Introduction to the X-ray Absorption Spectroscopy (XAS)

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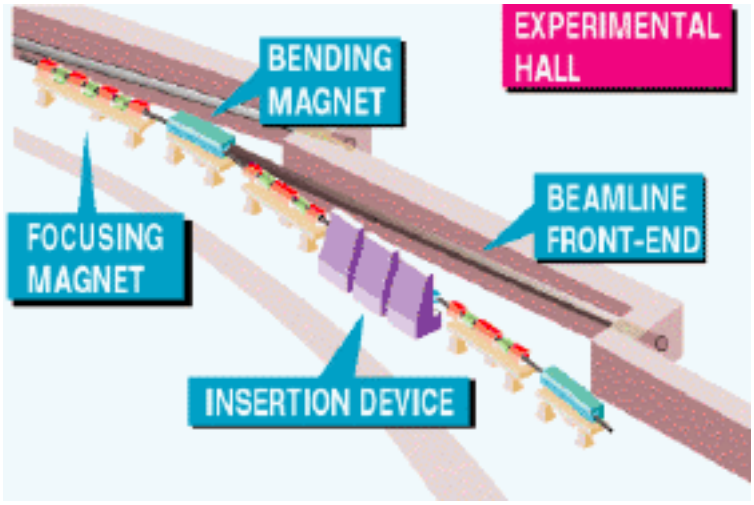
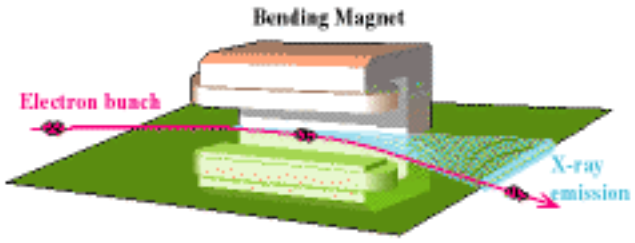
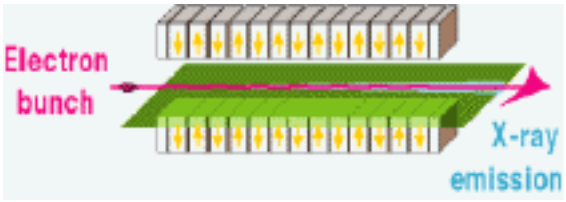
Synchrotron Radiation Sources



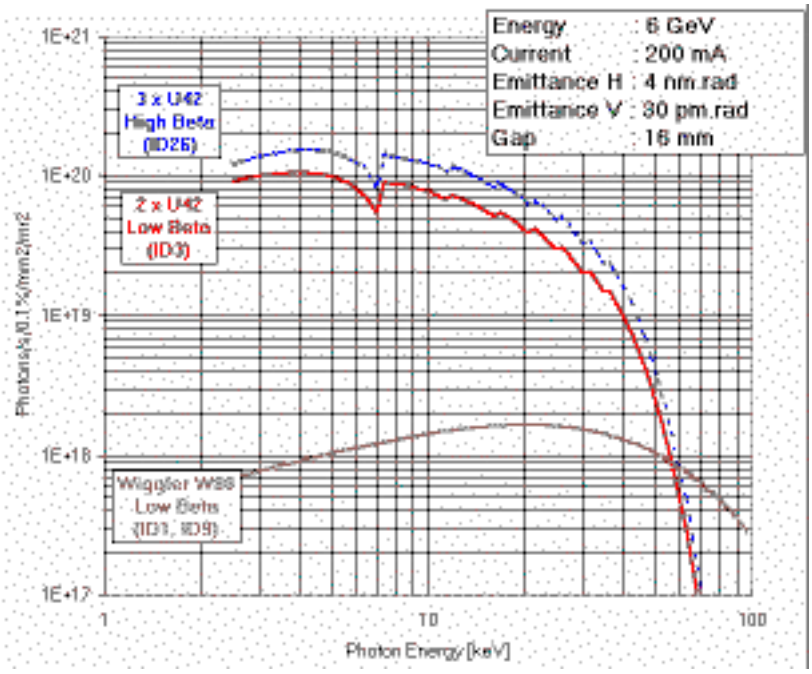
Location of the different sources in the tunnel



Emission from a bending magnet



Emission from an insertion device



Comparison between the brlliance of undulators and wigglers.

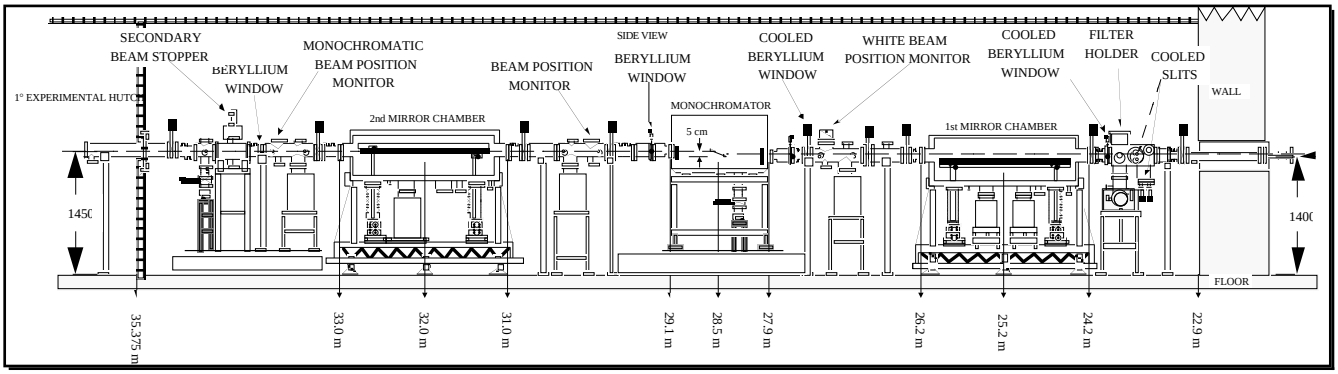
The GILDA Beamline

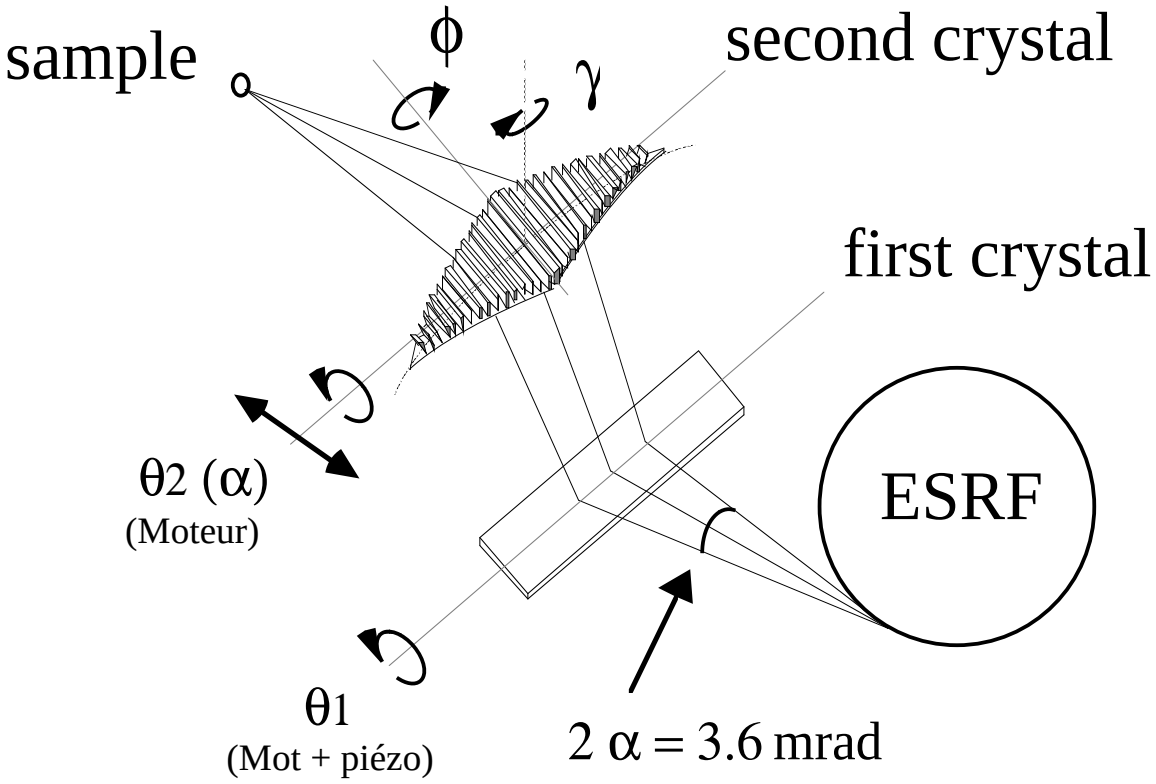
http://www.esrf.fr/exp_facilities/BM8/handbook/handbook.htm

BM8 at ESRF

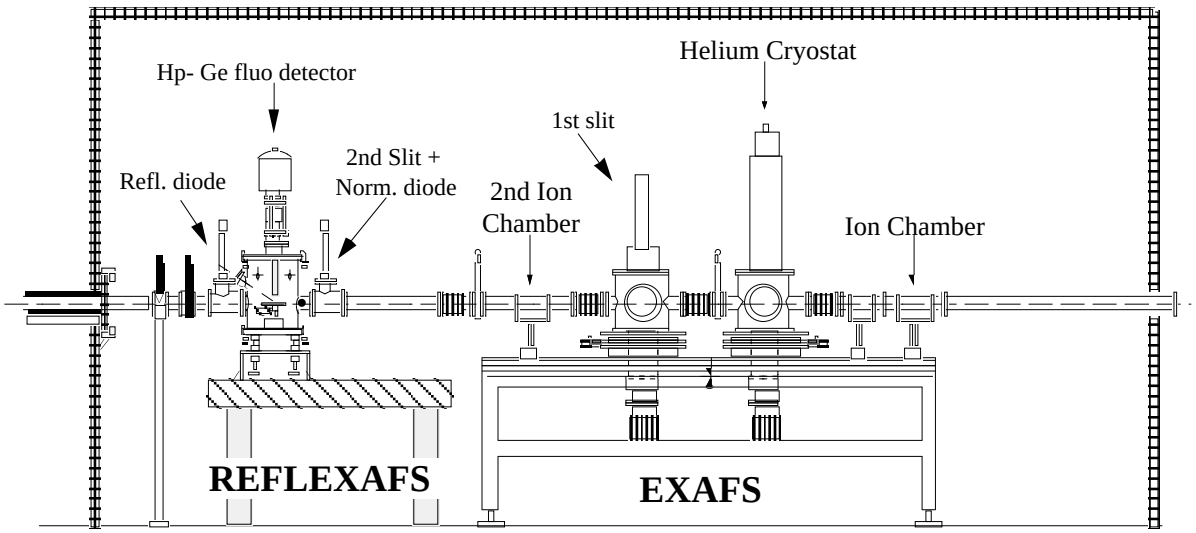
Energy range	5-70 KeV
Flux on the sample	10^8 - 10^{10} ph/s
Beam size on the sample	2 mm
Energy Resolution	$\Delta E/E \approx 10^{-4}$
Crystals	Si (311), Si(511)

