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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 V

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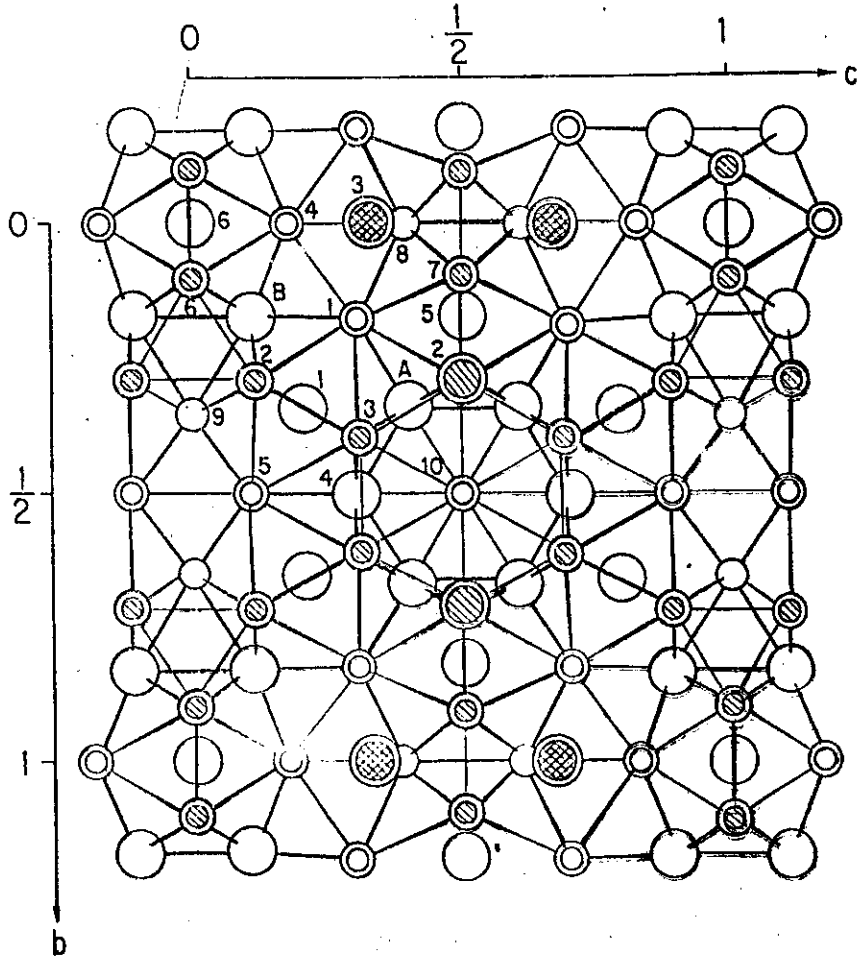
CRYSTAL STRUCTURE OF $Mg_{51}Zn_{20}$ (Mackay et al.)
SECTION OF THE UNIT CELL BETWEEN −0.25 and +0.25

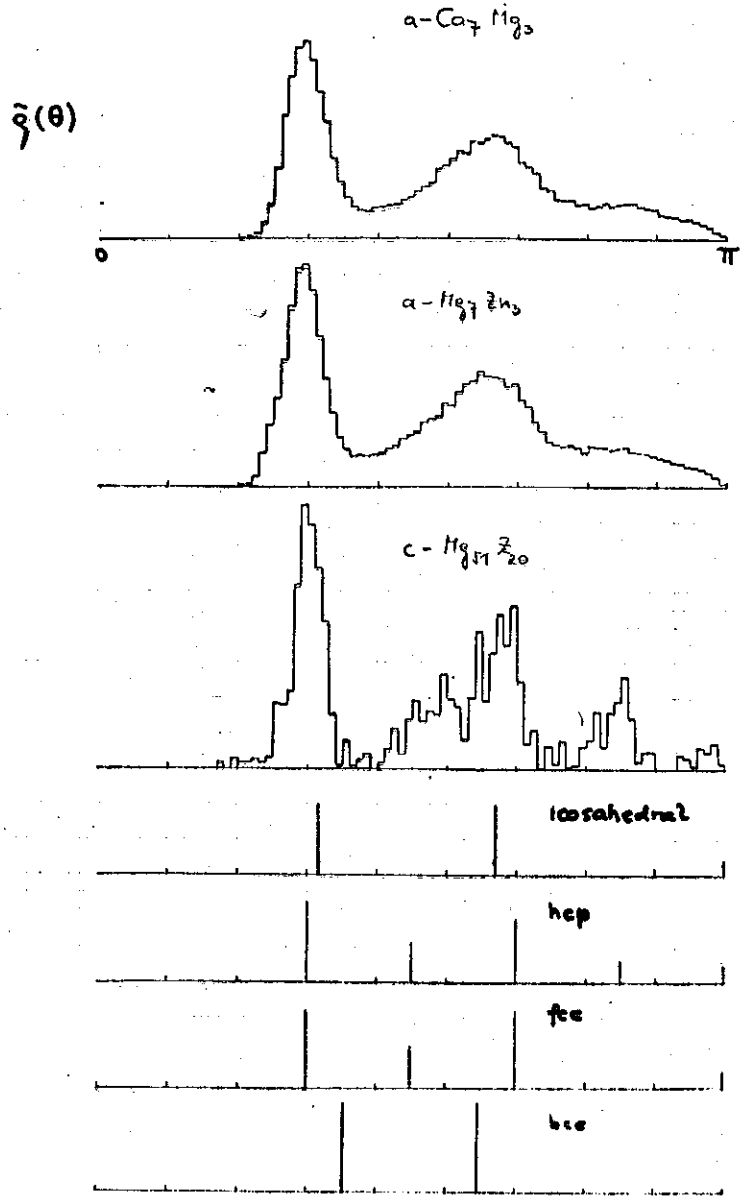


○ : Zn, A, B (x≒0) ○ : Mg (x=0)
◎ : 2Zn(x≒±0.16) ◎ : 2Mg(x≒±0.11)
◎ : 2Zn(x≒±0.21) ◎ : 2Mg(x≒±0.18)

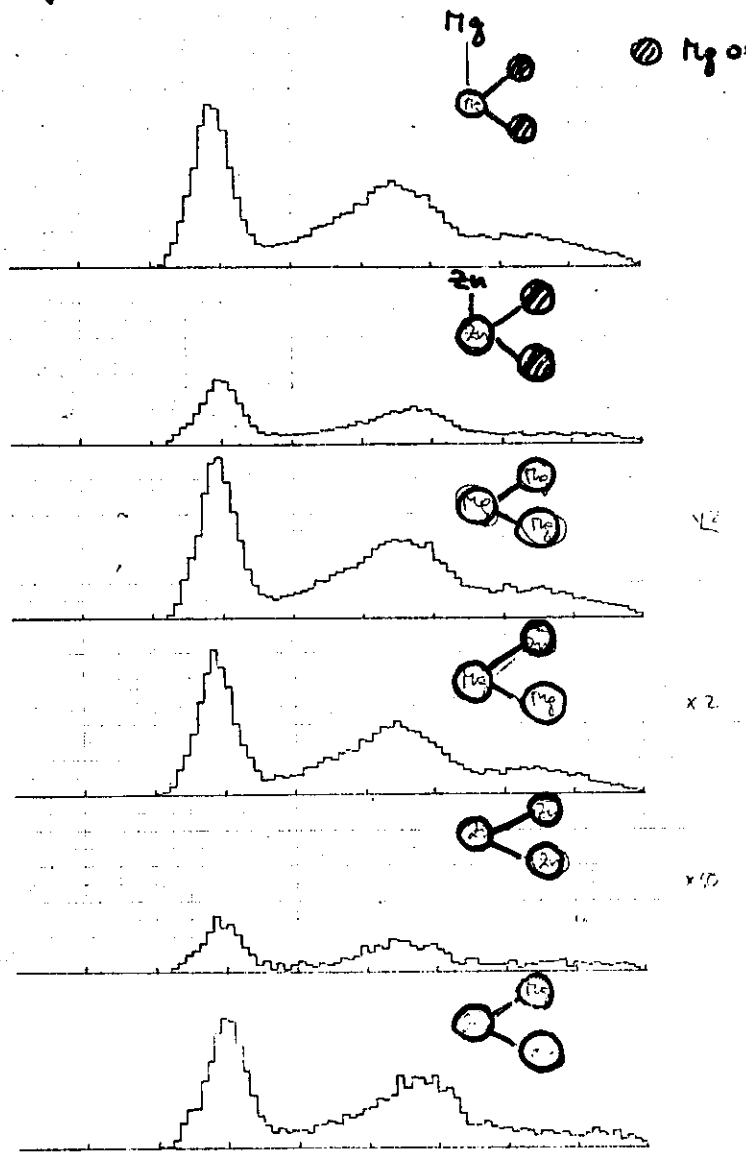
Fig.1

Bond-angle distribution function (total)
= radial average over three-body correl. fct.

$$\tilde{g}(\theta) \sim \int_0^{R_M} g^{(3)}(R_{12}, R_{13}, \theta)\, d^3R_{12}\, d^3R_{13}$$



Bond angle distribution functions (partial)



DEFECTS IN AMORPHOUS METALS

ATOMIC LEVEL STRESSES

$$\sigma_i^{\alpha\beta} = \frac{1}{2\Omega} \sum_{j \neq i} \frac{\partial \phi(r_{ij})}{\partial r_{ij}} \frac{r_{ij}^{\alpha} r_{ij}^{\beta}}{r_{ij}}$$

Classical potentials (see Born + Huang)

