



UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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H4.SMR/1013-38

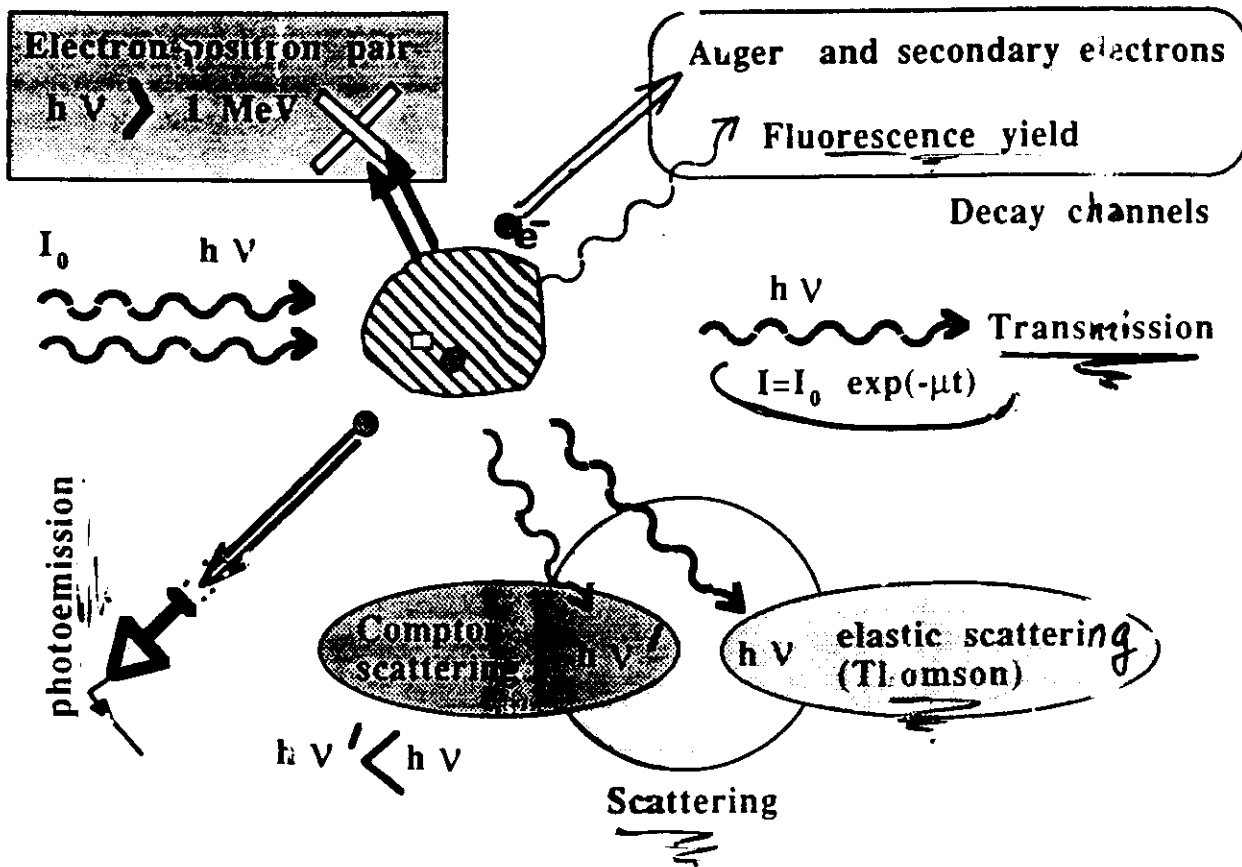
**SCHOOL ON THE USE OF SYNCHROTRON RADIATION
IN SCIENCE AND TECHNOLOGY:
*"John Fuggle Memorial"***

3 November - 5 December 1997

Miramare - Trieste, Italy

EXAFS Introduction

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



• 1 photon IN / 1 photon OUT
 Diffusion \bar{e} Thomson $(\frac{8\pi}{3} r_e^2)$

• 1 photon IN / c photon OUT
 \bar{e} IN ABSORPTION
 \bar{e} OUT PHOTOEMISSION

$h\nu$ (100eV \rightarrow 50 KeV)
 INTERACTIONS WITH ELECTRONS ARE IMPORTANT

I.D. SECTIONS EFFICACES D'INTERACTION (Atomiques)

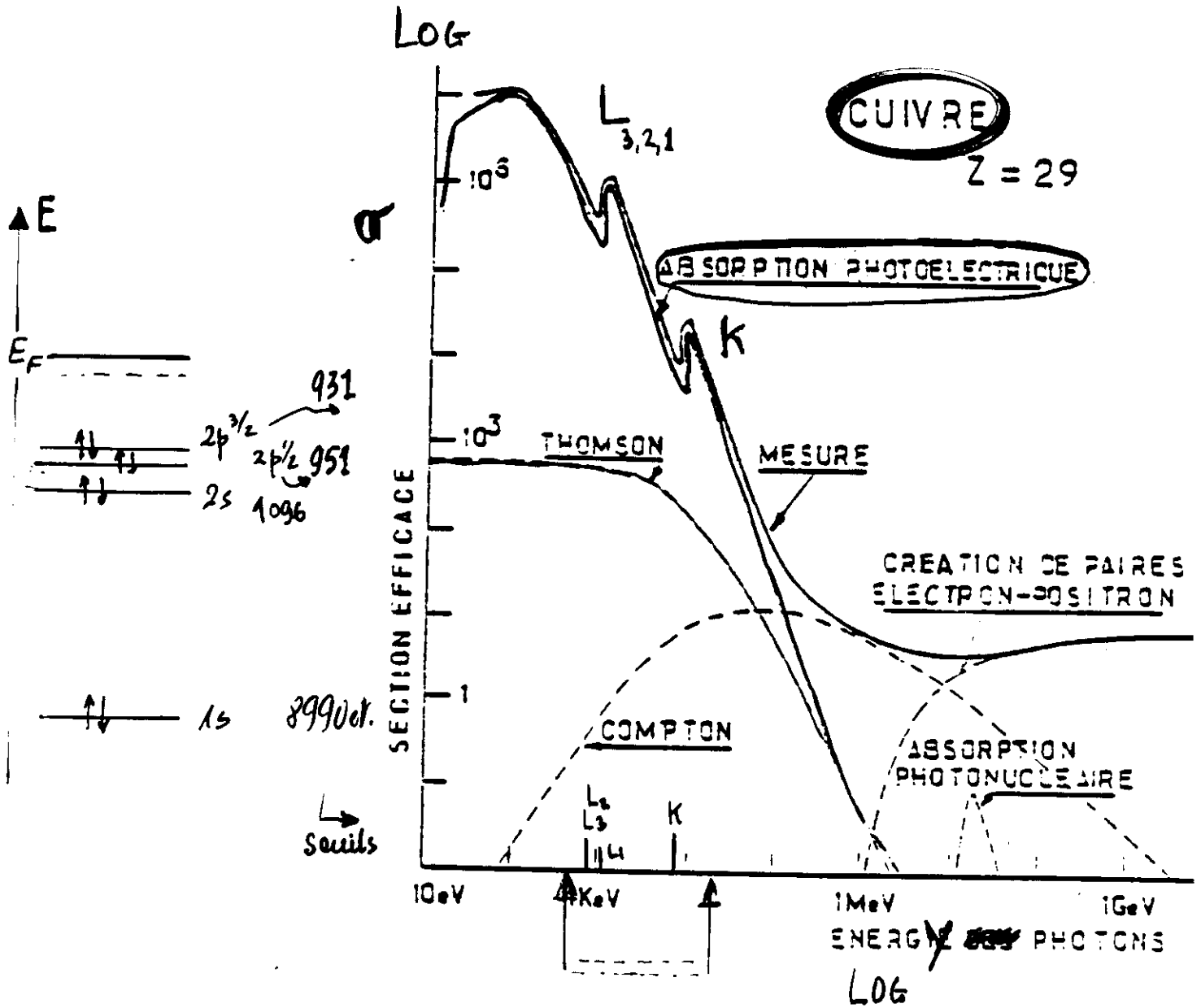
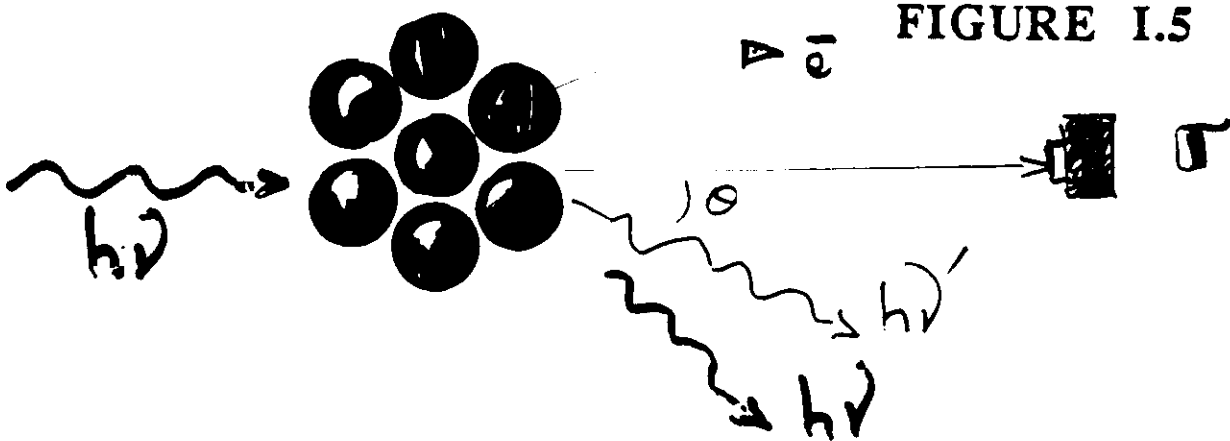


FIGURE I.5



The x-ray absorption cross-section

The Golden Rule $W = e\vec{r} \cdot \vec{E}$

$$\sigma = (2\pi/\hbar) \sum_f |\langle f | W | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

Expansion up to the electric quadrupole term

$$\exp[i(\vec{k} \cdot \vec{r})] \approx 1 + i\vec{k} \cdot \vec{r}$$

$\lambda \gg r$

Absorption cross-section including electric dipole and quadrupole contributions

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \left\{ \sum_f \underbrace{|\langle f | \hat{\epsilon} \cdot \vec{r} | i \rangle|^2}_{\text{Dipolar}} \delta(E_f - E_i - \hbar\omega) + \sum_f (1/4) \underbrace{|\langle f | \hat{\epsilon} \cdot \vec{r} \vec{k} \cdot \vec{r} | i \rangle|^2}_{\text{Quadrupolar}} \delta(E_f - E_i - \hbar\omega) \right\}$$

4 TOOLS

- SELECTIVITY $\hbar\omega$ (E_i)
- DICHRUISMS $\vec{E} \cdot \vec{r}$ ($\vec{e} \cdot \vec{z}$ or $(E_x - iE_y)(x + iy)$)
- SELECTION RULES dipole $\Delta l = \pm 1$
- FINAL STATE RELAXATION $\leq |f\rangle$

Règles de sélection dipolaires

Absorption

 l, s, J, m_j

 INITIAL
 Δ
 FINAL

$$\Delta J = 0, \pm 1$$

 sauf $J=J'=0$

$$\Delta l = \pm 1$$

$$\Delta m_j = 0, \pm 1$$

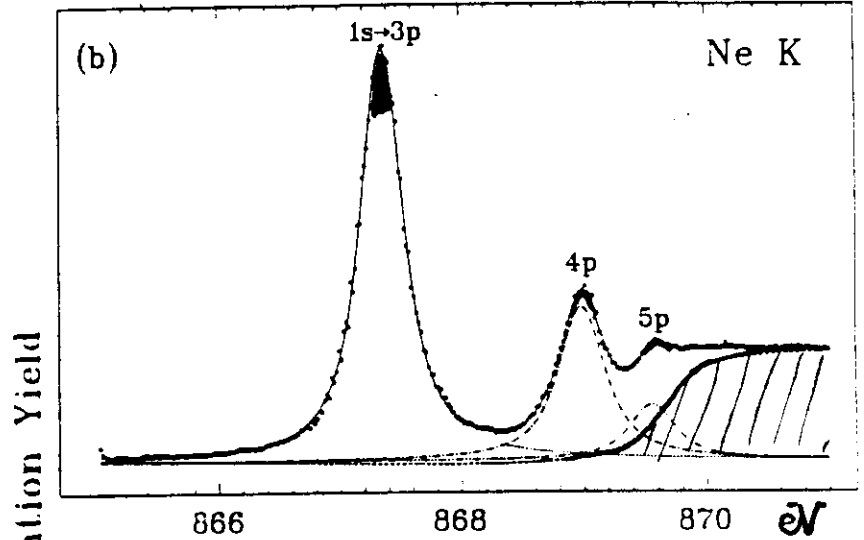
 \vec{E}

$$\Delta s = 0$$

$$|f\rangle = |1s^1 \dots \dots, np^1\rangle$$

Ne

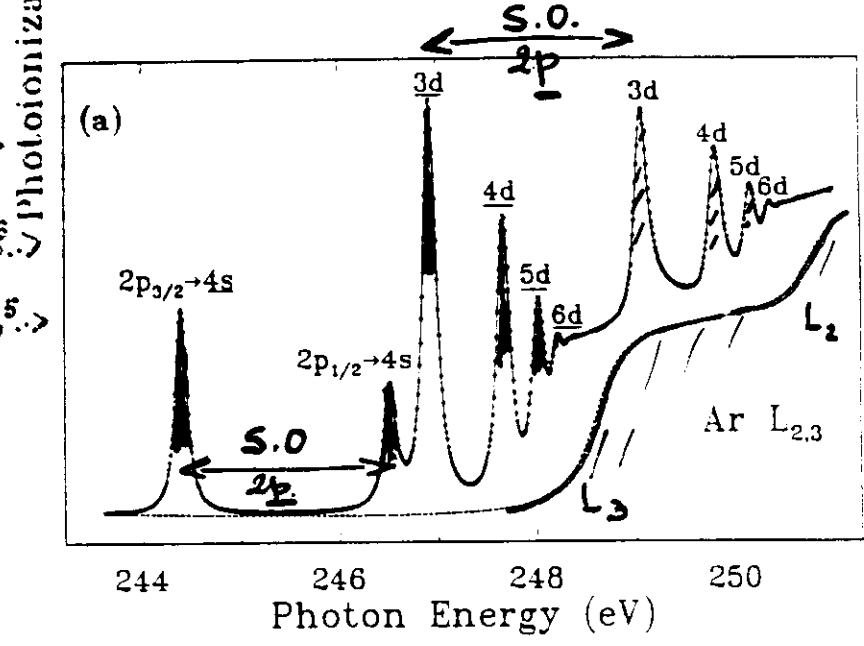
$$|i\rangle = |1s^2 2s^2 2p^6\rangle$$



Ar

$$|i\rangle = |1s^2 2s^2 2p^6 3s^2 3p^6\rangle$$

$$|f\rangle \quad \vec{J} = \vec{L} + \vec{S} \quad \left\{ \begin{array}{l} \uparrow\downarrow \quad 1/2 \quad \dots \quad 2p^5 \dots \\ \uparrow\uparrow \quad 3/2 \quad \dots \quad 2p^5 \dots \end{array} \right.$$



$$|f\rangle_{\alpha} = | \dots 2p^5 \dots \dots n d^1 \dots \rangle \quad n \geq 3$$

$$|f\rangle_{\beta} = | \dots 2p^5 \dots \dots n s^1 \dots \rangle \quad n \geq 4$$

