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**Research Workshop in Condensed Matter,
Atomic and Molecular Physics
(22 June - 11 September 1992)**

**Working Party on:
"Energy Transfer in Interactions with
Surfaces and Adsorbates"
(31 August - 11 September 1992)**

"Phonon at Surfaces and their Excitation by External Probes"

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Phonon at Surfaces and their excitation by external probes

by

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I aknowledge:

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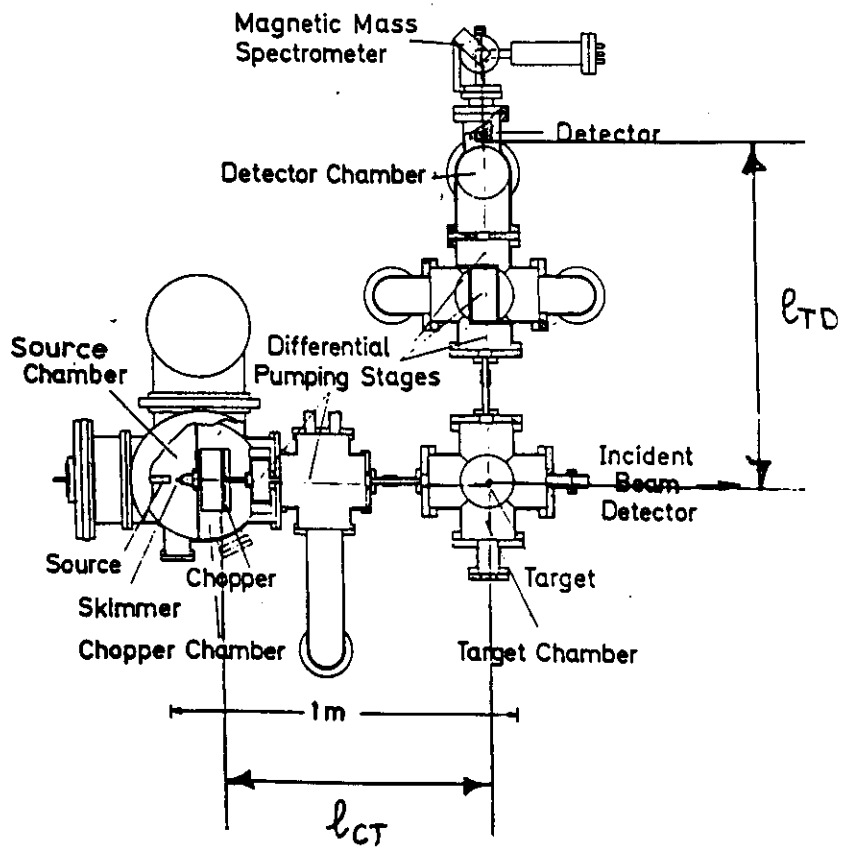
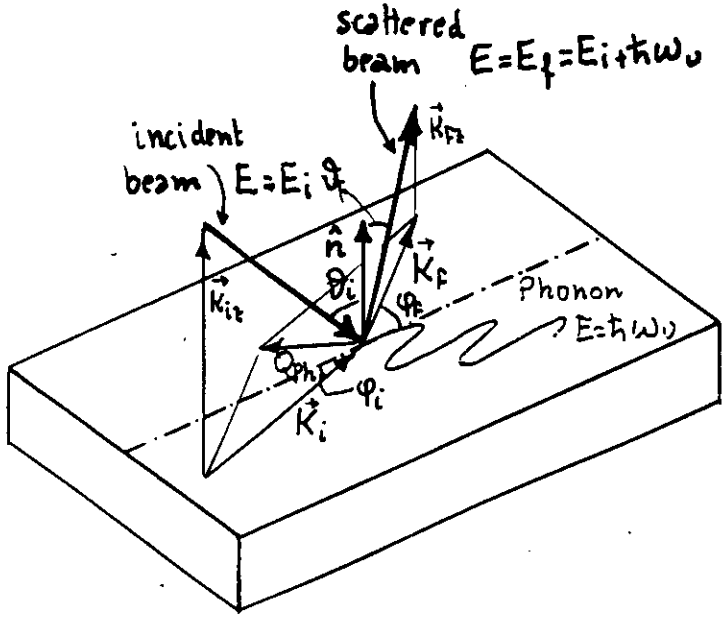
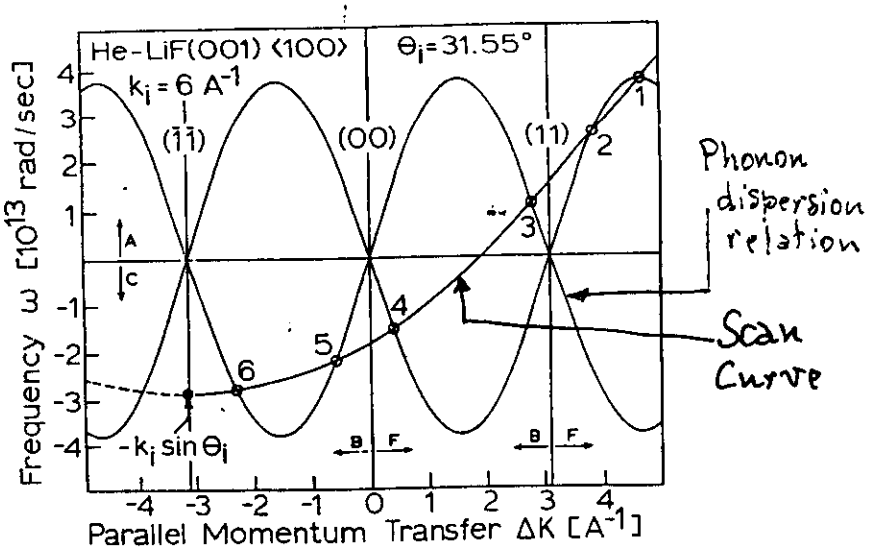
R.F. Wallis and A.A. Maradudin, Irvine USA
A. Quong, Washington
J.P. Toennies, Gottingen RFT

