

Basics of EXAFS Data Analysis

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EXAFS Analysis

Honeywell

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Data processing overview

- Introduction to Artemis
- Modeling Cu foil
- Background subtraction using theory
- Modeling U to determine neighboring atom type
- Multiple data set modeling

- M Newville. "IFEFFIT: interactive EXAFS analysis and FEFF fitting." J. Synch. Rad. **8**: pp 322-324, 2001. <http://cars9.uchicago.edu/ifeffit/>
- J J Rehr. "*Ab initio* multiple scattering X-ray absorption fine structure and X-ray absorption near edge structure code". University of Washington: pp, 1995. <http://leonardo.phys.washington.edu/feff/>
- E A Stern, M Newville, B Ravel, Y Yacoby and D Haskel. "The UWXAFS analysis package: Philosophy and details." Physica B **208 & 209**: pp 117-120, 1995.

Artemis

Theory

Variables

Data: input
from Athena

Project
Name:

Menus:

Fit:
optimize
variables

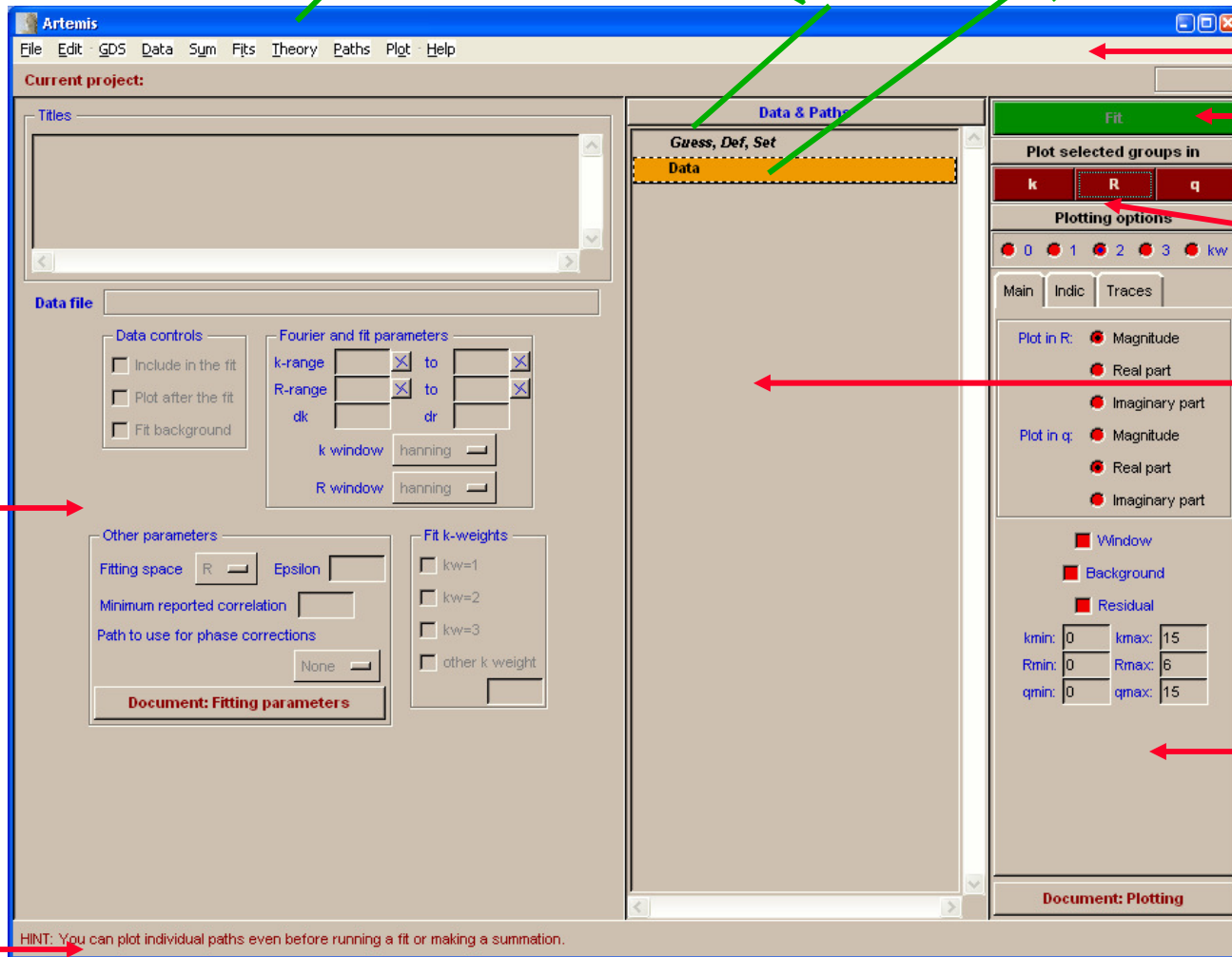
Plot and Do
buttons:

Data and
Paths:
Changes data
display area

Plotting
parameters

Data
display
area:
Changes
depending on
selected
information from
Data and Paths
list

Echo Area:
Messages from
Artemis



Reading in χ Data

➤ File: open data file: F:\lfeffit\examples\Artemis\Cu\cu010k.chi

Artemis

File Edit GD5 Data Sym Fits Theory Paths Plot Help

Current project: modified

Titles

Cu foil at 10K
cu010k.dat : this file is part of the uwxafs 3.0
data taken at NSLS beamline X-11A Sept 1992
by M Newville, B Ravel, and Y Zhang
foil of 99.999 Cu rolled and annealed to ~12 micr

Data file cu010k.chi

Data controls

☒ Include in the fit
☒ Plot after the fit
☐ Fit background

Fourier and fit parameters

k-range 2 to 22.95
R-range 1 to 3
dk 1 dr 0.0
k window Hanning
R window Hanning

Other parameters

Fitting space R Epsilon 0
Minimum reported correlation 0.25
Path to use for phase corrections None
Document: Fitting parameters

Fit k-weights

☒ kw=1
☐ kw=2
☐ kw=3
☐ other k weight

Data & Paths

Guess, Def, Set
cu010k.chi

Fit

Plot selected groups in
k R q

Plotting options

0 1 2 3 kw

Main Indic Traces

Plot in R: ☒ Magnitude
☐ Real part
☐ Imaginary part

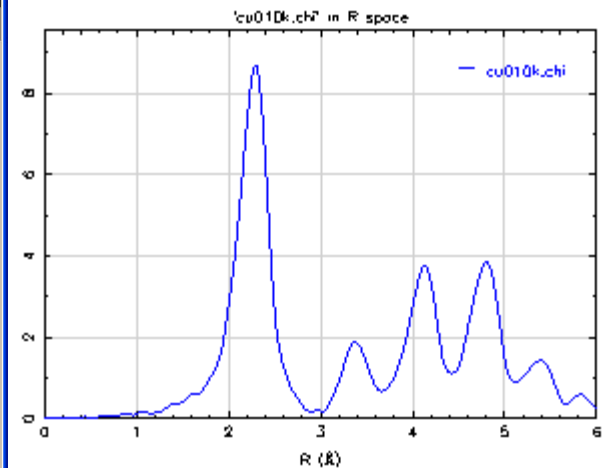
Plot in q: ☒ Magnitude
☐ Real part
☐ Imaginary part

☐ Window
☐ Background
☐ Residual

kmin: 0 kmax: 15
Rmin: 0 Rmax: 6
qmin: 0 qmax: 15

Document: Plotting

Read data from C:\Program Files\lfeffit\examples\Artemis\Cu\cu010k.chi



Data plotted in R-space

Message from Artemis

Reading Data from Athena Project

- File: open data file: F:\Ifeffit\examples\Athena\demos\align_merge.prj

The screenshot displays the Artemis software interface. The main window is titled "Artemis" and contains several panels. On the left, the "Athena project" panel shows a list of data records: "Fe/Ga alloy scan 1", "Fe/Ga alloy scan 2", and "Fe/Ga alloy scan 3". A red arrow points to this list with the text "list of data from Athena". In the center, the "Plot as ..." panel shows various options for plotting the data, including $\chi(k)$, $|\chi(R)|$, $|\chi(q)|$, $\text{Re}[\chi(R)]$, $\text{Re}[\chi(q)]$, $\text{Im}[\chi(R)]$, and $\text{Im}[\chi(q)]$. A red arrow points to this panel with the text "Plot the data". Below this, the "Import these data" button is highlighted, with a red arrow pointing to it and the text "Import the selected data set". On the right, the "Data & Paths" panel shows the file "cu010k.chi" selected. To the right of the main window, a plot titled "Fe/Ga alloy scan 1" is shown, displaying a blue line graph of $|\chi(q)|$ versus q (Å⁻¹). A red arrow points to this plot with the text "Selected data set plotted". The plot shows a series of peaks, with the most prominent one around $q = 2.5$ Å⁻¹. The plot is titled "Fe/Ga alloy scan 1" and the y-axis is labeled $|\chi(q)|$ (Å⁻¹).

Atoms page

➤ File: open file: F:\lfeffit\examples\Artemis\Cu\atoms.inp

The screenshot shows the Artemis software interface with the following components and annotations:

- Atoms Tab:** Located at the top left of the main window.
- Title lines:** The text "Cu 222" in the title bar area.
- Structural Information:** The left panel containing fields for Space group (fcc), A (3.61000), B, C, Alpha, Beta, Gamma, Cluster size (7.00000), Edge (K), and Shift vector (0, 0, 0).
- Atom with a core hole:** A red circle highlights the "1" in the "Core" column of the atom list table.
- Always much larger than paths used in fit:** Points to the "Data & Paths" panel.
- Absorption edge:** Points to the "Edge" field in the structural information panel.
- Make input (feff.inp) for theoretical calculation (FEFF):** Points to the "Run Atoms" button.
- Message from Artemis:** Points to the status bar at the bottom showing "Importing crystallography file ... done!".
- Select FEFF Calculation to Display This page:** Points to the "FEFF0" entry in the "Data & Paths" panel.

The interface also includes a "Fit" panel on the right with "Plot selected groups in" (k, R, q) and "Plotting options" (Magnitude, Real part, Imaginary part) for both R and q. The status bar at the bottom shows "Document: Atoms" and "Document: Plotting".

Theory input page (feff.inp)

➤ Click “Run Atoms”

The screenshot shows the Artemis software interface. The main window displays the 'feff.inp' file with the following content:

```
* This feff6 input file was generated by Artemis 0.
* Atoms written by and copyright (c) Bruce Ravel, 1
*
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *
* total mu*x=1:      4.06 microns, unit edge step
* specific gravity = 8.971
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *
* Normalization correction: 0.00046 ang^2
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *
*
* +-----+
* The following crystallographic data were used:
*
* title      Cu 222
* space = F m -3 m
* a = 3.610 b = 3.610 c = 3.610
* alpha = 90.0 beta = 90.0 gamma = 90.
* core = Cu edge = K
* atoms
* ! elem  x      y      z      tag
* Cu 0.00000 0.00000 0.00000
*
* -----
* TITLE Cu 222
*
* HOLE 1 1.0 * Cu K edge (8979.0 eV), second nu
*
* mphase,mpath,mfeff,mchi
* CONTROL 1 1 1 1
* PRINT 1 0 0 0
```

Annotations on the left side of the image:

- Feff.inp Tab**: Points to the 'feff.inp' tab in the top left.
- Absorption lengths**: Points to the line 'total mu*x=1: 4.06 microns, unit edge step'.
- normalization correction**: Points to the line 'Normalization correction: 0.00046 ang^2'.
- Crystallographic information From atoms.inp**: Points to the section 'The following crystallographic data were used:'.
- title lines**: Points to the line 'TITLE Cu 222'.
- hole number**: Points to the line 'HOLE 1 1.0 * Cu K edge (8979.0 eV), second nu'.

Annotations on the right side of the image:

- Select FEFF Calculation to Display This page**: Points to the 'FEFF0' entry in the 'Data & Paths' panel.

The 'Data & Paths' panel on the right shows the 'Guess, Def, Set' section with 'cu010k.chi' and 'FEFF0' listed. The 'Fit' panel on the far right shows 'Plot selected groups in' with 'k', 'R', and 'q' selected, and 'Plotting options' with '0', '1', '2', '3', and 'kw' selected.

Theory input page (feff.inp)

➤ Scroll feff.inp page downward

Feff.inp Tab

Core Hole and S02 value

Toggle switches for different FEFF modules and output max path length

Control over the number of output paths

Atomic potential index list

Index value For atomic potentials

List of atomic positions

Select FEFF Calculation to Display This page

Artemis

File Edit GDS Data Sum Fits Theory Paths Plot Help

Current project: modified

Atoms feff.inp Interpretation

HOLE 1 1.0 * Cu K edge (8979.0 eV), second nu

* mphase,mpath,mfeff,mchi

CONTROL 1 1 1 1

PRINT 1 0 0 0

RMAX 7.0

*CRITERIA curved plane

*DEBYE temp debye-temp

NLEG 4

POTENTIALS

* ipot Z element

0 29 Cu

1 29 Cu

ATOMS * this list contains

* x y z ipot tag

0.00000 0.00000 0.00000 0 Cu

1.80500 1.80500 0.00000 1 Cu_1

-1.80500 1.80500 0.00000 1 Cu_1

1.80500 -1.80500 0.00000 1 Cu_1

-1.80500 -1.80500 0.00000 1 Cu_1

1.80500 0.00000 1.80500 1 Cu_1

-1.80500 0.00000 1.80500 1 Cu_1

0.00000 1.80500 1.80500 1 Cu_1

0.00000 -1.80500 1.80500 1 Cu_1

1.80500 0.00000 -1.80500 1 Cu_1

-1.80500 0.00000 -1.80500 1 Cu_1

0.00000 1.80500 -1.80500 1 Cu_1

Run Feff Document: Feff and it's input file

Running atoms ... done!

Data & Paths

Guess, Def, Set

cu010k.cif

FEFF

Fit

Plot selected groups in

k R q

Plotting options

0 1 2 3 kw

Main Indic Traces

Plot in R: Magnitude

Real part

Imaginary part

Plot in q: Magnitude

Real part

Imaginary part

Window

Background

Residual

kmin: 0 kmax: 15

Rmin: 0 Rmax: 6

qmin: 0 qmax: 15

Document: Plotting

Theory input page (feff.inp)

➤ Scroll feff.inp page downward and to the right

Check that the atomic
Distances from the absorbing atom
Are reasonable

Artemis

File Edit GDS Data Sym Fits Theory Paths Plot Help

Current project: modified

Atoms feff.inp Interpretation

* this list contains 135 atoms

y	z	ipot	tag	distance
0.00000	0.00000	0	Cu	0.00000
1.80500	0.00000	1	Cu_1	2.55266
1.80500	0.00000	1	Cu_1	2.55266
1.80500	0.00000	1	Cu_1	2.55266
-1.80500	0.00000	1	Cu_1	2.55266
0.00000	1.80500	1	Cu_1	2.55266
1.80500	1.80500	1	Cu_1	2.55266
-1.80500	1.80500	1	Cu_1	2.55266
0.00000	-1.80500	1	Cu_1	2.55266
0.00000	-1.80500	1	Cu_1	2.55266
1.80500	-1.80500	1	Cu_1	2.55266
-1.80500	-1.80500	1	Cu_1	2.55266
0.00000	0.00000	1	Cu_2	3.61000
0.00000	0.00000	1	Cu_2	3.61000
-3.61000	0.00000	1	Cu_2	3.61000
0.00000	3.61000	1	Cu_2	3.61000
0.00000	-3.61000	1	Cu_2	3.61000
1.80500	1.80500	1	Cu_3	4.42133
1.80500	1.80500	1	Cu_3	4.42133
3.61000	1.80500	1	Cu_3	4.42133
3.61000	1.80500	1	Cu_3	4.42133
-1.80500	1.80500	1	Cu_3	4.42133
-1.80500	1.80500	1	Cu_3	4.42133
-3.61000	1.80500	1	Cu_3	4.42133
-3.61000	1.80500	1	Cu_3	4.42133
1.80500	3.61000	1	Cu_3	4.42133
1.80500	3.61000	1	Cu_3	4.42133

Run Feff Document: Feff and it's input file

Running atoms ... done!

