



H4.SMR/1013-39

**SCHOOL ON THE USE OF SYNCHROTRON RADIATION  
IN SCIENCE AND TECHNOLOGY:  
*"John Fuggle Memorial"***

**3 November - 5 December 1997**

***Miramare - Trieste, Italy***

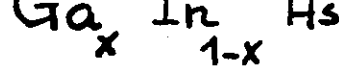
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***EXAFS - Part II***

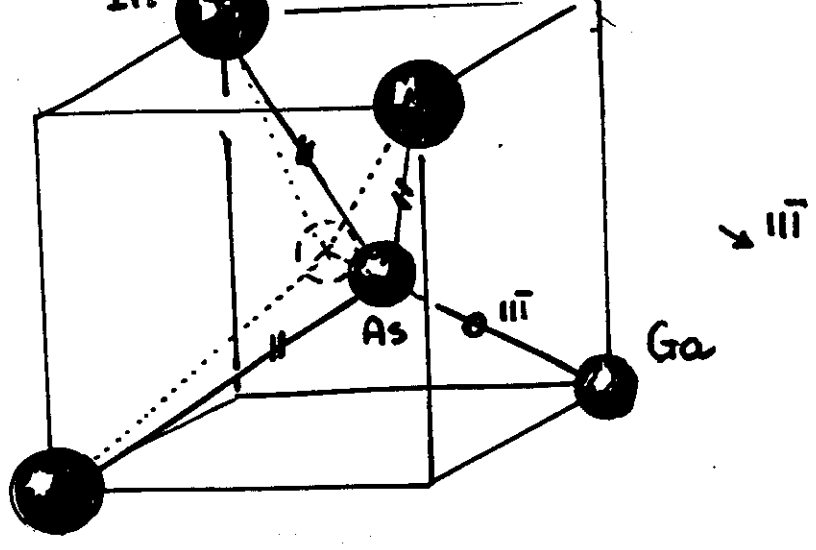
**A. Fontaine  
Laboratoire Louis Neel  
Grenoble, France**

# ILLUSTRATIONS

- 1. VIRTUAL CRYSTAL  
    & REAL CRYSTAL  
    as given by X-Ray Diff  
    as given by  
    the COMPLEMENTARY.  
    CONTRIBUTION of  
    EXAFS
- 2. IMPURITY in ALLOY  
    LOCAL Elastic CORE effect  
    & VEGARD LAW
- 3. CLUSTERING in ALLOY  
    in RARE GAS MATRIX
- 4. POLARISATION & SENSITIVITY TO ANISOTROPY  
    ORIENTATION of CHEMICAL BOND on SURFACE  
    SINGLE CRYSTAL INVESTIGATION
- 5. NEAR EDGE SPECTRA IN RARE EARTH.
- 6. SIMULATION of XANES for ZnS.



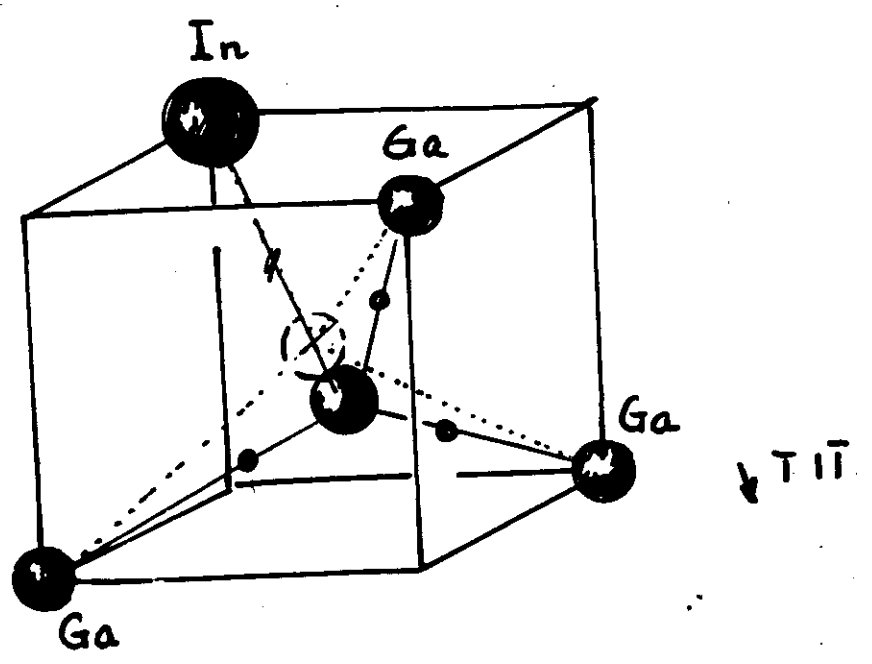
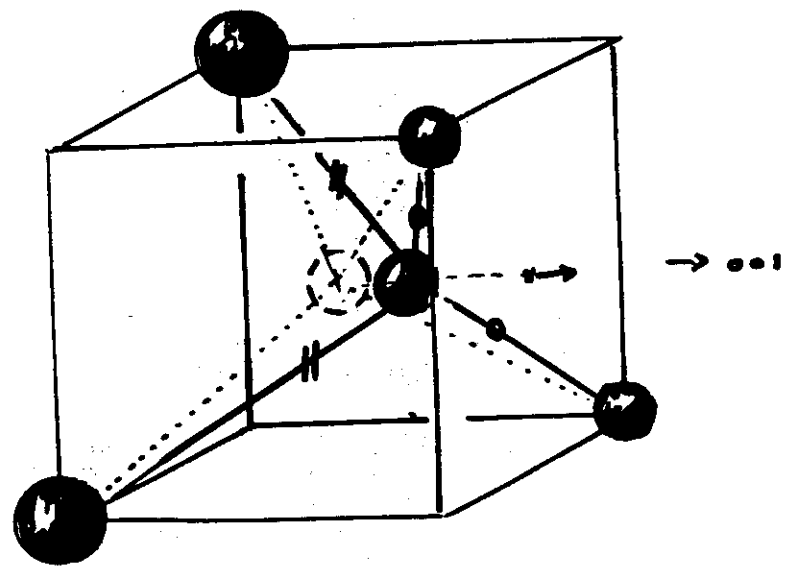
"x" to tune  
 1) lattice parameter  
 2) band gap



• DIFFRACTION  
 → AVERAGE CRYSTAL (VIRTUAL)

• EXAFS  
 → LOCAL ORDER  
 SELECTIVE PROBE

5 "environments"

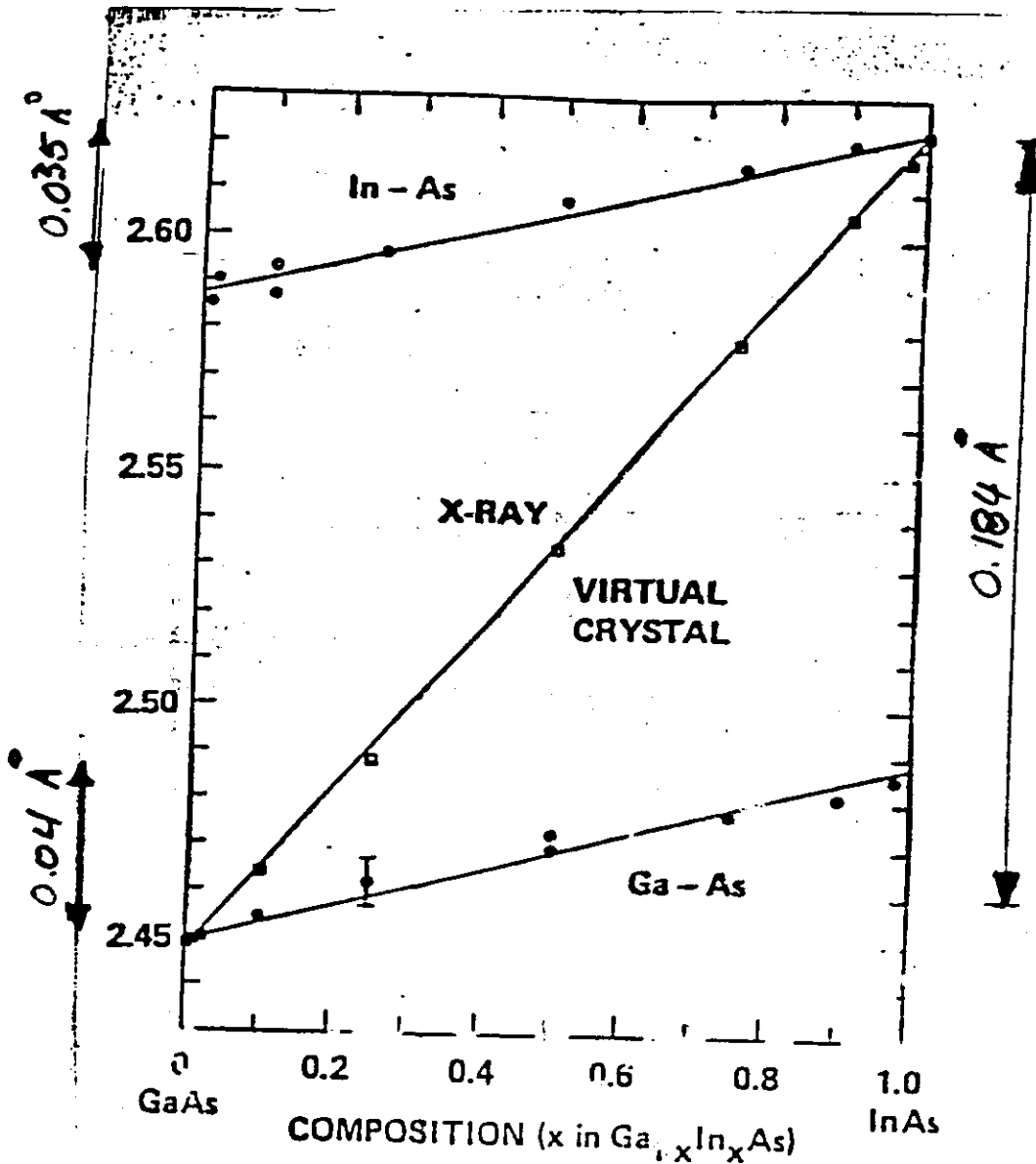


PSEUDO BINARY ALLOY.

# Local Structure of Pseudobinary Alloys

J.B. Boyce and J.C. Mikkelsen, Jr.

Xerox Palo Alto Research Center, 3333 Coyote Hill Road  
Palo Alto, CA 94304, USA



$$\frac{\delta b}{\delta a} \text{ Ga-As}$$

lattice parameter

$$\propto \frac{1}{\text{Bulk modulus}}$$

IONIC  
COVALENT

$\frac{1}{6}$

soft

J.B. Boyce and J.C. Mikkelsen, Jr.

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Palo Alto, CA 94304, USA

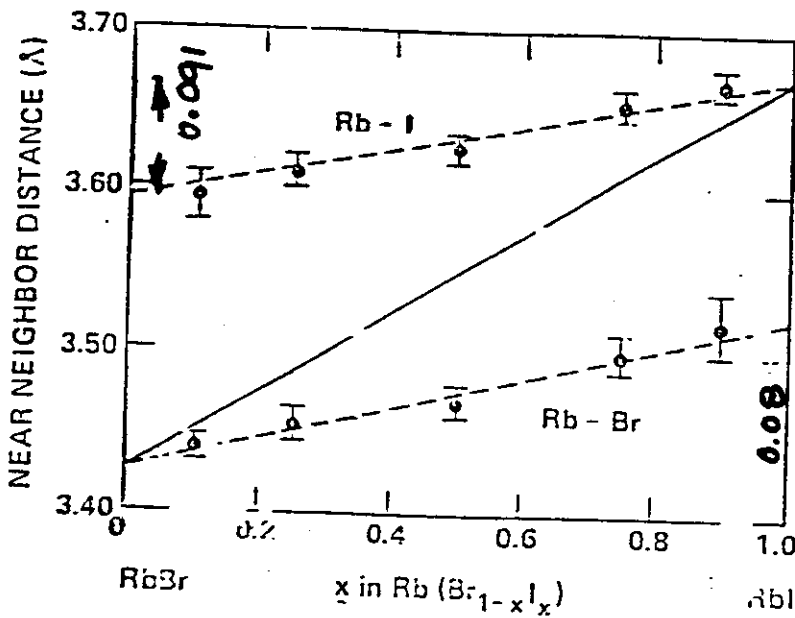
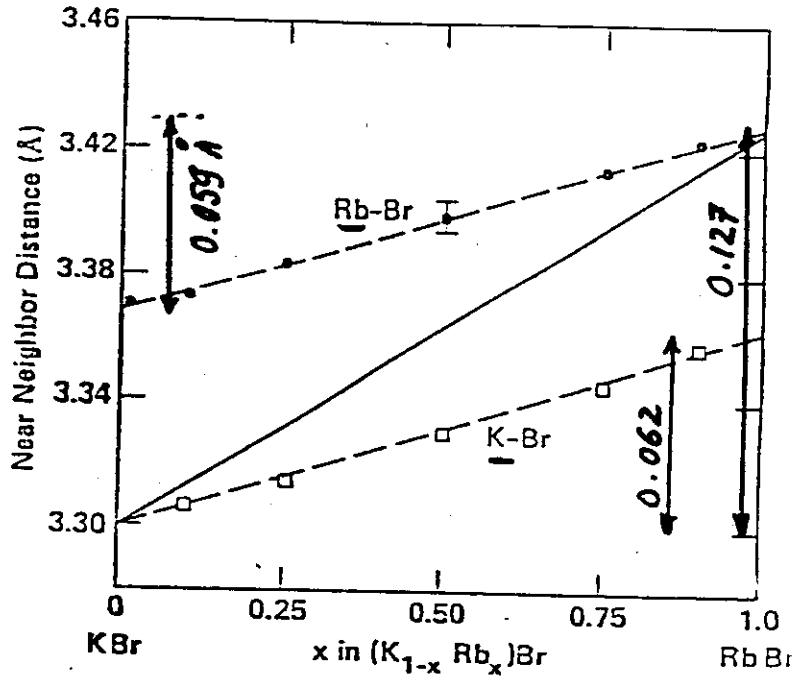
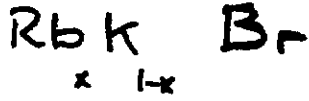
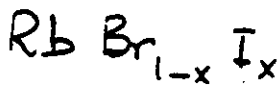


Fig. 3. Rb-Br and Rb-I first neighbor distances as a function of composition in  $Rb(Br_{1-x}I_x)$ .

3 edges



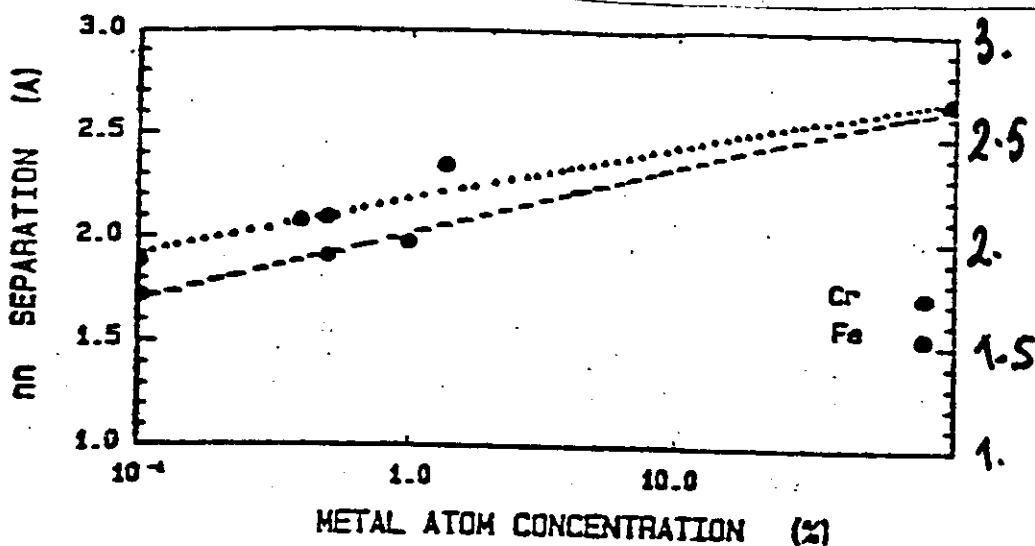
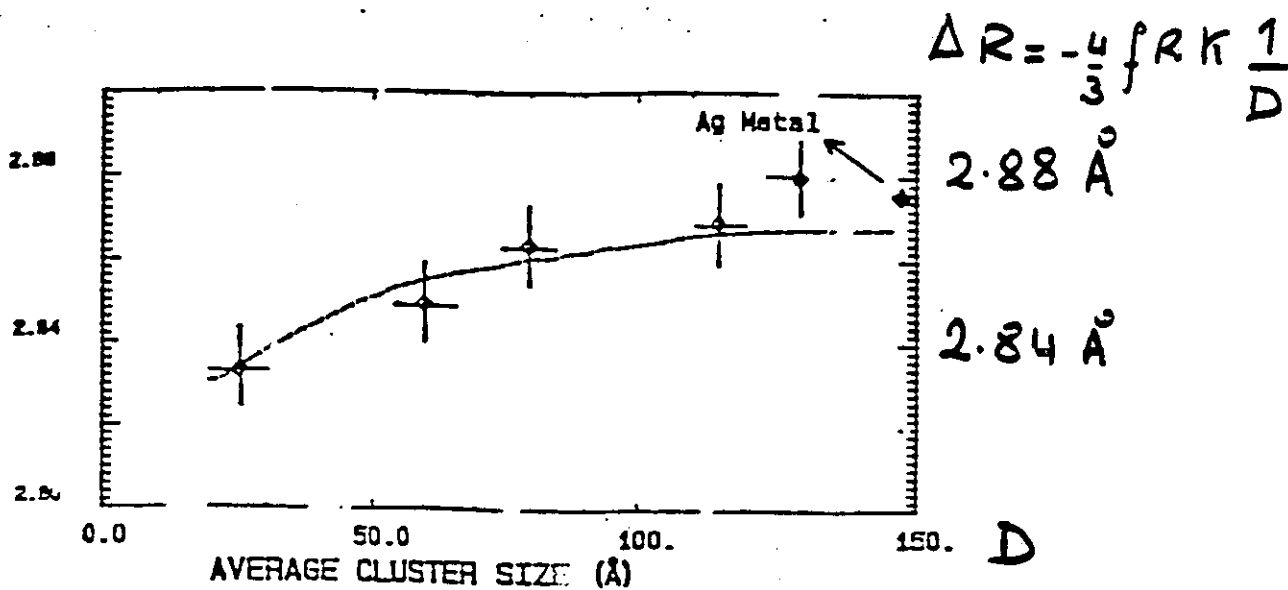
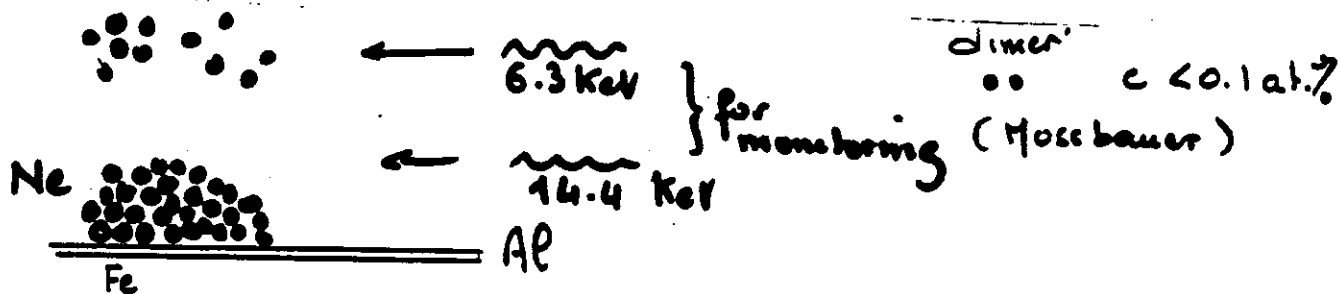
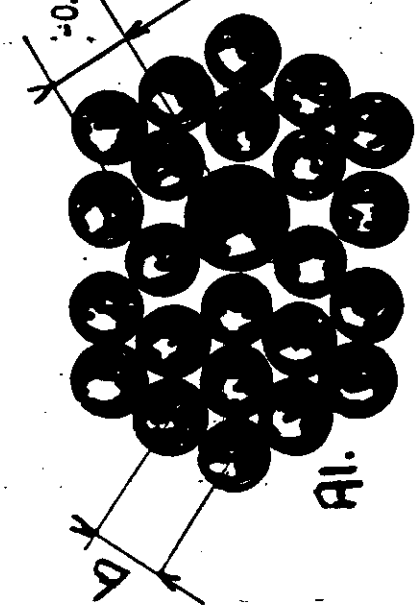
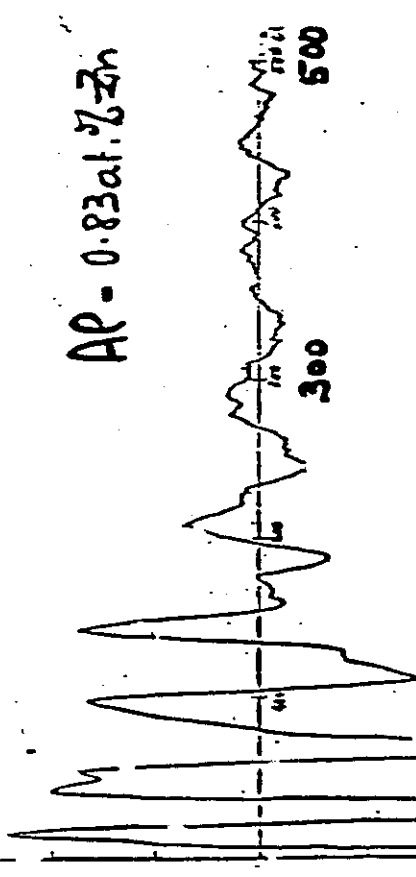