Status and perspectives of high-resolution spectroscopy in the soft x-ray range (invited)

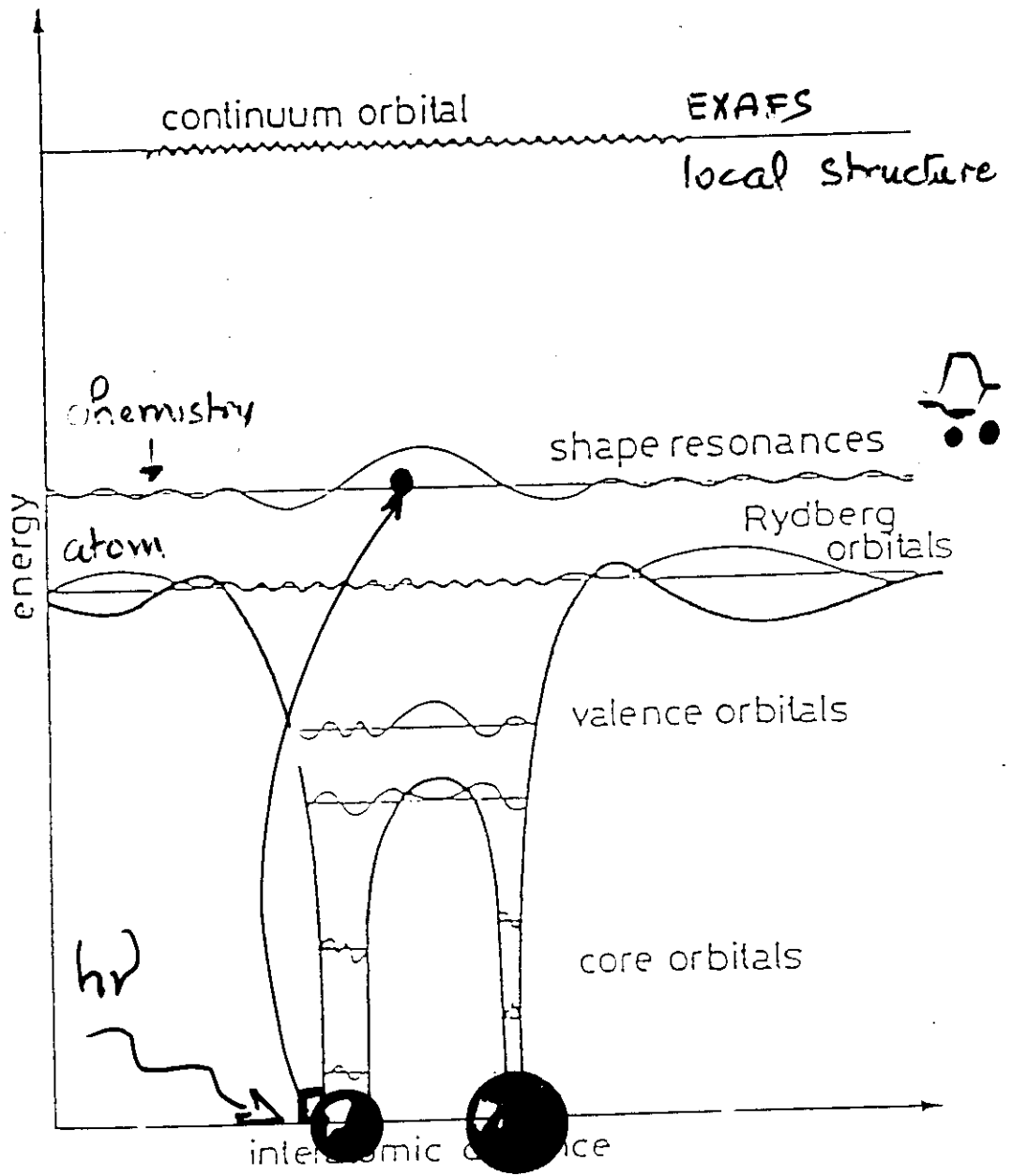
G. Kaindl, M. Domke, C. Laubschat, E. Weschke, and C. Xue
 Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, W-1000 Berlin 33, Germany
 (Presented on 18 July 1991!)

Soft x-rays \iff Allow High energy-Resolution
 MORE INFORMATIONS
 ACCESSIBLE

③

②

①



CORE HOLE in the final state

Status and perspectives of high-resolution spectroscopy in the soft x-ray range (invited)

G. Kaindl, M. Domke, C. Laubschat, E. Weschke, and C. Xue
 Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, W-1000 Berlin 33, Germany

(Presented on 18 July 1991)

SHAPE RESON.

Vibrational fine struct.
 Double excitation

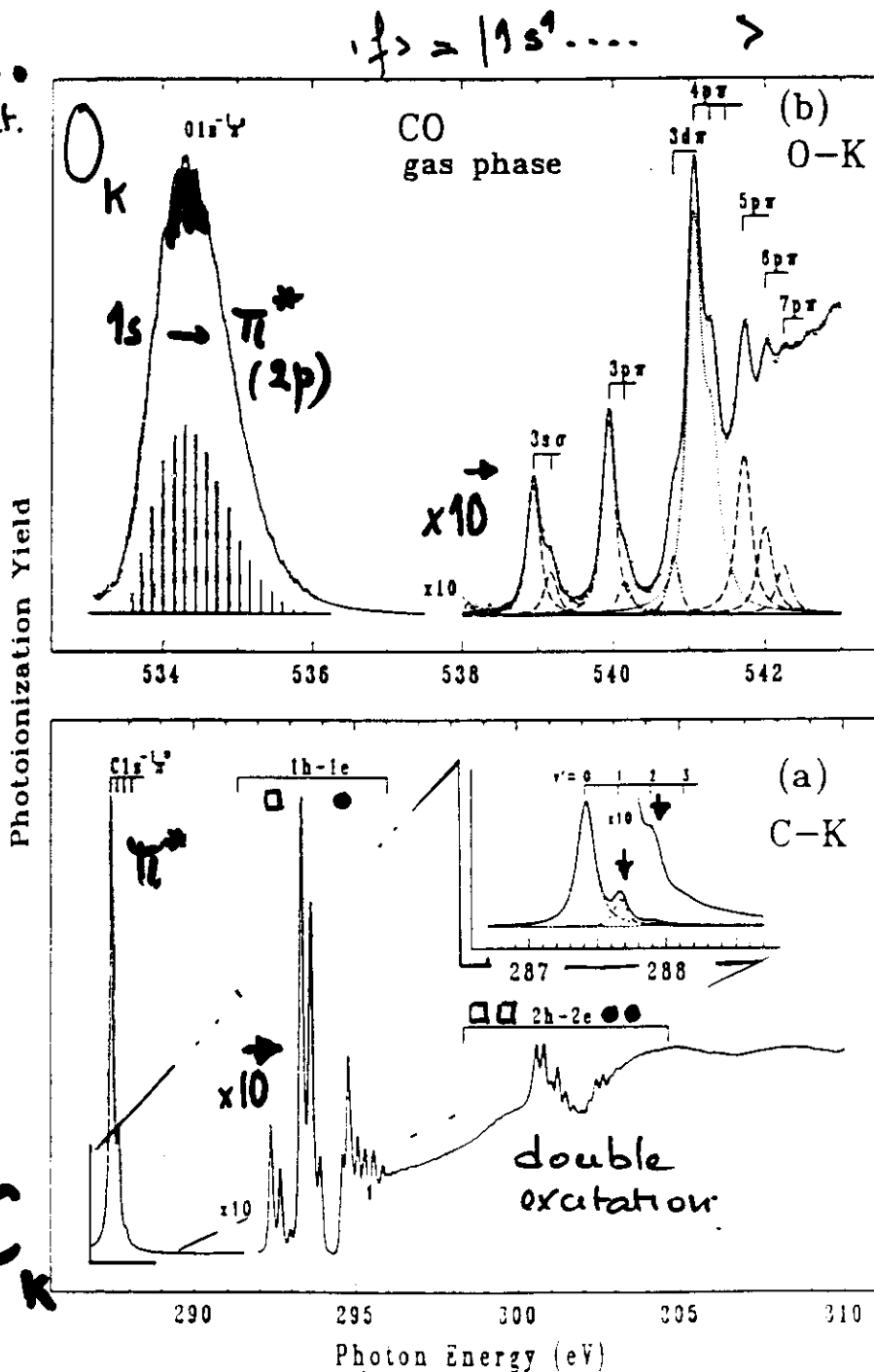
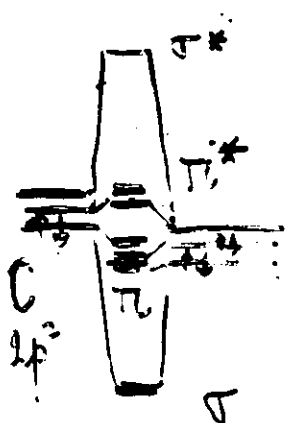
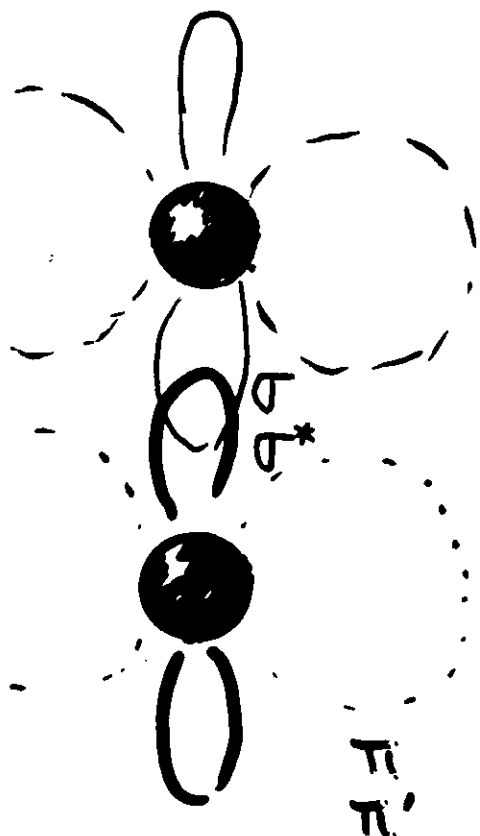
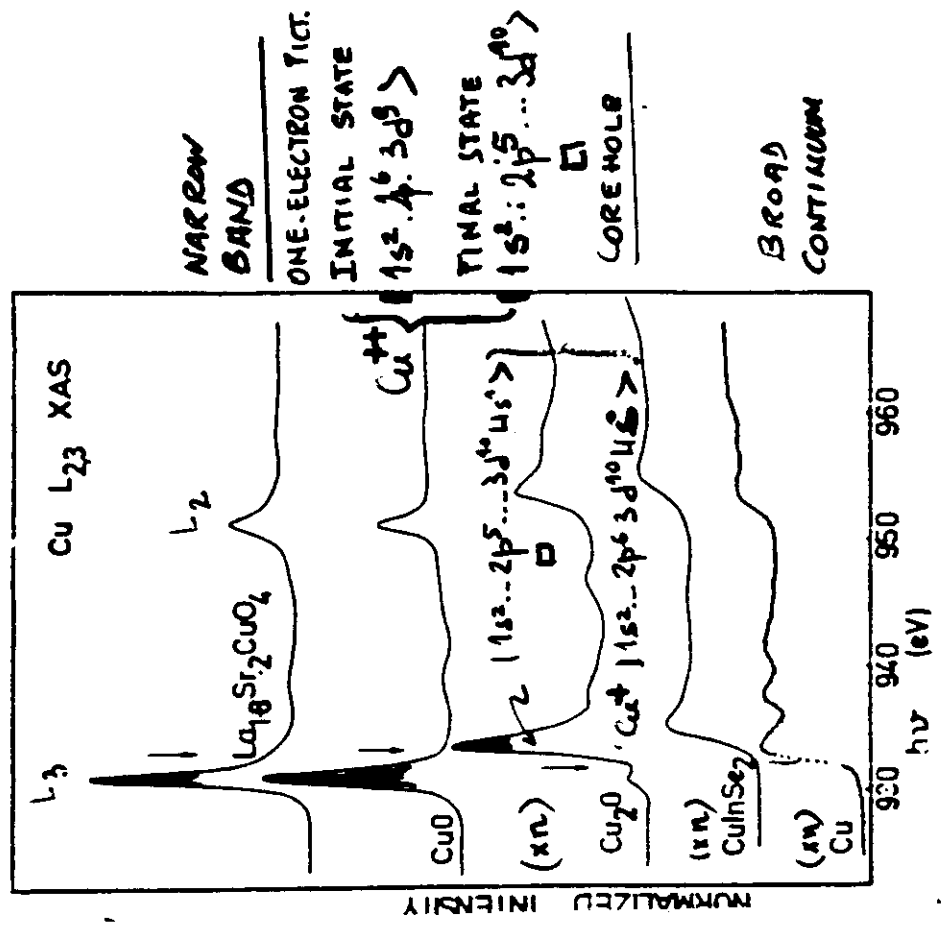
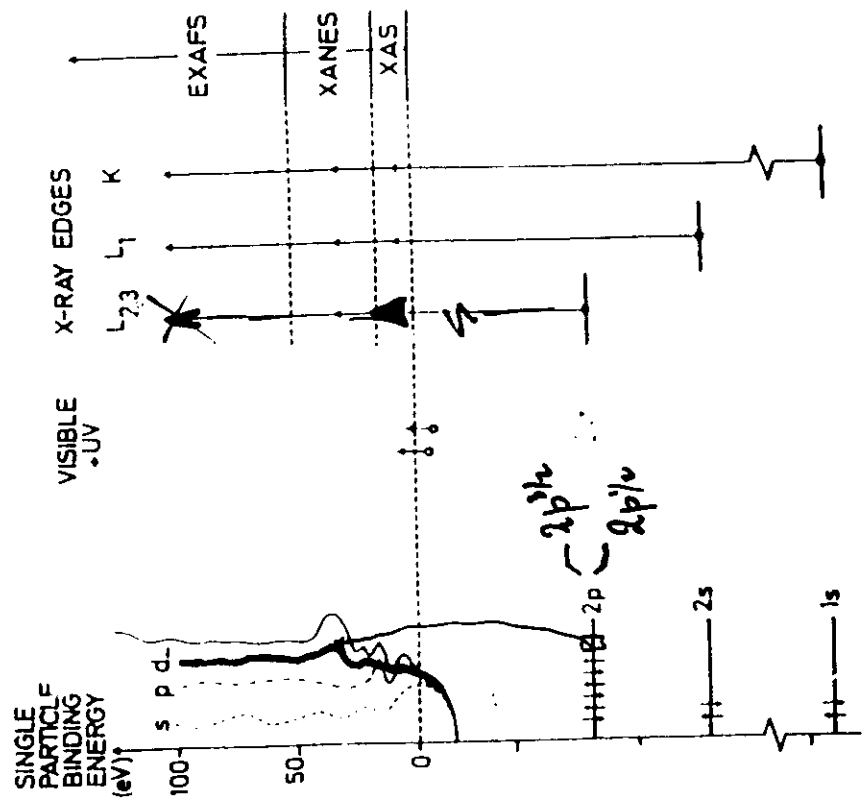
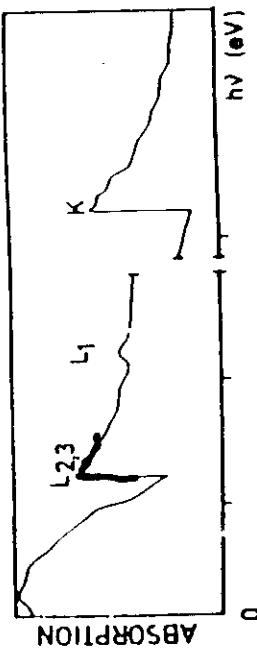
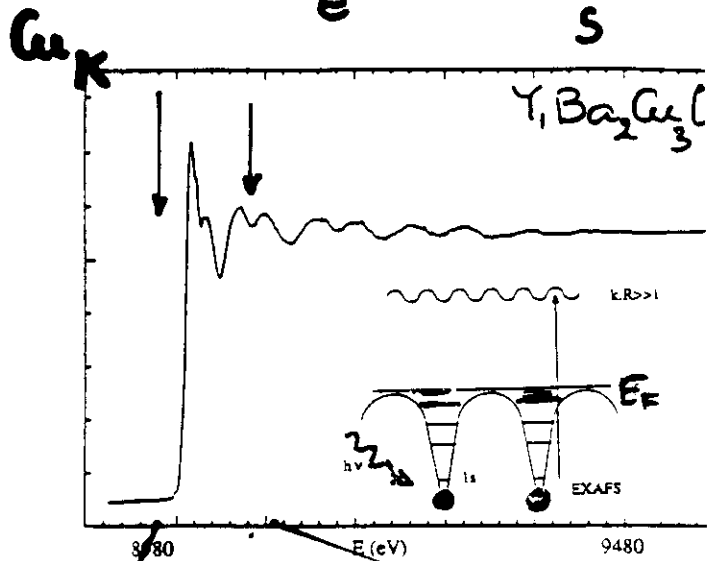
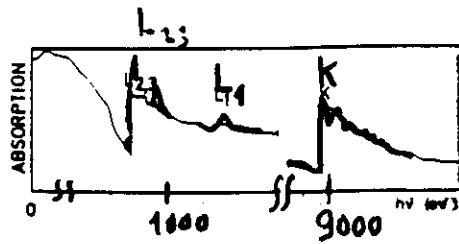
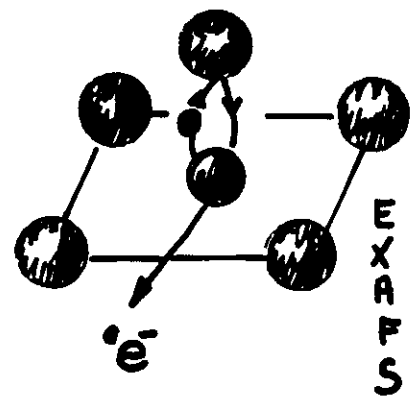