Data & Paths

Guess, Def, Set

cu010k.chi

FEFF0

Select FEFF Calculation to Display This page

Fit

Plot selected groups in

k R q

Plotting options

0 1 2 3 kw

Main Indic Traces

Plot in R: Magnitude Real part Imaginary part

Plot in q: Magnitude Real part Imaginary part

Window Background Residual

kmin: 0 kmax: 15

Rmin: 0 Rmax: 6

qmin: 0 qmax: 15

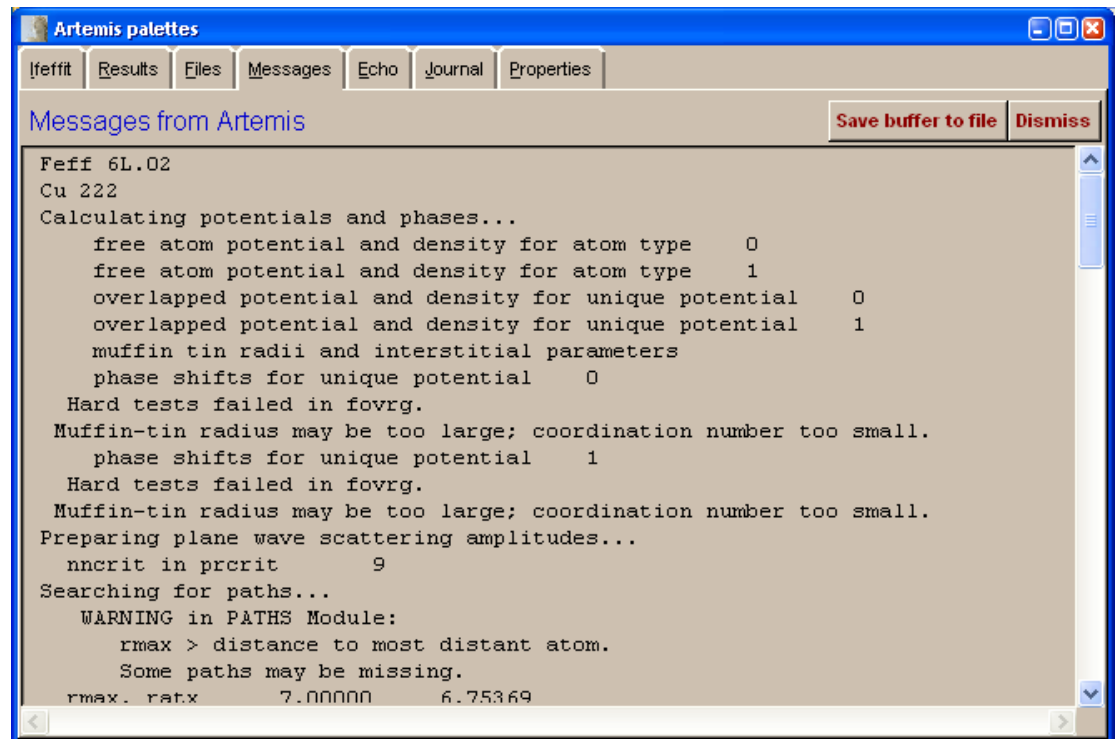
Document: Plotting

Running Feff

Text messages during Feff calculation

- **Artemis Palettes**

- **lfeffit:** Shows the interface from Artemis to lfeffit. Artemis is just a nice interface to lfeffit. lfeffit does the work!
- **Results:** Shows the results page from a fit of the theory to the data.
- **Files:** Shows data files.
- **Messages:** Shows output from Feff.
- **Echo:** Shows entire message from Artemis Echo area
- **Journal:** Useful place to make notes.
- **Properties:** Notes about the current project file.



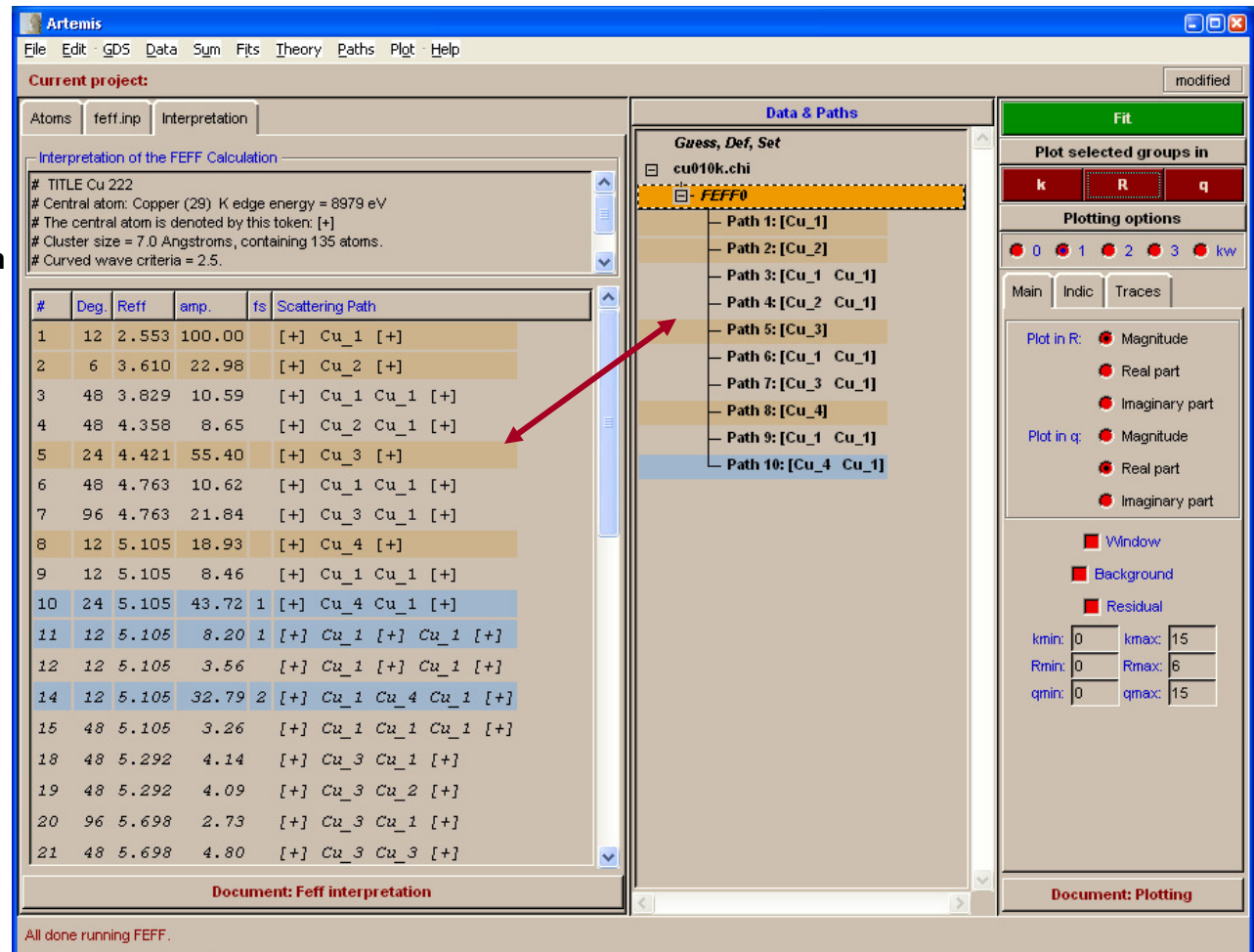
The screenshot shows the 'Artemis palettes' window with the 'Messages' tab selected. The title bar reads 'Artemis palettes'. Below the title bar are tabs for 'lfeffit', 'Results', 'Files', 'Messages', 'Echo', 'Journal', and 'Properties'. The 'Messages' tab is active, showing a text area with the following content:

```
Feff 6L.02
Cu 222
Calculating potentials and phases...
  free atom potential and density for atom type      0
  free atom potential and density for atom type      1
  overlapped potential and density for unique potential      0
  overlapped potential and density for unique potential      1
  muffin tin radii and interstitial parameters
  phase shifts for unique potential      0
Hard tests failed in fovrg.
Muffin-tin radius may be too large; coordination number too small.
  phase shifts for unique potential      1
Hard tests failed in fovrg.
Muffin-tin radius may be too large; coordination number too small.
Preparing plane wave scattering amplitudes...
nncrit in prcrit      9
Searching for paths...
WARNING in PATHS Module:
  rmax > distance to most distant atom.
  Some paths may be missing.
rmax. ratx      7.000000      6.75369
```

At the top right of the Messages tab, there are two buttons: 'Save buffer to file' and 'Dismiss'.

Feff paths: feffxxx.dat

- **Degen:** Degeneracy of the path (number of identical scattering paths)
- **reff:** Initial half path length (bond length for single scattering path)
- **amp:** Estimate of amplitude of path relative to first path.
- **fs:** Number of forward scattering events.
- **scattering path:** atoms scattering photoelectron, [+] symbol represents core atom.



S I Zabinsky, J J Rehr, A Ankudinov, R C Albers and M J Eller. "Multiple-scattering calculations of X-ray-absorption spectra." *Phys. Rev. B* **52**(4): pp 2995-3009, 1995.

Path Description

➤ Click on Path1 in the Data & Paths list

Artemis
File Edit GDS Data Sym Fits Theory Paths Plgt Help

Current project:
FEFF0: Path 1: [Cu_1]

☒ Plot after the fit ☒ Include in the fit
☒ Make this path the default after the fit

[+] Cu_1 [+]

2 legs Reff=2.5527 amp=100.000 degen=12

leg 1: 0.00000 1.80500 -1.80500 1 Cu
rleg=2.5527 beta=180.000

leg 2: 0.00000 0.00000 0.00000 0 Cu
rleg=2.5527 beta=180.000

Path parameter math expressions

label:
N: 12 ☒ S02: amp
delE0: enot
delR: delr
sigma^2: ss
Et:
3rd:
4th:

Data & Paths

Guess, Def, Set

- ☒ cu010k.chi
- ☒ FEFF0
- Path 1: [Cu_1]**
- Path 2: [Cu_2]
- Path 3: [Cu_1 Cu_1]
- Path 4: [Cu_2 Cu_1]
- Path 5: [Cu_3]
- Path 6: [Cu_1 Cu_1]
- Path 7: [Cu_3 Cu_1]
- Path 8: [Cu_4]
- Path 9: [Cu_1 Cu_1]
- Path 10: [Cu_4 Cu_1]

Fit

Plot selected groups in

☒ k ☒ R ☒ q

Plotting options

Main Indic Traces

Plot in R: ☒ Magnitude ☒ Real part ☒ Imaginary part

Plot in q: ☒ Magnitude ☒ Real part ☒ Imaginary part

☒ Window ☒ Background ☒ Residual

kmin: 0 kmax: 15
Rmin: 0 Rmax: 6
qmin: 0 qmax: 15

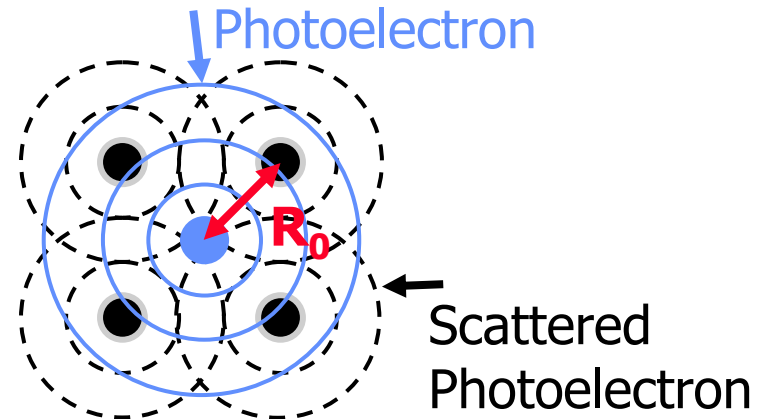
Document: Paths and path parameters

Document: Plotting

All done running FEFF.

The EXAFS Equation

- E. A. Stern and S M Heald Basic principles and applications of EXAFS. Handbook of Synchrotron Radiation. E. E. Koch. New York, North-Holland. **10**: pp 995-1014, 1983.
- E. A. Stern. "Theory of the extended x-ray-absorption fine structure." Phys Rev B **10**(8): pp 3027-3037, Oct 1974.
- E A Stern. "Structural determination by X-ray Absorption." Contemp. Phys **19**(4): pp 239-310, 1978.



$$\chi(k) = \sum_i \chi_i(k)$$

with each path written as:

$$\chi_i(k) = \left(\frac{(N_i S_0^2) F_i(k)}{k R_i^2} \sin(2k R_i + \phi_i(k)) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda(k)) \right)$$

$$R_i = R_0 + \Delta R$$

$$k^2 = 2 m_e (E - E_0) / \hbar$$

$F_i(k)$ effective scattering amplitude
 $\phi_i(k)$ effective scattering phase shift
 $\lambda(k)$ mean free path
 R_0 initial path length

N_i degeneracy of path
 S_0^2 passive electron reduction factor
 E_0 energy shift
 ΔR change in half-path length
 σ_i^2 mean squared displacement

Feff calculates the theoretical scattering amplitude $F(k)$ effective, hence the name Feff.

Path Parameters

- To produce a theoretical model each path must have a value for each of these parameters.
- Artemis makes a guess for these expressions.
- These values can originate from numbers or math expressions.

