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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

EXAFS STUDIES OF AMORPHOUS SOLIDS AND LIQUIDS

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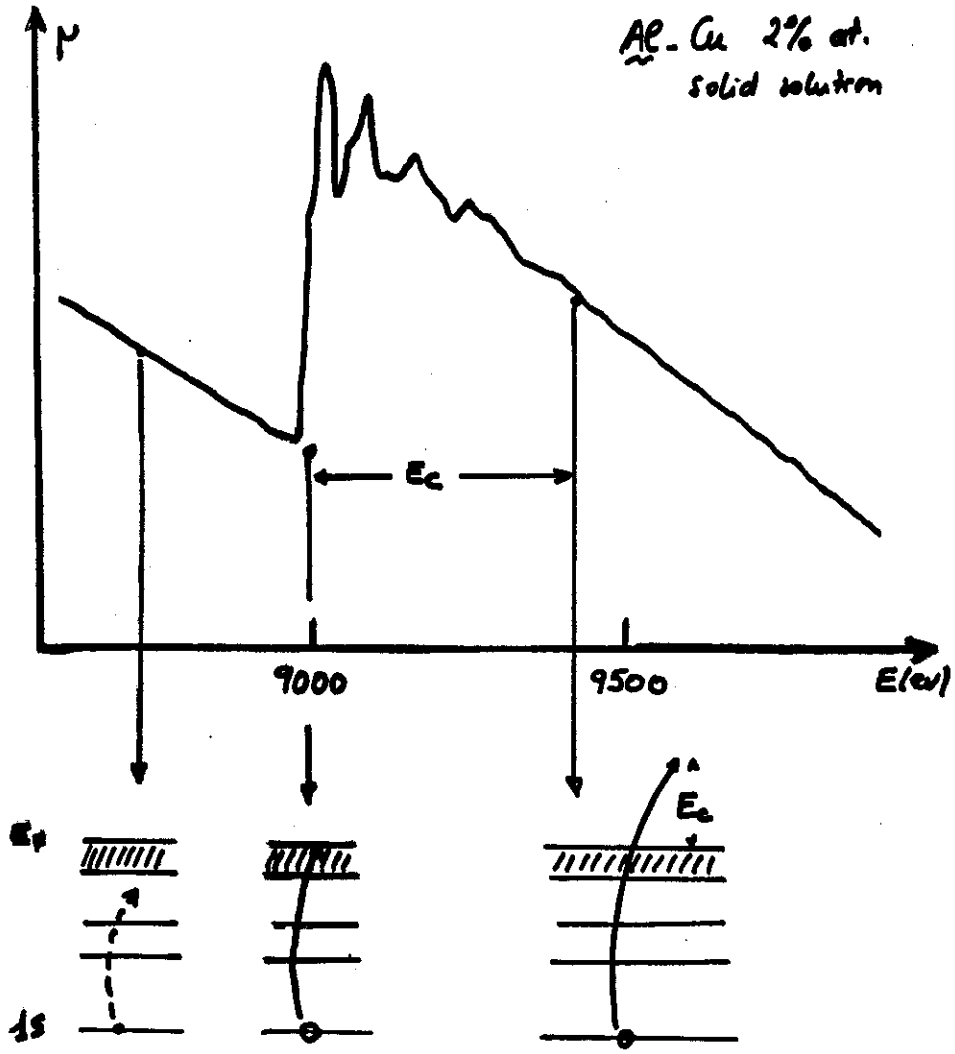
Extended X-ray Absorption Fine Structure

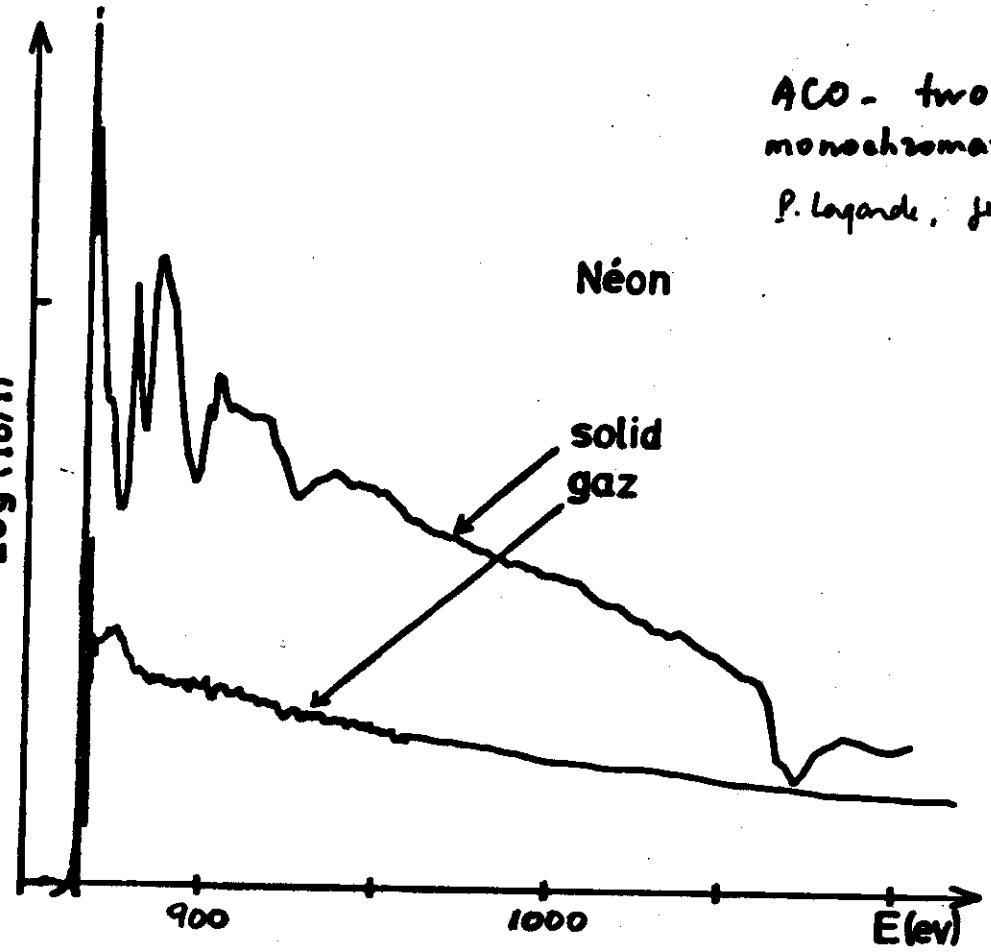
1. Introduction.
   General presentation of Exafs
2. The physical model.
   The Exafs formula
3. Experimental problems
4. Data analysis. Strenghts and limitations.
5. Examples of applications
6. The case of non-harmonic systems
   Formalism to be used
7. Examples on amorphous materials.

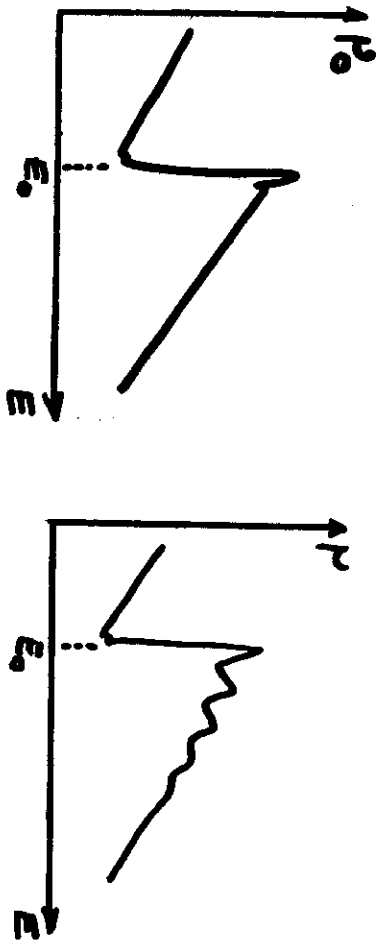


Kronig (1930) ; Stern, Sayers, Lytle (1972)

ACO - two crystals monochromator KAP

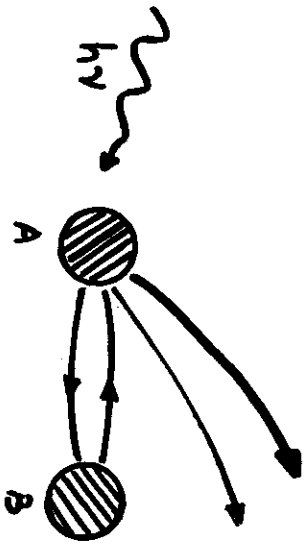
P. Lagarde, JM Estera, D. Raoux





Stern, Sayers, Lytle
Ashley and Doniach

$$\chi = \frac{\rho - \rho_0}{\rho_0}$$



Physical interpretation of Exafs

Modulations of the wavefunction of the final state of the photoelectron by diffraction of this electron on the neighbors

↳ interference effects.

Hypothesis

- single electron - single scattering (cf LEED)
- scattering weak
- short range domain seen by the photoelectron

Ashley, Doniach
Lee and Pendry

Absorption coefficient = Fermi's golden rule

$$\mu = \frac{2\pi}{\hbar} \sum_f |\langle i|H|f\rangle|^2 \, \delta(E_i - E_f)$$

$$= \frac{2\pi}{\hbar} |\langle i|H|f\rangle|^2 \, n(E)$$

Kronig 1930

Stern, Sayers, Lytle SRO

$H = \vec{\epsilon} \cdot \vec{r}$ = dipolar Hamiltonian for optical absorption

$$|f\rangle = |f_0 + \delta f\rangle$$

$|f_0\rangle$ = atomic outgoing wavefunction

$|\delta f\rangle$ = scattered part.

By expanding μ on $|\delta f\rangle$ to the second order terms, one obtains

$$\mu = \frac{2\pi}{\hbar} n(E) \left[|\langle i|H|f_0\rangle|^2 + 2\,Re\langle i|H|f_0\rangle\langle i|H|\delta f\rangle^* \right]$$

then

$$\chi(E) = \frac{\mu - \mu_0}{\mu_0} = 2\,Re\,\frac{\langle i|H|\delta f\rangle^*}{\langle i|H|f_0\rangle^*}$$

We have to calculate $|\delta f\rangle$

1- $|\delta f\rangle$ = outgoing wave with a phase shift δ_1'

$= Y_{1,0}(\vec{r})\, h_1(kr)\, e^{i\delta_1'}$

↳ Hankel function.

