INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

INTERNATIONAL CENTRE FOR SCIENCE AND HIGH TECHNOLOGY
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H4.SMR/676-21

SECOND SCHOOL ON THE USE OF SYNCHROTRON RADIATION IN SCIENCE AND TECHNOLOGY:
"JOHN FUGGLE MEMORIAL"

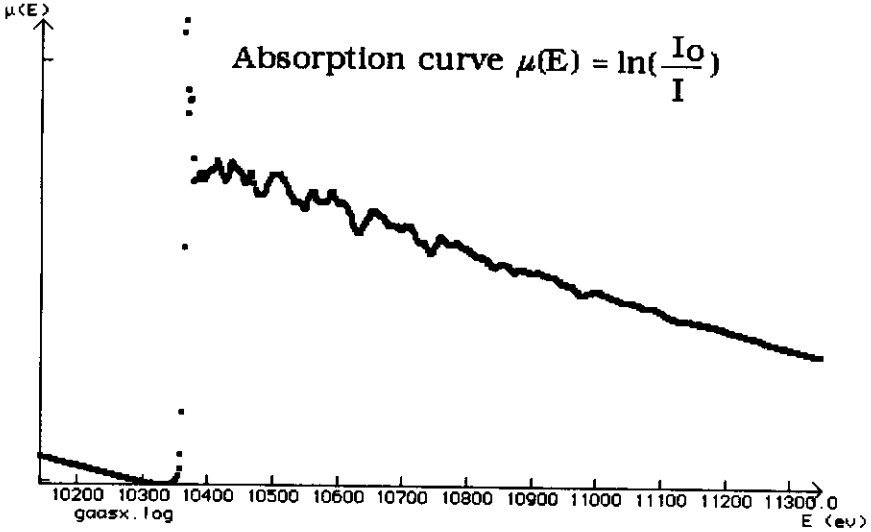
25 October - 19 November 1993

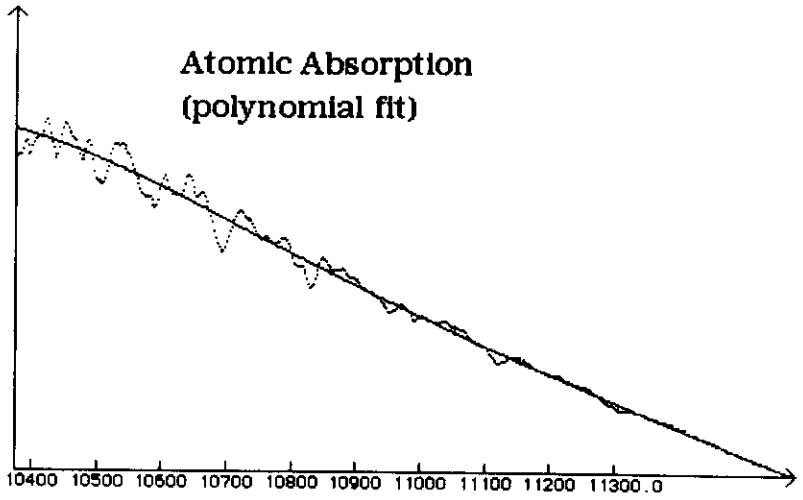
Miramare - Trieste, Italy

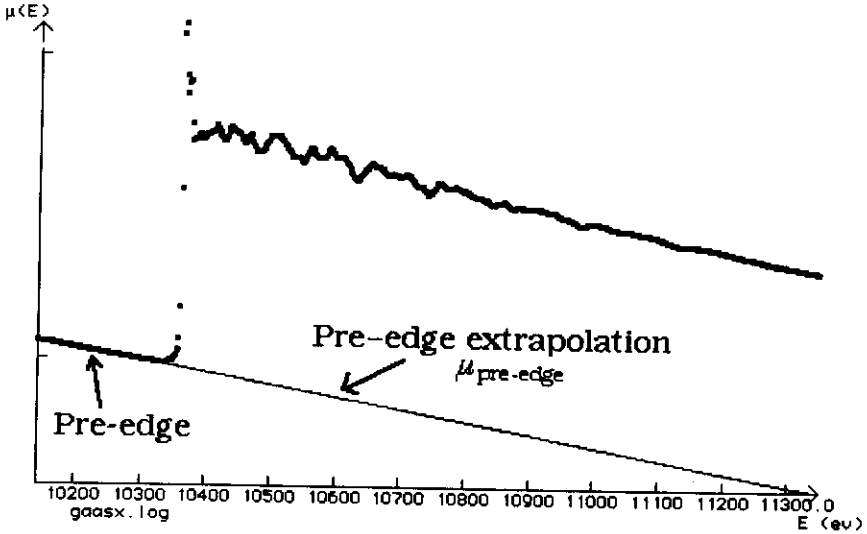
EXAFS DATA PROCESSING

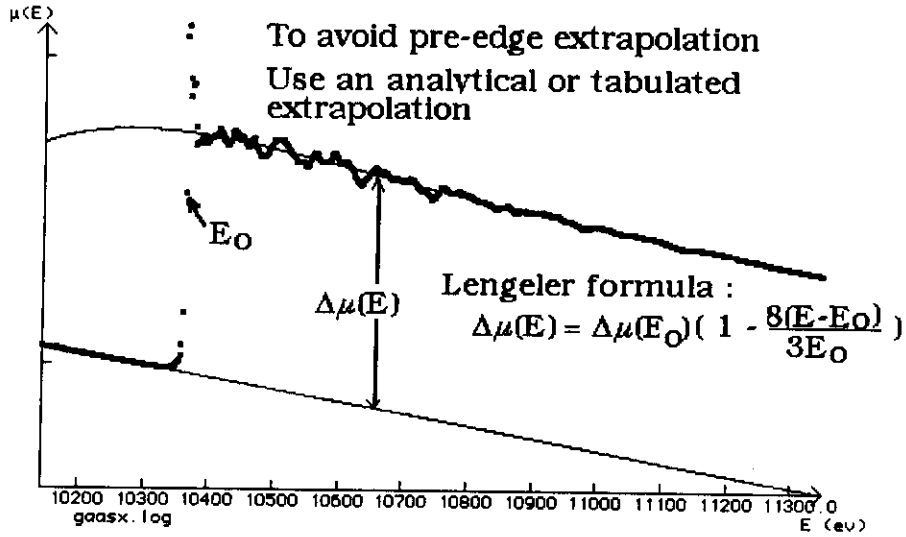
EXAFS DATA PROCESSING

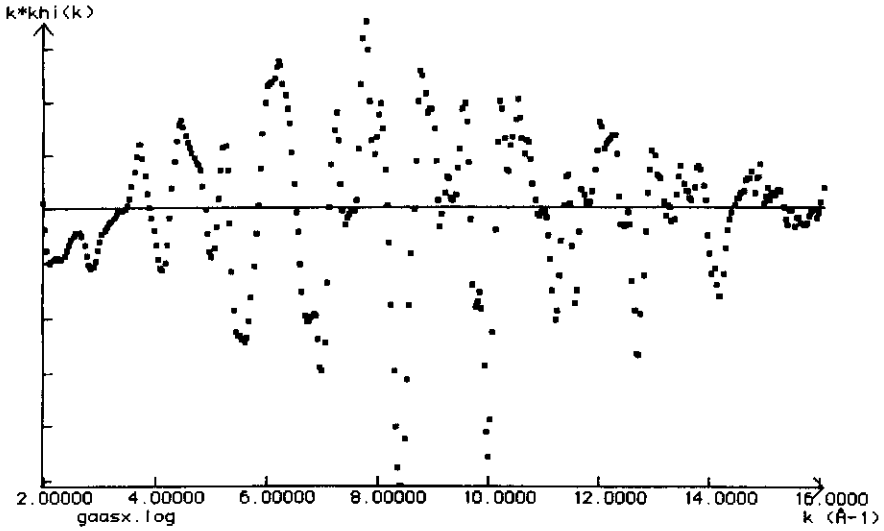
A. Michalowicz
L.U.R.E.
Orsay, France.

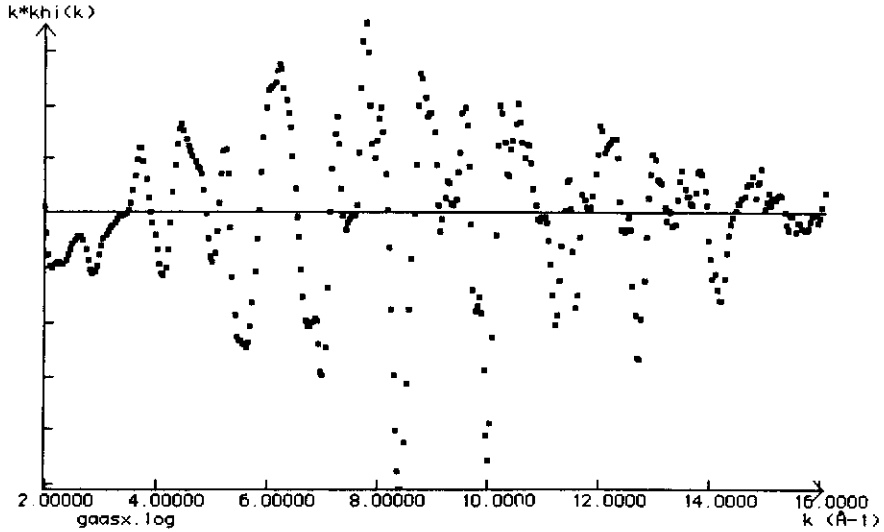

μ(E)
