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# Tutorial on XAFS data Analysis

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**“Gilberto Vlaic” XVII School on  
Synchrotron Radiation: Fundamentals,  
Methods and Applications**

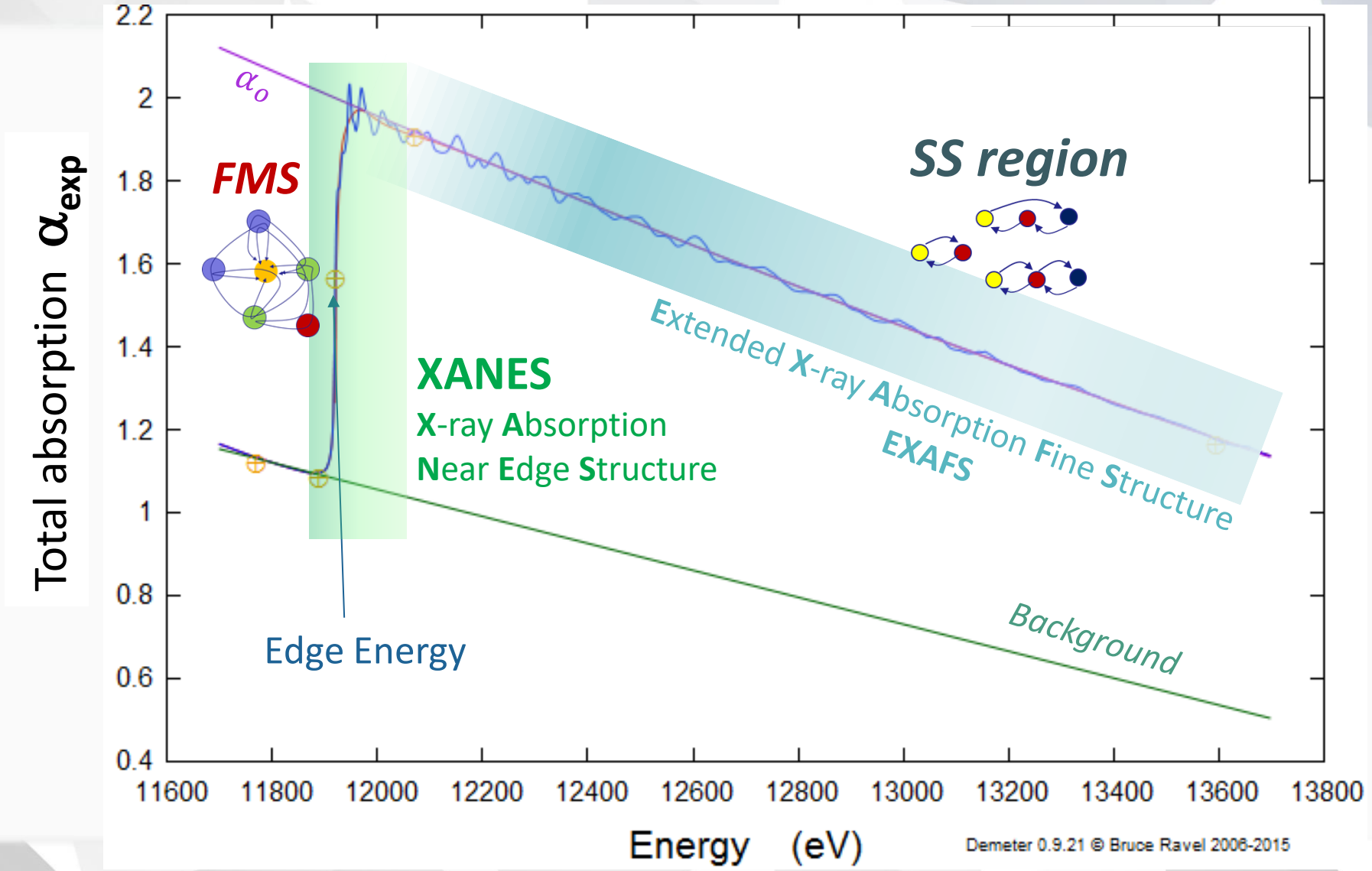
*Muggia (Italy), 16 - 26 September 2024*



ROMA  
TRE  
UNIVERSITÀ DEGLI STUDI



# The XAS spectrum





# Software

## Mandatory

- **XAFS data analysis software** (Demeter)
- **Curve fit** (FitYk)
- **Data manipulation** (EXCEL, ORIGIN, Gnuplot, ....)

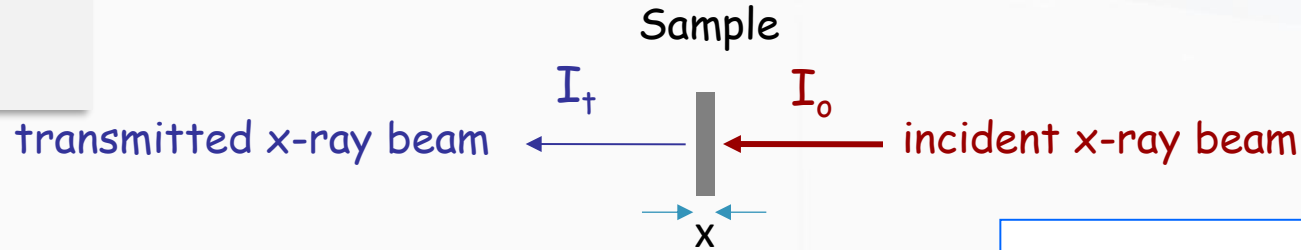
## Useful:

- **Database** of crystallographic structures (WEB)
- Atomic **Structure visualization** programs (VESTA)

# XAFS data collection is *conceptually* simple

Bulk samples  
High concentration  
 $\mu x \sim 0.1 - 1.5$

## Transmission geometry



$$I_t = I_0 e^{-\mu \cdot x}$$

$\mu$  = Linear absorption coefficient

$$\mu x = \ln \frac{I_0}{I_t}$$

Low concentration:  
 $\mu x \ll 0.1$

## Fluorescence geometry

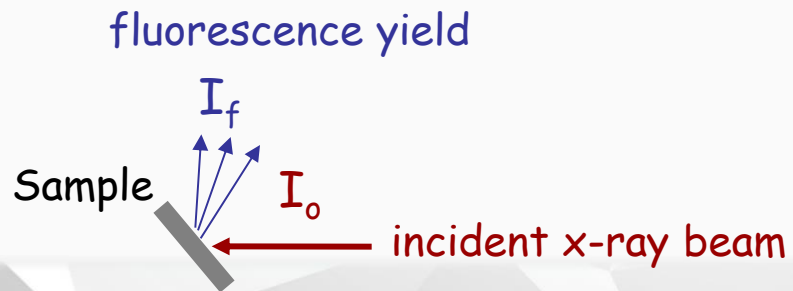
$$I_f \propto I_0 - I_t = I_0(1 - e^{-\mu x})$$

$$\mu \cdot x \ll 1$$

$$e^{-\mu x} \simeq 1 - \mu x$$

$$I_f \simeq I_0 \mu \cdot x$$

$$\mu x \simeq \frac{I_f}{I_0}$$



# File Format: search for the right columns

```

37 # Channel 1: gain 1E07V/A
38 # Channel 2: gain 1E07V/A
39 # Channel 3: gain 1E09V/A
40 # Channel 4: gain 1E09V/A
41 # DCM Crystal: Si111
42 #enc_energy mono_energy mono_bragg Step_Pos mono_Xlvert undulat
43 6963.15265954 6962.02206072 16.5019561813 898303 10.0639281062
44 6963.18693091 6962.09736453 16.5017999313 898260 10.0639158992
45 6963.3150513 6962.21432913 16.5015030563 898187 10.0639027156 7
46 6963.39128526 6962.31527448 16.5012569626 898120 10.0638900203
47 6963.46688033 6962.41622289 16.5010108688 898061 10.0638787898
    
```

$\mu$  absorption signal measured in fluorescence geometry

Energy  $I_o$   $I_{trasm}$  and/or  $I_{fluo}$

Energy and detector Intensities for Transmission or fluorescence

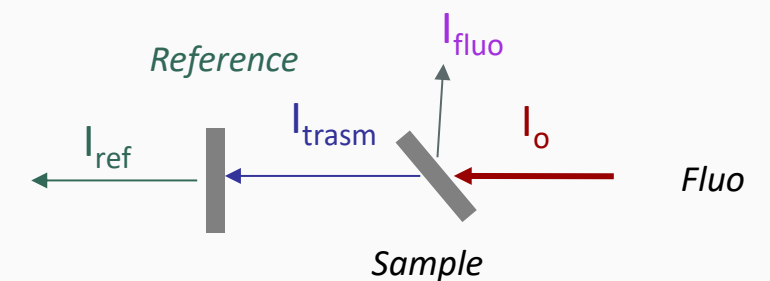
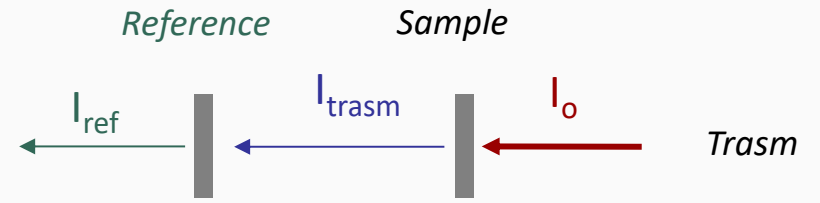
$I_{ref}$

Reference signal, for energy calibration

$$\ln\left(\frac{I_o}{I_{trasm}}\right) \quad \ln\left(\frac{I_{trasm}}{I_{ref}}\right) \quad \frac{I_{fluo}}{I_o}$$

$\mu$  absorption signal

$\mu_{ref}$  ref absorption signal



# XAFS data analysis Software


## IXAFS organization

IXAS RESOURCES

- XAS Research Review
  - About Web Magazine
  - Current Issue
  - Future Issue
  - Publishing Policy
  - Manuscript Submission
  - Manuscript Template
  - Editors
- News
- IXAS Info Plaza
  - Events
  - Job and Fellowship Info
  - FL Info Plaza
- Archives
- Related Organizations
- Links to SR facilities
- Database
- Supporting Corporations
- XAFS Conferences
  - Previous XAFS Conferences
  - Recent Trends
  - Scientific Trends
  - XAFS 15 (2012)
  - XAFS 16 (2015)
  - XAFS 17
  - Photo Gallery
- Books and Codes ←
- Miscellaneous
- Standardization
  - XAFS Standards & Criteria –Background
  - IXAS Strategy toward Standardization
  - Data Format
- Tutorial materials ←

- Easy to use (**not on Mac-OS!**)
- free
- based on FEFF6 and IFEFFIT

Demeter



X-ray Absorption Spectroscopy Using Feff and Iffeffit.

Windows Users:

[View On GitHub](#)

Demeter © 2006-2015 Bruce Ravel

[bruceravel.github.io/demeter/](http://bruceravel.github.io/demeter/)

Simple and easy to use data analysis software, freeware, based on FEFF6 and IFEFFIT

Download and install it



Google search:

[demeter EXAFS](#)

# GnXAS Software

## INTRODUCTION to GNXAS

[http://gnxas.unicam.it/pag\\_gnxas.html](http://gnxas.unicam.it/pag_gnxas.html)

The GNXAS package is an advanced software for EXAFS data analysis based on multiple-scattering (MS) calculations and a rigorous fitting procedure of the raw experimental data. The main characteristics of the software are:

- atomic phase shifts calculations in the muffin-tin approximation based on atom self-consistent relativistic calculations. Account for the neighbors is taken.
- Inclusion of inelastic losses through complex Hedin-Lundqvist potential.
- Calculation of MS signals associated with two, three, and four atom configurations using advanced algorithms.
- Use of an advanced fitting procedure that allows:
  - to fit simultaneously any number of spectra containing any number of edges,
  - to use directly the raw data without any pre-analysis,
  - to account for complex background multi-electron excitation features,
  - to use various model peaks for the pair, triplet and quadruplet distribution functions, including non Gaussian models and extremal cases. In all cases absolute parameters can be fitted,
  - to treat liquid phase or disordered systems and extract reliable  $g(r)$  functions in the short range,
  - to perform a rigorous statistical error analysis and plot two-dimensional correlation maps,
  - To provide a flexible scientific tool for EXAFS data analysis where the user has access to every stage of the calculation. **GNXAS is not a black box.**

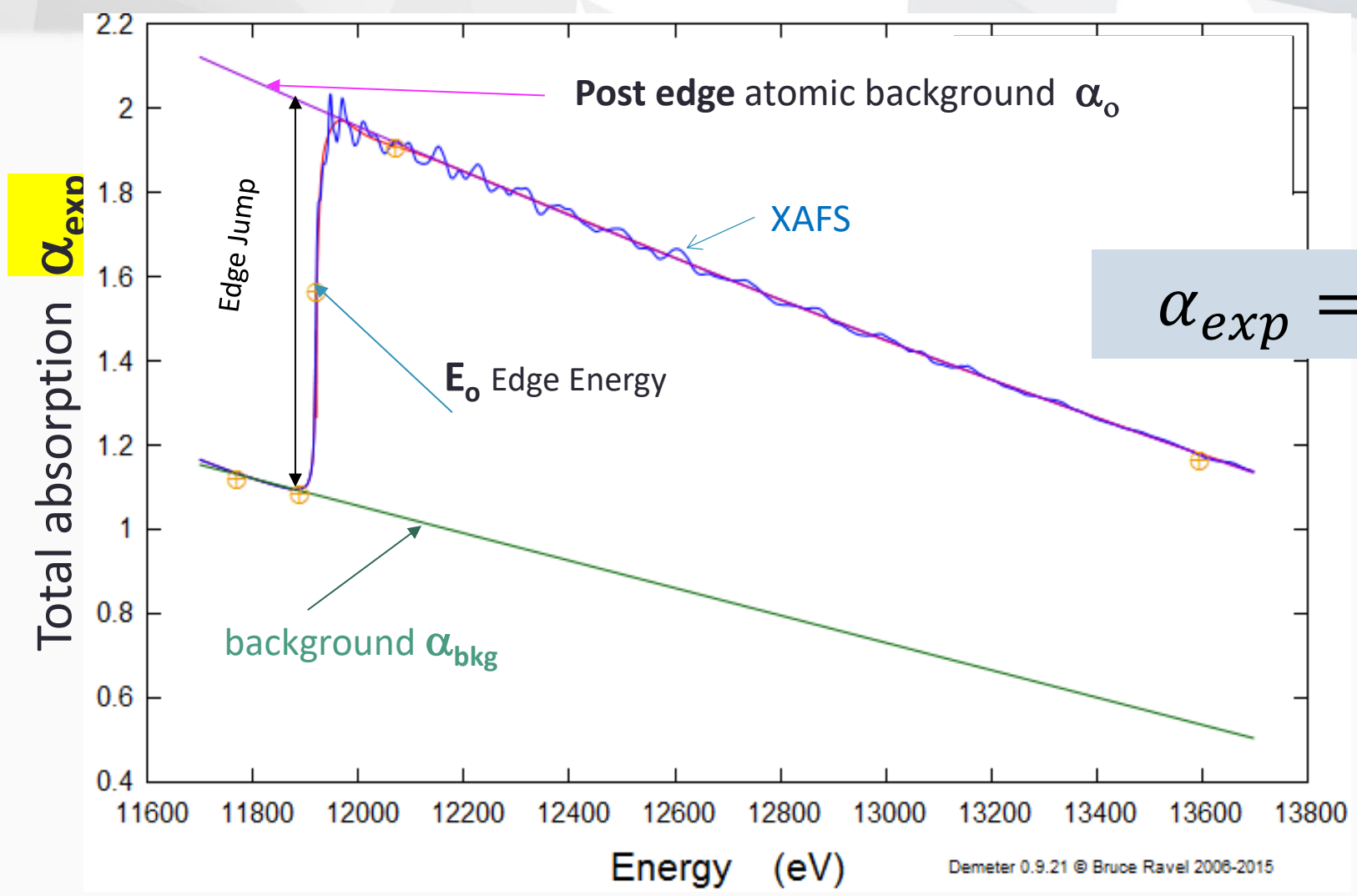


The analysis of uncertainties and error bars is a key issue for reliable understanding and discussion of XAFS results.





# The Experimental XAS signal $\alpha_{exp}$



- Sample holder
- Container
- Windows
- Air
- Other edges
- ....

$$\alpha_{exp} = \mu_x t + \text{All the rest}$$

**x: the edge of interest**  $\alpha_{bkg}$

$$\alpha_{exp}^{Trsm} = \ln \left( \frac{I_o}{I_t} \right)$$

$$\alpha_{exp}^{Fluo} = \left( \frac{I_{fluo}}{I_o} \right)$$

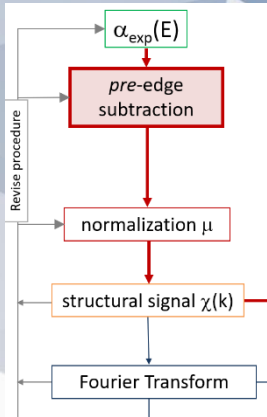
# Normalized XAS $\mu(E)$

## 1. Remove pre-edge

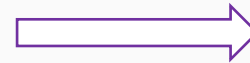
$\mu_x t$  is the absorption due to the edge of interest

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

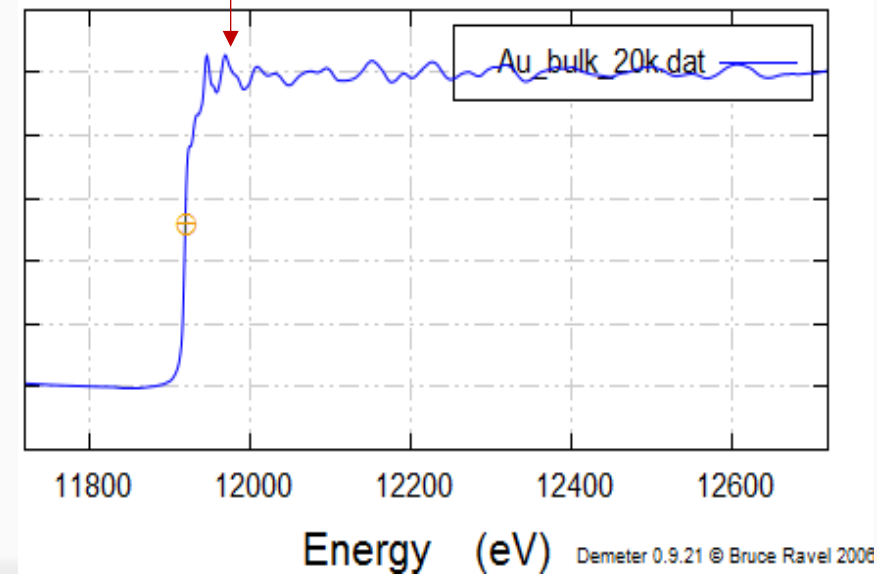
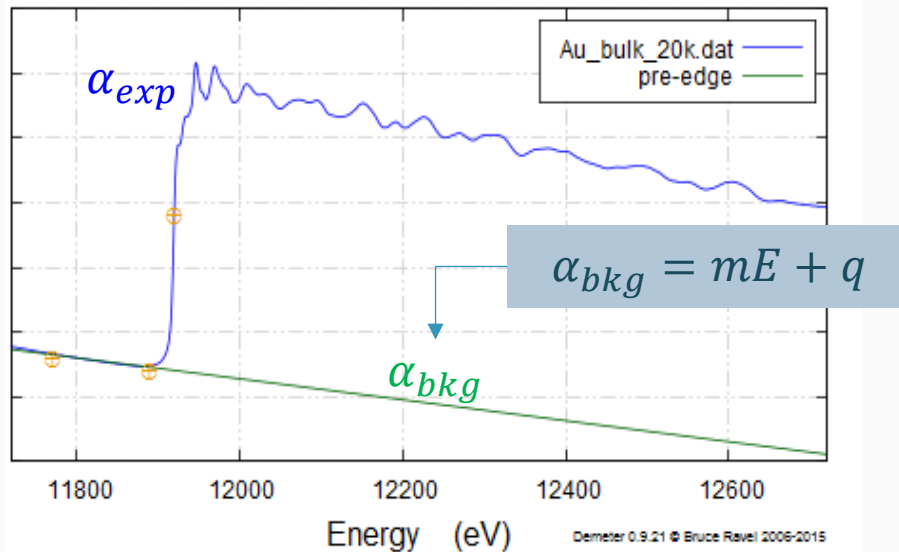
Everything being: other absorption edges, air, sample holder, matrices, chamber windows, etc...



