Tutorial on XAFS data Analysis

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Muggia (Italy), 16 - 26 September 2024

The XAS spectrum

XAFS data ANALYSIS:
from experimental data to (quantitative) structural information
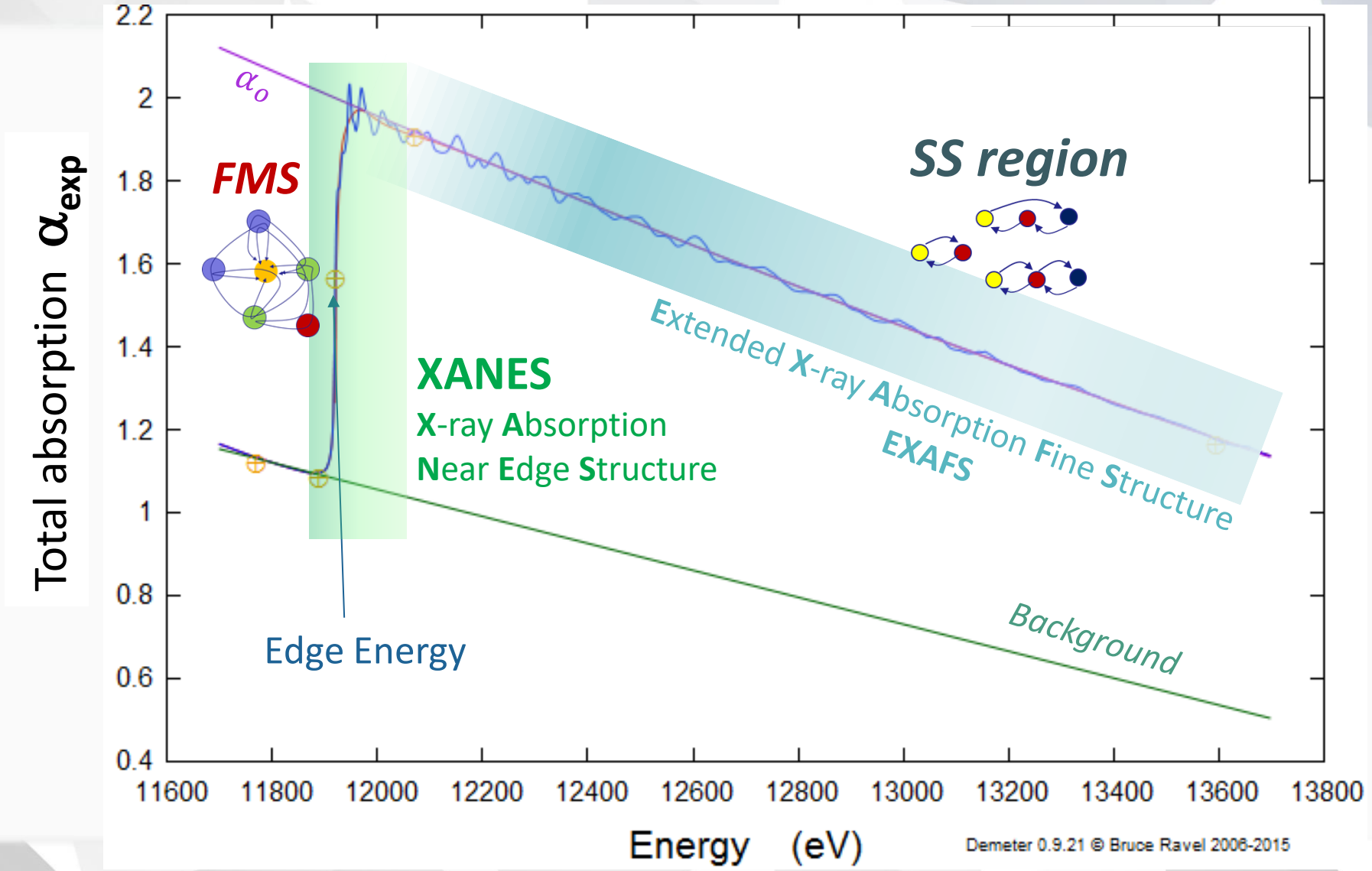
Software

Mandatory

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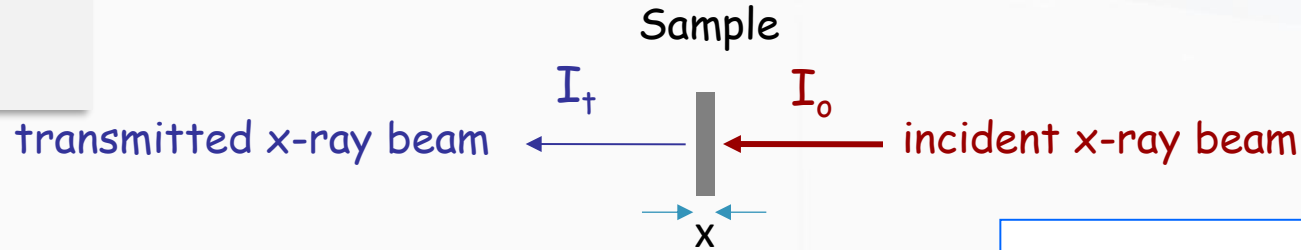- **Data manipulation** (EXCEL, ORIGIN, Gnuplot, ….)

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

Sample

I_t I_o

transmitted x-ray beam ← incident x-ray beam

x

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

μ = Linear absorption coefficient

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

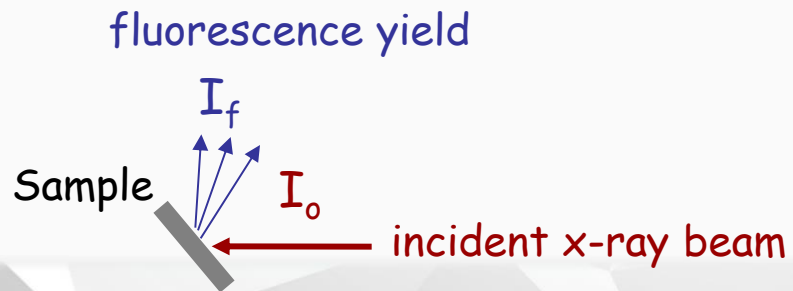Low concentration:
$\mu x \ll 0.1$

Fluorescence geometry

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

$\mu \cdot x \ll 1$

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

fluorescence yield

I_f

Sample I_o

incident x-ray beam

$$I_f \simeq I_o \mu \cdot x$$

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

```
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_X1vert 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
```

μ absorption signal measured in fluorescence geometry

Energy I_o I_{trasm} and/or I_{fluo} I_{ref} $\ln\left(\dfrac{I_o}{I_{trasm}}\right)$ $\ln\left(\dfrac{I_{trasm}}{I_{ref}}\right)$ $\dfrac{I_{fluo}}{I_o}$

Energy and detector Intensities for Transmission or fluorescence

Reference signal, for energy calibration

μ absorption signal

μ_{ref} ref absorption signal

Reference   *Sample*

I_{ref} ← I_{trasm} ← I_o ←   *Trasm*

Reference

I_{fluo}

I_{ref} ← I_{trasm} ← I_o ←   *Fluo*

Sample
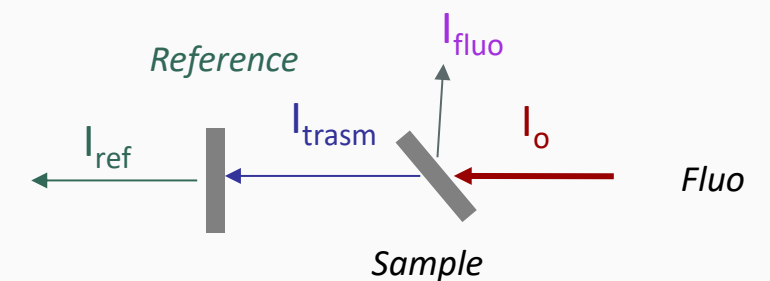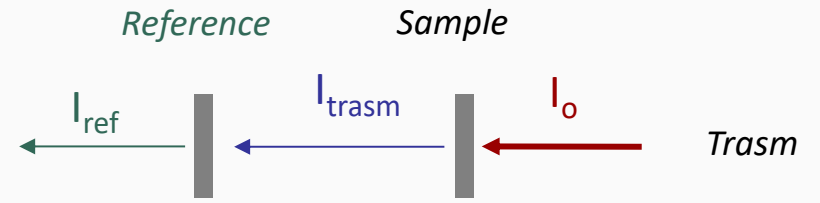
XAFS data analysis Software

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 ←

http://www.ixasportal.net/ixas/

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

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

Demeter

X-ray Absorption Spectroscopy Using Feff and Ifeffit.

Windows Users:

View On GitHub

Demeter © 2006-2015 Bruce Ravel

GnXAS Software

http://gnxas.unicam.it/pag_gnxas.html

The GNXAS package is and advanced software for EXAFS data analysis based on multiple-scattering (MS) calculations and a rigorous fitting procedure of the raw experimental data. The main characteristic 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 α_{exp}

Post edge atomic background α_o

XAFS

Edge Jump

E_o Edge Energy

background α_{bkg}

Total absorption α_{exp}

Demeter 0.9.21 © Bruce Ravel 2006-2015
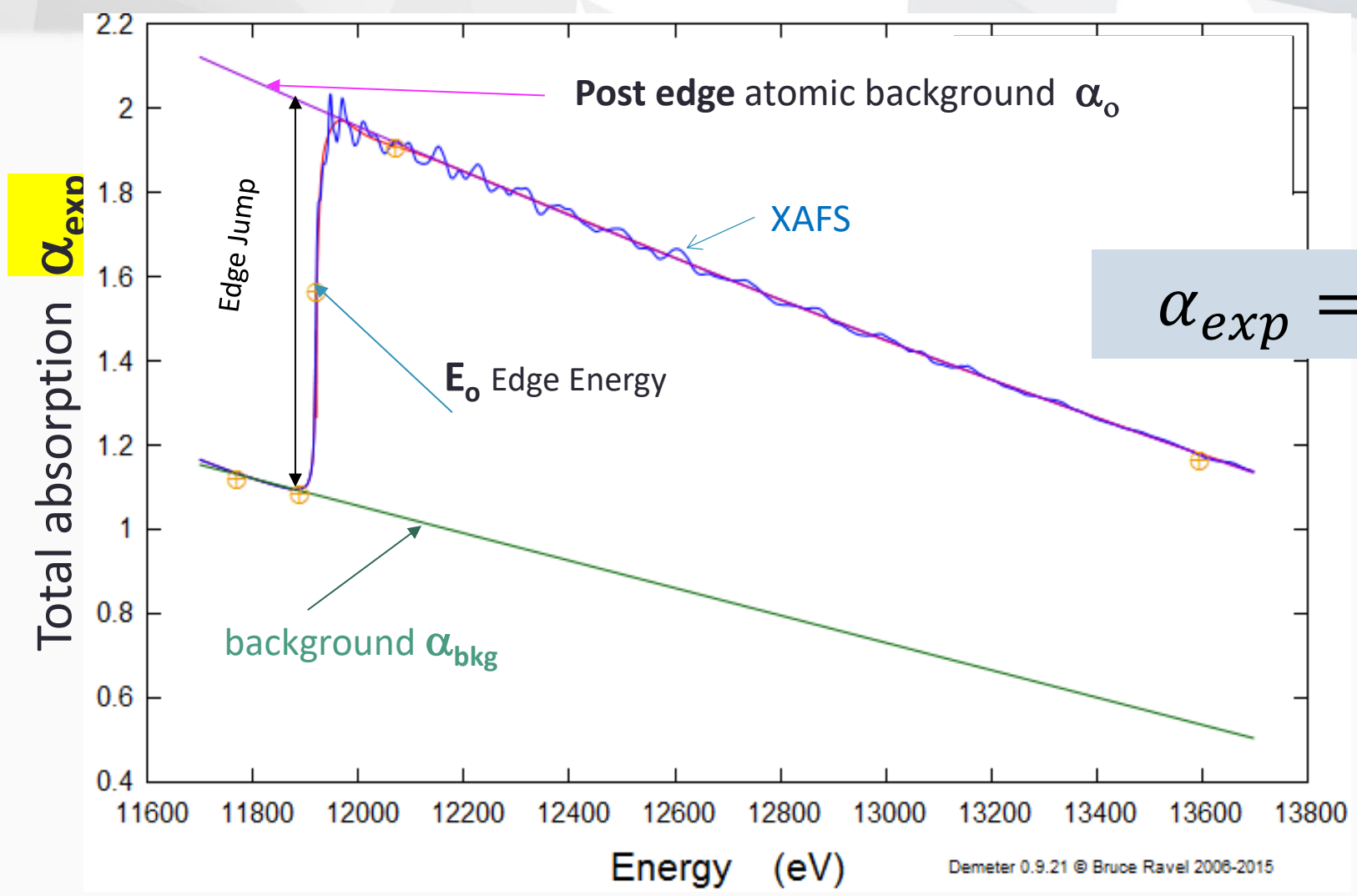
Sample holder
Container
Widows
Air
Other edges
....

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

x: the
edge of interest

α_{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

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

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

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

$$\alpha_{bkg} = mE + q$$

How to get the normalized χ(k)

2. <u>**Normalization**</u>

$\alpha_{exp}(E)$

pre-edge subtraction

Revise procedure

normalization μ

structural signal χ(k)

Fourier Transform
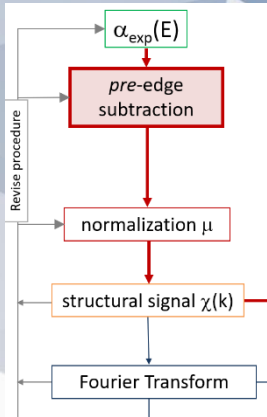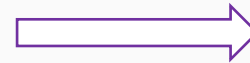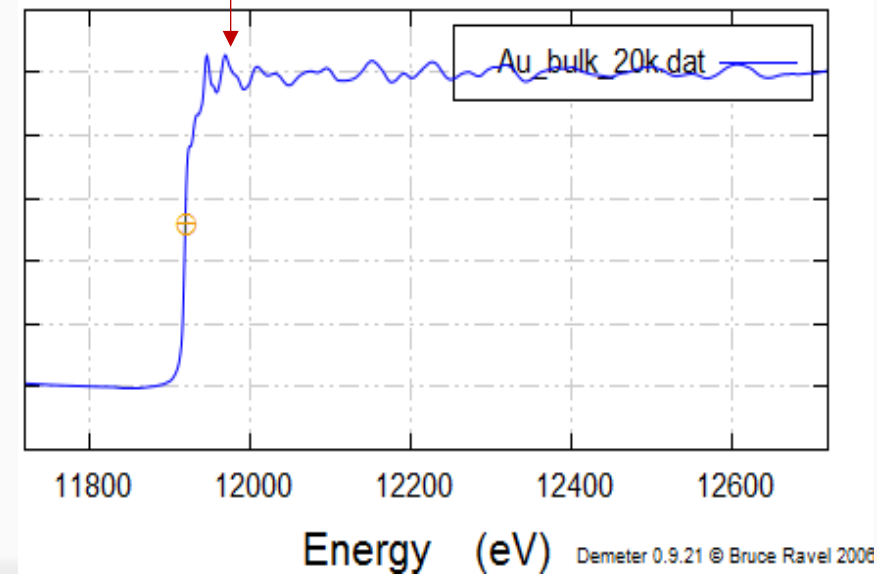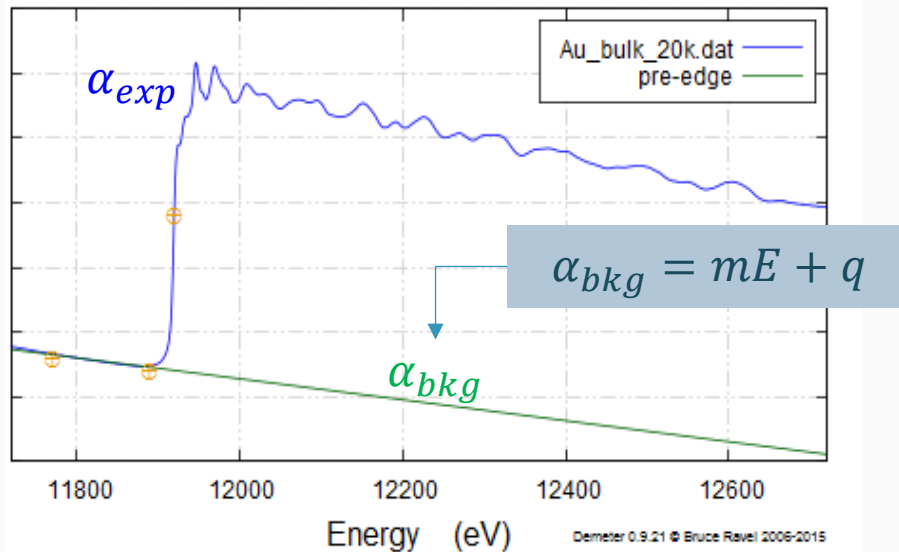
isolated absorber

perturbation from neighbour potentials

$$\mu_x t \simeq \mu_o (1 + \chi) t$$

$$\alpha_{norm} = \frac{\alpha_x}{\alpha_o} = \frac{\cancel{\mu_o}(1 + \chi)\cancel{t}}{\cancel{\mu_o}\cancel{t}}$$

