Today's outline - March 26, 2020 (part A)

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- Introduction to x-ray absorption spectroscopy

Today's outline - March 26, 2020 (part A)

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Homework Assignment #05:
Chapter 5: 1, 3, 7, 9, 10
due Thursday, April 02, 2020

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- Introduction to x-ray absorption spectroscopy

Homework Assignment #05:
Chapter 5: 1, 3, 7, 9, 10
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Homework Assignment #06:
Chapter 6: 1,6,7,8,9
due Tuesday, April 14, 2020

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:

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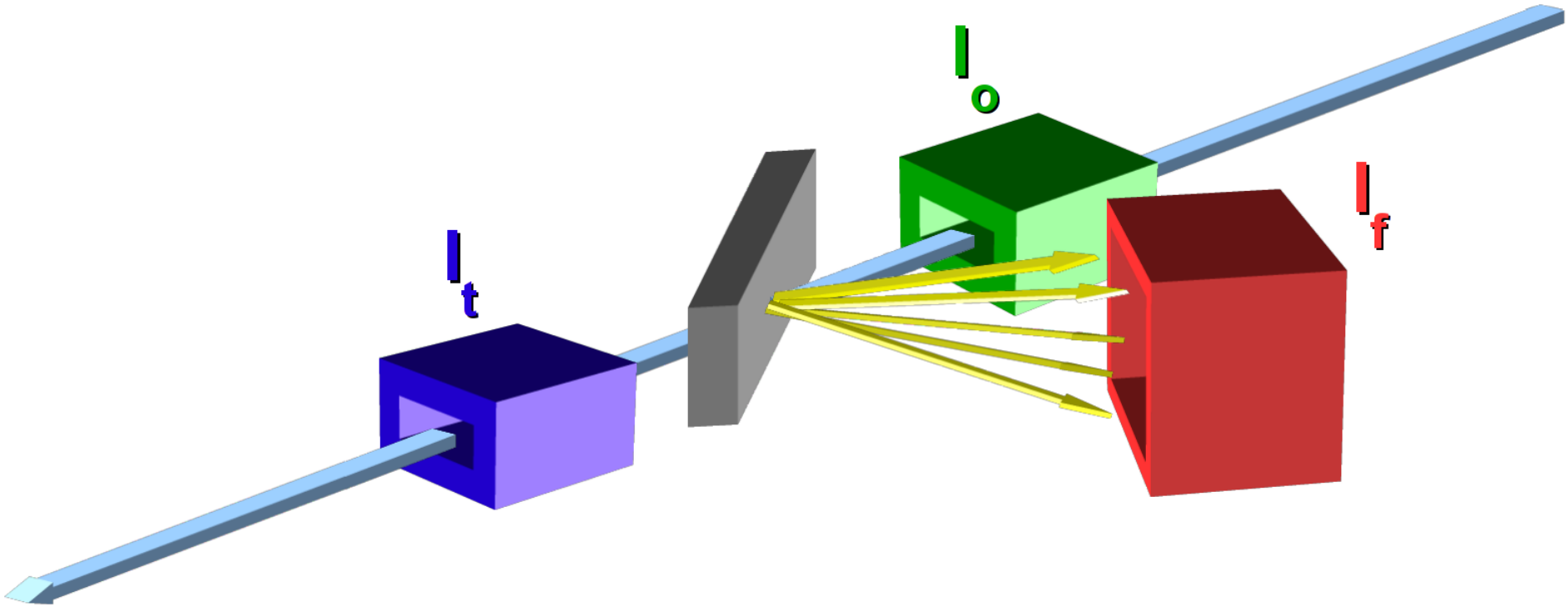
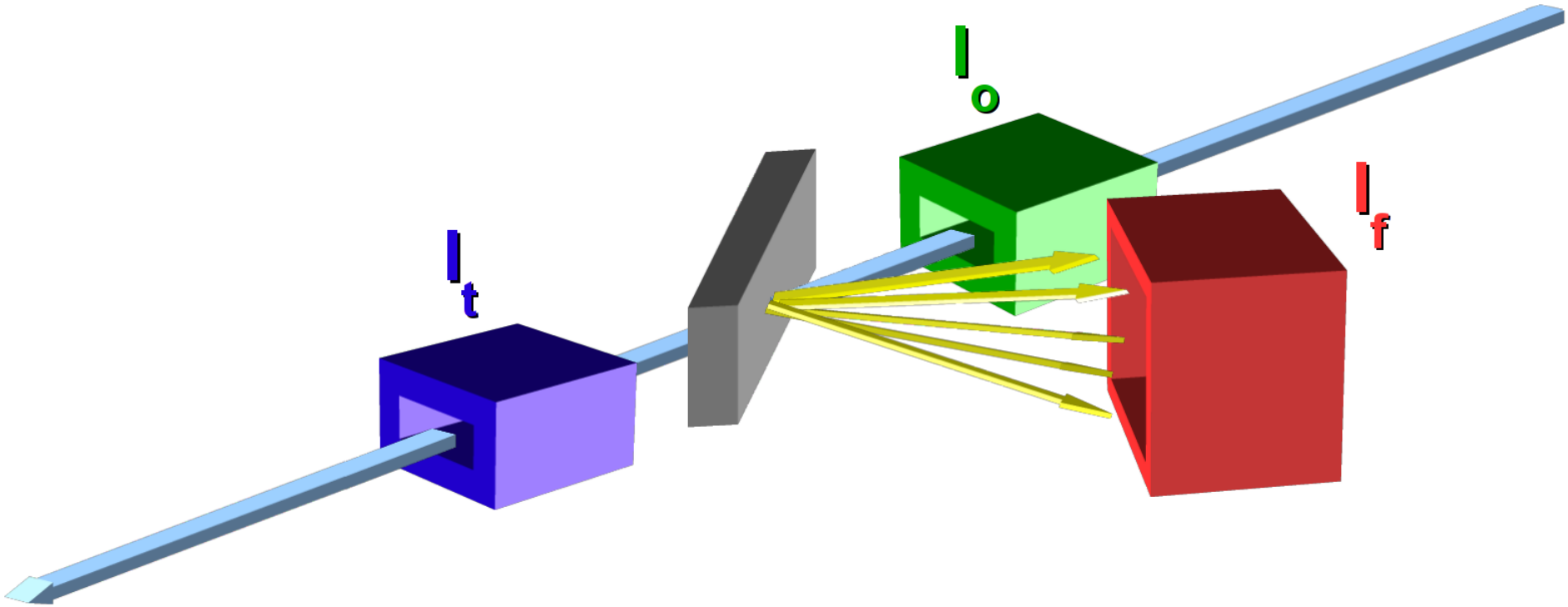
- applies to any element
- works at low concentrations
- has minimal sample requirements

The EXAFS experiment



The EXAFS experiment

I_o = incident intensity



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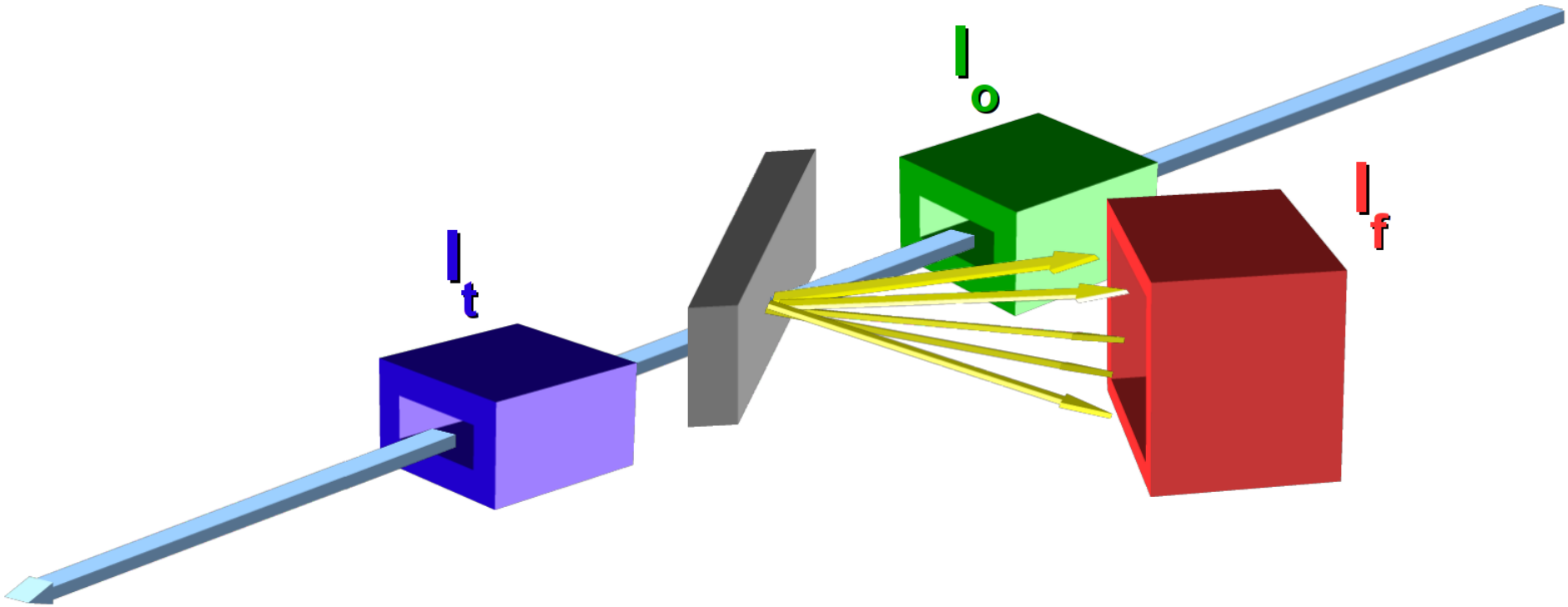

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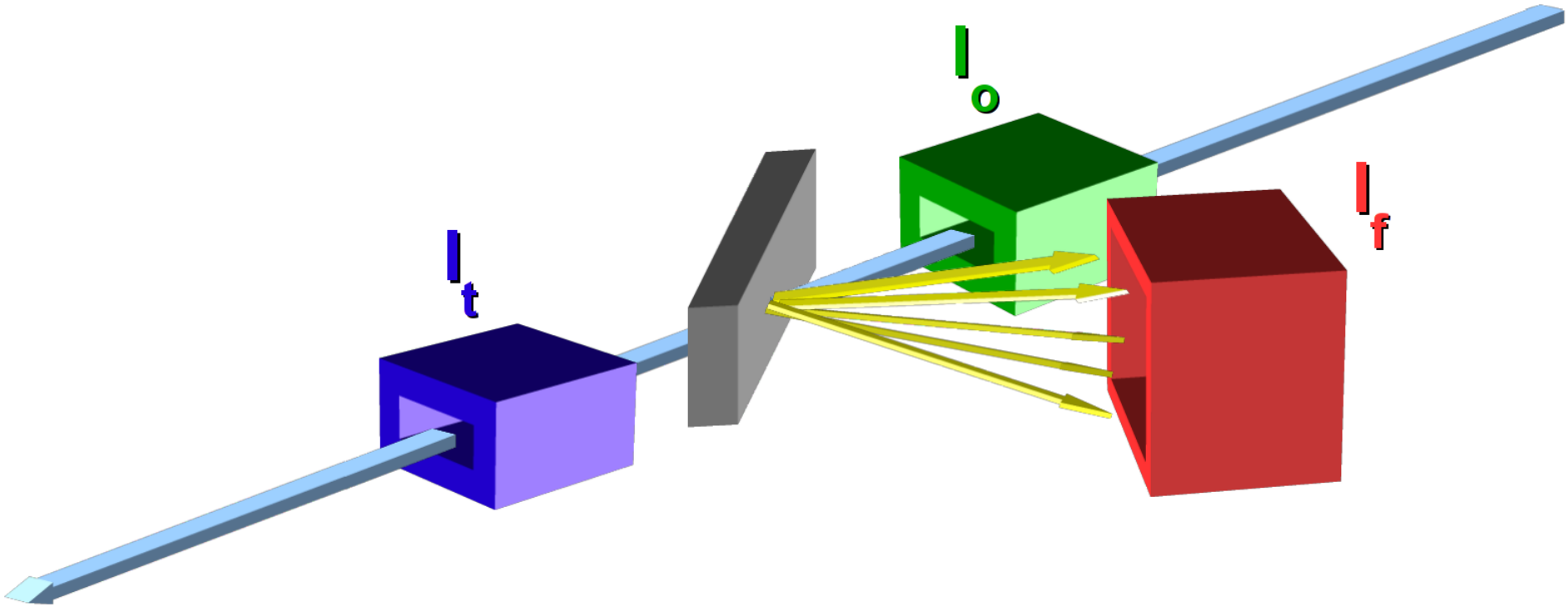

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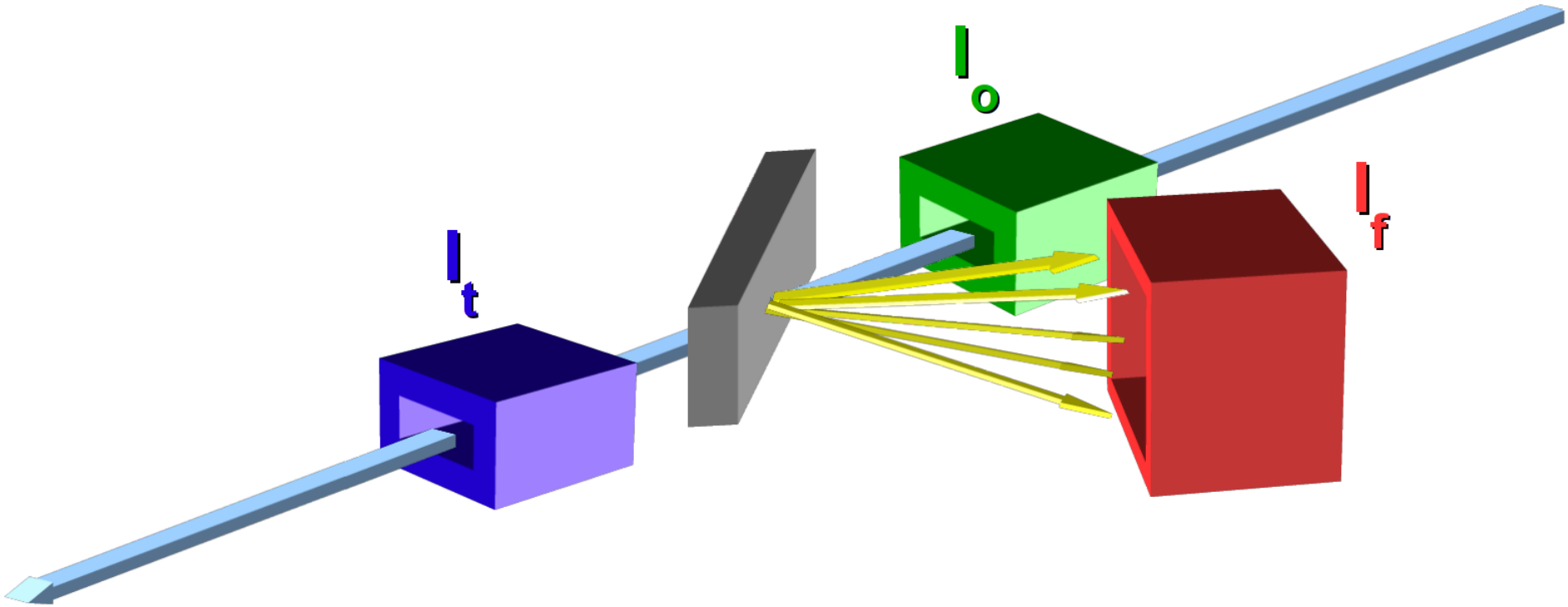

$$I_t = I_o e^{-\mu(E)x}$$

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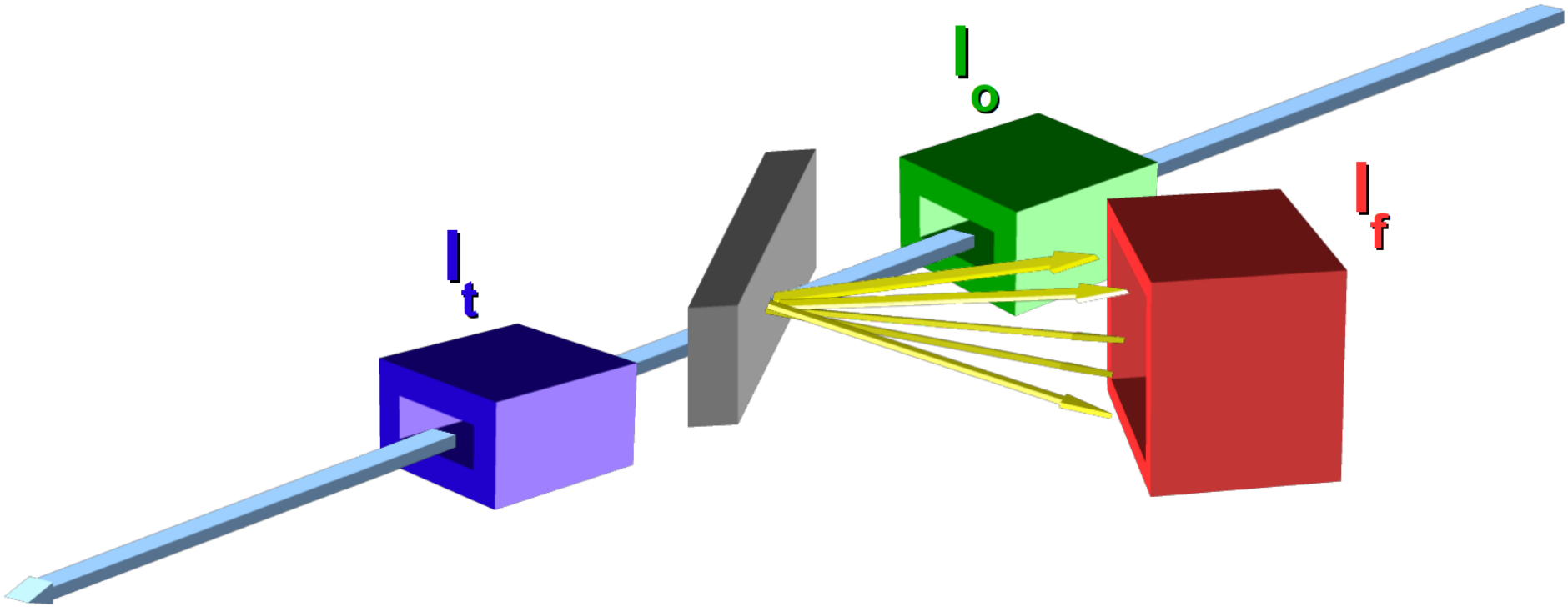

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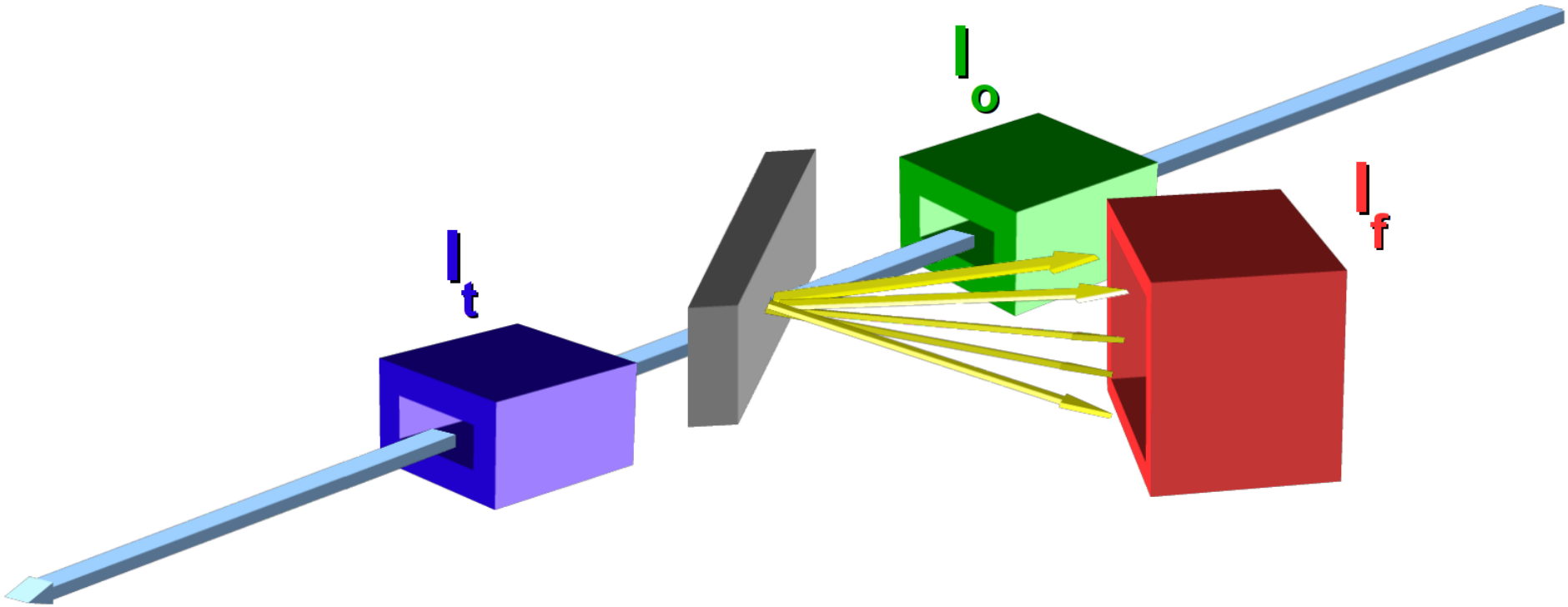

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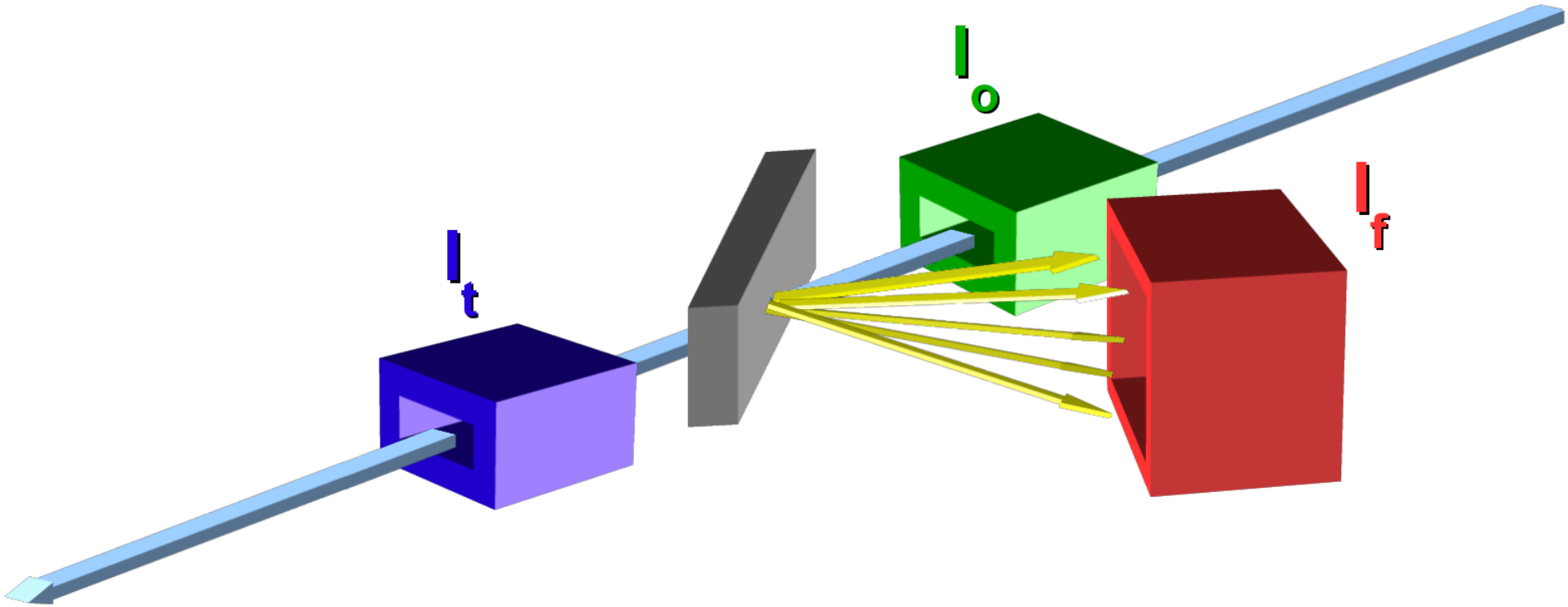
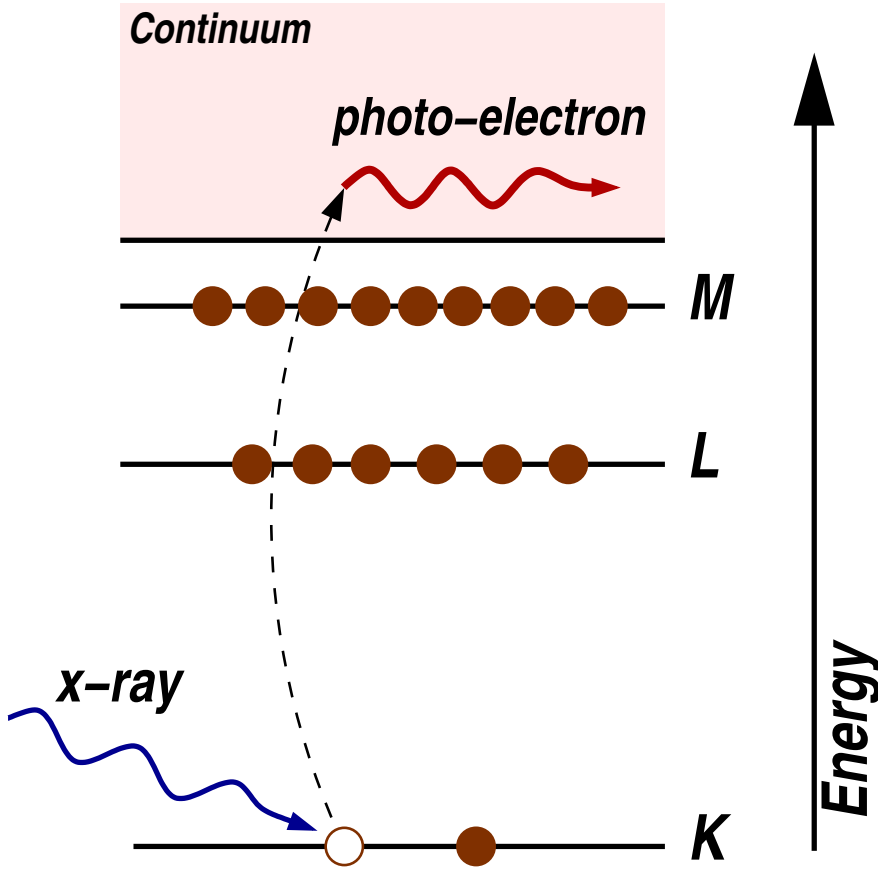


$$I_t = I_o e^{-\mu(E)x} \quad \longrightarrow \quad \mu(E)x = \ln\left(\frac{I_o}{I_t}\right) \qquad \mu(E) \propto \frac{I_f}{I_o}$$

