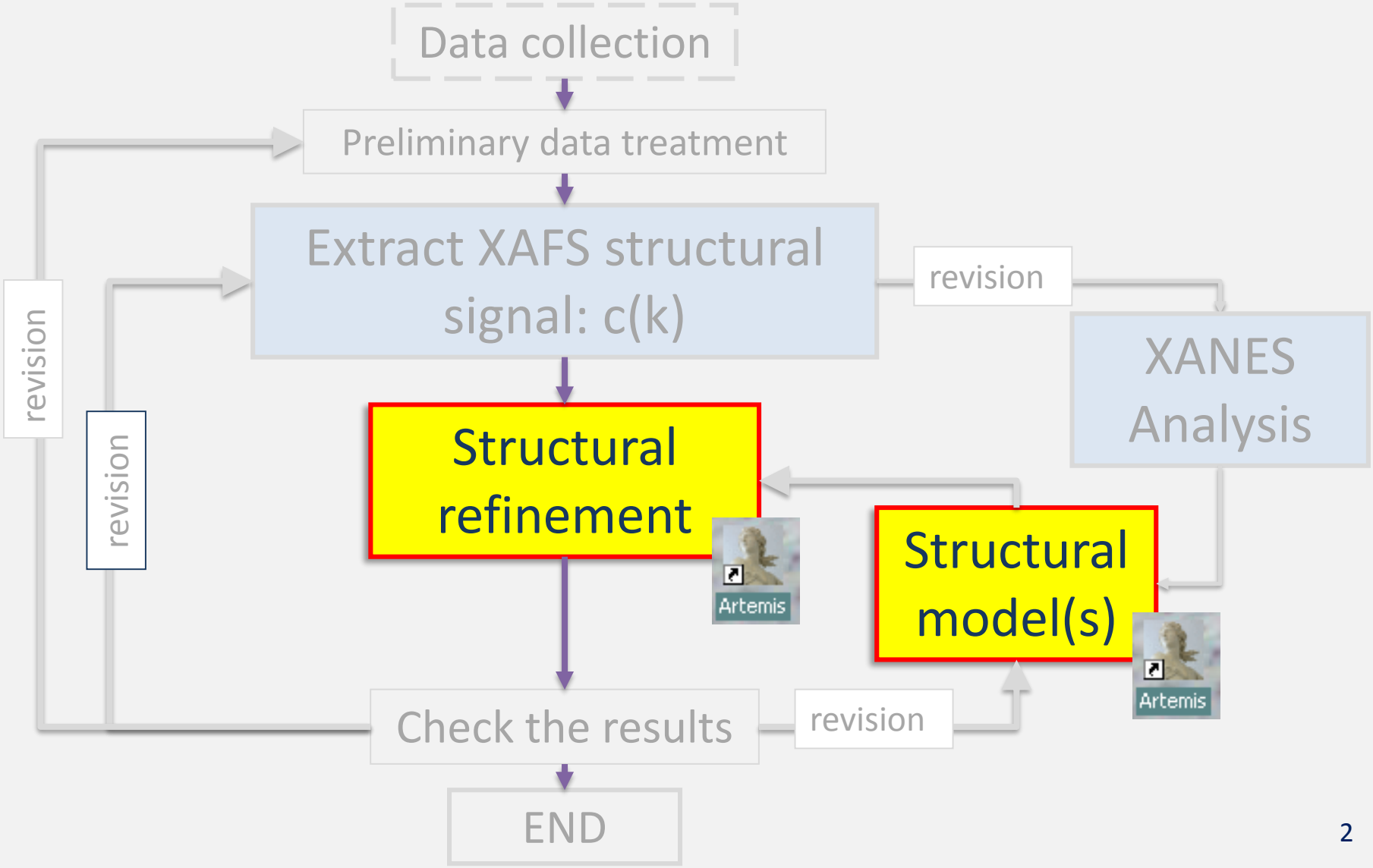
Data analysis of XAFS data

1. XAFS data analysis and related software
2. From XAS to XAFS: data treatment procedures
3. **Training: EXAFS data refinement**
4. Training: XANES data analysis

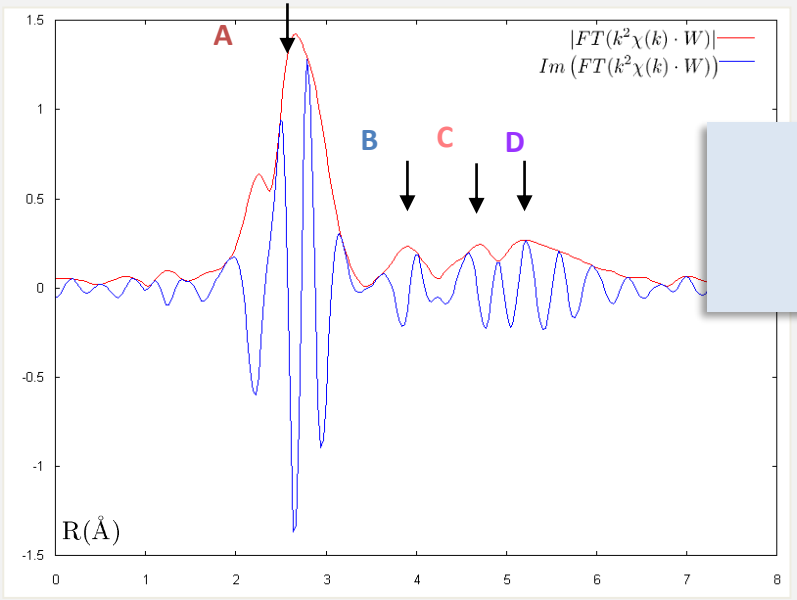
https://tinyurl.com/SRSelettra2021

Contacts:
Prof. Carlo Meneghini
Dip. Di Scienze, Università Roma Tre, Roma
carlo.meneghini@uniroma3.it

XAFS data ANALYSIS: from the experimental data to structural details

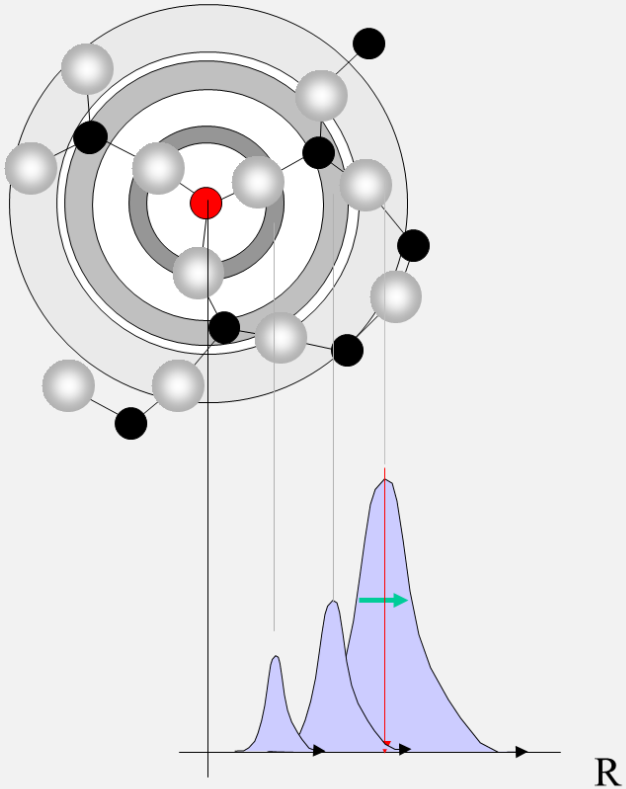


The EXAFS standard formula



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

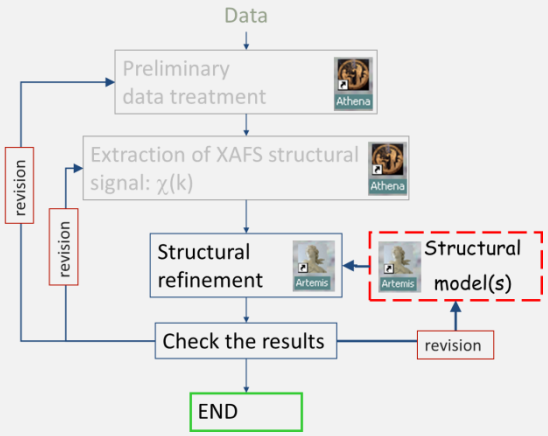
$$A_j = S_o^2 \frac{N_j}{r_j} |f_j| e^{-2k^2\sigma_j^2}\, e_j^{-\frac{2r_j}{\lambda}}$$



parameters

f_j = photo-electron scattering amplitude
ψ_j = photo-electron scattering phase
λ = photo-electron mean free path
S_o^2 = many body losses

