

# 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

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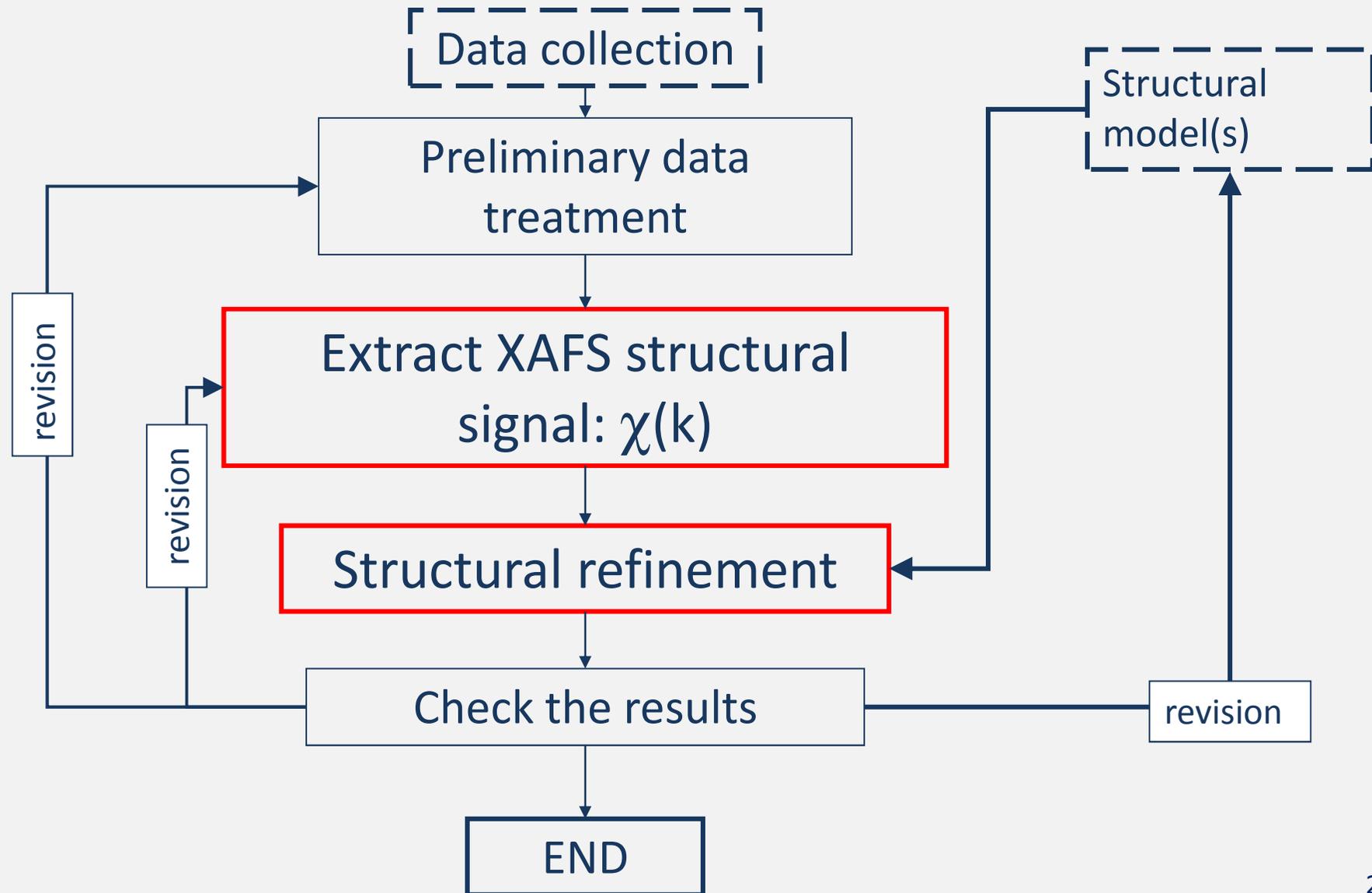
[carlo.meneghini@uniroma3.it](mailto:carlo.meneghini@uniroma3.it)

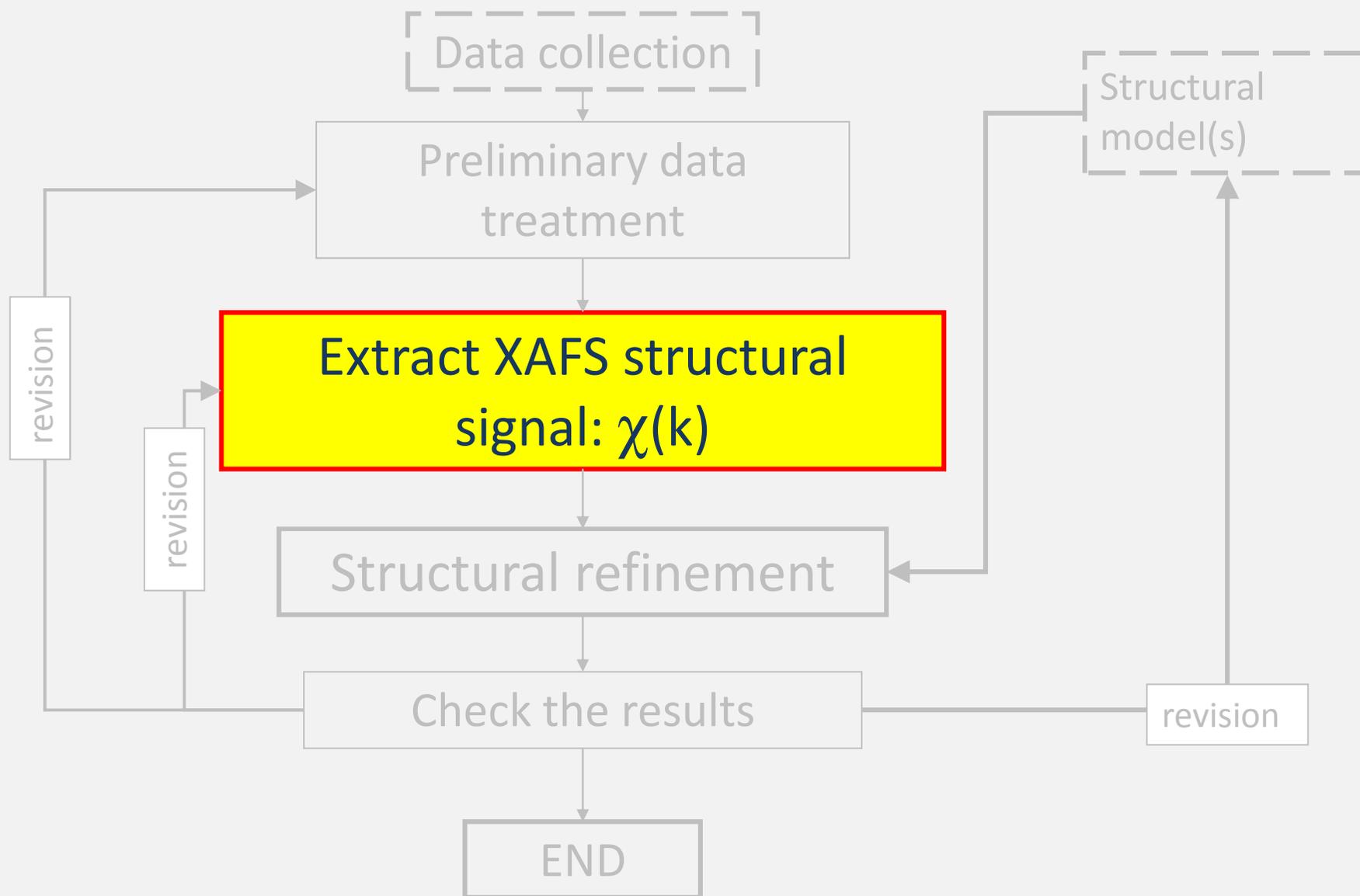


XIV School on Synchrotron Radiation:  
*Fundamentals, Methods and Applications*  
Muggia, Italy / 18-29 September 2017



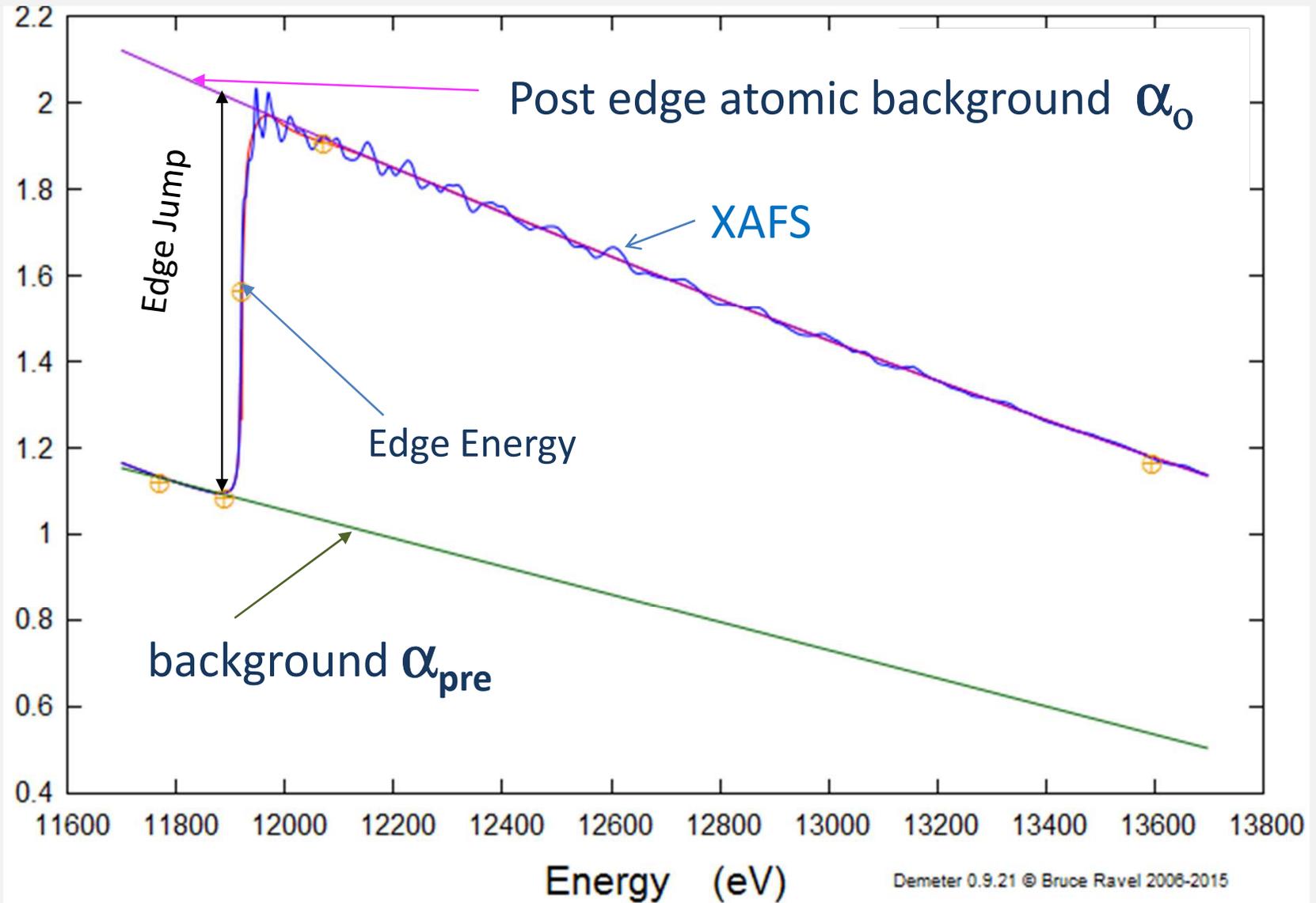
# flow-chart from the experimental data to data fit





