XAFS
Training on data Analysis

1. XAFS data analysis software
2. **From XAS to XAFS: how to deal with the data**
3. Training: EXAFS data refinement
4. Training: Linear combination analysis of XANES

Contacts:

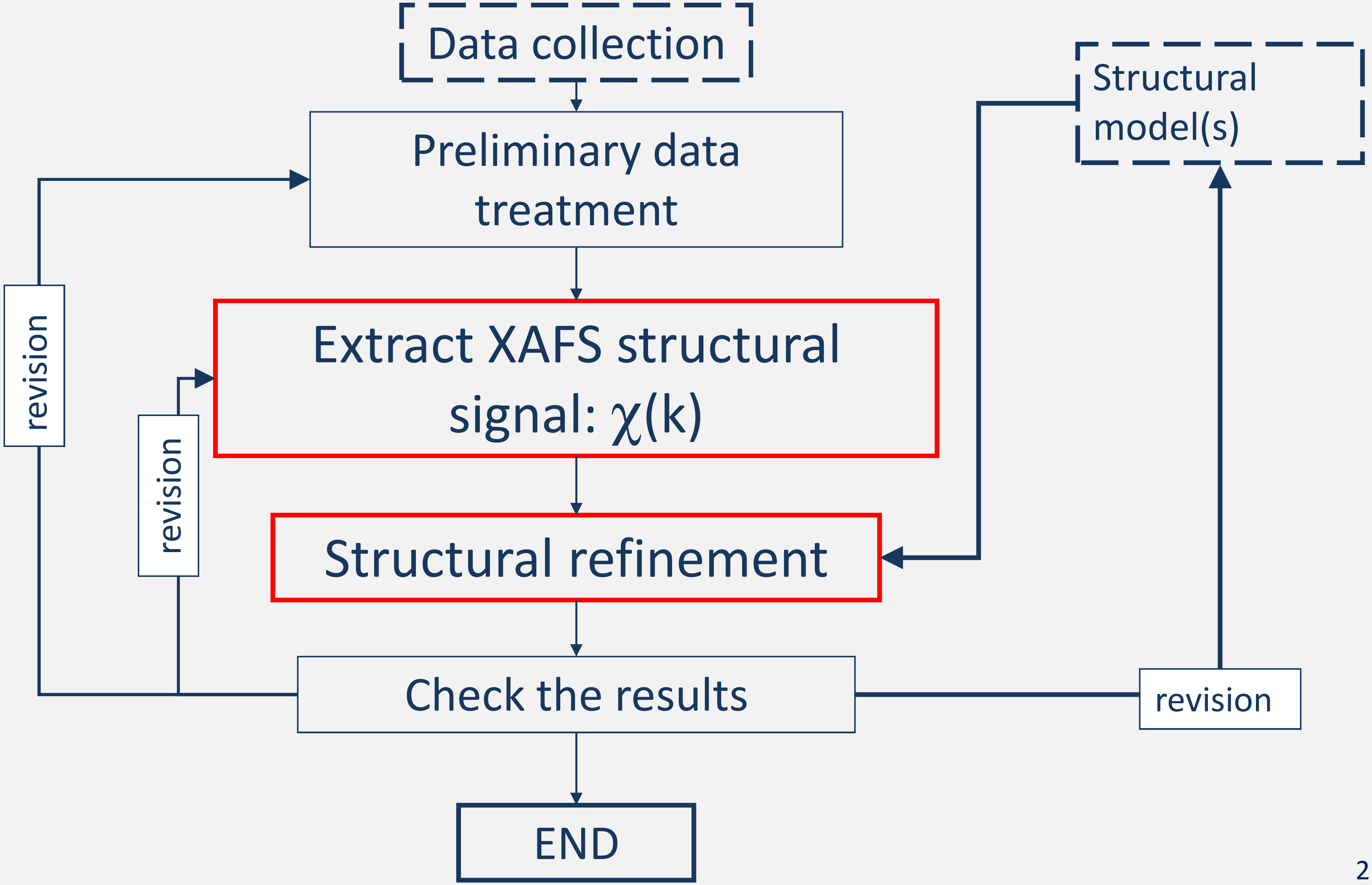
Prof. Carlo Meneghini

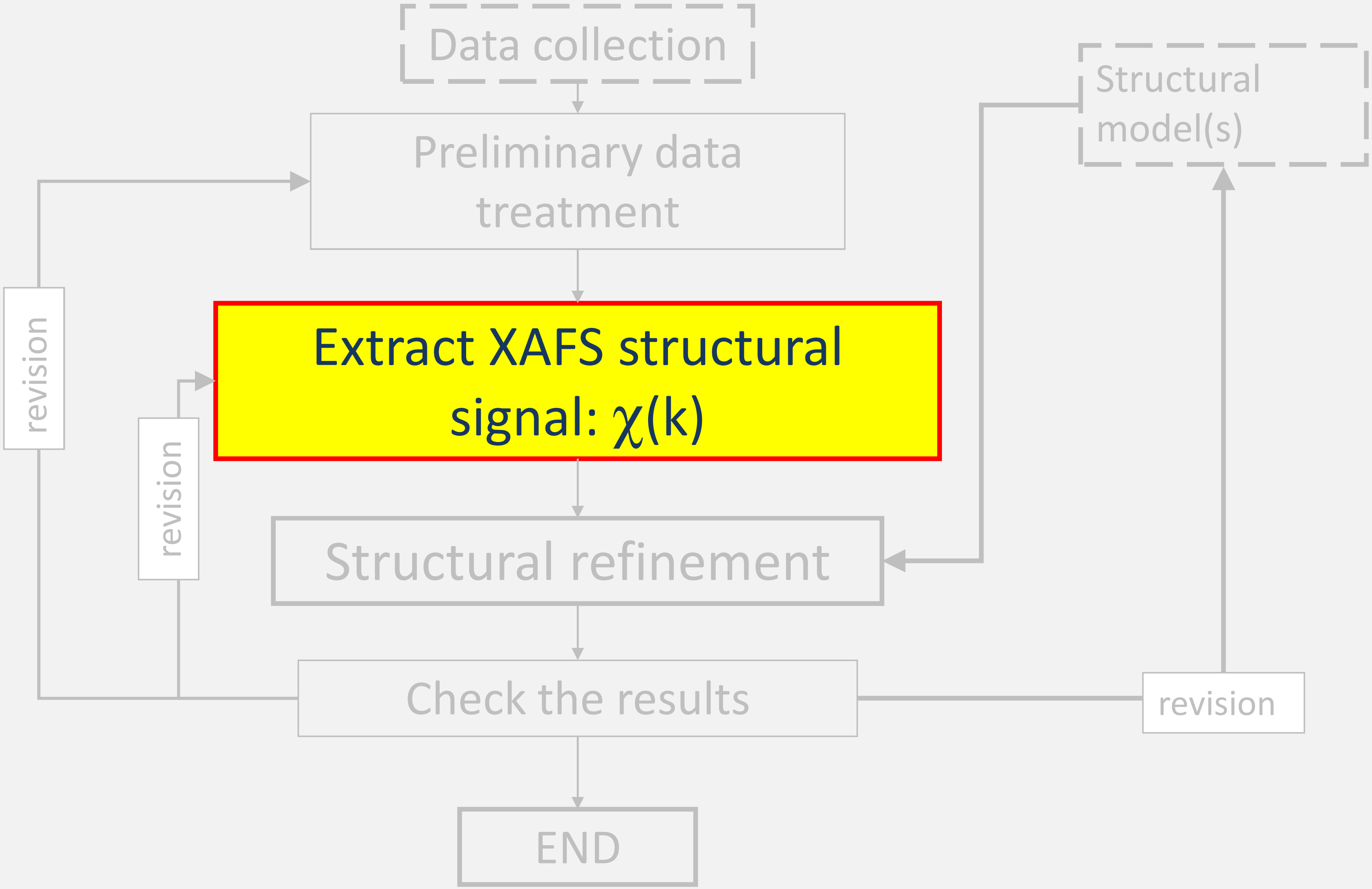
Dip. Di Scienze, Università Roma Tre, Roma

carlo.meneghini@uniroma3.it

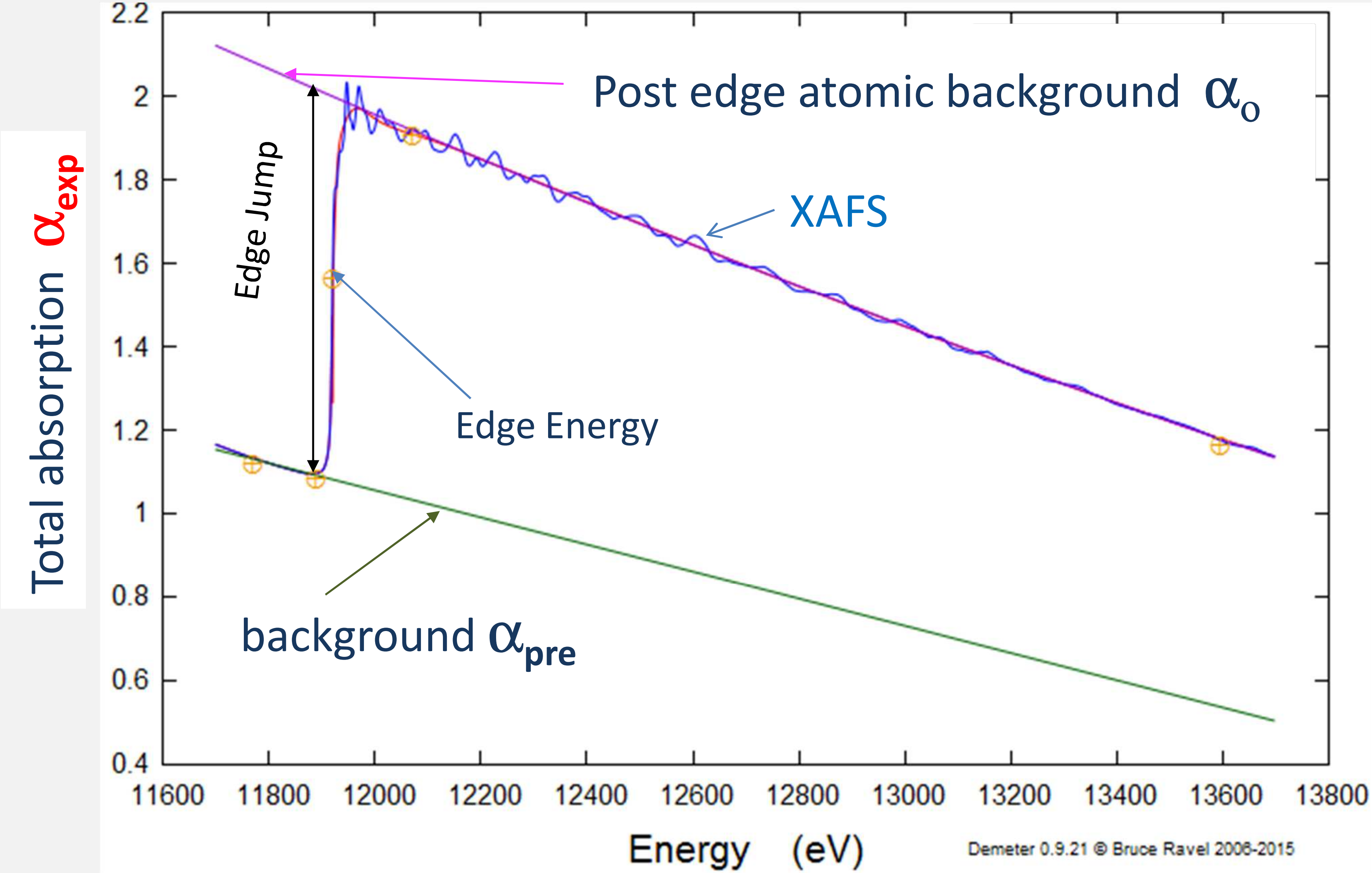
XIV School on Synchrotron Radiation:
Fundamentals, Methods and Applications
Muggia, Italy / 18-29 September 2017