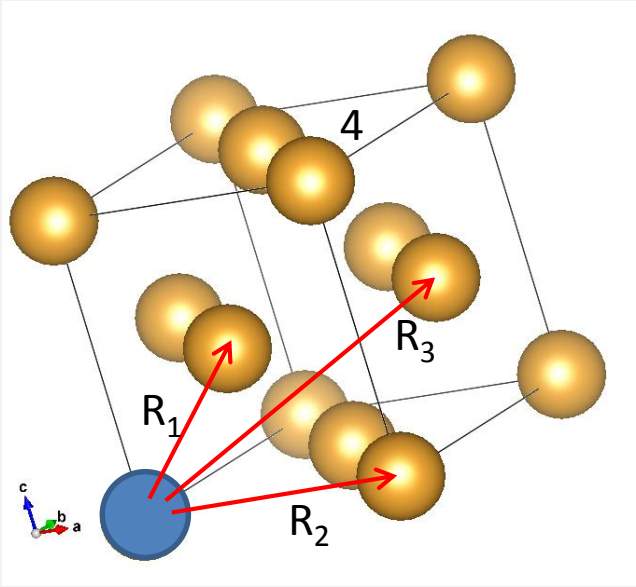
Structure
N_j = multiplicity (coordination number)
r_j = half path length (coordination distance)
σ_j^2 = variance of the path length distribution
(Mean Square Relative Displacement: MSRD)



Structural model & Data refinement

We will analyze Cu EXAFS firstly

1. search Cu metal structure (cif)
2. visualize with Vesta
3. draw a local structure model
4. draw a local cluster with Atoms



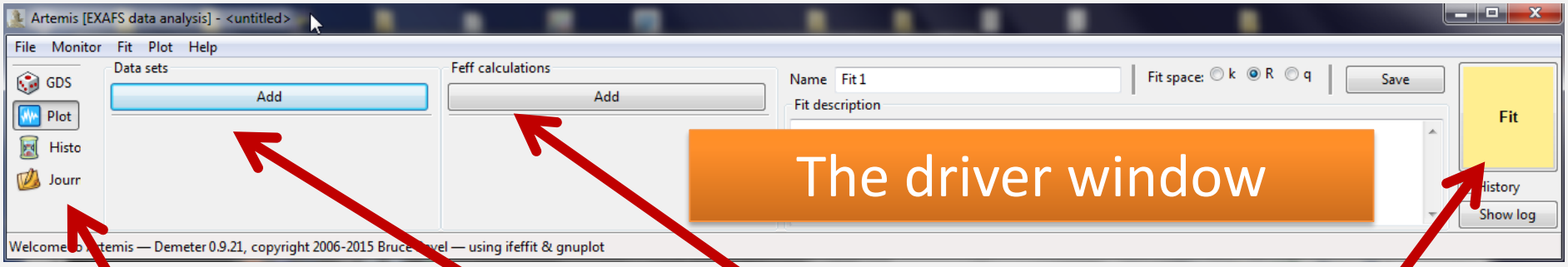
icsd_43493_Copper.cif

Cu metal
SPG: fcc, f m 3 m (# 220)
a = 3.61 A
Cu 0.0 0.0 0.0

Sh	R	N	R_{Cu}(A)
I:	$a/\sqrt{2}$	12	2.553
II:	a	6	3.610
III:	$a\sqrt{3/2}$	24	4.421
IV:	$a\sqrt{2}$	12	5.105
V:	$a\sqrt{5/2}$	24	5.708
....			

Start Arthemis

better on la larger monitor!



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

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

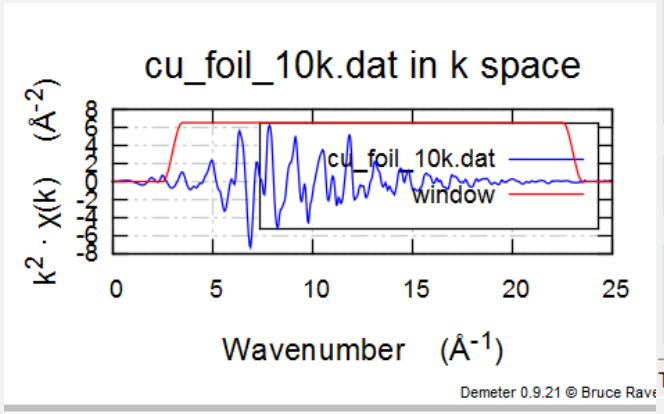
2:add a Structure .cif or Feff file

4

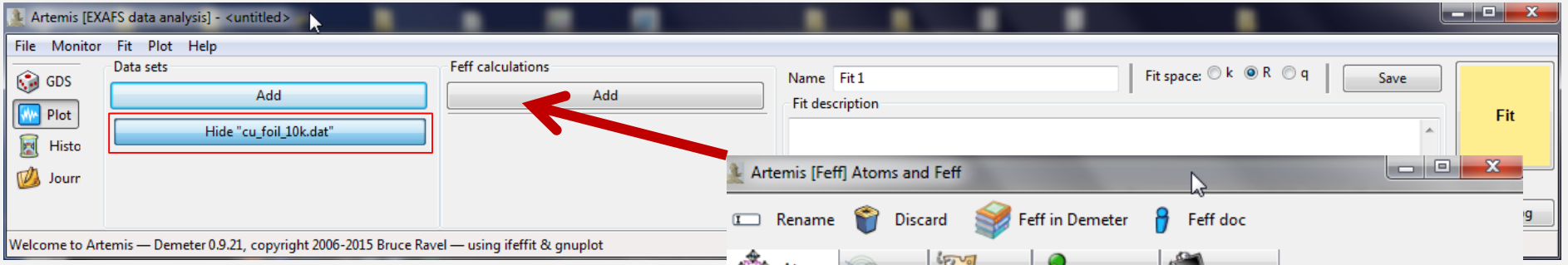
Start fit

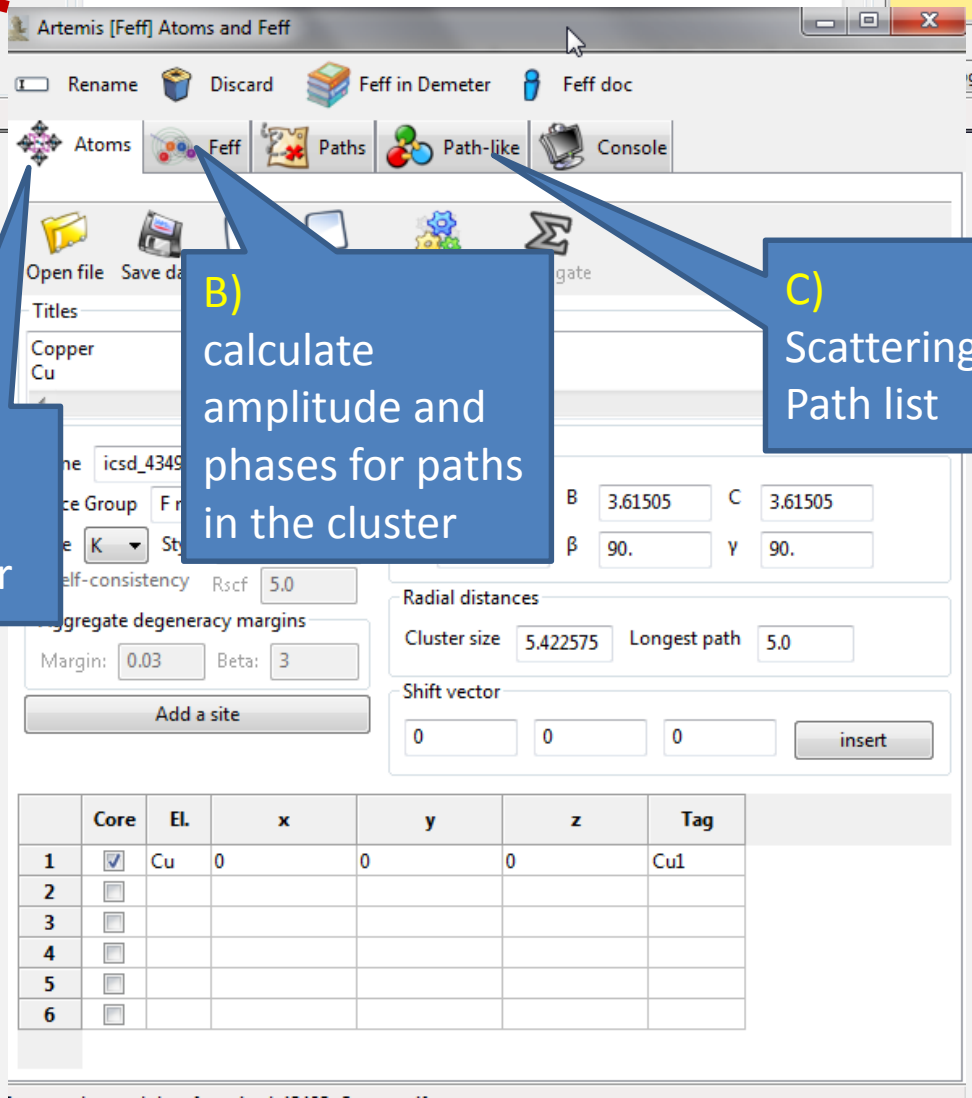
1: add χ(k) or Athena project

Inport the XAFS data from the Athena Project



2: add model structure (cif or simple pair)



