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SPRING COLLEGE IN MATERIALS SCIENCE

ON

"METALLIC MATERIALS"

(11 May - 19 June 1987)

ELECTRONIC STRUCTURE AND PHASE STABILITY
(Part II)

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II BAND STRUCTURE CALCULATIONS

II 1 Introduction

Our aim is to discuss the many assumptions with special attention concerning the results energy calculations and their limitations

(i) general principles of a band str. calc. local density approximation.

(ii) one electron states for periodic potentials

(iii) simple models to get general trends (chapter III)

II 2 DENSITY FUNCTIONAL FORMALISM.

2.1 Pb: find the solutions $\Psi_n(r_1 \dots r_N)$, E_n ($n=0$ = GROUND STATE) for

$$\mathcal{H} = T + \mathcal{U} + V_{ext} \quad (N_{el} \to \infty \text{ MACROSC. LIM!})?$$

$$\begin{cases} T = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 & \text{KINETIC ENERGY} \\ \mathcal{U} = \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} & \text{COULOMB ENERGY} \\ V_{ext} = \sum_i v_{ext}(r_i) & \text{EXT. POT}^{\text{L}} \text{ (NUCLEI, } \dots \text{)} \end{cases}$$

Two theorems

(a) The ground state energy E_0 (or the thermodyn. potential) is a universal functional of the density $n(r) = N\sum_{\sigma_i}\int|\Psi_0(r, r_2 \cdots r_N)|^2 d\sigma_2 \dots d\sigma_N$

(b) The ground state energy E_0 is the same as the corresponding energy for non interacting el. i.e. potential $v(r)$

(a) v_{ext} is a functional of $n(r)$ (up to a constant from)

if: $v_{ext} \to \Psi_0 \; E_0 \Rightarrow n(r) \Rightarrow E_0' < \langle\psi|\mathcal{H}'|\psi\rangle = E_0 + \int n(v'-v)$

and $v'_{ext} \to \Psi_0' \neq \Psi_0, E_0'$ $\qquad E_0 < \langle\psi'|\mathcal{H}|\psi'\rangle = E_0' + \int n'(v-v')$

$\Downarrow$

$v'_{ext} = v_{ext}$

$$\begin{cases} E(n(r)) = \int v_{ext}(r)\, n(r)\, dr + F(n(r)) \\ F(n(r)) = \frac{1}{2}\int\frac{n(r)\,n(r')}{|r-r'|} + G(n(\psi)) \end{cases}$$

(b) introduce an auxiliary system of non interacting electrons with the same density $n(r)$ as the real density

$$\mathcal{H}_0 = T + V \qquad V = \sum_i v(r_i) \; ?$$

$$n(r) = \sum_k f_k |\psi_k(r)|^2$$

$$\mathcal{H}_0 = \sum_i h_0(i) \qquad \begin{cases} h_0 = -\frac{\hbar^2}{2m}\nabla^2 + v \\ h_0\psi_k = \epsilon_k\psi_k \end{cases}$$

$$\begin{cases} G(n(r)) = T_0(n) + E_{xc}(n(r)) \\ T_0(n) = \langle\Psi_0^0|T|\Psi_0^0\rangle \quad (\Psi_0^0 \text{ G.S for } \mathcal{H}_0) \end{cases}$$

$$\begin{cases} E(n(r)) = T_0(n(r)) + \int v_{ext}(r)n(r)dr + \frac{1}{2}\int\frac{n(r)n(r')}{|r-r'|}dr\,dr' + E_{xc} \\ E(n(r)) = \langle\Psi_0^0|\mathcal{H}^0|\Psi^0\rangle = T_0(n(r)) + \int v(r)\,n(r)\,dr \end{cases}$$

GROUND STATE ENERGY (minimization): $\frac{\delta E}{\delta n(\psi)} = 0$

$$v(r) = v_{ext}(r) + v_{coul}(r) + v_{xc}(r)$$

(c) Local density approximation

$$E_{xc}(n(r)) = \int n(r)\,\epsilon_{xc}(n(r))\,dr$$

$\epsilon_{xc}(n)$ for an homogeneous el. gas

(d) Extension to the magnetic systems

$E_{xc}(n_\uparrow, n_\downarrow)$ $\qquad n = n_\uparrow + n_\downarrow$

the effects of exchange and correlations being included in a potential $v_{xc}(r)$

$$v(r) = v_{ext} + e^2\underbrace{\int \frac{n(r')\,dr'}{|r-r'|}}_{\text{COULOMB POTENTIAL}} + v_{xc}(r)$$

<u>The local density approximation</u>

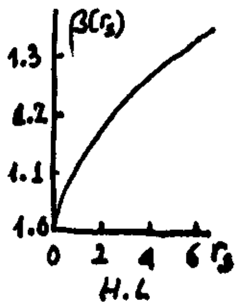
$$v_{xc}(r) = \frac{d}{dn}\left(n(r)\,\epsilon_{xc}(n)\right)_{n=n(r)} = \mu_{xc}(n(r))$$

$\epsilon_{xc}(n)$ IS THE EXCHANGE CORRELATION ENERGY PER ELECTRON FOR AN HOMOGENEOUS GAS OF DENSITY n ... which is accurate by known!

exchange part $v_x = \frac{d}{dn}\left(n(r)\, n^{1/3} \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\right) = \mu_{xx}$

$\sim n^{1/3}$

$= \frac{2}{3} v_{SLATER}$



$\mu_{xc}(n) = \beta(n)\,\mu_x(n)$

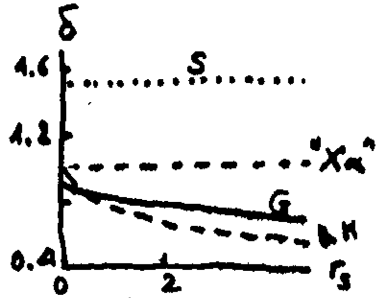
$\beta(r_s) = 1 + 0.545\, r_s \log(1 + 11.4/r_s)$

It can be extended to magnetic systems

$\zeta = \frac{m}{n}$

$v_{xc}^{\pm}(r_s, \zeta) = \mu_x(r_s)\left(\beta(r_s) \pm \frac{1}{3}\frac{\delta(r_s)\,\zeta}{1 \pm \gamma\zeta}\right)$

$\delta(r_s) = 1 - .036\, r_s - 1.36\, r_s/(1+10\, r_s)$ $\quad \gamma = 0.297$



$v_{slater} = \langle v_x \rangle$ average of an exchange potential for an homogeneous el gas $\sim n^{1/3}$

$(v_x)v_{..} = \alpha\, v_{slater}$ α fitted to some of prop.

3 Discussion

- THE L.D.A. ALLOW TO DETERMINE GROUND ST. PROPERTIES E_0, $n(r)$, $m(r)$, B, χ ...
- THE AUXILIARY FUNCTIONS $\psi_k(r)$ HAVE NO ∅ MEANING ... "IN PRINCIPLE" BUT...
- IT'S TEMPTING TO IDENTIFY $(\epsilon_k, \psi_k(r))$ TO THE ELEMENTARY EXCITATIONS (h, e) FOR THE REAL SYSTEM. AND—
- IT WORKS ≅ WHEN THE EFFECTS OF CORRELATION ARE NOT TOO IMPORTANT

Ex 1 Cu w/Ni

Ex 2 E_g for Si or GaAs (th. ≈ .25 eV of E_g^{exp}) 6

4. FORCES AND PRESSURE RELATIONS

homog. compression ep: monoatomic syst

- $p = -\frac{dE_0}{dV}$ $\quad p(V_0) = 0$ $\quad V_0 = N_a \Omega_a$ (eq. volume)

B = bulk modulus $= K^{-1} = -\frac{dp}{d\log V}\Big|_{V_0}$

E_c = cohesive energy per atom $= -\int_{V_0}^{\infty} p\,dV = -3\int p V d\log s$

(s = radius of the atomic sphere).

