



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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H4.SMR/676-33

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

25 October - 19 November 1993

Miramare - Trieste, Italy

UV and X ray interaction with matter

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UV and X ray interaction with matter

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Contents:

1. Quasiparticles in matter
2. The electromagnetic field
and its coupling to matter
3. Applications

(2)

Adiabatic approximation (to handle a system of electrons $[i=1, \dots, N]$ and nuclei $[\nu=1, \dots, N']]$)

$$H = T_e + V_{ee} + V_{en} + T_n + V_{nn}$$

$T \equiv$ kinetic energy
 $V \equiv$ potential energy

where:

$$T_e = \sum_{i=1}^N \frac{p_i^2}{2m}$$

$$T_n = \sum_{\nu=1}^{N'} \frac{p_\nu^2}{2M_\nu}$$

$$V_{en} = \sum_{i=1}^N \sum_{\nu=1}^{N'} \frac{-z_\nu e^2}{|r_i - R_\nu|}$$

$$V_{ee} = \frac{1}{2} \sum_{i,j=1}^{N'} \frac{e^2}{|r_i - r_j|}$$

$$V_{nn} = \frac{1}{2} \sum_{\nu,\mu=1}^{N'} \frac{z_\nu z_\mu e^2}{|R_\nu - R_\mu|}$$

Two adiabatic eigenvalue problems are obtained:
 the first is for electrons

$$\textcircled{\text{I}} \quad H_e \varphi_e(r, R) = [T_e + V_{ee} + V_{en} + V_{nn}] \varphi_e(r, R) = \epsilon_e(R) \varphi_e(r, R)$$

and the second for the nuclei

$$\textcircled{\text{II}} \quad H_n^{(e)} \chi_{\lambda e}(R) = [T_n + \epsilon_e(R)] \chi_{\lambda e}(R) = E_{\lambda e} \chi_{\lambda e}(R)$$

(3)

ELECTRONS IN CRYSTALS

Density-functional Kohn-Sham theory

"Real" crystal (interacting electrons)

$$H_e(N) = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + v(r_i) \right] + \frac{1}{2} \sum_{i,j=1}^N \frac{e^2}{r_{ij}} + \frac{1}{2} \sum_{k,l=1}^{N'} \frac{Z_k Z_l e^2}{R_{kl}}$$

$$v(\vec{r}) = \sum_{k=1}^{N'} \frac{-Z_k e^2}{|\vec{r} - \vec{R}_k|}$$

Equivalent Kohn-Sham system (non-interacting electrons with same particle density)

$$\tilde{H}(N) = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + v_{\text{eff}}(\vec{r}_i) \right] + \frac{1}{2} \sum_{k,l=1}^{N'} \frac{Z_k Z_l e^2}{R_{kl}}$$

$$\begin{cases} v_{\text{eff}}(\vec{r}) = v(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r}) \\ v_H(\vec{r}) = e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \\ v_{xc}(\vec{r}) = F[n(\vec{r})] = \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} \end{cases}$$

STANDARD BAND-STRUCTURE SCHEME

for solving the Kohn - Sham equations.

$$1. \quad \tilde{H} \Psi_{m,k}(\mathbf{r}) = \varepsilon_m(\mathbf{k}) \Psi_{m,k}(\mathbf{r})$$

$$\tilde{H} = \frac{p^2}{2m} + \underbrace{V_n(\mathbf{r}) + V_e(\mathbf{r})}_{\rightarrow V_{eff}(\vec{r})}$$

$$V_e(\mathbf{r}) = V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$2. \quad \rho(\mathbf{r}) = e \sum_{m,k} |\Psi_{m,k}(\mathbf{r})|^2$$

$$3a. \quad V_{xc}(\mathbf{r}) = F[\rho(\mathbf{r})]$$

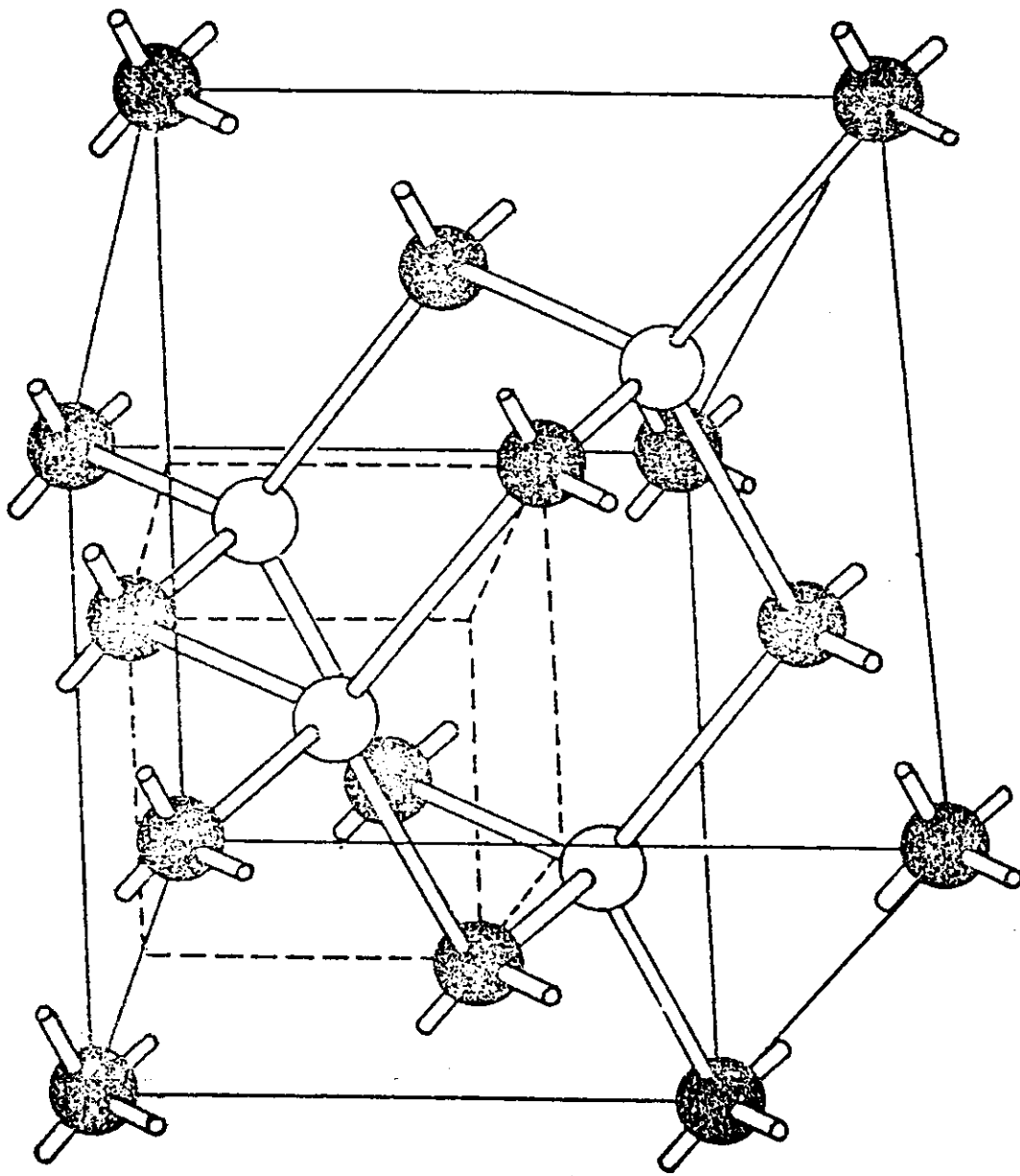
$$3b. \quad \Delta V_H(\mathbf{r}) = -4\pi e \rho(\mathbf{r})$$

which implies two constants of integration.

Standard scheme sets:

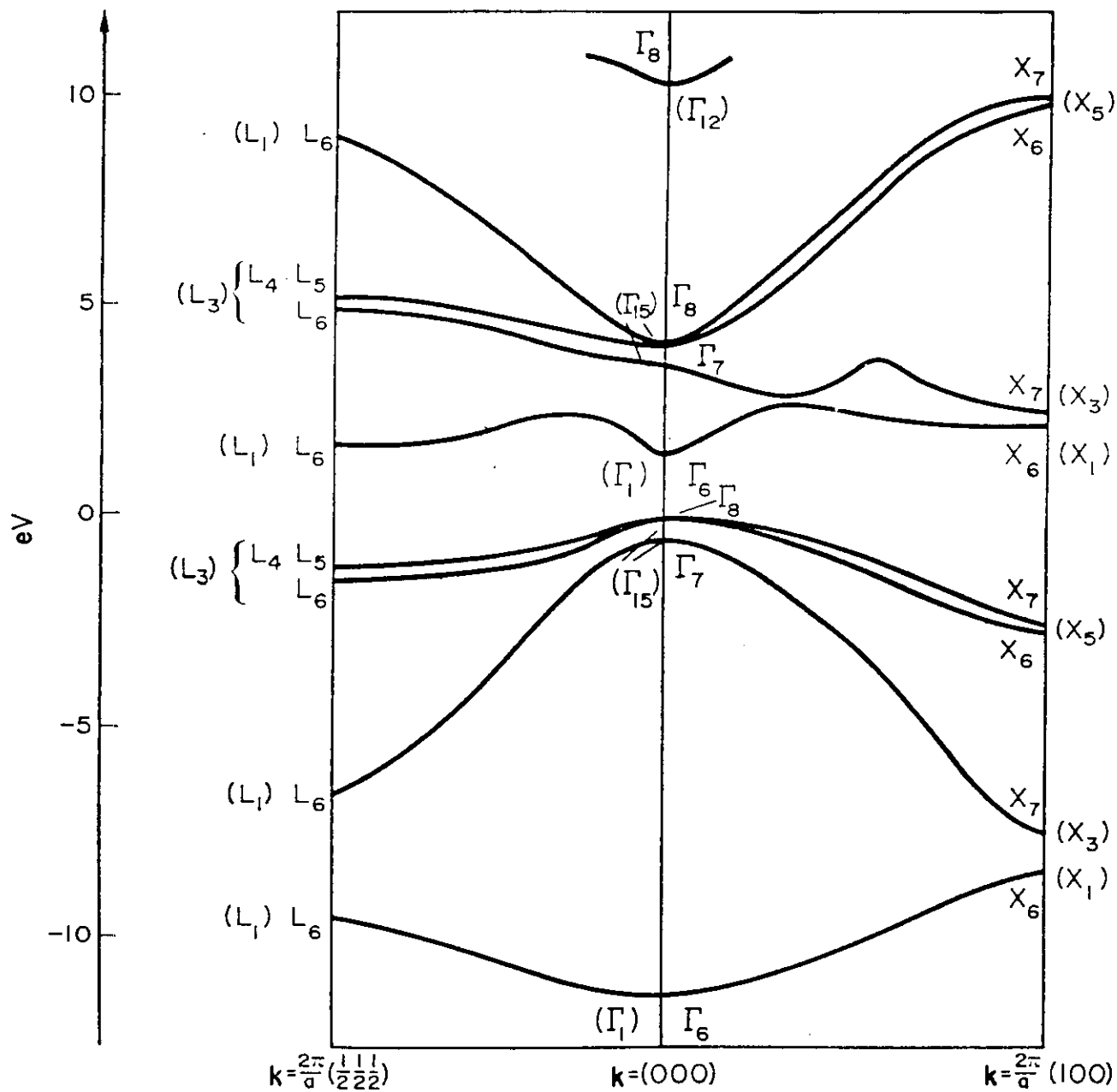
$$(i) \quad \int_{\Omega} \nabla V_H(\mathbf{r}) d^3r = \langle \mathbf{E} \rangle = 0$$

$$(ii) \quad \int_{\Omega} V_H(\mathbf{r}) d^3r = \langle V_H \rangle = 0.$$



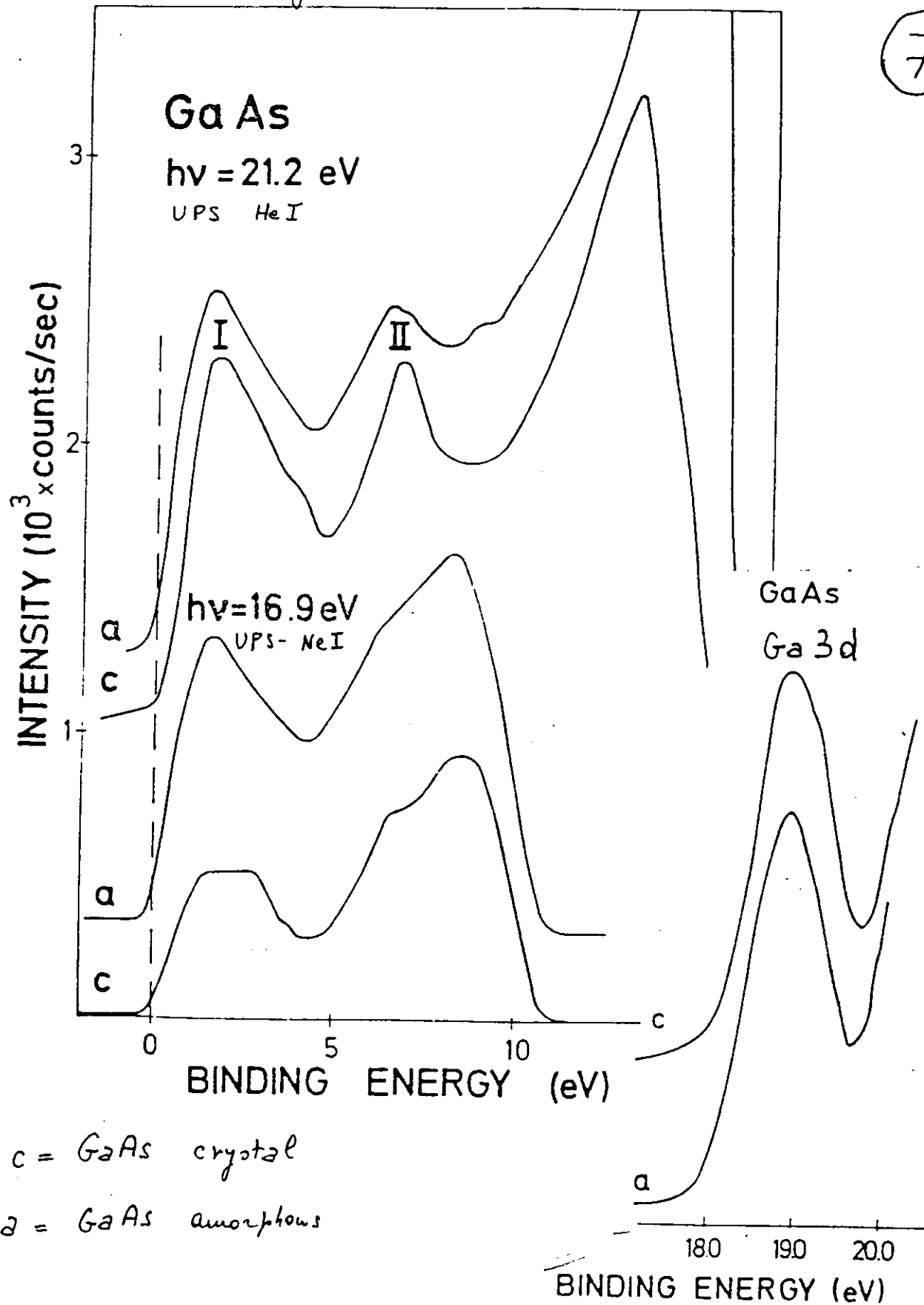
Zinc-blende crystal lattice.

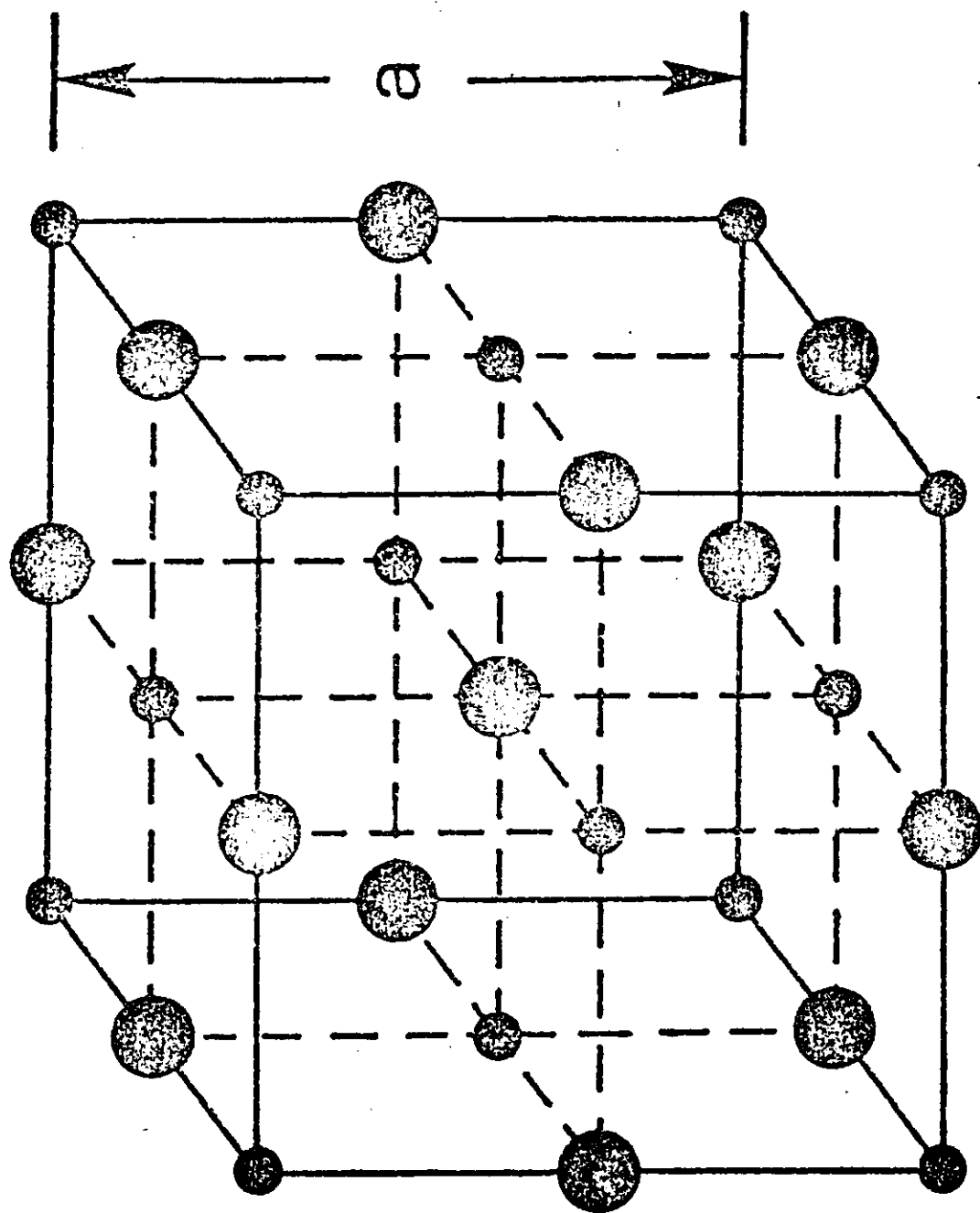
Each atom has tetrahedral coordination (4 neighbours).
 Applies to most cubic semiconductors (GaAs, InAs, InP, ZnSe).



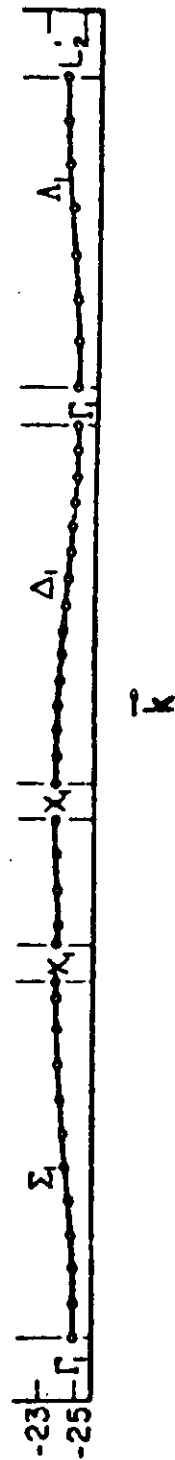
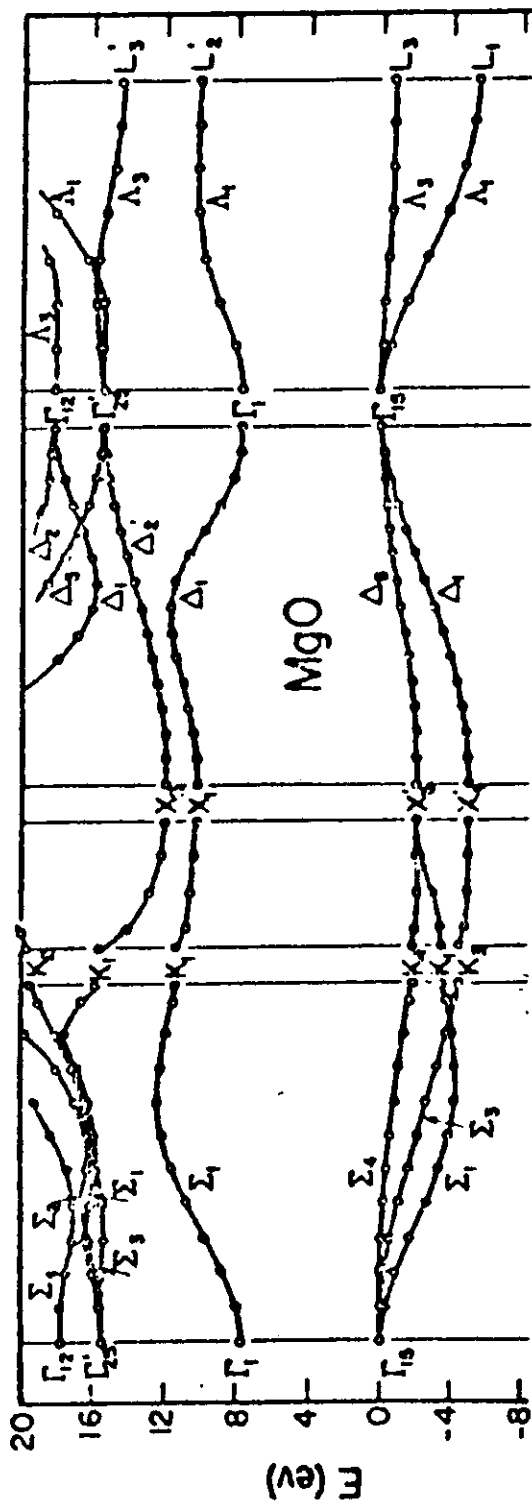
Energy bands for GaAs with the inclusion of spin-orbit interaction. The irreducible representations for the states of the simple group are supplied in brackets.

Valence-band density of states of crystal-GaAs and amorphous-GaAs measured by UPS. Notice similarity.



