XAS exercises

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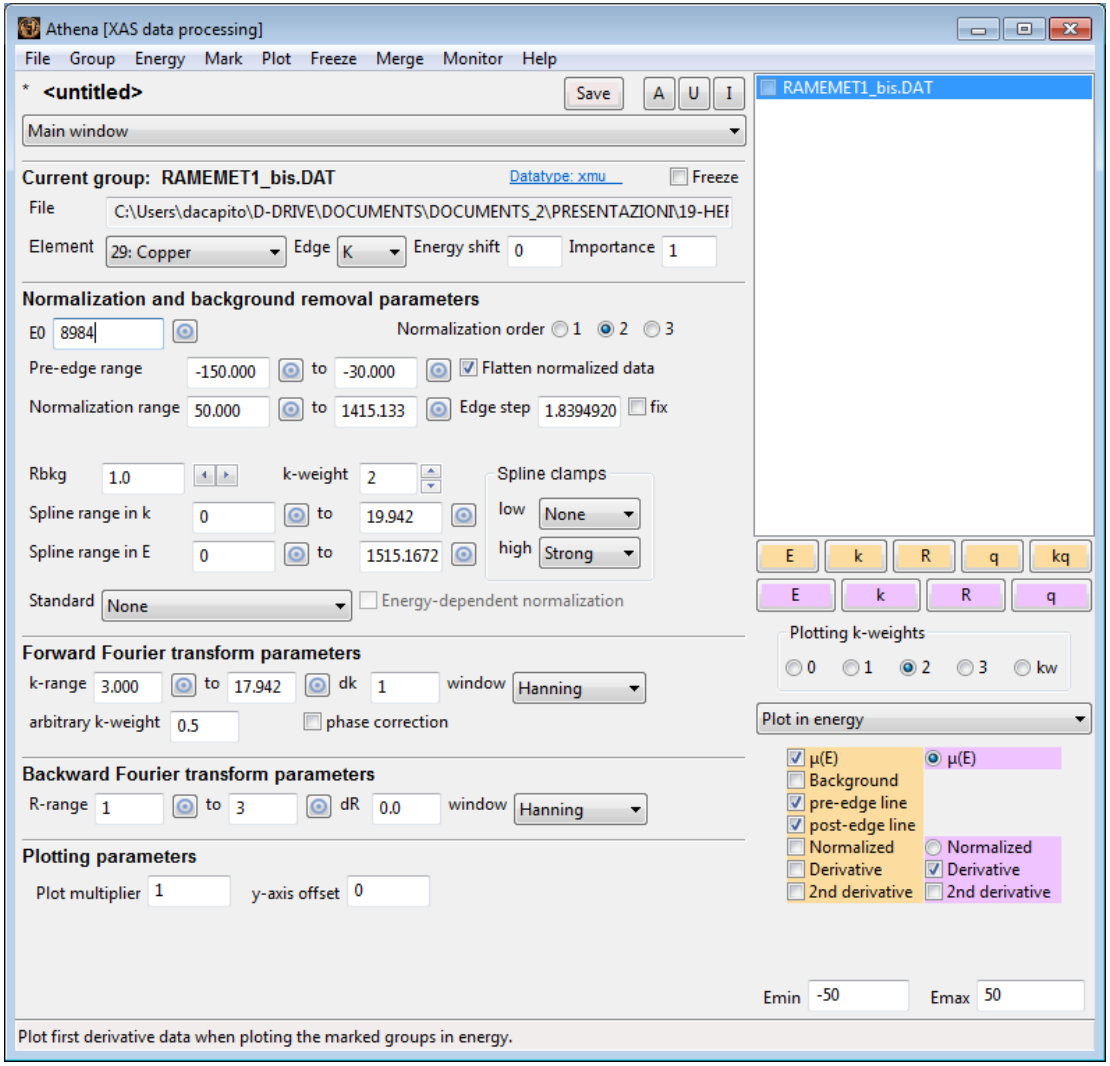
Layout

- Data treatment
- EXAFS
  - 1st shell fitting
  - Multi shell fitting
- Perspectives and conclusion

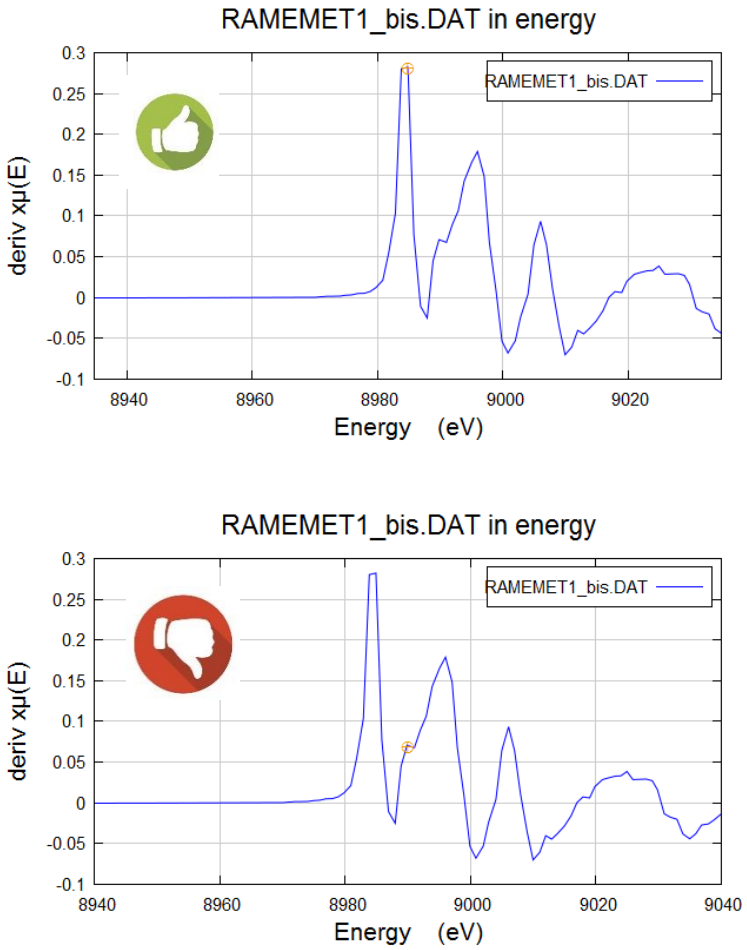
Data treatment

- DEMETER code
  - https://bruceravel.github.io/demeter/
  - ATHENA
    - Data extraction, treatment, XANES analysis
  - ARTEMIS
    - Data EXAFS fitting
  - FEFF
    - Ab-initio xas paths calculations
    - Ab-initio XANES calculations

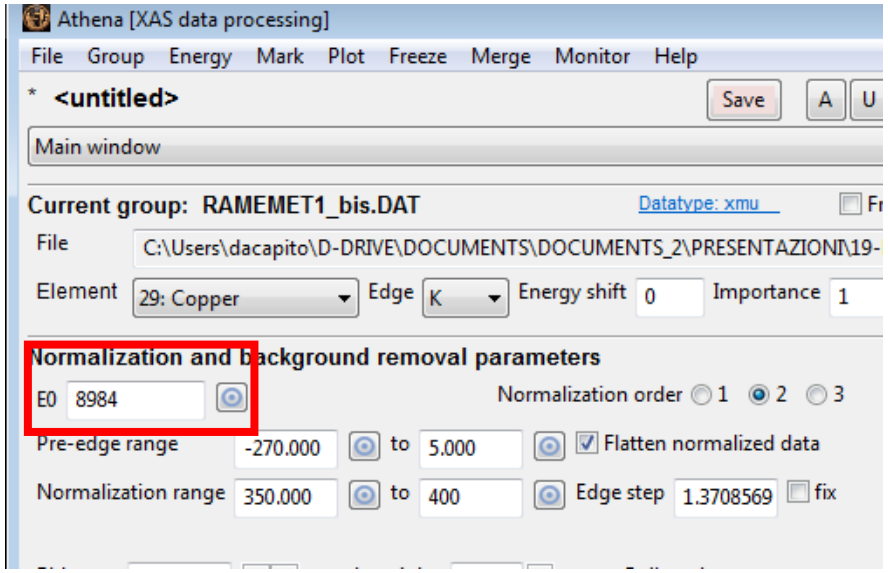
ATHENA


Athena [XAS data processing]
File Group Energy Mark Plot Freeze Merge Monitor Help
<untitled>
Save
A U I
Main window
Current group: RAMEMET1_bis.DAT
Datatype: xmu
Freeze
File
C:\Users\dacapito\D-DRIVE\DOCUMENTS\DOCUMENTS_2\PRESENTAZIONI\19-HEI
Element
29: Copper
Edge
K
Energy shift
0
Importance
1
Normalization and background removal parameters
E0
8984
Normalization order
1
2
3
Pre-edge range
-150.000
to
-30.000
Flatten normalized data
Normalization range
50.000
to
1415.133
Edge step
1.8394920
fix
Rbkg
1.0
k-weight
2
Spline clamps
Spline range in k
0
to
19.942
low
None
Spline range in E
0
to
1515.1672
high
Strong
Standard
None
Energy-dependent normalization
Forward Fourier transform parameters
k-range
3.000
to
17.942
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
RAMEMET1_bis.DAT
E
k
R
q
kq
E
k
R
q
Plotting k-weights
0
1
2
3
kw
Plot in energy
μ(E)
Background
pre-edge line
post-edge line
Normalized
Derivative
2nd derivative
μ(E)
Normalized
Derivative
2nd derivative
Emin
-50
Emax
50
Plot first derivative data when ploting the marked groups in energy.

Edge position

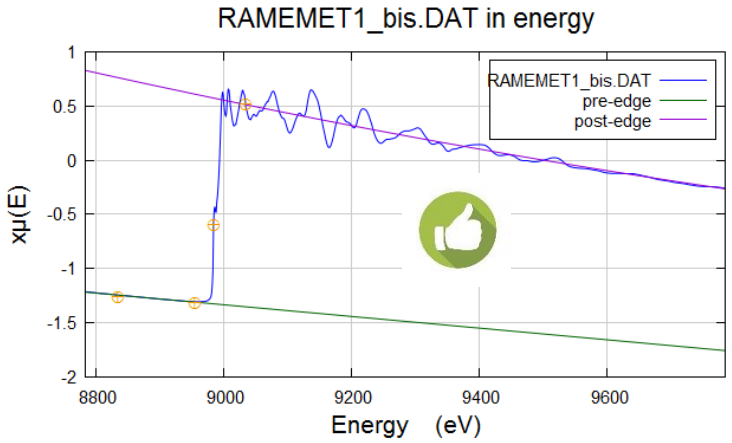


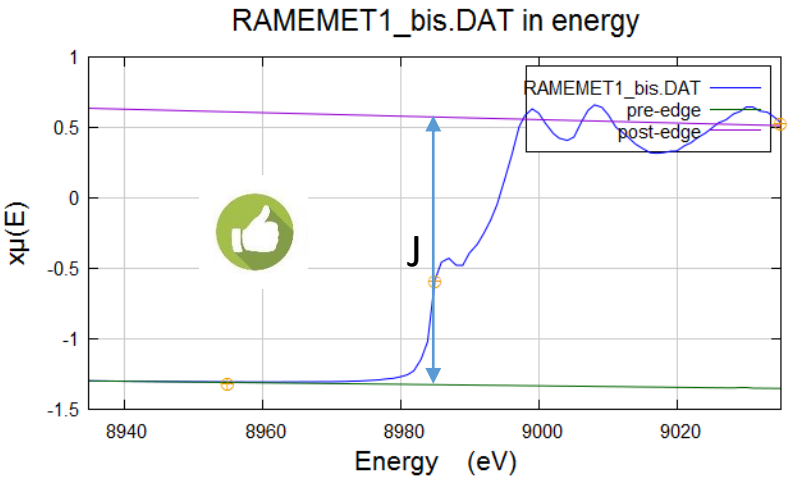
Edge == 1st inflection point of the derivative $\delta\mu/\delta E$



