INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392 I

SMR/94-17

SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

PAIR POTENTIALS IN AMORPHOUS METALLIC ALLOYS: ORDER, STABILITY AND DYNAMICS

Lecture III

J. HAFNER

Inst. für Theoretische Physik
Technische Universität Wien
Karlsplatz 13
A-1040 Wien
Austria

Summary of 2nd lecture

Construction of a pseudopotential:

- Operator approach
  - optimized OPW-pseudopotentials
    "hard core"
- Scattering approach
  - HAA-type potentials
    fitted to non linear charge density
    "soft core"

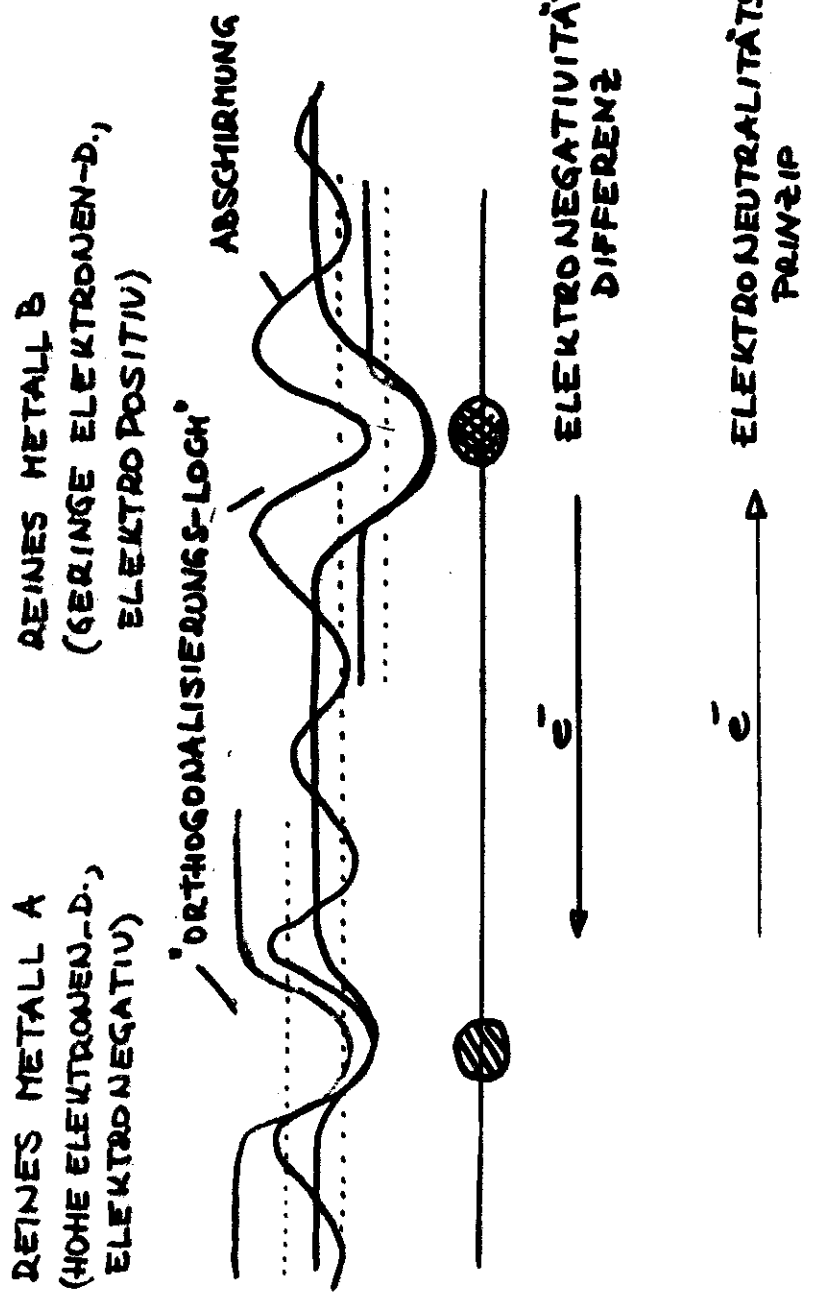
Exchange and correlation in the screening function

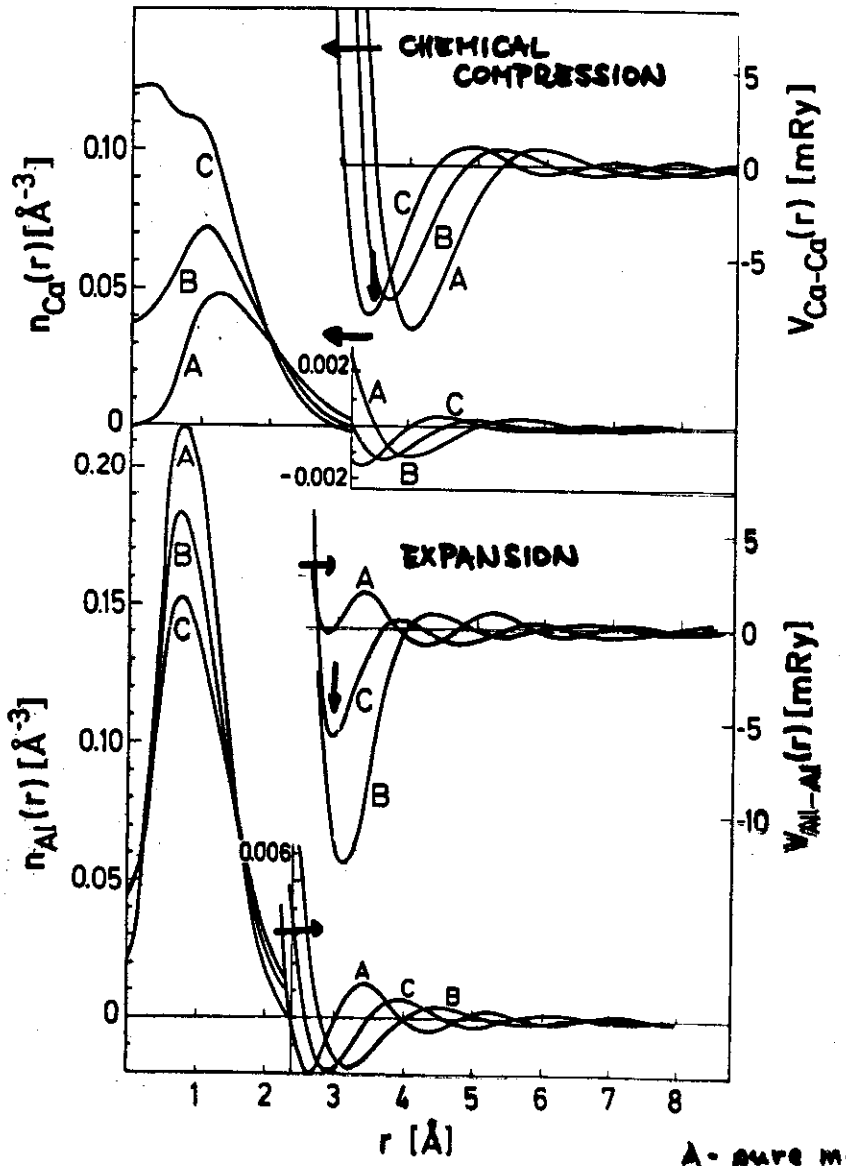
- Very important
- Require: - satisfaction of compress. sum rule
  - realistic e-e short range correl.