VOLUME-DEPENDENT INTERACTIONS

$$\sigma_i^{\alpha\beta} = \frac{1}{2\Omega} \sum_{j \neq i} \left(\frac{\partial V_{eff}(r_{ij},\Omega)}{\partial r_{ij}} \frac{r_{ij}^{\alpha} r_{ij}^{\beta}}{r_{ij}} + \Omega \frac{\partial V_{eff}(r_{ij},\Omega)}{\partial \Omega} \delta_{\alpha\beta} \right) - \frac{\partial E_0}{\partial \Omega}$$

$$E = E_0(\Omega) + \frac{1}{2} \sum_{ij}{}' V_{eff}(r_{ij},\Omega)$$

HYDROSTATIC STRESS

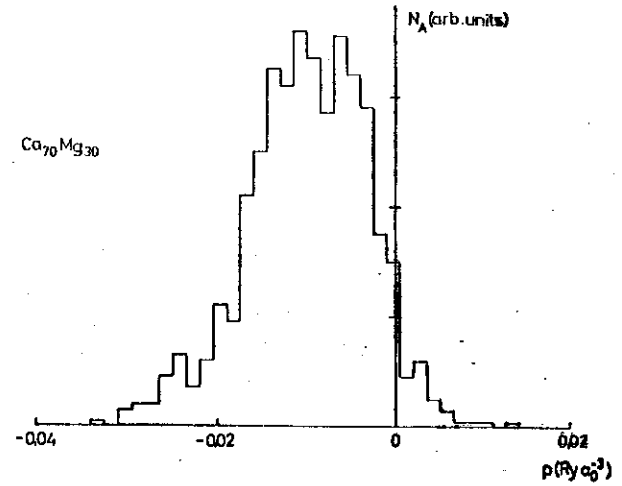
$$p_i = \frac{1}{3} \sum_{\alpha} \sigma_i^{\alpha\alpha}$$

SHEAR STRESS

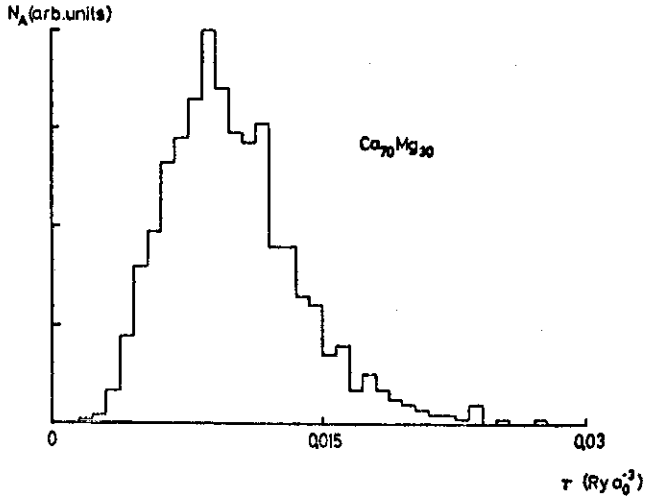
$$\tau_i = \left\{ (\sigma^{12})^2 + \frac{1}{4} (\sigma^{22} - \sigma^{11})^2 \right\}^{1/2}$$

ATOMIC LEVEL STRESSES

HYDROSTATIC STRESS p



SHEAR STRESS τ



EGAMI, SROLOVITZ AND HAFNER

ELASTIC AND MECHANICAL PROPERTIES OF METALLIC GLASSES

DENSITY $\rho_a < \rho_c$ by a few %

BULK MODULUS $B_a \sim B_c$

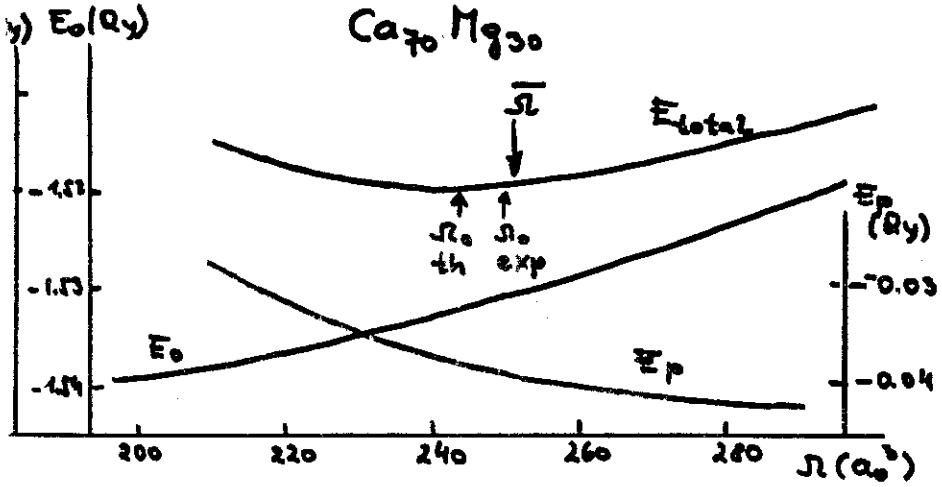
SHEAR MODULUS $E_a < E_c$

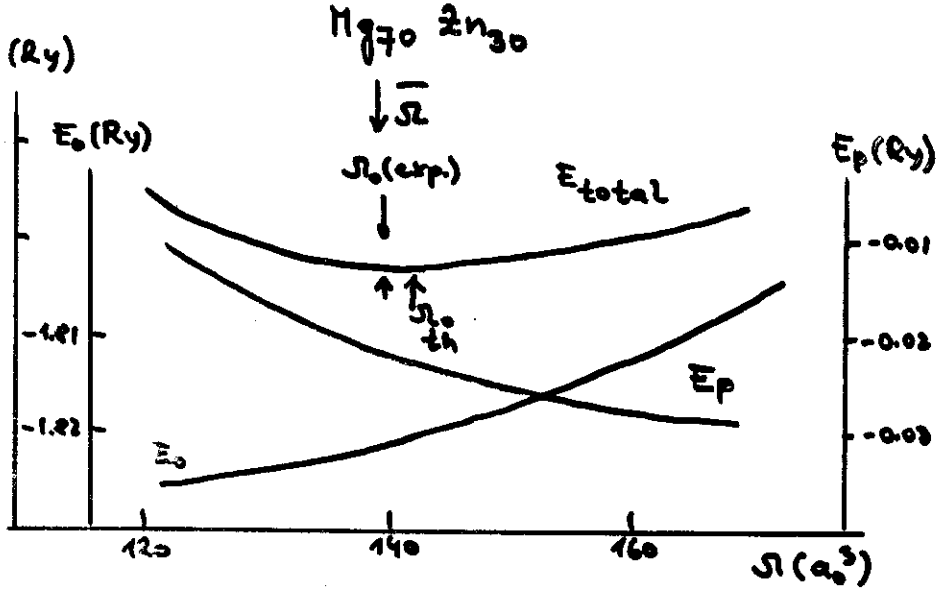
softening of shear shift vert by 20-30%, due to relaxation of internal stresses — allowed in the amorphous state, but forbidden in the crystal due to symmetry constraints

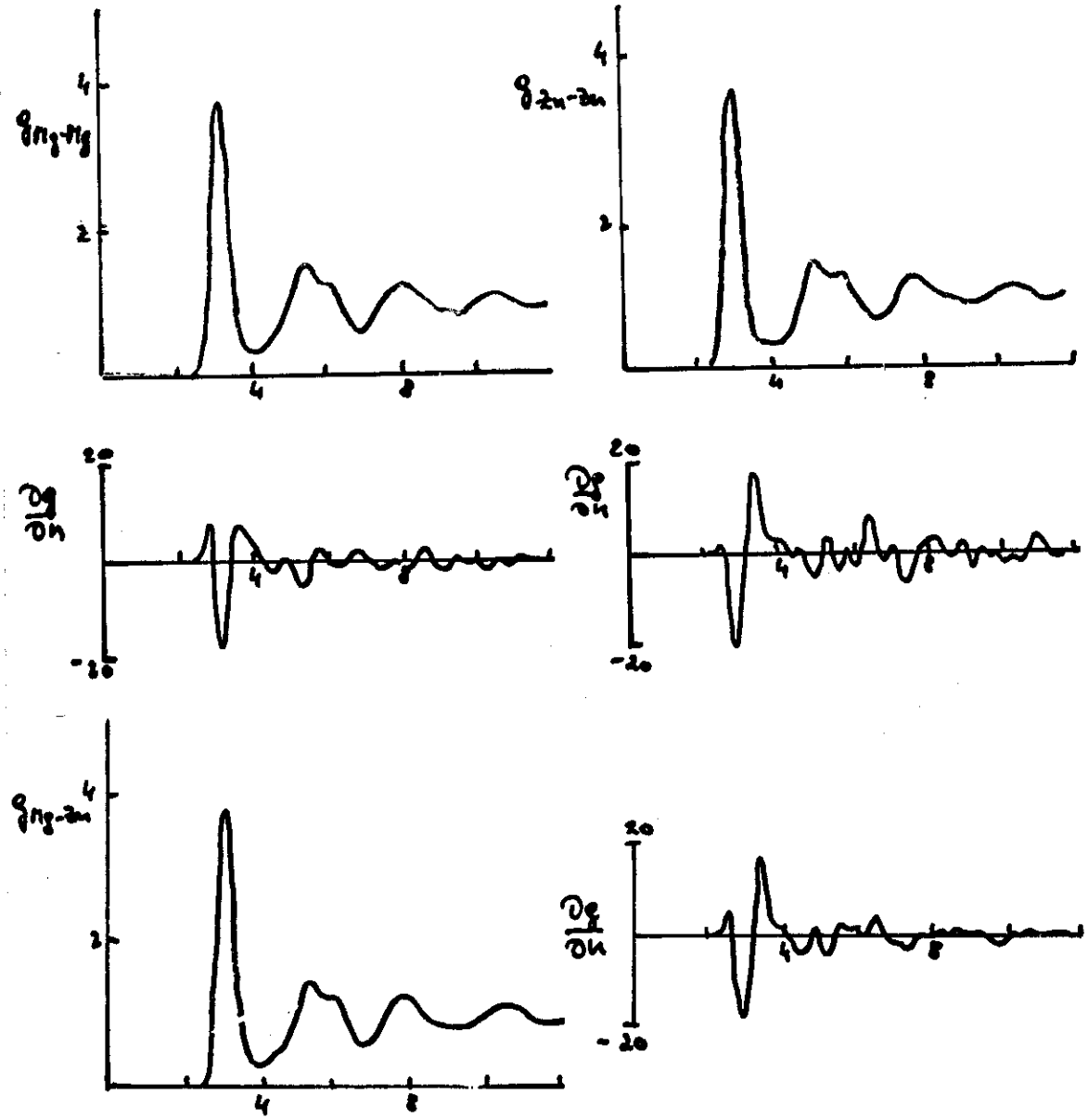
Theory: Cluster relaxation:

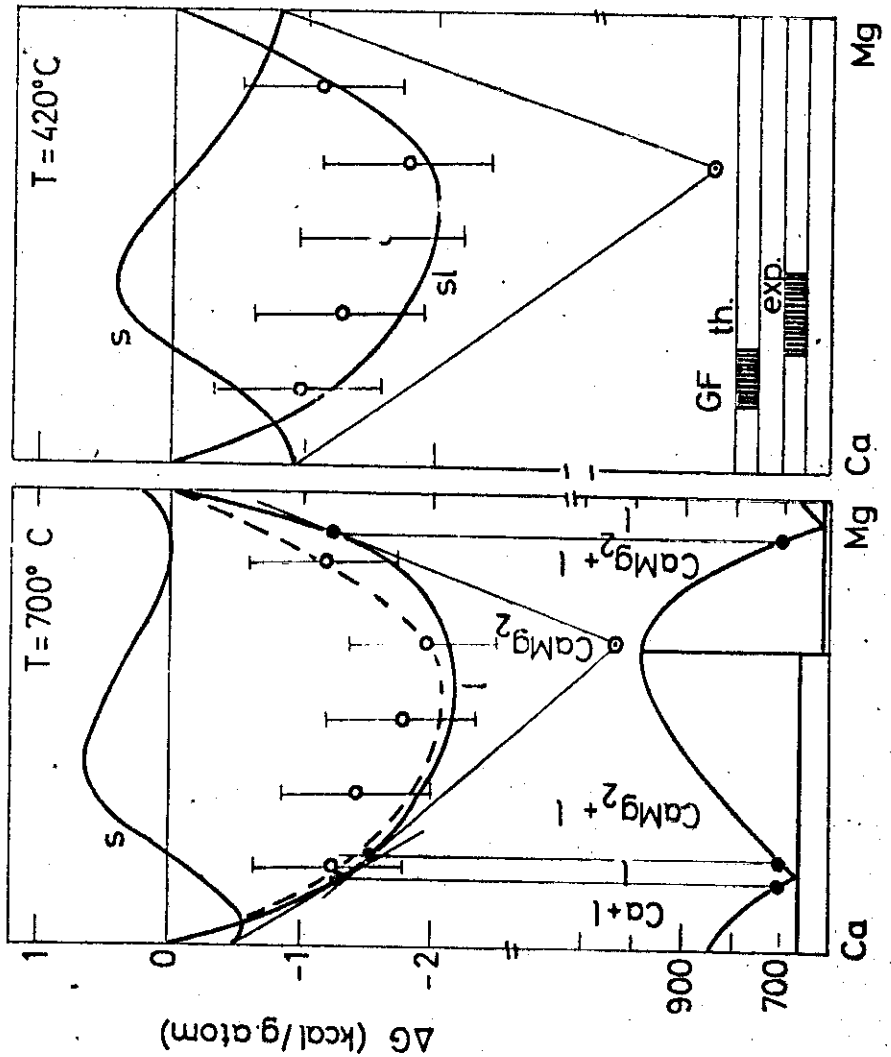
1) Relax the Cluster
2) Deform —«——
3) If necessary (volume change), adjust potentials

⇒ Energy as a function of the strain parameter


$Ca_{70}Mg_{30}$
E_0(Ry)
$\bar{\Omega}$
E_{total}
Ω_0 th
Ω_0 exp
E_p (Ry)
E_0
E_p
-1.83
-1.84
-0.03
-0.04
200
220
240
260
280
Ω (a_0^3)


$Mg_{70}Zn_{30}$
(Ry)
$\bar{\Omega}$
E_0(Ry)
Ω_0(exp.)
E_{total}
E_p(Ry)
Ω_0 th
E_p
E_0
-1.81
-1.82
-0.01
-0.02
-0.03
120
140
160
Ω (a_0^3)


g_{Mg-Mg}
g_{Zn-Zn}
g_{Mg-Zn}
$\frac{\partial g}{\partial u}$
$\frac{\partial g}{\partial u}$
$\frac{\partial g}{\partial u}$
4
8
20
-20



GLASS-FORMING ABILITY

a) THERMODYNAMIC ASPECTS

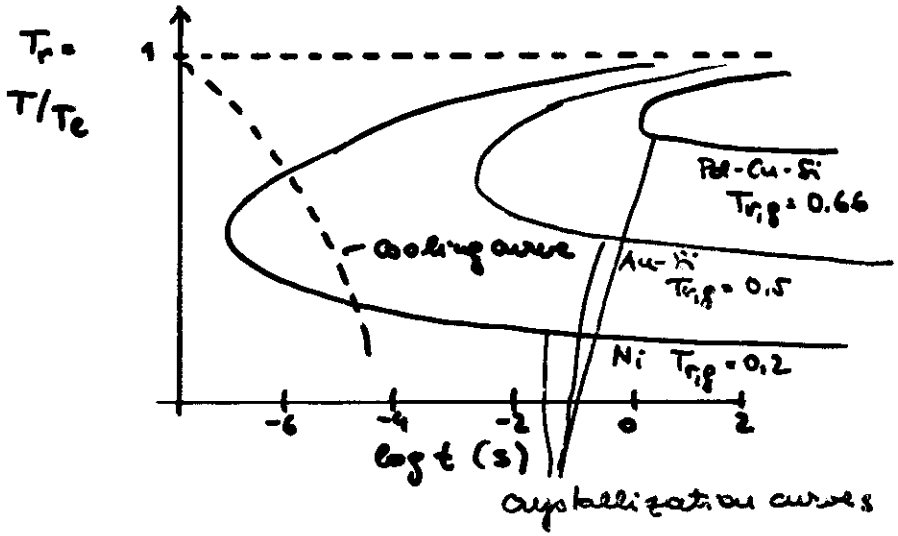
LOW ENTHALPY OF THE SUPERCOOLED LIQUID RELATIVE TO THE STABLE CRYSTALLINE STATE,

NO COMPETING <u>SIMPLE</u> CRYST. COMPOUNDS

b) KINETIC ASPECTS

DAVIES-UHLMANN THEORY OF CRYSTALLIZATION

→ Time-Temperature-Transformation diagram



→ RELEVANT PARAMETER FOR CRYSTALLIZATION KINETICS:

REDUCED GLASS-TEMPERATURE

$$T_{rg} = T_g / T_e$$

THEORIES FOR GLASS-TRANSITION

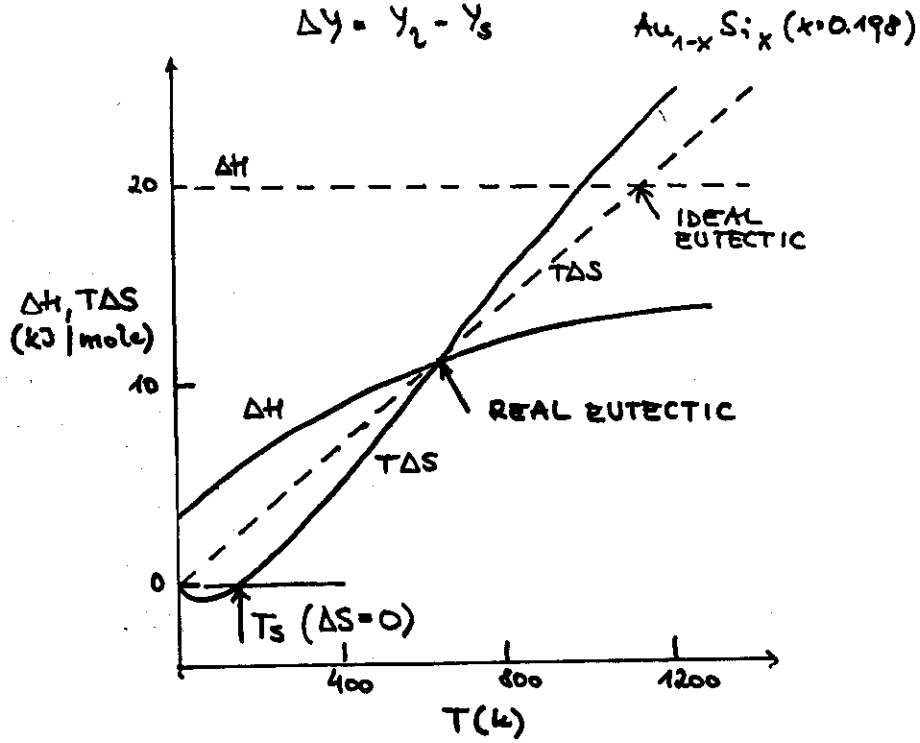
1. ENTROPY-THEORY (Gibbs, DiMarzio . . . .)
   VANISHING EXCESS ENTROPY OF THE SUPERCOOLED LIQUID RELATIVE TO THE SOLID
   ⇒ IDEAL GLASS TRANSITION (2nd ORDER)

