An Introduction to X-ray Absorption Spectroscopy

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These notes borrow heavily on the work of Matthew Newville and Bruce Ravel and in the same spirit as they intended, these notes too are open to others for sharing provided that proper attribution is given.

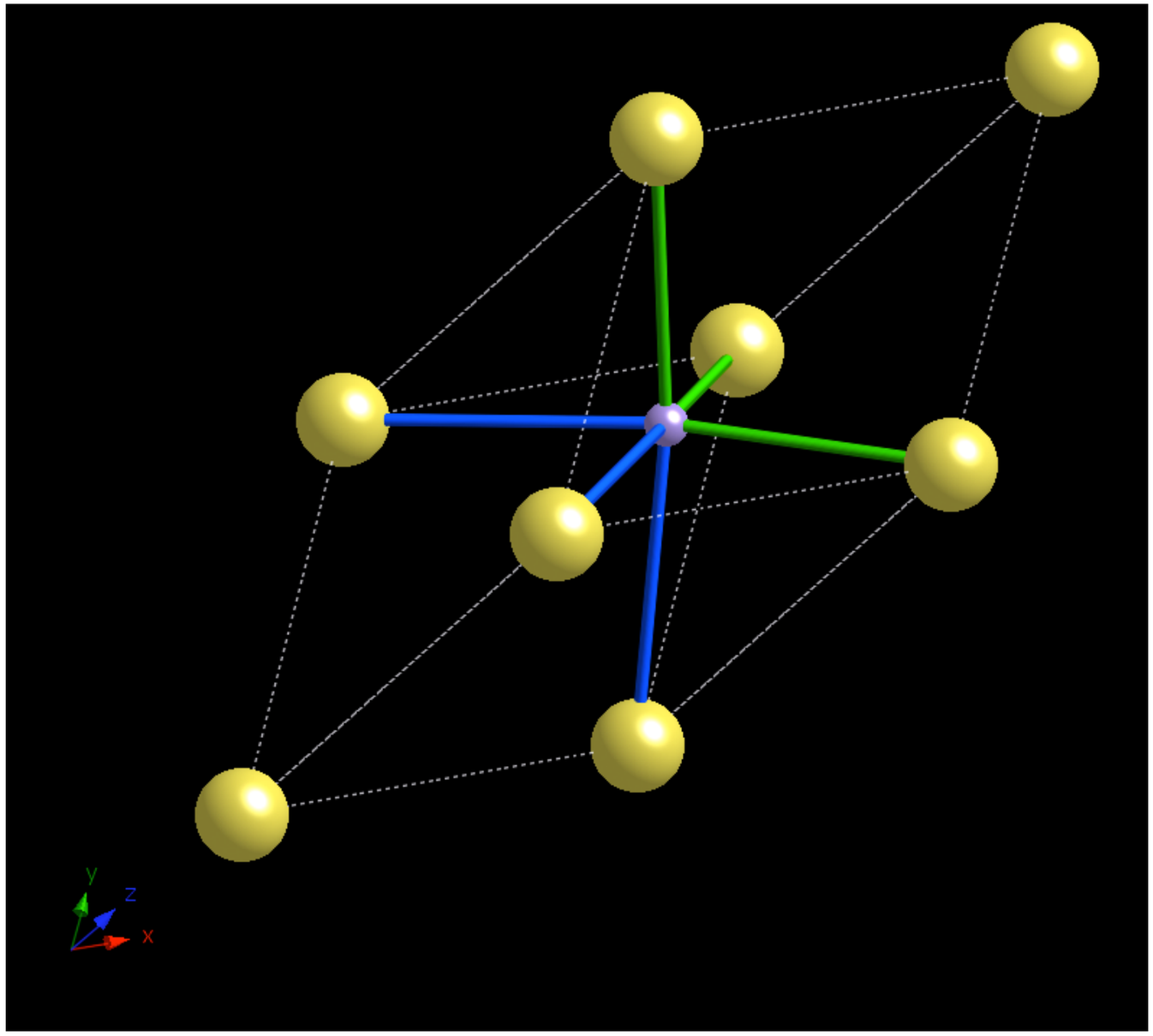
What is XAFS
(X-ray Absorption Fine-Structure)

- XAFS (also XAS) refers to the modulation of the x-ray absorption coefficient near and above an absorption edge.
- XAFS is elementally selective and can explore the local atomic environment about the absorbing atom

XAFS Characteristics

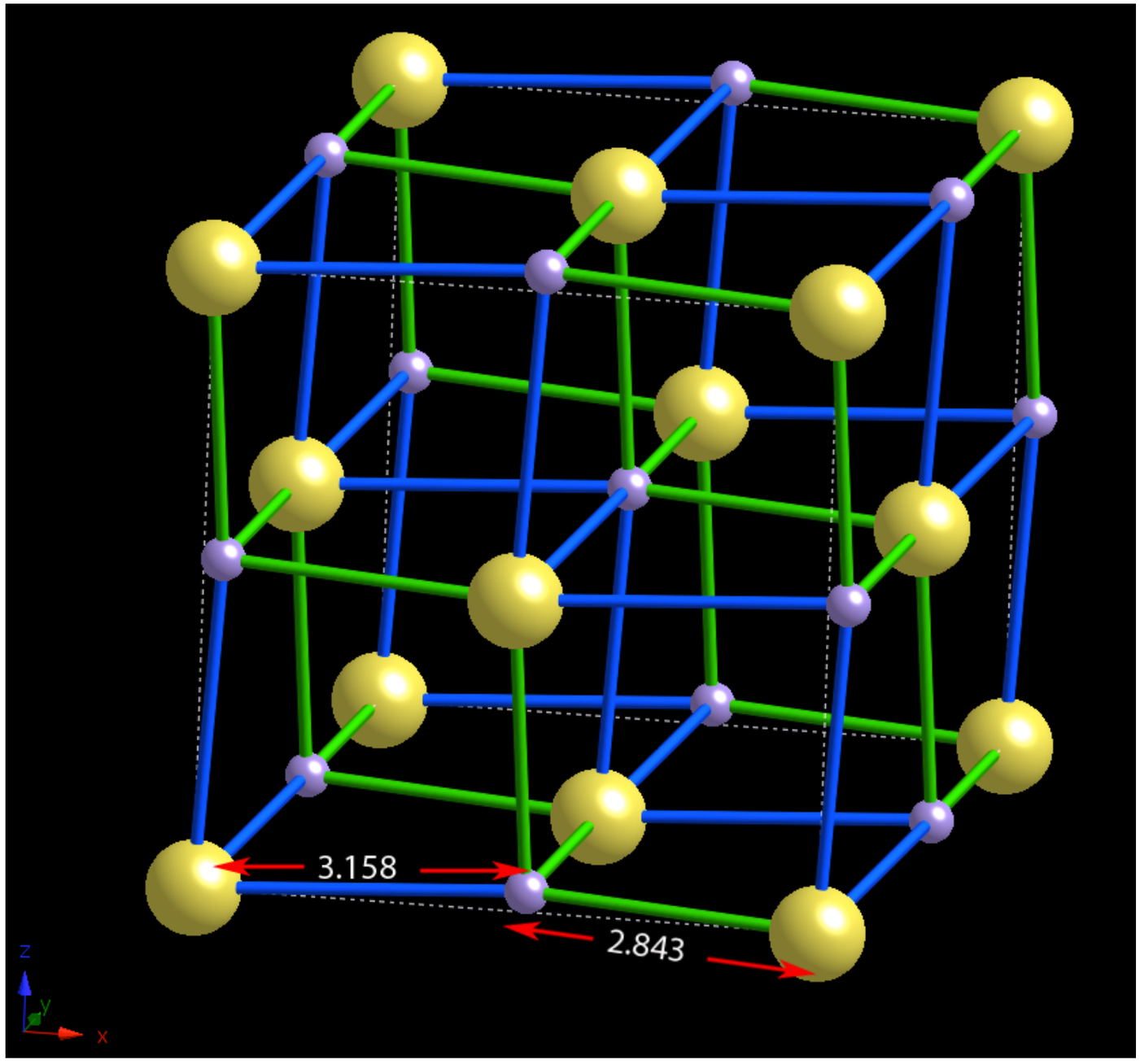
- elementally selective
- local atomic coordination
- chemical / oxidation state
- applies to any element
- works at low concentrations
- small sample volumes (even monolayers)

GeTe "ideal" Structure



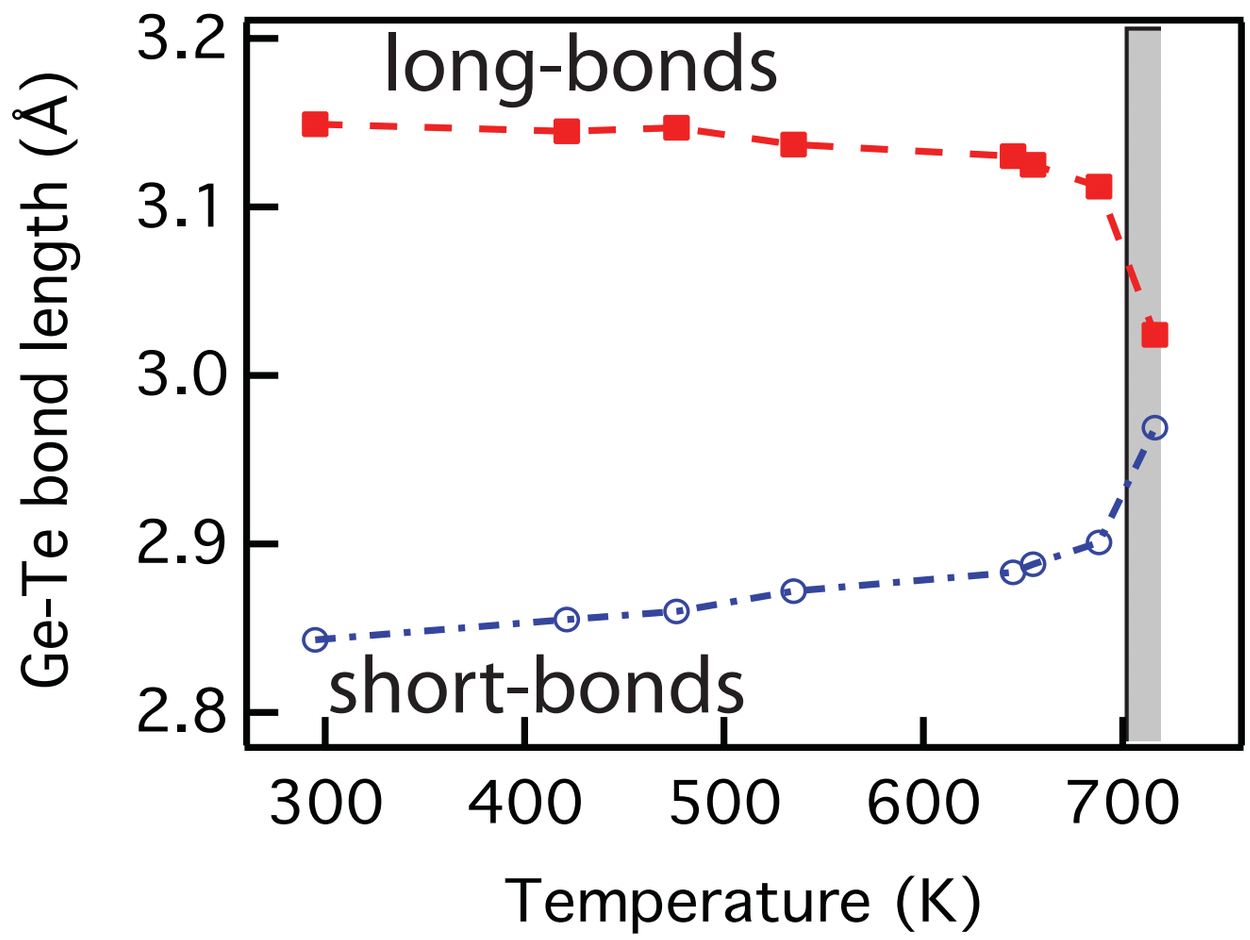
- Rhombohedral symmetry but more easily visualized as distorted rocksalt structure.

GeTe "ideal" Structure



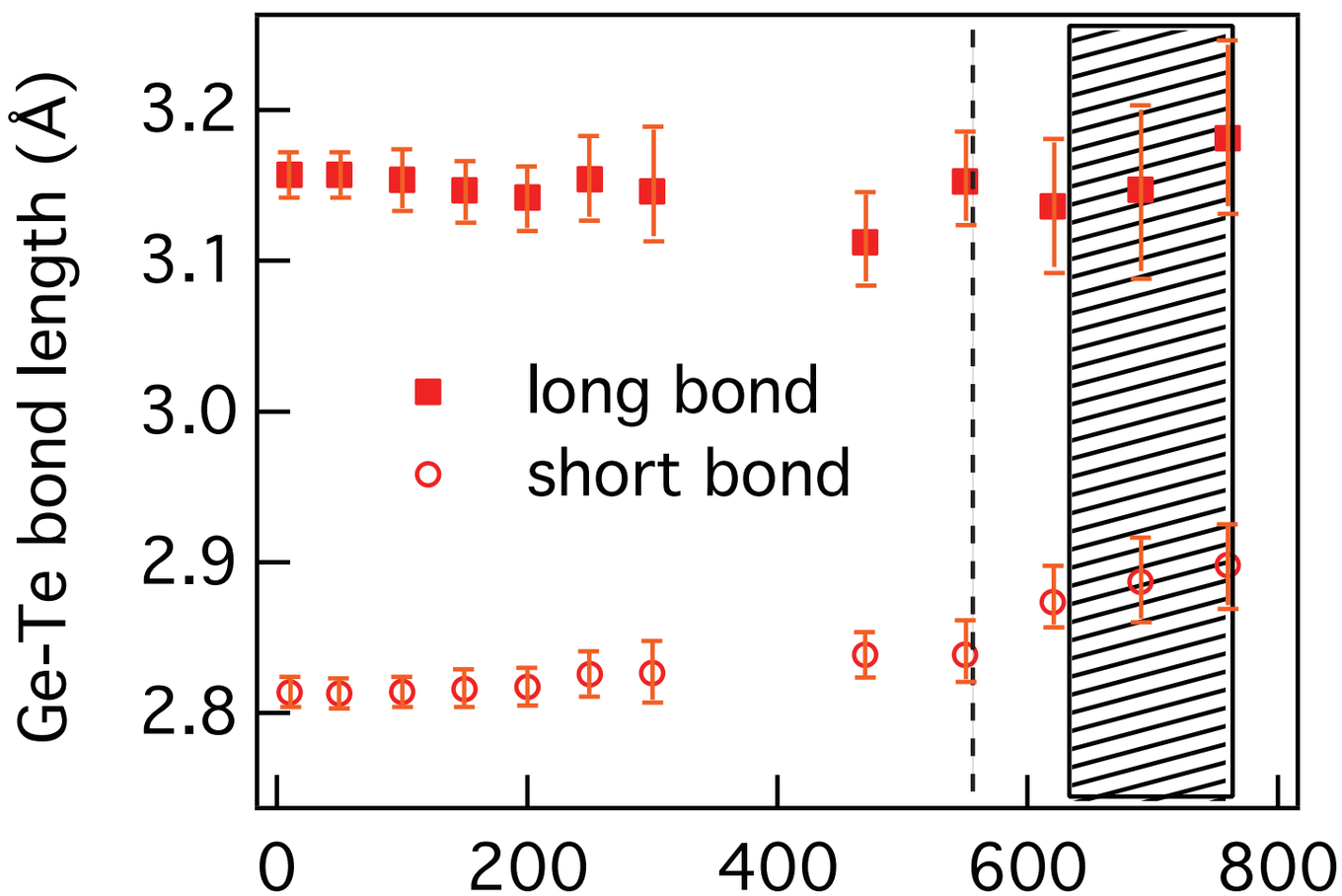
- Rhombohedral symmetry but more easily visualized as distorted rocksalt structure.

GeTe Diffraction



- Neutron powder diffraction shows long- and short-bonds calculated from average structure become equal at T_c

XAFS measurements

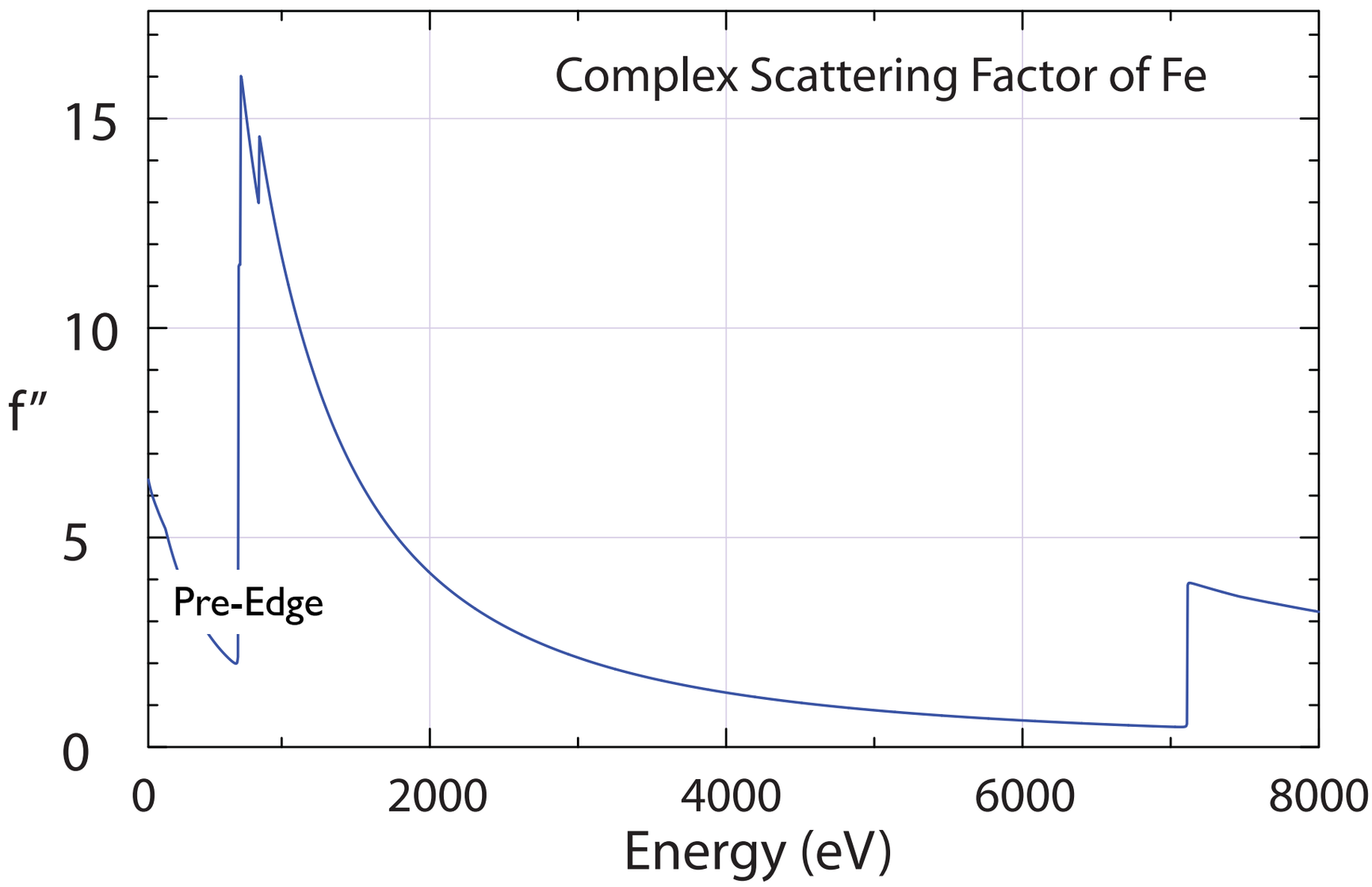


- Analysis showed that rhombohedral distortion existed up to and beyond T_c

XAFS is a local and Diffraction is a (longer) range probe

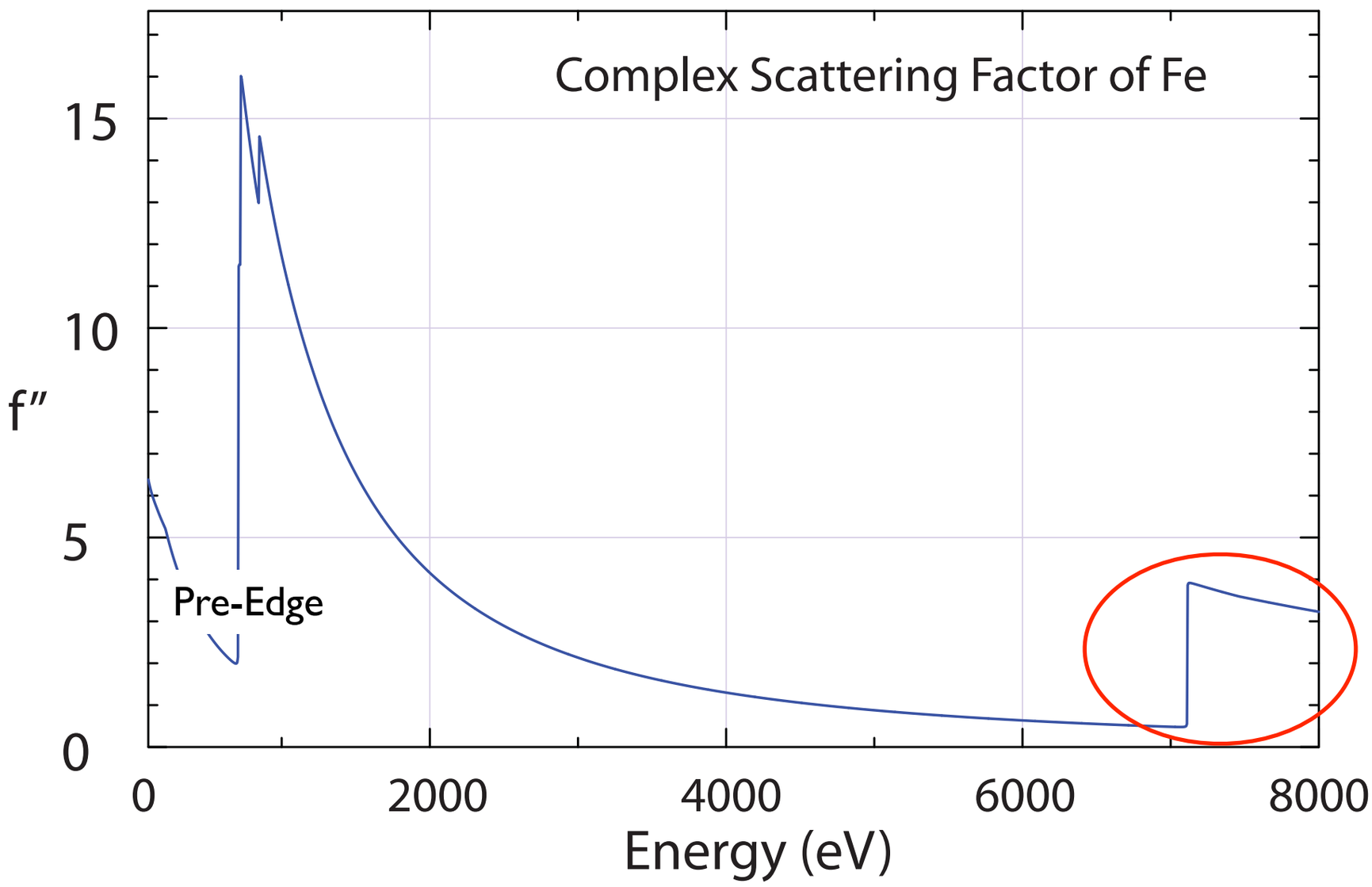
P. Fons, A. V. Kolobov, M. Krbal, J. Tominaga, K. Andrikopoulos, S. Yannopoulos, G. Voyiatzis, and T. Uruga. Phase transitions in crystalline GeTe: Pitfalls of averaging effects. Phys. Rev. B, 82(15):155209, 2010.

XAFS Example



Modulation of the x-ray absorption above the edge constitutes the XAFS signal

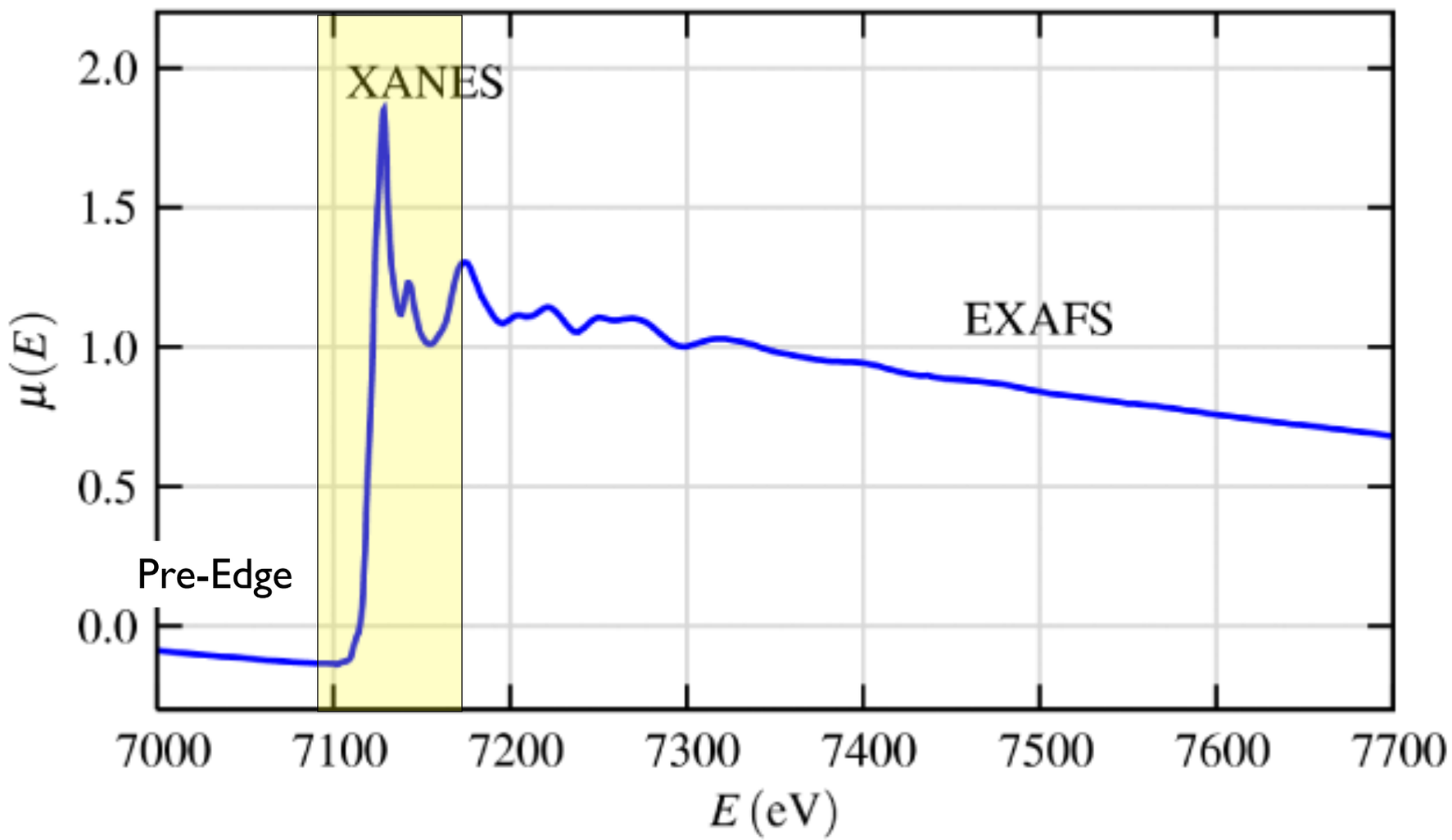
XAFS Example



Modulation of the x-ray absorption above the edge constitutes the XAFS signal

XAFS Example

Fe *K*-edge XAFS for FeO:



Modulation of the x-ray absorption above the edge constitutes the XAFS signal

XANES vs. EXAFS

- XANES X-ray Absorption Near-Edge Spectroscopy (0-40 eV)
- EXAFS Extended X-ray absorption Spectroscopy (40-1000 eV)

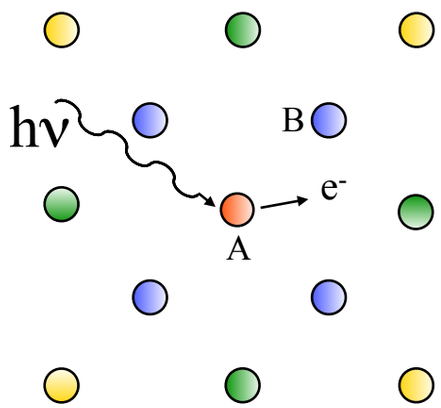
XANES and EXAFS are labels for two parts of the same spectra. They are distinguished due to the approximations used in the analysis of data

XANES region: The energy of the photoelectron (PE) is small, the mean free path long (nm) and PE interactions strong requiring more time consuming cluster calculations

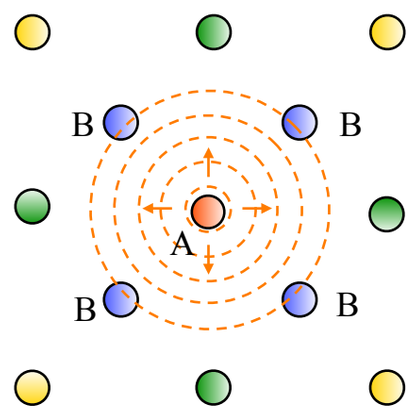
EXAFS region: The PE energy is higher and scattering can be treated as a finite series of interactions that can be well approximated by the the EXAFS equations we will encounter.

A visual interpretation of XAFS

Photon In

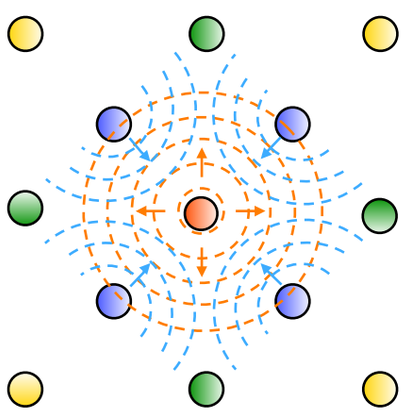


Photoelectron out



$$\left|f_0\right\rangle \propto \frac{e^{i\vec{k}\vec{r}+\delta_A}}{2kr}$$

For a s-state core level, an outgoing spherical wave moves out from the absorbing atom.

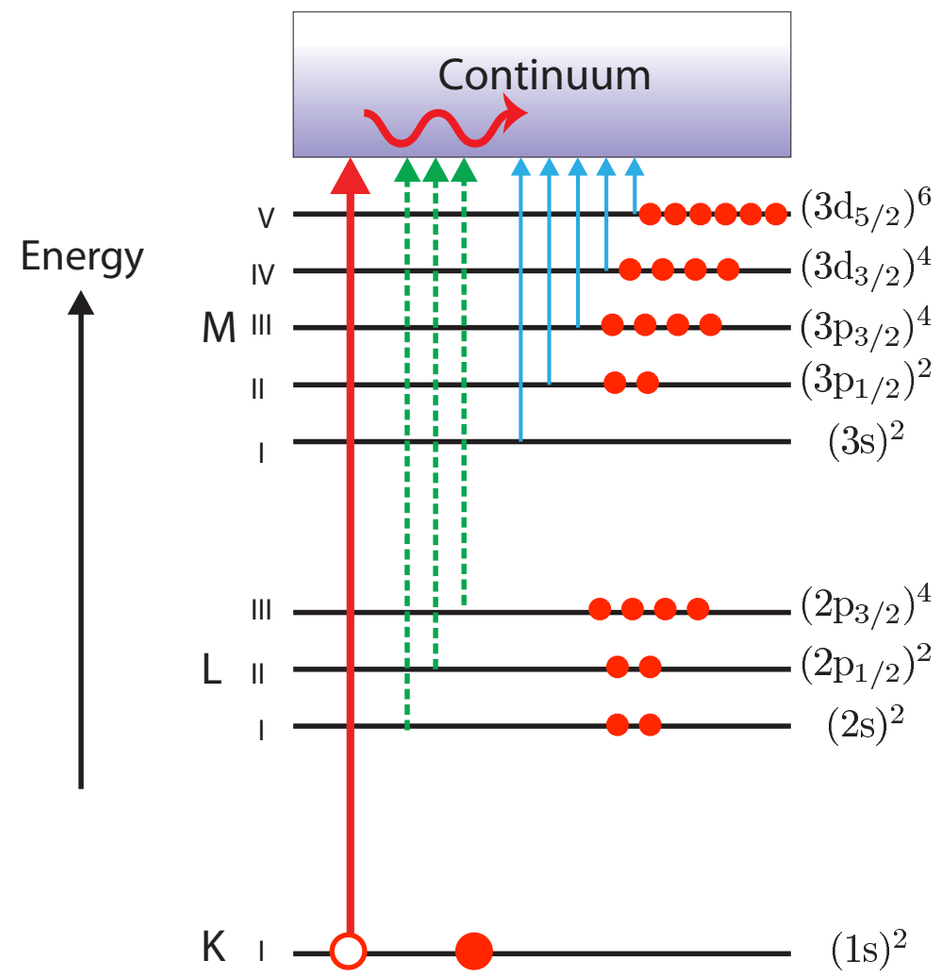


The outgoing spherical wave is scattered by the (coloumb) potentials of neighbor atoms causing interference with itself. The absorbing atom serves both as the source of the photoelectron and the detector. In other words, the XAFS signal reflects the local neighborhood about the absorbing atom.