Absorption curve $\mu(E) = \ln(\frac{I_0}{I})$
10200 10300 10400 10500 10600 10700 10800 10900 11000 11100 11200 11300.0
gaasx.log
E (ev)


Atomic Absorption
(polynomial fit)
10400 10500 10600 10700 10800 10900 11000 11100 11200 11300.0


μ(E)
Pre-edge extrapolation
$\mu_{pre\text{-}edge}$
Pre-edge
10200 10300 10400 10500 10600 10700 10800 10900 11000 11100 11200 11300.0
gaasx.log
E (ev)

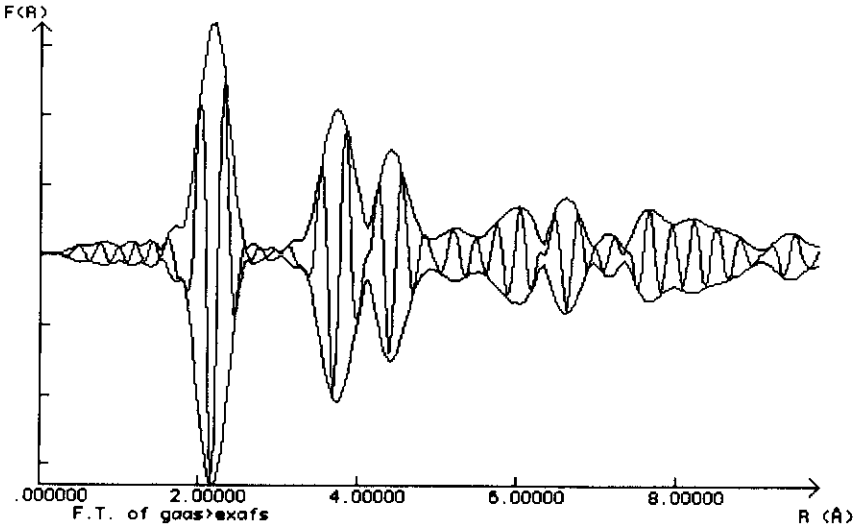

μ(E)
To avoid pre-edge extrapolation
Use an analytical or tabulated extrapolation
E_0
$\Delta\mu(E)$
Lengeler formula :
$\Delta\mu(E) = \Delta\mu(E_0)(1 - \frac{8(E-E_0)}{3E_0})$
10200 10300 10400 10500 10600 10700 10800 10900 11000 11100 11200 11300.0
gaasx.log
E (ev)