2. FREE VOLUME THEORY (Cohen, Turnbull, Grest . . . .)
   PERCOLATION TRANSITION IF AVERAGE FREE VOLUME DROPS BELOW A CRITICAL VALUE
   ⇒ CRITICAL INCREASE IN VISCOSITY
   ⇒ 1st ORDER TRANSITION

3. TRANSITION TO NON-ERGODIC STATE

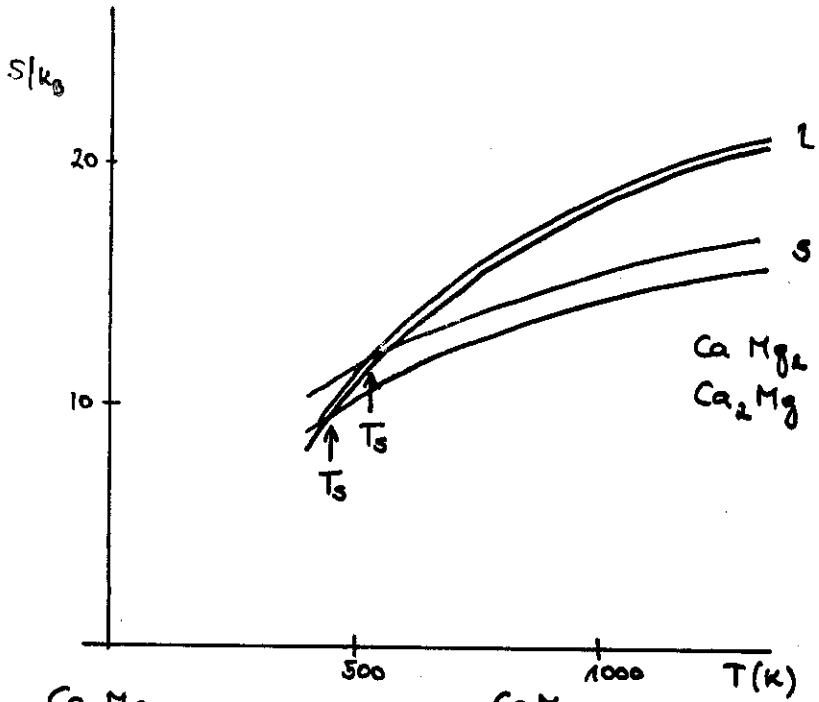
GLASS TRANSITION
AND KAUZMANN'S PARADOXON

$$\Delta S = S_c - S_a < 0$$



CASTANET ET AL.
ALLEN, WRIGHT + CONNELL

GLASS TRANSITION AND GLASS-FORMING ABILITY
IN CA-MG ALLOYS



Ca_2Mg

$T_s \approx T_g = 530\ K$

$T_l = 1023\ K$

$T_{gr} = \frac{T_g}{T_l} = 0.51$ (exp. 0.45)

$CaMg_2$

$T_s \approx T_g = 450\ K$

$T_l = 1180\ K$

$T_{gr} = 0.39$

DAVIES-UHLMANN THEORY OF TRANSFORMATION KINETICS

$\dot{T}_c \sim 4 \times 10^4\ K\,s^{-1}$ $\qquad$ $\dot{T}_c \sim 2 \times 10^7\ K\,s^{-1}$

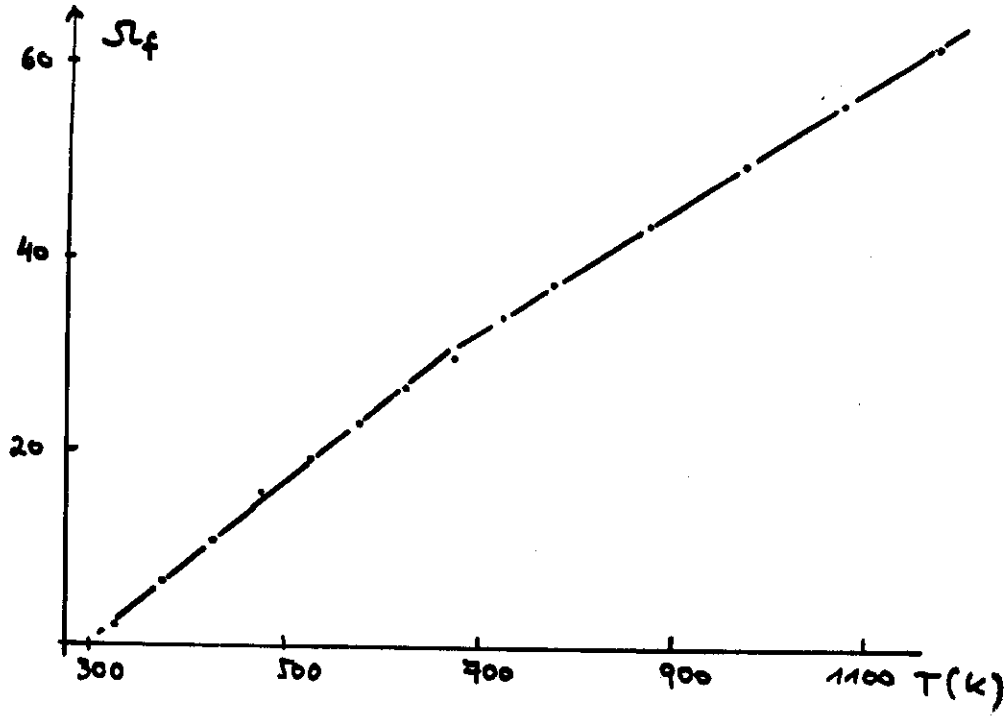
FREE VOLUME-APPROACH TO VISCOSITY

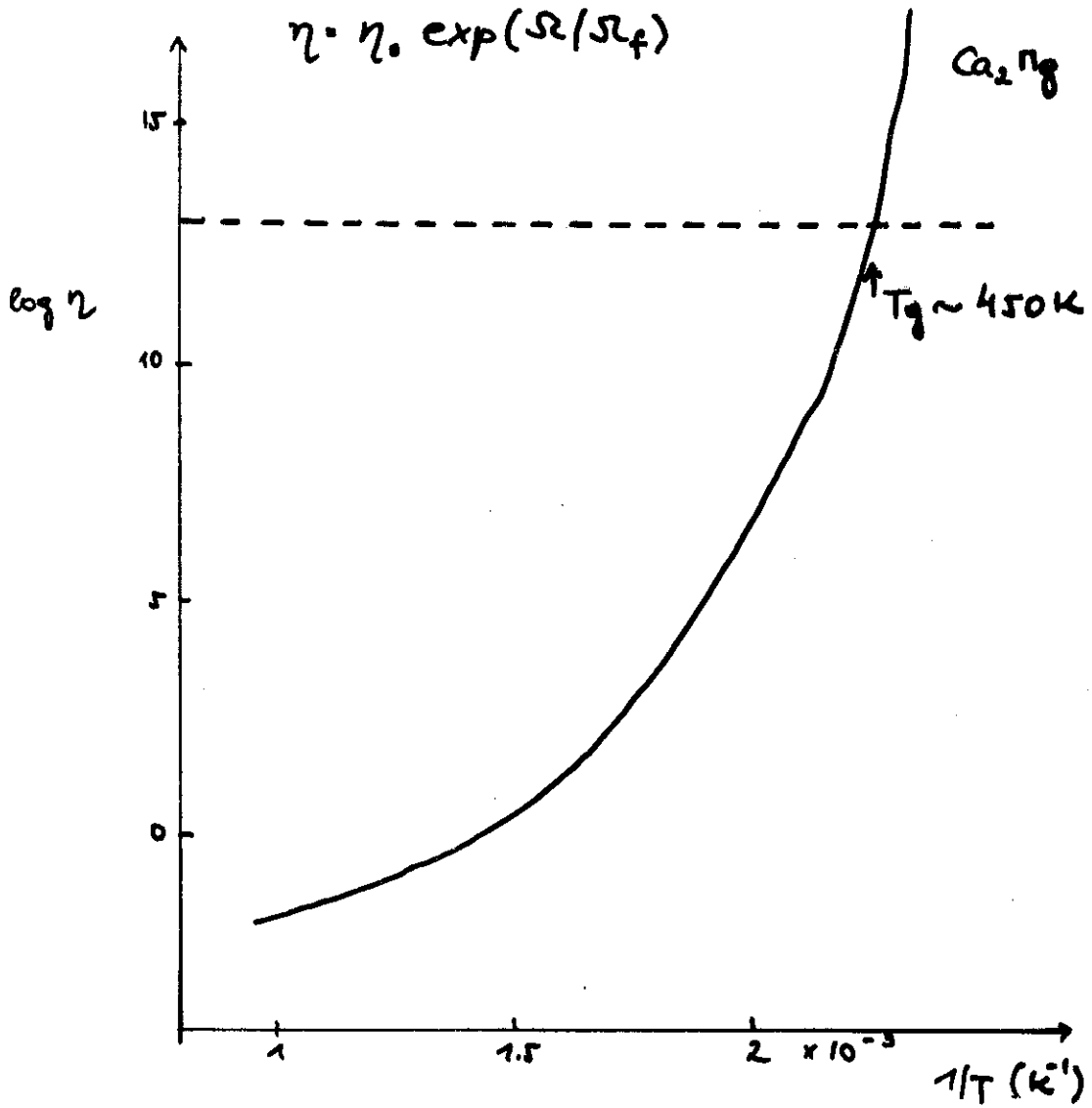
$\eta = \eta_0 \exp(\Omega/\Omega_f)$

η_0 from Enskog-Theory at $T = T_M$

$\Omega_f = \Omega - \Omega_0 = \Omega(\eta = 0.636)$

$\Omega = \Omega(T)$ from thermodyn. variational calculation





DYNAMICAL PROPERTIES OF AMORPHOUS ALLOYS

EQUATION OF MOTION METHOD

NEWTONIAN EQUATION OF MOTION

$$\ddot{u}_{i\alpha}(t) = m_i^{-1} F_{i\alpha}(t) = m_i^{-1} \sum_{j\beta} \phi_{\alpha\beta}(i,j,t)\, u_{j\beta}(t)$$

