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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 IV

J. HAFNER

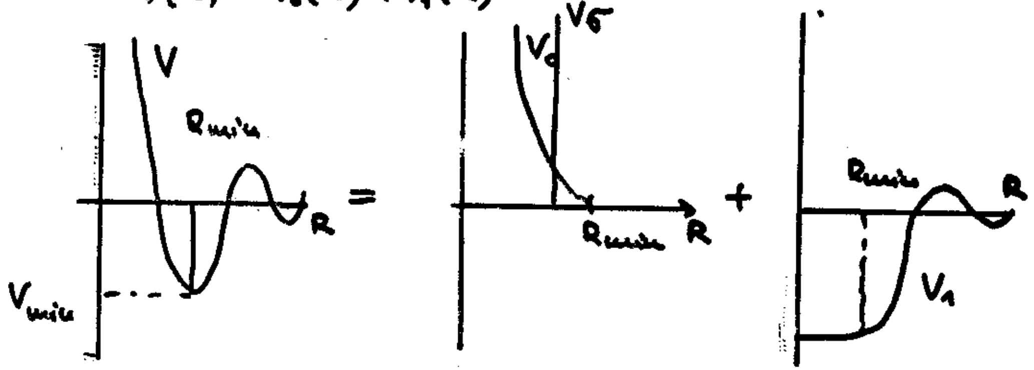
Inst. für Theoretische Physik
Technische Universität Wien
Karlsplatz 13
A-1040 Wien
Austria

BEYOND HARD SPHERES

a) Soft-repulsive potentials

Weeks-Chandler-Andersen Theory (WCA)

$V(R) = V_0(R) + V_1(R)$



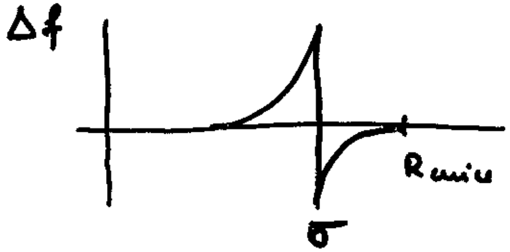
$V_0(R) = V(R) + V_{min}$ $R \le R_{min}$ repulsive

$V_1(R) = V(R)$ $R > R_{min}$

$\quad = V_{min}$ $R \le R_{min}$ } attractive

Mayer function $\quad f(R) = e^{-\beta V(R)}$

$$\Delta f(R) = f_0(R) - f_\sigma(R) = e^{-\beta V_0(R)} - e^{-\beta V_\sigma}$$



Functional Taylor-series in $\Delta f(R)$

$$F = F_\sigma + \int \left.\frac{\delta F[f(R)]}{\delta f(R)}\right|_0 \Delta f(R)\, d^3R + \dots$$

$$\frac{\delta F[f]}{\delta f(R)} = \frac{1}{2} n^2 y(R) = \frac{1}{2} n^2 e^{\beta V(R)} g(R)$$

$$y(R) = e^{\beta V(R)} g(R)$$

$$F = F_\sigma + \underbrace{\frac{n^2}{2}\int y_\sigma(R)\,\Delta f(R)\, d^3R}_{} + \dots$$

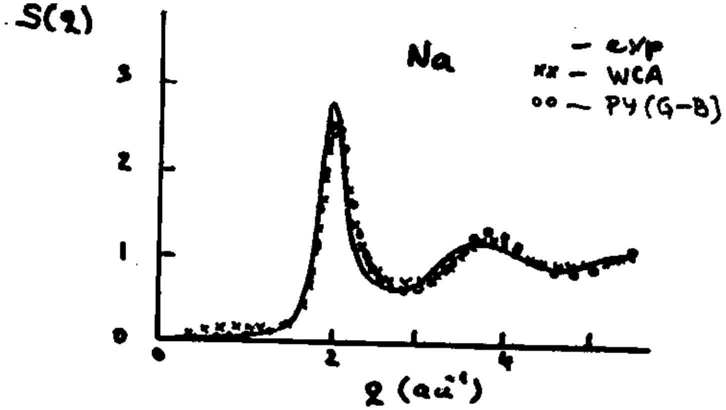
choose σ so that $= 0$

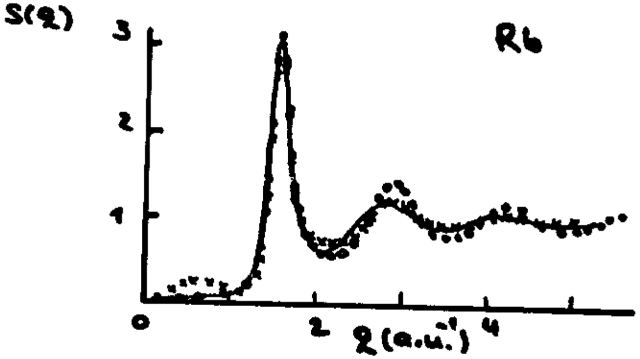
Condition for effective hard-core diameter

$$\int y_\sigma(R)\,\Delta f(R)\, d^3R = \int y_\sigma(R)\left[e^{-\beta V_0(R)} - e^{-\beta V_\sigma}\right] d^3R = 0$$

$$g(R) = g_\sigma(R) + y_\sigma(R)\left[e^{-\beta V_0(R)} - e^{-\beta V_\sigma}\right]$$

static structure factor, thermodynamics





Kumaravadivel + Evans '77

b) <u>Attractive potentials</u>

Ornstein-Zernike relation

$$h(R) = c(R) + n\int d^3R' \, c(|\vec{R}-\vec{R}'|)\, h(\vec{R}')$$

+ RPA for attractive part

$$c(R) = c_0(R) \qquad R \le \sigma \qquad (*)$$

$$= c_0(R) + \phi(R) \qquad R > \sigma \qquad \phi(R) = -\beta V_1(R)$$

$\rightsquigarrow$ RPA: unrealistic $g(R)$ for $R < \sigma$

Require: $g(R) = 0 \qquad R \le \sigma$

define: $g(R) \equiv g_0(R) + \tau(R) \qquad (**)$

Insert (*) and (**) in Fourier-transformed OZ-relation:

$$\left.\begin{array}{l} \hat{h}(q) = \hat{c}(q) + n\,\hat{c}(q)\,\hat{h}(q) \\ \hat{c}(q) = \hat{c}_0(q) + \hat{\phi}(q) \\ \hat{g}(q) = \hat{g}_0(q) + \hat{\tau}(q) \end{array}\right\} \rightsquigarrow$$

$$\hat{\tau}(q) = \frac{S_0(q)\,\hat{\phi}(q)\,S_0(q)}{1 - n\,S_0(q)\,\hat{\phi}(q)}$$