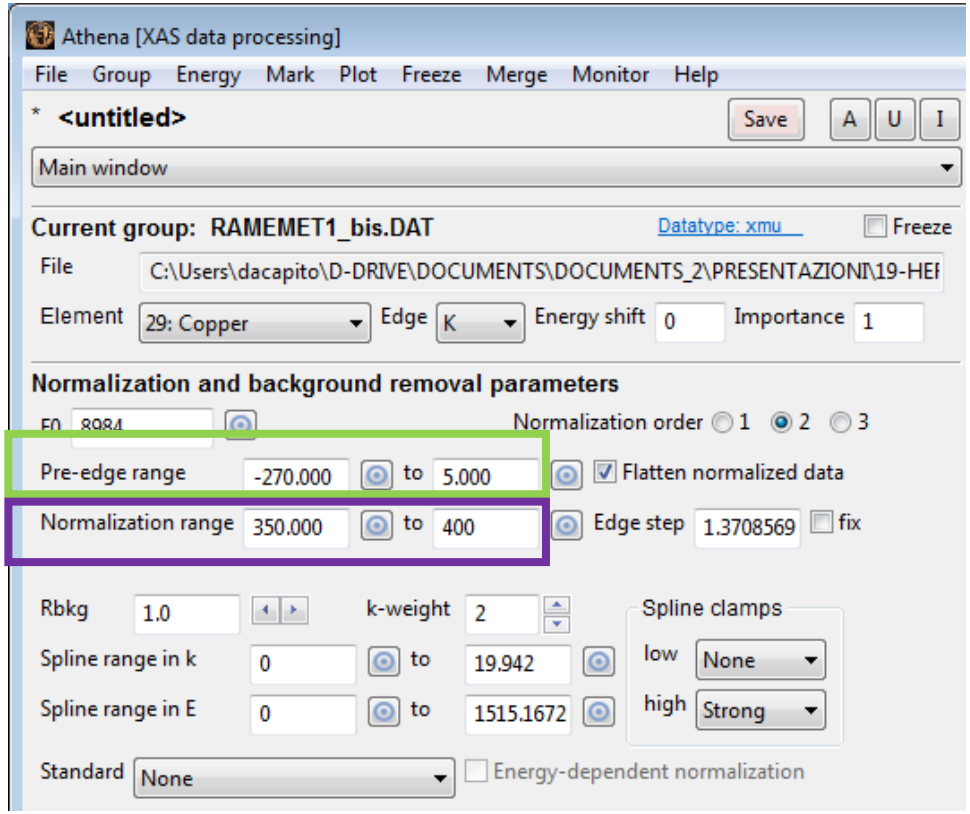
Data Normalization

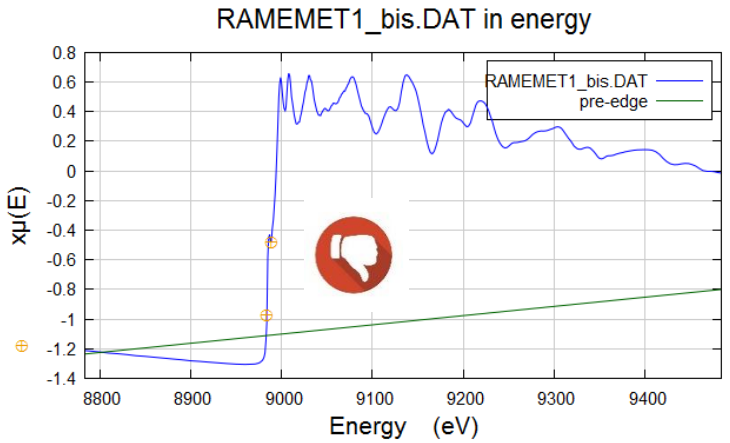
Edge step J calculation

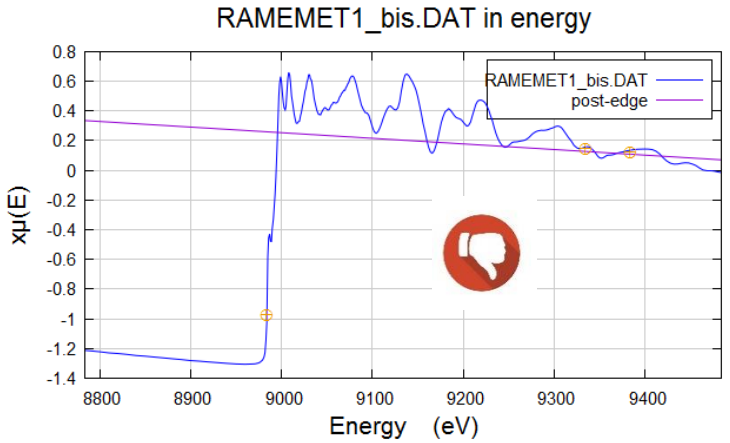




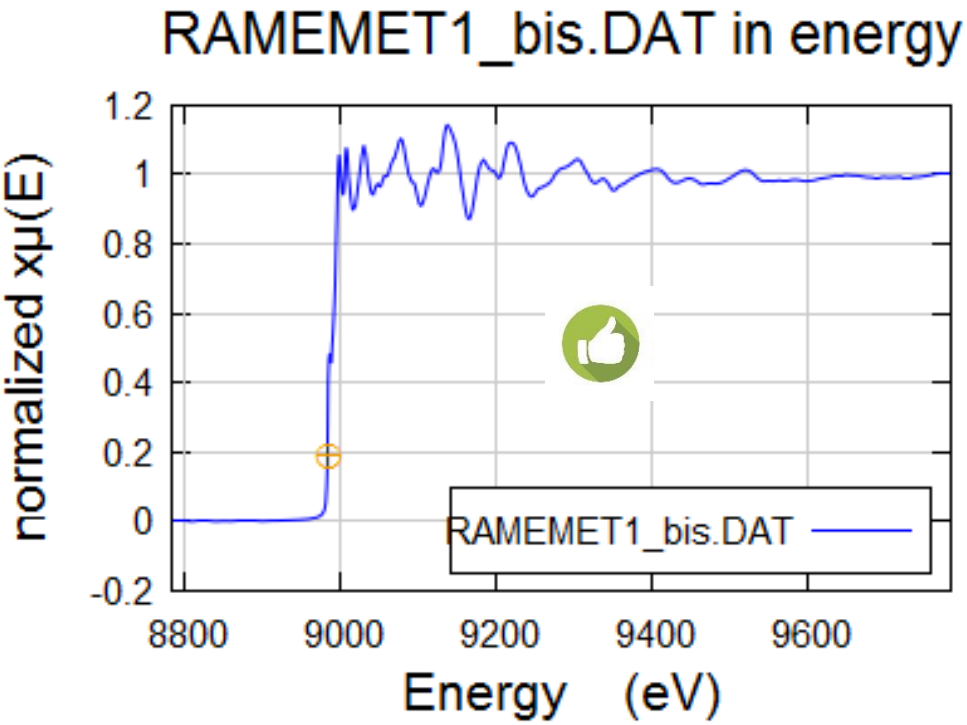
Data Normalization





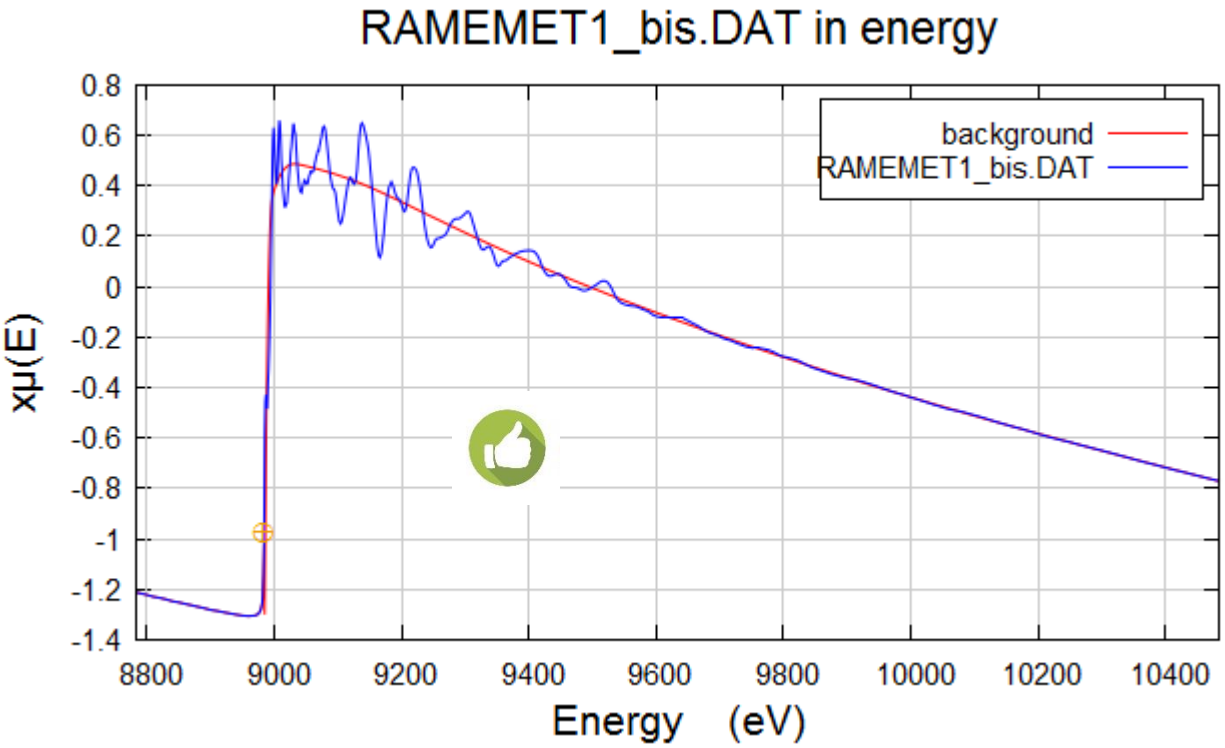


Normalized data

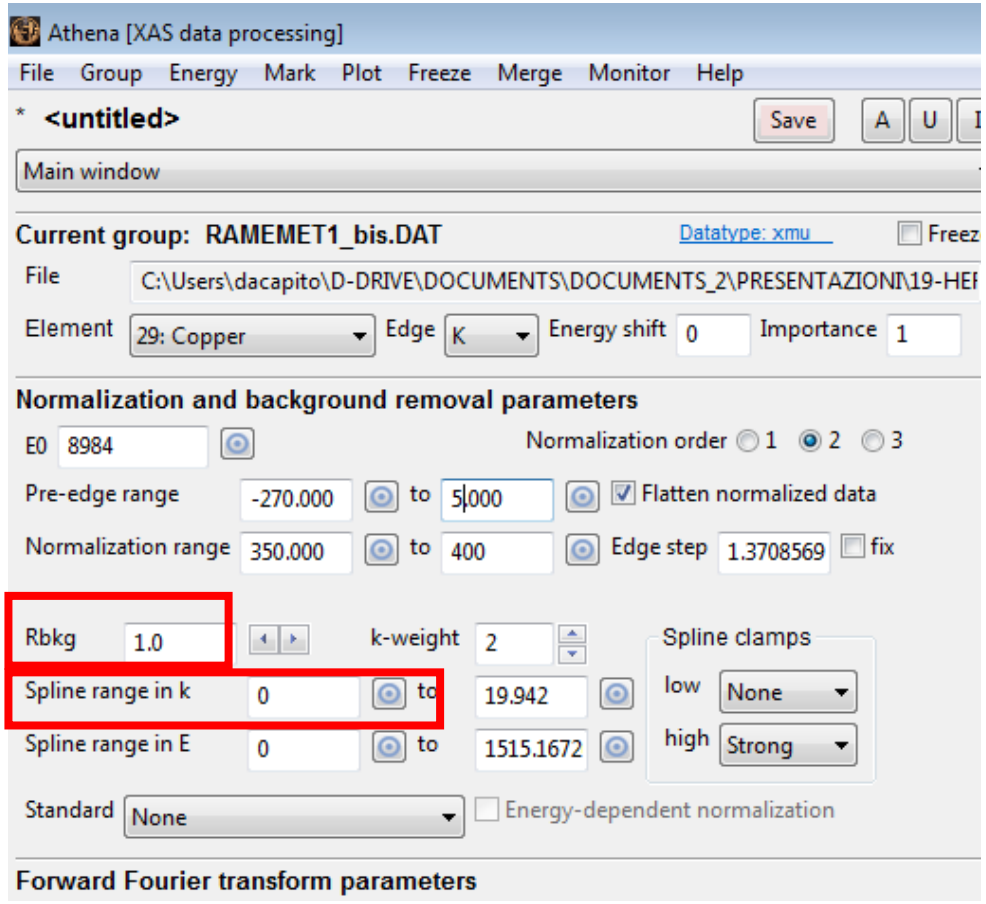


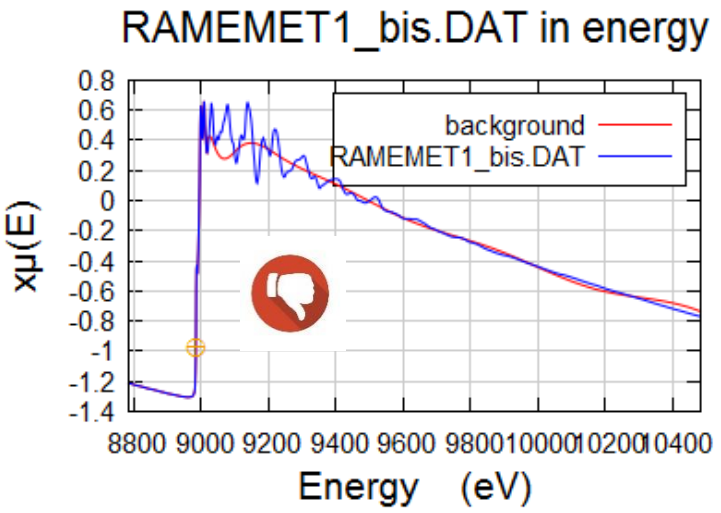
Very important for XANES

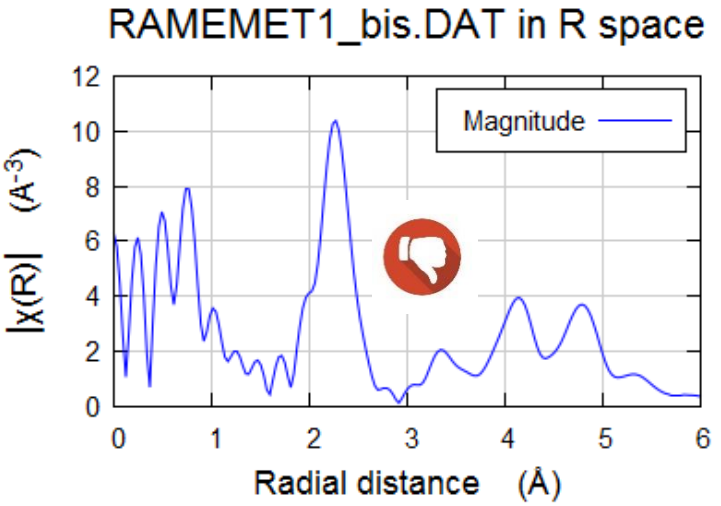
Background subtraction



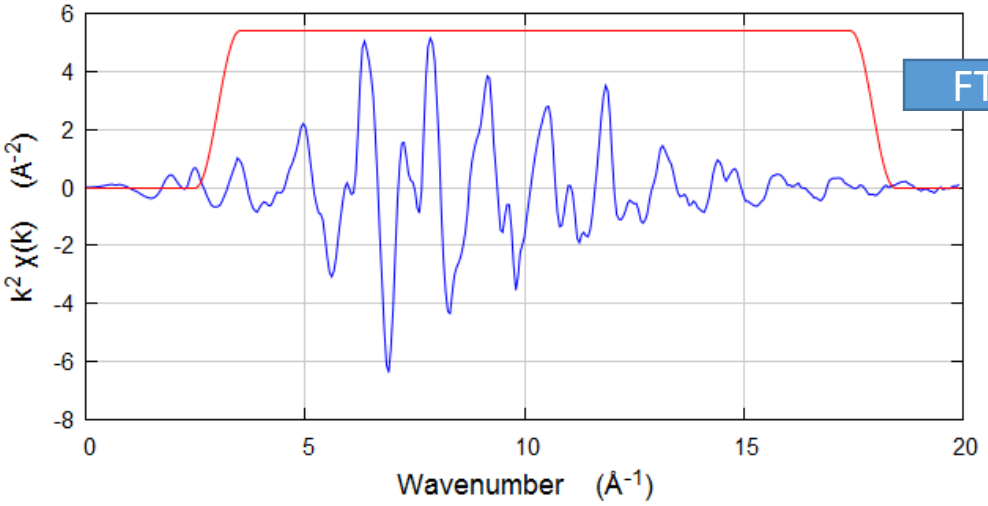
Bad bkg subtraction



