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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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ELECTRONIC STATES IN DISORDERED SYSTEMS

(Part I)

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ELECTRONIC STATES IN DISORDERED SYSTEMS

—•—

SRO
Local order → "Electronic states" → Electr. φ. propr → Transport / optical / magn etic...

Electronic struct → local order stability

for

- metallic alloys + simple ½ cond (Si)
- amorphous metals + am. ½ cond

ELECTRONIC STATES IN DISORDERED SYSTEMS

Introduction

—•—

1 Disordered states

a) classification

- "weakly" disordered — localized part weak
- "strongly" disordered — extended large

⇓

CONV^T EXPANSION FROM THE PERIODIC CRYSTAL

b) substit.' - disorder alloys → subst / interst.

∃ PERIODIC EMPTY LATTICE →

c) topological disorder

geometric with local constraints → steric / covalent ...

expansion from the gas ??

e) Examples: - liquids
- metallic amorphous (chem + top...) Si...
- ½ cond^{rs}

f) quenched ... disorder

2 Local order (notation)

site $\underline{\lambda}$

a) binary alloy $A_c B_{1-c}$

- OCCUPATION NUMBERS $\{p_{\underline{\lambda}}\}$ ⇔ CONFIGURATION

$$p_{\underline{\lambda}} = \begin{cases} 1 & \text{if occ by } A \\ 0 & \text{otherwise} \end{cases}$$

- CORRELATION FUNCTIONS.

$\langle p_{\underline{\lambda}} \rangle = c$ Concentration

$\lambda \neq \mu$ $\langle p_{\underline{\lambda}} p_{\underline{\mu}} \rangle = \langle p_{\underline{\lambda}} \rangle \langle p_{\underline{\mu}} \rangle = s(\lambda - \mu)$ → S.R.O. param. RX, Neutrons...

$\lambda \neq \mu \neq \rho \neq \lambda$ $\langle p_{\underline{\lambda}} p_{\underline{\mu}} p_{\underline{\rho}} \rangle = \dots$

- LOCAL ORDER

distribution of numbers, distances, angles → EXAFS

symmetry → NMR

b) amorphous systems

$g^{i_1 \dots i_s}_{\underline{\lambda}_1 \dots \underline{\lambda}_s}$

3 METHOD

1 • ONE ELECTRON THEORY.

2 • A SIMPLE MODEL FOR THE STUDY OF ELECTRONIC STATES OF METALS AND SEMICONDUCTORS: THE TIGHT BINDING APP.

3 • ELECTRONIC STATES IN DISORDERED SYST.
- 1 QUALITATIVE DISCUSSION
- 2 GENERAL RESULTS (T.B.A.)

4 APPLICATION TO
- ALLOYS
- AMORPHOUS SYSTEMS ↗ METALS ↘ 1/2 CONDUCTORS

I

ELECTRONIC STRUCTURE . BAND STRUCTURE

1. FOR A GIVEN IONIC CONFIGURATION WE HAVE TO CALCULATE THE ELECTRONIC ENERGY (neglect at this stage of the electron phonon interaction - adiabatic appr.):

$$U = U_{ion} + U_{el}$$

• LET US INTRODUCE THE "BEST" (AS POSSIBLE!) APPROXIMATION TO THE ELECTRONIC ENERGY BY A ONE ELECTRON PICTURE ("BAND THEORY")

IN SUCH AN APPROXIMATION, EACH ELECTRON MOVES INDEPENDENTLY OF THE OTHERS (UNCORRELATED MOTION) BUT IN THE:
(1) AVERAGE POTENTIAL OF THE OTHER ELECTRONS
(2) IONIC POTENTIAL $V_{ion}(\underline{r})$

$$\begin{cases} \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\underline{r})\right]\psi_\alpha(\underline{r}) = \epsilon_\alpha \psi_\alpha(\underline{r}) \\ V(\underline{r}) = V_{ion}(\underline{r}) + V_{el}(\underline{r}) \end{cases}$$

$V_{el}(\underline{r})$ occurs from the coulomb interaction ($V_c(\underline{r})$) and from the exchange-correlation correction ($V_{xc}(\underline{r})$)

$$\begin{cases} V_{el}(\underline{r}) = V_c(\underline{r}) + V_{xc}(\underline{r}) \\ V_c(\underline{r}) = \int \frac{n(\underline{r}')\,d\underline{r}'}{|\underline{r}-\underline{r}'|} \end{cases}$$

$n(\underline{r})$ is the number of electrons per unit volume

$$n(\underline{r}) = \sum' |\psi_\alpha(\underline{r})|^2 \quad (' \text{ for occupied states})$$

2. KOHN SHAM THEOREM: IT CAN BE SHOWN THAT THE ENERGY U_{el} IS EXACTLY GIVEN BY:

$$U = \langle T\rangle + \langle V_{ion}\rangle + \langle V_c\rangle + E_{xc}(n(\underline{r}))$$

WHERE:
1. T is the kinetic energy

$$\langle T\rangle = \sum' \langle \psi_\alpha | -\frac{\hbar^2}{2m}\nabla^2 | \psi_\alpha\rangle$$

2. V_{ion}, the INTERACTION BETWEEN IONS AND ELECTRONS

$$\langle V_{ion}\rangle = \int n(\underline{r})\, V_{ion}(\underline{r})\, d\underline{r}$$

3. V_c the coulomb energy

$$\langle V_c\rangle = \int \frac{n(\underline{r})\, n(\underline{r}')}{|\underline{r}-\underline{r}'|}\, d\underline{r}\, d\underline{r}'$$

4. $E_{xc}(n)$ IS THE "UNKNOWN" (!!) EXCHANGE-CORRELATION TERM WHICH DEPENDS ONLY ON $n(\underline{r})$

and ϵ_α BEING GIVEN BY:

$$V_{xc}(\underline{r}) = \frac{\delta E_{xc}(n(\underline{r}))}{\delta n(\underline{r})}$$

ϵ_α CAN BE CONSIDERED APPROXIMATELY AS ... TATION ENERGIES

---

3 THIS THEOREM IS USELESS IF WE DON'T USE APPROXIMATE (KNOWN) VALUES FOR $V_{xc}(\underline{r})$ (or E_{xc}). THE MOST POPULAR APPROXIMATION (not the best) IS THE Xα APPROXIMATION WHICH RESULTS FROM 2 APPR.:

(a) $E^{xc}(n(\underline{r})) \cong \int n(\underline{r})\, \epsilon_{xc}(n(\underline{r}))\, d\underline{r}$ LOCAL A...

WHERE $\epsilon_{xc}(\underline{r})$ is the exchange correlation energy per electron of an homogeneous gas with the same density.

(b) $V^{xc}(\underline{r}) = -3e^2\alpha\left(\frac{3n(\underline{r})}{4\pi}\right)^{1/3}$ (Xα APP)

α is A PARAMETER ($\alpha \sim 1, \frac{2}{3}$) WHICH WILL BE FITTED USING SOME PHYSICAL PROPERTY.
$\alpha = 1$ (Slater) $V^{xc}(\underline{r})$ is the average exchange potential of a free electron gas
$\alpha = \frac{2}{3}$ (Kohn, Gaspard)

USING SUCH APPROXIMATIONS U_{el} is only approximately calculated:

$$U_{el} = U_{el}^0 + U_{el}^1$$

THE LAST TERM RESULTS FROM 'RESIDUAL' EXCHANGE AND CORRELATION CONTRIBUTIONS WHICH CANNOT BE DESCRIBED IN SUCH A SIMPLE SCHEME: SPIN FLUCTUATIONS (MAGNETIC) TERMS ... CONTRIBUTIONS, CHARGE FLUCTUATIONS

Ex: IN A MAGNETIC SYSTEM (Fe IMPORTANT!) THE GROUND STATE ($T = 0K$) CAN BE WELL DESCRIBED BY SUCH SELF CONSISTENT CALCULATIONS (the value of magnetic moment, the elastic constant ...) BUT THE EXCITATIONS (COLLECTIVE) WHICH ARE IMPORTANT FOR THE THERMODYNAMIC PROPERTIES (EVEN FOR $T > T_c$, CURIE TEMPERATURE!) ARE NOT INCLUDED IN U_{el}^0

U_{el}^0 includes magnetic contribution ... but not the "spin fluctuation" term!

Note: (1) When U_{el}^0 is evaluated in the HARTREE FOCK theory, i.e. when we take only account exchange, by definition $U_{el}^1 = U_c$ is the correlation energy.
(2) However, usually, the band structure calculations are done in a LOCAL APPROXIMATION such as Xα

4 BAND STRUCTURE - METALS AND ALLOYS

FOR PERFECT METALS, THE POTENTIAL $V(\underline{r})$ 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:
- LOW CONCENTRATION LIMIT: DILUTE ALLOYS: STUDY OF THE SPATIAL DEPT. " " " ENERGY SPECTR.
- CONCENTRATED ALLOYS: " " " " "
- WILL SHOW THE GENERAL FEATURES ASSOCIATED WITH DISORDER!

2 → FOR THE EXPLICIT CALCULATION OF ENERGIES, ONE TROUBLE... 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 WHICH PHYSICAL PROPERTIES

CLASSIFICATION OF METALS

- NORMAL METALS
  those which are bonded by 'sp' electrons with 'd' or 'f' shells playing no significant rôle.
  conduction electrons are nearly free
  { $\epsilon_{\underline{k}}$ practically given by F.E model perturbed only near the Brillouin zone.
  { $\psi_{\underline{k}}(\underline{r})$ 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
  { n d states localized ($r_n \sim 0.5$ Å)
  { (n+1)s " EXTENDED AS VAL FUNCTIONS OF NORM. METALS
  METALS ARE CHARACTERIZED BY
  . NARROW 'd' BAND WIDTH (tight binding like)
  . AND WIDE 'sp' : bands HYBRIDIZED!
- 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-6s)
- 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; ES. 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

FREE ELECTRON
↓
NEARLY FREE ELECTRON — 1st order perturbation theory valid for normal metals (small parameter $\frac{V(\underline{k})}{\epsilon_F}$)

$V(\underline{k}) = \frac{1}{\Omega}\int V(\underline{r}) e^{-i\underline{k}\underline{r}}\, d\underline{r}$

Ω atomic volume, $\underline{k}$ reciprocal lattice vectors

provided we replace potential by pseudopotentials (to define) (cf Hafner)

↑

$r_0 > b$

$r_0 < b$ 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

IT'S NOW POSSIBLE TO COMPUTE SELF CONSISTENTLY THE BAND STRUCTURE OF ALL METALS BY A NUMBER OF METHODS (K.K.R., SCLCAO ...) BUT THE PREVIOUS MODELS (NFE, T.B.A) ALLOW TO DISCUSS THE PHYSICS IN A MUCH SIMPLER (PEDAGOGICAL) WAY.

NFE → Hafner's lectures

IN THE FOLLOWING WE WILL USE THE T.B.A (mostly) FOR THE CALCULATION OF THE CORRESPONDING "PARAMETERS" (energy levels, overlap and transfer integrals) SEE FOR EXAMPLE "..." PAPER BY BULLETT (Vol 35 Solid State Physics).

II THE TIGHT BINDING APPROXIMATION

II.1. General

(a) $\{\phi_{i\underline{l}}\}$ $\quad \langle \phi_{i\underline{l}} | \phi_{j\underline{m}} \rangle = S^{ij}_{\underline{l}-\underline{m}} \simeq \delta^{ij}\delta_{\underline{l}\underline{m}}$ (restriction)

$\underline{l}$ $(1, \dots N_a)$

i $(1, \dots s)$

$h \leftrightarrow \begin{cases} \epsilon_i(\underline{l}) = \langle i\underline{l}|h|i\underline{l}\rangle & i=j \\ \beta^{ij}(\underline{l},\underline{m}) = \langle i\underline{l}|h|j\underline{m}\rangle & \underline{l}\neq\underline{m} \end{cases}$

(b) $\begin{cases} h\psi = \epsilon\psi \\ \psi = \sum A_{i\underline{l}}(\underline{k})\,\phi_{i\underline{l}}(\underline{r}); \end{cases}$ "if perfect crystal (Bloch)" $\Rightarrow A_{i\underline{l}} = \frac{1}{\sqrt{N_a}} e^{i\underline{k}\cdot\underline{a}_{\underline{l}}}$

$\sum_{j\underline{m}} \langle i\underline{l}|h|j\underline{m}\rangle A_{j\underline{m}}(\underline{k}) = \epsilon \sum_{j\underline{m}} \langle i\underline{l}|j\underline{m}\rangle A_{j\underline{m}}$

$\| \langle i\underline{l}|h|j\underline{m}\rangle - \epsilon \langle i\underline{l}|j\underline{m}\rangle \| = 0$

(c) Example 1

non degenerate orbital - perfect crystal, $\underline{\delta}=?$

$\psi(\underline{r}) = \frac{1}{\sqrt{N_a}} \sum_{\underline{l}} e^{i\underline{k}\cdot\underline{l}} \phi_{\underline{l}}(\underline{r})$

$\epsilon_{\underline{k}} = \epsilon_0 + \sum_{\underline{m}(\neq\underline{l})} \beta(\underline{l}-\underline{m})\, e^{i\underline{k}\cdot(\underline{l}-\underline{m})}$

→ simple cubic (β non zero but n.n only)

$\epsilon_{\underline{k}} = \epsilon_0 + 2\beta(\cos k_x a + \cos k_y a + \cos k_z a)$

bonding $\quad -6|\beta| \le \epsilon_{\underline{k}} \le +6|\beta|$ $\quad$ anti-bonding

$\underline{k}=\underline{0}$ $\qquad$ $(\underline{k} = \frac{\pi}{a}(1,1,1))$

→ fcc lattice (β non zero for nn only)

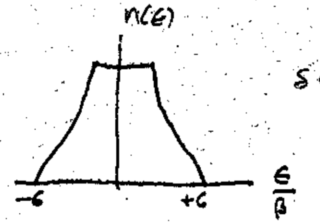
$\epsilon_{\underline{k}} = -4\beta\left(\cos\frac{k_x a}{2}\cos\frac{k_y a}{2} + \cos\frac{k_y a}{2}\cos\frac{k_z a}{2} + \cos\frac{k_x a}{2}\cos\frac{k_z a}{2}\right)$

bonding → $-12\beta \le \epsilon_{\underline{k}} \le 4\beta < 12\beta$

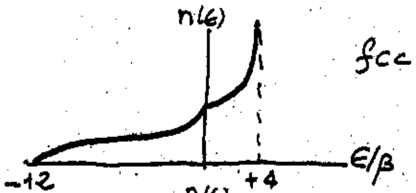
THE "TOTALLY" ANTIBONDING STATE DOES NOT EXIST IN f.c.c. LATTICES (see later / special $(\frac{2\pi}{a}, \frac{\pi}{a}, 0)$ ← frustration!