$$\alpha_{exp} = \alpha_x + \alpha_{bkg}$$



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



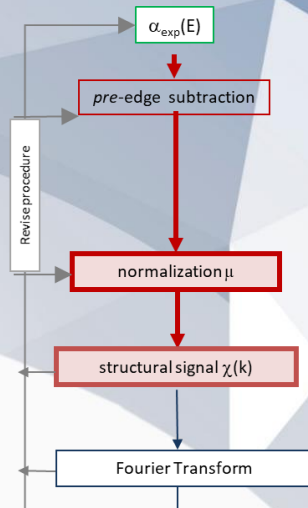
# How to get the normalized $\chi(k)$

## 2. Normalization

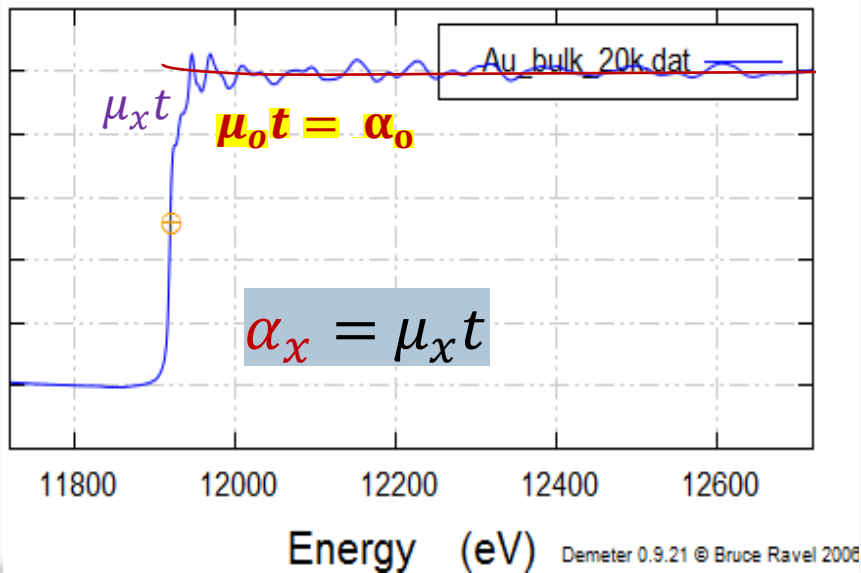
isolated absorber

$$\mu_x t \approx \mu_0 (1 + \chi) t$$

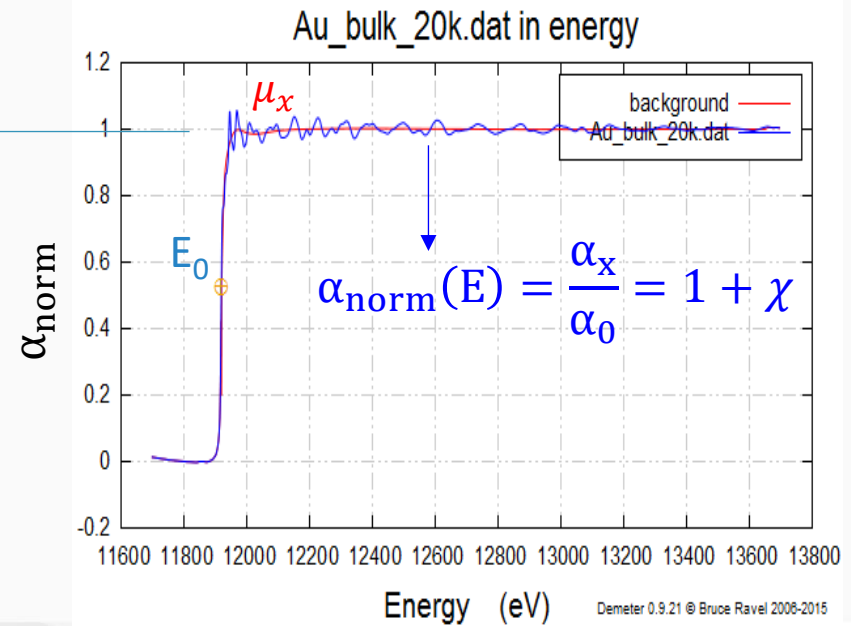
perturbation from neighbour potentials



$$\alpha_{\text{norm}} = \frac{\alpha_x}{\alpha_0} = \frac{\mu_0 (1 + \chi) t}{\mu_0 t}$$



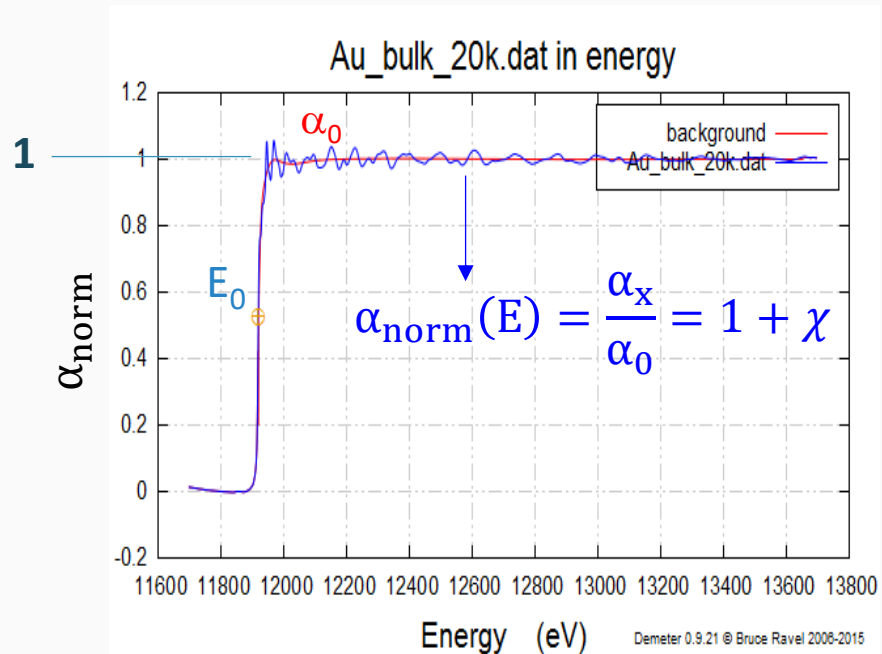
$$\alpha_{\text{norm}} = 1 + \chi$$



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

## 2. Normalization

$$\alpha_{norm} = 1 + \chi$$



$\alpha_0$  is calculated empirically as a smooth curve across the data.

Requirements for  $\alpha_0$ :

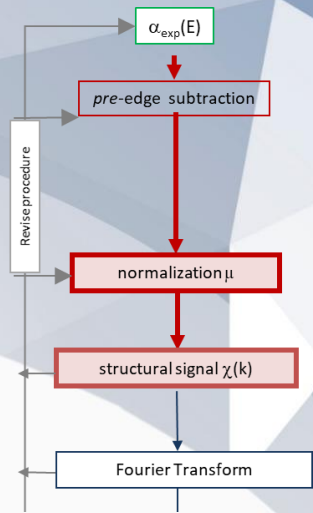
1) Smooth enough

not to remove atomic structure features

2) Structured enough

to remove not structural background

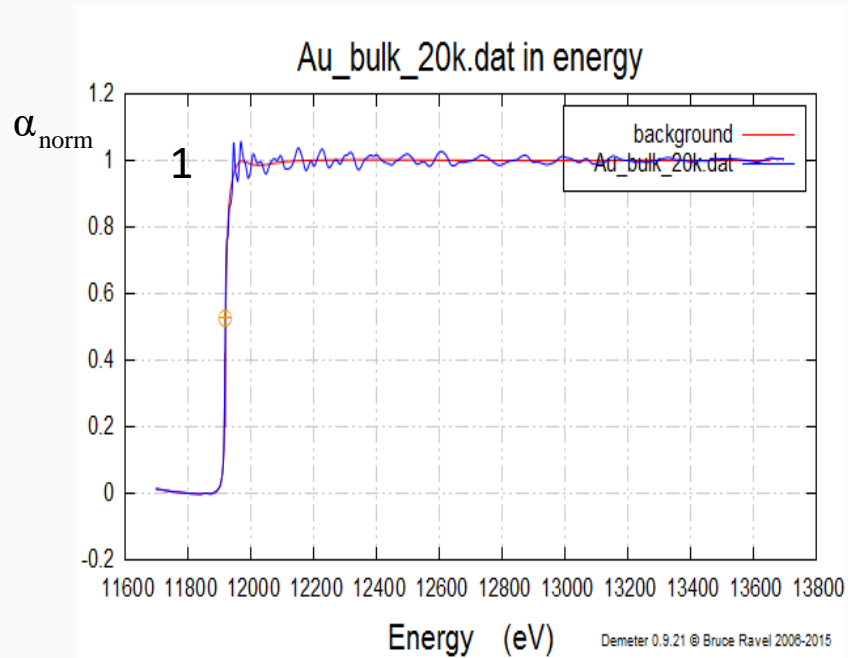
All the programs for XAFS data analysis calculate  $\alpha_0$  applying **different** but **equivalent** methods



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

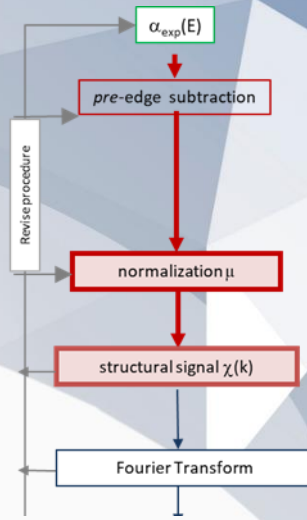
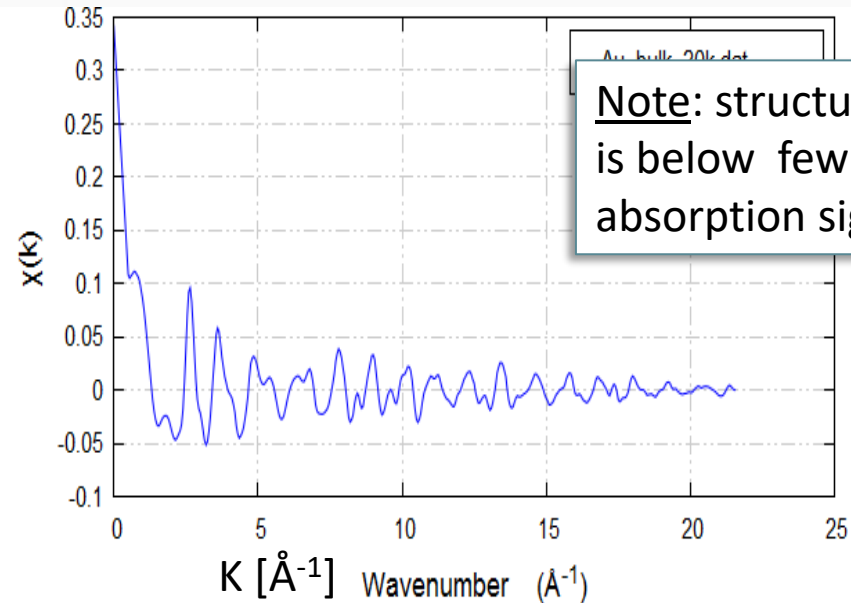
## 3. the structural EXAFS signal $\chi$

$$\alpha_{norm} = (1 + \chi)$$



$\chi$  = EXAFS structural signal

$$\chi = 1 - \alpha_{norm}$$

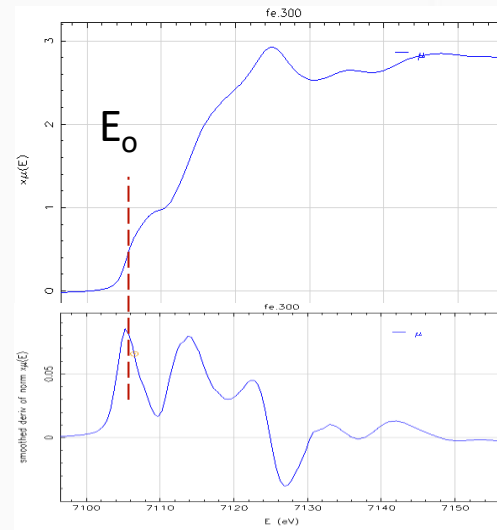
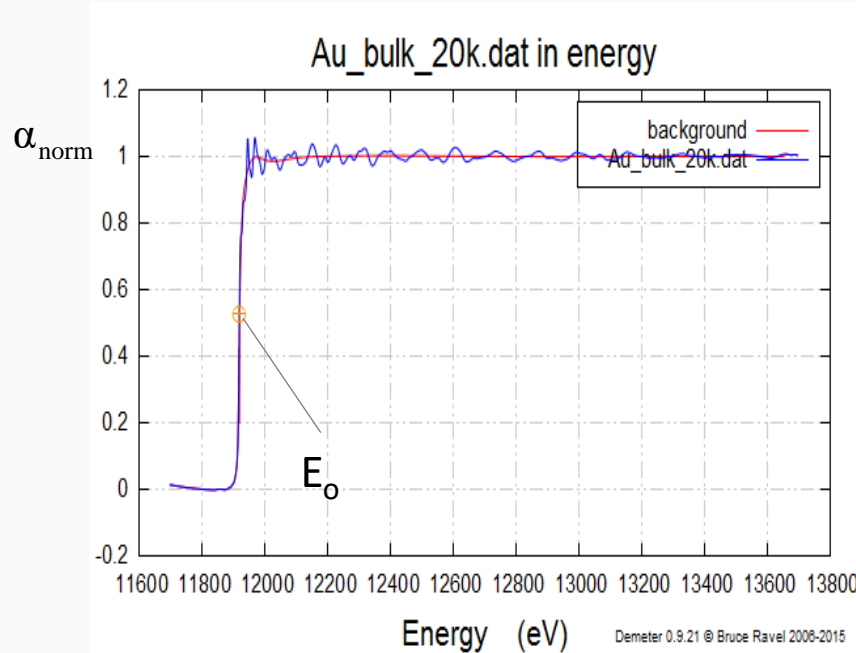
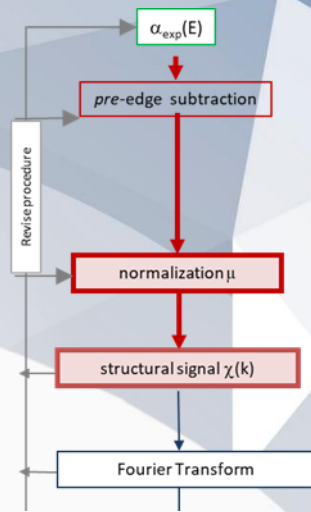


# How to get the normalized $\chi(k)$

## 4. the photoelectron wave vector $k$

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

$$k = \frac{1}{\hbar} \sqrt{2m_e(E - E_0)}$$



Edge energy is selected (*roughly*)

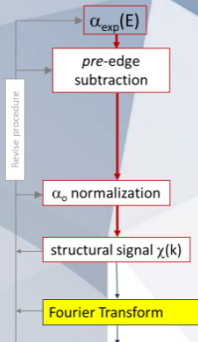
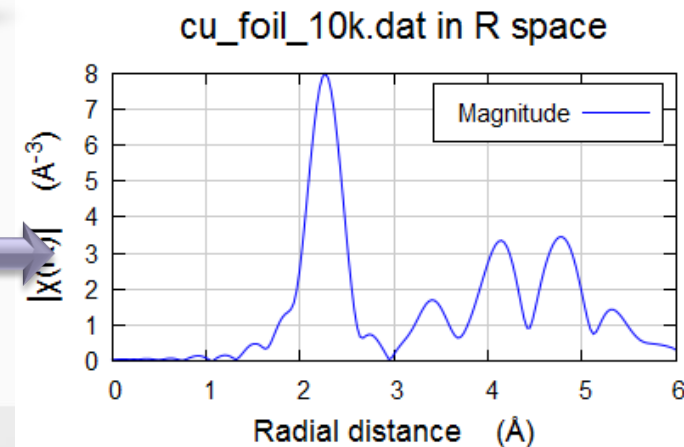
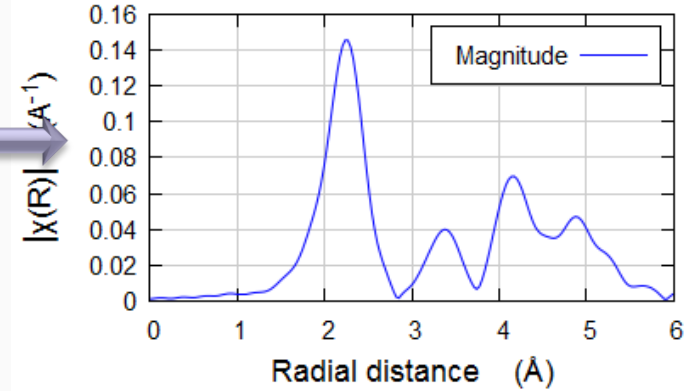
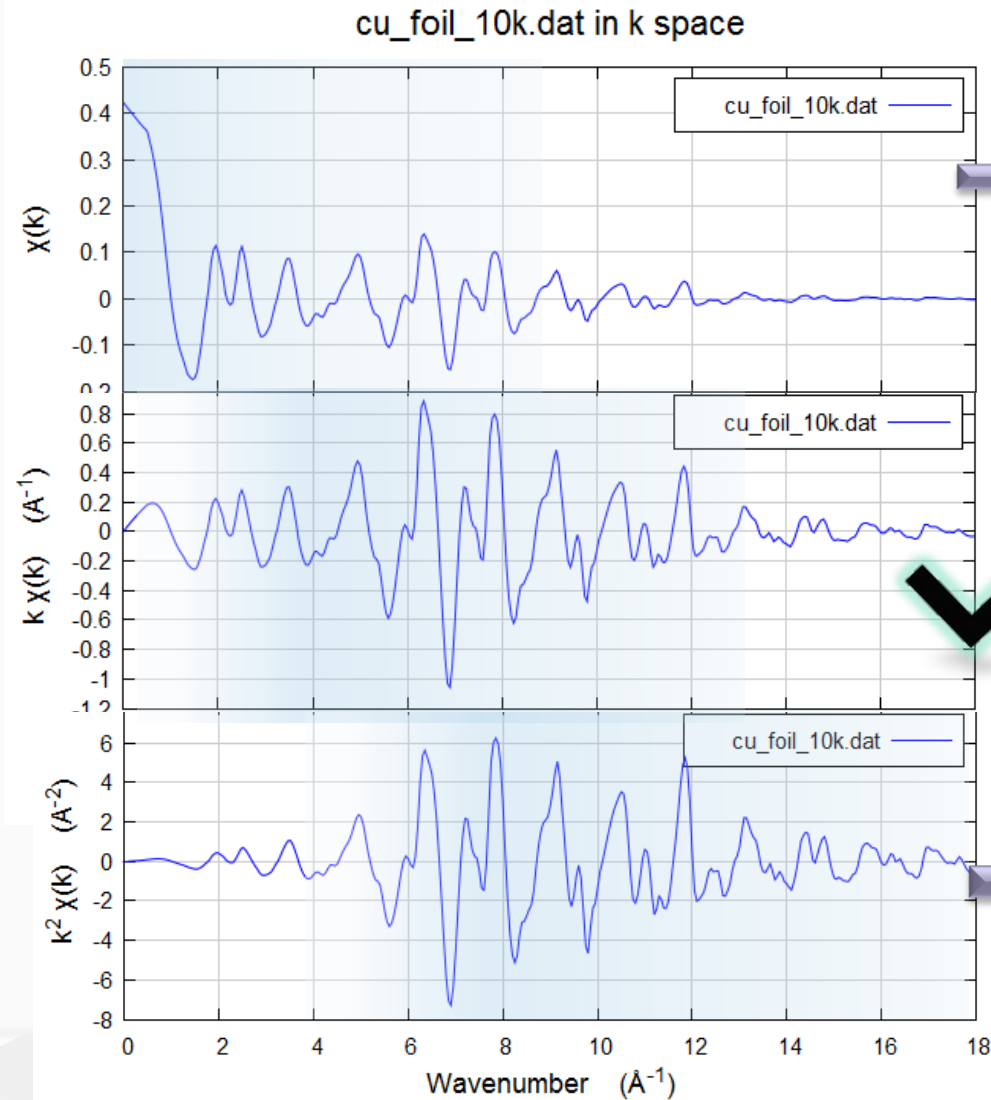
Metals: at the first inflection point of  $\alpha_{\text{nor}}$   
Oxides: where  $\alpha_{\text{nor}} \approx 0.5$