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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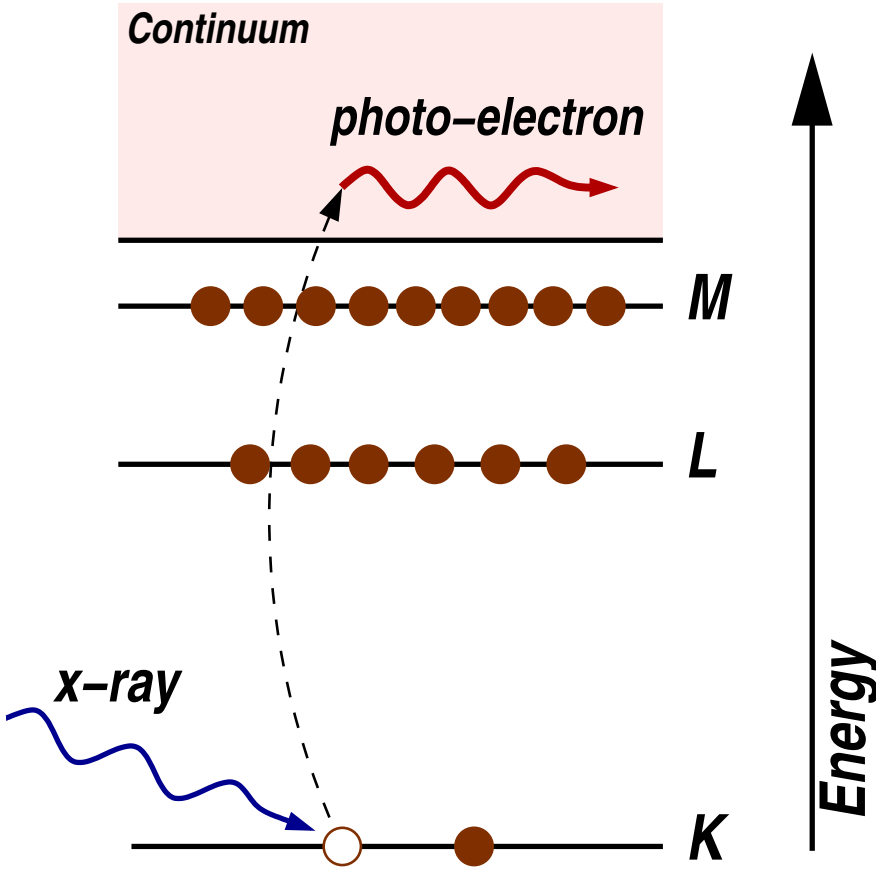

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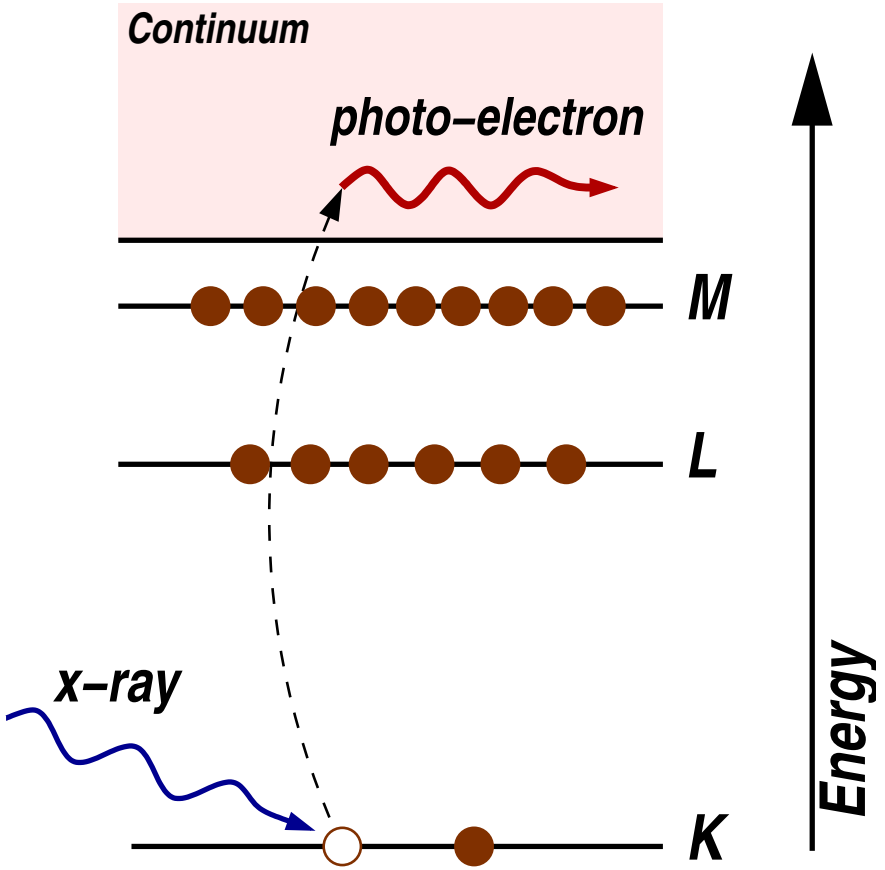

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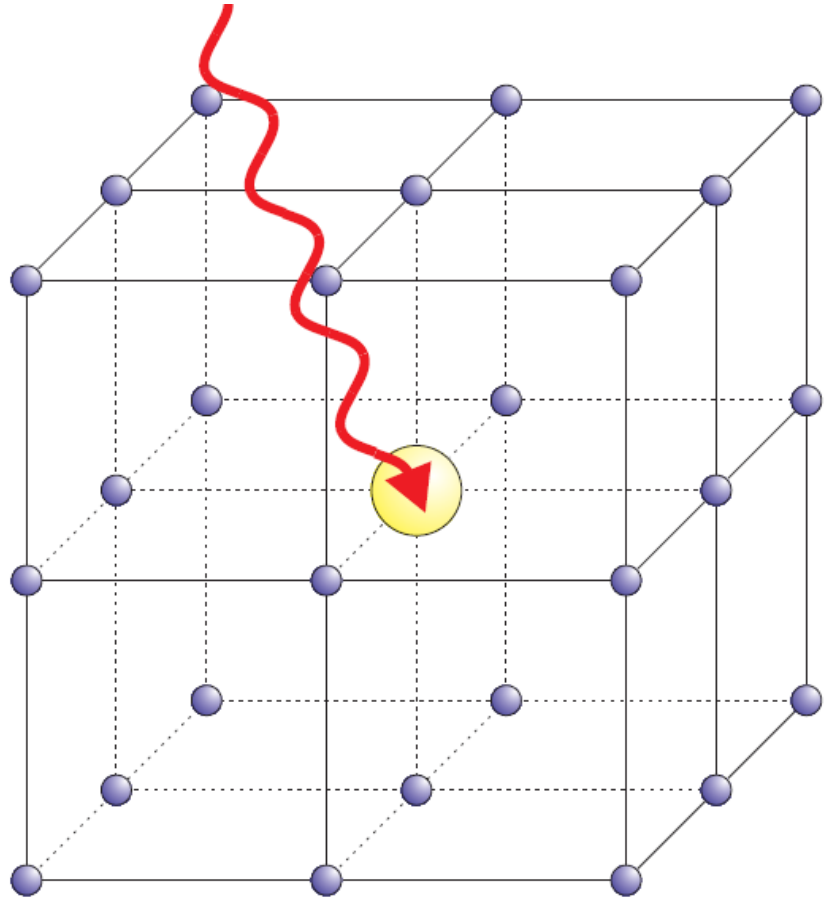

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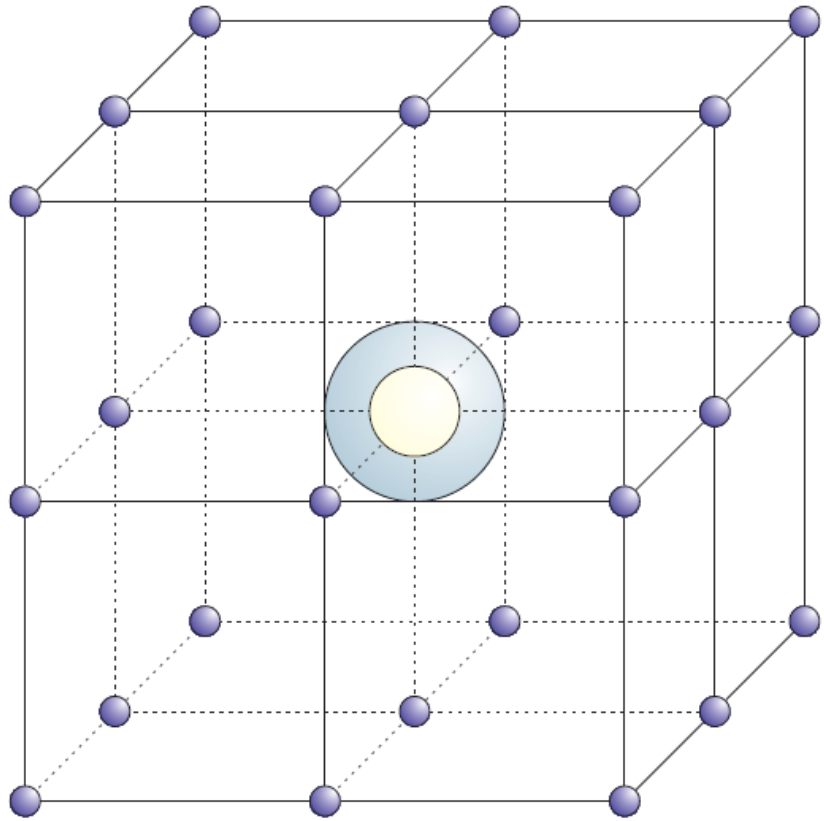

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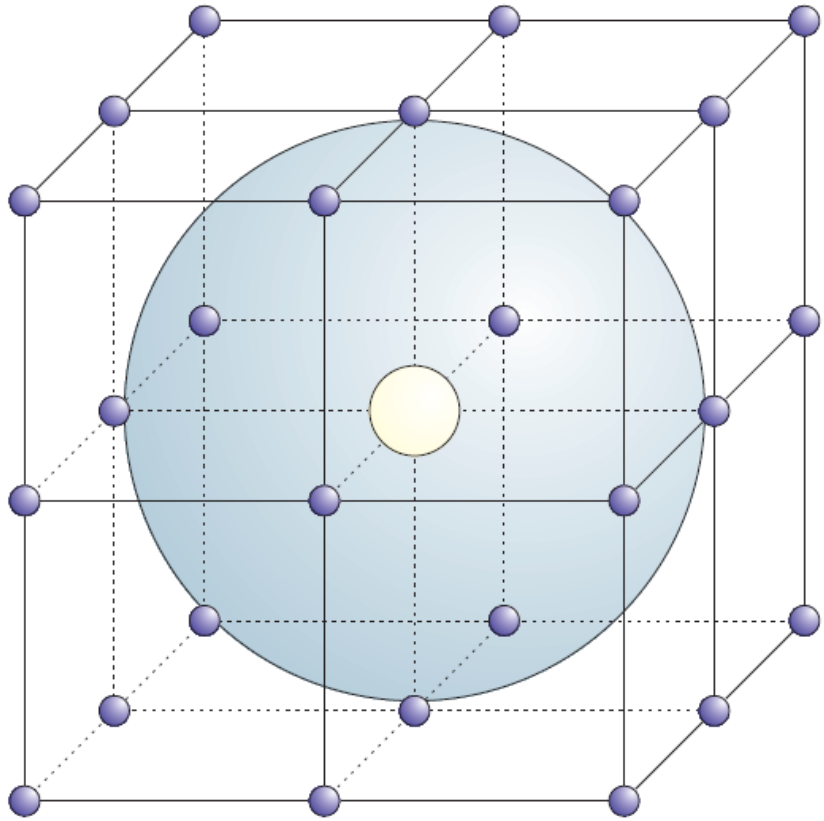

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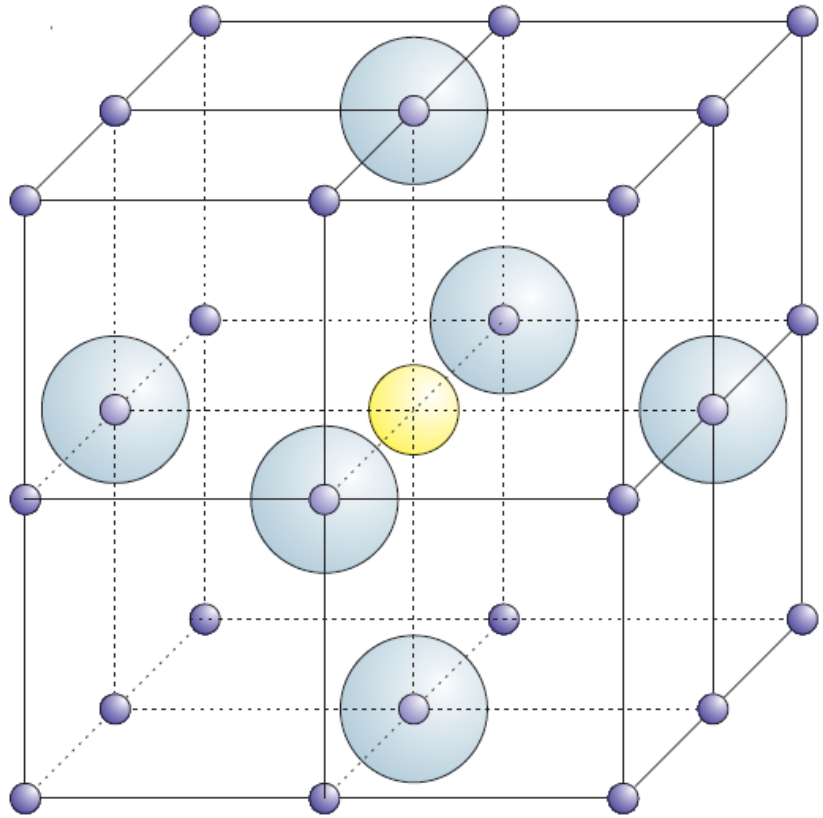

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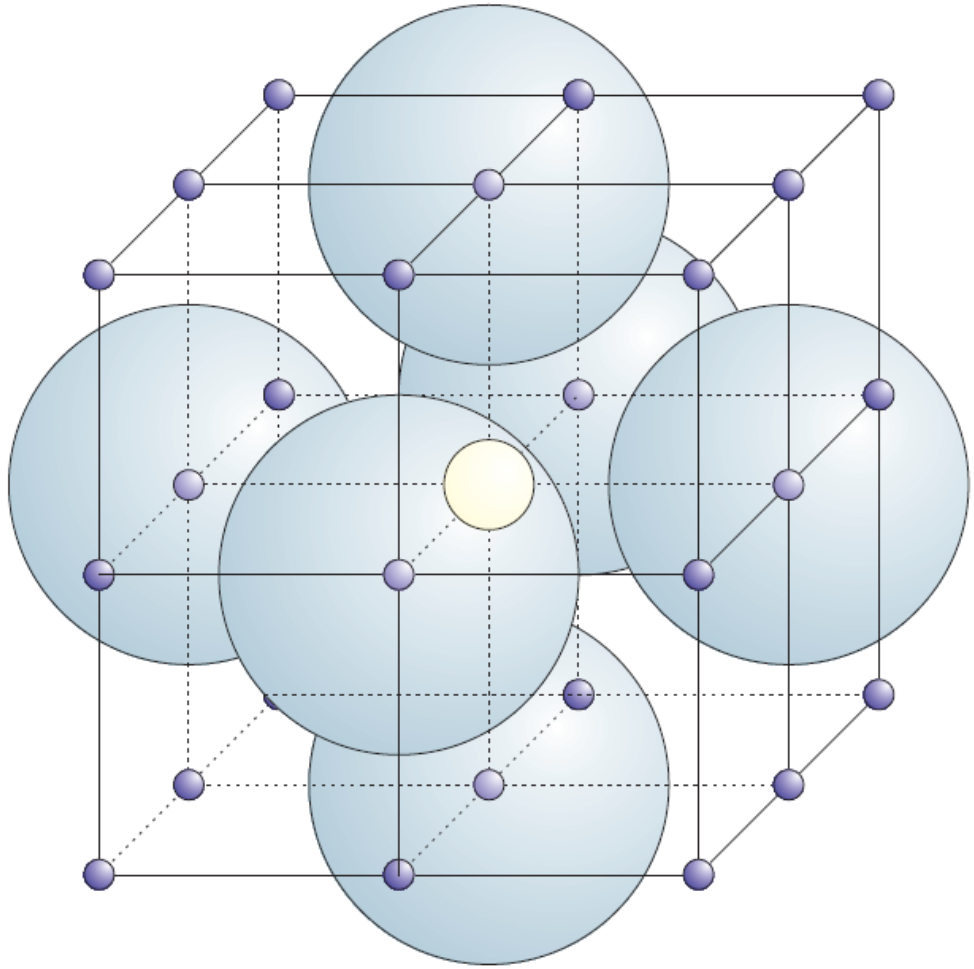

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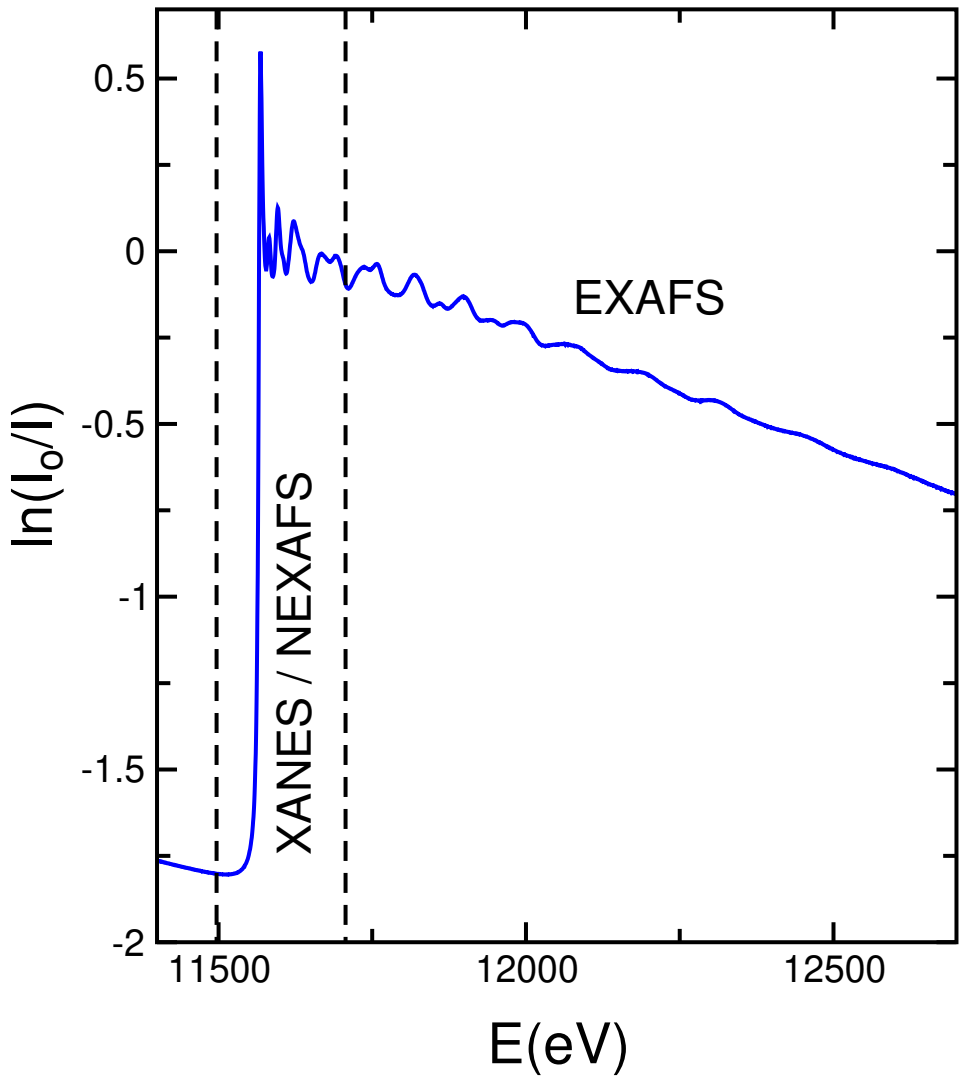
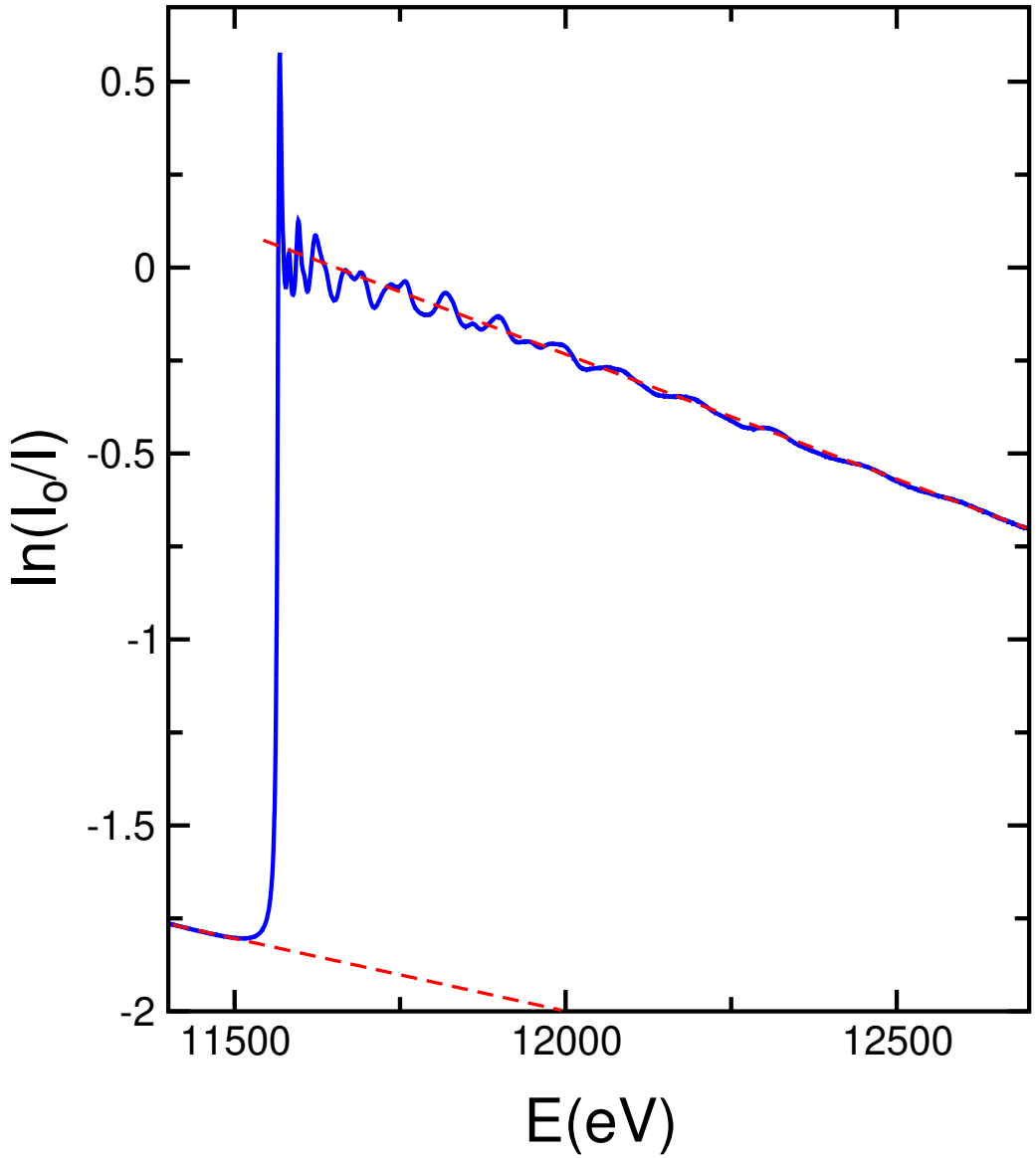
Any excess energy from the x-ray is given to an ejected photoelectron, which expands as a spherical wave, reaches the neighboring electron clouds, and scatters back to the core hole, creating interference patterns called XANES and EXAFS.



EXAFS data extraction

normalize by fitting pre-edge and post-edge trends



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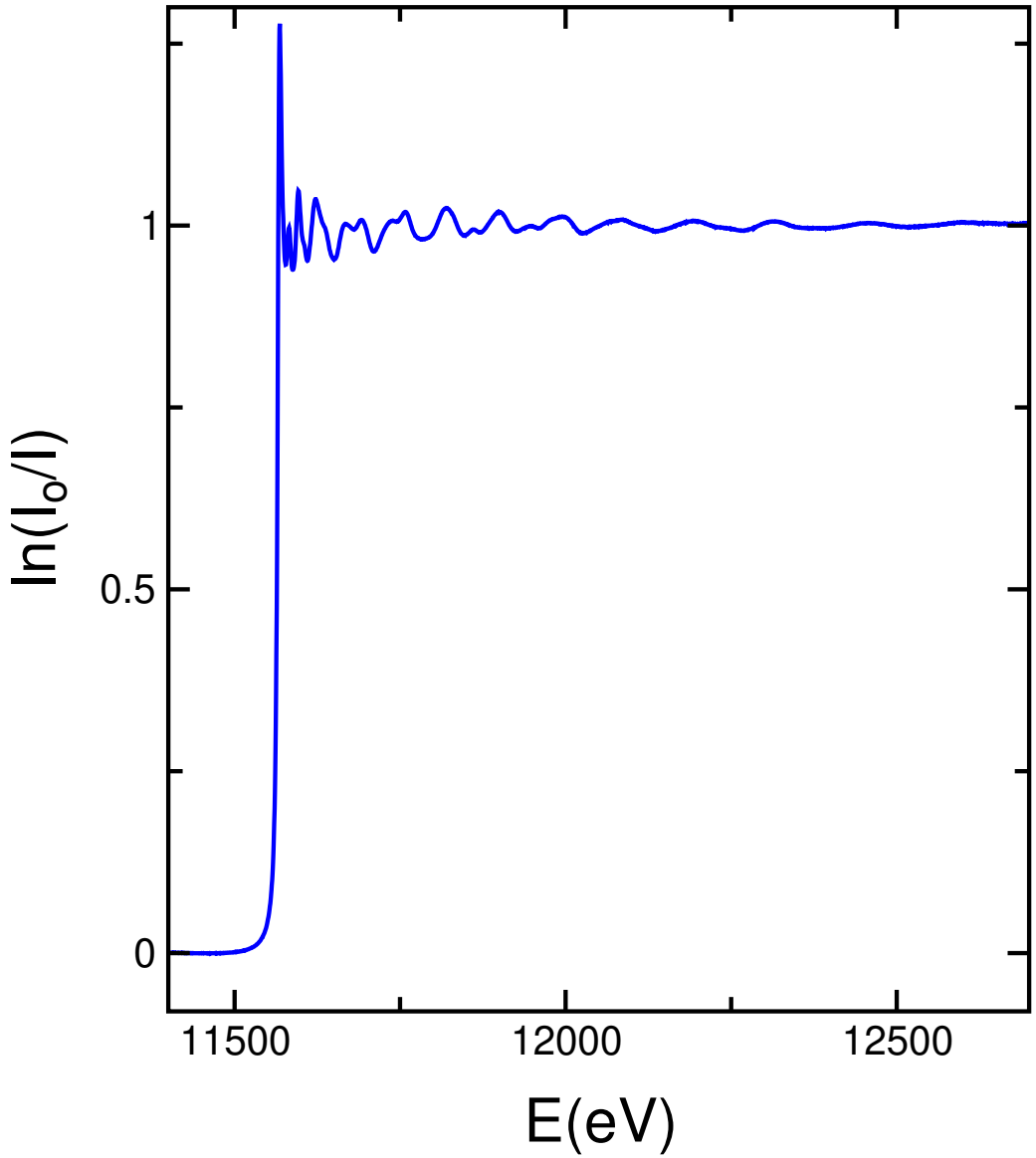