Energy range



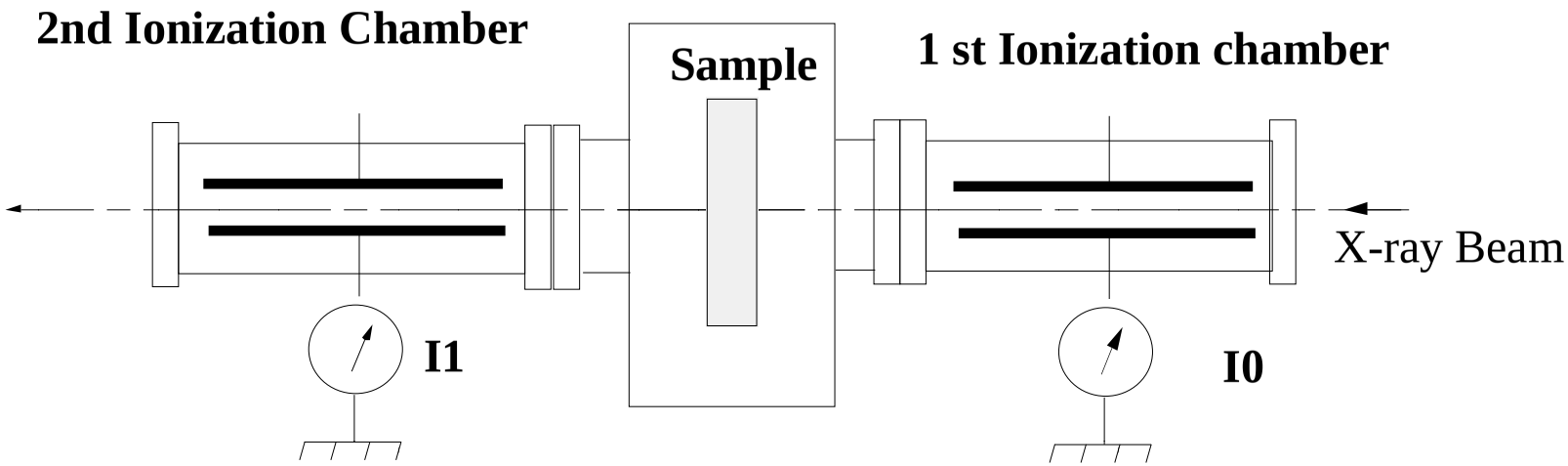


EXAFS HUTCH



Collection modes	• Transmission (Concentrated samples) • Fluorescence (Diluted samples) • Total & Partial electron Yield • Total reflection • Optical luminescence
Detectors	• Ion Chambers • 13 element High purity Ge • Electron multiplier • Si PIN diodes
Ancillary equipment	• Criostat/oven (77<T<500 K) • Liquid He criostat (4<T<300 K) • 1T Magnet

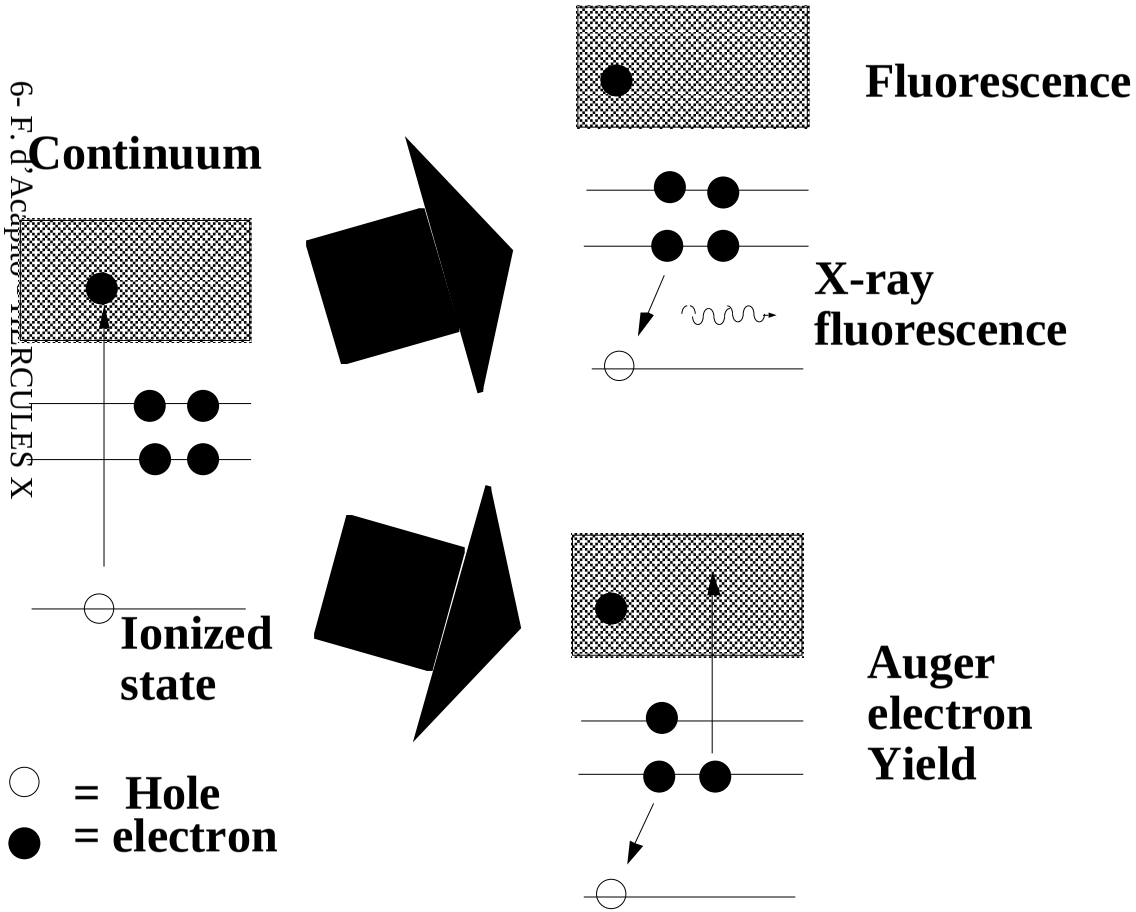
Measuring the X-ray absorption coefficient



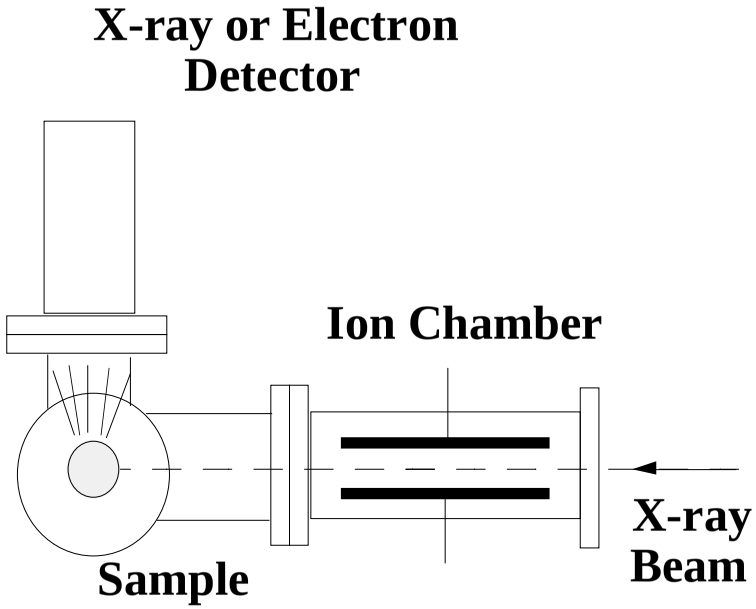
$$I1 = I0 * \exp(-\mu x)$$

$$\mu = -\ln(I1/I0)$$

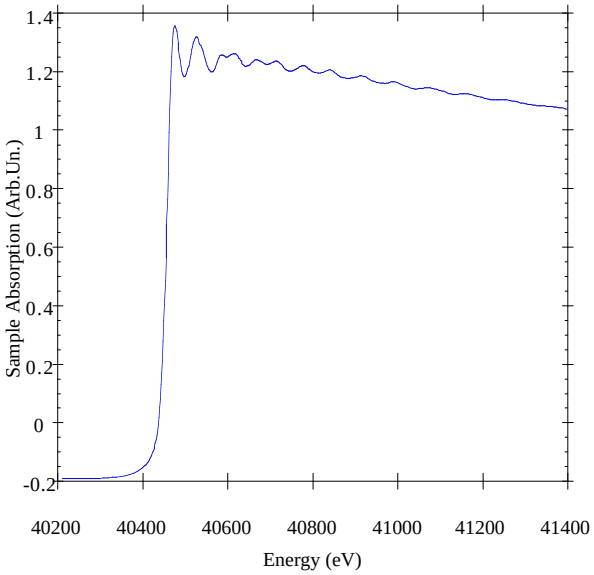
Indirect methods



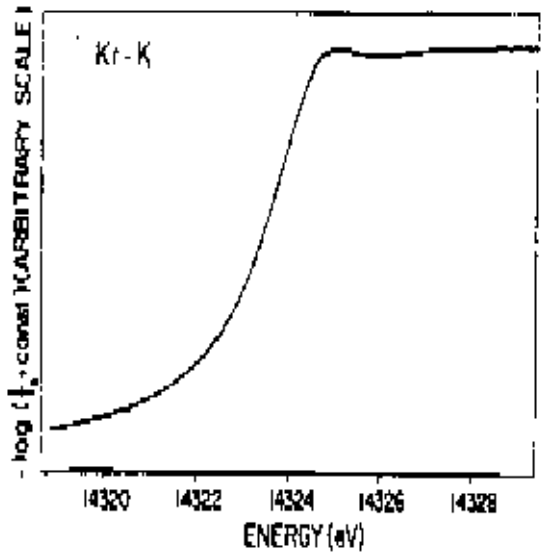
Experimental apparatus



Extended **X**-ray **A**bsorption **F**ine **S**tructure



Absorption spectrum of Crystalline CeO2



Absorption Spectrum of gaseous Kr

General Features:

I) Chemical Selective

II) Information about the local structure

Information provided

(for the first coordination shells)

I) Nearest neighbor nature and number (±0.5)

II) Interatomic distances (± 0.02 Å)

Debye-Waller Factors σ^2 (± 10%)

EXAFS Theory

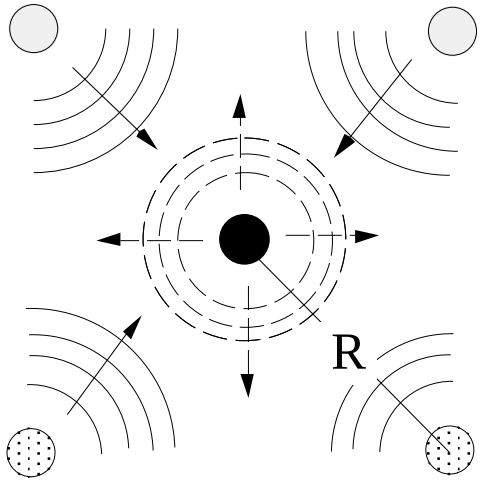
Absorption Coefficient μ from the Fermi Golden Rule

$$\mu = \left| < i \mid \bar{\mathbf{p}} \cdot \bar{\mathbf{A}} \mid f > \right|^2$$

$<i| = <1s|, <2s|, <2p_{1/2}|, <2p_{3/2}|$

$$< f \mid_{\text{isolated atom}} = \frac{e^{-i \bar{k} \bar{r}}}{k\, r} Y_{l,\, m}$$

$$< f_{\text{atom in a cluster}} \mid = ?$$



● = Absorbing Atom

○ = Backscattering Atom

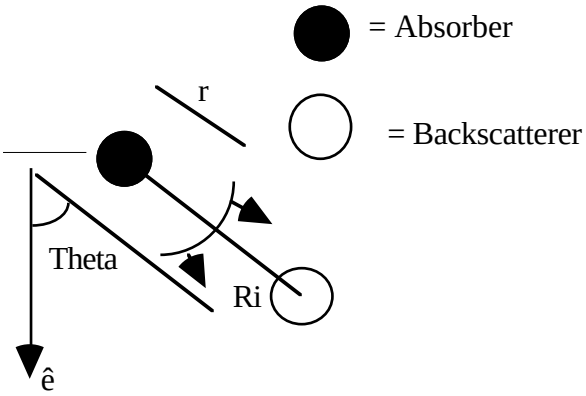
Definition of the oscillatory function χ

$$\chi \doteq \frac{\mu - \mu_{\text{atomic}}}{\mu_{\text{atomic}}}$$

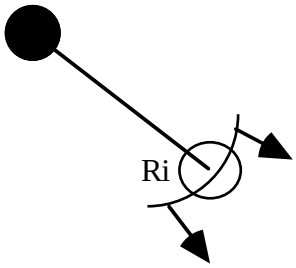
EXAFS formula

$$\chi = 3\, S_0^2 \sum_j \frac{N_j}{k\, R_j^2} A(k,R_j) \sin\left[2kR_j + \varphi(k,R_j) + 2\delta_c(k)\right] e^{-2k^2\sigma^2}\, e^{-2R_j/\lambda} \left(\hat{e} \cdot \hat{R}_j\right)^2$$