flow-chart
from the experimental data to data fit

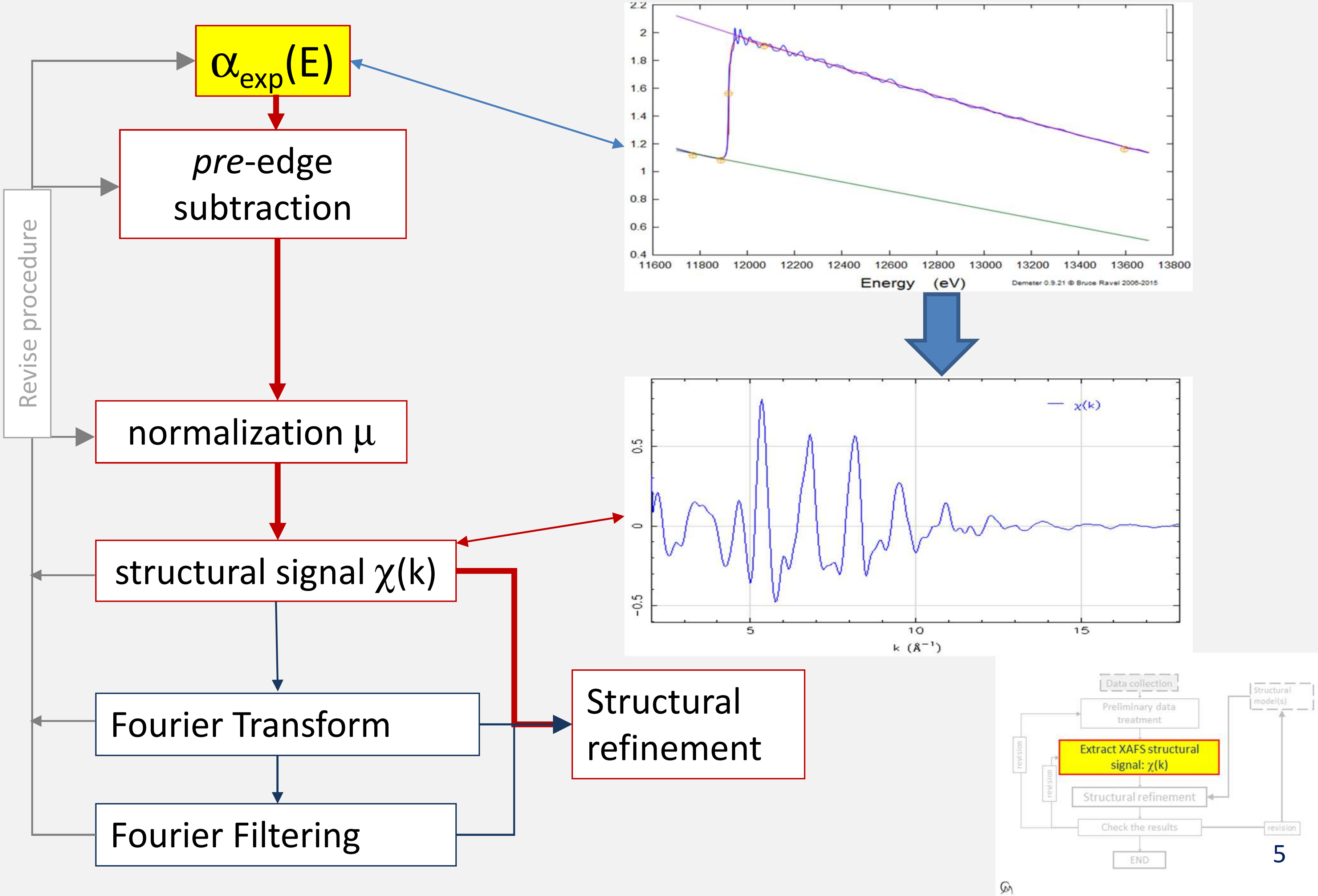



Data collection
Preliminary data treatment
Extract XAFS structural signal: χ(k)
Structural refinement
Check the results
END
Structural model(s)
revision
revision
revision

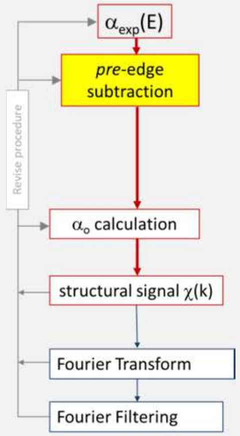
Characteristics of a XAS spectrum



How to get the normalized χ(k)



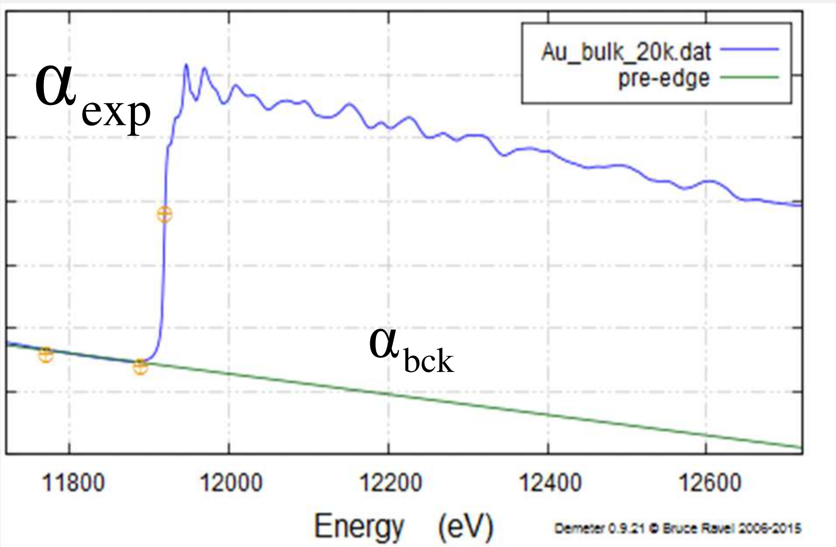
How to get the normalized $\chi(k)$



1. Remove pre-edge

$$\alpha_{exp} = \alpha_x + \alpha_{bck} = \mu_x t + \alpha_{bck}$$

$$\alpha_x = \mu_x t = \alpha_{exp} - \alpha_{bck}$$

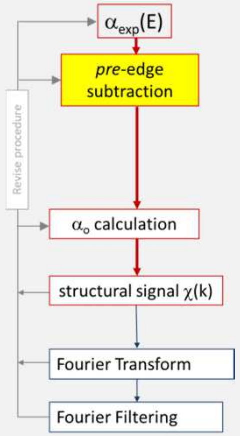


$\mu_x t$ is the absorption due to the edge we are working on

α_{bck} is the absorption due to **everything** except **$\mu_x t$**

Everything being: other absorption edges, air, sample holder, matrices, chamber windows, etc…

How to get the normalized $\chi(k)$



1. Remove pre-edge

$$\alpha_{exp} = \alpha_x + \alpha_{bck} = \mu_x t + \alpha_{bck}$$

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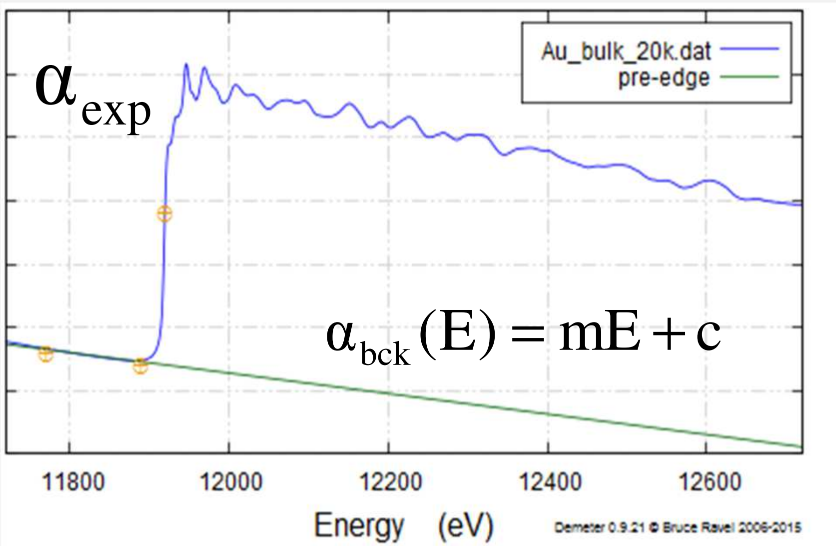
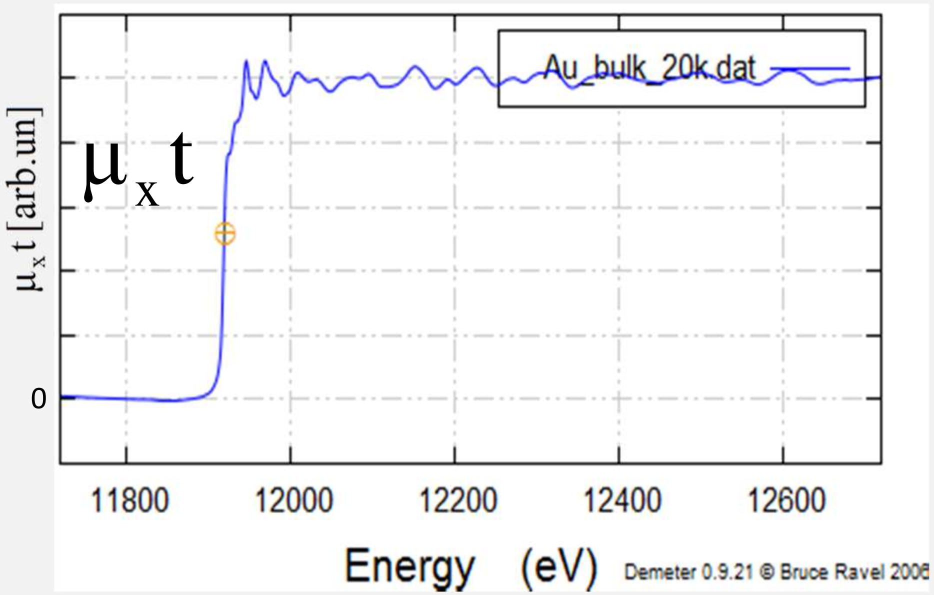
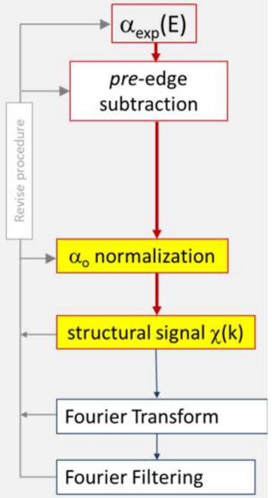




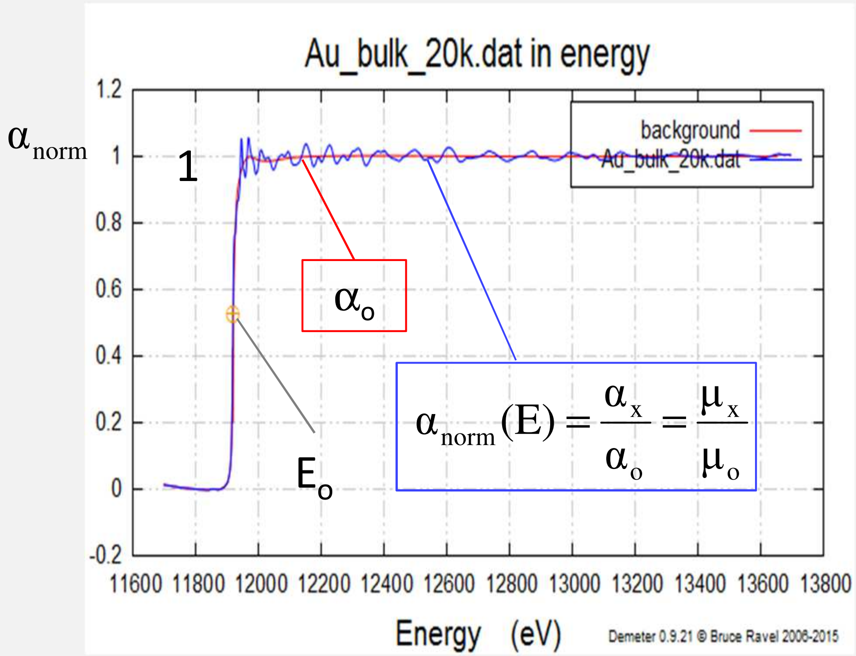
The pre-edge is simulated as a linear regression of data before the edge energy

