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Research Workshop in Condensed Matter, Atomic and Molecular Physics (22 June - 11 September 1992)

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"The Electronic Structure of Random $A^{III}B^{V}$ and $A^{II}B^{VI}$ Semiconductor Alloys by TB-LMTO Method"

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These are preliminary lecture notes, intended only for distribution to participants.

THE ELECTRONIC STRUCTURE OF RANDOM $A^{III}B^{V}$ AND $A^{II}B^{VI}$ SEMICONDUCTOR ALLOYS BY TB-LMTO METHOD

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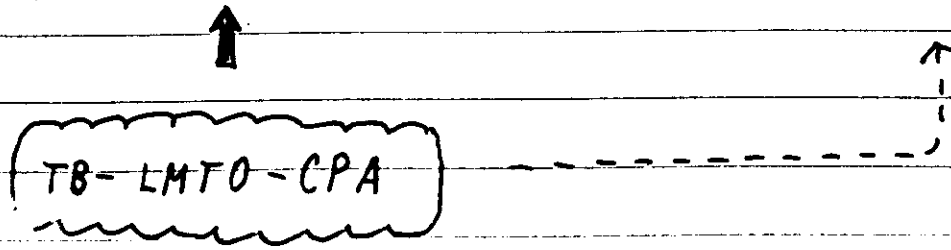
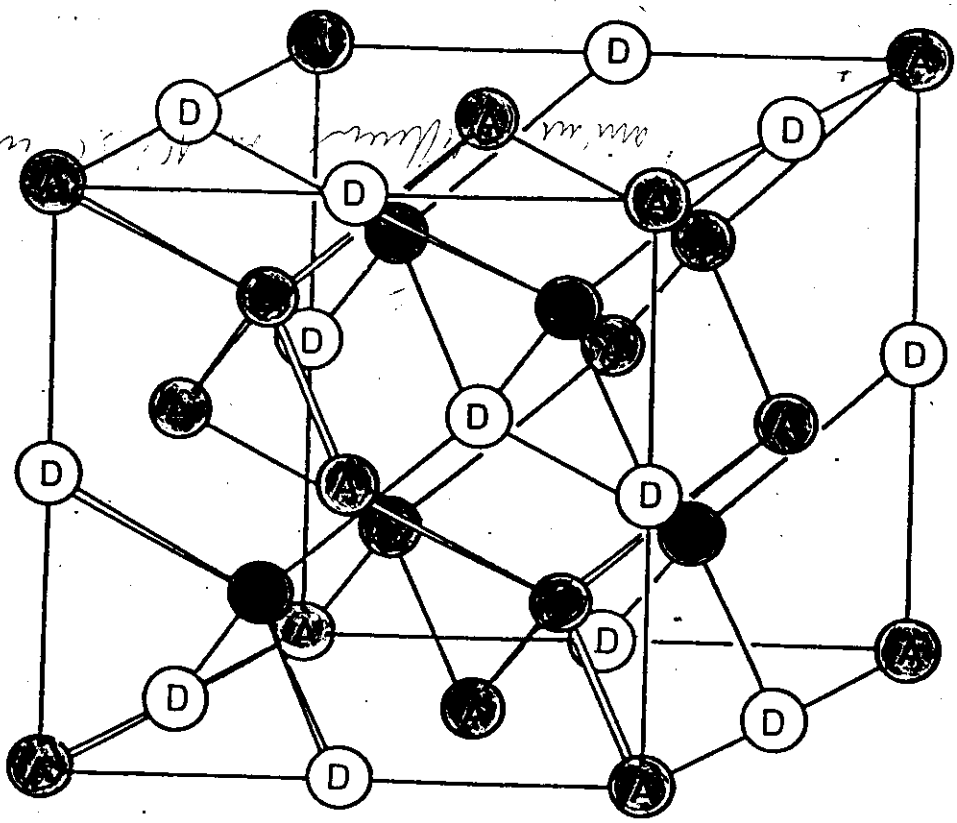
ELECTRONIC STRUCTURE OF RANDOM SEMICONDUCTORS

difficult problem, two approaches

A. Configurational averaging (CPA)	B. Representative configuration (supercell)
- concentration trends, damping of el. states	- structural distortions directly
- minimal basis set	- ab initio approach, standard techniques
- structural distortions via hopping integrals	
■ empirical theory, off-diagonal disorder	■ artificial geometry, no damping





Empty-sphere concept

bcc = 4 fcc sublattices A, B, C, D

Structure	A	B	C	D
diamond	C	C	E	E
ZnS	Zn	S	E_1	E_2
NaCl	Na	E	Cl	E
CaF_2	Ca	F	E	F
(DO_3)	Fe^A	Fe^B	Fe^C	Si^D

HAMILTONIAN FOR RANDOM ALLOYS

orthogonal LMTO-repres

$$H_{RL,R'L'} = C_{RL}\,\delta_{RR'}\delta_{LL'} + \Delta_{RL}^{1/2}\left\{S^0(1-\gamma S^0)^{-1}\right\}_{RL,R'L'}\Delta_{R'L'}^{1/2}$$

$$O_{RL,R'L'} = \delta_{RR'}\delta_{LL'} \qquad R/L = \ell m \ldots \text{site/orbital index}$$

Empty sphere concept $\Rightarrow$ close-packed filling

bcc (a/2) 4 fcc, origins at lattice points on bcc body-diagonal

$\Downarrow$

S^0 - canonical structure constant, do not depend on lattice constant

Example: zinc-blende $A_x B_{1-x} C$ alloy

fcc(1): cations A/B
fcc(2): anions C $\Rightarrow$ AC/BC
fcc(3): different ES
fcc(4): from AC/BC

Unified description: diamond, ZnS, NaCl, CaF_2

Potential parameters : $X = C, \Delta, \gamma$

$X_{RL} \Rightarrow$ randomly $X_L^{(1)}(x)$, $X_L^{(2)}(1-x)$

Physical meaning :

$$P_\ell^0(E) = (E - C_\ell) / (\Delta_\ell + \gamma_\ell (E - C_\ell)) \propto \operatorname{cotg} \eta_\ell(E)$$

PP depend on : - type of atom
- lattice constant

PP are obtained from first-principles as solutions of SE for LDA-potentials in atomic spheres centred at R

Feature :

