XAFS
Experimental &data Analysis

1. XAFS data analysis software
2. From XAS to XAFS: how to deal with the data
3. **Training: EXAFS data refinement**
4. Training: Linear combination analysis of XANES

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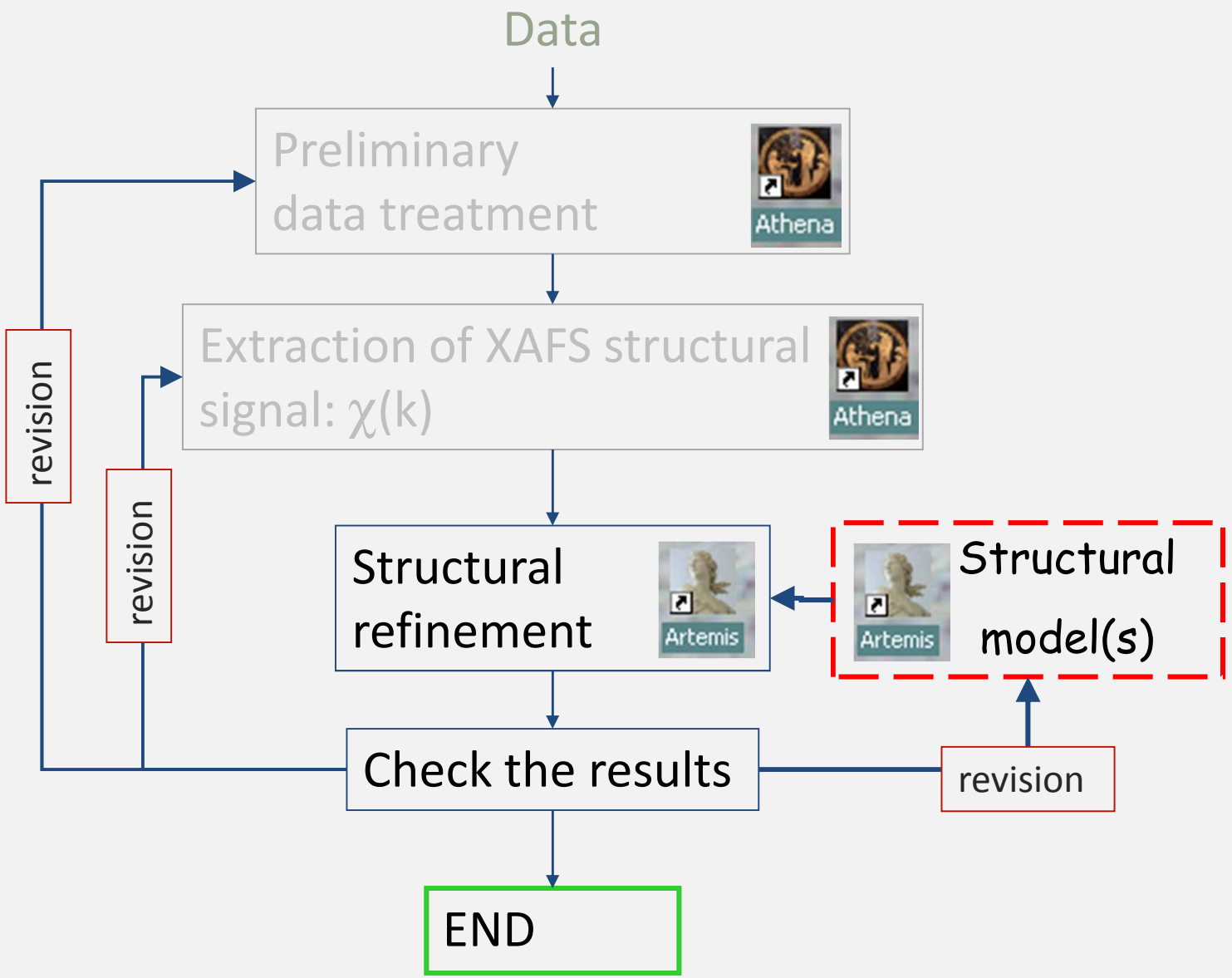
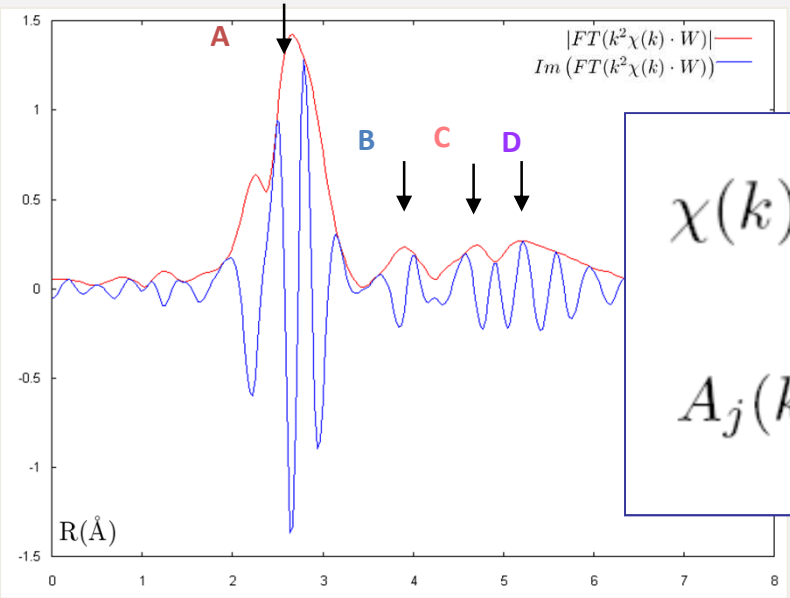
Data Refinement



