Basics of EXAFS Data Analysis

Shelly Kelly
EXAFS Analysis

Honeywell

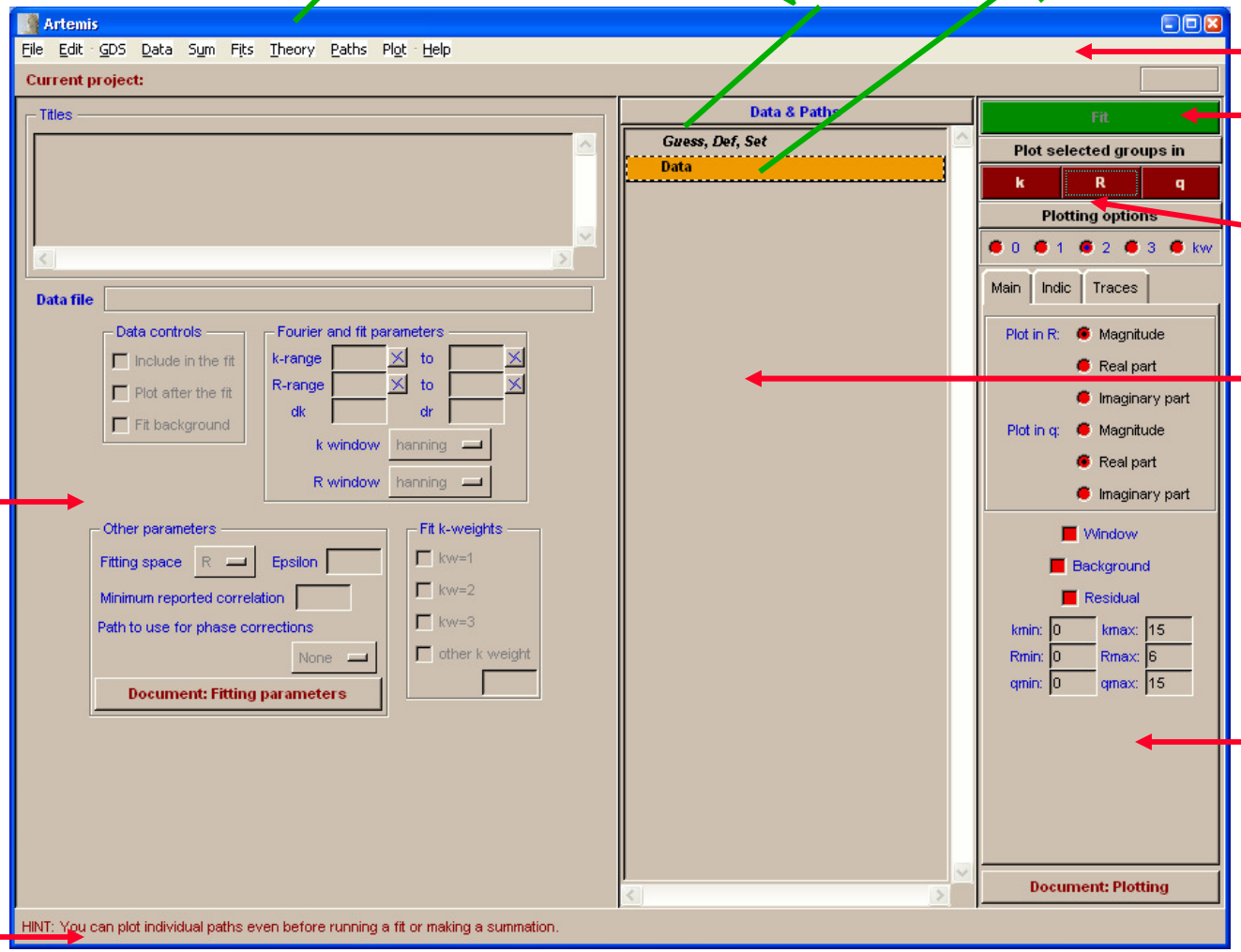
Data processing overview

UOP
A Honeywell Company

- **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



Project Name:

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

Echo Area:
Messages from Artemis

Menus:

Fit:
optimize variables

Plot and Do buttons:

Data and Paths:
Changes data display area

Plotting parameters

Reading in χ Data

A Honeywell Company

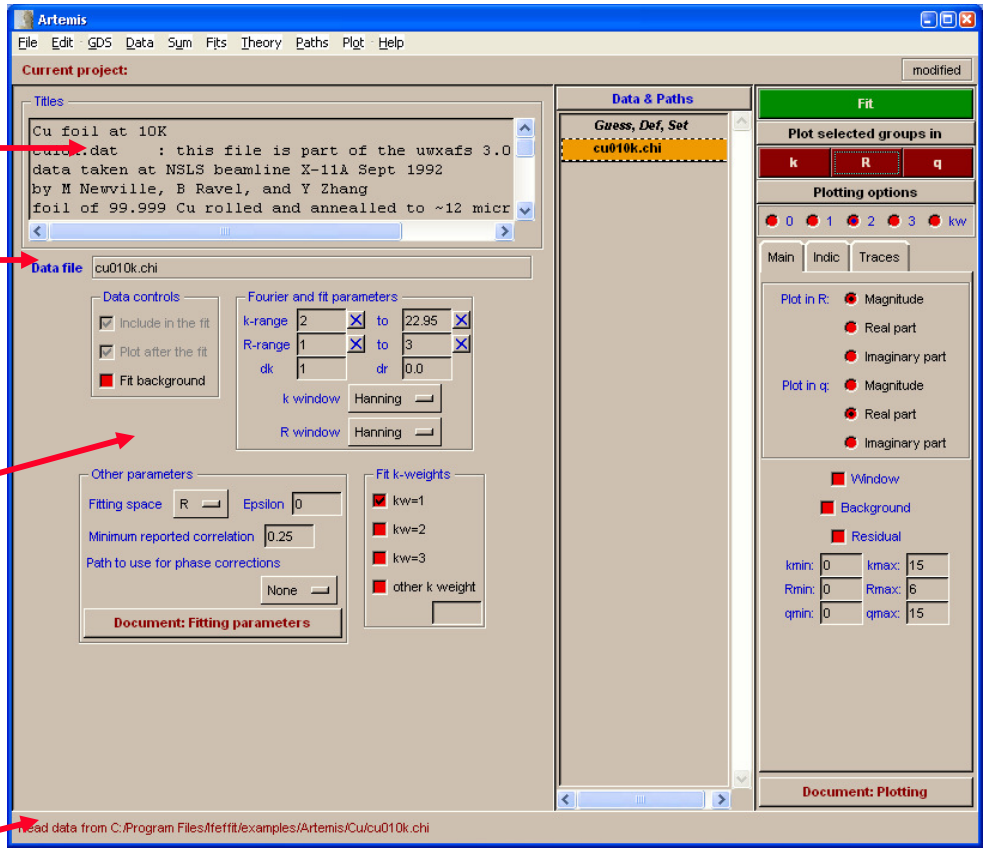
➢File: open data file: F:\Ifeffit\examples\Artemis\Cu\cu010k.chi

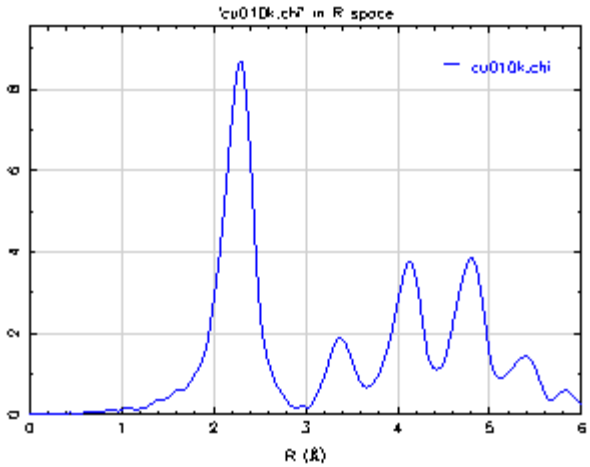
Title lines from data file

data file name

Fourier transform parameters

Message from Artemis



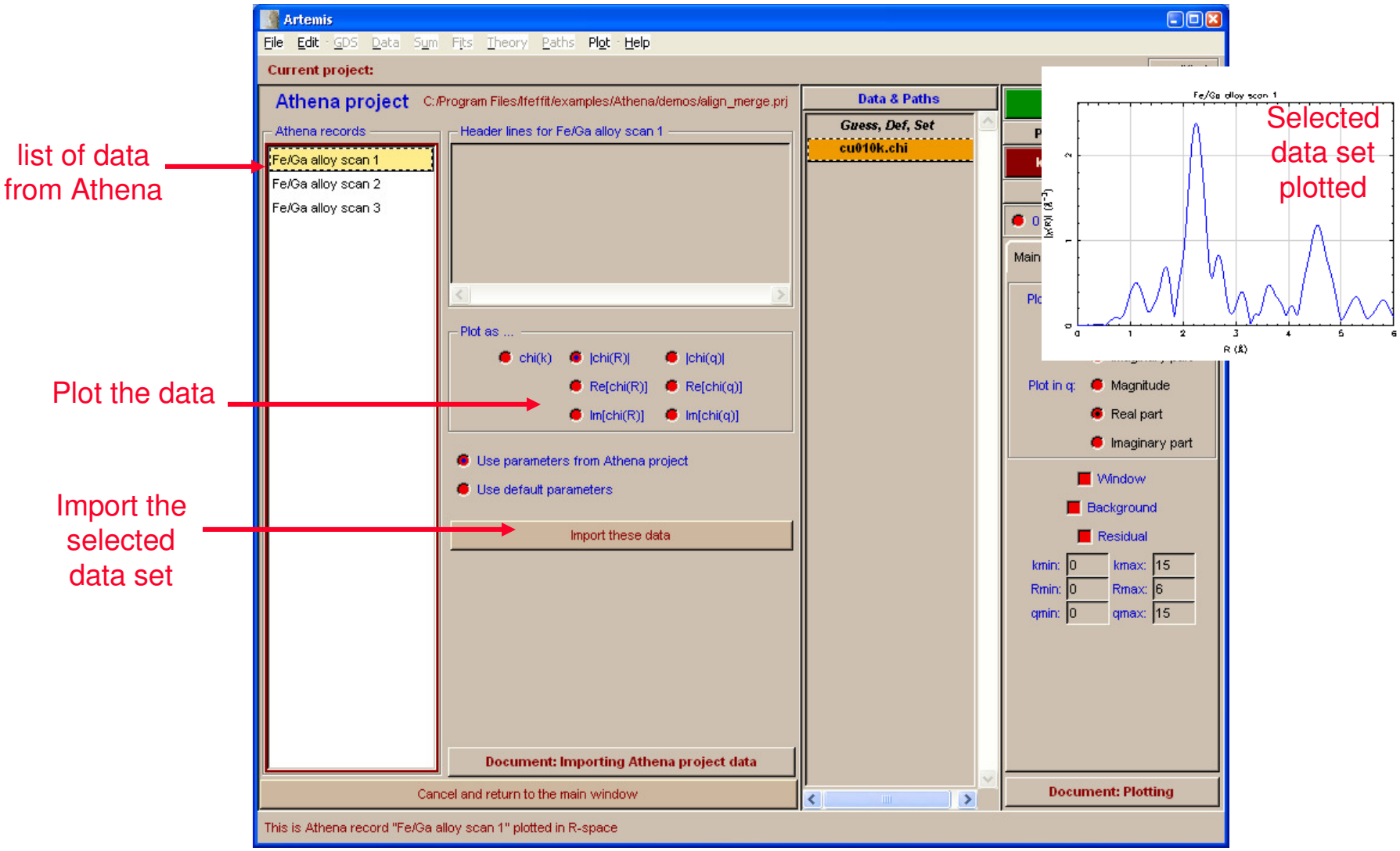


Data plotted in R-space

Reading Data from Athena Project

A Honeywell Company

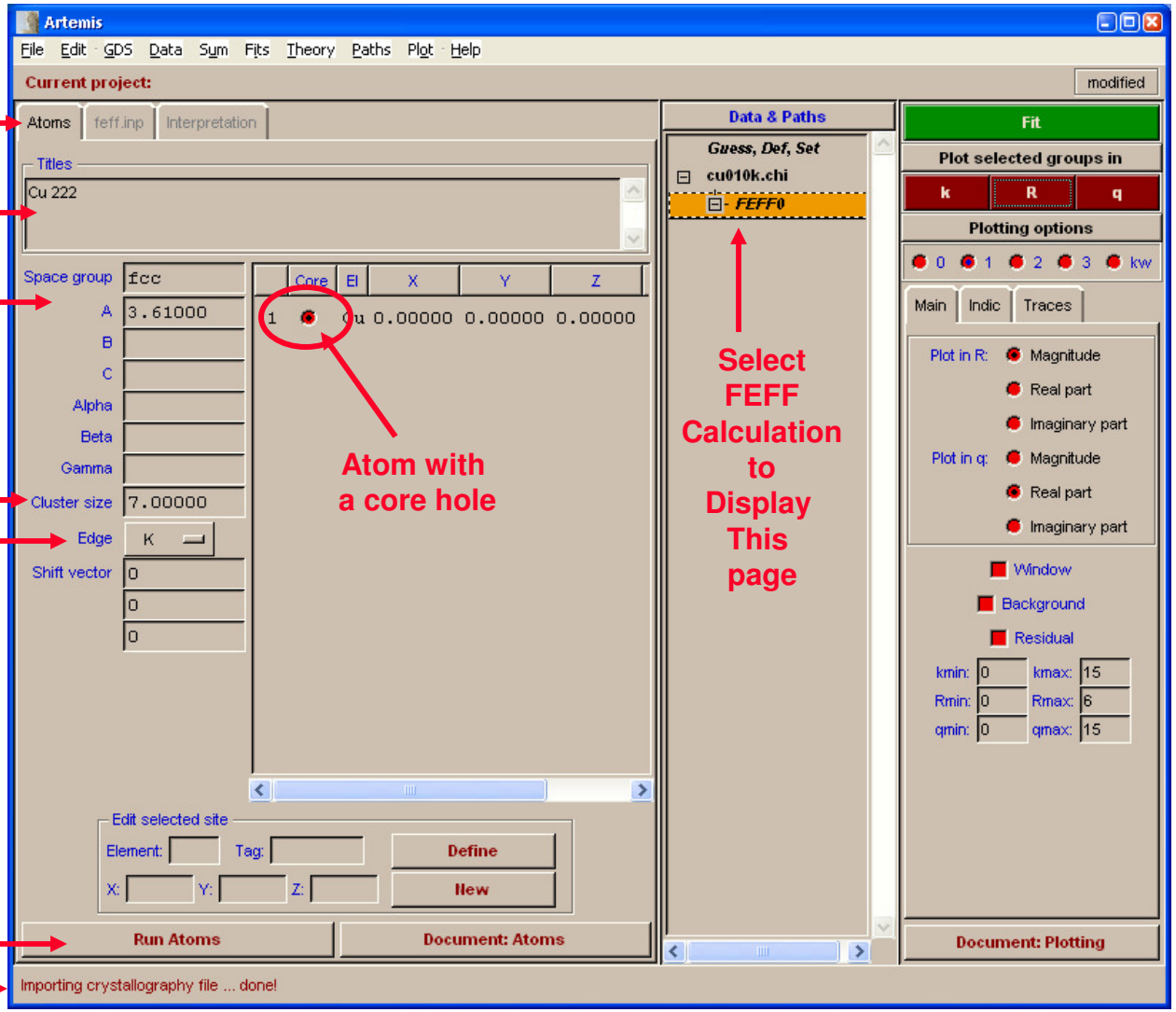
➢File: open data file: F:\Ifeffit\examples\Athena/demos/align_merge.prj



Atoms page

A Honeywell Company

➢File: open file: F:\Ifeffit\examples\Artemis\Cu\atoms.inp



Theory input page (feff.inp)

A Honeywell Company

➢Click “Run Atoms”