- <u>Th (Andersen)</u>

$$p = -\delta E_{bs}/\delta V$$

$$E_{bs} = \int^{\epsilon_F} n(\epsilon)\,\epsilon\, d\epsilon$$

δ = variation with a frozen potential in the atomic sphere approximation (ASA) (neglecting the interstitial region)

$\Omega_a = \frac{4\pi}{3} s^3$

$$\begin{cases} 3pV = -\frac{\delta E_{bs}}{\delta \log s} = \sum_\ell 3p_\ell V \quad \text{(spherical potentials inside the AS)} \\ 3p_\ell V = \int^{\epsilon_F} n_\ell(\epsilon)\, s\, \phi_\ell^2(\epsilon,s)\left\{(D_\ell(\epsilon)+\ell+1)(D_\ell(\epsilon)-\ell) + (\epsilon - \epsilon_{xc})s^2\right\} \end{cases}$$

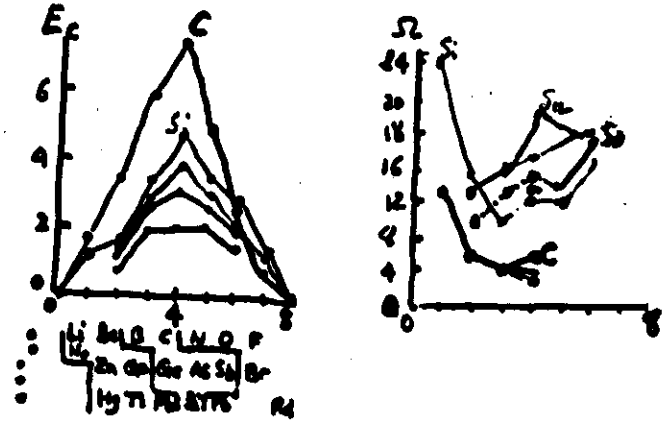
$D_\ell(\epsilon) = \frac{s\,\phi_\ell'(s,\epsilon)}{\phi_\ell(\epsilon,s)}$ $\quad$ (Pettifor, Nieminen Hodges)

⇒ EQUATION OF STATE $pV = f(V)$ easy to calculate from

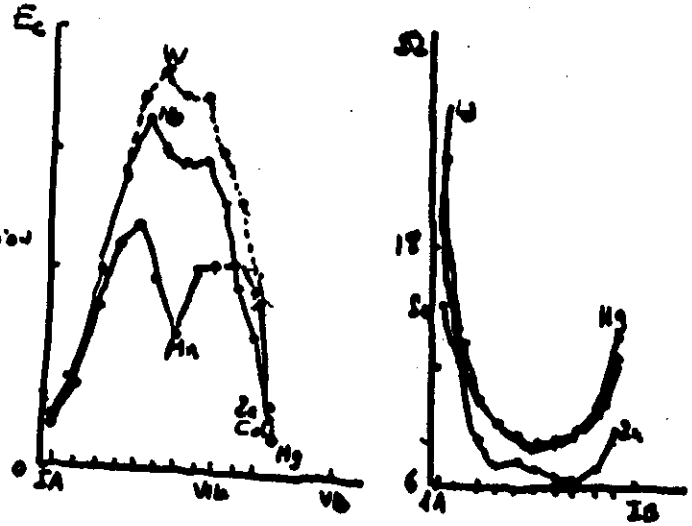
[illegible] ... and D_ℓ ...

COHESIVE ENERGIES AND ATOMIC VOL (exp)

"sp" ELEMENTS



TRANSITION METALS

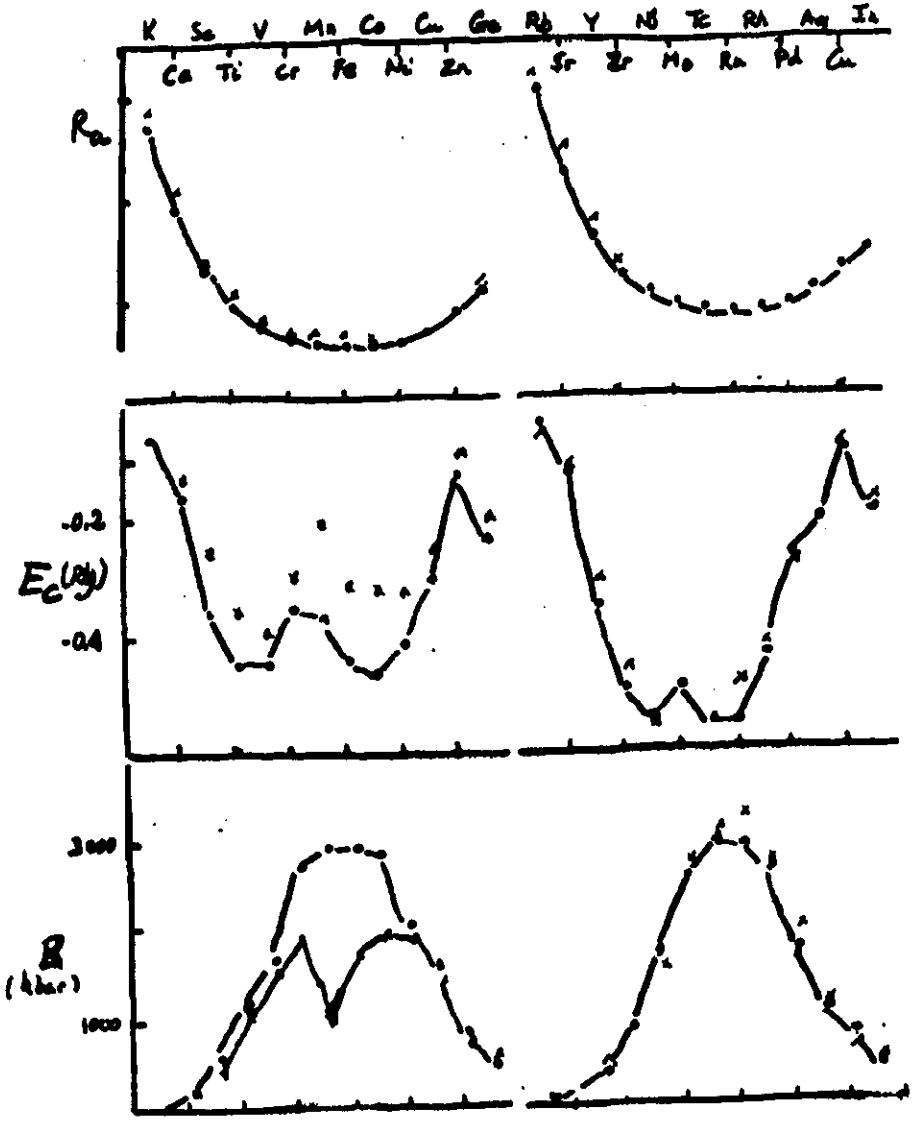


NOTE THAT : - THE COHESIVE ENERGY IS MAX WHEN THE 'sp' OR d BANDS ARE HALF FILLED
- THE ATOMIC VOLUME IS MINIMUM WHEN THESE BANDS ARE HALF FILLED (apart from large exceptions)

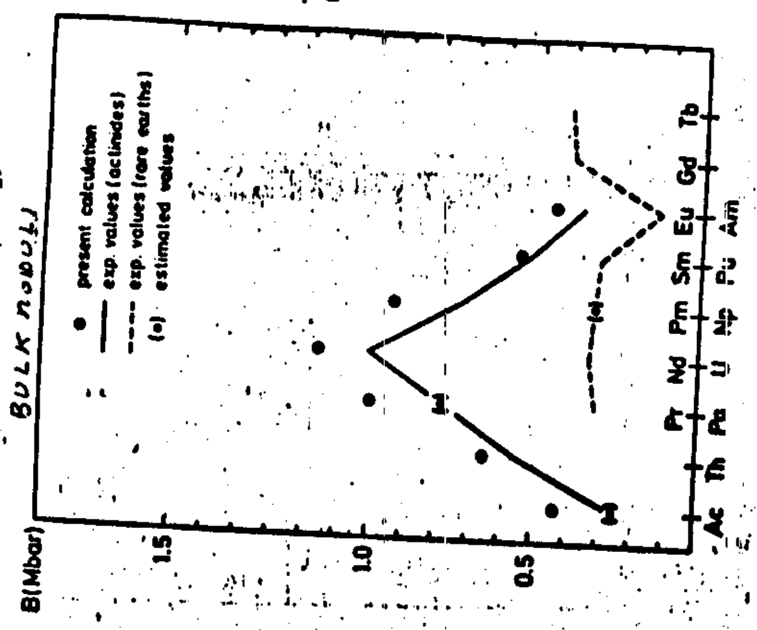
$E_c = E_{at} - E$ Ω is the atomic volume

