

# Introduction to *ab-initio* methods for EXAFS data analysis

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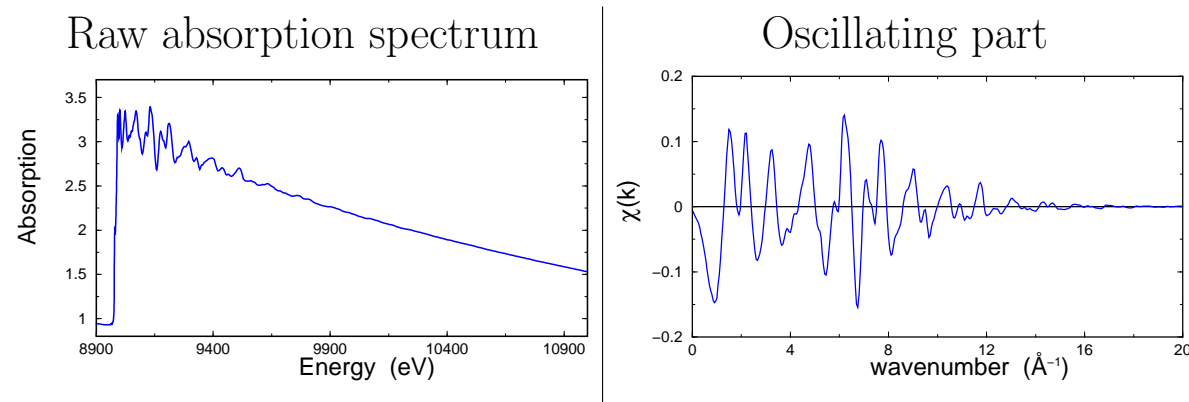
June 15, 2005

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# 1 Data analysis methods

In an EXAFS experiment, the absorption coefficient  $\mu$  is collected:



but only the oscillating part contains the information on the local structure like coordination numbers, bond lengths, bond length distribution [1].

The quantitative analysis method consist in:

- Extract the Oscillating part ( $\chi$  function) from the absorption  $\mu$ .
- Filter the desired signal  $\chi$
- Fit the  $\chi$  to a suitable model

Consider the basic EXAFS formula:

$$\chi(k) = S_0^2 \frac{NA(k)}{kR^2} e^{\frac{-2R}{\lambda}} \sin(2kR + \phi(k) + \phi_c) e^{-2k^2\sigma^2} \quad (1)$$

The *traditional* way of analyzing EXAFS data is to use empirical standards, often in conjunction with Fourier filter techniques.

In this approach, an *unknown* structure (blue parameters) is studied by extracting the backscattering parameters from the experimental spectrum of a *known* model compound.

In this lecture, the use of *ab-initio* methods and in particular the University of Washington XAFS package (UWXAFS) in EXAFS analysis based on [theoretical standards](#) will be discussed. This method uses theoretical calculations to provide the [red parameters](#) and has to be used in a variety of cases, namely:

- no empirical standards are available
  - non-resolved shells (BCC 1 – 2<sup>nd</sup> shell)
  - complex structures
- strong Multiple Scattering effects involved
  - collinear configurations (FCC 4<sup>th</sup> shell)

## 2 X-ray absorption cross section

### 2.1 General formulation

When measuring the X-ray absorption coefficient we measure the (mainly) dipole mediated transition of an electron from a deep core state  $|i\rangle$  to an unoccupied state  $|f\rangle$ . From the Fermi Golden Rule

$$\mu(E) \propto \sum_{f}^{E_f > E_F} \langle f | \hat{\epsilon} \cdot \mathbf{r} | i \rangle^2 \delta(E_f) \quad (2)$$

There are two ways to solve this equation [2]:

- Find an expression for  $|i\rangle$  and  $|f\rangle$  and evaluate directly the integral.
- Use the Green function method where only the potential and the initial state are needed

## 2.2 The Multiple Scattering approach

In the Green function method the X-ray absorption cross section is written as [3],[4], [5]:

$$\mu(E) \propto -\frac{1}{\pi} \Im \langle i | \hat{\epsilon}^* \cdot r G(r, r', E) \hat{\epsilon} \cdot r' | i \rangle \Theta(E - E_F) \quad (3)$$

Where:

$$G(r, r', E) = \frac{1}{E - H + i\eta}$$

(E= photon energy, H = one-particle Hamiltonian)

That can be explicitated as [4]:

$$\mu(E) \propto \mu^{at} \Im \left\{ \frac{1}{\sin^2 \delta_{L_0}^0} \frac{1}{2^{L_0+1}} \sum_{m_0} [T((1 - GT)^{-1})_{L_0, L_0}^{0,0}] \right\}$$

Where:

T= Atomic Scattering matrix

$$T = \begin{pmatrix} t_0 & 0 & \dots \\ 0 & t_1 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

Scattering from  $i^{th}$  atom

G Propagator matrix

$$G = \begin{pmatrix} 0 & G_{0,1} & \dots \\ G_{1,0} & 0 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

Propagation from  $i^{th}$  to  $j^{th}$  atom

The  $(1 - GT)^{-1}$  term can be approximated by a serie expansion

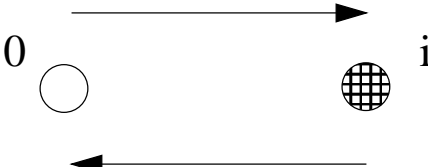
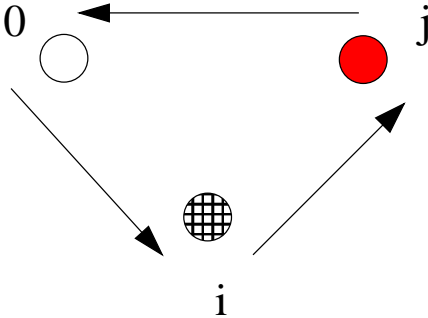
$$T(1 - GT)^{-1} \approx \sum_n [T(GT)^n]$$

Yelding:

$$\mu(E) \propto \mu^{at} \Im \left\{ \frac{1}{\sin^2 \delta_{L_0}^0} \frac{1}{2^{L_0+1}} \sum_{m_0} \underbrace{\sum_n [T(GT)^n]_{L_0, L_0}^{0,0}}_{Multiple Scattering} \right\} \quad (4)$$

Physical meaning of the various terms:

Note: '0' Indicates the absorber, i and j neighbors.

Math term	Picture	Meaning
$T_0 G_{0,i} T_i G_{i,0} T_0$		Single Scattering
$T_0 G_{0,i} T_i G_{i,j} T_j G_{j,0} T_0$		Double Scattering
$\vdots$	$\vdots$	$\ddots$

The convergence of the serie in (4) is achieved under strict conditions on the energy



range and scattering amplitudes (see [3]).

Moreover (4) is not generally reducible to a simple analytical expression. However it has been found [5], [6] that each of the various terms of the expansion of (4) can be written as:

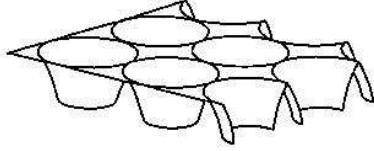
$$\chi_{\Gamma}(k) = \left( S_0^2 e^{-2\sigma^2 k^2} \right) \Im \left( \frac{f_{eff}}{kR^2} e^{2i(kR+\phi)} \right) \quad (5)$$

Here  $\Gamma$  is the path index and  $f_{eff}$  and  $\phi$  are the effective amplitude and phases of the path under analysis. These quantities can be thus calculated separately and then introduced in a fitting procedure.

## 2.3 Computing theoretical terms

Here we describe the steps in the generation of theoretical paths:

1.

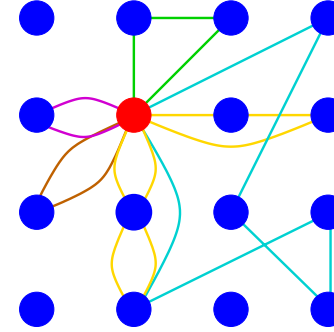


### Compute atomic potentials and phase shifts

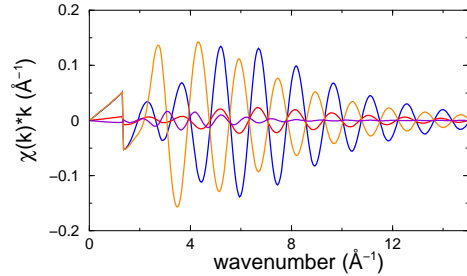
Use neutral, free, atomic spheres to construct a muffin tin potential. The embedded atoms are spherical and the interstitial region is flat.

### Find all scattering geometries in a cluster

2. Use a heap to construct successively higher orders of MS paths. In this way *all* possible scattering geometries are found in a cluster up to a specified order.



3.

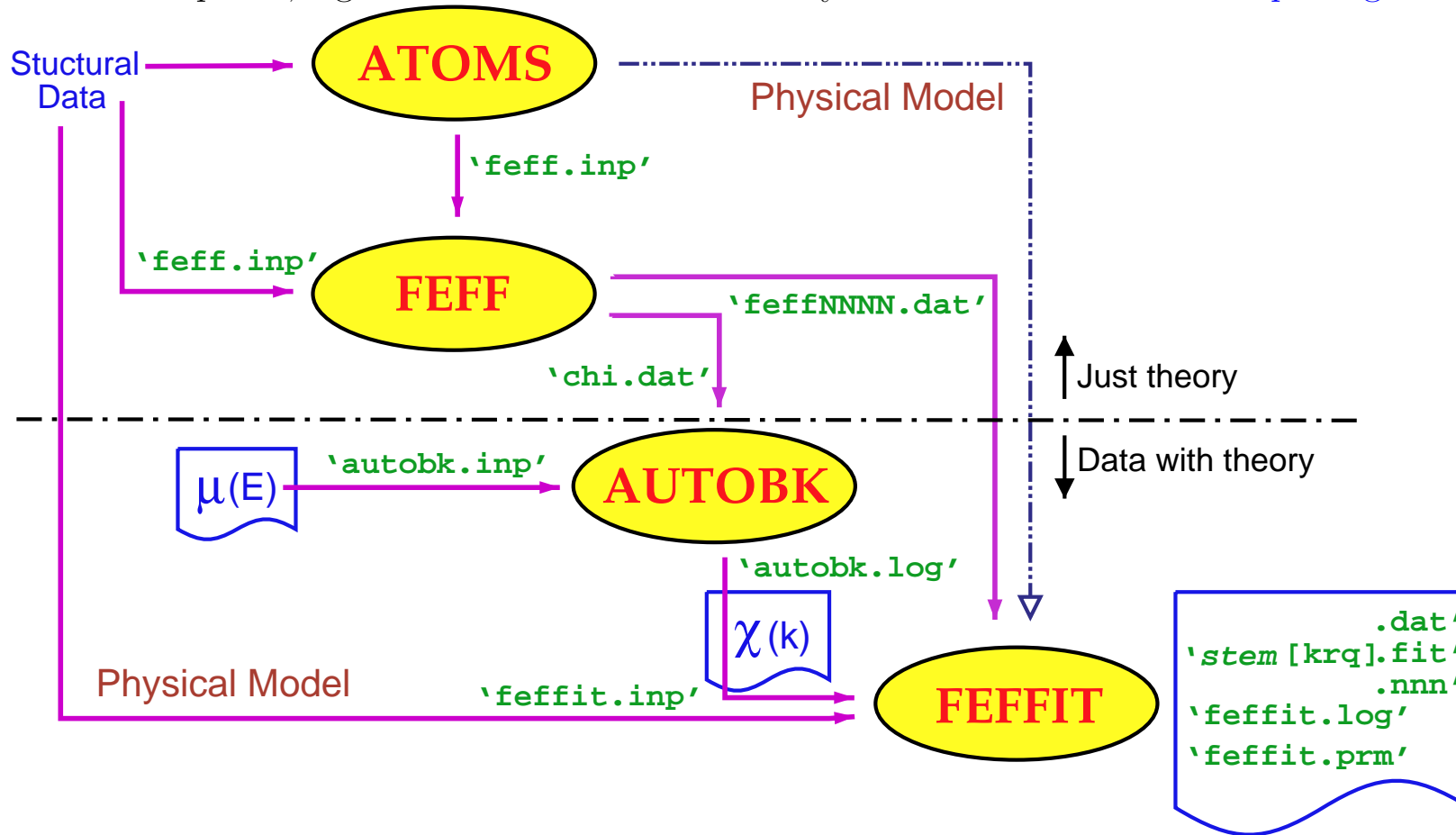


### Compute the contribution from each path

Using the list of enumerated paths and the atomic potentials, compute the curved-wave, effective scattering amplitudes and phase shifts for all paths. Polarization is considered *a priori* for all paths.

### 3 Overview of the UWXAFS package

The package UXWAFS [7] contains all the programs necessary to the generation of the theoretical paths, signal extraction and fit. Here you find [a flowchart of the package](#):



The UWXAFS package is made-up of 4 main programs

**ATOMS** Atoms takes the crystallographic data of the compound of interest and generates a suitable file for the program Feff. The file contains the atomic coordinates in the crystal up to a certain distance from the absorber and some control cards for Feff

**FEFF** Starting from the atomic coordinates Feff calculates the amplitude and phases of scattering paths up to a given order and 'intensity'.

**AUTOBK** Used to extract EXAFS  $\chi(k)$  part from the absorption spectrum

**FEFFIT** Fits the EXAFS spectrum with a theoretical model based on the paths calculated by Feff.

Making a [comparison with another package](#) (*GNXAS*) we can here resume sinoptically the operations of the various programs:

UWXAFS	GNXAS	Operation
ATOMS	CRYMOL, GNPEAK	Atomic coordinates generation
FEFF	GNPEAK, GNXAS	Path search and signal calculation
AUTOBK	No analogous	EXAFS signal extraction
FEFFIT	FITHEO	Signal fitting

Here we will provide a brief introduction to the use of the package. For a complete description and program manuals refer to the project home page [7] on the Web.