How to get the normalized $\chi(k)$

2. **Normalization**, χ and k



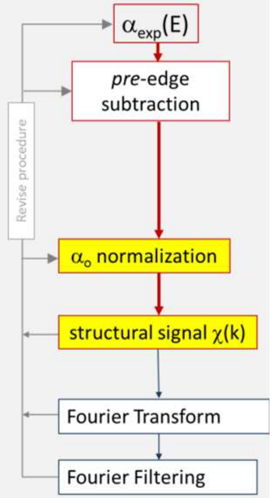
$$\mu_x t = \mu_O (1+\chi) t \Longrightarrow \mu_x = \frac{\mu_o (1+\chi) t}{\mu_o t} = \alpha_{norm}$$



α_o is calculated empirically as a smooth curve across the data.
Different programs for XAFS data analysis apply different (generally equivalent) methods

Requirements for α_o :
1) Smooth enough to not remove true structural features
2) Structured enough to remove not structural background structures

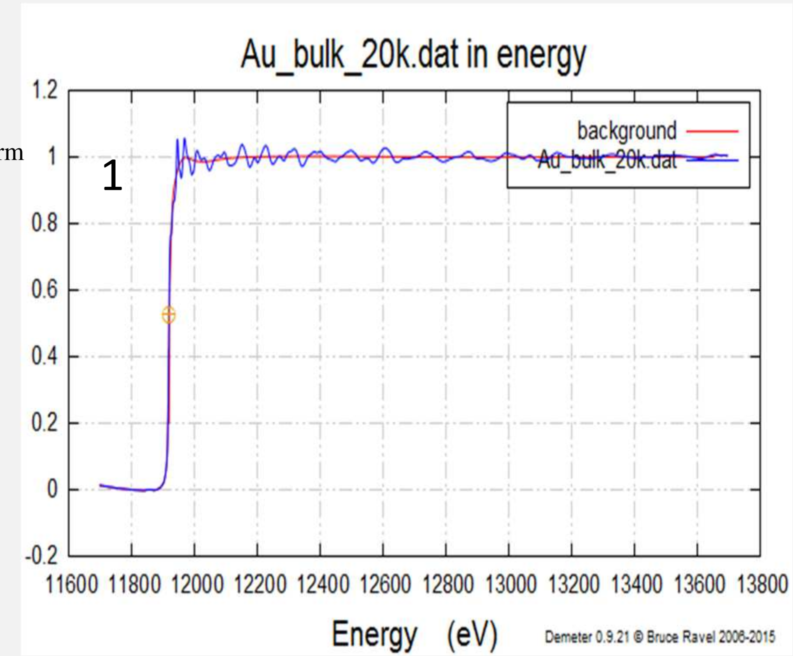
How to get the normalized $\chi(k)$

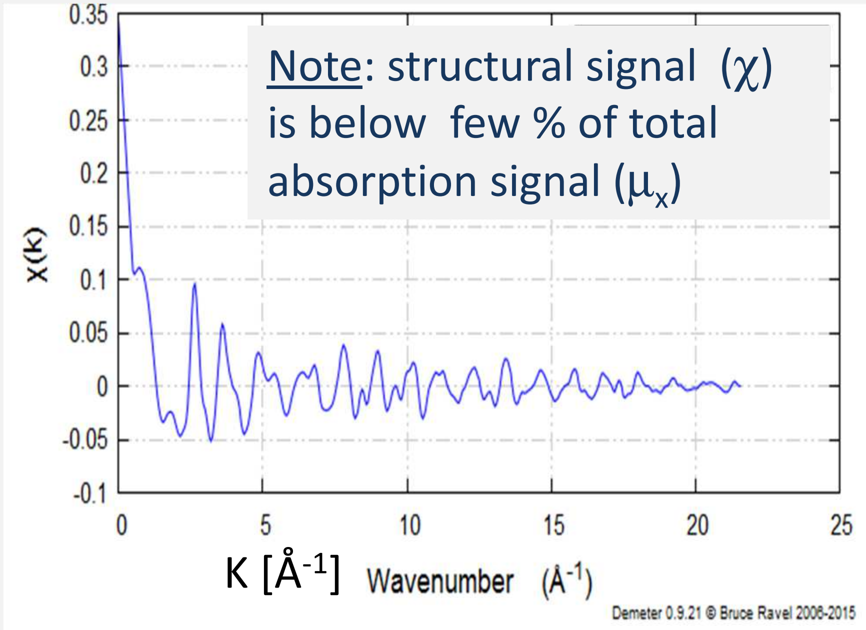


2. Normalization, χ and k

$$\mu_x = \mu_O (1 + \chi) \Longrightarrow \chi = \frac{\mu_x t - \mu_O t}{\mu_O t} = \frac{\alpha_x - \alpha_O}{\alpha_O}$$

α_{norm} 1

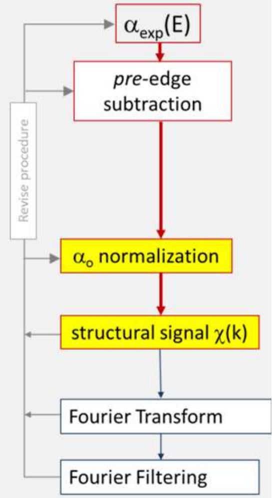




K [Å^{-1}]

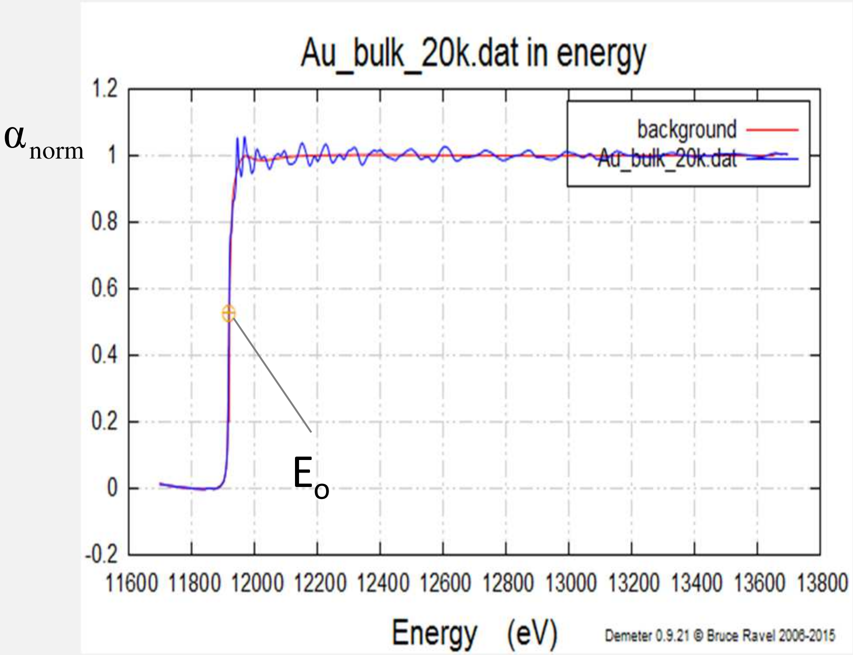
Note: structural signal (χ) is below few % of total absorption signal (μ_x)

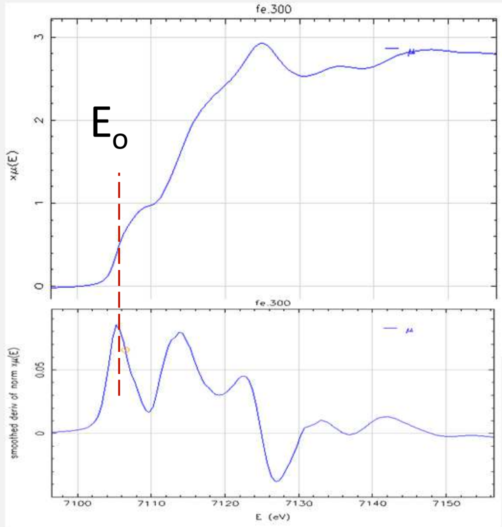
How to get the normalized χ(k)



2. Normalization, χ and **k**

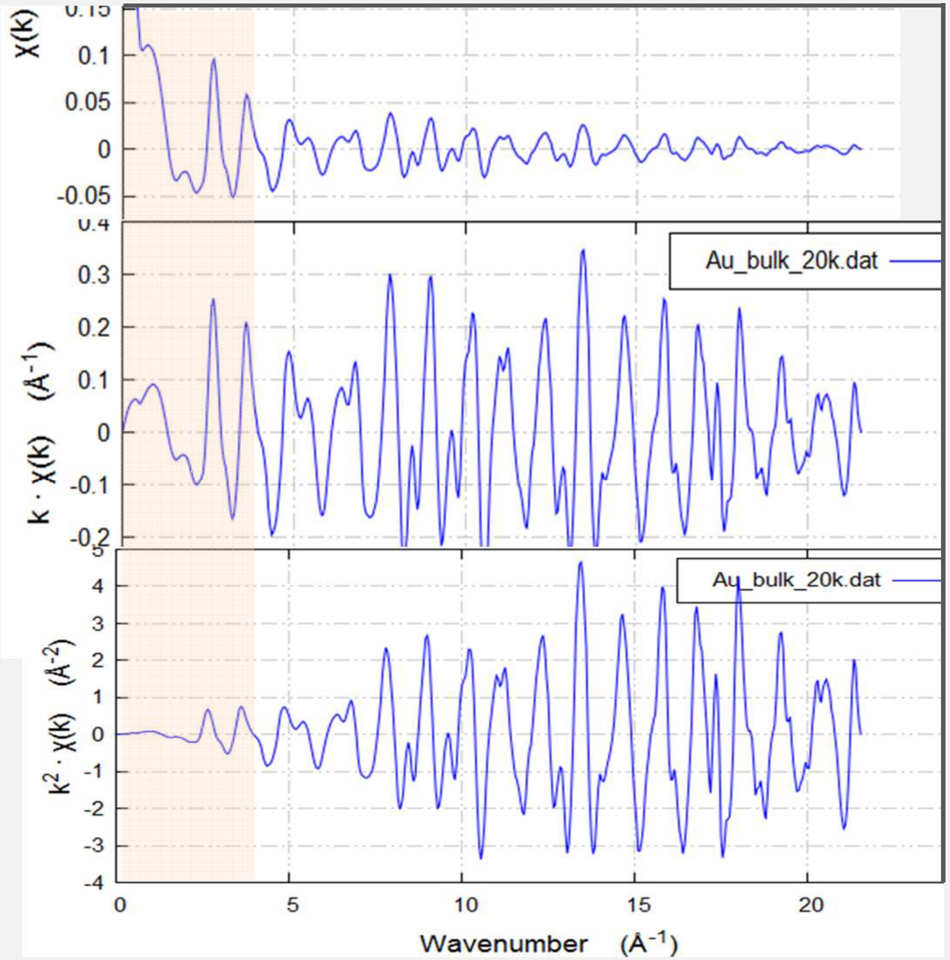
$$k = \sqrt{[2m(E_{h\nu} - E_0)/\hbar^2]}$$





Edge energy is selected at the first inflection point of α_{nor} or where α_{nor} =0.5
It will be refined during the analysis.