# Characteristics of a XAS spectrum

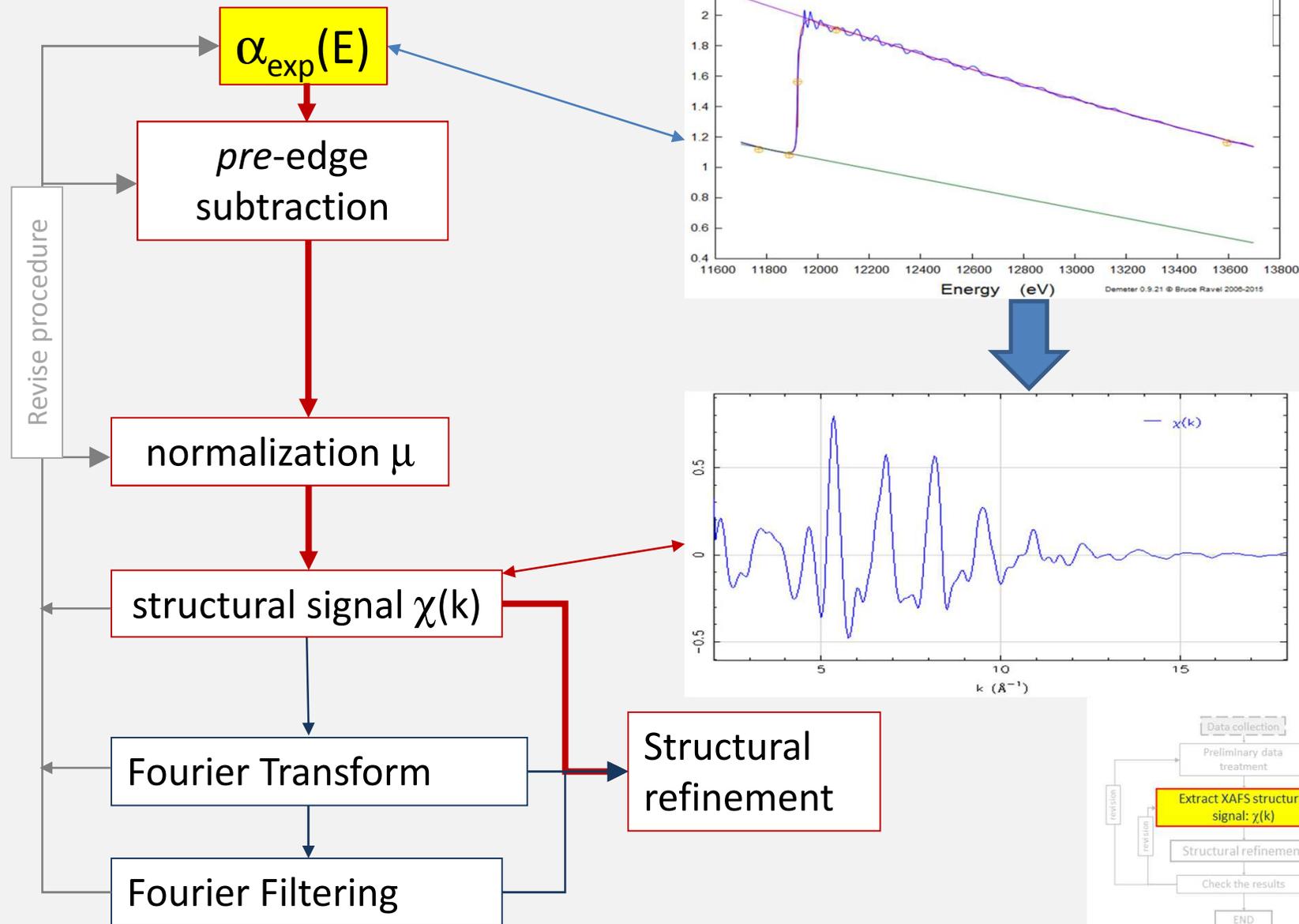
Total absorption  $\alpha_{\text{exp}}$



Demeter 0.9.21 © Bruce Ravel 2008-2015



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

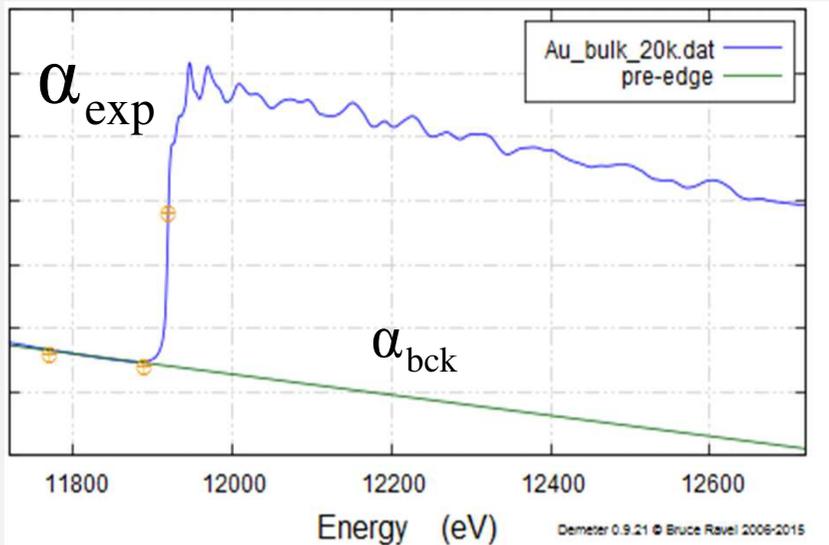
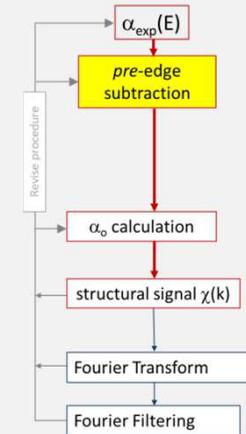


# How to get the normalized $\chi(k)$

## 1. Remove pre-edge

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

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



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

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

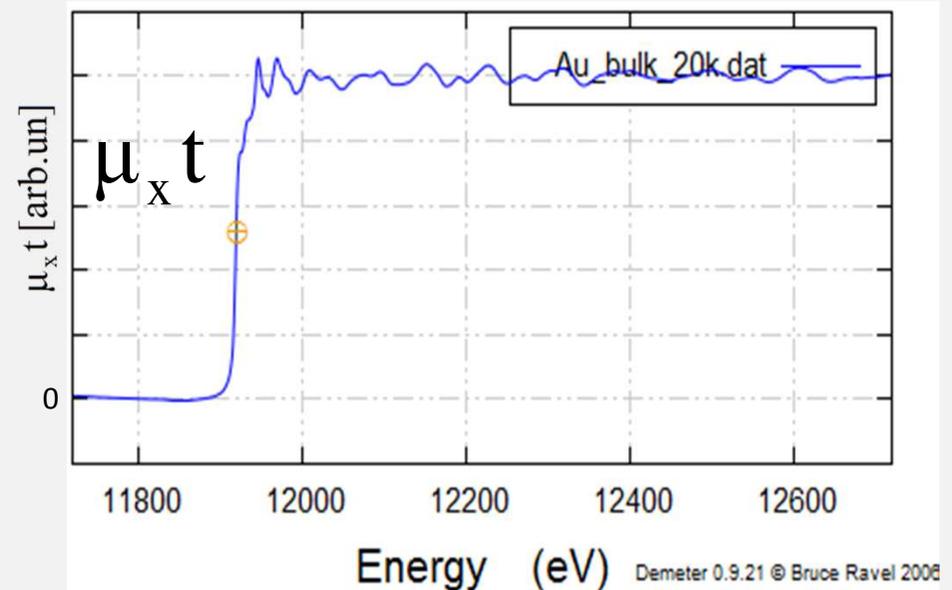
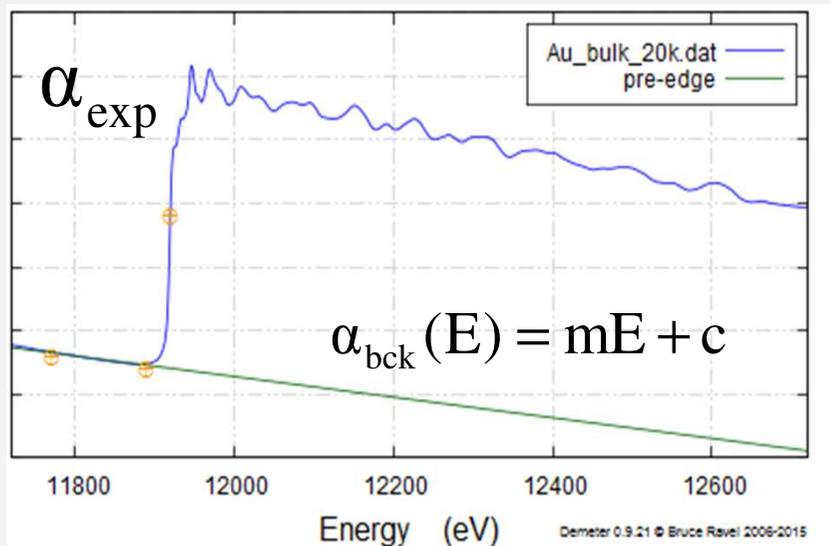
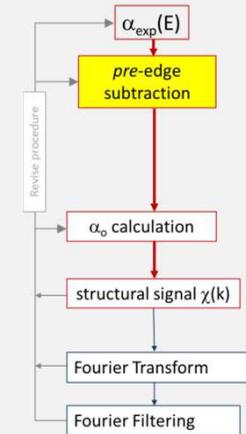
Everything being: other absorption edges, air, sample holder, matrices, chamber windows, etc...

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

## 1. Remove pre-edge

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

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

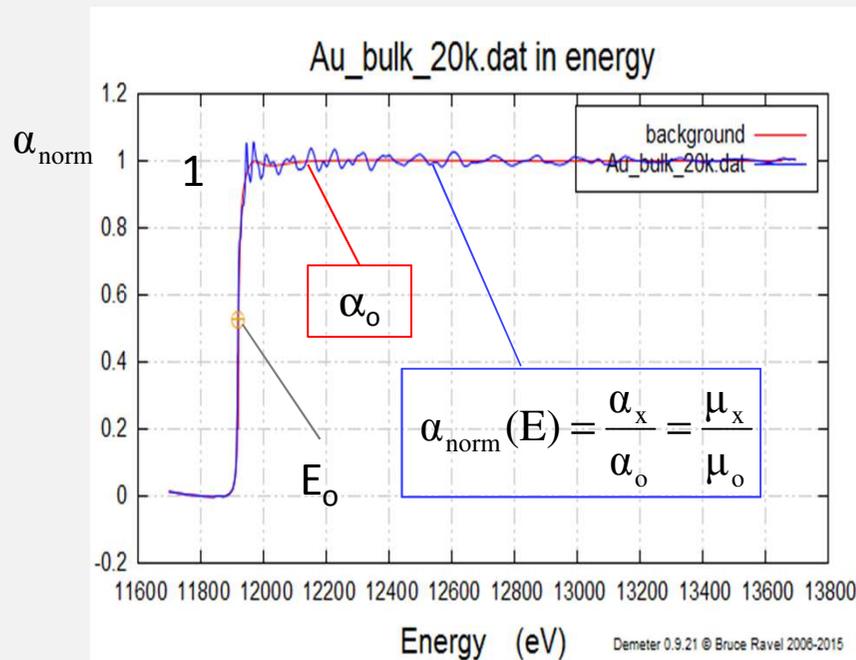
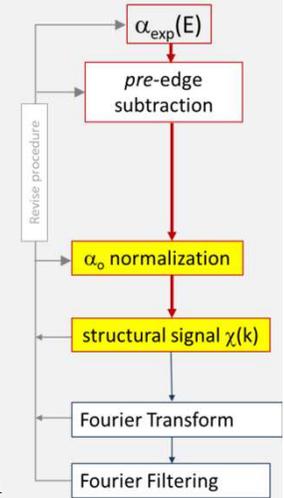


The pre-edge is simulated as a linear regression of data before the edge energy

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

## 2. Normalization, $\chi$ and $k$

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



$\alpha_o$  is calculated empirically as a smooth curve across the data.

