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SPRING COLLEGE IN MATERIALS SCIENCE

ON

"METALLIC MATERIALS"

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ELECTRONIC STRUCTURE AND PHASE STABILITY
(Part III)

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III ELECTRONIC STRUCTURE OF ORDERED AND DISORDERED SYSTEMS - GENERAL TRENDS -

III 1 Introduction : THE TIGHT BINDING METHOD

1 We use the simplest model to discuss the general features of ORDERED and disordered systems :

'THE TIGHT BINDING METHOD'

- This method is sufficient to exhibit the general trends in terms of few physical parameters.
- It allows to get a reasonable description of the 'd' band structure of TM (transition metals) and of the energetics of metals alloys and compounds
- Moreover, it's possible now to determine from 1st principles calculations (augmented meth.) T.B. parameters in a simple way

2 We will consider the following points :

- determination of the local electronic structure (recursion method or moments method)
- discussion of the general features of the electronic spectra of ordered and disordered alloys, the role of topological and chemical order.

3 T.B model

In the following we will consider mostly the simplest 'one orbital per site(λ)' model :

$$\varphi_\alpha(r) = \sum_\lambda A^\alpha(\lambda)\,\phi(\lambda, r)$$

NOTATIONS: $\phi(\lambda) \equiv |\lambda\rangle$

We assume for simplicity that $\langle \phi(\lambda) | \phi(\mu) \rangle = \delta_{\lambda\mu}$

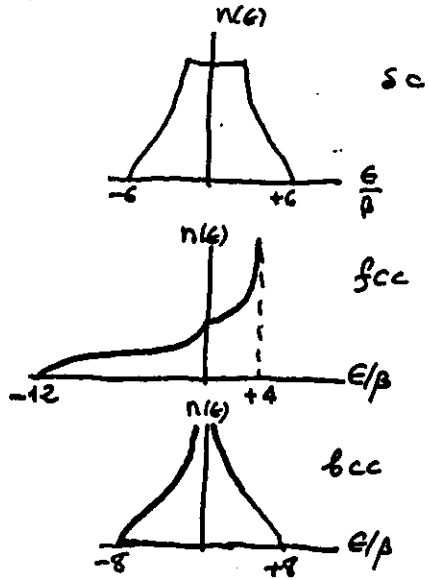
The matrix elements of h are (first simplest)

$\langle \lambda | h | \lambda \rangle = \epsilon_\lambda$ energy levels

$\langle \lambda | h | \mu \rangle = t(\lambda\mu)$ or $\beta(\lambda\mu)$ TRANSFER INTEGRAL

In the simplest situation, it's assumed that the t are non zero only for nearest neighbours so that the electronic structure is determined only by :

{ Structure ; ϵ_0 ; W bandwidth or β



← THESE D.O.S. FOR 1 ORBITAL PER SITE ARE VERY ≠ FROM ACTUAL D.O.S IN TM (OR NORMAL METALS.!!). (see below)

$|\epsilon - \epsilon_0| \leq \pi|\beta|$ ← Hadamard Gershgorin criterion (later)

coordination number ← perfect crystal

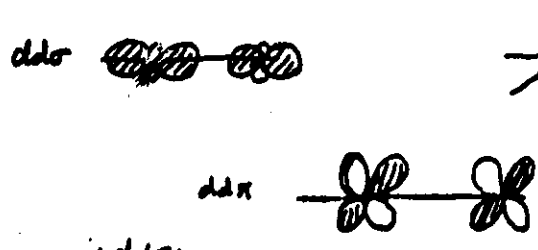
② Example 2 T.B 'd' Band of TM.

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

$\Gamma_{25'}$ Γ_{12}

cubic symmetry $\epsilon_i(\lambda) = \epsilon_i$ $\epsilon(\Gamma_{25'})$ ⇓ ≷ $\epsilon(\Gamma_{12})$

$\beta_{ij}(l-n)$ → $dd\sigma$, $dd\pi$ $dd\delta$



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

NOTE THAT WITH THESE ASSUMPTIONS, THE D.O.S. ARE ≡ TO THOSE

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

(a) density of states, local density of states — density of states (at

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

$\rightarrow$ relation with the resolvent

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

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

$\rightarrow$ electronic density and local density of states

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

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

$\rightarrow$ TBA and partial densities of states

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

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

$$n_{ij}(\epsilon,\lambda,\mu) = \Big\{\sum_\alpha A_i^{\alpha*}(\lambda)\,A_j^\alpha(\mu)\,\delta(\epsilon-\epsilon_\alpha) + (\text{c.c. with } \lambda\leftrightarrow\mu)\Big\}\frac{1}{2}$$

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

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

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

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

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

$\rightarrow$ Perfect crystal

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

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

(b) Problem:

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

recall that the direct diagonalization of the hamiltonian in the Bloch representation has:

- difficult for complex structures (AlSi, Amorphous, surfaces, ...)
- cannot be used for disordered systems

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

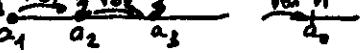
- moments methods (Gyorffy Lechmann and Stocks and Williams)
- recursion method (Haydock, Heine, Kelly, ...)

in the recursion method, one obtains 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 ($\langle n|h|m\rangle \equiv 0$ $|n-m|>1$)

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



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

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

$$= G^0 + G^0 v\, G$$

Example: 1 T.B band $\epsilon_{ii}=0$; $d=1$

G^0 absorption of an array at the end of a $1/\infty$ chain

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

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

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

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

⑥ RECURSION METHOD

$h = \sum_{\alpha}^{\infty} \epsilon_\alpha |\alpha\rangle\langle\alpha| + \sum_{\alpha\neq\beta}^{\infty} \beta_{\alpha\beta} |\alpha\rangle\langle\beta|$ → $n(\epsilon, \Delta\epsilon)$, $n(\epsilon, \Delta\epsilon \to 0)$??

1. Starting from a localized state $|1\rangle$ build a great orthogonal basis set $|n\rangle$ from the recurrence relations:

$$\begin{cases} |1\rangle = |0\rangle \\ |2\rangle = h|1\rangle - a_1|1\rangle \quad (2|1)=0 \Rightarrow a_1 = (1|h|1)/(1|1) \\ |3\rangle = h|2\rangle - a_2|2\rangle - b_1|1\rangle ; \ (2|2)=(3|1)=0 \\ \dots\dots \\ |n+1\rangle = h|n\rangle - a_n|n\rangle - b_{n-1}|n-1\rangle ; \ (n+1|2)=0 \quad r\le n \\ \dots\dots \end{cases}$$

a_n and b_{n-1} are defined by (1)(2) below and $(r|n+1)=0$ $\forall r\le n$:

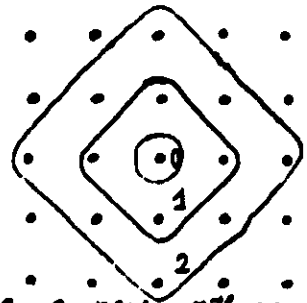
+ $\boxed{a_n = \dfrac{(n|h|n)}{(n|n)} \in \mathbb{R}}$ ← $(n|n+1)=0$ (1)

+ $(m|n+1) = 0 \quad \forall m \le n-1$ since $\begin{cases} h|n\rangle \supset |n\pm 1\rangle \text{ if} \\ (r|n)=0 \ \forall r\le n-1 \end{cases}$
(by recurrence) $(m|h|n\rangle = [(m|h]|n\rangle = 0$ ←

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

+ $\boxed{\dfrac{(n+1|h|n)}{(n-1|n-1)} = b_{n-1}}$ ← $(n-1|n+1)=0$ (2)

+ $|1\rangle, |2\rangle, \dots |n\rangle$ spread out further and further away from the central $|0\rangle$ where local density of states we describe



Up to between 1st and 2nd n.n.

+ They define a new orthonormalized set $\frac{|n\rangle}{\sqrt{(n|n)}}$; in this representation

• define (H_{nn}): $H_{nn} = \dfrac{(n|h|n)}{(n|n)}$, $H_{n,n} = \dfrac{(n-1|h|n)}{\sqrt{(n-1|n-1)(n|n)}}$ $n \ge 1$

$\begin{cases} \dots \\ = a_n \\ \dots \end{cases}$ $= \sqrt{\dfrac{(n-1|n-1)}{\dots}} \cdot b_{n-1}$

$\overbrace{(n-1|}\ h|n\rangle = [(n|+a_n(n-1|+b_{n-1}(n-2|]|n\rangle = (n|n\rangle$

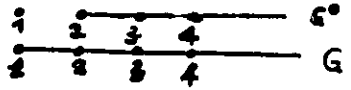
$H_{n+1,n} = b_{n-1}\sqrt{\dfrac{(n+1|n+1)}{(n|n)}} = \sqrt{\dfrac{(n|n)}{(n-1|n-1)}}$ → $\begin{cases} b_{n-1} = \dfrac{(n|n)}{(n-1|n-1)} \in \mathbb{R}_+ \\ H_{n-1,n} = \sqrt{b_{n-1}} \end{cases}$

← equivalent semi-infinite linear chain

2. Introduce the resolvent

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

relate G_{00} to G_{22} (System equations are previously)



$$\begin{cases} G_{11} = G^\circ_{11} + G^\circ_{11}\sqrt{b_1}G_{20} \\ G_{20} = G^\circ_{22}\sqrt{b_1}G_{21} \end{cases} \Downarrow \qquad \begin{cases} G^\circ_{00} = \dfrac{1}{z-a_1} \\ G^\circ_{22} = g_2 \end{cases}$$

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

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 $-\frac{1}{\pi}\mathrm{Im}\, G_{00}(\epsilon+i0) = n_0(\epsilon)$ is given by a continuous fraction:

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

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

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

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 (1952)

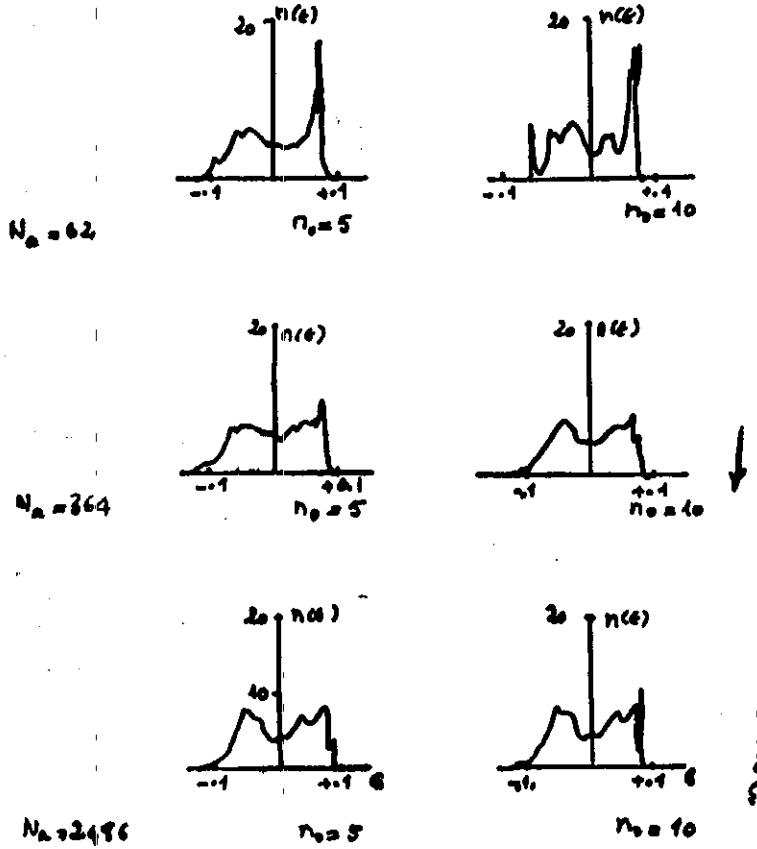
• When there is no gap (replace for $n > n_0$ a_n and b_n (resp) by a and b i.e:

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

...ch can be extended to off diagonal matrix elements of the Green function $G_{\lambda\mu}$

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

- The recursion method allows the calculation of properties of disordered systems (direct space calculation) - It is rapidly convergent ($\eta_0 \simeq 10, 15$)



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

For $N_a = 10^3$ at $n_0 = 10$, this density of states is the density of states of the d-band of infinite crystalline solids.

