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

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

25 October - 19 November 1993

Miramare - Trieste, Italy

Interaction of X-Rays with Matter:

X-Ray absorption fine structure

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

INTERACTION of X-RAYS with MATTER:

X-RAY ABSORPTION FINE STRUCTURE

>100eV <50KeV

Z

A. FONTAINE ICTP
- LURE · ORSAY · F. NOV 93 -

- 1 - INTRODUCTION

Cross sections, Fermi Golden Rule, Lines & Continuum.
EXAFS.
Decay Channels, Core Hole Width
Absorption in x-ray optics, & detection

- 2 - EXAFS

Local atomic structure
Brief theory, main approximations, model.
Data collection.
Data Analysis

- 3 - XANES : Cu K. edge.

Electronic properties

- 4 - Polarized X. rays. → Structure
→ Magnetism.

A HISTORY OF X-RAY ABSORPTION FINE STRUCTURES

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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.

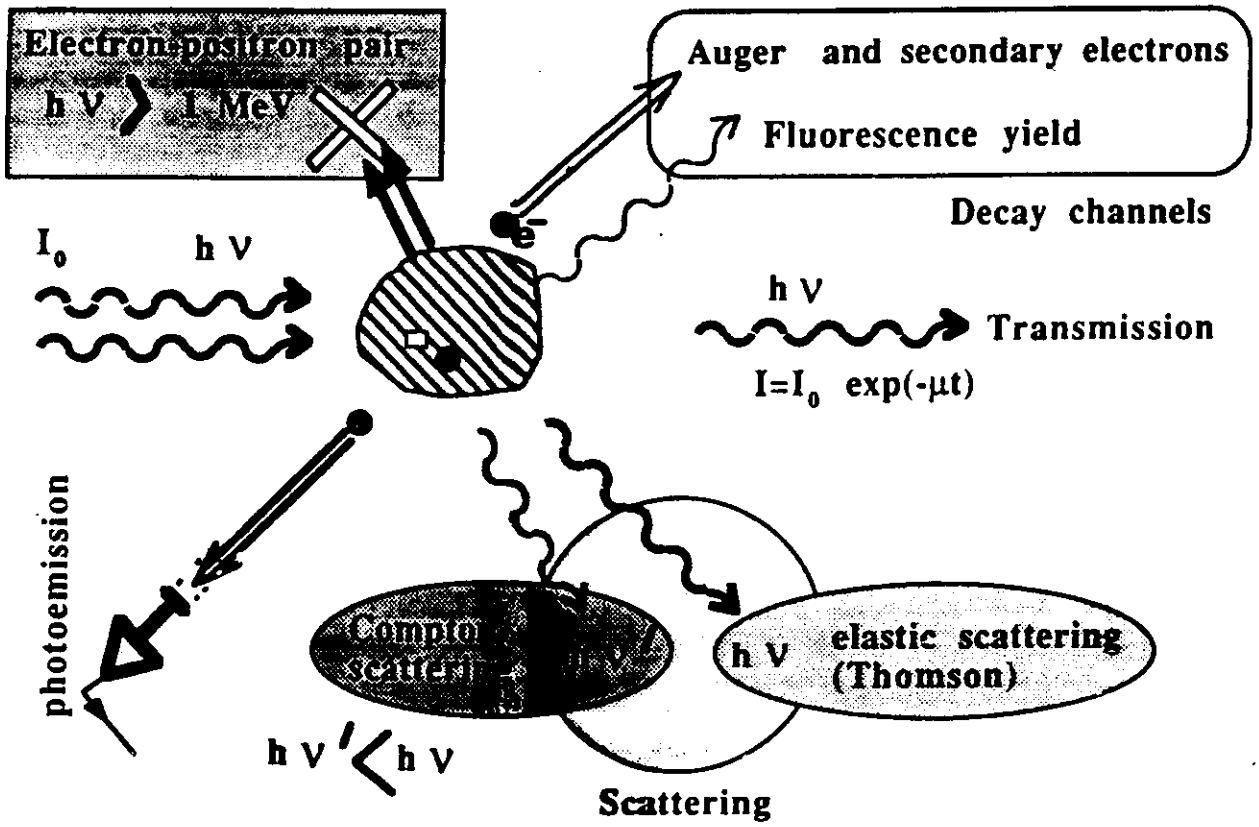
(1) That very day Wilhelm Conrad Röntgen was studying the discharge of electricity in rarefied gases by operating a Hittorf tube (some kind of Crookes tube) wrapped in a black cardboard. Some distance apart, there was a screen covered with barium platinum cyanide. Much to his surprise Röntgen saw the 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")".

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

(2) The study of the influence of X-rays on matter began immediately. In the course of

(3) 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

(4) 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 d'un [illegible]



- 1 photon IN / 1 photon OUT

  Diffusion $\bar{e}$ Thomson $\left(\frac{8\pi}{3} r_e^2\right)$

- 1 photon IN / 0 photon OUT

  $\bar{e}_\gamma$ IN ABSORPTION

  $\bar{e}_\gamma$ OUT PHOTOEMISSION

$\hbar\omega$ (100 eV → 50 KeV)

INTERACTIONS with ELECTRONS ARE IMPORTANT

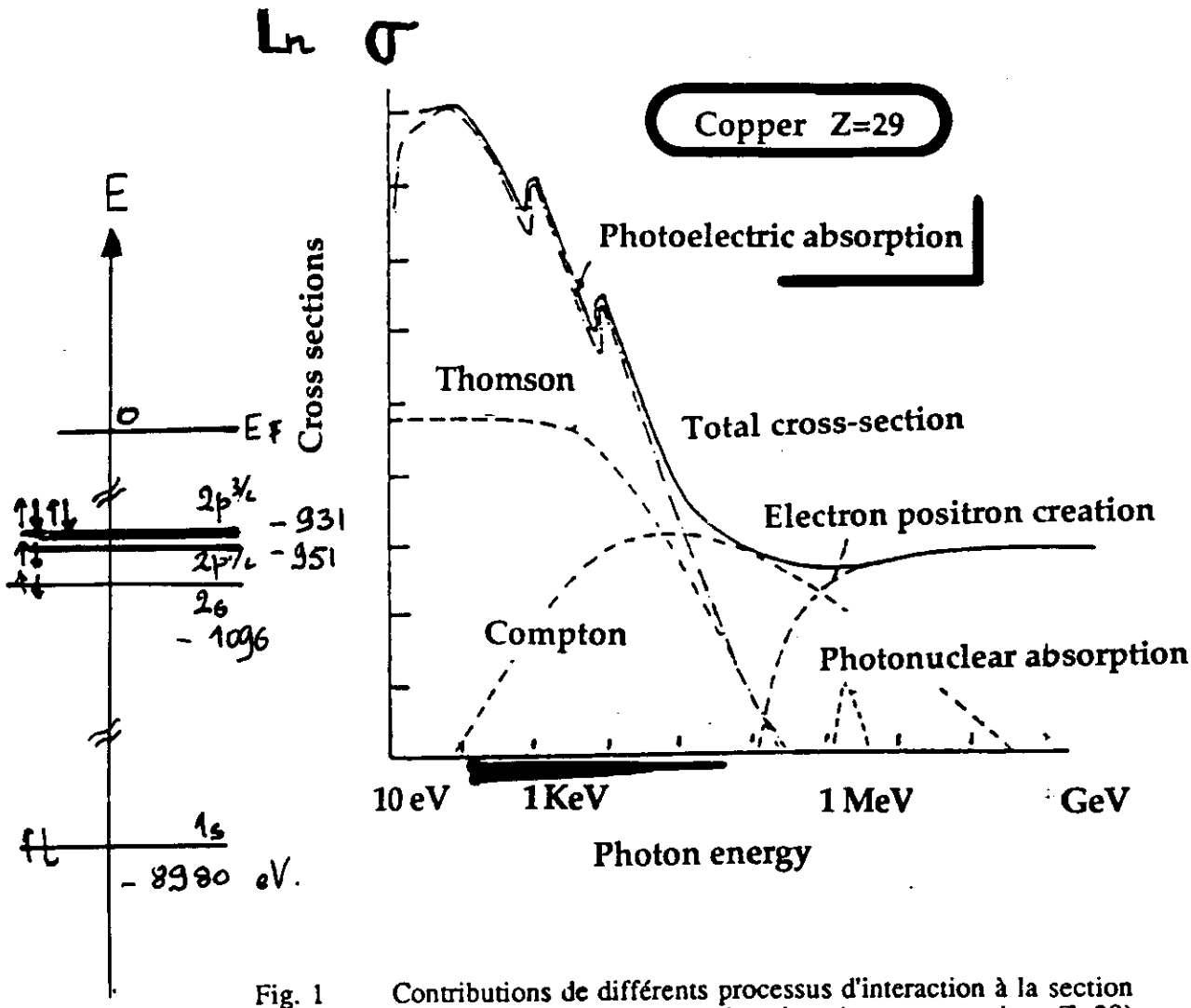
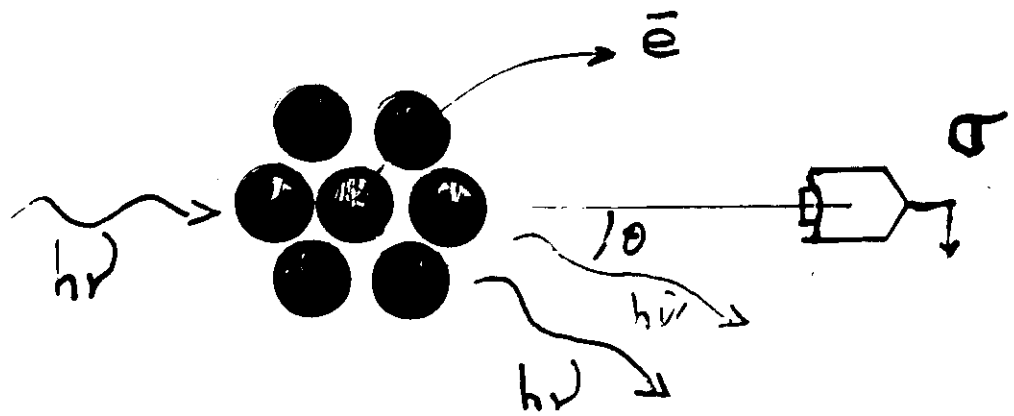


Fig. 1 Contributions de différents processus d'interaction à la section efficace totale pour l'atome de cuivre (numero atomique Z=29) [d'après Hubbel-1971].