2- Hypothesis of the use of the asymptotic limit for $h_1(kr)$ → plane wave

$$|\delta f\rangle = Y_{1,0}\, i\, \frac{e^{ikr}}{2kr}\, e^{i\delta_1'}$$

3- Scattering is weak → Born diffusion described by a scattering function $f(\theta)$

$$f(\theta) = \frac{1}{2ik} \sum_\ell (2\ell+1)\left(e^{i\delta_\ell}\sin\delta_\ell\right) P_\ell(\cos\theta)$$

$$f(\pi,k) = \frac{1}{2ik} \sum_\ell (-1)^\ell (2\ell+1)\left(e^{2i\delta_\ell} - 1\right)$$

4- $|\delta f\rangle$ has to be calculated at the site of the central atom since $|i\rangle$ is very localized → $r = R$ = interatomic distance

$$\chi(E) = -\frac{1}{kR^2}\, |f(\pi)|\, \sin(2kR + 2\delta_1' + \varphi)$$

5- Take into account

- the mean free path of the photoelectron
- the fluctuations of the distance R
- a scale factor due to atomic processes

$$\boxed{\chi(E) = \sum_j -\frac{N_j}{kR_j^2}\, S(k)\, e^{-2\sigma_j^2 k^2}\, e^{-\frac{2R_j}{\lambda(k)}}\, |f_j(\pi)|\, \sin(2kR_j + 2\delta_1' + \varphi_j(k))}$$

Experimental methods

Samples

Size of the beam ~ 5 x 40 mm²

Thickness ~ 10 μ for Cu

↳ cf. neutrons

Sensitivity

- in fluorescence mode $C \sim 10^{-5}$ M
- surface experiments

  10^{13} atoms in the beam (I/Cu)

Allaratus

- X-ray source with white spectrum
- monochromator
- I and I_0 detection

Conventional X-ray tube → few days

Synchrotron radiation → few minutes

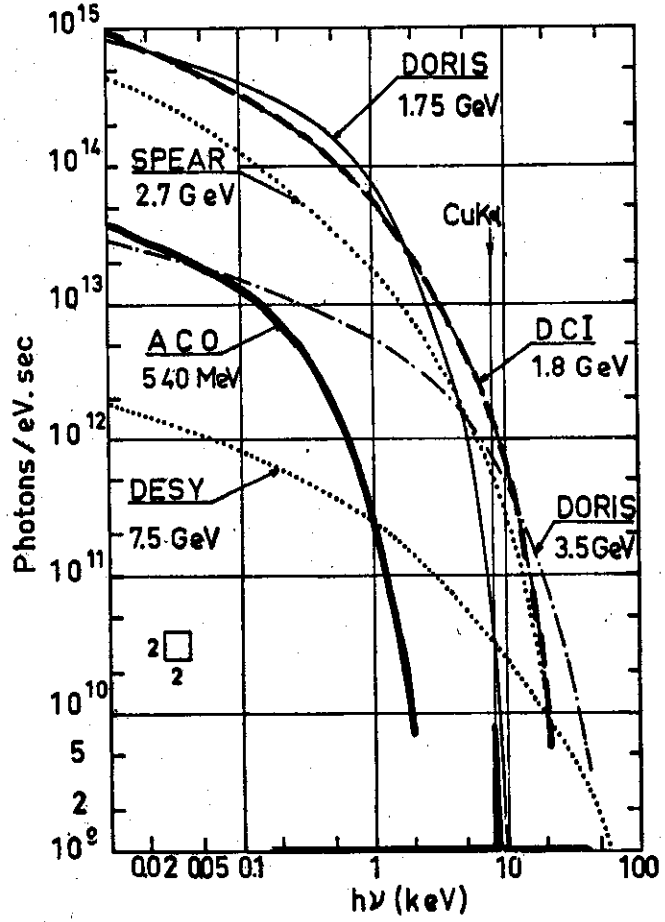
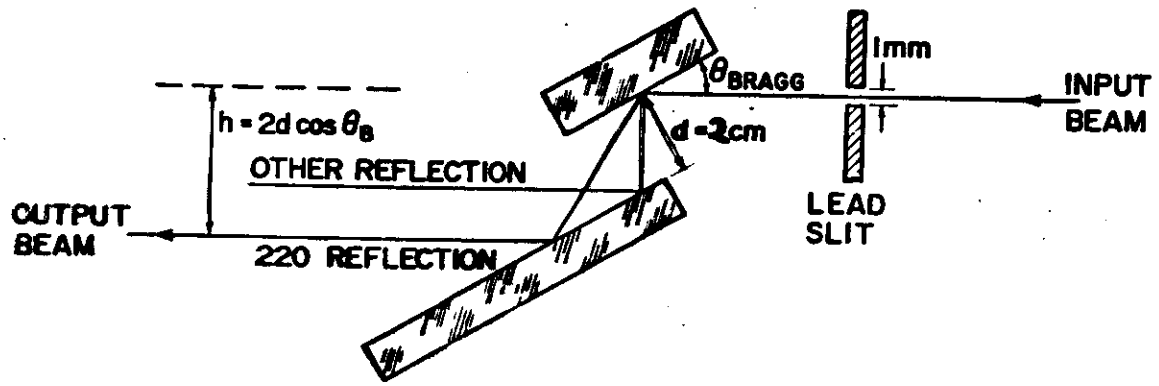
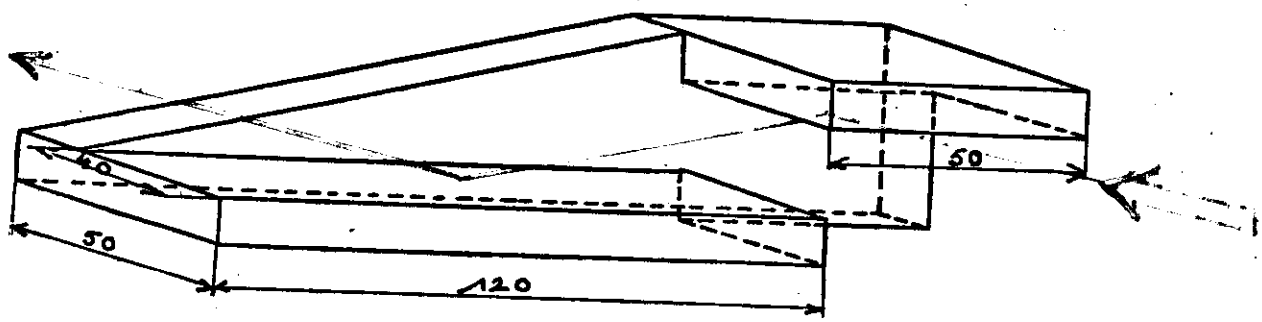
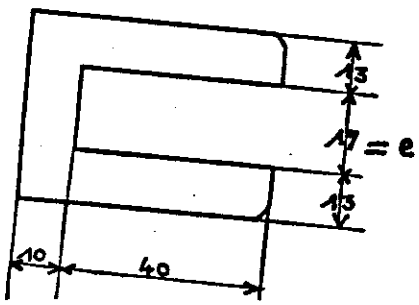


Fig. 28

CHANNEL CUT CRYSTAL MONOCHROMATOR

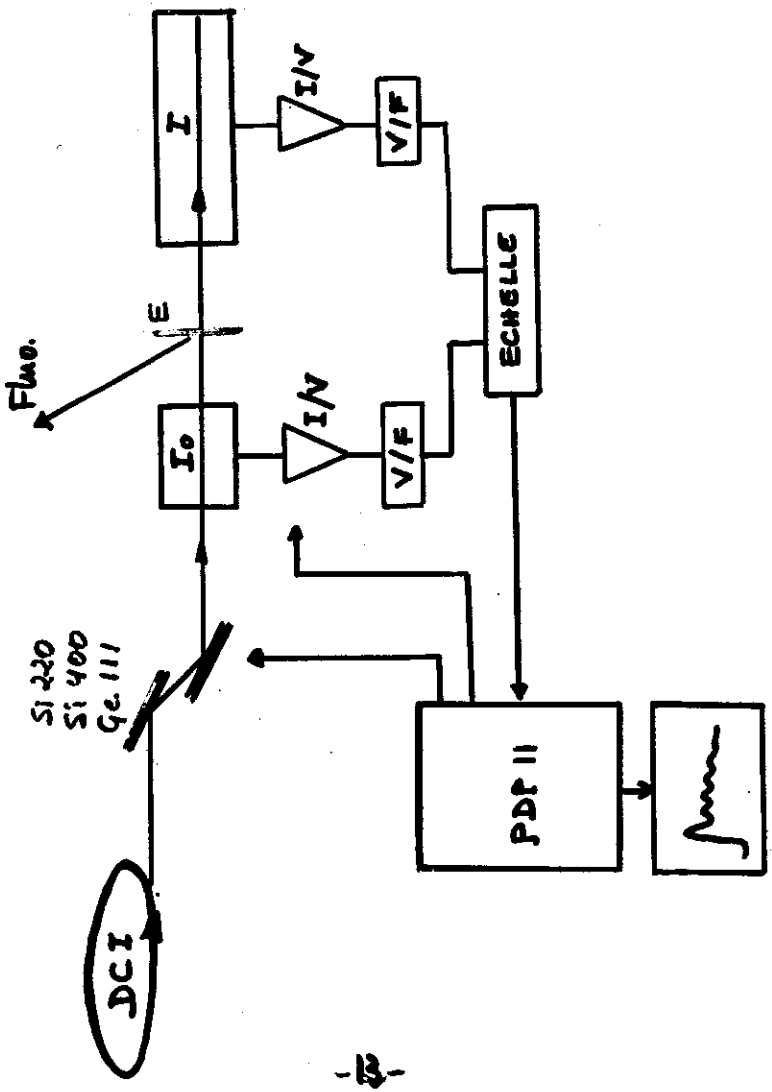






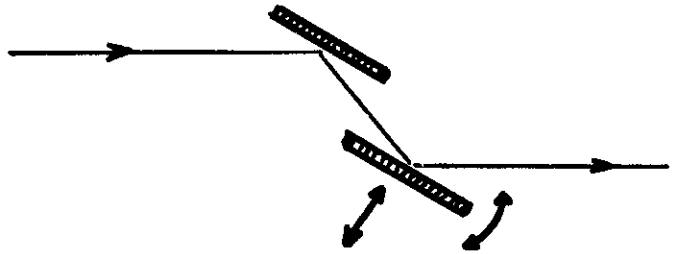
Si (400)

values in mm.