④ Spectral moments

⑧ $|z| \to \infty$ $(z \neq \epsilon_\alpha)$

$$G_{\lambda\lambda}(z) = \langle\lambda|\frac{1}{z-\hat{H}}|\lambda\rangle = \frac{1}{z} + \frac{\mu_1^\lambda}{z^2} + \frac{(\mu_2^\lambda)}{z^3} \cdots \quad (H^n)_{\lambda\lambda} = \mu_n^\lambda$$

(we dropped the degeneracy index for simplicity)

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

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

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

⑨ Examples

$\mu_0^\lambda = 1$ $\quad \mu_1^\lambda = \epsilon_\lambda$ $\quad \mu_2^\lambda = \epsilon_\lambda^2 + \sum_\beta \beta_{\lambda\beta}^2$ (non deg TB band)

↑ CENTER (choice 0) ↑ WIDTH

μ_3 comes from triangles → = 0 in ALTERNANT STRUCTURE FOR WHICH THERE IS NO TRIANGLES

→ ≠ 0 otherwise

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

⇒ $n(\epsilon) = n(-\epsilon)$ for alt lattice $(\epsilon_\lambda = 0)$

For non degenerate bands μ_p obtained by world counting techniques:

$$\mu_p = \nu_p \beta^p \quad \text{(all } \beta \text{ equals to for } n \text{ a)}$$

ν_p number of closed walks of length p

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

diamond structure $\nu_p = (p!)^2 \sum \frac{(2p)!}{(\alpha!)^4 (\beta!)^4}$ with $\alpha+\beta = p$

Otherwise: the use of a computer is required!

⑩ The band is characterized by: (i) μ_2 the average energy (ii) μ_2 the bandwidth, (iii) the asymmetry $\mu_3/\mu_2^{3/2}$

ALTERNANT STRUCTURES: Structures that can be partitioned in two subsets A and B, the nn of an A atom is a B atom and vice versa

ex: linear chain, diamond cubic, body centered cubic

④ The coefficients a_i, b_i are obtained from the moments

$a_1 = \mu_1 = 0$ (origin)
$b_1 = \mu_2$
$a_2 = \mu_3/\mu_2$
$a_3 = (\mu_4\mu_2 - \mu_2^3 - \mu_3^2)/\mu_2^2 \ldots$
....

$a_n = f(\mu_0, \ldots \mu_{2n-1})$
$b_n = f(\mu_0, \ldots \mu_{2n})$

III GENERAL FEATURES OF THE ELECTRONIC SPECTRUM OF CONCENTRATED ALLOYS

④ (a) choice of a simple band model (cf previously)

- "1 NON DEGENERATE TIGHT BINDING BAND" ISSUED FROM 1 "s" ORBITAL PER EACH SITE $\underline{i}$, $\phi(\underline{i},\varepsilon)$
THE WAVE FUNCTIONS FOR THE CRYSTAL ARE THEN IN L.C.O.A:

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

- WE ASSUME THAT:

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

AND WE DEFINE
THE ENERGY LEVELS: $\varepsilon_{\underline{i}} = \langle \phi(\underline{i}) | \mathcal{H} | \phi(\underline{i}) \rangle$ (61)
THE TRANSFER INTEGRALS: $\beta_{\underline{i}\underline{k}} = \langle \phi(\underline{i}) | \mathcal{H} | \phi(\underline{k}) \rangle$ (62)
FROM THE CRYSTALLINE HAMILTONIAN $\mathcal{H}$ $(\underline{i} \neq \underline{k})$

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

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

ARE OBTAINED FROM THE N EQUATIONS

$$(\varepsilon_{\underline{i}} - \varepsilon) A^{\alpha}(\underline{i}) + \sum_{\underline{k} \neq \underline{i}} \beta_{\underline{i}\underline{k}}\, A^{\alpha}(\underline{k}) \qquad \underline{i} = 1, \ldots N \qquad (63)$$

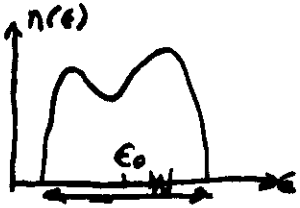
- THE SOLUTION IS OBVIOUS FOR A PURE METAL
i.e. WHEN $\varepsilon_{\underline{i}} = \varepsilon_0$ (whatever $\underline{i}$), $\beta_{\underline{i}\underline{k}} = \beta(\underline{i}-\underline{k})$

IT'S:

$$A^{\alpha}(\underline{i}) = \frac{e^{i\underline{k}\cdot\underline{i}}}{\sqrt{N}} \qquad , \varepsilon_{\underline{k}} = \varepsilon_0 + \sum_{\underline{i} \neq \underline{k}} \beta(\underline{i}-\underline{k}) e^{i\underline{k}\cdot(\underline{i}-\underline{k})} \qquad (64)$$

$\alpha = \underline{k}$

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!)

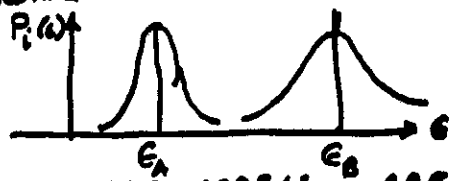
(b) Simple models for disorder.

FOR A GIVEN CONFIGURATION (i.e. FOR A SET OF VALUES OF p_i^A) THE DISORDERED STATE HAS TO BE REPRESENTED BY A CONSISTENT SET OF PARAMETERS

$|\phi(\lambda)\rangle$, ϵ_λ $\beta_{\lambda\lambda'}$

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

- FOR EXAMPLE, ϵ_λ DEPENDS NOT ONLY ON THE NATURE OF THE ATOM IN λ 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→∞)

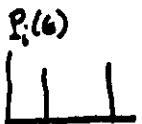


example.

- TWO SIMPLE MODELS ARE USED:

(i) ϵ_λ AND $\beta_{\lambda\lambda'}$ ARE ASSUMED TO BE ONLY DEPEND ON THE NATURE CHEMICAL OF THE ATOMS IN λ AND. THE ALLOY IS THEN CHARACTERIZED BY THE PARAMETERS:

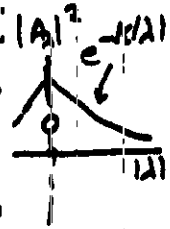
ϵ_A, ϵ_B ; $\beta_{AA}(\underline{\lambda})$, $\beta_{AB}(\underline{\lambda})$, $\beta_{BB}(\underline{\lambda})$



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

, 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 PROBABILITY. (number of electrons...)



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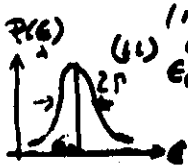


(ii) ϵ_λ ARE FLUCTUATING AROUND AND AVERAGE VALUE ϵ_0 AND $\beta_{\lambda\lambda'}$ ARE ASSUMED TO BE NON RANDOM.

- THE FLUCTUATIONS OF ENERGY LEVELS $\delta\epsilon_i$ ARE MUCH LARGER THAN THE FLUCTUATIONS WHICH OCCUR FROM THE NATURE OF ATOMS (RANDOM POTENTIAL)

- THE MODEL (i) IS USED TO DESCRIBE THE ELECTRONIC STRUCTURE OF TRANSITION ALLOYS (C.P.A).
- THE MODEL (ii) IS USED TOO 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)

(3) WE WILL DISCUSS ESSENTIALLY THE MODEL (i) WITH 2 NEAR. C

(a) ONE IMPURITY STATES (CAVITY) AB

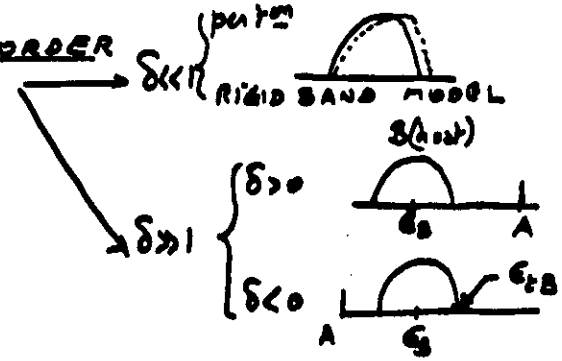
LET US STUDY QUALITATIVELY THE CASE OF "D.D." AND OF "O.D"

c.1 DIAGONAL DISORDER

TWO LIMITS

$N_A = N_B = N$

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



- WHEN δ IS SMALL THE PERTURBATION THEORY IS VALID AND EACH SATE IS DISPLACED BY:

$$\epsilon_k^A \to \Delta\epsilon_k^{B,A} = \langle \psi_k^B | \Delta V^{B,A} | \psi_k^B \rangle = \frac{1}{N} W \delta \quad (66)$$

THE PERTURBATION ΔV IS

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

WHEN A IS INTRODUCED IN B (0 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 0 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

$$|A_\lambda|^2 \sim \exp -\kappa|\lambda| \quad (67)$$

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 $\delta_c \sim 1$

c2 OFF DIAGONAL DISORDER.