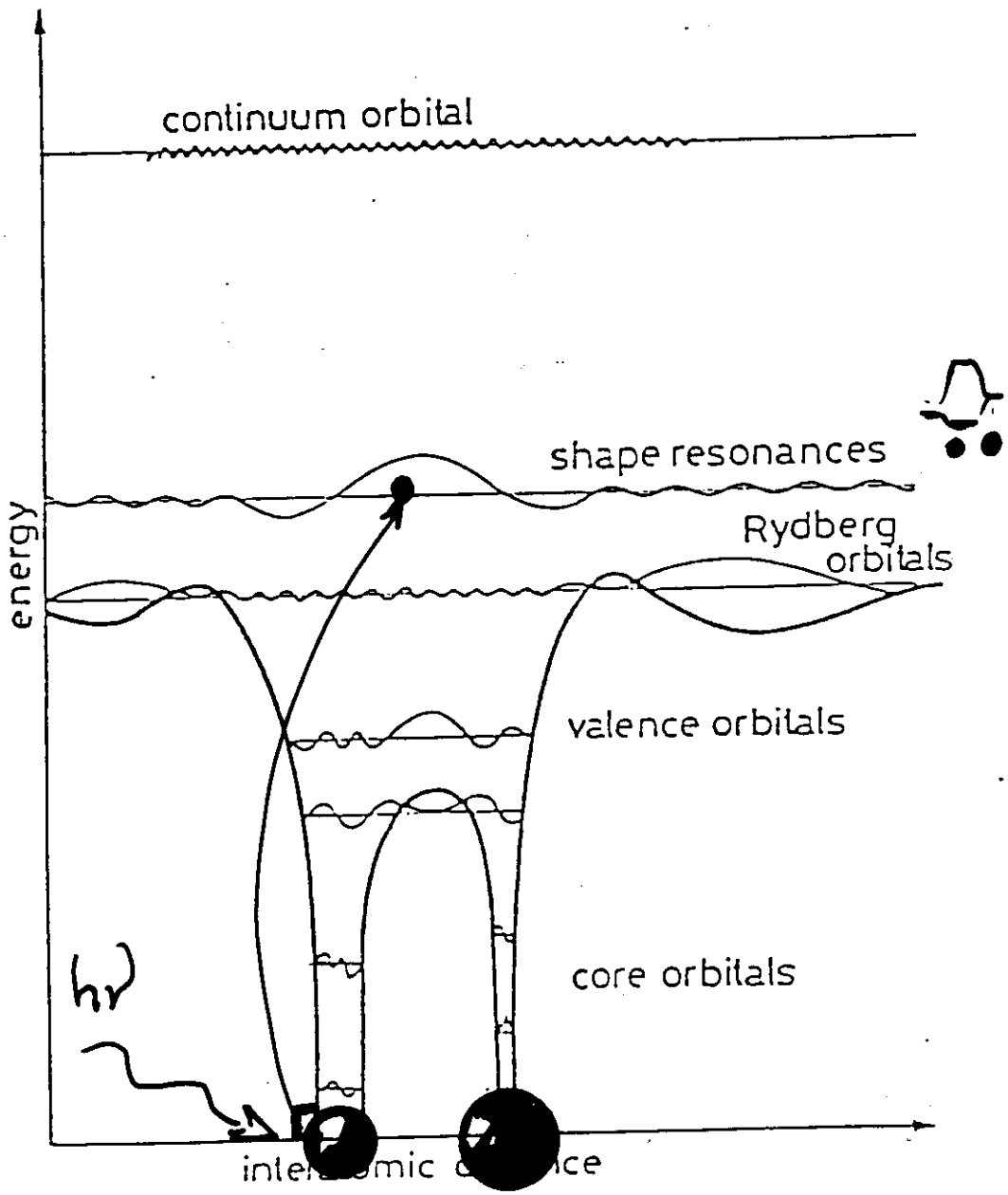
FERMI GOLDEN RULE

$$\sigma(\omega) = 4\pi^2\alpha\hbar\omega \sum_f |\langle f|\, \vec{\varepsilon}\cdot\vec{r}\, |i\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

4 TOOLS

$\|i\rangle$	~~Site~~ el. selectivity
$\Delta\ell = \pm 1$	Selection rules
$\vec{\varepsilon}\cdot\vec{r}$	Polarization dep.
$\|f\rangle$	Final state Relax.

ONE ELECTRON PICTURE + "INGREDIENTS"


continuum orbital
shape resonances
Rydberg
orbitals
energy
valence orbitals
core orbitals
hν

II .2

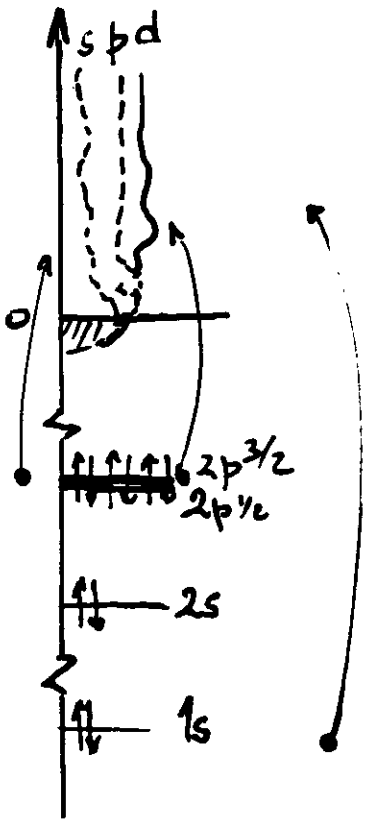
$|i\rangle = |1s^2 2s^2 2p^6\rangle$

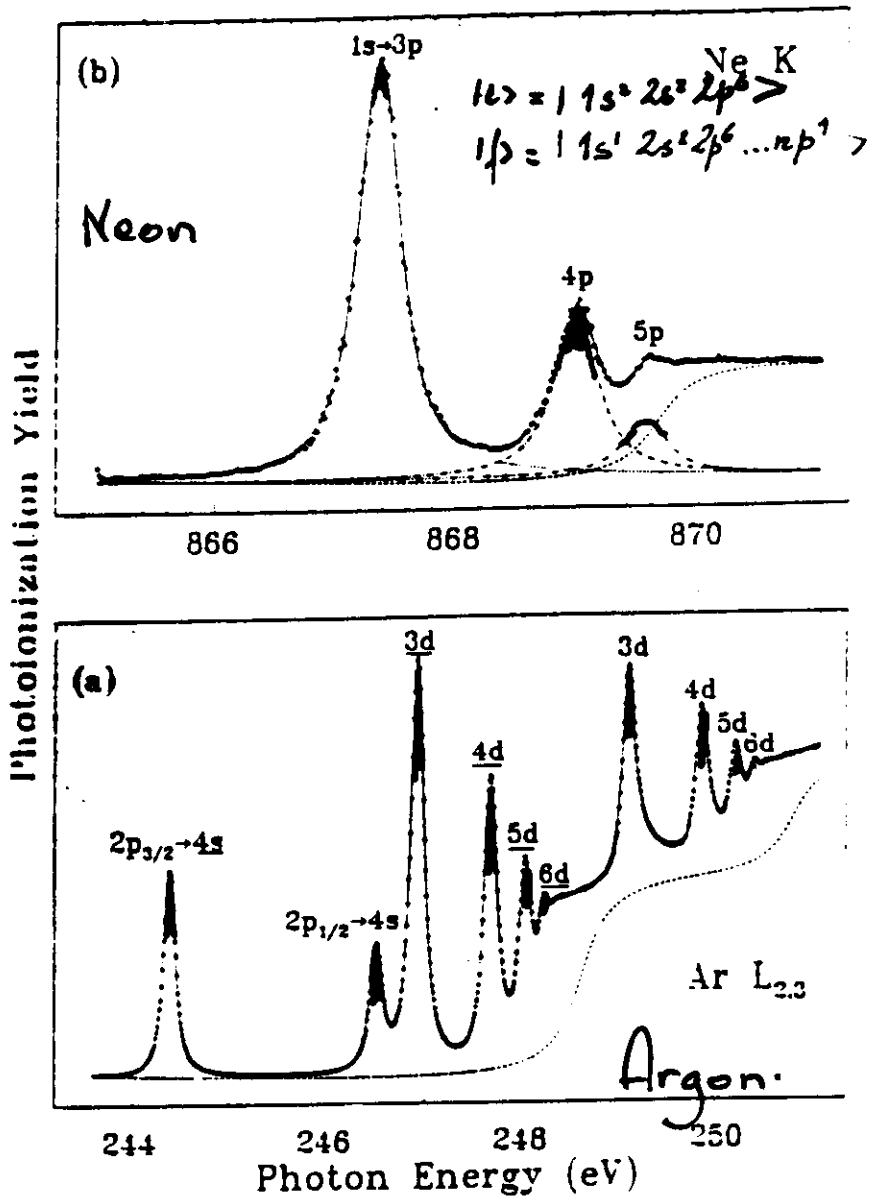
$|f\rangle = |1s^1 2s^2 2p^6 np^1\rangle$

. core hole.
+ photoelectron.

. dipolar $\Delta l = \pm 1$

s → p
p → d
p → s





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 ⟹ ALLOWS HIGH RESOLUTION
⇓
MORE INFORMATIONS ACCESSIBLE.

92·8

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

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SHAPE RESON.
Vibrational fine struct.
Double excitation