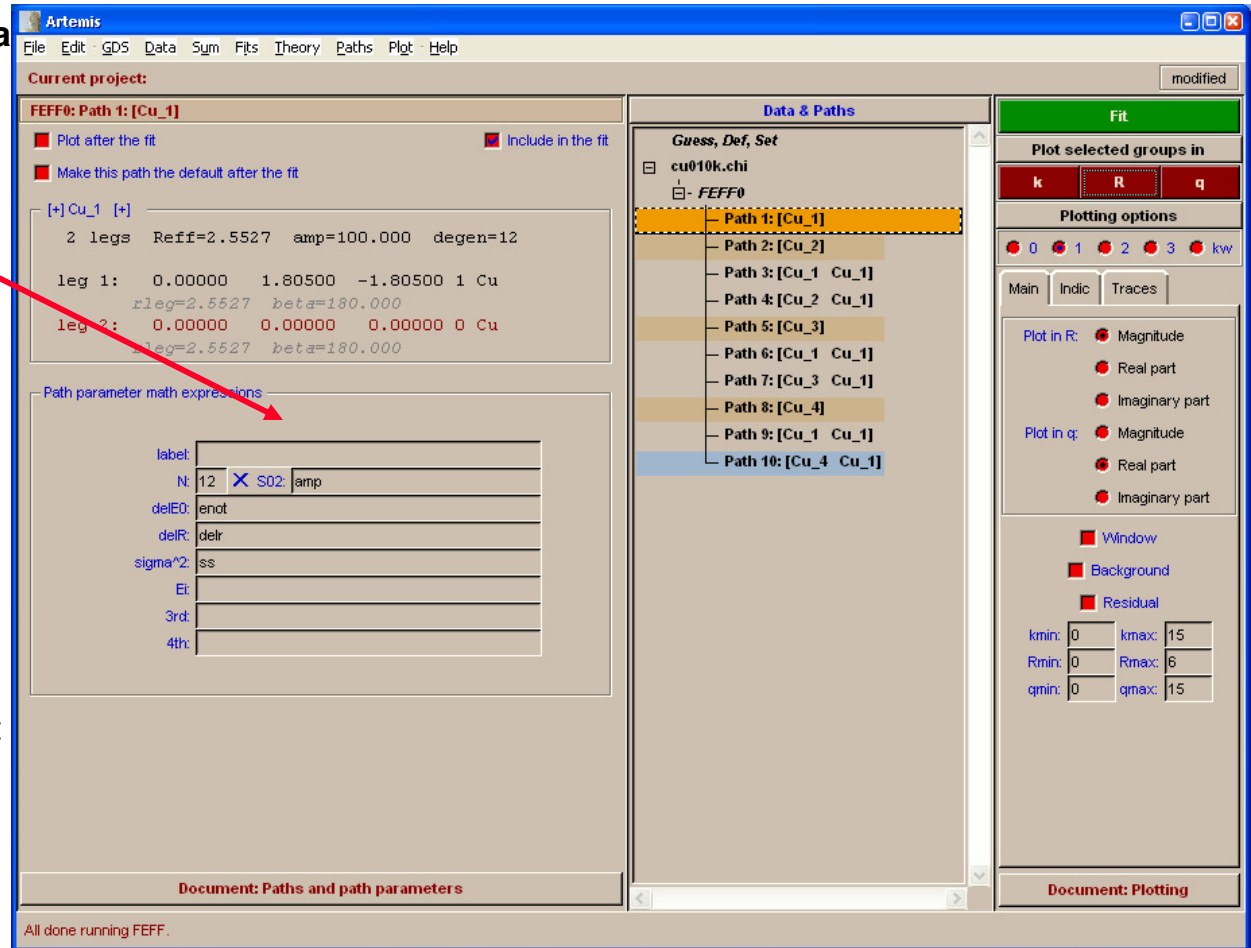
S02 passive electron reduction factor

N degeneracy of path

E0 energy shift

delR change in half-path length

sigma^2 mean squared displacement of the half path length

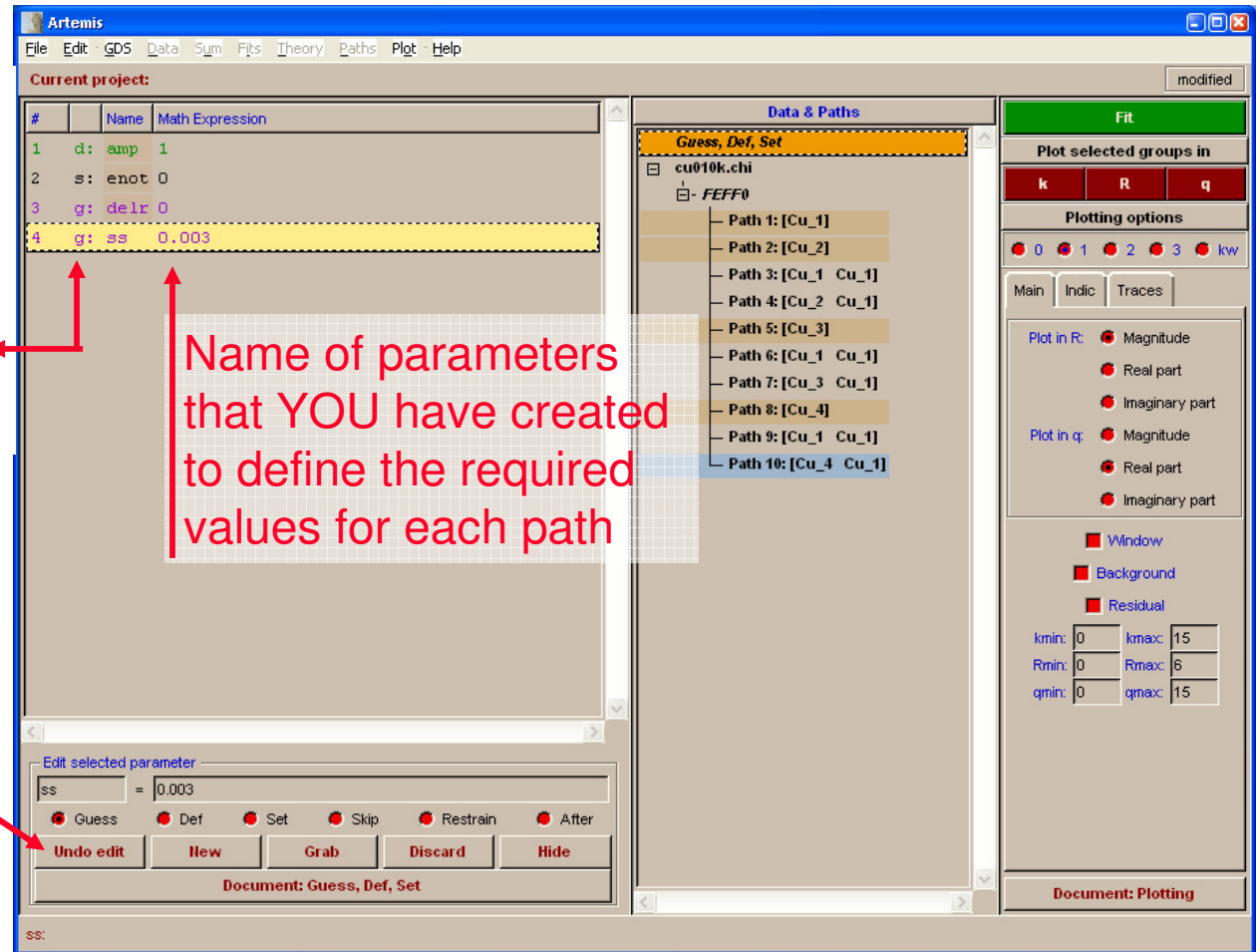


➤ Click "Guess, Def, Set" in the Data & Paths list

EXAFS parameters

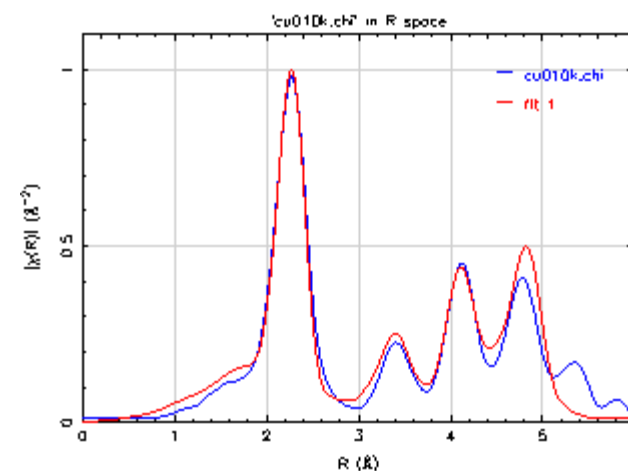
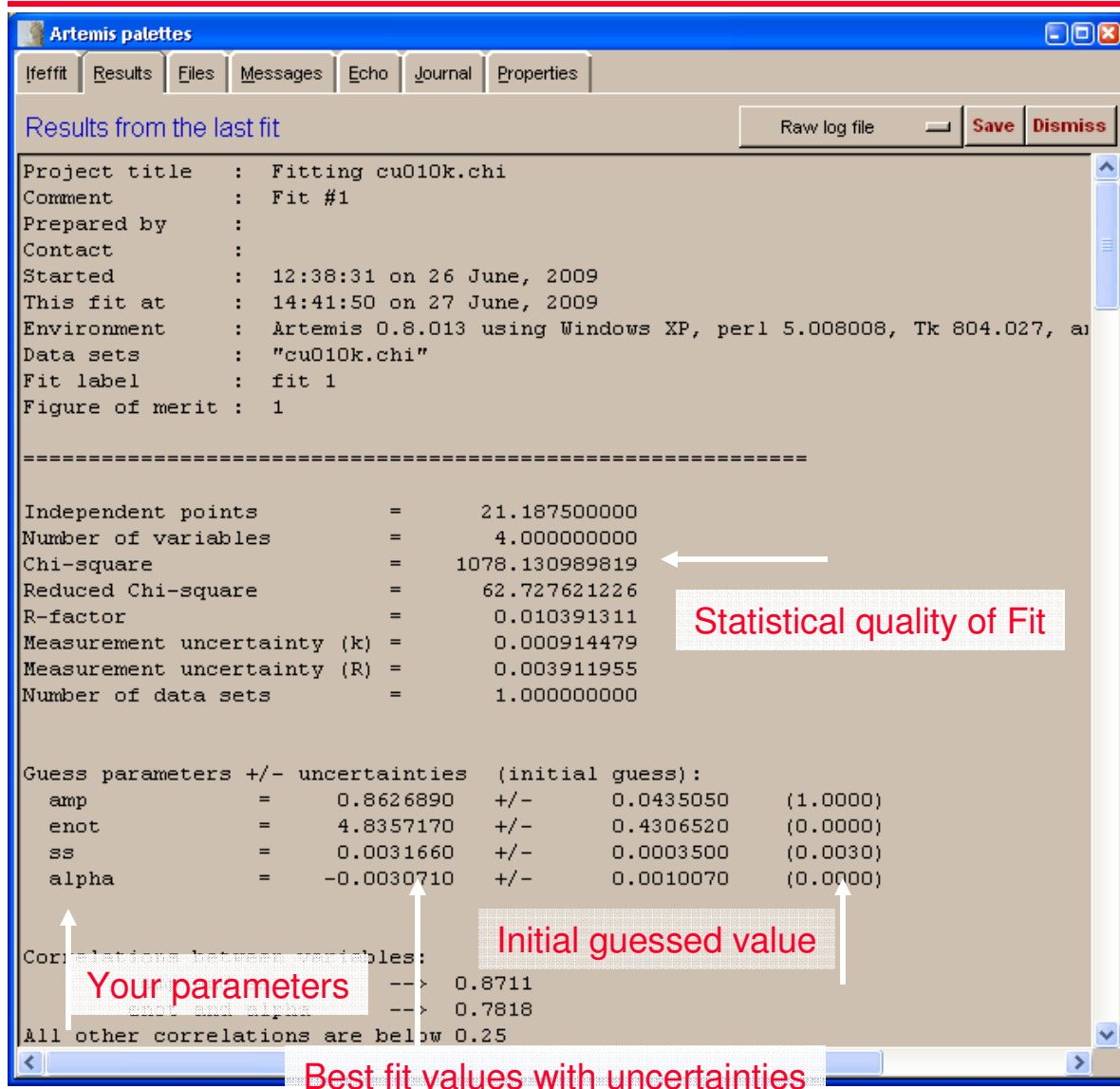
- **Guess:** Optimize parameter in fit.
- **Def:** Define a parameter to a given value but re-evaluate it during the fit
- **Set:** Set a value to a given value. Determine value once.
- **Skip:** Do not use this parameter.
- **Restrain:** penalty that can be added to the fit.

- **Define:** Define parameter to value given.
- **New:** Make a new parameter.
- **Grab:** Set the value to the best-fit value from the fit.
- **Discard:** remove parameter.
- **Hide:** Hide editing area



➤ Click "Fit" to optimize these values

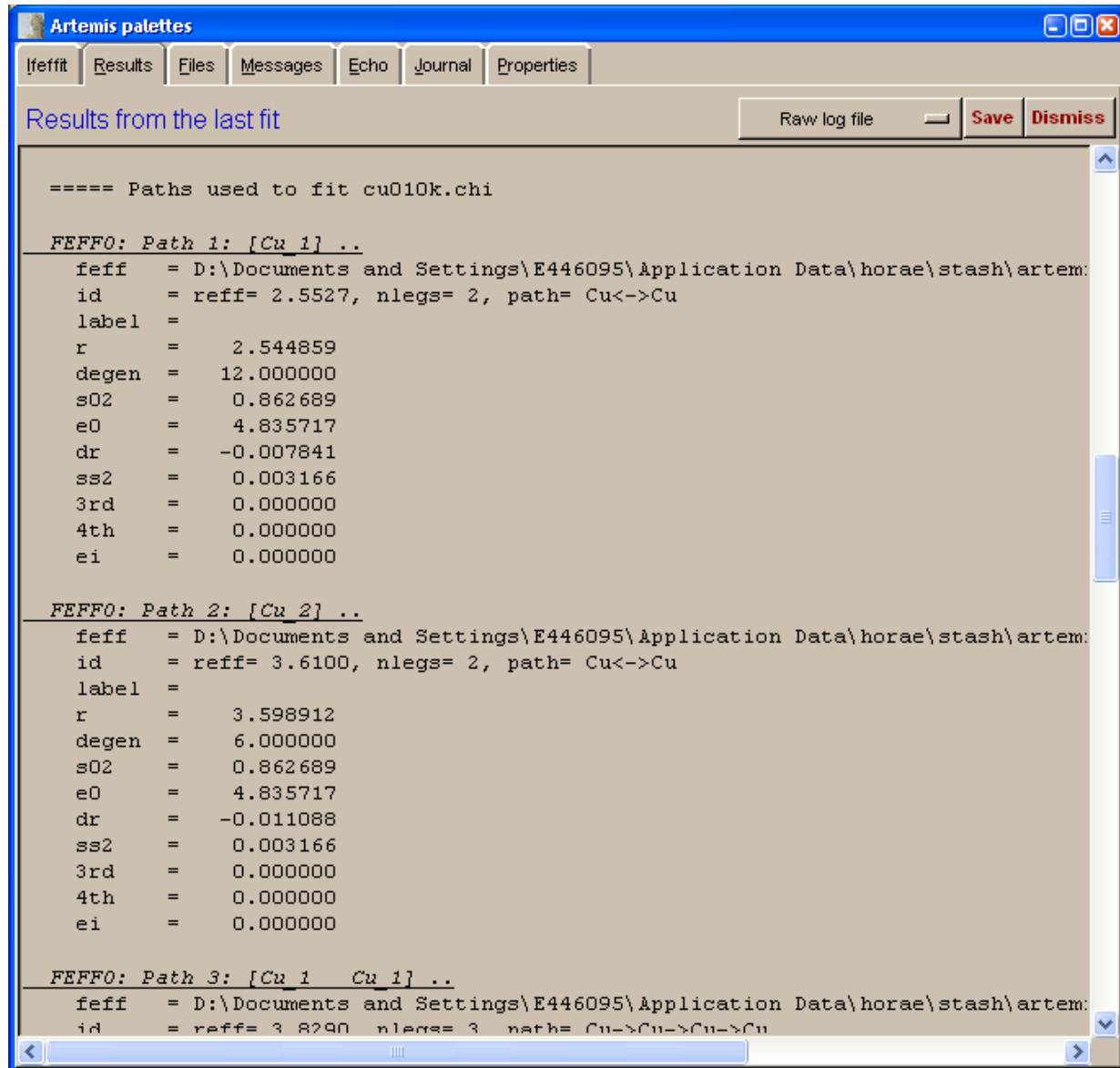
Fit Results



Fit Results

The value used for each EXAFS parameter for each path included in the fit.

Used as a diagnostic tool when models do not work as expected



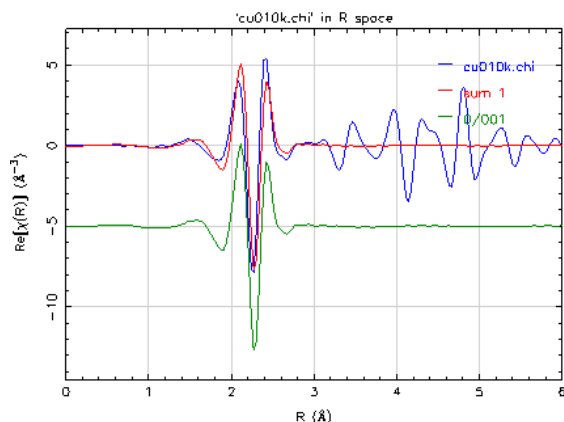
```
==== Paths used to fit cu010k.chi

FEFFO: Path 1: [Cu_1] ..
feff = D:\Documents and Settings\E446095\Application Data\horae\stash\artem:
id = reff= 2.5527, nlegs= 2, path= Cu<->Cu
label =
r = 2.544859
degen = 12.000000
s02 = 0.862689
e0 = 4.835717
dr = -0.007841
ss2 = 0.003166
3rd = 0.000000
4th = 0.000000
ei = 0.000000

FEFFO: Path 2: [Cu_2] ..
feff = D:\Documents and Settings\E446095\Application Data\horae\stash\artem:
id = reff= 3.6100, nlegs= 2, path= Cu<->Cu
label =
r = 3.598912
degen = 6.000000
s02 = 0.862689
e0 = 4.835717
dr = -0.011088
ss2 = 0.003166
3rd = 0.000000
4th = 0.000000
ei = 0.000000

FEFFO: Path 3: [Cu_1 Cu_1] ..
feff = D:\Documents and Settings\E446095\Application Data\horae\stash\artem:
id = reff= 3.8290, nlegs= 3, path= Cu->Cu->Cu->Cu
```

Example: Cu foil



GSD Info

Artemis

File Edit GDS Data Sum Fits Theory Pal

Current project: C:/Program Files/lfeffit/examp

#	Name	Math Expression
1	g: amp	0.9
2	g: enot	0
3	g: delr	0
4	g: sigsq	0.003
5	d: signor	0.00052

Path Info

Plot after the fit ☒ Include in the fit ☒

Make this path the default after the fit ☒

[+] Cu_1 [+]

2 legs Reff=2.5527 amp=100.000 degen=12

leg 1: 0.00000 1.80500 -1.80500 1 Cu
xleg=2.5527 beta=180.000

leg 2: 0.00000 0.00000 0.00000 0 Cu
xleg=2.5527 beta=180.000

Path parameter math expressions

label:

N: 12 ☒ S02 amp

delE0: enot

delR: delr

sigma^2: sigsq + signor

Ei:

3rd:

4th:

Guess, Def, Set

cu010k.chi

Sum

sum 1

FEFF0

feff0001.dat

feff0002.dat

feff0003.dat

feff0004.dat

feff0005.dat

Data Parameters

Data file: cu010k.chi

Data controls

☒ Include data in the fit?

☒ Plot data after the fit?

☒ Fit background

Fourier and fit parameters

k-range: 2.5 to 18

R-range: 1.396 to 2.793

dk: 1 dr: 0.5

k window: Hanning

R window: Hanning

Other parameters

Fitting space: R Epsilon: 0

Minimum reported correlation: 0.25

Path to use for phase corrections: None

Document: Fitting parameters

Fit k-weights

☒ kw=1

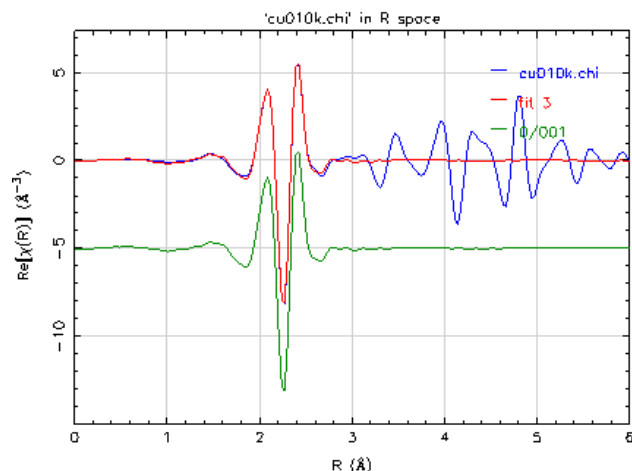
☒ kw=2

☒ kw=3

☒ other k weight

- Example from c:\Program Files\lfeffit\examples\Artemis
- Set up variables for first shell and give them reasonable values
- Sum paths to see how the theory corresponds to the data
- Notice strong signal due to 1st Cu neighbor is in about the right place for the data. Overall shape is similar
- Make sure that fit range is appropriate and choose kw for fit

Cu First Shell Model Results



GSD Info

Artemis

File Edit GDS Data Sym Fits Theory Paths Plot Help

Current project: C:/Program Files/feffit/examples/Artemis/Cu

#	Name	Math Expression
1	g: amp	0.908747 (0.020905)
2	g: enot	5.487727 (0.267428)
3	g: delr	-0.004584 (0.001284)
4	g: sigsqr	0.002945 (0.000132)
5	d: signor	0.00052

Results Info

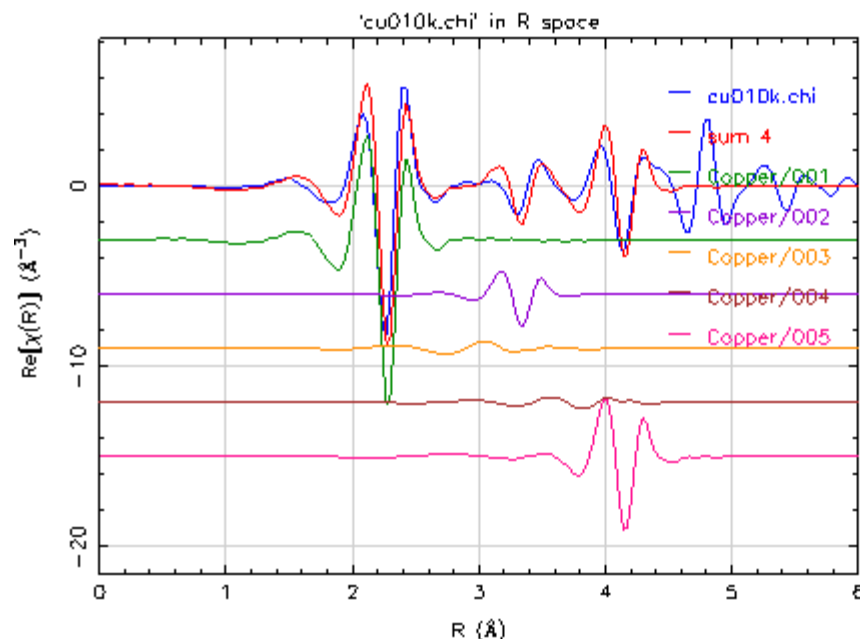
```
Independent points      =      13.579101562
Number of variables    =      4.0000000000
Chi-square             =     259.769677739
Reduced Chi-square     =     27.118375982
R-factor               =      0.001326741
Measurement uncertainty (k) =    0.001130698
Measurement uncertainty (R) =    0.004441269
Number of data sets    =      1.0000000000

Guess parameters +/- uncertainties (initial guess):
amp      =    0.9087470 +/-    0.0209050
enot     =    5.4877270 +/-    0.2674280
delr     =   -0.0045840 +/-    0.0012840
sigsqr   =    0.0029450 +/-    0.0001320

Def parameters (using "FEFF0: feff0001.dat"):
signor   =    0.0005200
```