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

$\mu_x t$

$\mu_o t = \alpha_o$

$$\boxed{\alpha_x = \mu_x t}$$

1

μ_x

E_0

$$\alpha_{norm}(E) = \frac{\alpha_x}{\alpha_0} = 1 + \chi$$

Au_bulk_20k.dat in energy

background
Au_bulk_20k.dat

Demeter 0.9.21 ® Bruce Ravel 2006-2015
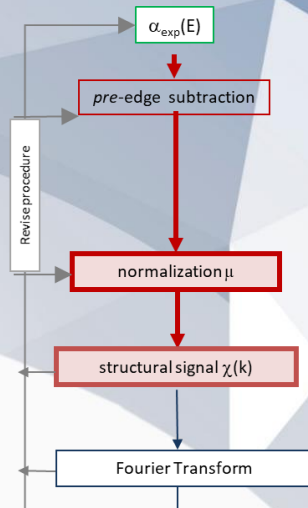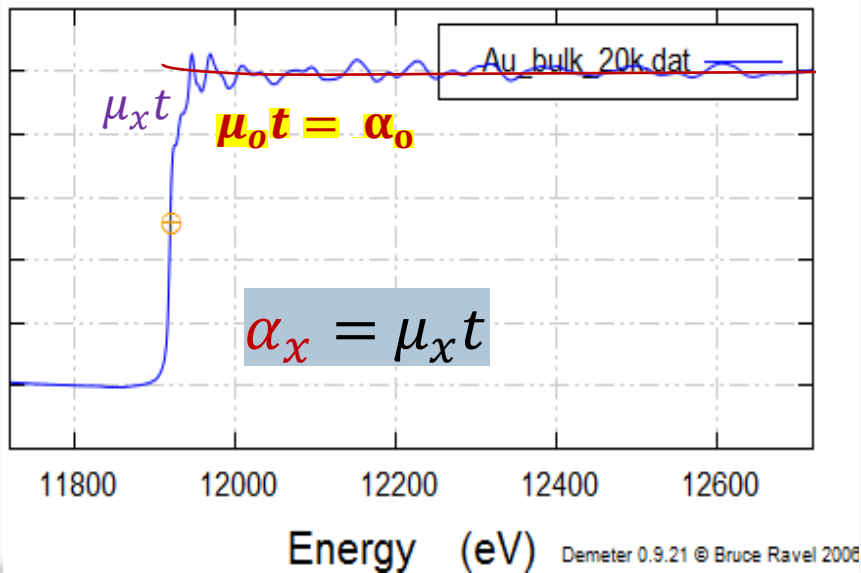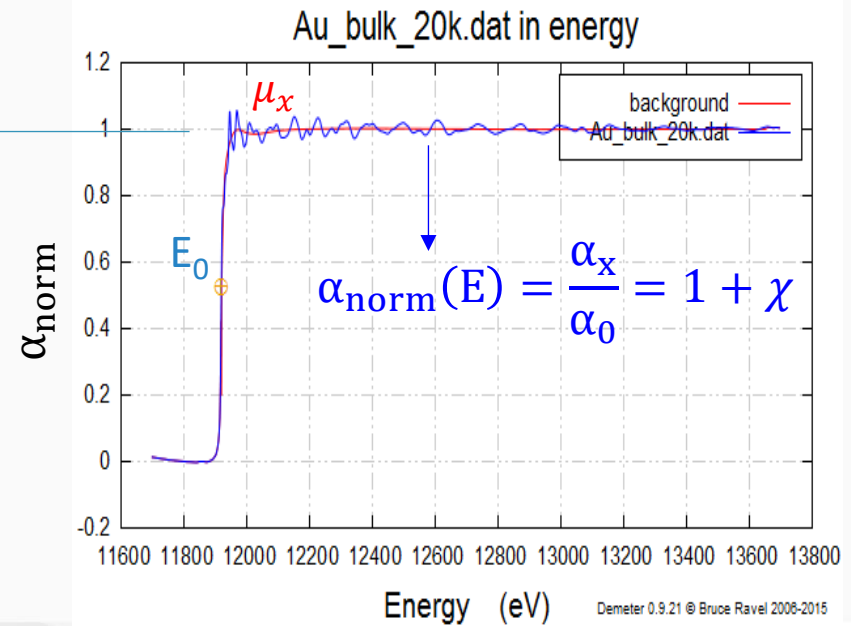
How to get the normalized χ(k)

2. **Normalization**

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

$$\alpha_{norm}(E) = \frac{\alpha_x}{\alpha_0} = 1 + \chi$$
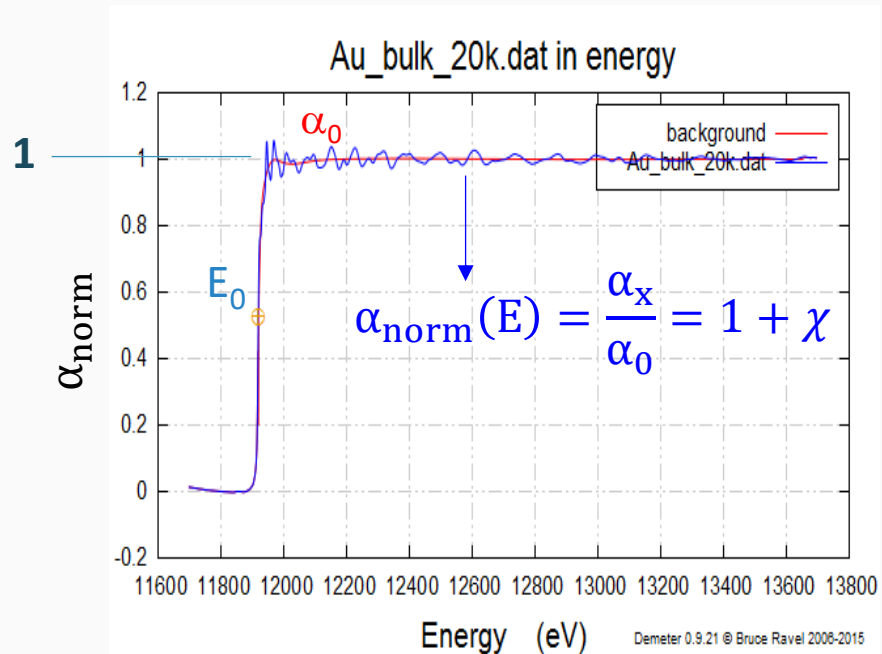
α_0 is calculated empirically as a smooth curve across the data.

Requirements for α_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 α_0 applying different but **equivalent** methods
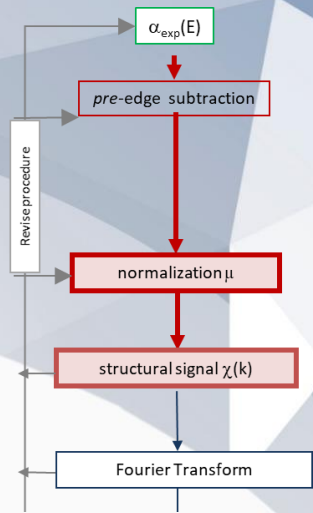
How to get the normalized χ(k)

3. the **structural EXAFS** signal χ

χ = EXAFS structural signal

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

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

Au_bulk_20k.dat in energy

background
Au_bulk_20k.dat

Energy (eV)

Demeter 0.9.21 © Bruce Ravel 2006-2015

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

K [Å⁻¹] Wavenumber (Å⁻¹)

Demeter 0.9.21 © Bruce Ravel 2006-2015

$\alpha_{exp}(E)$

pre-edge subtraction

Revise procedure

normalization μ
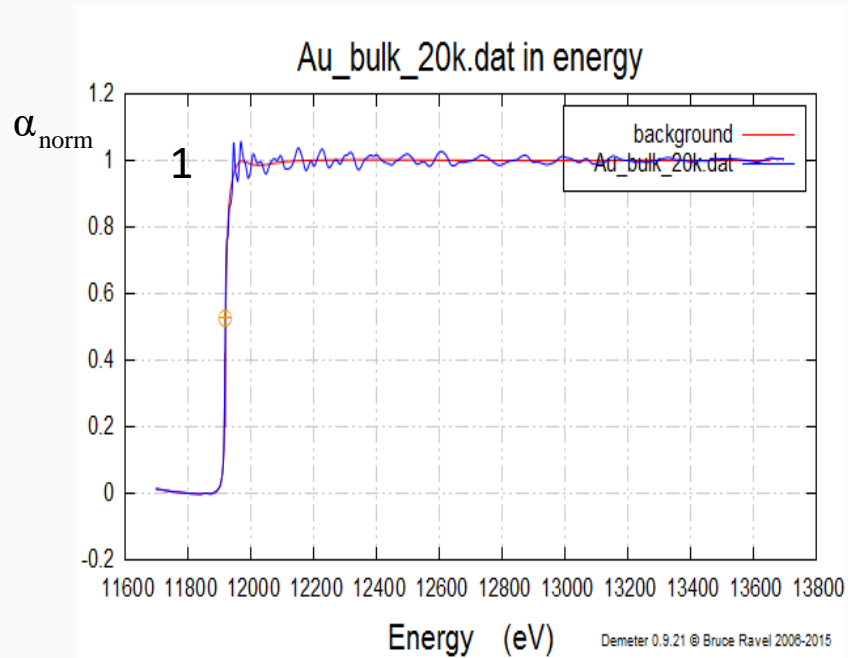
structural signal χ(k)

Fourier Transform
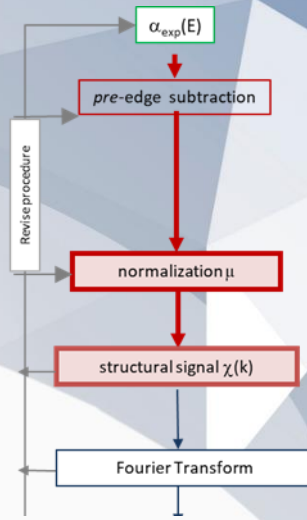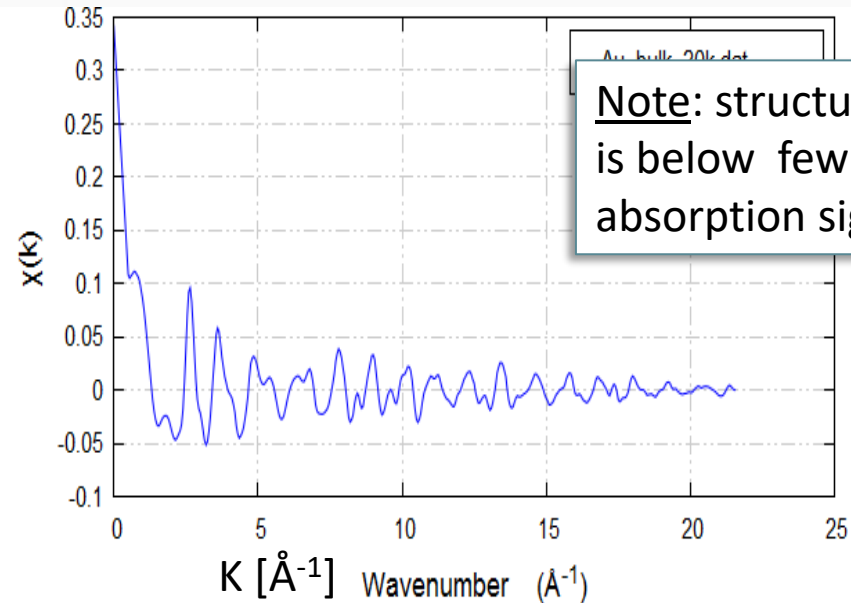
How to get the normalized χ(k)

4. the photoelectron wave vector k

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

$$k = \frac{1}{\hbar}\sqrt{2m_e(E - E_o)}$$
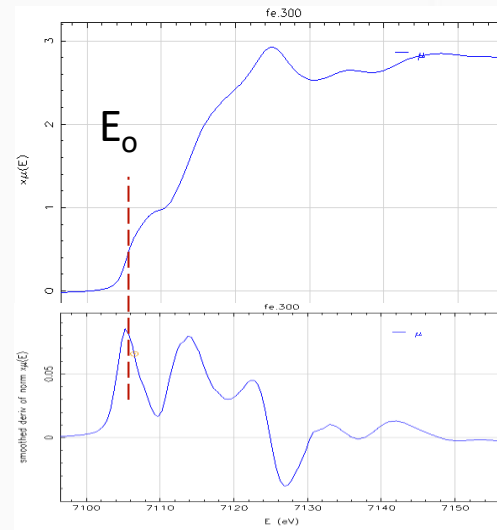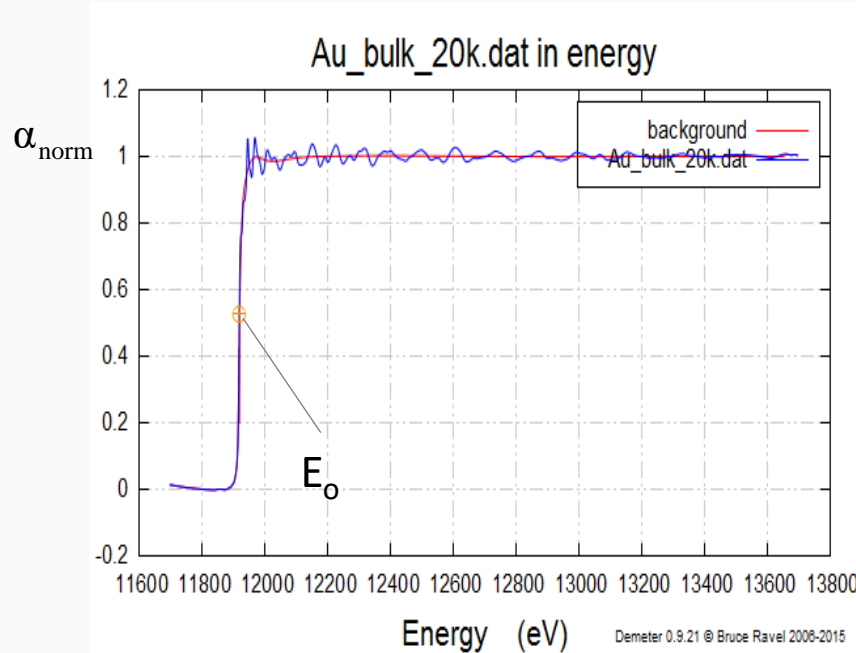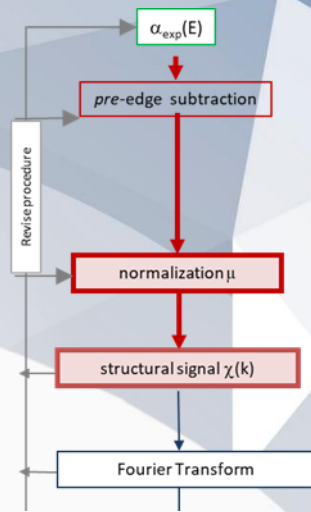
Edge energy is selected (*roughly*)

<u>Metals</u>: at the **first inflection point of α_{nor}**
<u>Oxides</u>: **where $\alpha_{nor} \simeq 0.5$**

It will be refined during the analysis.

