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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

ELECTRONIC STATES IN DISORDERED SYSTEMS

(Part II)

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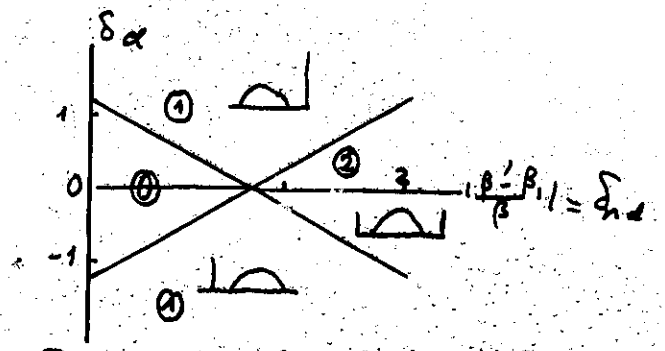
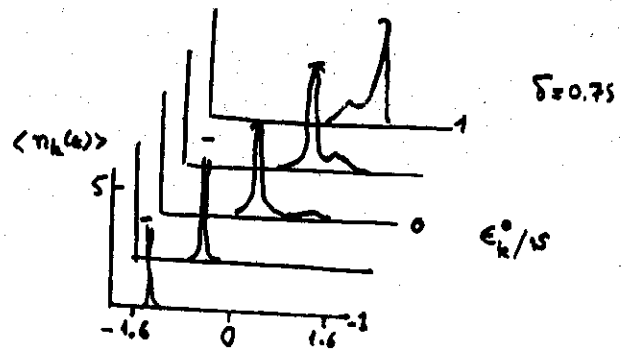
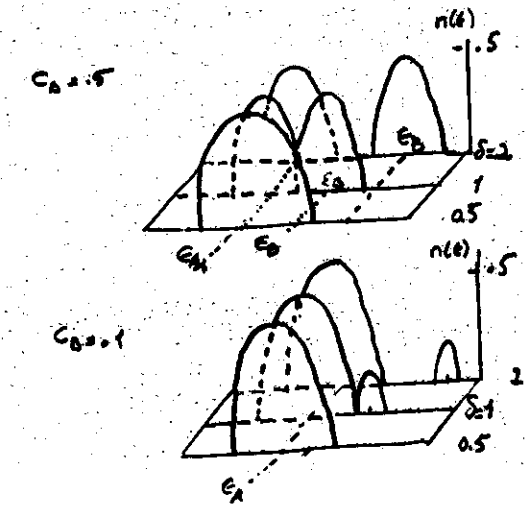
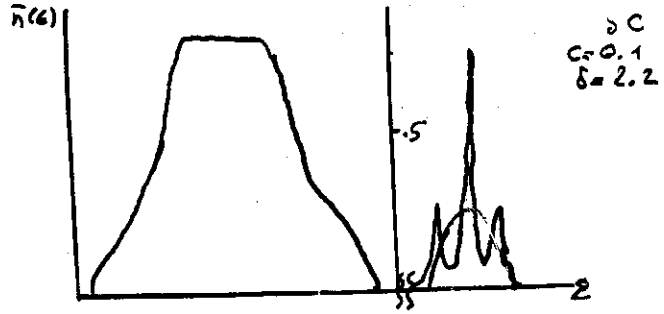


Bound states for D and off D D.



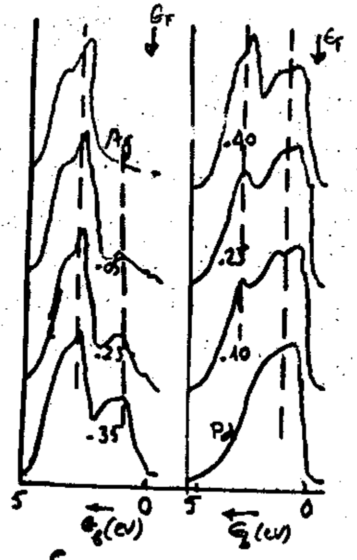
Spectral density calc by C.P.A.





ELECTRONIC STRUCTURE OF SOME DISORDERED SYSTEMS.

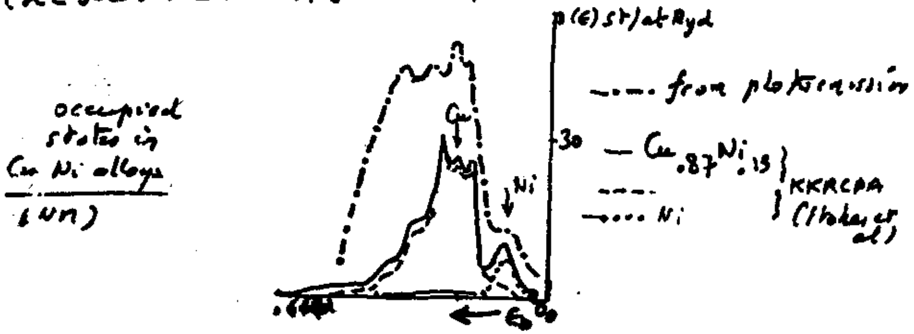
III . AMORPHOUS ½ COND, METALS AND ALLOYS
. SUBSTITUTIONAL BINARY ALLOYS



Photoemission spectra of Pd Ag alloys
(see the split Band regime)