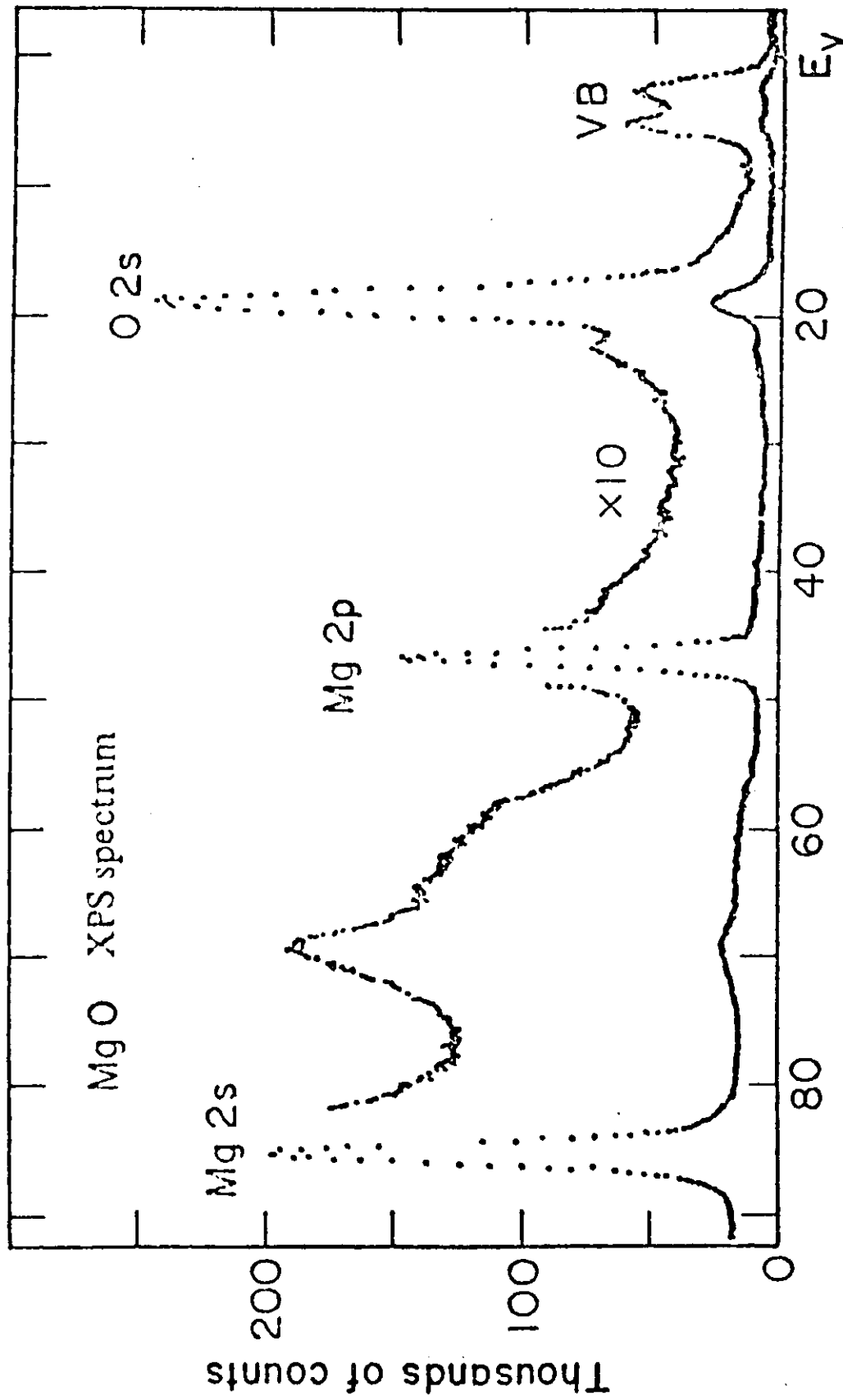


Rock salt crystal lattice. Each atom has octahedral coordination (6 neighbors). Applies to many ionic solids (MgO , NaCl , NiO , ...)

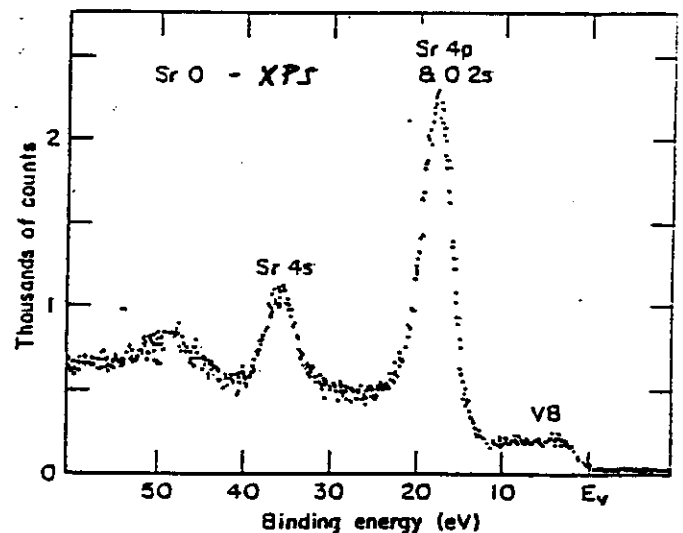
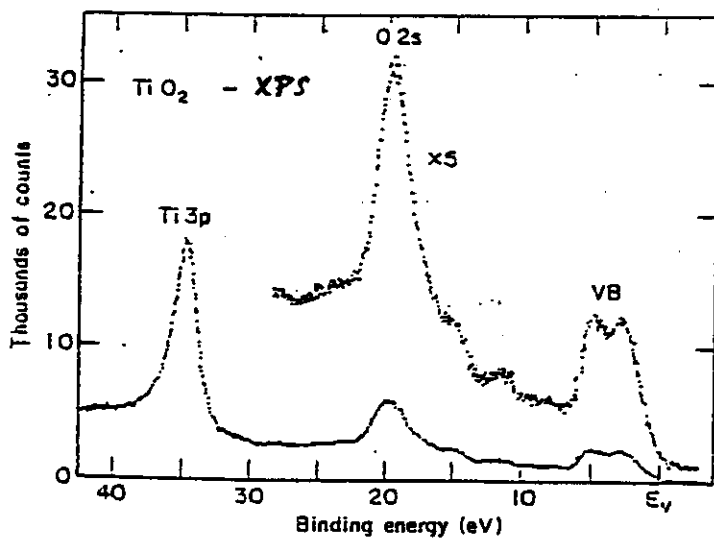
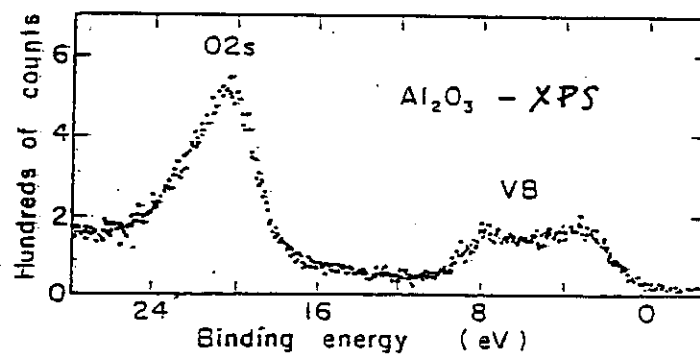
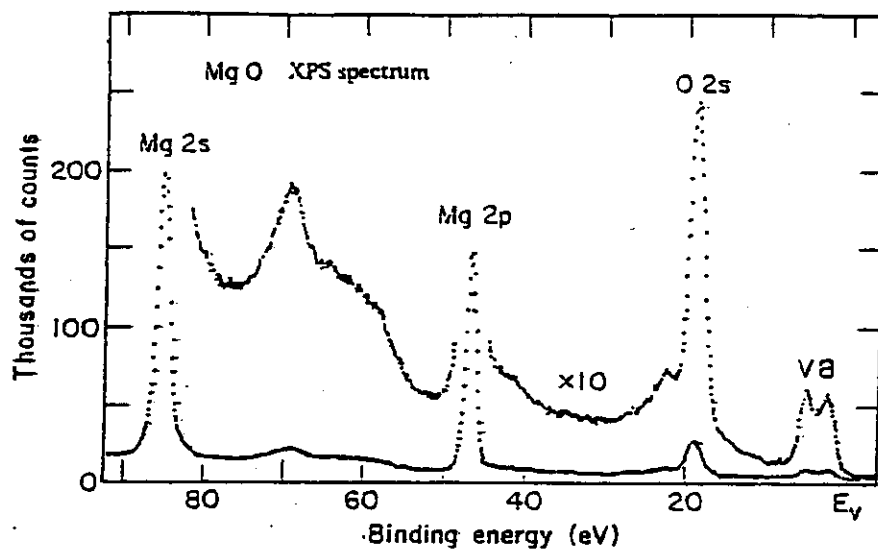


Electronic energy band structure of MgO.

Spin-orbit interaction is not included.



Valence- and core-band density of states of MgO measured by XPS. Upper valence band (VB) corresponds to O 2p bands.

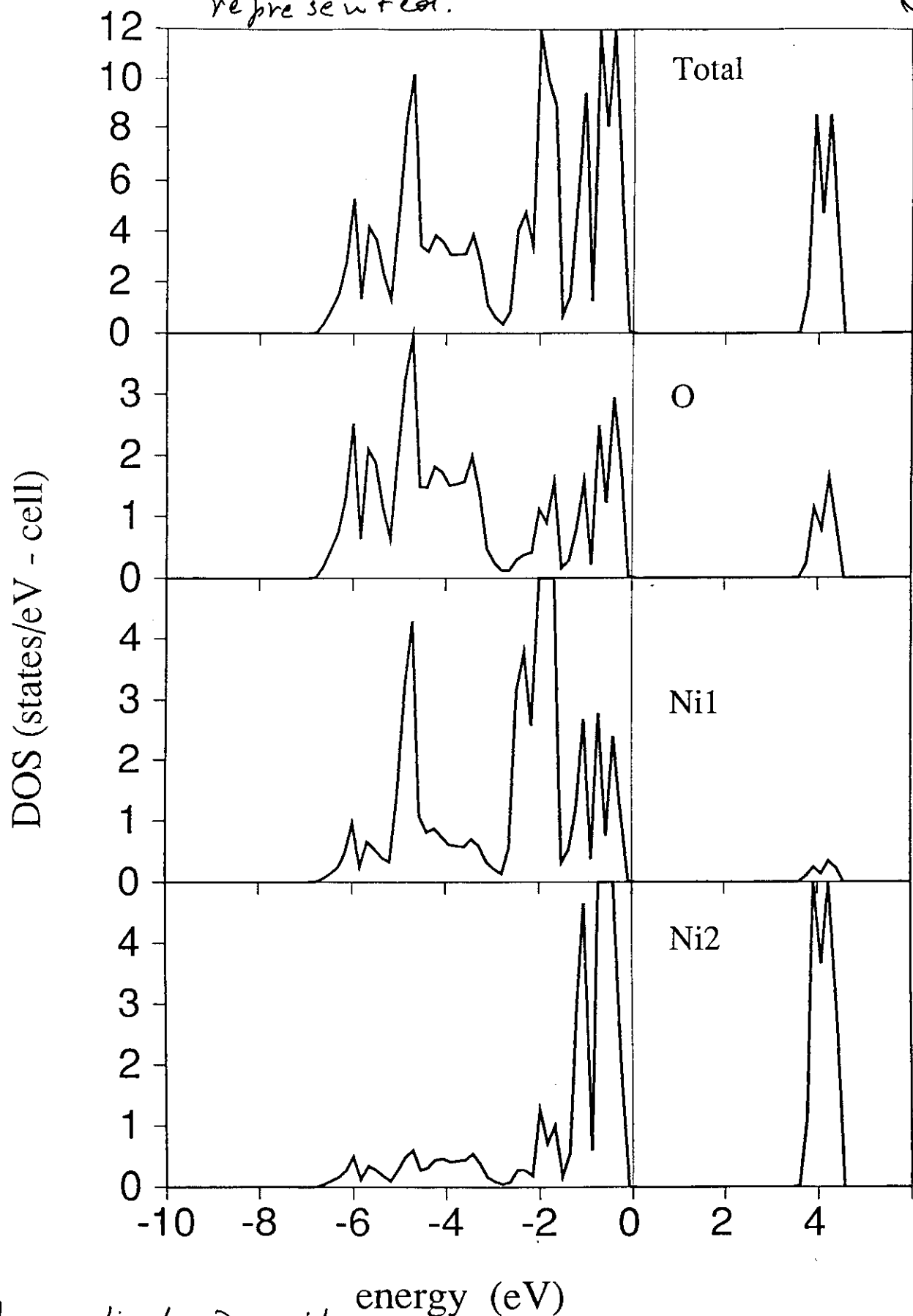


Al K α XPS spectra of several oxides

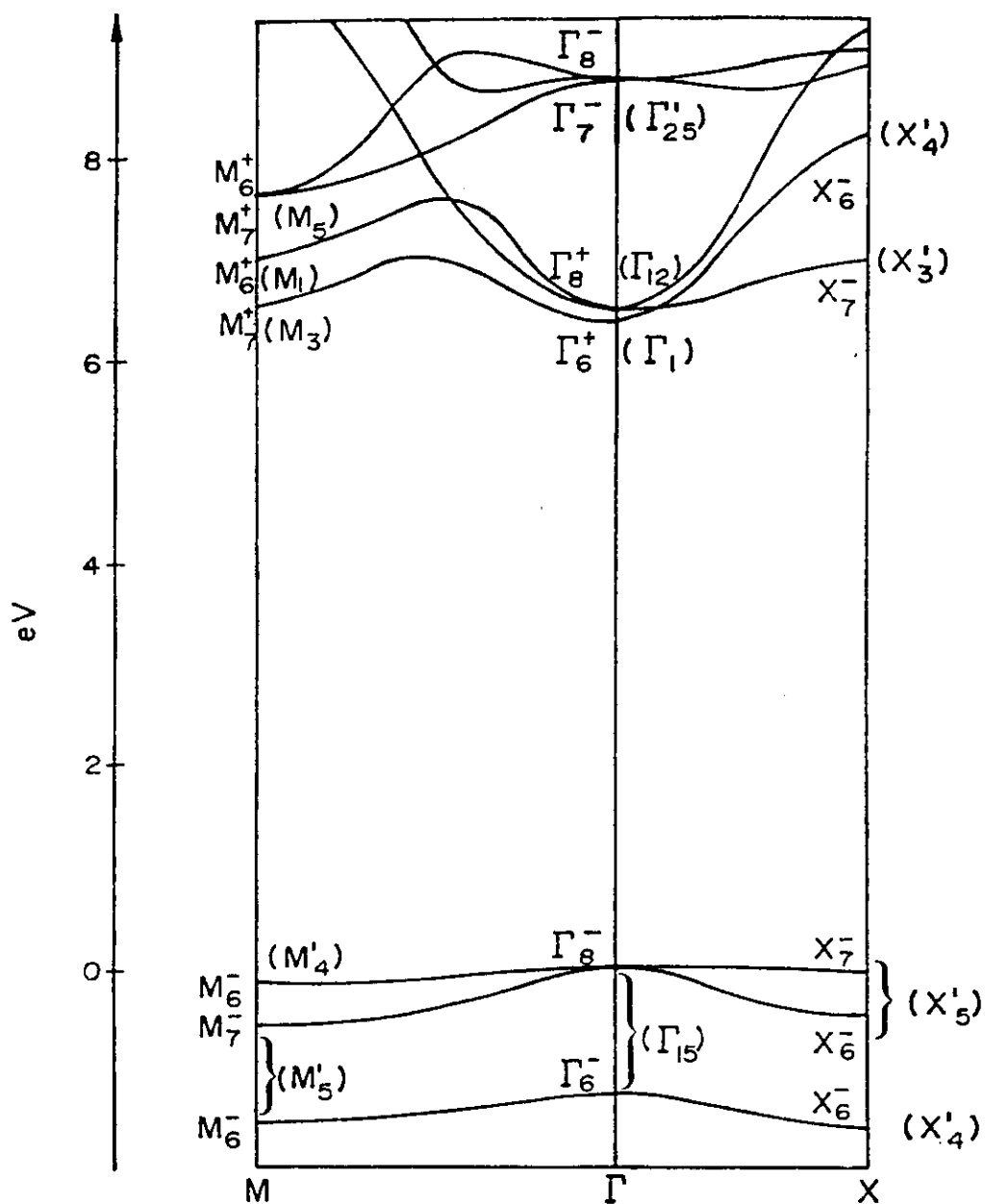
Notice similarity of O 2s and O 2p structures in different compounds.

Total and partial (atomic) densities of states in NiO - Spin ↑ states only are represented.

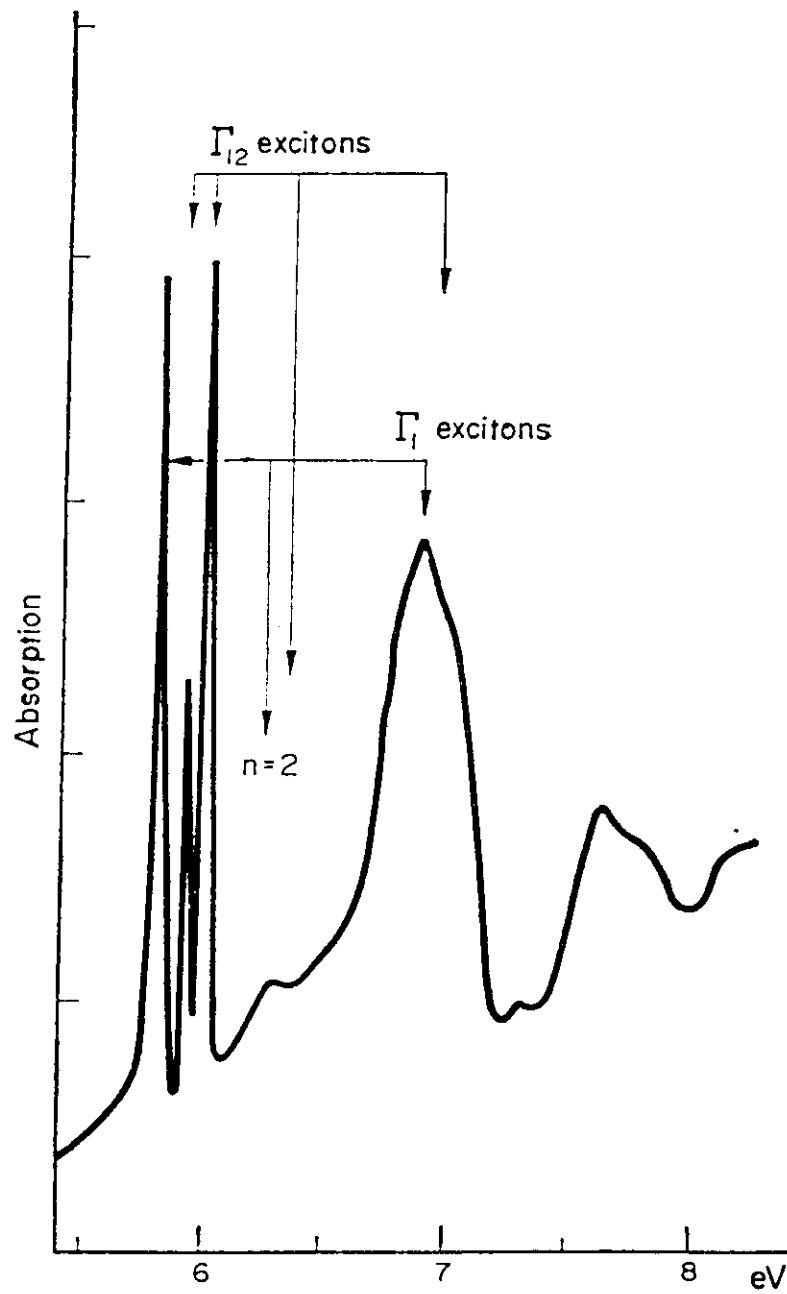
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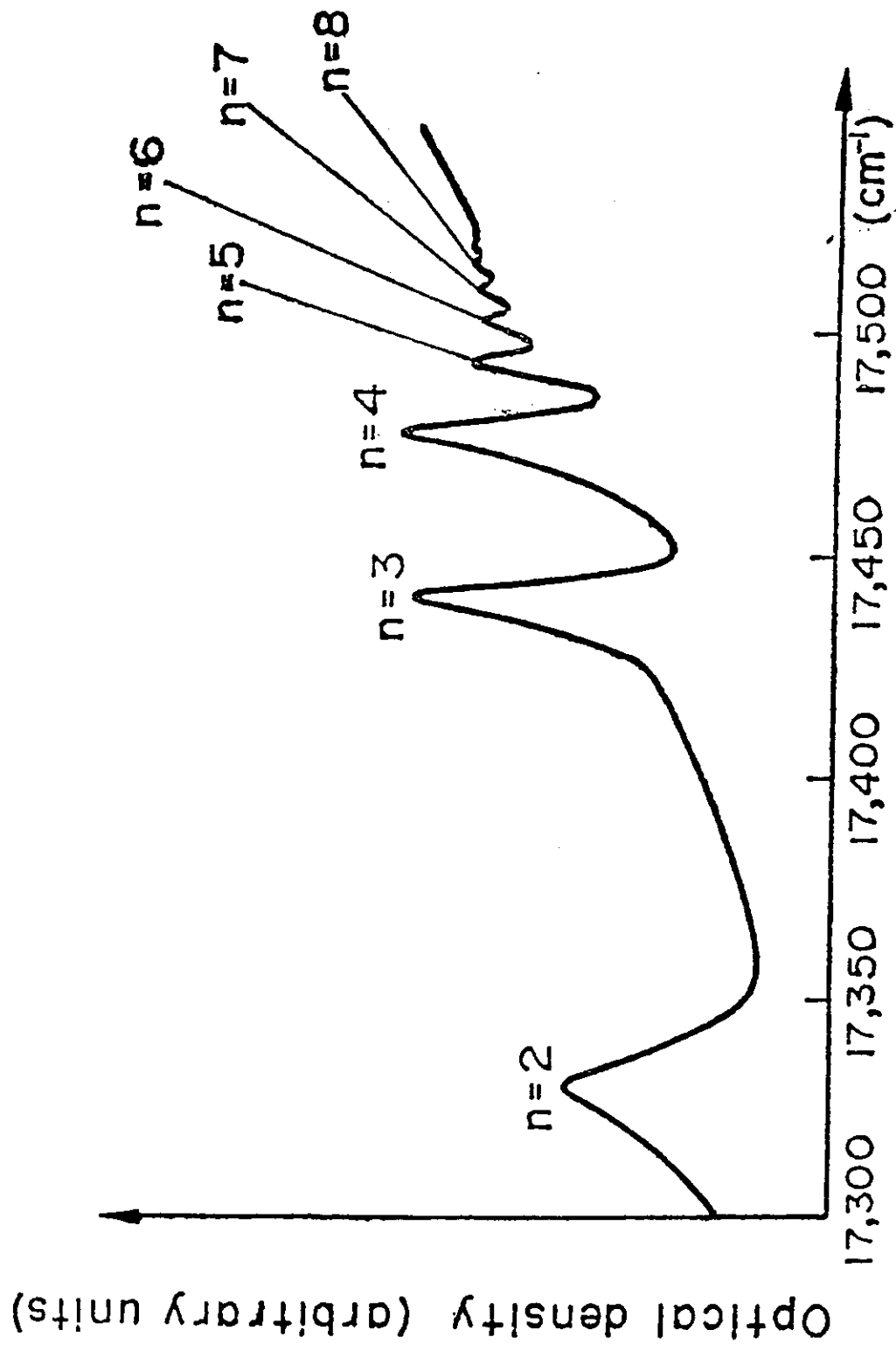
Theoretical Density of states of NiO for both occupied ($E < 0$) and empty states ($E > 0$) -



Energy bands for CsI. The notations appropriate to double group representations are used. The notations appropriate to simple group representations are given in parentheses.



Absorption spectrum at 10K of thin CsI film. (After Tee-garden and Baldini) The interpretation of exciton peaks is due to Onodera .



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Optical density for the yellow exciton series of Cu_2O at 4.2K.