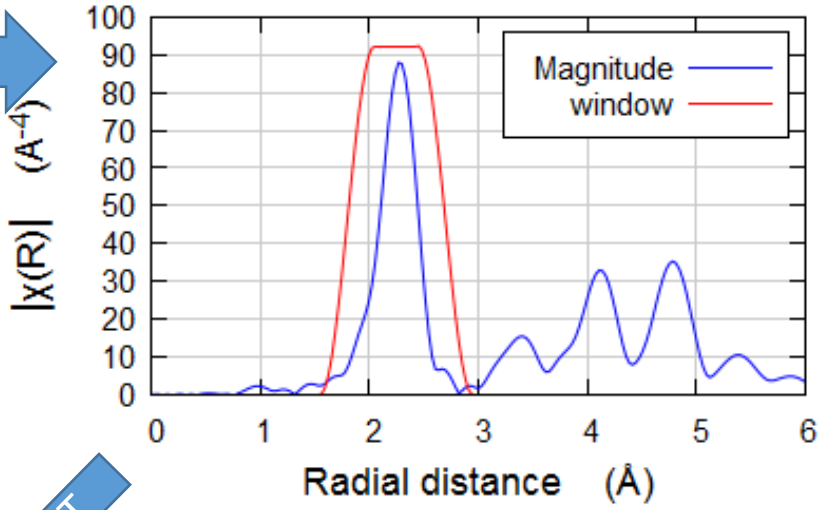




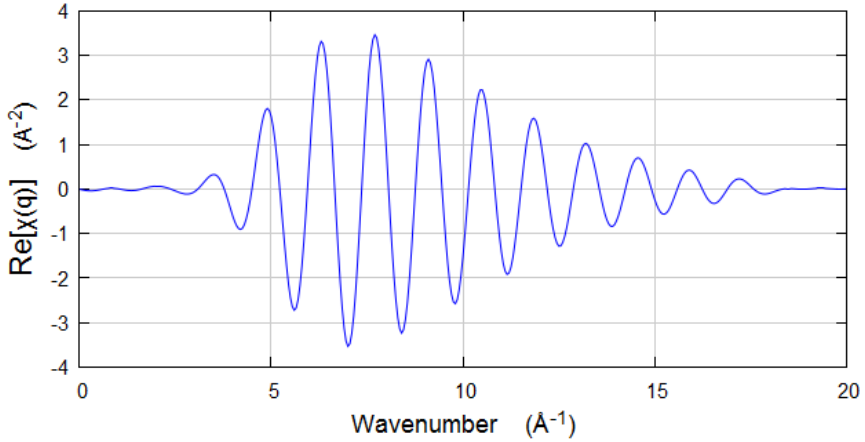
Data extraction



FT



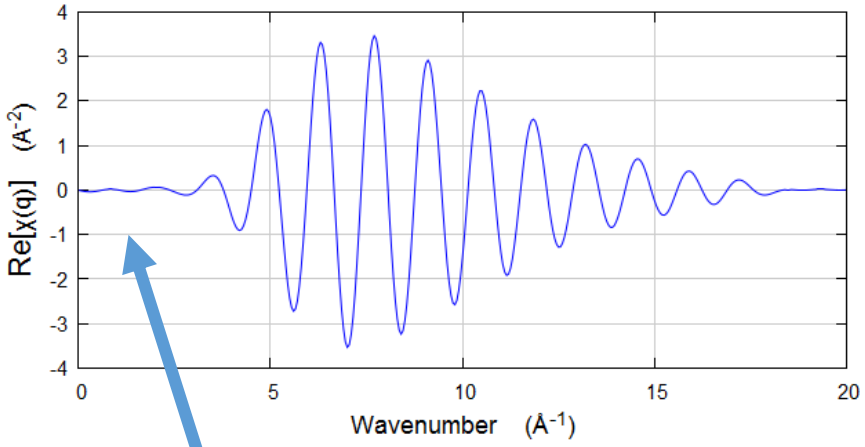
BFT



Important for EXAFS analysis

An example of EXAFS data analysis Metallic copper

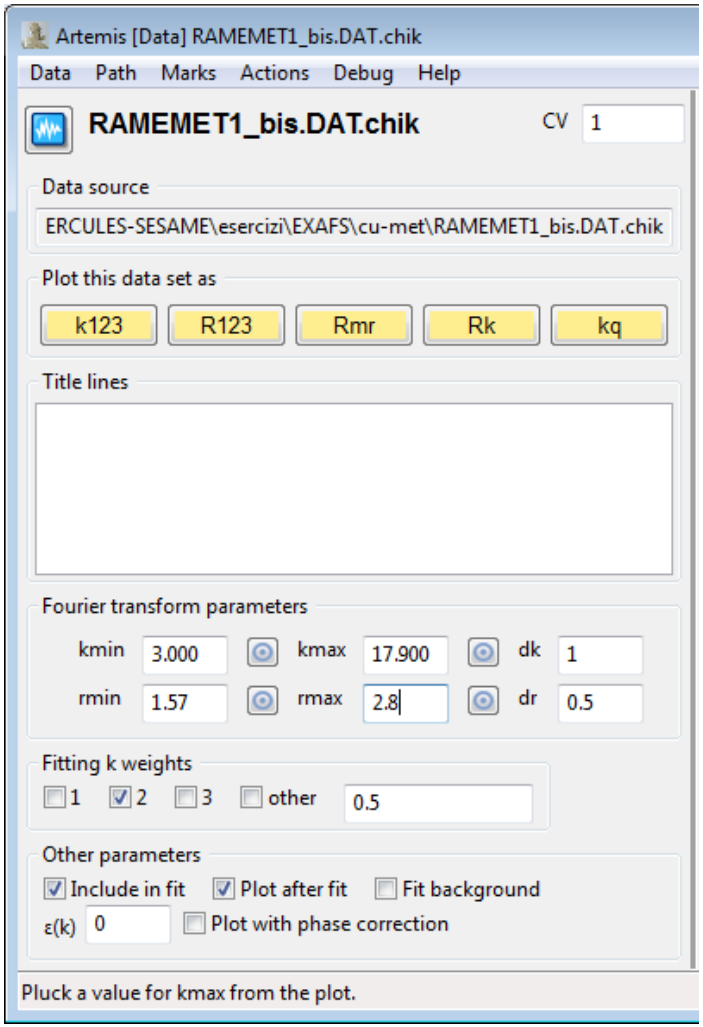
XAS data fitting

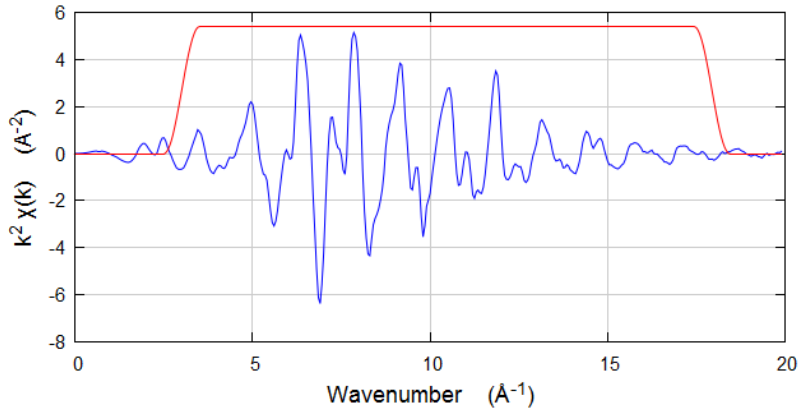


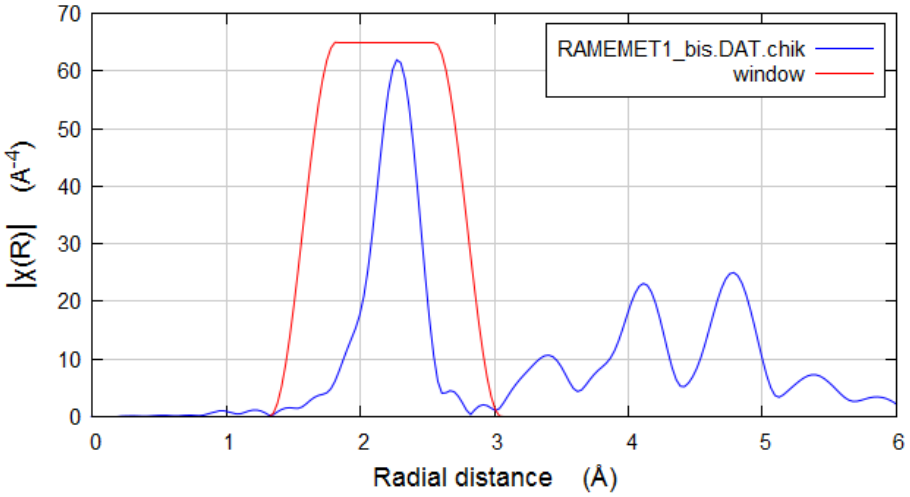
Ab initio calculated functions

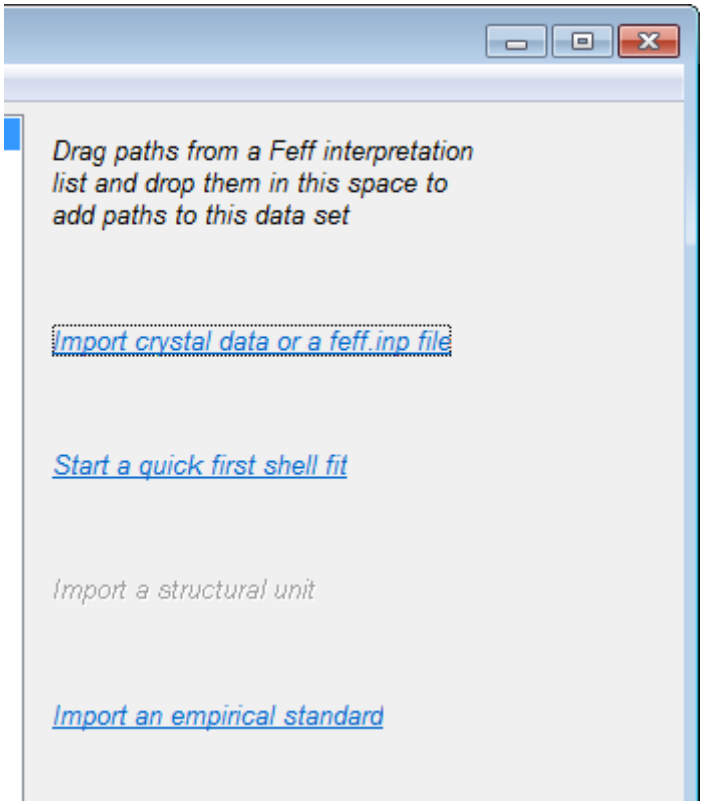
$$\chi(k) = S_0^2 \frac{NA(k)}{kR^2} e^{\frac{-2R}{\lambda}} sin(2kR + \phi(k) + \phi_c) e^{-2k^2\sigma^2}$$

