Today's Outline - October 31, 2016

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Homework Assignment #05:
Chapter 5: 1, 3, 7, 9, 10
due Wednesday, November 02, 2016

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Homework Assignment #05:
Chapter 5: 1, 3, 7, 9, 10
due Wednesday, November 02, 2016

Homework Assignment #06:
Chapter 6: 1,6,7,8,9
due Monday, November 14, 2016

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due Monday, November 14, 2016

No class on Wednesday, November 09, 2016

Final projects & presentations

In-class student presentations on research topics

- Choose a research article which features a synchrotron technique
- Get it approved by instructor first!
- Schedule a 15 minute time on Final Exam Day (tentatively, Monday, December 5, 2016, will confirm times)

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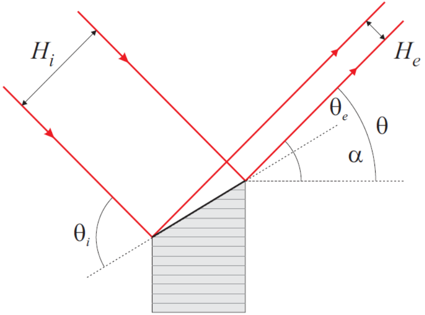
Final project - writing a General User Proposal

- Think of a research problem (could be yours) that can be approached using synchrotron radiation techniques
- Make proposal and get approval from instructor before starting
- Must be different techique than your presentation!

Asymmetric geometry

In general the diffracting planes are not precisely aligned with the surface of the crystal.



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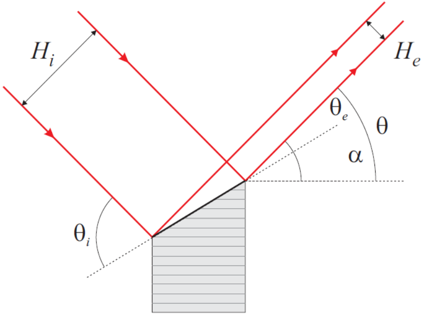
Parameterized by the asymmetry angle $0 < \alpha < \theta_{Bragg}$



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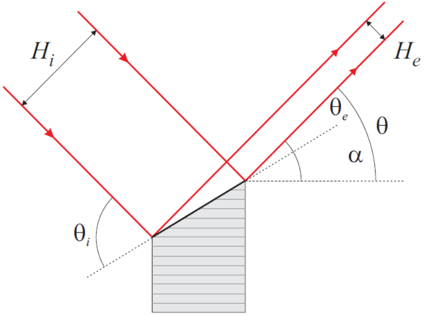

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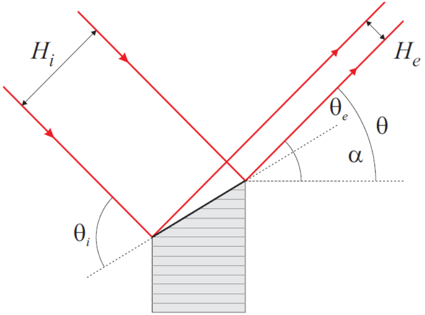

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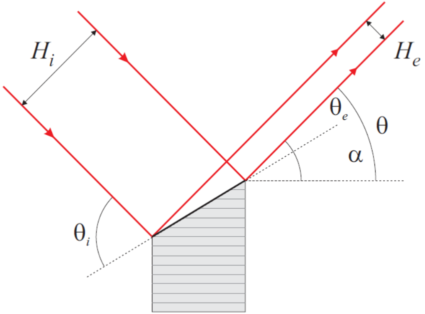

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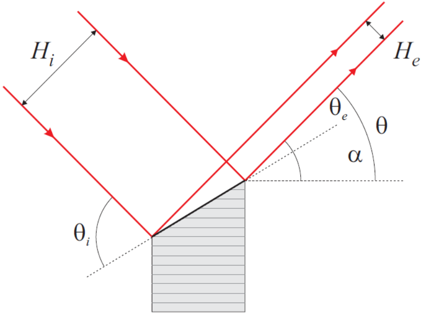

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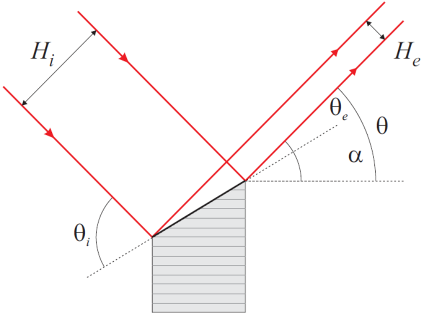

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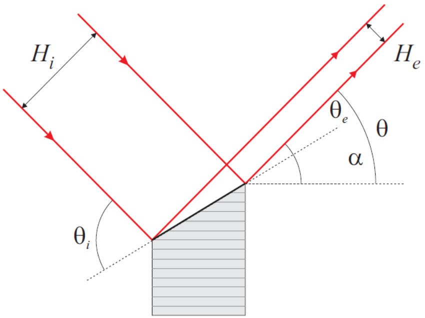

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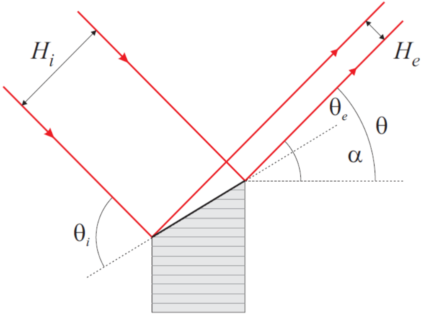

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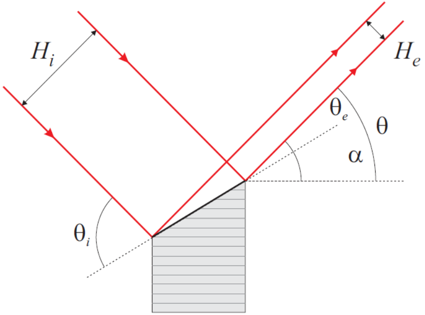