## 4 (TK)ATOMS

In order to generate the correct EXAFS signals it is mandatory to use a system with electron densities, bond distances and angles as much similar as possible to the sample in analysis.

For (strained, doped, ...) crystals the starting model will be the (undistorted, undoped, ...) crystal, for amorphous samples it is preferable to use a crystalline compound with similar composition.

The instructions for the program are contained in a control file named *atoms.inp*.  
The *atoms.inp* file for crystalline Cu

```
title Cu crystal fcc
```

```
space F M 3 M
```

```
a 3.618
```

```
rmax 5.73
```

```
core Cu1
```

```
edge K
```

```
atom
```

```
  Cu 0.0 0.0 0.0 Cu1
```

```
-----
```

It is made up of a series of commands ('space', 'a', 'core') followed by the related value.

In this way the space group, cell dimensions and prototypical atoms are specified. These informations can be found from different sources like:

- R.N.G. Wychoff's *Crystal Structures* [8]. A quite popular book on crystal structures.
- The ICSD database [9] This is a powerful and complete database with more than 76,500 entries in its complete form.

You can access this database and enter the details of your structure, namely the elements name and number:

ICSD for WWW - Mozilla Firefox

File Edit View Go Bookmarks Tools Help

http://icsd.ill.fr/icsd/index.php?action=Search&page=1&nb\_row: Go

Customize Links Free Hotmail Windows Media Windows

Authors/Code Years Journal Title/Comment Help

Elements Element Count Mineral Name ANX Formula Pearson Symbol

System Laue Class Centering Space Group Cell Size/Mass

Remarks Min. Distance Distance Select Distance Range Co-ordin.

**Search** Reset

**Query :** (EL\_COUNT = "1") AND el0.el\_symbol = 'Cu'

Select All / None 9 Results References EndNote **Details** Bonds Pattern Structure

Year	Authors	Struct. Formula	sgr	Mineral Name
<input checked="" type="checkbox"/> 1988	Suh, I.-K.;Ohta, H.;Waseda, Y.	Cu	FM3-M	Copper
<input type="checkbox"/> 1963	Srinavasa Rao, S.;Anantharaman, T.R.	Cu	FM3-M	Copper
<input type="checkbox"/> 1961	Otte, H.M.	Cu	FM3-M	
<input type="checkbox"/> 1953	Swanson, H.E.;Tatge, E.	Cu	FM3-M	Copper
<input type="checkbox"/> 1933	Owen, E.A.;Yates, E.L.	Cu	FM3-M	Copper
<input type="checkbox"/> 1926	Holgersson, S.	Cu	FM3-M	Copper
<input type="checkbox"/> 1925	Westgren, A.;Phragmen, G.	Cu	FM3-M	Copper
<input type="checkbox"/> 1923	Young, J.F.T.	Cu	FM3-M	Copper
<input type="checkbox"/> 1914	Bragg, W.L.	Cu	FM3-M	Copper

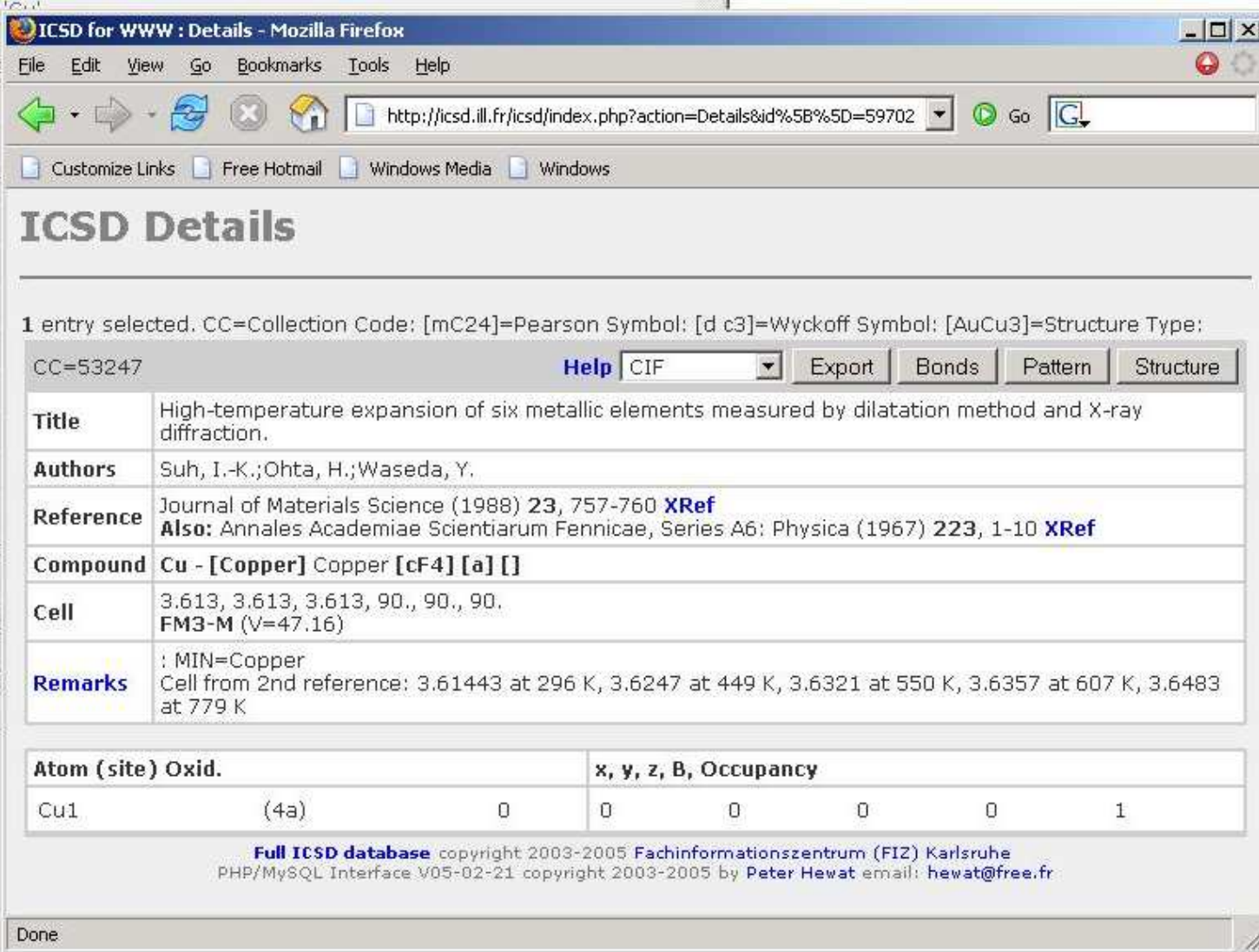
Page : [1](9 results) 10 results per page.

Full ICSD database copyright 2003-2005 Fachinformationszentrum (FIZ) Karlsruhe  
 PHP/MySQL Interface V05-02-21 copyright 2003-2005 by Peter Hewat email: hewat@free.fr

Done



The database prompts you a series of structures that you can select and see the details:



ICSD for WWW : Details - Mozilla Firefox

File Edit View Go Bookmarks Tools Help

http://icsd.ill.fr/icsd/index.php?action=Details&id%5B%5D=59702 Go

Customize Links Free Hotmail Windows Media Windows

## ICSD Details

1 entry selected. CC=Collection Code: [mC24]=Pearson Symbol: [d c3]=Wyckoff Symbol: [AuCu3]=Structure Type:

CC=53247 [Help](#)

<b>Title</b>	High-temperature expansion of six metallic elements measured by dilatation method and X-ray diffraction.
<b>Authors</b>	Suh, I.-K.; Ohta, H.; Waseda, Y.
<b>Reference</b>	Journal of Materials Science (1988) <b>23</b> , 757-760 <a href="#">XRef</a> Also: Annales Academiae Scientiarum Fennicae, Series A6: Physica (1967) <b>223</b> , 1-10 <a href="#">XRef</a>
<b>Compound</b>	Cu - [Copper] Copper [cF4] [a] []
<b>Cell</b>	3.613, 3.613, 3.613, 90., 90., 90. FM3-M (V=47.16)
<b>Remarks</b>	: MIN=Copper Cell from 2nd reference: 3.61443 at 296 K, 3.6247 at 449 K, 3.6321 at 550 K, 3.6357 at 607 K, 3.6483 at 779 K

Atom (site)	Oxid.		x, y, z, B, Occupancy
Cu1	(4a)	0	0 0 0 0 1

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PHP/MySQL Interface V05-02-21 copyright 2003-2005 by Peter Hewat email: [hewat@free.fr](mailto:hewat@free.fr)

Done

The output of the program is the *feff.inp* file that is the input for the following program

(feff).

Recently a new version with an improved User interface is now available with the name of TKATOMS:

TkAtoms

Atoms
Absorption
Powder
DAFS

File
Clear
Data
Preferences
Help


**Atoms: make atomic clusters from crystallographic data**

Cluster Size: 6.00000
Run Atoms

Shift Vector: 0, 0, 0

Output file types feff

IO Fill Gases
N2 0.00
Ar 0.00
Kr 0.00


Titles: Cu Metal fcc

Space Group f m -3 m
Browse Space Groups

Edge:

A 3.61500
Alpha

B
Beta

C
Gamma

**Unique Crystallographic Sites**
Number of Sites: 4
Add 1 Site

	Core Elem.	X	Y	Z	Tag	Occ.	
1	Cu	0.000000	0.000000	0.000000		1	Clear
2		0	0	0		1	Clear
3		0	0	0		1	Clear

With TKATOMS you can also create input files for other XAS data analysis programs (CRYMOL) and the .pdb file for the visualization of your cluster with RASMOL.

## 5 **FEFF**

The Feff program [10], [11] performs a serie of tasks with the aim of [generating the theoretical signals](#) to be used at the fitting stage. The main actions in a run for EXAFS analysis are listed below:

- Calculation of atomic potentials in the Muffin Tin approximation from the given cluster
- Calculation of the phase shifts
- Analysis of the cluster with identification of the multiple scattering paths
- Calculation of the signals.

All these operations are sequentially done by a serie of [\*modules\*](#).

Here we show an example of input file *feff.inp*:

```
* This feff.inp file generated by ATOMS, version 2.50
* ATOMS written by and copyright (c) Bruce Ravel, 1992-1999
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *
*      total mu =      2538.9 cm^-1, delta mu =      2196.1 cm^-1
*      specific gravity = 8.911, cluster contains 79 atoms.
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *
*      mcmaster corrections: 0.00052 ang^2 and 0.514E-06 ang^4
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- *

TITLE   Cu crystal fcc
EDGE     K
S02      1.0

*      pot    xsph  fms   paths genfmt ff2chi
CONTROL  1      1      1     1      1      1
PRINT    1      0      0     0      0      3

*      r_scf   [ l_scf  n_scf  ca ]
*SCF      5.62829  0      15    0.1

*      ixc    [ Vr  Vi ]
EXCHANGE  0      0    0
EXAFS    20
RPATH    11
NLEG     4

*      kmax   [ delta_k  delta_e ]
*XANES    4.0     0.07    0.5
*      r_fms   [ l_fms ]
*FMS      5.62829    0
*
*RPATH    0.10000
*      emin  emax  resolution
```

```

*LDOS      -20    20    0.1

POTENTIALS
*   ipot    z [ label    l_scmt  l_fms  stoichiometry ]
      0    29   Cu      -1      -1      0
      1    29   Cu      -1      -1      1

ATOMS
  0.00000    0.00000    0.00000    0   Cu1    0.00000
  0.00000   -1.80900    1.80900    1   Cu1    2.55831
  1.80900    0.00000    1.80900    1   Cu1    2.55831
(follow the positions of the atoms up to the 5th shell)
END

```

The calculation proceed as follows: first of all the program is instructed that a K edge spectrum has to be calculated (*EDGE* card). Then the various modules of the program are marked to be run (1) or not (0) in sequence (*CONTROL* card) performing the following operations:

**pot** Calculates the (atomic, muffin tin) scattering potentials.

**xsph** Calculates the phase shifts.

**fms** Full multiple scattering calculation of the absorption cross section. Not used in the present example.

**paths** path identification

**genfmt** Scattering amplitude calculation.

**ff2chi** Output of the various theoretical paths on a file.



The card *EXCHANGE* defines the potential type to be used, *ixc*=0 corresponding to the complex Hedin-Lunqvist potential.

There are cards that give to the program some limits for the calculation. Here card *EXAFS* limits the maximum *k* for the calculation to  $20 \text{ \AA}^{-1}$ , the maximum length (complete trip) for a path to be considered in the calculation (*RPATH* card) is  $11 \text{ \AA}$  and scattering paths up to  $4^{th}$  order ('leg', see next section).

