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SPRING COLLEGE IN MATERIALS SCIENCE

ON

"METALLIC MATERIALS"

(11 May - 19 June 1987)

ELECTRONIC STRUCTURE AND PHASE STABILITY
(Part I)

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ELECTRONIC STRUCTURE AND PHASE STABILITY

METALLIC SYSTEMS

I INTRODUCTION

1a) "build" new phases from at, clust, md-
- det (descr) their struct
- predict their occurence
  their properties → MECHAN, OPT, ELMAGN, TRANSP (supra), CAT
- «design» ←

b) Use of
- electronic structure
- statistical physics

c) Examples:
(i) HIGH TEMPERATURE ALLOYS
superalloys (heterogeneous) γ, γ' Ni_3Al
(ii) NEW SUPERCONDUCTORS $La_{2-x}M_xCuO_4$
«ceramics» Y---Cu---O
(iii) AMORPHOUS $NiZr$, FeP, ...

2 ORDER- DISORDER

2-1 TOPOLOGICAL DISORDER

ORDERED	TOPOLOGICAL DISORDER
(i) crystalline : 3x periodic	(ii) AMORPHOUS
(ii) quasicrystalline	(iii) LIQUID
"LRO" → lattice	"S.R.O"
$n_{at}(r)$	$g_{at}(r)$

«ground state» → H.T.O order → «ensemble average»

2-2 ALLOY PHASES AND CHEMICAL DISORDER

- START FROM SIMPLE LATTICES
- BUILD ORDERED STRUCTURES A_cB_{1-c} (O.S.) FROM SIMPLE TO MORE AND MORE COMPLEX BY ADDING PERIODIC 1D DEFECTS

Examples

1a) CuAu ($L1_0$) CoFe (B_2) simple O.S
Cu_3Au ($L1_2$)
fcc bcc

b) substoechiometric alloys
"simple ordering on a sublattice"
ex: carbides, nitrides.

c) long periods CuAu, CuPd
$TiAl_3$
TOWARD AN ∞ OF STRUCTURES.

2a polytypes
- Co V alloys
- M_3 alloys, $Zr(Fe,Cr)_2$

A B C A B A
(fcc) (hcp)

2 ORDER - DISORDER amorphous alloys

2.3 Low dimensionality. (→ 2D, 1D)

2D : Intercalation chemistry

Examples • TM dichalcogenides

• graphite + → metal (alkaline RE..)

→ molecules

1D
organic compounds
(transport
magnetism)

0D
small particles
(catalysis
magnetism)

2.4. ARTIFICIAL STRUCTURES (AS)

1D periodic modulations AB AB—

- composition superlattices
- coherent and incoherent interfaces
- periodic and aperiodic

order in A.S vs order in ~~opposite~~ bulk?

Ex : GeSi, on AlAs Ex : Ru Ir, NiCr... diffusion?

2.5 ORDER / MIXING } vs SEGREGATION ?

Ex 1 Cu Ni (mixing - segr) ← diffn Lig

Ex 2 $C_c R_{1-c}$ order - segr vs concentration c

2.6 PHASE STABILITY (ϕ St)

• Compare the (free) energies of the various ϕ ?
Is det de ϕ St

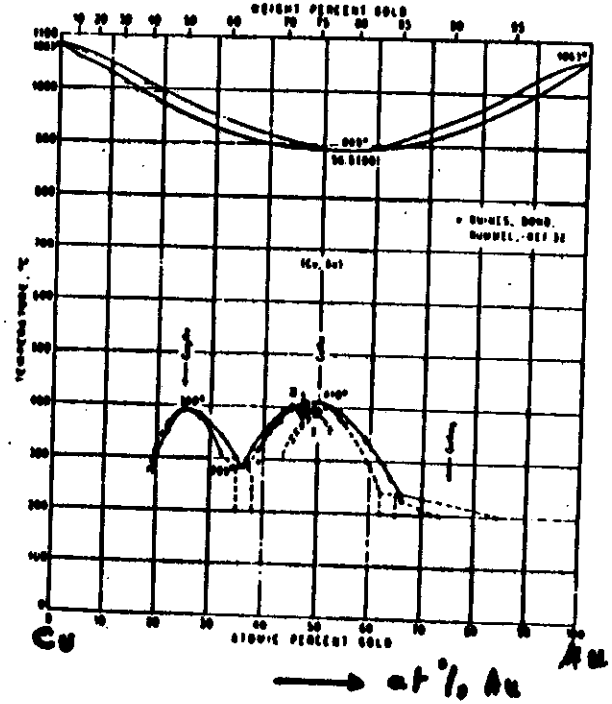
[→ various orders on the same lattice → St st
→ compare for ϕ lattices, ~~diffent~~

ΔH (or ΔE) $\Delta E = E - c_A E_A - c_B E_B$

mixing energy
formation "

IN THE FOLLOWING TRANSPARENCIES, WE PRESENT QUALITATIVELY SOME REPRESENTATIVE EXAMPLES OF THE ORDERED STRUCTURES. WE WILL STUDY LATER THEIR EXAMPLES FROM AN EL STR POINT OF VIEW

ONE OF THE SIMPLES PHASE DIAGRAM WITH O.S.



d'après Hansen (1958)