FIG. 3. Photoionization spectra of gas-phase CO close to (a) the C-K and (b) the O-K thresholds. The dominant spectral features in both spectra from excitations of C-1s and O-1s electrons, respectively, into the lowest unoccupied molecular state of Π symmetry; the resolved vibrational structure of the C 1s $\rightarrow \pi^*$ resonance is presented in the inset of (a). The less intense spectral features at higher photon energies (enhanced by a factor of 10 in both cases) stem from 1s-Rydberg-state transitions with vibrational fine structure as well as double excitations (in the C-K case).

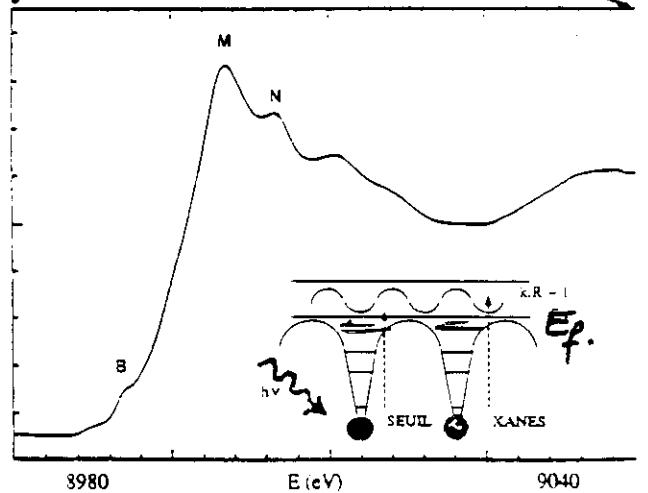


↑ SPIN-ORBIT
 ↓ CORE HOLE
 SELECTION RULES: Δl = ±1

KRONIG 1925

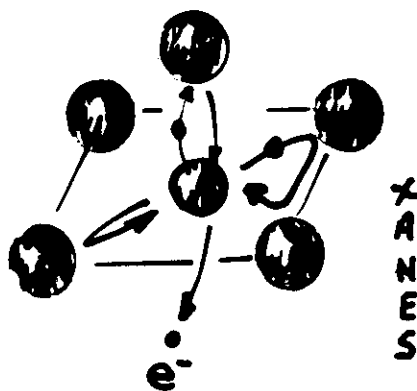
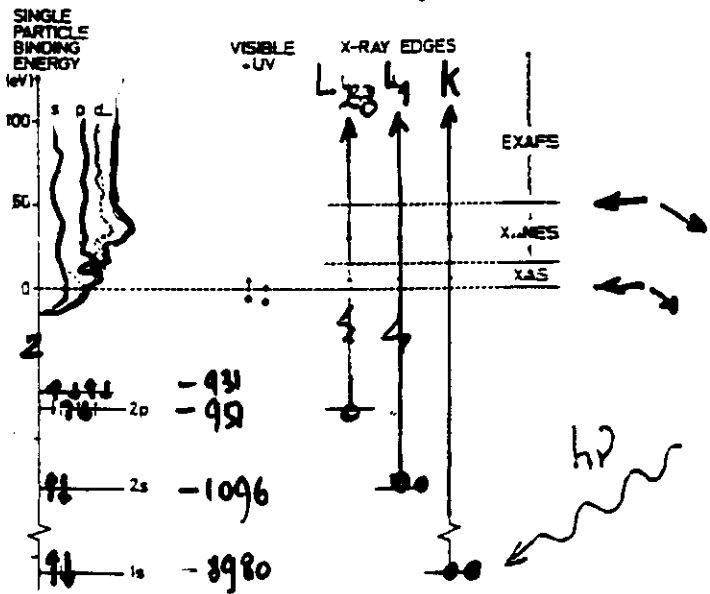


Spectre complet d'Exafs ou les oscillations s'étendent au-delà de 600 eV après seuil.



Présentation du seuil d'absorption de $Y_1Ba_2Cu_3O_{6.5}$ où l'on peut analyser pratiquement les transitions B, M et N proches du seuil, en termes d'orbitales moléculaires. Au delà de 20 eV on est dans le domaine du Xanes.

3 Séparation schématique d'un spectre d'absorption en trois zones.



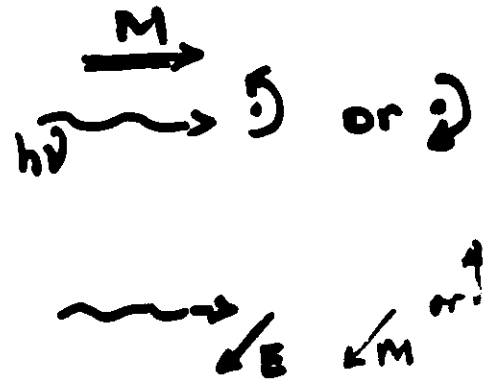
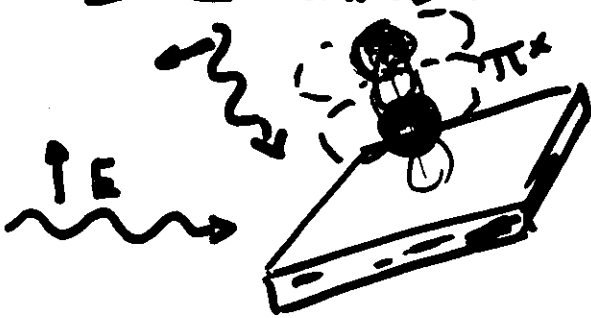
CORE HOLE WELL SCREENED
 DOOZLY SCREENED
 * B identification of CuF:

SUMMARY

I. INTERACTION: **DIPOL. ELECTRIC**
and

II. X.A.S. **Atom-selective**
DOS-selective

III **POLARISATION** **DEPENDENT**



IV **Multiplets** $\langle f |$
or
Multiple scattering

CORE HOLE
PHOTO electron
→ **FINAL STATE**

or
Single scattering EXAFS
(+E)

V **SIMPLICITY** of **INITIAL STATE**

$|i\rangle$
GROUND STATE

II

EXAFS

Model : single scattering
of the photoelectron

Data analysis scheme
tutorials

III

Data Collection

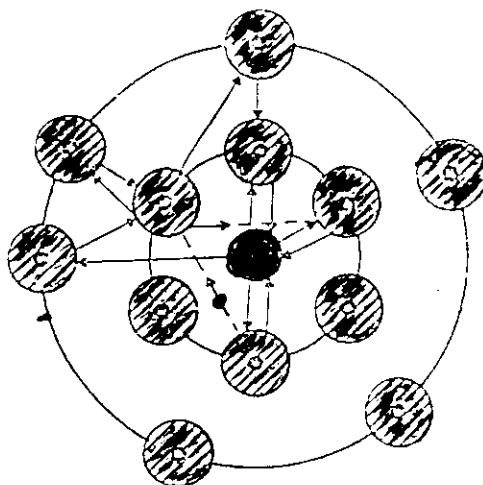
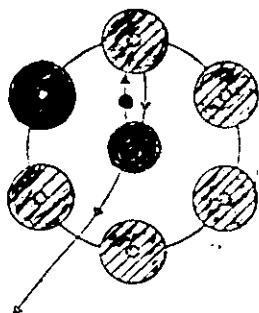
Examples. *

III.3 EXAFS & XANES: SCATTERING MODEL 97-1

EXAFS

XANES

- Absorbing Atom
- Photoelectron

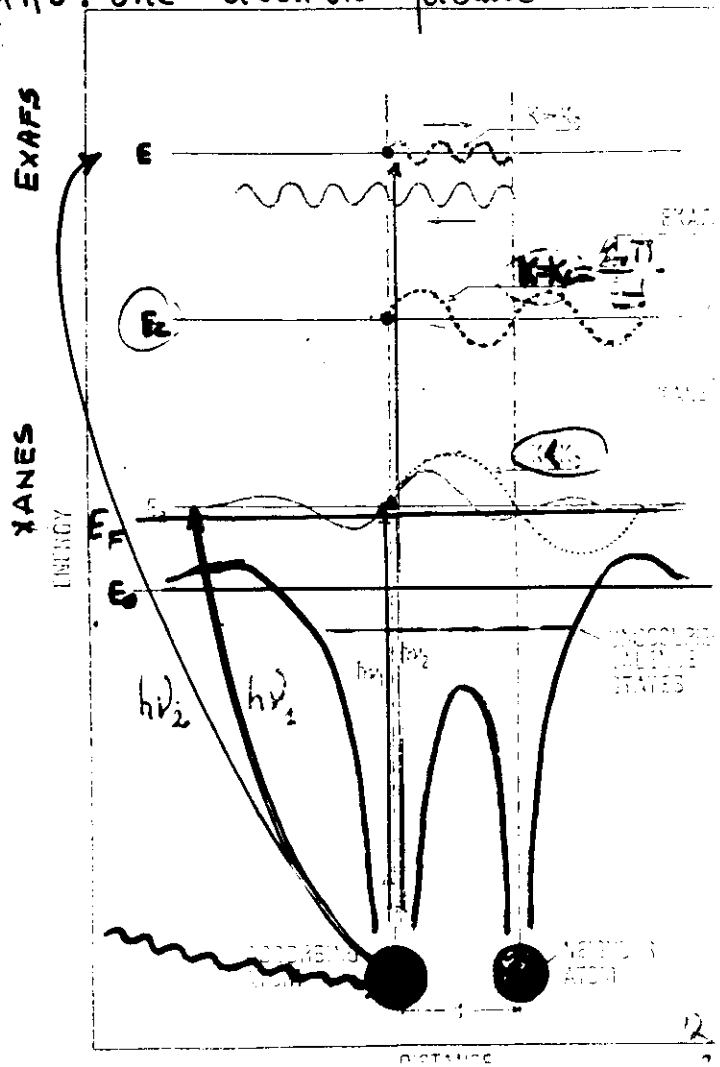
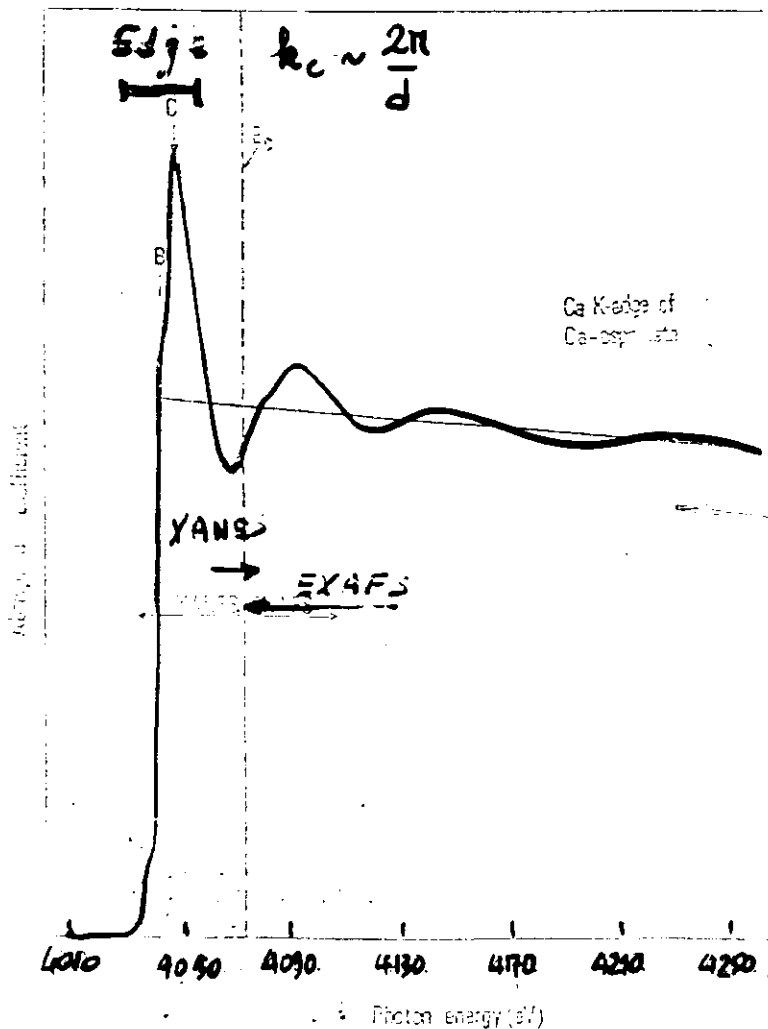


$$\mu \sim \sum_f |\langle f | \vec{R} \cdot \vec{E} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

$$|f\rangle = |f_0\rangle + (\text{scattered wavelets})$$

isolated atom neighbours.