Different programs for XAFS data analysis apply different (generally equivalent) methods

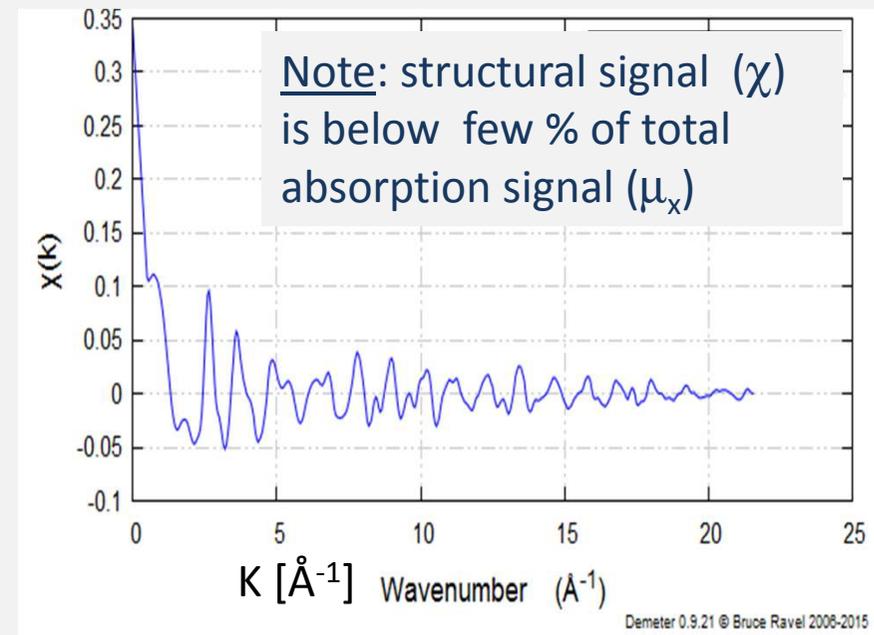
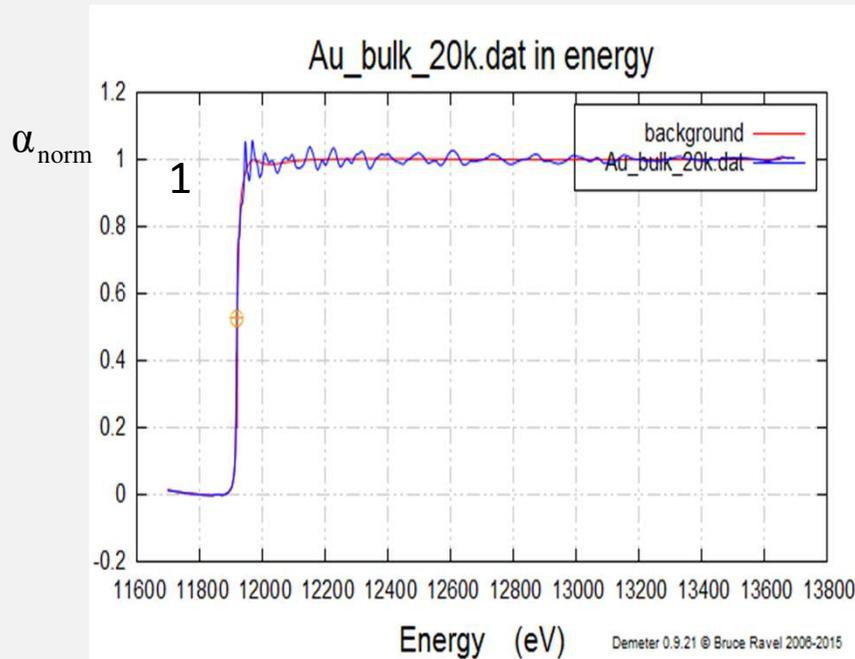
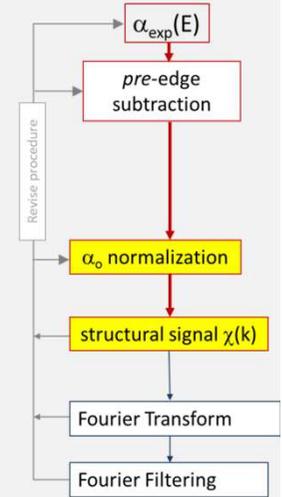
Requirements for  $\alpha_o$ :

- 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, $\chi$ and $k$

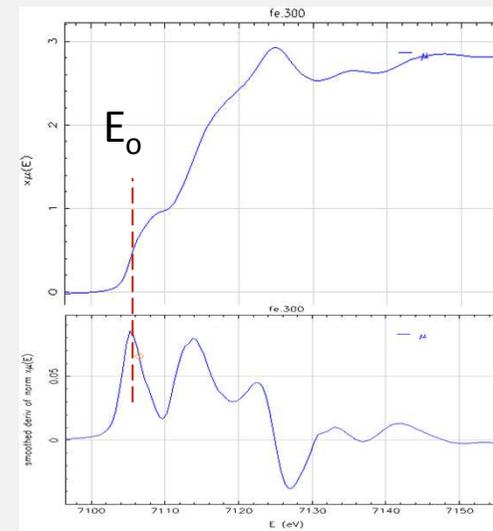
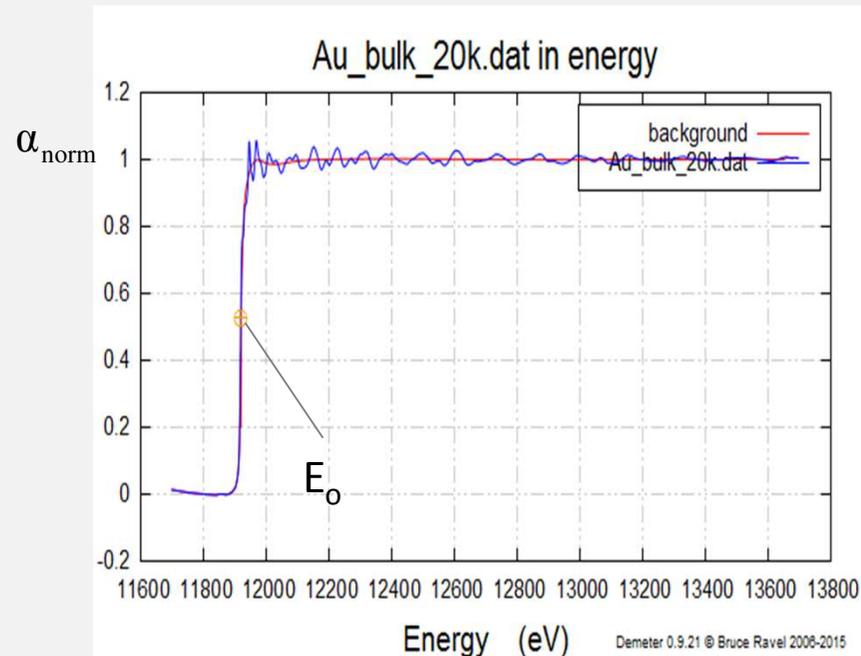
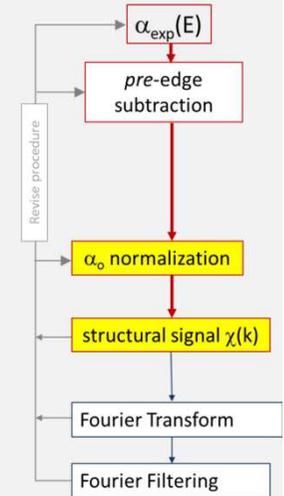
$$\mu_x = \mu_o (1 + \chi) \quad \longrightarrow \quad \chi = \frac{\mu_x - \mu_o}{\mu_o} = \frac{\alpha_x - \alpha_o}{\alpha_o}$$



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

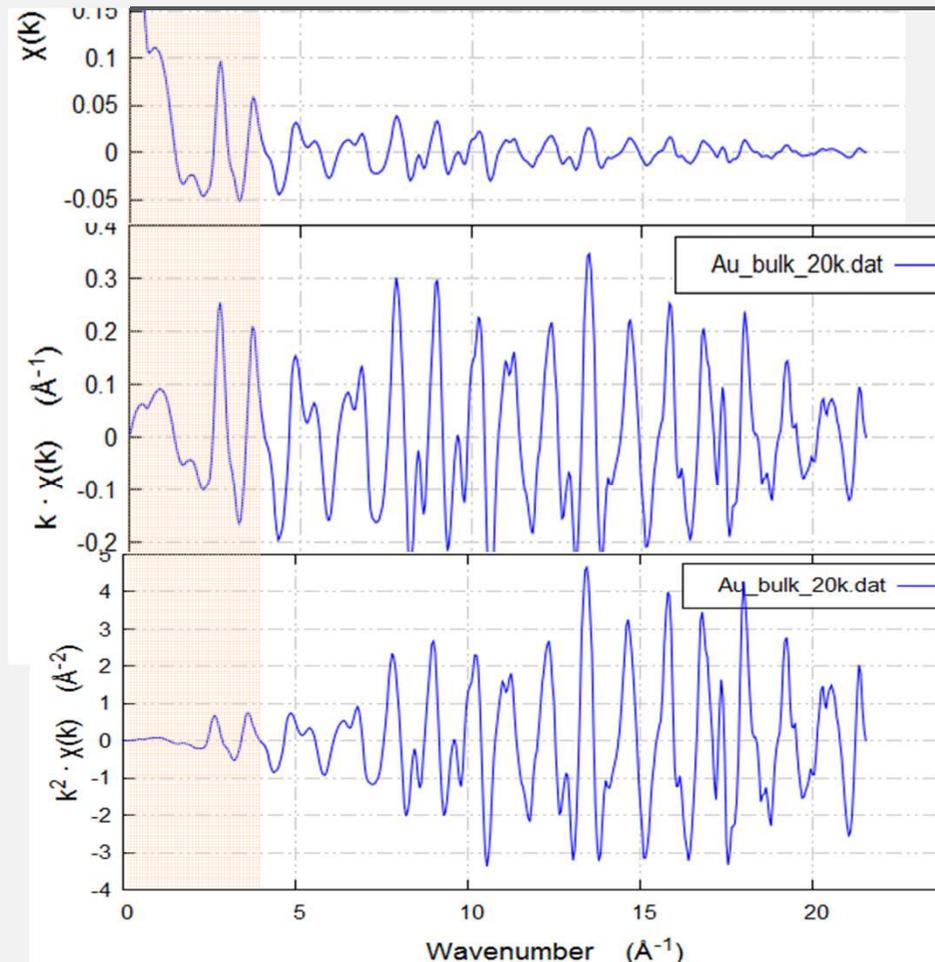
## 2. Normalization, $\chi$ and $\underline{k}$

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



Edge energy is selected at the first inflection point of  $\alpha_{\text{norm}}$  or where  $\alpha_{\text{norm}} = 0.5$   
It will be refined during the analysis.