Separability of structural $\propto$ atom-dependent parts of alloy Hamiltonian

MODELLING OF BOND-LENGTH VARIATIONS

S^0 - same for any lattice constant

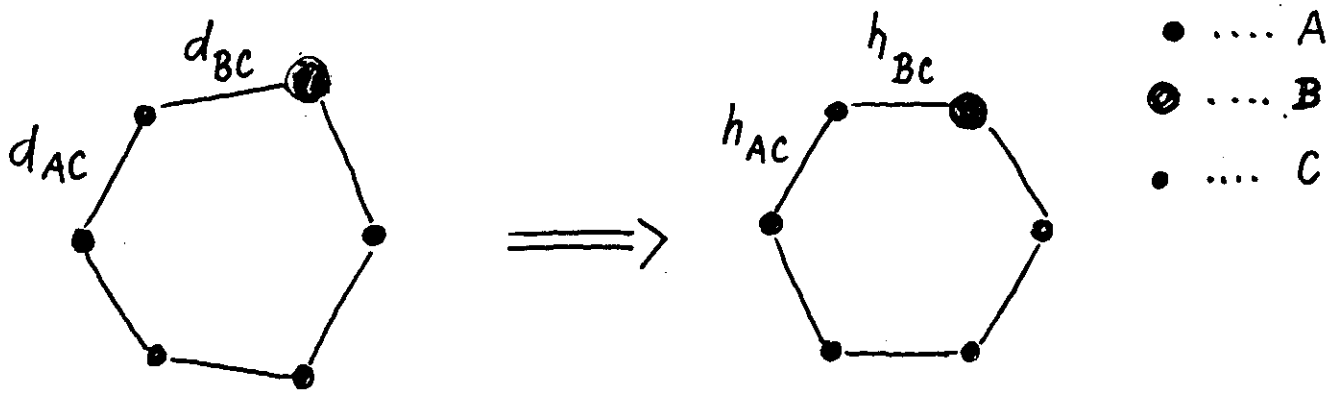
C, Δ, γ - evaluated from LDA-potentials in their WS spheres $\Longrightarrow$ bond lengths

Bond-length variations $\Longrightarrow$

differences in AC/BC hopping elements via potential parameters

(off-diagonal disorder)

Actual: Model:



different bond-lengths ($d_{AC} \neq d_{BC}$)

different hoppings ($h_{AC} \neq h_{BC}$)

THEORETICAL TECHNIQUES

Coherent potential approximation :

$\langle G(z) \rangle = \langle (z.1 - H)^{-1} \rangle \Longrightarrow$ diagonal / off-diagonal (bond-length)

Cannot be treated in CPA without limitations in orthogonal LMTO repres

Solution : separability of structural (S^0) / atom-dependent parts (C, Δ, γ) + transformation from orthogonal to auxiliary LMTO repres

$G(z) \Longrightarrow g^{\beta}(z) = (P^{\beta}(z) - S^{\beta})^{-1}$

(exact scaling transf)

S^{β} → non-random

$P^{\beta}(z)$ → site-diagonal & random (CPA applies)

Final step: $\langle g^{\beta}(z) \rangle \Longrightarrow \langle G(z) \rangle$

(exact scaling transf)

Minimal basis set:

sp^3d^5 - LMTO's on each atom/ES $\Rightarrow$ 36 x 36 format of CPA

Use of all orbitals: unphysical & undesirable

36 LMTO's = $\mathcal{L} + \mathcal{H}$ subsets, $\dim(\mathcal{L}) \approx$ 3-4 times less

$\mathcal{L}$-subset: minimal basis, accurate in a given E-range & treated exactly within CPA

$\mathcal{H}$-subset: its influence via simplified linearization scheme based on Löwdin downfolding applied in a suitably chosen LMTO repres; consistent approximate CPA treatment

Properties:

(i) No loss of accuracy in chosen E-range

(ii) Theory provides a way how to choose $\mathcal{H}$-LMTO repres

(iii) $\mathcal{L}$-sets in alloys same for AC & BC

Division into $\mathcal{L}$ & $\mathcal{H}$ sets depends on:

(i) Material - elemental, $A^{III}B^{V}$, $A^{II}B^{VI}$ etc

(ii) Lattice structure - diamond, ZnS, NaCl, CaF_2

(iii) Energy region - gap, valence bands, conduction states etc

Examples:

Si or GaAs: (diamond / ZnS)

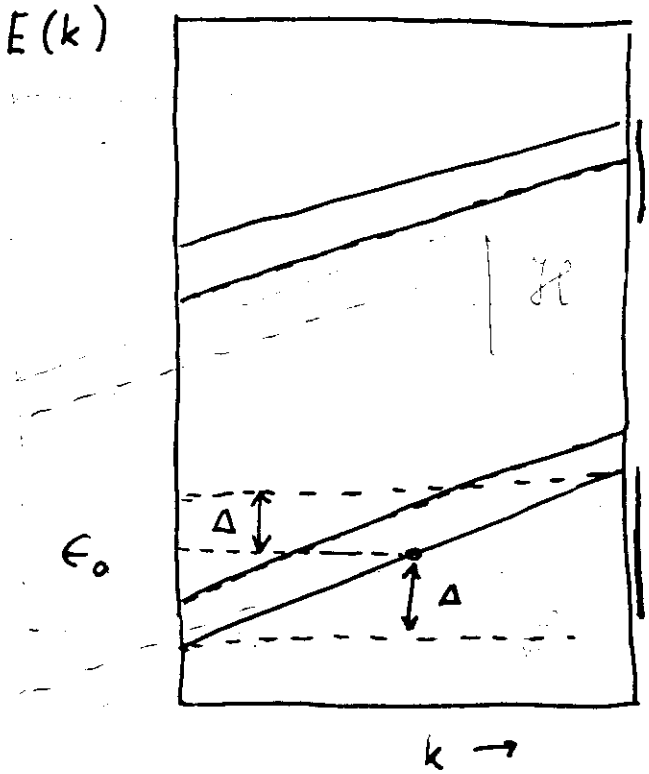
$Si(sp^3)\ Si(sp^3)\ E(s)\ E(s)$
$Ga(sp^3)\ As(sp^3)\ E_1(s)\ E_2(s)$
} 10 x 10 valence & low conduc.

CdTe (ZnS)

$Cd(sp^3)\ Te(p^3)\ E_1(s)\ E_2(s)$ - 9x9, gap
$Cd(d^5)\ Te(s)$ - 6x6, low valence

CdF_2 (CaF_2)

$Cd(sd^5)\ F(p^3)\ E(s)\ F(p^3)$ - 13x13, valence



— unhybridized $\epsilon_{\mathcal{L}}(k)$, $\epsilon_{\mathcal{H}}(k)$

— hybridized bands $E_{\mathcal{L}}(k)$, $E_{\mathcal{H}}(k)$

$$G(E) = \begin{pmatrix} E - \epsilon_{\mathcal{L}}(k) & -f_{\mathcal{L}\mathcal{H}} \\ -f_{\mathcal{H}\mathcal{L}} & E - \epsilon_{\mathcal{H}}(k) \end{pmatrix}^{-1} \quad (2\times 2)$$

gives hybridized bands $E_{\mathcal{L}}(k)$, $E_{\mathcal{H}}(k)$

As $\Delta \ll$ separation of $\epsilon_{\mathcal{L}}$, $\epsilon_{\mathcal{H}}$ bands, for $E \in \epsilon_0 \pm \Delta$ it holds $E - \epsilon_{\mathcal{H}} \approx \epsilon_0 - \epsilon_{\mathcal{H}}$

$$G_{\mathcal{L}\mathcal{L}}(E) = \frac{1}{E - \epsilon_{\mathcal{L}}(k) - \Pi_{\mathcal{L}}(k)} \quad (1\times 1), \qquad \Pi_{\mathcal{L}}(k) = \frac{f_{\mathcal{L}\mathcal{H}} f_{\mathcal{H}\mathcal{L}}}{\epsilon_0 - \epsilon_{\mathcal{H}}(k)}$$