Photoelectric Effect

- An x-ray is absorbed via the photoelectric effect in which E_{photon} induces a transition from a core-level to a continuum state
- The atom is left in an excited state with an empty level (core hole)
- Excess energy becomes kinetic energy of ejected photoelectron

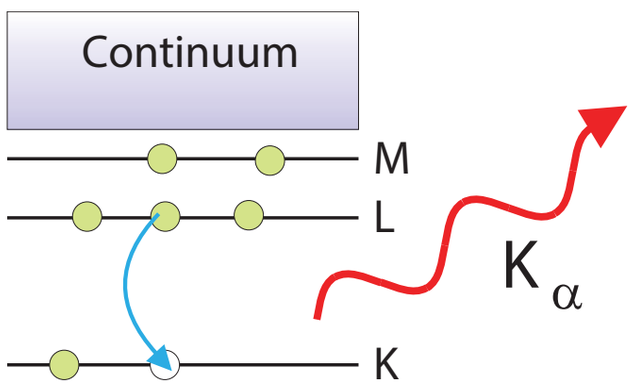
$$E_{Kinetic} = h\nu - E_{Edge}$$

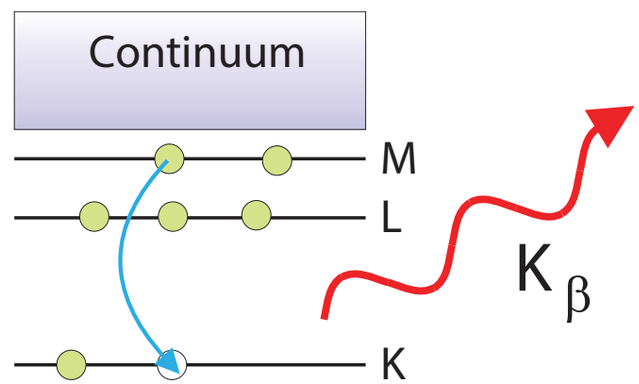


A K-shell excitation

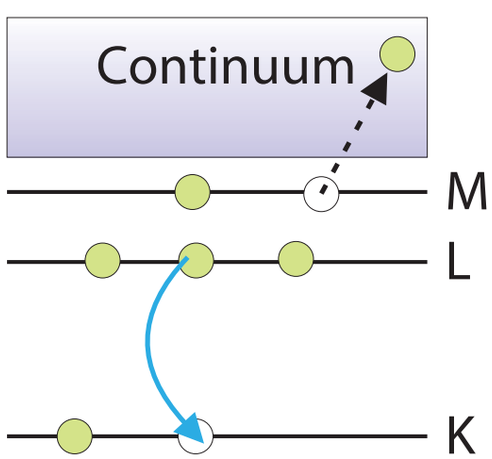
Recombination Processes

When a core-hole is created, the absorbing atom is in an excited state and can return to the ground state via Auger electron emission (AES) or X-ray fluorescence (XRF)





XRF: photon out. E_{photon} is element specific and offers a way to measure XAFS signals selectively and with great sensitivity



AES: Unlike XRF which has an (energy dependent escape depth typically in tens of μm in the hard x-ray region, AES is a surface sensitive detection technique

Linear Absorption Coefficient

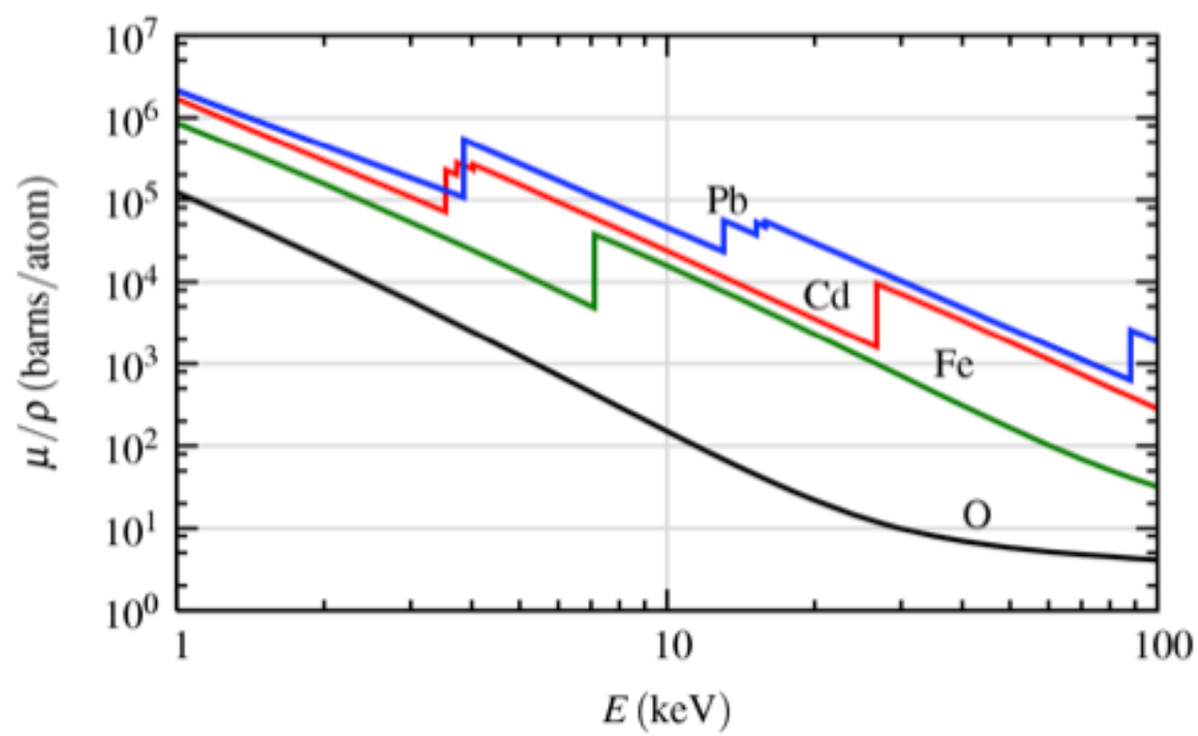
The intensity of an x-ray beam passing through matter can be described by

$$I = I_0 e^{-\mu t}$$

where I_0 is the initial intensity, t is the sample thickness, and μ is the x-ray absorption coefficient

μ depends on the x-ray energy, the atomic number Z of the absorber, the density ρ, and the atomic mass A

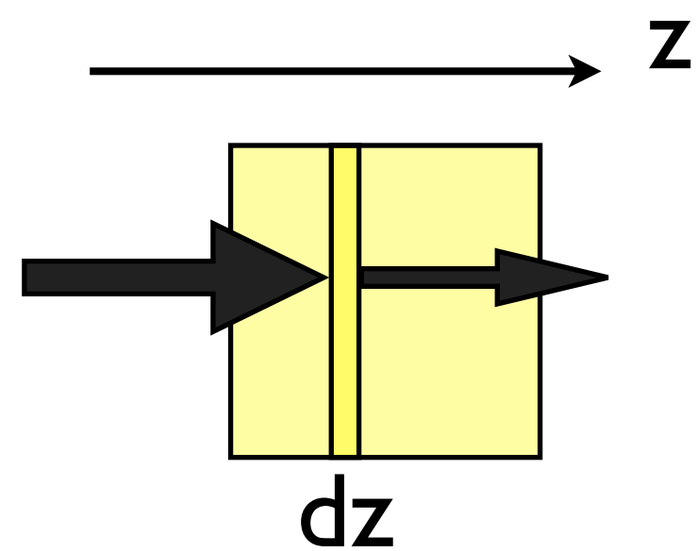
$$\mu \propto \frac{\rho Z^4}{A E^3}$$



Absorption in a Compound

The loss in a slice of thickness dz

$$dI = -I(z)\mu dz$$



The number of absorption events W is thus

$$W = I(z)\,\rho_{at}\,\sigma_a\,dz = I(z)\mu\,dz$$

$$\mu = \rho\sigma_a = \left(\frac{\rho_m N_A}{M}\right)\sigma_a$$

where

ρ_{at} = atomic number density

σ_a= atomic cross section

μ for a compound can thus be calculated as

$$\mu(E) = \sum_j \rho_{at}^j \sigma_j$$

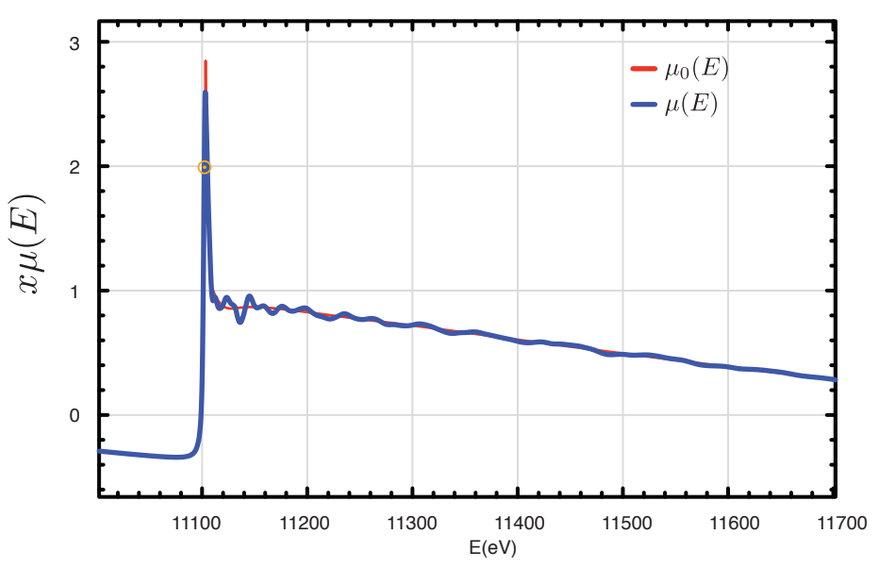
EXAFS

Extended X-ray Absorption Fine Structure

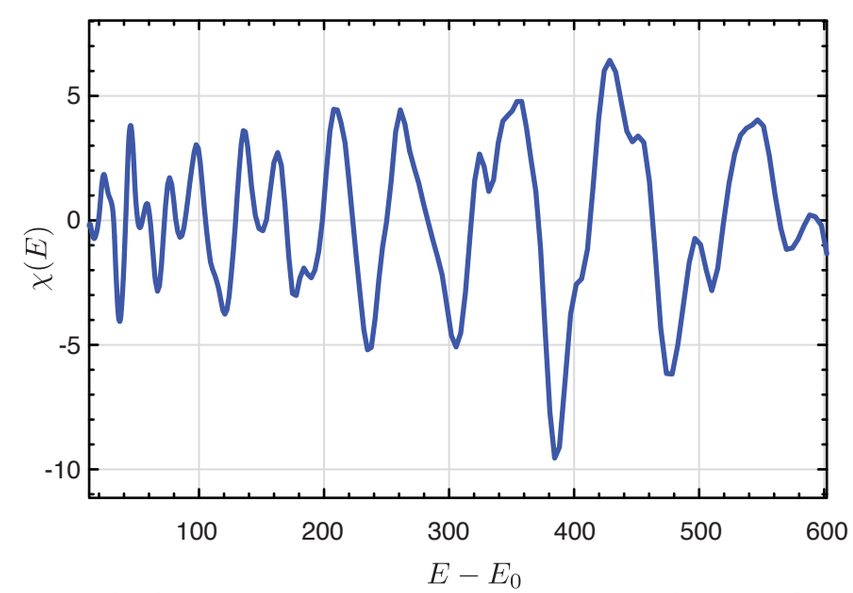
We are interested in the interference function in the absorption signal as it contains information about local structure

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E_0)}$$

By subtracting away the smooth atomic "bare atom" (μ_0) background and dividing by the edge step $\Delta\mu_0$ we can find the oscillations χ normalized to a single absorption event



$\mu(E)$ and smooth μ_0 for GeTe



$\mu(E)$ and smooth μ_0 for GeTe with E_0=11103 eV

EXAFS Equation

While the XANES region requires calculations, the EXAFS region can be fit using the EXAFS Equation

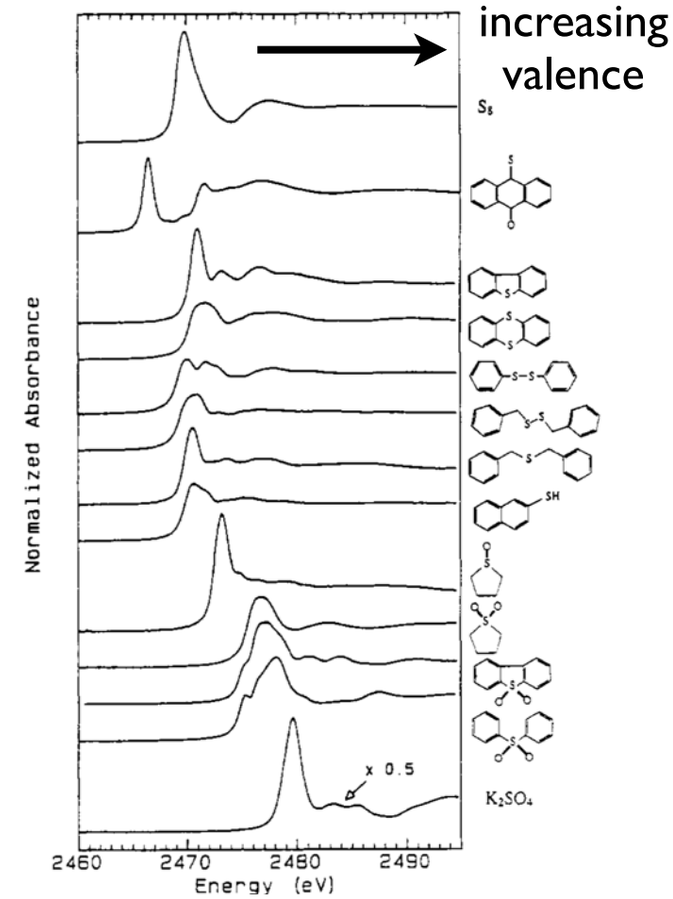
$$\chi(k) = \sum_i \frac{N_i S_0^2 F_i(k)}{k R_i^2} \sin(2kR_i + \delta_i(k))$$

Here $F_i(k)$ and $\delta(k)$ encompass the photoelectric scattering properties of the *i*th neighboring atom. If we know F and δ, we can fit:

R the distance to the neighboring atom *i*
N coordination number of the neighboring atom
σ^2 mean squared disorder

Both $F_i(k)$ and $\delta(k)$ depend on the atomic number Z so the type of atom surrounding the absorbing atom

XANES



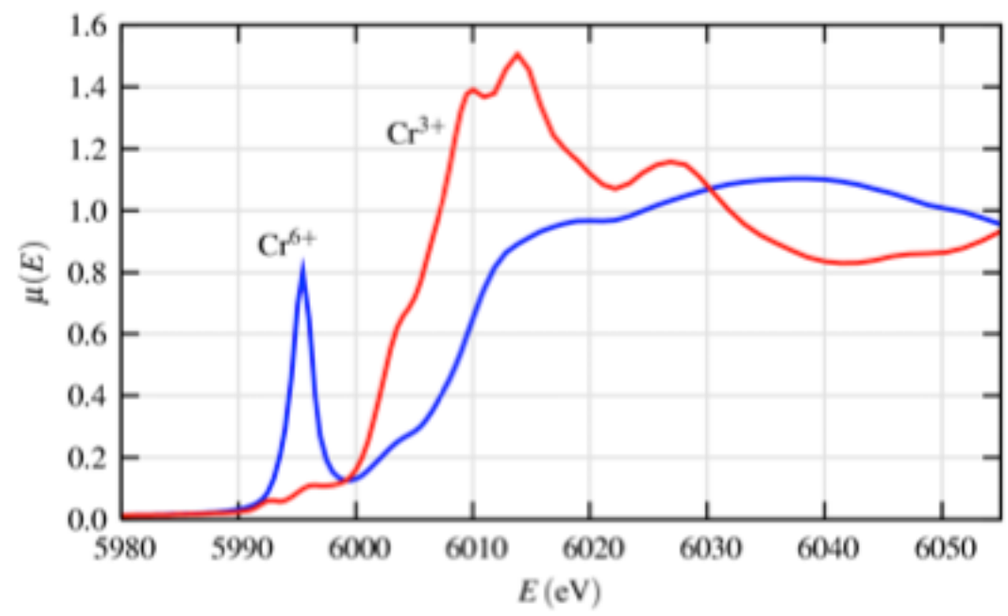
XANES region (absorption edge) can be used to determine chemical valence

Unlike EXAFS contains bond angle information although not simply extracted

Spectra can be added to match experimental spectra revealing the local chemical environment

For light elements XANES spectra can reveal the conduction band DOS

XANES edge for S compounds in different oxidation states

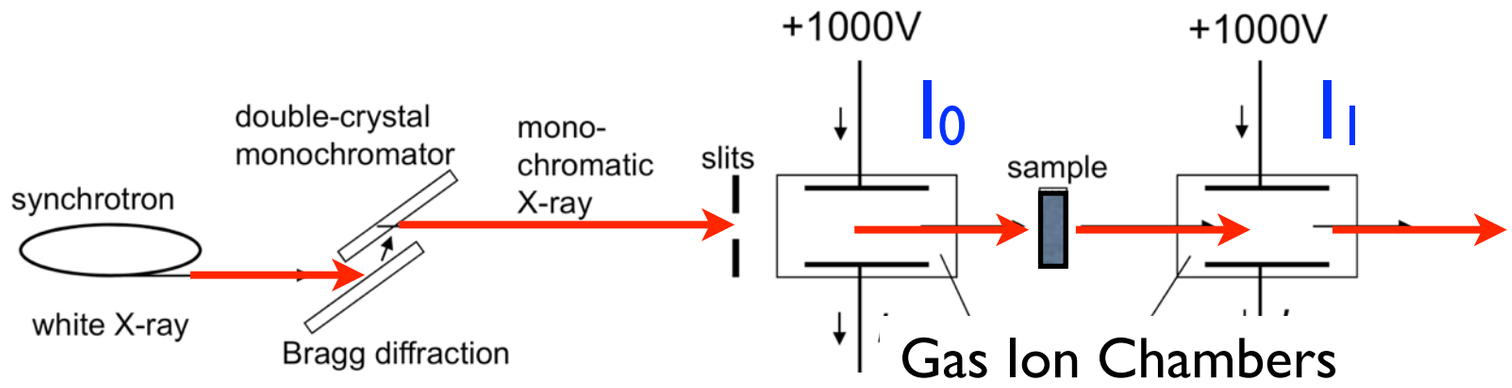


XANES spectra for Cr^{6+} and Cr^{3+}

Measurement Techniques

- We would like to measure a signal proportional to the number of x-rays absorbed
  - Transmission (directly measure the transmitted beam)
  - Fluorescence (measure the outgoing photon when the core hole recombines: see slide 8)
  - Electron Yield/Conversion Electron Yield (measure the Photoelectron/Auger electron signal)

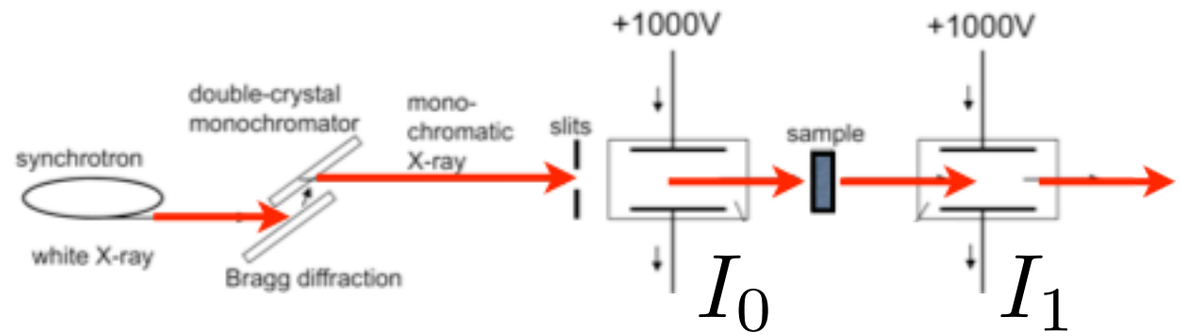
Transmission



$$\mu(E)t = -ln(I/I_0)$$

- For concentrated samples, transmission is often best technique for XAFS, but proper sample preparation is required
- Want $\mu_{\mathrm{Above}} - \mu_{\mathrm{Below}} = \Delta\mu \quad \ni \quad 1 < \Delta\mu < 3$
- For Fe foil Δμ=1 requires 3.7 μm thick foil!
  often solution is to make BN+sample powder pellet
- samples must be uniform without pinholes
- the grain size must be smaller than the absorption length

Why are Pinholes bad?



μ is defined by

$$I_1/I_0 = \left\langle e^{-\mu(E)t} \right\rangle$$

where <> represents the spatial average

What is actually measured is

$$t\mu_{\text{eff}} = \ln I_0/I_1 = \ln \left\langle e^{-\mu(E)t} \right\rangle$$

If the thickness t is the same everywhere, the brackets vanish and something proportional to μ(E) is measured

If t varies, the response is non-linear and not proportional to μ(E)

Example

A hypothetical sample consists of 90% uniform material S with 10% pinholes.

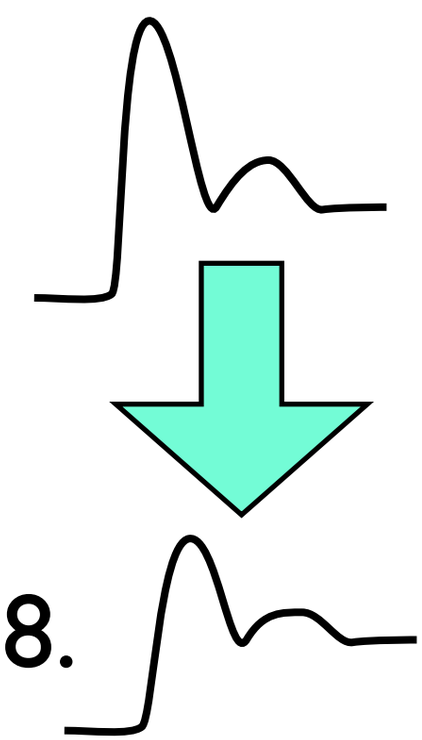
The edge jump is 4 and μ modulation is 0.1

Transmission of each part

$\hbar\nu$	$E < E_{\text{edge}}$	$E > E_{\text{edge}}$	
χ	0	0	0.1
T_{holes}	1	1	1
T_S	1	e^{-4}	$e^{-4.4}$

The net transmission is $0.90 \times T_S + 0.1 \times T_{\text{hole}}$

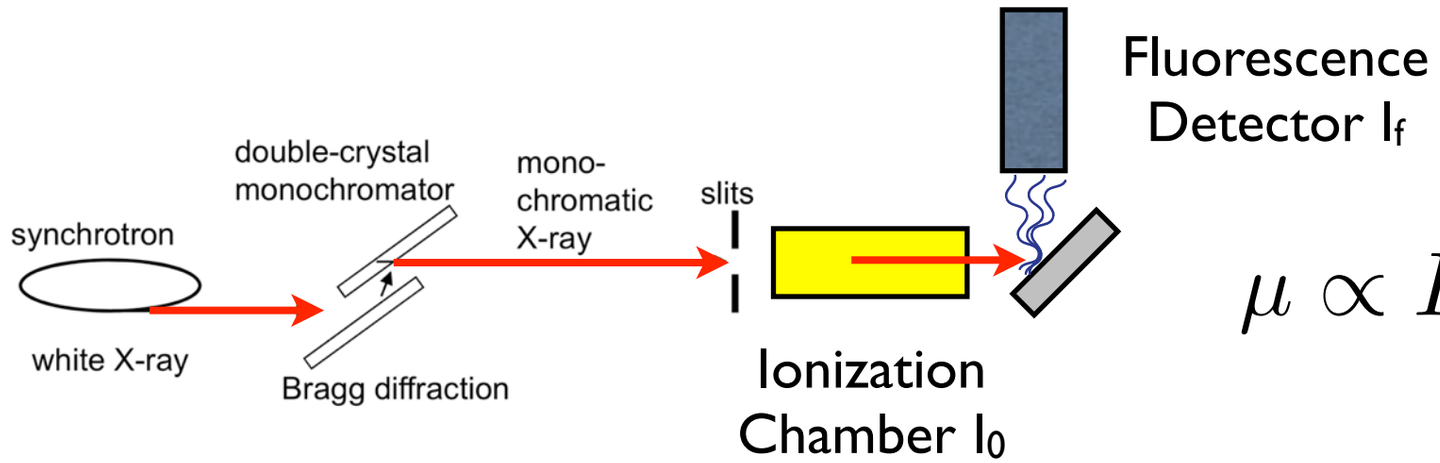
$\hbar\nu$	$E < E_{\text{edge}}$	$E > E_{\text{edge}}$	
T	1	$0.1 + 0.9e^{-4}$	$0.1 + 0.9e^{-4.4}$
T	1	0.116484	0.11105
μ=log(T)	0	2.15000	2.19778



Instead of χ~0.1, the calculated χ is ~0.048.

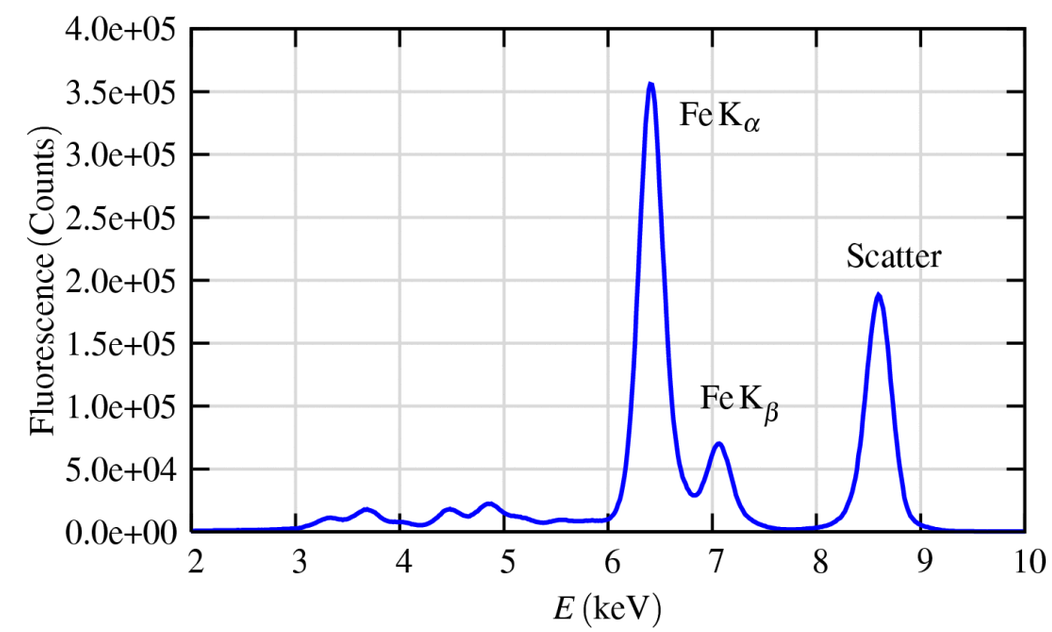
The spectra is "compressed"

Fluorescence Measurements



$$\mu \propto I_f / I_0$$

- Concentrations down to the ppm level can be measured
- Background from other signals can dominate leading to dead time poor S/N
- Sample non-uniformity big problem (I_0 correction can fail)
- Self-absorption (concentrated samples) can lead to effects similar to pinholes in transmission



X-ray Fluorescence Spectrum

Fluorescence Measurements

- For a good fluorescence experiment

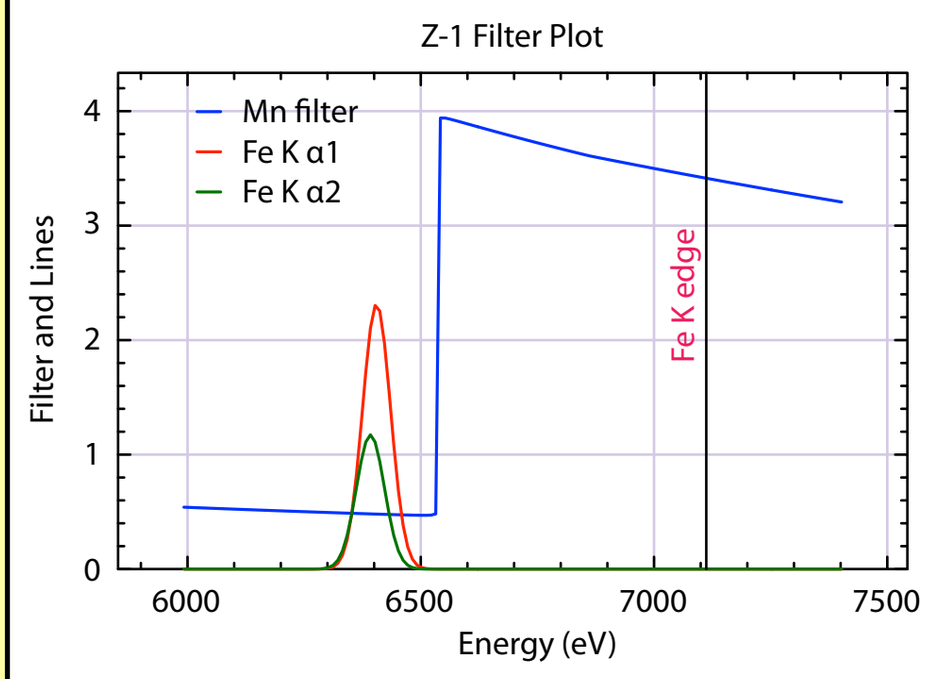
  Energy Discrimination: Eliminate unwanted energy photons by physical or electronic filter

  Solid Angle: As emitted XRF photons are isotropic, maximize solid angle

An example of physical filtering is the use of a so-called "Z-1" filter.

For example, the Fe Kα emission lines are located below the K-edge of the next "Z-1" element down, Mn.

Can be used with a detector with no energy resolution or to reduce flux to reduce dead time for energy discriminating fluorescence detector



Fe Kα emission lines and a "Z-1" Mn filter

Experiment Design

Important considerations for designing an XAFS experiment include:

Monochromatic x-rays: Need x-rays with a small energy spread or bandwidth $\Delta E \approx 1$ eV at 10 keV. Second harmonics of the monochromator need to be eliminated

Linear Detectors: The XAFS $\chi(k) \sim 10^{-2}$ or smaller, so we need many photons and detectors that are very linear in x-ray intensity (ion chambers). This usually means using a synchrotron source.

Well-aligned Beam: The x-ray beam hitting the detectors has to be the same beam hitting the sample.

Homogeneous sample: For transmission measurements, we need a sample that is of uniform and appropriate sample thickness of $\Delta\mu \sim 1$ absorption lengths. It should be free from pinholes. Powders need to be very fine-grained.

Counting Statistics: $\mu(E)$ should have a noise level of about 10^{-3}. That means we need to collect at least $\sim 10^6$ photons. For very low concentration samples, this may require hours of counting time.

An EXAFS Experiment

- To collect EXAFS data, we need to scan a monochromatic x-ray beam through the edge. Typical ranges are below
- In the EXAFS region, it is common to step in constant k

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} = \sqrt{0.262(E - E_0)}$$

- If errors are the result of Poisson statistics to have a 1% statistical error will require $\sqrt{N}/N=0.01 \Rightarrow 10{,}000$ counts

Typical Ranges for XANES and EXAFS

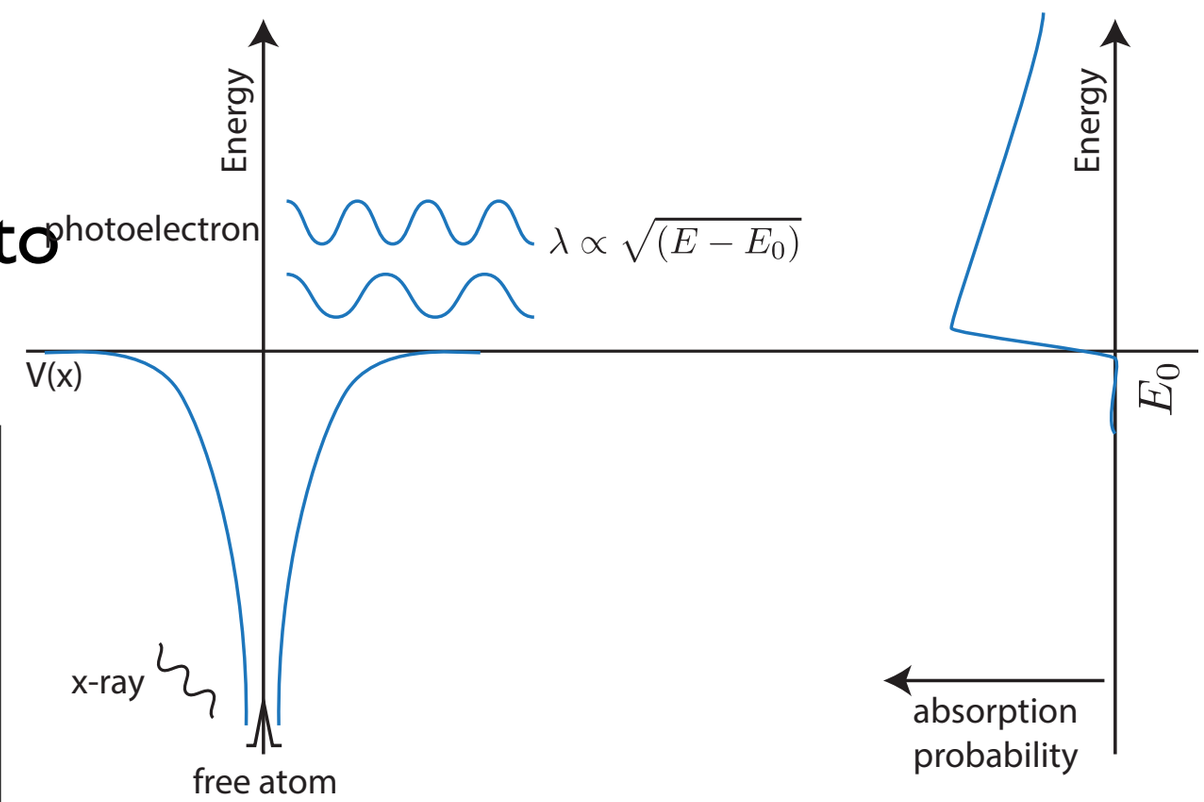
Region	Start E (eV)	End (eV)	Step (eV)
Pre-edge	-200	-20	5
XANES	-20	40	0.25-0.50
EXAFS	30	~800	0.05 $Å^{-1}$

Free Atom Absorption

Upon absorption of an x-ray with energy E_0 by a free atom, a core hole is created with K.E. (E-E_0). The core hole is filled by another electron (fluorescence) or an Auger process occurs and another e^- is ejected

A transition can only occur if there is an empty state for the core electron to move into.

Transitions into the continuum lead to large increases in absorption

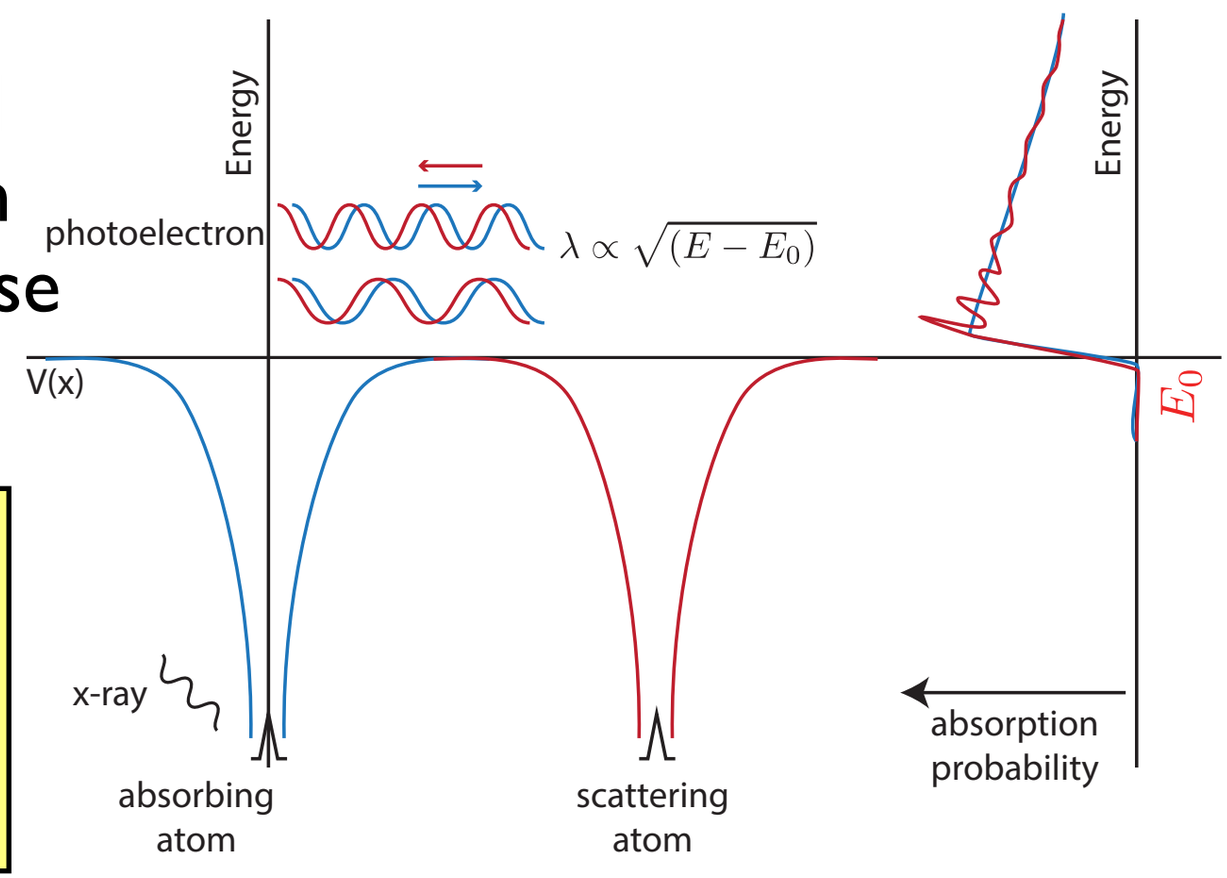


μ increases sharply at E_0 edge for a free atom and monotonically decreases with increasing energy

Backscattering

The photoelectron propagates outward in the form of a spherical wave (for k-shell holes) and parts of the wavefunction scatter off surrounding atoms and return to the absorbing atom.
The backscattered photoelectron will then interfere with itself.