# Inspect $k^n \chi(k)$

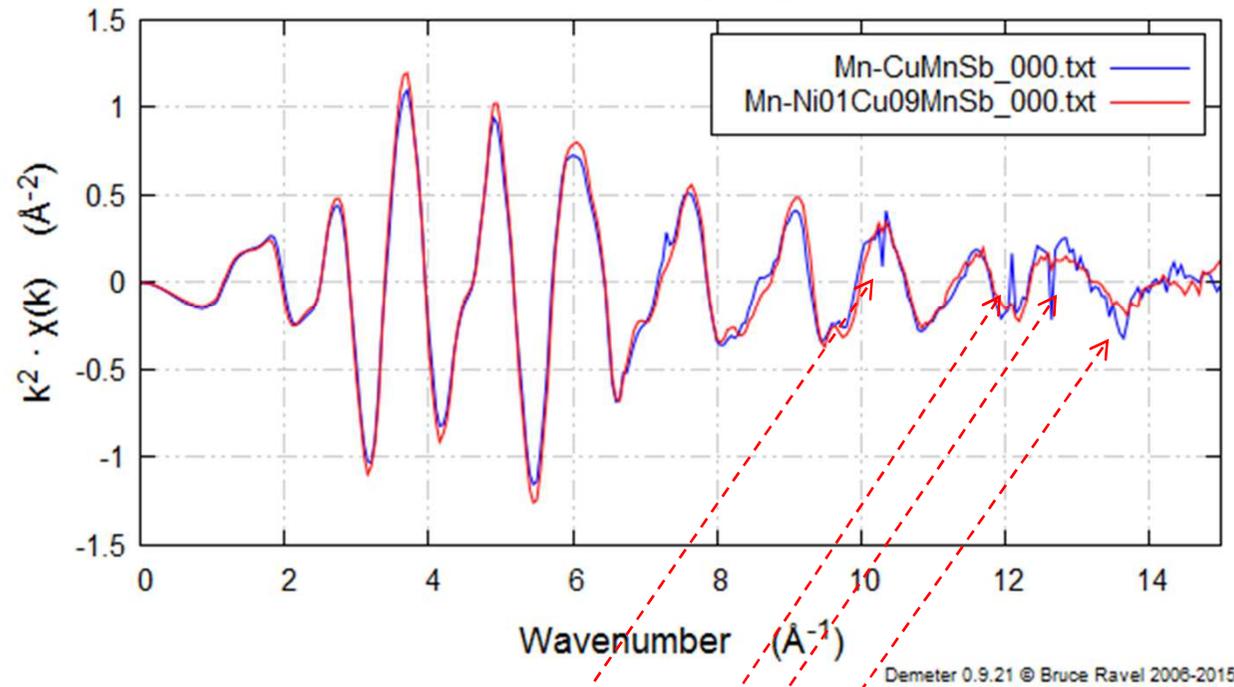


$k^n \chi(k)$  weighting highlights different features in the spectrum: high (low)  $n$  enhance high (low)  $k$ -regions

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

# Inspect $k^n \chi(k)$

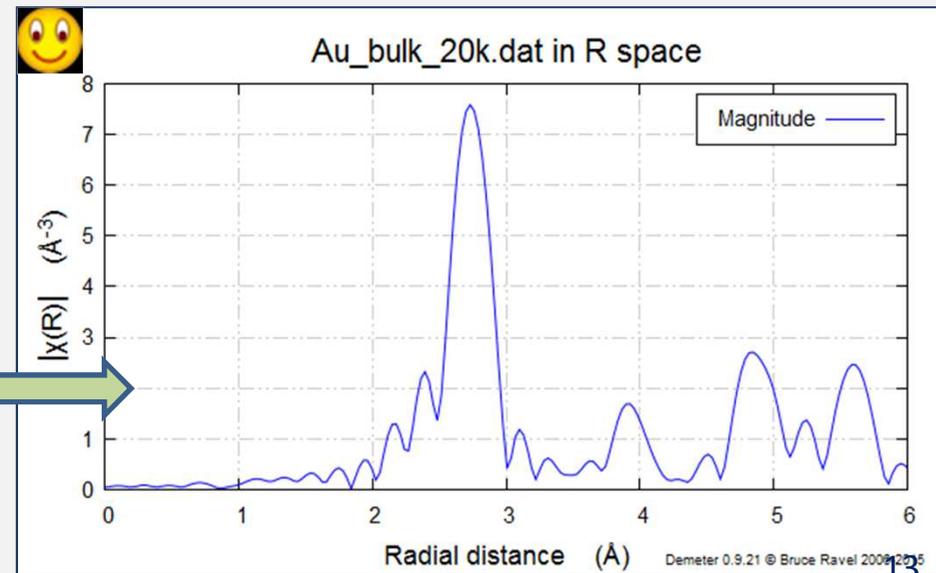
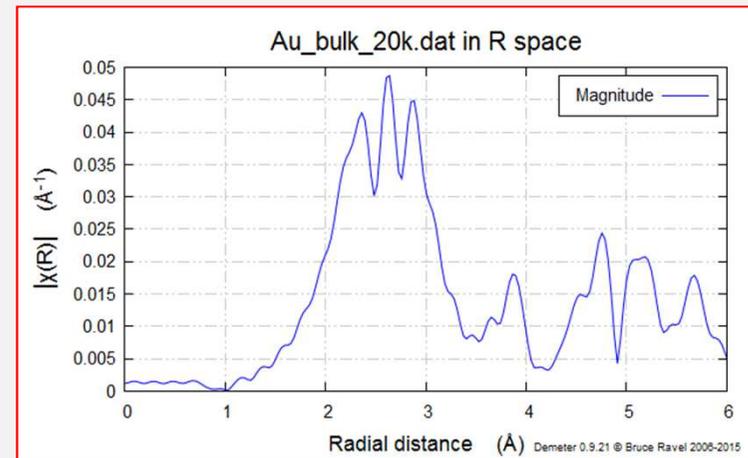
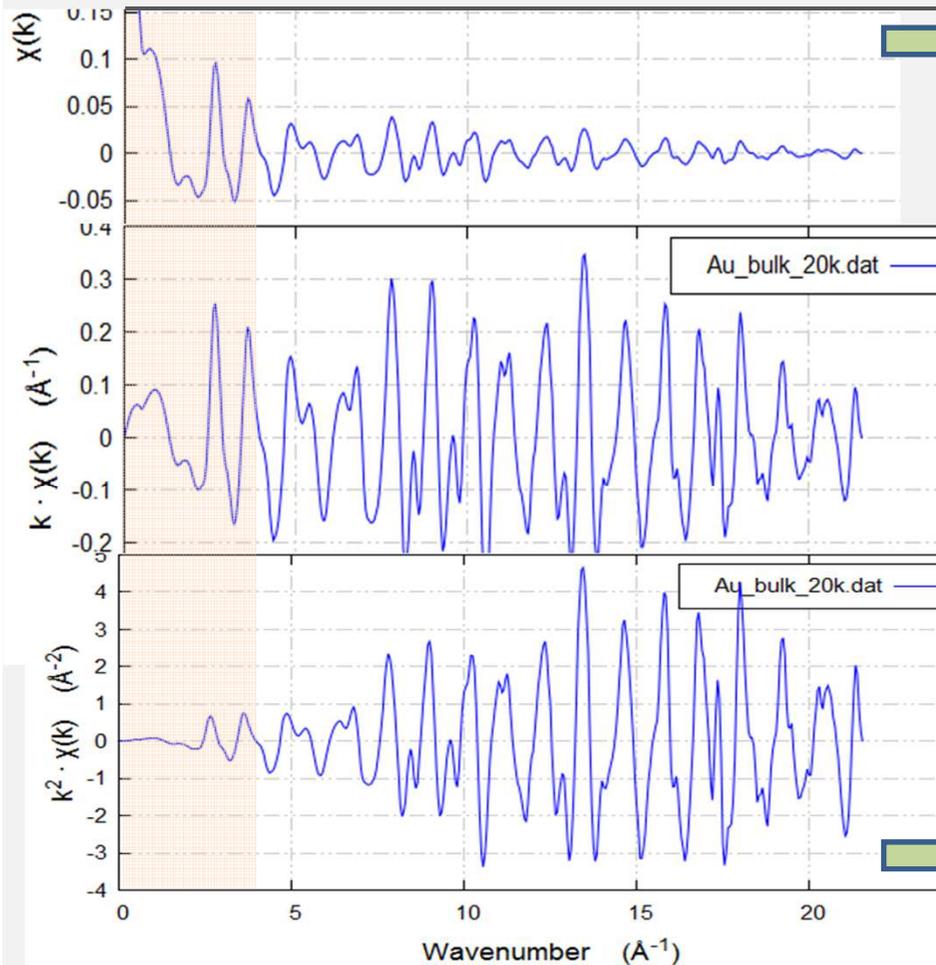
Quality of the data



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

# Qualitative local structure

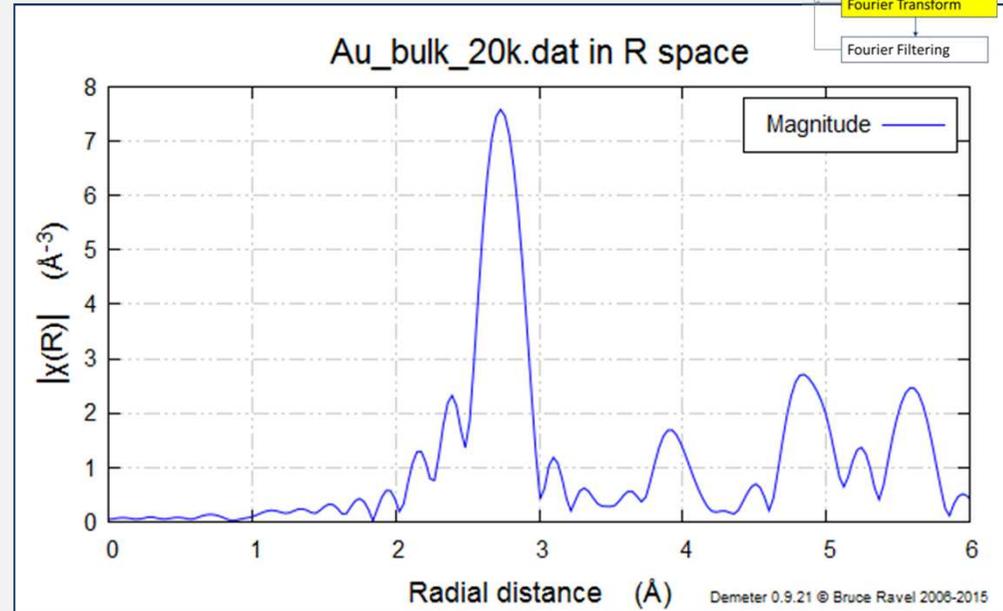
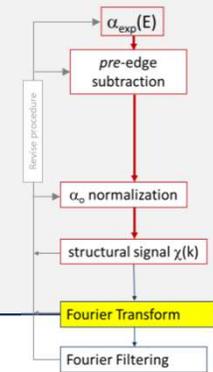
## 3. Fourier transform



