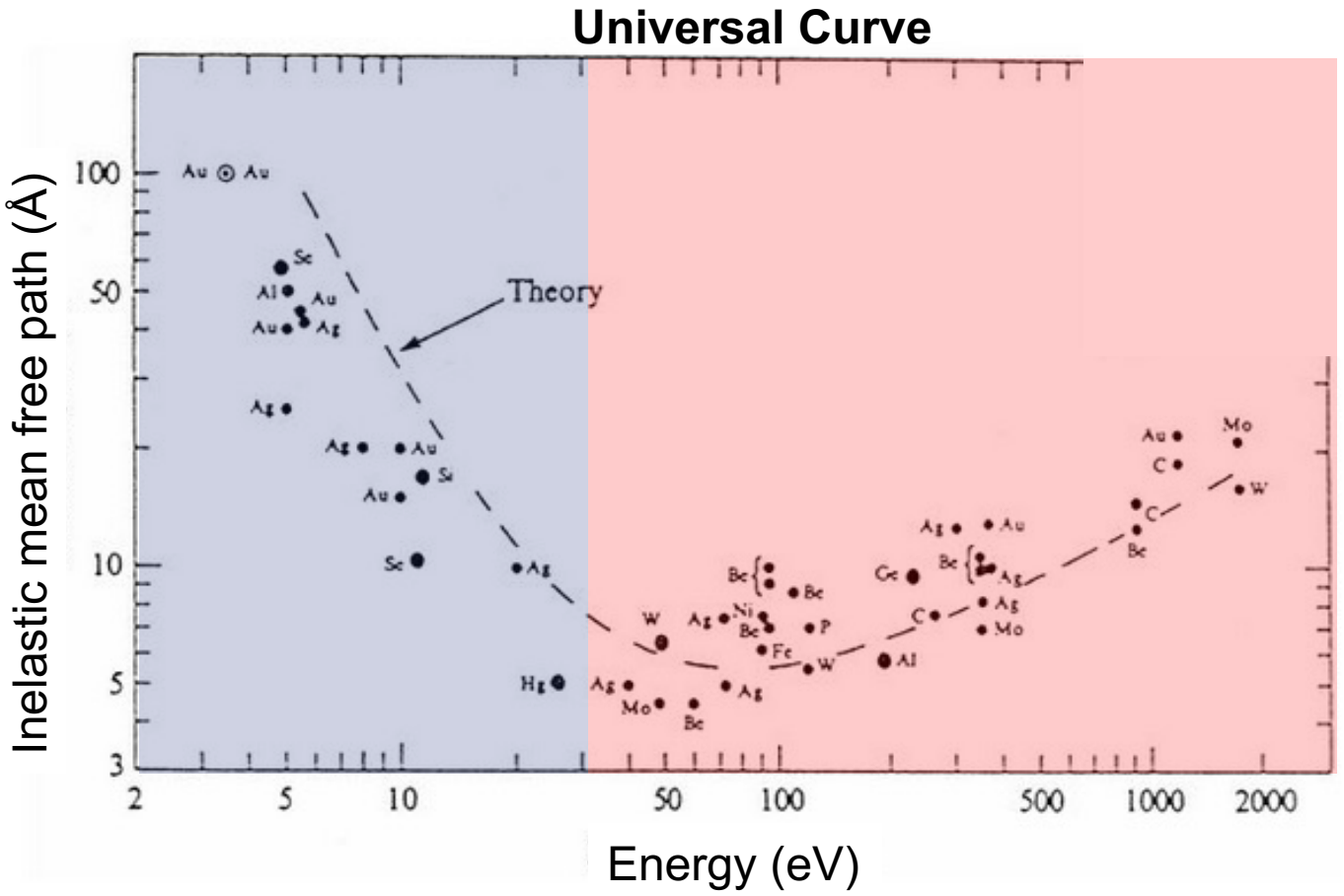


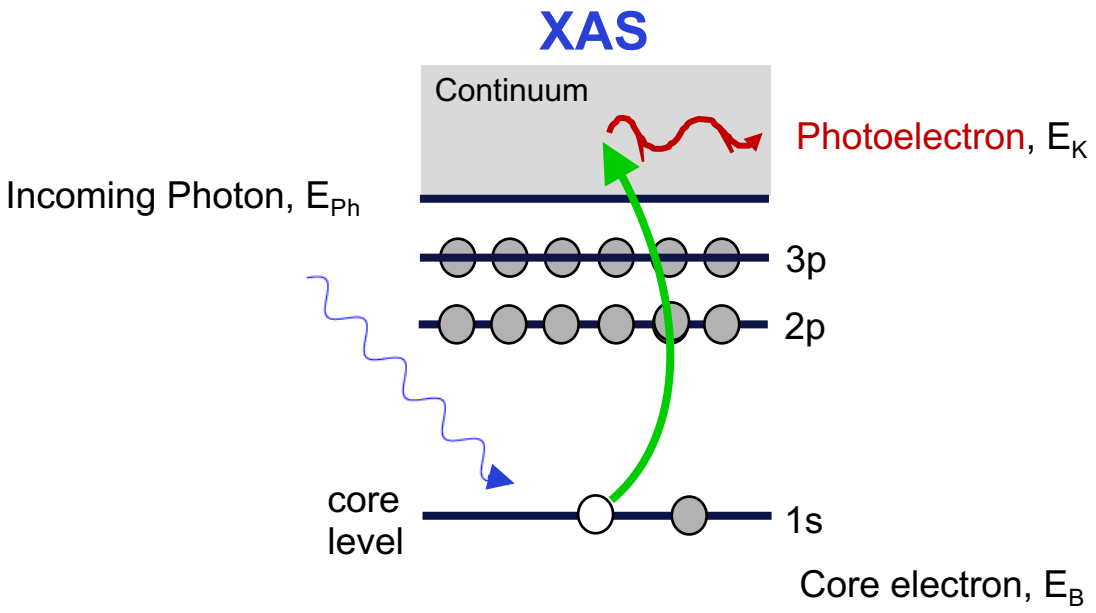
- **Local structure**
  - near neighbor distances
  - number and type of neighbors
  - static and thermal relative displacements



The kinetic energy of the photoelectron is important….

- “how far do electrons travel before loosing their energy”

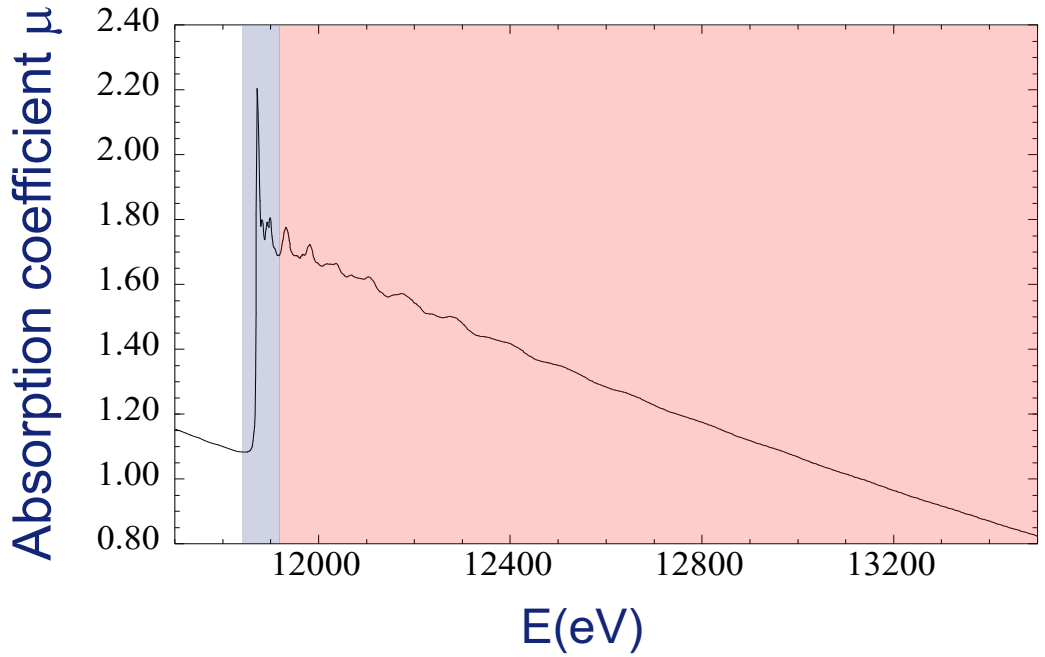




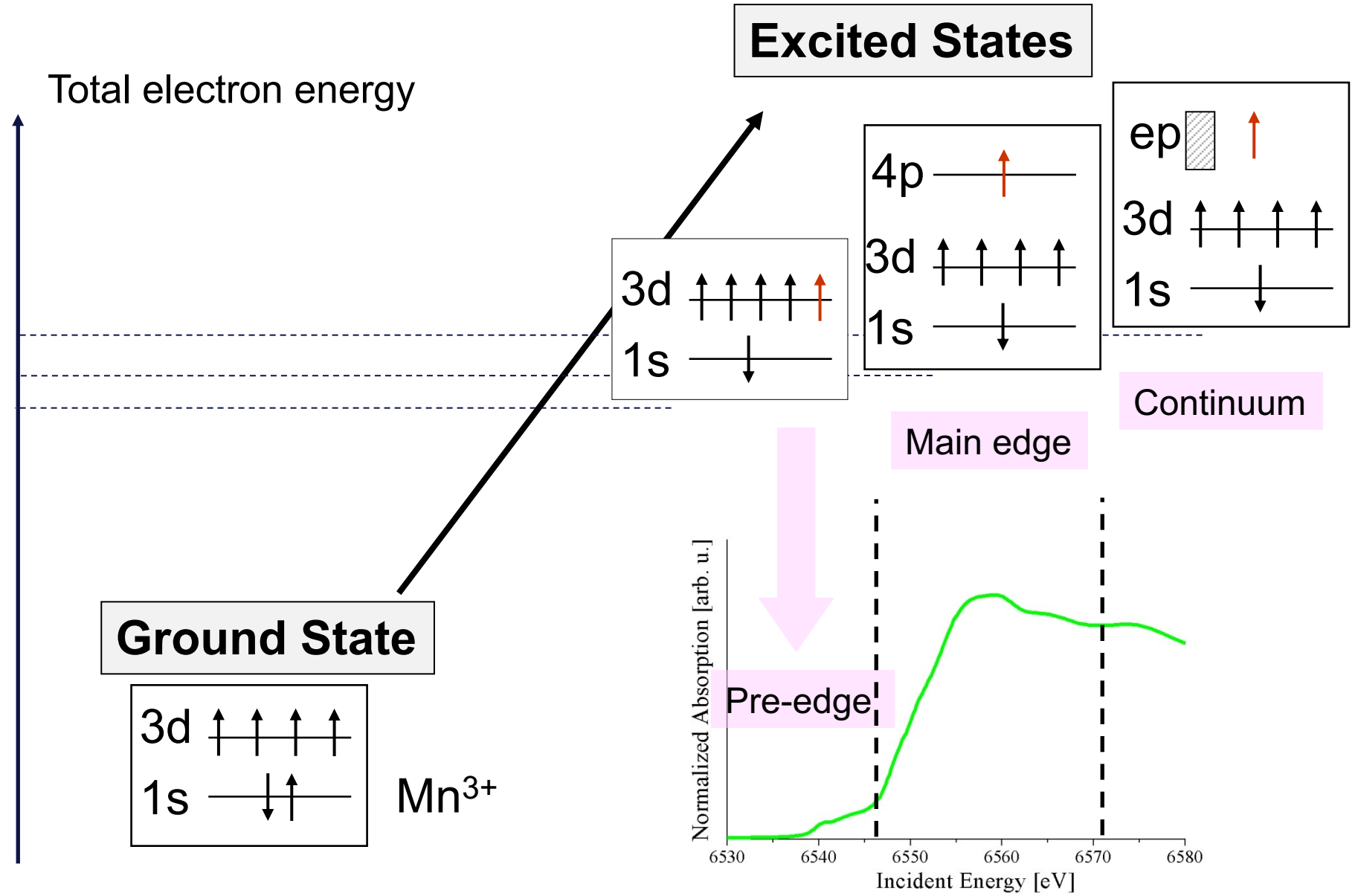
- Any excess energy from the X-ray is given to the ejected photoelectron.
- The kinetic enegy of the photoelectron is: $E_{Kinetic} = E_{Ph} - E_B$