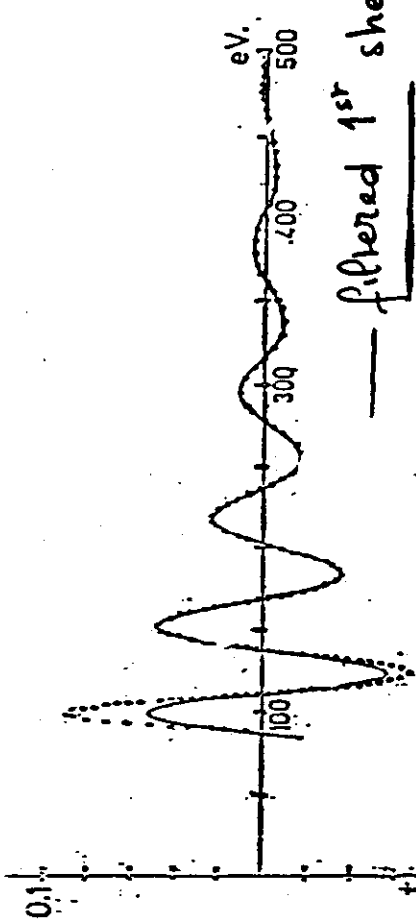
Fig. 1. nn separation vs. metal atom concentration



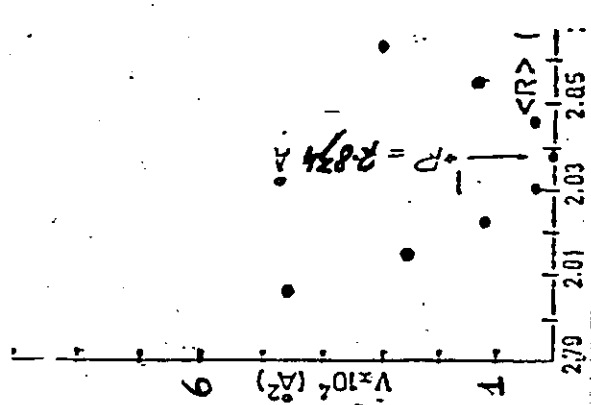
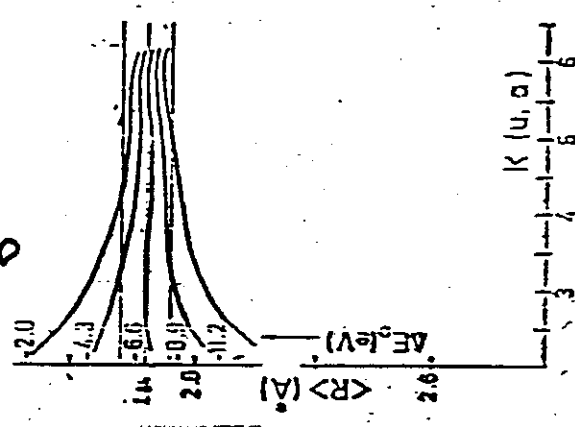
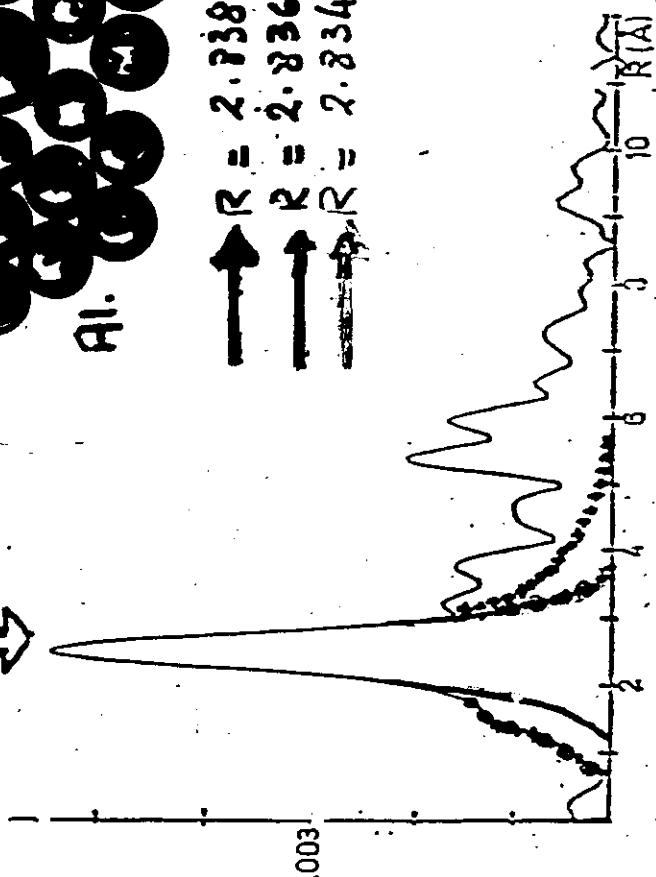
g. 3. nn separation vs. cluster size for Ag in Ar.



- ↑ R = 2.738 Å
- ↑ R = 2.836 Å
- ↑ R = 2.834 Å



... 12 Al 2.835 Å



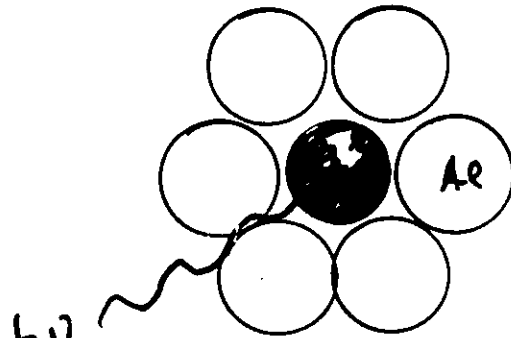
MIMAUT, FONTAINE, LAGRÈGE, RAOUX, SAGOC, SPANJAARD

J. of Phys. Met. F. 11 (13N) 1981

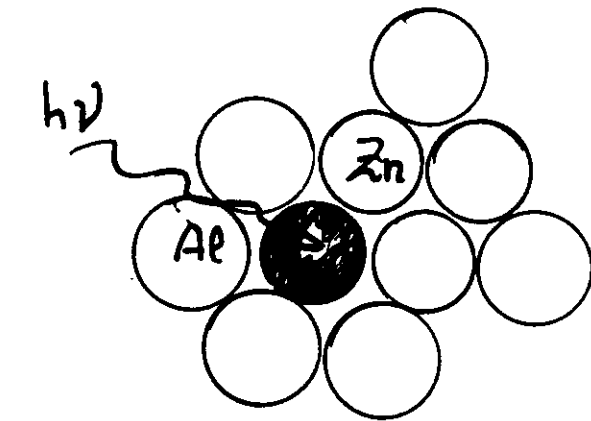
# ANNEALING of Al-Zn cat% alloys

$h\nu$   
Zn-ked<sub>c</sub>

Metastable  
Solid  
Solution.



Guinier-Preston  
Zones



Small clusters



increasingly  
large clusters

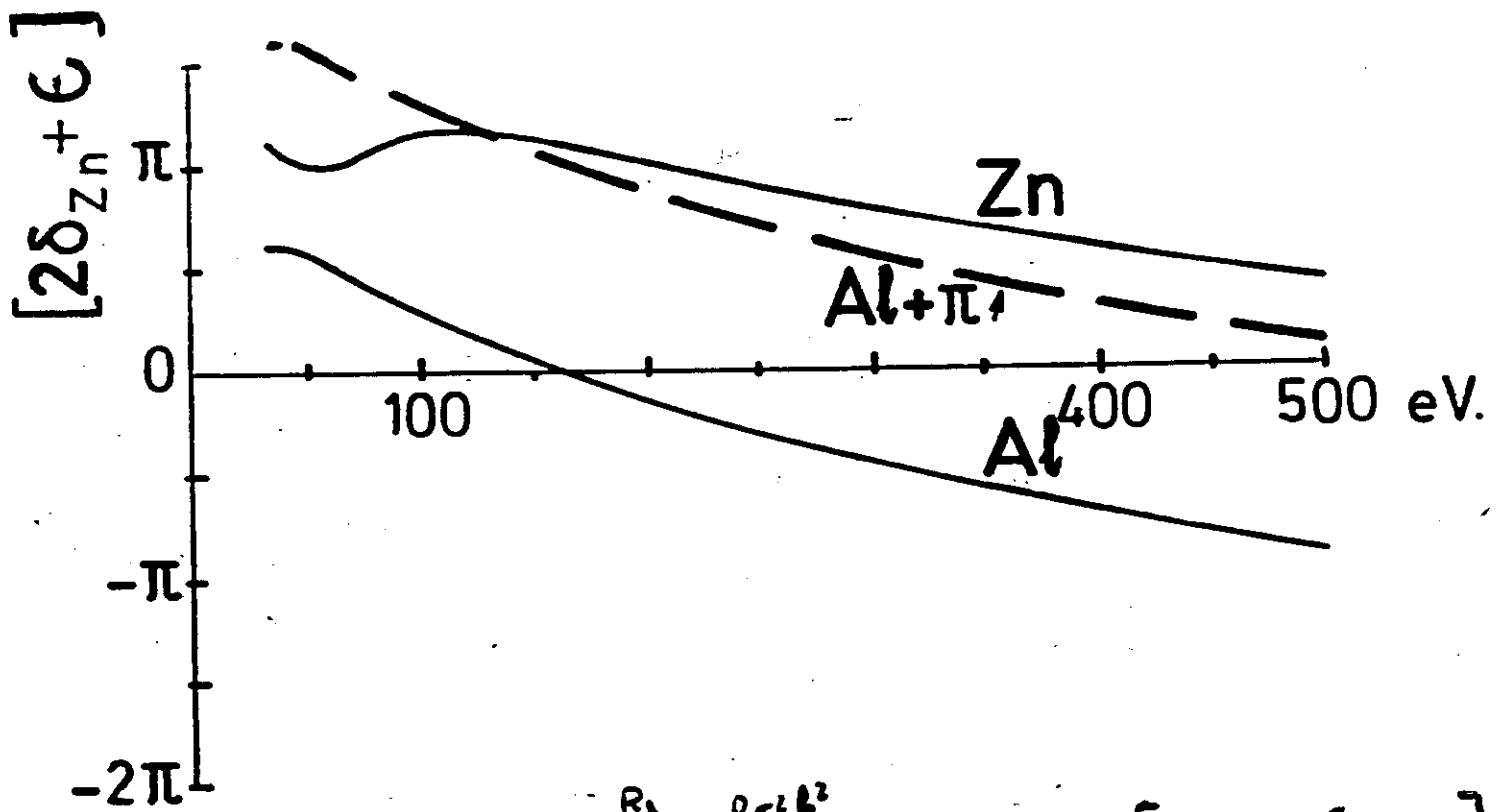
parameters

c

Temperature

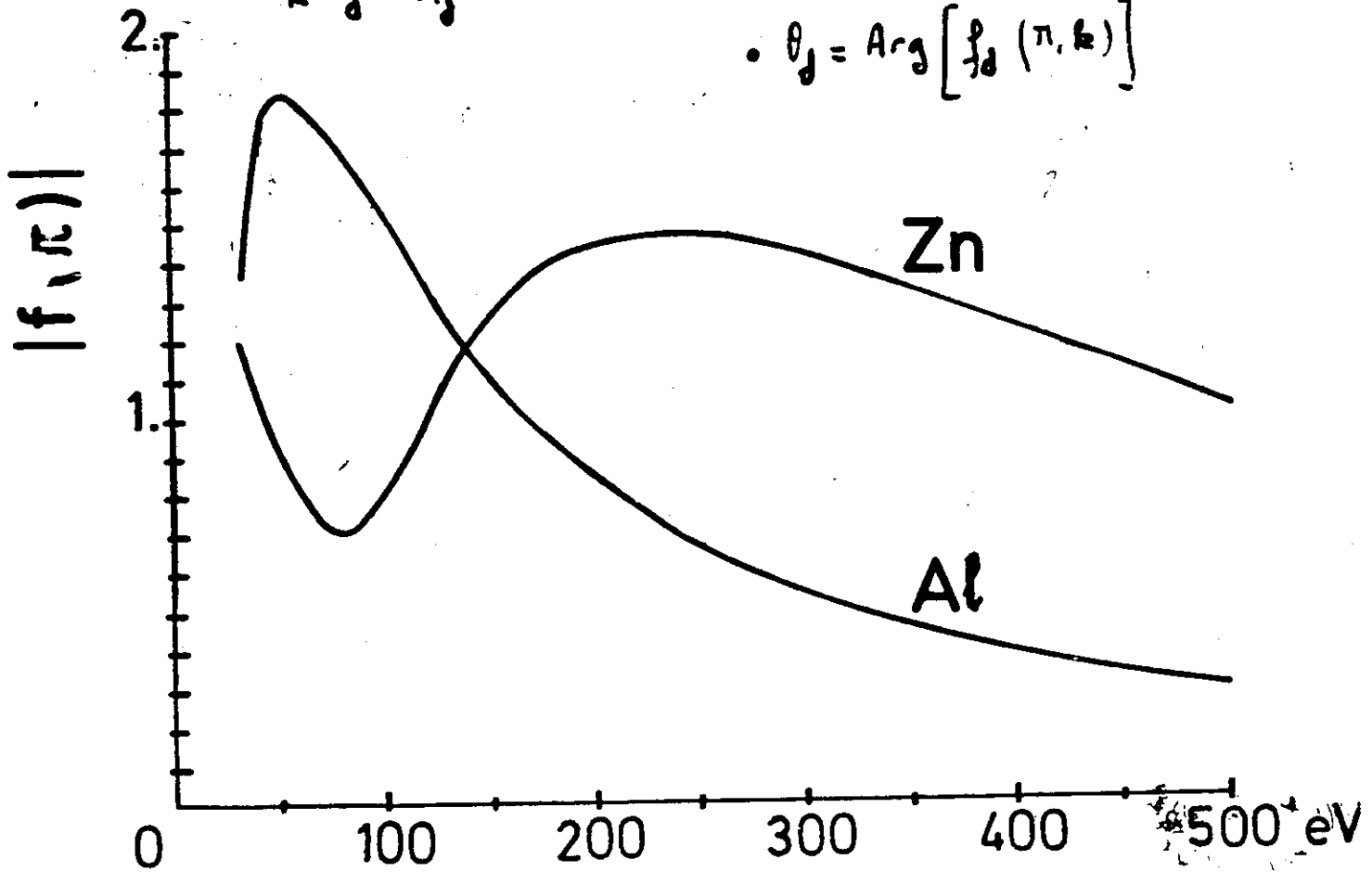
Time

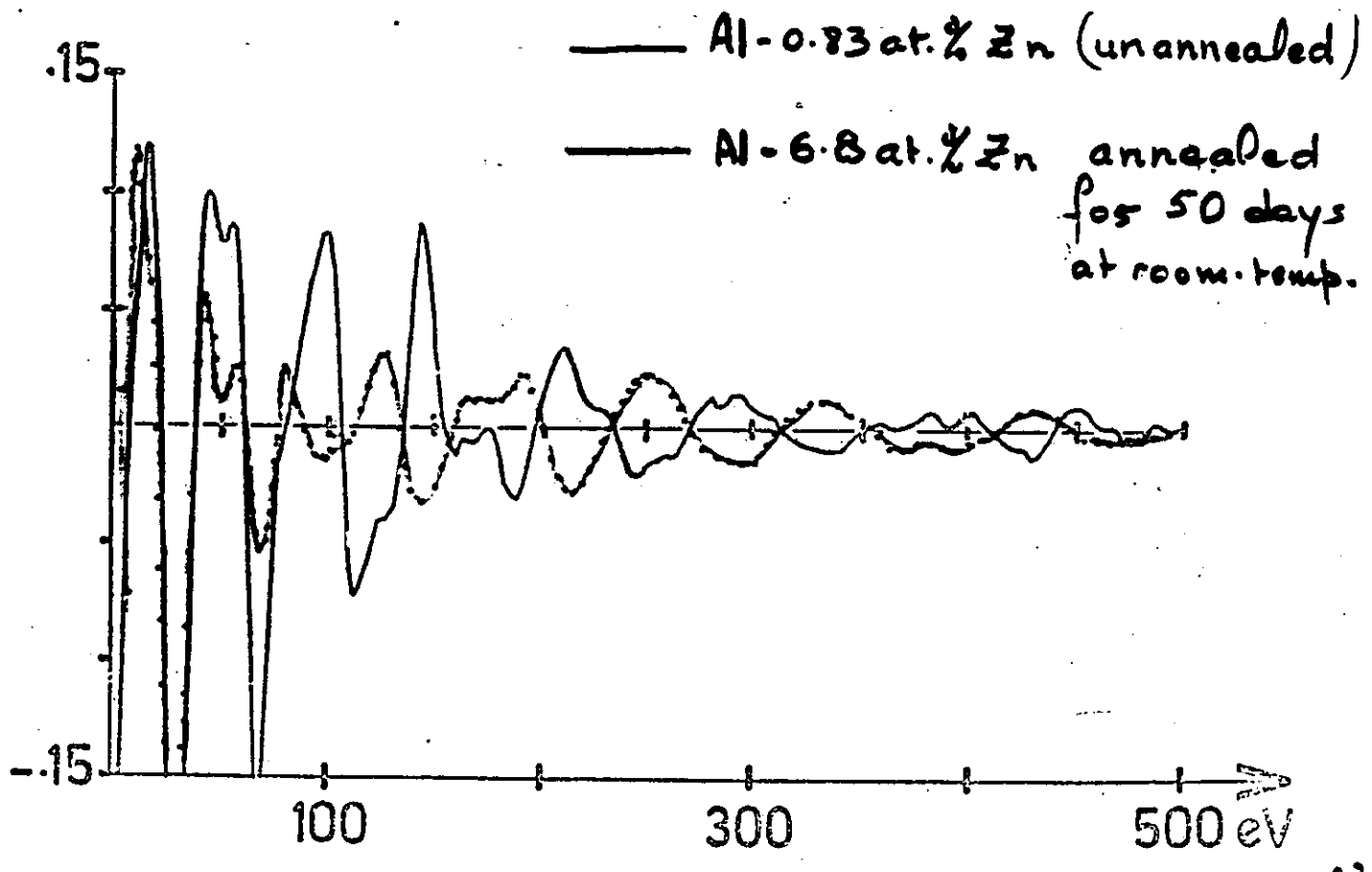
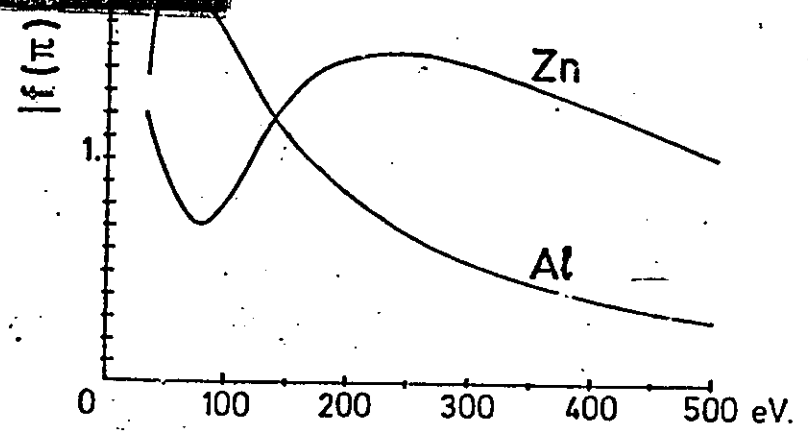
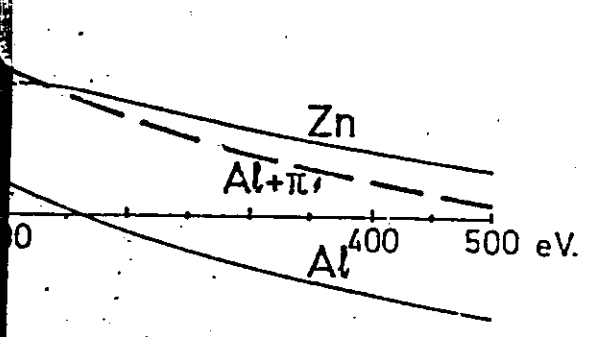
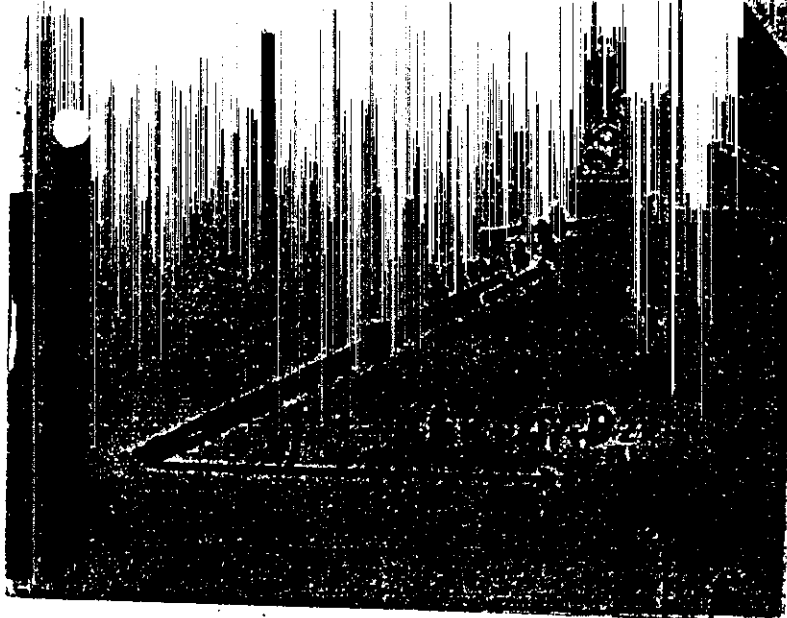