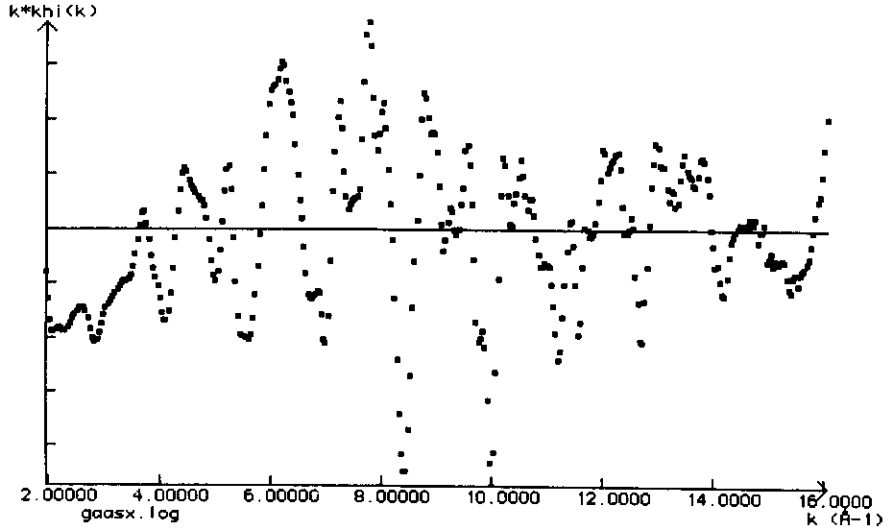


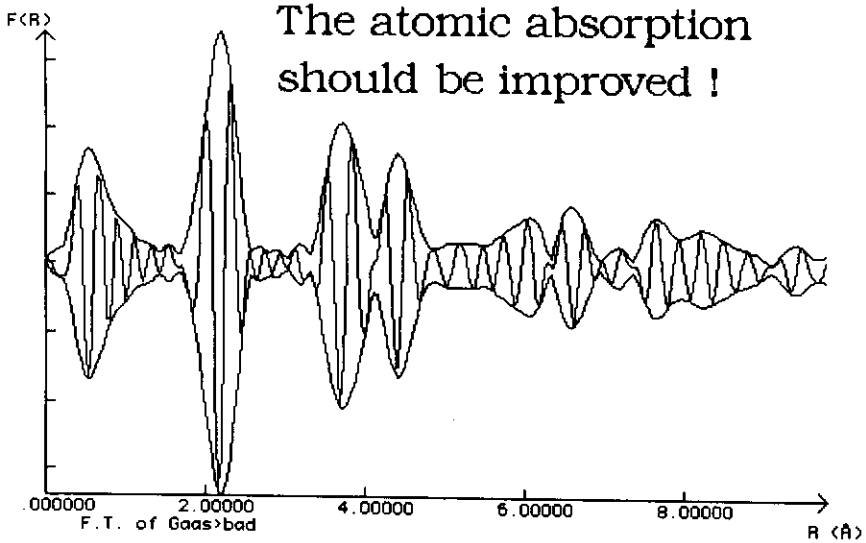


$$\chi(k) = \frac{\mu - \mu_{atomic}}{\Delta\mu}$$

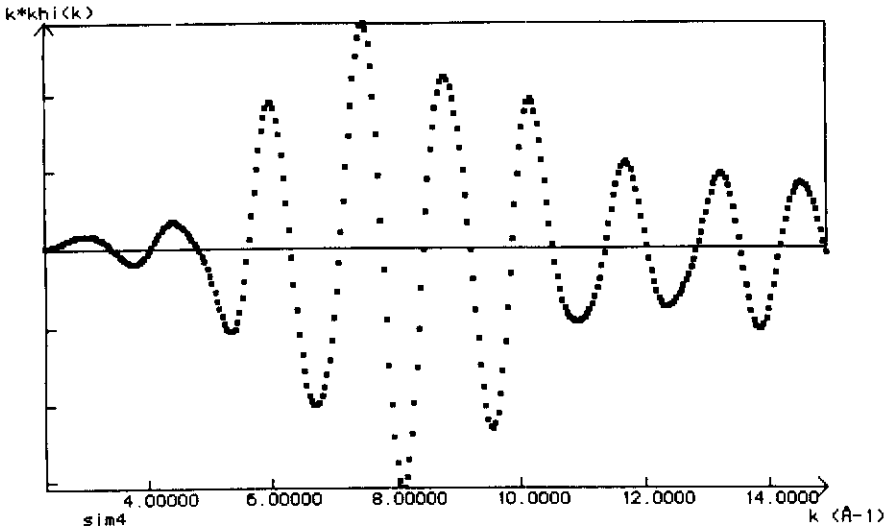
$$k = \sqrt{\frac{2m_e}{\hbar^2}(E - E_o)}$$