Qualitative local structure: pseudo distribution function

3. Fourier transform (k-weight)

Cu
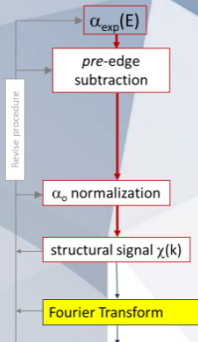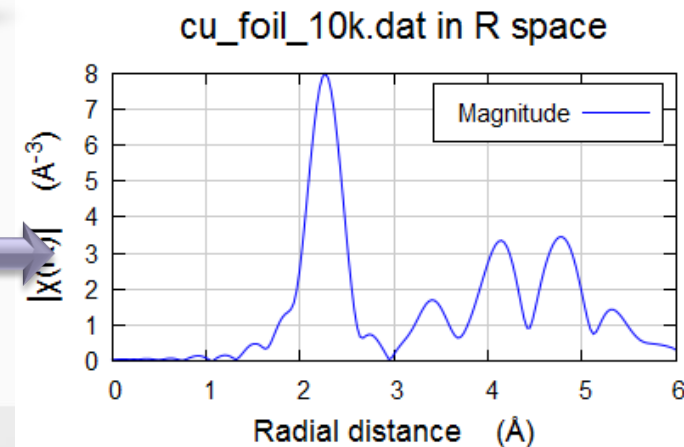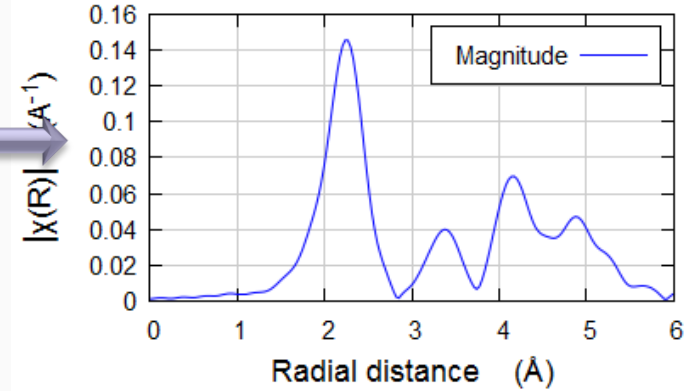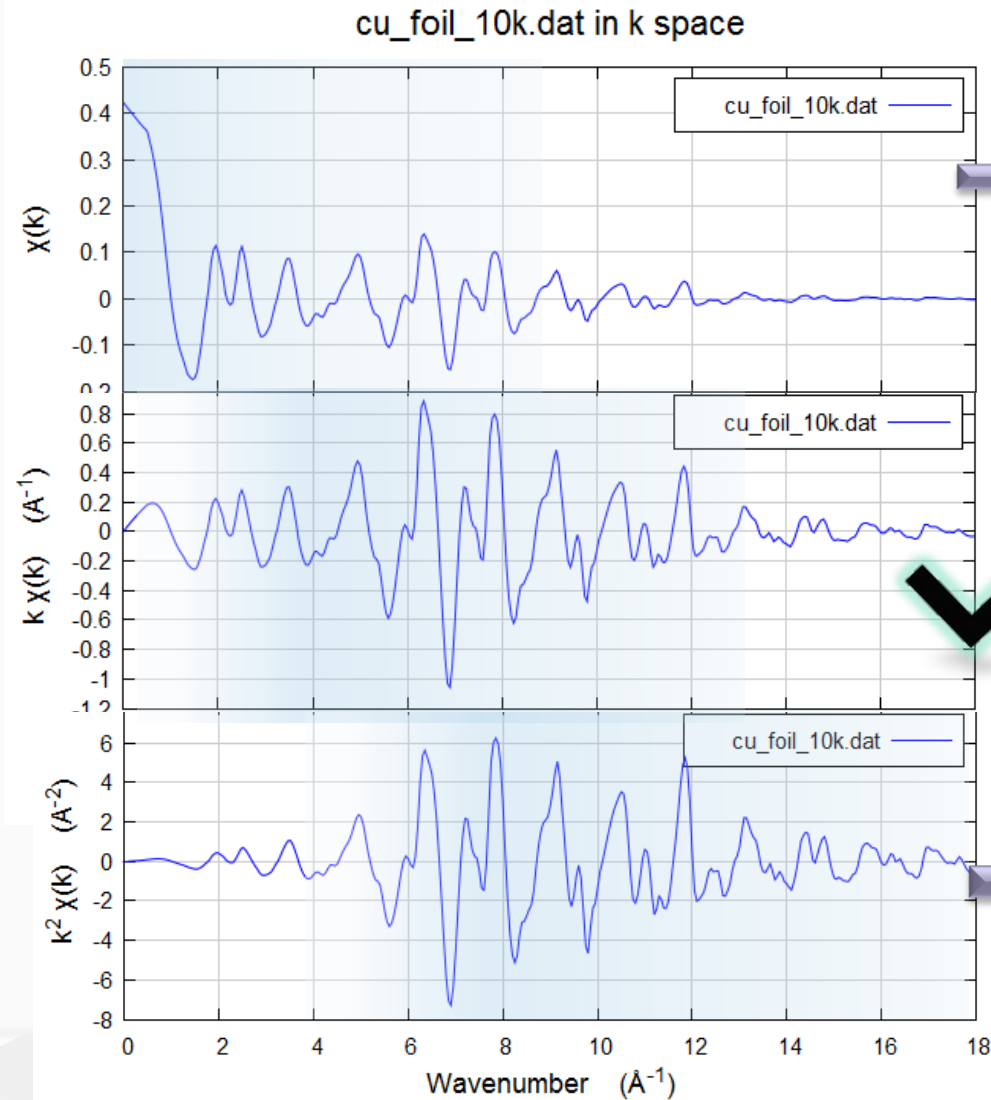
Qualitative local structure: pseudo distribution function

3. Fourier transform

|FT| shows more <u>intuitively</u> the main structural features in the real space:
the FT modulus represents a **pseudo-radial distribution function** 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

Pseudo radial-distribution function

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

$$A_j = S_o^2 \frac{N_j}{R_j^2}|f_j|e^{-2k^2\sigma_j^2}\, e_j^{-\frac{2r_j}{\lambda}}$$
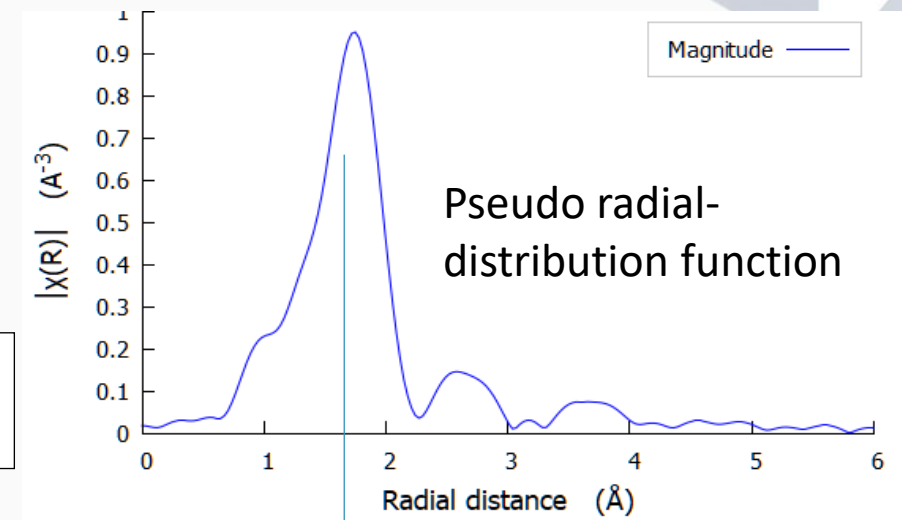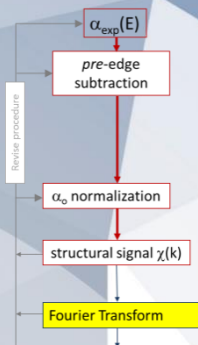
$$R_{true} \simeq R_{FT} + 0.5\text{Å}$$

Extract the XAFS signal (in short)

$$\alpha_{exp} = \mu_x t + \alpha_{pre}$$

$\alpha_{exp}(E)$

pre-edge subtraction

$$\alpha_x = \mu_x t$$

XANES analysis

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

α_o normalization

$$\chi_{exp} = \alpha_{norm}\text{-}1$$

χ_{exp}

structural signal $\chi(k)$

Fourier Transform

Structural refinement

Revise procedure

Check your data:

cu_foil_10k.dat in k space
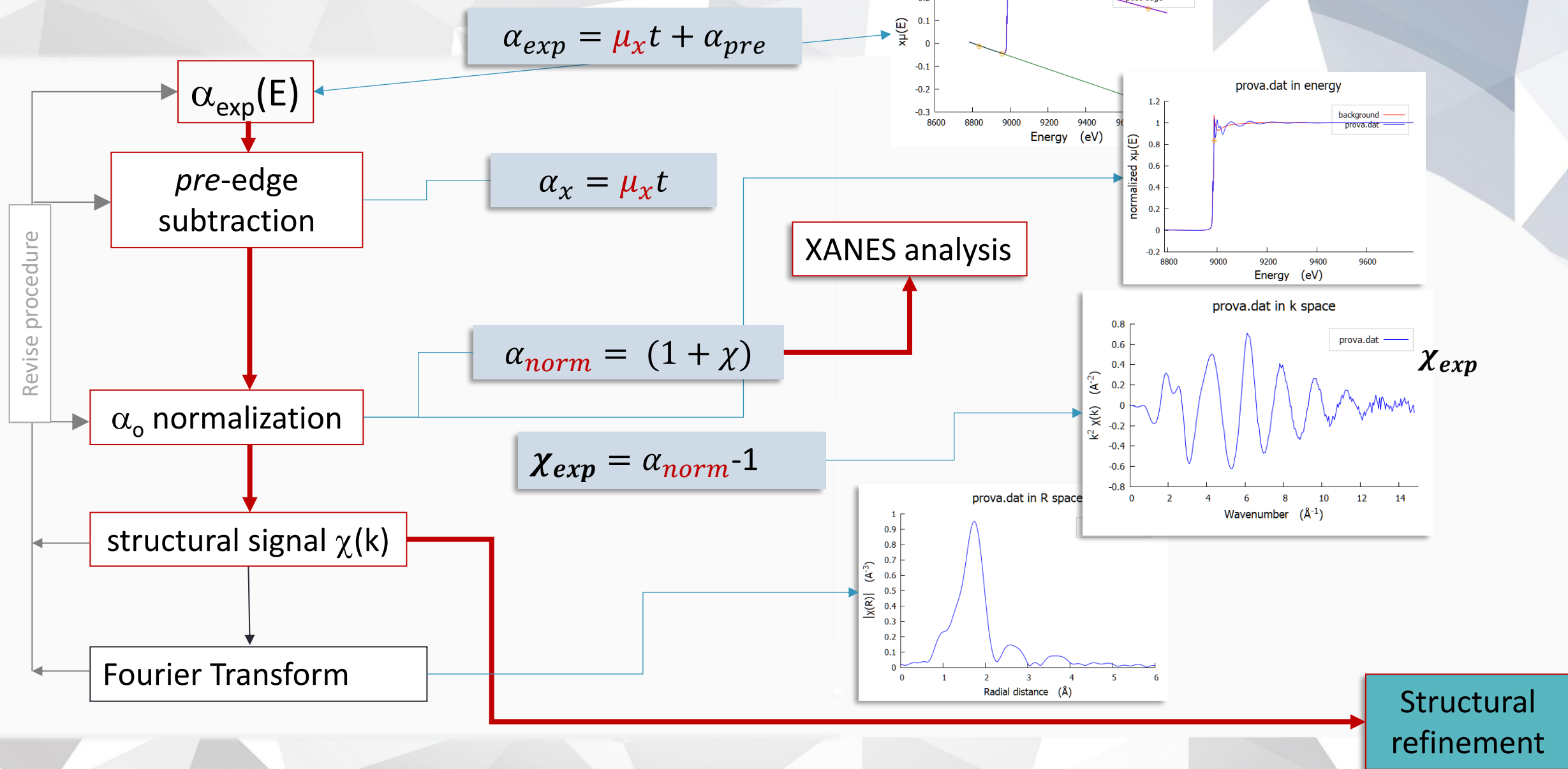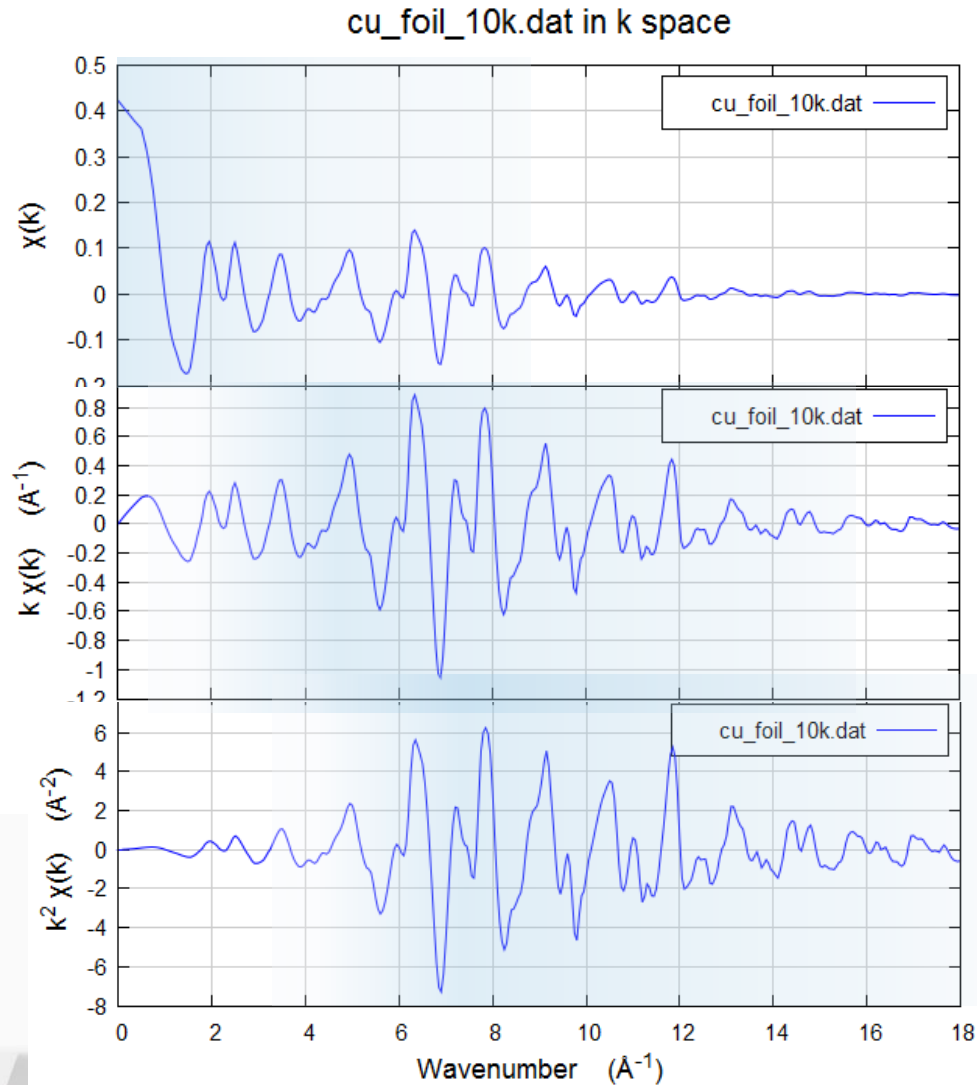
Inspect $k^n\chi(k)$

$k^n\chi(k)$ 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 not linear effects (mean free path)