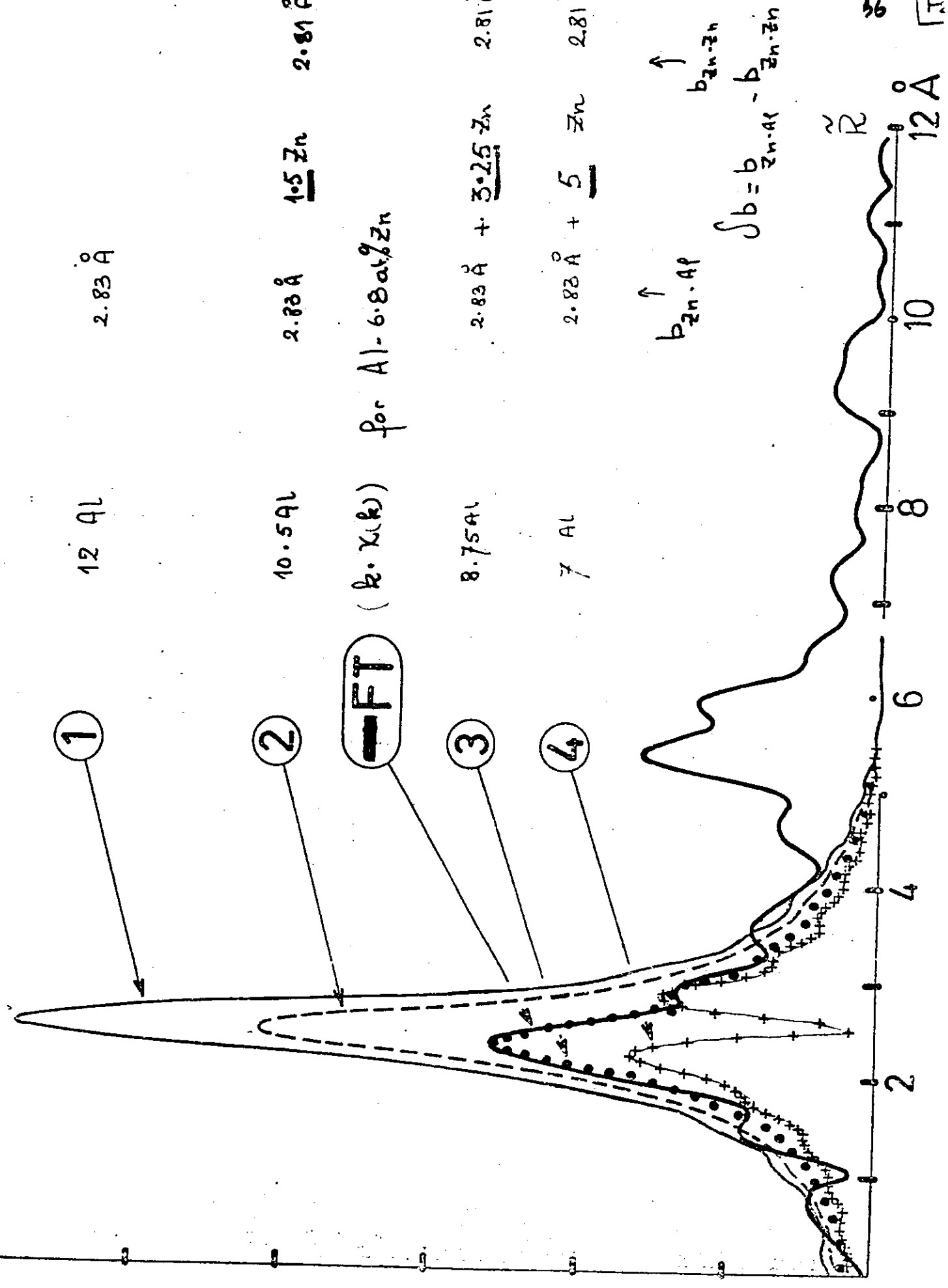
$$\chi(k) = -\frac{1}{2} \sum_d \frac{R_d}{Z_d} e^{-\frac{R_d}{R_d} i k} e^{-2\sigma_d^2 k^2} |f_d(\pi, k)| \sin [2kR_d + 2\delta_d + \theta_d(k)]$$

•  $\theta_d = \text{Arg} [f_d(\pi, k)]$





1.00  
39



12 Al 2.83 Å

10.5 Al 2.83 Å 1.5 Zn 2.81 Å

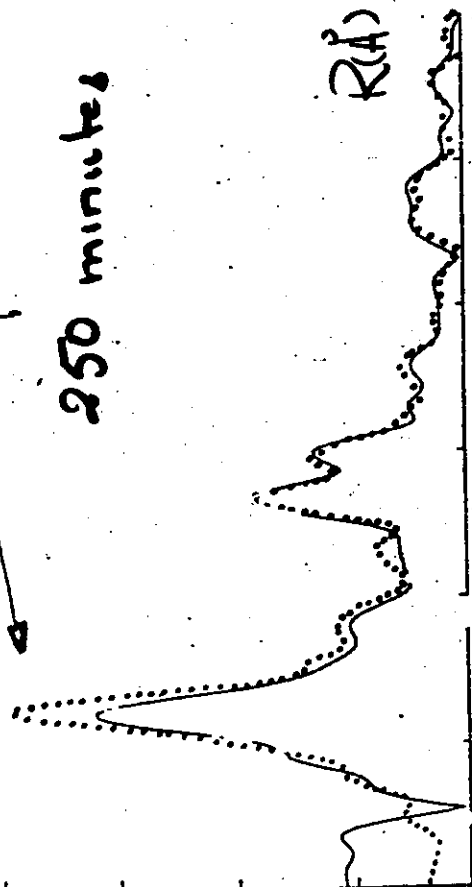
8.75 Al 2.83 Å + 3.25 Zn 2.81 Å

7 Al 2.83 Å + 5 Zn 2.81 Å

AP. 4.4 at. % Zn

AS-quenched.

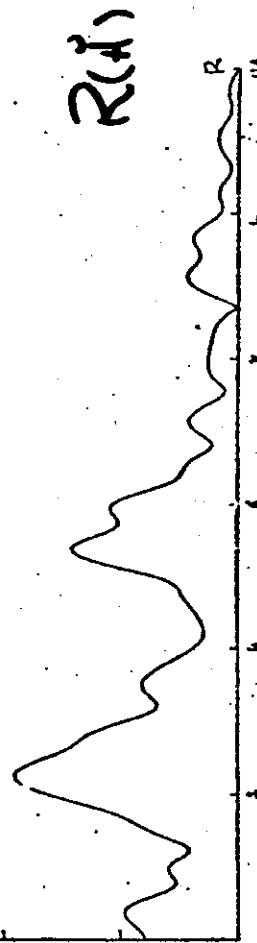
250 minutes



2 4 6 8 10

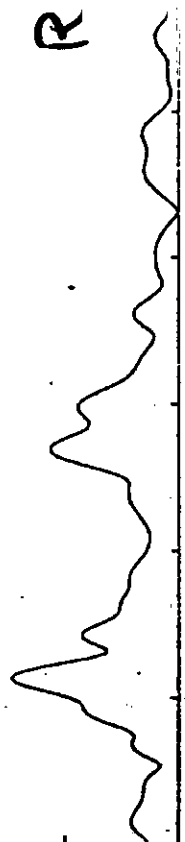
AP. 4.4 at. % Zn

490 minutes | annealed at room temperature for:



cu

720 minutes (12h)