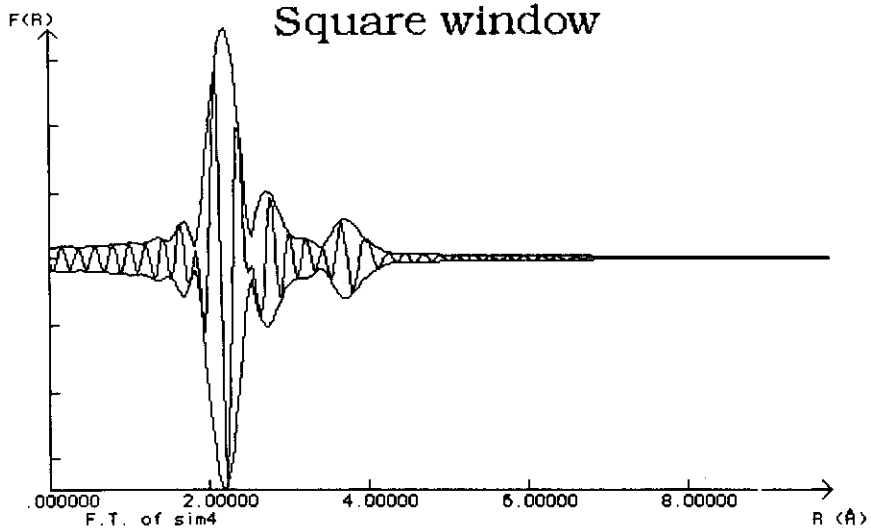


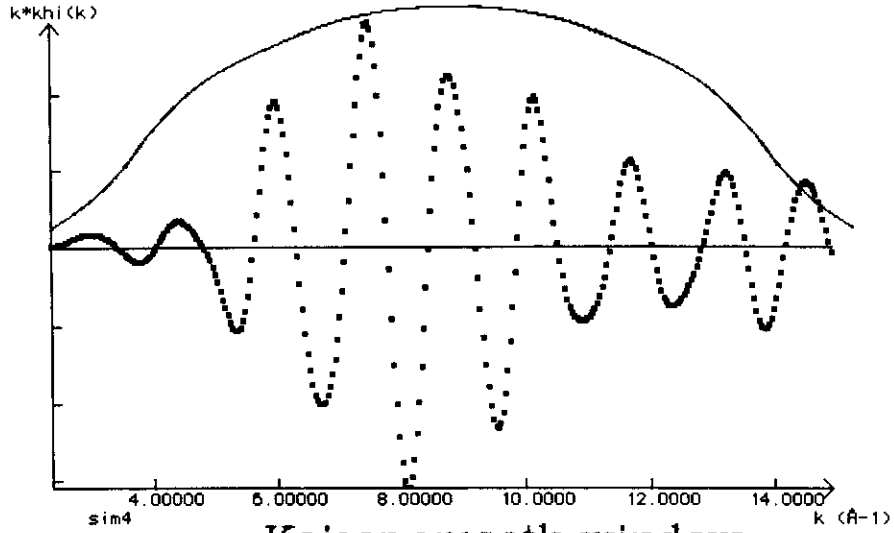


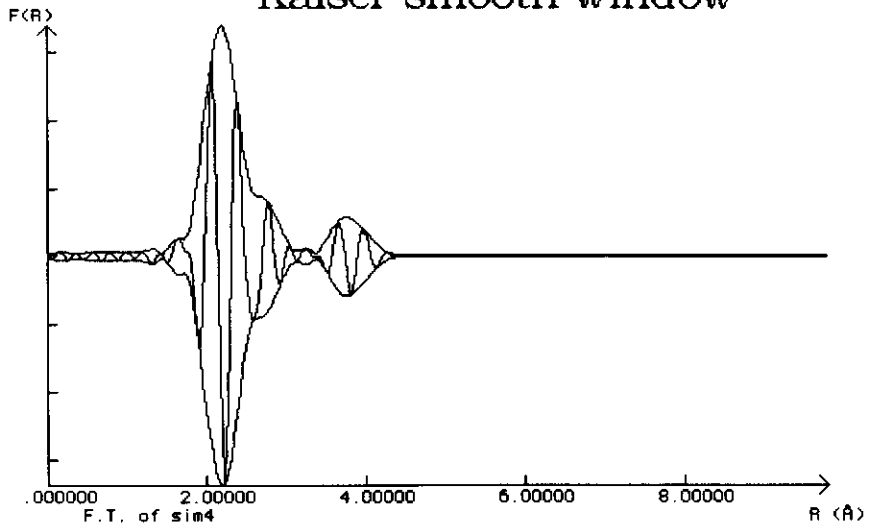


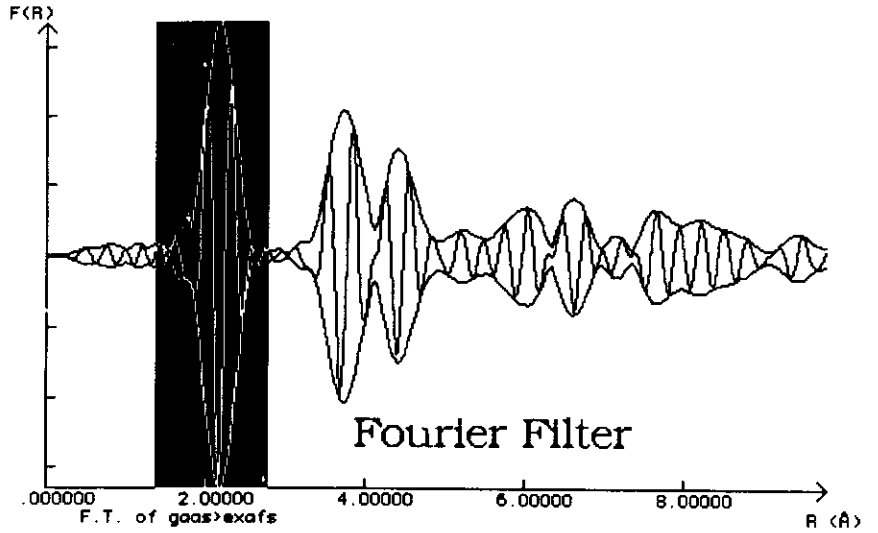
FOURIER TRANSFORM AND FILTERING

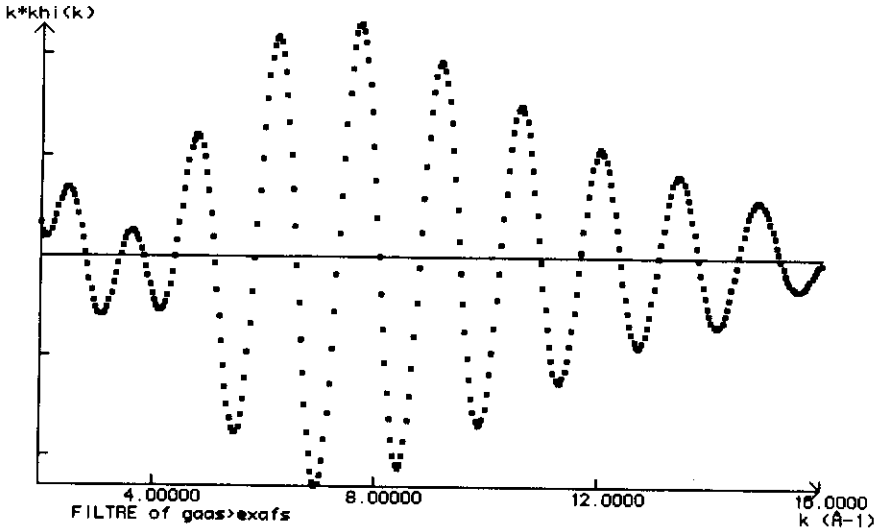

k*khi(k)
4.00000
6.00000
8.00000
10.0000
12.0000
14.0000
k (Å-1)
sim4


Square window
F(R)
.000000
2.00000
4.00000
6.00000
8.00000
R (Å)
F.T. of sim4


k*khi(k)
4.00000
6.00000
8.00000
10.0000
12.0000
14.0000
k (Å-1)
sim4


Kaiser smooth window
F(R)
.000000
2.00000
4.00000
6.00000
8.00000
R (Å)
F.T. of sim4





THEORY-EXPERIENCE FITTING

$$k\chi(k) = \sum_{i=1}^{n} \frac{N_i}{R_i^2} \exp(-2\sigma_i^2 k_i^2 - \frac{2R_i}{\lambda}) A_i(k_i,R_i,\pi) \sin[2k_iR_i+\Phi_i(k_i,R_i,\pi)]$$

$$k_i = \sqrt{\frac{8\pi^2 m_e}{h^2}(h\nu - E_o - \Delta E_o)}$$

Amplitude parameters

N : number of scatterers

σ : Debye-Waller factor (Damping coefficient)