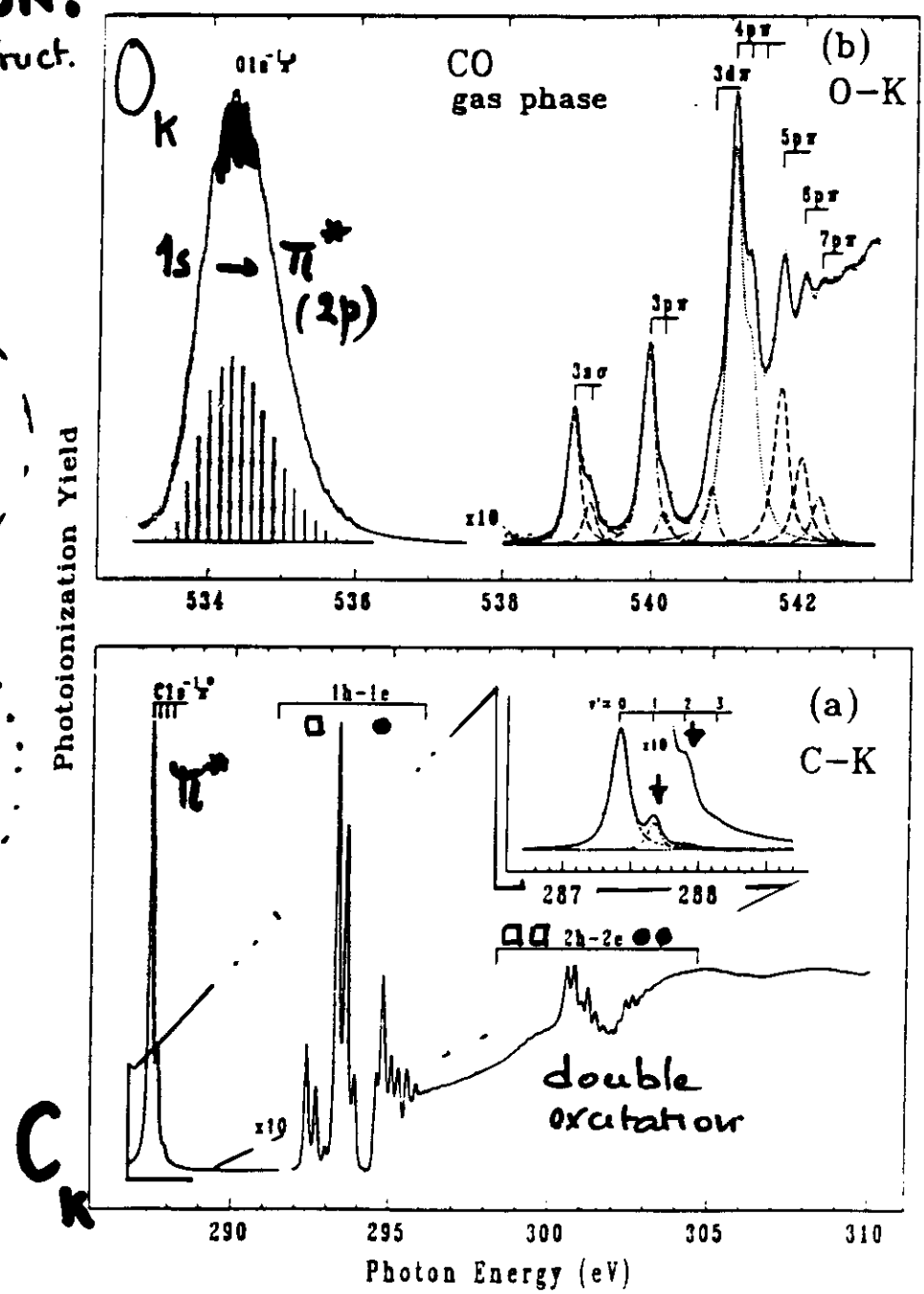


FIG. 3. Photoionization spectra of gas-phase CO close to (a) the C-*K* and (b) the O-*K* thresholds. The dominant spectral features in both spectra from excitations of C-1*s* and O-1*s* electrons, respectively, into the lowest unoccupied molecular state of Π symmetry; the resolved vibrational structure of the C $1s^{-1}\pi^*$ 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 $1s \rightarrow$ Rydberg-state transitions with vibrational fine structure as well as double excitations (in the C-*K* case).

92.25bis
-9B

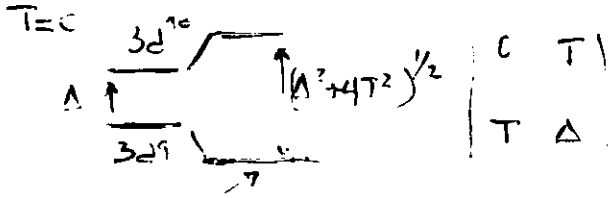
Cu

L_3 , L_2 edges.

Ability to identify valencies

- Cu^{I} GROUND STATE $|1s^2 .. 2p^6 . 3d^{10}>$
  final State $|1s^2 .. 2p^5 .... 3d^{10} 4s^1>$
  weak oscillator strength

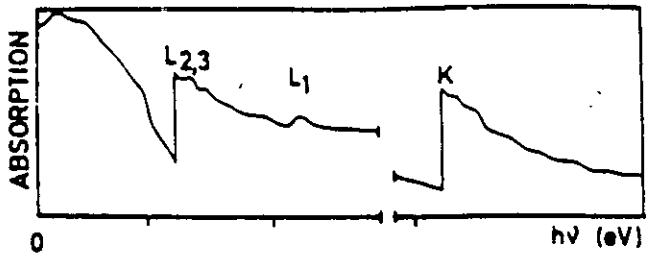
- Cu^{II} GROUND STATE

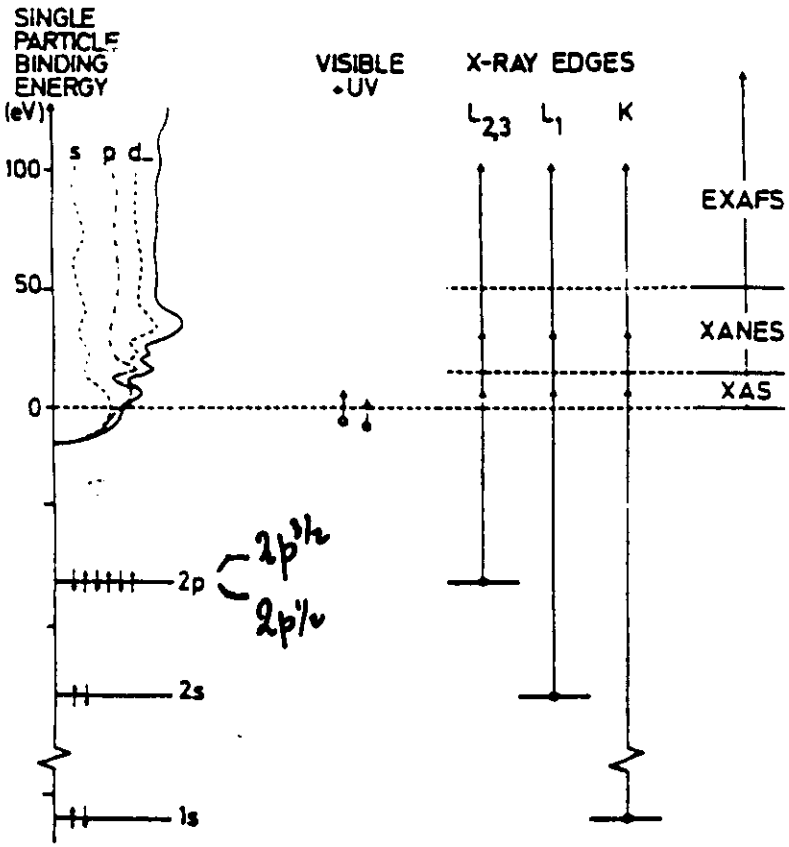


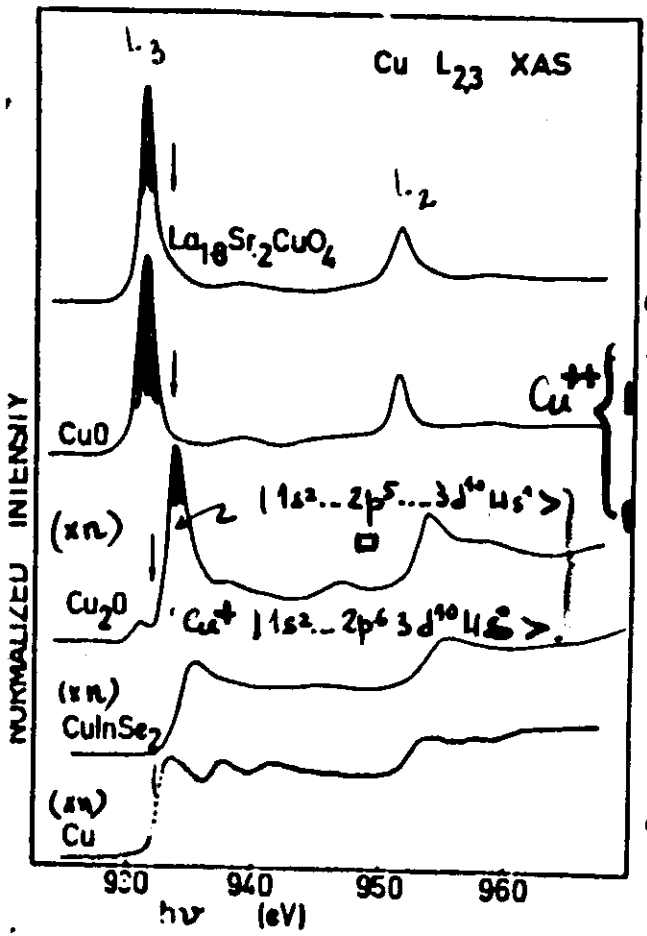
$\alpha_c \,|\, 1s^2 \ldots 3d^9 > \quad + \beta_c \,|\, 1s^2 \ldots 3d^{10} \underline{L}$

final state $|1s^2 2p^5 .. 3d^{10}>$ essentially 0

Intensity $\propto \alpha_0^2$ $(4s^1)$







NARROW BAND

ONE-ELECTRON PICT.

INITIAL STATE

$1s^2.\underline{2p}^6.3d^9\rangle$

FINAL STATE

$1s^2.:\underline{2p}^5...3d^{10}\rangle$

$\underline{\ }$ CORE HOLE

BROAD CONTINUUM

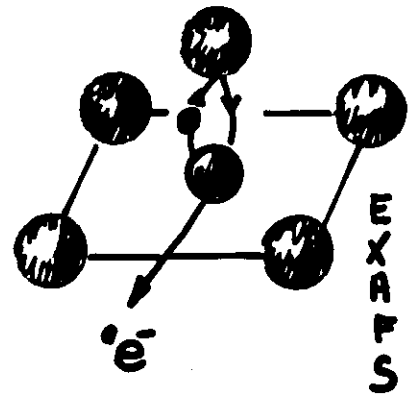
SPIN-ORBIT

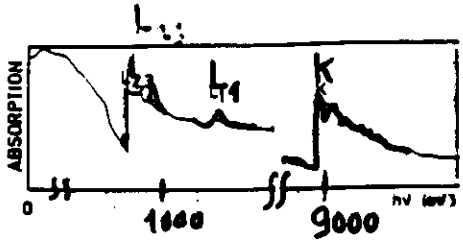
CORE HOLE

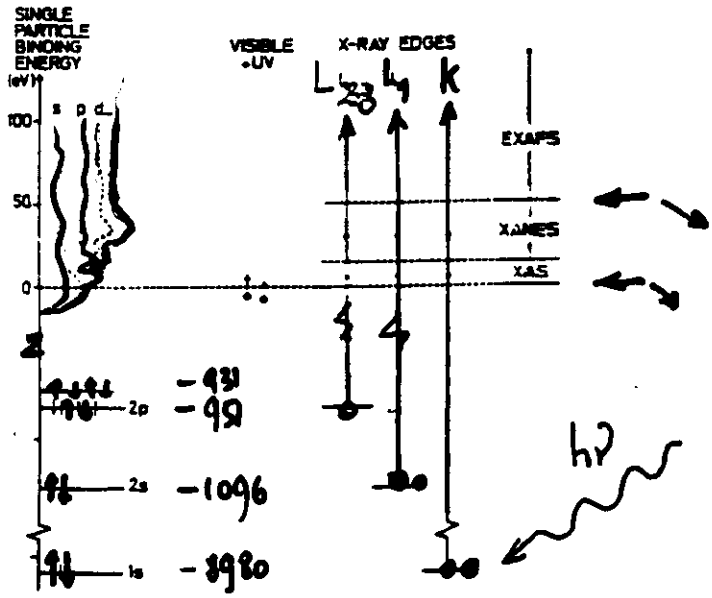
SELECTION RULES : $\Delta\ell = \pm 1$

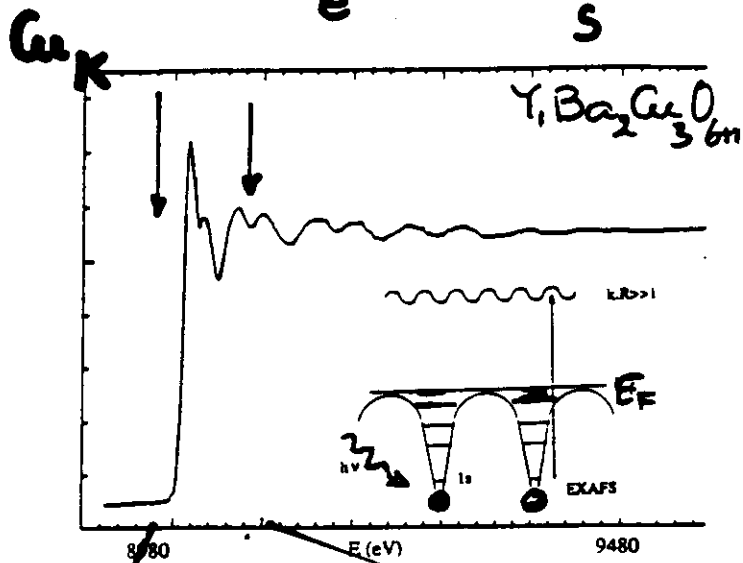
KRONIG 1925

92.