Check the FT

cu_foil_10k.dat in R space
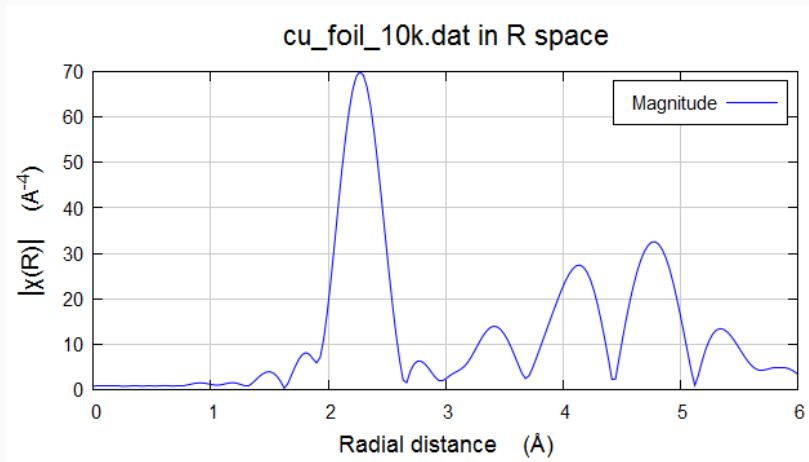
Unphysical peak (below 1 Å!)
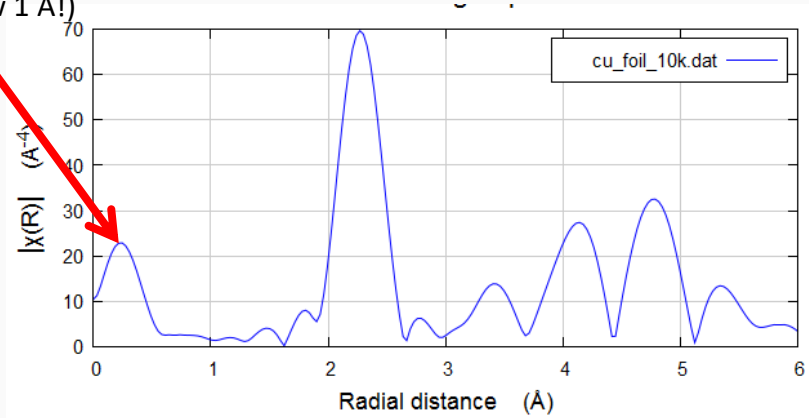
FT features:
Artifacts, distortions, noise, may suggests bad extraction, noise on the data, etc...

i.e.: intense peaks in the low R region (≈ less than 1Å) may signify errors in the extractions

Qualitative local structure: pseudo distribution function
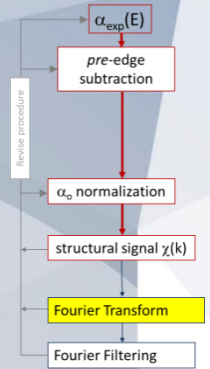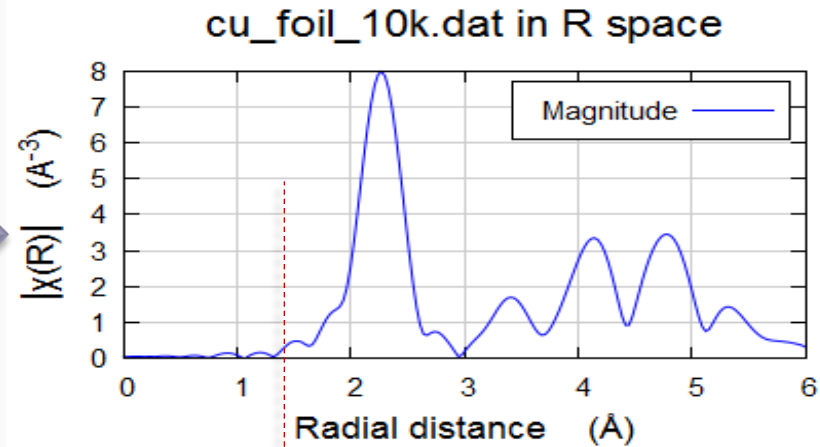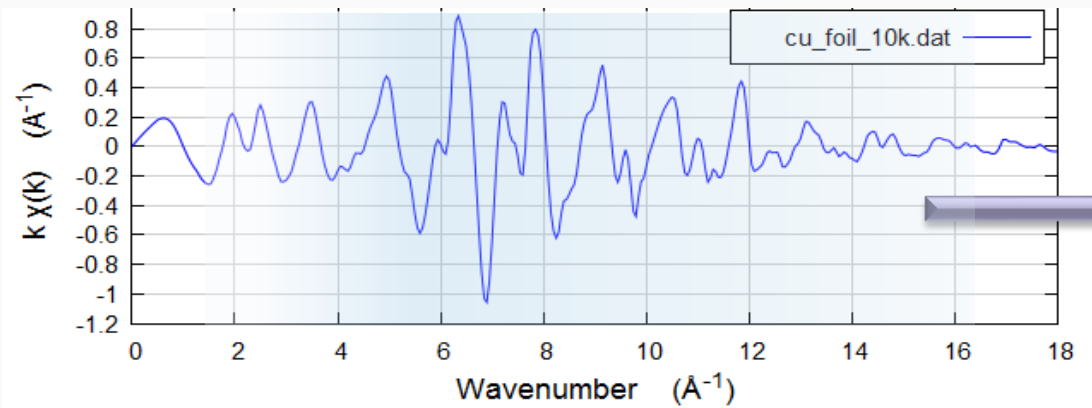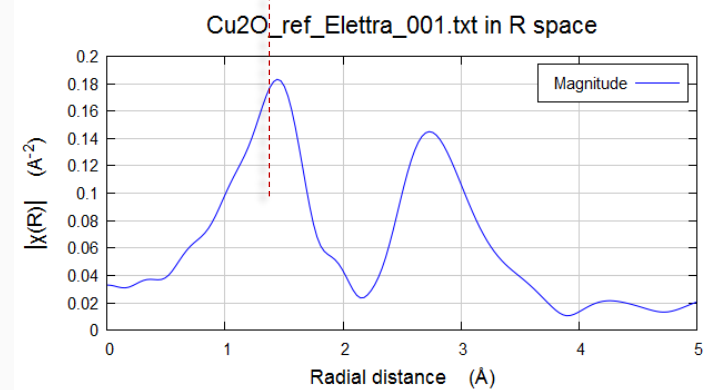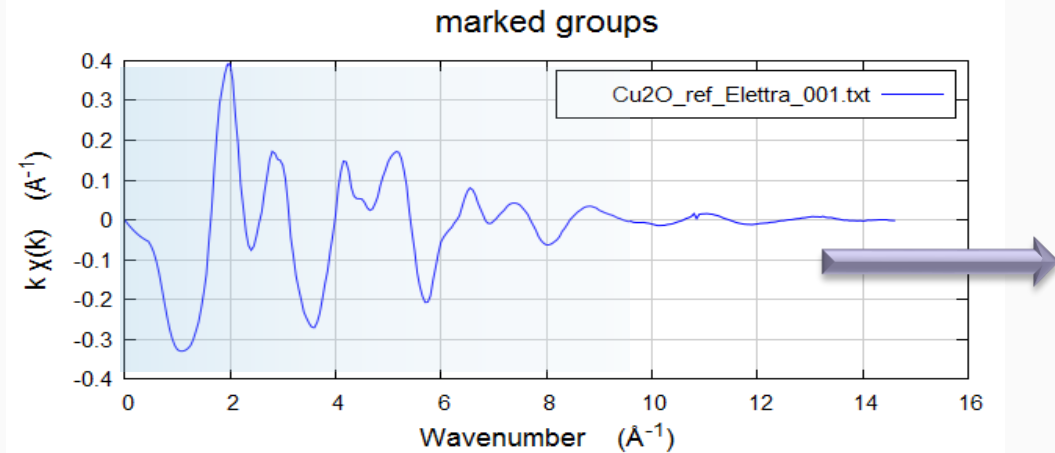
Qualitative local structure: pseudo distribution function

Cu_2O
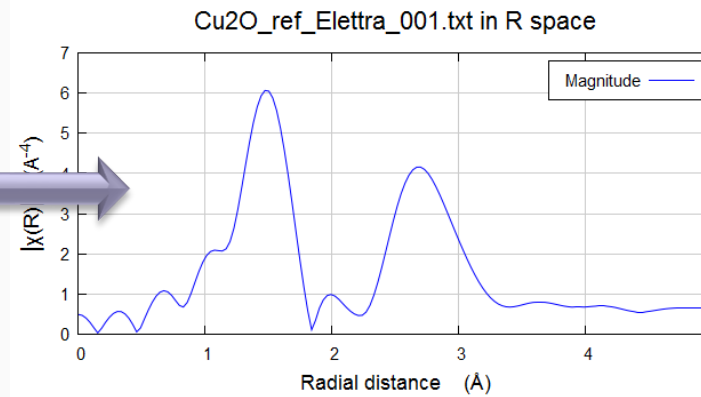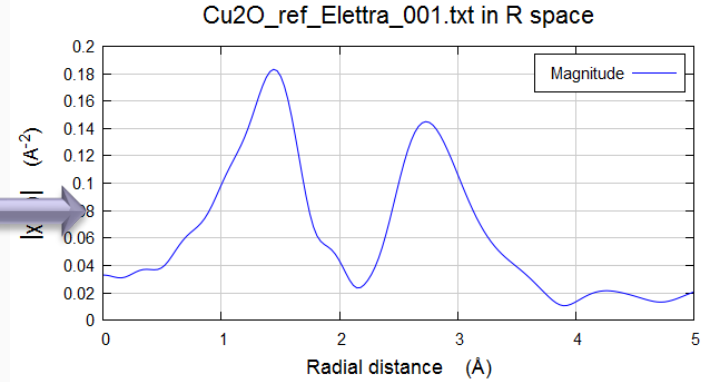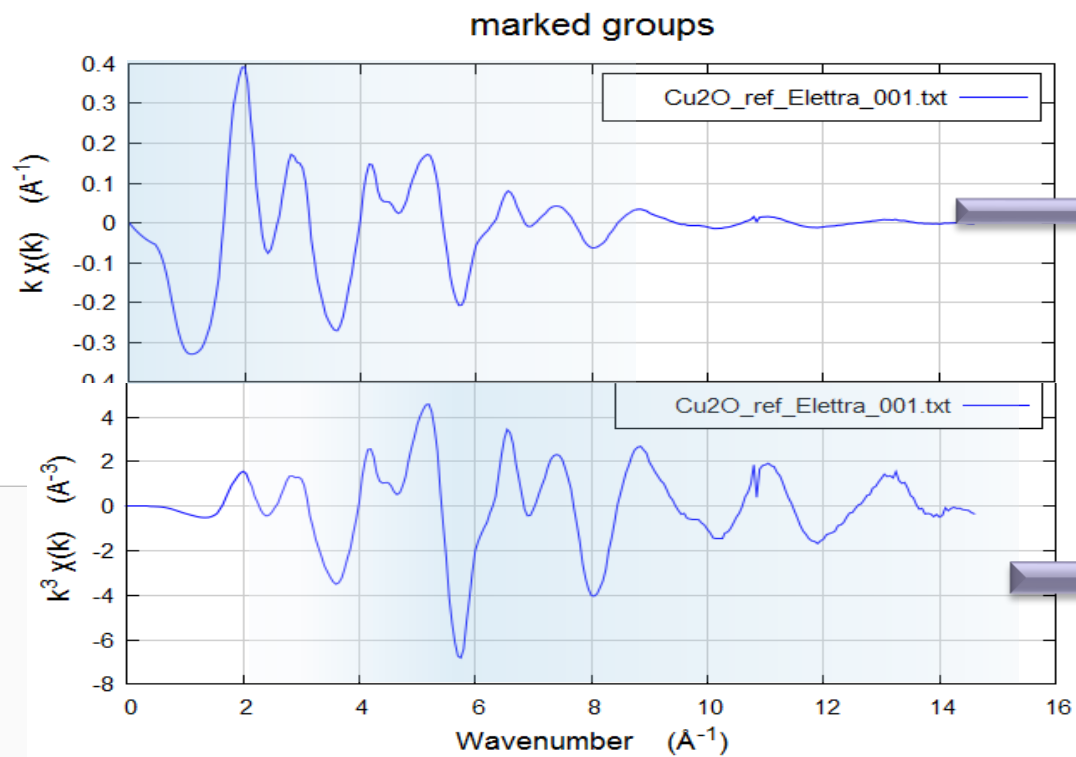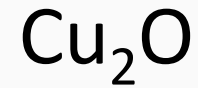
Software

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

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

Hands-on

https://tinyurl.com/Xafs2024
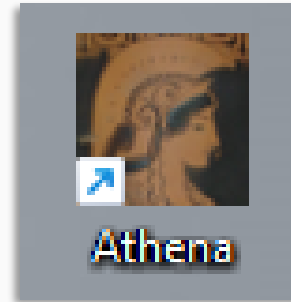
BiLaFeO_LCA
Cu-complex
Iridium_XANES
ok_Cu_Foil
ok_Fe_foil

https://tinyurl.com/Xafs2024DB

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

Structure Visualizers
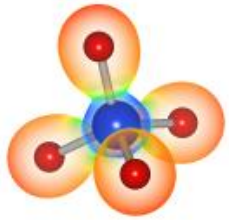
VESTA
Visualization for Electronic and STructural Analysis

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

Google search:
Vesta Download
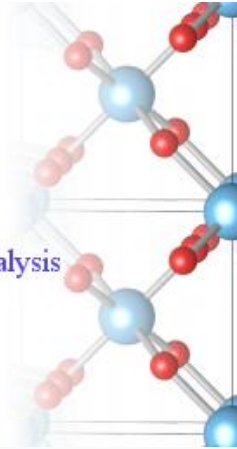
Cu-Complex *Cu_Complex8*

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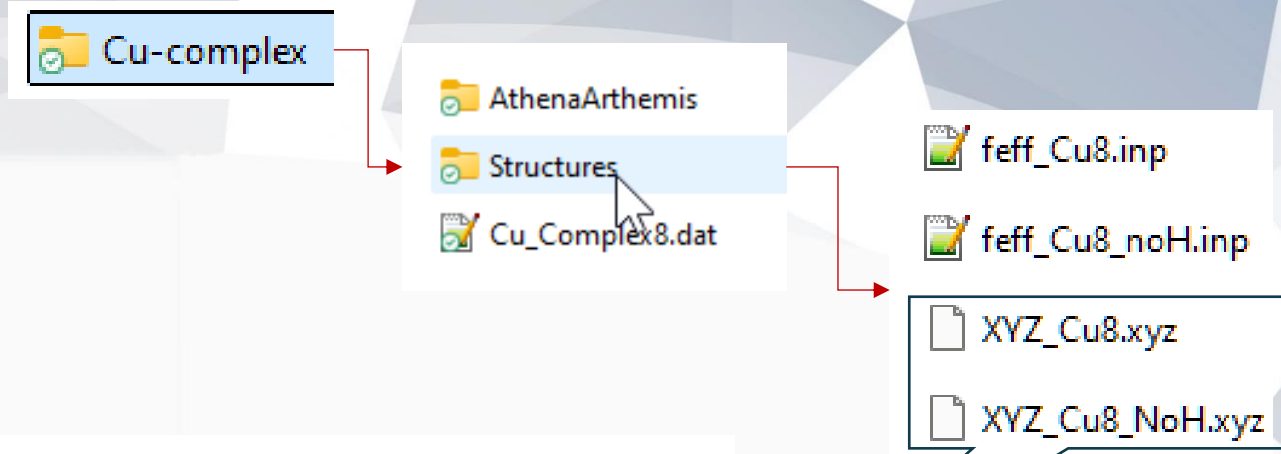

```
35
DFT simulation
Cu    0.00000    0.00000    0.00000    0.00000
N     1.77890    0.14844   -1.16253    2.13025
N     1.11941   -0.19745    1.80976    2.13712
P    -1.32133    1.85547   -0.08482    2.27945
P    -1.01833   -1.98718   -0.46346    2.28050
N     2.90255    0.58244   -0.52071    3.00585
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
```
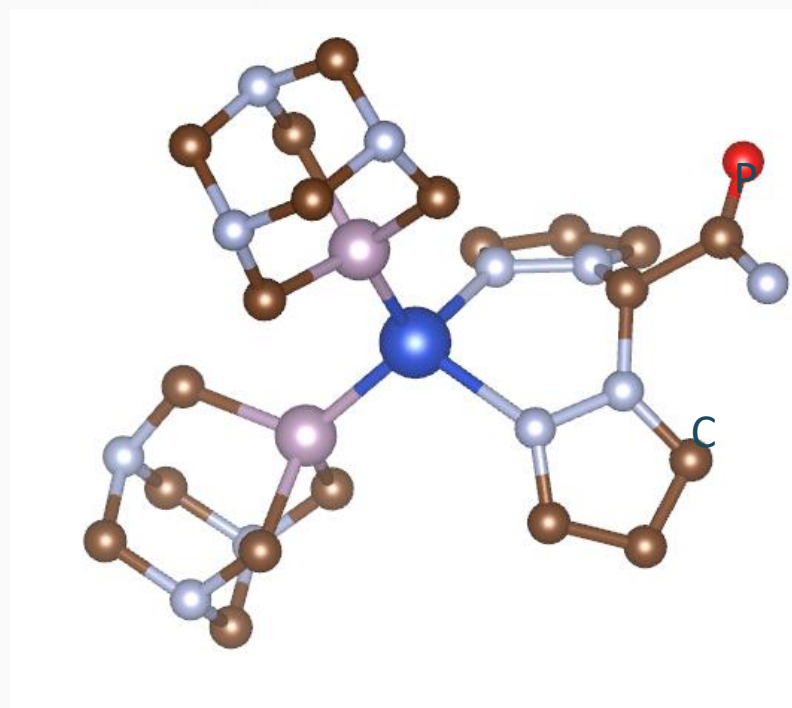
Cu-Complex