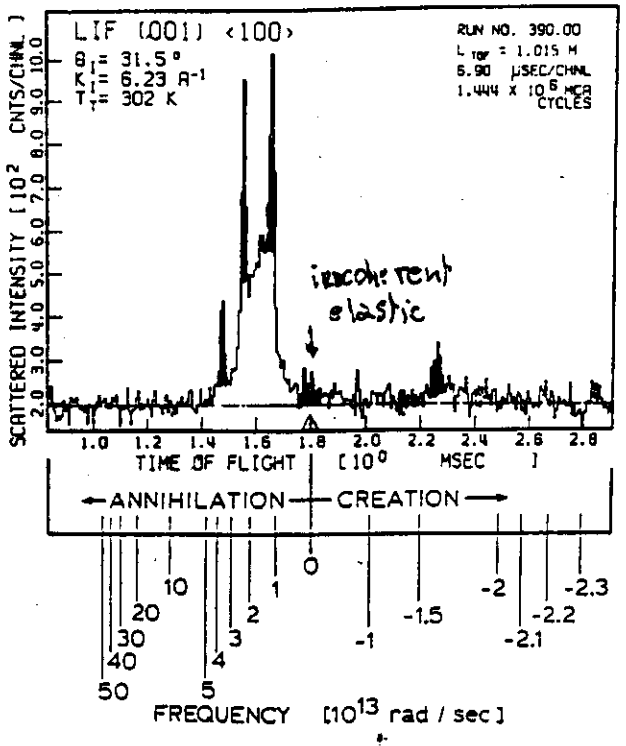


$$t = \frac{\ell_{CT}}{v_i} + \frac{\ell_{TD}}{v_f} = \text{time-of-flight}$$

$$E_f = \frac{1}{2} m_{He} \frac{\ell_{TD}^2}{\left(t - \frac{\ell_{CT}}{v_i}\right)^2}$$