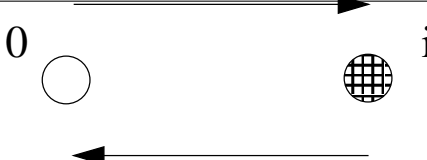
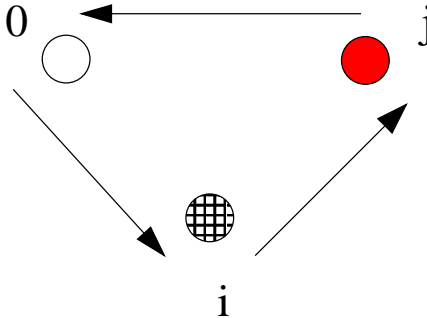
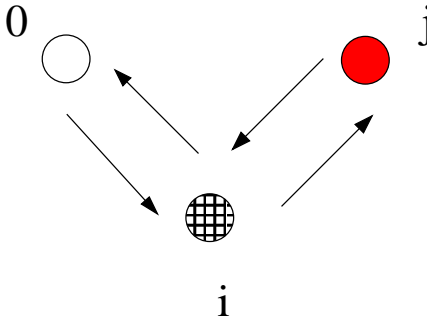
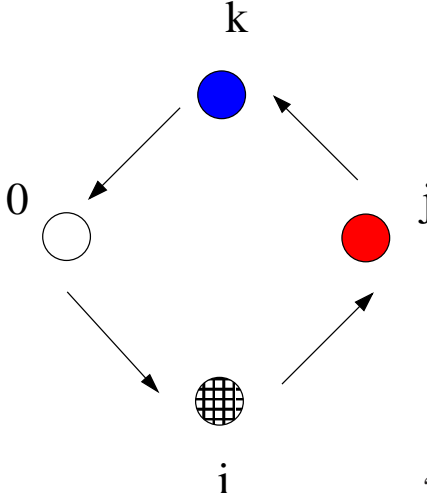
Cards like *SCF*, *XANES*, *FMS*, *LDOS* are not needed for calculations to be used in an EXAFS analysis so are commented with a \* character.

Then the program is instructed on how associate the various potentials to the different atoms in the cluster through the *POTENTIAL* card.

For different chemical species a different potential number is associated (1, 2, ...) potential 0 is always related to the photoemitter. In the following *ATOMS* card the spatial position and the potential associations are explicitated. It must be underlined that all the phase shifts (central atom, first and farther neighbors) are calculated starting from the same cluster.

## 5.1 Scattering paths in Feff

The scattering order of a path can be defined as the number of lines (legs) you draw between scatterers to describe the process under analysis as shown below:

	a two legged-path
	a three legged-path
	a four legged-path
	26 another four legged-path

Here '0' denotes the photoabsorber.

If a same 'loop' (same bonds and angles but different involved atoms except the absorber) is found in different atomic arrangements the associated path is said to be 'degenerate' and the degeneration is calculated and accounted for in the path amplitude. Moreover: the same loop can be run in clockwise or counterclockwise direction: this also is accounted for as a 'degeneration' of the path <sup>1</sup>. These degenerations can be removed when calculating the path amplitude accounting for the polarization (see below).

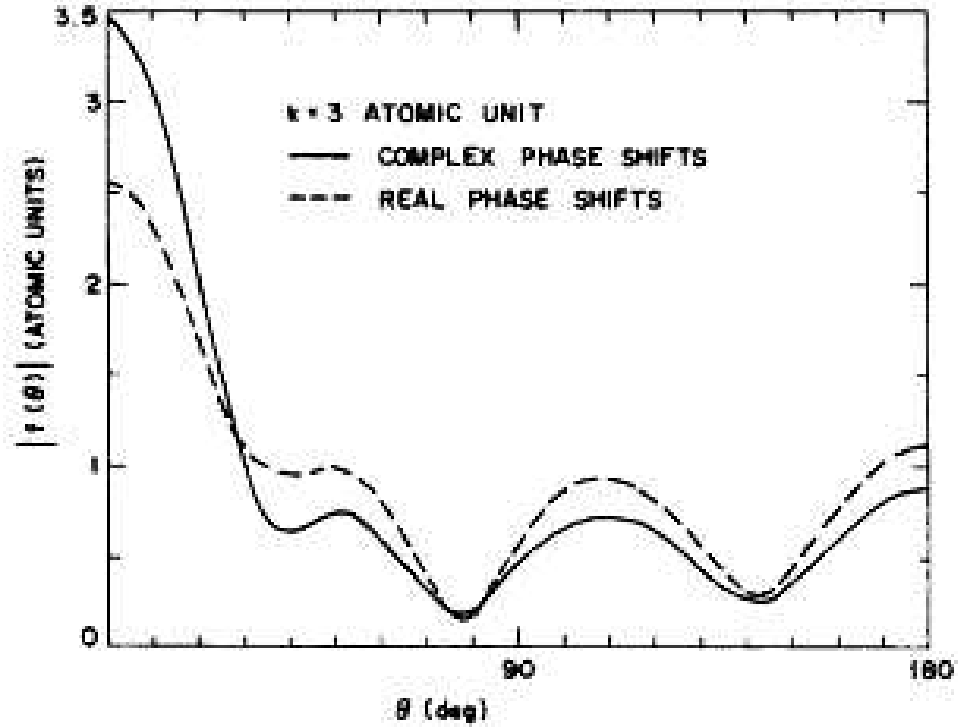
When considering a given atomic arrangement a [limited number of different paths](#) have to be considered to correctly account for the its contribution ot the total  $\chi$  signal. For the three atoms 0, i, j a good choice is to consider:

- 0 - i 2 legged path
- 0 - j 2 legged path
- 0 - i - j - 0 3 legged path
- 0 - i - j - i - 0 4 legged path

The importance of the 3 and 4 legged paths grow dramatically as the  $\hat{0ij}$  angle approaches 180 deg (i.e. collinear configuration and 0 deg angle scattering on i). As shown in the following picture (Cu atom, plane wave approx. [12])

---

<sup>1</sup>For this reason the degeneration of double scattering paths found by feff are twice those found by GNXAS that does not account for the 'rotation' sense.



the modulus of the scattering amplitude  $|f(\theta)|$  exhibits a marked maximum at 0 deg (forward scattering).

Finally, couple of points need a particular attention when comparing with the GNXAS code:

- The calculated amplitude of a given MS path is valid only for the geometric arrangement considered. The derivatives of amplitude and phase of the path respect to the path length and path angles are not calculated. This has to be considered when an-

alyzing samples with MS paths exhibiting different geometries with respect to the model, especially for the bond angles.

- For what concerns disorder each path is considered to be damped by a Debye-Waller like factor  $e^{-\sigma^2 k^2}$  where  $\sigma^2$  contains bond length and bond angle disorder (thermal or configurational). There is no explicit separation between the two contributions.

## 5.2 Some useful commands

**POLARIZATION** Feff is thought for working also on single crystals. A special card *POLARIZATION* acting on **xsph** module has be used to obtain the correct signal amplitude with the X-ray polarization vector along a given direction.

POLARIZATION x, y, z

means that the polarization vector has components x, y, z accordingly to the coordinates specified in *ATOMS*. Namely for an hexagonal system POLARIZATION 0, 0, 1 calculates the signals with the polarization parallel to the ‘c’ axis.

**CRITERIA** In principle a huge number of multiple scattering paths are present in a given atomic arrangement. Fortunately their amplitude drops rapidly with the path length and the number of scattering events.

In order to account only for the most important paths Feff sorts the paths found from the pure ‘geometrical’ analysis by their ‘amplitude’ [10]. The amplitude is taken as

$$\int_{k\text{space}} |\chi(k)| dk$$

in plane wave approximation. After sorting only paths with amplitude above a given cutoff are re-calculatd in curved-wave approximation. Among these only those above a second cutoff are considered and written on file.

The card CRITERIA (acting on the [genfmt](#)) module controls these cutoff values:

```
CRITERIA cw pw
default pw = 2.5 %
default cw = 4%
```

where cw is the curved wave cutoff, and pw is the plane wave cutoff. Default values are in percent of the largest path. This represents a 'smart' way to minimize the number of paths to be considered in the model.



### 5.3 Output files

Among the files produced by Feff some of them need particular attention. They are all in ASCII format and can be easily listed for checking:

`feffXXXX.dat` This file contains the major parameters of the associated  $XXXX^{th}$  path. It looks like this:

```
Cu crystal fcc                      Feff  8.00
Abs   Z=29 Rmt= 1.414 Rnm= 1.460 K  shell
Pot 1 Z=29 Rmt= 1.361 Rnm= 1.398
Gam_ch=1.729E+00 H-L  exch
Mu=-3.268E+00 kf=1.831E+00 Vint=-1.605E+01 Rs_int= 1.980
Path   1  icalc      2
-----
 2 12.000   2.5583   2.6431  -3.26835 nleg, deg, reff, rnrnav(bohr), edge
   x     y     z   pot at#
   0.0000  0.0000  0.0000  0  29 Cu   absorbing atom
   0.0000  1.8090  1.8090  1  29 Cu
   k  real[2*phc]  mag[feff]  phase[feff]  red factor  lambda  real[p]@#
0.000  3.6837E+00  0.0000E+00 -5.0825E+00  9.885E-01  1.6150E+01  1.8324E+00
0.100  3.6842E+00  4.9963E-02 -5.5819E+00  9.887E-01  1.6173E+01  1.8350E+00
0.200  3.6856E+00  9.7959E-02 -6.0572E+00  9.892E-01  1.6239E+01  1.8429E+00
0.300  3.6877E+00  1.4233E-01 -6.5099E+00  9.900E-01  1.6345E+01  1.8558E+00
```

where the various columns contain:

- `k` the photoelectron wavevector
- `real[2*phc]` the central atom phase \* 2
- `mag[feff]` the path amplitude

- `phase[feff]` the backscatterer phase
- `phase[feff]` the central atom reduction factor
- `lambda` the photoelectron mean free path
- `real[p]` the real part of the photoelectron momentum

This file is directly usable with the *feffit* program or, suitably manipulated, with a generic EXAFS fitting program.

[list.dat](#) The ‘list.dat’ file resumes some basic informations on the calculations on the various scattering paths. For each (numbered by ‘pathindex’ that also gives the name to the corresponding feffXXX.dat file) it is indicated:

- the  $\sigma^2$  factor considered (if any)
- the amplitude ratio respect to the first path
- the degeneracy (that, in case of single scattering path is the number of neighbors)
- the scattering order
- the effective path length (half the loop length, for single scattering coincides with the bond length).

Here we show a typical output for this file:

```

Cu crystal fcc                                     Feff  8.00
Abs   Z=29 Rmt= 1.414 Rnm= 1.460 K  shell
Pot 1 Z=29 Rmt= 1.361 Rnm= 1.398
Gam_ch=1.729E+00 H-L  exch
Mu=-3.268E+00 kf=1.831E+00 Vint=-1.605E+01 Rs_int= 1.980
-----
pathindex    sig2    amp ratio    deg    nlegs    r effective
    1         0.00000    100.000    12.000     2     2.5583
    2         0.00000     23.042     6.000     2     3.6180
    3         0.00000     11.967    48.000     3     3.8375
    4         0.00000      9.198    48.000     3     4.3673
    5         0.00000    55.644    24.000     2     4.4311
    6         0.00000    11.632    48.000     3     4.7739
    7         0.00000    24.567    96.000     3     4.7739
    8         0.00000    19.047    12.000     2     5.1166
    9         0.00000      9.492    12.000     3     5.1166

```

10	0.00000	43.979	24.000	3	5.1166
11	0.00000	8.413	12.000	4	5.1166
12	0.00000	4.189	12.000	4	5.1166
14	0.00000	31.858	12.000	4	5.1166

[path00.dat](#) This file contains a more exhaustive description of the paths permitting their identification. Here is a typical output:

```

Cu crystal fcc
Rmax 11.2566, keep limit 0.000, heap limit 0.000
Plane wave chi amplitude filter 2.50%
-----
  1   2 12.000 index, nleg, degeneracy, r= 2.5583
    x      y      z      ipot label      rleg      beta      eta
0.000000  1.809000  1.809000  1 'Cu      '      2.5583 180.0000  0.0000
0.000000  0.000000  0.000000  0 'Cu      '      2.5583 180.0000  0.0000
  2   2  6.000 index, nleg, degeneracy, r= 3.6180
    x      y      z      ipot label      rleg      beta      eta
0.000000  3.618000  0.000000  1 'Cu      '      3.6180 180.0000  0.0000
0.000000  0.000000  0.000000  0 'Cu      '      3.6180 180.0000  0.0000
  3   3 48.000 index, nleg, degeneracy, r= 3.8375
    x      y      z      ipot label      rleg      beta      eta
-1.809000  1.809000  0.000000  1 'Cu      '      2.5583 120.0000  0.0000
-1.809000  0.000000 -1.809000  1 'Cu      '      2.5583 120.0000  0.0000
 0.000000  0.000000  0.000000  0 'Cu      '      2.5583 120.0000  0.0000
  4   3 48.000 index, nleg, degeneracy, r= 4.3673
    x      y      z      ipot label      rleg      beta      eta
 0.000000  3.618000  0.000000  1 'Cu      '      3.6180 135.0000  0.0000
-1.809000  1.809000  0.000000  1 'Cu      '      2.5583  90.0000  0.0000
 0.000000  0.000000  0.000000  0 'Cu      '      2.5583 135.0000  0.0000

```

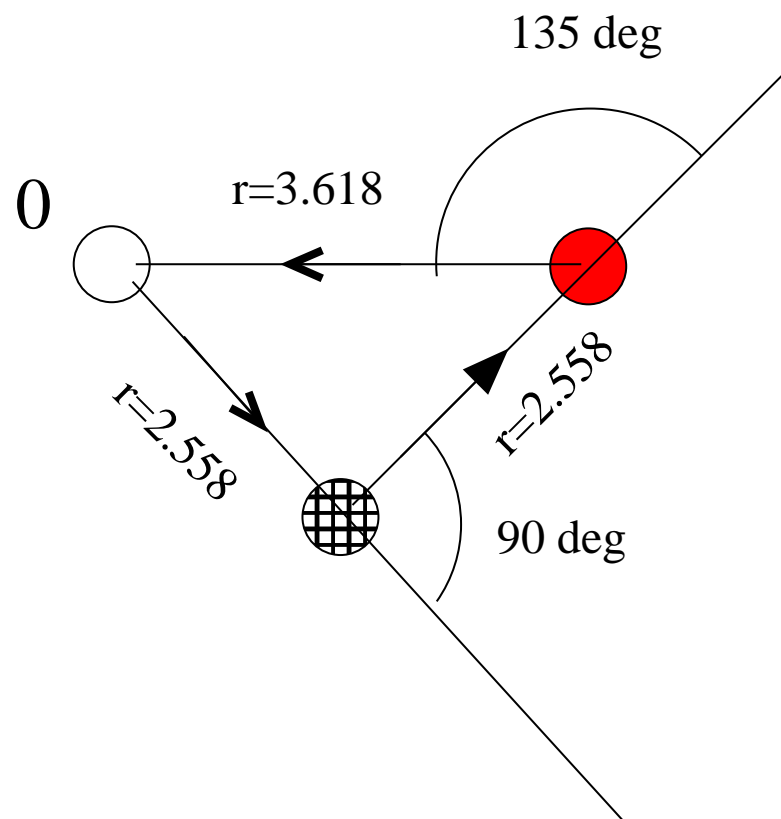
For each path it is indicated the number, scattering order and degeneracy. Then the atomic coordinates of the related atomic configuration follow with the potentials associated to each atom and the atom tags.