Explains why XANES and EXAFS cannot be analyzed in the same way

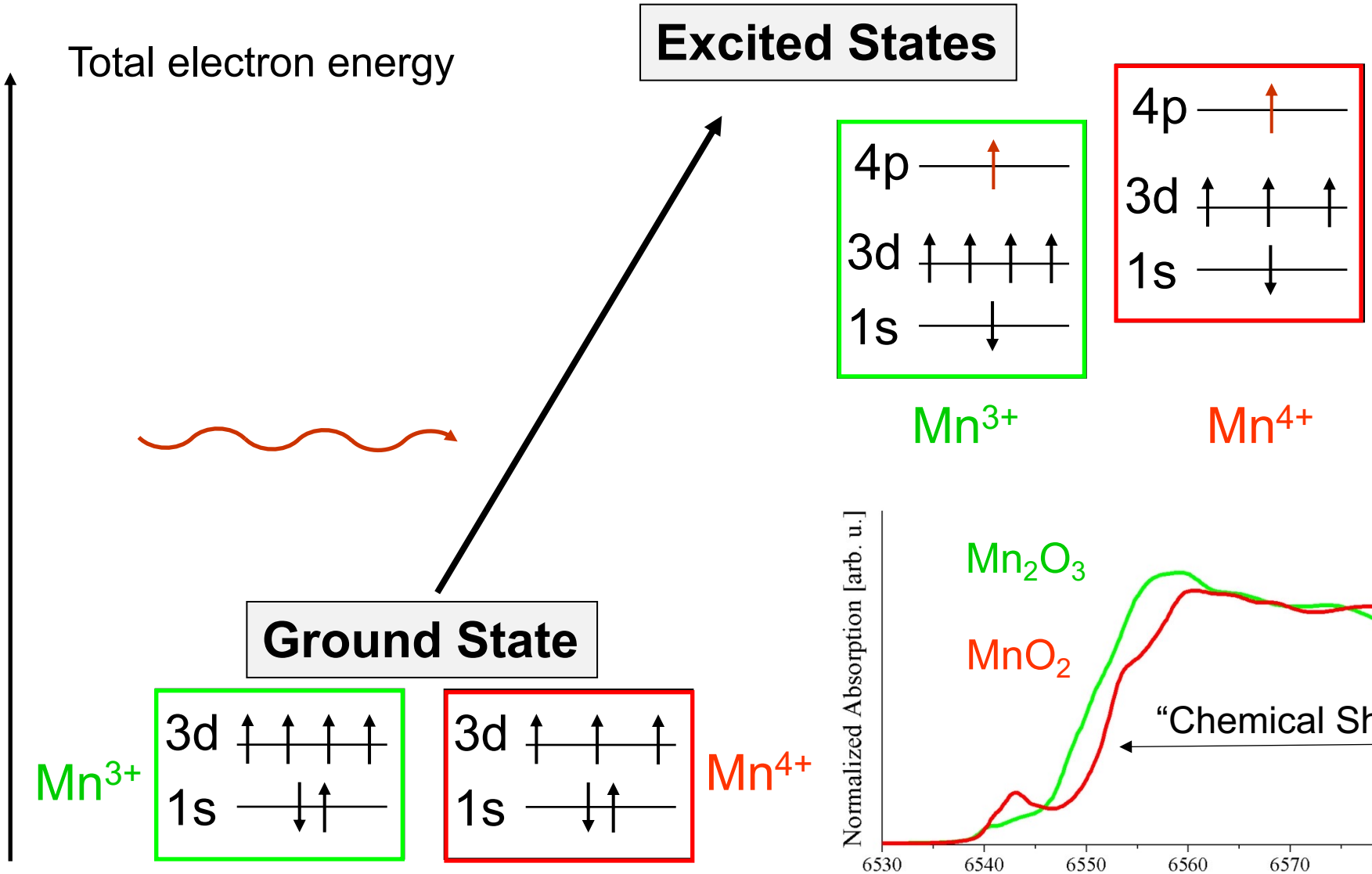
- Approximations can be used to interpret EXAFS, that are not valid for XANES
- Cannot be analyzed in the same way
- Different information content.



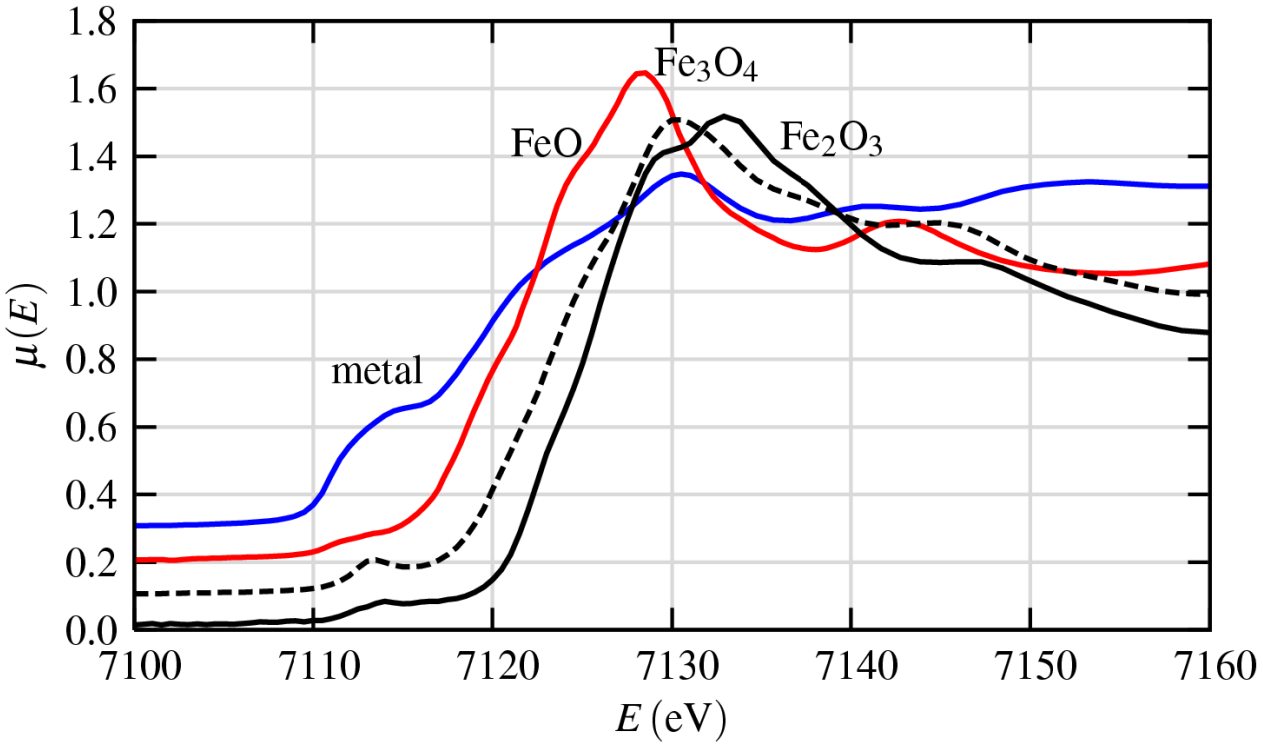
X-ray absorption near edge spectroscopy (XANES)



XANES: onset of absorption sensitive to oxidation state of absorber



Edge shifts and pre-edge peaks in Fe oxides by Fe_K XANES



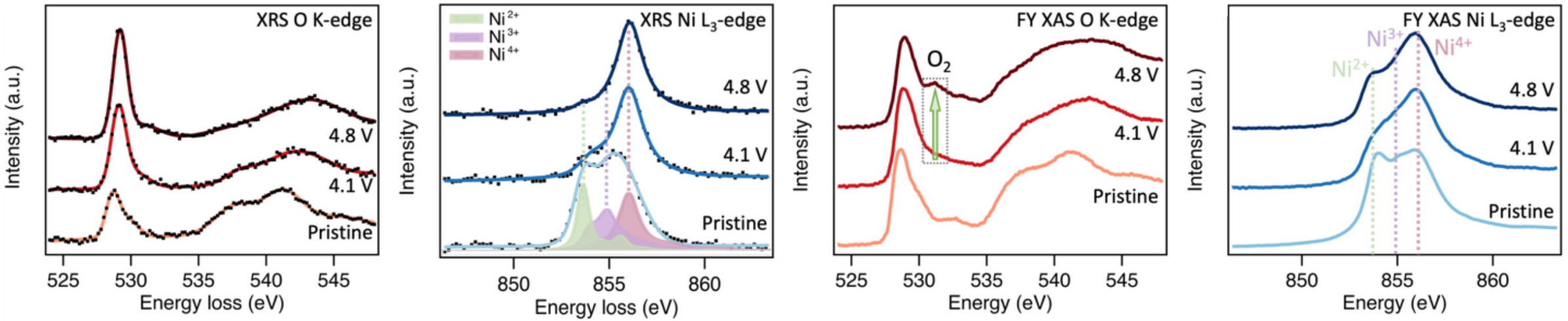
- The shift of the edge position can be used to determine the valence state
- The heights and positions of pre-edge peaks can also be reliably used to determine Fe^{3+}/Fe^{2+} ratios (and similar ratios for many cations).

Redox dynamics in lithium-ion battery cathodes

L. An et al. Energy Environ. Sci. (2024)

Towards lower-cost, longer-lasting lithium-ion batteries for green transportation

- Top candidate for enhanced charge storage and stability over thousands of cycles → $LiNiO_2$ cathodes
- Batteries degrade and lose capacity rapidly → need to understand exactly how O and Ni exchange electrons deep within the bulk material during operation to stop this degradation
- Need depth-resolved analysis of redox process, to distinguish reversible bulk redox activities from near-surface degradation



- X-ray Raman spectroscopy/scattering @ID20 ESRF
- **Hard X-rays** (10keV): **penetrates (~10 µm)** inside battery cell to map electronic changes in real time (*operando*).
- Redox process involves Ni-O rehybridization throughout the bulk of $LiNiO_2$

- FY-XANES spectroscopy @B07-B DLS
- **Soft X-rays** → information depth ~ **200 nm**
- Surface degradation leads to Ni reduction and trapping of molecular O_2 → development of a denser NiO-like reduced surface layer that hinders Li transport.

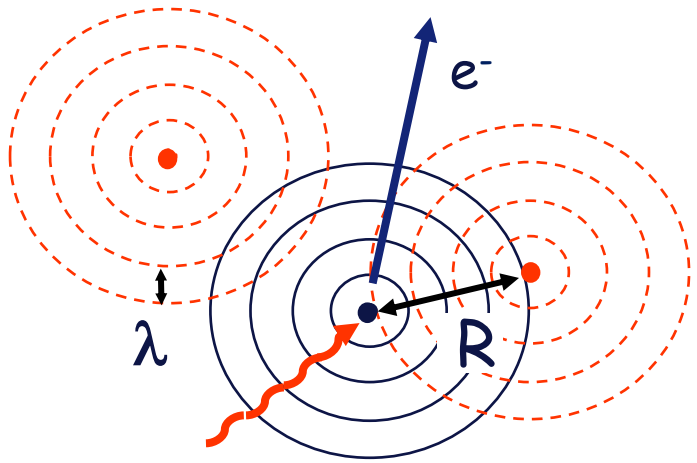
Extended X-ray absorption fine structure (EXAFS): measuring local structure

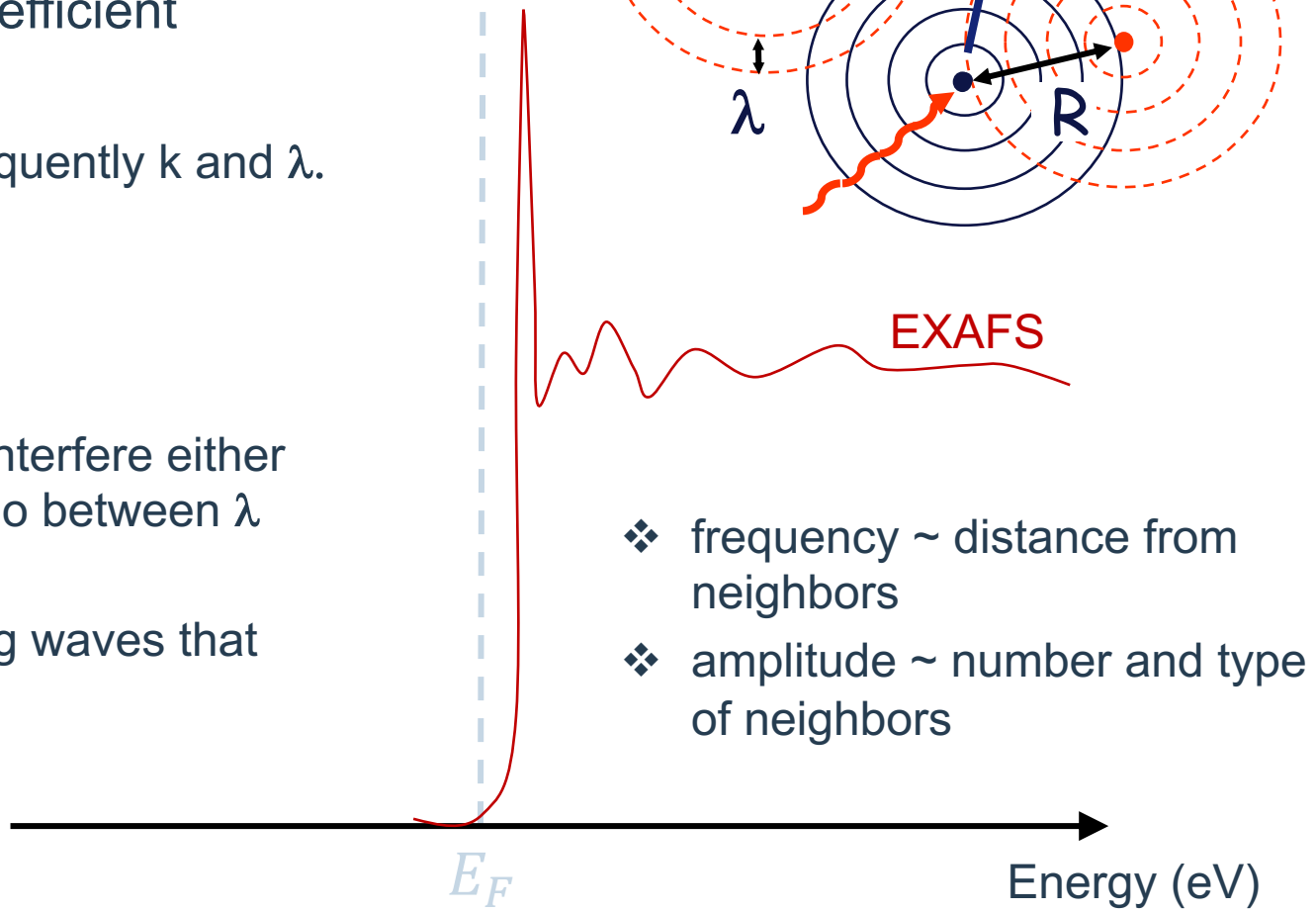
- Due to a quantum effect, the autointerference of photoelectron wave modifies the absorption coefficient value:

1. As E is scanned above E_0, E_{kin} is varied, and consequently k and λ.

$$E_{kin} = E - E_0 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

2. The outgoing and backscattered parts of the wave interfere either constructively or destructively, depending on the ratio between λ and R.
3. It is the interference between outgoing and incoming waves that gives rise to the sinusoidal variation of μ(E)





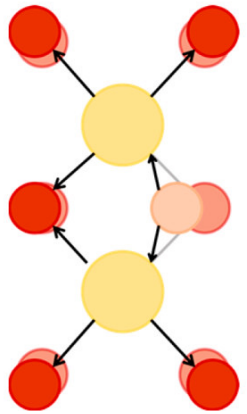
- ❖ frequency ~ distance from neighbors
- ❖ amplitude ~ number and type of neighbors

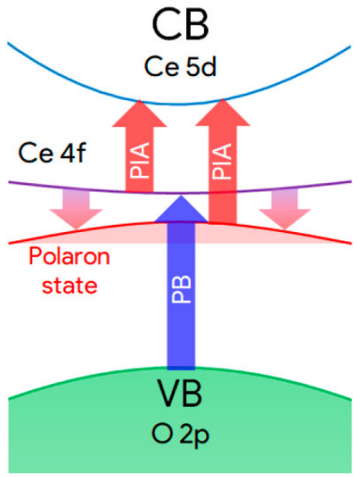
Structure and electronic properties of excited states in CeO_2 by fs-resolved Ce L_3 XAS

Improving water splitting processes for hydrogen production

- Coupling between excited states and LO phonons → polarons
- How does this influence functionality of photocatalytic materials

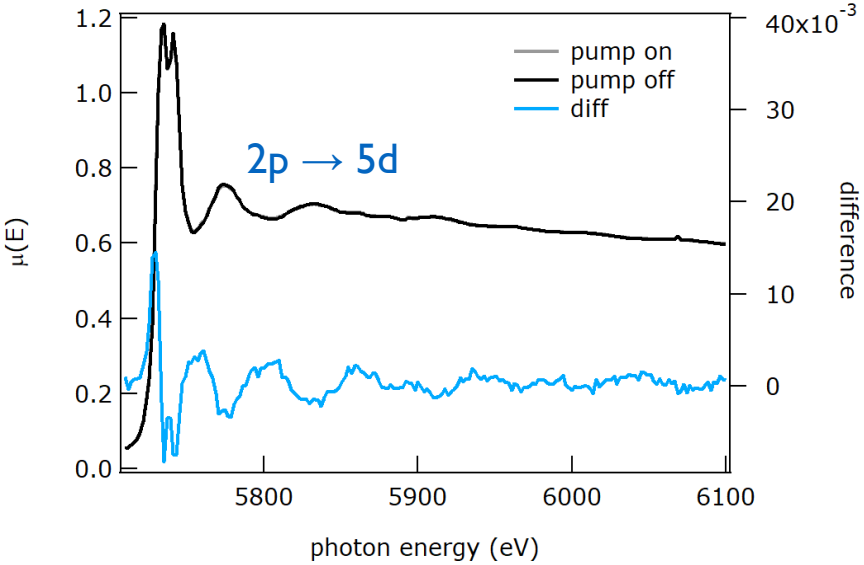
photoinduced structura distortion consistent with the formation of a small polaron state



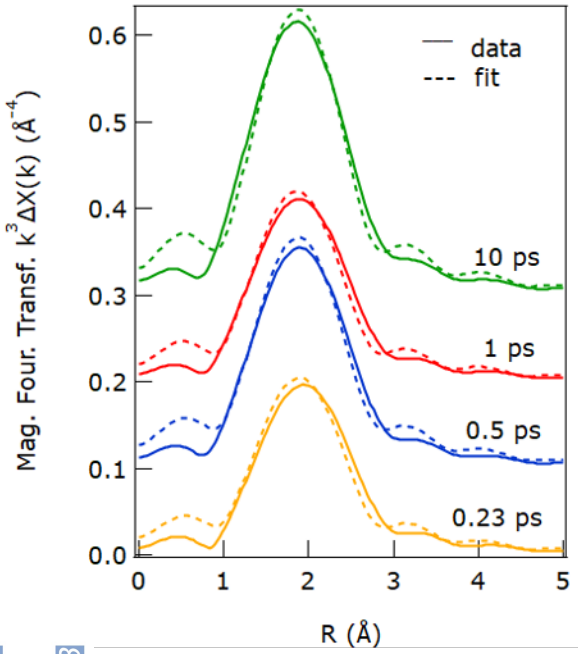


Cresi et al. *JPCL* **11**, 5686 (2020)

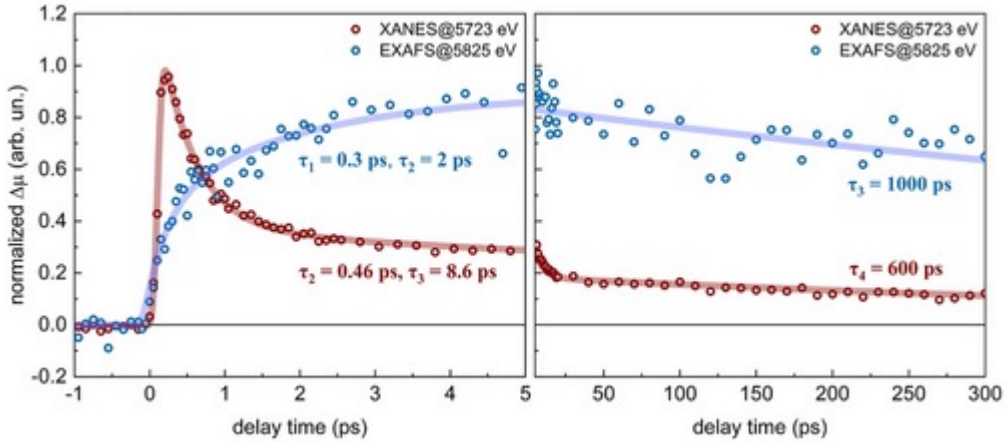
pump-probe Ce L_3 edge EXAFS at Δt=2 ps



ΔR_{Ce-O} → + 0.13 Å



Electronic → 300 - 500 fs Structural → 600 ps – 1ns



FXE@EuXFEL fs-resolved XAS

European XFEL

CNRNANO MODENA S3

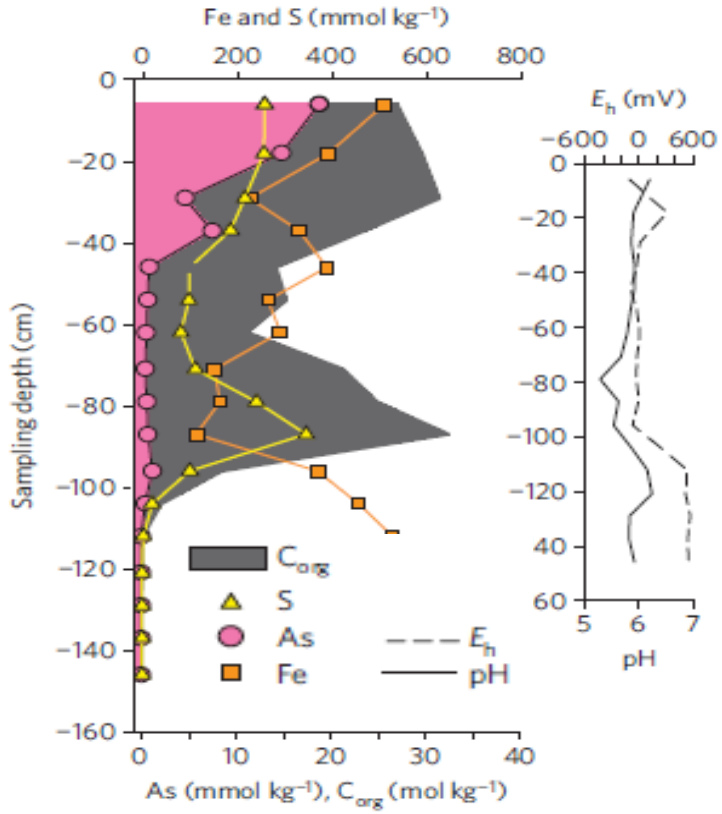
S. Pelatti, ...& P. Luches, Adv. Electron. Mater.11, no. 18 (2025): e00429

Arsenic sequestration by organic sulphur in peat by As_K EXAFS

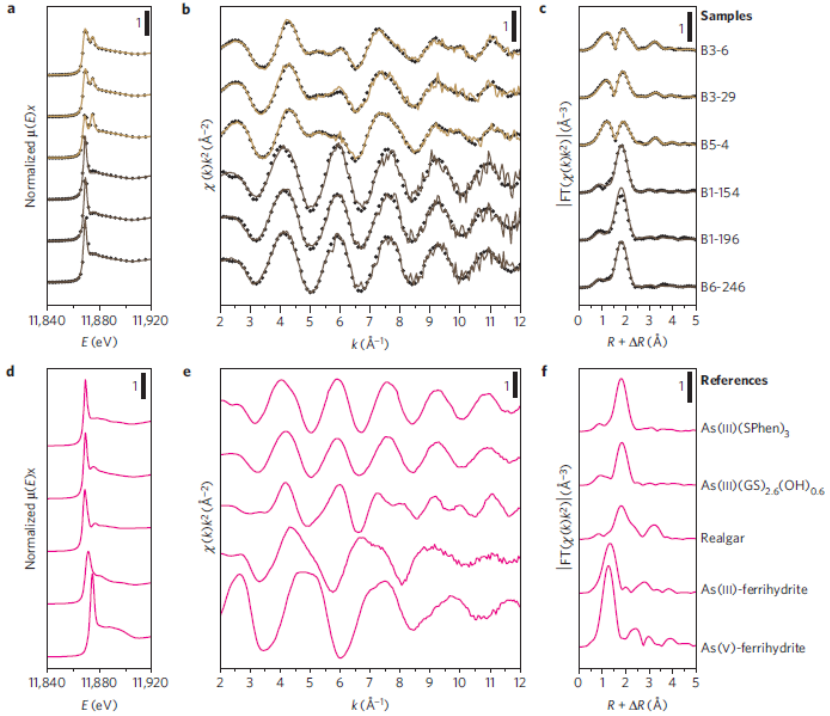
Does natural organic matter serve as geochemical trap for As ?

- Wetlands cover more than 6% of the global ice-free land area
- Play major role in storage, transformation, mobilization of trace elements

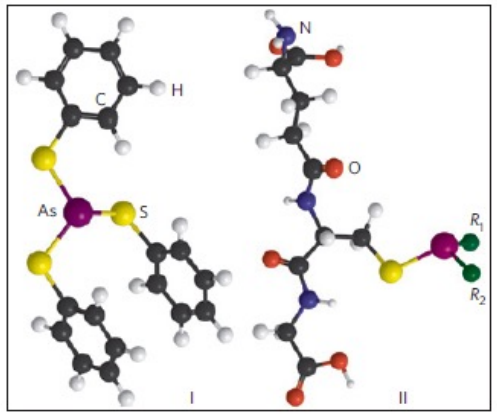
Peat samples collected from a naturally arsenic-enriched wetland in Switzerland.



As_K EXAFS (3-1000 ppm)



Trap: covalent bonds between As^{+3} and organic S groups



- Spectroscopic evidence for As binding to peat
- Identified dominating binding mechanism
- Quantified extent of As binding to peat

As_K FY XAS @ BM23 ESRF

Langner Nature Geoscience 2012

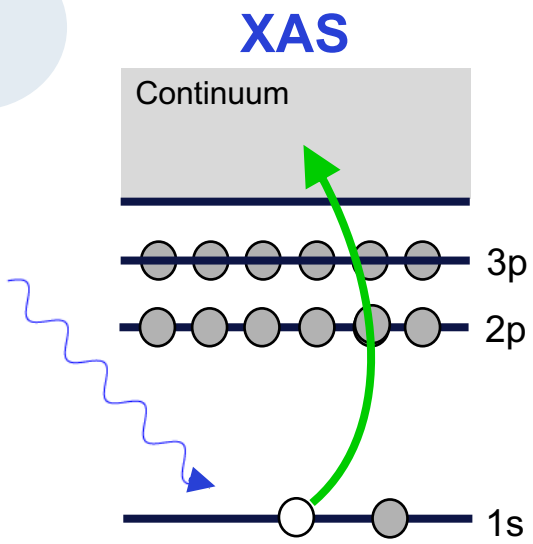
Outline

- Radiation – matter interaction
- Experimental Techniques
  - Based on Scattering
    - ► Elastic Scattering
    - ► Inelastic Scattering
  - Based on Photoelectric Absorption
    - ► Core-hole Spectroscopies
      - X-ray Absorption Spectroscopy
      - X-ray Emission Spectroscopy, RIXS, X-ray Raman
      - X-ray Polarization Dependent Spectroscopies
      - X-ray Photoemission Spectroscopy
  - Imaging Methods