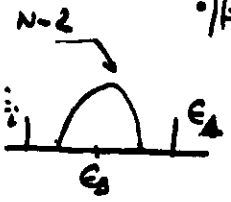
$\beta_{AB}=\beta'$ $\beta_{BB}=\beta$ $(\epsilon_A=\epsilon_B)$ (limited on the nearest neighbours)

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

R.B.M. $\epsilon_k^{B\to A}=\frac{1}{N}\Delta\beta(k)$ $\Delta\beta(k)\propto\sum_{\underline{\lambda}}\beta'(\underline{\lambda})\beta(\underline{\lambda})e^{i\underline{k}\cdot\underline{\lambda}}$

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

$|\psi_s\rangle=\frac{1}{\sqrt{n}}\sum|\phi(\underline{\lambda})\rangle$



THIS STATE MIXES WITH ϕ ON THE SITE OCCUPIED BY A WITH TWO {BONDING / ANTIBONDING} STATES WHOSE ENERGIES ARE

$\epsilon_l\simeq\epsilon_B-\beta'$ $\epsilon_u=\epsilon_B+\beta'$

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

. WHEN β'/β THEIR EXTENSION INCREASES

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

c3 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 $c\nearrow$ FOR D.D.

(NOTE: THE C.D. IS USEFUL FOR SUPERALLOYS!)

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

WE CAN EXPAND IN SUCC. POWERS OF P_λ or c:

$\Delta n(\epsilon,P_\lambda)=Nn_B(\epsilon)+\sum_{\underline{\lambda}}P_{\underline{\lambda}}\Delta n_A(\epsilon)+\frac{1}{2}\sum_{\underline{\lambda}\neq\underline{\mu}}P_\lambda P_\mu\Delta n_A(\epsilon,\underline{\lambda},\underline{\mu})+\dots$

OR AVERAGING OVER ALL CONFIGURATIONS:

$\Delta\bar{n}(\epsilon,c)=Nn_B(\epsilon)+Nc\,\Delta n_A(\epsilon)+\frac{1}{2}N\sum_{\mu\neq 0}\langle P_0P_\mu\rangle\Delta n_A(\epsilon,\underline{\lambda})+\dots$

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

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

$\Delta n_A(\epsilon,\underline{\lambda})$ — — —

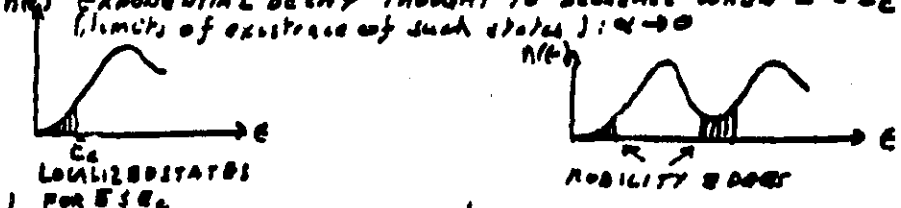
SEE REMARKS IN THIS LECTURES!!!

- In the case of strong disorder ($\delta \gg 1$) it's (more or less) intuitive that the sign (and the amplitude) of the wave function vary at random from site to site

Anderson finds that the states are localised when

$$\delta = \frac{\Gamma_{coord}}{W} > 5 \quad (\text{for } z = 6)$$

- When this condition is not satisfied only some of 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 $E \to E_c$ (limits of existence of such states): $\alpha \to 0$



IMPORTANT!

- THESE STATES DO NOT CONTRIBUTE TO THE CONDUCTIVITY (WHEN THE CONDUCTIVITY COMES FOR $T \to 0$ AND WHEN E_F IS IN A LOCALIZED REGION WE HAVE AN INSULATOR!).

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)

(5) (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 $\underline{k}$, 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.

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

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

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

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

$\lambda \sim a$

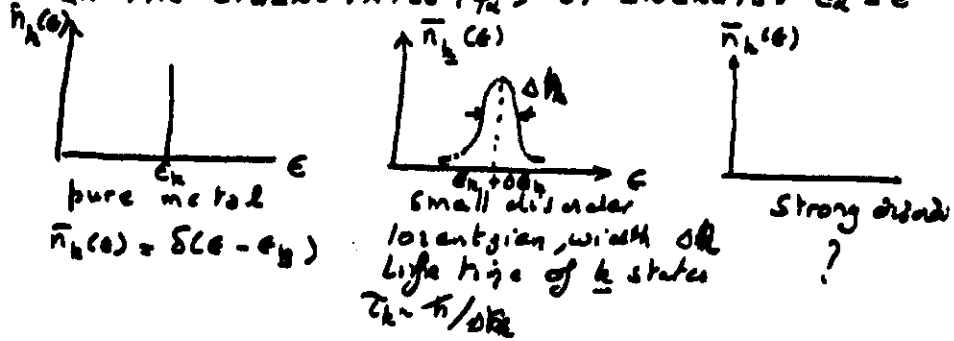
"λ cannot be smaller than a" (cf Mott Davis)
When Γ/β is large i.e. when the disorder is large "there is no more phase relations between functions on the neighbouring sites"

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

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

$$= \frac{1}{N} \langle \sum_\alpha K \, \Psi_{\underline{k}} | \Phi_\alpha \rangle |^2 \, \delta(E - E_\alpha) \rangle$$

IT'S THE AVERAGE WEIGHT OF THE $\Psi_{\underline{k}}$ STATES IN THE EIGENSTATES $|\Phi_\alpha\rangle$ OF ENERGIES $E_\alpha = E$



(6) DENSITY OF STATES, AVERAGED MEDIUM, GREEN FUNCTION

- THE AVERAGED DENSITY OF STATES $\bar{n}(\epsilon)$ IS GIVEN BY:

$$\bar{n}(\epsilon) = \frac{1}{N}\left\langle \sum_{\alpha} \delta(\epsilon - \epsilon_\alpha) \right\rangle = \frac{1}{N} \mathrm{Tr} \langle \delta(\epsilon - \mathcal{H}) \rangle = \sum_{\underline{k}} \bar{n}_{\underline{k}}(\epsilon) \quad (72)$$

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 RELATE THE RESOLVENT (or "Green function")

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

DEFINED FOR z OUTSIDE OF THE EIGENVALUES ϵ_α

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

- TO THE DENSITY OF STATES

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

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

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

$$\langle G(z) \rangle = \left\langle \frac{1}{z - \mathcal{H}} \right\rangle = \left\langle \frac{1}{z - \mathcal{H}_0 - \Sigma(z)} \right\rangle \quad (73)$$

Σ REPLACES V (THE RANDOM POTENTIAL)

$\mathcal{H} = \mathcal{H}_0 + V$ FOR A DOPED $\begin{cases} \mathcal{H}_0 = \sum \beta_{\underline{k}\alpha} |\alpha\rangle\langle\alpha| \\ V = \sum p_i \varepsilon_i |i\rangle\langle i| \end{cases}$

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:

$$\langle \phi(\underline{i}) | \Sigma | \phi(\underline{j}) \rangle \neq 0 \qquad \underline{i} \neq \underline{j} \quad (74)$$

BUT THESE MATRIX ELEMENTS DEPEND ON $\underline{i} - \underline{j}$

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

MORE PRECISELY WE ASSUMED THE TRANSLATIONAL INVARIANCE AVERAGING SO THAT:

- THE EFFECTIVE HAMILTONIAN FOR THE AVERAGE MEDIUM

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

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

ARE DIAGONAL IN THE BASIS OF BLOCH STATES $|\psi_{\underline{k}}\rangle$:

$$\langle \psi_{\underline{k}} | \langle G(z) \rangle | \psi_{\underline{k}'} \rangle = \delta_{\underline{k}\underline{k}'} \frac{1}{z - \epsilon^0_{\underline{k}} - \Sigma(\underline{k}, z)} \quad (76)$$

THE SPECTRAL DENSITY CAN THEN BE WRITTEN AS:

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

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

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

— Roughly lorentzian of width Γ small disorder (Σ_R, Σ_I smooth in $\underline{k}$)

(7) Local densities of states

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

$$n(\epsilon, \underline{i}) = \sum_{\alpha} |\varphi_\alpha(\underline{i})|^2 \delta(\epsilon - \epsilon_\alpha) \quad (78)$$

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

$$n(\epsilon, \underline{i}) = \sum_{\alpha} |\langle \phi(\underline{i}) | \psi_\alpha \rangle|^2 \delta(\epsilon - \epsilon_\alpha) \quad (79)$$

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

Note:

(a)

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

$|\langle \underline{k}0|\underline{k},t\rangle|^2 = P_{\underline{k}}(t)$ = probability of finding the electron at time t in state $\underline{k}$ knowing it was in this state at $t=0$

It is related to the usual Green Function

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

or:

$$G_{\underline{k}}(t) = -i\theta(t)\sum' |\langle k|\psi_\alpha\rangle|^2 e^{-i\epsilon_\alpha t/\hbar}$$

F.T: $G_{\underline{k}}(\epsilon+i0) = \int_0^\infty \frac{dt}{\hbar} e^{i(\epsilon+i0)t} G_{\underline{k}}(t) = \sum_\alpha' \frac{|\langle k|\psi_\alpha\rangle|^2}{\epsilon_+ - \epsilon_\alpha + i0}$

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

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

(b) If $G_{\underline{k}}(\epsilon) = (\epsilon_+ - \epsilon_k' - i\Delta)^{-1}$ $\qquad \Delta_k = \mathrm{Im}\,\Sigma_k(\epsilon_k')$

$$G_{\underline{k}}(t) = \int \frac{d\epsilon}{2\pi} e^{-i\epsilon t/\hbar} G_{\underline{k}}(\epsilon) = -i\theta(t) e^{-i\epsilon_k' t/\hbar} e^{-\Delta_k t/\hbar}$$

$$P_{\underline{k}}(t) = \exp -2\Delta_k t/\hbar$$

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

(c) C.P.A (Coherent potential approximation) for DL

METHOD

- It's a simple "one site" approximation to the calculation of the electronic spectrum which is exact in the limiting cases (i) Dilute limit, (ii) Atomic limit (iii) Split band (iv) perturbation limit: in this sense it's an "interpolation" between exact results!
- THE SIMPLEST WAY TO DERIVE IT:

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

$$\langle \phi_\lambda^n | \Sigma | \phi_\mu^{n'} \rangle = \delta_{\lambda\mu}\sigma(z) \qquad (\text{see})(80)$$

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

$$\boxed{\bar{n}(\epsilon) = \sum c_i n_i(\epsilon)}$$ (see)(83)

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

$$\bar{n}(\epsilon) = -\frac{2}{\pi}\mathrm{Im}\langle 0|(G(\epsilon+i0))|0\rangle$$

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).