*It will be refined during the analysis.*

# Qualitative local structure: pseudo distribution function

## 3. Fourier transform (k-weight)

Cu



# Qualitative local structure: pseudo distribution function

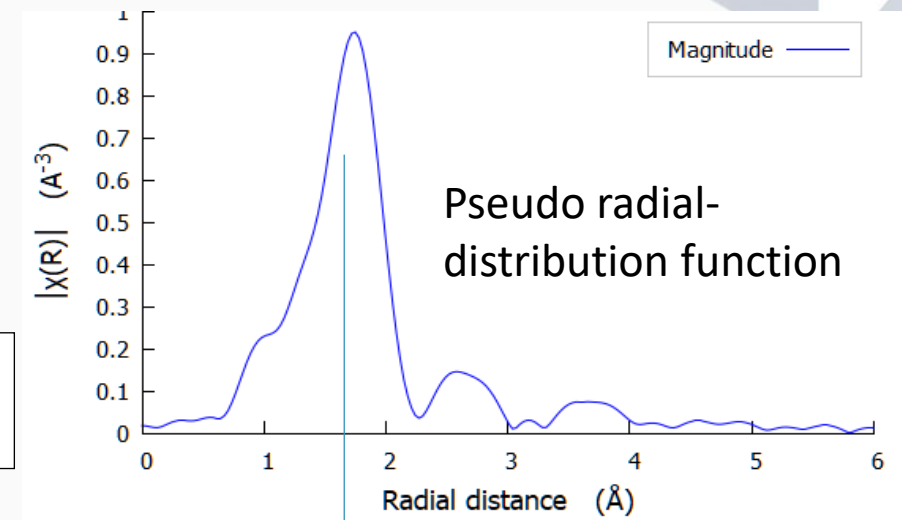
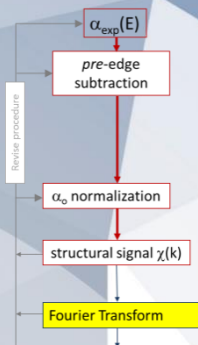
## 3. Fourier transform

|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

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

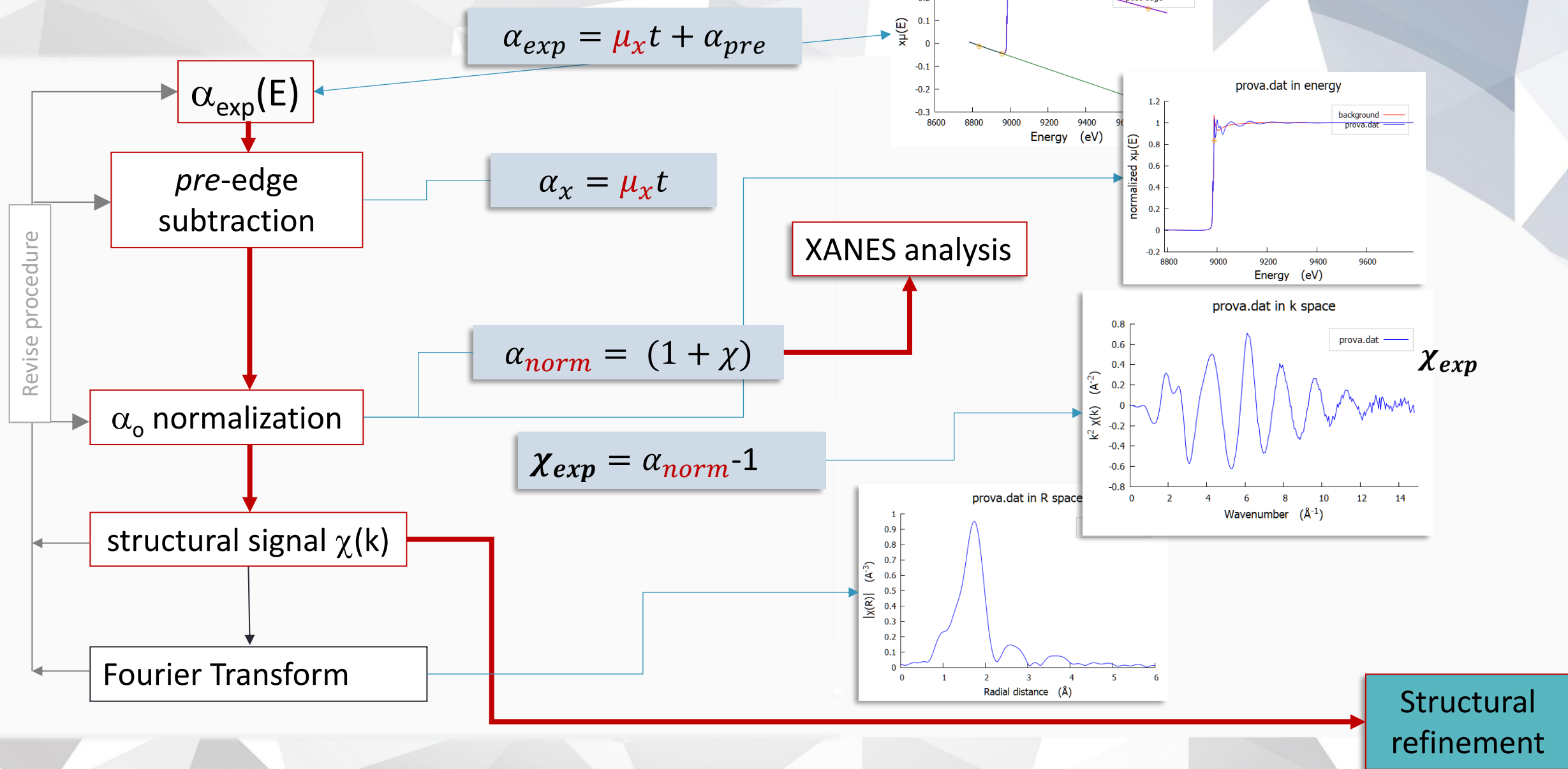
$$A_j = S_o^2 \frac{N_j}{R_j^2} |f_j| e^{-2k^2 \sigma_j^2} e_j^{-\frac{2r_j}{\lambda}}$$



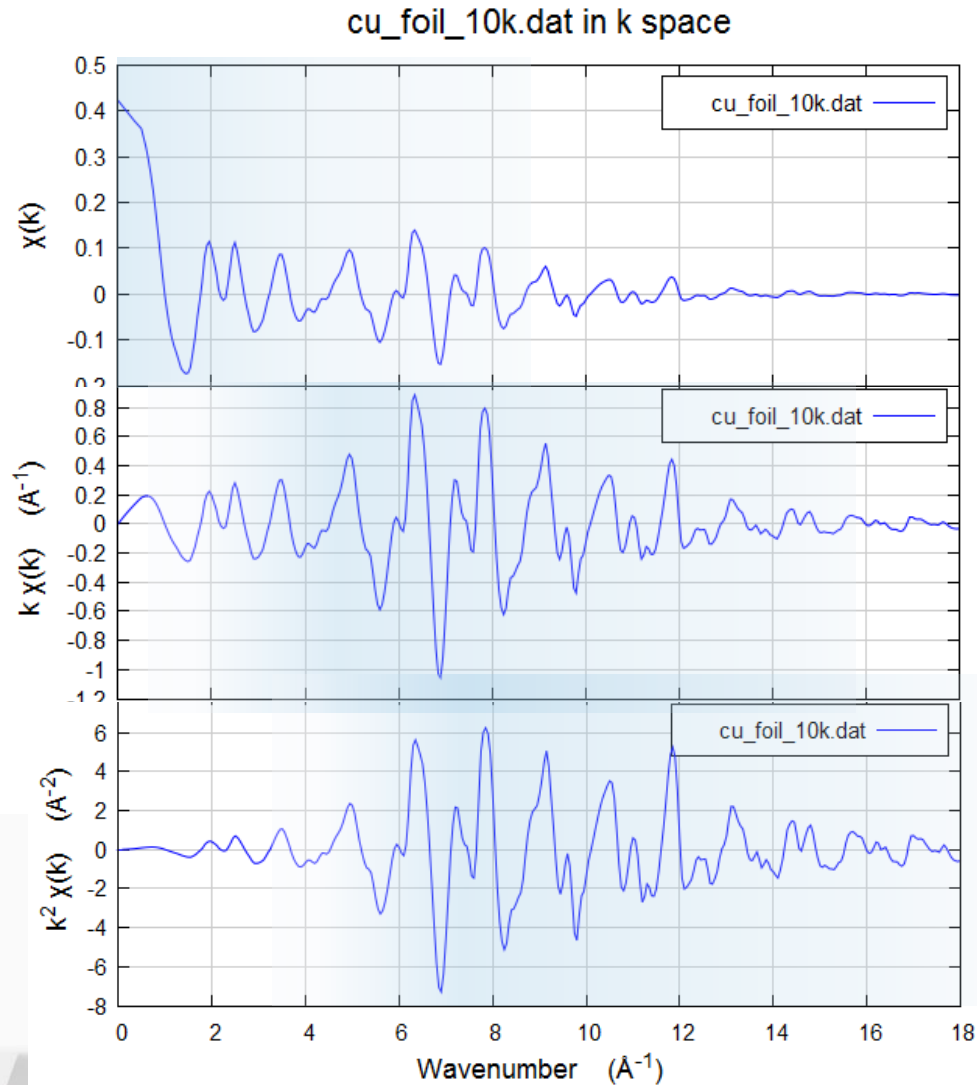
$$R_{true} \approx R_{FT} + 0.5 \text{\AA}$$



# Extract the XAFS signal (in short)



# Check your data:

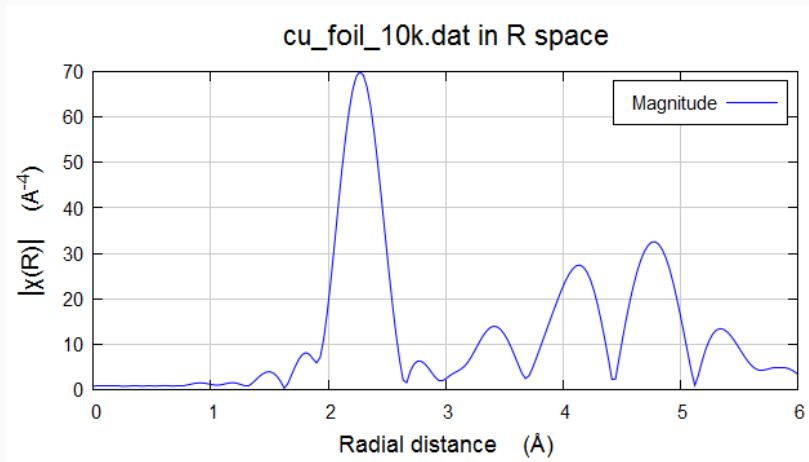


## Inspect $k^n \chi(k)$

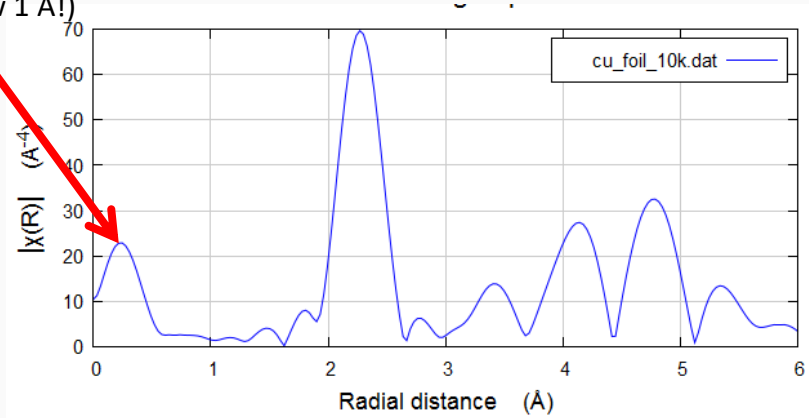
$k^n \chi(k)$  weighting highlights different features in the spectrum: high (low)  $n$  enhance high (low)  $k$ -regions

**Note:** low  $k$ -region ( $k < 3$ ) is generally affected by larger inaccuracies and is difficult to analyse due to **multiple scattering** contributions (XANES-FMS region) and other non-linear effects (mean free path)

# Check the FT

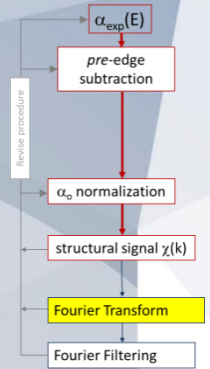


Unphysical peak  
(below 1  $\text{\AA}$ !)

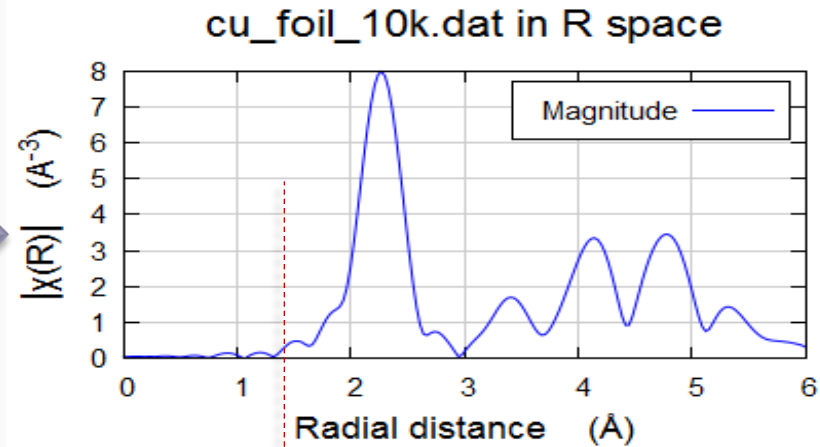
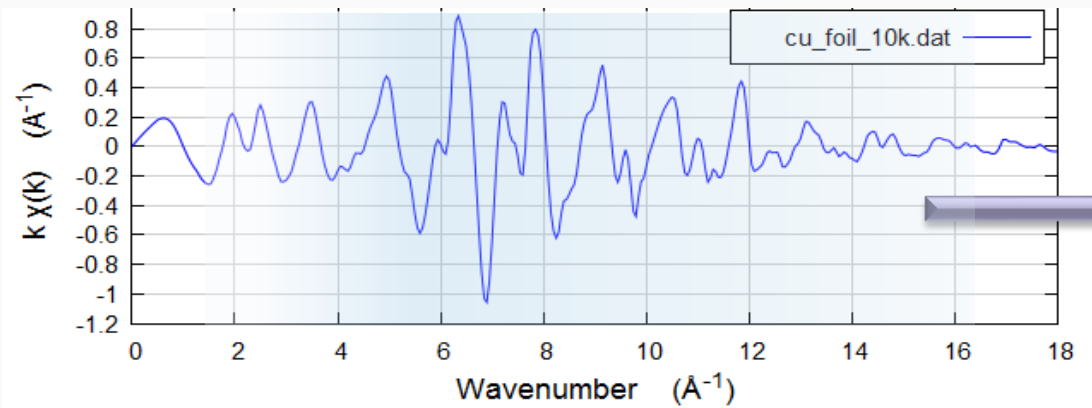


FT features:  
Artifacts, distortions, noise, may suggest bad extraction, noise on the data, etc...

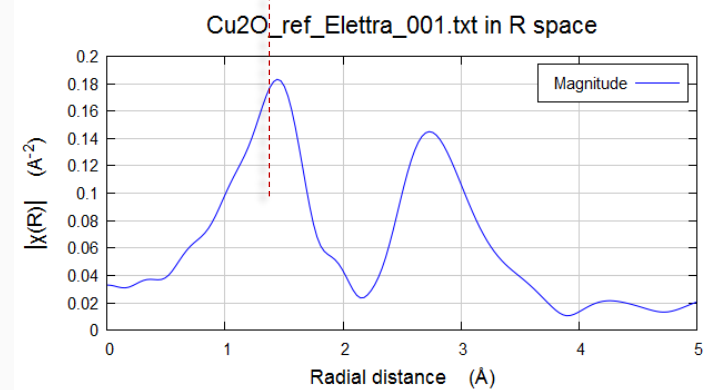
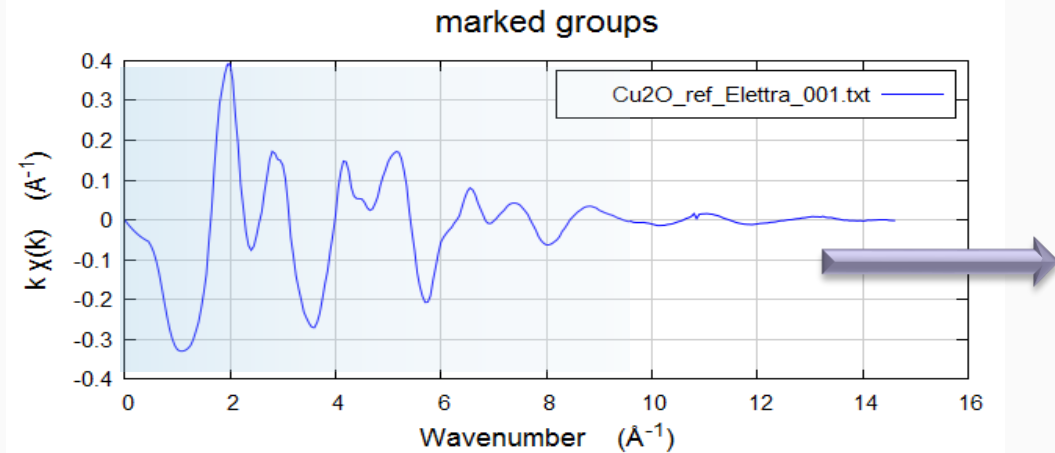
i.e.: intense peaks in the low R region ( $\approx$  less than 1 $\text{\AA}$ ) may signify errors in the extractions



# Qualitative local structure: pseudo distribution function

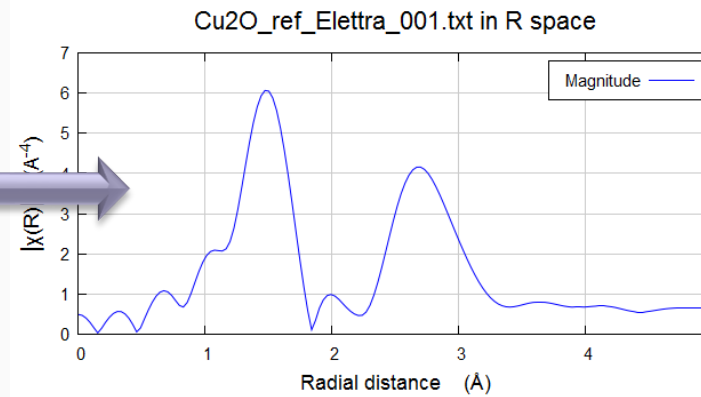
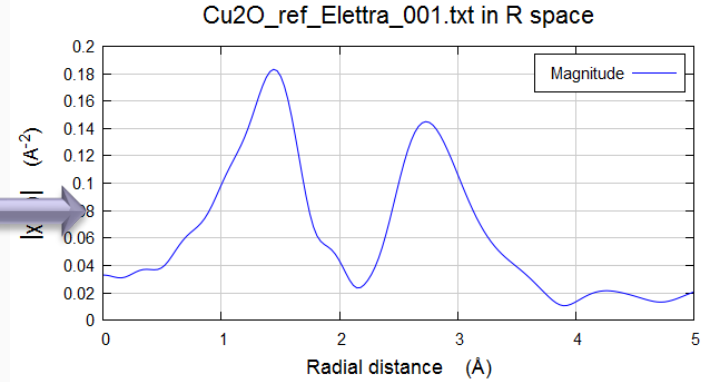
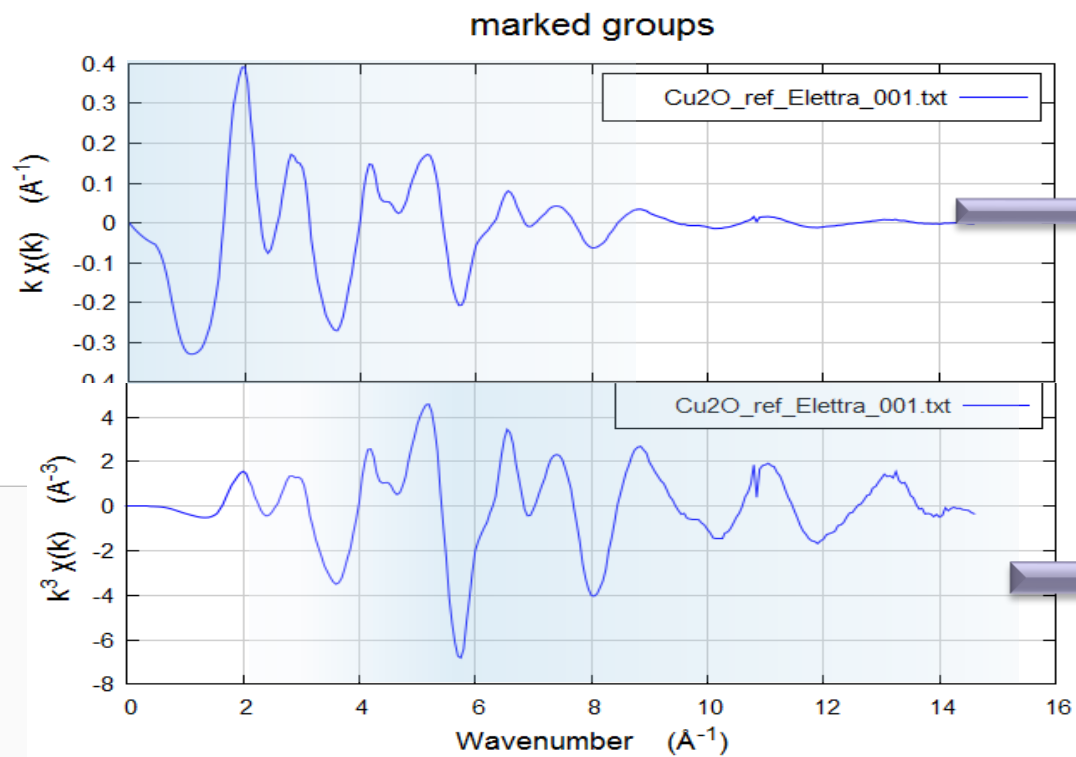
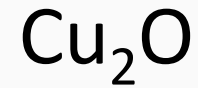


Cu



$\text{Cu}_2\text{O}$

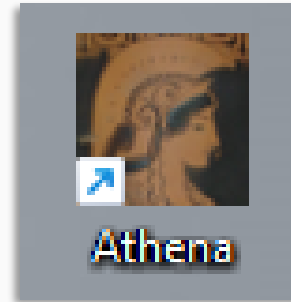
# Qualitative local structure: pseudo distribution function



# Software

- Download **Demeter** and install it
- Start **Athena**

Starting XAFS data analysis on IOS may be a challenging task !