- Import files

Cu_Complex8.dat

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

Cu_Complex8

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

21/09/2024

Note:
Always save data and project for future use
you have many options!
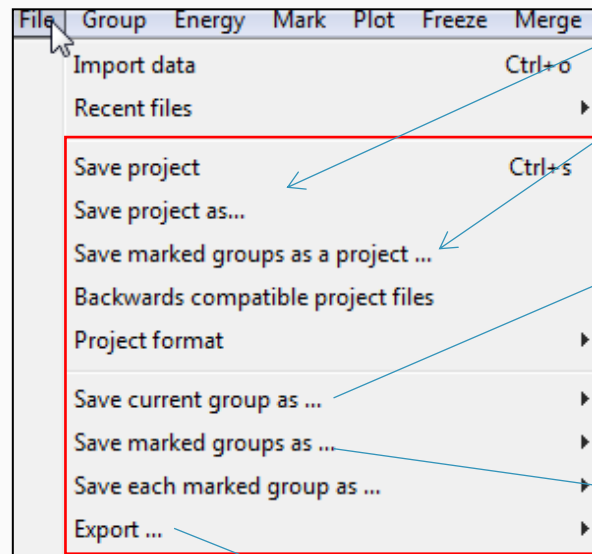
Save the entire project for reuse.

Save selected groups for separate use

| File | Group | Energy | Mark | Plot | Freeze | Merge |

Import data — Ctrl+o
Recent files ▶

Save project — Ctrl+s
Save project as...
Save marked groups as a project ...
Backwards compatible project files
Project format ▶

Save current group as ... ▶
Save marked groups as ... ▶
Save each marked group as ... ▶
Export ... ▶

μ(E)
norm(E)
χ(k)
χ(R)
χ(q)

μ(E)
norm(E)
deriv(μ(E))
deriv(norm(E))
second(μ(E))
second(norm(E))

χ(k)
kχ(k)
k^2χ(k)
k^3χ(k)

|χ(R)|
Re[χ(R)]
Im[χ(R)]
Pha[χ(R)]

|χ(q)|
Re[χ(q)]
Im[χ(q)]
Pha[χ(q)]

Excel report on all groups
Excel report on marked groups

Empirical standard

21/09/2024

Crystallographic structures DBs

http://www.webelements.com/

- Crystallography Open Database (COD)

www.crystallography.net
- WWW-MINCRYST

database.iem.ac.ru/mincryst/
- American Mineralogist Crystal Structure DB
- 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
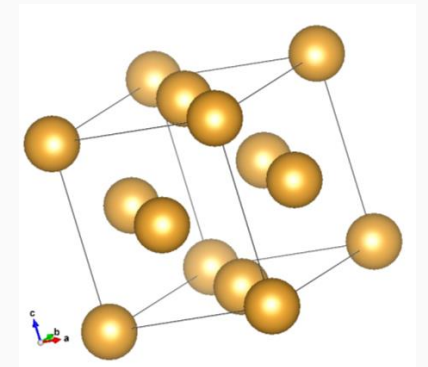
4. Fe (bcc) and Cu (fcc) XAFS

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

fcc (Fm-3m)

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

Bcc (Im3m)

$$R_1 = a\sqrt{3}/2 \qquad N_1 = 8$$
$$R_2 = a \qquad\qquad N_2 = 6$$
$$R_2 = a\sqrt{2} \qquad N_3 = 12$$

cu_foil_10k.dat
FeFoilRT_000.txt

|χ(R)| (Å⁻³) vs Radial distance (Å)

Demeter 0.9.21 © Bruce Ravel 2006-2015
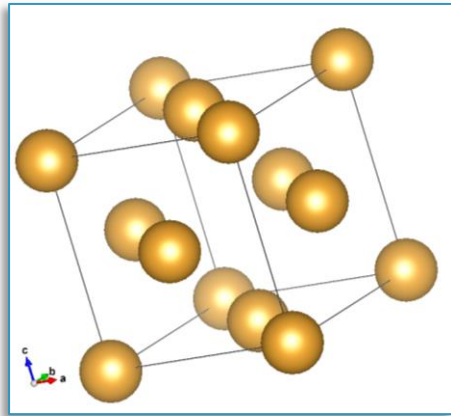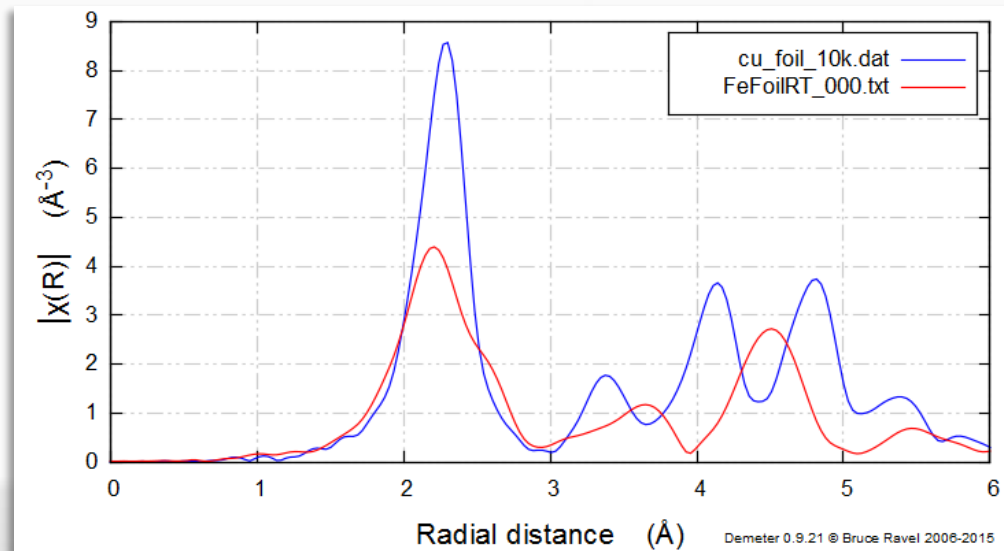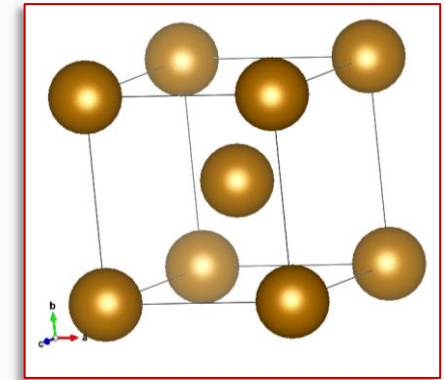
XAFS data analysis: Overview
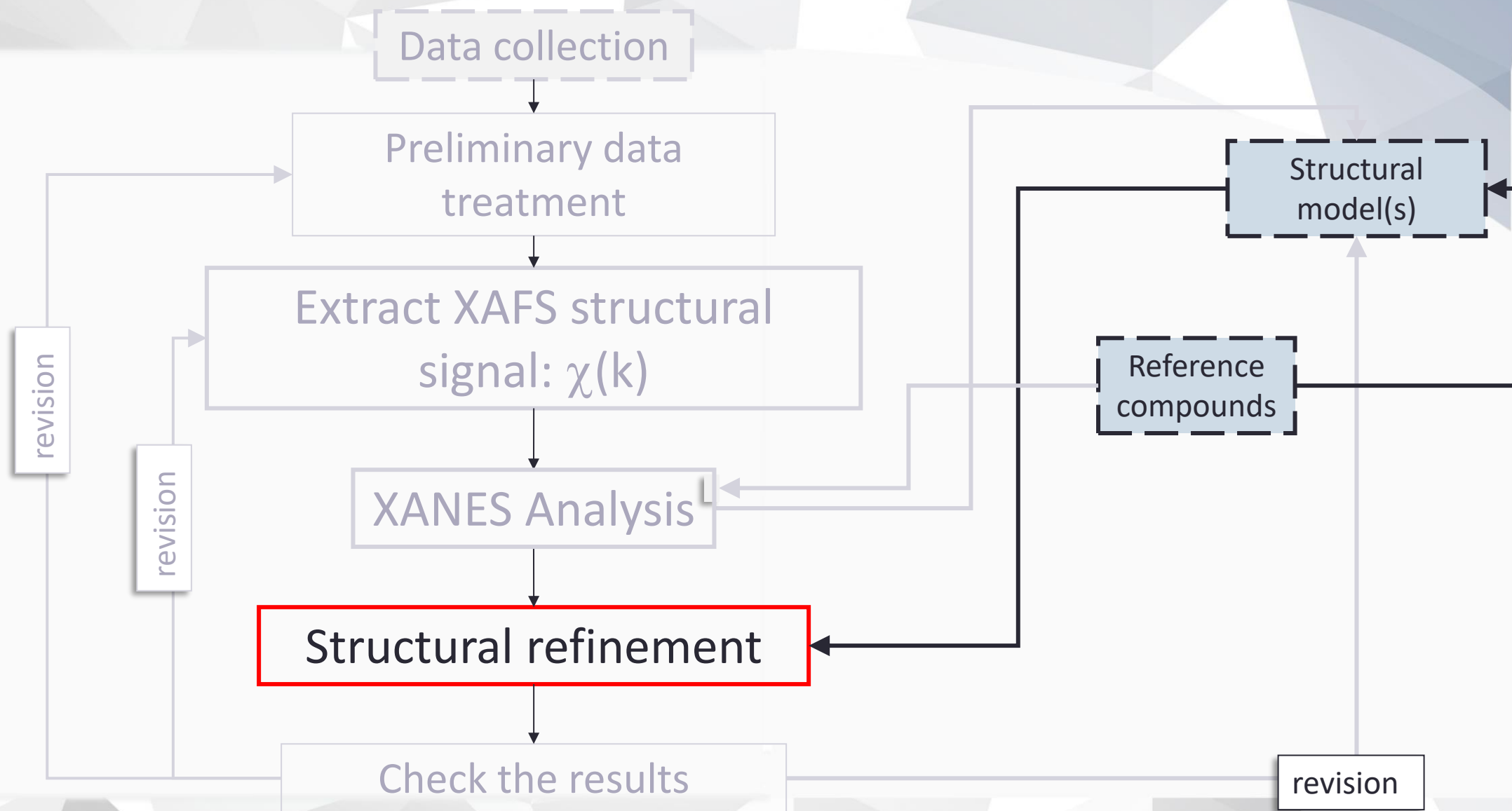
The EXAFS standard formula

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

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

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

parameters

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

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

λ = 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)

σ_j^2 = variance of the path length distribution

(Mean Square Relative Displacement: MSRD)

We will analyze Cu Complex8 EXAFS
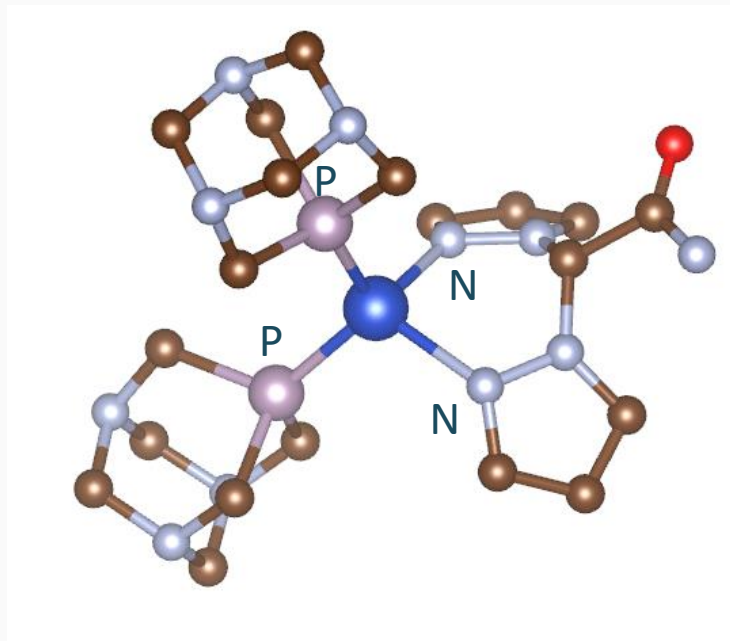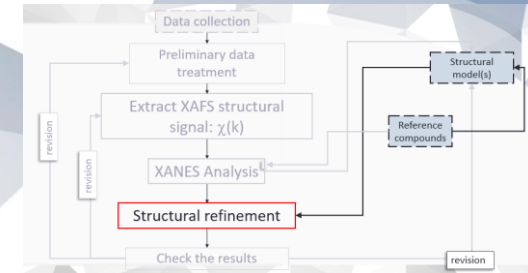
feff_Cu8_noH.inp

* 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   Cu38   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!

