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U.S. DEPARTMENT of ENERGY

Introduction to X-ray Absorption Spectroscopy

Slides adapted from materials by Bruce Ravel (NIST & NSLS-II) and Eli Stavitski (NSLS-II)

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3/10/2026

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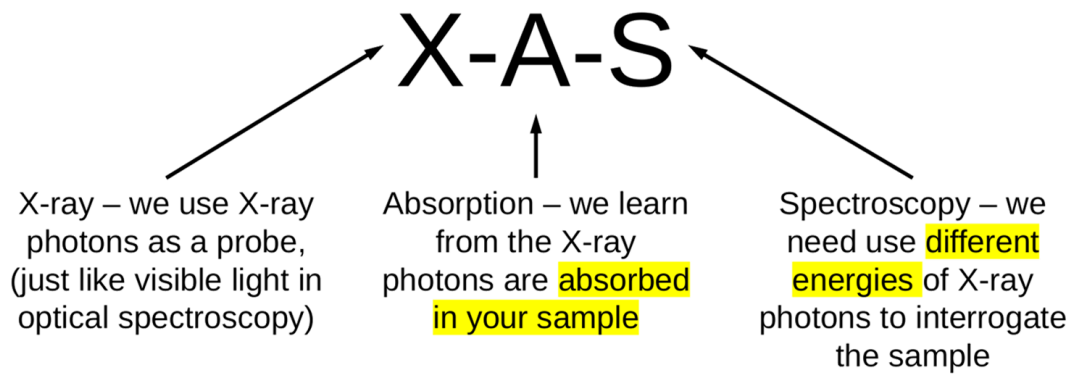
Outline

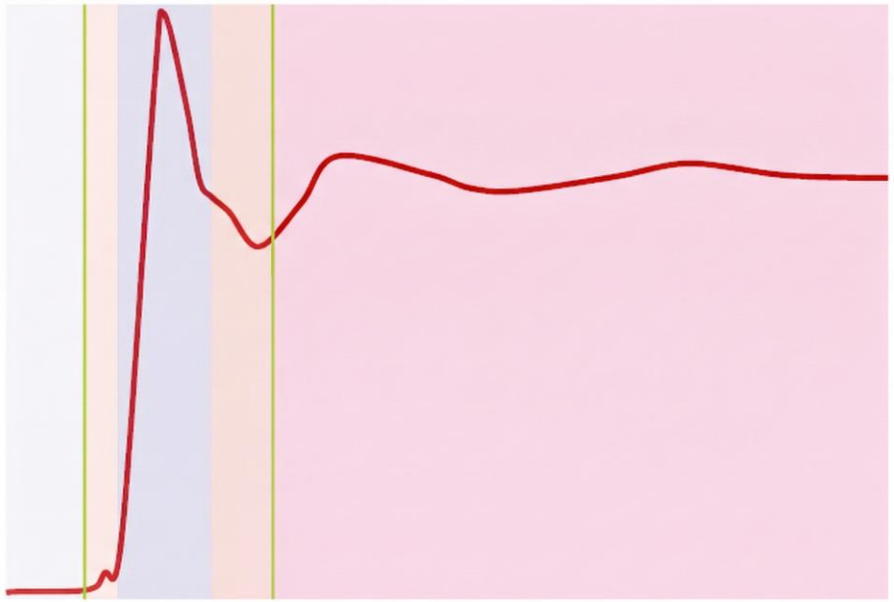
- What is XAS?
- Basic physics of X-ray absorption
- Beamline setup and detection
- What XAS can tell us

What is XAS?

X-ray Absorption Spectroscopy (XAS) measures how the X-ray absorption coefficient changes near an absorption edge.



XAFS	X-ray Absorption Fine-Structure Spectroscopy (= XAS)
XANES	X-ray Absorption Near-Edge Spectroscopy
EXAFS	Extended X-ray Absorption Fine-Structure
NEXAFS	Near Edge X-ray Absorption Fine Structure



No absorption – X-ray photon energy is too low	
XANES	Pre-edge region – transitions within the atom (e.g., 1s→3d)
	White line – transition to just above Fermi levels (e.g., 1s→4p)
	This region often contains signatures spectral features
EXAFS – where oscillations occur	

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History of XAS

Discovery of X-ray → **Early Observations** → **Development of EXAFS theory** → **Modern XAS**

1895
Röntgen
Discovered X-rays

Maurice de Broglie (1913)
First absorption edge measured

Fricke (1920)
First fine structure

Kossel (1920)
First theory of XANES

Hanawalt (1931)
EXAFS in gases, temperature effect

Kronig (1931)
First EXAFS theory

Cauchois (1932)
Curved crystal spectrograph

Hayasi (1936, 1949)
Theory of EXAFS

Sawada (1955)
Amorphous/crystalline polymorphs

Shiraiwa (1958)
Improved theory

Kostarev (1939, 1946)
Theory and measured EXAFS in single crystals

Kozlenkov (1960)
Improved theory

Van Nordstrand (1960)
Instrumentation, fingerprint ID, used XAS to characterize catalysts

Lytle (14 July 1960)
Boeing (BSRL)

Krogstad (1960)
Personal communication

Lytle (1962)
Particle-in-a-box model

Prins (1964)
Helped Name EXAFS

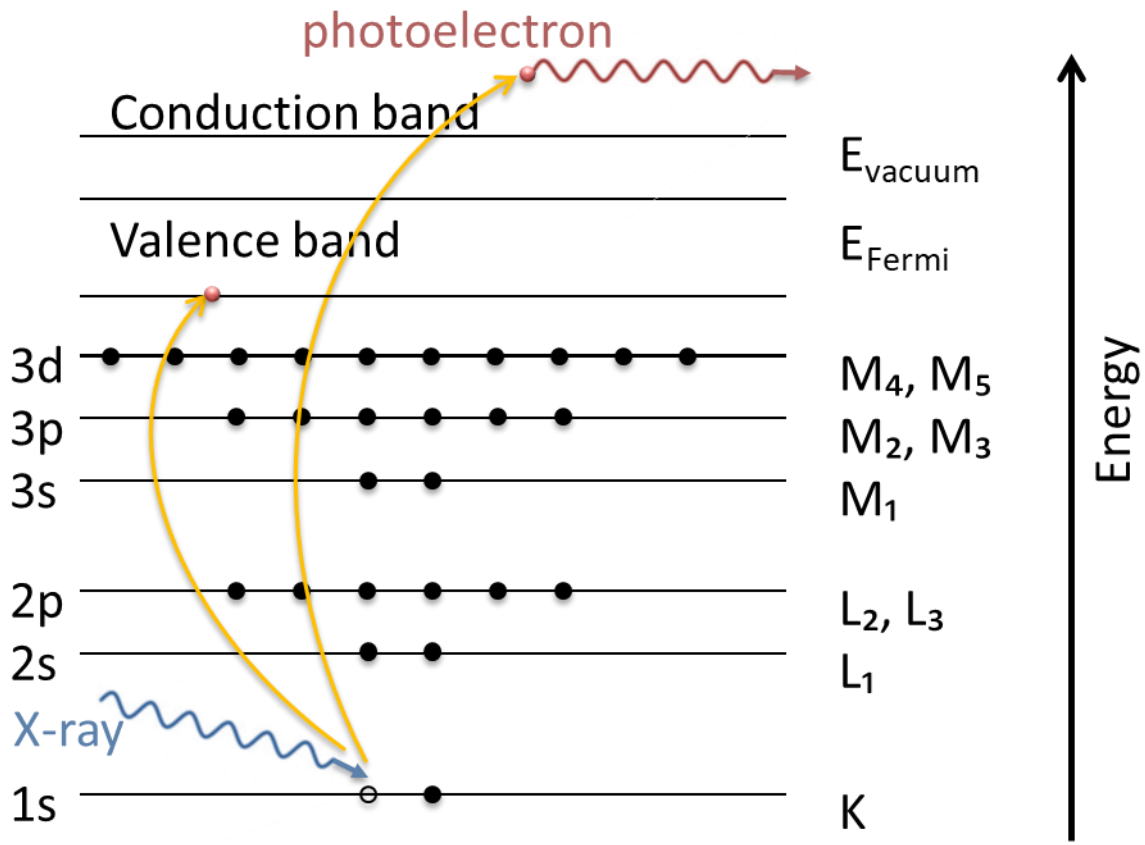
Parratt (1965)
Personal communication;
Rev. Mod. Phys. (1959).31, 616

Sayers, Stern, Lytle (1968–1971)
Modern theory, Fourier transform of EXAFS

Sayers, Stern, Lytle (1974) – First synchrotron XAS (SSRL)

Basic physics of XAS

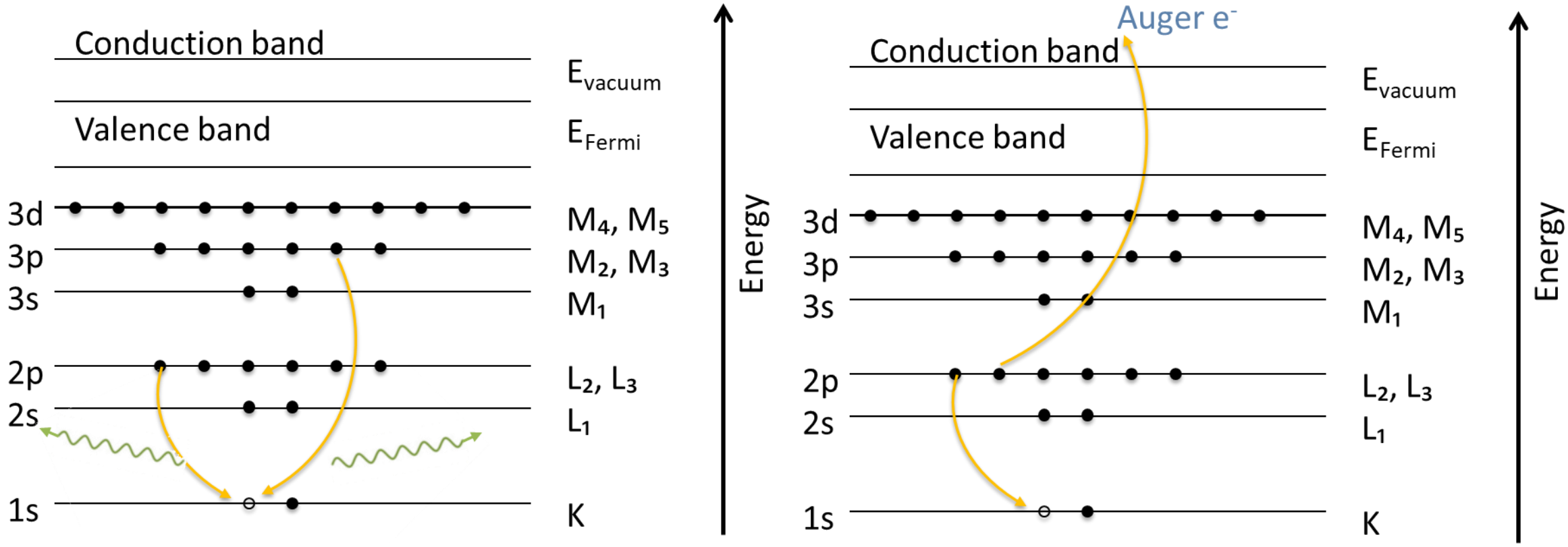
- XAS is an inner-shell spectroscopy because X-rays interact with core electrons (1s, 2s, 2p).
- An X-ray photon excites a core electron into an unoccupied state or into the continuum.
- X-ray absorption occurs through the photoelectric effect.



Basic physics of XAS

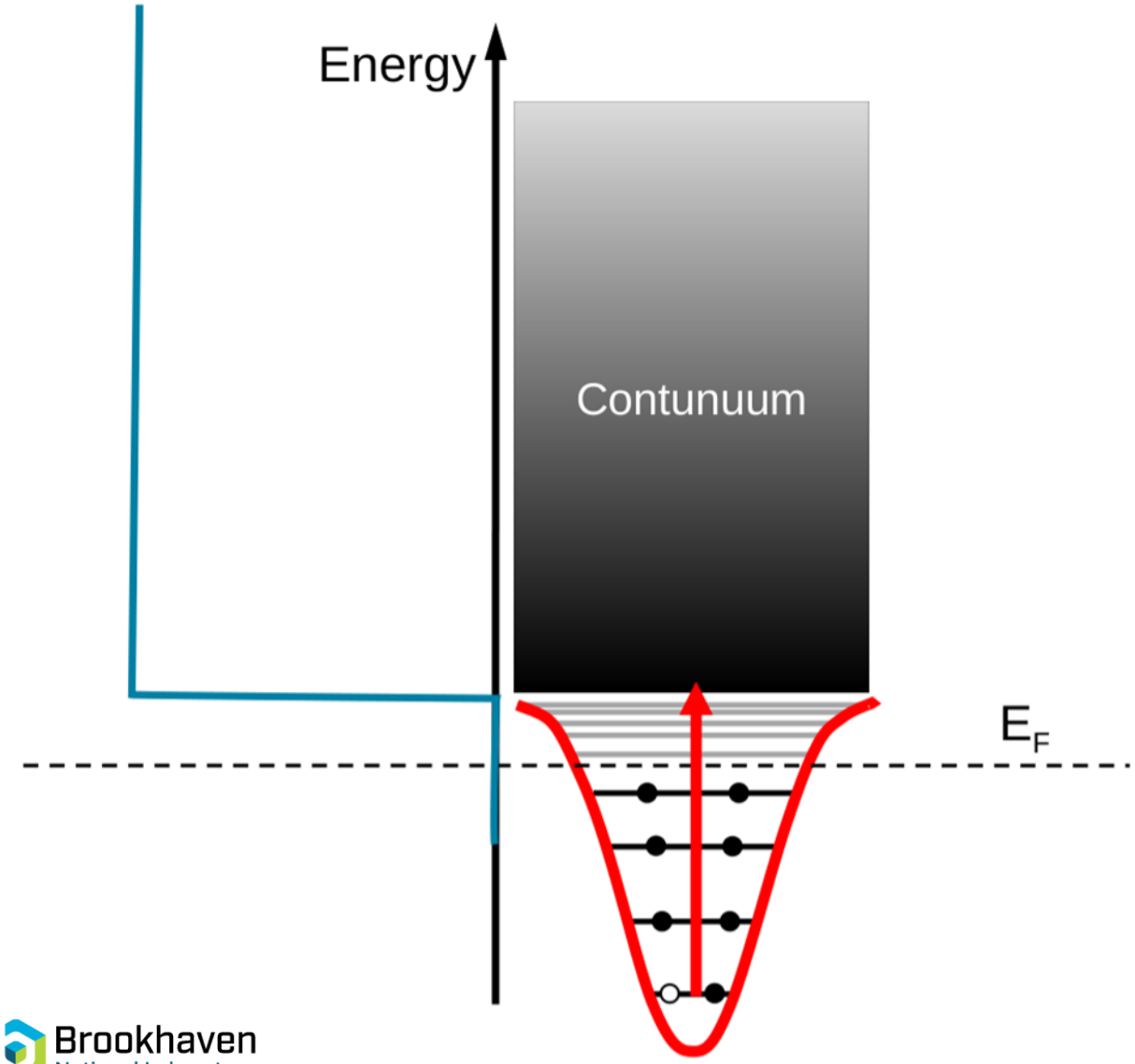
After X-ray absorption, the atom relaxes as a higher-energy electron fills the core hole.
Two common decay pathways:

- Fluorescent X-ray
- Auger electron



Core-hole lifetime: a few femtoseconds→
lifetime broadening introduces energy uncertainty

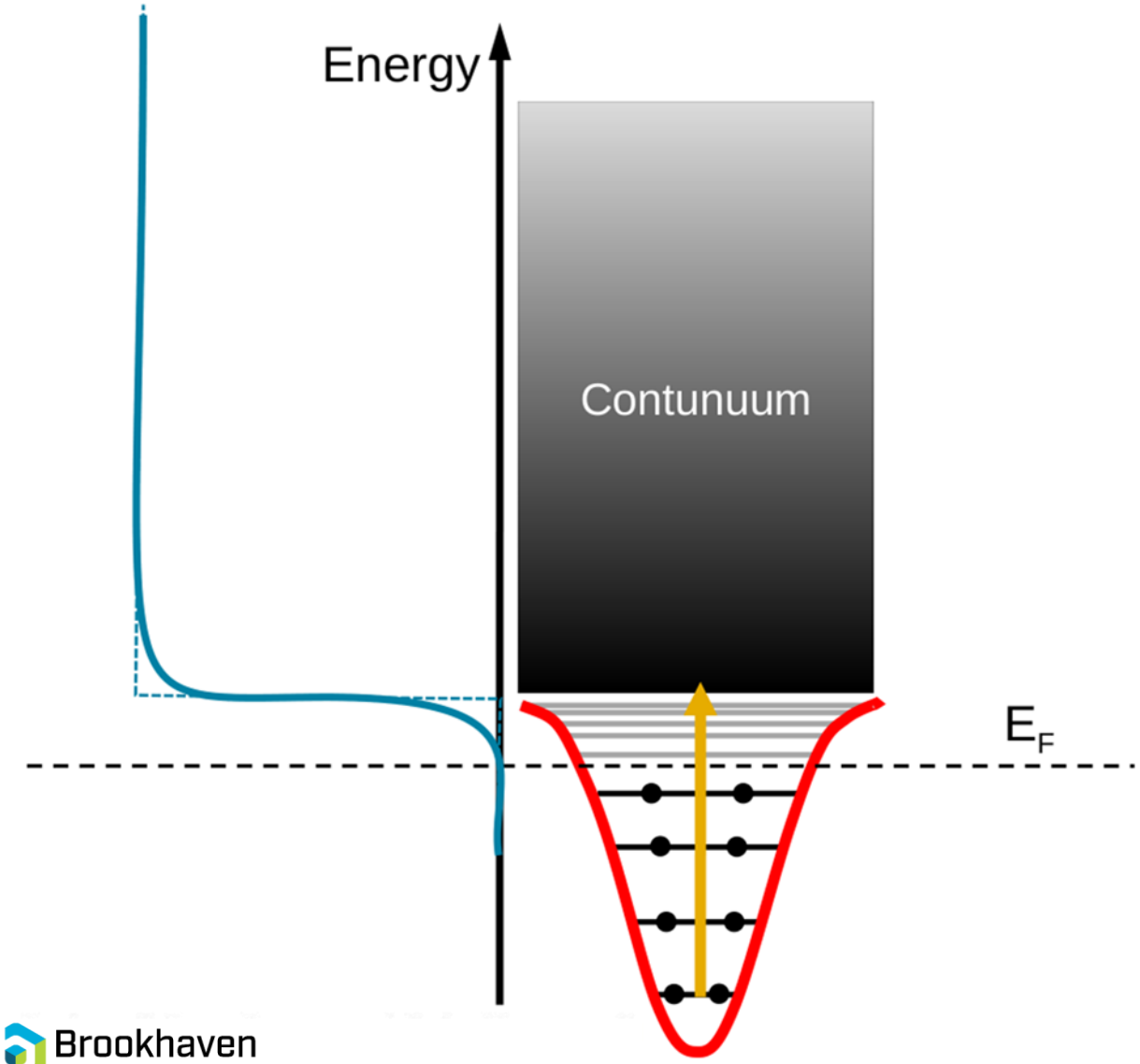
Processes behind X-ray absorption (1)



Example: K-edge of a 3d element

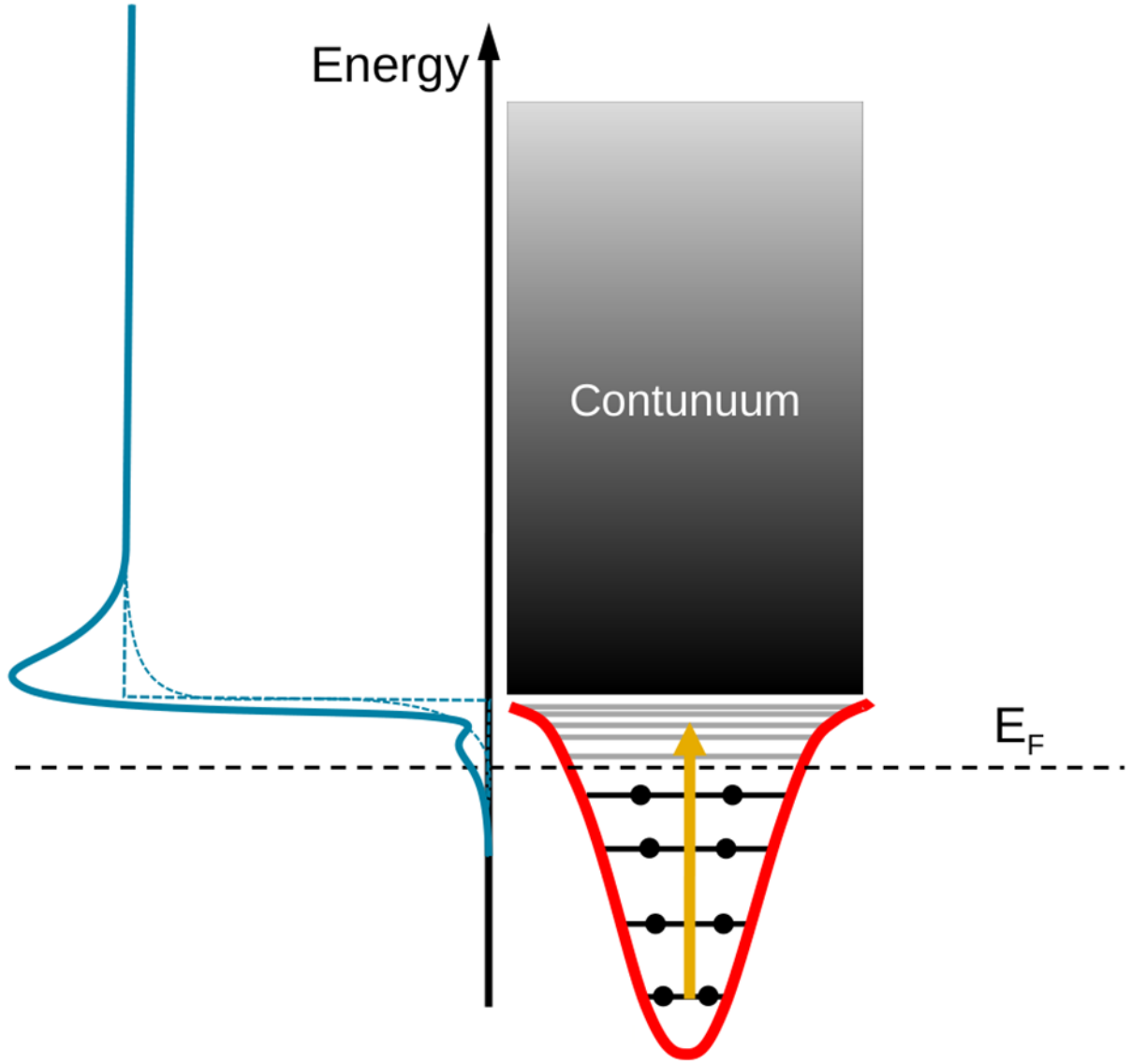
- When the photon energy exceeds the binding energy of a core electron, a photoelectron is emitted.
- This produces the sharp rise in absorption known as the absorption edge.

Processes behind X-ray absorption (2)



- Once the 1s electron is ejected, the core hole is filled within femtoseconds.
- Because the core-hole lifetime is short, the excited state has an intrinsic energy uncertainty.
- This lifetime broadening is typically on the order of 1 to several eV.

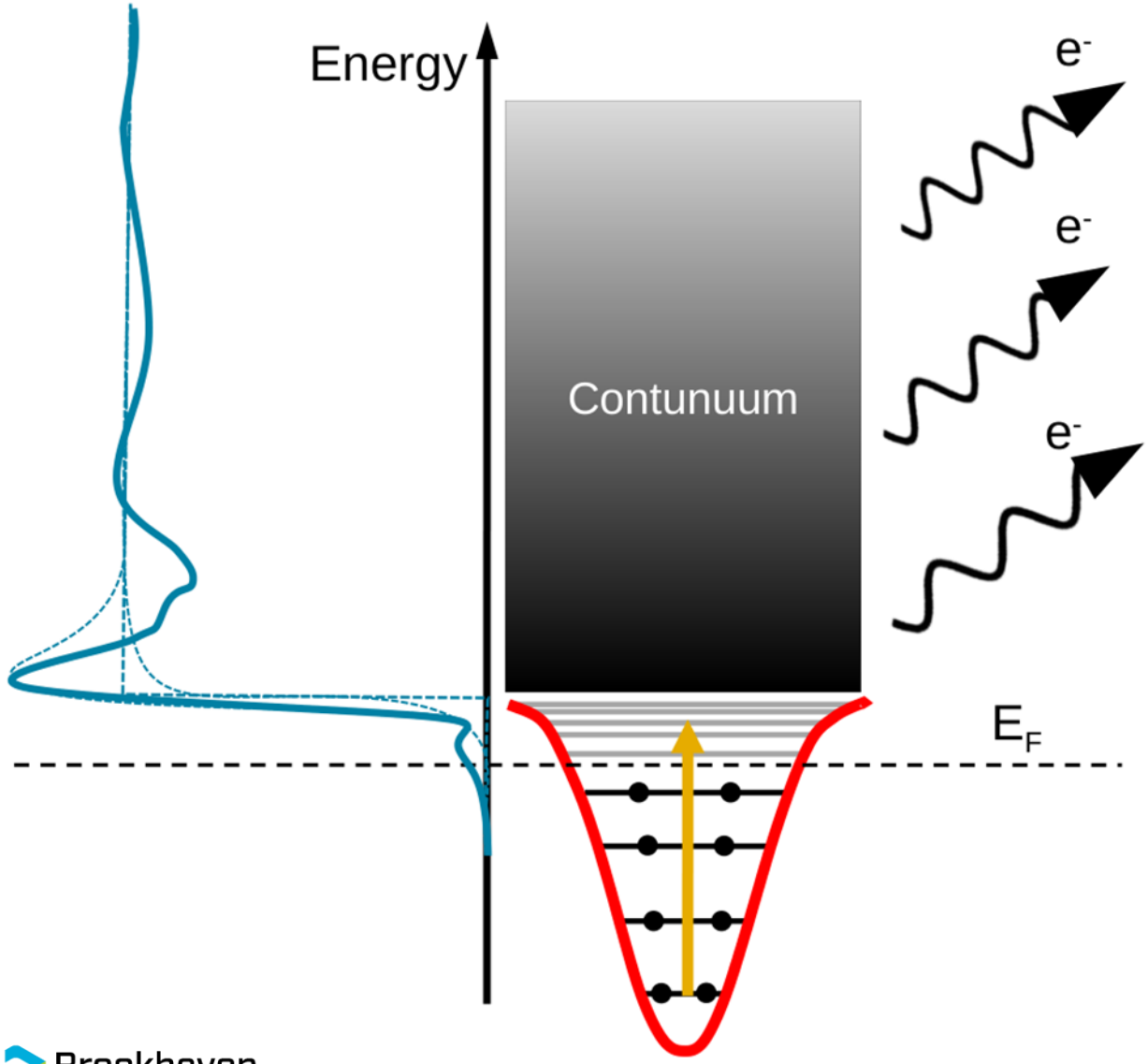
Processes behind X-ray absorption (3)



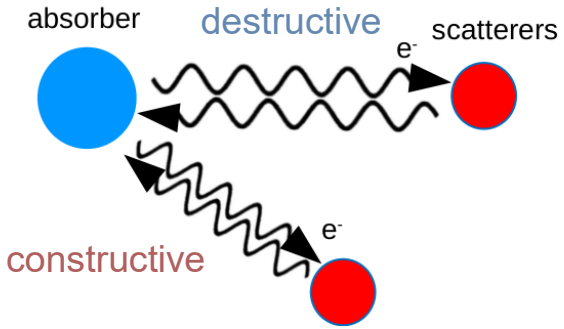
- Now consider the unoccupied states just above the Fermi level.