$$-\frac{2}{\pi}\mathrm{Im}\langle 0|G(\epsilon+i0)_{\begin{smallmatrix}\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\end{smallmatrix}}^{\begin{smallmatrix}\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\end{smallmatrix}}|0\rangle = -\frac{2}{\pi}\mathrm{Im}\langle 0|G(\epsilon+i0)_{\begin{smallmatrix}\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\end{smallmatrix}}^{\begin{smallmatrix}\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\end{smallmatrix}}|0\rangle \times c_A$$
$$-\frac{2}{\pi}\mathrm{Im}\langle 0|G(\epsilon+i0)_{\begin{smallmatrix}\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\end{smallmatrix}}^{\begin{smallmatrix}\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot\end{smallmatrix}}|0\rangle \times c_B$$

or:

$$\langle 0|(G(\epsilon+i0))|0\rangle = \sum_i c_i \langle 0|G_i(\epsilon+i0)|0\rangle$$
$$F(\epsilon) = \sum_i c_i F_i(\epsilon).$$

THIS CONDITION IS EASILY ANALYTICALLY EXPRESSED:

$$G_i(z) = \frac{1}{z - H_{\text{eff}} + (\epsilon_i - \Sigma)|0\rangle\langle 0|} = \langle G(z)\rangle + \langle G(z)\rangle(\epsilon_i - \Sigma)G_i(z)$$

or taking the matrix element $\langle 0|\ G_i\ |0\rangle$

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

$$1 = \sum_i \frac{c_i}{1-(\epsilon_i - \Sigma(z))F(z)}$$ (91) CPA condition

(3) 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 ($\epsilon_i = \epsilon_A$ for all i 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

$$E = \int^{E_F} n(\epsilon)\,\epsilon\, d\epsilon \quad \text{(band term)}$$

ARE PROPERLY WELL REPRESENTED BY CPA. (They are basic definitions of the properties depending only from one energy (ϵ_F) for ex. el. specific heat coefficient 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 it destroys the possibility of gaps

— 2 The CPA can be extended to take into account of the local environment (CPA, 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

(4) SELF CONSISTENT CALCULATION: for each spin σ

LDA $\Rightarrow$ $\hat{h} = -\frac{\hbar^2}{2m}\nabla^2 + v^{ion} + v^c[n(r)] + v^{xc}[n(r)]$

$\Downarrow$

$[\psi_\alpha, \epsilon_\alpha]$; $\hat{h}\psi_\alpha = \epsilon_\alpha \psi_\alpha$

$\Downarrow$

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

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

$$\delta\epsilon_{i\sigma} = \delta\langle i|\hat{h}|i\rangle = U_i\,\delta n_{i\bar{\sigma}} - J_i\,\delta n_{i\sigma} + O(\delta n_{i\sigma}^2)$$

KEEPING ONLY INTRAATOMIC INTEGRALS

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

σ : spin ± 1

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

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

$\Downarrow$

FRIEDEL OSCILLATIONS: IMPURITY INDUCED

DENSITY VARIATION: $\Delta n(r) \underset{r\to\infty}{\sim} A\frac{\cos(2k_F r + \phi_F)}{r^3}$

$2k_F$ diameter of the Fermi surface

IMPURITY POTENTIAL $\Delta V(r) = V^{alloy}_{host}(r) \sim \frac{\cos(2k_F r + \phi_F')}{r^3}$

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

HOST ENERGY LEVELS $\Delta\epsilon_i \sim$ " 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 the origin with the energy $\Delta\mathcal{E}(R) = Z'\Delta V(R) \sim \frac{\cos(2k_F r + \phi_F)}{r^3}$)

WHICH DETERMINE [illegible]

SPECTRAL BOUNDS IN DISORDERED SYSTEMS.

bounds related to the possibility of building up bonding and antibonding states ie to topological properties

1 HADAMARD GERSCHGORIN CRITERION

1 non deg TB band

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

$$|\epsilon - \epsilon_\alpha| \leq \sum_{\mu \neq \alpha} |\beta_{\alpha\mu}| \frac{|A_\mu|}{|A_\alpha|}$$

consider α | $|A_\alpha| \geq |A_\mu| \quad \forall \mu \neq \alpha \Rightarrow$

$$|\epsilon - \epsilon_\alpha| \leq \sum'_\mu |\beta_{\alpha\mu}|$$

$$\Downarrow$$

$$\epsilon \in \bigcup_\alpha \mathcal{D}_\alpha \qquad \mathcal{D}_\alpha = \{z : |z - \epsilon_\alpha| \leq \sum'_\mu |\beta_{\alpha\mu}|\}$$

If we have only a periodic crystal, $\epsilon_\alpha = 0 \Rightarrow |\epsilon| \leq \sum |\beta|$ / $\beta_{\alpha\mu} \neq 0$ only betw. n.n.

2 PERRON FROBENIUS THEOREM

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

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

Ex: $x_{\alpha\mu} = \epsilon_\alpha \quad \forall \alpha, \mu \neq \alpha \quad \beta_{\alpha\mu} < 0 \quad \lambda_{max} = -\epsilon_{min} \Rightarrow$

The lower state corresponds always to a non degenerate bonding state (for crystal and for any disordered)

3 MIN MAX THEOREM (Courant-Hilbert vol 1)

$\hat{H}$ = hamiltonian operator

- order the eigenvalues $\lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_N$
- define a subspace generated by k-1 states $|\psi_i\rangle$, $\mathcal{E}_{k-1}$
- calculate $\max_{\psi \in \mathcal{E}_{k-1}} \langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle$
- minimize this value when varying the $\mathcal{E}_{k-1}$ state; thus:

$$\lambda_k = \min_{\mathcal{E}_{k-1}} \max_{\psi \in \mathcal{E} - \mathcal{E}_{k-1}} \langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle$$

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

$$\boxed{\lambda_{k+m} \leq \lambda^{(m)}_k \leq \lambda_k} \qquad (C1)$$

- $\max_{\mathcal{E} - \mathcal{E}^{(m)}} \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq \max_{\mathcal{E} - \mathcal{E}^{(m)}} \frac{\langle \psi | H^{(m)} | \psi \rangle}{\langle \psi | \psi \rangle}$ ($\langle \psi | \psi^{(m)} \rangle = 0$, $\langle \psi | H | \psi \rangle$ / $\langle \psi | \psi \rangle > 0$)

Rolician constraints $\Rightarrow \pi_k \geq \pi_p$ (weaker p constraints)

$\Rightarrow \lambda^{(m)}_k \leq \lambda_k$

- $\lambda^{(m)}_k = \min_{\mathcal{E}_k} \max_{\substack{\langle \psi | H | \psi \rangle \geq 0 \\ \langle \psi | \psi \rangle = 0}} \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq \lambda_{k+m} = \min_{\mathcal{E}_k} \max$

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

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

Applications

@ disordered alloy: $A_c B_{1-c}$ only B.D ($\epsilon_A - \epsilon_B \neq 0$) GAMS

- project on the space $\mathcal{E}^{(A)}$ spanned by the A atoms ($\dim \mathcal{E}^A = c N_a$) $\mathcal{E}^{(B)} = \mathcal{E} - \mathcal{E}^A$ and from (C1):

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

- if H°_A is the hamiltonian of the pure metal A

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

since $(H^\circ_A)^{(A)} = H^{(A)}$

- if (for example) $\delta < 0 \quad H - H^{(B)}_A > 0$ from (C2)

$$\epsilon_k(H^{(B)}_A) \leq \epsilon_k(H) \qquad (2)$$

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

$$\underbrace{\epsilon_{k+(1-c)N_a}(H^{(B)}_A)}_{(C2)} \leq \epsilon_{k+N_a(1-c)}(H) \leq \underbrace{\epsilon_k(H^{(B)}_A \leq \epsilon^\circ_k}_{(C1)}$$

$\downarrow$

- Hence:

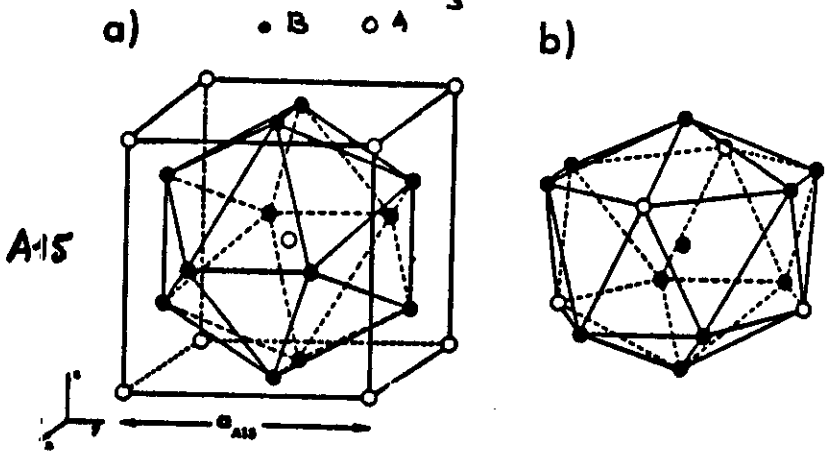
$$\begin{cases} \epsilon_N(H) = \epsilon_{min} \geq \epsilon^{(B)}_{min} A & (k = N_a c) \\ \epsilon_{1+N_a(1-c)} \leq \epsilon^\circ_{max} A & (k = 1) \end{cases}$$

III 4- QUALITATIVE DISCUSSION OF THE IMPORTANCE OF CHEMICAL AND TOPOLOGICAL (DIS) ORDERS ON THE DENSITY OF STATES OF TM ALLOYS.