(remember: $S_0 = (1 - n\hat{c}_0)^{-1} = 1 + n\hat{h}_0$)

integral equation for τ

Variational solution:

define:

$$A[\phi] = \frac{1}{(2\pi)^3 n}\int d^3q \left\{ n\, S_0(q)\, \hat{\phi}(q) + \ln\left[1 - n\, S_0(q)\, \hat{\phi}(q)\right]\right\}$$

$$\rightarrow \quad \frac{\delta A[\phi]}{\delta \hat{\phi}(q)} = -\frac{n}{(2\pi)^3}\, \hat{c}(q)$$

$$\frac{\delta A[\phi]}{\delta \phi(R)} = -n\, c(R) = 0 \qquad R < \sigma$$

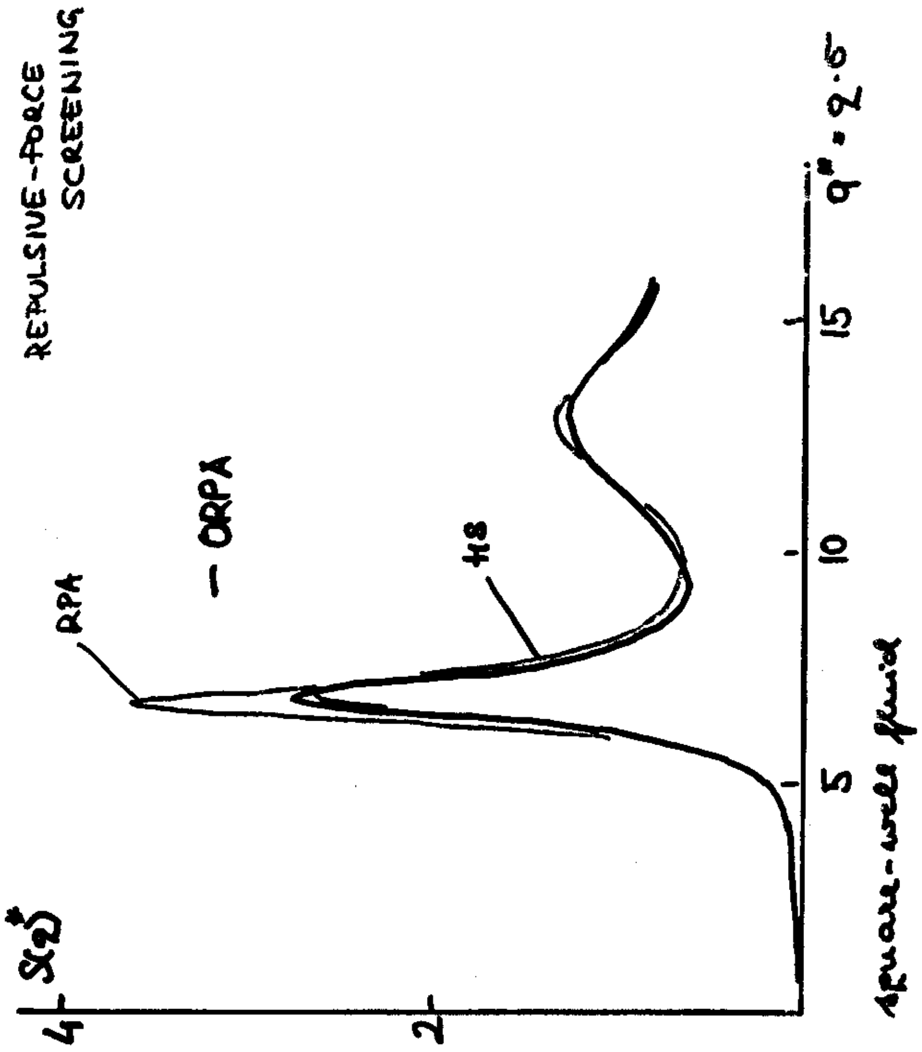
ORPA
MSA

$$F = F_0 - \frac{n^2}{2}\beta \int d^3R\, V_1(R)\, g_0(R) - \frac{1}{2n} F[\phi(R)]$$

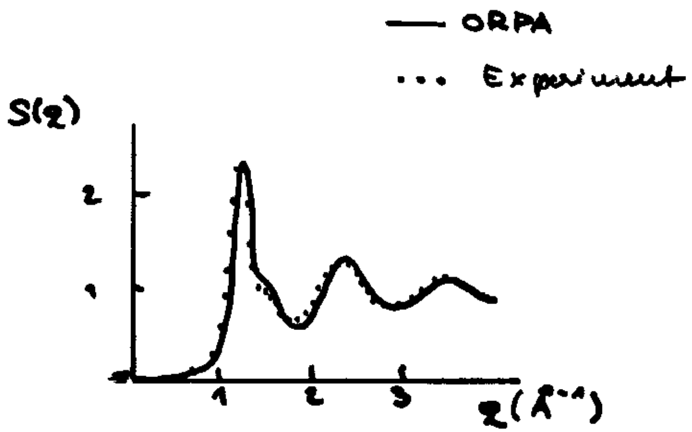
free energy:

→ free energy is stationary with respect to the optimized potential $\phi(R)$

(Andersen et. al.)



Liquid Ga (Regnault et al)