New developments

* Two crystals monochromators



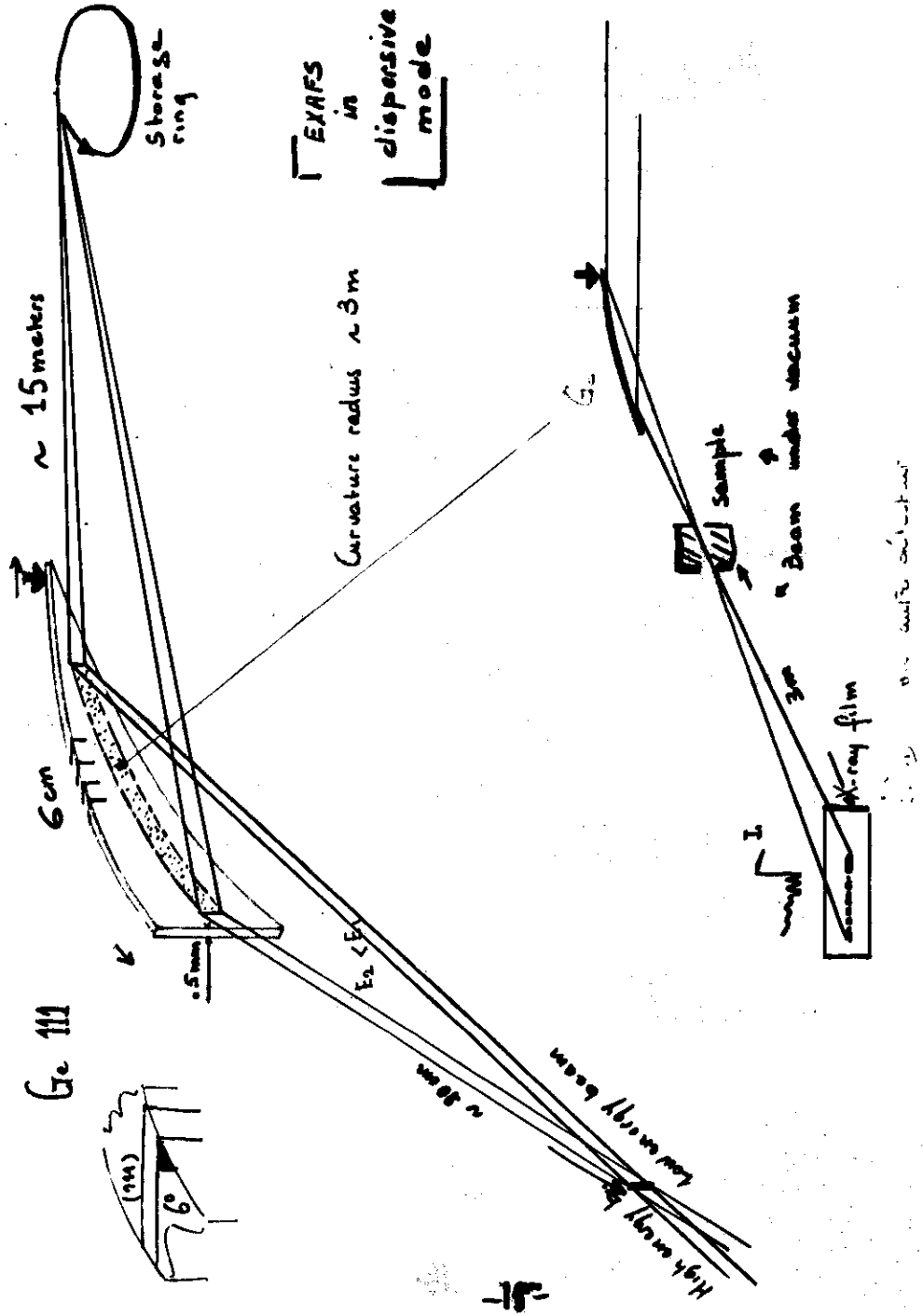
Advantages

. rotation of the second crystal versus the first one removes the harmonics

. translation of the 2d crystal makes the exit beam fixed

. focusing by curving the crystals

* Exafs in dispersive mode.



Data analysis. Strenghts and limitations

$$\chi(k) = -\sum_j \frac{N_j}{k R_j^2} S(k)\, e^{-\frac{2R_j}{\lambda}}\, e^{-2\sigma_j^2 k^2} \cdot |f_j(\pi)| \sin\left[2kR_j + \Phi_j\right]$$

a) . Electronic terms . λ, $f(\pi)$, δ_i'

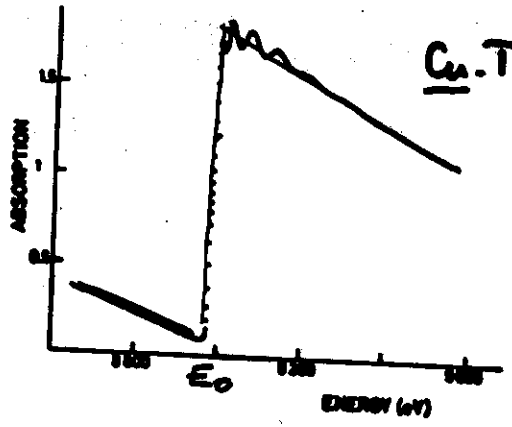
b) . Structural terms . N, R, σ

If a) are known, Exafs is a structural tool which gives b)
↳ g(R)

$\Phi_j(k) \simeq ak + b \rightarrow$ F.T $\rightarrow$ peaks at distances R_j shifted by a

Stern, Sayers, Lytle

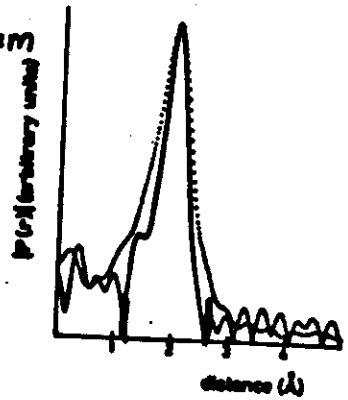
1. Extraction of Exafs data
   - μ - edge
   - atomic absorption
   - $\chi(E) = \frac{\mu}{\mu_0} - 1$



⇓

2. Fourier transform

   filtering of the shell



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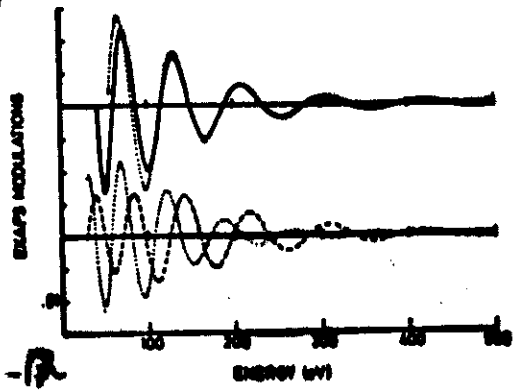
3. Back. Fourier transform

   - theoretical fit using calculated phase shifts

   ↓

   N, R, σ



Absorption edges. Selectivity

Absorption edges are well separated

ex	Al	1560 ev
	Si	1836 ev
	Fe	7111 ev
	Ni	8300 ev
	Cu	8990 ev

Exafs is a selective method

compare to X. rays or neutrons

All elements are accessible (K or L edges)

Advantage in { biophysics, solutions, catalysts ... etc..

Mathematics are not very complicated

I- Phase shifts

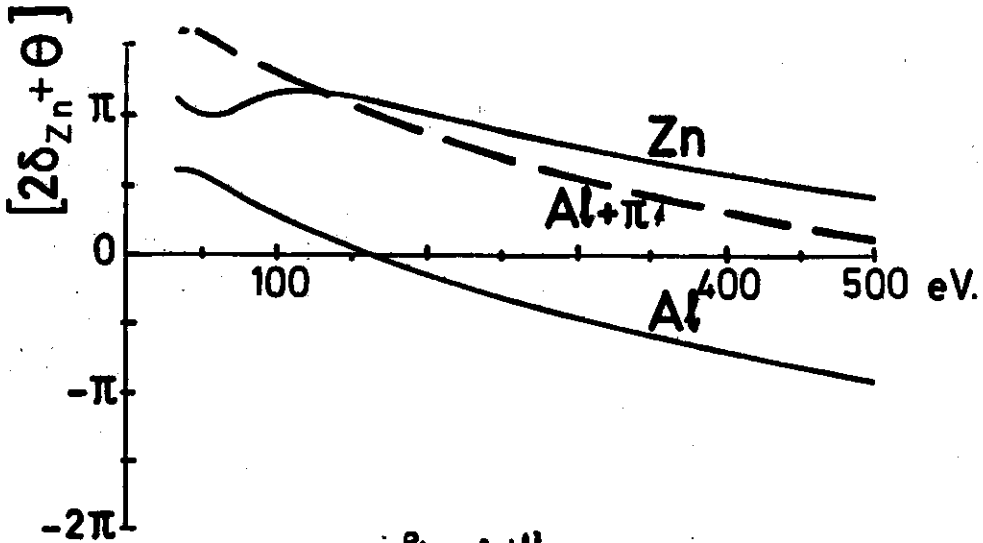
* Transferability = phase shifts are transferable from one couple A-B to another one if distances and chemistry are not too different.
  - good for $\phi(k)$ → $\Delta R \sim 0.02$ Å
    ex Ge. GeO_2. Ge_2H_6
  - less accurate for $|f(\pi)|$ $\Delta R \sim 10\%$
  - better when $Z \nearrow$