Introduction

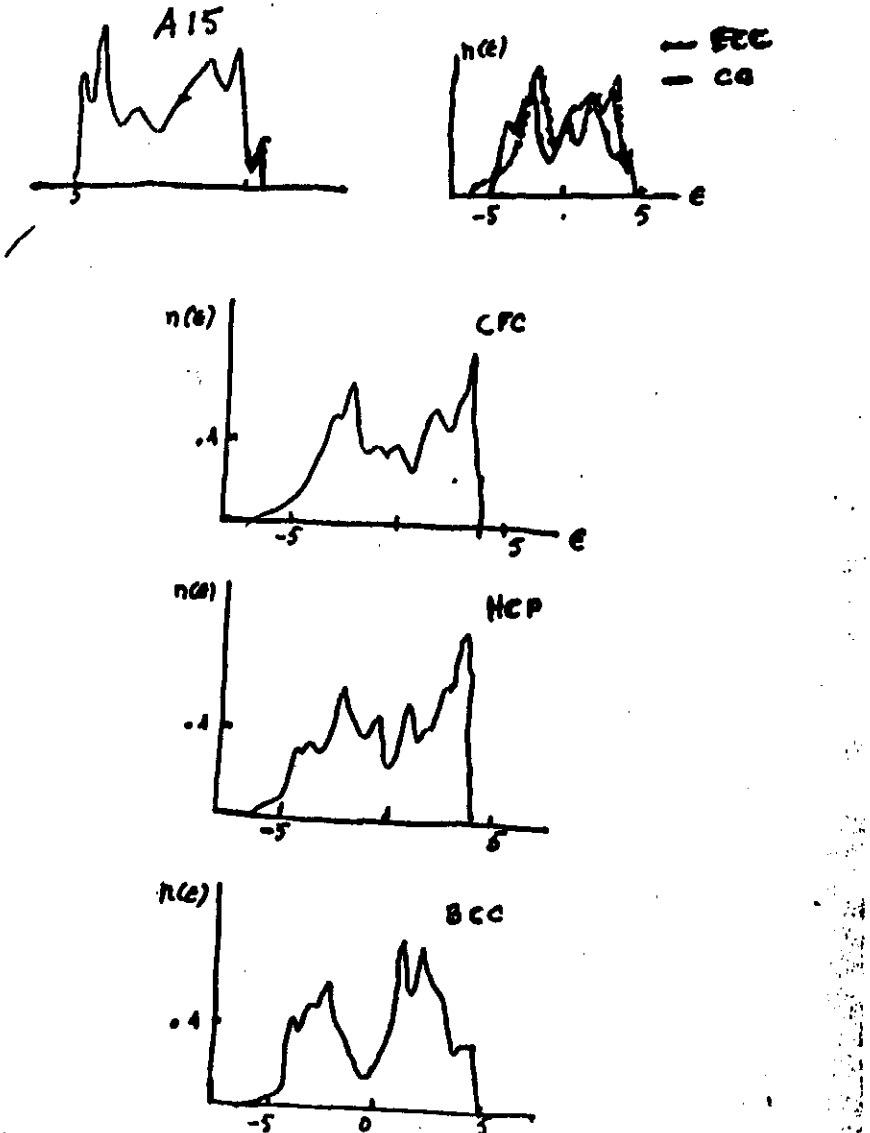
- Our aim is to show the effects of various (dis) orders on the D.O.S of TM alloys We emphasize the roles of (1) topological order
  (2) chemical order in x compounds
  (3) atomistic disorder in x alloys.
  (4) topological and chemical disorder
  (5) off diagonal disorder in some peculiar compounds.
- The general trends we show will be useful later to discuss qualitatively the phase stability (next chapter) However, the discussion shows that the trends for the phase stability cannot be found directly from the DOS (except in special cases)

A_3B



- The lattice is characterized by change in the three directions ox, oy, oz
- The usual order in this lattice corresponds to the figure, the impurity atoms B occupying the bcc lattice

1a THE ROLE OF TOPOLOGICAL ORDER IN THE D.O.S OF SEVERAL CRYSTALLINE STRUCTURES WITH THE SAME ATOMIC VOLUME



NOTE THAT, FOR PURE METALS, 4 TOPOLOGICAL ORDERS DO NOT INTRODUCE EASILY INTERPRETABLE CHANGES IN D.O.S

1b THE EFFECT OF TOPOLOGICAL ORDER ON THE "d" D.O.S OF TM.

amorphous metals

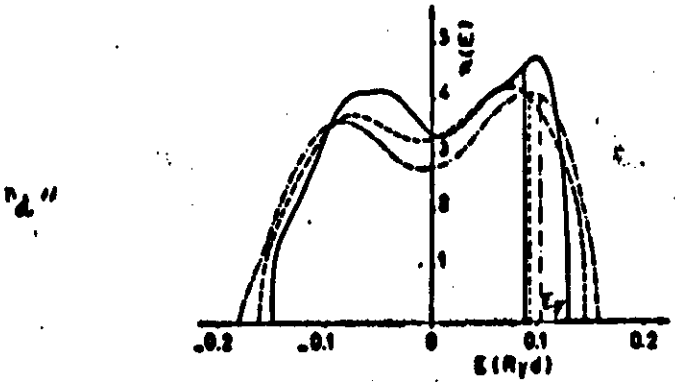


Fig. 2 : Density of d-states using H.R.(—), L.J. (—), and T.H.(-·-·-) models.

- The density of states $\bar{n}(\varepsilon)$ is not sensitive to the details of the model used for the determination of the structure (RANDOM PACKING OF HARD SPHERES starting from triangles with more number of tetrahedra and icosahedra)

from F. CYROT LACKMANN et al.

- THE VAN HOVE PEAKS HAVE DISAPPEARED SO THAT WE OBTAIN A

"structure less average density of states"

WHICH IS - IN SOME SENSE - THE AVERAGE OF THE PREVIOUS D.O.S (See next chapter)

-2- THE ROLE OF CHEMICAL ORDER ON THE D.O.S

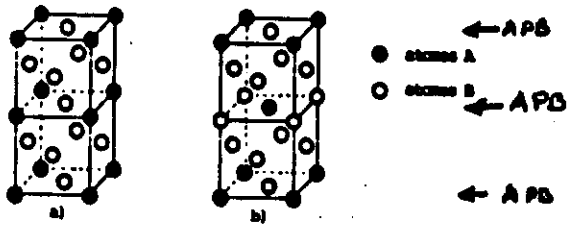


Fig. 1. a) structure ordonnée Li_2 (type Cu_3Au) pour un alliage binaire A_3B (ou AB_3). Deux mailles élémentaires sont représentées pour la comparaison avec la structure DO_{22}.

b) structure ordonnée DO_{22} pour un alliage binaire A_3B (ou AB_3)

"Cu_3Au"

"Cu_3Au" ⇒ DO_{22}

Going from $L1_2 \rightarrow DO_{22}$ LEADS TO VERY SMALL CHANGES OF $n(\epsilon)$

(a) THE INCREASE OF δ LEADS PROGRESSIVELY TO THE "SPLIT BAND REGIME" ⇒

APd_3

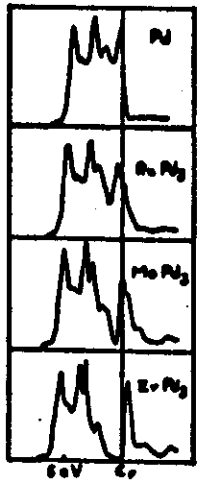


Fig. 2a. Densités d'états d'alliages ordonnés (type Cu_3Au), calculées par la méthode KKR (d'après réf. 177).

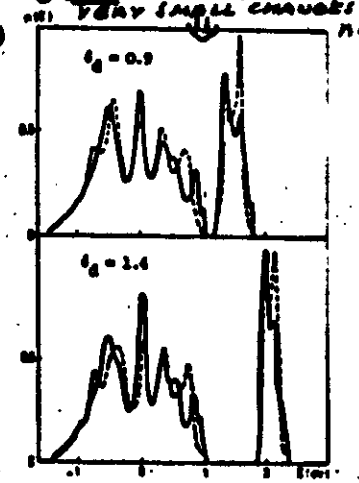


Fig. 2b. Densités d'états "d" des structures Li_2 et DO_{22}, calculées par la méthode de récursion.

— DO_{22}

— Li_2

(d'après réf. 154)

$\frac{\epsilon_A - \epsilon_B}{W}$ ↗ from Ru to Zr

↓

SPLIT BAND

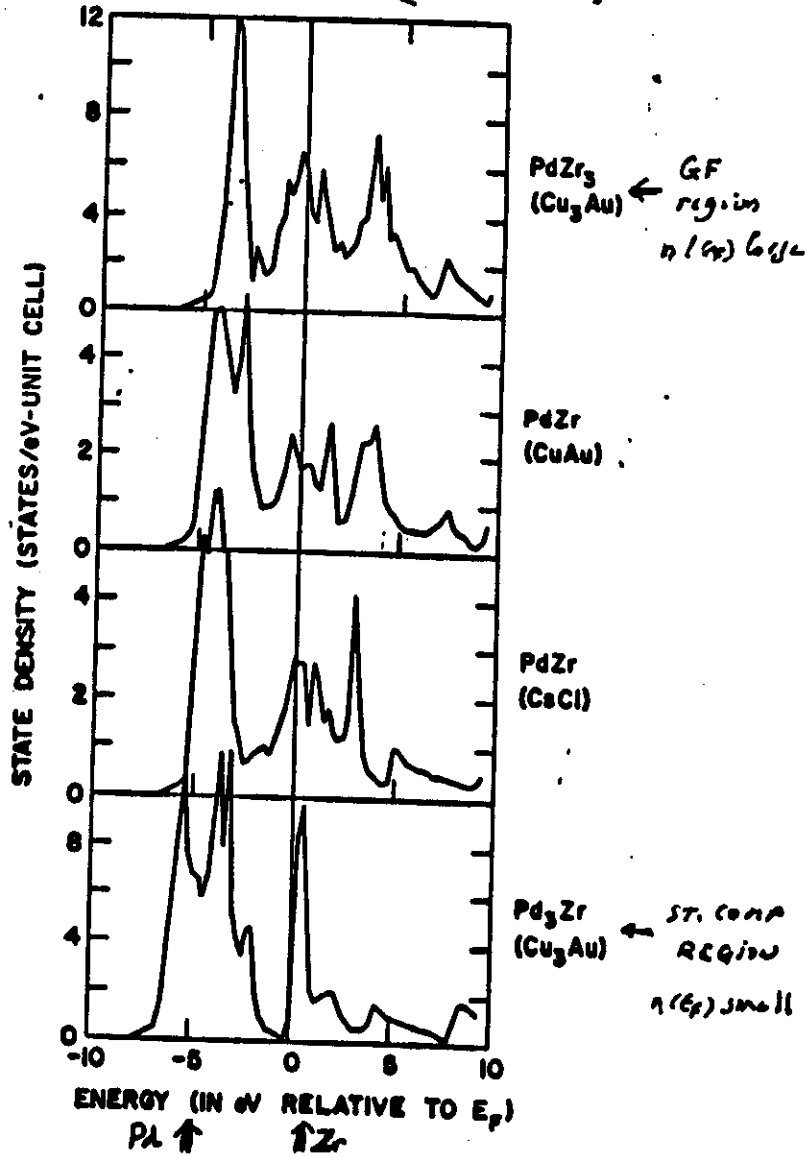
↓

$n_{DO_{22}}(\epsilon) - n_{L1_2}(\epsilon)$?

