Today's Outline - April 07, 2015

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- PHYS 570 days at 10-ID

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- Final Exam and General User Proposals

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Homework Assignment #06:
Chapter 6: 1,6,7,8,9
due Tuesday, April 14, 2015

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Homework Assignment #06:
Chapter 6: 1,6,7,8,9
due Tuesday, April 14, 2015

No class on Thursday, April 09, 2015

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1. April 10, 2015, 09:00 – 16:00
2. April 24, 2015, 09:00 – 16:00

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6. Let me know when you plan to come!

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 (Tuesday, May 5, 2015)

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Final project - writing a General User Proposal

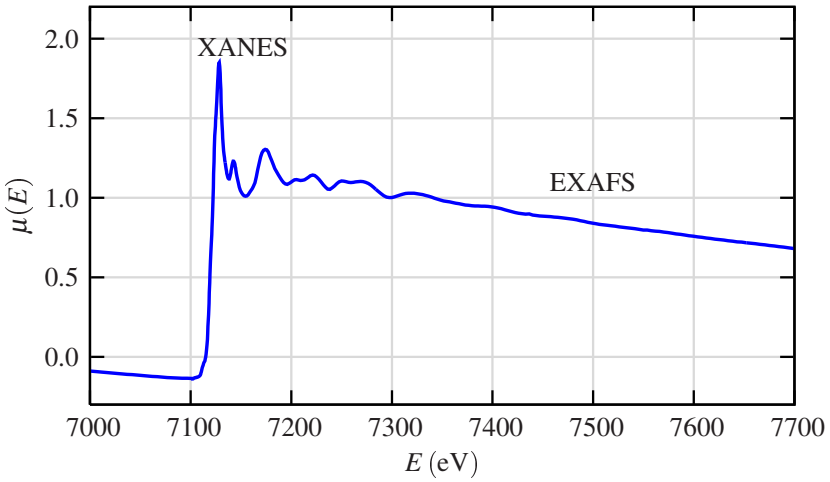
- Think of a research problem (could be yours) that can be approached using synchrotron radiation techniques
- Make proposal and get approval from instructor before starting
- Must be different techique than your presentation!

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.



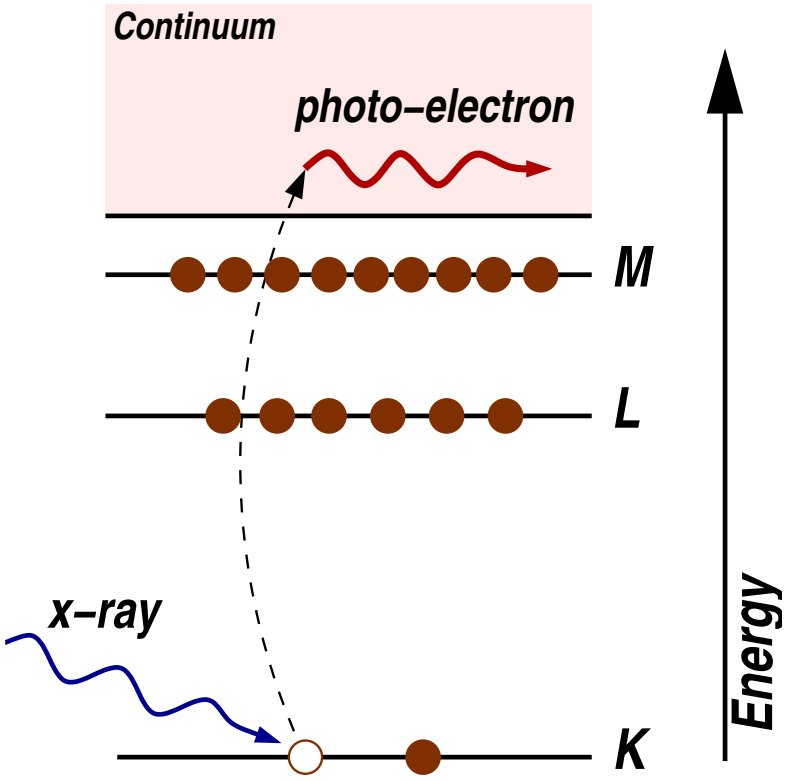
Fe *K*-edge XAFS for FeO

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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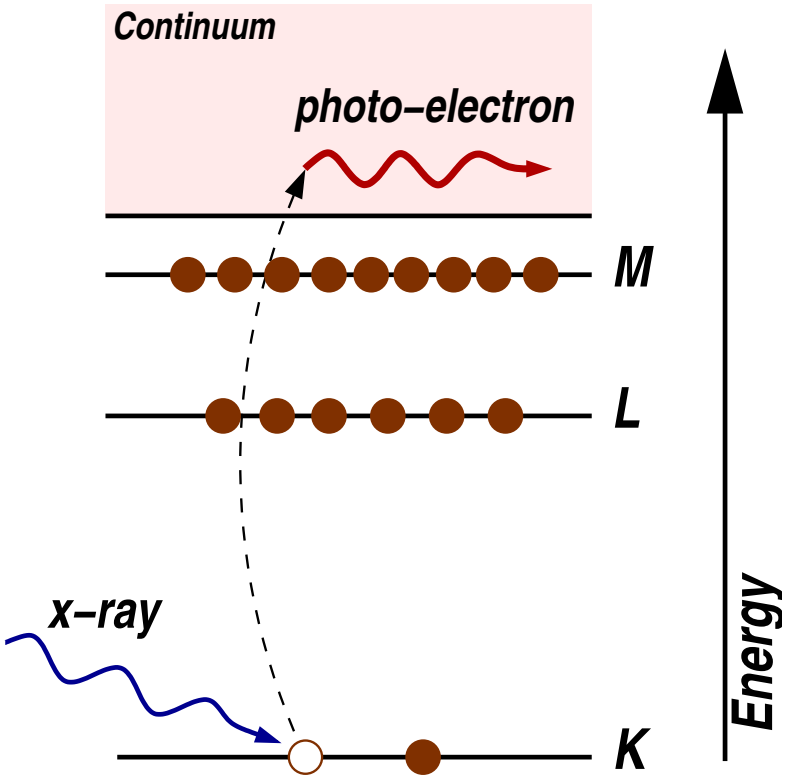

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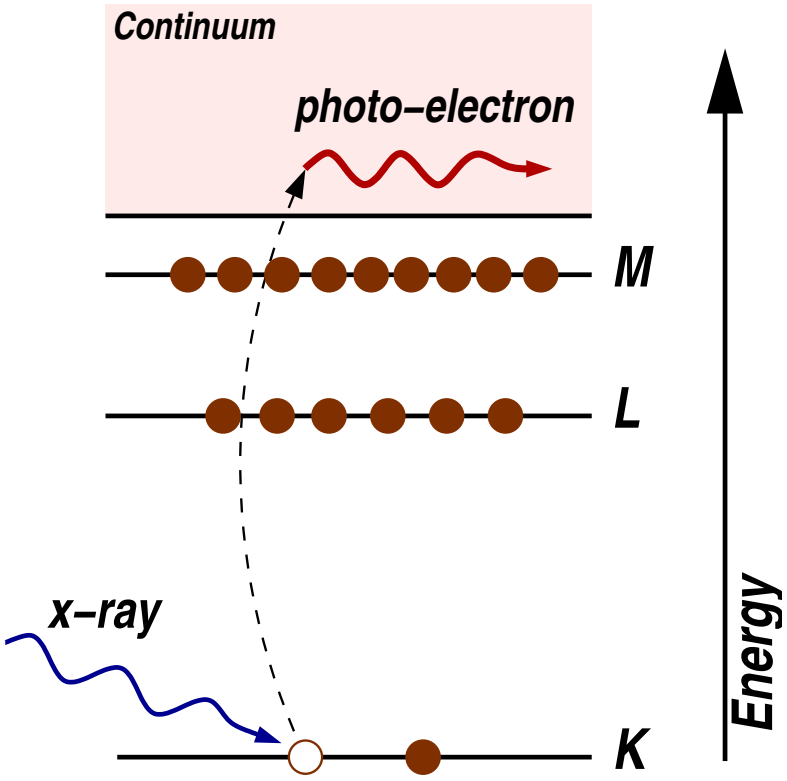

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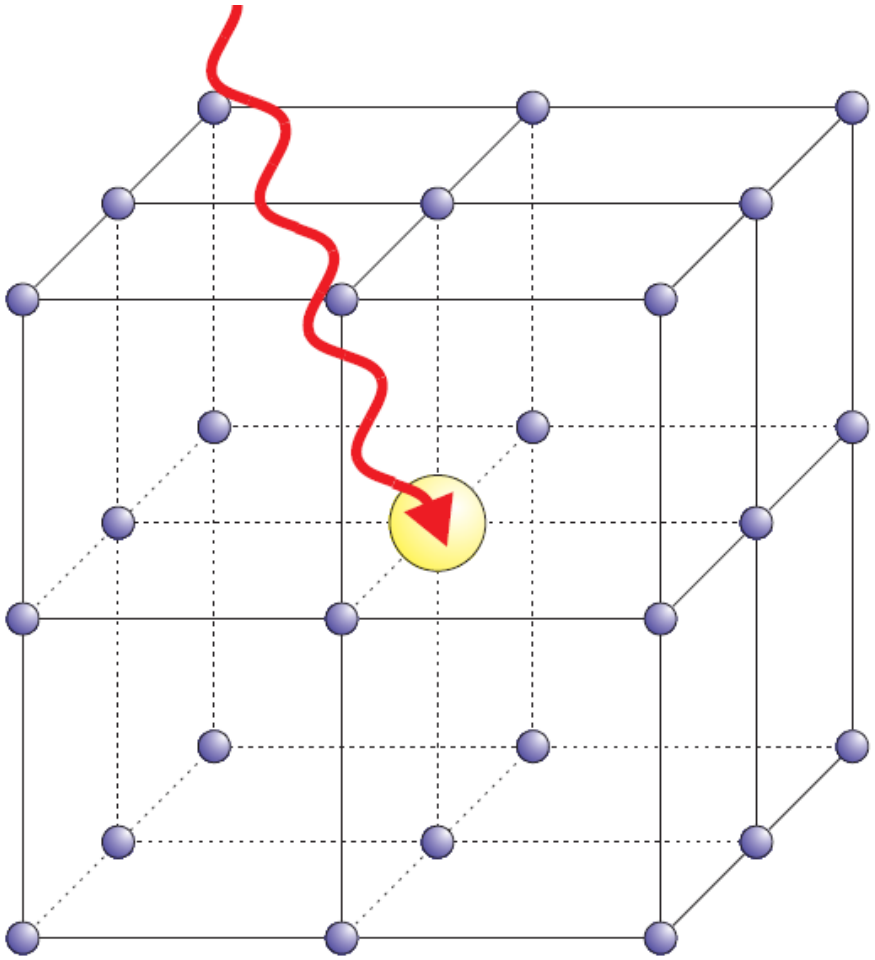

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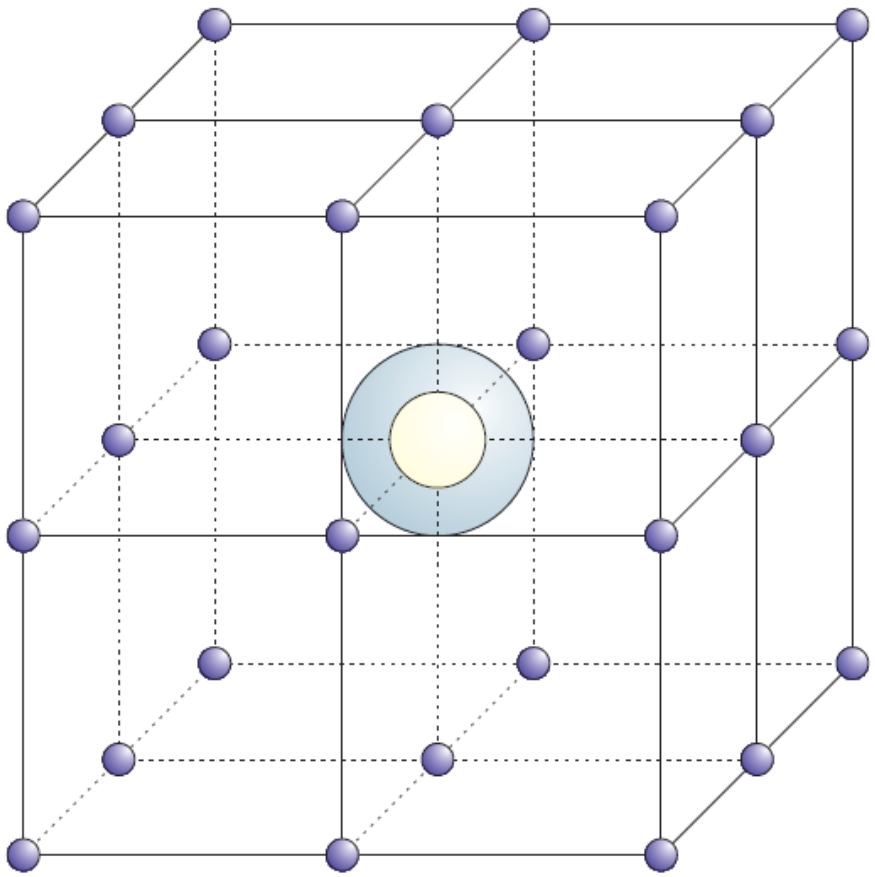

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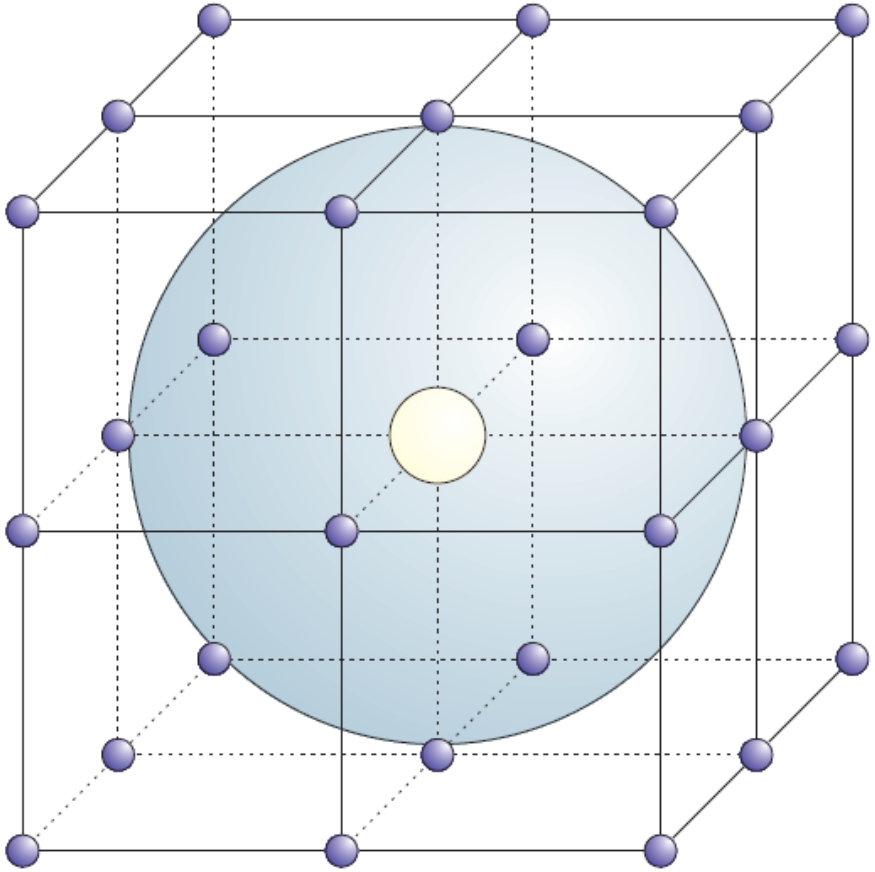

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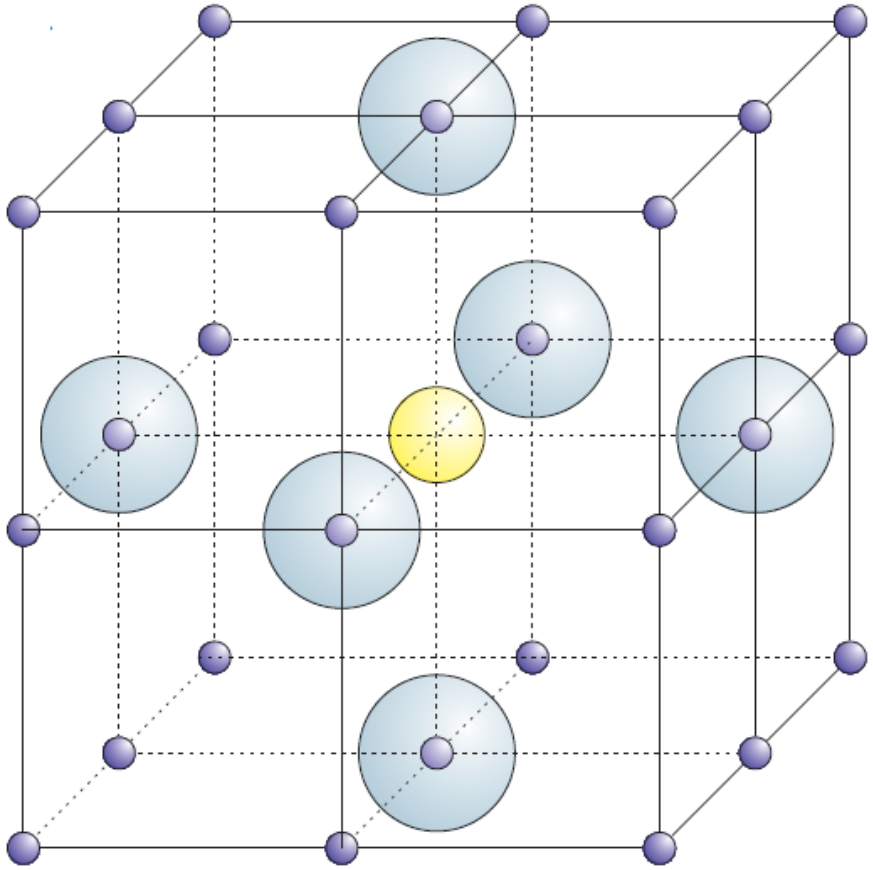

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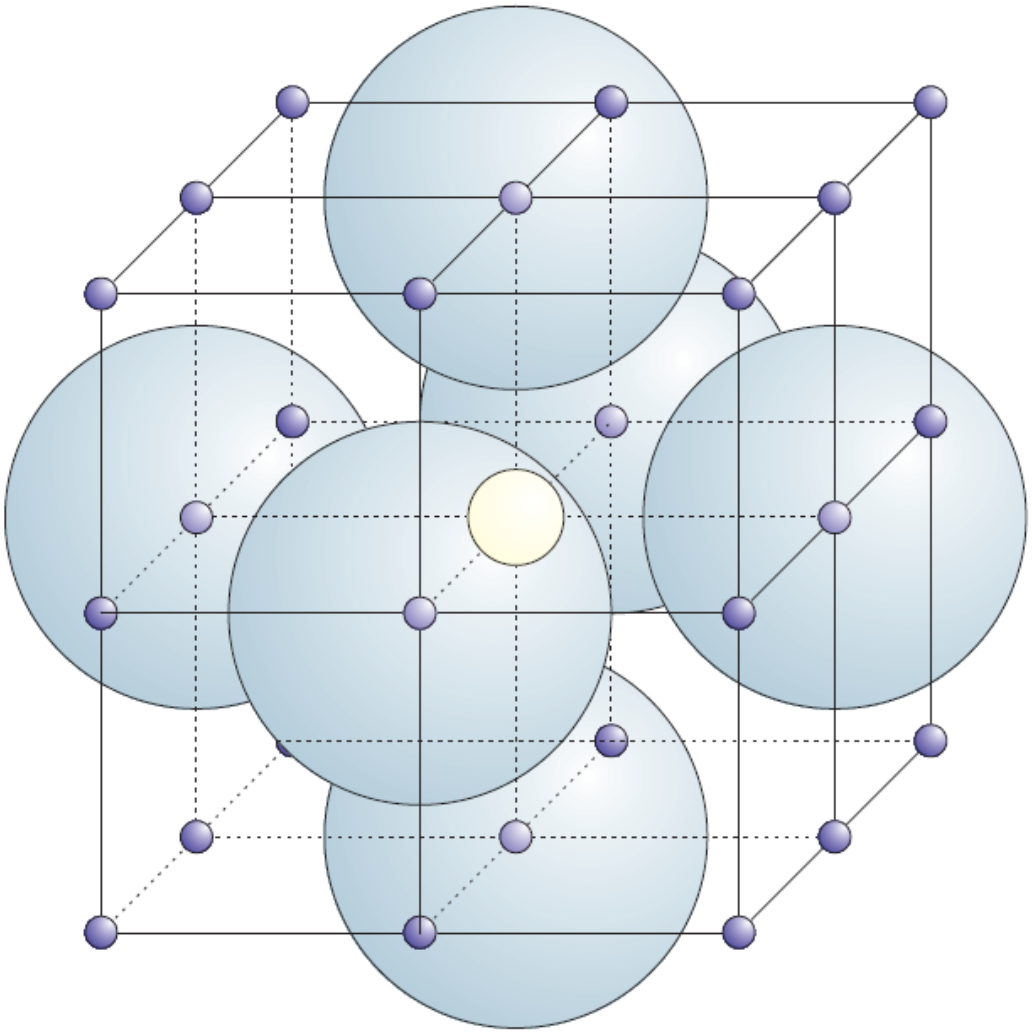