Feff.inp Tab

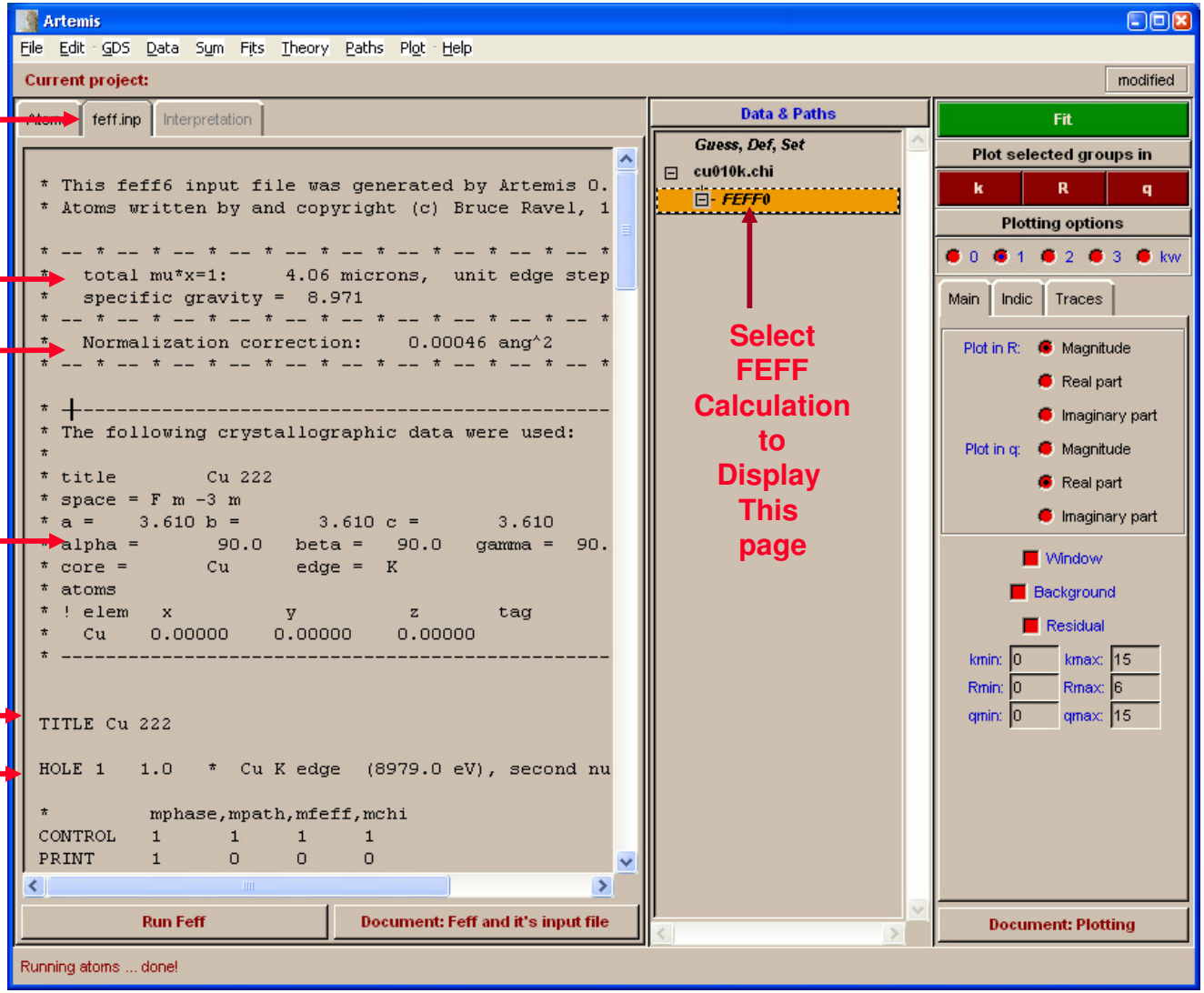
Absorption lengths

normalization correction

Crystallographic information From atoms.inp

title lines

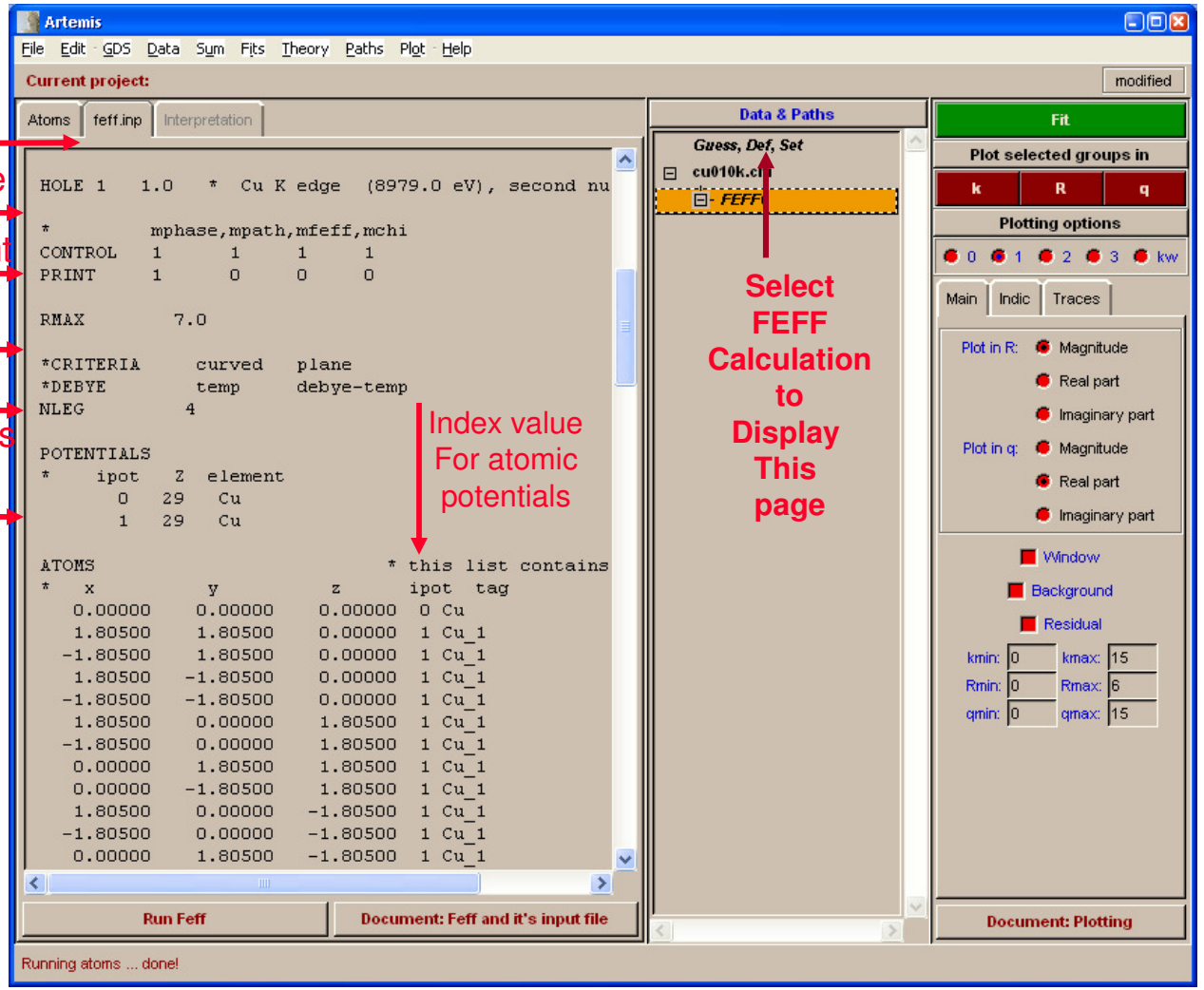
hole number



Theory input page (feff.inp)

A Honeywell Company

➢Scroll feff.inp page downward

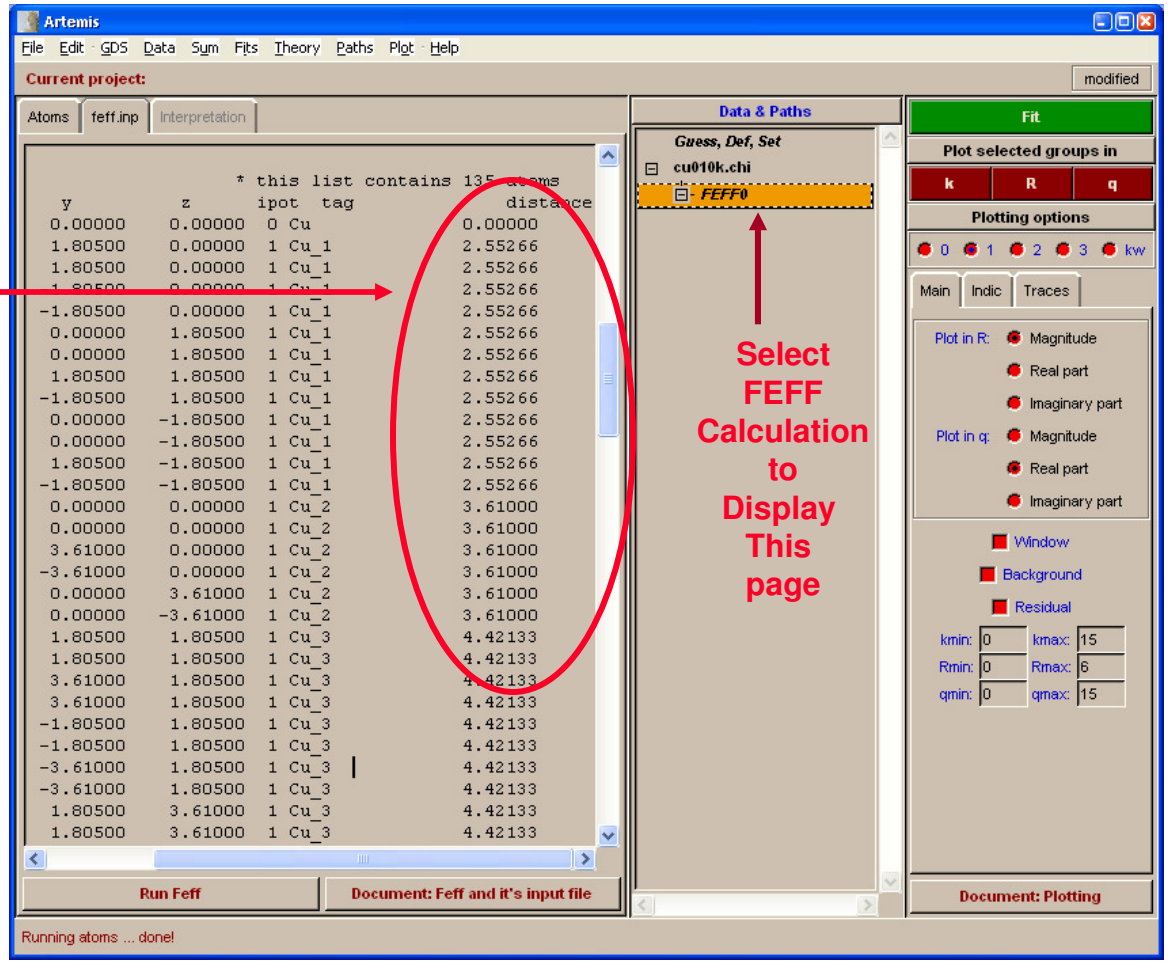


Theory input page (feff.inp)

A Honeywell Company

- Scroll feff.inp page downward and to the right

Check that the atomic Distances from the absorbing atom Are reasonable

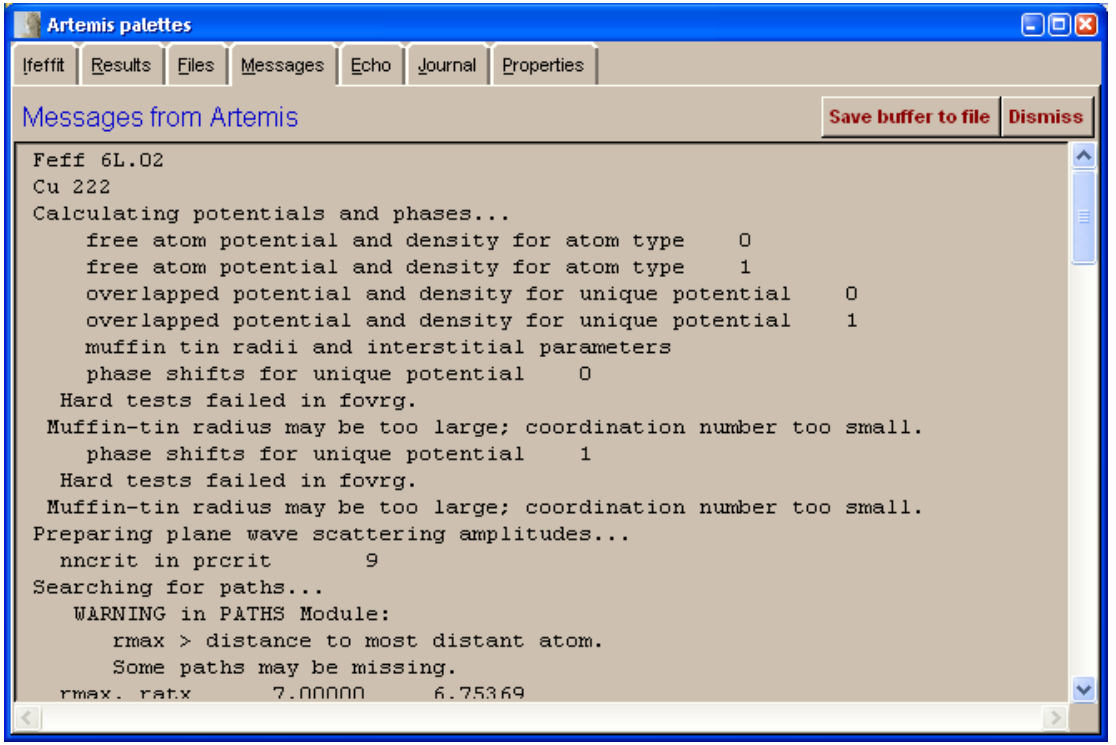


Running Feff

A Honeywell Company

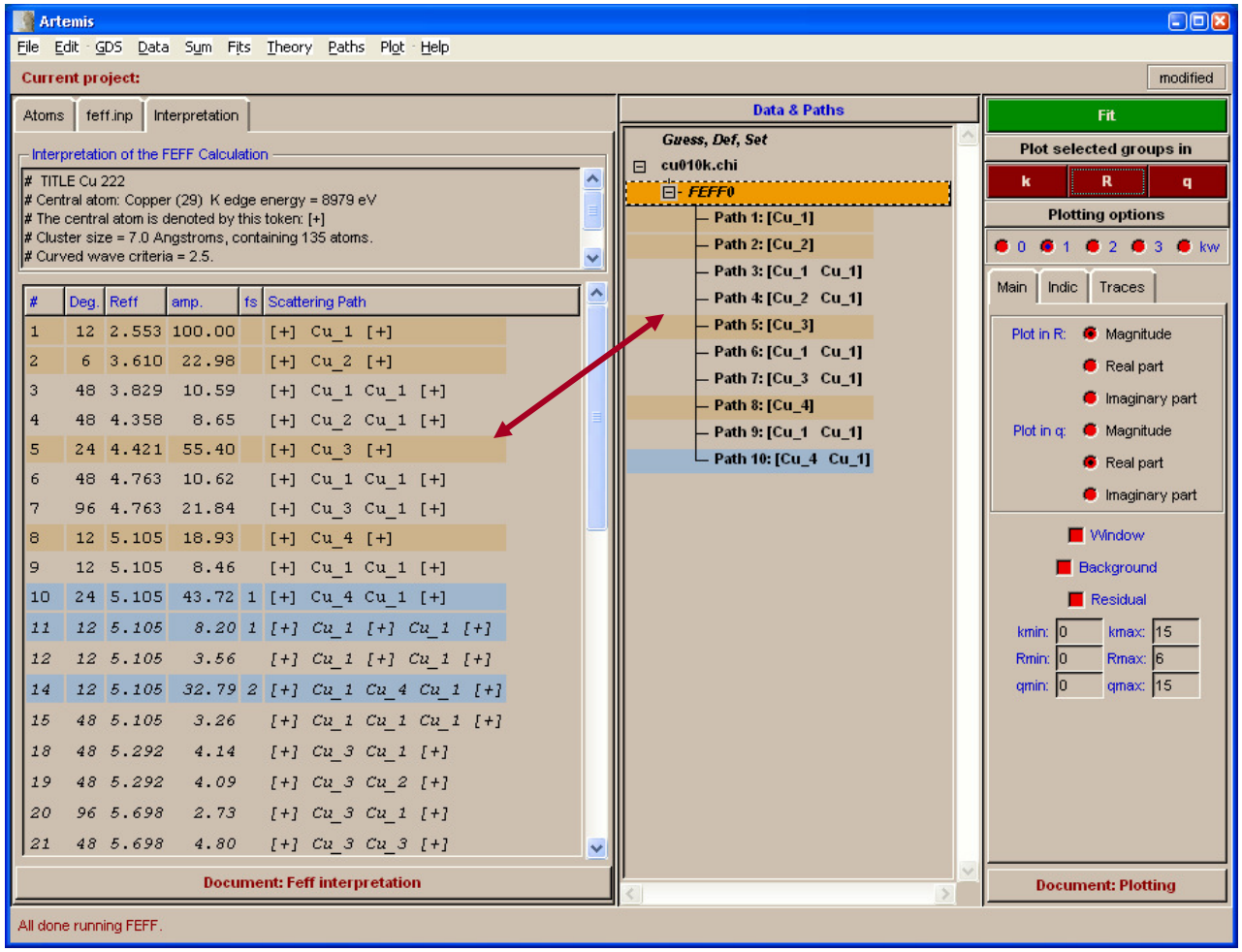
Text messages during Feff calculation

- **Artemis Palettes**
  - **Ifeffit: Shows the interface from Artemis to Ifeffit. Artemis is just a nice interface to Ifeffit. Ifeffit 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.**



Feff paths: feffxxxx.dat

- **Degen:** Degeneracy of the path (number of identical scattering paths)
- **reff:** Inital 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.

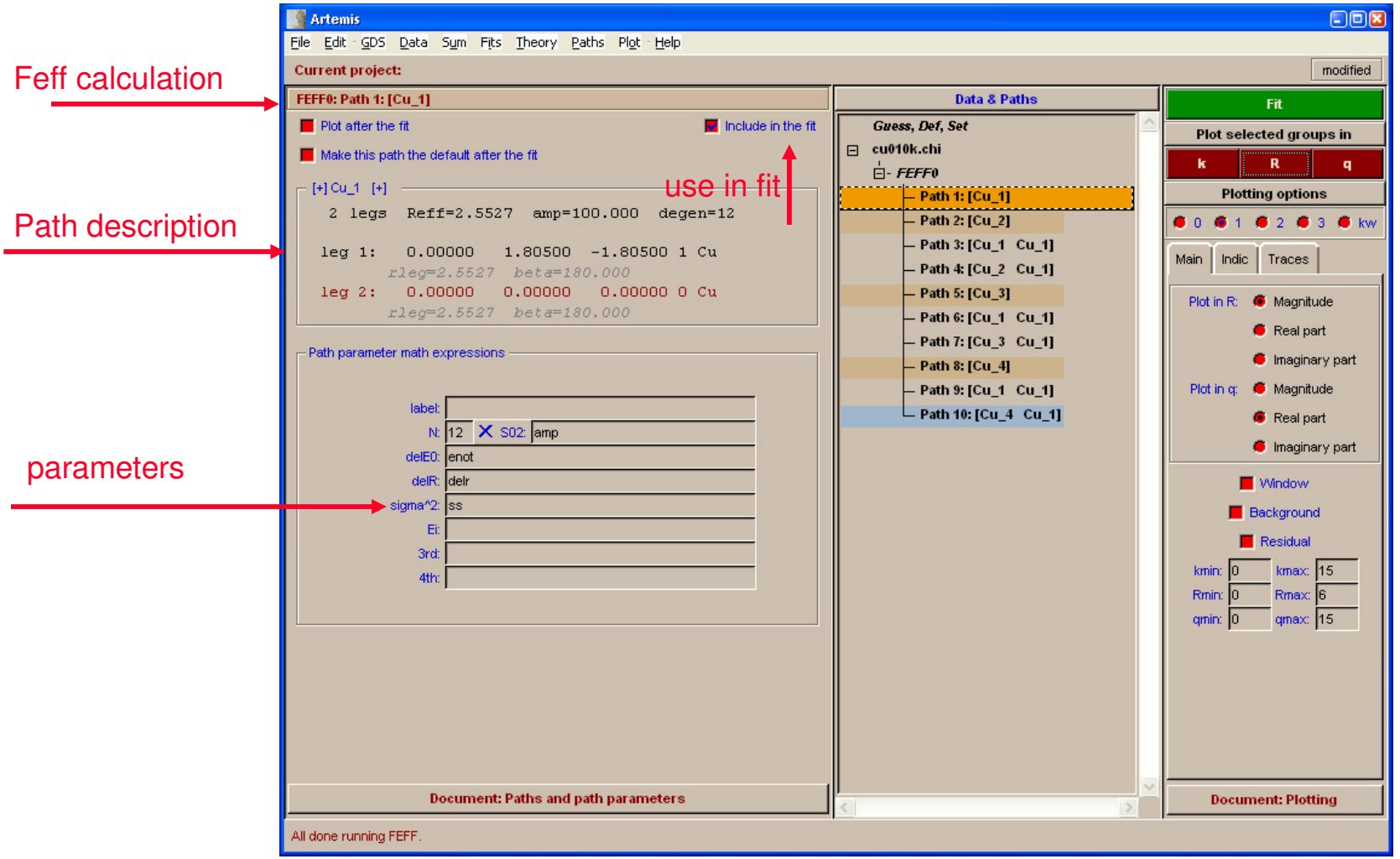


S I Zabinsky, J J Rehr, A Ankudinov, R C Albers and M J Eller. "Multiple-scattering calculations of X-ray-absorption spectra." Phys. Rev. B **52**(4): pp 2995-3009, 1995.