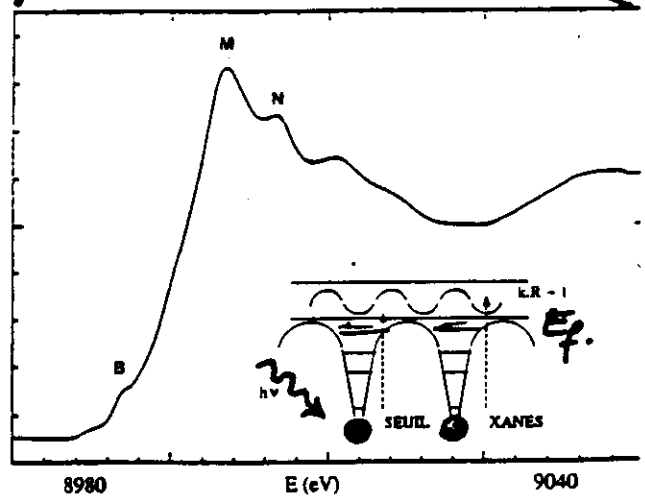




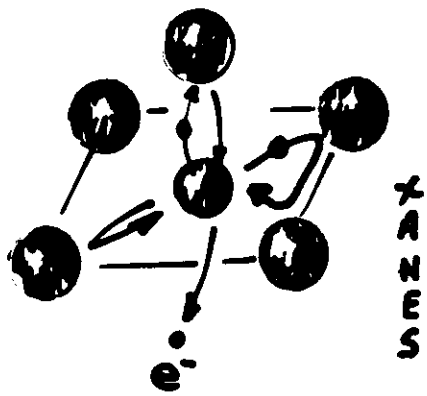




Spectre complet d'Exafs où les oscillations s'étendent au-delà de 600 eV après seuil.



Présentation du seuil d'absorption de $Y_1Ba_2Cu_3O_{6+\xi}$ 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.

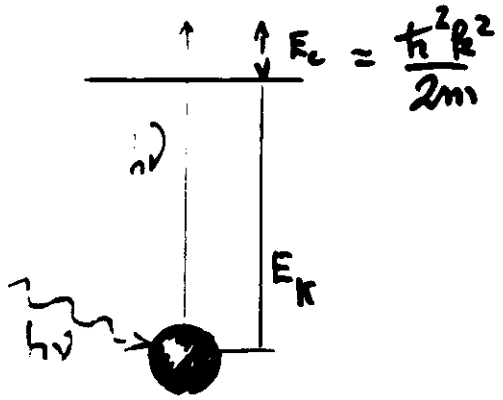
EXAFS.

92-K

1 PHOTON. Seuil K

$h\nu > K\text{-edge}_{Cu} \simeq 8979.3\ eV$ (E_K)

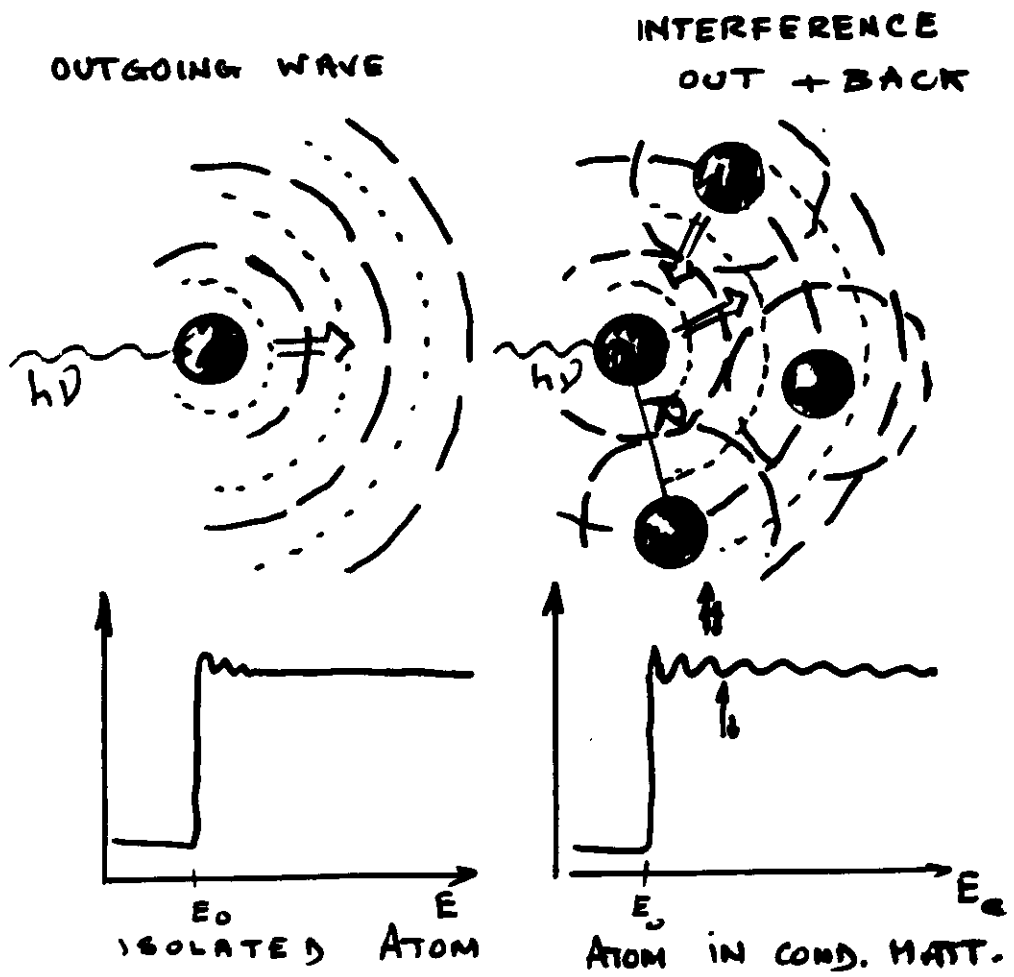
2 PHOTOELECTRON



$|f_0\rangle$ $|f_0 + \sqrt{f}\rangle$

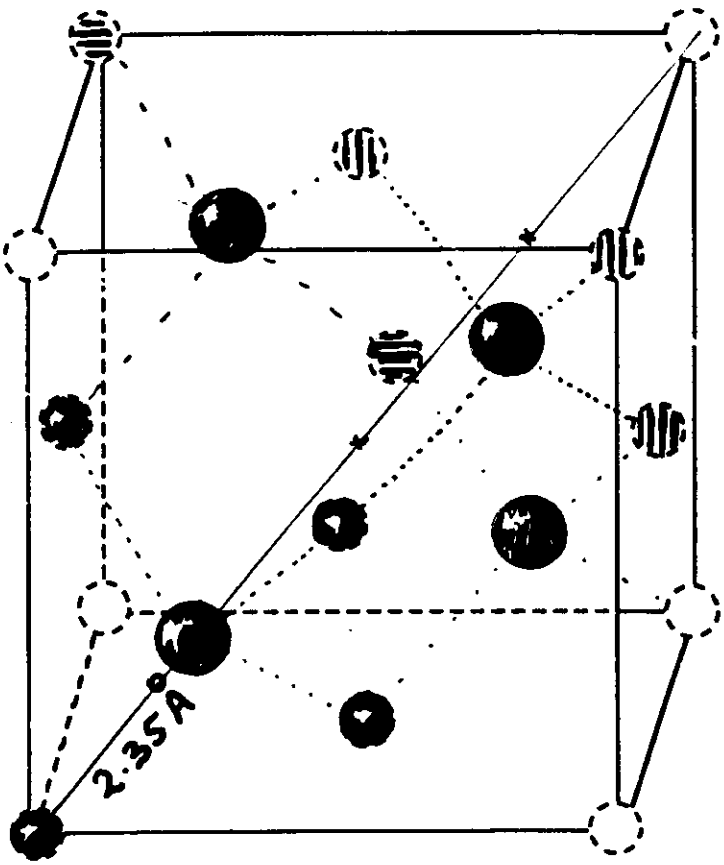
3 ABSORPTION.