- Data and Model are in good agreement
- GSD values are reasonable

Cu: Three Shell Model



Path Info

Make this path the default after the fit

[+] Cu_1 [+]

2 legs Reff=2.5527 amp=100.000 degen=12

leg 1: 0.00000 1.80500 -1.80500 1 Cu
rleg=2.5527 beta=180.000

leg 2: 0.00000 0.00000 0.00000 0 Cu
rleg=2.5527 beta=180.000

Path parameter math expressions

label:

N: 12 ☒ S02 amp

delE0: enot

delR: alpha*reff

sigma^2: debye(temp, theta) + signor

Et:

3rd:

4th:

cu010k.chi

Copper

- feff0001.dat
- feff0002.dat
- feff0003.dat
- feff0004.dat
- feff0005.dat
- feff0006.dat
- feff0007.dat
- feff0008.dat
- feff0009.dat
- feff0010.dat
- feff0011.dat
- feff0012.dat
- feff0014.dat
- feff0015.dat

GSD Info

Artemis

File Edit GDS Data Sum Fits Theory

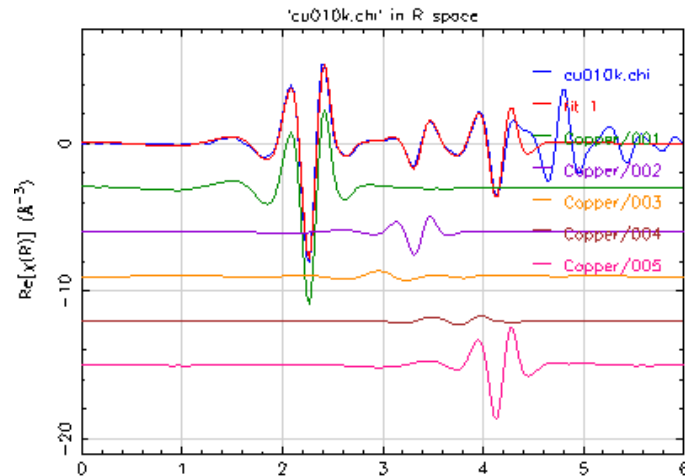
Current project: C:/Program Files/feffit/e

#	Name	Math Expression
1	g: amp	1
2	g: enot	0
3	g: alpha	0
4	s: temp	10
5	g: theta	350
6	s: signor	0.00052

- Use alpha to define path lengths
- Use Debye temperature to define σ^2 values
- Each Single scattering path fits into a specific signal in the data

Fitting results for three shell fit to Cu

Results Info



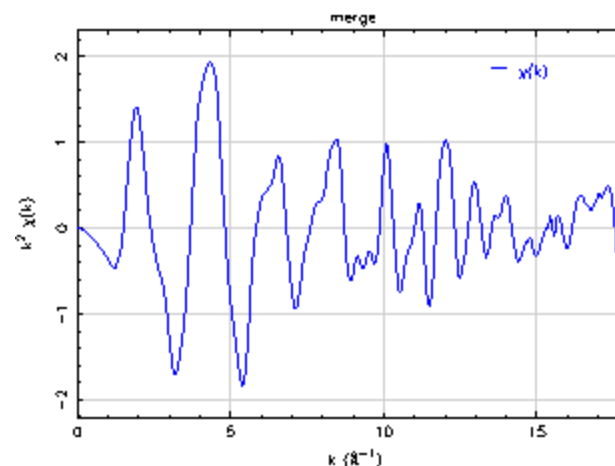
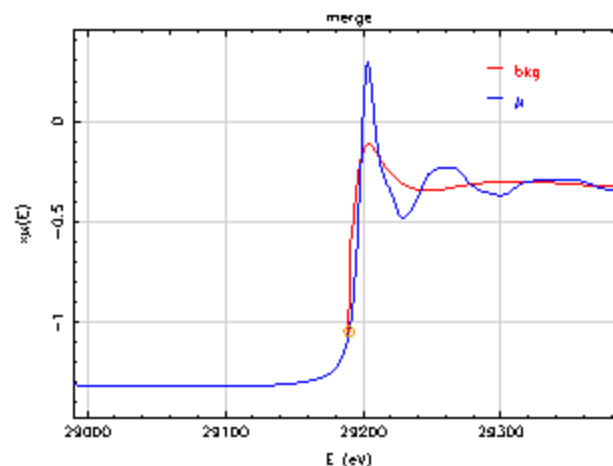
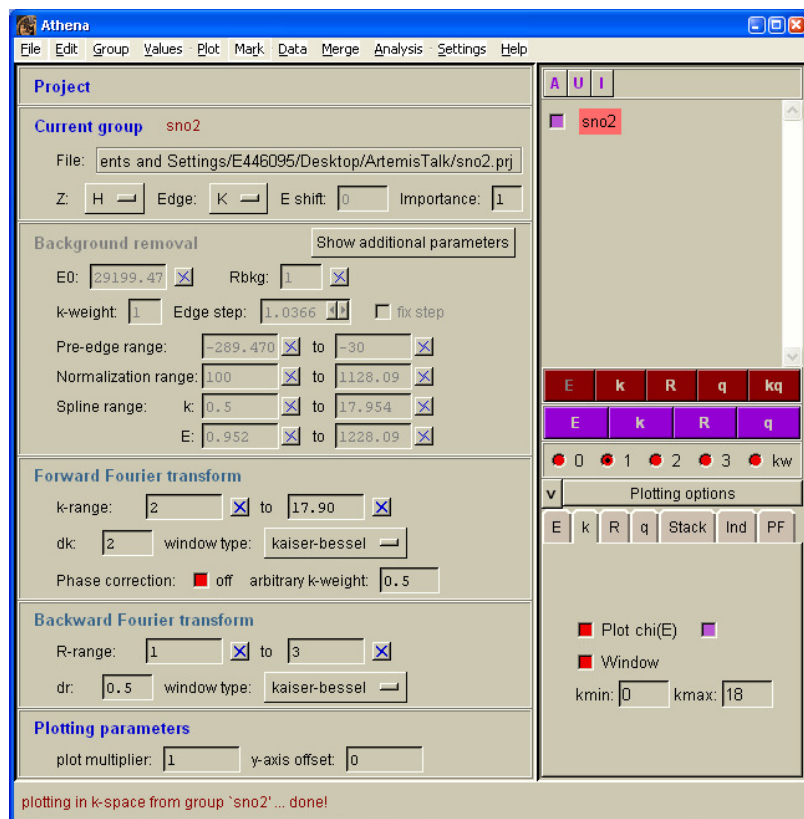
GSD Info

#	Name	Math Expression
1	g: amp	0.966074 (0.066731)
2	g: enot	5.725481 (0.383385)
3	g: alpha	0.000953 (0.001063)
4	s: temp	10
5	g: theta	286.435582 (41.176460)
6	s: signor	0.00052

Artemis palettes			
Results from the last fit			
Independent points	=	25.669921875	
Number of variables	=	4.000000000	
Chi-square	=	2356.356799399	
Reduced Chi-square	=	108.738592275	
R-factor	=	0.023004147	
Measurement uncertainty (k)	=	0.001106115	
Measurement uncertainty (R)	=	0.004671217	
Number of data sets	=	1.000000000	
Guess parameters +/- uncertainties (initial guess):			
amp	=	0.9660740 +/- 0.0667310	(1.0000)
enot	=	5.7254810 +/- 0.3833850	(0.0000)
alpha	=	0.0009530 +/- 0.0010630	(0.0000)
theta	=	286.4355820 +/- 41.1764600	(350.0000)

- There is more to this example on your computer
 - Modeling more shells and modeling temperature dependent spectra series

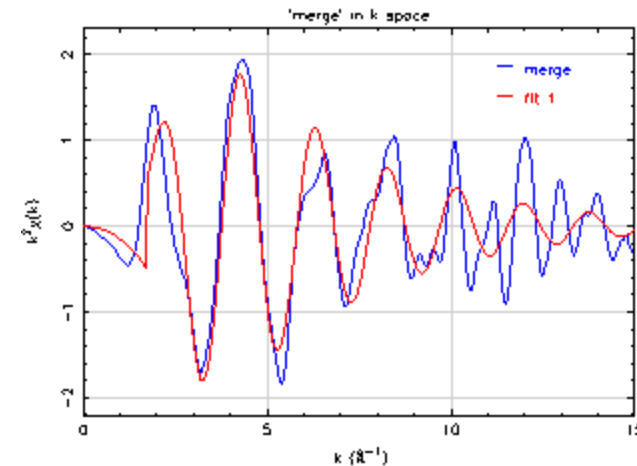
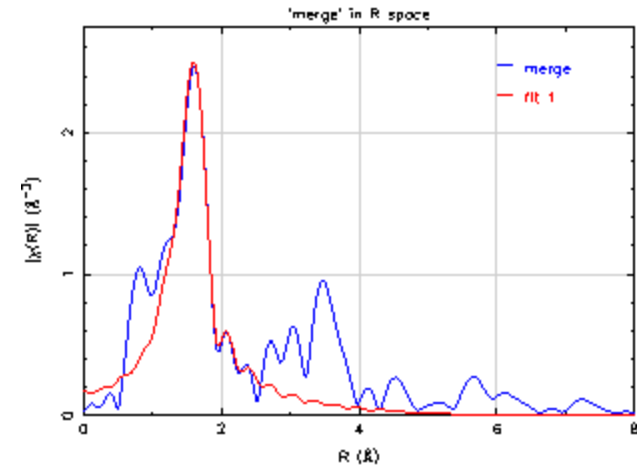
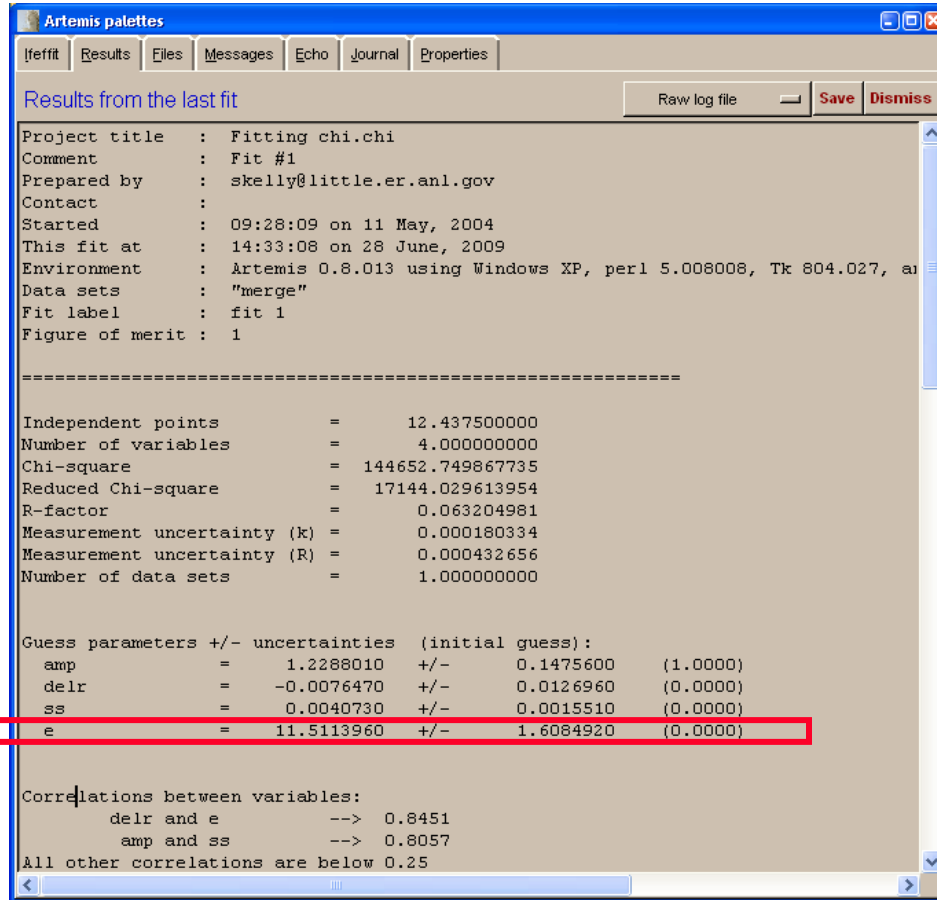
Example #2: Align SnO_2 EXAFS Spectra to Theory



- E0 is somewhere on the edge
- Using default parameters

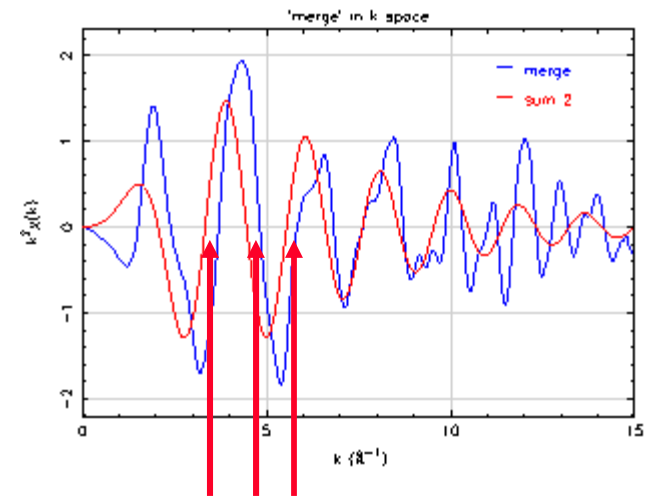
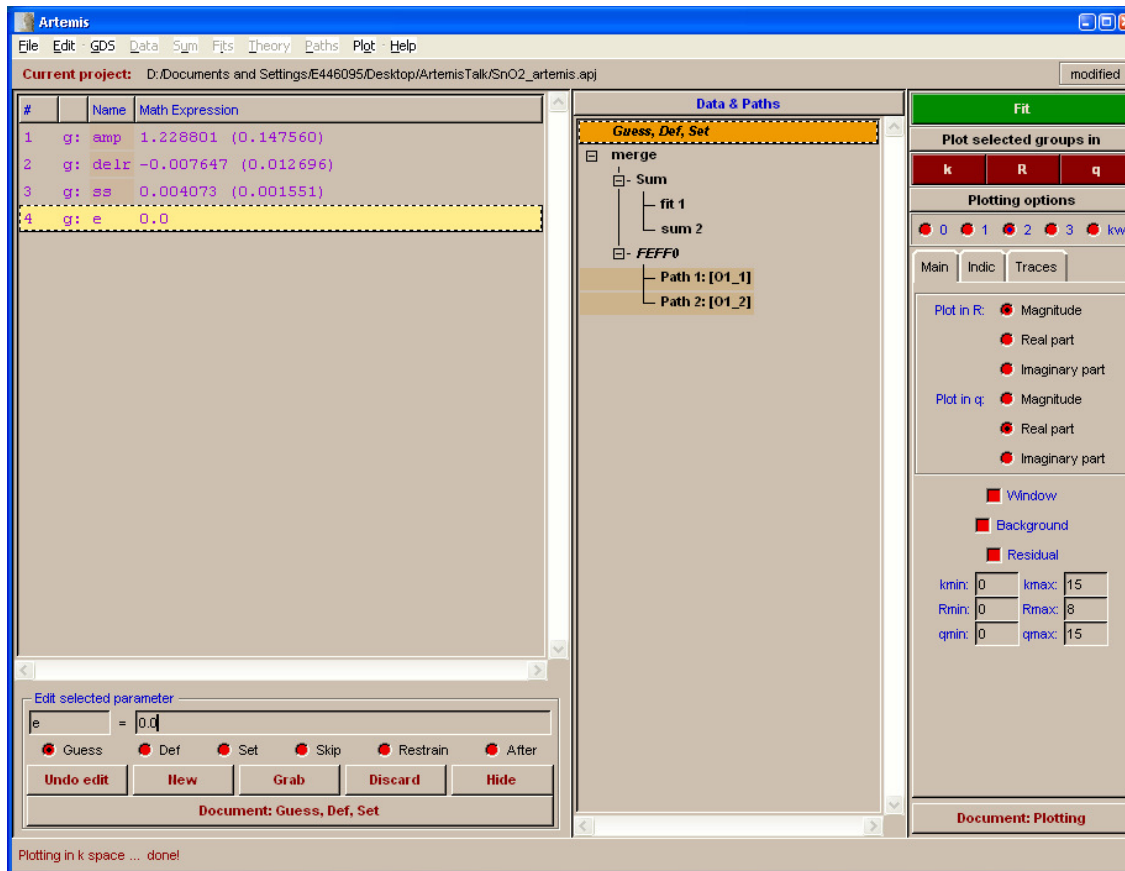
M Newville, B Ravel, D Haskel and E A Stern. "Analysis of multiple scattering XAFS data using theoretical standards." *Physica B* 208 & 209: pp 154-156, 1995.

Fit of first Shell



- E0 could be smaller
- Background needs to be adjusted
- More information:
- M Newville, B Ravel, D Haskel and E A Stern. "Analysis of multiple scattering XAFS data using theoretical standards." *Physica B* 208 & 209: pp 154-156, 1995.