Path Description

A Honeywell Company

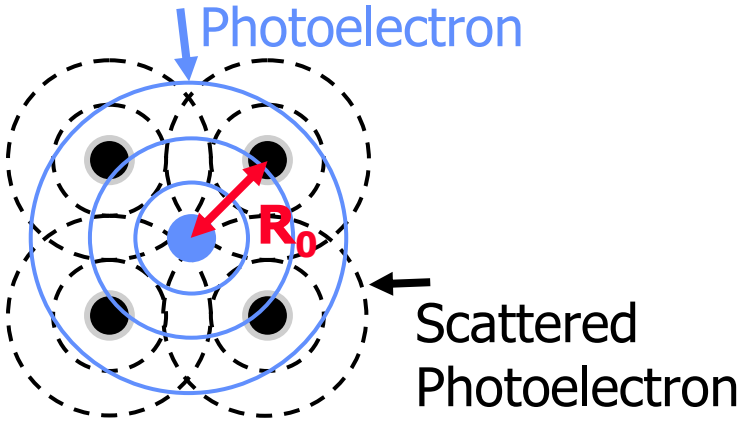
➢Click on Path1 in the Data & Paths list



The EXAFS Equation

UOP
A Honeywell Company

- E. A. Stern and S M Heald Basic principles and applications of EXAFS. Handbook of Synchrotron Radiaction. 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.



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

with each path written as:

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

$$R_i = R_0 + \Delta R$$

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

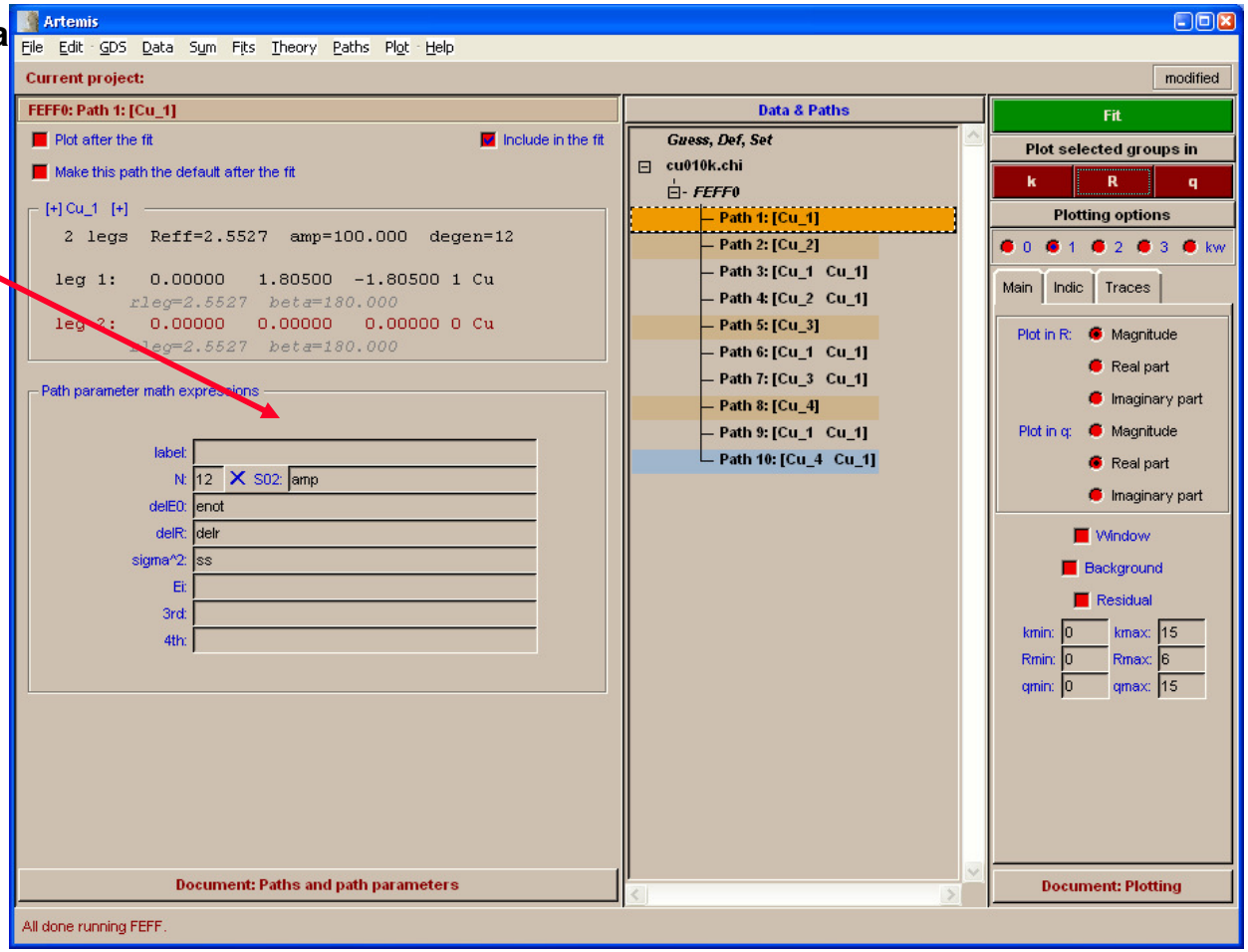
$F_i(k)$ effective scattering amplitude
$\varphi_i(k)$ effective scattering phase shift
$\lambda(k)$ mean free path
R_0 initial path length

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

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

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

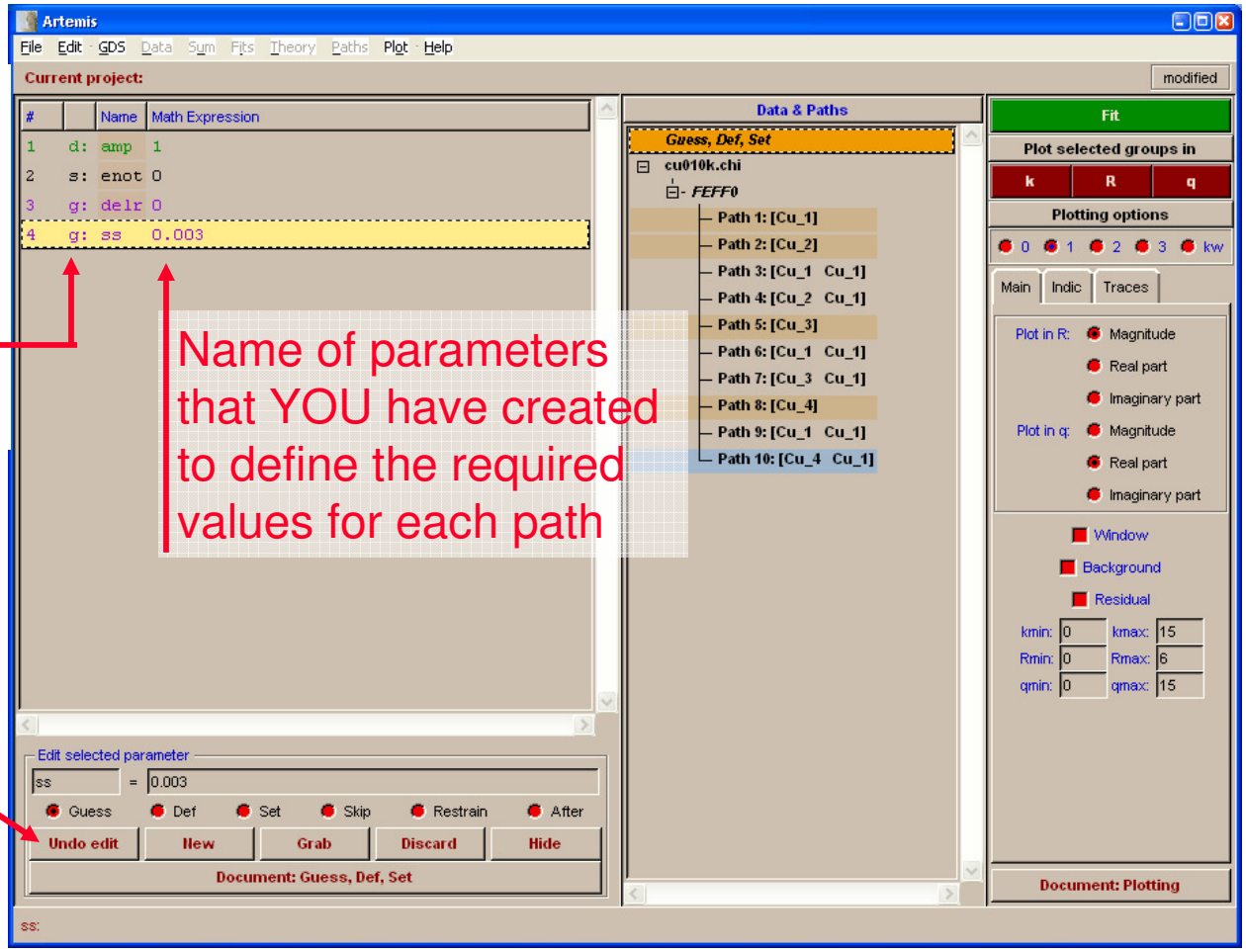
delR change in half-path length

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

A Honeywell Company

Artemis palettes

Ifeffit | Results | Files | Messages | Echo | Journal | Properties

Results from the last fit — Raw log file | Save | Dismiss

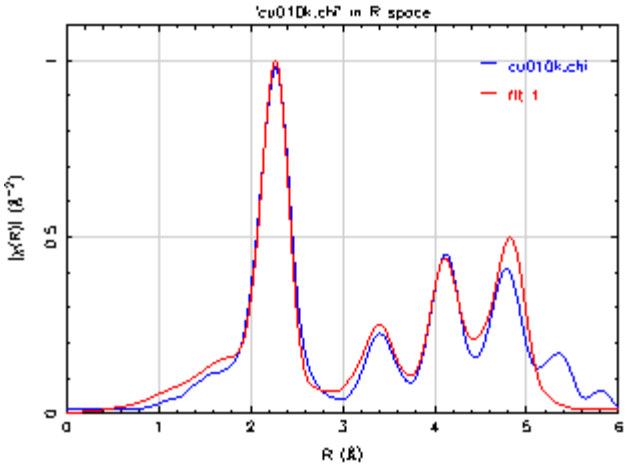
```
Project title    :  Fitting cu01Ok.chi
Comment          :  Fit #1
Prepared by      :
Contact          :
Started          :  12:38:31 on 26 June, 2009
This fit at      :  14:41:50 on 27 June, 2009
Environment      :  Artemis 0.8.013 using Windows XP, perl 5.008008, Tk 804.027, a
Data sets        :  "cu01Ok.chi"
Fit label        :  fit 1
Figure of merit  :  1

============================================================

Independent points           =      21.187500000
Number of variables          =       4.000000000
Chi-square                   =    1078.130989819
Reduced Chi-square           =      62.727621226
R-factor                     =       0.010391311
Measurement uncertainty (k)  =       0.000914479
Measurement uncertainty (R)  =       0.003911955
Number of data sets          =       1.000000000


Guess parameters +/- uncertainties  (initial guess):
  amp              =     0.8626890   +/-       0.0435050     (1.0000)
  enot             =     4.8357170   +/-       0.4306520     (0.0000)
  ss               =     0.0031660   +/-       0.0003500     (0.0030)
  alpha            =    -0.0030710   +/-       0.0010070     (0.0000)


Cor[illegible]bles:
                                 -->  0.8711
                                 -->  0.7818
All other correlations are below 0.25
```

Statistical quality of Fit

Initial guessed value

Your parameters

Best fit values with uncertainties

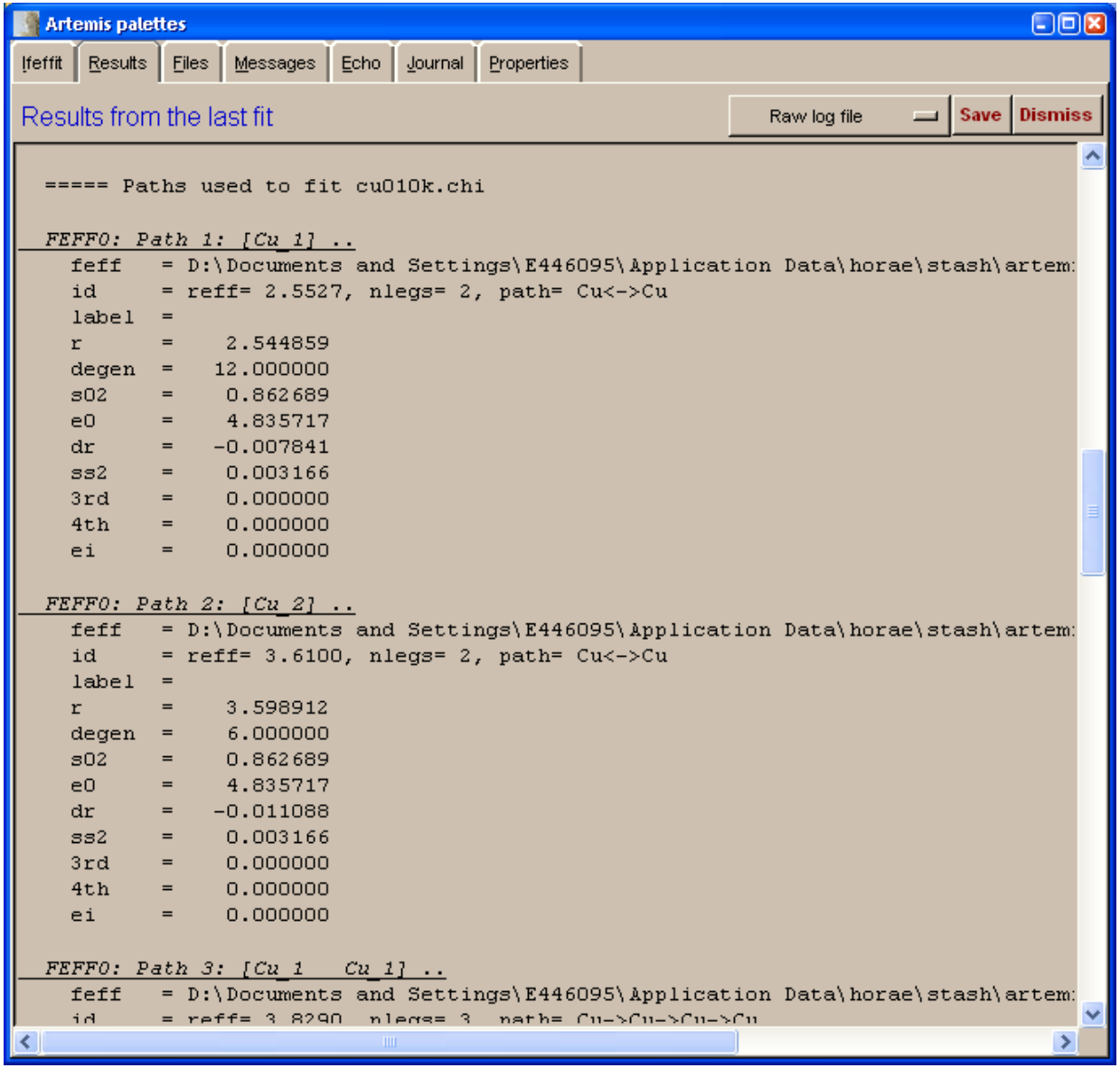


Fit Results

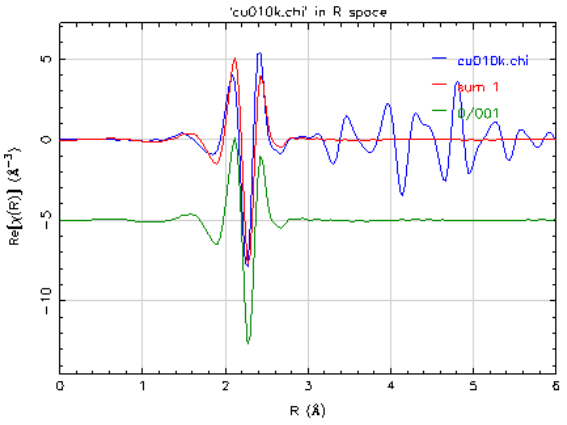
A Honeywell Company

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

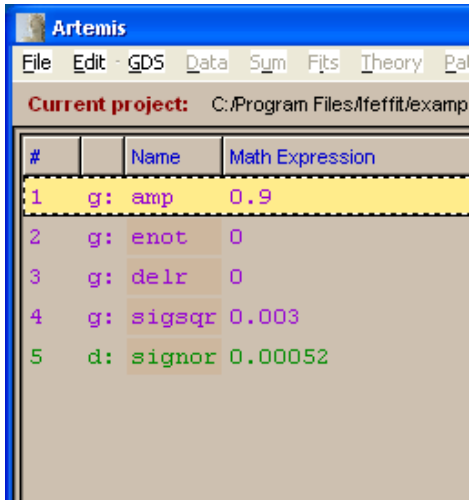
Used as a diagnostic tool when models do not work as expected