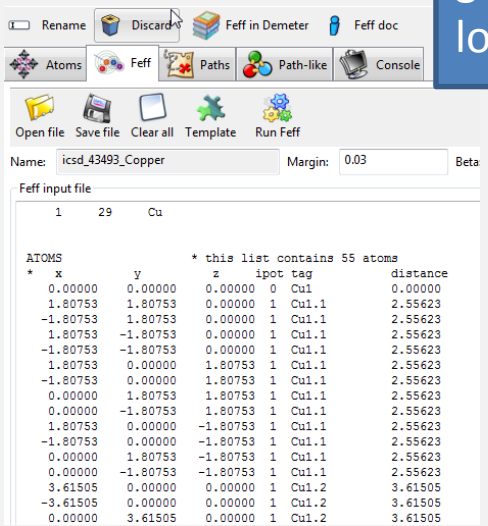


I. Run Atoms
II. check paths
III. Run Feff
IV. look at the path list

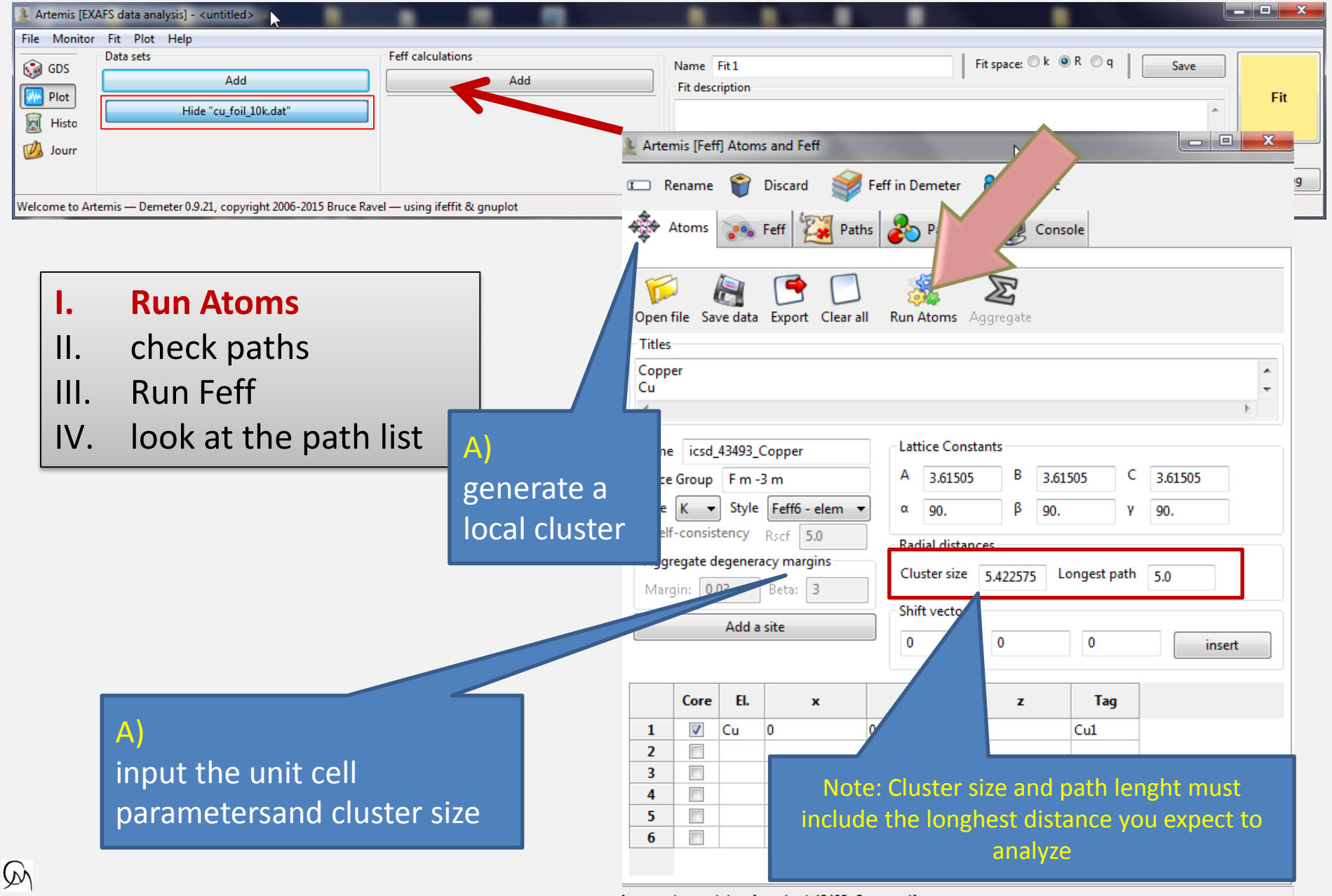
A) generate a local cluster

B) calculate amplitude and phases for paths in the cluster

C) Scattering Path list



2: add model structure (cif or simple pair)



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

2: add model structure (cif or simple pair)

Artemis [EXAFS data analysis] - <untitled>

File Monitor Fit Plot Help

GDS Plot Histo Jourr

Data sets: Add | Hide "cu_foil_10k.dat"

Feff calculations: Add

Welcome to Artemis — Demeter 0.9.21, copyright 2006-2015 Bruce Ravel — using ifeffit & gnuplot

Rename | Discard | Feff in Demeter | Feff doc

Atoms | Feff | Paths | Path-like | Console

Open file | Save file | Clear all | Template | Run Feff

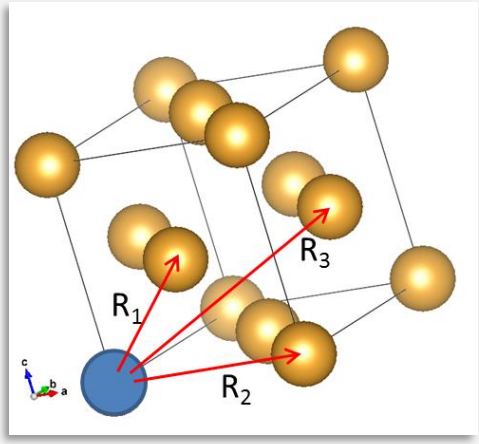
Name: icsd_43493_Copper Margin: 0.03 Beta

Feff input file

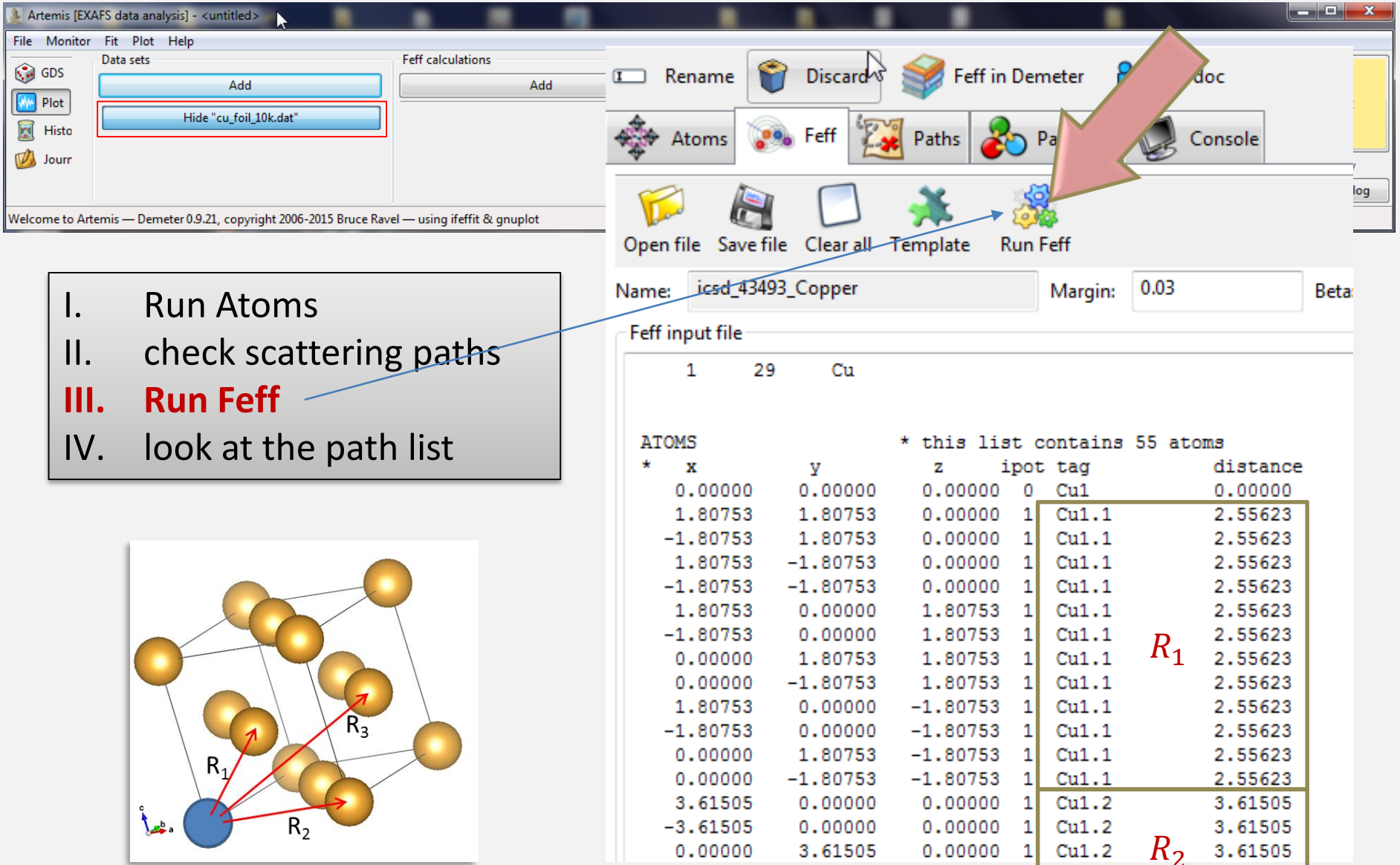
```
     1      29      Cu


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
```