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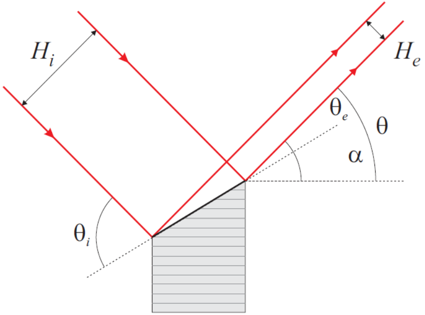

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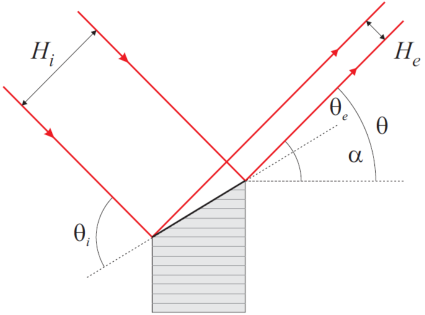

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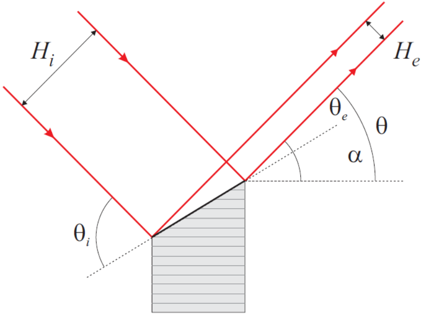

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Rocking curve measurements

The measured “rocking” curve from a two crystal system is a convolution of the Darwin curves of both crystals.

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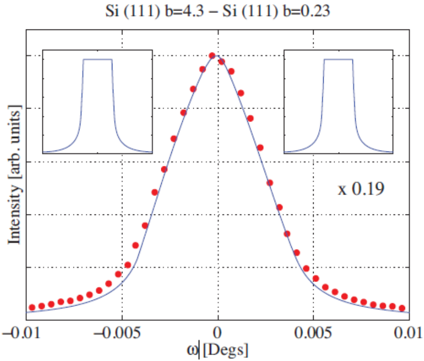

output divergence on left, input divergence on right

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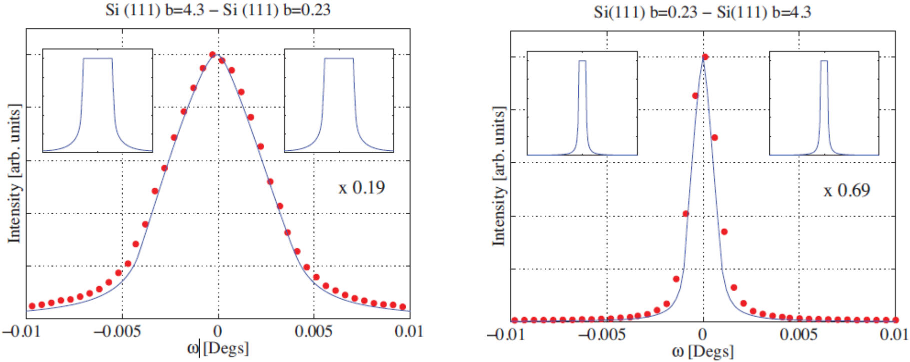

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Rocking curve measurements

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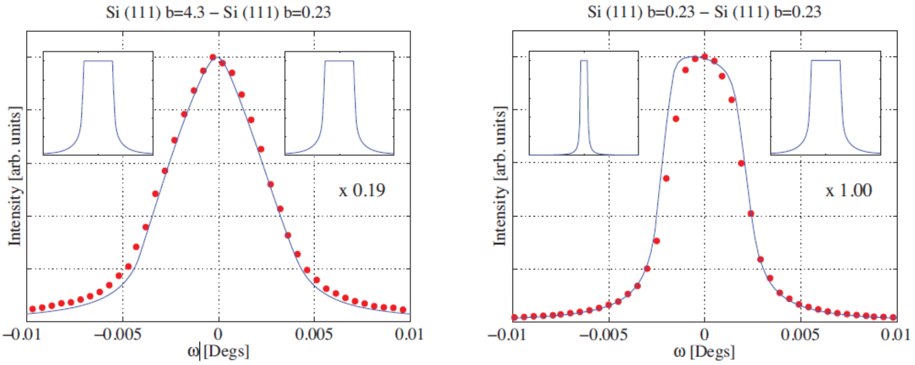

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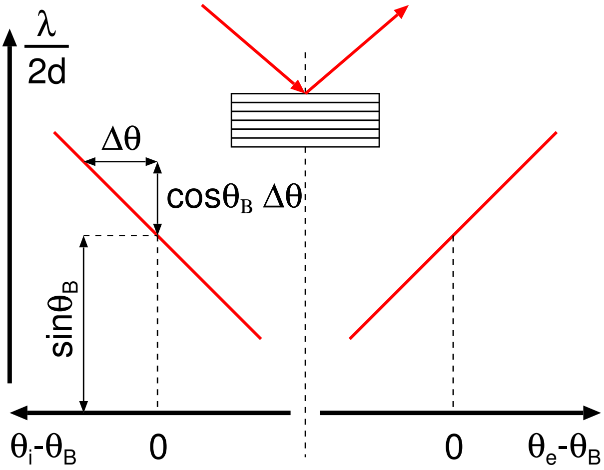
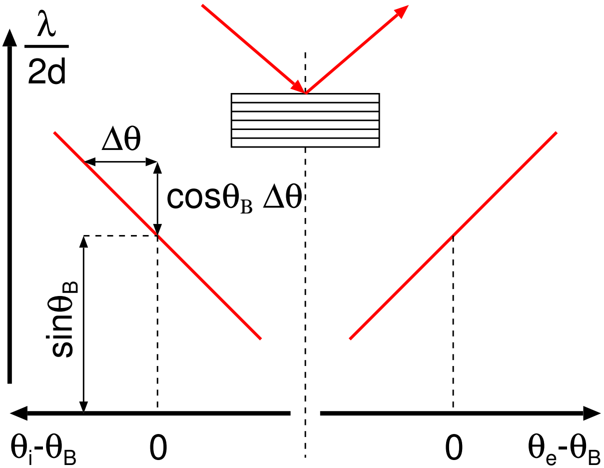
Dumond diagram: no Darwin width

Transfer function of an optical element parameterized by angle and wavelength.