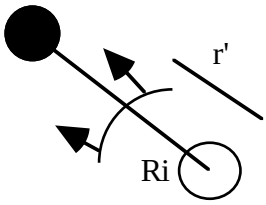
Amplitude of the backscattered electron wave



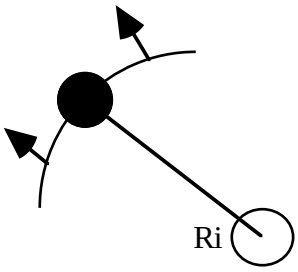
$$e^{i\partial}\,\frac{e^{ikr}}{kr}\cos\theta$$



$$e^{i\partial}\,\frac{e^{ikR_i}}{kR_i}\cos\theta$$



$$e^{i\partial}\,\frac{e^{ikR_i}}{kR_i}\cos\theta\;T(k)\;e^{i\beta}\,\frac{e^{ikr}}{kr}$$



$$\frac{e^{i\left(2kR_i+2\partial+\beta\right)}}{\left(kR_i\right)^2}\cos\theta\;T(k)$$

General formulation

Green function formalism

$$\sigma = \sigma_{at}\ \mathrm{Im}\left\{ \frac{1}{\sin^2\delta^0_{L_0}} \frac{1}{2\ L_0 + 1} \sum_{m_0} \left[T\ (I-GT)^{-1} \right]^{0,0}_{L_0,L_0} \right\} \approx \sigma_{at}\ \mathrm{Im}\left\{ \frac{1}{\sin^2\delta^0_{L_0}} \frac{1}{2\ L_0 + 1} \sum_{n} \left[\sum_{m_0} \left[T\ (GT)^{n} \right]^{0,0}_{L_0,L_0} \right] \right\}$$

T= Atomic Scattering Matrix

G= Propagator matrix

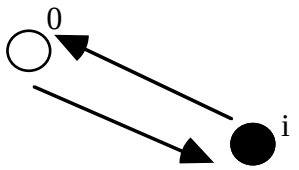
$$T = \begin{pmatrix} t_0 & 0 & \cdots & 0 \\ 0 & t_1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & t_n \end{pmatrix} \qquad G = \begin{pmatrix} 0 & G_{0,1} & \cdots & G_{0,N-1} \\ G_{1,0} & 0 & \cdots & G_{1,N-1} \\ \vdots & \vdots & \ddots & \vdots \\ G_{N-1,0} & G_{N-1,1} & \cdots & 0 \end{pmatrix}$$

$$T^{i,\,j}_{L,\,L'} = \delta(i,\,j)\ \delta(L,\,L')\ \exp(i\partial^l_i)\ \sin(\partial^l_i)$$

$$G^{i,\,j}_{L,\,L'} = \delta_{ij}\ \sqrt{4\pi\ (2l+1)\ (2l'+1)} \times$$
$$\times \sum_{L''} \left[\sqrt{(2l''+1)} \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & l'' \\ m & -m' & m'-m \end{pmatrix} (-1)^{m'}\ \ i^{l'+1}\ {}^{+}h(kR_{ij})\ Y_{l'',\,m'-m}(\hat{R}_{ij}) \right]$$

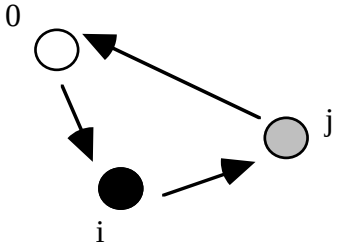
The scattering cross section σ can be approximated by the so-called Multiple Scattering serie made up of terms like:

Single Scattering (SS)



$T_0 G_{0,\,i} T_i G_{i,\,0} T_0$

Multiple Scattering (MS)
(double scattering)



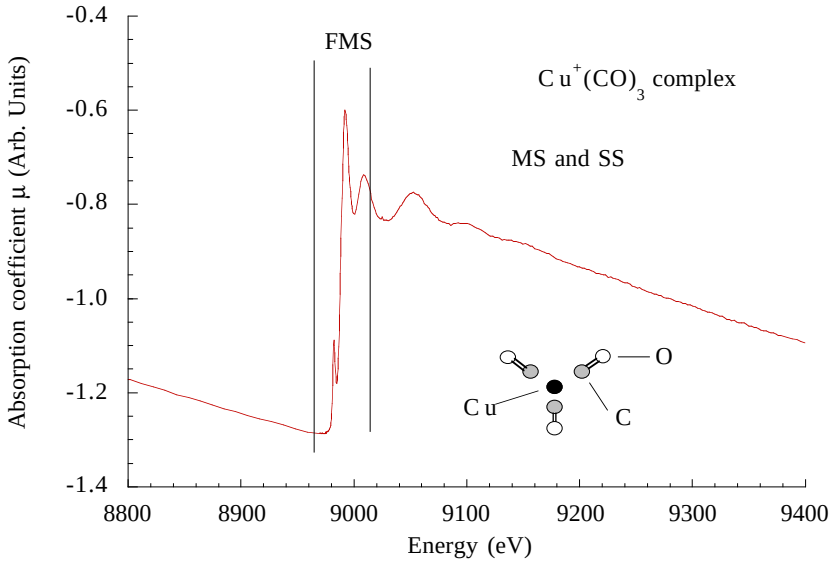
$T_0 G_{0,\,i} T_i G_{i,\,j} T_j G_{j,\,0} T_0$

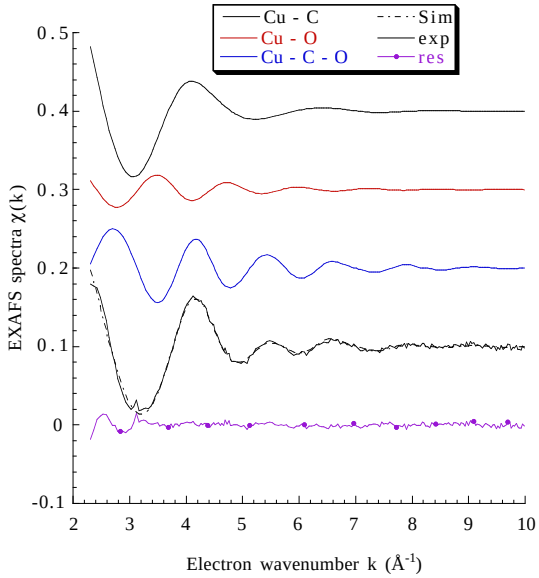
Full Multiple Scattering
(FMS)

All possible paths

$$\left(\frac{T}{I - GT} \right)^{0,\,0}_{L_0,\,L_0}$$

A FMS-MS-SS investigation: the structure of the $Cu^{+}(CO)_3$ complex





Contribution to the total EXAFS signal:

Cu-C SS; Cu-O SS; Cu-C-O MS.

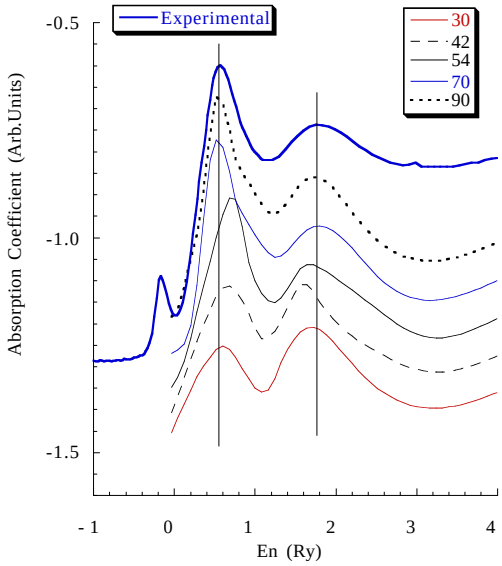
Quantitative analysis

$N^{Cu-CO} = 3 \pm 0.3$

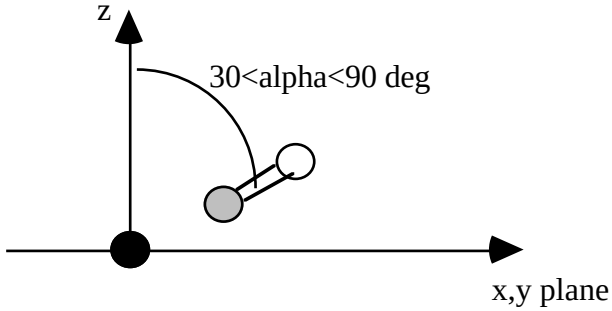
$R^{Cu-C} = 1.93 \pm 0.02$ Å

$R^{C-O} = 1.12 \pm 0.03$ Å

$\Theta^{Cu-CO} = 180 \pm 5$ deg



FMS simulation of the XANES region for different alpha angle values



Example of a quantitative EXAFS analysis.

Determination of the Cu-Cu distance in the Cu_2O compound

Recall of the EXAFS formula in the single scattering framework

$$\chi = 3\, S_0^2 \sum_j \frac{N_j}{k\, R_j^2} A(k,R_j) \sin\left[2kR_j + \varphi(k,R_j) + 2\delta_c(k)\right] e^{-2k^2\sigma^2} e^{-2R_j/\lambda} \left(\hat{e}\cdot\hat{R}_j\right)^2$$

The analysis method:

1) Evaluation of the *amplitude* $\tilde{A}(k, R_j)$

$$S_0^2 A(k, R_j) \exp(-2R_j/\lambda)$$

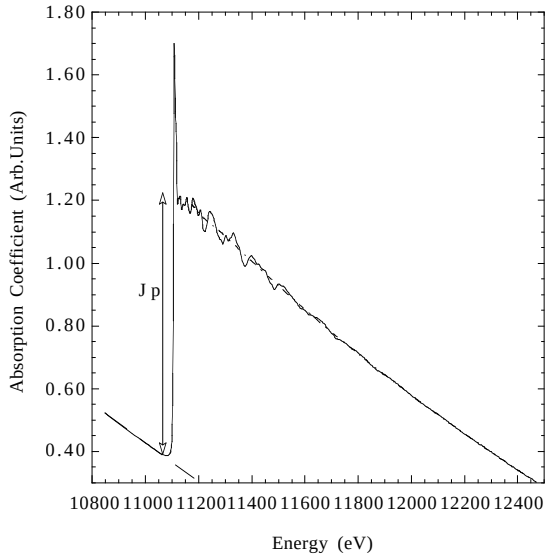
and *phase* $P(k, R_j)$

$$[\phi(k, R_j) + 2\delta_c(k)]$$

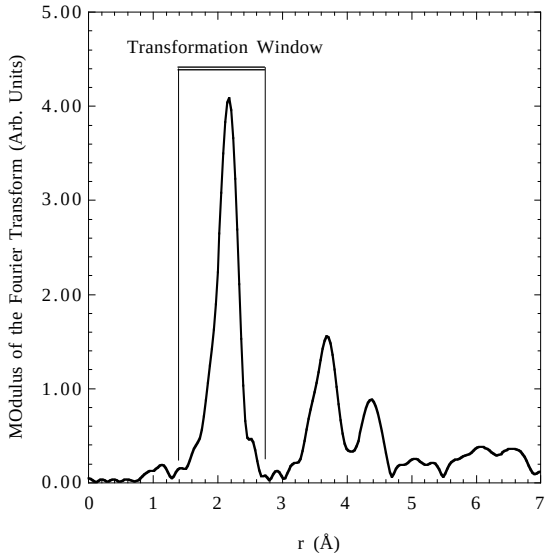
terms from a compound with known structural parameters

2) Use of the cited terms in the determination of N_j, σ_j and R_j of the unknown compound.

