# Today's outline - October 28, 2021

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Reading Assignment: Chapter 7.4

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Homework Assignment #05:
Chapter 5: 1,3,7,9,10
due Tuesday, November 02, 2021

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- EXAFS theory
- Local structure of nanoferritic alloy steels
- In situ studies of methanol fuel cells

Reading Assignment: Chapter 7.4

Homework Assignment #05:
Chapter 5: 1,3,7,9,10
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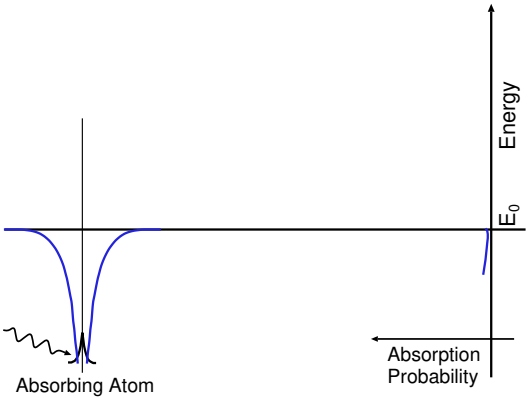
Homework Assignment #06:
Chapter 6: 1,6,7,8,9
due Tuesday, November 16, 2021

# X-ray absorption by a free atom




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

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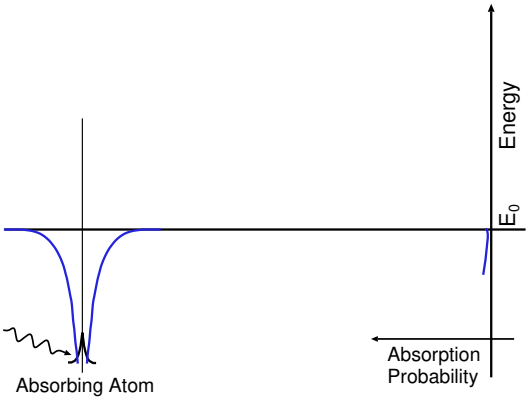


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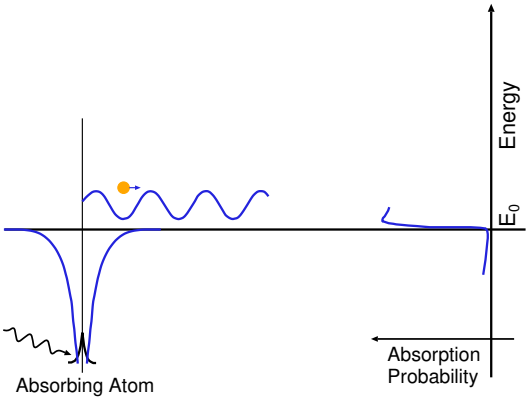


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Once the x-ray energy is large enough to promote a core-level to the continuum, there is a sharp increase in absorption.

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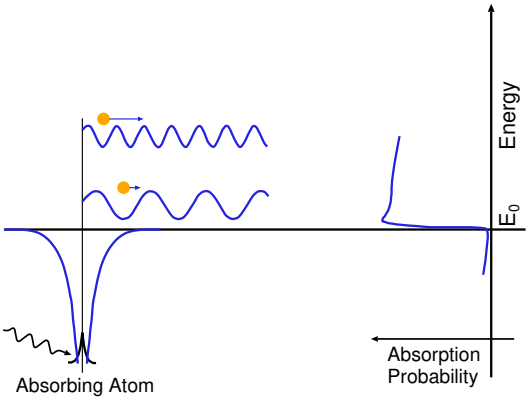


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$\mu(E)$ has a sharp step at the core-level binding energy, and is a smooth function of energy above this absorption edge.

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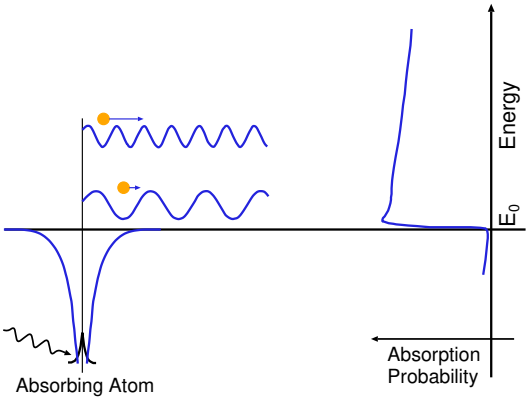


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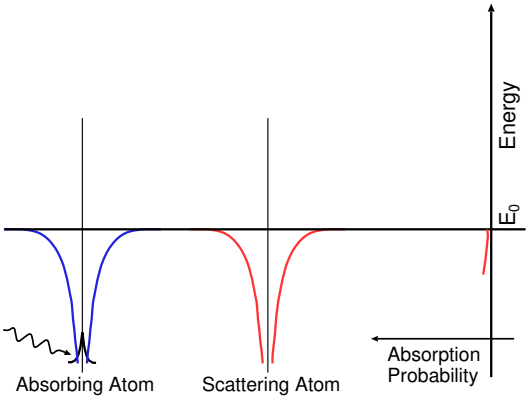
$\mu(E)$ has a sharp step at the core-level binding energy, and is a smooth function of energy above this absorption edge.