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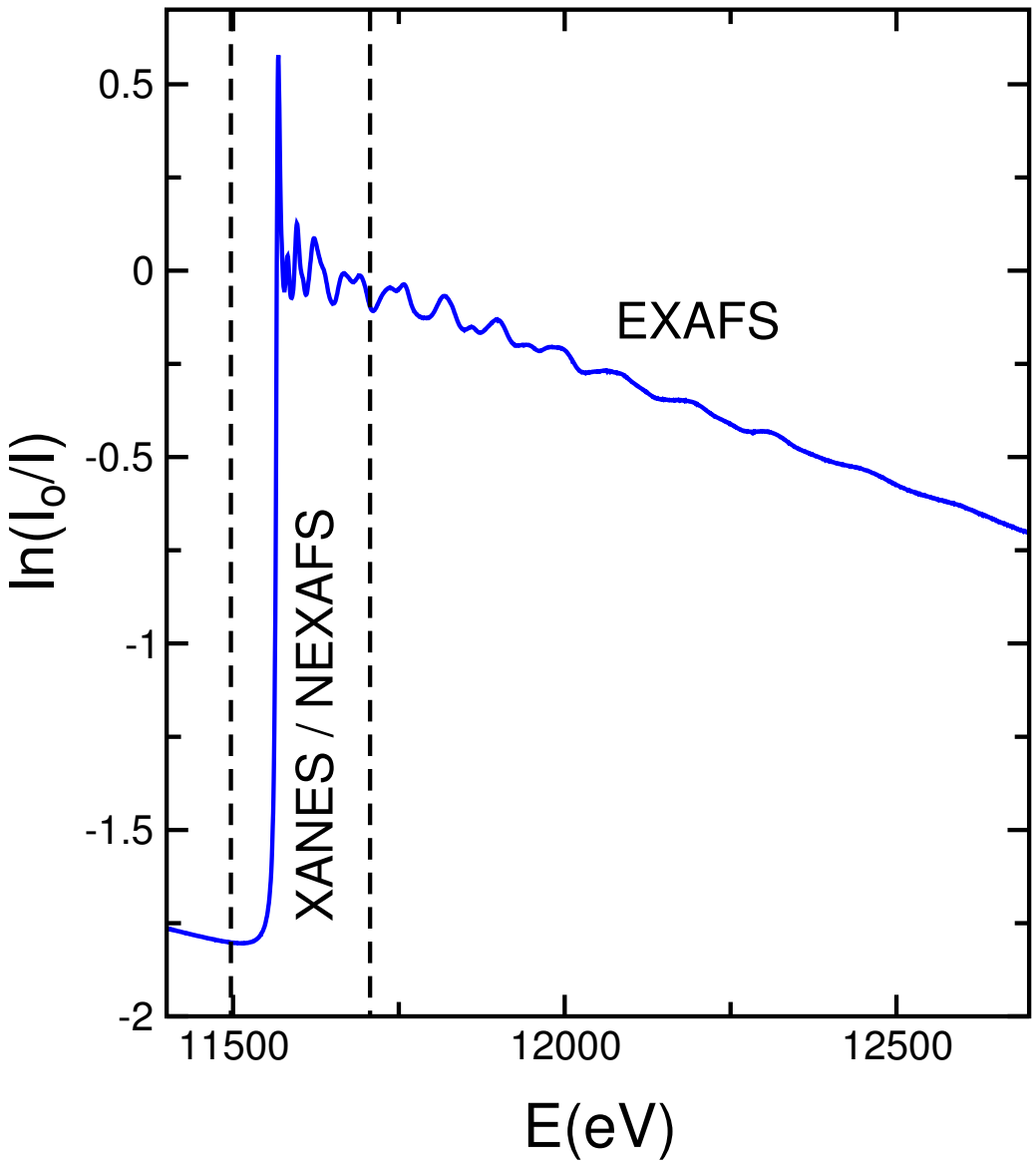
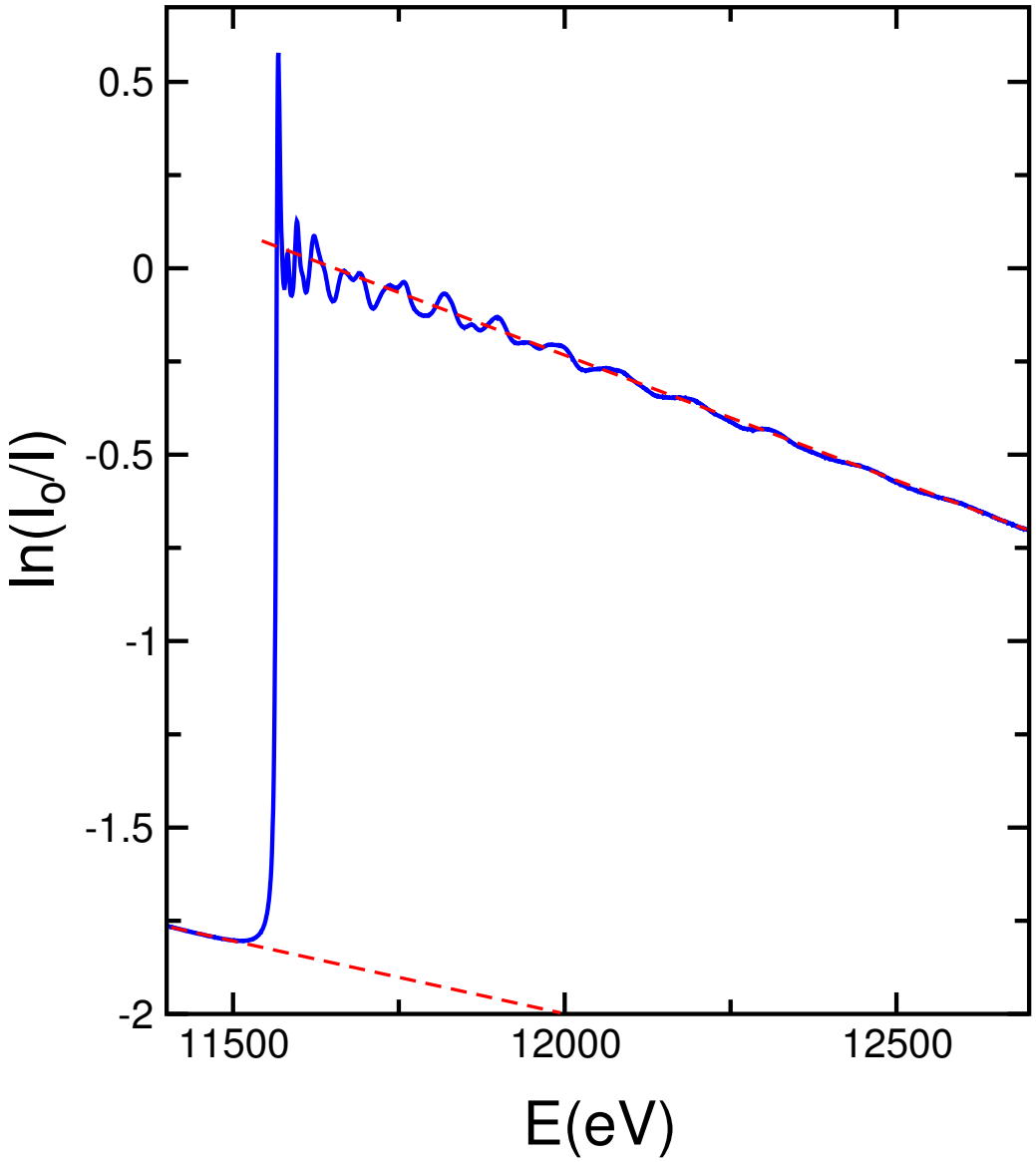
Any excess energy from the x-ray is given to an ejected photoelectron, which expands as a spherical wave, reaches the neighboring electron clouds, and scatters back to the core hole, creating interference patterns called XANES and EXAFS.



EXAFS data extraction

normalize by fitting pre-edge and post-edge trends



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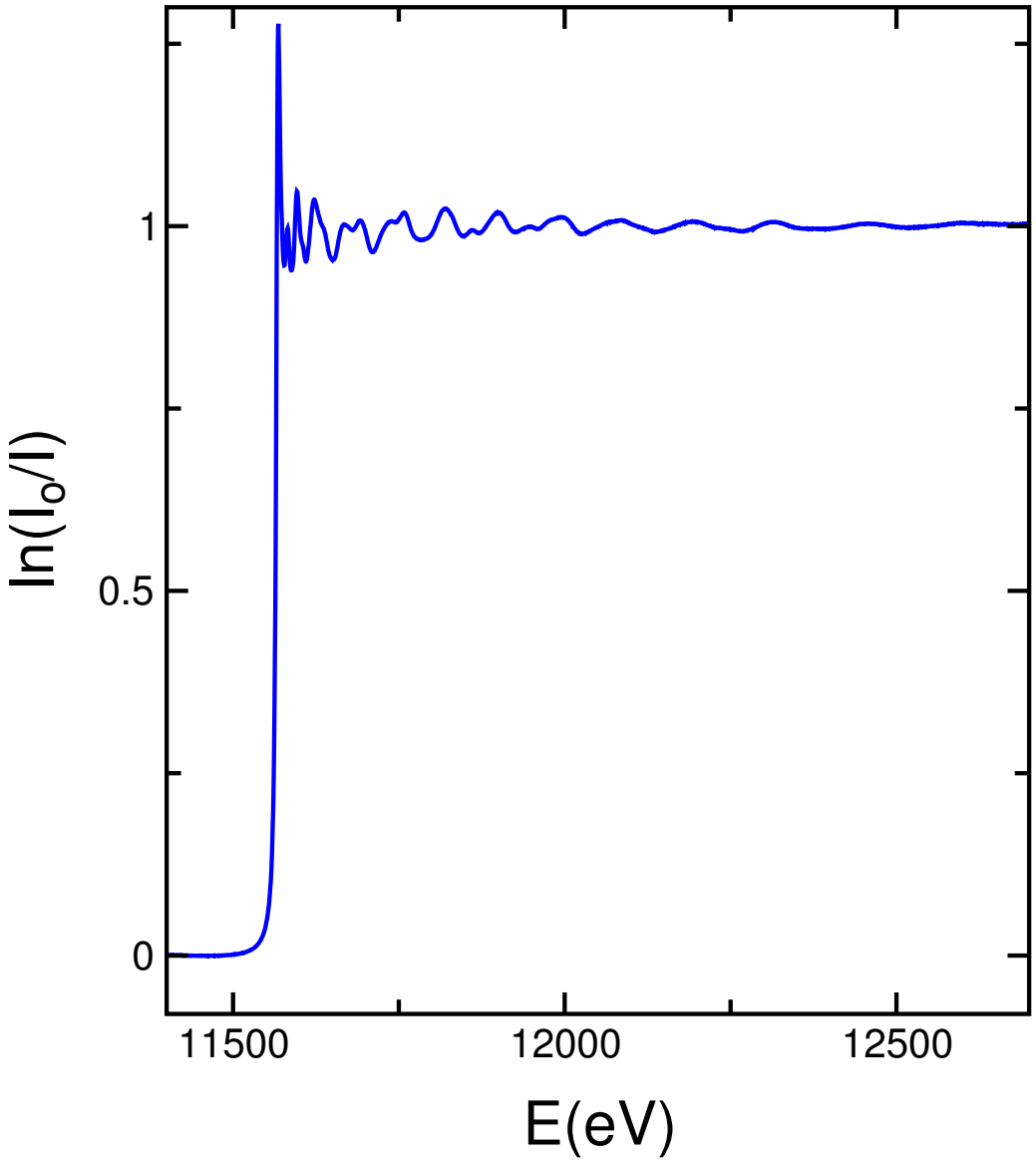

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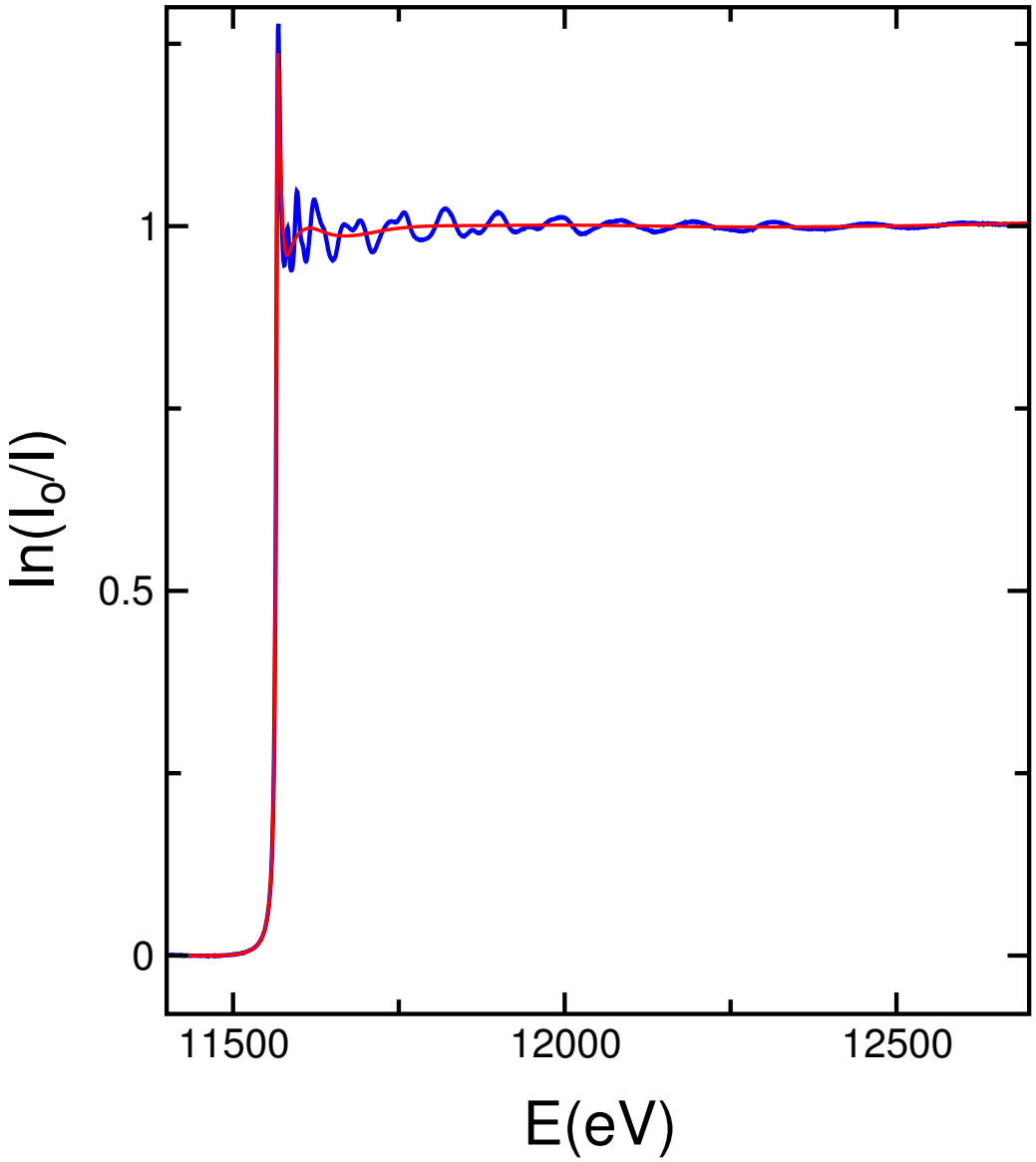

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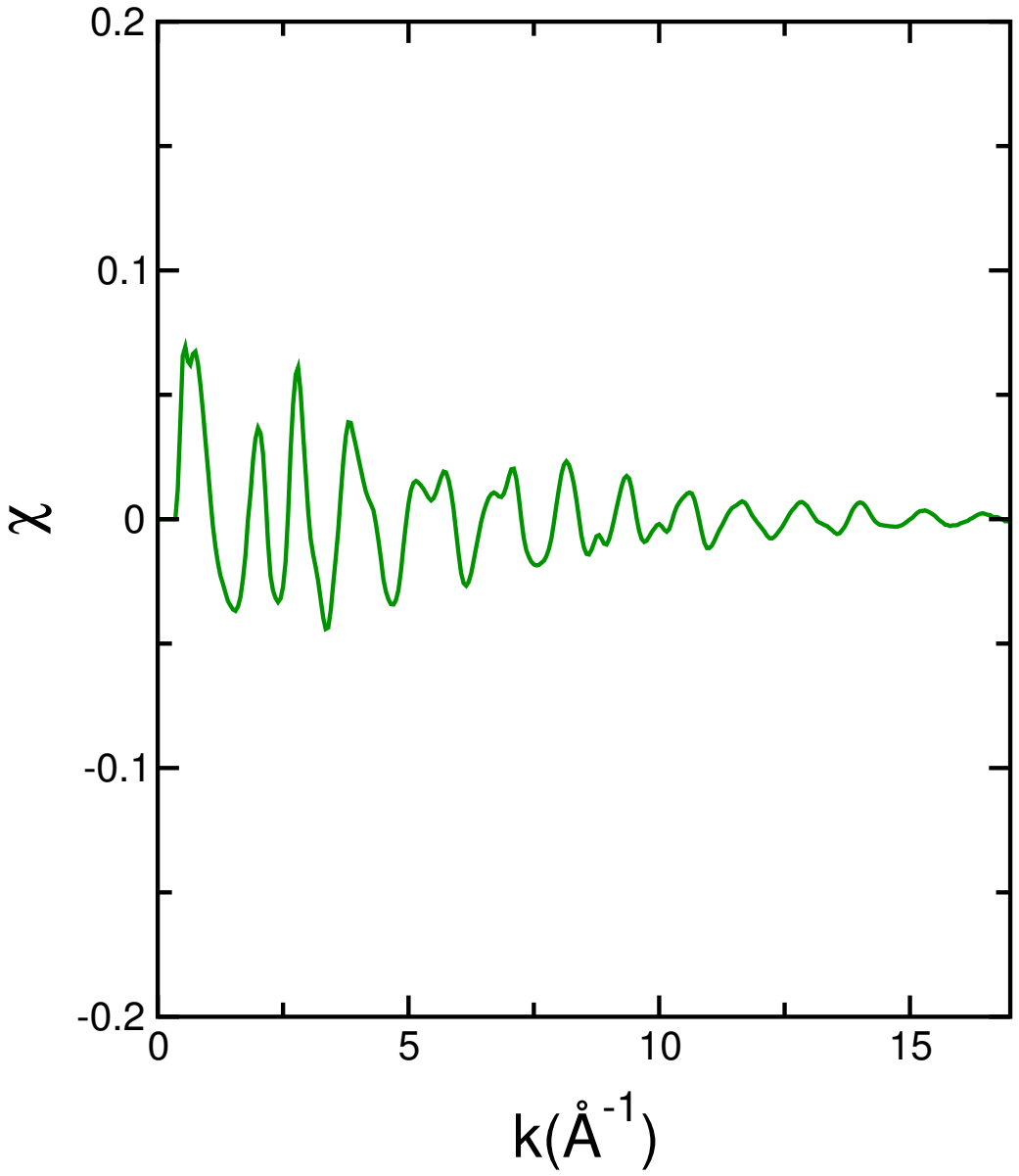