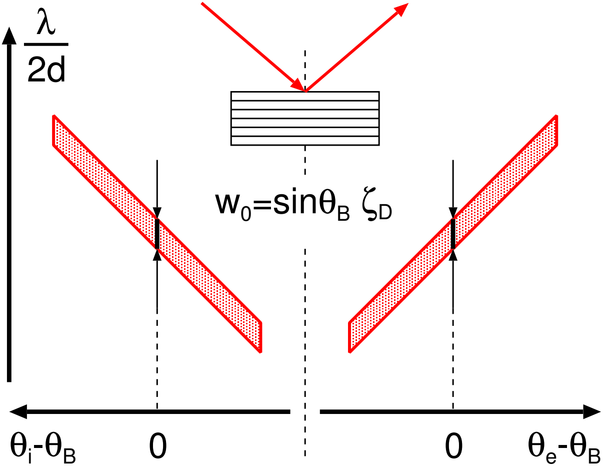
Dumond diagram: no Darwin width

Transfer function of an optical element parameterized by angle and wavelength. Here Darwin width is ignored.



Dumond diagram: symmetric Bragg

Including the Darwin width, we have a bandpass in wavelength.



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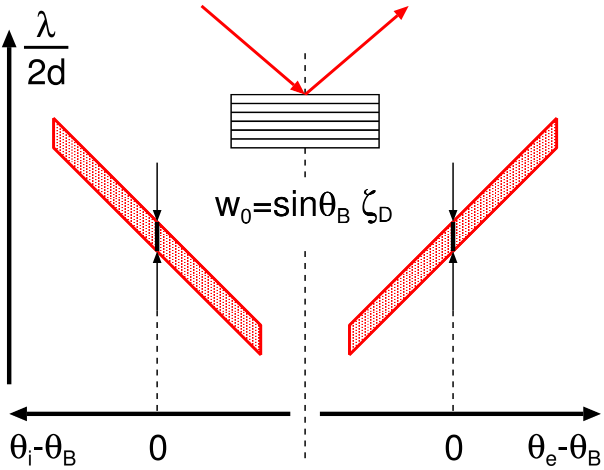
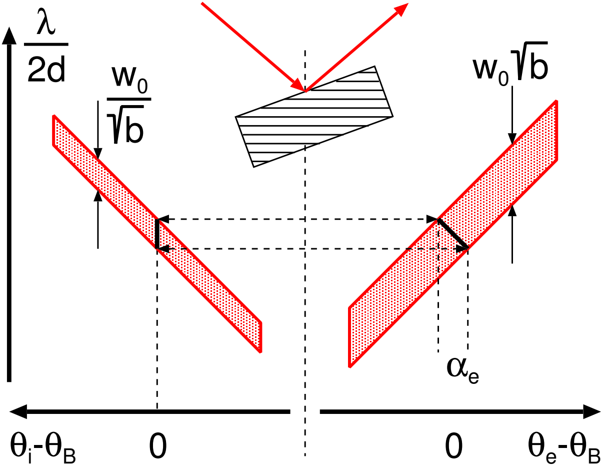
Including the Darwin width, we have a bandpass in wavelength. If input beam is perfectly collimated, so is output (vertical black line).

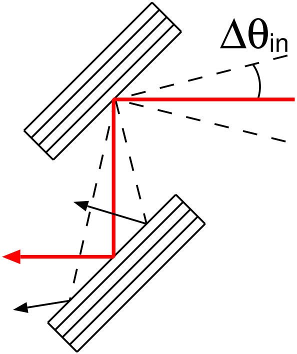


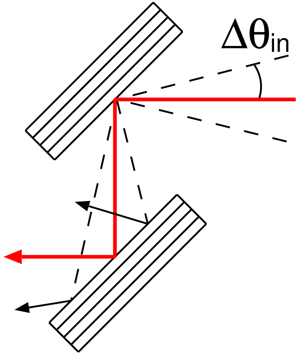
Dumond diagram: asymmetric Bragg

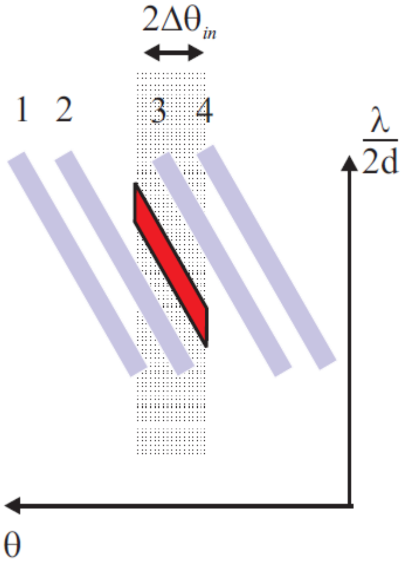
For asymmetric crystal, the output beam is no longer collimated but acquires a divergence α_e



Double crystal monochromators




Δθin


2Δθin
1
2
3
4
λ/2d
θ

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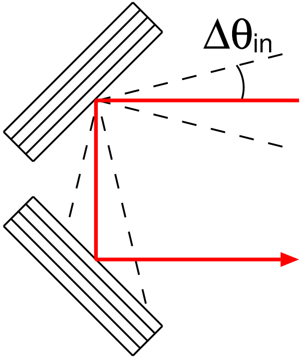