↳ band shift

Result:

$E_{\mathcal{L}}(k)$ nearly exact, $E_{\mathcal{H}}(k)$ does not described

DOWNFOLDING TO MINIMAL ($\mathcal{L}$) BASIS SET

We divide full space: $\mathbb{1} = \mathcal{L} + \mathcal{H}$

Blocks of averaged resolvent (downfolding).

$$\langle G(z)\rangle_{SS'} = \Lambda^{\wedge}_{S}(z)\,\delta_{SS'} + M^{\wedge}_{S}(z)\,\langle \hat{g}(z)\rangle_{SS'}\,M^{\wedge}_{S'}(z), \qquad S,S' = \mathcal{L},\mathcal{H}$$

$$\langle \hat{g}(z)\rangle_{\mathcal{L}\mathcal{H}} = \langle \hat{g}(z)\rangle_{\mathcal{L}\mathcal{L}}\; S^{\wedge}_{\mathcal{L}\mathcal{H}}\; F^{\wedge}_{\mathcal{H}\mathcal{H}}(z)$$

$$\langle \hat{g}(z)\rangle_{\mathcal{H}\mathcal{L}} = F^{\wedge}_{\mathcal{H}\mathcal{H}}(z)\; S^{\wedge}_{\mathcal{H}\mathcal{L}}\; \langle \hat{g}(z)\rangle_{\mathcal{L}\mathcal{L}}$$

$$\langle \hat{g}(z)\rangle_{\mathcal{H}\mathcal{H}} = F^{\wedge}_{\mathcal{H}\mathcal{H}}(z) + F^{\wedge}_{\mathcal{H}\mathcal{H}}(z)\; S^{\wedge}_{\mathcal{H}\mathcal{L}}\,\langle \hat{g}(z)\rangle_{\mathcal{L}\mathcal{L}}\; S^{\wedge}_{\mathcal{L}\mathcal{H}}\; F^{\wedge}_{\mathcal{H}\mathcal{H}}(z)$$

$$\langle \hat{g}(z)\rangle_{\mathcal{L}\mathcal{L}} = \left(P^{\wedge}_{\mathcal{L}}(z) - S^{\wedge}_{\mathcal{L}\mathcal{L}} - S^{\wedge}_{\mathcal{L}\mathcal{H}}\, F^{\wedge}_{\mathcal{H}\mathcal{H}}(z)\, S^{\wedge}_{\mathcal{H}\mathcal{L}}\right)^{-1} \quad \text{and}$$

$$F^{\wedge}_{\mathcal{H}\mathcal{H}}(z) = \left(P^{\wedge}_{\mathcal{H}}(z) - S^{\wedge}_{\mathcal{H}\mathcal{H}}\right)^{-1}$$

Advantage: all blocks are expressed via $\langle \hat{g}(z)\rangle_{\mathcal{L}\mathcal{L}}$ to be approximated. Specifically, we look for approximate form of $F^{\wedge}_{\mathcal{H}\mathcal{H}}(z)$ which is numerically demanding (repeated evaluation of matrix inversions of dim($\mathcal{H}$) for many z and k-vectors)

Approximate form of $F^{\beta}_{\mathcal{H}\mathcal{H}}(z)$:

(i) we choose the energy range of interest for $\mathcal{L}$-states centred around the energy ε_0, where we need a proper description

(ii) we transform to a new representation $\beta = (\beta_{\mathcal{L}}, \beta_{\mathcal{H}})$ such that

$$P^{\beta}_{\mathcal{H}}(\varepsilon_0) = 0$$

(equation for $\beta_{\mathcal{H}}$; $\beta_{\mathcal{L}}$ = screened NTO repres)

Solution : $\mathcal{H}$-states lie outside the energy range of $\mathcal{L}$-states (weak hybridization), so that

$$\mathrm{Im}\, P^{\beta}_{\mathcal{H}}(\varepsilon_0) \approx 0, \quad P^{\beta}_{\mathcal{H}}(z) \approx x\, P^{\beta,1}_{\mathcal{H}}(z) + (1-x)\, P^{\beta,2}_{\mathcal{H}}(z)$$

$$\beta_{\mathcal{H}} = \bar{f}_{\mathcal{H}} + \frac{\bar{\Delta}_{\mathcal{H}}}{\varepsilon_0 - \bar{C}_{\mathcal{H}}} \qquad (\bar{X} \equiv x X^1 + (1-x) X^2)$$

Because $\| P^{\beta}_{\mathcal{H}}(z) \| \gg \| S^{\beta}_{\mathcal{H}\mathcal{H}} \|$ for z around ε_0, we can write

$$F^{\beta}_{\mathcal{H}\mathcal{H}}(z) \approx \frac{d}{dz}\left(P^{\beta}_{\mathcal{H}}(z)\right)^{-1}_{\varepsilon_0}(z-\varepsilon_0) \equiv \frac{\bar{V}^{\beta}_{\mathcal{H}} - z}{\bar{\Gamma}^{\beta}_{\mathcal{H}}}$$

$$\bar{V}^{\beta}_{\mathcal{H}} = \bar{C}_{\mathcal{H}} - \frac{\bar{\Delta}_{\mathcal{H}}}{\bar{f}_{\mathcal{H}} - \beta_{\mathcal{H}}}, \qquad \bar{\Gamma}^{\beta}_{\mathcal{H}} = \frac{\bar{\Delta}_{\mathcal{H}}}{(\bar{f}_{\mathcal{H}} - \beta_{\mathcal{H}})^2}$$

Using this approximate form

$$\langle g^{\wedge B}(z)\rangle_{LL} = \left(P_L^{\wedge}(z) - S_{LL}^{\wedge B} - \Pi_{LL}^{\wedge B}(z) \right)^{-1}$$

$$\Pi_{LL}^{\wedge B}(z) = S_{Lh}^{\wedge} \{ \bar{V}_{he}^{\wedge} / \bar{\Gamma}_{he}^{\wedge} \} S_{hL}^{\wedge} - z\, S_{Lh}^{\wedge} \{ 1/\bar{\Gamma}_{he}^{\wedge} \} S_{hL}^{\wedge}$$

Advantage: trivial z-dependence of $\Pi_{LL}^{\wedge}$ as compared to $F_{hehe}^{\wedge}$; consistent approximation for other blocks of $\langle G \rangle$

Features

(i) The CPA eqs are solved only in the small L-block (all other blocks of $\langle G \rangle$ expressed via $\langle g^{\wedge} \rangle_{LL}$)

(ii) significant numerical simplification while retaining essentially the same accuracy in the energy region of interest around ε_0

(iii) Method is inherent to TB-LMTO & change of screening of downfolded h-states }

(iv) $\Pi_{LL}^{B} = A_{LL} - z\, B_{LL}$ ← corrects 0 } when going back to L-repres
↑ corrects H

CHOICE OF POTENTIAL PARAMETERS

■ Approximate bond-lengths preservation in alloys:

$d_{AC}(x) \neq d_{BC}(x) \approx const \Longrightarrow$ EXAFS, $A_x B_{1-x} C$ alloy

(ZnS : $A^{III}B^{V}$, $A^{II}B^{VI}$)