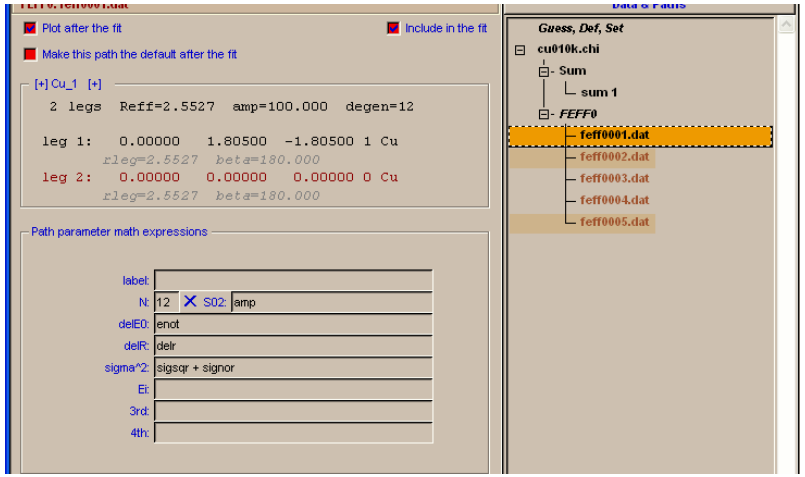
Example: Cu foil



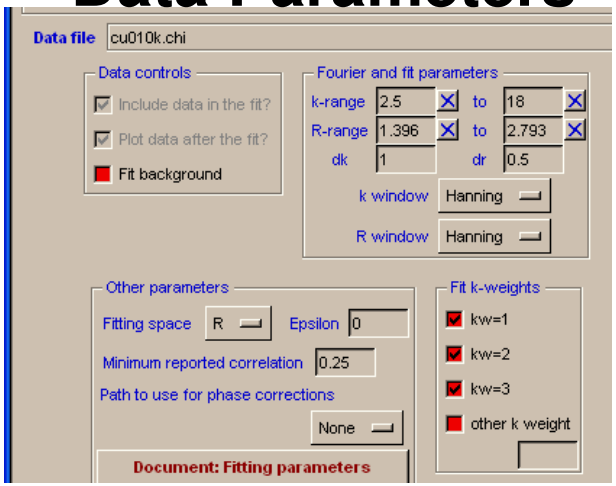
GSD Info



Path Info



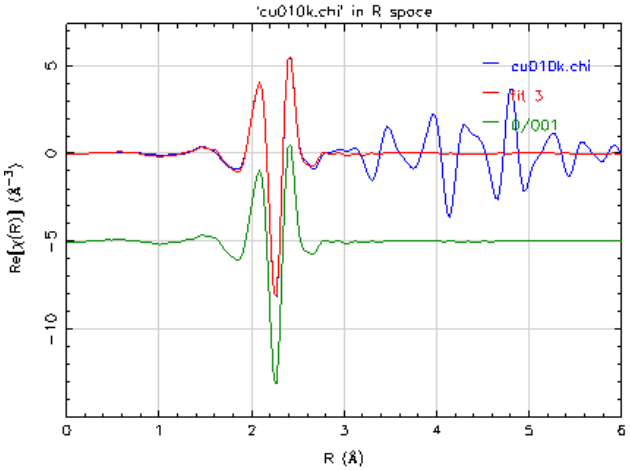
Data Parameters



- Example from c:\Program Files\Ifeffit\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

A Honeywell Company



Results Info

```
Independent points               =      13.579101562
Number of variables              =       4.000000000
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              =       1.000000000


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
```

GSD Info

Artemis

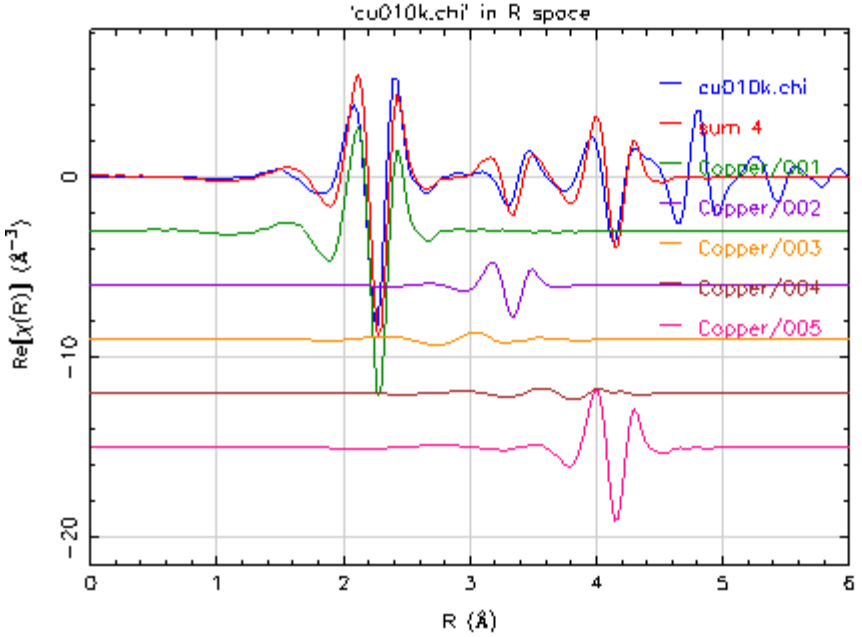
File Edit GDS Data Sum Fits Theory Paths Plot He

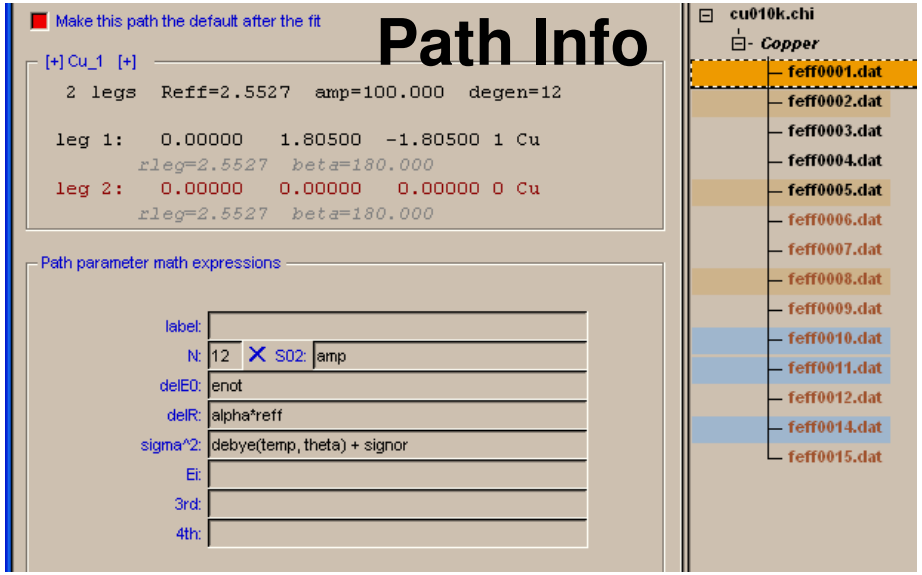
Current project: C:/Program Files/Ifeffit/examples/Artemis/Cu

#		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

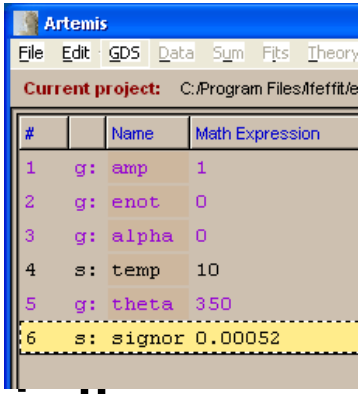
- Data and Model are in good agreement
- GSD values are reasonable

Cu: Three Shell Model



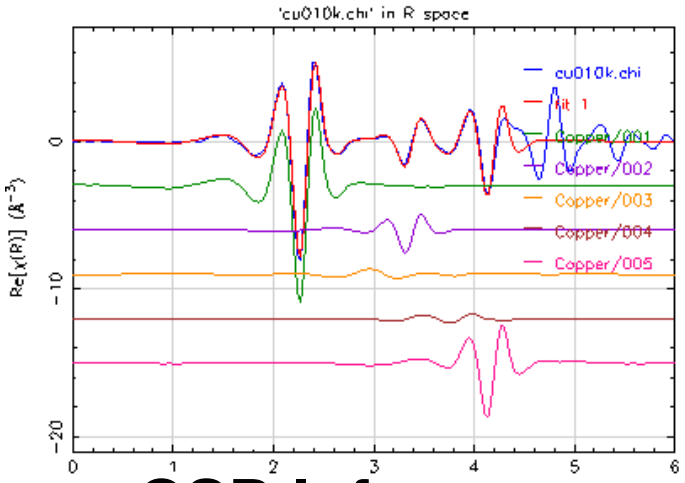


GSD Info

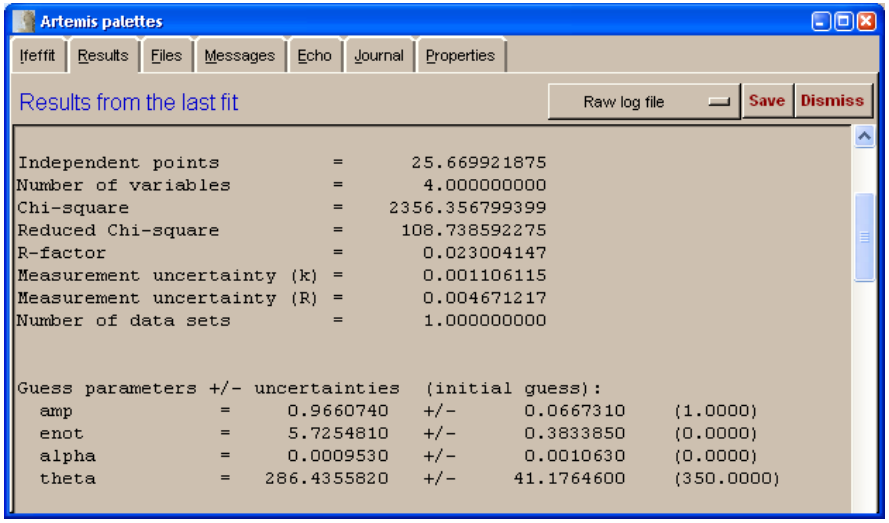


- Use alpha to define path lengths
- Use Debye temperature to define σ^2 values
- Each Single scattering path fits into a specific signal in the data

Fitting results for three shell fit to Cu



Results Info



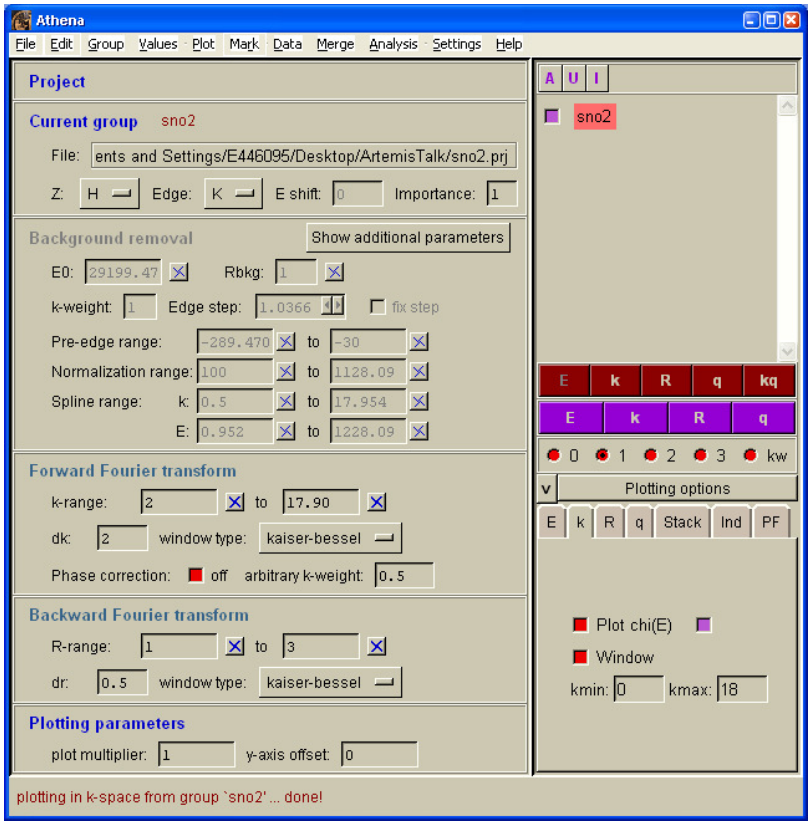
GSD Info

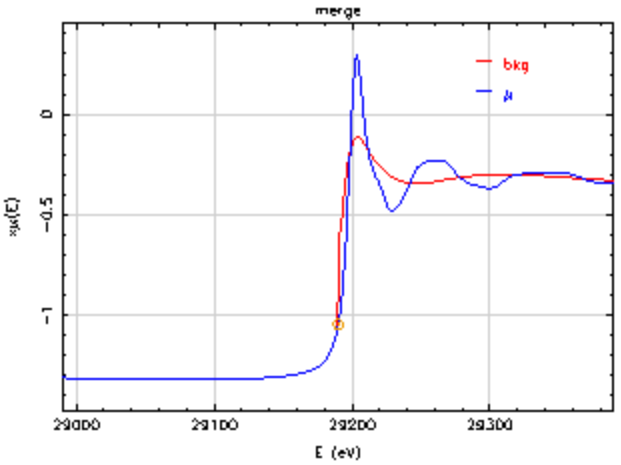
#		Name	Math Expression
1	g:	amp	0.966074 (0.066731)
2	g:	enot	5.725481 (0.383385)
3	g:	alpha	0.000953 (0.001063)
4	s:	temp	10
5	g:	theta	286.435582 (41.176460)
6	s:	signor	0.00052

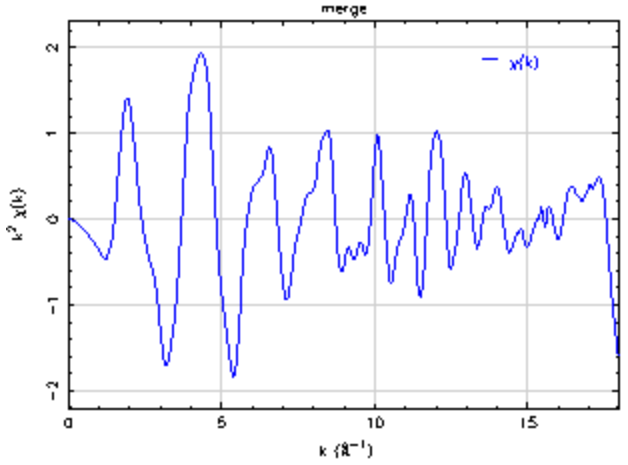
- There is more to this example on your computer
  - Modeling more shells and modeling temperature dependent spectra series