- According to the dipole selection rule, 1s → 4p transitions are dipole allowed and therefore give strong absorption.
- 1s → 3d transitions are dipole forbidden, but weak quadrupole transitions may become observable depending on symmetry.

Processes behind X-ray absorption (4)



- In condensed matter, the emitted photoelectron is scattered by neighboring atoms.
- The outgoing and back-scattered photoelectron waves interfere.
- This interference modulates the absorption coefficient and gives rise to EXAFS oscillations.



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Selection rules

The absorption probability is determined by the transition matrix element between the initial and final states.
This transition probability can be derived from Fermi's Golden Rule.

$$\mu(E) \propto \sum_f \left| \langle \psi_f | \hat{\epsilon} \cdot \mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} | \psi_i \rangle \right|^2$$

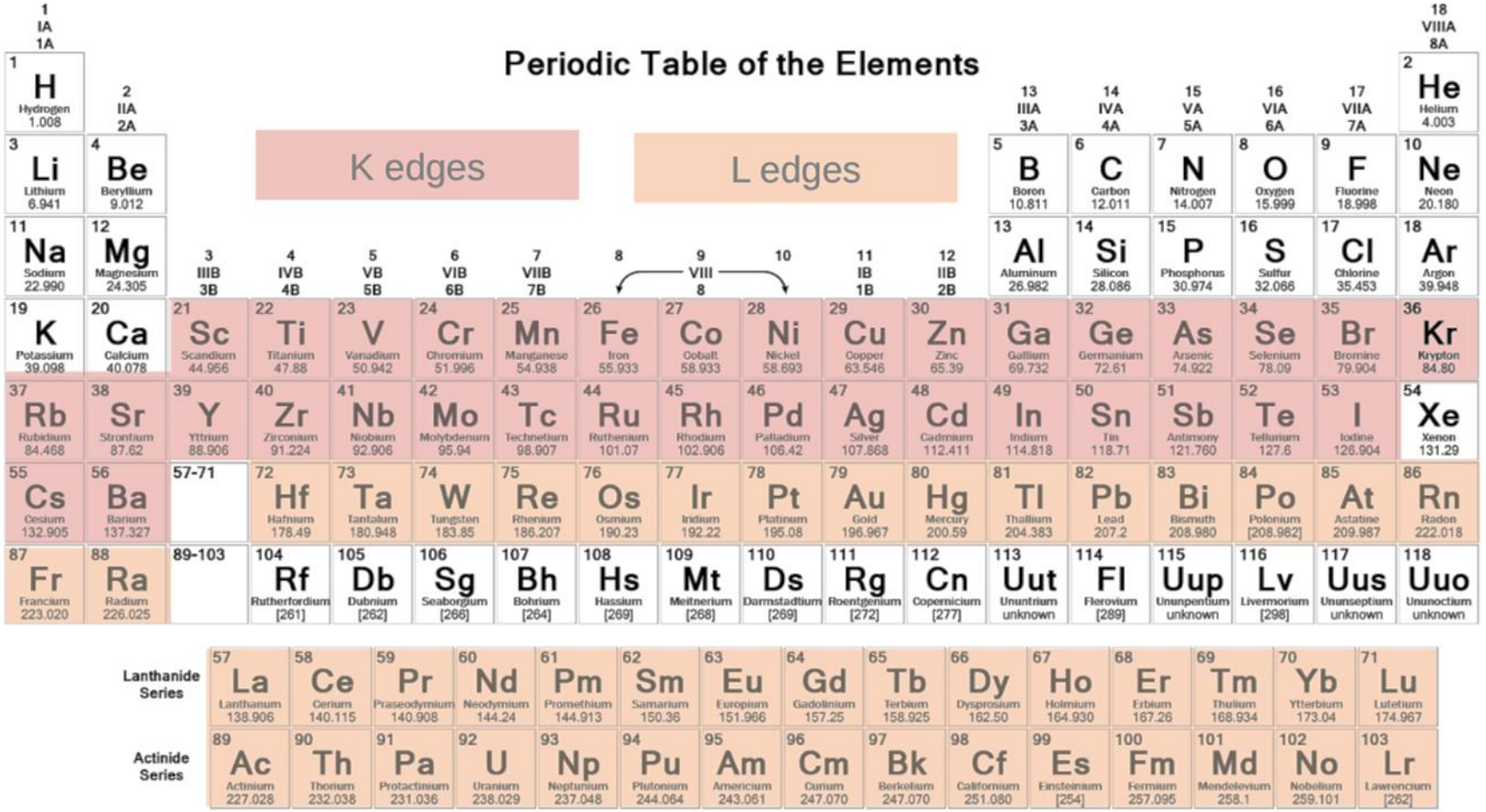
Dipole selection rule: $\Delta l = \pm 1$

Initial state:		final state:
K-edge: 1s (n=1,l=0,m=0)	→	p
L1-edge: 2s (n=2,l=0,m=0)	→	p
L2-edge: 2p (j=1/2) (n=2,l=1)	→	d(&s)
L3-edge: 2p (j=3/2) (n=2,l=1)	→	d(&s)

Selection rules for discrete transitions can be found here,
https://physics.nist.gov/Pubs/AtSpec/node17.html

More in Lecture **3** by Jorge Moncada Vivas:
XANES: fundamentals and analysis

What elements can we probe with hard X-rays?



21 Sc Scandium 44.95591	
K 1s	4492 eV
L_1 2s	498 eV
L_2 $2p_{1/2}$	403 eV
L_3 $2p_{3/2}$	398 eV

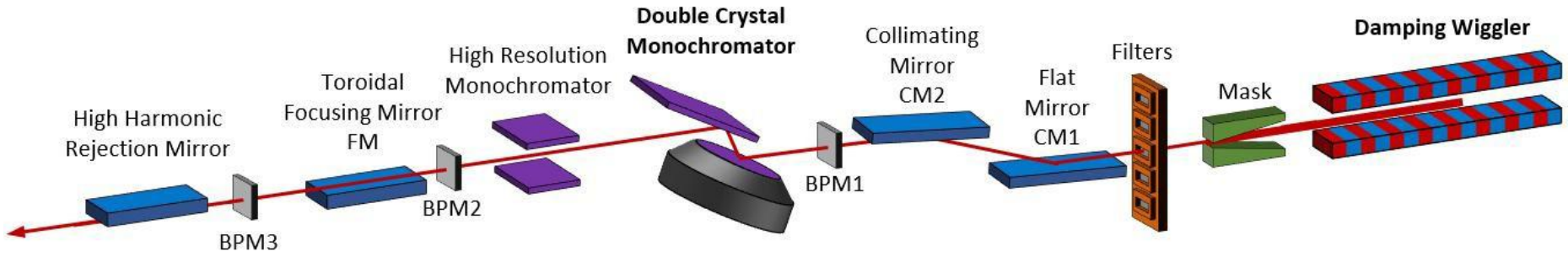
92 U Uranium 238.03	
K 1s	115606 eV
L_1 2s	21757 eV
L_2 $2p_{1/2}$	20948 eV
L_3 $2p_{3/2}$	17166 eV

- XAS is element specific: each element has characteristic absorption edge energies.
- With hard X-rays, we can probe many K and L edges across the periodic table.

Typical layout of an XAS beamline

detectors | slits | (mirror) | monochromator | (mirror) | source

X-ray direction

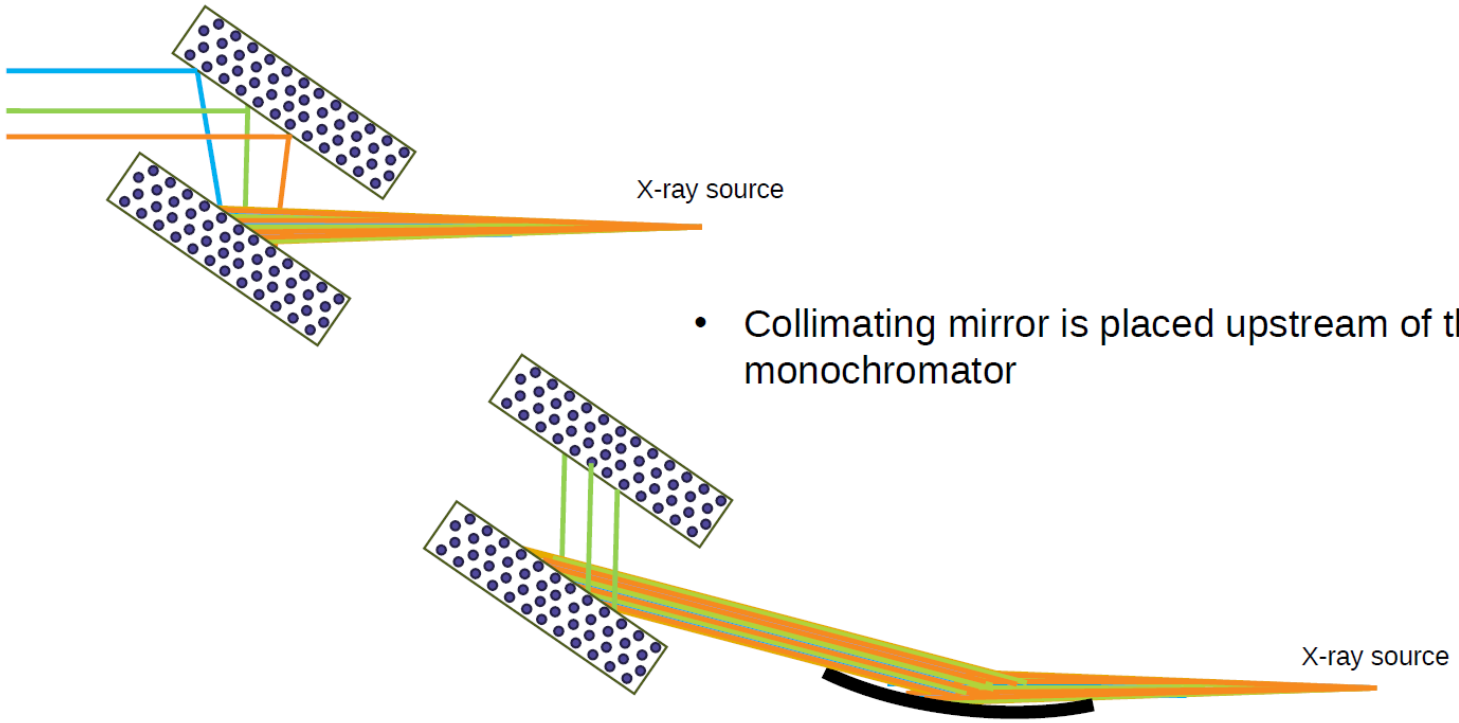


Simplest XAS beamline:
- monochromator

Modern XAS beamline:
- collimating mirror
- monochromator
- focusing mirror
- harmonic rejection mirror

Collimating mirror

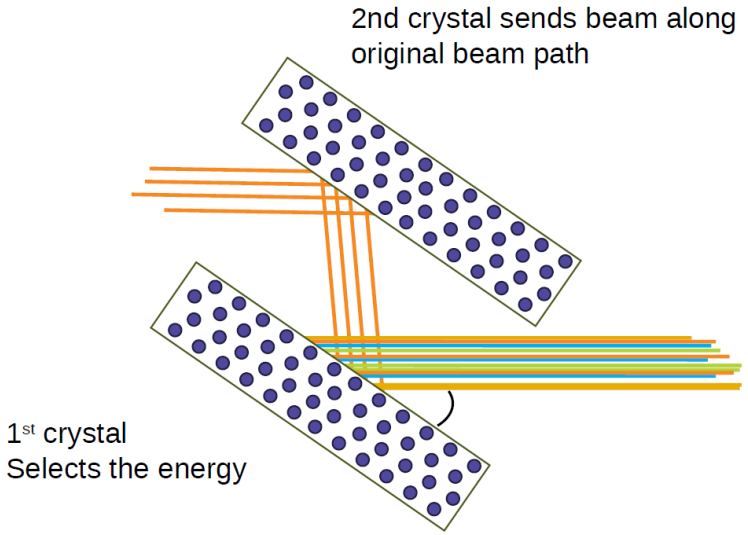
- Makes the divergent rays from the source more parallel.
- This helps ensure that X-rays hit the monochromator crystal at nearly the same angle, improving energy resolution.

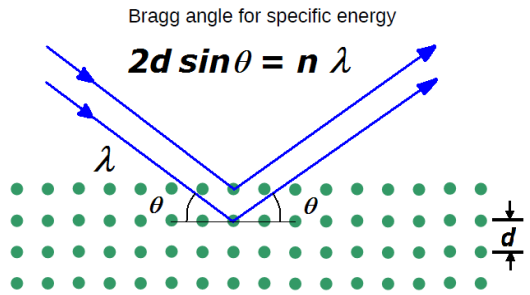


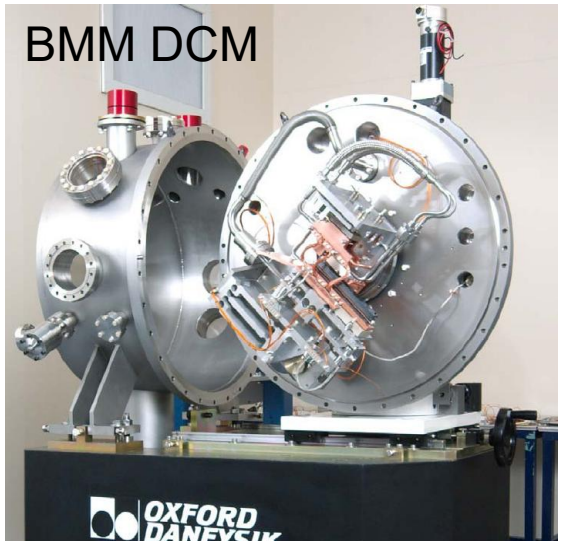
QAS collimating mirror

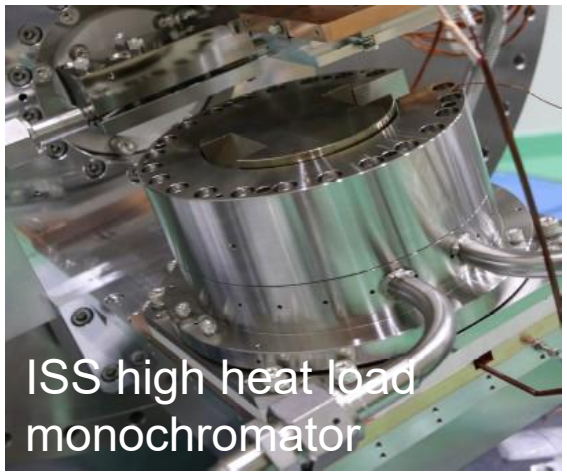
Monochromator

- Uses Bragg diffraction from Si crystals to select a narrow energy bandwidth from the incoming beam.
- The X-ray energy is tuned by rotating the crystal angle.