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

1: add χ(k) or Athena project

3: Define parameters
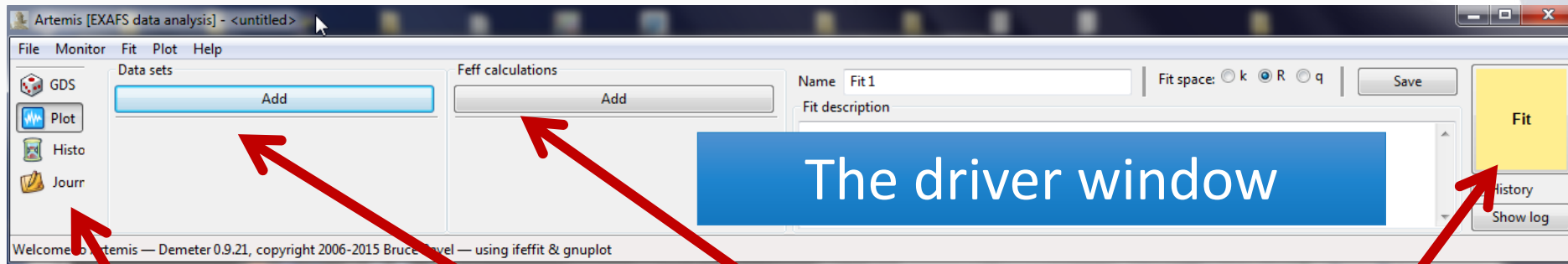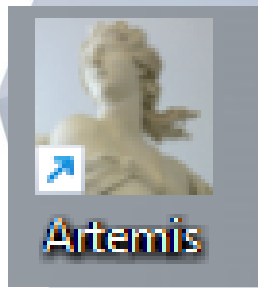
3
select **refinement pram**., plot, etc...
USE GDS button

Note:
Initialize to >0
the σ^2 parameters

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

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
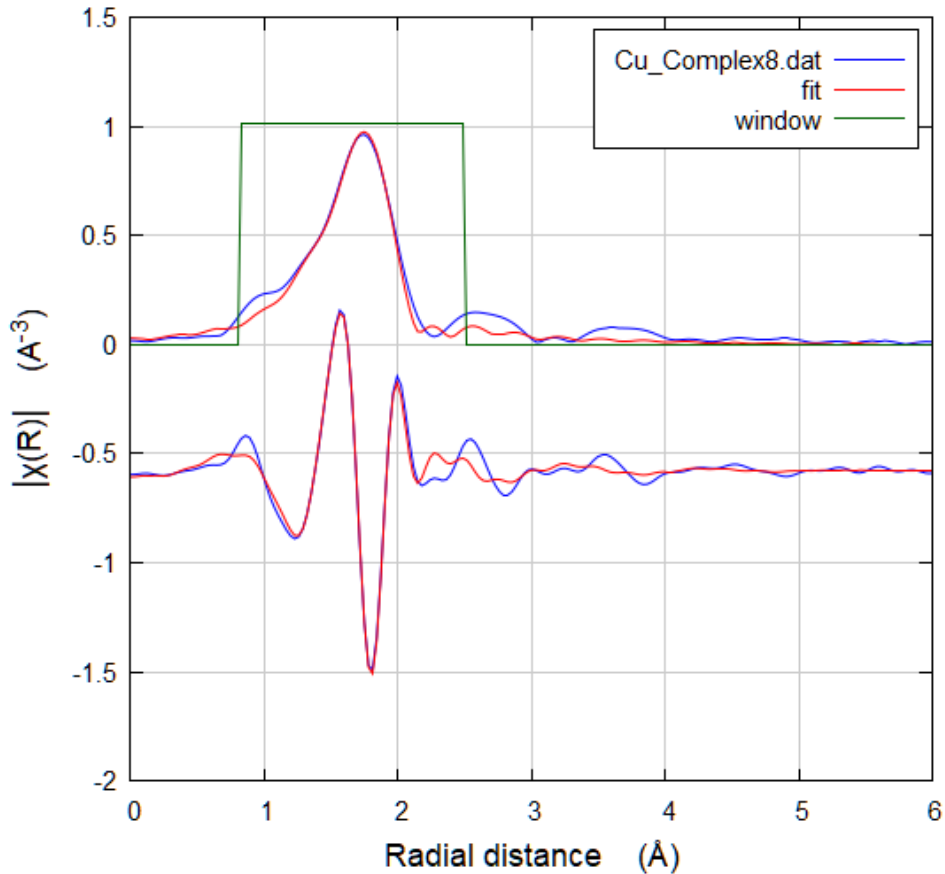
4: FIT

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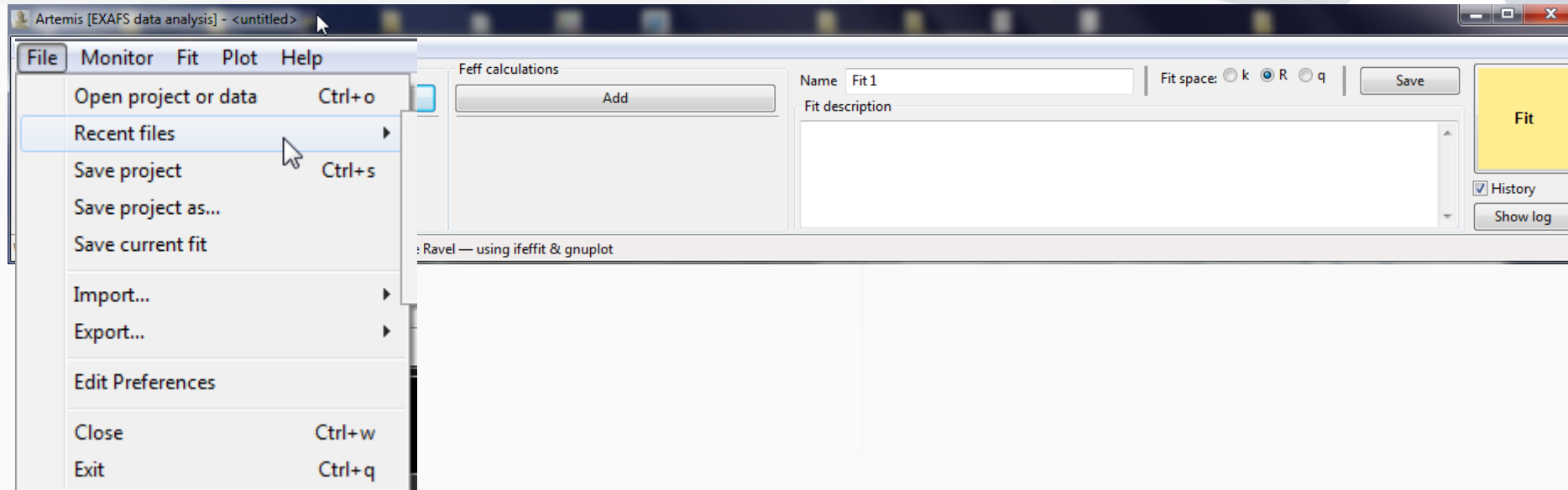
6: Check your results and your hypothesis about local atomic structure… if mismatches check hypothesis, extraction, quality of the data…

2': generate crystallographic model structure
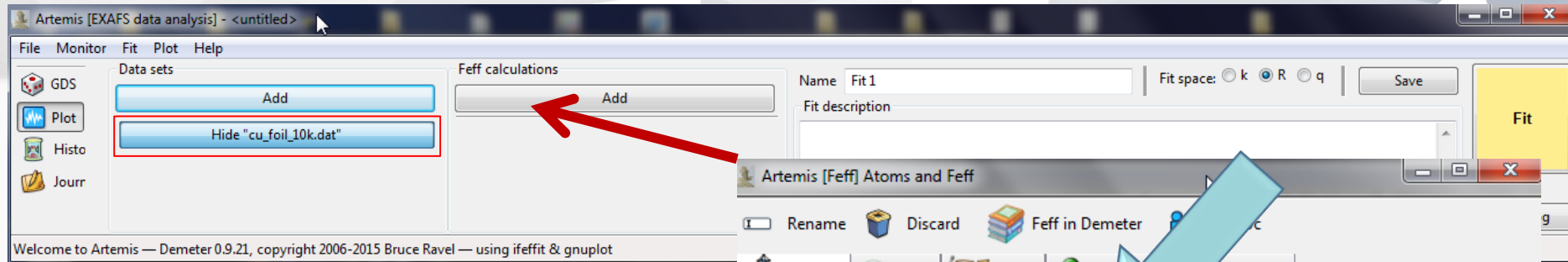
I. **Run Atoms**
II. check paths
III. Run Feff
IV. look at the path list

A) generate a local cluster

A) input the unit cell parametersand cluster size

Note: Cluster size and path lenght must include the longhest distance you expect to analyze

caused by electronic transitions (mainly dipole) to **empty bound states** near the Fermi level.
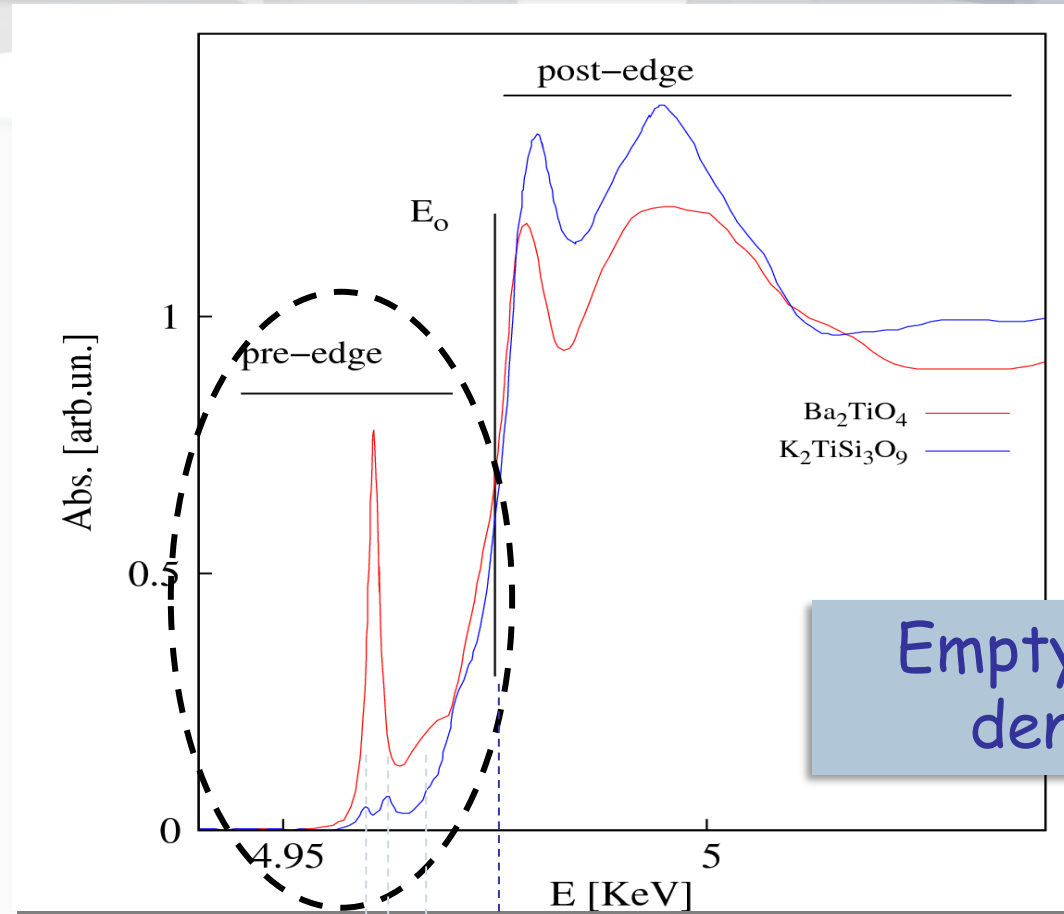
Empty state density
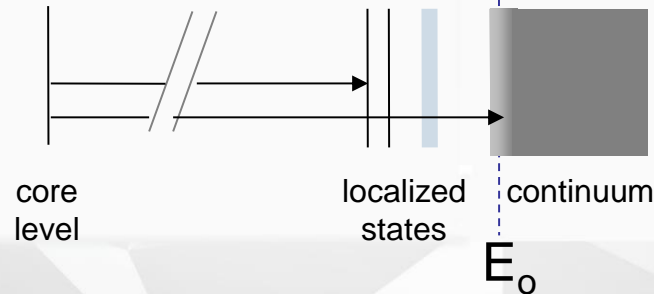
Note: it's complementary to the XPS, probing the occupied density of states.

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
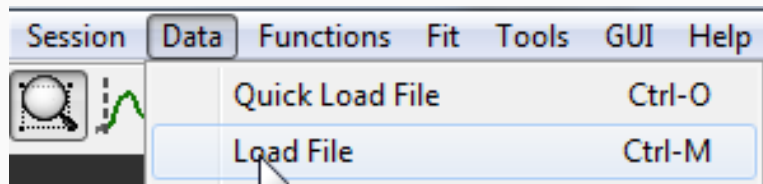
3. Select the Edge region

right click = erase
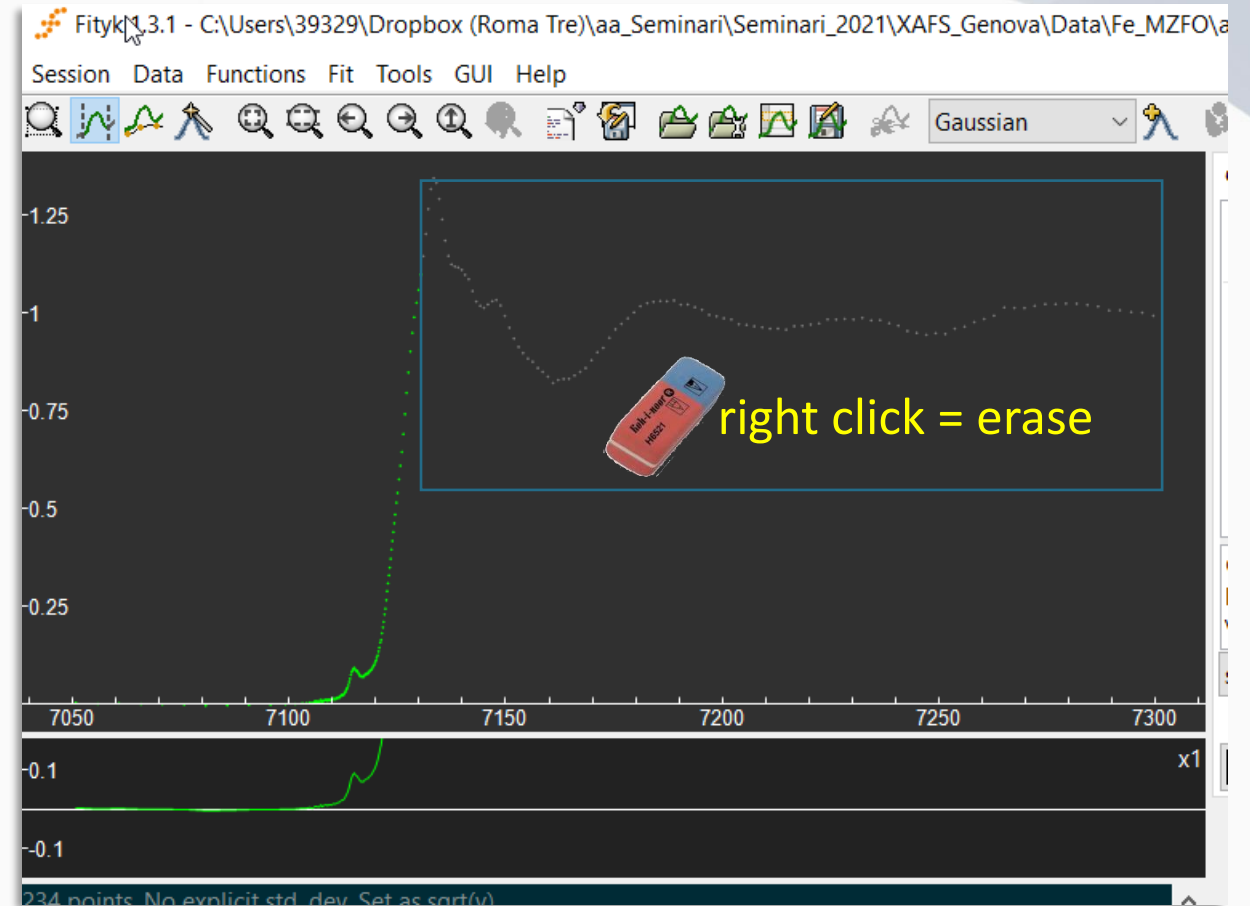
Analysis of the pre-edge: Peak fitting
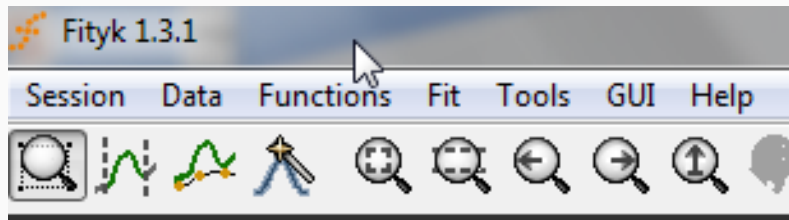
All_L3_norm_XANES.nor

1. Add models
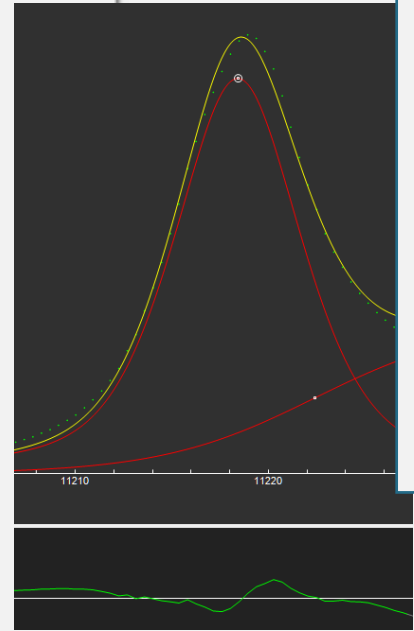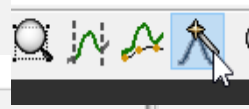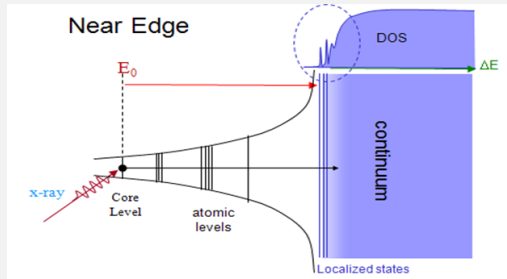
Define reasonable initial values for the parameters

2. Add constraints

Sigmoid: maximum ~ 1

Gaussian: same HWHM

No recipe: trial and error!