CONCENTRATION - FLUCTUATIONS

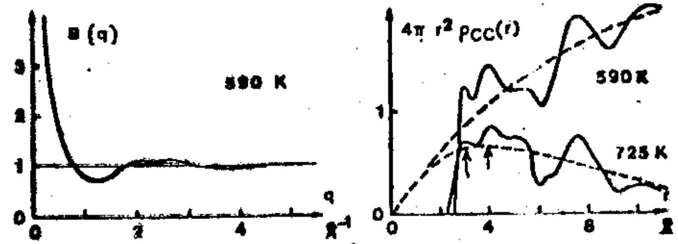


Fig. 1 and 2 S(q) and $4\pi r^2 \rho_{CC}(r)$ of liquid Li 61 Na 39

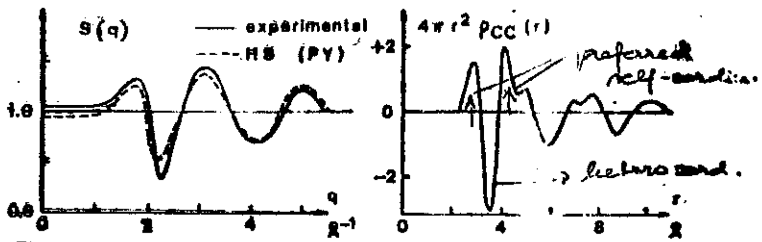


Fig. 3 and 4 S(q) and $4\pi r^2 \rho_{CC}(r)$ of liquid Li 62 Ca 38

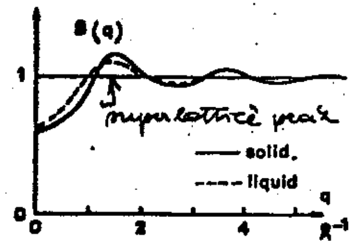


Fig. 5 S(q) of Li 70 Mg 30

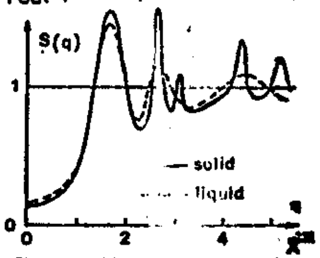


Fig. 6 S(q) of Li 55 Ag 45

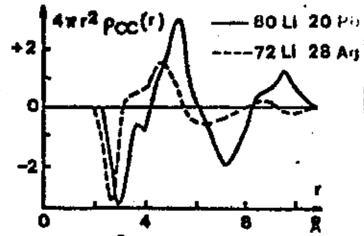
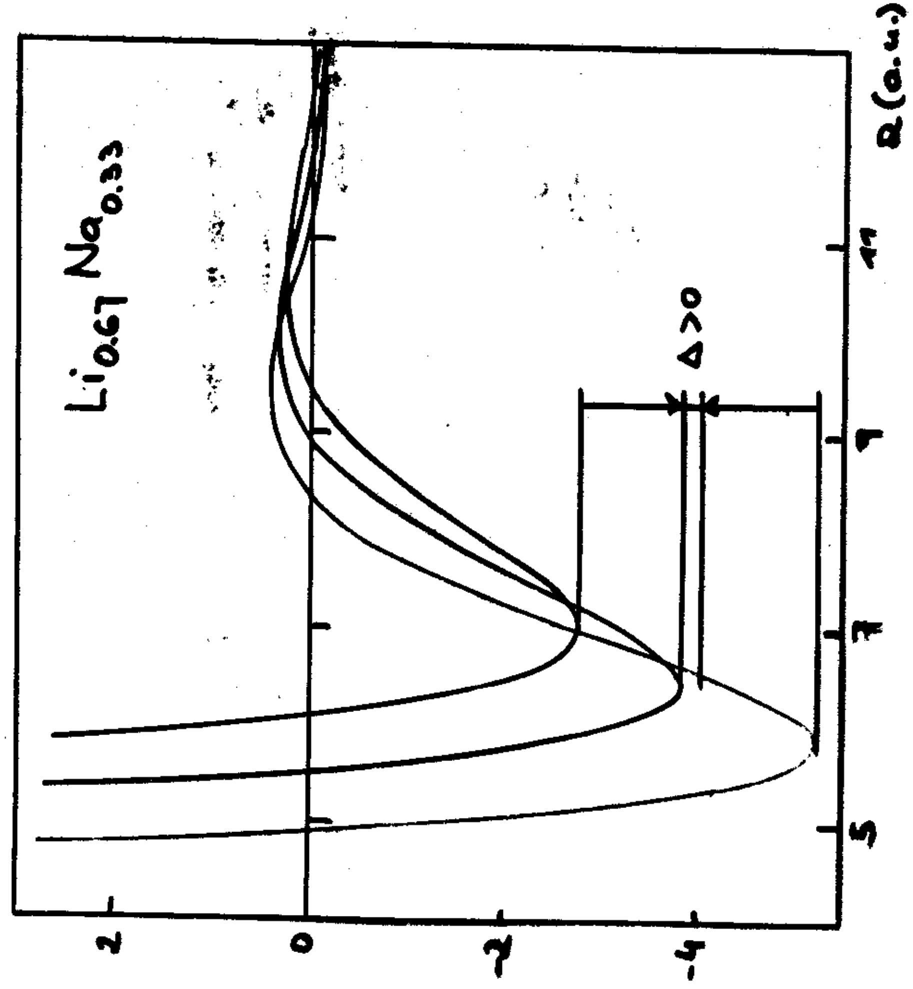
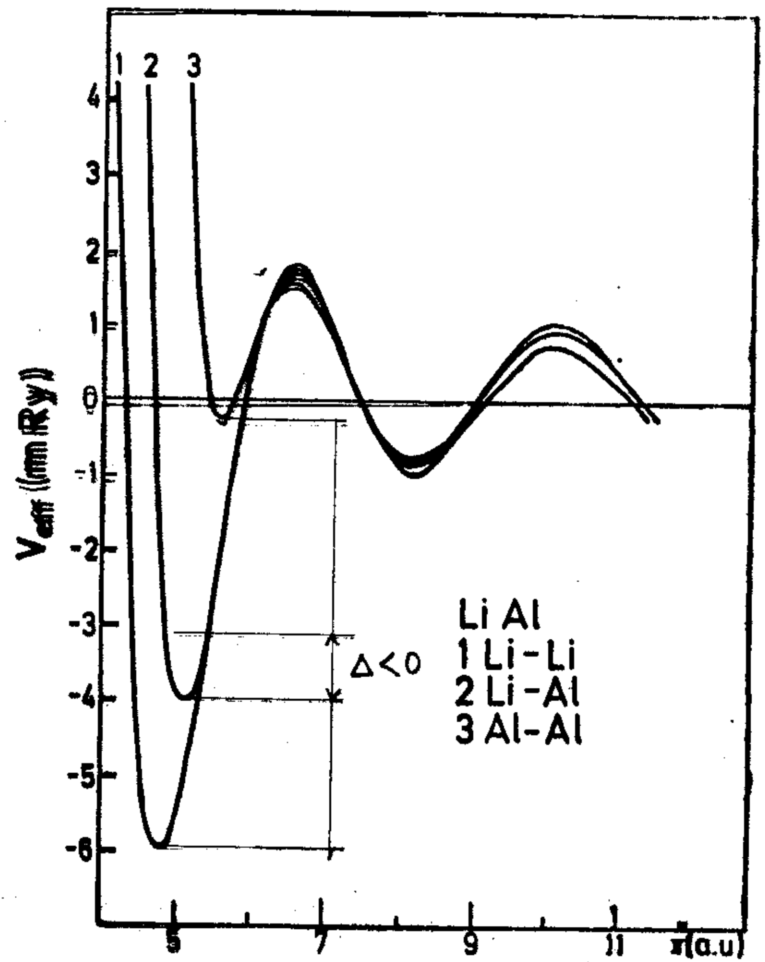