Modelling : sc pp for AC/BC at experimental lattice constants $a_{AC} \neq a_{BC}$

(volume varies linearly with x)

Example: $ZnS - Cd_x Hg_{1-x} Te$ ($a \approx 6.48\,\text{Å}$)

$CaF_2 - Cd_x Pb_{1-x} F_2$ ($a_{CdF_2} \approx 5.40\,\text{Å}$, $a_{PbF_2} \approx 5.94\,\text{Å}$)

■ Linear variation of bond-lengths with composition:

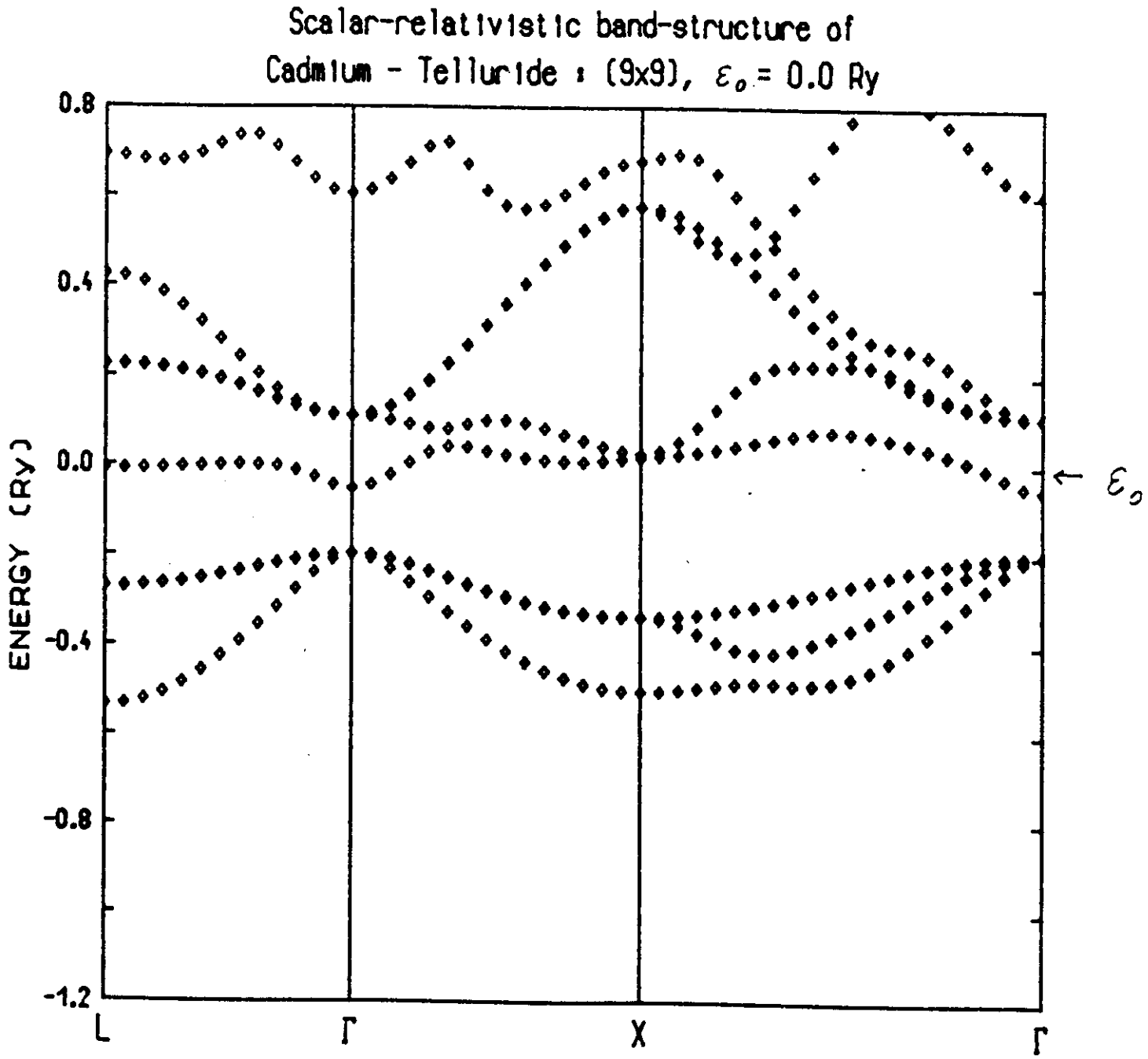
$d_{AC}(x) = d_{BC}(x)$, proportional linearly to x

Modelling : sc pp evaluated for experimental $a(x)$, same for $AC \propto BC$

More sophisticated choice : sc pp for $A_n B_{4-n} C_4$ ($n=0,1,2,3,4$) supercells at experimental $a(x)$, $x = 0, 0.25, 0.5, 0.75, 1.0$ (16 atoms/cell)

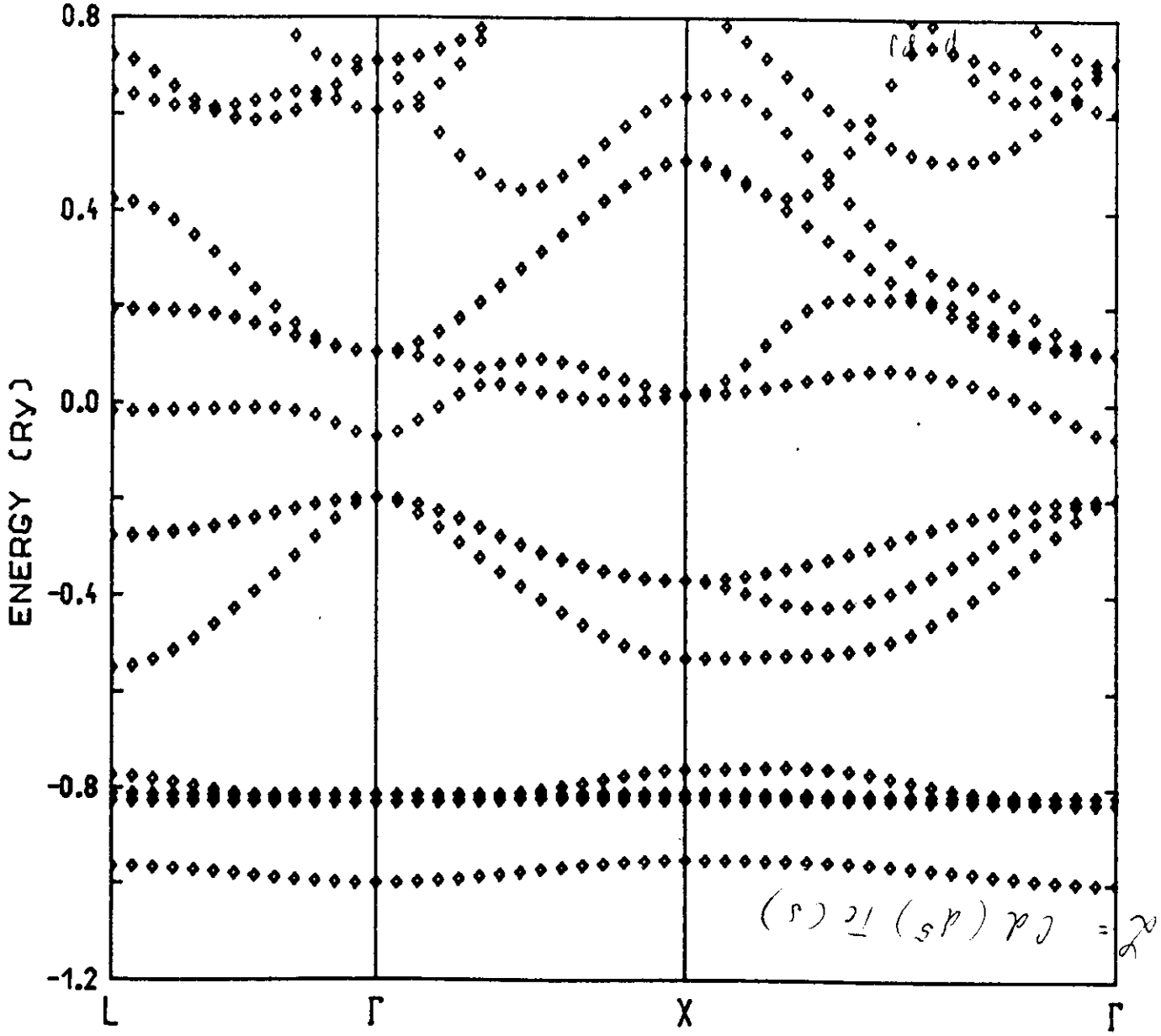
Example: $CaF_2 - Cd_x Pb_{1-x} F_2$, $a(x) = x\, a_{CdF_2} + (1-x)\, a_{PbF_2}$