Exafs is a comparative method

* Use of calculated phase-shifts

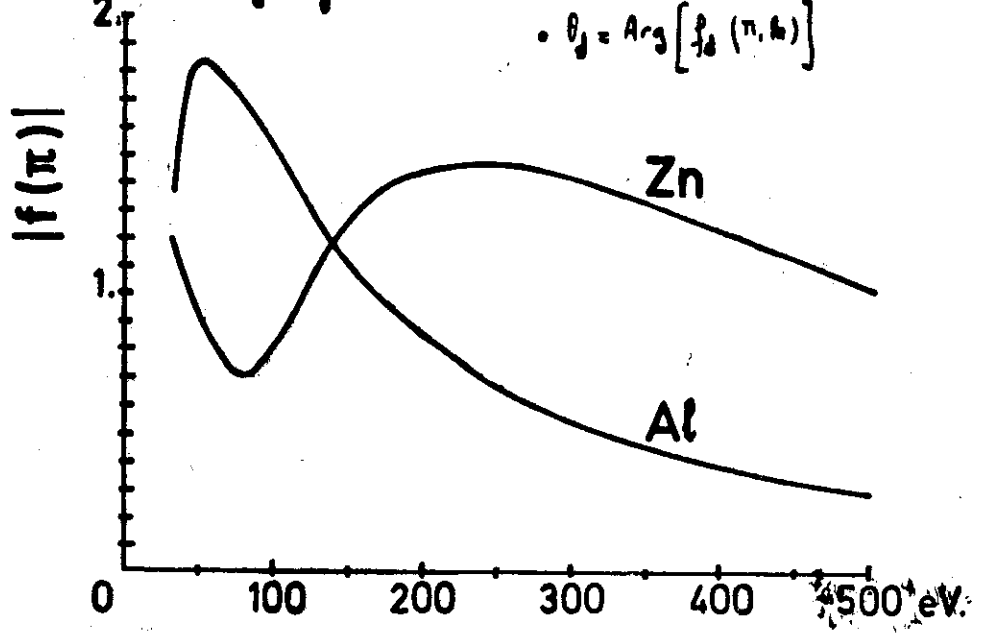
A shift of E_0 (± 10 ev) takes into account of valence bands effects.

B. K. Teo. and P. Lee
P. Eisenberger et. al. (Ge)
P. Lagarde et. al ($ZnBr_2$)
E. Stern ($|f(\pi)|$)



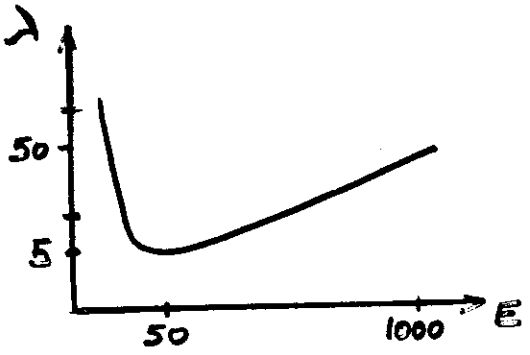
$$\chi(k) = -\frac{1}{k}\sum_j \frac{N_j}{R_j^2} e^{-\frac{R_j}{\lambda(k)}} e^{-2\sigma_j^2 k^2} |f_j(\pi,k)| \sin\left[2kR_j + 2\delta_1 + \theta_j(k)\right]$$

- $\theta_j = \mathrm{Arg}\left[f_j(\pi,k)\right]$



2. Mean free path

Reduction factor



$$\lambda \sim \frac{k}{\Gamma}$$

$$\Downarrow$$

$$e^{-\frac{2R}{\lambda}} \sim e^{-\frac{2\Gamma R}{k}}$$

Mean free path ⟷ information lost

at large R ⟷ model non valid

at small k (valence band effects)

Exafs studies the local order

$S(k)$ due to shake-up
shake-off processes

in general $S(k) \sim$ cte $\sim .8$

E. Stern

3. Other hypothesis

* Plane wave approximation

  less good for light elements
  small k

  J.B. Pendry
  R.F. Pettifer

* Single-scattering

  involves large R paths

* Screening of the potential

  small k values

  C. Noguera et. al

Effects of disorder in EXAFS

Harmonic approximation → the Debye-Waller term

Beni and Platzmann (76)

Time scale { absorption 10^{-16} s ; vibrations 10^{-12} s } → average.

Central atom $\vec{r_o} = \vec{r_o^0} + \vec{u_o}$

Scatterer $\vec{r_j} = \vec{r_j^0} + \vec{u_j}$

$$r = |r_{oj}| = |\vec{r_j^0} - \vec{r_o^0} + \vec{u_j} - \vec{u_o}|$$

$$\simeq r_{oj}^0 + |(\vec{u_j} - \vec{u_o})_{//}| + \frac{|(\vec{u_j} - \vec{u_o})_{\perp}|^2}{2 r_{oj}^0}$$

$$= r_{oj}^0 + u_{//} + \frac{u_{\perp}}{2 r_{oj}^0}$$

We have to take

$$\langle \sin(2k r_{oj} + \phi) \rangle$$

$$= \sin(2k r_{oj}^0 + \phi) \langle \cos(2k u_{//} + k \frac{u_{\perp}^2}{r_{oj}^0}) \rangle$$

$$+ \cos(2k r_{oj}^0 + \phi) \langle \sin(2k u_{//} + k \frac{u_{\perp}^2}{r_{oj}^0}) \rangle$$

1st term

$$\langle \cos(2k u_{//} + k \frac{u_{\perp}^2}{r_{oj}^0}) \rangle$$

$$= \langle \cos 2k u_{//} \rangle \langle \cos k \frac{u_{\perp}^2}{r_{oj}^0} \rangle$$

$$- \langle \sin(2k u_{//}) \rangle \langle \sin k \frac{u_{\perp}^2}{r_{oj}^0} \rangle$$

since $u_{//}$ and $u_{\perp}$ are independant

$$\langle \cos 2k u_{//} \rangle \sim 1 - 2k^2 \langle u_{//}^2 \rangle = 1 - 2k^2 \sigma_{//}^2$$

$$\cos k \frac{u_{\perp}^2}{r_{oj}^2} \sim 1 - \text{4° order terms}$$

$$\langle \sin 2k u_{//} \rangle \sim 2k \langle u_{//} \rangle + \text{3° order terms} \overset{//}{0} \text{ (harmonic)}$$

$$\langle \sin k \frac{u_{\perp}^2}{r_{oj}^0} \rangle \sim k \frac{\langle u_{\perp}^2 \rangle}{r_{oj}^0} = k \frac{\sigma_{\perp}^2}{r_{oj}^0}$$

To the 2nd order

$$\langle \cos(2k u_{//} + k \frac{u_{\perp}^2}{r_{oj}^0}) \rangle \sim 1 - 2\sigma^2 k^2 \sim e^{-2\sigma^2 k^2}$$

and it can be easily shown that the second terms averages to zero.

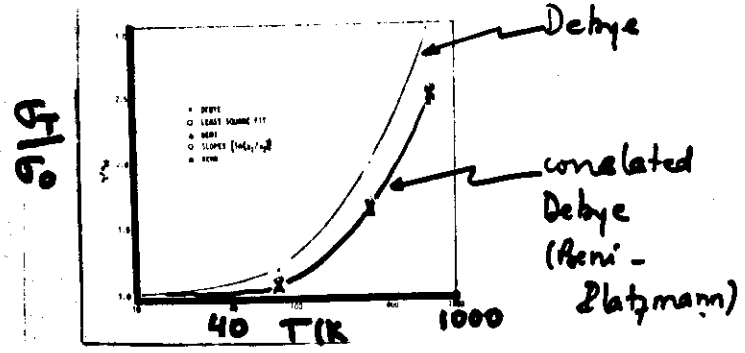
In the harmonic approximation, the effect of disorder can be described by a Debye-Waller like term $e^{-2k^2\sigma^2}$

Relation between σ(Exafs) and σ(X-rays)

Only correlated motions contribute to Exafs (relative displacements)

$$\sigma^2(\text{Exafs}) \sim \sum_{q,\ \text{phonons}} 2\langle u^2\rangle (1-\cos qR)$$

- the acoustic modes do not appear
- $\sigma^2(\text{Exafs}) \sim 2 * \sigma^2(\text{X-rays})$
- Einstein model is a good approximation for $\sigma^2(T)$



D.W. factor for crystalline Cu (Greegor and Lytle 1979)

Covalent systems

$$\text{Log}\frac{\chi_1}{\chi_2} = \log\frac{N_1}{N_2} - 2(\sigma_1^2-\sigma_2^2)k^2$$

at the maxima.

Ex: a-Ge and c-Ge (Crozier et al.)

$\sigma^2 = f(T)$ fitted with Einstein model

θ_E = 360 K (am.)
θ_E = 381 K (crys.)