CALCULATION OF THE COHESIVE ENERGY, WIGNER SEITZ RADIUS AND BULK MODULUS FOR TM OF THE 1st AND 2nd SERIE

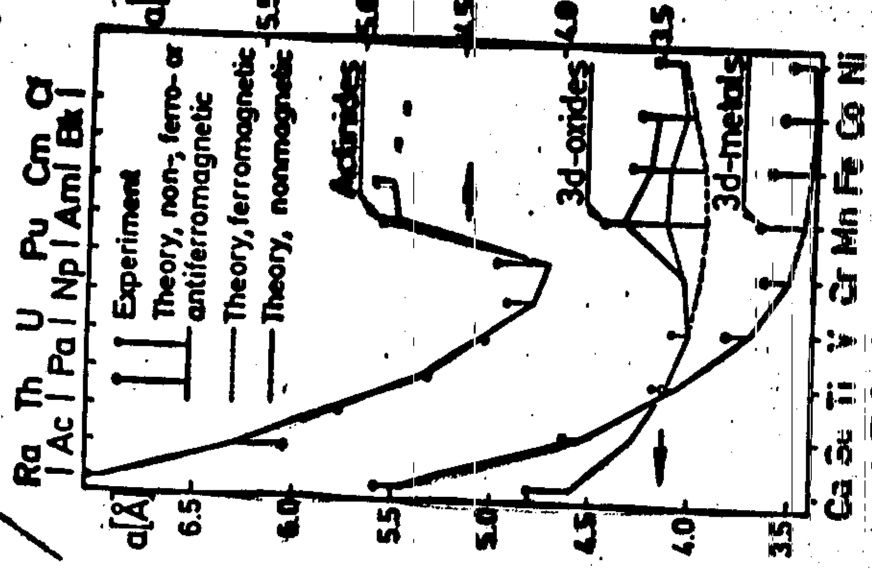
NOTE THE DEVIATIONS DUE TO "STRONG" CORRELATIONS AND MAGNETISM IN THE 1st SERIE



Cohesive energy, Wigner Seitz radius R_{ws} and bulk compressibility of transition metals of 1st and 2nd serie (calc. x exp)

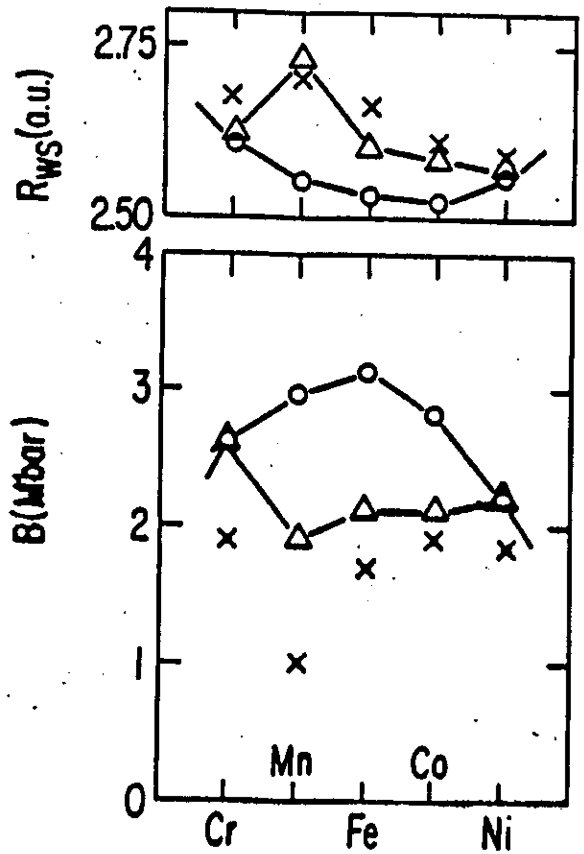


(from OK Andersen) (1985)



NOTE THE EFFECT OF MAGNETISM (→ INCREASE a) ... "Am ACTINIDES"

THE EFFECT OF MAGNETISM ON ATOMIC VOLUMES



(from Janak et al)

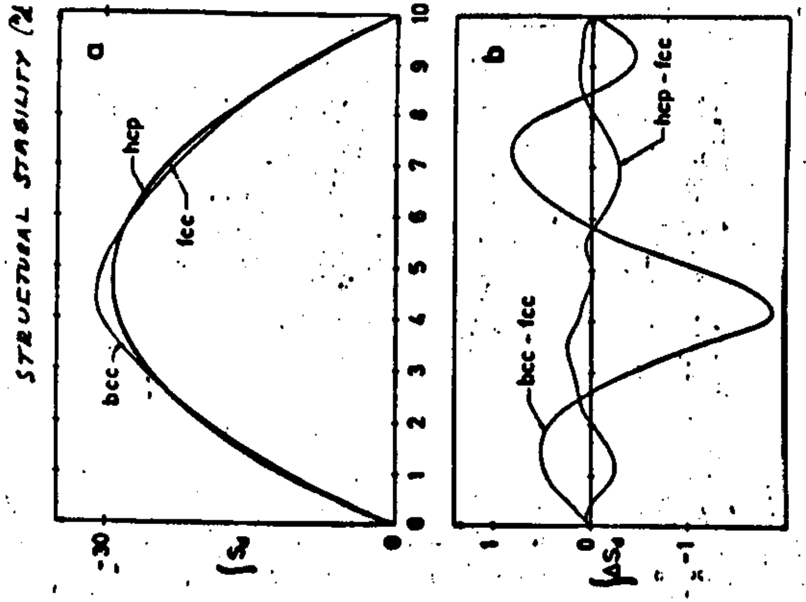
× exp
Δ magn calc
o paramagn "

$\Delta E_m = E(m) - E(0) = \overset{0}{\Delta E_{bs}} - \frac{\overset{0}{I} m^2}{2}$

$-\frac{\partial \Delta E_m}{\partial \Omega} = p_m \Rightarrow p_m = -\partial \Delta E_{bs}/\partial \Omega$

$W \sim \Omega^{-5/3}$ ... $n(\epsilon, W) = n(\frac{\epsilon}{W}, 1) W \Rightarrow$ $p_m = \frac{5}{3} \Delta E_{bs}(m) > 0$

STRUCTURAL STABILITY (N d)

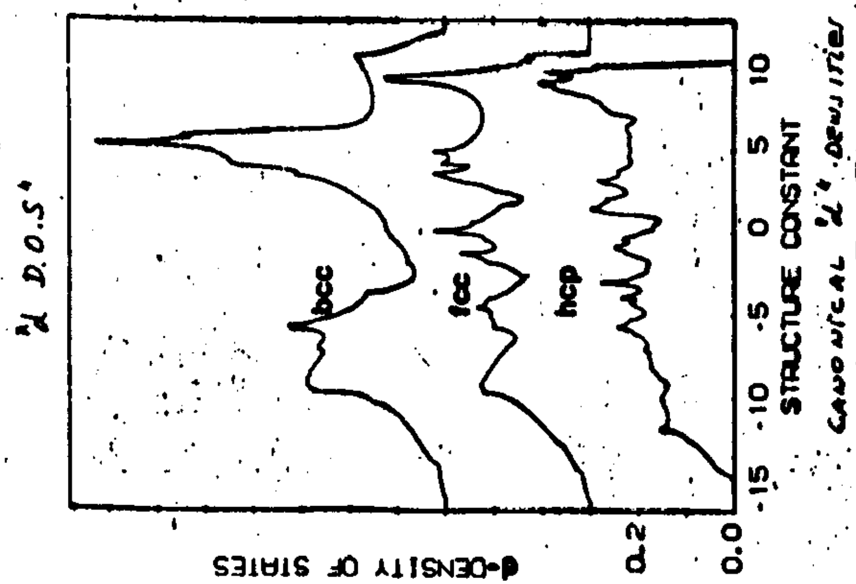


STRUCTURAL STABILITIES FROM CANONICAL 'd' BANDS

NOTE THAT THE bcc IS THE MOST STABLE STATE (FOR N=9, Pd) IN LCN REDUCTION WITH Bpp

[redacted] from OK Andersen

'd' D.O.S'