$\mathcal{L}$: $Cd(sp^3)$ $Te(p^3)$ $E_1(s)$ $E_2(s)$

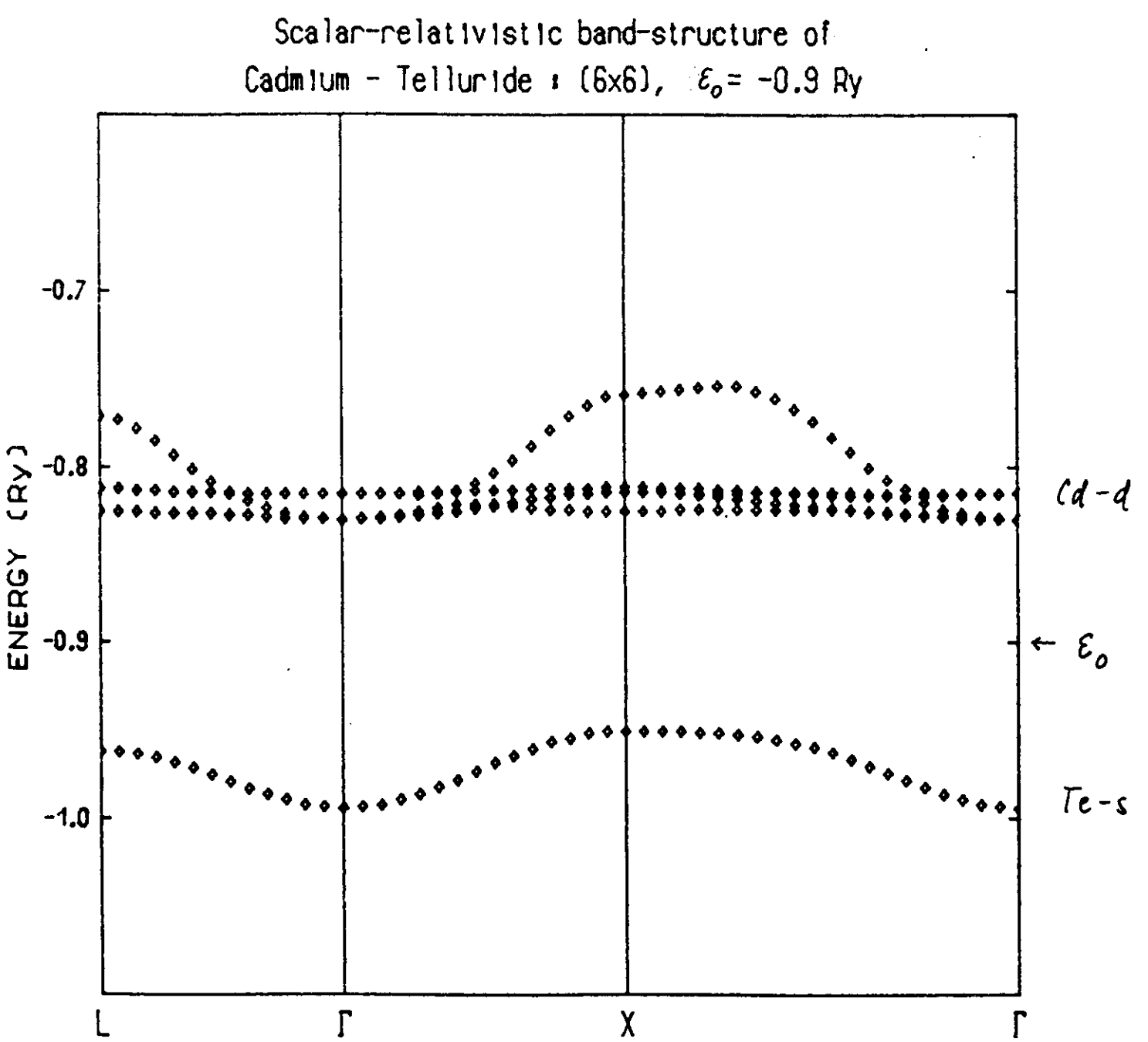


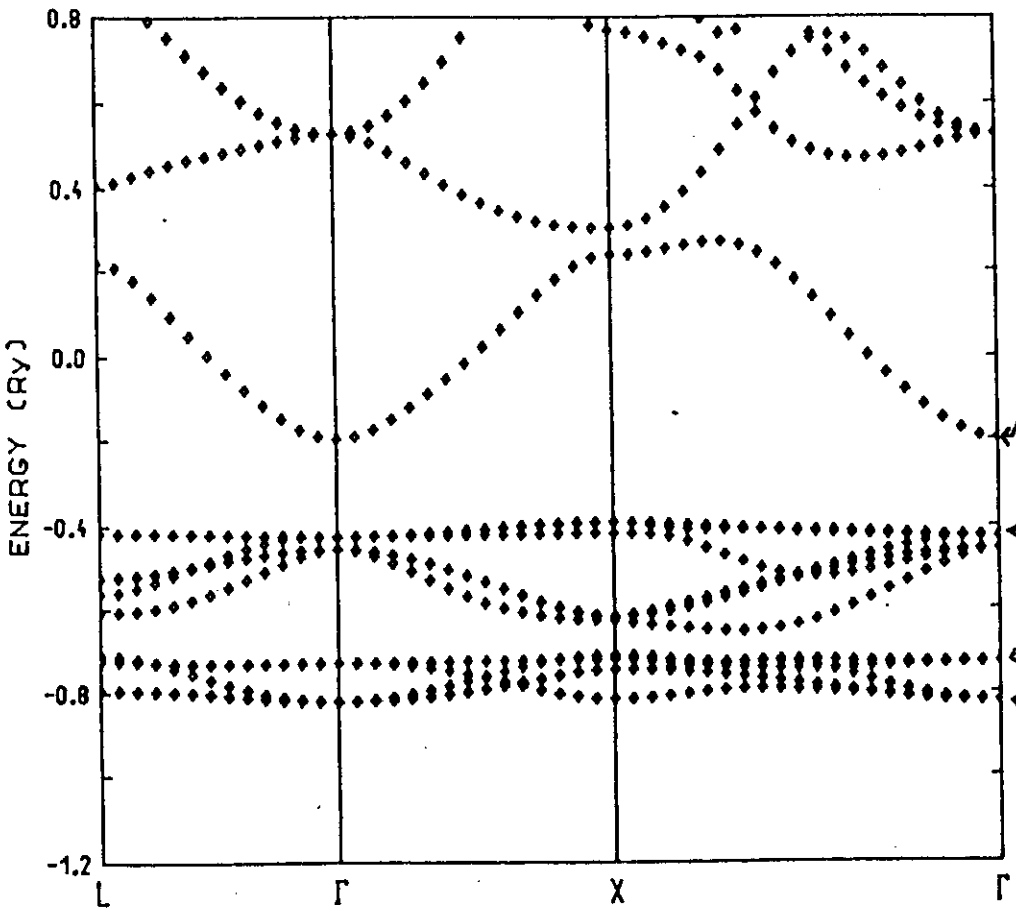
Full basis set :

$Cd(sp^3d^5)\ Te(sp^3d^5)\ E_1(sp^3d^5)\ E_2(sp^3d^5)$