# Hands-on

<https://tinyurl.com/Xafs2024>

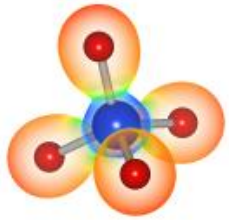
BiLaFeO\_LCA  
Cu-complex  
Iridium\_XANES  
ok\_Cu\_Foil  
ok\_Fe\_foil



<https://tinyurl.com/Xafs2024DB>

1. **Cu-Complex** (Amorphous)
2. *Cu K edge XAFS* (fcc)
3. *Fe K edge XAFS* (bcc)

# Structure Visualizers

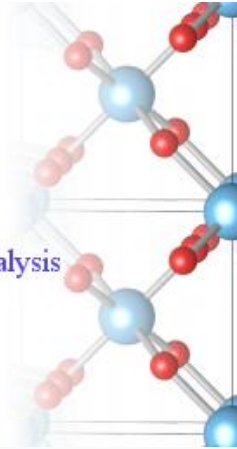


## VESTA

Visualization for Electronic and SStructural Analysis

<http://jp-minerals.org/soft/en/>

Google search:  
Vesta Download



Download it

	x	y	z	Occ.	B	Site	Sym.
1 Au Au1	0.00000	0.00000	0.00000	1.000	1.000	4a	m-3m

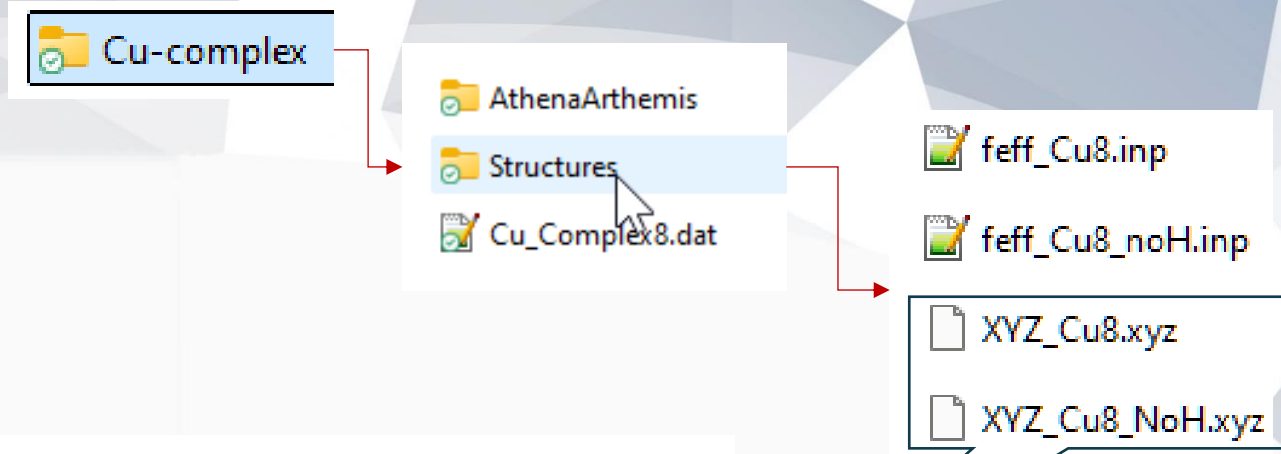
Number of polygons and unique vertices on isosurface = 0 (0)  
14 atoms, 0 bonds, 0 polyhedra; CPU time = 38 ms



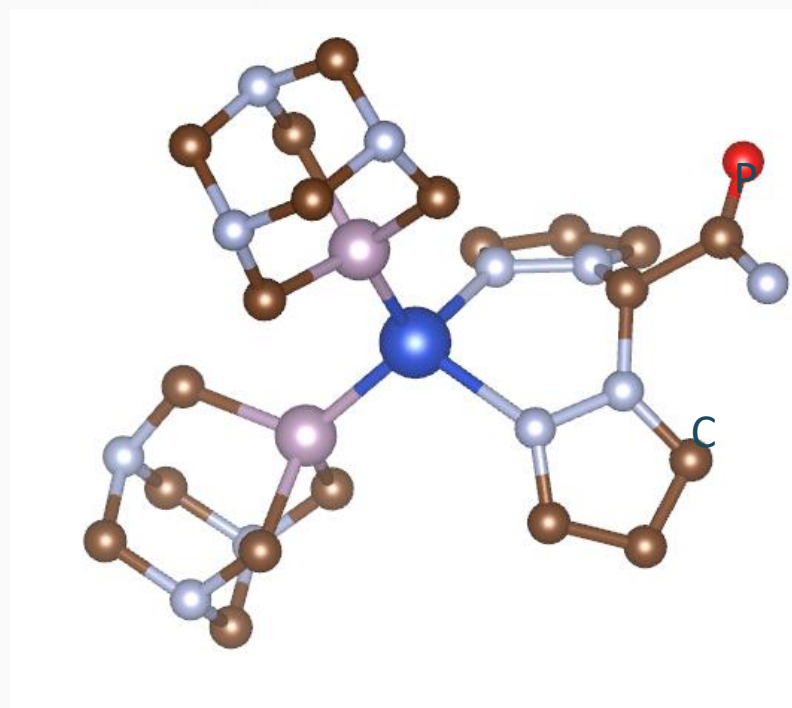
# Cu-Complex

## *Cu\_Complex8*

- Import files
- Take confidence with the GUI
- Use automatic extraction
- check extraction parameters and procedures
- save files and plots



```
35
DFT simulation
Cu  0.00000  0.00000  0.00000  0.00000
N   1.77890  0.14844 -1.16253  2.13025
N   1.11941 -0.19745  1.80976  2.13712
P  -1.32133  1.85547 -0.08482  2.27945
P  -1.01833 -1.98718 -0.46346  2.28050
N   2.90255  0.58244 -0.52071  3.00585
N   2.38749  0.30983  1.80623  3.00975
C   2.69897  1.25819  0.74902  3.07059
C   2.22515 -0.50587 -2.24895  3.20390
C   1.11069 -1.11210  2.79534  3.20692
C  -3.10470  1.76240  0.58409  3.61751
```



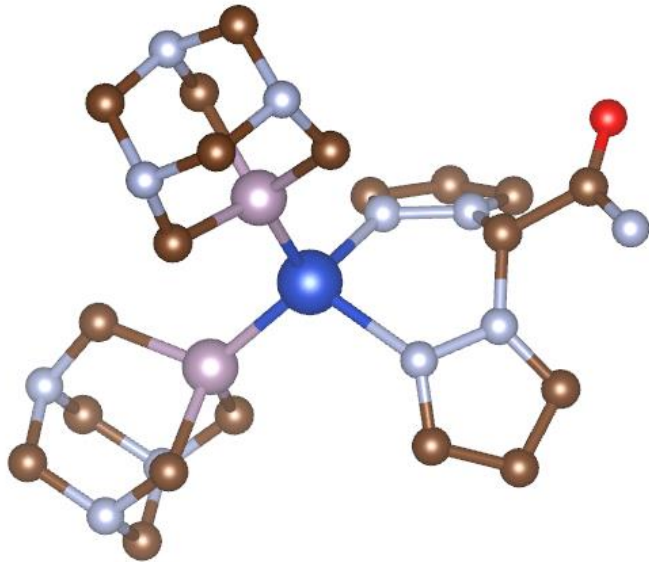
N

# Cu-Complex

- Import files

**Cu\_Complex8.dat**

- Take confidence with the GUI
- Use automatic extraction
- check extraction parameters and procedures
- save files and plots



File Group Energy Mark Plot Freeze Merge Monitor Help

\* <untitled> Save A U I

Main window

Current group: Cu\_Complex8\_Absorption\_N.dat Datatype: xmu Freeze

File C:\Users\carlo\Desktop\Cu-complex\Cu\_Complex8\_Absorption\_N.dat

Element 29: Copper Edge K Energy shift 0 Importance 1

Normalization and background removal parameters

E0 8986.68 Normalization order 1 2 3

Pre-edge range -150,000 to -30,000 Flatten normalized data

Normalization range 50,000 to 800 Edge step 0.3709005 fix

Rbkg 1.0 k-weight 2 Spline clamps

Spline range in k 0 to 14.863 low None

Spline range in E 0 to 841.65888 high Strong

Standard None Energy-dependent normalization

Forward Fourier transform parameters

k-range 3,000 to 12,863 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

E k R q kq

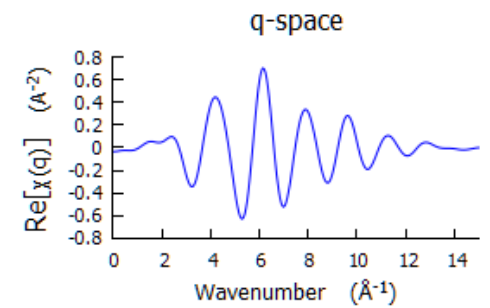
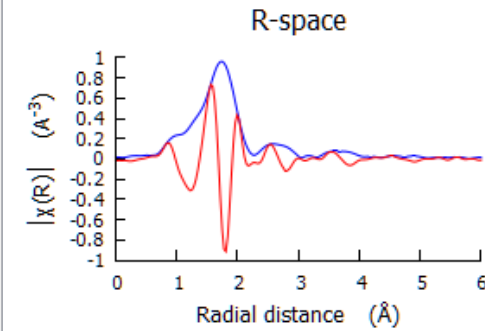
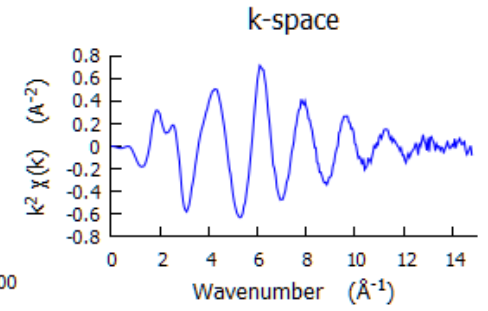
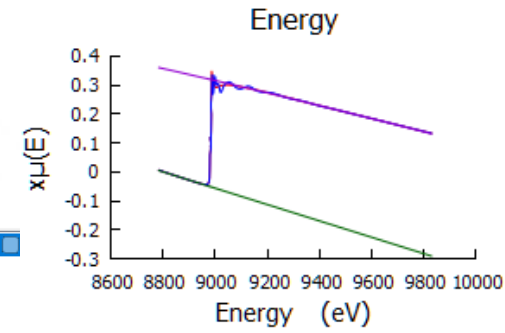
E k R q

Plotting k-weights

0 1 2 3 kw

Plot in R-space

Magnitude Envelope Real part Imag. part Phase Window



**Cu\_Complex8**

# 1. Cu K edge XAFS

1

## 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

6

7

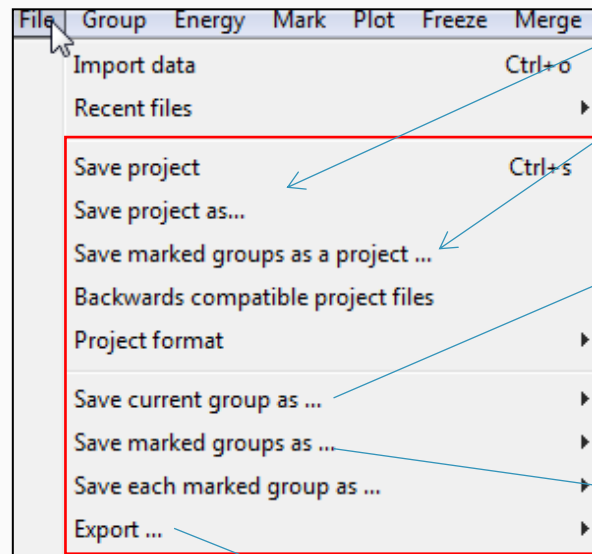
8-10

11

The screenshot shows the Athena XAS data processing software interface. The main window is titled 'Athena [XAS data processing]'. The current group is 'cu\_foil\_10k.dat'. The element is '29: Copper' and the edge is 'K'. The background removal and normalization parameters are set with E0 at 8977.58, Rbkg at 1.0, and normalization order at 3. The forward Fourier transform parameters are set with k-range from 3.000 to 23.019 and dk at 1. The backward Fourier transform parameters are set with R-range from 1 to 3 and dR at 0.0. The plotting parameters are set with a plot multiplier of 1 and a y-axis offset of 0. The interface includes a menu bar (File, Group, Energy, Mark, Plot, Freeze, Merge, Monitor, Help), a toolbar (Save, A, U, I), and a right-hand panel for plotting options (E, k, R, q, kq) and plotting k-weights (0, 1, 2, 3, kw). The bottom status bar indicates the data was imported from 'C:\Users\CarloNew\Dropbox\Seminar\_Malu\_2015\dat\Cu\_Foil\cu\_foil\_10k.dat'.

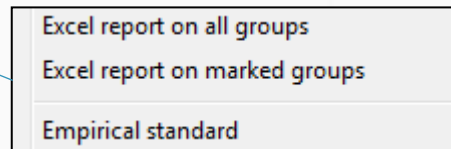
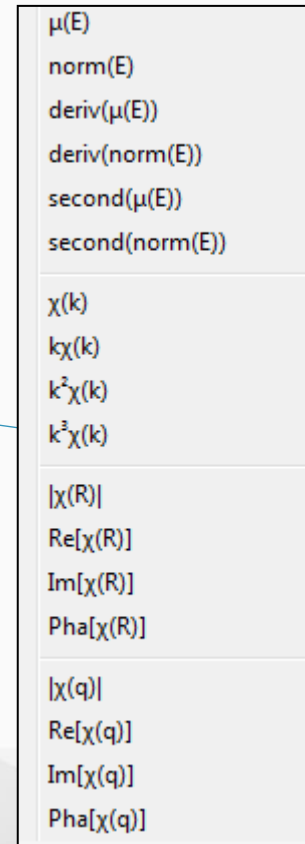
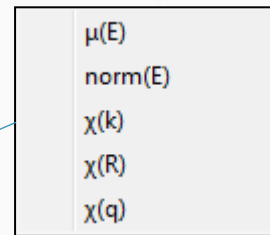
## Note:

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



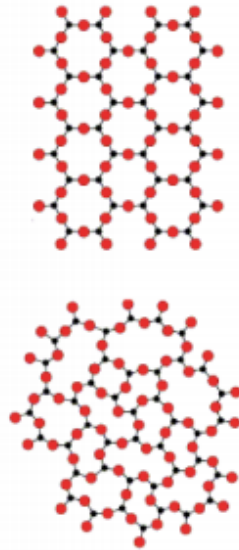
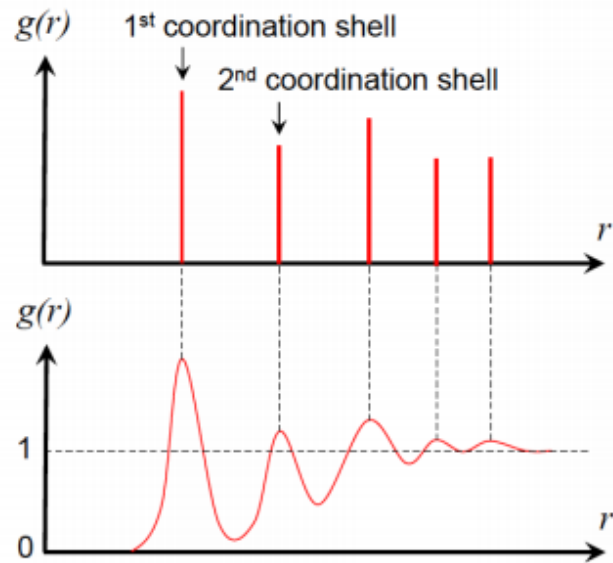
Save the entire project for reuse.

Save selected groups for separate use



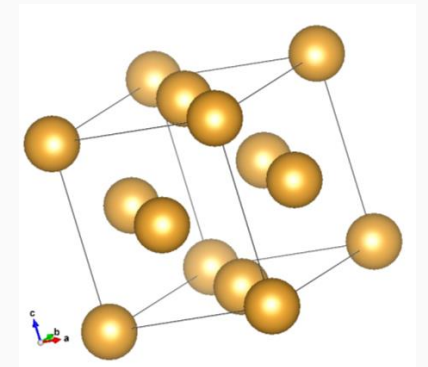
# Crystallographic structures DBs

<http://www.webelements.com/>



- Crystallography Open Database (COD)  
[www.crystallography.net](http://www.crystallography.net)
- WWW-MINCRYST  
[database.iem.ac.ru/mincryst/](http://database.iem.ac.ru/mincryst/)
- American Mineralogist Crystal Structure DB  
[rruff.geo.arizona.edu/AMS/amcsd.php](http://rruff.geo.arizona.edu/AMS/amcsd.php)
- ICSD: inorganic chemistry database (guest) - FIZ Karlsruhe
- Google Scholar
- <http://www.webelements.com/>

***Chemical bonds locally preserve also in disordered phases distances and angles like the crystallographic counterparts***

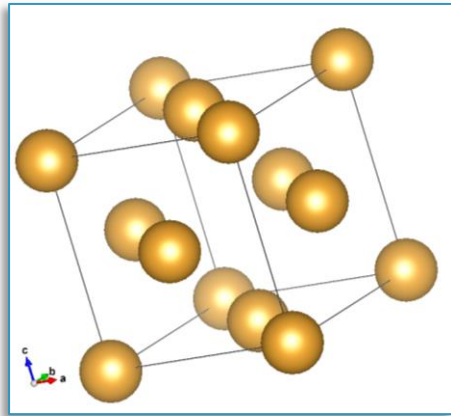


# 4. Fe (bcc) and Cu (fcc) XAFS

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

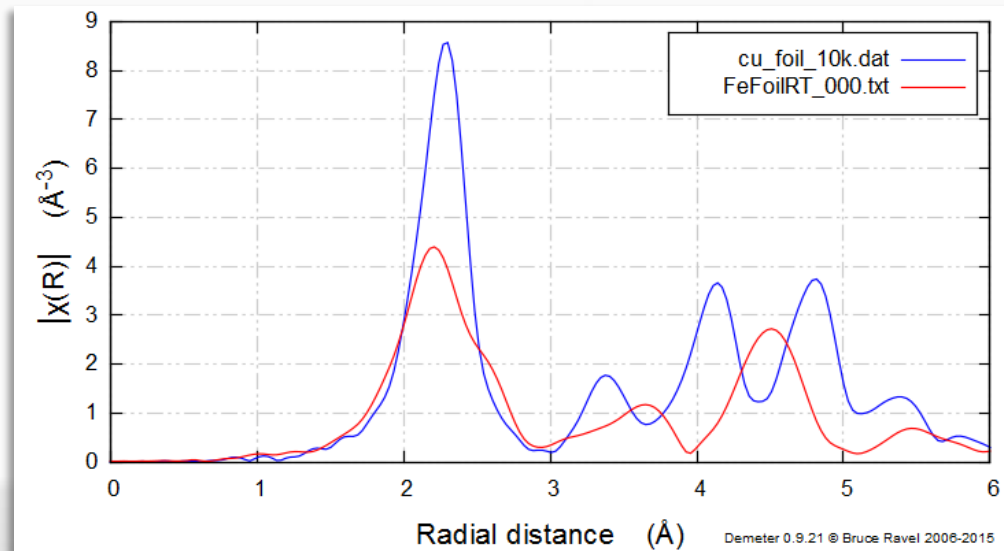
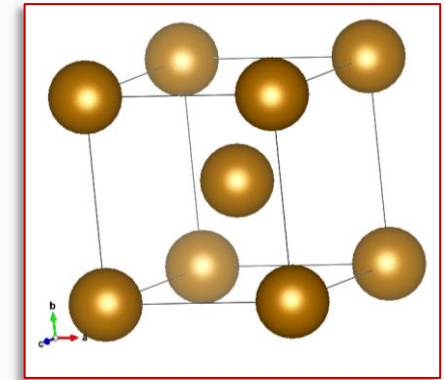
fcc  
(Fm-3m)