There must be empty states at $(E-E_0)$ at the absorbing atom μ to be non-zero.
The amplitude of the backscattered wavefunction at the absorbing atom and its variation with energy give rise to oscillations in μ that are XAFS.



XAFS is thus caused by the photoelectron interfering with itself due to the presence of neighboring atoms

EXAFS: Physics

Now let us find a simple form for χ. First we note that the initial state is a core state and we wish to find the effect of backscattering on the final state. If we recall the definition for μ(E)

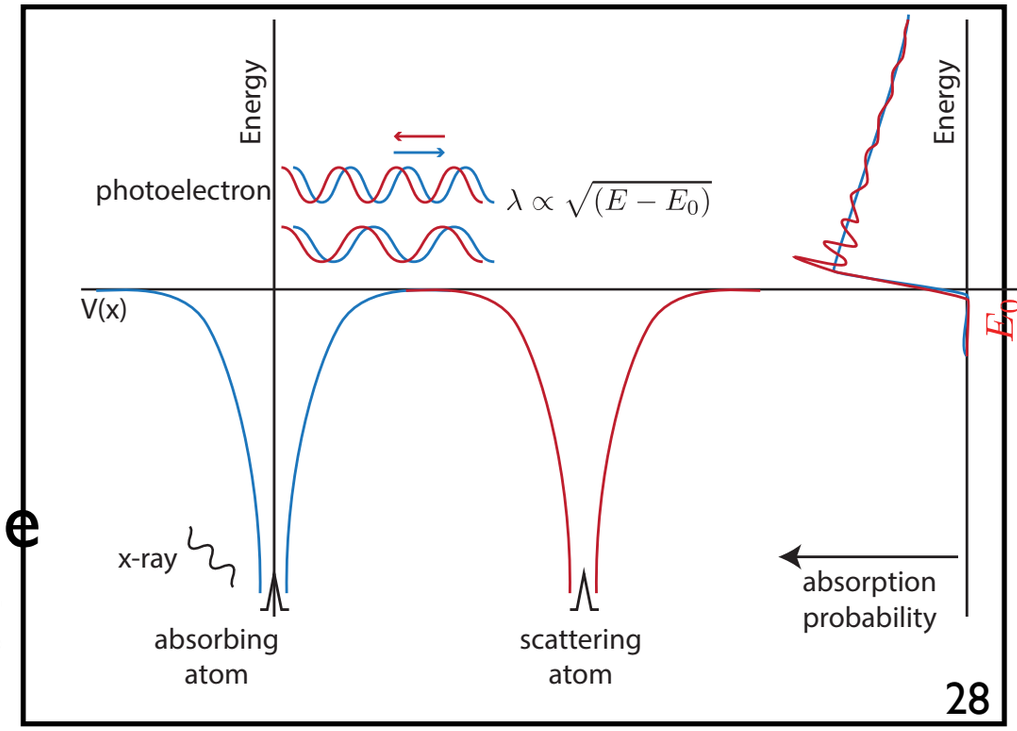
$$\mu(E) = \mu_0(E)\,[1 + \chi(E)] \qquad \chi(k) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E_0)}$$

μ describes a transition between states and can be written in terms of Fermi's golden rule: $\mu(E) = |\langle i|\mathcal{H}|f\rangle|^2$

Note that the initial state $|i\rangle$ is a core state and a photon; this state is not changed by the presence of a neighboring atom

H is the interaction. In the dipole approximation $\mathcal{H} = e^{ikr} \sim 1$

$|f\rangle$ is the final state which consists of a photoelectron, a core hole, and no photon. The photoelectron is scattered by the neighboring atom.



EXAFS: Physics

EXAFS is a "final state effect". As the initial state is deep and localized, it changes little due to neighboring atoms. The final state $|f\rangle$ does however change due to backscattering from a neighboring atom. If $|f_0\rangle$ is the final state of an isolated atom, the final state is $|f\rangle = |f_0 + \Delta f\rangle$ expanding in μ to second order gives:

$$\mu(E) \sim |\langle i|\mathcal{H}|f_0\rangle|^2 \left[1 + \frac{\langle i|\mathcal{H}|\Delta f\rangle \langle f_0|\mathcal{H}|i\rangle^*}{|< i|\mathcal{H}|f_0 >|^2} + \text{C.C.}\right]$$

as $\mu(E) = \mu_0 (1 + \chi(E))$ where $\mu_0 = |\langle i|\mathcal{H}|f_0\rangle|^2$ implies,

$$\chi(E) \sim \langle i|\mathcal{H}|f\rangle \sim \langle i|\Delta f\rangle$$

If we take the initial state as a delta function δ(0), X becomes

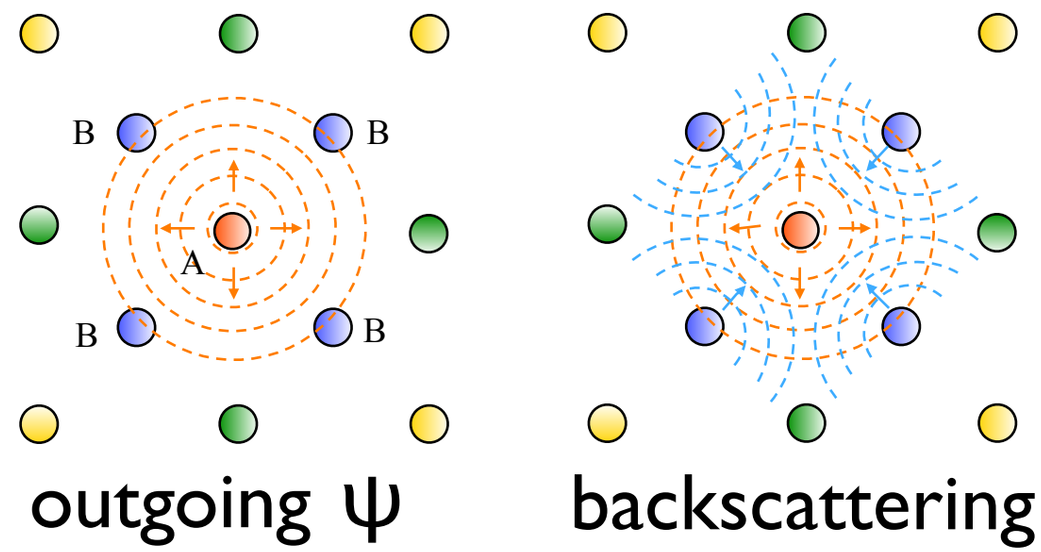
$$\chi(E) \sim \int dr\ \delta(r)\ \psi_{\text{scatt}}(r) = \psi_{\text{scatt}}(0)$$

Conclusion: χ is the part of the photoelectron wavefunction that is backscattered to the origin by neighboring atoms

EXAFS: A simple picture

If $\chi \sim \psi_{\mathrm{scatt}}(0)$, we can understand by following the photoelectron ψ_P's path

- ψ_P leaves the absorbing atom
- part of ψ_P scatters off a nearby atom
- returns to the absorbing atom



With a spherical wave e^{ikr}/kr for the outgoing photoelectron and a scattering atom at distance r=R,

$$\chi = \frac{e^{ikr}}{kr}\left[2kf(k)e^{i\delta}\right]\frac{e^{ikr}}{kr} + \mathrm{C.C.}$$

where scattering from the neighboring atom gives rise to the amplitude f(k) and phase shift δ(k) to the photoelectron

EXAFS: A simple picture

Combining all terms, we get the expression for a single scattering atom

$$\chi(k) = \frac{f(k)}{kR^2} \sin\left[2kR + \delta(k)\right]$$

If N atoms are present with a thermal and static disorder of σ^2 (which give the mean square displacement in R, we find

$$\chi(k) = \frac{N f(k)\, e^{-2k^2\sigma^2}}{kR^2} \sin\left[2kR + \delta(k)\right]$$

In a real structure, there are neighbors at different distances and a sum must be taken

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

EXAFS: A simple picture

To get the expression, $$\chi(k) = \frac{f(k)}{kR^2} \sin\left[2kR + \delta(k)\right]$$

We used a spherical wave (e^{ikr}/kr) for the photoelectron, but we must take into account inelastic scattering processes. To do this, we include a damping function representing that limits how far a photoelectron can travel and still return to interfere coherently

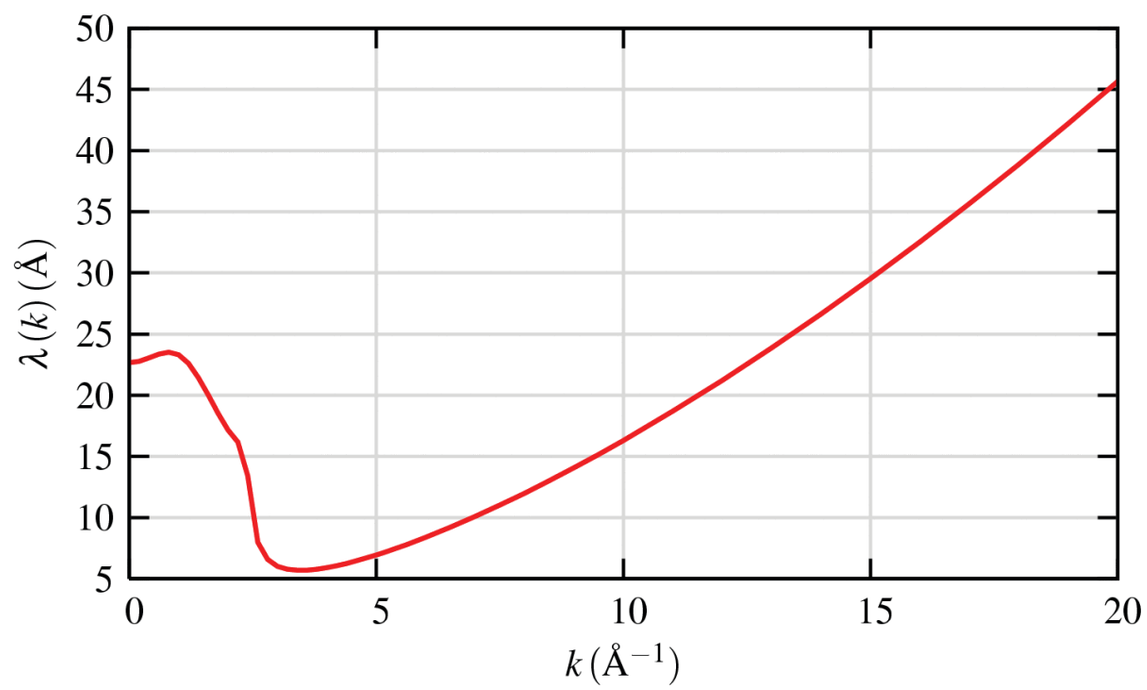
$$\boxed{\psi(k,r) \sim \frac{e^{ikr} e^{-r/\lambda(k)}}{kr}}$$

Here λ is the mean free path (and includes core-hole lifetime effects)

This leads to our first version of the EXAFS equation

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

Mean Free Path



The mean free path λ depends on k, but λ < 25 Å for the EXAFS range. The λ term and R^{-2} lead to EXAFS being a short range probe.

Note that λ and R^{-2} get large for low k (e.g. the XANES region)

Amplitude Reduction Term

The one remaining correction term in the EXAFS equation is the Amplitude Reduction Factor or S_0^2 . This term is due to the relaxation of the other electrons in the atom due to the presence of a core hole.

$$S_0^2 = \left| \left\langle \phi_f^{N-1} | \phi_0^{N-1} \right\rangle \right|^2$$

Here the $\left\langle \phi_f^{N-1} \right|$ term accounts for the relaxation of the N-1 electrons left behind with the core hole relative to the same electrons in the unexcited atom $\left| \phi_0^{N-1} \right\rangle$. In fitting the EXAFS equation, S_0^2 is often taken as a constant $0 < S_0^2 < 1$.

While great strides have been taken into calculations of λ and S_0^2, typically S_0^2 is still taken as a constant for the absorbing atom in fitting data.

This and other issues make the accuracy in determining R (phases) better than N (amplitudes)

The EXAFS Equation

The EXAFS equation thus takes the form

$$\chi(k) = \sum_i \frac{N_i S_0^2 f_i(k)}{kR_i^2} \sin(2kR_i + \delta_i(k)) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)}$$

The sum is taken over all "shells" of atoms or "scattering paths" for the photoelectron.

If we know the scattering properties of: $f_i(k)$ and $\delta(k)$ as well as $\lambda(k)$, we can determine:

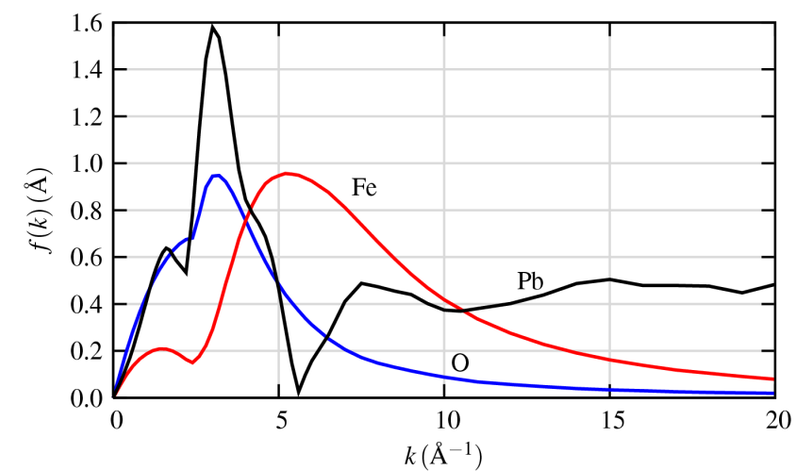
N the coordination number about the absorbing atom
R the distance to the nearest atom
σ^2 the mean-squared disorder of the corresponding neighbor distance

As the amplitude $f(k)$ and phase-shift $\delta(k)$ depend on atomic number, XAFS is also sensitive to the Z of the neighboring atom.

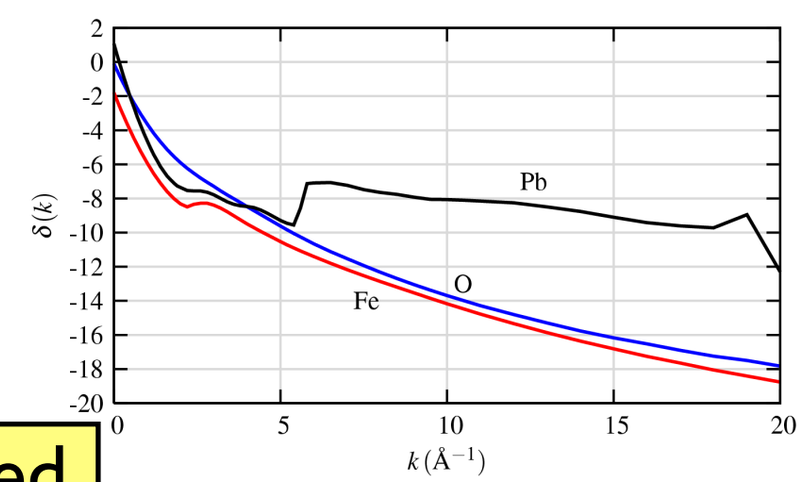
Scattering amplitude f(k) and phase-shift δ(k) examples

The scattering amplitude f(k) and phase-shift(k) depend on atomic number and can be calculated.

The scattering amplitude f(k) peaks at different k-values and goes to larger k-values as Z increases. Note the structure in f(k) for heavy elements like Pb.



The phase-shift δ(k) changes abruptly for large Z. The Z of a neighboring atom can typically be determined ±3 using phase-shifts.



Accurate values for f(k) and δ(k) can be calculated using first-principles code such as FEFF9.

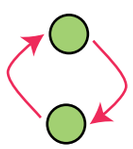
Using feff to calculate f(k) and δ(k)

- Feff is a real-space Greens function code that solves the scattering problem and computers the *effective scattering amplitude* $f_i(k)$ and phase-shift $\delta_i(k)$ a given path i.
- Input to Feff (version 9 at the moment) consists of specifying the location of atoms in space, their (Z) types, and the absorbing atom. The resulting f(k),δ(k), and λ for each path are saved in files feff0001.dat, feff0002.dat, etc.
- Recent fitting programs use feff directly to model EXAFS data.
- A structure close to unknown is sufficient for feff input and fitting allows the refinement of distances and coordination numbers.

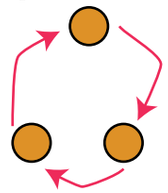
Multiple Scattering

The path sum in the EXAFS equation can include many shells (1st, 2nd, 3rd nearest-neighbors). For paths beyond the nearest neighbor path, multiple-scattering paths can become important

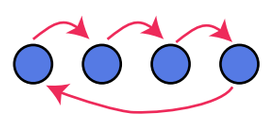
single scattering



triangular paths



focused multiple scattering paths



For multiple scattering paths, the amplitude depends on scattering angles.

For triangular paths with 45 <θ< 135° not strong, but may be many in number.

For linear-paths, with angles θ~180°, are very strong: the photoelectron can be focused from one atom to the next

For nearest-neighbor analysis, multiple scattering is rarely needed.

Multiple scattering strongest for θ>150°

Fitting Strategy

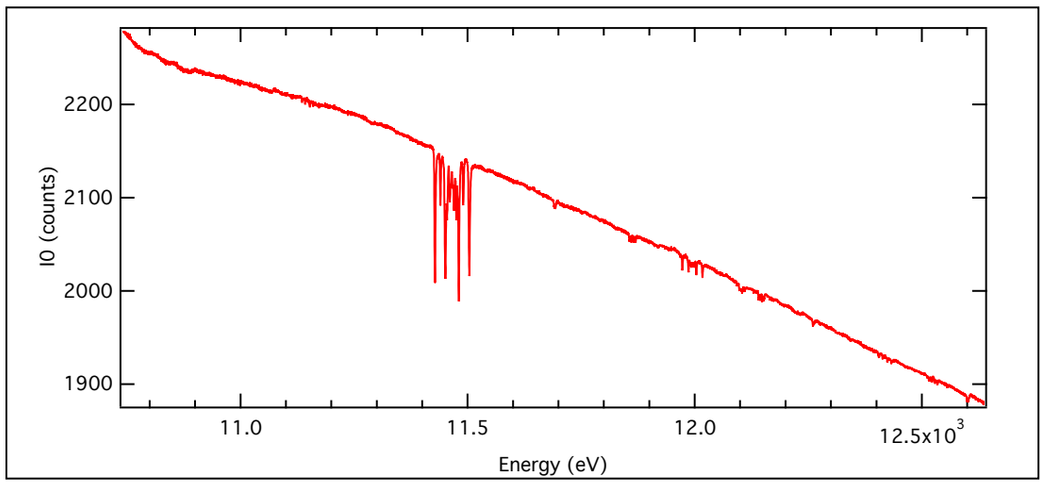
- Convert measured intensities to $\mu(E)$
- Subtract a smooth *pre*-edge function to eliminate background from instruments or other edges
- Normalize $\mu(E)$ to go from 0 to 1 so that it represents the absorption of one x-ray photon.
- Remove a smooth post-edge background function to approximate $\mu_0(E)$ to determine $\chi(k)$
- Convert E to k-space
- Assign a k-weighting function to $\chi(k)$ and the Fourier Transform to real space
- Isolate the $\chi(k)$ for a particular "shell" by Fourier filtering

Next: Model $f(k)$ and $\delta(k)$ to fit $\chi(k)$

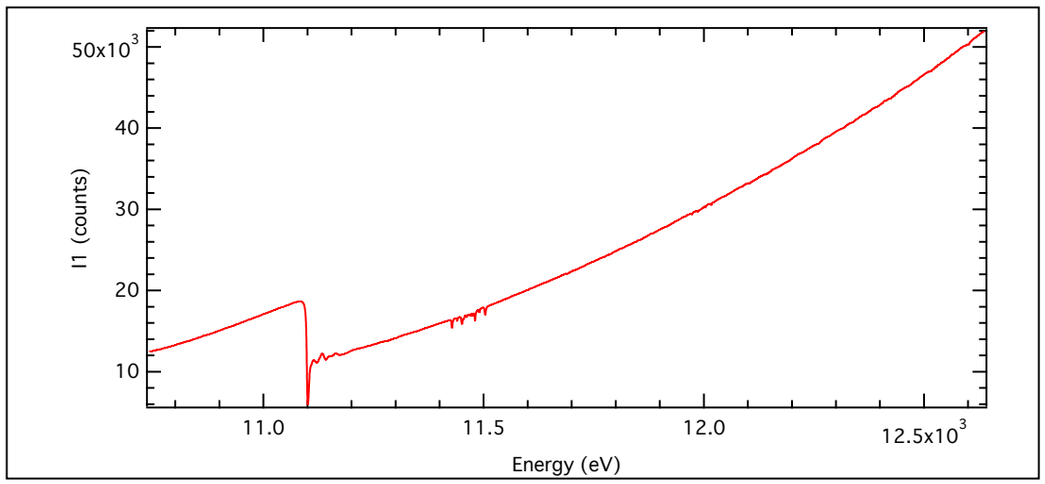
Data Reduction: Transmission

Converting raw measured intensities (in transmission) to μ(E)

I_0



I

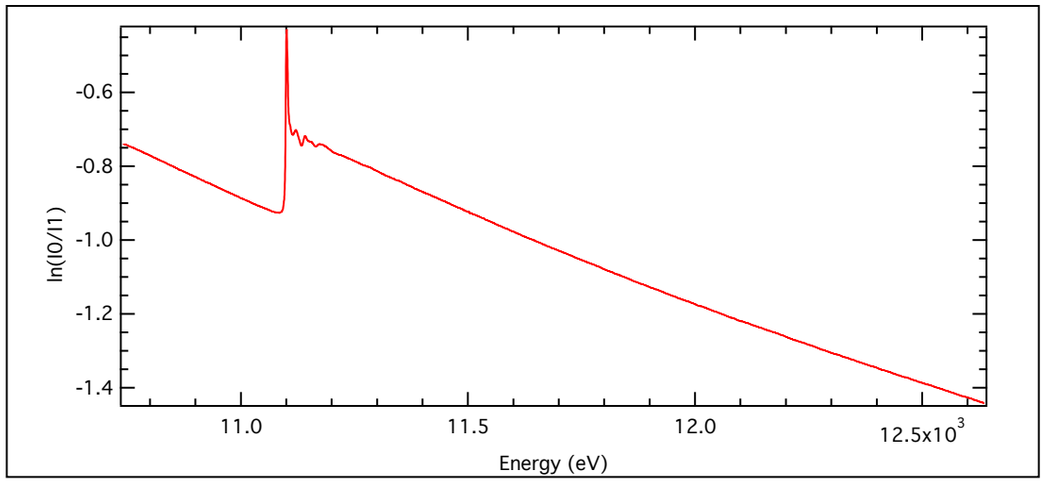


$-\ln(I/I_0)$

For XAFS in transmission

$$I = I_0 e^{-\mu(E)t}$$

$$\mu(E)t = -\ln(I/I_0)$$

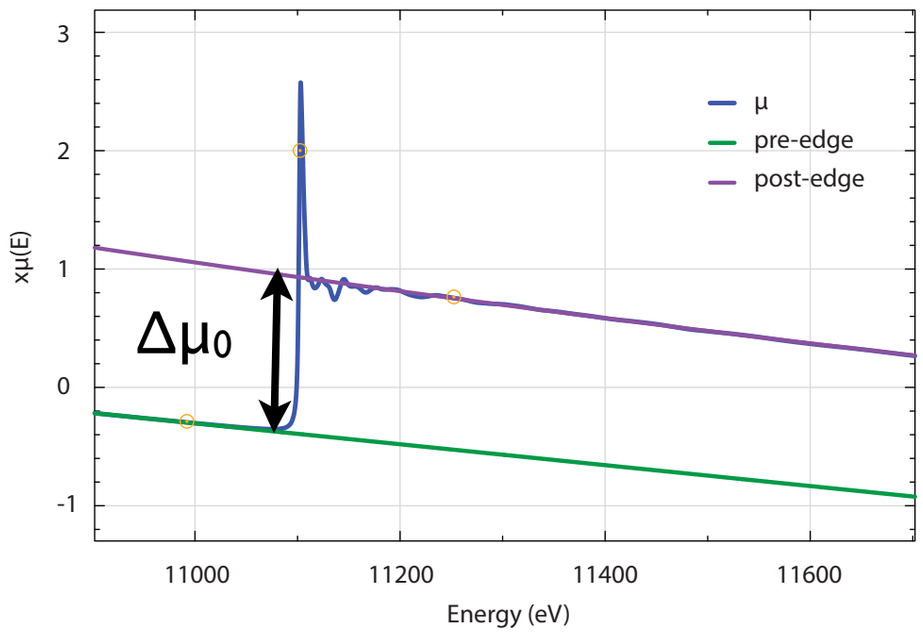


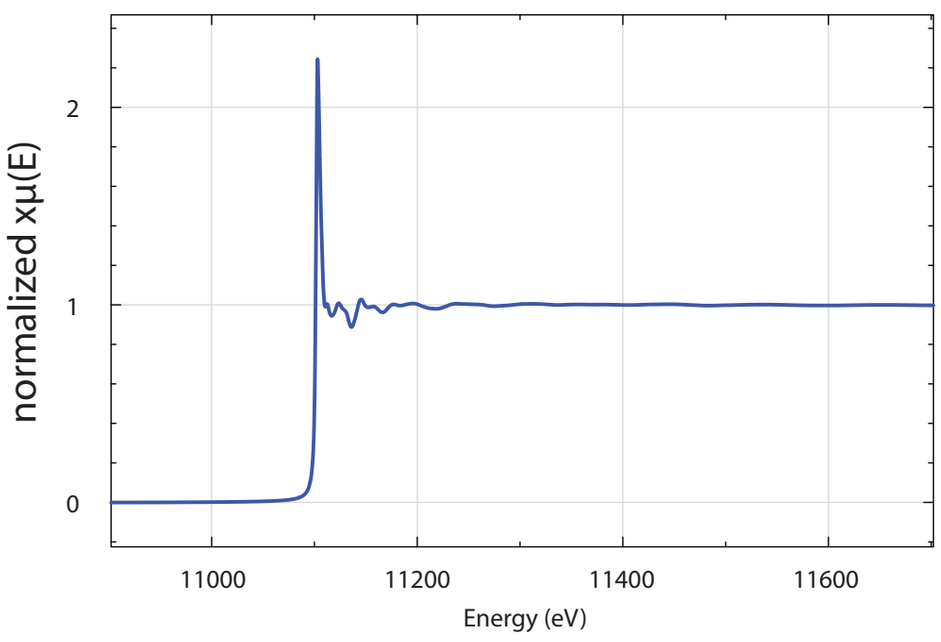
Software

- Some free data processing programs
- Demeter: A comprehensive system for processing and analyzing X-ray Absorption Spectroscopy data. (Linux, Windows, Mac-version available)
  - http://bruceravel.github.io/demeter/
- Athena (data processing) Artemis (fitting)
  - Macintosh version iXAFS
    - installable using the demeter package from macports http://www.macports.org (install demeter)
- lfeffit mailing list (artemis, athena, demeter)

Data Reduction: Athena

GeTe at 300 K @bl01b1





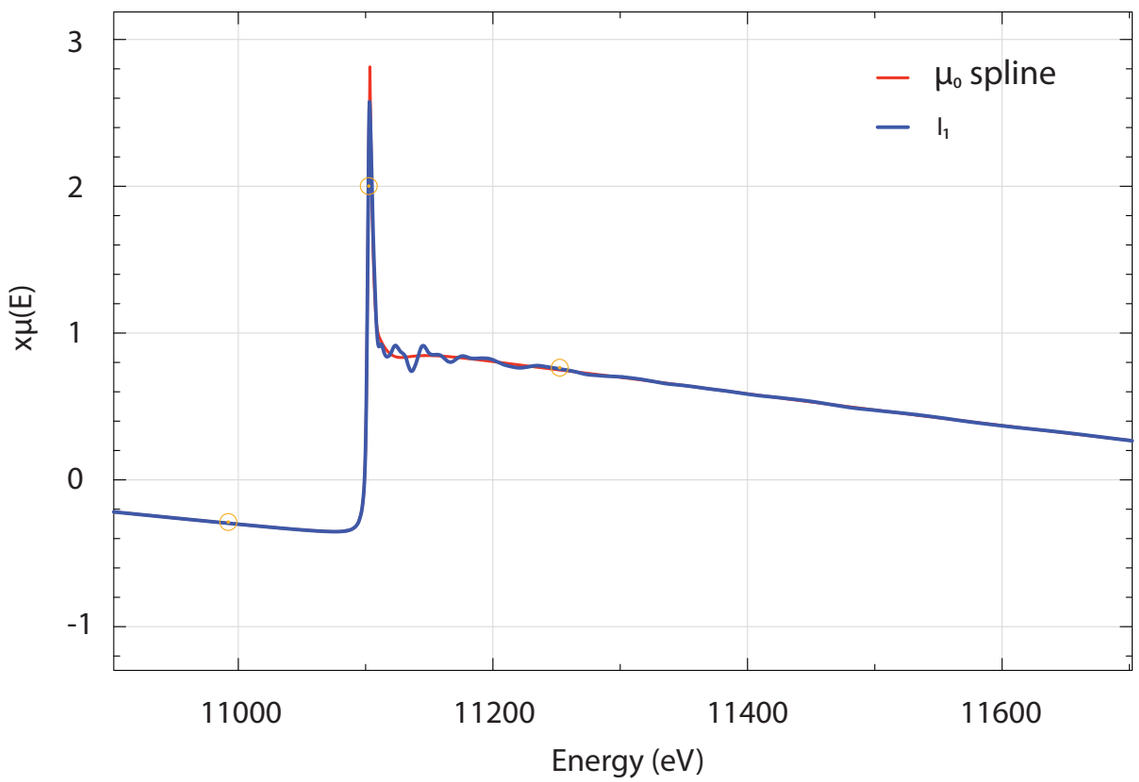
Pre-Edge Subtraction

Pre-Edge subtraction removes the effect of other edges/ background effects

Normalization

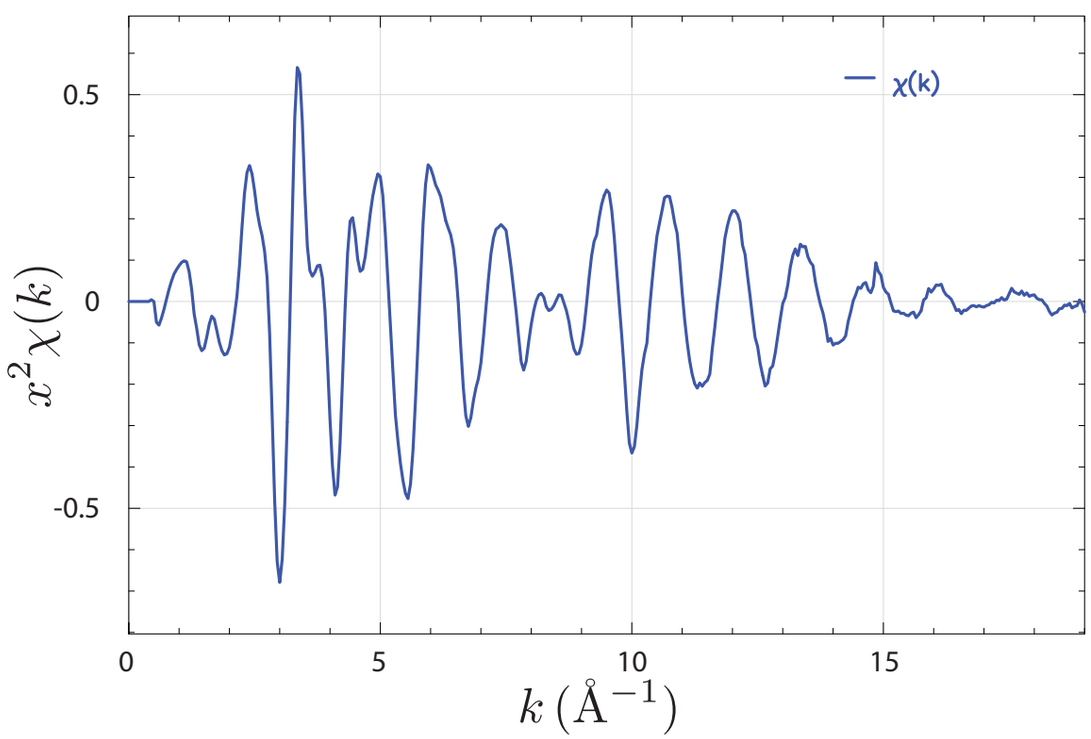
Post-edge subtraction determines $\Delta\mu_0$ so the EXAFS event is for a single x-ray photon