∃ Triangles △

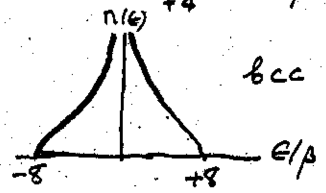
{ Structure,
ϵ_0
W band width



sc



fcc



bcc

$|\epsilon - \epsilon_0| \leq Z|\beta|$ ← Hadamard Gershgorin criterion (later) | perfect crystal |

Z coordination number

(d) Example 2 T.B 'd' bands of T.M.

$\phi_i(r)$ $i = 1, 2, 3$ $\begin{cases} \frac{xy}{r^2} f(r) \\ \frac{yz}{r^2} f(r) \\ \frac{zx}{r^2} f(r) \end{cases}$ $\begin{cases} \frac{x^2-y^2}{r^2} f(r) \\ \frac{3z^2-r^2}{r^2} f(r) \end{cases}$

Γ'_{25} Γ_{12}

cubic symmetry $\epsilon_i(\lambda) = \epsilon_i$ $\epsilon(\Gamma'_{25}) \simeq \epsilon(\Gamma_{12})$

$\beta_{ij}(\lambda - \mu) \Rightarrow dd\sigma, dd\pi, dd\delta$

ddσ



ddδ

ddπ


$\left|\frac{dd\sigma}{dd\pi}\right| \sim 2$ $dd\sigma \simeq 0.5\,eV$ (Ni)

(e) Example 3 SEMI CONDUCTOR BAND STRUCTURE

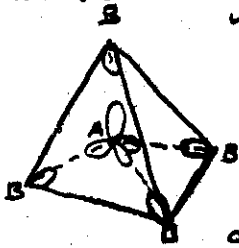
1 – sp^3 orbitals and tetracoordinated semicond^{rs}

orbitals on λ pointing in the (111), (1$\bar{1}\bar{1}$), ($\bar{1}$1$\bar{1}$), ($\bar{1}\bar{1}$1) direct

i =

$$|\lambda i\rangle = \begin{cases} (111) \rightarrow \frac{1}{2}\left(|\lambda s\rangle + |\lambda p_x\rangle + |\lambda p_y\rangle + |\lambda p_z\rangle\right) \\ (1\bar{1}\bar{1}) \rightarrow \text{"}\left(\text{"} + \text{"} - \text{"} - \text{"}\right) \\ (\bar{1}1\bar{1}) \rightarrow \text{"}\left(\text{"} - \text{"} + \text{"} - \text{"}\right) \\ (\bar{1}\bar{1}1) \rightarrow \text{"}\left(\text{"} - \text{"} - \text{"} + \text{"}\right) \end{cases}$$

This new basis set allows to get directly the most important transfer integrals β.



2 – energy and transfer integrals

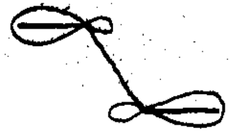
$$\begin{cases} \langle \lambda j|h|\lambda j\rangle = \frac{\epsilon_s + 3\epsilon_p}{4} = \epsilon_0 = 0 & \text{(choice of the origin)} \\ \langle \lambda j|h|\lambda j'\rangle = \frac{\epsilon_s - \epsilon_p}{4} = \Delta < 0 & j' \neq j \end{cases}$$


Δ


β

$\beta = \frac{1}{4}\left(\beta_{ss} + 2\sqrt{3}\beta_{s\sigma} + 3\beta_{\sigma\sigma}\right)$


β_ϵ


β_t


β'

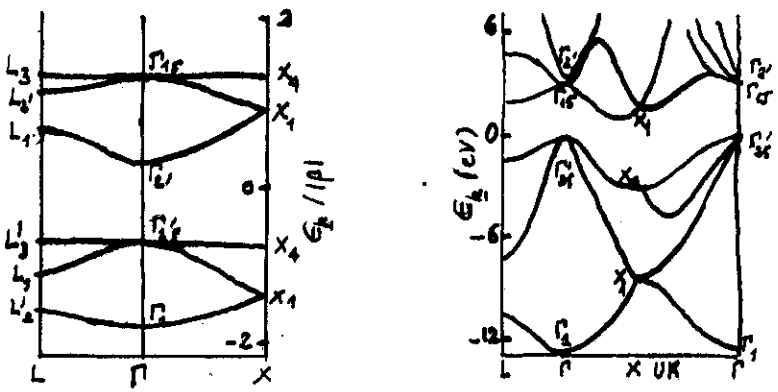

γ

(Si) $\beta = -3.6\,eV$ $\Delta = -1.47\,eV$ $\beta' = -.545\,eV$

$\beta_\epsilon = -.27\,eV$ $\beta_t = .27\,eV$

TWO METHODS FOR DET^{N} OF ϵ_j ↗ RECIPROCAL SPACE $\det|\underline{\underline{h}}(k) - \epsilon\,\underline{\underline{S}}(k)| = 0$
↘ REAL SPACE

Direct band structure calculations



(a) (b) Si

the $\Delta = -\frac{1}{4}$, $\beta = -1$, others β, γ are zero
T.B.A

Chadi Phys Rev B.16 3572 (1977)

Leman Friedel J. Appl Phys 33, 281 (1962)
Weaire Thorpe Phys Rev B 4 2508 (1971).

Comparison of the T.B band structure when only Δ and β are non zero with the Si band structure

Spectrum bounds (chap 3)

These bounds can be obtained directly (see next section). They can be also deduced from general theorems (mini-max theorem, see later) when β, Δ (only) are $\neq 0$.

$|\beta| > |\Delta| >$ other transfer integrals $\Rightarrow$ several approx.

(a) molecular model $\quad \epsilon = \pm\beta + \epsilon_0$ (β only is non zero)

(b) β and Δ only are non zero (see below)

§ Leman Friedel – Thorpe – Weaire theorem (homopolar a.t) C, Si, Ge

Notation $|ij>$

$$|\psi> = \sum a_{ij} |ij> \qquad (\beta, \Delta \text{ non zero})$$

$$\begin{cases} <ij| \quad \Delta \sum_{j' \neq j} a_{ij'} + \beta a_{ji} = E a_{ij} \quad (1) \\ <ji| \quad \Delta \sum_{i' \neq i} a_{ji'} + \beta a_{ij} = E a_{ji} \quad (1') \end{cases}$$

$$S_i = \sum_j a_{ij} \qquad S_j = \sum_{i'} a_{ji'}$$

S_i ? a_{ji}

$$\begin{cases} (E+\Delta) a_{ij} = \Delta S_i + \beta a_{ji} \\ (E+\Delta) a_{ji} = \Delta S_j + \beta a_{ij} \end{cases} \quad a_{ij}$$

$$\begin{cases} \sum_j \{(E+\Delta)^2 - \beta^2\} a_{ij} = \Delta(E+\Delta) S_i + \beta\Delta S_j \\ \sum_i \{(E+\Delta)^2 - \beta^2\} a_{ji} = \Delta(E+\Delta) S_j + \beta\Delta S_j \end{cases}$$

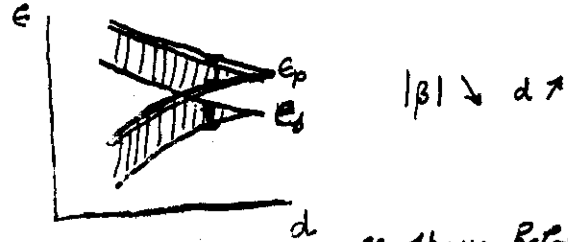
$$\epsilon \left(\frac{(E-\Delta)^2 - (\beta^2 + 4\Delta^2)}{\beta\Delta} \right) S_i = \sum_j S_j \Rightarrow \begin{cases} S \neq 0 \\ S = 0 \end{cases}$$

(a) $S \neq 0$

band structure for a T.B. band issued from non deg TB orbitals with

$$\beta = 1 \qquad \epsilon = \frac{(E-\Delta)^2 - \beta^2 + 4\Delta^2}{4\beta\Delta}$$

$-4 \leq \epsilon \leq +4 \Rightarrow$ hence the following spectrum:



as shown below

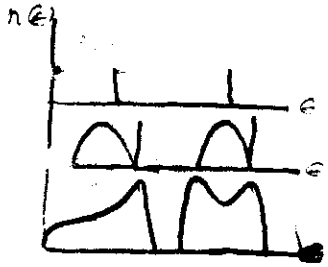
$((\epsilon-\epsilon_d)(\epsilon-\epsilon_p)-\beta^2)(\epsilon-\epsilon_p)\leq 0 \qquad (\epsilon_d=3\Delta,\ \epsilon_p=-\Delta)$

$\frac{\beta}{\Delta}\leq 2$ $\begin{cases}\epsilon_d+\beta\leq\epsilon\leq\epsilon_d-\beta\\ \epsilon_p+\beta\leq\epsilon\leq\epsilon_p-\beta\end{cases}$ $\qquad$ $\frac{\beta}{\Delta}\geq 2$ $\begin{cases}\epsilon_d+\beta\leq\epsilon\leq\epsilon_p+\beta\\ \epsilon_d-\beta\leq\epsilon\leq\epsilon_p-\beta\end{cases}$

$\epsilon_d+\beta$ $\epsilon_d+\beta$ $\epsilon_p+\beta$ $\epsilon_p-\beta$ $\qquad$ $\epsilon_d+\beta$ $\epsilon_p+\beta$ $\epsilon_d-\beta$ $\epsilon_p-\beta$

$\underline{\Delta=0}$ $\begin{cases}\epsilon=-\Delta\pm\beta\\ =\epsilon_p\pm\beta\end{cases}$ 2 flat "p" bands

(Si)



no Δ model $\beta\neq 0$, $\Delta=0$

$\beta,\Delta\neq 0$

realistic band structure

The previous result is equally valid for a "perfect" amorphous covalent N_2 and N if we neglect flat Δ,β

perfect $\Leftrightarrow$ each atom has still a ~~perfect~~ local tetrahedral environment (CRN)

They can be extended to various situations as shortly below

4 Extension of the Lemon Friedel Thorpe Weaire to heteropolar lattice $A^N B^{8-N}$

Two sublattices A, B

Two hybrid orbitals levels ϵ_A, ϵ_B

$\psi=\sum_{ij} a_{ij}|ij\rangle+\sum_{ij} b_{ij}|ij\rangle$

a_{ij} $\begin{cases}\epsilon\, a_{ij}=\epsilon_A a_{ij}+\Delta_A\sum_{j'\neq j} a_{ij'}+\beta\, b_{ij}\\ \epsilon\, b_{ij}=\epsilon_B b_{ij}+\Delta_B\sum_{i'\neq i} b_{i'j}+\beta\, a_{ij}\end{cases}$ $\uparrow b_{ij}$

$\Downarrow$

Σ_j' $\begin{cases}f(\epsilon)\, a_{ij}=\Delta_A(\epsilon-\epsilon_B+\Delta_B)S_i^A+\beta\Delta_B S_j^B\\ \Sigma_i' \quad f(\epsilon)\, b_{ij}=\Delta_B(\epsilon-\epsilon_A+\Delta_A)S_j^B+\beta\Delta_A S_i^A\end{cases}$

$f(\epsilon)=(\epsilon-\epsilon_A+\Delta_A)(\epsilon-\epsilon_B+\Delta_B)-\beta^2$

(a) pure "p" flat band

$S_i^A=0=S_j^B$ $\Rightarrow$ $a_{ij}\neq 0$ $b_{ij}\neq 0$

$(\epsilon-\epsilon_A+\Delta_A)(\epsilon-\epsilon_B+\Delta_B)-\beta^2=0$

$\epsilon_A-\Delta_A=\epsilon_p^A$

$\epsilon=\frac{\epsilon_p^A+\epsilon_p^B}{2}+\frac{1}{2}\left((\epsilon_p^A-\epsilon_p^B)^2+4\beta^2\right)^{1/2}$

(b) broad 'sp' band

Σ_j', Σ_i' $\Rightarrow$ $\phi_A S_i^A=\sum_j S_j^B$

$\phi_B S_j^B=\sum_i S_i^A$

$i=A,B$ $\quad$ $\bar{i}=\bar{B},\bar{A}$

$\phi_i=\dfrac{(\epsilon-\epsilon_i+\Delta_i)(\epsilon-\epsilon_{\bar{i}}+\Delta_{\bar{i}})-\beta^2-4\Delta_i(\epsilon-\epsilon_{\bar{i}}+\Delta_{\bar{i}})}{\beta\Delta_{\bar{i}}}$

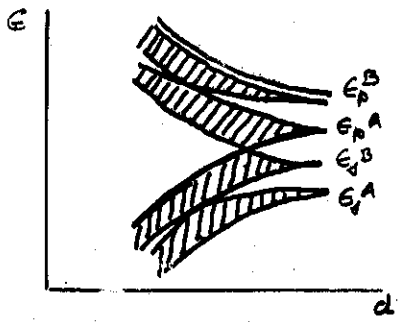
$\Rightarrow(\phi_a\phi_b-4)S_i^A=\sum_j S_j^A$ fcc lattice

$\Rightarrow 4\leq(\phi_a\phi_b-4)\leq 12$ $\Leftrightarrow 0\leq\phi_a\phi_b\leq 16$

generalized-S of the previous relation (homop)

new gaps

$\Rightarrow$ see fig below



5 Generalizations

– extension to tetraedral 1/2 condrs AX_2 (SiO_2, SiS_2 ...)
ABX_4 ($AlPO_4$)
....

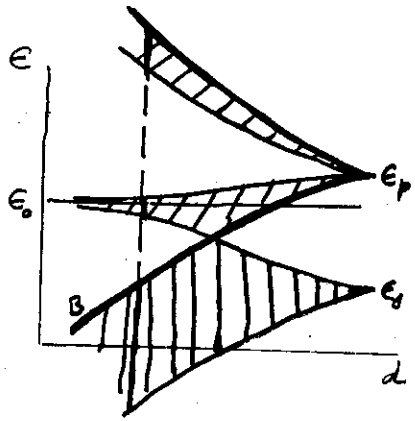
– extension to sp^n $n=2$ $d=1$ ——— 2σ 4π ⅄ hexagonal layer
$n=3$ $d=2$

– extension to incomplete octets (broken σ Bonds)

corrugated layer 3 (sp^3)

zigzag chain 2 (sp^3)

etc...