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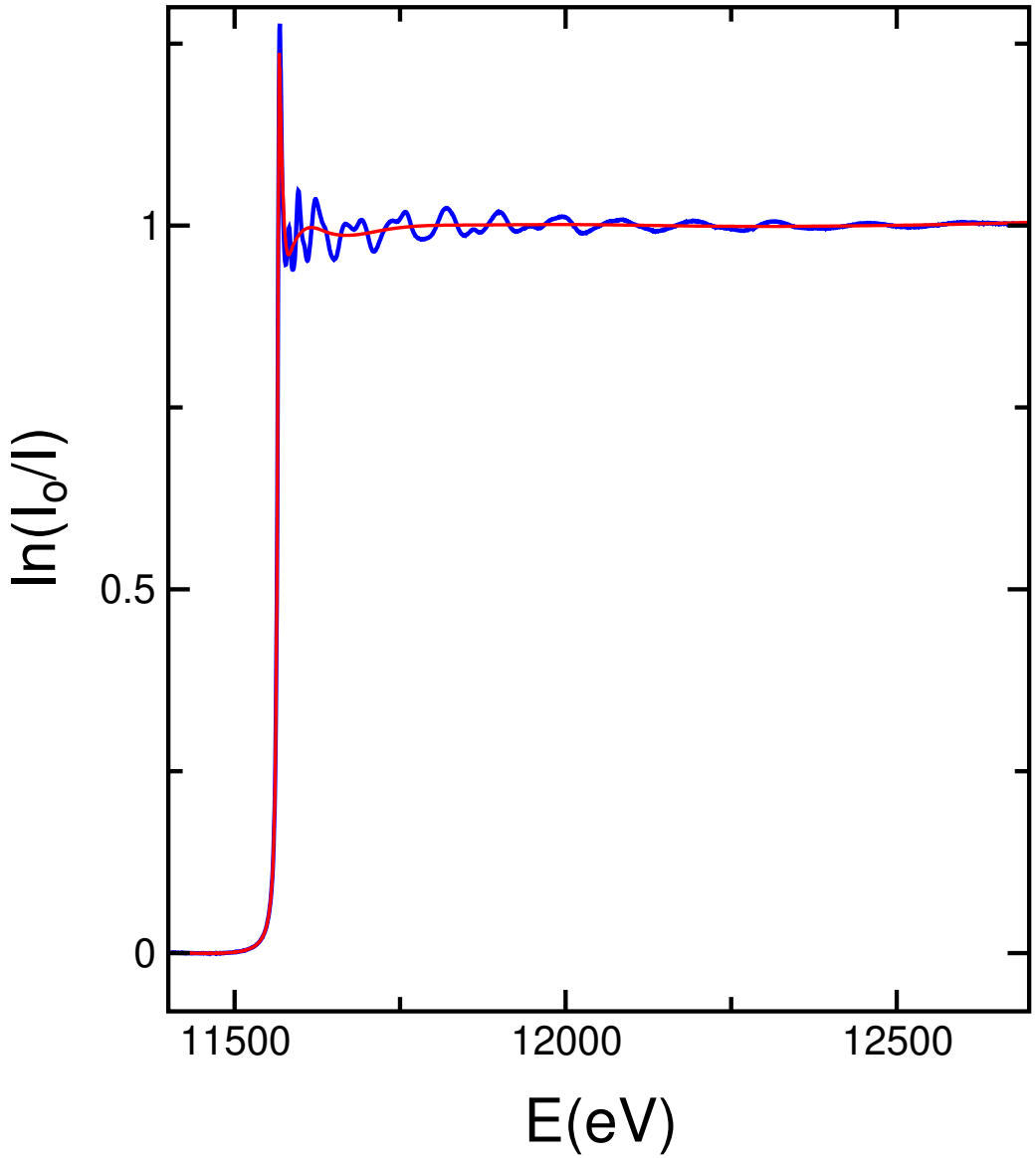

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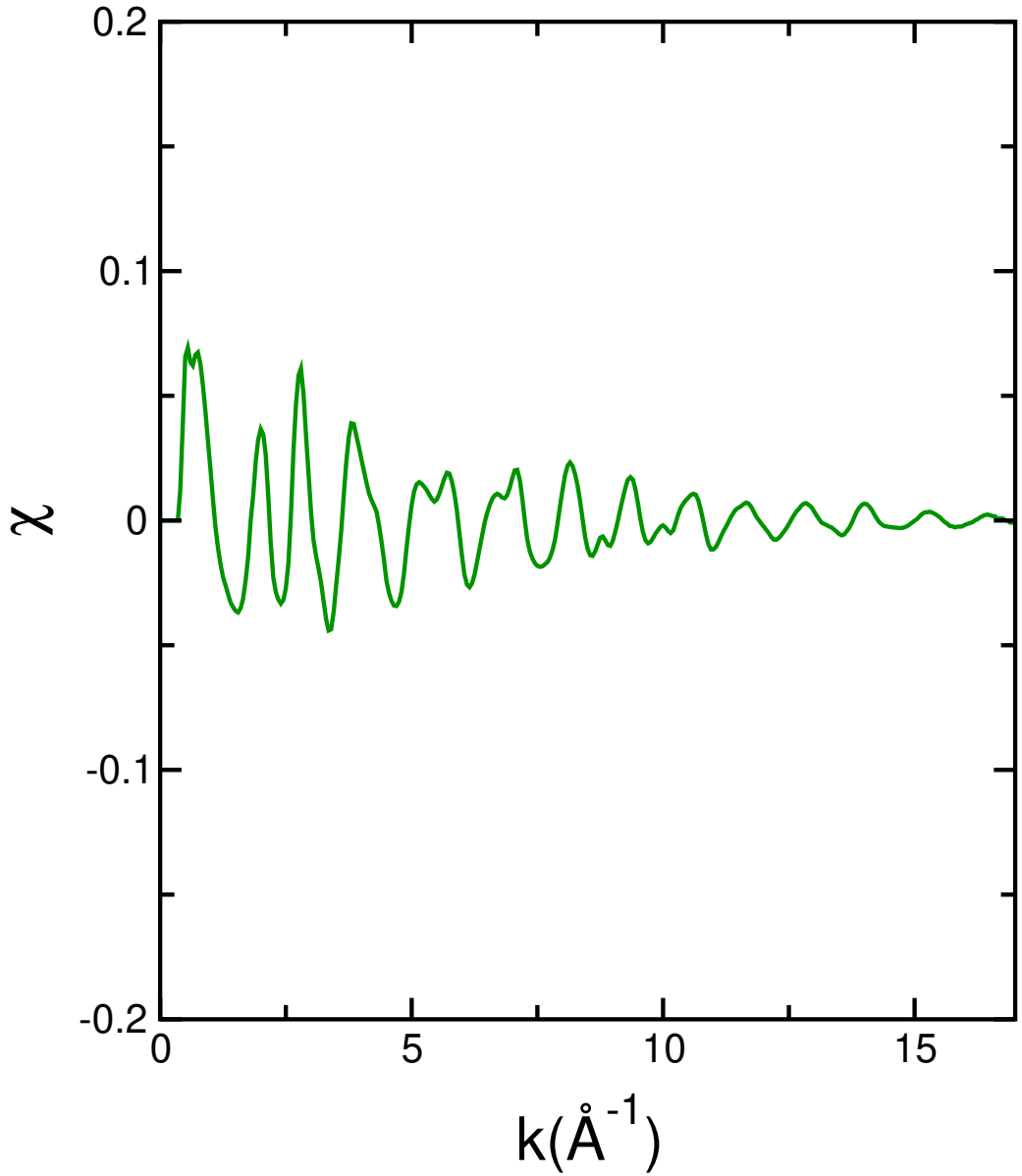

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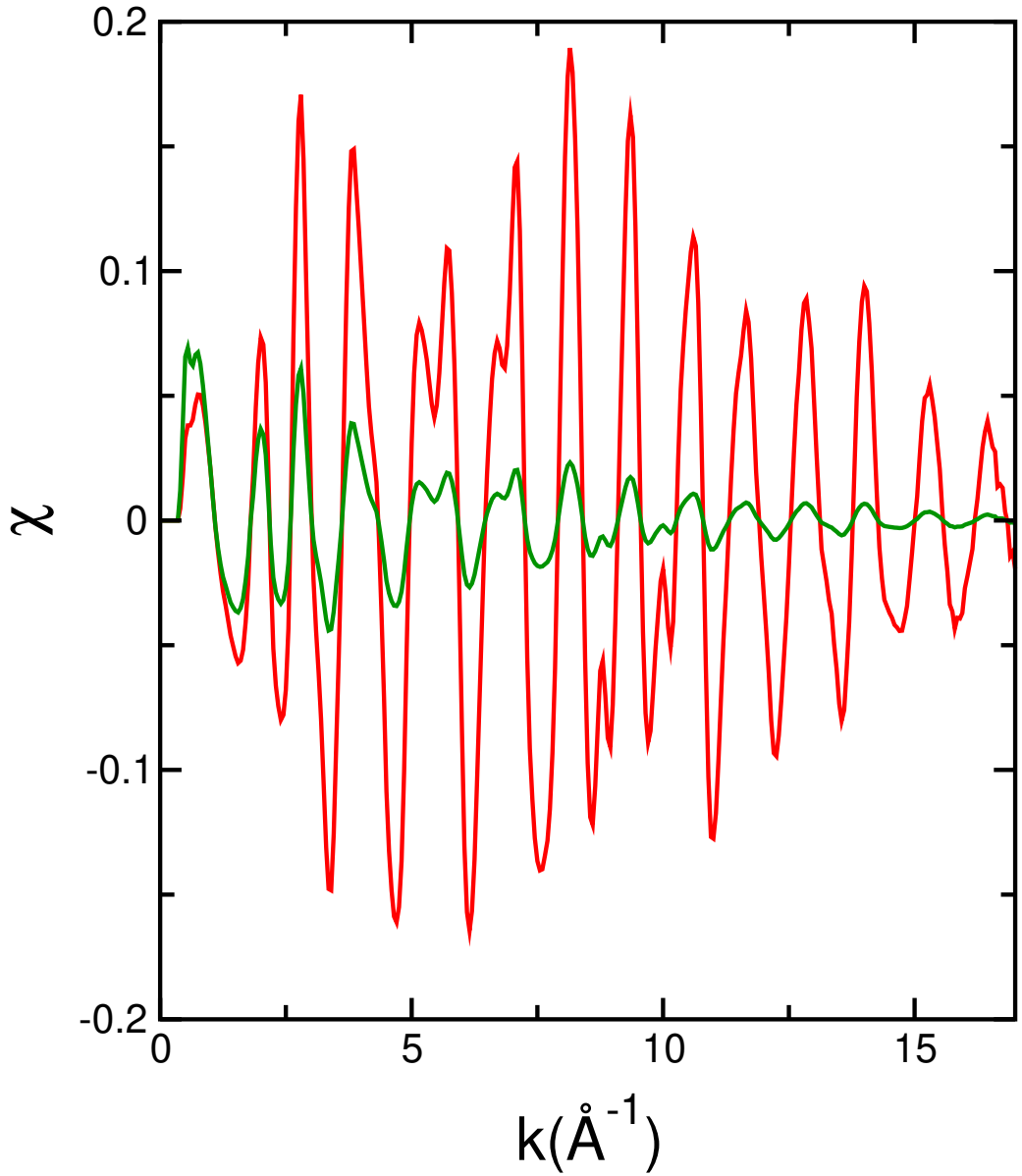

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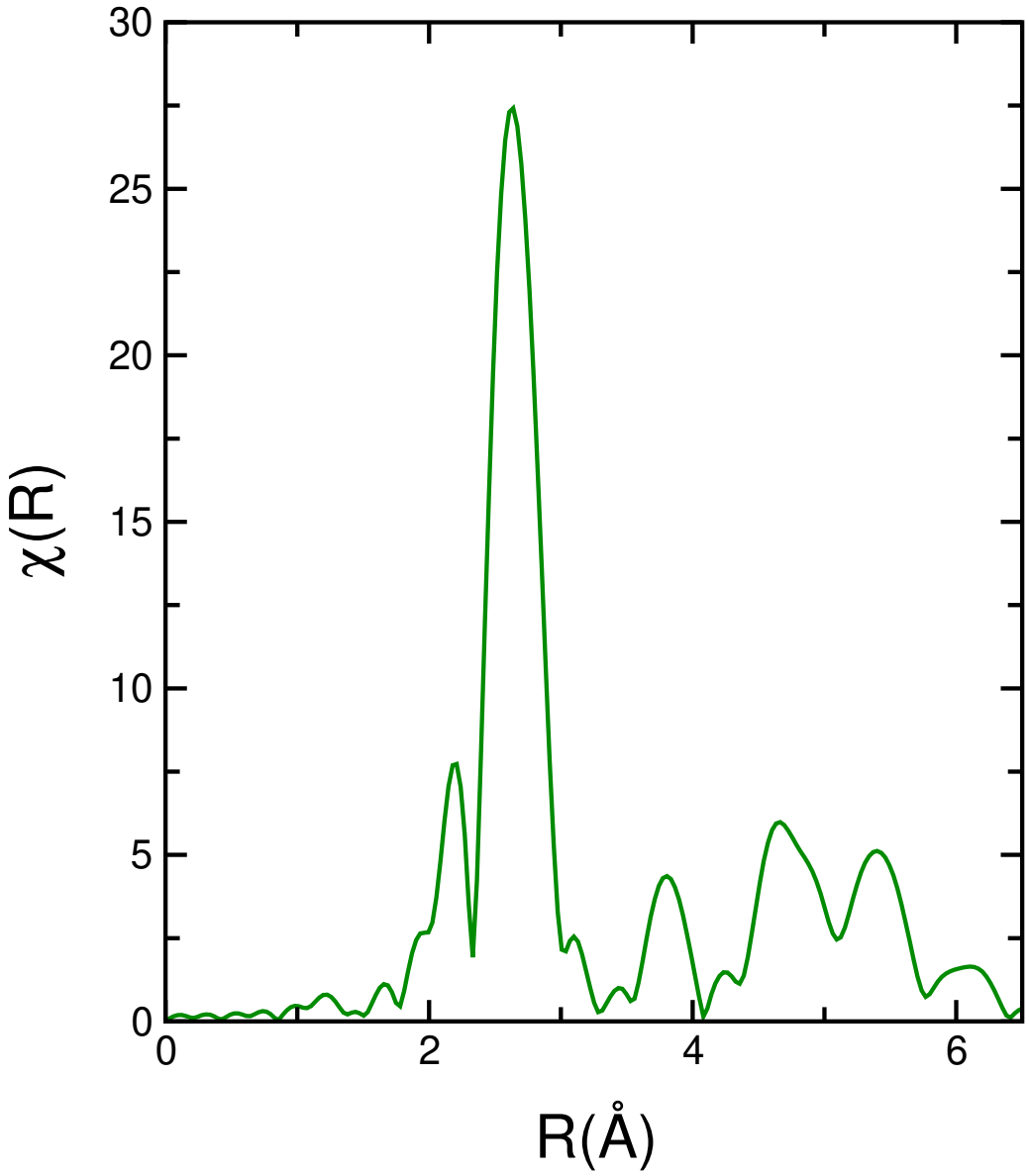
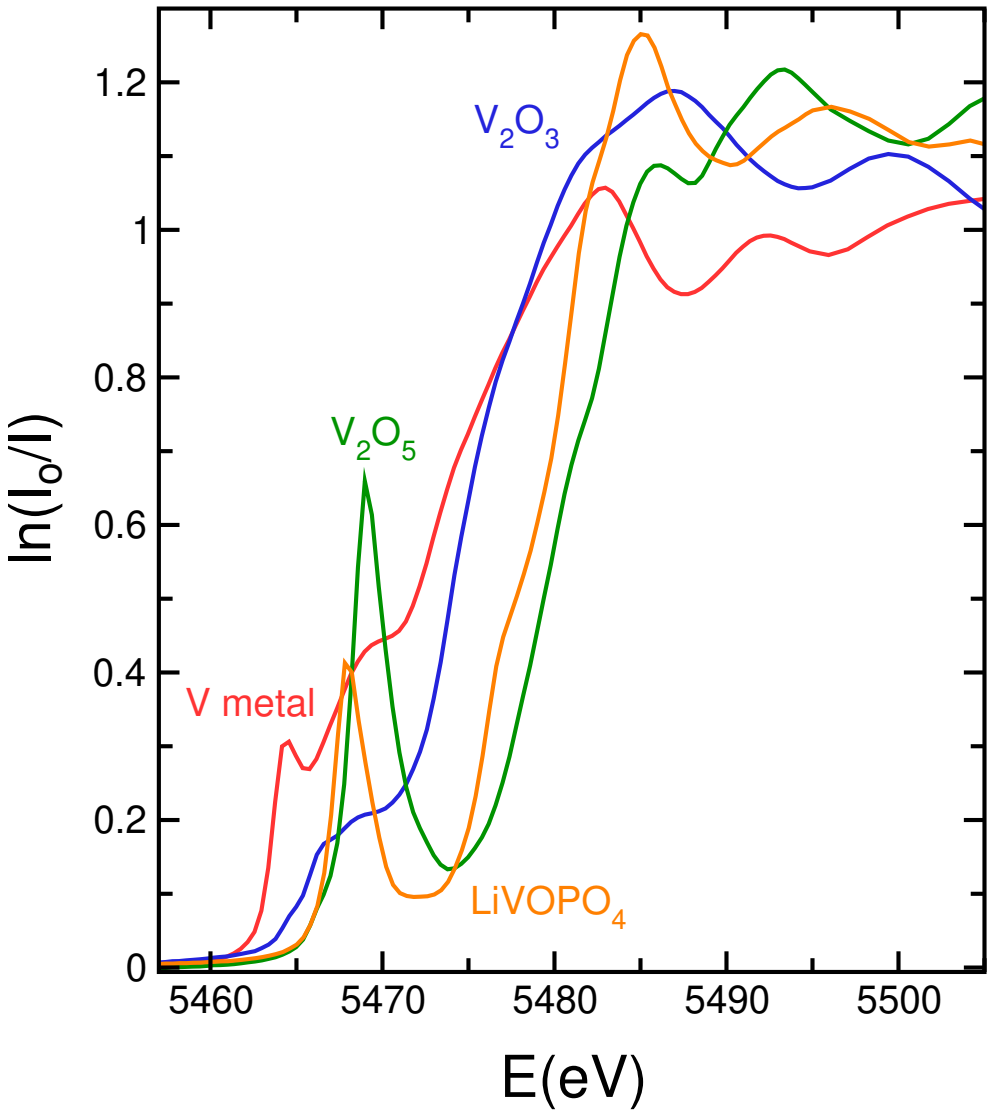
Fourier transform to get real space EXAFS



XANES edge shifts and pre-edge peaks



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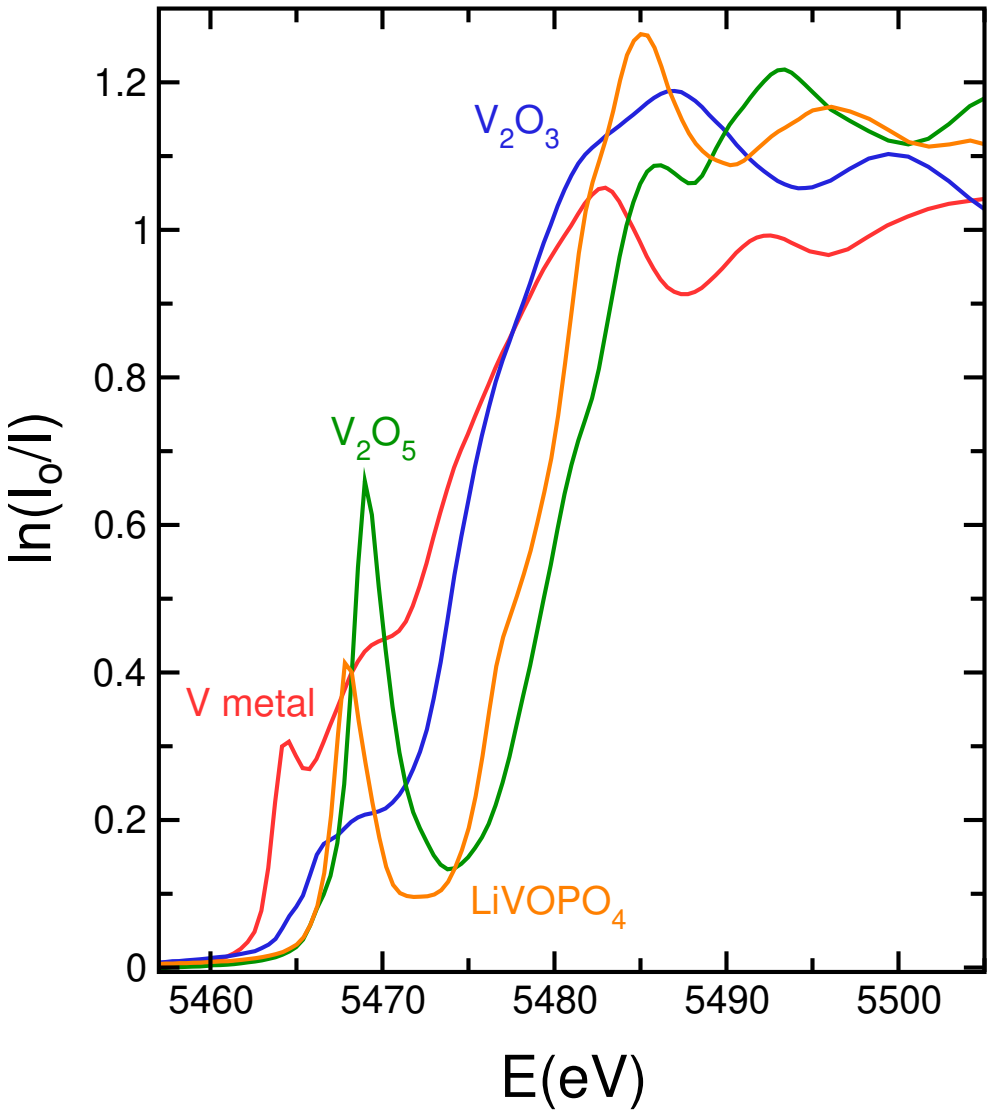

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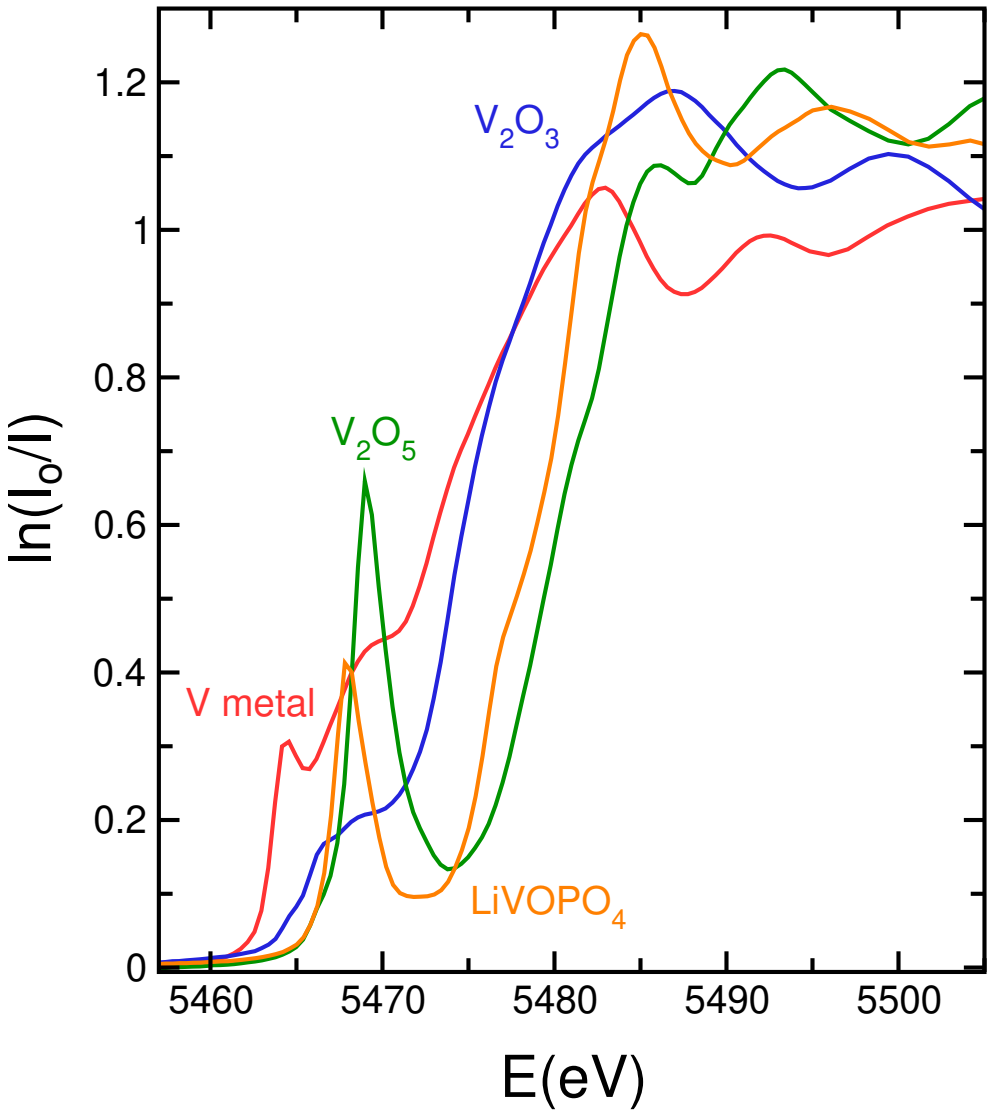

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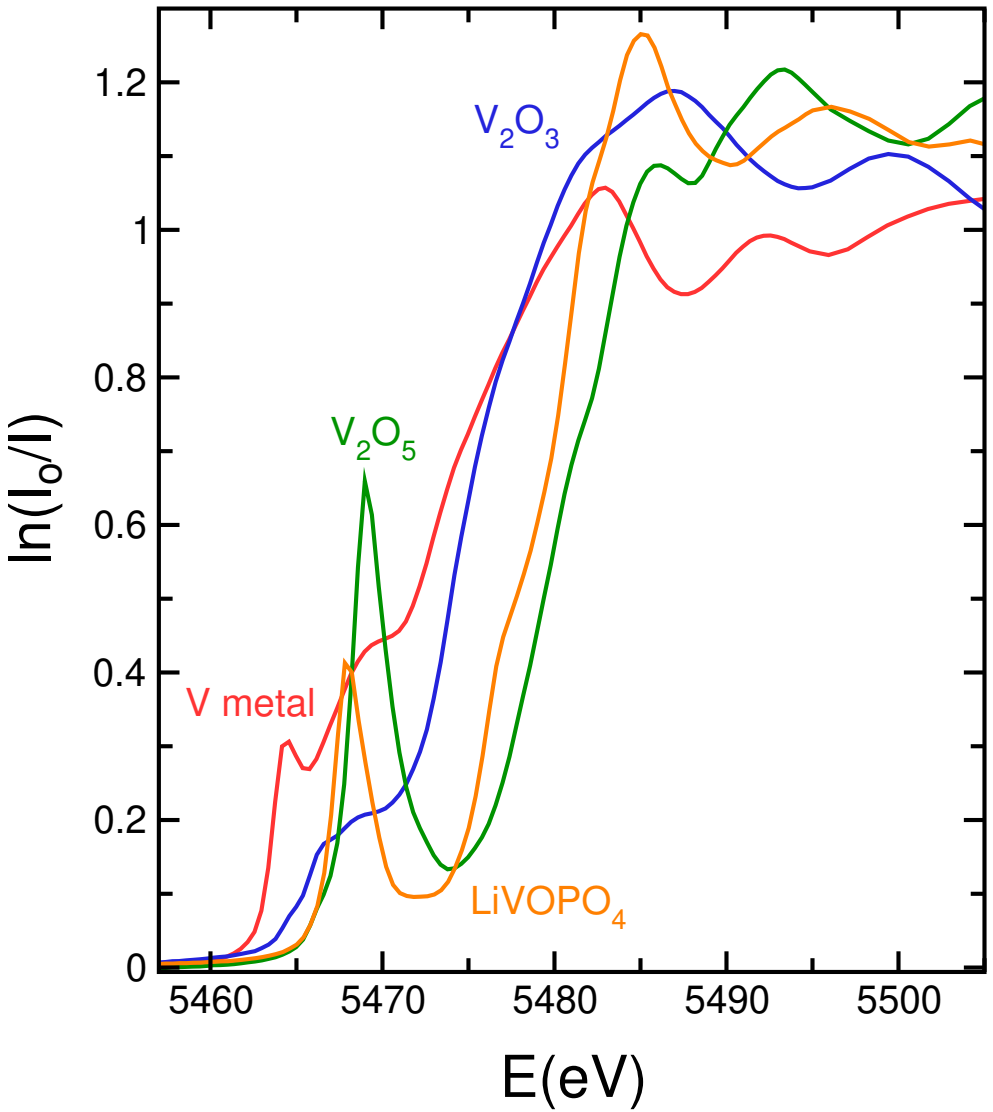

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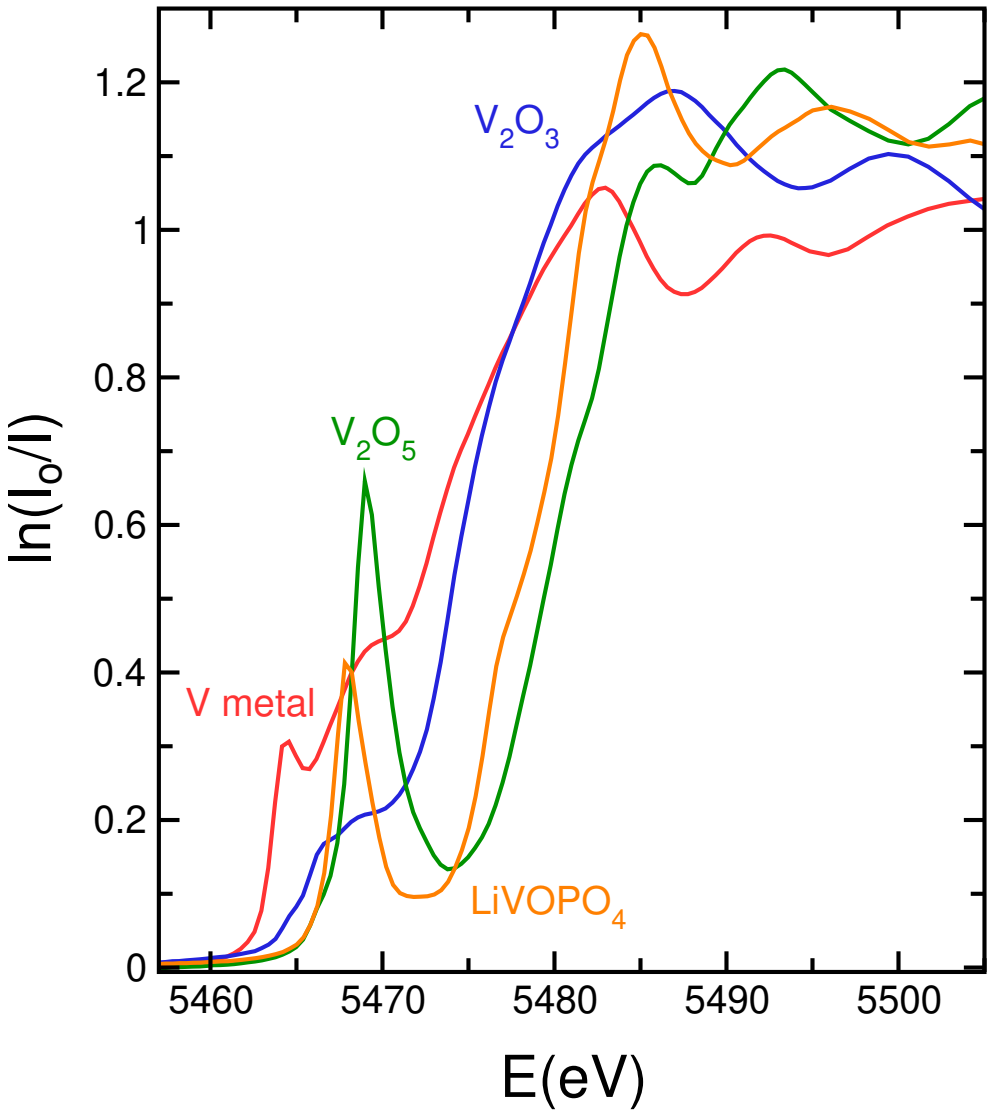

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Modern codes, such as FEFF9, are able to accurately compute XANES features.