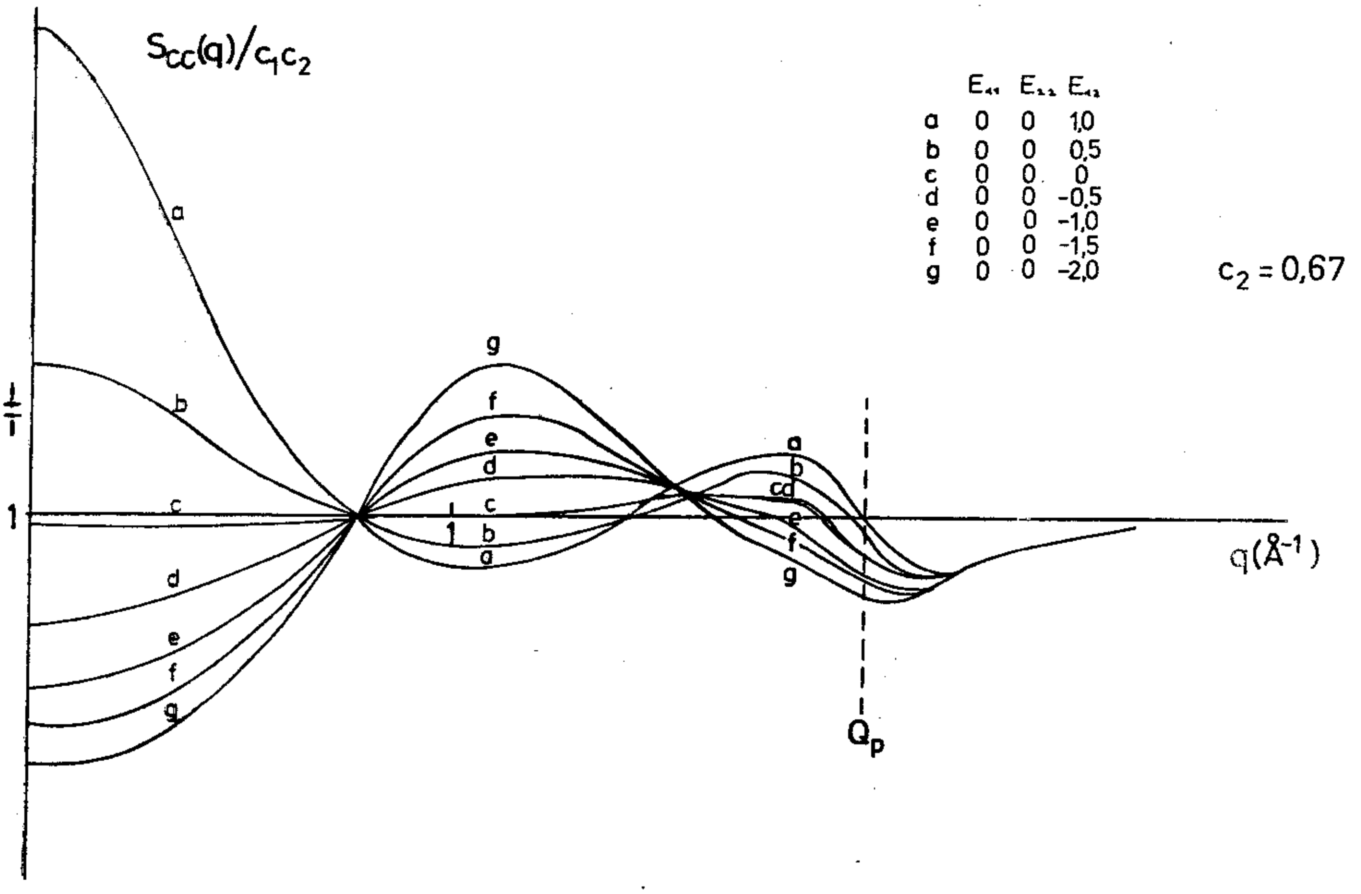
Fig. 9 $4\pi r^2 \rho_{CC}(r)$ of Li/Pb, Ag

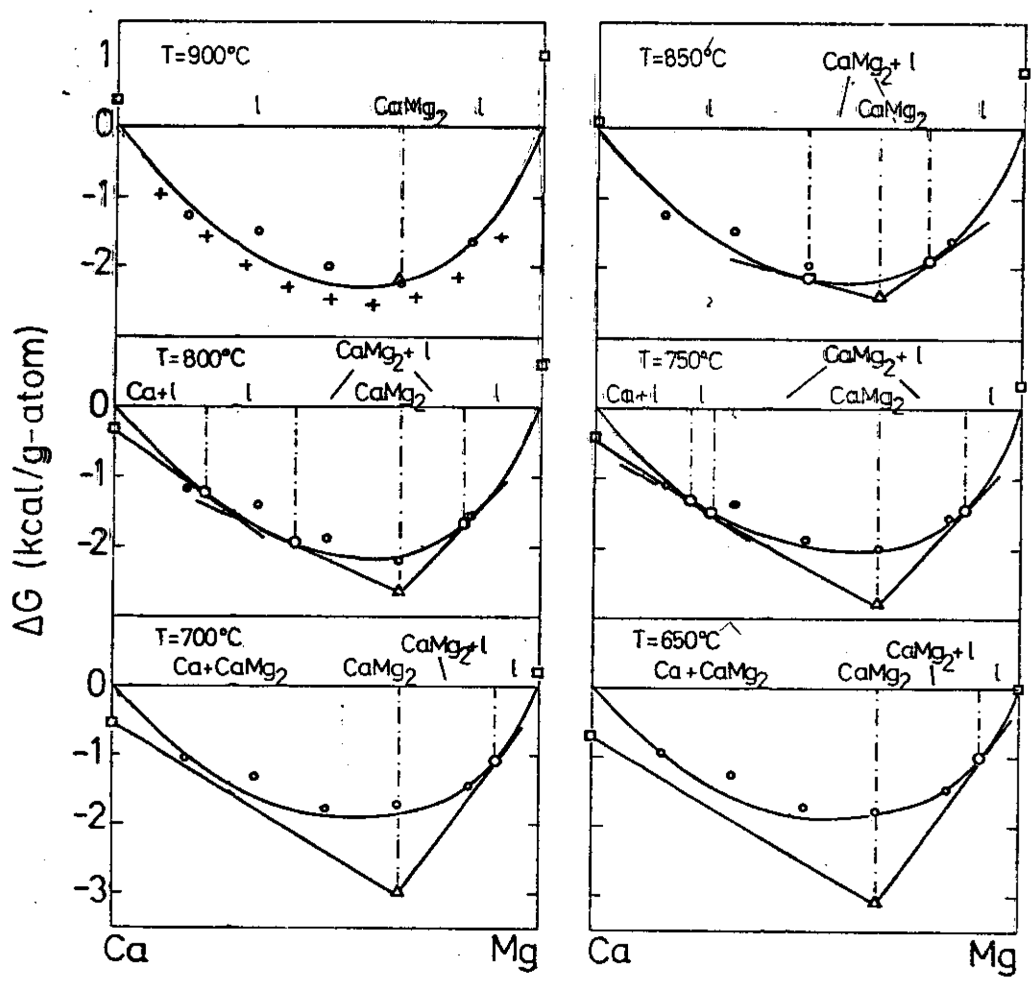


Li0.67 Na0.33
Δ>0
R (a.u.)