Pseudopotentials in alloys

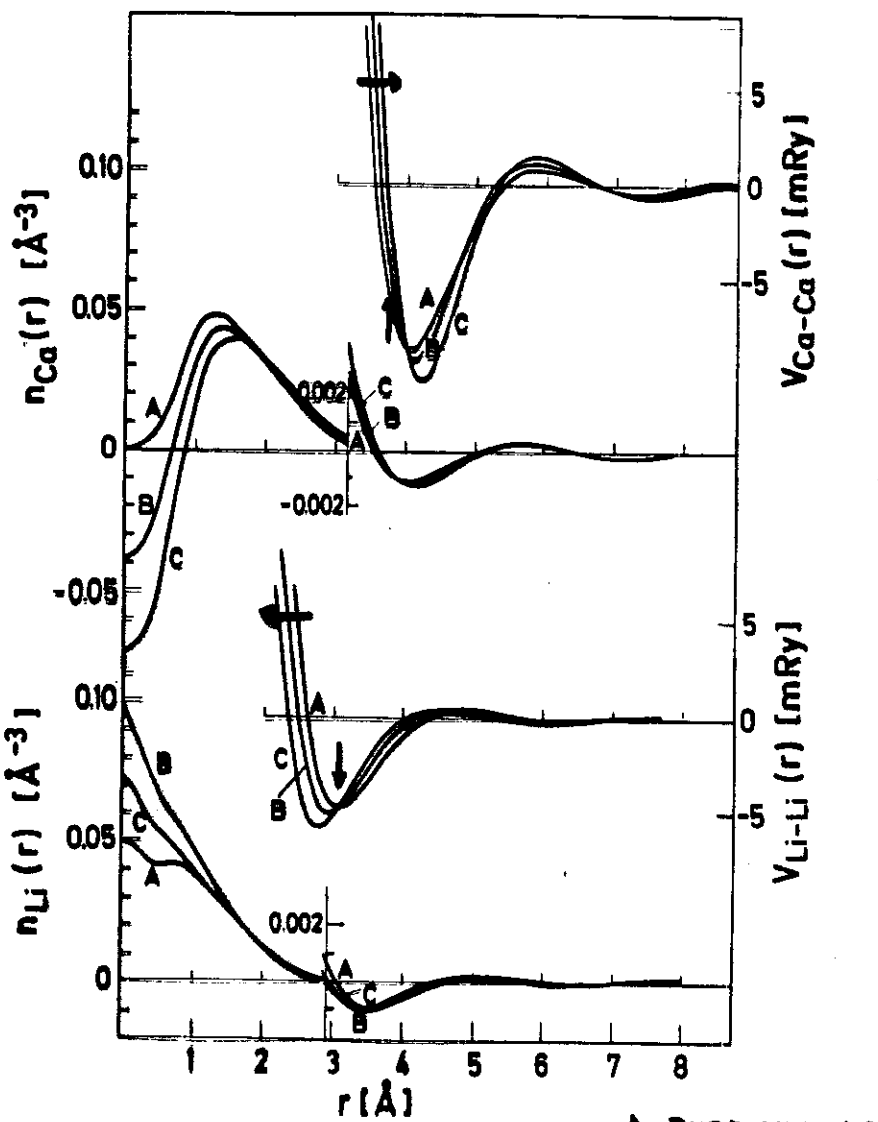
PP concentration dependent due to

- change in core-shift
- change in orthogonalization charges
- different energy-dependence
- shift of Fermi-level (different screening)





A - pure metals
B - Ca_2Al
C - $CaAl_2$

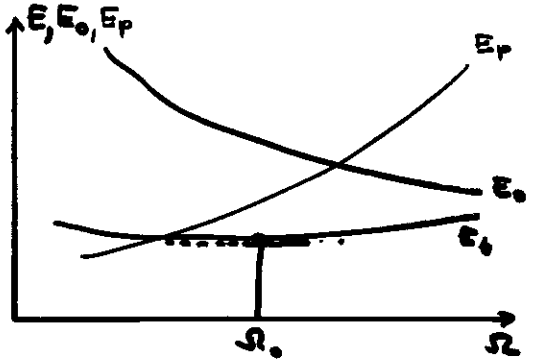


A - PURE METALS
B - Ca_2Li
C - $CaLi_2$

PHASE STABILITY IN PURE METALS AND CRYSTALLINE ALLOYS

- PURE METALS

EQUILIBRIUM VOLUME DETERMINED BY COMPETING VOLUME AND PAIR FORCES



$E = E_\Omega + E_P$

97-99% 1-3%

$p = p_\Omega + p_P$

$>0 \quad <0$

$B = B_\Omega + B_P$

$>0 \quad >0$

EQUILIBRIUM N.N. DISTANCE

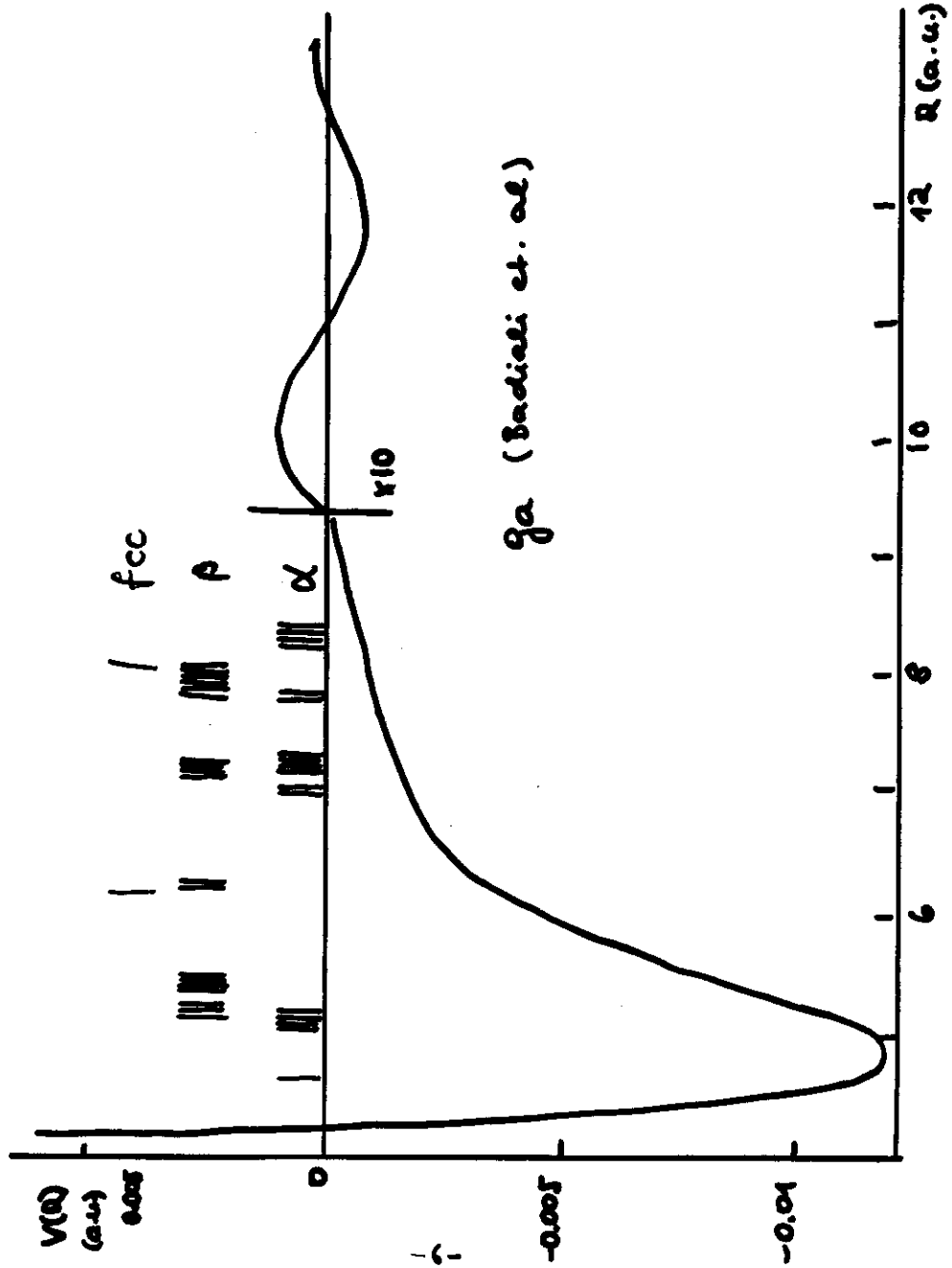
≅ POSITION OF ATTR. MIN. IN V(R)