X-ray absorption by a free atom

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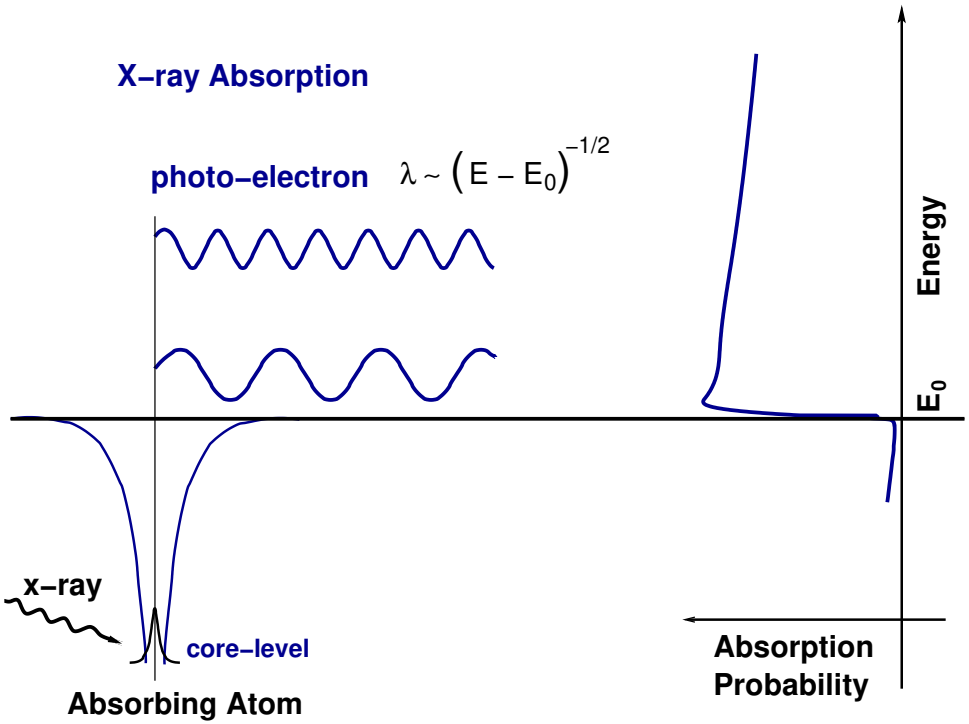

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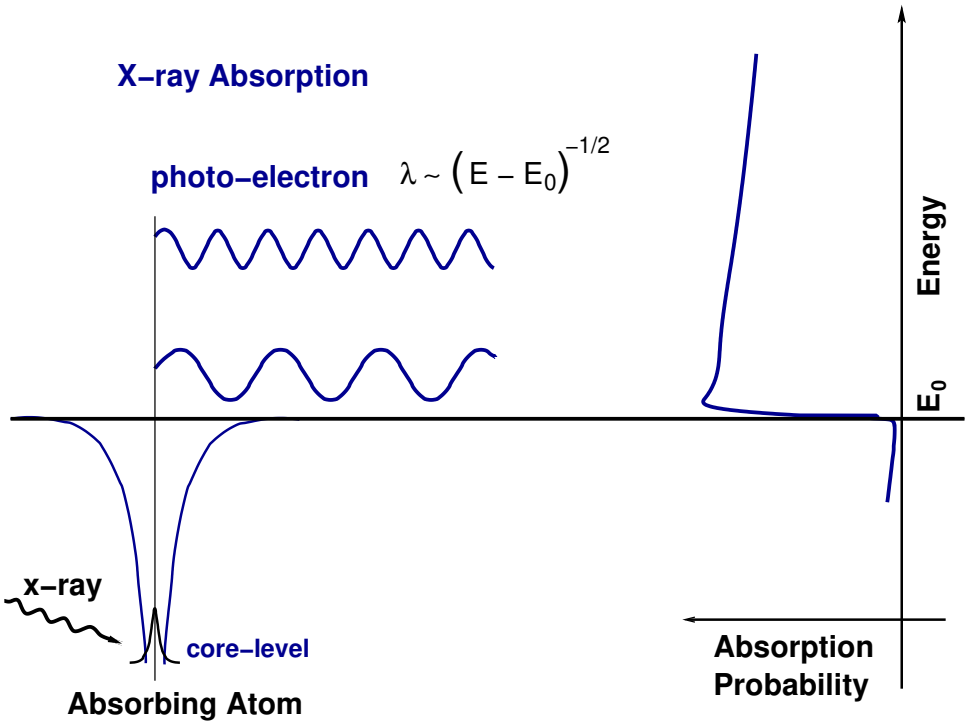

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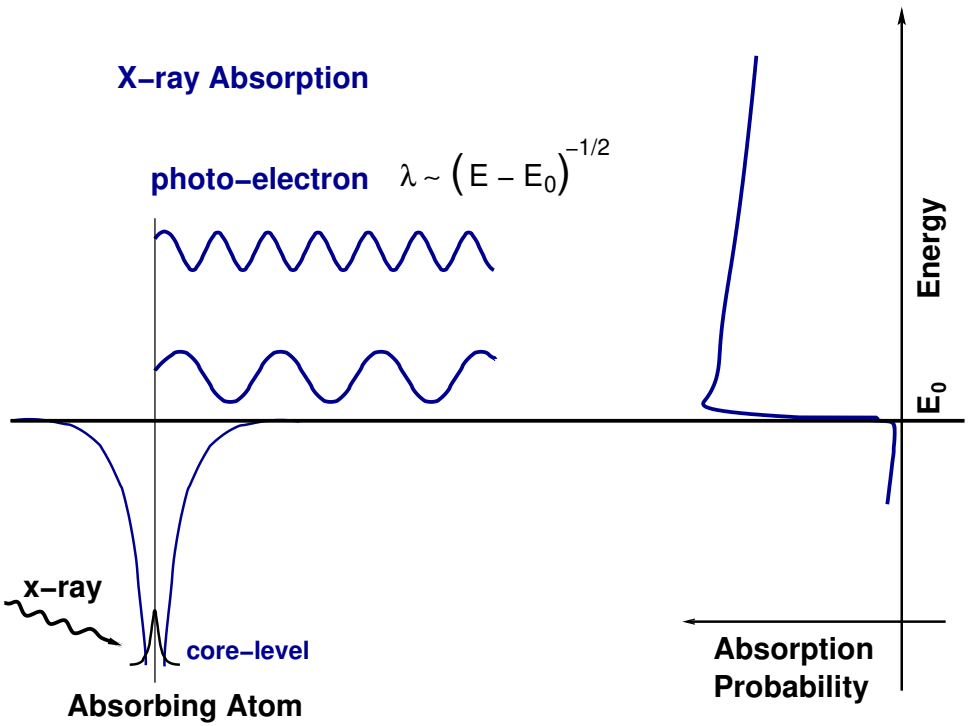

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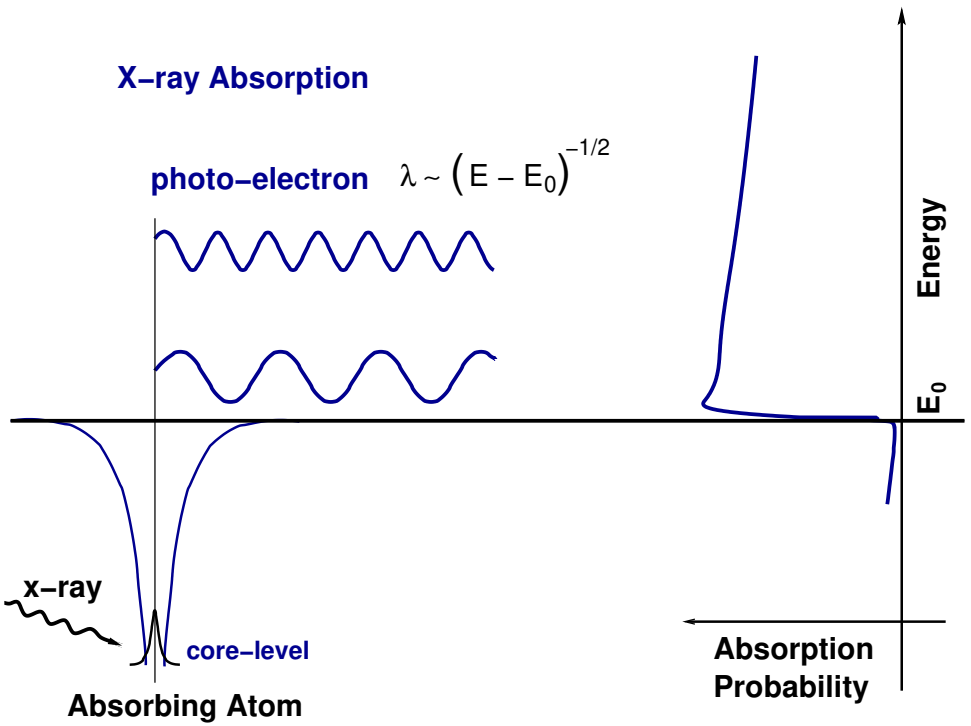

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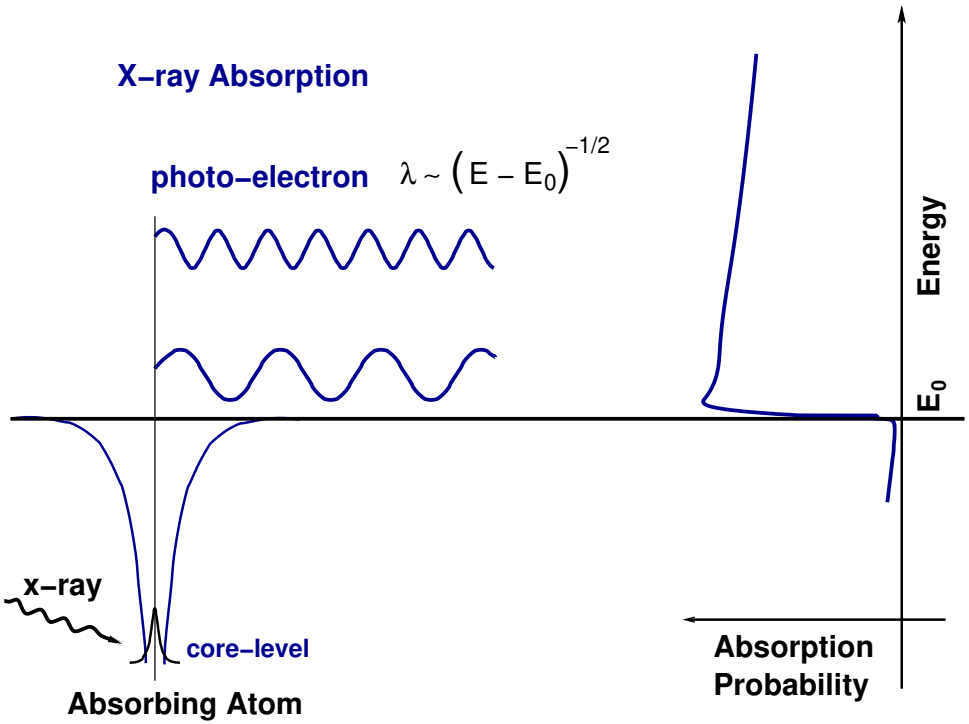
Once the x-ray energy is large enough to promote a core-level to the continuum, there is a sharp increase in absorption.

X-ray absorption by a free atom

An atom absorbs an x-ray of energy E, destroying a core electron with energy E_0 and creating a photoelectron with energy $(E - E_0)$. The core hole is eventually filled, and a fluorescence x-ray or Auger electron is ejected from the atom.



x-ray absorption needs an available state for the photoelectron to go into

No available state:
No absorption

Once the x-ray energy is large enough to promote a core-level to the continuum, there is a sharp increase in absorption.

$\mu(E)$ has a sharp step at the core-level binding energy, and is a smooth function of energy above this absorption edge.

X-ray absorption with photoelectron scattering

With another atom nearby, the ejected photoelectron can scatter from a neighboring atom and return back to the absorbing atom

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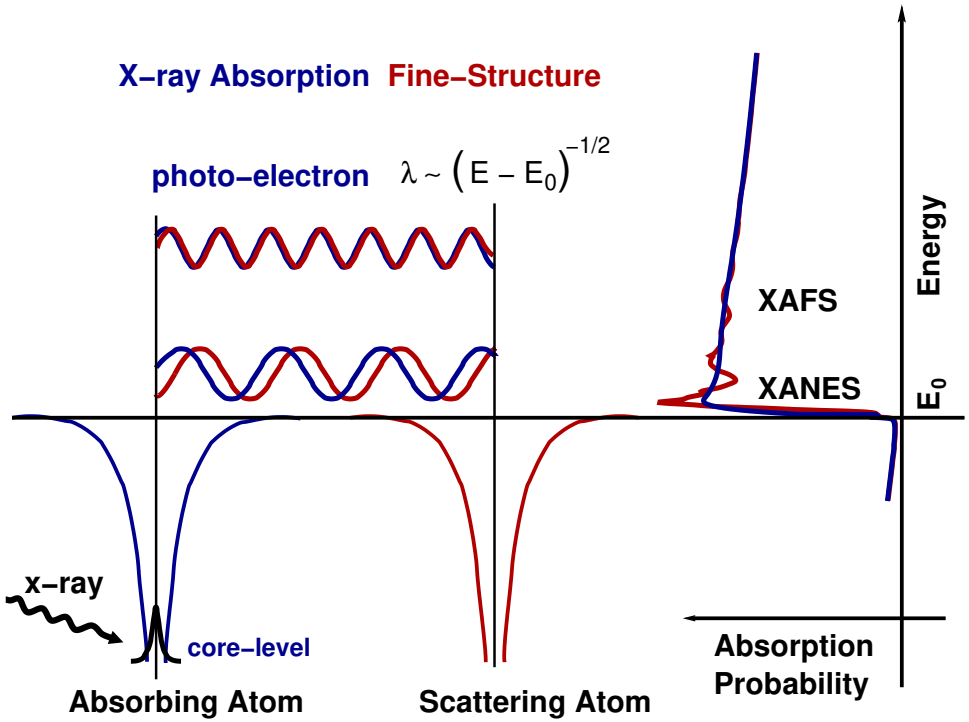

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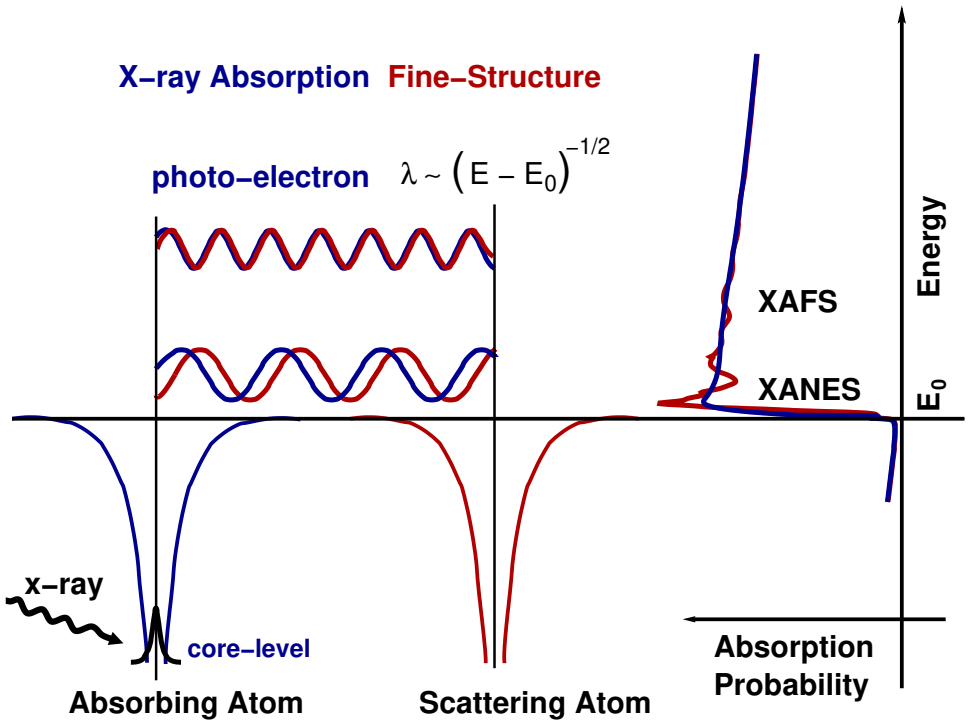

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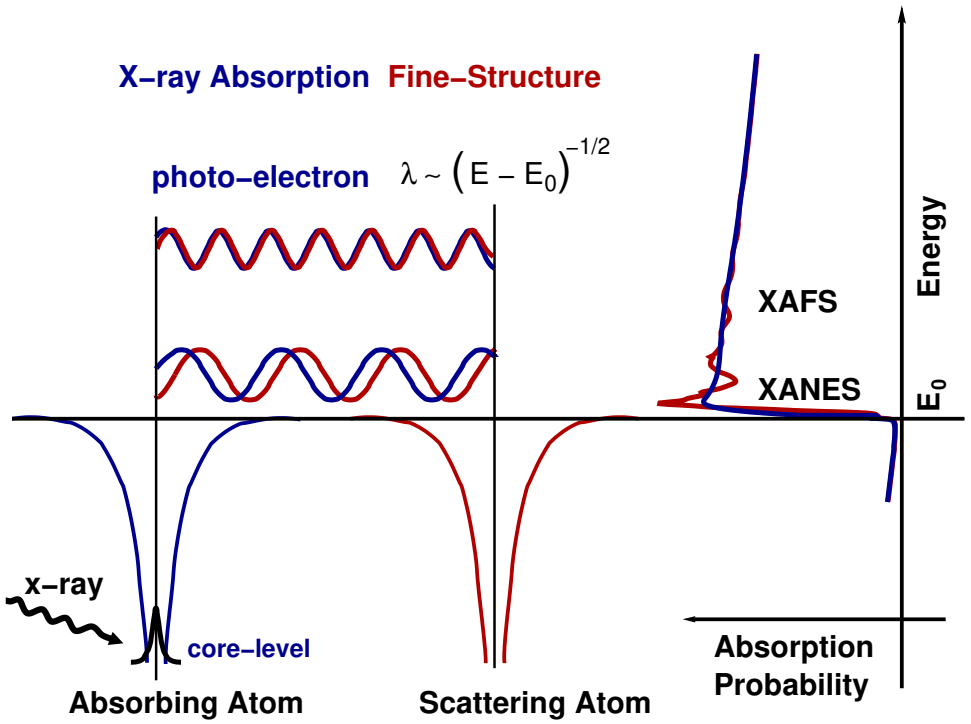

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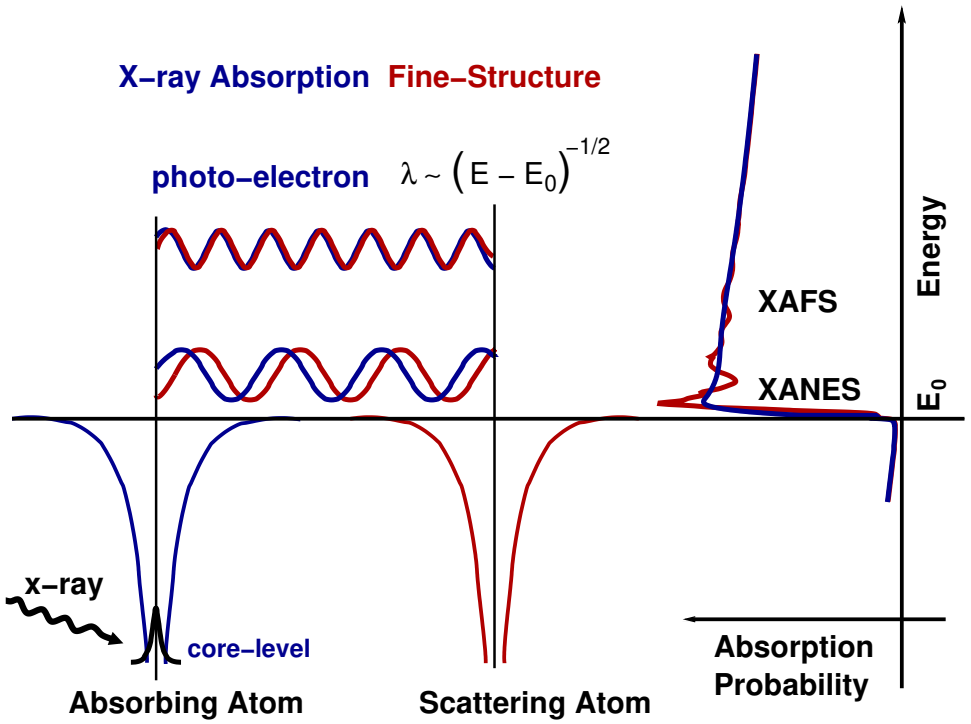

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The amplitude of the back-scattered photoelectron at the absorbing atom will vary with energy, causing the oscillations in $\mu(E)$

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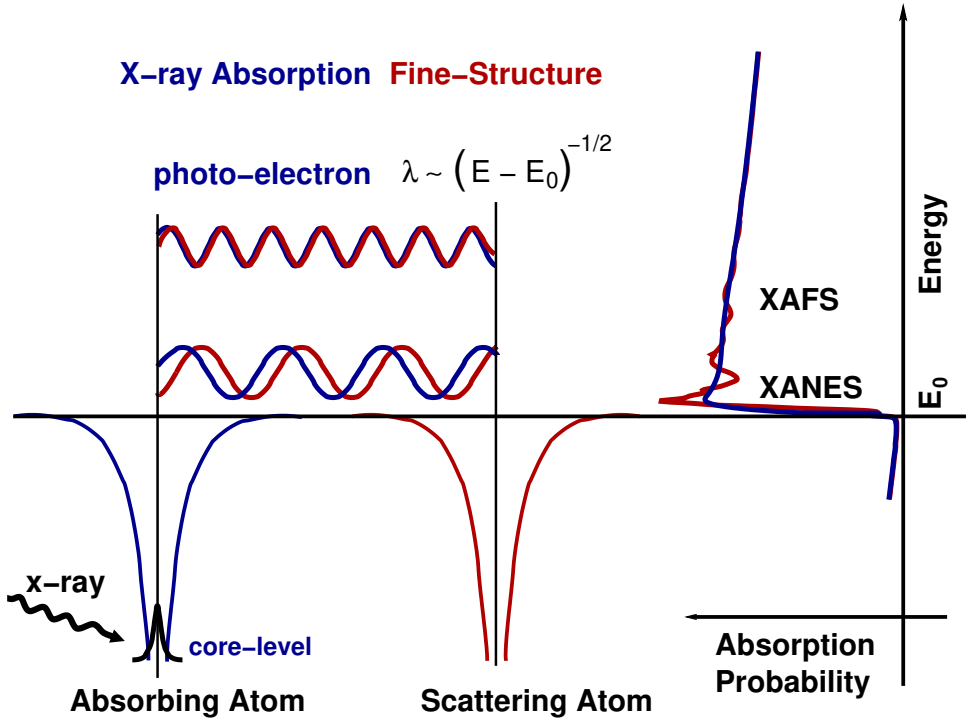
We have seen how this works qualitatively, now let's look at how first order perturbation theory can give a quantitative theory