$\mathcal{L}$: $Cd(d^5)\,Te(s)$





minimum Γ

Bottom of cond. band

admixture of Cd-s, F-p

Valence band

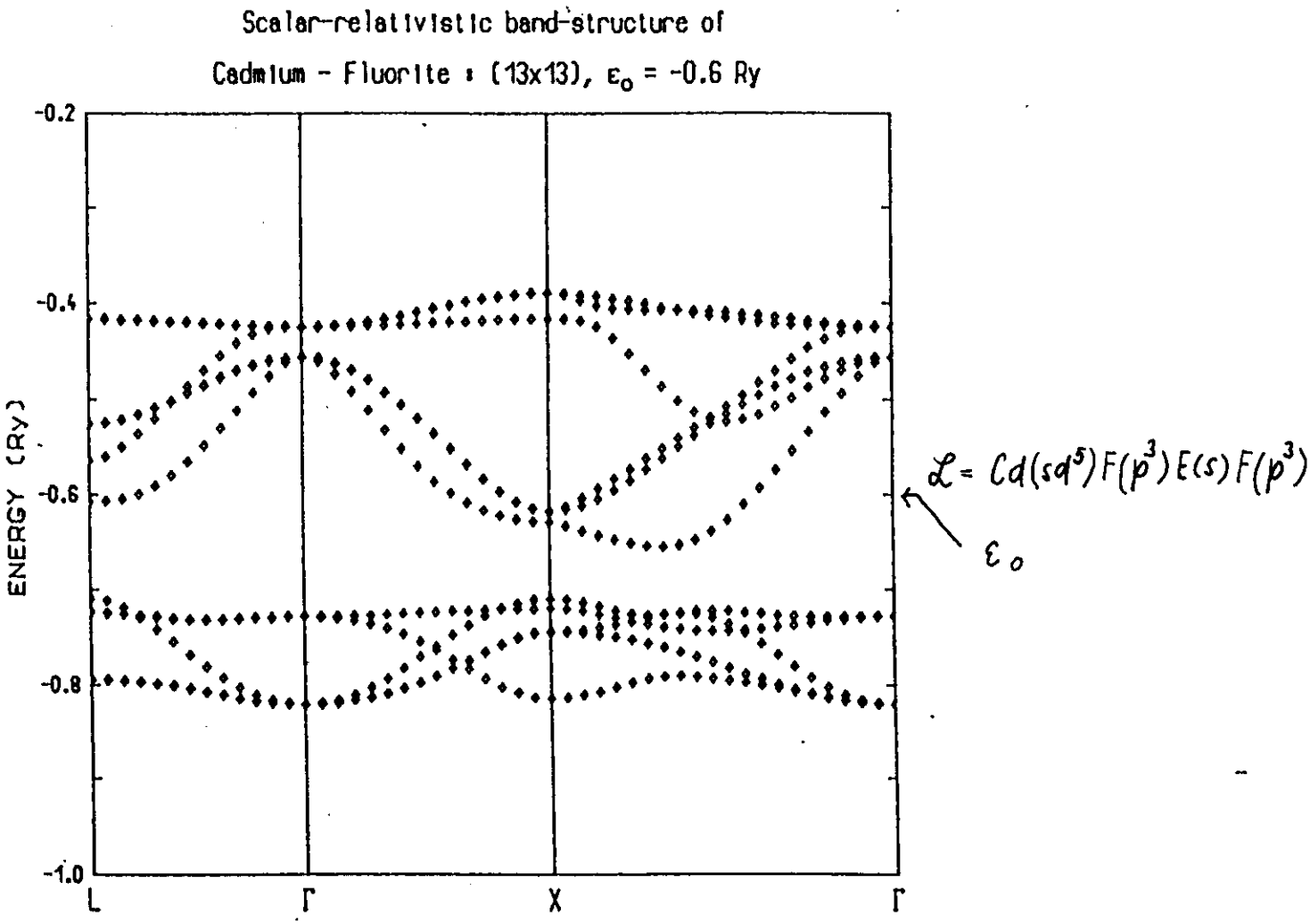
strong p-d hybridization of F-p and Cd-d, while bottom is dominated)