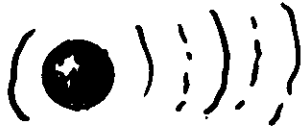
XAS: one electron picture



Heuristic derivation

$$\mu = \sum_f |\langle i | \vec{R} \cdot \hat{E} | f \rangle|^2 \int (\vec{E}_f \cdot \vec{E}_i - \hbar \omega)$$

ISOLATED ATOM



$$|f_0\rangle \sim \frac{e^{i(kR_f + \delta'_i)}}{2kR_f}$$

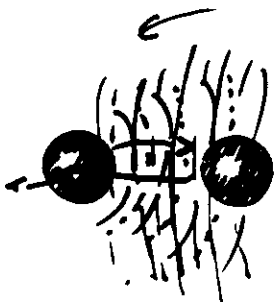
ANG. $Y_{l,0}(\frac{\vec{R}}{R})$ RAD. $h_l^l(kR)$ PHASE. $e^{i\delta'_l(k)}$

≡ OUT GOING WAVE

~ plane wave @ R_f

SURROUNDED EMITTER

$$|f\rangle = |f_0\rangle (1 + \chi)$$



Back scattering

$$f_f(\pi, k) = \frac{1}{2ik} \sum_l (2l+1) (e^{2i\delta'_l} - 1) P_l(-1)$$

Coming back on the central atom

$$\frac{e^{ikR_f}}{R_f} e^{i\delta'_i(k)}$$

$[2\delta'_l + \theta'_l]$

EXAFS SIGNAL
for
a

SINGLE BACKSCATTERER

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} = \frac{-|f_f(\pi, k)|}{k R_f R_f} \sin(2kR_f + \dots)$$

- $\chi(k) = \frac{\mu - \mu_0}{\mu_0}$

- $\chi(k) = -\frac{1}{k} \sum_j \frac{1}{R_j^2} |f_j(\pi, k)| \sin(2k R_j + 2\phi_j(k) + \theta)$

Powder
or
cubic lattice \sum_{N_j} shell

$\times e^{-2\sigma_j^2 k^2} \times e^{-\frac{R_j}{\lambda}}$

- $\frac{\hbar^2 k^2}{2m} = E - E_0$

origin of the kinetic energy

- $e^{-\frac{R_j}{\lambda}}$

mean free path of the photoelectron

- $e^{-2\sigma_j^2 k^2}$

D.N.

static or dynamic disorder

ADVANTAGES of EXAFS.

(i) SELECTIVITY of the "ELECTRON" SOURCE

Cu K 8979.8 Zn K 9659 EUL_{III} 6977 eV.

(ii) GOOD ACCURACY IN BOND LENGTH DET

0.01 Å

(iii) CHEMICAL IDENTIFICATION of NEIGHBORS

& COORDINATION NUMBER

ΔZ large enough, $\pm \frac{1}{4}$ in best cases
(out of 12)

NEEDS

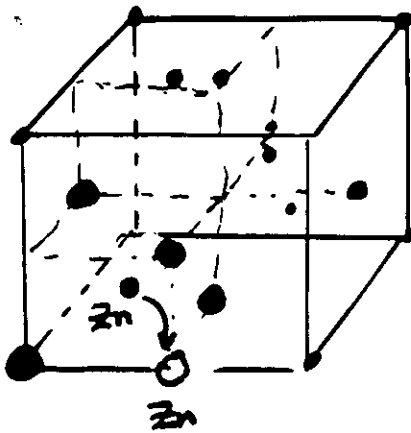
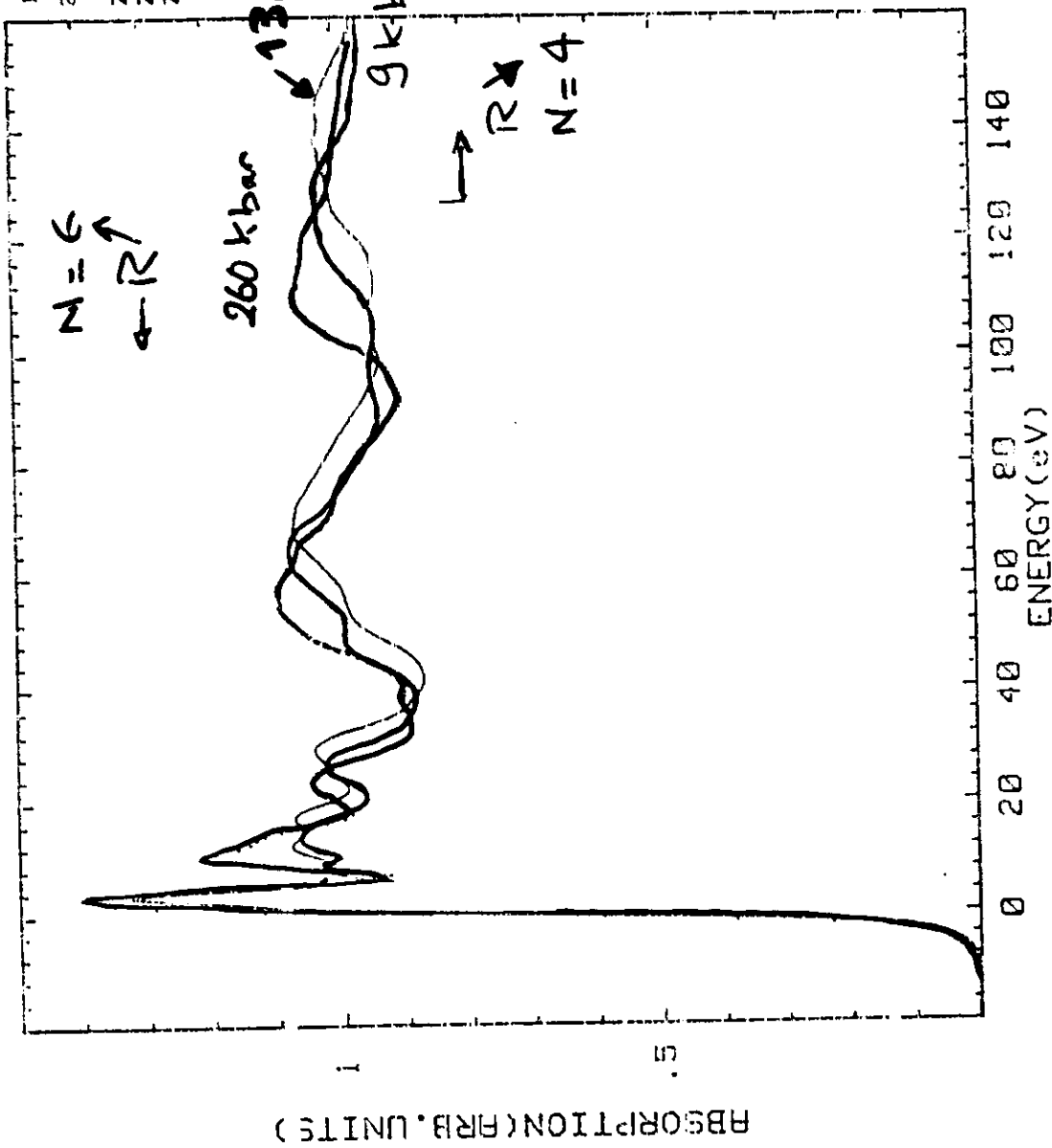
PHASE SHIFTS

& BACKSCATTERING AMPLITUDES

$$\text{MAX} \leftrightarrow 2R + \uparrow = \frac{\pi}{2} + n\pi$$

14 Jun 1990
15:54:21
20 100 20 95

Z1S9
Z1S180
Z1S260

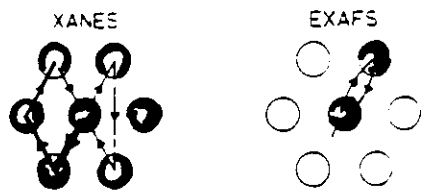


zinc blende (4)

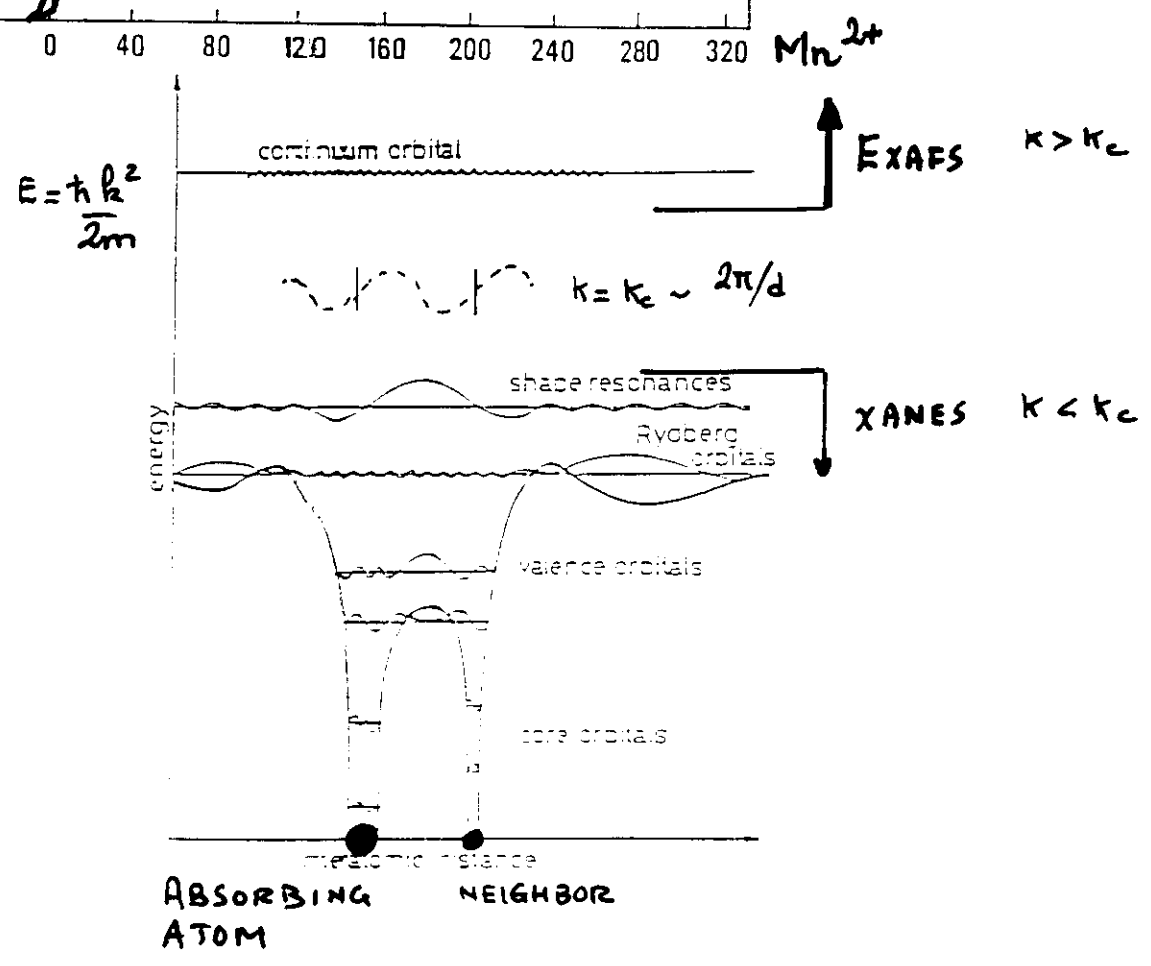
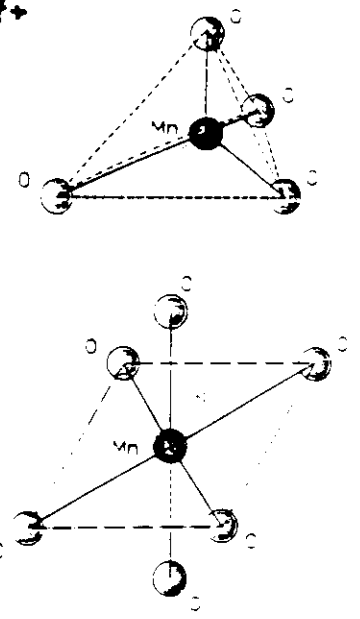
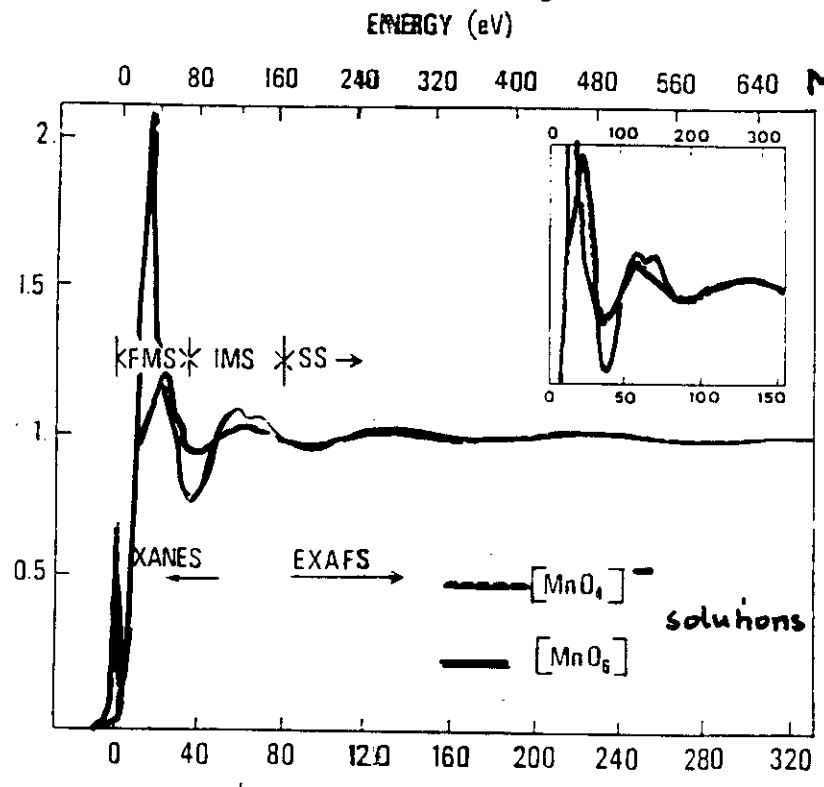
ZnS

Zn k-edge

ZnS



Mn dans des sites octaédrique et tétraédrique



SUMMARY

EXAFS \approx SPHERICAL LEED

\approx DIFFRACTION OF LOW ENERGY ELECTRON

where the SOURCE OF \bar{e} is
INSIDE THE SAMPLE
ON A SELECTED ATOM

EXAFS and OTHER SCATTERING TECHNIQUES

◆ X-RAY SCATT. PAIR CORRELATION FUNCT.
Binary alloy $\left. \begin{matrix} AA \\ AB \\ BB \end{matrix} \right\}$

Bad News EXAFS does not see long distances

Good News EXAFS is accurate to evaluate local ORDER

◆ NEUTRONS $b > 0$ $b < 0$
GOOD CONTRAST
EXAFS $f(\pi, k)$ & its PHASE

◆ X-Ray WEAKER INTERACTION THAN γ
STRONGER ——— THAN γ

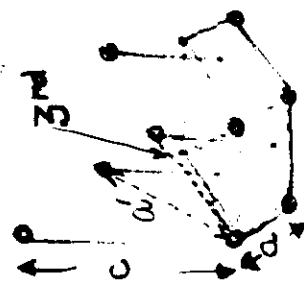
Hard X-rays Sample "REASONABLE VOLUME"

III.3 c

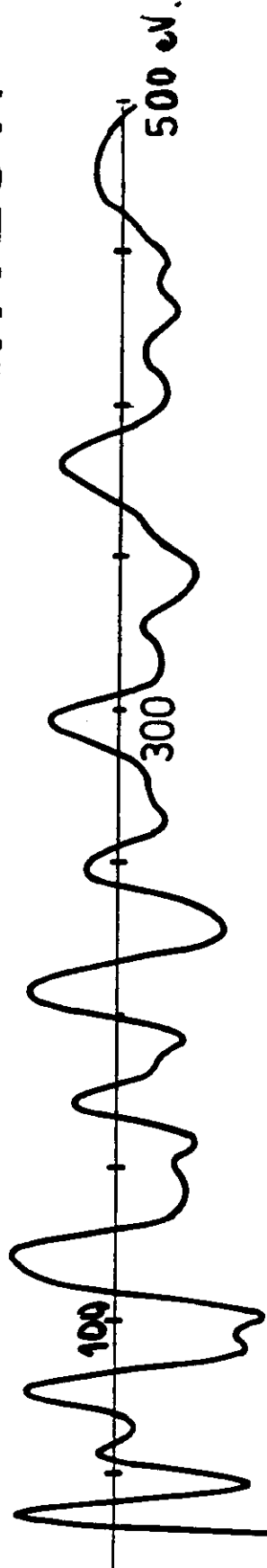
DEBYE - WALLER DAMPING

$a = 2.912 \text{ \AA}$
 $a = 2.66 \text{ \AA}$
 $c/a = 1.86$
 $\nu_3 = 3.925 \text{ \AA}$ at 25 K.