X-ray absorption: Fermi's golden rule

$$\mu(E) = \mu_0(E) + \Delta\mu(E)$$



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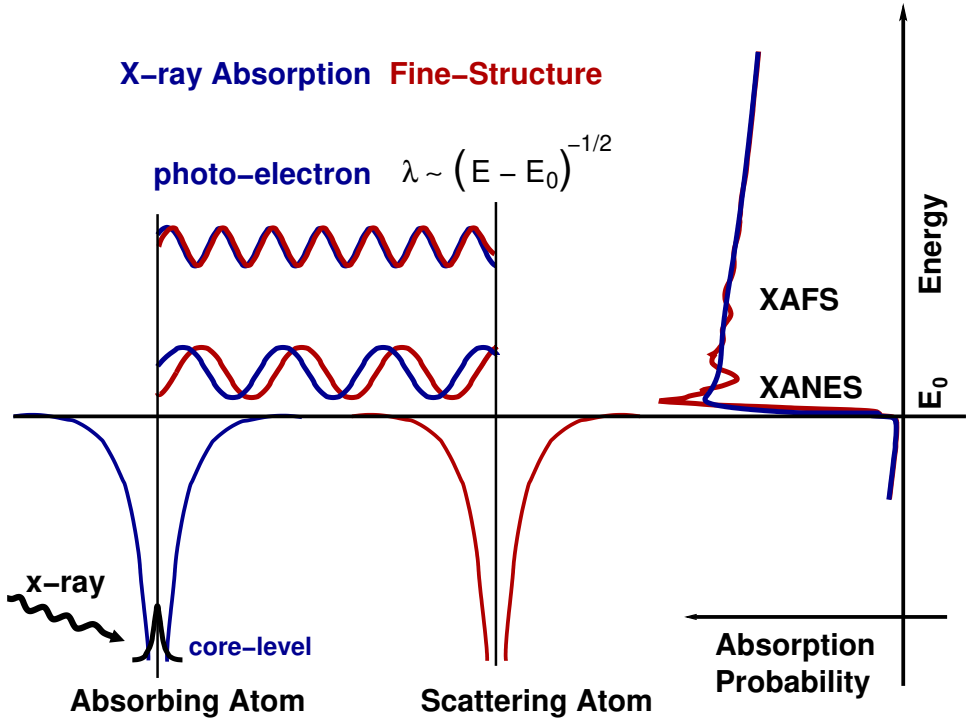

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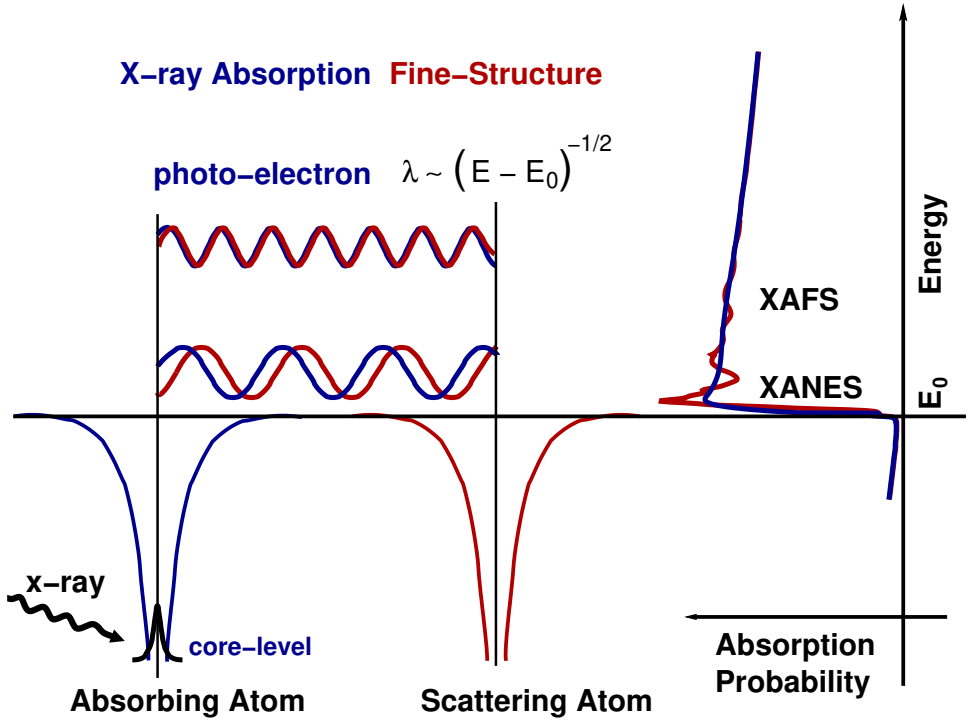

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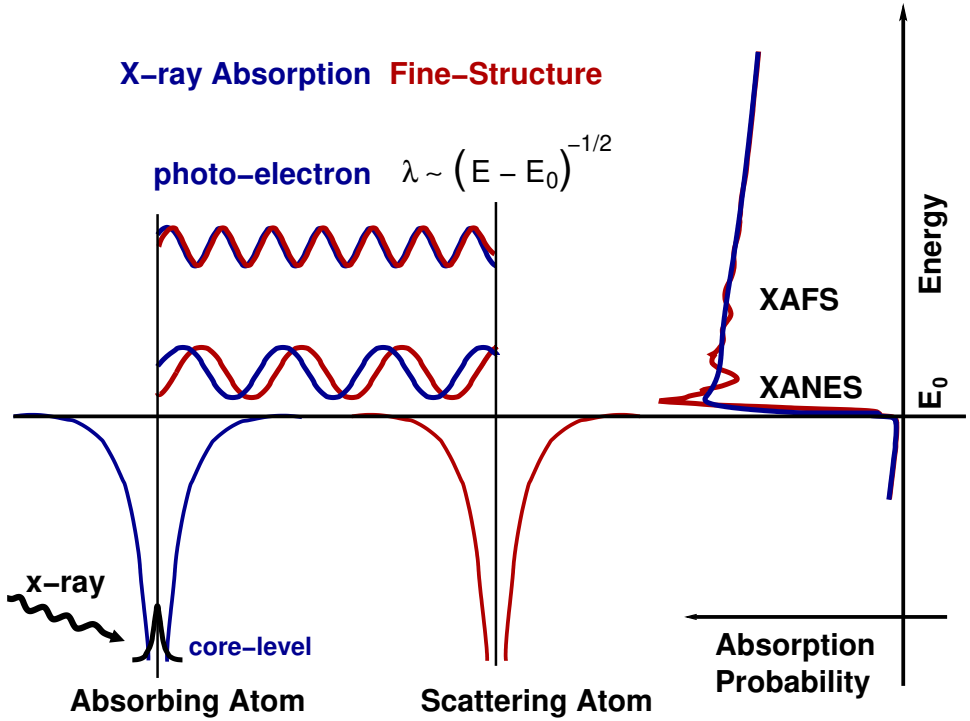

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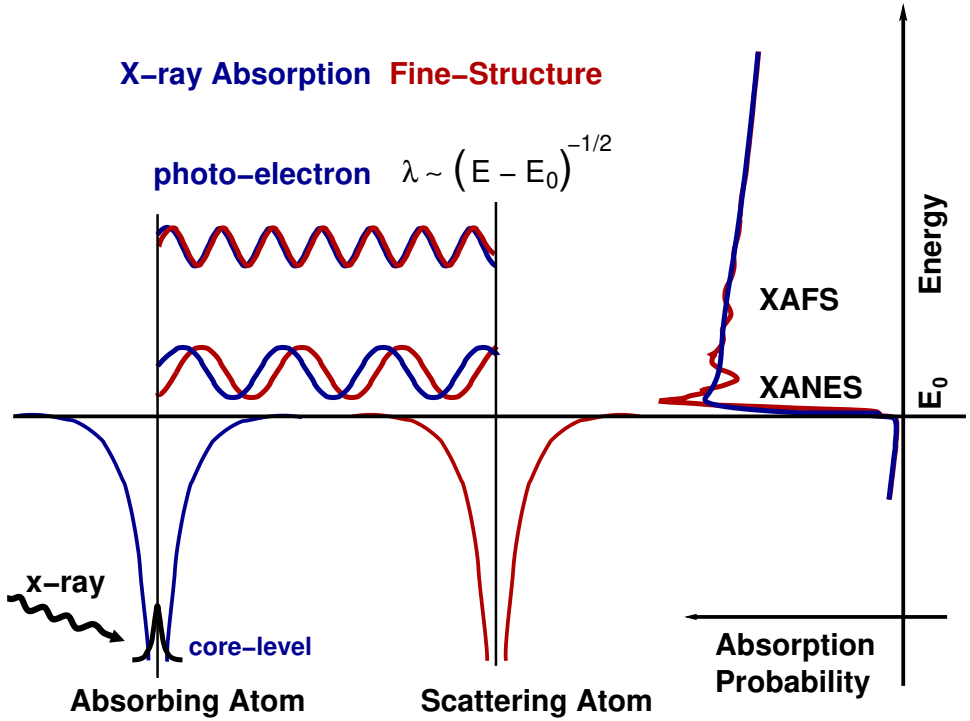

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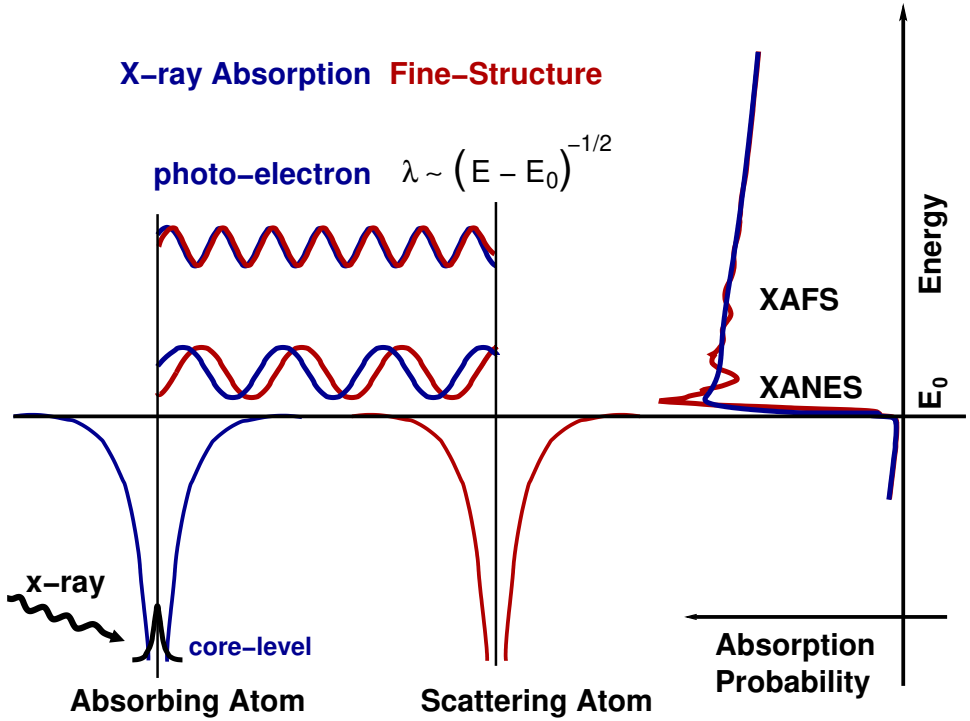

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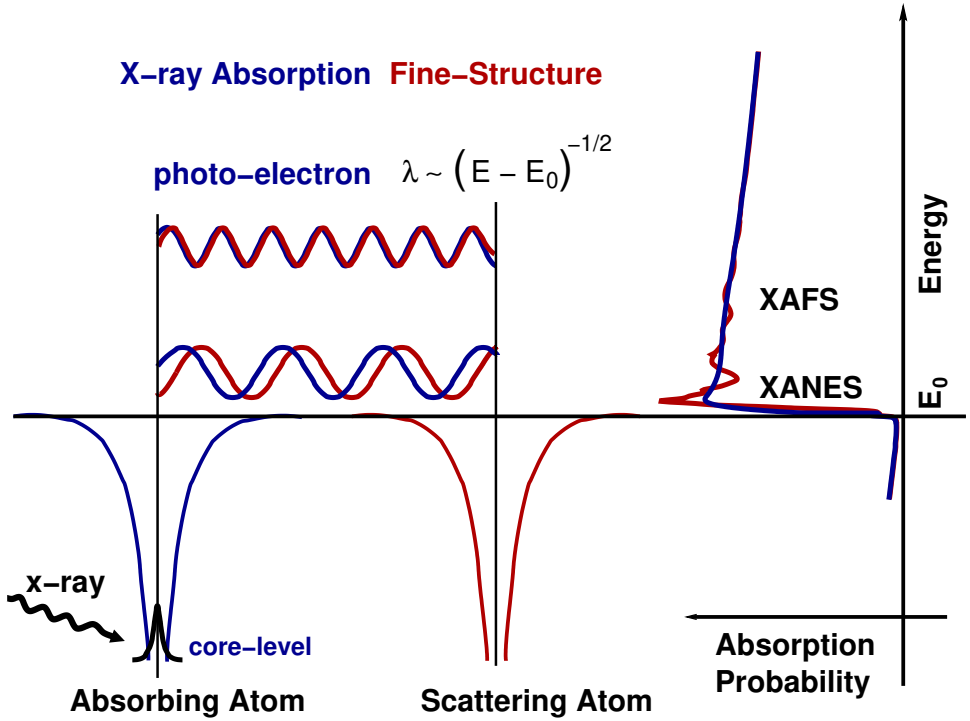

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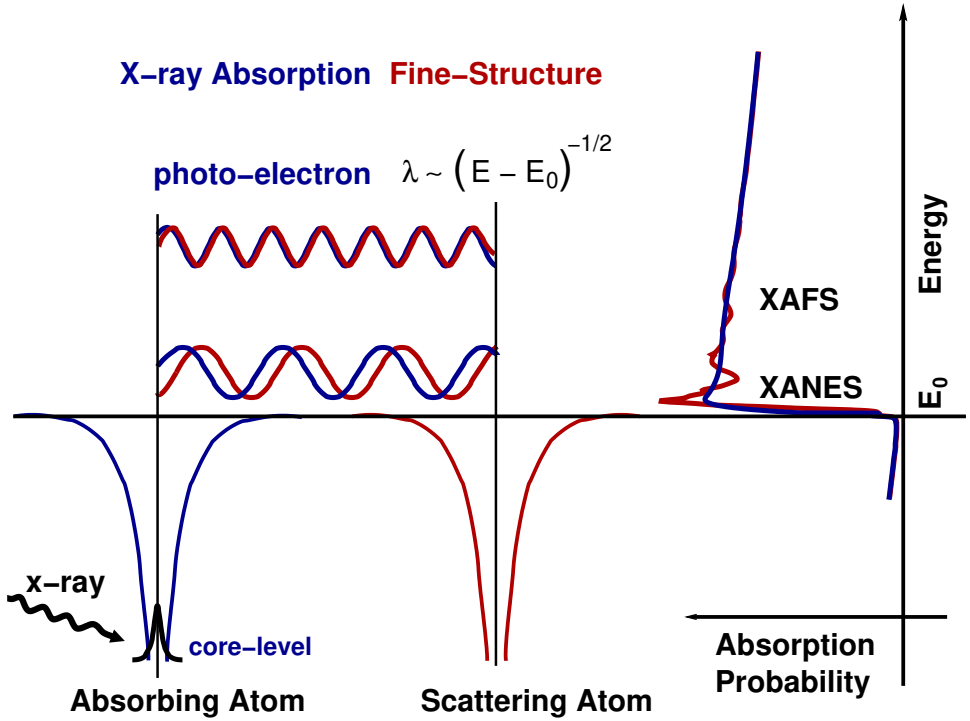

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$|f\rangle$ is the final state which has a photoelectron, a hole in the core, and no photon. This is altered by the neighboring atom: the photoelectron scatters.

μ and χ and the photoelectron wavefunction

Writing $|f\rangle = |f_0 + \Delta f\rangle$, where Δf gives the change in photoelectron final state due to backscattering from the neighboring atom, we can expand μ to get

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Compare this to $\mu(E) = \mu_0(E)[1 + \chi(E)]$ and we see that

$$\mu_0(E) \sim |\langle i|\mathcal{H}|f_0\rangle|^2 \qquad \text{atomic background}$$

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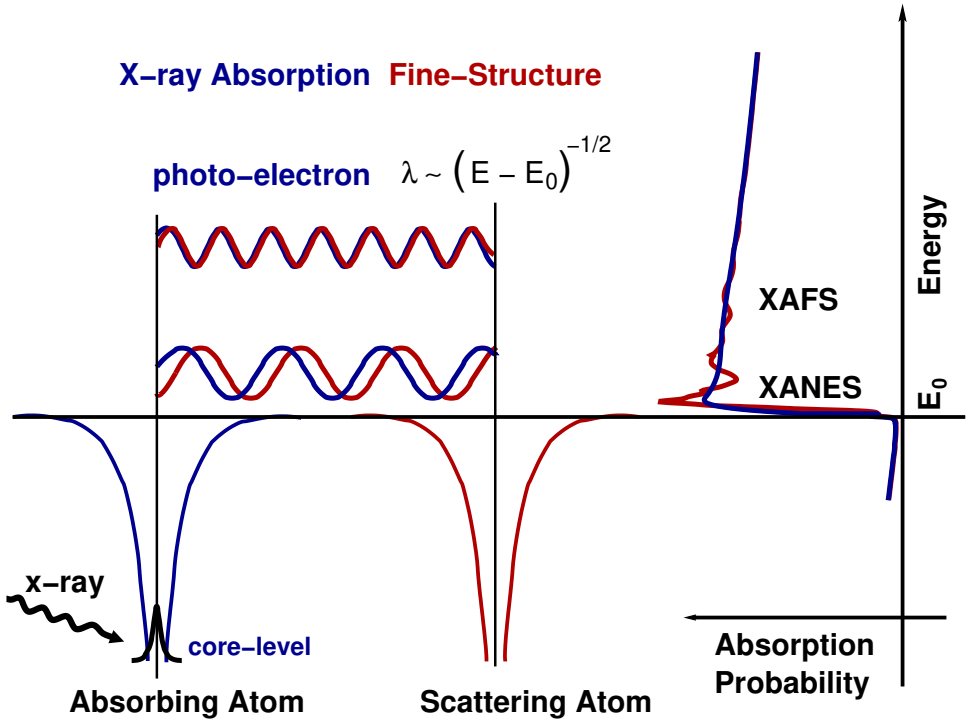
Computing the scattered wavefunction

Assume that emitted photoelectron is a spherical wave



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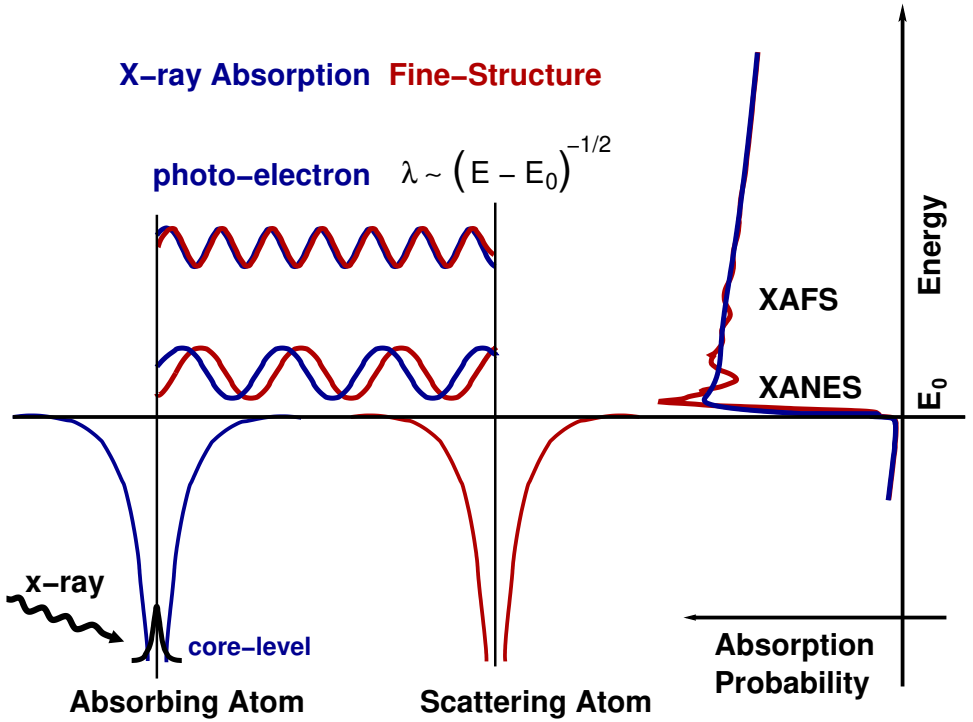

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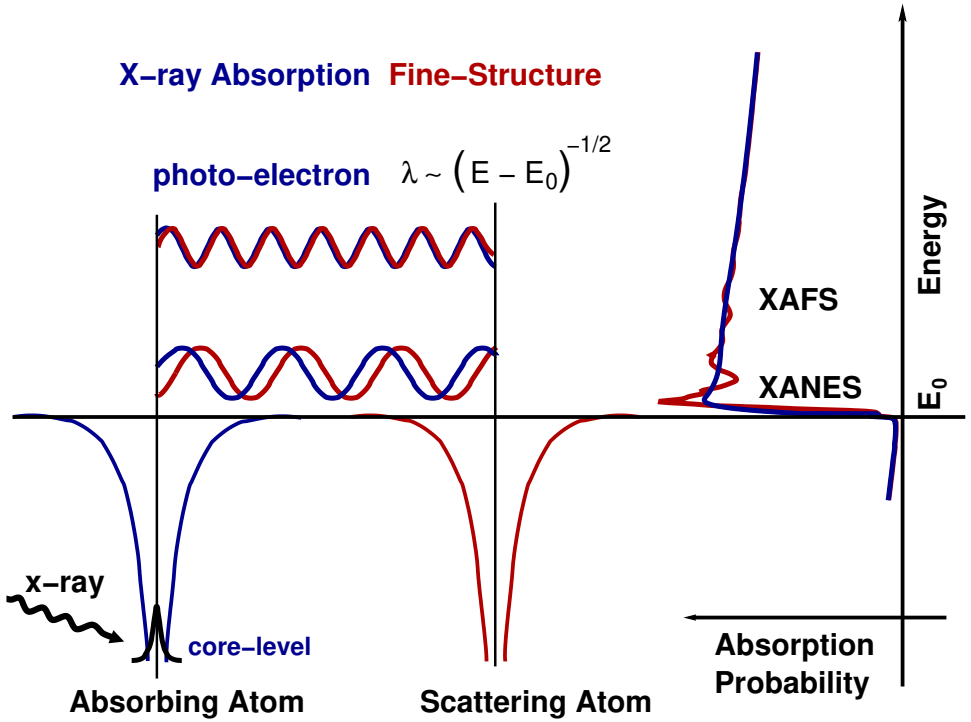

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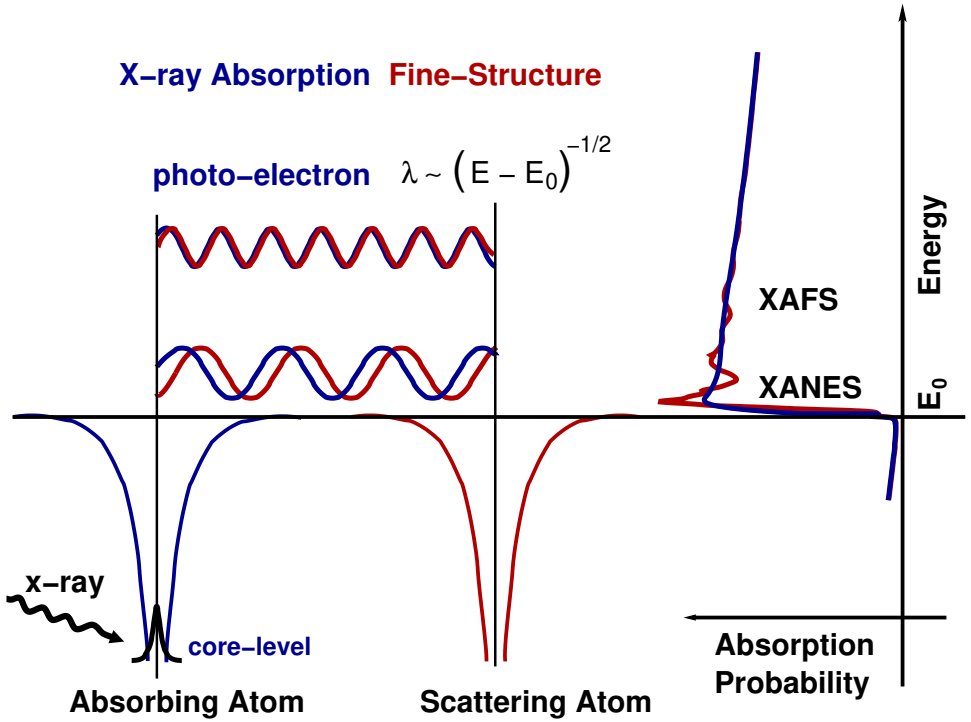

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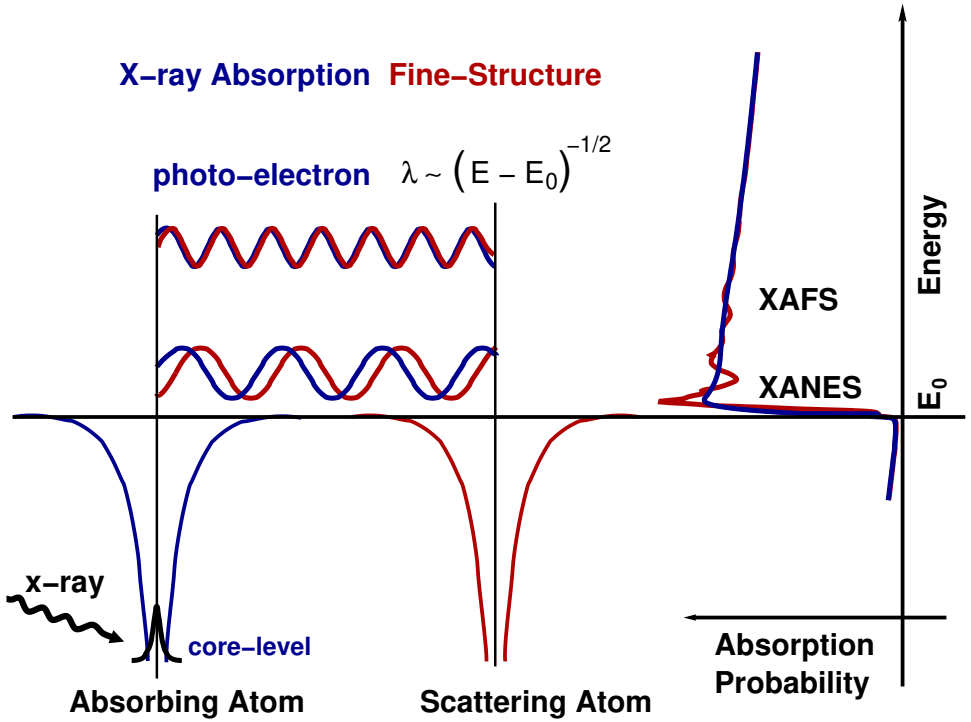

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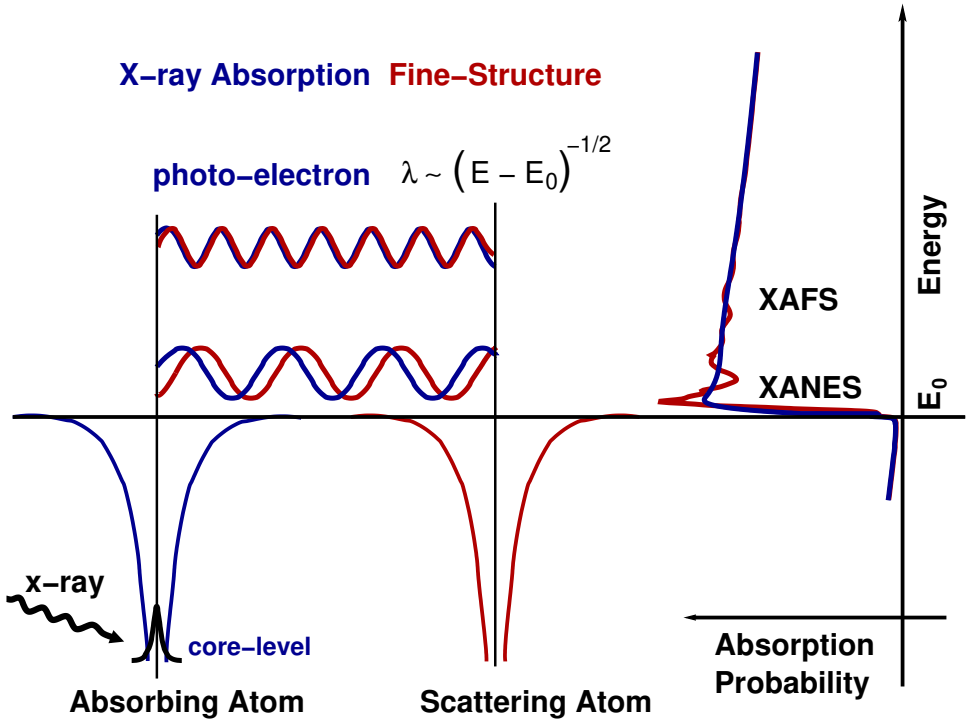