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

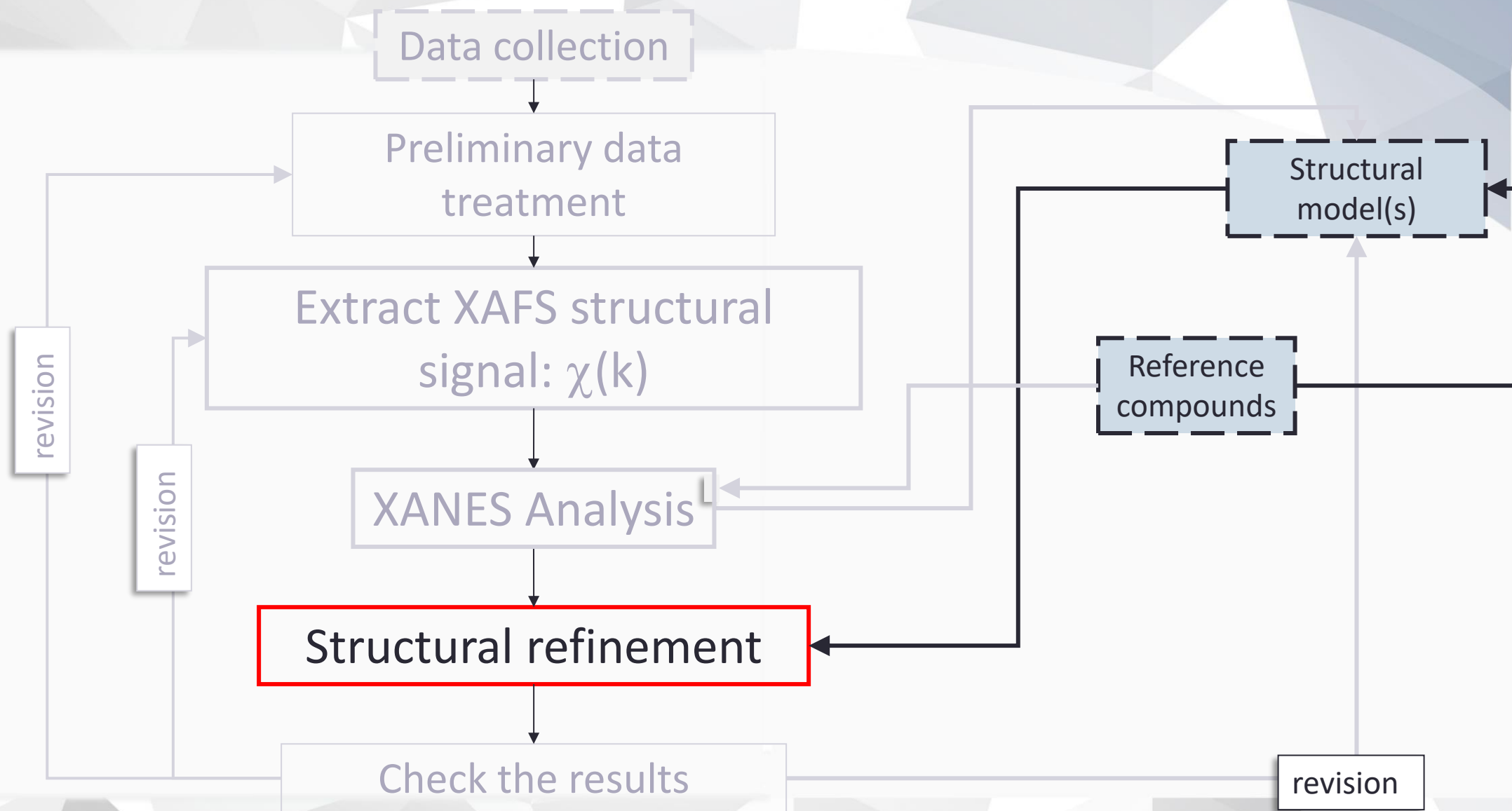


Bcc  
(Im3m)

$$\begin{aligned} R_1 &= a\sqrt{3}/2 & N_1 &= 8 \\ R_2 &= a & N_2 &= 6 \\ R_3 &= a\sqrt{2} & N_3 &= 12 \end{aligned}$$



# XAFS data analysis: Overview



# The EXAFS standard formula

$$\chi_j(k) = \frac{1}{k} A_j(k, R_j) \sin\left(2kR_j + \phi_j(k)\right)$$

$$A_j(k, R_j) = \frac{S_o^2 N_j}{R_j^2} |f_j(k, R_j)| e^{-2k^2 \sigma_j^2} e^{-\frac{2R_j}{\lambda}}$$

$$k = \frac{2\pi}{\lambda_e} = \hbar^{-1} \sqrt{2m_e(E - E_o)}$$

## parameters

$f_j(k, R_j)$  = photo-electron scattering amplitude

$\phi_j(k)$  = photo-electron scattering phase

$\lambda$  = photo-electron mean free path

$S_o^2$  = many body losses

$E_o$  = Edge energy shift

## Structure

$N_j$  = multiplicity (coordination number)

$R_j$  = half path length (coordination distance)

$\sigma_j^2$  = variance of the path length distribution

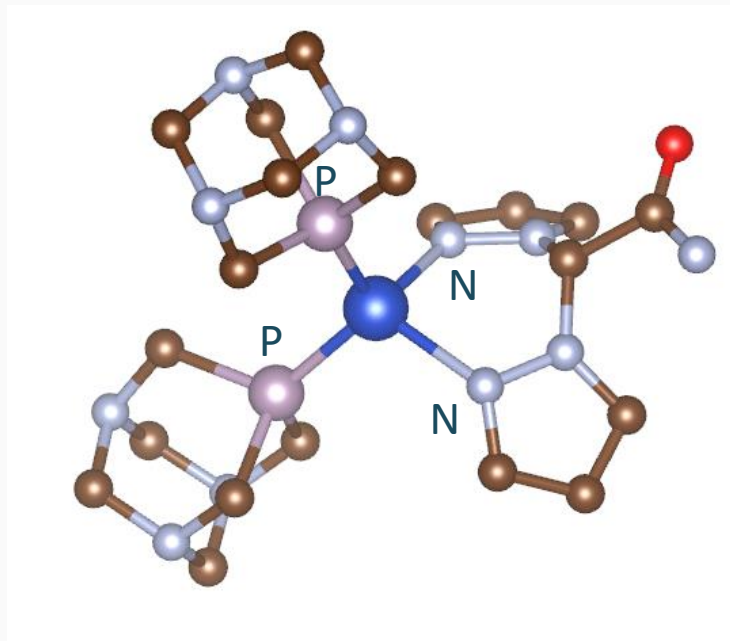
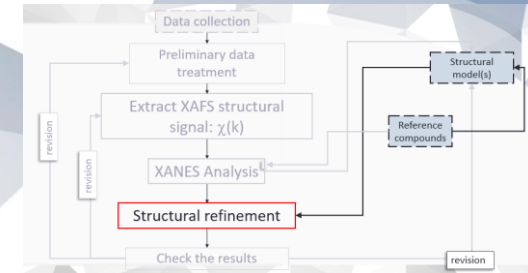
(Mean Square Relative Displacement:  
MSRD)





# Structural model & Data refinement

## We will analyze Cu Complex8 EXAFS



- feff\_Cu8.inp
- feff\_Cu8\_noH.inp
- XYZ\_Cu8.xyz
- XYZ\_Cu8\_NoH.xyz

## feff\_Cu8\_noH.inp

\* This feff6 file was generated by Demeter 0.9.26  
 \* Demeter written by and copyright (c) Bruce Ravel, 2006-2018

HOLE 1 1.0 \* FYI: (Cu K edge @ 8979 eV, 2nd number is S0^2)

CONTROL 1 1 1 1  
 PRINT 1 0 0 0

RMAX 7.0

POTENTIALS

* ipot	Z	tag
0	29	Cu
1	7	N
2	3	C
3	15	P

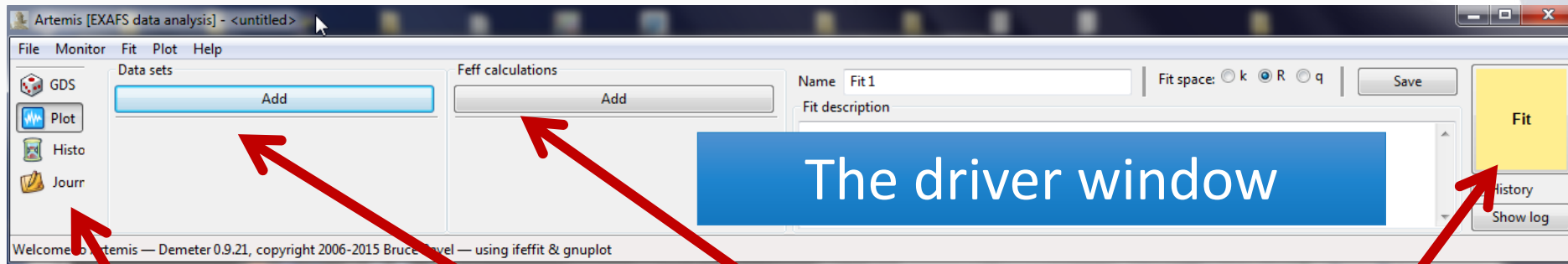
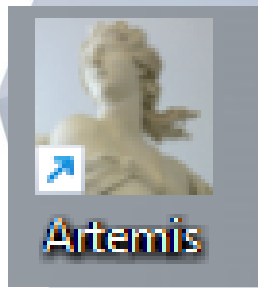
ATOMS \* this list contains 131 atoms

* x	y	z	ipot	tag	distance
0.00000	0.00000	0.00000	0	<b>Cu38</b>	0.00000
1.77890	0.14844	-1.16253	1	N1.1	2.13025
1.11941	-0.19745	1.80976	1	N3.1	2.13712
-1.32133	1.85547	-0.08482	3	P2.1	2.27945
-1.01833	-1.98718	-0.46346	3	P1.1	2.28050
2.90255	0.58244	-0.52071	1	N2.1	3.00585
2.38749	0.30983	1.80623	1	N4.1	3.00975

....  
 END

# Start Arthemis

*better on a larger monitors!*



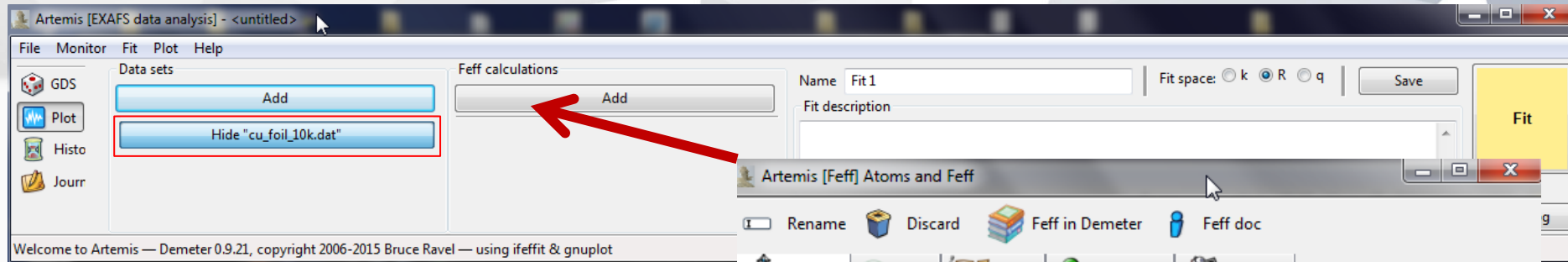
3  
select  
**refinement**  
pram., plot,  
etc...

1  
add EXAFS  
 $\chi(k)$  or  
athena project

2  
add a  
Structure  
.cif or Feff file

4  
Start fit

# 2: add model structure (cif or simple pair)



- I. Run Atoms
- II. check paths
- III. Run Feff
- IV. look at the path list

A) for crystals generate a local cluster

B) calculate amplitude and phases for paths in the cluster

C) Scattering Path list

```
Artemis [EXAFS data analysis] - <untitled>
File Monitor Fit Plot Help
Data sets
Add
Hide "cu_foil_10k.dat"
Feff calculations
Add
Name Fit 1
Fit space: k R q
Save
Fit
Welcome to Artemis — Demeter 0.9.21, copyright 2006-2015 Bruce Ravel — using ifeffit & gnuplot
```

Artemis [Feff] Atoms and Feff

Rename Discard Feff in Demeter Feff doc

Atoms Feff Paths Path-like Console

Open file Save da

Titles

Copper

Cu

icsd\_4349

Group F r

K St

-consistency Rscf 5.0

Aggregate degeneracy margins

Margin: 0.03 Beta: 3

Add a site

Radial distances

Cluster size 5.422575 Longest path 5.0

Shift vector

0 0 0 insert

	Core	EL	x	y	z	Tag
1	<input checked="" type="checkbox"/>	Cu	0	0	0	Cu1
2	<input type="checkbox"/>					
3	<input type="checkbox"/>					
4	<input type="checkbox"/>					
5	<input type="checkbox"/>					
6	<input type="checkbox"/>					

Artemis [Feff] Atoms and Feff

Rename Discard Feff in Demeter Feff doc

Atoms Feff Paths Path-like Console

Open file Save file Clear all Template Run Feff

Name: icsd\_43493\_Copper Margin: 0.03 Beta

Feff input file

```
1 29 Cu
ATOMS * this list contains 55 atoms
* x y z ipot tag distance
0.00000 0.00000 0.00000 0 Cu1 0.00000
1.80753 1.80753 0.00000 1 Cu1.1 2.55623
-1.80753 1.80753 0.00000 1 Cu1.1 2.55623
1.80753 -1.80753 0.00000 1 Cu1.1 2.55623
-1.80753 -1.80753 0.00000 1 Cu1.1 2.55623
1.80753 0.00000 1.80753 1 Cu1.1 2.55623
-1.80753 0.00000 1.80753 1 Cu1.1 2.55623
0.00000 1.80753 1.80753 1 Cu1.1 2.55623
0.00000 -1.80753 1.80753 1 Cu1.1 2.55623
1.80753 0.00000 -1.80753 1 Cu1.1 2.55623
-1.80753 0.00000 -1.80753 1 Cu1.1 2.55623
0.00000 1.80753 -1.80753 1 Cu1.1 2.55623
0.00000 -1.80753 -1.80753 1 Cu1.1 2.55623
3.61505 0.00000 0.00000 1 Cu1.2 3.61505
-3.61505 0.00000 0.00000 1 Cu1.2 3.61505
0.00000 3.61505 0.00000 1 Cu1.2 3.61505
```

# 1: add $\chi(k)$ or Athena project

Artemis [EXAFS data analysis] - <untitled>

File Monitor Fit Plot Help

Data sets **Add**

Feff calculations **Add**

Name: Fit 1

Fit space:  $k$

Fit description

Artemis: Import from Athena project file

Cu\_Complex8.dat

1 **Athena\_Cu\_Complex8.prj**

Artemis [Data] Cu\_Complex8.dat

Plot as:  $\mu(E)$ ,  $|X(R)|$ ,  $Re[X(R)]$ ,  $Im[X(R)]$

Take parameters: Project file, Artemis default, Current value

Fourier transform parameters:  $k_{min}$ ,  $k_{max}$ ,  $dk$ ,  $r_{min}$ ,  $r_{max}$ ,  $dr$

Fitting  $k$  weights:  $k_1$ ,  $k_2$ ,  $k_3$ , other,  $\epsilon(k)$

Other parameters: Include in fit, Plot after fit, Fit background, Plot with phase correction

Artemis [Feff] Atoms and Feff

2 **feff\_Cu8\_noH.inp**

Artemis [Feff] Atoms and Feff

Name: feff\_Cu8\_noH

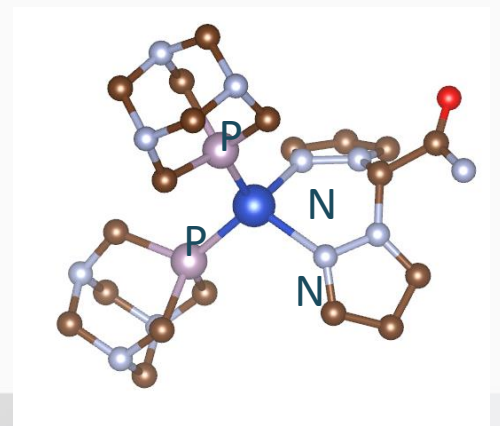
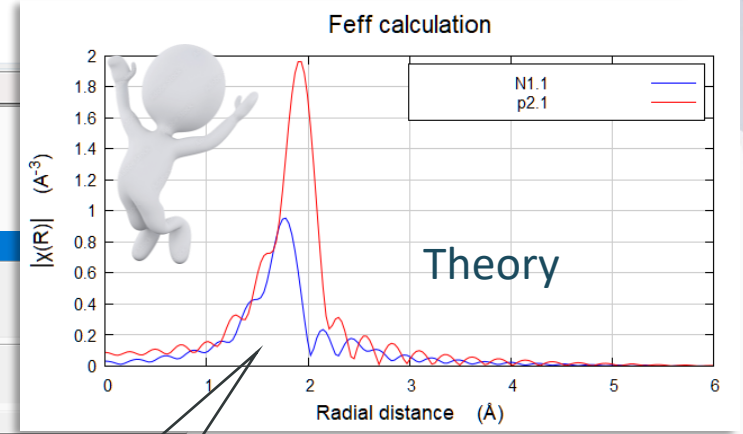
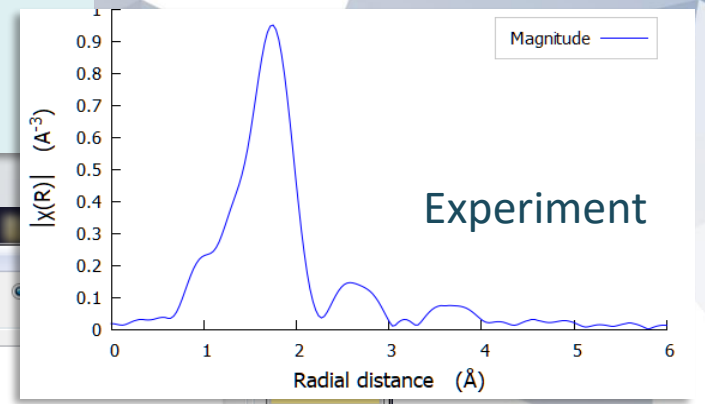
Feff input file

```
* This feff6 file was generated by Demeter
* Demeter written by and copy
*
* total mu*x=1: 2719.699 mi
* specific gravity: 0.116
* normalization correction:
*
HOLE 1 1.0 * FYI: (C
* mphase,mpath,mfeff,
CONTROL 1 1 1 1
PRINT 1 0 0
RMLX = n
```

Description

```
# This paths.dat file was written by Demeter 0.9.26
# Distance fuzz = 0.030 A
# The central atom is denoted by this token: @
# Cluster size = 5.00 A, containing 34 atoms
# 63 paths were found within 5.000 A
# Forward scattering cutoff 20.00
```

Degen	Reff	Scattering path	Rank	Type
1	2.00	@ N1.1 @	10...	single scatte
2	2.00	@ p2.1 @	91.12	single scatte
3	2.00	@ N2.1 @	43.00	single scatte
4	1.00	@ C7.1 @	8.23	single scatte
5	2.00	@ C1.1 @	14.81	single scatte
6	4.00	@ N1.1 N2.1 @	32.90	obtuse triang
7	4.00	@ N1.1 C1.1 @	22.09	obtuse triang
8	2.00	@ N1.1 C1.1 N1.1 @	9.12	dog-leg
9	2.00	@ N1.1 N2.1 N1.1 @	8.78	dog-leg
10	3.00	@ C37.1 @	16.22	single scatte
11	2.00	@ C31.1 @	10.65	single scatte
12	2.00	@ N1.1 N3.1 @	3.36	other double
13	1.00	@ C36.1 @	5.17	single scatte



## 2: drag and drop relevant paths to the data window

The screenshot displays the Artemis software interface. The main window is titled "Artemis [Data] Cu\_Complex8.dat" and contains a "Data" window with a list of paths. Two paths are selected: "[feff\_Cu8\_noH] N1.1" and "[feff\_Cu8\_noH] p2.1". These paths are being dragged from the "Scattering Paths" table to the "Data" window. The "Data" window also shows a "CV" field set to 1 and a "Plot after fit" checkbox checked. The "Scattering Paths" table is shown below, with columns for Degen, Reff, Scattering path, Rank, and Type. The first two rows are highlighted in blue, corresponding to the selected paths. The "Description" field contains the following text:

```
# This paths.dat file was written by Demeter 0.9.26
# Distance fuzz = 0.030 A
# The central atom is denoted by this token: @
# Cluster size = 5.00 A, containing 34 atoms
# 63 paths were found within 5.000 A
# Forward scattering cutoff 20.00
```

The "Scattering Paths" table is as follows:

	Degen	Reff	Scattering path	Rank	Type
1	2.00	2.134	@ N1.1 @	10...	single scatte
2	2.00	2.280	@ p2.1 @	91.12	single scatte
3	2.00	3.008	@ N2.1 @	43.80	single scatte
4	1.00	3.071	@ C7.1 @	8.23	single scatte
5	2.00	3.205	@ C1.1 @	14.81	single scatte
6	4.00	3.253	@ N1.1 N2.1 @	32.90	obtuse triang
7	4.00	3.342	@ N1.1 C1.1 @	22.09	obtuse triang
8	2.00	3.478	@ N1.1 C1.1 N1.1 @	9.12	dog-leg
9	2.00	3.499	@ N1.1 N2.1 N1.1 @	8.78	dog-leg
10	3.00	3.633	@ C37.1 @	16.22	single scatte

## 2: Define parameters

[icsd\_434] Cu1.1  
[icsd\_434] Cu1.2  
[icsd\_434] Cu1.3  
[icsd\_434] Cu1.4  
[icsd\_434] Cu1.1 Cu1.4  
[icsd\_434] Cu1.1 Cu1.4 Cu1.1

[icsd\_43493\_Copper] Cu1.1  
 Include path  Plot after fit  
 Use this path for phase corrected plotting.  
@ Cu1.1 @  
(0001) single scattering, high (100.00)

x	y	z	i
1.807530	1.807530	0.000000	
0.000000	0.000000	0.000000	

Label: Reff=2.556, nleg=2, degen=12

N: 12  
SO<sup>2</sup>: So2  
ΔE0: De\_0  
ΔR: dr\_1  
ss\_1

right click for options

SO<sup>2</sup>  
Clear SO<sup>2</sup>  
Export this SO<sup>2</sup> to every path in THIS Feff calculation  
Export this SO<sup>2</sup> to every path in THIS data set  
Export this SO<sup>2</sup> to every path in EVERY data set  
Export this SO<sup>2</sup> to marked paths in THIS data set  
Grab SO<sup>2</sup> from previous path  
Grab SO<sup>2</sup> from next path

Give a name to each parameter to adjust

**NOTE:**  
DE and So2 should be the same for absorbers in the same structure

# 3: Define parameters

Artemis [EXAFS data analysis] - <untitled>

File Monitor Fit Plot Help

Data sets: Add

Feff calculations: Add

Name: Fit1 | Fit space:  k  R  q | Save

Fit description

Fit

History  Show log

Welcome to Artemis - Demeter 0.9.21, copyright 2006-2015 B...