1. Radiation field in vacuum

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- choice of gauge for scalar and vector potentials $\left\{ \begin{array}{l} \varphi(\vec{r}, t) = 0 \\ \vec{\nabla} \cdot \vec{A}(\vec{r}, t) = 0 \end{array} \right.$
- Vector potential for monochromatic radiation

$$\vec{A}(\omega; \vec{r}, t) = A_0(\omega) \vec{\eta} \left[e^{i(\vec{k} \cdot \vec{r} - \omega t + \delta_\omega)} + \text{c.c.} \right]$$

$$\text{where } \omega = |\vec{k}|c \quad \text{and } \vec{\eta} \cdot \vec{k} = 0$$

$$|\vec{\eta}| = 1 \quad \vec{\eta} = \text{vector of polarization}$$

- Electric and magnetic fields

$$\left\{ \begin{array}{l} \vec{E}(\omega; \vec{r}, t) = -2\omega A_0(\omega) \vec{\eta} \sin(\vec{k} \cdot \vec{r} - \omega t + \delta_\omega) \\ \vec{E} \parallel \vec{\eta} \end{array} \right.$$

$$\left\{ \begin{array}{l} \vec{B}(\omega; \vec{r}, t) = -2 A_0(\omega) \vec{k} \times \vec{\eta} \sin(\vec{k} \cdot \vec{r} - \omega t + \delta_\omega) \\ \vec{B} \perp \vec{k} ; \quad \vec{B} \perp \vec{\eta} \end{array} \right.$$

2. Coupling to quantum systems

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- One particle with mass m and charge q

$$h_0 = \frac{\vec{p}^2}{2m} + V(\vec{r}, \vec{\sigma})$$

$$\left\{ \begin{array}{l} \vec{p} \rightarrow \vec{p} - \frac{q}{c} \vec{A}(\omega; \vec{r}, t) \\ h_0 \rightarrow h \end{array} \right\} \text{ in presence of radiation field}$$

$$h = h_0 + \frac{q}{mc} \vec{p} \cdot \vec{A}(\omega; \vec{r}, t)$$

where second order terms in A have been neglected (low radiation intensity)

- N particles with masses m_i and charges q_i

$$H_0 = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + U$$

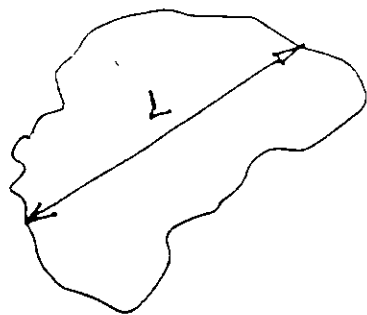
$$H = H_0 + \sum_{i=1}^N - \frac{q_i}{m_i c} \vec{p}_i \cdot \vec{A}(\omega; \vec{r}_i, t)$$

- Coupling operator to be used in time-dependent perturbation theory

$$W = \sum_{i=1}^N - \frac{q_i A_0(\omega)}{m_i c} \vec{\eta} \cdot \vec{p}_i \left[e^{-i(\vec{k} \cdot \vec{r}_i - \omega t + \delta_\omega)} + \text{c.c.} \right]$$

3. Dipole approximation

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L = linear dimension of quantum system

If $kL \ll 1$ the coupling operator can be approximated as:

$$W \simeq - \frac{A_0(\omega)}{c} \left[e^{-i(\omega t - \delta_\omega)} + \text{c.c.} \right] \sum_{i=1}^N \frac{q_i}{m_i} \vec{\eta} \cdot \vec{P}_i$$

and its matrix element between initial state $|\psi_0\rangle$ and final state $|\psi_f\rangle$ becomes

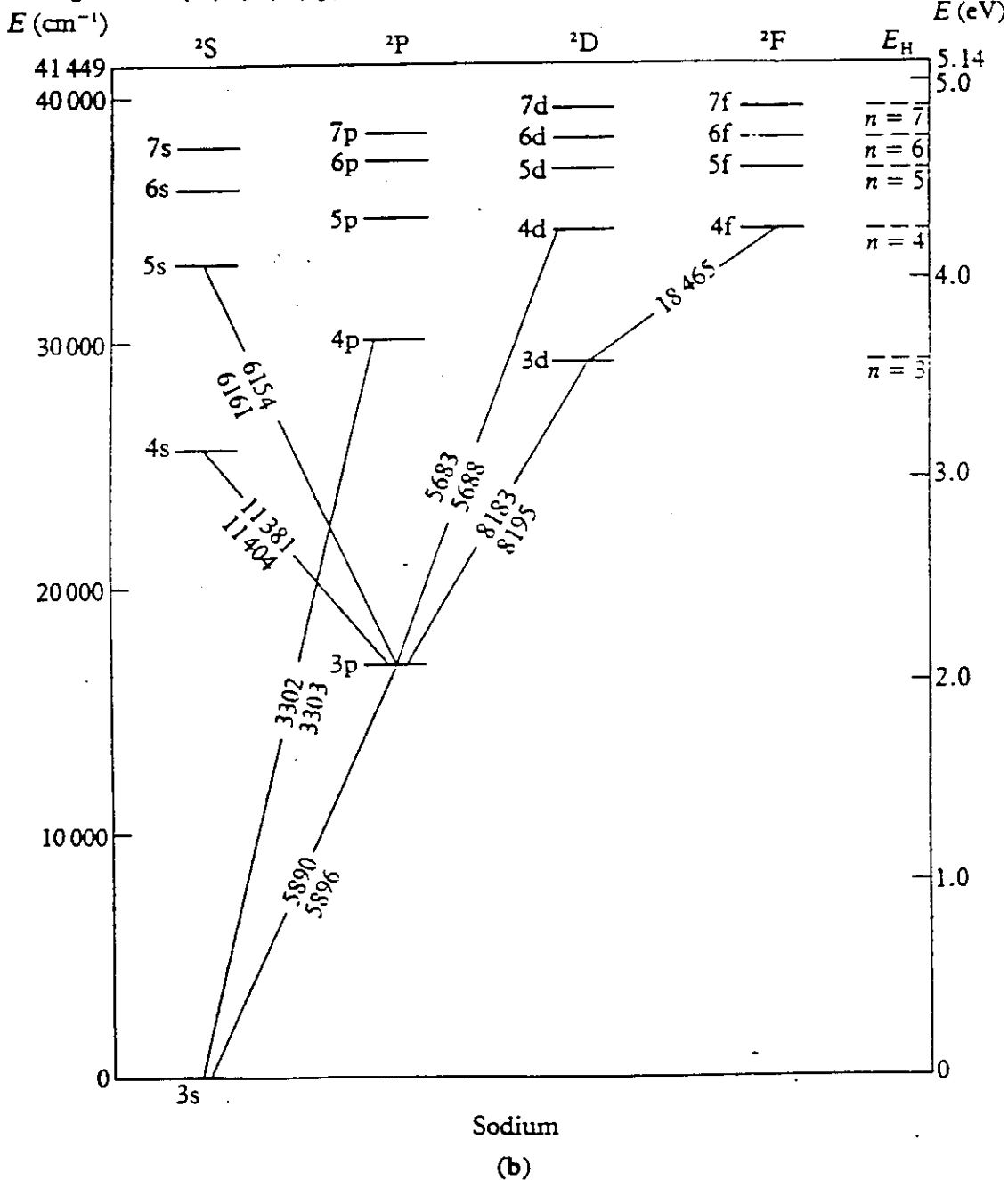
$$\begin{aligned} \langle \psi_f | W | \psi_0 \rangle &= - \frac{A_0(\omega)}{c} \left[e^{-i(\omega t - \delta_\omega)} + \text{c.c.} \right] \sum_{i=1}^N \frac{q_i \vec{\eta}}{i\hbar} (\bar{E}_0 - \bar{E}_f) \langle \psi_f | \vec{r}_i | \psi_0 \rangle \\ &= \frac{i A_0(\omega)}{\hbar c} \left[e^{-i(\omega t - \delta_\omega)} + \text{c.c.} \right] (\bar{E}_0 - \bar{E}_f) \vec{\eta} \langle \psi_f | \sum_{i=1}^N q_i \vec{r}_i | \psi_0 \rangle \end{aligned}$$

where $\sum_{i=1}^N q_i \vec{r}_i$ is the electric dipole operator of the system.

In the above derivation, use has been made of the relationship

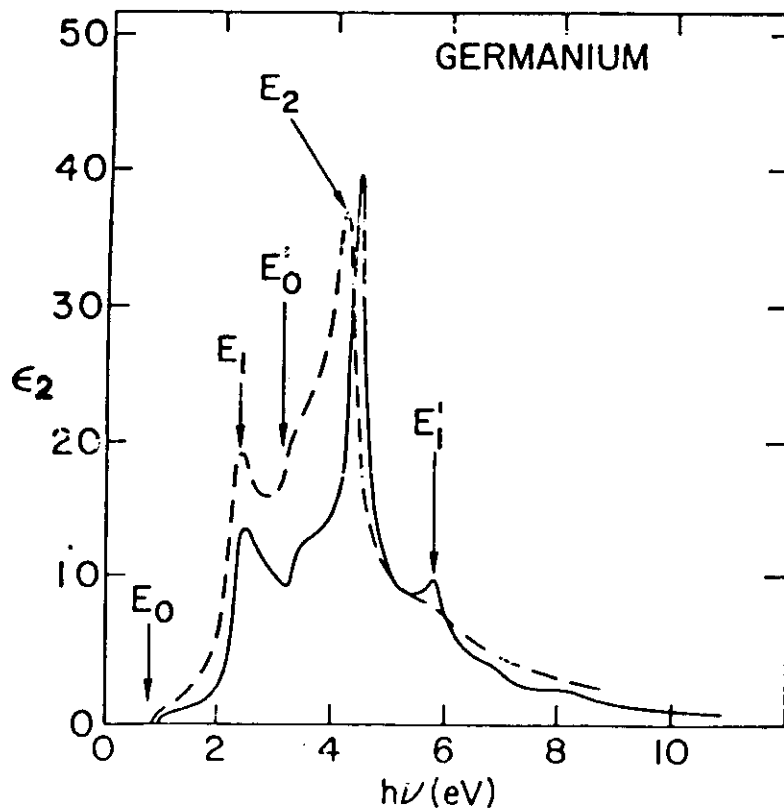
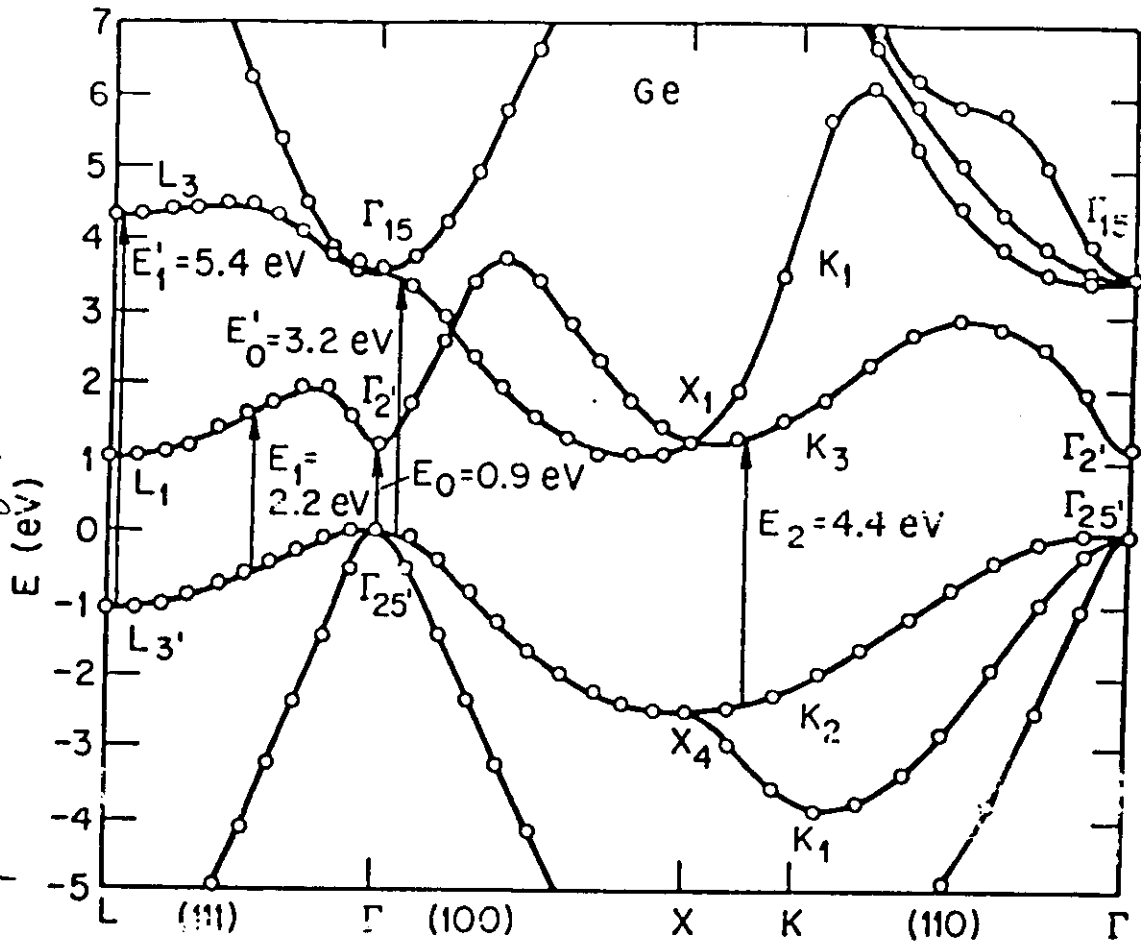
$$\vec{P}_i = (i\hbar)^{-1} [\vec{r}_i, H_0] .$$

Configuration: $(1s)^2 (2s)^2 (2p)^6 nl$



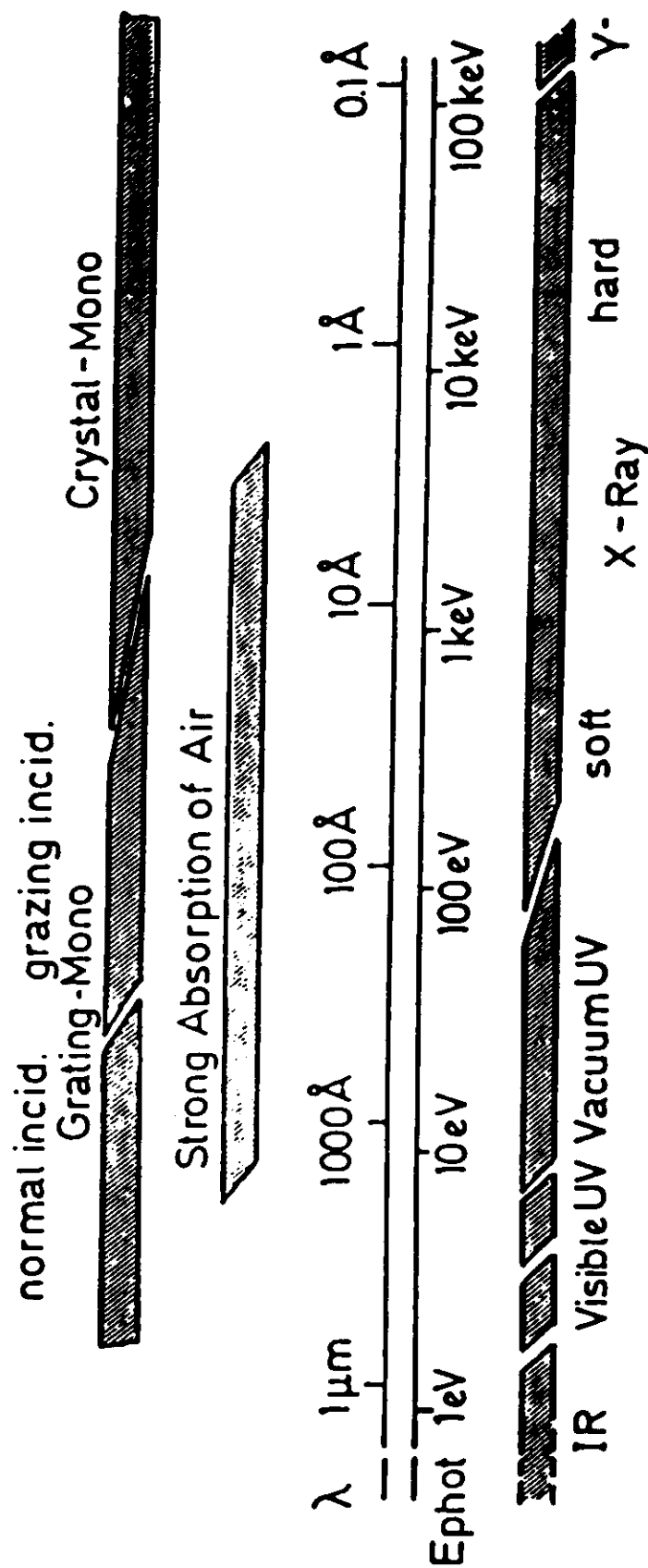
Allowed optical transitions in atomic sodium. Notice selection rule $\Delta l = \pm 1$, $l = \text{angular momentum}$.

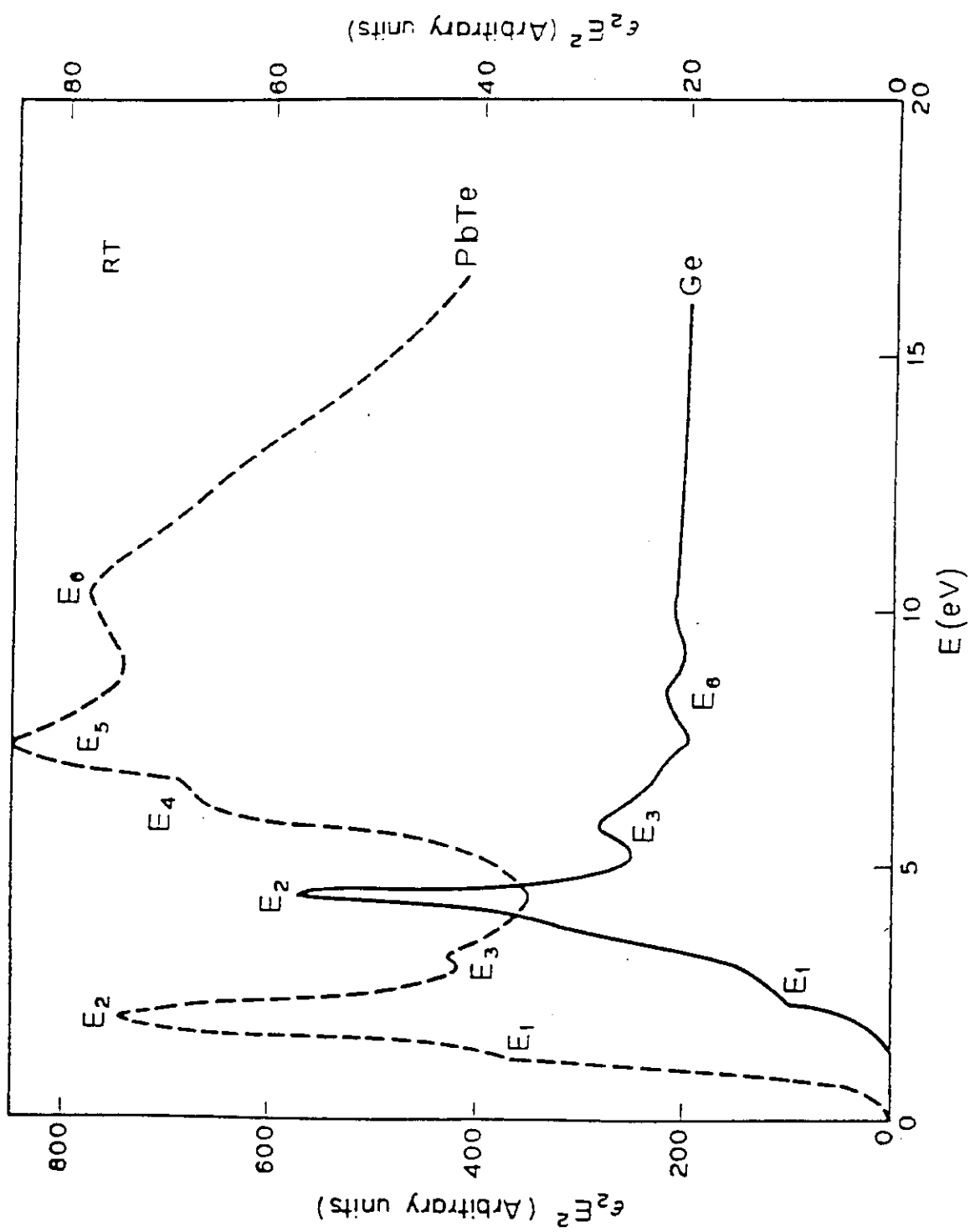
Energy bands of Ge close to the
fundamental gap.



Energy dependence of the imaginary part of the dielectric function of Ge. Experimental data (solid line) from H. R. Philipp and H. Ehrenreich, Phys. Rev. 129, 1550 (1963), calculated spectrum (broken line)