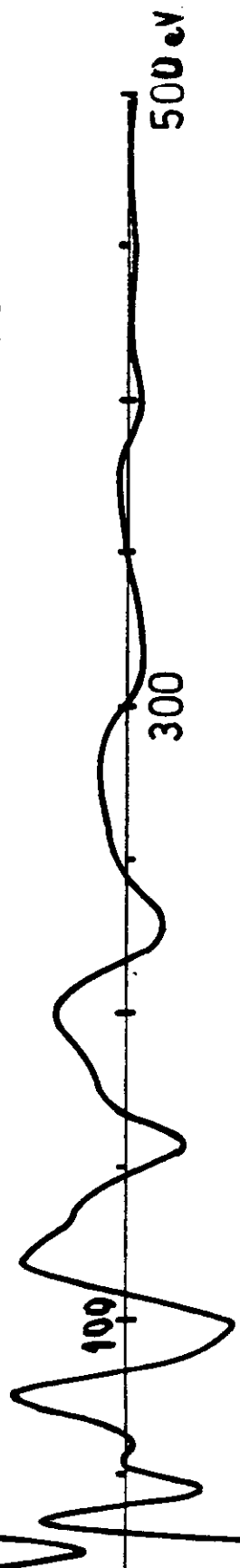
crystallographic data.



Zn: 25 K



Zn: 300 K

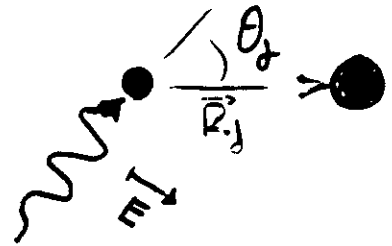


Décalage thermique croît avec la n° couche

Rabe et al. : Ge, Au Analyse avec Einstein

$$X(r_2) = - \frac{\frac{1}{2} \frac{d^2 \langle \sigma \rangle}{dt^2}}{k R_j^2} \sin(2k R_j + \phi) \quad 3 \cos^2 \theta_j$$

$$\cos \theta_j = (\vec{E}, \vec{r}_j)$$



$$\text{AVERAGING} \quad \longrightarrow \langle 3 \cos^2 \theta_j \rangle = 1$$

ASSUMPTIONS

- 1 \bar{e} transition
+ INGREDIENT (core hole relaxation)
 - Plane wave
 - SINGLE SCATTERING
- } NOT NECESSARY
USED for
1) SAKE OF CLARITY
2) PRACTICAL APP.

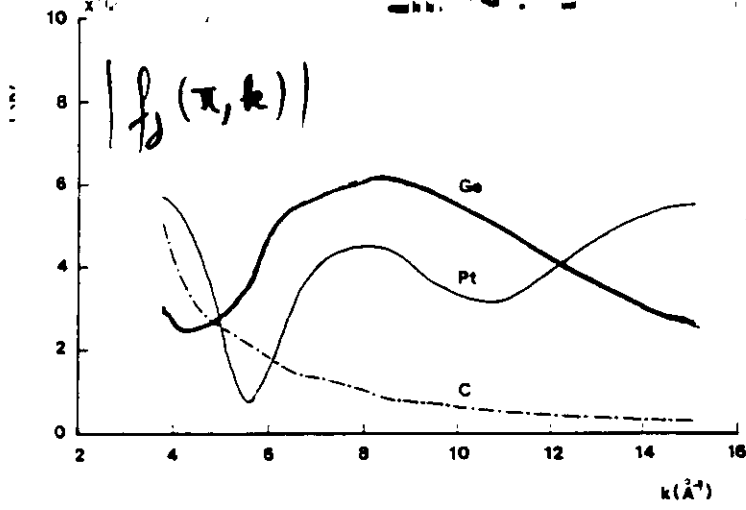


Figure 6.4. Theoretical backscattering amplitudes versus k for C ($Z = 6$), Ge ($Z = 32$), and Pt ($Z = 78$) after Teo and Lee (14).

\neq amplitudes

Pt

Ge

C

Total phase

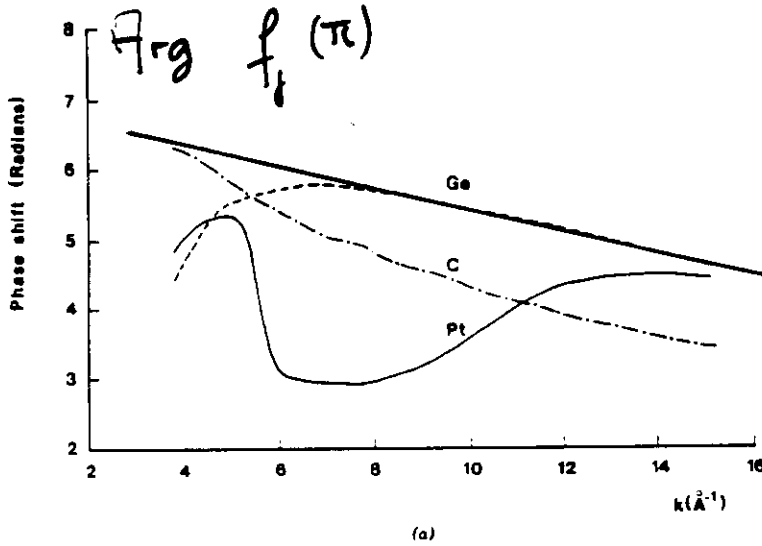
$$2kR_j + \psi(k)$$

$$\psi(k) = 2\delta_1(k) + \theta_j(k)$$

$$\left\langle \frac{1}{2} \frac{d\psi(k)}{dk} \right\rangle \lesssim 0.40$$

low Z elements

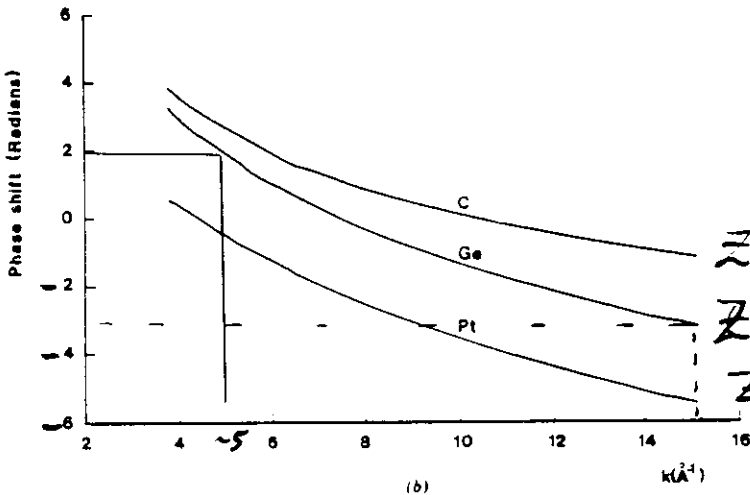
high Z : $\psi(k)$ non monotoneous.



average slope

$$-0.15 \text{ \AA}$$

$$\frac{d\theta_j}{d(2\theta)} \sim 0.05 \text{ \AA}$$



$Z = 6$
 $Z = 32$
 $Z = 78$

C
Ge
Pt



$$\left\langle \frac{1}{2} \frac{d(2\delta_1)}{dR} \right\rangle = -0.5 \text{ \AA}$$

$$\text{Phase} = 2kR_j + 2\delta_1(k) + \theta(k)$$

\downarrow 85% \downarrow 13% \downarrow 2%

\Rightarrow VERY GOOD EVALUATION of DISTANCES

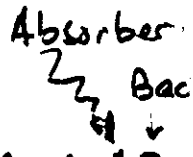
III 5.2

Phase shifts & amplitudes

* Theoretical evaluations

Excellent for phase shifts

GOOD for AMPLITUDES

* Best procedure to evaluate ϕ for the AB 

a/ Measure a well-known sample with a simple lattice with a structure close to the UNKNOWN sample with A as absorber B as backscatterer

b/ Extract phase shift $\phi(k)$ and amplitudes $|f(\pi, R)|$

c/ Transfer into the data analysis of the unknown sample.

* KEEP STANDARDS & INVESTIGATED SAMPLES AS CHEMICALLY CLOSE AS POSSIBLE

* WELL-CONDITIONED PROBLEM HIGH PRESSURE EXP. SAMPLE @ $P=0 \Rightarrow$ STANDARD

III. 4 EXAFS: LOCAL & SELECTIVE PROBES
useful for

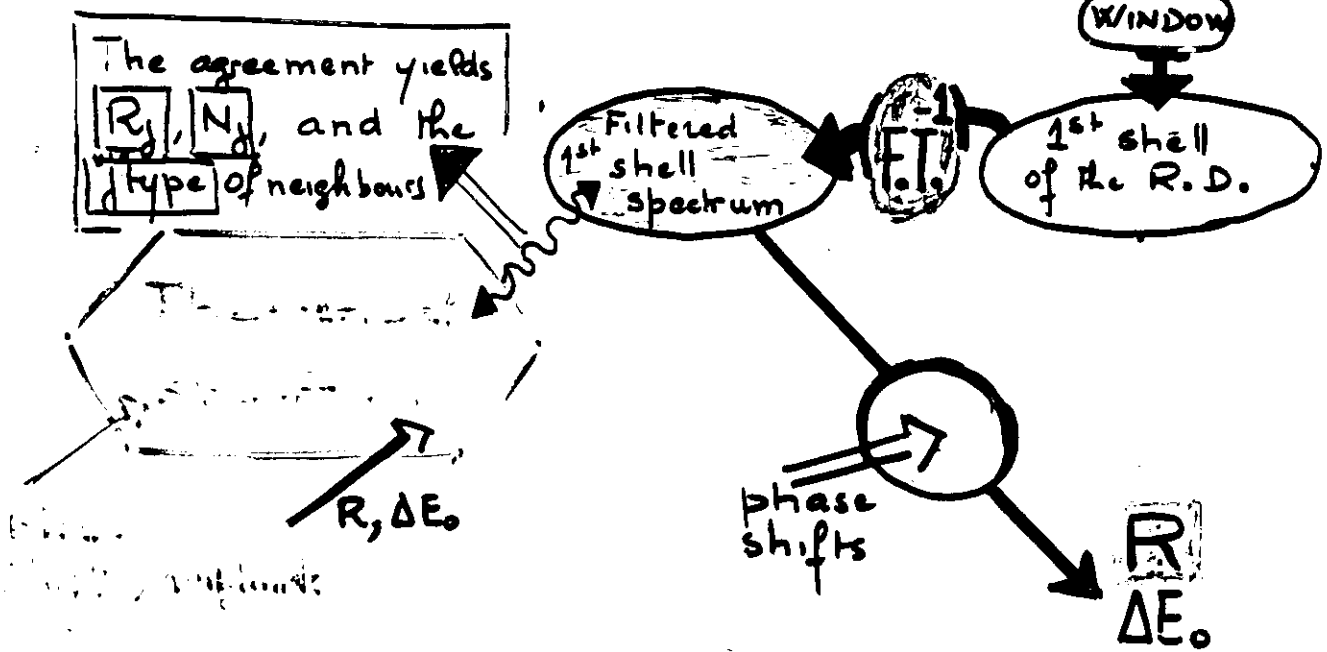
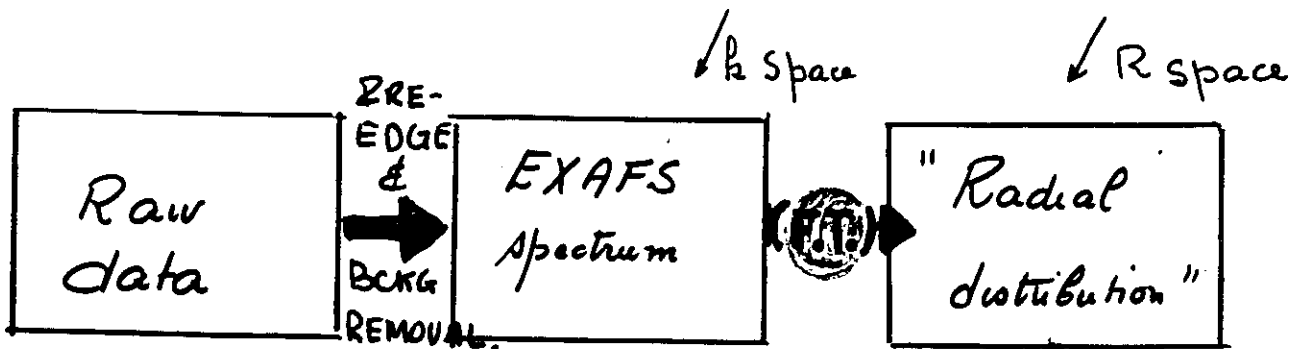
- isolated IMPURITY in a MATRIX.
local distortion
- local symmetry determination.
tetra or octahed. sites
- small particles
Clusters (metallization), catalysis
- dilute samples

SURFACE PHYSICS	< monolayer on SURFACE (EXAFS)
PHYSICS	Phase transformation Actual phase of sandwiched film. Thin films -- , Supra
BIO PHYSICS	Fe in Hemoglobin. Reactivity CO , O_2
GEO PHYSICS	High Pressure, High Temp.
CHEMISTRY	In-situ experiments Battery, Electrochemical
MATERIALS SCIENCE	Subconductors Semiconductors Insulators Magnets, Alloys --

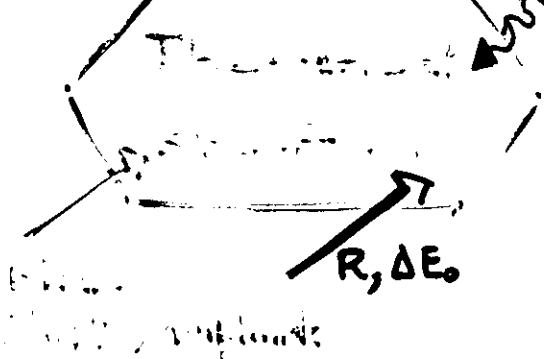
II.2 DATA ANALYSIS

Q/ SCHEME

$$\left\{ \begin{array}{l} \Delta E_0 = E_0 - E_{\text{Threshold}} \\ \frac{k^2 k^2}{2m} = E - E_0 \end{array} \right.$$