$k(2\pi)$



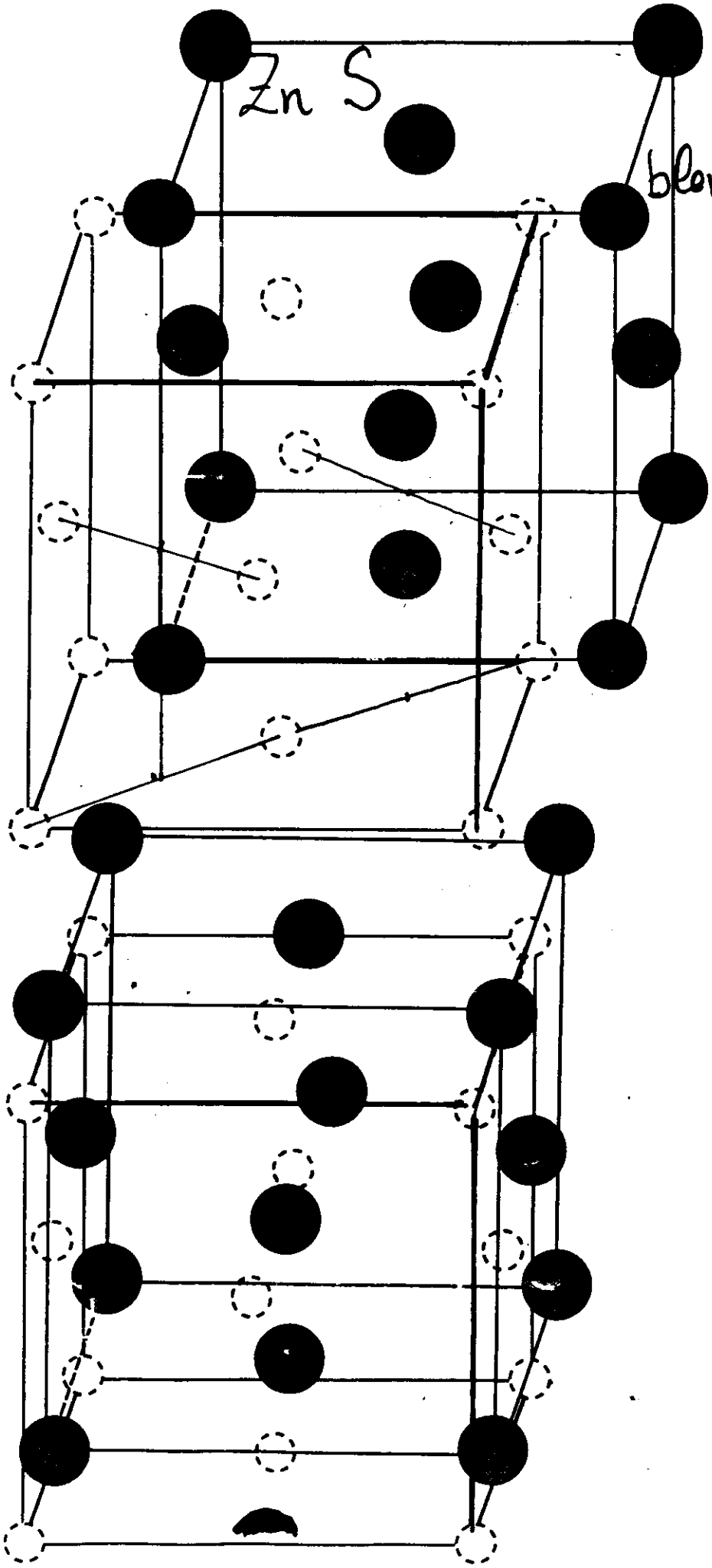
Zn S

4S @ 2.35 Å

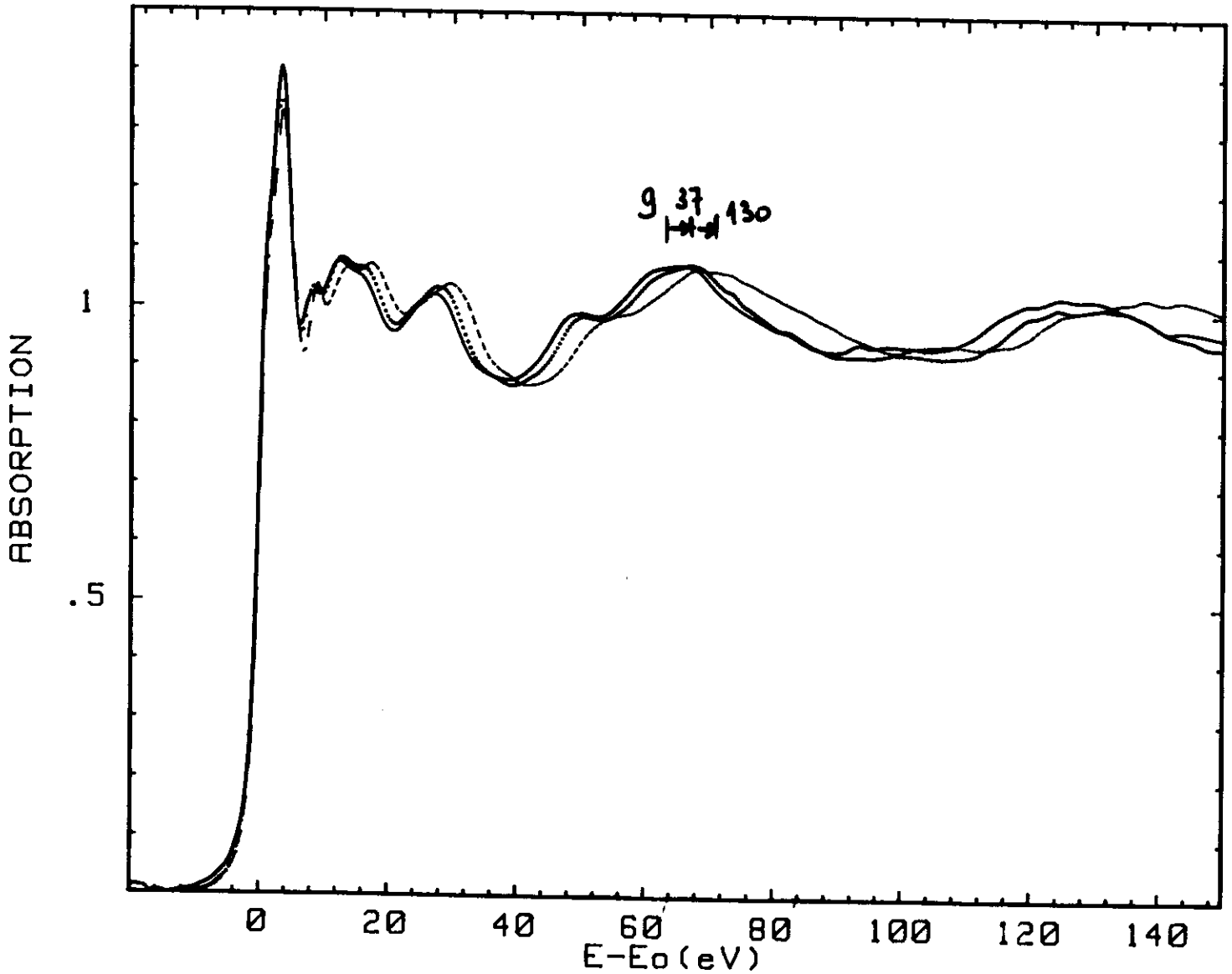


ZnS

92-12



Rock salt



Kbar

9, 37, 130

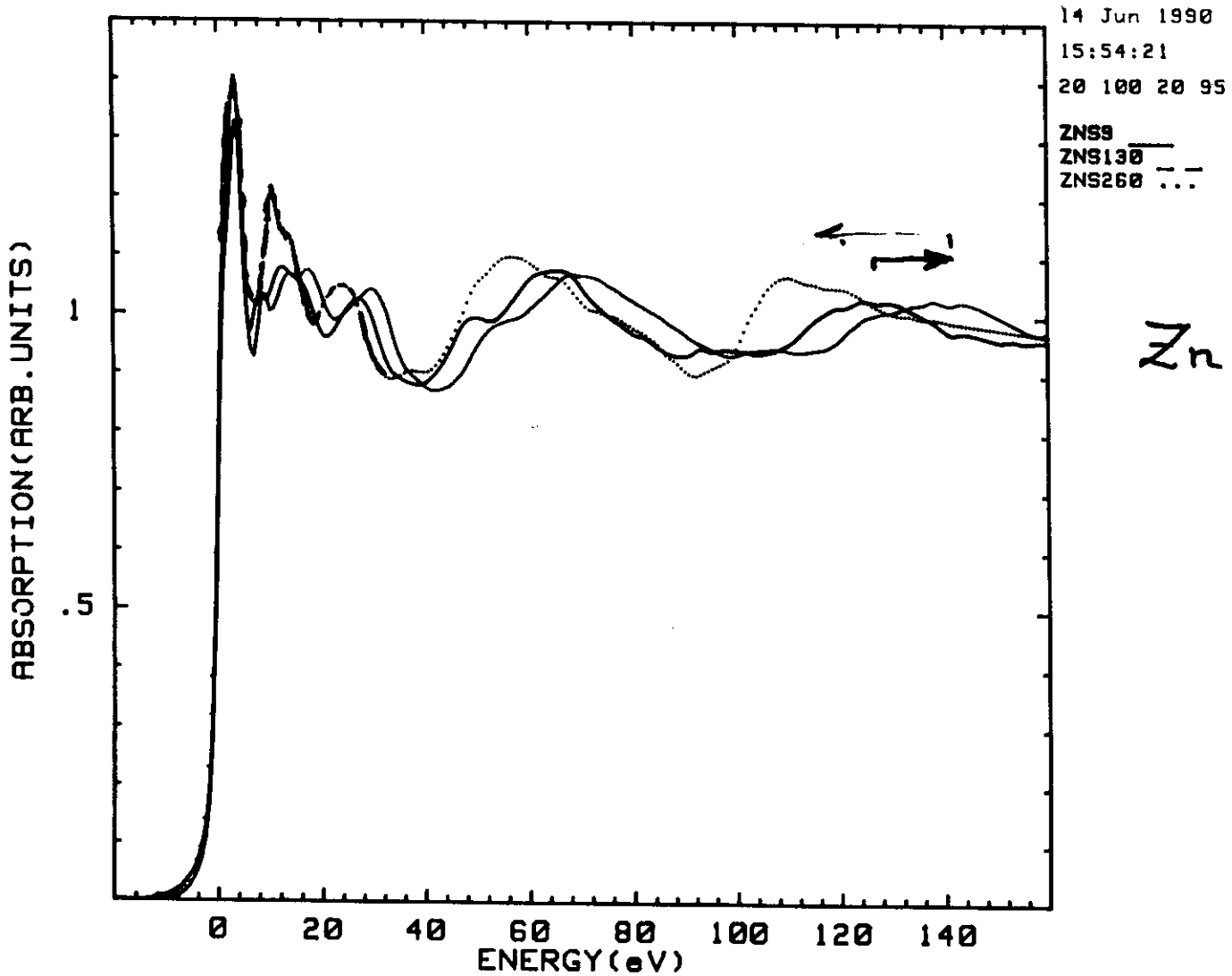
ZnS

blende

$\hbar^2k^2/2m$

Kinetic energy of the photoelectron.