* ϵ_i WITH SAME %d FROM δ

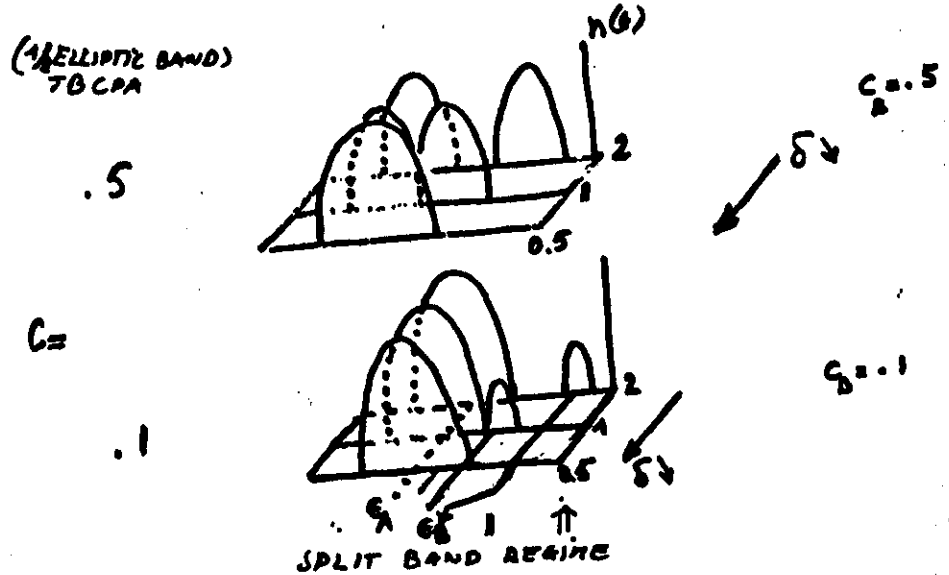
THE ROLE OF THE O.S ON THE DOS

- EACH MINORITY ATOM A (AB_3) IS SURROUNDED ONLY BY * MAJ. AT
  IN THE Cu_3Au, CuAu, CsCl STRUCT.
- THE BAND WIDTH OF PURE Zr IS ≥ THE BANDWIDTH OF Pd
  " " " < " " "

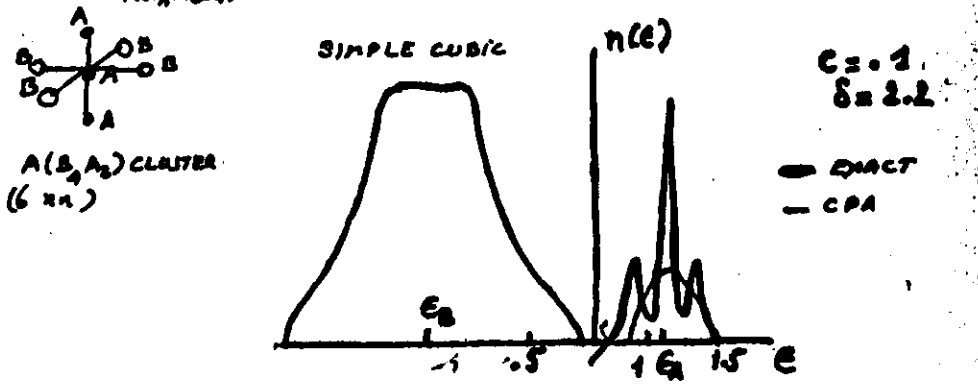


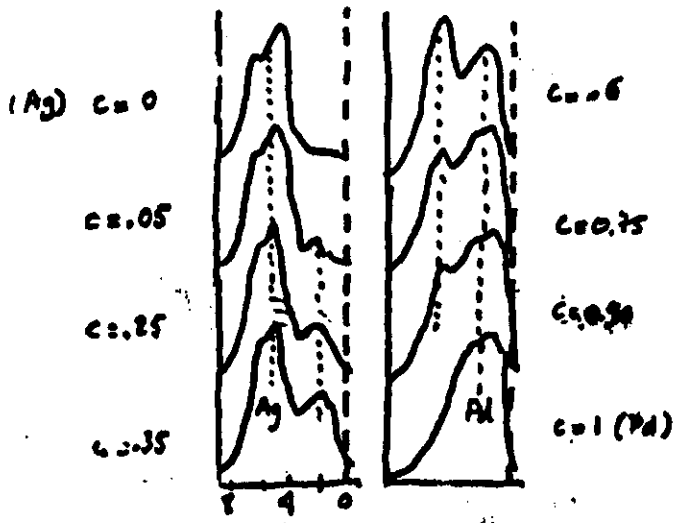
- A PSEUDO GAP IS OBSERVED WHEN THE MAJORITY ε_F HAS THE SMALLEST BAND WIDTH (Pd_3Zr), THE Zr 'd' STATES BEING QUASI ATOMIC (from MORUZZI et al)
- STRONG ↓ STABILITY OCCURS FOR Pd_3Zr WHEREAS GLASS FORMING

3 DISORDERED ALLOYS: CPA and D.O.S.



- THE CPA DOES NOT TAKE INTO ACCOUNT THE FLUCTUATIONS OF A DENSITIES OF STATES $n_A(E)$ WITH ENVIRONMENT
- IT DOES NOT ACCURATELY REPRESENT THE MINORITY BAND (in the split band regime) WHERE IS DOMINATED BY ENVIRONMENT EFFECTS (Three most probable cluster configurations AB_nA_{6-n}) OCCUR IN THE FIG

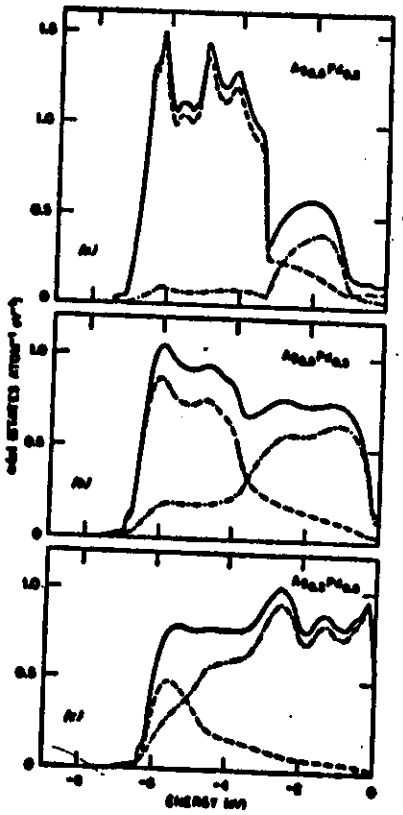




$Pd_{1-c}Ag_c$
(from Wallden et al)

THE PHOTOEMISSION SPECTRA SHOW CLEARLY THAT THESE ALLOYS CORRESPOND C TO THE SPLIT BAND REGIME

in the separation between the Ag and Pd d-scattering resonances. In fig. IV.7 we collect together the self-consistent total and component densities of states for the three alloys considered, the corresponding non-self-consistent results are shown in fig. II.1. Insofar as the positions of the Pd and Ag sub-bands are concerned it appears that the self-consistent results are in slightly better agreement with the UPS results displayed in fig. II.1.



SCKKR CPA Calculations of Pd Ag (M. Stocks et al)

COMPARE WITH TBI EXPERIMENT!

Fig. IV.7. Total and component densities of states for three $Ag_c Pd_{1-c}$ alloys calculated using the self-consistent KKR-CPA. The key is as in Fig. IV.4

THE IRRELEVANCE OF THE VCA IN Pd Ag ALLOYS

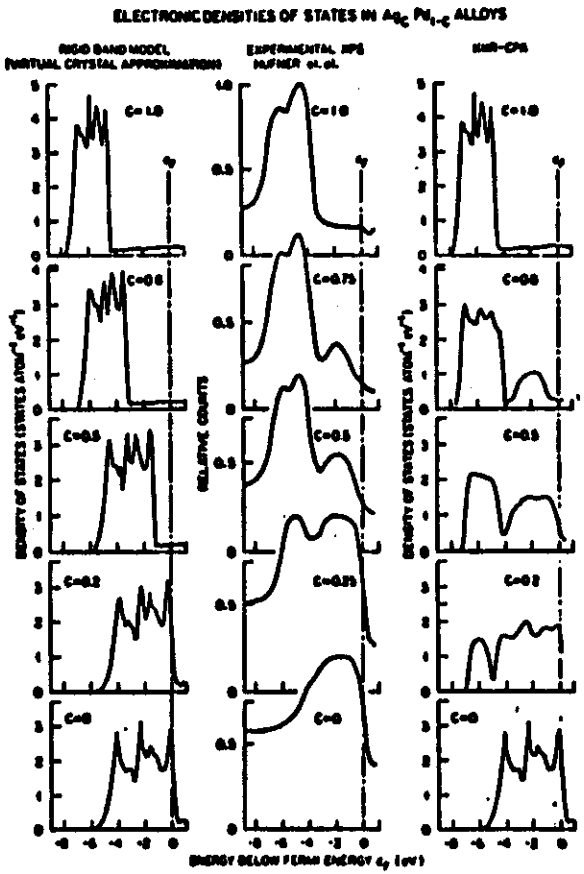


Fig. III.1. Densities of states for $Ag_c Pd_{1-c}$ alloys.

Left column : Densities of states calculated according to the virtual crystal approximation.
Centre column : Experimental XPS spectra (Hüfner et al).
Right column : Densities of states calculated according to the KKR-CPA.

(from M. Stocks et al)

THE ROLE OF SELF CONSISTENCY TO DETERMINE THE D.O.S OF DISORDERED ALLOYS

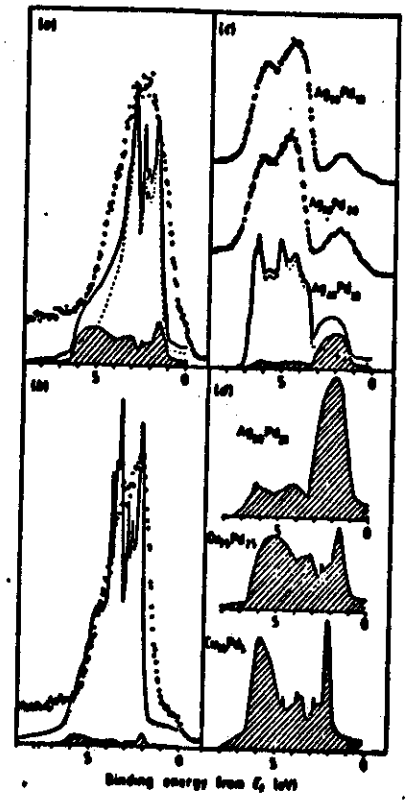


Fig. IV.15. The dots show photoelectron spectra from the conduction bands of $Cu_{.2}Pd_{.8}$ (a), $Cu_{.5}Pd_{.5}$(b), $Ag_{.5}Pd_{.5}$ and $Ag_{.8}Pd_{.2}$(c). The full curves show the total density of states given by SCF-KKR-CPA calculations for $Cu_{.7}Pd_{.3}$ (a), $Cu_{.5}Pd_{.5}$(b) and $Ag_{.6}Pd_{.4}$(c). The contributions to the total densities of states made by Pd are shown shaded and the contributions from Cu and Ag are shown by the broken curves. Figure V.2(d) shows the calculated Pd densities of states per Pd site.