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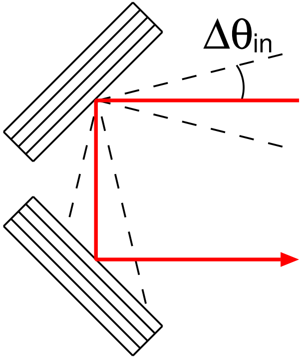
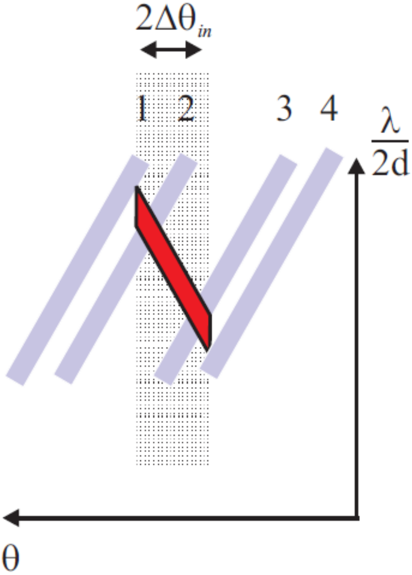
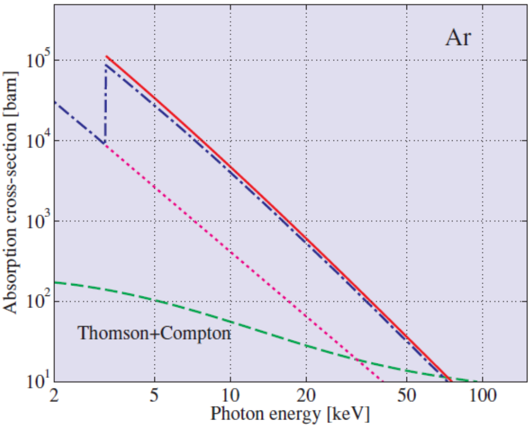




Total cross section



The total cross-section for photon "absorption" includes elastic (or coherent) scattering, Compton (inelastic) scattering, and photoelectric absorption.

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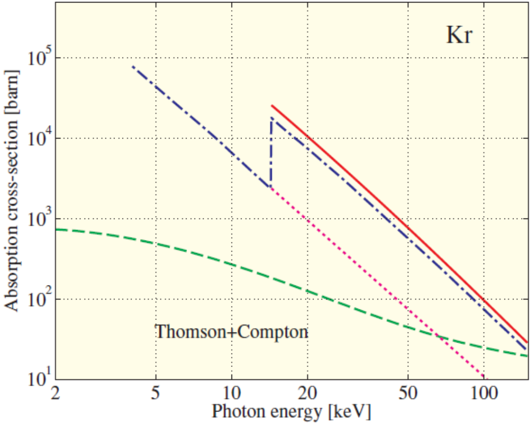

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Characteristic absorption jumps depend on the element

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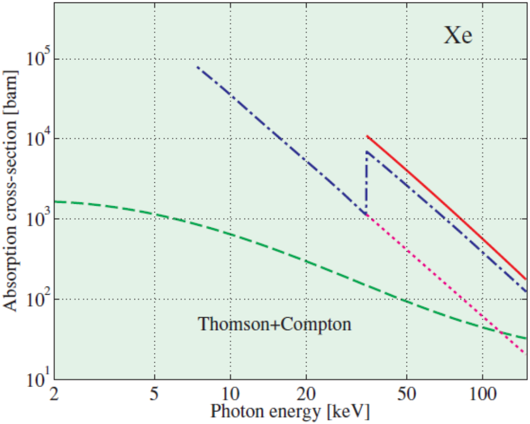

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These quantities vary significantly over many decades but can easily put on an equal footing.

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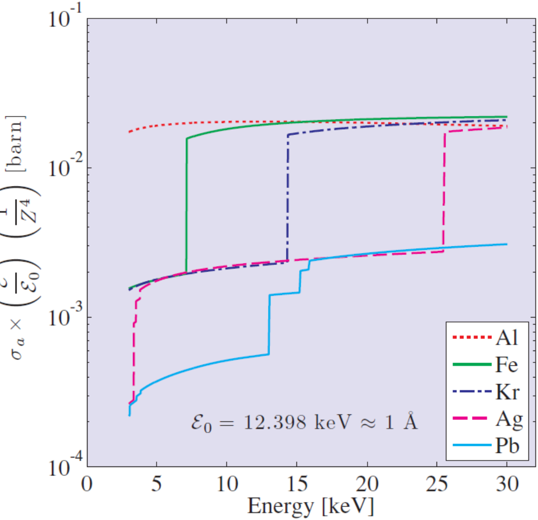

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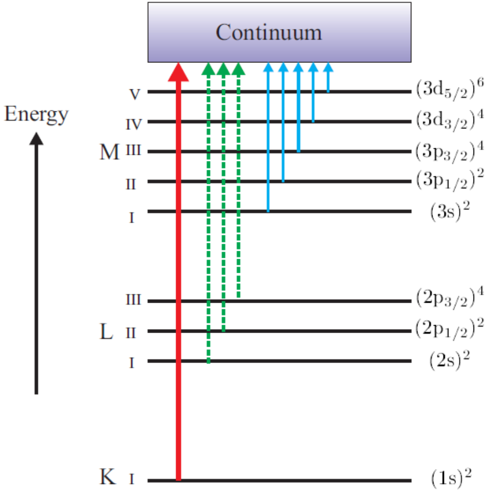

remarkably, all values lie on a common curve above the K edge and between the L and K edges and below the L edge

Calculation of σ_a

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The first term gives absorption

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$$\vec{A} = \hat{\varepsilon}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega}}\left[a_k e^{i\vec{k}\cdot\vec{r}} + a_k^\dagger e^{-i\vec{k}\cdot\vec{r}}\right]$$

The first term gives absorption while the second produces Thomson scattering so we take only the first into consideration now.