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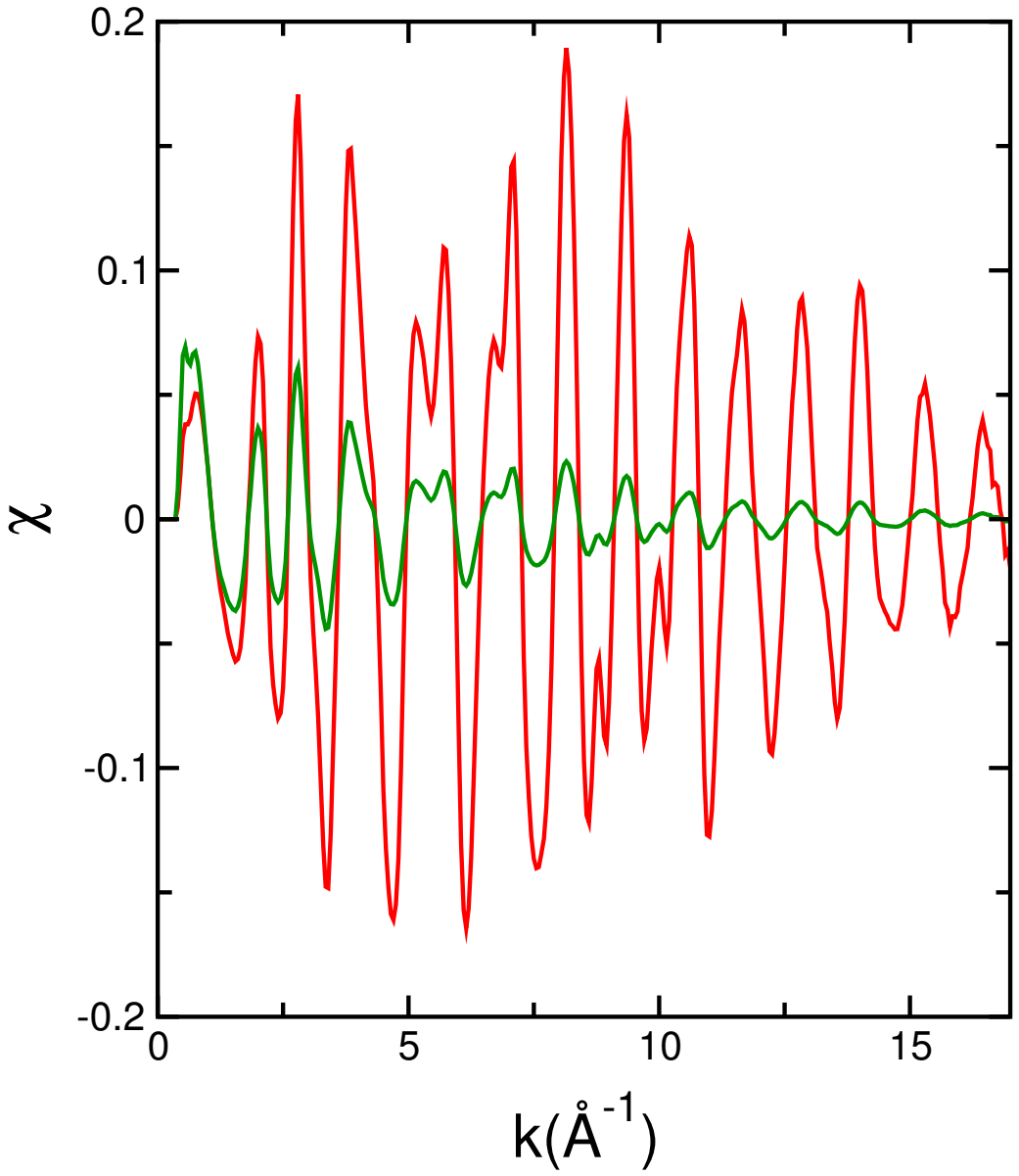

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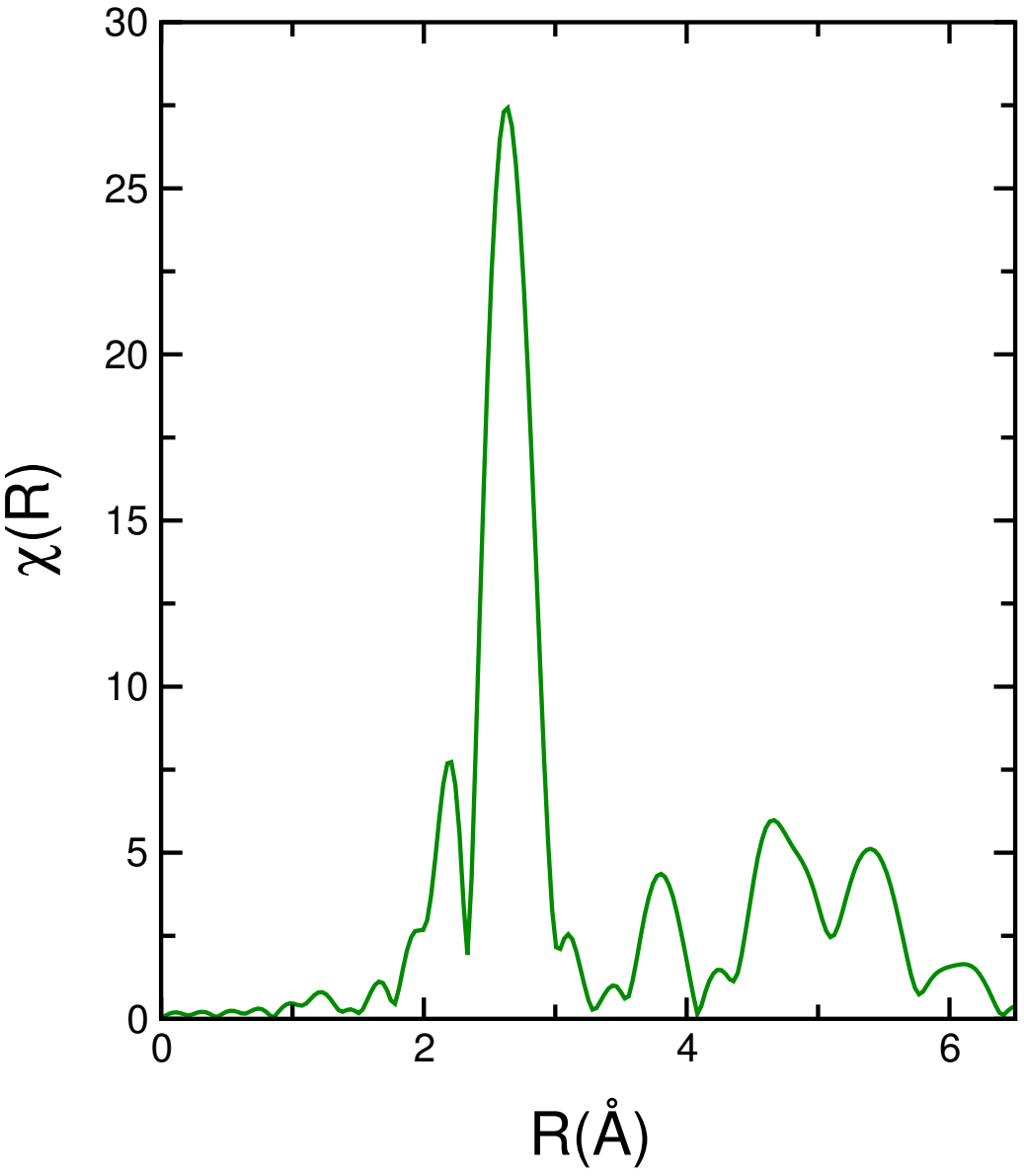
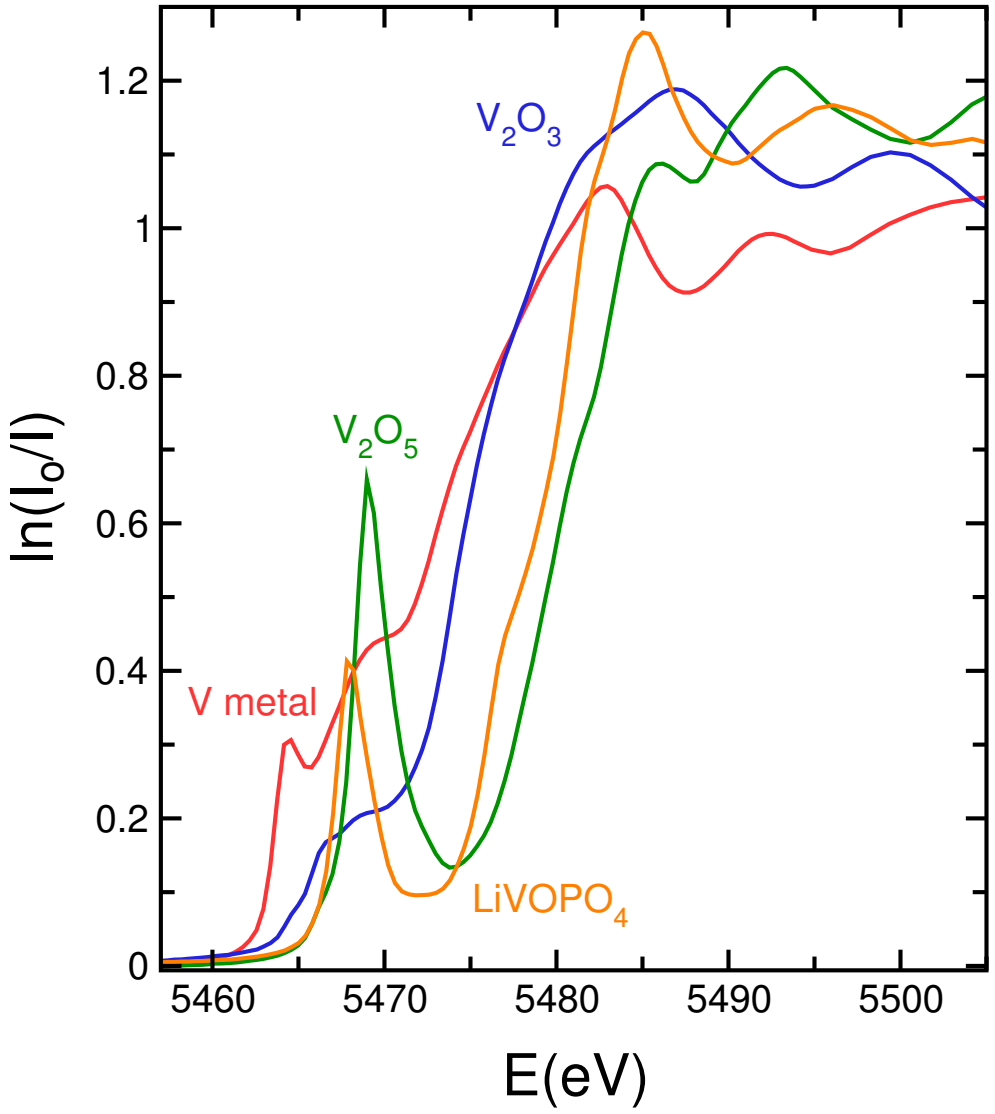
Fourier transform to get real space EXAFS



XANES edge shifts and pre-edge peaks



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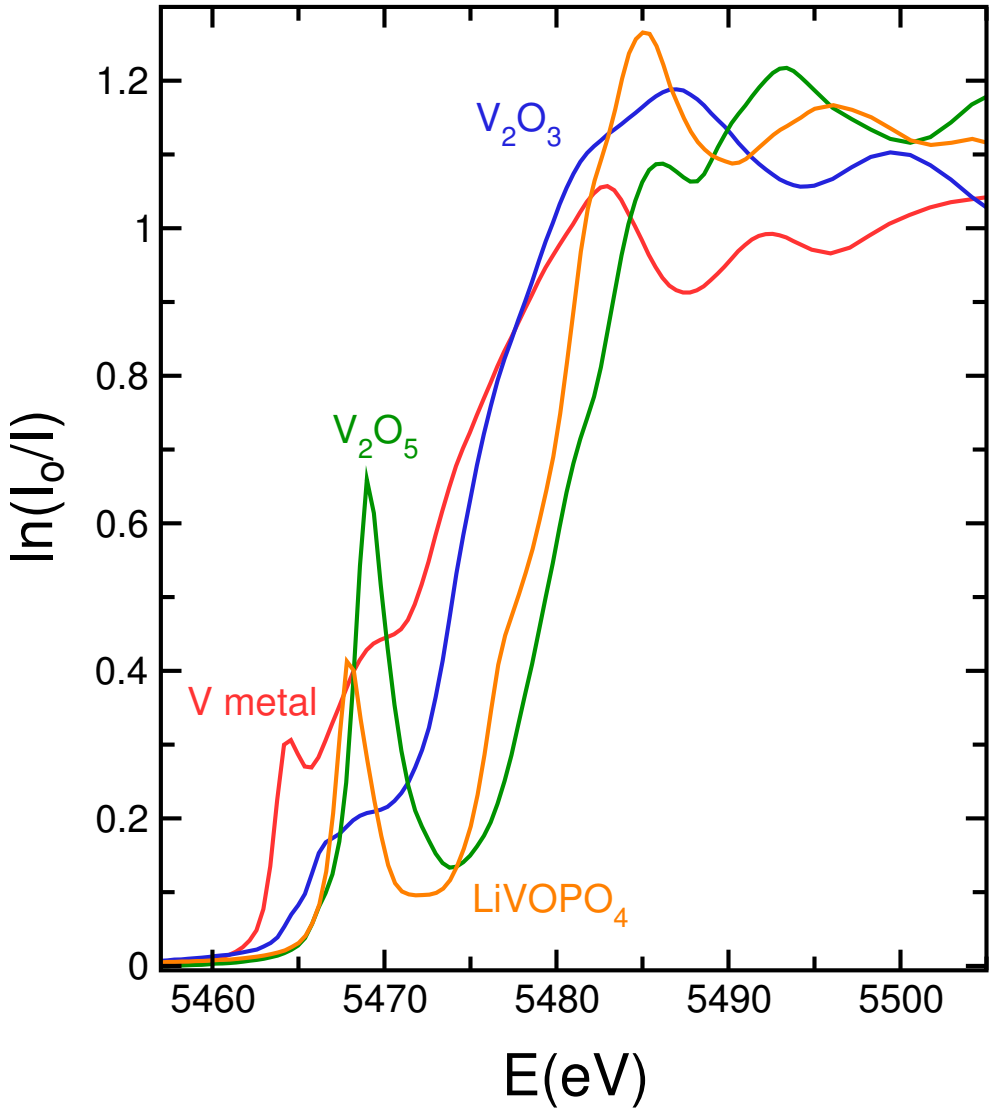

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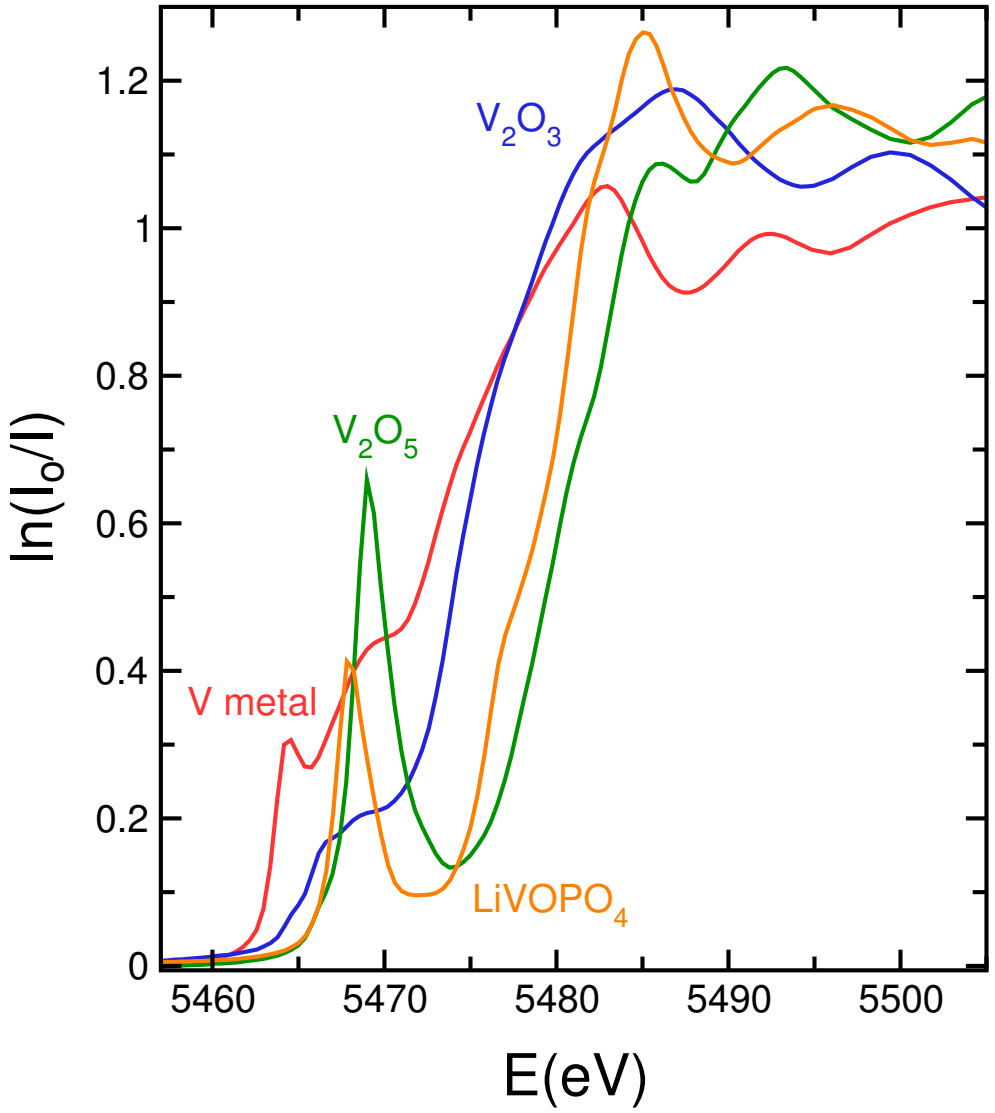

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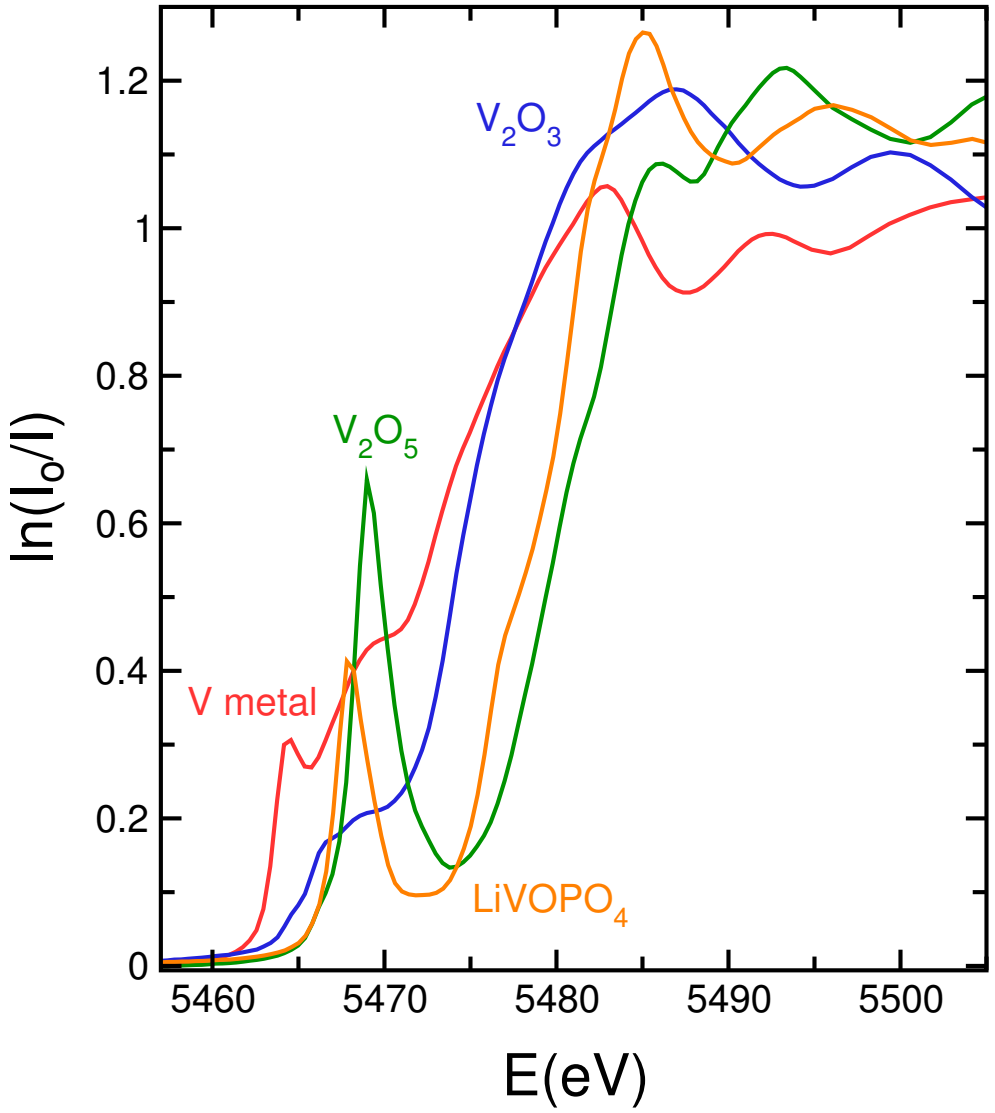