— "IN PRIOR" Cu Pd AND Pd Ag ALLOYS ARE BOTH IN THE SPLIT BAND REGIME. A SC CALCULATION SHOWS THAT THE ALLOYING LEADS TO $\epsilon_{Pd} \simeq \epsilon_{d_0}$ IN $Cu_c Pd_{1-c}$ ALLOYS: A UNIQUE PEAK IS OBSERVED IN THE PHOTOEMISSION SPECTRA OF SUCH COMPOUNDS (from Stocks et al.)

Cu Pd. ALLOYS

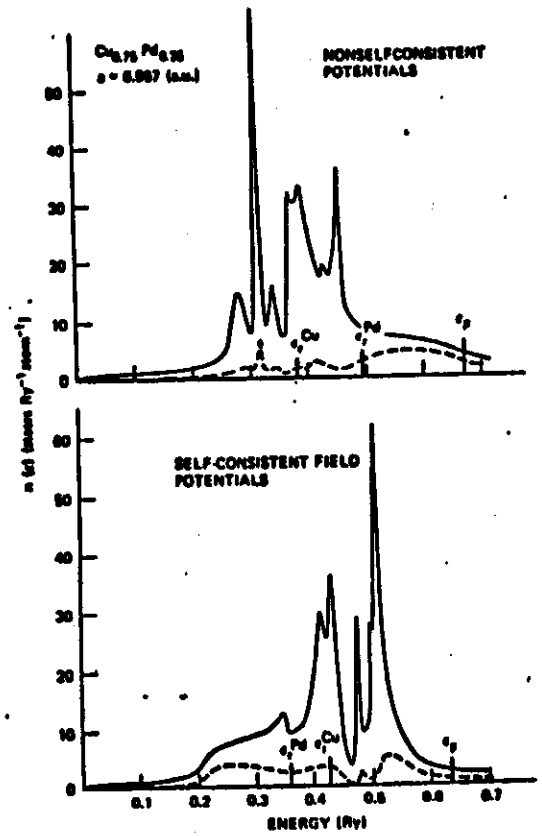
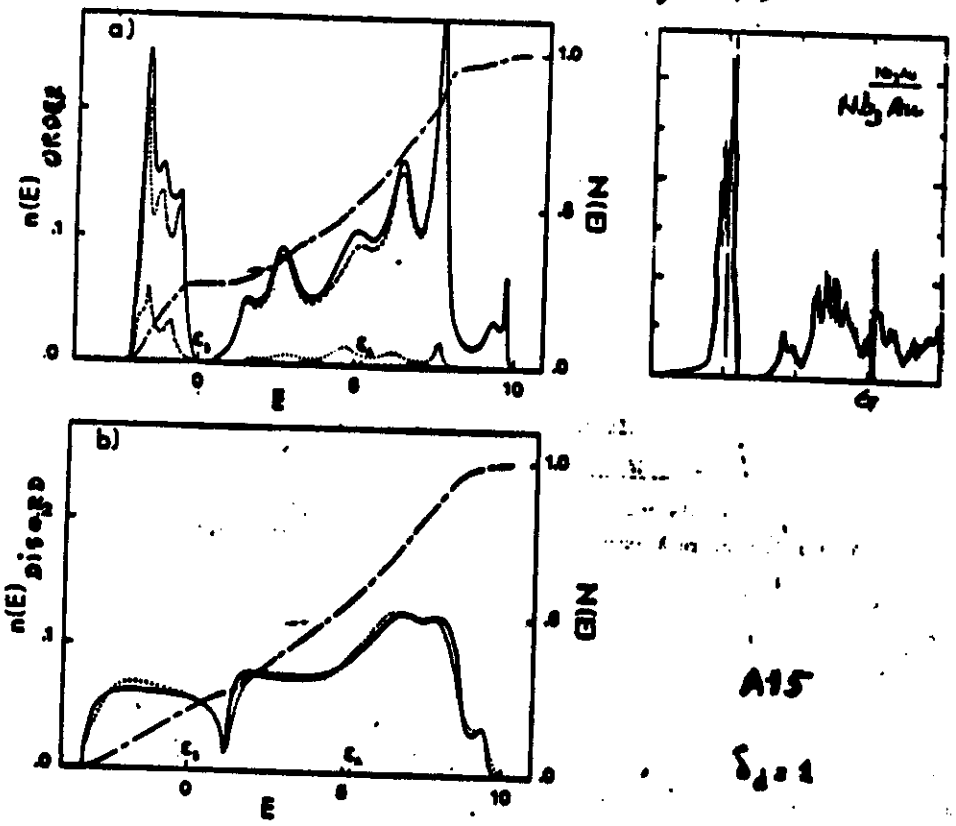


Fig. IV.14. Upper : Total (solid) and palladium component (dash) densities of states for $Cu_{.75}Pd_{.25}$ for nonselfconsistent potentials. The densities of states were calculated using the 6-shell cluster method.
Lower : Same as upper except for the self-consistent potentials.
(from Stocks et al.)

ORDERED AN DISORDERED SYST PRESENT NEARLY IDENTICAL D.O.S (crystalline)



order % disorder
(crystalline)

FOR LARGE δ VALUES, THE D.O.S IS MOSTLY DETERMINED BY THE FLUCTUATIONS OF ENERGY LEVELS - IN THE DISORDERED STATE THE D.O.S IS SMOOTHED AND THE PSEUDO GAP MORE OR LESS FILLED.

Alliage	$\bar{n}_0$	Δn_0	δ_0	$n_{ord.}(\epsilon_F)$	$n_{dés.}(\epsilon_F)$	$\gamma_0^{ord.}$	$\gamma_0^{dés.}$	$\gamma^{ord.}_{exp.}$	λ
Ti_3Pt	4,50	6	1,4	1,388	1,236	3,28	2,90	6,7	0,73
V_3Pt	5,25	8	1,6	1,670	1,336	3,93	3,16	7,2	0,82
Cr_3Pt	6,00	4	1,0	1,727	1,683	4,18	4,00	8,5	1,07

(γ_{ord} is (some hotes) larger than γ_{dis} !)

from P. TURCHI (Thesis 1980)

-4- THE ROLE OF TOPOLOGICAL DISORDER ON THE D.O.S OF [illegible] COMPOUNDS

(4a)

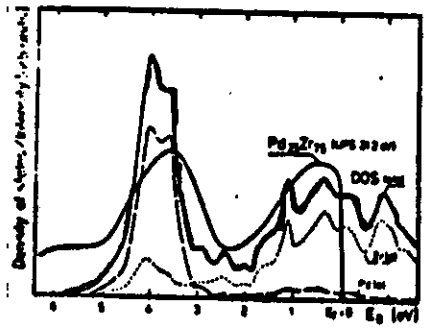


Fig.7 Calculated total (s,p,d) and partial d-density of states DOS of the crystalline compound $PdZr_3$ with Cu_3Au symmetry and the UPS spectrum of glassy $Pd_{25}Zr_{75}$.

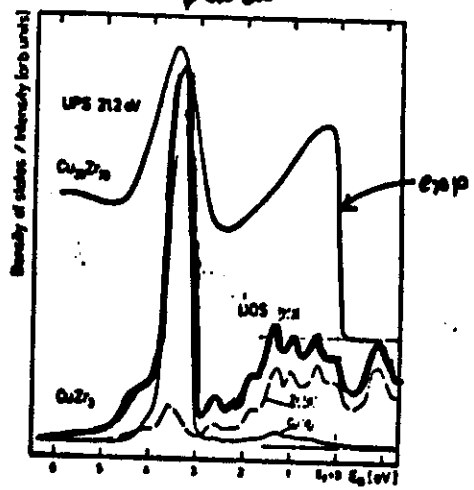


Fig.8 Calculated total (s,p,d) and partial d-density of states of the crystalline compound $CuZr_3$ with Cu_3Au symmetry and the UPS spectrum of glassy $Cu_{25}Zr_{75}$.

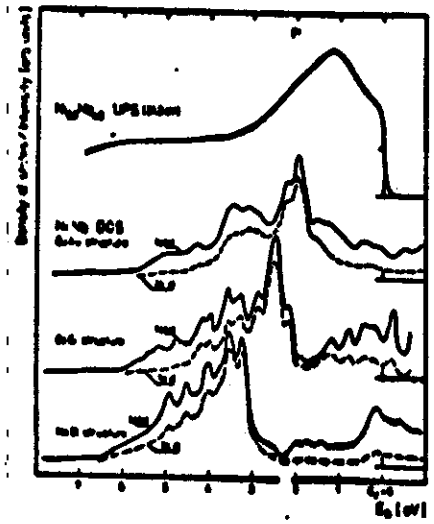


Fig.9 Calculated total (s,p,d) density of crystalline NiMb with NaCl, CsCl and Cu_3Au structure and the UPS spectrum of glassy $Ni_{60}Nb_{40}$. For comparison the partial Ni d-densities of states are shown.

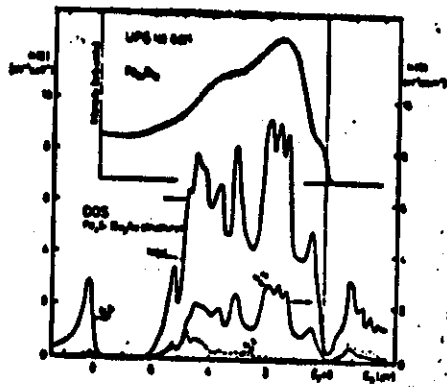
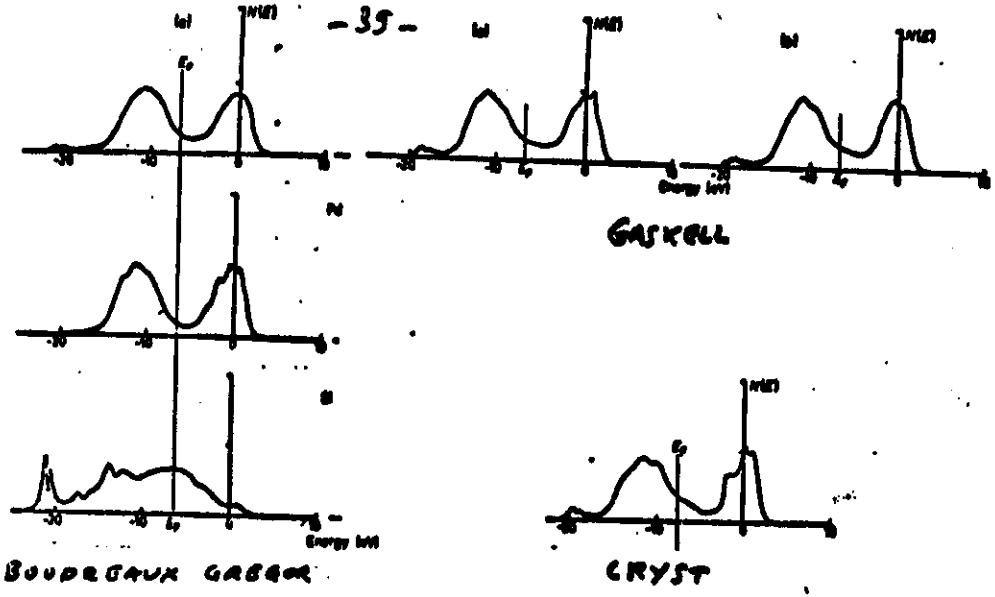


Fig.10 The calculated total and partial density of states of Pd_3Si in the Cu_3Au structure and the UPS spectrum of glassy $Pd_{84}Si_{16}$.

importance of topological disorder?!

from H.J. Güntherodt (LAM4)

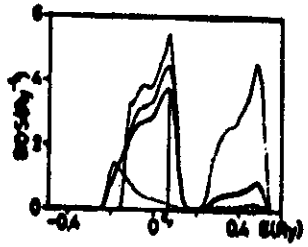
THE IMPACT OF TOPOLOGICAL ORDER INTRODUCES NO QUALITATIVE



Pd_3Si:

from Kelly et al.