$\rightsquigarrow$ DIFFERENCE EQUATION (Δ ... TIMESTEP)

$$\vec{u}_i(t+\Delta) = \vec{u}_i(t-\Delta) - 2\vec{u}_i(t) + \Delta^2 m_i^{-1} \vec{F}_i(t) + O(\Delta^4)$$

VIBRATIONAL DOS

$$g(\omega) = -\frac{2\omega}{\pi} \operatorname{Im} \operatorname{Tr} G(\omega^2 + i\varepsilon)$$

$$\int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle u_{i\alpha}(t) u_{j\beta}(0) \rangle = -\operatorname{Im} G_{\alpha\beta}(i,j,\omega^2 + i\varepsilon$$

$$\rightsquigarrow g(\omega) = \frac{2\omega}{\pi} \operatorname{Re} \int_0^{\infty} \sum_{i,\alpha} u_{i\alpha}(t)\, u_{i\alpha}(0)\, e^{i\omega t}\, dt$$

$$\approx \frac{2\omega}{\pi} \operatorname{Re} \int_0^{T} \sum_{i,\alpha} u_{i\alpha}(t)\, u_{i\alpha}(0)\, e^{i\omega t} f(t/T)\, dt$$

PROJECTED DOS (ONTO A SET OF INITIAL CONDITIONS $u_{i\alpha}(0)$)

RECURSION METHOD

$$G_{\alpha\beta}(ij,\omega^2+i\varepsilon) = \langle u_{i\alpha}|(\omega^2 I - D + i\varepsilon)^{-1}|u_{j\beta}\rangle$$

$$D_{\alpha\beta}(ij) = M_i^{-1/2}\,\phi_{\alpha\beta}(ij)\,M_j^{1/2}$$

NEW BASIS SET σ: ORTHONORMAL
D TRIDIAGONAL

$$\sigma_0 = u_{i\alpha}$$

$$b_1\sigma_1 = D\sigma_0 - a_0\sigma_0$$

RECURSION RELATION

$$b_{n+1}\sigma_{n+1} = D\sigma_n - a_n\sigma_n - b_n\sigma_{n-1}$$

$$\rightsquigarrow \quad a_n = \langle\sigma_n|D|\sigma_n\rangle$$

$$b_n = \langle\sigma_{n-1}|D|\sigma_n\rangle = \langle\sigma_n|D|\sigma_{n-1}\rangle$$

$$\rightsquigarrow \quad D = \begin{bmatrix} a_0 & b_1 & & \\ b_1 & a_1 & b_2 & \\ & b_2 & a_2 & b_3 \\ & & b_3 & a_3 & \ddots \end{bmatrix}$$

CONTINUED FRACTION REPRES. FOR $G_{\alpha\alpha}(ii,\omega^2)$

$$G_{\alpha\alpha}(ii,\omega^2) = \cfrac{1}{\omega^2 - a_0 - \cfrac{b_1^2}{\omega^2 - a_1 - \cfrac{b_2^2}{\omega^2 - a_2 - \cdots}}}$$

INITIAL CONDITIONS

a) $\vec{u}_i(0) = 1 \quad \vec{u}_j(0) = 0 \quad \forall\, j \neq i$

$\rightsquigarrow$ LOCAL DOS

b) STATISTICALLY DISTRIBUTED PHASES

$\vec{u}_j(0) = e^{i\phi_{j\alpha}}$, $0 \leq \phi_{j\alpha} \leq 2\pi$ RANDOM NUMBERS

$\rightsquigarrow$ TOTAL DOS

c) SINGLE PLANE WAVE

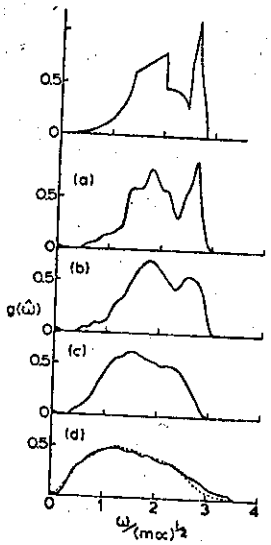
$\vec{u}_j(0) = \vec{e}_\alpha \exp(i\vec{q}\vec{R}_j)$ $\vec{e}_\alpha$ Polarisation vector

$\rightsquigarrow$ DOS OF STATES WITH CONSTANT WAVE VECTOR $\vec{q}$
DYNAMICAL STRUCTURE FACTOR

$$S(\vec{q},\omega) = \frac{1}{2\pi}\sum_{ij} e^{-i\vec{q}(\vec{R}_i - \vec{R}_j)} \int_{-\infty}^{\infty} e^{i\omega t}\,\vec{q}\cdot\vec{u}_i(t)\,\vec{u}_j(0)\,dt$$

REHR + ALBEN:

DENSITY OF STATES

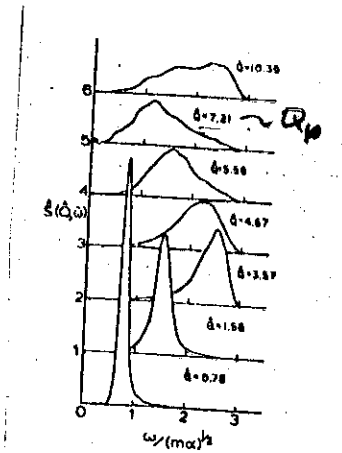


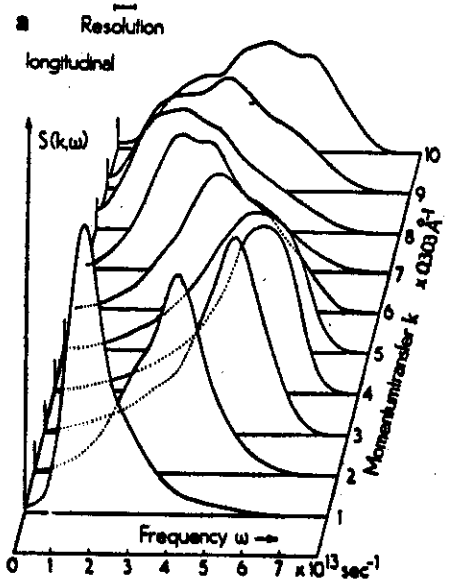
FCC- CRYSTAL

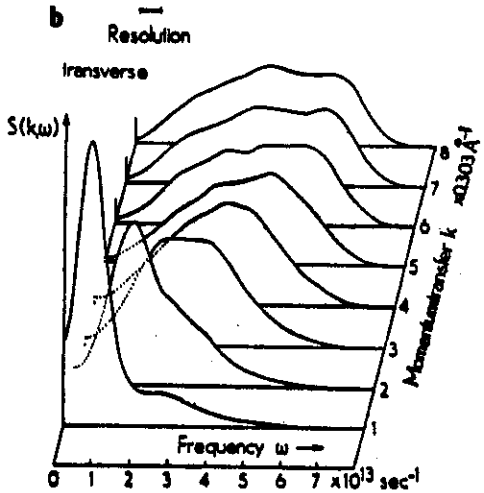
480-ATOM FCC CLUSTER

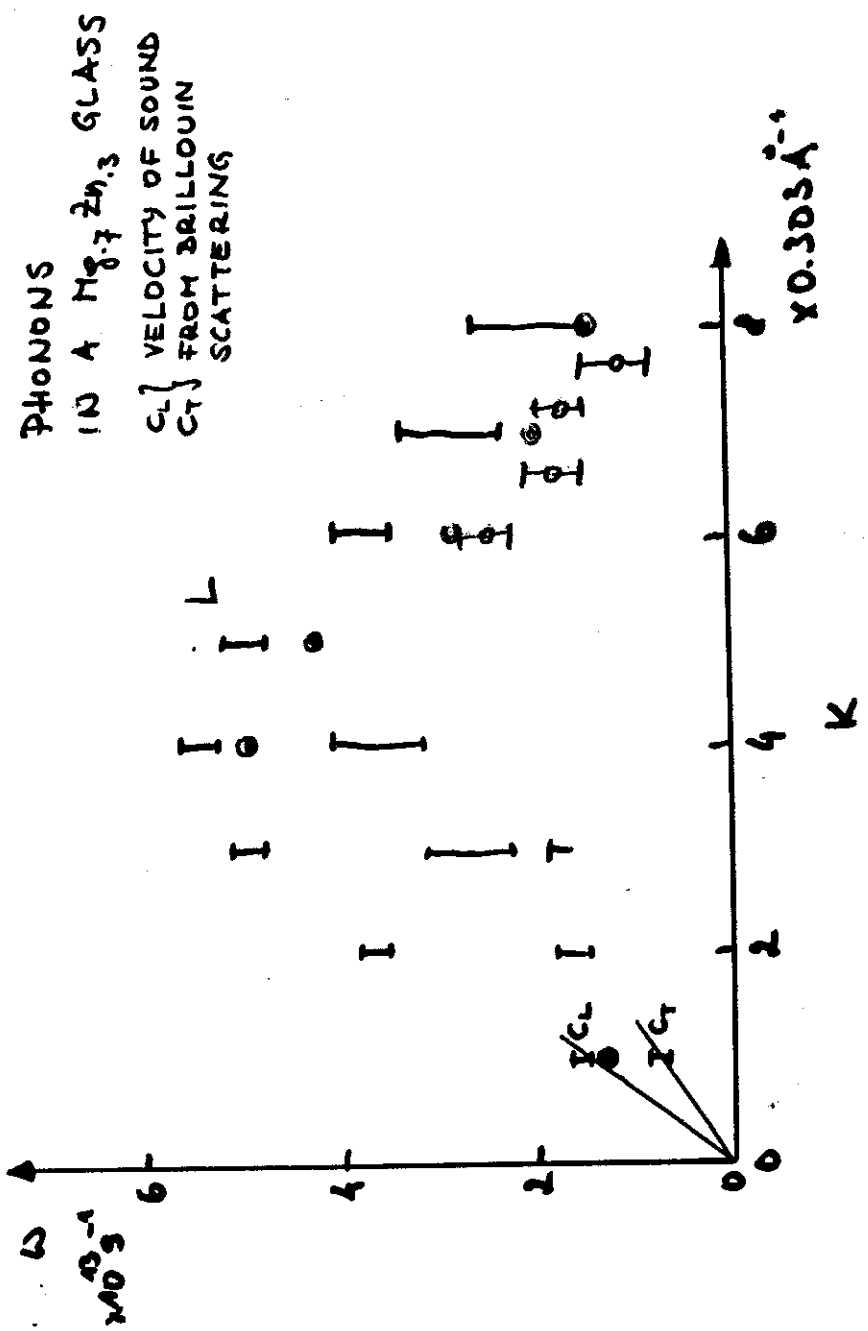
300-ATOM AMORPHOUS MODEL
- CONSTANT FORCES
- MORSE-POTENTIAL
- LENNARD-JONES-POT.