R_1 R_2

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

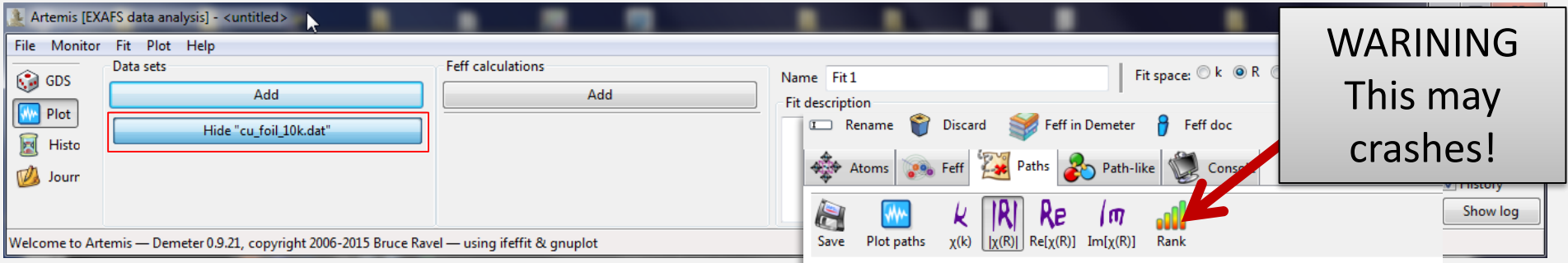


2: add model structure (cif or simple pair)



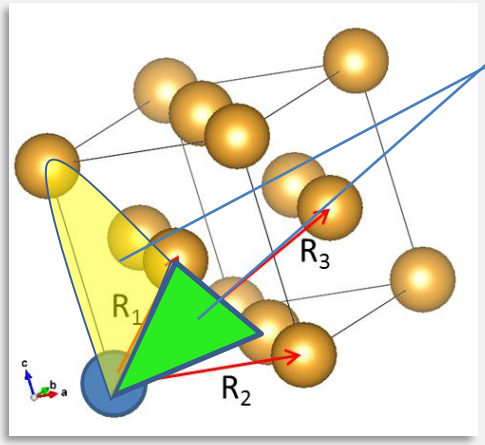
I. Run Atoms
II. check scattering paths
III. Run Feff
IV. look at the path list

2: add model structure (cif or simple pair)



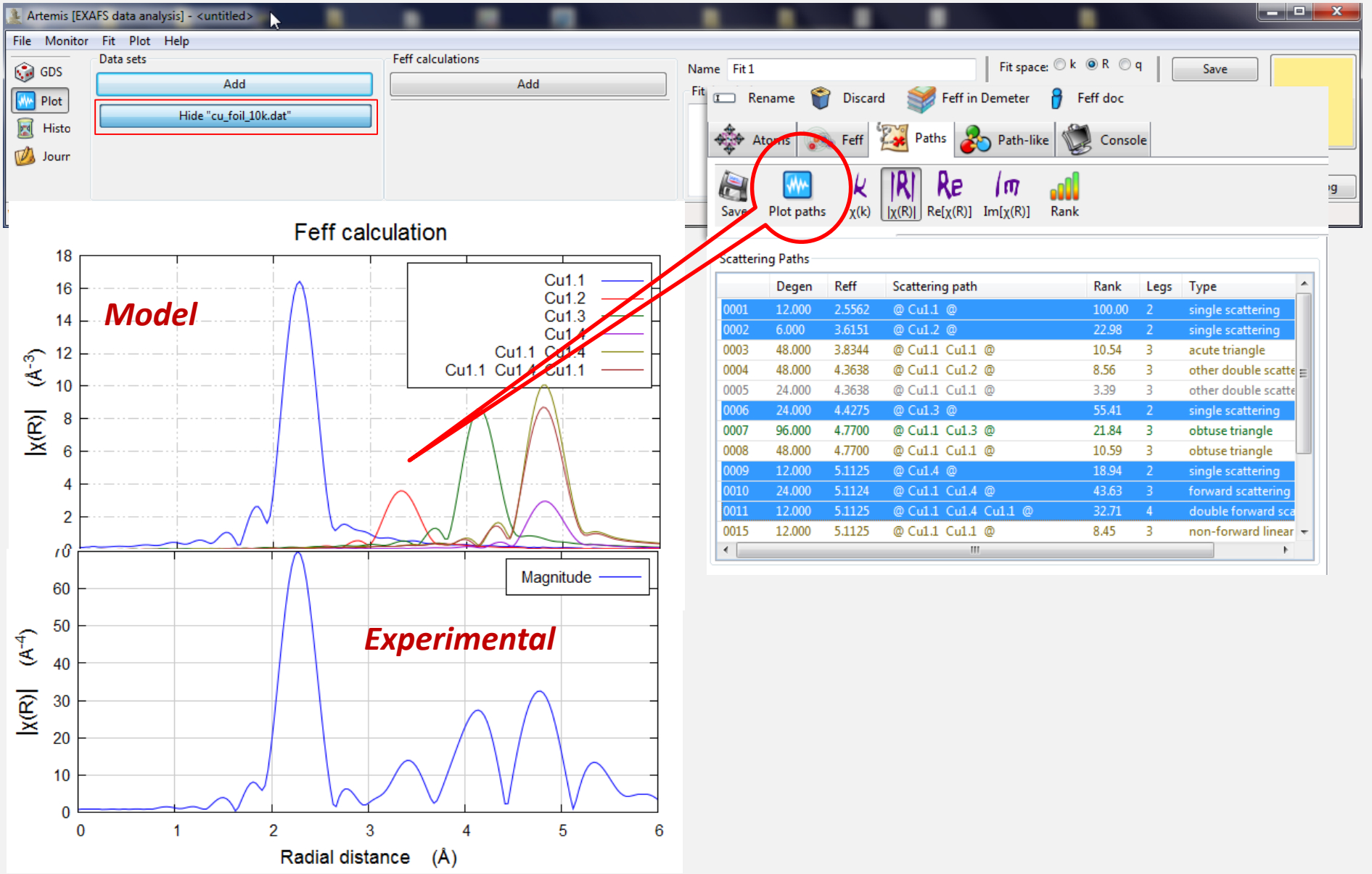
WARINING
This may crashes!

Recognize path relevance looking at the Rank &/or at the plots

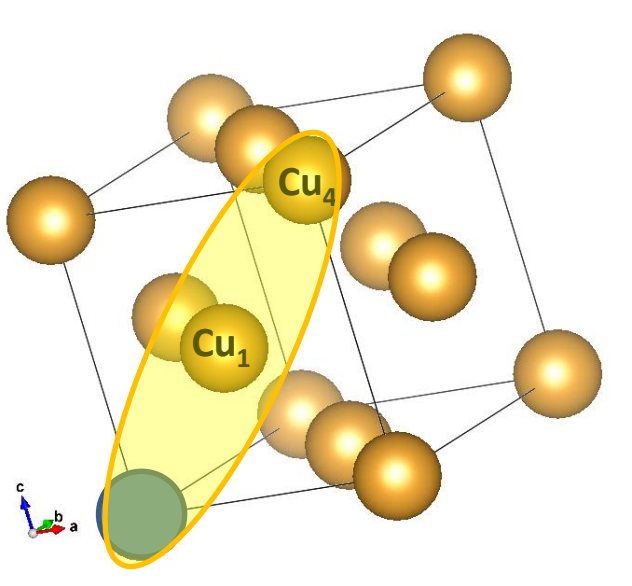


Path geometry

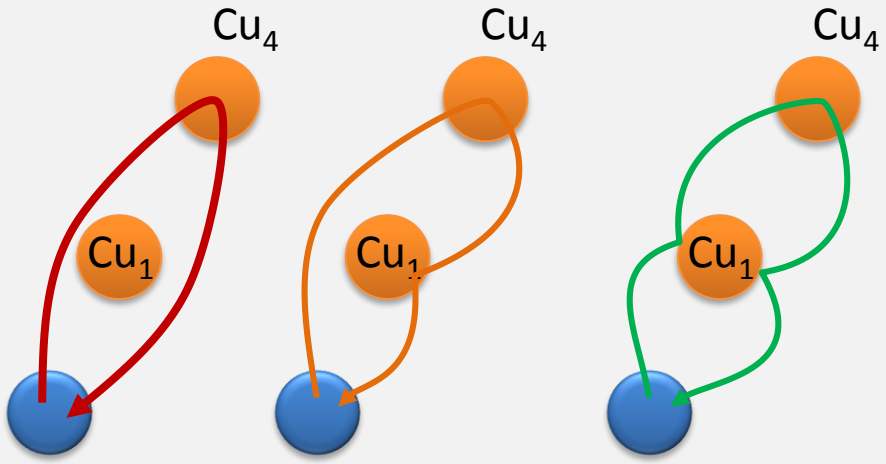
2: add model structure (cif or simple pair)