CANONICAL 'd' DENSITIES OF STATES FOR TM (from O.K. Andersen)

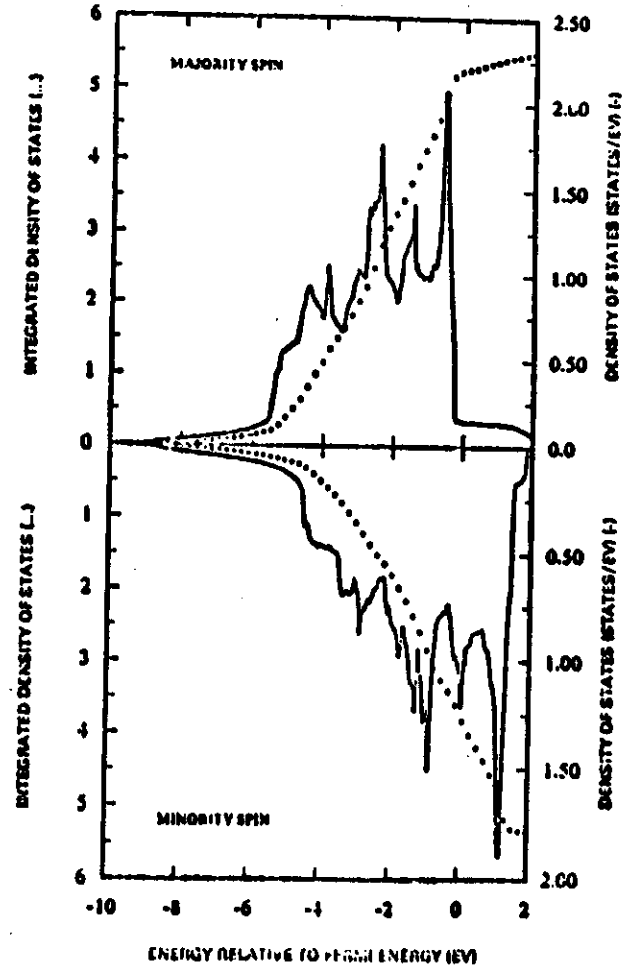
D.O.S OF FERROMAGNETIC COBALT

— THE 'd' BANDS ARE (ROUGHLY) RIGIDLY SHIFTED:

$$\begin{cases} \Delta E(m) = \varepsilon_{d\uparrow} - \varepsilon_{d\downarrow} \simeq \alpha m & \alpha \sim 0.5\text{-}0.7 \text{ eV} \\ m = n_{\uparrow} - n_{\downarrow} \end{cases}$$

EFFECTS OF SPIN POLARIZATION

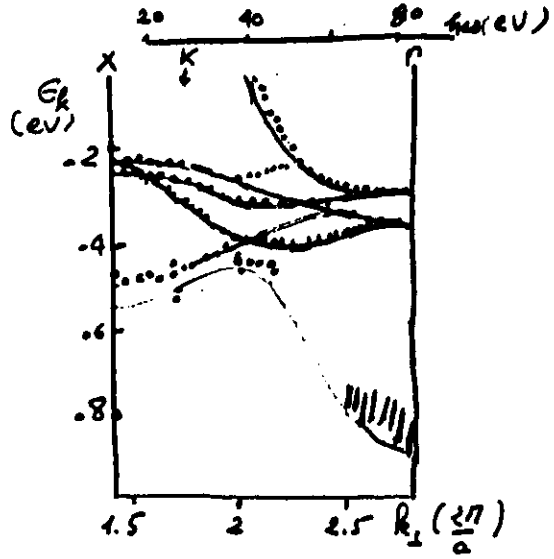
Cobalt



Cobalt is a strong ferromagnet i.e. $n_{d\uparrow} = 5$ (filled majority band)

$m = n_{\uparrow} - n_{\downarrow} = 1.7$

EXCITATIONS AND ONE EL STATES



C. (110)

THE ONE ELECTRON STATES ϵ_k AS CALCULATED BY "BURDICK" ARE IN AGREEMENT WITH THE E. EXCITATIONS OBTAINED EXPERIMENTALLY BY ANGULAR RESOLVED PHOTOEMISSION (ARPES) (from Thiry et al 1979)

III.50.

IN NICKEL THE EXCITATIONS OBTAINED BY ARPES ARE STILL RELATIVELY WELL DEFINED BUT THEIR SPECTRUM (i.e ϵ_k) IS NARROWER THAN THE L.D.A ONE ELECTRON SPECTRUM: CORRELATIONS INTRODUCE QUANTITATIVE BUT NOT QUALITATIVE CHANGES ON THE SPECTRUM OF ONE EL. EXC.

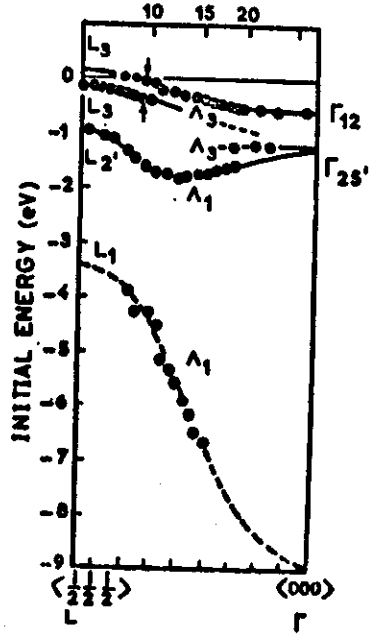


Fig. 2c : Angular photoemission of ferromagnetic nickel (from [3]). Two 'd' states observed for k near L (noted ↑↓) are identified to spin splitted states ($A_{3\uparrow}$, $A_{3\downarrow}$). The band width and the spin splitting are much smaller than the corresponding quantities deduced theoretically by band calculations. (See below)

ARPES SPECTRA

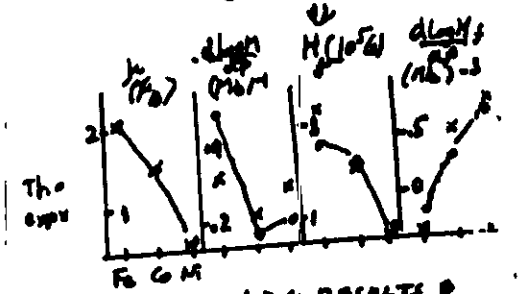
A SATELLITE (which is not predicted by one electron calcl) appears 6eV below the E_F and results from the correlated movement of 2 holes ⇒ THIS IS RELATED TO THE NARROWING OF OUR BAND

EXCITATIONS

The occupied width of Ni d bands W_{occ} is smaller exp'ly than theoretically

	W_{occ} exp	W_{occ} H_h	Δ exp	Δ H_h
Fe	3.1	3.5	1.5	1.5
Co	3.8(L_1)	4.7	0.9 1.2	1.55 1.2
COMPARE ⇒ Ni	3.4	4.7	(0.3L)	0.65

GROUND STATE PROP



LDA RESULTS ● exp ▲ " × " FOR THE MAGNETIZATION μ_s HYPERFINE FIELD H_{hf} $\frac{d\ln\mu_s}{dp}$, $\frac{d\ln H_{hf}}{dp}$

GOOD AGREEMENT FOR G.S PROPERTIES

from bcc (½) -13- OB

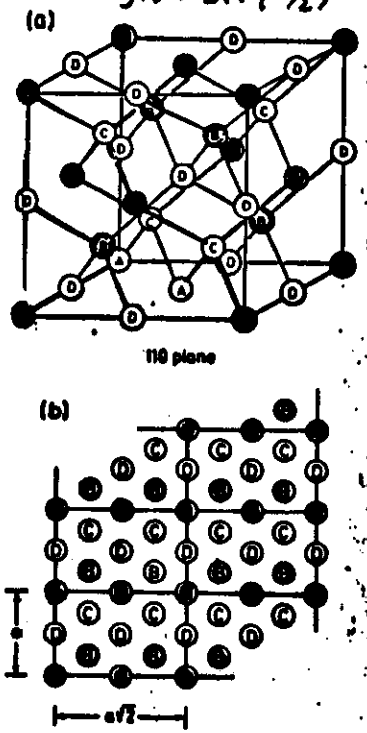


FIG. 1. (a) Face-centered-cubic structure with four basis atoms. The lattice constant is a. (b) (110) plane of the structure shown in Table II.