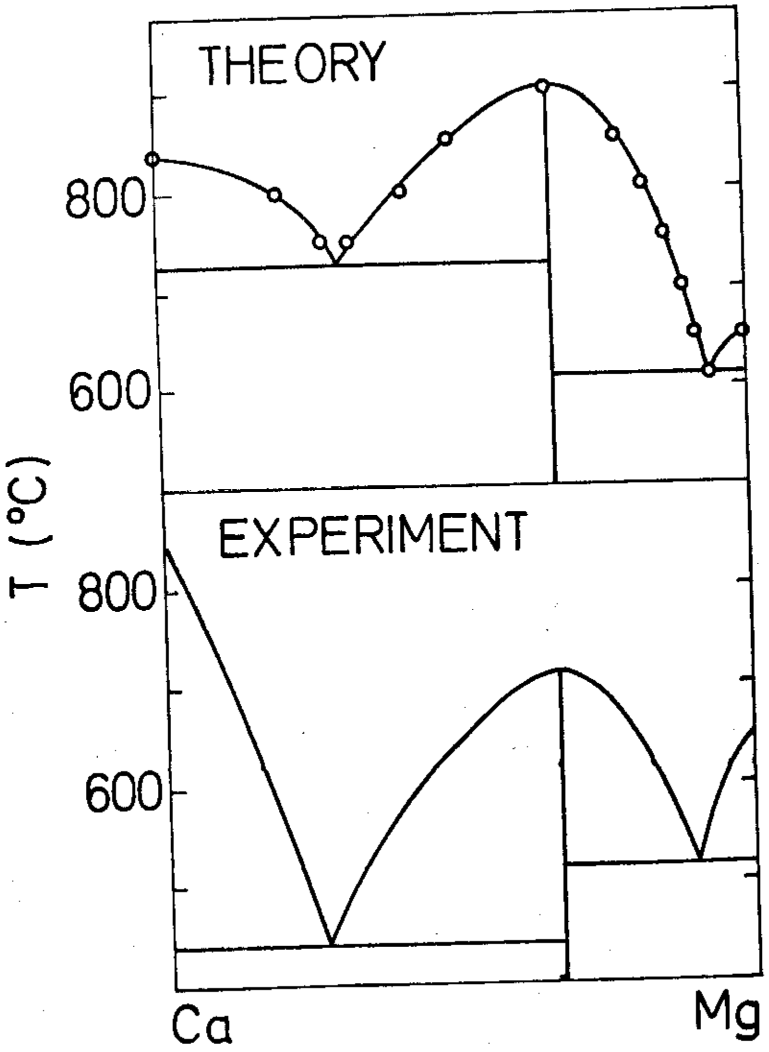


1 2 3
Veff (mRy)
r(a.u)
Δ<0
Li Al
1 Li-Li
2 Li-Al
3 Al-Al





Ab-initio construction of phase-diagram



AMORPHOUS METALLIC ALLOYS
– METALLIC GLASSES

Transition metals – metalloids
Pd-Si, Fe-B, Ni-P

Transition-metals – transition metals
Cu-Zr, Ni-Nb

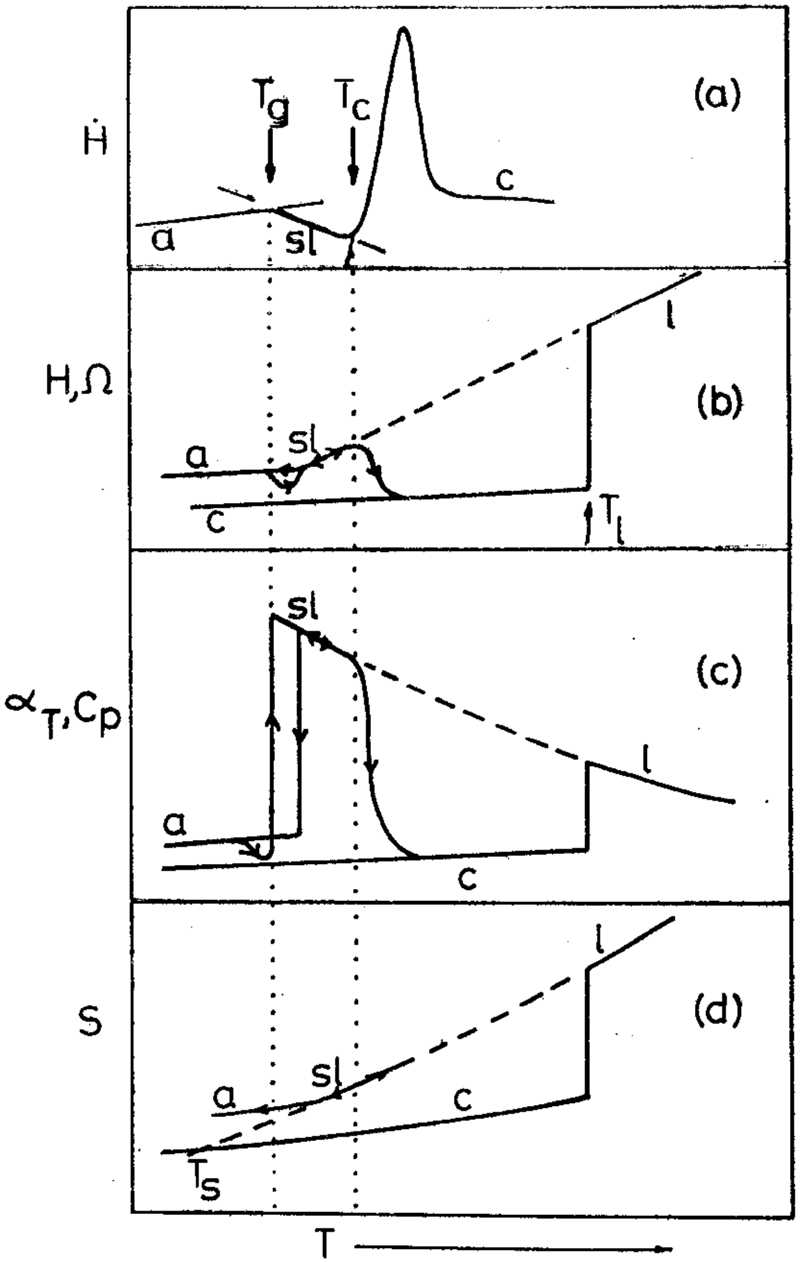
Transition-metals – lanthanides
Gd-Co, Tb-Fe, Au-La