Artemis [GDS] Guess, Def, Set parameters

	Type	Name	Math expression
1	guess	So2	0.8
2	guess	De_0	0.0
3	guess	dr_1	0.0
4	guess	ss_1	0.003
5	guess	dr_2	0.0
6	guess	ss_2	0.003
7	guess	dr_3	0.0
8	guess	ss_3	0.003
9	guess	dr_4	0.0
10	guess	ss_4	0.003
11	guess	ss_41	0.003
12	guess	ss_42	0.003

Note:  
Initialize to >0  
the  $\sigma^2$  parameters

Note:  
Constraint to physical  
meaning structural  
parameters (es. MS paths)

3  
select refinement  
param., plot, etc...  
USE GDS button

# 3: Define parameters

Artemis [EXAFS data analysis] - <untitled>

File Monitor Fit Plot Help

Data sets Add Feff calculations Add Name Fit1 Fit space:  k  R  q Save Fit

Artemis [Data] cu\_foil\_10k.dat

Welcome to Data Parameters Marks Actions Debug Help

cu\_foil\_10k.dat CV 1

Data source: o\_Malu\_2015\data\ok\_Cu\_Foil\EXAFS\_extraction\athena\_Cu10k.prj, 1

Plot this data set as:

Title lines

Fourier transform parameters

kmin	3.000	<input checked="" type="radio"/>	kmax	23.019	<input checked="" type="radio"/>	dk	1
rmin	1	<input checked="" type="radio"/>	rmax	3	<input checked="" type="radio"/>	dr	0.0

Fit  Fit background  Base correction

[icsd\_434] Cu1.1  
[icsd\_434] Cu1.2  
[icsd\_434] Cu1.3  
[icsd\_434] Cu1.4  
[icsd\_434] Cu1.1 Cu1.4  
[icsd\_434] Cu1.1 Cu1.4 Cu1.1

Actions Debug Help

Make VPath from marked	Alt+Shift+v
Transfer marked	Alt+Shift+t
Compute bond valence sum	Alt+Shift+b
Include marked	Alt+Shift+c
Exclude marked	Alt+Shift+x
Discard marked	
Plot marked after fit	Alt+Shift+p
Plot no paths after fit	Alt+Shift+u

Note: Run fit starting with first shell then add progressively far away contributions

Note: FT range must include the last shell you want to fit

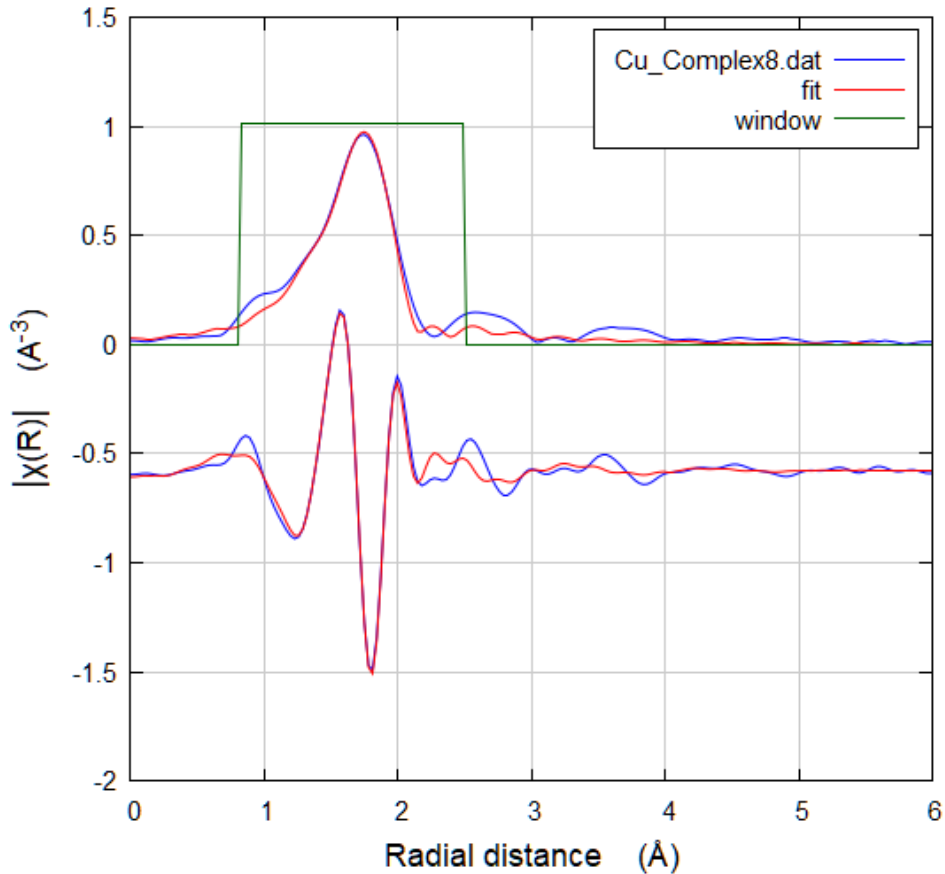
run Fit



# 4: FIT



Cu\_Complex8.dat in R space



```
Independent points      : 10.3359375
Number of variables    : 5
Chi-square             : 907.1668222
Reduced chi-square     : 170.0107661
R-factor               : 0.0179542
Number of data sets   : 1
```

```
Happiness = 100.00/100          color = #D8E796
***** Note: happiness is a semantic parameter and should *****
***** NEVER be reported in a publication -- NEVER! *****
```

guess parameters:

```
DE_0      = -7.33133652  # +/-  4.43267763  [0]
Dr_1      = -0.03011728  # +/-  0.02457603  [0]
ss_1      =  0.01171751  # +/-  0.01516697  [0.00300]
Dr_2      = -0.05100508  # +/-  0.01036517  [0]
SS_2      =  0.00513951  # +/-  0.00188231  [0.00300]
```

Correlations between variables:

```
ss_1 & de_0      --> -0.9224
ss_2 & ss_1      --> -0.9072
ss_2 & de_0      -->  0.8636
dr_2 & de_0      -->  0.5498
ss_2 & dr_1      --> -0.5275
```

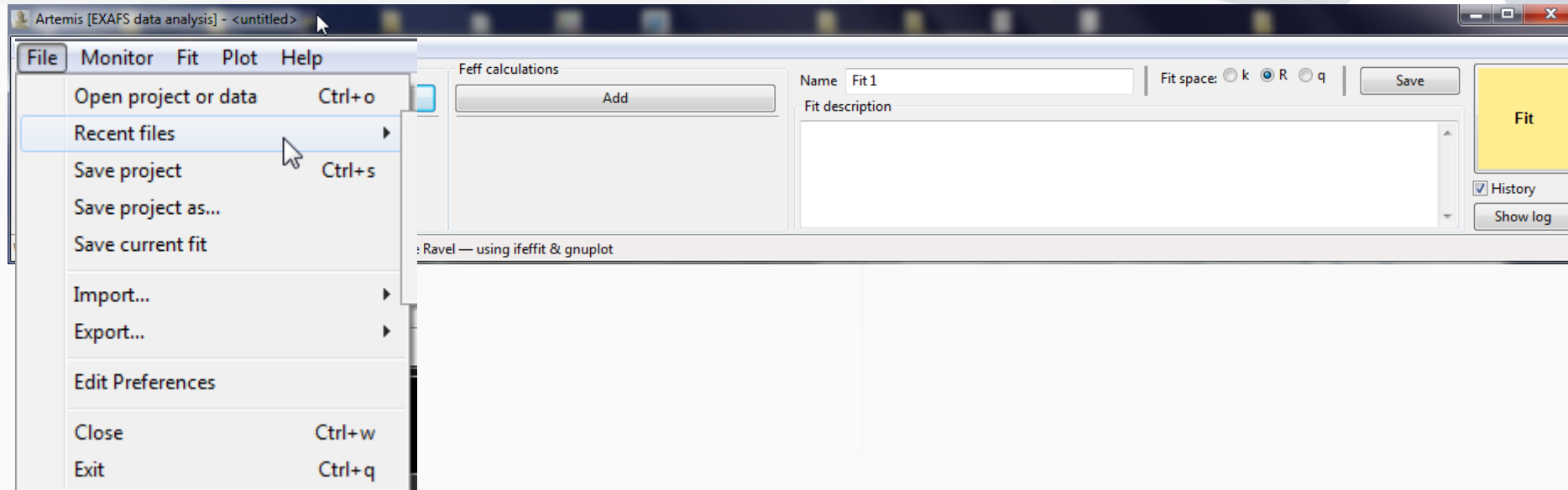
All other correlations below 0.4

N	S02	sigma^2	e0	delr	Reff	R
2.000	1.000	0.01172	-7.331	-0.03012	2.13370	2.10358
2.000	1.000	0.00514	-7.331	-0.05101	2.28000	2.22900

**Note:**

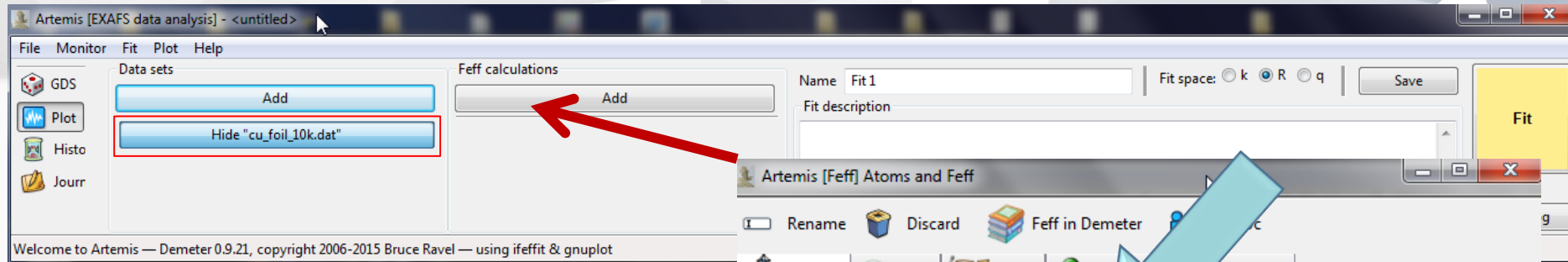
Check modulus and  
real(imaginary) parts

## 5: Always save best fit and output files



6: Check your results and your hypothesis about local atomic structure... if mismatches check hypothesis, extraction, quality of the data...

# 2': generate crystallographic model structure



- I. Run Atoms
- II. check paths
- III. Run Feff
- IV. look at the path list

A)  
generate a  
local cluster

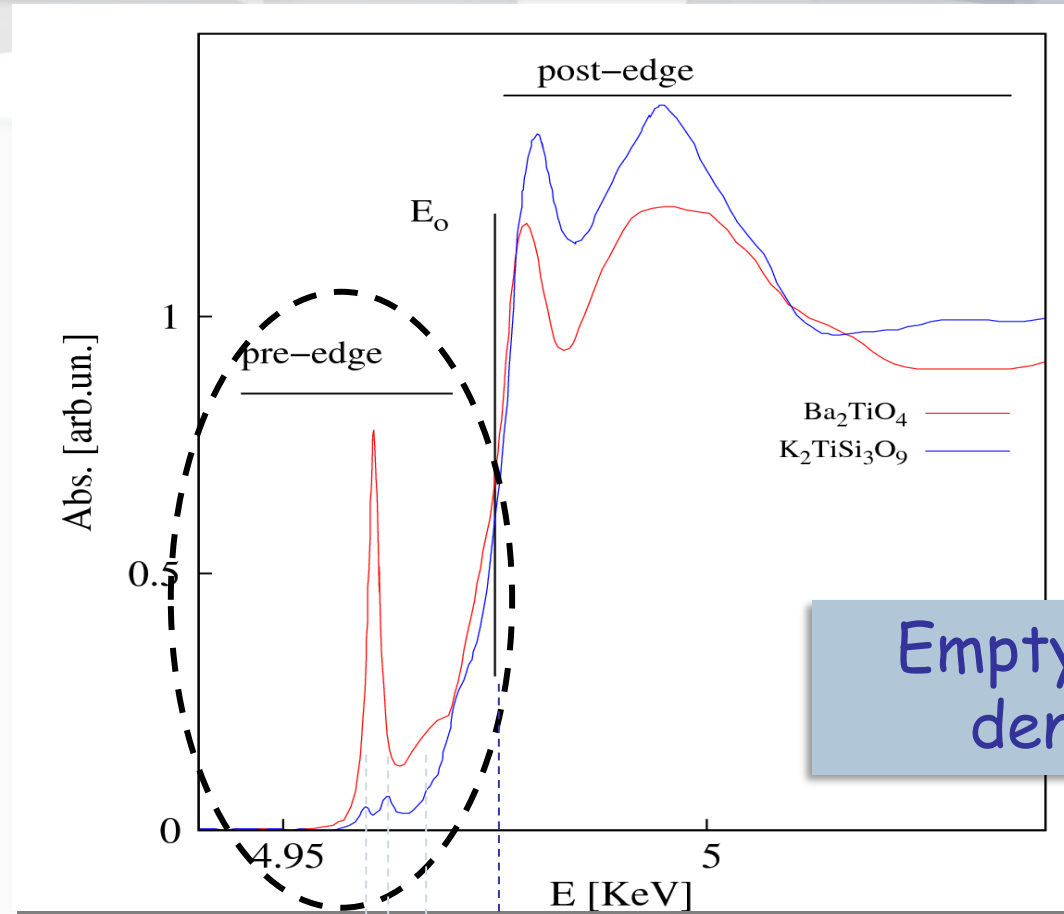
A)  
input the unit cell  
parameters and cluster size

	Core	EL	x	y	z	Tag
1	<input checked="" type="checkbox"/>	Cu	0	0		Cu1
2	<input type="checkbox"/>					
3	<input type="checkbox"/>					
4	<input type="checkbox"/>					
5	<input type="checkbox"/>					
6	<input type="checkbox"/>					

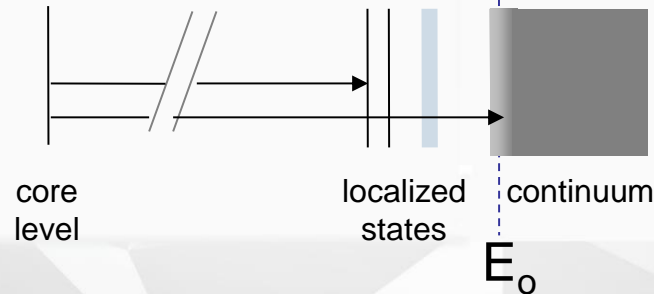
Note: Cluster size and path length must include the longest distance you expect to analyze

# The Pre-edge region

caused by electronic transitions (mainly dipole) to empty bound states near the Fermi level.



Empty state density



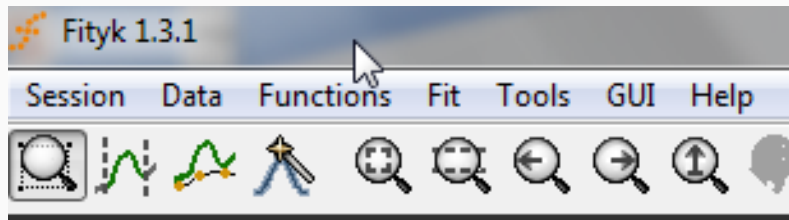
Note: it's complementary to the XPS, probing the occupied density of states.

# Analysis of the pre-edge: Peak fitting

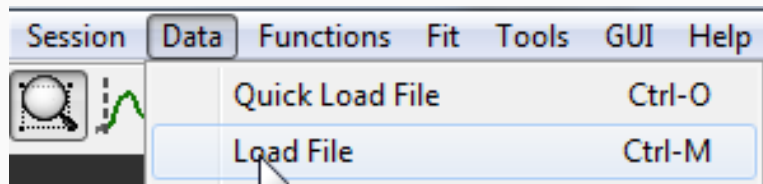
0. Load, manage and save normalized spectra (Athena)

All\_L3\_norm\_XANES.nor

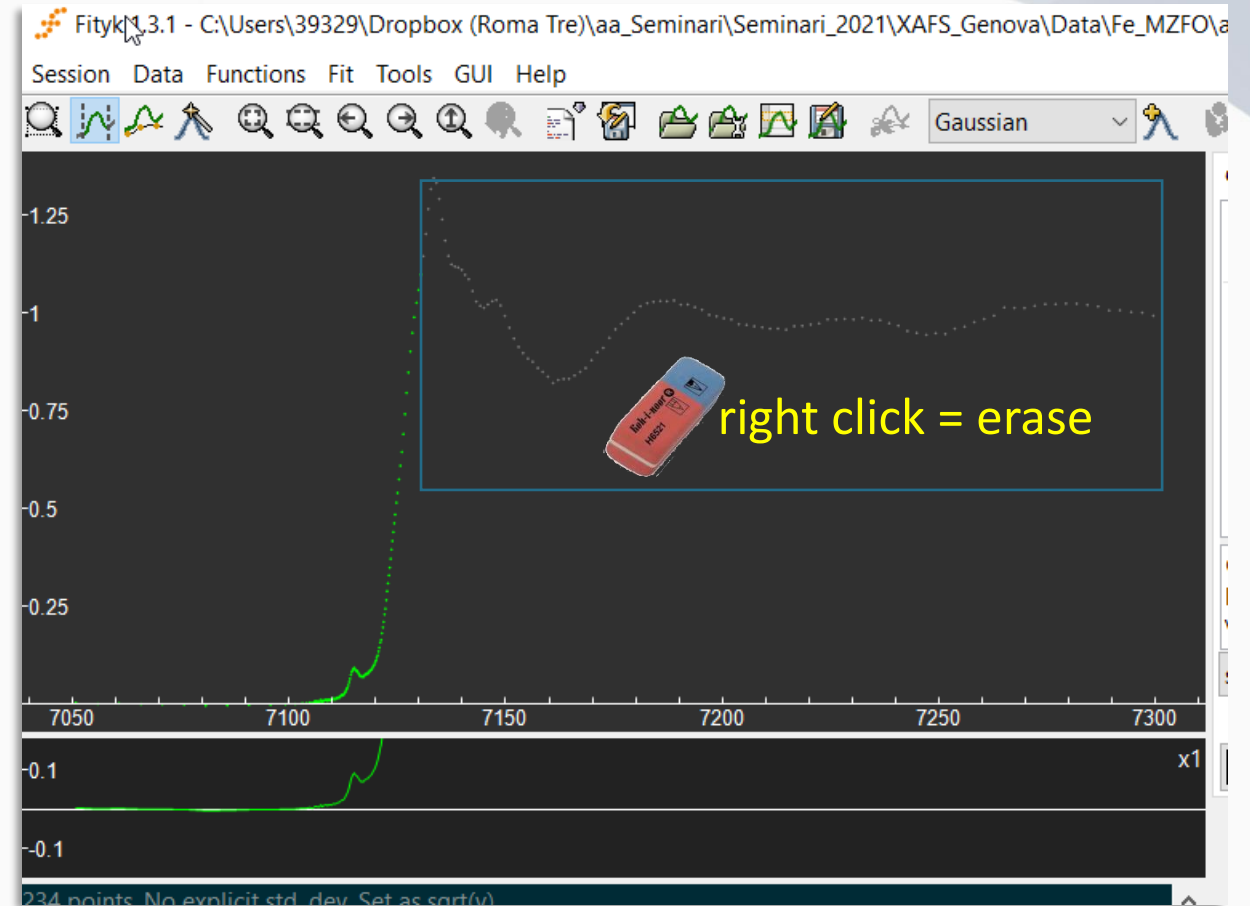
## 1. Start Fityk



## 2. Load the normalized spectrum



## 3. Select the Edge region



# Analysis of the pre-edge: Peak fitting

All\_L3\_norm\_XANES.nor

## 1. Add models

Functions Fit Tools GUI Help

Function Type

Definition Manager

Guess Peak

Auto-Freeze

Export Peak Parameters

Export Formula

Export Points

Constant

Linear

Quadratic

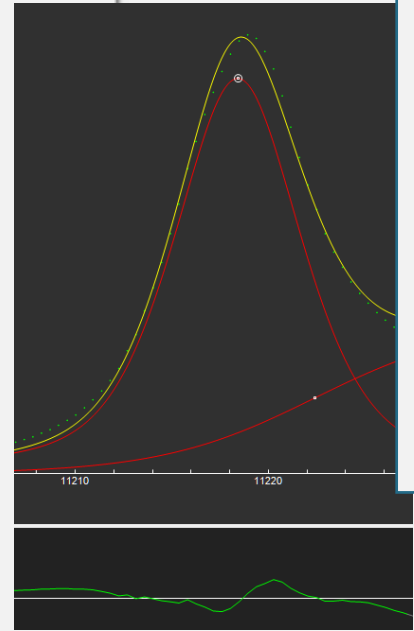
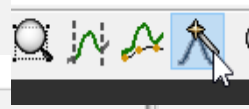
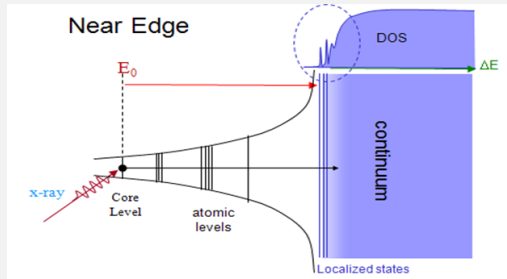
Cubic

Polynomial4

Polynomial5

Polynomial6

Gaussian



Define reasonable initial values for the parameters

## 2. Add constraints

Parameters for %\_1 : Sigmoid:

- lower: 0.025
- upper: 1
- xmid: 7123.96
- wsig: 1.835

Parameters for %\_1 : Sigmoid (constraints):

- lower: 0
- upper: 1
- xmid: 11565
- wsig: 4

Parameters for Sigmoid:

- height: 0.06166939
- center: 7115.407
- hwhm: 2.048429

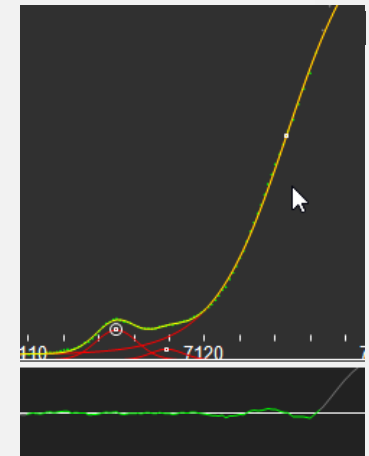
Parameters for Gaussian: same HWHM

Buttons: manual add, add i, same HWHM for all functions

No recipe:  
trial and error!