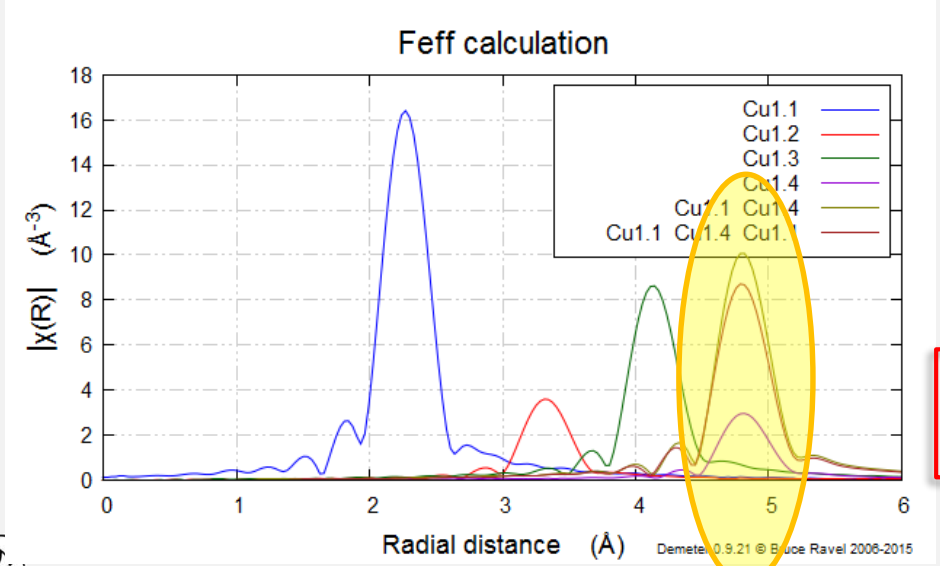
2: Check paths by relevance: **Multiple scattering**