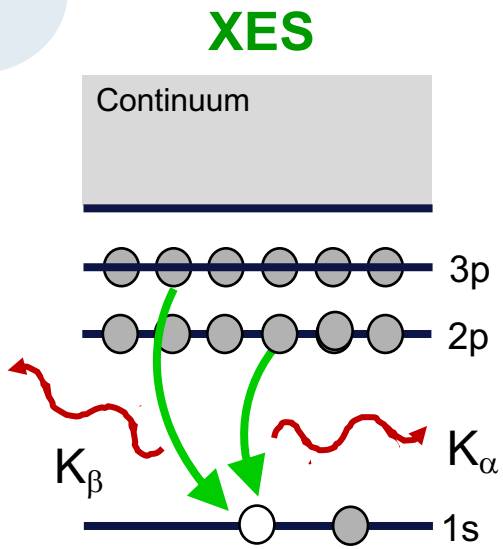
Pause : 11h40-11h50

X-Ray Emission Spectroscopy: XES

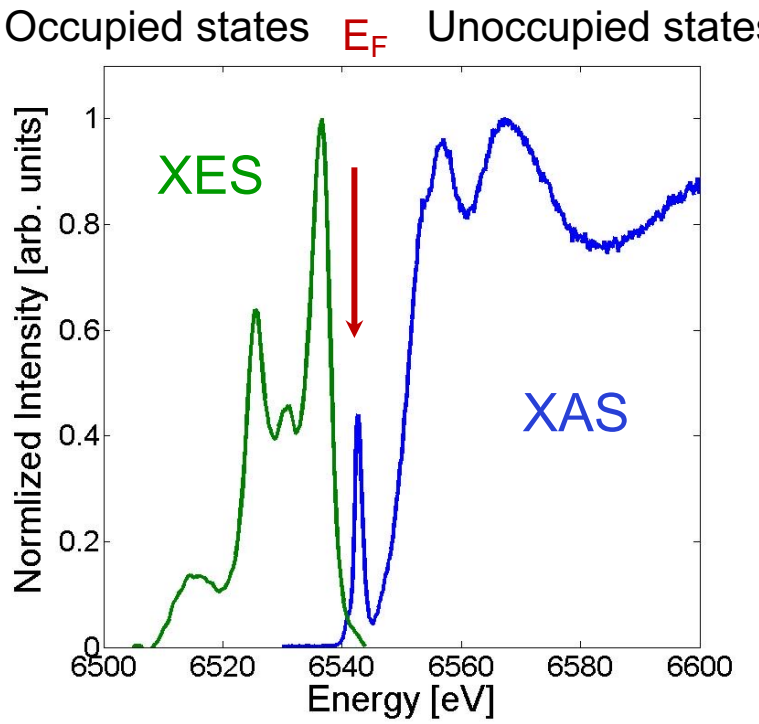
1



2

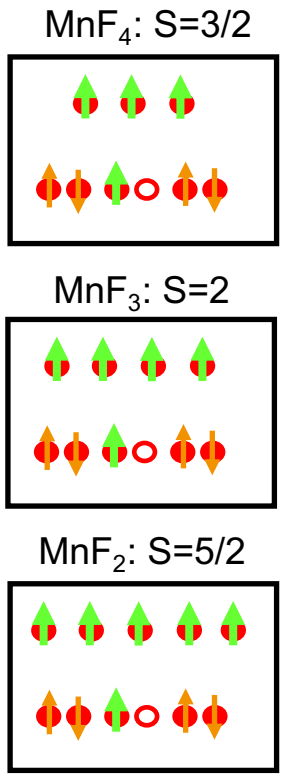


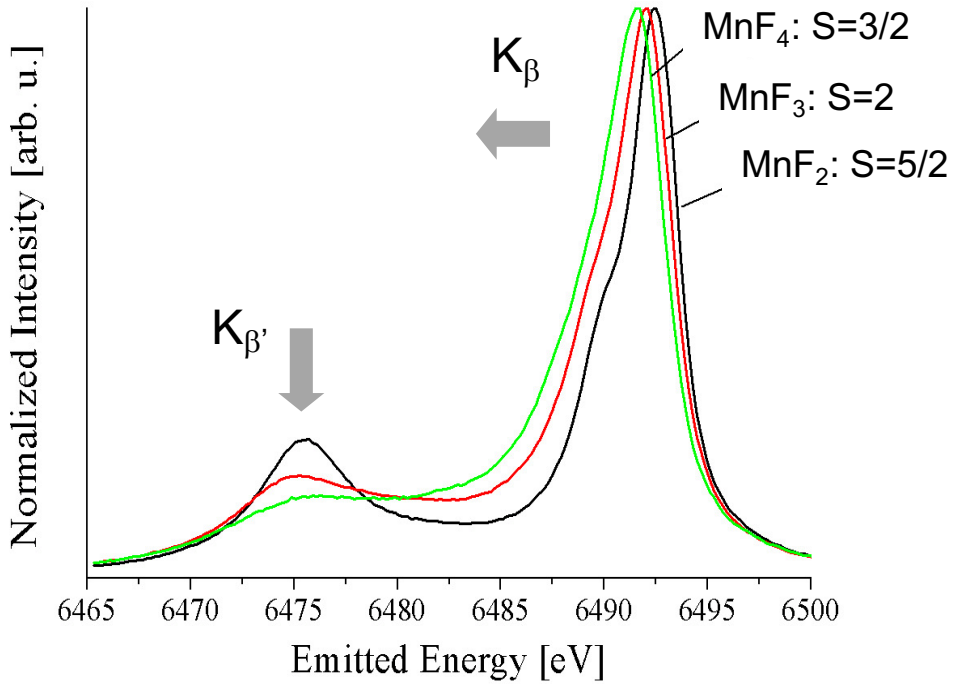
- K_α and K_β : non-resonant XES
  - Incident photon energy is far from absorption edge
  - Photoelectron well into continuum

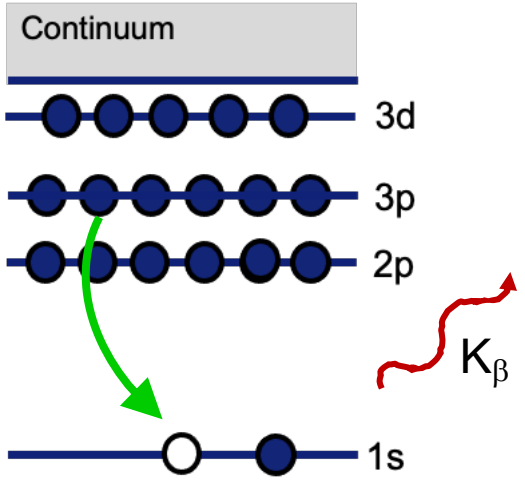


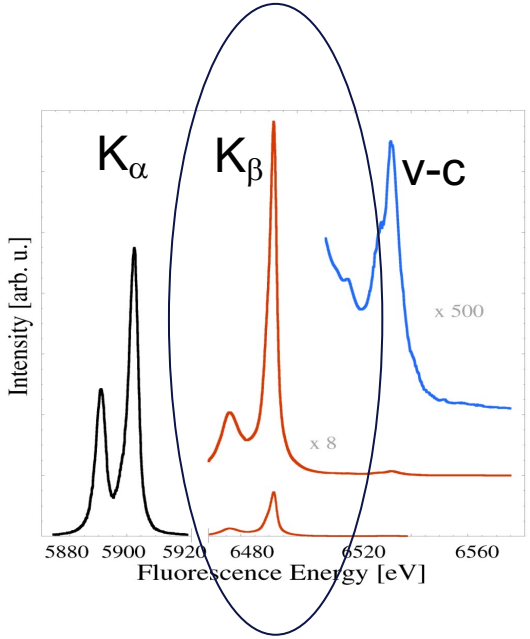
Valence band spin state by K_β XES

- Local magnetic moment
- Spin transitions



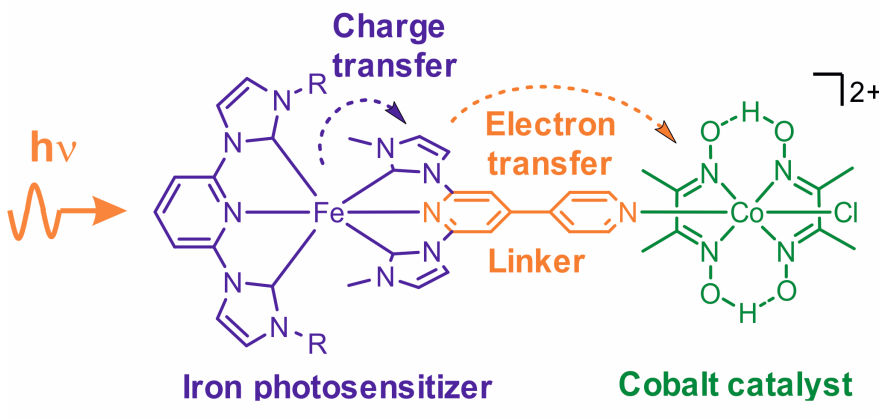


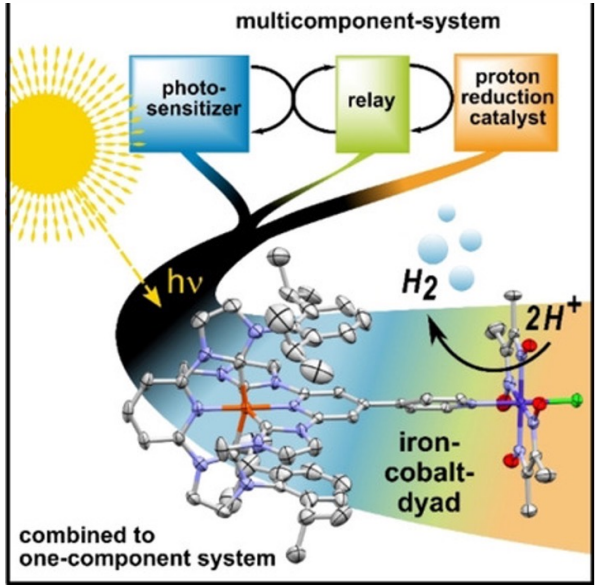




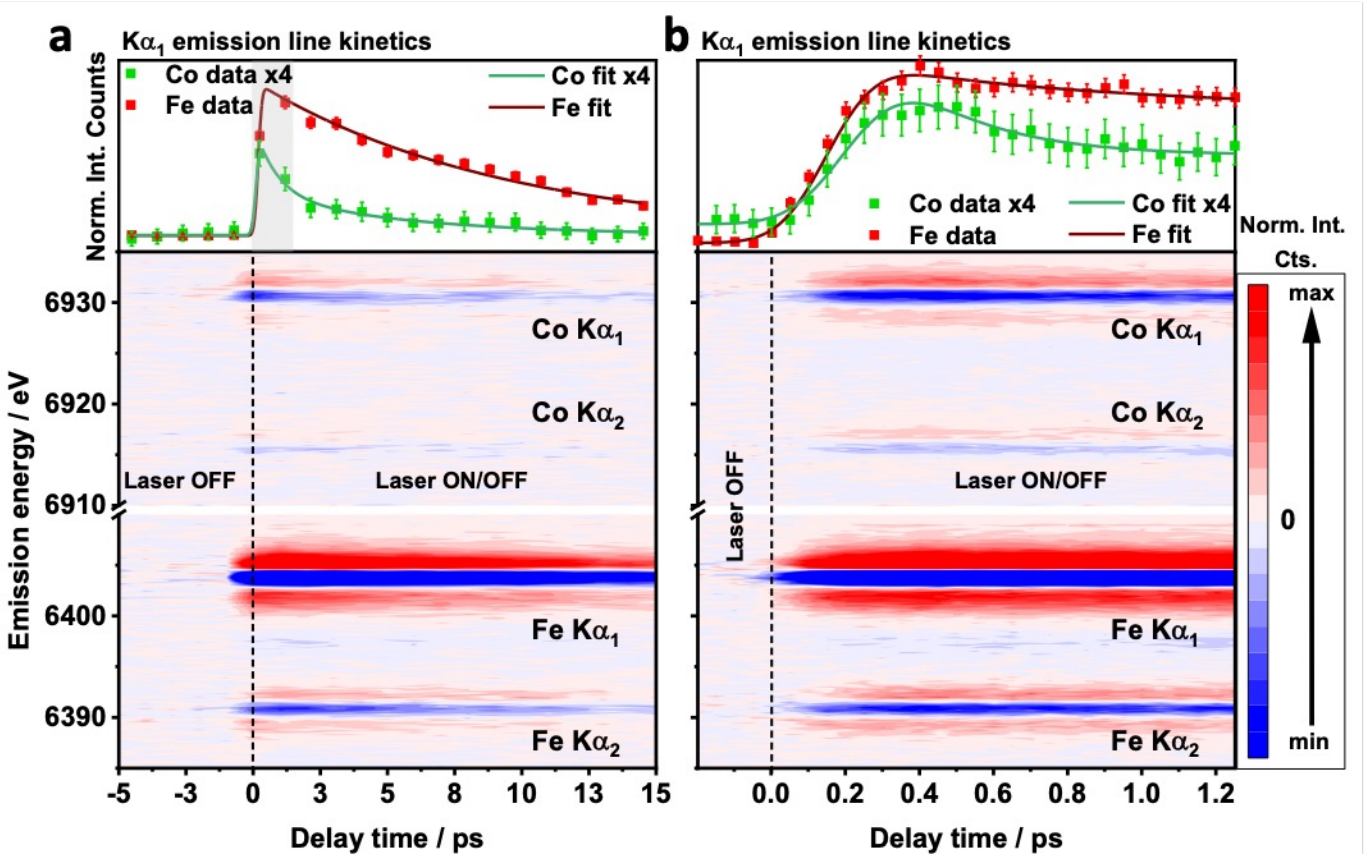
Excited State Landscape in a Base Metal Dyad by fs-resolved K_α XES