Inspect $k^n\chi(k)$

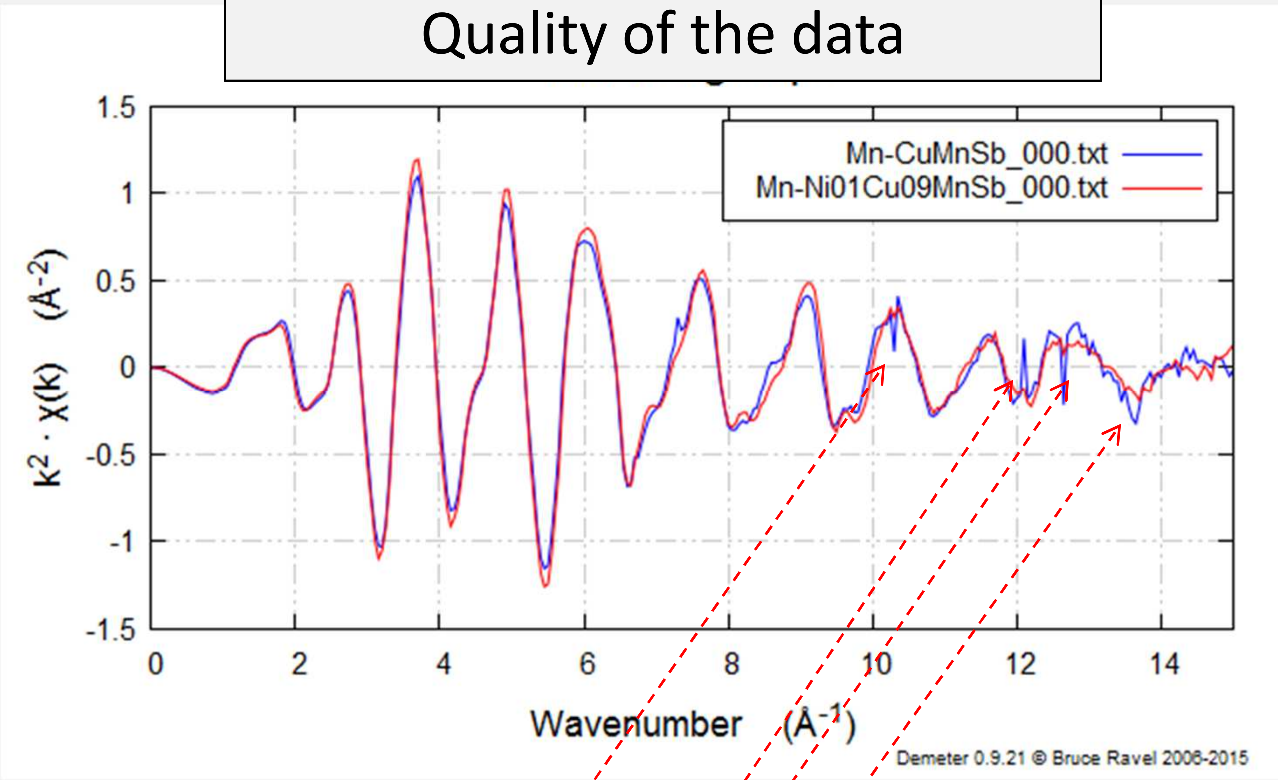


$k^n\chi(k)$ weighting highlights different features in the spectrum: high (low) n enhance high (low) k-regions

Note: low k-region is generally affected by larger inaccuracies and difficult to analyse due to intense multiple scattering contributions

Inspect $k^n\chi(k)$

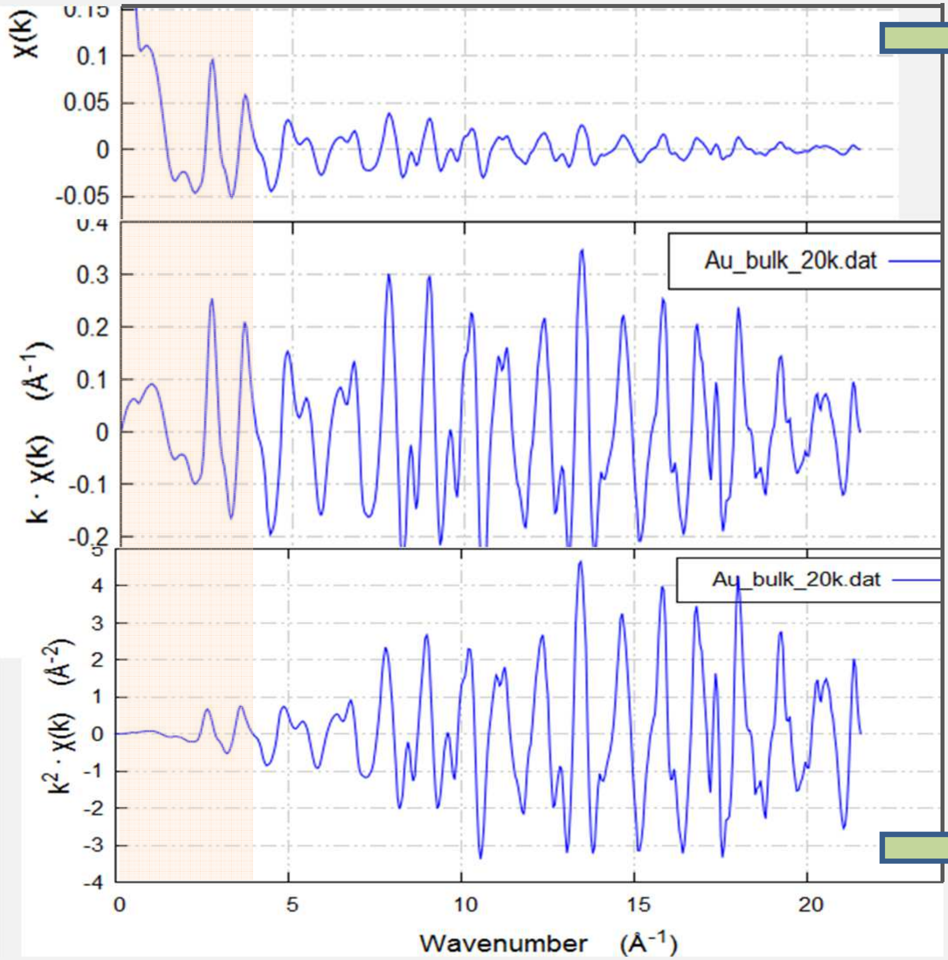
Quality of the data

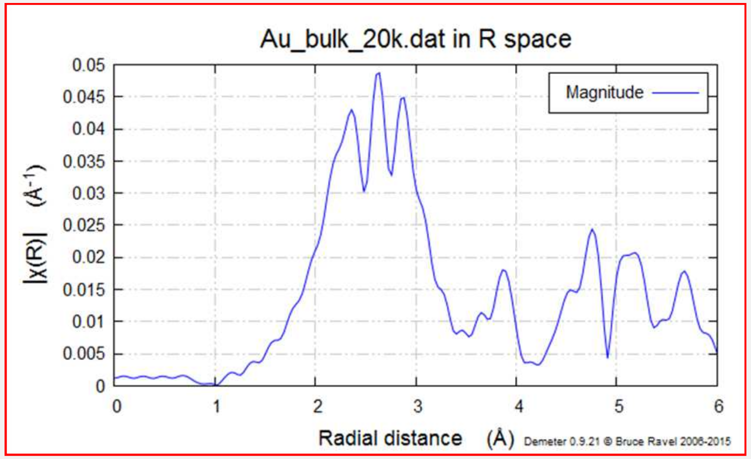


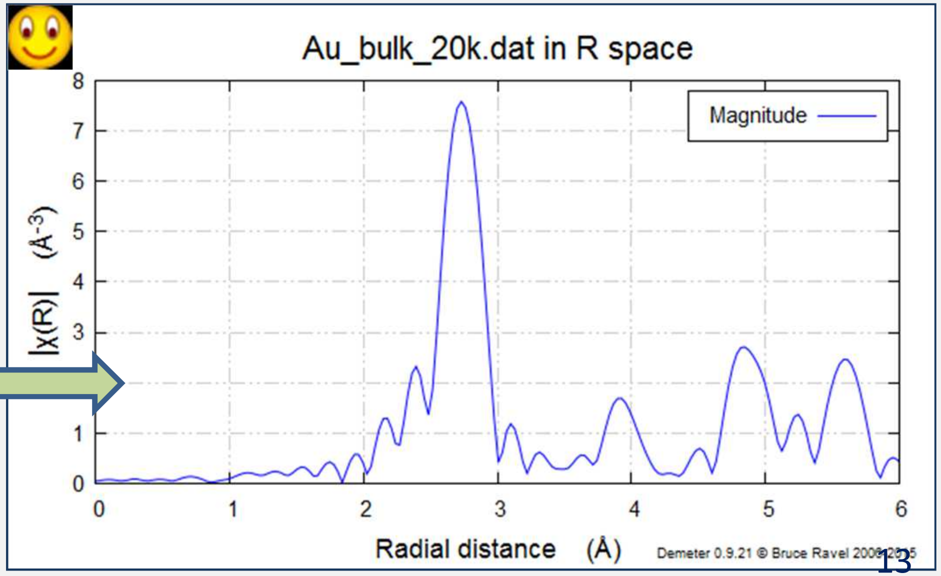
Check for distortions in the spectra, correct or cut the data and retain only the "good" regions"