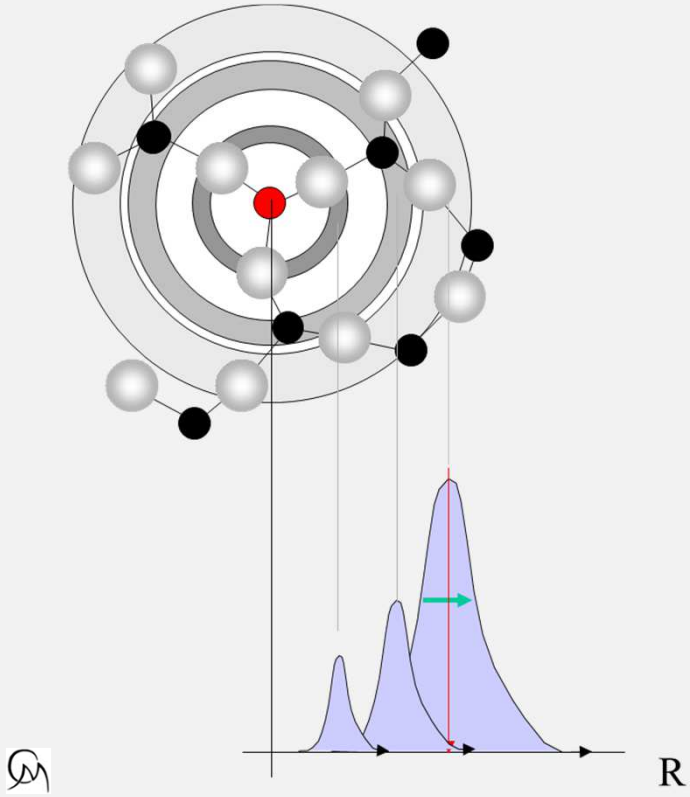
The EXAFS standard formula



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

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

$$k = \sqrt{\frac{2m}{\hbar}(E - (Eo + \Delta E))}$$



parameters

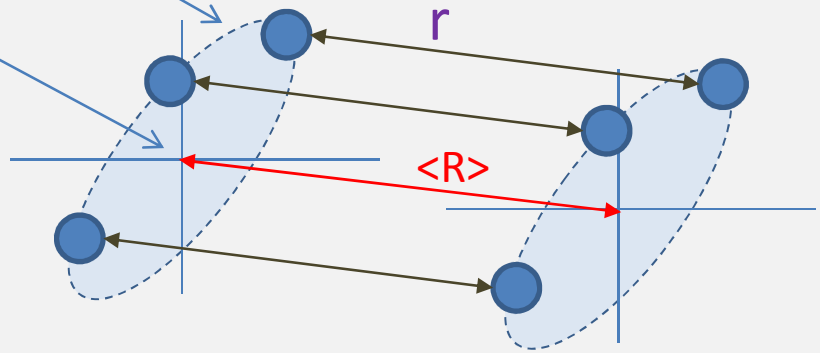
$f_j(r,k)$ = photo-electron scattering amplitude
$\psi_j(r,k)$ = photo-electron scattering phase
λ = photo-electron mean free path
S_o^2 = many body losses
ΔE = energy shift

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)

MSRD and σ^2

Thermal ellipsoids

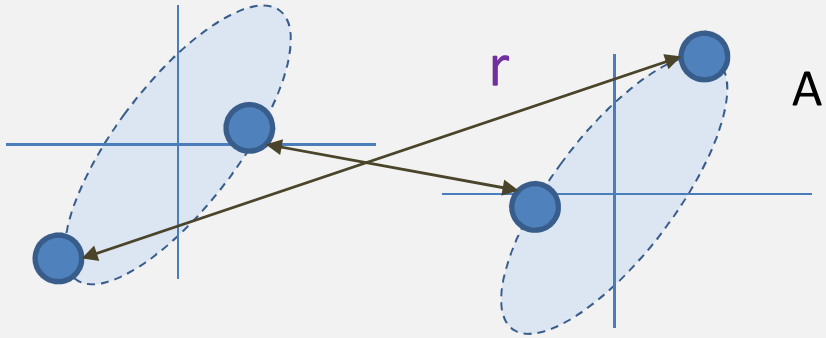
Average position (XRD lattice)



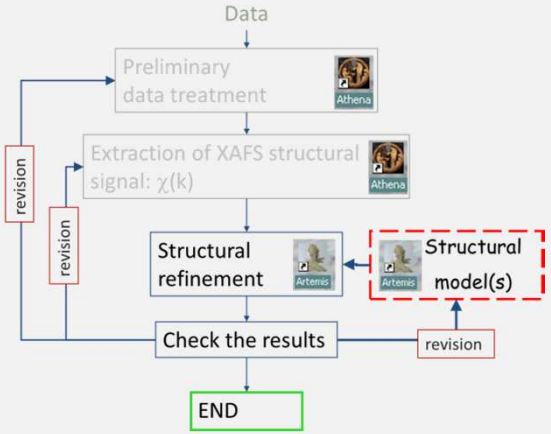
<R> = Average distance (XRD)

r = XAFS instantaneous distance

Correlated displacement:
MSRD < U_{XRD}



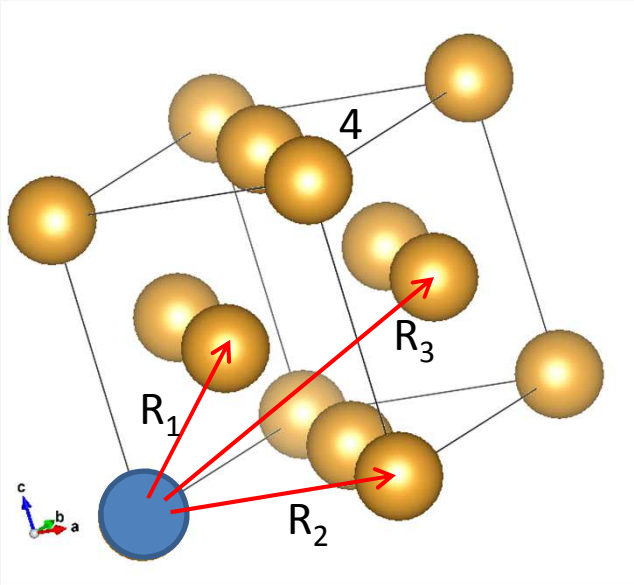
Anti-correlated displacement:
MSRD > U_{XRD}



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



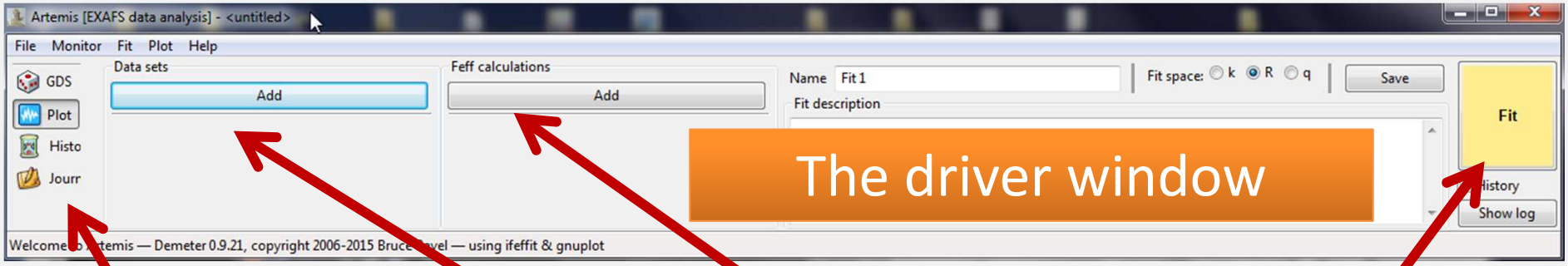
icsd_43493_Copper.cif

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!