QAS Channel-Cut monochromator

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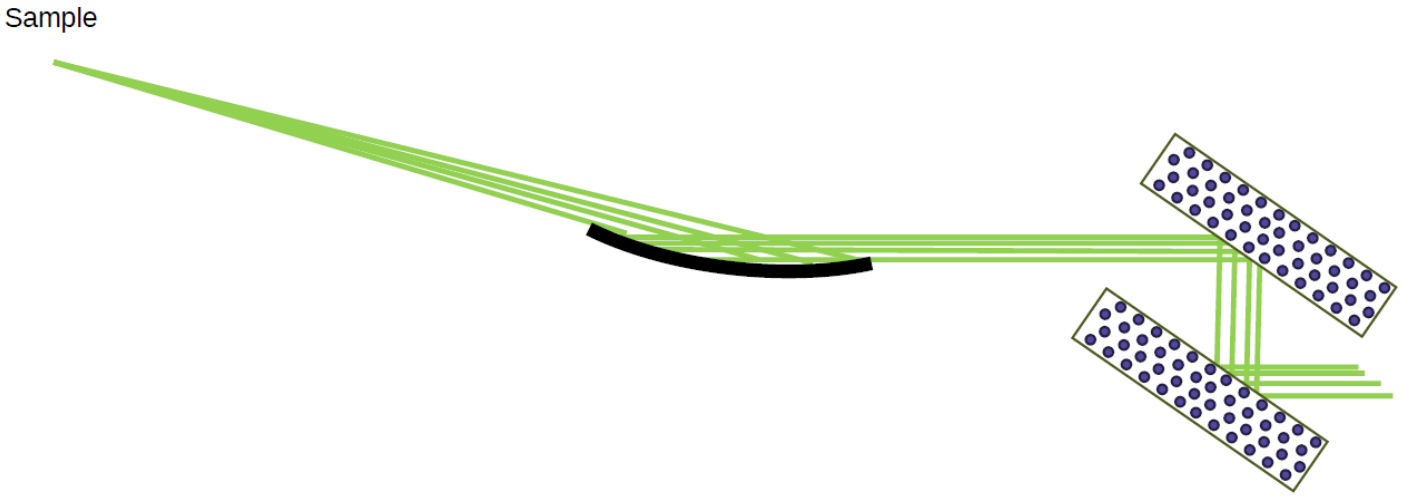
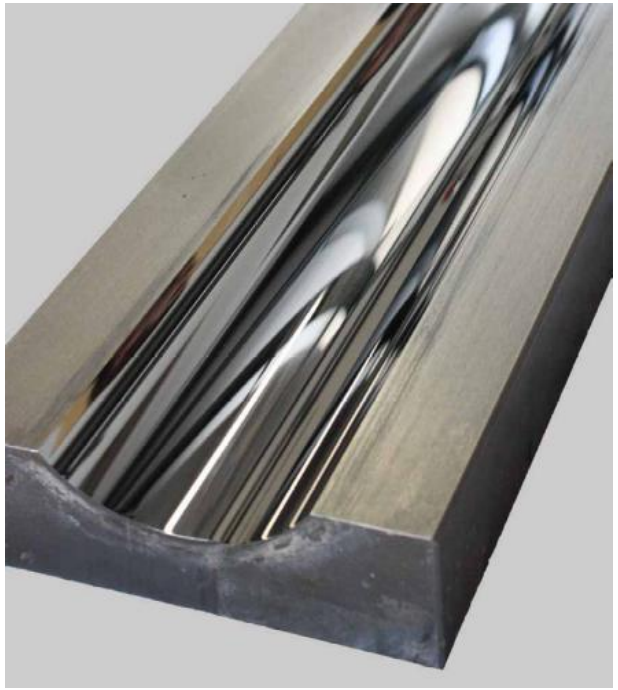
Focusing mirror

- Collimation mainly occurs vertically, while the beam continues to expand horizontally.
- The focusing mirror controls the beam size at the sample, from micrometers to millimeters depending on the application.





https://crystal-scientific.com/mirror_cylindrical.html

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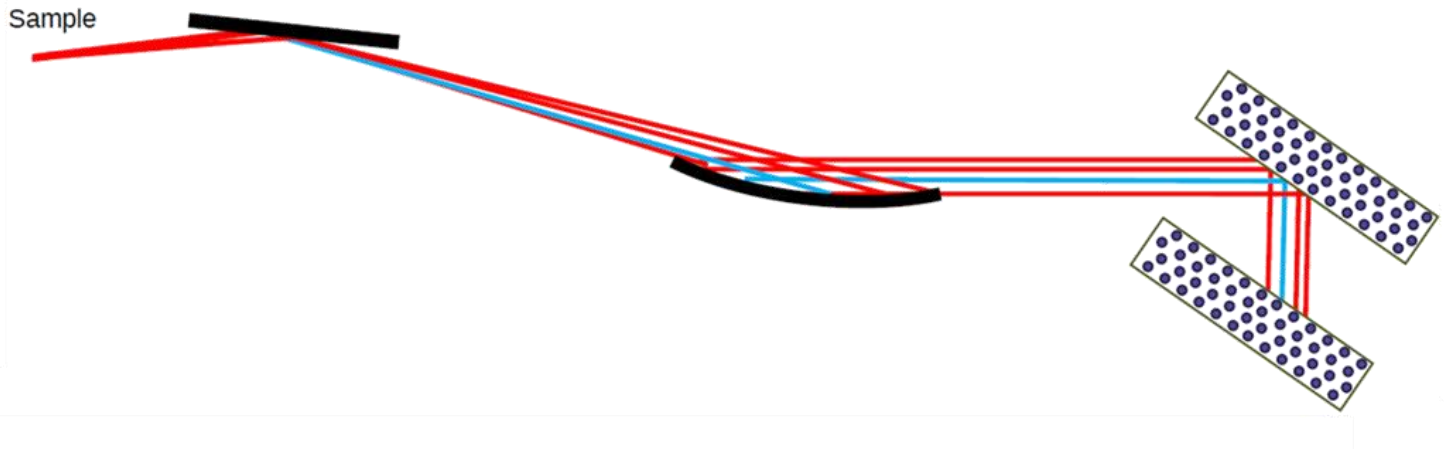
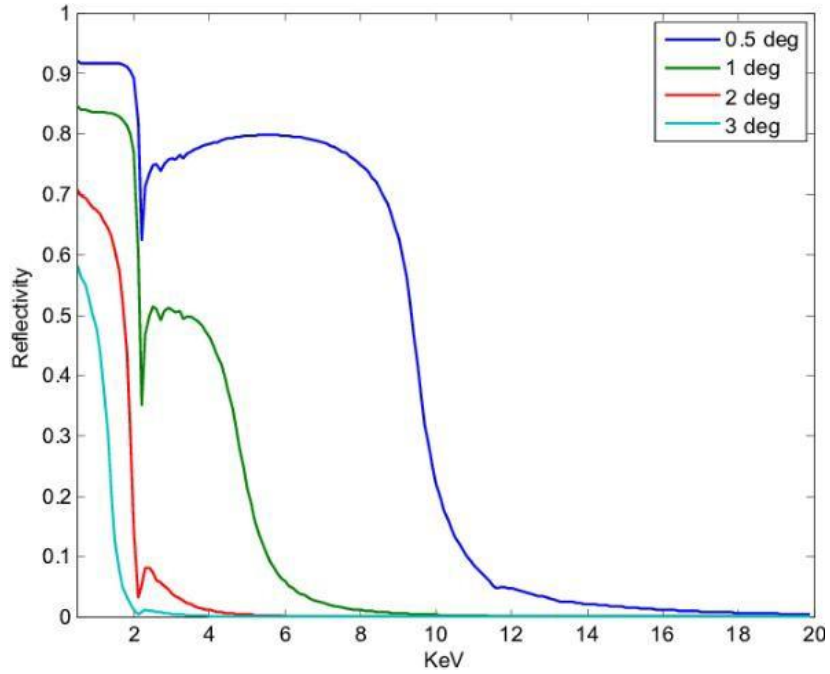
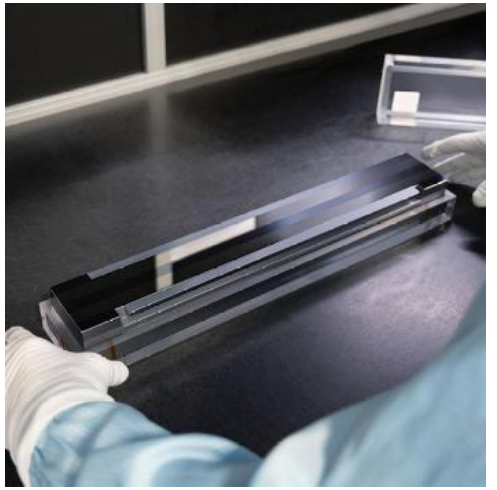
Harmonic Rejection mirror

- Higher-order harmonics from the monochromator can contaminate the beam.
- A harmonic rejection mirror suppresses these unwanted higher-energy photons.

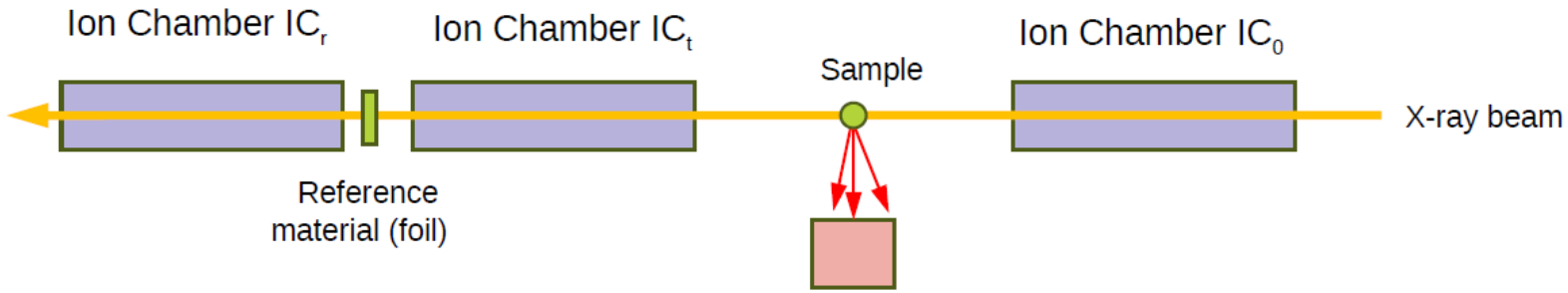






https://www.zeiss.com/semiconductor-manufacturingtechnology

Detectors for XAS



Detection mode:

- Transmission mode: ion chambers

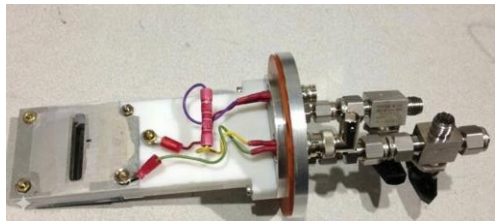
https://xds-oxford.com/products/

https://www.mirion.com/products/technologies/

https://www.hitachi-hightech.com/us/en/products

- Fluorescence mode: Integrating or energy-discriminating fluorescence detectors

- Electron yield



Choosing the detection mode

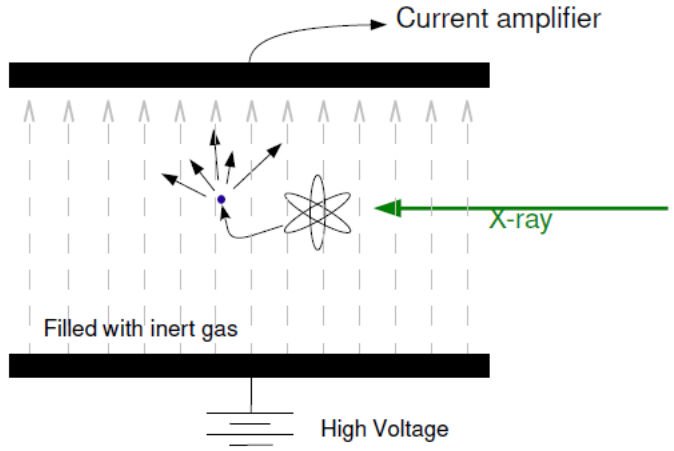
- Transmission: concentrated, not too thick, edge step >0.1, <2.0
- Fluorescence: dilute samples: < 0.1 absorption length edge step
- Electron yield: concentrated, thick or surface-sensitive measurements.

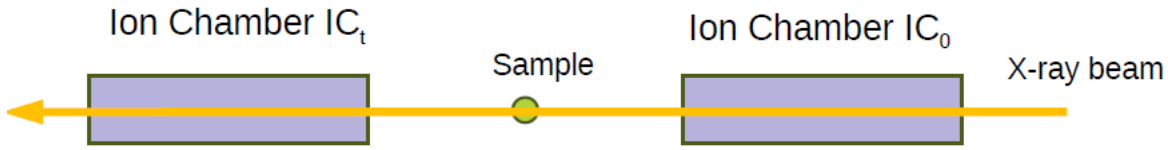
Good sample preparation is essential for success!