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 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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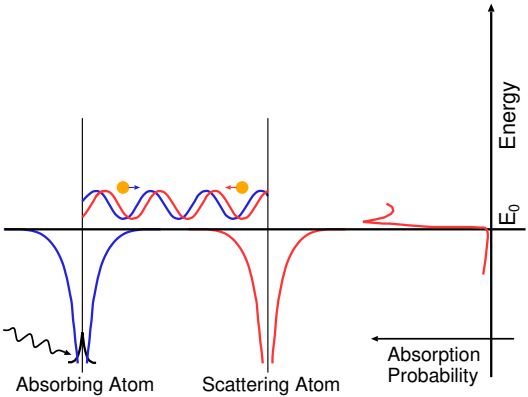


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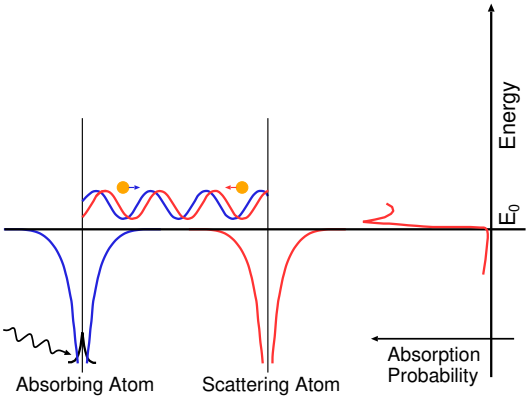


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In the XANES region $\mu(E)$ depends on the density of electron states with energy $(E - E_0)$, at the absorbing atom with the appropriate symmetry ($\Delta l = \pm 1$, $\Delta m = 0, \pm 1$)

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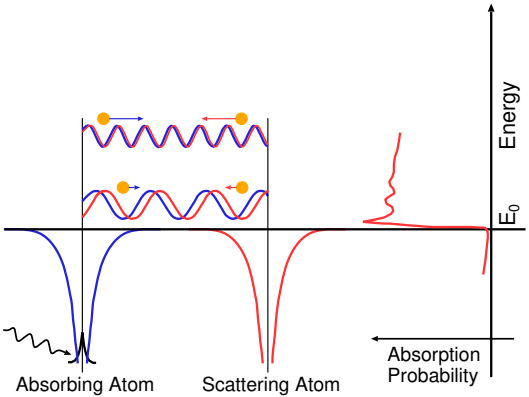


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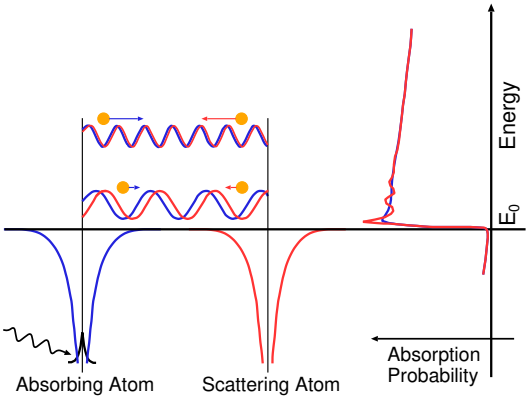


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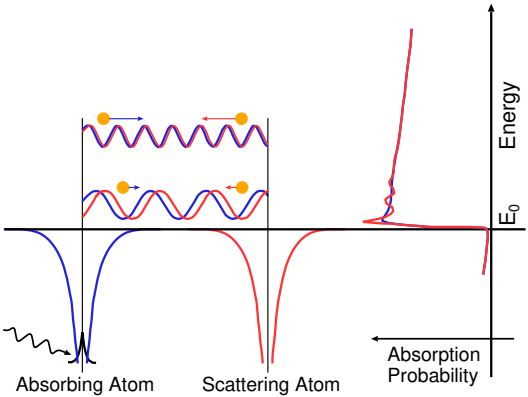
The amplitude and phase of the back-scattered photoelectron at the absorbing atom will vary with energy, causing the oscillations in $\mu(E)$

# X-ray absorption: Fermi's golden rule




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

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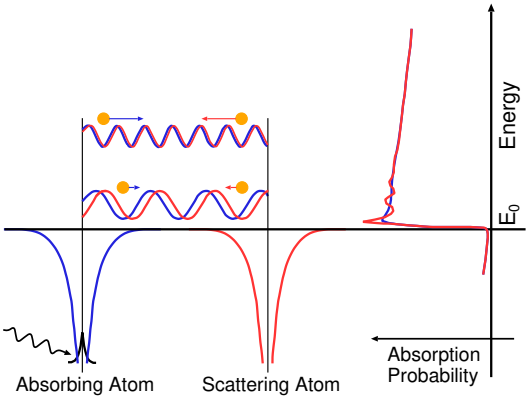


$$\mu(E) = \mu_0(E) + \Delta\mu(E) = \mu_0(E)[1 + \chi(E)]$$

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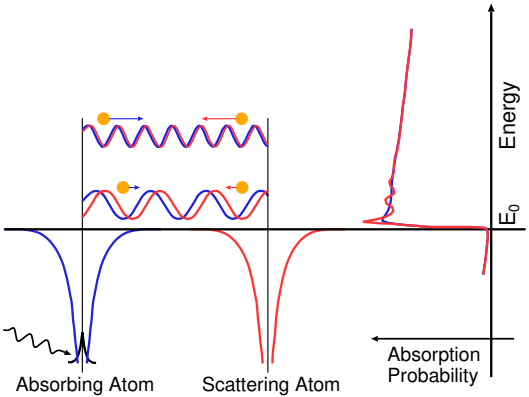


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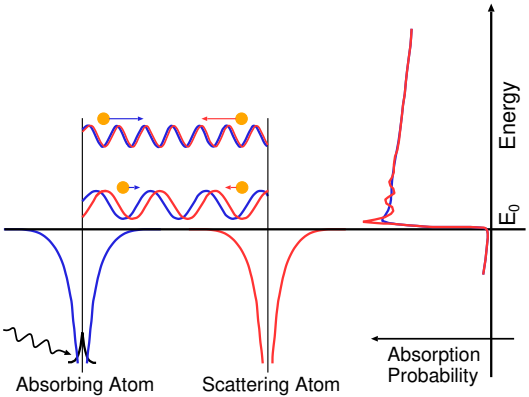