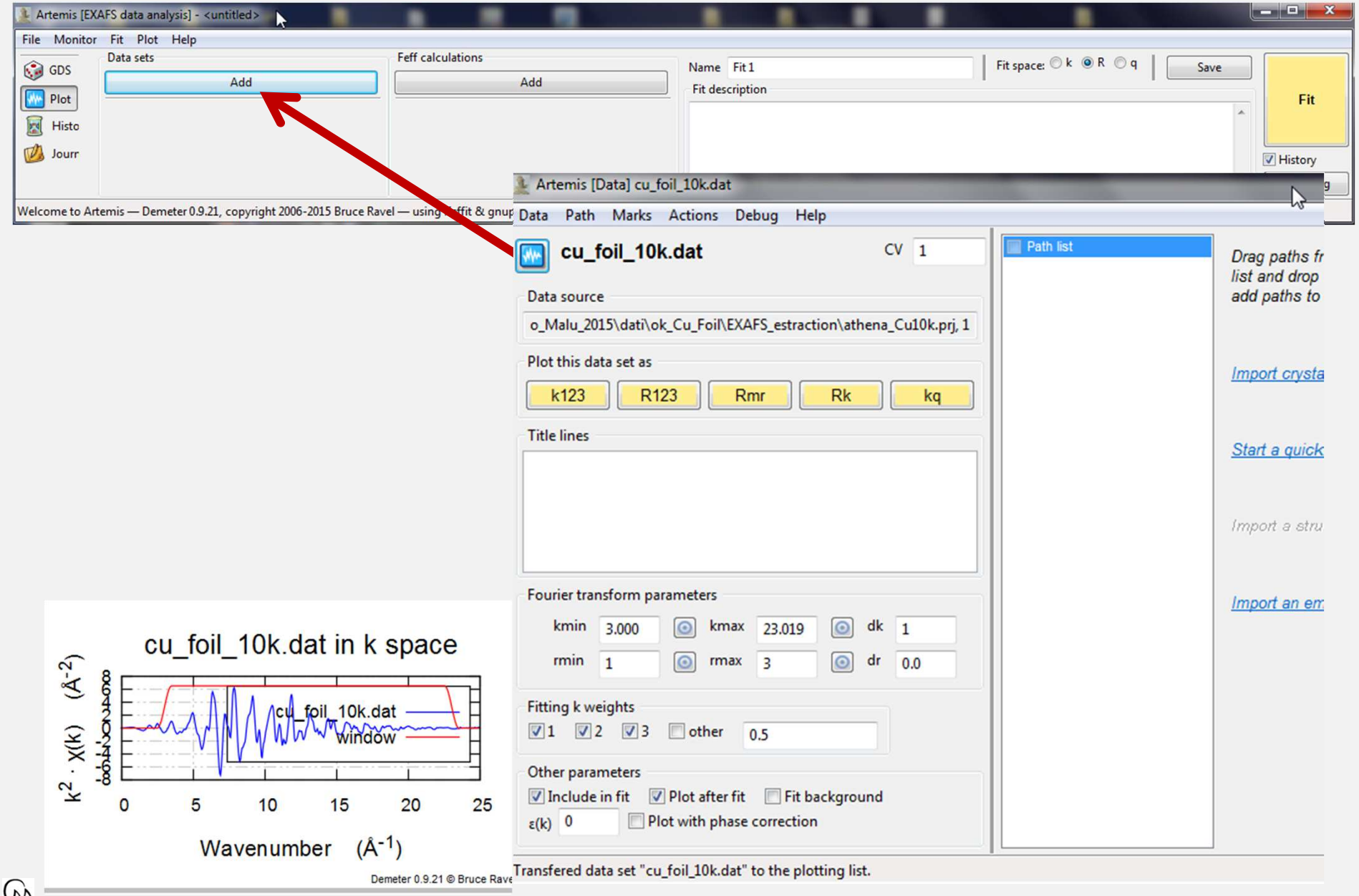
1
add EXAFS
χ(k) or
athena project

2
add a
Structure
.cif or Feff file

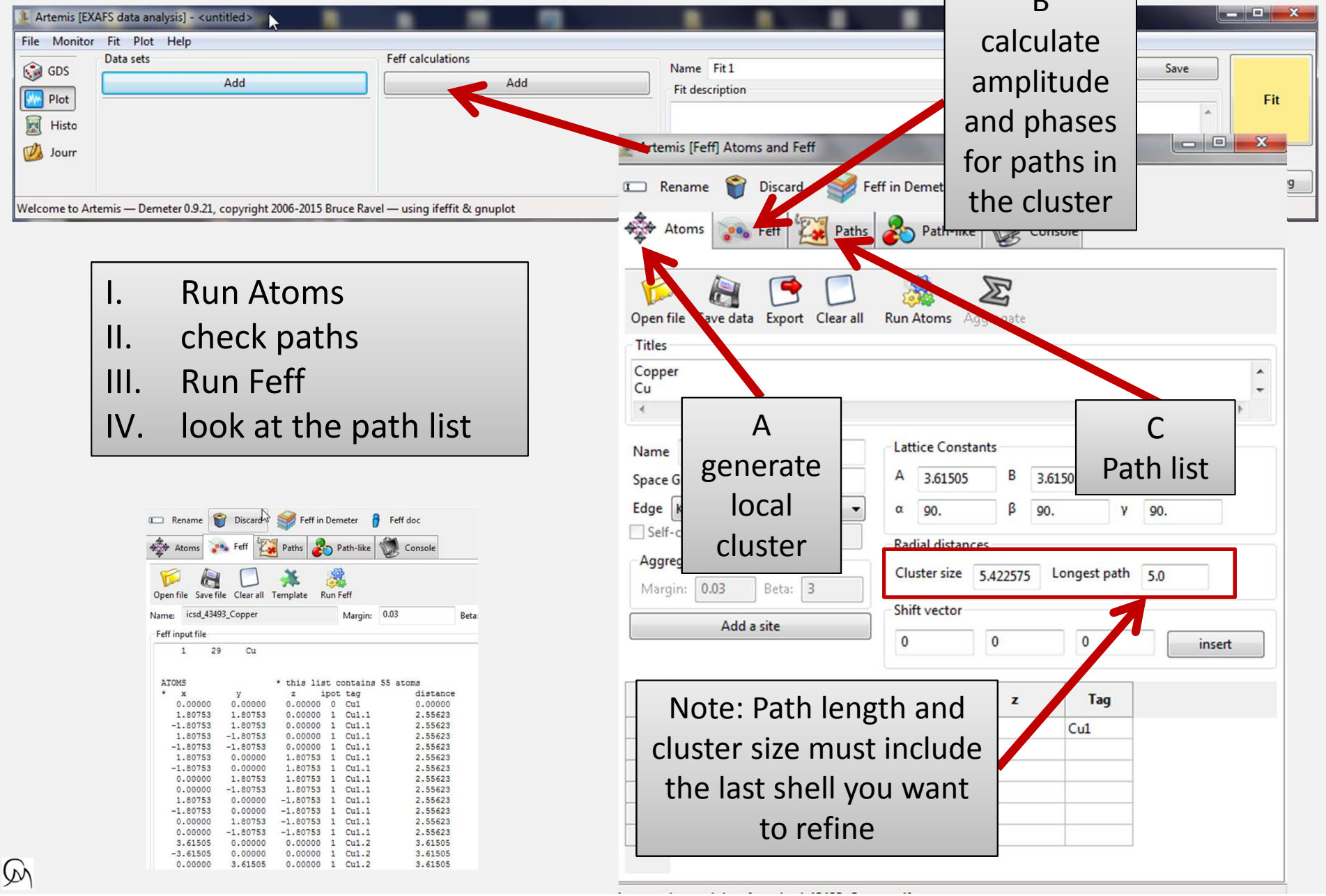
3
select
refinement
pram., plot,
etc...