CPA calculations can be done in the same way for opt prop. conductivity... (see ref)

WE PRESENTED TBCPA BUT KKR CPA (MULT T.B BANDS) is possible...
(see below: calculation for CuNi in a KKRCPA calc)



introduction

ⓐ • Topological disorder
Amorphous ½ cond's
metals (?)

↦ small fluctuations of local env't ⇒ small fluct^ns of n(E)
↦ difficult to study: (recursion, moments) ⇒ transport opt...?
↦ Stability ~ g(r), local env't ?
- orders of magnitude of energies
- no pair interactions to study the structural part of the energy (compare with Hafner's lectures.

ⓑ • crystalline Binary T.M. alloys | chemical disorder

↦ can be large ⇒ Large variations of n(E) (split band regime)
↦ C.P.A. allows to study physical properties (transport, optical, magnetic...)
↦ Perturbation theory allows to (i) determine the structural part of the energy which determines SRO (local order) (ii) investigate stable phases.
⇒ simple model to study the effects of T ?

① Amaphous ½ cond^{rs}. (tetracond.) III

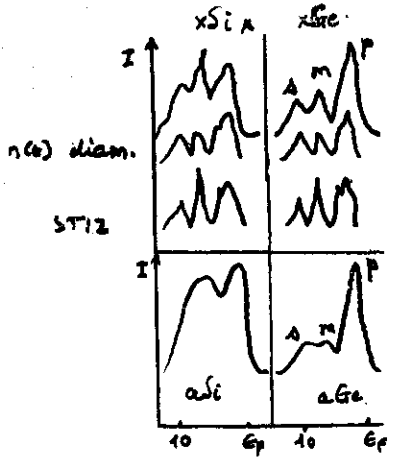
ⓐ. STRUCTURE

- small fluctuations of the bond lengths (≈ 1%)
  angles (≈ 10%)
- $\bar{z} = 4$ ideal = without dangling bonds
- defects ?

CONTINUOUS RANDOM NETWORK (CRN)

Contains usually five fold seven fold rings (Polk)
However Connell Temkin's model does not contain odd membered rings.

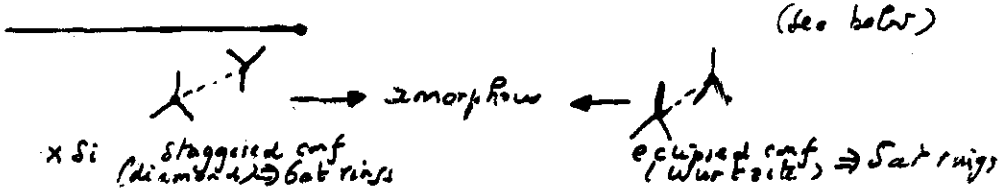
ⓑ. Photoemission and electronic structure

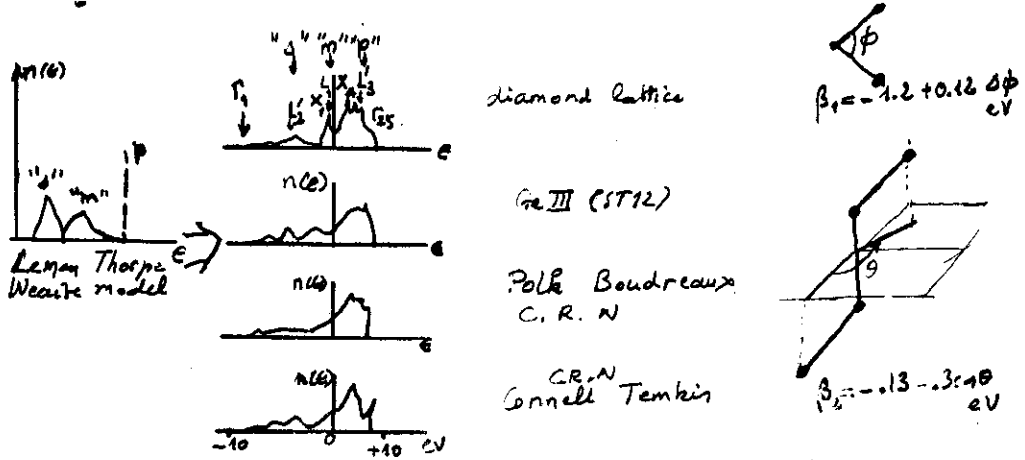


in crystalline Si 3 peaks
's' bottom of the valence band
'p' top " " "
mixed in the middle — — —