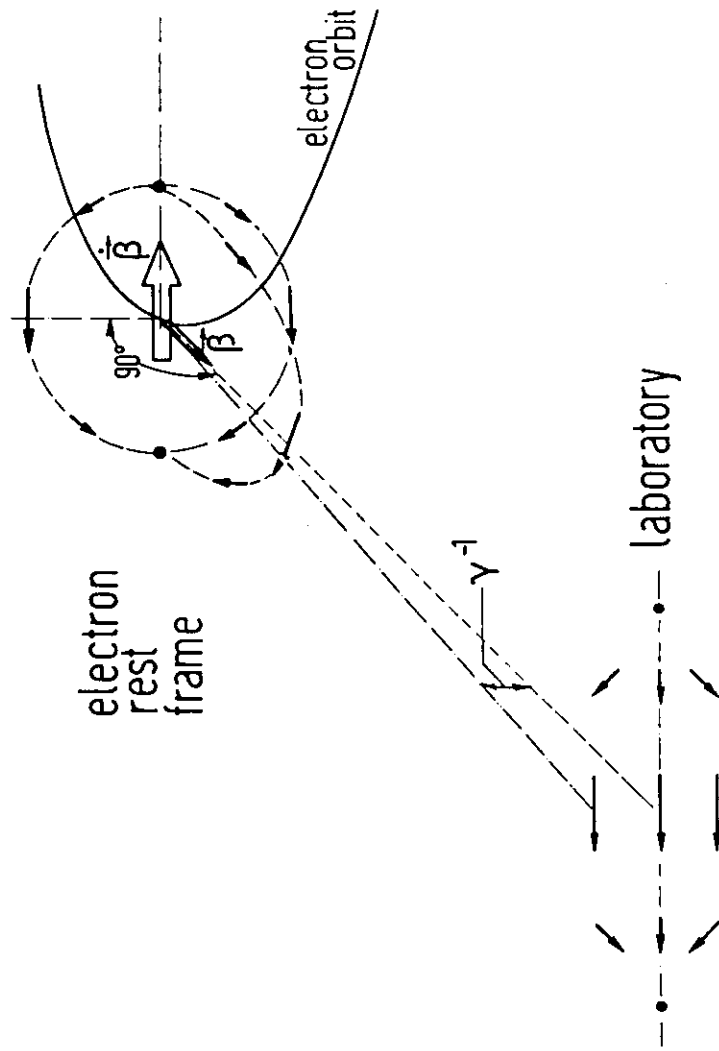
SPECTRAL REGIONS FOR USING SYNCHROTRON RADIATION





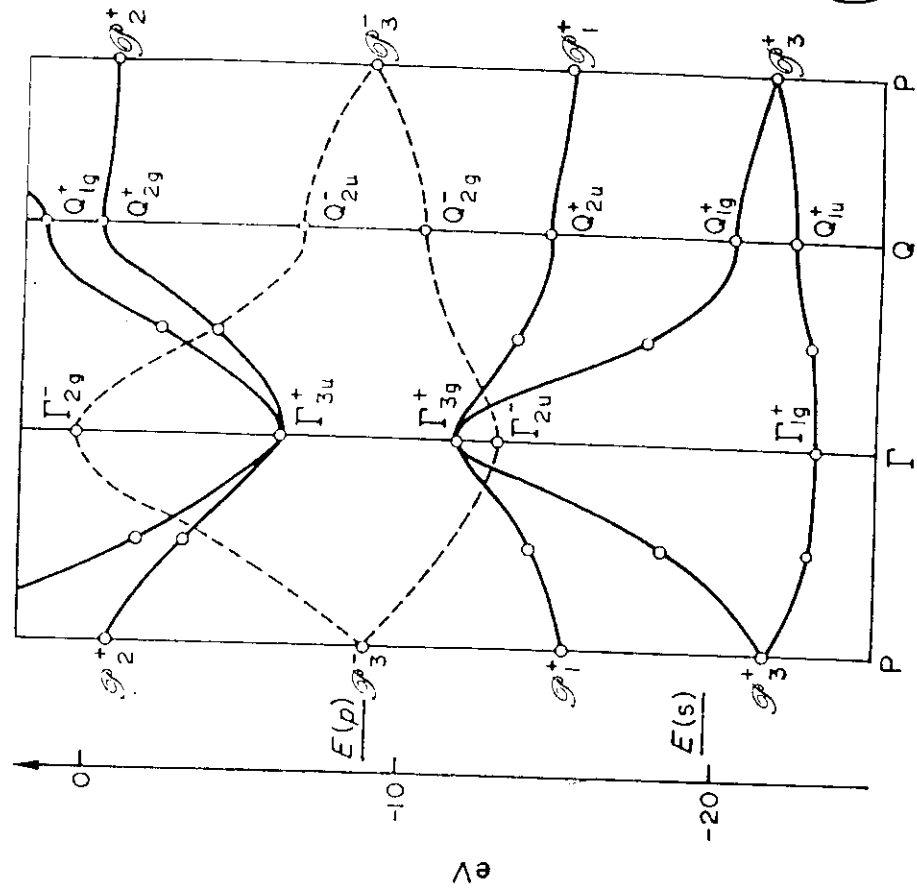
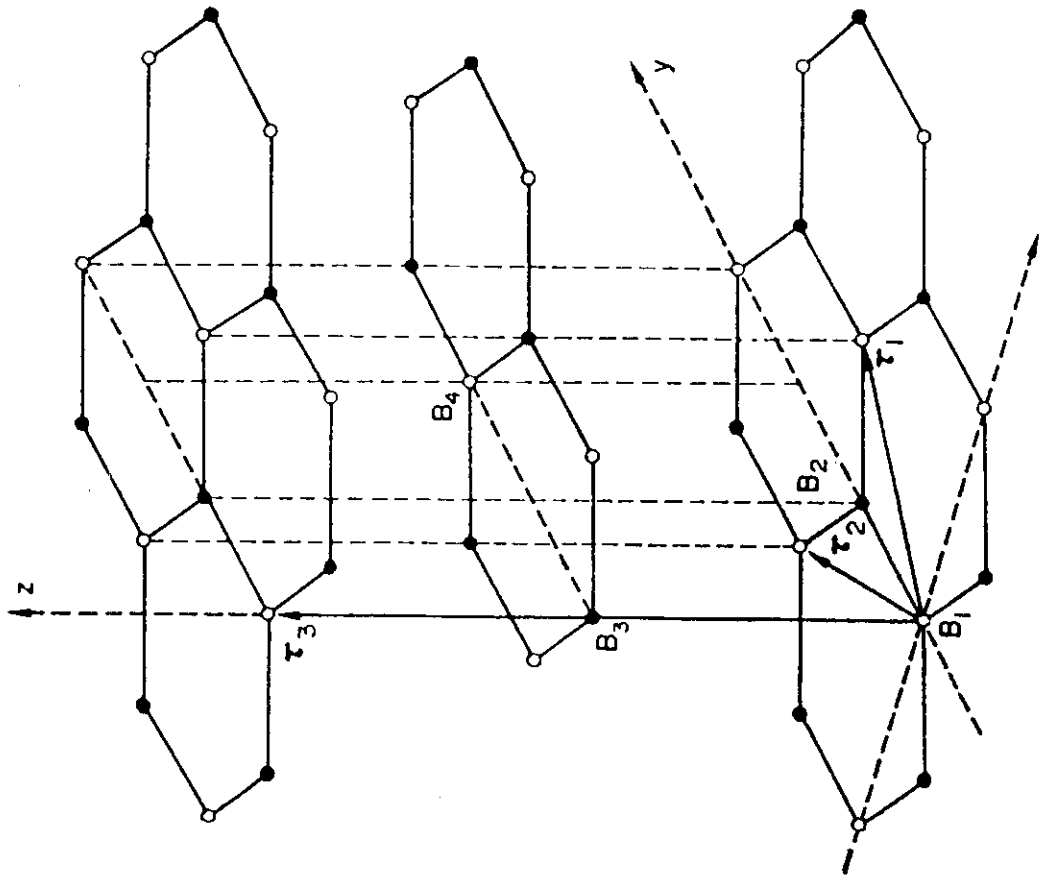
The density of states function $\epsilon_2 E^2$ for Ge and PbTe derived from normal incidence reflectance data.

Both materials are cubic. No optical anisotropy is observed.

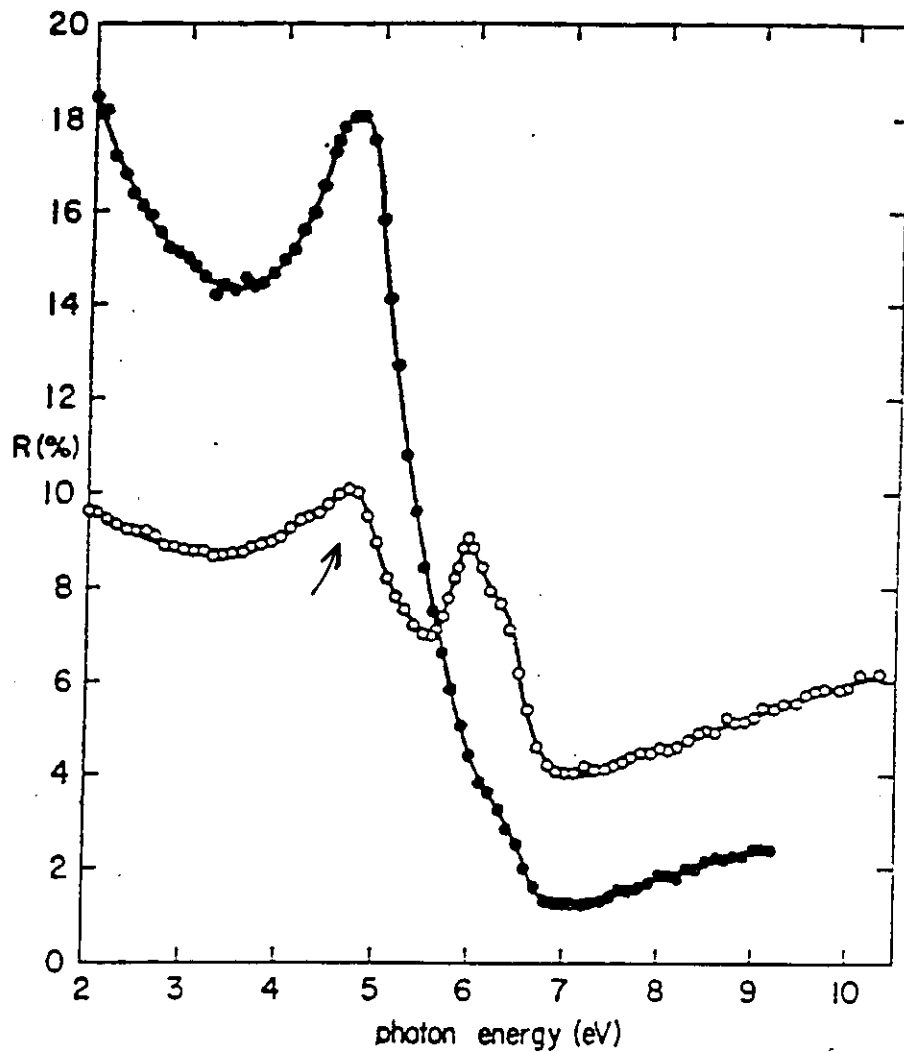


Non-relativistic dipole radiation pattern and its appearance after the relativistic angle transformation. Arrows indicate direction and magnitude of the electric vector

Polarization of synchrotron light.

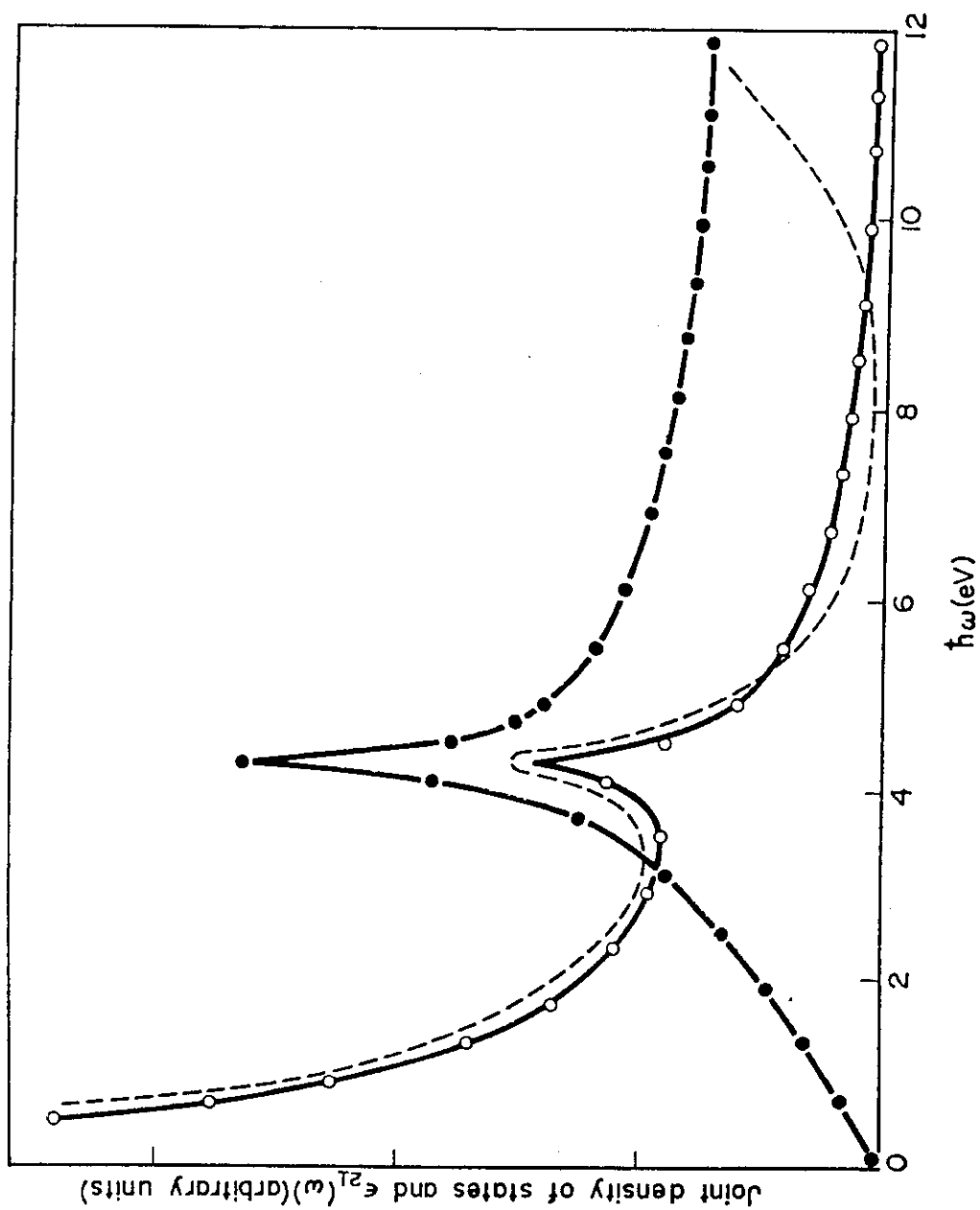


Energy bands for two-dimensional graphite. Bands even (odd) with respect to the σ_h reflection are denoted by continuous (broken) lines. The energies of the valence states of carbon atom are also shown.

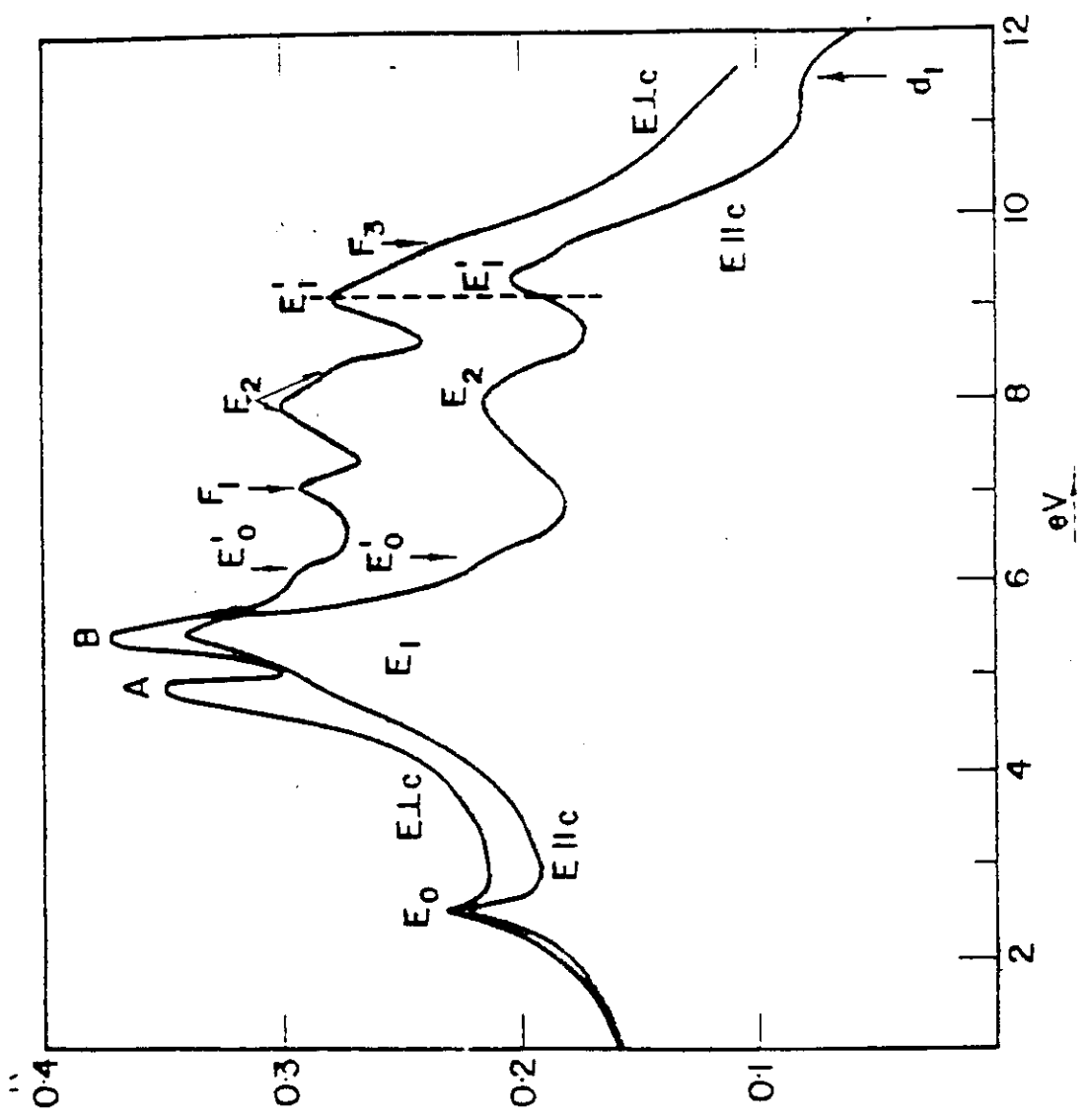


Reflectivity of polished pyrolytic graphite for (●) $E \perp c$ and (○) $E \parallel c$ under near-normal incidence.

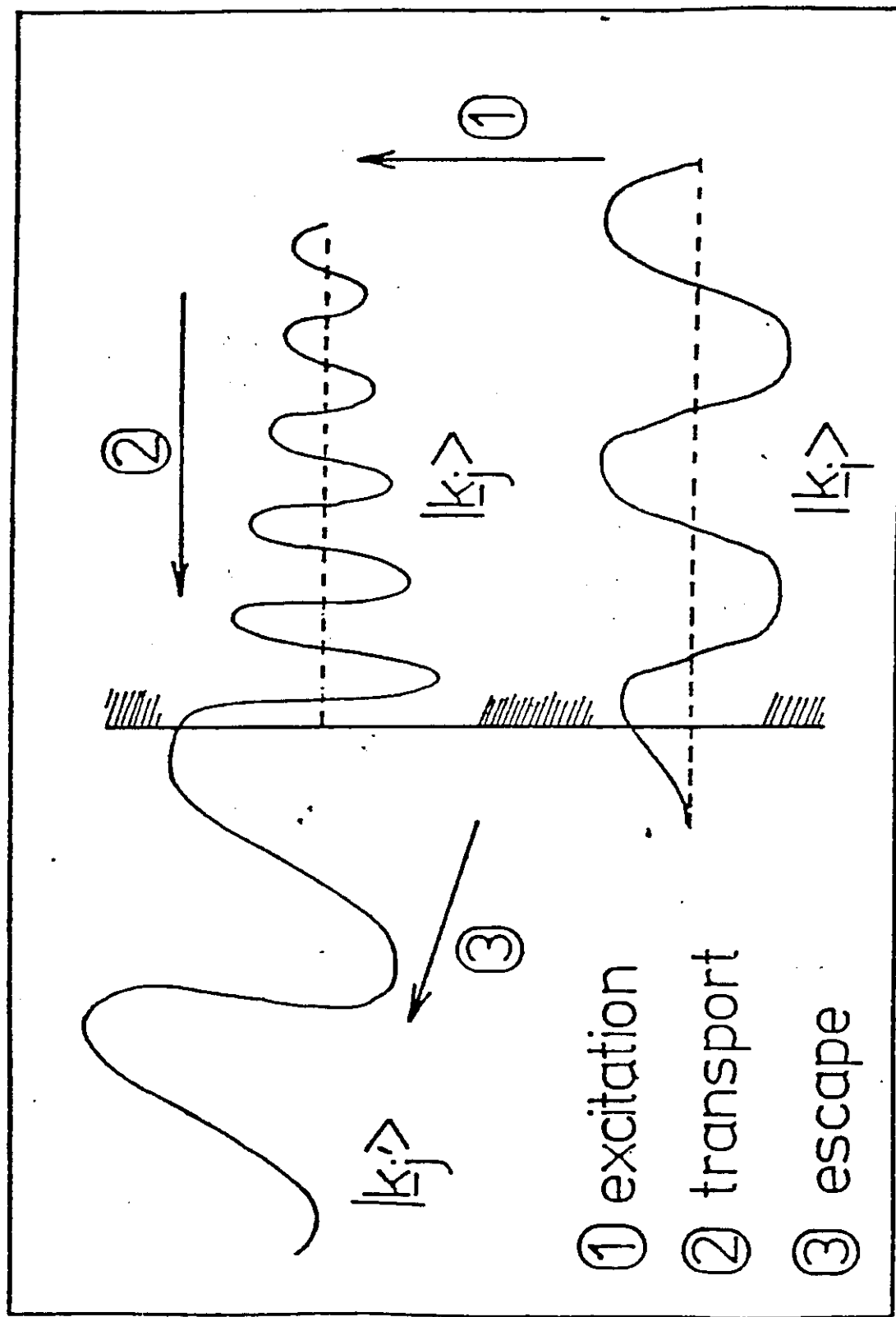
The arrow indicates a residue of the $E \perp c$ spectrum. Should not be there for perfect normal incidence and perfect sample.



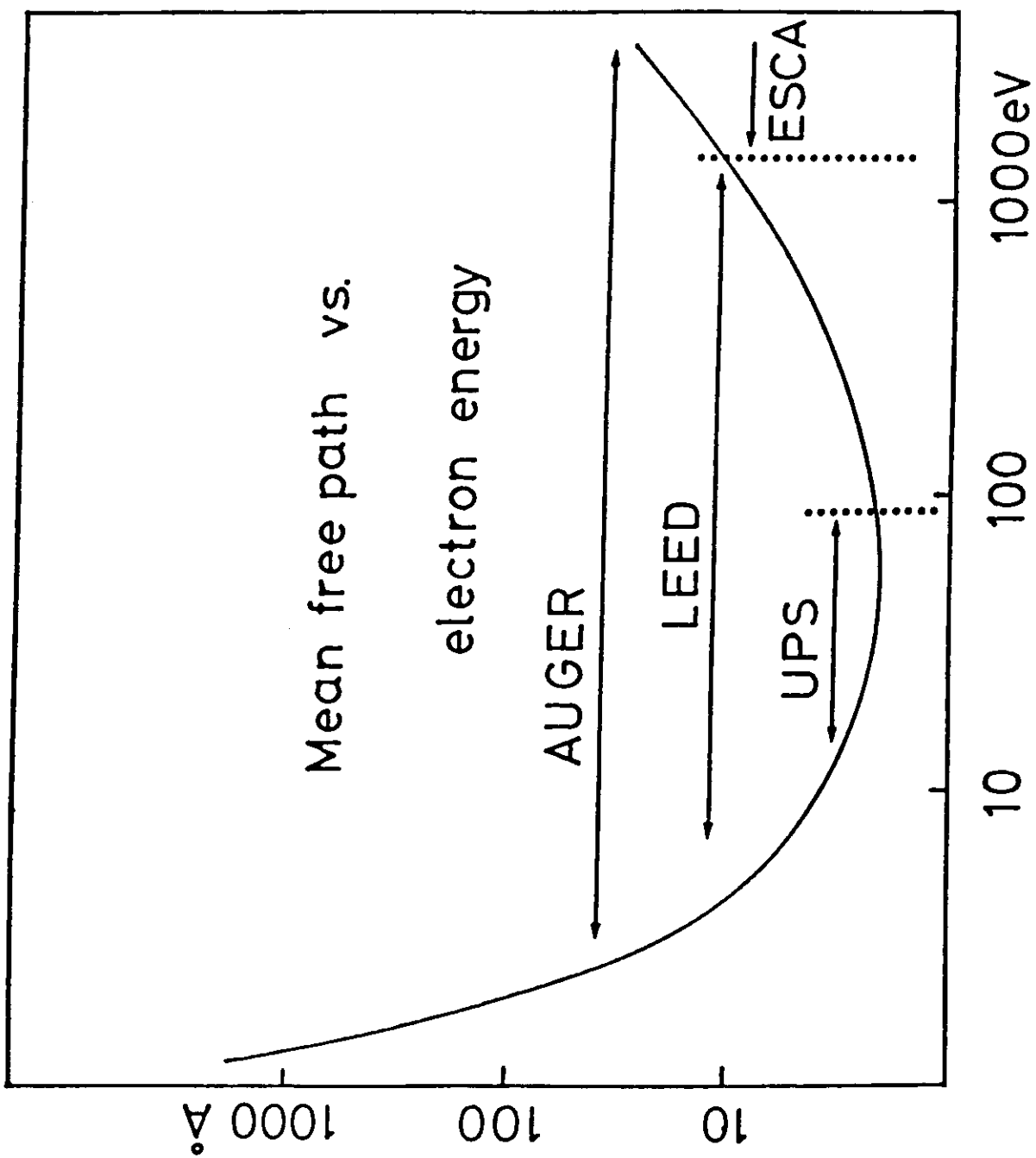
Joint density of states (solid circles) and imaginary part of the dielectric constant (open circles) computed from the π bands of two-dimensional graphite. The experimental dielectric function of Taft and Philipp is also given.