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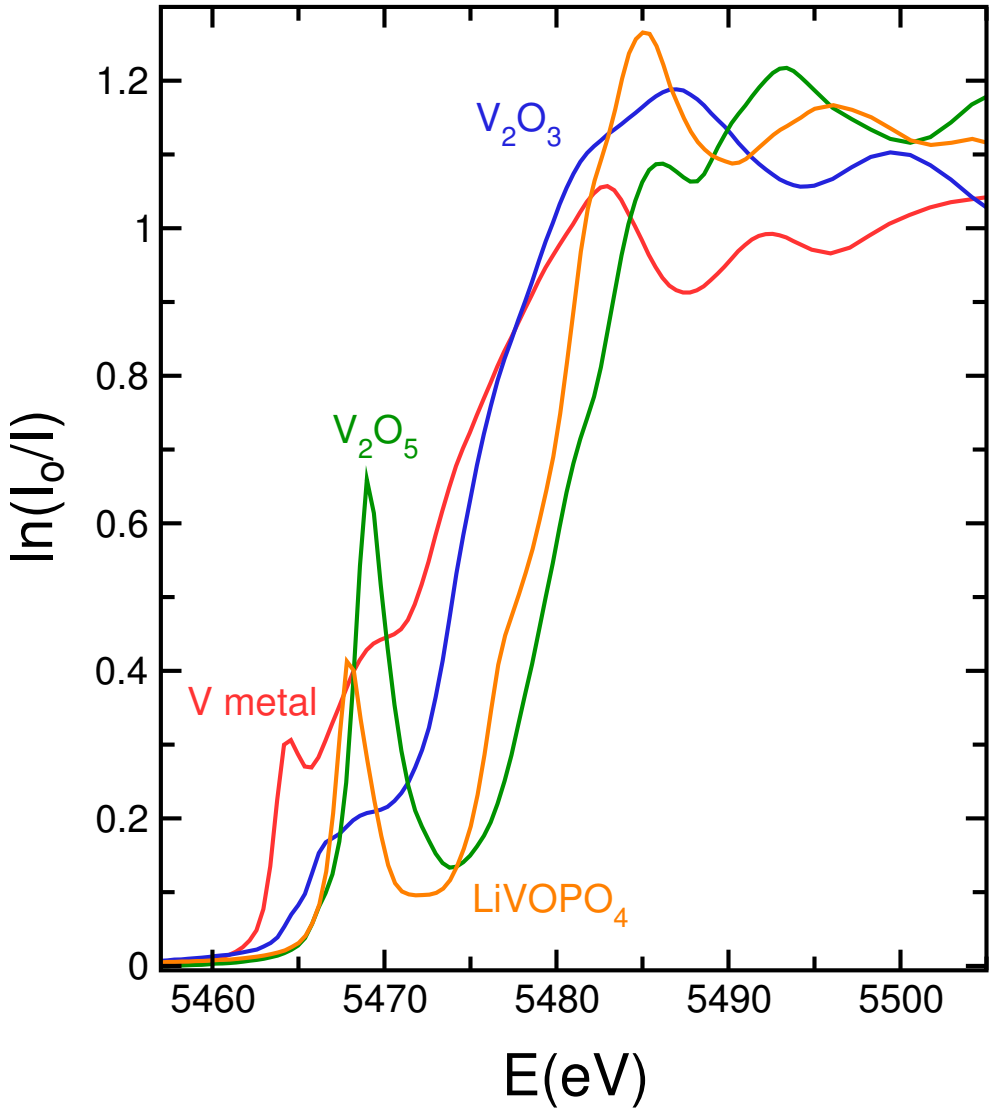

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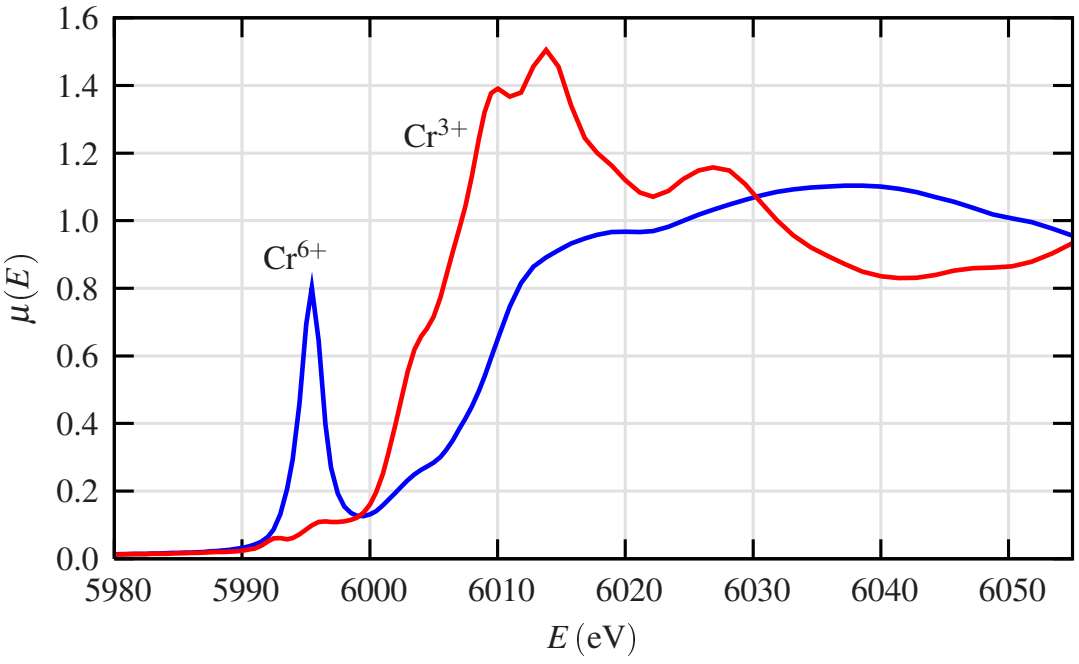
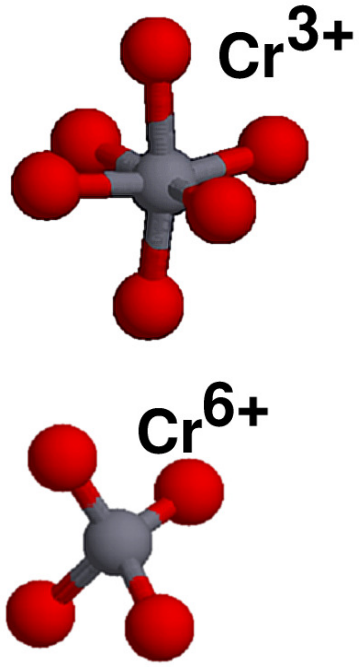
Modern codes, such as FEFF9, are able to accurately compute XANES features.

Coordination chemistry





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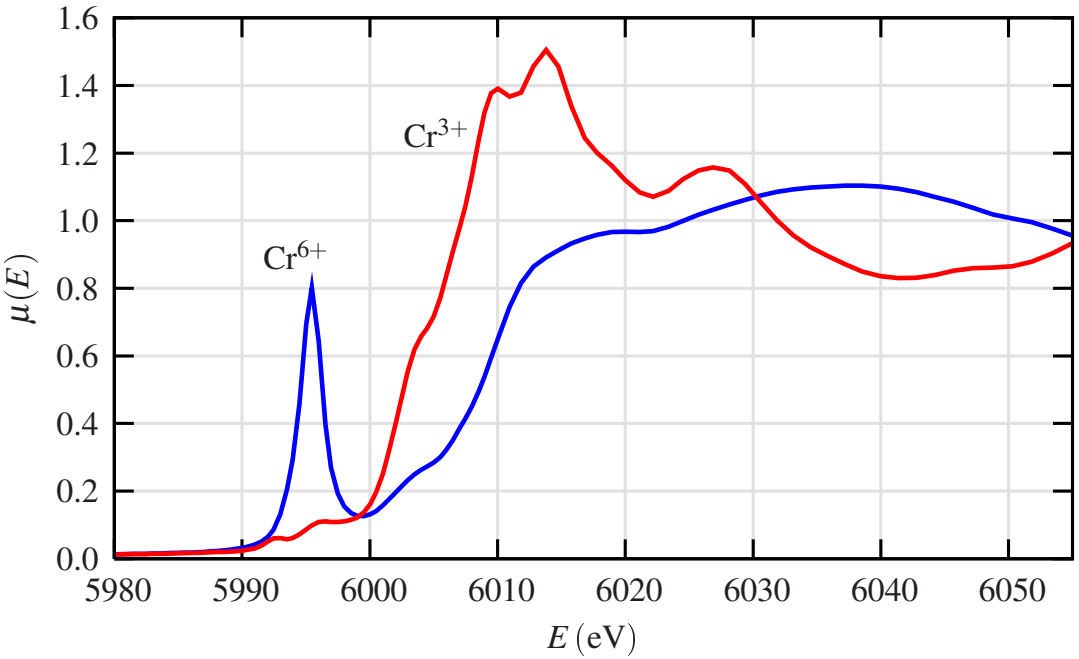

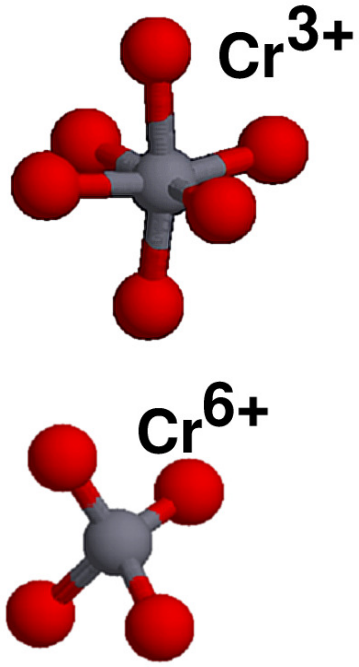

The XANES of Cr^{3+} and Cr^{6+} shows a dramatic dependence on oxidation state and coordination chemistry.

For ions with partially filled *d* shells, the *p*-*d* hybridization changes dramatically as *regular octahedra* distort, and is very large for *tetrahedral* coordination.

This gives a dramatic *pre-edge peak* – absorption to a localized electronic state.

XAFS Theory: 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 photo-electron with energy $(E - E_0)$. The core hole is eventually filled, and a fluorescence x-ray or Auger electron is ejected from the atom.

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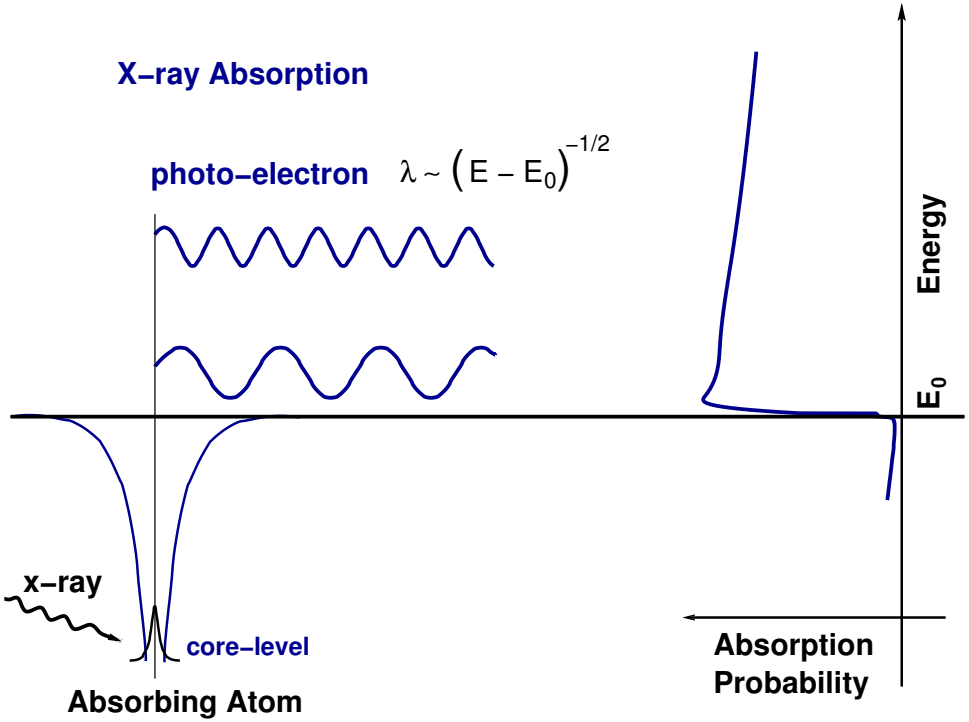

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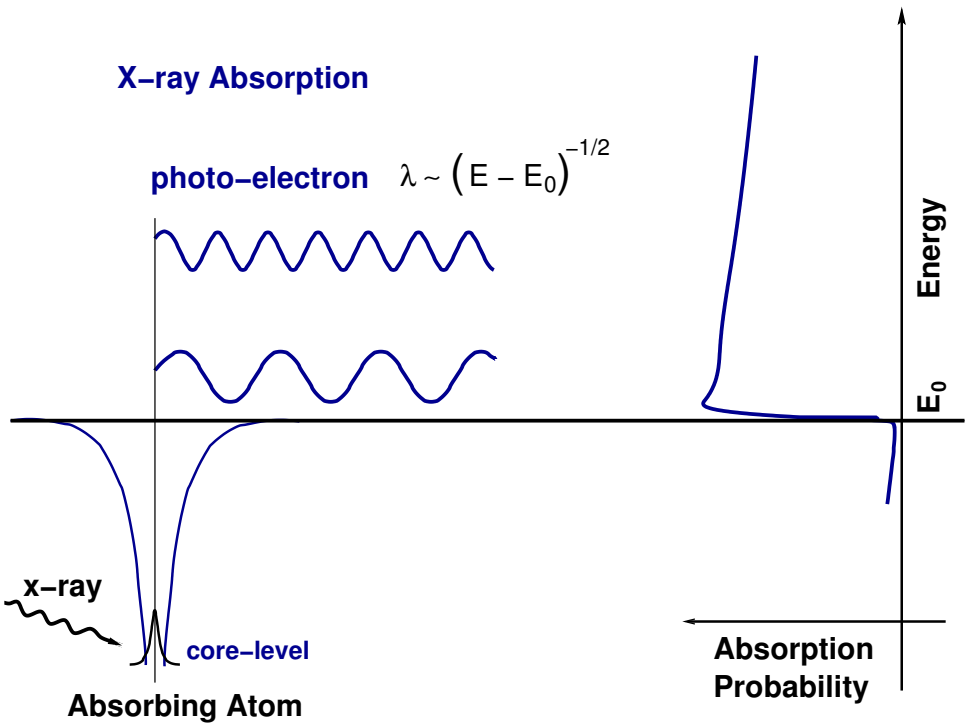

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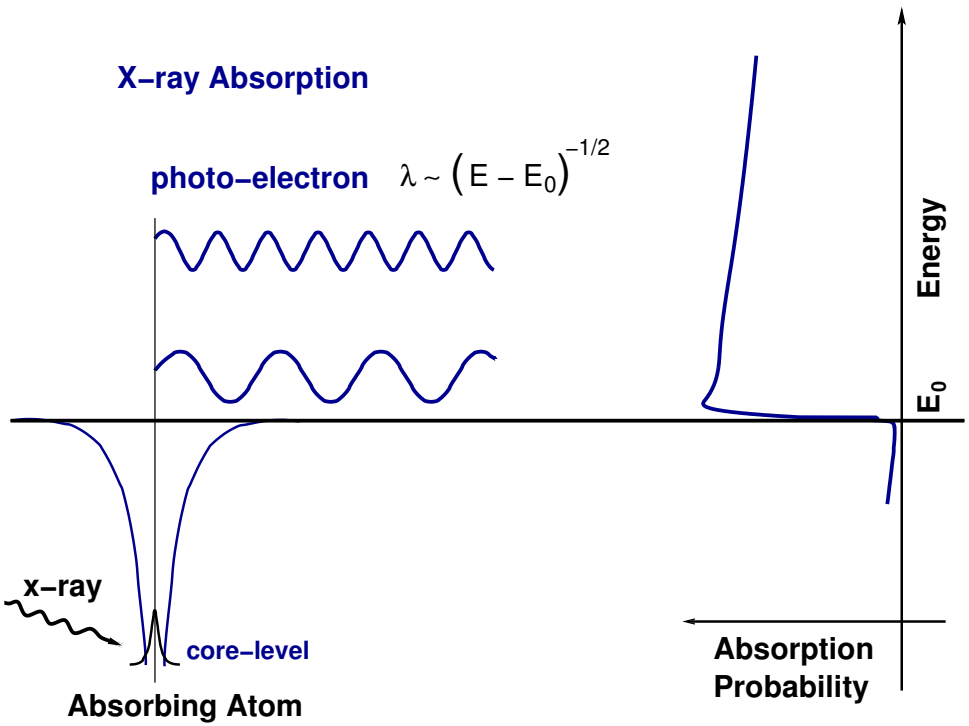

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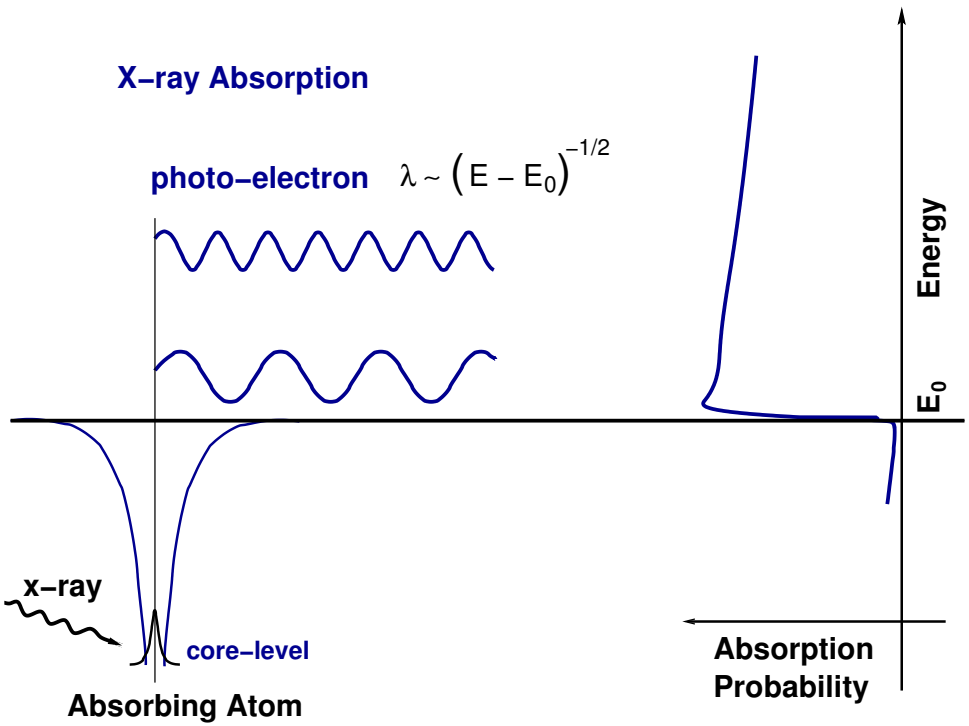

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Once the x-ray energy is large enough to promote a core-level to the continuum, there is a sharp increase in absorption.

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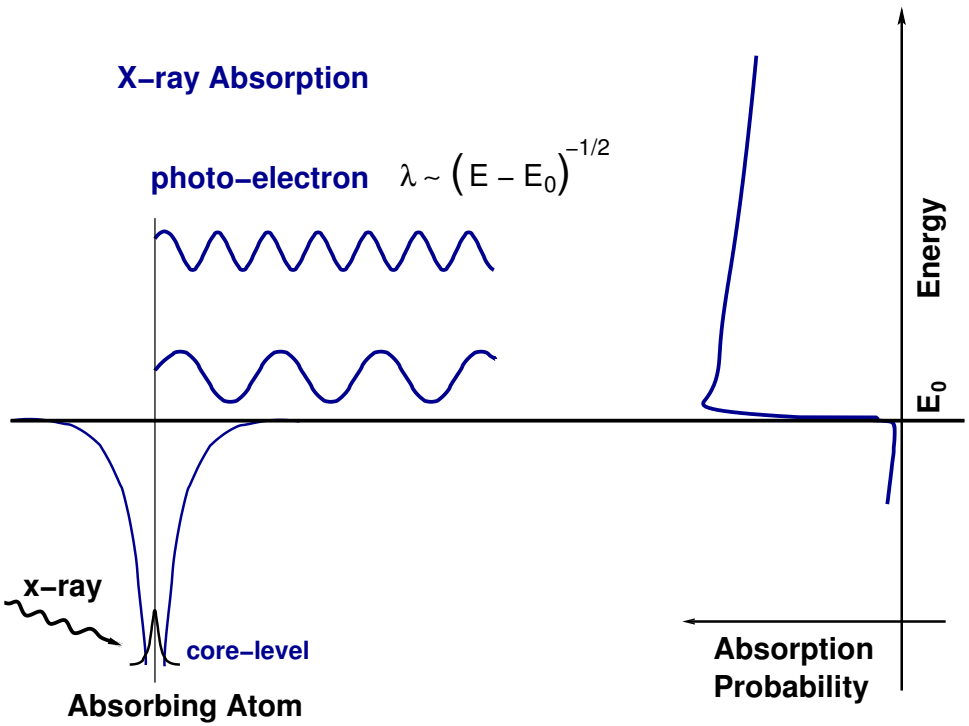

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$\mu(E)$ has a sharp step at the core-level binding energy, and is a smooth function of energy above this absorption edge.