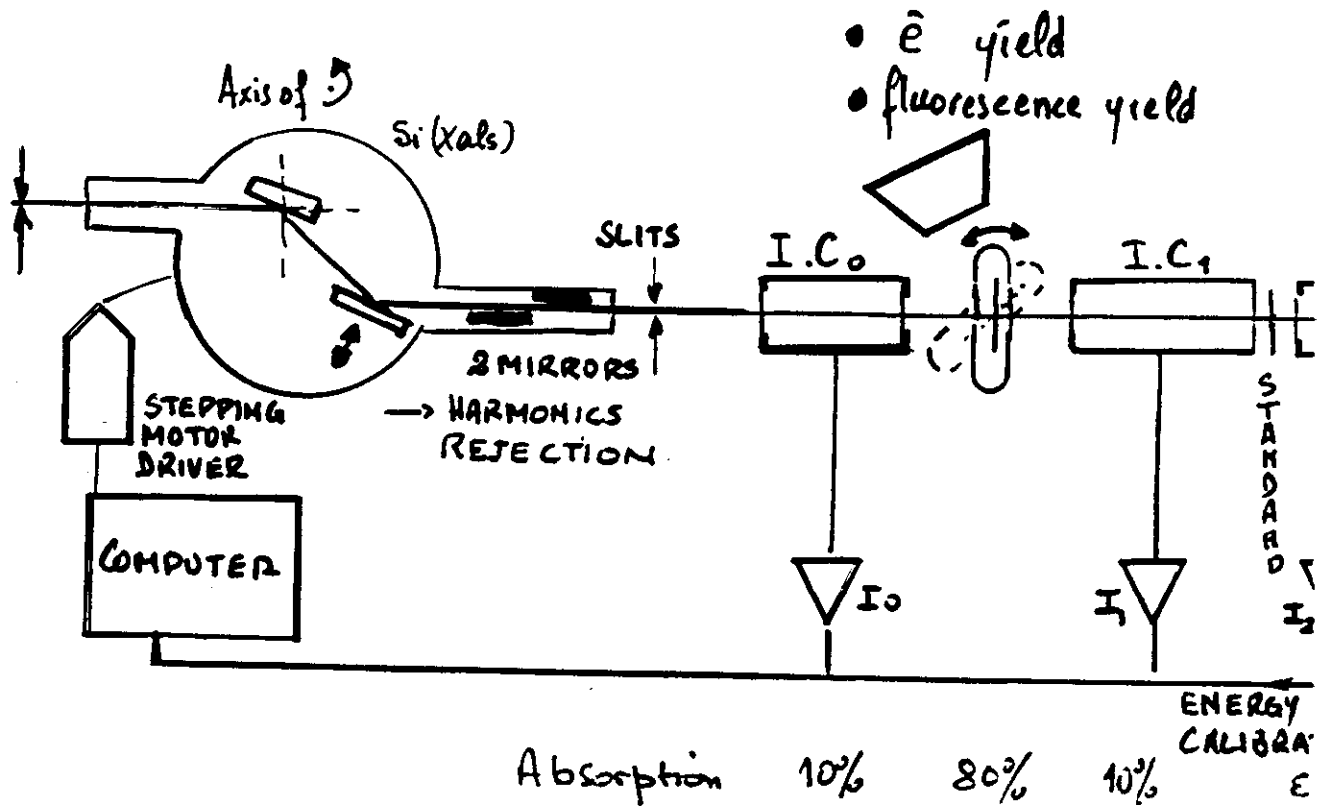


20 days

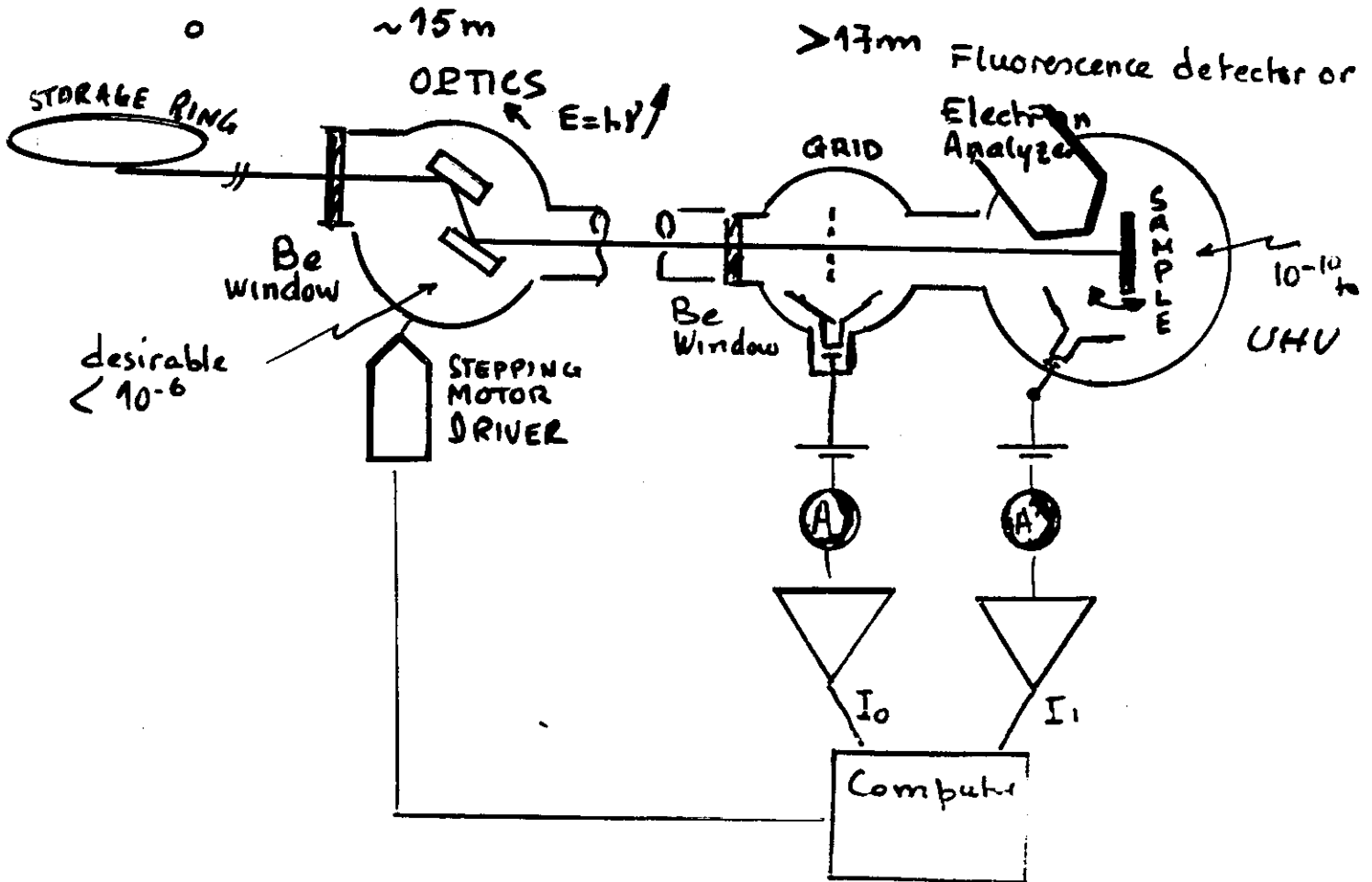


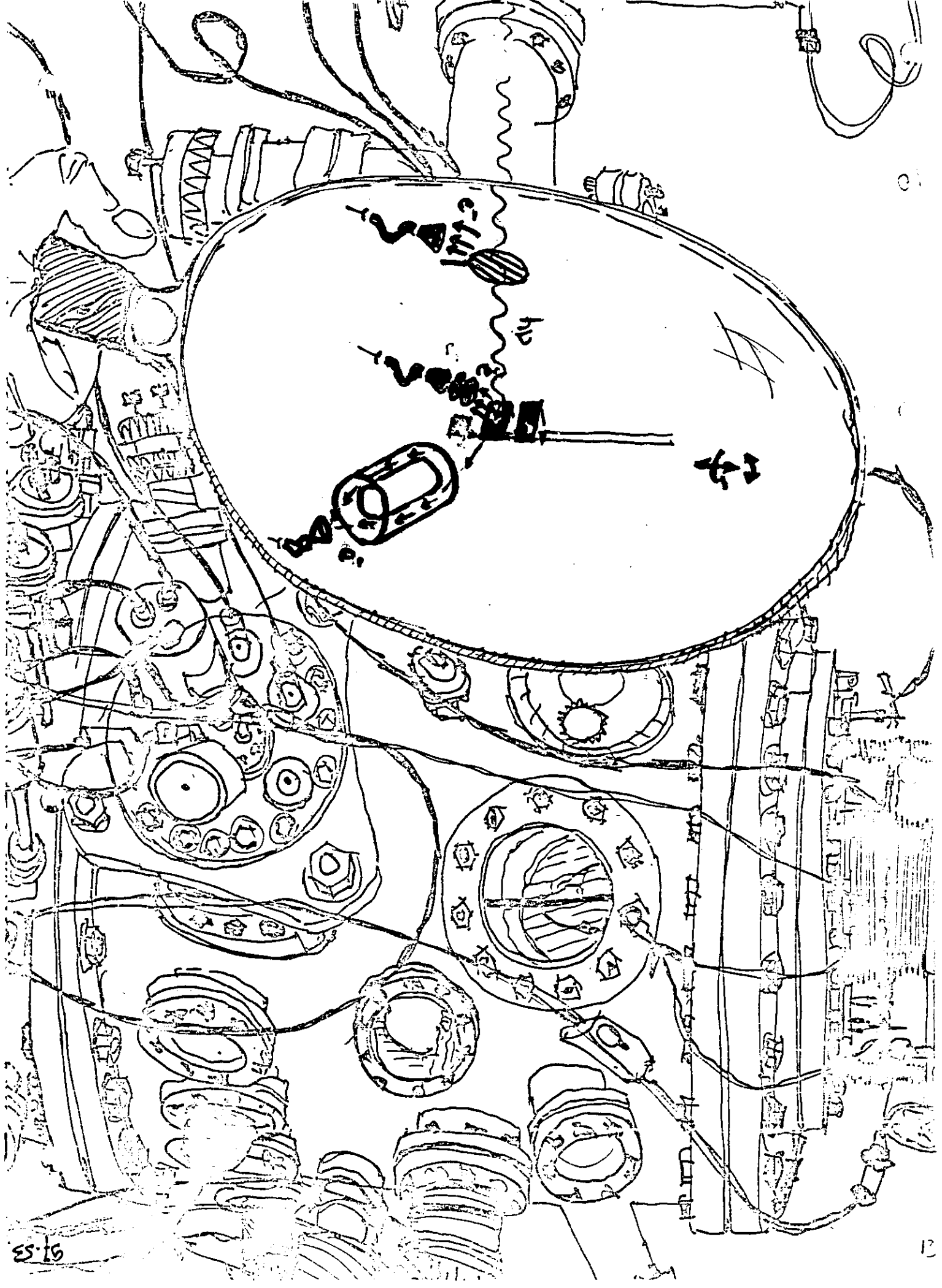
a) Two - CRYSTAL

SET-UP



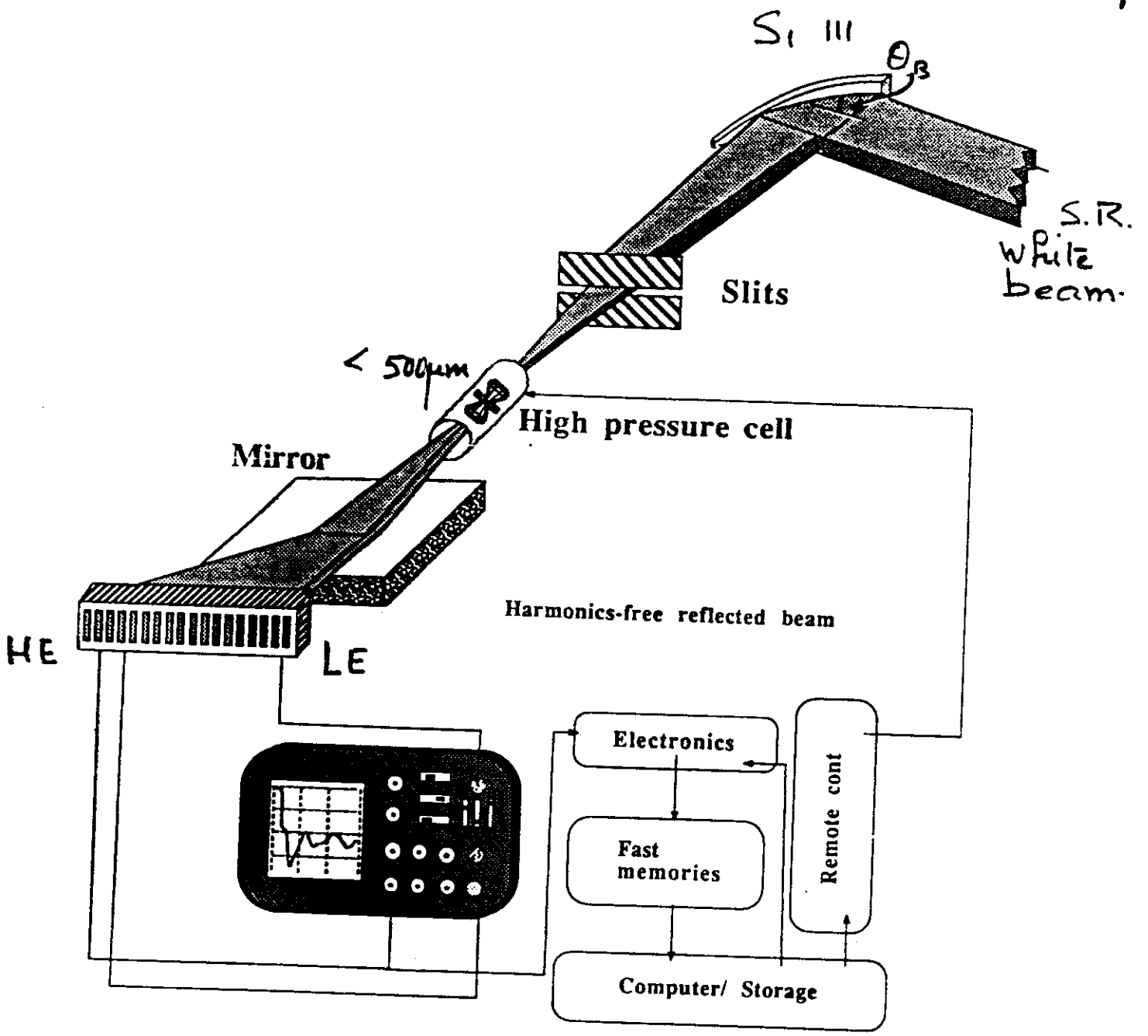
SEXAFS Configuration



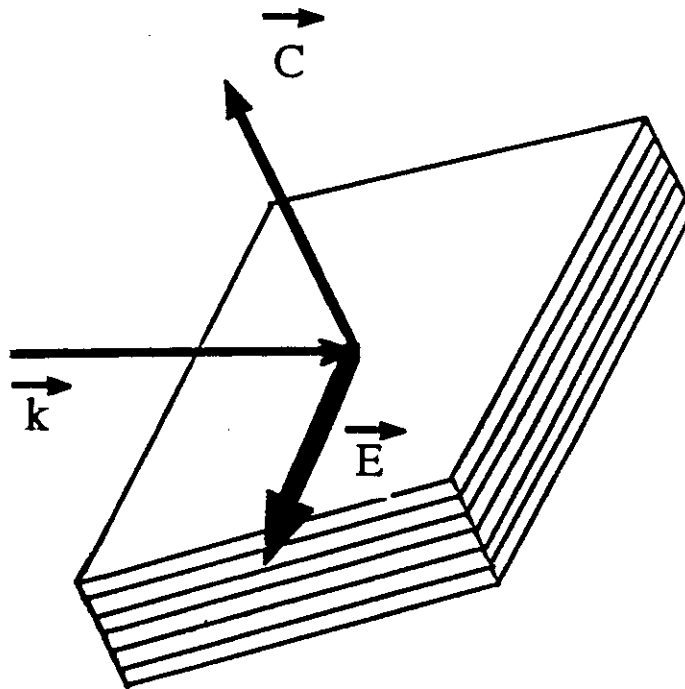


67.53

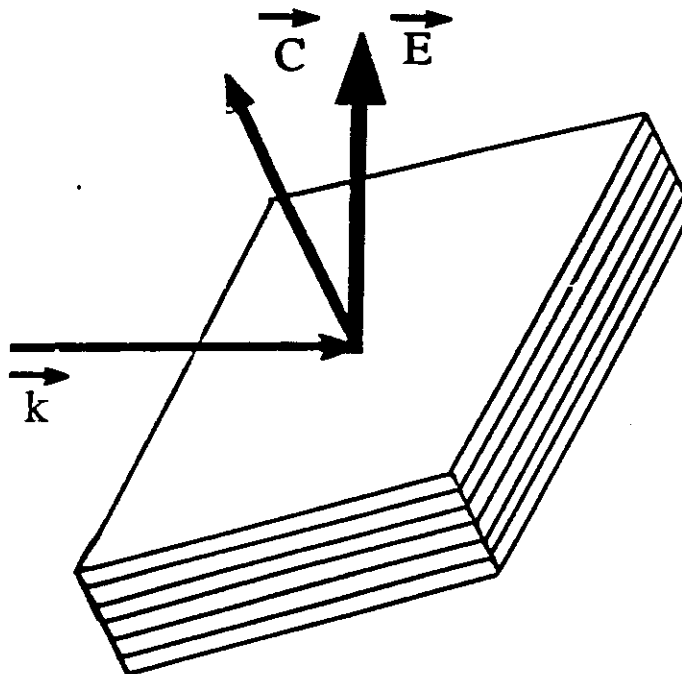
13



Schematic layout of the Energy-Dispersive Spectrometer

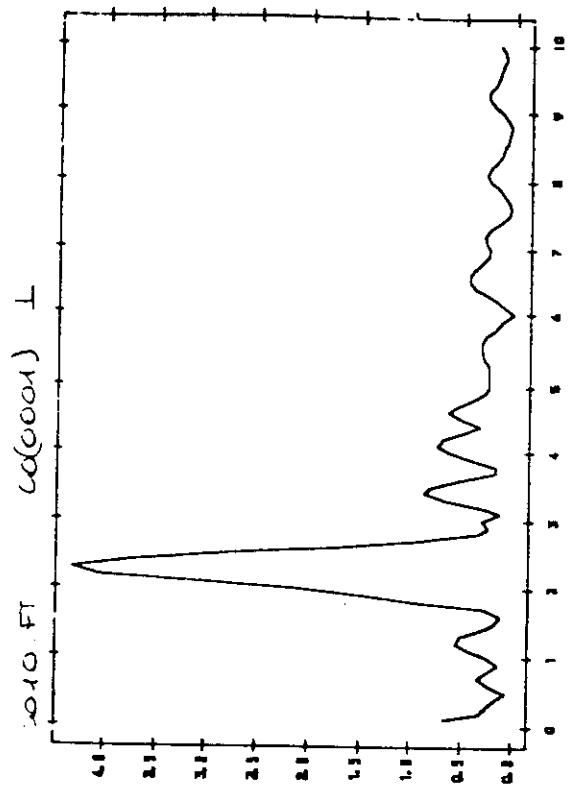
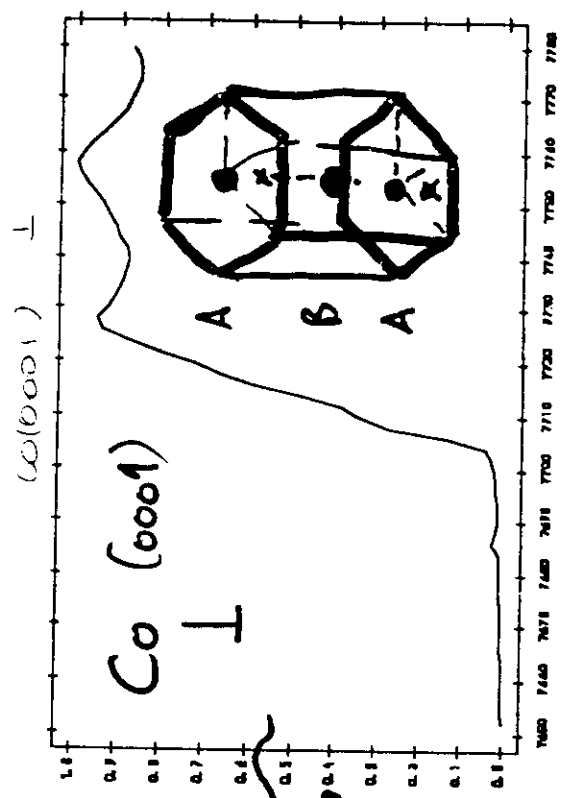
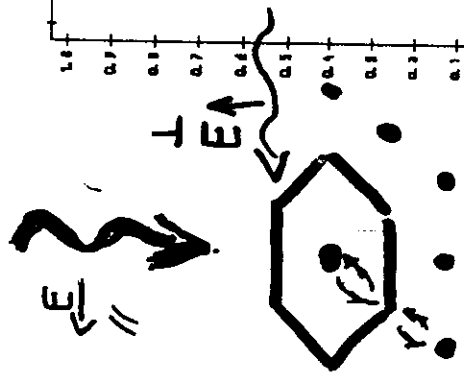
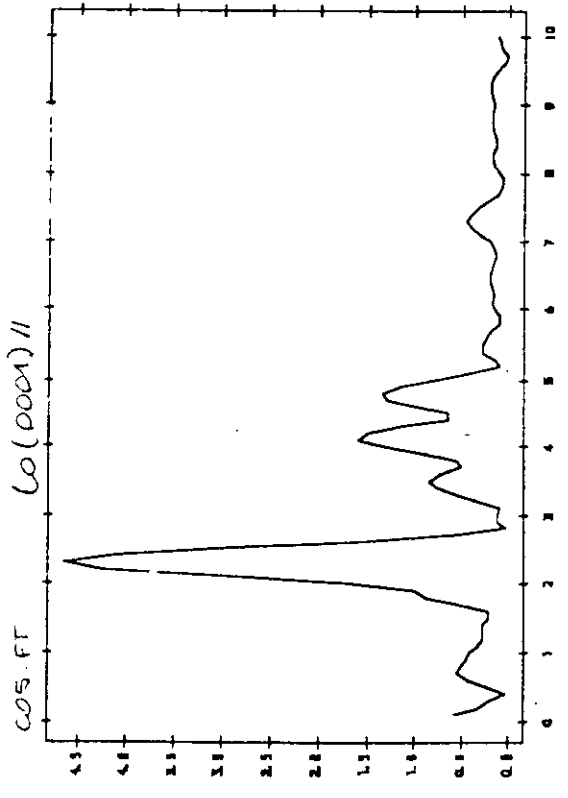
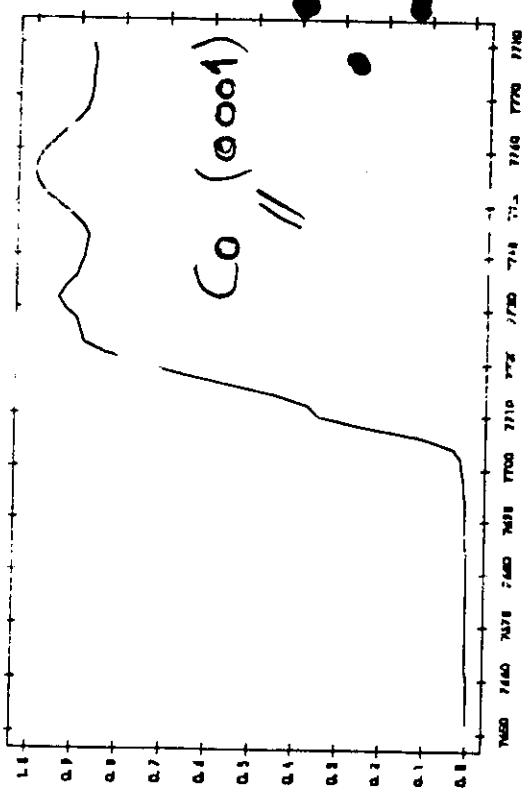


In plane polarisation

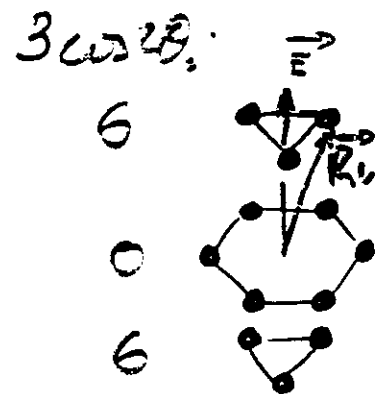
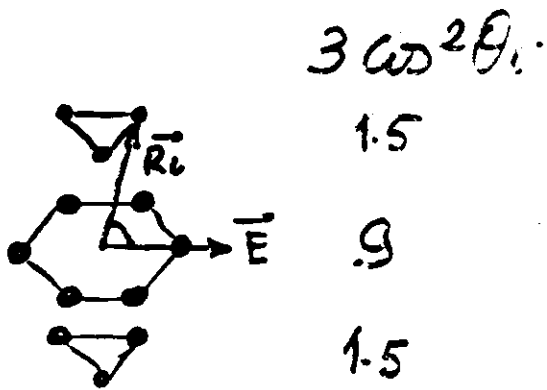
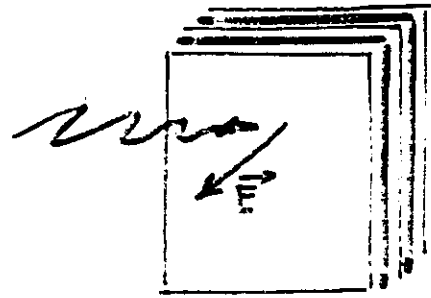
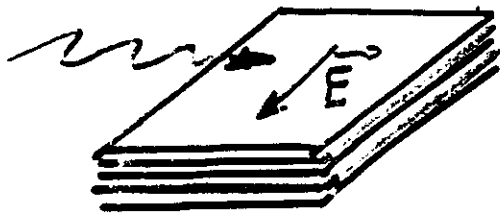


Perpendicular to the plane polarisation





# Glancing angle Geometry



not perfect hcp

$$1.5 + \delta$$

$$9 - 2\delta$$

$$1.5 + \delta$$

$$6$$

$$0$$

$$6$$

# MULTILAYERS.

- OPTICS                      x-Ray
- MAGNETISM

## 2D                      stacking and

- NEW                      STRUCTURES

GROWTH                      Substrate                      *Nature  
orientation  
Roughness  
Temperature*

- NEW MAGNETIC PROPERTIES

Giant Magnetoresistance , Perpendicular Anisotropy  
Spin-Valve , Oscillatory Coupling

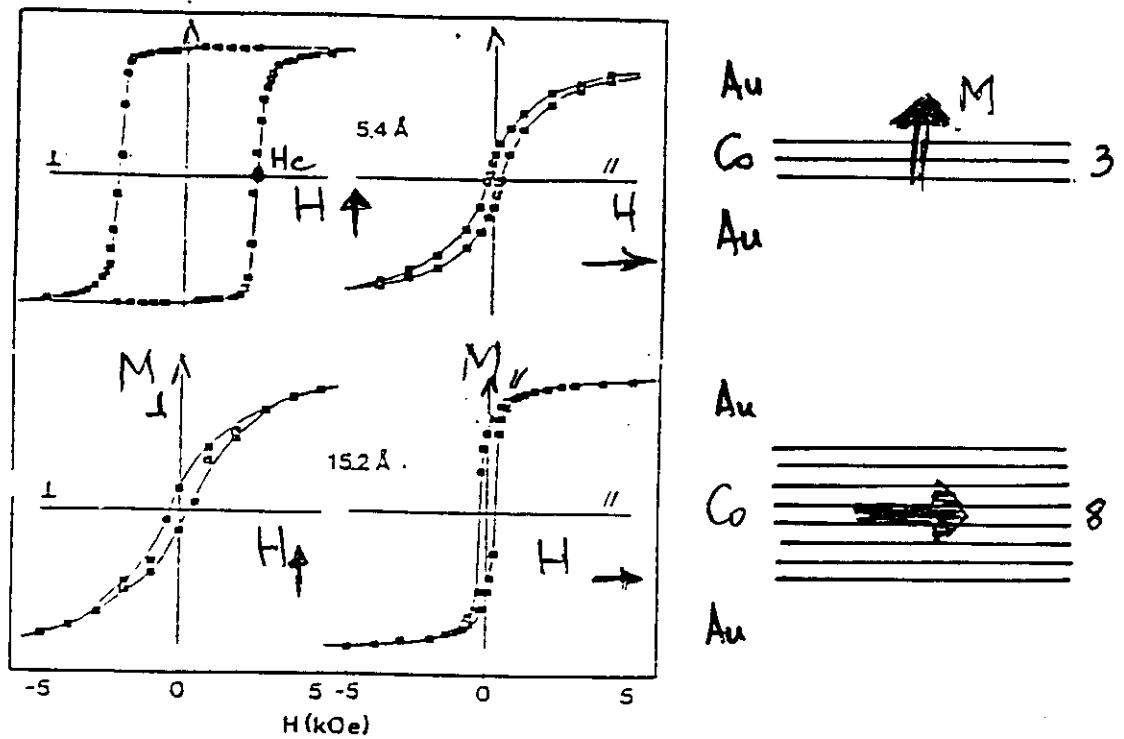
J. Grunberg et al. , A. Fert et al. , S. Parkin , J. Stöhr et al.  
R. Coe et al. , S. Saito , E. Freltoft et al. , ... 18

# Multicouches magnétiques

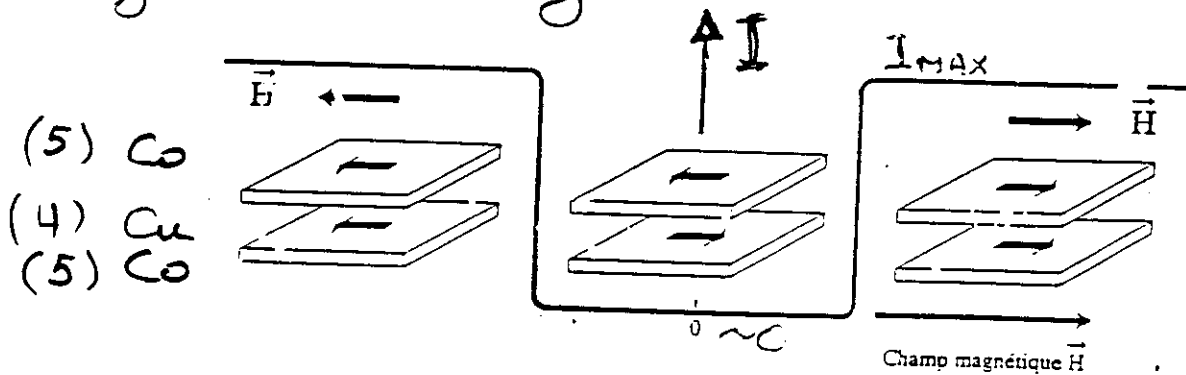
Media

Tête de lecture

Aimantation perpendiculaire



Magnétorésistance géante



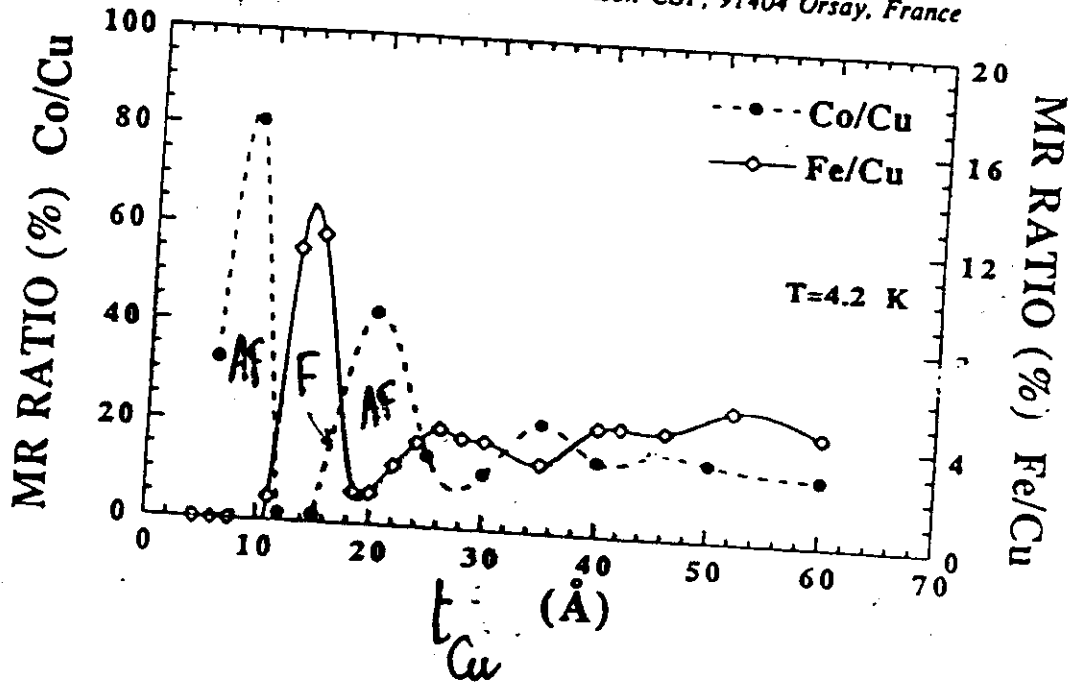
PERMALLOY - 3%  
MULTICOUCHEs  $\approx$  100%

# Oscillatory interlayer exchange and magnetoresistance in Fe/Cu multilayers

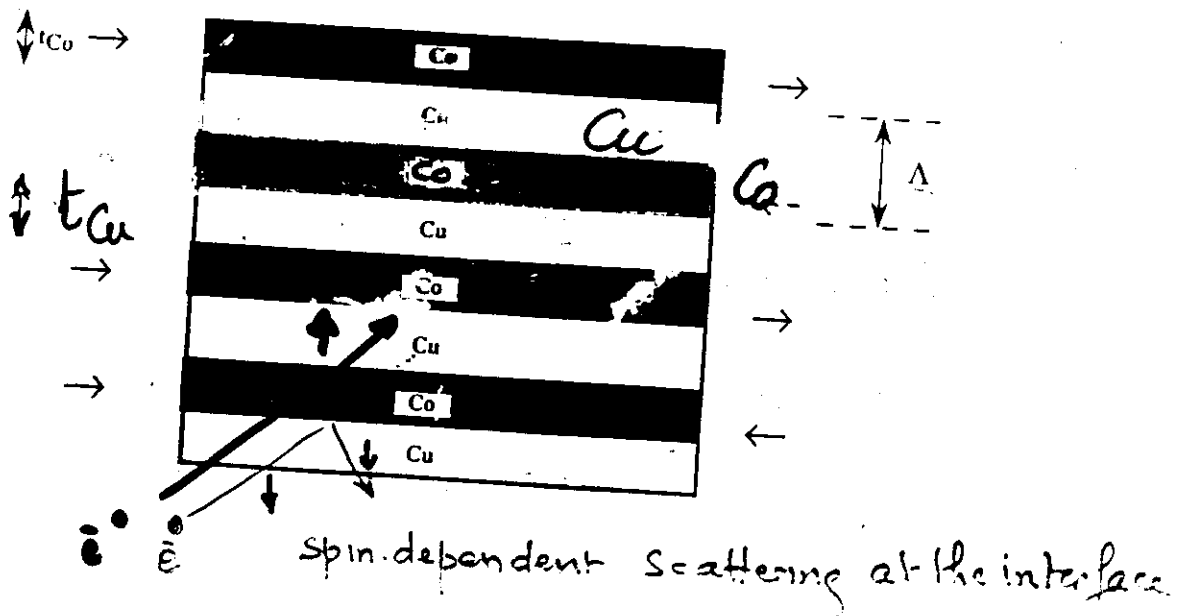
F. Petroff, A. Barthélemy, D. H. Mosca,\* D. K. Lottis, and A. Fert  
*Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France*

P. A. Schroeder, W. P. Pratt, Jr., and R. Loloee  
*Department of Physics and Astronomy and Center for Fundamental Materials Research,  
 Michigan State University, East Lansing, Michigan 48824*

S. Lequien  
*Laboratoire Central de Recherches Thomson-CSF, 91404 Orsay, France*



⇒ Giant Magnetoresistance.