Data Reduction: Athena



Post-Edge Background

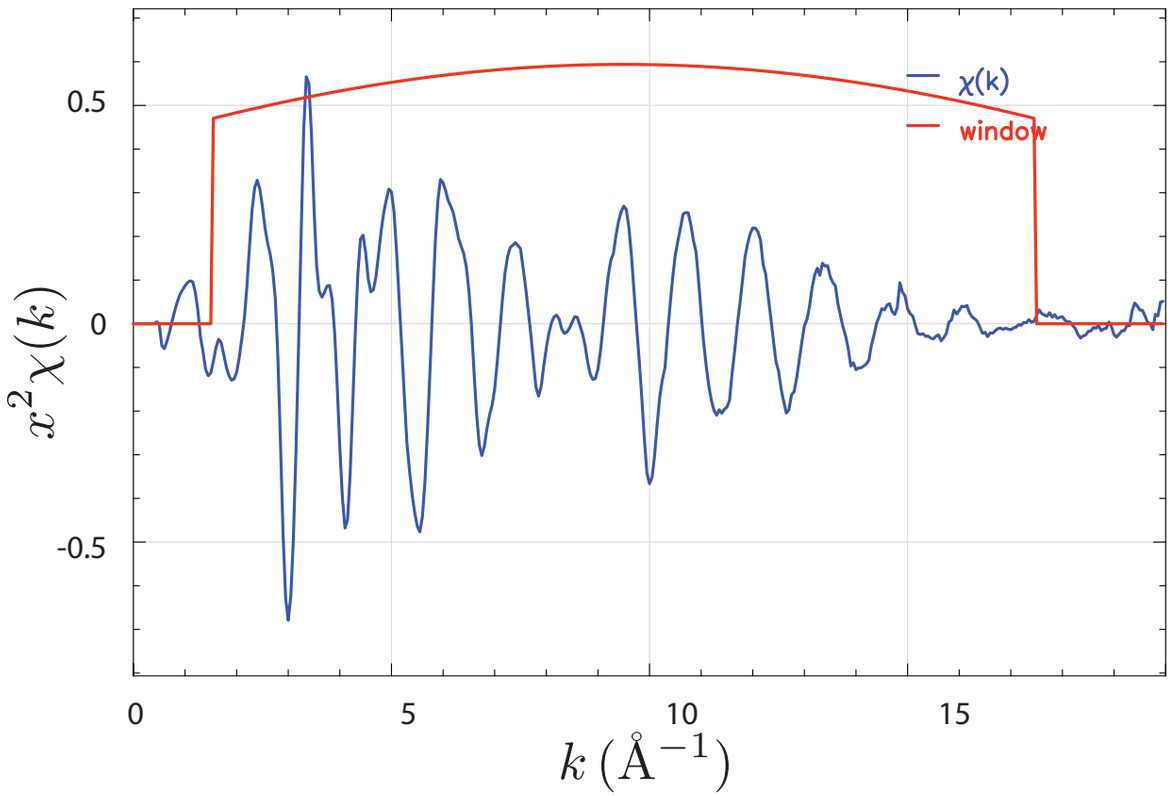
$\mu_0(E)$ is approximated by a smooth spline with no Fourier components in the EXAFS region (k-space)



k^2 Weighted χ Function

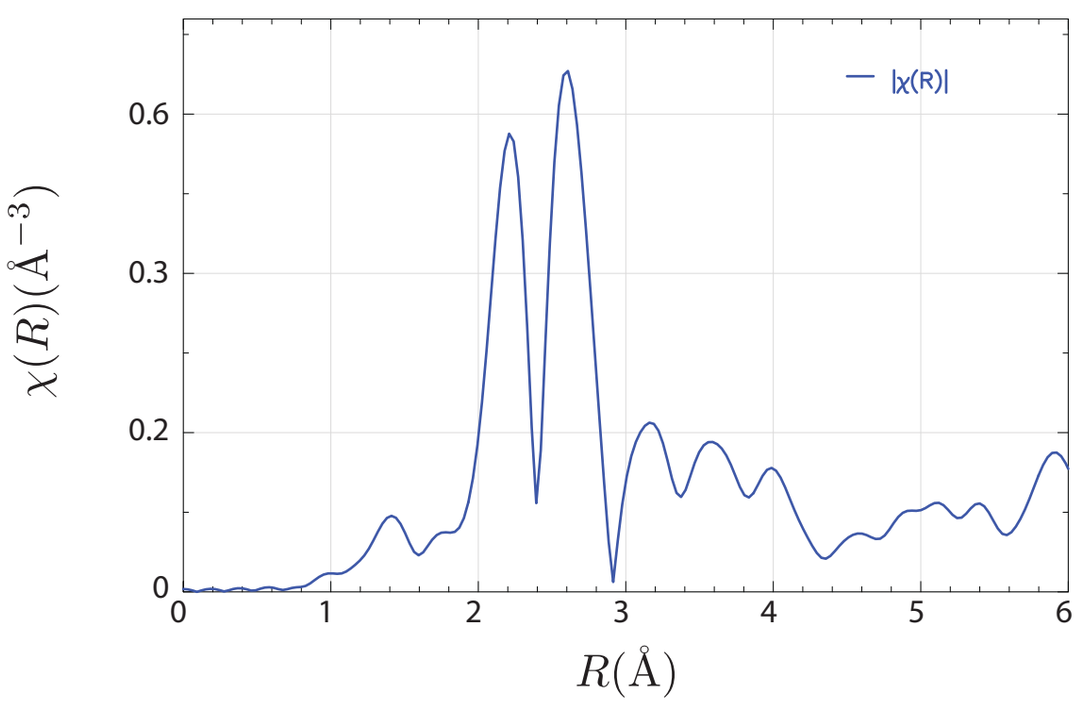
After subtraction of spline approximation to $\mu_0(E)$, convert to momentum units

Data Reduction: Athena



k-weighted $\chi(k)$: $k^2\chi$

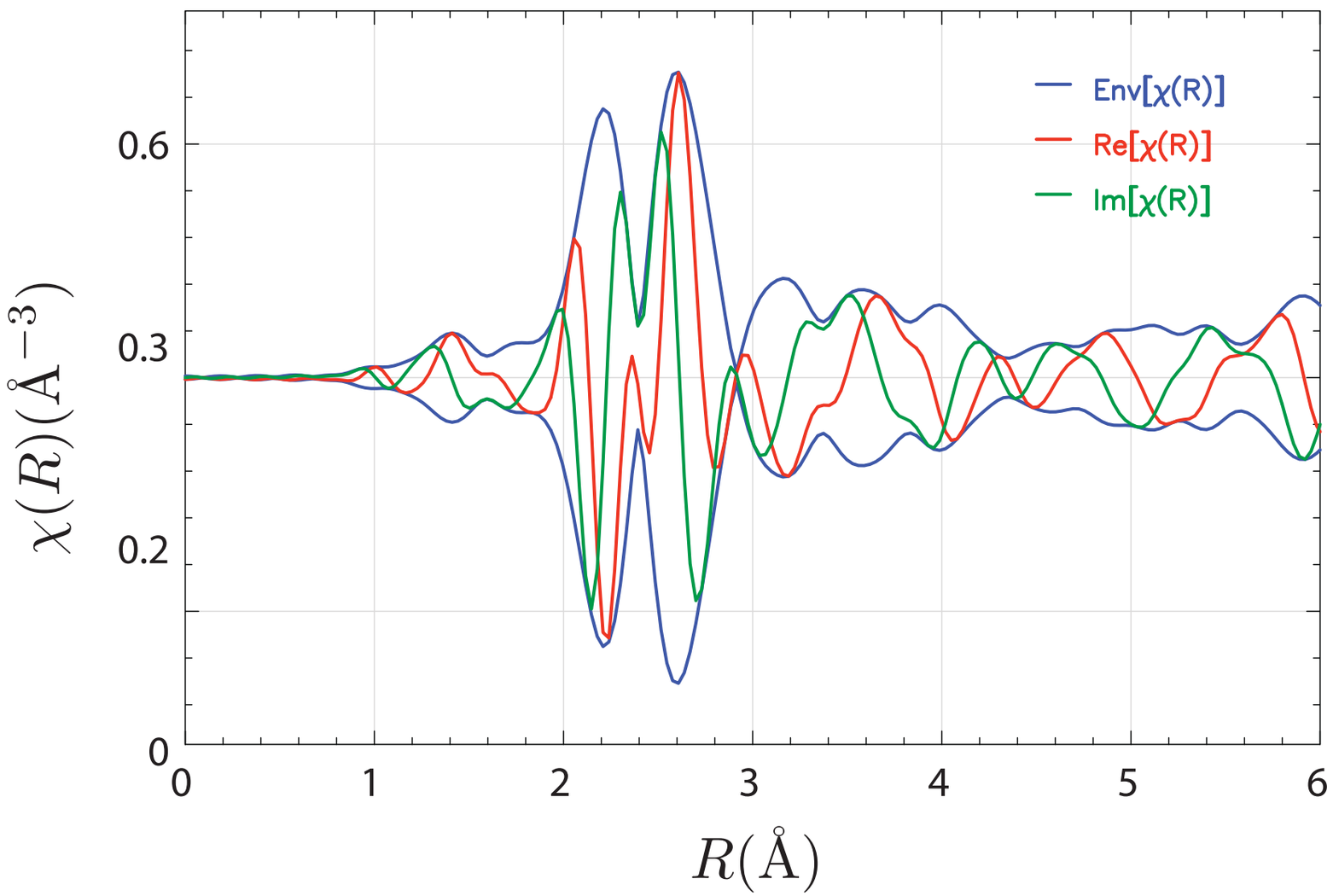
$\chi(k)$ is composed of sine waves from individual paths so we will transform to R-space. Use a apodization window to avoid "ringing" effects



$\chi(R)$

The Fourier Transform of $k^2\chi$ has two main peaks. The spectra are shifted with respect to the true bond lengths due to the phase-shift $\delta(k)$. A shift of 0.5Å is typical

Data Reduction: Athena



χ(R) is complex. Often only the magnitude is shown.

χ(R) is not a radial distribution function, but an interference function

In data fitting, both the real and imaginary parts are used

The Information Content of EXAFS

The number of parameters obtainable from a single set of data is limited:

$$N \sim \frac{2\Delta k \Delta R}{\pi}$$

Here Δk and ΔR are the k- and R-ranges of the data used. For typical ranges of k=[3,12]$Å^{-1}$ and R=1,3] Å, there are about 11.5 statistical degrees of freedom or parameters that can be fit from EXAFS.

The "Goodness of Fit" statistics and corresponding confidence in the measured parameters need to reflect this limitation.

It is often important to constrain parameters R, N, and σ^2 for different paths or even different data sets (different T, element edges etc.)

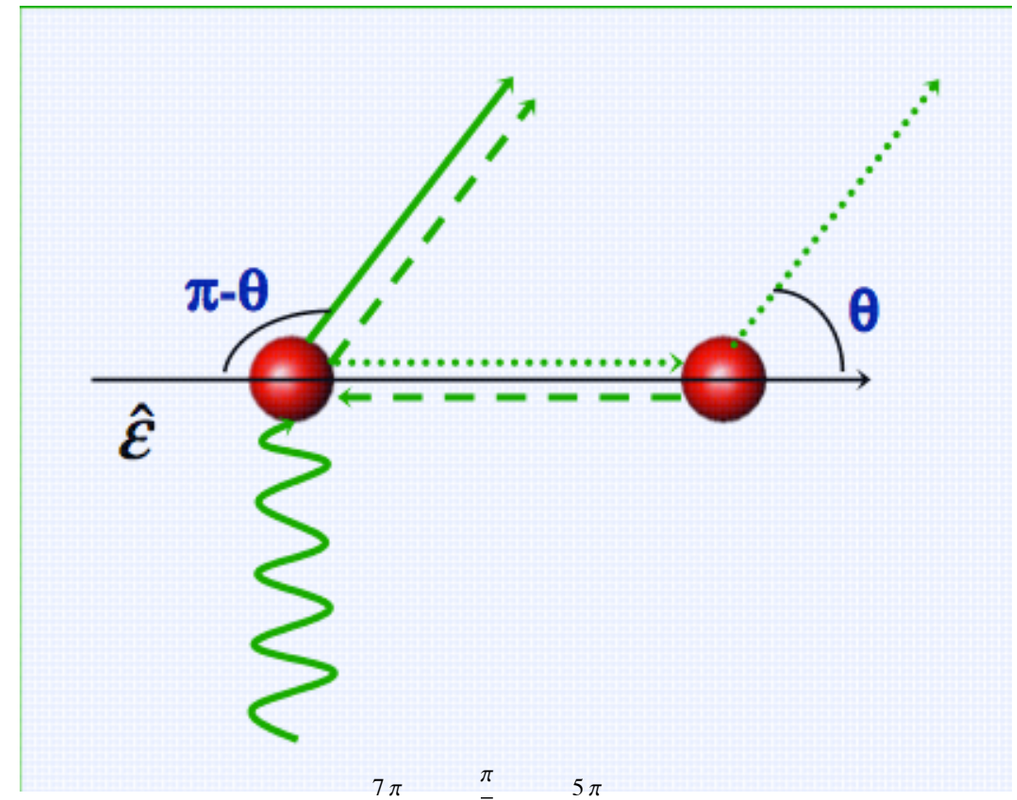
We can use chemical plausibility to weed out bad results or incorporate additional known data (coordination, Bond Valence Model etc.) to improve the quality of the fit.

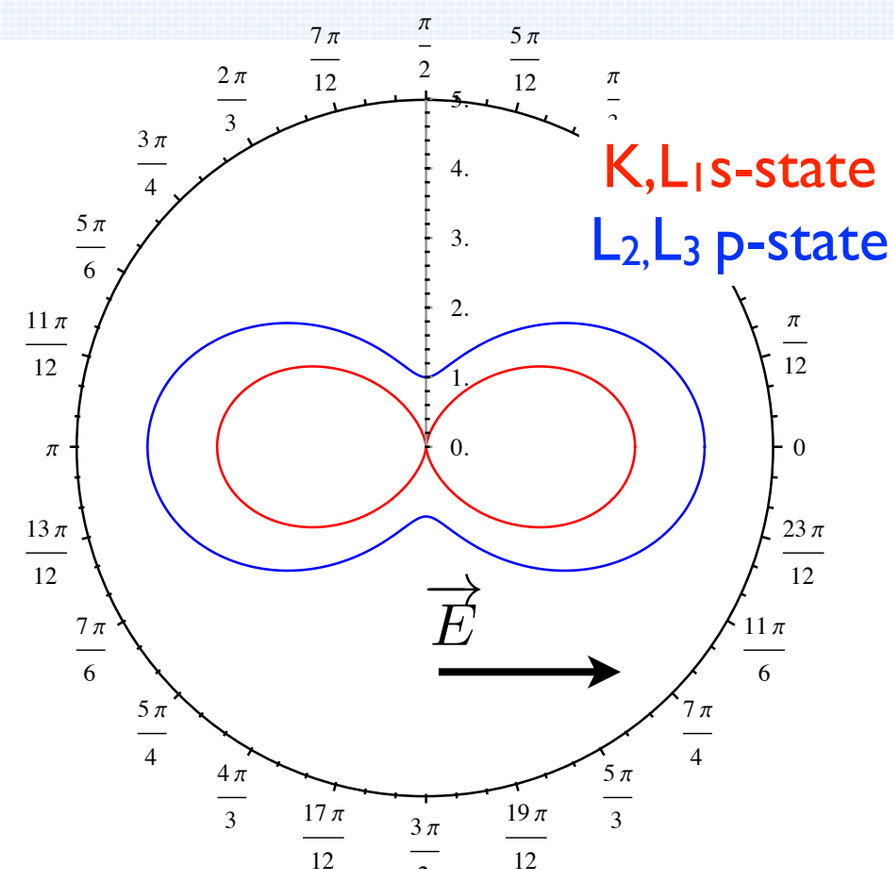
Polarization Dependence

- The ($\hat{e}$ · r) of the dipole approximation leads to an orientation dependence of χ that depends on the type of edge
  - K,L_1 Edges
  - L_2 L_3 Edges (assuming d-like final state) $3\cos^2\theta$

$$-\frac{1}{2}\left(1+3\cos^2\theta\right)$$

For systems with symmetry lower than cubic, polarization can be used as a tool to check for the anisotropy of a structure

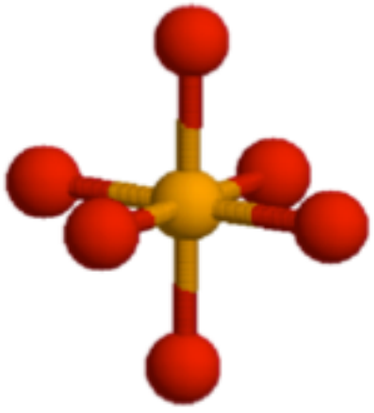




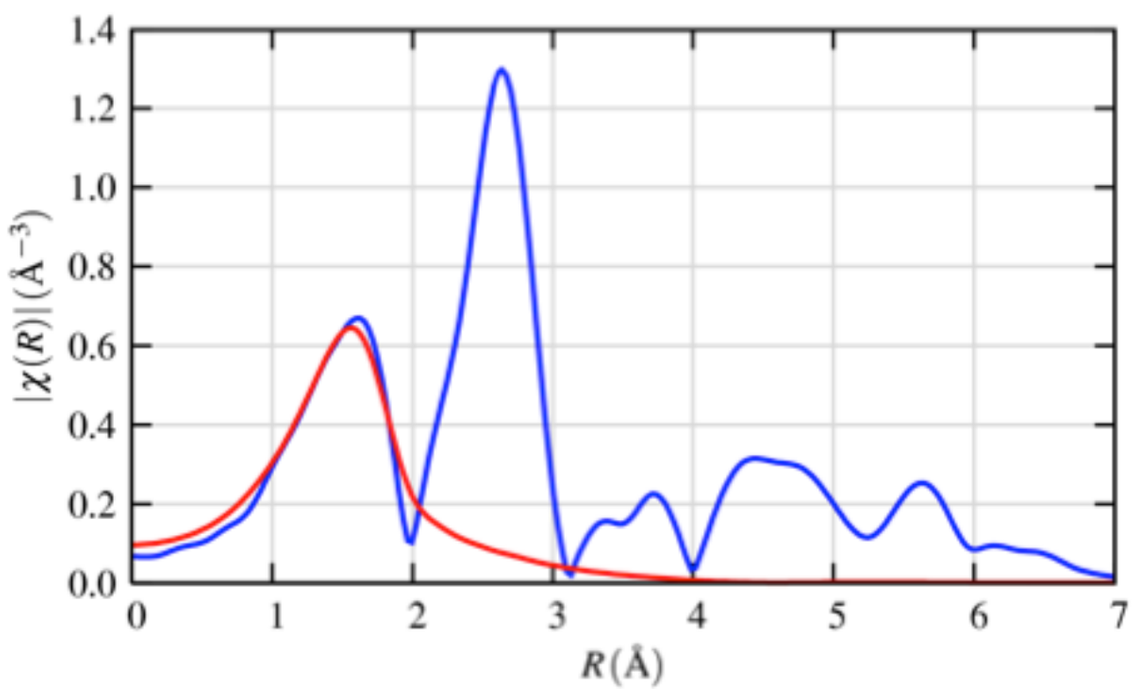
A Fitting Example

FeO has a rock-salt structure.

To model the FeO EXAFS, we calculate the scattering amplitude $f(k)$ and phase-shift $\delta(k)$, based on a guess of the structure, with Fe-O distance $R = 2.14\,\text{Å}$ (a regular octahedral coordination).



We'll use these functions to *refine* the values R, N, σ^2, and E_0 so our model EXAFS function matches our data.

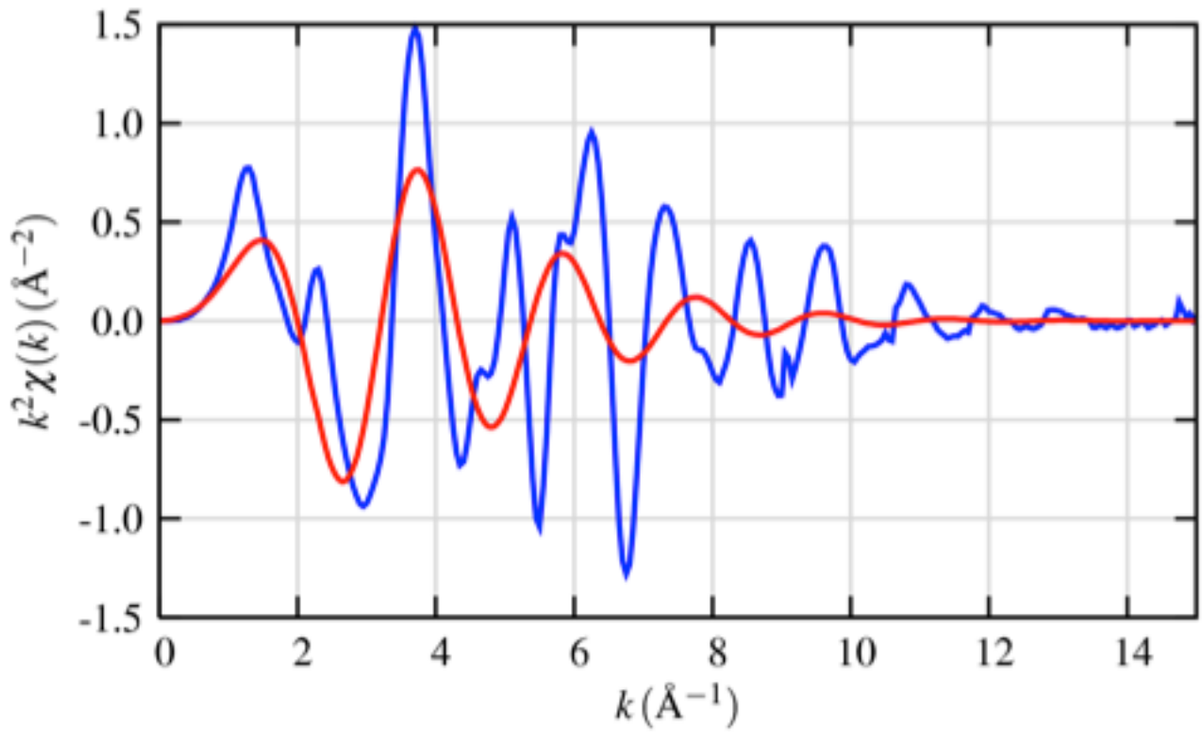


$|\chi(R)|$ for FeO data and 1st shell fit.

Fit results:

$$
\begin{aligned}
N &= 5.8 \pm 1.8 \\
R &= 2.10 \pm 0.02\text{Å} \\
\Delta E_0 &= -3.1 \pm 2.5 \text{ eV} \\
\sigma^2 &= 0.015 \pm 0.005 \ \text{Å}^2
\end{aligned}
$$

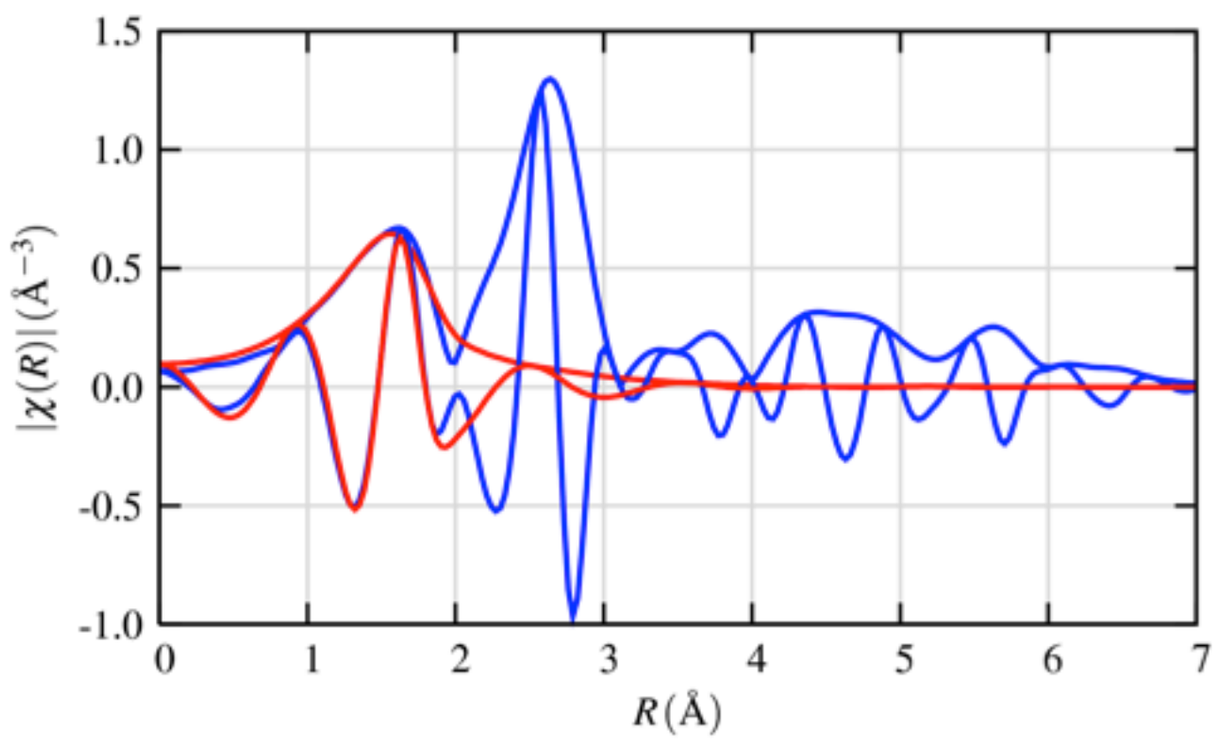
A Fitting Example



1st shell fit in k space.

The 1st shell fit to FeO in k space.

There is clearly another component in the XAFS!



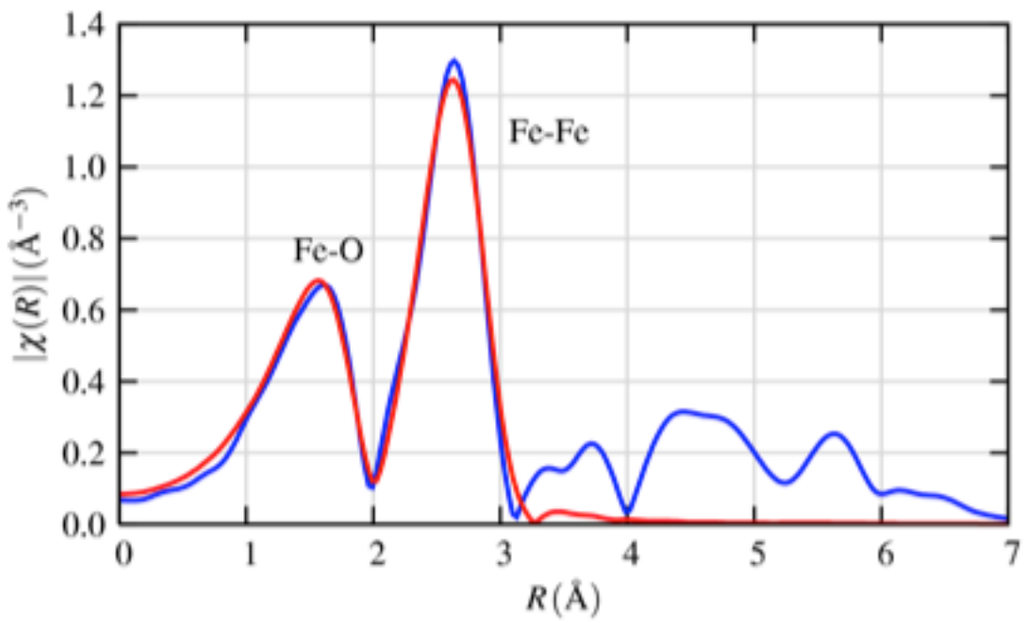
1st shell fit in R space.

$|\chi(R)|$ and $\mathrm{Re}[\chi(\mathrm{R})]$ for FeO (blue), and a 1st shell fit (red).

Though the fit to the magnitude didn't look great, the fit to $\mathrm{Re}[\chi(\mathrm{R})]$ looks very good.

A Fitting Example

Adding the second shell Fe to the model, with $f(k)$ and $\delta(k)$ for Fe-Fe, and refining R, N, σ^2:



$|\chi(R)|$ data for FeO (blue), and fit of 1st and 2nd shells (red).

These results are consistent with the known values for crystalline FeO:
6 O at 2.13Å, 12 Fe at 3.02Å.

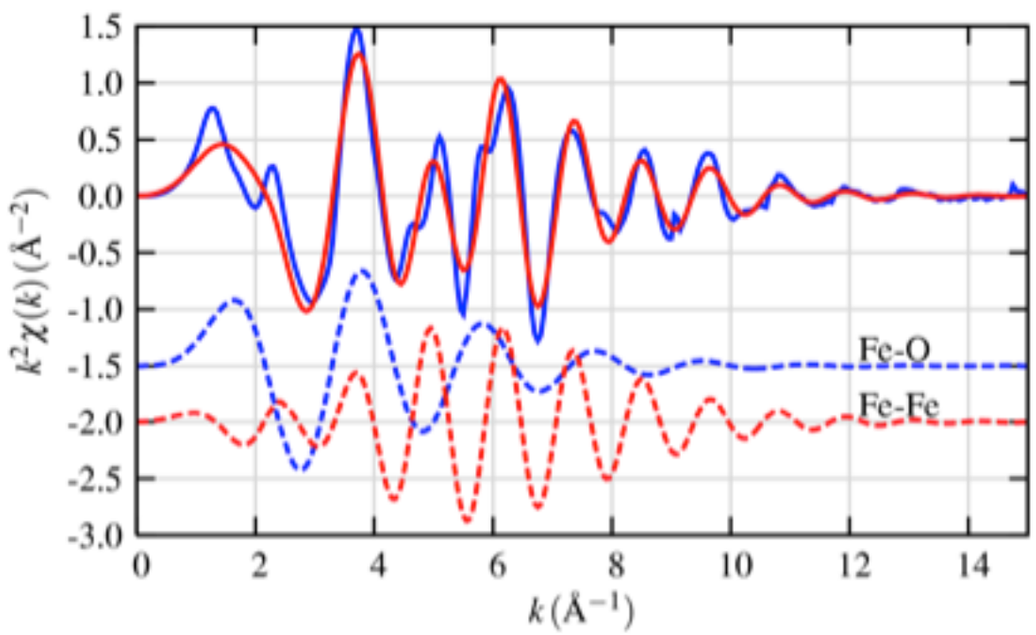
Fit results: Statistics: $R \approx 0.016$ $\chi^2_\nu \approx 100$.

Shell	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

These are typical even for a "very good fit" on known structures.
The calculation for $f(k)$ and $\delta(k)$ are good, but not perfect!

A Fitting Example

Other views of the data and fit:

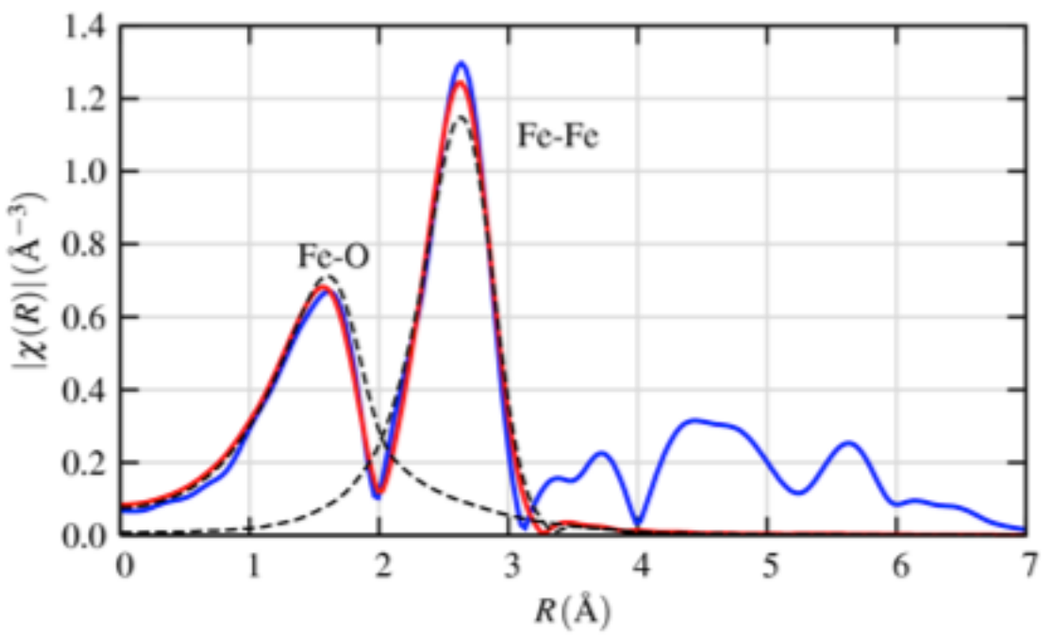


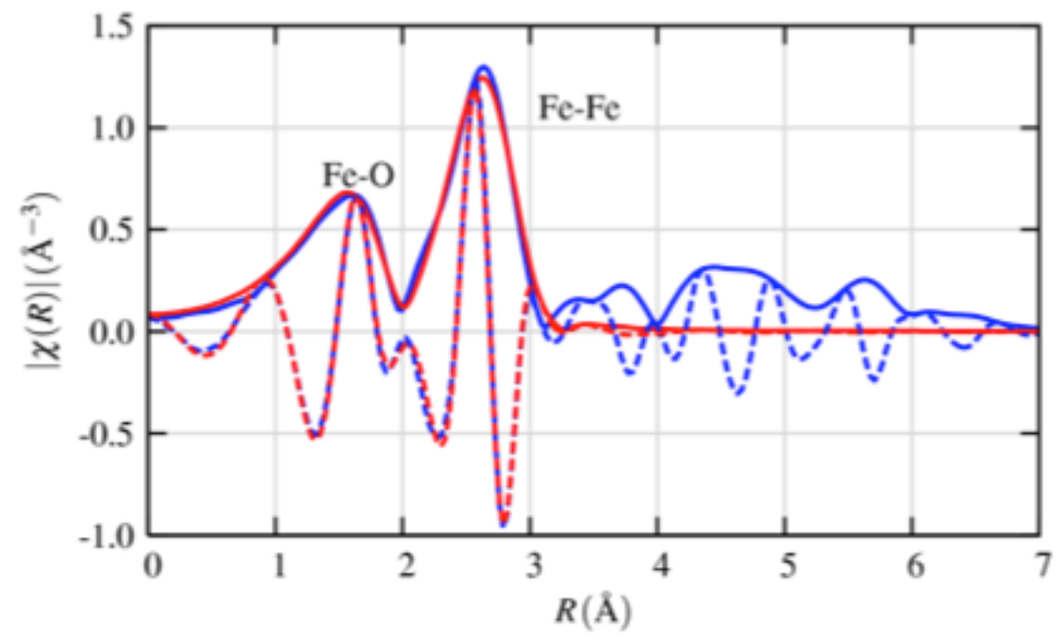
The Fe-Fe EXAFS extends to higher-**k** than the Fe-O EXAFS.

Even in this simple system, there is some *overlap* of shells in **R**-space.

The agreement in $\mathrm{Re}[\chi(\mathrm{R})]$ look especially good – this is how the fits are done.

Of course, the modeling can get more complicated than this!