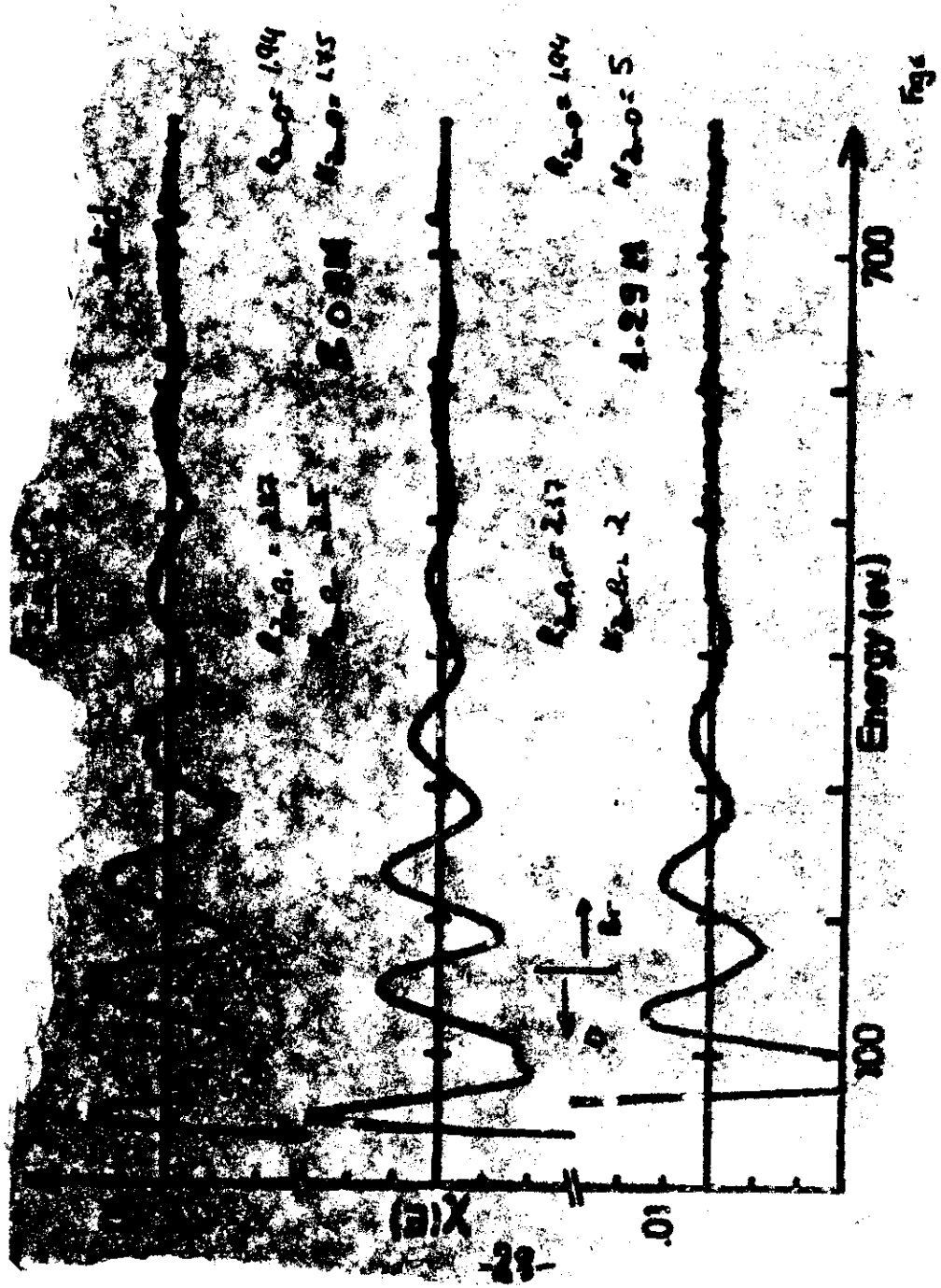
↳ just change in static disorder

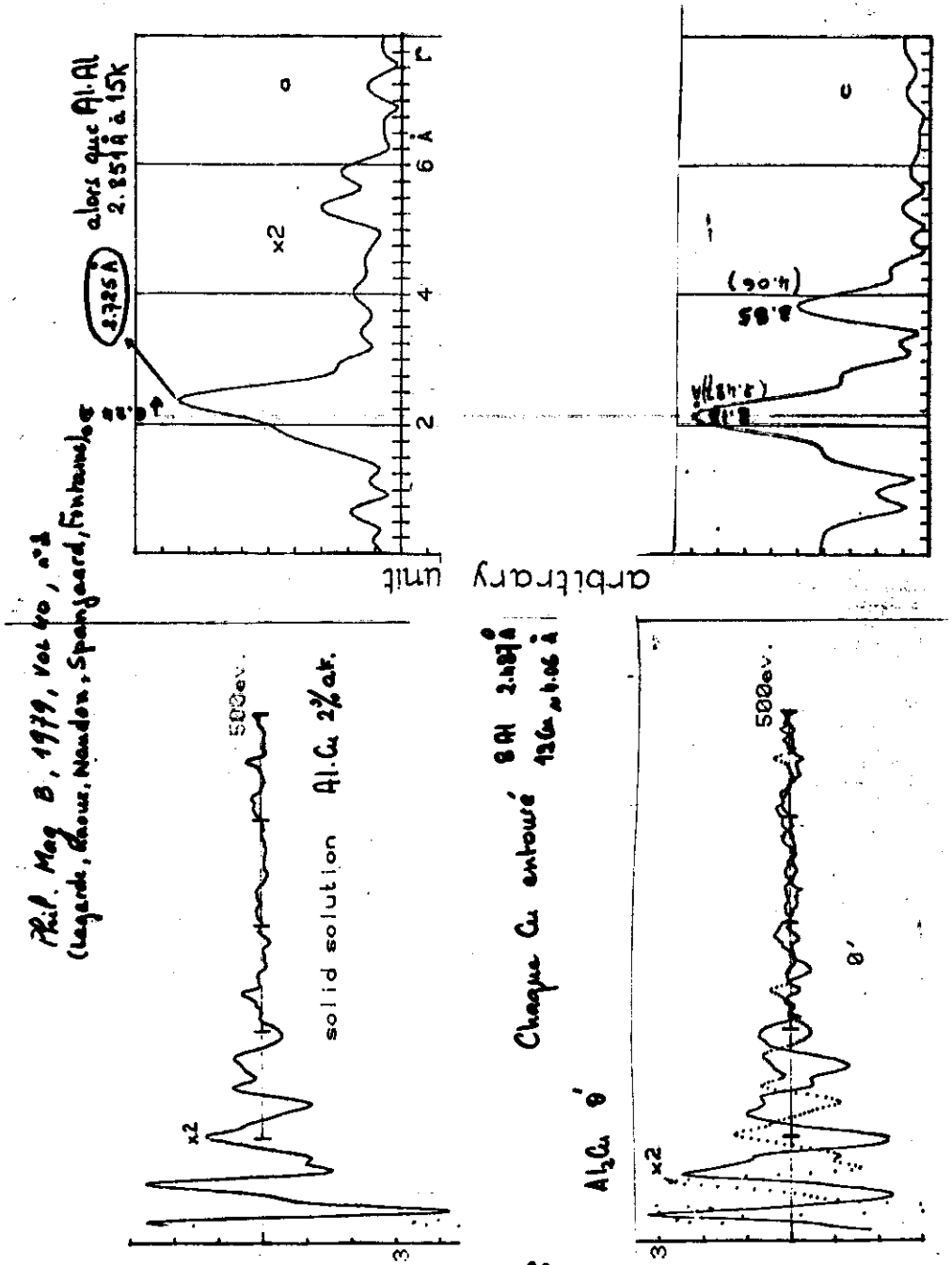
Domains of application

In general systems

- disordered (amorphous)
- diluted (solutions - biophysics catalysts)

Exafs is interesting when other methods (diffraction - microscopy) are inefficient.





The case of non-harmonic systems

Eisenberger and Brown.

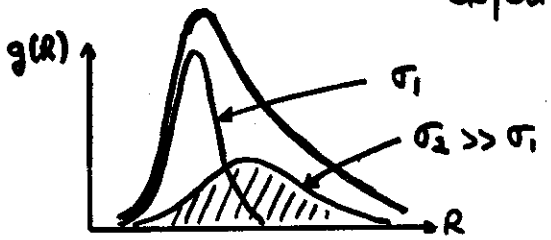
- Exafs model non valid for $k < 3\ \text{Å}^{-1}$

  ↓

  information at large R permanently lost.

  (Fourier-Yevick RDF)

- Large effect of σ^2 on the experimental data



$$e^{-2k^2\sigma_2^2} \ll e^{-2k^2\sigma_1^2}$$

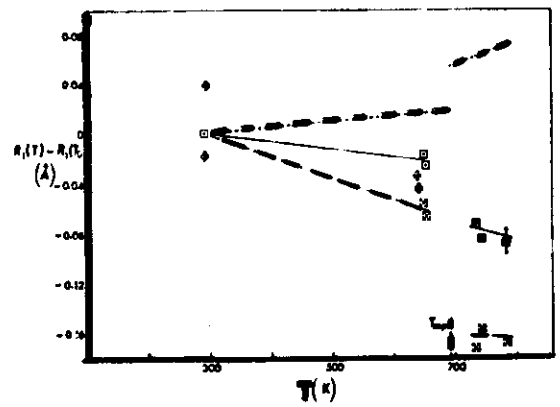
- Anharmonicity has two effects
  - measured distances are too short
  - coordination numbers are too small

  by using the harmonic approx.

- Ex. Zn metal on the c-direction between 20 K and 300 K

Exafs	X-rays
5 % contraction	2 % expansion

ΔR



Temperature dependance of the n. n. dist. R in Zn (Cargill and Seary, 1980)

— — from thermal expansion data

— + — from the magnitude of F.T. of Exafs

Formalism to be used

$$\chi(k) = -\frac{f(\pi)}{k}\int_0^\infty \underbrace{g(r)\frac{e^{-\frac{r}{\lambda}}}{r^2}}_{f(r)=f(\bar{r}+x)} \sin(2kr+\phi)\,dr$$

expanding the sine

$$\chi'(k) = \sqrt{A_k^2+S_k^2}\,\sin(2k\bar{r}+\phi+\Sigma_k)$$

with
$$\begin{cases} A_k = \int_{-\infty}^{+\infty} f(\bar{r}+x)\sin 2kx\,dx \\ S_k = \int_{-\infty}^{+\infty} f(\bar{r}+x)\cos 2kx\,dx \\ \Sigma_k = \text{Arctg}\,(A_k/S_k) \end{cases}$$

$\Sigma_k \longrightarrow$ change in distance

$\sqrt{A_k^2+S_k^2} \longrightarrow$ change in coord. nb.

Eisenberger. Brown.