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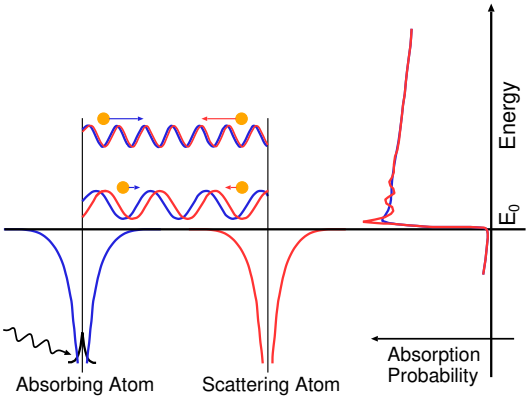


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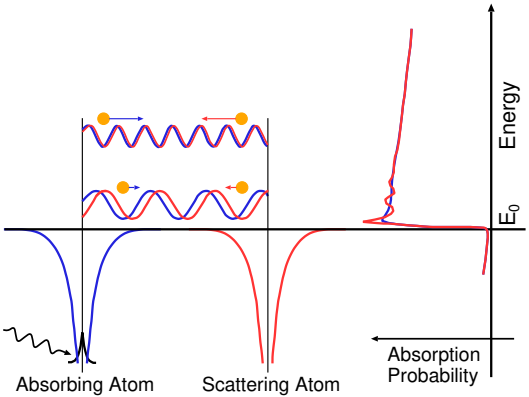


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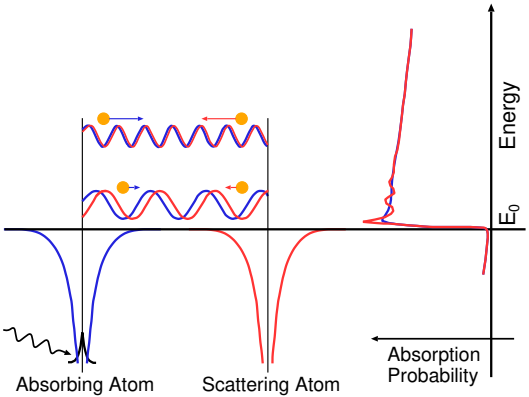


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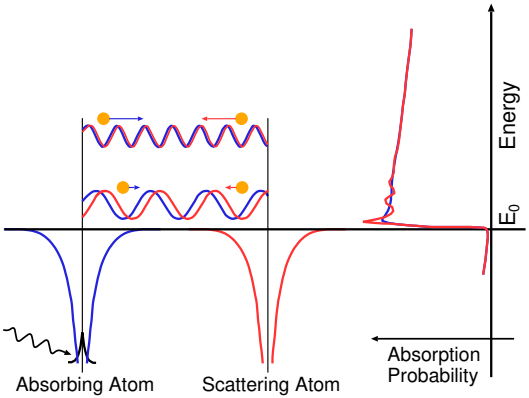


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$|f\rangle$ is the final state which has a photoelectron, a hole in the core, and no photon. This is altered by the neighboring atom: the photoelectron scatters.

# $\mu$ and $\chi$ and the photoelectron wavefunction

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

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

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\chi(E) &\sim \langle i|\mathcal{H}|\Delta f\rangle \sim \langle i|\Delta f\rangle && \text{XAFS oscillations}
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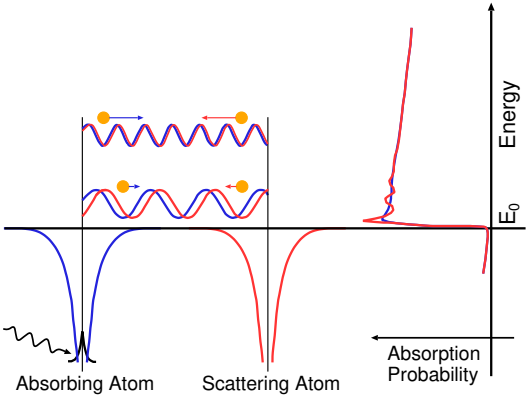


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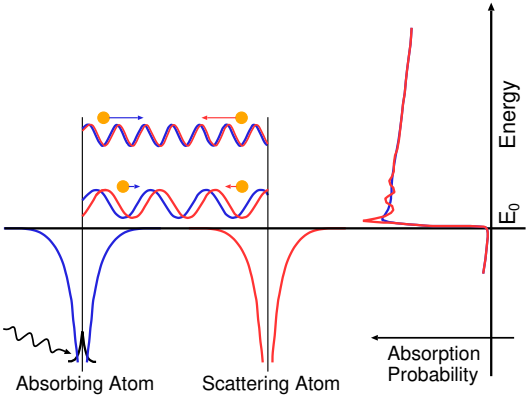


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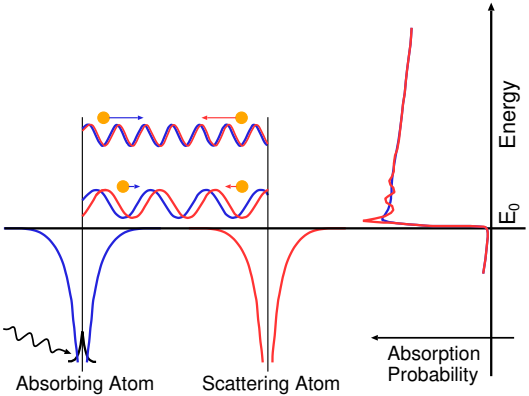


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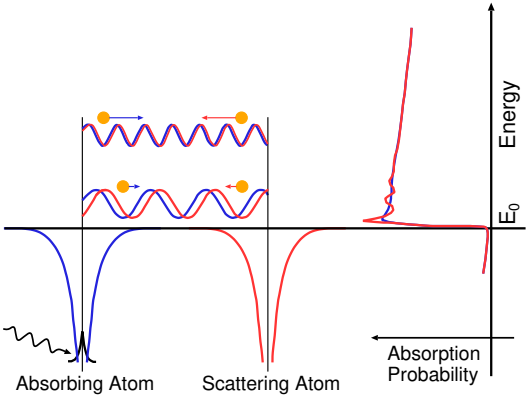