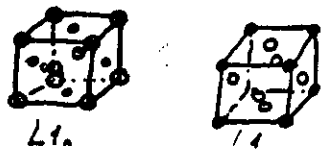
• THREE ORDERED PHASES

fcc latt. $Cu Au_I$ $L1_0$

$Cu_3 Au$ $L1_2$ + "LONG PERIODS" $Cu Au_{II}$

$Cu Au_3$

• A
○ B

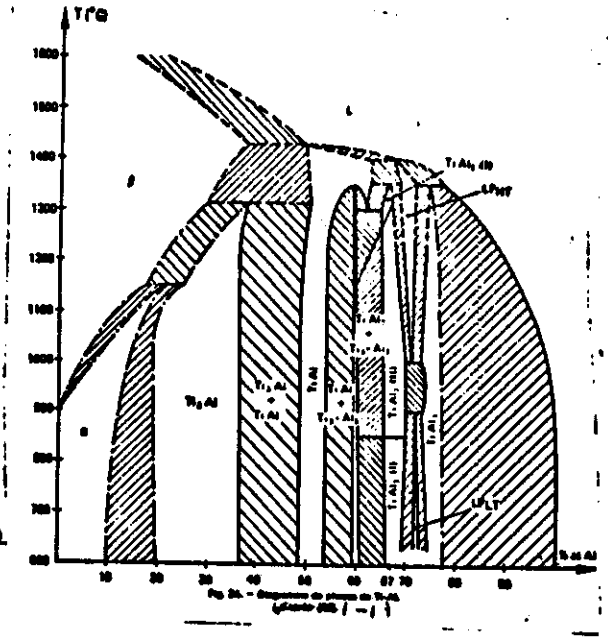


$L1_0$ $L1_2$

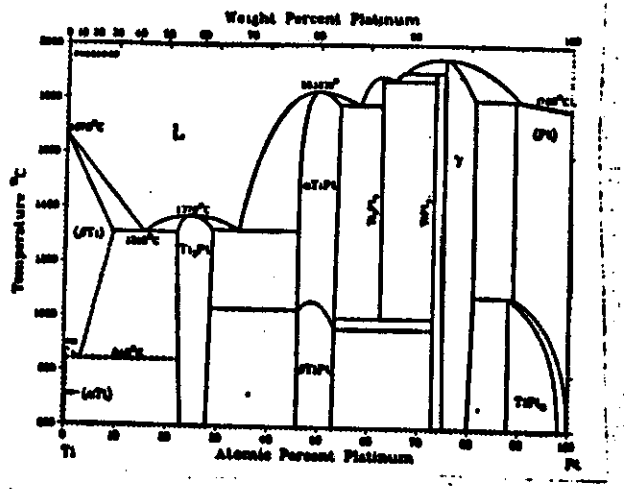
(5)

$TiAl_3$ and TiPt ϕ DIAGRAMS

NOTE THE REGIONS OF THE ϕ DIAGR FOR WHICH LONG RANGE ORDER VARIANTS ARE OBSERVED LP_{HT}, LP_{LT} (for the structures see below)



Assessed Ti-Pt Diagram



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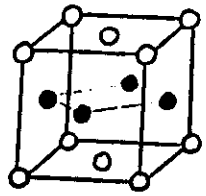
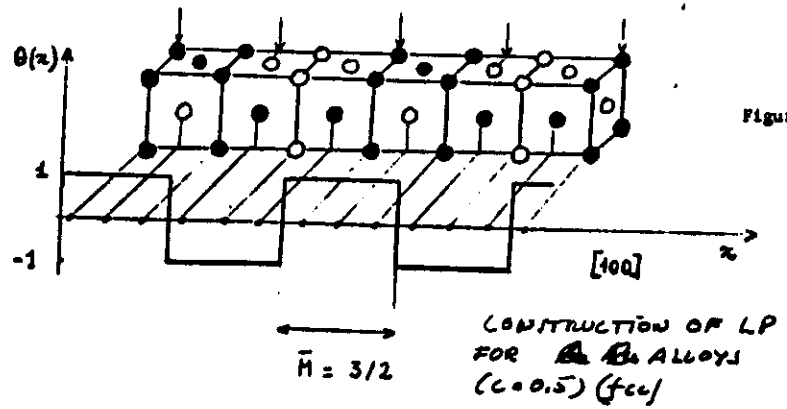


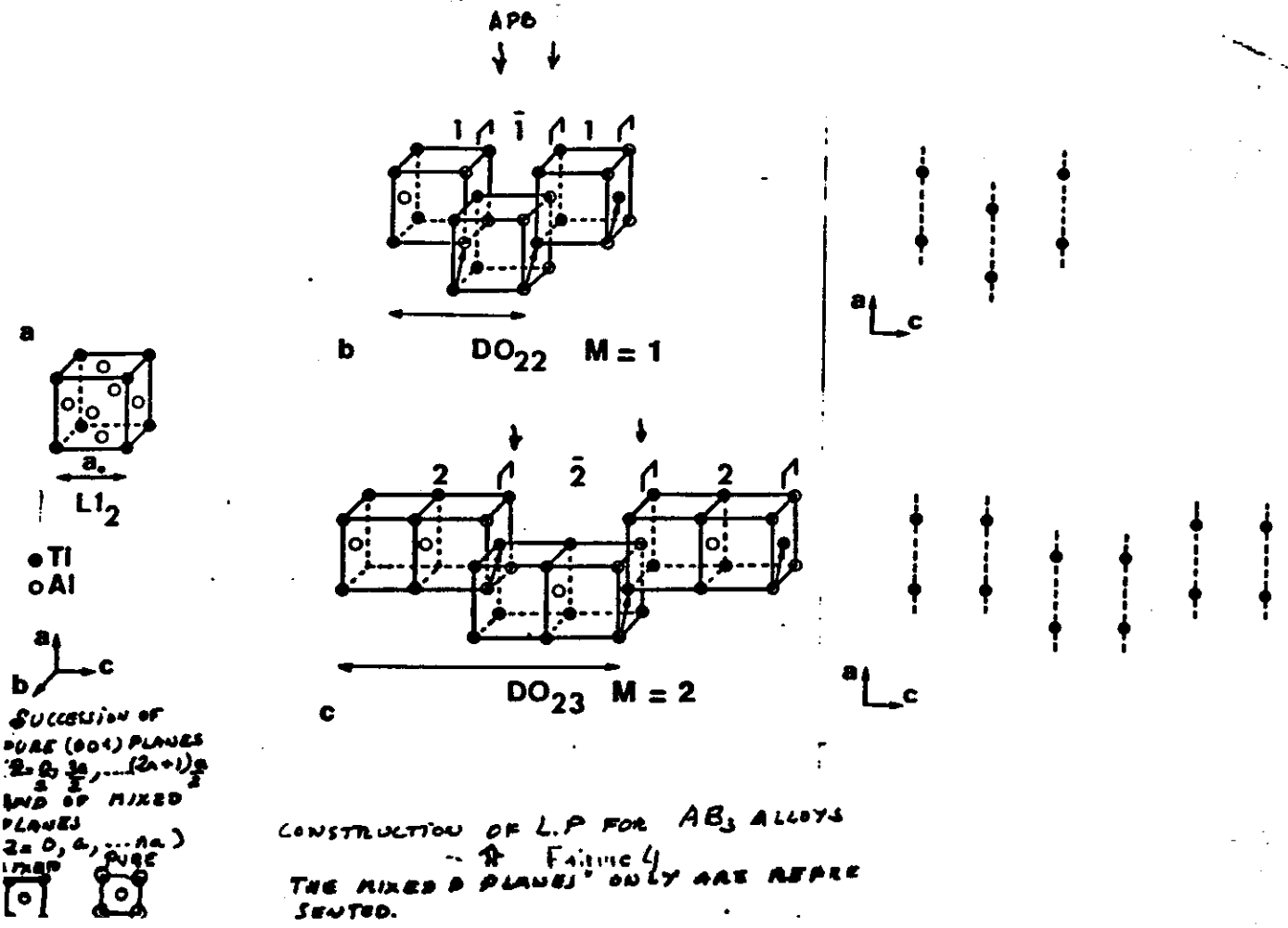
$L1_2$.