E_0 ? 9659. $E_k = h\nu - E_0$

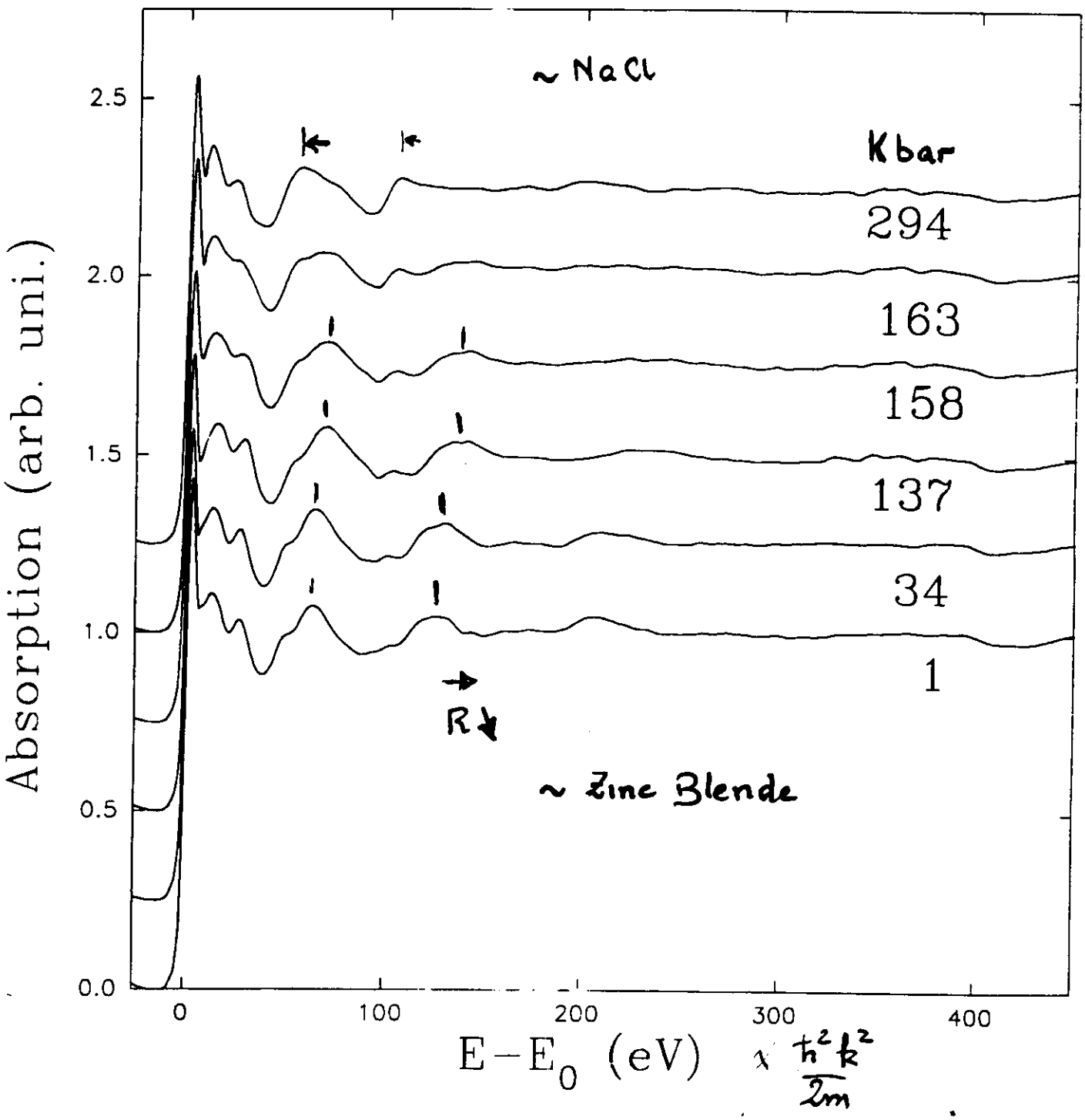


ZnS 130 9 kbar 260 w. NaCl.

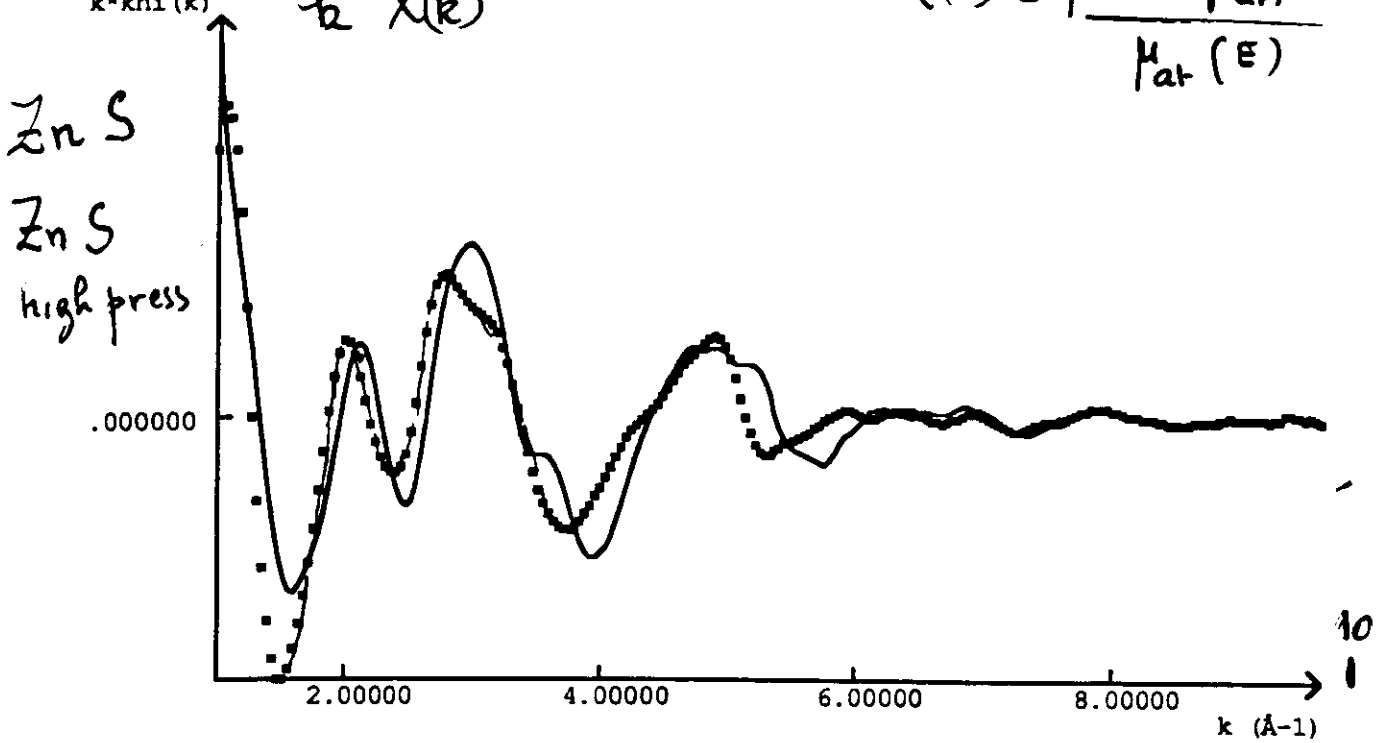
92-14

Zn K-edge
~ 9660 eV

ZnS



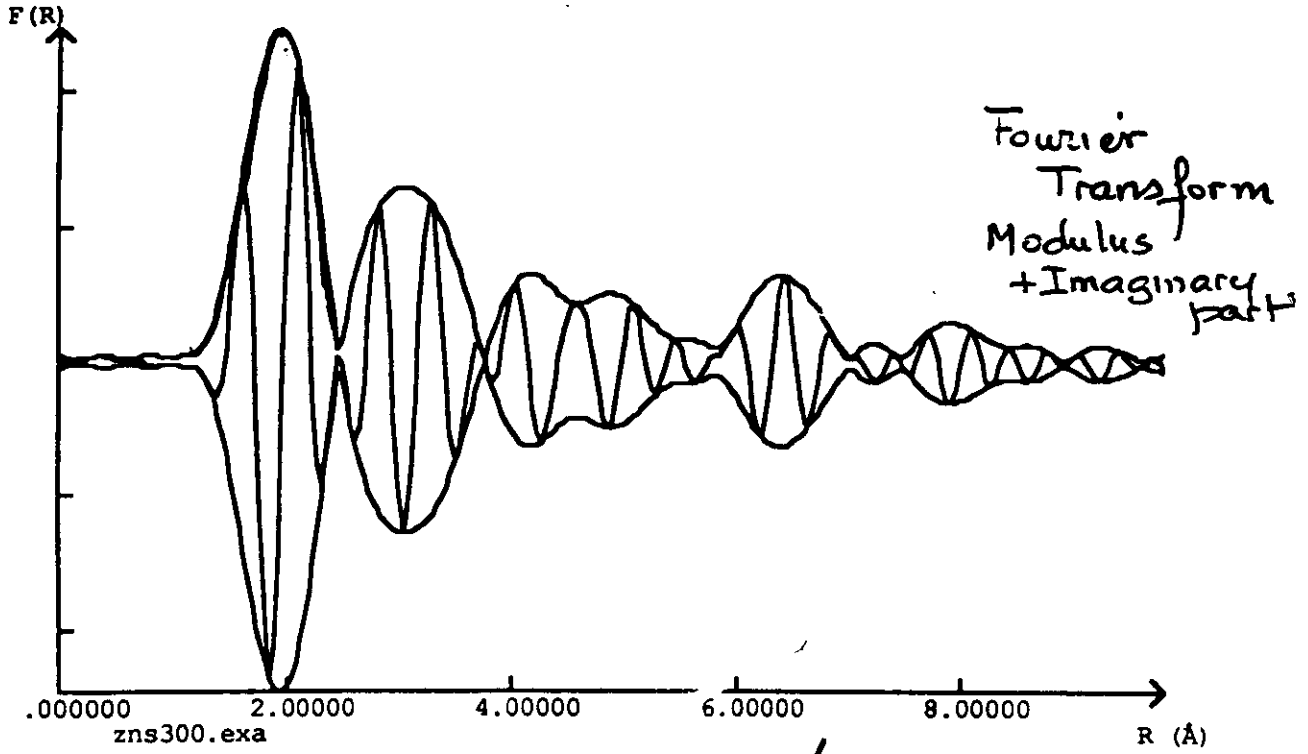
$\chi(E) = \dfrac{\mu(E) - \mu_{at}(E)}{\mu_{at}(E)}$