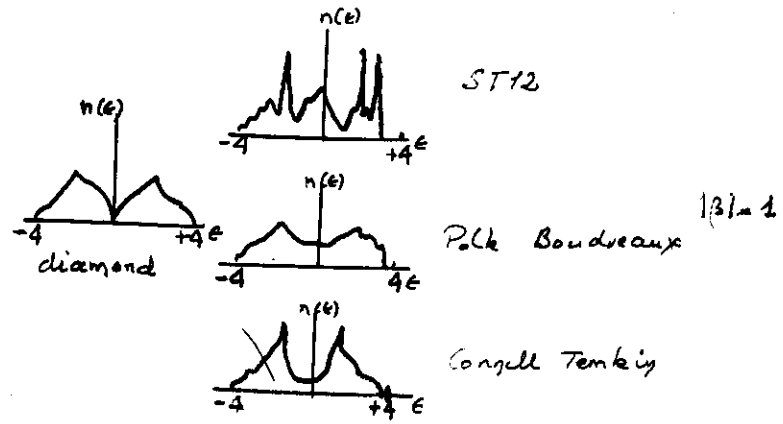
in amaphous Si 2 peaks:

- Note that the 'p' peak is not modified by disorder ($\epsilon_p - |\beta|$) of the simplified LFTW model
- Relation with the one Bond TB model ⇒ disorder affects only the central dip and the width of the VB according to the existence of odd membered rings.





The valence bands of Si atoms on Diff^{t} lattices



TB band issued from 's' from degenerate orbitals allow creation of non bonding states ($\epsilon = 0$) odd membered rings prevent the construction of the totally Antibonding state (ST12 and Polk B.)

The filling of the pseudo gap can be understood as follows (Gaspard): (crude model)

$n(\epsilon)$ = average of eigenvalues of rings of diff lengths Broadened (from their interaction)

$\beta = 1$ the ϵ_ℓ of a ring of length n are

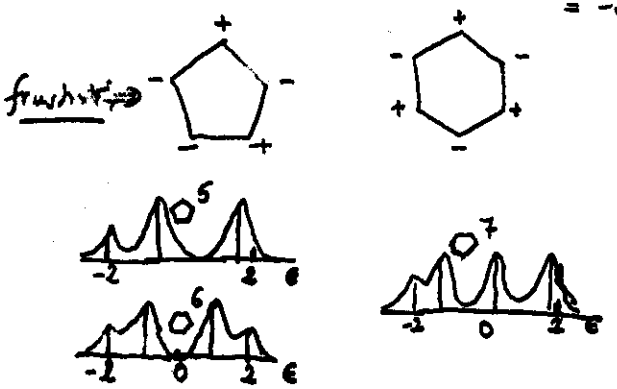
$$\epsilon_\ell = -2\cos\frac{2\pi\ell}{n} \quad (\ell = 0, 1, \dots n-1)$$

$\epsilon = -2$ $\ell = 0$ (bonding state)

$\epsilon = 2$ $\ell = \ell_p = \frac{n}{2}$ $\epsilon_{\frac{n}{2}} = -2\cos\pi = 2$ even $n = 2p$

$\ell = p$ $\epsilon_p = -2\cos\frac{2\pi p}{2p+1}$ odd $n = 2p+1$

$= -2\cos(\pi)(1+\frac{1}{2p+1})\dots$

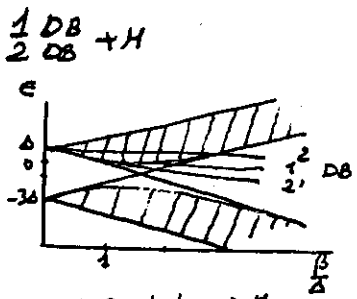


⑥ Hydrogenated amorphous Si

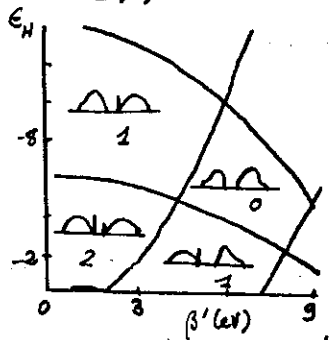
- removal of the states from the gap
- widening of the optical gap
- alteration of both the VB and CB $n(\epsilon)$

Density of states of hydrogenated a Si (crude model)