DYNAMICAL STRUCTURE FACTOR:









SYMMETRIZED ONE-PHONON DYNAM. STRUCT. FACTOR

$$S_1(\vec{Q},\omega) = e^{-\beta\hbar\omega/2} N^{-1} \sum_{l,m} e^{-i\vec{Q}(\vec{R}_l-\vec{R}_m)} e^{-2W_{lm}(\vec{Q})} S_{lm}(\vec{Q},\omega)$$

NORMAL MODE EXPANSION

$$S_{lm}(\vec{Q},\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle \vec{Q}\cdot\vec{u}_l(t)\ \vec{Q}\cdot\vec{u}_m(0)\rangle_{\text{Therm. Av.}}$$

$$= N^{-1} \sum_{\vec{q}j} S^{lm}_{\vec{q}j}(\vec{Q},\omega)\, e^{i\vec{q}(\vec{R}_l-\vec{R}_m)}$$

$$S^{lm}_{\vec{q}j}(\vec{Q},\omega) = \frac{\pi\hbar}{M} \frac{(\vec{Q}\cdot\vec{\varepsilon}_l(\vec{q}j))(\vec{Q}\cdot\vec{\varepsilon}^{*}_m(\vec{q}j))}{\omega(\vec{q}j)} \times \left\{ (n(\vec{q}j)+1)\,\delta(\omega-\omega(\vec{q}j)) + n(\vec{q}j)\,\delta(\omega+\omega(\vec{q}j)) \right\}$$

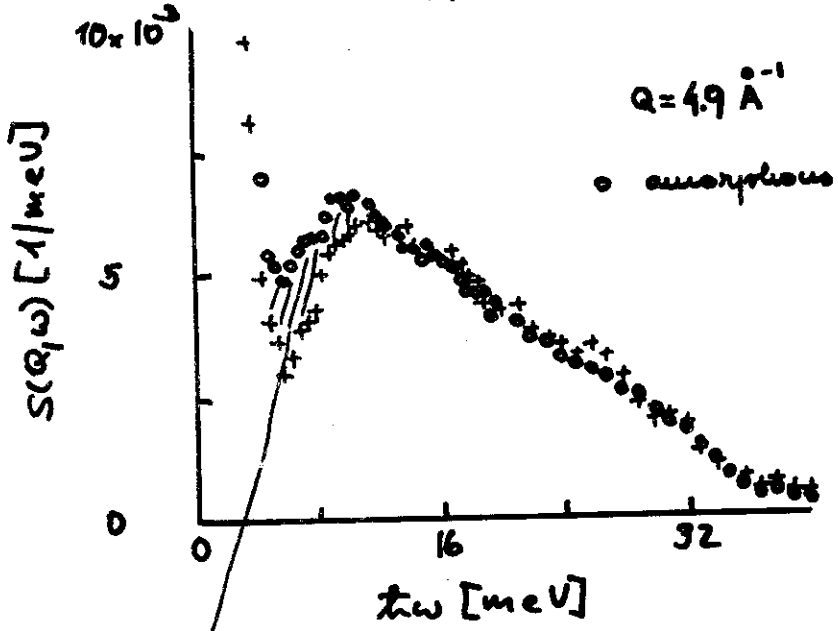
Ass.: Polarization vector slowly varying (long-wavel.)

Def.: $S(\vec{k}) \equiv N^{-1} \sum_{l,m} e^{-i\vec{k}(\vec{R}_l-\vec{R}_m)} - N\delta_{\vec{k},0}$

STATIC STRUCTURE FACTOR

$$S_1(\vec{Q},\omega) = \underbrace{\sum_j S_{\vec{Q}j}(\vec{Q},\omega)}_{\text{NORMAL (BRILLOUIN) SCATTERING}} + \underbrace{N^{-1} \sum_{\vec{q}j} S(\vec{Q}-\vec{q})\, S_{\vec{q}j}(\vec{Q},\omega)}_{\text{"DIFFUSE UMKLAPP SCATTERING"}}$$

$Mg_{70}Zn_{30}$

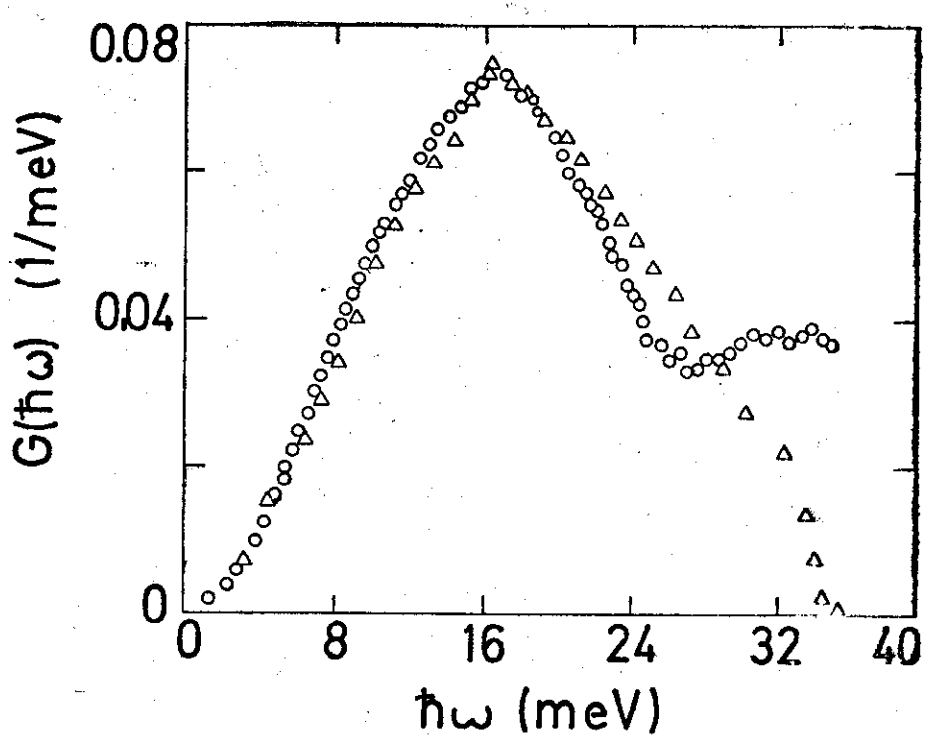


additional low energy excitations in the metallic glass (inelastic neutron scattering, Fuck et al.)

PHONON-DOS $Ca_{70}Mg_{30}$

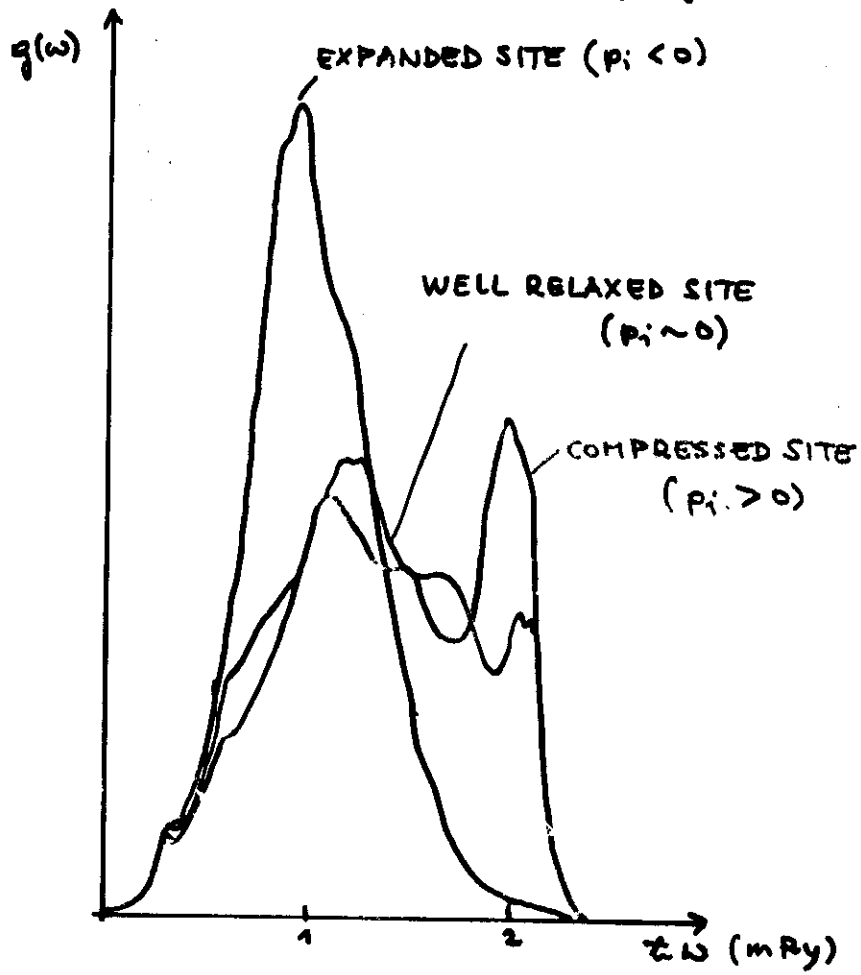
Δ THEORY (Kaplan)

○ EXP. (Fuck et al.)