If desired it is possible to modify the atomic positions to generate (with a successive

run of **genfmt** paths with new configurations using the previously calculated potentials. This can be useful when the sample is found to have different arrangements respect to the model crystal.

The successive numbers are added to better describe the path but are not considered by **genfmt**. *rleg* is the leg length, *beta* indicates the photoelectron scattering angle. Namely for path 4 in the previous example if we start from atom with potential ‘0’ (the absorber at 0.0, 0.0, 0.0) going to the first scatterer the photoelectron travels for 2.558 Å then scatters on the neighbor at (-1.809, 1.809, 0.00) with an angle of 90 deg, travels again for 2.558 Å scatters of 135 deg on the neighbor at (0.0, 3.618, 0.0) and travels for 3.618 Å before coming back to the absorber.

The picture below describes path 4 with bond lengths and angles evidenced.



## 6 AUTOBK

AUTOBK [13] is used to extract the oscillating EXAFS part  $\chi(k)$  from the raw absorption spectrum. The  $\chi$  function is taken as:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)} \quad (6)$$

Where  $E_0$  is the absorption edge energy,  $\mu_0(E)$  the atomic-like absorption past the edge,  $\Delta\mu_0(E)$  the jump at the edge step. Usually  $\chi$  is expressed as a function of the photoelectron wavevector  $k$

$$k = \sqrt{\frac{2m}{\hbar}}(E - E_0) \approx 0.51\sqrt{(E - E_0)} \quad (7)$$

It uses a cubic splines to approximate the atomic background  $\mu_0(E)$ . The spline is adjusted by minimizing the difference (spline-spectrum) above the edge in fourier space below a given  $R$  value  $R_{bkg}$ . A value of  $R_{bkg} = 1\text{\AA}$  is taken by default and user can change it to change the spline *stiffness*  $\{higher R_{bkg}\} \iff \{floppier function\}$  taking care to ensure  $R_{bkg} < 2 \times R_{first\_shell}$ .

Here you find an example of input file:

```
Title = cu
data = cu.mu
out = cu
Rbkg = 1.0
kmin = 1.1
e0 = 8983.3
-----
```



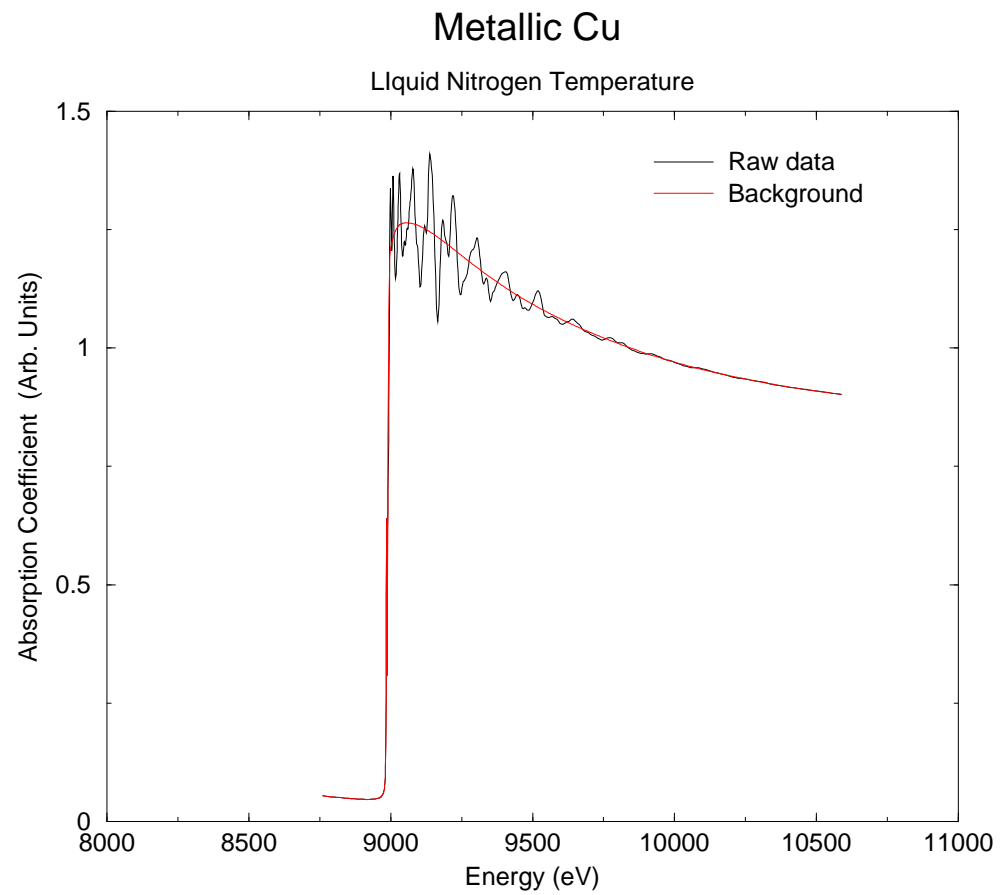
The most important output files are:

**\*e.bkg** : the background file

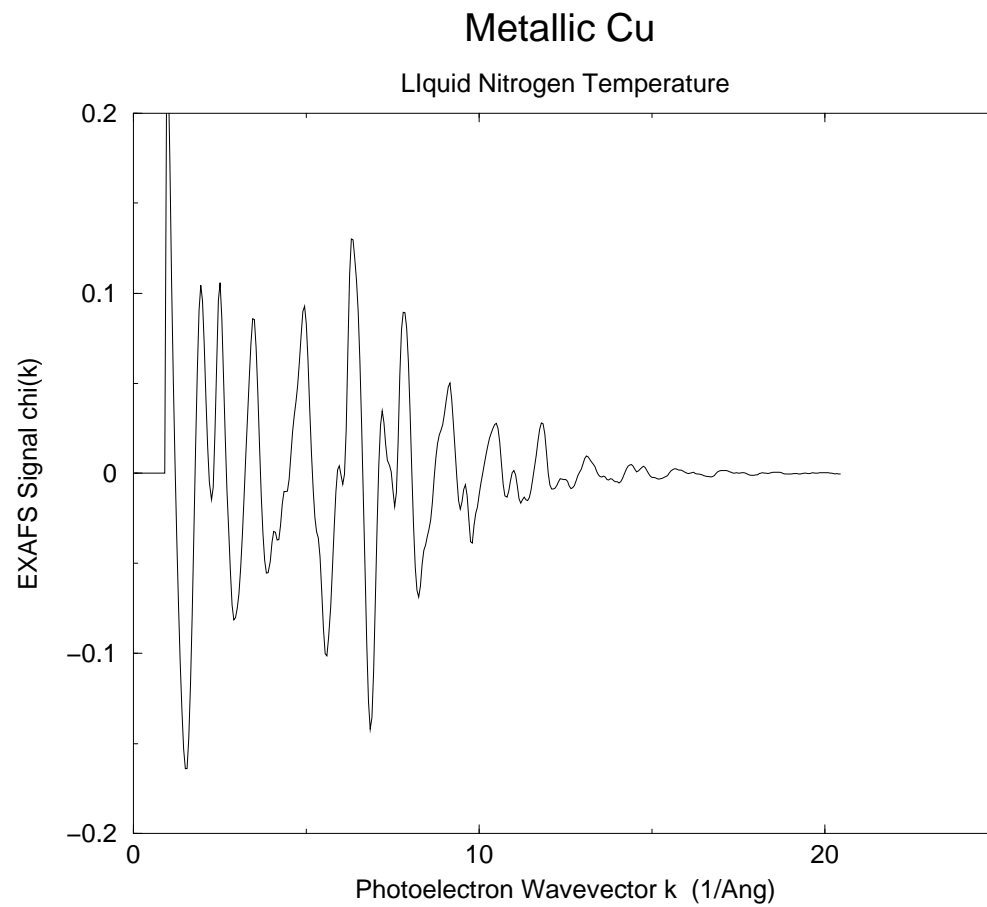
**\*k.chi** : the extracted EXAFS spectrum  $\chi(k)$ .

**autobk.log** : text file containing details on the background subtraction

Here you have an example on the output from autobk:



Absorption and calculated background



The extracted EXAFS  $\chi(k)$  function.

## 7 FEFFIT (ARTEMIS)

Program FEFFIT [14] permits a quantitative analysis of EXAFS data starting from theoretical paths calculated with FEFF.

The basic idea stems from the assumption that in the EXAFS region the spectrum is obtainable as sum of individual path signals as follows:

$$\chi(k) = \sum_{\Gamma} \chi_{\Gamma}(k) = S_0^2 \sum_{\Gamma} \frac{N F_{eff}}{k R^2} e^{\frac{-2R}{\lambda}} \sin(2kR + \phi_{eff} + \phi_c) e^{-2k^2 \sigma^2} \quad (8)$$

Where the sum runs over all the paths single or multiple scattering. Quantities in red are calculated by FEFF, quantities in blue are usually the unknown of the problem. In particular they are:

- $k$  The photoelectron wavevector.
- $\chi(k)$  The EXAFS signal.
- $S_0^2$  The amplitude reduction factor.
- $F_{eff}$  The effective curved-wave backscattering amplitude.
- $\phi_c$  The total central atom phase shifts.
- $\phi_{eff}$  The backscatterer phase shift.
- $\lambda$  The photoelectron mean free path.

- $\sigma^2$  The mean square fluctuation of R (Debye-Waller factor).
- $R$  The path half length (bond length in single scattering paths).
- $N$  The number of neighbors.

The separation between the various terms can be done by working on Fourier Transforms of the  $\chi(k)$ . This permits also the analysis of the spectrum on a limited number of shells.

The program minimizes the function

$$\chi^2 = \sum_{i=1}^N \left( \frac{f_i^{data} - f_i^{model}}{\epsilon_i} \right)^2 \quad (9)$$

where  $f_i$  can be the real plus imaginary part of the FT or the back-transformed spectrum. The minimum is found with a Levenberg-Marquardt algorithm.

FEFFIT is controlled by an input file called *feffit.inp* that contains the commands to run the fit. The commands can be grouped by action as follows:

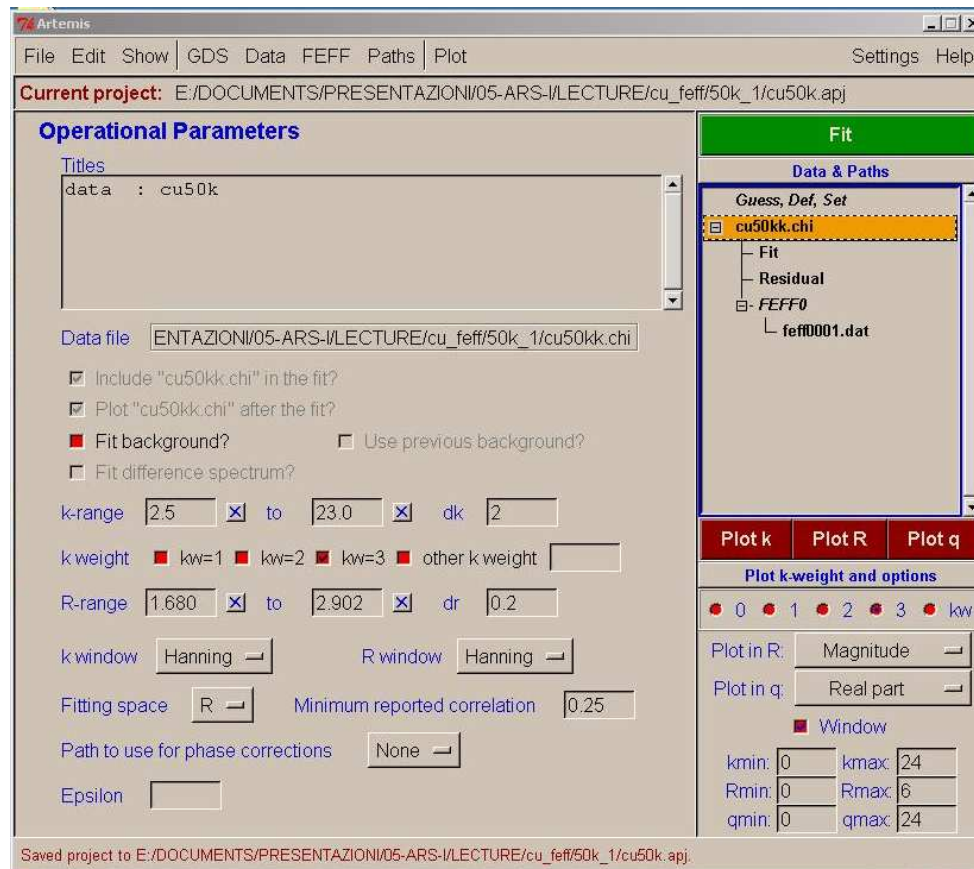
- fitting control (regions, weights, ...)
- definition of variables
- definition of the paths

The fit can be done both on the back-transformed space or in Fourier space, so minimizing the manipulation of the spectra. In this latter case both Real and Imaginary parts are considered with equal weight (default choice). For a detailed description of the program please refer to [14] and to the feffit manual available on the web page [15].