# Qualitative local structure

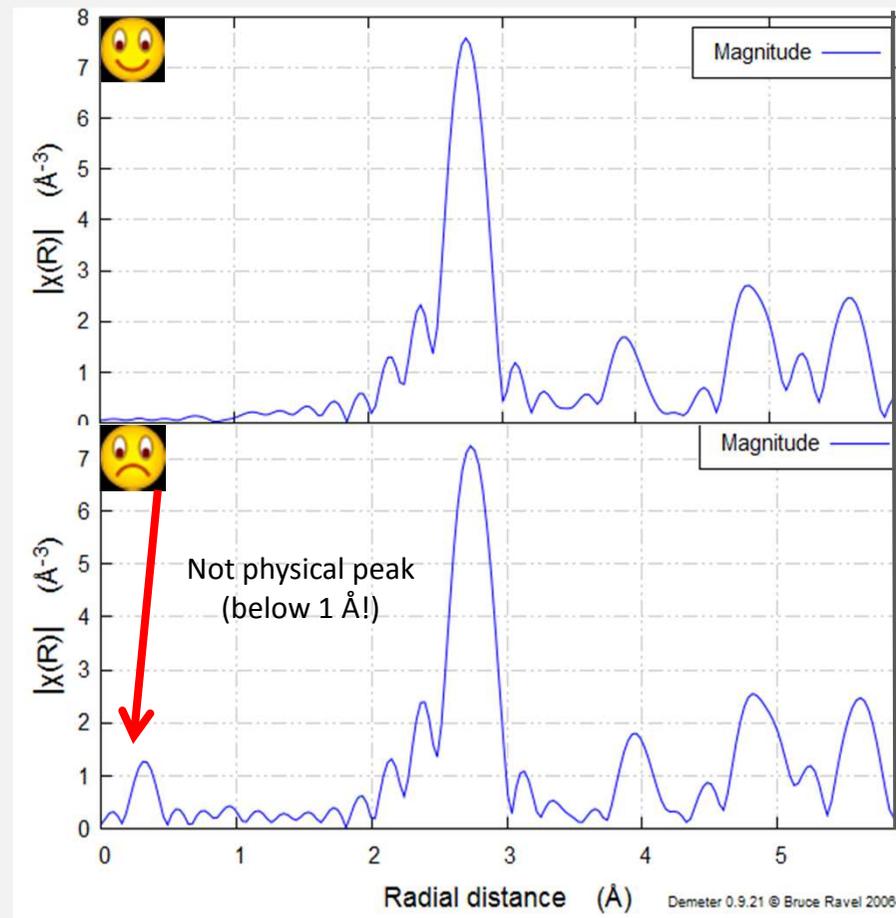
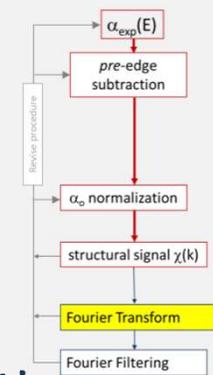
## 3. Fourier transform

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



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

# Check FT



FT features give suggestions about the extraction procedure:

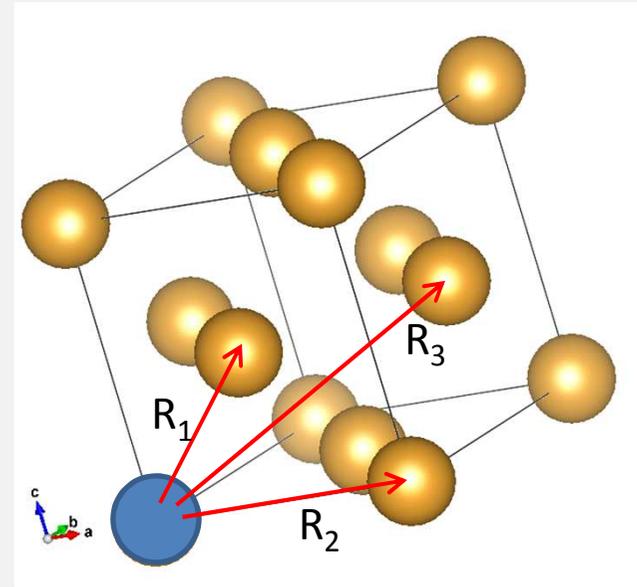
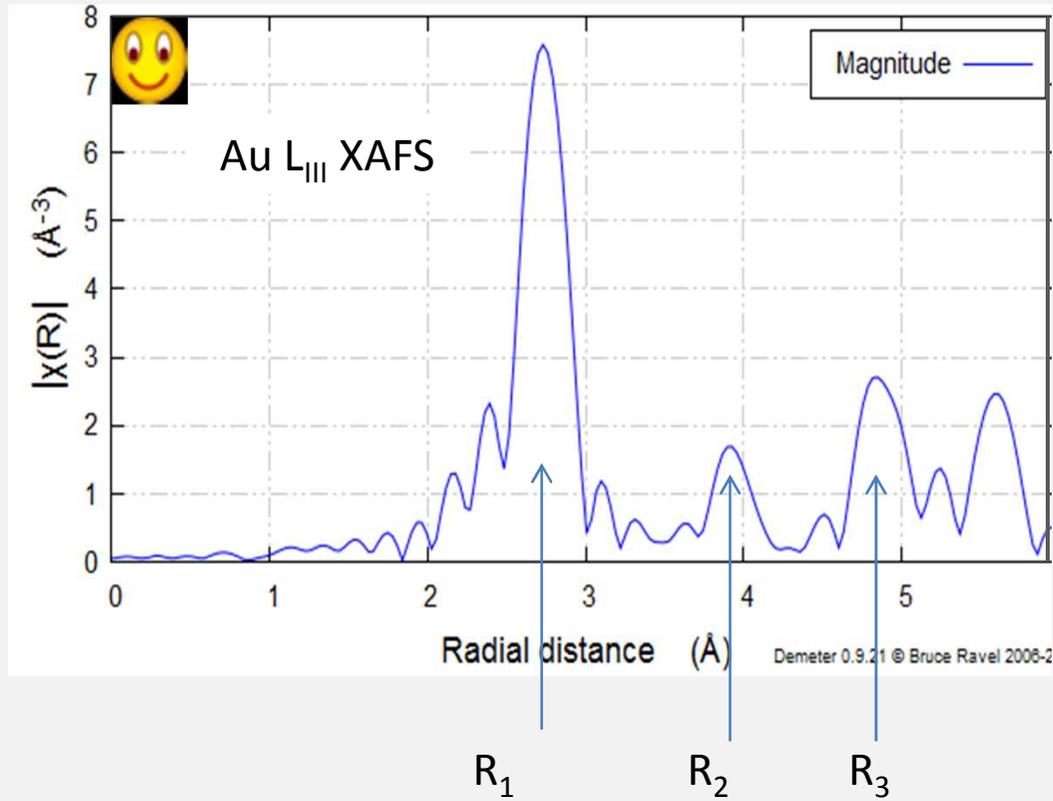
Artifacts, distortions, noise, may suggest bad extraction, noise on the data, etc...

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



# FT and expected atomic structure

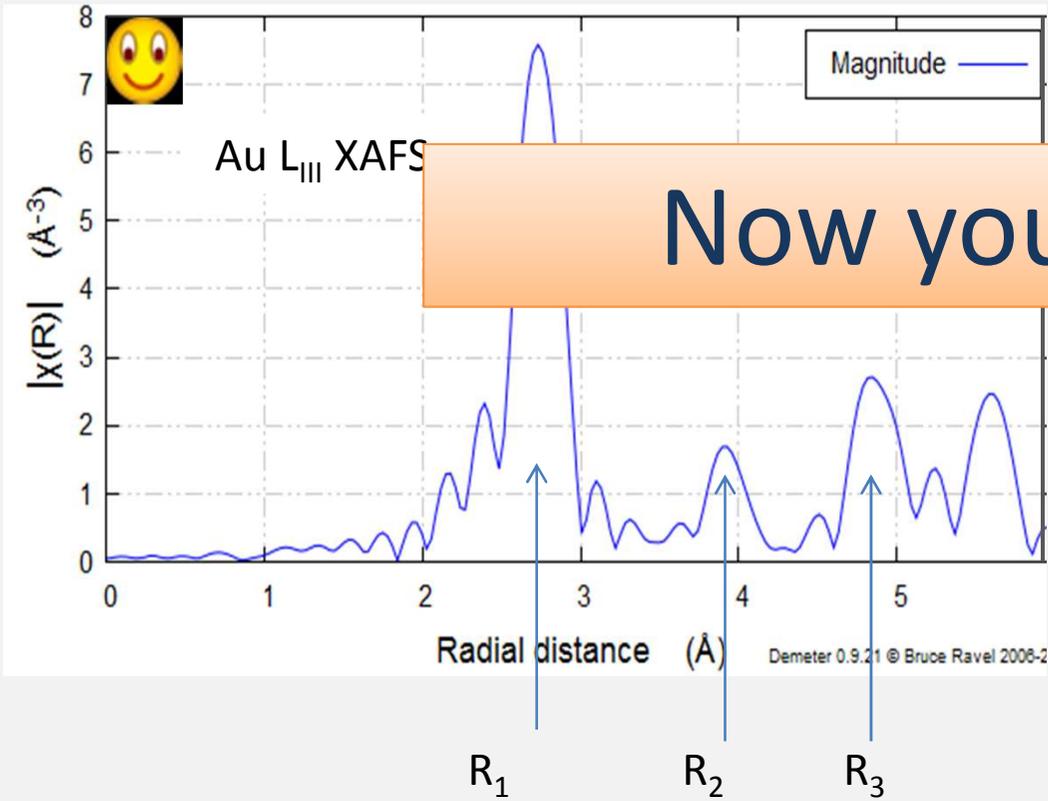
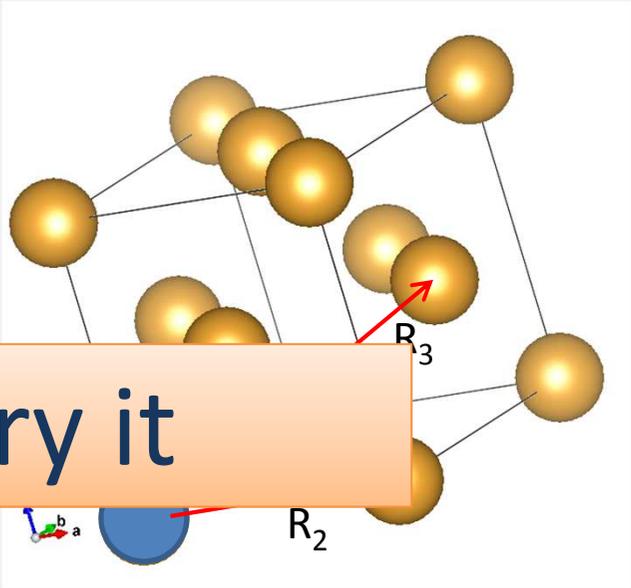
Look at the FT features and compare the structure you expect



$R_1 = a/\sqrt{2}$	$N_1 = 12$
$R_2 = a$	$N_2 = 6$
$R_3 = a\sqrt{6}/2$	$N_3 = 24$

# FT and expected atomic structure

Look at the FT features and compare the structure you expect



Now you try it

$R_1 = a/\sqrt{2}$	$N_1 = 12$
$R_2 = a$	$N_2 = 6$
$R_3 = a\sqrt{6}/2$	$N_3 = 24$



# 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

## Basic features

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

## Modify extraction parameters

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

## k-Weighting

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

## Back Fourier

11. Range and window

The screenshot shows the Athena software interface for XAFS data processing. The main window displays the current group 'cu\_foil\_10k.dat' and various parameters for data extraction and plotting. The interface is annotated with yellow boxes and red arrows pointing to specific features:

- 1**: Points to the 'File' menu.
- 2**: Points to the plot type buttons (E, k, R, q, kq).
- 3**: Points to the 'Current group' field.
- 4**: Points to the 'Edge' dropdown menu.
- 5**: Points to the 'Normalization order' radio buttons.
- 6**: Points to the 'Pre-edge range' input fields.
- 7**: Points to the 'Spline range in k' input fields.
- 8-10**: Points to the 'Forward Fourier transform parameters' section, including 'k-range', 'arbitrary k-weight', and 'window'.
- 11**: Points to the 'Plotting parameters' section, including 'Plot multiplier' and 'y-axis offset'.