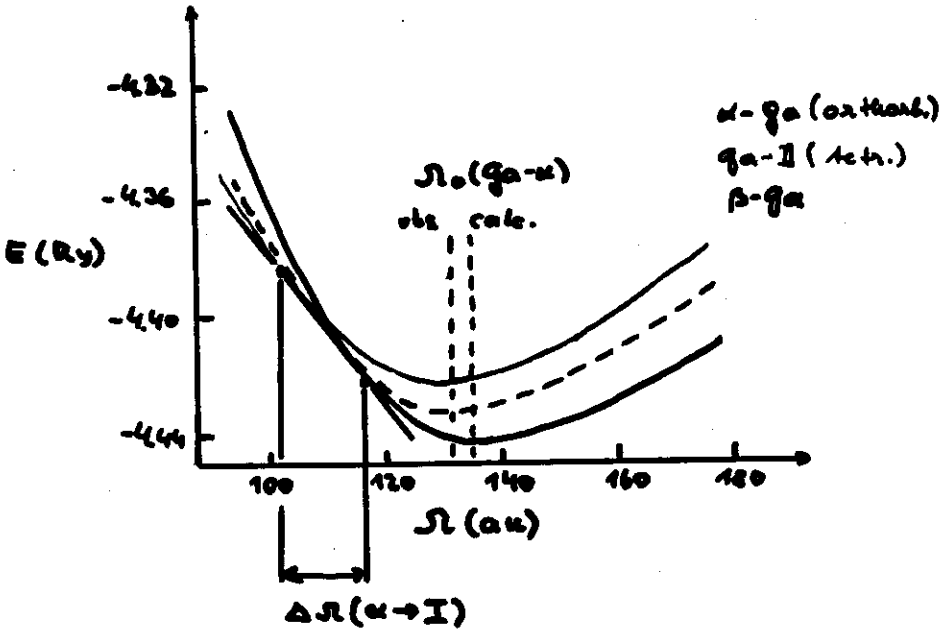
↷ CLOSE-PACKED STRUCTURE (Na, Mg, Al)

≠ POSITION OF ATTR. MIN. IN V(R)

↷ DISTORTED, OPEN STRUCTURE

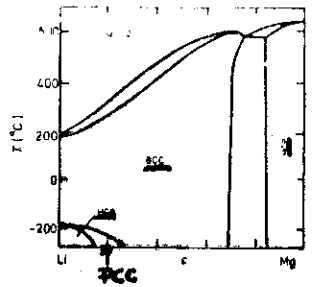
e.g. Ga, Sn





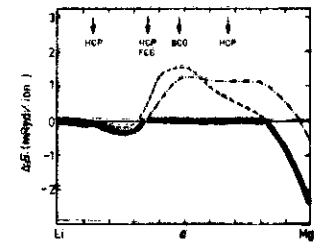
Pressure-induced structural phase transformations in solid Ca

Li-Mg



PHASENDIAGRAMM

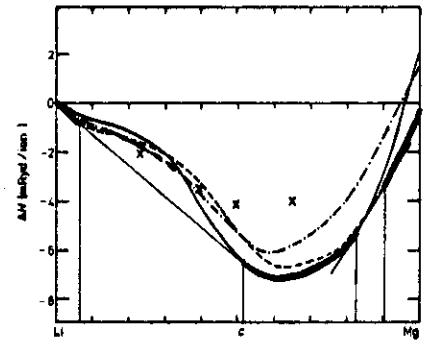
Figure 1. Phase diagram of the Li-Mg system (schematical).



STRUKTURELLE ENERGIEDIFFERENZEN

↓ ~ $Q = 2k_F$

Figure 2. Structural energy differences ΔE relative to the BCC phase. The vertical arrows mark the concentrations at which the Fermi sphere touches a Jones-zone plane.



BILDUNGSENTHALPIE

— BCC
— HCP
— FCC

Figure 7. Heat of formation ΔH (— BCC, -- HCP, -·- FCC) against concentration. The common tangent construction for the stability limits of the different phases is indicated. The crosses refer to the heat of formation measured by Mashkovetz and Puchkov (1965) for the liquid alloys.

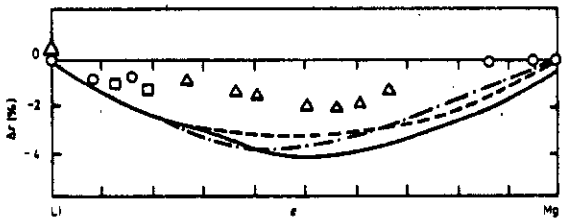


Figure 3. Deviations of the mean atomic radius from Vegard's rule (in percent). Full curve BCC phase, broken HCP, chain FCC (theoretical); Δ BCC, ○ HCP, □ FCC (experimental, as referenced in the text).

BINARY ALLOYS

Finnis '74:

For local pseudopotentials (pure metal)

$$E_\Omega = \underbrace{2E_{eg} - 2E_0 B_{eg}}_{\Downarrow} + \underbrace{\frac{1}{2} V^{(2)}_{ind}(0)}_{\frac{1}{N}\sum_{\underline{q}} F(q)}$$

"free electron" contribution to the heat of formation (Pettifor '81)

$$\Delta H_{eg} = -\frac{5}{9}\bar{Z}\left(2.21 - 0.641\bar{r}_s - 0.023\bar{r}_s^2\right)\left[\Delta\left(\frac{1}{r_s}\right)\right]^2$$

(1) loss of exchange and correlation energy on alloying destabilizes the alloy

(2) relaxation of kinetic energy on alloying stabilizes the alloy

(1) dominates at low electron densities — small — high —

$\bar{Z}$ .. average valence

$\bar{r}_s$ .. average electron dens. parameter

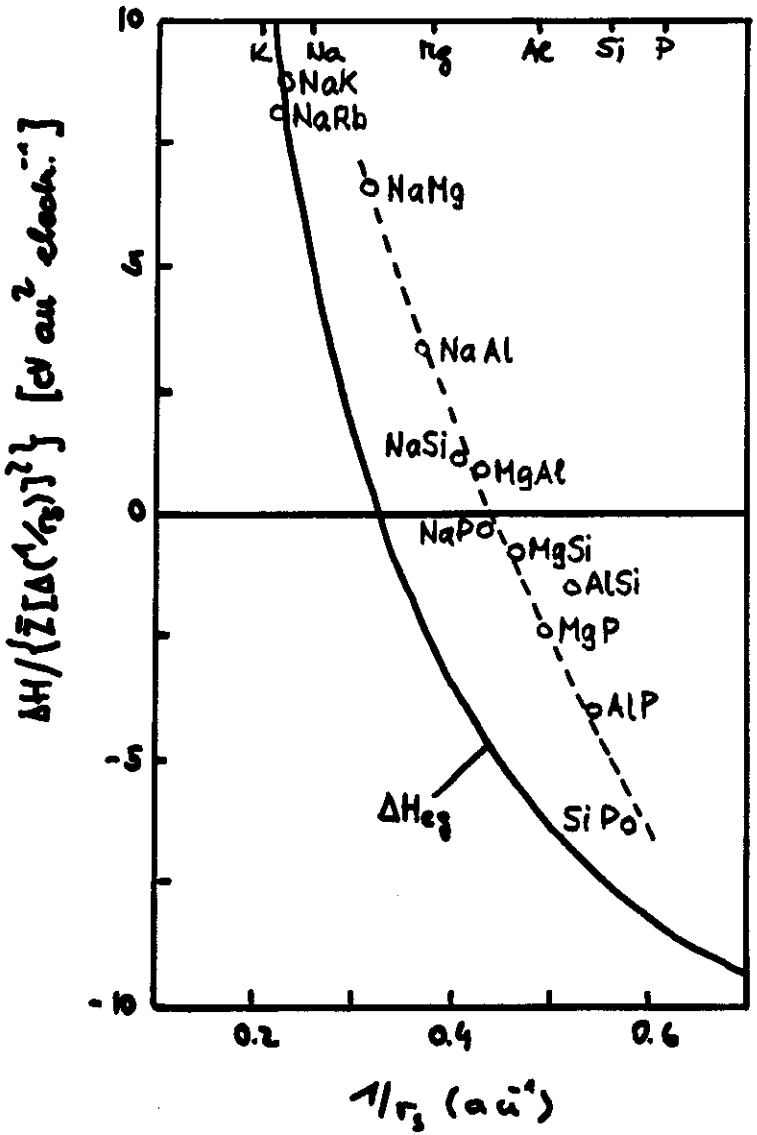
$\Delta\left(\frac{1}{r_s}\right)$ .. difference in the av. electron density parameter