4
Start fit

1: add χ(k) or 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

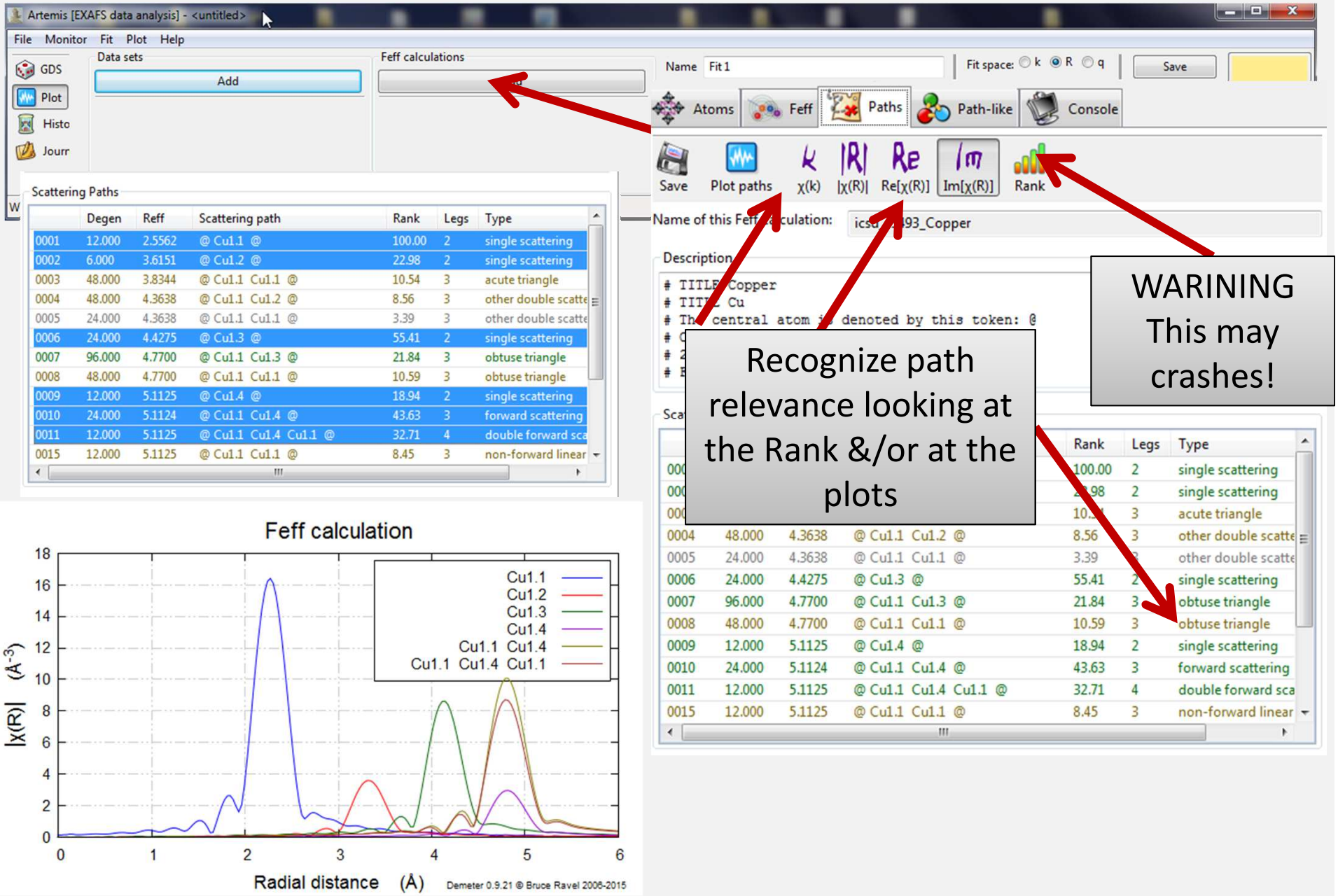
B calculate amplitude and phases for paths in the cluster

A generate local cluster

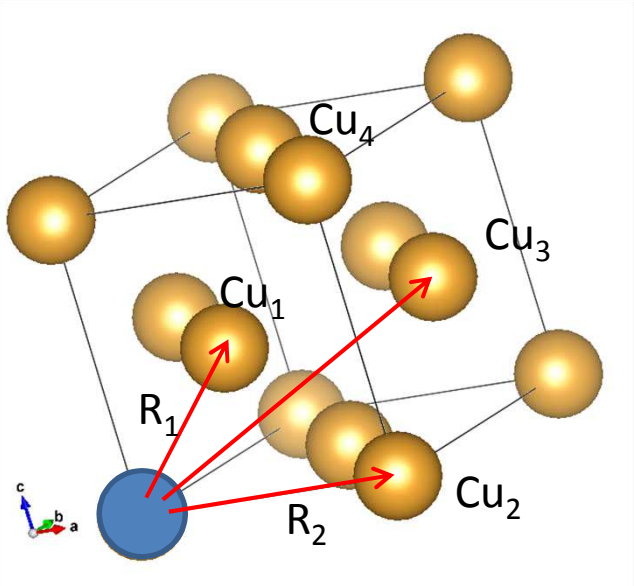
C Path list

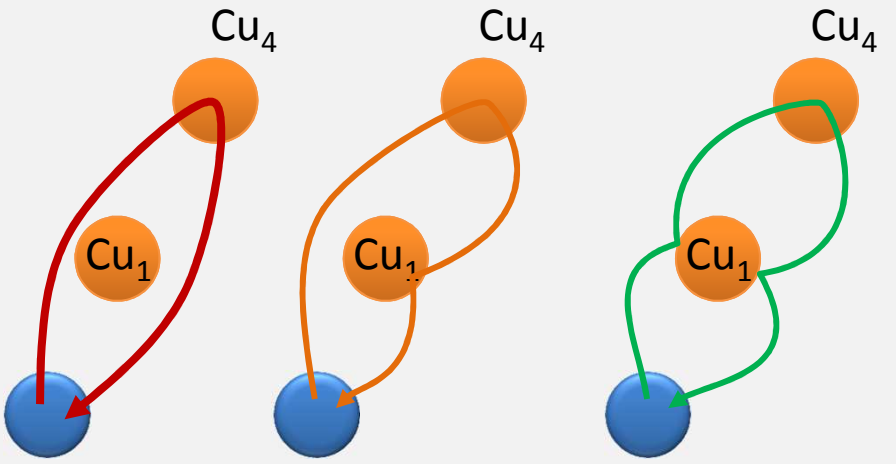
Note: Path length and cluster size must include the last shell you want to refine