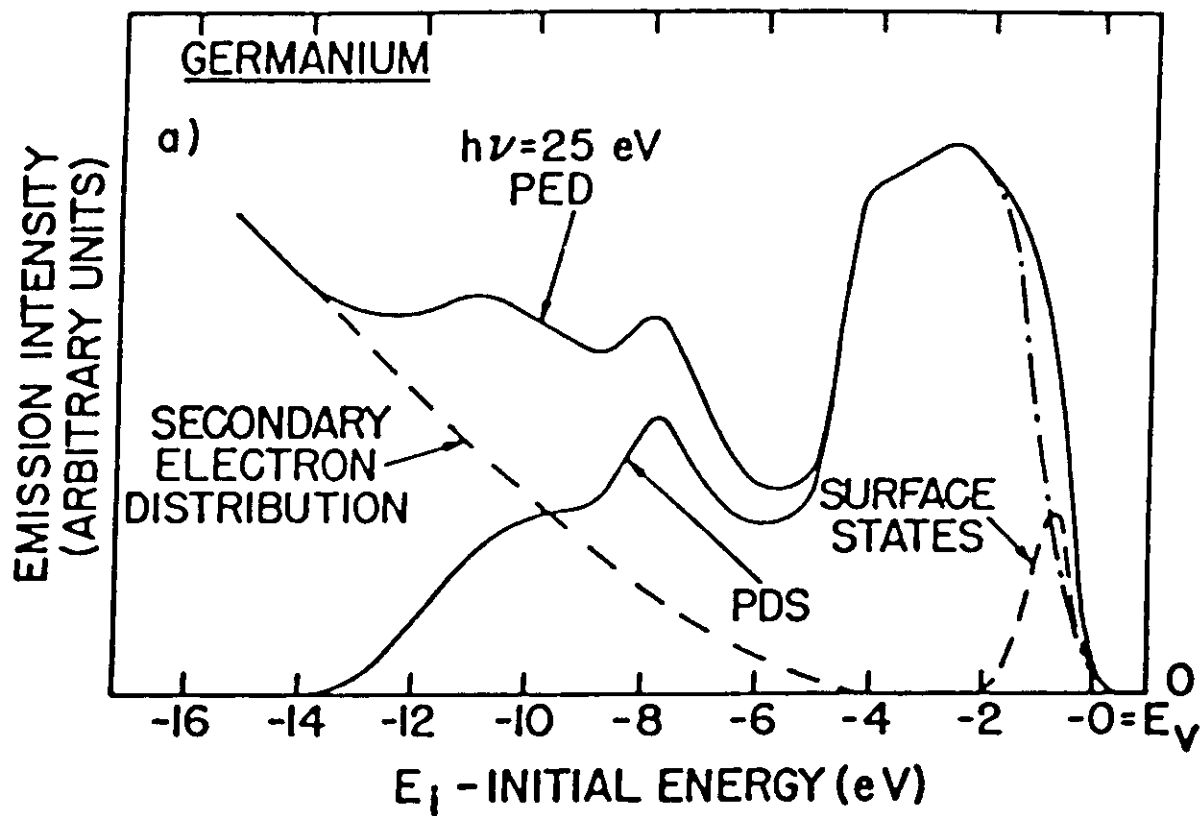


Room temperature reflectivity of hexagonal CdS for $E_{\perp} c$ and $E_{\parallel} c$ (Cardona and Harbeke).

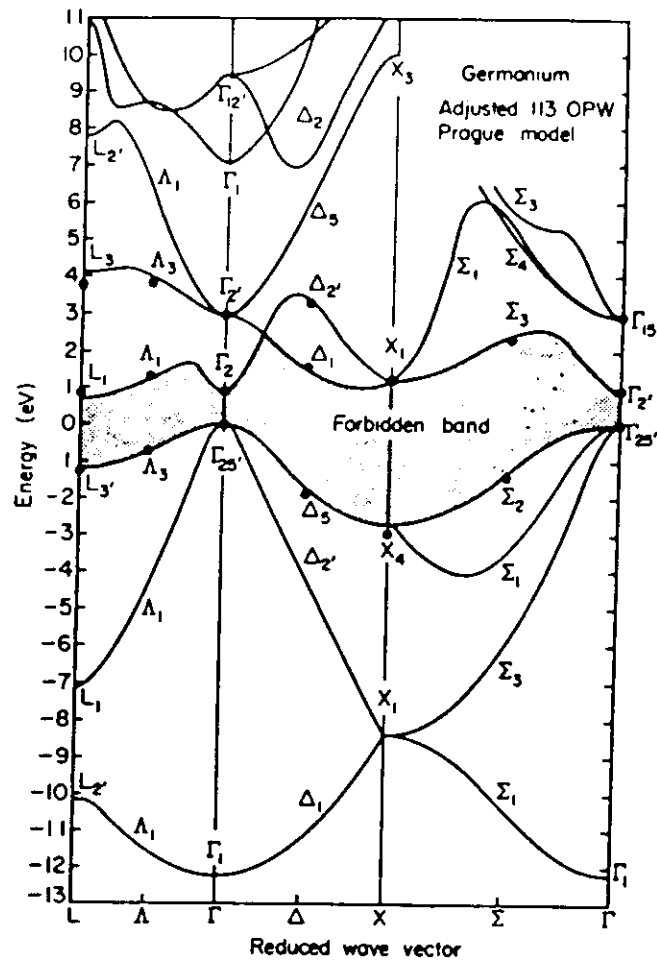


Scheme of photoemission experiment.

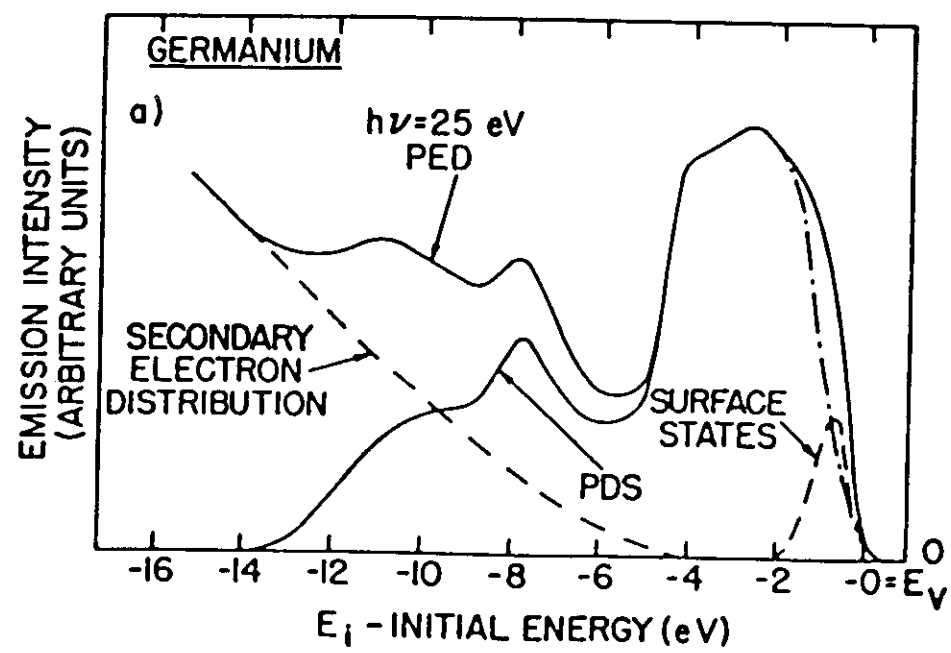


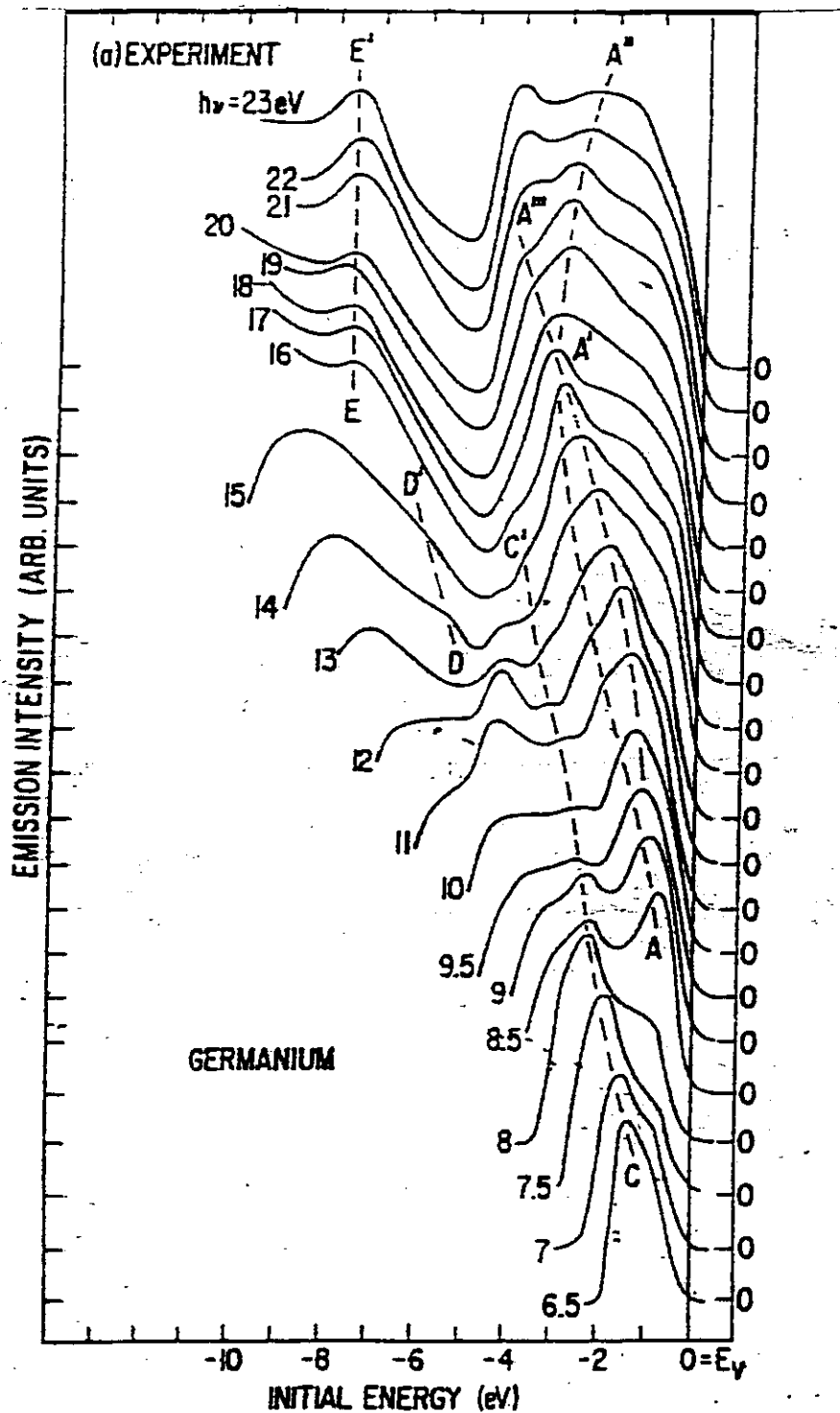


Photoemission intensity and photoemission density of states of Ge. (W. D. Grobman, D. E. Eastman, and J. L. Freeouf, Phys. Rev. 12B, 4405 (1975))

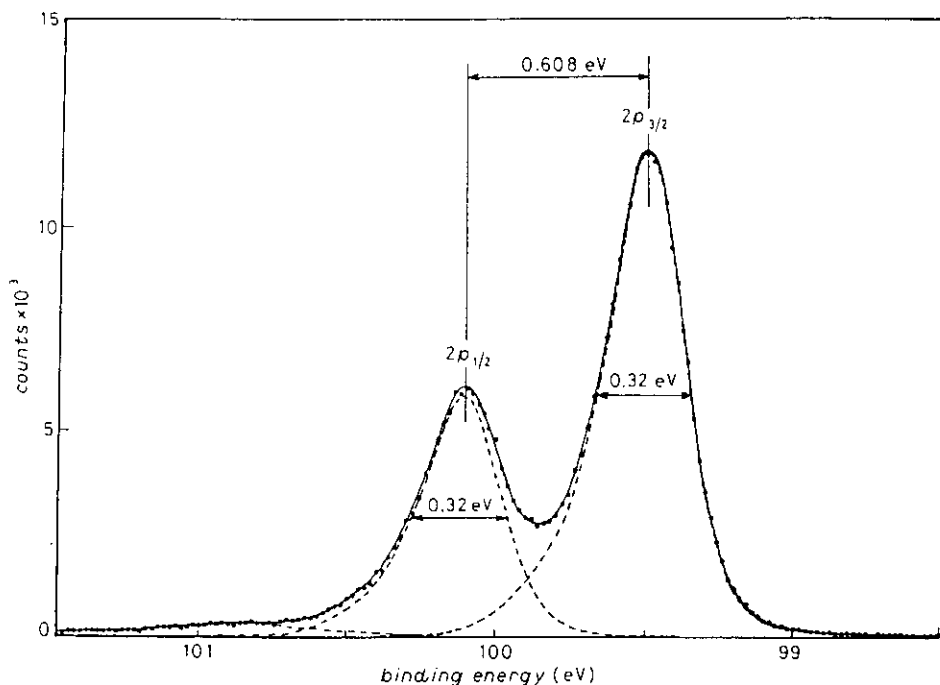


Energy band structure of germanium, with spin-orbit splitting neglected. Representative points of the pseudopotential interpolation scheme fitted to this adjusted OPW band model are indicated by the heavy dots (after Herman *et al.*, 1967a,b).



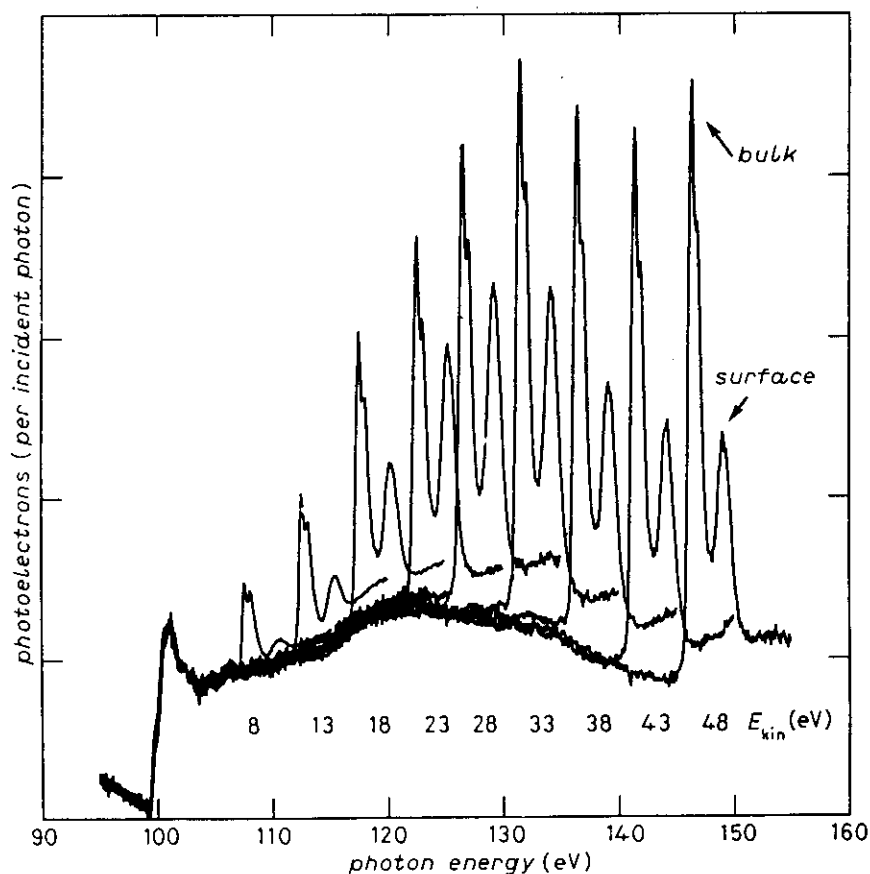


Final-state effects in low-energy UPS
data in Ge.

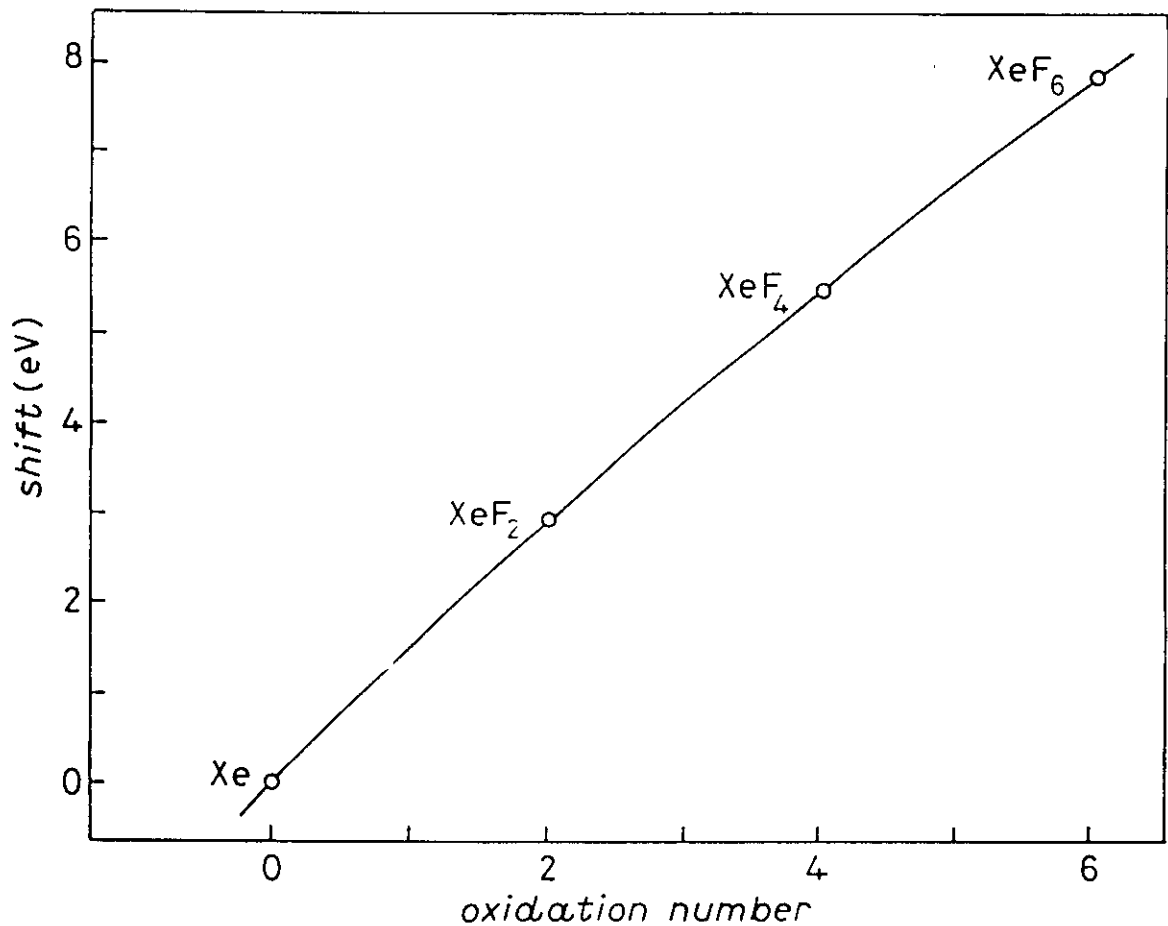


The Si2p core level of bulk Si measured by X-ray photoelectron spectroscopy (from ref. [9]); Si(111), $T = 300$ K, $\theta = 45^\circ$.

Notice core spin-orbit separation.



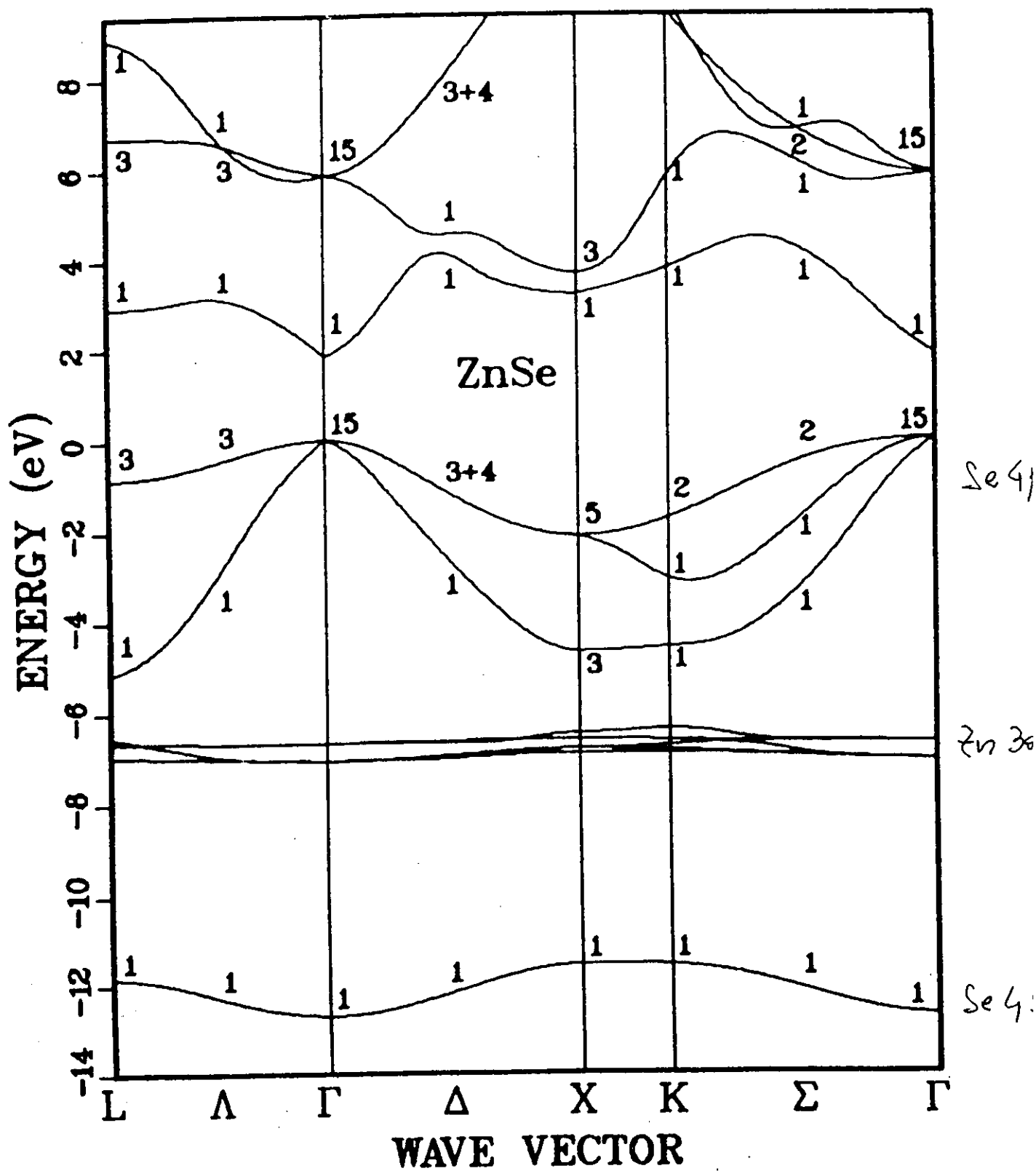
Constant-final-state spectra for oxygen on Si(100) exhibiting energy-dependent variations in the photoionization cross-section and in the escape depth. A maximum in the surface-to-bulk intensity ratio is reached at about 130 eV photon energy.