Fix/release refinement parameters to avoid correlations

3. Fit
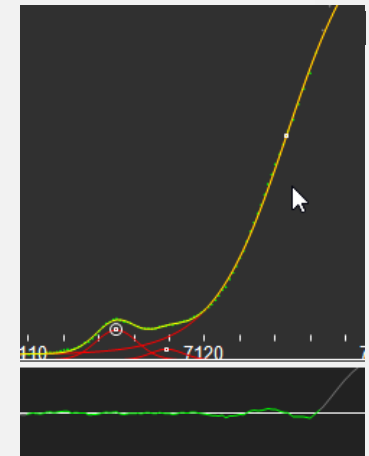
Analysis of the pre-edge: Peak fitting

All_L3_norm_XANES.nor
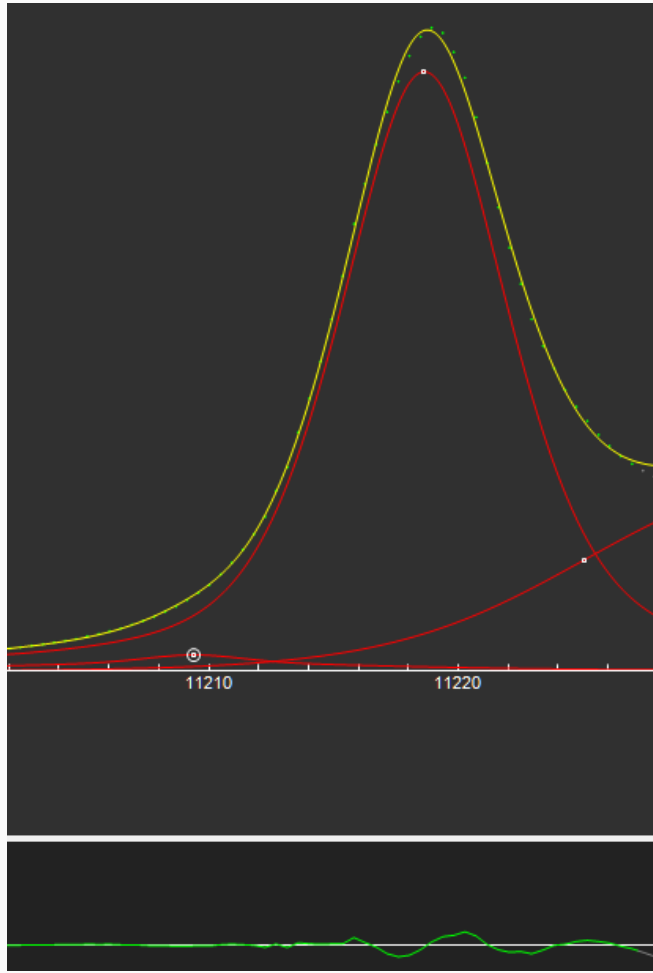
4. save
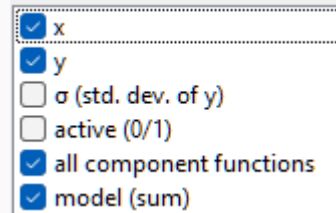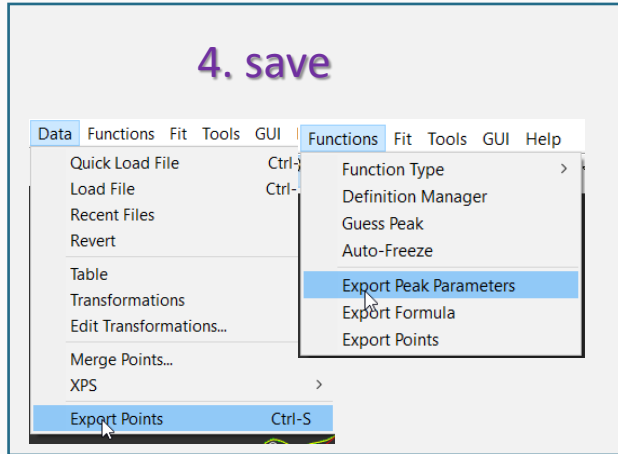
No recipe:
trial and error!

Check the residual

Analysis of the pre-edge: Peak fitting

Sr_prj

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 $2p$-$5d_{5/2}$
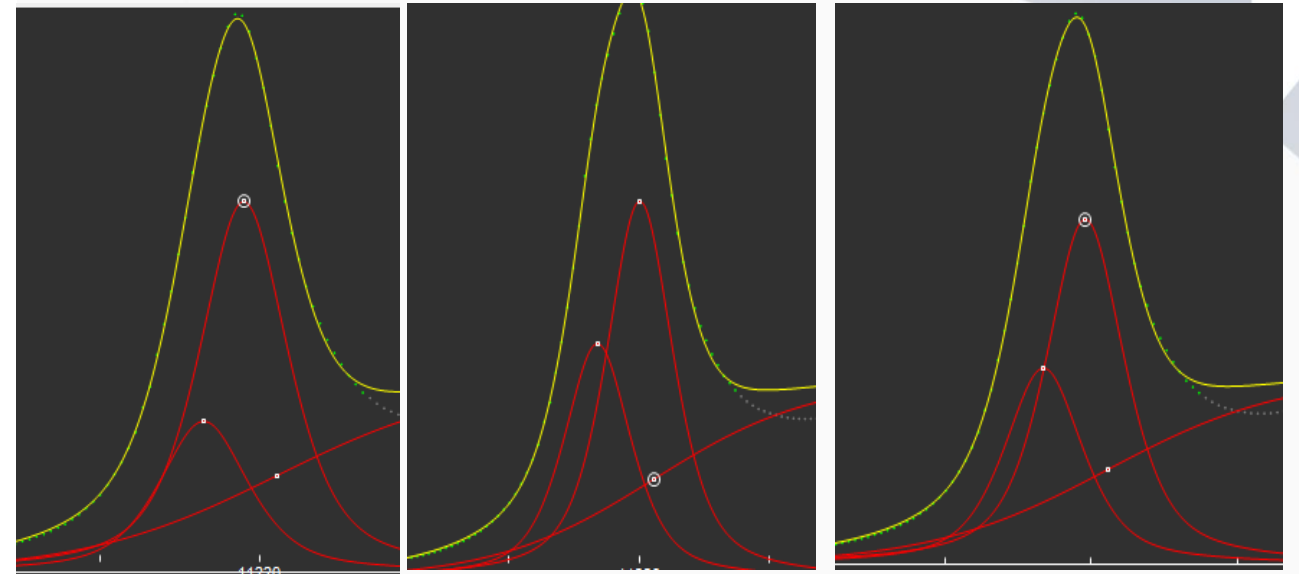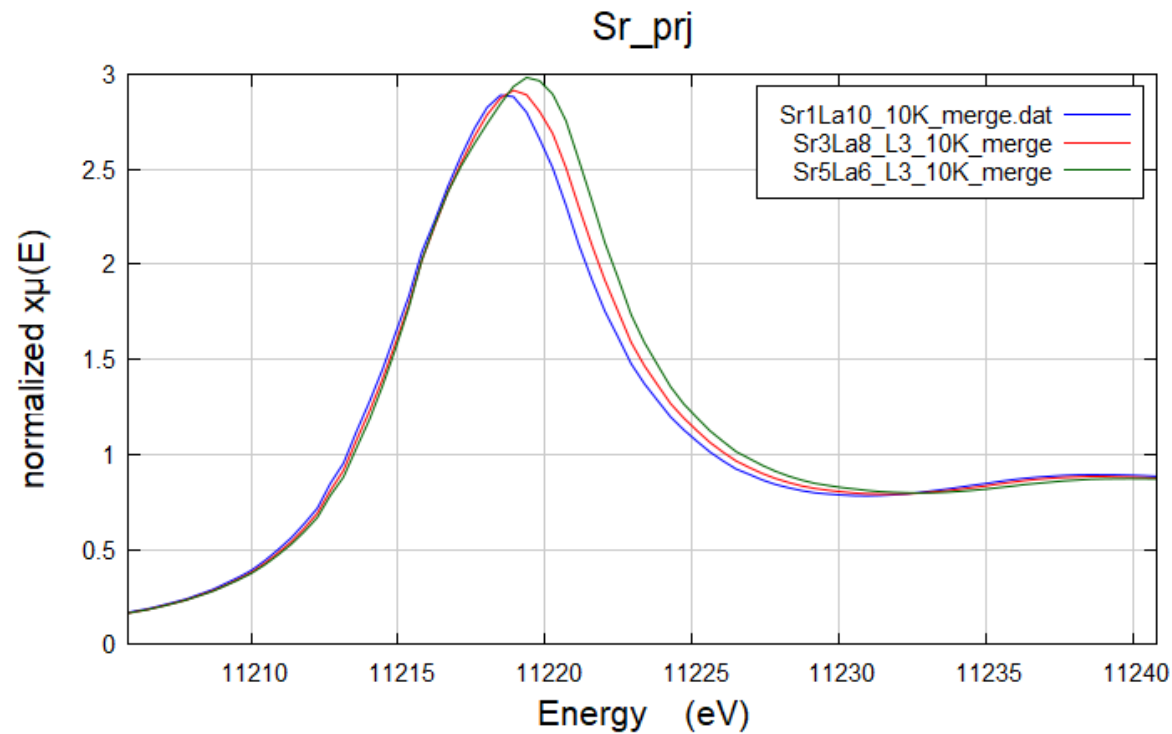
XANES change slightly from Sr1 to Sr3 to Sr5 pointing out a progressive widening of the t_{2g}-e_g energy difference

Edge region: a valuable fingerprint for chemical speciation
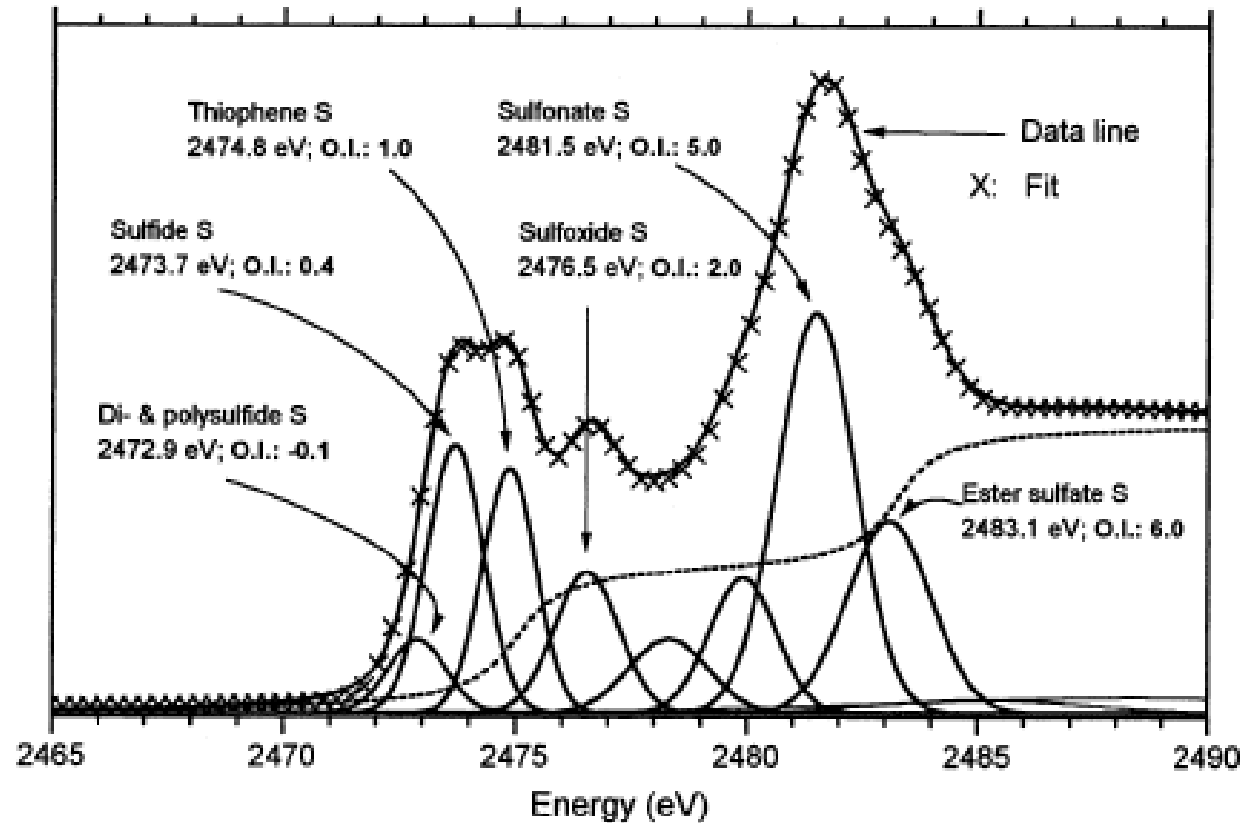
A. Vairavamurthy / Spectrochimica Acta Part A 54 (1998) 2009–2017

chemical speciation of Sulphur in humic substances

Analysis of the XANES: chemical speciation in mixtures

Linear Combination Analysis (LCA)

Linear Combination Fit (LCF)

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

$$R^2 = \sum_i \left(\mu^{exp}(E_i) - \mu^{th}(E_i) \right)^2$$
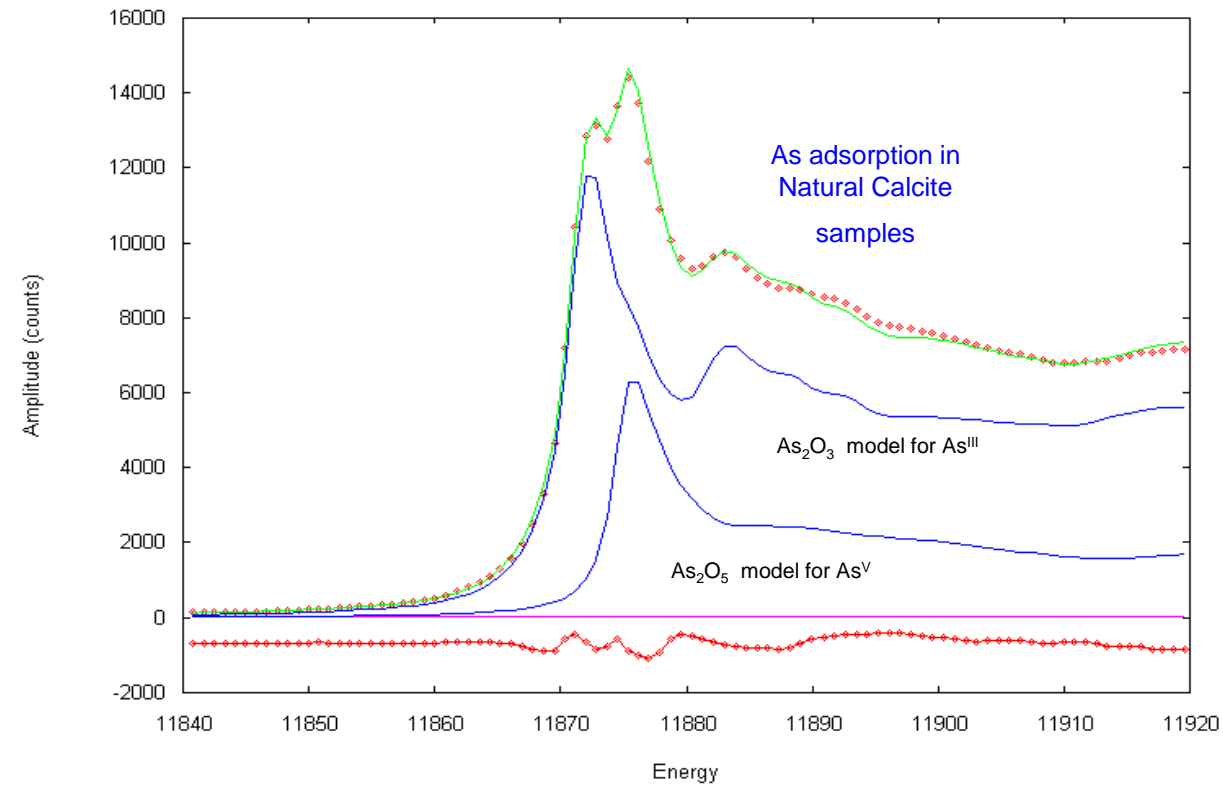
As adsorption in Natural Calcite samples

As_2O_3 model for As^{III}

As_2O_5 model for As^V

Arsenic uptake by natural calcite: An XAS study

F. Bardelli [a], M. Benvenuti [b], P. Costagliola [b,*], F. Di Benedetto [b,c], P. Lattanzi [d], C. Meneghini [e], M. Romanelli [e], L. Valenzano [f]

Analysis of the XANES: chemical speciation in mixtures

Magnetic properties of La doped $Bi_{1-x}La_xFeO_3$ improves doping with La till x~0.2 then M suddenly drops down.