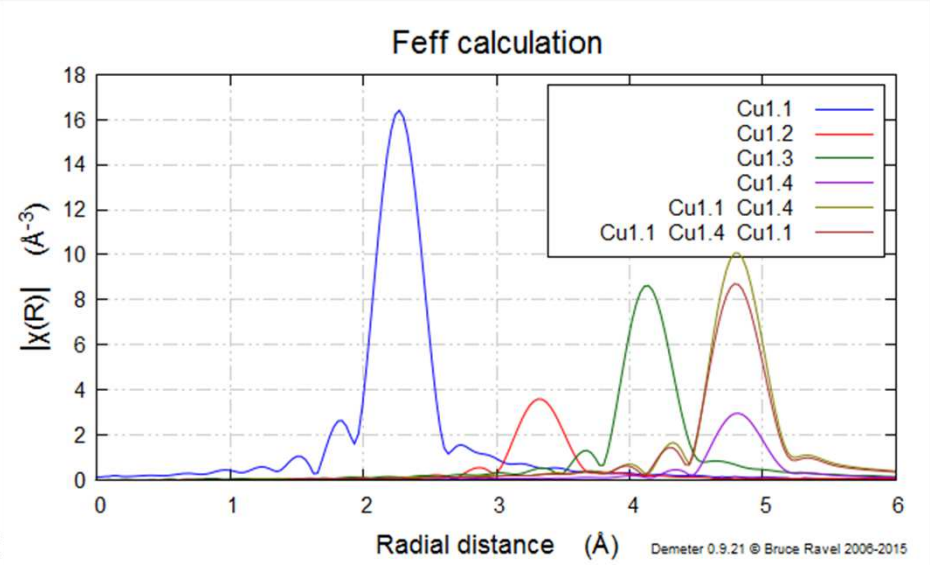
2: add model structure (cif or simple pair)