In the following examples we will approach the fit of the EXAFS spectrum of a [Cu metallic foil at 50 K](#). The fit will be done on the first shell and then on the first 4 shells evidencing the role of multiple scattering contributions.

## 7.1 Metallic Cu, $I^{st}$ shell

Also in the case of FEFFIT a new version of the program has been recently released with an improved user interface. The new code is called ARTEMIS and the picture below presents the input page:



ARTEMIS needs the following inputs:

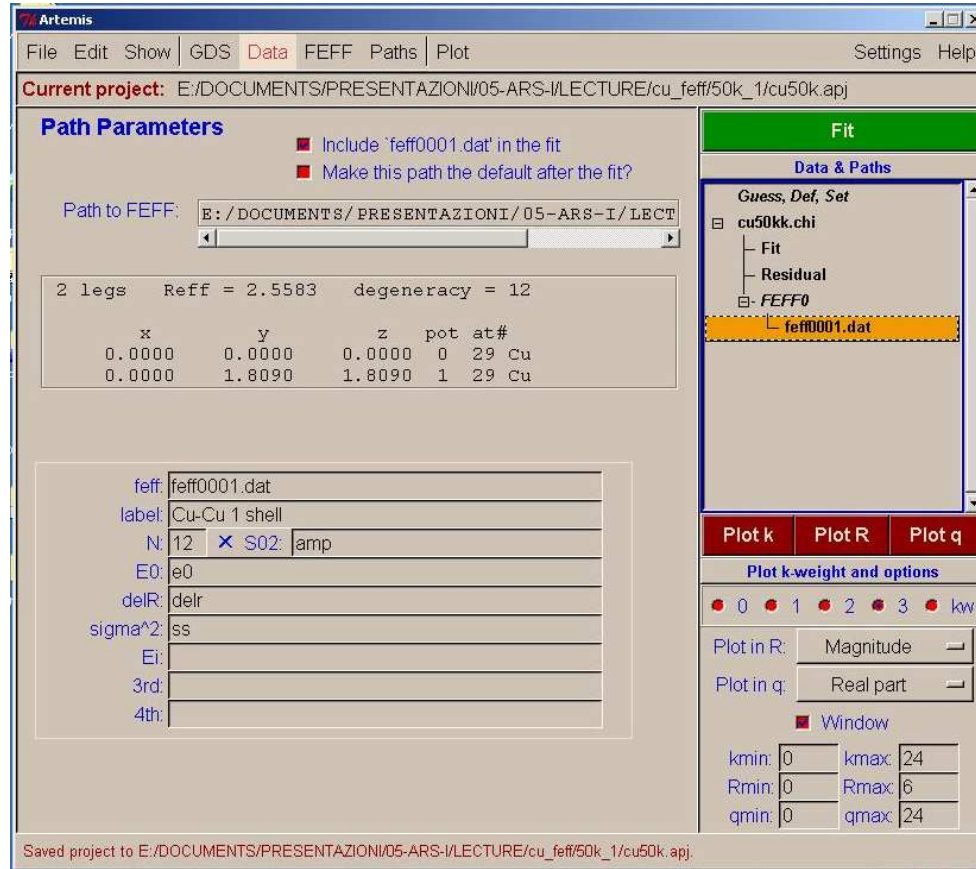
- an experimental  $\chi(k)$  spectrum, extracted (namely) with autobk.
- the feffxxxx.dat theoretical paths generated by feff

Successively, the details for FT transformation and fit have to be added like:

- *krange* The range in k space for FT
- *kweight* n in the  $k^n$  weight for exp. data
- *dk* The 'width' of the window
- *kwindo* The window type (see manual)
- *R-range* The fit range in R space (if used)
- *Fitting space* Can be k, R or q.

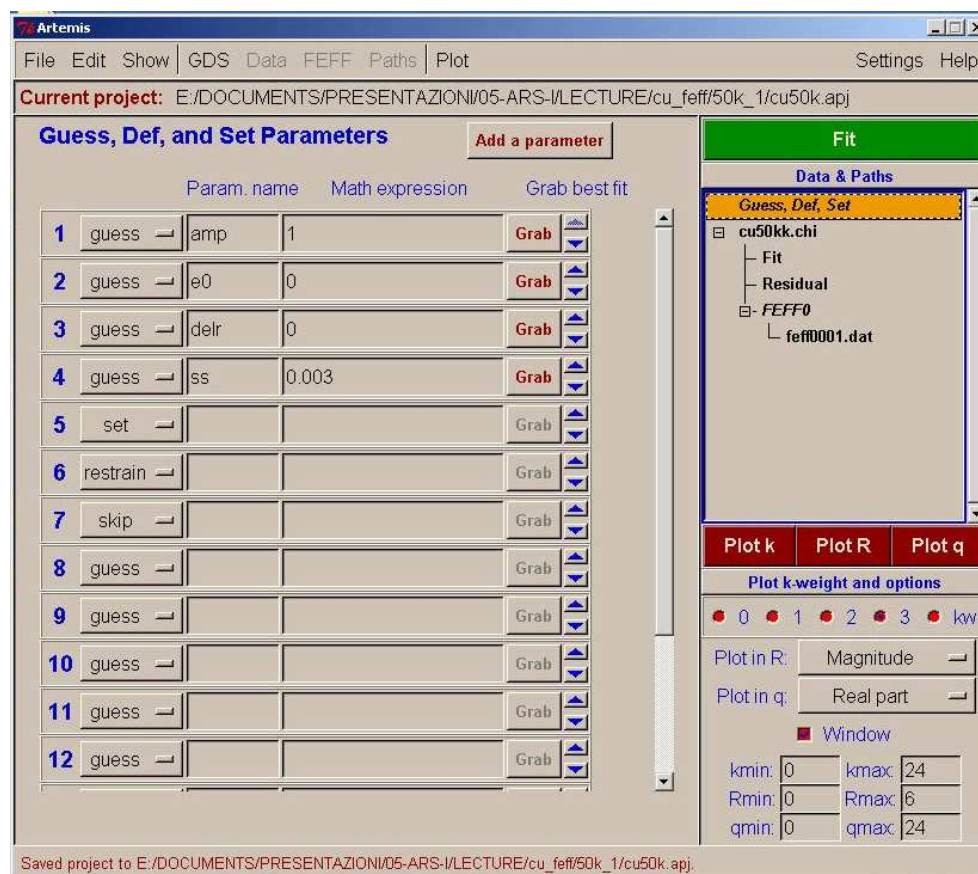
The theoretical paths to be used for the fit can be added under the menu **FEFF**  $\rightarrow$  **Add a feff path** and a window pops up with the details of the path:





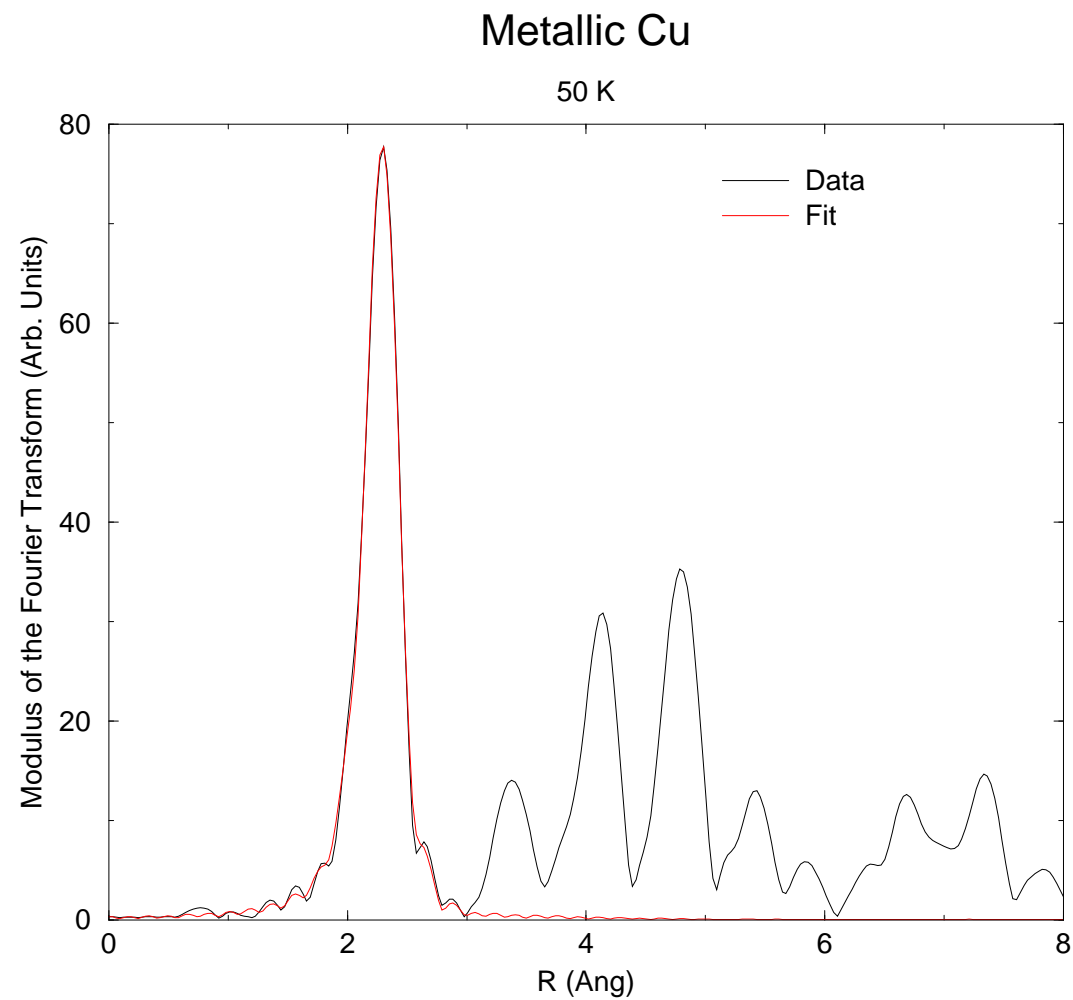
For each path (only one in this case) a name for each variable has to be chosen to be used in the following section. In this case we considered the number of neighbors 12 so we decide to fix the  $S_0^2$  parameter, the edge shift  $\Delta E_0$ , the deviation from the theoretical bond length  $\Delta R$  and the Debye-Waller factor  $\sigma^2$ .

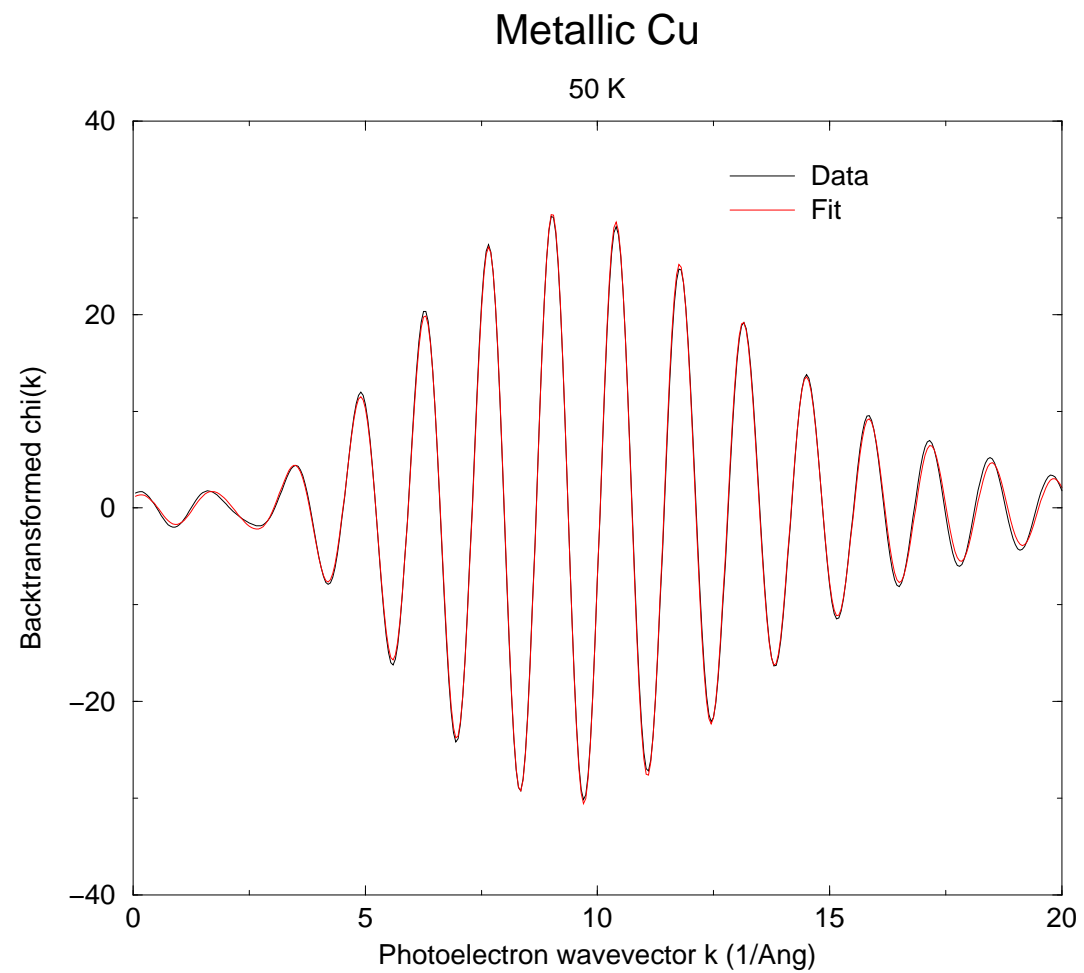
Finally the *user variables* to be fitted are declared with the **guess** or **set** commands with their initial values:



**Set** can be also used to define relations between the variables that represents one of the major points of the *feffit* program. This permits to reduce the free parameters by introducing a little physics in the problem. Eventually clicking the **FIT** button starts the fit. *feffit* (and ARTEMIS) use equation (8)

to fit data in a given  $R$  range. In this way only paths with a length less than  $R$  have to be considered in the fit permitting the analysis on a limited frequency region of the spectrum. The results of the fits are shown below:





The results of the fits are written in the file *\*.log*

Project title : Fitting cu50kk.chi  
Prepared by :  
Contact :  
Started : 13:34:36 on 7 June, 2005  
This fit at :  
14:05:24 on 7 June, 2005  
Environment : Artemis 0.6.009 using Windows 2000,  
perl 5.006001, Tk 800.023, and Ifeffit 1.2.5

=====

Independent points=15.577148437  
Number of variables=4.000000000  
Chi-square=142.413269537  
Reduced Chi-square=12.301238971  
R-factor=0.002368169  
Measurement uncertainty (k)=0.000205961  
Measurement uncertainty (R)=0.405209346  
Number of data sets=1.000000000

Guess parameters +/- uncertainties:

amp	=	0.8806861	+/-	0.0260147
e0	=	4.0043504	+/-	0.4398137
delr	=	-0.0031570	+/-	0.0014421
ss	=	0.0036016	+/-	0.0001231

Correlations between variables:

amp and ss	-->	0.8741
e0 and delr	-->	0.8716

All other correlations are below 0.25

===== Data set cu50kk.chi =====

file: E:/DOCUMENTS/PRESENTAZIONI/05-ARS-I/LECTURE/cu\_feff/50k\_1/cu50kk.chi

title lines:

data : cu50k

k-range = 2.500 - 23.000

dk = 2.000

k-window = hanning

k-weight = 3

R-range = 1.680 - 2.902

dR = 0.200

R-window = hanning

fitting space = R

background function = none

phase correction = none

These are not yet computed quite right in all situations...

Chi-square for this data set = 284.82654

R-factor for this data set = 0.00237

===== Paths used to fit cu50kk.chi

FEFF0: feff0001.dat

feff = E:\DOCUMENTS\PRESENTAZIONI\05-ARS-I\LECTURE\cu\_feff\feff\feff0001.dat

id = reff = 2.5583, degen = 12.0, path: Cu->Cu->Cu

r = 2.555143

reff = 2.558300

degen = 12.000000

```

n*s02    =    0.880686
e0        =    4.004350
dr        =   -0.003157
reff+dr   =    2.555143
ss2       =    0.003602

```

The fields in the file are generously commented so you can easily find all the infos you need.

As a general rule in the first part the results on the 'fitted' variables are resumed together with the statistical analysis of the fit (  $\chi^2$  analisys, error analysis, correlations, ...). Then the fit conditions ( weight, boundaries, ...) are shown.

Finally the results on the path variables are resumed. Note a few tricks:

- Take care to the relations you established between path and user variables.
- For the bond length R the actual fitted variable is delR. To know the R value you have to see the value of {reff + delR}
- *feffit* considers by default the path with its geometrical degeneracy. So in this case we got 12 neighbours (degen) without explicitly telling the program as it went from the calculation. If the number of neighbors is your unknown you have to run the program with the N card = 1 and attribute to each path an amplitude  $S_0^2 \times N$  where  $S_0^2$  is found from a reference compound and  $N$  is the number of neighbors to be fitted.

## 7.2 Error analysis

A few considerations now on the error analysis made by *feffit*. The fitting routine works through the minimization of a  $\chi^2$ -like function like that in eq. (9). For the correct statement of such a function (in order to perform a statistical analysis on it) it is mandatory to correctly determine the noise *Epsilon* on the data. When working in Fourier Transformed space it is hard to establish a relation between the noise you can estimate on the spectrum (by the square root of counts or by empirical techniques) and the error that propagates through the fourier filter. An accurate error analysis is necessary to:

- decide whether what we have found is a good fit or not
- attribute error bars to the best-fitting quantities

*feffit* has an automatic routine that determines the 'noise' on the data from the residual extracted from the Fourier Transformed data between  $R = 15 - 25$  Å. In this way values of the  $\chi_\nu^2$  ( $\chi$ -square function divided by the number of free parameters  $\nu$ ) well above 1 are obtained even for the best looking fits, preventing a correct statistical analysis. Feffit circumvents this problem by calculating the parameters uncertainties by multiplying the square root of the diagonal elements of the correlation matrix by  $\sqrt{\chi_\nu^2}$ . This is equivalent to rescale *Epsilon* to obtain a  $\chi_\nu^2 = 1$  that is to assume *a priori* the goodness of the fit and attributing to statistical *noise* the misfit.



### 7.3 Multiple Scattering analysis

In the Fourier Transform of the metallic Cu foil several coordination shells are well visible above the first.

Also from the *feff* calculation (file list.dat) several higher order paths (3 and 4 legged) result to have a considerable amplitude.

coordination shells can give a deeper insight in the material structure. Moreover for such task the inclusion of Multiple Scattering (MS) paths is mandatory.

selected the stronger paths to be considered. By constructing our model we only have to avoid parameter proliferation due to the increased number of paths.

parameters can easily linked so minimizing the number of free parameters.

fit of metallic Cu:

```
Title = cu50k data = cu50kk.chi
allout T
%
%---FT parameters -----
kmin = 1.7 kmax = 20 dk = 3 kweight = 3.0
% -----
%
%
% --- Fit details -----
rmin = 1.7 rmax = 5.1 epsdat 1.33e-3
%-----
%
%
% ---- User variables -----
set sigm_mcm = 0.00052 set temp = 50
```

```

%
guess e0          = 0.0 guess s02      = 1.0 guess exp_param = 0.00 guess
Debye_temp = 315
% -----
%
%
%
% --- Global parameters -----
s02      0      s02
e0        0      e0
delr      0      reff * exp_param
sigma2    0
debye (temp, Debye_temp) + sigm_mcm
% -----
%
%
% -----Path list -----

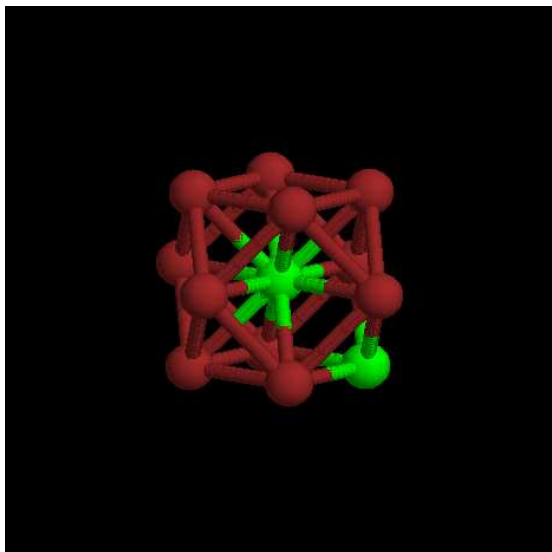
Path      1      ../feff/feff0001.dat Id      single scattering 1st shell
Path      2      ../feff/feff0002.dat Id      ss II shell
Path      3      ../feff/feff0003.dat Id      ms 60 deg triangles
Path      5      ../feff/feff0005.dat Id      ss III shell
Path      6      ../feff/feff0006.dat Id      ms 120 deg
Path      7      ../feff/feff0007.dat Id      ms 120 deg
Path      8      ../feff/feff0008.dat Id      ss 4th shell
Path     10      ../feff/feff0010.dat Id      ms 4th shell Cu*-Cu-Cu
Path     13      ../feff/feff0014.dat Id      ms 4th shell Cu*-Cu-Cu-Cu

end

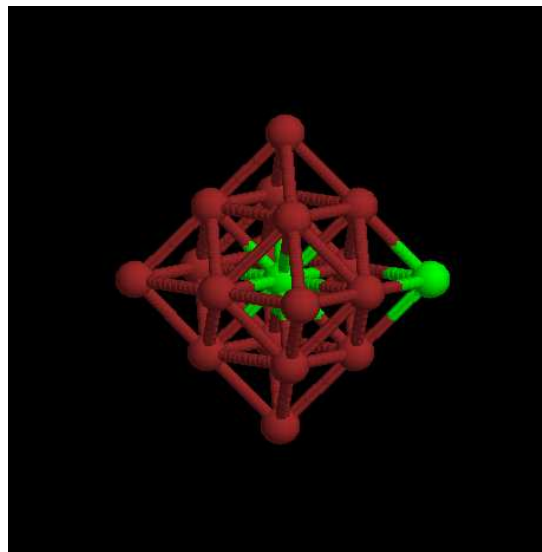
```

Here the path list includes:

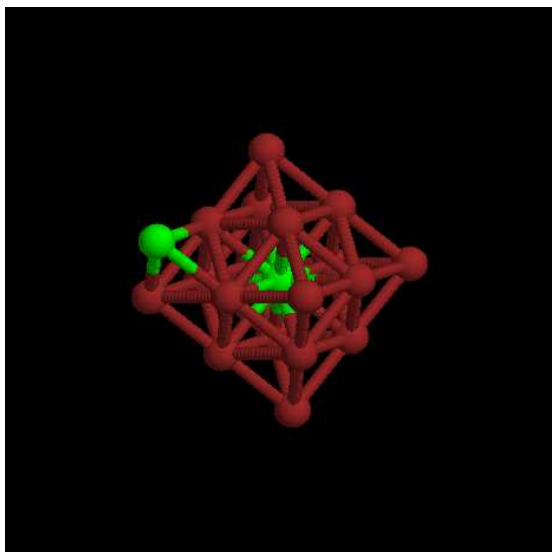
- [Single scattering](#) paths from the first to the fourth shell (paths 1, 2, 5, 8)