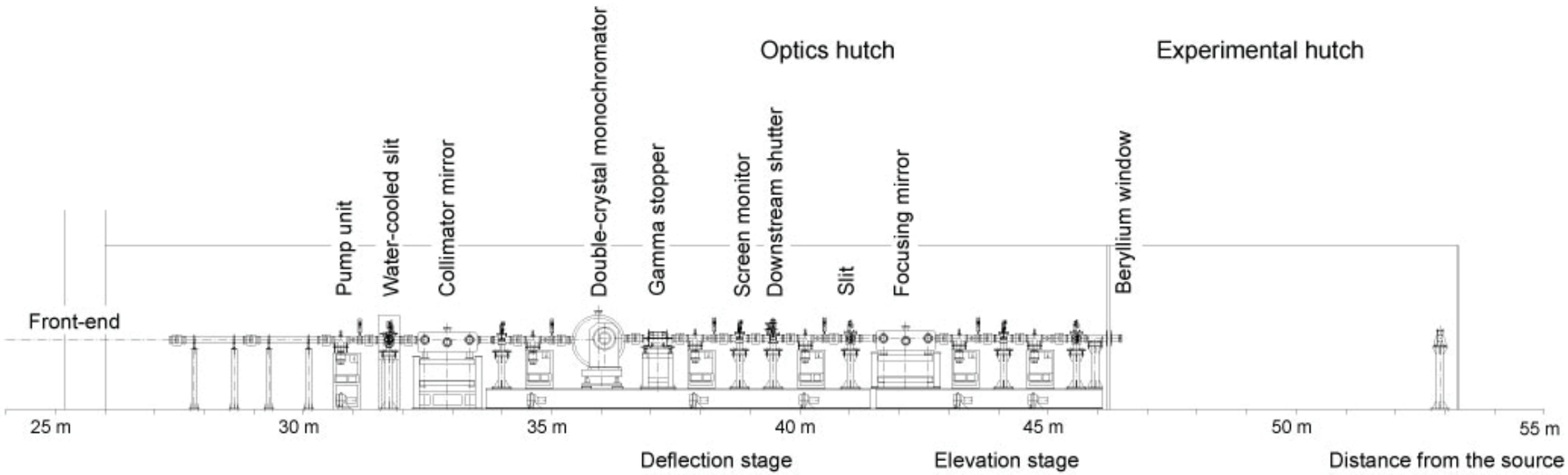




Experimental Considerations

- In what follows a brief introduction to some of the components of a beamline will be shown

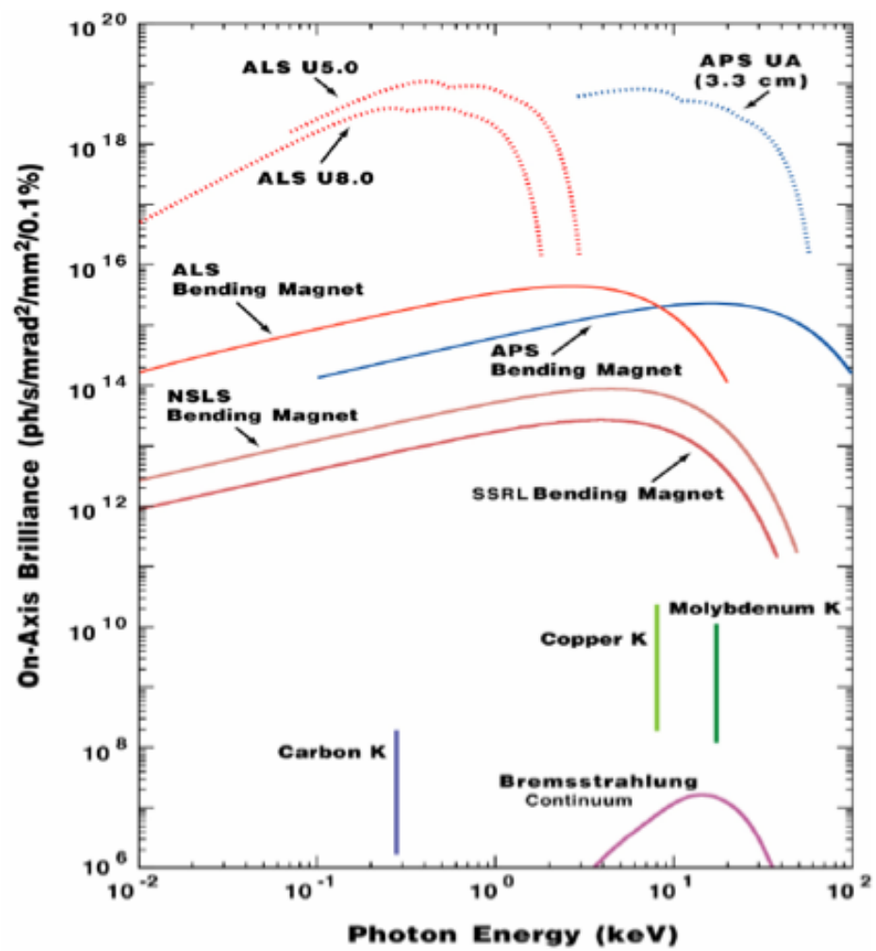
BL01B1

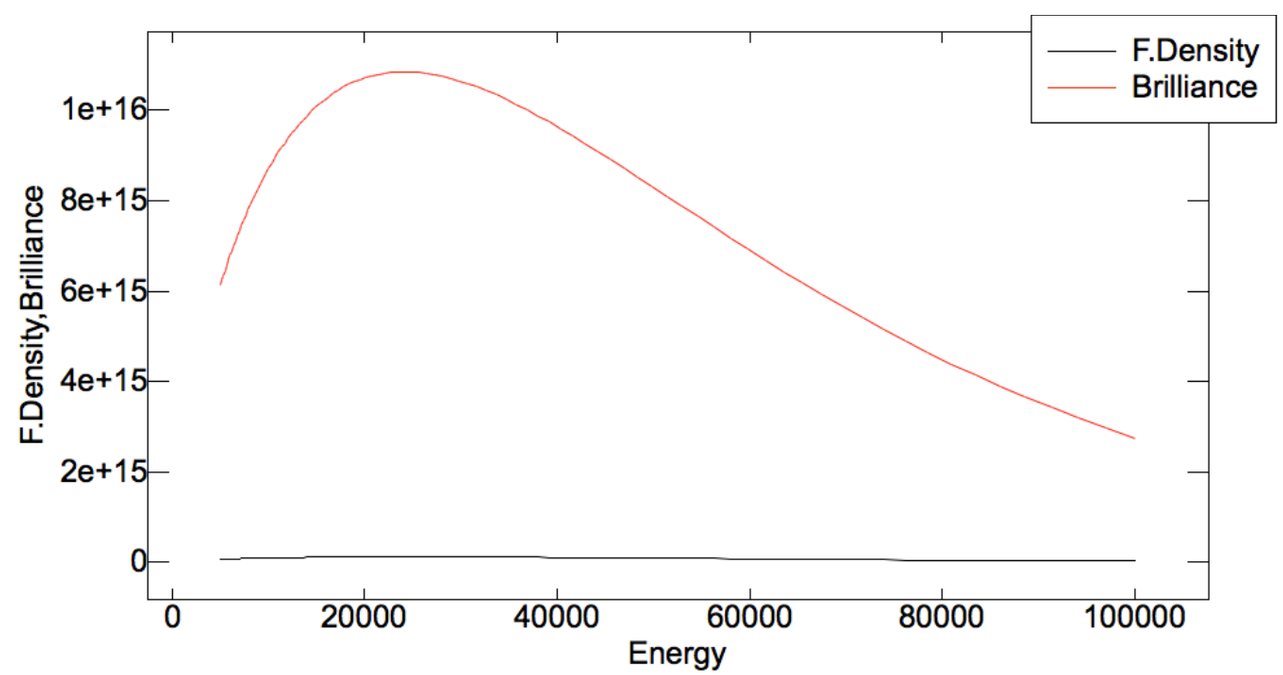


- Si double monochromator (111), (311), or (733)
- Focusing harmonic rejecting mirrors
- automatic adjustment of beam location with energy
- energy range 4.5-110 keV

Bl01B1 Energy Dependence

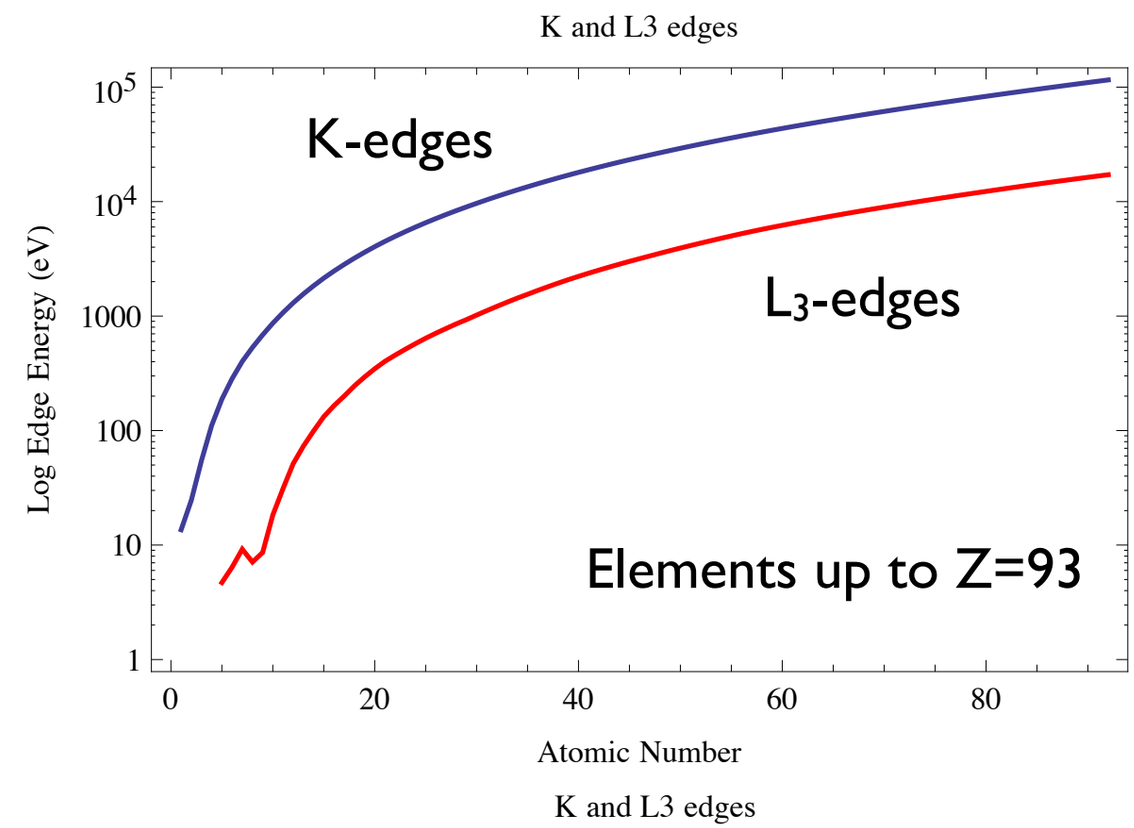
- The energy dependence of x-rays from bl01b1 as predicted by the program SPECTRA (http://radiant.harima.riken.go.jp/)





Absorption Edges

- K Edge Energies $\propto Z^2$
- Elements with Z>18 have either a K or an L-edge accessible between 3 and 35 keV
- Soft x-ray XAFS possible as well
- Edges with E<3 keV require special preparation (vacuum) while edges over E>35 keV can suffer from reduced cross section, Compton scattering, and multielectron effects. (3 keV<E<35 keV Hard X-ray region easy to measure in)

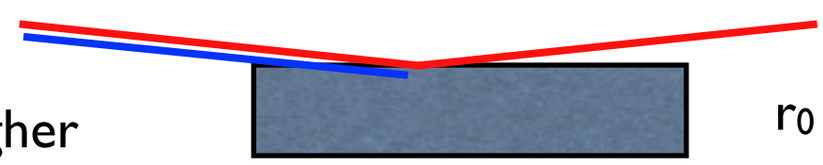


Harmonic Rejection

- As the monochromator lets through x-rays that satisfy the Bragg condition ($\lambda=2d \sin\theta$) not only λ, but $\lambda/2$, $\lambda/3$ (higher harmonics) are transmitted as well.
- At bl01b1, higher harmonics are rejected using a mirror, for a fixed wavenumber k, x-rays will not reflect for angles greater than the critical angle α_c.

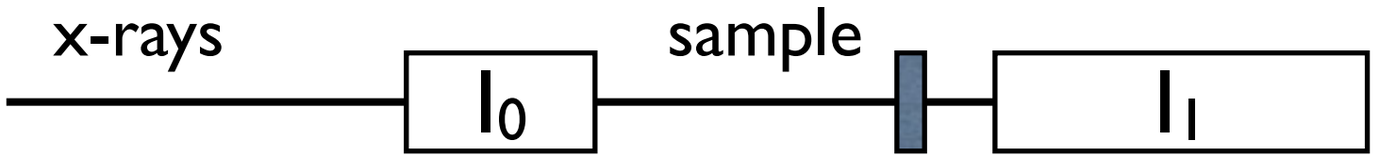
$$\alpha_c = \sqrt{2\delta} = \frac{4\pi\rho r_0}{k}$$

ρ number density of coating
r_0 electron scattering length=2.82 x 10^5 Å
k = incident wavevector



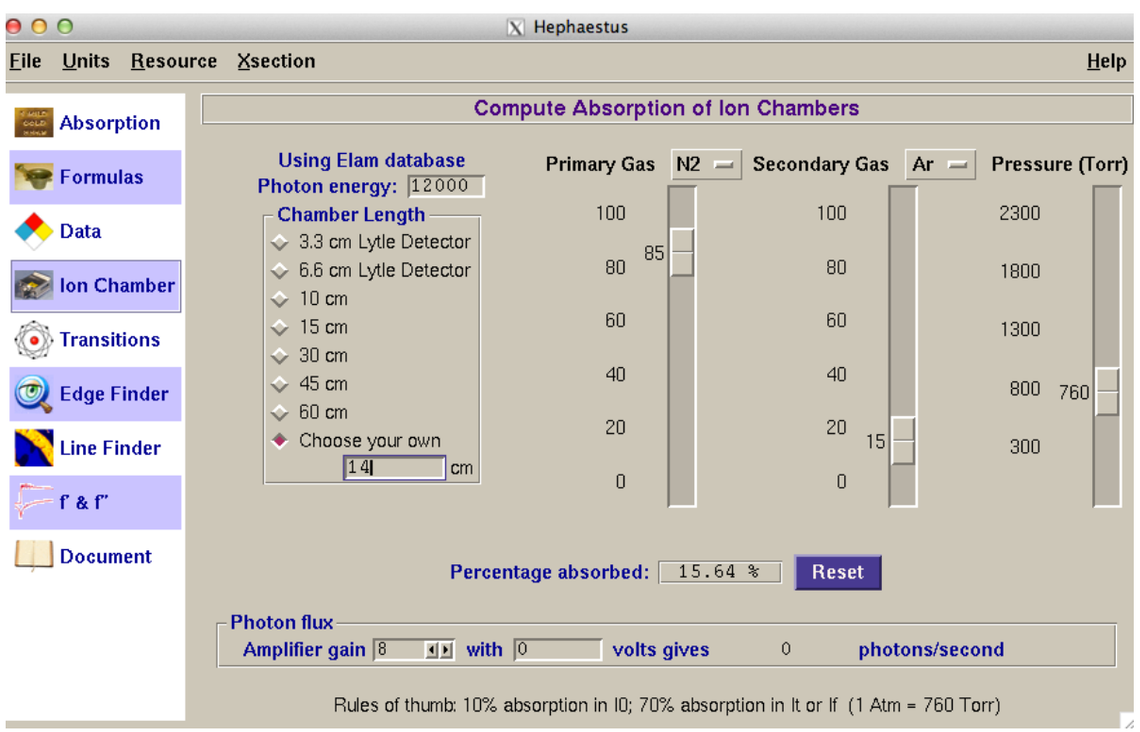
fundamental λ is reflected but higher harmonic $\lambda/2$ and above are not

Measurement Techniques



- The intensity of the synchrotron varies with time. It must be normalized. Typically this is done by using an ion chamber which measures the current of ionized gas between two capacitors.

  - To optimized statistics without too much signal attenuation, the I_0 chamber should operate at about 15% attenuation. I_1 should be about 85%.



Hephaestus can help.
At 12 keV, a 140 mm Ion Chamber will absorb 15% of the incoming signal if a N_2/Ar mixture in a ratio of 85:15 is used.

Absorption Length

- Absorption Length μ is
  - distance over which the incident intensity decreases by a factor of 1/e (37%)
  - an important factor in designing EXAFS experiments and should be calculated

$$f_i = \frac{M_i}{\sum_i M_i}$$

$$\mu = \rho \sum_i (f_i \sigma_i)$$

sample calculation for GeTe

ρ=6.212 gm/cm^3, f_i(Ge)= f_i(Te) =1/2

above edge @11.4 keV σ_{Ge}=22,340 Barns, σ_{Te}=22,380 Barns

```
In[342]:= σ[Ge] = 185.359 cm^2 / gm; σ[Te] = 105.629 cm^2 / gm;

In[344]:= μ = (6.212 gm / cm^3) (f[Ge] σ[Ge] + f[Te] σ[Te])

Out[344]= 835.838 / cm

In[345]:= absorptionlength = 10^4 (μm / cm) (1 / μ)

Out[345]= 11.964 μm
```

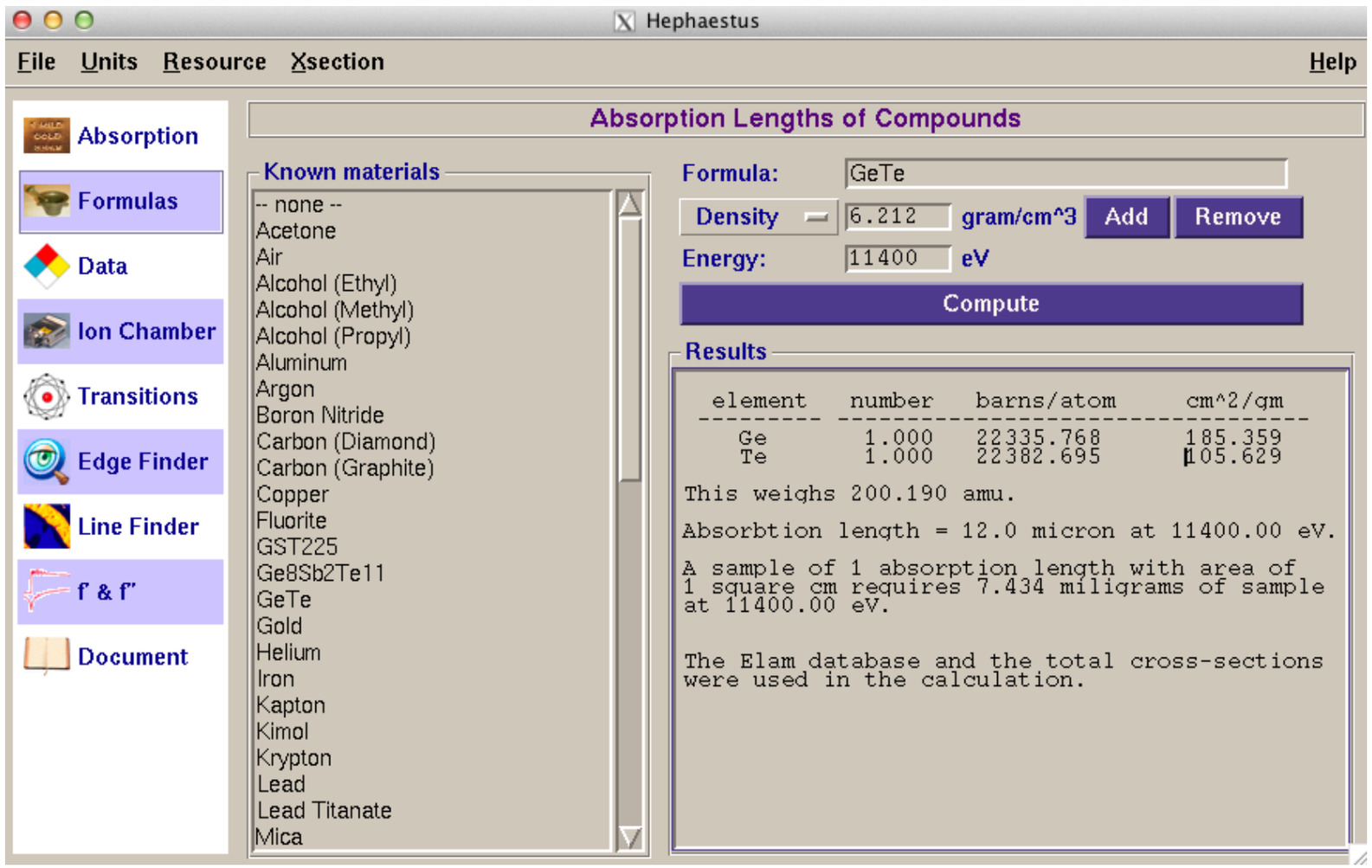
where a Barn is 10^{-24} cm^2

The 1/μ length is about 10 μm

Absorption Length

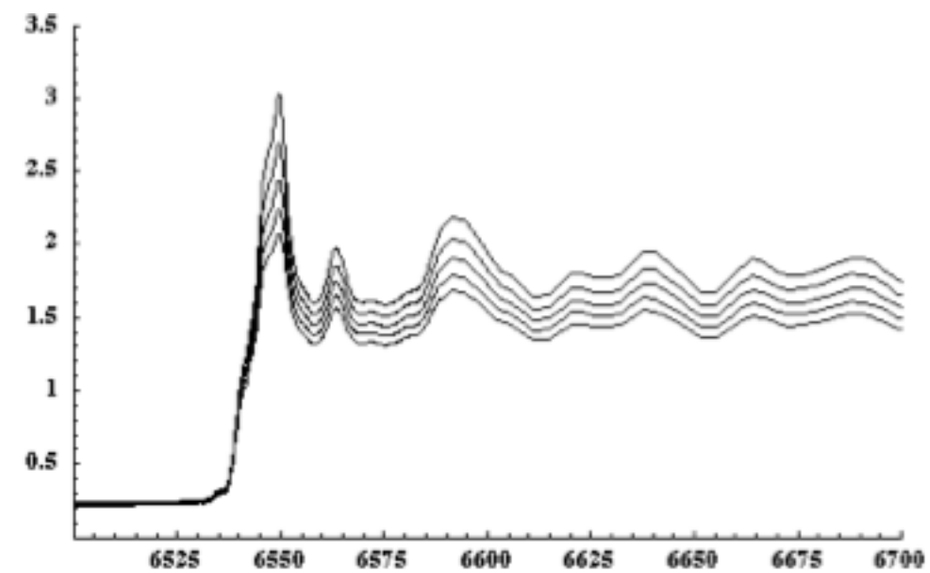
- One can also calculate the absorption length using Hephaestus (part of the Horae suite). http://cars9.uchicago.edu/ifeffit/Downloads

- or http://macports.org "port install demeter"



Absorption Lengths and Particle Size

- It is important to keep particle size below one absorption length
  - This leads to sample areas that are opaque and gaps that distort the "white line" and affects σ^2 as well
- Samples should be uniform on the length scale of the absorption length (small particles must be used)

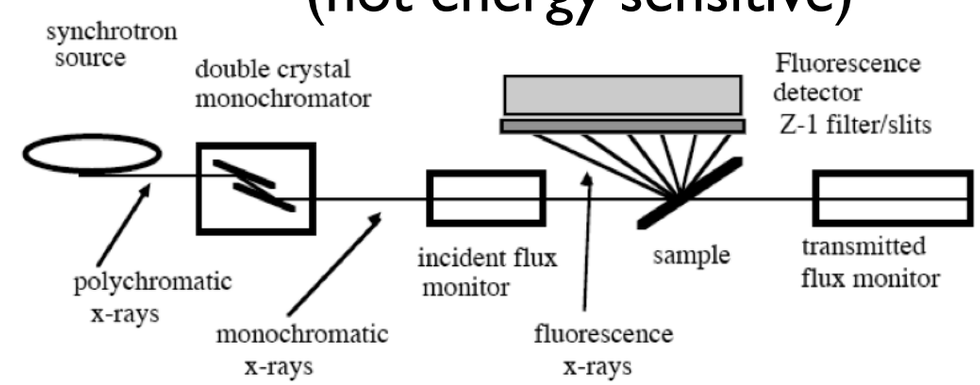


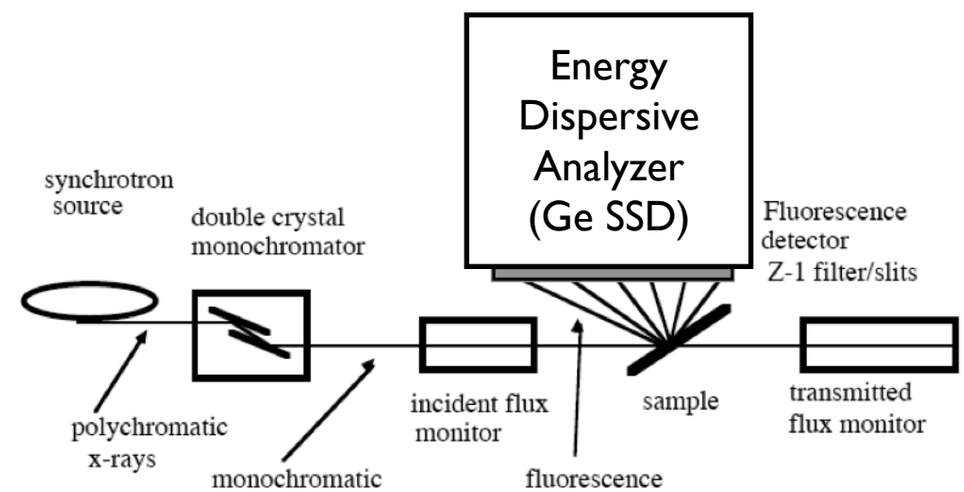
MnO spectra as a function of particle size (10% leakage)

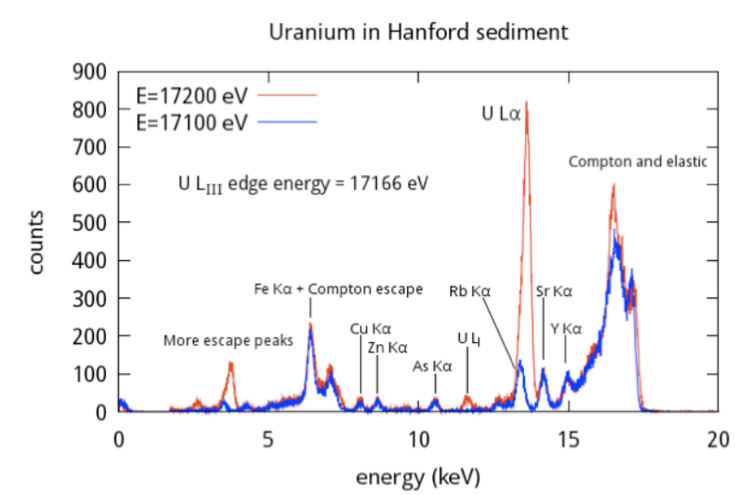
X-ray Fluorescence

- X-ray fluorescence is highly sensitive
- A good sample is:
  - dilute (to avoid self absorption)
  - homogeneous (I_0 will not divide out if sample is non-uniform)
- If there is only one strong fluorescence, a Lytle-Heald detector can be used (ion-chamber)
- If several elements are present, an energy dispersive (Ge SSD) can be used, but dead time can be a problem.

Lytle-Heald Detector
(not energy sensitive)



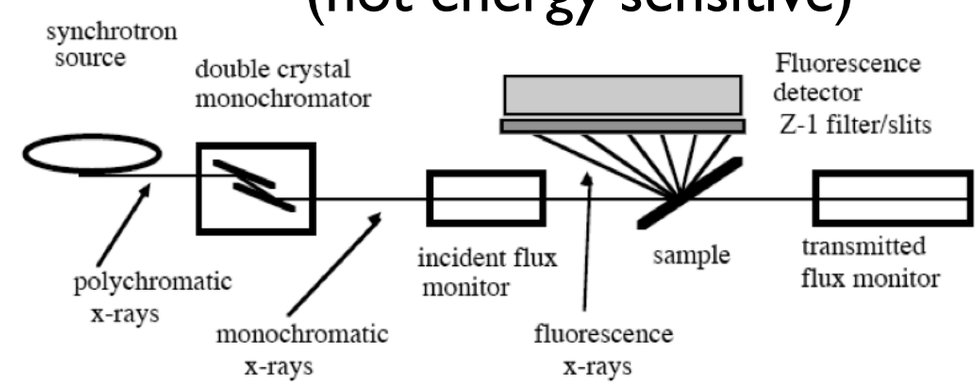


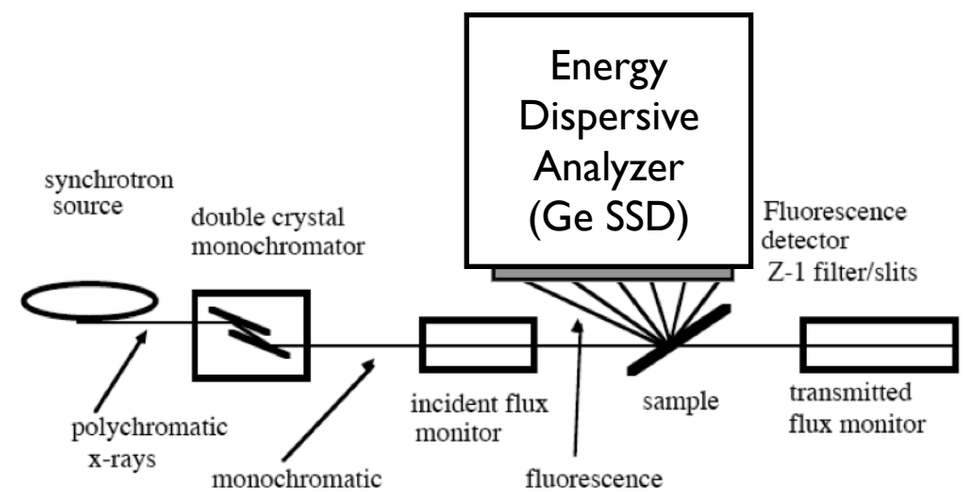


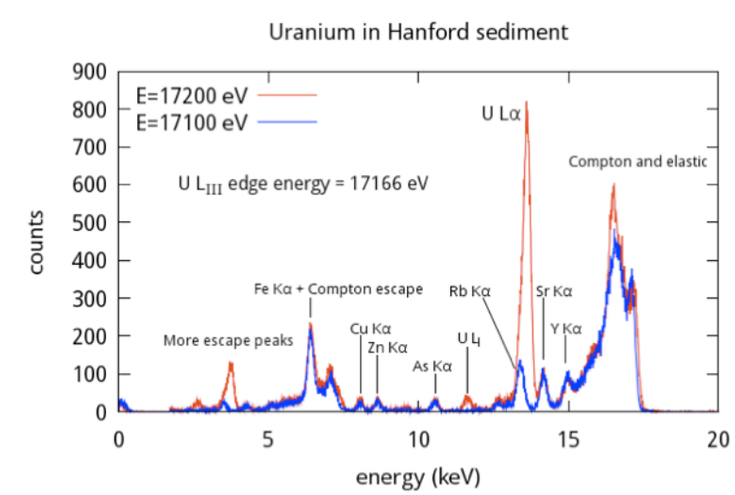
X-ray Fluorescence (cont.)

- Self-absorption can significantly distort signal.
  - Correction possible
    Athena/Demeter offer correction
    Booth and Bridges, Physica Scripta **T115,** 202 (2005)
- Dead time of detector can distort features (e.g. white line)
  - Correction possible
- Diffraction (e.g. from single crystal substrates) can be lead to strong glitches
  - can be reduced by averaging signal while rotating sample slightly

Lytle-Heald Detector
(not energy sensitive)



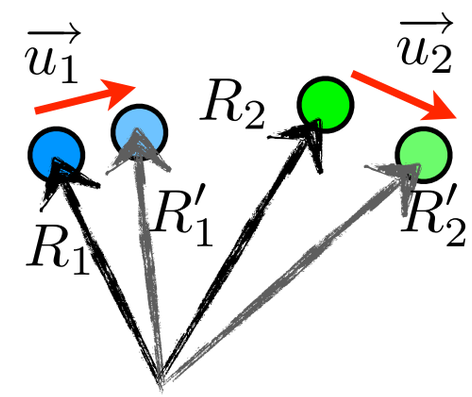




Disorder in EXAFS and diffraction

In diffraction, we define single center displacement parameters u

$$u_1^2 = \left\langle (\overrightarrow{R_1'} - \overrightarrow{R_1})^2 \right\rangle, \;\; u_2^2 = \left\langle (\overrightarrow{R_2'} - \overrightarrow{R_2})^2 \right\rangle$$



In EXAFS, we define correlated displacement parameters also known as Mean Squared Relative Displacement (MRSD)

$$\sigma_{12}^2 = \left\langle \left[(\overrightarrow{R_2'} - \overrightarrow{R_1'}) - (\overrightarrow{R_2} - \overrightarrow{R_1}) \right]^2 \right\rangle = \left\langle \left[(\overrightarrow{R_2'} - \overrightarrow{R_2}) - (\overrightarrow{R_1'} - \overrightarrow{R_1}) \right] \right\rangle$$

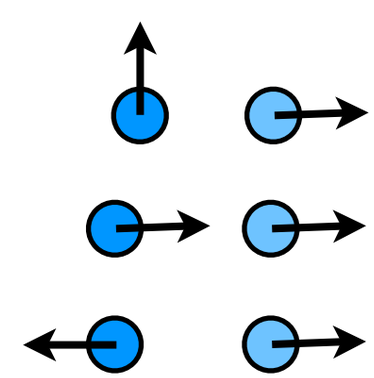
$$= u_1^2 + u_2^2 - 2\left\langle (\overrightarrow{u_1} \cdot \overrightarrow{u_2}) \right\rangle = u_1^2 + u_2^2 - 2u_1 u_2 \left\langle \hat{u_1} \cdot \hat{u_2} \right\rangle$$

If $|u_1| = |u_2|$

$$\sigma^2 = 2u^2, \;\; \text{if} \;\; \hat{u_1} \cdot \hat{u_2} = 0$$

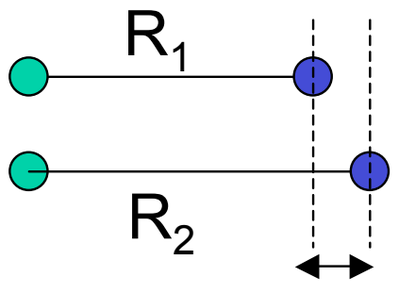
$$\sigma^2 = 0, \;\; \text{if} \;\; \hat{u_1} \cdot \hat{u_2} = 1$$

$$\sigma^2 = 4u^2, \;\; \text{if} \;\; \hat{u_1} \cdot \hat{u_2} = -1$$

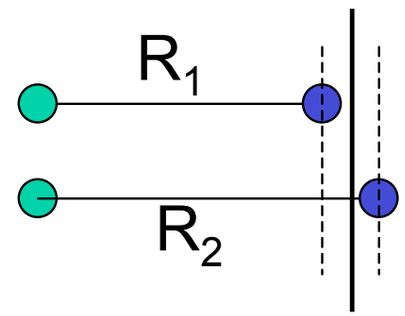


Spatial Resolution (Beats)

The ability to resolve two distances "close" to each other.