Qualitatively:

$\Delta = 0$: broken bond $\Leftrightarrow$ $\epsilon = 0$ ($\beta = 0$, $\sigma^*(1)$ at 0)

1 broken (sp^3) bond ⇓
one band in the middle of the gap!

$\Delta \neq 0$ ⇒ band of broken bonds

II 2 LOCAL ELECTRONIC STRUCTURE AND RECURSION (MOMENTS) METH.

ⓐ density of states, local density of states — density of states / at

→ • $\begin{cases} n(\epsilon) = \frac{1}{N_a}\sum_\alpha \delta(\epsilon-\epsilon_\alpha) = N_a^{-1}\,\mathrm{Tr}\,\delta(\epsilon-h) \\ h\psi_\alpha = \epsilon_\alpha\psi_\alpha \end{cases}$ $\epsilon_\alpha, \psi_\alpha$ eigenstates

→ relation with the resolvent

$$\frac{1}{\epsilon-\epsilon_\alpha+i0} = \mathcal{P}\frac{1}{\epsilon-\epsilon_\alpha} - \pi i\,\delta(\epsilon-\epsilon_\alpha)$$

⇓

$$\begin{cases} G(z) = \frac{1}{z-h} \\ n(\epsilon) = \frac{1}{N_a} - \frac{2}{\pi}\,\mathrm{Tr}\,G(\epsilon+i0) \end{cases}$$

→ electronic density and local density of states

$$n(\underline{r}) = \sum_{\alpha\ \mathrm{occ}} |\psi_\alpha(\underline{r})|^2 = \int f(\epsilon)\, n(\epsilon,\underline{r})\, d\epsilon$$

$$n(\epsilon,\underline{r}) = \sum_\alpha |\psi_\alpha(\underline{r})|^2\,\delta(\epsilon-\epsilon_\alpha)$$

→ TBA and partial densities of states

$$\psi_\alpha(\underline{r}) = \sum_{i,\lambda} A_i^\alpha(\lambda)\,\phi_{i\lambda}(\underline{r}) \qquad \phi_{i\lambda}(\underline{r}) \in \mathbb{R}$$

$$n(\epsilon,\underline{r}) = \sum n_{ij}(\epsilon,\lambda,\mu)\,\phi_{i\lambda}(\underline{r})\,\phi_{j\mu}(\underline{r})$$

$$n_{ij}(\epsilon,\lambda,\mu) = \Big\{\sum_\alpha A_i^\alpha(\lambda)\,A_j^\alpha(\mu)\,\delta(\epsilon-\epsilon_\alpha) + \Big\{\begin{matrix}(\lambda=\mu)\\(\lambda\neq\mu)\end{matrix}\Big\}\Big\}\frac{1}{2}$$

$\lambda=\mu$ local density of states for the orb. $i\lambda$

$\lambda\neq\mu$ interference — " — (bonding)

Relation between $n(\epsilon,\lambda,\mu)$ and $G(z)$

$$n_{ij}(\epsilon,\lambda,\mu) = -\frac{1}{2\pi}\mathrm{Im}\{\langle\phi_{i\lambda}|\,G(\epsilon+i0)\,|\phi_{j\mu}\rangle - \langle\phi_{j\mu}|G(\epsilon-i0)|\phi_{i\lambda}\rangle\}$$

Proof: $G(z) = \sum_\alpha |\psi_\alpha\rangle \frac{1}{z-\epsilon_\alpha}\langle\psi_\alpha|$

→ Perfect crystal

$n(\epsilon,\underline{\lambda}) \equiv n(\epsilon,\lambda,\lambda) = n(\epsilon)$ λ sites

$n_{ij}(\epsilon,\underline{\lambda},\underline{\mu}) \equiv n_{ij}(\epsilon,\lambda-\mu)$

(b) Problem:

determine directly the local density of states (without using the Bloch representation)

state that the direct diagonalization of the hamiltonian in the Bloch representation is:

- difficult for complex structures (A15, chevrel, σ ...)
- cannot be used for disordered systems

2 (≃ equivalent) methods have been used to determine the local properties

— moments method (Cyrot Lackmann and Gaspard ...)

— recursion method (Haydock, Heine, Kelly ...)

In the recursion method, we obtain directly the coefficients $(a_i\ b_i)$ of the expansion of $G_{00}(z)$ (continuous fraction):

$$G_{00}(z) = 1/z-a_1-b_1/z-a_2-b_2/z-a_3-b_3 \ldots /z-a_n-b_n/\ldots$$

by: (i) defining a new representation $\{|n\rangle\}$ $(n=1,2,\ldots\infty)$ in which h is tridiagonalized $(\langle m|h|n\rangle = 0$ $|n-m|>1)$

(ii) showing that G_{00} can be written as a continuous fraction is the equivalent chain problem

$$\underset{a_1}{1} \overset{\sqrt{b_1}}{—} \underset{a_2}{2} \overset{\sqrt{b_2}}{—} \underset{a_3}{3} \quad \overset{\sqrt{b_{n-1}}}{—} \underset{a_n}{n}$$

In the moment approach which is less efficient the moments are calculated and the coefficients a_n, b_n are related to these moments.

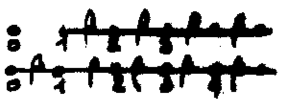
Note

Dyson equation: $G = (z-h)^{-1}$ $\quad G^0 = (z-h^0)^{-1}$ $\quad h = h^0 + v$

$$(z-h)^{-1} = (z-h_0)^{-1}[(z-h_0-v)+v](z-h_0-v)^{-1}$$
$$= G^0 + G^0 v G$$

Examples: 1 T.B band $E_0 = 0$; dot

h^0, h



G^0, G — absorption of an atom out the end of a 1/2 ∞ chain

$$\begin{cases} G_{00} = G^0_{00} + G^0_{00} v_{01} G_{10} \\ G_{10} = G^0_{11} v_{10} G_{00} \end{cases}$$

$$G^0 \begin{cases} G^0_{00} = 1/z \\ G^0_{0i} = 0 \quad i \neq 0 \end{cases}$$

$$v \begin{cases} v_{0i} = 0 \quad i \neq 1 \\ v_{01} = \beta \end{cases}$$

$$G_{00} = (z-\beta^2 G^0_{11})^{-1}$$

(c) RECURSION METHOD

$$h = \sum_{\lambda}' \epsilon_\lambda |\lambda\rangle\langle\lambda| + \sum_{\lambda\mu}' \beta_{\lambda\mu} |\lambda\rangle\langle\mu| \quad \rightarrow n(\epsilon,\lambda),\ n(\epsilon,\lambda\mu)\,??$$

1 • Starting from a localized state $|0\rangle$ build a new orthogonal basis set $|n\rangle$ from the recurrence relation:

$$\begin{cases} |1\rangle = |0\rangle \\ |2\rangle = h|1\rangle - a_1|1\rangle & \langle 2|1\rangle = 0 \Rightarrow a_1 = \langle 1|h|1\rangle/\langle 1|1\rangle \\ |3\rangle = h|2\rangle - a_2|2\rangle - b_1|1\rangle; & \langle 3|2\rangle = \langle 3|1\rangle = 0 \\ \ldots \\ |n+1\rangle = h|n\rangle - a_n|n\rangle - b_{n-1}|n-1\rangle; & \langle n+1|r\rangle = 0 \quad r \leq n \\ \ldots \end{cases}$$

a_n and b_{n-1} are defined by (1)(2) below and $\langle r|n+1\rangle = 0$ $\forall r \leq n$.

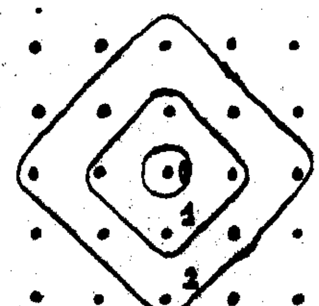
+ $\boxed{a_n = \dfrac{\langle n|h|n\rangle}{\langle n|n\rangle}} \in \mathbb{R}$ $\quad \Leftarrow \langle n|n+1\rangle = 0 \quad (1)$

+ $\langle m|n+1\rangle = 0$ $\forall m \leq n-1$ (by recurrence) since $\begin{cases} h|m\rangle \supset |m\rangle \\ \langle r|n\rangle = 0 \ \forall r \leq n-1 \end{cases}$

$$\langle m|h|n\rangle = [\langle m|h]|n\rangle$$
$$= [\langle m+1| + a_m^* \langle m| + b_{m-1}^* \langle m-1|]|n\rangle = 0$$

+ $\boxed{\dfrac{\langle n-1|h|n\rangle}{\langle n-1|n-1\rangle} = b_{n-1}}$ $\quad \Leftarrow \langle n-1|n+1\rangle = 0 \quad (2)$

+ $|1\rangle, |2\rangle, \ldots |n\rangle$ spread out further and further away from the central $|0\rangle$ whose local density of states we desire



β to first and 2nd n.n.

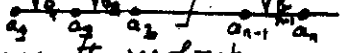
+ they define a new orthonormalized set $\dfrac{|n\rangle}{\sqrt{\langle n|n\rangle}}$; in this representation

• define H_{nm}: $H_{nn} = \dfrac{\langle n|h|n\rangle}{\langle n|n\rangle}$, $H_{n-1\,n} = \dfrac{\langle n-1|h|n\rangle}{\sqrt{\langle n-1|n-1\rangle\langle n|n\rangle}}$ $n \geq 1$

$$\begin{cases} H_{nn} = a_n & H_{n-1\,n} = \sqrt{\dfrac{\langle n-1|n-1\rangle}{\langle n|n\rangle}}\, b_{n-1} \\ H_{nm} = 0 & |n-m| > 1 \end{cases}$$

$(n-1|H|n) = [E_n + \beta_{n-1}(n-1| + \beta_{n-2}(n-2|]\,|n) = \beta_{n-1}|n-1)$

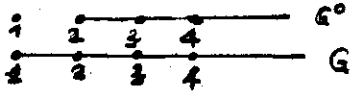
$H_{n,n+1} = \beta_{n-1}\sqrt{\frac{\langle n+1|n+1\rangle}{\langle n|n\rangle}} = \frac{\langle n|n\rangle}{\langle n-1|n-1\rangle}$ $\Rightarrow \begin{cases} \beta_{n-1} = \frac{\langle n|n\rangle}{\langle n-1|n-1\rangle} \in \mathbb{R}_+ \\ H_{n-1,n} = \sqrt{\beta_{n-1}} \end{cases}$



⇐ equivalent semi-infinite linear chain

2. Introduce the resolvent

$$G_{00} = \langle 0|\frac{1}{z-h}|0\rangle = (\delta|\frac{1}{z-h}|\delta)$$



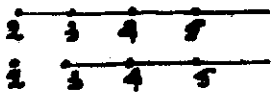
relate G_{00} to G_{22} (Dyson equations as previously)

$$\begin{cases} G_{11} = G^\circ_{11} + G^\circ_{11}\sqrt{b_1}\,G_{10} \\ G_{21} = G^\circ_{22}\sqrt{b_1}\,G_{01} \end{cases} \qquad \begin{cases} G^\circ_{00} = \frac{1}{z-a_1} \\ G^\circ_{22} \equiv g_2 \end{cases}$$

$$\Downarrow$$

$$G_{00} = \frac{1}{z-a_1-b_1 g_2(z)}$$

relate $G^\circ_{22} = g_2$ to g_3



$$g_2(z) = \frac{1}{z-a_2-b_2 g_3(z)}$$

etc...

Conclusion: The local density of state $-\frac{1}{\pi}\mathrm{Im}\,G_{00}(E+i0) = n_0(E)$ is given by a continuous fraction:

$$G_{00} = \frac{1}{z-a_1} - \frac{b_1}{|z-a_2} - \frac{b_2}{|z-a_3} - \cdots - \frac{b_n}{|z-a_{n+1}} - \cdots$$

3. It can be shown that (1) when the spectrum is connected and bounded:

$a_n \xrightarrow[n\to\infty]{} a$ $\qquad b_n \to b = \frac{W^2}{4}$

where a is the middle of the band
W " " band width.

(2) when the spectrum presents gaps a_n and b_n present oscillations. (Turbhi et al (1982)

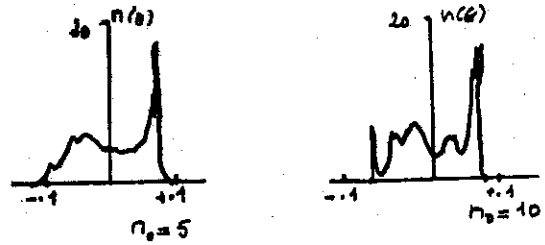
- When there is no gap replace for $n > n_0$ a_n and b_n (resp) by a and b i.e:

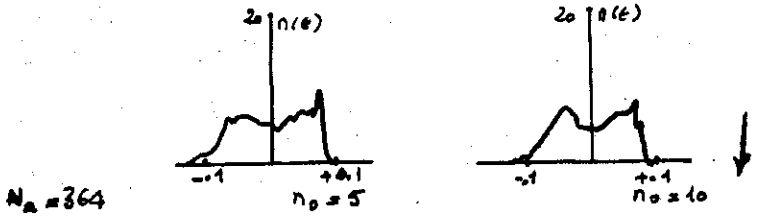
$$g_{n_0} = \frac{1}{z-a-b g_{n_0}} \qquad g_{n_0} = \frac{1}{2b}\left(z-a-\sqrt{(z-a)^2-4b}\right)$$

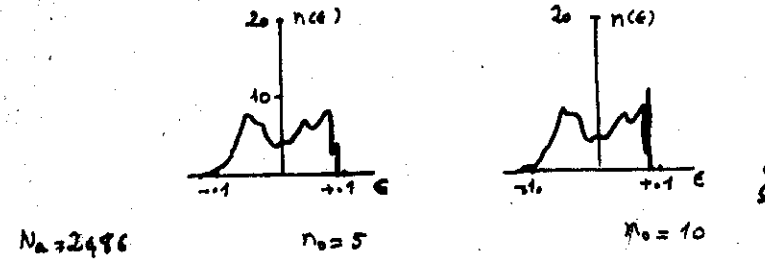
- It can be extended to off diagonal matrix elements of the Green function $G_{i\pm}$

$$G_{i\pm} = \frac{1}{4}\left[G_{i+\pm,i+\pm} - G_{i\pm,i-\pm}\right]$$

- The recursion method allows the calculation of properties of disordered systems (direct space calculation) - It is rapidly convergent ($n_0 \simeq 10, 15$)







Smoothed local density of states of d orbitals of fcc clusters of various sizes

For $N_a \geq 10^3$ at $n_0 > 10$, this density of states is the density of states deduced from band structure calc.