97-61

# STRUCTURES of.

(2D + epitaxy) systems

WELL-CONDITIONED PROBLEM

for EXAFS

- not too many elements
- simple structures
- benefit from linear polarization of S.R.

- ANSWER is LOCAL ORDER

STRAIN & ANISOTROPY.

TO BE PERFORMED TOGETHER WITH DIFFRACTION.  
WITH EXP.

### Structure of Thin Metastable Epitaxial Fe Films on Cu(100): Reconstruction and Interface Ordering by Coating

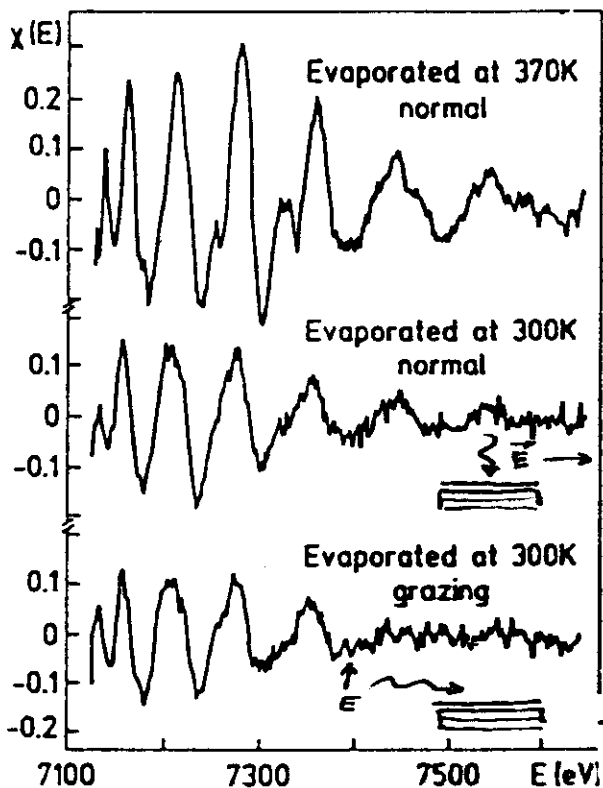
H. Magnan, D. Chandesris, B. Villette, O. Heckmann, and J. Lecante

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université de Paris-Sud, F-91405 Orsay, France  
and Service de Physique des Atomes et des Surfaces, Centre d'Etudes Nucléaires, F-91191 Gif-sur-Yvette, France

$$\chi(k) = -\frac{1}{kz} \sum_j \frac{1}{R_j^2} 3 \cos^2 \theta_j \exp(-2\sigma_j k^2) \exp\left(-\frac{2R_j}{\lambda(k)}\right) f_j(\pi, k) \sin[2kR_j + \tau(k)]$$

with

$$\tau(k) = 2\tilde{J}(k) + \arg f_j(\pi, k)$$

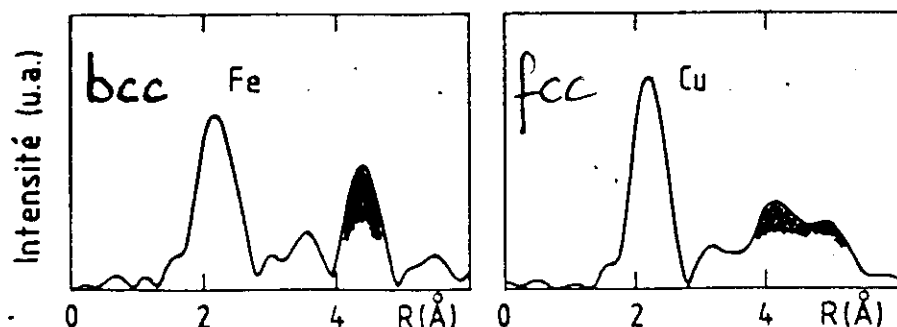
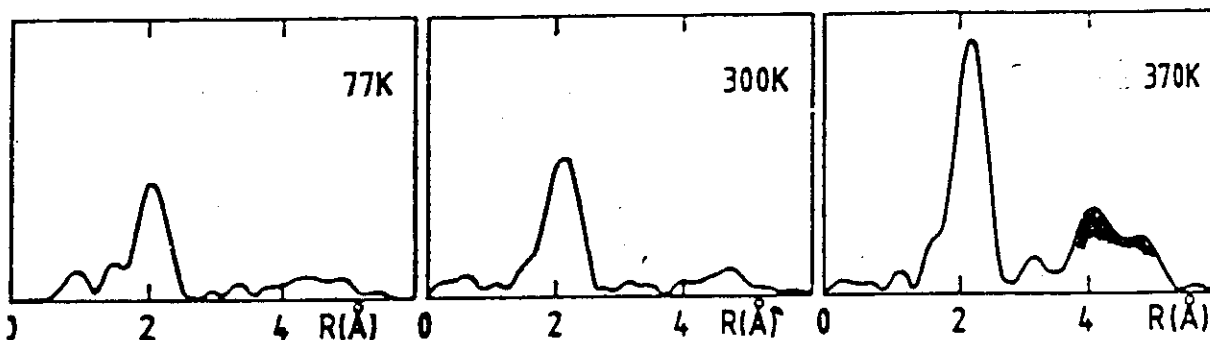


EXAFS

F.T.  $\Delta E$  window

$F(R) \approx$  "Rad. dist"

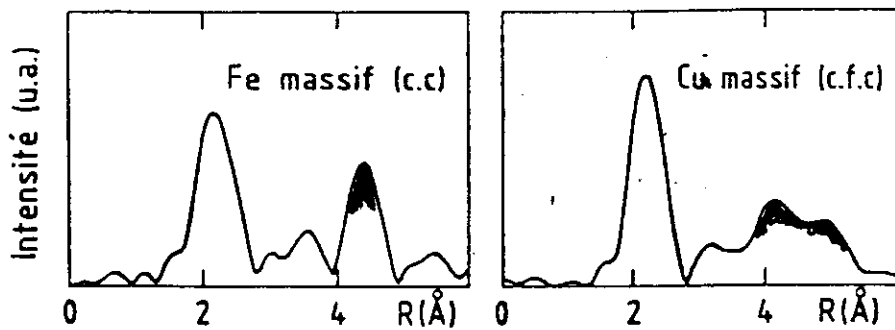
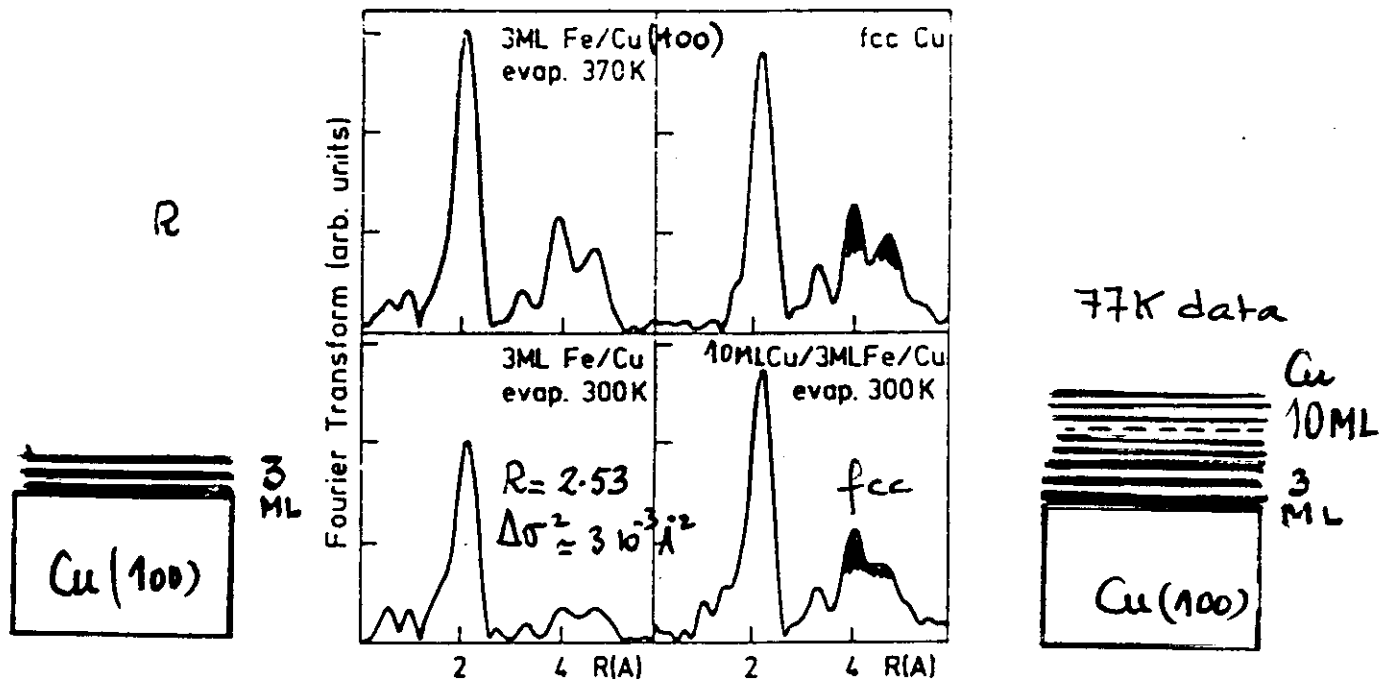
Fe K-edge: 3.5 ML on Cu(100)  
(77K data)



### Structure of Thin Metastable Epitaxial Fe Films on Cu(100): Reconstruction and Interface Ordering by Coating

H. Magnan, D. Chandesris, B. Villette, O. Heckmann, and J. Lecante

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université de Paris-Sud, F-91405 Orsay, France  
and Service de Physique des Atomes et des Surfaces, Centre d'Etudes Nucléaires, F-91191 Gif-sur-Yvette, France

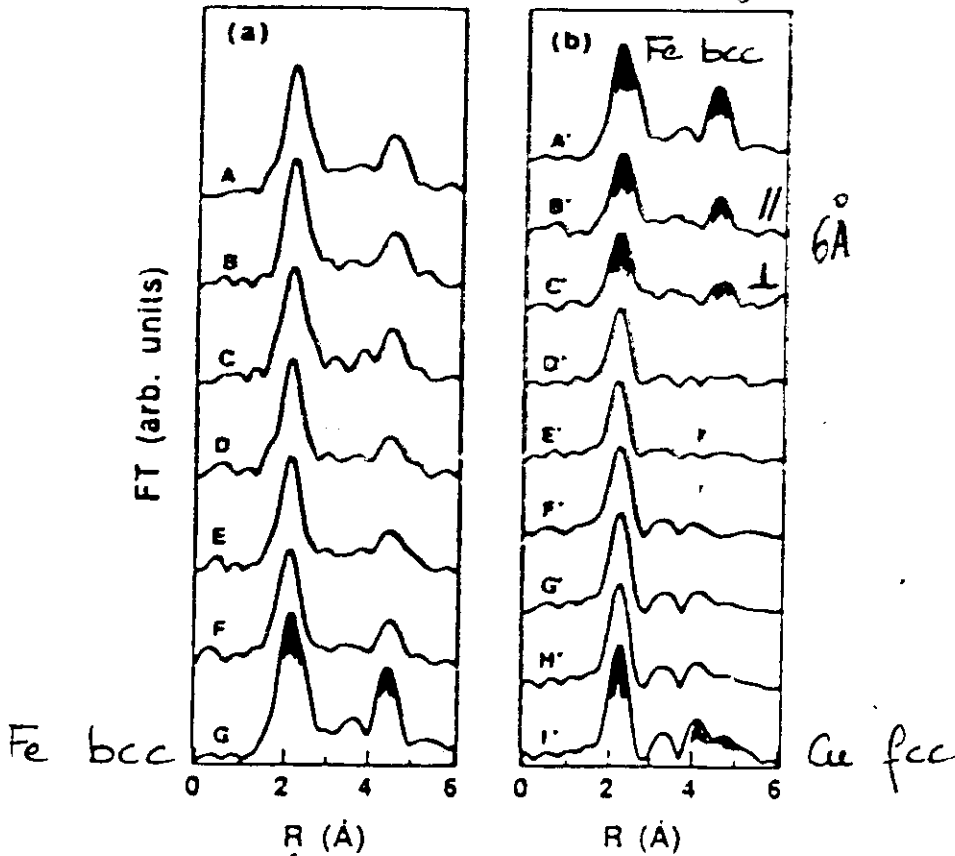
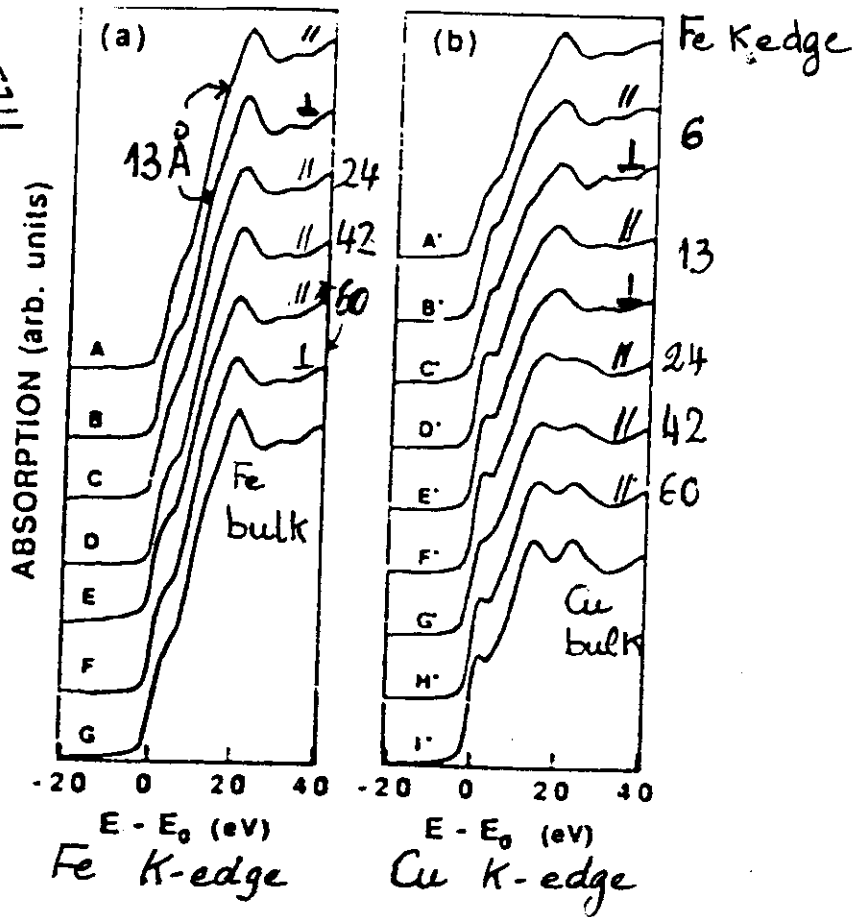
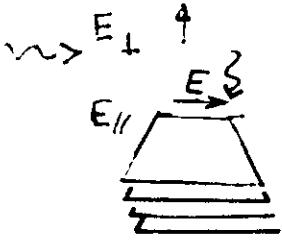




Structural characterization of Fe/Cu multilayers by x-ray absorption spectroscopy

S. Pizzini, et al.  
F. Pfeiffer

60 ( 15 Å.Fe, t<sub>Cu</sub>(Cu) )



bcc  
6 Å  
fcc + disorder ↓  
with t<sub>Cu</sub>  
(see BP IV 2)

IV. 3. Fe-Co multilayers

• lateral dimension  $\gg$  thickness  
~ superlattices

• NMR

• XANES & EXAFS

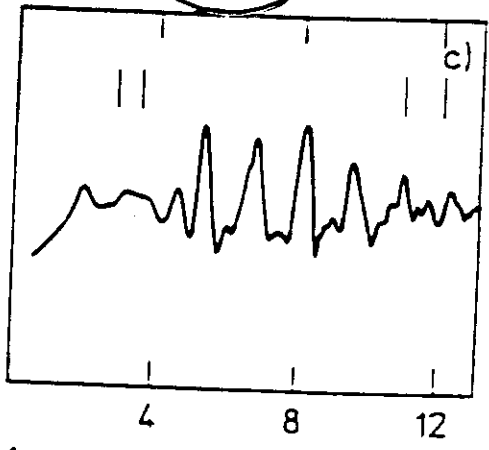
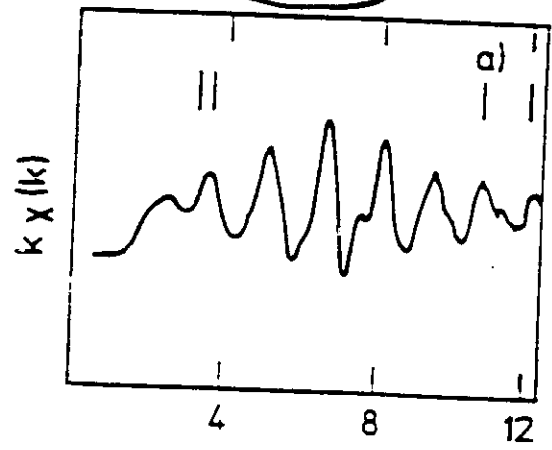
evidence Co stacking to be "bcc"



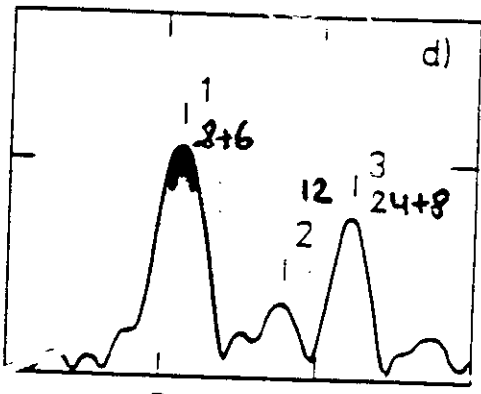
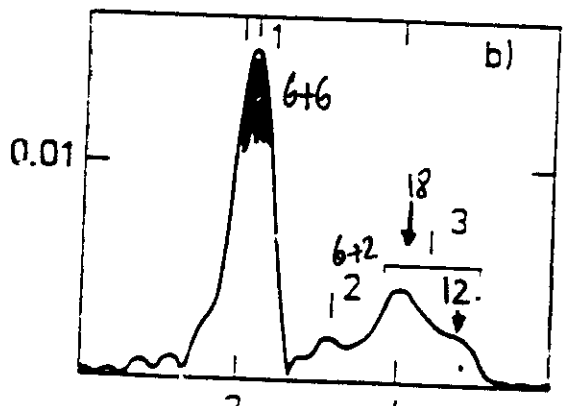
N	R (Å)	N	R (Å)
8	2.485	6	2.49
6	2.87	6	2.51
12	4.05	6	3.54
24	4.75	2	4.07
8	4.97 (*)	18	4.34
6	5.74 (*)	12	4.78
		6	5.02 (*)