Using light for a sustainable production of molecular hydrogen





FXE@EuXFEL Ultrafast Two-Color XES



M. Nowakowski… & M. Bauer, Adv. Sci. 11, 2404348 (2024)

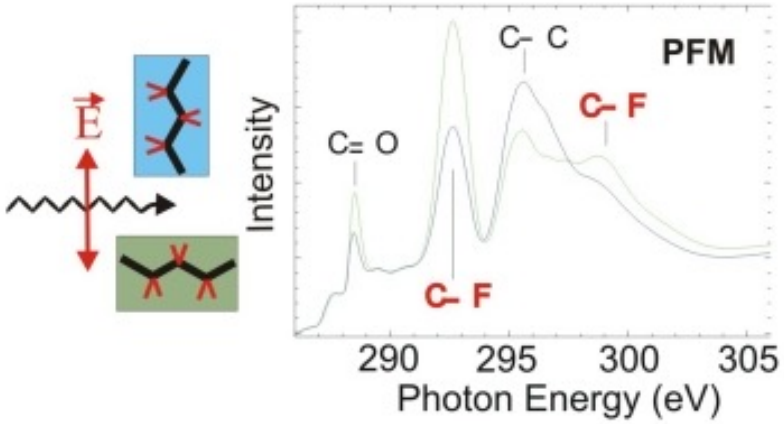
Outline

- Radiation – matter interaction
- Experimental Techniques
  - Based on Scattering
    - ▶ Elastic Scattering
    - ▶ Inelastic Scattering
  - Based on Photoelectric Absorption
    - ▶ Core-hole Spectroscopies
      - X-ray Absorption Spectroscopy
      - X-ray Emission Spectroscopy, RIXS, X-ray Raman
      - X-ray Polarization Dependent Spectroscopies
      - X-ray Photoemission Spectroscopy
  - Imaging Methods

Polarisation Dependent X-ray Spectroscopies

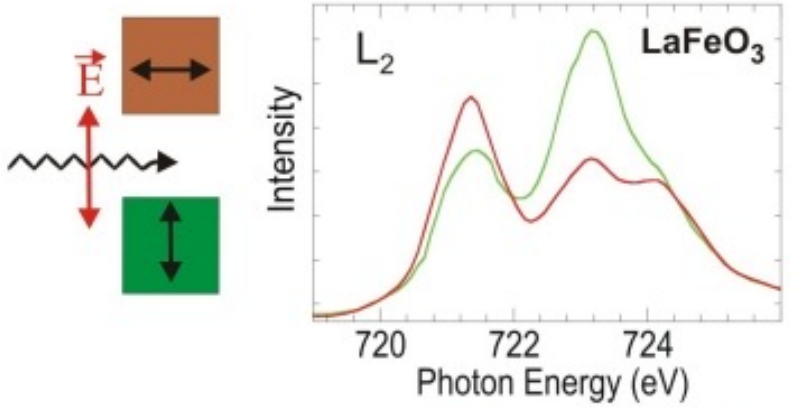
X-ray Linear Dichroism

Stöhr *et al.*, Phys. Rev. Lett. **47**, 381 (1981)



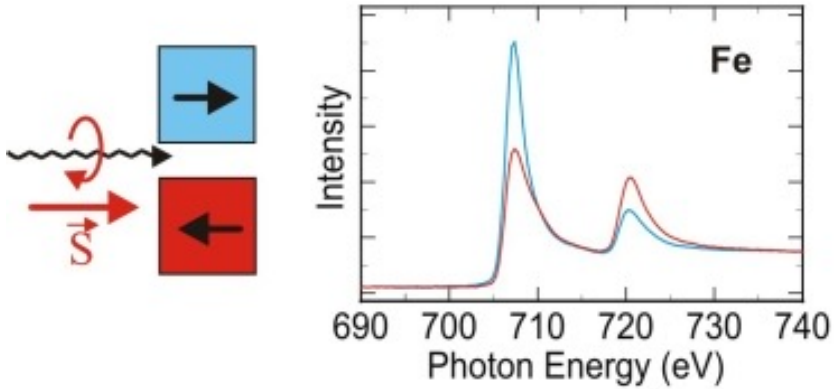
X-ray Magnetic Linear Dichroism

Van der Laan *et al.*, Phys. Rev. B **34**, 6529 (1986)



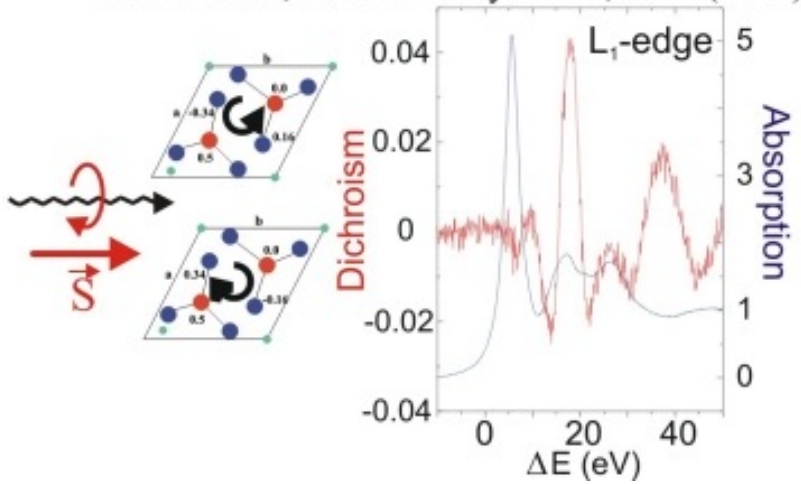
X-ray Magnetic Circular Dichroism

Schütz *et al.*, Phys. Rev. Lett. **58**, 737 (1987)



X-ray Natural Circular Dichroism

Goulon *et al.*, J. Chem. Phys. **108**, 6394 (1998)

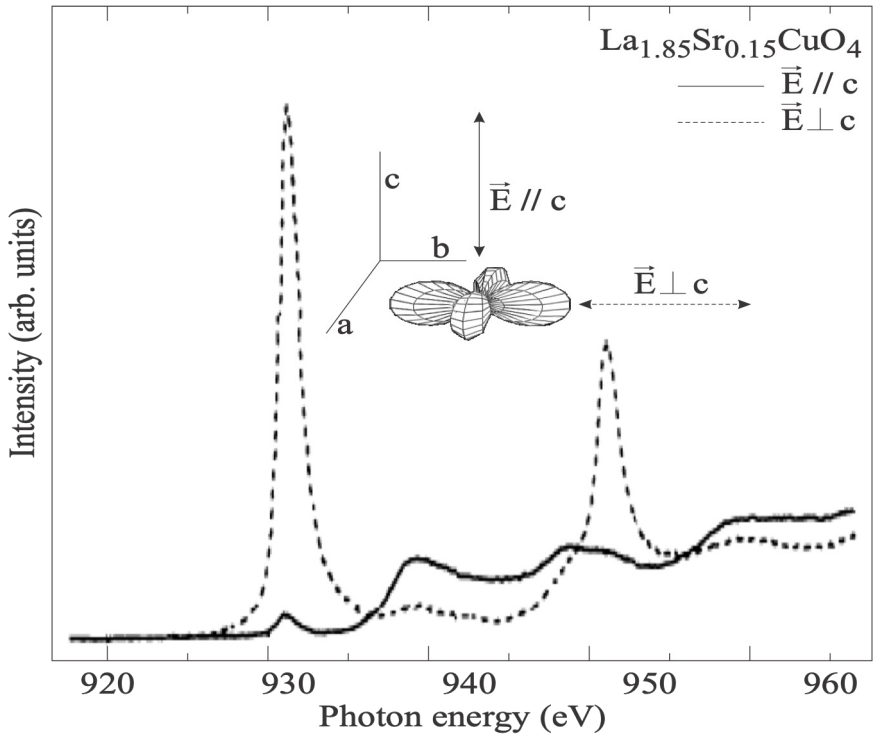


X-ray Linear Dichroism

- Dependence of absorption on relative orientation between x-ray polarization and crystallographic axis
- $\vec{\varepsilon}$: search-light for no. of valence holes in different directions

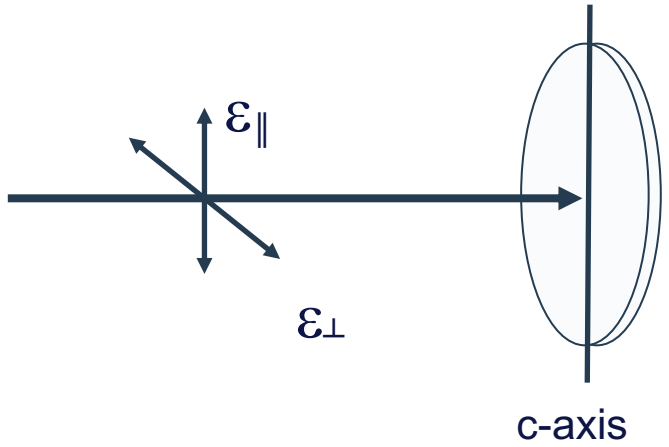
$$XLD = \frac{\mu^{//} - \mu^{\perp}}{\mu^{//} + \mu^{\perp}} \qquad \mu^{//} : \vec{\varepsilon} \,//\, \vec{c} \qquad \mu^{\perp} : \vec{\varepsilon} \perp \vec{c}$$

Cu $L_{2,3}$ edge



C. T. Chen et al PRL 68, 2543 (1992)

linearly polarized X-rays



- The polarisation dependence → symmetry of empty orbitals
- Sensitive to 3d orbital occupation along polarization direction

X-ray Magnetic Circular Dichroism

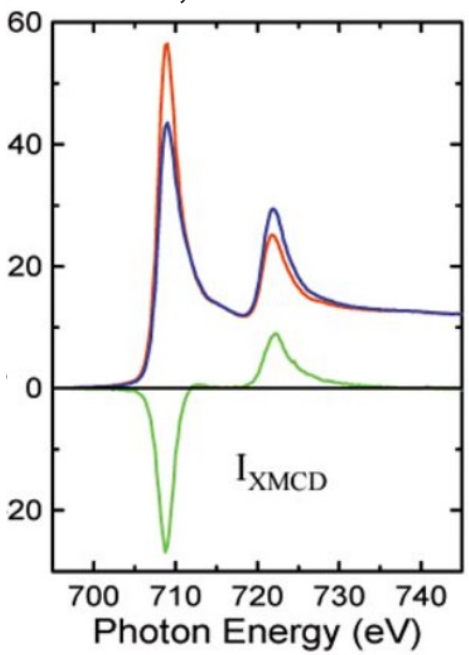
- To make the absorption process spin dependent
  - circularly polarized photons
  - transfer their angular momentum to photoelectron

$$XMCD = \frac{\mu^L - \mu^R}{\mu^L + \mu^R}$$

μ^L : absorption coefficient using CPL

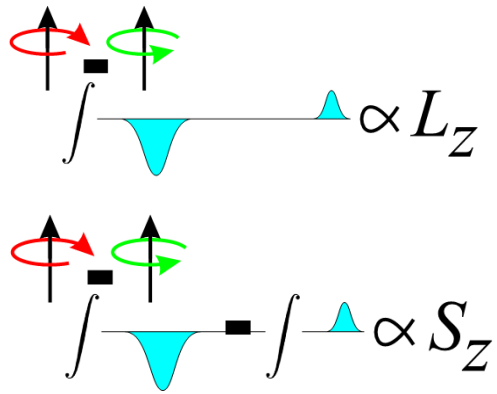
μ^R : absorption coefficient using CPR

Fe $L_{2,3}$-edge XMCD



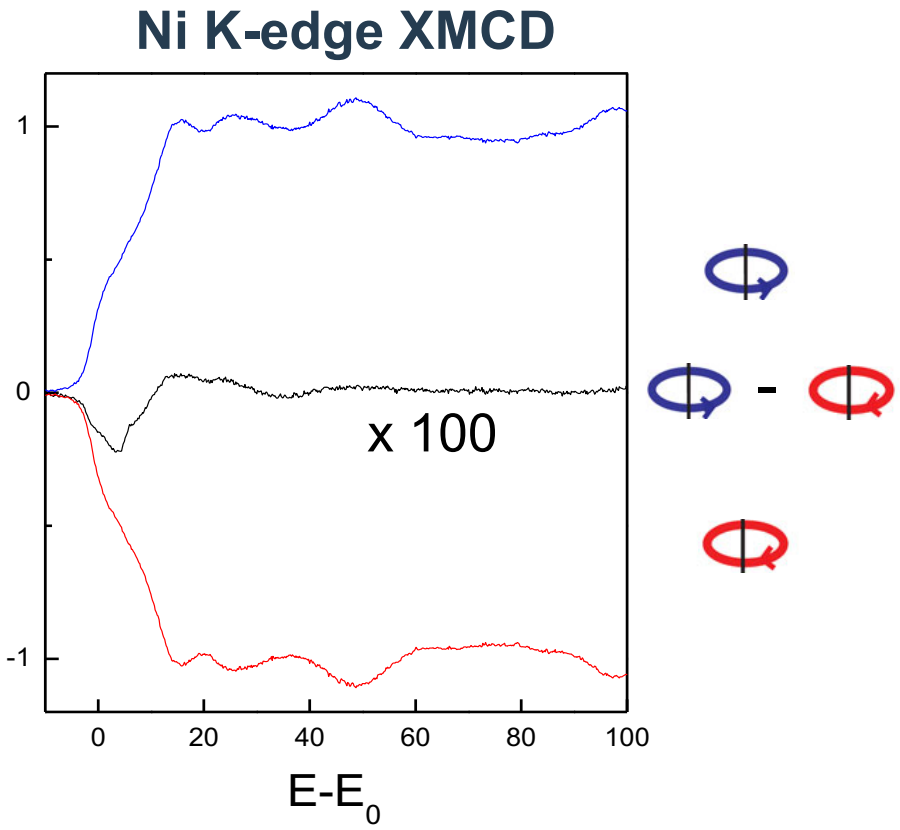
L-edge XMCD (2p → 3d)
Direct probe of valence band magnetization