Qualitative local structure

3. Fourier transform

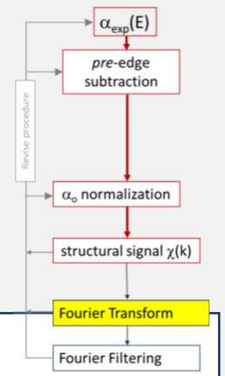




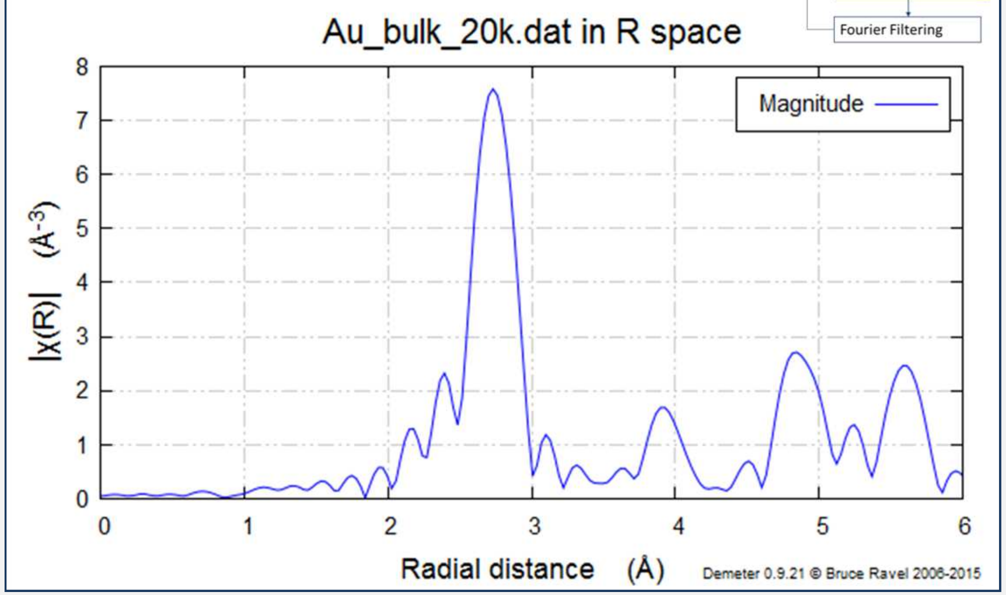


Qualitative local structure

3. Fourier transform

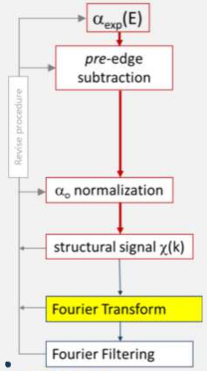


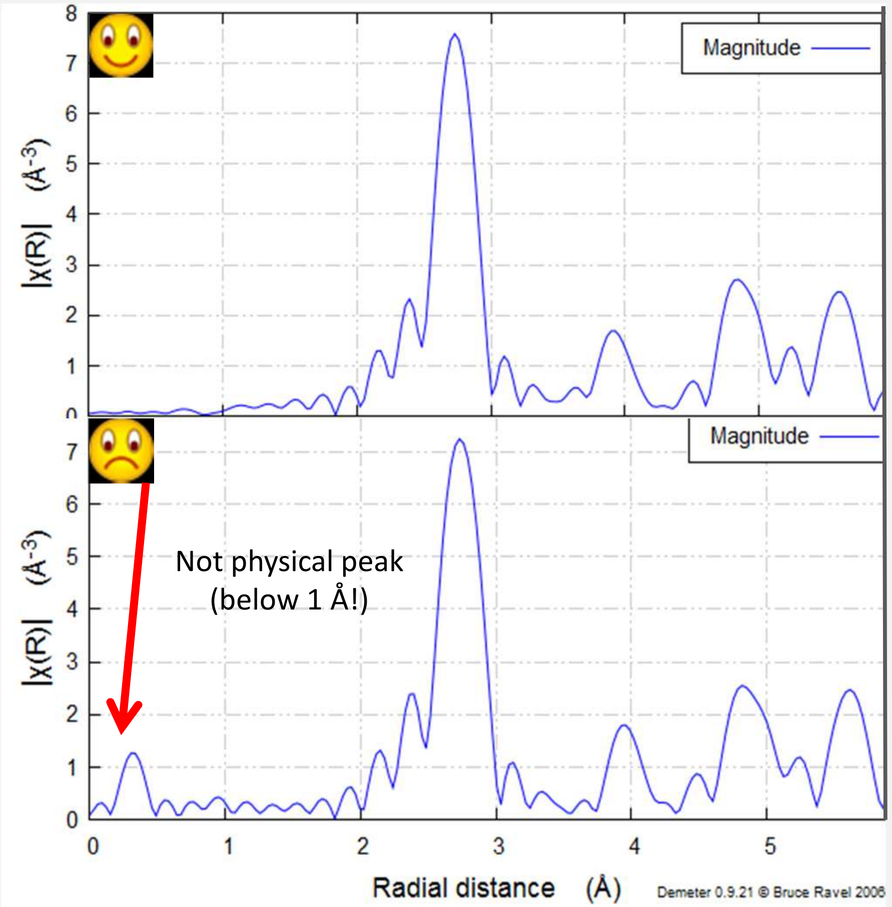
|FT| shows more <u>intuitively</u> the main structural features in the real space: the FT modulus represents a <u>pseudo-radial distribution function</u> modified by the effect of <u>amplitude</u>, <u>phase</u> and <u>mean free path</u> parameters.



Peak positions (phase shift corrected) => neighbour shells
Peak amplitude and shape => number and type of neigbours

Check FT



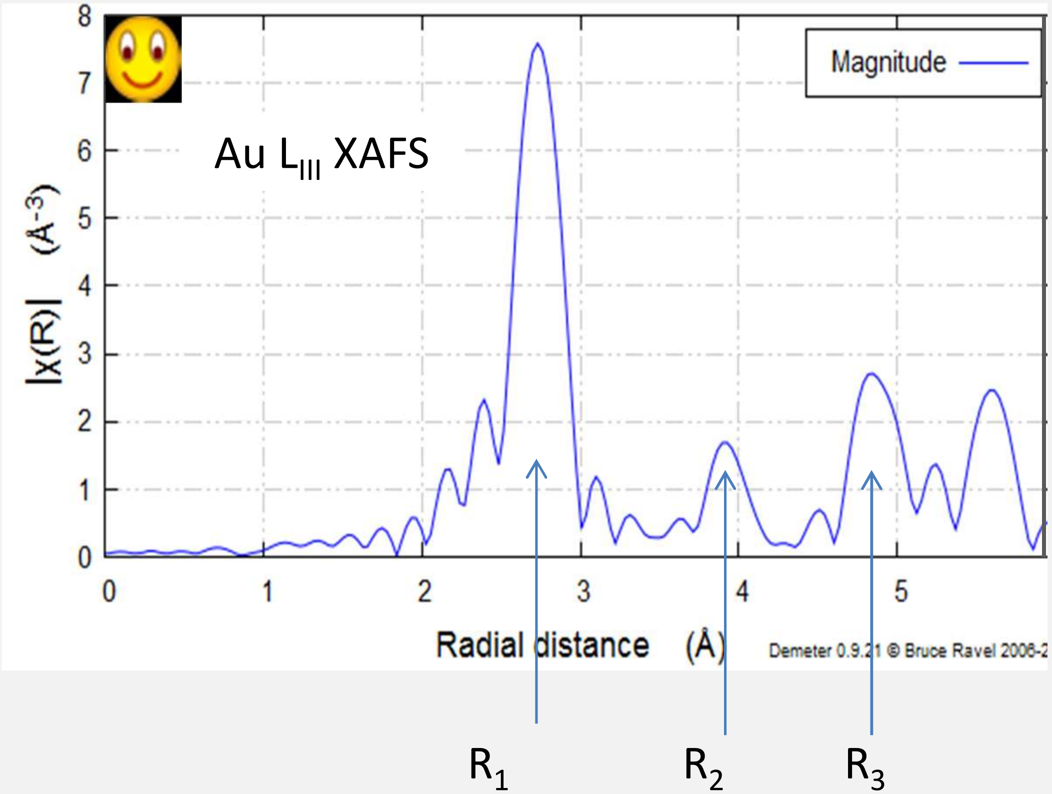


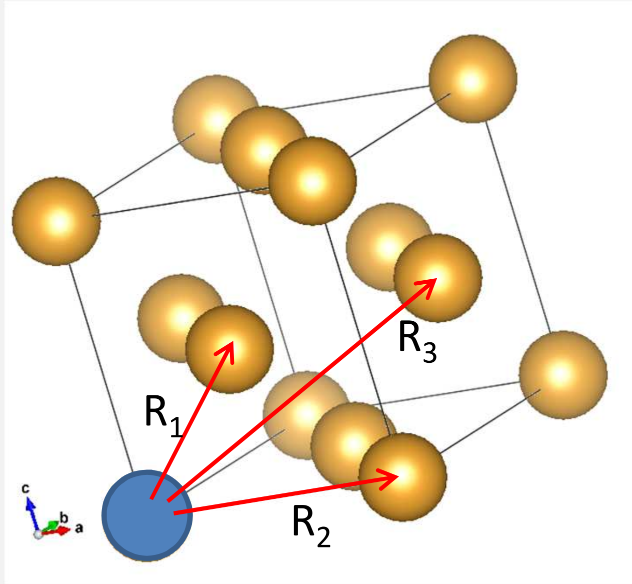
FT features give suggestions about the extraction procedure:
Artifacts, distortions, noise, may suggests bad extraction, noise on the data, etc…

Intense peaks in the low R region (less than 1Å) may signify errors in the extractions

FT and expected atomic structure

Look at the FT features and compare the structure you expect





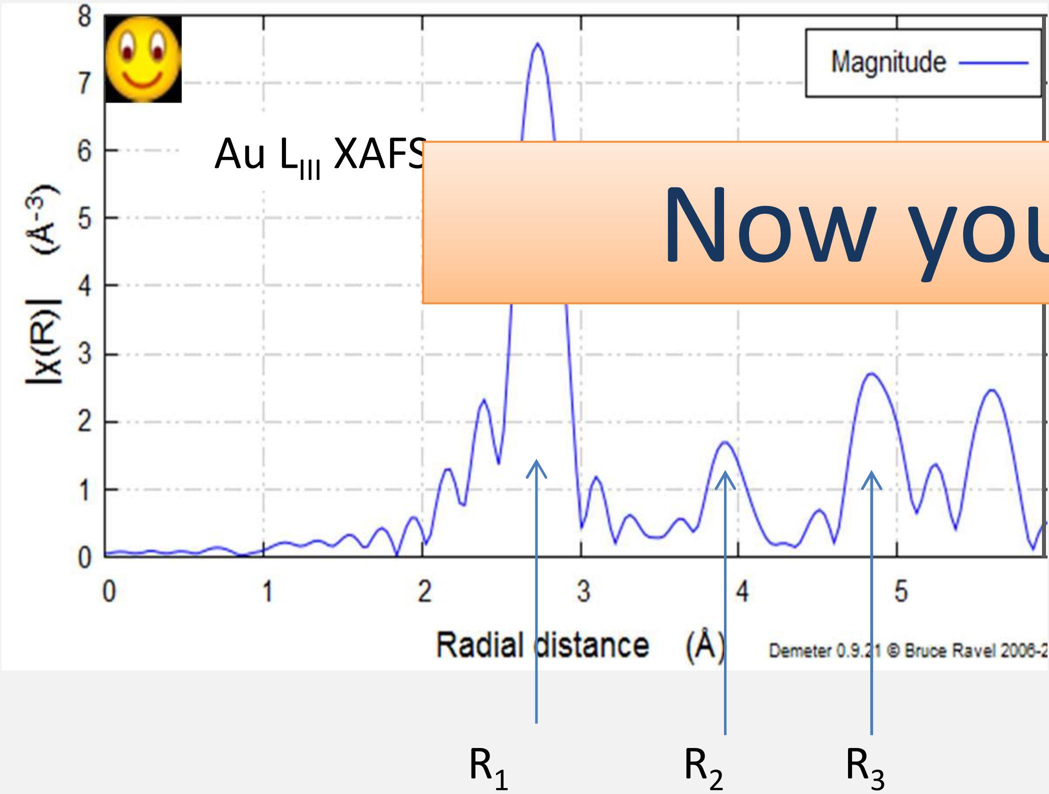
$$R_1 = a/\sqrt{2} \qquad N_1 = 12$$

$$R_2 = a \qquad N_2 = 6$$

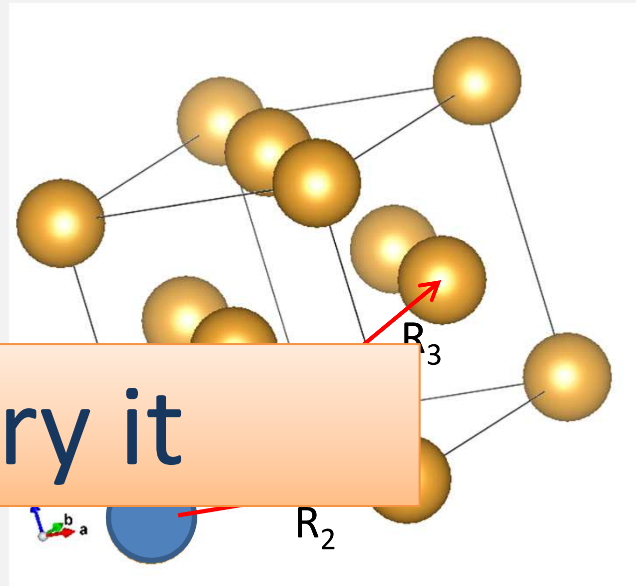
$$R_3 = a\sqrt{6}/2 \qquad N_3 = 24$$

FT and expected atomic structure

Look at the FT features and compare the structure you expect



Now you try it



$$R_1 = a/\sqrt{2} \qquad N_1 = 12$$

$$R_2 = a \qquad N_2 = 6$$

$$R_3 = a\sqrt{6}/2 \qquad N_3 = 24$$

Exercises

I. Download Demeter and install it
II. Start Athena

Examples and exercises

Copper (**Cu**) metal foil Download **Cu_Foil.zip** folder

Gold (**Au**) metal foil (Room temperature and 20 K)

Download **Au_Foil.zip** folder

Iron (**Fe**) metal foil (Room temperature)