$\Delta H > \Delta H_{eg}$

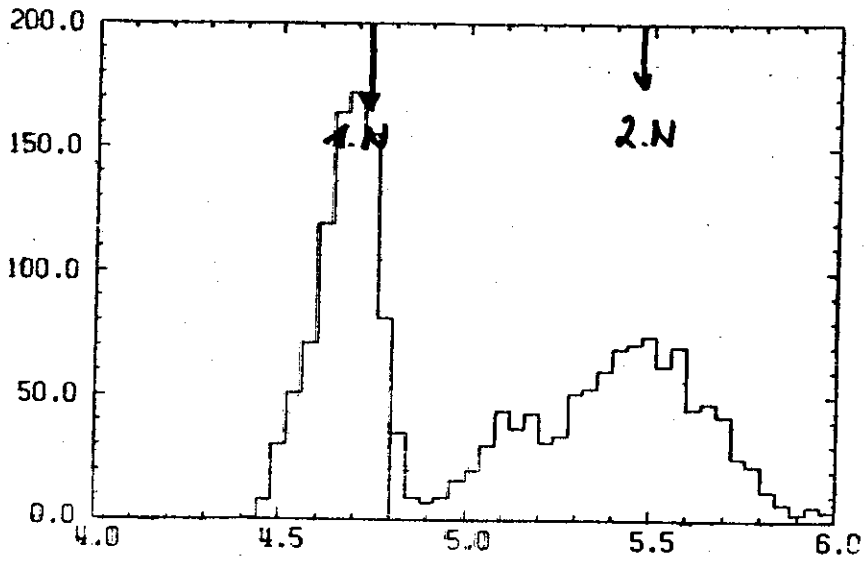
$\Rightarrow \Delta H_p + \Delta\left(\frac{1}{2} V^{(2)}_{ind}(0)\right) > 0$

pair interactions destabilize mixed crystals

Pettifor and Gelatt



o LDF-band structure calculation (assuming CsCl-structure)

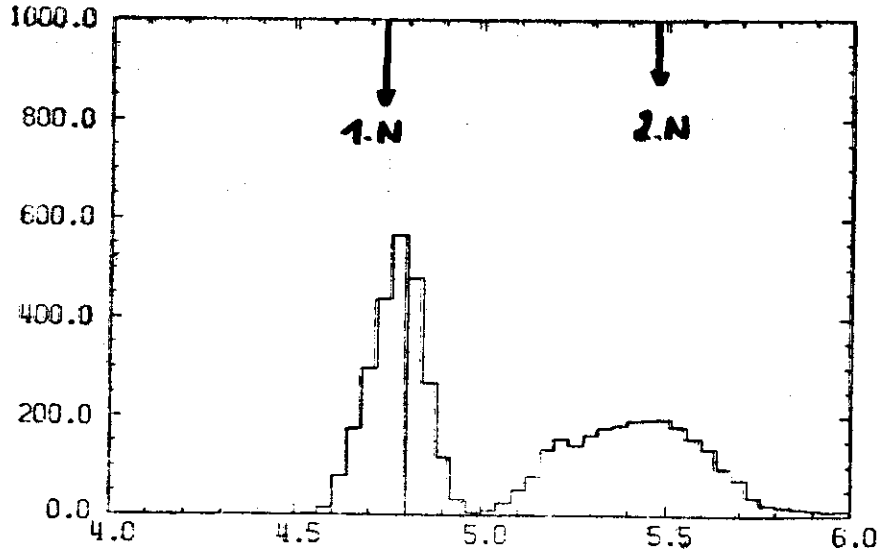


RDF(R), K29-RB71, PARTIELL K, HA1(100)

STATISCHE GITTERVERZERRUNGEN IN K-Rb

v. HEIMENDAHL u. HAFNER (1974)

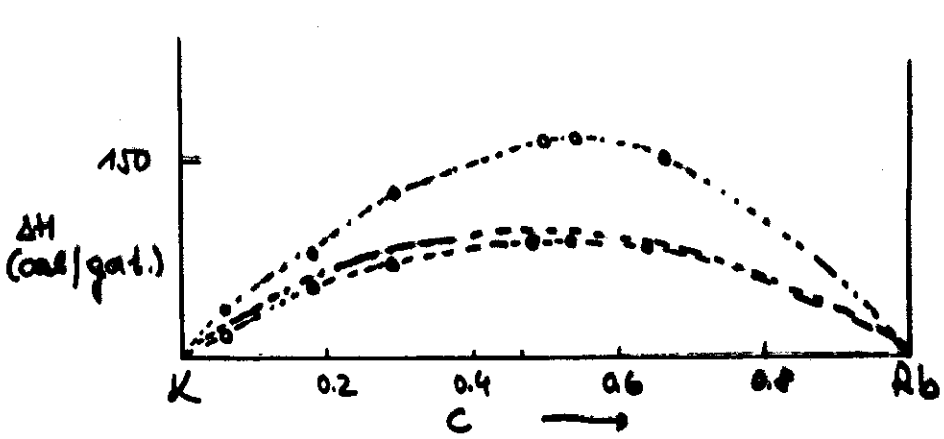
STATIC LATTICE DISTORTIONS



RDF(R), K29-RB71, PARTIELL SB, HA1(100)

RADIALE VERTEILUNGSFUNKTION

K-Rb



-·o·· with relaxation
-·o— without relaxation
— · · exp. (estimated from ΔH of liquid alloys and the entropy and heat of fusion)

ORDER-DISORDER TRANSITIONS

COMPLETE DISORDER

$$E = E_R + \frac{1}{N}\sum_{i<j} \bar{V}(R_{ij}) + \Delta E_{bs}$$

$$\Delta E_{bs} = \frac{c(1-c)}{N}\sum_{\vec{q}} F(q)$$

LONG-RANGE ORDER

BRAGG-WILLIAMS ORDER PARAMETERS η

$\eta = (f_\alpha - c)/(1-c)$ f_α.. fraction of sites of type α occupied by A-atoms

$$W(\vec{q}) = S(\vec{q})\left\{\bar{w}(q) - c\eta\Delta w(\vec{q})\right\} + \eta\, S_A(q)\Delta w(\vec{q})$$

Leung '79

SHORT-RANG ORDER

WARREN-COWLEY ORDER PARAMETERS α_i

$$|D(\vec{q})|^2 = \frac{c(1-c)}{N}\sum_i \alpha(R_i)\, e^{-i\vec{q}\vec{R}_i}$$

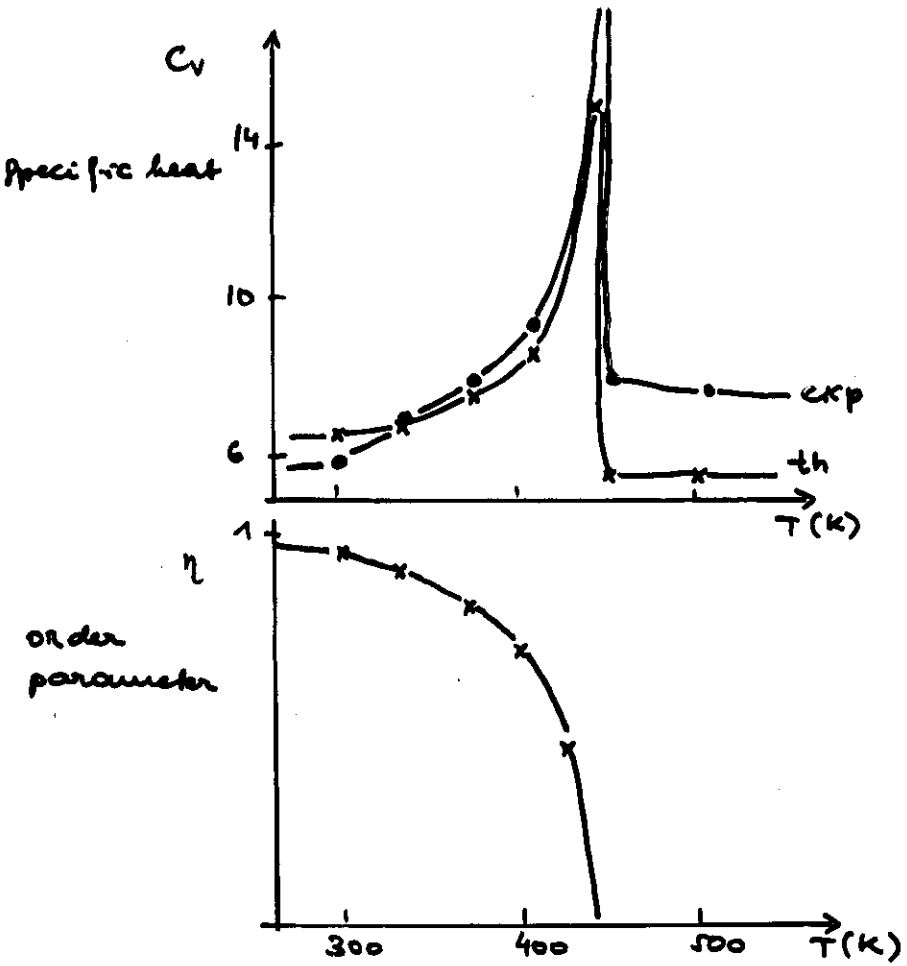
$$E = E_R + \frac{1}{N}\sum_{i<j} \bar{V}(R_{ij}) + c(1-c)\sum_i N_i\,\alpha(R_i)\,\Delta V(R_i)$$