$\lambda = \frac{k}{\Gamma}$: mean free path of photoelectrons

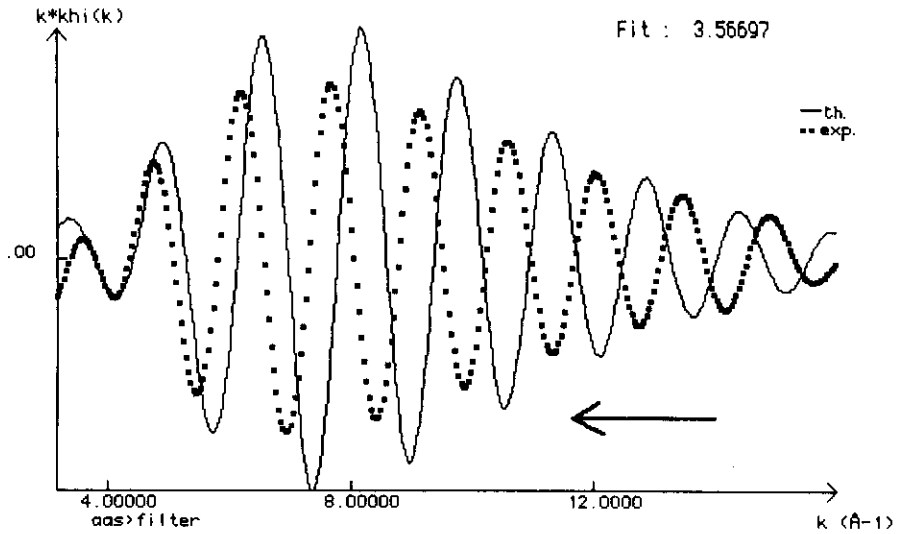
Phase parameters

R : Absorber-Scatterer distance

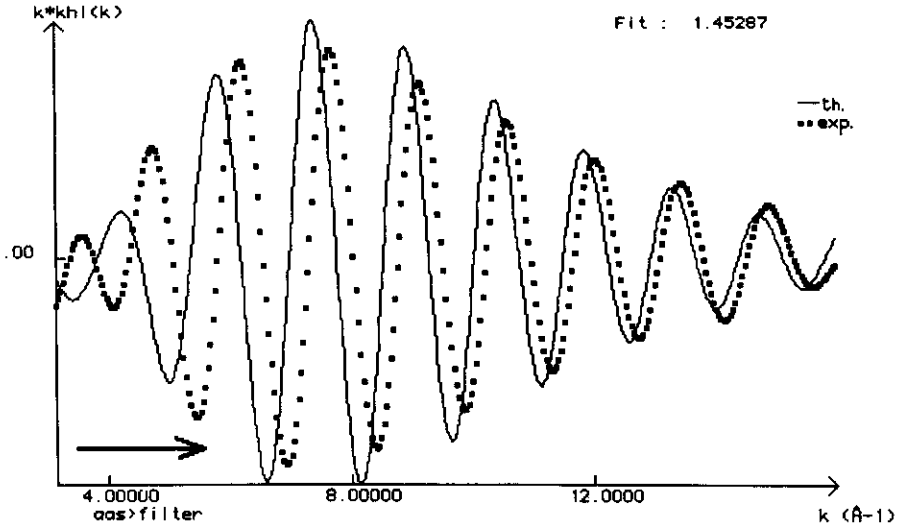
ΔE_o : Energy shift

A : scattering amplitude

Φ : total phase shift

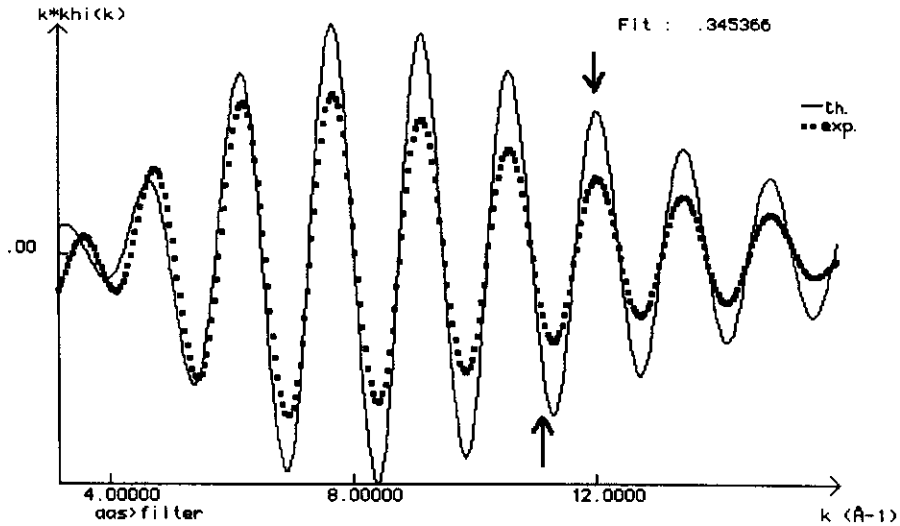


The fit is worse at the end of the spectrum => increase R



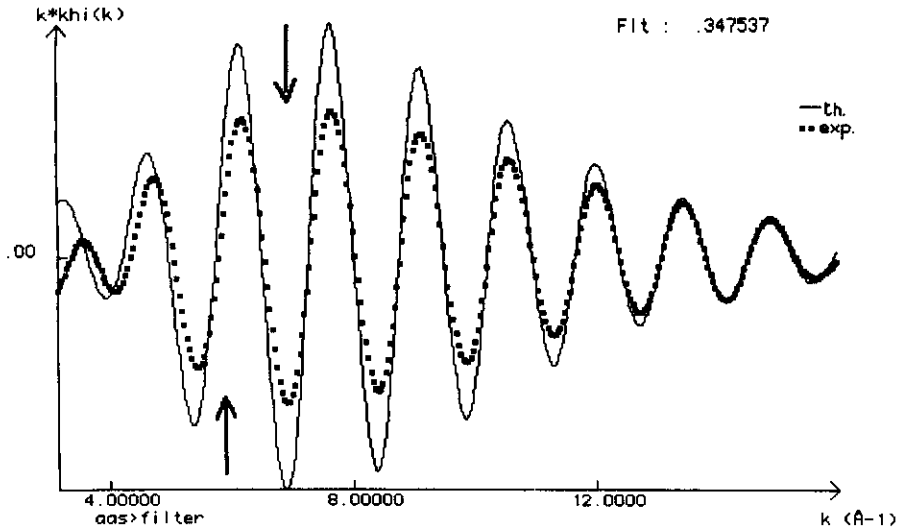
The fit is worse at the begining

=> increase E_0



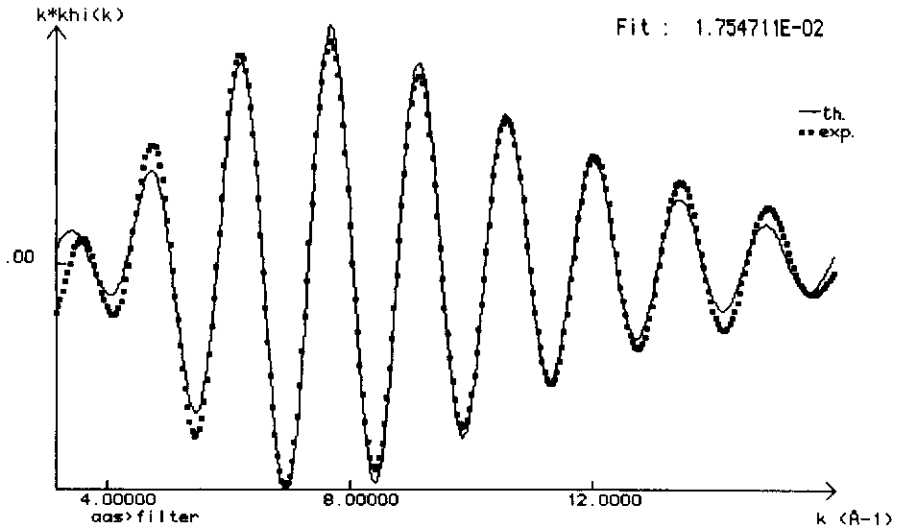
The fit is worse at the end

=> increase σ



The fit is worse at the begining

=> increase Γ

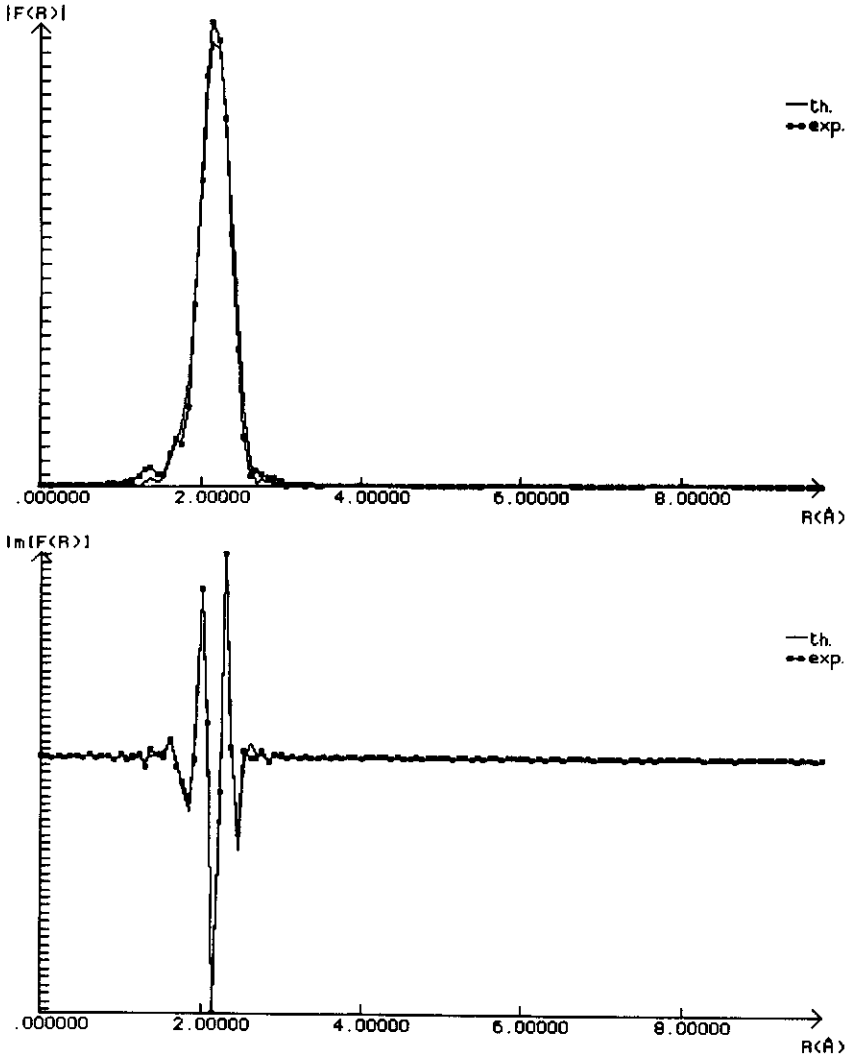


Result after an automatic fit

DANGER !!!

Fitting Γ and σ together <=> Fitting N