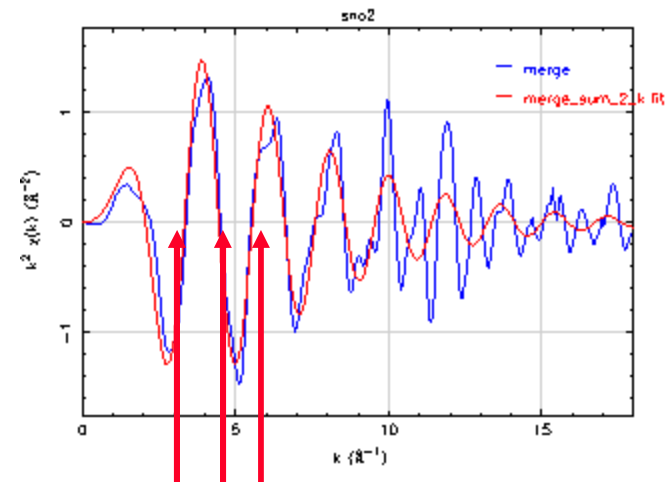
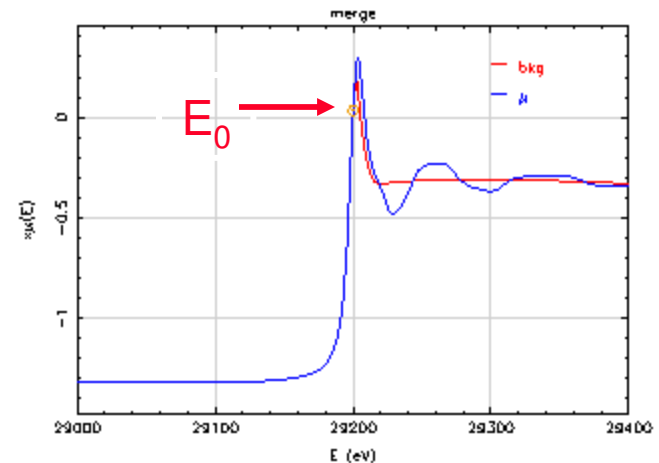
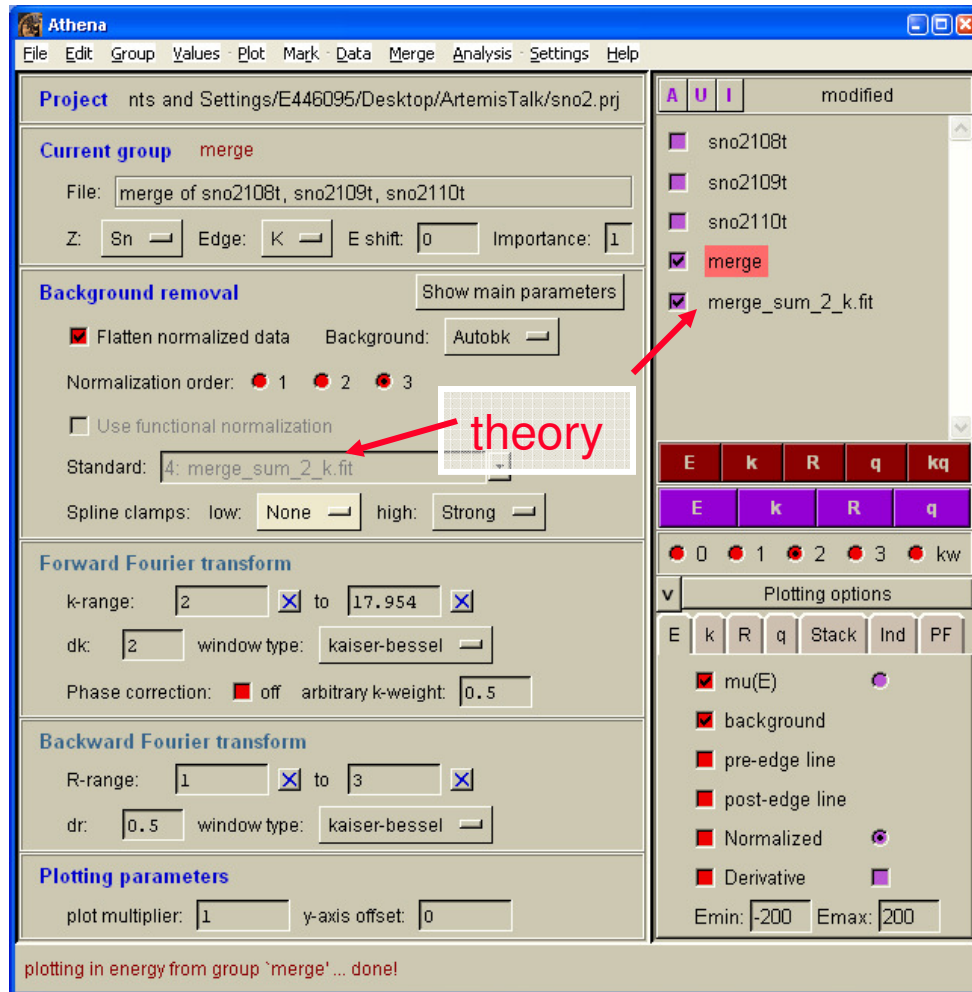
Create first shell model with $\Delta E=0$



Data and theory are not aligned

- Set parameters to their best-fit values by using the Grab button.
- Set $e=0$.
- Sum all paths to make model spectrum with $E=0$.

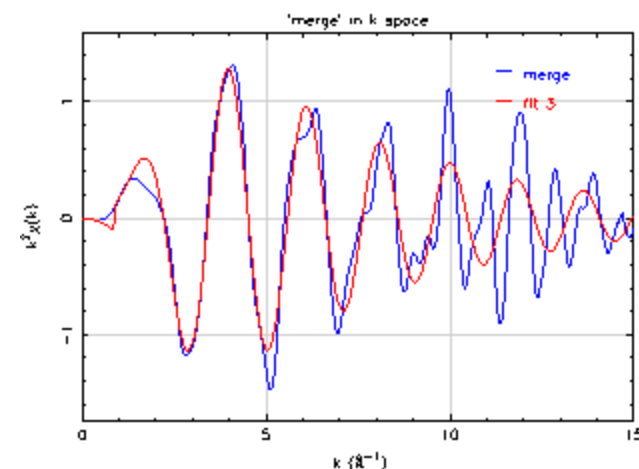
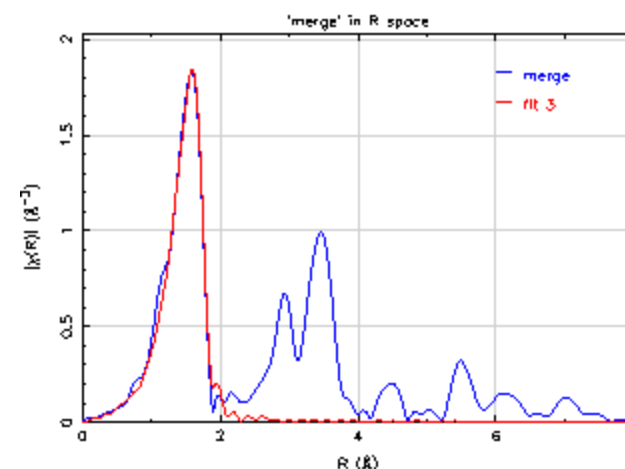
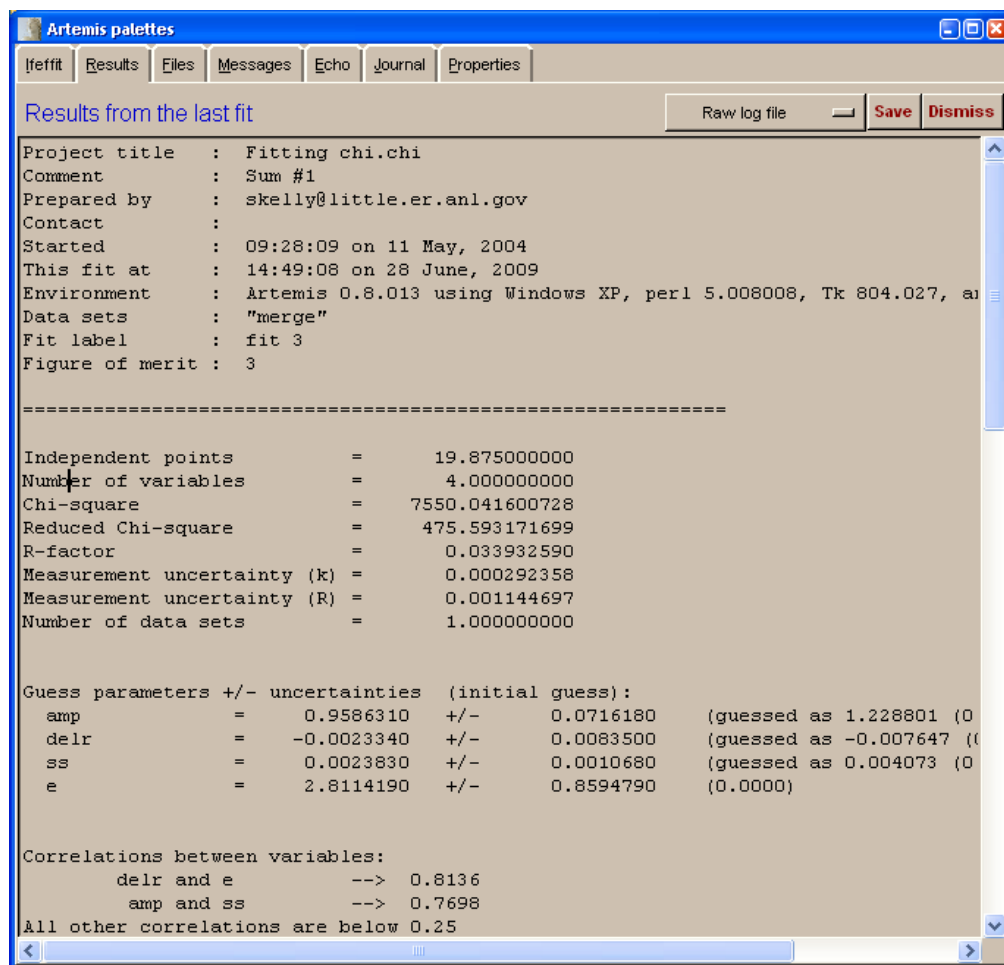
Background corrected and energy aligned by using theory



Data and theory are aligned

- Read the theory into Athena
- Select your data and use the theory as a standard
- Adjust E0 so that the data and theory are aligned at low k values

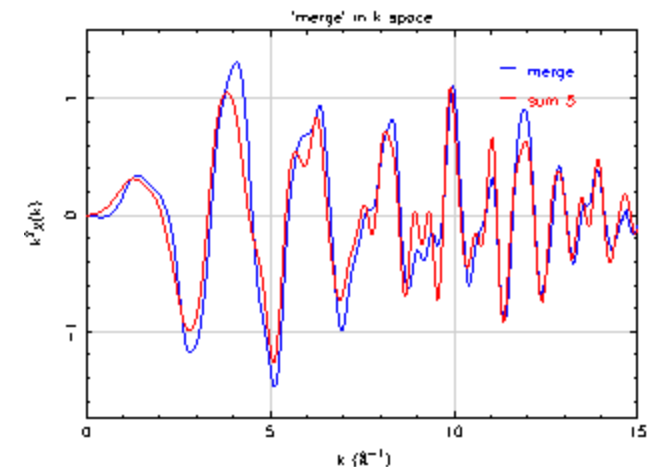
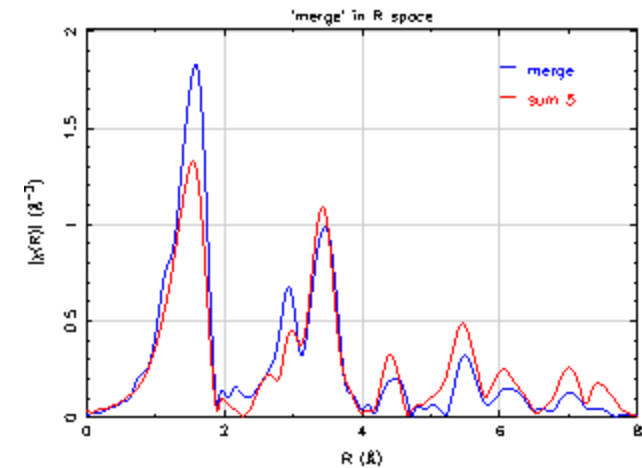
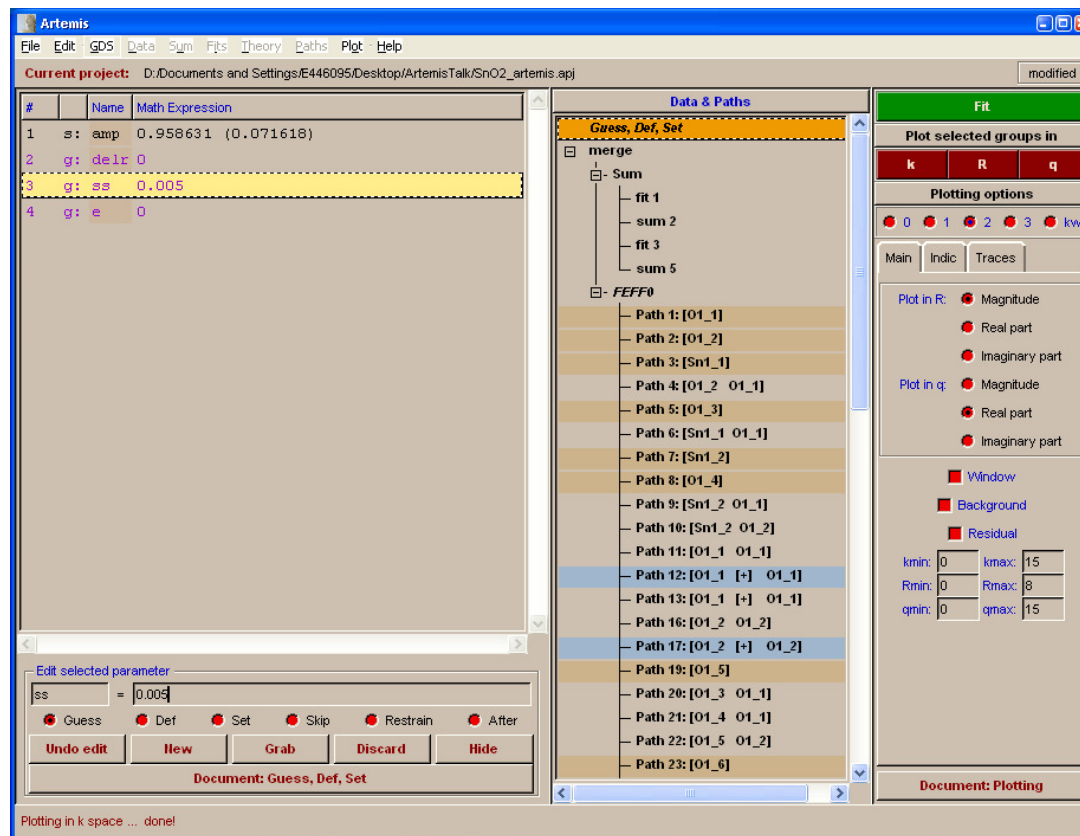
Fit to first shell with background adjusted



- Read the chi(k) data back into Artemis and fit the first shell

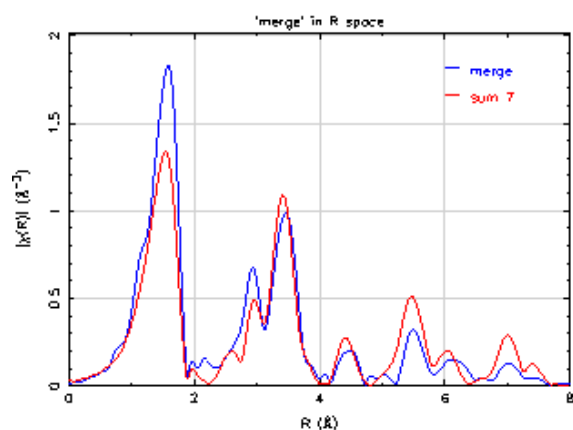
Example 3: Modeling a metal-oxide (SnO_2)

- Compare the sum of all 69 paths to the data

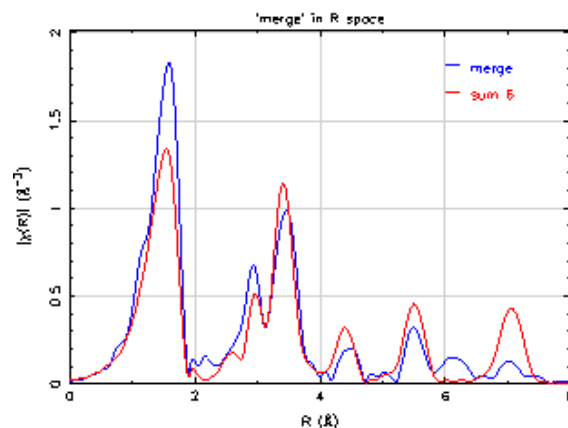


How many paths are required?