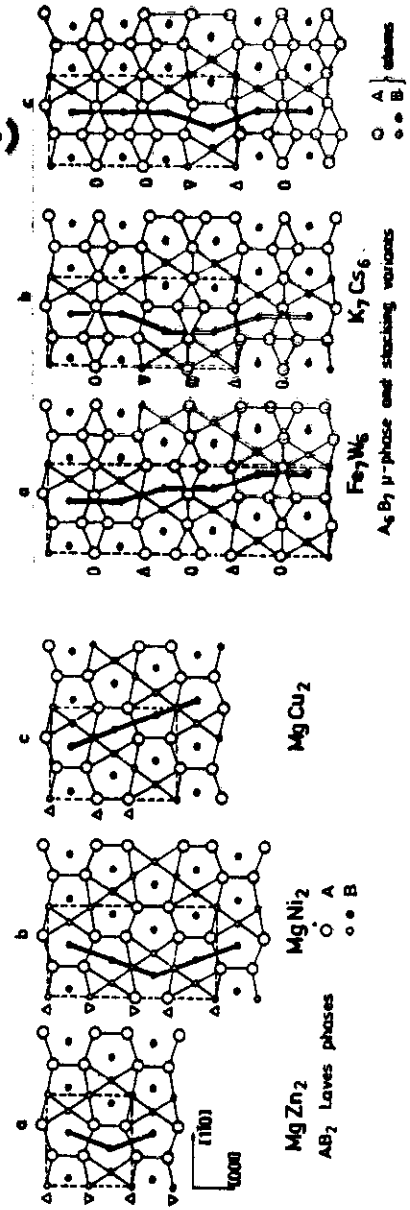
num of coordination shells of radius R_i, coord. no. N_i

ORDER-PARAMETERS DETERMINED BY VARIATIONAL CONDITION

$$\left(\frac{\partial F}{\partial \eta}\right)_{R,T} = 0 \qquad \left(\frac{\partial F}{\partial \alpha_i}\right)_{R,T} = 0$$

LANGREICHWEITIGE ORDNUNG IN Mg_3Cd (LEUNG ET AL.)
LONG RANGE ORDER





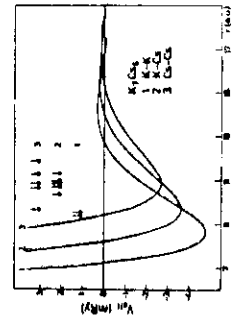


FIG. 9. Effective interionic pair potentials in K_7Cs_6. The arrows indicate interatomic distances occurring in the observed K_7Cs_6 structure.

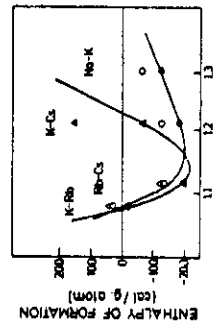


FIG. 10. Enthalpies of formation of intermetallic compounds against the ratio of the atomic radii of the components. Δ Laves phase $C14$ (ideal structural parameters), ▲ Laves phase $C14$ (calculated structural parameters), ○ K_7Cs_6 structure (observed structural parameters), ● K_7Cs_6 structure (calculated structural parameters).

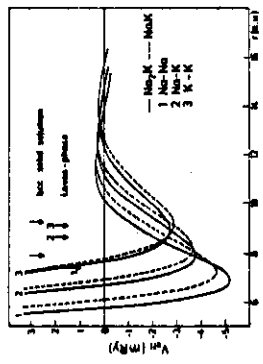
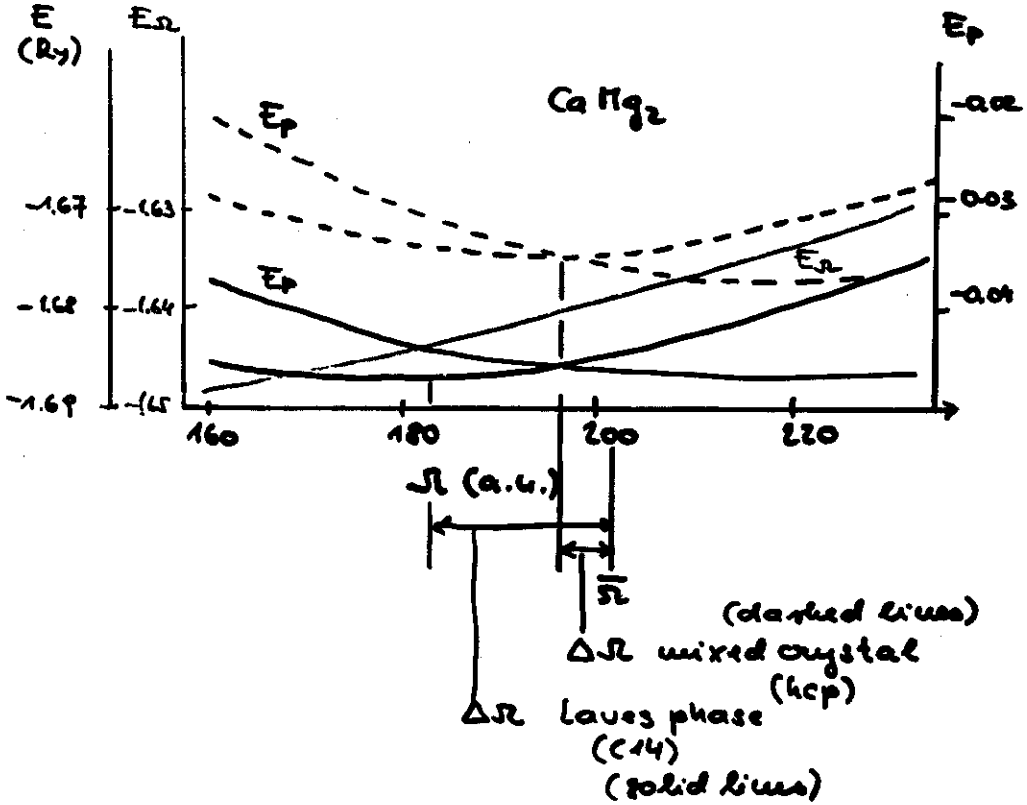


FIG. 6. Effective interionic pair potentials for Na_2K and NaK (solid and broken lines, respectively) at the equilibrium volume. The arrows indicate the nearest-neighbor distances in the $C14$ and in the bcc structures.

Volume of formation in mixed crystals and intermetallic compounds



STRUCTURE AND THERMODYNAMICS OF LIQUID METALS AND ALLOYS

Calculation of the structure from the interionic forces

i) by solving one of the integral equations of the theory of liquid and liquid mixtures: difficult, successful for some cases, but not even attempted for alloys

ii) by computer simulation: hard numerical work, very successful, confirms validity of DRT and OPW-pair potentials. But is it a theory?

iii) by thermodynamic perturbation theory

THERMODYNAMIC VARIATIONAL METHOD

Gibbs-Bogoljubov inequality

$$F \leq F_0 + \langle V \rangle_0$$

F_0: free energy of a reference system

$\langle V \rangle_0$: expectation value of the perturbation

upper bound to exact free energy

Reference systems:

Hard-spheres: analytic solution of PY-equ., quite realistic $S(q)$ or semi-empirical Verlet-Weis $S(q)$

One-component plasma:

analytic thermodynamic functions,
approx. analytic $S(q)$

HS: N. Jones '73 — OCP: Ross + DeWitt '80
Stroud + Ashcroft — Parmentello et al '81
Young et al.
Kafuri
⋮

Na, K, Rb, Cs : $F_{OCP} < F_{HS}$ S_{OCP} slightly better

Li, polyvalent metals : $F_{HS} < F_{OCP}$ S_{HS} better

HS: corrections for soft repulsive potentials and attractive potentials possible

OCP: how to go beyond G-B method?