The software window shows the following parameters:

- Current group: cu\_foil\_10k.dat
- File: C:\Users\CarloNew\Dropbox\Seminar\_Malu\_2015\dat\Cu\_Foil\cu\_foil\_10k.dat
- Element: 29: Copper
- Edge: K
- Energy shift: 0
- Importance: 1
- Background removal and normalization parameters:
  - E0: 8977.58
  - Rbkg: 1.0
  - Flatten normalized data:
  - Algorithm: Autobk
  - k-weight: 2
  - Normalization order: 3
  - Pre-edge range: -150.000 to -30.000
  - Edge step: 2.3266765
  - Normalization range: 150.000 to 2284.890
  - Spline range in k: 0 to 25.019
  - Spline range in E: 0 to 2384.8608
  - Spline clamps: low (None), high (Strong)
- Standard: None
- Forward Fourier transform parameters:
  - k-range: 3.000 to 23.019
  - dk: 1
  - window: Hanning
  - arbitrary k-weight: 0.5
  - phase correction:
- Backward Fourier transform parameters:
  - R-range: 1 to 3
  - dR: 0.0
  - window: Hanning
- Plotting parameters:
  - Plot multiplier: 1
  - y-axis offset: 0

The plot area on the right shows the 'Plot in R-space' section with the following options:

- Magnitude
- Envelope
- Real part
- Imag. part
- Phase
- Window

Plotting k-weights:  0  1  2  3  kw

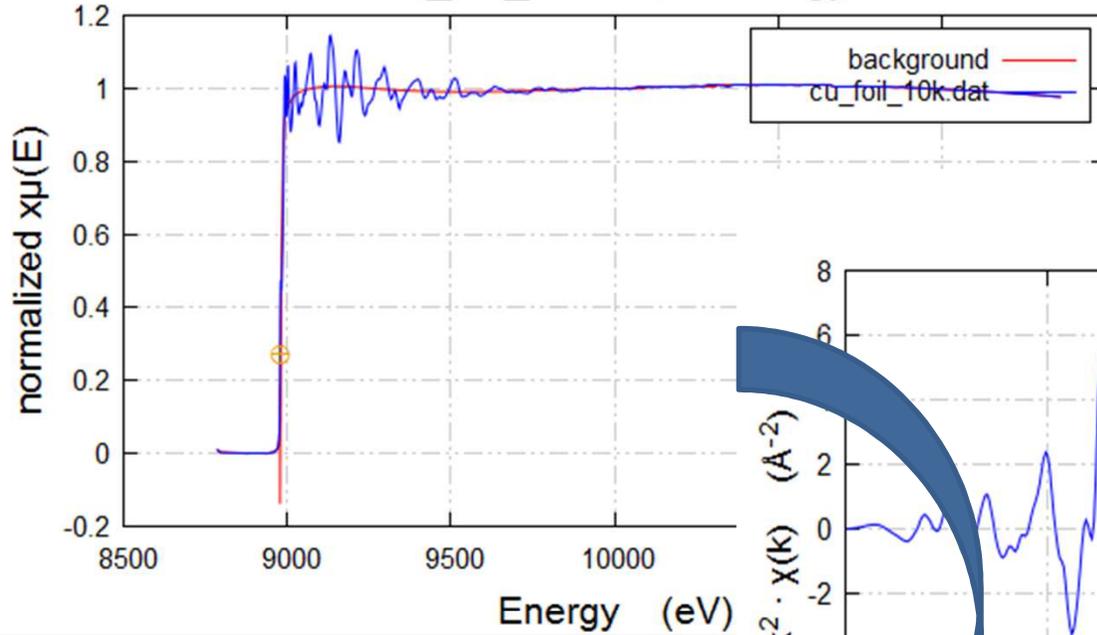
Rmin: 0 Rmax: 6

Imported cu\_foil\_10k.dat from C:\Users\CarloNew\Dropbox\Seminar\_Malu\_2015\dat\Cu\_Foil\cu\_foil\_10k.dat

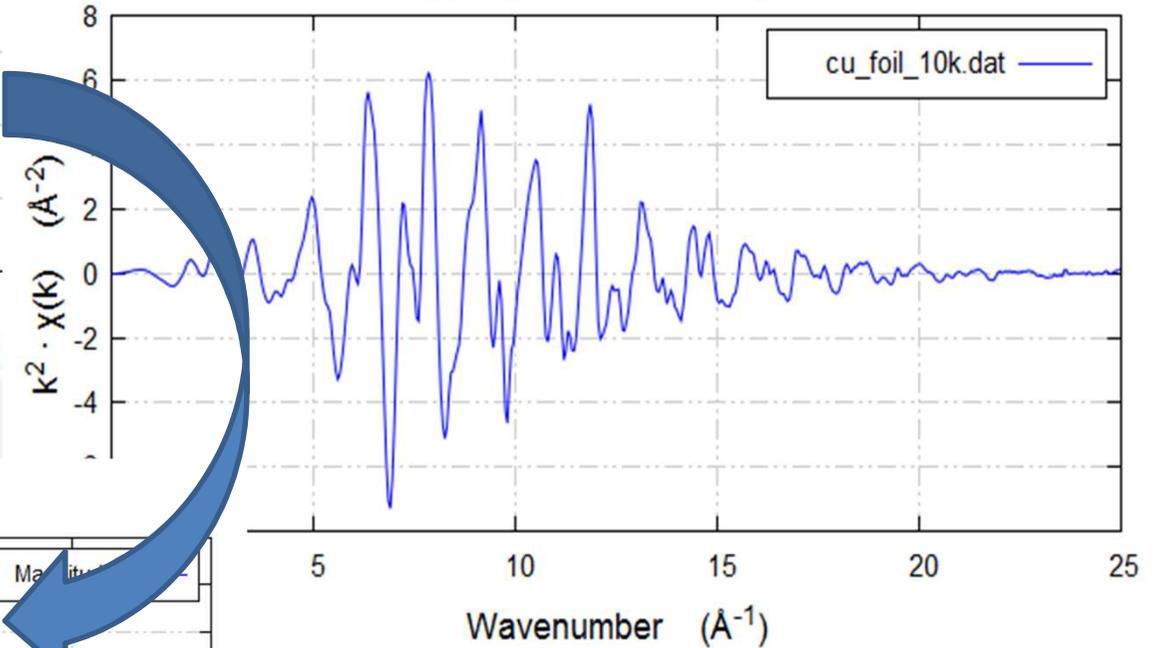


# Cu K edge XAFS

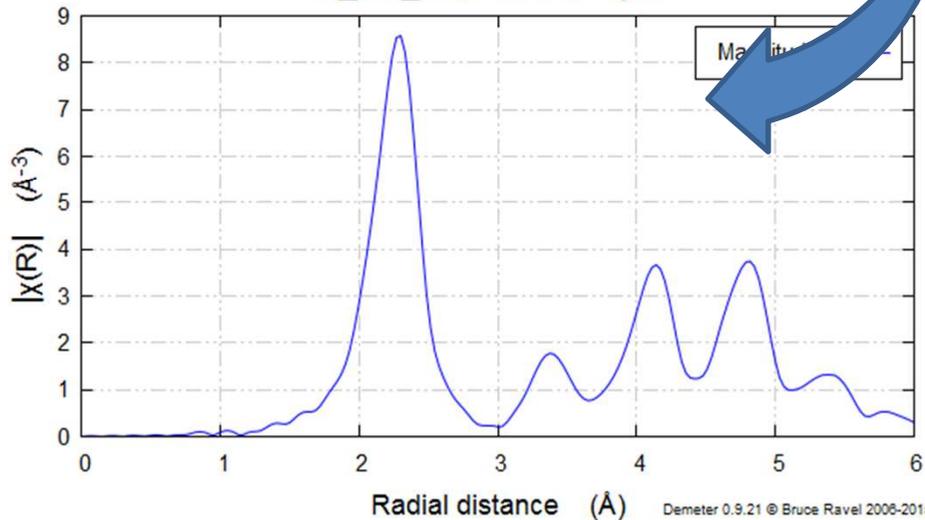
cu\_foil\_10k.dat in energy



cu\_foil\_10k.dat in k space

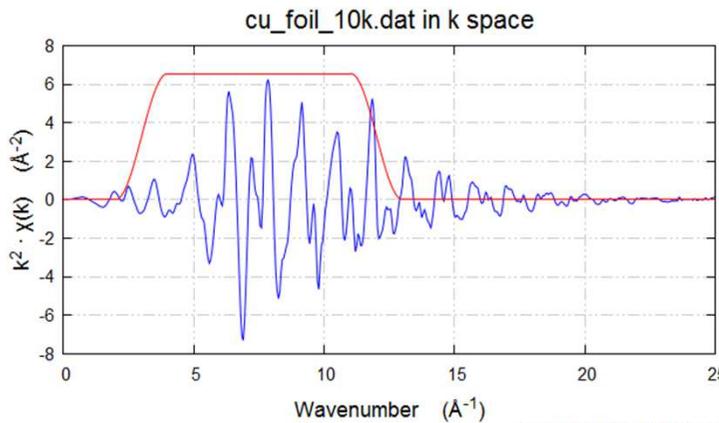
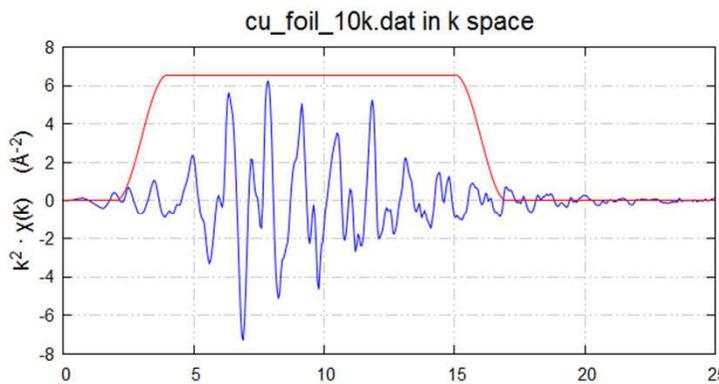
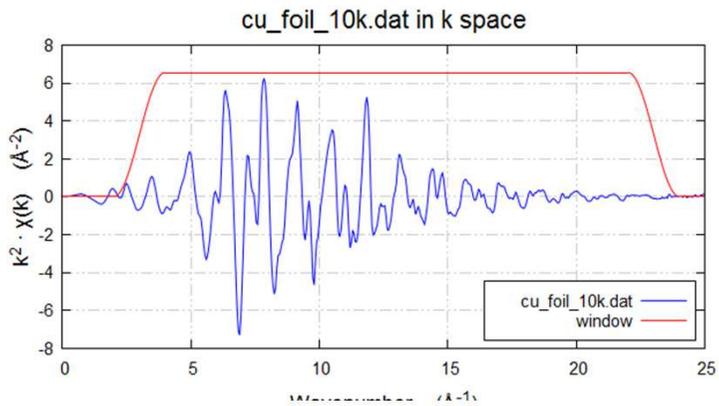