Ex	Str	A	B	C	D
Cs	bcc	Cs	Cs	Cs	Cs
CsCl	B_2	Cs	Cl	Cl	Cs
B_3Si_1	B_3	Si	Si	E	E
GaAs	BSb	Ga	As	E_1	E_2
NaTl	B_{32}	Na	Tl	Na	Tl
Cu_2MnAl	L_{21}	Cu	Mn	Al	Cu
NaCl	B1	Na	E	E	Cl
CaF	C1	Ca	F	F	E
MgLiSb	$C1_3$	Sb	Mg	Li	E
MgCuSb		Sb	Cu	E	Mg

SEMICONDUCTOR GaAs

good agreement for the equation of state even if the gap is uncorrect! (E.S. prop)

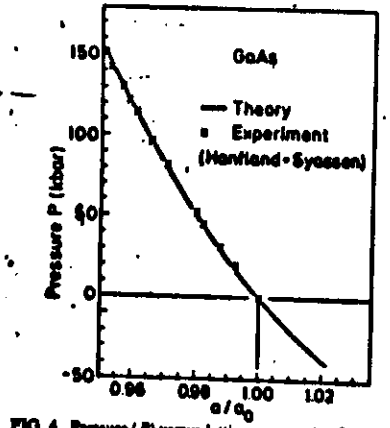
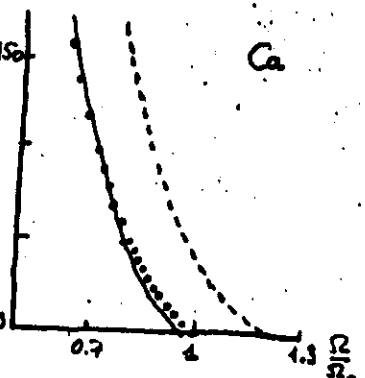


FIG. 4. Pressure (P) versus lattice constant (a) for GaAs calculated (solid line) from self-consistent relativistic LMTO band structures. The "empty spheres" are included (cf. Sec. III), and the Ga 3d core states are "relaxed." The crosses indicate experimental results by Hanfland and Syassen (Ref. 57). The equilibrium lattice constant is denoted a_0 (=5.654 Å).

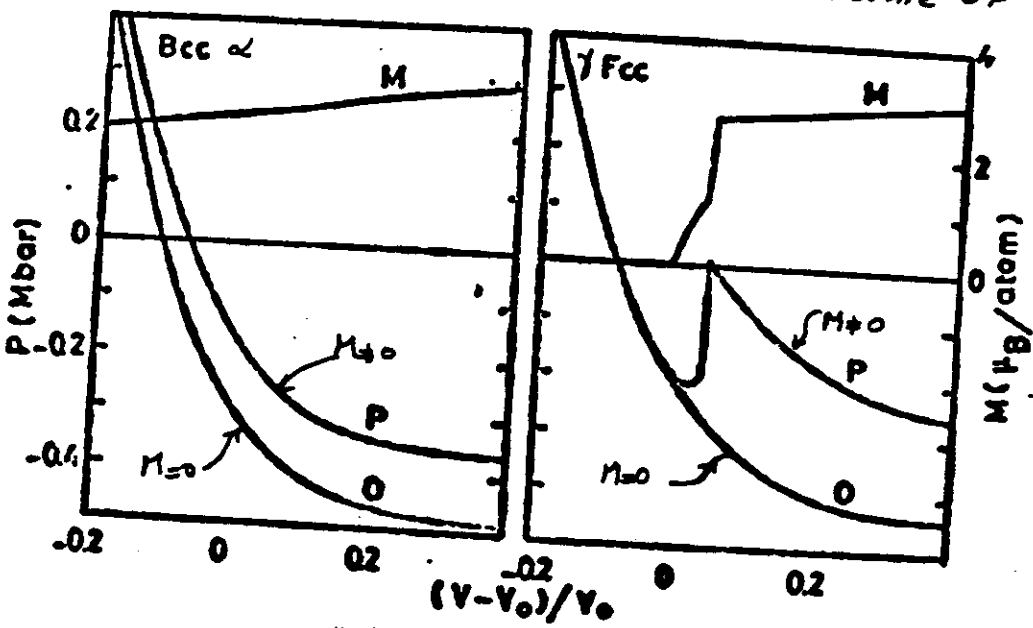
ALKALINE EARTH



The theoretical eq. of state is in agreement with the exp one for a pressure (P) in expansion taking into account of the sp-d hybridization (Generalized pseudopotential theory Moriarty 1983)

-15-

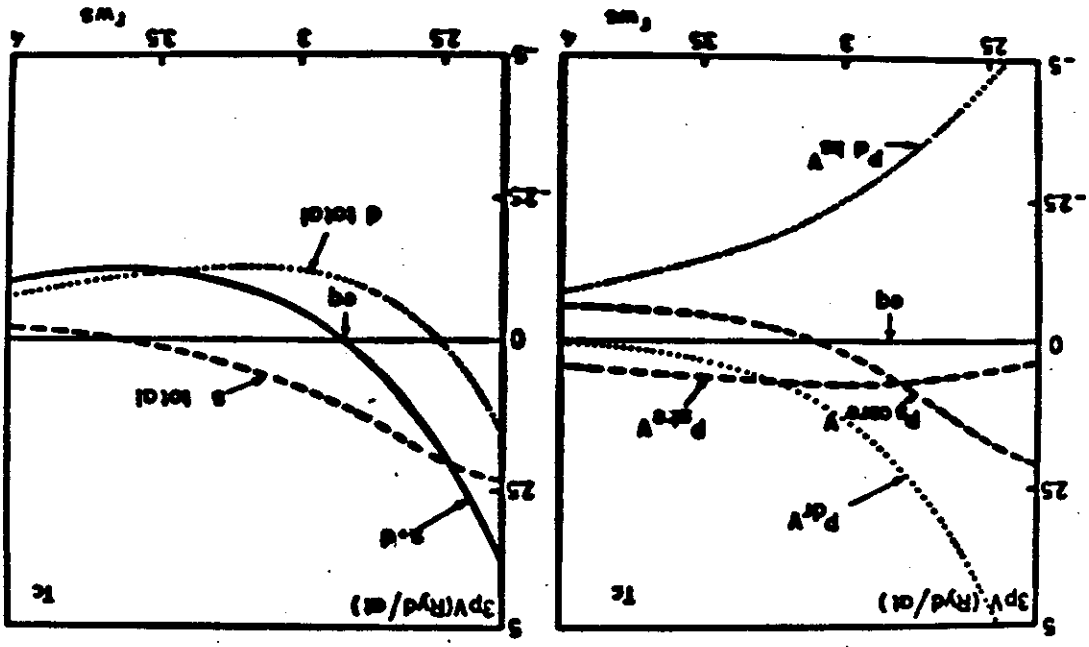
ROLE OF THE MAGNETISM (FERRO) ON THE EQUATION OF STATE OF Fe



← γ Fe has in that calc the eq state at $\beta = \alpha(1)$ with $M = 0$ and $M \neq 2\mu_B$ for (2) $E(2) - E(1) \simeq 8 MRL$

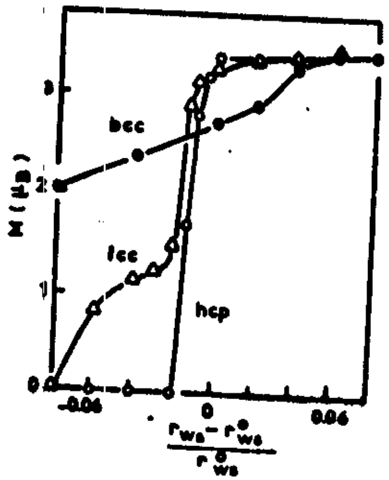
THE solution "0" is obtained when the constraint M=0. is imposed

-19-



TH. EQUATION OF STATE FOR A TM (TC)

THE CHANGE OF MAGN. MOMENTS WITH VOLUME (as calculated in the LDA) OR P.