HS: $F \leq E_0 + E_{bs} + E_{cs} + \underbrace{\frac{3}{2} k_B T}_{\text{kin. energy}} - TS_{HS} - \underbrace{\frac{1}{2}\gamma^2 T^2}_{\text{ideal electronic entropy}}$

$= E_R + E_p + \dots\dots$

$\vec{q}$-space
$$\begin{cases} E_0 = \frac{1}{2} E_{ii} + \frac{3}{5}\varepsilon_F/R_0 \\ E_{bs} = E_2 = \frac{n_0}{(2\pi)^3}\int F(q)\, S_{HS}(q)\, d^3q \\ E_{cs} = \frac{Z^2 e^2}{\pi}\int_0^\infty (S_{HS}(q) - 1)\, d^3q \end{cases}$$

$\vec{r}$-space
$$\begin{cases} E_R = E_0 + \frac{1}{N}\sum_q F(q) + \lim_{R\to 0}\left(\frac{4\pi Z^2 e^2}{R} + F(R)\right) \\ E_p = \frac{n_0}{2}\int g_{HS}(R)\, V(R)\, d^3R \end{cases}$$

VARIATIONAL CONDITION: $\left(\frac{\partial F}{\partial \sigma}\right)_{R,T} = 0$

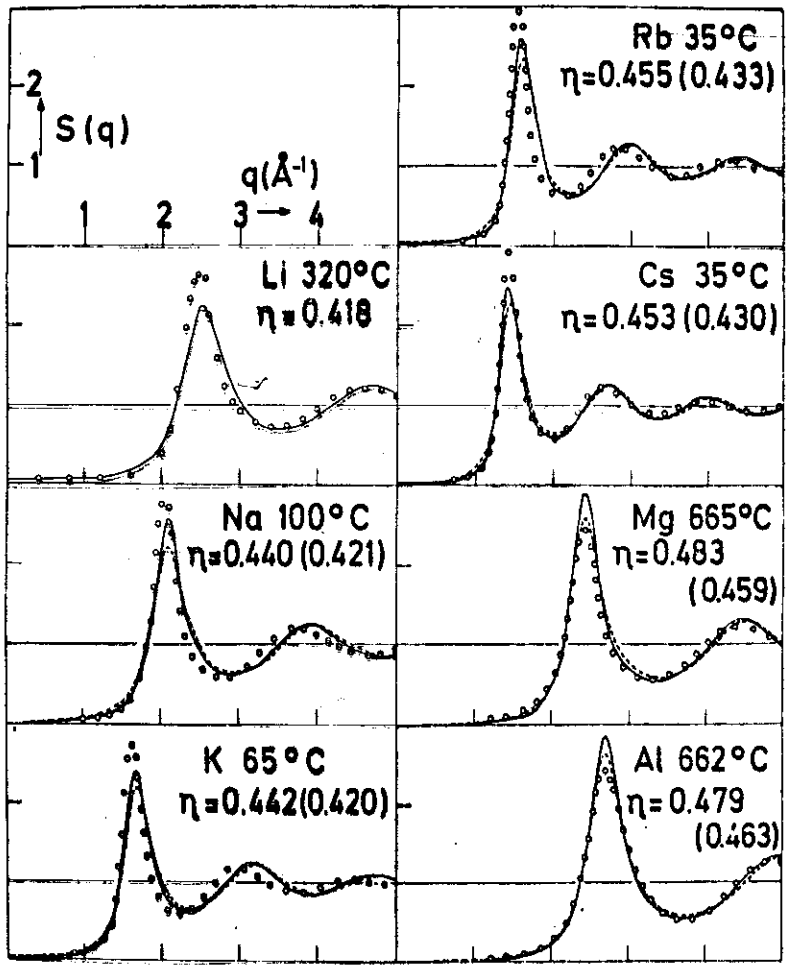


Fig. 1

Thermodynamic properties of liquid metals close to their melting point, as calculated with the GB-HS variational technique (Hoover '77)

a) Excess entropy $-S_e/k_B$

	th.	exp
Li	3.75	3.70
Na	3.47	3.55
K	3.41	3.51
Rb	3.65	3.63
Cs	3.60	3.56
Mg	4.10	3.45
Al	4.18	3.60

b) Bulk modulus B_T (10^{10} dyn cm^{-2})

	th		exp
	Mot.	dyn.	
Li	8.1	9.3	11.5
Na	3.7	3.8	5.3
K	1.7	1.8	2.6
Mg	21.6	19.7	20.4
Al	37.4	30.7	41.3

c) Thermal expansion coeff. α (10^{-4} K^{-1})

	th.	exp
Li	3.9	3.2
Na	5.2	2.8
K	6.4	2.9
Mg	1.71	1.66
Al	1.19	1.22

d) Specific heat

	C_p/k_B		C_V/k_B		$\gamma = C_p/C_V$	
Li	4.3	3.7	3.4		1.3	
Na	4.0	3.8	2.9	3.4	1.4	1.1
K	4.6	3.9	3.3	3.4	1.4	1.1
Rb	5.0	3.8	3.4	3.3	1.5	1.2
Cs	5.4	3.9	3.2	3.2	1.7	1.2
Mg	4.2	4.0	3.2	3.0	1.3	1.3
Al	3.9	3.5	3.2	2.7	1.2	1.25

Gibbs-Bogoljubov method for liquid mixtures

$$E_0 = \sum_{A,B} E_{0i} + \frac{N}{2}\left(c\,\phi_A + (1-c)\,\phi_B\right)/\Omega_0$$

$$E_{bs} = \frac{\Omega_0}{(2\pi)^3}\int_0^\infty \sum_{\substack{i,j \\ A,B}} (c_i c_j)^{1/2} F_{ij}(\underline{q})\, S_{ij}(\underline{q})\, d^3q$$

↑ Ashcroft-Langreth partial structure f.

$$= \frac{\Omega_0}{(2\pi)^3}\int_0^\infty \left(F_{NN}(q) S_{NN}(q) + 2F_{Nc}(q) S_{Nc}(q) + S_{cc}(q) F_{cc}(q)\right) d^3q$$

↑ Bhatia-Thornton

$$E_{cs} = \frac{e^2}{\pi}\int_0^\infty \sum_{\substack{i,j \\ A,B}} (c_i c_j)^{1/2} z_i z_j \left(S_{ij}(q) - 1\right) dq$$

$$= \frac{e^2}{\pi}\int_0^\infty \left\{\bar{z}^2\left(S_{NN}(q) - 1\right) - 2\bar{z}\Delta z\, S_{Nc}(q) - \Delta z^2\left(S_{cc}(q) - c(1-c)\right)\right\} d^3q$$

$$E_R = E_0 + \frac{1}{2}\left[c V_{AA}(0) + (1-c) V_{BB}(0)\right] - \lim_{R\to 0} \sum_{\substack{i,j \\ A,B}} c_i c_j \left(\frac{4\pi z_i z_j e^2}{\Omega_0 R^2} + F_{ij}(R)\right)$$

$$E_p = \frac{n_0}{2} \sum_{\substack{i,j \\ A,B}} c_i c_j \int g_{ij}(R)\, V_{ij}(R)\, d^3R$$

$$= \frac{n_0}{2}\int \left[g_{NN}(R)\,\bar{V}(R) + 2 g_{Nc}(R)\, V_{Nc}(R) + g_{cc}(R)\,\Delta V(R)\right] d^3R$$

Variational conditions:

$$\left(\frac{\partial F}{\partial \sigma_A}\right)_{\sigma_B, \Omega, T} = 0 \qquad \left(\frac{\partial F}{\partial \sigma_B}\right)_{\sigma_A, \Omega, T} = 0$$