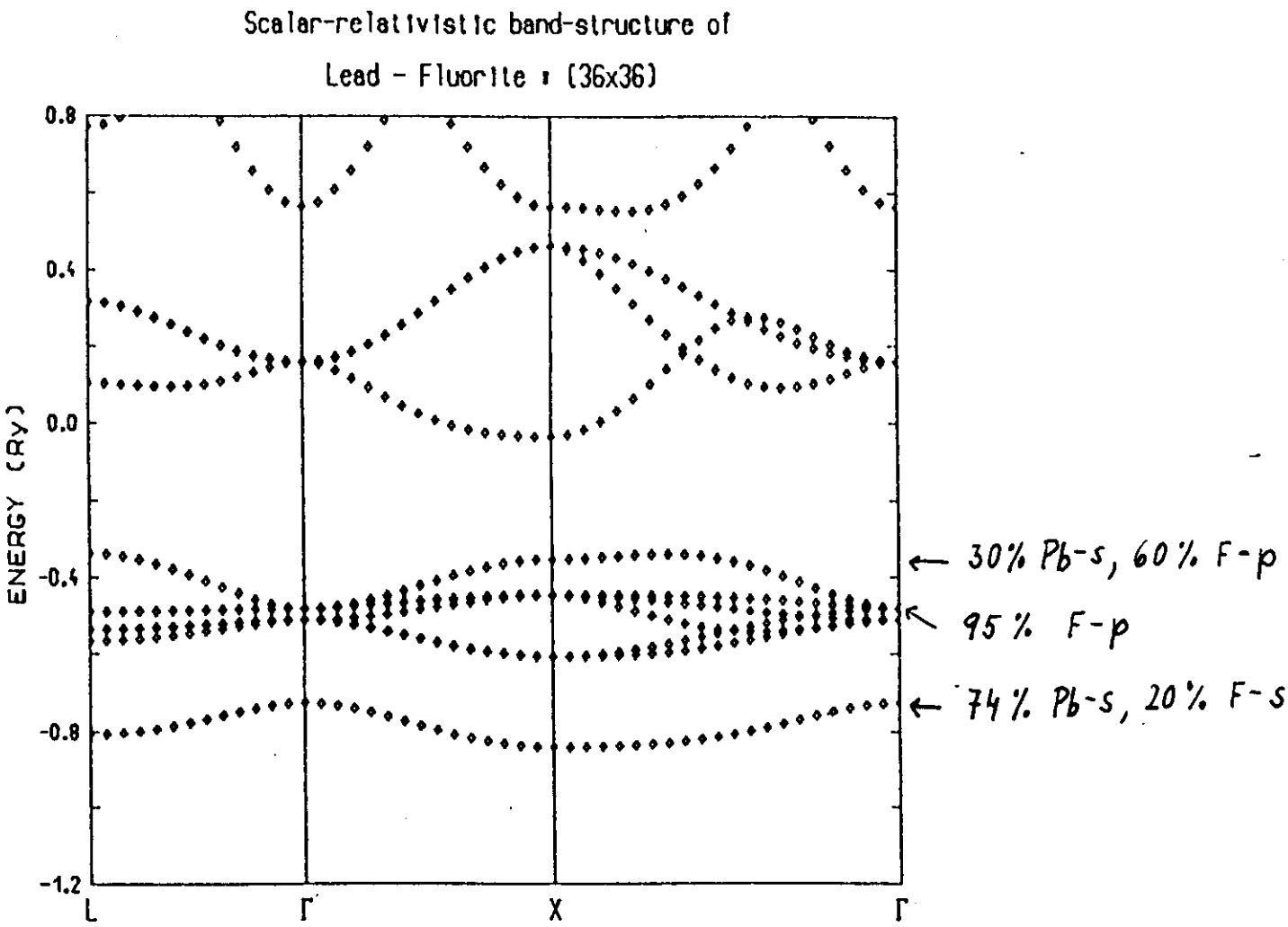
Cd-d
40% Cd-s, 37% F-p
23% F-s

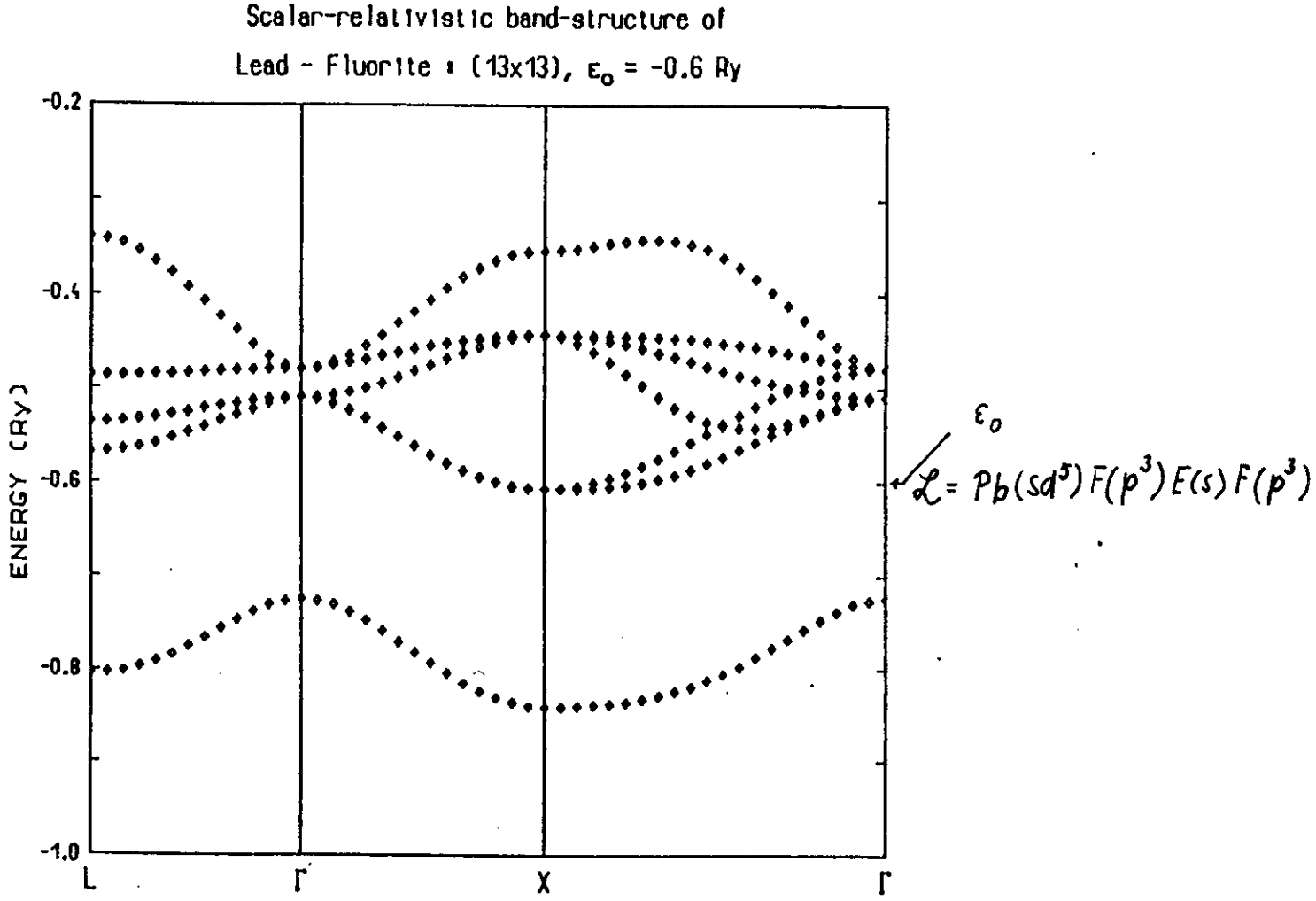
← 68% F-p; 30% Cd-d

98% Cd-d

← 68% F-p, 30% Cd-d

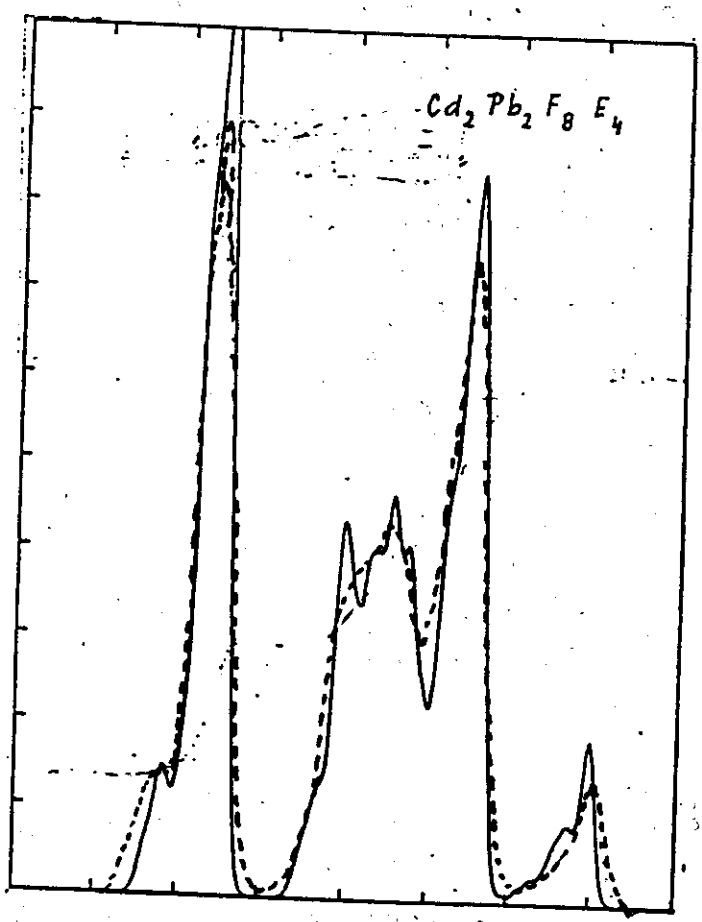

Scalar-relativistic band-structure of
Cadmium - Fluorite : (13x13), ε_0 = -0.6 Ry
-0.2
-0.4
-0.6
-0.8
-1.0
ENERGY (Ry)
L
Γ
X
Γ
$\mathcal{L} = Cd(sd^5)F(p^3)E(s)F(p^3)$
ε_0


Scalar-relativistic band-structure of
Lead - Fluorite : (36x36)
ENERGY (Ry)
0.8
0.4
0.0
-0.4
-0.8
-1.2
L
Γ
X
Γ
← 30% Pb-s, 60% F-p
← 95% F-p