Figure 4.3



CONSTRUCTION OF LP FOR [illegible] ALLOYS ($c = 0.5$) (fcc)

Figure 4.4



CONSTRUCTION OF L.P FOR AB_3 ALLOYS
→ Fairme 4
THE MIXED B PLANES ONLY ARE REPRESENTED.

(2)

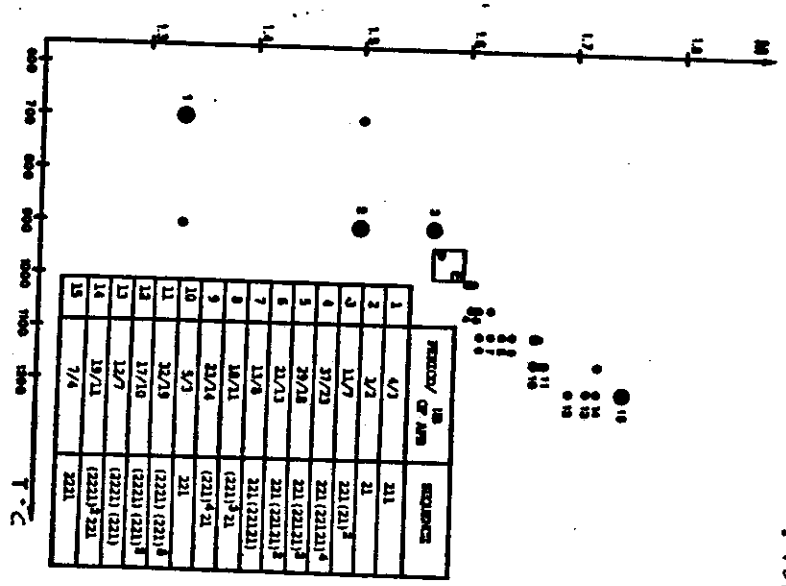


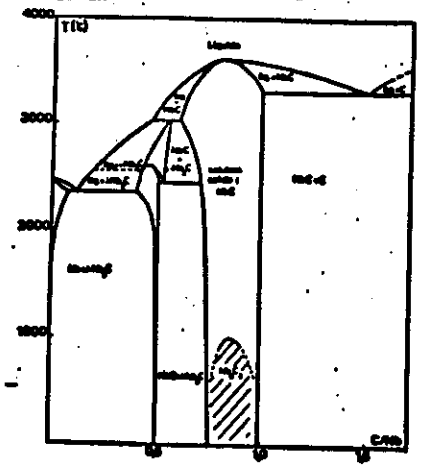
Fig 19 Lorieau et al 1975

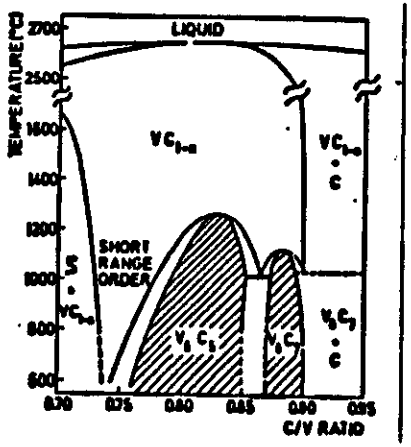
PERIODS OF THE OBSERVED L.P. FOR VA RICH T (observation by HREM).

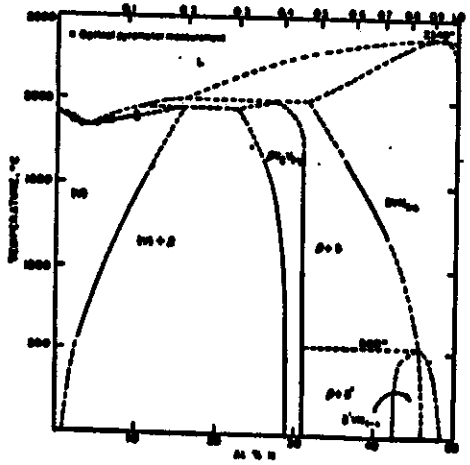
Ti Al3

(1)

PHASE DIAGRAMS OF SUBSTOECHIOMETRIC [redacted] CARBIDES







ORDER IN SUBSTOECHIOMETRIC CARBIDES AND NITRIDES
(Structure "Na Cl" B1)

- ONE OF THE fcc SUBLATTICES IS ONLY OCCUPIED BY TM ATOMS
- ONE OF THE fcc SUBLATTICES IS OCCUPIED BOTH BY C (or N) AND BY VACANCIES. : THE VACANCIES ARE ORDERED ON THIS fcc SUBLATTICE ACCORDING TO THE CLASSICAL O.S WE DESCR. PREVIOUS

[O.S for vacancies on the metalloid fcc sublat.]

carbides
- $L1_1$ "Cu Au" — Ti_2C, Zr_2C, Y_2C, Sc_2C, Gd_2C Dy_2C, Ho_2C Er_2C
- 11 "A_3B" — Nb_6C_5, V_6C_5, Ta_6C_5

nitrides
- DO_{22} "$TiNi_3$" — Nb_4N_3
- 40 "A_2L_2" — Ti_2N, Mo_2N

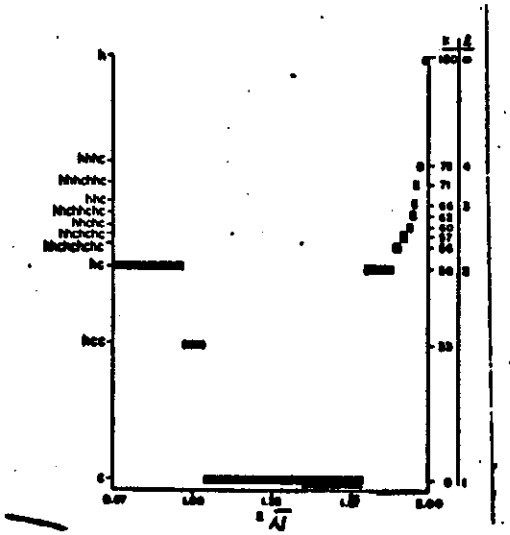
(from de Novion et al)

1. Note : $L1_1$ IS THE STRUCTURE OBTAINED ON AN fcc LATTICE BY OCCUPYING THE SUCCESSIVE (111) PLANES BY A AND B ATOMS
   40 IS THE STRUCTURE OBTAINED FROM $L1_0$ BY INTRODUCING THE PREVIOUS ABB on ALL PLANES ⊥ na.