Why?

Above x~0.2 $LaFeO_3$ phase separate out (solution limit) worsening the overall property of the system

$Bi_{1-x}La_xFeO_3$

× % La

$Bi_{0.5}La_{0.5}FeO_3$ exp.
fit
residual
$LaFeO_3$
$Bi_{0.8}La_{0.2}FeO_3$

La solution limit x ~ 0.2
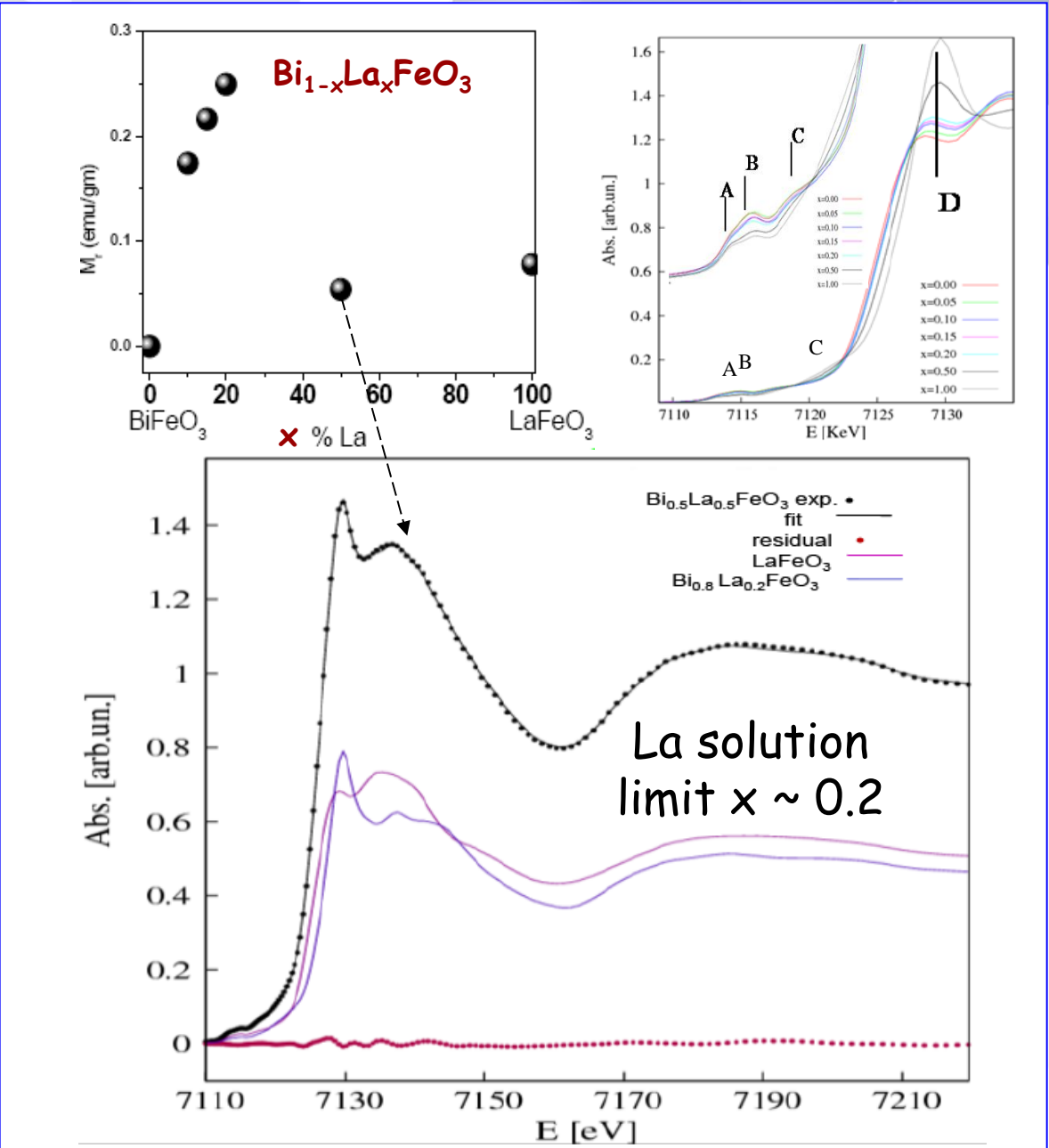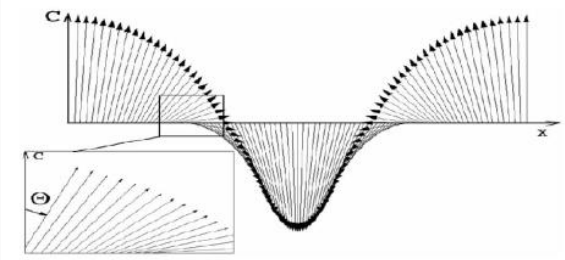
Data on: LCA-BiLaFeO

Nome

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

$Bi_{0.5}La_{0.5}FeO_3$
$Bi_{0.8}La_{0.2}FeO_3$
$Bi_{0.9}La_{0.1}FeO_3$
$BiFeO_3$
La_0FeO_3

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

marked groups

Compare spectra with the end compounds

Check for data alignment

Compare spectra with the end compounds

Athena [XAS data processing]

File   Group   Energy   Mark   Plot   Freeze   Merge   Monitor   Help

* **<untitled>**   Save   A   U   I

Linear combination fitting

Fit range: -20   to   30

Fitting space
  ● norm μ(E)   ○ deriv μ(E)   ○ χ(k)

Standards | Fit results | Combinatorics | Sequence

	Standards	Weight	E0	Fit E0	Required
1:	BiFeO3.jmp	0.500	0	✓	✓
2:	LaFeO3.jmp	0.500	0	✓	✓

☑ Bi50La50FeO3.jmp
☑ Bi80La20FeO3.jmp
☑ Bi90La10FeO3.jmp
☑ BiFeO3.jmp
☑ LaFeO3.jmp

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 analys
Peak fitting
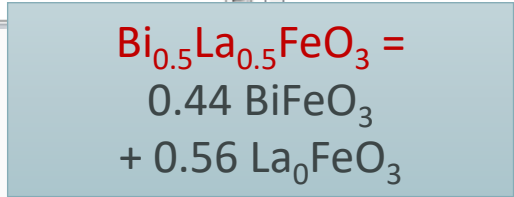Log-ratio/phase-difference a
Difference spectra

$Bi_{0.5}La_{0.5}FeO_3 =$
$0.44\ BiFeO_3$
$+ 0.56\ La_0FeO_3$

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
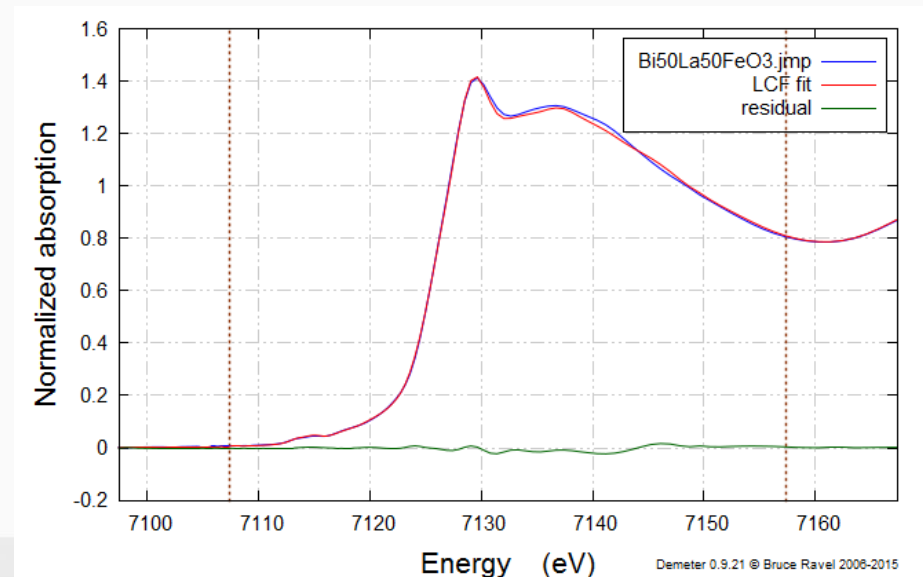Noise added to data: 0
R-factor = 0.0001869
Chi-square = 0.00614
Reduced chi-square = 0.0000534

.	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
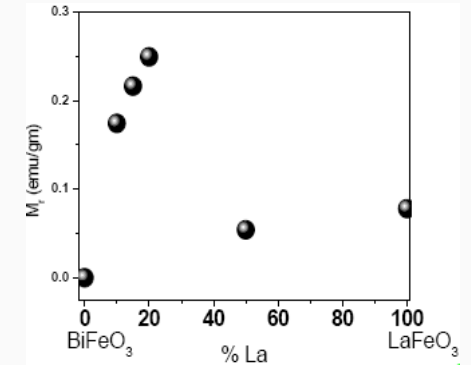
Chi-square = 0.0061
Reduced chi-square = 0.000053

Chi-square = 0.00124
Reduced chi-square = 0.000011
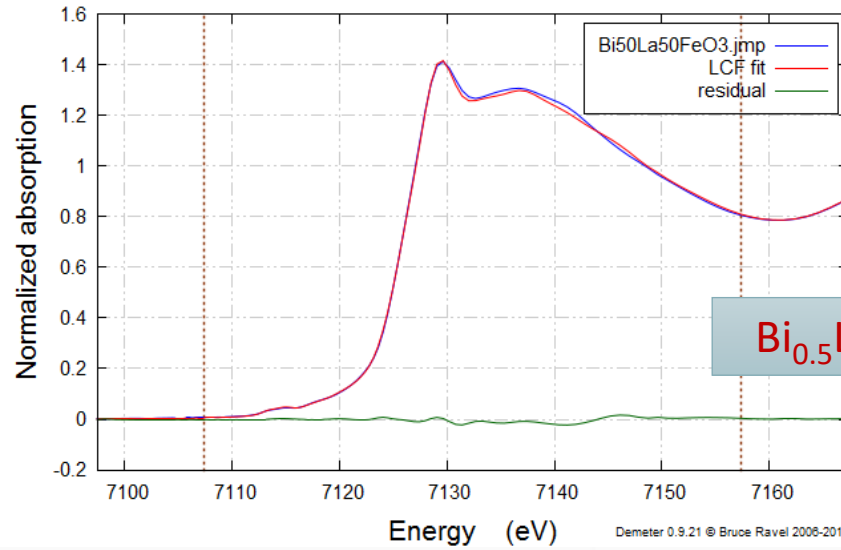
$Bi_{0.5}La_{0.5}FeO_3$ = 44% $BiFeO_3$ + 56% $LaFeO_3$
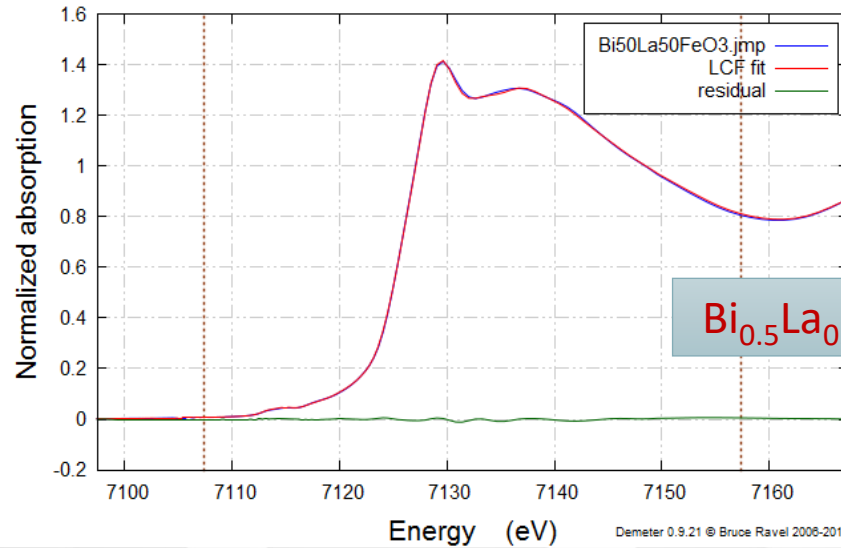
$Bi_{0.5}La_{0.5}FeO_3$ = 53% $Bi_{0.8}La_{0.2}FeO_3$ + 47% $LaFeO_3$

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
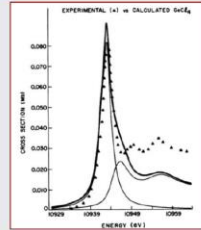
Theory
Tyson, Hodgson, Natoli, Benfatto Phys. Rev. B 465997 (1992)
A. Filipponi et al. Phys. Rev. B 52, 12122 (1995)
Ankudinov et al. Phys Rev. B 58, 7565 (1998)
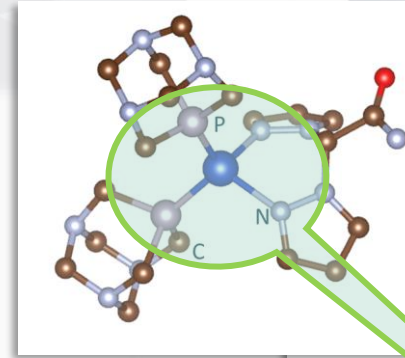J. Rehr Rev. Mod. Phys. 72, 621 (2000)

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

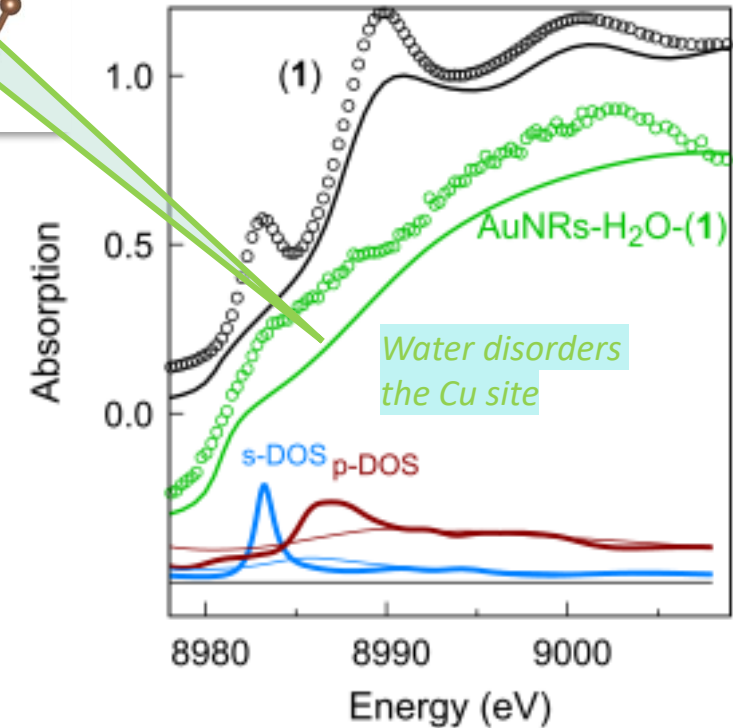Cu-site local modification in Cu-AuNP+water solution

Water disorders the Cu site

Figure 8. The experimental XANES data (circles) and model curves (full lines) of complex 1 (black) and AuNRs-H2O-(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-H2O-(1) model (thin lines).

Thanks for…

Carlo Meneghini

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16-26.09.2024