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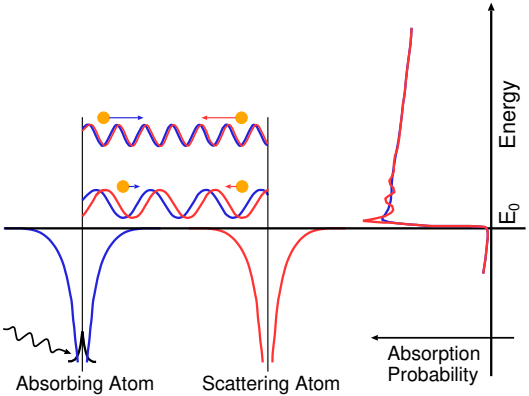


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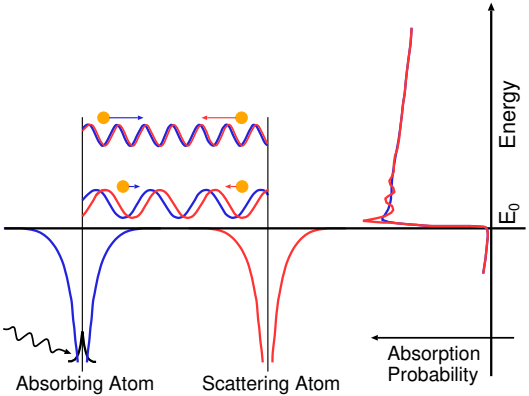


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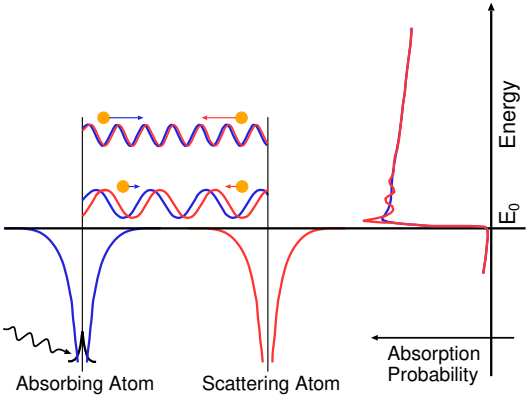


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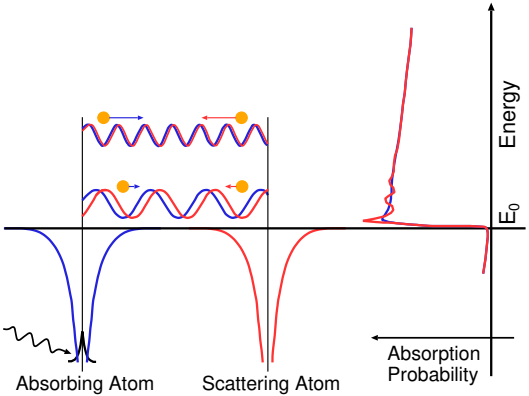


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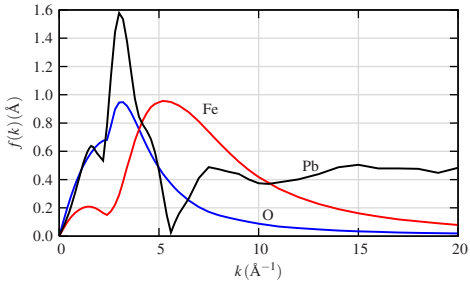

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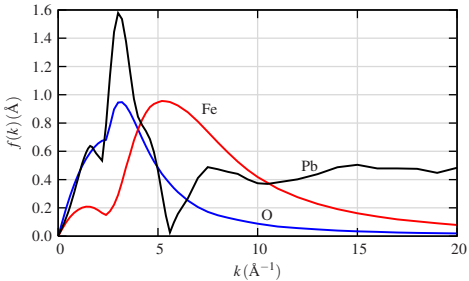

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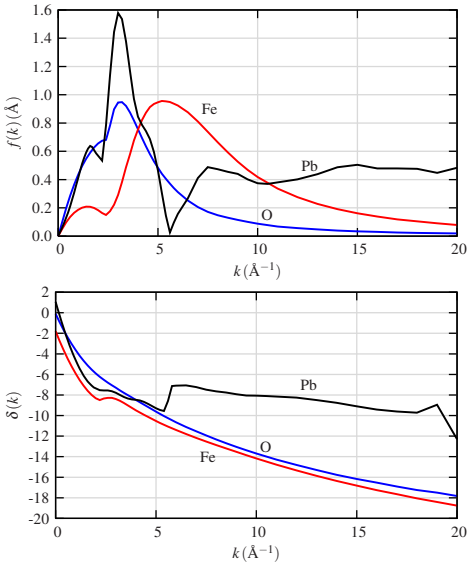

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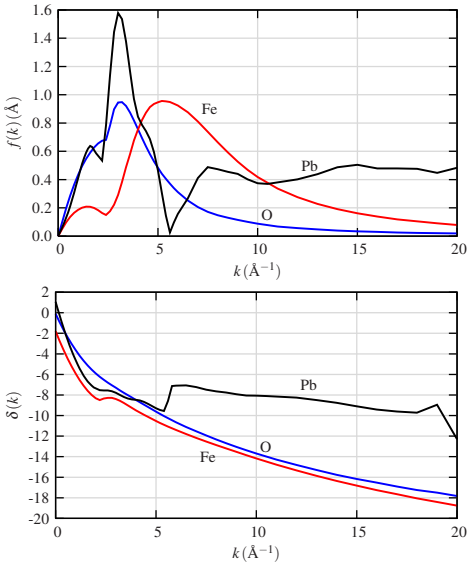