② Spectral moments

① $|z| \to \infty$ $(z \neq \epsilon_\lambda)$

$$G_{\lambda\lambda}(z) = \langle\lambda| \frac{1}{z-\hat{h}} |\lambda\rangle = \frac{1}{z} + \frac{h_{\lambda\lambda}}{z^2} + \frac{(h^2)_{\lambda\lambda}}{z^3} + \dots + \frac{(h^n)_{\lambda\lambda}}{z^{n+1}} + \dots$$

(we dropped the degeneracy index for simplicity)

$$\begin{cases} G_{\lambda\lambda}(z) = \sum_{n=0}^{\infty} \frac{\mu_n^\lambda}{z^{n+1}} \\ \mu_n^\lambda = \langle\lambda| H^n |\lambda\rangle = \int n(\epsilon,\lambda)\, \epsilon^n \, d\epsilon \end{cases} \leftarrow n^{th} \text{ moment of the local density of states}$$

$$\mu_n^\lambda = \sum_{\lambda_1 \dots \lambda_{n-1}} H_{\lambda\lambda_1} H_{\lambda_1\lambda_2} \cdots H_{\lambda_{n-1}\lambda}$$

= sum of the contributions of all closed walks of length n which can be drawn on the lattice

② Examples

$\mu_0^\lambda = 1$ $\quad \mu_1^\lambda = \epsilon_\lambda$ $\quad \mu_2^\lambda = \epsilon_\lambda^2 + \sum_p \beta_{\lambda p}^2$ (sum over bonds)

↑ CENTER (choice 0) ⇑ WIDTH

μ_3 comes from triangles → $=0$ in ALTERNANT STRUCTURES OR WHEN THERE IS NO TRIANGLES

→ $\neq 0$ otherwise

the same for μ_{2n+1} $\forall n > 1$ (no circuits with odd length for alt. lattices $(\epsilon_\lambda = 0)$)

$\Rightarrow n(\epsilon) = n(-\epsilon)$ for alt lattice

For non degenerate bands μ_p obtained by walk counting techniques:

$$\mu_p = \nu_p \beta^p \quad \text{(all } \beta \text{ equals } +0 \text{ for } n \neq 0)$$

ν_p number of closed walks of length p

linear chain $\mu_{2p} = 2p!/(p!)^2$

diamond structure $\nu_p = (p!)^2 \sum_{s=0}^{p} \frac{(2s)!\,(2p-2s)!}{(s!)^4 (p-s)^2}$

Otherwise: the use of a computer is required!

③ The band is characterized by: (i) μ_2 the average energy (ii) μ_2 the bandwidth, (iii) the asymmetry $\mu_3/\mu_2^{3/2}$

④ The coefficients a_i, b_i are obtained from the moments

$a_1 = \mu_1 = 0$ (origin)

$b_1 = \mu_2$

$a_2 = \mu_3/\mu_2$

$a_3 = (\mu_4 \mu_2 - \mu_2^3 - \mu_3^2)/\mu_2^2 \dots$

....

ALTERNANT STRUCTURES: Structures that can be partitioned in two sublattices L ($L = A, B$); the nn. of an A site is a B site and of an B site is an A site

Ex: linear chain, simple cubic, body centered cubic

III GENERAL FEATURES OF THE ELECTRONIC SPECTRUM OF CONCENTRATED ALLOYS

(1) (a) choice of a simple band model (of the theory)

- "1 NON DEGENERATE TIGHT BINDING BAND" ISSUED FROM 1 "S" ORBITAL PER ELEMENTARY SITE $\underline{i}$, $\phi(\underline{i},\underline{r})$

THE WAVE FUNCTIONS FOR THE CRYSTAL ARE THEN IN L.C.O.A:

$$\Psi_\alpha(\underline{r}) = \sum_{\underline{i}} A_\alpha^{\underline{i}}(\underline{i})\,\phi(\underline{i},\underline{r}) \qquad (59)$$

- WE ASSUME THAT

$$\langle \phi(\underline{i}) | \phi(\underline{k}) \rangle = \delta_{\underline{i}\underline{k}} \qquad (60)$$

AND WE DEFINE

- THE ENERGY LEVELS: $\epsilon_{\underline{i}} = \langle \phi(\underline{i}) | \mathcal{H} | \phi(\underline{i}) \rangle$ (61)
- THE TRANSFER INTEGRALS: $\beta_{\underline{i}\underline{j}} = \langle \phi(\underline{i}) | \mathcal{H} | \phi(\underline{j}) \rangle$ (62)

FROM THE CRYSTALLINE HAMILTONIAN $\mathcal{H}$ $(\underline{i} \neq \underline{j})$

- THE WAVE FUNCTIONS $|\Psi_\alpha\rangle$ AND THE ENERGIES ϵ_α

$$\mathcal{H}|\Psi_\alpha\rangle = \epsilon_\alpha |\Psi_\alpha\rangle$$

ARE OBTAINED FROM THE N EQUATIONS

$$(\epsilon_{\underline{i}} - \epsilon)\,A^{\alpha}(\underline{i}) + \sum_{\underline{j}\neq\underline{i}} \beta_{\underline{i}\underline{j}}\,A^{\alpha}(\underline{j}) \qquad \underline{i} = 1, \ldots, N \qquad (63)$$

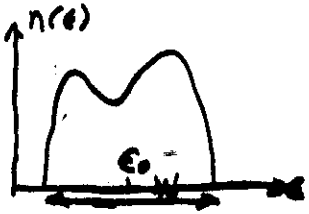
- THE SOLUTION IS OBVIOUS FOR A PURE METAL i.e. WHEN $\epsilon_{\underline{i}} = \epsilon_0$ (whatever $\underline{i}$) , $\beta_{\underline{i}\underline{j}} = \beta(\underline{i}-\underline{j})$

IT'S:

$$A^{\alpha}(\underline{i}) = \frac{e^{i\underline{k}\cdot\underline{i}}}{\sqrt{N}} \quad , \quad \epsilon_{\underline{k}} = \epsilon_0 + \sum_{\underline{j}\neq\underline{i}} \beta(\underline{i}-\underline{j})\,e^{i\underline{k}\cdot(\underline{j}-\underline{i})} \qquad (64)$$

$\alpha = \underline{k}$

THE BAND IS CHARACTERIZED BY TWO PARAMETERS



- ITS POSITION "CENTER" ϵ_0
- ITS WIDTH $W \sim 2z\beta$ (z coordination number, β = integral between nearest neighbours)

ADVANTAGES:

- IT'S THE SIMPLEST MODEL TO DISCUSS THE FEATURES OF THE DISORDER EFFECTS
- WITH SOME COMPLICATIONS, IT WILL REPRESENT THE 'd' BANDS OF TRANSITION METALS WHICH DETERMINE THE THERMODYNAMIC PROPERTIES. (5 ORBITALS PER SITE!)

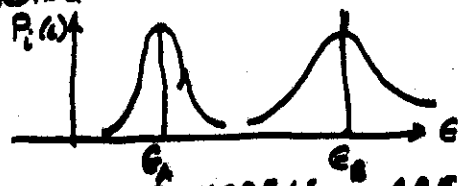
(b) simple models for disorder.

FOR A GIVEN CONFIGURATION (i.e. FOR A SET OF VALUES OF $p_{\underline{i}}^{i}$) THE DISORDERED STATE HAS TO BE REPRESENTED BY A CONSISTENT SET OF PARAMETERS

$|\Phi A\rangle$, $\epsilon_{\underline{i}}$, $\beta_{\underline{i}\underline{j}}$

WHICH DEPEND ON $\{p_{\underline{i}}^{i}\}$.

- FOR EXAMPLE, $\epsilon_{\underline{i}}$ DEPENDS NOT ONLY ON THE NATURE OF THE ATOM IN $\underline{i}$ BUT ALSO ON ITS ENVIRONMENT; THE ENERGIES OF A AND B ATOMS ARE DISTRIBUTED AROUND AN AVERAGE VALUES ϵ_A, ϵ_B: ACCORDING PROBABILITY LAWS: $P_A(\epsilon_A)$, $P_B(\epsilon_B)$ $(N \to \infty)$

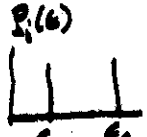


example.

- TWO SIMPLE MODELS ARE USED:

(1) $\epsilon_{\underline{i}}$ AND $\beta_{\underline{i}\underline{j}}$ ARE ASSUMED TO BE ONLY DEPENDENT ON THE NATURE CHEMICAL OF THE ATOMS IN $\underline{i}$ AND $\underline{j}$. THE ALLOY IS THEN CHARACTERIZED BY THE PARAMETERS:

$$\epsilon_A, \epsilon_B \quad ; \quad \beta_{AA}(\underline{i}), \beta_{AB}(\underline{i}), \beta_{BB}(\underline{i})$$



$$\mathcal{H}(p_{\underline{i}}^{i}) = \sum_{\underline{i}} p_{\underline{i}}^{i}\,\epsilon_i |\lambda\rangle\langle\lambda| + \sum_{\underline{i},\underline{j}} p_{\underline{i}}^{i}\,p_{\underline{j}}^{j}\,\beta_{ij}(\underline{i}-\underline{j})\,|\lambda\rangle\langle\mu| \qquad (65)$$
$\lambda \neq \mu$

- notation $|\lambda\rangle = |\phi(\underline{\lambda})\rangle$
- THE ENVIRONMENT EFFECTS ARE NEGLECTED
- PERHAPS NOT TOO BAD AT 50% BUT CERTAINLY NOT PHYSICALLY VALID FOR $c \to 0$ ($\delta\epsilon/\epsilon_A \to 0$)
- ALL THE ATOMS i HAVE THE SAME PROPERTIES.... (number of electrons...)

$\epsilon_{\underline{i}}$ ARE FLUCTUATING AROUND AND AVERAGE VALUE ϵ_0 AND $\beta_{\underline{i}\underline{j}}$ ARE ASSUMED TO BE NON RANDOM.

- THE FLUCTUATIONS OF ENERGY LEVELS DO ARE MUCH LARGER THAN THE FLUCTUATIONS WHICH OCCUR FROM THE NATURE OF ATOMS (RANDOM POTENTIAL)

TRONIC STRUCTURES OF [illegible] (C.M.A).

• THE MODEL (1) IS USED SO OFTEN TO STUDY LOCALIZATION (Anderson's model of disorder)

DEFINITIONS

THE FLUCTUATIONS OF ϵ_i DEFINE THE "DIAGONAL DISORDER (D.D)" ——— .. (β ——— "OFF ———.

——— (O.D)

(2) WE WILL DISCUSS ESSENTIALLY THE MODEL (1) WITH 2 VER. OF

(a) ONE IMPURITY STATES ($\epsilon_A \neq \epsilon_B$) A B

LET US STUDY QUALITATIVELY THE CASE OF "D.D." AND OF "O.D"

c 1 DIAGONAL DISORDER

TWO LIMITS

$N_A = N_B = N$

$\frac{\epsilon_A - \epsilon_B}{W} = \delta$

$\delta \ll 1$ (perturb.) → RIGID BAND MODEL

$\delta \gg 1$ → $\delta > 0$: B (host), ϵ_B, A

$\delta < 0$: A, ϵ_B, ϵ_{LB}

• WHEN δ IS SMALL THE PERTURB THEORY IS VALID AND EACH SATE IS DISPLACED BY:

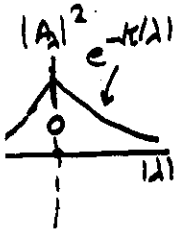
$\epsilon_k^B \rightarrow \Delta\epsilon_k^{B,A} = \langle \psi_k^B | \Delta V^{B,A} | \psi_k^B \rangle = \frac{1}{N} W \delta$ (6)

THE PERTURBATION ΔV IS

$\Delta V^{B,A} = (\epsilon_A - \epsilon_B) |0\rangle\langle 0|$

WHEN A IS INTRODUCED IN B (@ site)

RIGID BAND MODEL



• WHEN $\delta \gg 1$ BOUND STATES

(N-1) EXTENDED STATES FOR $\epsilon \in [\epsilon_B \pm \Psi]$ WITH NO ELECTRONIC DENSITY ON THE SITE @ OCCUPIED BY A (WHEN $\delta \to \infty$), 1 BOUND STATE LOCALIZED ON THE A ATOM. (FOR $\epsilon \simeq \epsilon_A$)

• WHEN δ DECREASES FROM ∞, THE BOUND STATE INCREASES IN SIZE

$|A_\lambda|^2 \sim \exp -\kappa|\lambda|$ (7)

WHERE $\kappa(\delta) \to 0$ WHEN THE BOUND STATE IS JUST ON THE BAND EDGE ($\epsilon_{LB} \simeq \epsilon_B$) i.e FOR $\delta = \delta_c$

• FOR $\delta < \delta_c$ NO MORE BOUND STATE $\delta_c \sim 1$

c 2 OFF DIAGONAL DISORDER

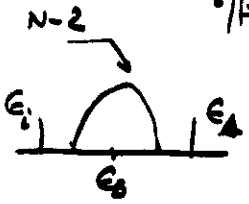
$\beta_{AB} = \beta'$ $\beta_{BB} = \beta$ ($\epsilon_A = \epsilon_B$) (limited on the nearest neighbours)

• $\left|\frac{\beta' - \beta}{\beta}\right| \ll 1$ PERTURBATION THEORY

R. Sm?? $\Delta\epsilon_k^{B \to A} = \frac{1}{N} \Delta\beta(k)$ $\Delta\beta(\lambda) = \sum_\lambda (\beta'(\lambda) - \beta(\lambda)) e^{ik\lambda}$

• $\left|\frac{\beta' - \beta}{\beta}\right| \gg 1$ 2 BOUND STATES: • BUILD WITH THE NEAREST NEIGHBOUR ORBITALS. $\phi(\lambda)$ THE SYMMETRIC STATE

$|\psi_s\rangle = \frac{1}{\sqrt{N}} \sum_n |\phi(\lambda)\rangle$



• THIS STATE MIXES WITH ϕ ON THE [redacted] SITE OCCUPIED BY A WITH TWO { BONDING / ANTIBONDING } STATES

WHOSE ENERGIES ARE

$\epsilon_i \simeq \epsilon_B - \beta'$ $\epsilon_A = \epsilon_B + \beta'$

WHEN $\beta'/\beta \to \infty$ THESE CLUSTER STATES ARE LOCALIZED (EQUALLY) ON A AND THE NEIGHBOUR

. WHEN β'/β THEIR EXTENSION INCREASES

. THEY DISAPPEAR WHEN $\beta/\beta' \sim \beta$.

c 3 CONCLUSION

ACCORDING TO THE VALUES OF δ, β'/β WE CAN HAVE VERY DIFFERENT FEATURES

0, 1 OR 2 BOUND STATES!