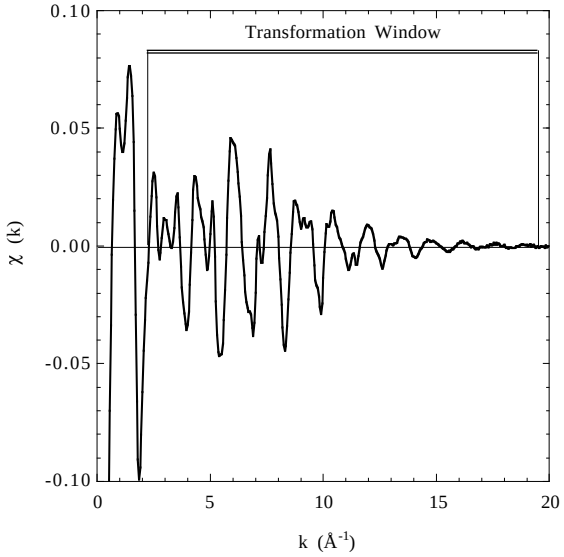
Extraction of the EXAFS signal



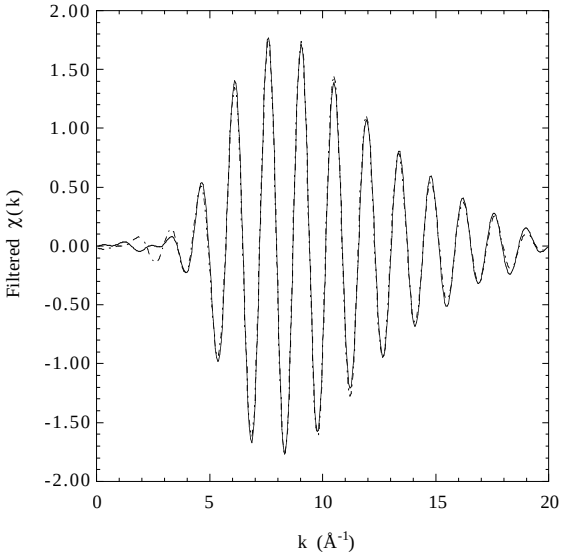
Step 1 Background subtraction & normalization



Step 3 Isolation of the interesting peak by back-transform



Step 2 Fourier Filtering of the spectrum



Step 4 fit to a model

Sample description

The model compound

Metallic Cu foil

Structure	fcc
1st shell nearest neighbours N:	12 Cu
1st shell Cu- Cu distance R:	2.5561 Å
1st shell Debye-Waller factor σ (77K)	0.057 Å

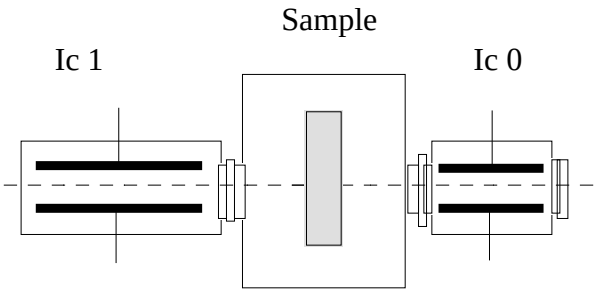
The 'unknown' compound

Crystalline Cu_2O powder

1st shell nearest neighbours:	2 O
1st shell Cu - O distance:	1.85 Å
2nd shell nearest neighbours:	12 Cu
2nd shell Cu - Cu distance:	3.019 Å

we will use the backscattering parameters of the Cu foil to extract the Cu-Cu distance in the oxide.

Experimental setup



a) Transmission Mode

Ic_0 filled with 1000 mbar N_2 Absorption =8%
Ic_1 filled with 300 mbar Ar Absorption = 80%
Samples at Liquid Nitrogen Temperature

Energy scan details

fixed energy step scan
$0.025\ Å^{-1} \leq \Delta k \leq 0.05\ Å^{-1}$

	Pre-edge Edge - 200 eV	Edge	1st zone Edge + 100 eV	2 zone Edge + 400 eV	3 zone k_{max}= 15$Å^{-1}$	
8800 eV	8970 eV	9010 eV	9079 eV	9379 eV	9840 eV	
	10 eV	0.5 eV	1 eV	2 eV	4 eV	
	17 pts	80 pts	69 pts	150 pts	115 pts	
	3 s	3 s	3 s	3 s	3 s	

Sample preparation

General rules: $\mu^{tot} < 2.5$

$\Delta\mu^{Cu} \approx 1$

Fundamental steps

1) Find the weight fraction of the components:

Cu_2O: Mw= 2* 63.54 + 16 = 143.08 g/Mol

$Wt\%^{Cu}$ = 2*63.54/143.08 = 88.81 %

$Wt\%^{O}$ = 16/143.08 = 11.18 %

2) Read the absortion cross sections on tables

σ^{8978}_{Cu} = 36.1 cm^2/g σ^{8980}_{Cu} = 287.2 cm^2/g

σ^{8980}_{O} = 7.5 cm^2/g

3) Calculate the sample weight for $\Delta\mu$=1 (typical S=1cm^2 pellet)

$\Delta\mu^{Cu} = \Delta\sigma^{Cu}$ [cm^2/g] * δ^{Cu} [g/cm^2]

$\delta^{Cu} = \Delta\mu^{Cu} / \Delta\sigma^{Cu}$ = 1/ (287.2 - 36.1) = 3.98 mg^{Cu}/cm^2

Powder weight P

$P = \delta^{Cu} * S / Wt\%^{Cu}$ = 3.98e-3 * 1 / 0.8881 = 4.48 mg^{Cu2O}

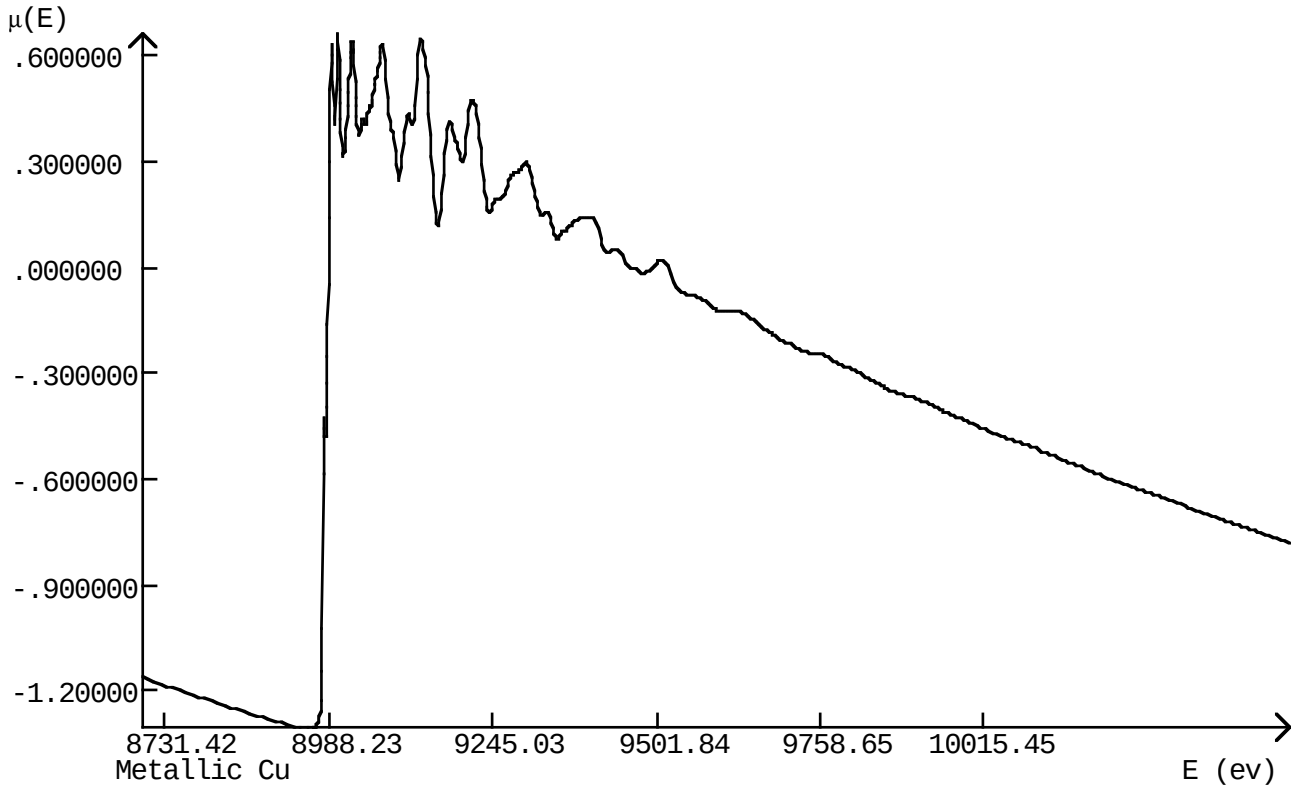
$\delta^{O} = P * Wt\%^{O} / S$= 0.5 mg^{O}/cm^2

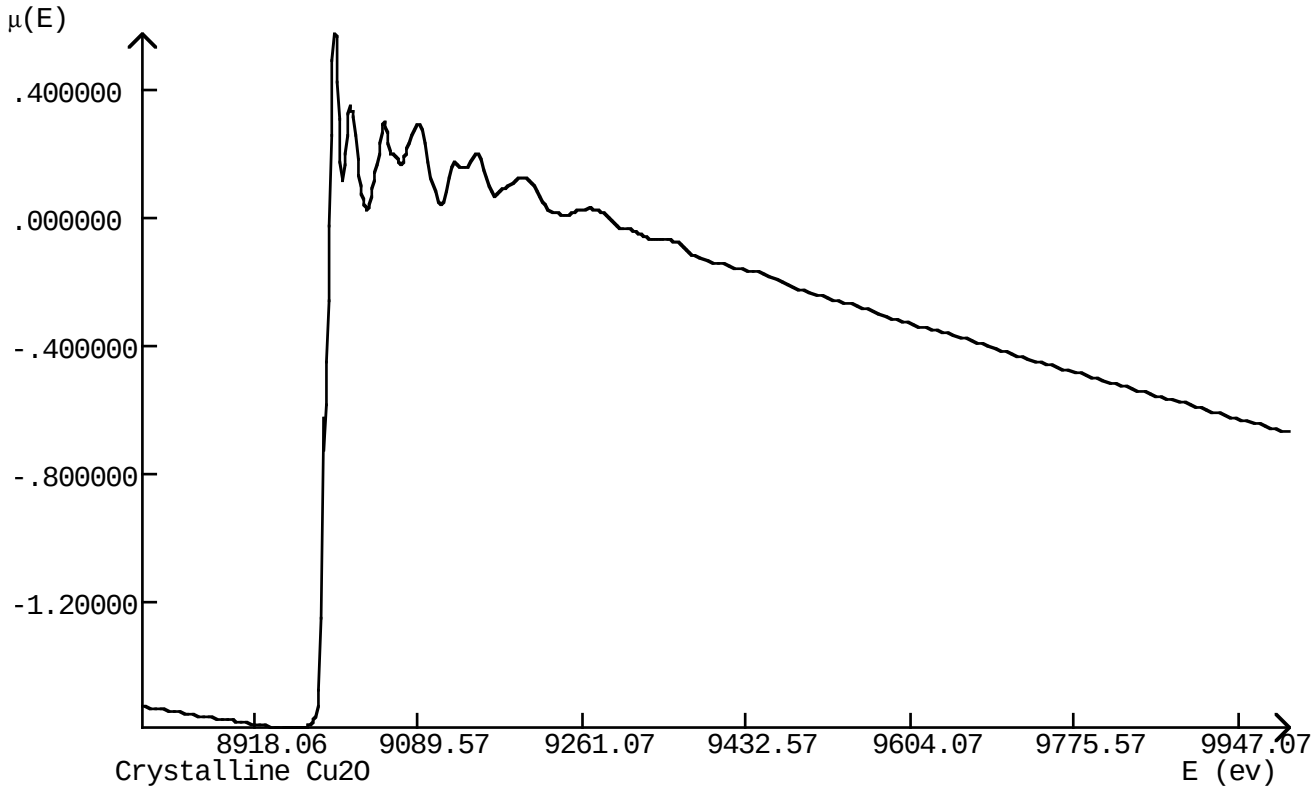
4) Check if the total μ<2.5

$\mu = \sigma^{8980}_{Cu} * \delta^{Cu} + \sigma^{8980}_{O} * \delta^{O}$ = 1.143 + 0.0037 = 1.147

Your 4.5 mg/cm² pellet is O.K.