4 APPROXIMATIONS FOR THE CALCULATION OF THE ONE ELECTRON STATES

① LDA

$$\begin{cases} h = -\frac{\hbar^2}{2m}\nabla^2 + v \\ v = v_{ext} + v_{coul} + v_{xc} \end{cases}$$

• $h\,\psi_\alpha = \epsilon_\alpha \psi_\alpha$, $n(r) = \sum_{occ} |\psi_\alpha|^2$ and $v_{coul}(n)$, $v_{xc}(n(r))$

② THE DISTRIBUTION OF ATOMS ON A GIVEN LATTICE IS KNOWN («conf»). USUALLY SPECIAL ASSUMPTIONS ARE DONE FOR THE SELF CONSISTENT CALCULATION OF ϵ_α ACCORDING TO THE CONSIDERED LATTICE AND AT. (use of the variat. meth.)

ⓐ WAVE FUNCTION

L. C. A. O.

CHOOSE ϕ^i_λ

$\psi_\alpha(r) = \sum_{\lambda i} A_{\lambda i}\, \phi^i_\lambda(r)$

$\phi^i_\lambda(r) = \phi^i(r - \lambda)$

λ = SITE , i = index for the orbitals of the considered set {i}.

{i} { SLATER FUNCTIONS, GAUSSIANS ...

AS LOCALIZED AS POSS.

2: they are not orthog.!

THE ENERGY LEVELS ARE GIVEN BY:

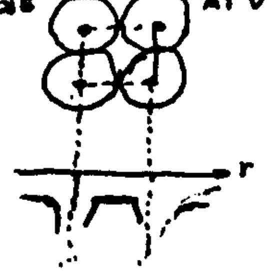
$\det | H^{ij}_{\lambda\mu} - \epsilon S^{ij}_{\lambda\mu} | = 0$

A SIMPLE SEC. EQ.

ⓑ POTENTIAL

MUFFIN TIN APPROX

CHOOSE "AT VOL"



V(r) (spherical approxim.) if r ∈ at sph.

C^{te} if r is in the int. reg.

VALID FOR COMPACT STRUCTURES

OPEN STRUCTURES ?

SURFACES ?

MOLECULES ?

Ex: KKR APW for perfect periodic systems.

IF WE ARE INTERESTED IN A LIMITED RANGE OF EN LINEARIZED METHODS ARE USED A.S.A.

L. MTO

LAPW

LOCALIZED ORBITALS CAN BE OBTAINED FROM LINEARIZED METH. ⇐

... CONSERVING PSEUDOPOTENTIALS

INTERCALATED GRAPHITE COMPOUNDS
- ANISOTROPY
- BONDING

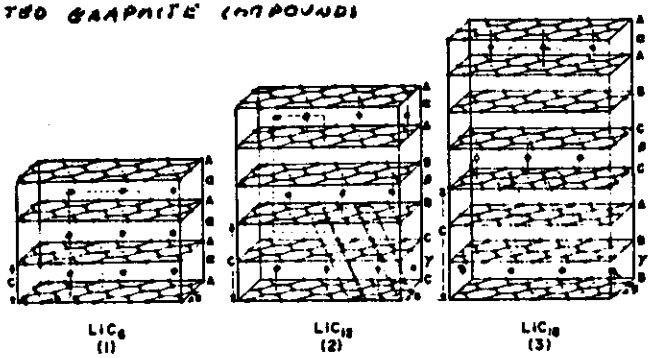


FIG. 1. Structures of Li-intercalated graphite compounds LiC_6 (stage 1), LiC_{12} (stage 2), and LiC_{18} (stage 3) assumed in present study. Carbon atoms are denoted by filled circles connected along nearest-neighbor bonds. Li atoms are denoted by unfilled circles. Primitive unit cells are indicated for each structure. Dashed rectangle in each structure denotes the plane used in contour plots shown in Figs. 2–7.

TABLE I. Lattice parameters for Li-intercalated graphite compounds.

LiC_6 (structure based on Ref. 9)

Primitive lattice vectors:

$\vec{T}_1 = a\sqrt{3}[(\sqrt{3}/2)\hat{x} + \frac{1}{2}\hat{y}]$,

$\vec{T}_2 = a\sqrt{3}[-(\sqrt{3}/2)\hat{x} + \frac{1}{2}\hat{y}]$,

$\vec{T}_3 = c_1\hat{z}$, $a = 2.485$ Å, $c_1 = 3.706$ Å

Atomic locations within unit cell:

C atoms: $\pm[\frac{1}{3}(\vec{T}_1+\vec{T}_2)+\frac{1}{3}\vec{T}_3]$

$\pm[\frac{1}{3}\vec{T}_1+\frac{1}{3}\vec{T}_3]$

$\pm[\frac{1}{3}\vec{T}_2+\frac{1}{3}\vec{T}_3]$

Li atom: 0

Symmetry directions:

$\Gamma \le k \le A$ $\vec{k} = x\vec{G}_3$ $0 \le x \le \frac{1}{2}$

$\Gamma \le k \le M$ $\vec{k} = x(\vec{G}_1 - \vec{G}_2)$ $0 \le x \le \frac{1}{2}$

$\Gamma \le k \le K$ $\vec{k} = x(\vec{G}_1 + \vec{G}_2)$ $0 \le x \le \frac{1}{2}$

LiC_{12} and LiC_{18} (assumed structures)

Primitive lattice vectors:

$\vec{T}_1 = a\sqrt{3}[(\sqrt{3}/2)\hat{x} + \frac{1}{2}\hat{y}]$, $\vec{T}_2 = a\sqrt{3}[-(\sqrt{3}/2)\hat{x} + \frac{1}{2}\hat{y}]$,

$\vec{T}_3 = (2a/\sqrt{3})\hat{y} + c_n\hat{z}$, $a = 2.485$ Å,

$c_2 = 7.056$ Å (LiC_{12}), $c_3 = 10.406$ Å (LiC_{18})

LiC_{12} and LiC_{18} (assumed structures continued)

Atomic locations within unit cells:

C atoms: $\pm\left|\left|\frac{1-2p_n}{3}\right|(\vec{T}_1+\vec{T}_2)+p_n\vec{T}_3\right|$

$\pm\left|\left|\frac{1-2p_n}{3}\right|\vec{T}_1 - \frac{2p_n}{3}\vec{T}_2 + p_n\vec{T}_3\right|$

$\pm\left|\frac{-2p_n}{3}\vec{T}_1 - \left|\frac{1+2p_n}{3}\right|\vec{T}_2 + p_n\vec{T}_3\right|$

$\pm\left|-\left|\frac{1+2p_n}{3}\right|(\vec{T}_1+\vec{T}_2)+p_n\vec{T}_3\right|$

$\pm\left|-\left|\frac{1+2p_n}{3}\right|\vec{T}_1 - \frac{2p_n}{3}\vec{T}_2 + p_n\vec{T}_3\right|$

$\pm\left|\frac{-2p_n}{3}\vec{T}_1 + \left|\frac{1-2p_n}{3}\right|\vec{T}_2 + p_n\vec{T}_3\right|$

$p_n = \frac{c_1}{2c_n}$ where $n = 2$ for LiC_{12} and 3 for LiC_{18}

Additional C atoms in LiC_{18}: $\pm[-\frac{1}{3}(\vec{T}_1+\vec{T}_2)+\frac{1}{3}\vec{T}_3]$