2: Check paths by relevance



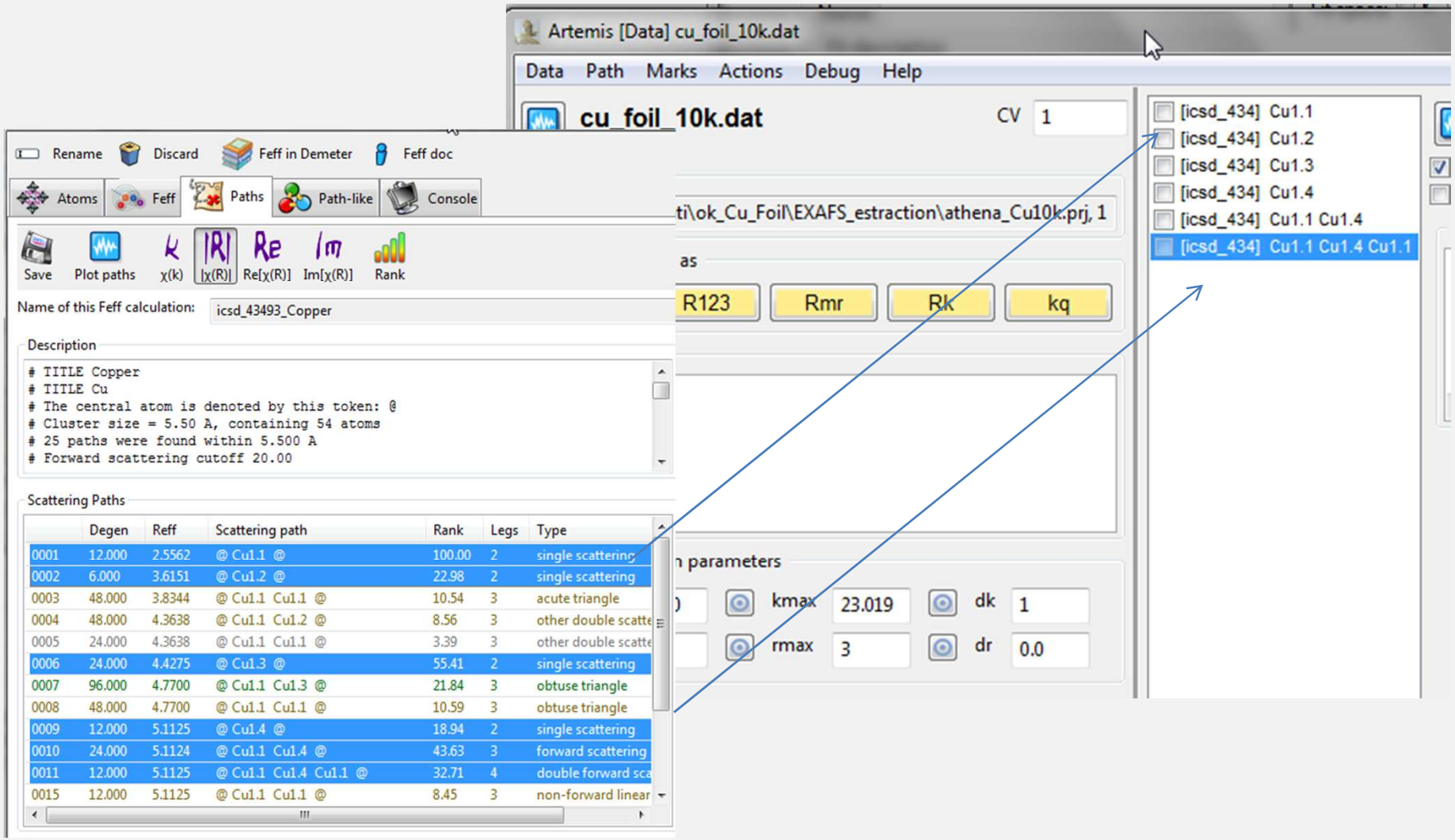




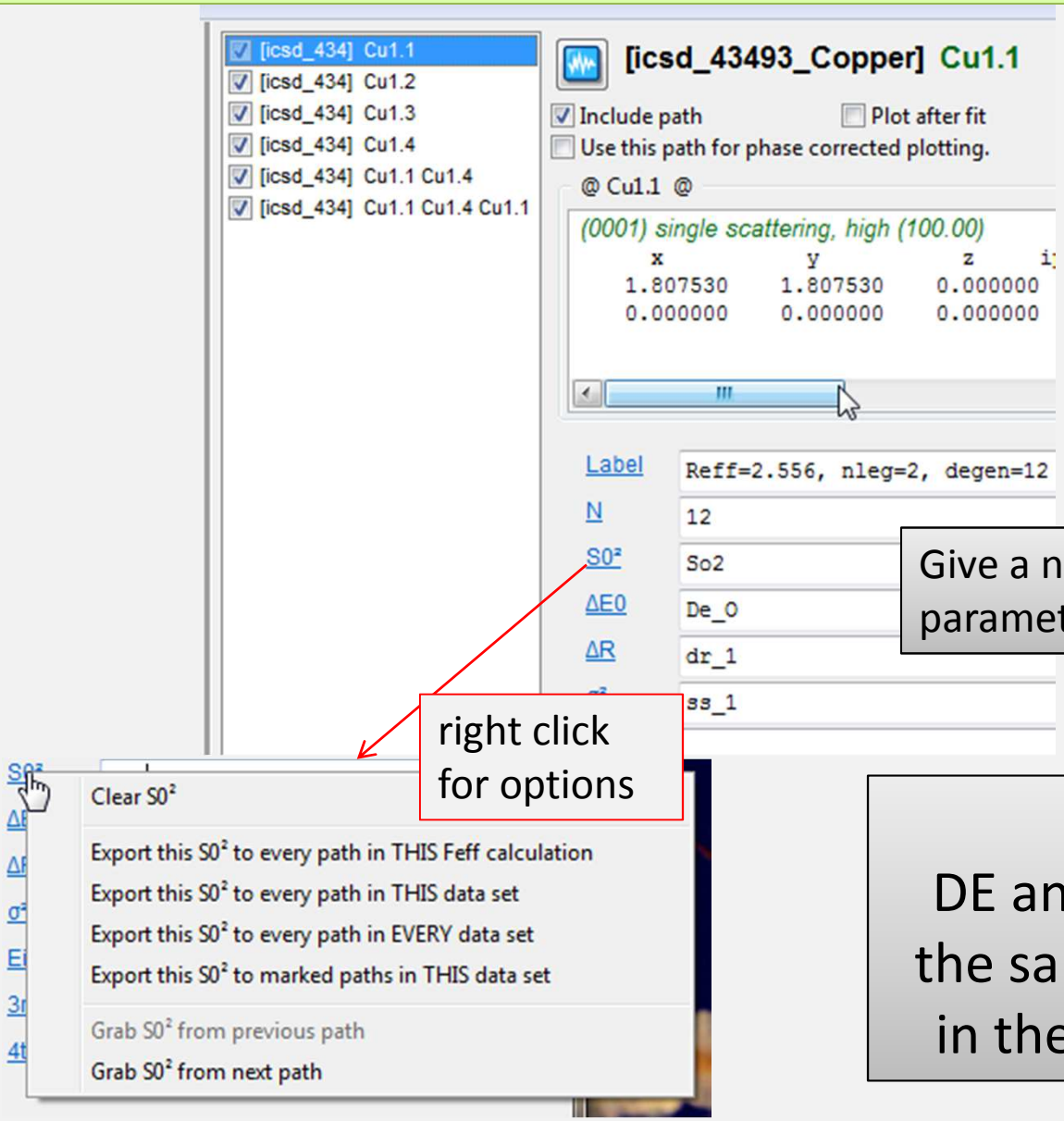
Scattering Paths

	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

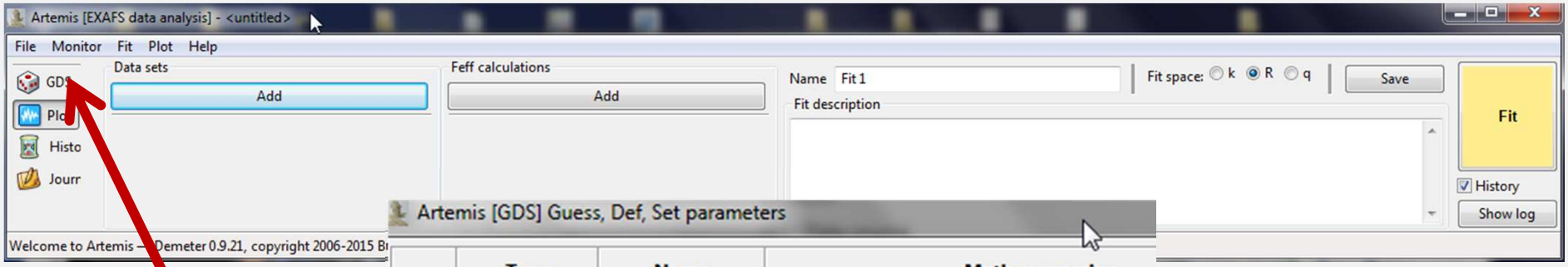


Give a name to each parameter to adjust