- A unique probe for element-specific spin- and orbital magnetization
- L_z and S_z can be evaluated directly from Sum Rules



B.T. Thole et al.; Phys. Rev. Lett. (1992)
P. Carra et al.; Phys. Rev. Lett. (1993)

X-ray Magnetic Circular Dichroism



$$XMCD = \frac{\mu^L - \mu^R}{\mu^L + \mu^R}$$

μ^L : absorption coefficient using CPL

μ^R : absorption coefficient using CPR

K-edge XMCD (1s → 4p)
Indirect information on valence band magnetization

→ Much smaller signal

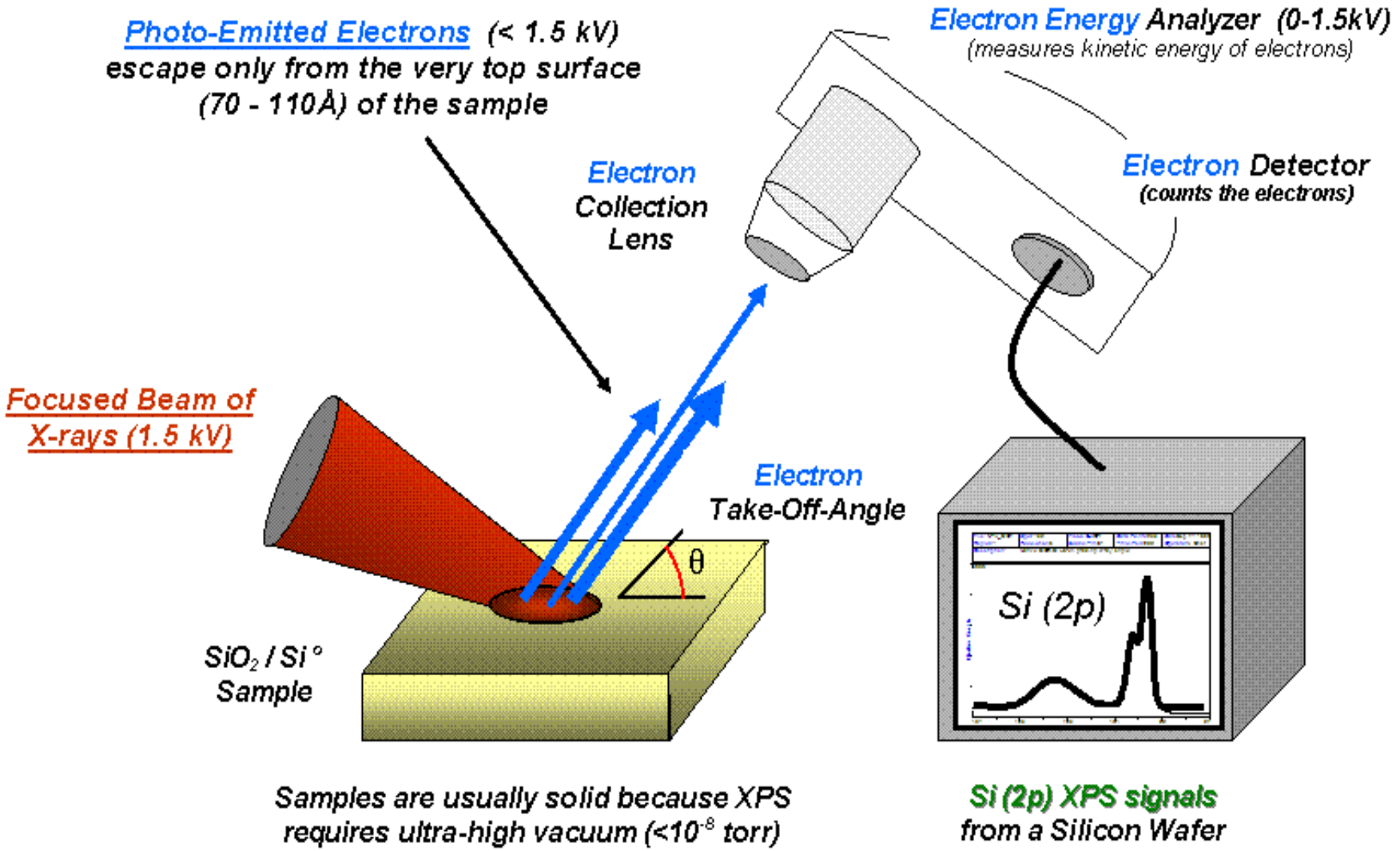
→ More difficult interpretation

- net magnetic moment on absorber
- sublattice magnetization
- changes in ferromagnetic order
- hybridization effects, induced moments

Outline

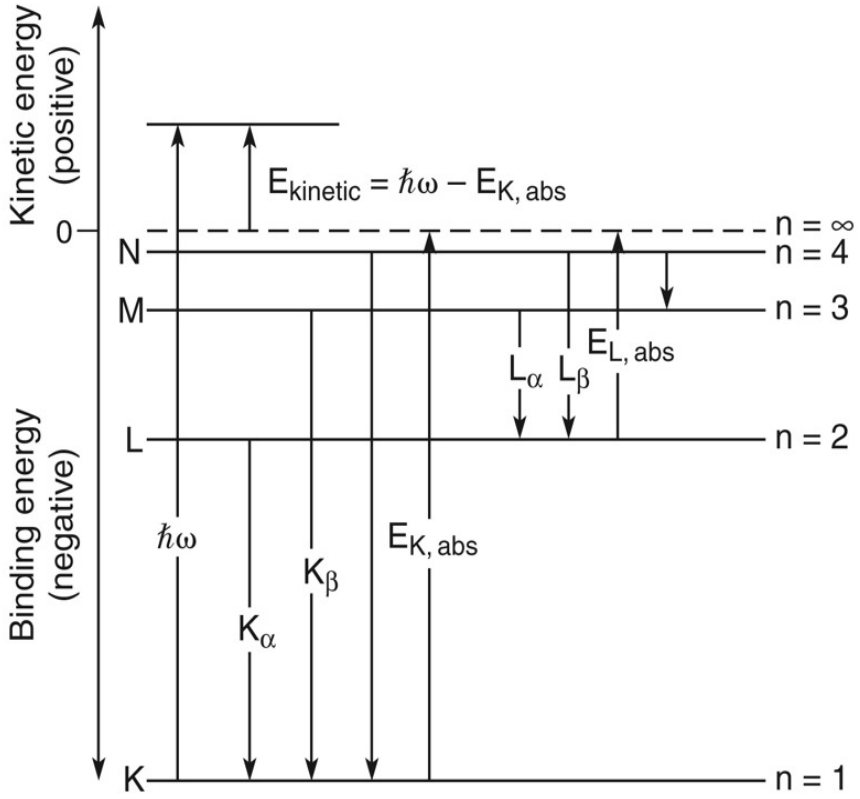
- Radiation – matter interaction
- Experimental Techniques
  - Based on Scattering
    - ▶ Elastic Scattering
    - ▶ Inelastic Scattering
  - Based on Photoelectric Absorption
    - ▶ Core-hole Spectroscopies
      - X-ray Absorption Spectroscopy
      - X-ray Emission Spectroscopy, RIXS, X-ray Raman
      - X-ray Polarization Dependent Spectroscopies
      - X-ray Photoemission Spectroscopy
  - Imaging Methods

X-ray Photoelectron Spectroscopy

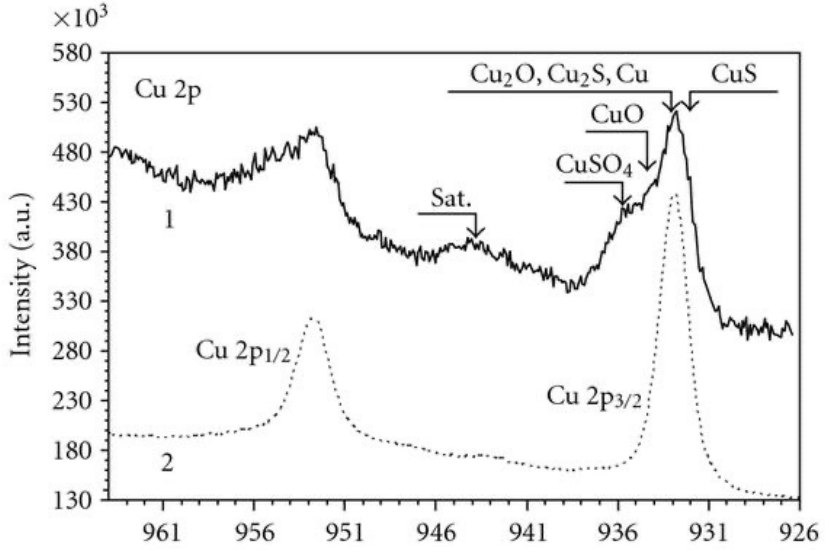


X-ray Photoelectron Spectroscopy for Chemical Analysis

- Binding energies of the measured electrons are characteristic of the chemical structure and molecular bonding of the material



Cu L_2 ($2p_{1/2}$) and L_3 ($2p_{3/2}$) photoemission



$$E_i = \hbar\omega - E_f - \phi$$

binding energy of electron

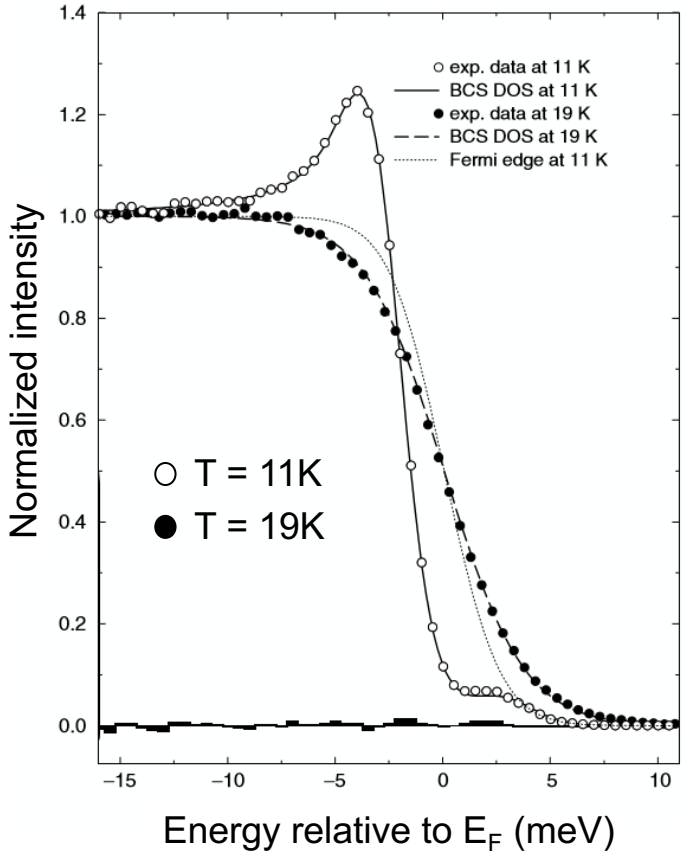
incoming photon energy → measured

kinetic energy of outgoing photoelectron → measured

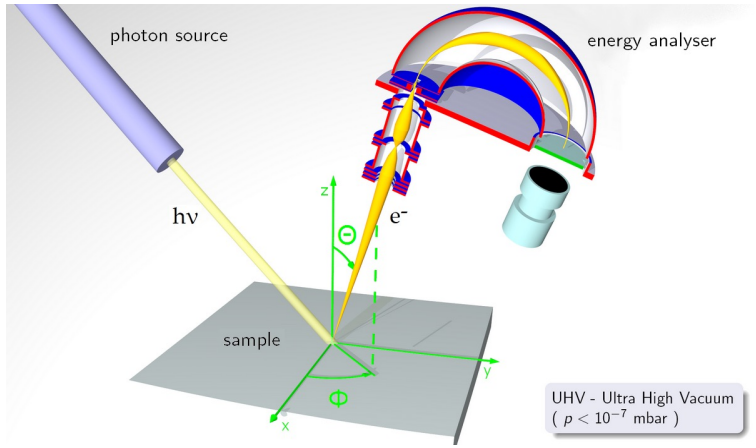
electron work function

Valence band photoemission & band structure determination

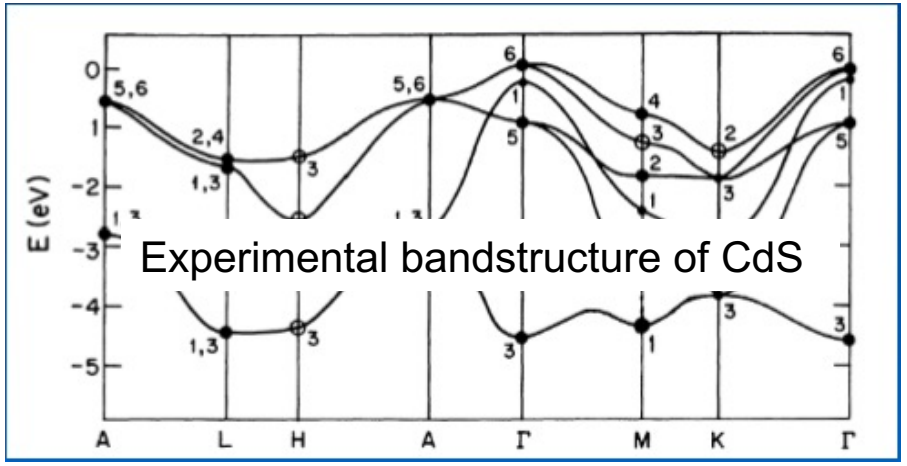
- Opening of the superconducting gap at T< Tc
- Less electron states at the Fermi level