$\pm[-\frac{1}{3}\vec{T}_1+\frac{1}{3}\vec{T}_3]$

$\pm[+\frac{1}{3}\vec{T}_2+\frac{1}{3}\vec{T}_3]$

Li atom: 0

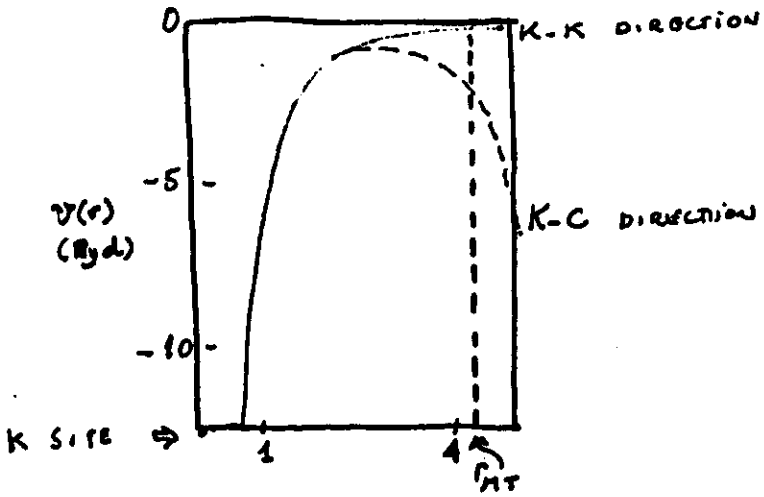
Symmetry directions:

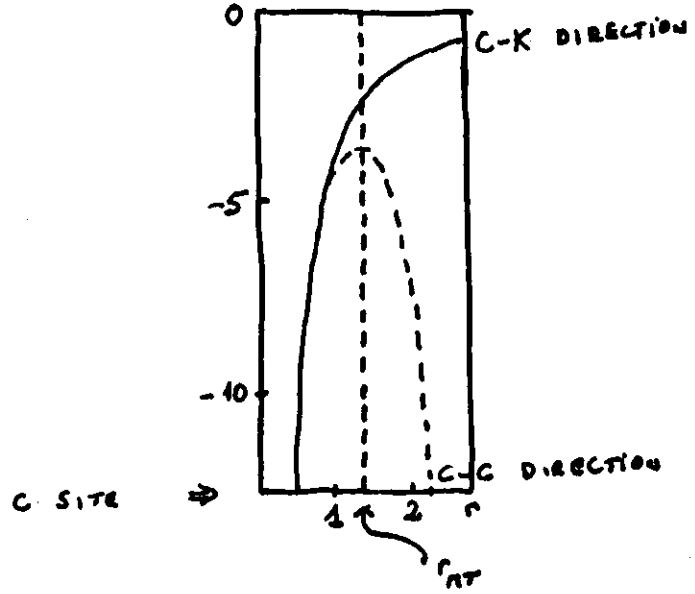
$\Gamma \le k \le A$ $\vec{k} = x\vec{G}_3$ $0 \le x \le \frac{1}{2}$

$\Gamma \le k \le M$ $\vec{k} = x(\vec{G}_1 - \vec{G}_2)$ $0 \le x \le \frac{1}{2}$

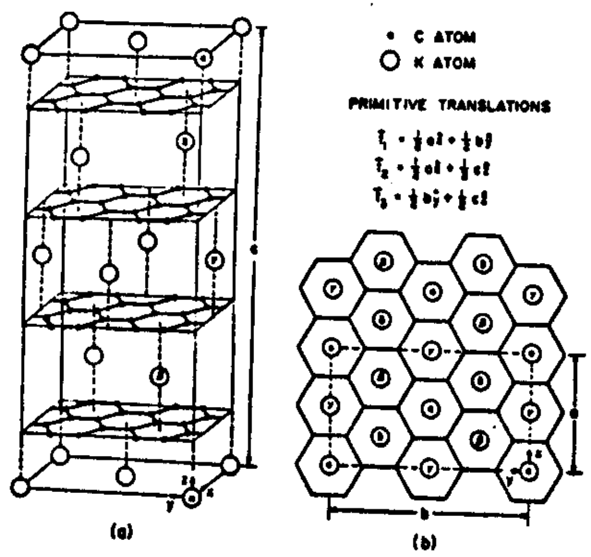
$\Gamma \le k \le K$ $\vec{k} = x(\vec{G}_1 + \vec{G}_2)$ $0 \le x \le \frac{1}{2}$

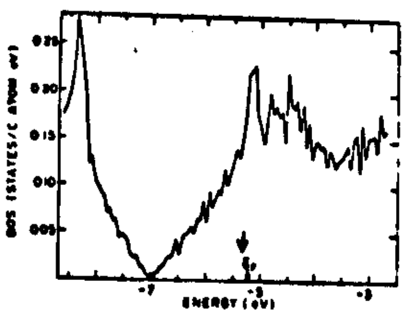
ANISOTROPIC COMPOUNDS
AND MT APPROXIMATION





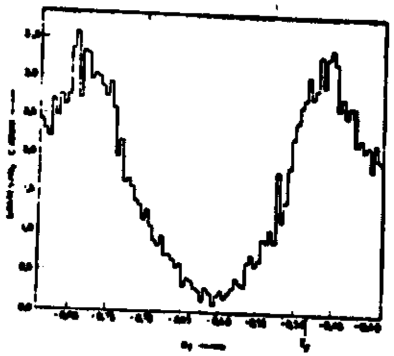
DONORS IN SATURATED C. RIGID BAND MODEL?





KC_8

di Vincenzo et al



LiC_6

Holwarth et al (1978)

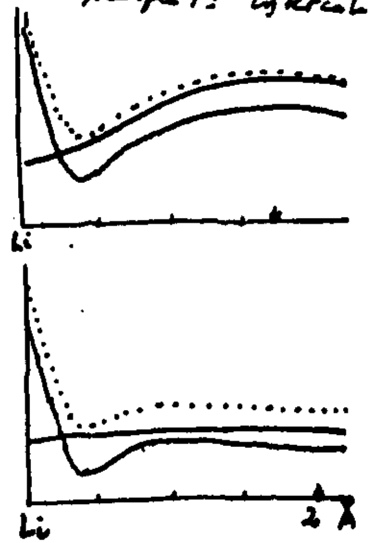
{AS FAR AS D.O.S ARE CONCERNED Li, K ACT AS A DONOR i.e. THE FERMI LEVEL WHICH WAS IN THE PSEUDO GAP OF GRAPHITE GOES UP TO ACCOMODATE THE SUPPLEMENTARY ELECTRON OF Li.

APPLY THE RIGID BAND MODEL IS VALID!

DEFINITION OF CHARGE TRANSFER IN A COMPOUND?

1. From the total charge of each Wigner cell ... and its ambiguity

Example 1: intercalate compounds LiC_6



— superimposed at densities from ionic Li^+ $2s^0$ C $2s^1 2p_{xy}^2 2p_z^{7/6}$

LiC_6 — band str

--- neutral Li $2s^1$ C $2s^1 2p_{xy}^2 2p_z^1$

[IN THIS CASE THE Li WAVE FUNCTION OVERLAPS STRONGLY WITH C SO THAT THE NOTION OF CT HAS NO MORE CLEAR MEANING.

center of C hexagon

Example 2 PdH — c.f. later (chapter III

Example 3 CsAu, CeO_2...

Example 4 CT in T.M. compounds

2. IN THE ATOMIC CELL AND IN T.M. THE CHARGE TRANSFER IS IN GENERAL SMALL EXCEPT IN SOME SPECIAL CASES WITH STRONG ELECTRONEGATIVITY & WHERE IT CAN ATTAIN ≈ 0.4, 0.5

Ex: YPd_3, VACANCY in FeAl □ ≈ 0.5

3. EXAMPLE OF THE DISTRIBUTION OF CHARGE IN $Cu_{0.75}Pd_{0.25}$

	non self consistent calc	self consistent
Q(Cu)	11.36 (MT 10.71)	11.05 (10.4)
Q(Pd)	9.93 (MT 9.17)	9.74 (9.1)
Q(intest)	0.65	0.75

THE SELF CONSISTENCY REDUCES THE CHARGE TRANSFER Cu IS QUASI NEUTRAL.