The agreement yields **R_j, N_j**, and the type of neighbours



HOMOGENEOUS SHELL

HOMOGENEOUS SHELL

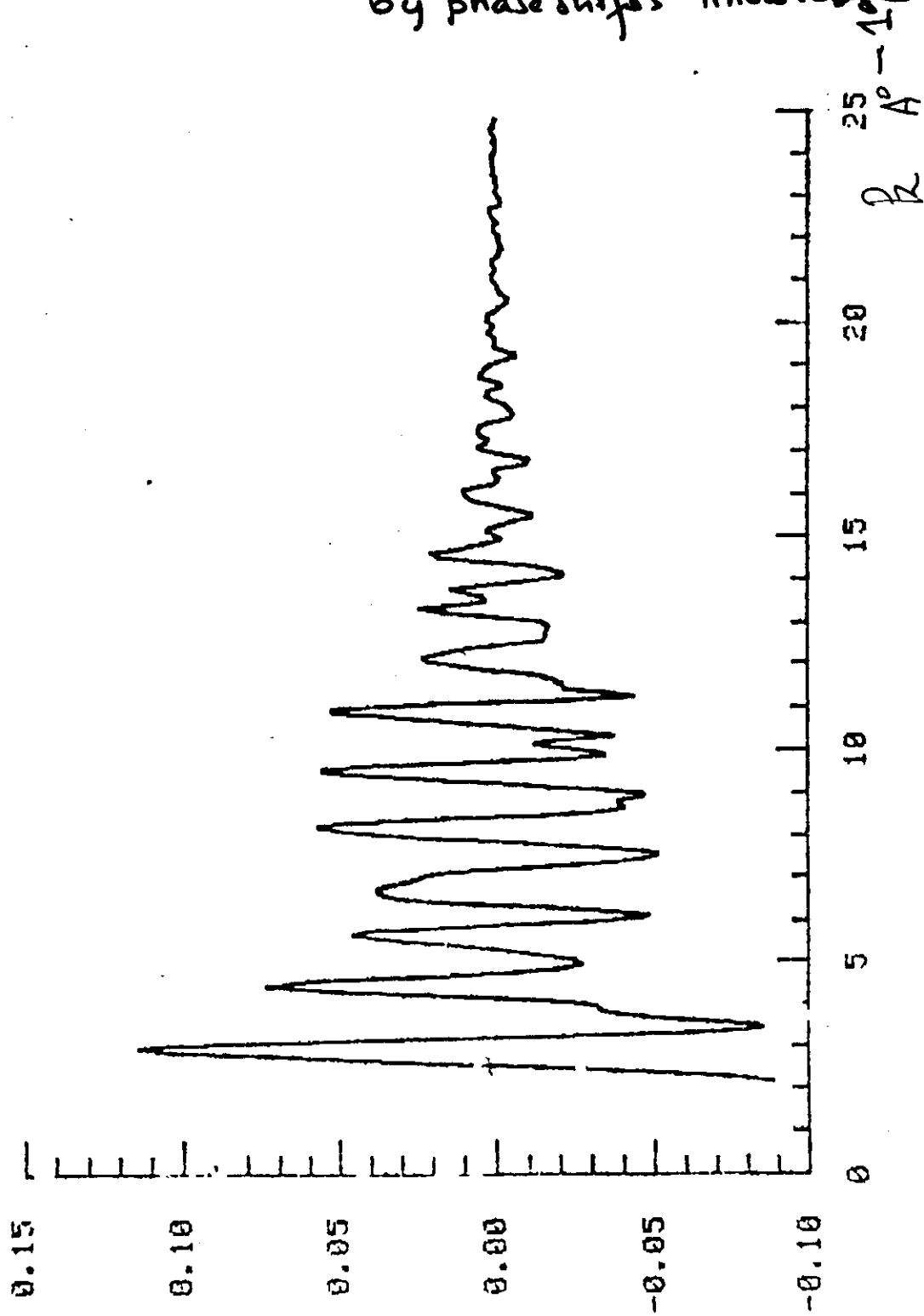
fitting

III. S.d

EXAFS SIGNAL

17 oscillations

⇒ Accuracy limited by phase shifts knowledge



Rhodium Foil. ^(-fc) (Data SSRL)

D. SAYERS. NCSU line I 5 Feb 81.

	shell #	k-range	λ	N	R	Δσ² · 10⁴ Å²	E ₀ (eV)	
MODEL ← → Phase shifts & Amplitude	1	5-17	2 ₁	12	2.69	2.23	-0.24	
	1	6-16	"	11.8	2.69	2.13	.42	
	2	5-17	"	4.77	3.80	1.96	-0.06	
	2	6-16	"	4.78	3.80	1.97	-0.24	
	3	5-17	"	24.7	4.67	3.12	-0.4	
	3	6-16	"	25.1	4.67	3.21	-0.4	
	4	5-17	"	12.1	5.38	3.14	+0.4	
	4	6-16	"	12.78	5.38	3.38	+0.2	
			A ⁻¹					

EXAFS ANALYSIS

Not "TOTALLY" SOLVED?

- Phase shifts and Amplitude TRANSFERABILITY
App. Muffin Tin

- Many body problems

BREAKTHROUGH

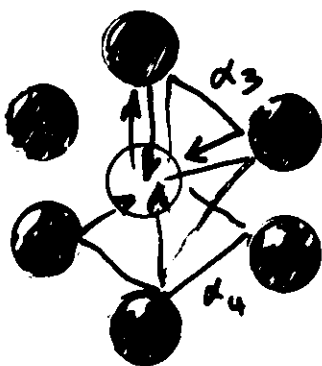
- MULTIPLE SCATTERING

C. Natoli

P. Durham

J. Rehr

(FEFF code)

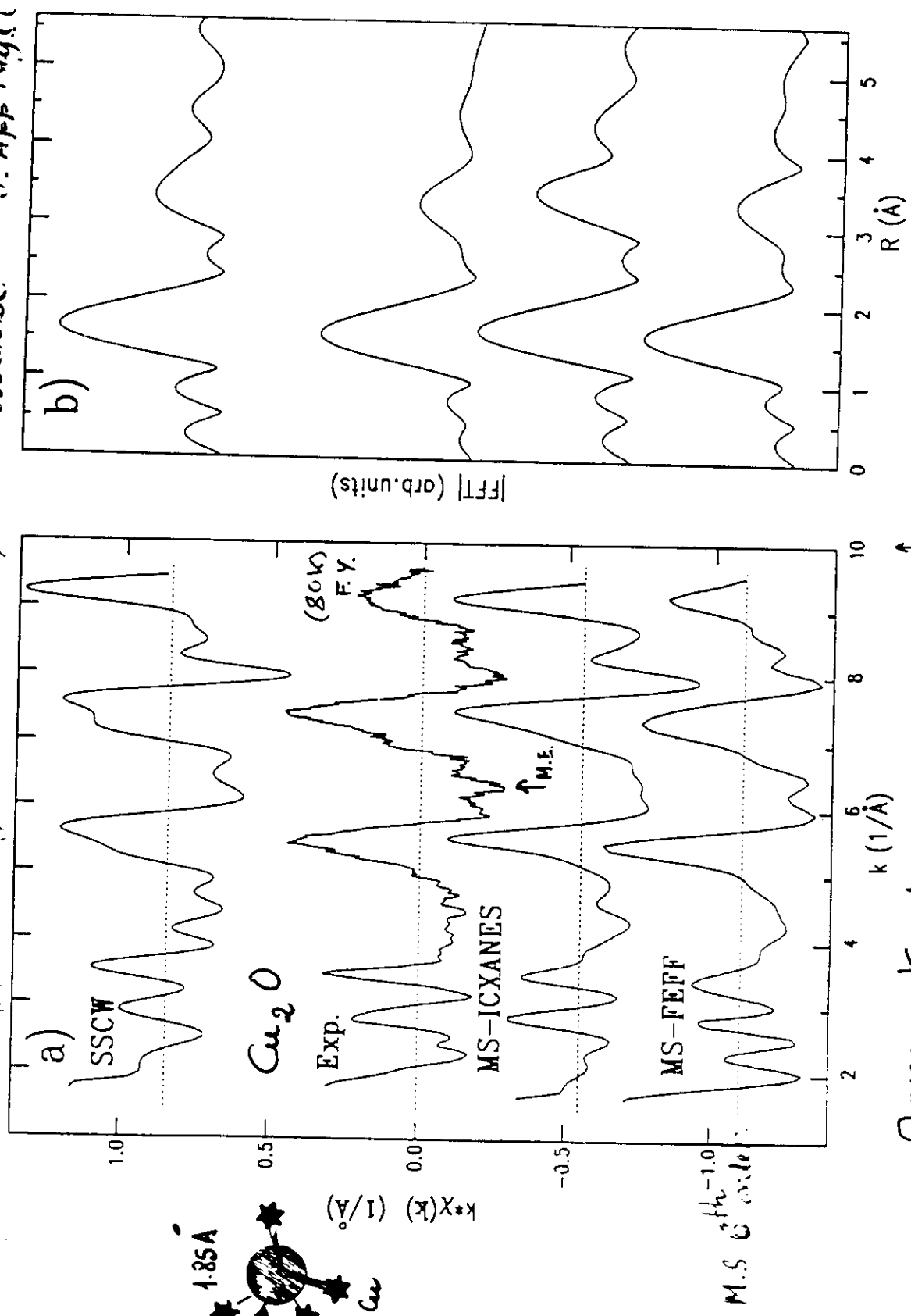


Long "multiple" paths

- Less efficient
- more numerous

- CUMULANT ANALYSIS σ^2, c^3 (T)

C. Dagg, L. Tröger, A. Brunnhs, K. Babenschke, J. Appl Phys (1993)



Oxygen K-edge \uparrow 3100V

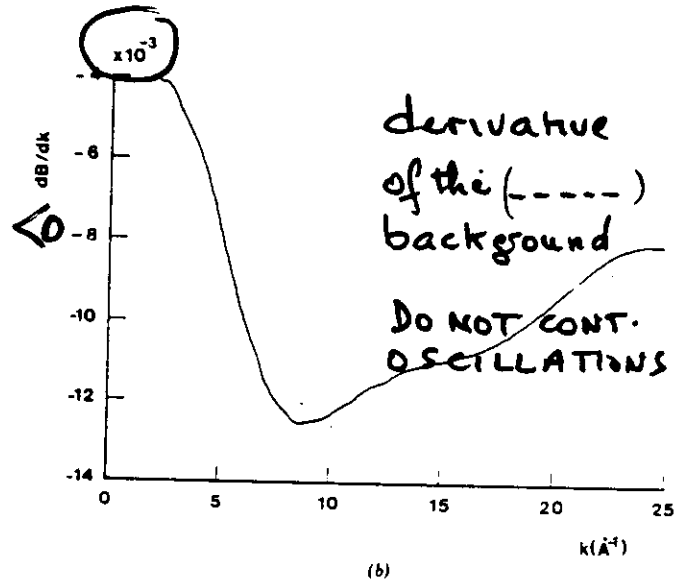
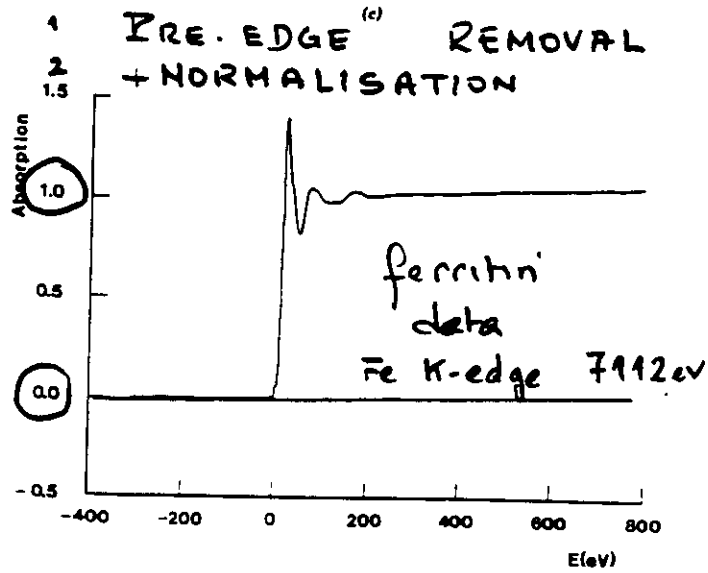
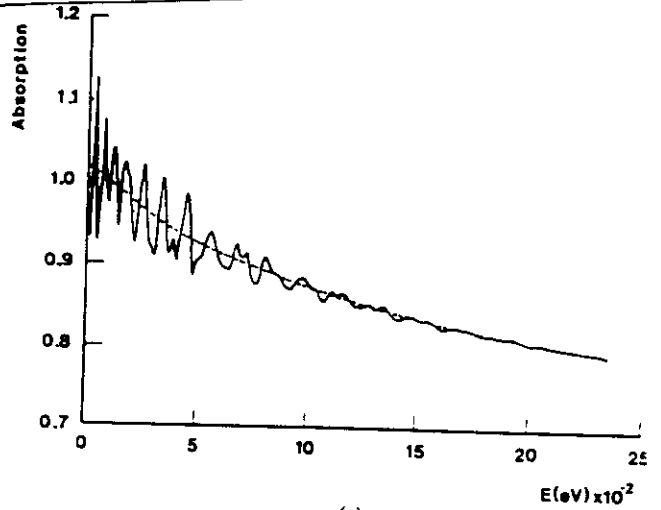
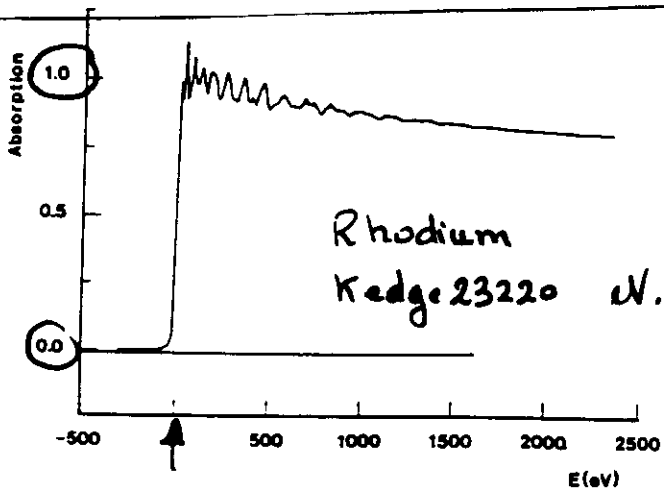


Figure 6.1. (Continued)

Figure 6.2. (a) The normalized data of Fig. 6.1c for rhodium metal showing on an expanded scale for the data above the edge. The calculated background curve used to extract the EXAFS is shown as a dashed line. (b) The derivative of this background curve versus the photoelectron wave vector k . (c) The normalized EXAFS for rhodium metal plotted versus k .

3 Choice of E_0 as the inflection point.

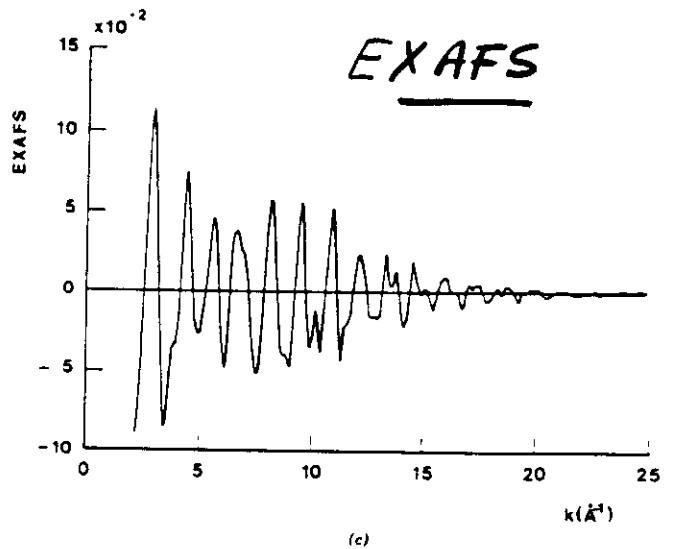


Figure 6.2. (Continued)

D. SAYERS, B.A. BUNKER
Ch 6. El Koningsberger, Zinnz
J. Wiley. Chemical Analysis 92

What do we (try to) learn?