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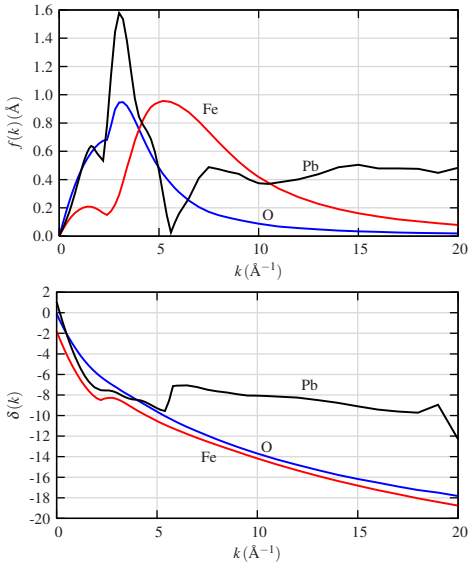

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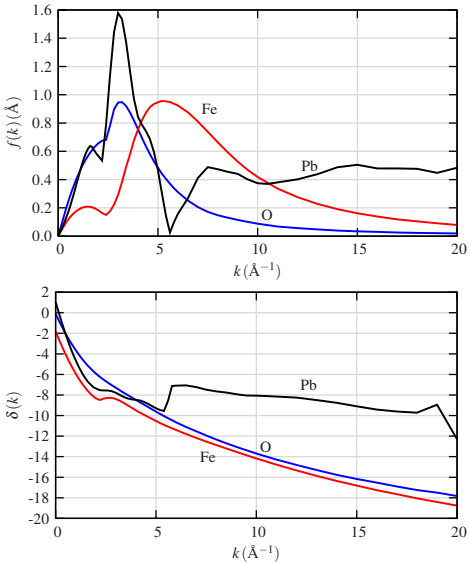
$Z$ can usually be determined to $\pm 5$. Fe and O can be distinguished, but Fe and Mn cannot be



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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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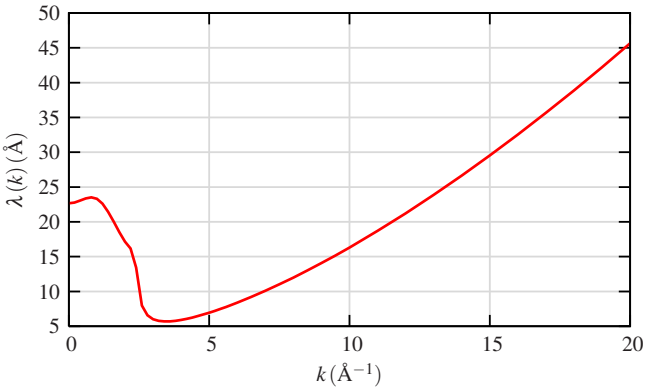

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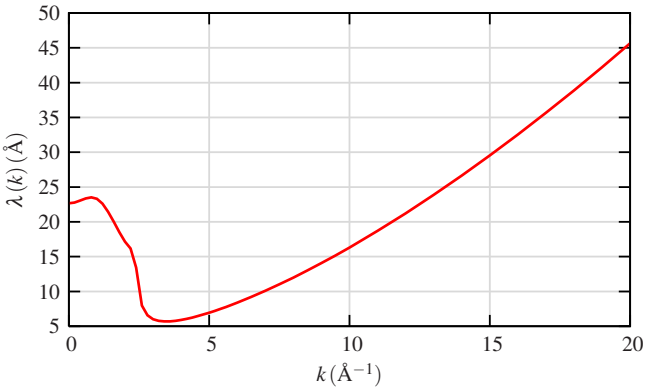

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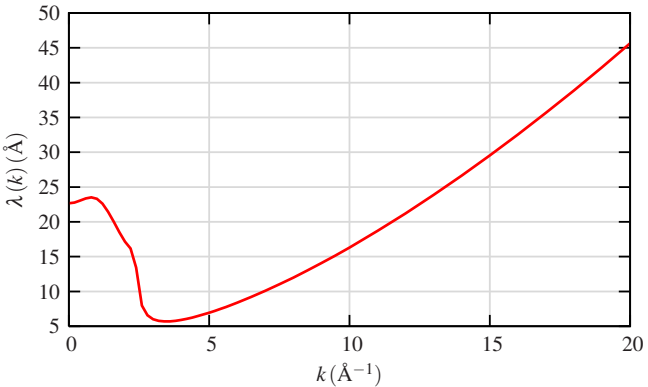


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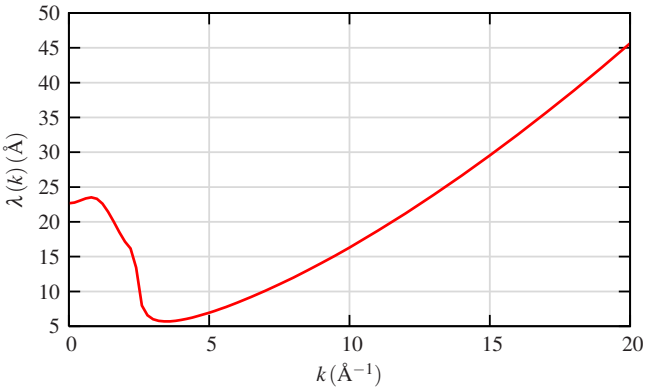


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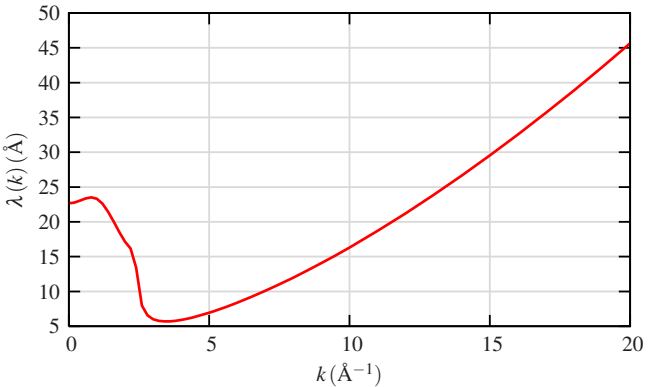


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for XANES ($k < 3\,\text{Å}^{-1}$), both $\lambda$ and $R^{-2}$ become large: making XANES not really a local probe

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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 $\sigma^2$ for scattering paths to neighboring atoms by fitting the data.