Focousing effect enhances the ultiple scattering from aligned configurations



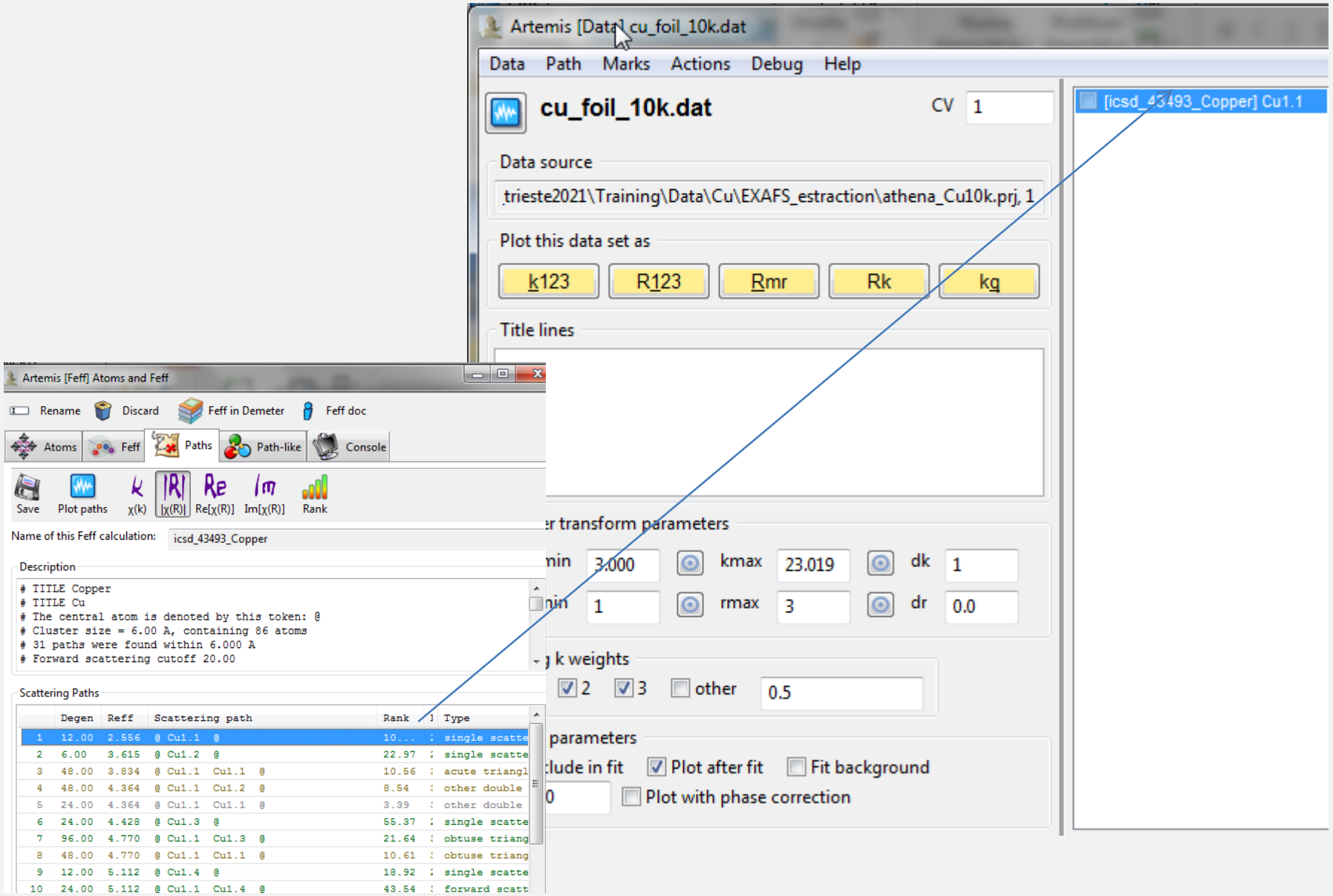
Cu1.4 Cu1.1-Cu1.4 Cu1.1-Cu1.4-Cu1.1



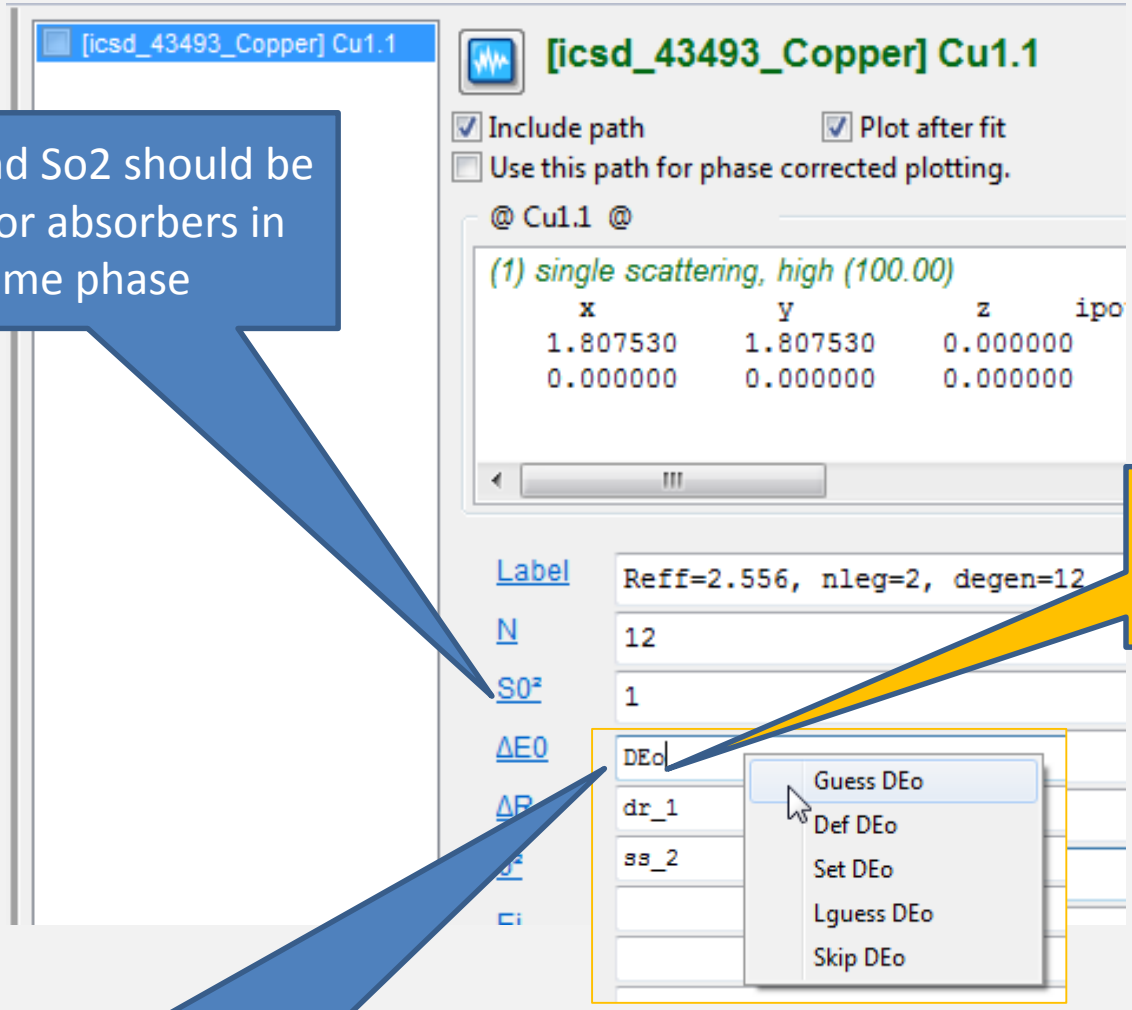
Scattering Paths

	Degen	Reff	Scattering path	Rank	Legs	Type
0001	12.000	2.5562	@ Cu1.1 @	100.00	2	single scattering
0002	6.000	3.6151	@ Cu1.2 @	22.98	2	single scattering
0003	48.000	3.8344	@ Cu1.1 Cu1.1 @	10.54	3	acute triangle
0004	48.000	4.3638	@ Cu1.1 Cu1.2 @	8.56	3	other double scatte
0005	24.000	4.3638	@ Cu1.1 Cu1.1 @	3.39	3	other double scatte
0006	24.000	4.4275	@ Cu1.3 @	55.41	2	single scattering
0007	96.000	4.7700	@ Cu1.1 Cu1.3 @	21.84	3	obtuse triangle
0008	48.000	4.7700	@ Cu1.1 Cu1.1 @	10.59	3	obtuse triangle
0009	12.000	5.1125	@ Cu1.4 @	18.94	2	single scattering
0010	24.000	5.1124	@ Cu1.1 Cu1.4 @	43.63	3	forward scattering
0011	12.000	5.1125	@ Cu1.1 Cu1.4 Cu1.1 @	32.71	4	double forward sca
0015	12.000	5.1125	@ Cu1.1 Cu1.1 @	8.45	3	non-forward linear