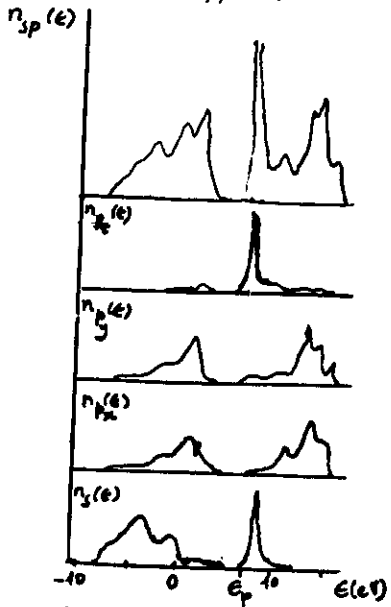
⑥ $\frac{1}{2}$ DB + H



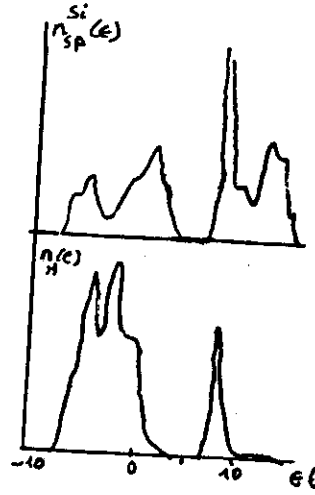
— D.B states in the Bethe Approximation



Nb of localized states in the gap



Density of state on a Si atom bearing a D.B pointing in the z direction and with 3 sp^2 backbonds (see the peak in the $n_{p_z}(\epsilon)$ for $\epsilon \simeq (\epsilon_s + 3\epsilon_p)/4$)



By hydrogenation the "p_z" DB is pushed in the conduction band and the local DOS for H has a 3 peak structure.

$\epsilon_s = 0$
$\epsilon_p = 7.2$ eV
$ss\sigma = -2.03$ eV
$sp\sigma = 2.55$ eV
$pp\sigma = 4.5$ eV
$pp\pi = -1.09$ eV

$ss\sigma_{HSi} = -2.5$ eV
$sp\sigma_{HSi} = 4$ eV
$\epsilon_H = -1$ eV !
resolution : 1eV !

$sp^{n-1} \Rightarrow$ $G_{db}(z) = \dfrac{1}{z - \dfrac{(n-1)\Delta^2}{z-(n-1)\Delta-\beta^2 G_{db}}}$ (Bethe lattice)

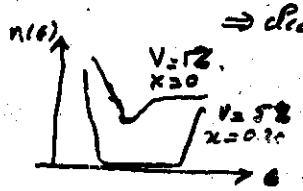
$\Downarrow$

; $G_H(z) = \dfrac{1}{z - \epsilon_H - \beta^2 G_{DB}(z)}$

db peak for $\beta/\Delta > \sqrt{n-1}$ at $\epsilon_{db} = (\epsilon_s + (n-1)\epsilon_p)/4$ with a weight $1-(n-1)\Delta^2\beta^2$

Lamache Gaspard J. de Phys C4 765 (1982)

⑥ "Simulation" with
- $\underline{\underline{x}}$ Si + random vacancies
  ⇒ D.B filling the gap
  + H (1, 2, 3, 4 H) attached to one of the DB (random)
  ⇒ clean the gap, narrows the gap
  Si:Hx

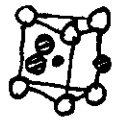


② Amorphous metallic alloys

ⓐ Structure

+ Dense Random Packing of hard spheres (DRPH)
  - absence of directional bonds
  - tendency for at to be packed as tightly as possible (without LRO)
  - starting from a triangle max of tetrahedra ⇒ icosaedra...
+ alloys ⇒ • DRPH with two hard sphere diameters
  ⇒ • Gaskell's model (for metal metalloïd)

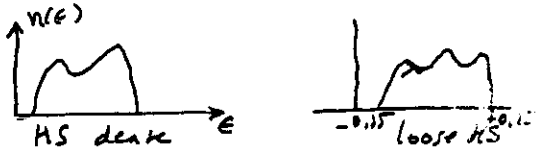
$(Me)_3 M$ prismatic units



SRO is the same as in the corresponding crystallic compound. (with the same composition) This last model is supported by a lot of experiments (ME, NMR... see Durand's lectures

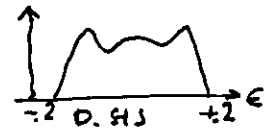
ⓑ Electronic structure

From FINNEY'S MODELS (Amorphous metals)



WA = WITH RELAXATION
LOCAL RADIAL DISTRIBUTION GOVERNS THE SHAPE OF n(E)
(shape of Voronoï Polyedra molecules)

relaxed Morse potential



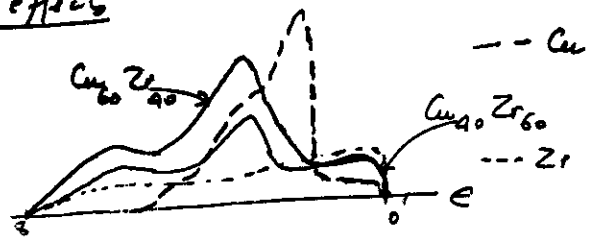
!!