2. Note also that in METALLIC SYSTEMS, THERE IS ONLY ONE "$L1_1$" STRUCTURE EXPERIMENTALLY OBSERVED ("CuPt") WHEREAS MANY SUBSTOECHIOMETRIC CARBIDES PRESENT THIS STRUCTURE AS A STABLE O.S. WHY ? SEE CHAPTER II.

POLYTYPES IN Mg BASED TERNARY ALLOYS

NOTATION : ABAB (h) ABC (c)

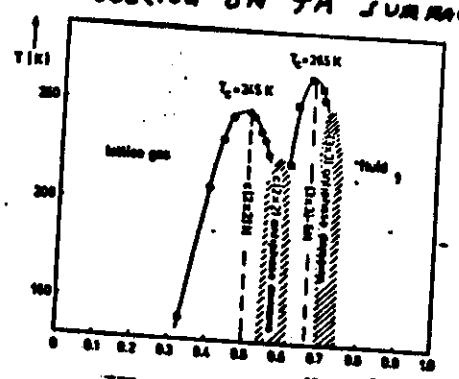


POLYTYPES VS THE AVERAGE NUMBER OF ELECTRONS $\bar{N}$.

(from Brunsma - Zangwill PRL 57 1414 (1986))

See also C.T Liu lectures

ORDERING ON TM SURFACES



Complete phase diagram of the hydrogen/iron(110) system. The full dots represent the experimentally determined data points; the hashed areas correspond to the regions where phase boundaries occur.

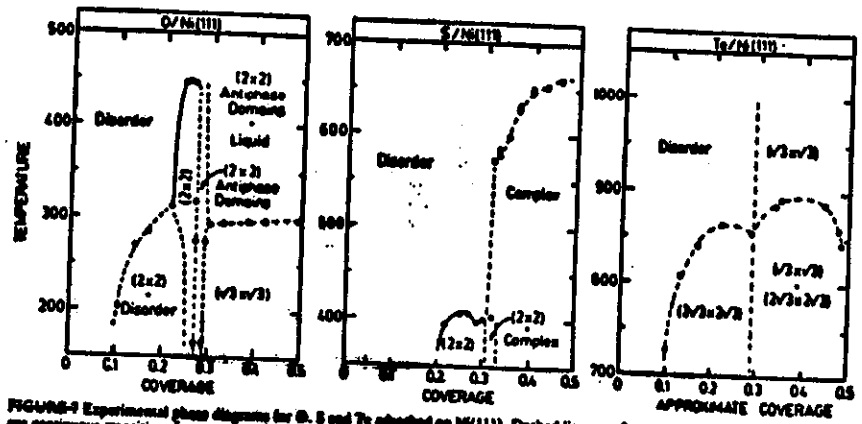
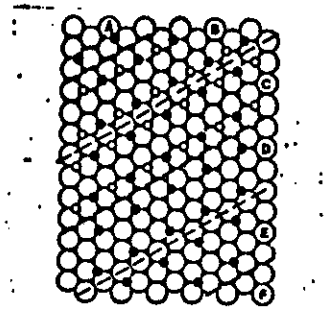


FIGURE 9 Experimental phase diagrams for O, S and Te adsorbed on Ni(111). Dashed lines are first-order transitions and solid lines are continuous transitions.



A domain of the $p(2\times2)$ structure with antiphase boundaries in between. Dashed lines in the figure show these boundaries. If atoms in a given domain occupy fcc sites, atoms in neighboring domains will be in hcp sites.

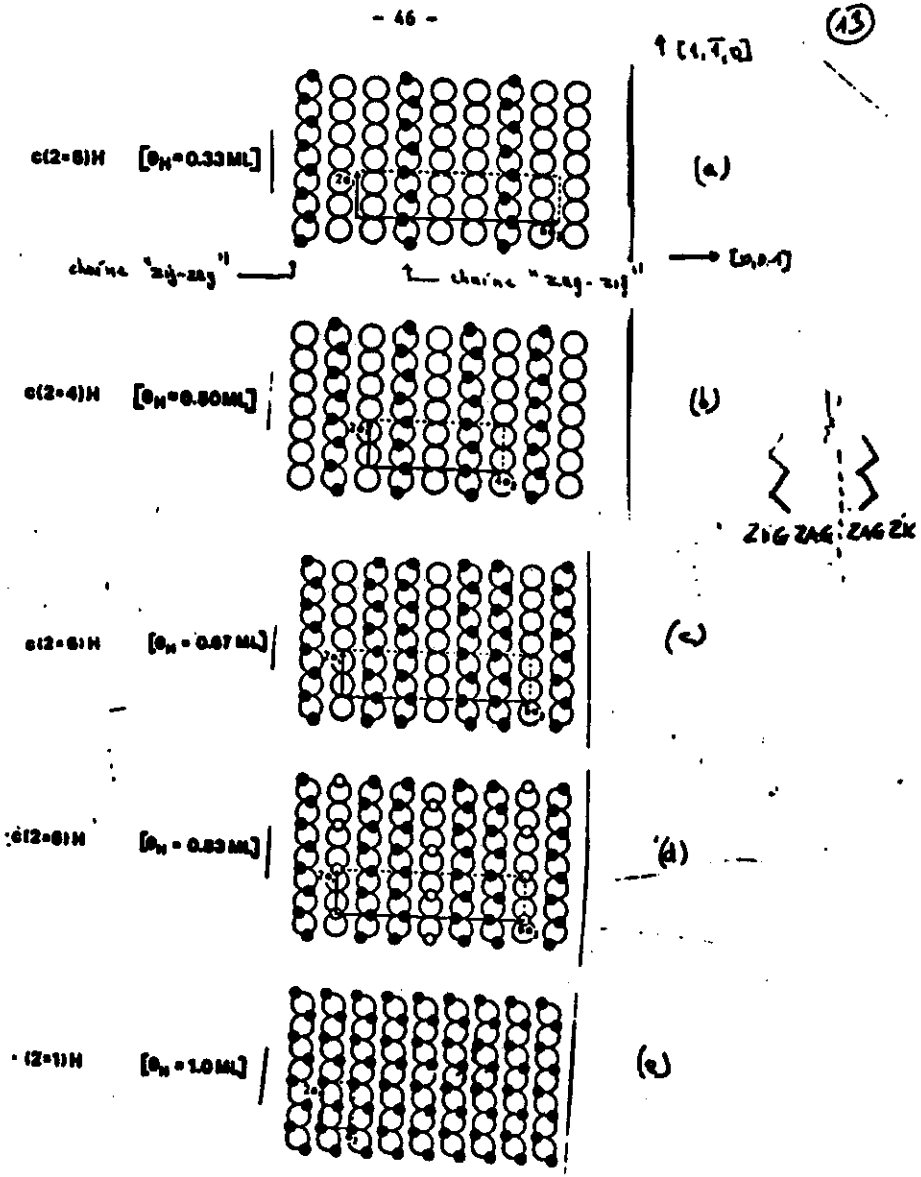
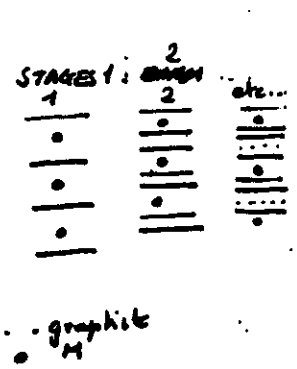
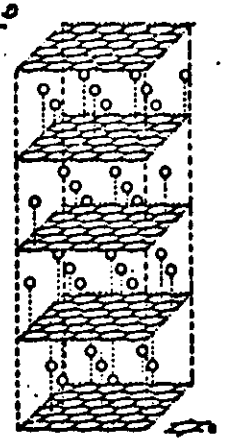