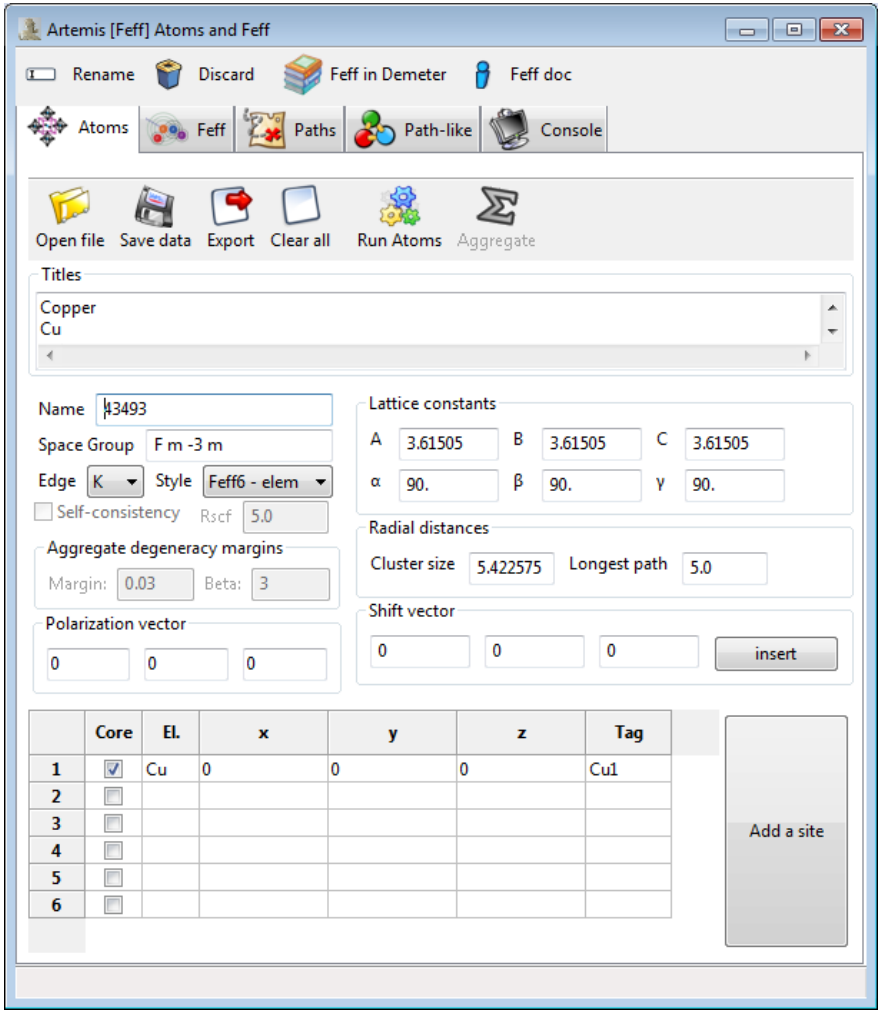
Fitting parameters


Artemis [Data] RAMEMET1_bis.DAT.chik
Data Path Marks Actions Debug Help
RAMEMET1_bis.DAT.chik
CV 1
Data source
ERCULES-SESAME\esercizi\EXAFS\cu-met\RAMEMET1_bis.DAT.chik
Plot this data set as
k123 R123 Rmr Rk kq
Title lines
Fourier transform parameters
kmin 3.000 kmax 17.900 dk 1
rmin 1.57 rmax 2.8 dr 0.5
Fitting k weights
1 2 3 other 0.5
Other parameters
Include in fit Plot after fit Fit background
ε(k) 0 Plot with phase correction
Pluck a value for kmax from the plot.

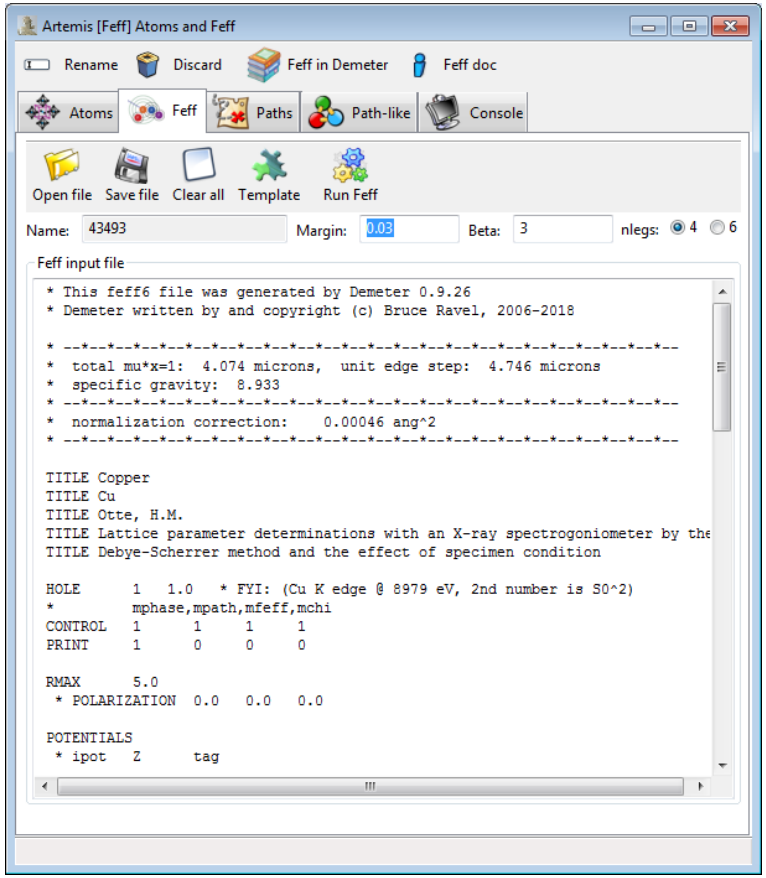

k² χ(k) (Å⁻²)
Wavenumber (Å⁻¹)

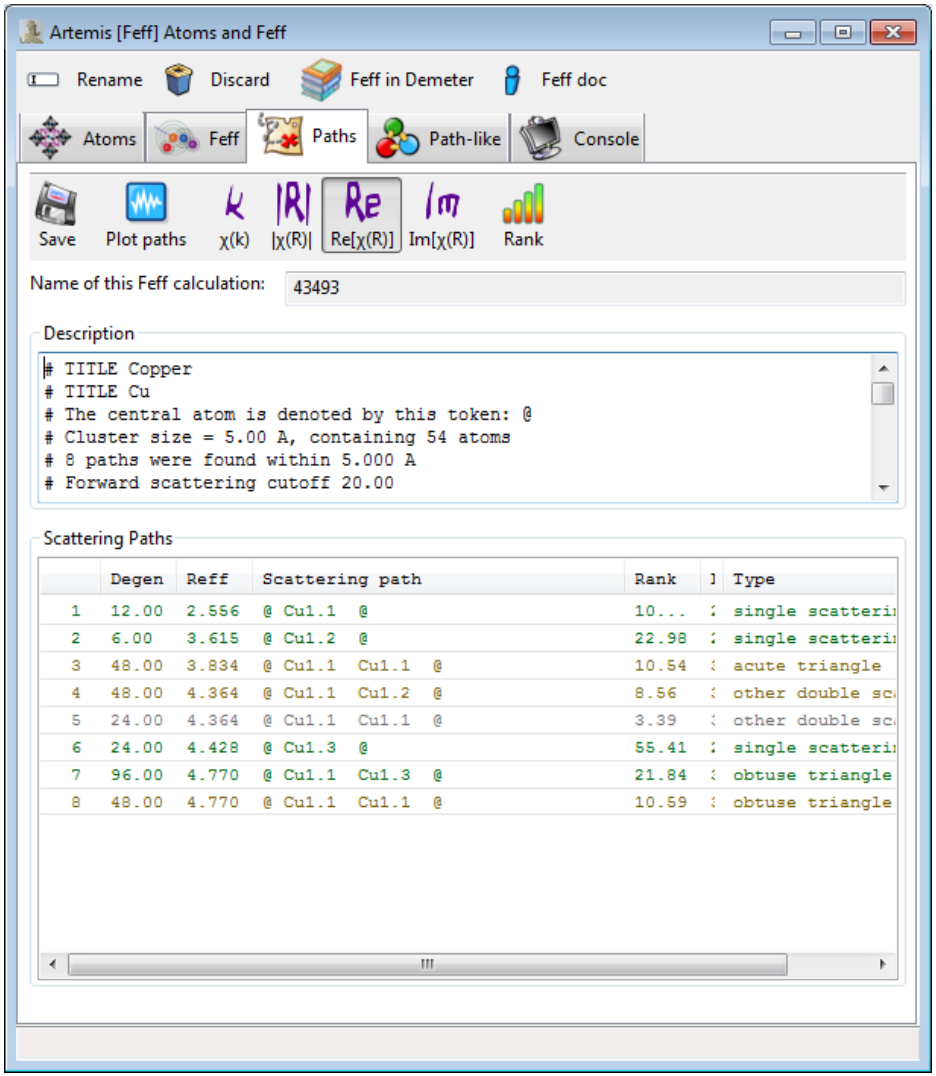

RAMEMET1_bis.DAT.chik
window
|χ(R)| (Å⁻⁴)
Radial distance (Å)

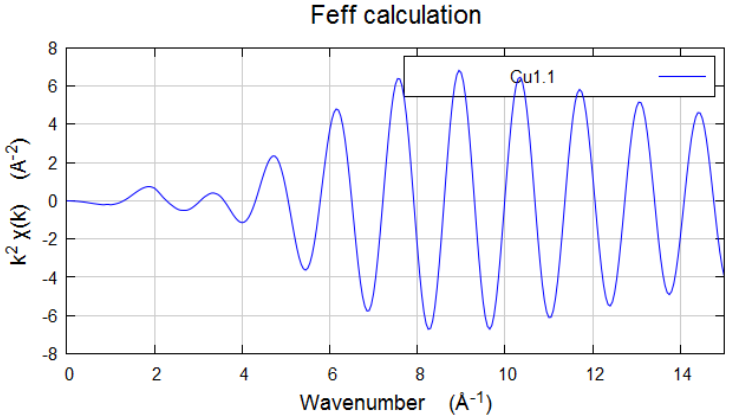


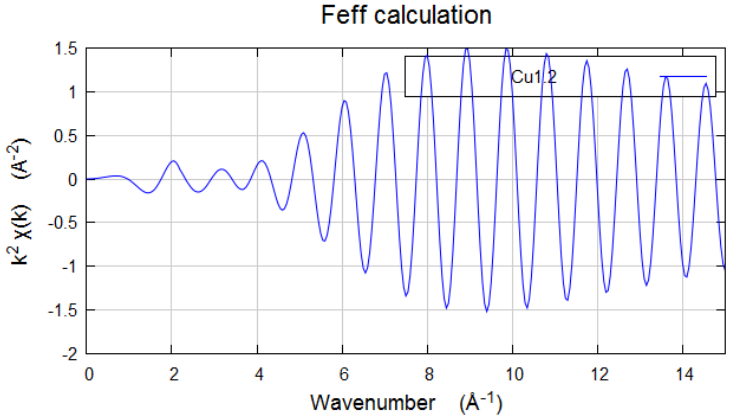


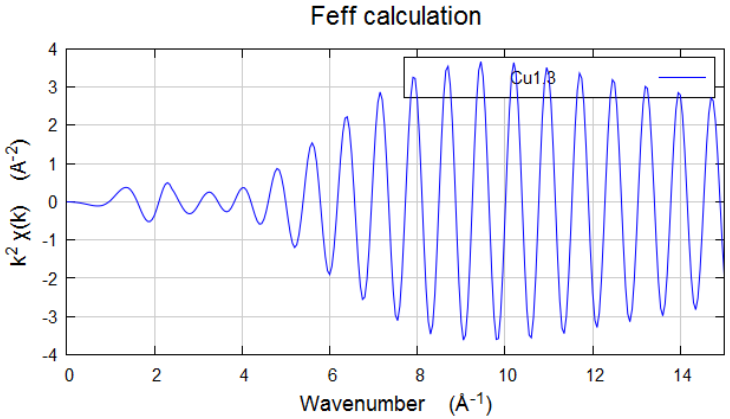
Import a .cif file

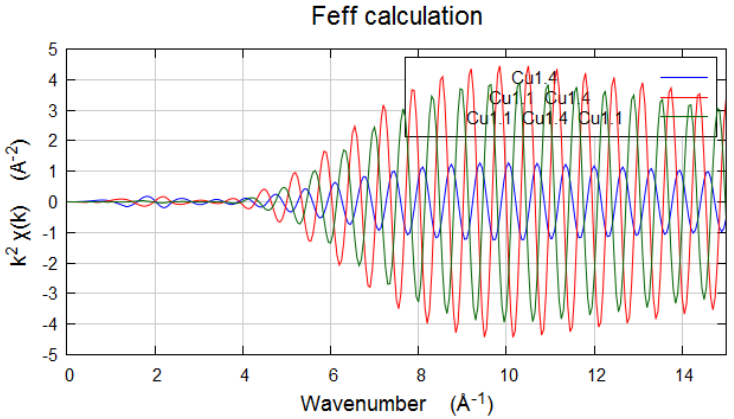

Artemis [Feff] Atoms and Feff
Rename
Discard
Feff in Demeter
Feff doc
Atoms
Feff
Paths
Path-like
Console
Open file
Save file
Clear all
Template
Run Feff
Name: 43493
Margin: 0.03
Beta: 3
nlegs: 4 6
Feff input file
* This feff6 file was generated by Demeter 0.9.26
* Demeter written by and copyright (c) Bruce Ravel, 2006-2018
* total mu*x=1: 4.074 microns, unit edge step: 4.746 microns
* specific gravity: 8.933
* normalization correction: 0.00046 ang^2
TITLE Copper
TITLE Cu
TITLE Otte, H.M.
TITLE Lattice parameter determinations with an X-ray spectrogoniometer by the
TITLE Debye-Scherrer method and the effect of specimen condition
HOLE 1 1.0 * FYI: (Cu K edge @ 8979 eV, 2nd number is S0^2)
* mphase,mpath,mfeff,mchi
CONTROL 1 1 1 1
PRINT 1 0 0 0
RMAX 5.0
* POLARIZATION 0.0 0.0 0.0
POTENTIALS
* ipot Z tag