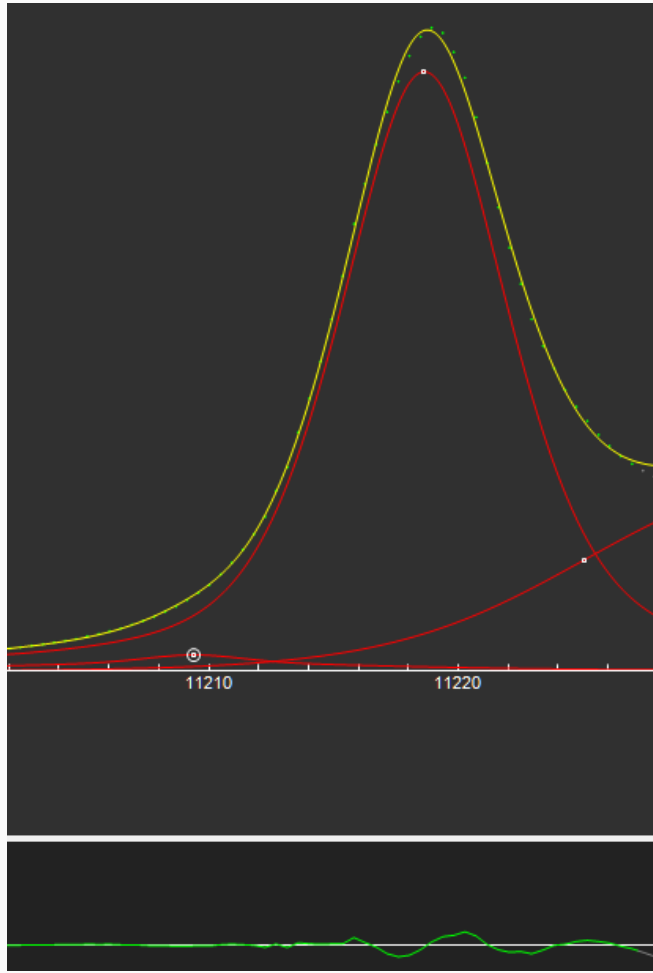
Fix/release refinement parameters to avoid correlations

## 3. Fit

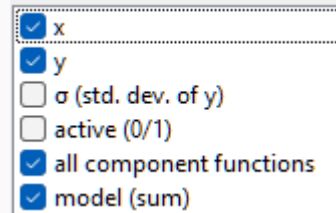
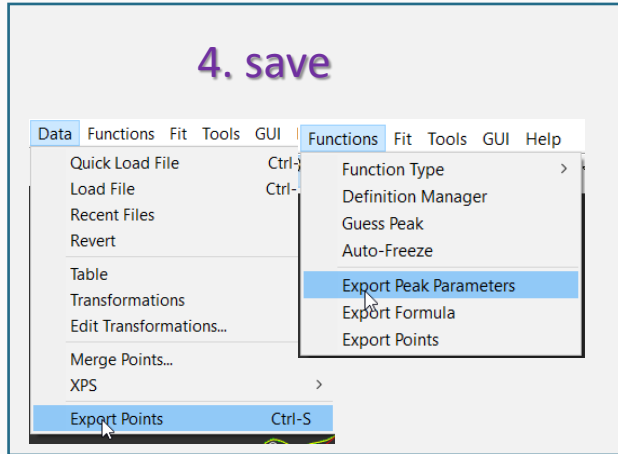


# Analysis of the pre-edge: Peak fitting

All\_L3\_norm\_XANES.nor



## 4. save

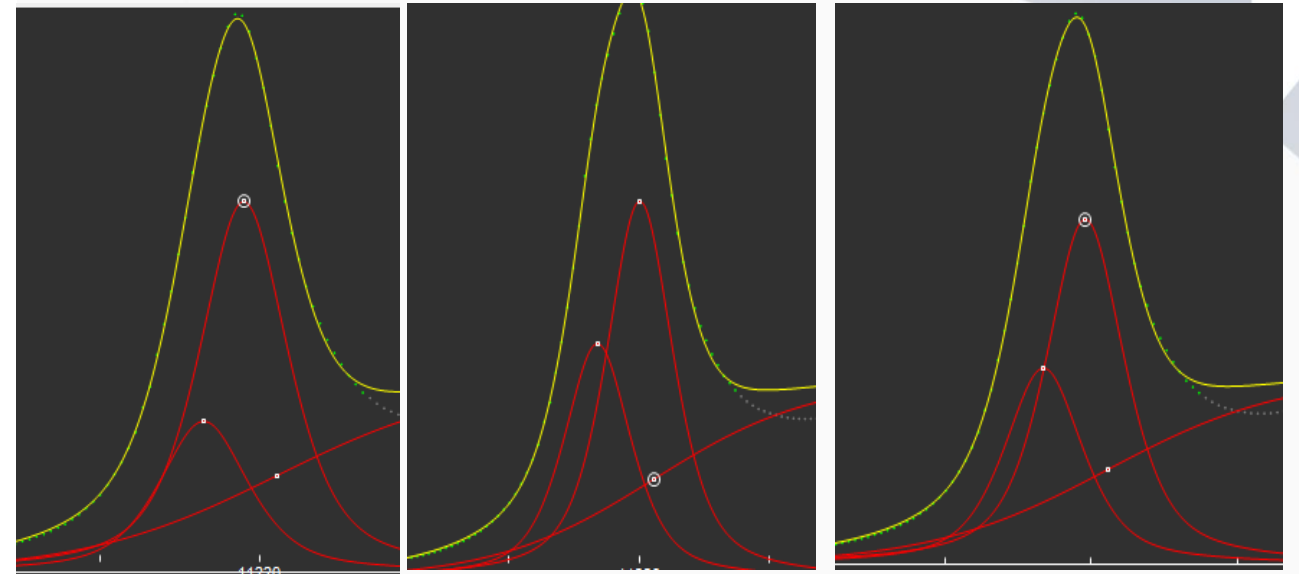
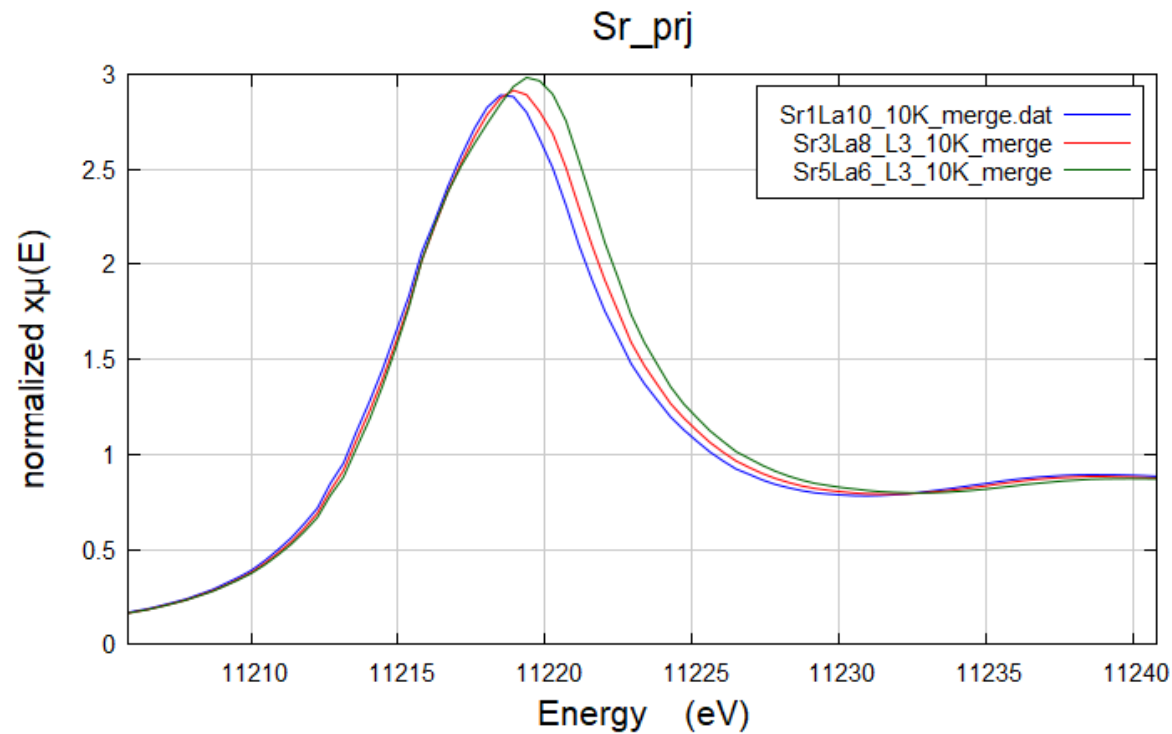


*No recipe:  
trial and error!*

*Check the residual*

# Analysis of the pre-edge: Peak fitting

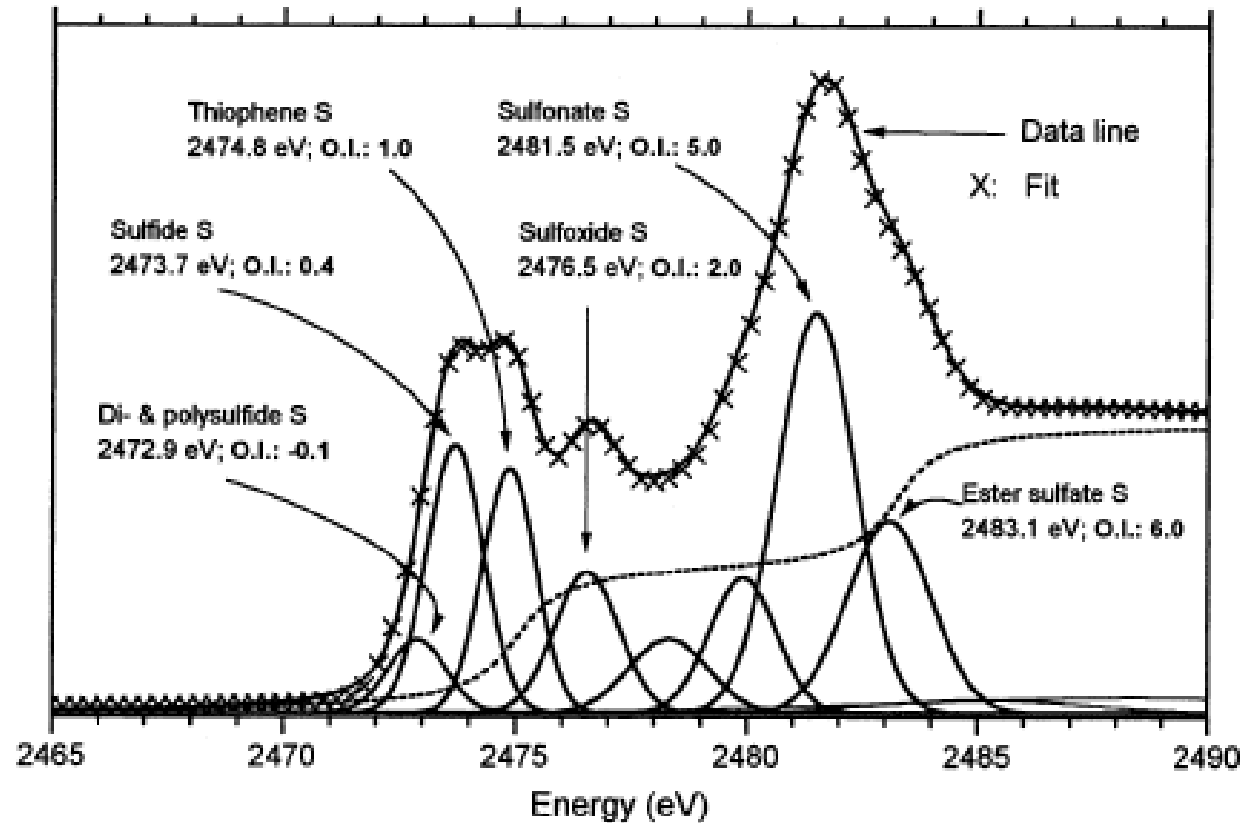
We fitted the XANES region at  $L_3$  and  $L_2$  edges with sigmoid function plus two Voigt peaks representing the transitions  $2p-5d_{3/2}$  and  $2p-5d_{5/2}$



XANES change slightly from Sr1 to Sr3 to Sr5 pointing out a progressive widening of the  $t_{2g}-e_g$  energy difference



# Edge region: a valuable fingerprint for chemical speciation



*A. Vairavamurthy / Spectrochimica Acta Part A 54 (1998) 2009–2017*

*chemical speciation of Sulphur  
in humic substances*

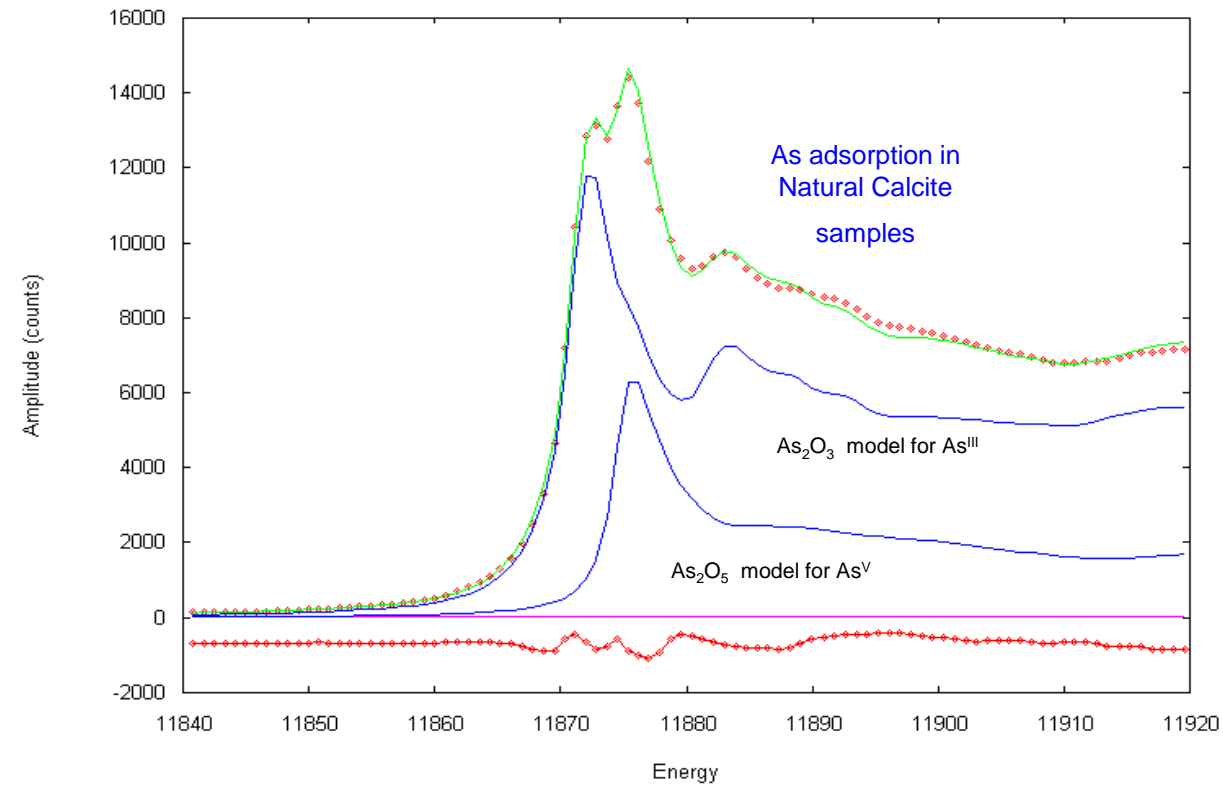
# Analysis of the XANES: chemical speciation in mixtures

## Linear Combination Analysis (LCA)

## Linear Combination Fit (LCF)

$$\mu^{th} = \sum_j \alpha_j \mu^{ref_j}$$

$$R^2 = \sum_i (\mu^{exp}(E_i) - \mu^{th}(E_i))^2$$



Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

Geochimica et Cosmochimica Acta 75 (2011) 3011–3023

Geochimica et  
Cosmochimica  
Acta

[www.elsevier.com/locate/gca](http://www.elsevier.com/locate/gca)

Arsenic uptake by natural calcite: An XAS study

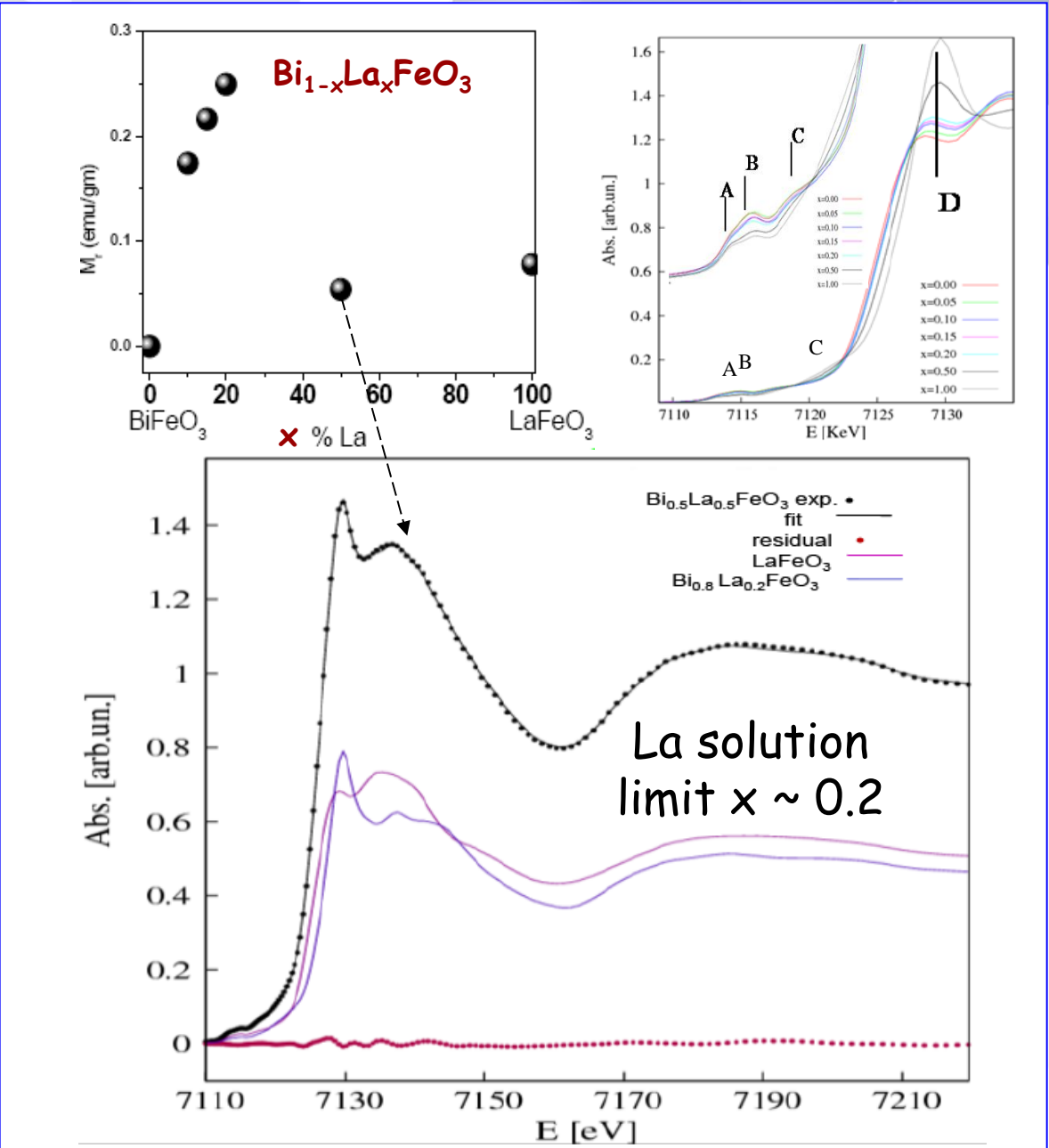
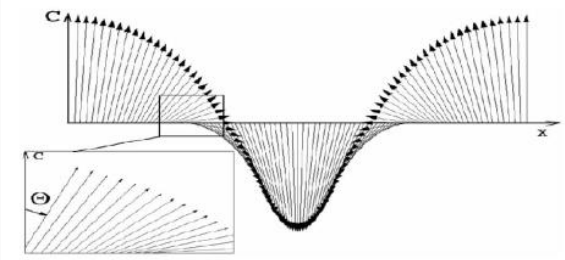
F. Bardelli<sup>a</sup>, M. Benvenuti<sup>b</sup>, P. Costagliola<sup>b,\*</sup>, F. Di Benedetto<sup>b,c</sup>, P. Lattanzi<sup>d</sup>,  
C. Meneghini<sup>e</sup>, M. Romanelli<sup>c</sup>, L. Valenzano<sup>f</sup>

# Analysis of the XANES: chemical speciation in mixtures

Magnetic properties of La doped  $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$  improves doping with La till  $x \sim 0.2$  then  $M_i$  suddenly drops down.