Fig. 21 (d'après |90c|)

Arrangements des adatomes d'hydrogène sur la surface (110) du nickel pour les structures ordonnées observées ($0 < \theta \leq 1$). Les grands cercles correspondent aux atomes de Ni, tandis que les petits cercles (noirs et blancs) correspondent aux atomes H. Notez qu'il y a trois types d'arrangements atomiques différents correspondant à la structure c(2x6).





Model for C_8K according to Rüdorff and Schulze (1954) showing the stacking of graphite layers (networks of small solid balls) and of potassium layers (networks of large hollow balls). The graphite and intercalate layers are arranged in an AαAβAγAδ stacking sequence, where A refers to the graphite layers and the greek letters to the intercalate layers.

Fig. 10b (d'après |10|)

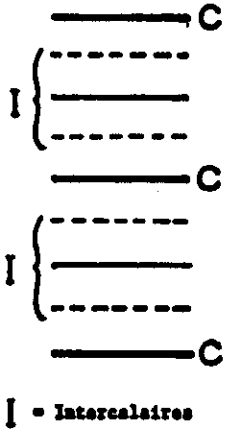
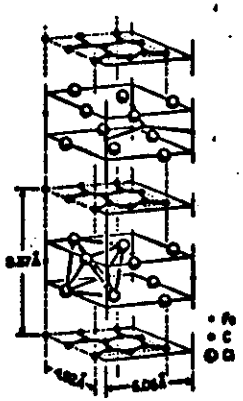


Fig. 10c



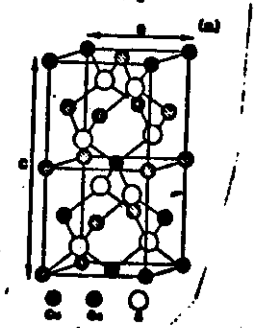
Schematic diagram of stage 1 graphite–$FeCl_3$ showing intercalate layers with the bulk $FeCl_3$ structure sandwiched between graphite planes. The intercalate layers are incommensurate with the graphite and the pertinent lattice constants are indicated. The octahedral coordination of the ferric ion is shown in the lower sandwich and the two inequivalent ferric ions are indicated on the upper sandwich.

Fig. 10d (d'après |10|)

SEMICONDUCTOR COMPOUNDS AND ARTIFICIAL STRUCTURES

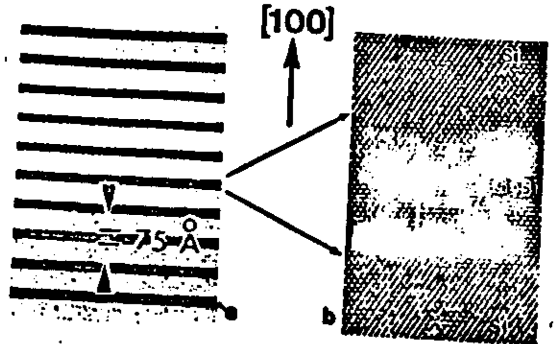
chalcopyrite

ABS_2



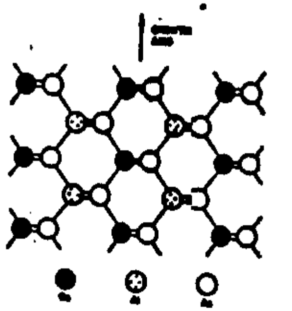
"diamond" lattice"

- one of the fcc lattice is occupied by S atoms
- the other one is occupied according to a structure 40 (see carbides) by A and B Atoms.



1. (a) Bright-field (b) Lattice images of the Ge–Si/Si SSL.

Ge Si / Si



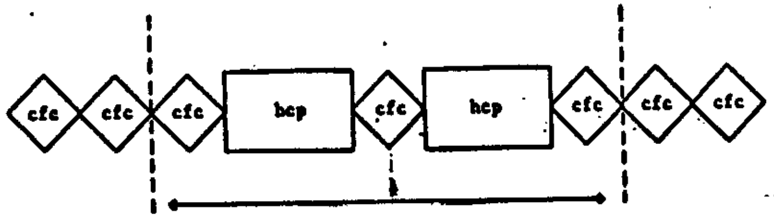
perfect long-range order in $Al_{0.5}Ga_{0.5}As$. Schematic diagram of a par

$Al_{0.5}Ga_{0.5}As$

METALLIC ARTIFICIAL STRUCTURES

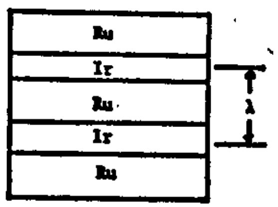
T=338C. $d = 500 \times 19$ Å

ABCA	CACA	BCAB	ABAB	CABC	BCBC	ABCA	.....
Ag	Ti	Ag	Ti	Ag	Ti	Ag	
cfc	hcp	cfc	hcp	cfc	hcp	cfc	



$d = 2000$ Å

Ru / Ir



$\lambda > 62$ Å Ir (hcp) Ru (fcc)

$\lambda < 41$ Å ($n < 10$) Ir

TiAg

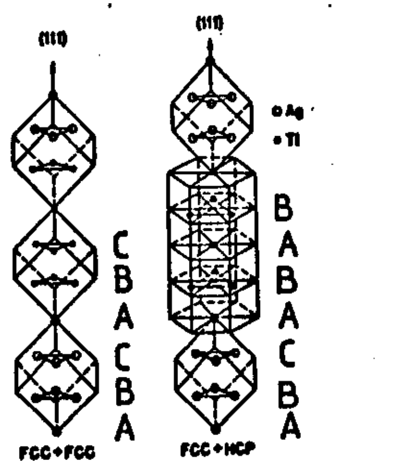


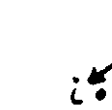
FIG. 3. Models of the structures found in Ti-Ag laminae: at the left, the fcc structure; at the right, the mixed fcc-hcp structure.