Example #2: Align SnO_2 EXAFS Spectra to Theory

A Honeywell Company







- **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

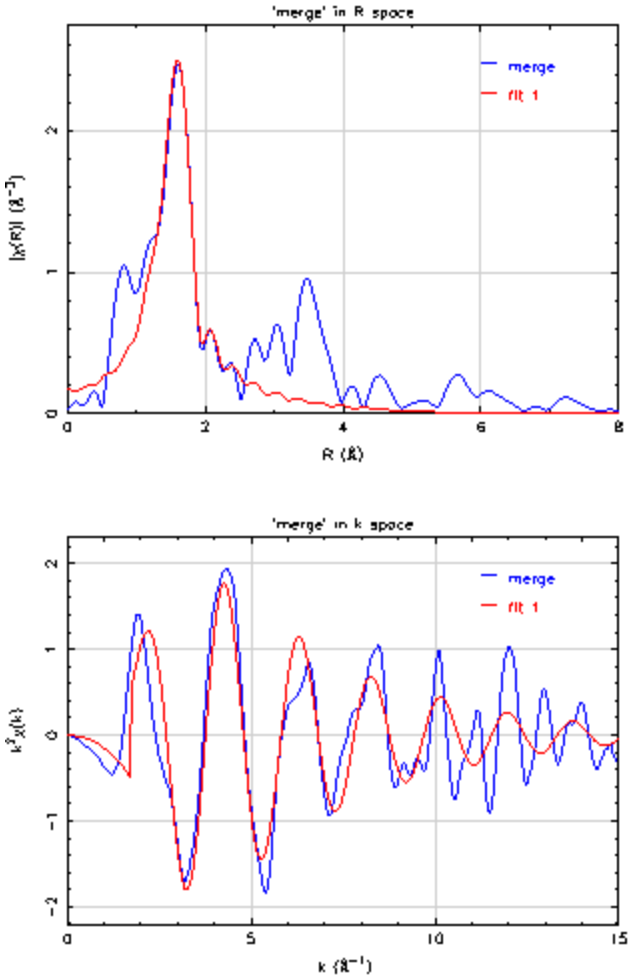
A Honeywell Company

Artemis palettes

Ifeffit | Results | Files | Messages | Echo | Journal | Properties

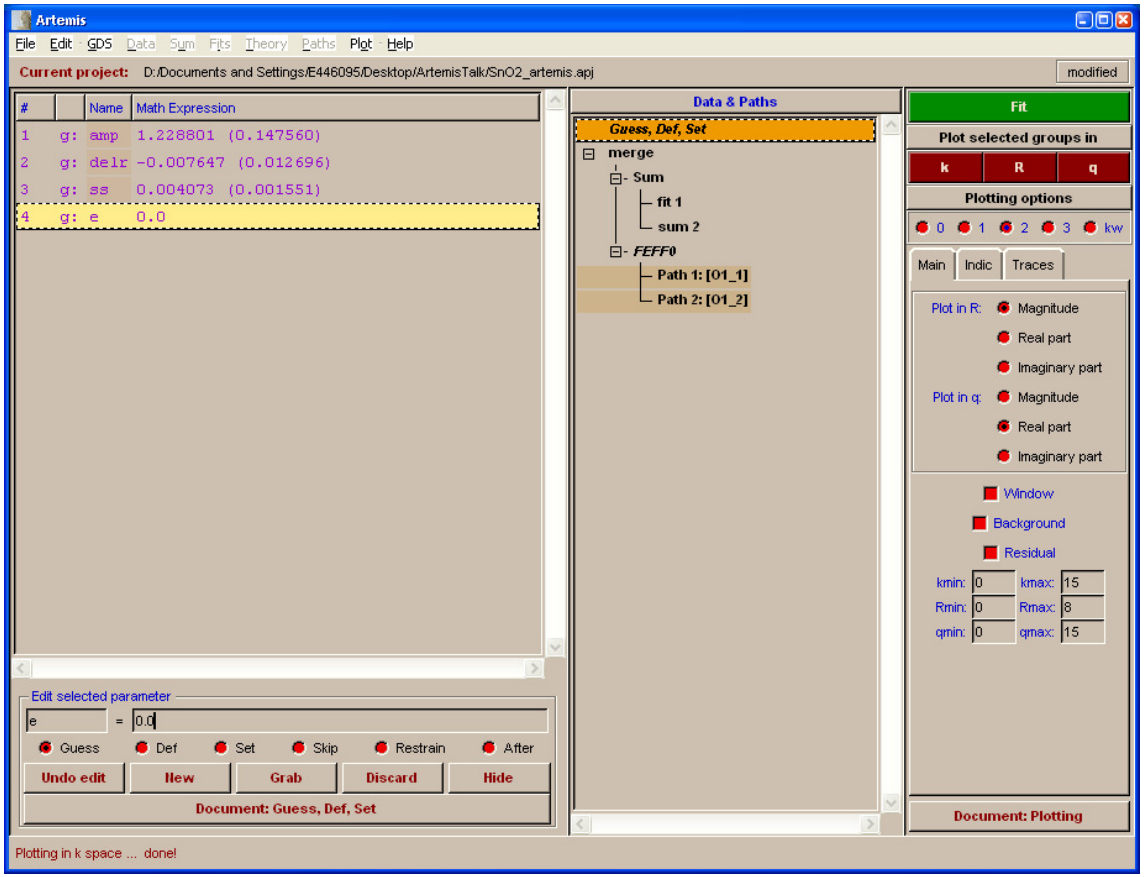
Results from the last fit — Raw log file — Save — Dismiss

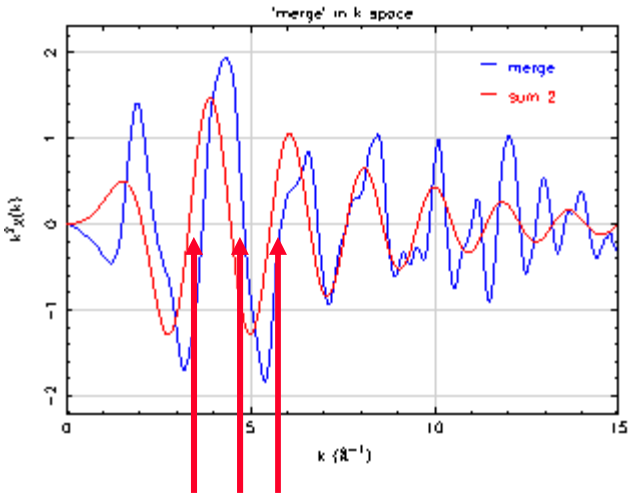
```
Project title   :  Fitting chi.chi
Comment         :  Fit #1
Prepared by     :  skelly@little.er.anl.gov
Contact         :
Started         :  09:28:09 on 11 May, 2004
This fit at     :  14:33:08 on 28 June, 2009
Environment     :  Artemis 0.8.013 using Windows XP, perl 5.008008, Tk 804.027, a
Data sets       :  "merge"
Fit label       :  fit 1
Figure of merit :  1

============================================================

Independent points           =      12.437500000
Number of variables          =       4.000000000
Chi-square                   =  144652.749867735
Reduced Chi-square           =   17144.029613954
R-factor                     =       0.063204981
Measurement uncertainty (k)  =       0.000180334
Measurement uncertainty (R)  =       0.000432656
Number of data sets          =       1.000000000


Guess parameters +/- uncertainties  (initial guess):
  amp             =     1.2288010   +/-       0.1475600     (1.0000)
  delr            =    -0.0076470   +/-       0.0126960     (0.0000)
  ss              =     0.0040730   +/-       0.0015510     (0.0000)
  e               =    11.5113960   +/-       1.6084920     (0.0000)


Correlations between variables:
        delr and e           -->  0.8451
         amp and ss          -->  0.8057
All other correlations are below 0.25
```



- **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 ΔE=0

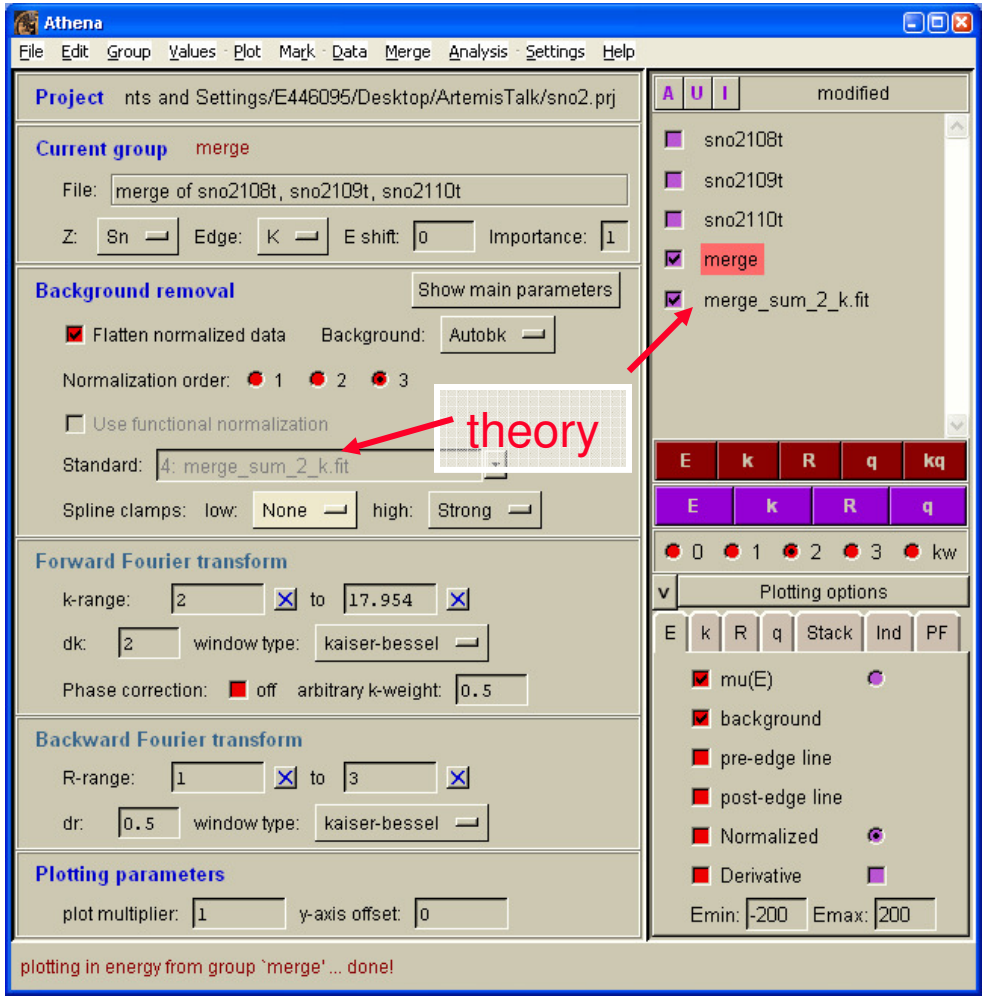


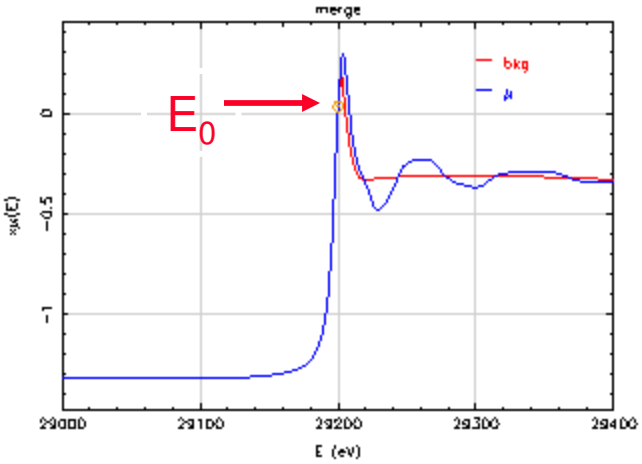


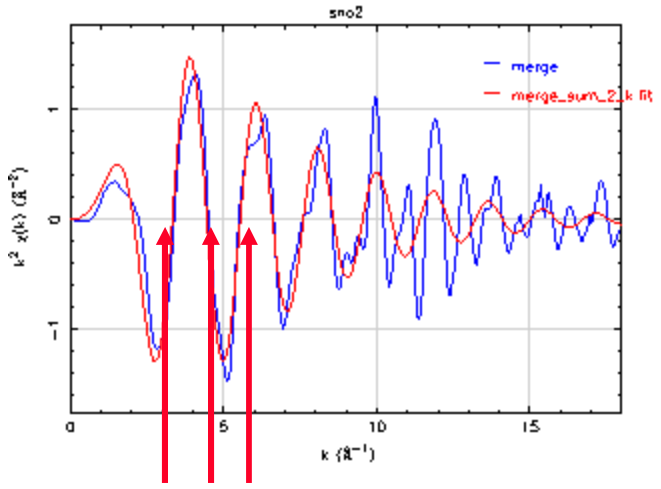
Data and theory are not aligned

- **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







- **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**

Data and theory are aligned

Fit to first shell with background adjusted

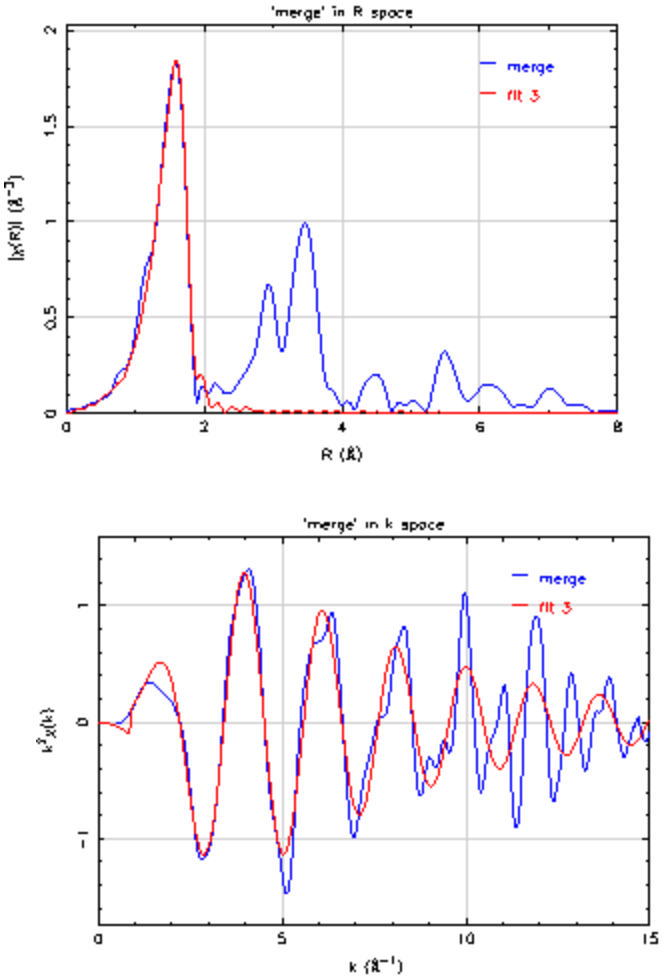
A Honeywell Company

Artemis palettes

Ifeffit | Results | Files | Messages | Echo | Journal | Properties

Results from the last fit — Raw log file — Save — Dismiss

```
Project title    :  Fitting chi.chi
Comment          :  Sum #1
Prepared by      :  skelly@little.er.anl.gov
Contact          :
Started          :  09:28:09 on 11 May, 2004
This fit at      :  14:49:08 on 28 June, 2009
Environment      :  Artemis 0.8.013 using Windows XP, perl 5.008008, Tk 804.027, a
Data sets        :  "merge"
Fit label        :  fit 3
Figure of merit  :  3

-------------------------------------------------------------

Independent points           =      19.875000000
Number of variables          =       4.000000000
Chi-square                   =    7550.041600728
Reduced Chi-square           =     475.593171699
R-factor                     =       0.033932590
Measurement uncertainty (k)  =       0.000292358
Measurement uncertainty (R)  =       0.001144697
Number of data sets          =       1.000000000


Guess parameters +/- uncertainties  (initial guess):
  amp             =     0.9586310   +/-      0.0716180    (guessed as 1.228801 (0
  delr            =    -0.0023340   +/-      0.0083500    (guessed as -0.007647 (
  ss              =     0.0023830   +/-      0.0010680    (guessed as 0.004073 (0
  e               =     2.8114190   +/-      0.8594790    (0.0000)


Correlations between variables:
       delr and e           -->  0.8136
        amp and ss          -->  0.7698
All other correlations are below 0.25
```

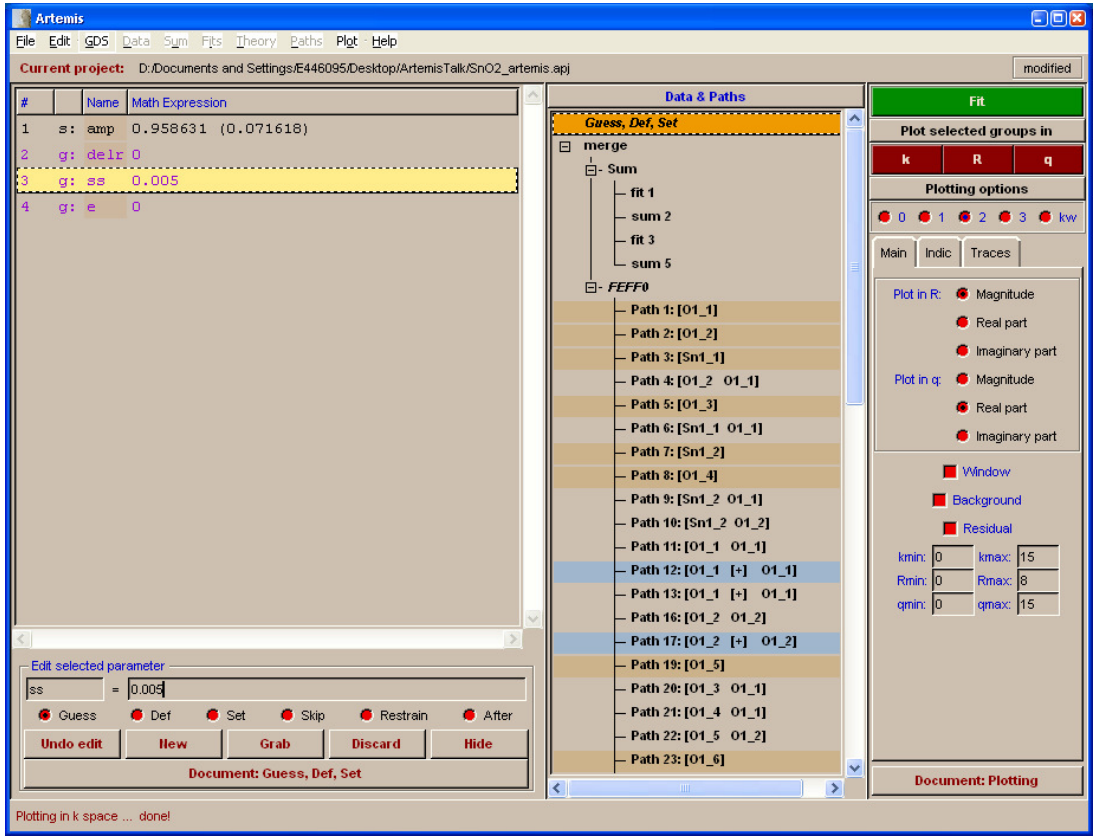


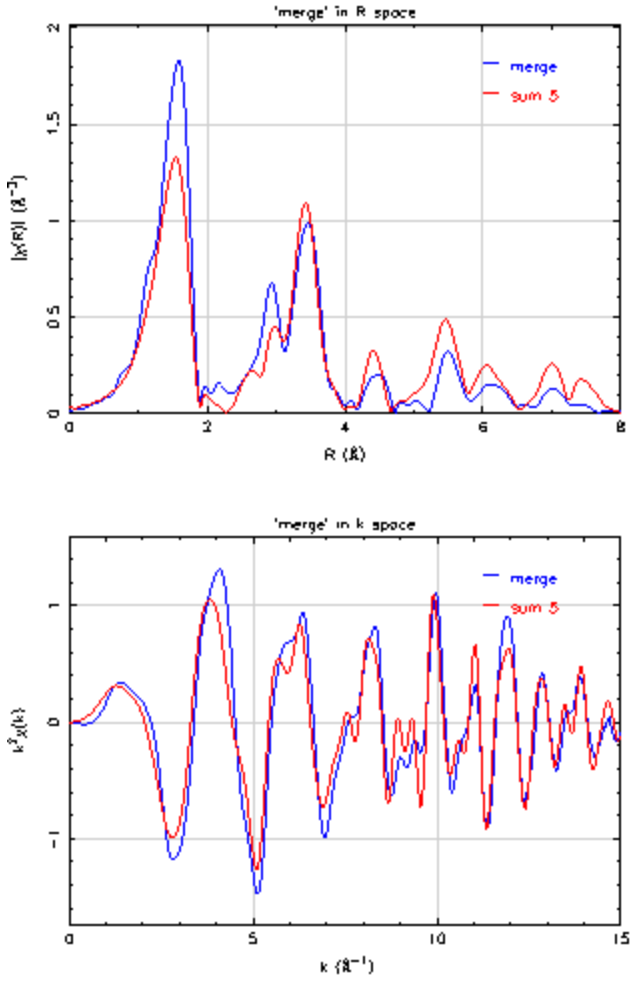
- **Read the chi(k) data back into Artemis and fit the first shell**