cu\_foil\_10k.dat in R space

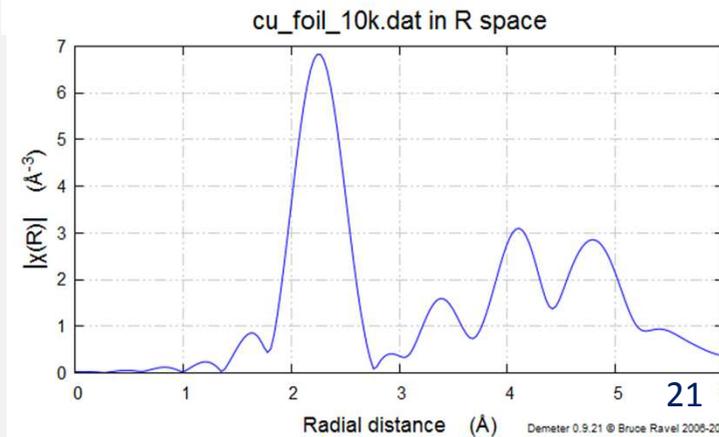
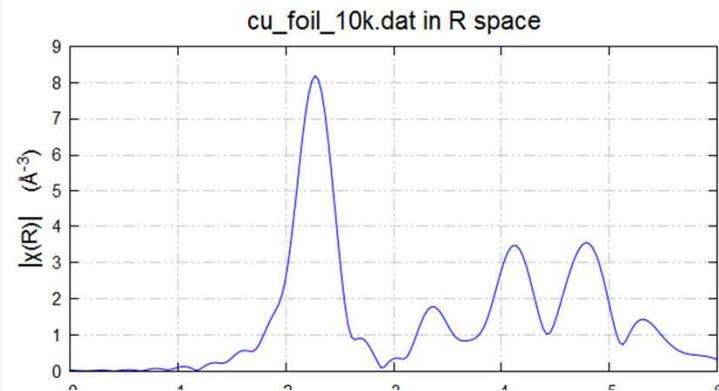
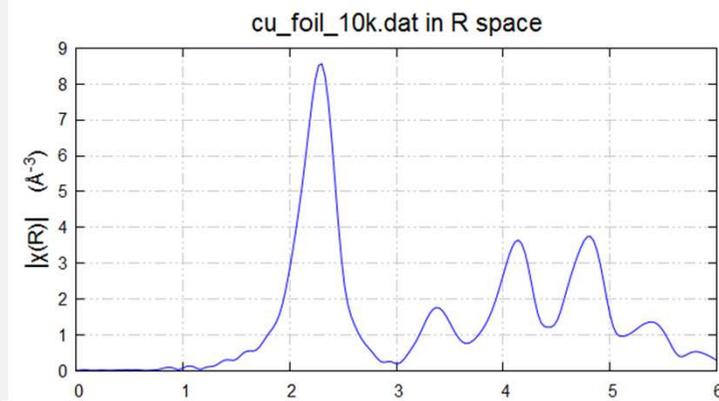


Demeter 0.9.21 © Bruce Ravel 2006-2015

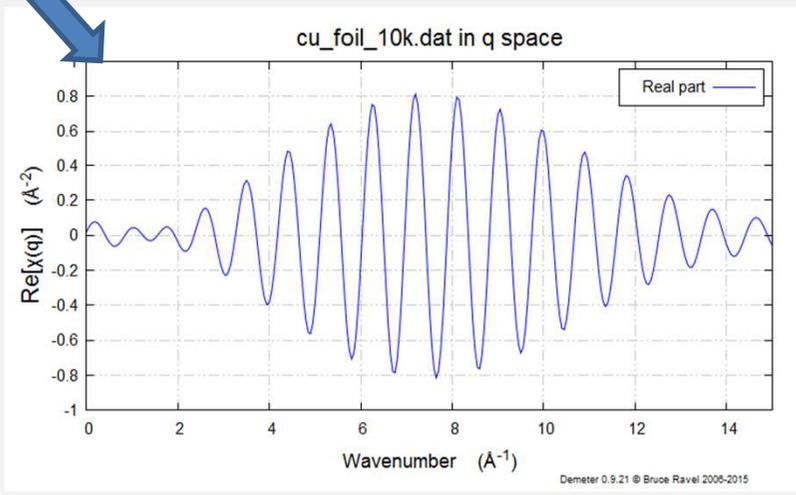
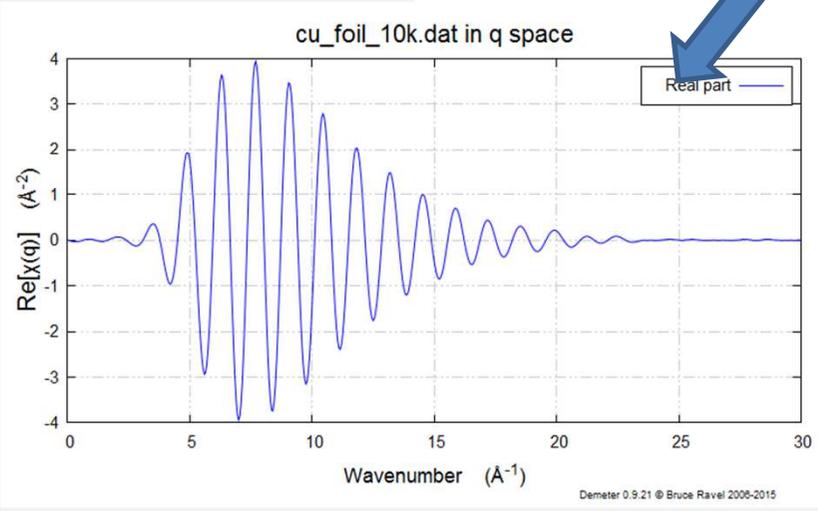
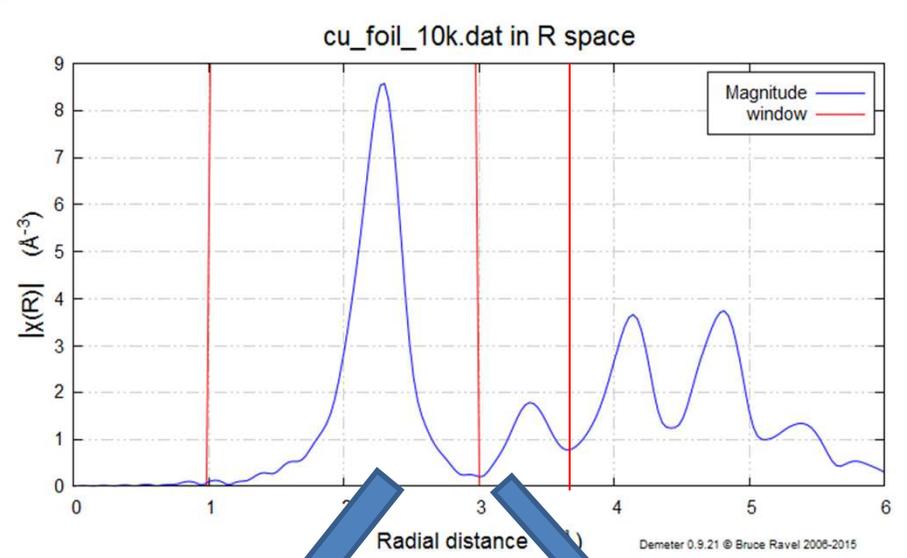
# FT window



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

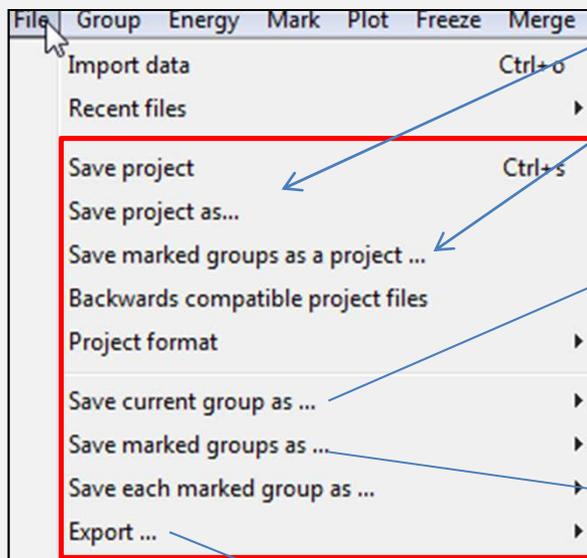
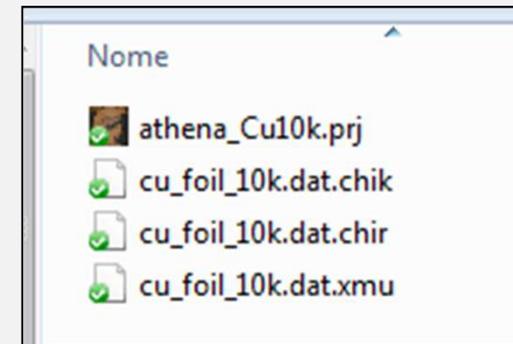


# Back-Fourier info



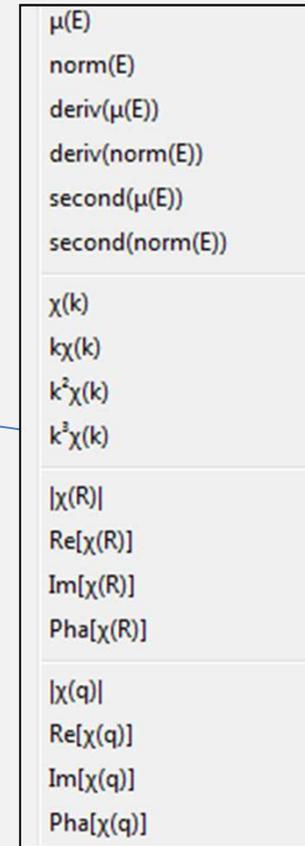
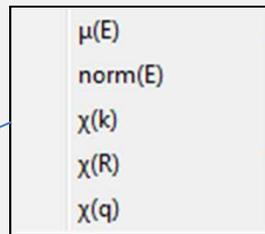
**Note:**

Always save data and project for future use  
you have many options!



Save the entire project for reuse.

Save selected groups for separate use

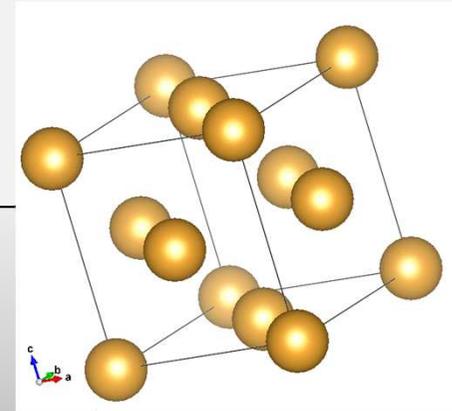


## 2. Au $L_{III}$ edge XAFS

Open [Au Foil.zip](#)