X-ray Absorption with Photo-Electron Scattering

With another atom nearby, the ejected photo-electron can *scatter* from a neighboring atom and return back to the absorbing atom.

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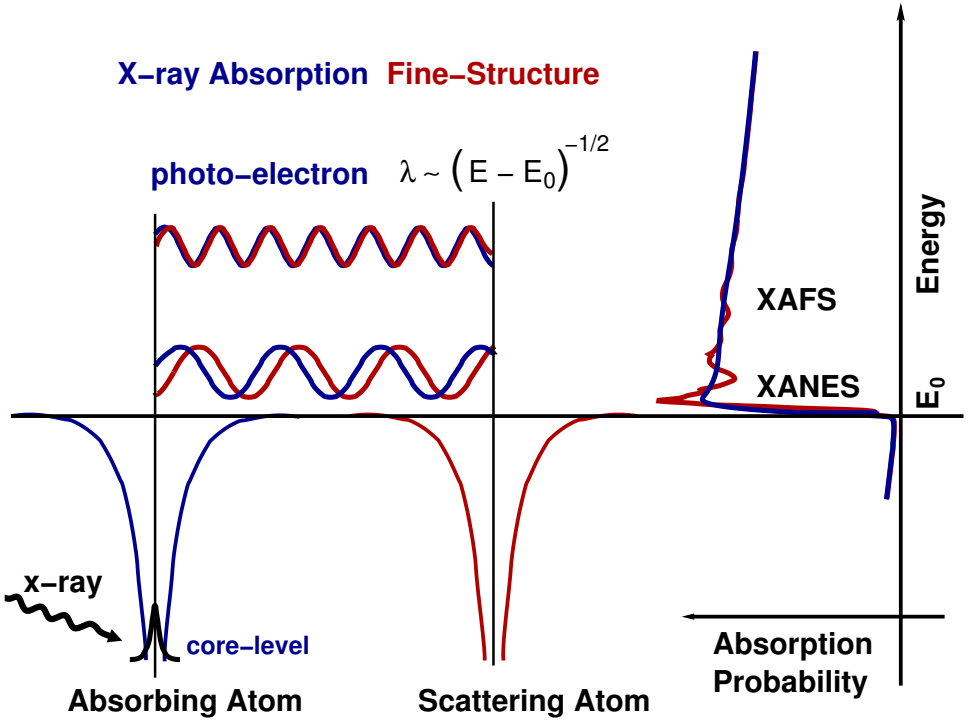

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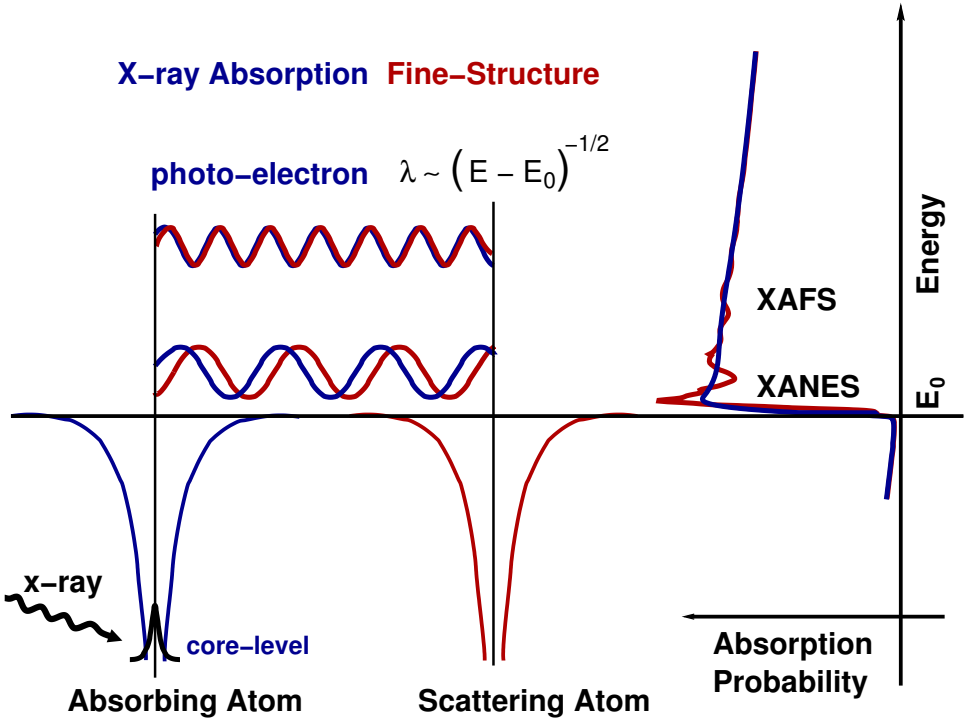

The photo-electron scattered back will interfere with itself.

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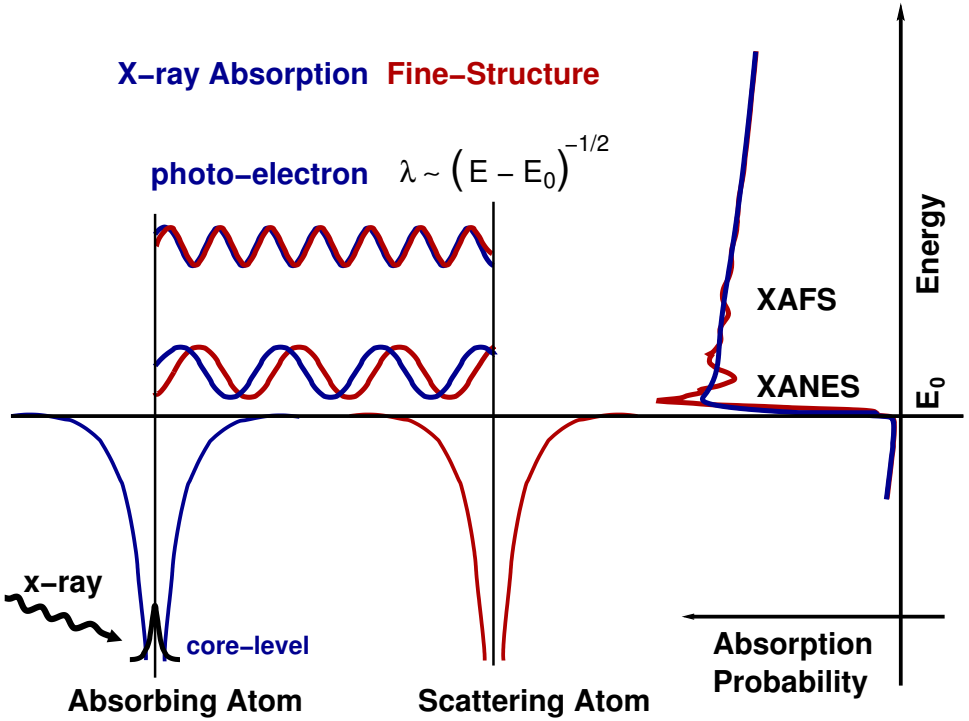

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The amplitude of the back-scattered photo-electron *at the absorbing atom* will vary with energy, causing the oscillations in $\mu(E)$ that are the XAFS. The XAFS oscillations are an interference effect of the photo-electron with itself, due to the presence of neighboring atoms.

X-ray Absorption: Fermi's Golden Rule

$$\mu(E) = \mu_0(E)[1 + \chi(E)]$$

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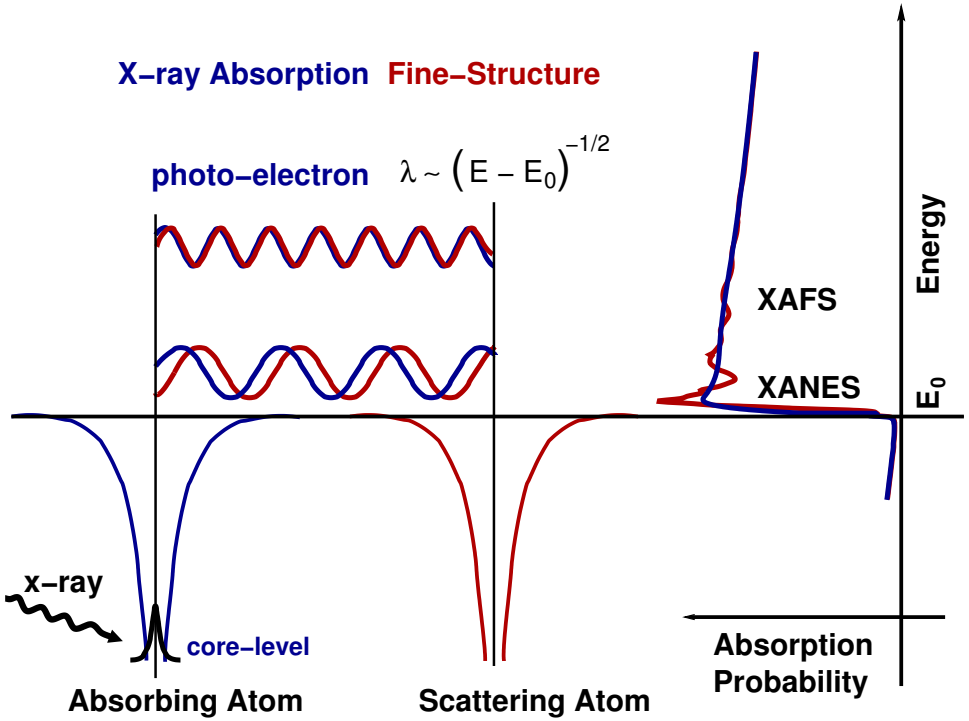
$$\mu(E) \sim |\langle i|\mathcal{H}|f\rangle|^2$$



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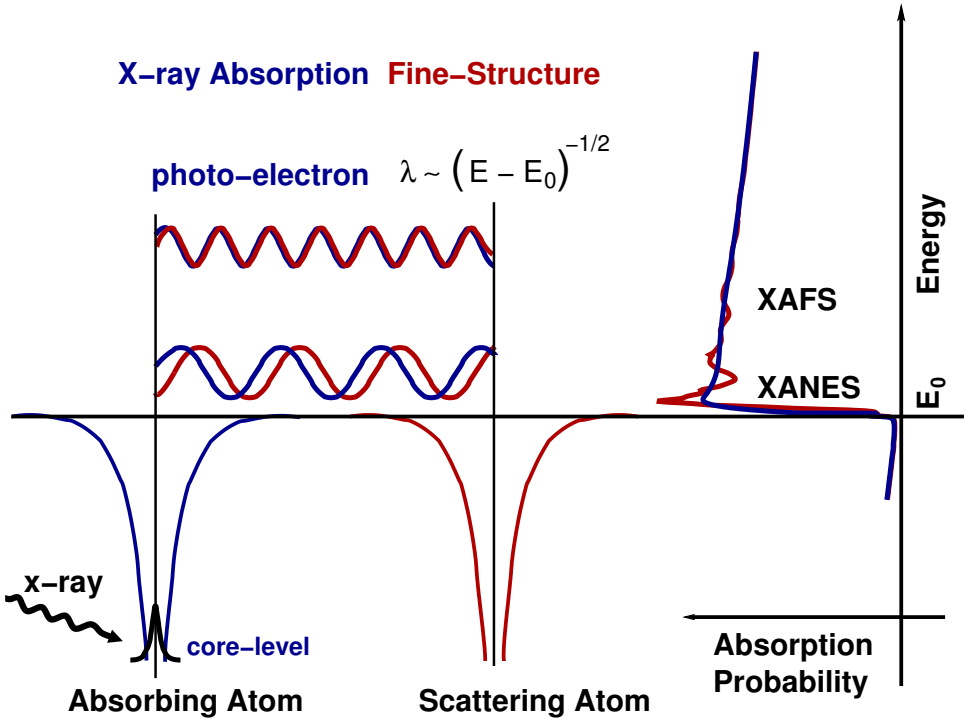

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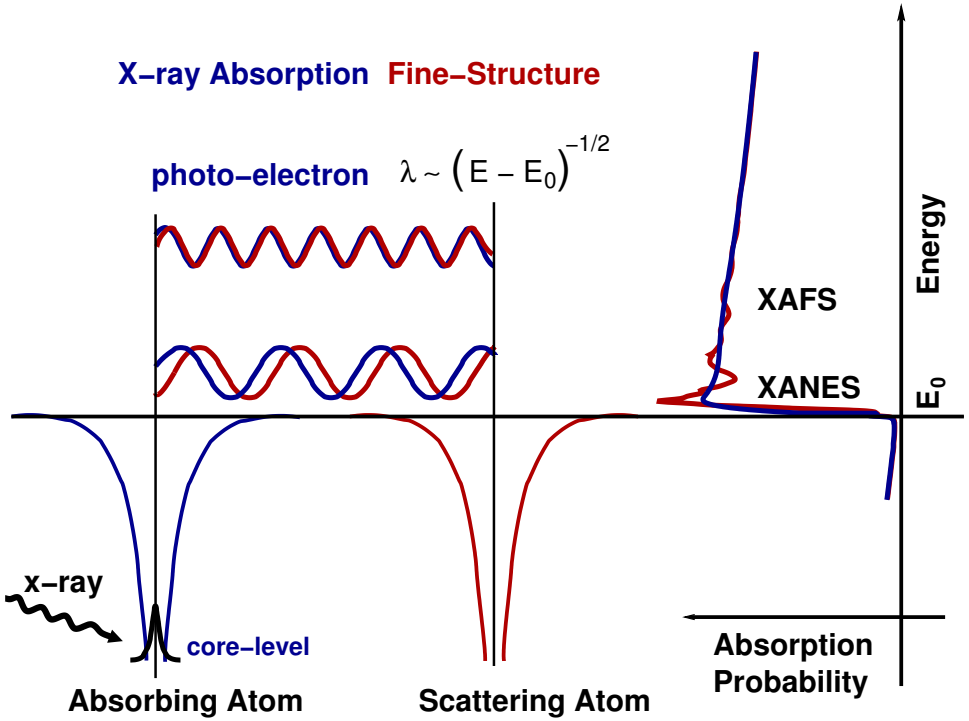

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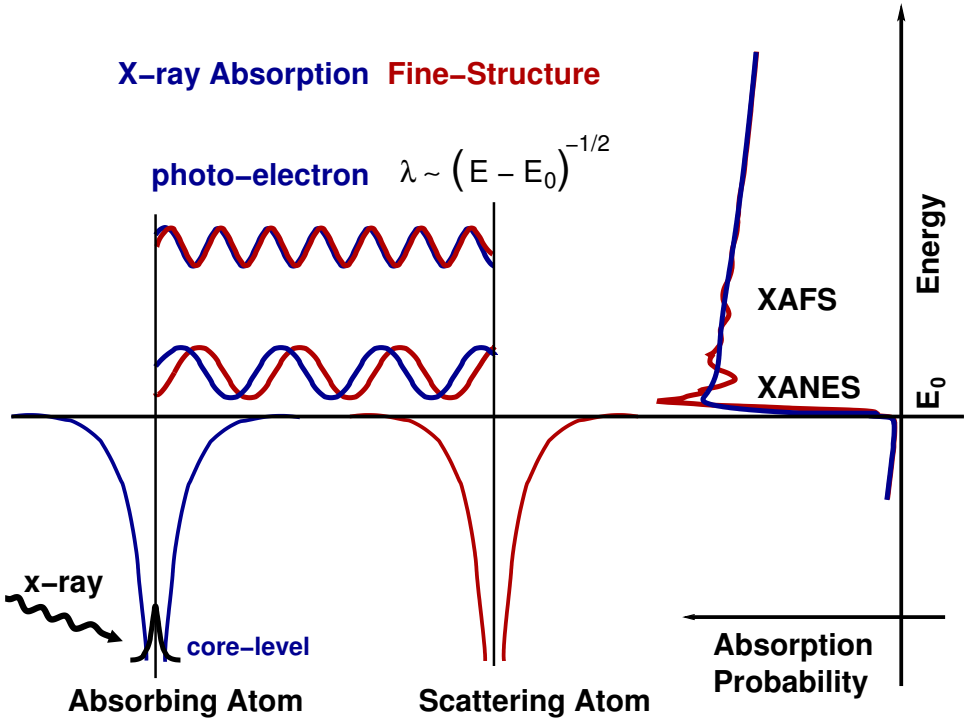

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$|f\rangle$ the *final state* has a photo-electron, a hole in the core, and no photon. This is altered by the neighboring atom: the photo-electron scatters.

μ and χ and the photo-electron wavefunction

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

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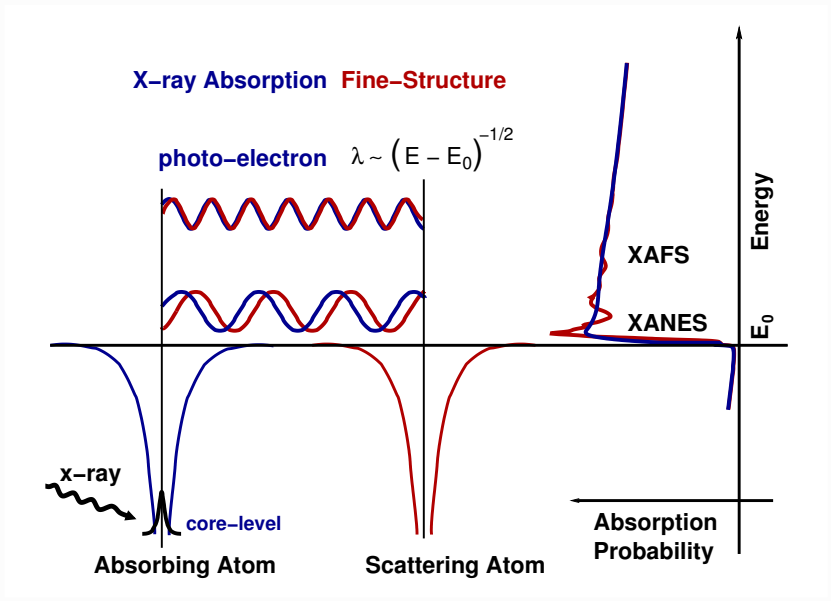
χ is due to the portion of the photo-electron wave-function at the absorbing atom caused that was scattered back by neighboring atoms.