Beware of the correlations !



What is the subject of
the practical works ?

Learn EXAFS data analysis
on an "easy" case : GaAs

Choose a specialised study
among the three propositions :

Phase transition under pressure
in ZnS

Local disorder effect in a
crystal : $Mn_{2x}Cu_{1-x}PS_3$

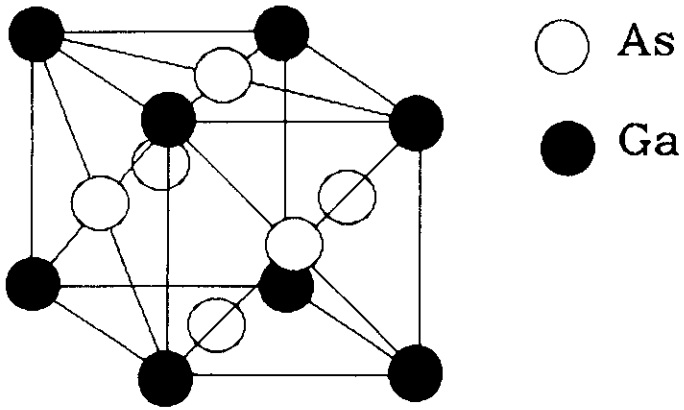
Structure of an inorganic molecule:
P_4Se_3

The structure of GaAs is given in the following picture. The corresponding X ray absorption spectrum are available in the file Gaasx.log

The crystallographic Ga-neighbour distances are :

Ga	As	D = 2.448 Å
Ga	Ga	D = 3.998 Å
Ga	As	D = 4.688 Å
Ga	Ga	D = 5.654 Å