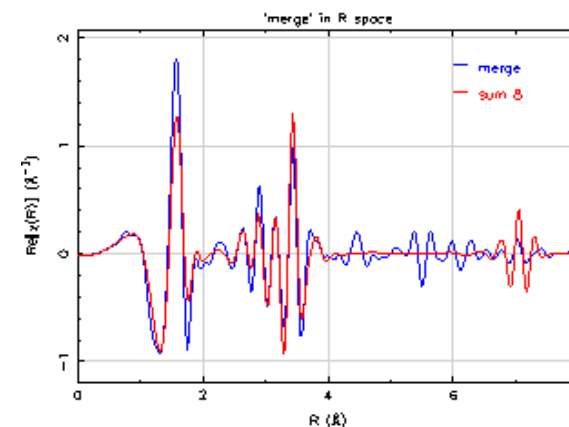
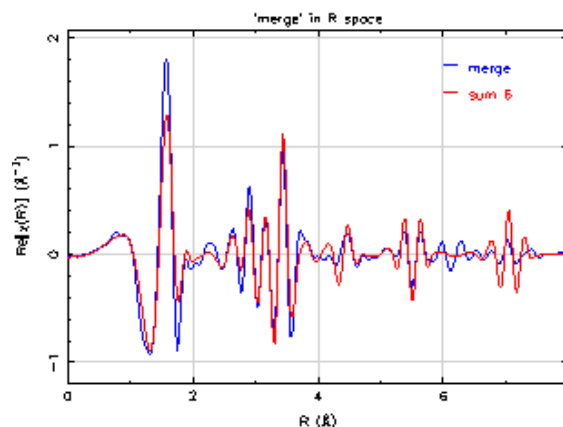
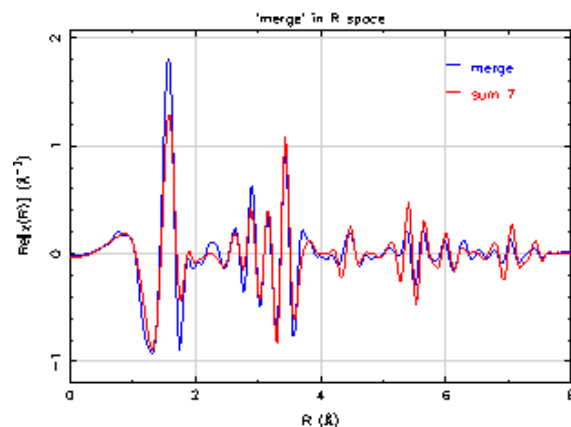
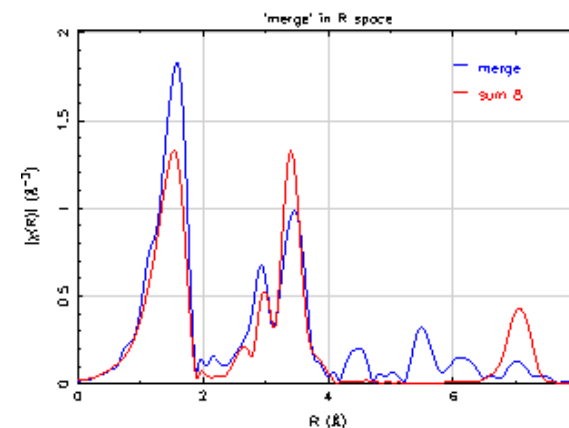
Minimum amplitude 5%
30 of 69 paths



Minimum amplitude 10%
18 of 69 paths



Minimum amplitude 15%
8 of 69 paths



All data is present in model

missing a little of the data

missing a lot of the data

Models to consider:

- **Δr :**
 - Symmetric expansion term: $\text{Alpha} * \text{reff.}$
 - Grouped depending on distance and atom types
 - Related to unit cell dimensions
- **ΔE :**
 - Energy shifts that depend on atom type
 - One energy shift for all paths
 - Two energy shifts, one for first shell and another for all other shells
- **σ^2 :**
 - Grouped depending on distance and atom types.
 - Use a Debye or Einstein model, with one or more characteristic temperatures.
 - Each shell with independent value.
 - Separate structural disorder from thermal disorder components.
- **S02:**
 - One S02 for all paths.
 - Approximate S02 from standards.
- **N:**
 - Determined by the crystal structure.
 - Fit a data series where N is expected to change.

Some EXAFS references

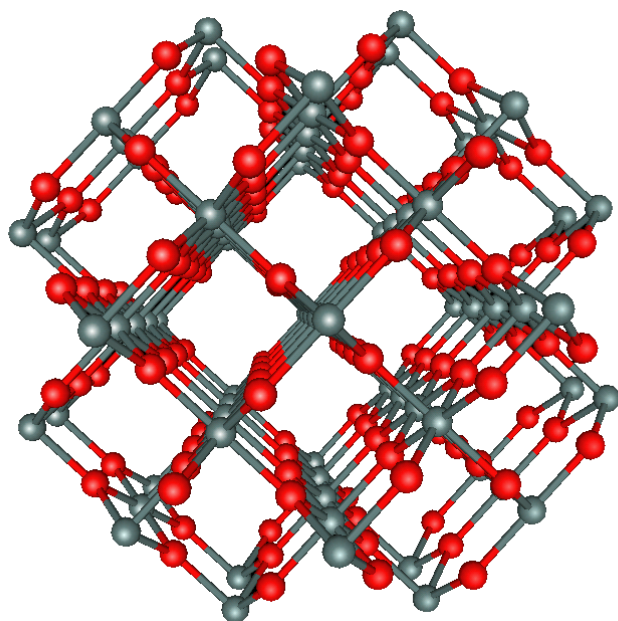
- Multiple edges, structural information: **B Ravel, E. Cockayne, M. Newville and K. M. Rabe. "Combined EXAFS and first-principles theory study of Pb_{1-x}GexTe." *Phys. Rev. B* 60(21): pp 14632–14642, Dec 1999**
- Structural information, bond angles: **A. I. Frenkel, E A Stern, A. Voronel, M. Qian and M Newville. "Solving the structure of disordered mixed salts." *Phys. Rev. B* 49(17 – 1): pp 11662–11674, May 1994.**
- Model two phases, then combined to model a mixture: **S. Kelly, R. Ingalls, F. Wang, B. Ravel and D. Haskel. "X-ray-absorption fine-structure study of the B1-to-B2 phase transition in RbCl." *Phys. Rev. B* 57(13): pp 7543–7550, April 1998**
- Determine neighbor atom types and number using standards: **S. D. Kelly, K. M. Kemner, J. B. Fein, D. A. Fowle, M. I. Boyanov, B. A. Bunker and N. Yee. "X-ray absorption fine-structure determination of pH dependent U-bacterial cell wall interactions." *Geochem. Cosmo. acta.* 66(22): pp 3855-3871, Nov 2002.**
- Multiple techniques: **P G Allen, J J Bucher, D L Clark, N M Edelstein, S A Ekberg, J W Gohdes, E A Hudson, N Kaltsoyannis, W W Lukens, M P Neu, P D Palmer, T Reich, D K Shuh, C D Tait and B D Zwick. "Multinuclear NMR, Raman, EXAFS, and X-ray diffraction studies of uranyl carbonate complexes in near-neutral aqueous solution. X-ray structure of [C(NH₂)₃]₆[(UO₂)₃(CO₃)₆] 6.5H₂O." *Inorg. Chem.* 34: pp 4797-4807, 1995.**
- Pressure dependent data: **A. I. Frenkel, F. M. Wang, S. Kelly, R. Ingalls, D. Haskel, E. A. Stern and Y. Yacoby, "Local structural changes in KNbO₃ under high pressure", *Physical Review B* 56, 10869, 1997.**
- Temperature dependent data: **D. Haskel, E.A. Stern, D.G. Hinks, A.W. Mitchell, J.D. Jorgensen, J.I. Budnick, "Dopant and Temperature Induced Structural Phase Transitions in La_{2-x}Sr_xCuO₄" *Physical Review Letters*, 76 (3) pg 439**
- Multiple edges, structural disorder: **S. Calvin, E. E. Carpenter, B. Ravel, V. G. Harris and S. A. Morrison. "Multiedge refinement of extended x-ray-absorption fine structure of manganese zinc ferrite nanoparticles." *Phys. Rev. B* 66: pp 224405, 2002.**
- Structural information from XANES and EXAFS: **B. Ravel, E. A. Stern, R. I. Vedrinskii and V. Kraizman. "Local structure and the phase transitions of BaTiO₃." *FERROELECTRICS* 206(1-4): pp 407-430, 1998.**
- Temperature dependence and nanoparticles: **A. I. Frenkel, C. W. Hills and R. G. Nuzzo. "A view from the inside: Complexity in the atomic scale ordering of supported metal nanoparticles." *JOURNAL OF PHYSICAL CHEMISTRY B* 105(51): pp 12689-12703, 2001.**
- Kelly, S. D.; Hesterberg, D.; Ravel, B. Analysis of soils and minerals using X-ray absorption spectroscopy. In *Methods of soil analysis, Part 5 -Mineralogical methods*; Ulery, A. L., Drees, L. R., Eds.; Soil Science Society of America: Madison, WI, USA, 2008; pp 367-463.

The Model for SnO₂ data

- **Δr** : symmetric expansion term: $\alpha * \text{reff.}$
- **ΔE** : Energy shifts that depend on atom type:
 - The first shell; E_{o1} ,
 - All other oxygen scattering events: E_{o2}
 - All tin scattering events: E_{sn}
- **σ^2** : Grouped depending on distance and atom types.
- **S_0^2** : one for all paths.
- **N** : determined from the crystal structure.

Final Model for SnO₂

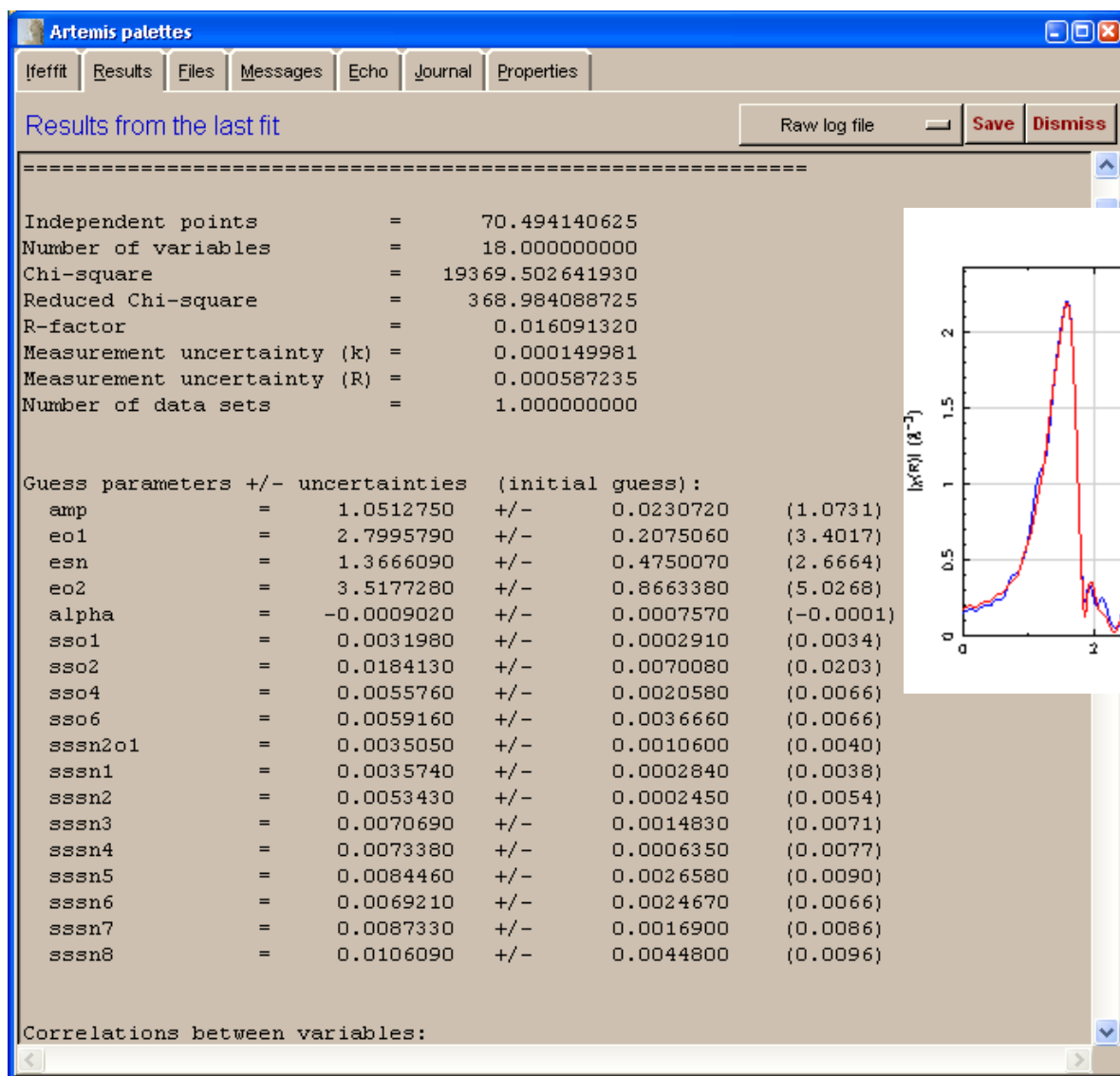
Includes all the
atoms shown here



Path	N	reff	ΔR	σ^2	ΔE
Sn-O1	4	2.0519	Alpha·reff	σ^2_{o1}	ΔE_{o1}
Sn-O2	2	2.0567	Alpha·reff	σ^2_{o1}	ΔE_{o1}
Sn-Sn1	2	3.1864	Alpha·reff	σ^2_{sn1}	ΔE_{sn}
Sn-O3	4	3.5906	Alpha·reff	σ^2_{o3}	ΔE_{o2}
Sn-Sn2	8	3.7093	Alpha·reff	σ^2_{sn2}	ΔE_{sn}
Sn-Sn2-O1	8	3.9090	Alpha·reff	σ^2_{sn2o1}	$0.5 \cdot \Delta E_{sn} + 0.5 \cdot \Delta E_{o1}$
Sn-Sn2-O2	8	3.9090	Alpha·reff	σ^2_{sn2o1}	$0.5 \cdot \Delta E_{sn} + 0.5 \cdot \Delta E_{o1}$
Sn-O5	8	4.2414	Alpha·reff	σ^2_{o5}	ΔE_{o2}
Sn-Sn3	4	4.7373	Alpha·reff	σ^2_{sn3}	ΔE_{sn}
Sn-O7	8	4.8006	Alpha·reff	σ^2_{o7}	ΔE_{o2}
Sn-Sn4	8	5.7092	Alpha·reff	σ^2_{sn4}	ΔE_{sn}
Sn-Sn5	8	5.8365	Alpha·reff	σ^2_{sn4}	ΔE_{sn}
Sn-Sn5-O1	8	5.8405	Alpha·reff	σ^2_{sn4}	$0.5 \cdot \Delta E_{sn} + 0.5 \cdot \Delta E_{o1}$
Sn-Sn5-O4	8	5.8405	Alpha·reff	σ^2_{sn4}	$0.5 \cdot \Delta E_{sn} + 0.5 \cdot \Delta E_{o2}$
Sn-O1-Sn5-O1	4	5.8444	Alpha·reff	σ^2_{sn4}	$0.33 \cdot \Delta E_{sn} + 0.66 \cdot \Delta E_{o1}$
Sn-O4-Sn5-O4	4	5.8444	Alpha·reff	σ^2_{sn4}	$0.33 \cdot \Delta E_{sn} + 0.66 \cdot \Delta E_{o2}$
Sn-Sn6-Sn1	4	6.3728	Alpha·reff	σ^2_{sn6}	ΔE_{sn}
Sn-Sn1-Sn6-Sn1	2	6.3728	Alpha·reff	σ^2_{sn6}	ΔE_{sn}
Sn-Sn7	4	6.6995	Alpha·reff	σ^2_{sn7}	ΔE_{sn}
Sn-Sn7-O2	4	6.6995	Alpha·reff	σ^2_{sn7}	$0.5 \cdot \Delta E_{sn} + 0.5 \cdot \Delta E_{o1}$
Sn-Sn7-O6	4	6.6995	Alpha·reff	σ^2_{sn7}	$0.5 \cdot \Delta E_{sn} + 0.5 \cdot \Delta E_{o2}$
Sn-Sn7-O6-O2	4	6.6995	Alpha·reff	σ^2_{sn7}	$0.33 \cdot \Delta E_{sn} + 0.33 \cdot \Delta E_{o1} + 0.33 \cdot \Delta E_{o2}$
Sn-O6-Sn7-O2	4	6.6995	Alpha·reff	σ^2_{sn7}	$0.33 \cdot \Delta E_{sn} + 0.33 \cdot \Delta E_{o1} + 0.33 \cdot \Delta E_{o2}$
Sn-O2-Sn7-O6-O2	4	6.6995	Alpha·reff	σ^2_{sn7}	$0.25 \cdot \Delta E_{sn} + 0.50 \cdot \Delta E_{o1} + 0.25 \cdot \Delta E_{o2}$
Sn-O6-Sn7-O6-O2	4	6.6995	Alpha·reff	σ^2_{sn7}	$0.25 \cdot \Delta E_{sn} + 0.25 \cdot \Delta E_{o1} + 0.50 \cdot \Delta E_{o2}$
Sn-Sn8	8	7.4187	Alpha·reff	σ^2_{sn8}	ΔE_{sn}
Sn-Sn8-Sn2	16	7.4187	Alpha·reff	σ^2_{sn8}	ΔE_{sn}
Sn-Sn2-Sn8-Sn2	8	7.4187	Alpha·reff	$4 \cdot \sigma^2_{sn2}$	ΔE_{sn}
Sn-Sn2-Sn8-Sn2	8	7.4187	Alpha·reff	σ^2_{sn8}	ΔE_{sn}
Sn-Sn9	16	7.6578	Alpha·reff	σ^2_{sn9}	ΔE_{sn}

- One S02-value was also determined in the fit.
- 30 paths used in final model.
- There are a total of 18 parameters in this model and 56 independent points in the data.