Download **Fe_foil.zip** folder

1. Cu K edge XAFS

<u>Basic features</u>

1. Import data
2. E, K, R, Q figures and plot parameters

<u>Modify extraction parameters</u>

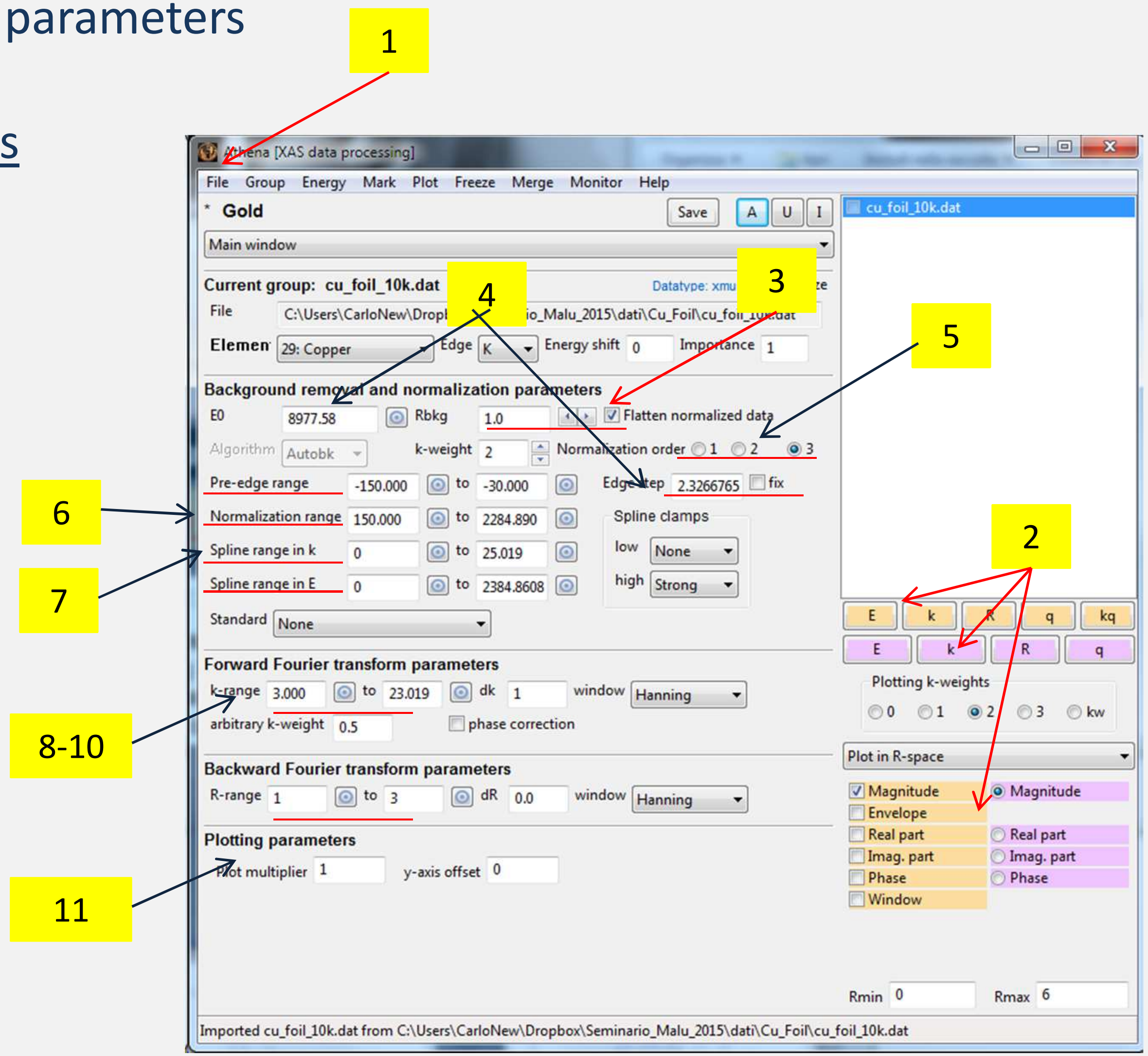
3. R_{bkg}
4. Edge Energy and step
5. Normalization order
6. Normalization range
7. Spline range