2: drag and drop relevant paths to the data window



2: Define parameters

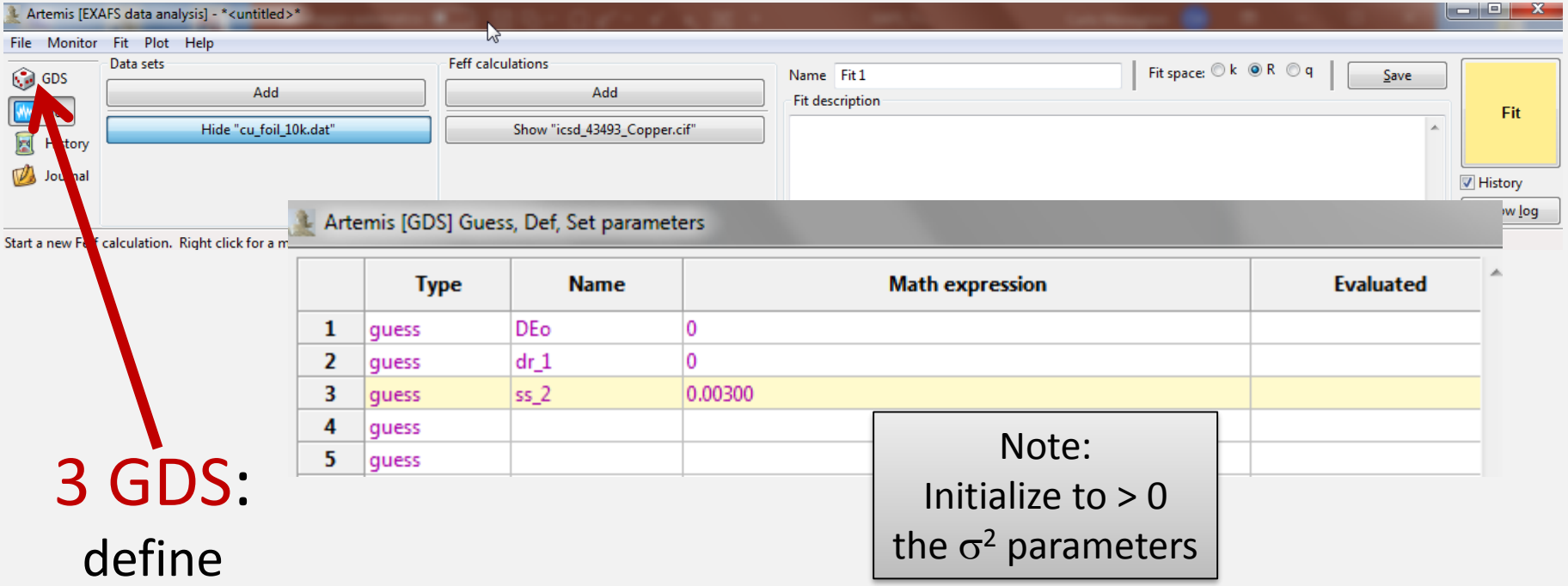


NOTE: DE and So2 should be the same for absorbers in the same phase

right click

You must provide a name to each parameter you want refine

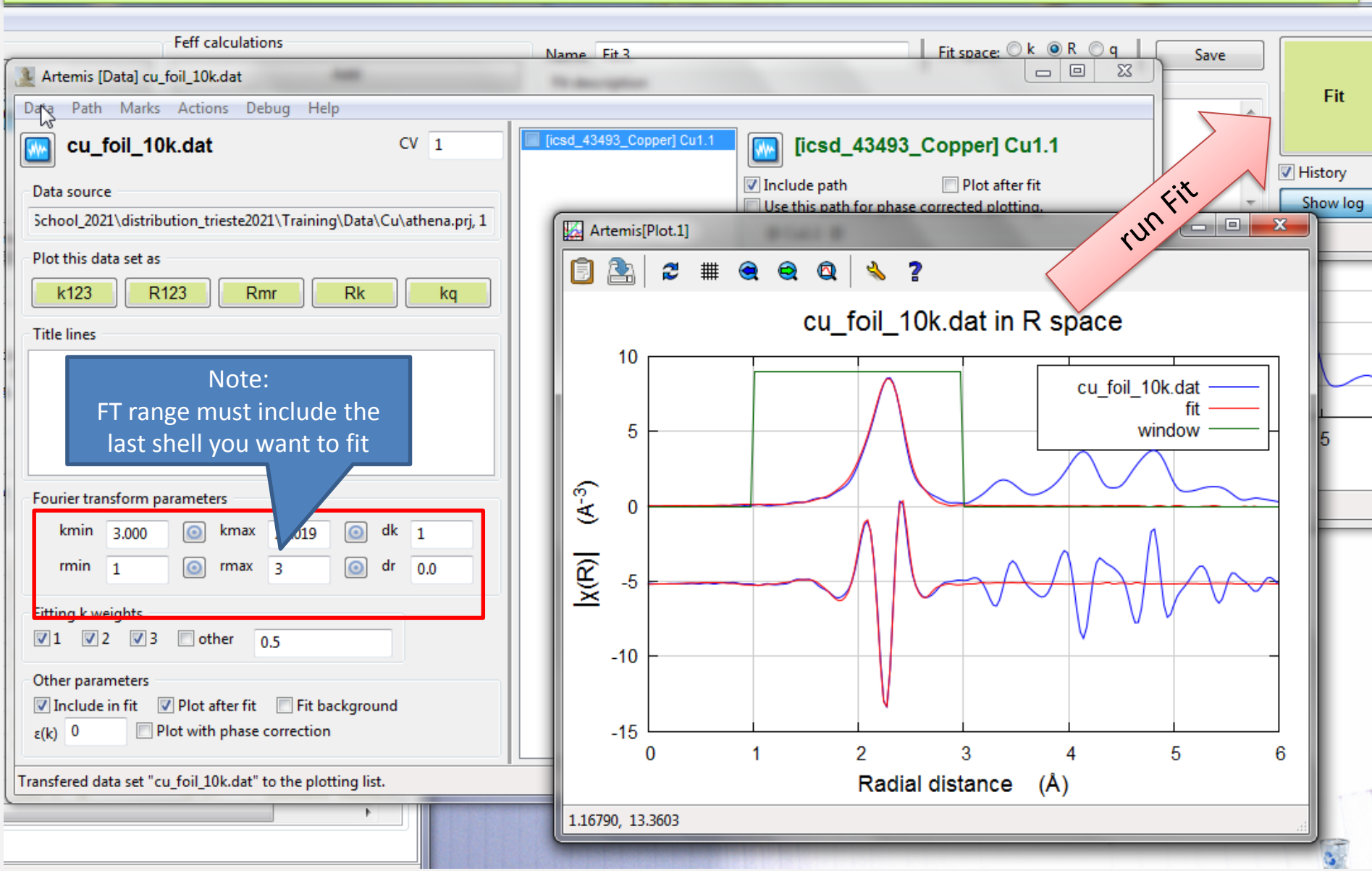
3: Define the refinement parameters



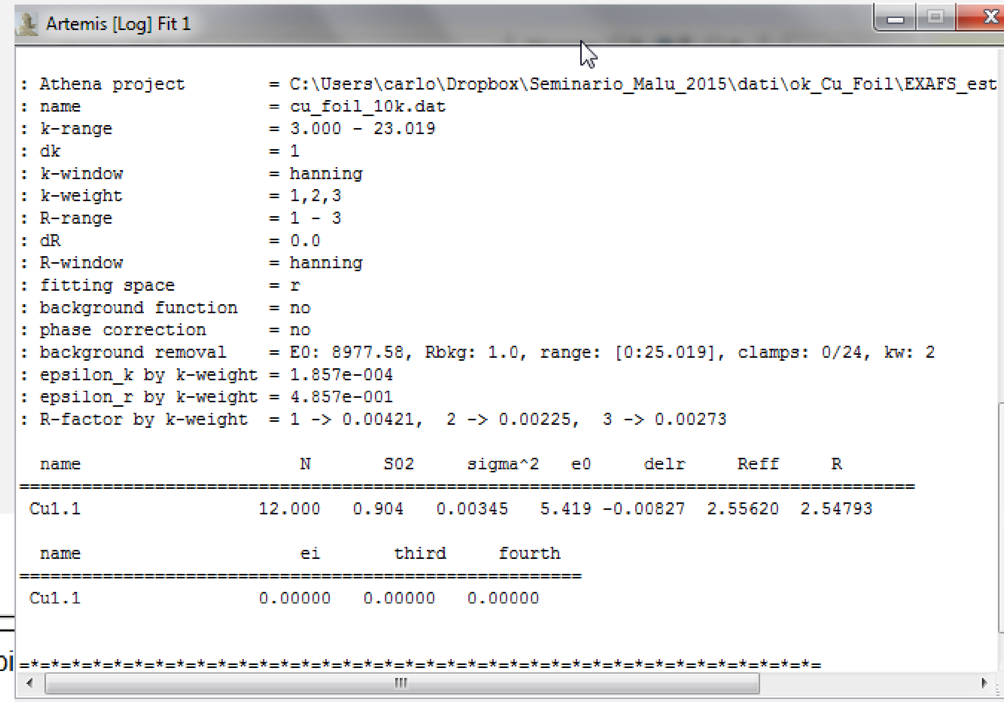
3 GDS: define **refinement prameters**

Note:
Initialize to > 0
the σ^2 parameters

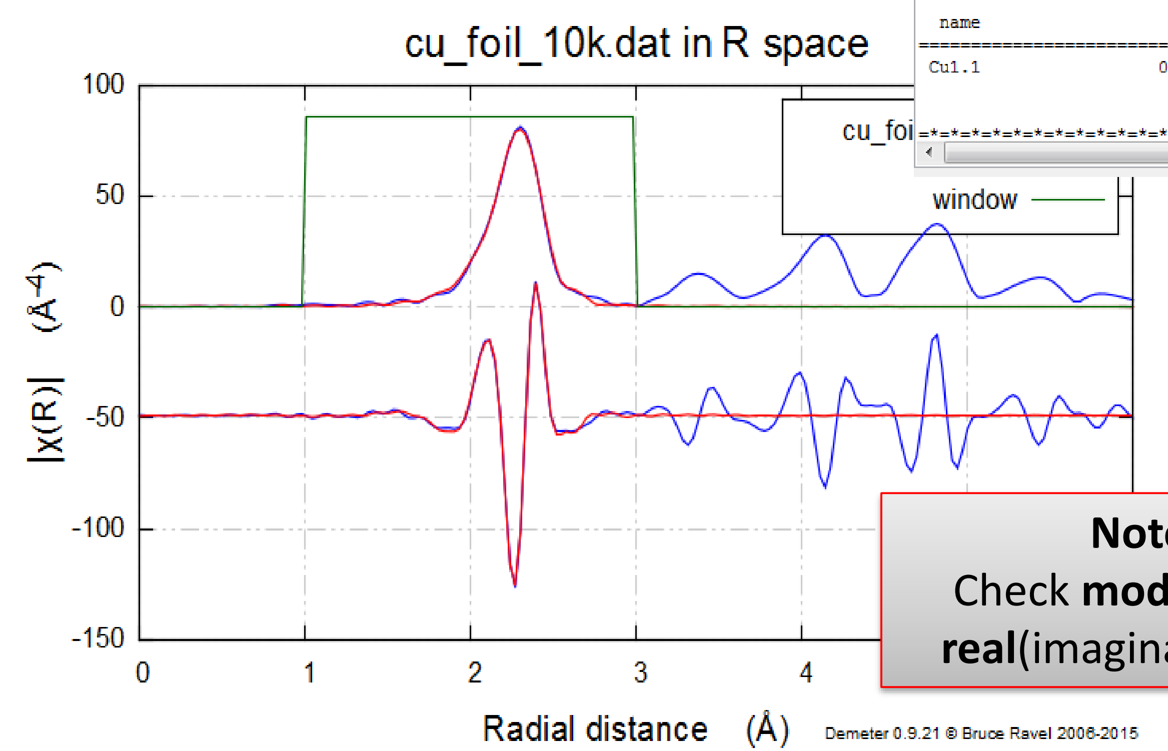
3: Best fit


Feff calculations
Name Fit 3
Fit space: k R q
Save
Fit
History
Show log
Artemis [Data] cu_foil_10k.dat
Data Path Marks Actions Debug Help
cu_foil_10k.dat
CV 1
Data source
School_2021\distribution_trieste2021\Training\Data\Cu\athena.prj, 1
Plot this data set as
k123 R123 Rmr Rk kq
Title lines
Note:
FT range must include the last shell you want to fit
Fourier transform parameters
kmin 3.000
kmax
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
Transfered data set "cu_foil_10k.dat" to the plotting list.
[icsd_43493_Copper] Cu1.1
[icsd_43493_Copper] Cu1.1
Include path
Plot after fit
Use this path for phase corrected plotting
run Fit
Artemis[Plot.1]
cu_foil_10k.dat in R space
cu_foil_10k.dat
fit
window
|χ(R)| (Å⁻³)
Radial distance (Å)
1.16790, 13.3603