Simple-metals – transition metals
Ca-Ni, Be-Ti

Simple-metals – lanthanides
Al-La, Ga-La

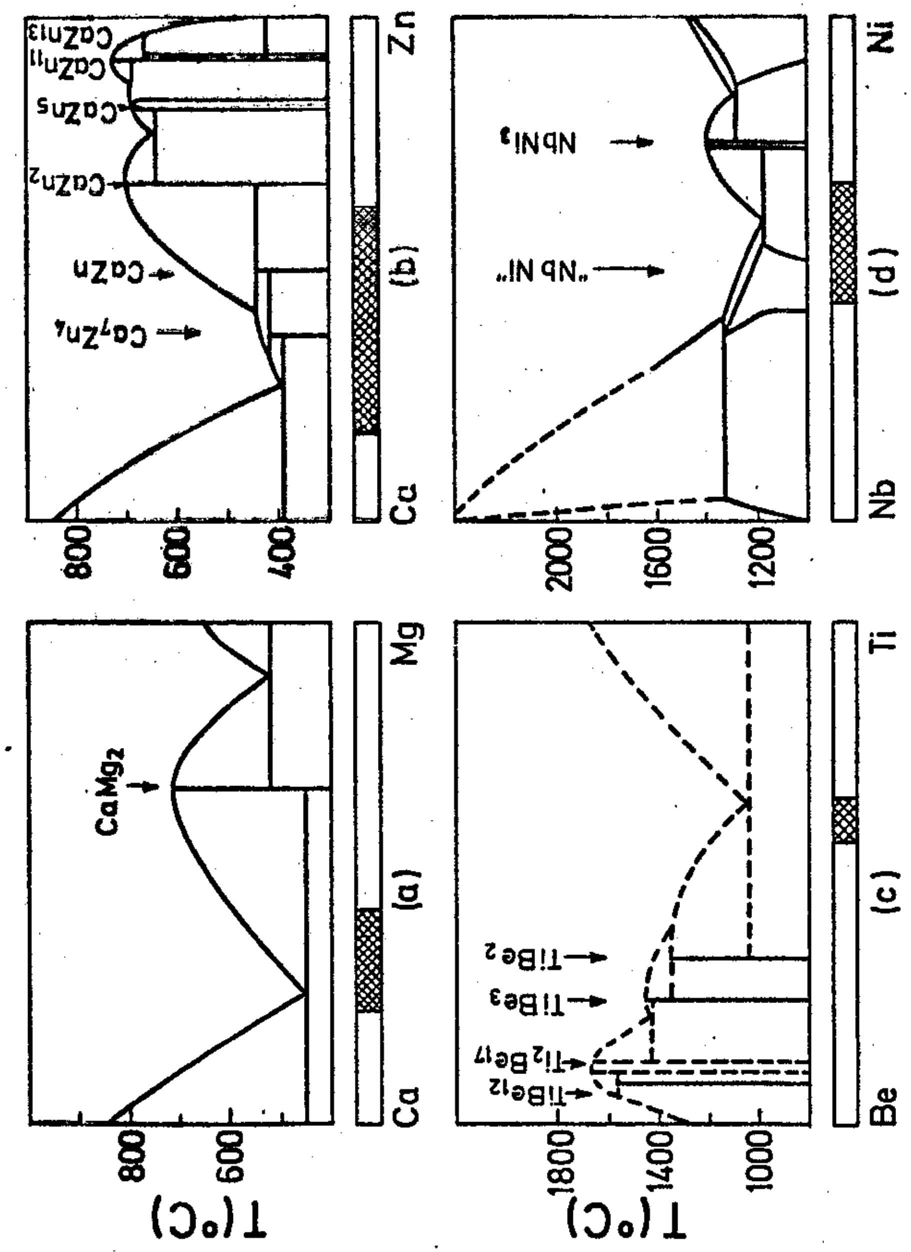
Simple-metals – simple metals
Mg-Zn, Ca-Mg, Ca-Al, Ca-Ga, Sr-Al

Simple metals – metalloids
Rb-O, Cs-O



Ḣ
H, Ω
α_T, C_p
S
(a)
(b)
(c)
(d)
T_g
T_c
T_l
T_s
a
sl
c
l
T

Fig. 2 (a)-(d)



T (°C)
800
600
400
2000
1600
1200
1800
1400
1000
Ca
Zn
Mg
Nb
Ni
Be
Ti
(a)
(b)
(c)
(d)
$CaZn_{13}$
$CaZn_{11}$
$CaZn_5$
$CaZn_2$
CaZn
Ca_7Zn_4
$CaMg_2$
$NbNi_3$
"Nb Ni"
$TiBe_2$
$TiBe_3$
Ti_2Be_{17}
$TiBe_{12}$

Fig. 1

$$\vec{F}(\vec{R}_i) = -\sum_{j\neq i} \vec{\nabla}\, v(|\vec{R}_i-\vec{R}_j|)$$

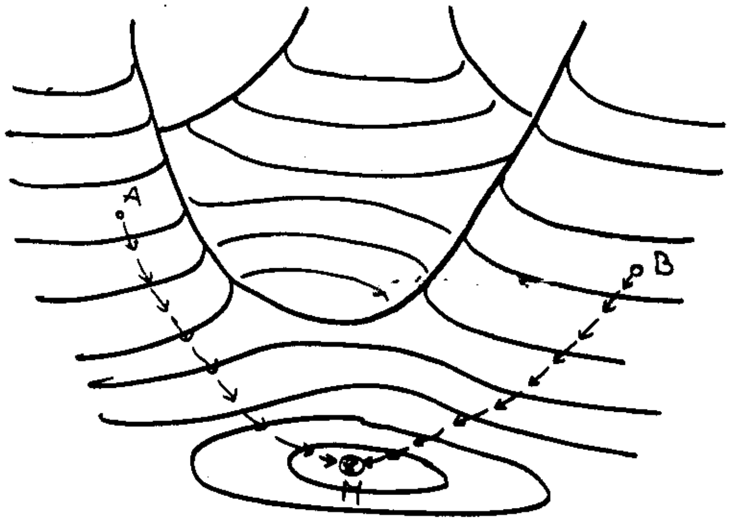
$$\vec{F}(\vec{R}_i+\delta\vec{R}_i) = \vec{F}(\vec{R}_i) + (\delta\vec{R}_i\cdot\vec{\nabla})\vec{F}(\vec{R}_i)$$