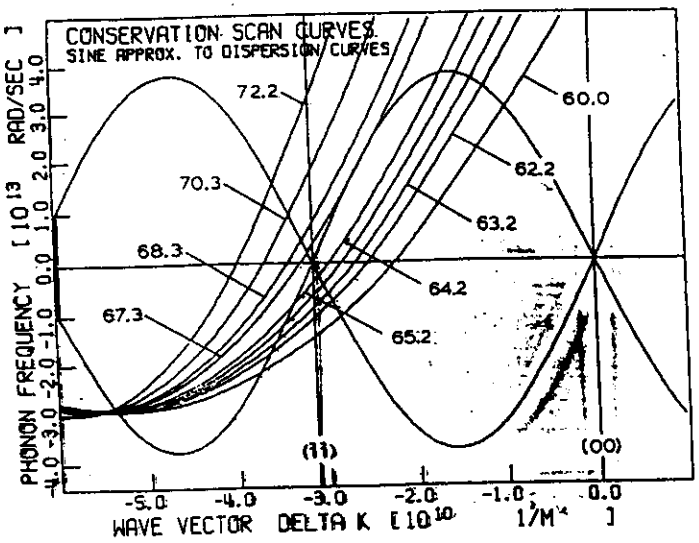


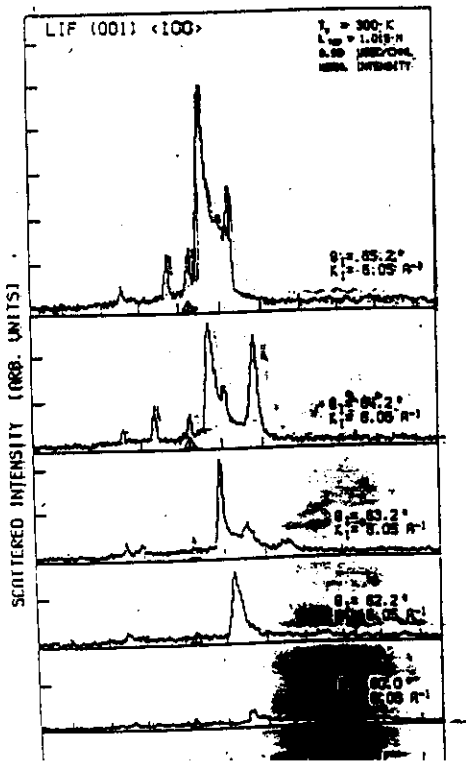
$\vec{K}_f = \vec{K}_i + \vec{Q} + \vec{G}$: "conservation of the lateral momentum"

$E_f = E_i \pm \hbar\omega_\nu(\vec{Q})$: conservation of the energy

Combining these two eqations we obtain the "Scan Curve"

$$\frac{\hbar^2}{2m_{He}\sin^2\vartheta_f}\left[K_i^2\left(1-\frac{\sin^2\vartheta_f}{\sin^2\vartheta_i}\right)+2\vec{K}_i\cdot(\vec{Q}+\vec{G})+|\vec{Q}+\vec{G}|^2\right]=\pm\hbar\omega_\nu$$





LATTICE DYNAMICS IN THE HARMONIC APPROXIMATION

In the Adiabatic Approximation the potential energy among the ions is given by:

$$\Phi([R]) = E_{el-ion} + E_{el-el} + E_{ion-ion}$$

where

$$\vec{R}(l\kappa) = \vec{R}^0(l\kappa) + \vec{u}(l\kappa)$$

l is the cell index and κ the basis index.

$$\Phi([R]) = \Phi_0 + \sum_{l\kappa\alpha} \phi_\alpha(l\kappa) u_\alpha(l\kappa) + \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \phi_{\alpha\beta}(l\kappa\ l'\kappa') u_\alpha(l\kappa) u_\beta(l'\kappa')$$

where the first and second order force constants tensors are given by:

$$\phi_\alpha(l\kappa) = \left(\frac{\partial \Phi}{\partial u_\alpha(l\kappa)} \right)_{R^0}$$

$$\phi_{\alpha\beta}(l\kappa\ l'\kappa') = \left(\frac{\partial^2 \Phi}{\partial u_\alpha(l\kappa) \partial u_\beta(l'\kappa')} \right)_{R^0}$$

In the harmonic approximation the Hamiltonian of the crystal is given by:

$$H = \sum_{l\kappa\alpha} \frac{p_\alpha^2}{2M_\kappa} + \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \phi_{\alpha\beta}(l\kappa\ l'\kappa') u_\alpha(l\kappa) u_\beta(l'\kappa')$$