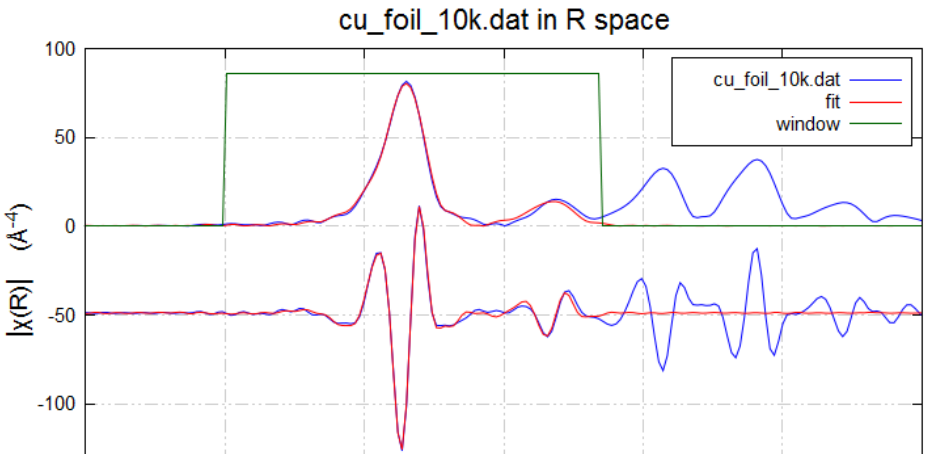
4: FIT

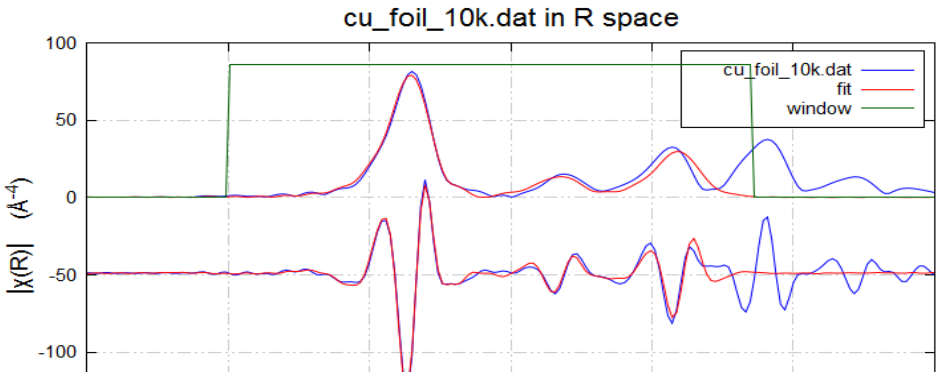


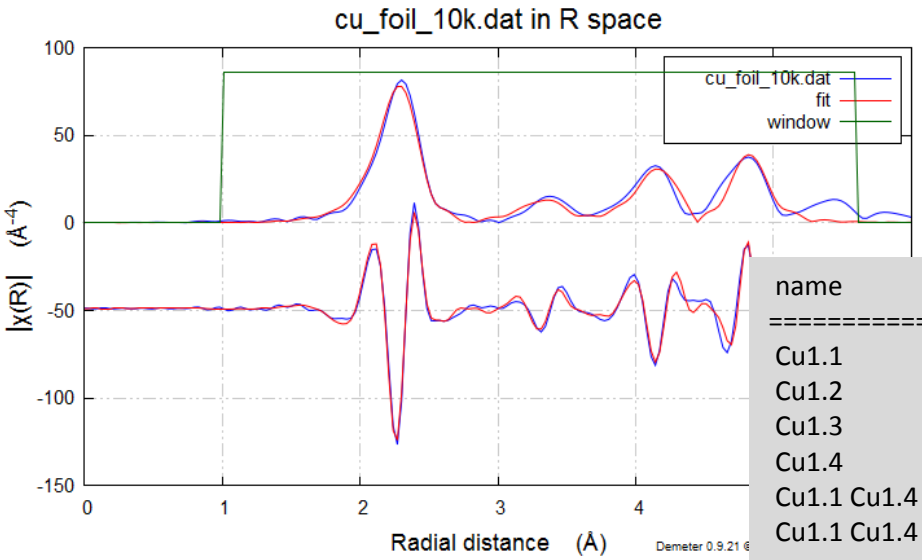
```
Artemis [Log] Fit 1

: Athena project        = C:\Users\carlo\Dropbox\Seminario_Malu_2015\dati\ok_Cu_Foil\EXAFS_est
: name                  = cu_foil_10k.dat
: k-range               = 3.000 - 23.019
: dk                    = 1
: k-window              = hanning
: k-weight              = 1,2,3
: R-range               = 1 - 3
: dR                    = 0.0
: R-window              = hanning
: fitting space         = r
: background function   = no
: phase correction      = no
: background removal    = E0: 8977.58, Rbkg: 1.0, range: [0:25.019], clamps: 0/24, kw: 2
: epsilon_k by k-weight = 1.857e-004
: epsilon_r by k-weight = 4.857e-001
: R-factor by k-weight  = 1 -> 0.00421,  2 -> 0.00225,  3 -> 0.00273

 name                        N       S02      sigma^2    e0      delr      Reff      R
=============================================================================================
 Cu1.1                   12.000    0.904    0.00345    5.419 -0.00827   2.55620   2.54793

 name                        ei        third       fourth
===========================================================
 Cu1.1                   0.00000    0.00000    0.00000

=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=*=
```



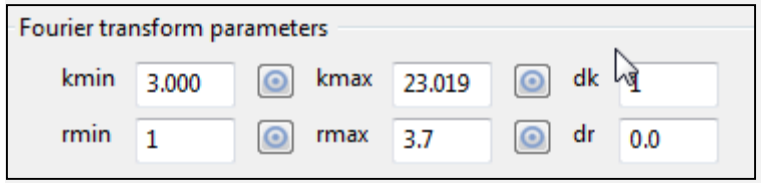
Note:
Check **modulus** and **real**(imaginary) parts







4: FIT, extend the analysis to further shells



Run fit starting with first shell then **add progressively further** contributions

Note:
extend your fit but: a large enough windows must be defined in the Athena project

name	N	S02	sigma^2	e0	delr	Reff	R
Cu1.1	12.000	0.980	0.00388	4.001	-0.01367	2.55620	2.54253
Cu1.2	6.000	0.980	0.00513	4.001	-0.02943	3.61510	3.58567
Cu1.3	24.000	0.980	0.00514	4.001	0.00381	4.42750	4.43131
Cu1.4	12.000	0.980	0.00092	4.001	0.00862	5.11250	5.12112
Cu1.1 Cu1.4	24.000	0.980	0.00271	4.001	0.00862	5.11250	5.12112
Cu1.1 Cu1.4 Cu1.1	12.000	0.980	0.00322	4.001	0.00862	5.11250	5.12112

3: Define parameters

Artemis [EXAFS data analysis] - <untitled>

File Monitor Fit Plot Help

GDS Plot Histo Journ

Data sets: Add

Feff calculations: Add

Name: Fit 1 | Fit space: k R q | Save

Fit description

Fit

History

Show log

run Fit

Artemis [Data] cu_foil_10k.dat

Data Path Marks Actions Debug Help

cu_foil_10k.dat CV 1

Data source

o_Malu_2015\dati\ok_Cu_Foil\EXAFS_estraction\athena_Cu10k.prj, 1

Plot this data set as

k123 R123 Rmr Rk kq

Title lines

Fourier transform parameters

kmin 3.000 kmax 23.019 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

[icsd_434] Cu1.1

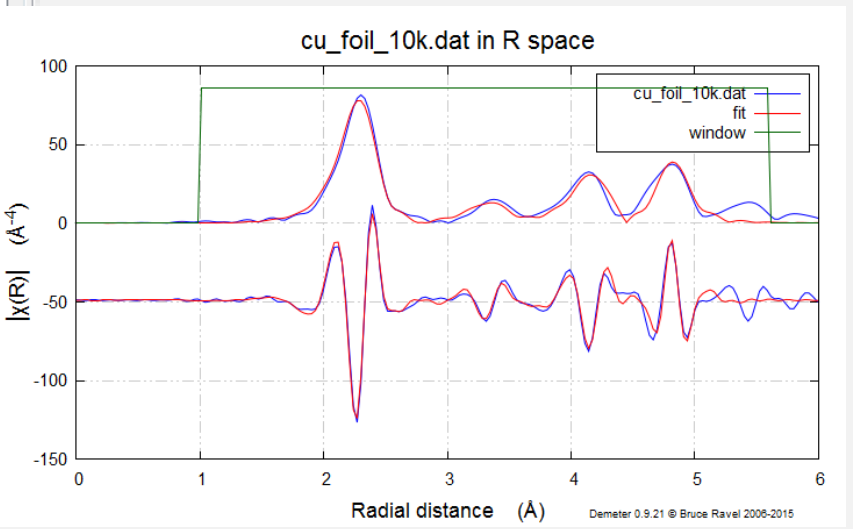
[icsd_434] Cu1.2

[icsd_434] Cu1.3

[icsd_434] Cu1.4

[icsd_434] Cu1.1 Cu1.4

[icsd_434] Cu1.1 Cu1.4 Cu1.1



4: Check best fit log file

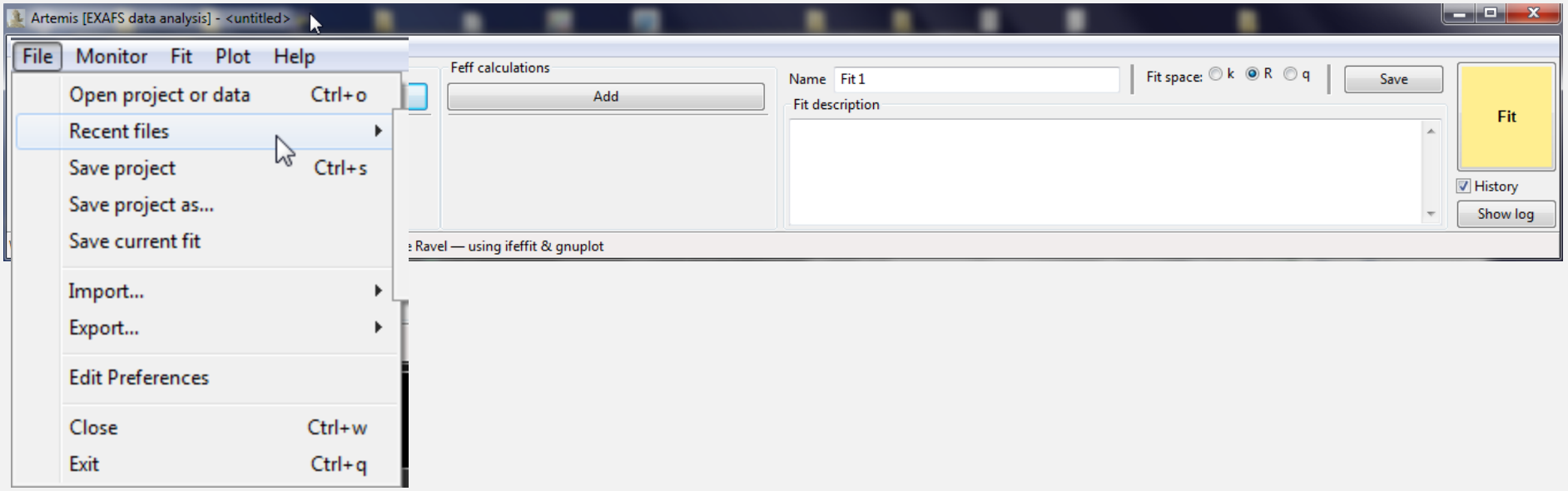
Note:
Keep correlations among the parameters low, maybe add physical meaning constraints.
Far away shell parameters are generally less accurate, use them with care

Correlations between variables:

ss_42 & ss_4	**--> 0.8812**
ss_1 & so2	**--> 0.8229**
ss_43 & ss_42	**--> 0.8137**
ss_43 & ss_4	**--> 0.8062**
dr_1 & de_0	--> 0.7729
ss_43 & dr_4	--> 0.7515
dr_3 & de_0	--> 0.6824
dr_3 & dr_1	--> 0.5290
ss_3 & so2	--> 0.5153
ss_42 & so2	--> 0.4289
ss_3 & ss_1	--> 0.4239

All other correlations below 0.4

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...

Your Exercises

Analyze the Fe structure