COBALT

FER



$k (\text{Å}^{-1})$



"hcp"

bcc

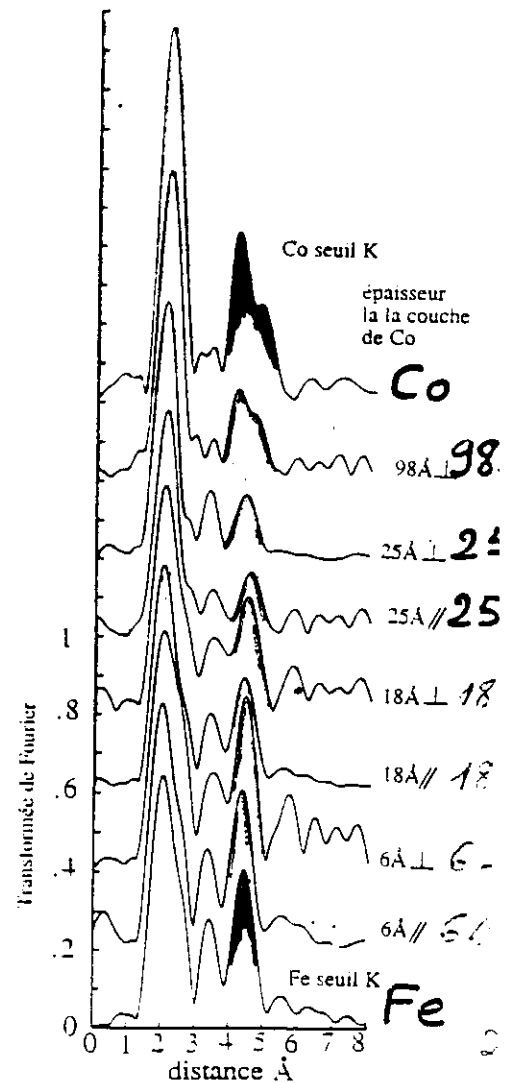
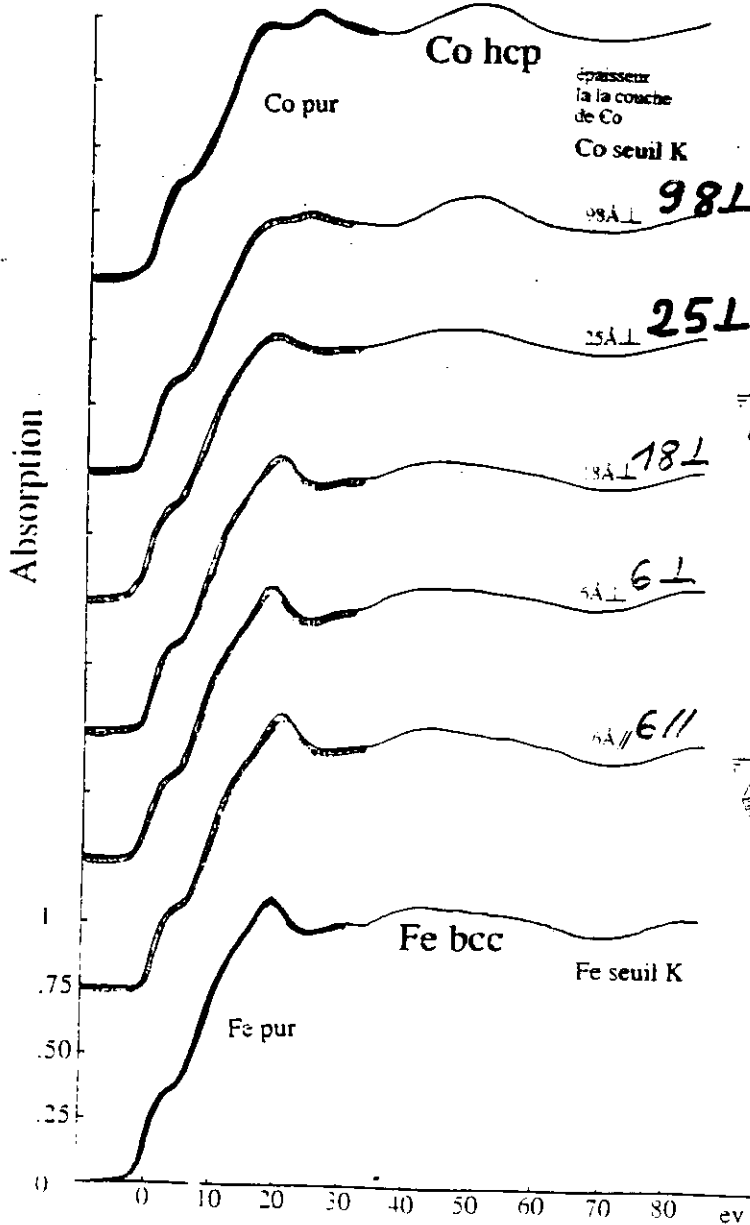
$R (\text{Å})$

# MULTICOUCHES Co/Fe

Phases métastables  $\longrightarrow$  Bidimensionnalité

Polarisation linéaire  $\longrightarrow$  Rayonnement Synchrotron

**Co bcc**



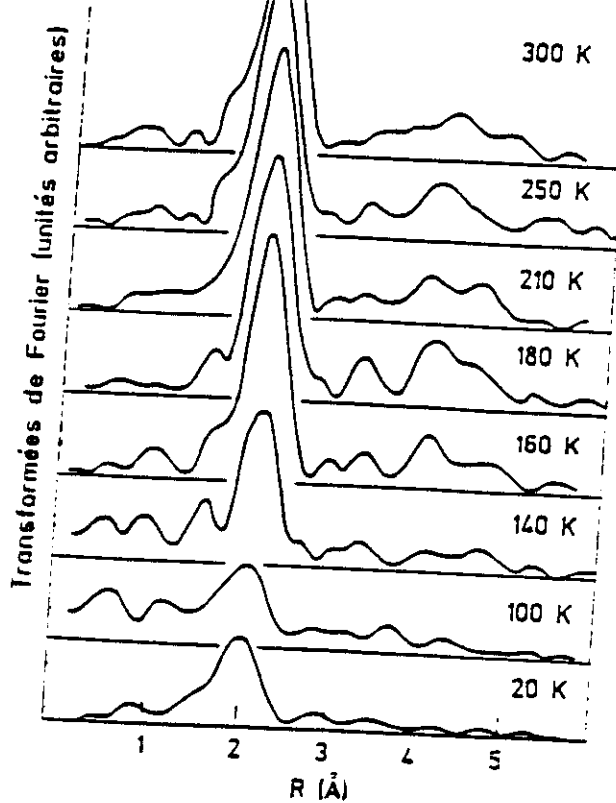


figure 3.18: cristallisation du cobalt amorphe. T.F. des spectres EXAFS pendant la remontée en température. à 160K l'échantillon est cristallisé. Les spectres EXAFS sont ici enregistrés à la température indiquée et non à basse température.

CRYST.

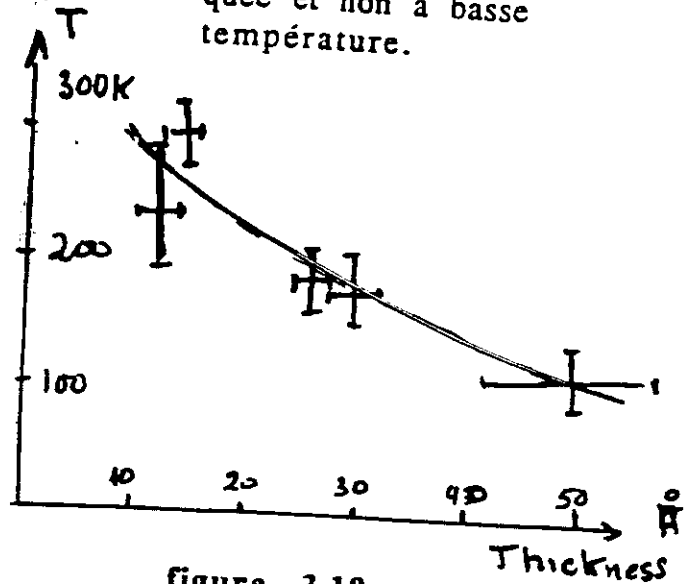
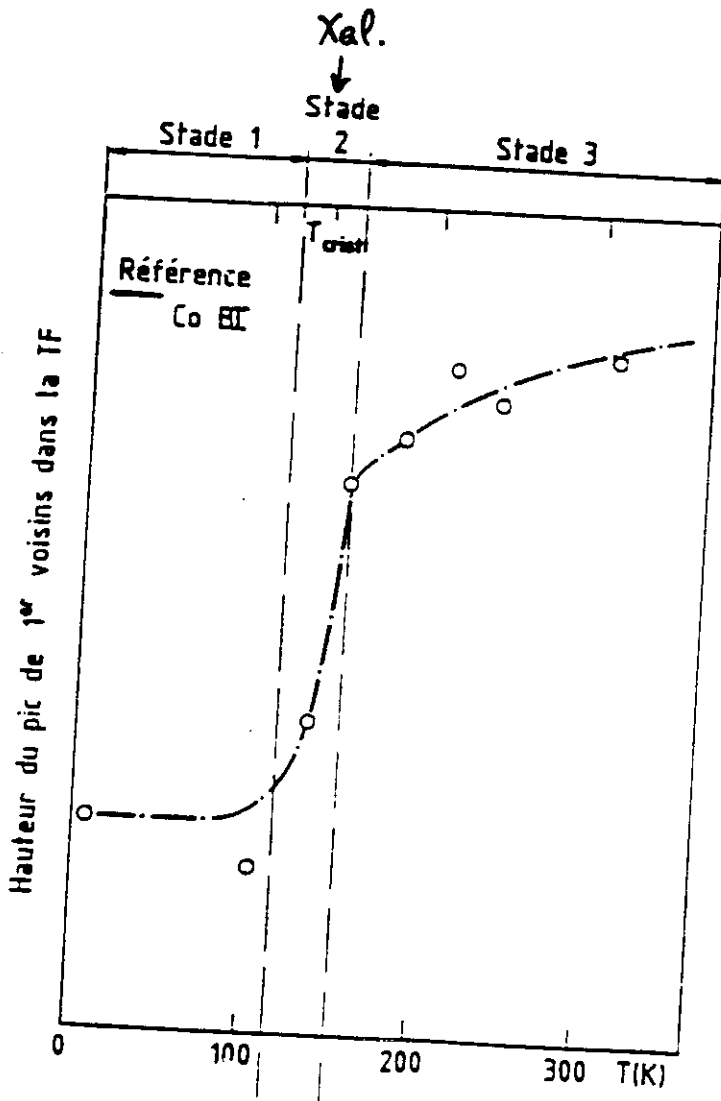


figure 3.19: Hauteur du pic de premiers voisins dans les transformées de Fourier de la figure 3.18 en fonction de la température, en comparaison avec la hauteur du pic de premiers voisins dans le cobalt massif à basse température. Mise en évidence de la cristallisation rapide des films de cobalt.



- Physics
- Aims of the EXAFS study
- Results
- Beatings
- Model of the new 2d stacking

- MBE on sapphire 1120 + RHEED  
 $10^{-10}$  torr

⇒ NEW STRUCTURES: 2D + EPITAXY.  
 Fe & Ru thicknesses as parameters

• RESULTS:

- DIFFRACTION      HEXAGONAL PACKING  
 $c/a = 1.55$       atomic volume  $12.8 \text{ \AA}^3$   
 $c = 4.15 \text{ \AA}$       bcc  $11.3 \text{ \AA}^3$   
    (13.566) hcp  $10.9 \text{ \AA}^3$

- MAGNETISM: (Mossbauer)
  - 2 dead Fe layers at each interface
  - IN-PLANE
  - Fe moment  $\sim 2\mu_B \equiv Fe_\alpha$  (bcc)
  - Theory hcp  $\leftrightarrow$  ANTIFERROMAGN.

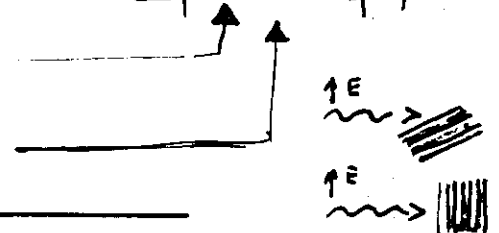


• AIMS: XAS investigation:

- REAL CRYSTAL / VIRTUAL CRYSTAL

• TOOLS

- Fermi GOLDEN RULE  $\propto \sum |k_i \cdot \vec{E} \cdot \vec{p}|^2 \rho$
- Atomic selectivity
- Linear polarisation

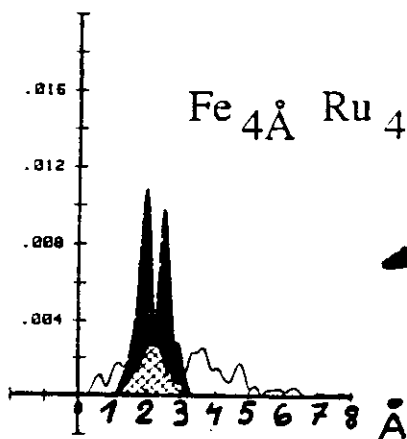
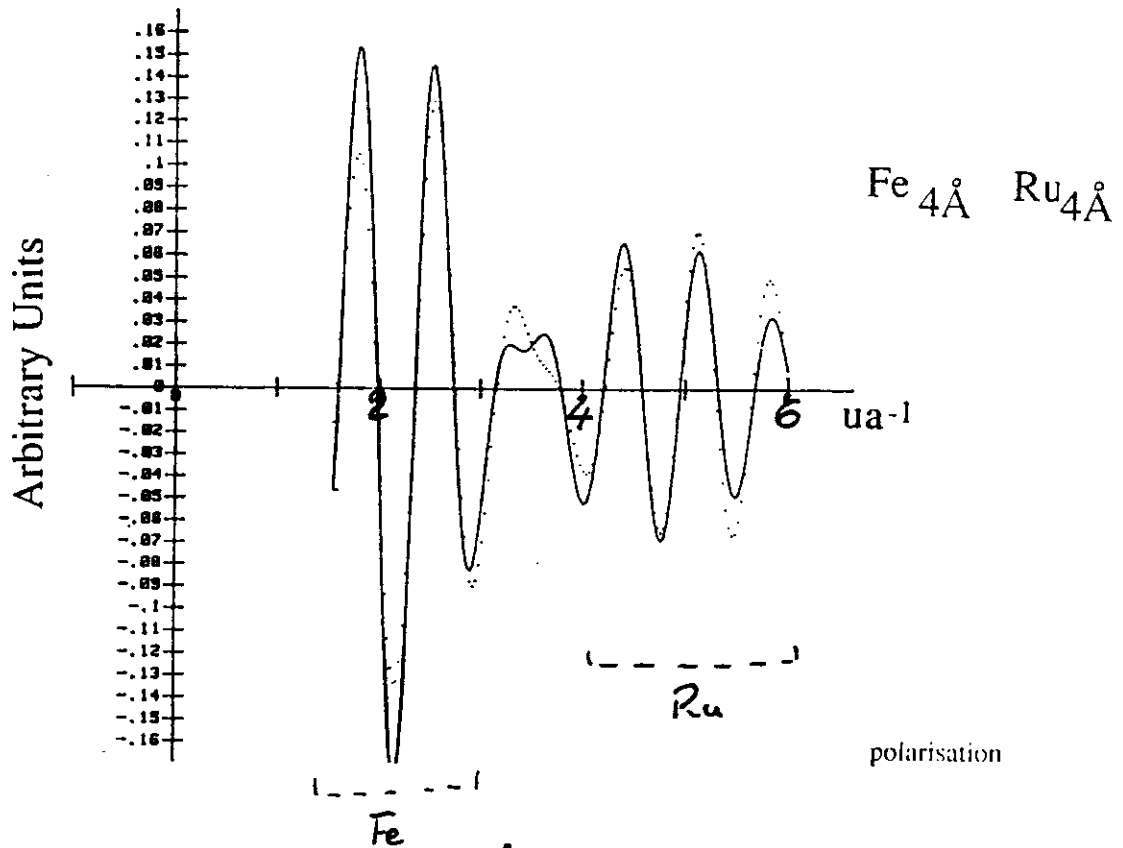


• RESULTS

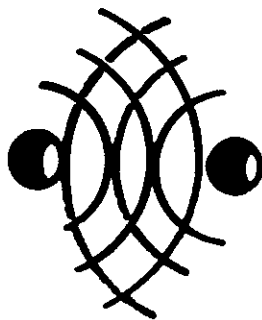
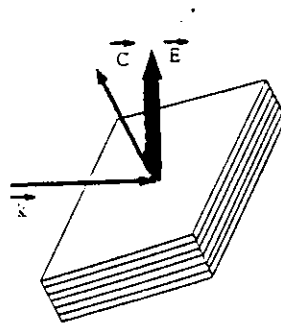
• PACKING IS HEXAGONAL BUT AB'AB'  
 $\neq$  bcc 'ABAB'

$$\chi(k) = -\frac{1}{k} \sum_j \frac{N_j}{R_j^2} 3 \cos^2 \theta_j \exp(-2\sigma_j^2 k^2) \exp\left(-\frac{2R_j}{\lambda(k)}\right) |F_j(\pi, k)| \chi$$

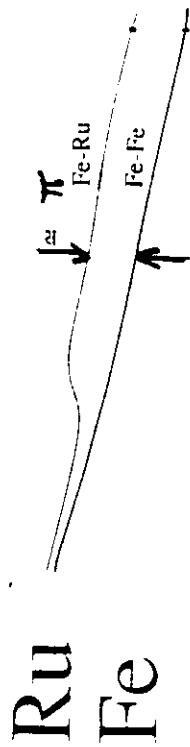
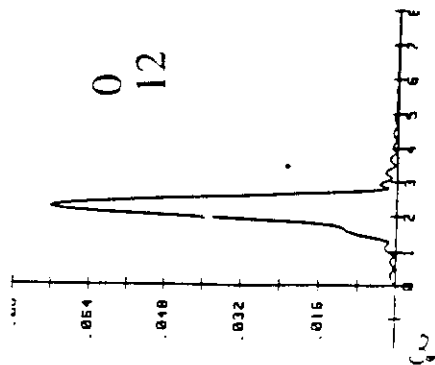
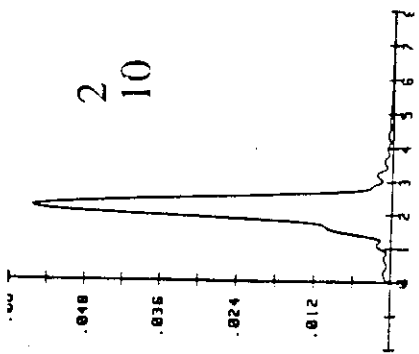
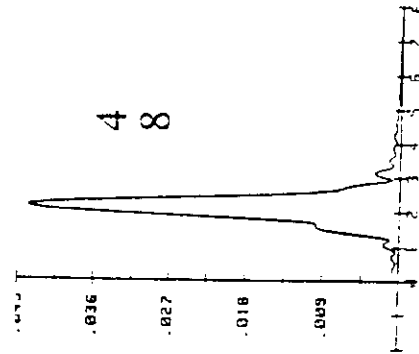
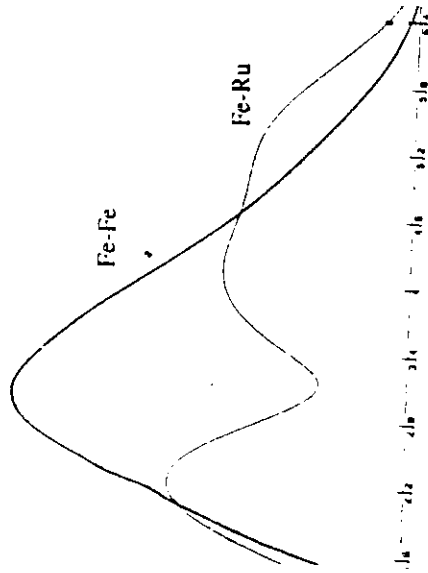
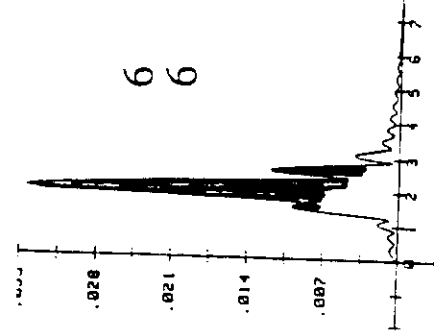
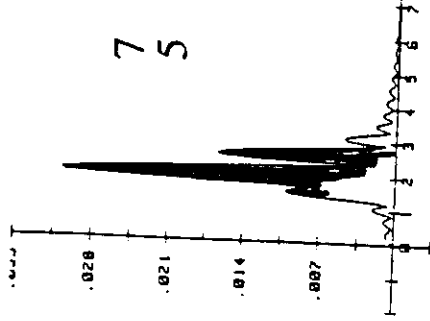
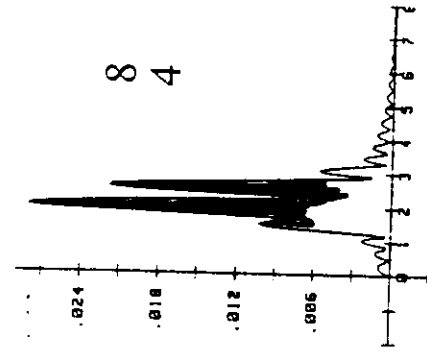
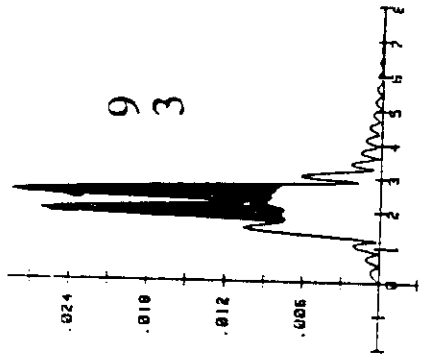
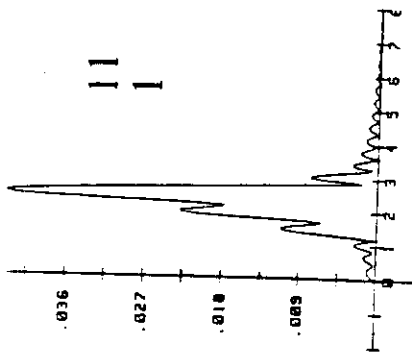
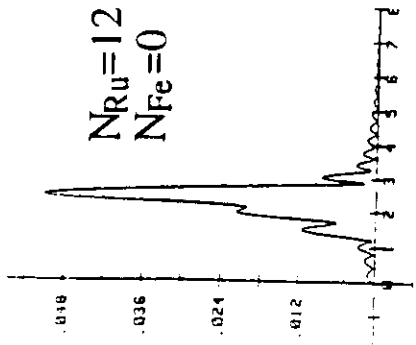
$$\sin\left(2kR_j + 2\delta(k) + \arg(F_j(\pi, k))\right)$$



T.F.