Why?

Above  $x \sim 0.2$   $\text{LaFeO}_3$  phase separate out (solution limit) worsening the overall property of the system



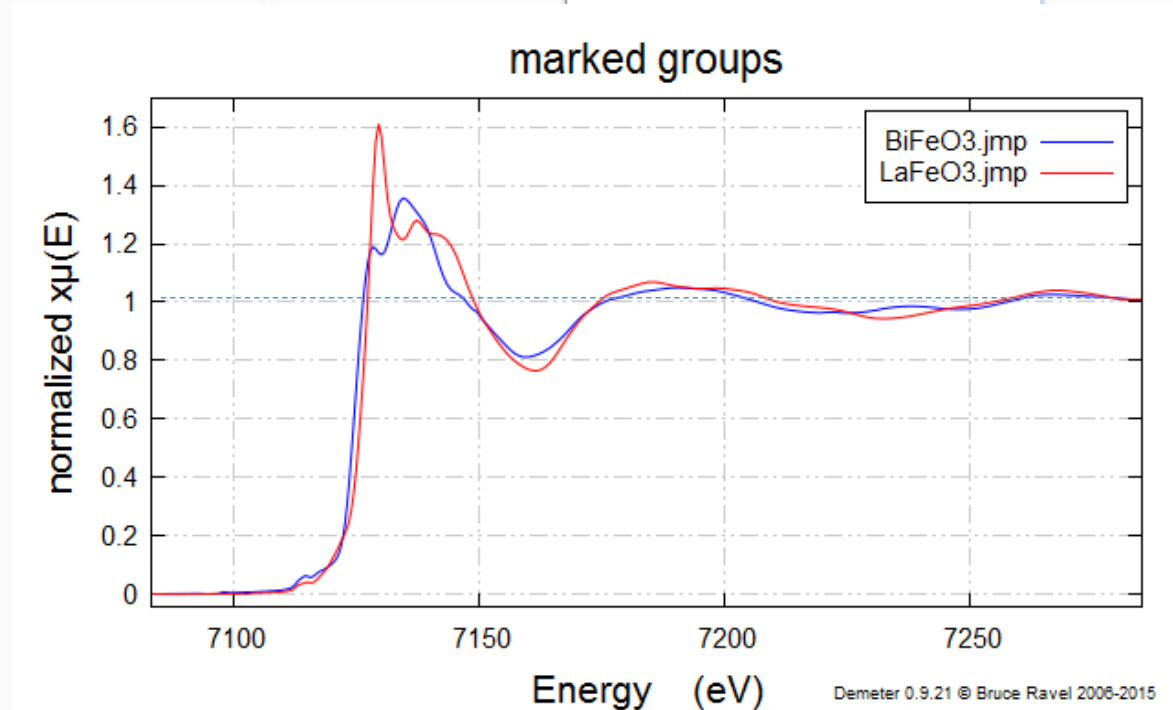
# Data on: LCA-BiLaFeO

Nome	
Bi50La50FeO3.jmp	$\text{Bi}_{0.5}\text{La}_{0.5}\text{FeO}_3$
Bi80La20FeO3.jmp	$\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$
Bi90La10FeO3.jmp	$\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$
BiFeO3.jmp	$\text{BiFeO}_3$
LaFeO3.jmp	$\text{La}_0\text{FeO}_3$

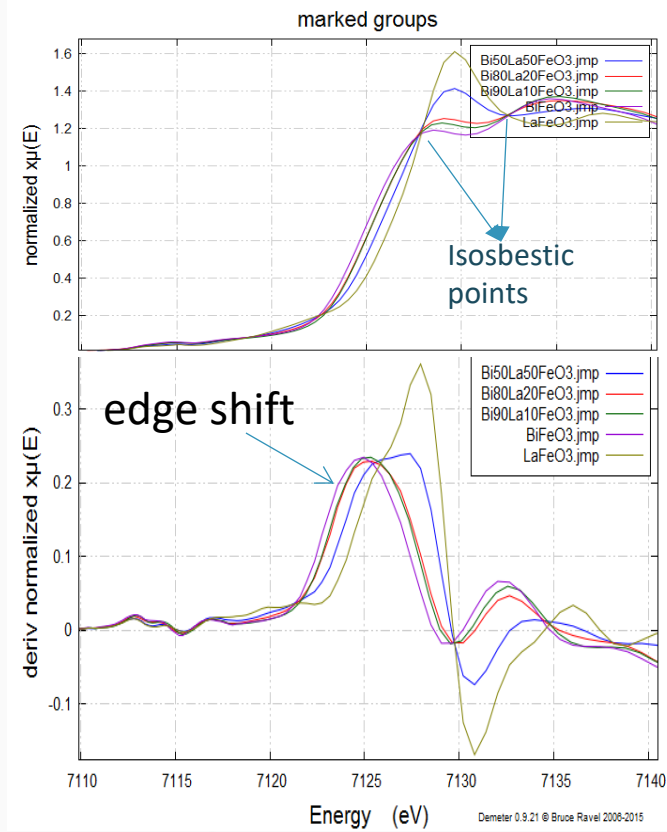
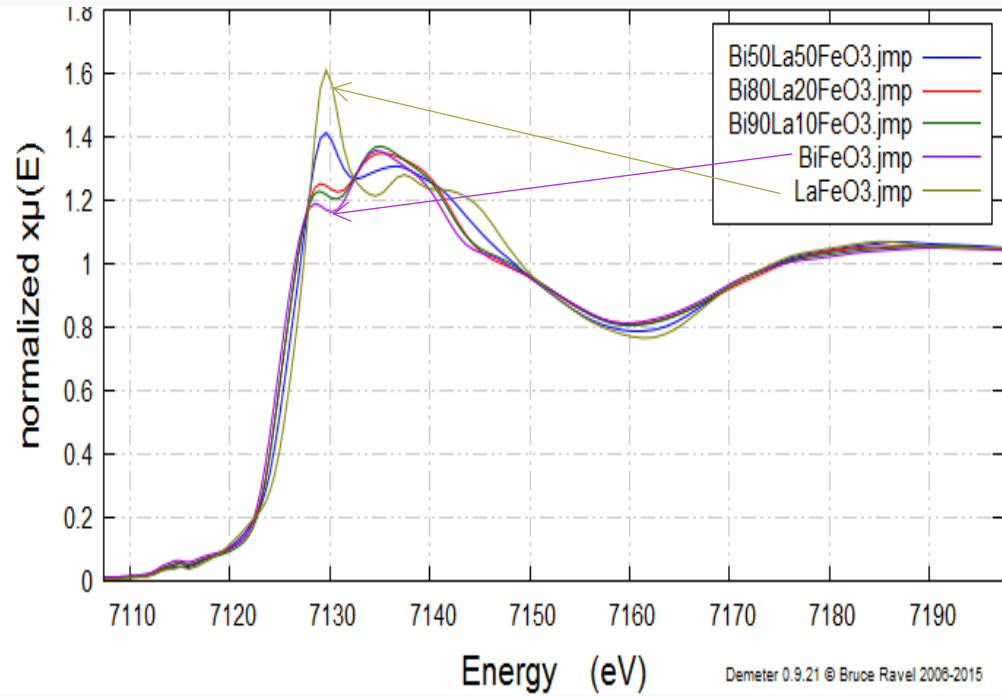
- Start Athena
- load all the files (columns 1,2)

Select range	Clear nu
Energy	<input checked="" type="radio"/> 1 <input type="radio"/> 2 <input type="radio"/> 3 <input type="radio"/> 4 <input type="radio"/> 5
Numerator	<input type="checkbox"/> 1 <input checked="" type="checkbox"/> 2 <input type="checkbox"/> 3 <input type="checkbox"/> 4 <input type="checkbox"/> 5
Denominator	<input type="checkbox"/> 1 <input type="checkbox"/> 2 <input type="checkbox"/> 3 <input type="checkbox"/> 4 <input type="checkbox"/> 5

- Bi50La50FeO3.jmp
- Bi80La20FeO3.jmp
- Bi90La10FeO3.jmp
- BiFeO3.jmp
- LaFeO3.jmp



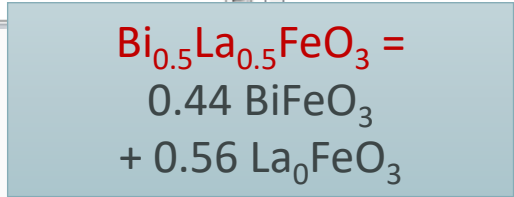
# Compare spectra with the end compounds



Check for data alignment

# Compare spectra with the end compounds

- Main window
- Main window
- Calibrate data
- Align data
- Rebin data
- Deglitch and truncate data
- Smooth data
- Convolute and add noise to data
- Deconvolute data
- Self-absorption correction
- Multi-electron excitation removal
- Copy series
- Data summation
- 
- Linear combination fitting
- Principle components analysis
- Peak fitting
- Log-ratio/phase-difference analysis
- Difference spectra
- 



LCF fit of Bi50La50FeO3.jmp as flattened  $\mu(E)$  from 7107.411 to 7157.411

Fit included 118 data points and 3 variables, and approximately 37.528 measurements

Weights sum to 1: yes

Weights forced between 0 and 1: yes

Overall e0 shift used: no

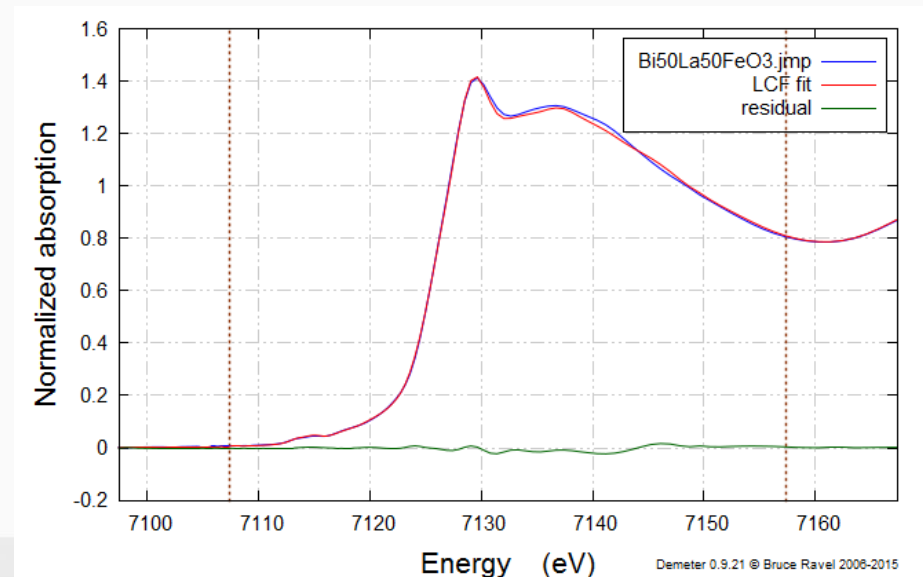
Noise added to data: 0

R-factor = 0.0001869

Chi-square = 0.00614

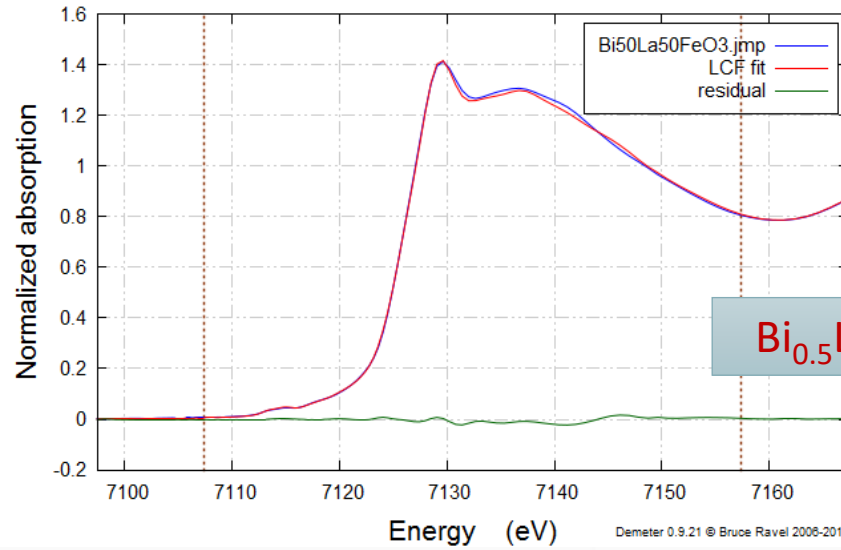
Reduced chi-square = 0.0000534

standard	weight	e0
BiFeO3.jmp	0.443 (0.008)	-0.008 (0.034)
LaFeO3.jmp	0.557 (0.008)	-0.119 (0.019)



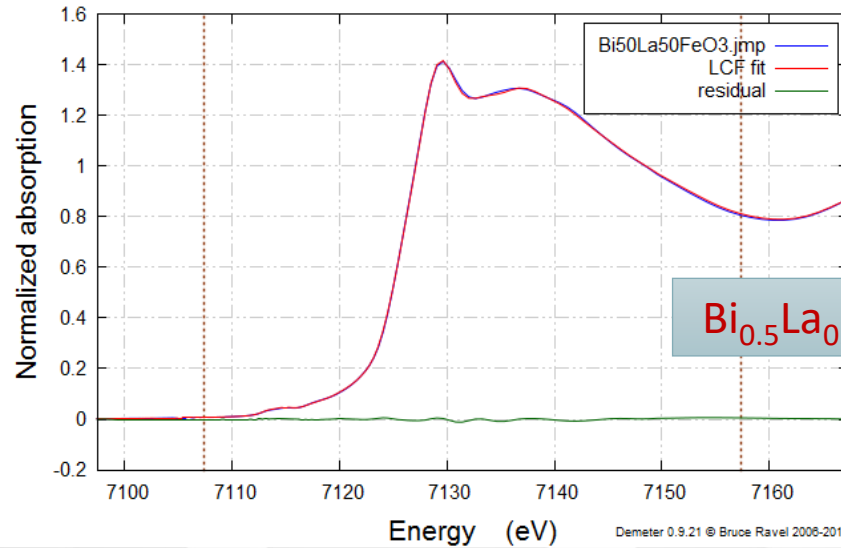
# Compare spectra with the end compounds

Chi-square = 0.0061  
 Reduced chi-square = 0.000053

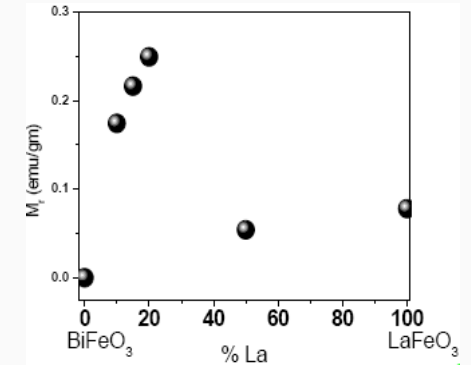


$\text{Bi}_{0.5}\text{La}_{0.5}\text{FeO}_3 = 44\% \text{ BiFeO}_3 + 56\% \text{ LaFeO}_3$

Chi-square = 0.00124  
 Reduced chi-square = 0.000011



$\text{Bi}_{0.5}\text{La}_{0.5}\text{FeO}_3 = 53\% \text{ Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3 + 47\% \text{ LaFeO}_3$



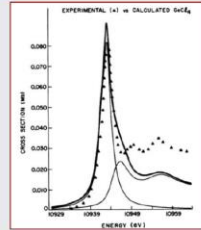
# Ab-Initio XANES modelling

## Toward a quantitative interpretation of XANES

### XANES development

Lee & Pendry Phys. Rev. B 11, 2795 (1975) (initial theory)  
C.R. Natoli et al. Phys. Rev. A, 22, (1980) (first calculations)

First-principles calculation of x-ray absorption-edge structure in molecular clusters  
C. R. Natoli, D. K. Misemer, S. Doniach, and F. W. Kutzler



### Theory

Tyson, Hodgson, Natoli, Benfatto Phys. Rev. B 465997 (1992)

A. Filippini et al. Phys. Rev. B 52, 12122 (1995)

Ankudinov et al. Phys. Rev. B 58, 7565 (1998)

J. Rehr Rev. Mod. Phys. 72, 621 (2000)

### programs for XANES:

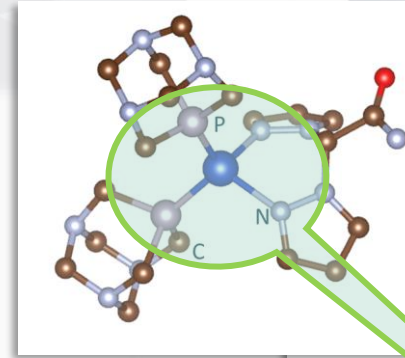
C. R. Natoli and M. Benfatto CONTINUUM, MXAN freeware

J. Rehr, Ankudinov FEFFx (x=6,8,9) freeware Licence

Y. Joly FDMNES freeware

## Ab Initio XANES modelling requires:

- long computation time 🤔
- specific skills 😎
- solid theoretical background 🧠
- **patience to manage long (and frustrating!) trial and errors procedures** 💣



Cu-site local modification in Cu-AuNP+water solution

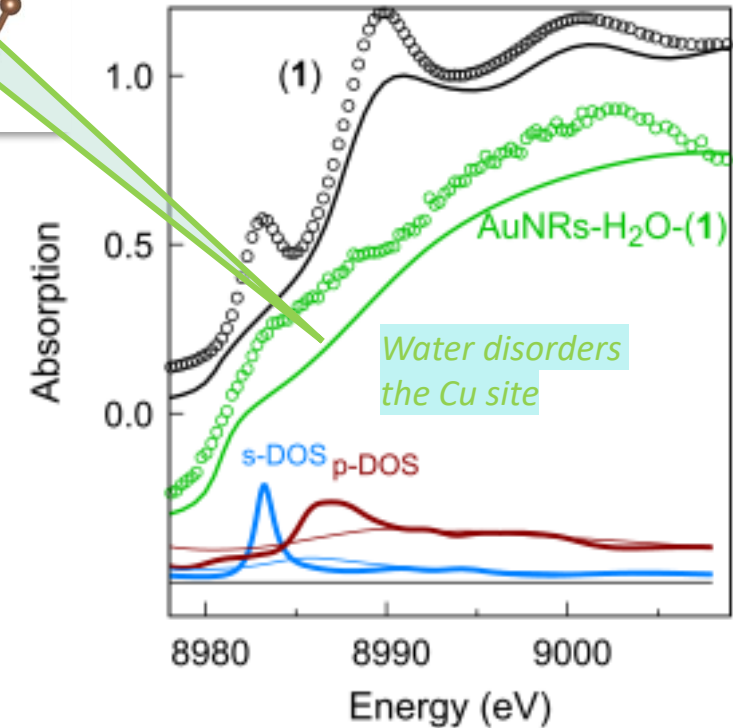


Figure 8. The experimental XANES data (circles) and model curves (full lines) of complex 1 (black) and AuNRs-H<sub>2</sub>O-(1) samples are shown, vertically shifted for clarity. Bottom curves represent the calculated Cu s- and p-density of states (DOS) for the complex 1 model (tick line) and for the AuNRs-H<sub>2</sub>O-(1) model (thin lines).



# Thanks for...

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