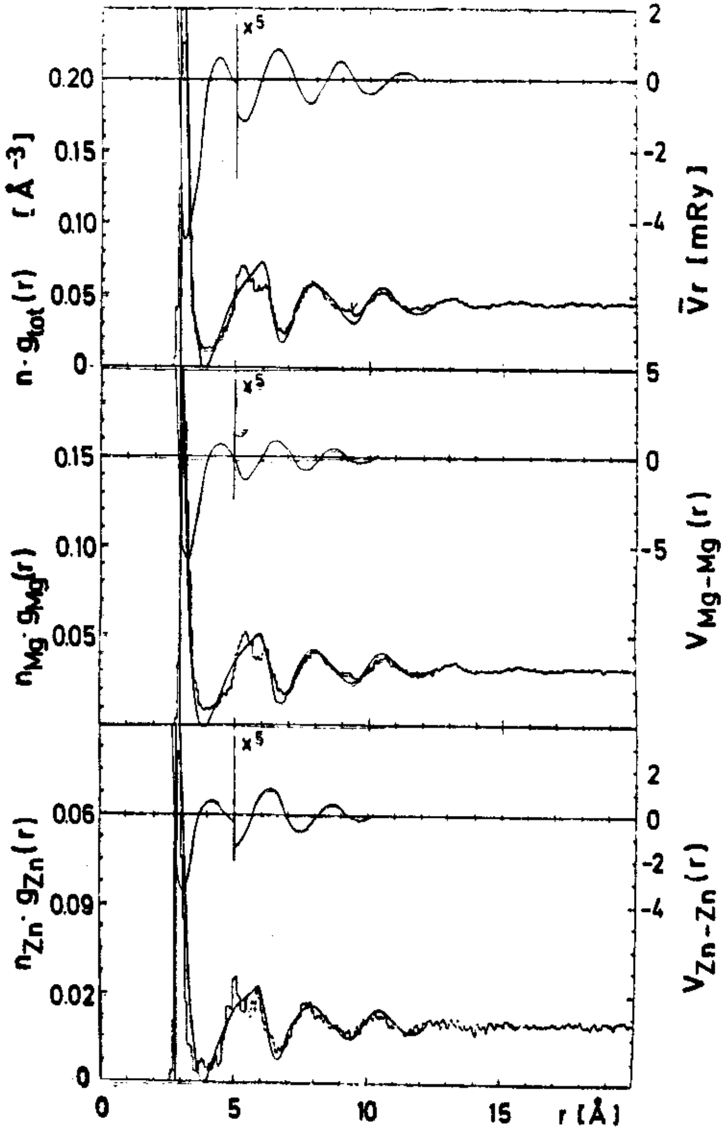
$$\vec{F}(\vec{R}_i+\delta\vec{R}_i) = \emptyset$$

$$-\vec{F}(\vec{R}_i) = (\delta\vec{R}_i\cdot\vec{\nabla})\vec{F}(\vec{R}_i) \rightarrow \delta\vec{R}_i \quad \forall i$$

$$\vec{R}_i{}' = \vec{R}_i + f\cdot\delta\vec{R}_i$$

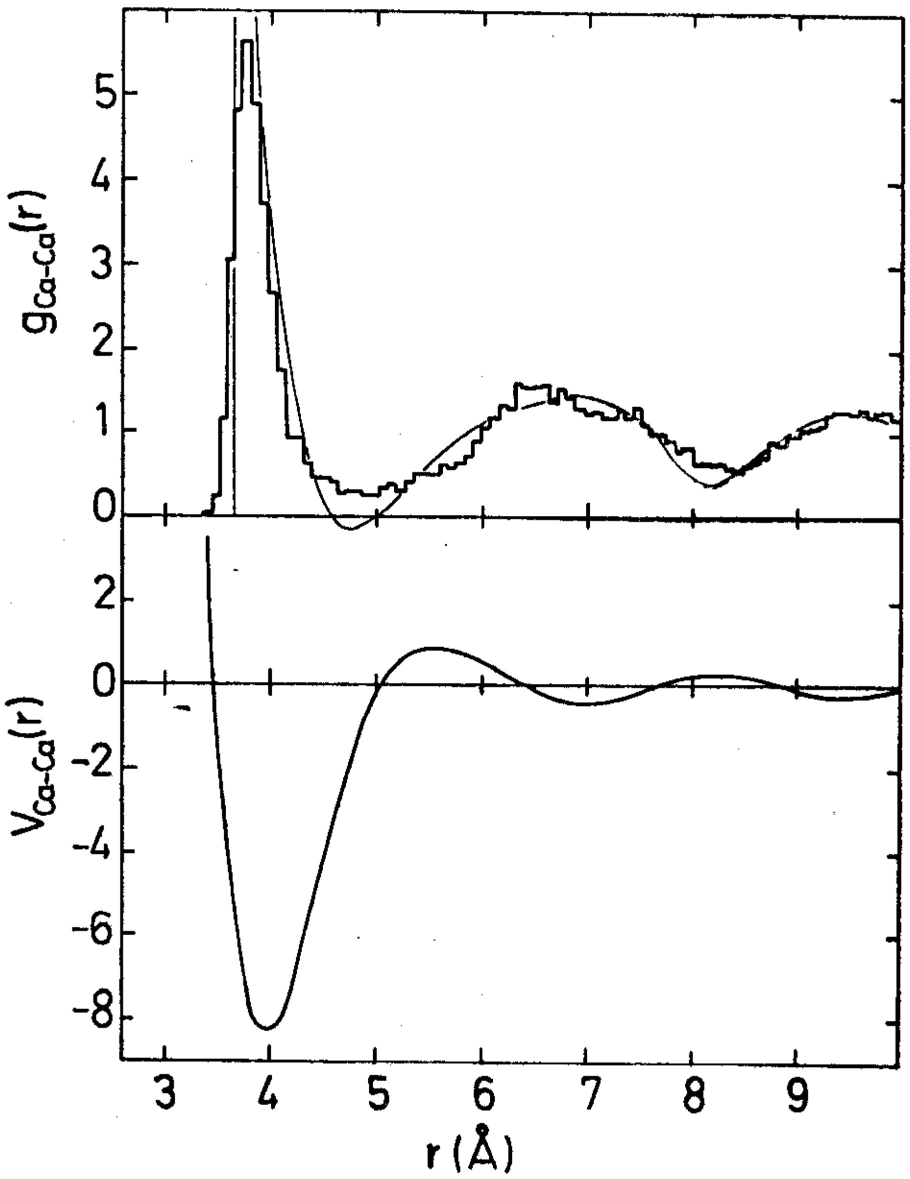
≙ ABSTIEG ENTLANG DES STEILSTEN GRADIENTEN AUF DER ENERGIE-HYPERFLÄCHE IM KONFIGURATIONSRAUM