Import Au\_bulk\_20k.dat

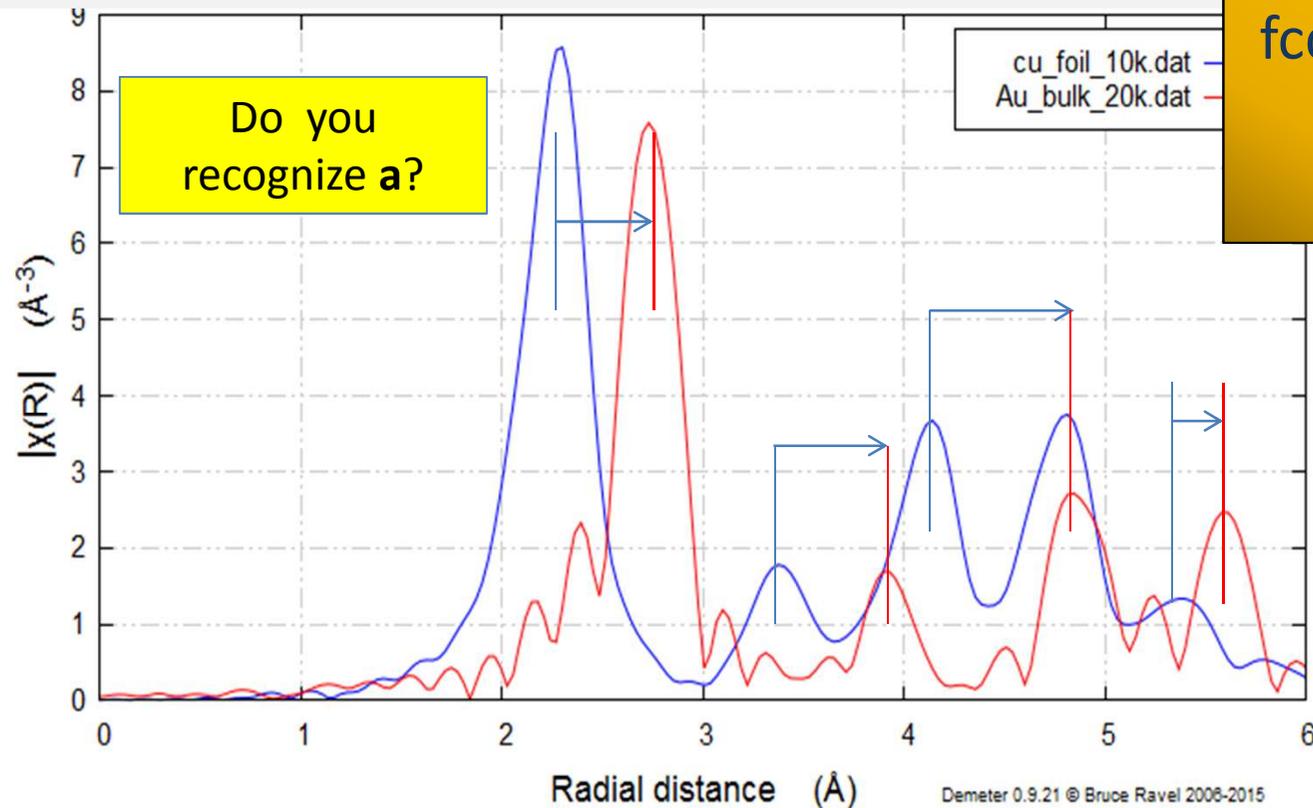
1. compare FT data for Cu and Au samples.



Au and Cu have  
fcc structure but:

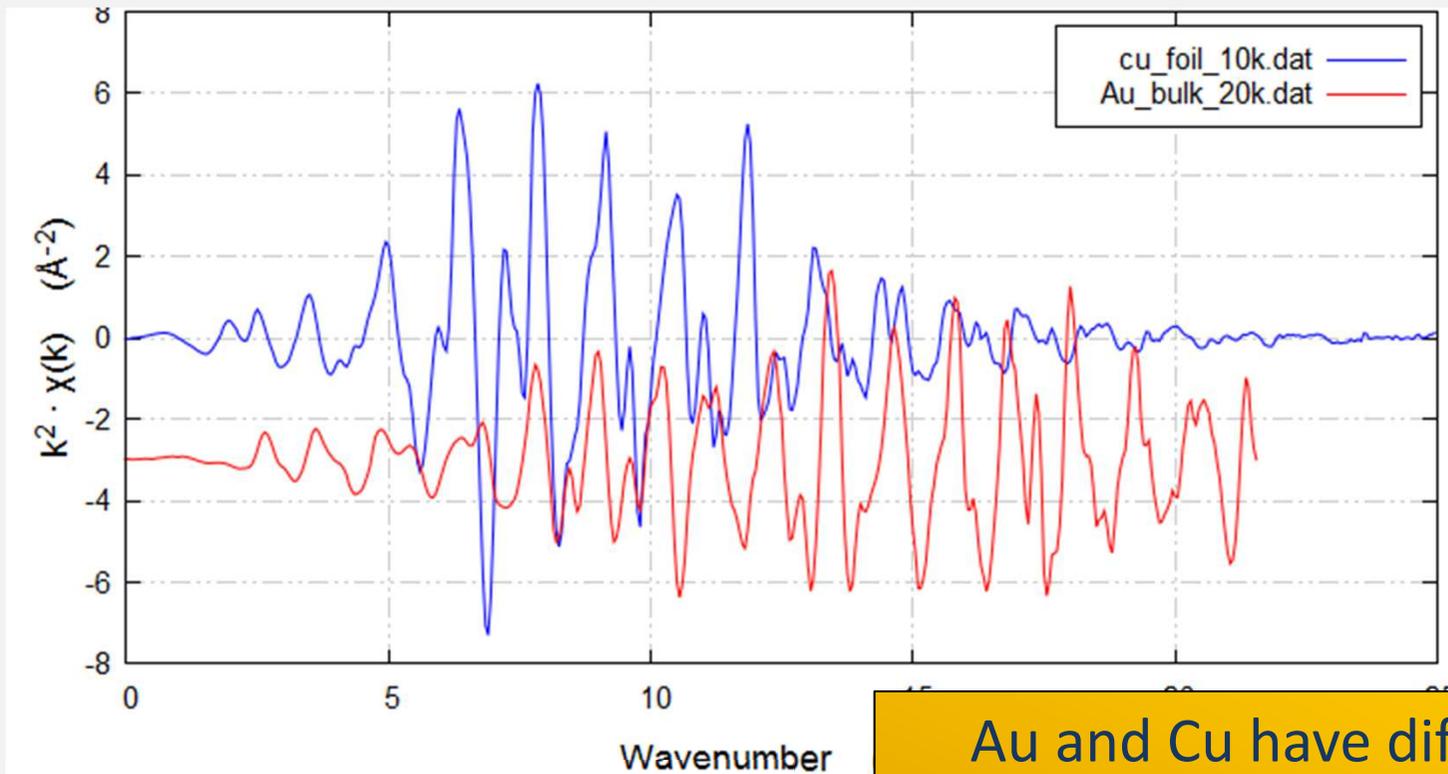
$$a_{Cu} = 3.61 \text{ \AA}$$

$$a_{Au} = 4.07 \text{ \AA}$$



# Au L<sub>III</sub> edge XAFS

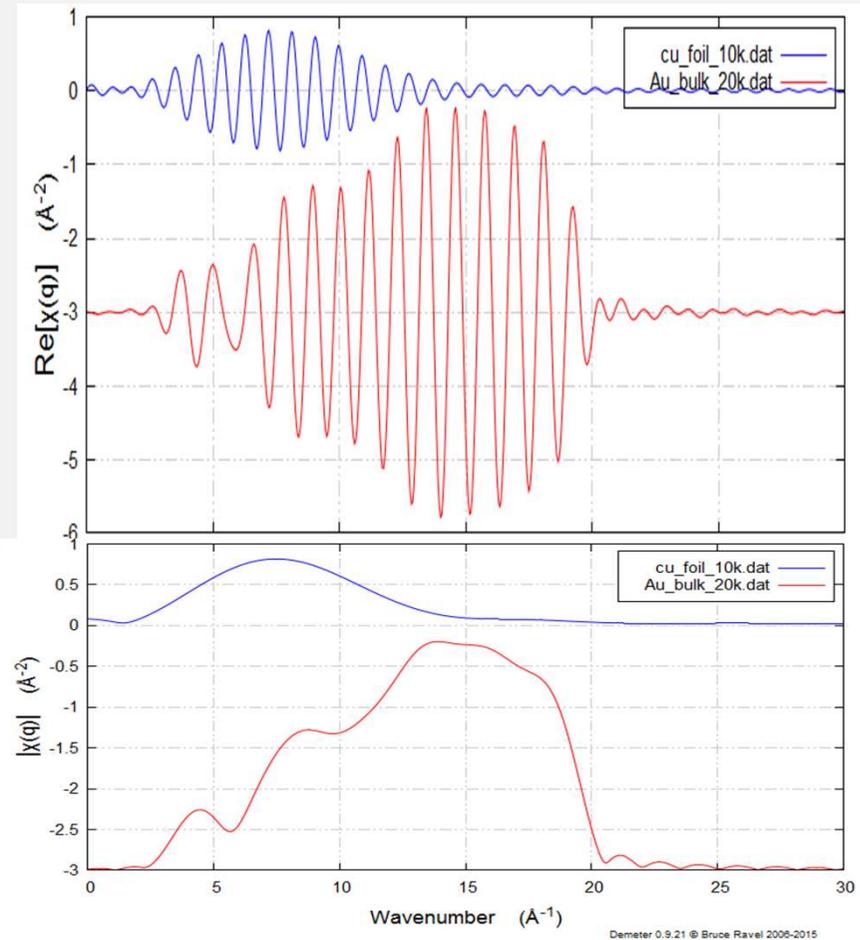
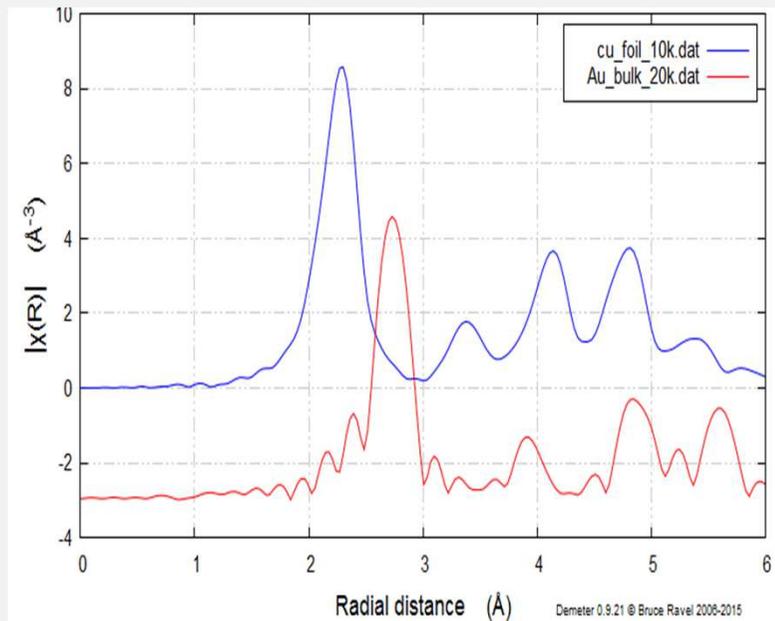
2. compare EXAFS spectra for Cu and Au samples.



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

Au and Cu have different  
Amplitude (A) and phase ( $\psi$ )  
functions:  
chemical selectivity

## 2. compare Back FT for Cu and Au samples.

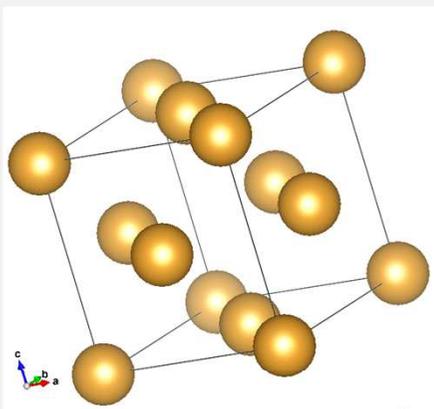


Au and Cu have different  
Amplitude (A) and phase ( $\psi$ )  
functions:  
chemical selectivity

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

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

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



**fcc**  
**(Fm-3m)**

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

$$R_2 = a \quad N_2 = 6$$

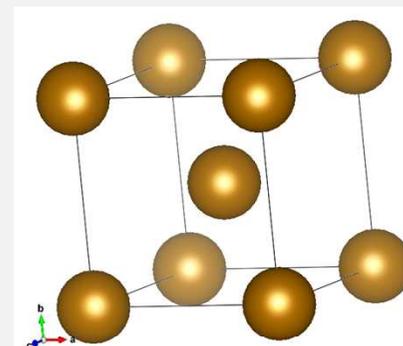
$$R_3 = a\sqrt{6}/2 \quad N_3 = 24$$

**Bcc**  
**(Im3m)**

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

$$R_2 = a \quad N_2 = 6$$

$$R_3 = a\sqrt{2} \quad N_3 = 12$$



$a_{Cu} = 3.61 \text{ \AA}$

$a_{Fe} = 2.86 \text{ \AA}$