σ_A, σ_B .. hard sphere diameters

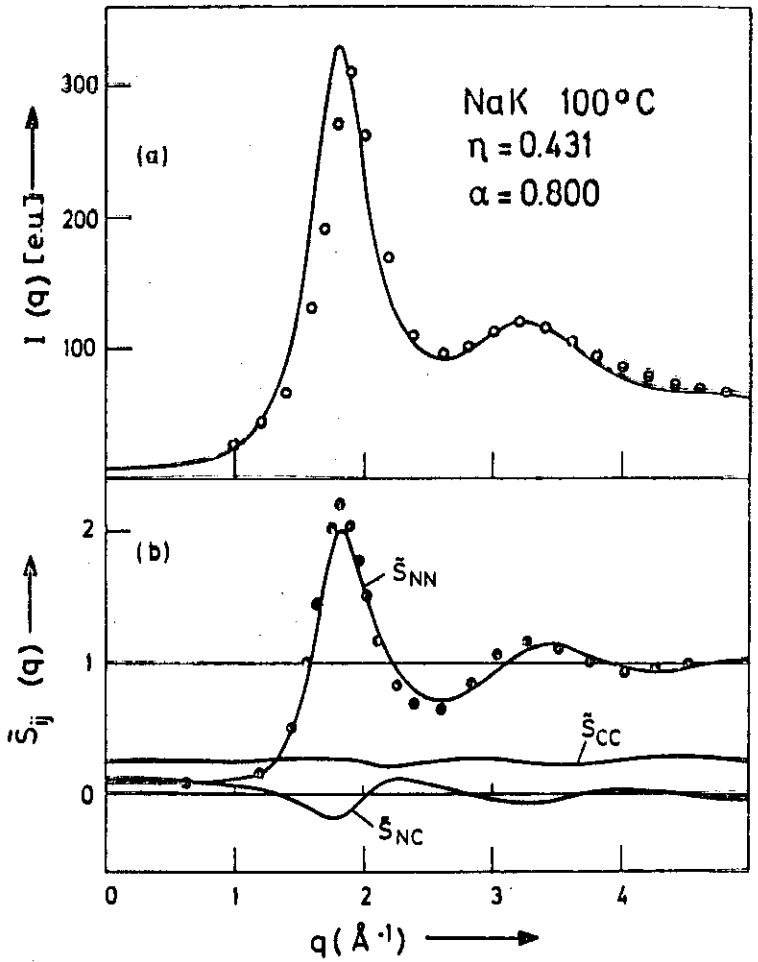
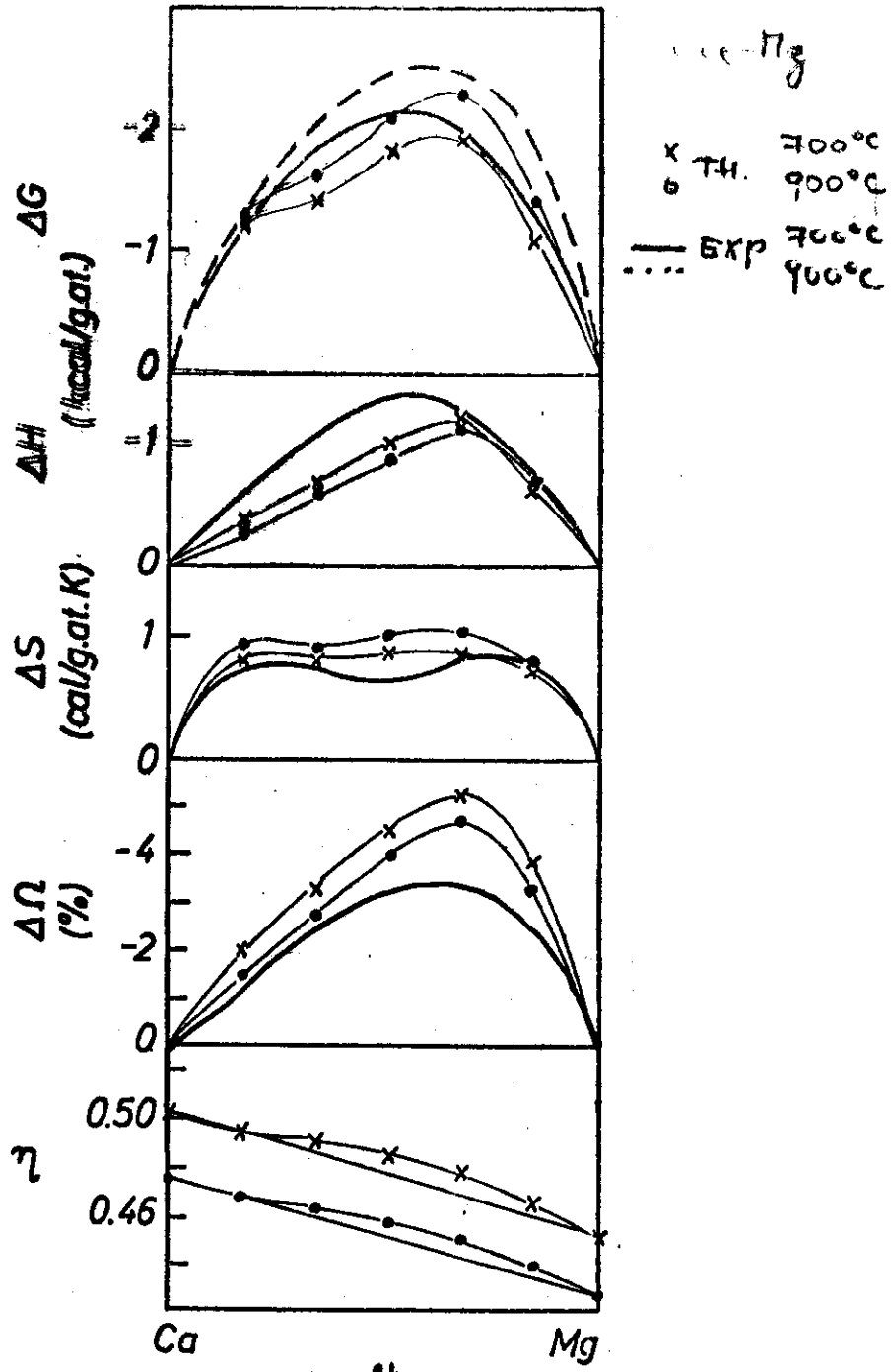
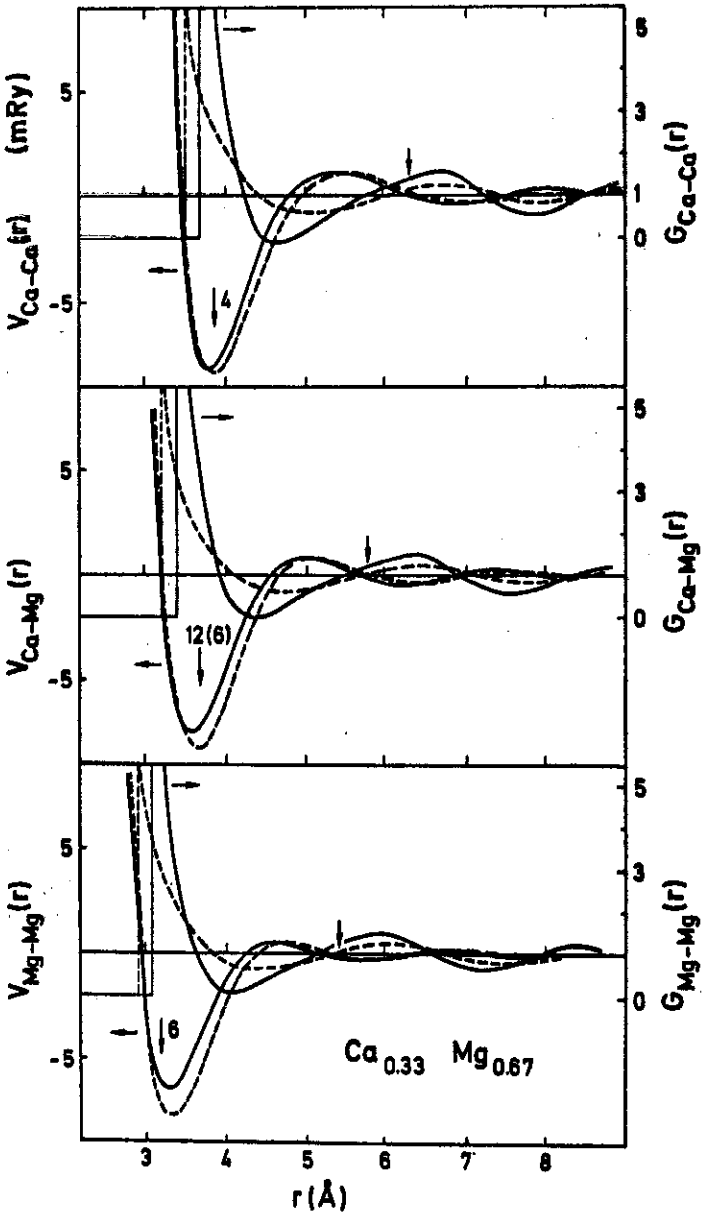
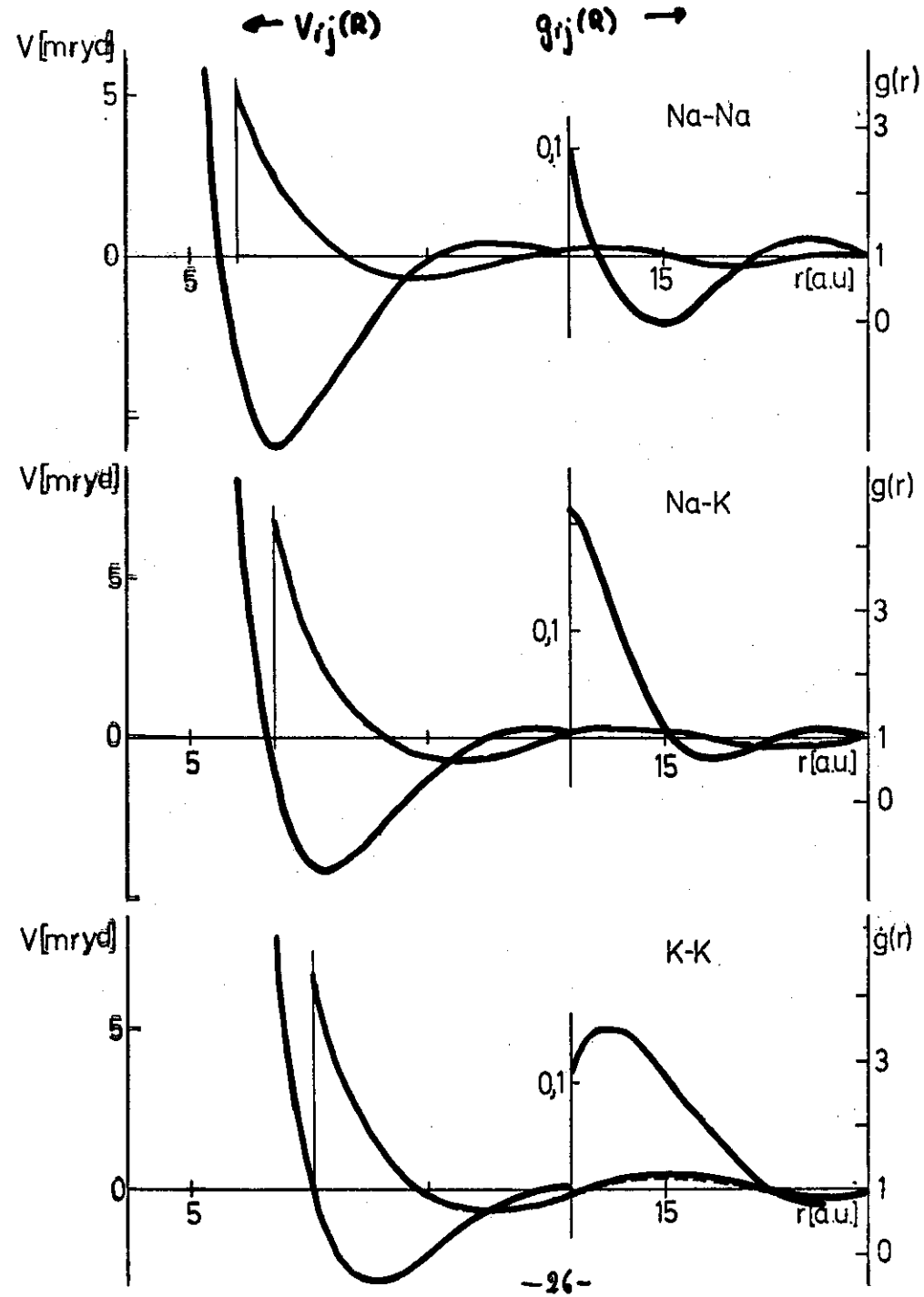