LET US NOW DISCUSS WHAT IS PASSING WHEN C. FOR D.D.

(Note: the O.D. IS USEFUL FOR INTER ALLOYS!)

(b) DILUTE ALLOYS $A_{1-c} B_c$: DIAGONAL DISORDER

WE CAN EXPAND IN SUCC. POWERS OF p_λ OR C

$N n(\epsilon, p_\lambda) = N n_B(\epsilon) + \sum_\lambda p_\lambda \Delta n_A(\epsilon) + \frac{1}{2} \sum_{\lambda\mu} p_\lambda p_\mu \Delta n_A(\epsilon, \lambda, \mu) + \ldots$

OR AVERAGING OVER ALL CONFIGURATIONS:

$N \overline{n}(\epsilon, c) = N n_B(\epsilon) + Nc\, \Delta n_A(\epsilon) + \frac{1}{2} N \sum_{\mu \neq 0} \langle p_0 p_\mu \rangle \Delta n_A(\epsilon, \lambda) + \ldots$

FOR MACROSCOPIC MEASUREMENTS WE NEED ONLY $\overline{n}$.

$\Delta n_A(\epsilon)$ VARIATION OF DENSITY OF STATES INTRODUCED BY ONE IMPURITY

$\Delta n_A(\epsilon, \lambda)$ — PAIR INTERACTION BETWEEN IMPURITIES $(0, \lambda)$

WHEN $\delta \gg 1$ PAIR INTERACTIONS DETERMINE A RANGE OF POSSIBLE BONDING AND ANTI BONDING STATES FOR THE VARIOUS DISTANCES (λ) OF THE ATOMS

© CONCENTRATED ALLOYS

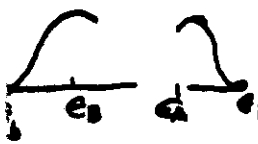
ONE EXPECTS TO HAVE FOR $\bar{\delta} \gg 1$ A SPECTRUM MADE OF TWO PARTS : (1) THE 1st IS CENTERED ON ϵ_A AND HAS WAVE FUNCTIONS MAINLY LOCALIZED ON A SITES WHEREAS (2) THE 2d IS CENTERED IN ENERGY ON ϵ_B AND HAS WAVE FUNCTIONS MAINLY LOCALIZED ON B SITES

HOWEVER!
- IS THERE STILL A GAP BETWEEN THESE TWO PARTS?
- ARE THERE LOCALIZED STATES?

1 THEOREM.
THE EIGENVALUES OF $\mathcal{H}$ ARE NECESSARILY IN THE ENERGY INTERVALS WHERE ARE THE EIGENVALUES OF PURE A AND PURE B SYSTEMS

⇒ WHEN THESE INTERVALS DO NO RECOVER ($\delta > 1$) THERE IS A GAP IT'S THE "SPLIT BAND REGIME"
LARGE DEVIATION FROM R.B.M!

2 FOR DIAGONAL DISORDER $\bar{n}(\epsilon, c)$ IS EXPONENTIALLY NEAR THE BAND EDGES OF PURE METALS "band tails"

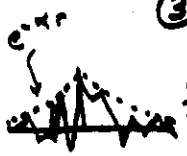


It's always possible to have a piece as large as possible wanted of pure B in a disordered system... but with small probability:

The volume L^3 of B is obtained with probability $\sim (1-c)^{L^3}$; the first state above the ~~bottom~~ ground state of this cube has $h \sim \frac{1}{L}$, $\Delta E \sim |\beta|/L^2$, $L^3 n(\epsilon) \sim \frac{L^2}{|\beta|}$

$$\Rightarrow \boxed{\bar{n}(\epsilon) \sim (1-c)^{L^3} \frac{1}{|\beta| L} \sim \sqrt{\Delta E}\, \exp -\alpha \Delta E^{-3/2}} \quad (\S 8)$$

ENVELOPES



③ LOCALIZED STATES : WAVE FUNCTIONS HAVE DECREASING ENVELOPES

THE STATES ~~ARE~~ LOCALIZED IF AN ELECTRON OF ENERGY E (± dE) IN VOLUME L^3 LARGE ENOUGH TO SATISFY UNCERTAINTY PRINCIPLE DOES NOT DIFFUSE AWAY.

THE EXISTENCE OF SUCH STATES HAVE BEEN EXTENSIVELY STUDIED IN THE ANDERSON'S MODEL FOR DISORDER.

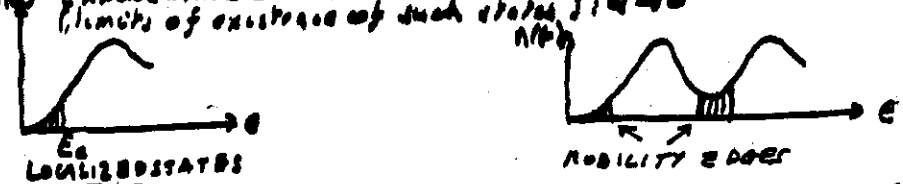
SEE CAMKELINUM LECTURES!!!

- In the case of strong disorder ($\bar{\delta} \gg 1$) it's clear that all the states (but the sign (and the amplitudes) of the wave functions vary at random from site to site.

Anderson finds that the states are localized when:

$$\delta = \frac{\text{Const}}{W} > 5 \quad (\text{for } \beta = 0)$$

- When this condition is not satisfied only some the states for some energy ranges of low density of states are thought to be localized (in the band tails) WITH CHARACTERISTIC EXPONENTIAL DECAY THOUGHT TO DECREASE WHEN $E \to \epsilon_c$ (limits of existence of such states) $\to 0$



- THESE STATES DO NOT CONTRIBUTE TO THE CONDUCTIVITY (WHEN THE CONDUCTIVITY COMES FOR $T \to 0$ AND WHEN $\delta > 5$ WE HAVE AN INSULATOR!).

EXPAND!

④ Simple limiting cases (soluble!)

(1) dilute limit ($c \to 0$)
(2) perturbation theory ($\delta \ll 1$) (cf chapter II)
(3) atomic limit $\beta \to 0$
(4) split band limit $\delta \to \infty$ (β fixed)

(3) (a) SPECTRAL DENSITIES

- THE WAVE VECTOR $\underline{k}$ CAN ONLY CHARACTERIZE THE ALLOY STATES WHEN THE DISORDER IS SMALL i.e. WHEN THE UNCERTAINTY IN k, Δk INTRODUCED BY SCATTERING IS SMALL AS COMPARED WITH k

$$\Delta k/k \ll 1 \qquad \Delta k\,\lambda \sim 1 \qquad (69)$$

WHERE λ IS THE MEAN FREE PATH.

$$\frac{1}{\lambda} = \frac{1}{v\tau} \sim 2\pi \cdot \Gamma^2 \frac{n(\epsilon)\Omega}{v} \qquad (\Omega \text{ at. volume})$$

FOR SIMPLE CUBIC CRYSTAL AND FOR k STATES AT THE BOTTOM OF THE BAND

$$m^* \sim \frac{1}{2\beta a^2},\ \Omega = a^3,\ v = \frac{\hbar}{m^*}\ n(\epsilon) = \frac{\hbar m^*}{2\pi^2} \Rightarrow$$

$$\frac{a}{\lambda} \sim \left(\frac{\Gamma}{\beta}\right)^2 \frac{1}{4\pi} \Rightarrow \Delta k \gtrsim k \text{ WHEN } \frac{\Gamma}{\beta} \gtrsim 3,4$$

$\lambda \sim a$ (cf Mott Davis)

"λ cannot be smaller than a" when the disorder is large

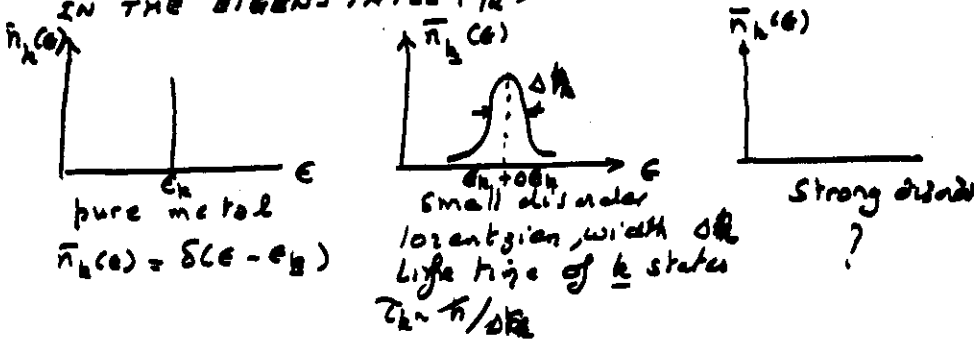
When Γ/β is large i.e. when the disorder is large "there is no more phase relations between functions on the various bonding sites"

- FOR LARGE DISORDER, WE CAN ONLY CONSIDER THE SPECTRAL DENSITY :

$$\bar{n}_{\underline{k}}(\epsilon) = \frac{1}{N} \langle \psi_{\underline{k}} | (\delta(\epsilon - \mathcal{H})) | \psi_{\underline{k}} \rangle \qquad (70)$$

$$= \frac{1}{N} \Big\langle \sum_{\alpha} K\, \psi_{\underline{k}} | \varphi_\alpha \rangle |^2\, \delta(\epsilon - \epsilon_\alpha) \Big\rangle$$

IT'S THE AVERAGE WEIGHT OF THE $\psi_{\underline{k}}$ STATES IN THE EIGENSTATES $|\varphi_\alpha\rangle$ OF ENERGIES $\epsilon_\alpha = \epsilon$



(4) DENSITY OF STATES, AVERAGED MOMENTUM, GREEN FUNCTION

- THE AVERAGED DENSITY OF STATES $\bar{n}(\epsilon)$ is given by:

$$\bar{n}(\epsilon) = \frac{1}{N}\Big\langle \sum_{\alpha} \delta(\epsilon - \epsilon_\alpha) \Big\rangle = \frac{1}{N} \mathrm{Tr} \langle \delta(\epsilon - \mathcal{H}) \rangle = \sum_{\underline{k}} \bar{n}_{\underline{k}}(\epsilon) \qquad (71)$$

THIS AVERAGED DENSITY $\bar{n}(\epsilon)$ WILL BE OFTEN SUFFICIENT FOR OUR PURPOSE - HOWEVER, NOTE THAT (OBVIOUSLY!) NOTHING CAN BE SAID ABOUT THE NATURE OF THE WAVE FUNCTIONS FROM $\bar{n}$!! (localized states or not ?)

- USING THE IDENTITY:

$$\lim_{\eta \to 0} \frac{1}{x + i\eta} = \lim_{\eta \to 0} \frac{x}{x^2 + \eta^2} - i \lim_{\eta \to 0} \frac{\eta}{x^2 + \eta^2} = \frac{\mathcal{P}}{x} - \pi i\, \delta(x)$$

- WE CALCULATE THE RESOLVENT (or "Green function")

$$G(z) = \frac{1}{z - \mathcal{H}}$$

DEFINED FOR z OUTSIDE OF THE EIGENVALUES ϵ_α

$$\langle \varphi_\alpha | G(z) | \varphi_\beta \rangle = \delta_{\alpha\beta} \frac{1}{z - \epsilon_\alpha} \qquad (z \neq \epsilon_\alpha) \quad (72)$$

- TO THE DENSITY OF STATES

$$n(\epsilon) = -\frac{1}{\pi} \mathrm{Im}\, G(\epsilon + i0)$$

$$\bar{n}(\epsilon) = -\frac{1}{\pi} \mathrm{Im}\, \mathrm{Tr} \langle G(\epsilon + i0) \rangle$$

- IT'S USEFUL TO INTRODUCE THE EFFECTIVE POTENTIAL "$\Sigma(z)$" BY :

$$\langle G(z) \rangle = \Big\langle \frac{1}{z - \mathcal{H}} \Big\rangle = \Big\langle \frac{1}{z - \mathcal{H}_0 - \Sigma(z)} \Big\rangle \qquad (73)$$

Σ REPLACES V (THE RANDOM POTENTIAL)

$$\mathcal{H} = \mathcal{H}_0 + V \text{ FOR A DOS } \begin{cases} \mathcal{H}_0 = \sum \beta_{\underline{k}\underline{k}'} |\underline{k}\rangle\langle\underline{k}'| \\ V = \sum p_i\, \epsilon_i\, |i\rangle\langle i| \end{cases}$$

WHEN WE AVERAGE OVER ALL CONFIGURATIONS.

- Σ IS IN GENERAL ENERGY (z) DEPENDENT
- IT'S NON LOCAL (IN GENERAL!) IN THE BASIS OF ATOMIC FUNCTIONS:

$$\langle \phi(\underline{l}) | \Sigma | \phi(\underline{l}') \rangle \neq 0 \qquad \underline{l} \neq \underline{l}' \qquad (74)$$

BUT THESE MATRIX ELEMENTS DEPEND ON $\underline{l} - \underline{l}'$

- IT'S NON REAL, THE IMAGINARY PART BEING ASSOCIATED TO THE "LIFE TIME" OF ELECTRONS IN THE AVERAGE MEDIUM.