Harmonic approximation if
$$\begin{cases} \frac{\langle x^2\rangle}{R} < .01\,\text{Å} \\ \frac{\langle x^2\rangle}{\lambda} < .01\,\text{Å} \\ k^3\langle x^3\rangle \ll 1. \end{cases}$$

Solutions

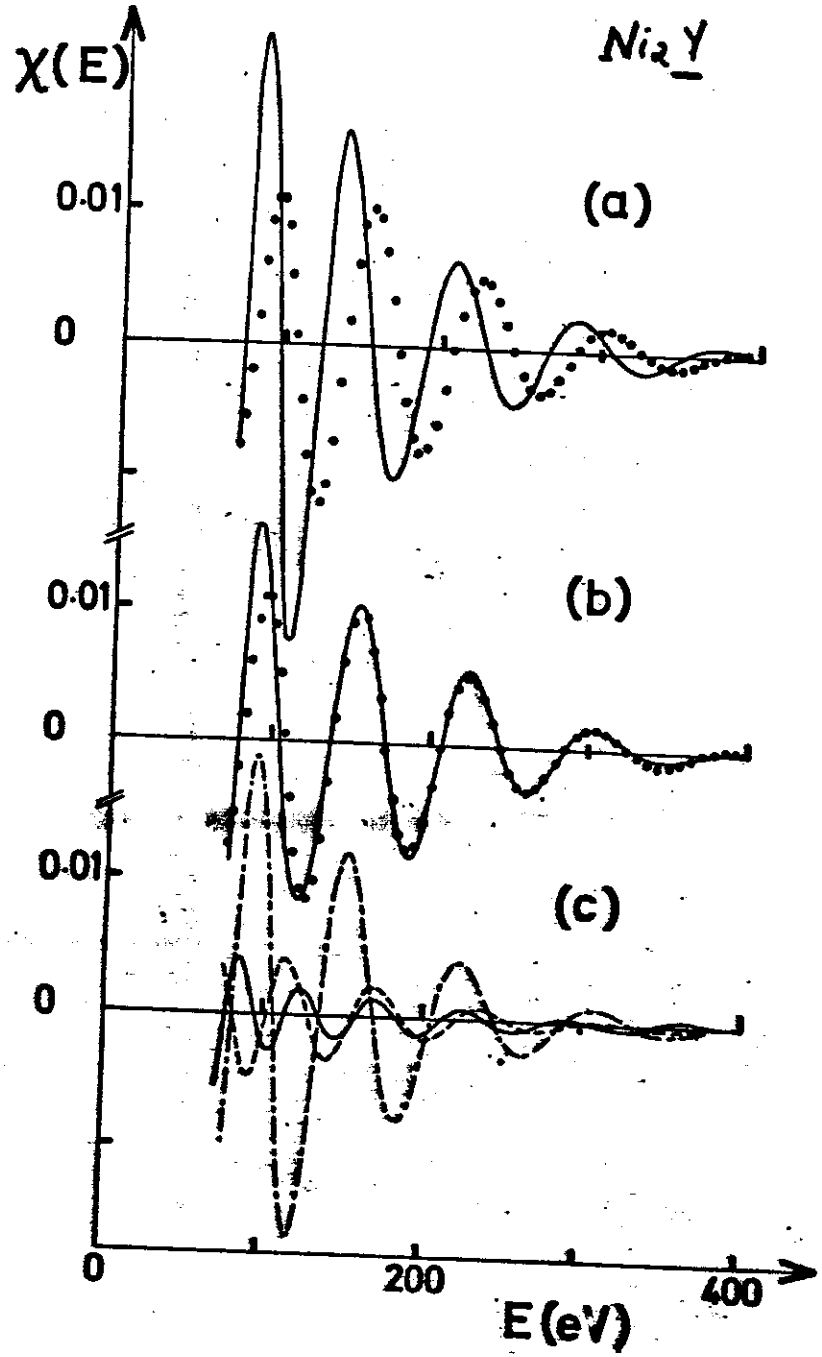
1- Exafs data and Exafs results have to fit other structural results
(X-rays or neutrons)

in X-rays { $k_{min} \sim 1 Å^{-1}$ → large R
{ $k_{max} \sim 10 Å^{-1}$ → $\delta R \sim .1 Å$.

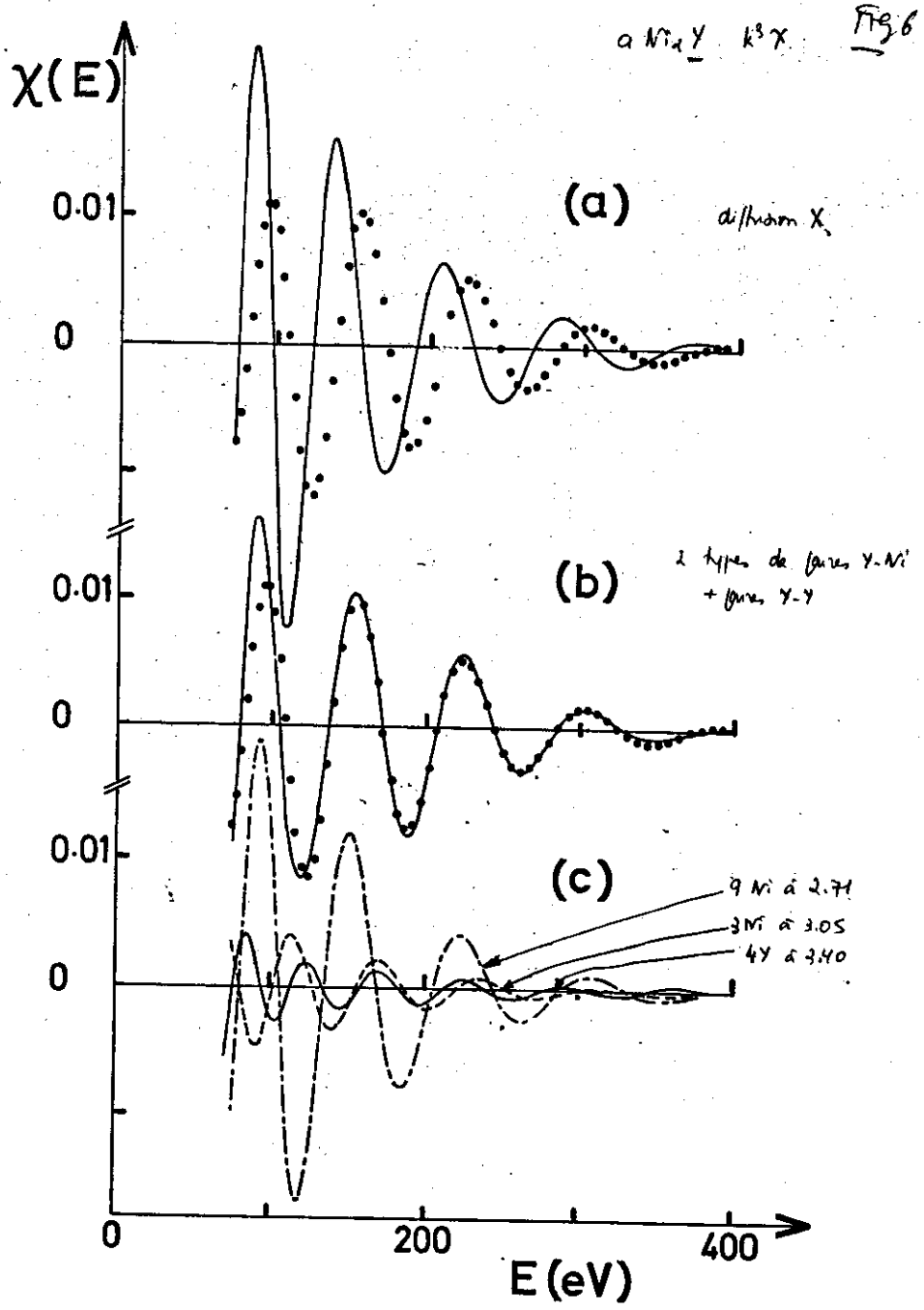
2- Expand g(R) Eisenberger Brown.
ex. Co.B (H. Dubois)

3- Use a model for g(R)

- two-shells gaussian RDF
ex Ni Y (A. Sadoc et al)
- $g(R) = A(R-R_0)^2 \exp[-B(R-R_0)]$ $R \geq R_0$
$= 0$ $R < R_0$
ex. Zn liquid (Crozier Seary)
- $g(R) = \exp -|R-R_1|/\sigma_1$ $R \geq R_1$
$= 0$ $R < R_1$
ex: Co P