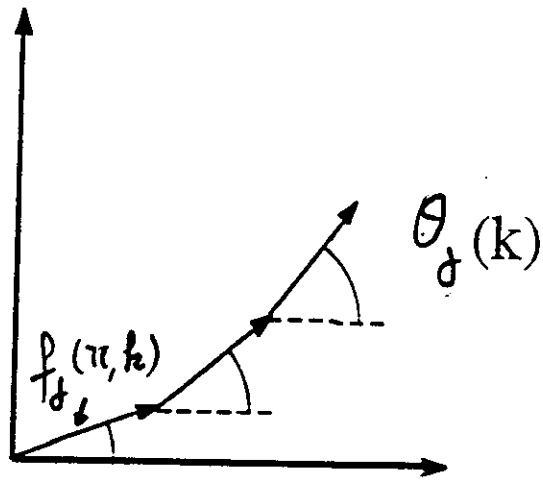


Ru  
Fe

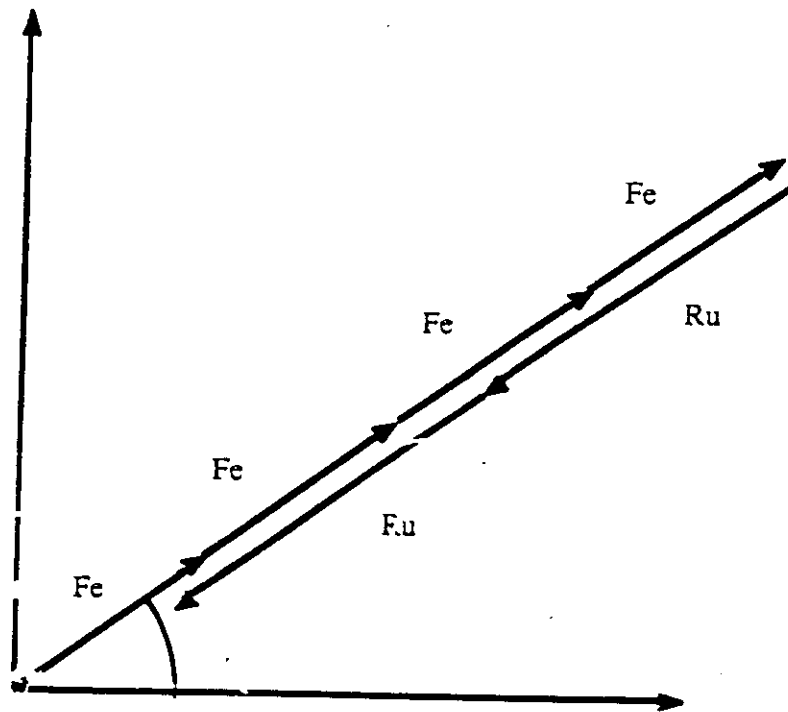
$\approx \pi$   
Fe-Ru  
Fe-Fe

0 12 10 8 7 6 5 4 3 2 1

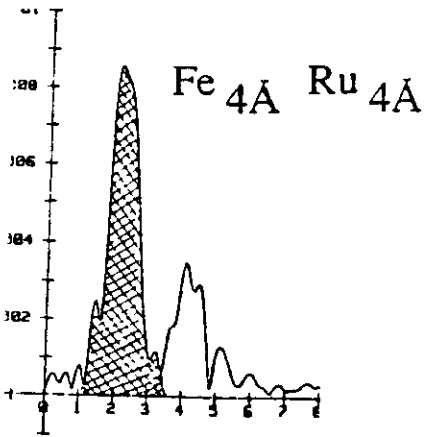
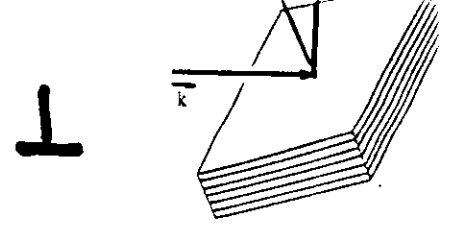
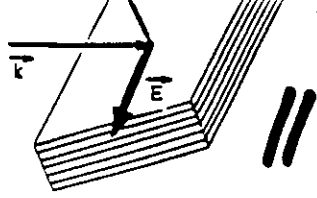
# SCHEMATIC FRESNEL DIAGRAM



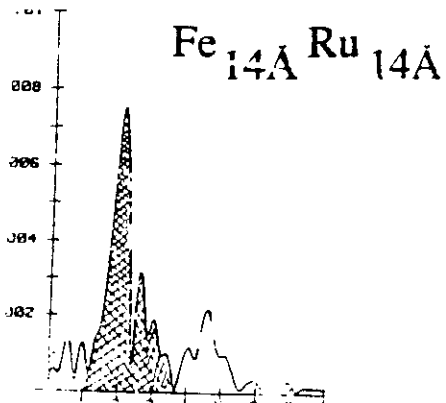
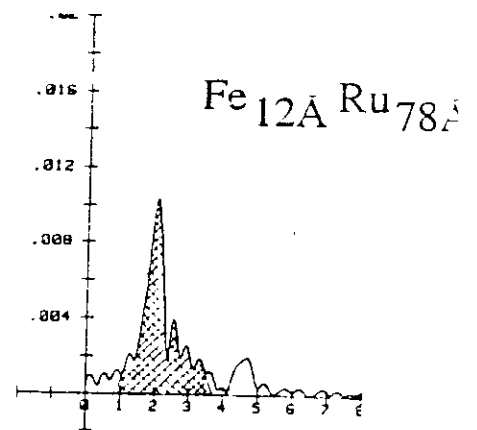
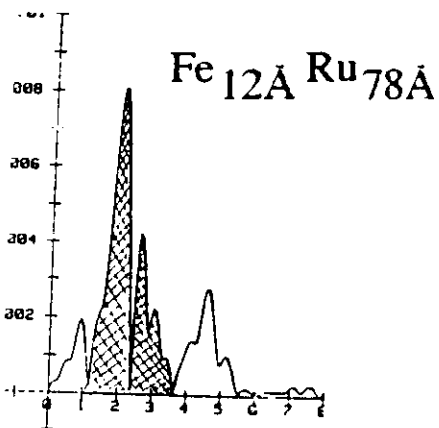
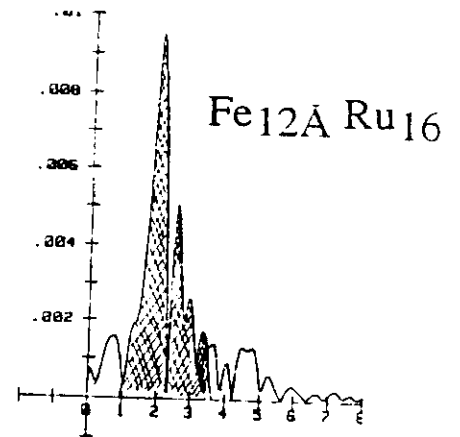
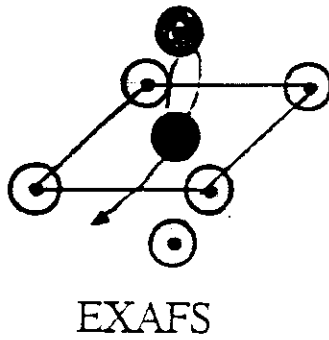
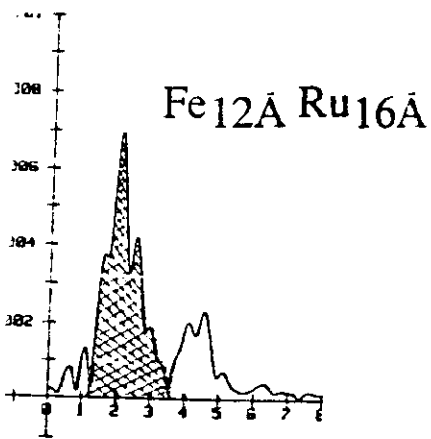
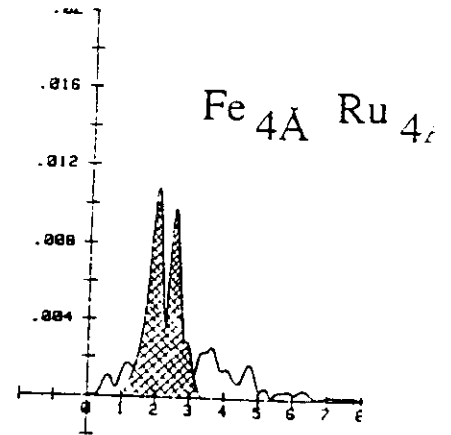
for a "h" value



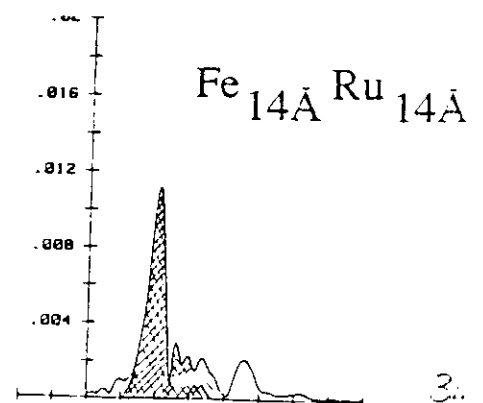
Pour des valeurs de k supérieures à  $3 \text{ ua}^{-1}$



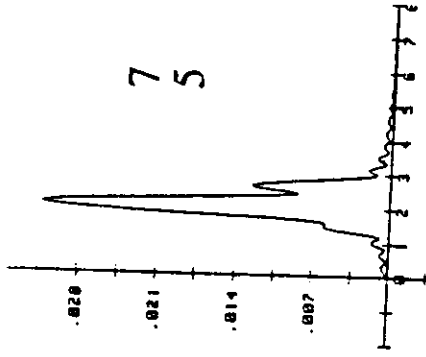
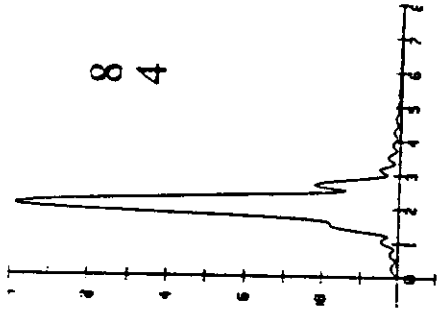
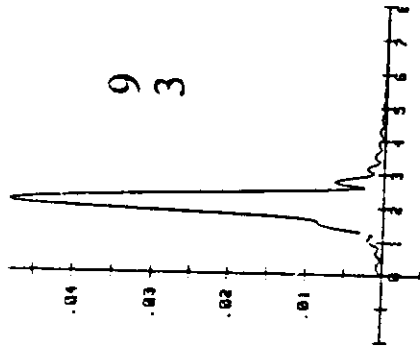
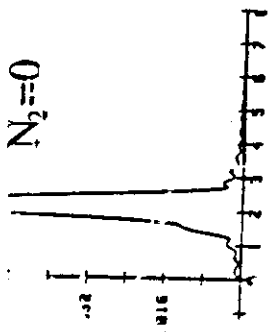
Fe/Ru



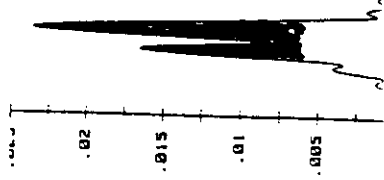
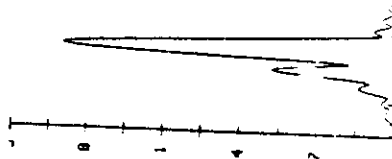
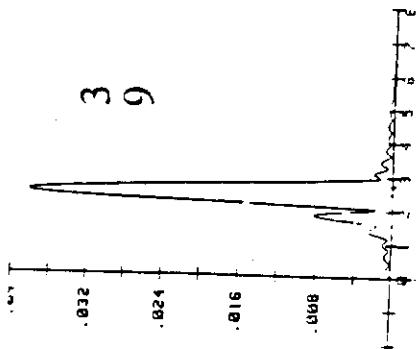
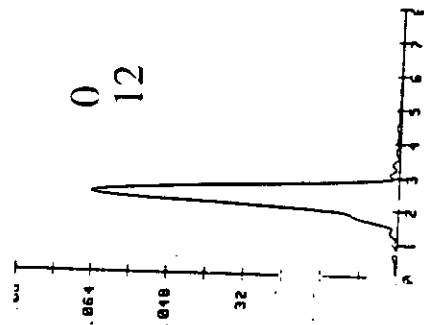
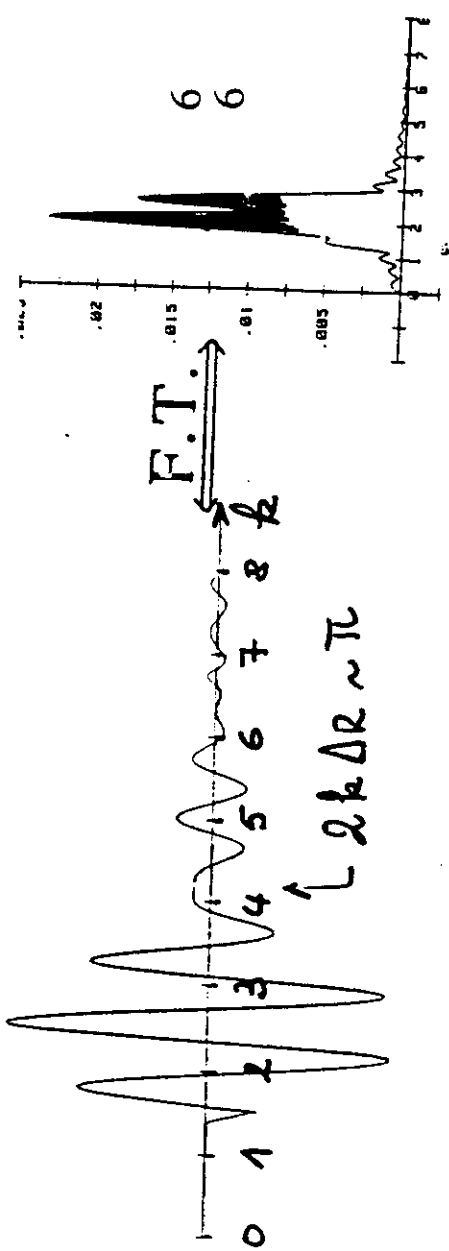
Fe / Fe+ΔR



$N_1=12$   
 $N_2=0$



$R_1=2.50\text{\AA}$   
 $R_2=2.75\text{\AA}$



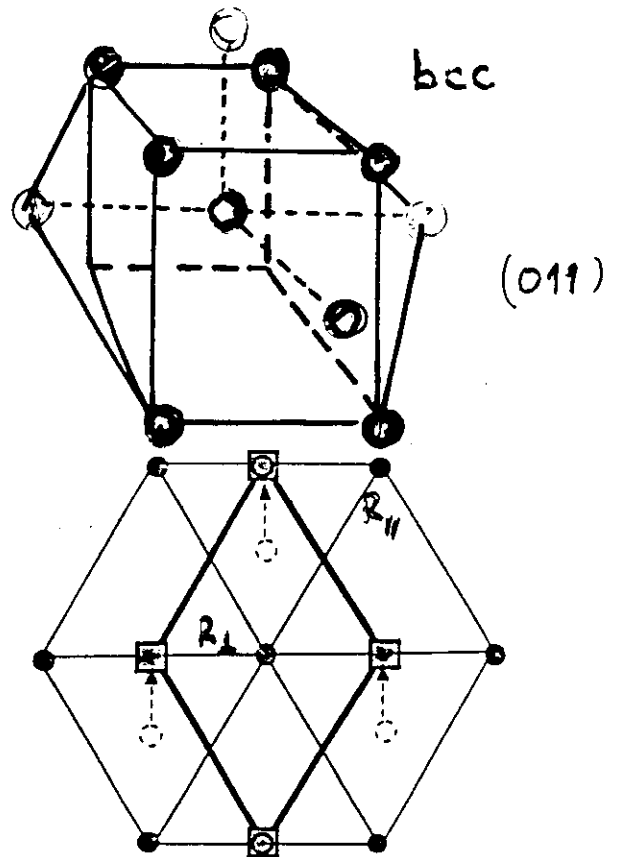
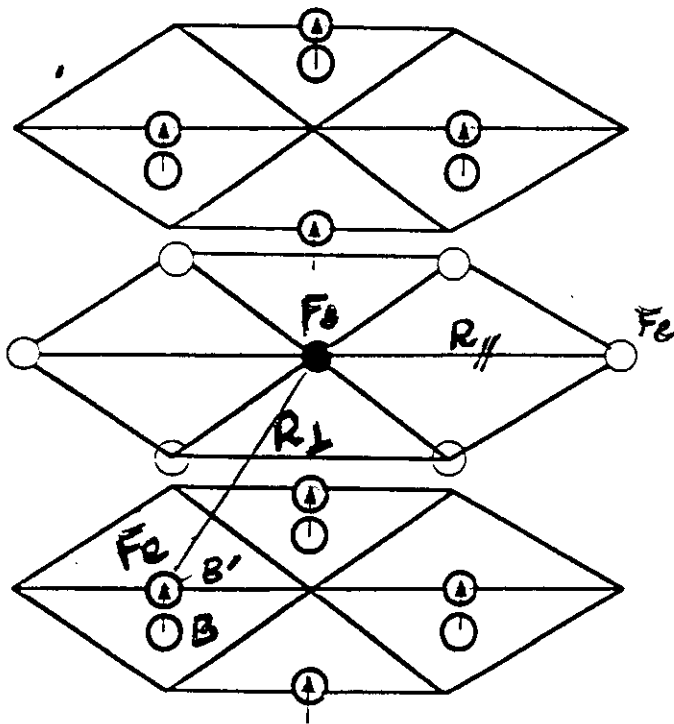
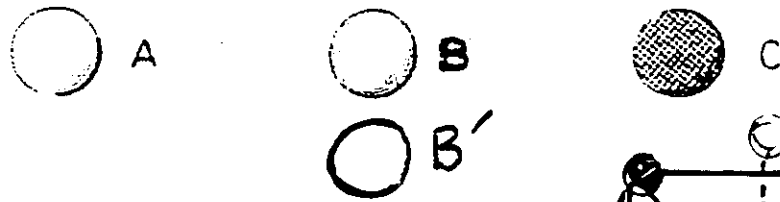
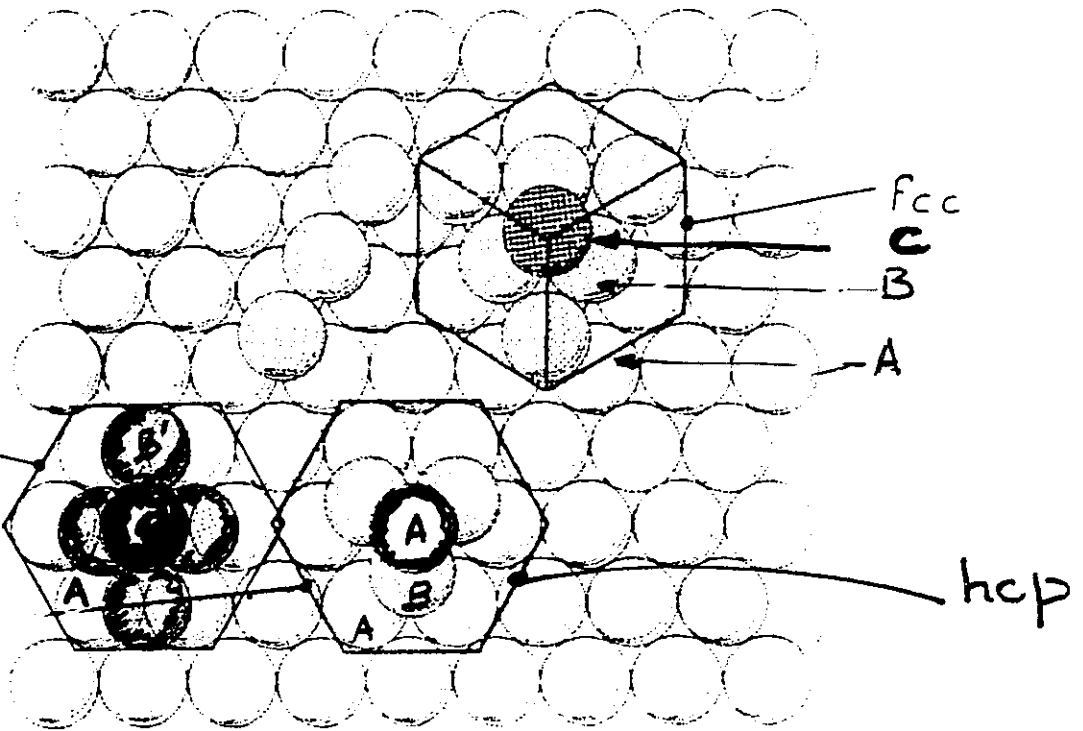
• hcp