5 BAND STRUCTURE. METALS AND ALLOYS

FOR PERFECT METALS, THE POTENTIAL $V(\vec{r})$ IS PERIODIC AND THE ELECTRONIC STATES DEFINE ENERGY BANDS. FOR THE STUDY OF ALLOYS, TWO QUESTIONS APPEAR:

1- WHAT ARE THE NEW FEATURES INTRODUCED BY THE DISORDER IN AN ALLOY? ARE BANDS STILL WELL DEFINED?

2- ARE SUCH FEATURES DIFFERENT GOING FROM ONE HOST TO ANOTHER?

- CAN THE ENERGY BE CALCULATED IN AN UNIFIED WAY?

1 → FOR THE FIRST QUESTION, IT'S CONVENIENT TO STUDY SUCCESSIVELY TWO LIMITS:

SEE PR MARCH LECTURES ⇒ • LOW CONCENTRATION LIMIT (out of the scope of this course) DILUTE ALLOYS: STUDY OF THE SPATIAL DEPT ENERGY SPACES

• CONCENTRATED ALLOYS: " " " " WILL SHOW THE GENERAL FEATURES ASSOCIATED WITH DISORDER

2 → FOR THE EXPLICIT CALCULATION OF ENERGIES, UNFORTUNATELY... IT'S (up to now!) NECESSARY TO USE APPROXIMATIONS WHICH ARE DIFFERENT FOR EACH "CLASS" OF METALS. WE DEFINE ACCORDING TO THEIR ELECTRONIC STRUCTURE... AND TO THEIR PHYSICAL PROPERTIES. THESE APPROXIMATIONS WILL BE USEFUL TO UNDERSTAND PHYSICALLY THE RESULTS WE OBTAIN BY MORE PRECISE "AB INITIO" BAND STRUCTURE CALC.

CLASSIFICATION OF METALS

• NORMAL METALS

Those which are bonded by 'sp' electrons with 'd' or 'f' shells playing no significant role.

conduction electrons are nearly free

$\{ \epsilon_{\vec{k}}$ practically given by F.E model perturbed only near the Brillouin zone.

$\{ \psi_{\vec{k}}(\vec{r})$ practically constant in most of the volume but oscillates in the core region to be orthogonalized to the inner states.

• TRANSITION METALS

ATOMS ARE CHARACTERIZED BY

{ nd states localized (r_M 0.5 Å)

{ (n+1)s " EXTENDED AS VAL FUNCTIONS OF NORM. METALS

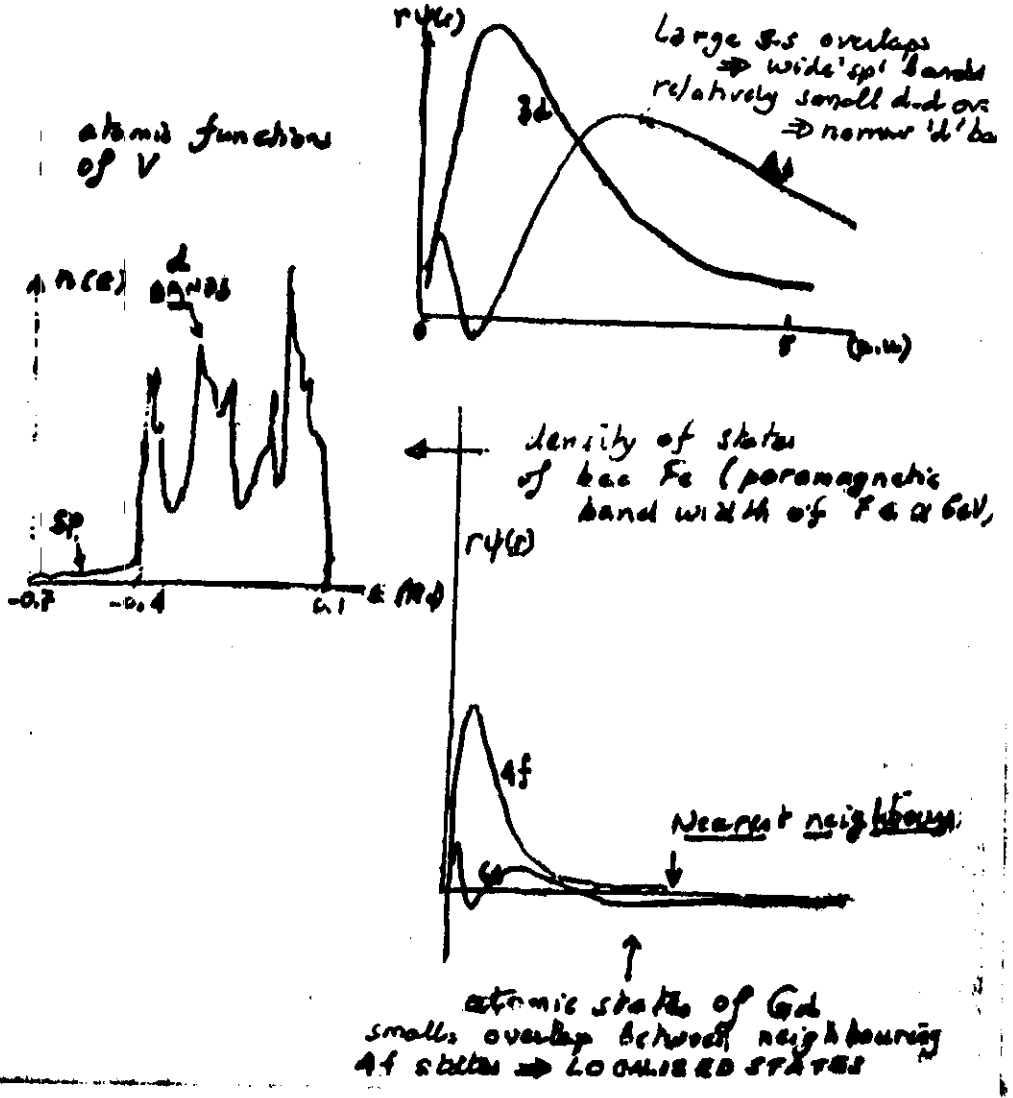
METALS ARE CHARACTERIZED BY

• NARROW nd BAND WIDTH (tight binding like)

• ... IN ALL BANDS

PERIODIC CHART OF ELEMENTS

														Li	Be		C
														Na	Mg	Al	Si	P
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm								



• RARE EARTH
ATOMIC STATE CHARACTERIZED BY
4f electrons localized as compared with 5d.6s
METALS CHARACTERIZED BY
{f: Localized states
{and bands similar to transitory elements (5d-6

• ACTINIDES
INTERMEDIATE SITUATION BETWEEN TRANSITION METALS AND R.E
ALONG THE ACTINIDE SERIE THE 5f SHELLS BE COME MORE CONTRACTED WHEN THE ACTINIDE IS HEAVIER
• AT THE BEGINNING OF THE SERIES 5f HAVE EXTENSIONS (relative to the nearest neighbour distance b) COMPARABLE TO d FUNCTIONS OF TRANSITION METALS; 5f, 6d HYBRIDIZED BANDS
• IN THE SECOND PART (after Cm) THEY ARE LOCALIZED AS 4f STATES OF RARE EARTHS

TWO EXTREME MODELS FOR THE BAND STRUCT

$r_0 \gg b$ FREE ELECTRON
↓
NEARLY FREE ELECTRON — 1st order perturbation theory valid for normal metals (small parameter $\frac{V(K)}{\varepsilon_F}$)

$V(K) = \frac{1}{\Omega}\int V(r) e^{-iKr}\,dr$

Ω atomic volume, K reciprocal lattice vectors
provided we replace potential by pseudopotential (Heading (cf Hafner)

↑

$r_0 < b$ TIGHT BINDING APPROX (LCAO) — • the properties of transition metals are roughly determined by d electrons which are well represented by LCAO (qualitatively)

$r_0 \ll b$ ATOMIC LIMIT

r_0 = atomic radius for valence electrons
b = distance between two nearest neighbours