Free electron approximation

In order to evaluate the M_{if} matrix element we define the initial and final states

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Thus

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The calculation is simplified if the interaction Hamiltonian is applied to the left since the final state has only a free electron and no photon

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The free electron state is an eigenfunction of the electron momentum operator

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$$M_{if} = \frac{e}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega}}\left[\hbar(\vec{q}\cdot\hat{\varepsilon})_e\langle 1|_\gamma\langle 1|e^{i\vec{k}\cdot\vec{r}}|1\rangle_\gamma|0\rangle_e + 0\right]$$

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$$ \begin{aligned} M_{if} &= \frac{e}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega}}\left[\hbar(\vec{q}\cdot\hat{\varepsilon})\,{}_e\langle 1|{}_\gamma\langle 1|e^{i\vec{k}\cdot\vec{r}}|1\rangle_\gamma|0\rangle_e + 0\right] \\ &= \frac{e\hbar}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega}}(\vec{q}\cdot\hat{\varepsilon})\,{}_e\langle 1|e^{i\vec{k}\cdot\vec{r}}|0\rangle_e \end{aligned} $$

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$$= \frac{e\hbar}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega}}(\vec{q}\cdot\hat{\varepsilon})_e\langle 1|e^{i\vec{k}\cdot\vec{r}}|0\rangle_e = \frac{e\hbar}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega}}(\vec{q}\cdot\hat{\varepsilon})\int \psi_f^* e^{i\vec{k}\cdot\vec{r}}\psi_i d\vec{r}$$

Photoelectron integral

$$M_{if} = \frac{e\hbar}{m}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega}}(\vec{q}\cdot\hat{\varepsilon})\int \psi_f^* e^{i\vec{k}\cdot\vec{r}}\psi_i d\vec{r}$$

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which is the Fourier transform of the initial state $1s$ electron wave function

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the overall matrix element squared for a particular photoelectron final direction (φ, θ) is

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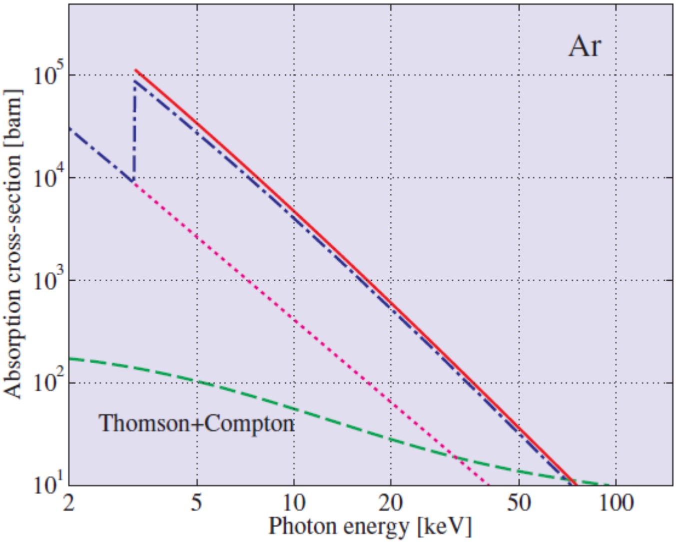
where the integral I_3 is given by

$$I_3 = \int \phi^2(\vec{Q}) q^2 \sin^2\theta \cos^2\varphi\, \delta(\mathcal{E}_f - \mathcal{E}_i) q^2 \sin\theta\, dq\, d\theta\, d\phi$$

Calculated cross section



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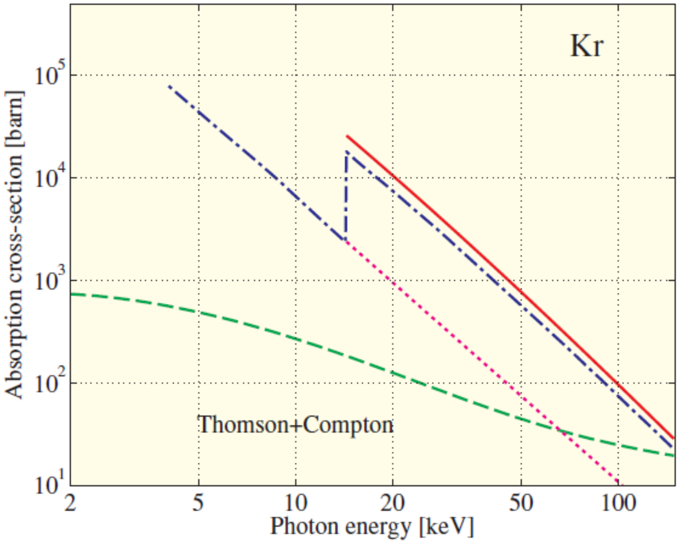

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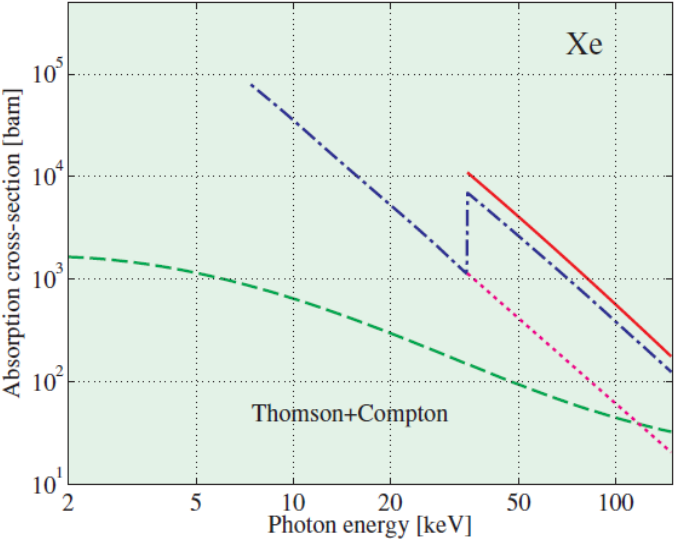
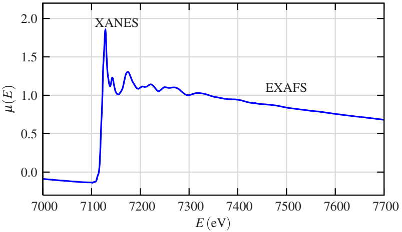


What is XAFS?