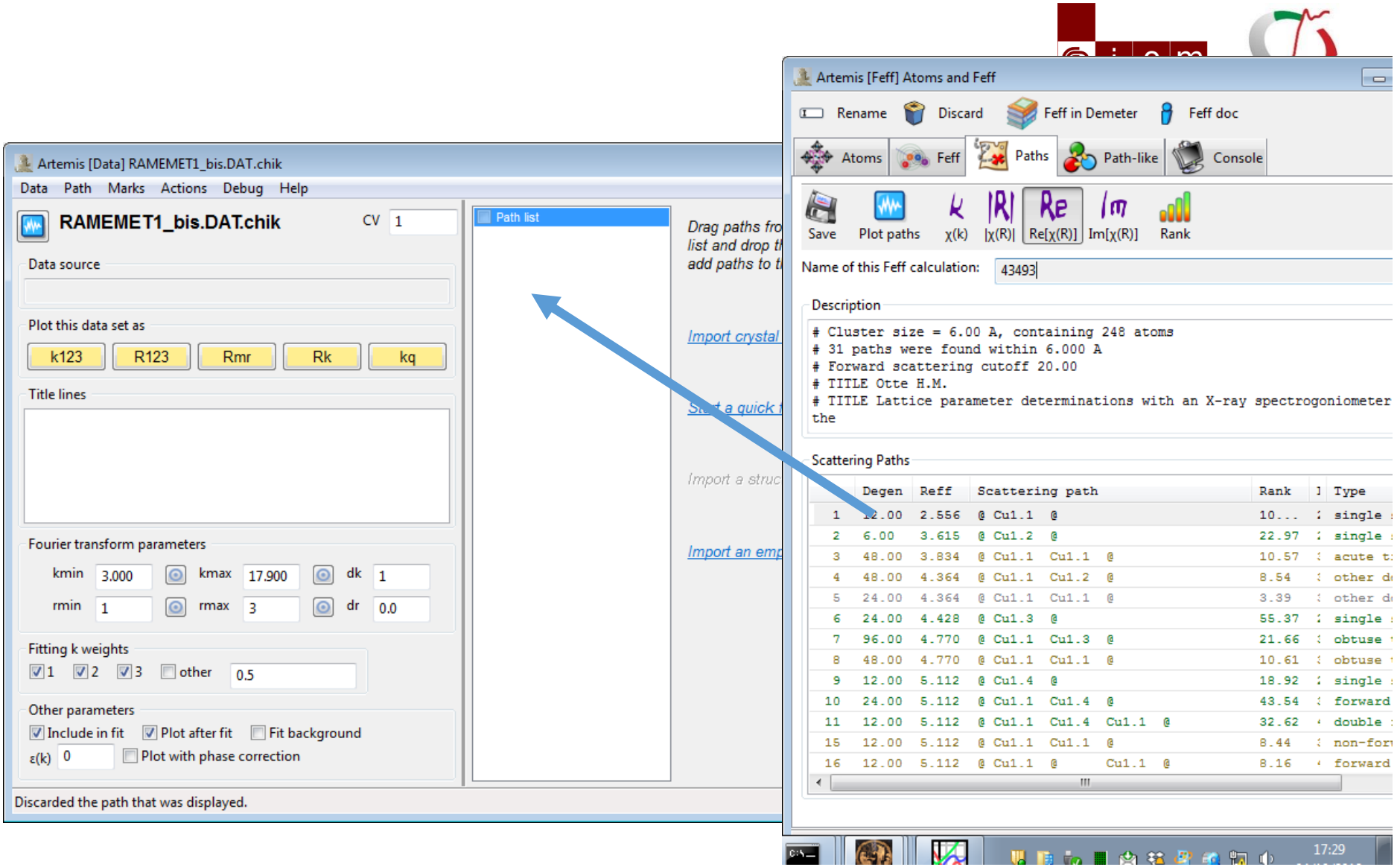

Artemis [Feff] Atoms and Feff
Rename
Discard
Feff in Demeter
Feff doc
Atoms
Feff
Paths
Path-like
Console
Save
Plot paths
χ(k)
|χ(R)|
Re[χ(R)]
Im[χ(R)]
Rank
Name of this Feff calculation: 43493
Description
TITLE Copper
TITLE Cu
The central atom is denoted by this token: @
Cluster size = 5.00 A, containing 54 atoms
8 paths were found within 5.000 A
Forward scattering cutoff 20.00
Scattering Paths
Degen Reff Scattering path Rank Type
1 12.00 2.556 @ Cu1.1 @ 10... single scatteri
2 6.00 3.615 @ Cu1.2 @ 22.98 single scatteri
3 48.00 3.834 @ Cu1.1 Cu1.1 @ 10.54 acute triangle
4 48.00 4.364 @ Cu1.1 Cu1.2 @ 8.56 other double sc
5 24.00 4.364 @ Cu1.1 Cu1.1 @ 3.39 other double sc
6 24.00 4.428 @ Cu1.3 @ 55.41 single scatteri
7 96.00 4.770 @ Cu1.1 Cu1.3 @ 21.84 obtuse triangle
8 48.00 4.770 @ Cu1.1 Cu1.1 @ 10.59 obtuse triangle

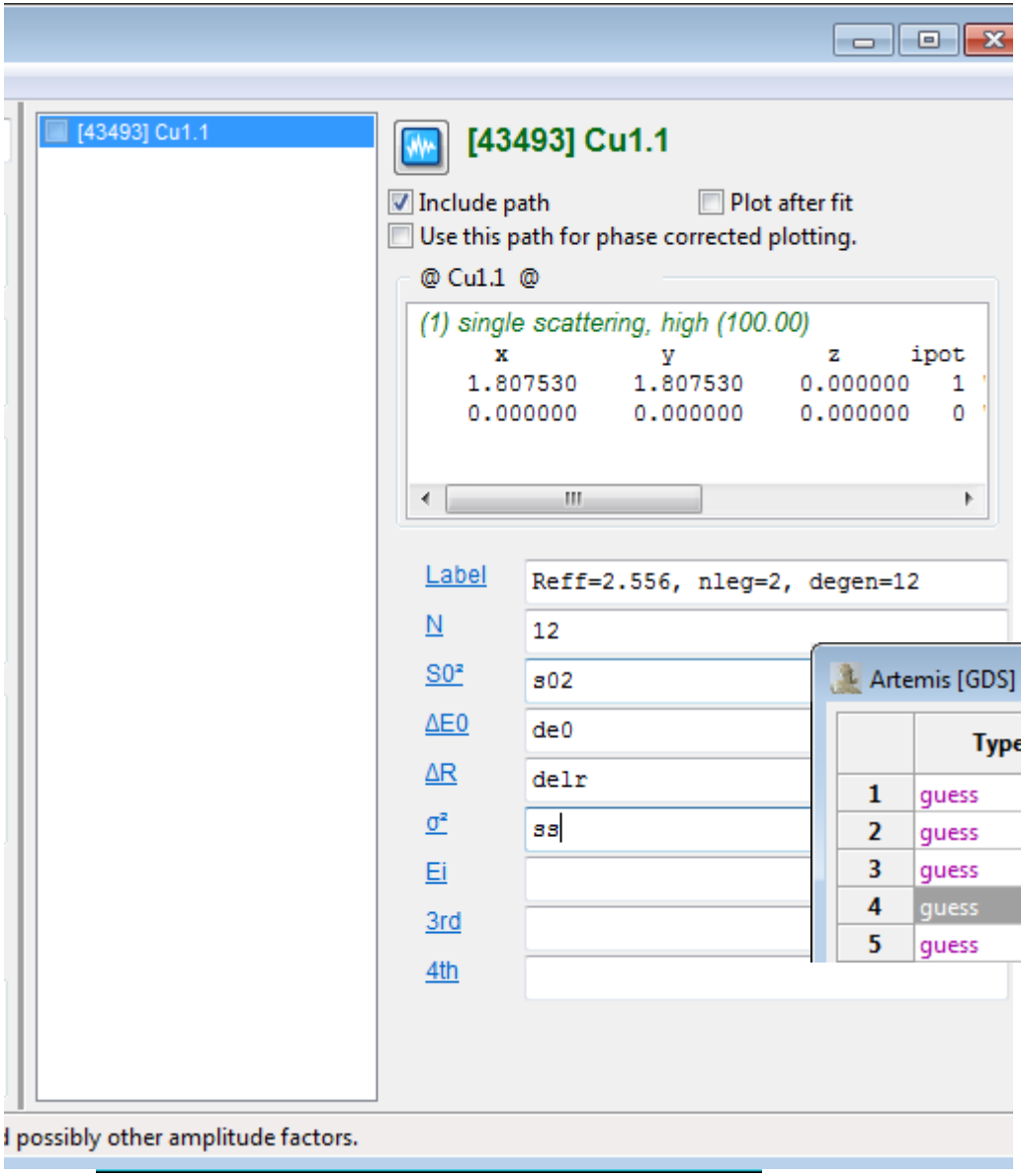

Feff calculation
Cu1.1
k² χ(k) (Å⁻²)
Wavenumber (Å⁻¹)

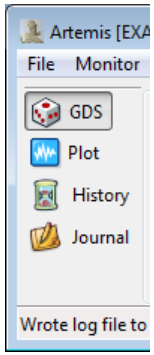

Feff calculation
Cu1.2
k² χ(k) (Å⁻²)
Wavenumber (Å⁻¹)

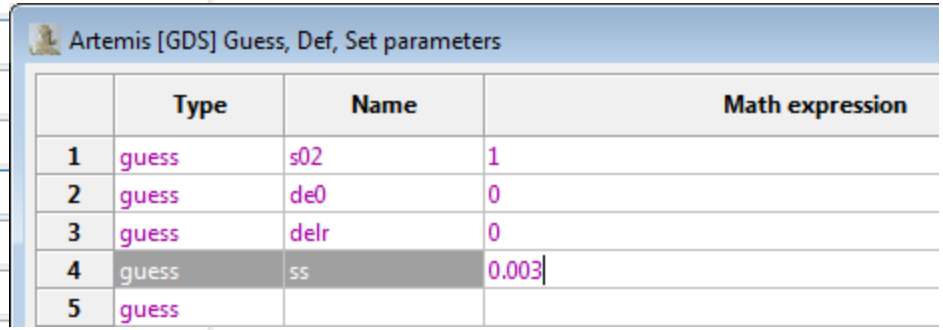

Feff calculation
Cu1.3
k² χ(k) (Å⁻²)
Wavenumber (Å⁻¹)


Feff calculation
Cu1.4
Cu1.1 Cu1.4
Cu1.1 Cu1.4 Cu1.1
k² χ(k) (Å⁻²)
Wavenumber (Å⁻¹)

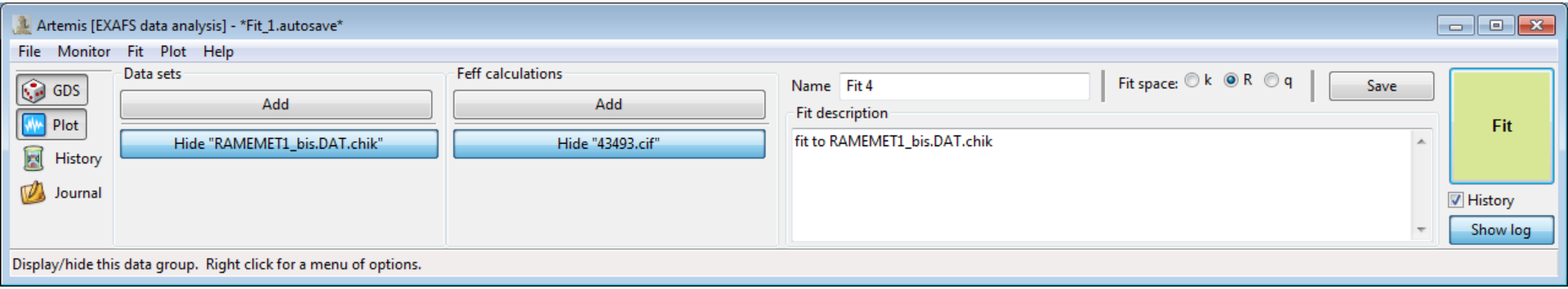

Artemis [Data] RAMEMET1_bis.DAT.chik
Data Path Marks Actions Debug Help
RAMEMET1_bis.DAT.chik
CV 1
Data source
Plot this data set as
k123 R123 Rmr Rk kq
Title lines
Fourier transform parameters
kmin 3.000 kmax 17.900 dk 1
rmin 1 rmax 3 dr 0.0
Fitting k weights
1 2 3 other 0.5
Other parameters
Include in fit Plot after fit Fit background
ε(k) 0 Plot with phase correction
Path list
Drag paths fro
list and drop t
add paths to t
Import crystal
Import a struc
Import an emp
Discarded the path that was displayed.
Artemis [Feff] Atoms and Feff
Rename Discard Feff in Demeter Feff doc
Atoms Feff Paths Path-like Console
Save Plot paths χ(k) |χ(R)| Re[χ(R)] Im[χ(R)] Rank
Name of this Feff calculation: 43493
Description
Cluster size = 6.00 A, containing 248 atoms
31 paths were found within 6.000 A
Forward scattering cutoff 20.00
TITLE Otte H.M.
TITLE Lattice parameter determinations with an X-ray spectrogoniometer
the
Scattering Paths
Degen Reff Scattering path Rank Type
1 12.00 2.556 @ Cu1.1 @ 10... single
2 6.00 3.615 @ Cu1.2 @ 22.97 single
3 48.00 3.834 @ Cu1.1 Cu1.1 @ 10.57 acute t
4 48.00 4.364 @ Cu1.1 Cu1.2 @ 8.54 other d
5 24.00 4.364 @ Cu1.1 Cu1.1 @ 3.39 other d
6 24.00 4.428 @ Cu1.3 @ 55.37 single
7 96.00 4.770 @ Cu1.1 Cu1.3 @ 21.66 obtuse
8 48.00 4.770 @ Cu1.1 Cu1.1 @ 10.61 obtuse
9 12.00 5.112 @ Cu1.4 @ 18.92 single
10 24.00 5.112 @ Cu1.1 Cu1.4 @ 43.54 forward
11 12.00 5.112 @ Cu1.1 Cu1.4 Cu1.1 @ 32.62 double
15 12.00 5.112 @ Cu1.1 Cu1.1 @ 8.44 non-for
16 12.00 5.112 @ Cu1.1 @ Cu1.1 @ 8.16 forward
17:29