The EXAFS Equation: simple description

With $\chi \sim \psi_{\rm scatt}(0)$, and a spherical wave for the photo-electron

$$\psi(k,r) = e^{ikr}/kr$$

we can model $\chi(k)$ as the photo-electron



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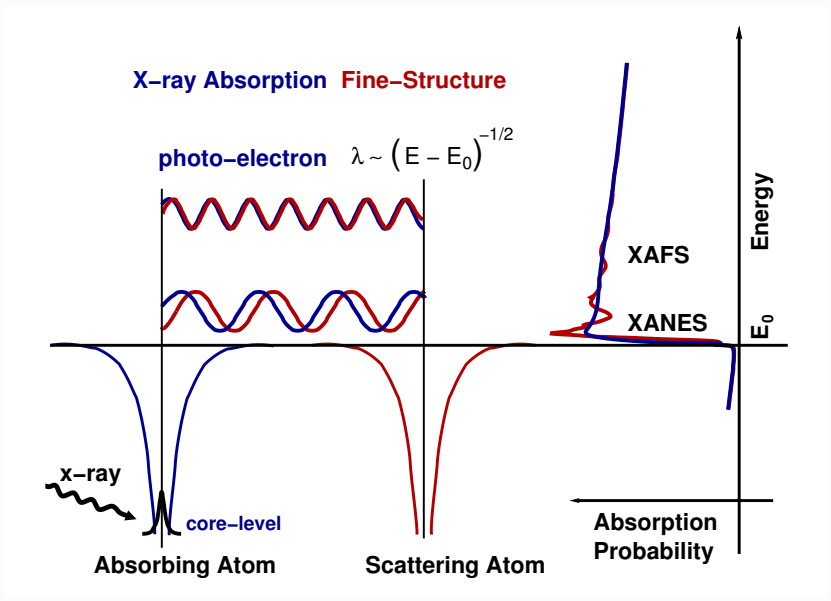

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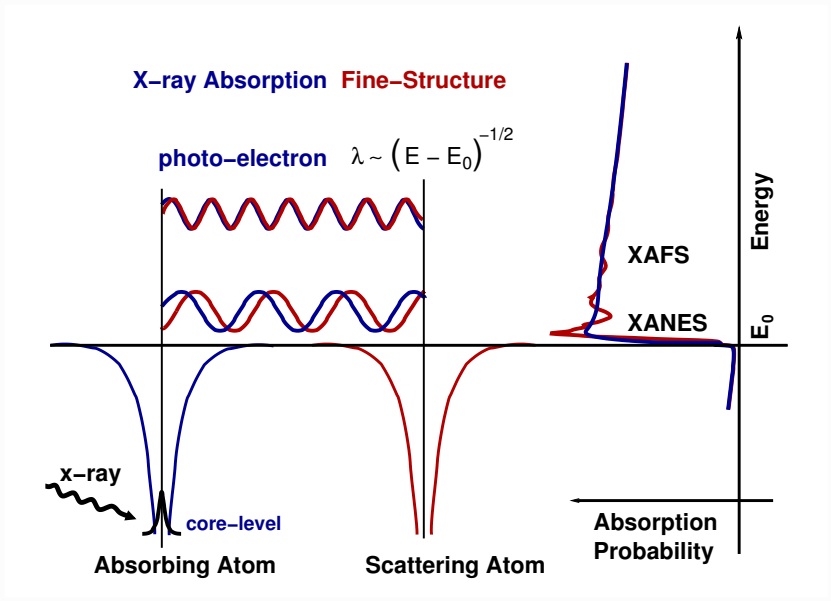

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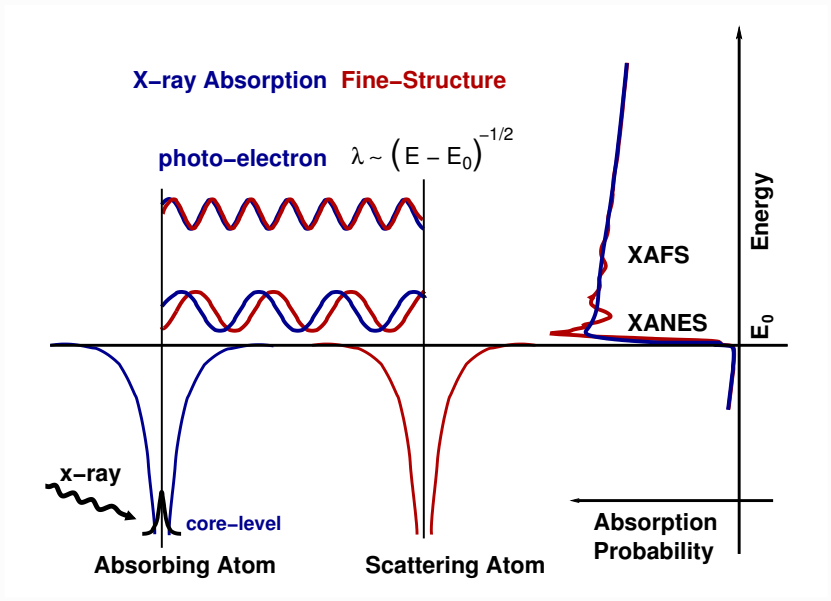

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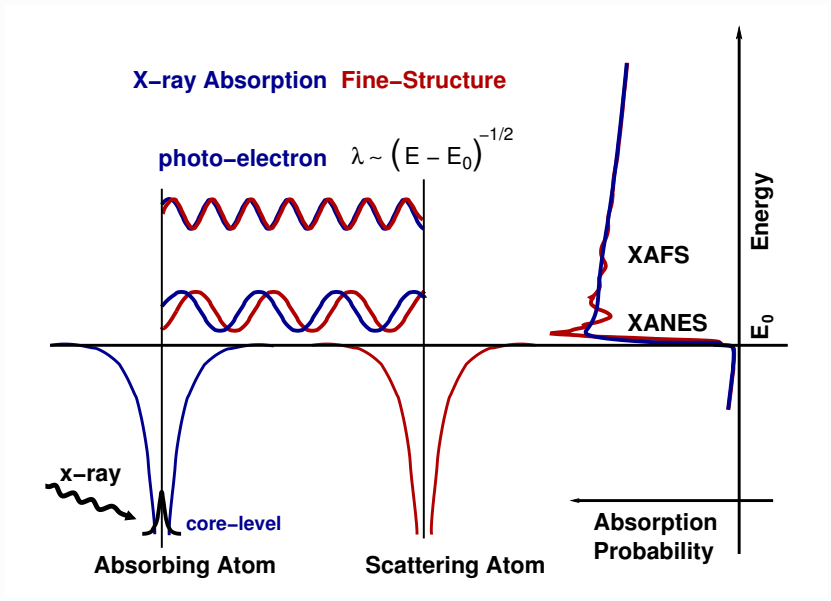

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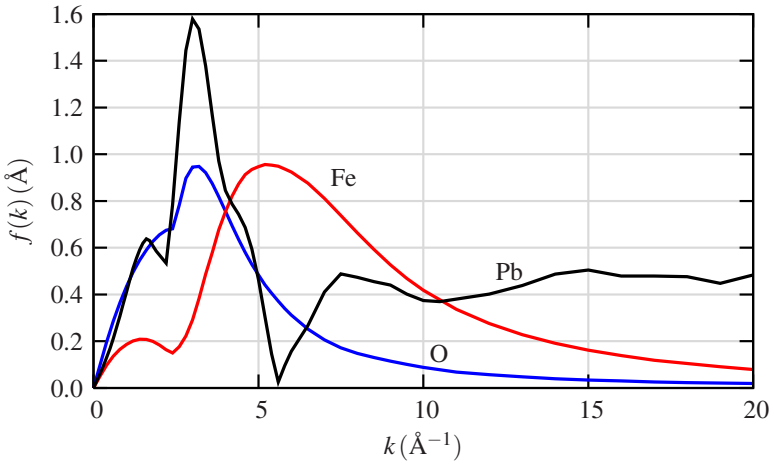
A real system has atoms at different distances and of different types. We add all these contributions to get a better version of the EXAFS equation:

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

Scattering Amplitude and Phase-Shift: $f(k)$ and $\delta(k)$

The scattering amplitude $f(k)$ and phase-shift $\delta(k)$ depend on atomic number.



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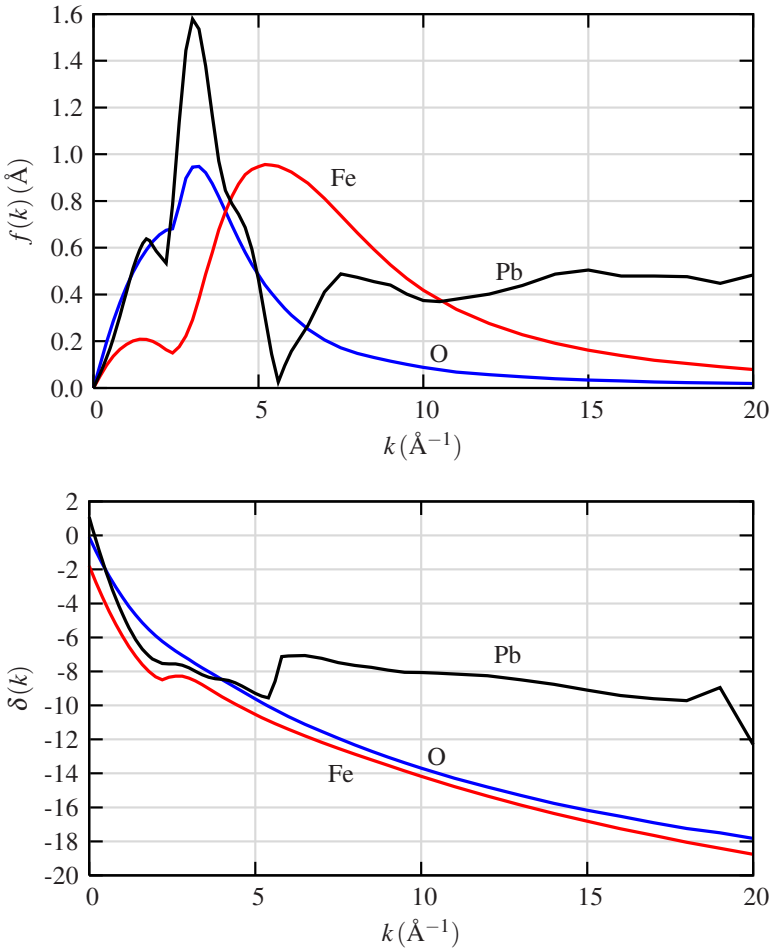

The scattering amplitude $f(k)$ peaks at different k values and extends to higher-k for heavier elements. For very heavy elements, there is structure in $f(k)$.

The phase shift $\delta(k)$ shows sharp changes for very heavy elements.

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

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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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To get to

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we used a spherical wave for the photo-electron: $\psi(k, r) \sim e^{ikr}/kr$.
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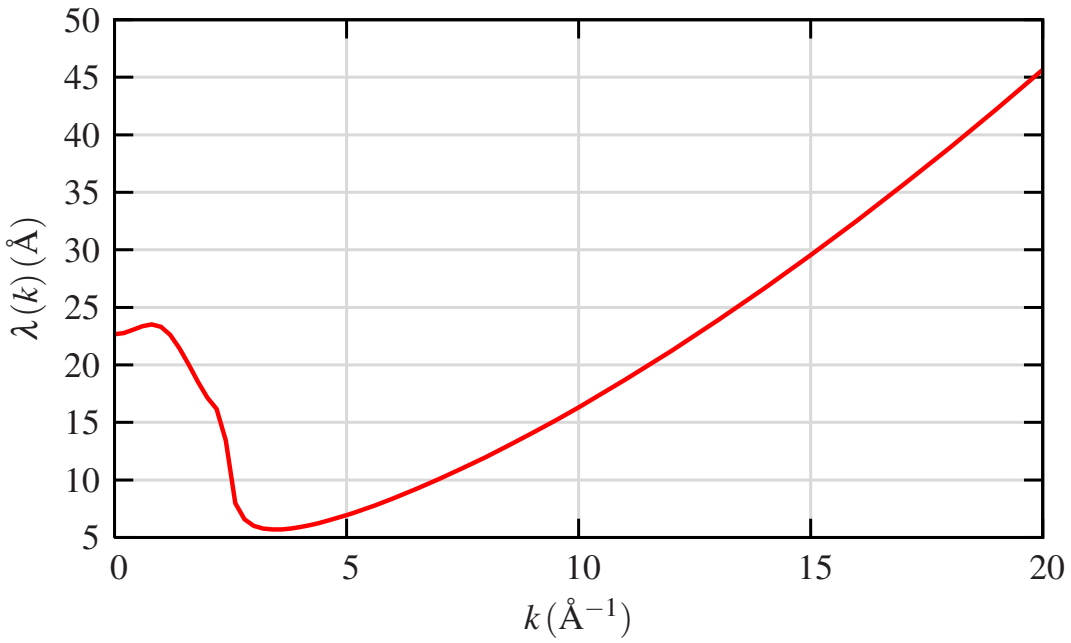

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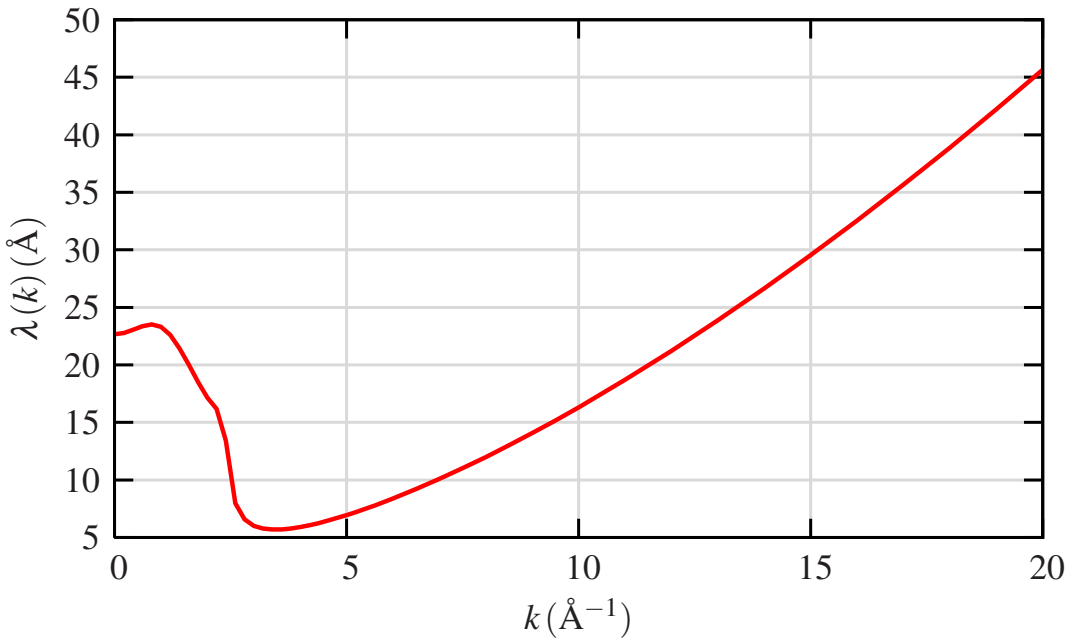

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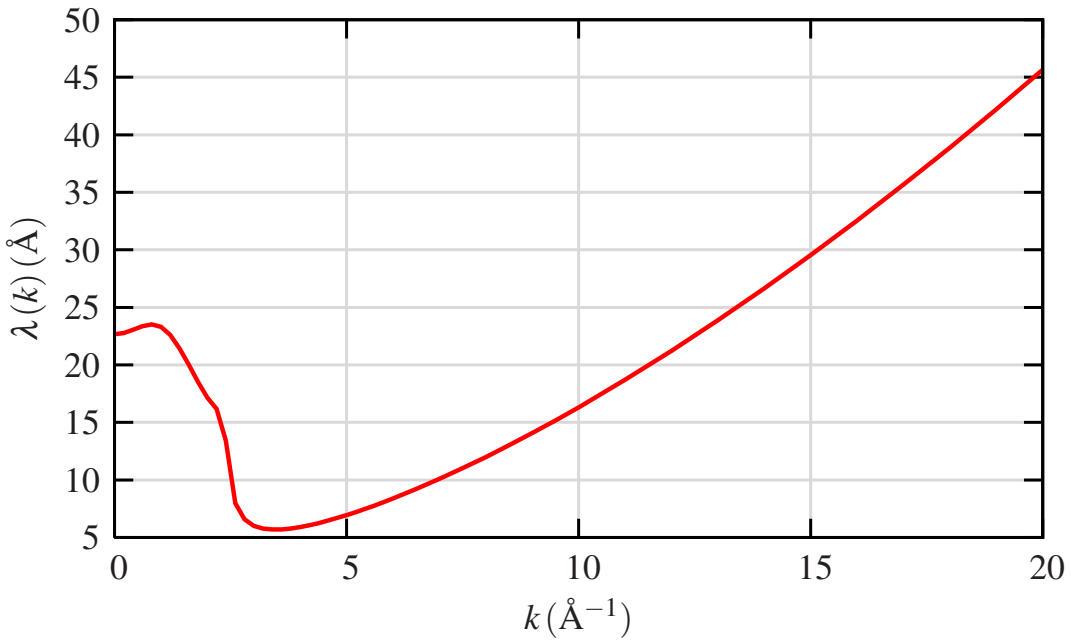

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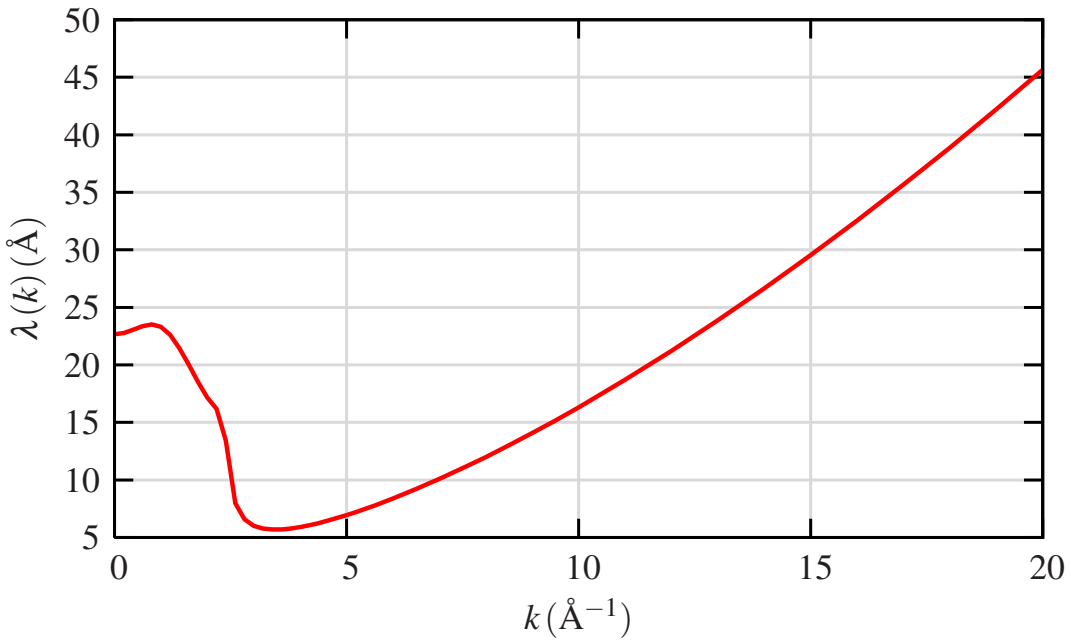

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- For XANES ($k < 3\,\text{Å}^{-1}$) Both λ and R^{-2} get large: XANES is not really a *local probe*.

S_0^2: Amplitude Reduction Term

Another important Amplitude Reduction Term is due to the relaxation of the *other electrons in the absorbing atom* to the hole in the core level:

$$S_0^2 = |\langle \Phi_f^{N-1} | \Phi_0^{N-1} \rangle|^2$$

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S_0^2 is usually taken as a constant:

$$\boxed{0.7 < S_0^2 < 1.0}$$

and is used as a Fitting Parameter that multiplies χ:

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Another important Amplitude Reduction Term is due to the relaxation of the *other electrons in the absorbing atom* to the hole in the core level:

$$S_0^2 = |\langle \Phi_f^{N-1} | \Phi_0^{N-1} \rangle|^2$$

$|\Phi_0^{N-1}\rangle = (N-1)$ electrons in unexcited atom.
$\langle \Phi_f^{N-1}| = (N-1)$ electrons, relaxed by core-hole.

S_0^2 is usually taken as a constant:

$$\boxed{0.7 < S_0^2 < 1.0}$$

and is used as a Fitting Parameter that multiplies χ:

S_0^2 is Completely Correlated with N (!!!)

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.