a Ni_2Y $k^3\chi$ Fig 6



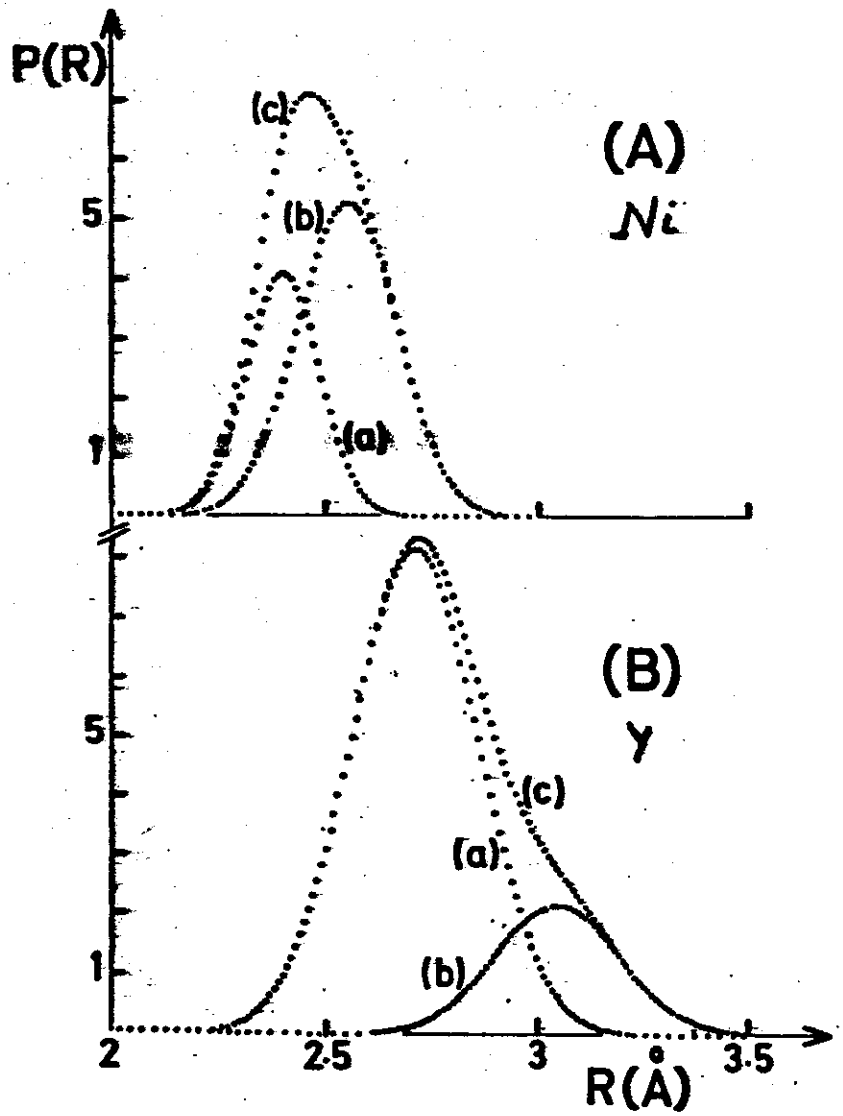
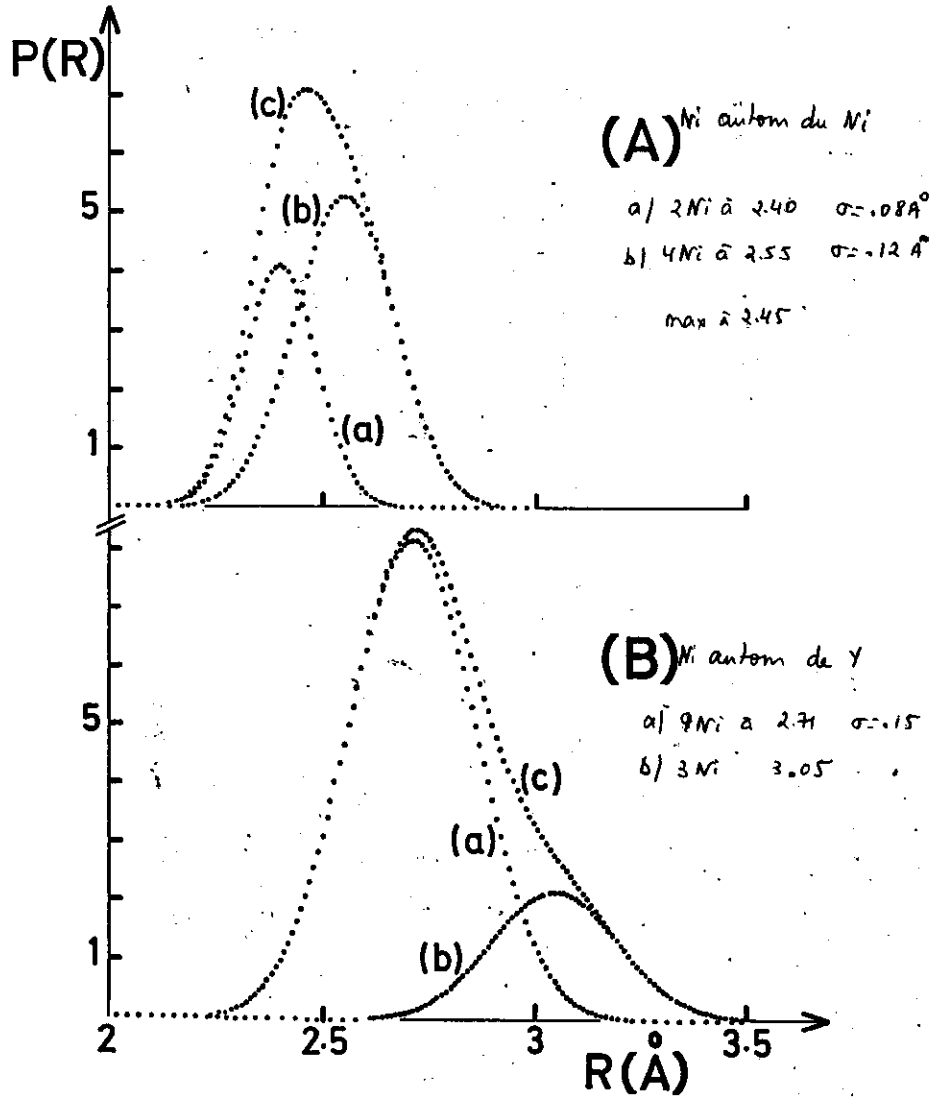


Fig 8

Ni2Y



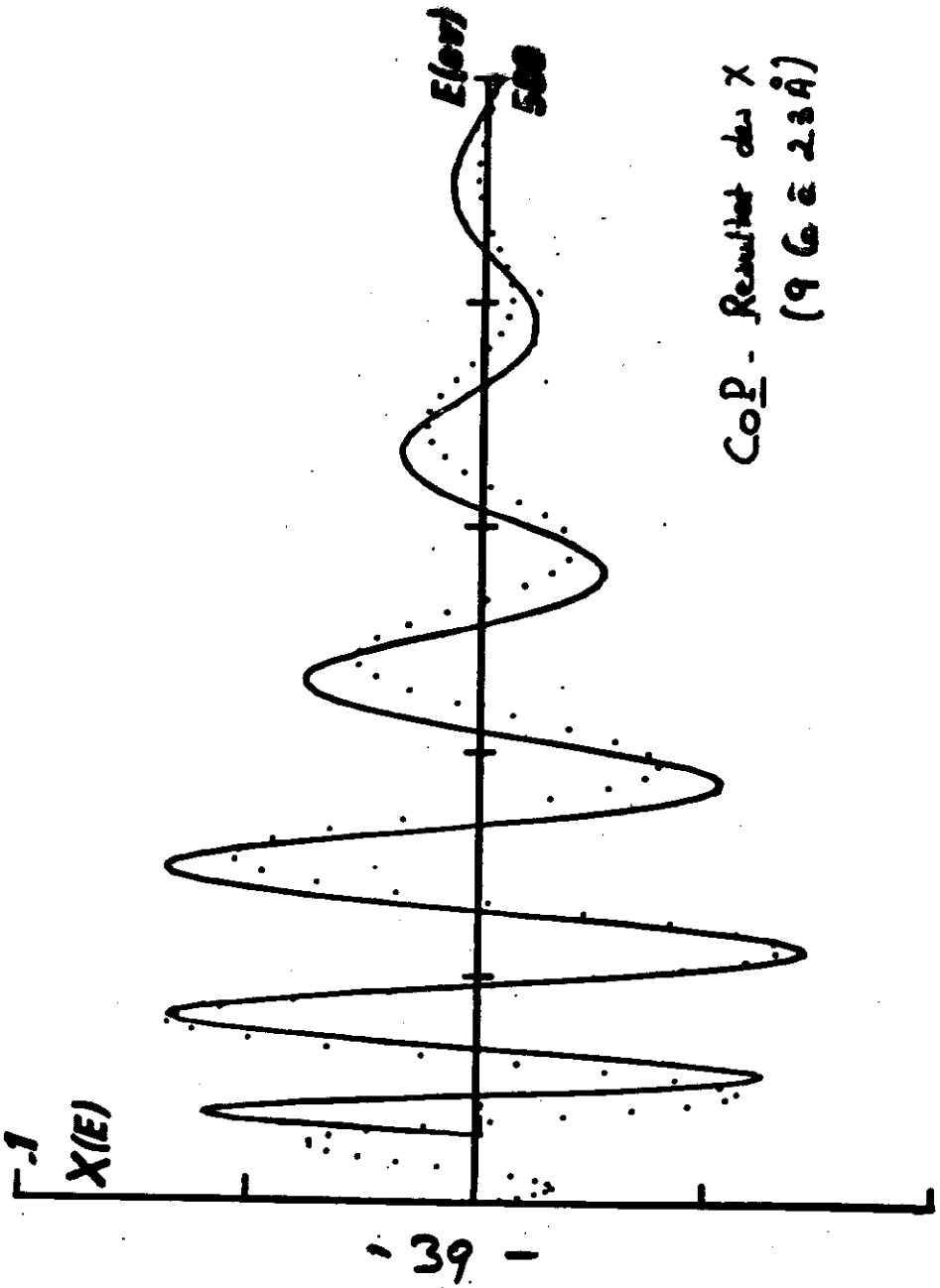
Ni_2Y

Distances

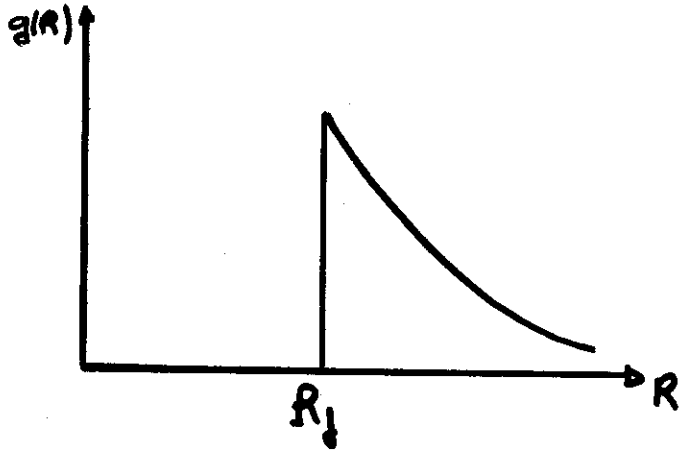
	Amorphous		Crystal
	Exafs	X-scattering	
Ni-Ni	2.40 2.55	2.48	2.54
Ni-Y	2.71 3.05	2.80	2.98
Y-Y	3.40	3.40	3.11

Coordination Numbers (statistical model)

Ni-Ni	2 4	5.5 (8)	6
Ni-Y	4.5 1.5	5 (4)	6
Y-Ni	9 3	12 (10.7)	12
Y-Y	4	4 (5.3)	4



Co P - Resultat des X
(9 Couches à 2,34 Å)