<u>k-Weighting</u>

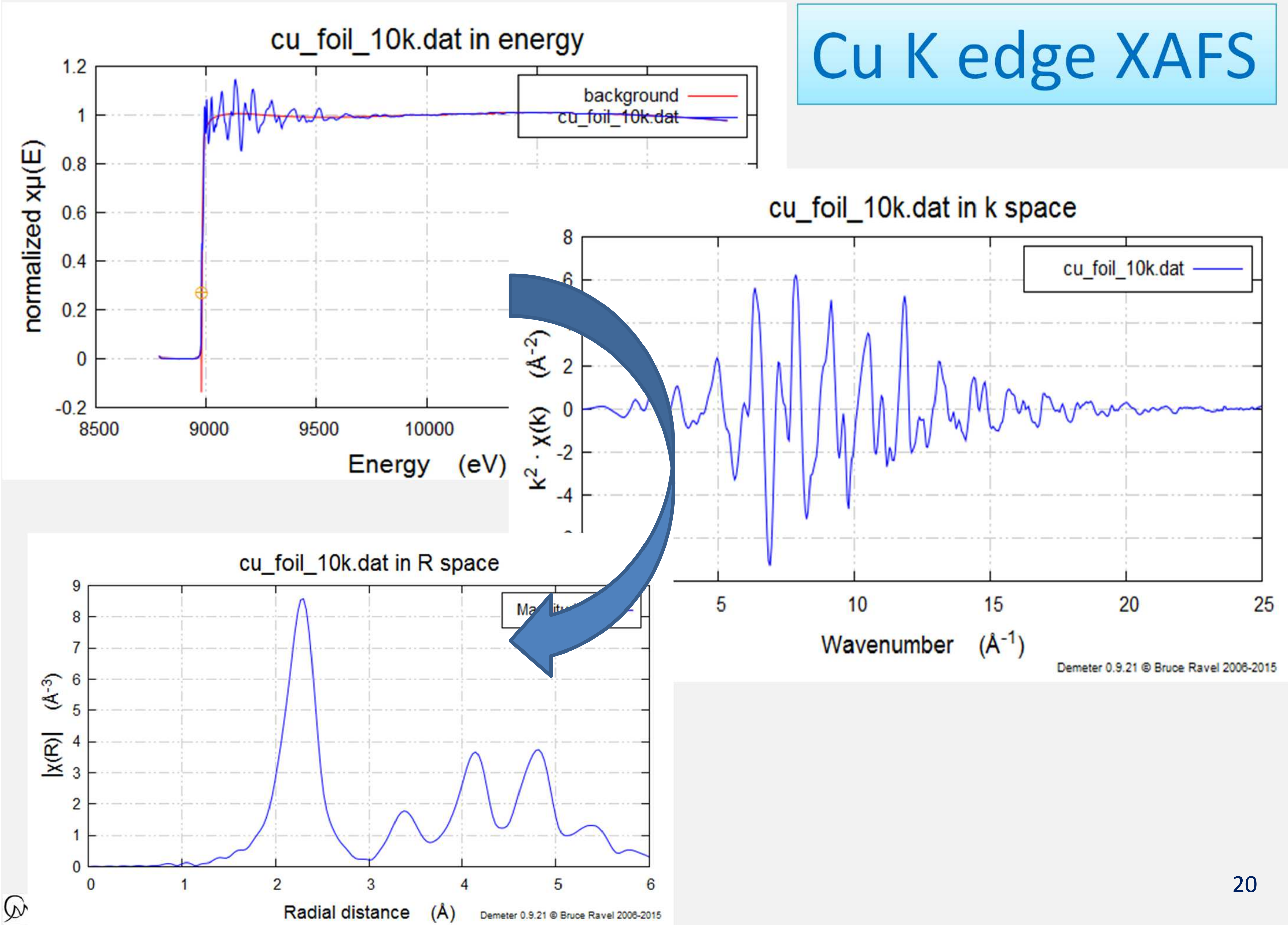
8. FT range
9. FT window
10. FT weight

<u>Back Fourier</u>

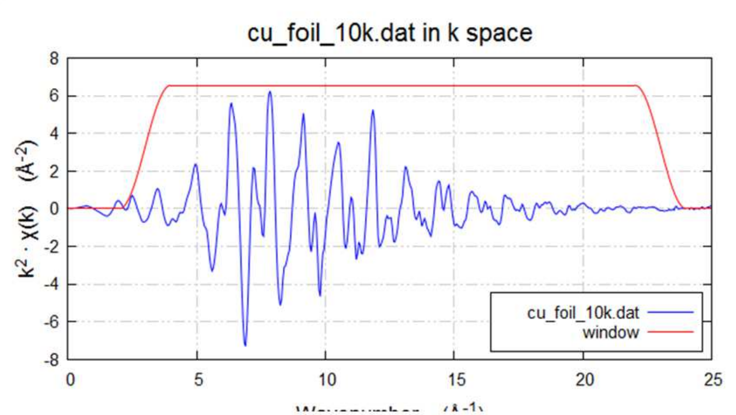
11. Range and window

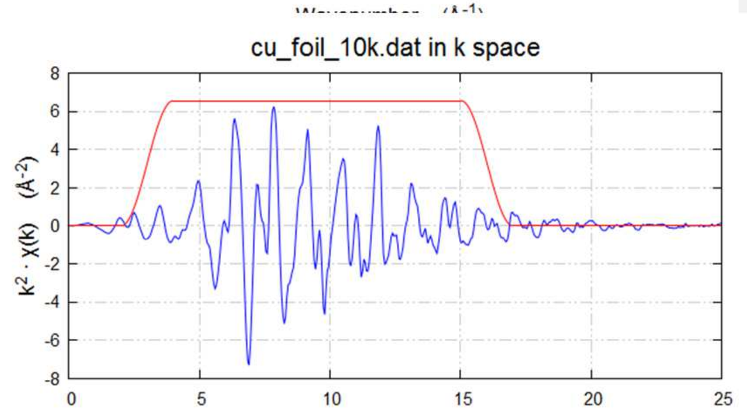


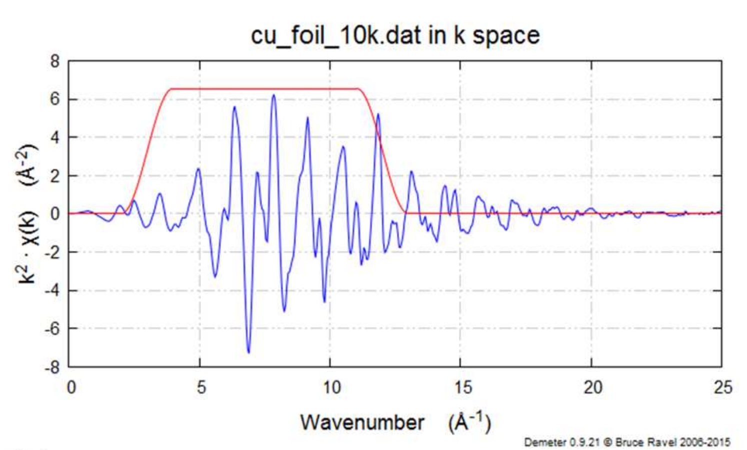
Cu K edge XAFS



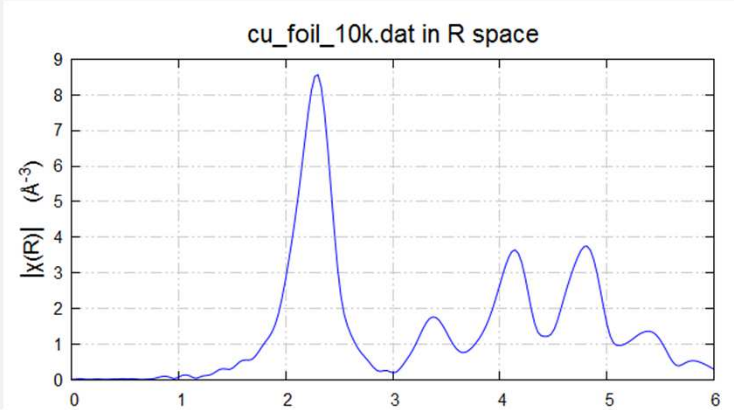
FT window

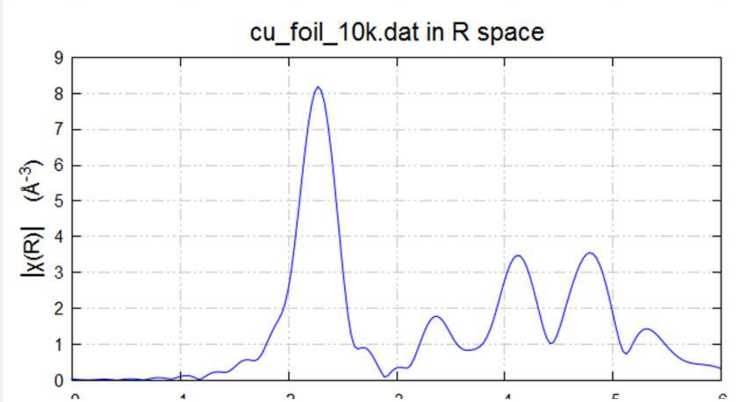


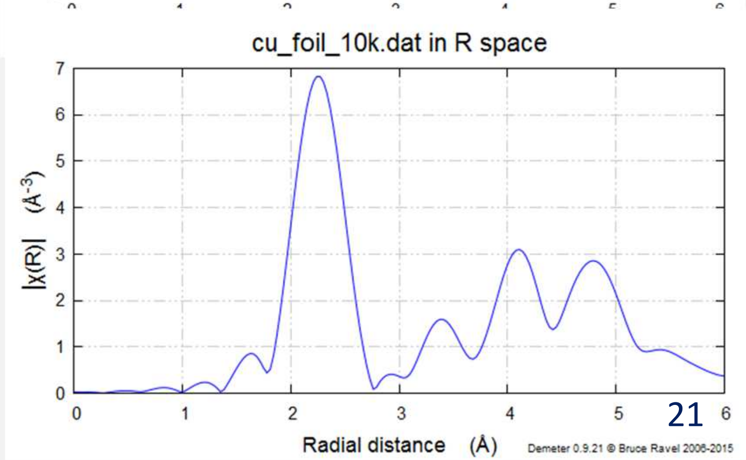




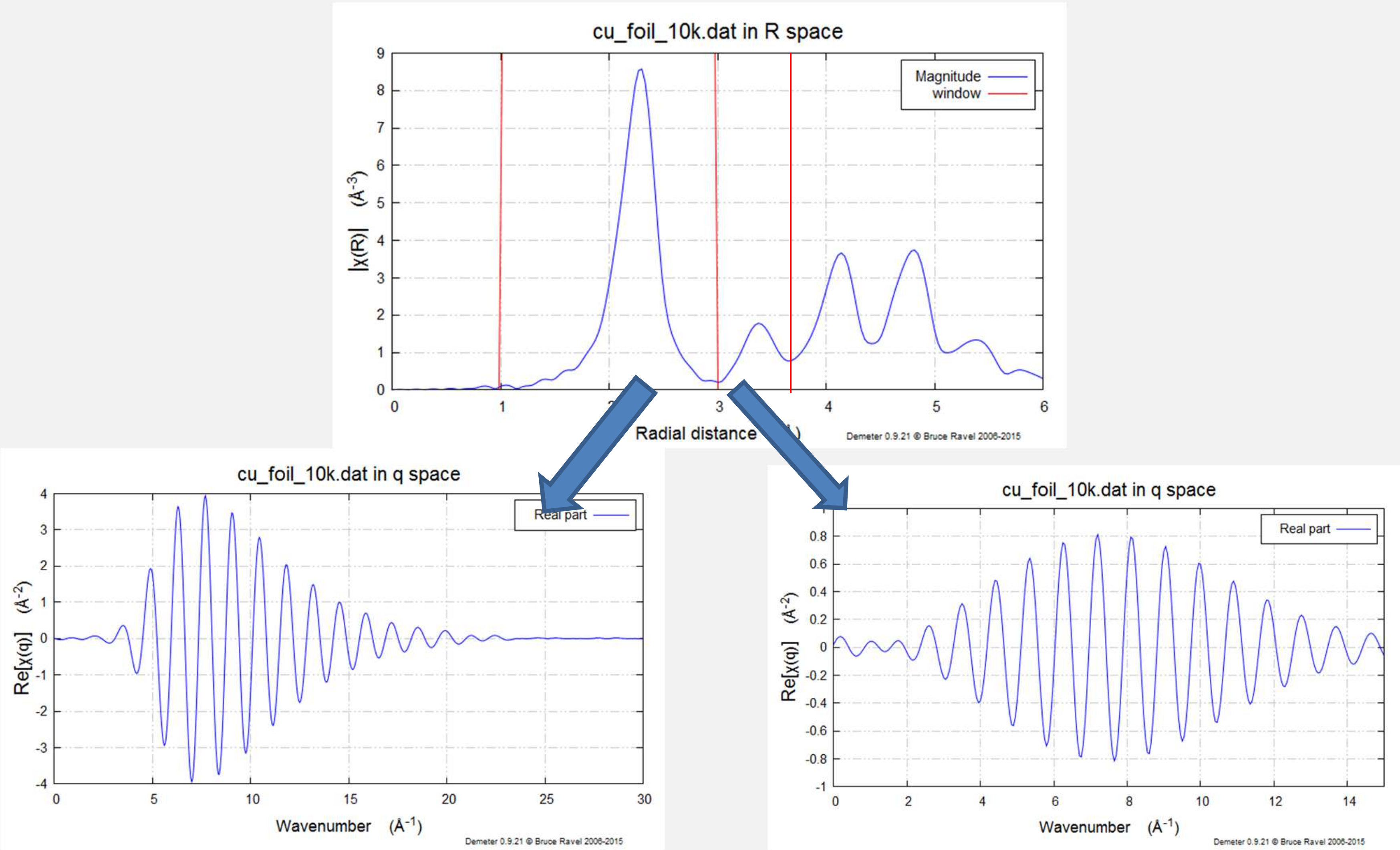
High quality data: main FT features does not change with windows







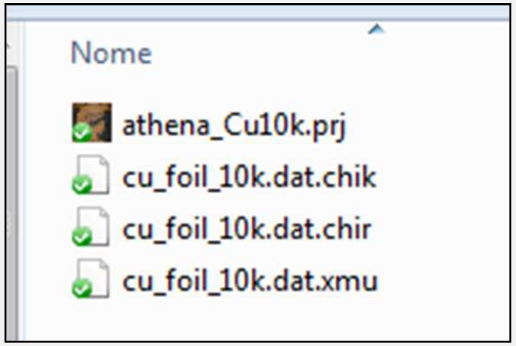
Back-Fourier info



Note:

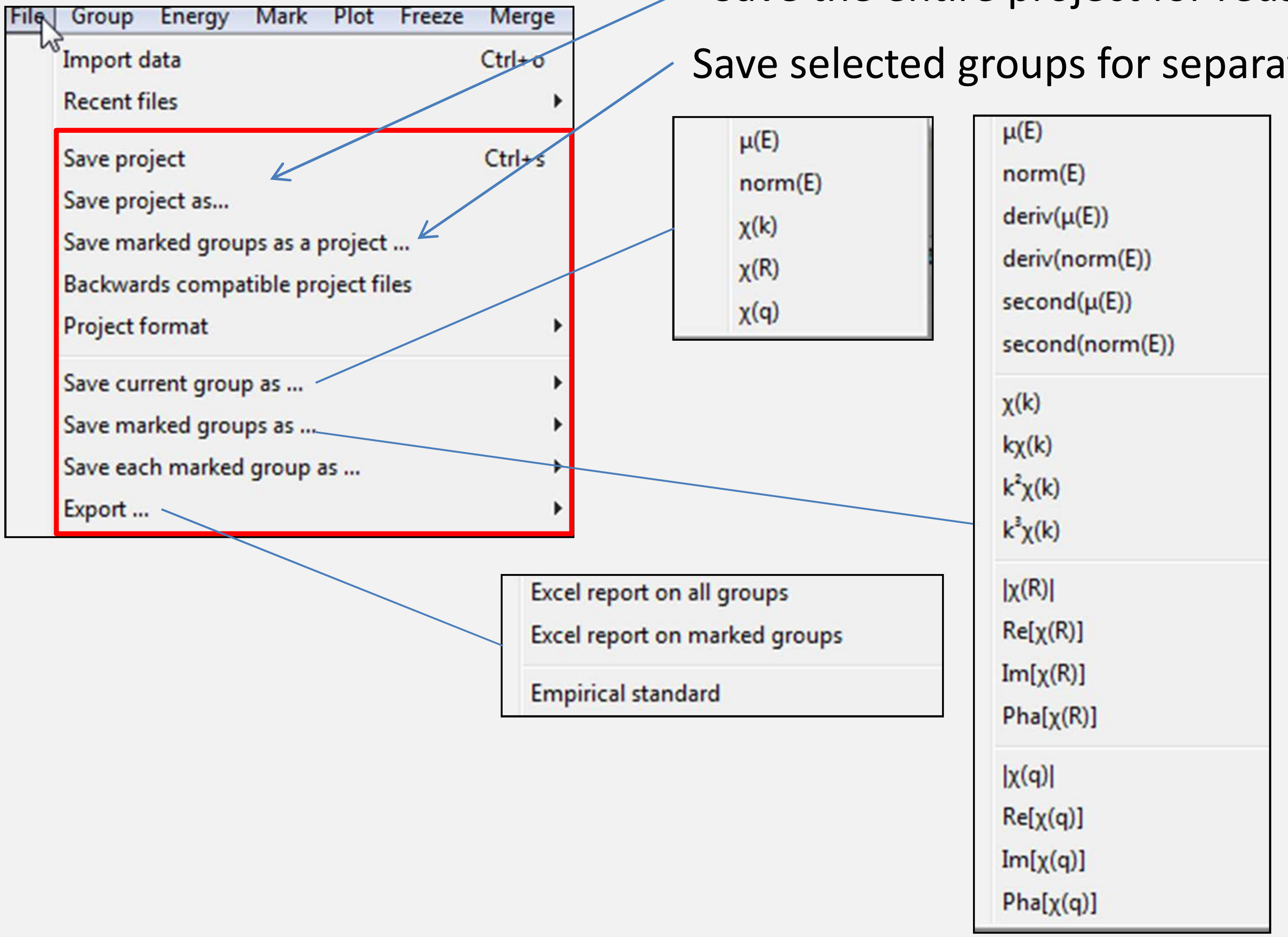
Always save data and project for future use

you have many options!

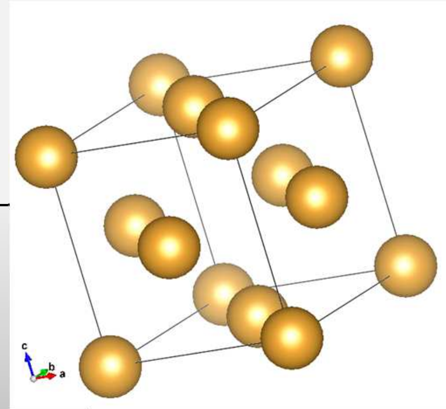


Save the entire project for reuse.