Aim of the Practical Work : try to simulate the EXAFS spectrum with the known structure and the McKale Phase shifts and amplitudes and fit to the experimental EXAFS spectrum.

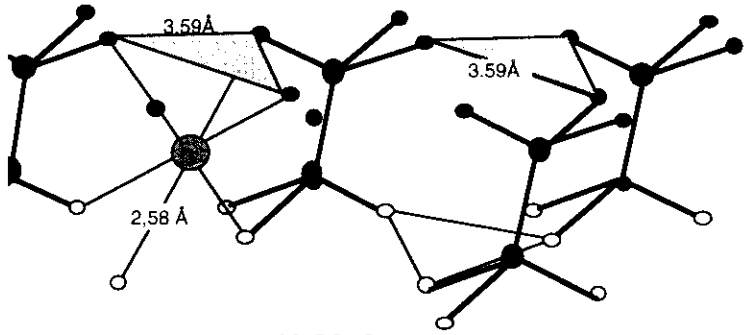


PARTIAL SUBSTITUTION OF MANGANESE(II) IONS BY COPPER(I) IN $MnPS_3$

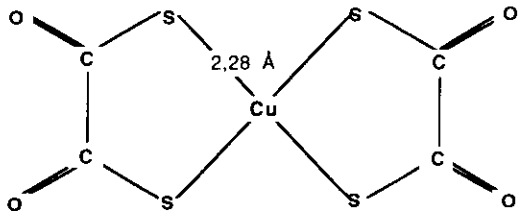
$Mn_{0.87}Cu_{0.26}PS_3$ is a compond obtained by direct synthesis from the elements in which 13 % of the Mn(II) ions have been replaced by 26 % of Cu(I).

a) EXAFS interpretation.
Use the Manganese and Copper edge spectra of $Mn_{0.87}Cu_{0.26}PS_3$ to determine the Cu-S and the Mn-S distances. The model compounds spectra are available : $MnPS_3$ and $K_2Cu(S_2C_2O_2)_2$.
Use McKale's Amplitudes and Phase Shifts and check their accuracy on the model compounds.