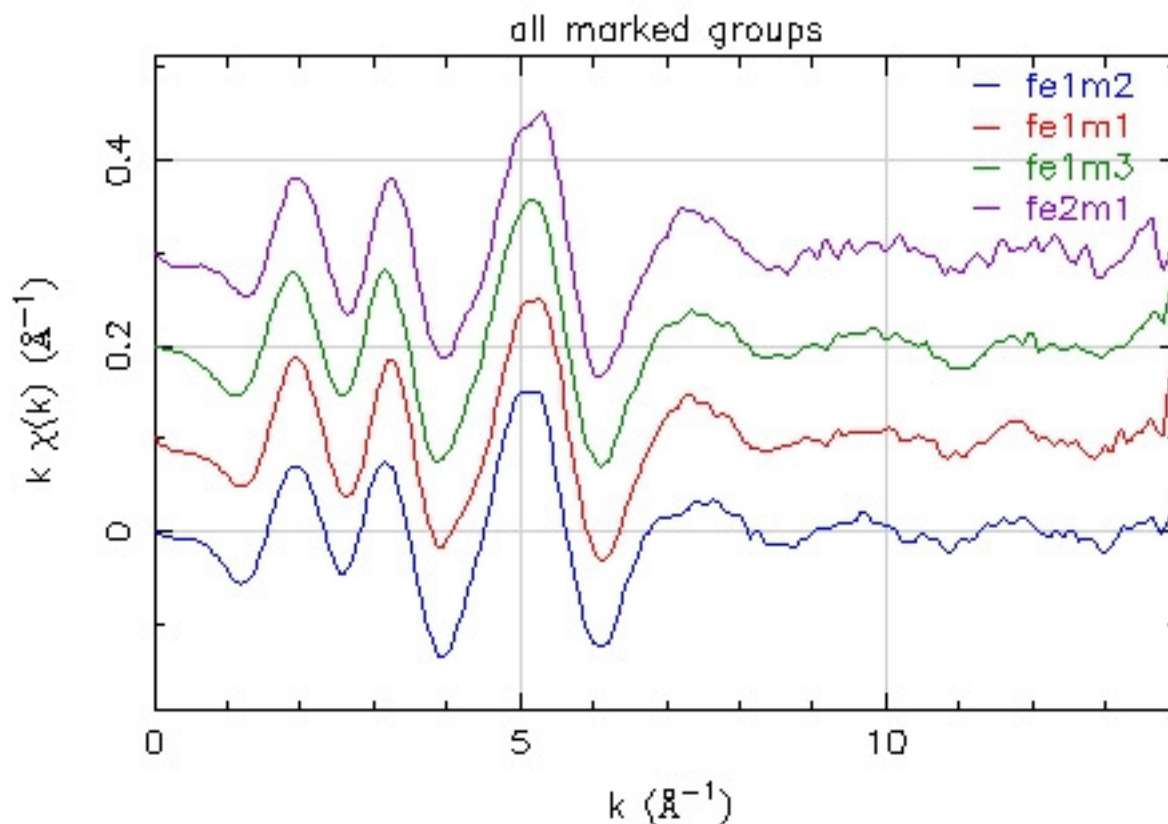
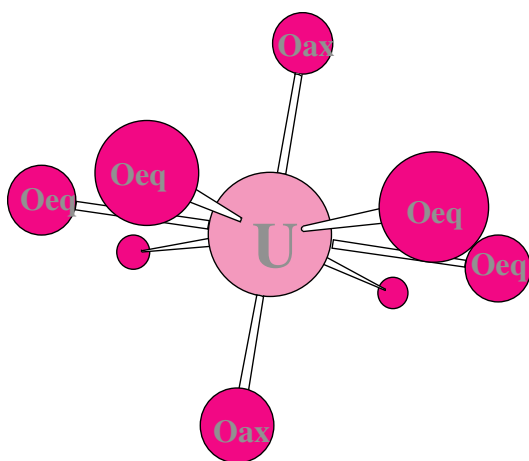
Final Model and Fit to SnO₂



- Typical values for EXAFS parameters
- Δr : less than 0.5 Å
- ΔE : less than 10 eV
- σ^2 : 0.003 to 0.020 Å²
- S02: 0.70 to 1.10

Example 4: Determining 2nd shell atom type and number

- Uranyl in equilibrium with a mixture of Fe-oxides and different microbial components.
- Possible second shell atoms, O, C, P, Fe, U.
- 30-50 combinations of these atoms were tested.
- Three of these tests are shown here:
 - C and Fe,
 - P and Fe,
 - Fe and Fe



Setting up a Uranyl Model

Artemis

File Edit GDS Data Sum Fits Theory Paths Plot Help

Current project: D:/Documents and Settings/E446095/Desktop/ArtemisTalk/Artemis1-TestPaths.apj

#	Name	Math Expression
5	g: noeq	2.683084 (0.982222)
6	g: deloeq	-0.169572 (0.021928)
7	g: ssoeq	0.004189 (0.003290)
8	--	-----
9	g: nfe2	0.399266 (0.219653)
10	g: delfe2	-0.144064 (0.051333)
11	d: ssfe2	ssfe1
12	--	-----
13	g: nc	1
14	g: delc	0
15	g: ssc	0.003
16	--	-----
17	np	1
18	delp	0
19	ssp	0.003
20	--	-----
21	nfe1	0.415675 (0.146499)
22	delfe1	0.047575 (0.035494)
23	ssfe1	0.003

Data & Paths

- chi_1.chi
 - Fit
 - FEFF0
 - Oax at 1.78
 - Oeq at 2.46
 - C at 2.85
 - U-Oax1-U-Oax1
 - U-Oax1-Oax2
 - U-Oax1-U-Oax2
 - FEFF1
 - P at 3.06
 - FEFF3
 - Fe at 3.53
 - FEFF4
 - Fe at 2.80

Fit

Plot selected groups in

k R q

Plotting options

0 1 2 3 kw

Main Indic Traces

Plot in R: Magnitude Real part Imaginary part

Plot in q: Magnitude Real part

Edit selected parameter

ssp = 0.003

Guess Def Set Skip Restrain After

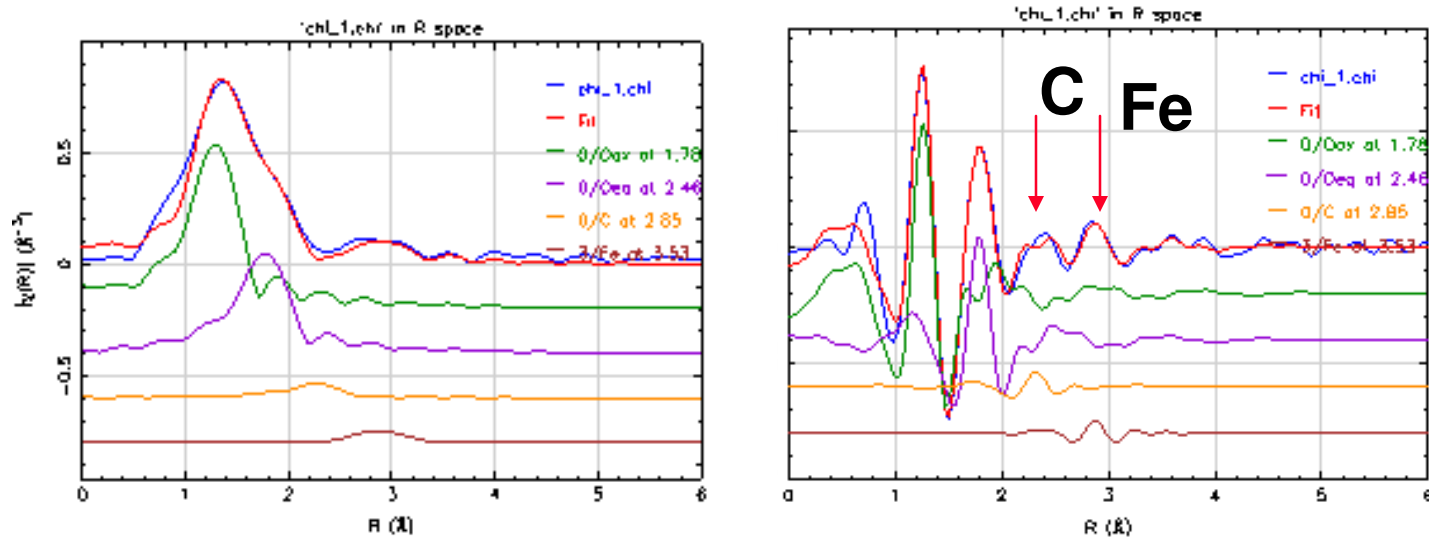
Undo edit New Grab Discard Hide

Document: Guess, Def, Set

ssp = -0.000673 +/- 0.019959

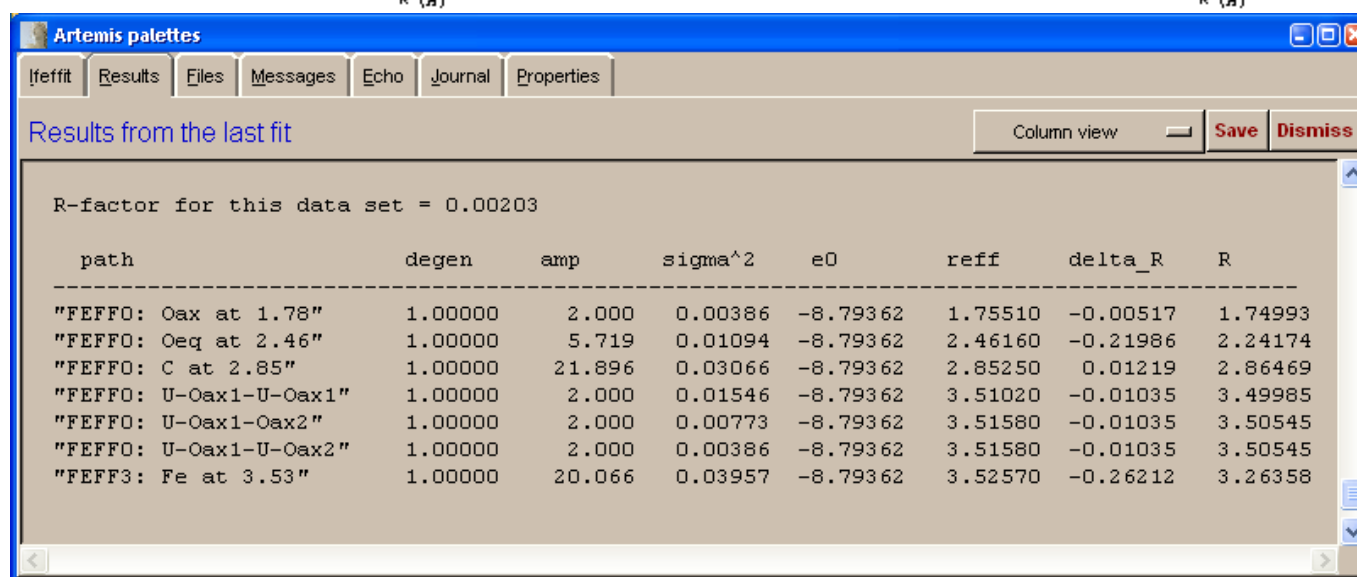
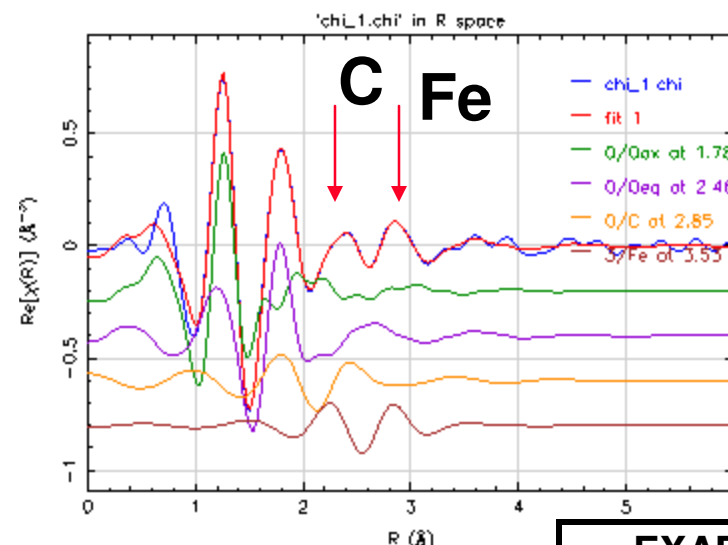
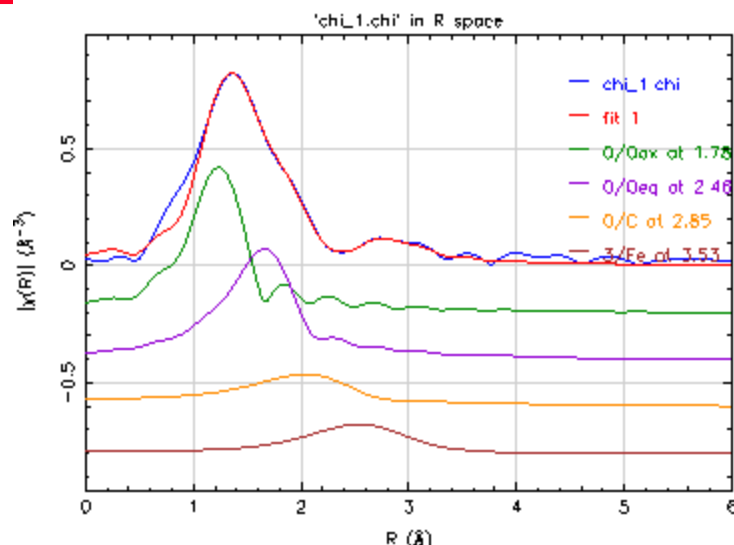
- Organization is key
- FEFF paths can be renamed
- Separators can be added to GDS page
- Variable names can have meaning
- Multiple FEFF calculations can be used in one model

Test data for C and Fe shells



- Place **C** and **Fe** shells in a “good” spot
 - set parameters – no fitting
 - monitor results and fit spectra
 - Needs to be done using real or imaginary part of FT, can not always be done using magnitude of FT.

Fit Results using C and Fe shells

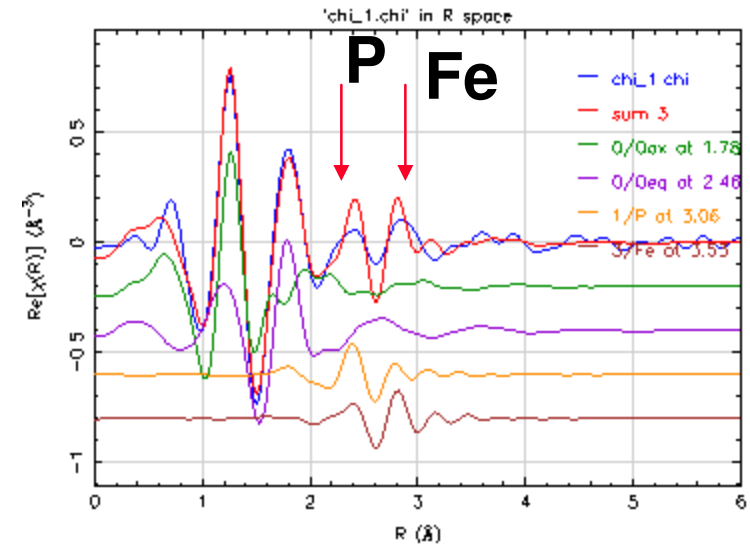
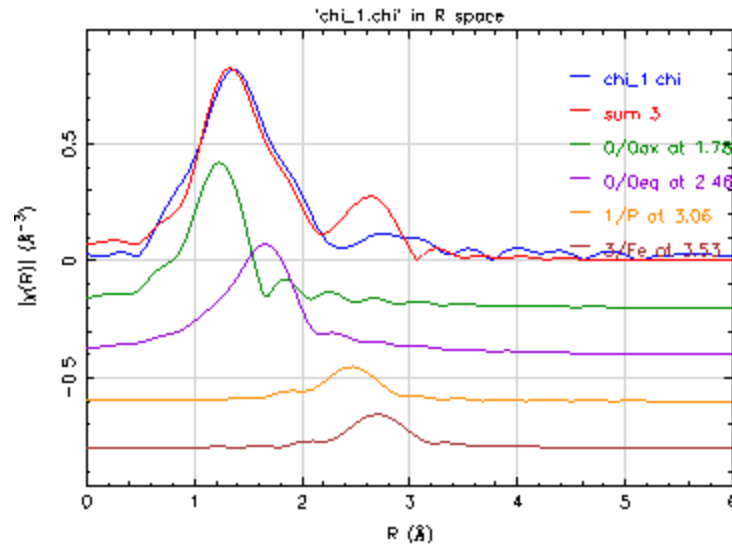