Example 3: Modeling a metal-oxide (SnO_2)

UOP
A Honeywell Company

- **Compare the sum of all 69 paths to the data**

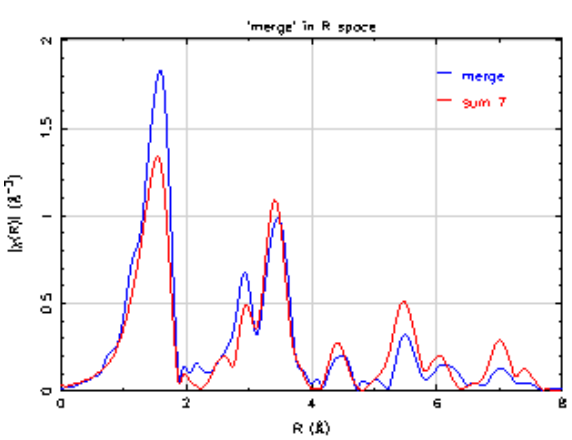


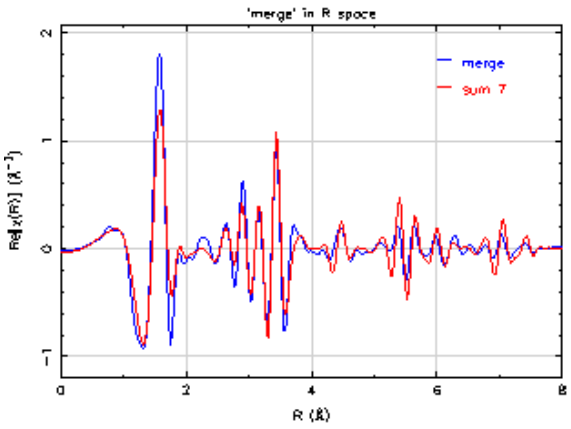


How many paths are required?

A Honeywell Company

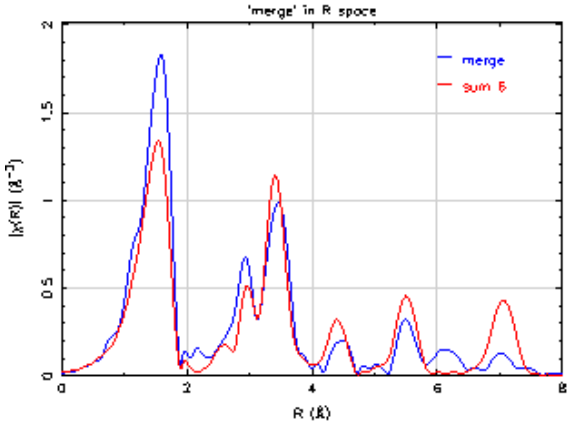
Minimum amplitude 5%
30 of 69 paths

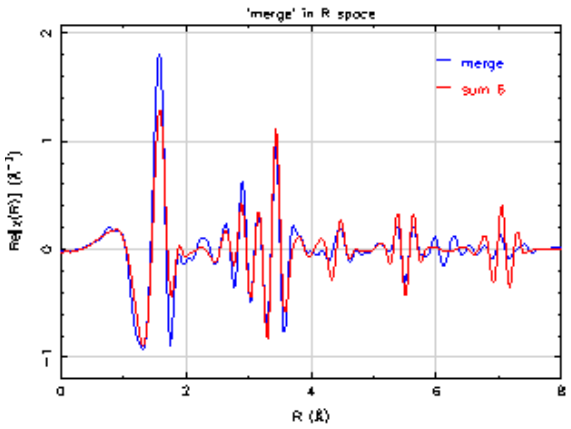




All data is present in model

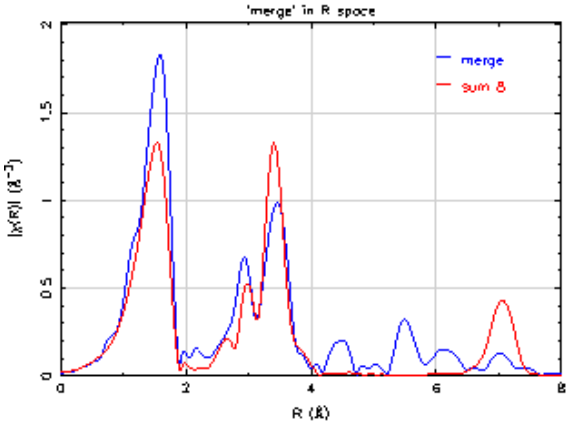
Minimum amplitude 10%
18 of 69 paths

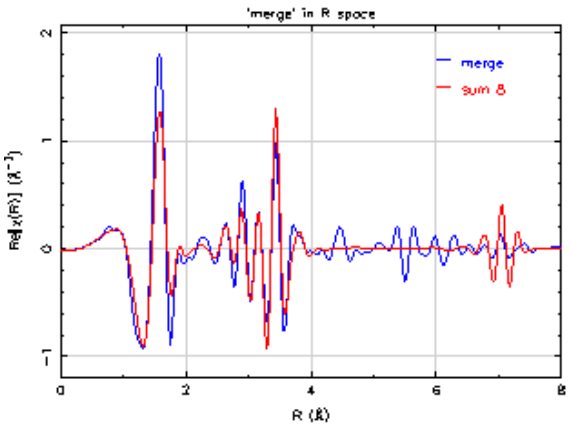




missing a little of the data

Minimum amplitude 15%
8 of 69 paths





missing a lot of the data

Models to consider:

UOP
A Honeywell Company

- Δr:
  - Symmetric expansion term: Alpha * 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 Einstien 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 were N is expected to change.

Some EXAFS references

UOP
A Honeywell Company

- Multiple edges, structural information: **B Ravel, E. Cockayne, M. Newville and K. M. Rabe. "Combined EXAFS and first-principles theory study of Pb1-xGexTe." 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] 6.5H20." 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 $La_{2-x}Sr_xCuO_4$” 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 SnO_2 data

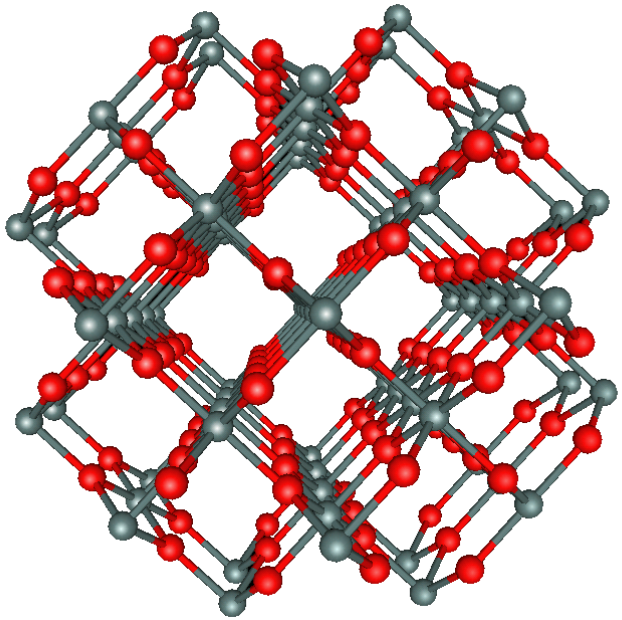
UOP
A Honeywell Company

- Δr: symmetric expansion term: alpha * reff.
- ΔE: Energy shifts that depend on atom type:
  - The first shell; Eo1,
  - All other oxygen scattering events: Eo2
  - All tin scattering events: Esn
- 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 SnO_2

UOP
A Honeywell Company

Includes all the atoms shown here



Path	*N*	*reff*	*ΔR*	σ^2	*ΔE*
Sn-O1	4	2.0519	**Alpha**·reff	**σ^2o1**	**ΔEo1**
Sn-O2	2	2.0567	Alpha·reff	σ^2o1	ΔEo1
Sn-Sn1	2	3.1864	Alpha·reff	**σ^2sn1**	**ΔEsn**
Sn-O3	4	3.5906	Alpha·reff	**σ^2o3**	**ΔEo2**
Sn-Sn2	8	3.7093	Alpha·reff	**σ^2sn2**	ΔEsn
Sn-Sn2-01	8	3.9090	Alpha·reff	**σ^2sn2o1**	0.5·ΔEsn+0.5·ΔEo1
Sn-Sn2-02	8	3.9090	Alpha·reff	σ^2sn2o1	0.5·ΔEsn+0.5·ΔEo1
Sn-O5	8	4.2414	Alpha·reff	**σ^2o5**	ΔEo2
Sn-Sn3	4	4.7373	Alpha·reff	**σ^2sn3**	ΔEsn
Sn-O7	8	4.8006	Alpha·reff	**σ^2o7**	ΔEo2
Sn-Sn4	8	5.7092	Alpha·reff	**σ^2sn4**	ΔEsn
Sn-Sn5	8	5.8365	Alpha·reff	σ^2sn4	ΔEsn
Sn-Sn5-01	8	5.8405	Alpha·reff	σ^2sn4	0.5·ΔEsn+0.5·ΔEo1
Sn-Sn5-04	8	5.8405	Alpha·reff	σ^2sn4	0.5·ΔEsn+0.5·ΔEo2
Sn-O1-Sn5-O1	4	5.8444	Alpha·reff	σ^2sn4	0.33·ΔEsn+0.66·ΔEo1
Sn-O4-Sn5-O4	4	5.8444	Alpha·reff	σ^2sn4	0.33·ΔEsn+0.66·ΔEo2
Sn-Sn6-Sn1	4	6.3728	Alpha·reff	**σ^2sn6**	ΔEsn
Sn-Sn1-Sn6-Sn1	2	6.3728	Alpha·reff	σ^2sn6	ΔEsn
Sn-Sn7	4	6.6995	Alpha·reff	**σ^2sn7**	ΔEsn
Sn-Sn7-O2	4	6.6995	Alpha·reff	σ^2sn7	0.5·ΔEsn+0.5·ΔEo1
Sn-Sn7-O6	4	6.6995	Alpha·reff	σ^2sn7	0.5·ΔEsn+0.5·ΔEo2
Sn-Sn7-O6-O2	4	6.6995	Alpha·reff	σ^2sn7	0.33·ΔEsn+0.33·ΔEo1+0.33·ΔEo2
Sn-O6-Sn7-O2	4	6.6995	Alpha·reff	σ^2sn7	0.33·ΔEsn+0.33·ΔEo1+0.33·ΔEo2
Sn-O2-Sn7-O6-O2	4	6.6995	Alpha·reff	σ^2sn7	0.25·ΔEsn+0.50·ΔEo1+0.25·ΔEo2
Sn-O6-Sn7-O6-O2	4	6.6995	Alpha·reff	σ^2sn7	0.25·ΔEsn+0.25·ΔEo1+0.50·ΔEo2
Sn-Sn8	8	7.4187	Alpha·reff	**σ^2sn8**	ΔEsn
Sn-Sn8-Sn2	16	7.4187	Alpha·reff	σ^2sn8	ΔEsn
Sn-Sn2-Sn-Sn2	8	7.4187	Alpha·reff	4·σ^2sn2	ΔEsn
Sn-Sn2-Sn8-Sn2	8	7.4187	Alpha·reff	σ^2sn8	ΔEsn
Sn-Sn9	16	7.6578	Alpha·reff	**σ^2sn9**	ΔEsn

- **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 SnO_2

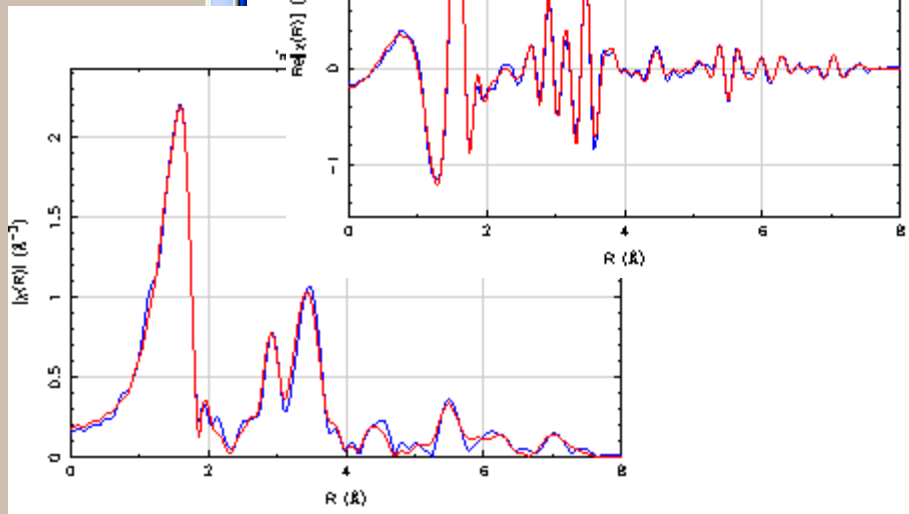
A Honeywell Company

Artemis palettes

Ifeffit | Results | Files | Messages | Echo | Journal | Properties

Results from the last fit — Raw log file — Save — Dismiss

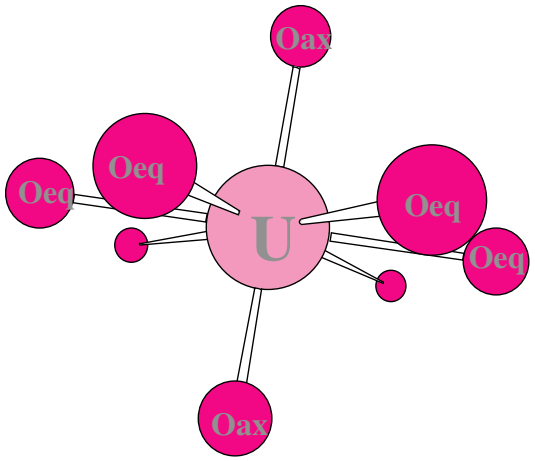
```
============================================================

Independent points               =      70.494140625
Number of variables              =      18.000000000
Chi-square                       =   19369.502641930
Reduced Chi-square               =     368.984088725
R-factor                         =       0.016091320
Measurement uncertainty (k)      =       0.000149981
Measurement uncertainty (R)      =       0.000587235
Number of data sets              =       1.000000000


Guess parameters +/- uncertainties  (initial guess):
   amp                =     1.0512750   +/-       0.0230720     (1.0731)
   eo1                =     2.7995790   +/-       0.2075060     (3.4017)
   esn                =     1.3666090   +/-       0.4750070     (2.6664)
   eo2                =     3.5177280   +/-       0.8663380     (5.0268)
   alpha              =    -0.0009020   +/-       0.0007570     (-0.0001)
   sso1               =     0.0031980   +/-       0.0002910     (0.0034)
   sso2               =     0.0184130   +/-       0.0070080     (0.0203)
   sso4               =     0.0055760   +/-       0.0020580     (0.0066)
   sso6               =     0.0059160   +/-       0.0036660     (0.0066)
   sssn2o1            =     0.0035050   +/-       0.0010600     (0.0040)
   sssn1              =     0.0035740   +/-       0.0002840     (0.0038)
   sssn2              =     0.0053430   +/-       0.0002450     (0.0054)
   sssn3              =     0.0070690   +/-       0.0014830     (0.0071)
   sssn4              =     0.0073380   +/-       0.0006350     (0.0077)
   sssn5              =     0.0084460   +/-       0.0026580     (0.0090)
   sssn6              =     0.0069210   +/-       0.0024670     (0.0066)
   sssn7              =     0.0087330   +/-       0.0016900     (0.0086)
   sssn8              =     0.0106090   +/-       0.0044800     (0.0096)


Correlations between variables:
```