The Manganese edge spectra are already available as EXAFS files : MnPS3.exa and MnCu.exafs.
For the Copper edge spectra you must use EXAFS program in order to extract the EXAFS signal from the absorption curve. These absorption curves are also provided : Cu4S.log for the model compound and CuMN.log for $Mn_{0.87}Cu_{0.26}PS_3$ at copper edge.

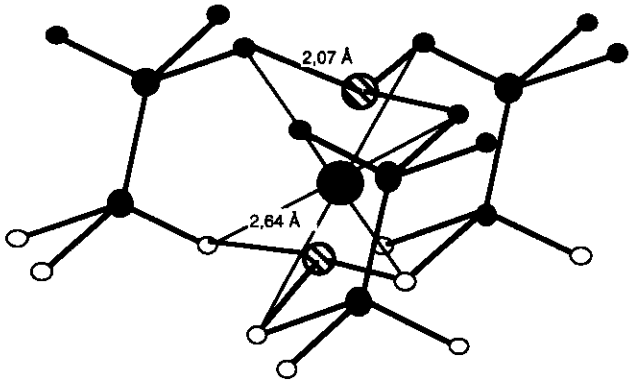


$MnPS_3$ Structure.



$Cu(S_2C_2O_2)_2^{2-}$ Structure

2) Discussion of the crystallographic and EXAFS results.



distance Cu-Cu : 3,003 Å

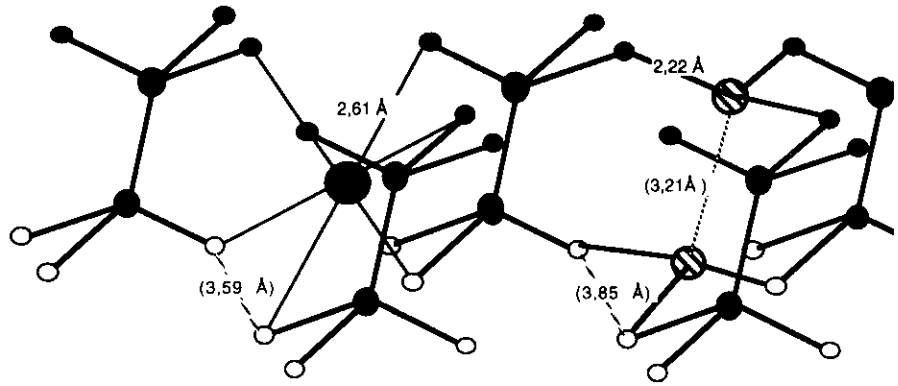
Cu
Mn
P
S

Crystallographic distances in $Mn_{0.87}Cu_{0.26}PS_3$.

Interpretation ?

Answer :

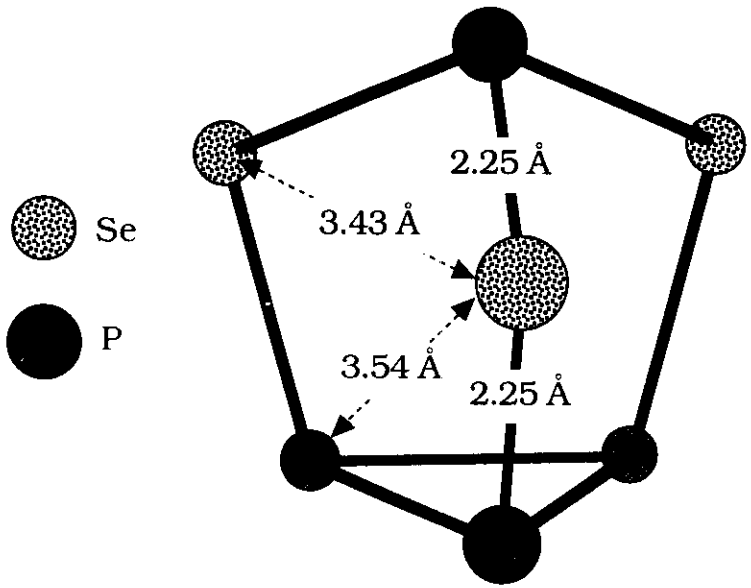
	DIFFRACTION	EXAFS
Mn-S	2.64 Å	2.61 Å
Cu-S	2.07 Å	2.22 Å



The two metallic sites must be separated. The crystallographic distances are averaged in a single site since the Cu sites are randomly distributed.

Reference :
MATHEY Y.,MICHALOWICZ A., TOFFOLI P., VLAIC G.,Inorg.Chem. (1984) 23,897

P_4Se_3 is an inorganic molecular compound. The molecular unit is represented in the following figure :



The X-Ray Absorption Spectrum of this compound recorded at 77 K is provided in the files PRICBT01.DAT, ..., PRICBT04.DAT

- Add the files with the Program LECTURE. If one file is incorrect you must eliminate it.

- Get the EXAFS spectrum with the program EXAFS

- Use the program FOURIER-FILTRE to obtain the Fourier transform and the Filtered EXAFS spectra
a) Only the first shell
b) The whole spectrum.

- Fit the first shell with the program ROUND MIDNIGHT
Use the known value of N to determine the best value of Γ

- Try to fit the total spectrum with the help of the known structure. The values of N_1, N_2 and N_3 are known and should be fixed.Γ should be also fixed to the value found in the previous question.

- Is the molecular structure of P_4Se_3 sufficient to modelise the EXAFS spectrum? What could you suggest to improve the fit ?

To answer to this question, try to use the comparison of $F_{exp}(R)$ and $F_{th}(R)$ as provided in ROUND MIDNIGTH.