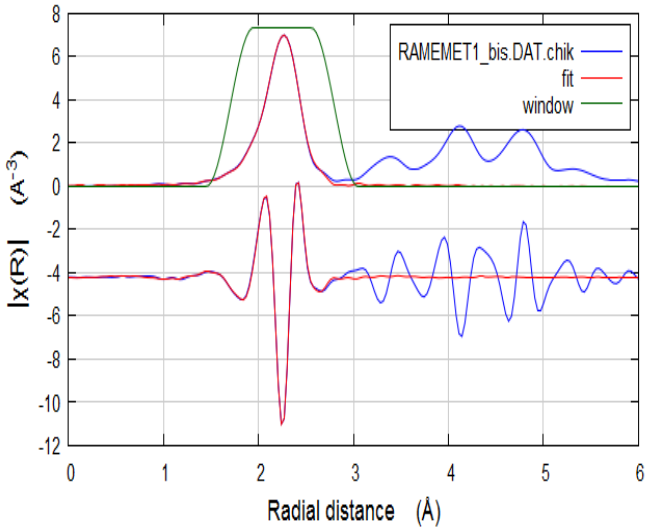

[43493] Cu1.1
[43493] Cu1.1
Include path
Plot after fit
Use this path for phase corrected plotting.
@ Cu1.1 @
(1) single scattering, high (100.00)
x y z ipot
1.807530 1.807530 0.000000 1
0.000000 0.000000 0.000000 0
Label
Reff=2.556, nleg=2, degen=12
N
12
S0²
s02
ΔE0
de0
ΔR
delr
σ²
ss
Ei
3rd
4th
possibly other amplitude factors.

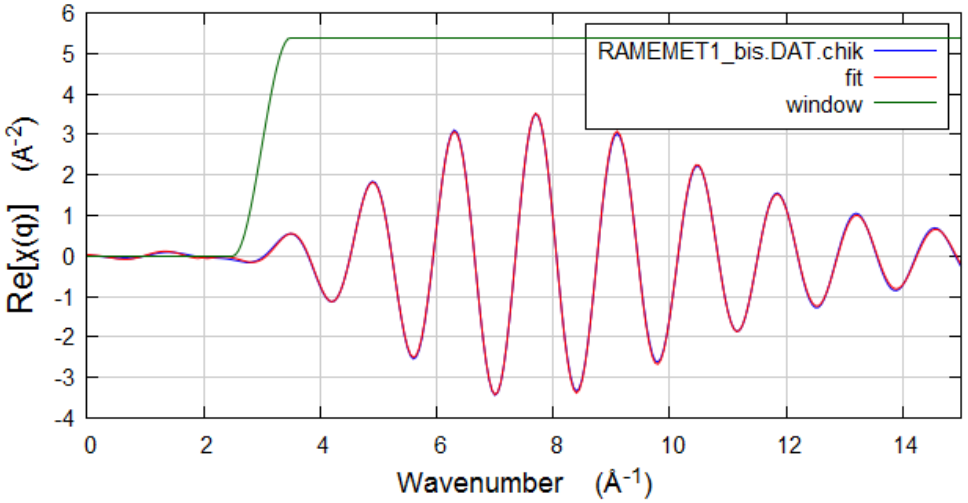

Artemis [EXA
File Monitor
GDS
Plot
History
Journal
Wrote log file to


Artemis [GDS] Guess, Def, Set parameters
Type Name Math expression
1 guess s02 1
2 guess de0 0
3 guess delr 0
4 guess ss 0.003
5 guess

Fit results


Artemis [EXAFS data analysis] - *Fit_1.autosave*
File Monitor Fit Plot Help
GDS
Plot
History
Journal
Data sets
Add
Hide "RAMEMET1_bis.DAT.chik"
Feff calculations
Add
Hide "43493.cif"
Name Fit 4
Fit space: k R q
Save
Fit description
fit to RAMEMET1_bis.DAT.chik
Fit
History
Show log
Display/hide this data group. Right click for a menu of options.


RAMEMET1_bis.DAT.chik
fit
window
|χ(R)| (Å⁻³)
Radial distance (Å)


RAMEMET1_bis.DAT.chik
fit
window
Re[χ(q)] (Å⁻²)
Wavenumber (Å⁻¹)

Fit results

```
guess parameters:
------------------------------------------------------------------------------
  s02                =    0.88351859    # +/-    0.02088049     [1]
  de0                =    4.59920280    # +/-    0.28462844     [0]
  delr               =   -0.01515839    # +/-    0.00141444     [0]
  ss                 =    0.00433382    # +/-    0.00014620     [0.003]
```

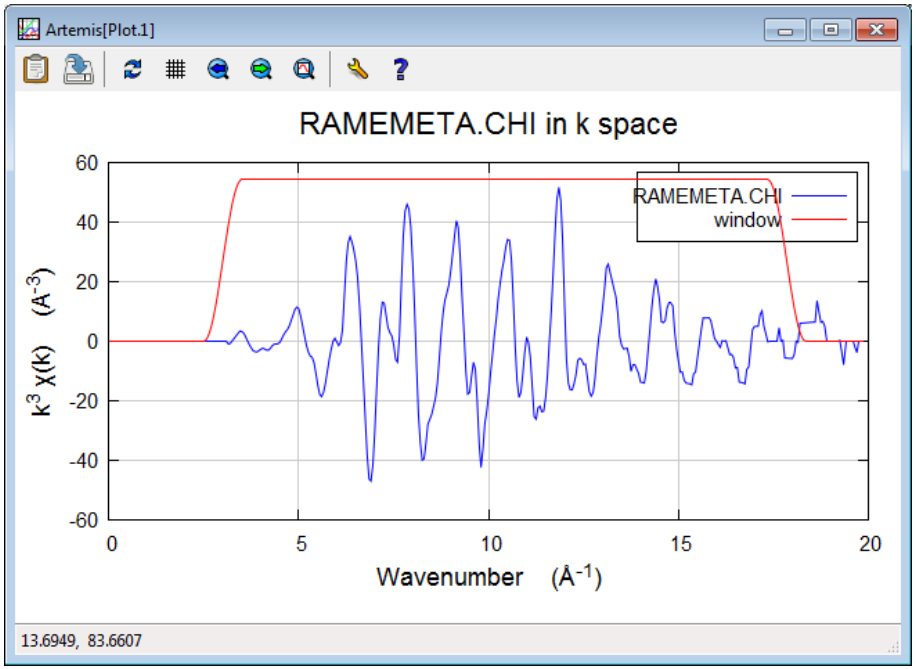
```
  name                N       S02     sigma^2   e0     delr     Reff     R
================================================================================
[43493] Cu1.1     12.000    0.884    0.00433    4.599 -0.01516  2.55620  2.54104

  name                ei       third     fourth
=================================================
[43493] Cu1.1     0.00000    0.00000    0.00000
```

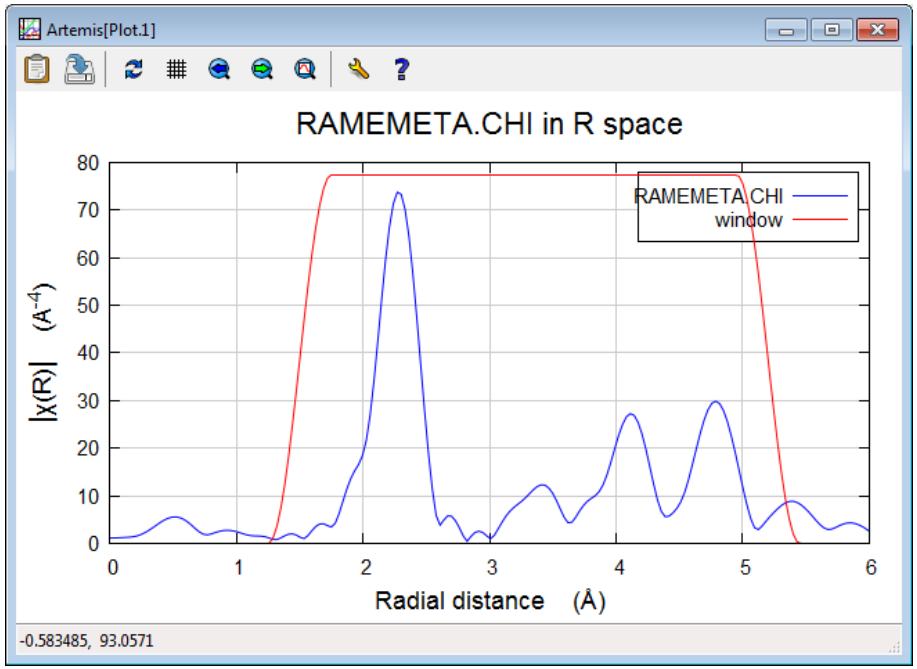
Multiple shell analysis

- General strategy
  - Increase the number of shells in the model
  - Do not let the number of free parameters proliferate

- Method
  - Use a common amplitude reduction factor and the crystallographic number of neighbors.
  - Structure homothety (i.e. all Rs are scaled by a common factor using the Reff variable)
  - Use built-in models (Debye or Einstein) for the calculation of DW factors.

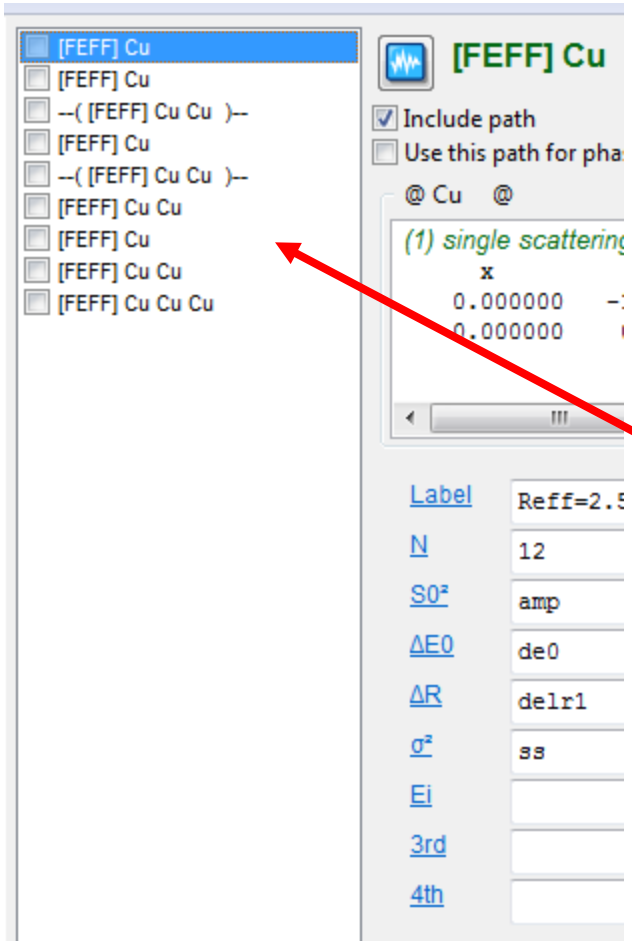
Data fitting

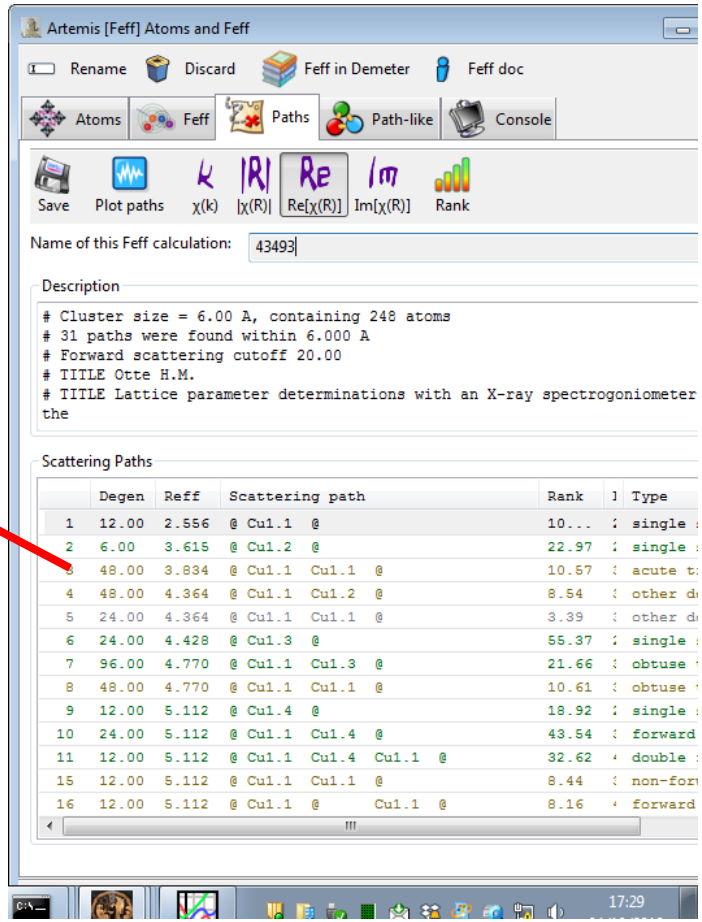




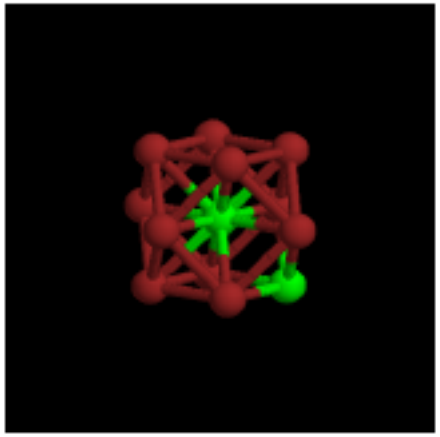
Increase the fitting range in R space up the max desired value