More in Lecture **5** at 4:15 pm by Steve Farrel : Sample preparation and environments: getting the most out of your science

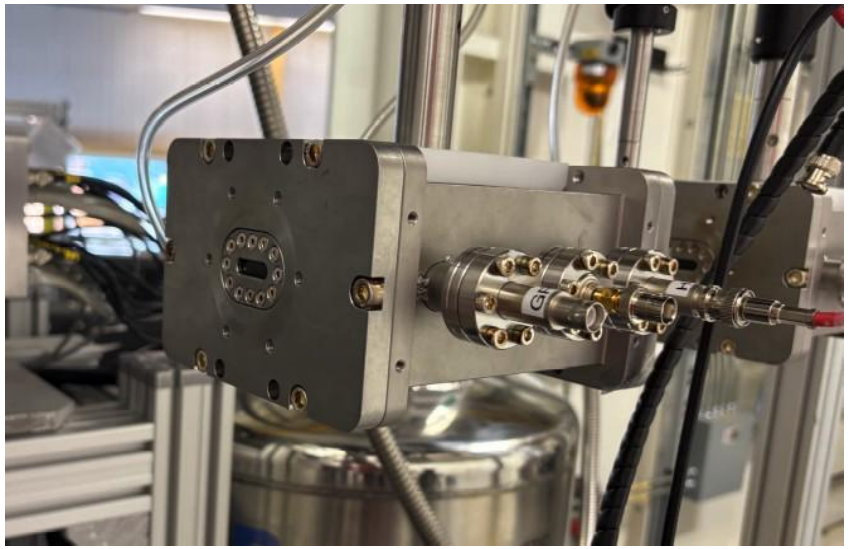
Detectors - ion chambers

- Gas-filled detectors operated under high voltage (typically 500–2000 V).
- X-ray photons ionize the gas, generating a measurable current proportional to photon flux.





In transmission XAS: μ(E) = ln (I0/It)



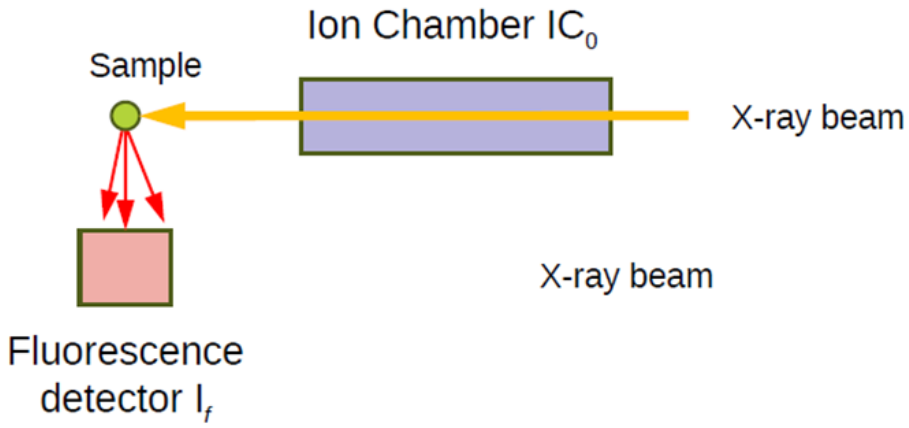
Detectors – Solid State detectors

- They are commonly used for dilute samples and fluorescence-mode XAS.

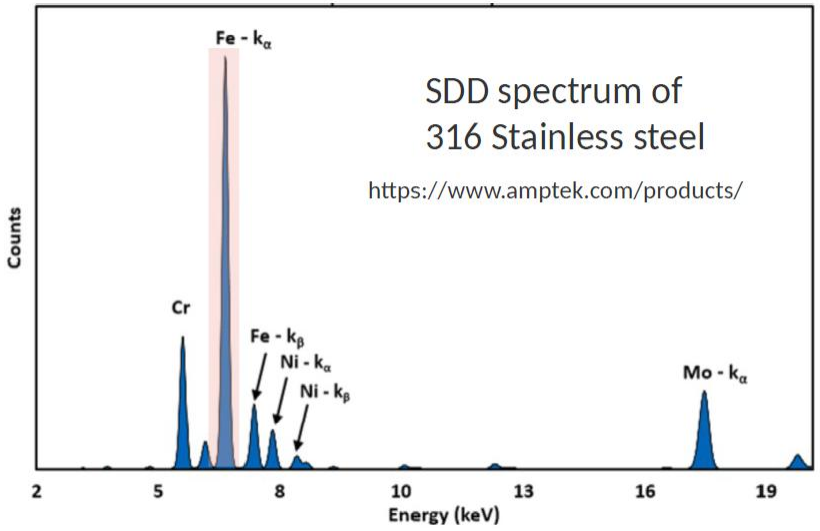
- Typical materials:
  - Si
  - Ge
  - CdTe

- X-ray photons generate electron–hole pairs, and the collected charge is proportional to the detected fluorescence signal.

Maximum count rates of several hundred KHz total (signal+background)/channel

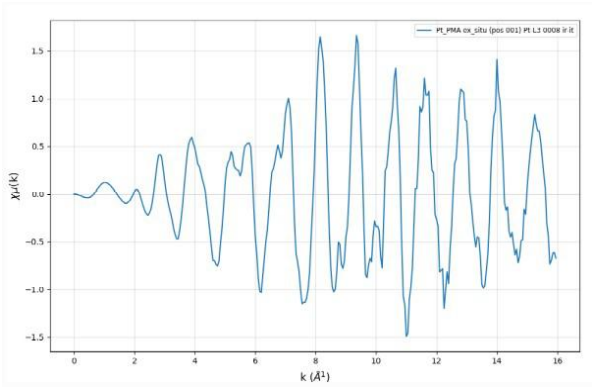


$\mu(E) \propto If/I0$

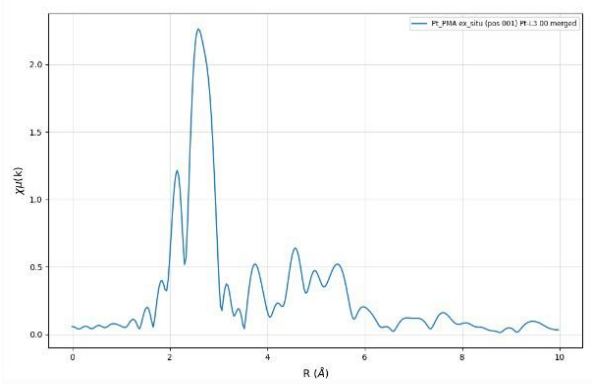


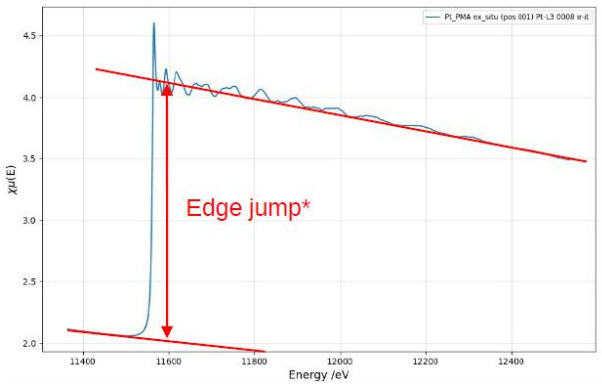
Data Reduction

- Apply instrumental Corrections (e.g. detector dead-time)
- Normalize data to unit edge step
- Convert from E → k
- Subtract the background
- Apply k-weighting
- Fourier transform to R space
- Fourier Filter to isolate shells (optional)

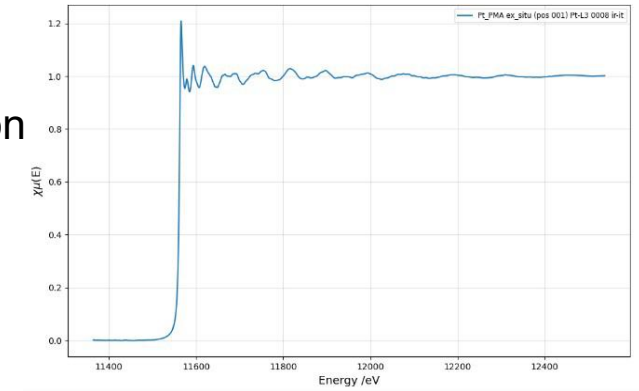


Fourier transform





Normalization



More in Lecture **2** at 11:10 am by Akhil Tayal:
Data reduction and background removal

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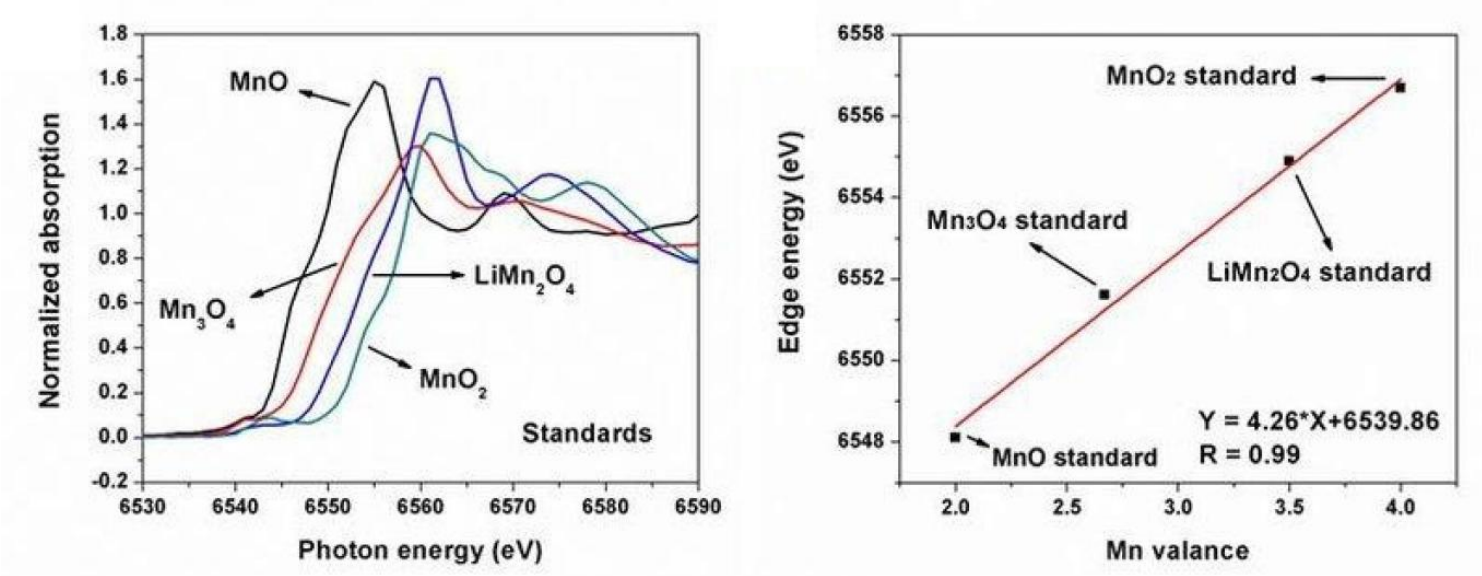
What can we learn from XANES

Oxidation and edge position

- The absorption edge shifts to higher energy as oxidation state increases due to weaker shielding effect of valence electrons and increase in Coulomb attraction.



This example shows a linear relationship between edge position and effective oxidation state (it's not always linear).

More in Lecture **3** by Jorge Moncada Vivas: XANES: fundamentals and analysis

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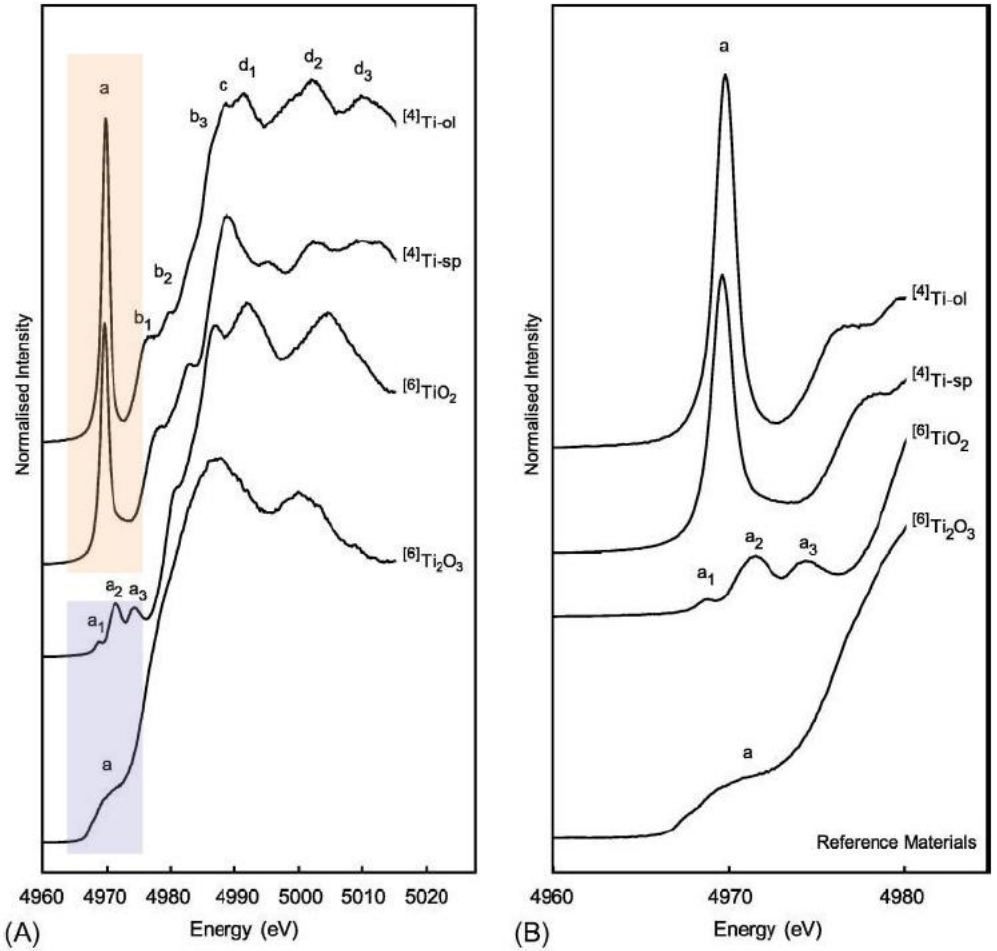
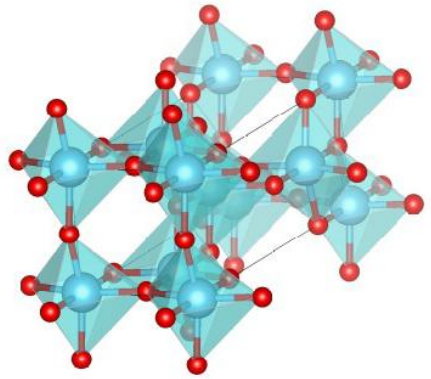
What can we learn from XANES