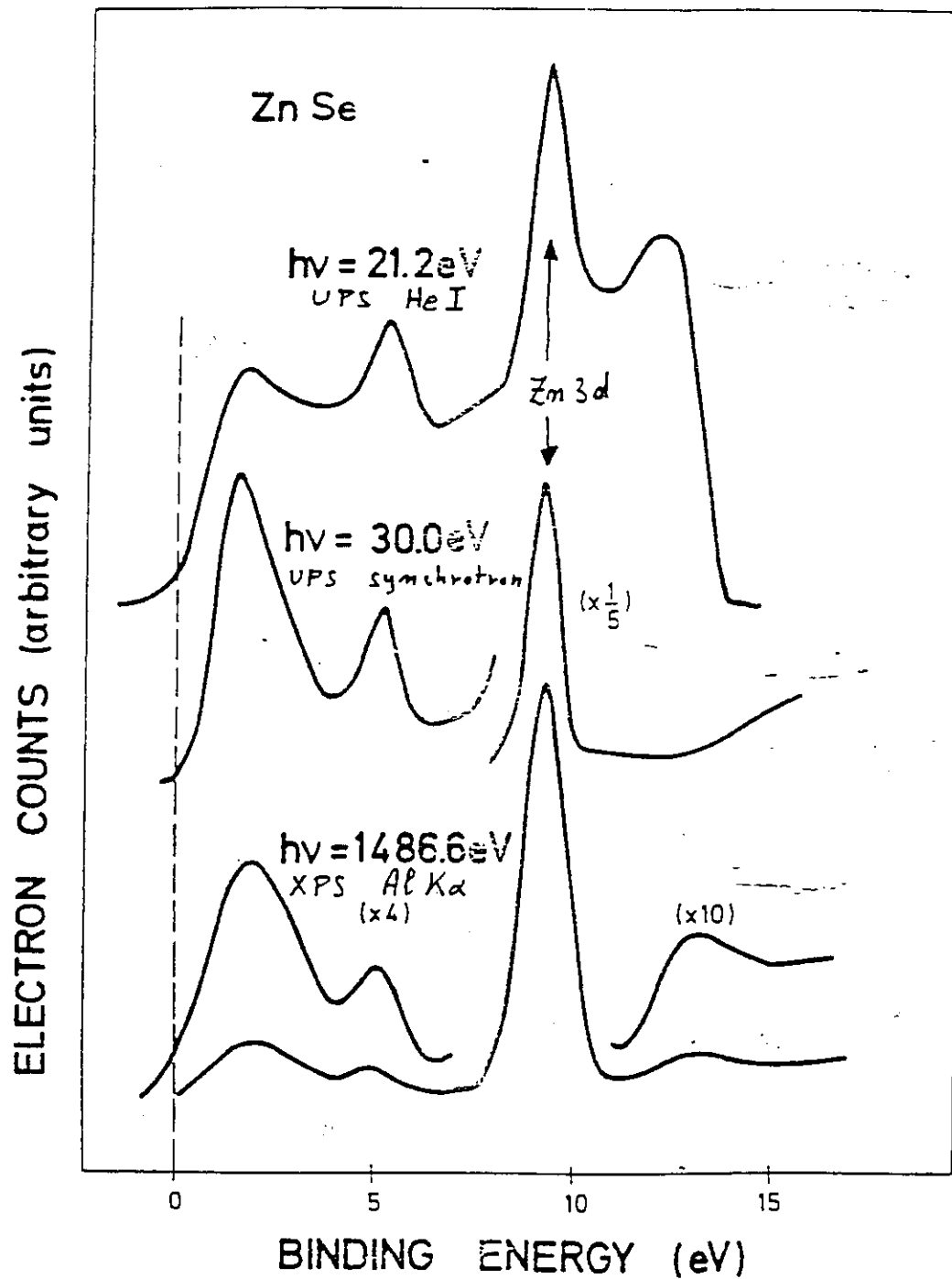
Measured binding energy shift for the xenon $3d_{5/2}$ electrons

Chemical shifts of Xe core levels
when atom is embedded in different
environments.

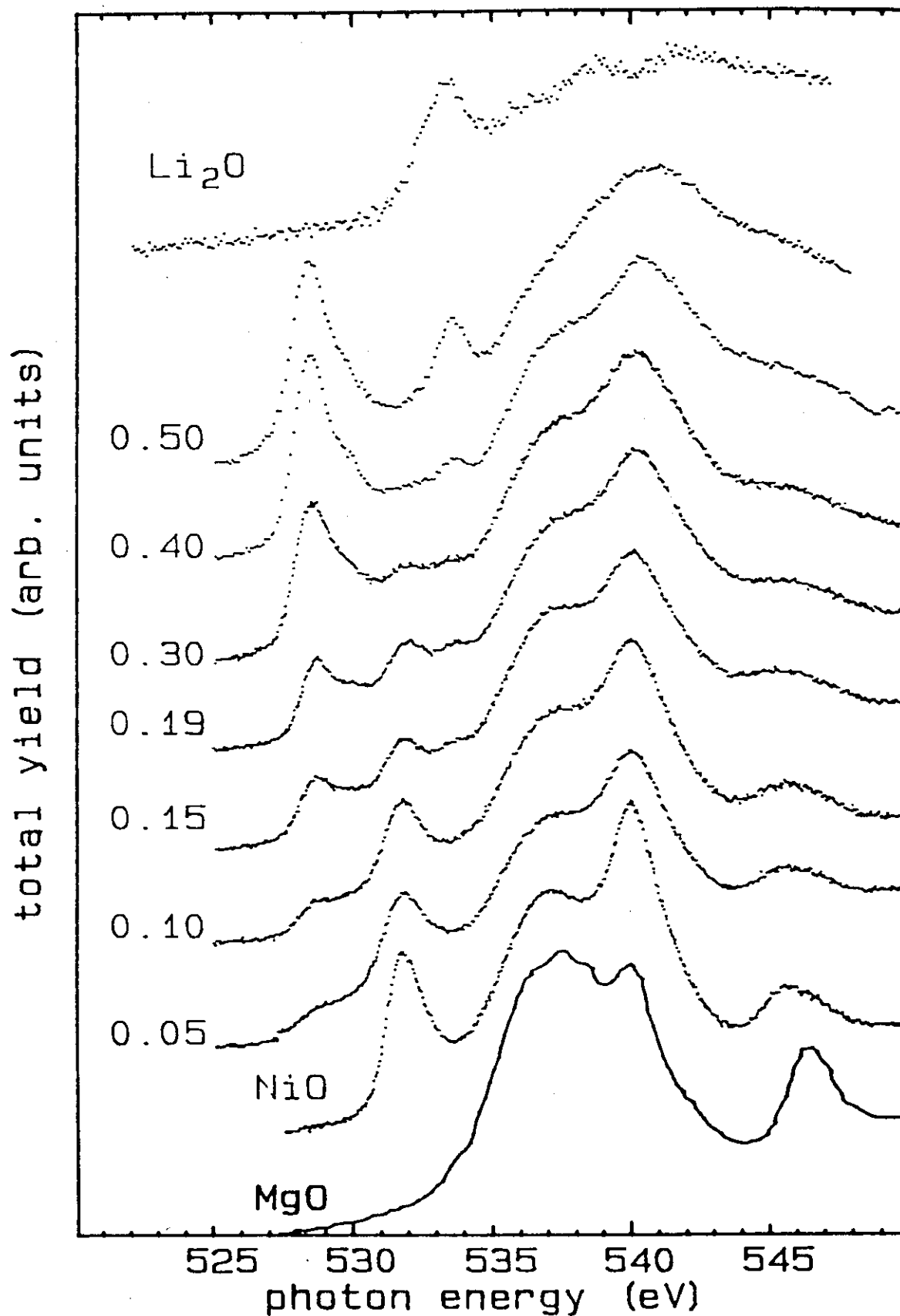
Chemical shifts increase (decrease)
binding energy of core levels of
positive (negative) atoms.



Energy - band dispersion of Zn Se
close to the fundamental gap.



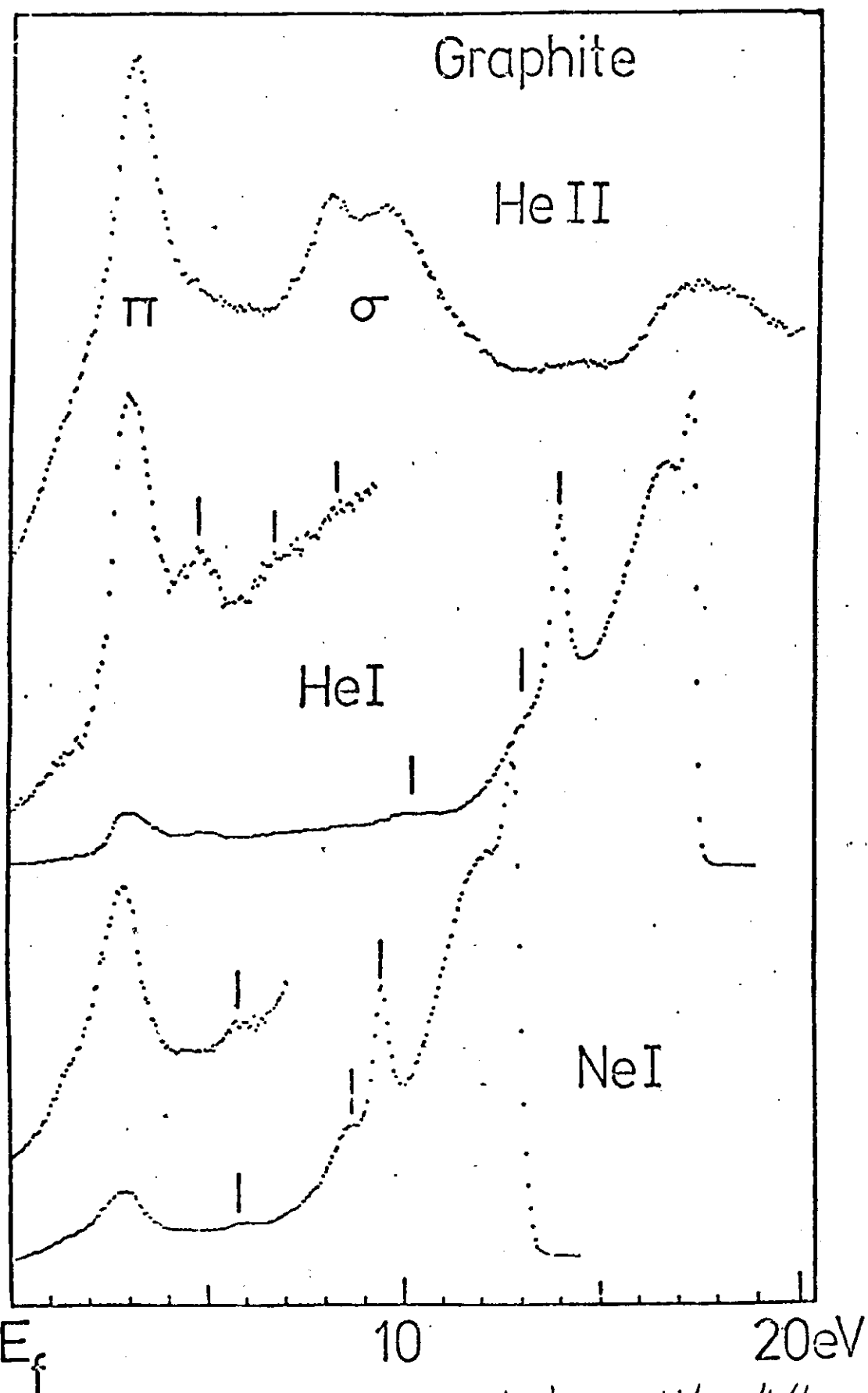
Photoemission spectra of ZnSe obtained with different photon sources. Notice sharp structure due to Zn 3d bands.



Oxygen K-edge absorption spectra of MgO

NiO, $\text{Li}_x\text{Ni}_{1-x}\text{O}$ for indicated values of x , and Li_2O .

K-edge spectra of Li-doped NiO give evidence that topmost occupied states in NiO derive also from $2p$ orbitals.



UPS spectra of graphite with different sources.

PHOTOEMISSION : SOURCES

1. UPS

5 - 100 eV

- Spectres atomiques
ou moléculaires

He I	21.2 eV
He II	40.8 eV
He II β	48.8 eV
Ne I	16.8 eV
Ne II	28.9 eV

- Synchrotron
(intensity + tunability +
polarization).

2. XPS (ESCA)

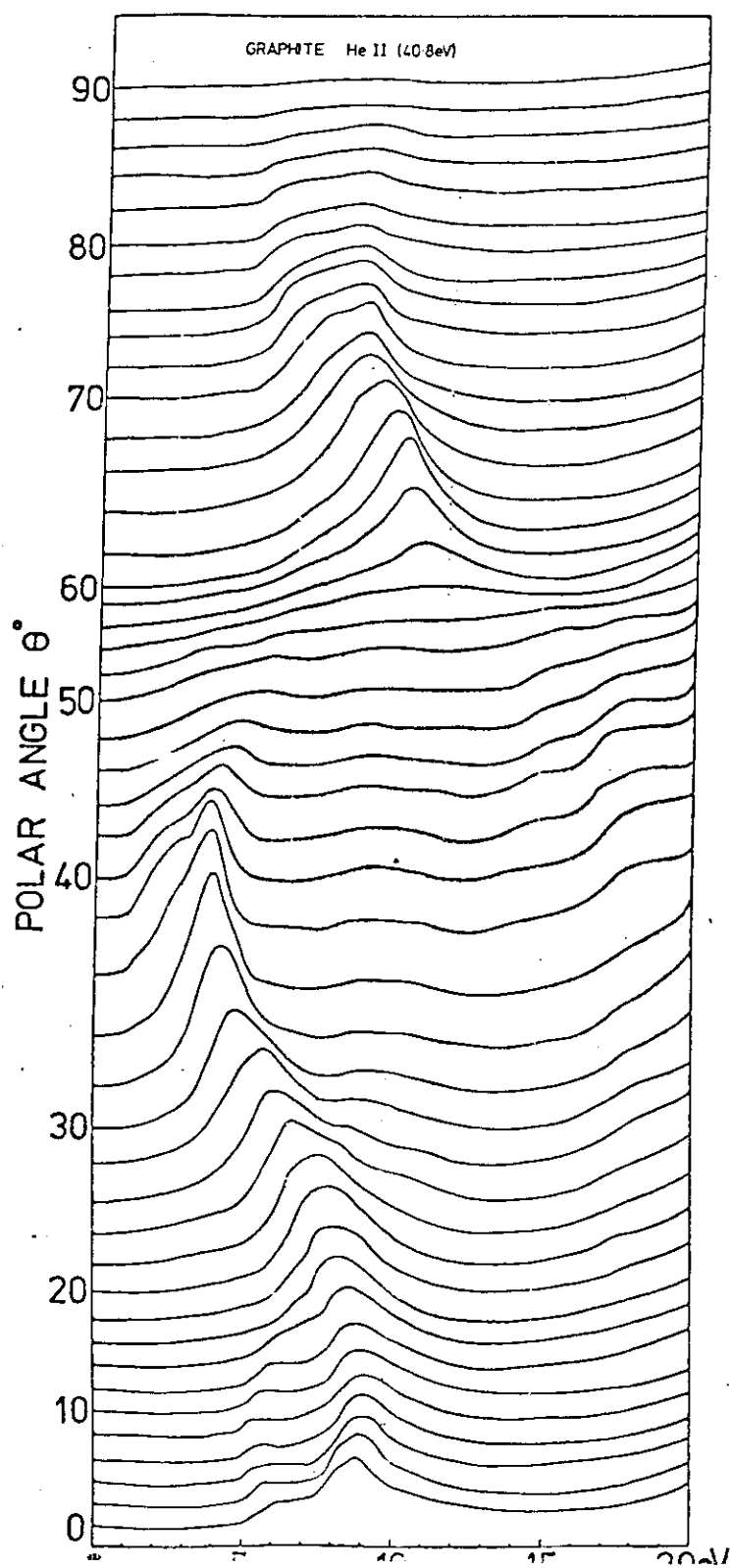
$\sim 10^3$ eV

- Rayons X - Emission
par atome

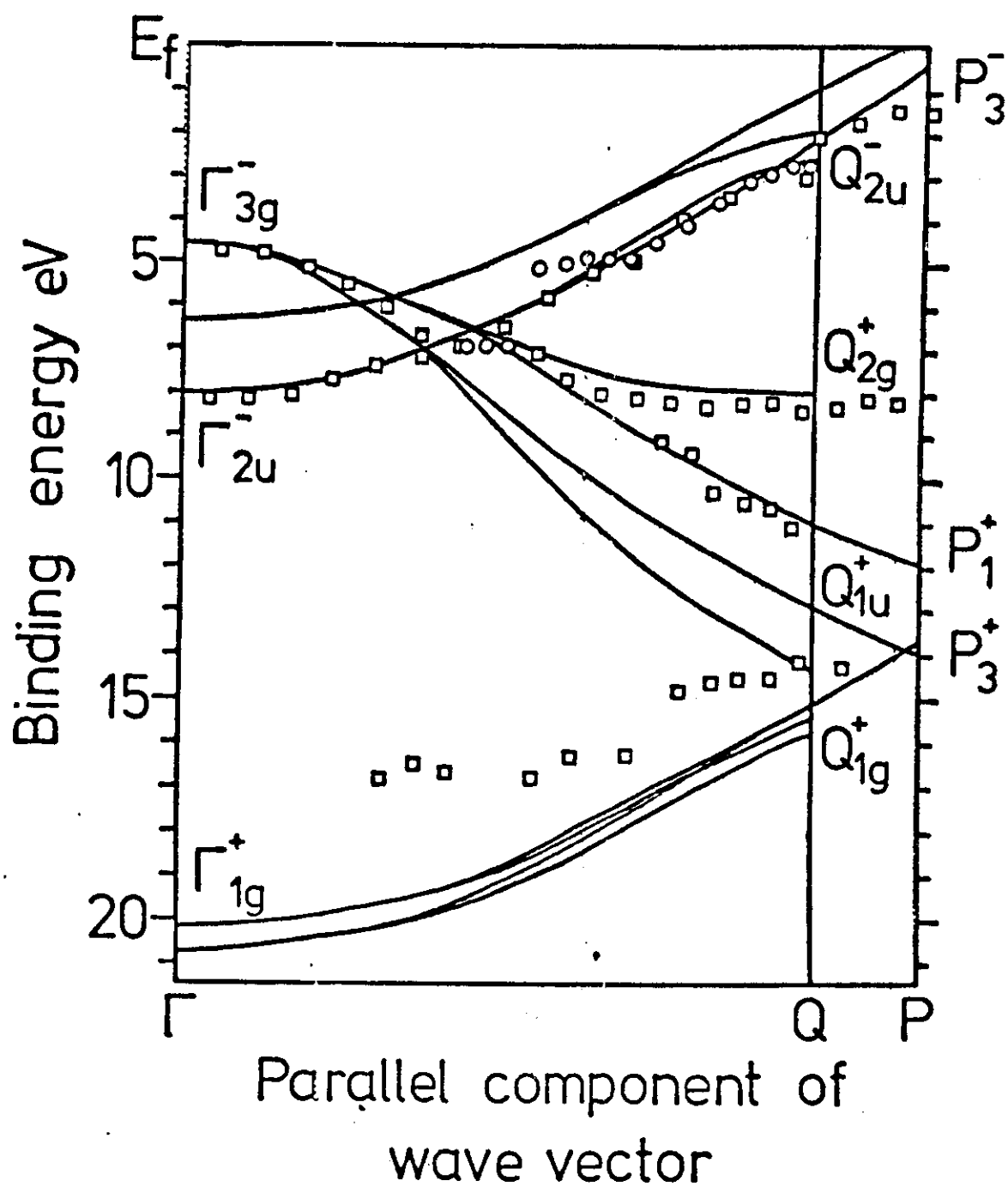
Mg K α 1253.6 eV

Al K α 1486.6 eV

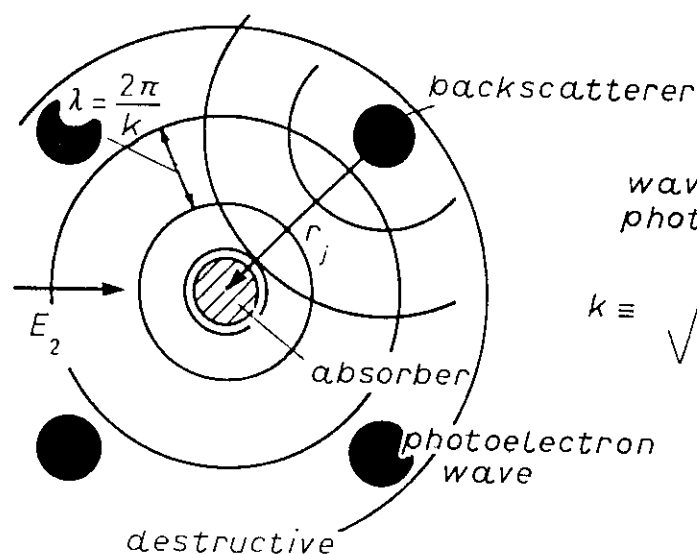
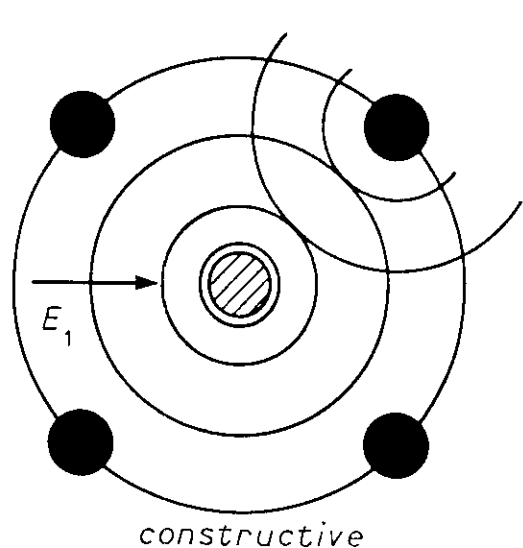
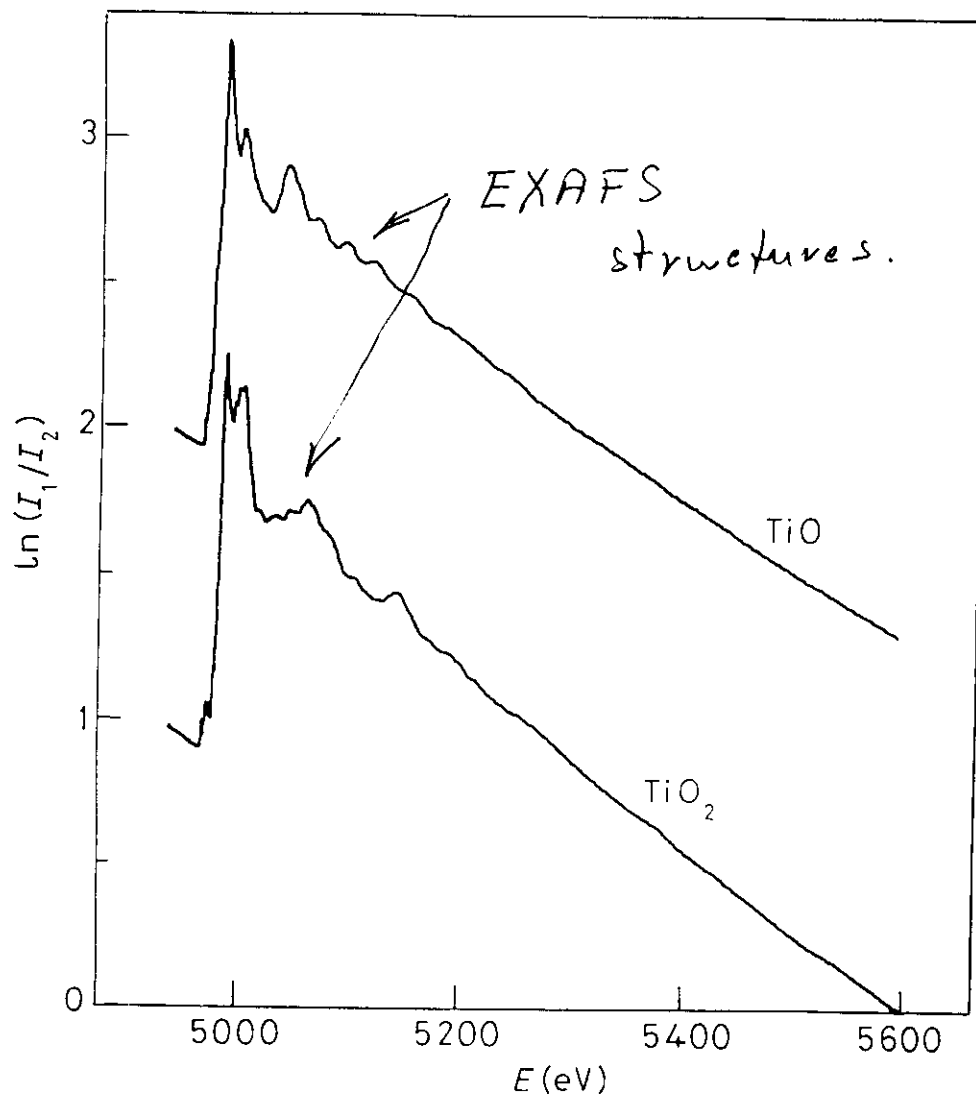
- Synchrotron (intensity +
tunability + polarization).