Building up the model

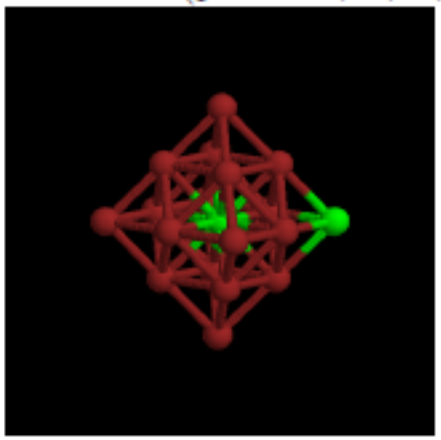




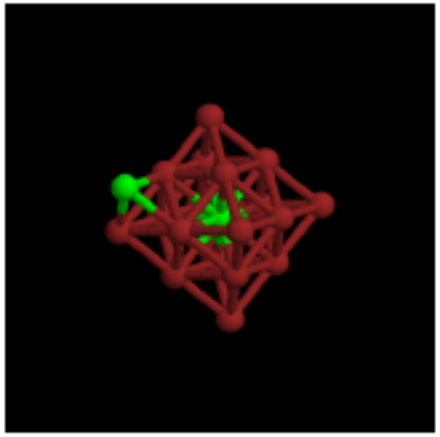
Single scattering paths from the first to the fourth shell (paths 1, 2, 5, 8)



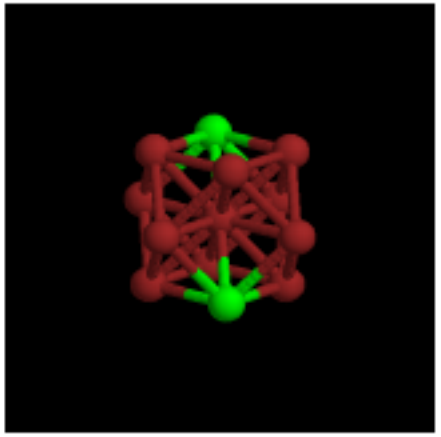
1st Shell (Path 1)



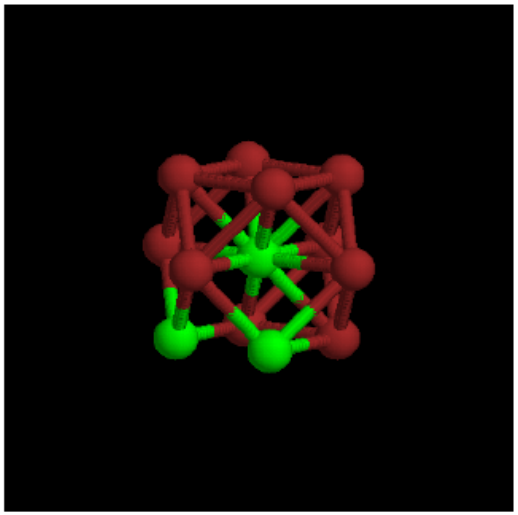
2nd shell (Path 2)



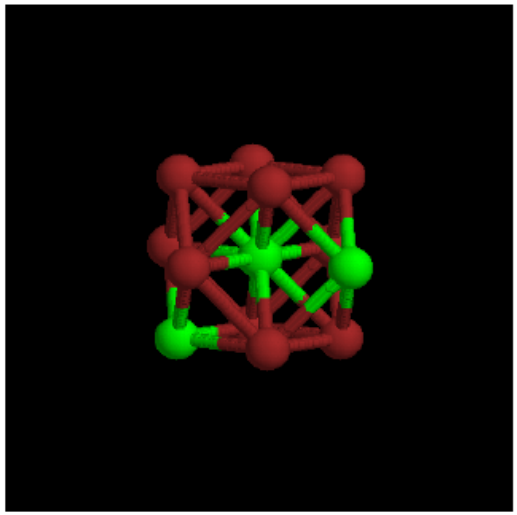
3rd shell (Path 5)



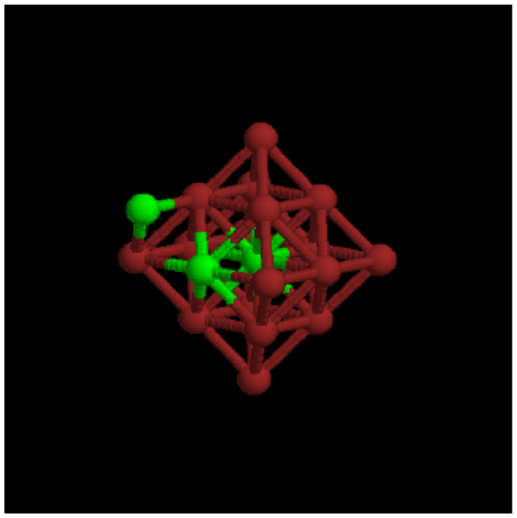
4th shell (Path 8)



Double scattering between absorber and 2 Nearest Neighbors (NN) with the absorber in the vertex of a 60 deg angle (path 3).

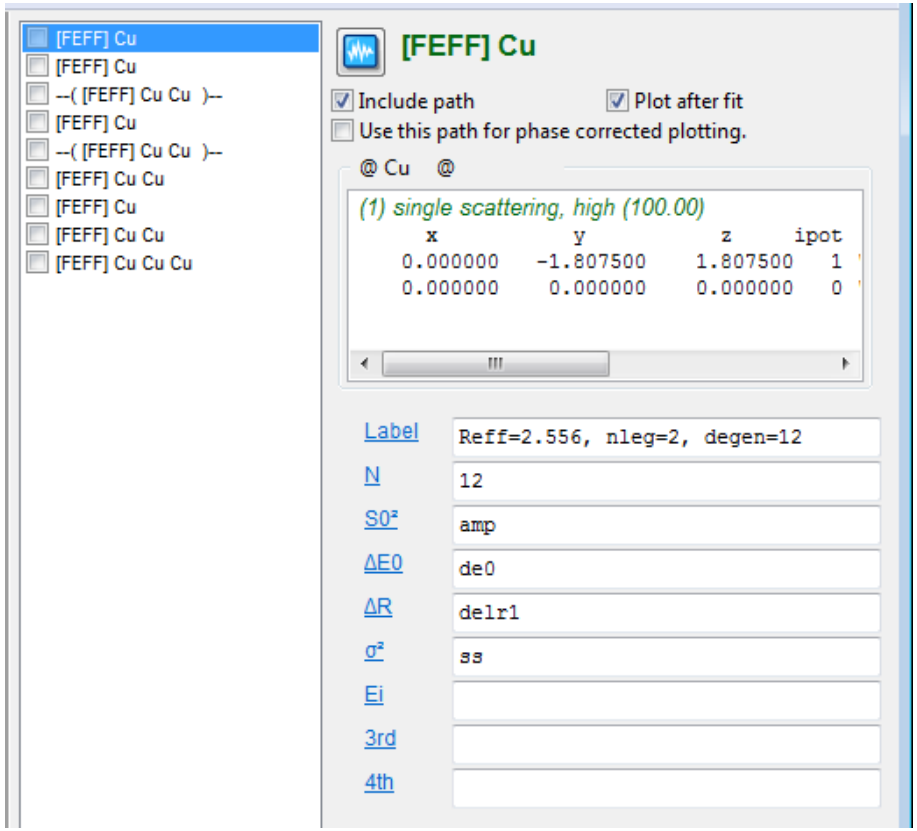


Double scattering between the absorber and 2 NN. The absorber is on the vertex of a 120 deg angle (path 6).

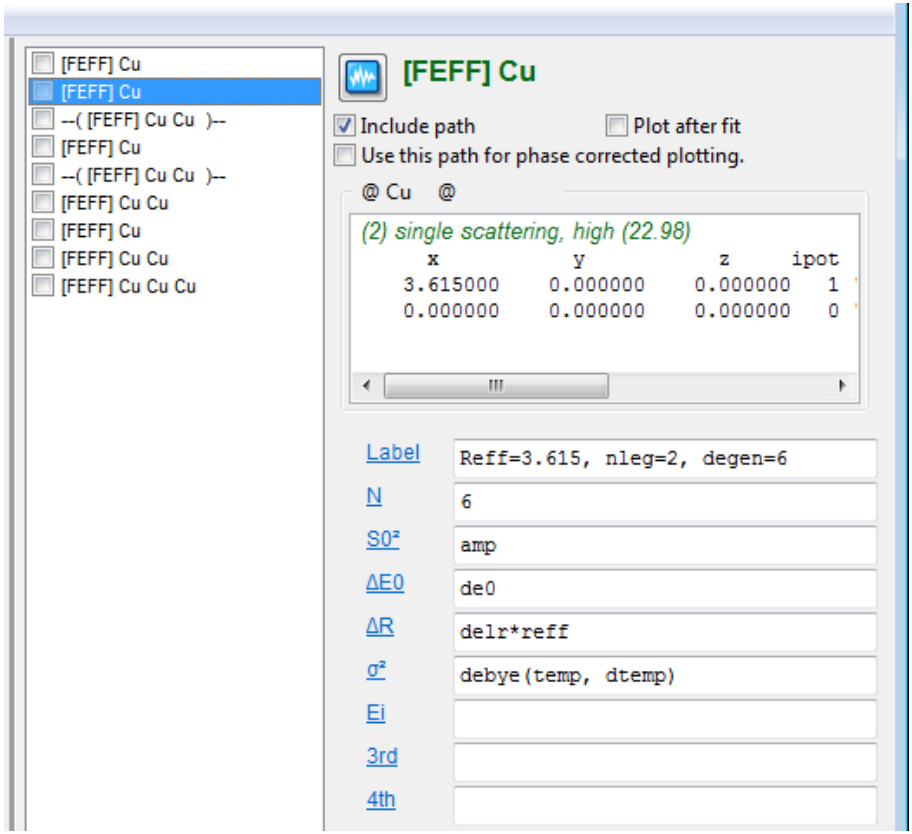


Double scattering between the absorber, a 1 NN and a 3 NN (path 7).