← 74% Pb-s, 20% F-s

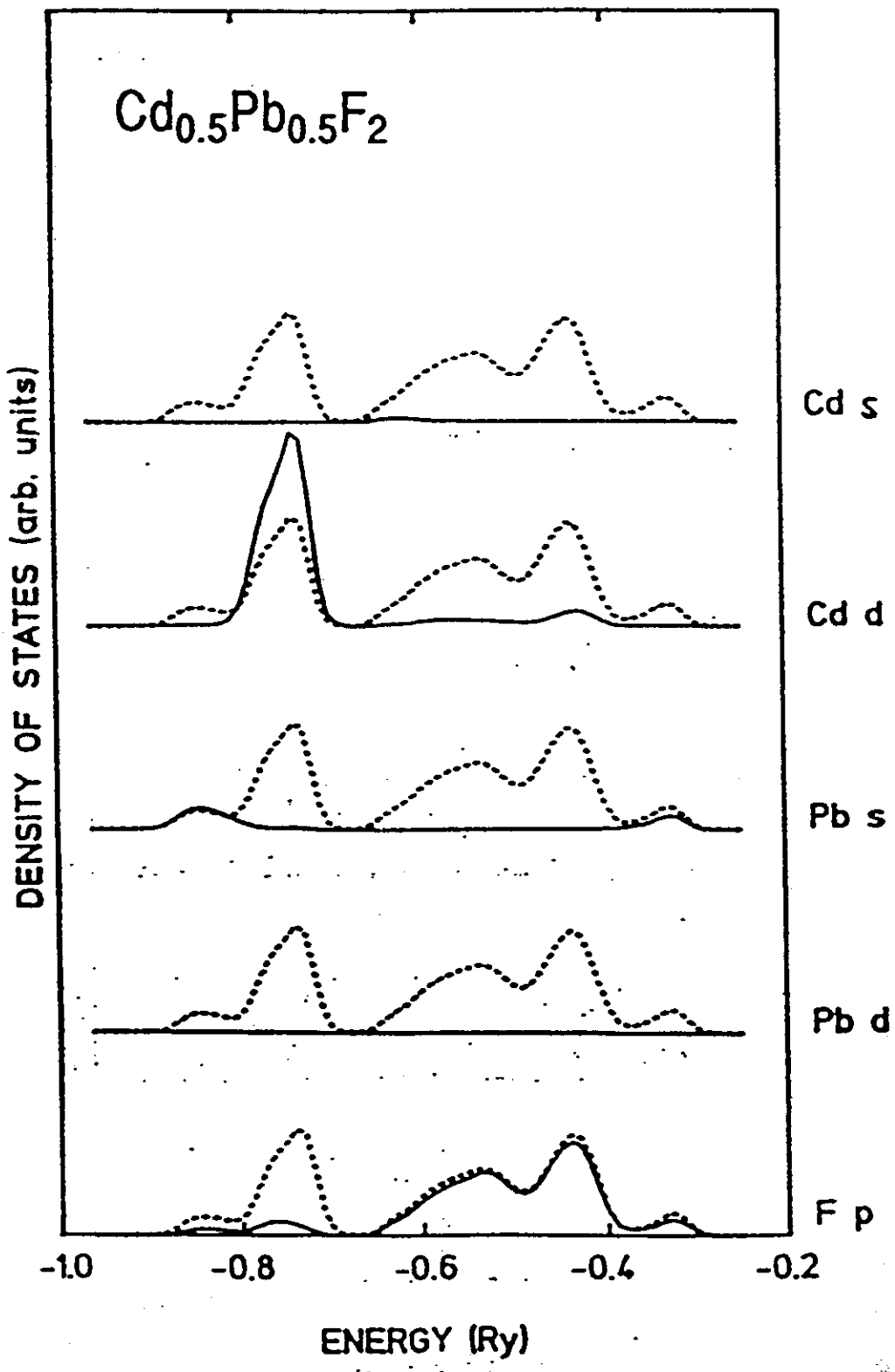

Scalar-relativistic band-structure of
Lead - Fluorite : (13x13), ε_o = -0.6 Ry
ENERGY (Ry)
-0.2
-0.4
-0.6
-0.8
-1.0
L
Γ
X
Γ
ε_o
$\mathcal{L}$ = Pb(sd^5) F(p^3) E(s) F(p^3)

LMTO CPA : ---- $Cd_{0.5}Pb_{0.5}F_2$

LMTO supercell : —— $Cd_2Pb_2F_8E_4$



$Cd_{0.5}Pb_{0.5}F_2$
Cd s
Cd d
Pb s
Pb d
F p
DENSITY OF STATES (arb. units)
ENERGY (Ry)
-1.0
-0.8
-0.6
-0.4
-0.2


$Cd_{0.5}Pb_{0.5}F_2$
DENSITY OF STATES (arb. units)
Cd s
Cd d
Pb s
Pb d
F p
-1.0
-0.8
-0.6
-0.4
-0.2
ENERGY (Ry)