3.88 Å

$R_{11} = 2.73 \pm 0.02$

→  $c = 4.18 \text{ \AA}$

New hexagonal packing but virtual crystal is "hcp"



F. BAUDET et al.

Cu<sup>2+</sup>  
in CUPRATES

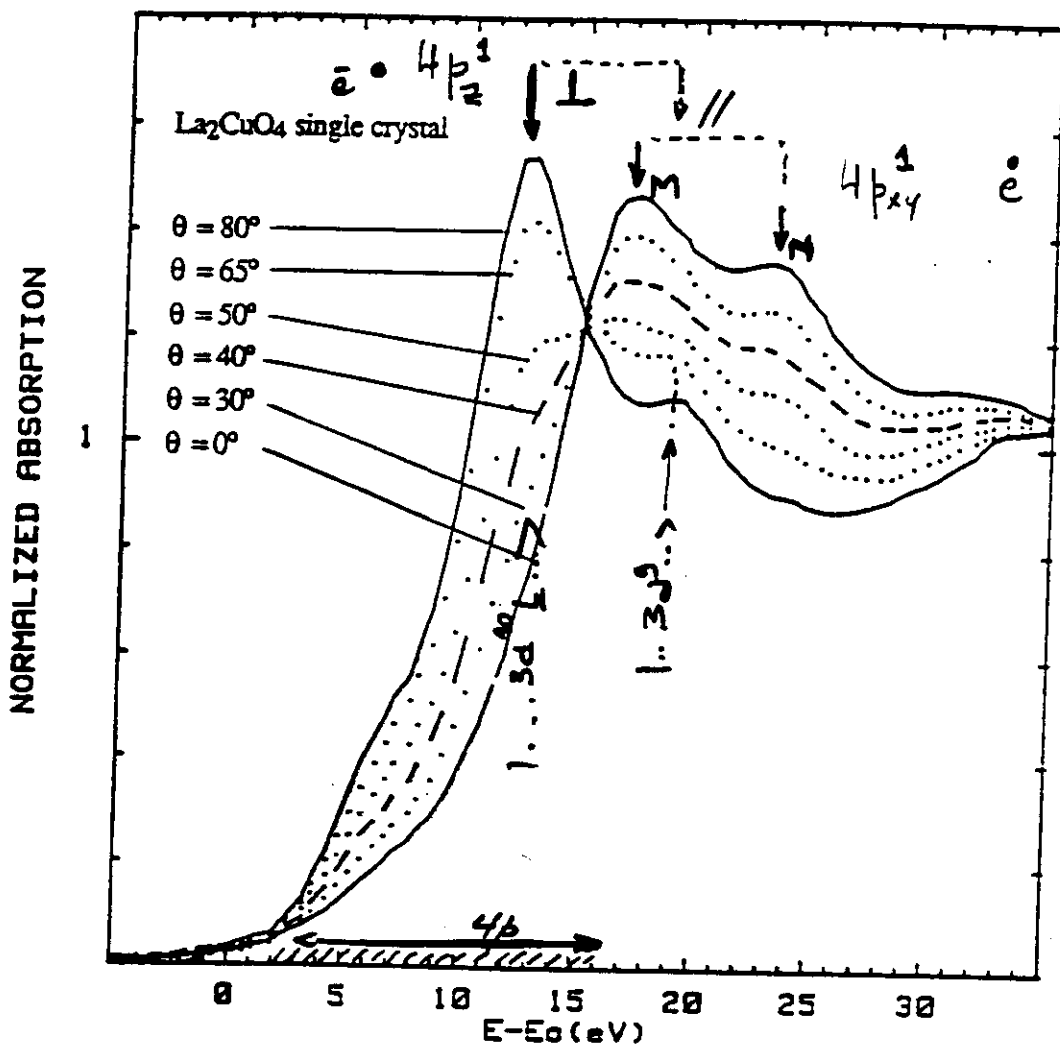
SQUARE PLANAR CLUSTER

GROUND STATE

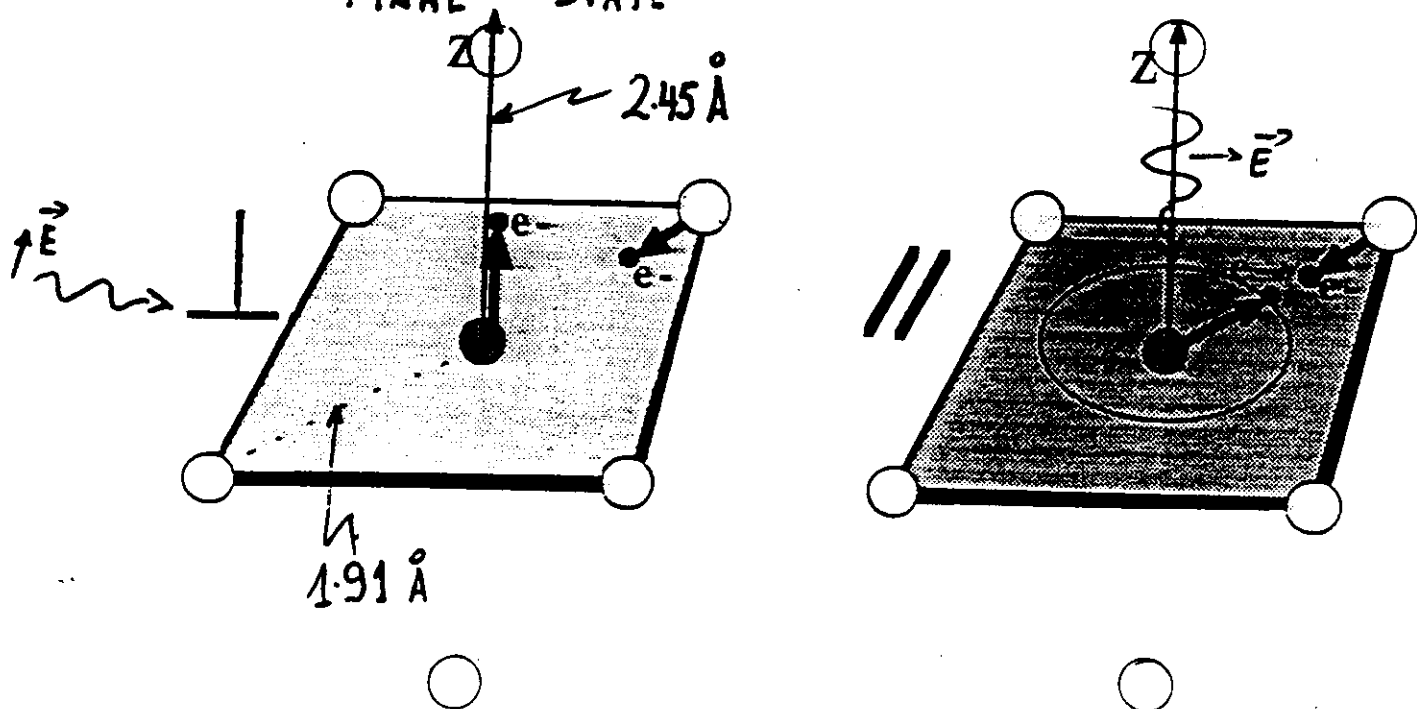
$$\sqrt{0.67} |1s^2 \dots 3d^9, \dots 2p^6\rangle + \sqrt{0.33} | \dots 3d^{10} \rangle$$

TOLENTINO  
FONTAINE  
et al.

HIGHLY  
CORRELATED  
SYSTEM  
&  
MANY BODY  
PROBLEMS



FINAL STATE

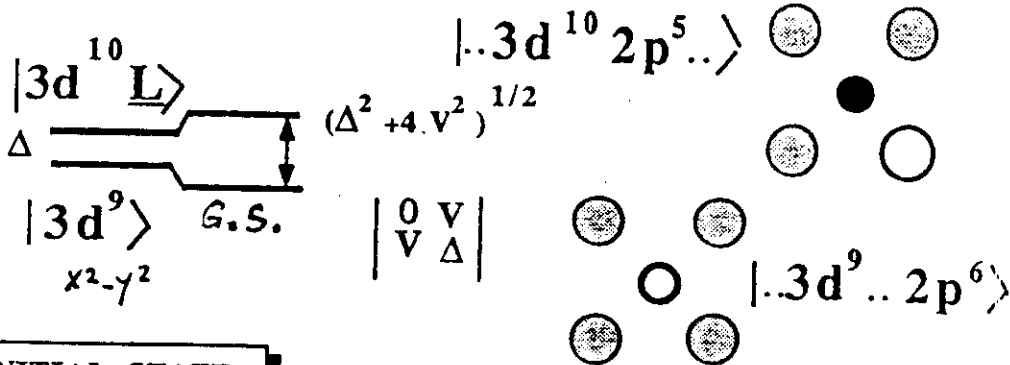


XAFS:

Cu K-edge of cuprates :  
what do we measure ?

~ ZSA  
model  
(1985)

$D_{4h}$

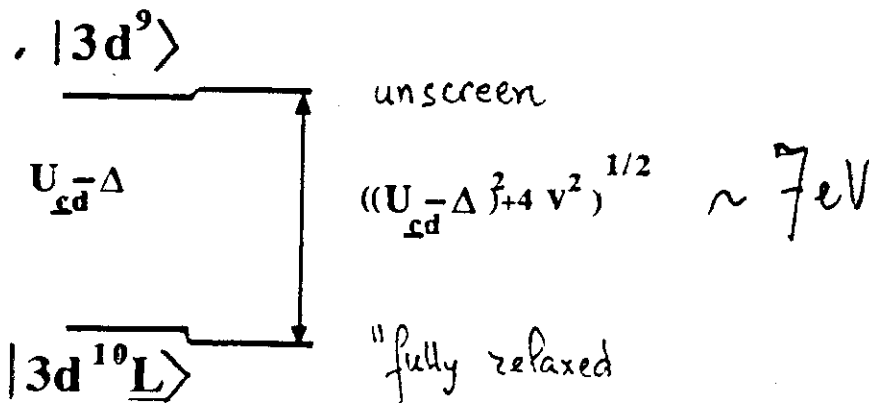


INITIAL STATE

The core level spectroscopy creates a deep core HOLE

→ Relaxation of all the LOCALIZED electrons  
of the probed ATOM

FINAL STATE  $\neq$  INITIAL STATE



1-XPS and K-edge XAS do not fill empty 3d states

2-L III do fill the d band. "ONE" FINAL STATE  $\langle P \in 10 \rangle$

$L_{II}$

115  
 Van der Laan  
 (ZRB . 1981)

$2p_{3/2}$

$2p_{1/2}$

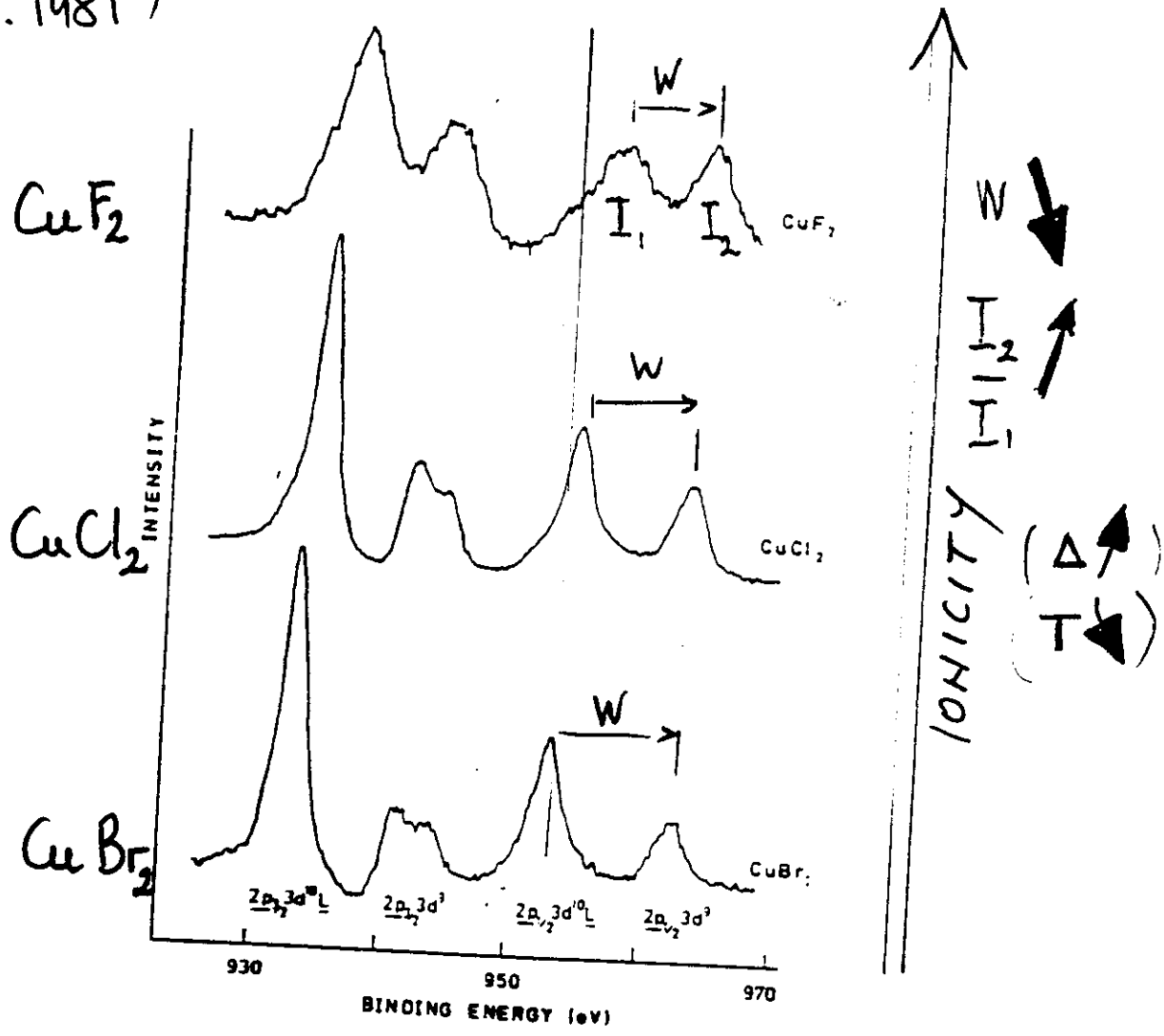
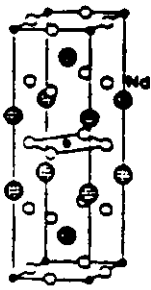


Fig.6 Spectres de photoémission d'électrons (XPS) des halogénures de cuivre  $\text{CuF}_2$ ,  $\text{CuBr}_2$ ,  $\text{CuCl}_2$  [d'après G. van der Laan et al-1981].





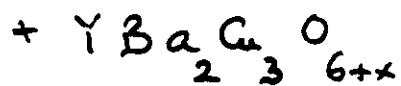
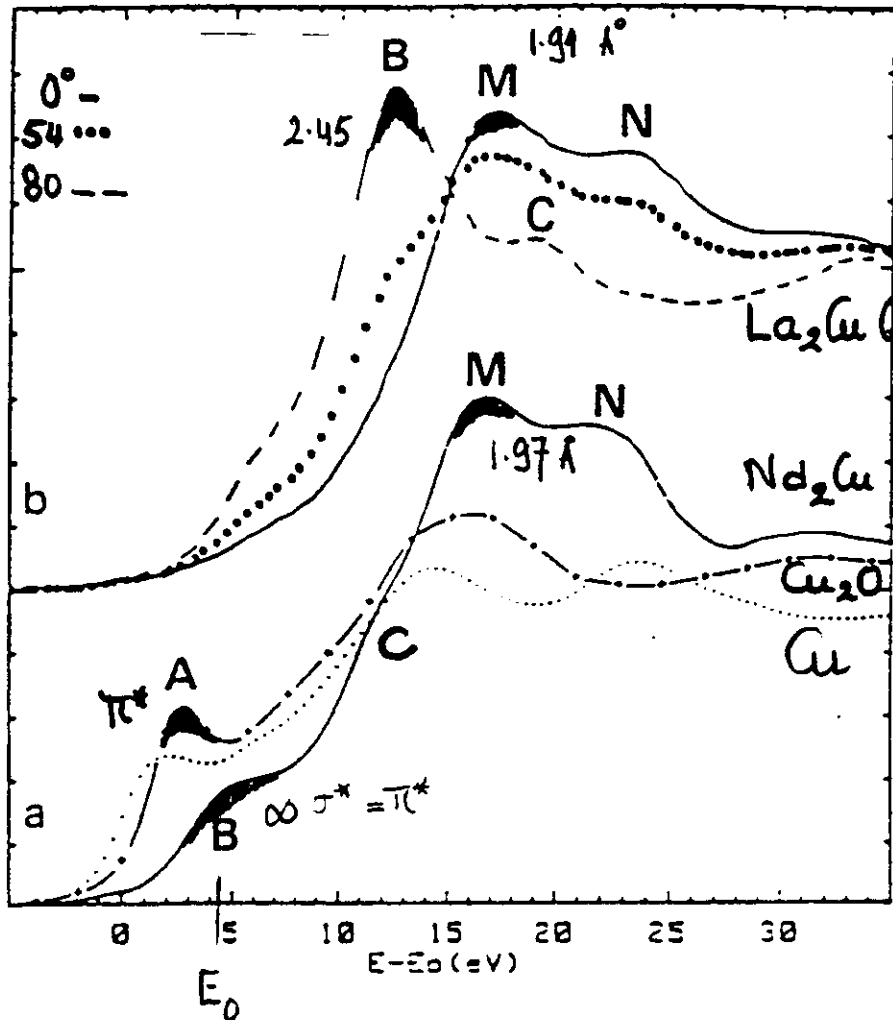
(a)



(b)



NORMALIZED ABSORPTION



Range of Cu-O distances

## A History of X-ray absorption fine structure (\*)

R. Stumm von Bordwehr

Laboratoire de Physique du Solide, Université de Nancy I, B.P. 239, F-54506 Vandoeuvre-lès-Nancy Cedex, France

**Résumé.** — Cette histoire de la spectroscopie de structure fine des seuils d'absorption X (XAFS) des origines à 1975 commence par présenter les premières observations de seuils d'absorption X ainsi que les dispositifs expérimentaux utilisés au début du siècle. Puis on décrit la découverte des structures fines et l'interprétation qu'en donne Kossel. On discute en détails les trois remarquables articles écrits par Kronig pour expliquer les XAFS dans les solides et les molécules. On montre comment Petersen a développé la théorie des XAFS des molécules et Smoluchowski celle des cristaux. Puis on passe en revue les contributions japonaises et soviétiques à cette spectroscopie jusqu'aux années soixante. On conclut par la description de la théorie actuelle des XAFS qui s'est développée au début des années soixante-dix. Bien que décrivant des nombreuses expériences, ce travail met l'accent sur l'évolution conceptuelle de l'interprétation des XAFS, en tenant compte des faux pas et des contributions négligées.

**Abstract.** — This historical account of X-ray absorption fine structure (XAFS) spectroscopy from the origin to 1975 begins with the first observations of X-ray absorption edges and the experimental setups used at the turn of the century. Then, the discovery of XAFS and Kossel's early interpretation are discussed. A close look is taken at the three outstanding papers written by Kronig to explain XAFS in solids and molecules. Petersen's development of XAFS in molecules and Smoluchowski's investigation of XAFS in crystals during the thirties are reviewed. Then, the Japanese and Soviet contributions to X-ray absorption spectroscopy up to the sixties are described. We conclude with the advent of the present understanding of XAFS developed in the early seventies. Although many experiments are presented, we emphasize the conceptual evolution of the interpretation of XAFS, including false steps and overlooked works.

*Il ne s'agit pas, en effet, pour faire un portrait, de reproduire avec une justesse mathématique, les proportions et les formes de l'individu ; il faut encore, et surtout, saisir et représenter en les justifiant et en les embellissant les intentions de la nature manifestées sur cet individu, avec les modifications ou les développements essentiels apportés par les habitudes, les idées, la vie sociale.*

André Adolphe Eugène Disderi

## Introduction.

By the above sentence [1.1], we would like to explain the reasons which lead us to the elaboration of this history of X-ray absorption fine structure (XAFS).

We do not intend to carry out an exhaustive work nor to seek accuracy and exactitude but we think that it is necessary to spur the memory of science, now and then,

(\*) This paper is dedicated to Ralph Kronig (Fig. 1.1).

A. von Bordwehr

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