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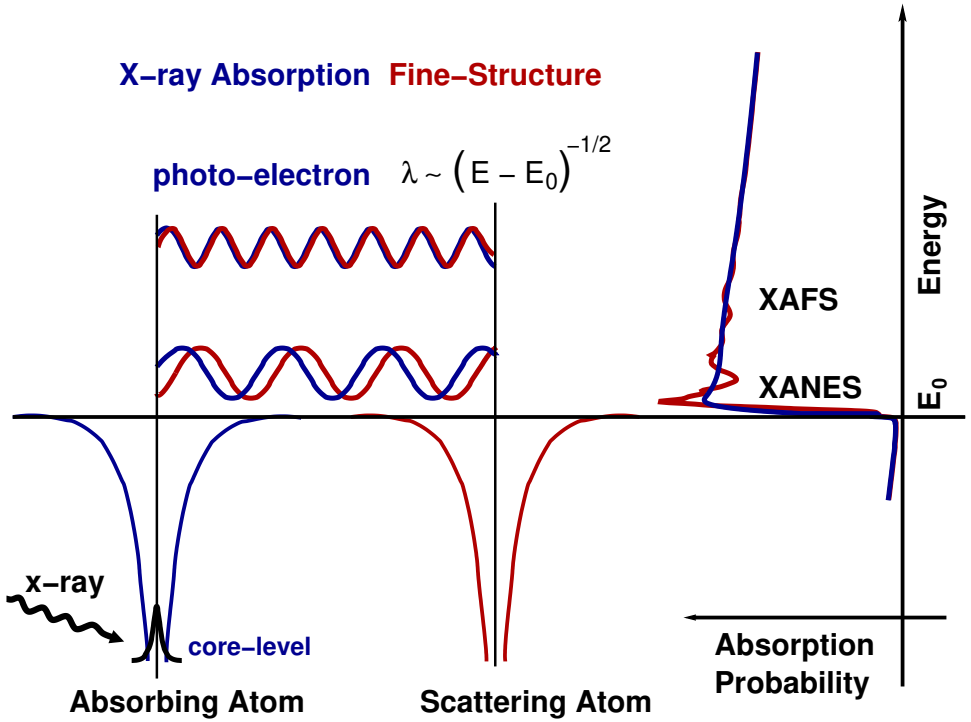

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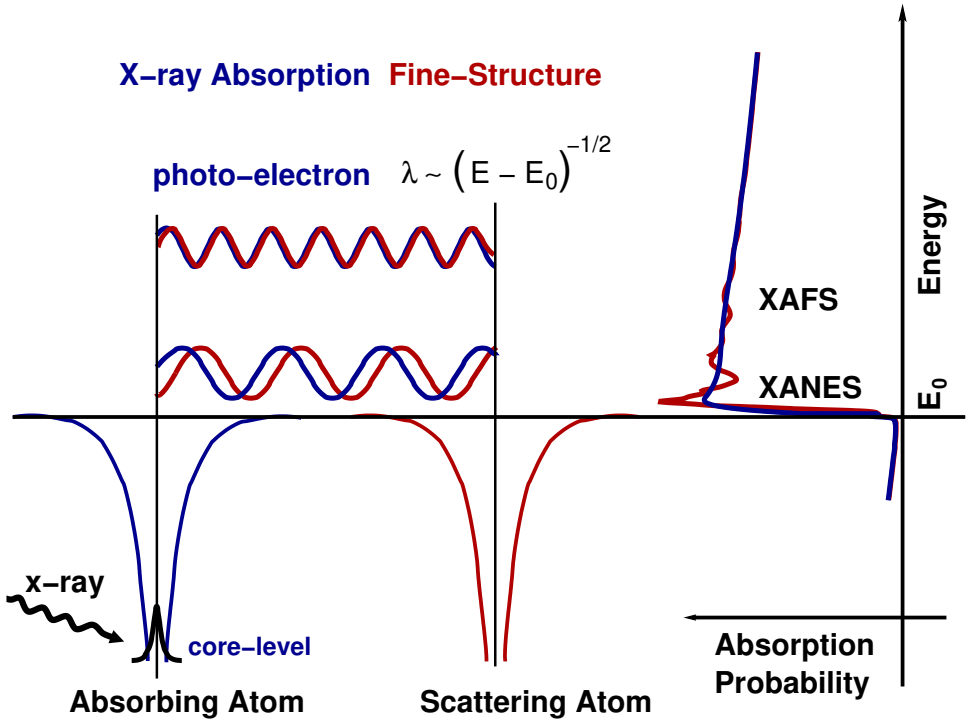

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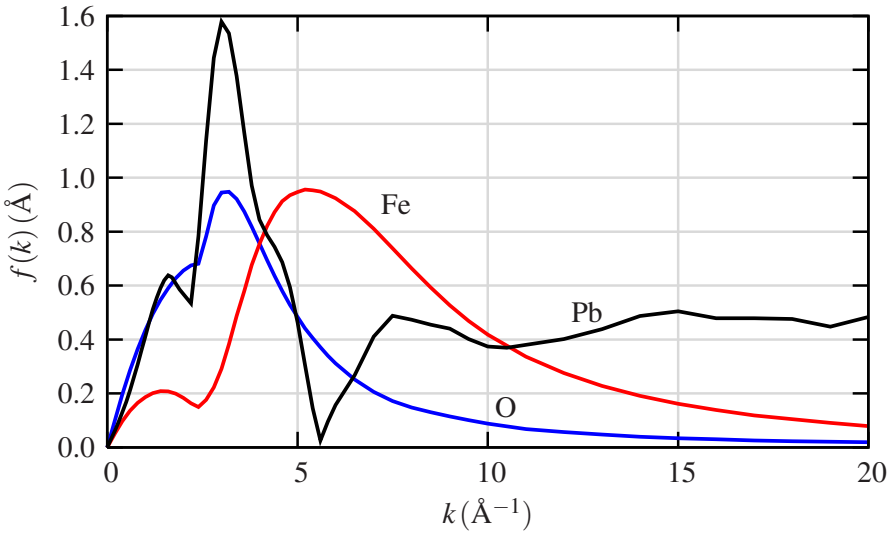

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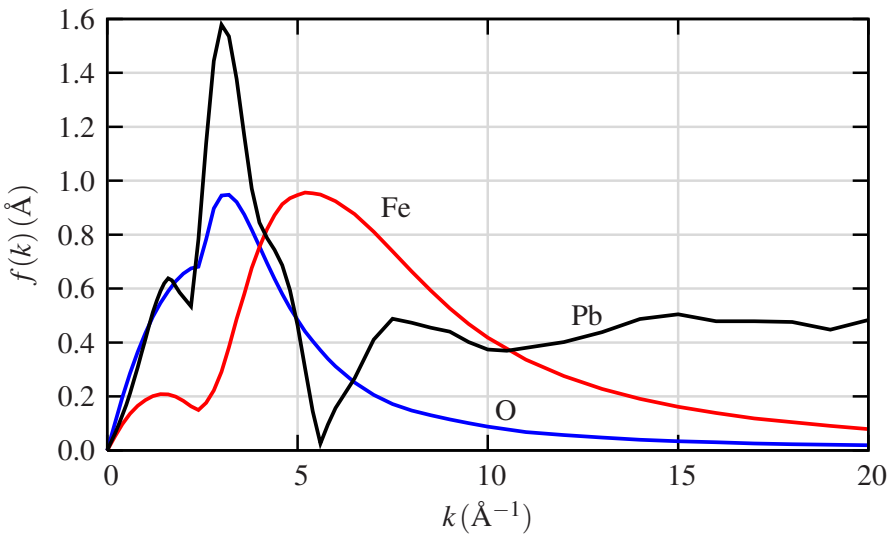

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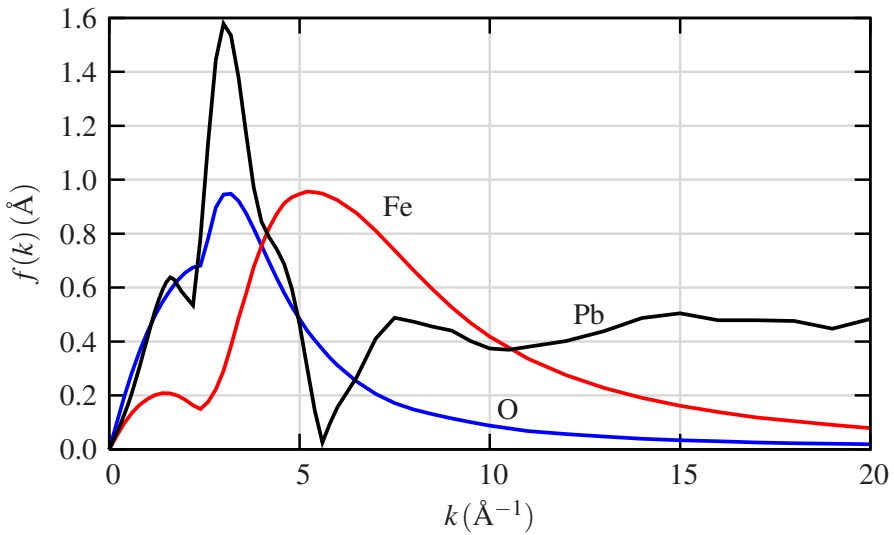

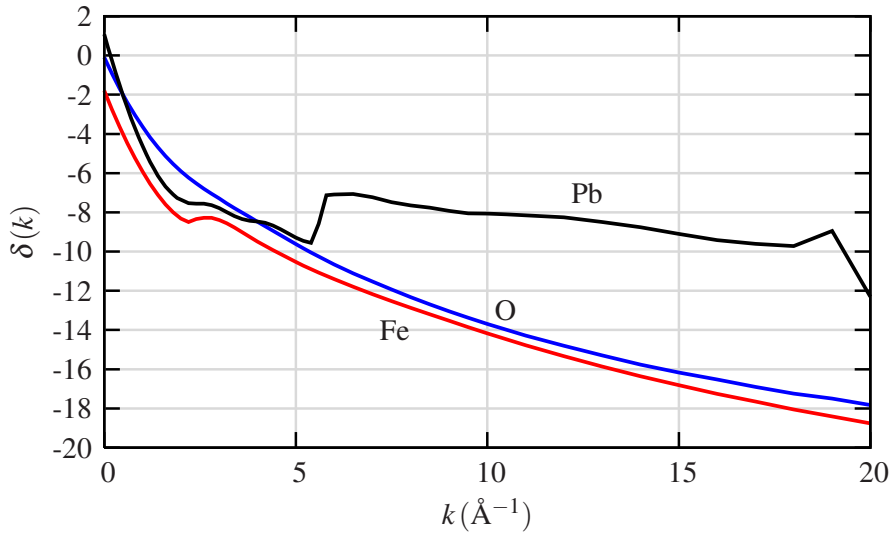

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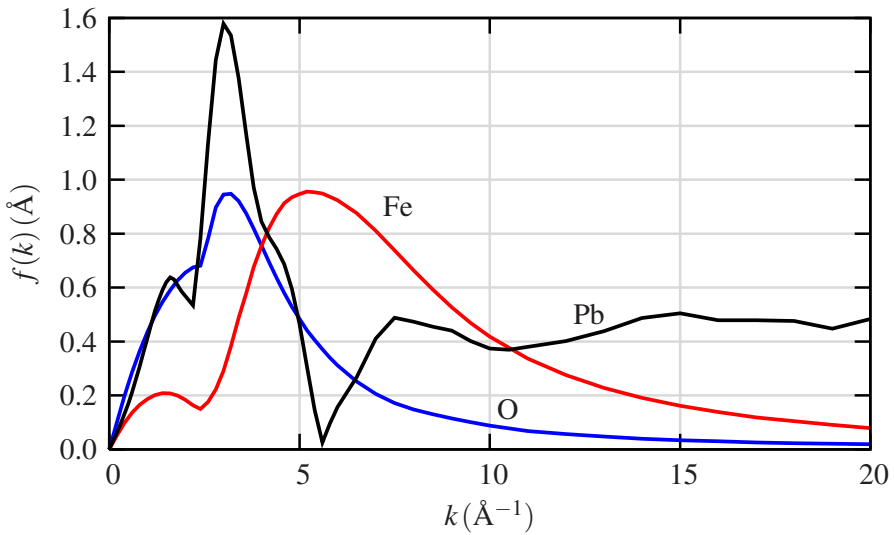

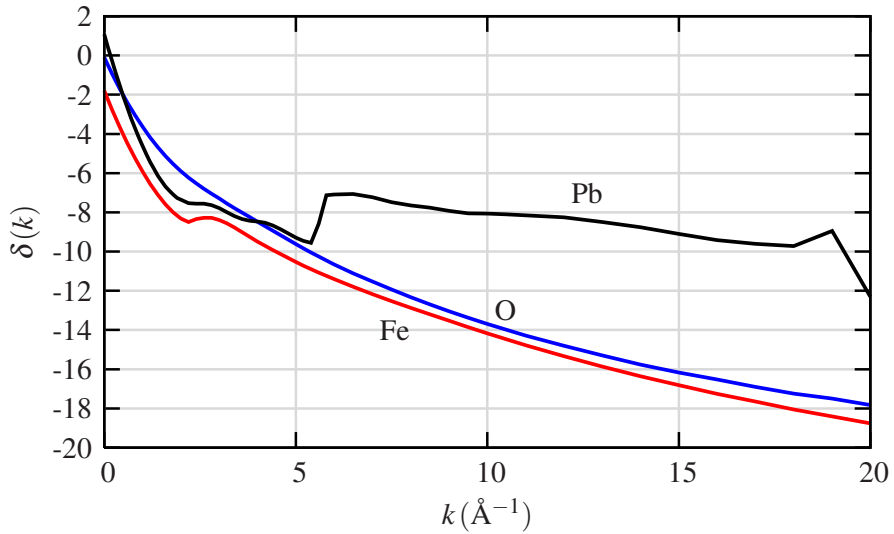

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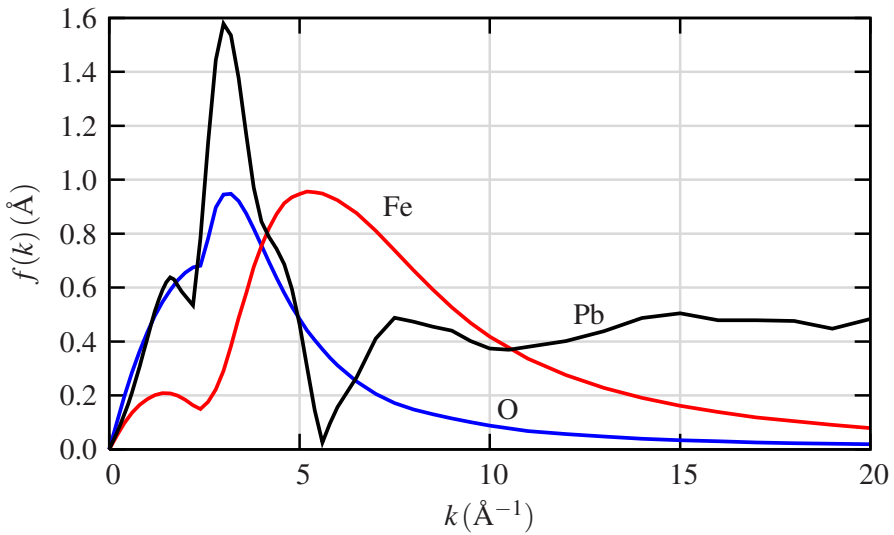

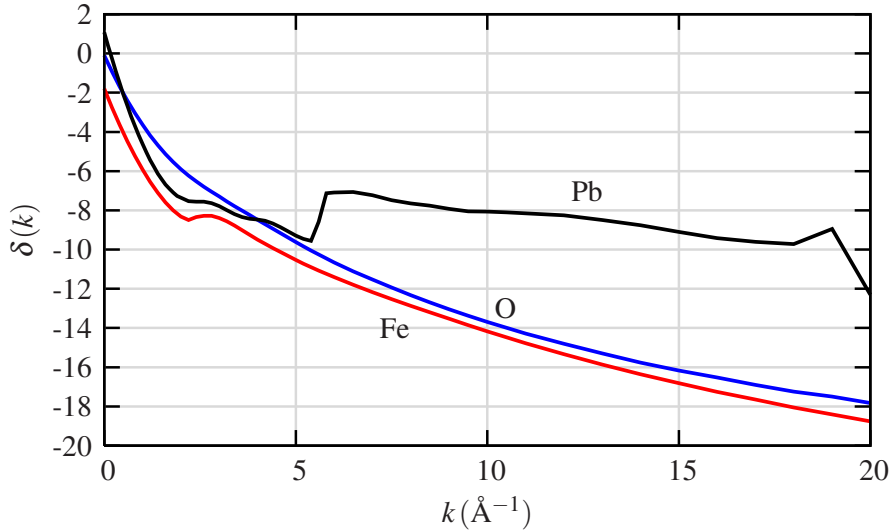

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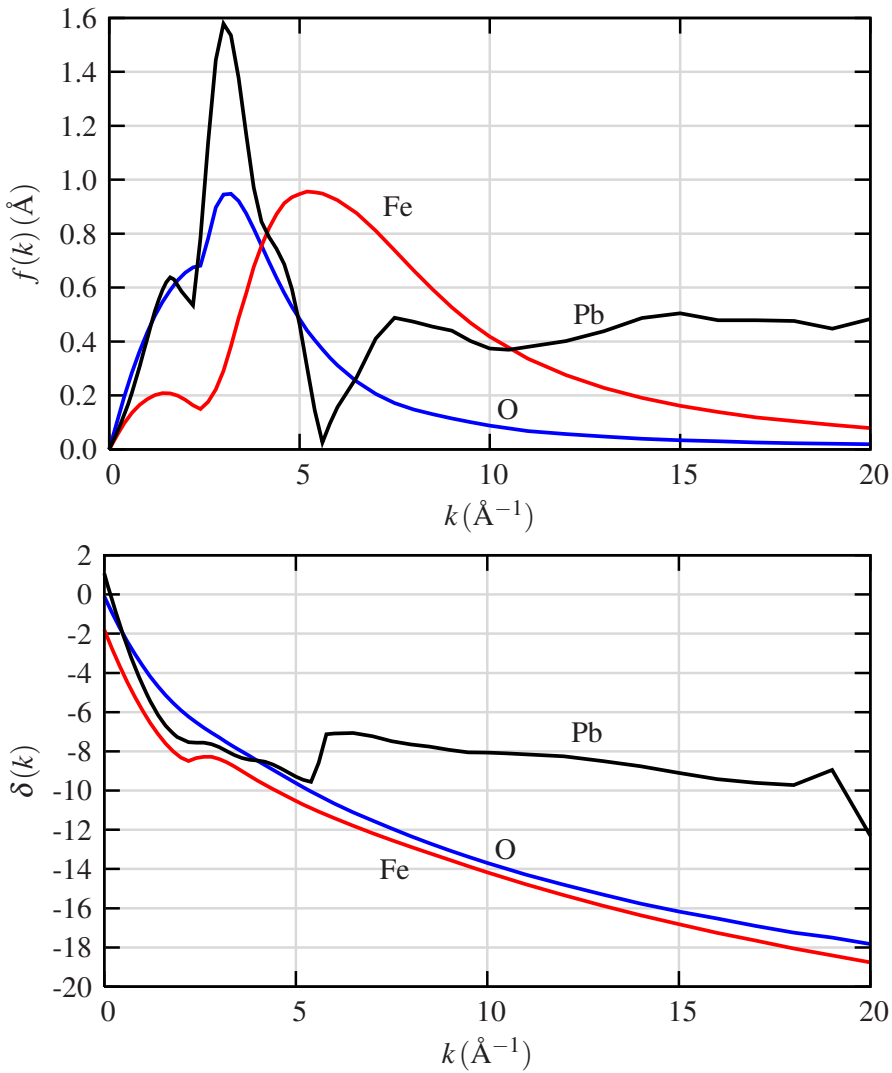

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Z can usually be determined to ± 5. Fe and O can be distinguished, but Fe and Mn cannot be

The EXAFS equation: What we left out

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Generally, the calculations (FEFF, etc) include these effects. We'll discuss of few of these in more detail ...

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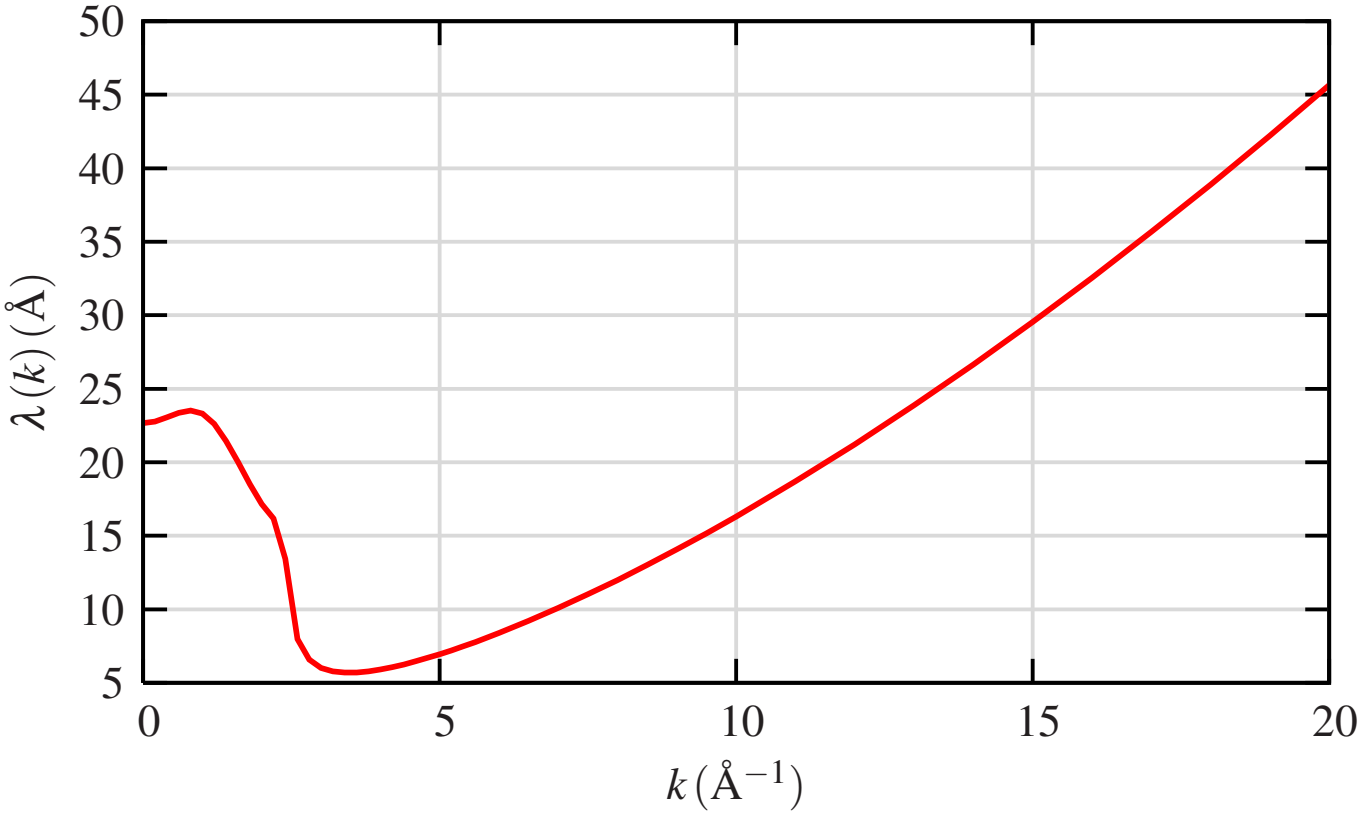

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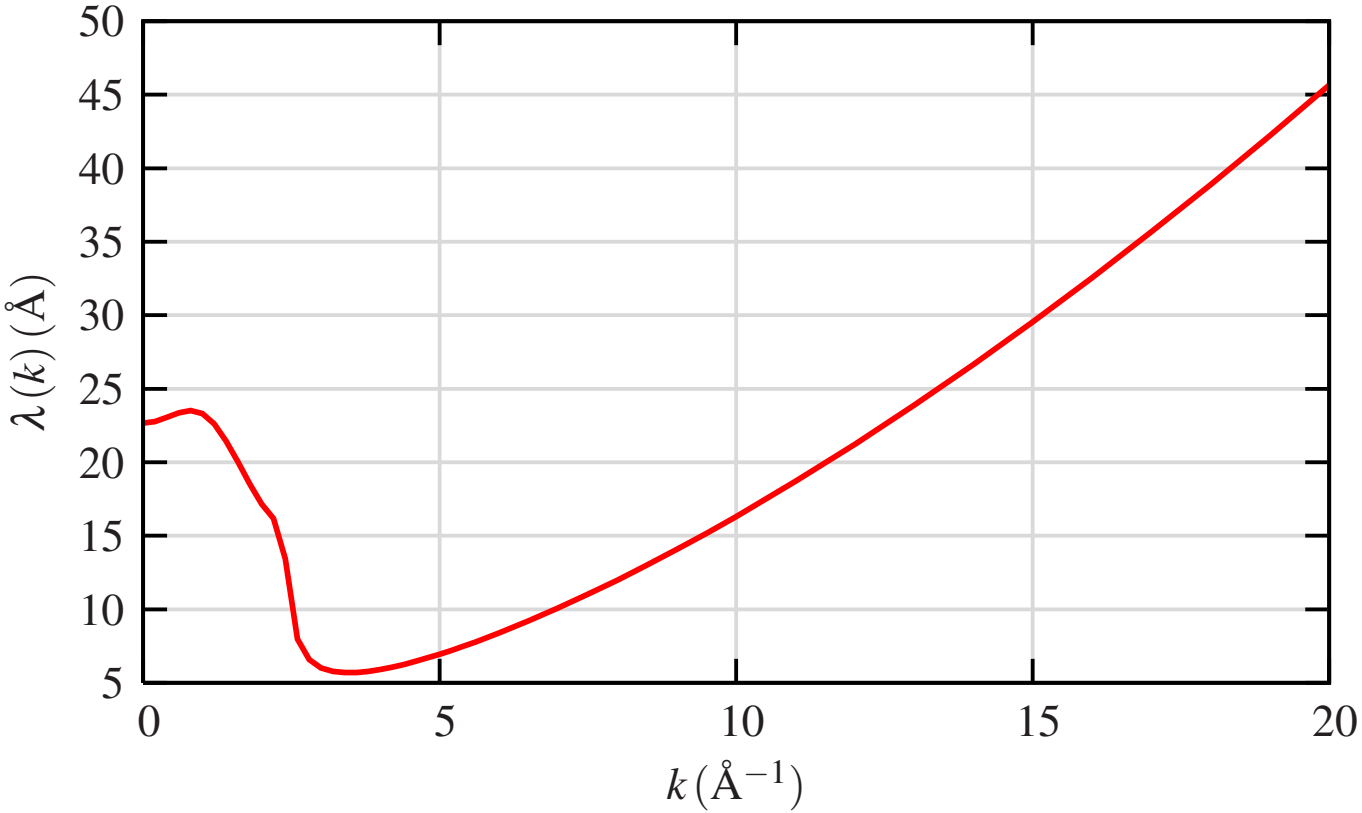