Fit parameters

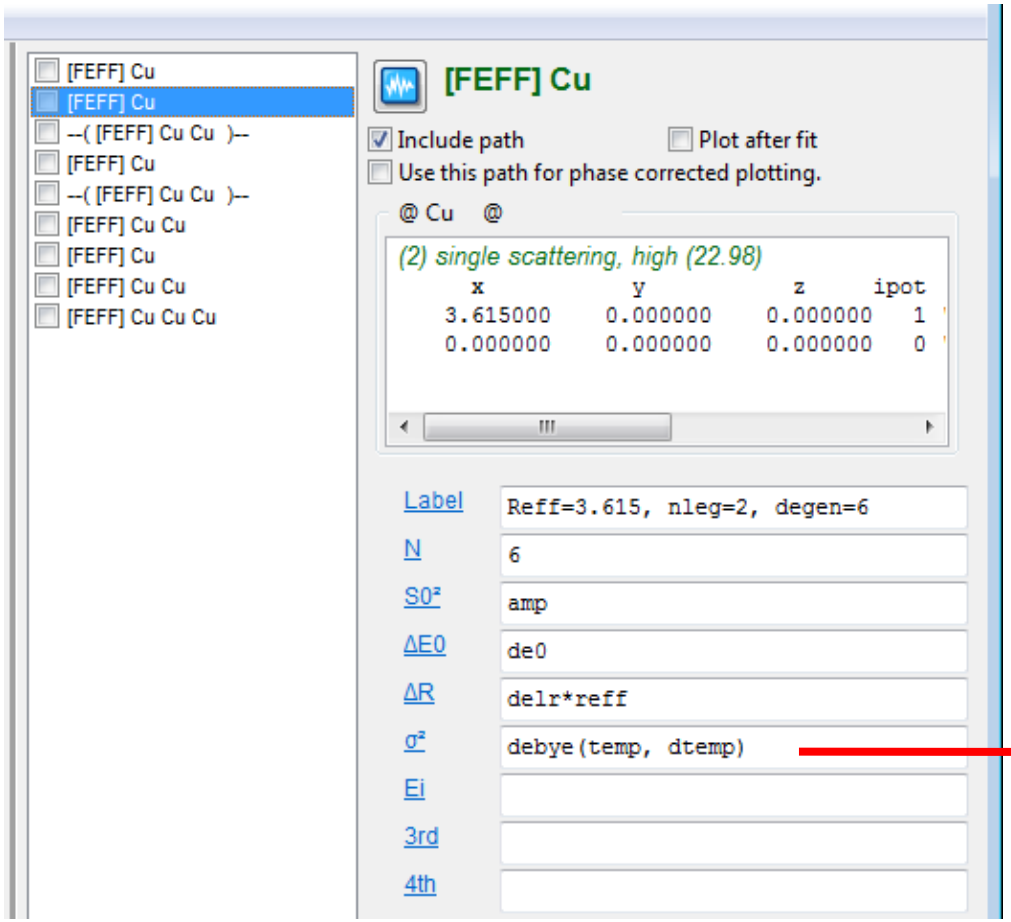


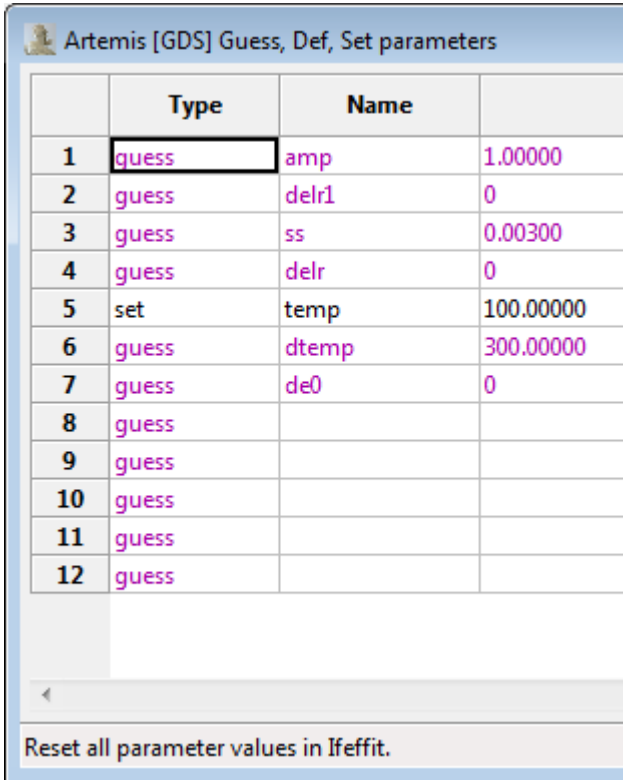
First shell



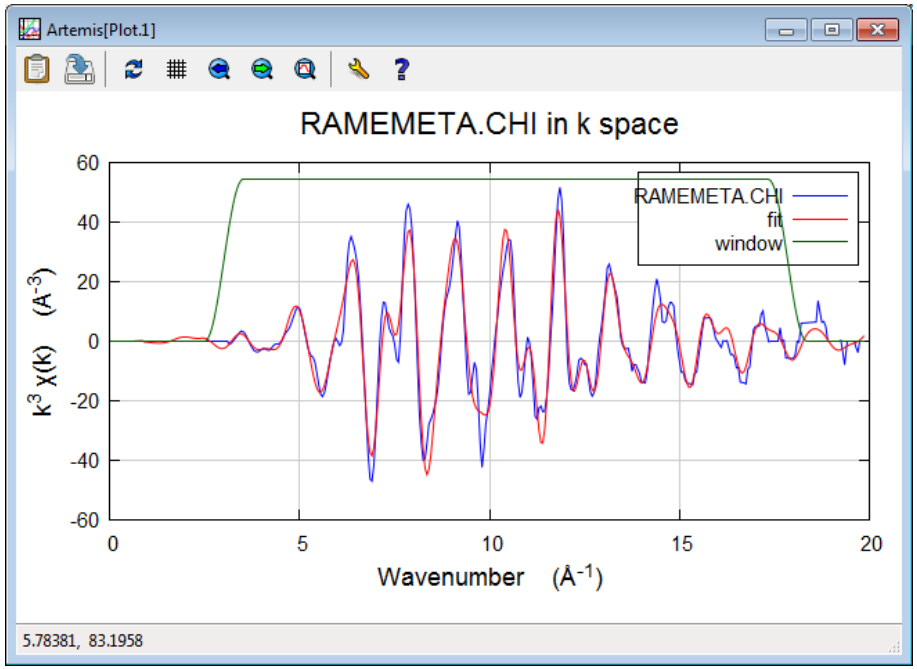
Other shells

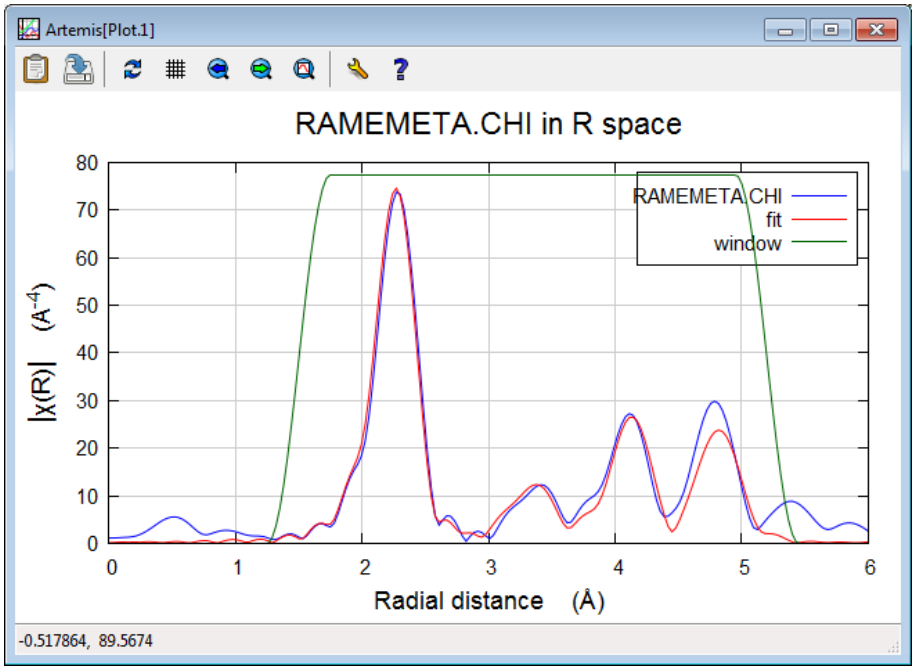
Note the special variable *Reff* and the function *Debye*


[FEFF] Cu
[FEFF] Cu
--([FEFF] Cu Cu)--
[FEFF] Cu
--([FEFF] Cu Cu)--
[FEFF] Cu Cu
[FEFF] Cu
[FEFF] Cu Cu
[FEFF] Cu Cu Cu
[FEFF] Cu
Include path
Plot after fit
Use this path for phase corrected plotting.
@ Cu @
(2) single scattering, high (22.98)
x y z ipot
3.615000 0.000000 0.000000 1
0.000000 0.000000 0.000000 0
Label
Reff=3.615, nleg=2, degen=6
N
6
S0²
amp
ΔE0
de0
ΔR
delr*reff
σ²
debye(temp, dtemp)
Ei
3rd
4th

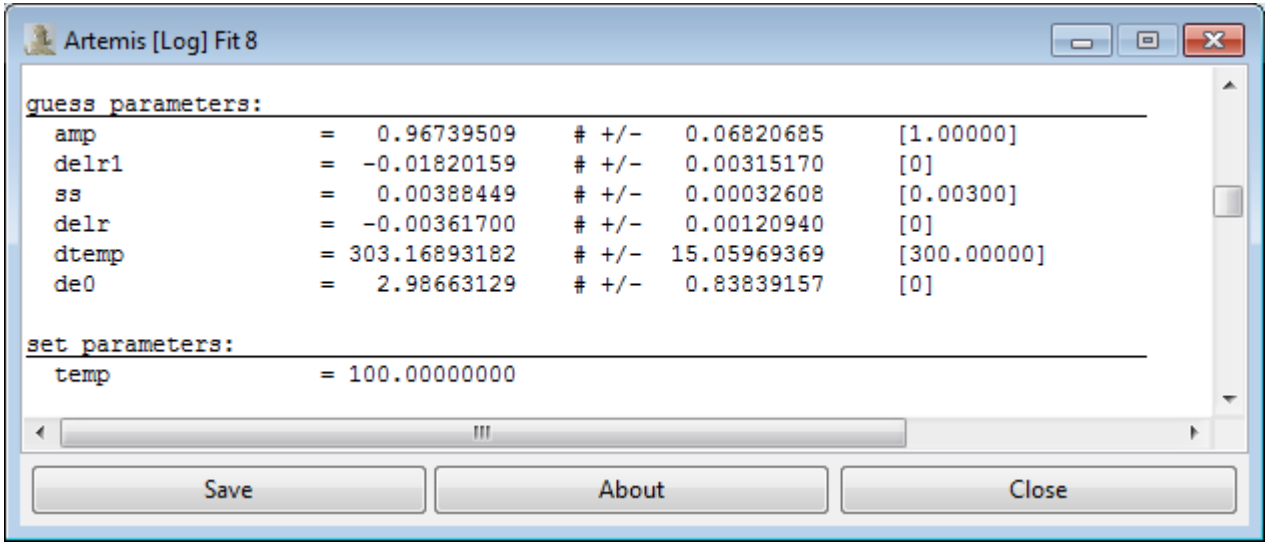

Artemis [GDS] Guess, Def, Set parameters
Type
Name
1 guess amp 1.00000
2 guess delr1 0
3 guess ss 0.00300
4 guess delr 0
5 set temp 100.00000
6 guess dtemp 300.00000
7 guess de0 0
8 guess
9 guess
10 guess
11 guess
12 guess
Reset all parameter values in Ifeffit.

Results


Artemis[Plot.1]
RAMEMETA.CHI in k space
RAMEMETA.CHI
fit
window
k³ χ(k) (Å⁻³)
Wavenumber (Å⁻¹)
5.78381, 83.1958

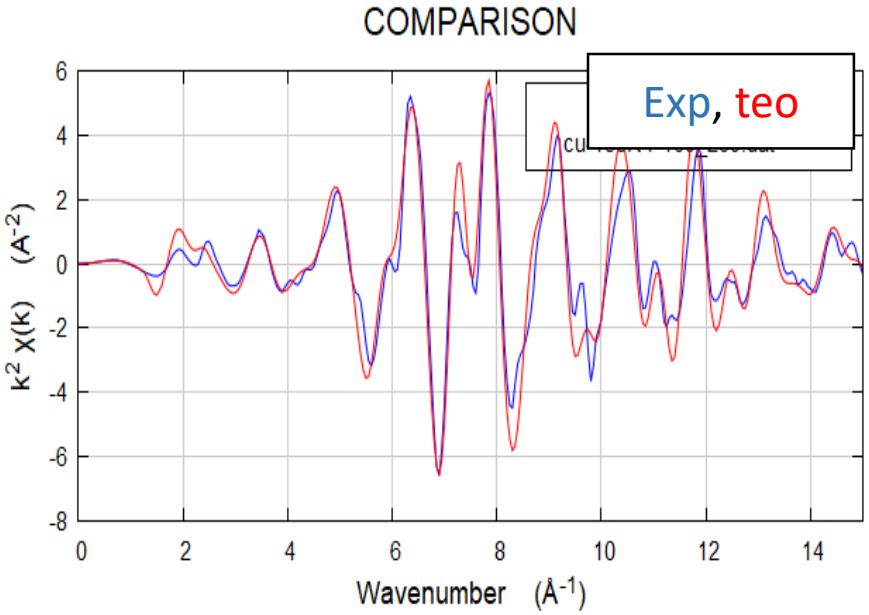

Artemis[Plot.1]
RAMEMETA.CHI in R space
RAMEMETA.CHI
fit
window
|χ(R)| (Å⁻⁴)
Radial distance (Å)
-0.517864, 89.5674

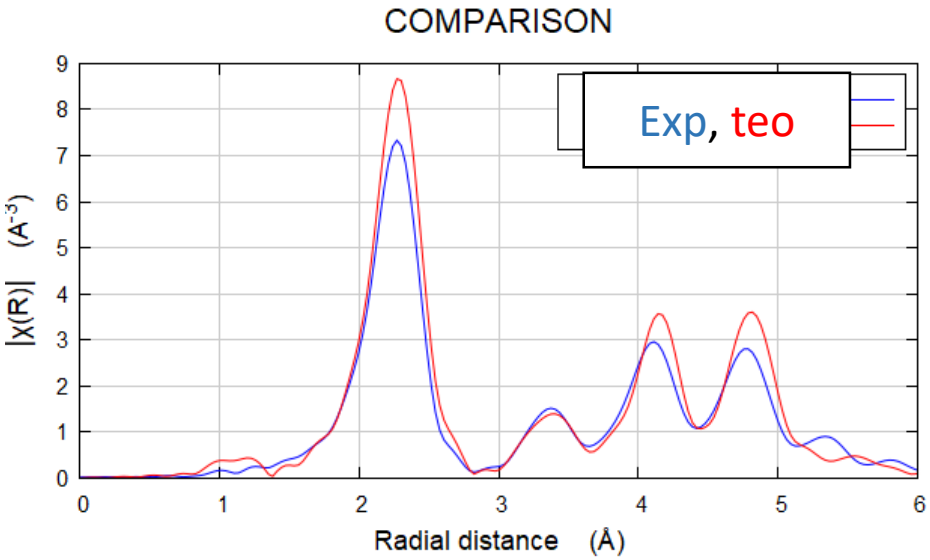
Results


Artemis [Log] Fit 8
guess parameters:
amp = 0.96739509 # +/- 0.06820685 [1.00000]
delr1 = -0.01820159 # +/- 0.00315170 [0]
ss = 0.00388449 # +/- 0.00032608 [0.00300]
delr = -0.00361700 # +/- 0.00120940 [0]
dtemp = 303.16893182 # +/- 15.05969369 [300.00000]
de0 = 2.98663129 # +/- 0.83839157 [0]
set parameters:
temp = 100.00000000
Save
About
Close

Perspective: ab initio modeling

Cu FCC, DFT-MD, 108 at cell, 1ps.
XAS from a 54 atm cluster, 5.2 Å, 100 frames





Conclusion

- XAS data treatment
  - Edge determination
  - Normalization
- EXAFS
  - Quantitative data analysis
  - Also Multiple Shell analysis possible