Save selected groups for separate use

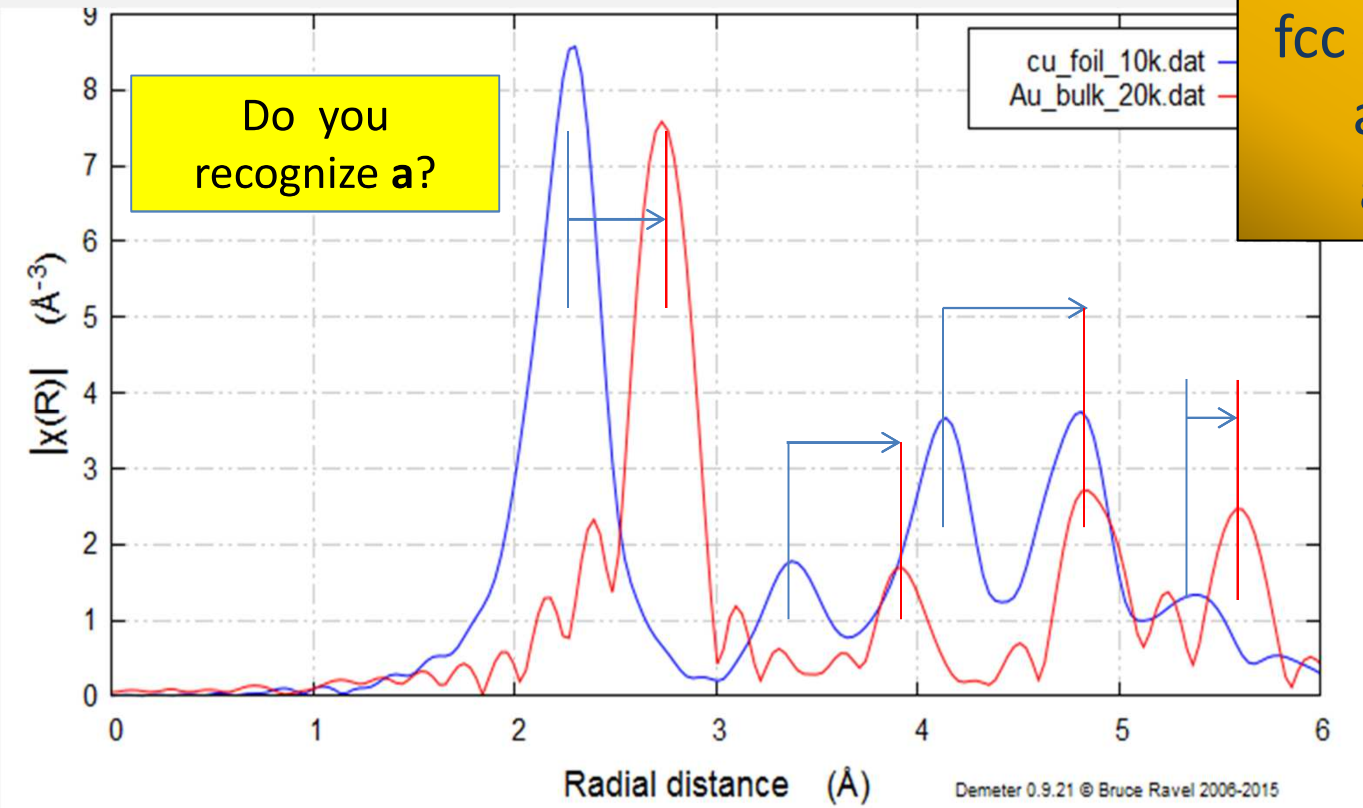


2. Au L_{III} edge XAFS



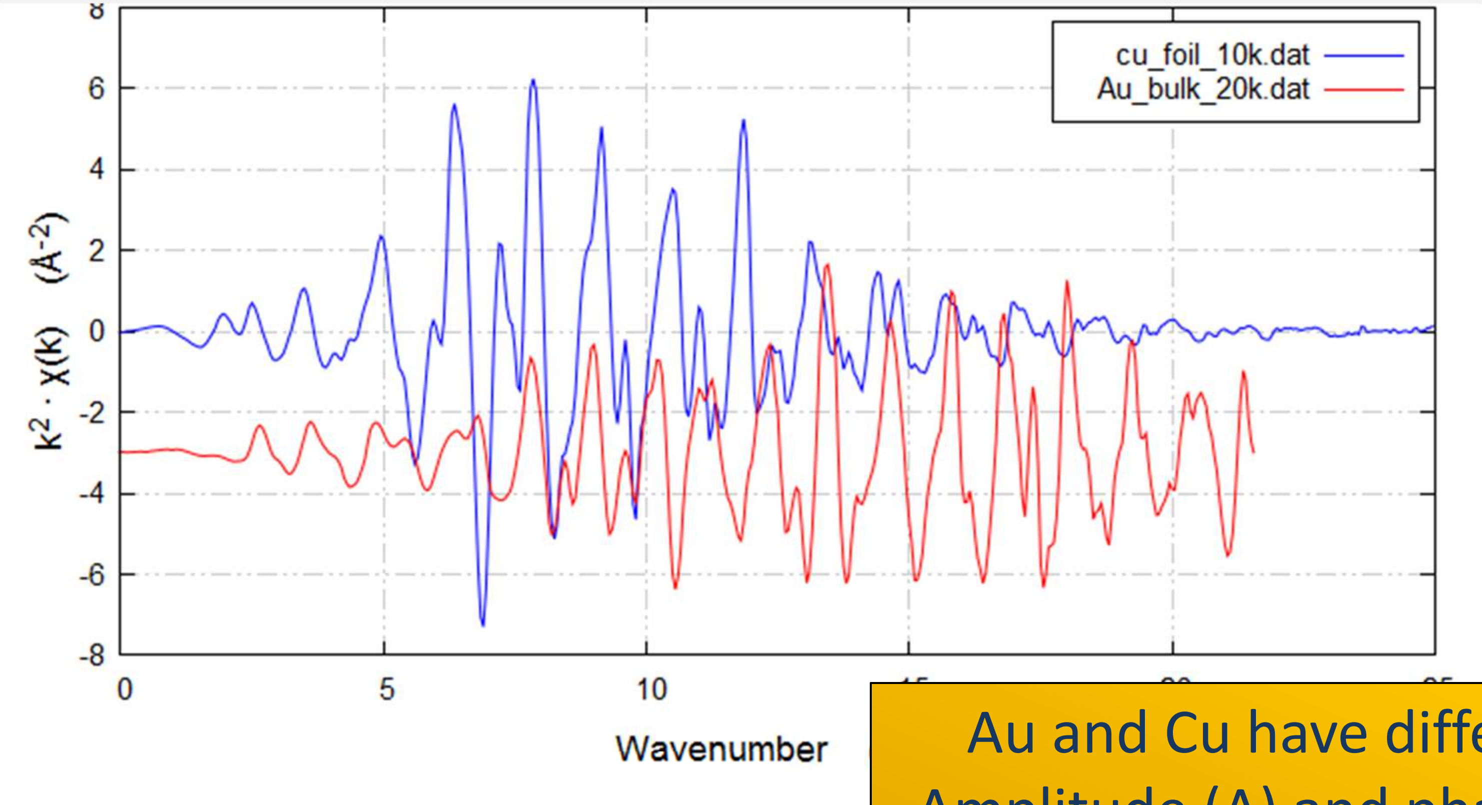
Open **Au_Foil.zip**
Import Au_bulk_20k.dat
1. compare FT data for Cu and Au samples.

Au and Cu have fcc structure but:
a_{Cu}= 3.61 A
a_{Au}=4.07 A



Au L_{III} edge XAFS

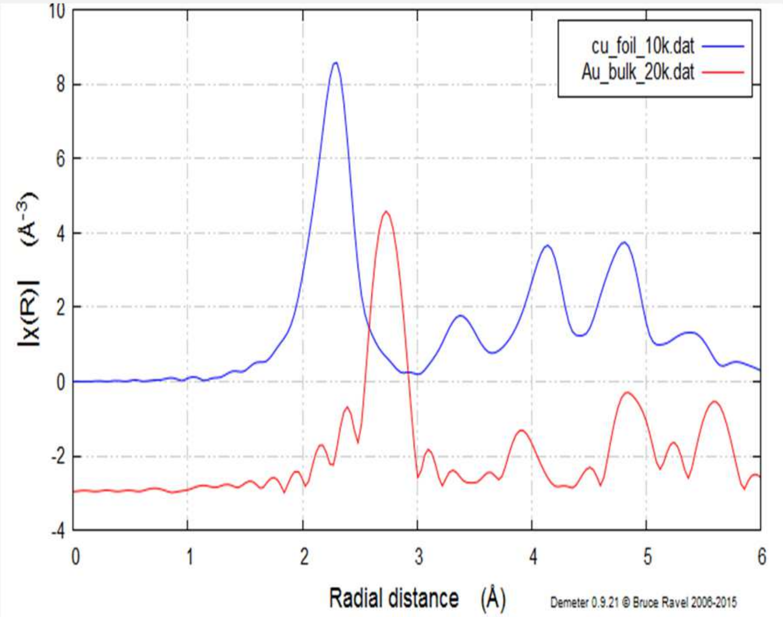
2. compare EXAFS spectra for Cu and Au samples.

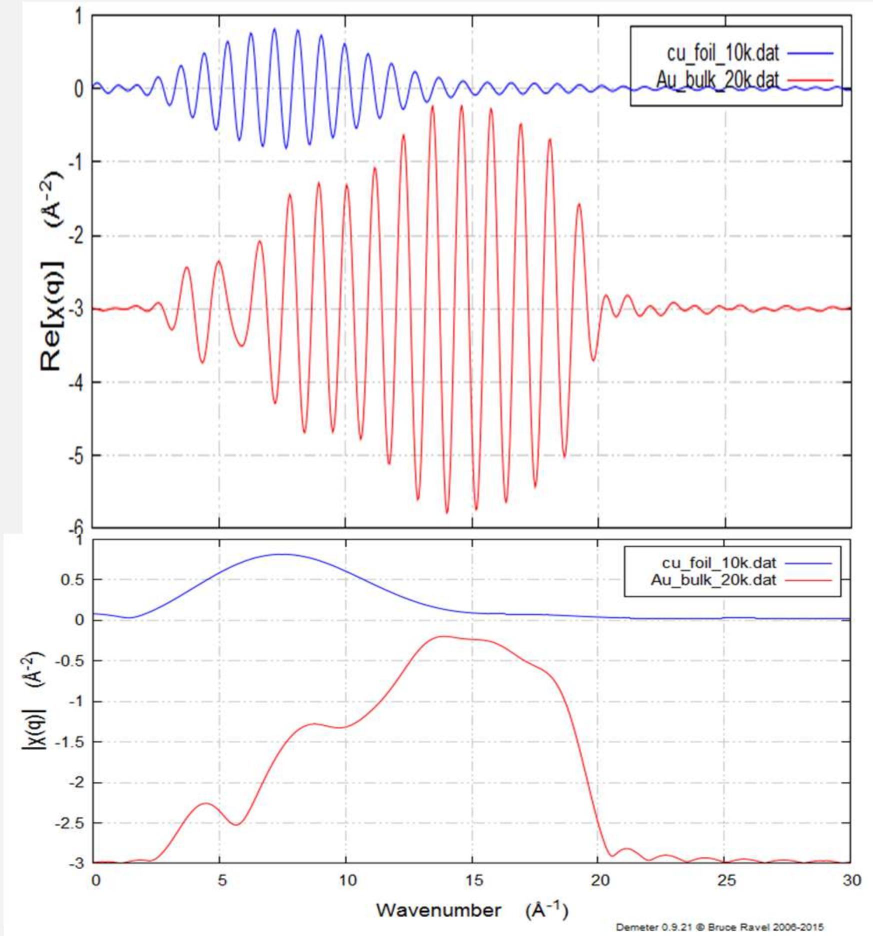


$$\chi(k) = \frac{1}{k}\sum_j A_j(k, r_j)\sin\big(2kr_j + \psi_j(k)\big)$$

Au and Cu have different Amplitude (A) and phase (ψ) functions:
chemical selectivity

2. compare Back FT for Cu and Au samples.



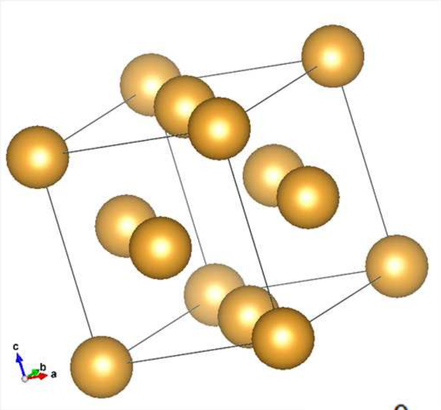


Au and Cu have different Amplitude (A) and phase (ψ) functions:
chemical selectivity

$$\chi(k) = \frac{1}{k}\sum_j A_j(k, r_j)\sin\left(2kr_j + \psi_j(k)\right)$$

3. Fe (bcc) and Cu (fcc) XAFS

Compare Cu and Fe EXAFS data: shows the effect of different crystallographic structure



fcc (Fm-3m)

$R_1 = a/\sqrt{2} \quad N_1 = 12$

$R_2 = a \quad N_2 = 6$

$R_3 = a\sqrt{6}/2 \quad N_3 = 24$

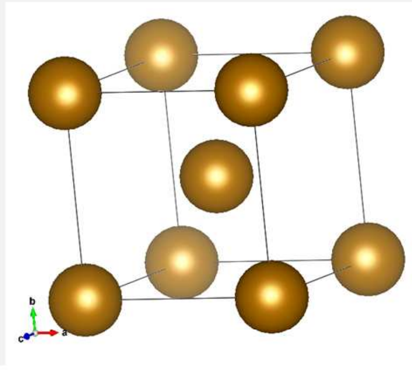
$a_{Cu} = 3.61$ A

Bcc (Im3m)

$R_1 = a\sqrt{3}/2 \quad N_1 = 8$

$R_2 = a \quad N_2 = 6$

$R_2 = a\sqrt{2} \quad N_3 = 12$



$a_{Fe} = 2.86$ A