AB ABNCB CB ≈≈≈ // CB CB // AC AC ≈≈≈ AC AC // ABAB≈≈≈
Ru Ir Ru Ir Ru

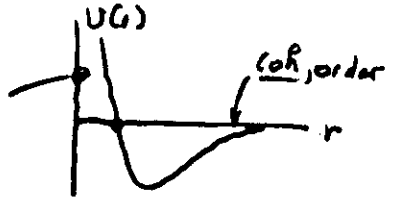
3 interatomic potentials, pair and multiple cluster interactions, and ϕ stability.

alloy $A_c B_{1-c}$

1 - Let assume $\exists \; v^{ij}(r)$



$$E_{conf} = \frac{1}{2} \sum_{R,ij} v^{ij}(R)$$



Up

2 On a lattice → Ising model

- a configuration $\equiv \{p_\lambda^i\}$

$$p_\lambda^i = \begin{cases} 1 & \text{if site } \lambda \text{ occ by } i \\ 0 & \text{otherwise} \end{cases}$$

- $$E_{conf} = \frac{1}{2} \sum_{\substack{i,j \\ \lambda\mu}} v_{\lambda\mu}^{ij} \, p_\lambda^i \, p_\mu^j$$

- BINARY ALLOY i = A, B

$$p_\lambda^B = 1 - p_\lambda^A \qquad p_\lambda^A = p_\lambda$$

$$E_{conf} = \frac{1}{2} \sum_{\lambda \neq \mu} v_{\lambda\mu} p_\lambda p_\mu - \tilde{\mu} \sum p_\lambda$$

$$v_{\lambda\mu} = v_{\lambda\mu}^{AA} + v_{\lambda\mu}^{BB} - 2 v_{\lambda\mu}^{AB}$$

- ISING NOTATION

$$p_\lambda = \frac{1+\sigma_\lambda}{2} \Rightarrow E_{conf} = \frac{1}{2} \sum_{\lambda\mu} v_{\lambda\mu} \sigma_\lambda \sigma_\mu - \sum_\lambda h_\lambda \sigma_\lambda$$

IN SUCH A CASE WE ARE INTERESTED BY:

- THE DETERMINATION OF THE ATOMIC ORDER: (possible intermetallic compounds ? the most stable at equilibrium ? order or segregation ?...)
- THE SHORT RANGE ORDER (SRO) IS DETERMINED BY:

$$\langle p_\lambda^i p_\mu^j \rangle = \begin{cases} \delta_{ij} c_i & \text{if } \lambda = \mu \\ c_i c_j - c_i c_j \frac{1}{N} \Phi_{\lambda\mu}^{ij}(\lambda - \mu) \end{cases}$$

(probability to have : i^{th} at λ and j^{th} at μ.

WHERE $\langle p_\lambda^i \rangle = c_i$ IS THE CONCENTRATION OF ATOM i

FOR A BINARY ALLOY $A_c B_{1-c}$:

$$\begin{cases} \langle p_\lambda^A p_\mu^A \rangle = c_A^2 + c_A c_B \, \alpha(\lambda - \mu) \\ \langle p_\lambda^A p_\mu^B \rangle = c_A c_B - c_A c_B \, \alpha(\lambda - \mu) \end{cases} \qquad \begin{matrix} S^{AB}(\lambda) = \alpha(\lambda) \\ \text{"SRO PARAMETERS"} \end{matrix}$$

$\alpha(\lambda)$ decreases with λ (oscillating) and tends to zero when $\lambda \to \infty$

- $\alpha_1 > 0$ (1 = 1st neighbor) → CLUSTERING (more A at 1st neighbor than the average when one of its neighbor is occupied by A
- $\alpha_1 < 0$ → ORDERING (less A, more B)

4 GENERAL TRENDS FOR SEGREGATION AND ORDER

GENERAL EMPIRICAL "RULES"

1. DISORDERED SYSTEMS AND COMPOUNDS

SOLID SOLUTIONS ⟷ INTERMETALLIC COMPOUNDS

SIZE EFFECT $\frac{\Delta r}{r} < .15$

ELECTRONEGATIVITY

$\Delta E_1 \cong A(\Delta\Omega)^2$ (Ω = at volume)

$\Delta E_2 \simeq -N_R \Delta\phi^2$

$$\Delta E = -P\Delta\phi^2 + Q\Delta n_{WS}^{2/3} \quad \text{(MIEDEMA)}$$

2 ORDERED STRUCTURE ON A LATTICE

FOR A GIVEN CONCENTRATION c TWO PARAMETERS (AT LEAST):

- AVERAGE NUMBER OF ELECTRONS PER ATOM (e/a) HUME ROTHERY

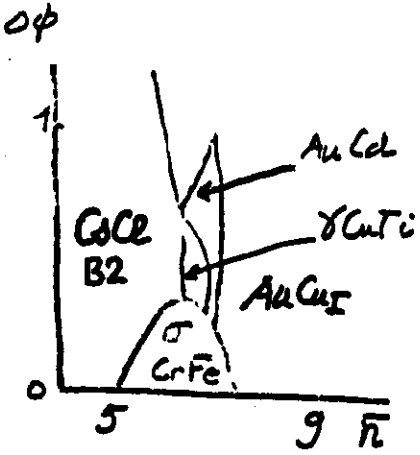
$$\bar{N} = c_A N_A + c_B N_B$$

- DIFFERENCE OF ELECTRONEGATIVITIES $\Delta\phi$

∴ DIFFERENCE OF VALENCE (ΔN)

↓

"STRUCTURAL MAPS"



3 EXAMPLE : PARAMETERS CHARACTERIZING AN ALLOY OF TRANSITION METALS:

FOR ORDERING ON A GIVEN LATTICE (fcc for example):

(i) CONCENTRATION c DETERMINES A SET OF POSSIBLE STRUCTURES

(ii) THE (e/a) FILLING OF THE BANDS

$$\bar{N} = c_A N_A + c_B N_B$$

(iii) $\Delta N = N_A - N_B$ CHARACTERIZES THE FLUCTUATION OF POTENTIALS

(iv) $\Delta S = \pm 1, \pm 2, 0$ CORRESPONDS TO THE SERIES (S = 1, 2, 3).