right click for options

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

3: Define parameters



3

select **refinement pram.**, plot, etc...
USE GDS button

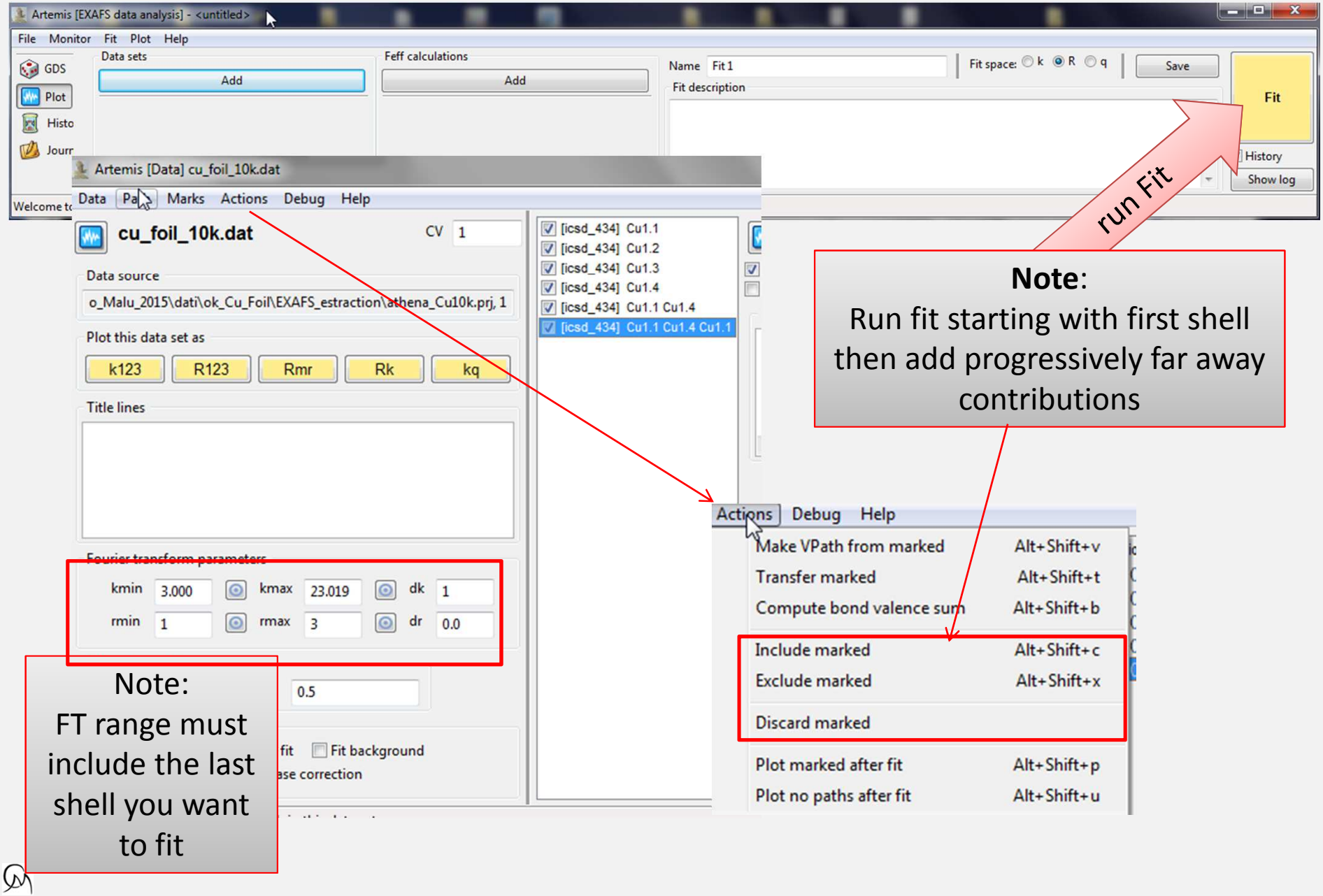
Artemis [GDS] Guess, Def, Set parameters