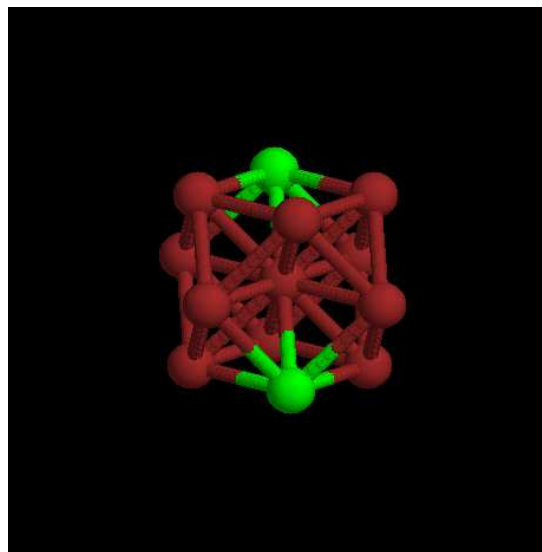
Path 1



Path 2



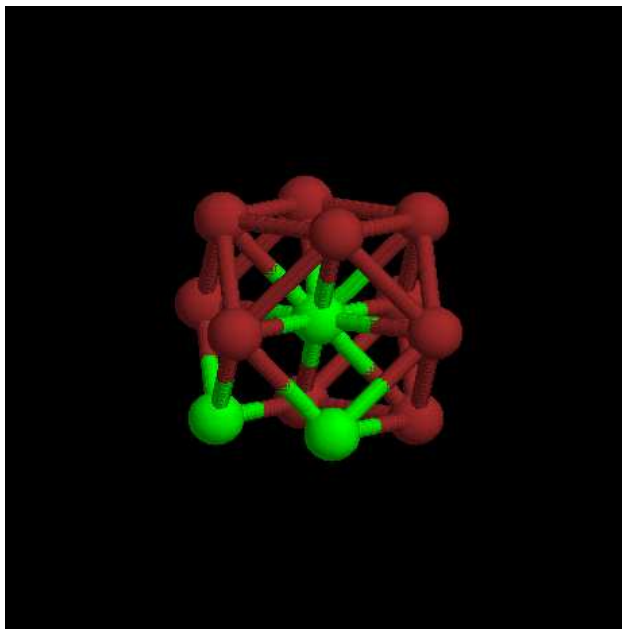
Path 5



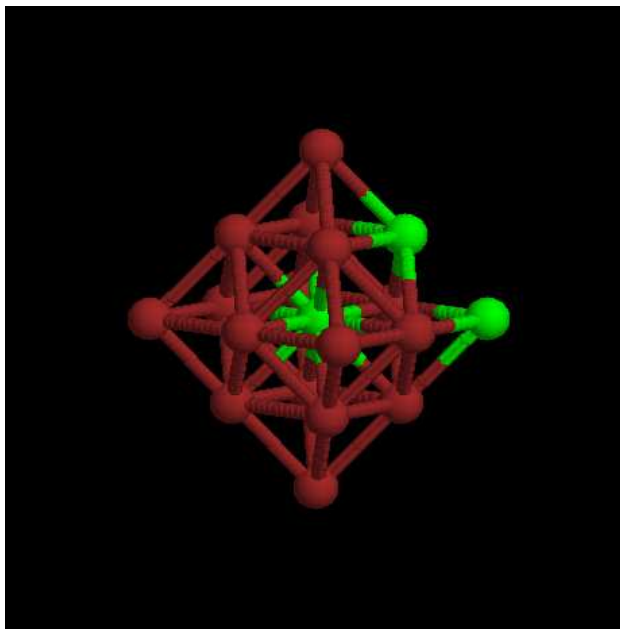
Path 8



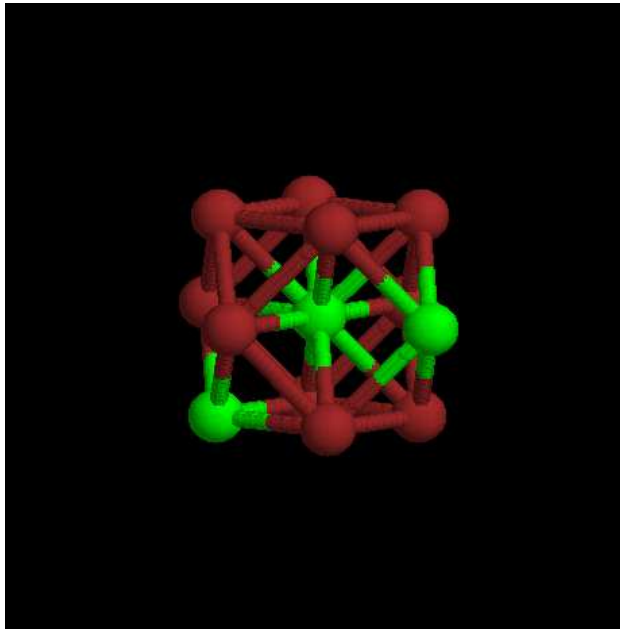
- Double scattering between absorber and 2 Nearest Neighbors (NN) with the absorber in the vertex of a 60 deg angle (path 3).



- Double scattering between absorber a first and a 2 neighbor with the absorber in the vertex of a 90 deg angle (path 4).

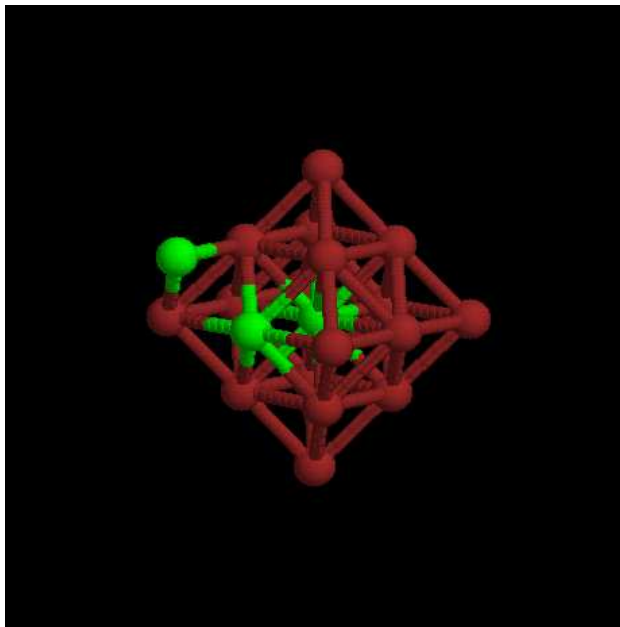


- Double scattering between the absorber and 2 NN. The absorber is on the vertex of a 120 deg angle (path 6)

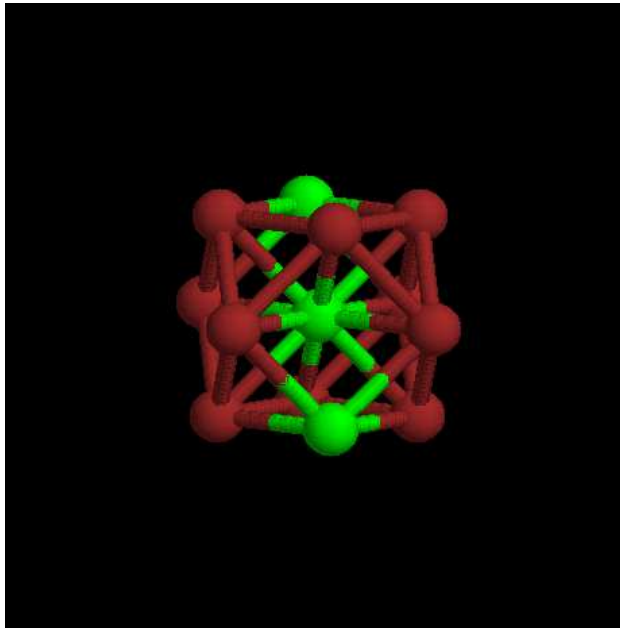




- Double scattering between the absorber a NN and a 3<sup>rd</sup> neighbor. The NN is in the vertex of a 120 deg angle (path 7).



- Double scattering between the absorber and two collinear NN the absorber in the middle of the chain (path 9)
- Double scattering between the absorber and collinear NN and 4<sup>th</sup> neighbor, the absorber at an edge of the chain (path 10)
- Triple scattering back and forth touching all the atoms in a configuration similar to path 9 (path 11)
- Triple scattering back and forth touching all the atoms in a configuration similar to path 10 (path 14)



The grouping of the parameters can be done as follows:

- a `common value of e0 and s02 can be used for all.`
- `an overall scaling of the path lengths` can be done by using the feffit function *reff*. This can be useful when treating global expansion due to doping, temperature, ...It can coupled to the delr variable of path 0 (so acting on all paths) with the command:

`delr 0 reff * exp_param`

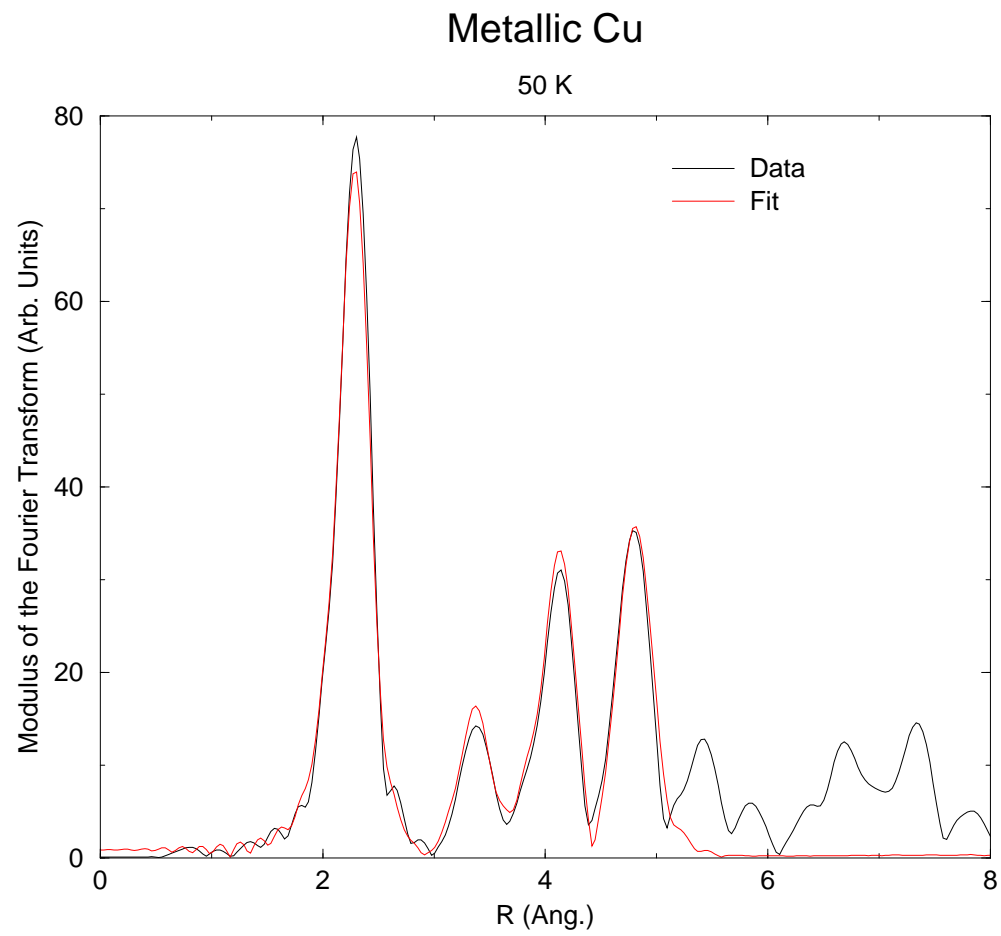
in this way for each path delr is calculated as a fraction exp\_param of the effective length reff. exp\_param is the only fitting parameter for the bond lengths.

- `A correlated Debye model for the Debye-Waller  $\sigma^2$  factors.` In principle they could be parametrized by knowing physical quantities of the system under analysis like the interatomic force constants [16] or the Debye (or Einstein) temperatures [17], [10]. In practice this works only on a few cases. When suitable the result of a feffit function

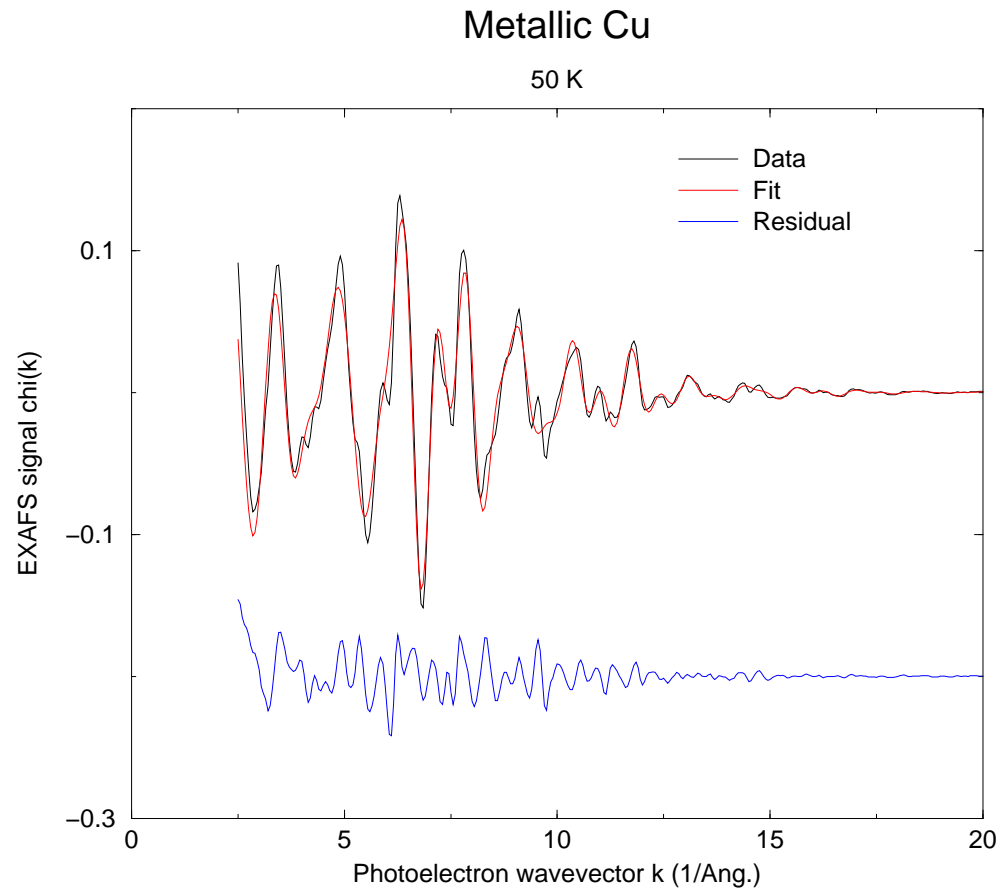
`debye (temp, debye_temp)`

can be associated to  $\sigma^2$  giving an estimated value knowing the temperature and the material Debye temperature. Associated to the 0<sup>th</sup> path it repeats this calculations for all the paths in the list.