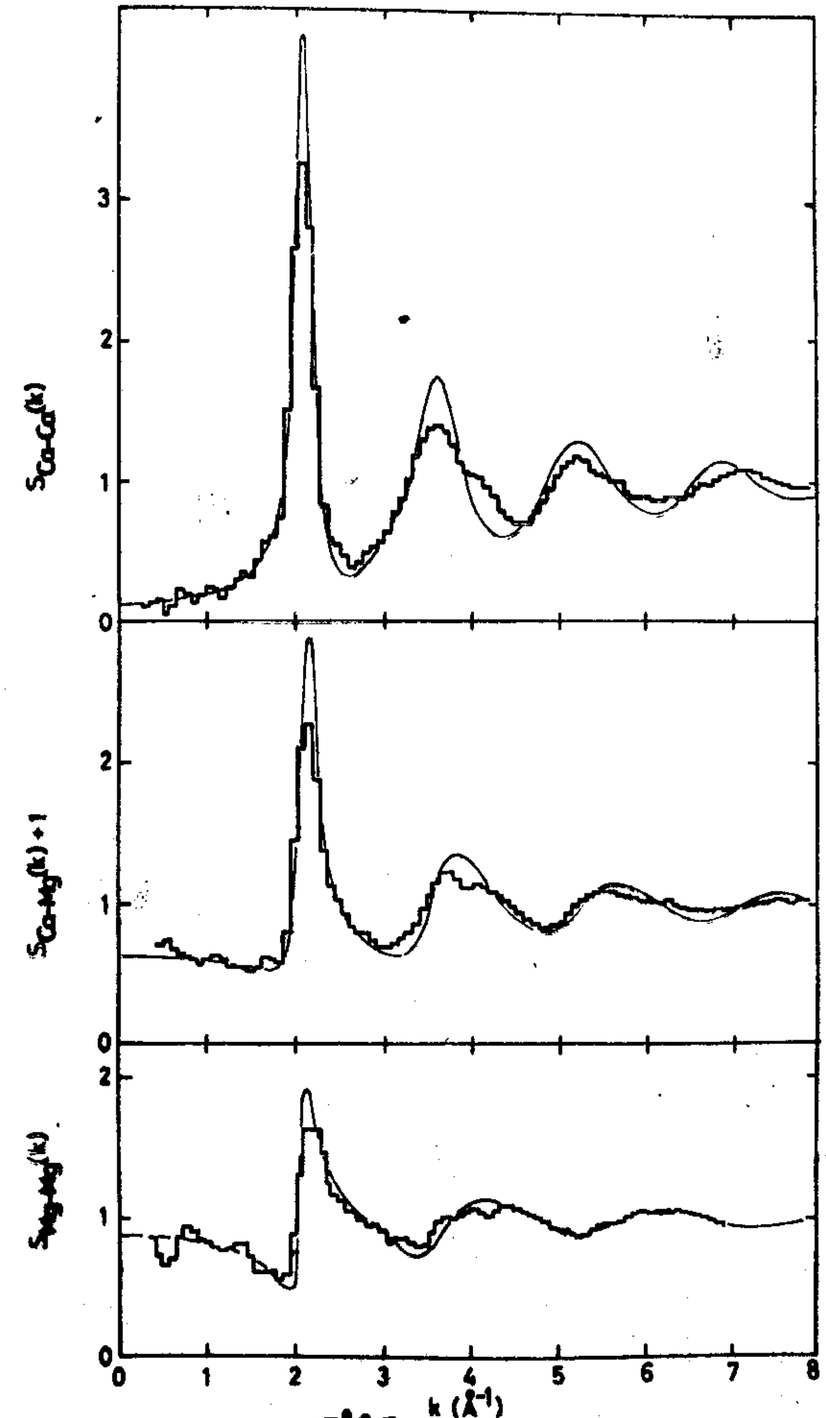




$Mg_{.70}Zn_{.30}$

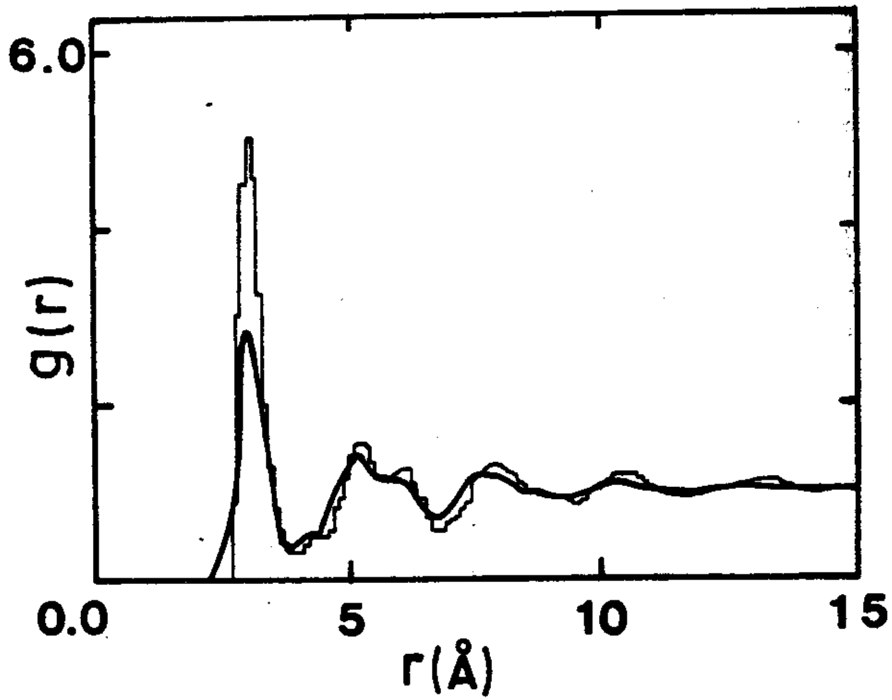
Ca.67 Mg.33

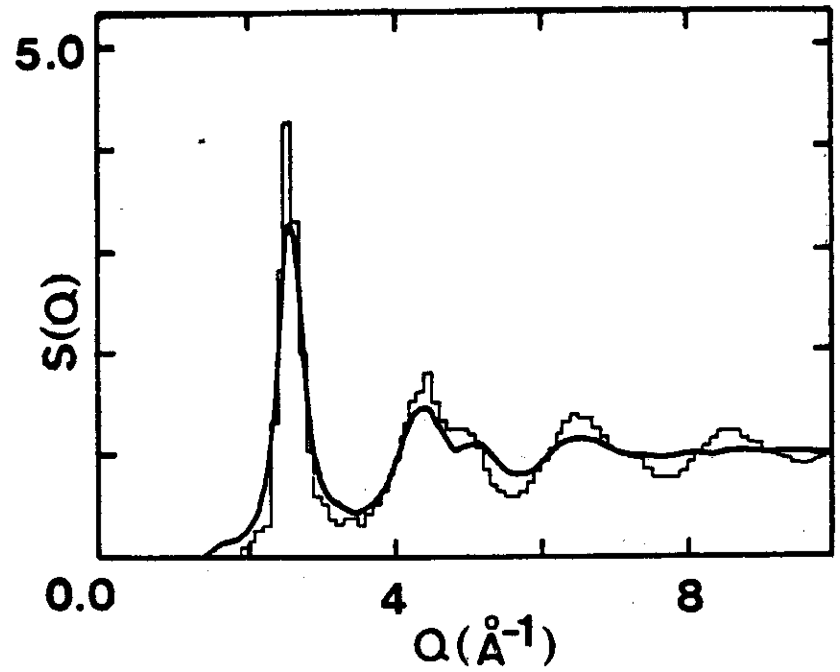




Histogram: Theory (Cluster-Relaxation, T=0 K)
Contin. Line: elastic neutron scattering
(room temperature)

$Mg_{70}Zn_{30}$





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