The absorption spectra:

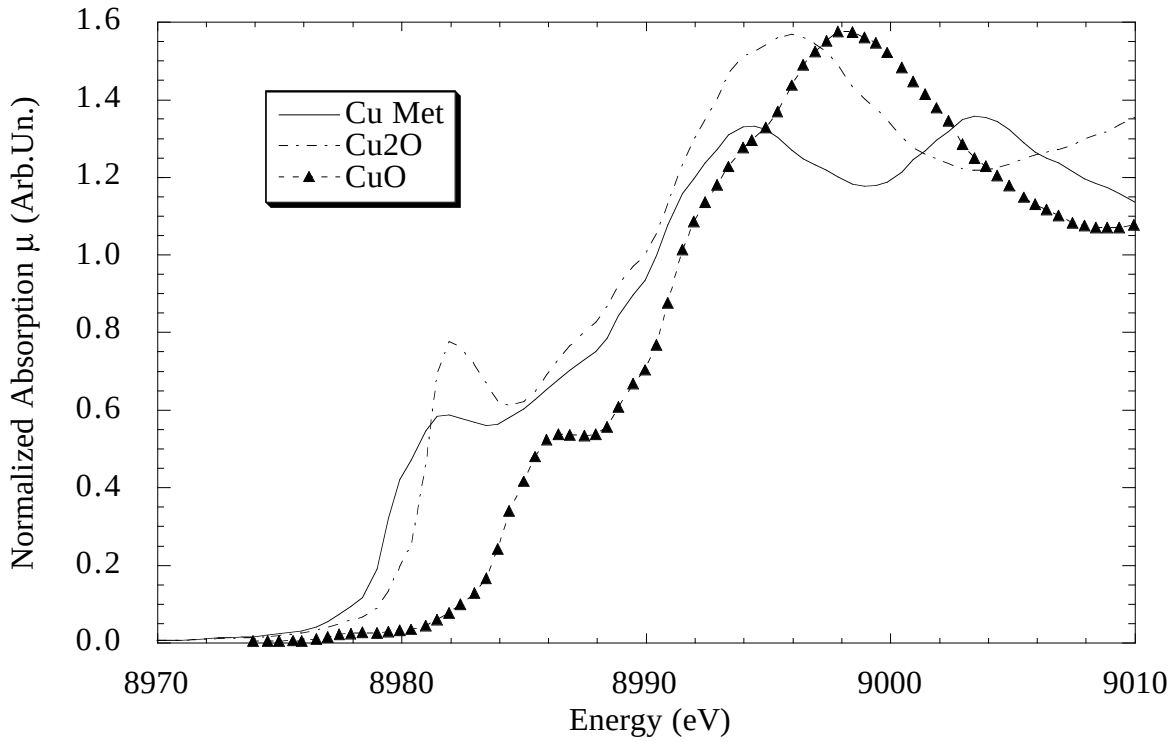


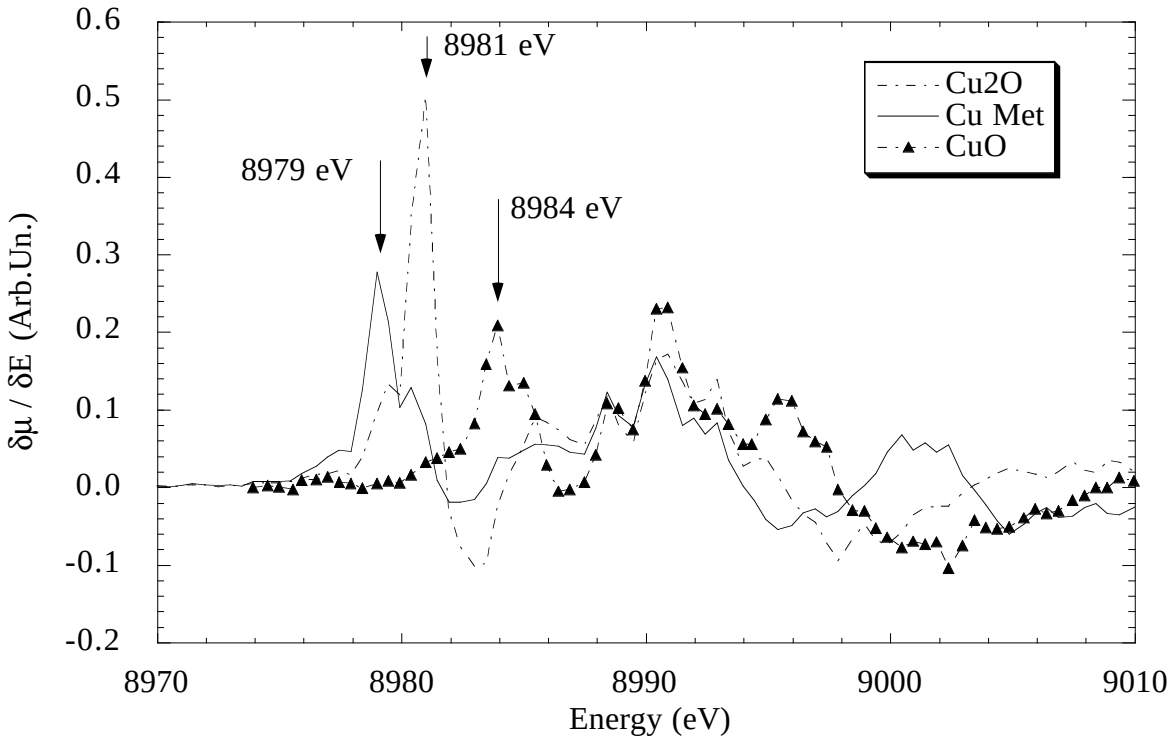


Edge analysis

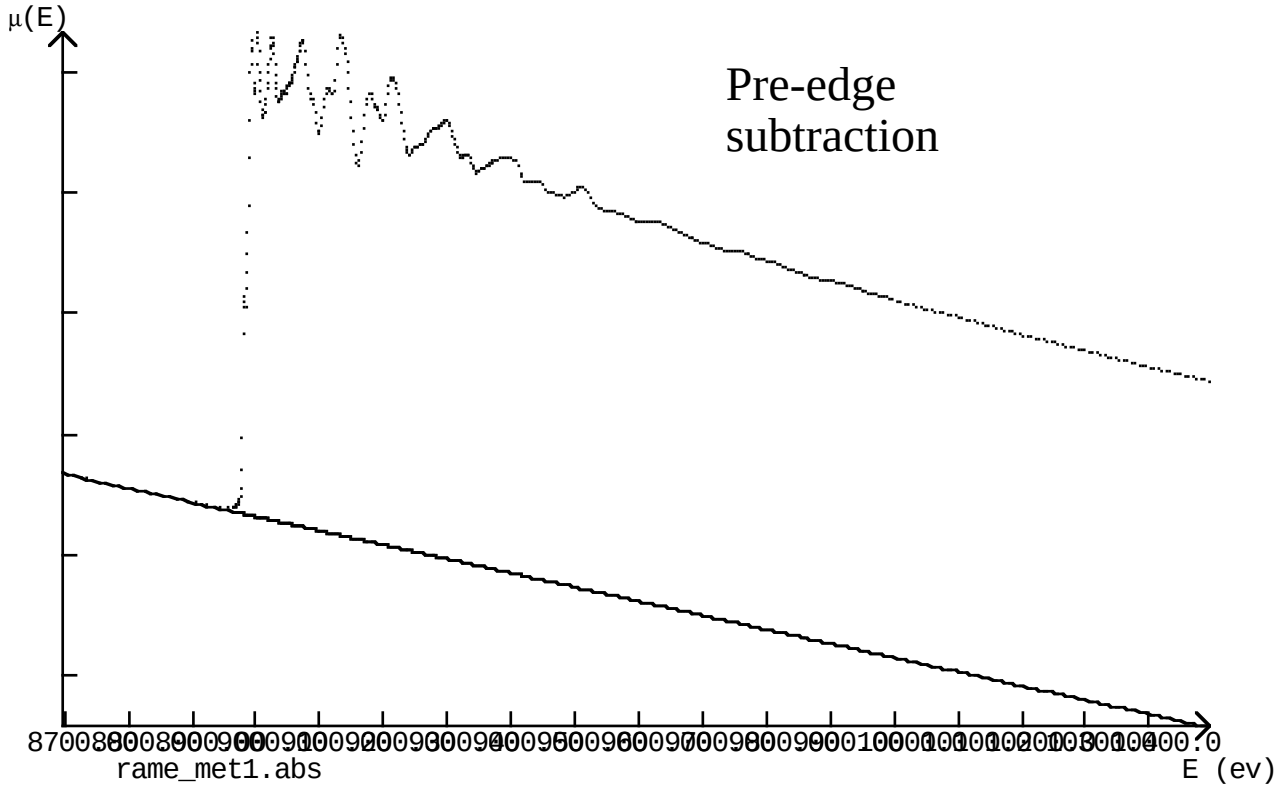
• The edge shape depends on the details of the local geometry around the absorbing atom.

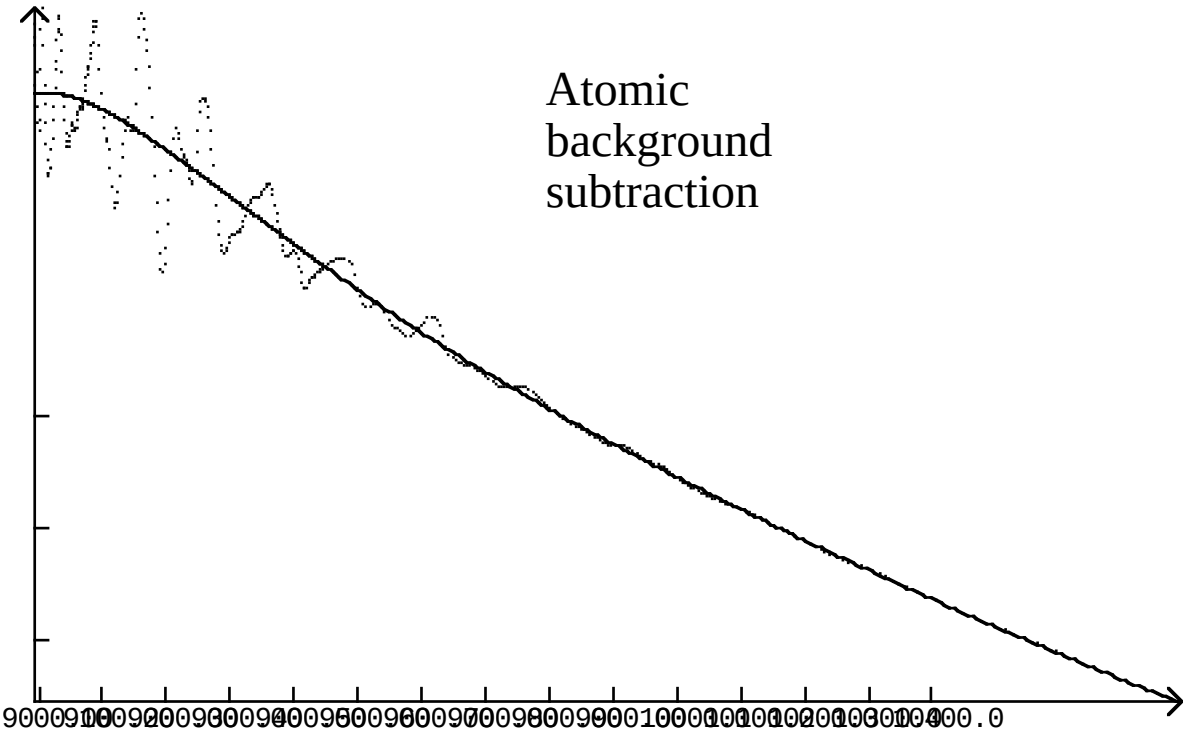
• The edge energy (first inflection point of μ) is related with the valence state of the absorber.