Sum over Paths and Multiple Scattering

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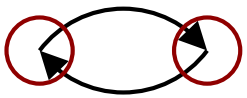

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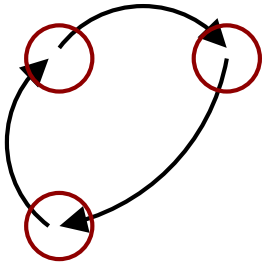
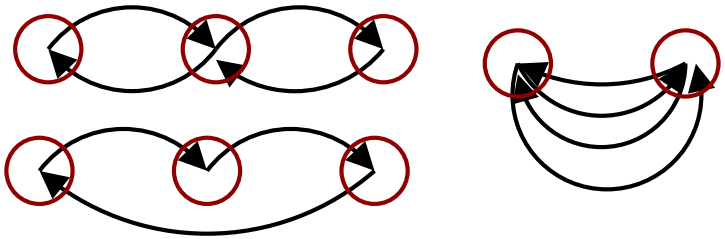


Focussed Multiple Scattering Paths



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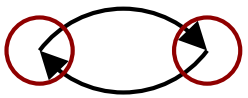

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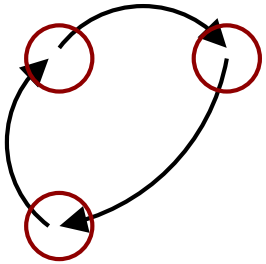

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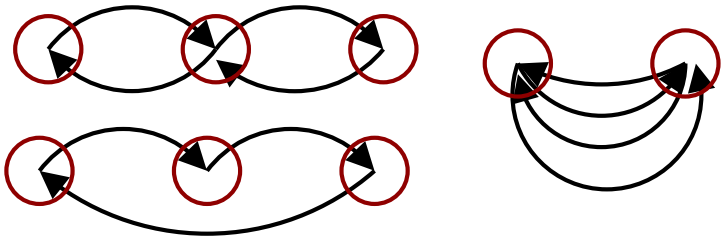

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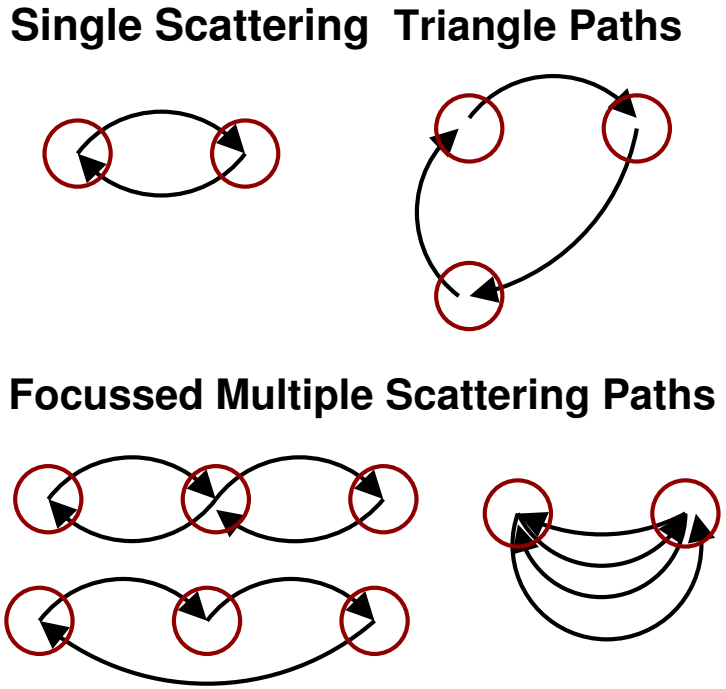

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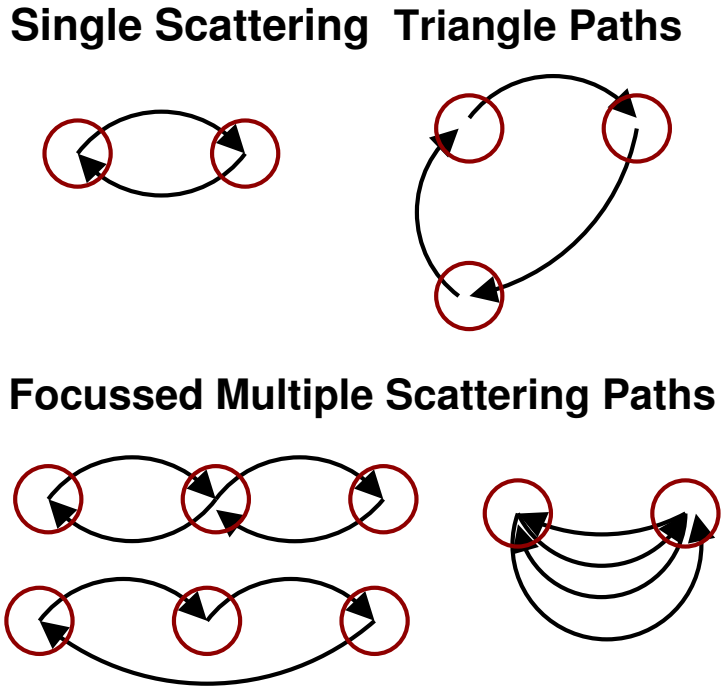

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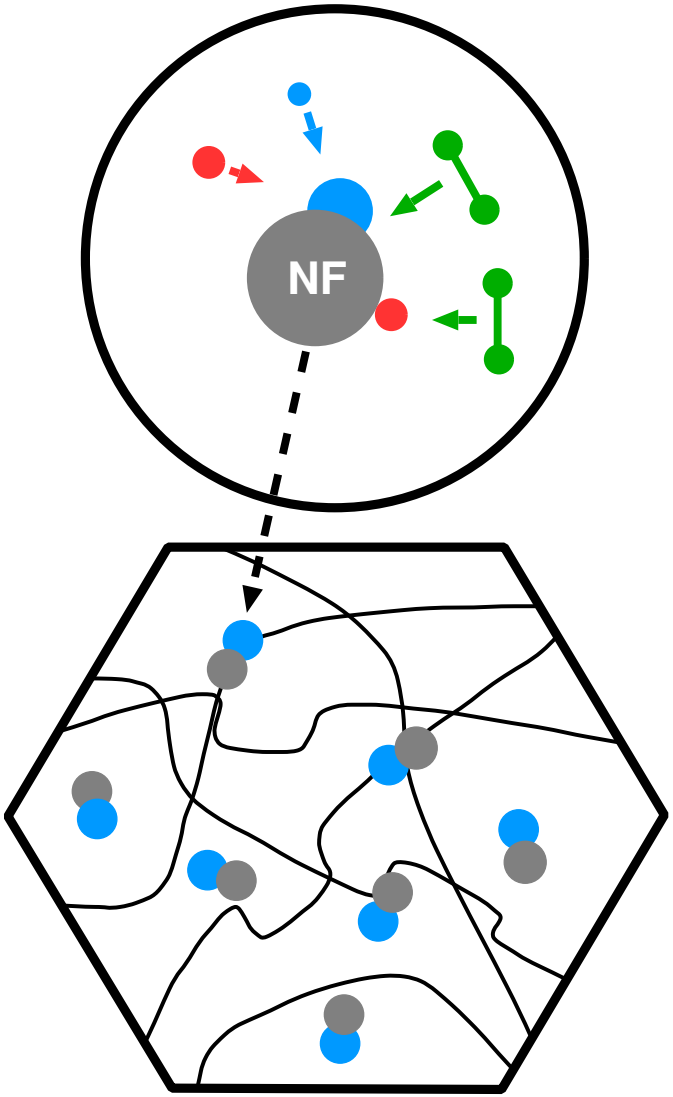
Multiple Scattering is strongest when $\theta > 150^\circ$.

The strong angular dependence can be used to measure bond angles.

For first shell analysis, multiple scattering is hardly ever needed.

Advantages of NFA steels



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

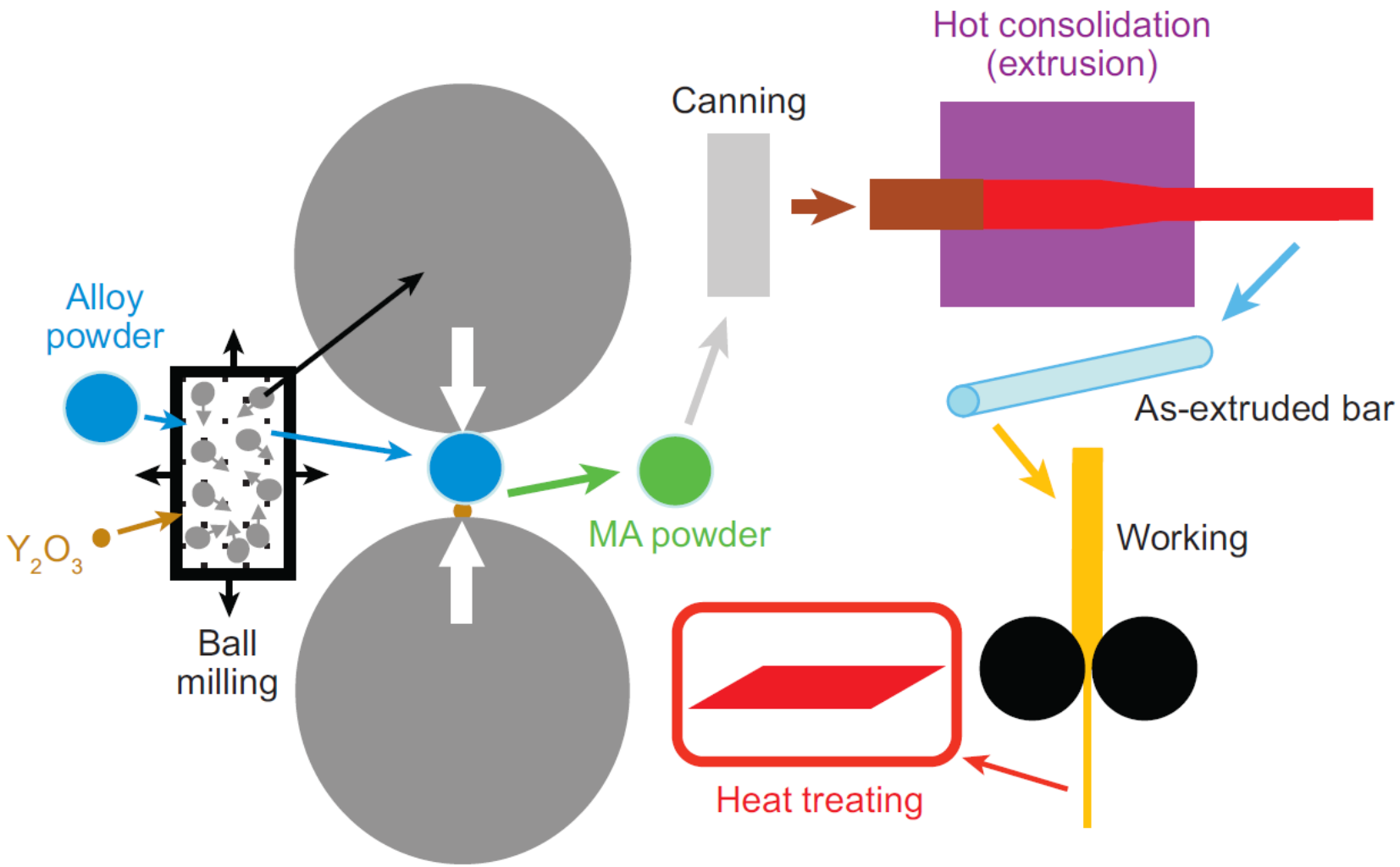
NFs trap helium in fine bubbles and prevent accumulation of high concentrations

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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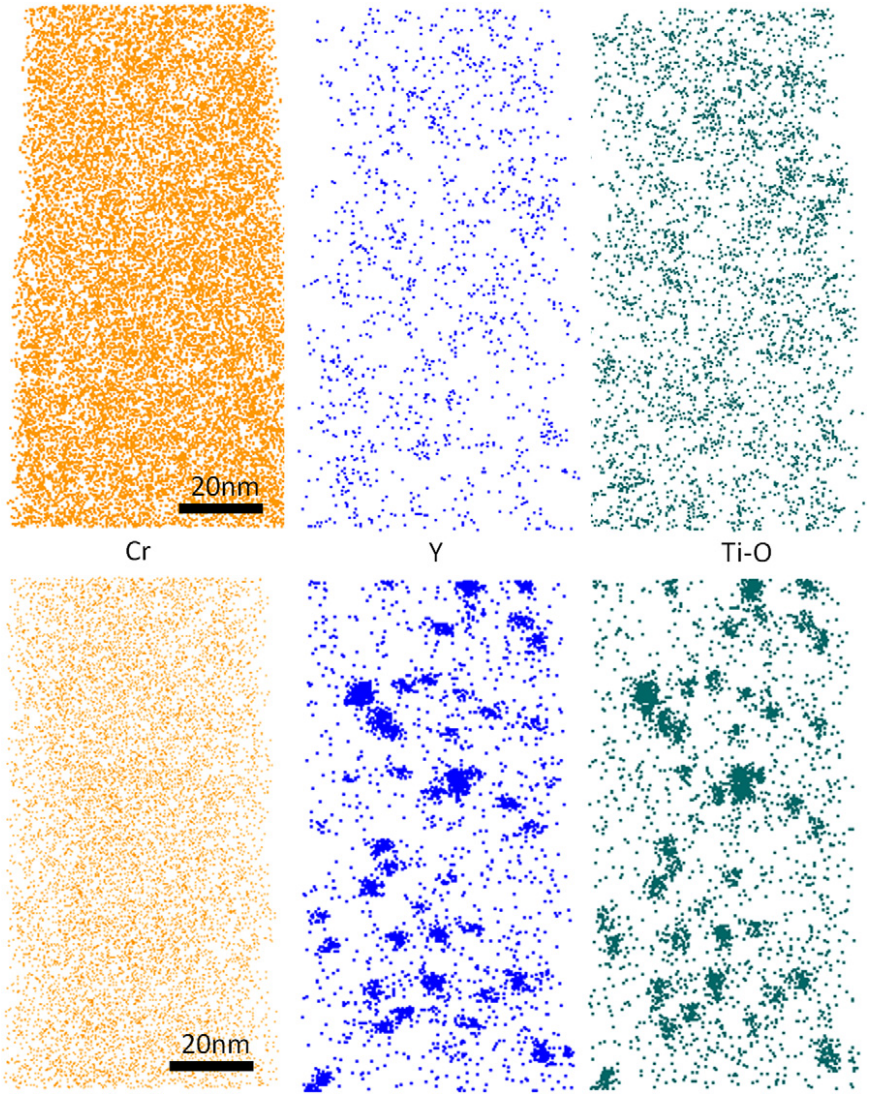
Atom probe tomography data



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

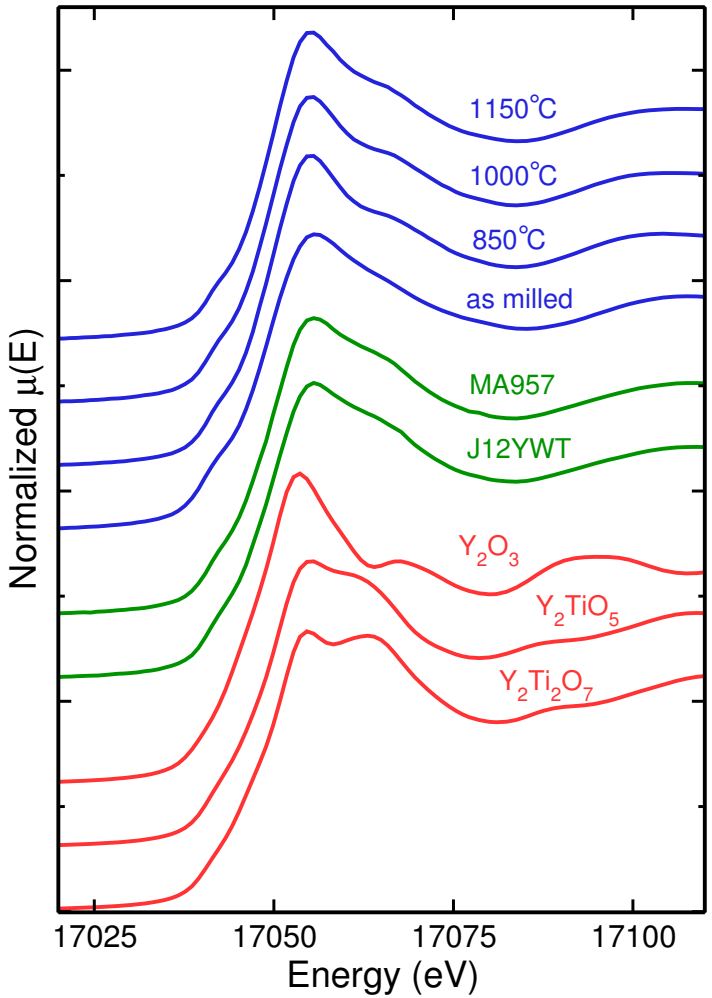
C.A. Williams, P. Unifantowicz, N. Baluc, G.D.W. Smith, and E.A. Marquis, *Acta Materialia* **61**, 2219–2235 (2013).

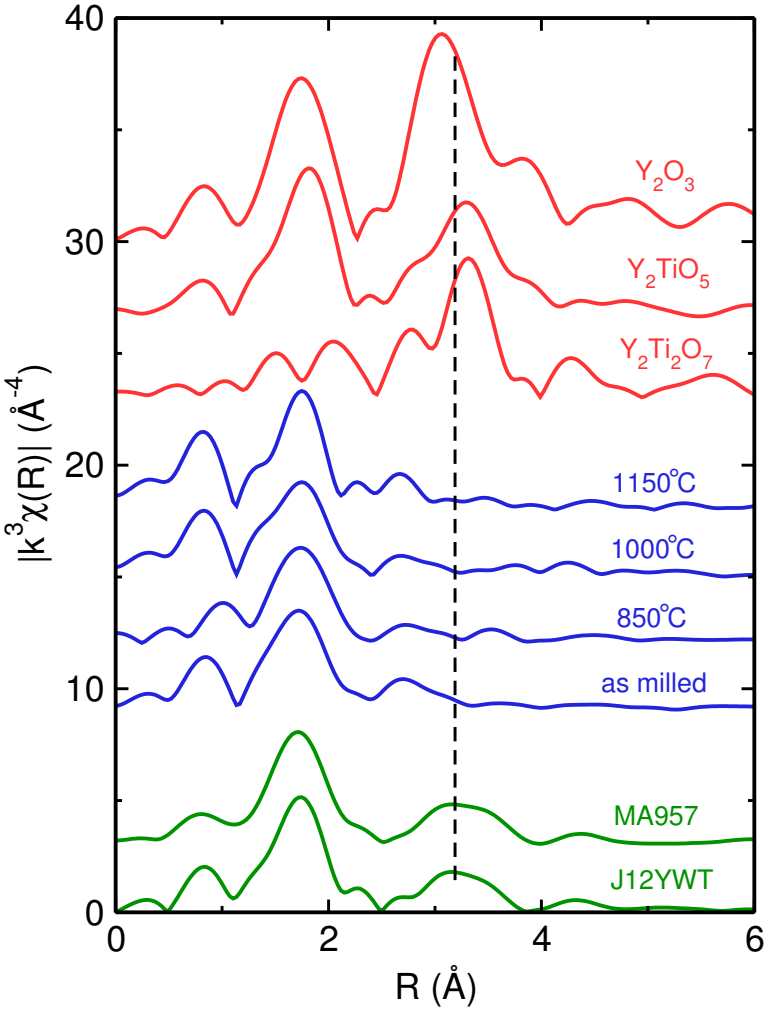
Samples studied

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.