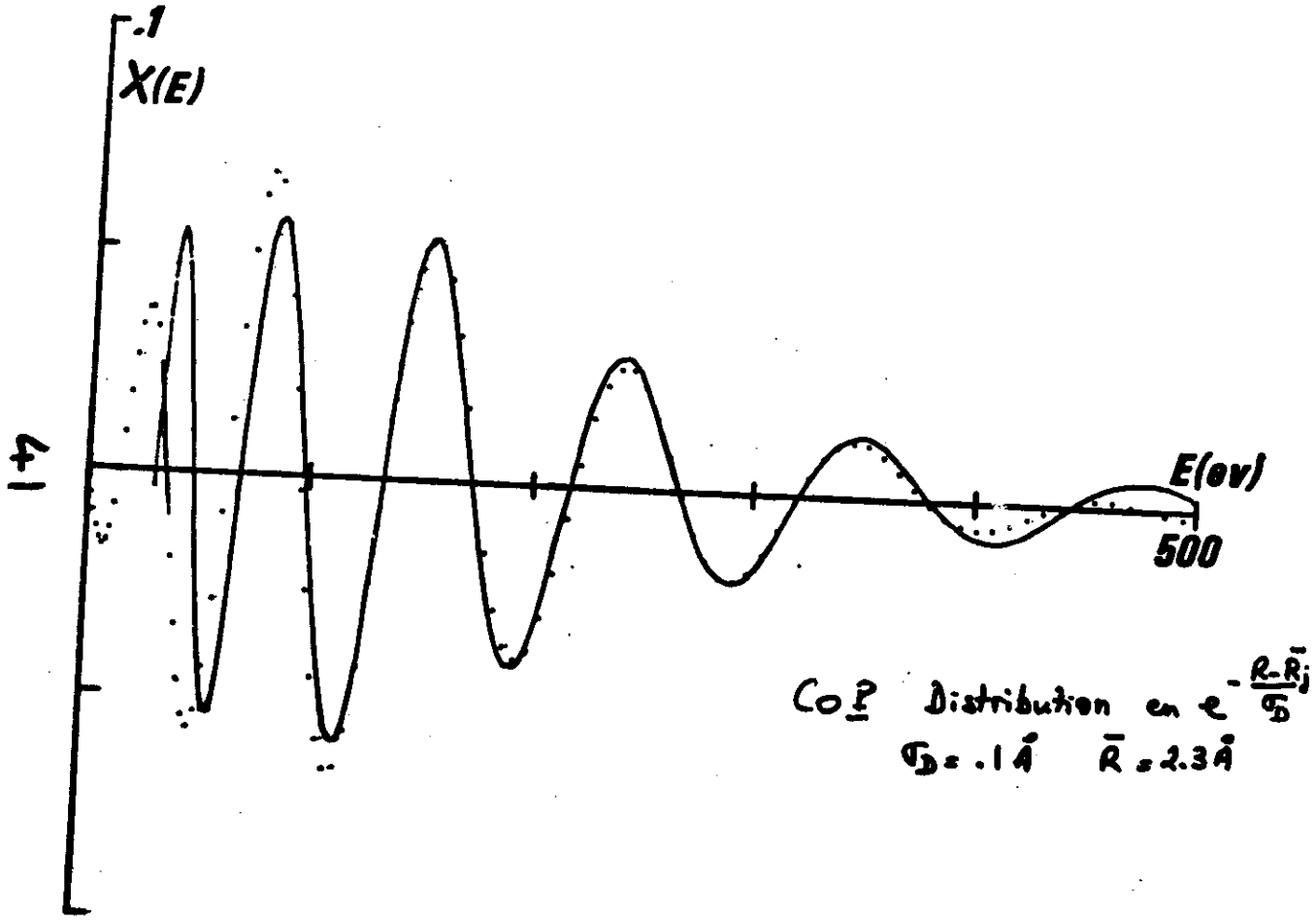


$$g(R) = 0 \qquad R < R_1$$

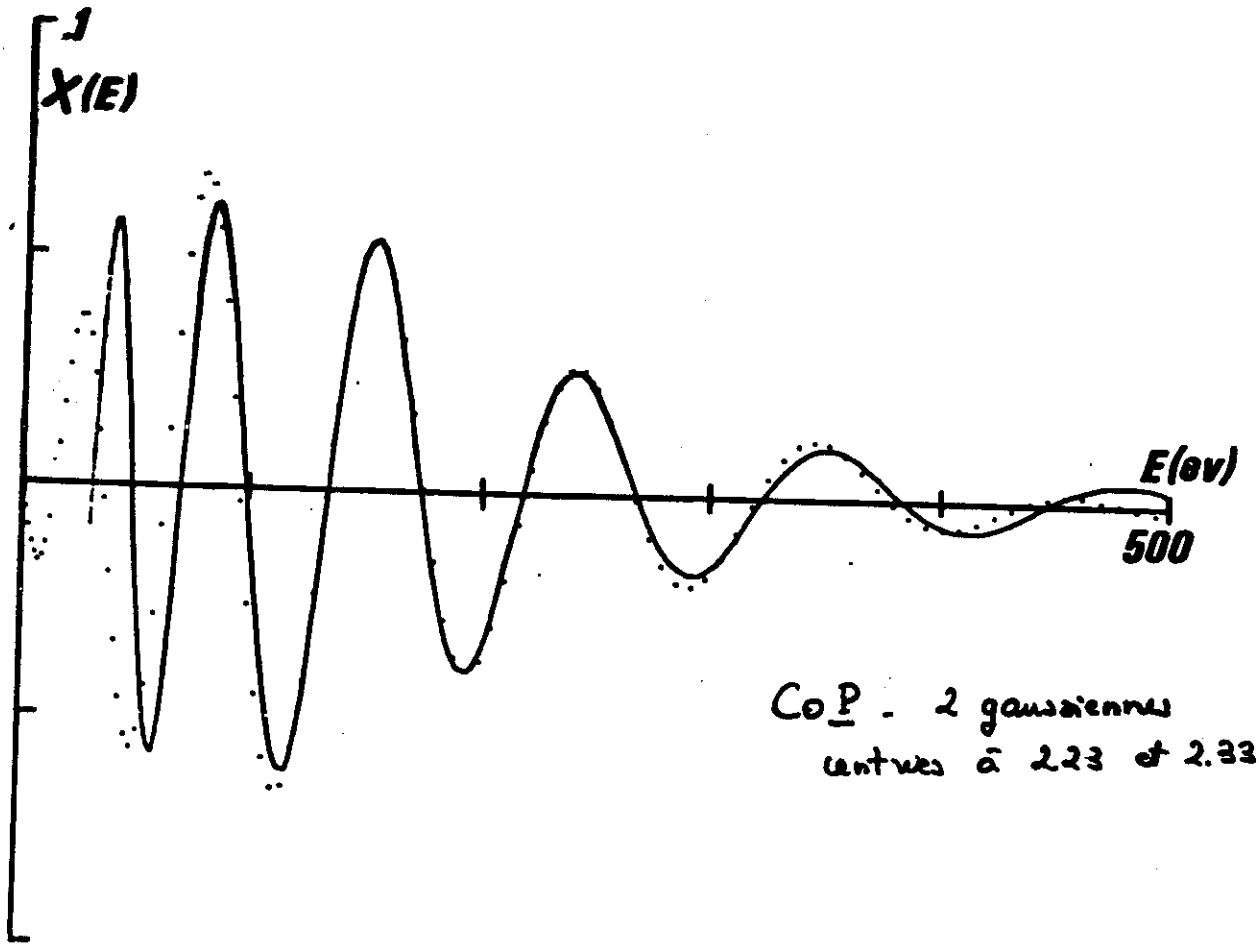
$$g(R) = \exp\left[-\left(\frac{R - R_1}{\sigma_D}\right)\right] \qquad R > R_1$$

$$\overline{R} = R_1 + \sigma_D$$

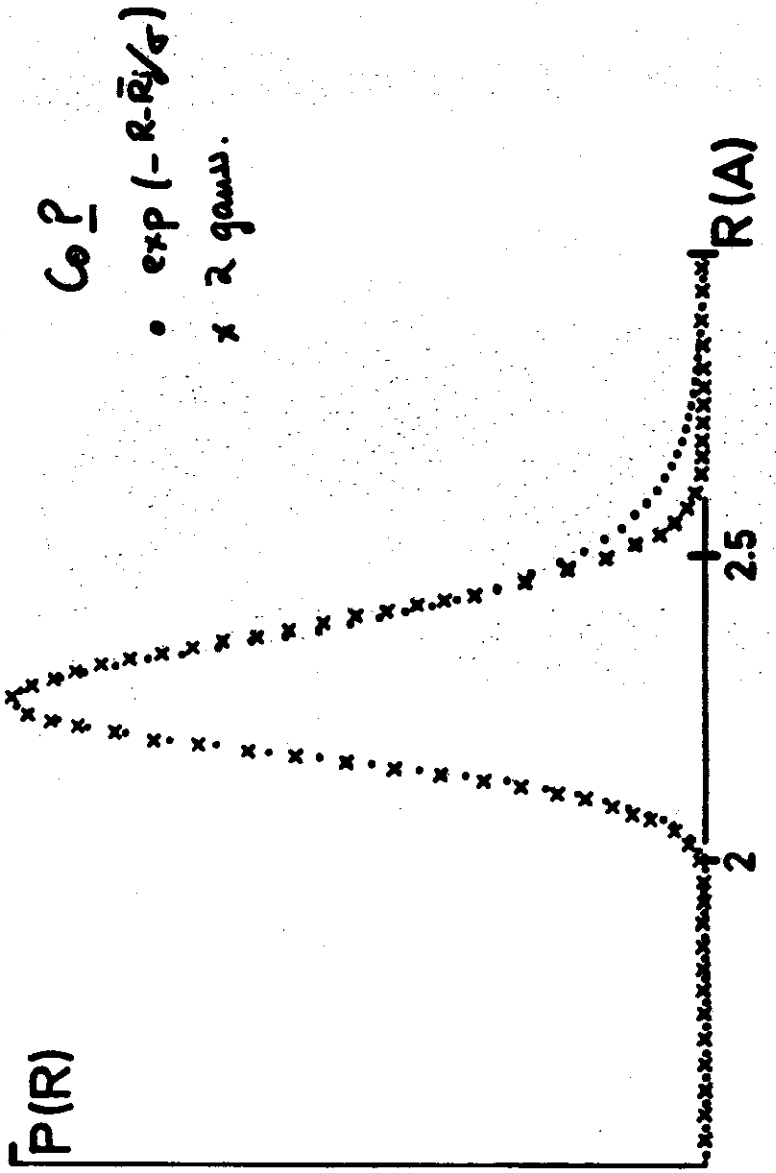
(Haensel et al.)



Co P Distribution en $e^{-\frac{R-\bar{R}_j}{\sigma_D}}$
$\sigma_D = .1\,\text{Å}$ $\bar{R} = 2.3\,\text{Å}$



Co P . 2 gaussiennes
centrées à 2.23 et 2.33 Å



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