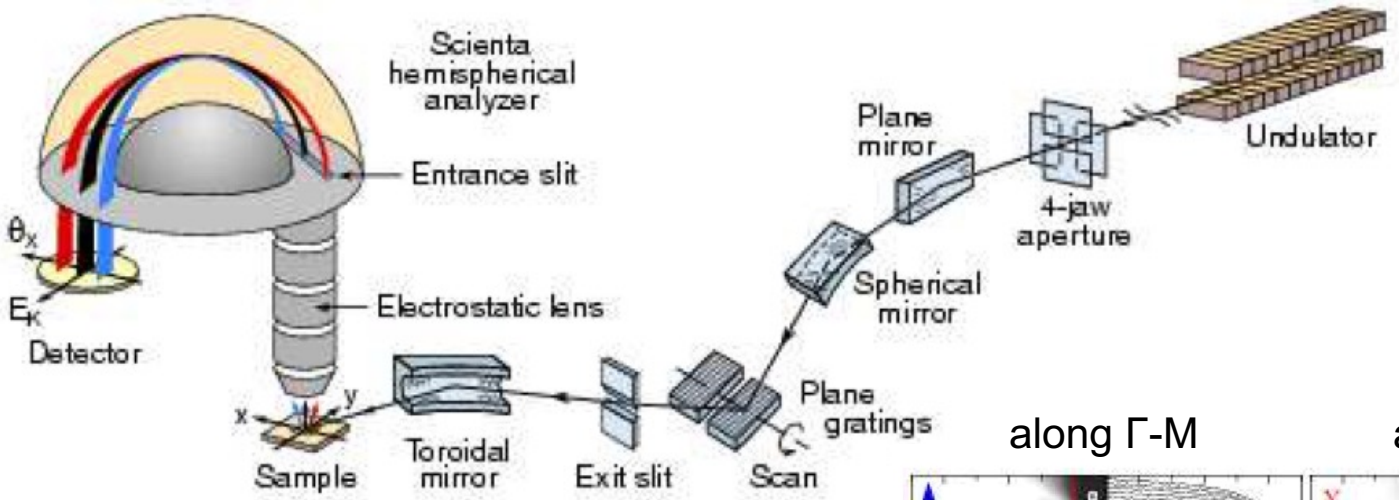
Angle-Resolved Photo-Electron Spectroscopy



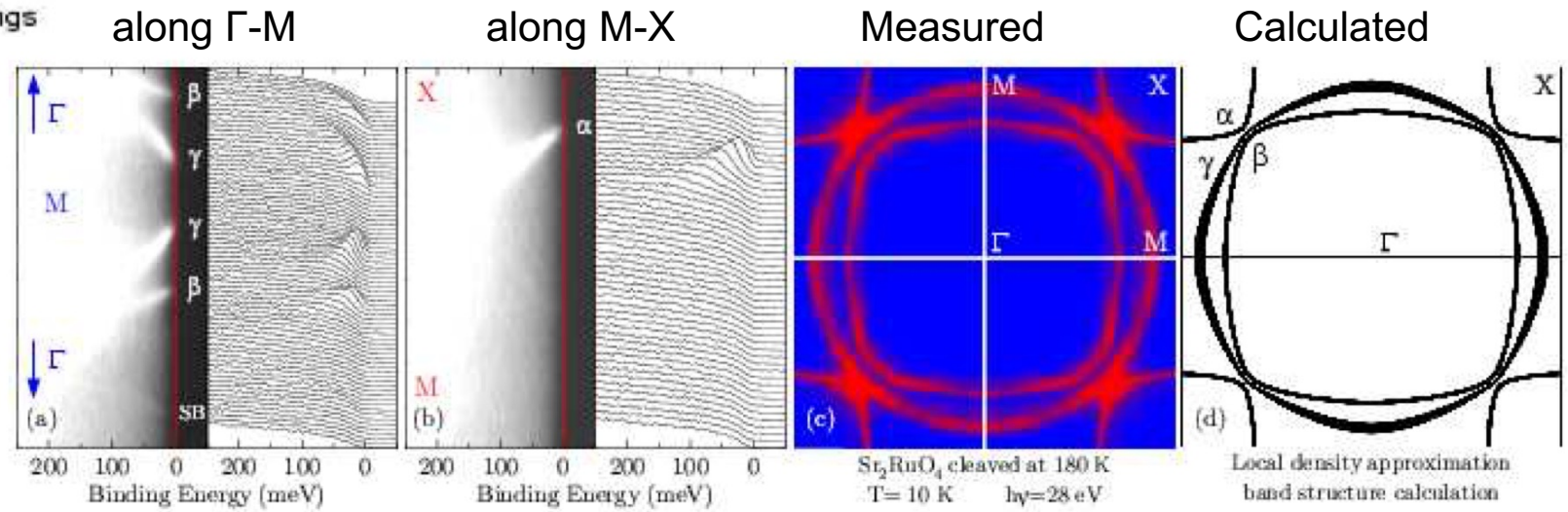
Distribution of electrons in reciprocal space



High resolution ARPES reveals Fermi surface in novel superconductors



- Novel superconductor Sr_2RuO_4
- Isostructural to the archetypal cuprate parent compound La_2CuO_4 (but RuO_2 planes replace the CuO_2 planes)
- Its low-energy electronic structure is characterized by three bands crossing the chemical potential



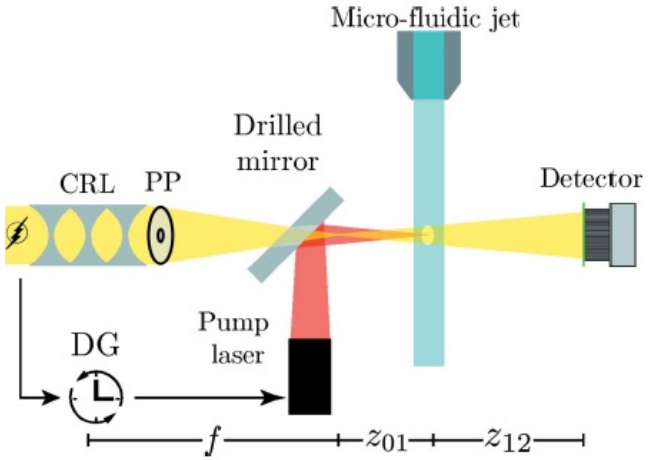
Damascelli A. et al., Reviews of Modern Physics 75.2 (2003): 473.

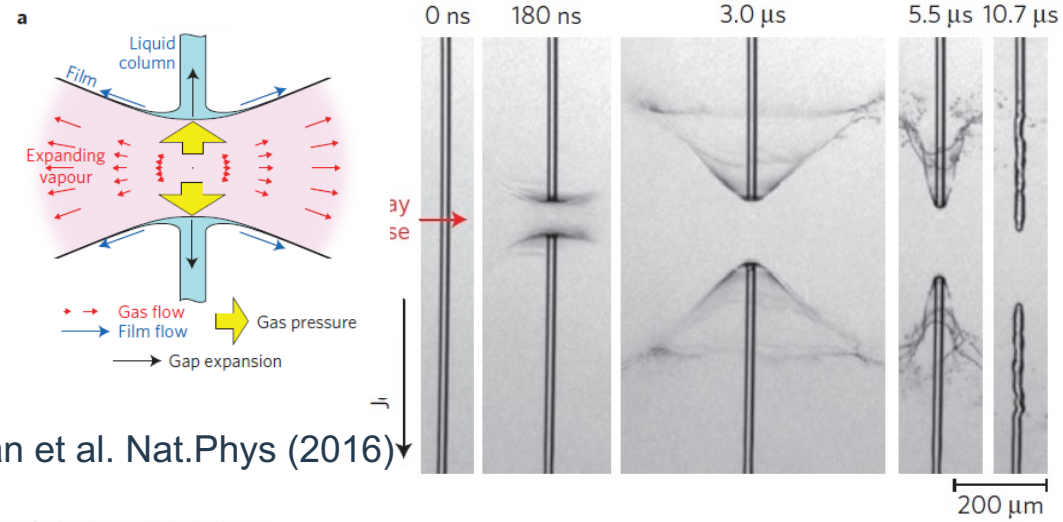
Outline

- Radiation – matter interaction
- Experimental Techniques
  - Based on Scattering
    - ► Elastic Scattering
    - ► Inelastic Scattering
  - Based on Photoelectric Absorption
    - ► Core-hole Spectroscopies
      - X-ray Absorption Spectroscopy
      - X-ray Emission Spectroscopy, RIXS, X-ray Raman
      - X-ray Polarization Dependent Spectroscopies
      - X-ray Photoemission Spectroscopy
  - Imaging Methods

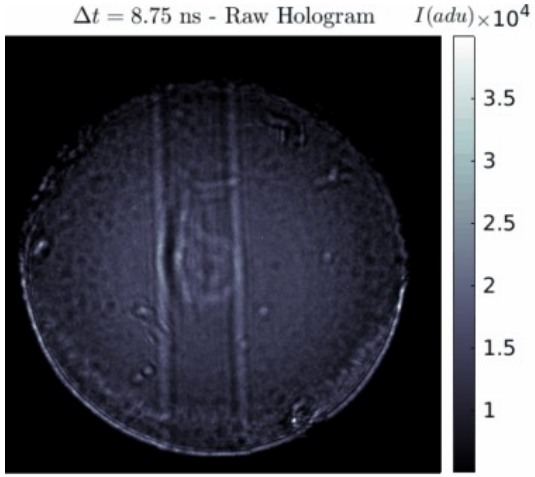
Density Imaging: Shock propagation by ultrafast holography

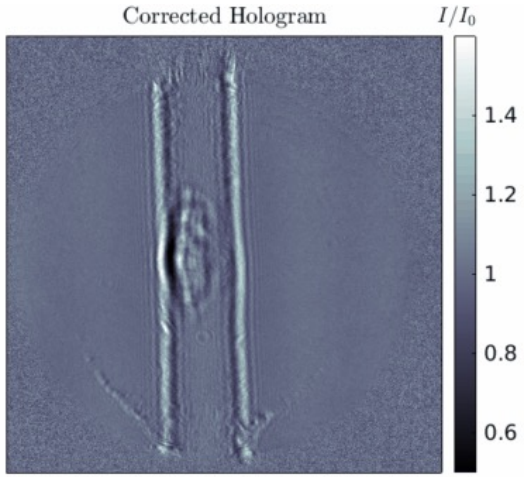
- Phase contrast imaging
  - Very sensitive to tiny changes in refractive index
  - Provides dentity profile

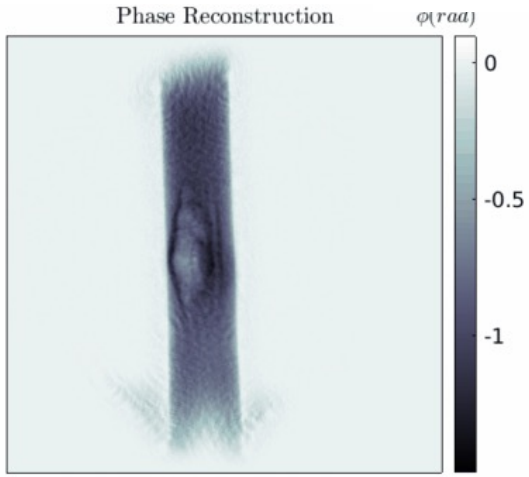


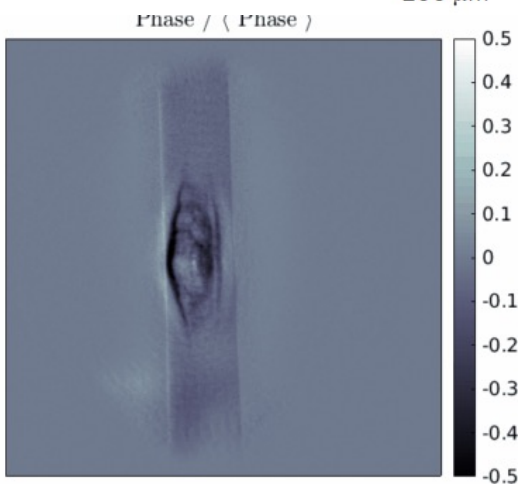


Stan et al. Nat.Phys (2016)









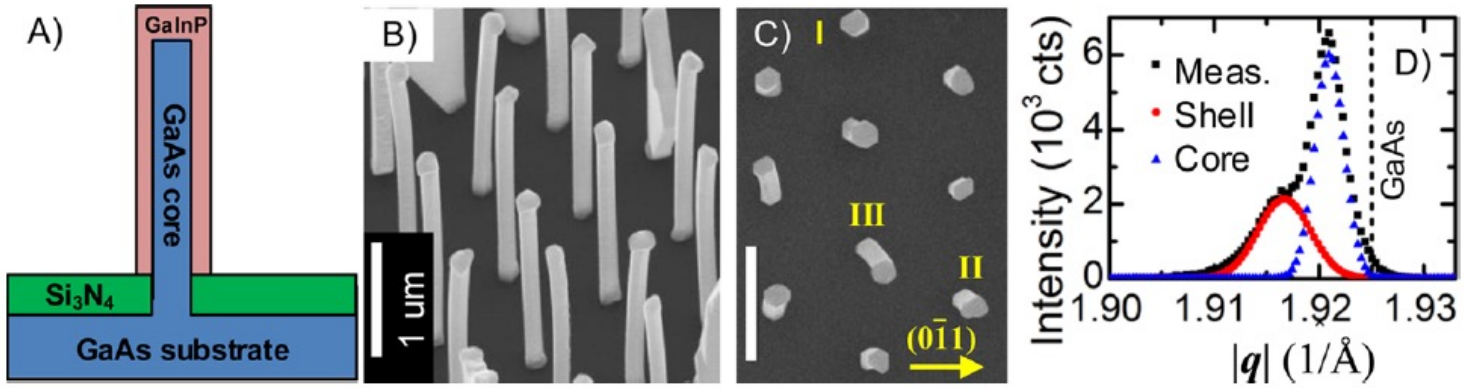
Johannes Hagemann *et al.* JSR (2021)