NAL INVARIANCE AVERAGING SO THAT:

- THE EFFECTIVE HAMILTONIAN FOR THE AVERAGE MEDIUM

$$\mathcal{H}_{eff} = \mathcal{H}_0 + \Sigma(z) \qquad (75)$$

- THE 'POTENTIAL OF THE AVERAGE MEDIUM' Σ
- AND $\langle G(z) \rangle$

ARE DIAGONAL IN THE BASIS OF BLOCH STATES $|\psi_k\rangle$:

$$\langle \psi_k | \langle G(z) \rangle | \psi_{k'} \rangle = \delta_{kk'} \frac{1}{z - \epsilon_k^0 - \Sigma(k,z)} \qquad (76)$$

THE SPECTRAL DENSITY CAN THEN BE WRITTEN AS:

$$\boxed{\bar{n}_k(\epsilon) = -\frac{1}{\pi} \frac{\mathrm{Im}\, \Sigma(k,z)}{|\epsilon - \epsilon_k^0 - \Sigma_R(k,z)|^2 + |\mathrm{Im}\, \Sigma(k,z)|^2}} \qquad (77)$$

$(\Sigma_R(k,z) = \mathrm{Re}\, \Sigma(k,z))$

AND $\tau_k \sim \hbar / |\mathrm{Im}\, \Sigma(k,z)|$

— Roughly lorentzian form for small disorder (Σ_R, τ_k smooth on k)

⑦ Local densities of states

- In an alloy, we can define the local density of state (per unit energy) by:

$$n(\epsilon, r) = \sum_\alpha |\varphi_\alpha(r)|^2 \delta(\epsilon - \epsilon_\alpha) \qquad (78)$$

- In a T.B. model we define the density of occupation of a given orbital by:

$$n(\epsilon, \alpha) = \sum_\alpha |\langle \Phi(r) | \psi_\alpha \rangle|^2 \delta(\epsilon - \epsilon_\alpha) \qquad (79)$$

- For the average medium $\langle n(\epsilon, \alpha) \rangle = \bar{n}(\epsilon)$

⑧

$$|\underline{k}, t\rangle = e^{-iht/\hbar} |k, 0\rangle$$

$|\langle \underline{k}' 0 | \underline{k}, t \rangle|^2 = P_{\underline{k}}(t)$ = probability of finding an el at time t in state $\underline{k}$ knowing it was in this state at $t=0$

It's related to the usual Green function

$$G_{\underline{k}}(t) = -i \langle \underline{k} 0 | \underline{k} t \rangle \quad t > 0$$
$$= 0 \quad t < 0$$

or:

$$G_{\underline{k}}(t) = -i\theta(t) \sum_\alpha |\langle k | \psi_\alpha \rangle|^2 e^{-i\epsilon_\alpha t/\hbar}$$

F.T: $G_k(\epsilon + i0) = \int_0^\infty \frac{dt}{\hbar} e^{i(\epsilon + i0)t} G_k(t) = \sum_\alpha \frac{|\langle k | \psi_\alpha \rangle|^2}{\epsilon - \epsilon_\alpha + i0}$

$$= \langle \underline{k} | G(\epsilon + i0) | \underline{k} \rangle$$

$$P_{\underline{k}}(t) = |G_k(t)|^2 \quad t > 0$$

⑨ If $G_{\underline{k}}(\epsilon) = (\epsilon - \epsilon_k' - i\Delta)^{-1}$ $\quad \Gamma_k = 2\,\mathrm{Im}\, \Sigma_k(\epsilon_k')$

$$G_k(t) = \int \frac{d\epsilon}{2\pi} e^{-i\epsilon t/\hbar} G_k(\epsilon) = -i\theta(t) e^{-i\epsilon_k' t/\hbar} e^{-\frac{\Gamma_k}{2\hbar} t}$$

$$P_k(t) = \exp -2\Gamma_k t/\hbar$$

A SIMPLE METHOD FOR THE CALCULATION OF $\bar{n}(\epsilon, c)$ ENERGIES

⑥ C.P.A (Coherent potential approximation) for DD

① METHOD

. It's a simple "one site" approximation to the calculation of the electronic spectrum which is aware of the limiting cases (i) dilute limit, (ii) zero mixt limit (iii) split band (iv) perturbation limit: in this sense it's an "interpolation" between exact results!

. THE SIMPLEST WAY TO OBTAIN IT:

(1) → $\Sigma(z)$ IS ASSUMED TO BE LOCAL:

$$\langle \phi(\lambda) | \Sigma | \phi(\mu) \rangle = \delta_{\lambda\mu}\, \sigma(z) \qquad (*)(80)$$

(2) → IT'S DERIVED FROM THE CONDITION (SELF CONSISTENCY)

$$\boxed{\bar{n}(\epsilon) = \sum_i c_i\, n_i(\epsilon)} \qquad (*)(81)$$

THE DENSITY OF STATES AT THE ORIGIN FOR THE AVERAGE MEDIUM:

$$\bar{n}(\epsilon) = -\frac{2}{\pi} \langle o | (G(\epsilon + i0)) | o \rangle$$

IS THE AVERAGE OF THE DENSITIES OF STATES OF THIS SAME SITE WHEN IT'S OCCUPIED BY AN A ATOM, $n_A(\epsilon)$ (PROBABILITY c_A) OR B ATOM, $n_B(\epsilon)$ (PROBABILITY c_B).

$$-\frac{2}{\pi}\langle o | G(\epsilon+i0), \begin{smallmatrix} \Sigma & \Sigma & \Sigma & \Sigma \\ \Sigma & \Sigma & \Sigma & \Sigma \\ \Sigma & \Sigma & \Sigma & \Sigma \end{smallmatrix} | o \rangle = -\frac{2}{\pi}\langle o | G(\epsilon+i0, \begin{smallmatrix} \Sigma & \Sigma & \Sigma & \Sigma \\ \Sigma & \Sigma & \Sigma & \Sigma \\ \Sigma & \Sigma & \Sigma & A \end{smallmatrix}) | o \rangle \times c_A$$

$$-\frac{2}{\pi}\langle o | G(\epsilon+i0, \begin{smallmatrix} \Sigma & \Sigma & \Sigma & \Sigma \\ \Sigma & \Sigma & \Sigma & \Sigma \\ \Sigma & \Sigma & \Sigma & B \end{smallmatrix}) | o \rangle \times c_B$$

or:

$$\langle o | (G(\epsilon+i0)) | o \rangle = \sum_i{}' c_i \langle o | G_i(\epsilon+i0) | o \rangle$$

$$F(\epsilon) = \sum_i c_i F_i(\epsilon).$$

THIS CONDITION IS EASILY ANALYTICALLY EXPRESSED:

$$G_i(z) = \frac{1}{z - H_{eff} + (\epsilon_i - \Sigma) | o \rangle \langle o |} = \langle G(z) \rangle + \langle G(z) \rangle (\epsilon_i - \Sigma) G_i(z)$$

or taking the matrix element $\langle o | G_i | o \rangle$

$$F_i(z) = F(z) + F(z)(\epsilon_i - \Sigma) F_i(z) \Rightarrow F_i(z) = \frac{F(z)}{1 - (\epsilon_i - \Sigma) F(z)}$$

$$\boxed{1 = \sum_i \frac{c_i}{1 - (\epsilon_i - \Sigma(z)) F(z)}} \qquad (*)(82)$$ CPA condition

② PROPERTIES

- IT PRESERVES THE ANALYTICAL PROPERTIES OF $\langle G(z) \rangle$ which means that $\bar{n}(\epsilon) \geq 0$ as it must!
- THE COMPARISON WITH NUMERICAL RESULTS SHOWS THAT THE SPECTRUM IS WELL REPRODUCED EXCEPT SMALL "STRUCTURES"

  Ex: cf fig (of p 58)(c) THE STRUCTURES CAN BE INTERPRETED BY LOCAL ENVIRONMENT EFFECTS. An atom A has different local densities of states according to its environment; the number of electrons on such atom fluctuates with environment... This shows the limit of the approximation we did ($\epsilon_\lambda = \epsilon_A$ for all λ sites occupied by A atoms...)

. HOWEVER, IT'S IMPORTANT TO KNOW THAT THE SPLIT BAND REGIME IS WELL REPRESENTED.

- INTEGRAL PROPERTIES SUCH AS THE ENERGY

  $E = \int n(\epsilon)\, \epsilon\, d\epsilon$ (band term)

  ARE PROBABLY WELL REPRESENTED BY CPA. (They are less sensitive than properties depending only from one energy (ϵ_F for ex. / specific heat coeff. γ)

- Note 1: the comparison of CPA with the "numerical results" can be done with "reconstruction" of $\bar{n}(\epsilon)$ by a moment method (see the next fig); this method introduces some broadening and underestimates the possibility of gaps

  2 The CPA can be extended to take into account of the local environment (CPA n, BRA): one writes

  $$\bar{n}(\epsilon) = \sum_i p_i(\epsilon)\, n_i^{(n)}(\epsilon, c)$$

  where $n_i^{(n)}$ is the density of an atom i surrounded by n atoms i (nearest neighbours) and by the average medium Σ determined by this condition

  For small δ values, CPA gives good results but for large δ values $\bar{n}(\epsilon)$ is no more ≥ 0 everywhere. It is possible to overcome numerically such difficulties but the analyticity of such approximations is not correct in general.

Ann 1 Energy levels and transfer integrals in a disordered system

(a) SELF CONSISTENT CALCULATION: for each spin σ

LDA $\Rightarrow$ $h_\sigma = -\frac{\hbar^2}{2m}\nabla^2 + V^{ion} + V^{e}[n(r)] + V^{xc}[n_\sigma(r)]$

$\Downarrow$

$[\psi_\alpha, \epsilon_\alpha]$; $h\psi_\alpha = \epsilon_\alpha \psi_\alpha$

$\Downarrow$

$n(r) = \sum_{\alpha\, occ} |\psi_\alpha(r)|^2$

IN A T.B.A THE SELF CONSISTENT ENERGY LEVELS (ϵ_λ) and TRANSFER INTEGRALS DEPEND ON (i) THE LATTICE TOPOLOGY (ii) THE CHEMICAL NATURE OF ATOMS ON λ. FOR EXAMPLE THE ENERGY LEVEL CHANGE INDUCED BY A MODIFICATION OF THE LOCAL ENVIRONMENT OF AN SITE λ (occupied by i at) IS

$$\delta\epsilon_{\lambda\sigma} = \delta\langle\lambda|h|\lambda\rangle = U_\lambda\,\delta n_\lambda - J_\lambda\,\delta n_{\lambda\sigma} + O(\delta n_{\lambda\sigma}^2)$$

KEEPING ONLY INTRAATOMIC INTEGRALS

$$U_\lambda = \int \phi_\lambda^2(r)\frac{e^2}{|r-r'|}\phi_\lambda^2(r')\,dr\,dr' \quad \text{(Coulomb term)}$$

σ : spin ± 1

$\delta n_\lambda = \sum_\sigma \delta n_{\lambda\sigma}$ = "charge transfer"

(b) EXAMPLE: 1 impurity in a metal (at the origin)

$\Downarrow$

FRIEDEL OSCILLATIONS: IMPURITY INDUCED

DENSITY VARIATION: $\Delta n(r) \underset{r\to\infty}{\sim} A\,\frac{\cos(D_F\, r + \phi_F)}{r^3}$

D_F diameter of the Fermi surface

IMPURITY POTENTIAL $\Delta V(r) = V_A(r) - V_B(r)$ (alloy, host) $\sim \frac{B\cos(D_F r + \phi_F')}{r^3}$

ELECTRIC FIELD $\mathcal{E}(r)$ $\sim$ "

HOST ENERGY LEVELS $\Delta\epsilon_\lambda$ $\sim$ " etc...

THESE LONG RANGE OSCILLATIONS DETERMINE LONG RANGE PAIR INTERACTIONS BETWEEN IMPURITIES (in a first order calc a point charge $Z'\delta(r-R)$ interact with the impurity at its origin with the energy $\Delta E(R) = Z'\Delta V(R) \sim \frac{\cos(D_F r + \phi_F)}{r^3}$)

WHICH DETERMINE SHORT RANGE ORDER (equil)

Annex [redacted] II 1

(a) Single impurity in a non deg. T.B. band

A (A, B) transition metals (for ex) 'd' bands

(a) assumption:

- A is characterized by the potential $\Delta V(1)$
- ΔV is mostly localized on A so that

$$\langle\lambda|\Delta V|\mu\rangle \simeq \Delta V\,\delta_{\lambda\mu}\,\delta_{\lambda 0} \quad (11)$$

or: $\Delta V = \Delta V\,|0\rangle\langle 0|$; $\Delta V = \epsilon_A - \epsilon_B$

(b) change in density of states

From the result of (84 p56 where $H_{eff}\to H_0$, $\Sigma\to\epsilon_B$)

$$\langle 0|G|0\rangle = \frac{G^0(0)}{1-\Delta V\,G^0(0)} \quad \text{where} \begin{cases}\langle 0|G^0|0\rangle = G^0(0) & (12)\\ G^0 = \frac{1}{z - H_0} & (H_0 \text{ host})\end{cases}$$

$$\langle\lambda|G|\lambda\rangle = G^0(0) + G^0(\lambda)^2\frac{\Delta V}{1-\Delta V G^0(0)} \quad \text{where } \langle\lambda|G^0|0\rangle = G^0(\lambda) = \langle 0|G^0|\lambda\rangle$$

The total density of states is:

$$N\,n(\epsilon) = -\frac{\mathrm{Im}}{\pi}\sum_\lambda \langle\lambda|G(\epsilon+i0)|\lambda\rangle \quad (13)$$

$$= -\frac{\mathrm{Im}}{\pi} N\left[G^0(0) + \frac{\Delta V}{1-\Delta V G^0(0)}\sum_\lambda G^2(\lambda)\right]$$

By definition: $\sum_\lambda |\lambda\rangle\langle\lambda| = 1$ (complete set)

$$\sum_\lambda G^2(\lambda) = \sum_\lambda \langle 0|G|\lambda\rangle\langle\lambda|G|0\rangle = \langle 0|G^2|0\rangle = -\langle 0|\frac{dG}{d\epsilon}|0\rangle$$

$$G^2(z) = \frac{1}{(z-H)^2} = -\frac{d}{dz}\frac{1}{z-H}$$

so that:

$$N\,\Delta n(\epsilon) = +\frac{\mathrm{Im}}{\pi}\frac{\Delta V}{1-\Delta V G^0(0)}\frac{d}{dz}G^0(z,0)\Big|_{z=\epsilon+i0}$$

$$N\,\Delta n(\epsilon) = -\frac{\mathrm{Im}}{\pi}\frac{d}{dz}\mathrm{Log}\,(1-\Delta V G^0(z,0))\Big|_{z=\epsilon+i0} \quad (15)$$

(c) Friedel's rule (in a metal)

THE TOTAL NUMBER OF DISPLACED STATES (BY THE IMPURITY IS (Friedel's rule)

$$\Delta Z = N\int_{-\infty}^{\epsilon_F}\Delta n(\epsilon)\,d\epsilon = \frac{1}{\pi}\mathrm{Arg}\,(1-\Delta V G^0(\epsilon_F+i0,0)) = \frac{\delta(\epsilon_F)}{\pi}$$

where $\delta(\epsilon_F) = \mathrm{Im}\,\mathrm{Log}\,(1-\Delta V G^0(\epsilon_F+i0,0))$ (16a)

(d) ΔV, determ:

ΔV is then determined by the Friedel's rule:

$\Delta Z = \delta(\epsilon_F)/\pi$ (16 b)

i.e when we know $G(\epsilon_F+i0,0)$ i.e. $n^0(\epsilon)$ of the host

recall!

$$G^0(\epsilon_F+i0,0) = -i\pi\,n(\epsilon) + \mathcal{P}\int\frac{n(\epsilon')\,d\epsilon'}{\epsilon-\epsilon'} \quad (17)$$

(As a first step, the screening is entirely known with this approximation of localized potential. But the result is not consistent since the localized potential distroys the Friedel's oscillations around the impurity

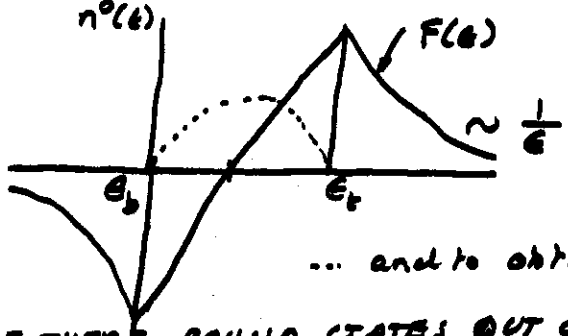
Note: Usually, two simple approximations to obtain the screening charge:
(i) the perturbation theory; it's self consistent but only valid for small δ or Δv or ΔZ
(ii) the localized potential approximation (this section) valid for all values of δ but, not consistent

---

(9) bound states

- For simple bands densities $n^0(\epsilon)$:

- IT'S EASY TO COMPUTE $F(\epsilon) = \mathcal{P}\int \frac{n(\epsilon')}{\epsilon-\epsilon'} d\epsilon'$ (numerically) ...