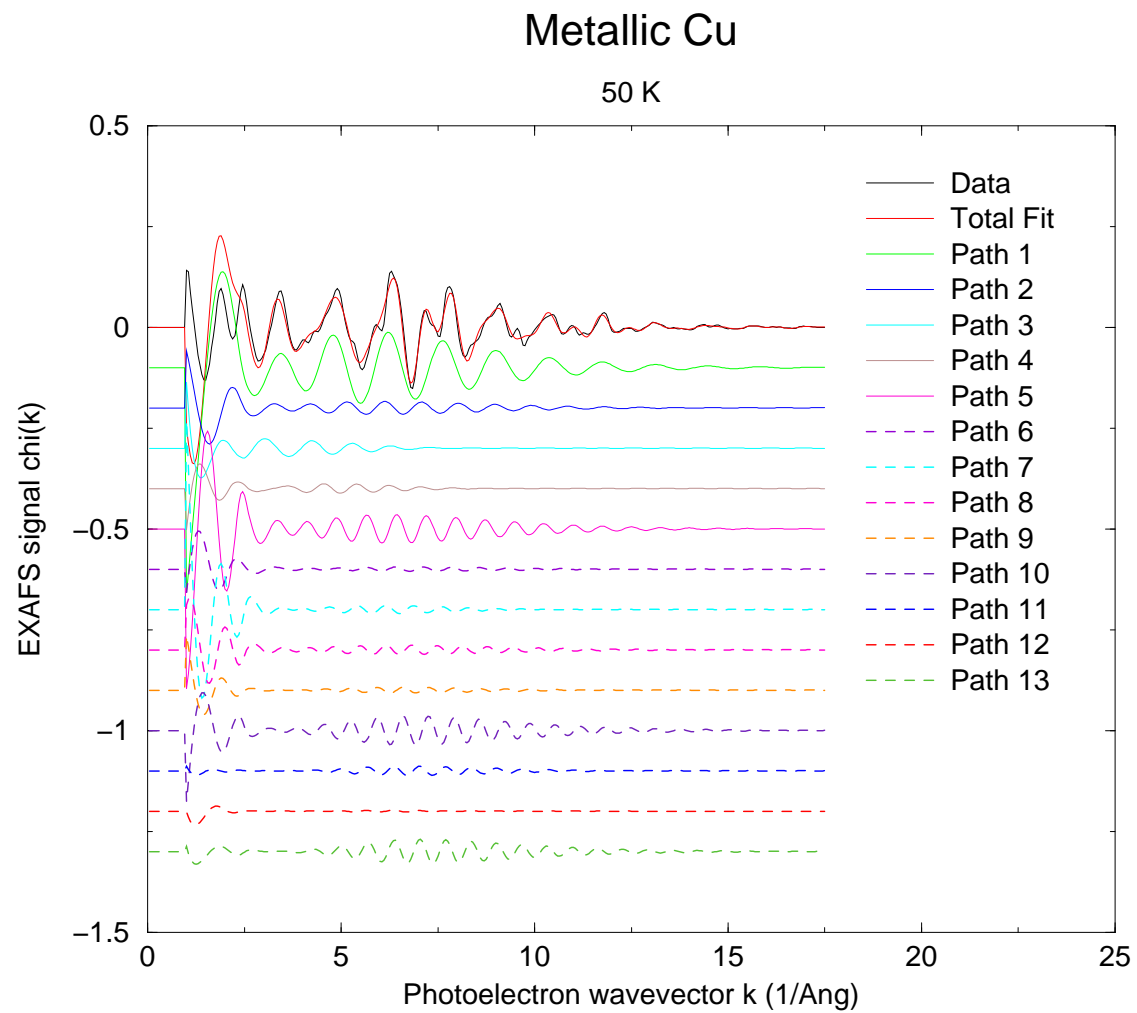
Following these prescriptions we end up to fit the spectrum of metallic Cu up to the fourth shell with 13 paths and only 4 free (e0, s02, exp\_param, Debye\_temp) parameters. The results are shown below:



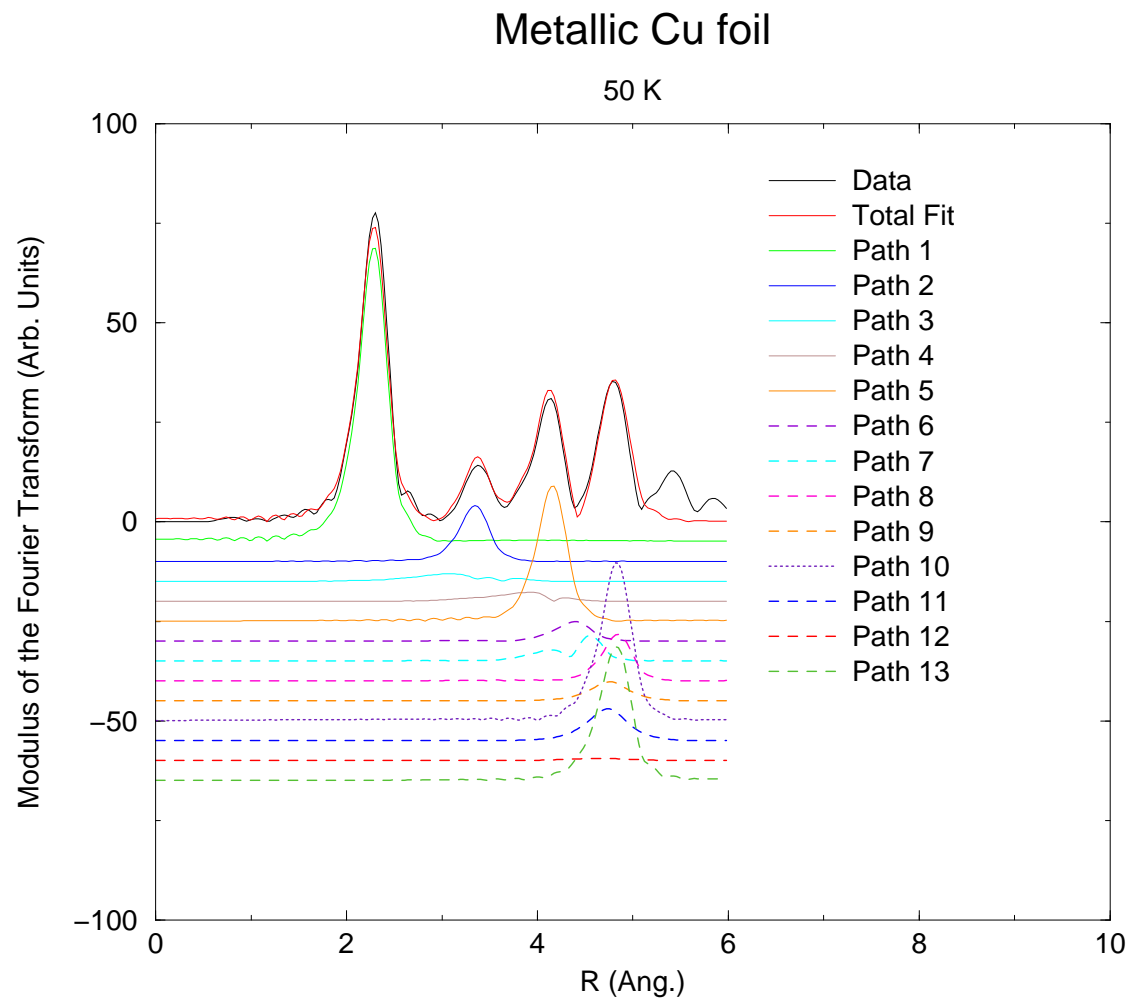
The Fourier Transform



The  $k$  space with the residual in evidence. The high frequency is due to the higher shells neglected in the fit.



The various fitting signals in  $k$  space



The various fitting signals in R space.

The results are shown in the *feffit.log* file:

```
feffit log file : version 2.32x 04-jan-1996
=====
```

input data file:

input data chi file = cu50kk.chi, skey = ASCII

-----  
fit results, goodness of fit, and error analysis:

independent points in data	=	38
number of variables in fit	=	4
degrees of freedom in fit	=	34
r-factor of fit	=	0.0274983
chi-square	=	65.0783386
reduced chi-square	=	1.9140688

feffit found the following values for the variables:

variable		best fit value	uncertainty	initial guess
e0	=	2.1270523	0.7010058	0.0000000
s02	=	0.9395413	0.0567436	1.0000000
exp_param	=	-0.0018812	0.0009045	0.0000000
debye_temp	=	304.9983826	19.1098671	315.0000000

correlation between variables

variable #1	variable #2	correlation
e0	exp_param	0.8820515
s02	debye_temp	-0.8783429

all other correlations are less than 0.2500000

>> ----- <<  
>> the uncertainties and correlations listed above are estimated <<  
>> under the assumption that the errors are normally distributed. <<  
>> <<  
>> the uncertainties given are estimated to increase the best-fit <<  
>> value of chi-square by the value of reduced chi-square. <<  
>> this assumes the fit is "good" and that the value of <<  
>> the measurement uncertainty was poorly estimated. <<  
>> ----- <<

user titles:

cu50k



```

input data chi file = cu50kk.chi, skey = ASCII
measurement uncertainty of data:
    ... in k-space      =      0.0013300
    ... in r-space      =      2.2689121
    ... in q-space      =      0.8162713
user-chosen weight for data =      1.0000000
weight used for chi-square =      2.7543547
independent points in data =      38
chi-square              =      65.0783386
r-factor                =      0.0274983
fitting was done in r-space
r range      = [  1.718058,  5.031457 ]

```

---

```

fourier transform information:
k range      = [  1.700000, 20.000000 ]
k weight     =      3.000000
dk1, dk2     =      3.000000,  3.000000
window type = hanning window sills
number of points in fft for fitting =   512
number of points in fft for outputs =  2048

```

---

```

feffit found the following values for the "fixed" values:
    sigm_mcm      =      0.0005200
    temp          =      50.0000000

```

---

```

path  feffnnnn.dat file name
1     ../feff/feff0001.dat
2     ../feff/feff0002.dat
3     ../feff/feff0003.dat
5     ../feff/feff0005.dat
6     ../feff/feff0006.dat
7     ../feff/feff0007.dat
8     ../feff/feff0008.dat
10    ../feff/feff0010.dat

```

13 ../feff/feff0014.dat

---

```

path  user identification
  1   single scattering 1st shell Cu-Cu
  2   I shell ss
  3   ds 60 deg triangles
  5   ss III shell
  6   ds 120 deg triangles
  7   ts 120 deg
  8   ss 4th shell
 10   double scattering 4th shell Cu*-Cu-Cu
 13   4th-scattering 4th shell Cu*=Cu=Cu

```

---

path	degen	amp	e0	{reff + delr}	delr	sigma2
1	12.00	0.9395	2.12705	2.5535	-0.00481	0.003932
2	6.00	0.9395	2.12705	3.6112	-0.00681	0.004508
3	48.00	0.9395	2.12705	3.8303	-0.00722	0.004358
5	24.00	0.9395	2.12705	4.4228	-0.00834	0.004455
6	48.00	0.9395	2.12705	4.7649	-0.00898	0.004553
7	96.00	0.9395	2.12705	4.7649	-0.00898	0.004553
8	12.00	0.9395	2.12705	5.1070	-0.00963	0.004418
10	24.00	0.9395	2.12705	5.1070	-0.00963	0.004418
13	12.00	0.9395	2.12705	5.1070	-0.00963	0.004418

---

path	ei	third	fourth
1	0.000000	0.000000	0.000000
2	0.000000	0.000000	0.000000
3	0.000000	0.000000	0.000000
5	0.000000	0.000000	0.000000
6	0.000000	0.000000	0.000000
7	0.000000	0.000000	0.000000
8	0.000000	0.000000	0.000000
10	0.000000	0.000000	0.000000
13	0.000000	0.000000	0.000000

---

It must be noted that the the noise level again was redefined to have a  $\chi_\nu^2 = 1$ . The fit slightly worser than the previous one at the first shell level because of the  $\sigma^2$  model: a fit with un-constrained sigmas results in a better agreement, anyways the value obtained for the Debye temperaure is  $305 \pm 19$  deg C near to the literature value 315 deg [17].

## 7.4 A tetrahedral compound: crystalline Ge

This is left as an exercise for the students. Here I will only suggest the *atoms.inp* file:

```
\title GE
space DIAMOND
a= 5.65735
rmax = 6      core= Ge

out = feff.inp

atom
! Type      x      y      z      tag
  Ge      0.125    0.125    0.125    Ge1
-----
```

Then proceed as follows:

- Calculate the cluster
- Calculate the theoretical paths
- Try a first shell fit
- try a multiple shell (and multiple scattering) fit up to the 3<sup>rd</sup> shell.

## 7.5 Advanced features

In the previous examples a quite standard analysis, though 'spiced up' by the MS treatment, was described. The UWXAFS package permits also more advanced features that will not be treated here but is well treated in the manuals:

**Non gaussian RDFs** Up to here we have tacitly assumed that the distribution of the atomic positions due to thermal vibration was of Gaussian nature. The Radial Distribution Functions (RDF) can be strongly asymmetric leading to an incorrect interpretation of the data [18]. A number of methods [5], have been developed to cope with this problem. Feffit implements non-gaussian RDFs in the framework of the cumulant expansion theory [19]; the 3<sup>rd</sup> and 4<sup>th</sup> that can be added as further Path parameters and included in the fit.

**Multiple datasets fit** In multielement compounds it is desirable having spectra at the edges of varios components to add up the information in the EXAFS fit. Feffit permits the simultaneous fit of a list of different datasets taken (namely) at different edges. The advantage is that a reduction of the total free parameter is achieved ( $R_{A-B}$  and  $\sigma_{A-B}^2$  measures at te A edge must be the same as  $R_{B-A}$  and  $\sigma_{B-A}^2$  measured at the B edge) and more physical results can be obtained. The same can be done on the same edge with data with an external parameter (temperature, pressure) variable.

**Background refinement** Up to here we have separated the EXAFS signal extraction and fit processes in two steps. At the fit stage a further refinement of the background

can be done with the main purpose of detect possible correlations between structural and background parameters. A dedicated card ( $bkg = T$ ) permits this operation that is made in practice by adding to the EXAFS formula a spline with a suitable number of knots.

## 8 Conclusion

Here we have briefly introduced the UWXAFS analysis package for EXAFS data. We warmly recommend the students to further train themselves on well known structures (bcc, zincblende, ...) to gain a full control of the various parts of the program before approaching a *real* unknown sample. Due to its introductory form this lecture is far from being exhaustive so we invite the students to refer to the programs manuals (available on the relative web pages). Another introductory course (to which a lot of pages of the present lecture are inspired) can be find in [20]. For further questions, feel free to contact me at the address: [dacapito@esrf.fr](mailto:dacapito@esrf.fr).

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