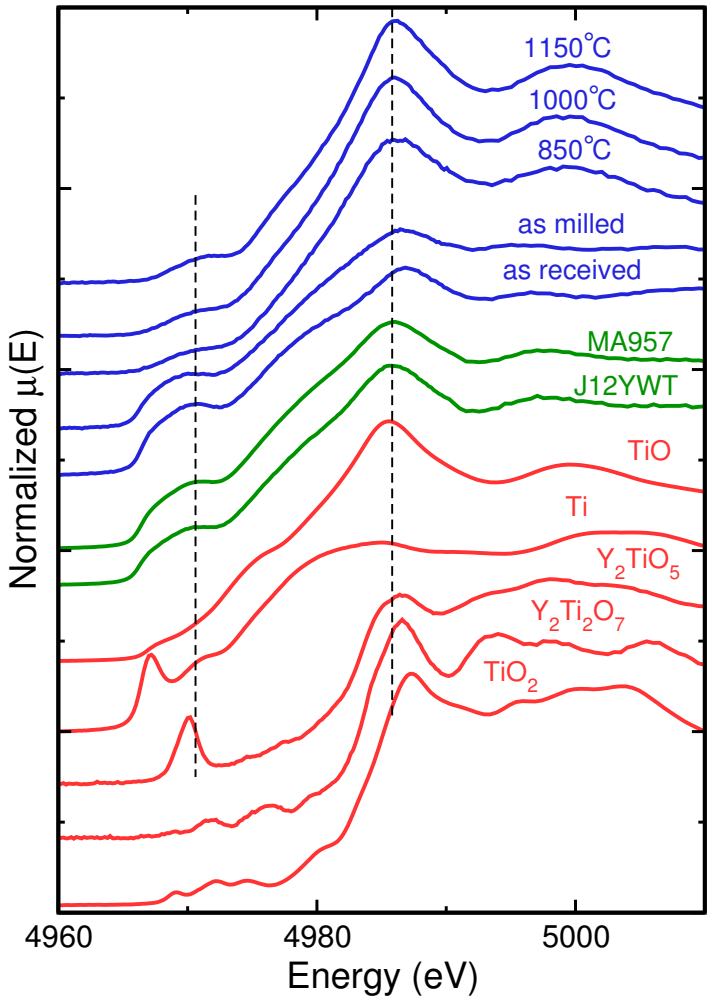
Yttrium edge data

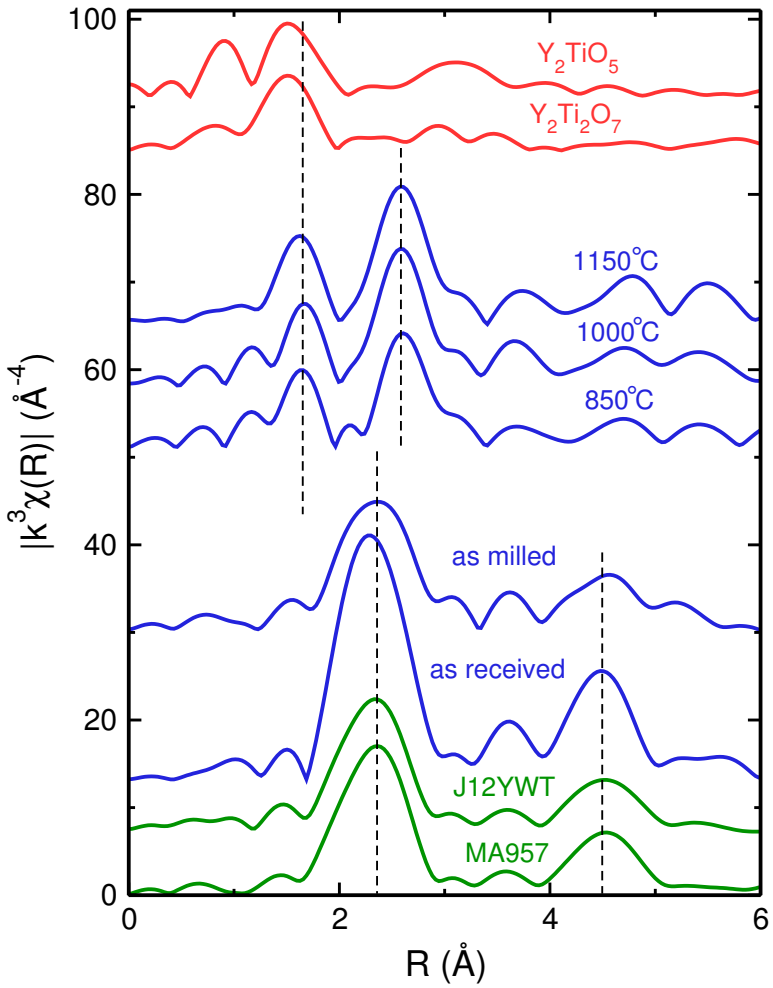




Edges show complex mixture; EXAFS of annealed powders indicate smaller NFs than commercial steels

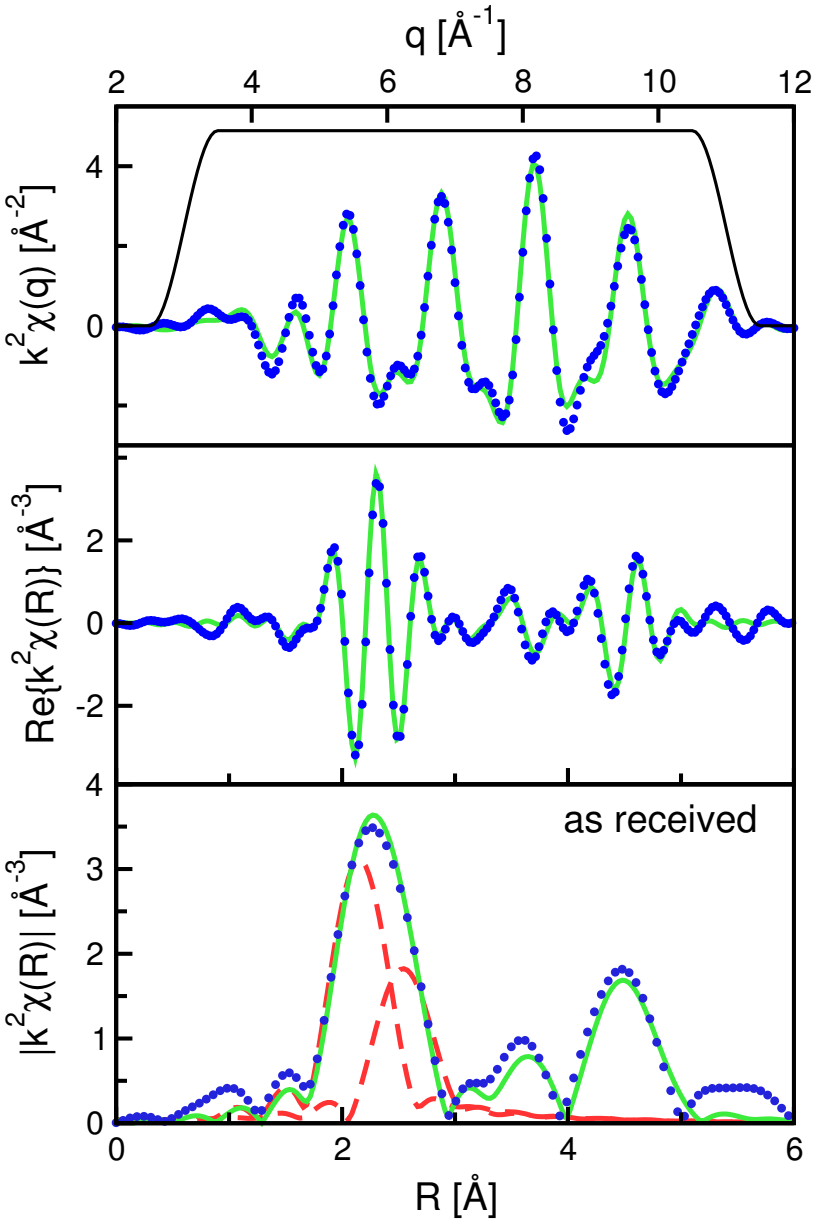
Titanium edge data





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 $\sim$ 2.6Å

Ti in BCC structure



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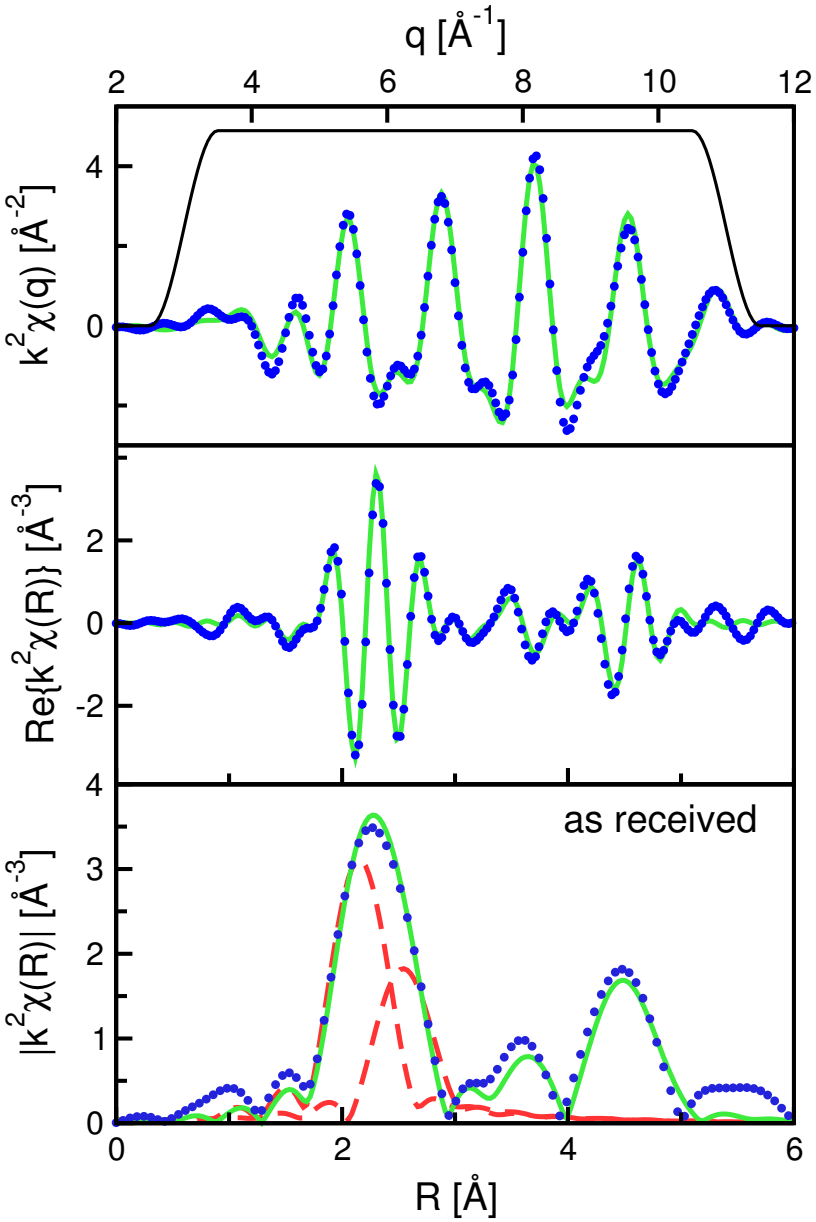

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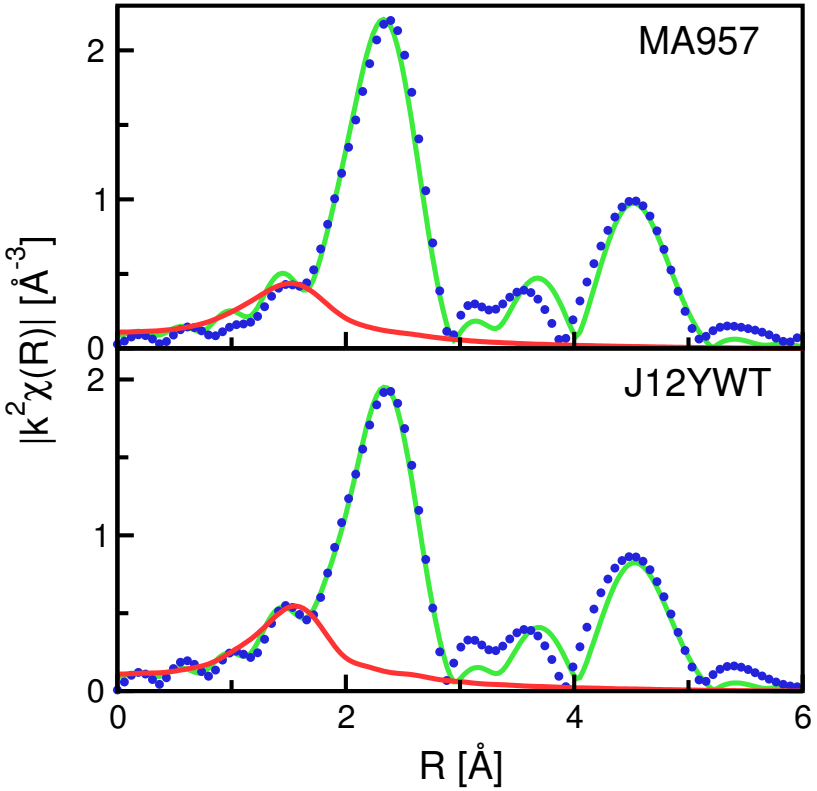
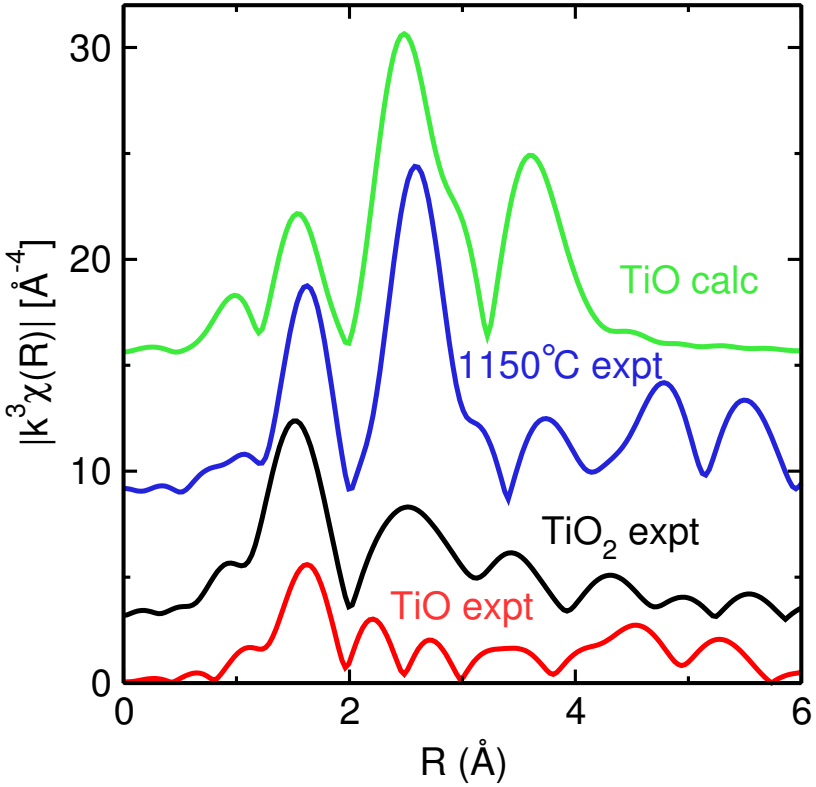


Commercial alloys fit with this model plus a small amount of Ti-O neighbors

Ti in TiO structure

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



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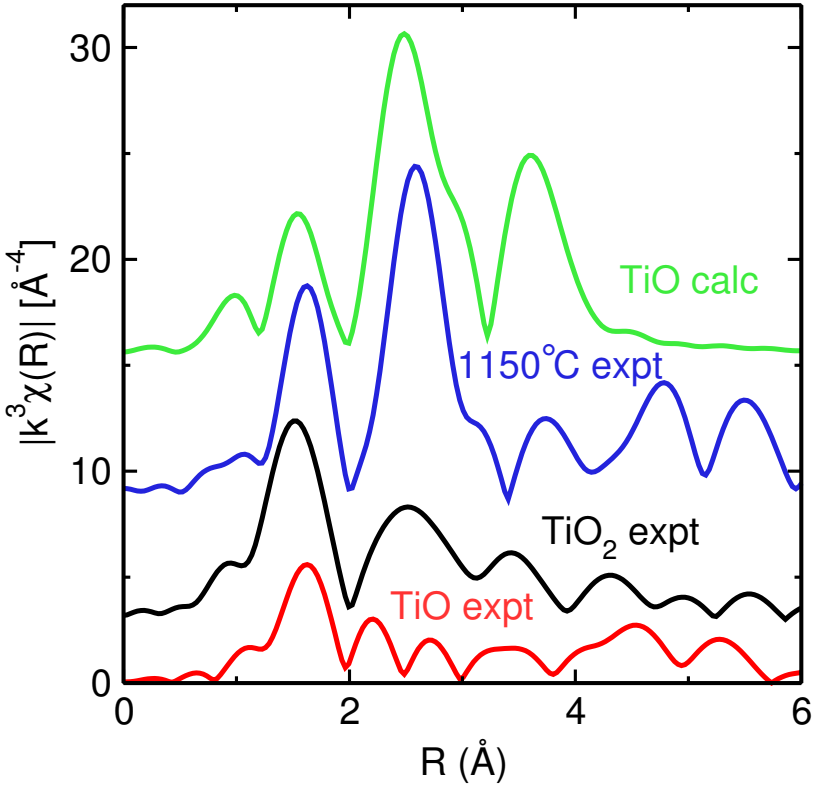

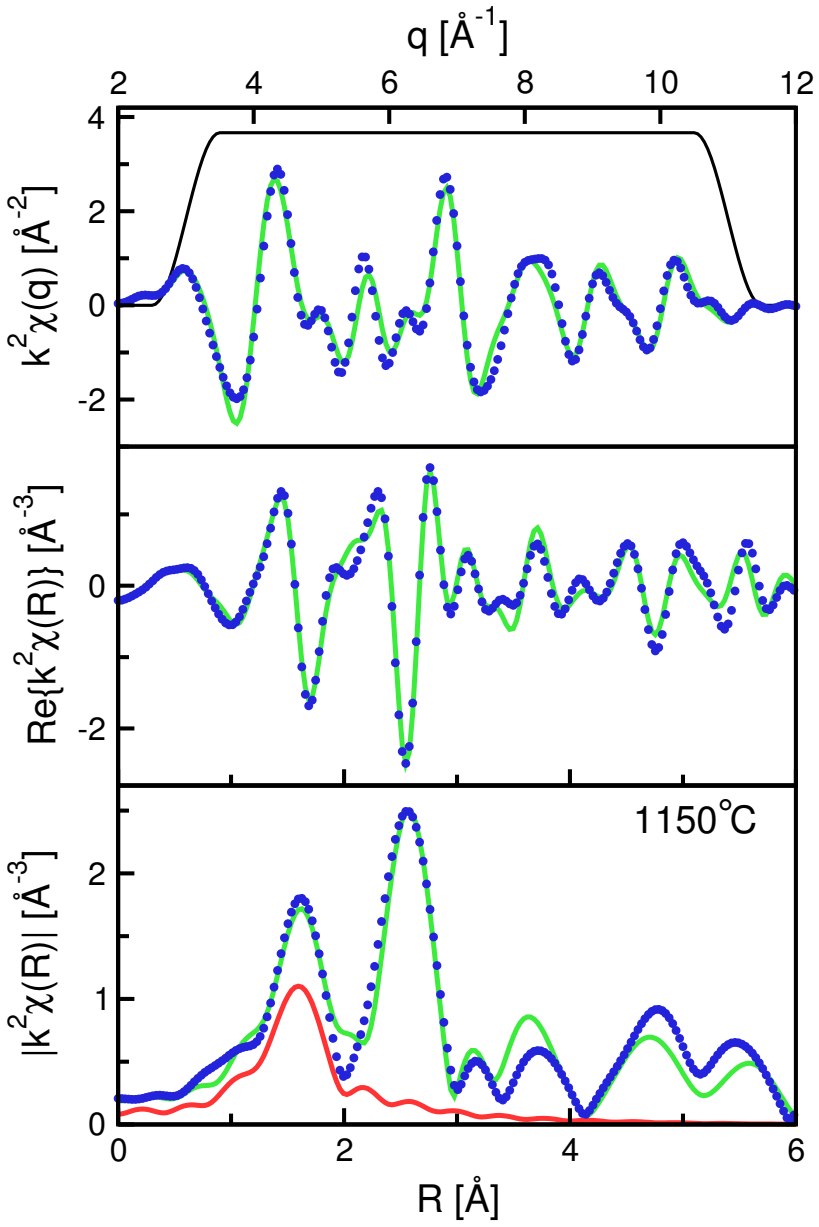

All can be fit with cubic TiO plus an additional Ti–O path, likely from complex Y–Ti–O oxides

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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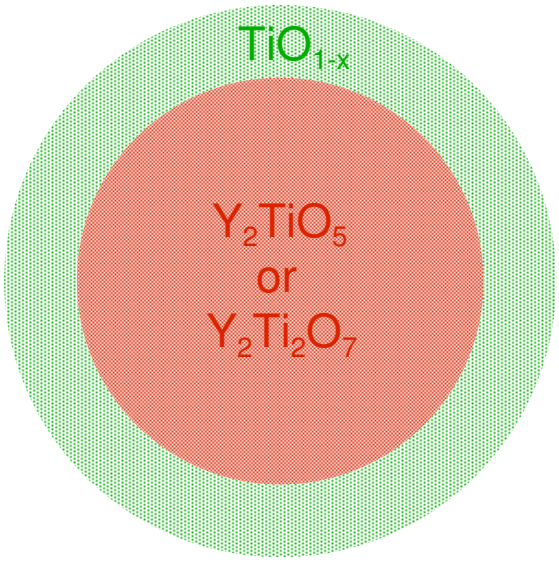

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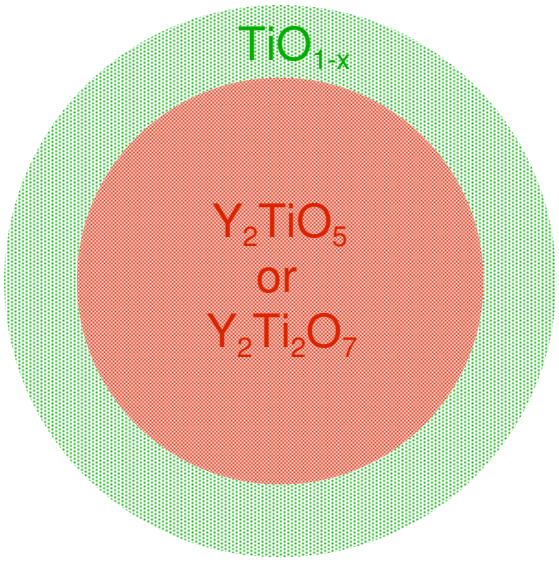

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S. Liu, G.R. Odette, and C.U. Segre, *J. Nucl. Mater.* **445**, 50-56 (2014).