ⓒ Electronic structure of amorphous metallic systems

Photoémission

MOSTLY alloy effects

METAL-METAL

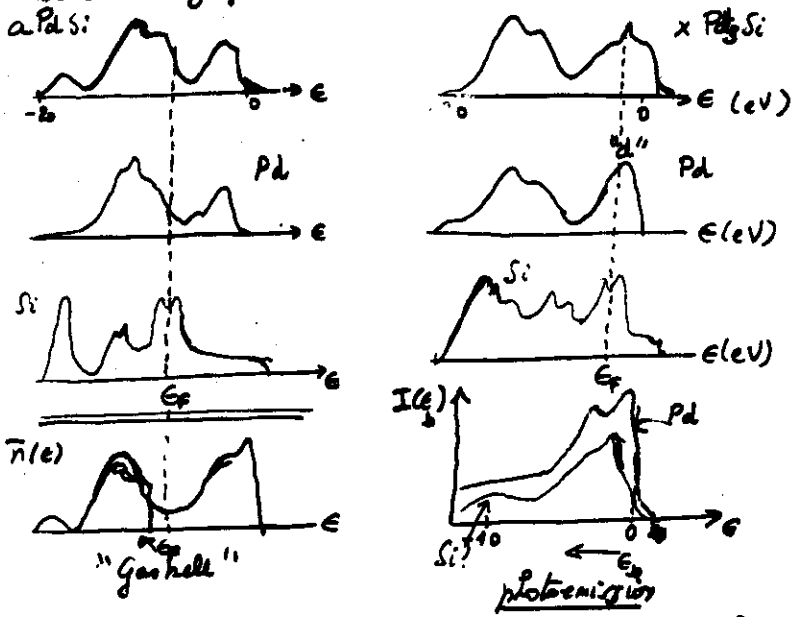


⇒ Split Band regime (of PdAg or...)

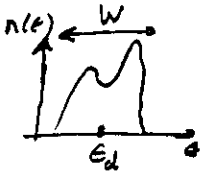
Metal Metalloid systems

Ni P , Pd Si ...

"Boudreaux Gregor"



- small differences between both calculations (â)
- state that the 'sp' states on Pd are not correctly treated (only one Pd s, p basis orbital)

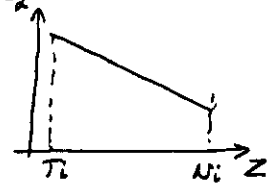


(3) ALLOYS OF TRANSITION METALS

NEGLECT of 'sp' STATES ⇒ T. B 'd' bands → / Canonical bands / dep on struct and scale W ϵ_d

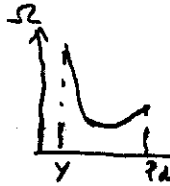
(a) The importance of disorder

D.D $\quad \epsilon_d \simeq -Z_{eV} + \epsilon_d^\circ$

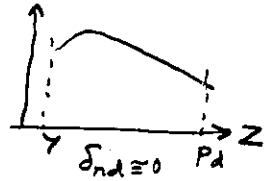


ODD

eq. latt $\qquad$ for equilibr.



Example VRh $\delta_d = .9$



(b) Split band regime

for a number of cases

Pd Ag, Cu Ni, ... Ni Ru ... Pt V etc..

(c) Phase stability and local order.