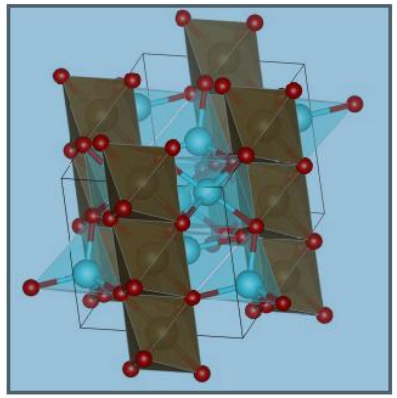
Pre-edge – local symmetry



Tetrahedral vs octahedral Ti



TiO_2

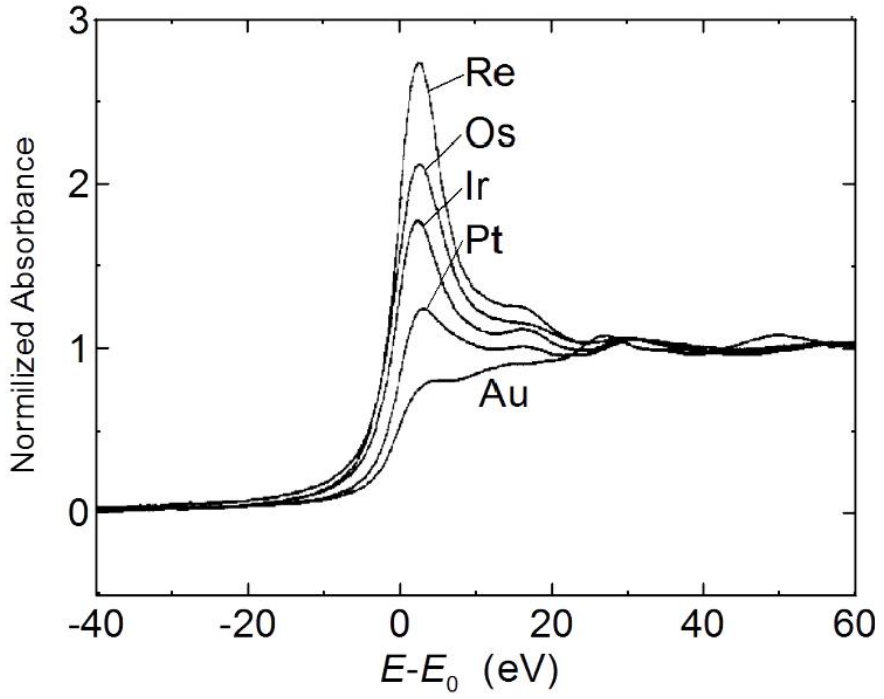


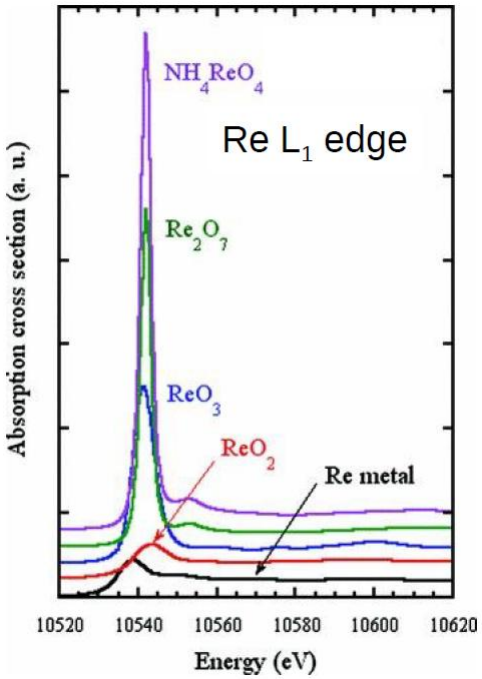
Fe_2TiO_4

- In tetrahedral coordination, Ti lacks inversion symmetry, allowing 1s → 3d transitions to gain dipole intensity through p–d mixing.
- As a result, the pre-edge feature becomes stronger.

What can we learn from XANES

White line intensity reflects the number of unoccupied d states.





75	76	77	78	79
Re	**Os**	**Ir**	**Pt**	**Au**
Rhenium	Osmium	Iridium	Platinum	Gold
186.207	190.23	192.22	195.08	196.967
$5d^5$	$5d^6$	$5d^7$	$5d^9$	$5d^{10}$

- For 5d elements, the white line arises from 2p3/2 → 5d transitions.
- White line intensity generally increases with the number of 5d holes.
- Gold shows little or no white line because excitation goes directly into the continuum.

J. Phys. Chem. 96 (1992) 4960

Phys. Rev. B 85, 125136 (2021)

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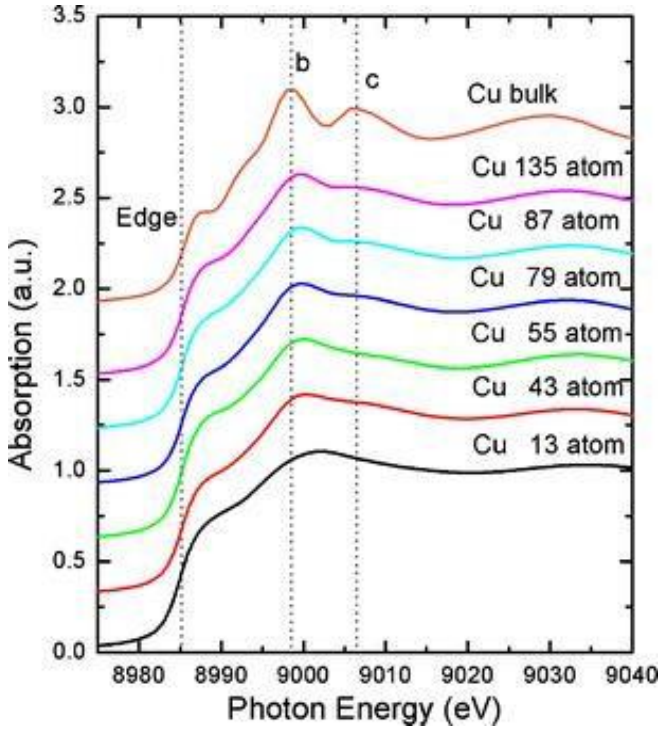
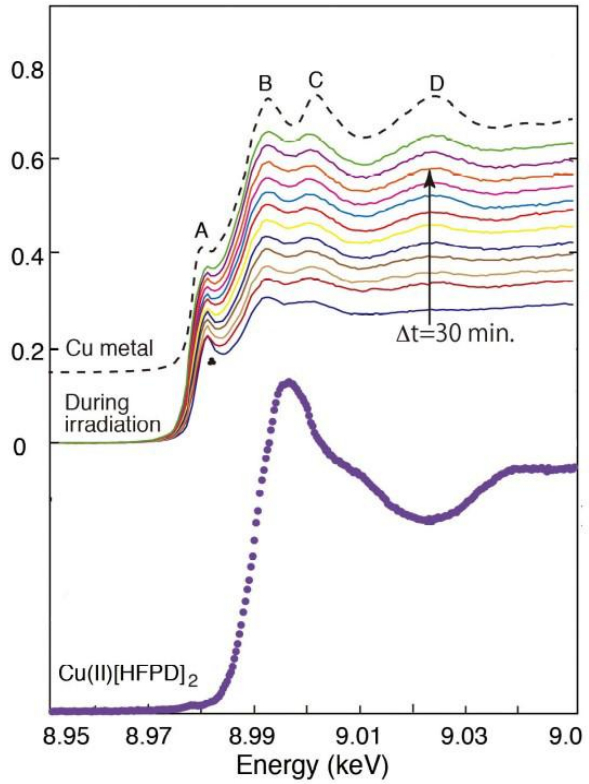
What can we learn from XANES

Nanoparticles vs bulk

Pronounced XANES features in bulk metals are often broadened or smeared in nanoparticles.



Analytical and Bioanalytical Chemistry 399, 3033–3040 (2011)



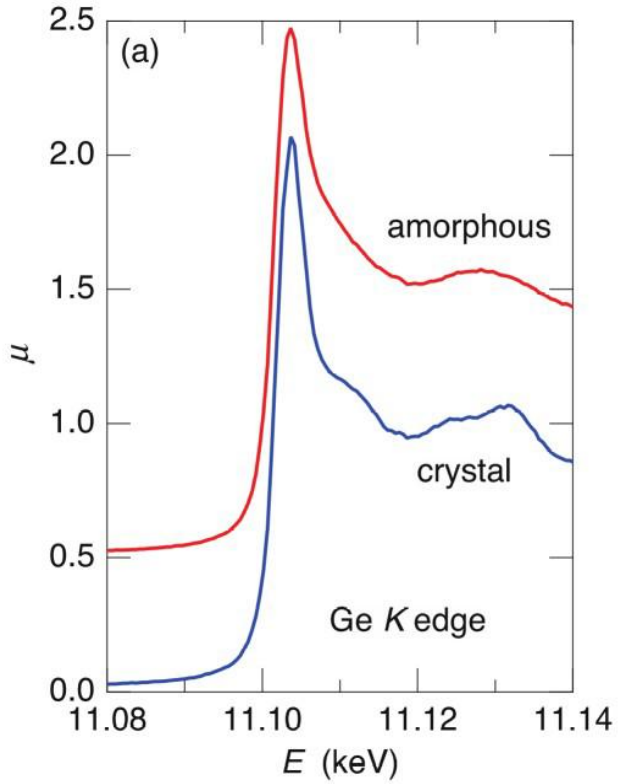
Scientific Reports 4, 7199 (2014)

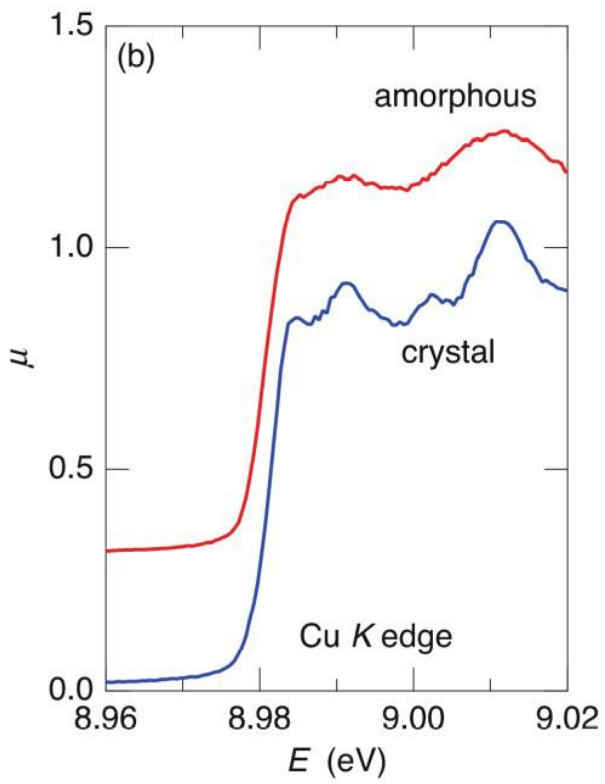
Here the Cu particles grow from solution under radiolysis. As the size increases, the features in XANES sharpen

What can we learn from XANES

Amorphous vs. crystalline materials

Similar to the nanoparticle/bulk comparison, spectral features in crystalline materials are often sharper than in amorphous materials.