EXAFS Parameters

σ^2 -values	-
Distances	+
Coordination numbers	-
ΔE -value	-

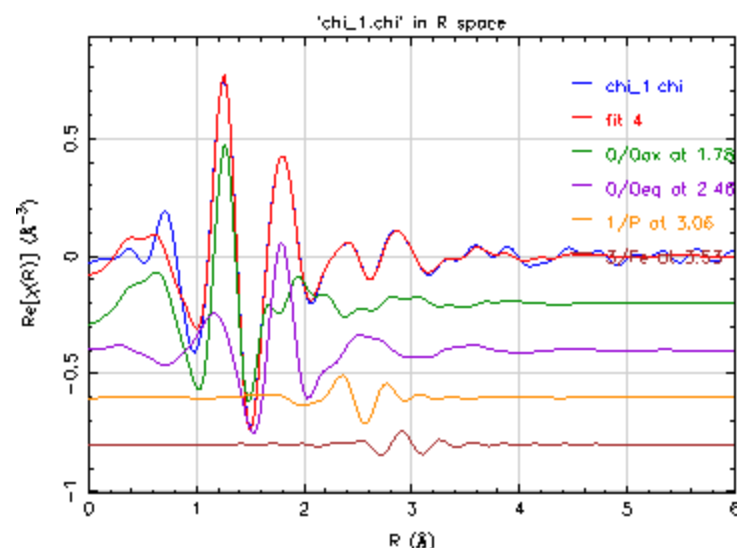
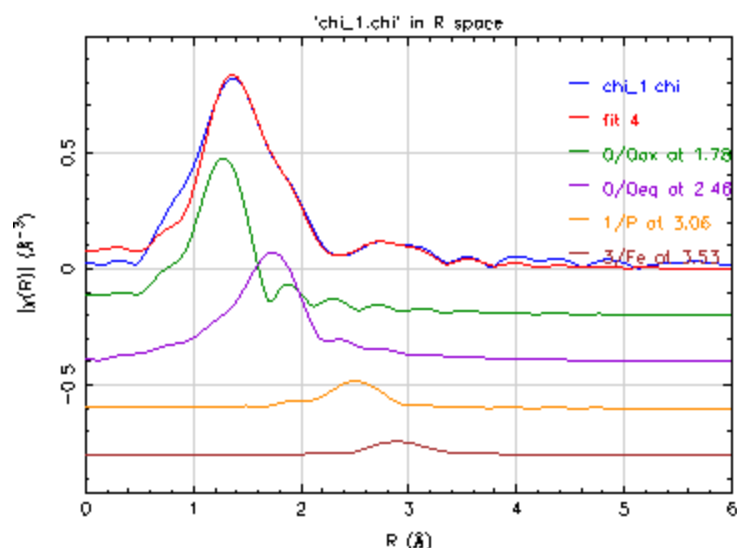
Signals became broad and unrealistic

Test data for P and Fe shells



- Place **P** and **Fe** shells in a “good” spot
 - set parameters – no fitting
 - monitor results and fit spectra

Fit Results using P and Fe shells



Artemis palettes

Results from the last fit

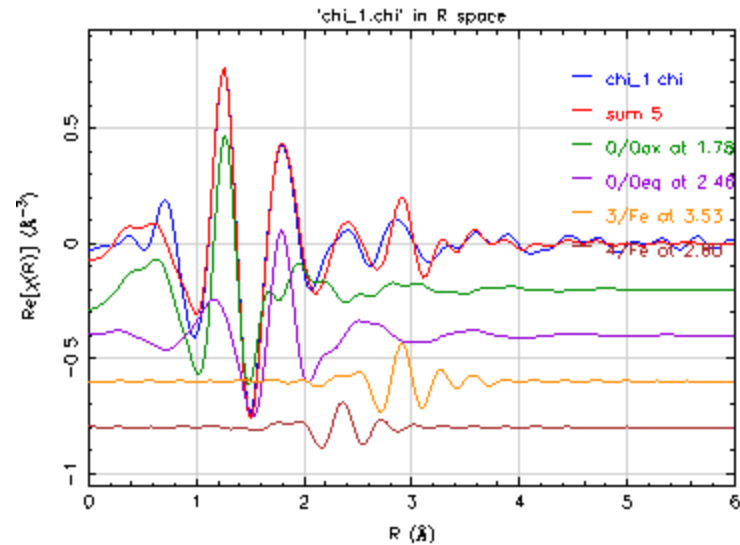
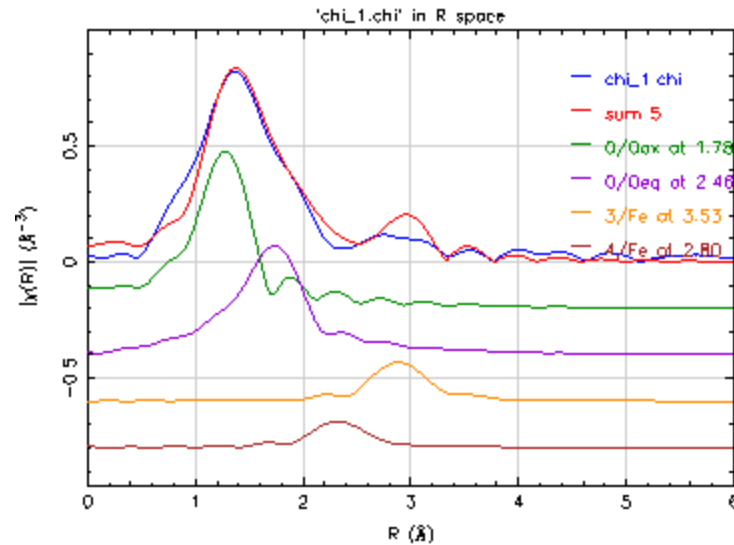
R-factor for this data set = 0.00264

path	degen	amp	sigma ²	e0	reff	delta_R	R
"FEFF0: Oax at 1.78"	1.00000	2.000	0.00351	-1.12310	1.75510	0.02066	1.77576
"FEFF0: Oeq at 2.46"	1.00000	4.615	0.00941	-1.12310	2.46160	-0.17609	2.28551
"FEFF0: U-Oax1-U-Oax1"	1.00000	2.000	0.01405	-1.12310	3.51020	0.04132	3.55152
"FEFF0: U-Oax1-Oax2"	1.00000	2.000	0.00702	-1.12310	3.51580	0.04132	3.55712
"FEFF0: U-Oax1-U-Oax2"	1.00000	2.000	0.00351	-1.12310	3.51580	0.04132	3.55712
"FEFF1: P at 3.06"	1.00000	0.835	0.00398	-1.12310	3.05550	0.00987	3.06537
"FEFF3: Fe at 3.53"	1.00000	0.276	0.00139	-1.12310	3.52570	-0.12876	3.39694

EXAFS Parameters

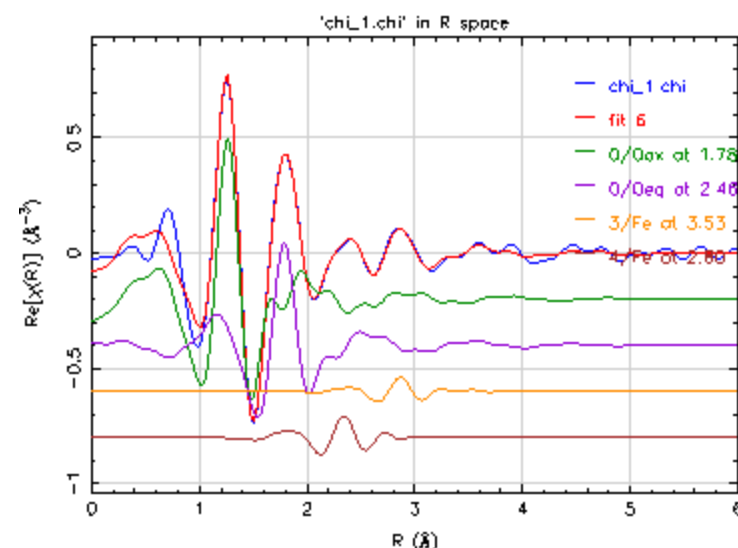
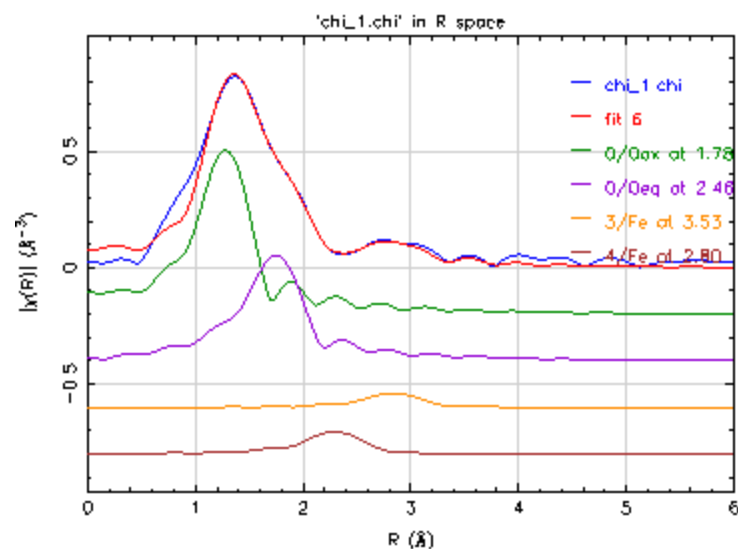
σ^2 -values	-
Distances	+
Coordination numbers	+
ΔE -value	+

Test data for Fe and Fe shells



- Place Fe and Fe shells in a “good” spot
 - set parameters – no fitting
 - monitor results and fit spectra

Fit Results using Fe and Fe shells



Artemis palettes

feffit Results Files Messages Echo Journal Properties

Results from the last fit

Column view Save Dismiss

R-factor for this data set = 0.00254

path	degen	amp	sigma ²	e0	reff	delta_R	R
"FEFF0: Oax at 1.78"	1.00000	2.000	0.00320	-0.59470	1.75510	0.01998	1.77508
"FEFF0: Oeq at 2.46"	1.00000	3.235	0.00594	-0.59470	2.46160	-0.17897	2.28263
"FEFF0: U-Oax1-U-Oax1"	1.00000	2.000	0.01280	-0.59470	3.51020	0.03995	3.55015
"FEFF0: U-Oax1-Oax2"	1.00000	2.000	0.00640	-0.59470	3.51580	0.03995	3.55575
"FEFF0: U-Oax1-U-Oax2"	1.00000	2.000	0.00320	-0.59470	3.51580	0.03995	3.55575
"FEFF3: Fe at 3.53"	1.00000	0.670	0.00830	-0.59470	3.52570	-0.16117	3.36453
"FEFF4: Fe at 2.80"	1.00000	0.669	0.00830	-0.59470	2.80090	0.03782	2.83872

EXAFS Parameters

σ^2 -values

+

Distances

+

Coordination
numbers

+

ΔE -value

+

Comparison of Models

Artemis

File Edit GDS Data Sum Fits Theory Paths Plot Help

Current project: D:\Documents and Settings\E446095\Desktop\ArtemisTalk\artemis1-TestPaths.apj

Examine log files

Current fit: fit Fe Fe

Fits

- fit C Fe
- sum 2
- sum 3
- fit P Fe
- sum 5
- fit Fe Fe

Choose a parameter

Statistical parameters

Get parameters from Guess, Def, Set list

Parameter report

Calculations

- ☒ Compute the average value
- ☒ Fit Einstein temp. to sigma² values

Absorber: ☐ Scatterer: ☐

☒ Prefer R-factor

☐ Prefer reduced chi-square

☒ Show y=0 in plot

Quick summaries of selected fits

Select all

Clear selection

Document: Log viewer

Loaded parameter list from GDS page

Data & Paths

Guess, Def, Set

- chi_1.chi
 - Fit
 - fit C Fe
 - sum 2
 - fit P Fe
 - sum 5
 - fit Fe Fe
 - FEFF0
 - Oax at 1.78
 - Oeq at 2.46
 - C at 2.85
 - U-Oax1-U-Oax1
 - U-Oax1-Oax2
 - U-Oax1-U-Oax2
 - FEFF1
 - P at 3.06
 - FEFF3
 - Fe at 3.53
 - FEFF4
 - Fe at 2.80

Fit

Plot selected groups in

k R q

Plotting options

0 1 2 3 kw

Main Indic Traces

Plot in R: ☒ Magnitude

☒ Real part

☒ Imaginary part

Plot in q: ☒ Magnitude

☒ Real part

☒ Imaginary part

☒ Window

☒ Background

☒ Residual

kmin: 0 kmax: 15

Rmin: 0 Rmax: 6

qmin: 0 qmax: 15

Document: Plotting

Quick summary

Artemis palette

Messages from Artemis

Save buffer to file

Dismiss

Project title : Fitting chi.chi

Comment : Sum #1

Figure of merit : 1

Fitting statistics

- Number of independent points : 12.251953125
- Number of variables : 12
- Chi-square : 1024.074456168
- Reduced chi-square : 4064.54377971
- R-factor : 0.002032495
- Measurement uncertainty (k) : 0.000141141
- Measurement uncertainty (R) : 0.000261597

Guess parameters

- eO1 = -8.7936210 +/- 27.0349090 (guessed as 1.202347 (3.389124))
- deloax = -0.0051730 +/- 0.0784490 (guessed as 0.026478 (0.019777))
- ssaox = 0.0038640 +/- 0.0023150 (guessed as 0.002833 (0.000755))
- ssoeq = 5.7190560 +/- 12.7930550 (guessed as 2.680084 (0.982222))
- deloeq = -0.2198580 +/- 0.1225970 (guessed as -0.169572 (0.021928))
- ssoeq = 0.0189370 +/- 0.0187410 (guessed as 0.004189 (0.003290))
- ndeo = 0.0660730 +/- 121.4045300 (guessed as 0.395266 (0.219553))
- delte2 = -0.2621230 +/- 0.2376720 (guessed as -0.144064 (0.051333))
- ssate2 = 0.0398700 +/- 0.1009870 (0.0050)
- ss = 21.8964850 +/- 216.6230520 (1.0000)
- delc = 0.0121930 +/- 0.1461970 (0.0000)
- ss = 0.0306560 +/- 0.1611940 (0.0030)

Project title : Fitting chi.chi

Comment : Sum #1

Parameter Report

Artemis palette

Messages from Artemis

Save buffer to file

Dismiss

Project title : Fitting chi.chi

Comment : Sum #1

report on "Statistical parameters"

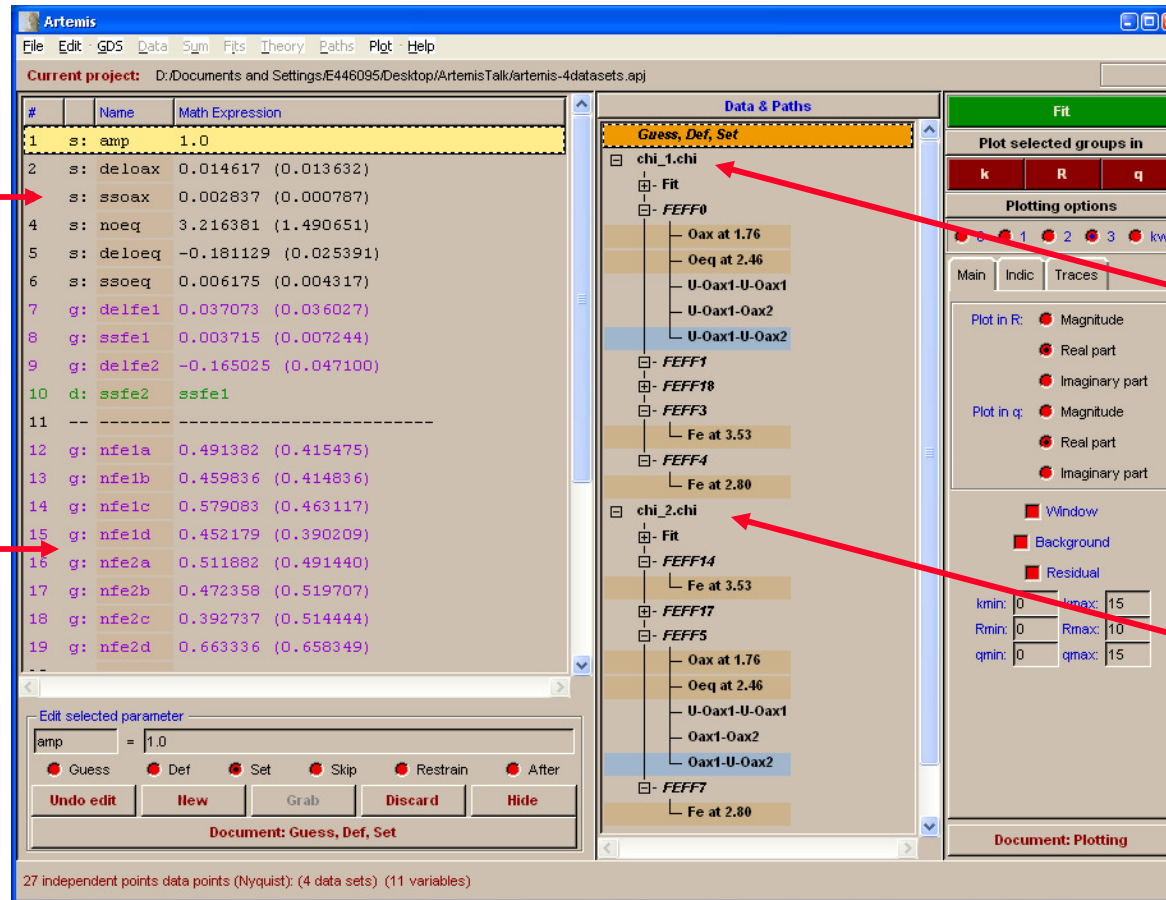
#	fit	FOM	R-factor	Reduced chi-square	Chi-square	ovar	ndp
1	fit C Fe	1	0.0020	4064.544	1024.074	12	12
4	fit P Fe	4	0.0026	7594.168	1913.374	12	12
6	fit Fe Fe	6	0.0025	1305.861	1634.877	11	12

- Models are saved in Artemis and can be compared or re-instated later

Multiple data set fit

Common
variables
for all 4
data sets

variables
for each
data set



Data set 1

Data set 2

- Fit 4 data sets
- Use K-weights of 1, 2 and 3
- Fit different N values for each data set
- Data series is needed to accurately determine the number of Fe atoms in the 2nd and 3rd shells

Modeling a Data Series