X-ray Absorption Fine-Structure (XAFS) is the modulation of the x-ray absorption coefficient at energies near and above an x-ray absorption edge. XAFS is also referred to as X-ray Absorption Spectroscopy (XAS) and is broken into 2 regimes:

XANES	X-ray Absorption Near-Edge Spectroscopy
EXAFS	Extended X-ray Absorption Fine-Structure

which contain related, but slightly different information about an element's local coordination and chemical state.



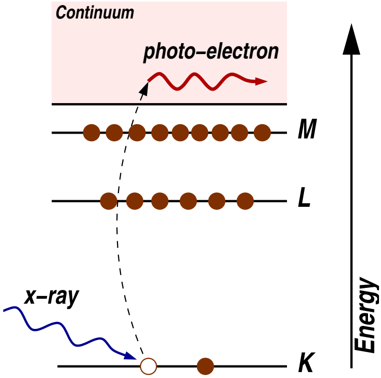
Fe K-edge XAFS for FeO

XAFS Characteristics:

- local atomic coordination
- chemical / oxidation state
- applies to any element
- works at low concentrations
- minimal sample requirements

The x-ray absorption process

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).



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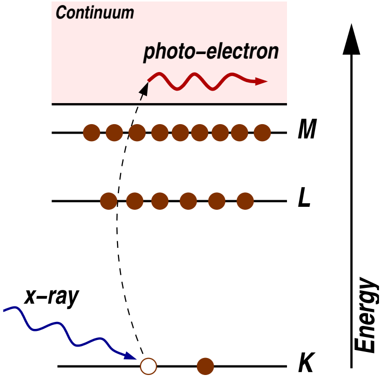
The atom is in an excited state with an empty electronic level: a core hole.



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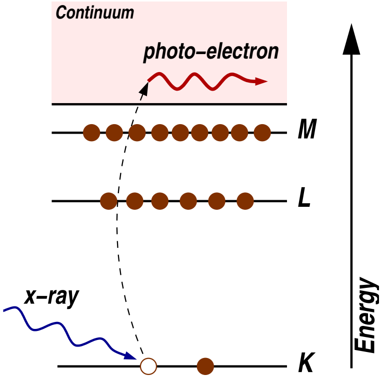

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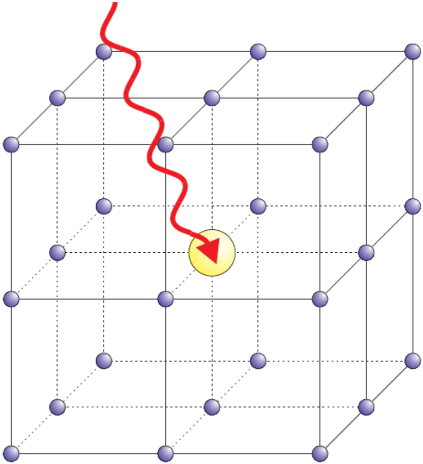

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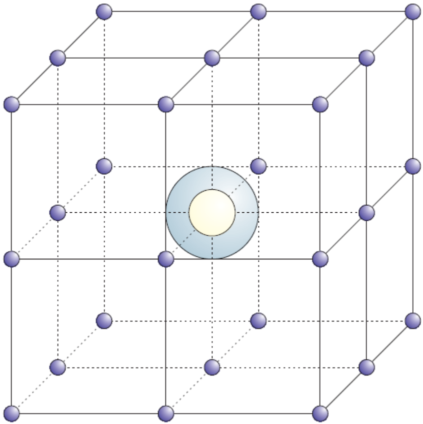

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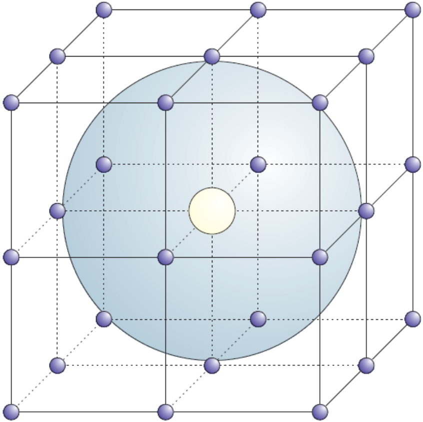
Any excess energy from the x-ray is given to an ejected photoelectron, which expands as a spherical wave, reaches the neighboring electron clouds



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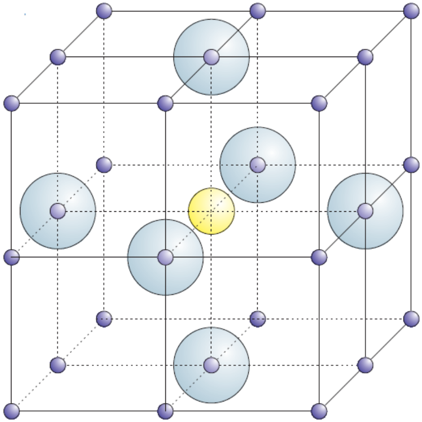
Any excess energy from the x-ray is given to an ejected photoelectron, which expands as a spherical wave, reaches the neighboring electron clouds, and scatters back to the core hole



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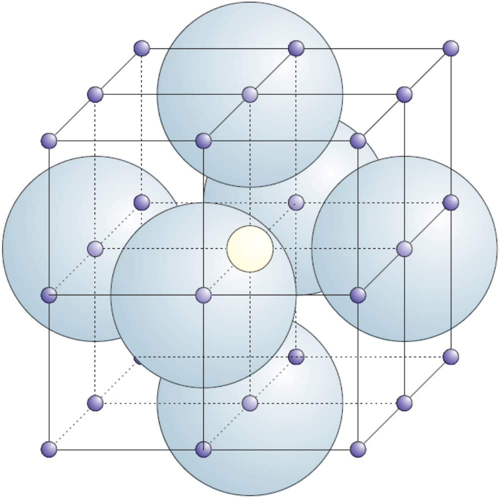