$E - E_0 \longrightarrow k$

$\hbar^2 k^2$

Im



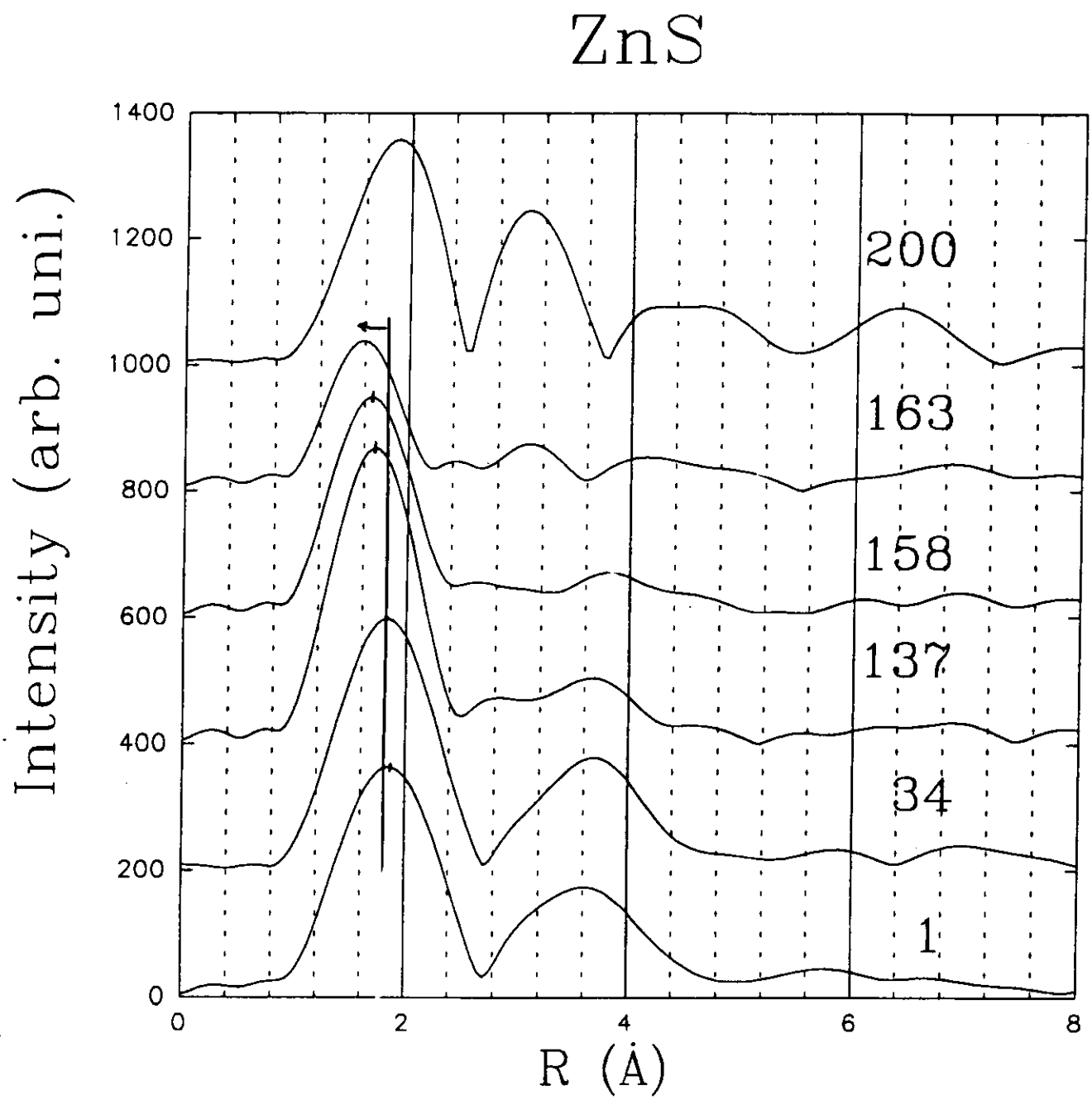
ϕ

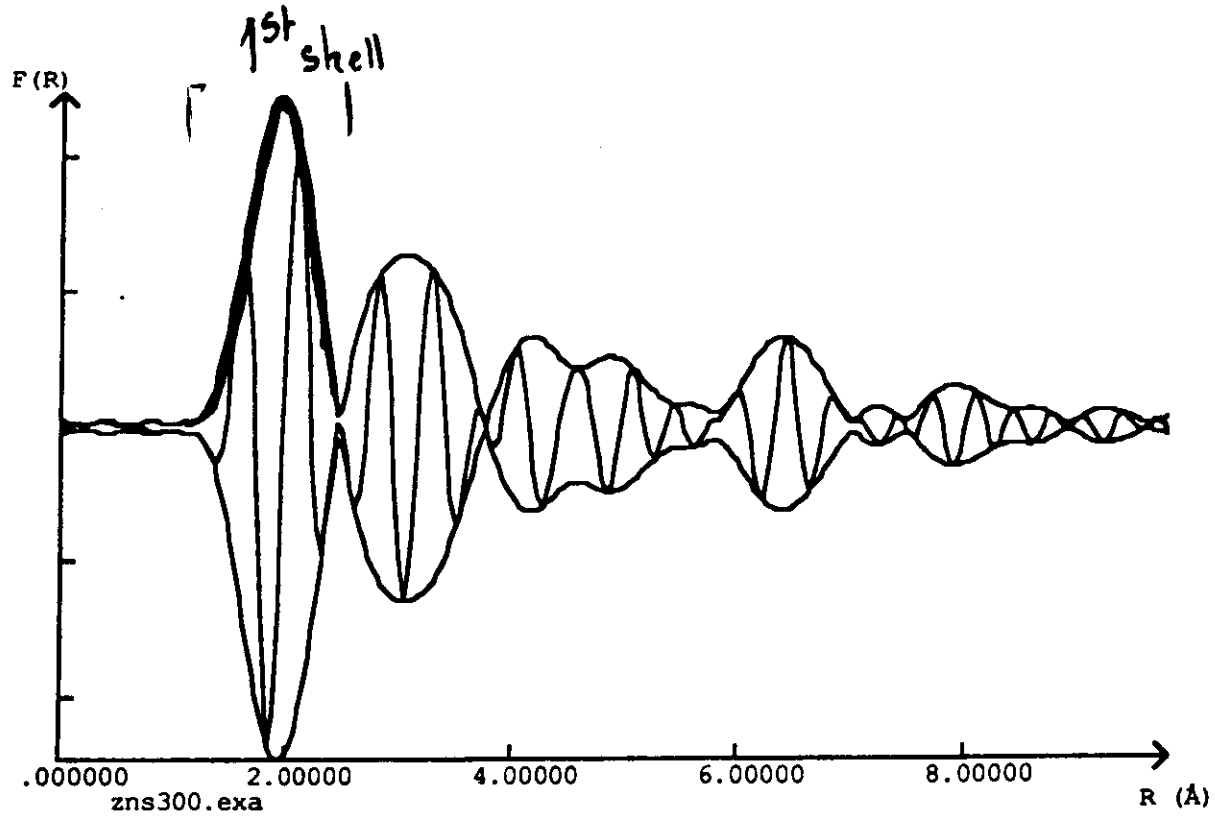
↑ ≠ 2.35 → Phase shifts are R dependent

$+ = 2kR + \phi(k)$

92-12

Zn K-edge





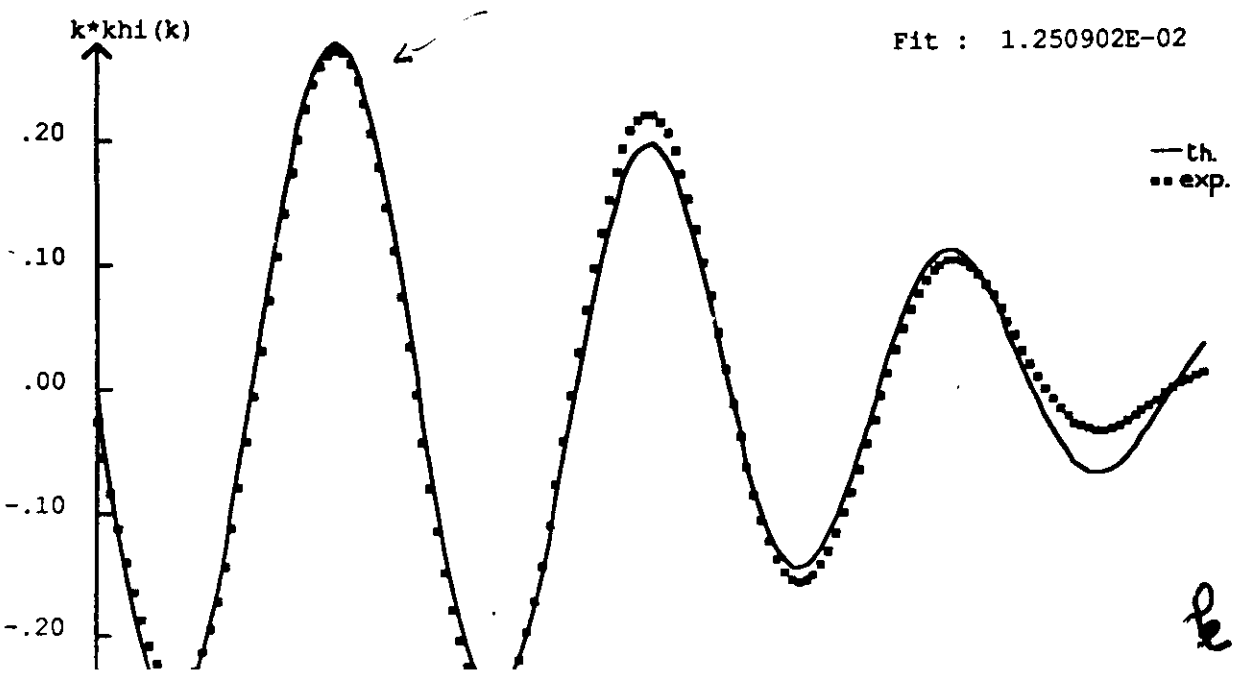
R(Å)