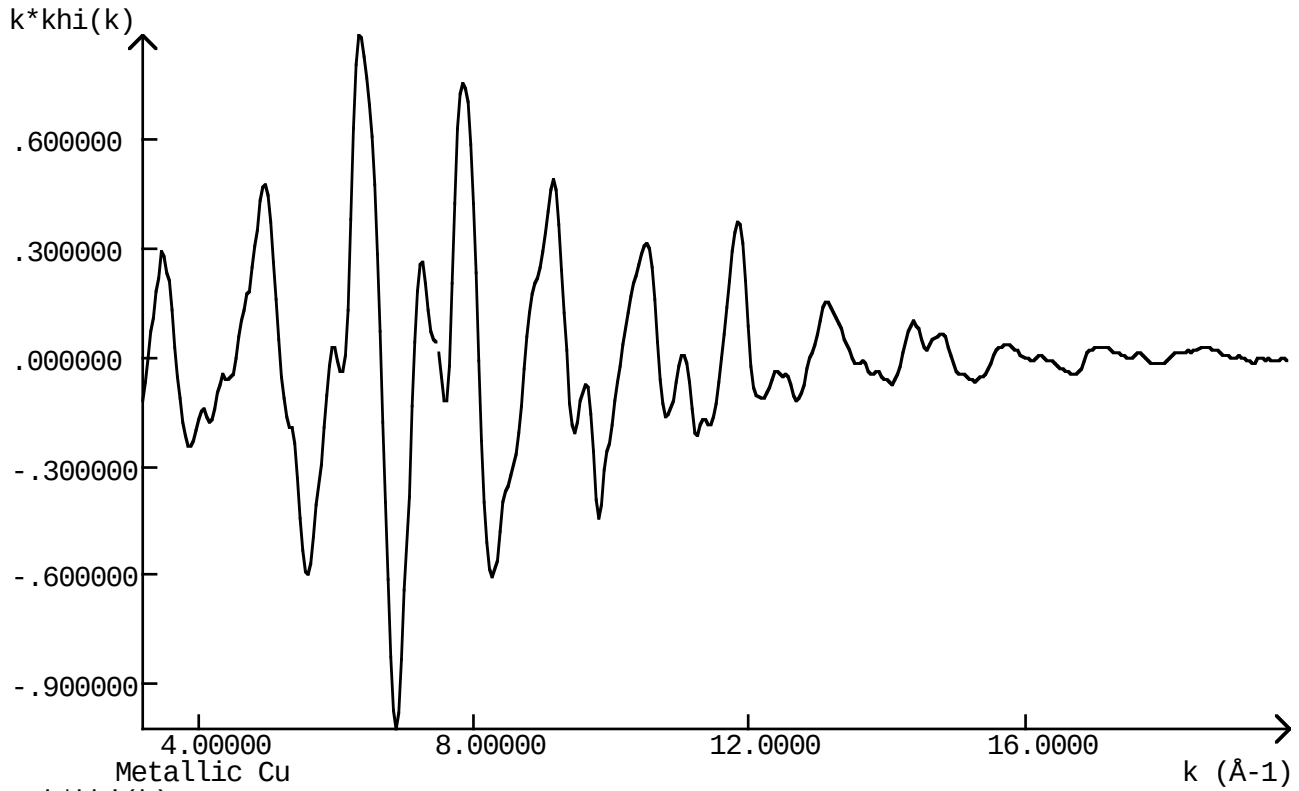


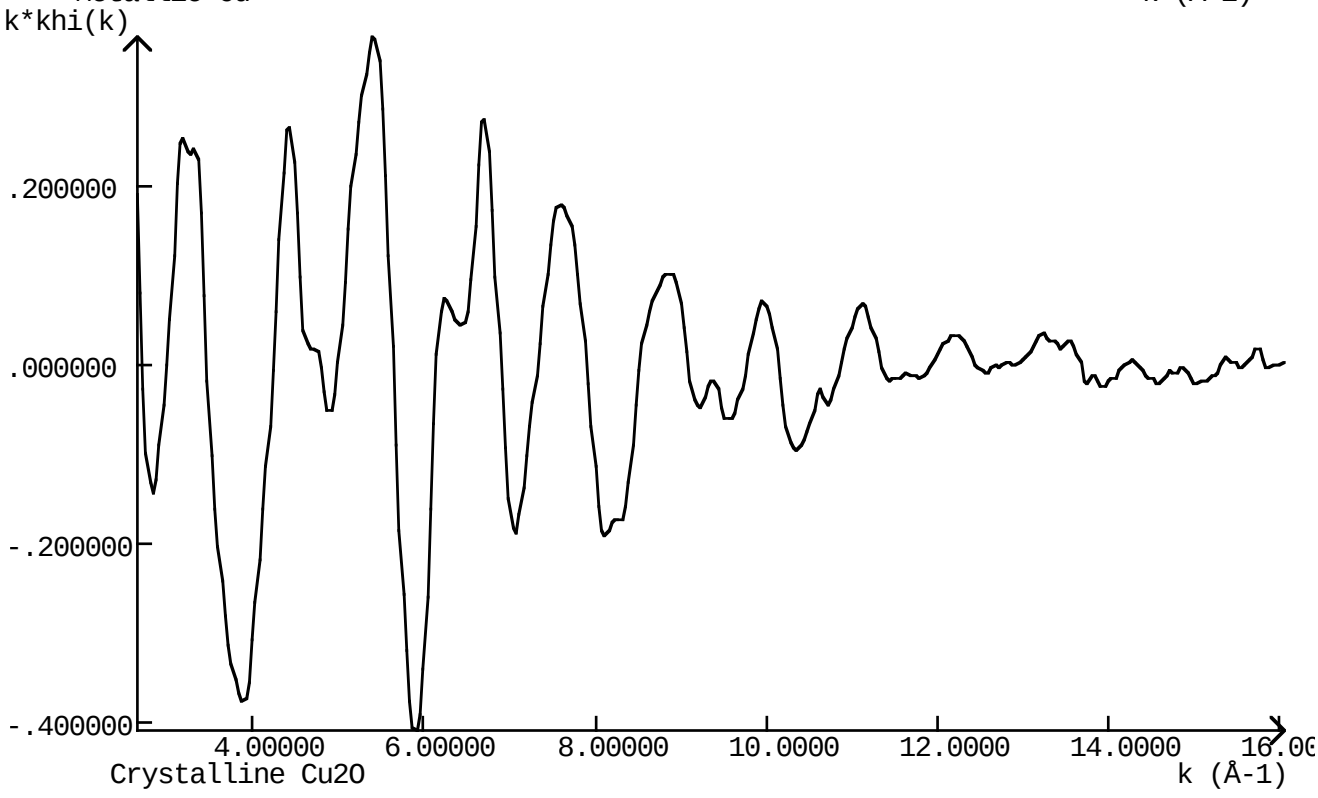
EXAFS signal extraction

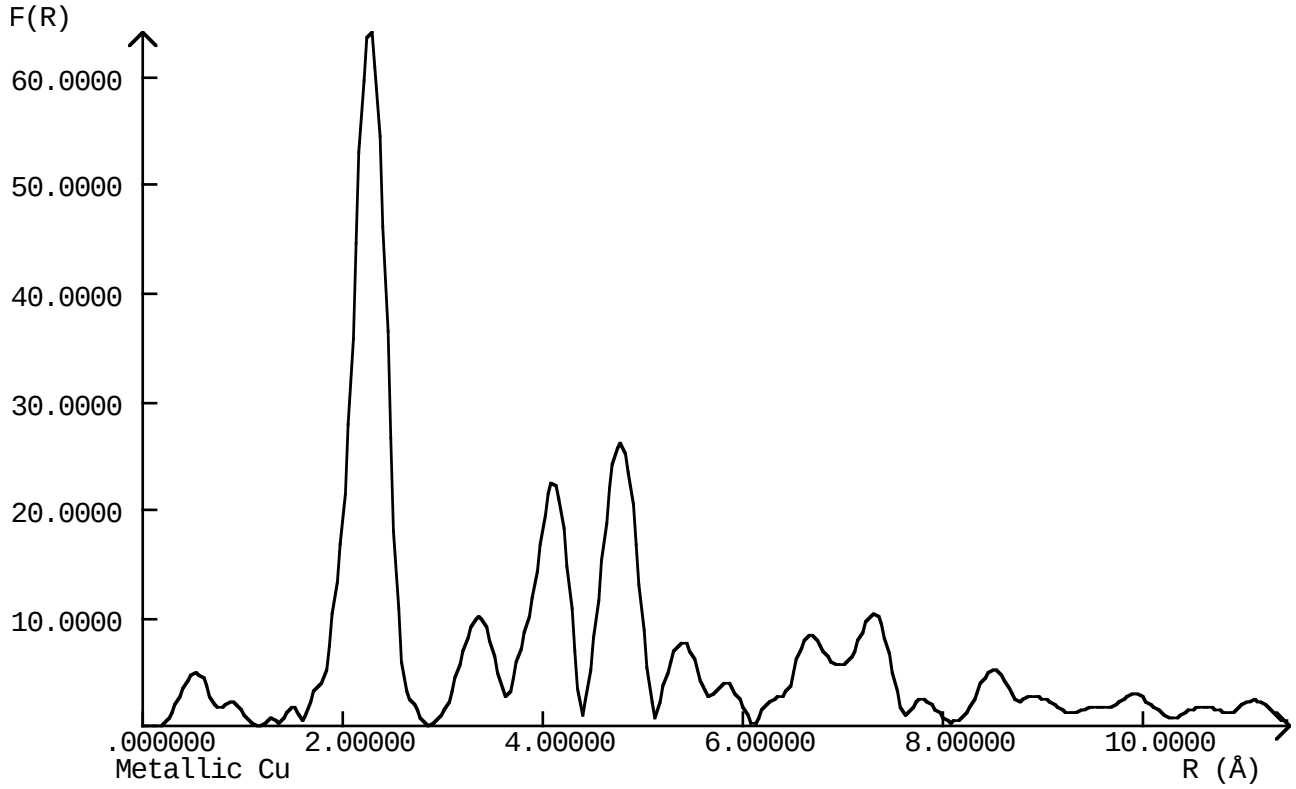


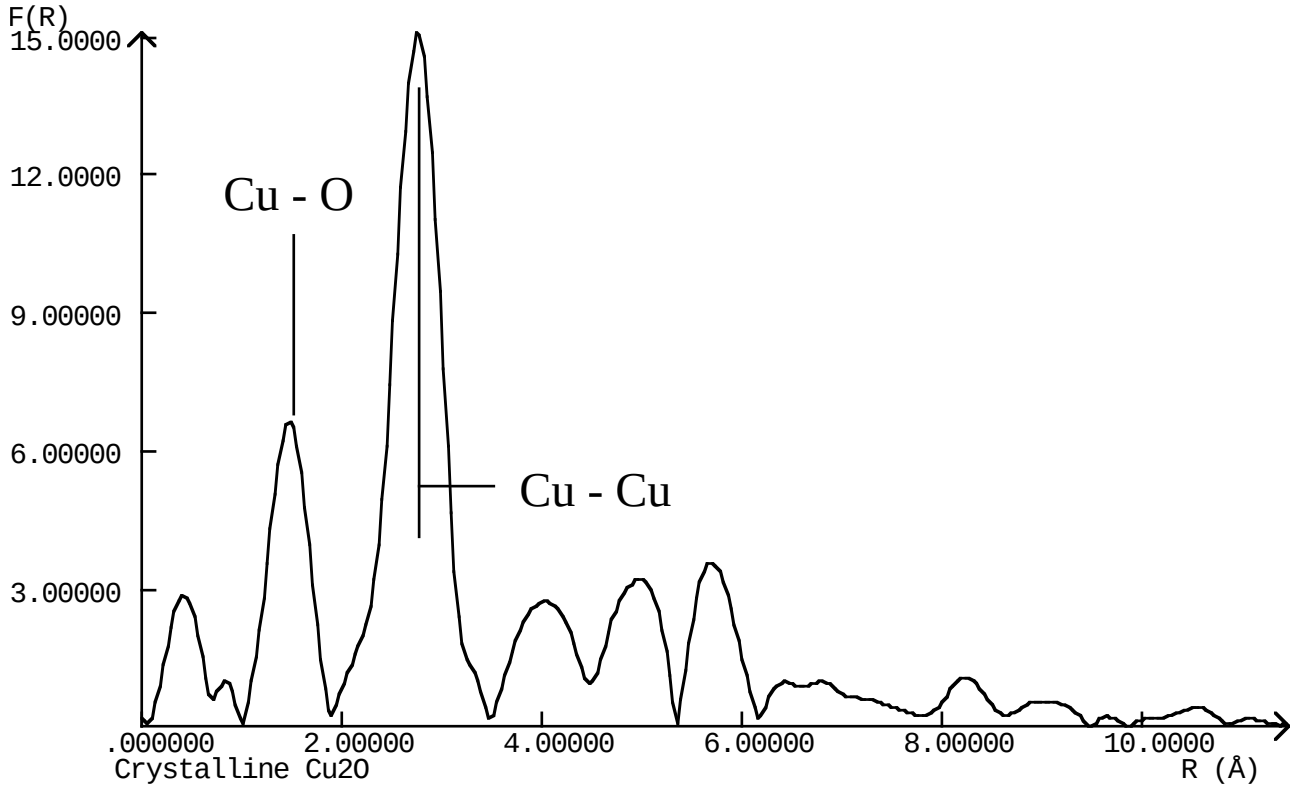


EXAFS spectra