NaK 100°C
η = 0.431
α = 0.800
(a)
(b)
I (q) [e.u.]
$\tilde{S}_{ij}$ (q)
$\tilde{S}_{NN}$
$\tilde{S}_{CC}$
$\tilde{S}_{NC}$
q (Å⁻¹)

Fig. 4


ΔG
ΔH (kcal/g.at.)
ΔS (cal/g.at.K)
Δ Ω (%)
η
Ca
Mg
x TH. 700°C
o TH. 900°C
EXP 700°C
EXP 900°C


$V_{Ca-Ca}(r)$ (mRy)
$G_{Ca-Ca}(r)$
$V_{Ca-Mg}(r)$
$G_{Ca-Mg}(r)$
$V_{Mg-Mg}(r)$
$G_{Mg-Mg}(r)$
4
12(6)
6
$Ca_{0.33}$ $Mg_{0.67}$
r(Å)


← $V_{ij}(R)$
$g_{ij}(R)$ →
V[mryd]
g(r)
Na-Na
Na-K
K-K
0,1
r[a.u]

References to 3rd lecture

Applications of pseudopotentials to structural stability

Pure metals:

General: V. Heine and J. Weaire, Sol. State Phys., vol. 24.

Sp-prob.: J.E. Inglesfield, J. Phys. C1, 1337 (1968)
J. Kaplan and O. Entin-Wohlman, Isr. J. Chem. Proc. Wis. 4, 37 (1970)

Pressure induced phase transitions:
J. Kaplan, Phys. Rev. B10, 4151 (1974)

Temperature-induced phase transitions:
T. Ebbajō and R. Pynn, J. Phys. F1, 744 (1971)
J. Kaplan, Z. Phys. B24, 41 (1976)

Mixed crystals:
P. Beaudamps et al., J. Phys. F4, 2017 (1975)
J. Kaplan, J. Phys. F6, 1243 (1976)
and references cited therein

Static lattice distortions:
J. Kaplan and J. Perez, to be published in J. Phys. F.

Ordering:
long-range: C. Zemp et al. J. Phys. F9, 179 (1979)
short-range: T.H. Hayes et al. Phys. Rev. 175, 699 (1968)
F.A. Khwaja et al., Phys. Stat. Sol. (b) 82, 701 (1977)
and references therein

Intermetallic compounds:
J. Kaplan, Phys. Rev. B15, 617 (1977); B19, 584 (1979);
B21, 406 (1980)

Structure and thermodynamics of liquid metals and alloys

g.BG-Ziegler variational technique

Pure metals, HS-reference system

PY-solutions: E. Thiele, J. Chem. Phys. 39, 474 (1963)
R.S. Wertheim, J. Math. Phys. 5, 927 (1964)
N.F. Carnahan and K.E. Starling, J. Chem. Phys. 51, 635 (1969)

G-B inequality: A. Isihara, J. Phys. A1, 539 (1968)

Applications: H. Jones, J. Chem. Phys. 57, 2640 (1971),
Phys. Rev. A8, 3215 (1973),
D. Stroud and N.W. Ashcroft, Phys. Rev. B5, 371 (1972)
J. Kaplan, Phys. Rev. A16, 351 (1977)

Pure metals, OCP-reference system:
H. Ross, Phys. Rev. B21, 3140 (1980)
H. Ross et al., Phys. Rev. (1981)
D.K. Chaturvedi et al., Physica 110B, 11 (1981)

Alloys, HS-reference system
I.H. Umar and W.H. Young, J. Phys. F4, 525 (1974)
J. Kaplan, Phys. Rev. A16, 351 (1977)
H. Ruppersberg, J. Phys. F (1981)