... and to obtain $\delta(\epsilon_F) \Rightarrow \Delta v$

- ARE THERE BOUND STATES OUT OF THE BAND ENERGIES? $A_\lambda \sim e^{-\kappa|\lambda|}$

i.e $\begin{cases} \psi(r) = \sum A_\lambda \phi_\lambda(r) \\ \mathcal{H}\psi = \epsilon\psi \end{cases}$ (19a) $\epsilon \notin [\epsilon_b, \epsilon_t]$?

$\mathcal{H} = \mathcal{H}_0 + \Delta v$

$\Rightarrow (\epsilon - \mathcal{H}_0)\psi = \Delta v \psi$ or $\psi = G(\epsilon)\Delta v \psi$ (19b)

or multiplying by $\langle 0|$ (19b)

$A_0 = \langle 0|G(\epsilon)|0\rangle \Delta v A_0$ (cf (11))

$A_0 \neq 0 \Rightarrow$ $\boxed{F(\epsilon)\Delta v = 1}$ CONDITION TO HAVE A BOUND STATE (19)

- bound states if Δv is large that this equation has a solution

For $F(\epsilon)$ or n^0: $\Delta v > 0$ when Δv of a bound state appear (see fig) first at the band edge for $\Delta v_c = F(\epsilon_t)$

$\Delta v < 0$ bound states of $\Delta v < F(\epsilon_b)$

- Extension: For $\boxed{\Delta v' < \Delta v < \Delta v_c}$ there is a bound state at the energy:

$F(\epsilon) = 1/\Delta v$

Multiplying (18b) by $\langle \lambda|$ we obtain:

$\boxed{A_\lambda = G(\epsilon_k, \lambda) A_0}$ (20)

ϵ_k

$G(\epsilon_k, \lambda) = \langle 0|G(\epsilon_k)|\lambda\rangle = \sum_k \frac{\langle 0|\psi_k\rangle\langle\psi_k|\lambda\rangle}{\epsilon_F - \epsilon_k}$ (21)

FOR PURE METALS, T.B. $\Rightarrow \psi_k(r) = \frac{1}{\sqrt{N}}\sum_\lambda e^{ikR_\lambda}\phi_\lambda(r)$

$\Rightarrow G(\epsilon_k, \lambda) = \frac{1}{N}\sum_k \frac{e^{ikR_\lambda}}{\epsilon_F - \epsilon_k}$ (22)

$G(\epsilon_k, \lambda)$ is decreasing exponentially at large $|\lambda|$:

$\epsilon_k \simeq \epsilon_b + \alpha k^2 \quad \alpha > 0$ (23)

$G(\epsilon_k, \lambda) \sim \int \frac{e^{ikR_\lambda}\, dk}{\epsilon_k - \epsilon_b - \alpha k^2} \sim \int \frac{e^{ikR_\lambda}}{\kappa^2 + k^2} dk$

$\boxed{\kappa^2 = \frac{\epsilon_b - \epsilon_k}{\alpha}}$ (24) $\sim \frac{e^{-\kappa|\lambda|}}{|\lambda|}$ or $\sim e^{-\kappa|\lambda|}$!

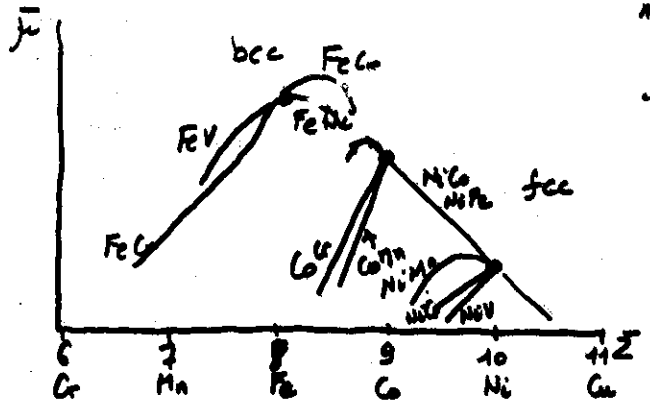
$\boxed{A_\lambda \sim A_0 e^{-\kappa|\lambda|}}$ (25)

A_0 determined by normalization condition !

- NOTE THAT THE EXTENSION TENDS TO Δv_c INFINITE ($\kappa \to 0$) when $\epsilon_k \to \epsilon_b$ or when the bound state energy tends towards the band edge energy ϵ_b (or ϵ_t) !

2. A simple example: alloys of transition metals; interpretation of the Pauling Slater curve.

1. The magnetic moments (per atom) $\bar{\mu}(c)$ of alloys $A_{1-c}B_c$ show systematic trends which can be easily expressed in terms of the existence or non existence of bound states



"Pauling Slater"

These magnetic moments are normalized vs. the average number of electrons of the alloy in the Pauling Slater curve

Let us consider only the case of nickel alloys

(a). HOST NICKEL IS A STRONG FERROMAGNET i.e. $n_\uparrow = 5$ $\quad n_\downarrow = 4.4 \Rightarrow m = 0.6\,\mu_B$.

(b) FOR SMALL ΔZ VALUES i.e. FOR POTENTIALS SO SMALL THAT THERE ARE NO BOUND STATES we have $\Delta Z_\uparrow = 0$ (occupied)

i.e. there is no change in the number of states in the $\uparrow$ band; it was full, it's still full (The density of states is deformed but all the states are still occupied!)

From Friedel's rule:

$$\Delta Z = \Delta Z_\uparrow + \Delta Z_\downarrow$$

$\Rightarrow \Delta Z_\uparrow = 0$, $\Delta Z_\downarrow = \Delta Z$

IT'S OBSERVED (see curve) for Ni Co, Ni Fe and

Ni Mn (low concentrations):

$$\bar{\mu}(c) = \mu_{Ni} + c[\Delta Z_\uparrow - \Delta Z_\downarrow]\mu_B \qquad (2c)$$

$$= \mu_{Ni} + \Delta Z\, \mu_B \quad \begin{pmatrix} Co & \Delta Z = -1 \\ Fe & \Delta Z = -2 \end{pmatrix} \ldots$$

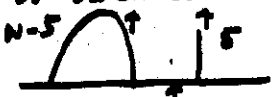
(c) for large ΔZ values, we observe deviations from this law (ex Ni Cr, Ni V.) i.e. there are non zero values of $\Delta Z_\uparrow$

(from expt we can deduce $\Delta Z_\uparrow$

(2d) $\begin{cases} \Delta Z = \Delta Z_\uparrow + \Delta Z_\downarrow \text{ (known)} \\ \frac{d\bar{\mu}}{dc}(c=0) = \mu_B(\Delta Z_\uparrow - \Delta Z_\downarrow) \end{cases} \Rightarrow \Delta Z_\uparrow$ (expt) $-5 < \Delta Z_\uparrow < 0$

(d). $\Delta Z_\uparrow$ can only be different from zero if some states have been repelled from the "d" band at energies $\varepsilon_k > \varepsilon_F$

If there is such a "d" level:



$\Delta Z_\uparrow = -5$!

(d). However, this ε_F level is degenerate with 'sp' bands so that there is a virtual bound state:

which is partially occupied and $\Delta Z_\uparrow$ is non integer

$\Rightarrow$ this has been also observed for other alloys! (with elts of 2nd and 3rd series...)

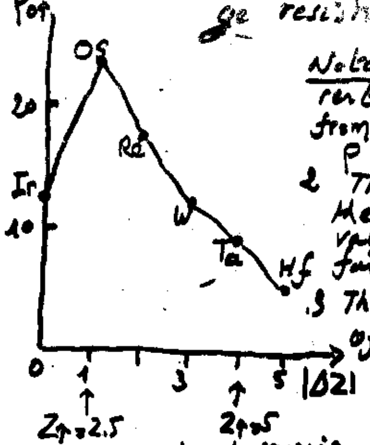
Note

1. Note that the physical properties of the alloys with V.B.'s are quite different from the others. The bound states are extended (not far from ε_F, then the Fermi energy) so THAT THE MAGNETIZATION IS MORE EXTENDED FAR FROM THE IMPURITY ($\sim \exp -\kappa\lambda$ $\kappa \sim 10\text{Å}^{-1}$!)

This extension has been measured by neutron diffusion

2. The extending suggests that the validity of the model for disorder (neglect of fluctuations of ε_i) will not be very good in such concentrated alloys (cf below)

3 The equivalence of v.b.s is clearly apparent experimentally by (a) large specific heat coefficients when the v.b.s sits at the Fermi level (Ni Rh for example) (b) large resistivities in the ↑ band for these alloys …



Max of resistivity coming from the v.b.s in the majority spin bands.

Note 1 The resistivities in ↑ and ↓ bands are different so that the observed resistivity (T = 0 K) results from the conduction in parallel of ↑ and ↓ bands:

$\rho = \rho_\uparrow \rho_\downarrow / \rho_\uparrow + \rho_\downarrow$.

2 The resistivities ρ_σ can be deduced by a study of the resistivity of ternary alloys $\rho(c_1, c_2)$ (Ni A B) varying c_1, c_2 and B, $\rho(c_1, c_2)$ being not a linear function of c_1, c_2 even if $\rho_\sigma(c_1, c_2) = c_1\rho_{1\sigma} + c_2\rho_{2\sigma}$ are.

3 The resistivity $\rho_\sigma = \frac{m}{n e^2} \times \frac{1}{\tau}$ comes from the scattering (mass m, nb = n) of conducting electrons in "d" bands.

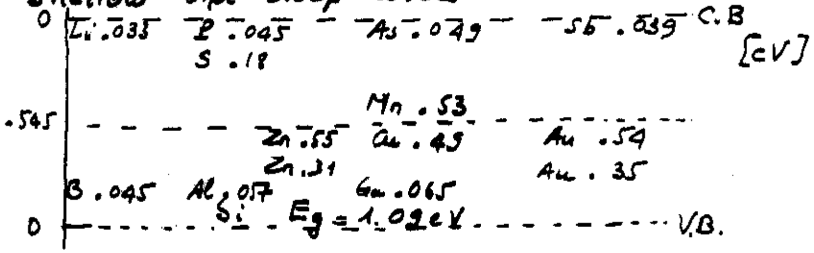
$\frac{1}{\tau} \sim \frac{2\pi}{\hbar} |V_{sd}|^2 n_{d\sigma}(\varepsilon_F, \sigma)$ where $n_{d\sigma}(\varepsilon_F, \sigma)$ is the density of states at the Fermi level of 'd' states on the impurity ($\sim \frac{\Delta}{\pi(\varepsilon_{d\sigma}^2 + \Delta^2)}$) MAX WHEN v.b.s at E_F (Rh)

B II CONCENTRATED ALLOYS OF TRANSITION METALS

See Alloys of TM

3 ELECTRONIC STRUCTURE OF DEFECTS IN 1/2 COND.

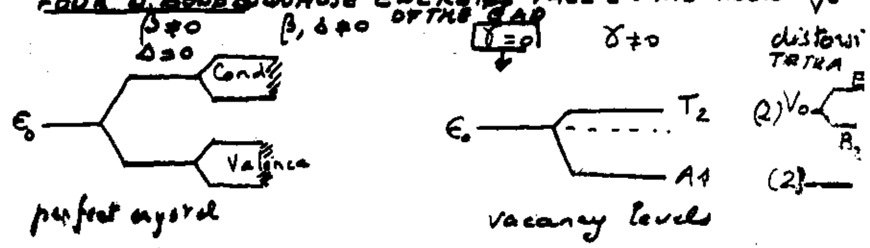
1. Shallow and deep levels



- shallow levels ⟹ extended part^{ons} ⟸ Bloch repr eff mass appr^{on}
  $\frac{m^*}{m} = .3$ $\epsilon = 11.7$ $E_B \simeq 10^{-2}$ eV, $a_{eff} \simeq 160 a_0$
- Deep levels ⟹ localized part^{ons} ⟸ direct space calc^{on}

2 The silicon vacancy

1. molecular model of the vacancy in a diamond type cry
FOUR D. BONDS WHOSE ENERGIES FALL IN THE MIDDLE OF THE GAP



A_1 $\sigma = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)$

$T_2 \begin{cases} t_x = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4) \\ t_y = \frac{1}{2}(-\phi_1 + \phi_2 + \phi_3 - \phi_4) \\ t_z = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 - \phi_4) \end{cases}$

⇑ MODIFIED BY DISTORSION AND BY MULTIPLET SPLITTING

- TB and S.C calculations

	TBA	Baraff	Pantelides
A1	-.88	-1.1	-.6
T2	.12	+.7	+.7

(Kauffer D) (eV)

& Green function method or recursion method

II 11

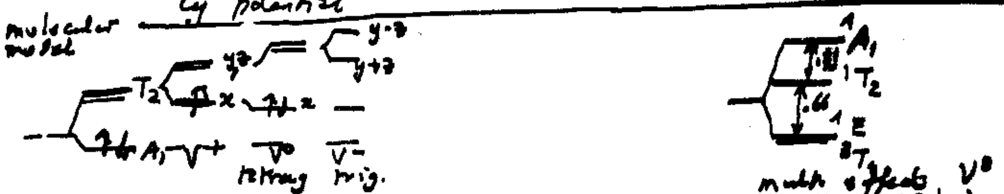
■ A lot of calculations (see References) were done for the vacancy in Si. The electronic structure is characterized by: (i) A LOCALIZED STATE T_2 IN THE GAP (ii) A RESONANT STATE NEAR THE TOP OF THE V.B. (see table)

- Self consistent calculations are needed to investigate the stability of the charge states (see Baraff et al)
- Multiplet effects and distortion effects must be taken into account... (see below)

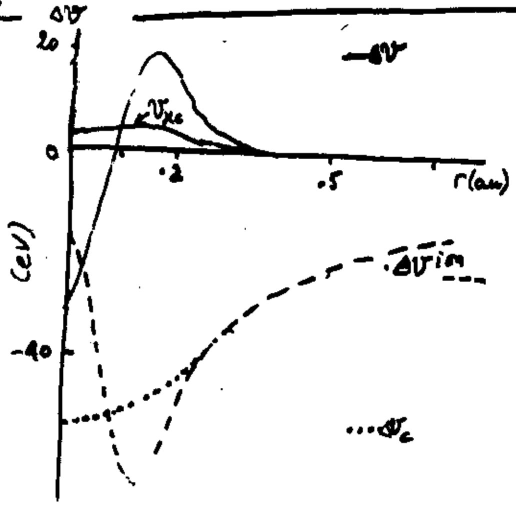
N.B.