$$\begin{cases} \Delta N \simeq \Delta\epsilon_d \sim \Delta\phi \\ \Delta\epsilon_d = \epsilon_A - \epsilon_B = \text{difference between the A and B energy levels in the metal} \\ \Delta W_d = W_A - W_B = f(\Delta Z, \Delta S). \end{cases}$$

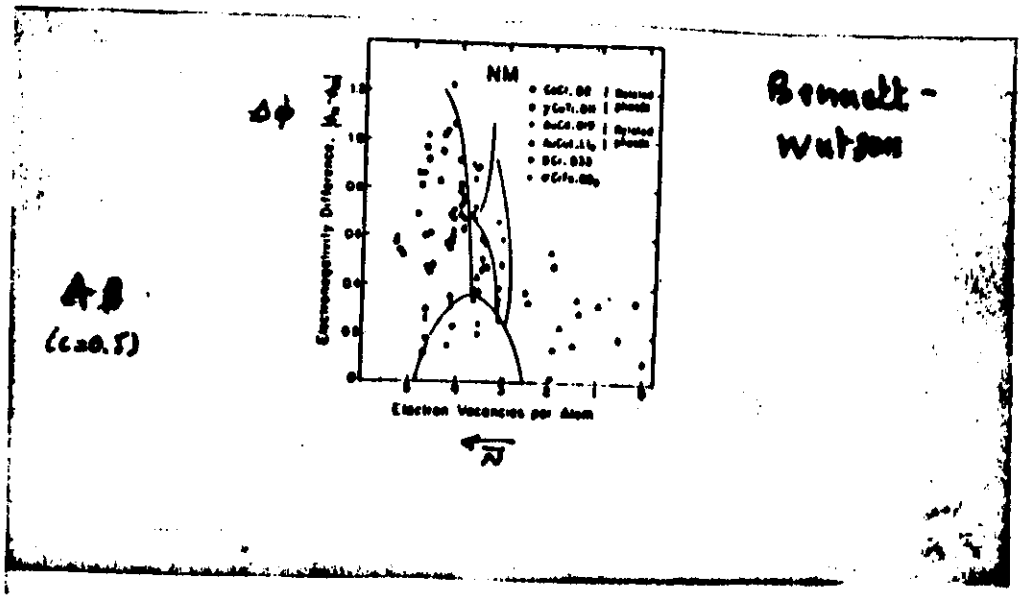
NOTE THAT A GOOD SEPARATION IS OBTAINED BY 2D MAPS FOR ALL CONCENTRATIONS !

4. STRUCTURAL MAPS AND ELECTRONEGATIVITY SCALE FOR p-d COMPOUNDS (Pettifor)

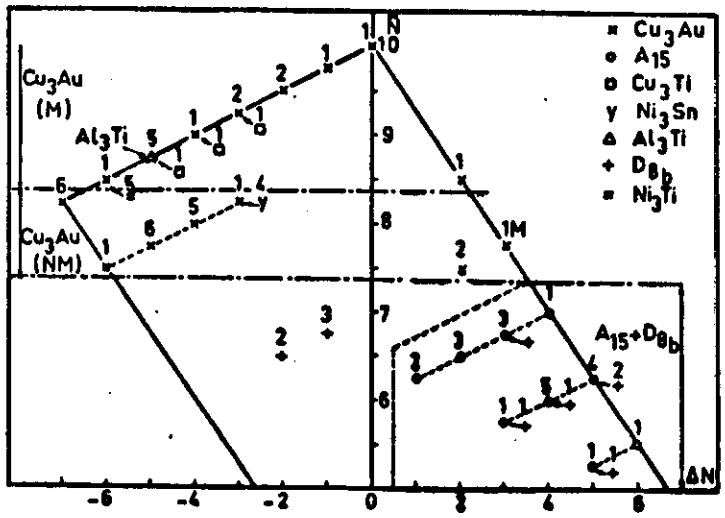
5 GLASS FORMING ABILITY

ΔH_m / r/R (Giessen)

and more complicated representation...



(23)

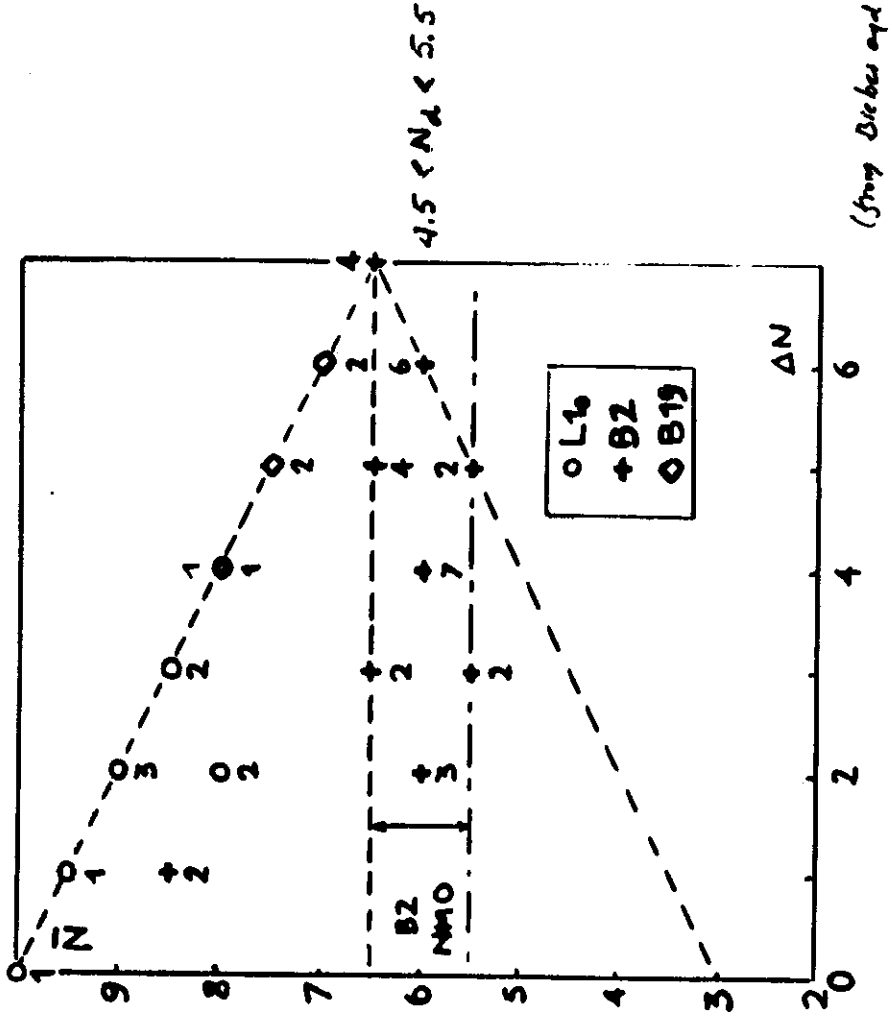


(from Brebec and Gautier)

Fig. IV.7.3. :

Cartes structurales phénoménologiques ($\bar{N}$, ΔN) pour les alliages de métaux de transition A_3B ; Cu_3Au (N) et Cu_3Au (NN) correspondent respectivement aux composés ferromagnétiques et paramagnétiques. Les nombres représentent le nombre de systèmes pour lesquels chaque SO a été observée.