OR



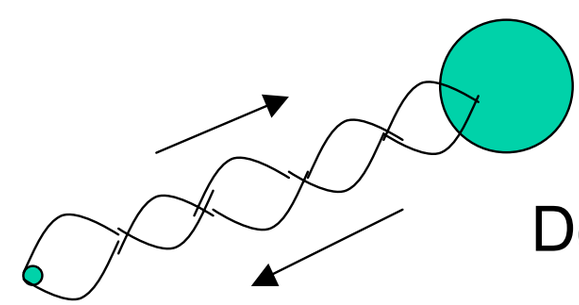
$$\langle R \rangle = (R_1 + R_2)/2$$

$$\sigma = \Delta R/2$$

Intuition: To resolve, ΔR needs to be a significant fraction of the smallest photoelectron wavelength

$$\Delta R \geq \frac{\lambda_{\min}}{4} = \frac{2\pi}{4k_{\max}} = \frac{\pi}{2k_{\max}}$$

$$\boxed{k_{\max} \geq \frac{\pi}{2\Delta R}}$$



De Broglie λ

$$k = \frac{2\pi}{\lambda}$$

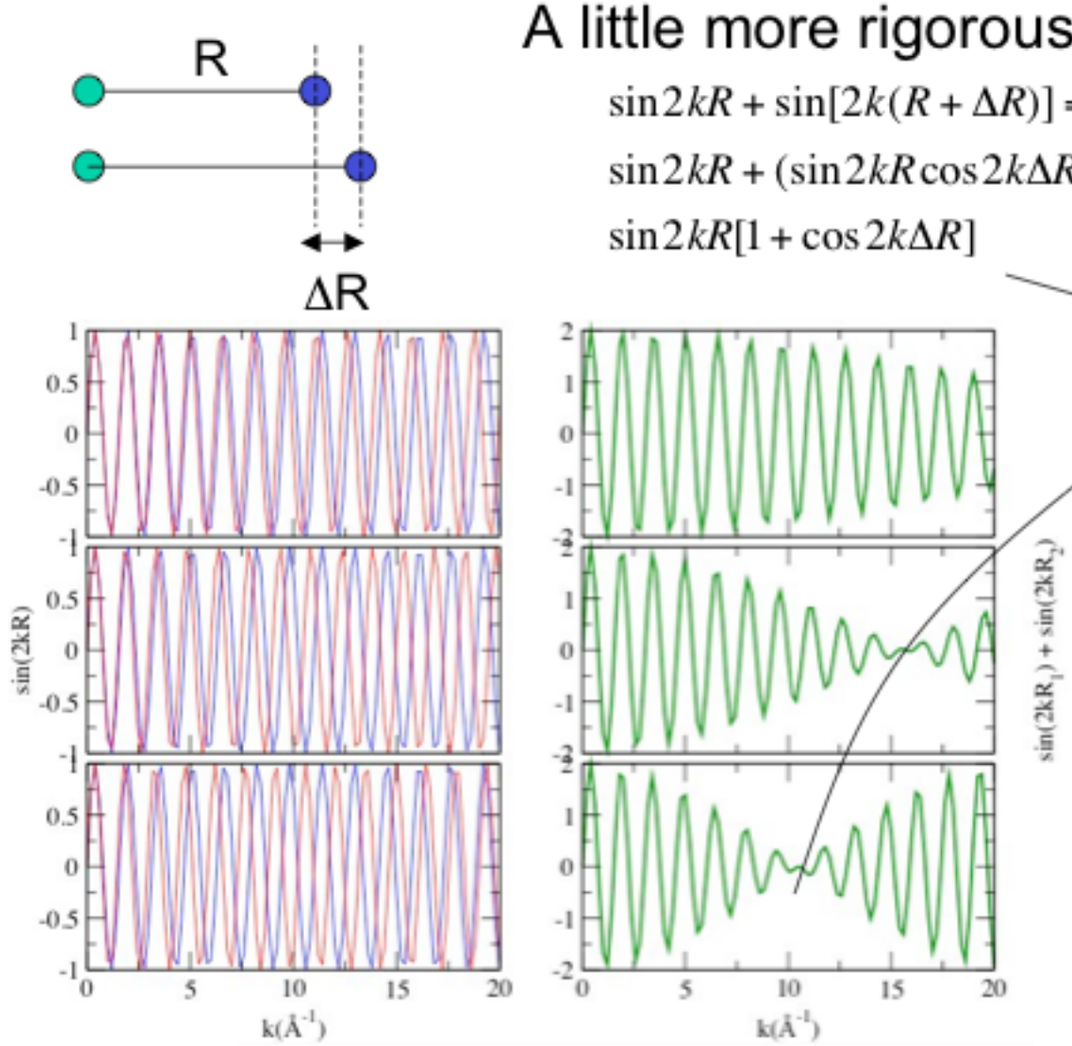
Spatial Resolution (Beats)

A little more rigorous derivation:

$$\sin 2kR + \sin[2k(R+\Delta R)] =$$
$$\sin 2kR + (\sin 2kR \cos 2k\Delta R + \cos 2kR \sin 2k\Delta R)$$
$$\sin 2kR[1+\cos 2k\Delta R]$$

Low "freq" modulation with beat at $2k\Delta R=\pi$

$$k_{beat} = \frac{\pi}{2\Delta R}$$



ΔR=0.05 Å

ΔR=0.1 Å

R=2.0Å

ΔR=0.15 Å

Features of XANES

- Pre-edge region
  - Features caused by dipole transitions to (empty) bound states.
  - Local geometry about absorbing atom
- Absorption Edge
  - ionization threshold to continuum states
  - Larger oxidation state (chemical shift) moves edge up in energy
- XANES region is characterized by multiple scattering. Includes information about bond angles and distances. Need to use simulation (Feff9) to understand structure

Selection Rules

XANES probes unoccupied electron states

- Dipole selection rule

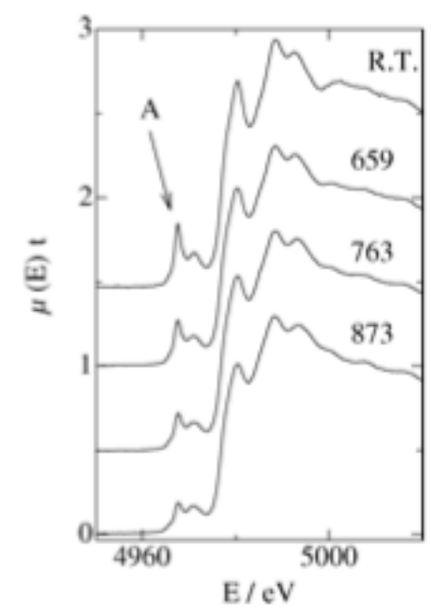
  Δl (*orbital angular momentum*) = ± 1, Δj (total *angular momentum*) = ± 1

- Edges
  - K-edge and L_1 Edges: s (l=0) → p (l=1)
  - L_2, L_3-Edges: p(l=1) → d(l=2) or s(l=0)
  - Note that states can mix hence by using the selection rules XANES can be used as a probe of hybridization

note that quadrupole transitions are possible but typically have about 1/100 of the strength of dipole transitions

K-edge Pre-Edge Peaks

- In a metal, a K-edge transition implies a s → p like transition
  - For Octahedral coordination site is centrosymmetric implying no p-d mixing (only weak quadrupole transitions)
  - p-d mixing becomes possible with distortion from octahedral point symmetry
  - tetrahedral site symmetry, largest pre-edge peaks

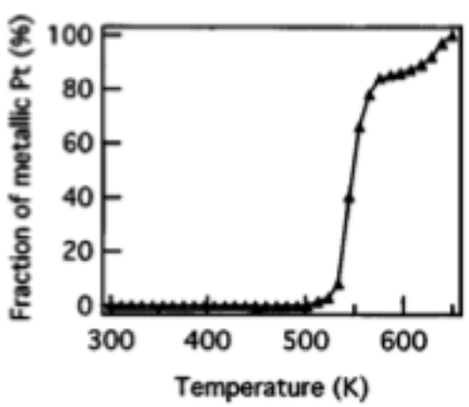


X-ray absorption near edge (XANES) spectra of Ti K-edge for $PbTiO_3$ a various temperatures.

Using XANES with mixtures

- The coherence length (the distance over which the multiple scattering occurs) in XANES is on the order of 1 nm
  - If the sample is homogeneous over distances of 1 nm, then different regions of the sample will add incoherently
    XANES(mixture) = Σf_i XANES$_i$

Example of the decomposition of $PtO_{1.6}$



G. 3. Fraction of metallic Pt phase obtained by reduction of a $PtO_{1.6}$ layer.

Example: The decomposition of $PtO_{1.6}$
All XANES spectra collected repeatedly during the thermal decomposition process could be fit by a weighted sum of Pt and the starting compound PtOx demonstrating that no intermediate phases were involved. The figure on the left shows the metal fraction allowing the kinetics of the reaction to be explored

Kolobov et al., *Appl. Phys. Lett. 86*, 12 (2005), 121909.

XANES Summary

- The XANES signal is significantly larger than EXAFS and exhibits little temperature dependence.
- XANES spectra can be used as a fingerprint and linear combination type analyses are easily carried out. Simple selection rule considerations can give considerable insight into the bonding in a sample.
- The multiple scattering present in XANES spectra make it more difficult to treat theoretically, but the real-space multiple scattering code Feff (now at version 9) allows calculation of theoretical spectra using only the coordinates and types of atoms in a cluster. http://leonardo.phys.washington.edu/feff/

XANES Software

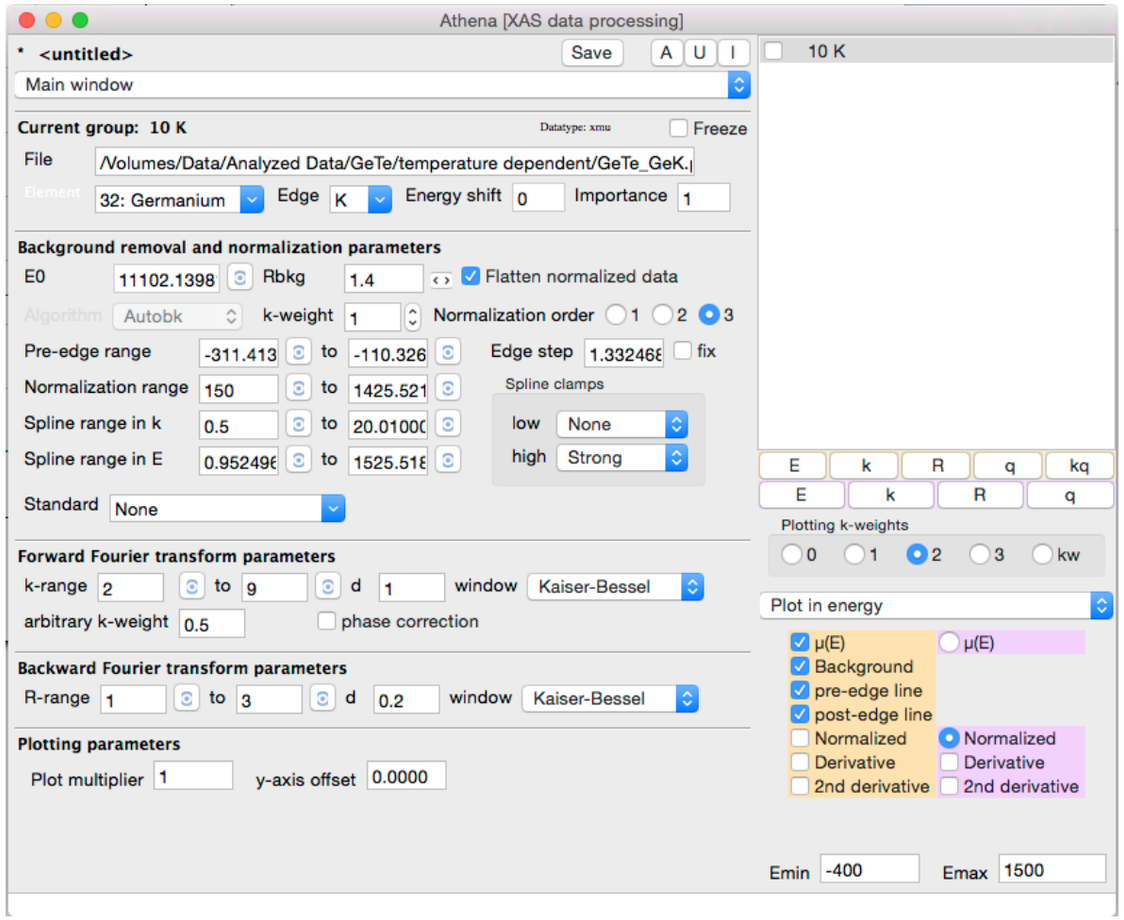
This list is inevitably incomplete

- Multiple Scattering Code
  - XANES EXAFS FEFF9 from http://leonardo.uwash.edu
  - EXCURVE http://ccpforge.cse.rl.ac.uk/gf/project/excurv/ Free
- Density-Functional Theory
  - XANES EXAFS Wien2K all electron code http://wien2k.at
  - XANES EXAFS CASTEP plane wave code
  - XANES EXAFS FMNES http://neel.cnrs.fr/spip.php?rubrique1007 Free

Quick Fit

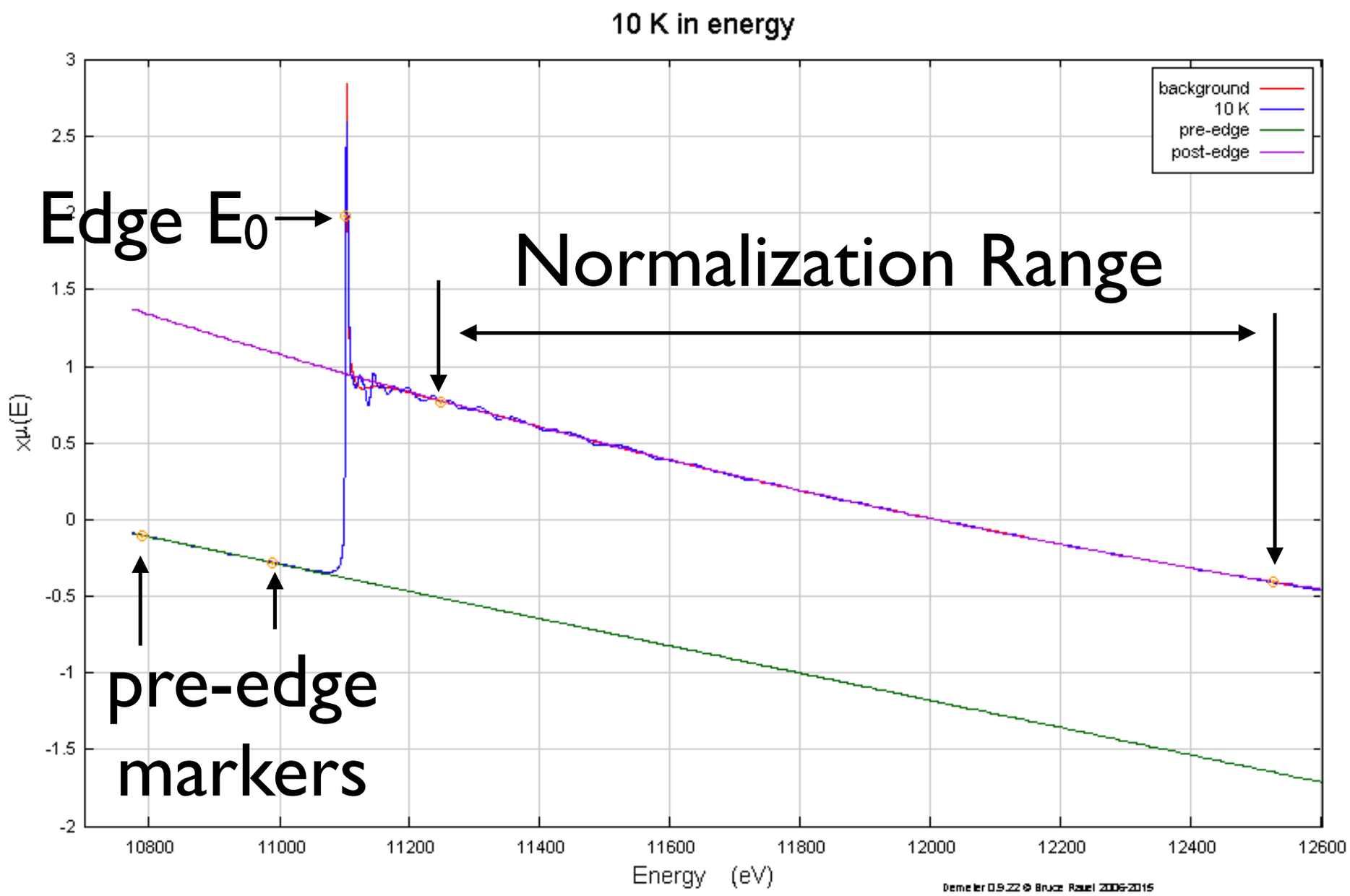
- If time allows, we shall review a quick fit of GeTe at the Ge edge. (an more complete tutorial would take several hours)
  - goal is to give a bird's eye overview of the fitting process
- Software: artemis and athena (horae suite)
- Steps
  - Athena: Background processing: using a spline to subtract background and obtain χ function
  - Artemis: Calculate theoretical paths for a model structure and fit to experimental χ data

Athena

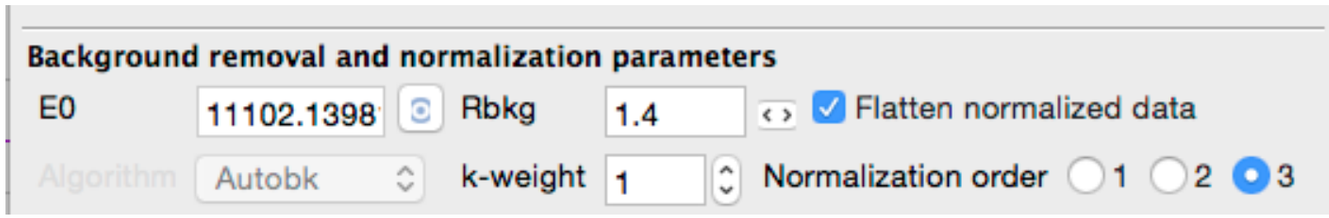


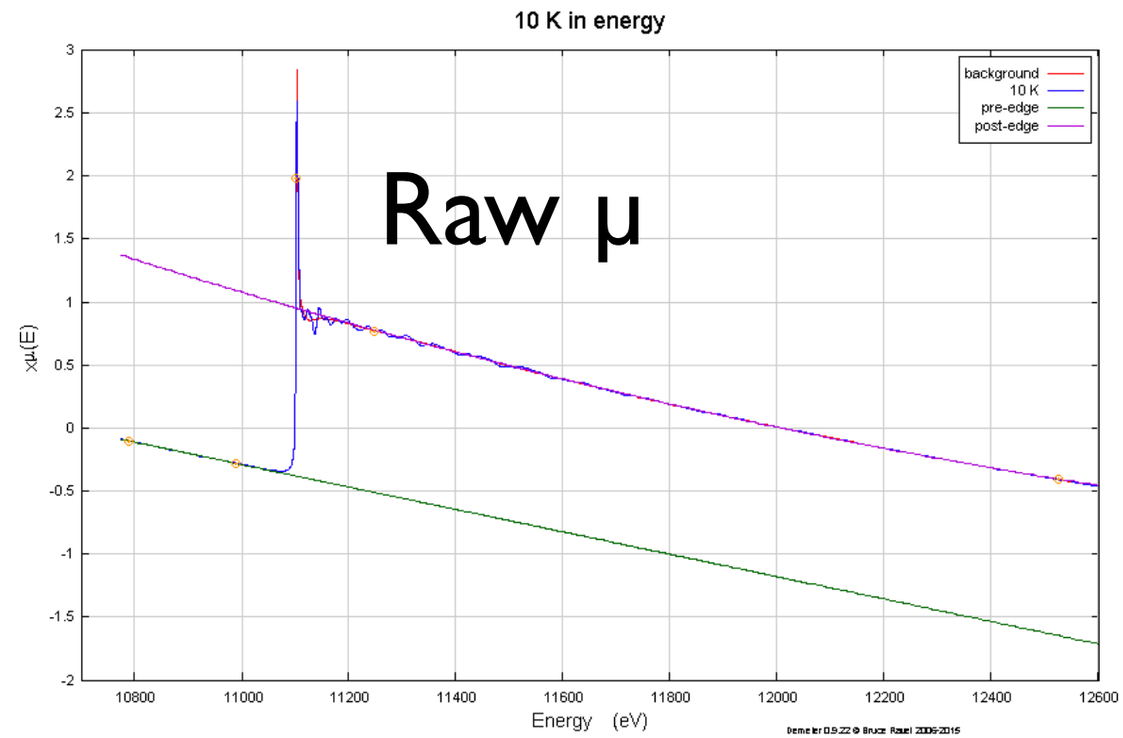
- Artemis is the Greek goddess of wisdom
- Read in 200K GeTe data taken at Ge K-edge
  - with plugin can read SPring-8 or KEK data directly
  - Fit linear pre-edge line to pre-edge region and polynomial spline to Normalization range
  - Subtract to get χ

Athena


10 K in energy
background
10 K
pre-edge
post-edge
Edge E0
Normalization Range
pre-edge
markers
xμ(E)
Energy (eV)
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
10800
11000
11200
11400
11600
11800
12000
12200
12400
12600

Edge Step Normalization

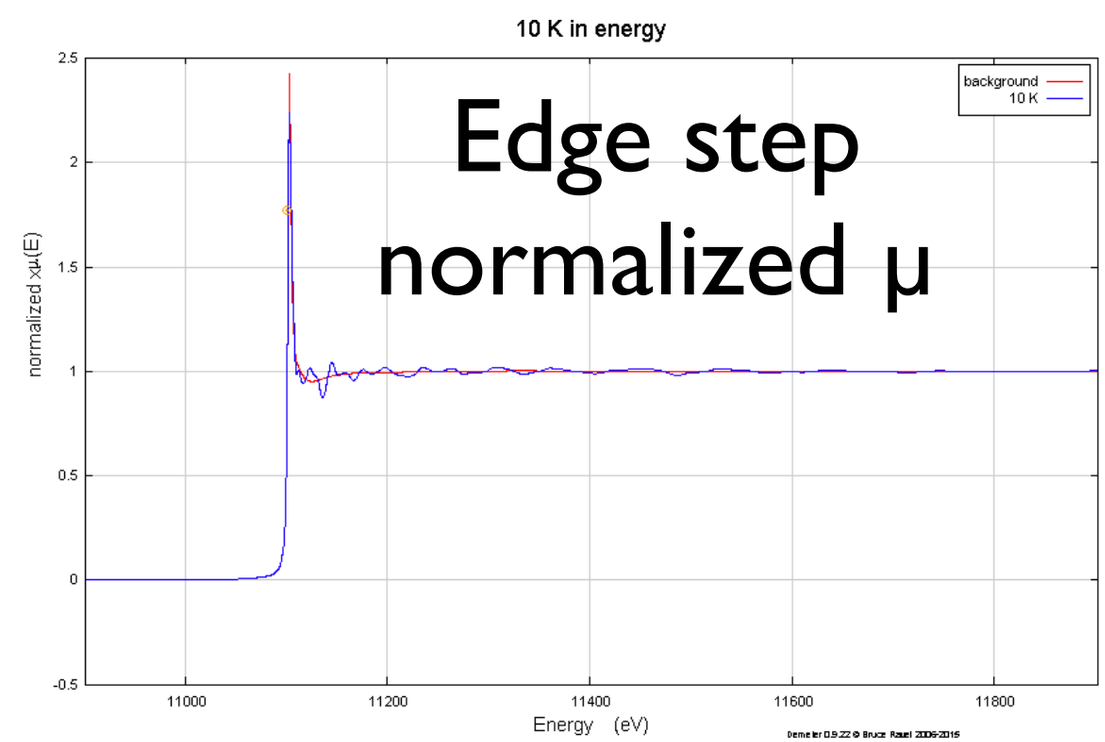




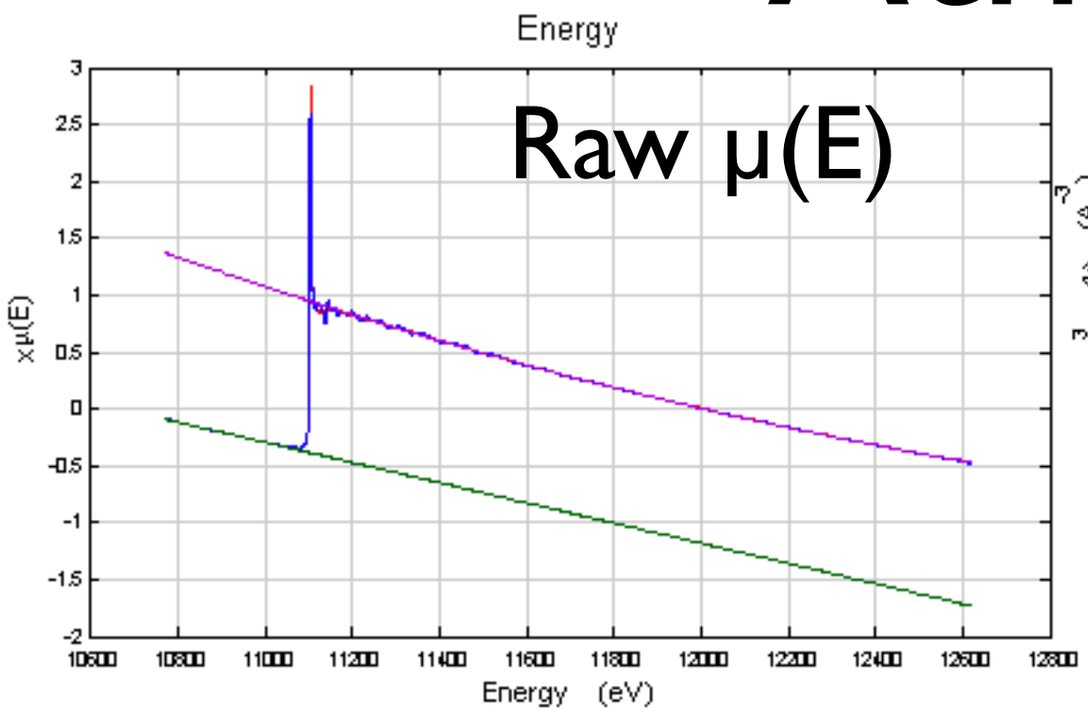
- Use a spline function with no real space contributions above 1.4 Å
- The E_0 value will be used to determine to zero of k

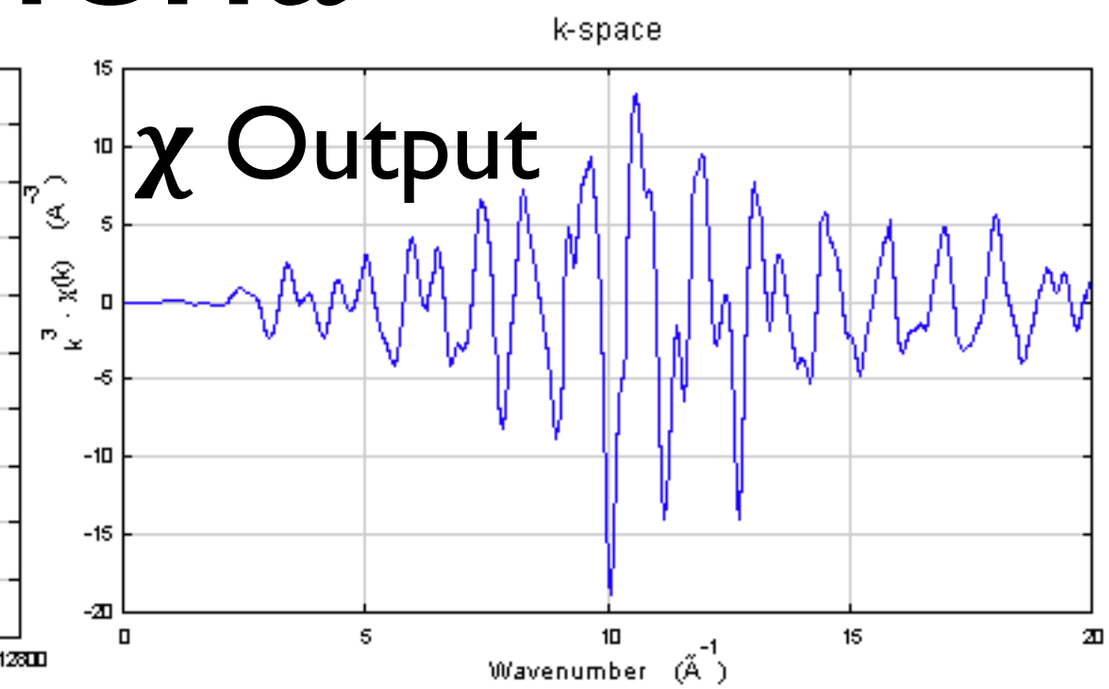
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} = \sqrt{0.262(E - E_0)}$$

- Subtract off spline to generate χ
- Save χ in a file for processing with athena

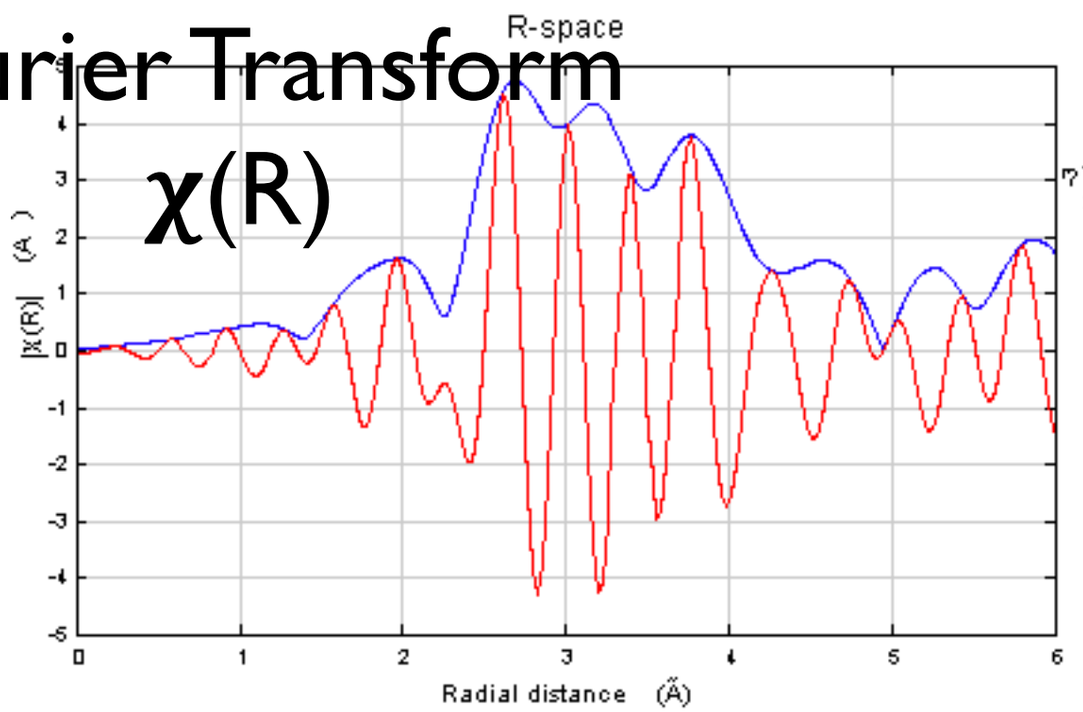


Athena

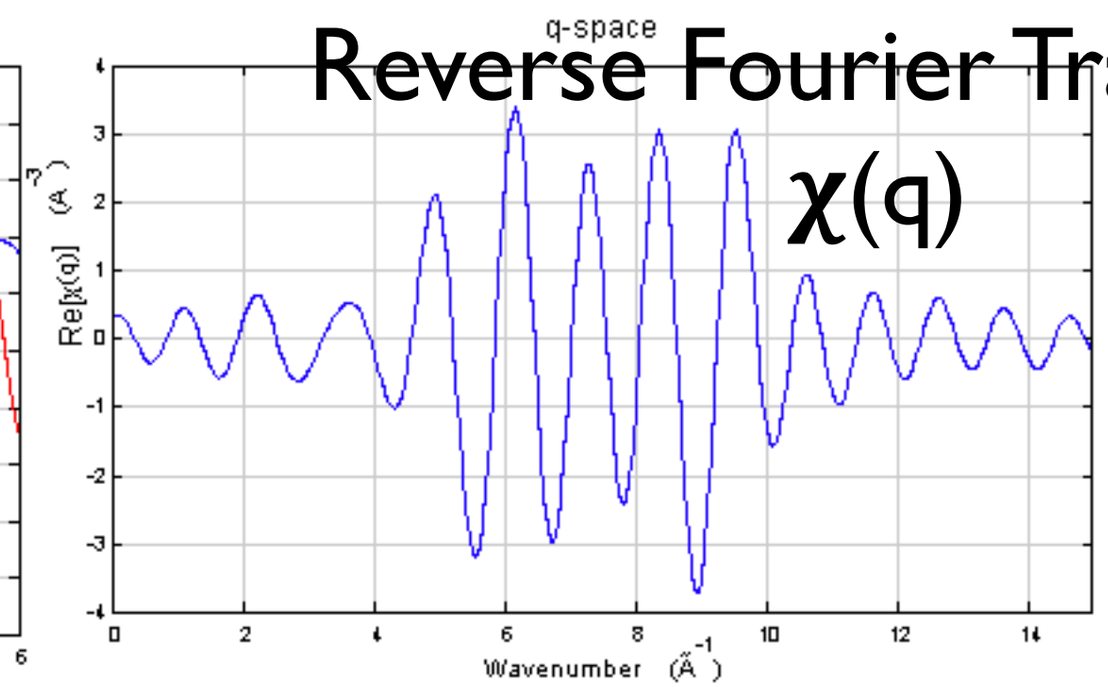




Fourier Transform



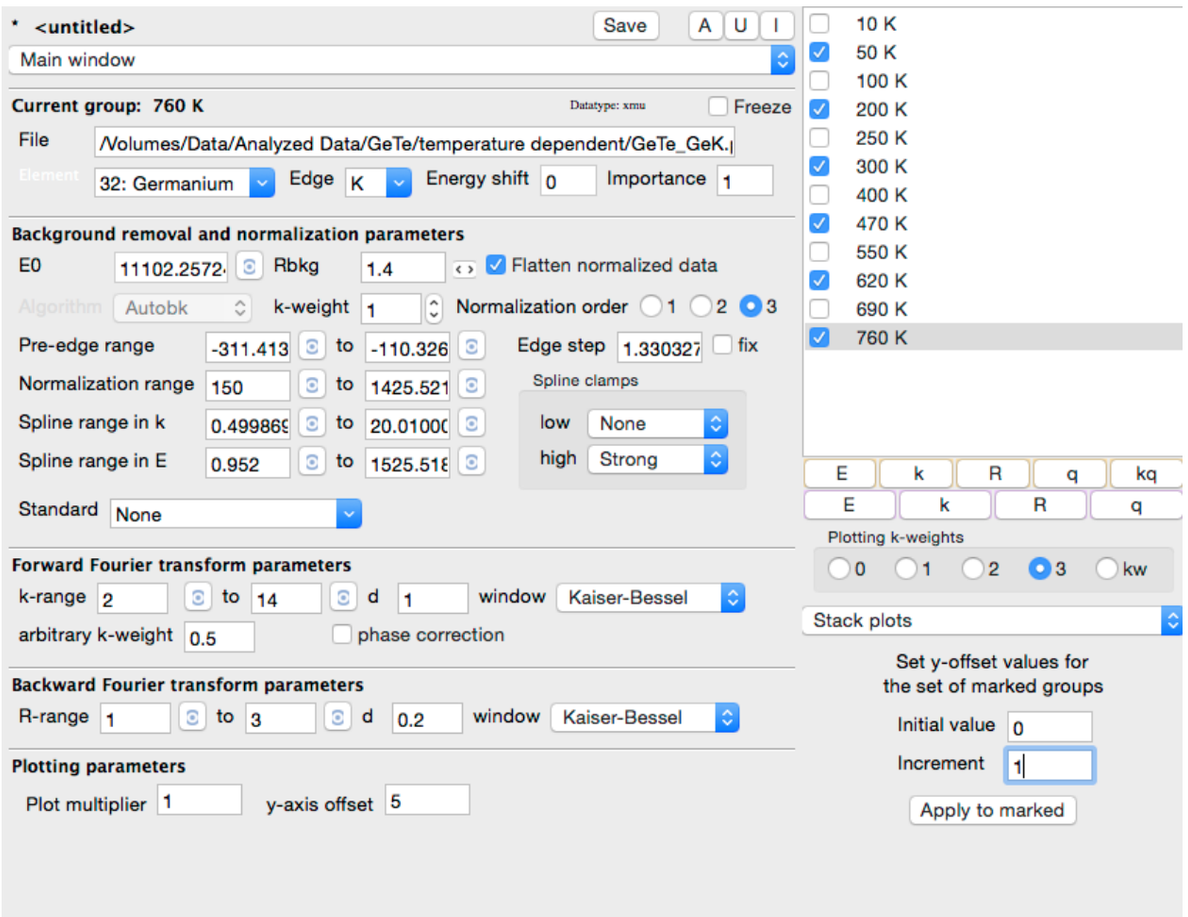
Reverse Fourier Transfo

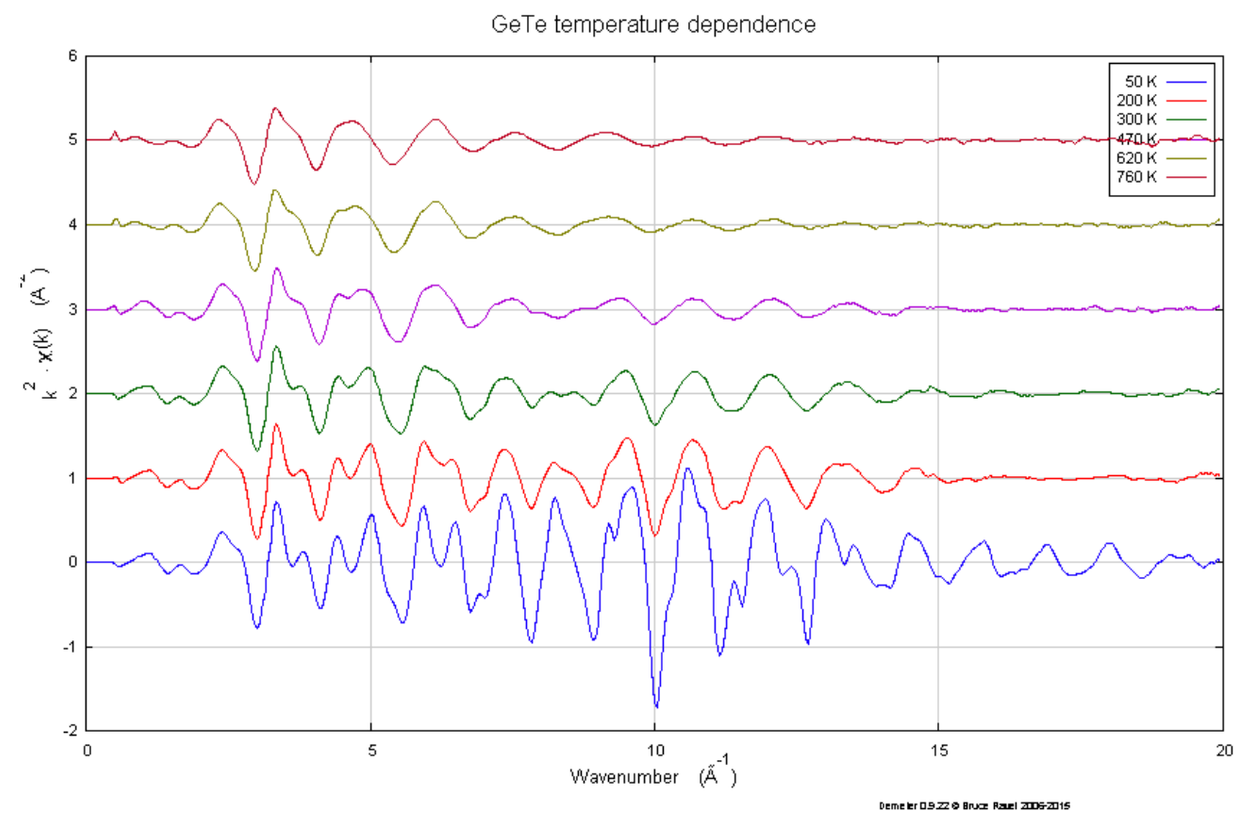


Athena

- Many bells and whistles to Athena
  - deglitching
  - linear component analysis (XANES)
  - principle component analysis (XANES)
  - self absorption corrections (fluorescence)
  - multi-electron effects removal
  - calculate differences between spectra
  - show many spectra and work in groups
  - and many more features …