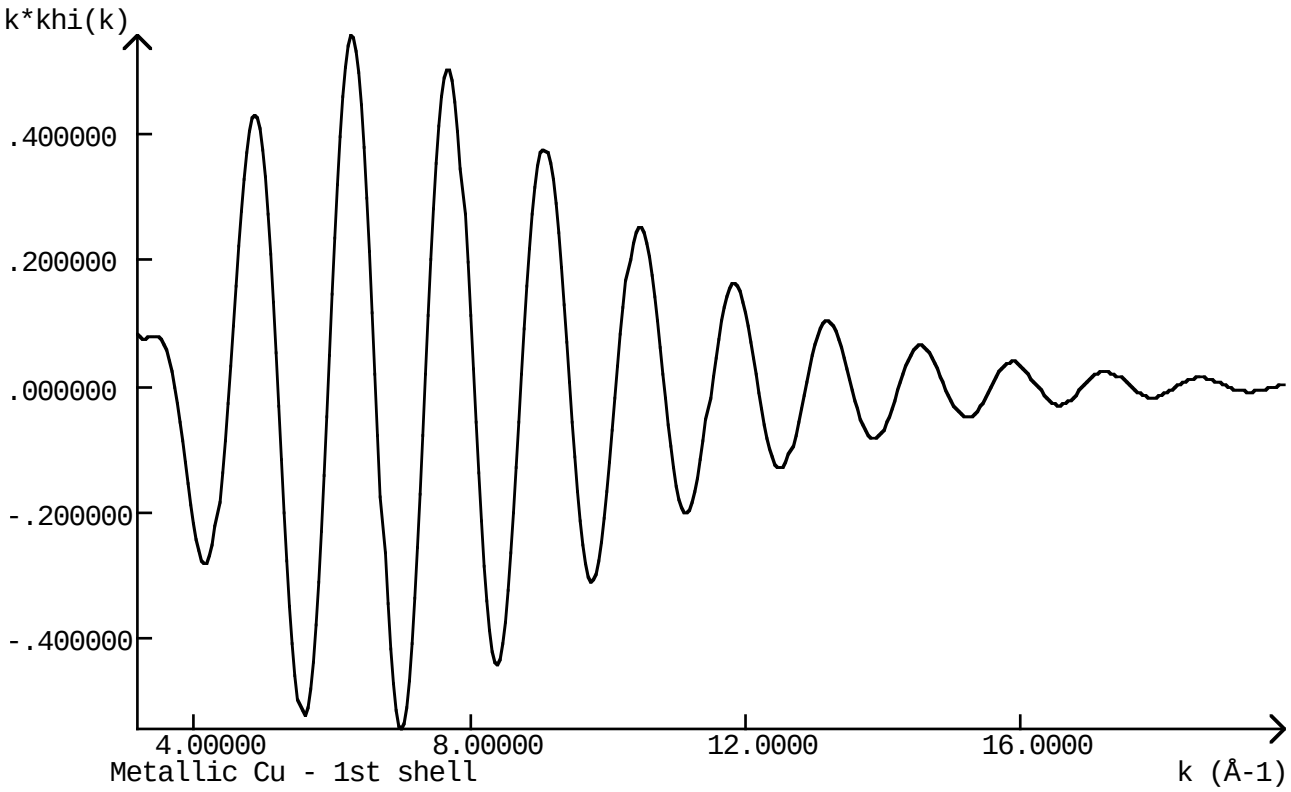


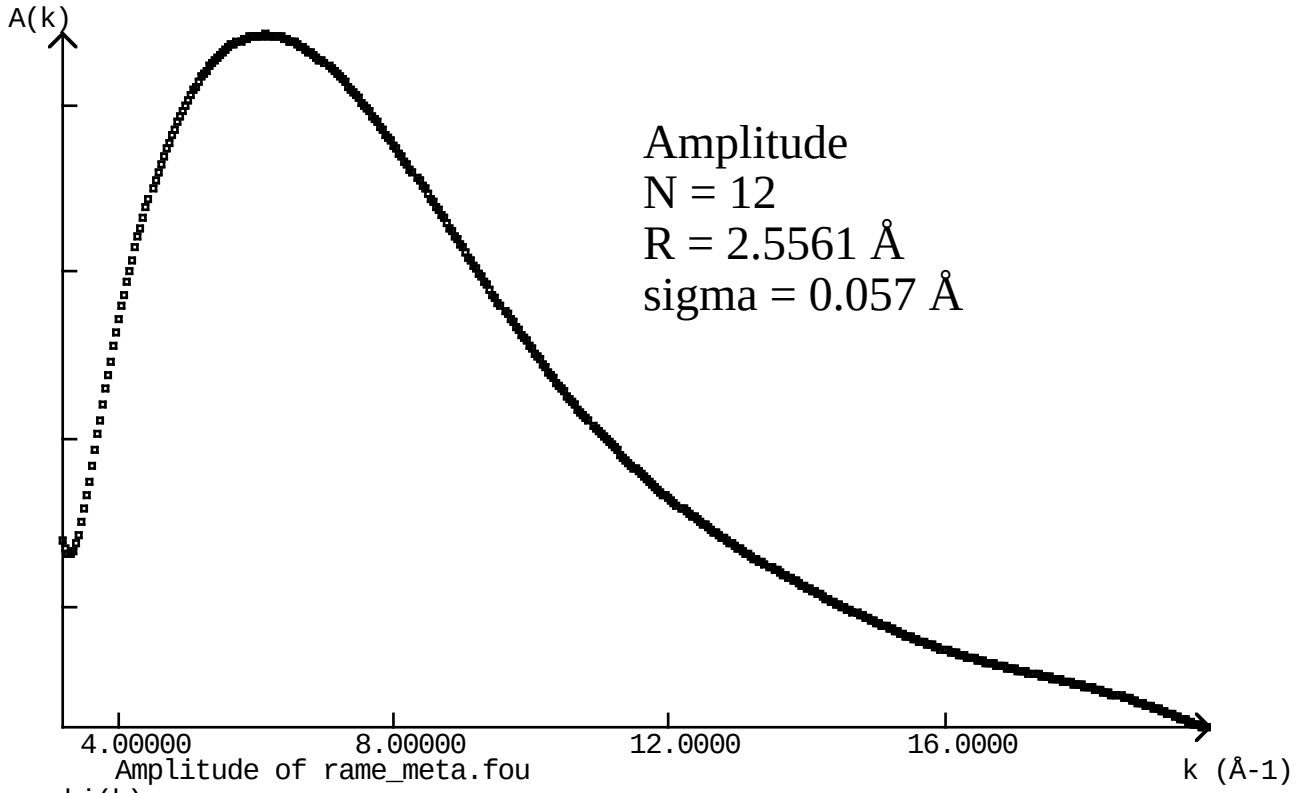


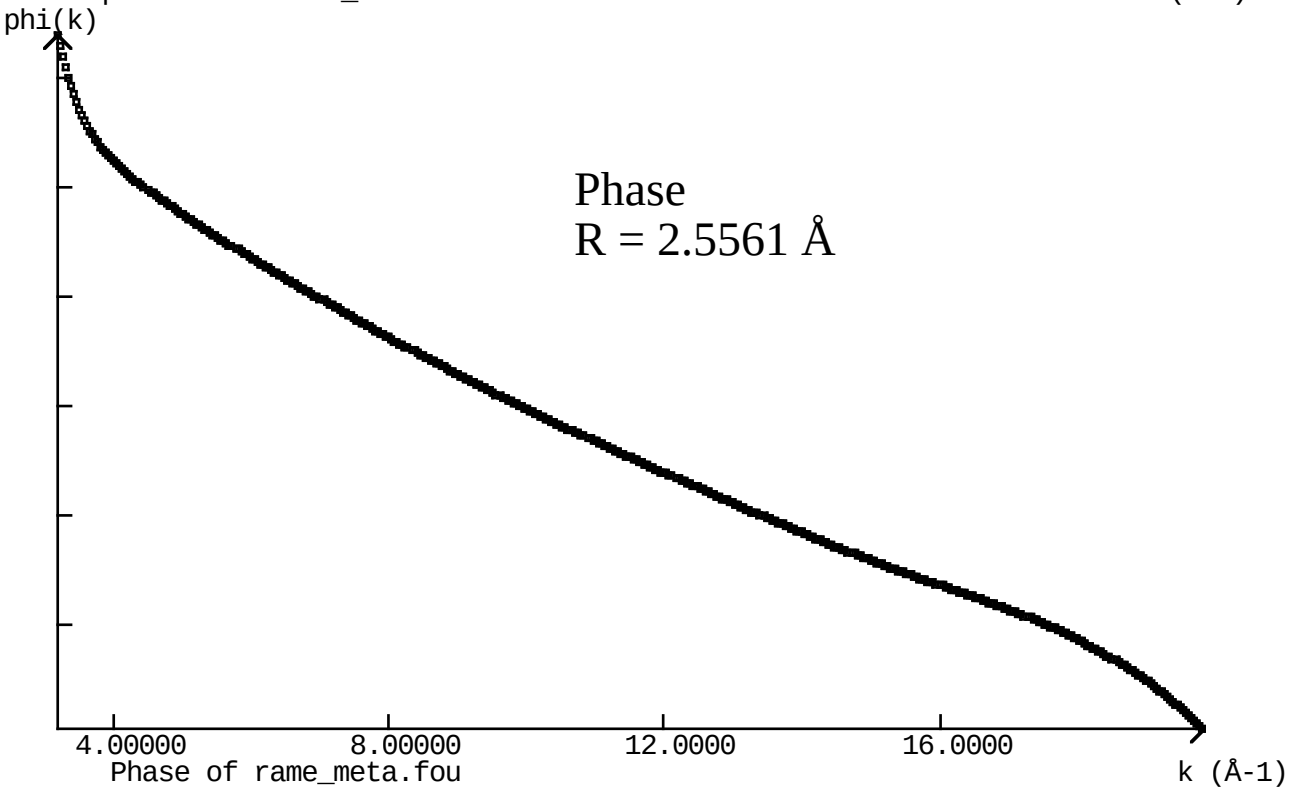

F(R)
60.0000
50.0000
40.0000
30.0000
20.0000
10.0000
.000000
2.00000
4.00000
6.00000
8.00000
10.0000
Metallic Cu
R (Å)