Angular-resolved photoemission (UPS)
in graphite.



Dispersion of valence bands in pyrrhite:
 Theory (lines), angular-resolved
 photoemission (squares).



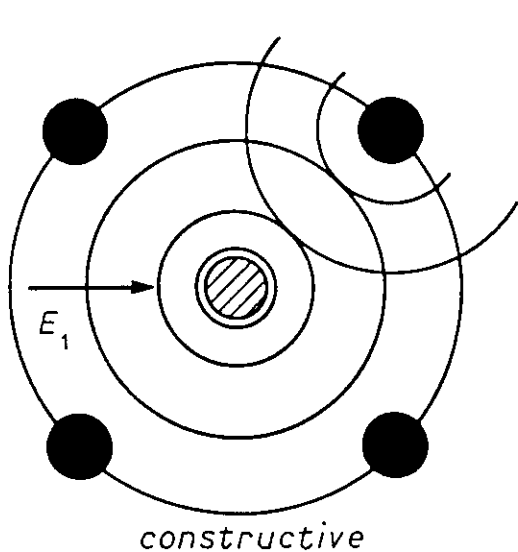
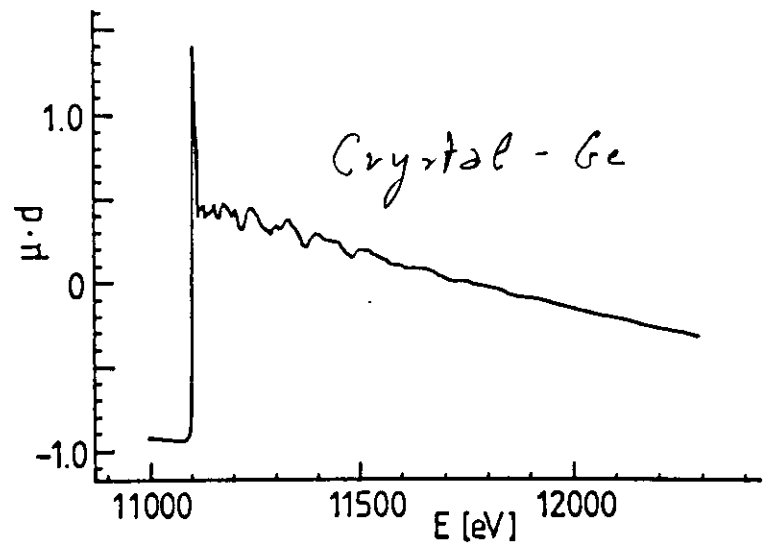
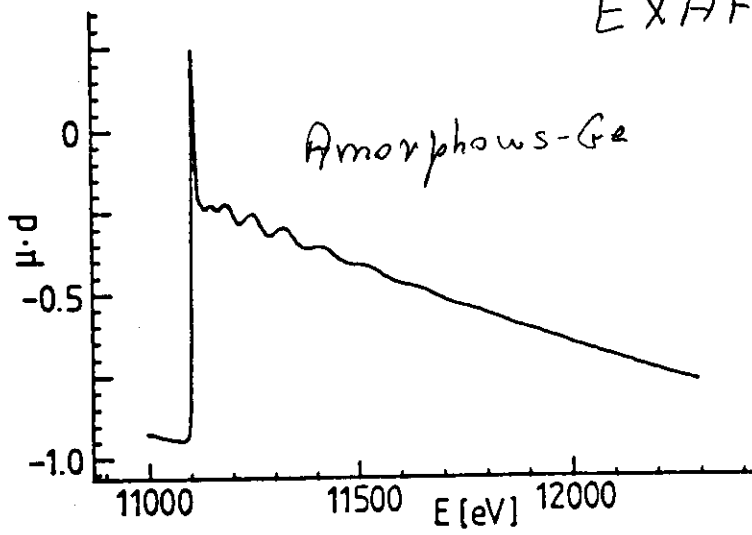
wave vector of photoelectron

$$k \equiv \sqrt{\frac{2m}{\hbar^2} (E - E_0)}$$

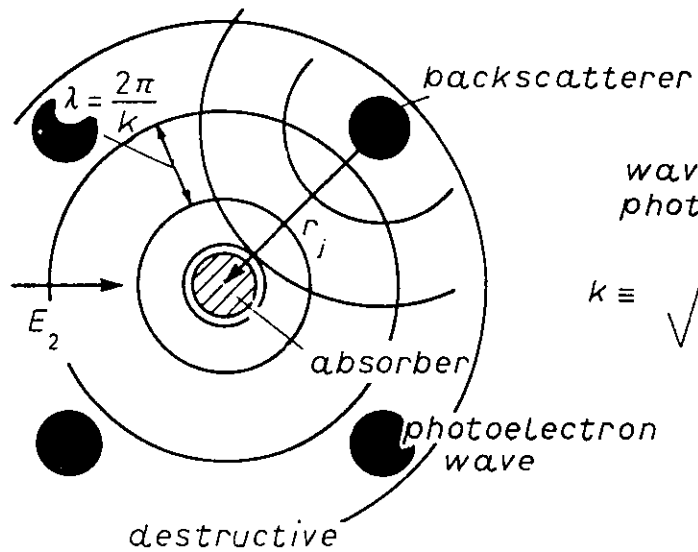
Scheme of interference in Extended X-ray Absorption Fine Structure (EXAFS).

EXAFS structure in Ge

43

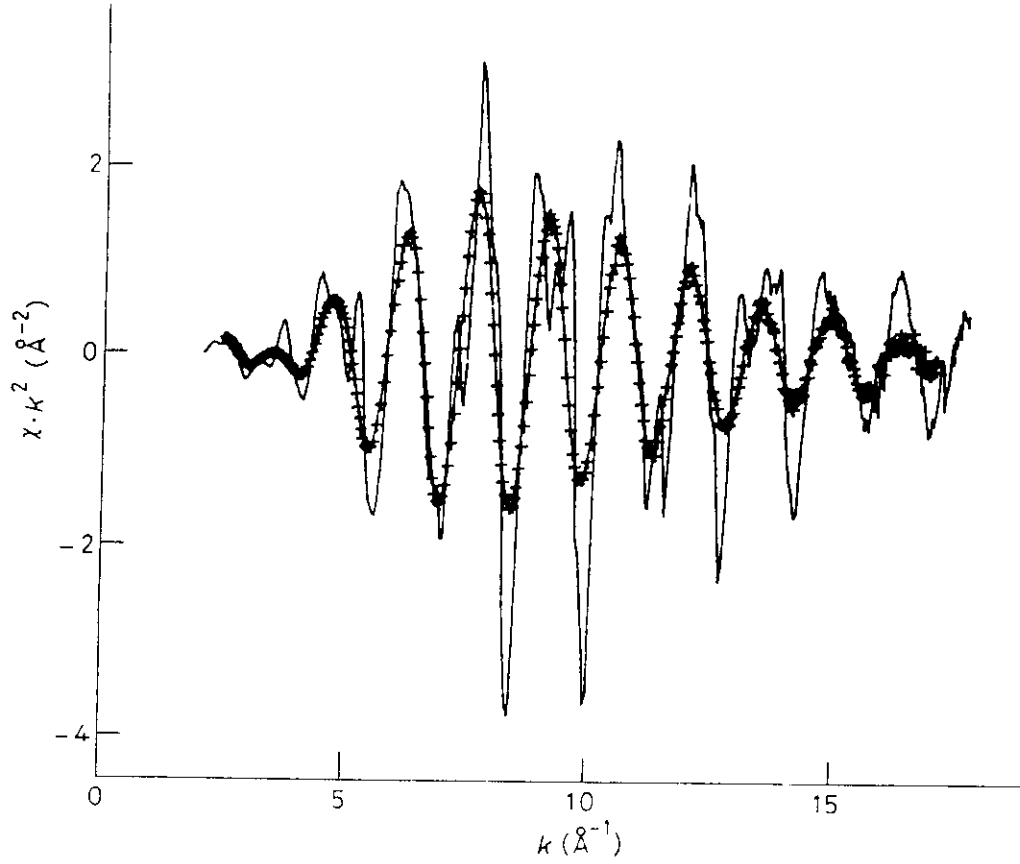


interference

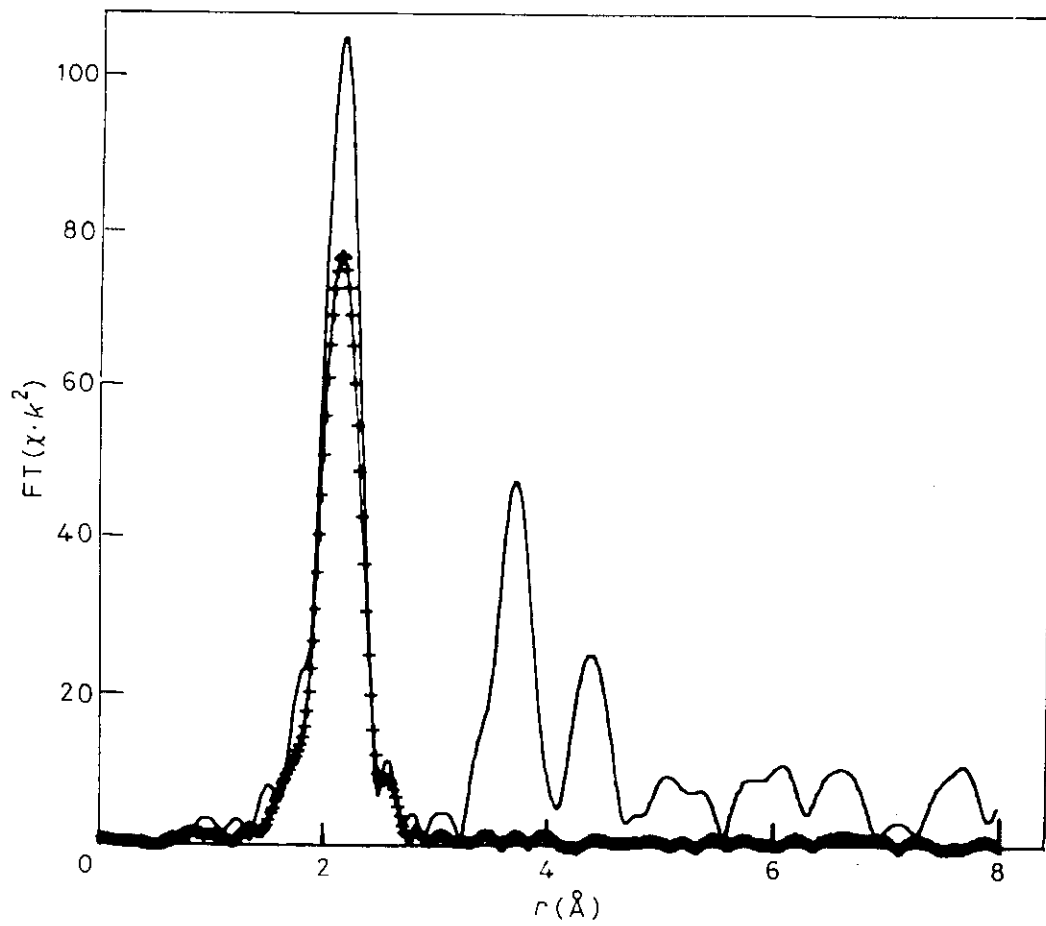


wave vector of photoelectron

$$k \equiv \sqrt{\frac{2m}{\hbar^2} (E - E_0)}$$

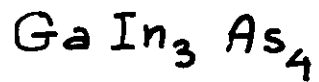


EXAFS $\chi \cdot k^2$ of a-Ge (-+-+ -) and c-Ge (—) measured at 77 K

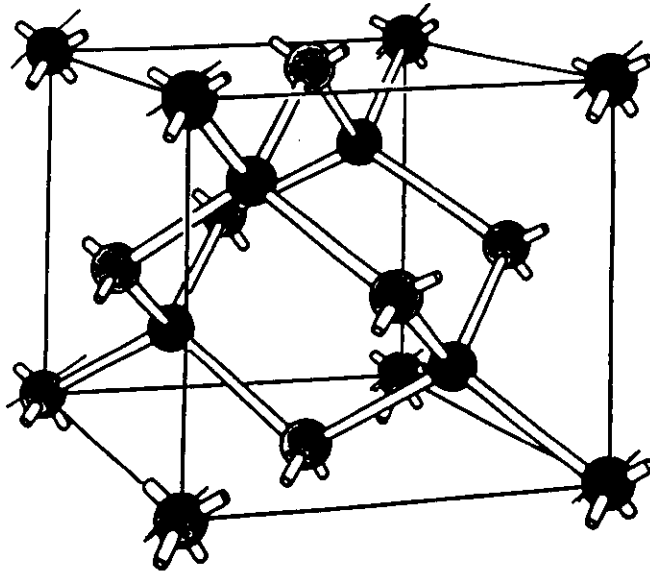


Fourier transforms of the EXAFS of a-Ge (-+-+ -) and c-Ge (—)

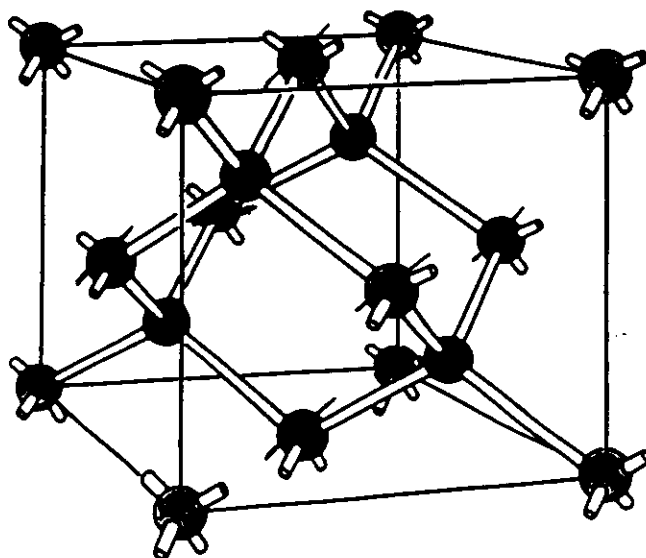
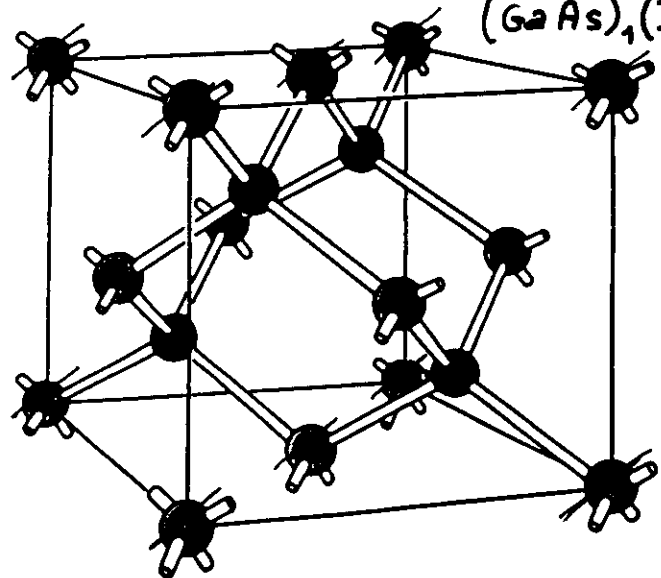
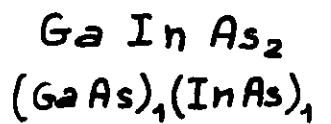
$$x = 0.75$$



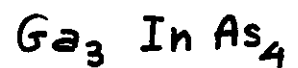
45



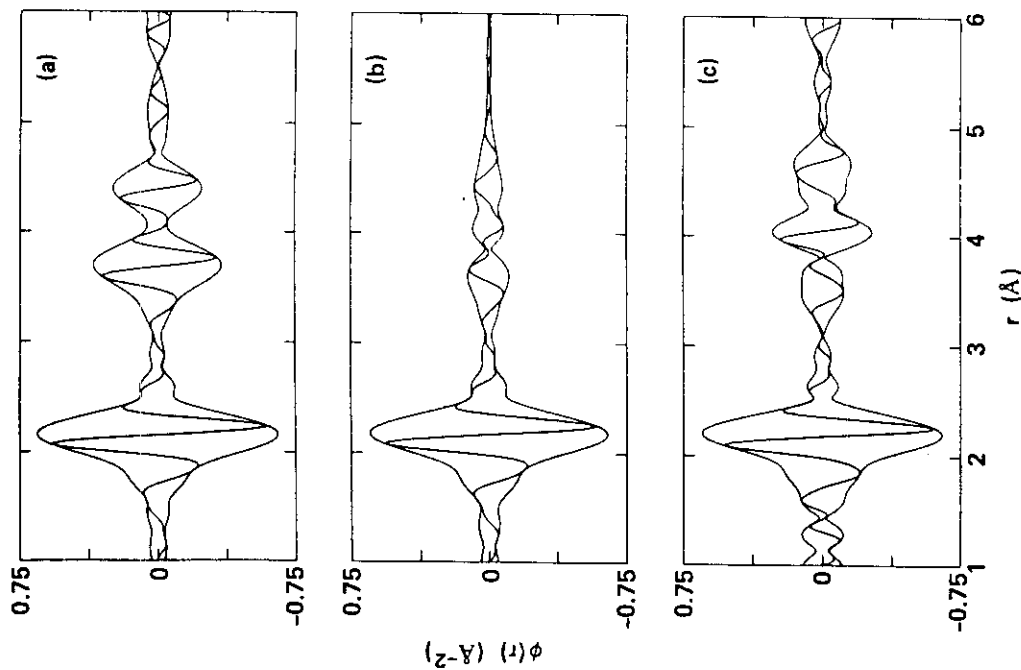
$$x = 0.50$$



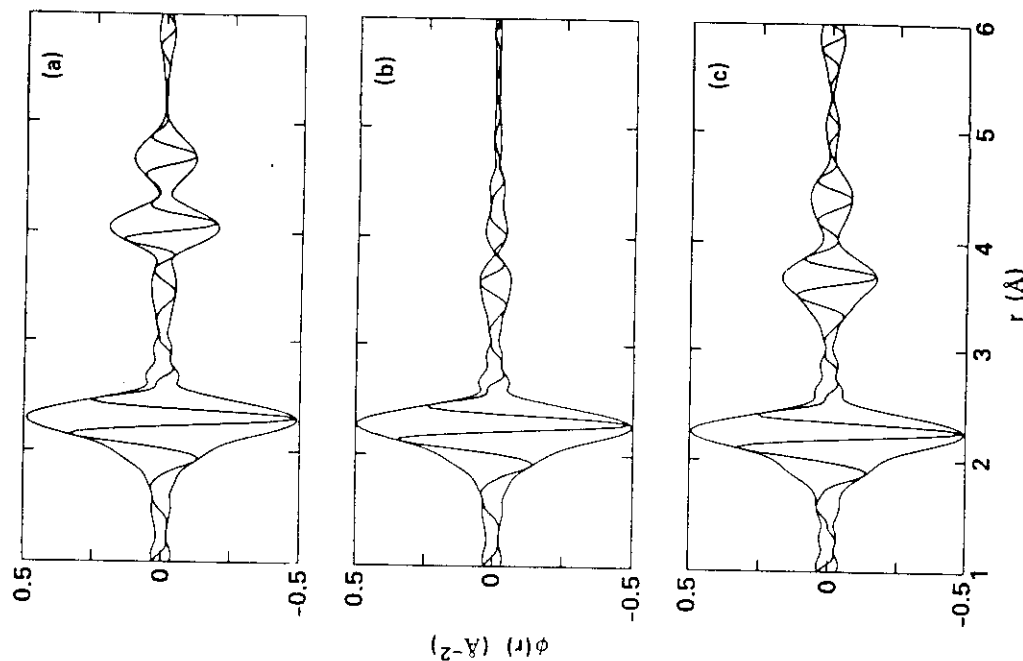
$$x = 0.25$$



Atomic distribution in $\text{Ga}_{2-x}\text{In}_x\text{As}$ alloys
for three different compositions.



Ga K-edge EXAFS in real space transformed using a window of $k = 3.56 - 15.65 \text{ \AA}^{-1}$ broadened by a Gaussian of width $0.7 \text{ \AA}^{-1}$ for (a) pure GaAs, (b) $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$, and (c) $\text{Ga}_{0.1}\text{In}_{0.9}\text{As}$. Note the similarity of the first-neighbor As peak position, width, and amplitude (i.e., similar r , σ , and N). The second-neighbor peaks, on the other hand, are quite different.



In K-edge EXAFS in real space transformed using a window of $k = 3.96 - 18 \text{ \AA}^{-1}$ broadened by a Gaussian of width $0.7 \text{ \AA}^{-1}$ for (a) pure InAs, (b) $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$, and (c) $\text{In}_{0.1}\text{Ga}_{0.9}\text{As}$, all at 77 K. Note the similarity of the first-neighbor As peak position, width, and amplitude (i.e., similar r , σ , and N). The second-neighbor peaks, on the other hand, are quite different.