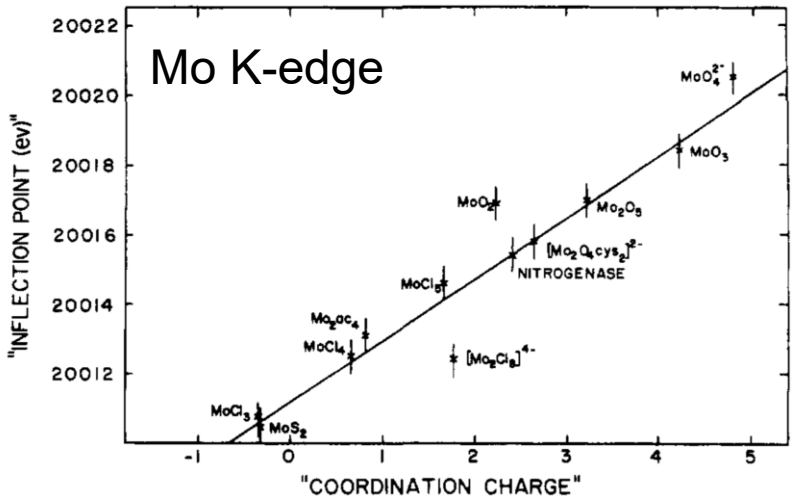


Phase-changing $GeCu_2Te_3$ material before and after annealing

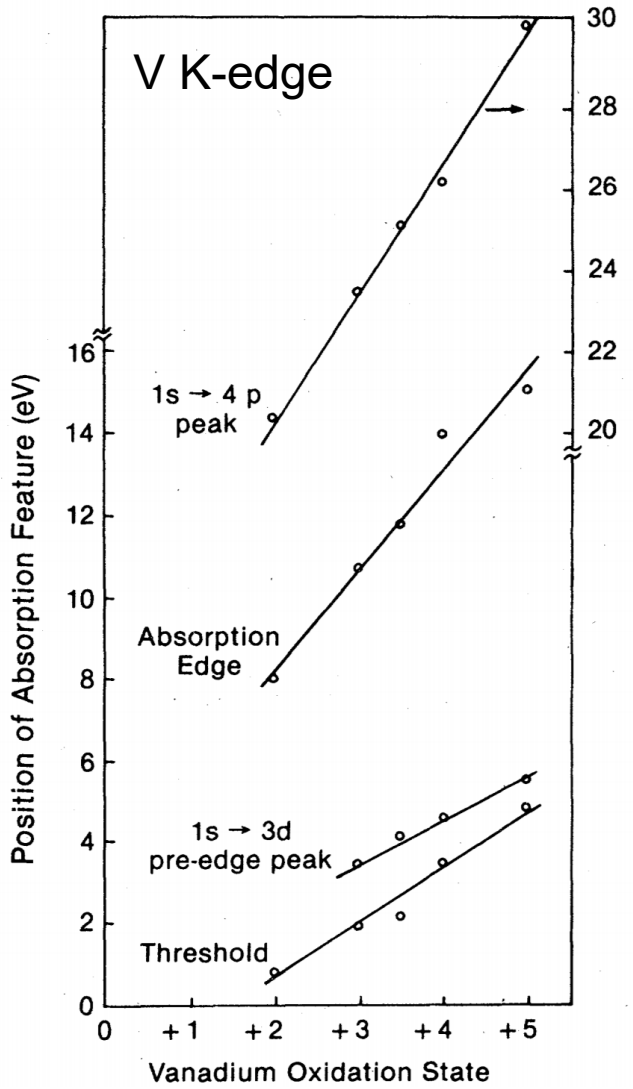
Journal of Optoelectronics and Advanced Materials 18, 248-253 (2016)

Linear Combination Fitting

- Assumption: the XANES signature of a collection of atoms is the linear sum of the XANES from individual components
- Requirements:
  - appropriate reference standards
  - well-normalized spectra
  - consistent normalization



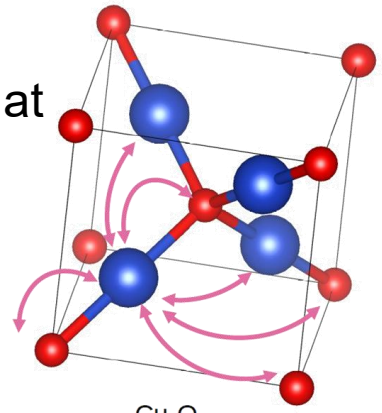
J. Am. Chem. Soc. 1976, 98, 5, 1287–1288



Phys. Rev. B 30, 5596

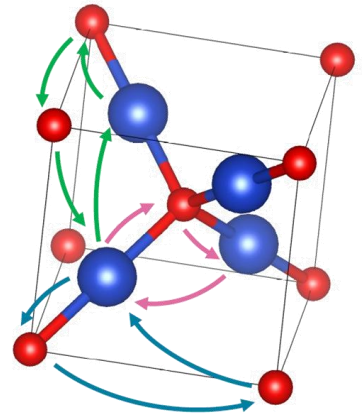
How does a single path look like

All “single” scattering paths are active at the same time

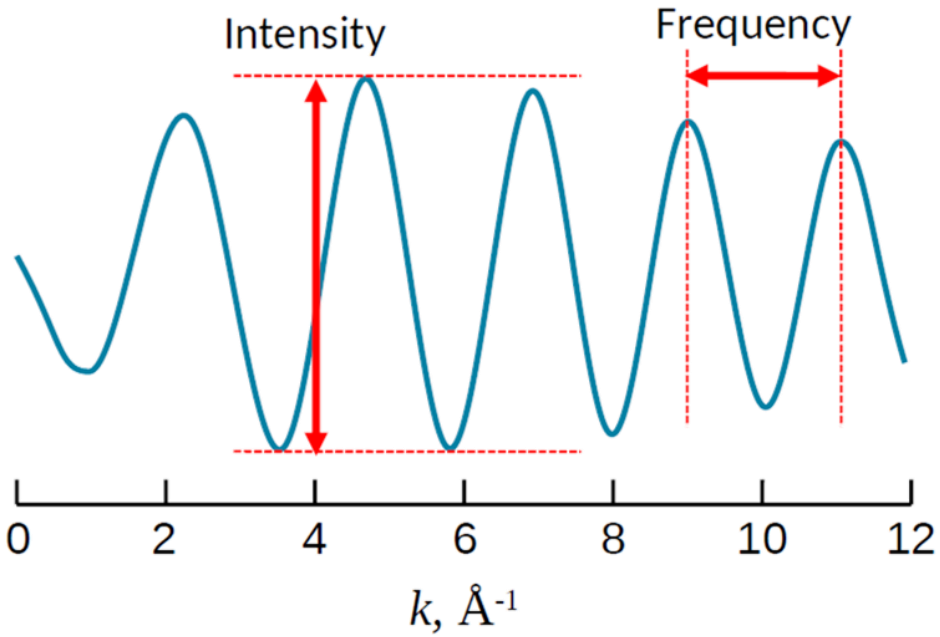


Cu_2O

Scattering between more than two atoms - multiple scattering - plays a significant role



A single scattering path contributes a damped sinusoidal oscillation in k-space.



Intensity is defined by
$S_0^2, N_j, f_j(k), \sigma_j^2, R_j$

Frequency is defined by
$R_j, \delta_j(k)$

EXAFS equation

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$

N_j	number of scattering atoms of type j
k	photoelectron wavenumber,
$f_j(k)$	scattering amplitude
R_j	distance to scattering atoms
σ_j^2	Debye-Waller factor
$\delta_j(k)$	phase shift introduced by atom j
S_0^2	amplitude reduction factor

…and we sum all the scattering paths together!

$f_j(k)$ and $\delta_j(k)$ are calculated (in this tutorial, using a code called FEFF*

* To attempt an EXAFS fit you NEED to know something about the structure

We determine N, R and σ_j^2 from the fit**

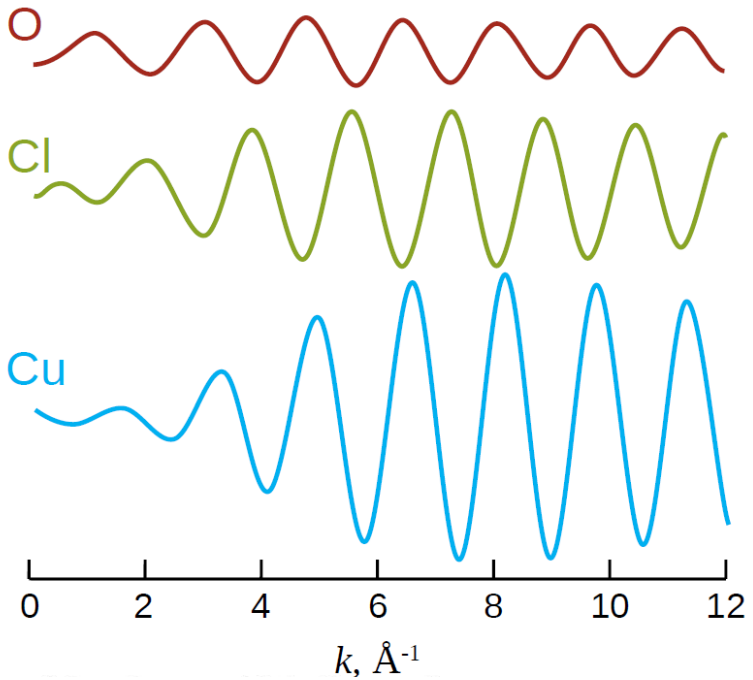
* S_0^2, N and σ_j^2 are correlated

More in Lecture 9 by Dali Yang: Understanding the EXAFS equation

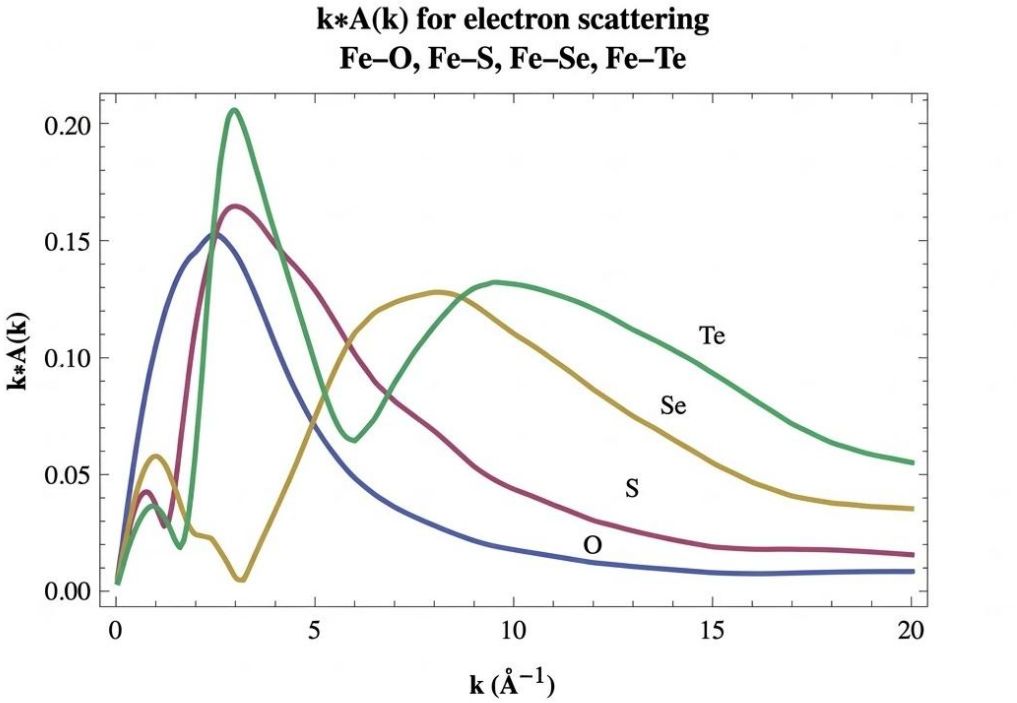
Scattering Amplitudes

- The scattering amplitude $f_j(k)$ depends on the identity of the neighboring atom.Heavier neighboring atoms generally scatter more strongly.

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$



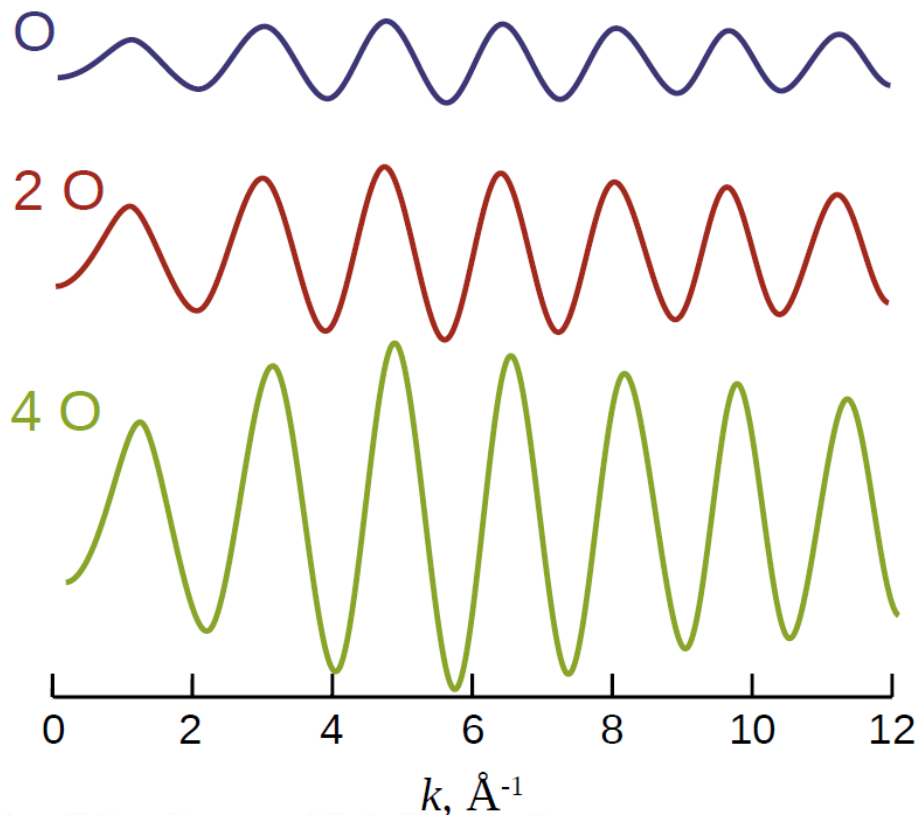
In this illustration, O, Cl, and Cu are shown at the same distance from the absorber for comparison purposes.