European
XFEL

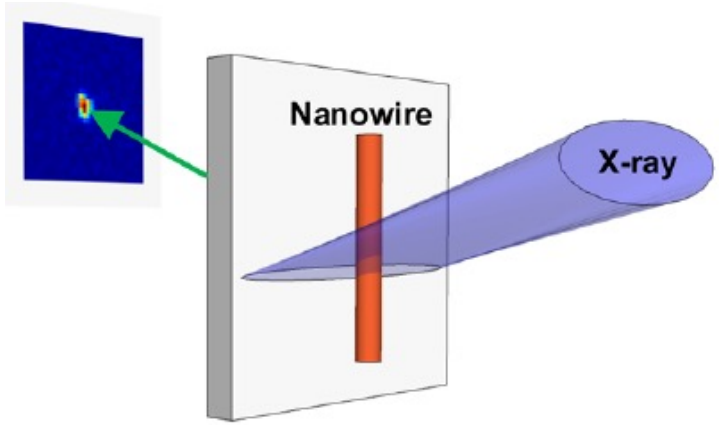
Strain Imaging: core-shell nanowires by nano-XRD

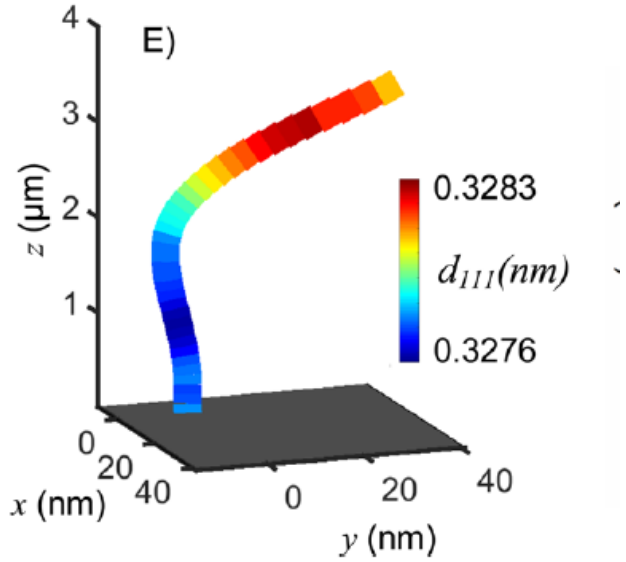
Towards high-efficiency solar cells, light-emitting diodes (LEDs), and nanoscale photodetectors

- GaAs-GaInP core shell nanowire
- Lab source XRD
  - few mm^2 spot
  - Measure (111) reflection – average over many wires
- «Nano-XRD» @ ID11 ESRF
  - Spot size 0.1 × 6 mm
  - Measure individual wires
  - Spatial variation of (111) lattice spacing in a bent nanowire



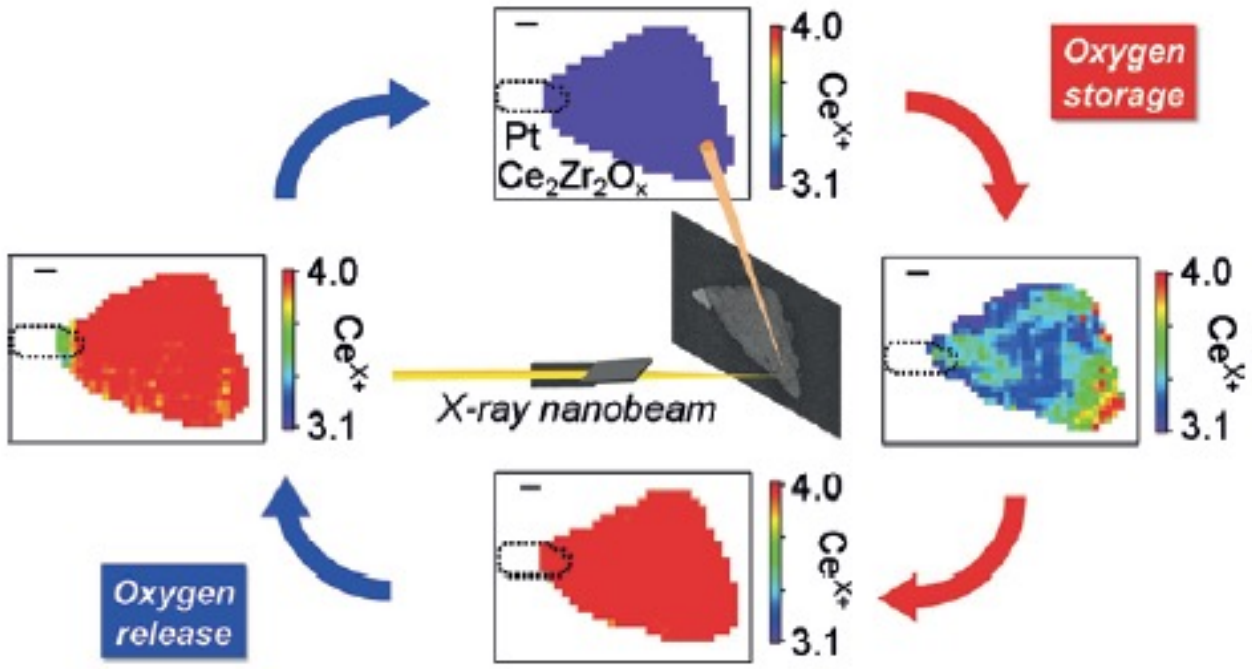
SEM





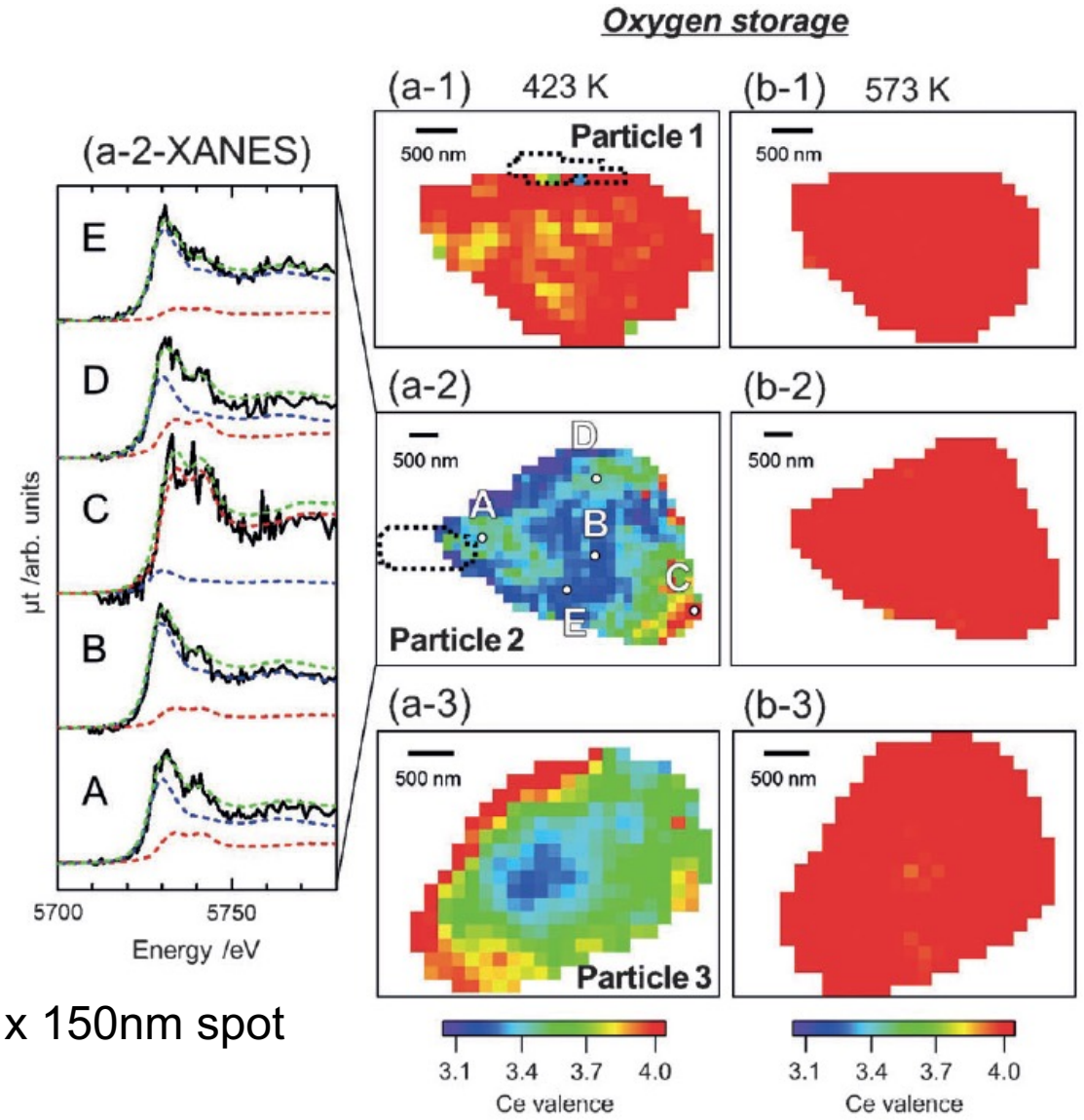
Wallentin et al, Nanoletters, 17, 4143 (2017)

Chemical Imaging: Oxygen diffusion in individual catalyst particle



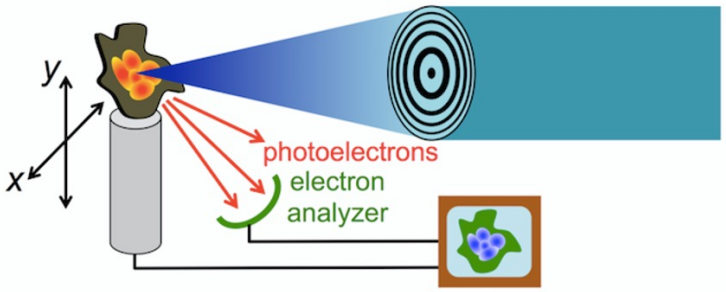
Matsui et al., Angew. Chem. Int. Ed. 2016, 55, 1 – 5

BL36XU, SPRING8

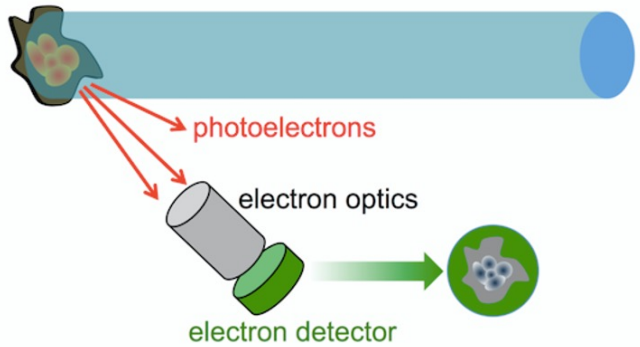


400 x 150nm spot

Photoelectron spectro-microscopy for chemical contrast



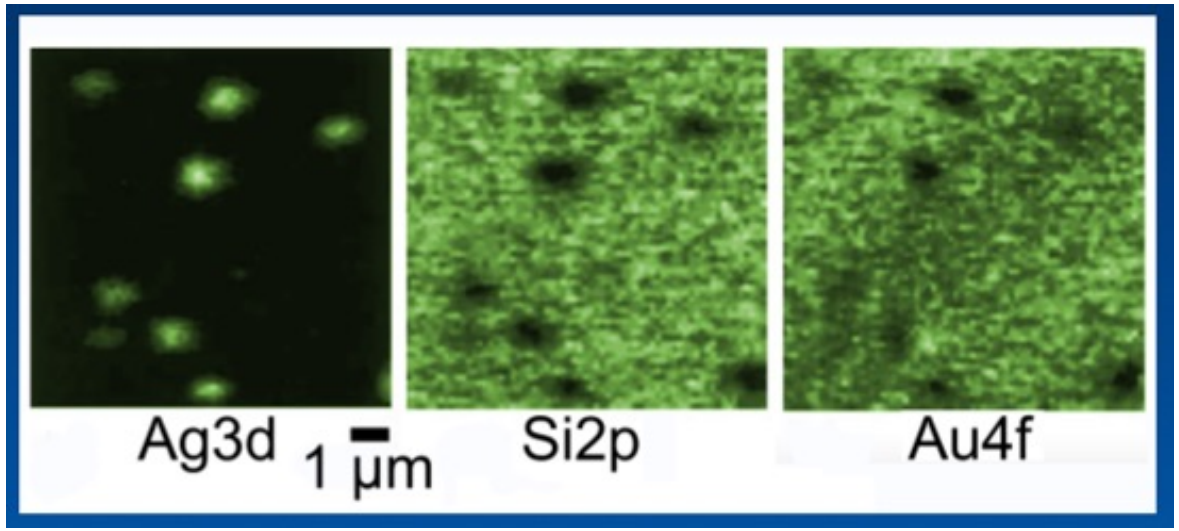
Scanning mode



Full field mode

Photoelectron images at different photoelectron energies

→ chemical contrast inversion



M. Marsi et al.; J. Elec. Spectros. 84, 73 (1997)

Thank you for your attention !