Multiple Data Sets



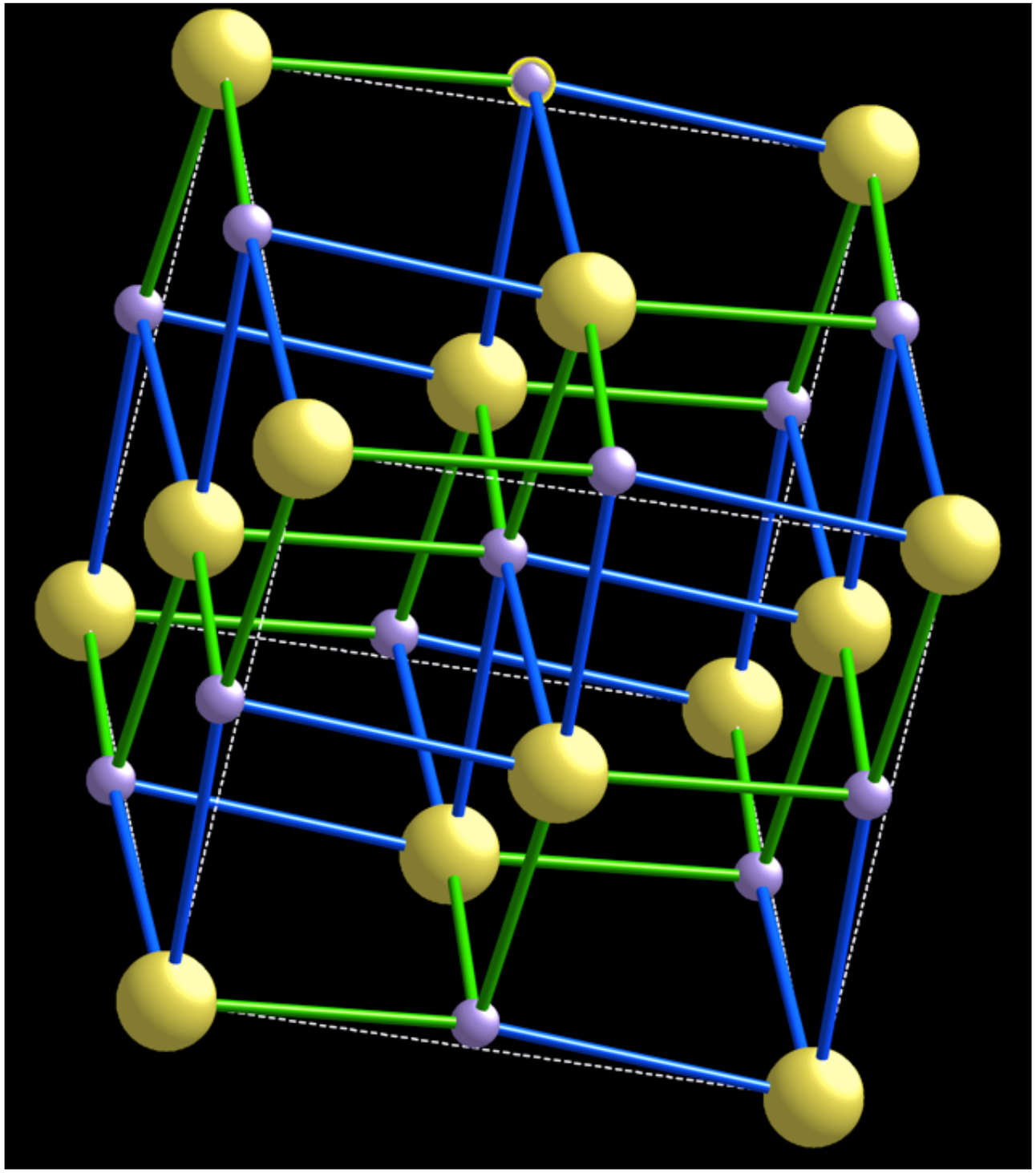


- Analyze multiple datasets to see
  - experimental trends with external variable, e.g. T
  - compare and adjust Athena processing parameters

GeTe Structure

The rhombohedral structure can be more easily be visualized as a non-primitive face centered cubic cell

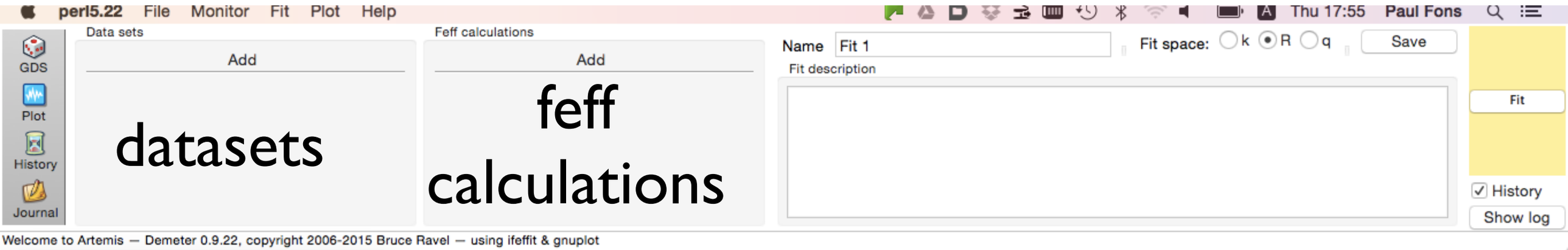
blue = 3.158 Å
green = 2.843 Å



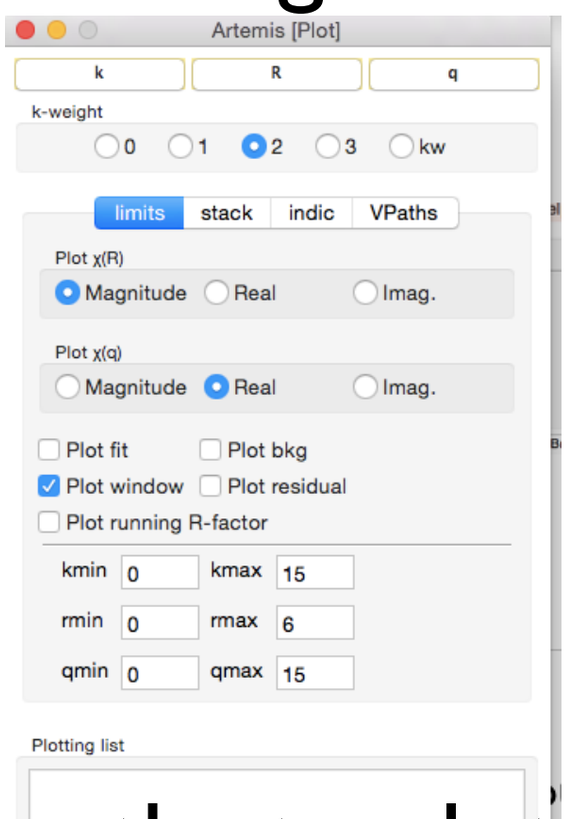
Artemis

- Artemis is the Greek goddess of the hunt
- Use for fitting against theoretical (feff) standards
- We will read in the 200K background subtracted GeTe data from Athena
  - Fit using two feff models
    - GeTe polycrystalline matrix
    - Ge (small amount of second phase)

Artemis Layout



Plotting Tools

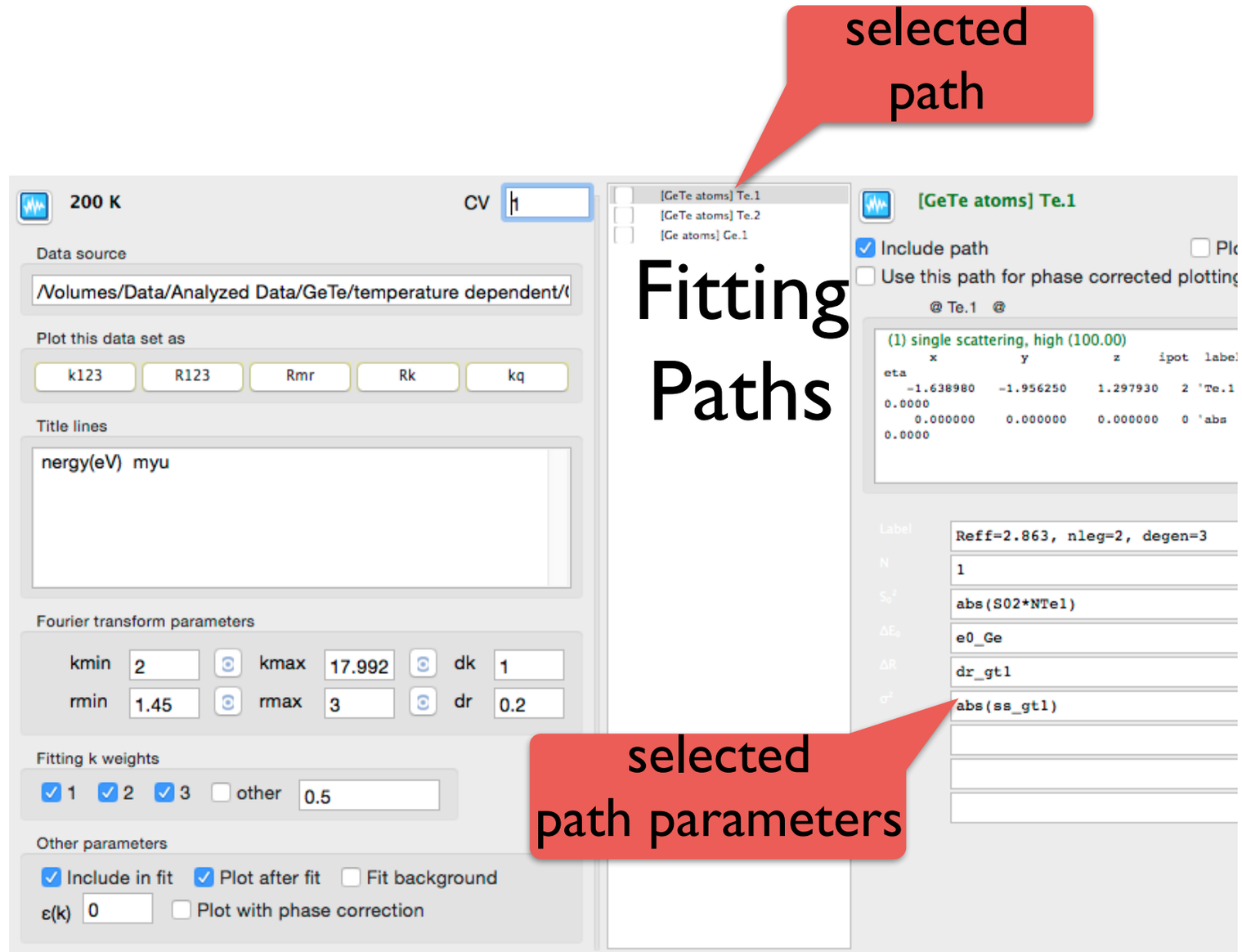


paths to plot

- Artemis can fit one or more datasets simultaneously (multiple edges, multiple temperatures, multiple pressures, etc.)
- older version of feff, feff6 (for EXAFS paths) built in - good for EXAFS but not for XANES
- fit EXAFS equation

Artemis

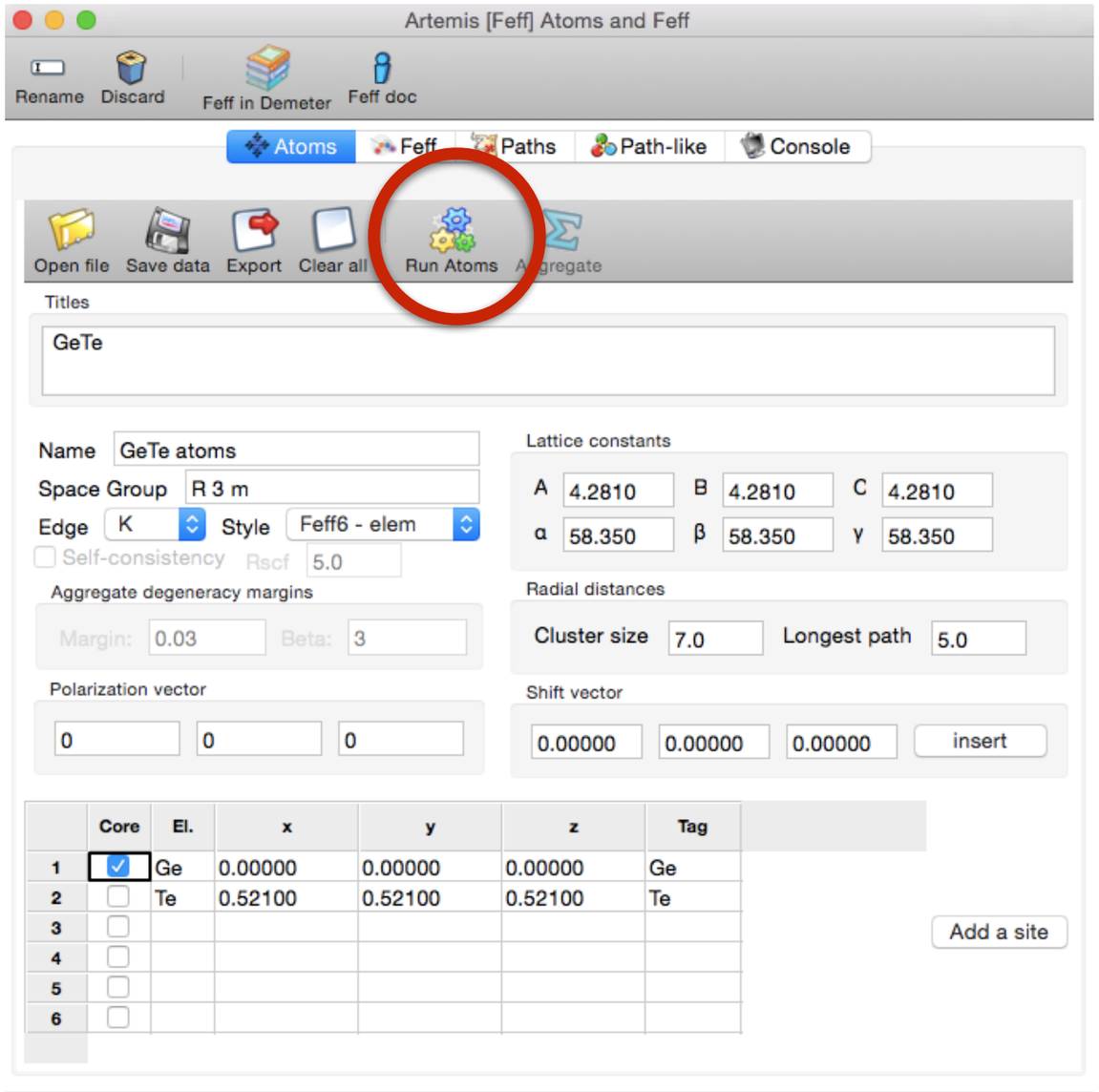
- Clicking on the Add button in the dataset box allows importing of data processed by Athena
  - the data is displayed
- It also cause a new fitting dialog box to open in which paths to be fitted can be added
- The fitting paths have to be generated by a feff calculation (next)



Each dataset has a corresponding Fit window

Artemis

- Clicking on the Add tab in the feff calculations brings up a dialog box for specifying the structure
- Running atoms generates a feff input file
  - make changes if necessary



Artemis

- Clicking on the Add tab in the feff calculations brings up a dialog box for specifying the structure
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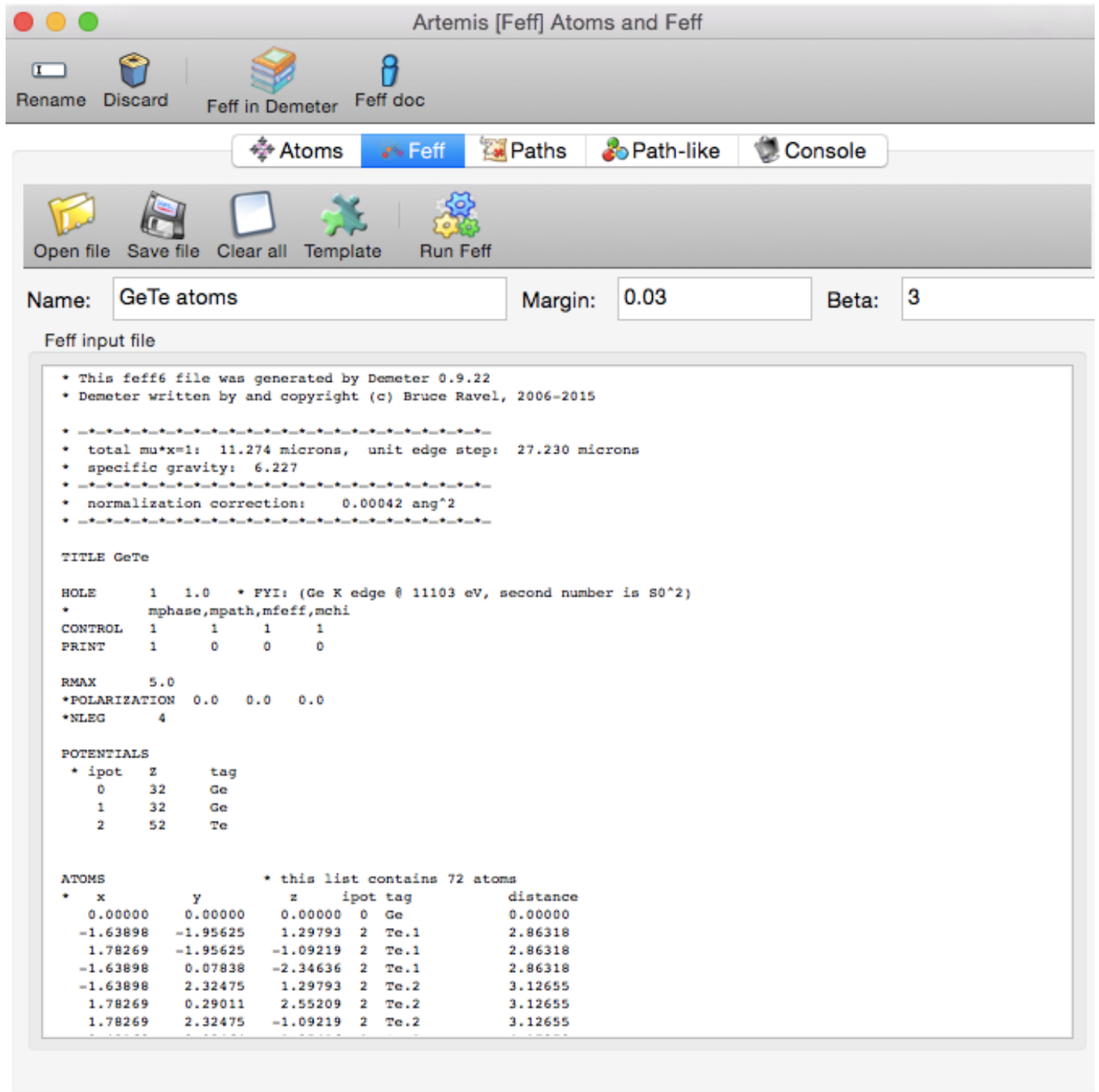
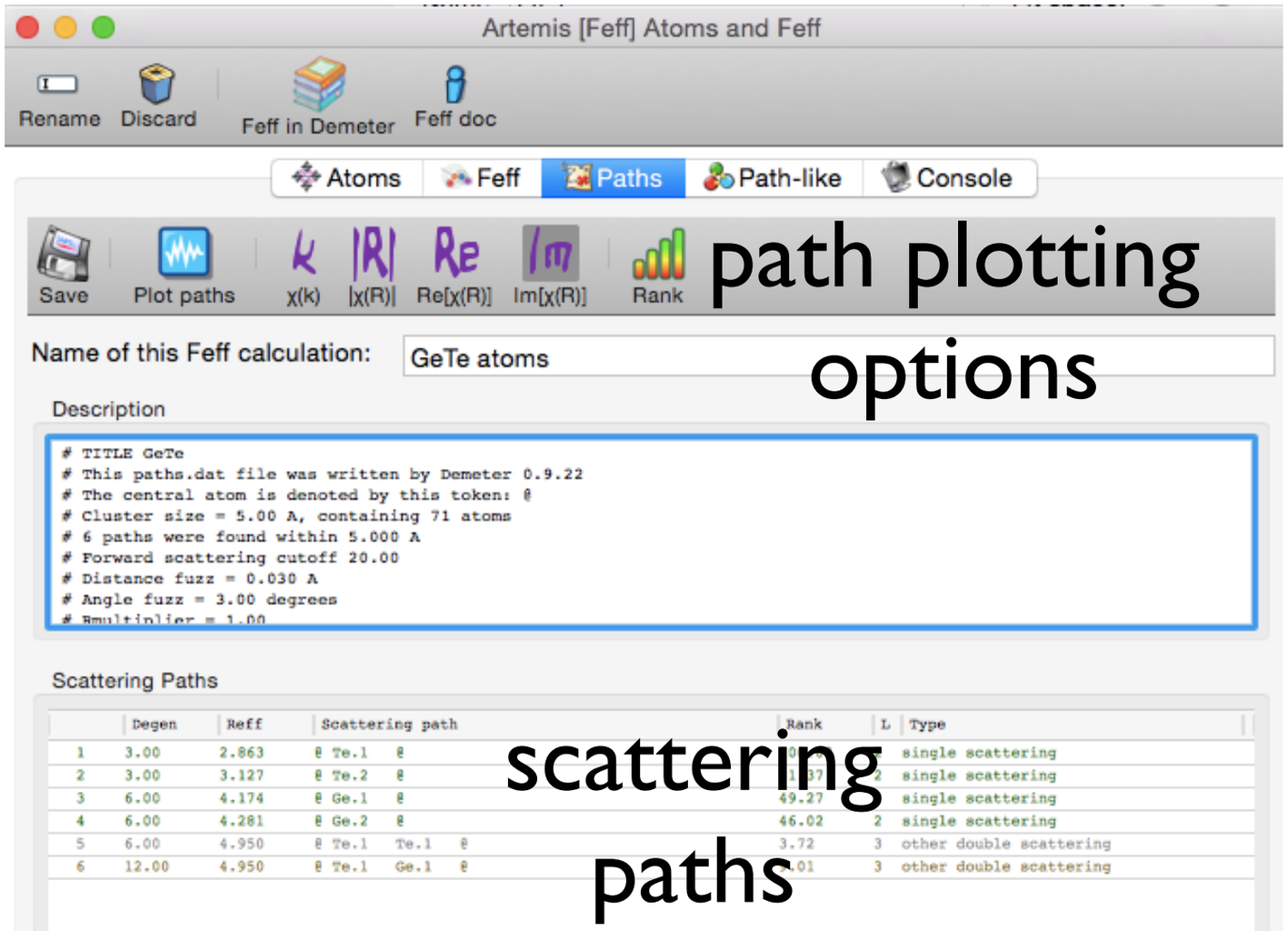
  - make changes if necessary



Artemis

- running the feff calculation
  - feff calculates important paths
  - Refine structure using these paths
  - Next we will specify parameters for each path from the EXAFS equation



$$\chi(k) = \sum_i \frac{N_i S_0^2 f_i(k)}{k R_i^2} \sin(2kR_i + \delta_i(k)) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)}$$

Artemis

- running the feff calculation
  - feff calculates important paths
  - Refine structure using these paths
  - Next we will specify parameters for each path from the EXAFS equation

Scattering Paths

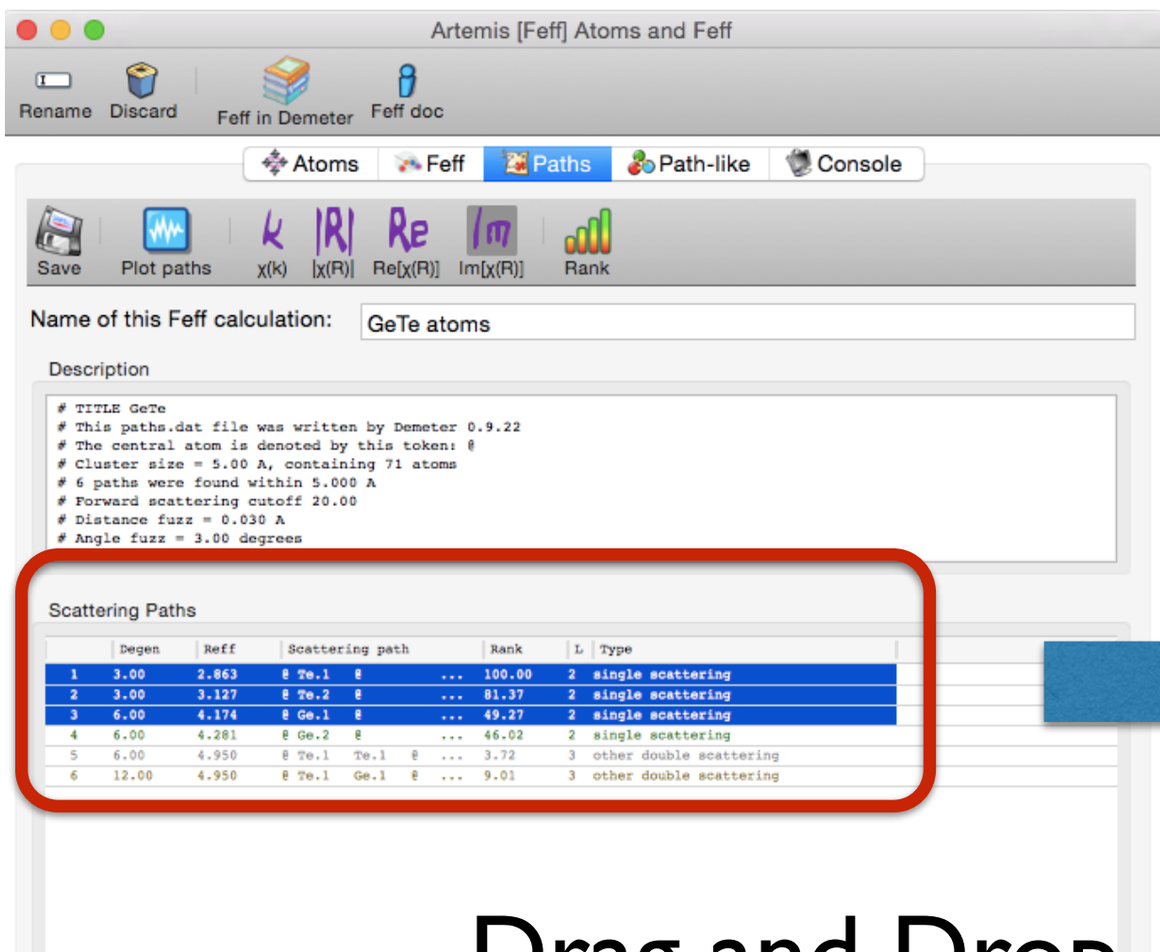
	Degen	Reff	Scattering path				Rank	L	Type
1	3.00	2.863	@ Te.1	@		...	100.00	2	single scattering
2	3.00	3.127	@ Te.2	@		...	81.37	2	single scattering
3	6.00	4.174	@ Ge.1	@		...	49.27	2	single scattering
4	6.00	4.281	@ Ge.2	@		...	46.02	2	single scattering
5	6.00	4.950	@ Te.1	Te.1	@	...	3.72	3	other double scattering
6	12.00	4.950	@ Te.1	Ge.1	@	...	9.01	3	other double scattering

$$\chi(k) = \sum_i \frac{N_i S_0^2 f_i(k)}{k R_i^2} \sin(2kR_i + \delta_i(k)) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)}$$