Brookhaven National Laboratory

Number of scatterers

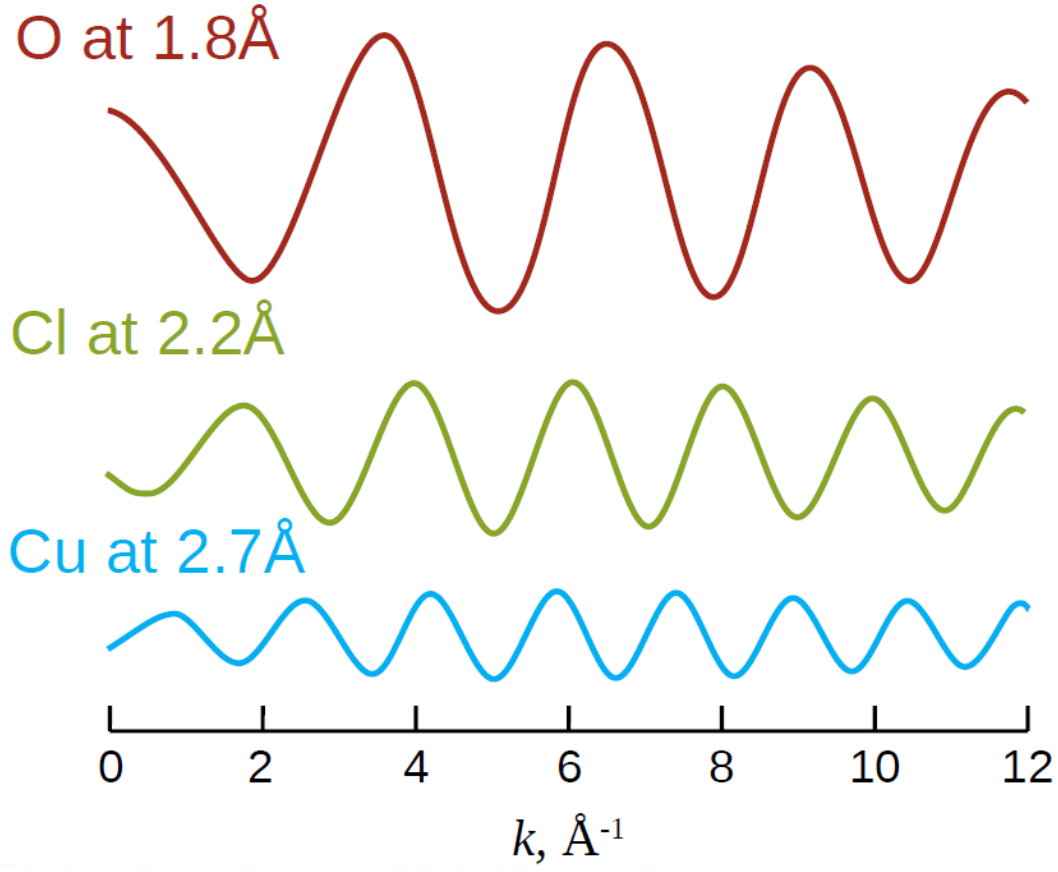
Larger coordination number increases EXAFS amplitude.

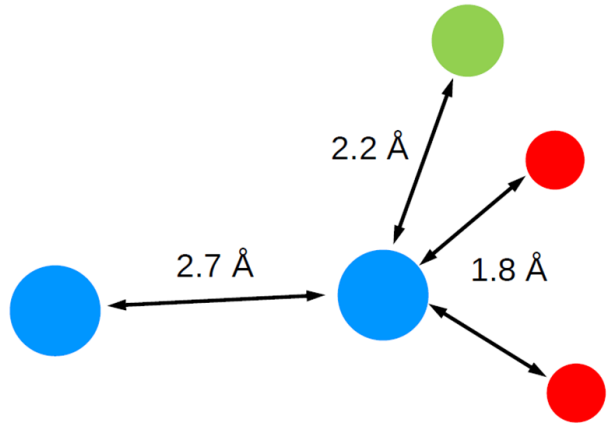


$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$

Distance to scatterers

As the scatterer moves farther away, the oscillation frequency increases while the amplitude decreases.



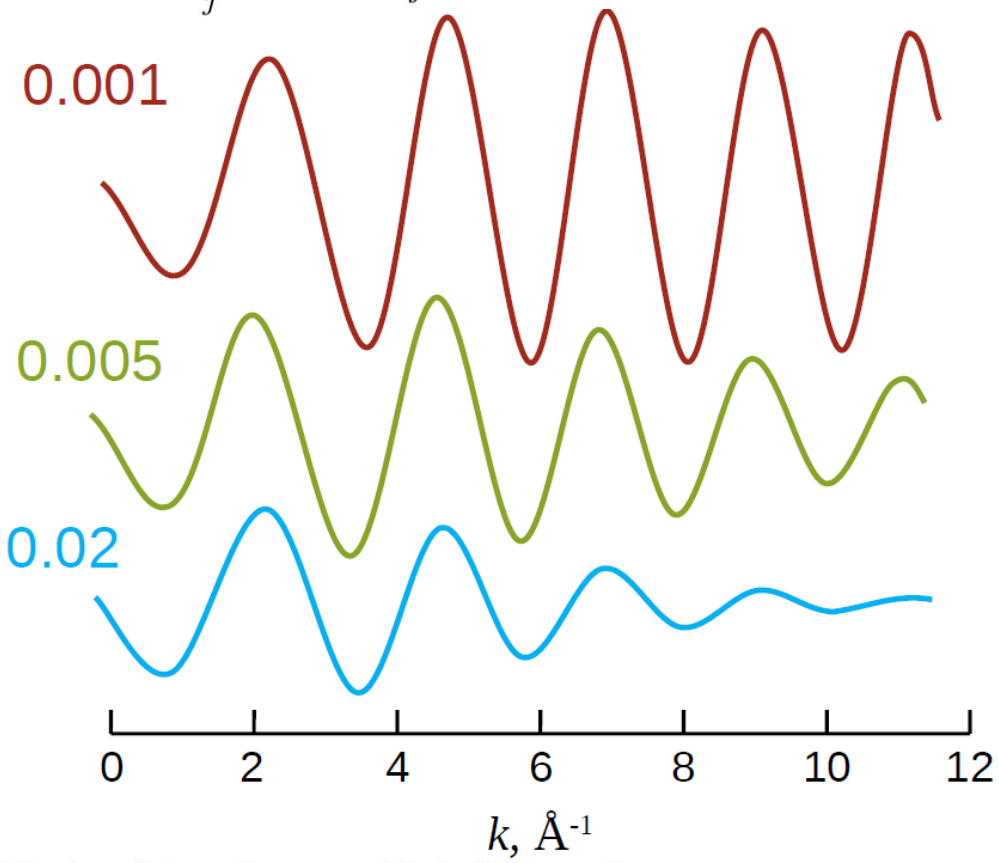


$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$

Debye-Waller factor

The Debye–Waller factor reflects disorder, including thermal and structural disorder.

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$



Difference of Debye-Waller factor in XRD vs EXAFS

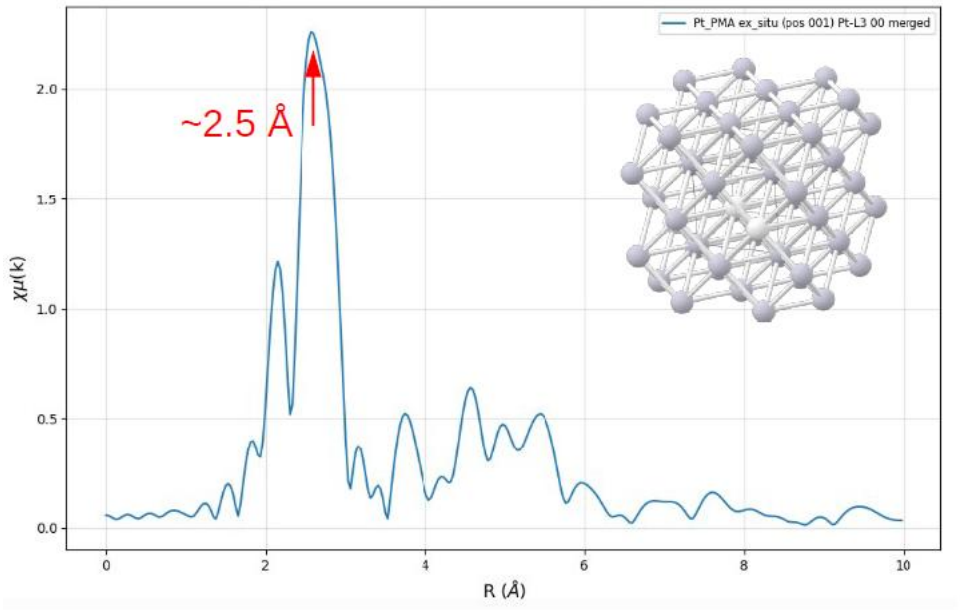
- In XRD: describes atomic displacement from lattice positions
- It reflects:
  - thermal vibration
  - positional disorder in the crystal lattice

- In EXAFS: describes fluctuations in the distance between the absorber and neighboring atoms
- it includes:
  - thermal vibration
  - structural disorder
  - distribution of bond lengths

EXAFS Debye–Waller factor is usually larger because it includes relative motion of two atoms.

Phase shift

Peaks in the Fourier transform do not appear exactly at the true interatomic distances.



The real Pt distance is 2.79 Å

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]\, S_0^2$$

$\delta_j(k)$ is an element specific phase shift that causes the distance in FT-EXAFS to underestimate the real one by up to 0.5 Å.

Amplitude reduction factor S_0^2

S_0^2 accounts for many-body amplitude reduction and is usually treated as an empirical fitting parameter.

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)] \, S_0^2$$

It is typically determined using a well-defined reference sample, such as a metal foil.

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)] \, S_0^2$$

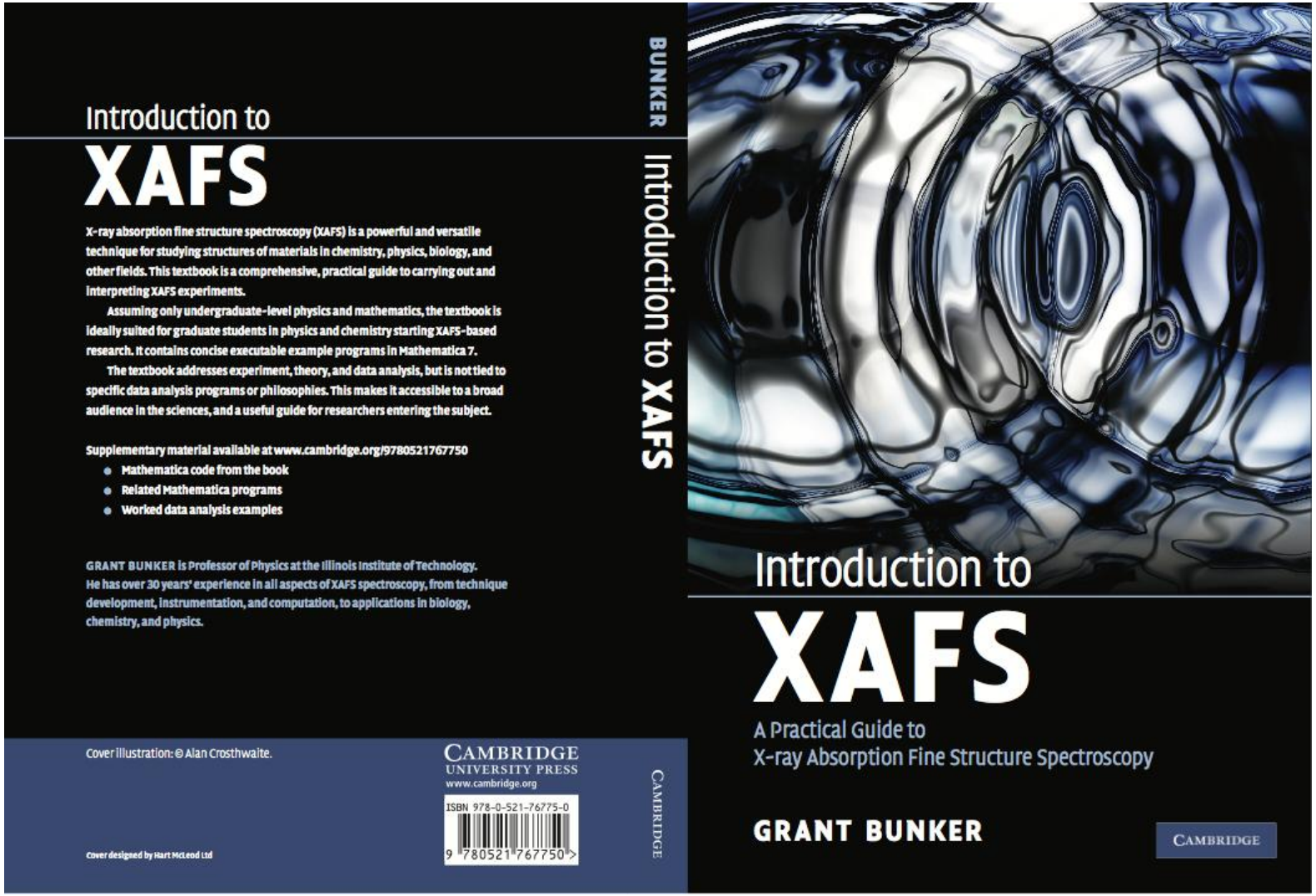
N_j and S_0^2 are correlated, so an incorrect S_0^2 leads to inaccurate coordination numbers.

More in Lecture **4** and **8** by Bruce Ravel:
EXAFS analysis I & II

What XAF spectroscopy can do — Key Takeaways

1. **Element-specific probing**
   - Individual elements in complex or heterogeneous materials can be studied independently.
   - All atoms of the selected element contribute — there are **no spectroscopically silent atoms.** However, very light atoms such as hydrogen scatter the photoelectron weakly and are often difficult to detect.
2. **Electronic structure information**: **oxidation state and orbital occupancy** can often be determined from **XANES**
3. **Local structural information:** precise information on **bond distances, coordination numbers, neighboring atom types** (Z can usually be determined to ±5), **and disorder**
4. Applicable to **crystalline and non-crystalline systems**
5. Works for **any phase of matter**: gas, liquid, or solid
6. **Works in realistic environments:** Measurements can be performed **in situ / operando**, under conditions close to the natural or working states.

Reference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Introduction to XAFS
Introduction to
XAFS
X-ray absorption fine structure spectroscopy (XAFS) is a powerful and versatile technique for studying structures of materials in chemistry, physics, biology, and other fields. This textbook is a comprehensive, practical guide to carrying out and interpreting XAFS experiments.
Assuming only undergraduate-level physics and mathematics, the textbook is ideally suited for graduate students in physics and chemistry starting XAFS-based research. It contains concise executable example programs in Mathematica 7.
The textbook addresses experiment, theory, and data analysis, but is not tied to specific data analysis programs or philosophies. This makes it accessible to a broad audience in the sciences, and a useful guide for researchers entering the subject.
Supplementary material available at www.cambridge.org/9780521767750
Mathematica code from the book
Related Mathematica programs
Worked data analysis examples
GRANT BUNKER is Professor of Physics at the Illinois Institute of Technology. He has over 30 years' experience in all aspects of XAFS spectroscopy, from technique development, instrumentation, and computation, to applications in biology, chemistry, and physics.
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