	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 σ^2 parameters

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

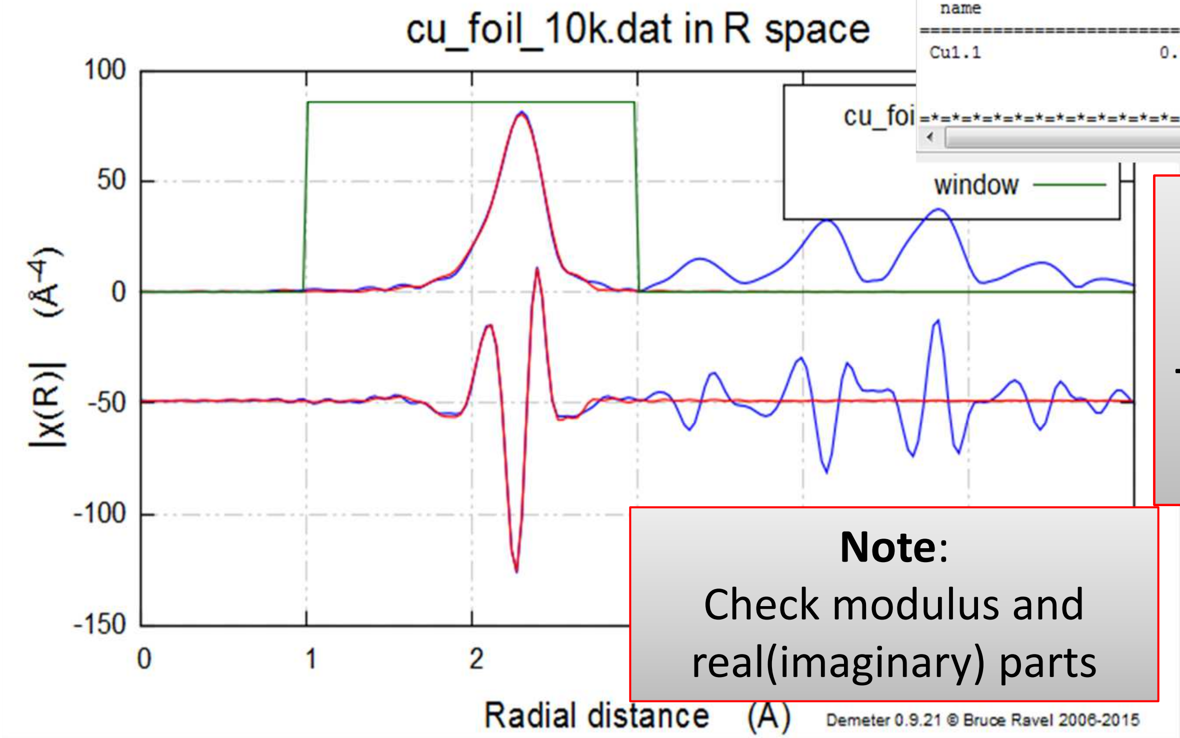
3: Define parameters



4: FIT

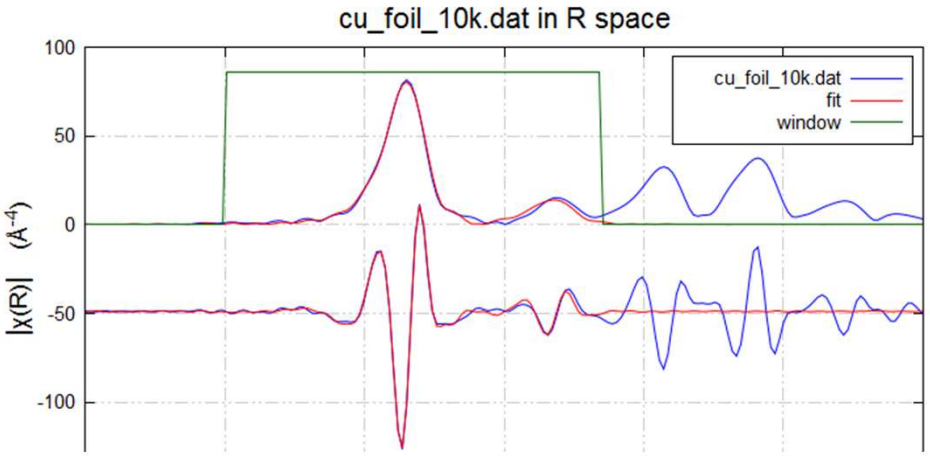
Artemis [Log] Fit 1

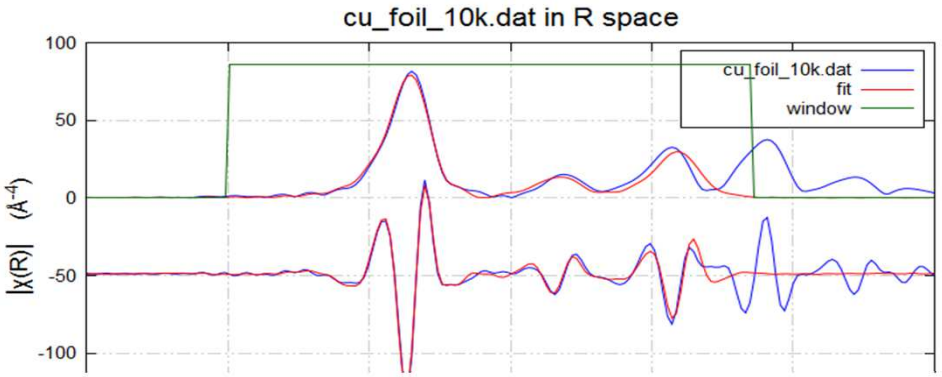
```
: Athena project        = C:\Users\carlo\Dropbox\Seminario_Malu_2015\dati\ok_Cu_Foil\EXAFS_est
: name                  = cu_foil_10k.dat
: k-range               = 3.000 - 23.019
: dk                    = 1
: k-window              = hanning
: k-weight              = 1,2,3
: R-range               = 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

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

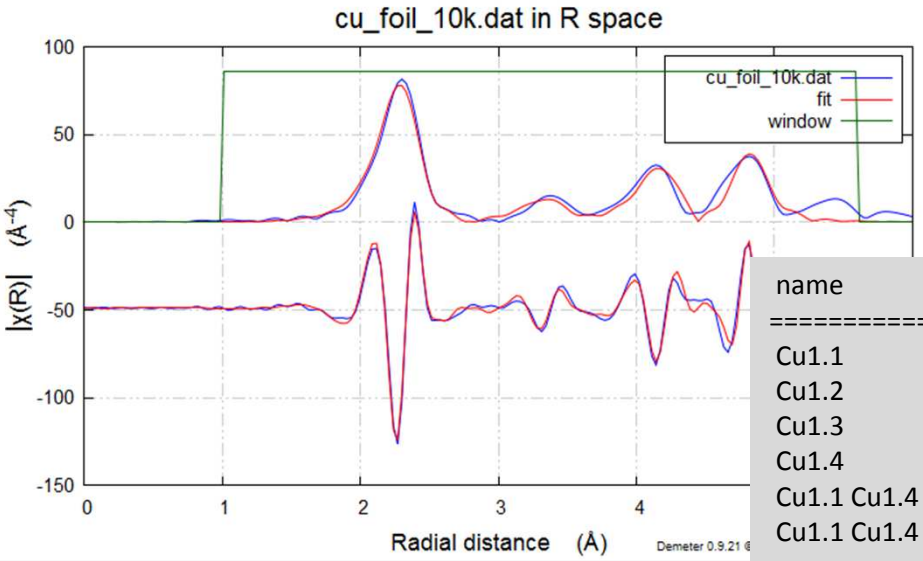


Note: alway use physical meaning constraints i.e. for Cu foil N_j are that of fcc structure

Note:
Check modulus and real(imaginary) parts







4: FIT, extend the analysis to further shells

Fourier transform parameters

kmin	3.000	kmax	23.019	dk	1
rmin	1	rmax	3.7	dr	0.0

Note:
shell 3 and 4 should be included together

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

4: Check best fit log file

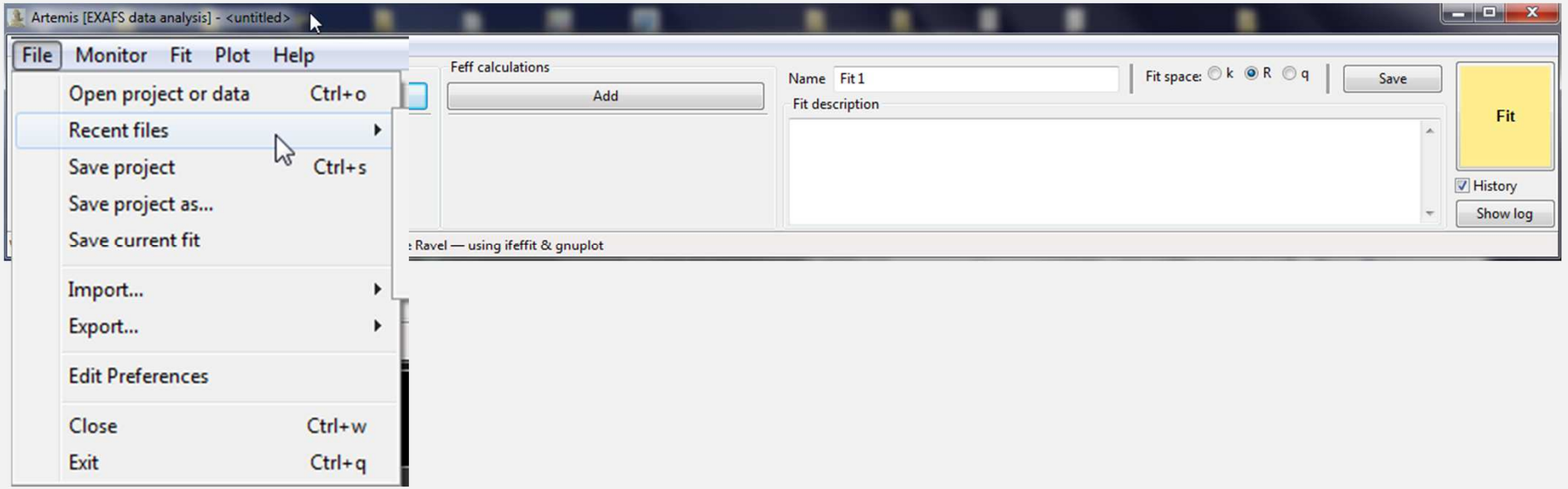
Note:
Keep correlations among the parameters low, maybe add physical meaning constraints.
Far away shell parameters are generally less accurate, use them with care

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

CoO-oxide directory contains Co K edge EXAFS spectra measured on CoO powders

1. Extract EXAFS signals and save data
2. Merge data
3. Analyze Co EXAFS signals

Fe-Temperature directory contains Fe EXAFS spectra measured on Fe foils at different temperatures..

1. Extract EXAFS signals
2. Qualitatively compare the data
3. Check the proper edge alignment
4. Analyze Fe EXAFS signals and account for structural changes as a function of temperature