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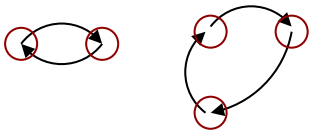

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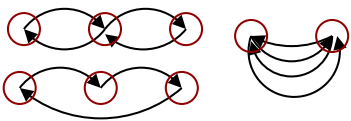

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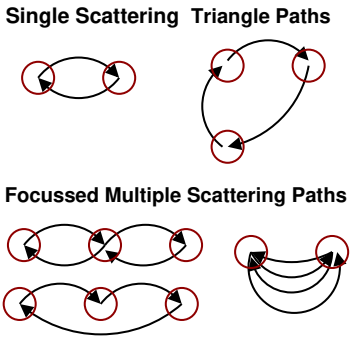


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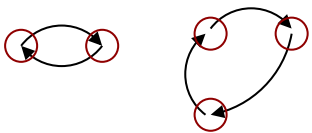

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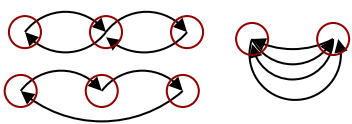

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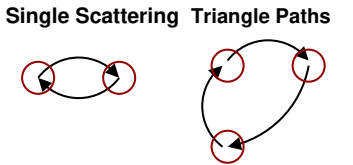


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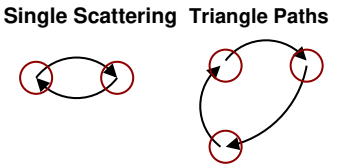


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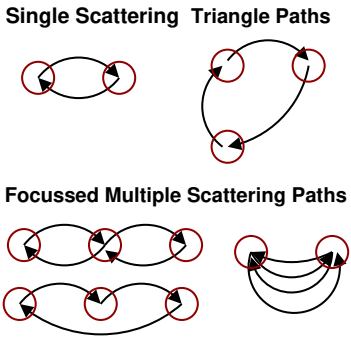


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For first shell analysis, multiple scattering is hardly ever needed

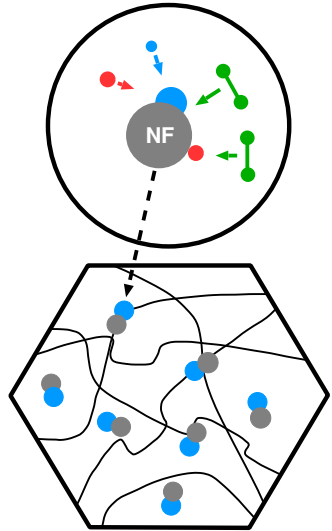
# Advantages of nanoferritic alloy (NFA) steels

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

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

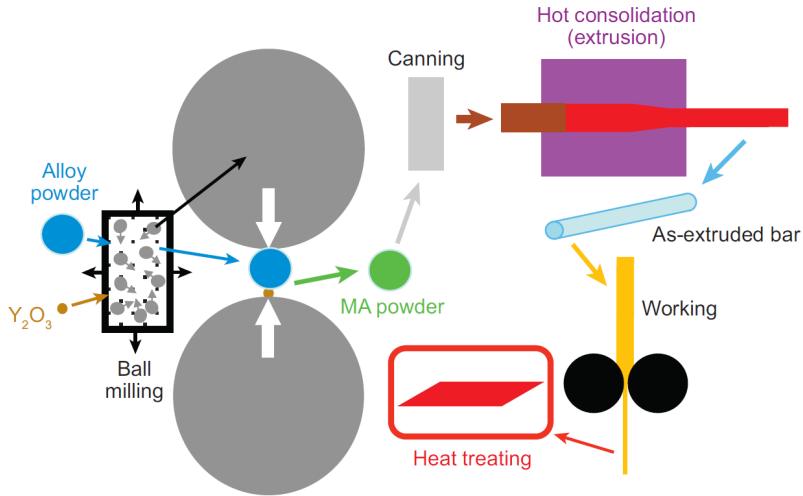
NFs maintain high stable sink densities for vacancy and self-interstitial atom defect annihilation

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



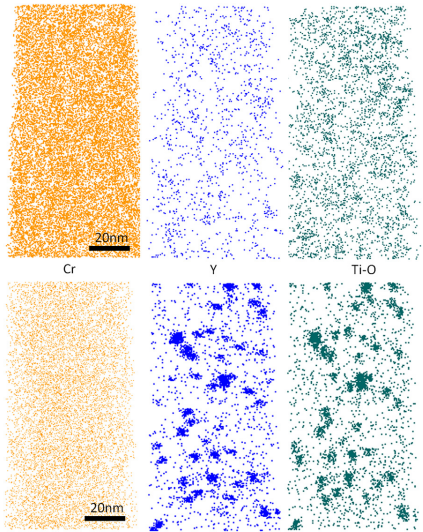

G.R. Odette, M.J. Alinger, and B.D. Wirth, *Annu. Rev. Mater. Res.* **38**, 471–503 (2008).