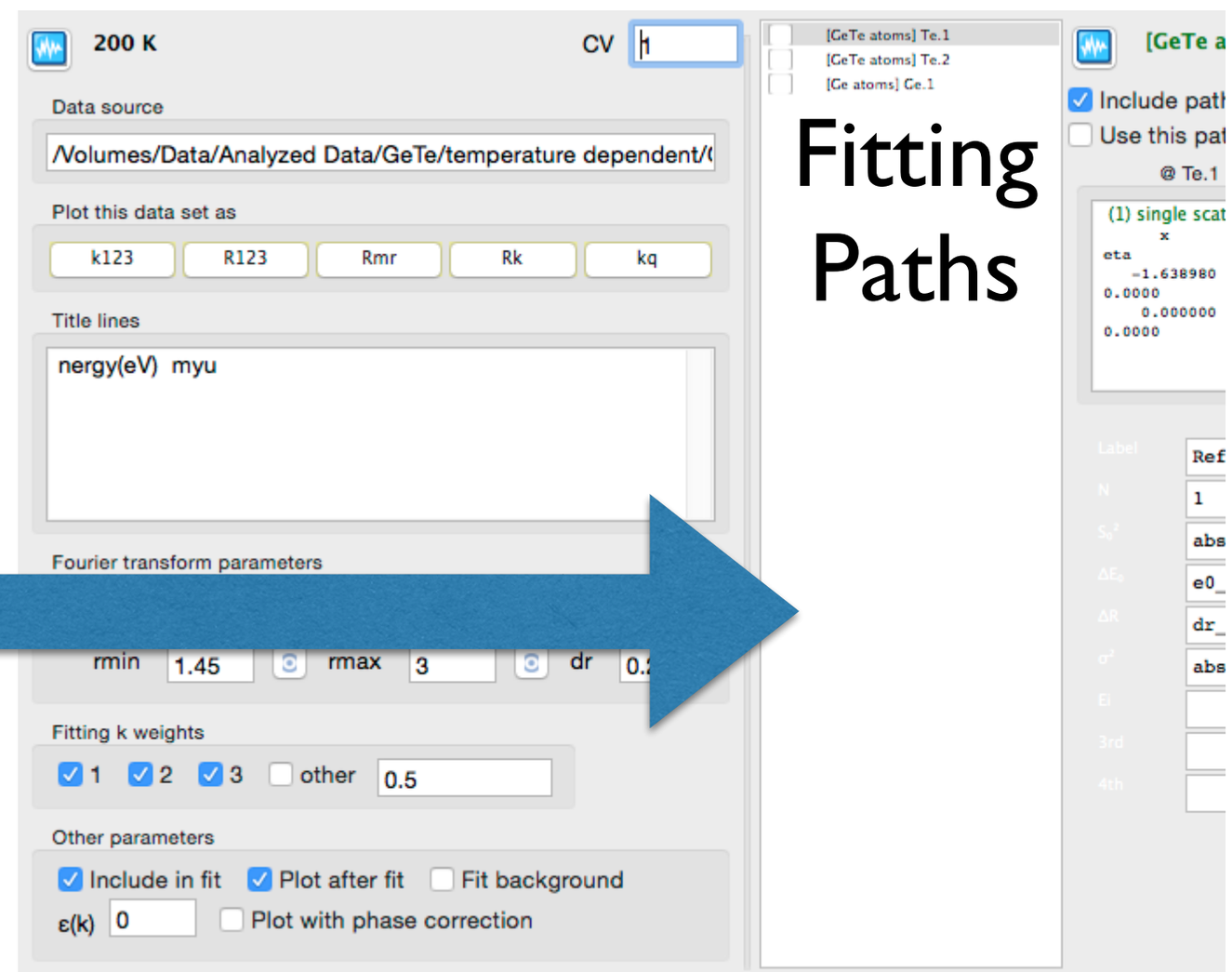
Artemis: Fitting paths

feff result window

dataset window

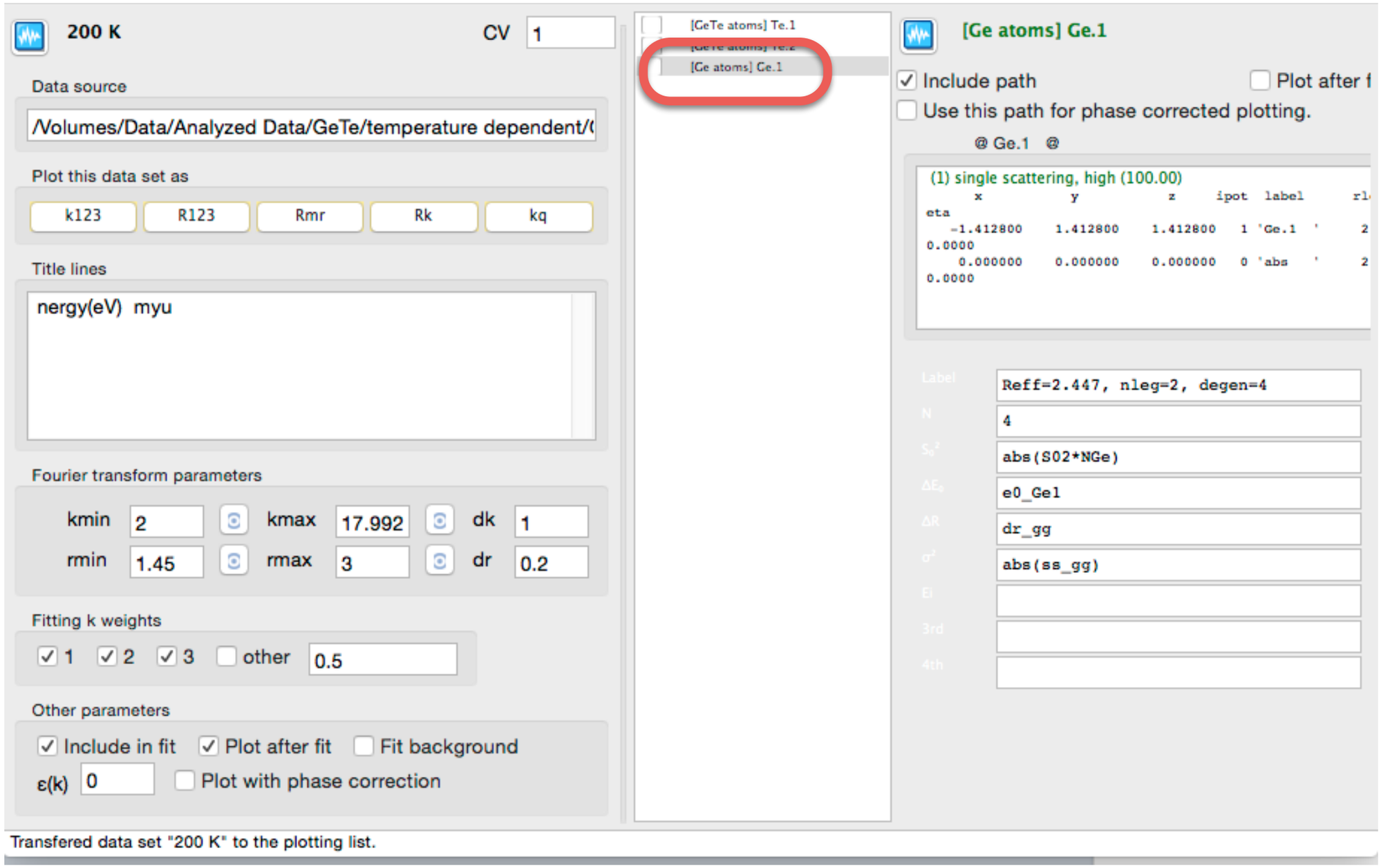


Drag and Drop



Fitting Paths

Artemis: FEFF calculations

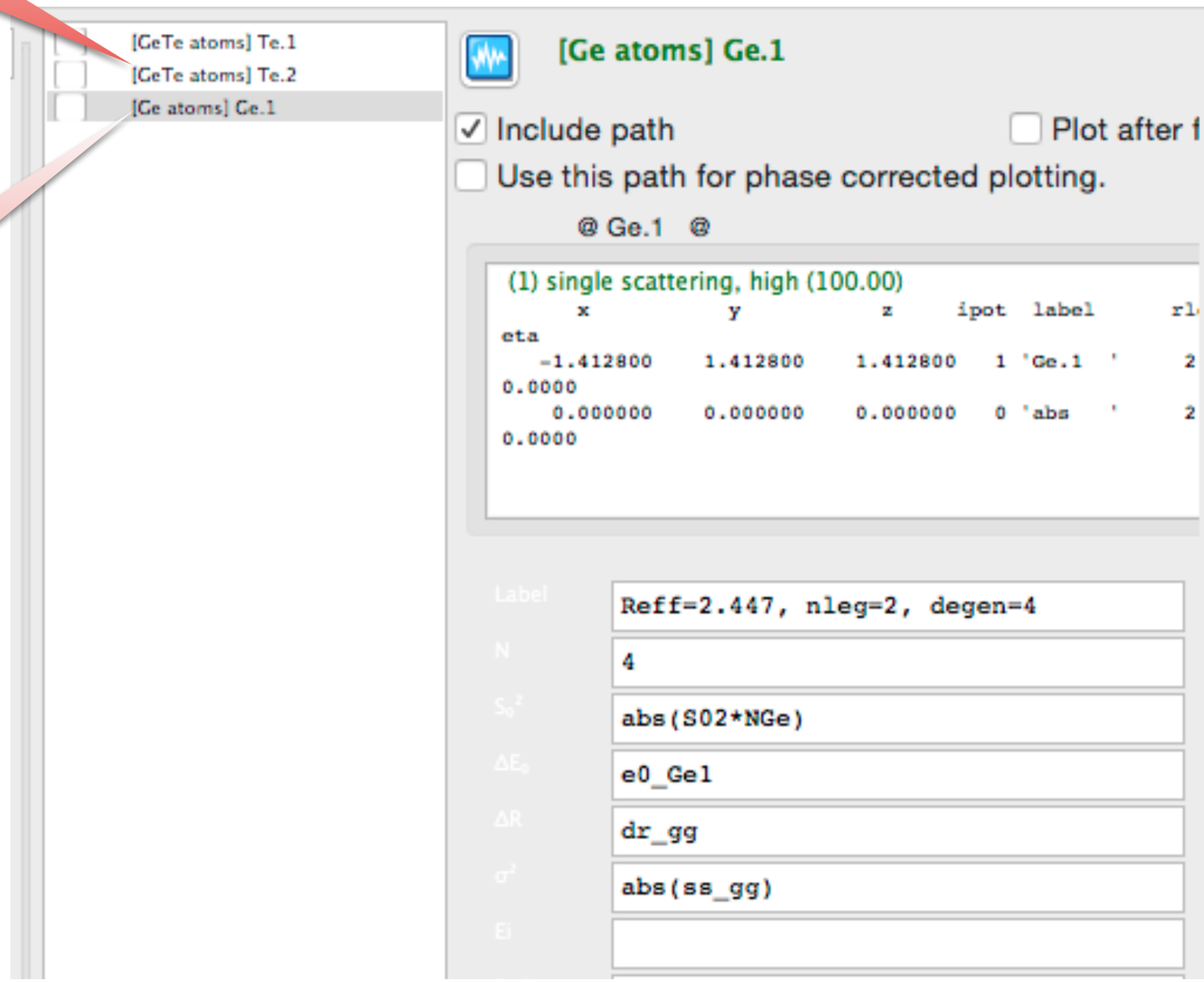


- In this case, we need a second model for Ge precipitates

Artemis: FEFF calculations

GeTe model

Ge model



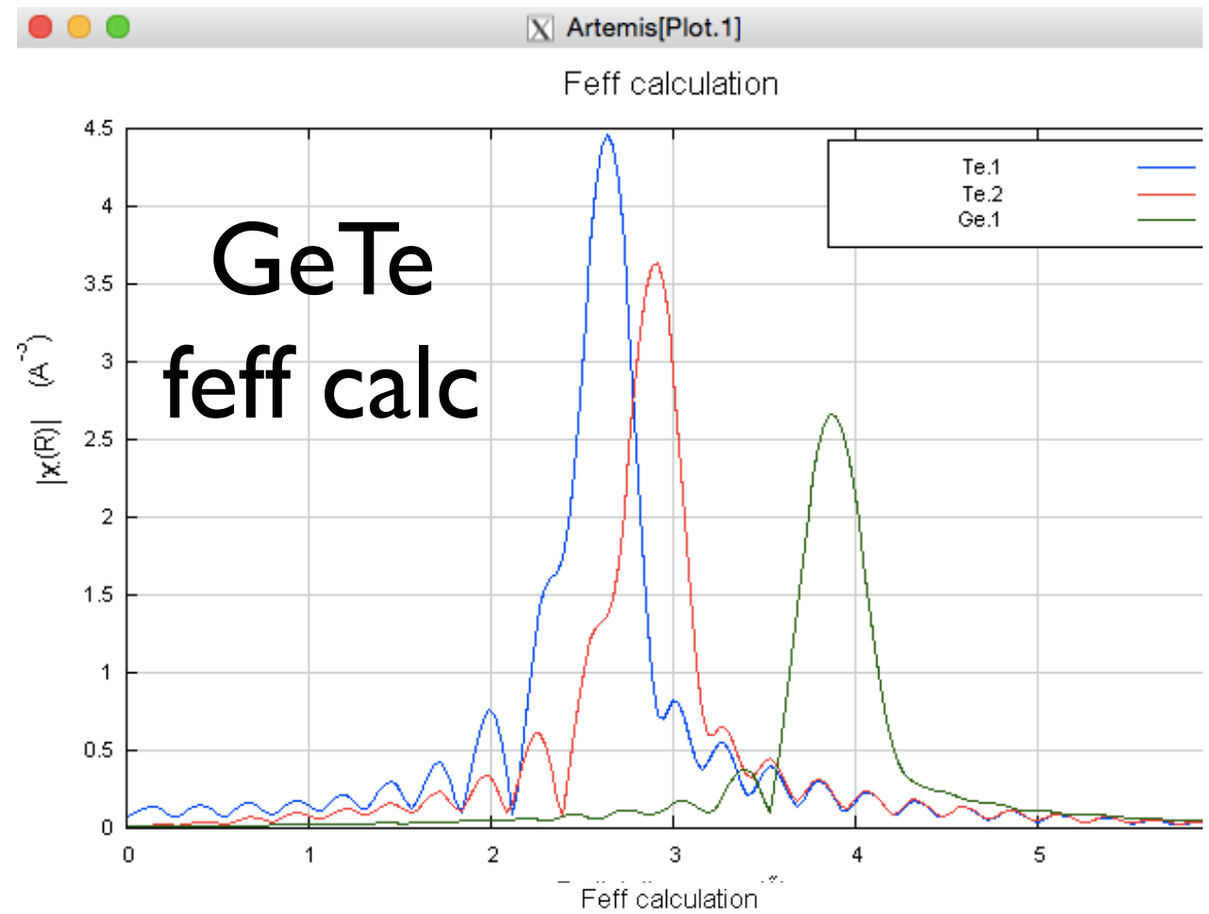
- In total we have three paths in our model:
  - 2 from GeTe
  - 1 from Ge

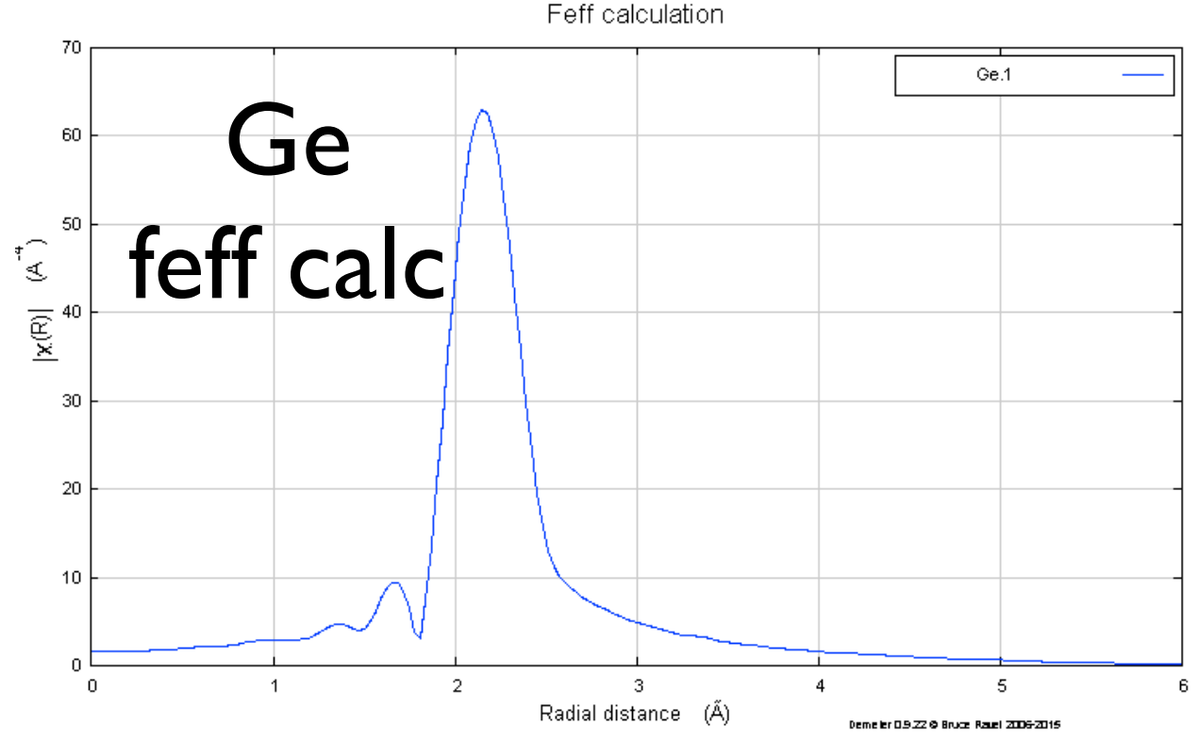
Artemis Fitting Paths

- In our example we have
  - carried out two feff calculations
    - GeTe
      - use the two NN paths from this
    - Ge
      - use the NN path from this
- Next step is to set up the fitting expressions

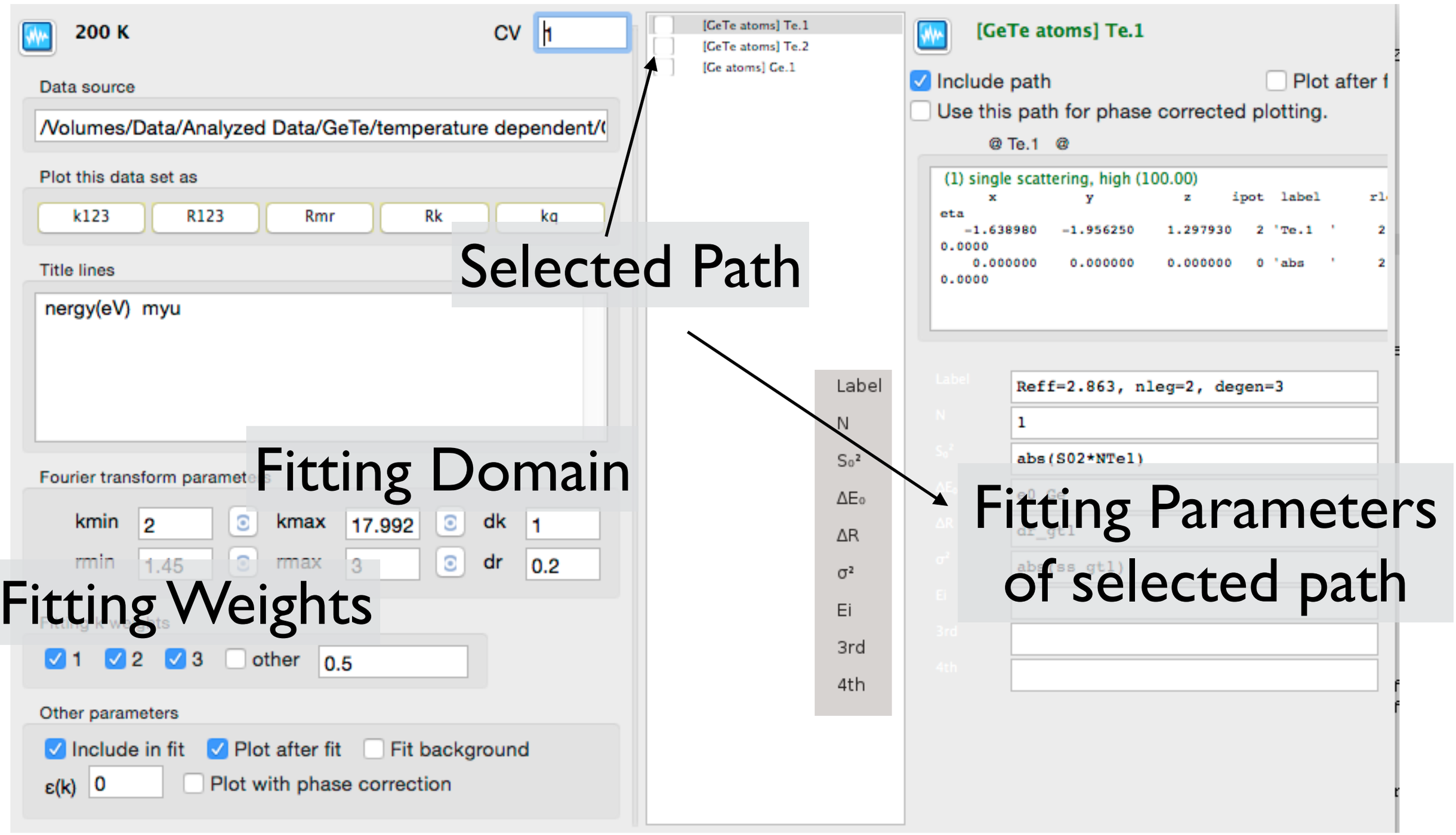
Artemis: path visualization

- We can for example plot the magnitude of first three paths for GeTe in real space using the plotting controls
- Note the phase shift results in the path lengths being smaller than in the actual structure
- We can do the same thing for the Ge feff model

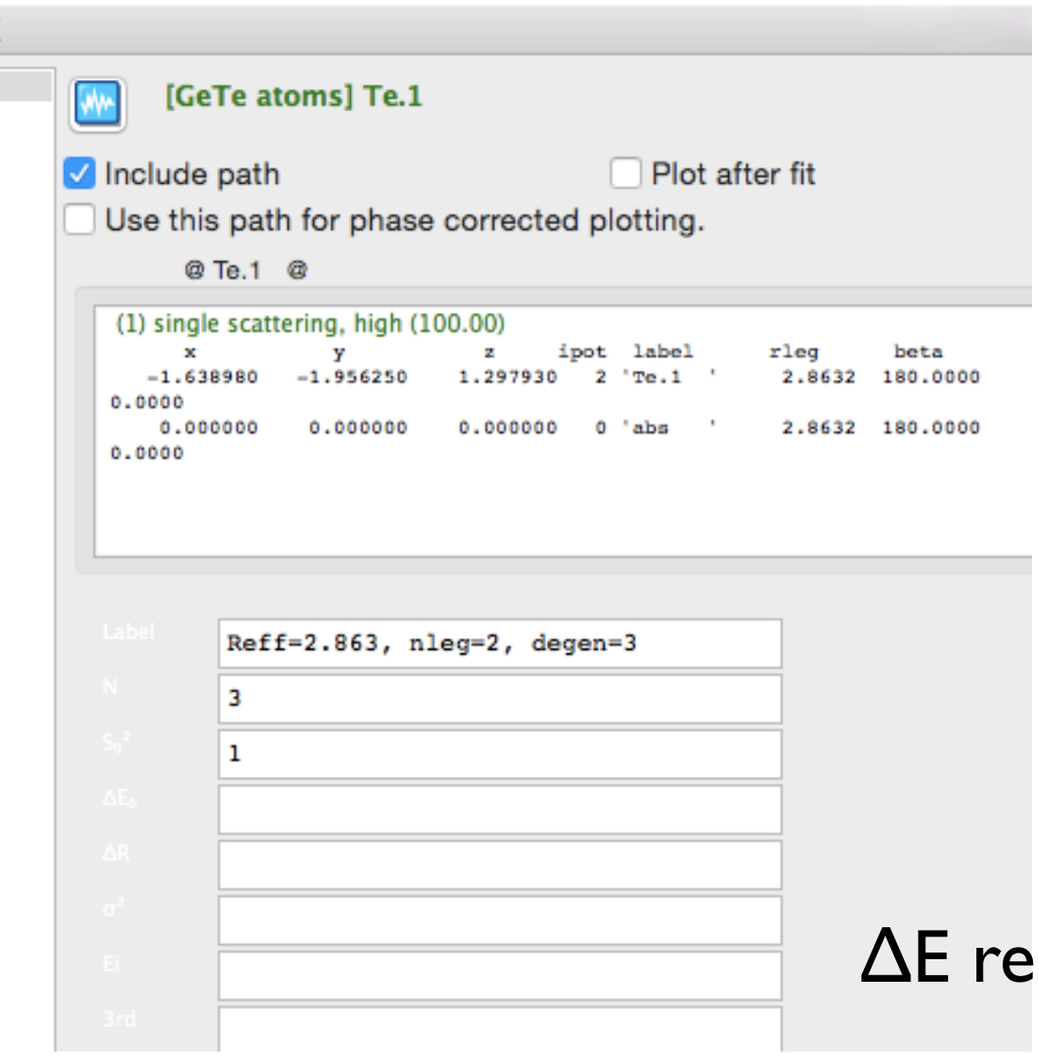


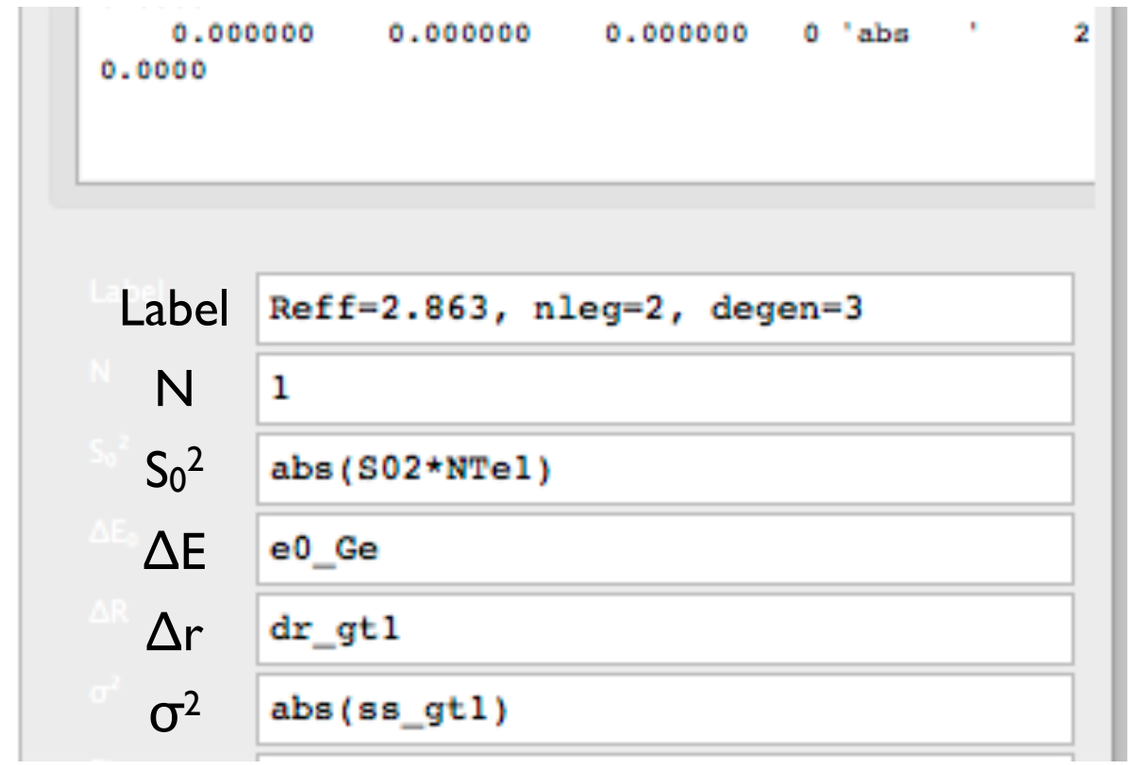


Artemis: Fitting Parameters



Fitting parameters





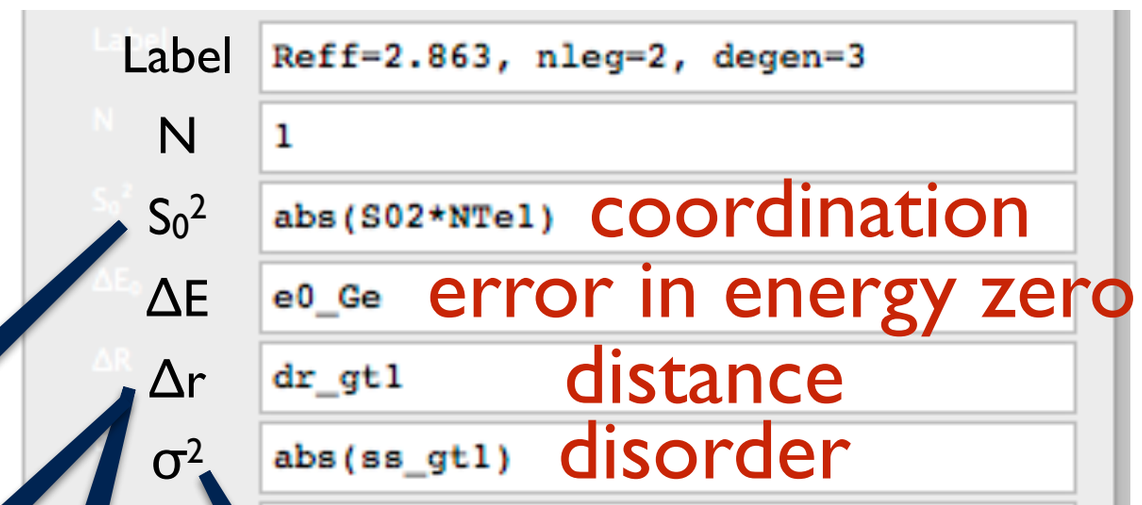
ΔE represents diff between energy zero of feff and expt

$$\chi(k) = \sum_i \frac{N_i S_0^2 f_i(k)}{k R_i^2} \sin(2kR_i + \delta_i(k)) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)}$$

$$R_i = R_0 + \Delta R \qquad k^2 = \frac{2m_e(E - E_0)}{\hbar}$$

Define expressions for paths

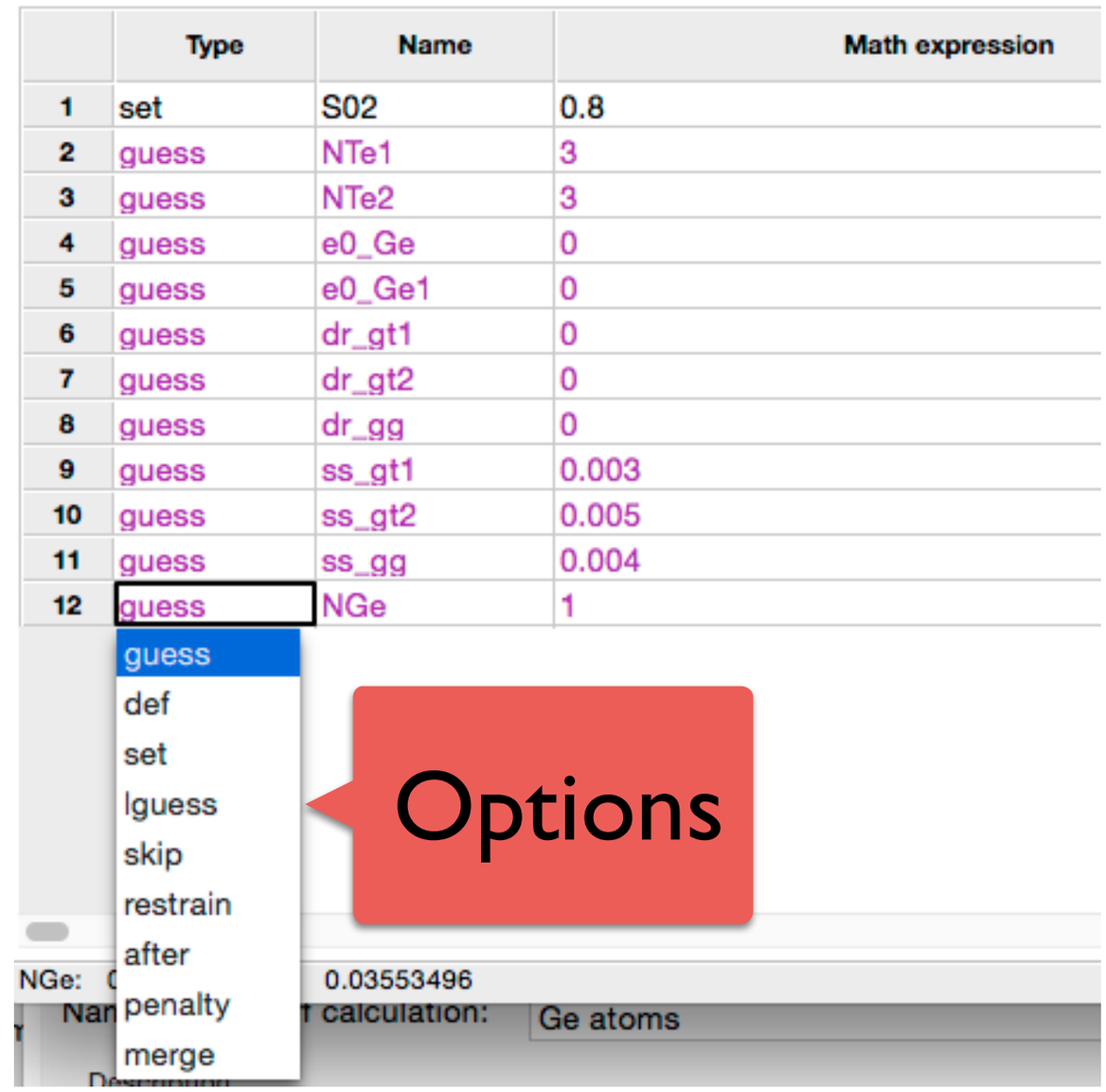
- For each path
  - we define math expressions for each EXAFS equation variable
  - These variables can be then be varied either individual or by mathematical expressions containing multiple variables



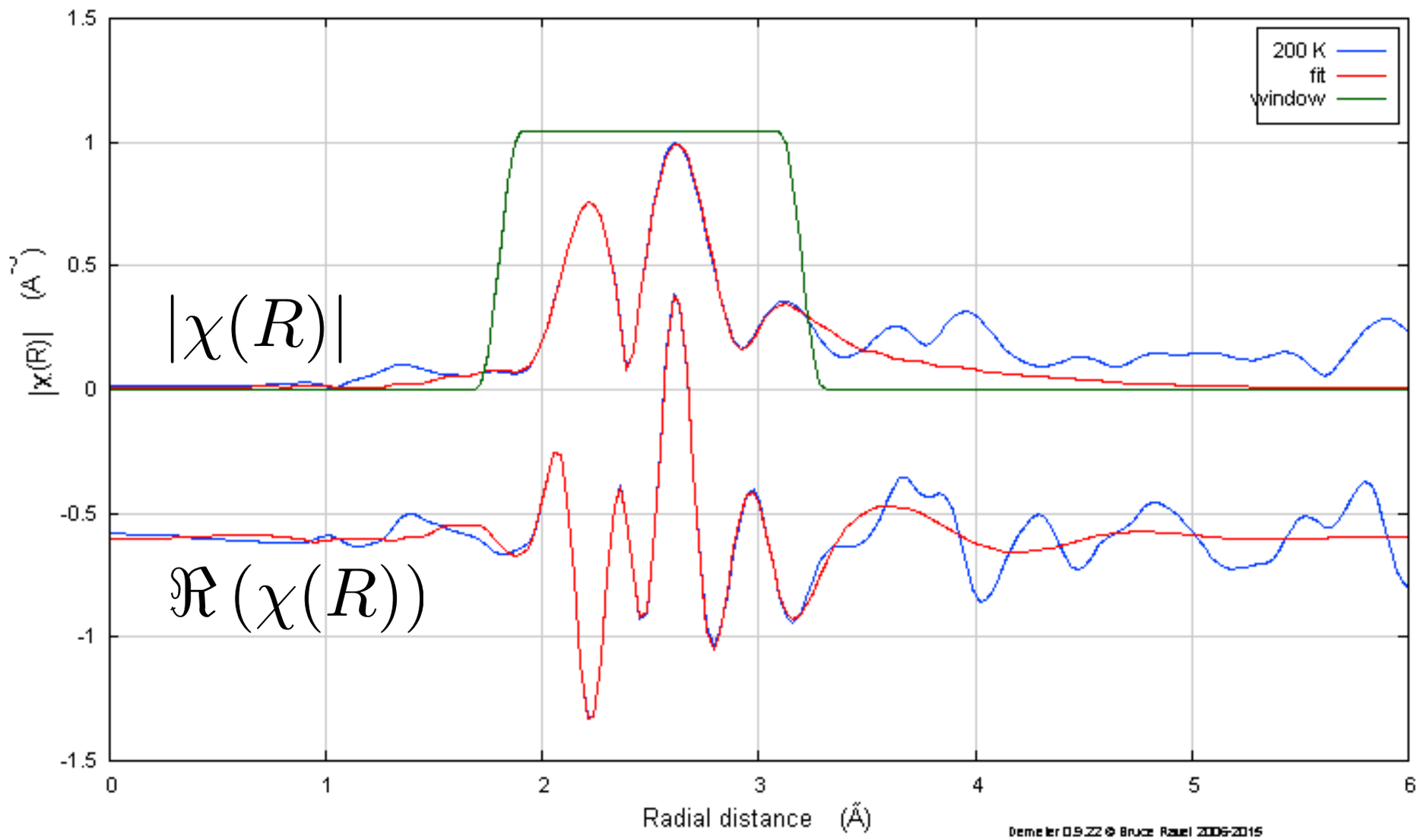
$$\chi(k) = \sum_i \frac{N_i S_0^2 f_i(k)}{k R_i^2} \sin(2kR_i + \delta_i(k)) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)}$$

GDS panel

- The GDS (guess, define, set) panel allows
  - defining a guess to be varied
  - a bounds restraint
  - a penalty function
  - all entries can be potentially complicated algebraic expressions



Artemis: Fit result



- Fit in real space from 1.8 to 3.2 Å: r-factor = 0.00373
- Display the Real part of the complex function χ as well as the magnitude

Artemis: Summary

- We have fit a 200K GeTe EXAFS spectra out to 1st NN
- There are many different options we have not touched upon in the software suite due to time limitations
- Some additional things we could do
  - Temperature dependence (multiple data sets)
  - Fitting simultaneously at more than one edge
  - Including multiple scattering paths
  - many more

Resources

- Books
  - XAFS for Everyone by Scott Calvin, CRC Press 2013.
  - Introduction to XAFS: A Practical Guide to X-ray Absorption Fine Structure Spectroscopy by Grant Bunker, Cambridge 2010.
  - X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES (Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications) by D. C. Koningsberger and R. Prins, John Wiley and Sons 1988.
  - Elements of Modern X-ray Physics by Jens Als-Nielsen and Des McMorrow, 2nd Ed. Wiley 2011.
- Review Articles
- Theoretical approaches to x-ray absorption fine structure by J. J. Rehr and R. C. Albers, Rev. Mod. Phys. 72 (3) 621-654 (2000)
- Internet
  - http://www.xafs.org International XAFS Organization

    This site has links to tutorials by synchrotron organizations and other useful information including an online magazine. Membership is free.