F(R)
15.0000
12.0000
9.00000
6.00000
3.00000
Cu - O
Cu - Cu
.000000
2.00000
4.00000
6.00000
8.00000
10.0000
Crystalline Cu2O
R (Å)

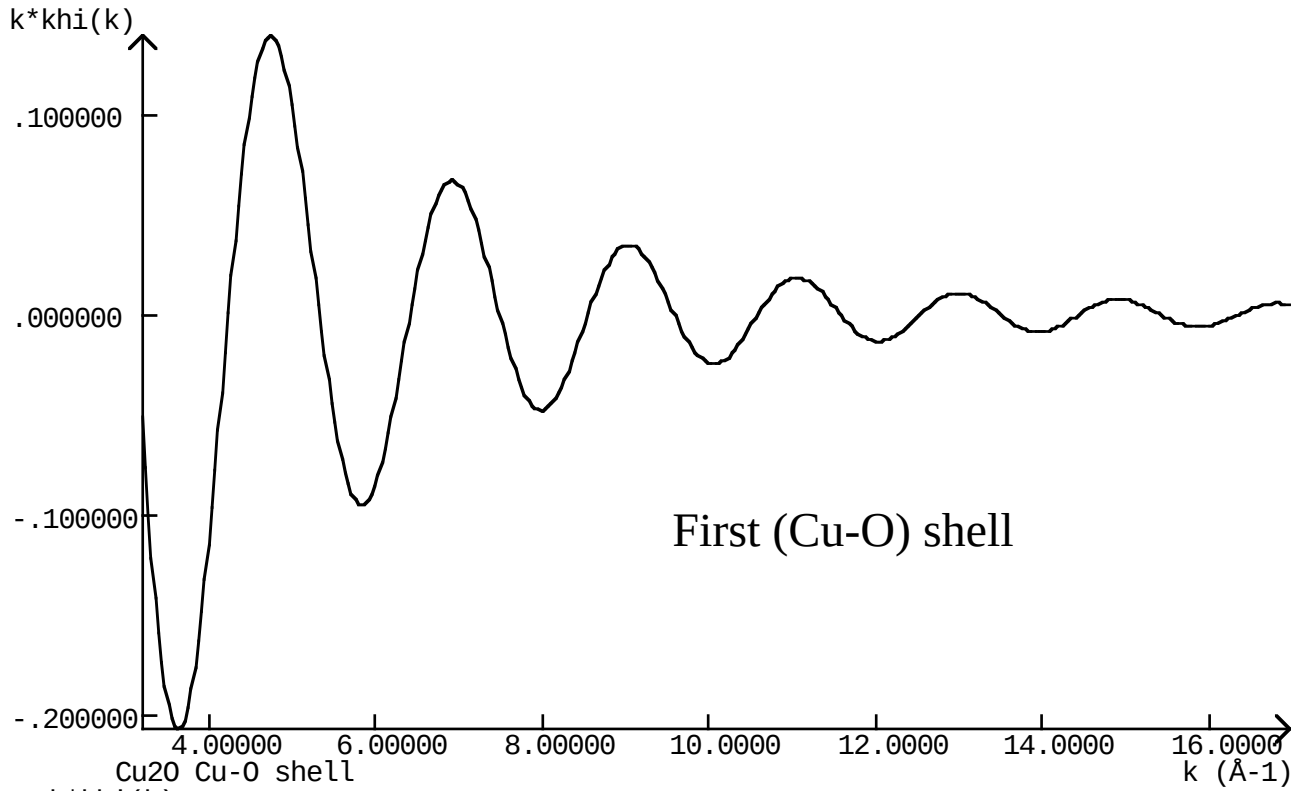
Calculation of the backscattering parameters

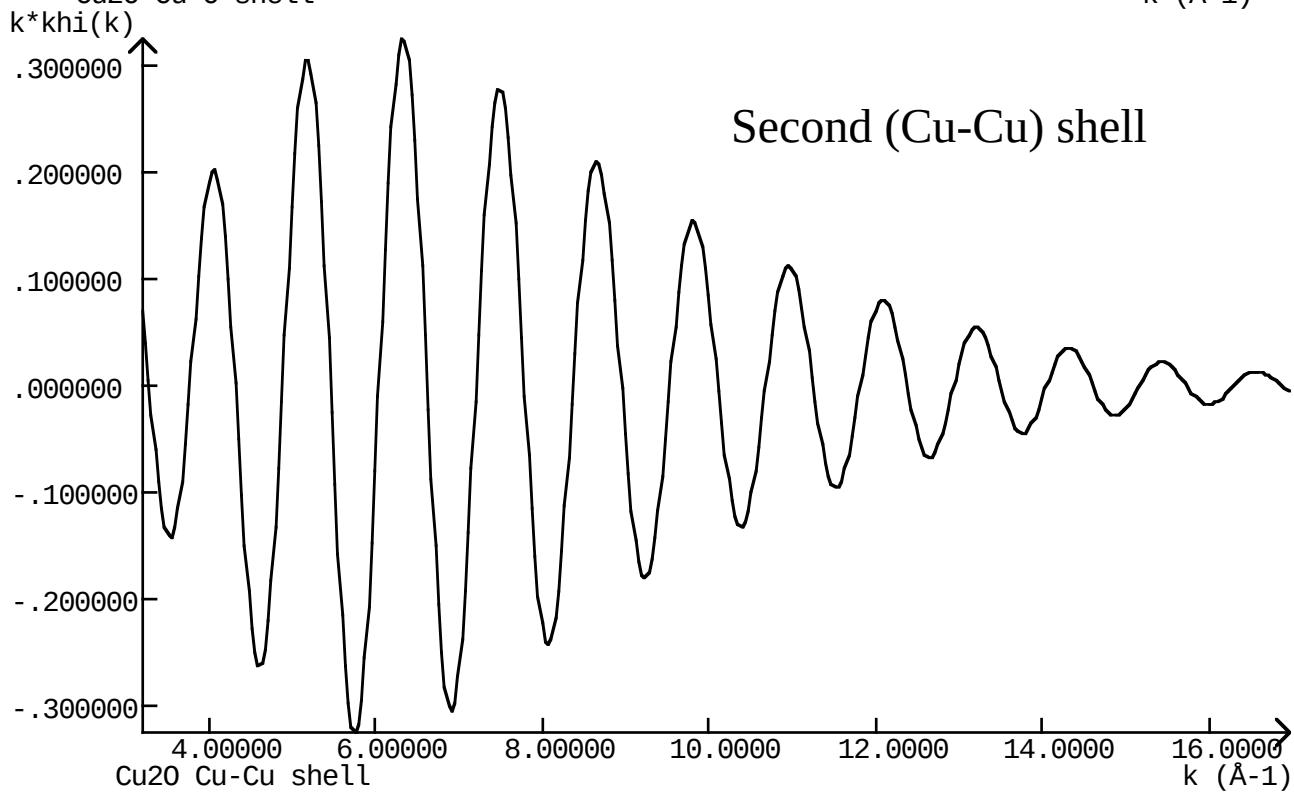



A(k)
Amplitude
N = 12
R = 2.5561 Å
sigma = 0.057 Å
4.00000
8.00000
12.0000
16.0000
Amplitude of rame_meta.fou
k (Å-1)

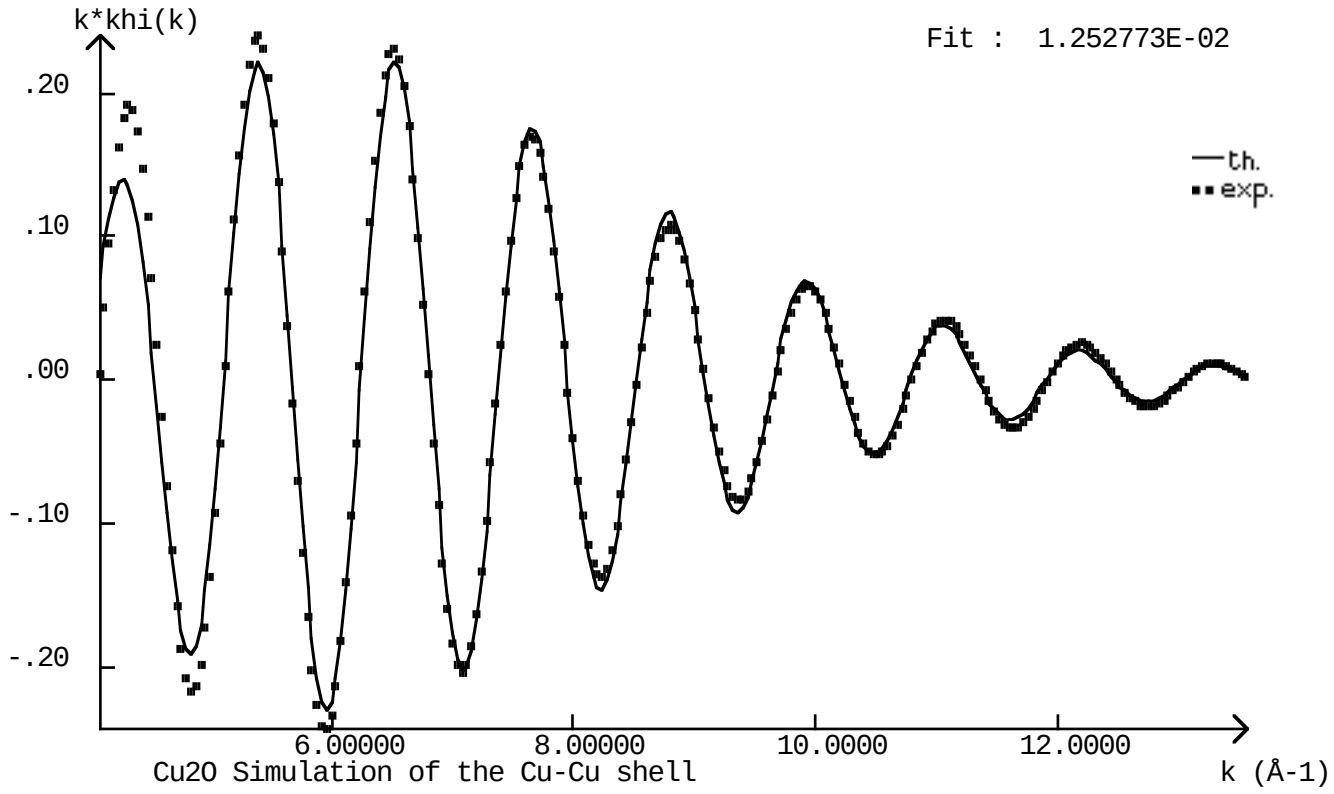

phi(k)
Phase
R = 2.5561 Å
4.00000
8.00000
12.0000
16.0000
Phase of rame_meta.fou
k (Å-1)

Back-Fourier transforms of the 'unknown' compound





The simulation



Results of the simulation

Parameter	Value
N	12.2 ± 0.5
R (Å)	3.03 ± 0.03
σ (* 10^{-2} Å)	9.3 ± 2

The results are in agreement with the crystallographic data !

Suggestions for further reading

General papers

P.A.Lee, P.H.Citrin, P.Eisenberger, B.M.Kincaid Rev.Mod. Phys. **53** (1981), 769

D.C.Köningsberger “X-ray Absorption”, Edited by D.C.Koningsberger and R.Prins, John Wiley ans Sons New York 1988

Useful links

(analysis programs and recent literature)

FEFF project ($)
http://leonardo.phys.washington.edu/

GNXAS Project (no $)
http://gnxas.unicam.it/

EXAFS analysis programs ($ and no $)
http://www.esrf.fr/computing/scientific/exafs/