ZnS

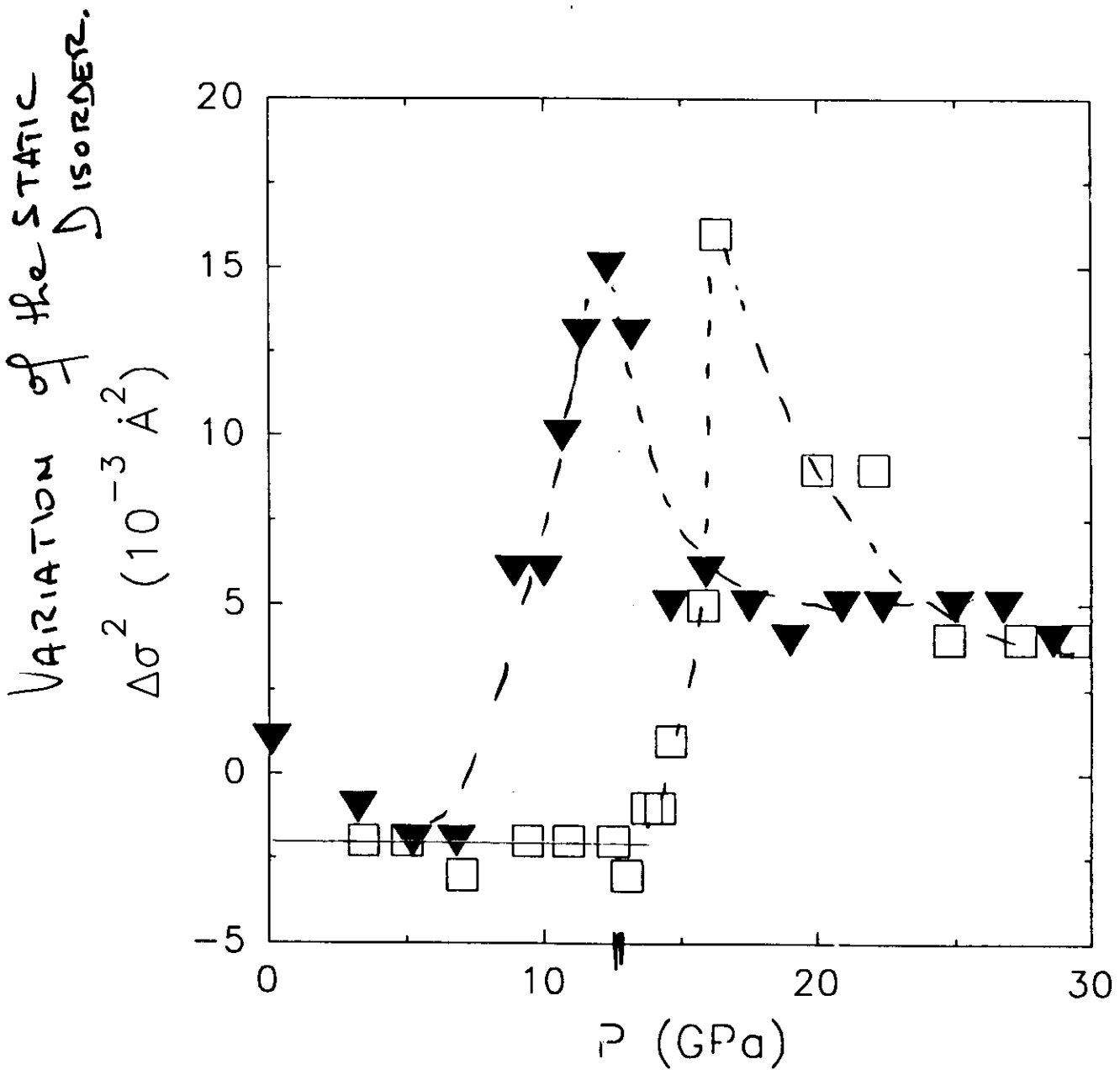
Zn K-edge

$(FT)^{-1}$

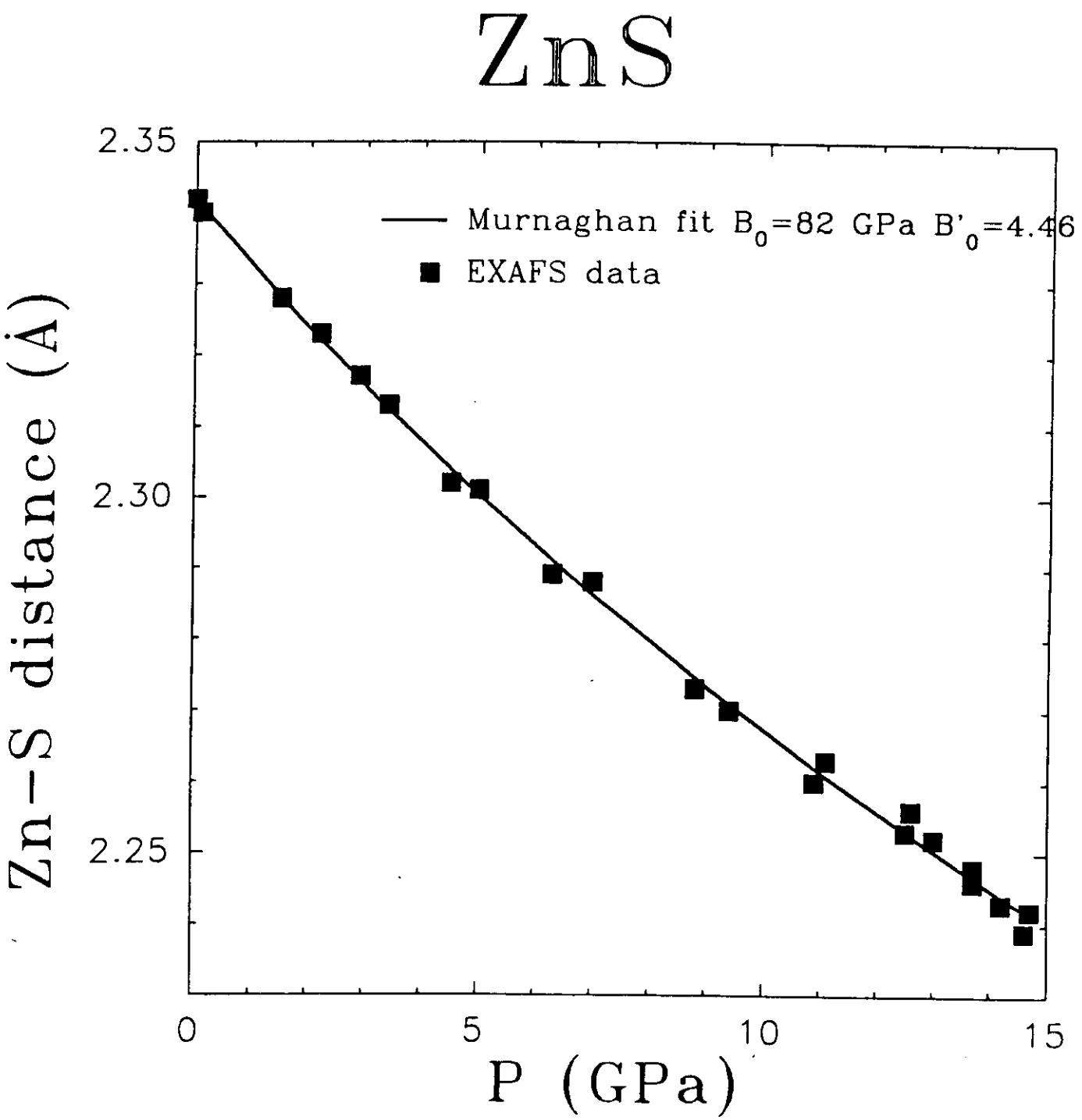
4 S @ 2.35 Å
6 S @ 2.45 Å

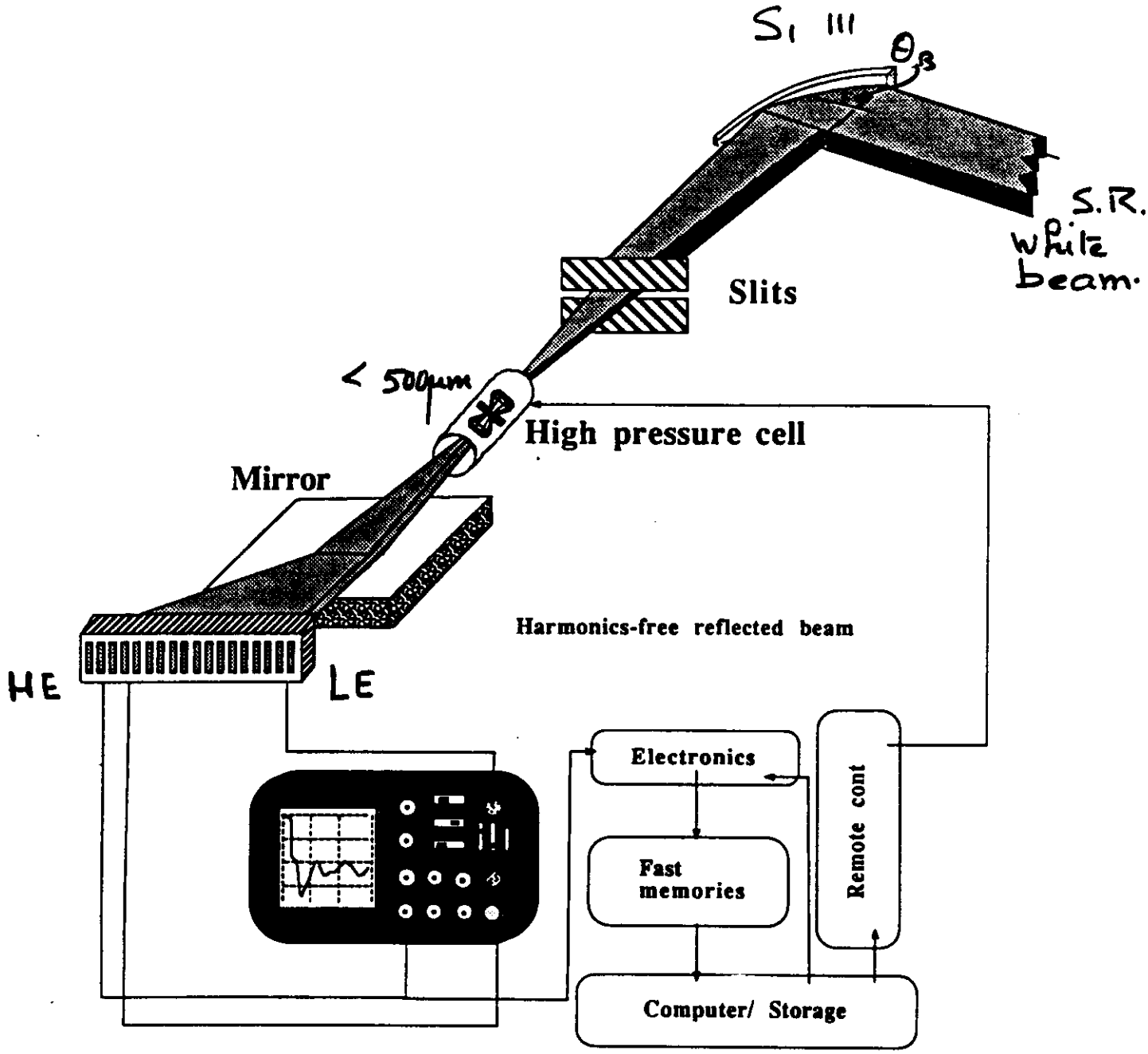


FIRST ORDER TRANSITION



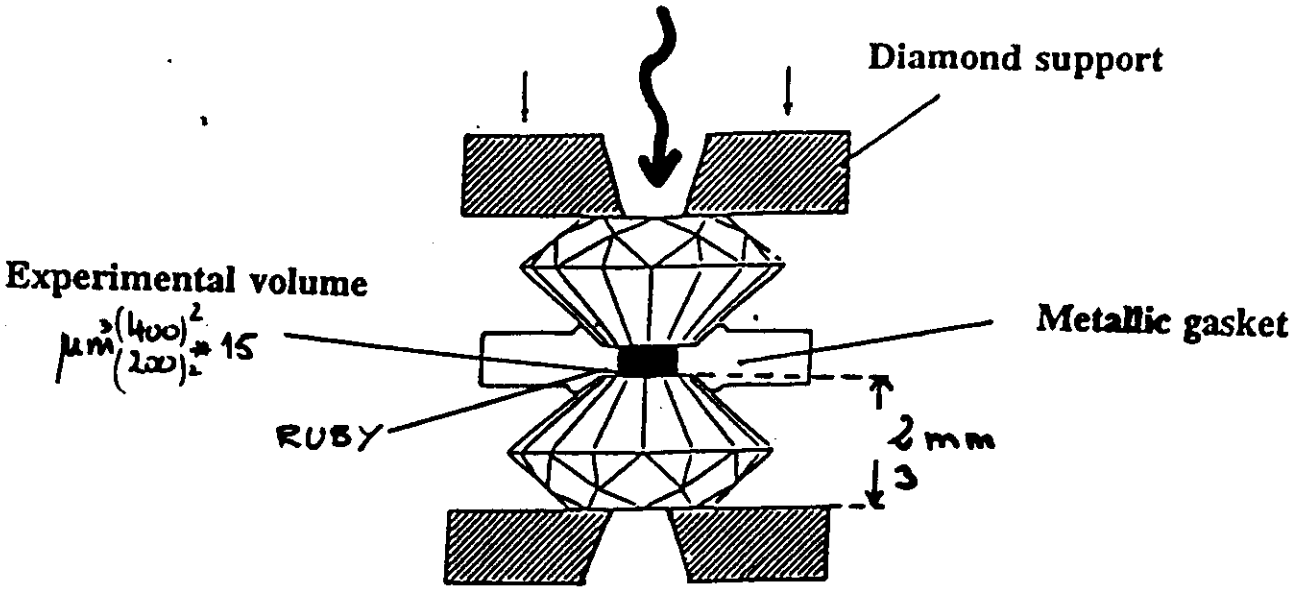
INHOMOGENEITY in the pressure cell.


ZnS
Murnaghan fit B_0=82 GPa B'_0=4.46
EXAFS data
Zn–S distance (Å)
2.35
2.30
2.25
0
5
10
15
P (GPa)



Schematic layout of theEnergy-Dispersive Spectrometer

Diamond Anvil Cell (DAC)



* Sample dimensions
* Diamond absorption

▸▸▸▸

Synchrotron Radiation

ALREADY SUGGESTED

ELECTRONIC
ATOMIC STRUCTURES & XAS

- EXAFS is A LOCAL PROBE
- ~~SITE~~ ELEMENT SELECTIVITY
- K space $\underset{FT^{-1}}{\overset{FT}{\longleftrightarrow}}$ R space