1. Orders of magnitude

Ei: PURE METALS ~ eV/at | COHESIVE ENERGY

↓

DISORDERED ALLOYS ~ $\frac{eV}{10}$/at | FORMATION ENERGY

↓

ORDER ON A LATTICE

↓

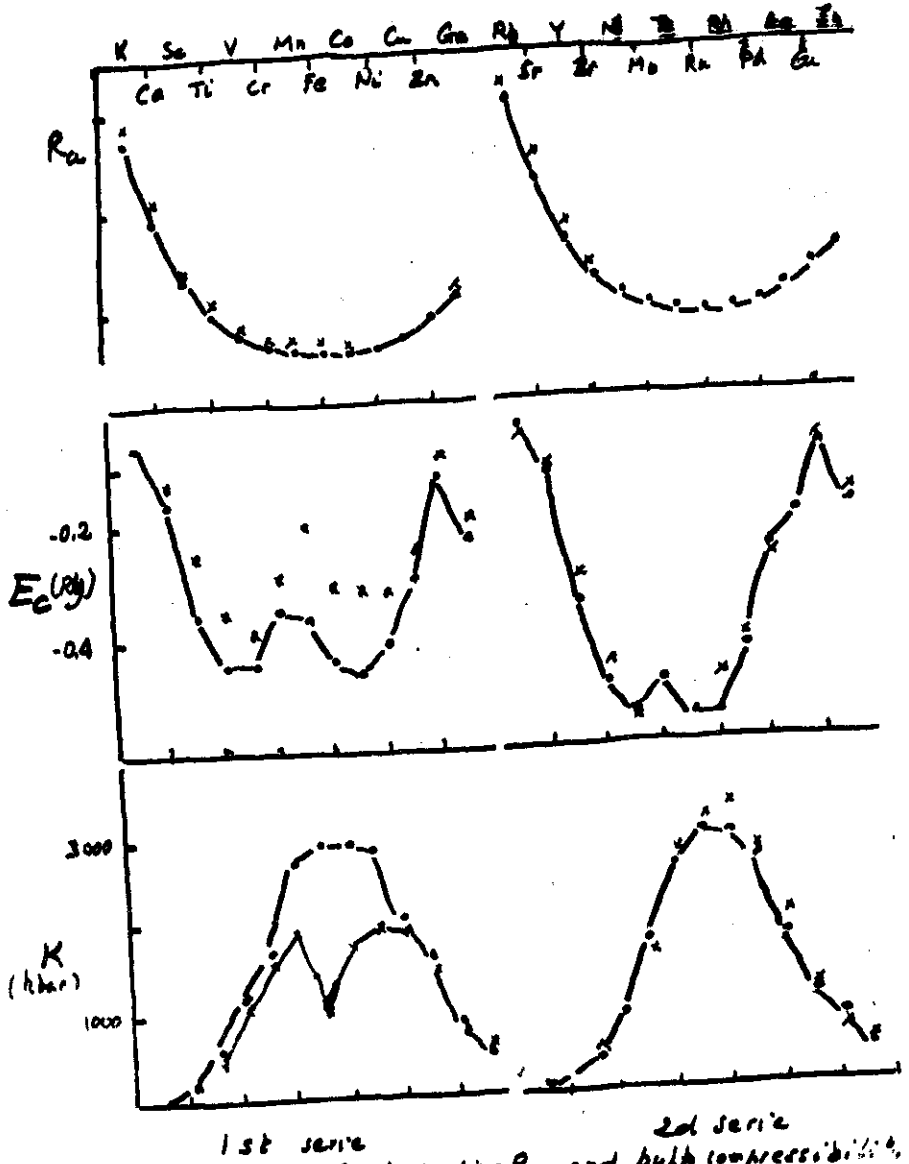
RELATIVE STABILITY OF DIFFERENT PHASES ~ $\frac{eV}{100}$/at | ORDERING ENERGIES

$E_c^i = |E(crystal)/N_a - E_{at}| = |E_i - E_{at}|$

$E_{form}(A_cB_{1-c}) = E_{dis\,all}(A_cB_{1-c}) - cE_A - (1-c)E_B$

$E_{ord}(A_cB_{1-c}) = E_{ord\,all}(A_cB_{1-c}) - E_{dis}(A_cB_{1-c})$

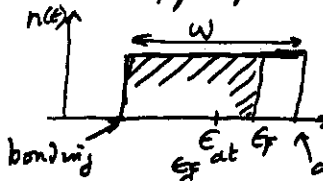
$\Delta E_{sf}(1\to 2) = E_{ord}^{(1)} - E_{ord}^{(2)}$ two phases 1, 2



Cohesive energy, Wigner Seitz radius Ra and bulk compressibility of transition Metals of 1st and 2d serie (oth. x exp.)

[2] Qualitatively

- For the cohesive energy : filling of the 'd' bands explains most of the $|E_c|$ value (max Z)



$$E_c = \int n(\varepsilon)[\varepsilon - \varepsilon_{at}]\,d\varepsilon$$

$$|E_c| \simeq \frac{W}{20}(n)(10-n)$$

EXPLAINS THE PARABOLIC VARIATION OF $|E_c|$ (Friedel)

$$n = 10\int_{-\frac{W}{2}+\varepsilon_{at}}^{\varepsilon_F} n(\varepsilon)\,d\varepsilon$$

- For the formation energy. C. P. A

Qualitatively change of E comes from change of Band width

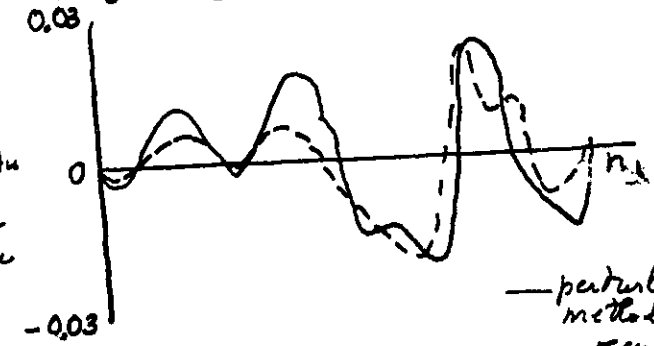
$$W_{all}^2(c) = z\beta^2 + c_A c_B(\varepsilon_A - \varepsilon_B)$$
$$= W^2\left[\frac{1}{4z} + \frac{2}{4}c_A c_B \delta^{-2}\right]$$