(24)



(from Brebec and Gautier)

HETTIPOR "CHEMICAL SCALE" FOR THE STUDY OF THE STABILITY OF AB COMPOUNDS

Fig. 1. - The chemical scale.

THE COARSE POLARIZATION FORAL MAP

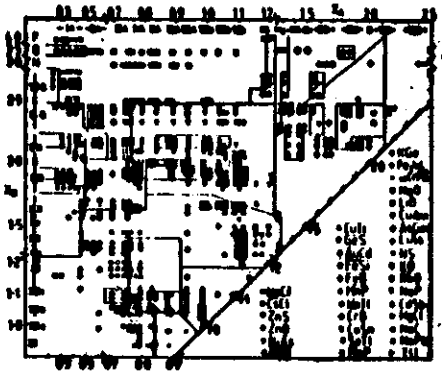


Fig. 2. - The (χ_A,χ_B) structure map for 534 AB compounds.

structural behaviour under pressure of the sp bonded III-V compounds AlP, AlAs, GaP, and GaAs has been investigated from first principles by Froyen and Cohen (14). Here we wish to study the pd bonded AB compounds which are located near the middle of Fig. 2. In particular, we wish to understand (15)

STRUCTURAL MAP (A. Hafner) FOR Sp-d COMPOUNDS

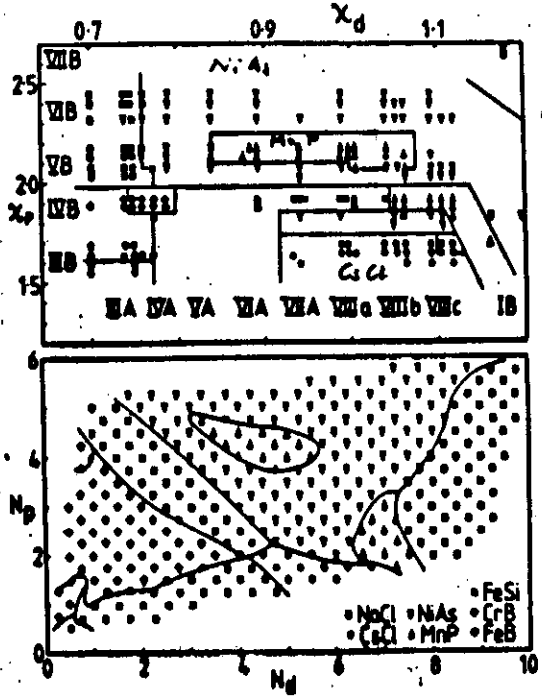


Fig. 3 -

Upper panel: The Structure map (χ_p,χ_d) for 160 pd bonded AB compounds, where χ_p and χ_d are the values of the chemical scale for the A and B elements respectively. The 2p elements are not included in the present figure.

Lower panel: The theoretical structure map (N_p,N_d) where N_p and N_d are the number of p and d valence electrons respectively on the CsCl lattice.

(Arno Hafner)

I: INTRODUCTION
- topological and chemical orders.
- eq. st and metastable structures: "order" in amorphous and artificial materials. General trends (structural maps).
- phase stability and pair potentials? If such potentials ∃ the results of Statistical ϕ can be used (ground states, ϕ diag...)

II ELECTRONIC STRUCTURE: GENERAL PRINCIPLES
- The Density Functional formalism and the L.D.A.
- Discussion. Validity of the results for G.S and excitations (??) in some examples.
- Force theorem and the equation of state (T=0K)
- The current approximations for the calculation of the one electron states - Brief comments on the definition of charge transfer.

III ELECTRONIC STRUCTURE OF ORDERED AND DISORDERED SYSTEMS: GENERAL TRENDS
- Introduction: the tight binding method
- Local electronic structure and recursion (moments) method.
- General features of the electronic structure of (concentrated) disordered alloys and ordered compounds. A simple method for the calculation of completely disordered alloys: the CPA.
- Discussion of the roles of the (1) topological disorder (2) chemical order in compounds (3) disorder in crystalline systems (4) topological disorder in O or D. alloys (5) ODD in intermetallic compounds and La_2CuO_4 systems ... ON THE D.O.S

PHASE STABILITY, PAIR POTENTIALS AND MULTIATOM INTERACTIONS
- Introduction: the various approaches for the expansion of the total energy in terms of multiatom interactions (MAI)
- The relevant energies for the study of ϕ stability. Orders of magnitude.
- Some examples: - formation energy of X and a alloys
  - structural stability of pure metals
  - relative stability of ϕ DS
- Qualitative discussion of the corresponding energies in terms of the D.O.S
  - cohesive energy (Friedel)
  - mixing energy for disordered alloys
  - structural stability
  - ordering energies
- Interatomic potentials and multiatom interactions
  - the various approaches
  - the general relation between perturbation expansions and MAI (cluster expansions)
  - the Generalized Perturbation method: principles and qualitative discussion of the results. (X or ORD)
  - the Linearized Green Function method (Top (DIS)ORD)
  - the generalized pseudopotential formalism (GPF)

V PHASE STABILITY AND ϕ DIAGRAMS USING CLUSTER EXPANSIONS.
- Introduction: the simultaneous use of electronic structure and of stat ϕ results. for T=0K and T≠0K
- GROUND STATE PHASE STABILITY
  - Ising models and O.S. stability: some examples (fcc lattice, mostly with APB energies, long periodic, polytypes ...)
  - Structural maps (GSM) for simple structures using the GPM. (Homogeneous states)
  - Ground state phase stability in binary alloys (heterogeneous states)
- PHASE DIAGRAMS CALCULATIONS
  - Determination of the configurational entropy (CVM, Monte Carlo) Sconf.
  - Prototype phase diagrams.
  - The liquid state of TM alloys from their electronic structures
  - a simple 1st pples ϕ diag. calculation
  - The role of vibrational and magnetic entropies.

VI CONCLUSION(S)