# Fabrication of NFA steels



# Atom probe tomography data

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

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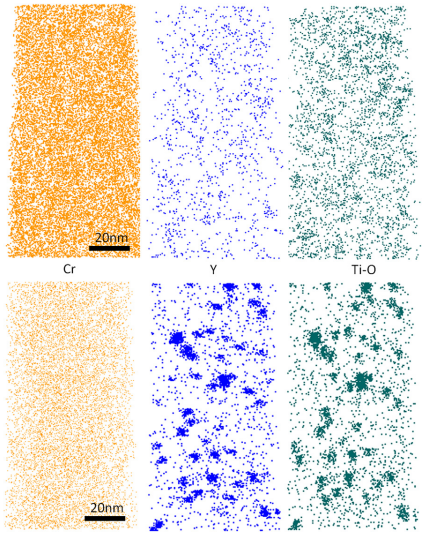


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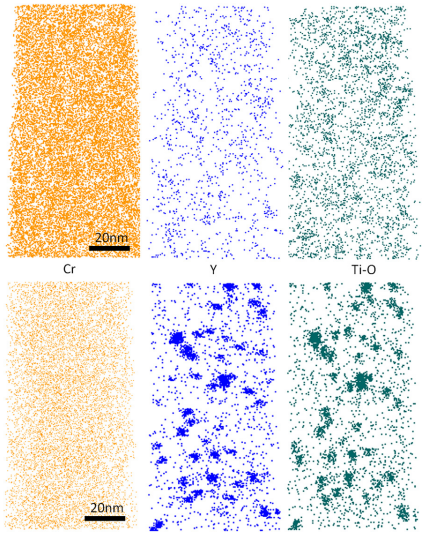
# Atom probe tomography data

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

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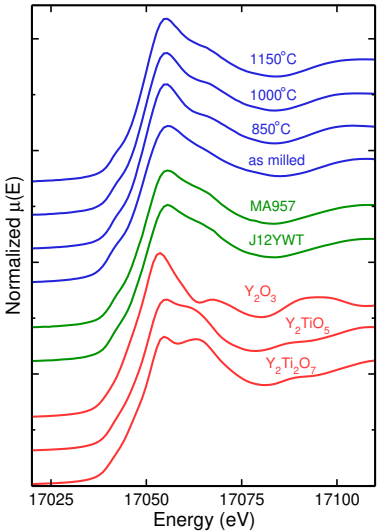
# Samples studied

| 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 of phases

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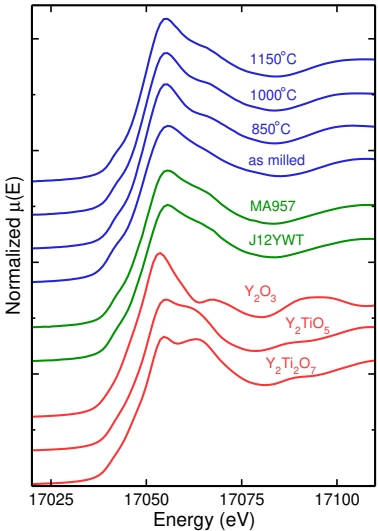
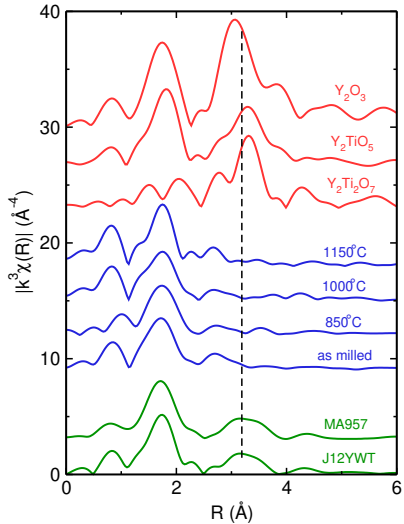
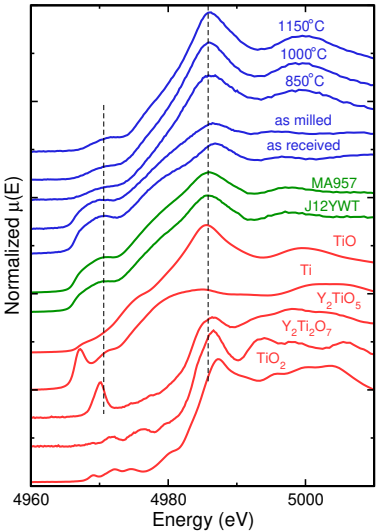



Edges show complex mixture of phases

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

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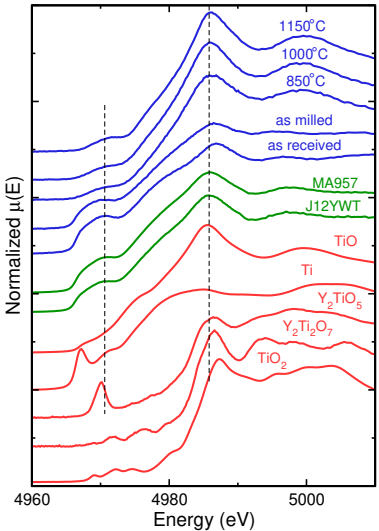


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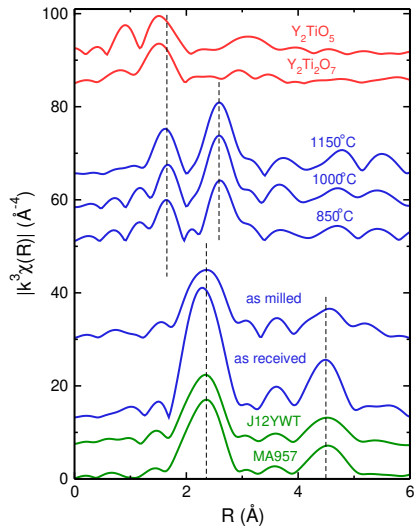
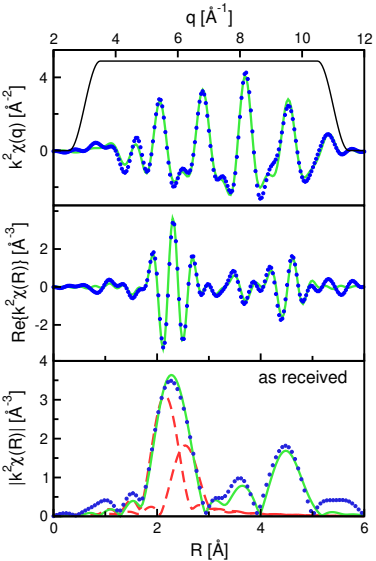
EXAFS shows a distinct heavy metal peak at $\sim 2.6$Å