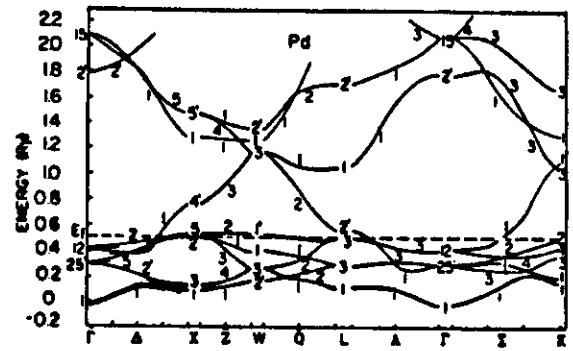
THE CHANGES OF TOPOLOGICAL ORDER DO NOT INTRODUCE IMPORTANT CHANGES IN THE D.O.S



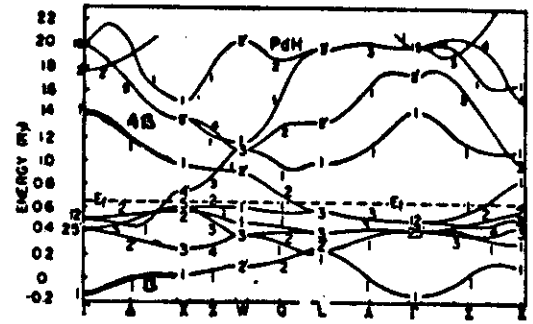
Pd_3P

from Fujiwara

(a) INTERSTITIAL COMPOUNDS : THE IMPORTANCE OF SD HYBRIDIZATION (OFF DIAG D.)



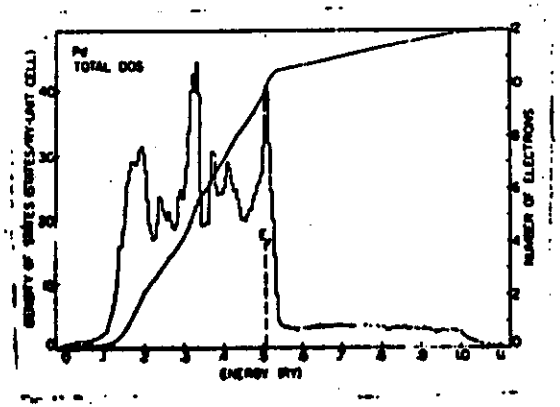
Pd

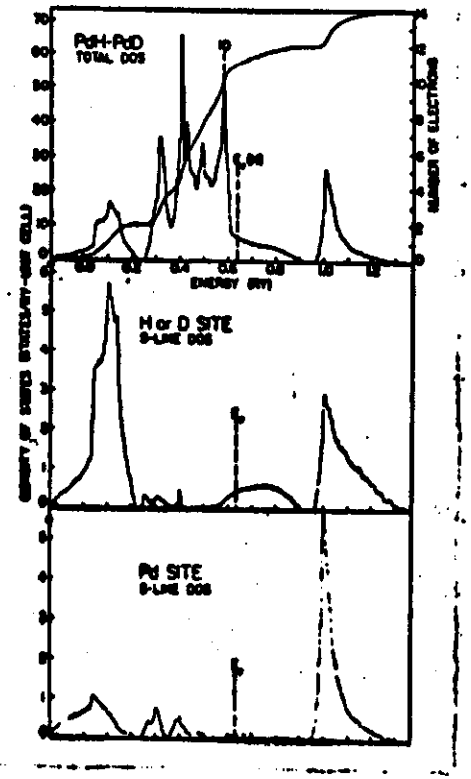


PdH

- STRONG HYBRIDIZATION LEADS TO BONDING (B) AND ANTIBONDING BANDS (AB) WHOSE STATES ARE EQUALLY DISTRIBUTED ON Pd AND H SITES
- THE FERMI LEVEL INCREASES GOING FROM Pd TO PdH AS SUGGESTED BY A RIGID BAND MODEL (H "DONE")
- BUT THE H ARE NOT REALLY "DONORS" SINCE THE BONDING BANDS HAVED "S" ELECTRONS ON THE H CELLS

STRONG (sp) - d HYBRIDIZATION IN PdH



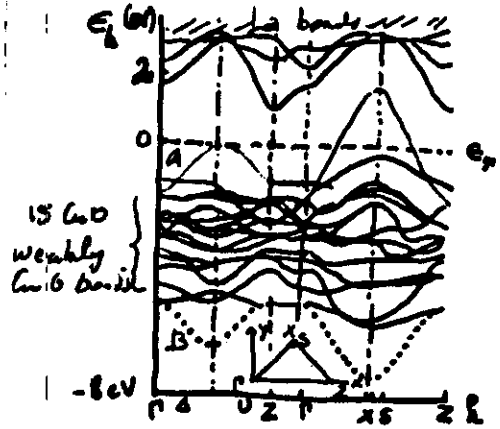


cf the DOS (sBlks) on the H site ⇒

(6) NEW SUPERCONDUCTORS ($(La_{1-x}La_{x}^{2+})_2Cu_2O_4$

THE BAND STR OF La_2CuO_4 EXHIBITS STRONG p d HYBRIZATION WITH Binding (B) AN ANTIBONDING (A) BANDS

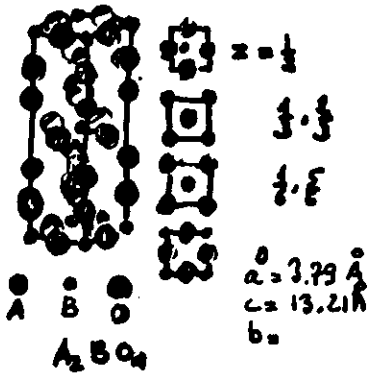
K_2NiF_4 structure



.... Bonding "pd BAND"

Strong pdσ INTERACTION BETWEEN Cu $d(z^2, y^2)$ and neighbouring $p(x,y)$ O orbitals

A — antibonding band (half filled)

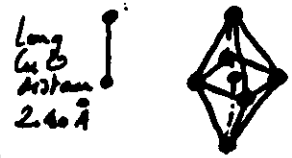


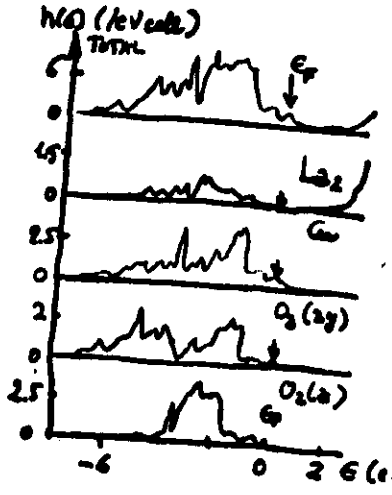
See the structure of Cu layers well separated from each other

Sucessive packing of

La O La_2CuO_4 La O

(B 1) perovskite (B1) etc...

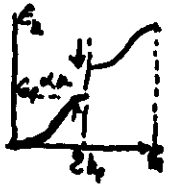




(from H. Mattheiss)

- THE PURE La_2CuO_4 HAS A STRUCTURE WHICH IS SLIGHTLY DIFFERENT FROM THE "K_2NiF_4" STRUCTURE. THE (CuO_6) OCTAHEDRA ARE SLIGHTLY TILTED AROUND ONE OF THE ORIGINAL [110] TETRAGONAL AXES (±5° AT 10 K) THE OCTAHEDRA SHARE CORNERS AND NEIGHBOURING OCTAHEDRA TILT IN OPPOSITE DIRECTIONS: THE OBSERVED CELL IS THEN DOUBLED IN THE BASAL PLANE ($\sqrt{2}a_0 \times \sqrt{2}a_0$) AND THE SYMMETRY IS LOWERED (from tetragonal to orthorhombic)

- THE MECHANISM OF THIS STRUCTURAL TRANSFORMATION CAN BE FOUND FROM THE TWO DIMENSIONAL NATURE OF THE HALF FILLED BAND (A) THE NEARLY PERFECT NESTING OF THE LARGE FERMI SURFACE SUGGESTS THE ∃ OF A CDW WITH $q_{CDW} = 2k_F = (\frac{1}{2}, \frac{1}{2}, 0)$



WHICH WOULD OPEN A GAP AT E_F STABILIZING THE DISTORTED PHASE (see next chapter) : THE PURE La_2CuO_4 IS A

La_2CuO_4 SEMICONDUCTOR

- SUPERCONDUCTIVITY IS INDUCED BY ADDING "IMPURITIES WITH ± VALENCES (divalent Sr, Ba, tetravalent lead) : THEIR ROLES WILL BE TO LOWER OR RAISE E_F AND THEN TO SUPPRESS THE FERROELASTIC STRUCTURAL TRANSFORMATION: THE "ALLOY" BECOMES A METAL - WHY IT'S SUPERCONDUCTING IS NOT CLEAR UP TO NOW (classical electron models, bipolarons, resonating valence bonds)

$La_{2-x}Ba_xCuO_{4\pm\delta}$ SUPERCONDUCTOR

- NOTE THAT THE PREVIOUS LDA (LMTO) calculation IS VALID ONLY IF ONE ASSUMES THAT STRONG CORRELATIONS ON Cu^{++} ARE NOT EFFECTIVE (at least qualitatively) : IT'S OK NOW!
- FINALLY, THE BEST SUPERCONDUCTORS KNOWN UP TO NOW ARE THE COMPOUNDS $YBa_2Cu_3O_{6.5+\delta}$ WHOSE STRUCTURE IS ...