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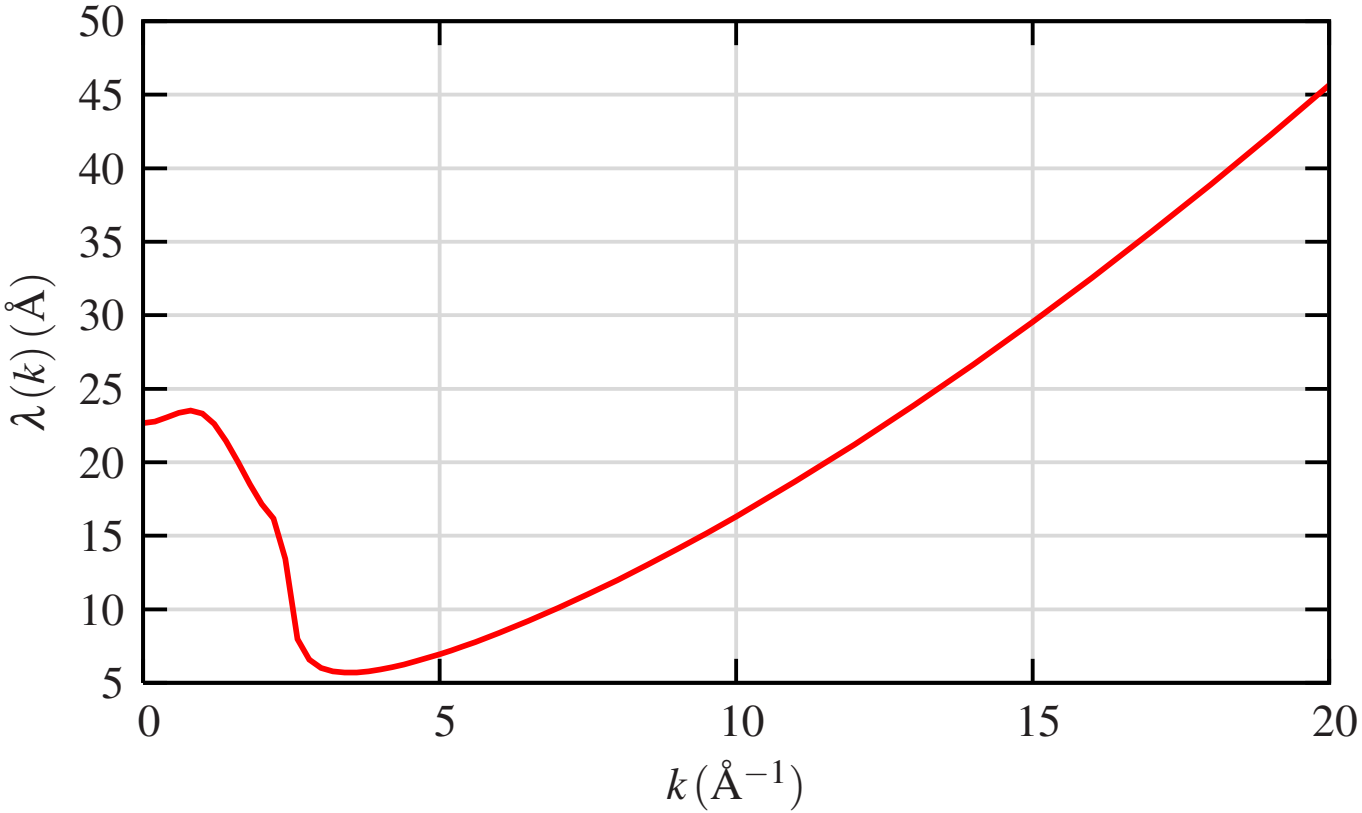

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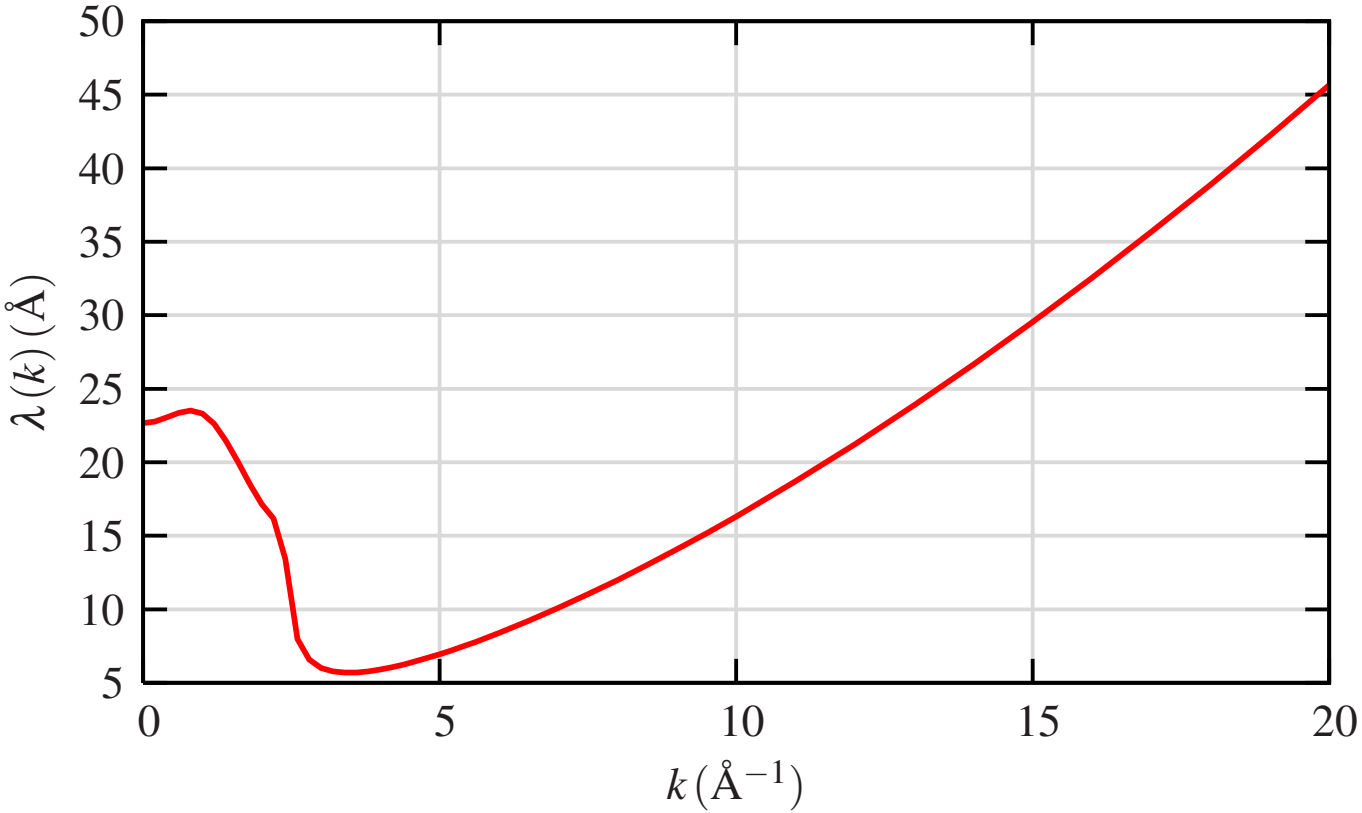

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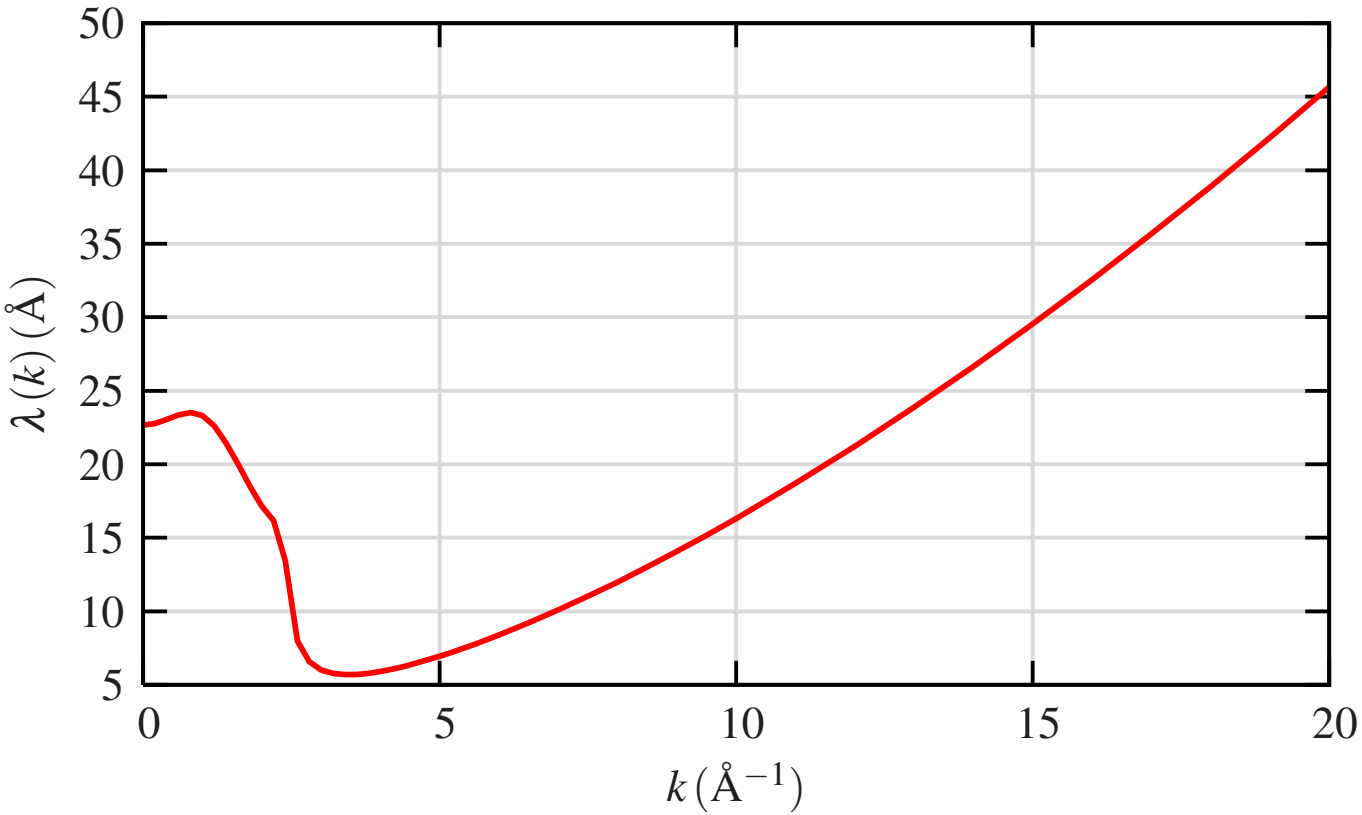

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- for XANES ($k < 3\,\text{Å}^{-1}$), both λ and R^{-2} become large: making XANES not really a local probe

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This, and other experimental and theoretical issues, make EXAFS amplitudes (and therefore N) less precise than EXAFS phases (and therefore R)

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Because we can compute $f(k)$ and $\delta(k)$, and $\lambda(k)$ we can determine Z, R, N, and σ^2 for scattering paths to neighboring atoms by fitting the data.

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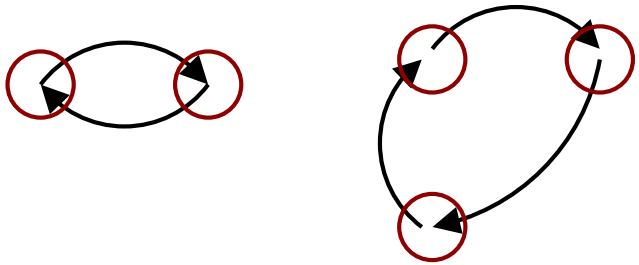

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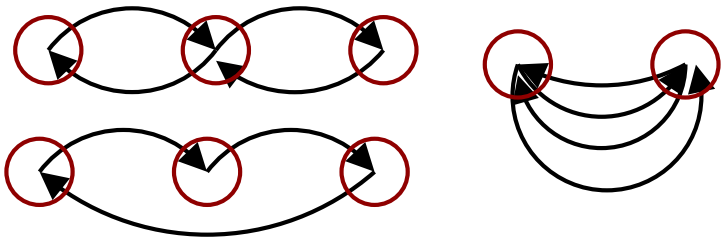

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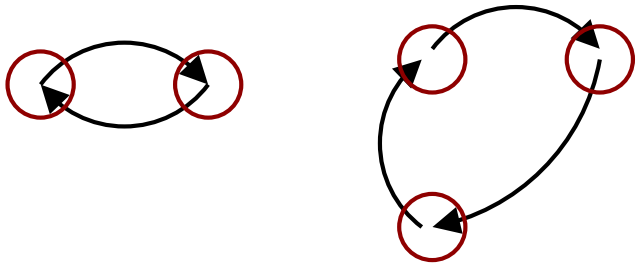

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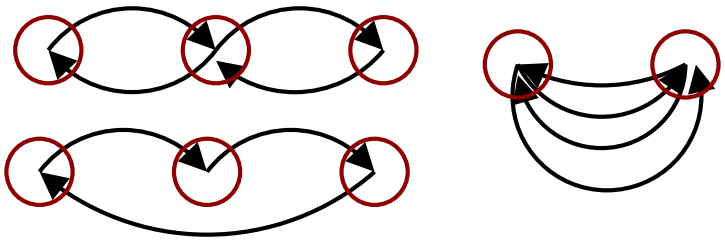

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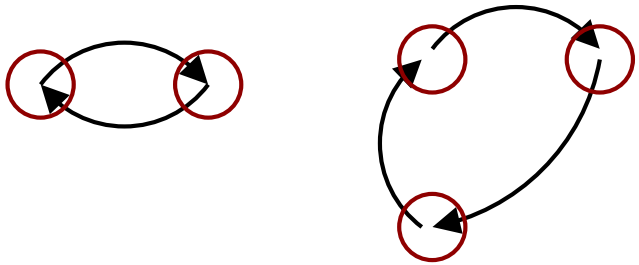

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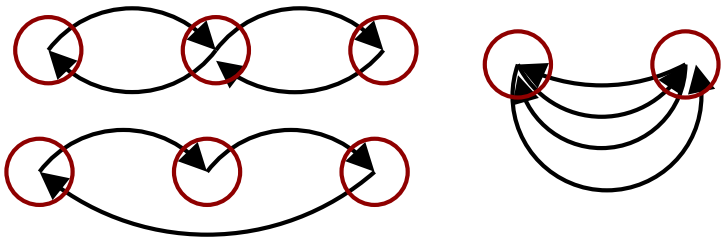

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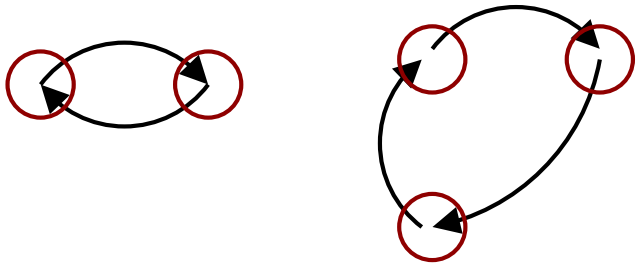

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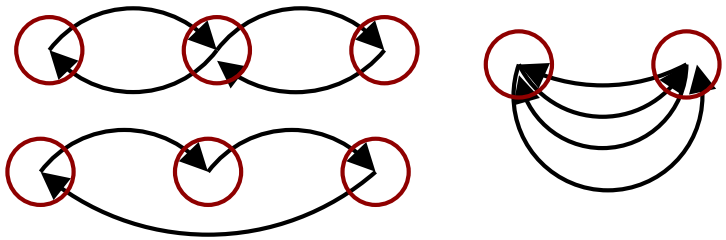

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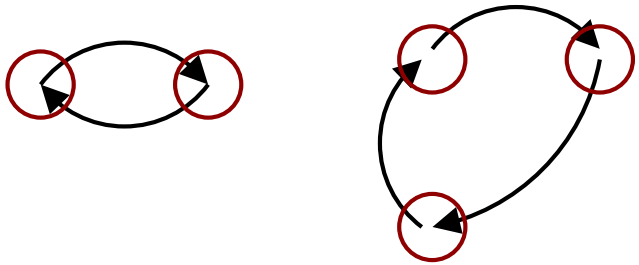

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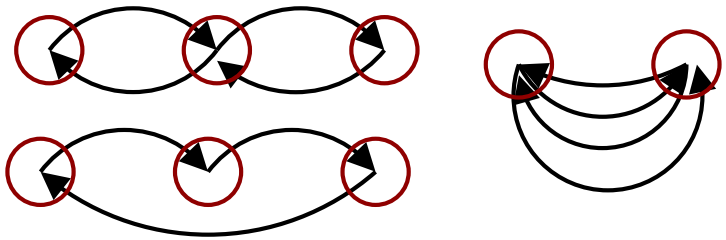

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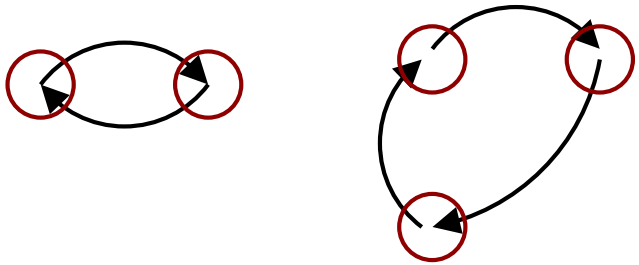

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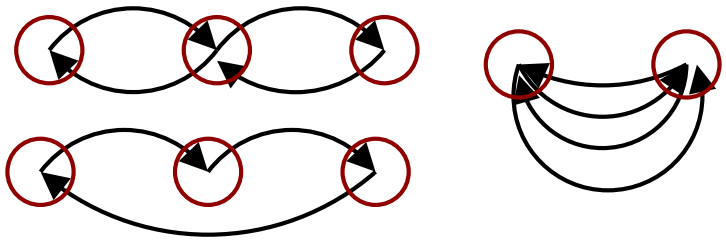

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For first shell analysis, multiple scattering is hardly ever needed

Today's Outline - March 26, 2020 (part C)

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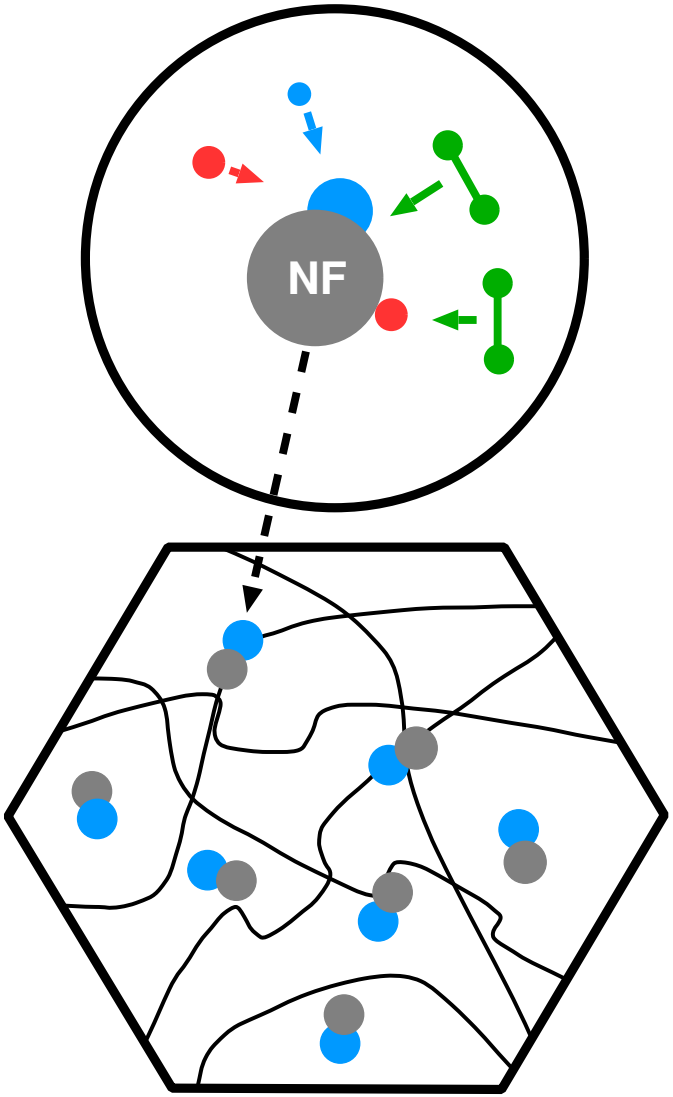
- Local structure of nanoferritic alloy steels

Advantages of nanoferritic alloy (NFA) steels



High density nanofeatures (NFs) and dislocations provide irradiation damage resistance

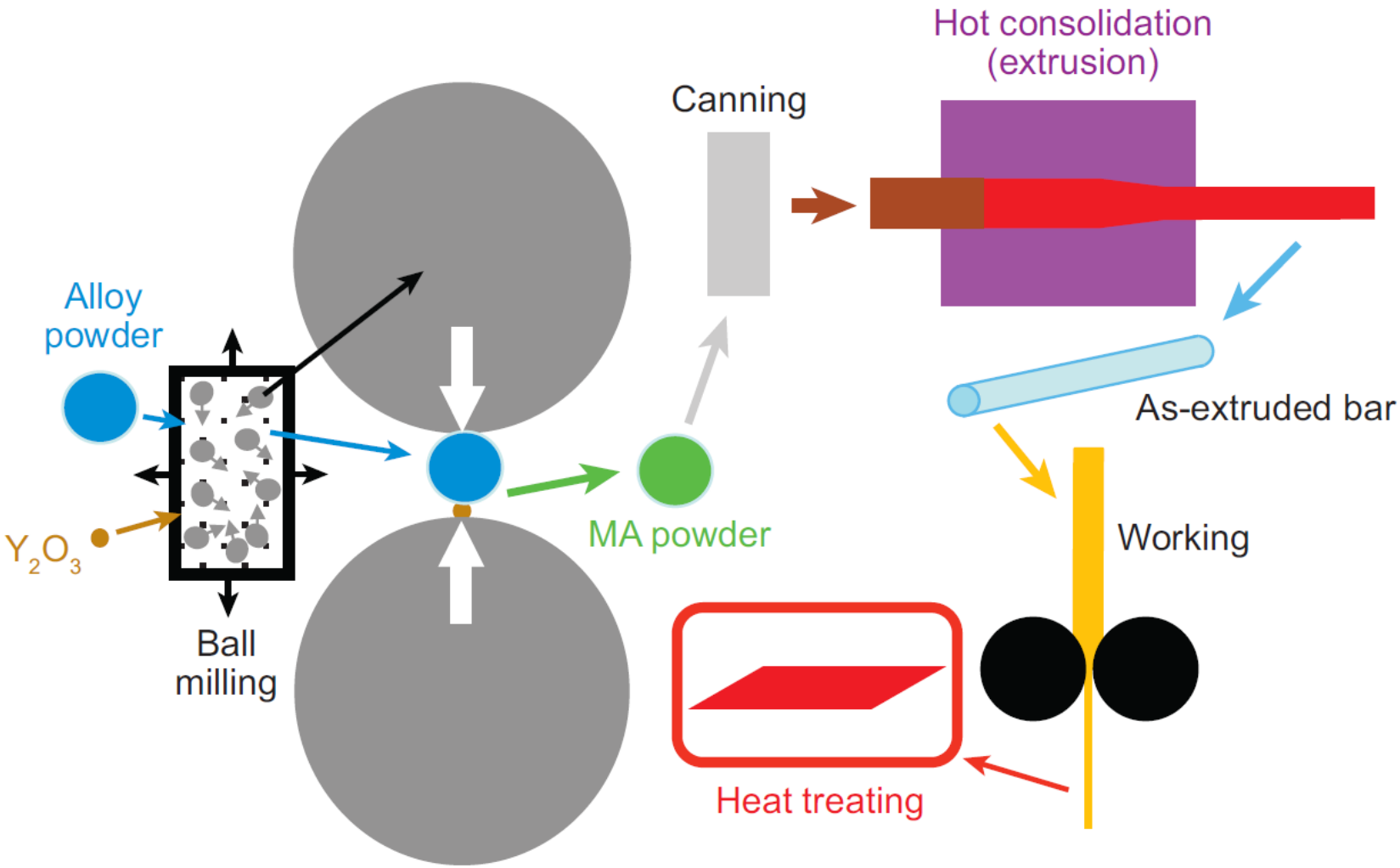
NFs trap helium in fine bubbles and prevent accumulation of high concentrations

NFs maintain high stable sink densities for vacancy and self-interstitial atom defect annihilation

NFs maintain high creep strength because of dislocation pinning, allowing operation at temperatures above the displacement damage regime

G.R. Odette, M.J. Alinger, and B.D. Wirth, *Annu. Rev. Mater. Res.* **38**, 471–503 (2008).

Fabrication of NFA steels



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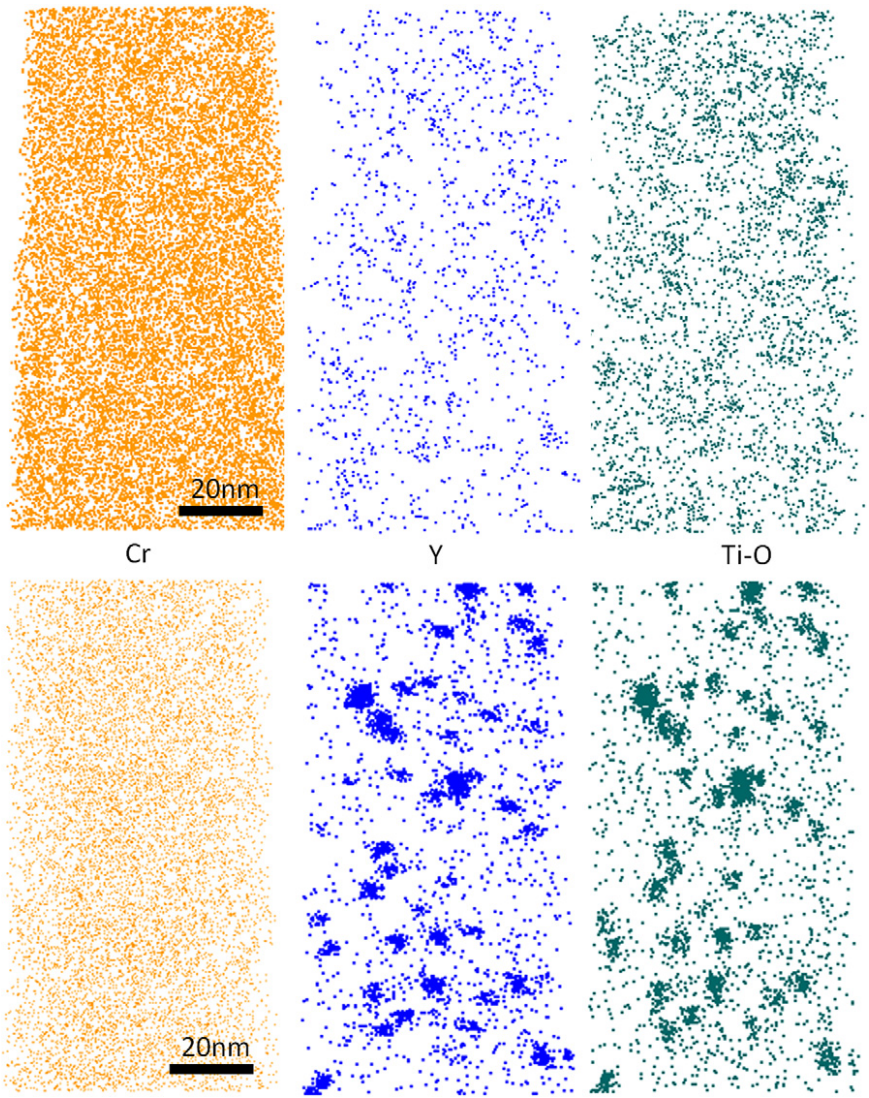
Atom probe tomography data



After mechanical alloying, Cr, Ti and Y are uniformly distributed throughout the solid

Consolidated materials show Ti-O and Y to be primarily co-localized in nanoclusters

Use XAS to understand the local structure of these nanoclusters

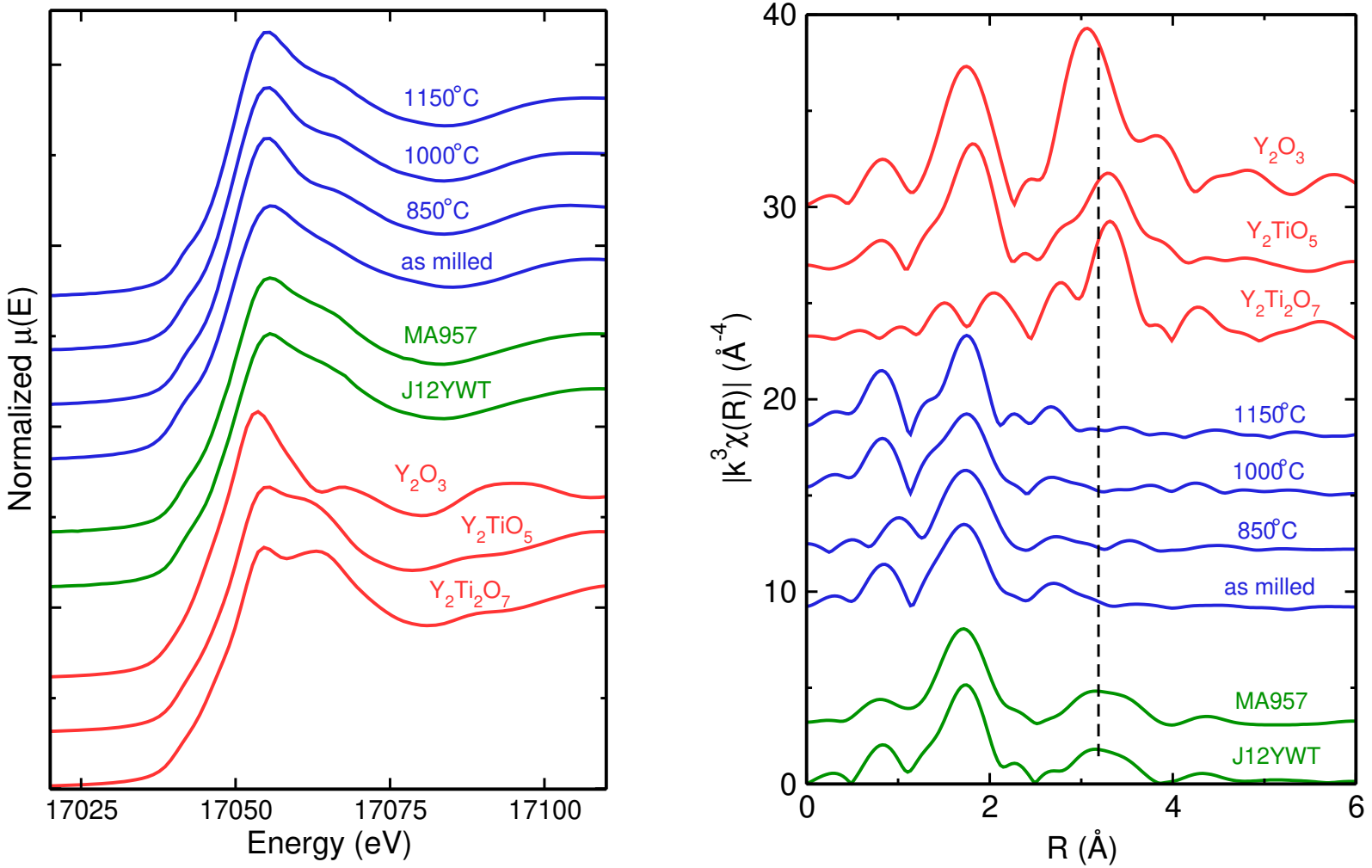
C.A. Williams, P. Unifantowicz, N. Baluc, G.D.W. Smith, and E.A. Marquis, *Acta Materialia* **61**, 2219–2235 (2013).