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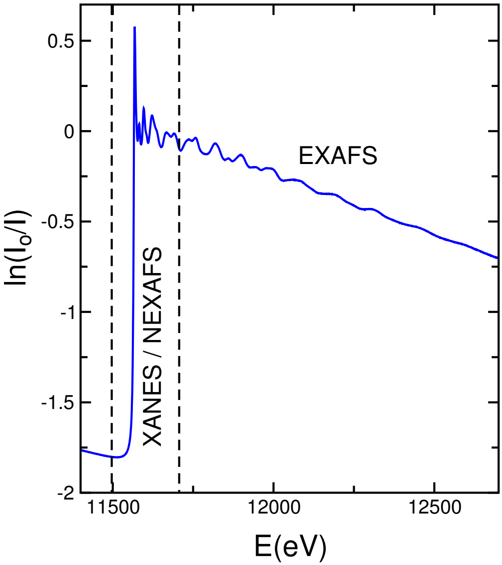
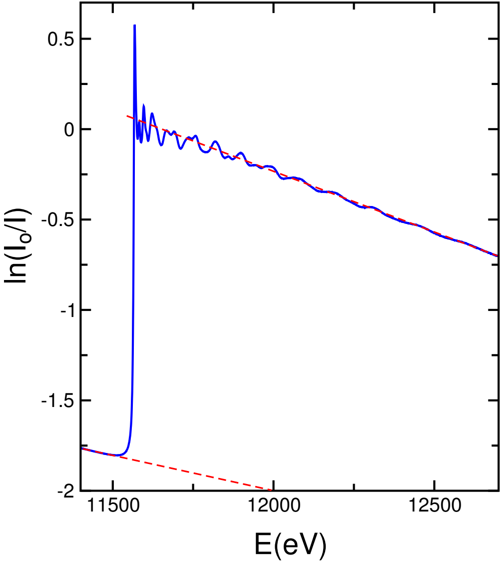
Any excess energy from the x-ray is given to an ejected photoelectron, which expands as a spherical wave, reaches the neighboring electron clouds, and scatters back to the core hole, creating interference patterns called XANES and EXAFS.



EXAFS data extraction

normalize by fitting pre-edge and post-edge trends



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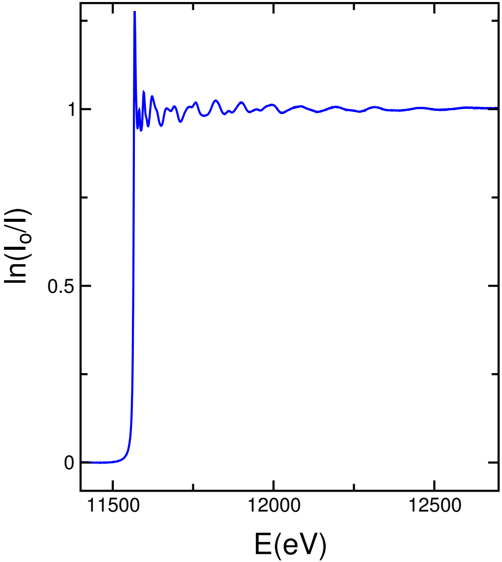
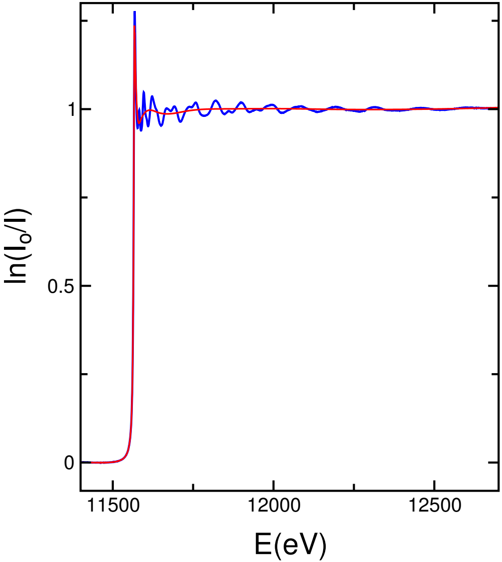


EXAFS data extraction

normalize by fitting pre-edge and post-edge trends

remove "smooth" μ_0 background



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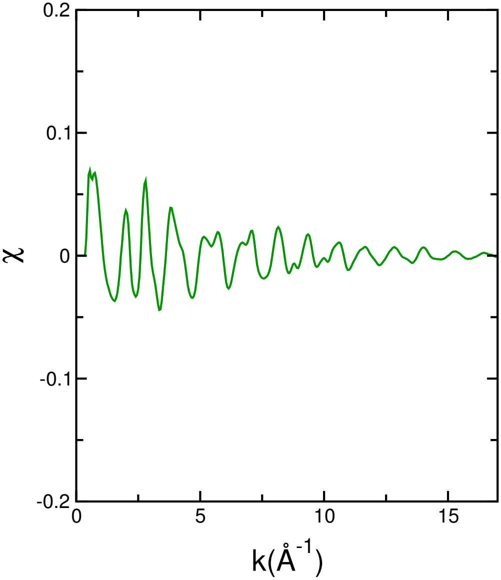
convert to photoelectron momentum space

$$k = \frac{2\pi}{hc}\sqrt{\mathcal{E} - \mathcal{E}_0}$$



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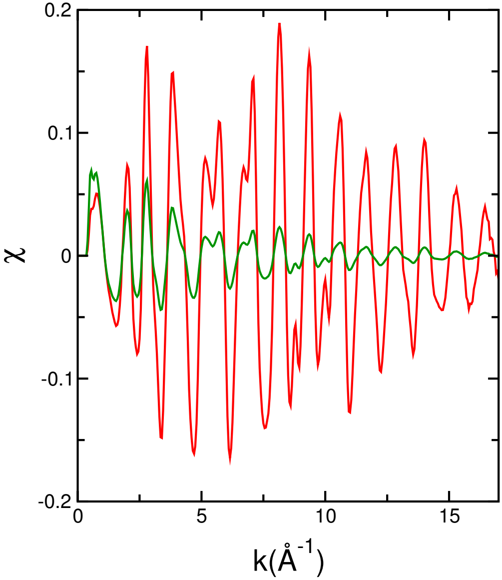
weight by appropriate power of k to obtain "good" envelope which clearly shows that EXAFS is a sum of oscillations with varying frequencies and phases