PHONON - LDOS

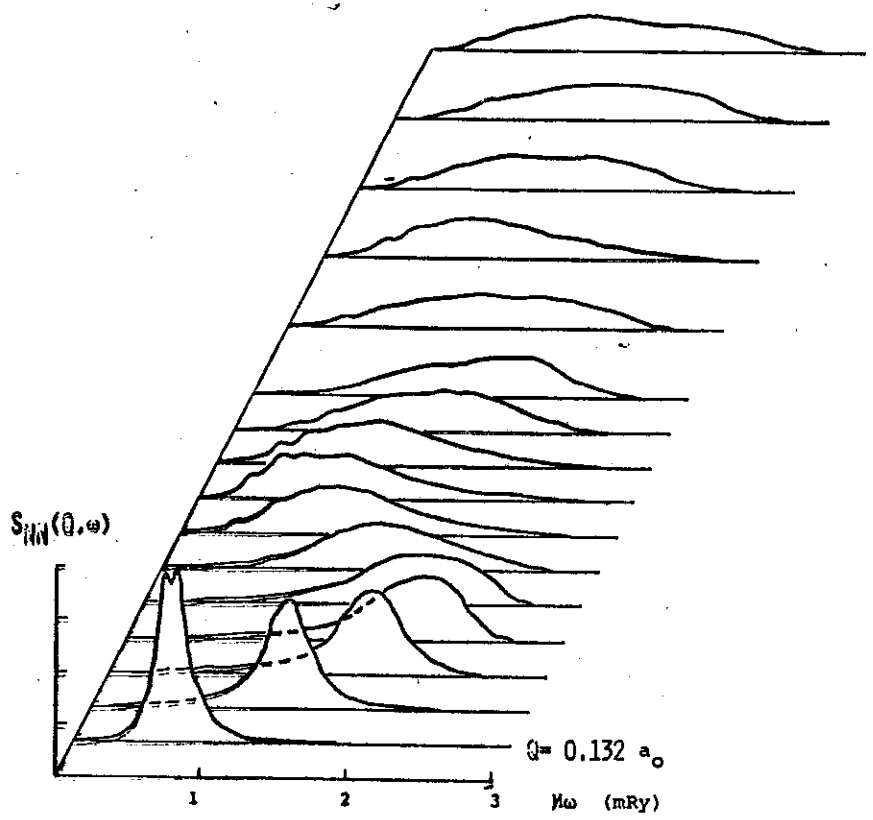
$Ca_{70}Mg_{30}$



$Ca_{70}Mg_{30}$

WAVE-NUMBER DEPENDENT VIBRATIONAL SPECTRUM

TOTAL: $S_{NN}(Q,\omega)$

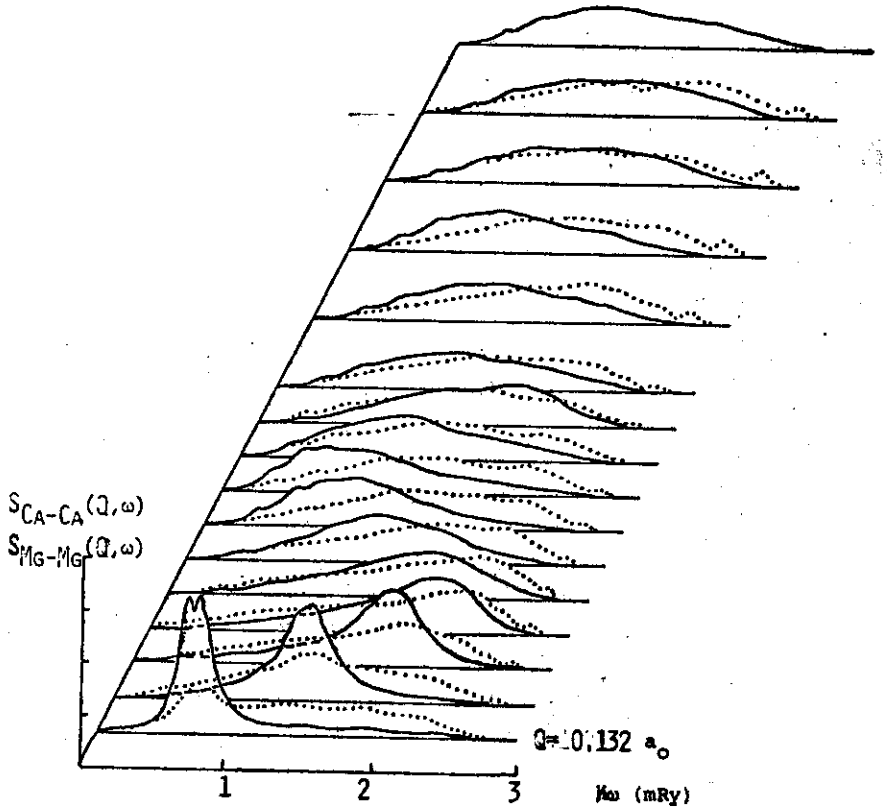


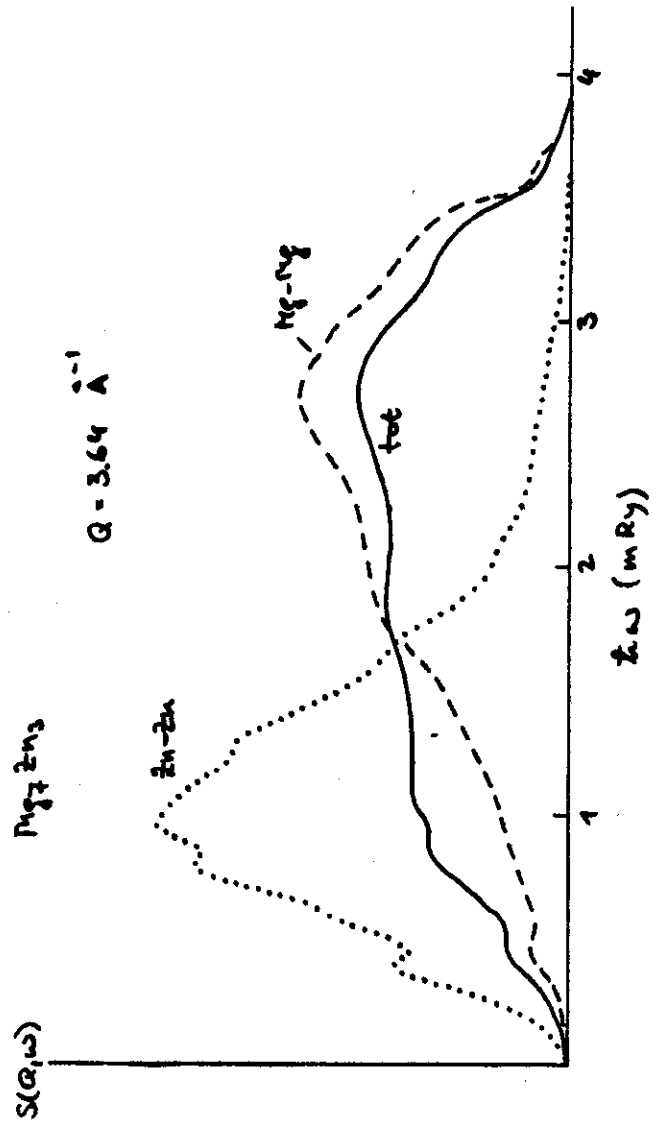
$Ca_{70}Mg_{30}$

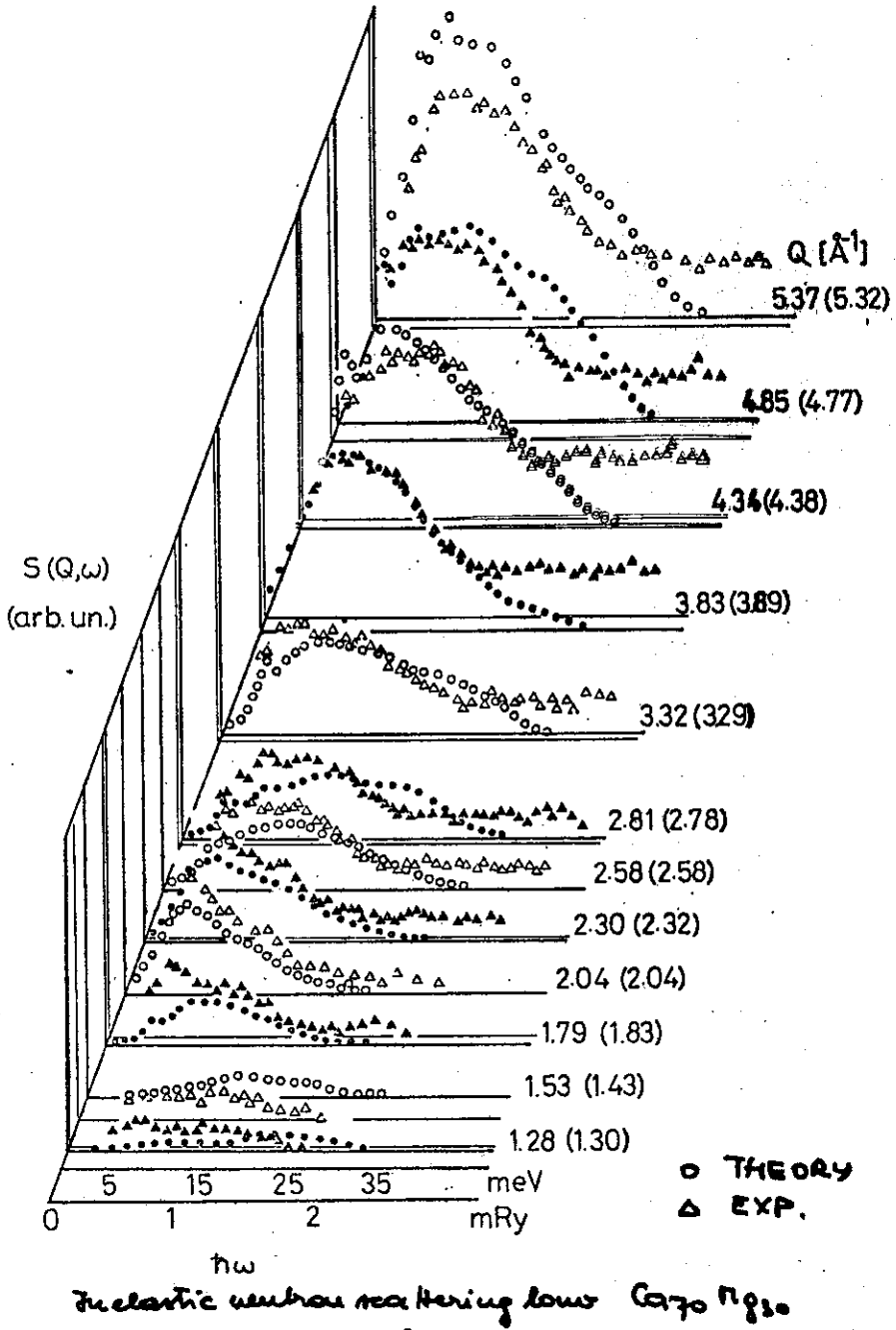
WAVE-NUMBER DEPENDENT VIBRATIONAL SPECTRUM

PARTIALS: $S_{Ca-Ca}(Q,\omega)$ _____