(47)

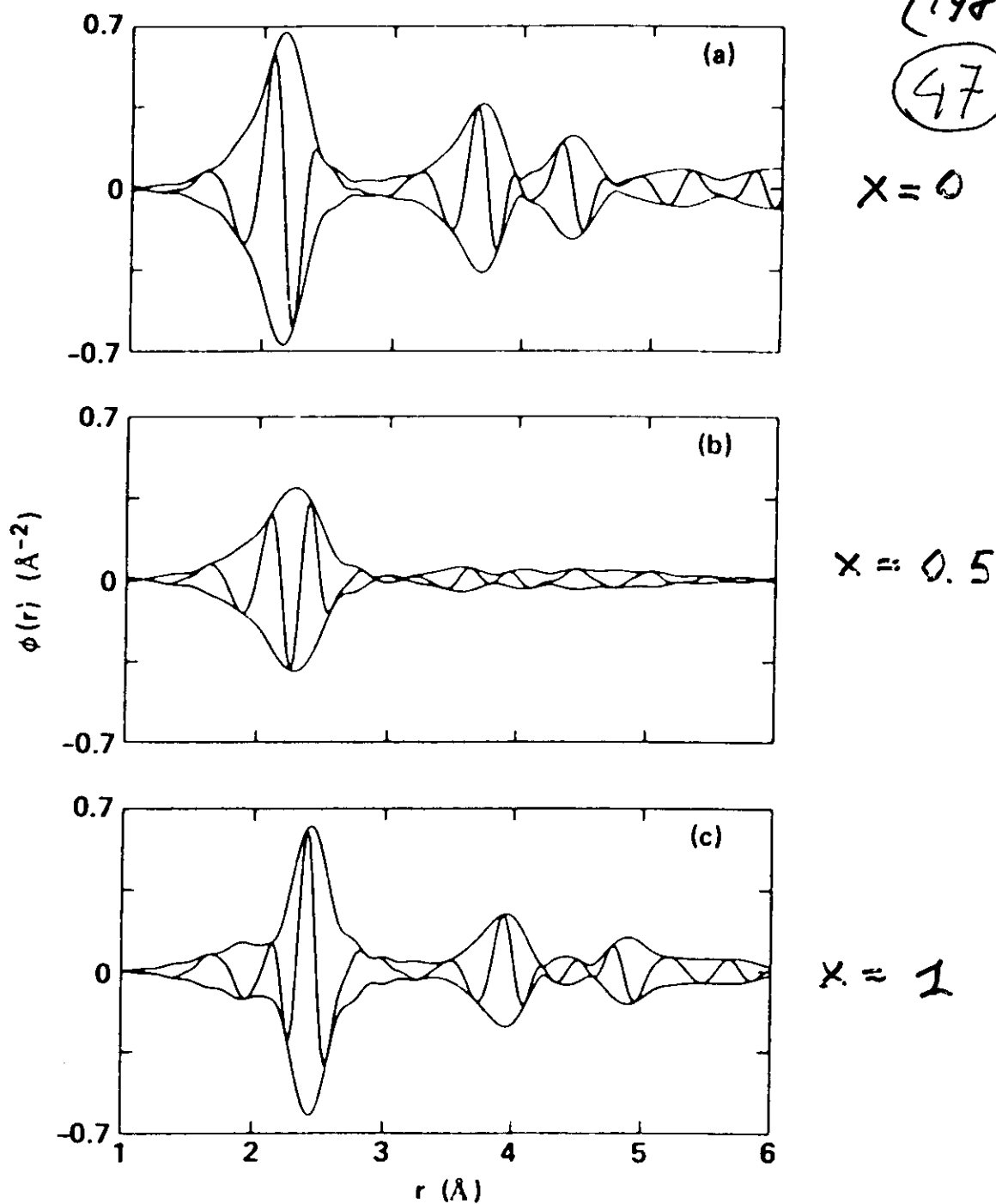


FIG. 7. As K -edge EXAFS in real space transformed using a window of $4.16\text{--}17.85\text{ \AA}^{-1}$ broadened by a Gaussian of width $0.7\text{ \AA}^{-1}$ for (a) pure GaAs, (b) $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$, and (c) pure InAs, all at 77 K. Note that, unlike the cation first-neighbor peaks of Figs. 3 and 4, the first-neighbor peaks here do differ.



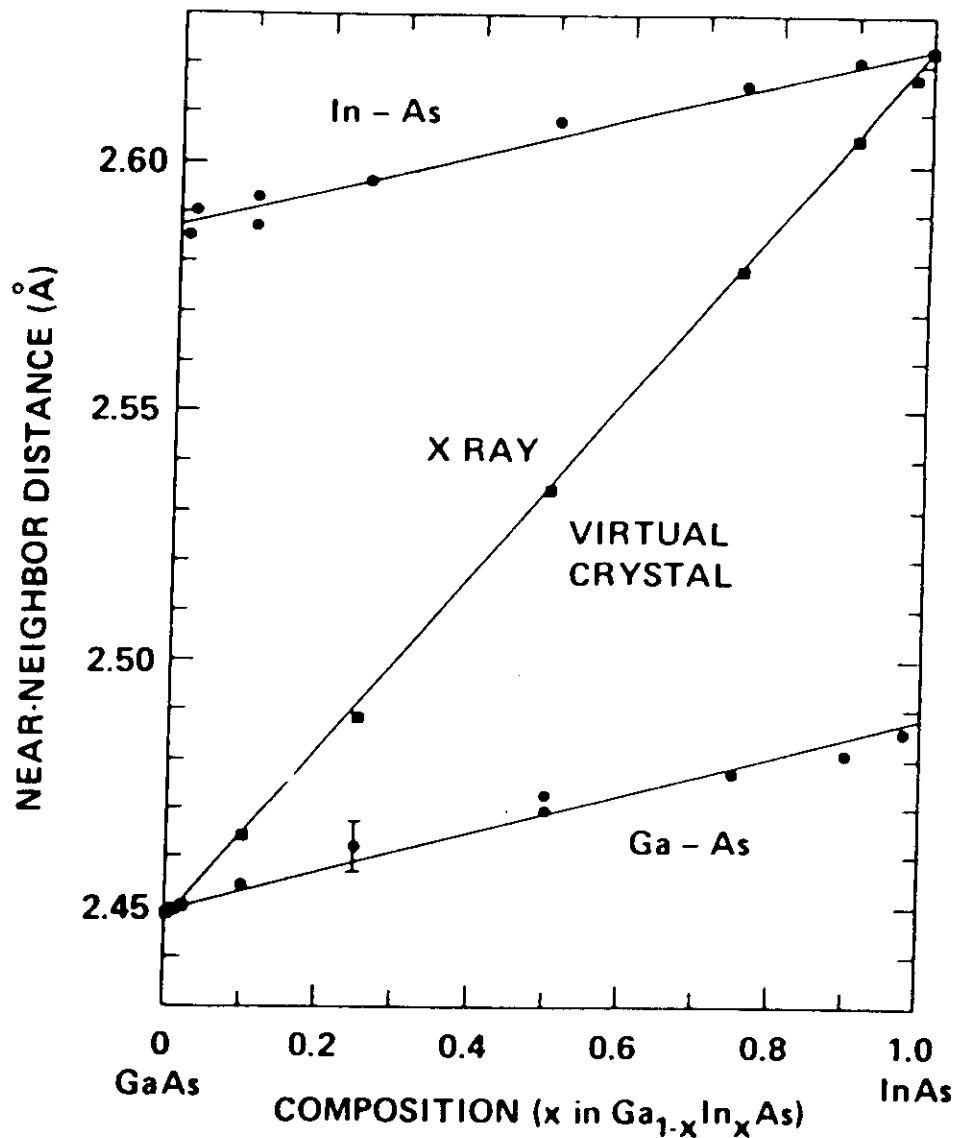
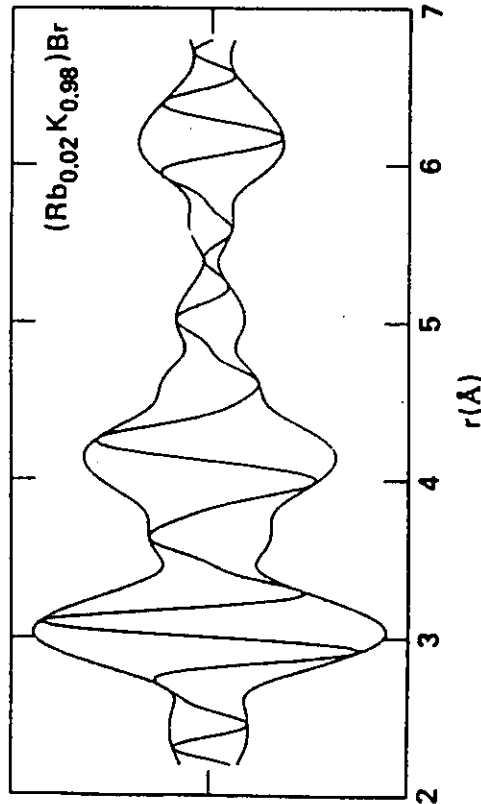
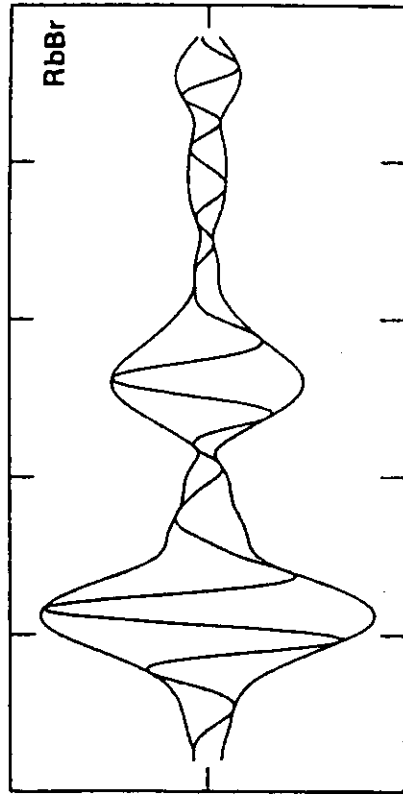


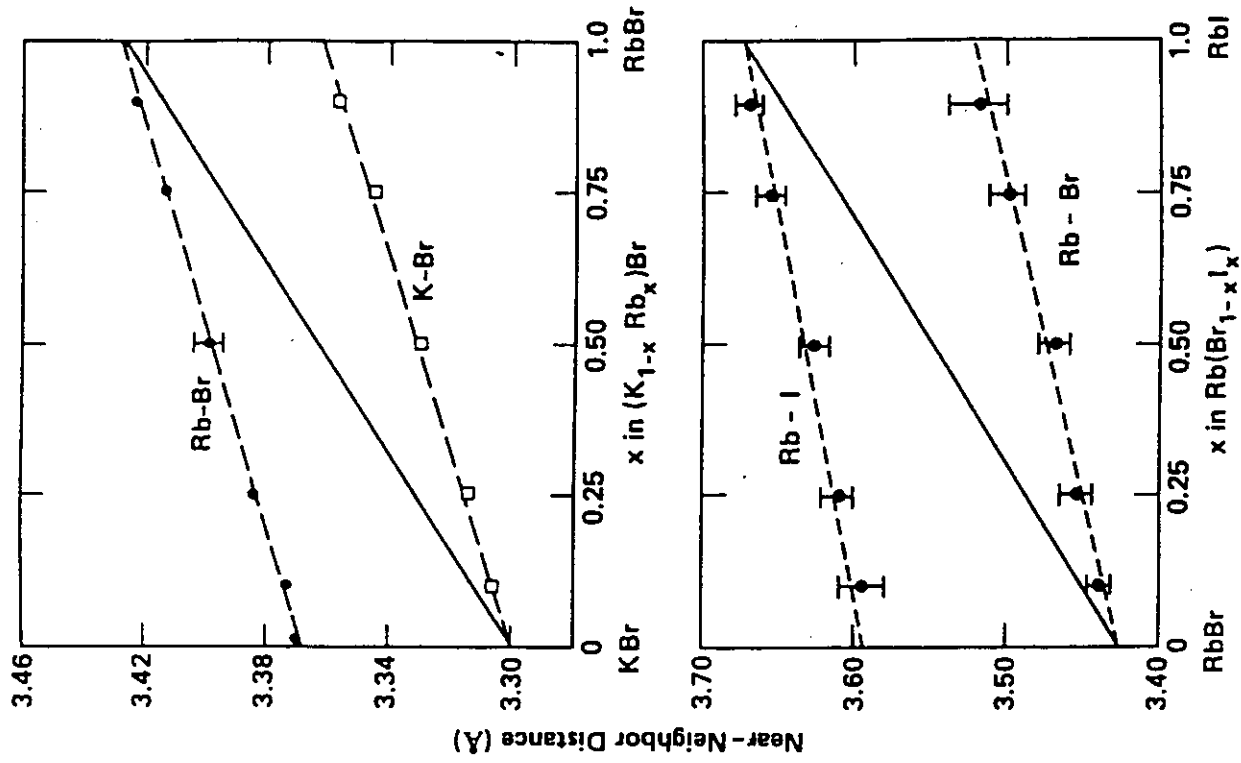
FIG. 6. Ga-As and In-As near-neighbor distances as a function of alloy composition. Middle curve is the VCA cation-anion bond length calculated from the measured x-ray lattice constant. The weighted average of the two NN distances agrees with the VCA (lattice constant) average.

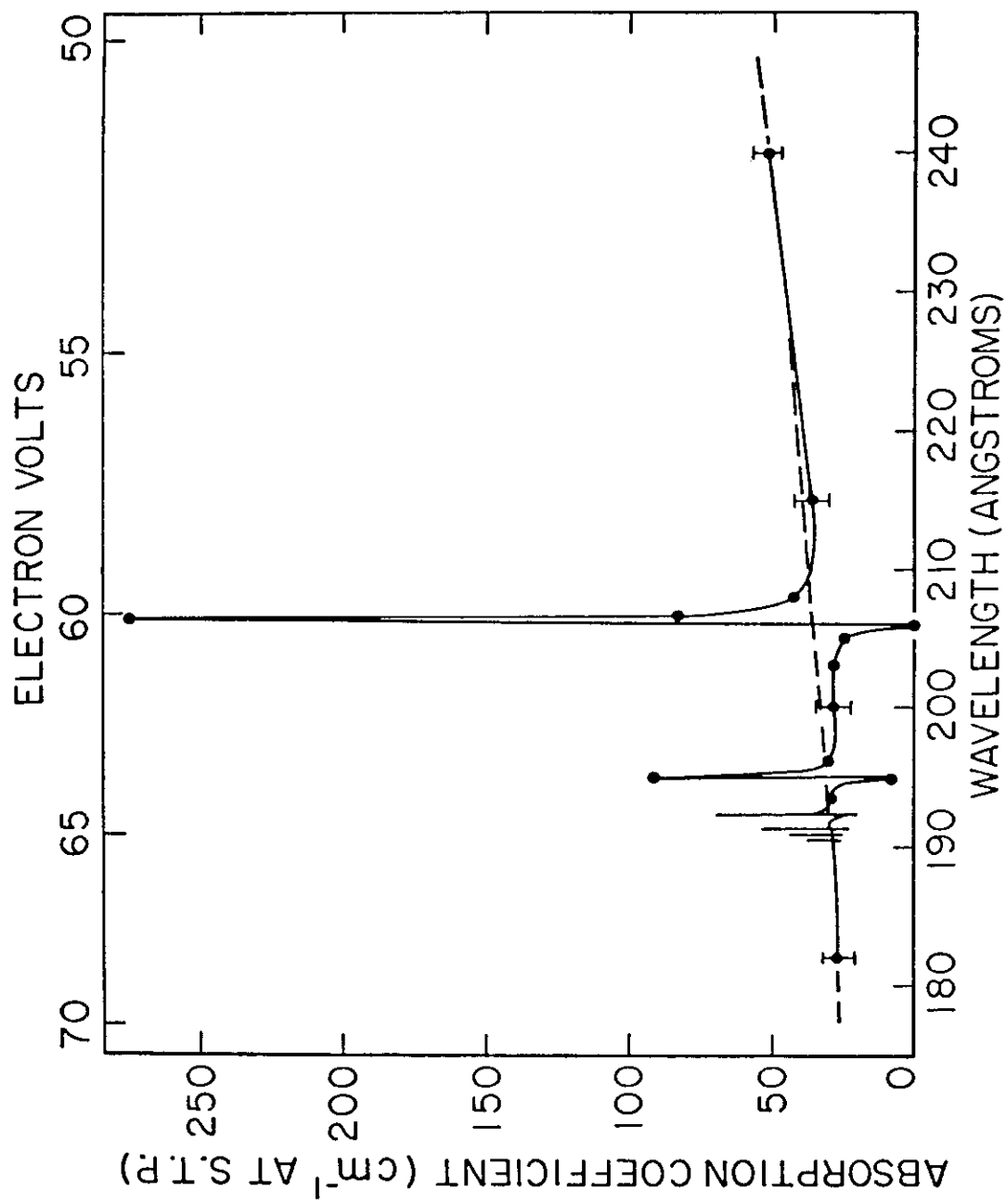
X-ray diffraction $\Rightarrow$ average distances

EXAFS $\Rightarrow$ atomic-scale investigation



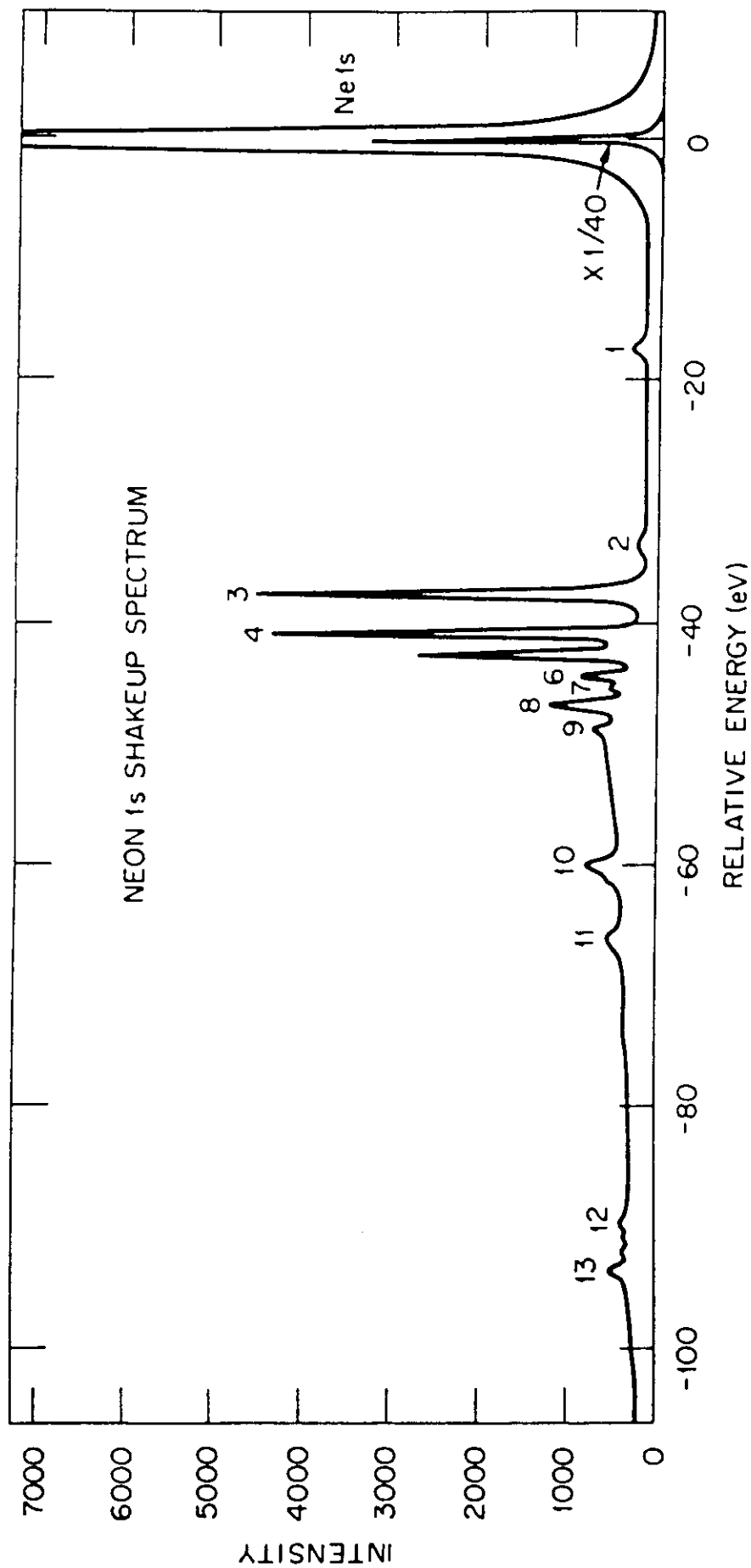
Real part and the magnitude (envelope curve) of the Fourier transform of k times the EXAFS, $\chi(k)$, on the Rb K edge of pure RbBr (upper drawing) and the alloy $(\text{Rb}_{0.02}\text{K}_{0.98})\text{Br}$ (lower drawing), both at 77 K. The data were transformed using a square window form $k = 2$ to $16 \text{ \AA}^{-1}$, broadened by a Gaussian of half-width $0.7 \text{ \AA}^{-1}$.



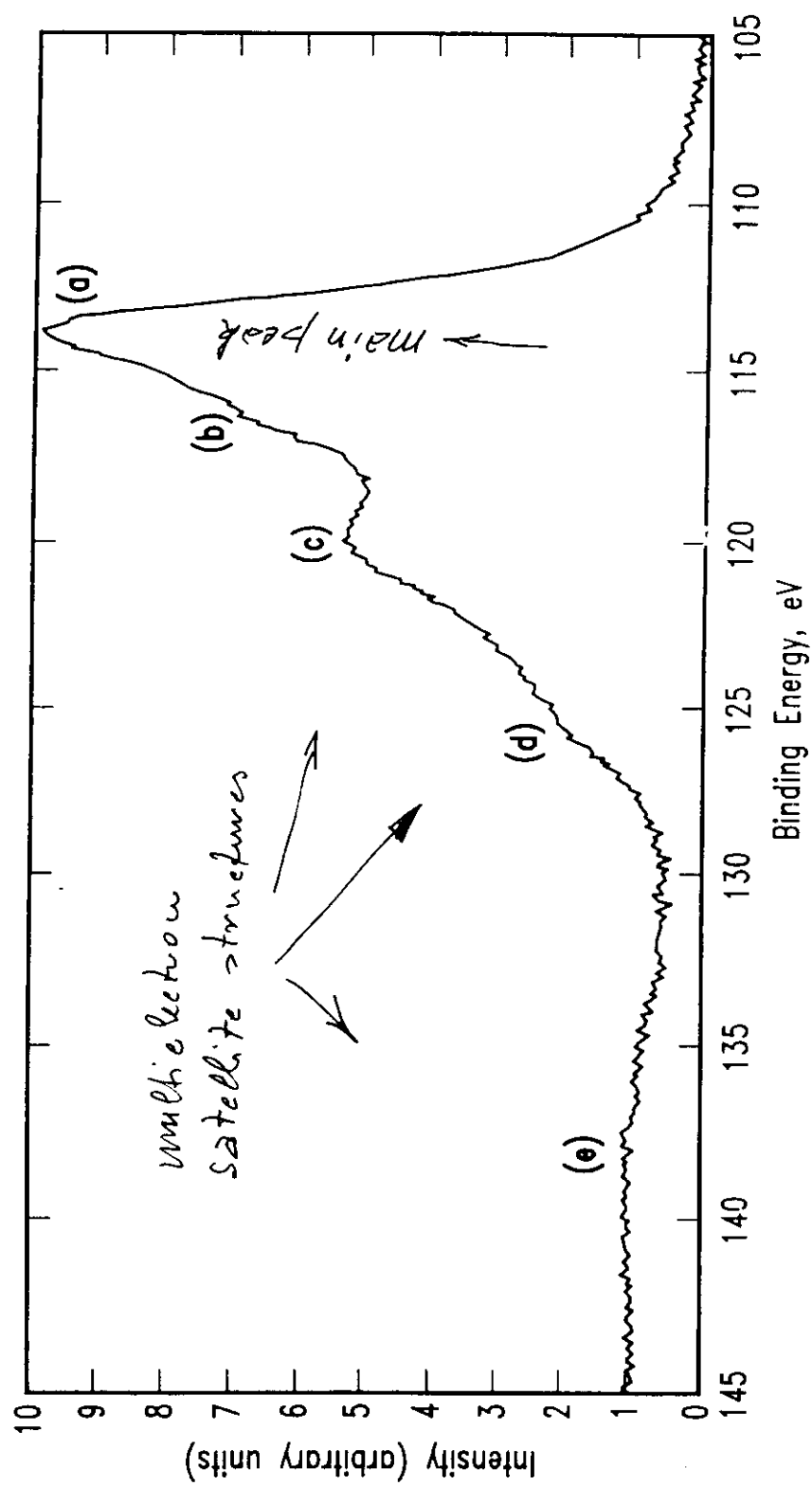


The absorption coefficient of helium in the 175-245-Å region. The solid curve connects the points at which the data were reduced in the present experiment. The dashed curve indicates the result of Lowry *et al.* (1965).

Many-electron effects in He: the $2s^1 n p^1$ series.



The Ne 1s photoelectron spectrum, showing the single-electron emission photopeak, the shakeup peaks involving (a) a 1s, 2p electron pair (lines 2-9), (b) a 1s, 2s pair (10, 11), and (c) the 1s, 2p² electrons (12, 13), and the KL double-electron ionization continuum (below $\Delta E = -47\text{eV}$). Excitation by monochromatized AlK α x rays with a bandwidth of 0.2eV (U. Gelius).



Ni 3s XPS spectrum measured at 80° take-off angle on the NiO(100) surface.