- high density of Si valence el ⇒ short range of the vacancy potential

molecular model



HOZE MODEL



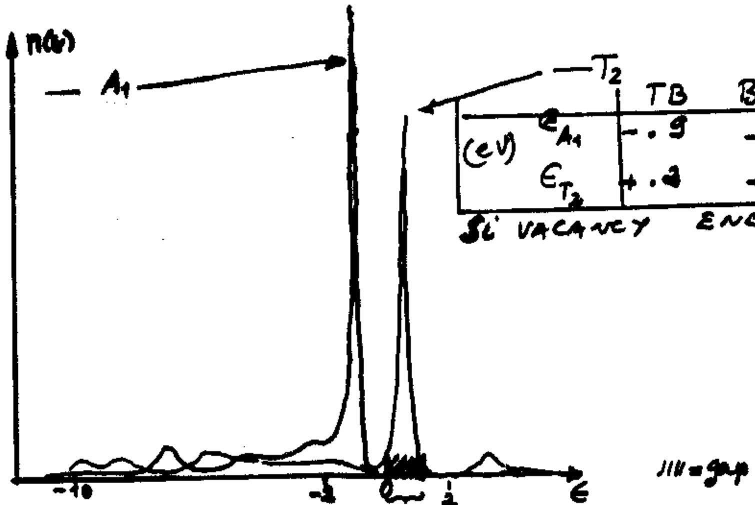
$\Delta V = \Delta V^{ion} + \Delta V^{el}$
$\Delta V^{el} = V_i^{c} + \Delta V^{xc}$

- ΔV^c related to $\Delta n(r)$ by Poisson eqn
- ΔV^{xc} by Slat $X\alpha$ approximation (Baraff et al)

n(r) calc self consistently by Thomas Fermi Approximation (Lannoo) approximating

$n(r) = \frac{1}{3\pi^2} k_F^3(r)$ $\frac{K^2 k_F^2(r)}{2m} = E_F - V(r)$

Fig 11



		TB	Baraff	Pantel.
(eV)	ϵ_{A_1}	−.9	−1.1	−.6
	ϵ_{T_2}	+.2	+.7	+.8

Si VACANCY ENERGY LEVELS

Local density of states for the A_1 and T_2 D.B of the Si vacancy (Kauffer et al PRB 8 (77) 4107). A_1 is a resonance in the V.B, T_2 is a localized level. RECURSION METHOD. (Note the resolution)

(B) CORRELATION EFFECTS

In the LDA:

$\epsilon_i = \frac{\partial E}{\partial n_i}$ ⇒ $\mathcal{E}_1(V^{2+} + e^- \to V^+) = \int_0^1 (\epsilon_n(T_2) - \epsilon(\Gamma))\,dn$ $e^-(\Gamma)$ $T_2^{\downarrow}$

E total energy
n_i = occupation number of an energy level ϵ_i

$\mathcal{E}_2(V^+ + e \to V^0) = \int_0^1 (\epsilon_{n+1}(T_2) - \epsilon(\Gamma))\,dn$

⇓

$U = \epsilon_2 - \epsilon_1 = \int_0^1 (\epsilon_{n+1}(T_2) - \epsilon_n(T_2))\,dn \simeq \epsilon_{3/2} - \epsilon_{1/2}$

⇓

$U \simeq 0.20 - 0.25\,eV$

(C) ANDERSON NEGATIVE U SYSTEM: V^+ ⇐ RELAXATION

V^+ unstable: $2V^+ \to V^0 + V^{2+}$ from J. Teller RELAXATION

linear J.T effect ⇒ $\Delta E(q, n) = -n\Gamma q + kq^2$

Γ: JT coupling, q displacement of one of the 4nn, k lattice constant

$\frac{\partial \Delta E}{\partial q} = 0 \Rightarrow \Delta E_0 = -n^2\frac{\Gamma^2}{4k}$; $q_n = n\Gamma/2k$

V^+ UNSTABLE IF $2\,\Gamma^2/4k < 4\Gamma^2/4k - U$

Annex 3

SPECTRAL BOUNDS IN DISORDERED SYSTEMS.

bounds related to the possibility of building up bonding and antibonding state i.e. to topological properties

1 HADAMARD GERSCHGORIN CRITERION

1 non deg TB band

$$(\epsilon - \epsilon_\lambda) A_\lambda = \sum_{\mu \neq \lambda} \beta_{\lambda\mu} A_\mu$$

$$|\epsilon - \epsilon_\lambda| \leq \sum_{\mu \neq \lambda} |\beta_{\lambda\mu}| \, |A_\mu / A_\lambda|$$

consider λ | $|A_\lambda| \geq |A_\mu|$ $\forall \mu \Rightarrow$

$$|\epsilon - \epsilon_\lambda| \leq \sum_\mu |\beta_{\lambda\mu}|$$

$$\Downarrow$$

$$\epsilon \in \bigcup_\lambda \mathcal{D}_\lambda \qquad \mathcal{D}_\lambda = \{z \mid |z - \epsilon_\lambda| \leq \sum_{\mu \neq \lambda} |\beta_{\lambda\mu}|\}$$

If we have only a perfect crystal, $\epsilon_\lambda = 0 \Rightarrow |\epsilon| \leq z|\beta|$
$\beta_{\lambda\mu} \neq 0$ only betw. n.n.

2 PERRON FROBENIUS THEOREM

$\underline{\underline{x}} = \{x_{\lambda\mu}\}$, $x_{\lambda\mu} > 0$ $\Rightarrow \lambda_{max} = \sup \lambda$ (where λ is an eigenvalue of x) positive real and non degenerate

$$\min_\mu \sum_\lambda x_{\mu\lambda} \leq \lambda_{max} \leq \max_\mu \sum_\lambda x_{\lambda\mu}$$

Ex: $x_{\lambda\lambda} = \epsilon_\lambda$ $\quad x_{\lambda\mu} = -\beta_{\lambda\mu}$ $\quad \lambda_{max} = -\epsilon_{min} \Rightarrow$
The lower state corresponds always to a non degenerate bonding state (for crystal and for any disordered state)

3 MIN MAX THEOREM (Courant-Hilbert Vol 1)

h = hermitian operator
- order the eigenvalues $\lambda_1 \geq \lambda_2 \ldots \geq \lambda_N$
- define a subspace generated by k-1 states $|y_i\rangle$, $\mathcal{E}_{k-1}$
- calculate $\max_{|x\rangle \in \mathcal{E}_{k-1}} \langle x|h|x\rangle / \langle x|x\rangle$
- minimize this value when varying the $\mathcal{E}_{k-1}$ state; then:

$$\lambda_k = \min_{\mathcal{E}_{k-1}} \max_{x \in \mathcal{E} - \mathcal{E}_{k-1}} \langle x|h|x\rangle / \langle x|x\rangle$$

C1: If $H^{(m)}$ is the projection of H in the space $\mathcal{E} - \mathcal{E}^{(m)}$ of dimension m; note $\lambda^{(m)}$ its eigenvalues and $|y_i\rangle$ a basis set of $\mathcal{E}^{(m)}$ $1 \leq i \leq m$

$$\boxed{\lambda_{k+m} \leq \lambda_k^{(m)} \leq \lambda_k} \quad (C1)$$

- $\max_{\mathcal{E} - \mathcal{E}^{(k)}} \dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq \max_{\mathcal{E} - \mathcal{E}^{(k)}} \dfrac{\langle\psi|H^{(m)}|\psi\rangle}{\langle\psi|\psi\rangle}$ $\quad$ ($\langle\psi|H^{(m)}|\psi\rangle = \langle\psi|H|\psi\rangle$, $\langle y_i|\psi\rangle = 0$)
  Relative constraints $\Rightarrow$ $k \to k + p$ (we add p constraints)
  $\Rightarrow \lambda_k^{(m)} \leq \lambda_k$
- $$\lambda_k^{(m)} = \min_{\mathcal{E}_k} \max_{\substack{\langle y_i|\psi\rangle = 0 \\ \langle y_j|\psi\rangle = 0}} \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq \lambda_{k+m} = \min_{\mathcal{E}_k, \mathcal{E}_m} \max \langle \ldots$$

C2 If $V = V^+$ is positive ($\langle y|V|y\rangle \geq 0$ $\forall y$)

$$\lambda_k(H+V) \geq \lambda_k(H) \qquad (C2)$$

Applications

(a) disordered alloy : $A_c B_{1-c}$ only DD ($\epsilon_A - \epsilon_B \neq 0$) GAP.
- project on the space $\mathcal{E}^{(A)}$ spanned by the A atoms (dim $\mathcal{E}^A = cN_a$) $\mathcal{E}^{(B)} = \mathcal{E} - \mathcal{E}^A$ and from (C1):

$$\epsilon_{k+N_a(1-c)} \leq \epsilon_k(H^{(A)}) \leq \epsilon_k(H) \qquad (\epsilon_k(H) = \epsilon_k)$$

- if H_A^0 is the hamiltonian of the pure metal A

$$\underbrace{\epsilon_{k+N_a(1-c)}(H_A^0)}_{\epsilon^0_{k+N_a(1-c)}} \leq \epsilon_k(H^{(A)}) \leq \underbrace{\epsilon_k(H_A^0)}_{\epsilon_k^0} \qquad (1)$$

since $(H_A^0)^{(A)} = H^{(A)}$
- if (for example) $\delta < 0$ $\quad H - H_A^0 > 0$ from (C2)

$$\epsilon_k(H_A^0) \leq \epsilon_k(H) \qquad (2)$$

- (1)+(2) $\Rightarrow$

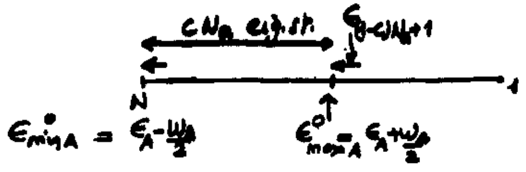
$$\underbrace{\epsilon_{k+(1-c)N_a}(H_A^0) \leq \epsilon_{k+N_a(1-c)}(H)}_{(C2)} \underbrace{\leq \epsilon_k(H_A^0) \leq \epsilon_k^0}_{(C1)}$$

$$\downarrow$$

- Hence:

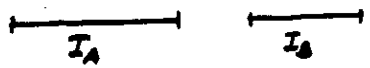
$$\begin{cases} \epsilon_N(H) = \epsilon_{min} \geq \epsilon^{(0)}_{min\,A} & (k = N_a c) \\ \epsilon_{1+N_a(1-c)} \leq \epsilon^0_{max\,A} & (k = 1) \end{cases}$$

⇒ N_A states lie in $I_A \equiv [\epsilon_A - \frac{W_A}{2}, \epsilon_A + \frac{W}{2}]$.



⇒ $I = \{\epsilon\} \in I_A \cup I_B$

$I_A = \{\epsilon^0_{An}\}$ $I_B = \{\epsilon^0_{Bn}\}$



⇒ gap if $I_A \cap I_B = \emptyset$

⑥ L.F.T.W. model

Th: if $H = H^0 + V$, H_0 and V having (resp. h_k and v_l) as eigenvalues, the eigenvalues ϵ_α of H are such that

$$\epsilon_\alpha \in \bigcup_k \mathcal{D}_k, \quad \epsilon_\alpha \notin \bigcap_k d_k$$

$$\mathcal{D}_k = \{z \mid |z - h_k| \le \max_l |v_l|\}$$

$$d_k = \{z \mid |z - h_k| < \min_l |v_l|\}$$

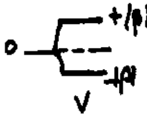
Proof: $(\epsilon_\alpha - H^0)|\psi_\alpha\rangle = \epsilon_\alpha|\psi_\alpha\rangle$ $\quad \langle\psi_\alpha|\psi_\alpha\rangle = 1$

$$\langle\psi_\alpha|(\epsilon - H^0)^2|\psi_\alpha\rangle = \langle\psi_\alpha|V^2|\psi_\alpha\rangle$$

$$\Rightarrow \min_k |\epsilon_\alpha - h_k| \le \max_l |v_l|$$

$$\max_k |\epsilon_\alpha - h_k| \ge \min_l |v_l| \qquad \text{QED}$$

Application LFWT model sp^n $n = 2, 3$



$V = \beta \sum_{i \neq i'} |i j\rangle\langle i' j|$

$H^0 = \Delta \sum |i j\rangle\langle i j'| = \epsilon_s \sum |s i\rangle + \epsilon_p \sum |p_i\rangle$

$\mathcal{D} = \{z \mid |z - \epsilon_s| \le |\beta|\}$

$d = \{z \mid |z - \epsilon_p| \le |\beta|\}$ ⇒ $\epsilon_\alpha \in \mathcal{D} \cup d$, $\notin \mathcal{D} \cap d$

$E_g \ge |(n+1)\Delta - 2|\beta||$ ⇒ ∃ energy gap in the atomic limit $(n+1)|\Delta| > 2|\beta|$

— covalent — $(n+1)|\Delta| < 2|\beta|$

- In the alternant lattices E_g is equal to its max value E_g^0
- Otherwise the bounds are not attained $E_g > E_g^0$
- For example the covalent gap increases when the structure of the amorphous state contains some closed circuits with an odd number of bonds

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