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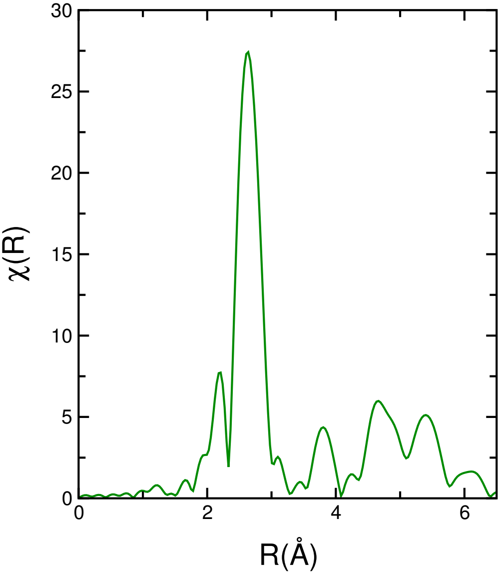
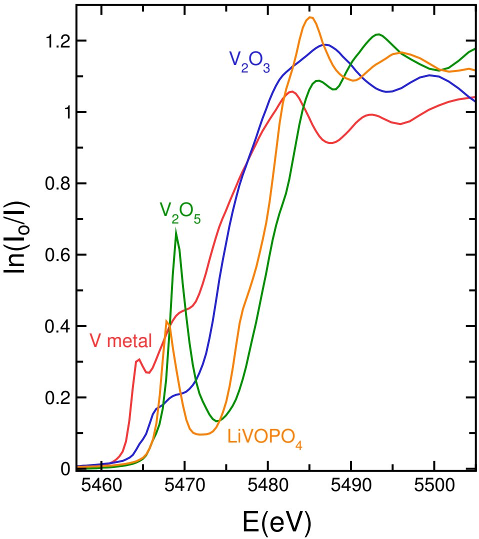
Fourier transform to get real space EXAFS



XANES edge shifts and pre-edge peaks



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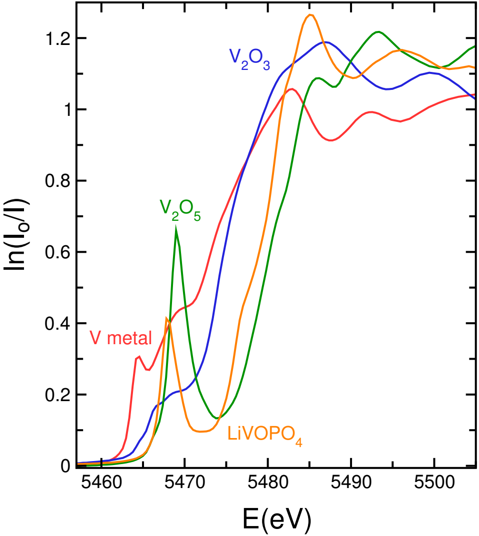

The shift of the edge position can be used to determine the valence state.

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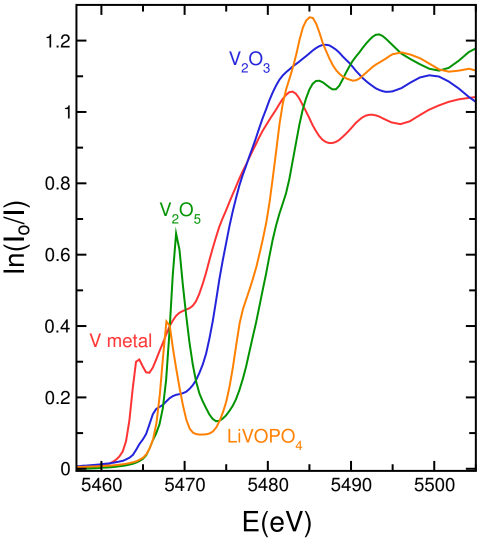

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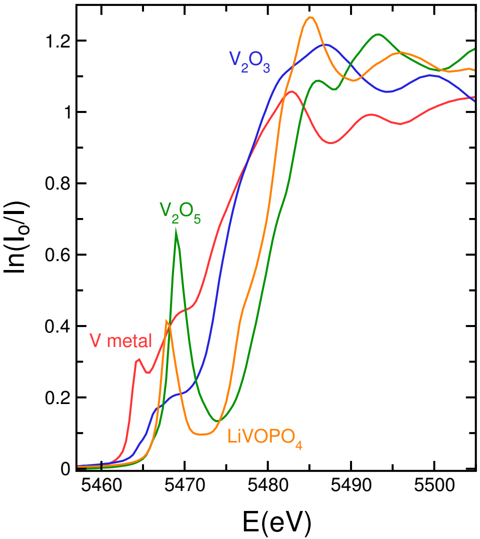

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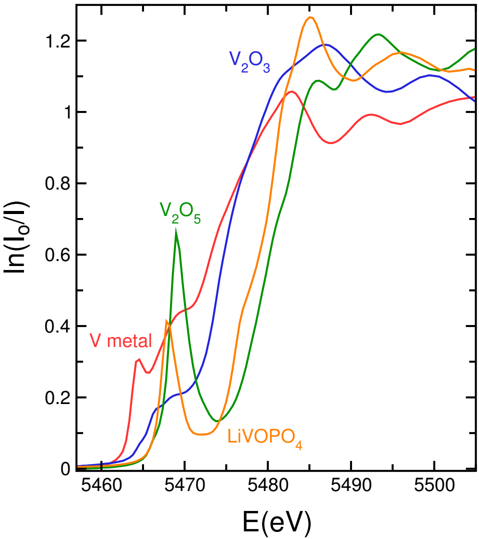

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Modern codes, such as FEFF9, are able to accurately compute XANES features.