⇒ increasing of bonding energy (at constt volume)

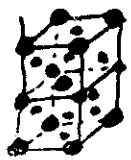
- For the ordering energy, relative stability !

band structure calculations ?
"perturbation" method ... valid for strong disorder

$\Delta E(Cu_3Au - Al_3Ti)$ $\delta = 0.9$



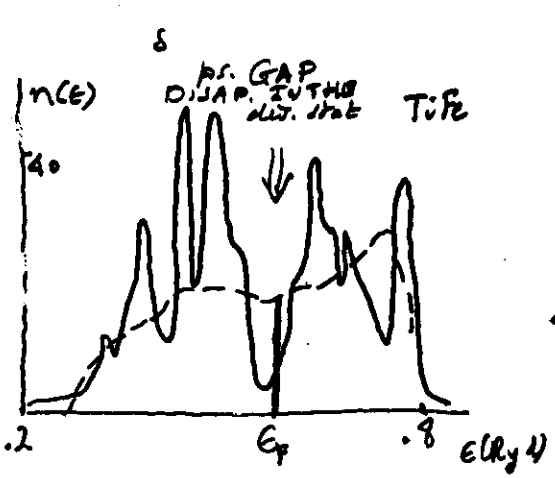
relative stability

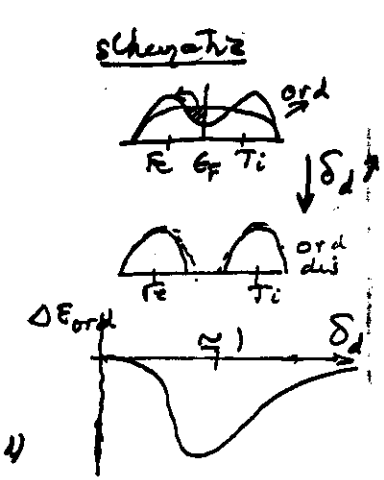


— perturbation method

– – – recursion method ($n_0 = 15$) (if $n_0 = 20$ better)

ordering energy





5) Generalized Perturbation Method

→ G.P.M ⟺ Cluster expansion for the total energy from a reference medium : i.e. THE DISORDERED STATE FOR THE CONSIDERED CONCENTRATION c

$$E(\{p_\lambda\}) = \bar{E} + \sum_\lambda p_\lambda p_\mu v(\lambda-\mu) + \sum_{\substack{\lambda\neq\mu\neq\nu \\ \rho+\sigma,\tau}} p_\lambda p_\rho w(\lambda-\mu,\rho-\sigma)+\cdots$$

bijection ⇒ (structural part)

It's convergent keeping only – pair interactions – up to 6th nn

(see previous Ising Ising-Ti Alg.).

→ Derivation ($\delta_{ord}=0$)

GPM (simple derivation) for a non deg TB band

- $E = -\frac{1}{\pi}\int f(\epsilon)\,\mathrm{Tr}\,\mathrm{Im}\,\mathrm{Log}\,G(\epsilon+i0)\,d\epsilon$
  $f(\epsilon)$ F. Dirac function
  $G(\epsilon+i0) = \frac{1}{\epsilon+i0-h}$ noted G
- Ref medium $\bar{H}$ (CPA)
- Hamiltonian for a configuration $\{p_\lambda\}$
  $h(\{p_\lambda\}) = \hat{h} = \bar{h} + V(\{p_\lambda\})$
  fluctuating part
  $(V = \sum p_\lambda^i \epsilon_\lambda^i \Leftarrow$ DD)
- Diagonal / off Diag. G
  $G = G^d + G^{nd}$ $(\langle\lambda|G^d|\lambda\rangle = \delta_{\lambda\mu}\langle\lambda|G|\lambda\rangle)$

$$\begin{cases} E = \bar{E} + \Delta E \\ \bar{E} = -\frac{1}{\pi}\int f(\epsilon)\,\mathrm{Tr}\,[\log \bar{G}(\epsilon) - \log(1-\bar{G}_{ii}V)] \\ \Delta E = \frac{1}{\pi}\int f(\epsilon)\,\mathrm{Tr}\log(1-G^{nd}t^d) \end{cases}$$

$(t_d = V/(1-G^d V)$)

- Expansion of ΔE / struct part)

$$\Delta E = -\frac{1}{\pi}\int f(\epsilon)\,\mathrm{Tr}\,G^{nd}t^d + \frac{1}{2}\mathrm{Tr}\,G^{nd}t^d G^{nd}t^d + \frac{1}{3}\mathrm{Tr}\,G^{nd}t^d G^{nd}t^d G^{nd}t^d + \cdots$$

pairs ⇒ (dumbbell) triplets ⇒ (triangle)

- Pair interactions for DD

$$V(\lambda-\mu) = -\frac{1}{\pi}\int_{\epsilon_F}^{\epsilon} d\epsilon\,(\Delta t)^2\,\bar{G}(R)^2\,d\epsilon$$