Samples studied

Sample name	Composition (wt %)					Processing
	Cr	Ti	Mo	W	Y_2O_3	
MA957	14	1	0.3		0.3	hot extruded @ 1150°C
J12YWT	12	0.4		3	0.25	hot extruded @ 1150°C
as received	14	0.4		3		as received powder
as milled	14	0.4		3	0.25	mechanically alloyed powder
850°C	14	0.4		3	0.25	powder annealed @ 850°C
1000°C	14	0.4		3	0.25	powder annealed @ 1000°C
1150°C	14	0.4		3	0.25	powder annealed @ 1150°C

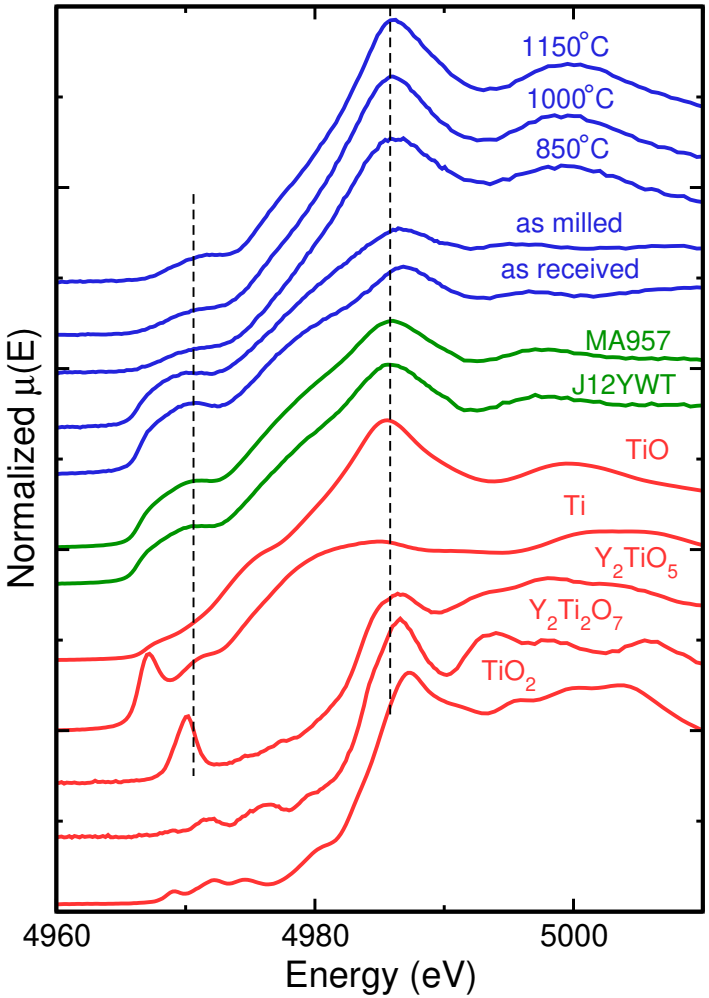
Samples consolidated from as milled powder by hot isostatic pressing were shown to be identical to annealed powders and are thus not discussed.

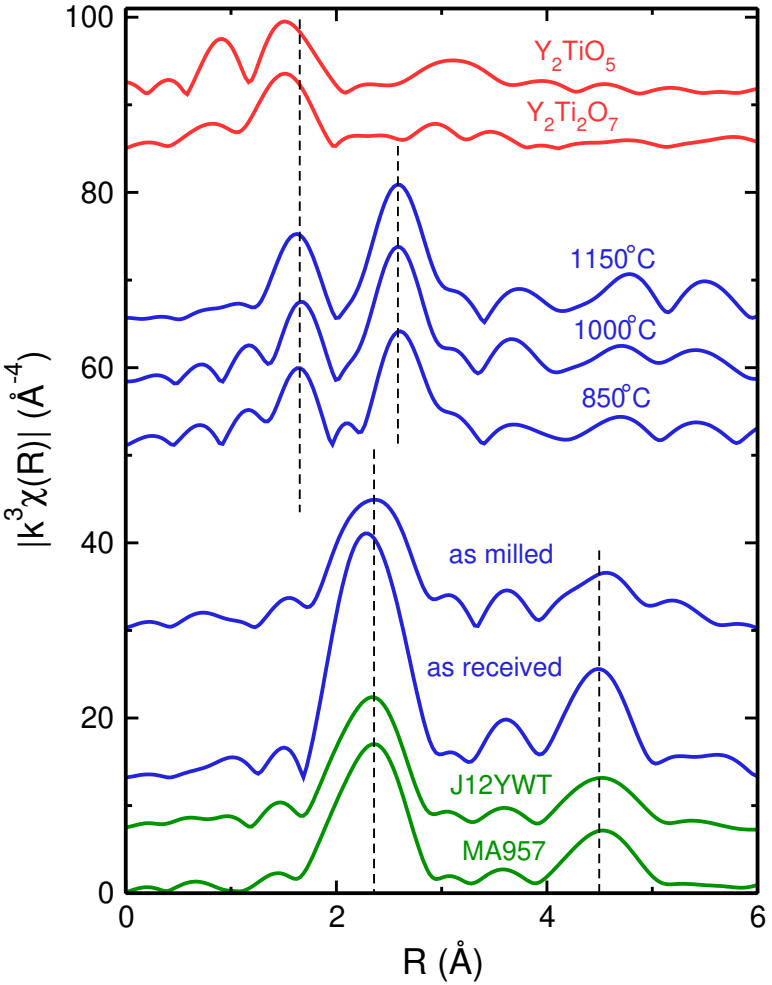
Yttrium edge data



Edges show complex mixture; EXAFS of annealed powders indicate smaller NFs than commercial steels

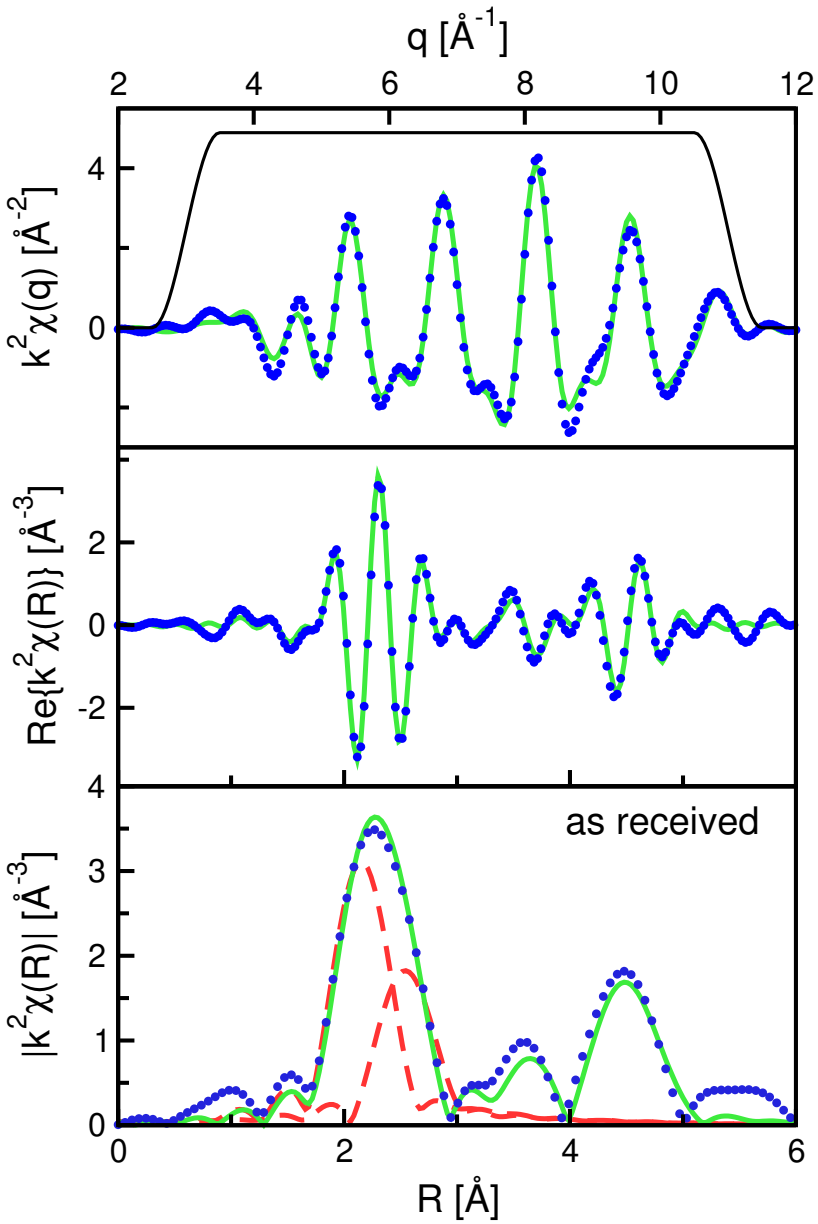
Titanium edge data





As received, as milled and commercial steels all show a metallic environment; annealed powder edges resemble TiO and EXAFS shows a distinct heavy metal peak at ~ 2.6Å

Ti in BCC structure



As received data can be fit with a simple BCC Fe model

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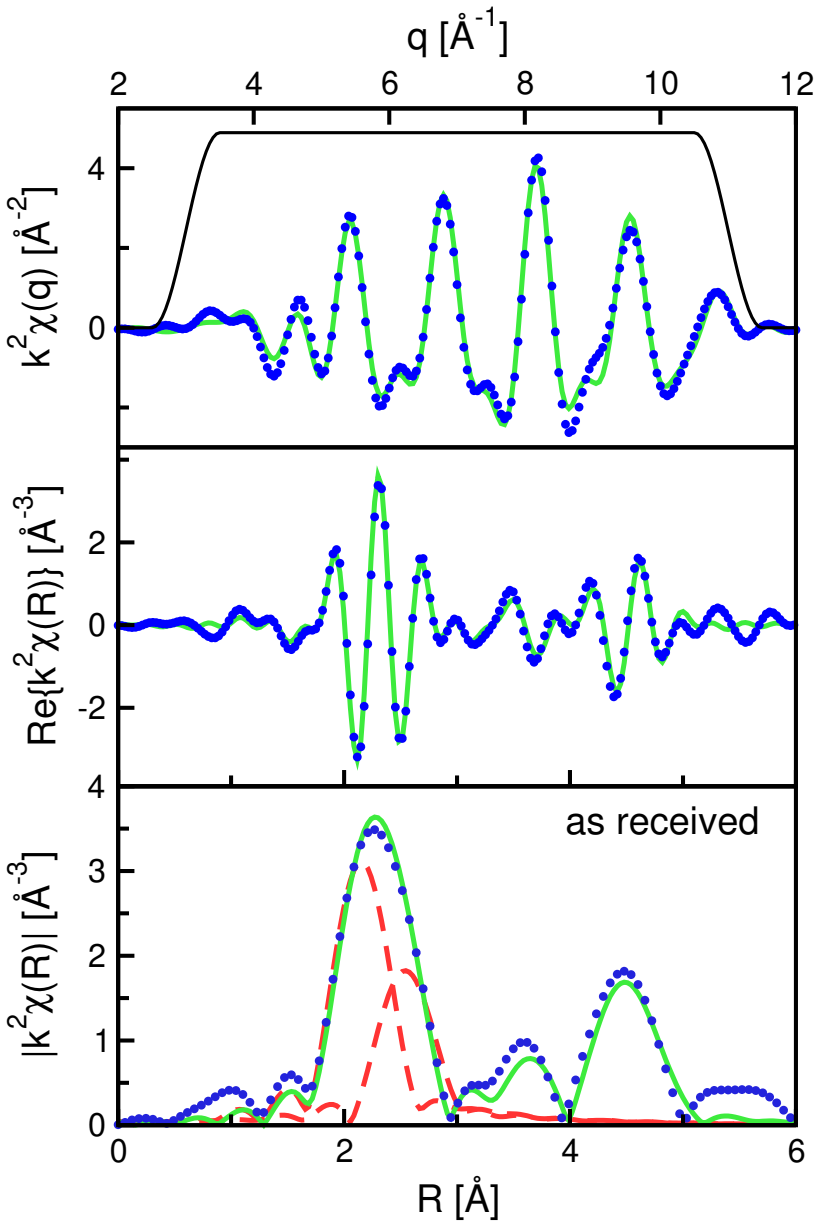

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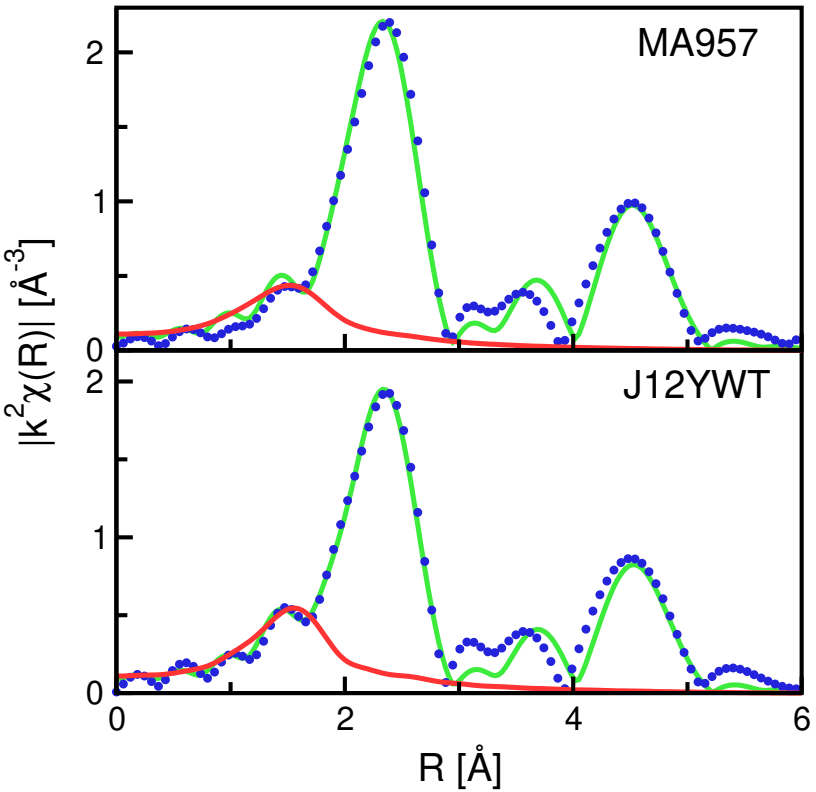
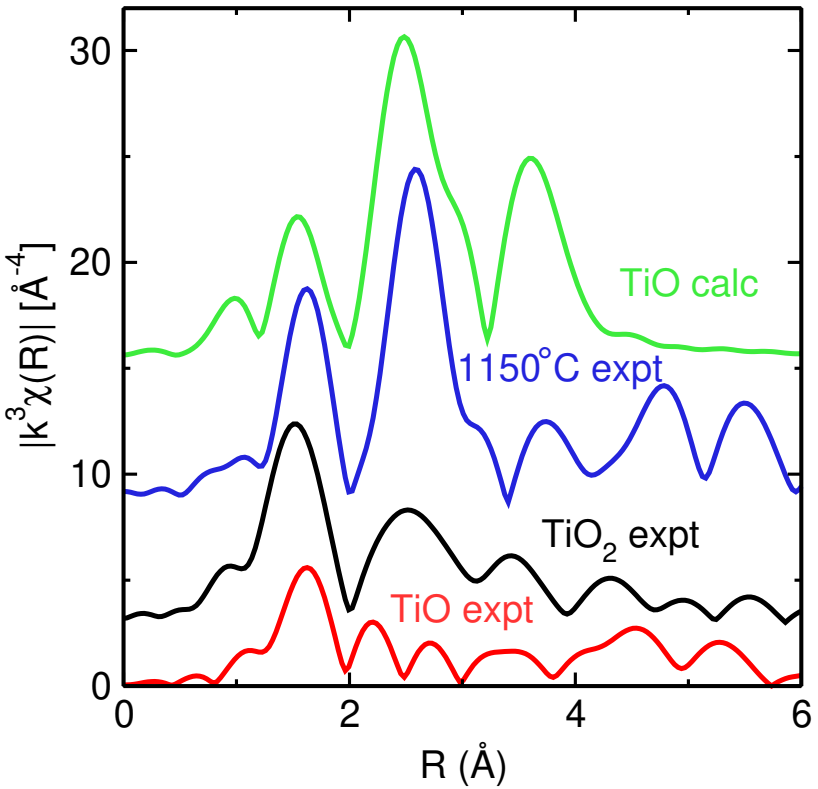


Commercial alloys fit with this model plus a small amount of Ti-O neighbors

Ti in TiO structure

Annealed powders have a remarkable resemblance to the cubic TiO calculated spectrum



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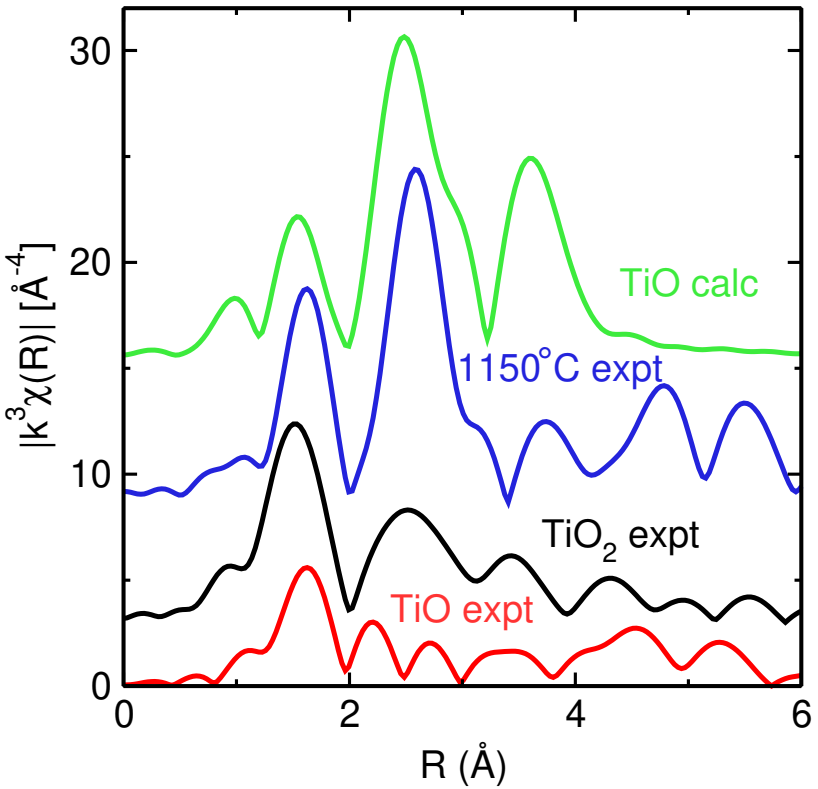
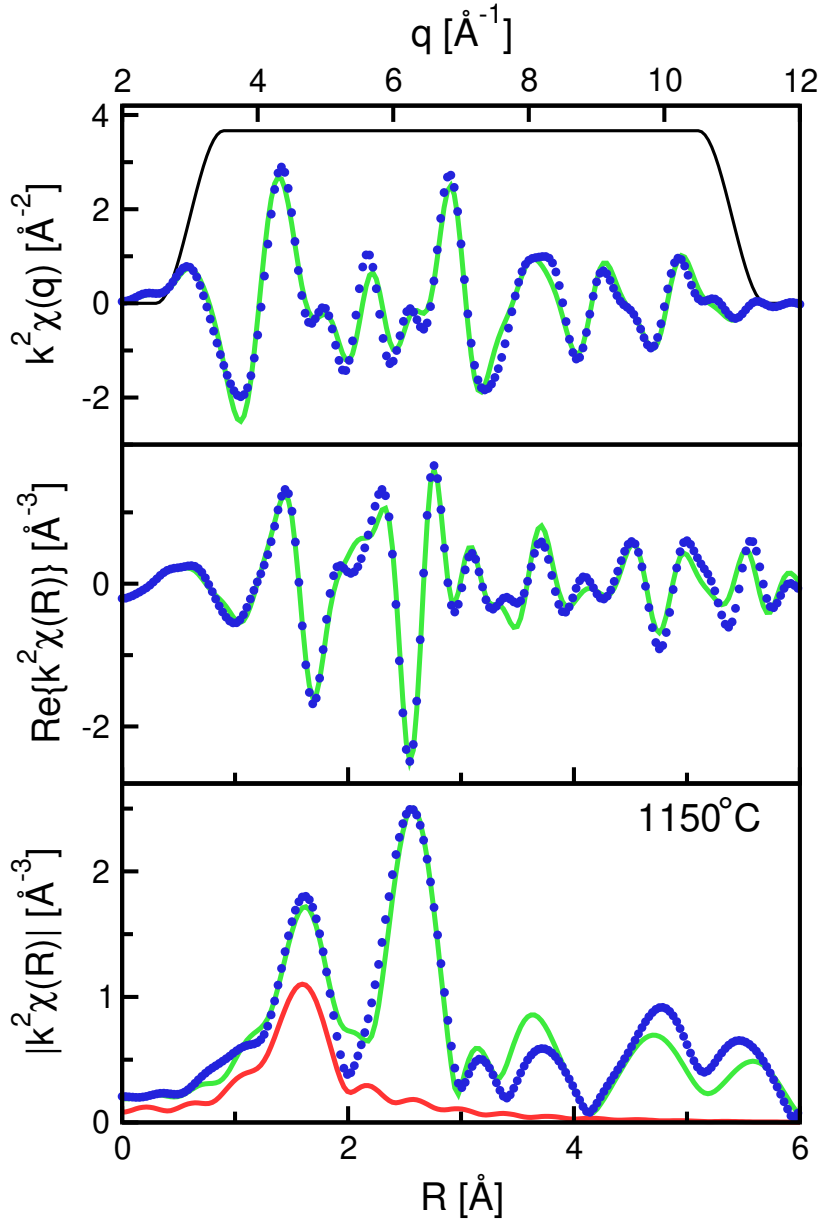


All can be fit with cubic TiO plus an additional Ti–O path, likely from complex Y–Ti–O oxides



The fate of Ti

Commercial steels retain Ti in a metallic BCC lattice for the most part

Annealed powders all have mixture of TiO-like structure and more complex oxides ($\sim$ 50% each)

Presence of this metastable cubic TiO suggests significant fraction of Ti on the surface of Y–Ti–O NFs (consistent with Marquis & Williams)

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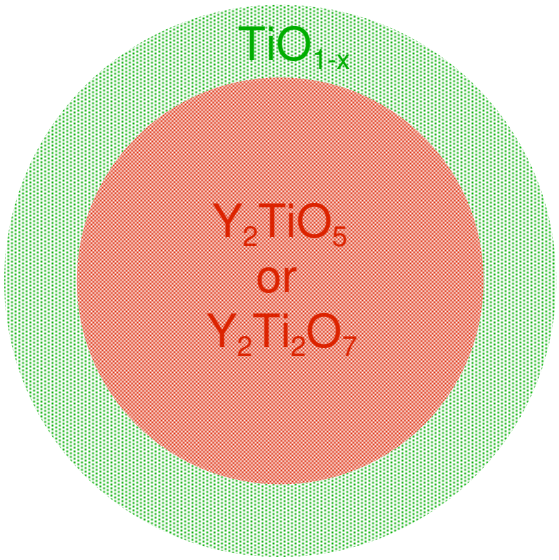

TiO cubic suboxide is stabilized on the surface of the Y–Ti–O nanoclusters

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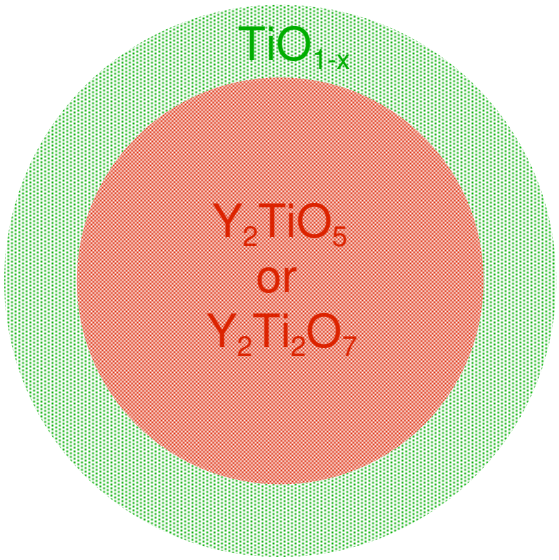

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S. Liu, G.R. Odette, and C.U. Segre, *J. Nucl. Mater.* **445**, 50-56 (2014).