1. FERMI GOLDEN RULE + DIPOLE APPROXIMATION

$$\mu \propto \sum_f |\langle f | \vec{E} \cdot \vec{r} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

- $|i\rangle$ site selectivity
- $|f\rangle$ 2DOS selectivity
+ selection rules
- $\vec{E} \cdot \vec{r}$ Anisotropy sensitivity \neq any sym. breaking
- $|f\rangle$ CORE-HOLE RELAXATION VALENCE SENSITIVITY

2. EXAFS

$$\chi(k) = -\frac{1}{k} \sum_j \frac{N_j}{R_j^2} 3 \cos^2 \theta_j \exp(-2.5j^2 k^2) \exp(-2R_j/\lambda(k))$$

$$|f_j(\pi, k)| \sin(2kR_j + 2\delta(k) + \arg f_j(\pi, k))$$

- Anisotropy sensitivity
- "SPHERICAL LEED" (Low Energy Electron Diff)
- Sensitivity to disorder.

EXAFS = STRUCTURAL PROBE with
LOCAL ABILITY, i.e.
for COORDINANCE

COMPLEX BACKSCATTERING AMPLITUDE
PHASE + AMPLITUDE

WHAT don't we learn ?

details
+

- XANES (multiple scattering) as a TOOL
to access to CORRELATION FUNCTION
BEYOND THE 2nd ORDER
- NEAR EDGE STRUCTURE in HIGHLY CORRELATED
SYSTEMS
(Rare earths, high T_c's)
as an electronic PROBE for
VALENCY
MAGNETISM
- HOW TO GO BEYOND THE ONE ELECTRON
PICTURE .

• -----
THEREFORE → EXTRA WORK

X-ray Absorption Principles, Applications, Techniques
of EXAFS, SEXAFS, XANES, ...
Ed. by J.C. Koningsberger, R. Prins, WILEY Interscience Pub.

HISTORY OF X-RAY ABSORPTION FINE STRUCTURES

R. Stumm von Bordwehr
Laboratoire de Physique du Solide
Université de Nancy I
B.P. 239, F-54506 Vandoeuvre-lès-Nancy

Annales de Phys.
1989/14 / Aout
p 377-400

1. The discovery of X-ray absorption edges

1.1. The prehistory

The question of the origins is always involved, but it would be difficult to date back the X-ray absorption spectroscopy before the eighth of November 1895 in the evening.

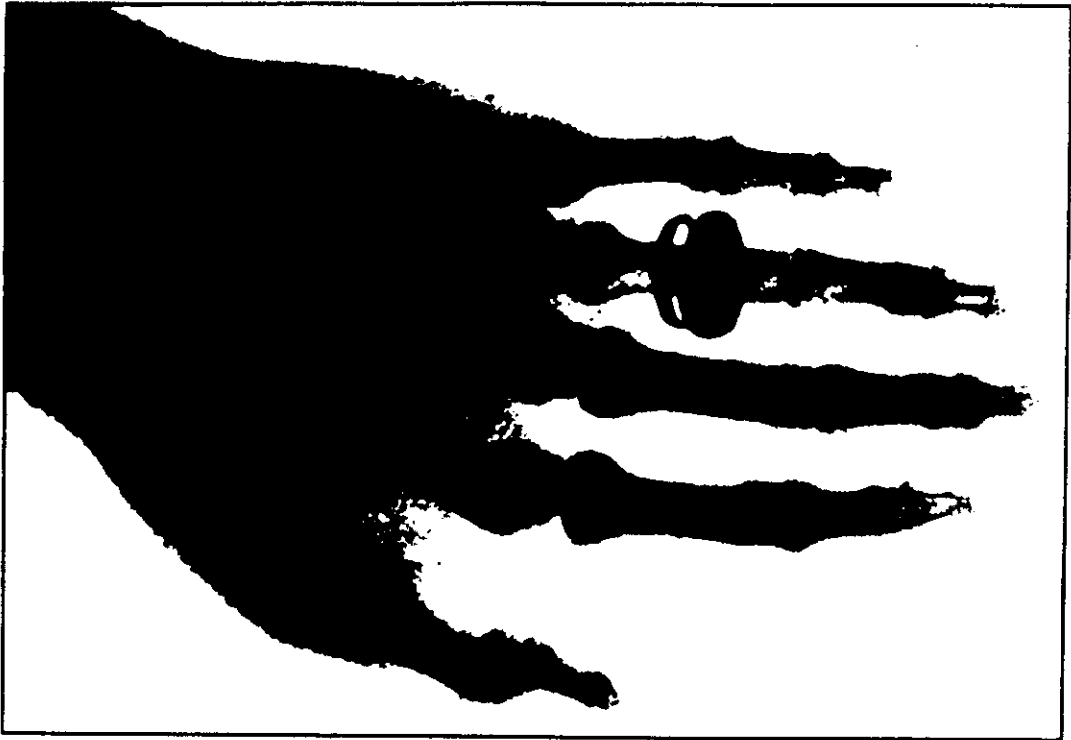
① That very day Wilhelm Conrad Röntgen was studying the discharge of electricity in rarefied gases by operating a Crookes tube (some kind of Crookes tube) wrapped in a black cardboard. Some distance apart, there was a screen covered with barium platinum cyanide. Much to his surprise Röntgen saw the screen glowing: the first X-ray was detected. He reported his observations in a local journal (Röntgen 1895) where, almost incidentally, he named the new rays in a footnote: "Der Kürze halber möchte ich den Ausdruck "Strahlen" und zwar zur Unterscheidung von anderen den Namen "X-Strahlen" gebrauchen (to shorten I shall use the designation "rays", and to differentiate it from the others the naming "X rays")".

② The news spread very fast over the world and created an extraordinary enthusiasm (rather comparable to the one caused by the high T_c superconductors almost a century later): only in 1896 more than 1000 papers were published on the subject (Segrè 1980).

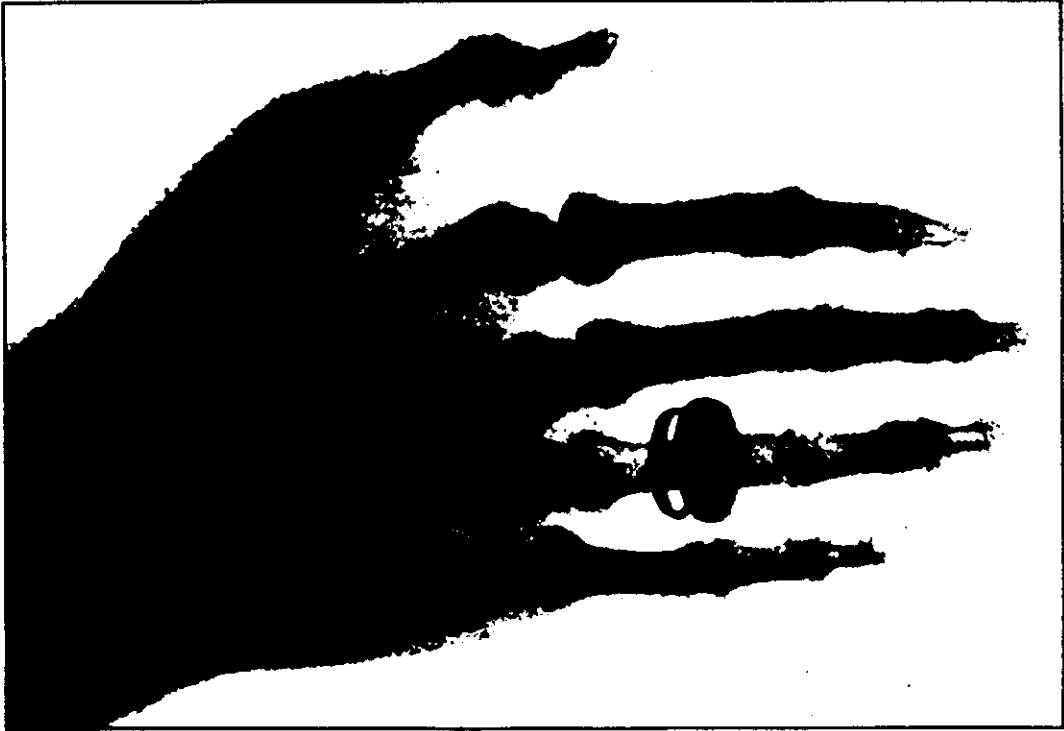
③ The study of the influence of X-rays on matter began immediately. In the course of experiments carried out in the laboratory of the Ecole Normale Supérieure, Jean Perrin (1897) noticed that the metals irradiated emitted charged particles. In 1898 Georges Sagnac discovered that "La surface d'un métal M, frappée par les rayons X, émet de nouveaux rayons que j'ai appelés rayons secondaires du métal M [... et qui ont] la propriété d'être absorbés complètement par le métal M qui les émet [?] (the surface of a metal M, receiving X-rays, emits new rays that I call secondary rays of the metal M and which have the property of being completely absorbed by the metal M which emits them)" (Sagnac 1898a). This was the first allusion to the fact that chemical elements could emit characteristic radiations. Three years later, Sagnac wrote a review article entitled "X-rays, matter and electricity", in which he came to the conclusion that: "Le pouvoir de transformation d'un métal vis-à-vis des rayons X [la fluorescence X] paraît distinguer ce métal d'un autre métal, sauf quand les poids atomiques sont assez voisins (Pb et Pt) ou que les métaux sont des éléments chimiques analogues (Fe et Ni). L'étude de l'action électrique d'un corps frappé par les rayons X permet d'y reconnaître la présence d'une petite quantité de..."

④

⑤



NOV 1895
London



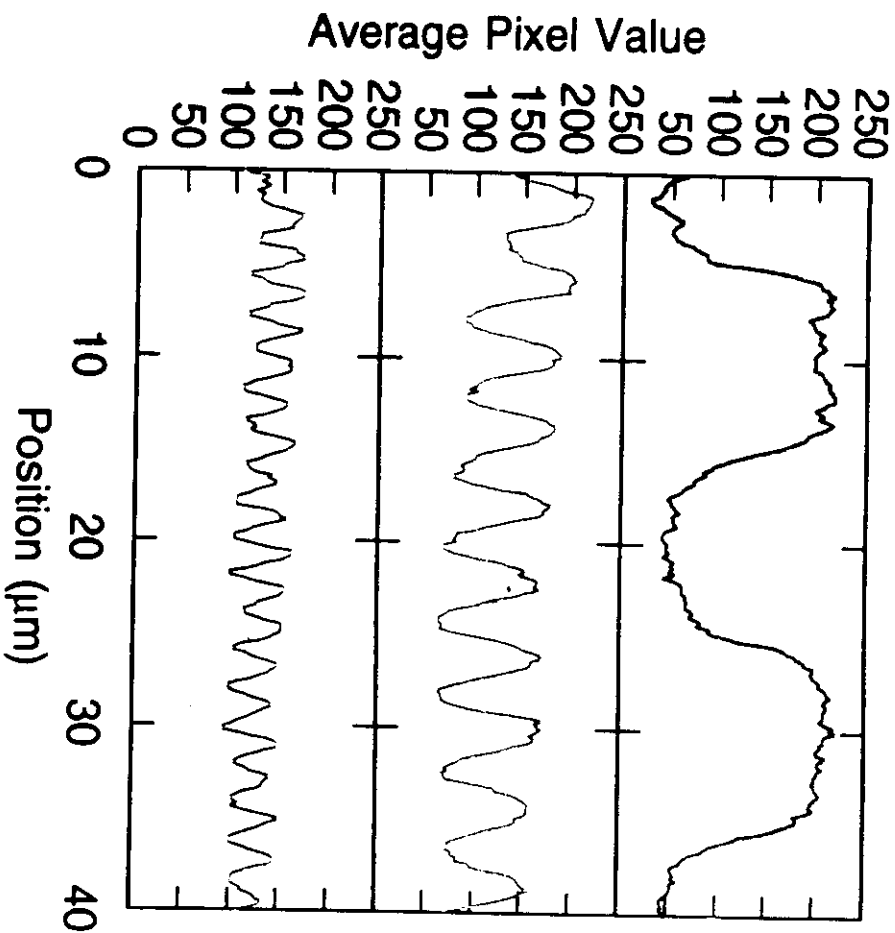
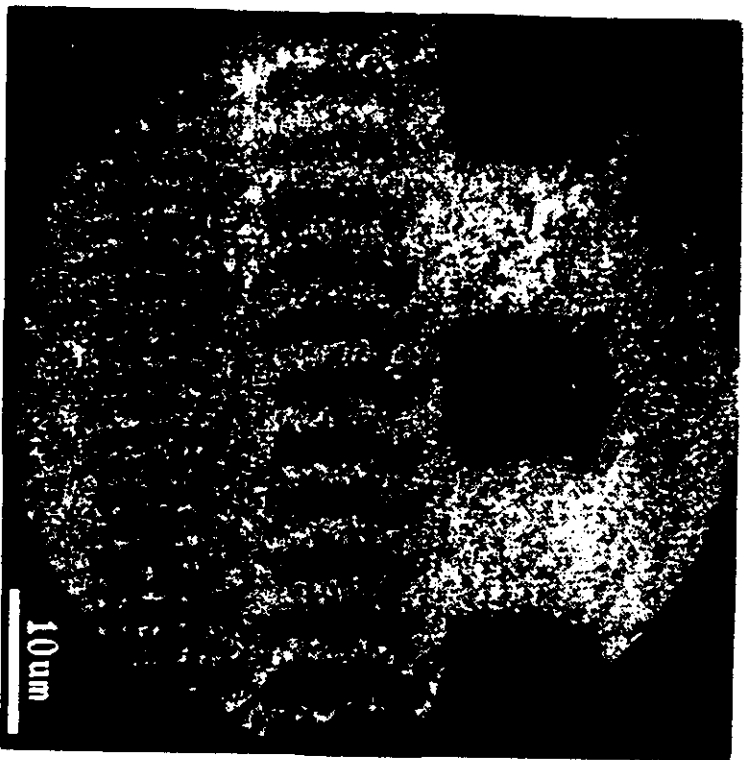


IMAGE =

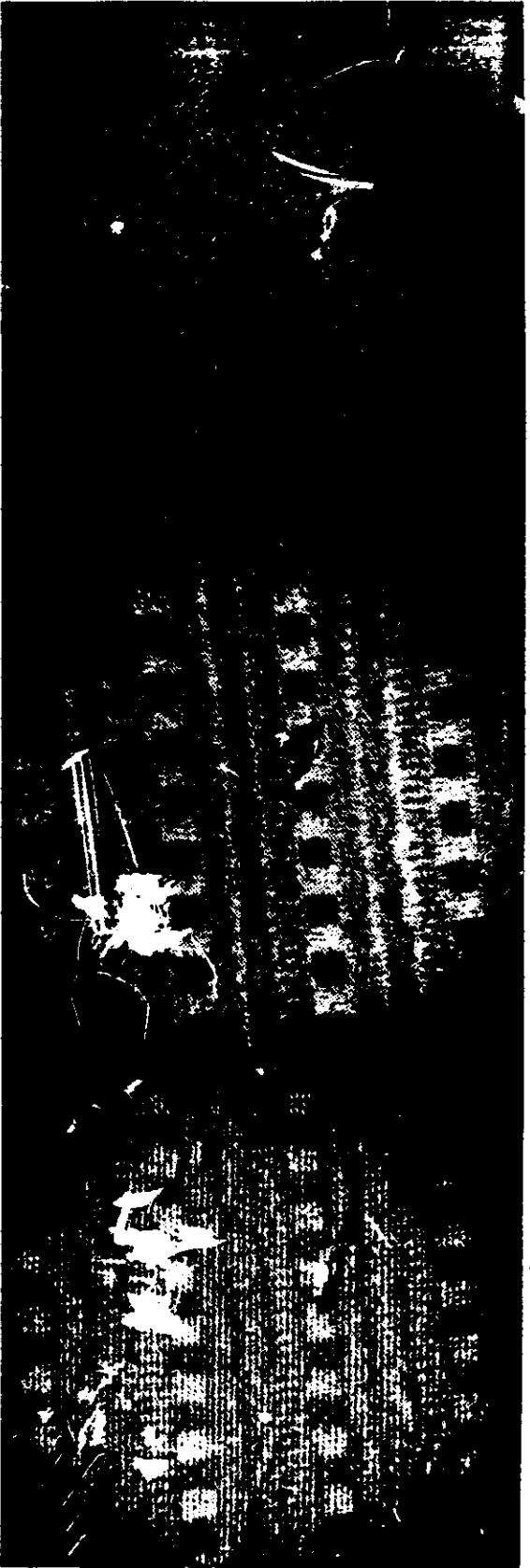
YMU HR_NIM

Co L₃ 778 eV
 (1. 193 eV)
 LEFT HANDED h_v?
 RIGHT HANDED h_v?