$G(R) = \langle 0|\bar{G}(\epsilon)|R\rangle$

- It's a cluster expansion in terms of $(t^d G^{nd})^n$ small parameter, $(t^d G^{nd}(R))^2$
- Better convergence for large δ
  $|G(R)| \sim \exp(-R/\lambda)$ λ = mean free path

6 Pair interactions for phase stab.

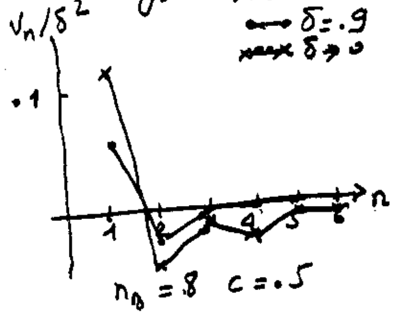
$V_{1-n} = V_1, V_2 \dots V_n$
nth n.n.

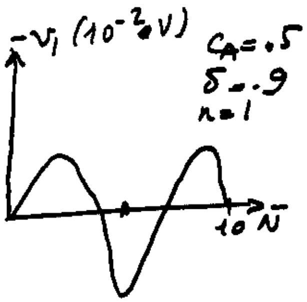
- scaling property for all binary alloys

$V_n = \overline{W}\ V_n$

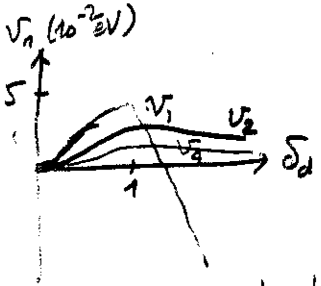
$V_n = V_n(c, \overline{N}, \delta_d, \delta_{nd})$

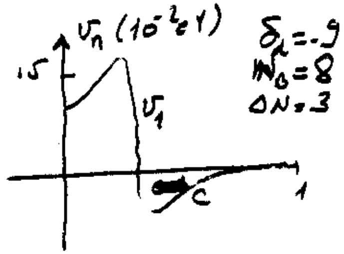
(i) range : short ranged for large disorders
(ii) band filling $\overline{N}$
sum rules ⇒ existence of a min. number of 0 for $V_n(\overline{N})$





"range"
(iii) disorder (δ) / can change of sign)



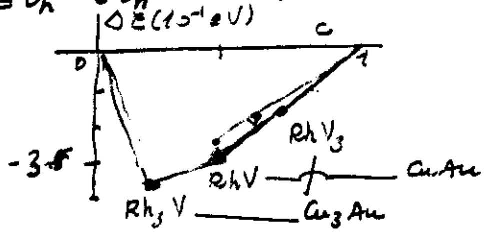


(iv) concentration / can also change of sign)

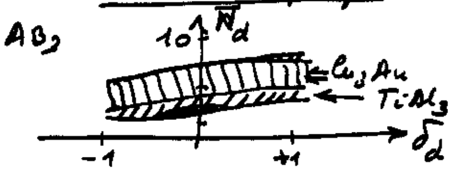
7 Most Stable O.S (T=0K) on a given lattice for a given c

MAPPING OF THE ELECTRONIC PB. ON AN EQUIVALENT 3D ISING MODEL WHOSE GROUND STATES IS KNOWN FOR SHORT RANGED INTONS
$\sigma(\Delta_{1-n}) = V_n$ ($V_n = 0$ n>4)

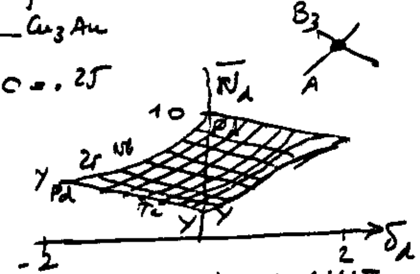
Ex VRh



8 Structural maps Ex. c=.25

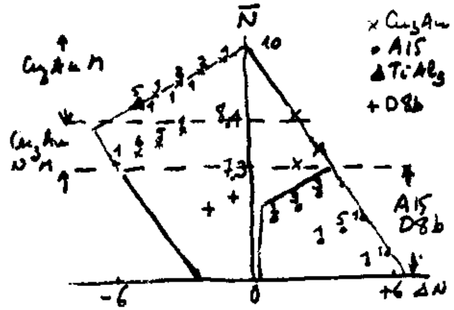


MOST STABLE PHASES FOR GIVEN (δ_d, N_d)



A PECULIAR SYST AB_3 CORRESPONDS TO A POINT IN THIS DIAGRAM

⇒ syst predictions for the phase stability and for SRO in such crystalline alloys (no. magn)
- magnetism ?
- self consistency ? ...



Experimental Structural map ($\overline{N}$, ΔN) for C=.25