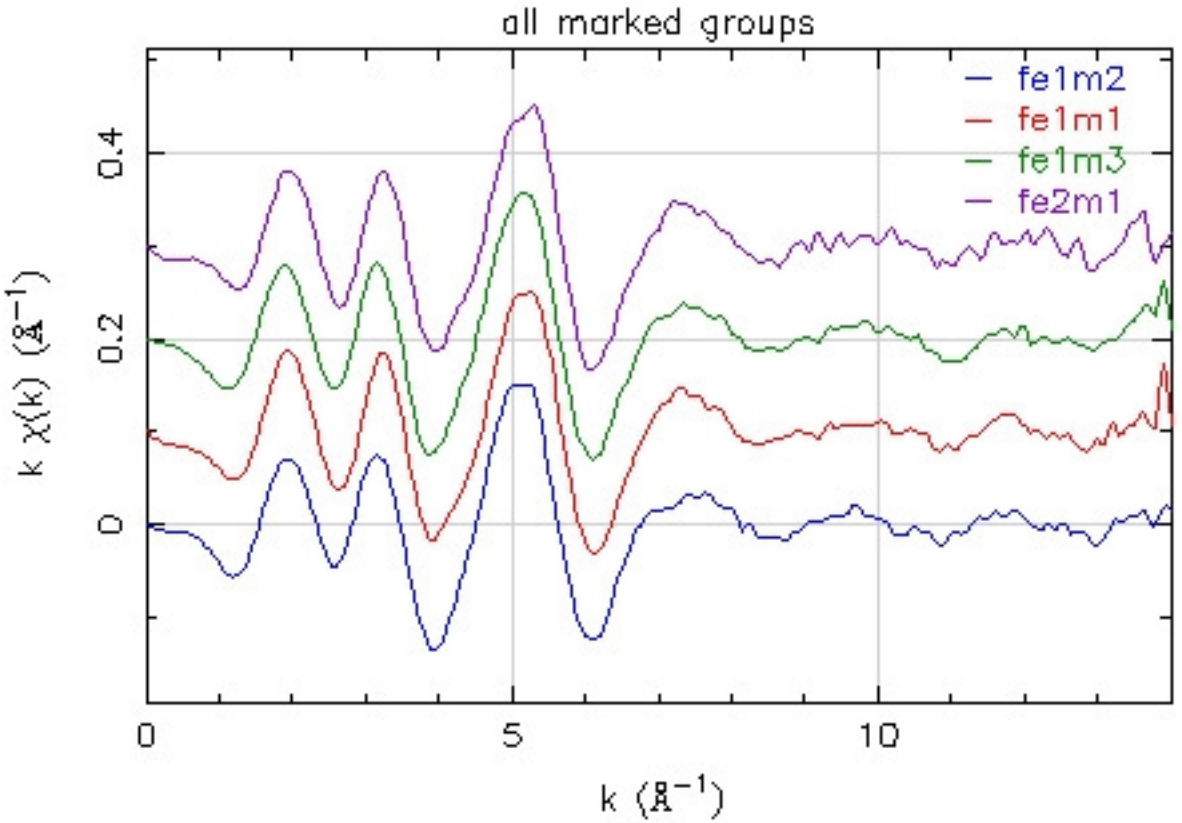


- **Typical values for EXAFS parameters**
- **Δr: less than 0.5 Å**
- **ΔE: less than 10 eV**
- **σ^2: 0.003 to 0.020 Å^2**
- **S02: 0.70 to 1.10**

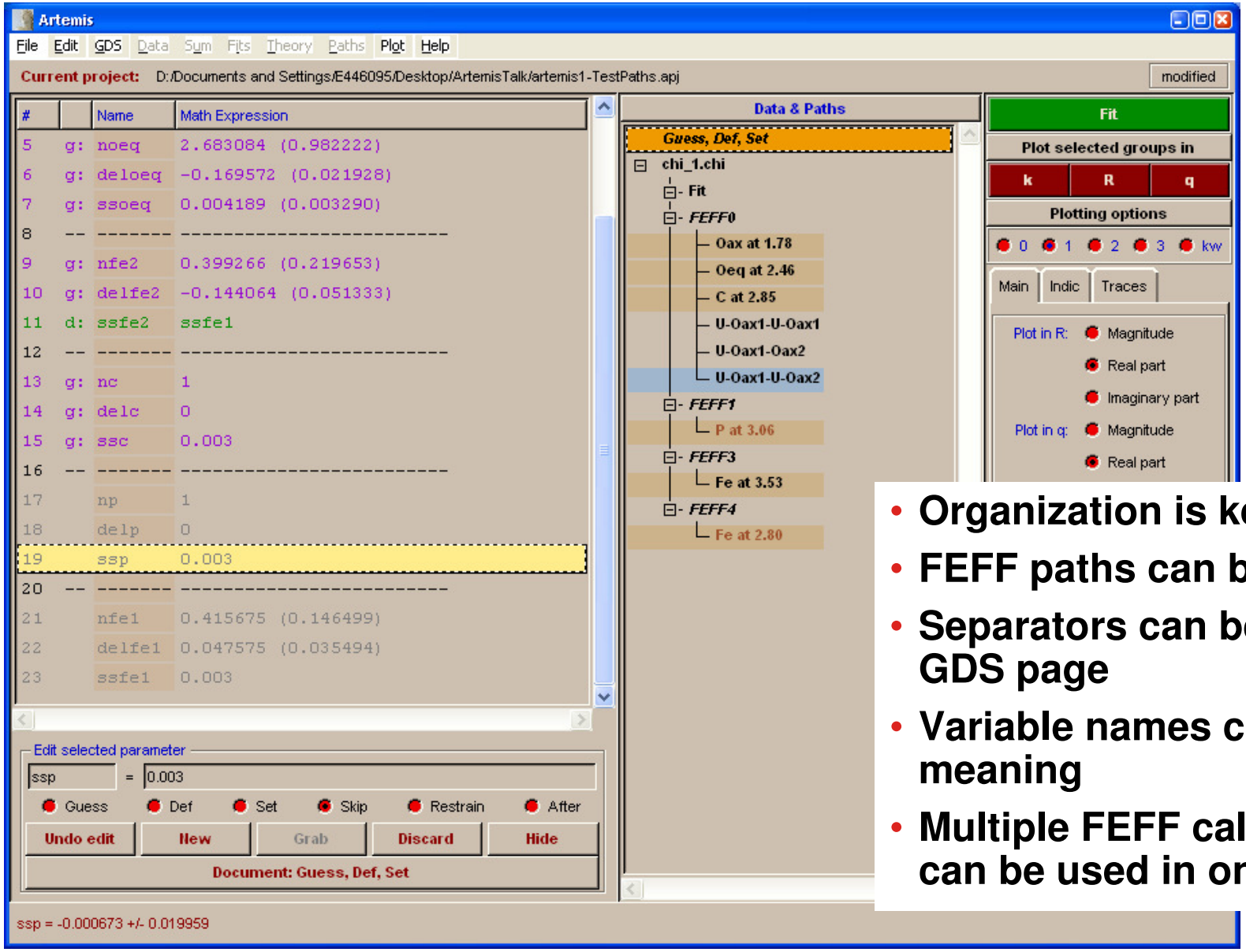
Example 4: Determining 2nd shell atom type and number

- 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



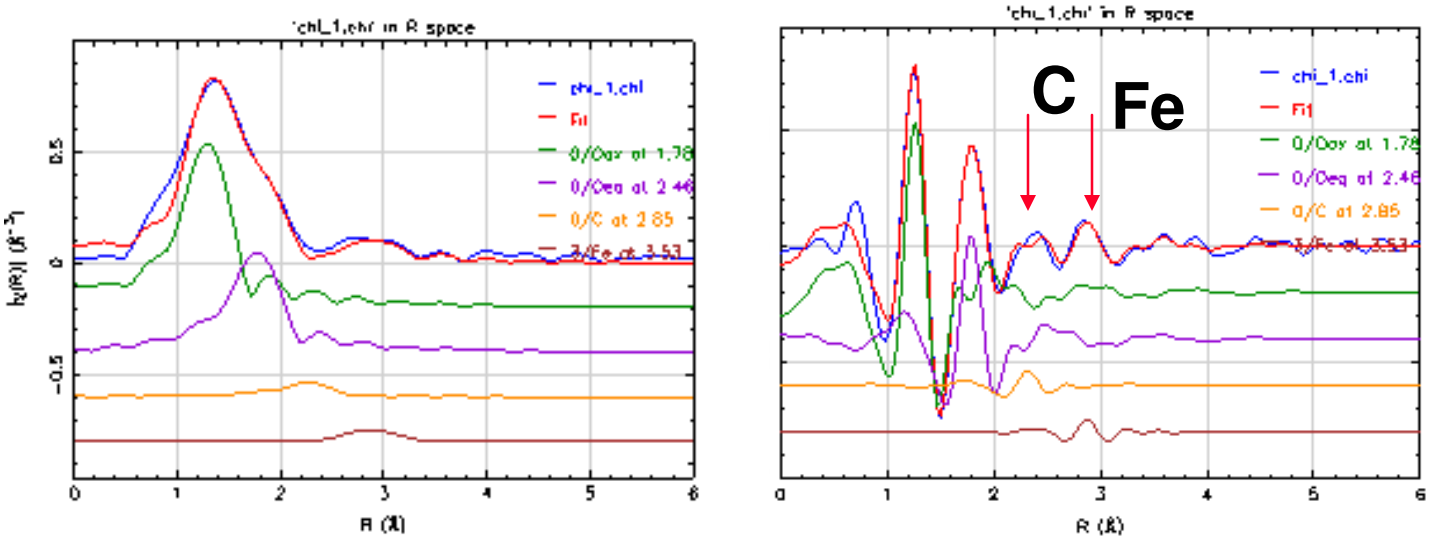


Setting up a Uranyl Model



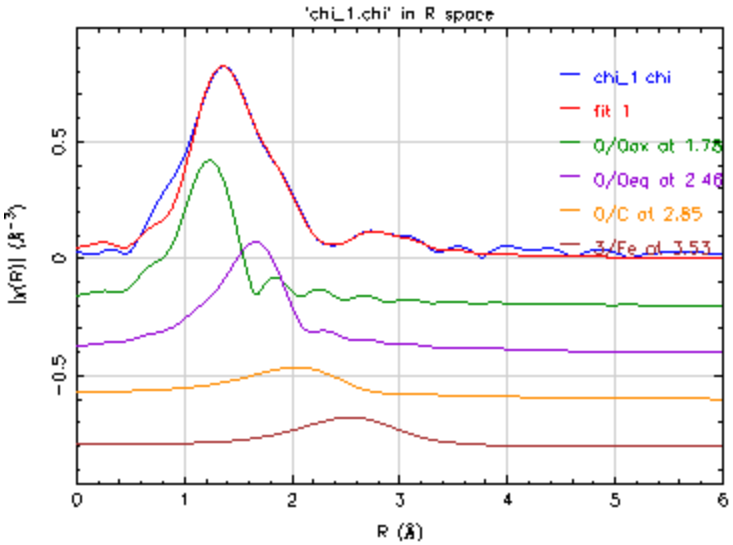
- Organization is key
- FEFF paths can be renamed
- Separators can be added to GDS page
- Variable names can have meaning
- Multiple FEFF calculations can be used in one model

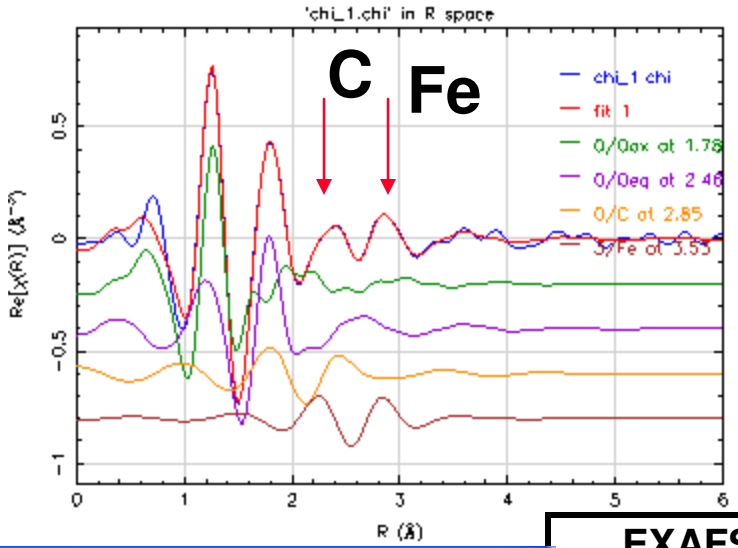
Test data for C and Fe shells

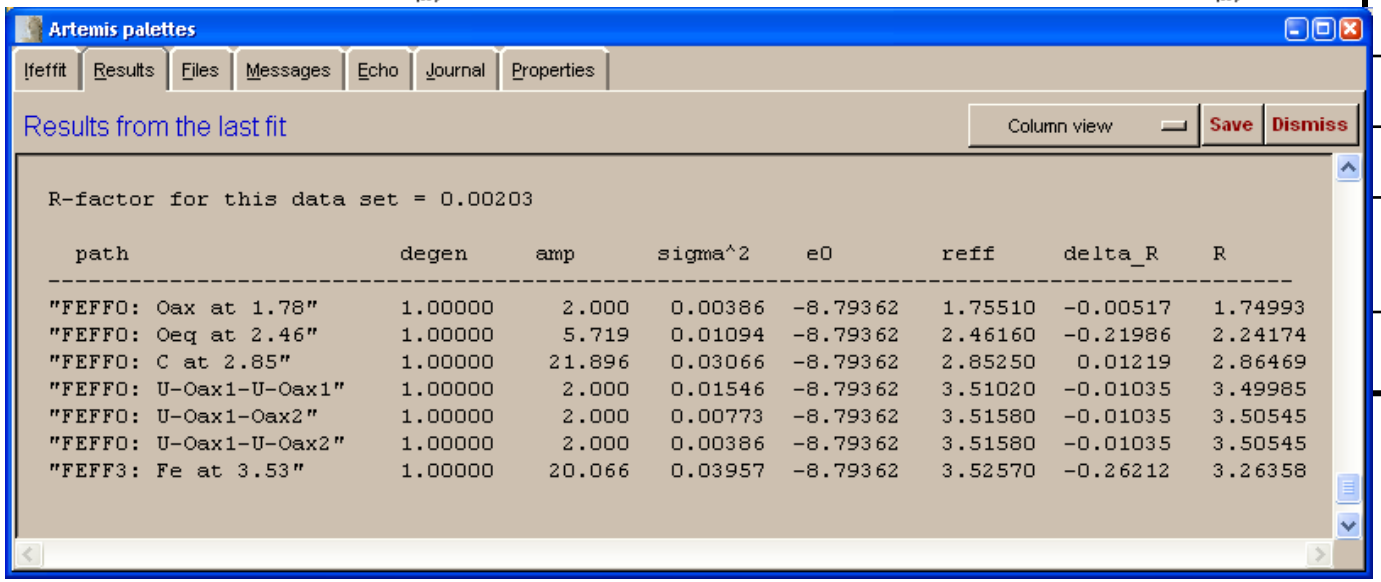


- **Place C and Fe shells in a "good" spot**
  - **set parameters – no fitting**
  - **monitor results and fit spectra**
  - **Needs to be done using real or imaginary part of FT, can not always be done using magnitude of FT.**

Fit Results using C and Fe shells



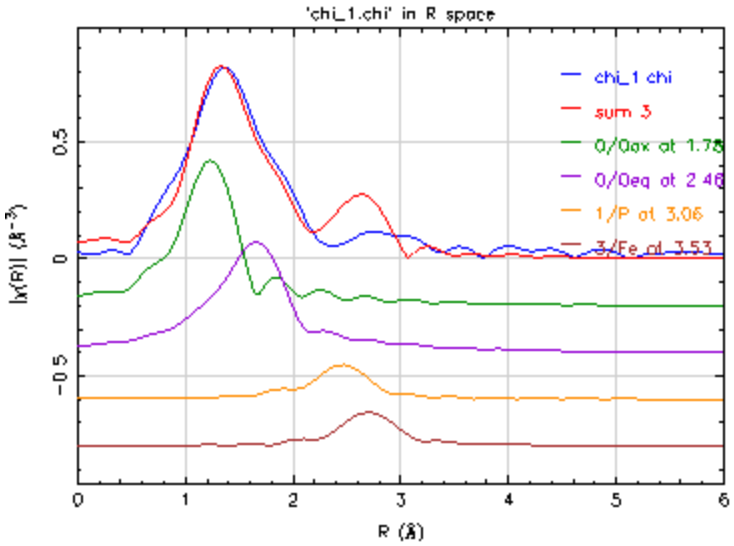


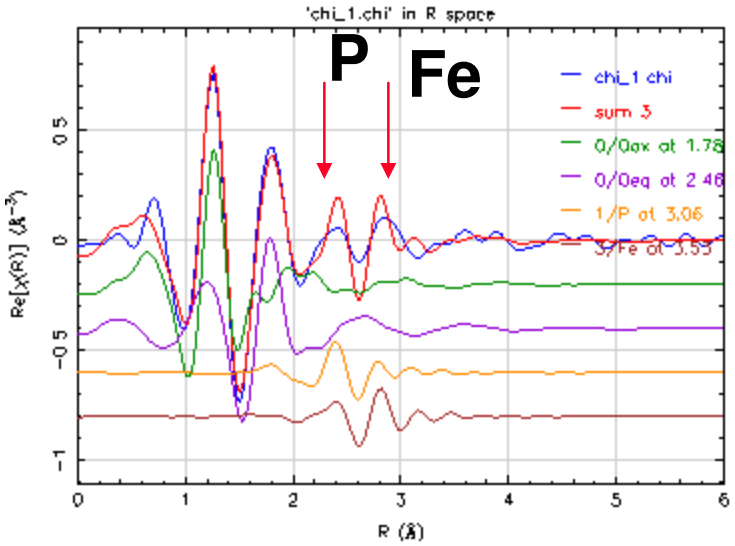


EXAFS Parameters	
σ^2-values	-
Distances	+
Coordination numbers	-
ΔE-value	-

Signals became broad and unrealistic

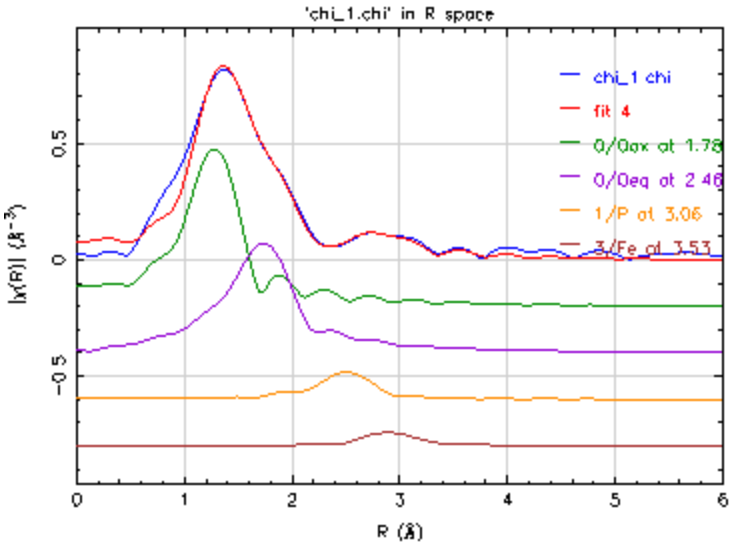
Test data for P and Fe shells

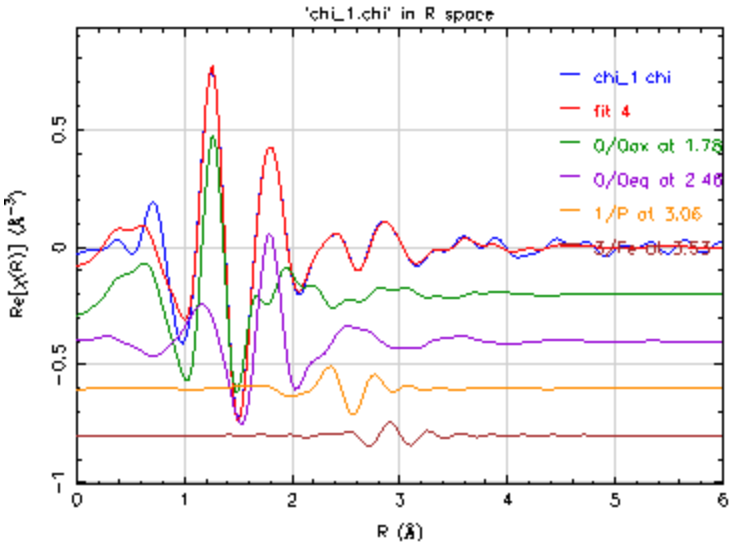




- **Place P and Fe shells in a "good" spot**
  - **set parameters – no fitting**
  - **monitor results and fit spectra**