J. Stöhr, B. Terner
 et al.

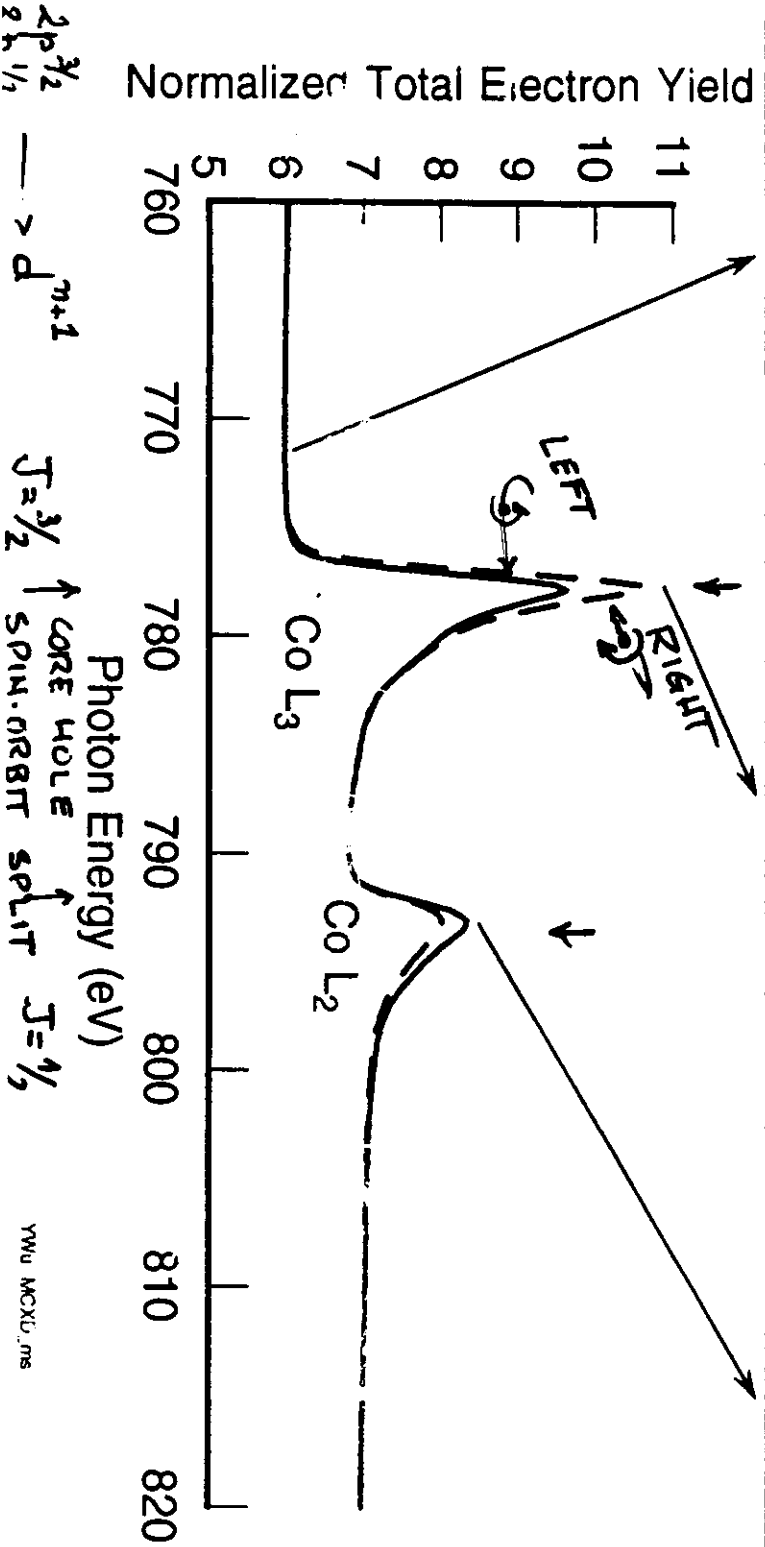
MCXD Microscopy

Diff. Image



778eV
LIII
793eV
LII
94
3.1

Fig. 2



J. STÖHR
or al.
(Nature)
93
T.B. Co
from
a
dark mat.

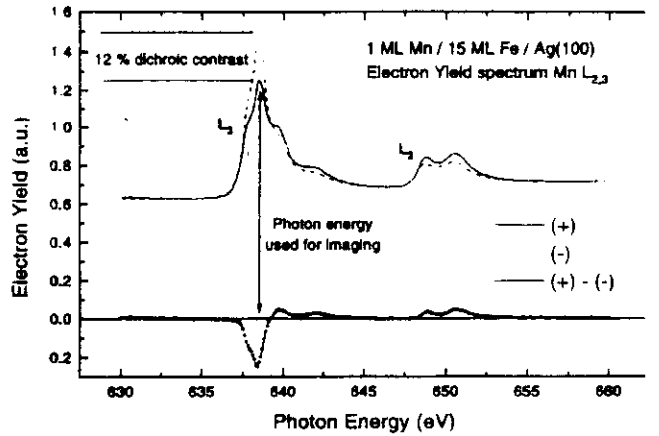
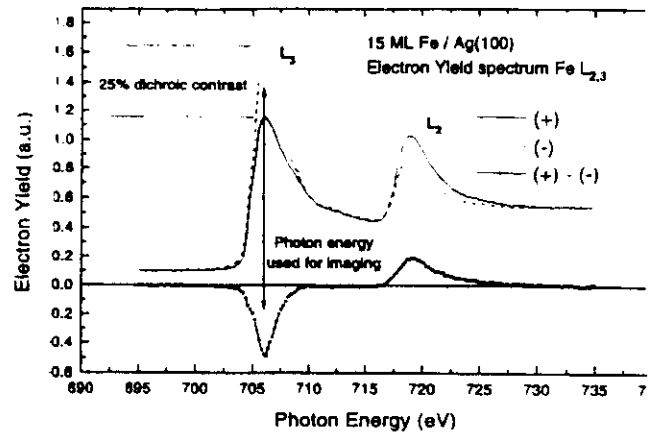
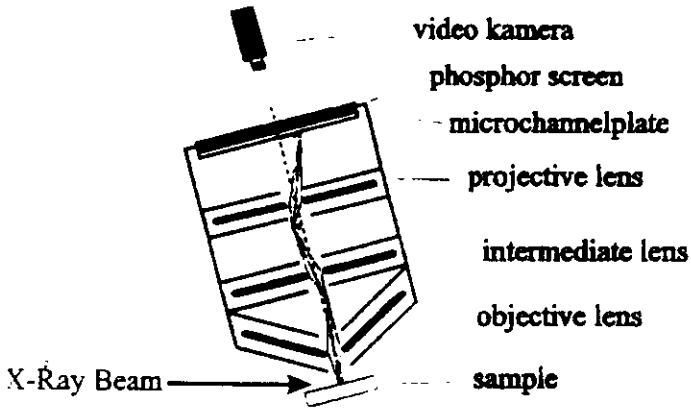
Stöhr et al

8378

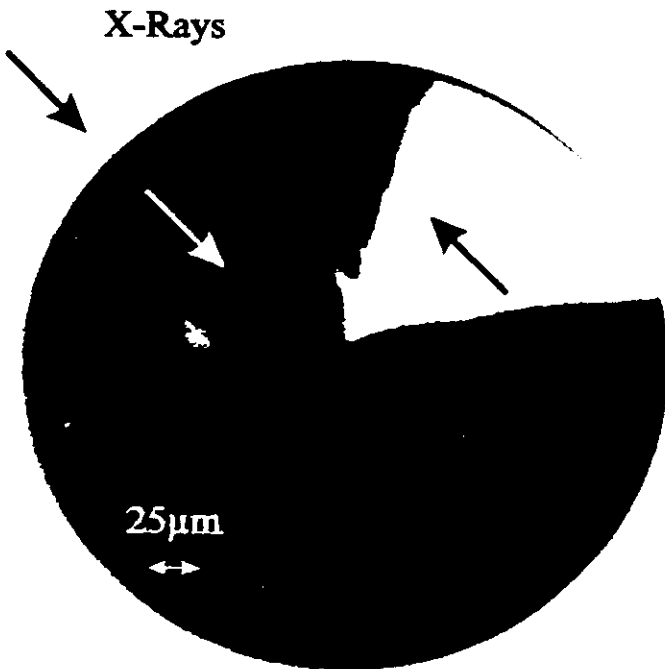
Microscopy of magnetic domains
in ultra-thin films
by x-ray dichroism

- D. Spanke, J. Dresselhaus, F.U. Hillebrecht, E. Kisker, University of Düsseldorf
- N.B. Brookes, J.B. Goedkoop, ESRF

Photo Emission Electron Microscope

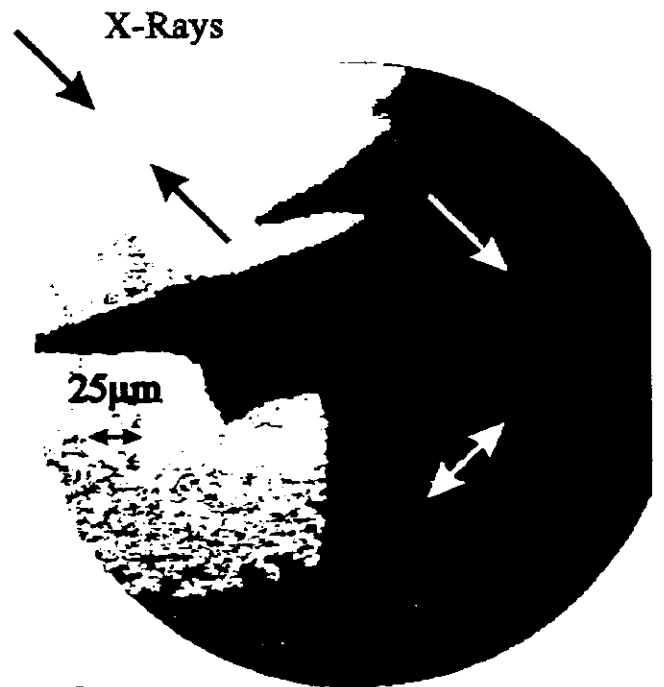


15 ML film of Fe on Ag (100)

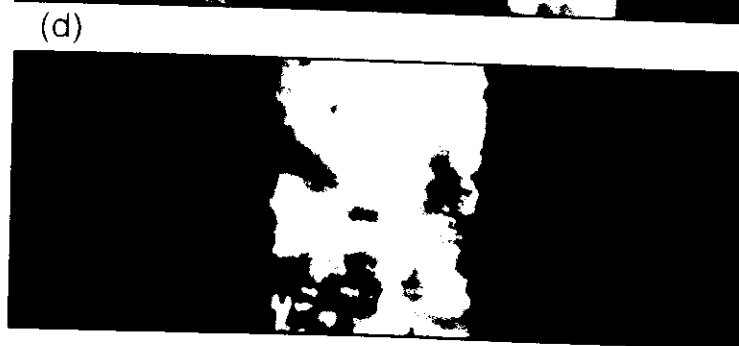
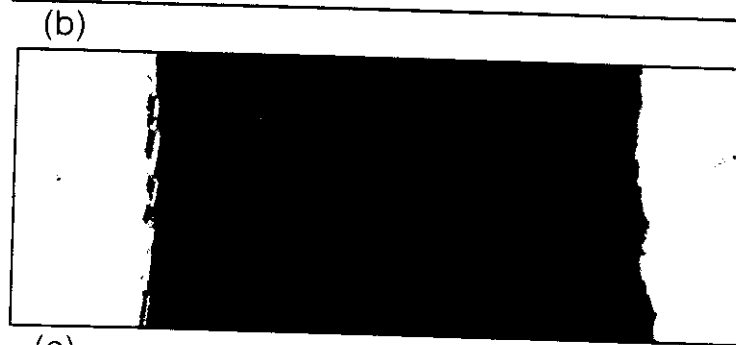
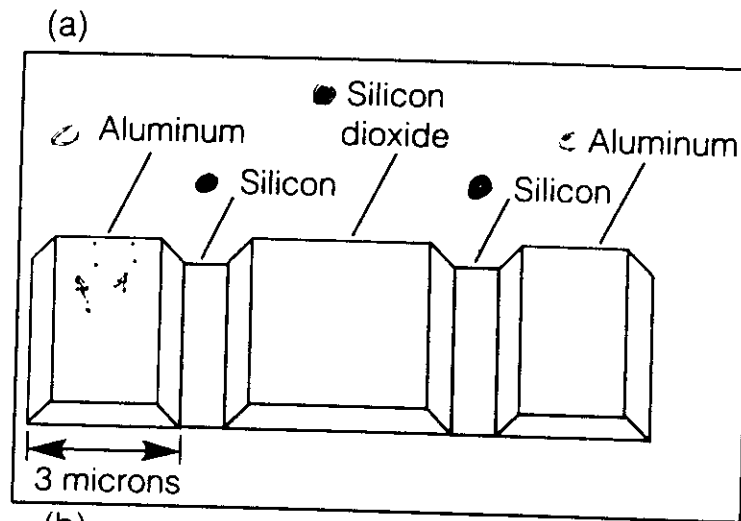


Three Domain directions
yellow: parallel to light helicity
blue: anti-parallel to light helicity
green: normal to light helicity

0.5 ML Mn on a 15 ML film of Fe on Ag (100)



Spectromicroscopy



PHOTON SOURCES

energy tunable
polarisation tunable

(SR)

element selectivity
spin sensitivity
monolayer sensitivity
anisotropic sensitivity

valence sensitivity

local environment probe

i.e structural electronic magnetic information