# Ti in BCC structure




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

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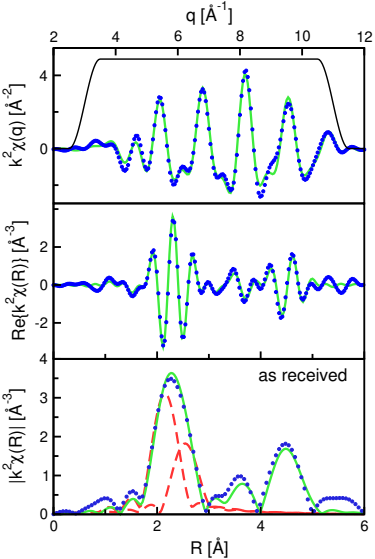


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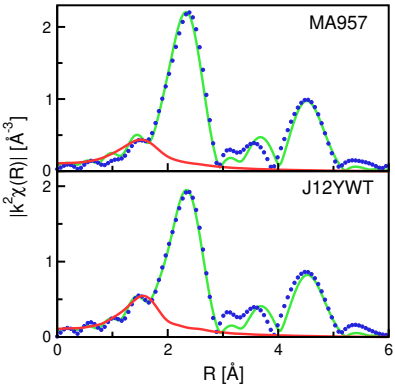

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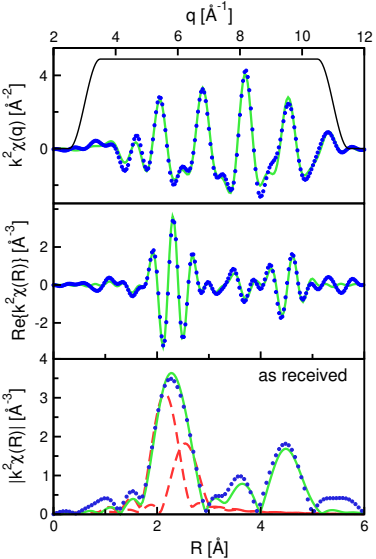


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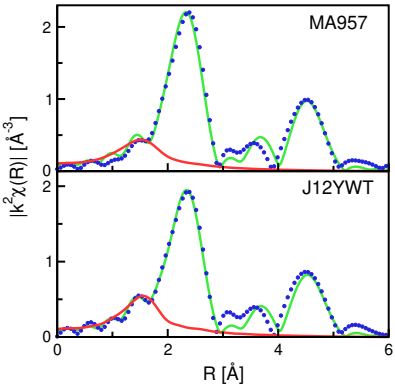
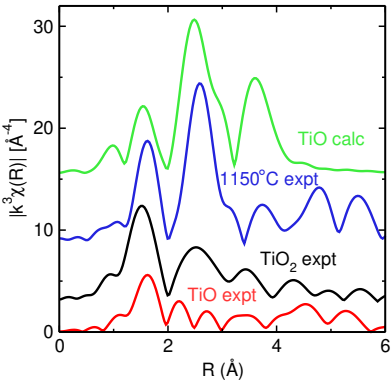



Commercial alloys fit with this model plus a small amount of Ti-O neighbors

# Ti in TiO structure

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



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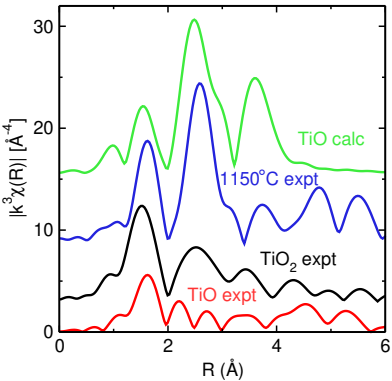
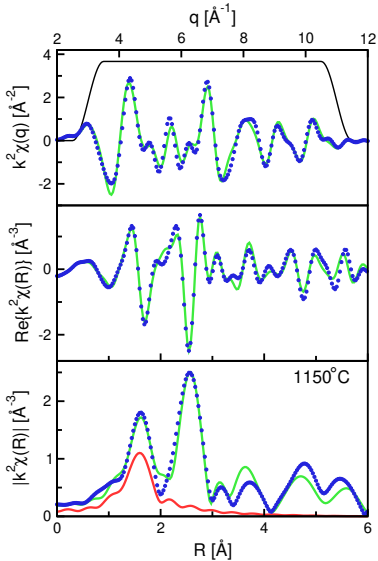



All can be fit with cubic TiO plus an additional Ti–O path, likely from complex Y–Ti–O oxides



# The fate of Ti

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

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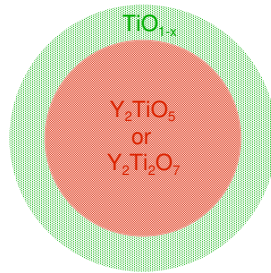
Annealed powders all have mixture of TiO-like structure and more complex oxides ($\sim$ 50% each)




"Evidence for core-shell nanoclusters in oxygen dispersion strengthened steels measured using x-ray absorption spectroscopy," S. Liu, G.R. Odette, and C.U. Segre, *J. Nucl. Mater.* **445**, 50-56 (2014).

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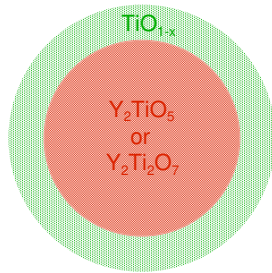


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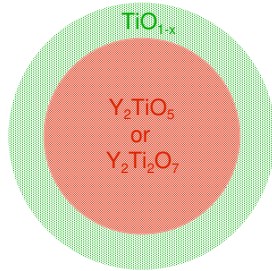
Presence of this metastable cubic TiO suggests significant fraction of Ti on the surface of Y–Ti–O NFs

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