Fit Results using P and Fe shells





Artemis palettes

Ifeffit | Results | Files | Messages | Echo | Journal | Properties

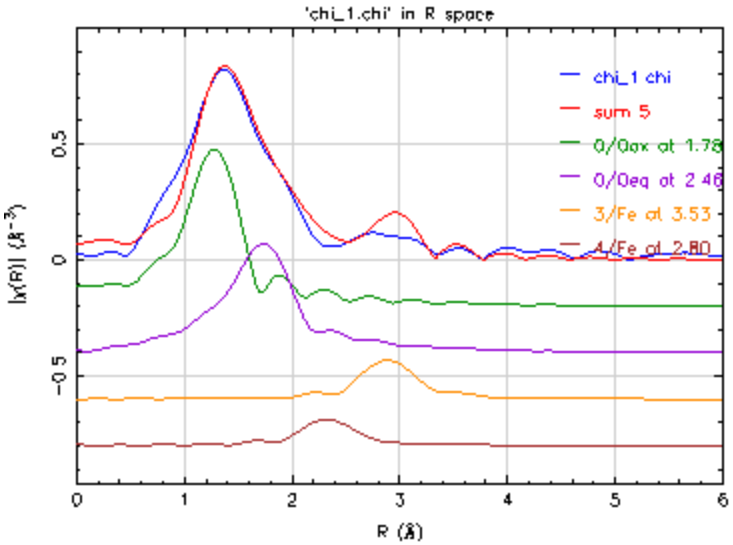
Results from the last fit — Column view | Save | Dismiss

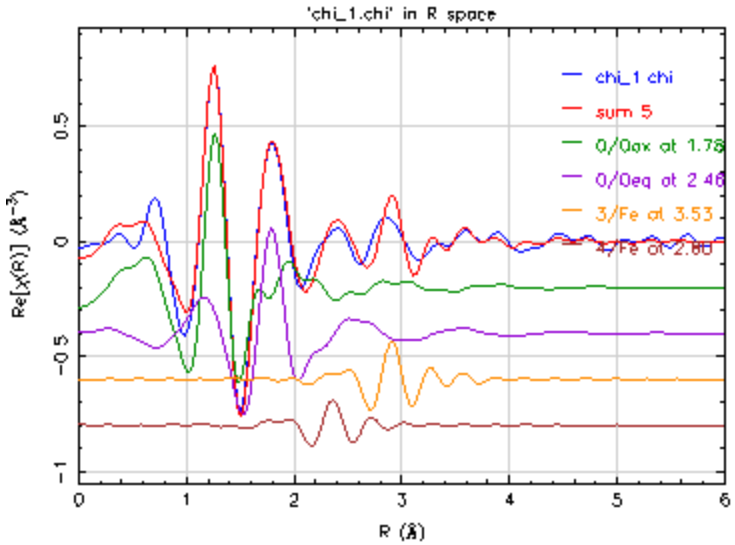
R-factor for this data set = 0.00264

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

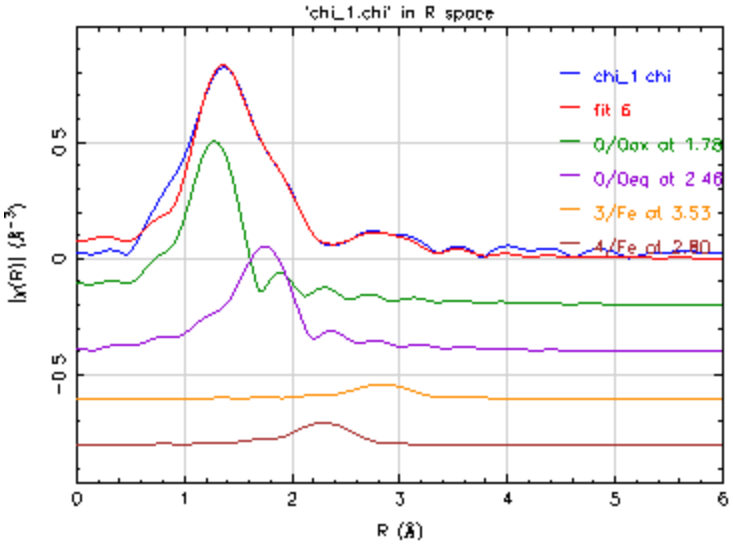


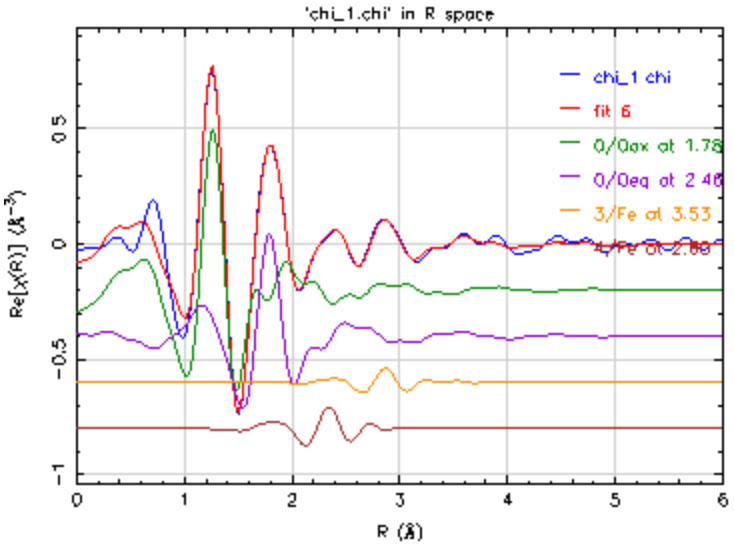


- **Place Fe and Fe shells in a "good" spot**
  - **set parameters – no fitting**
  - **monitor results and fit spectra**

Fit Results using Fe and Fe shells

A Honeywell Company





Artemis palettes

Ifeffit | Results | Files | Messages | Echo | Journal | Properties

Results from the last fit — Column view — Save — Dismiss

R-factor for this data set = 0.00254

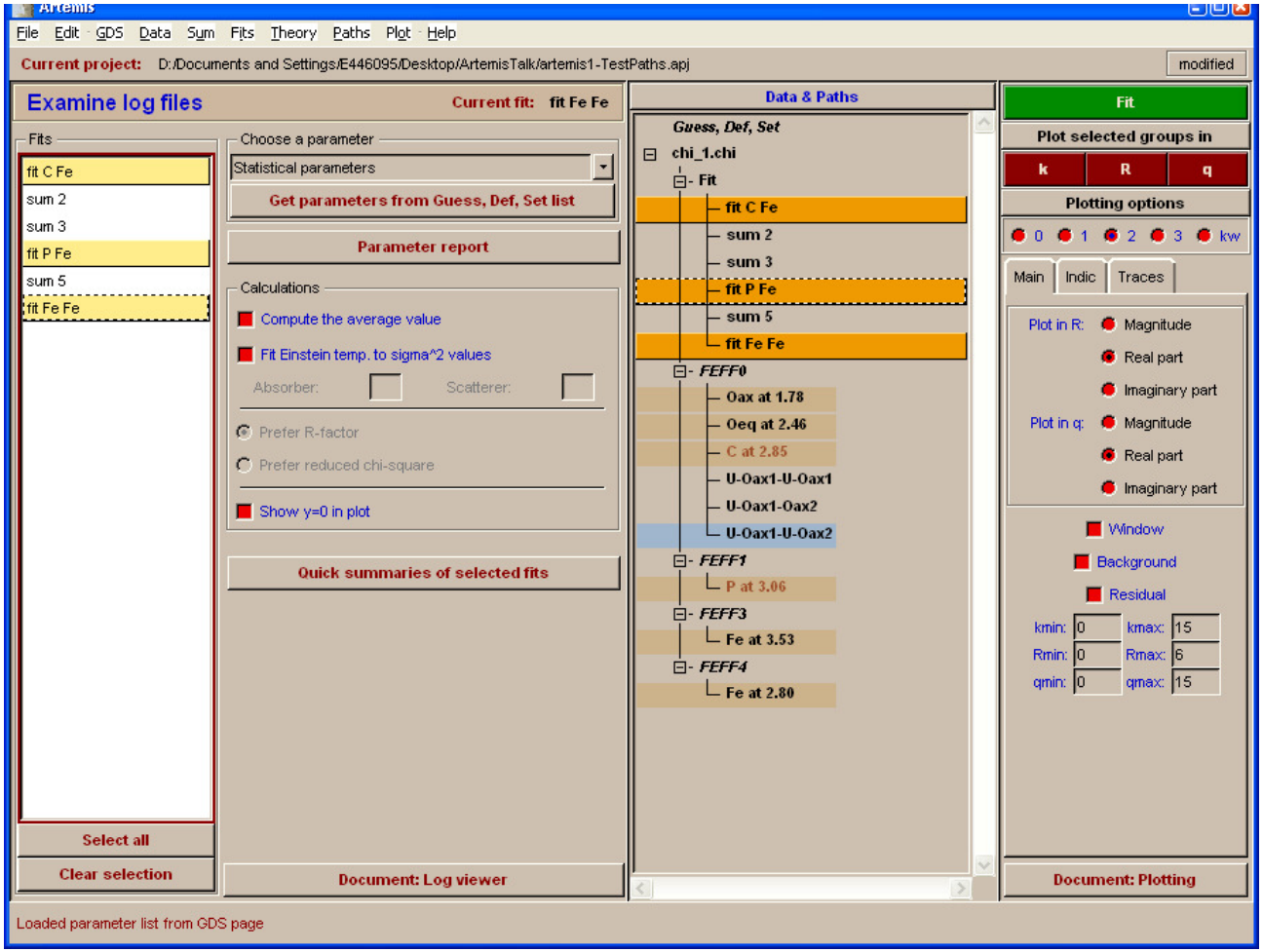
path	degen	amp	sigma^2	e0	reff	delta_R	R
"FEFF0: Oax at 1.78"	1.00000	2.000	0.00320	-0.59470	1.75510	0.01998	1.77508
"FEFF0: Oeq at 2.46"	1.00000	3.235	0.00594	-0.59470	2.46160	-0.17897	2.28263
"FEFF0: U-Oax1-U-Oax1"	1.00000	2.000	0.01280	-0.59470	3.51020	0.03995	3.55015
"FEFF0: U-Oax1-Oax2"	1.00000	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	+

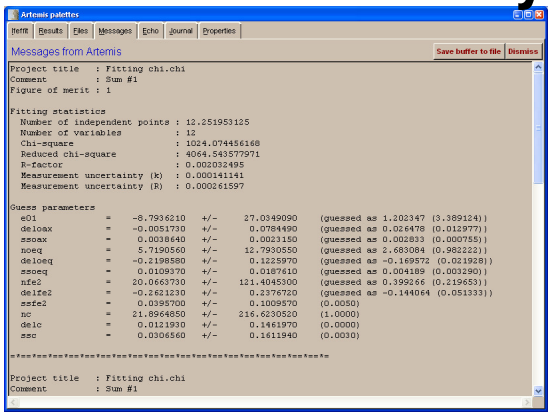
File Number

Comparison of Models

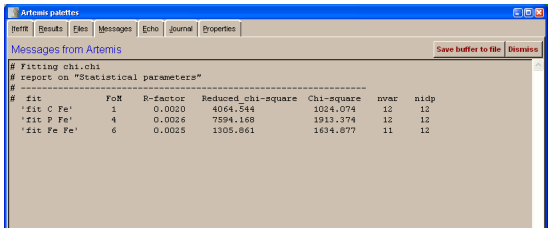
UOP
A Honeywell Company



Quick summary



Parameter Report



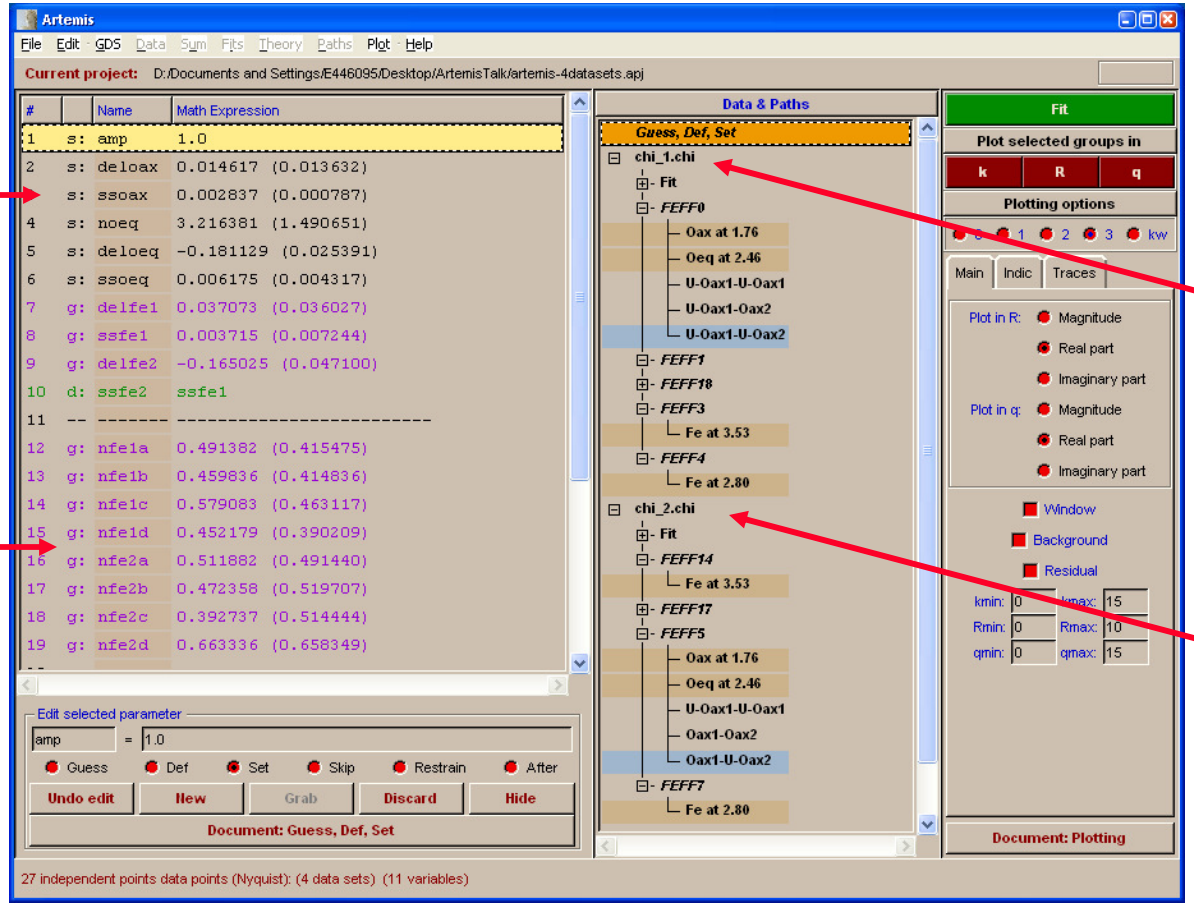
- **Models are saved in Artemis and can be compared or re-instated later**

Multiple data set fit

A Honeywell Company

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

A Honeywell Company

Artemis palettes

Ifeffit | Results | Files | Messages | Echo | Journal | Properties

Results from the last fit

```
Environment      :  Artemis 0.8.013 using Windows XP, perl 5.008008, Tk 80
Fit label        :  fit Fe Fe
Data sets        :  "chi_1.chi", "chi_2.chi", "chi_3.chi", "chi_4.chi"
Figure of merit :  7

============================================================


Fitting statistics
  Number of independent points : 26.578125000
  Number of variables          : 11
  Chi-square                   : 9490.351885016
  Reduced chi-square           : 609.210151094
  R-factor                     : 0.057174889
  Measurement uncertainty (k)  : 0.000196055
  Measurement uncertainty (R)  : 0.000220316

Guess parameters
  delfe1          =     0.0422810   +/-      0.0123250     (guessed as 0.0
  ssfe1           =     0.0050600   +/-      0.0047000     (guessed as 0.0
  delfe2          =    -0.1704970   +/-      0.0137850     (guessed as -0.
  nfe1a           =     0.5063030   +/-      0.2914520     (guessed as 0.4
  nfe1b           =     0.5505380   +/-      0.3310320     (guessed as 0.4
  nfe1c           =     0.6513330   +/-      0.3598810     (guessed as 0.5
  nfe1d           =     0.4671820   +/-      0.2862200     (guessed as 0.4
  nfe2a           =     0.5683350   +/-      0.3168750     (guessed as 0.5
  nfe2b           =     0.5138540   +/-      0.3234190     (guessed as 0.4
  nfe2c           =     0.4784870   +/-      0.3155270     (guessed as 0.3
  nfe2d           =     0.7617610   +/-      0.4179530     (guessed as 0.6

Def parameters (using "FEFF0: Oax at 1.76")
```