$S_{Mg-Mg}(Q,\omega)$ .....

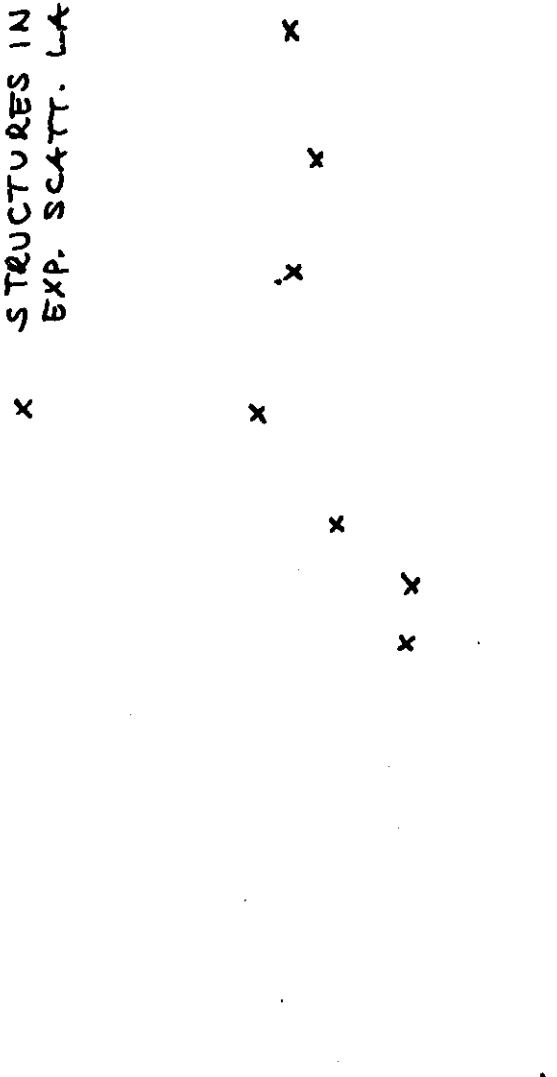


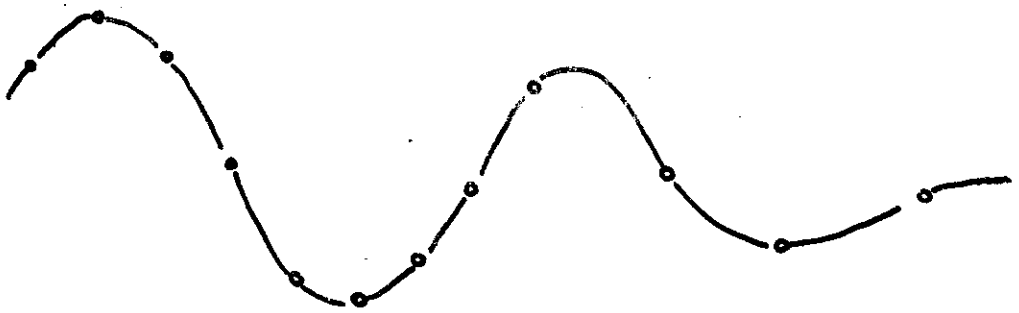


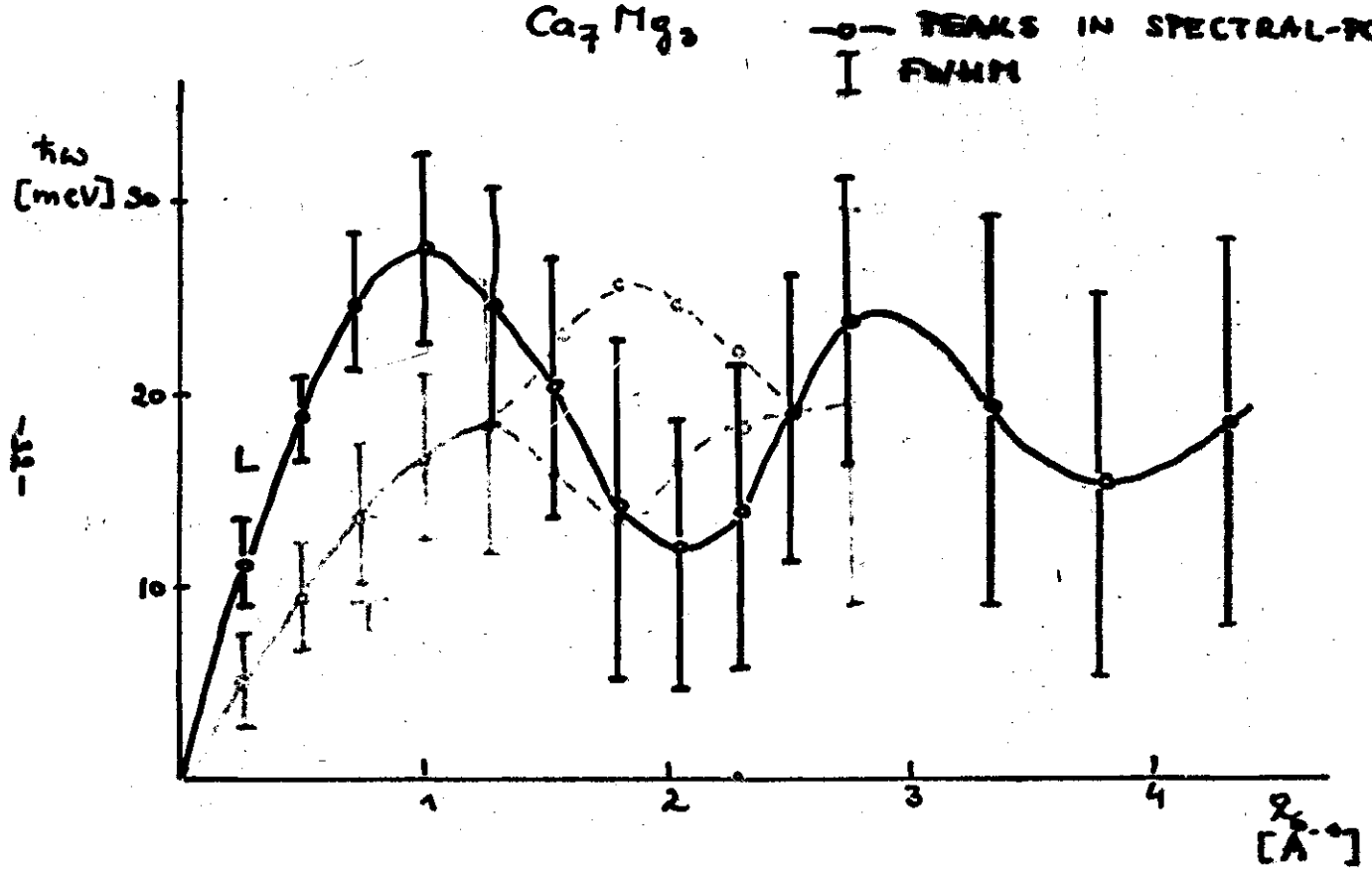


Inelastic neutron scattering law $Ca_{70}Mg_{30}$

STRUCTURES IN THE EXP. SCATT. LAW




—o— PEAKS OR SHOULDERS
IN THE INELAST. NEUTR
SCATTERING


Ca_7Mg_3
—o— PEAKS IN SPECTRAL-PDF
I FWHM
ħω [meV]
30
20
10
L
1
2
3
4
Q [Å⁻¹]