By using the Hamilton equations

$$\dot{u}_\alpha(l\kappa) = \frac{\partial H}{\partial p_\alpha(l\kappa)} = \frac{p_\alpha(l\kappa)}{M_\kappa}$$

$$\dot{p}_\alpha(l\kappa) = -\frac{\partial H}{\partial u_\alpha(l\kappa)} = -\sum_{l'\kappa'\beta} \phi_{\alpha\beta}(l\kappa\ l'\kappa') u_\beta(l'\kappa')$$

we obtain the equation of motion in the form:

$$M_\kappa \ddot{u}_\alpha(l\kappa) = -\sum_{l'\kappa'\beta} \phi_{\alpha\beta}(l\kappa\ l'\kappa') u_\beta(l'\kappa')$$

The atomic displacement $\vec{u}$ can be written in the Bloch form:

$$u_\alpha(l\kappa) = \frac{1}{\sqrt{M_\kappa}} e_\alpha(\kappa) e^{i\vec{q}\cdot\vec{R}^0(l) - i\omega t}$$

and the equation of motion reduces to:

$$\omega^2(\vec{q}j) e_\alpha(\kappa, \vec{q}j) = \sum_{\kappa'\beta} D_{\alpha\beta}(\kappa\kappa'|\vec{q}) e_\beta(\kappa', \vec{q}j)$$

$$D_{\alpha\beta}(\kappa\kappa'|\vec{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{l'} \phi_{\alpha\beta}(0\kappa\ l'\kappa') e^{-i\vec{q}\cdot\vec{R}^0(l')}$$

The dynamical matrix D is an Hermitian $3r \times 3r$ matrix, where r is the number of the atoms in the unit cell.
The index j designates the phonon branch and for each value of $\vec{q}$

$$j = 1, 2, ..., 3r$$

The eigenvalues fulfill the orthonormality and the completeness relations:

$$\sum_{\alpha,\kappa} e_\alpha^*(\kappa, \vec{q}j) e_\alpha(\kappa, \vec{q}j') = \delta_{jj'}$$

$$\sum_{j} e_\alpha^*(\kappa, \vec{q}j) e_\beta(\kappa', \vec{q}j) = \delta_{\alpha\beta}\delta_{\kappa\kappa'}$$

The eigenvalues are real and because of the time reversal:

$$\omega^2(\vec{q}j) = \omega^2(-\vec{q}j)$$

and

$$e_\alpha^*(\kappa, \vec{q}j) = C e_\alpha(\kappa, -\vec{q}j)$$

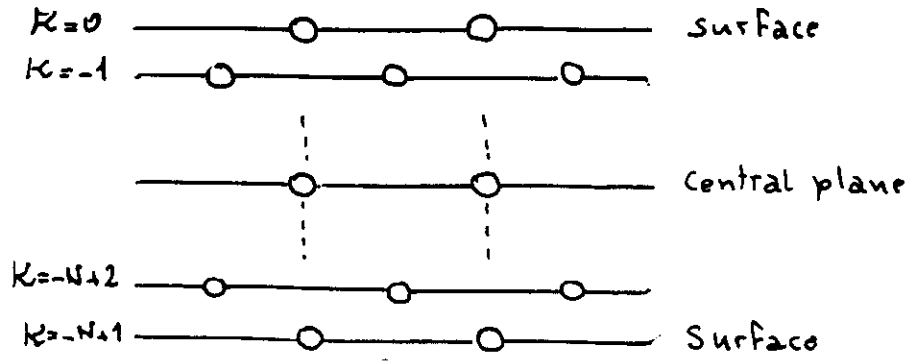
Usually the complex constant phase C is choosen to be 1.

For each normal mode

$$u_\alpha(l\kappa) = \frac{1}{\sqrt{M_\kappa}} e_\alpha(\kappa, \vec{q}j) e^{i\vec{q}\cdot\vec{R}^0(l) - i\omega(\vec{q}j)t}$$

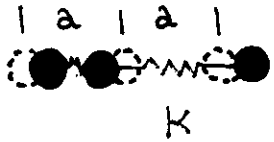
For a semiinfinite Bravais crystal or a finite slab

l twodimensional lattice vector
κ crystal plane index
j eigenvalue index $\quad 1, ..., 3N$



BORN-VON KARMAN METHOD

Es. Unidimensional chain



Taking into account only first nearest neighbours interactions the total energy is

$$\Phi = \frac{1}{2} K \sum_l (u_l - u_{l-a})^2$$

The equation of motion of an atom in the chain is:

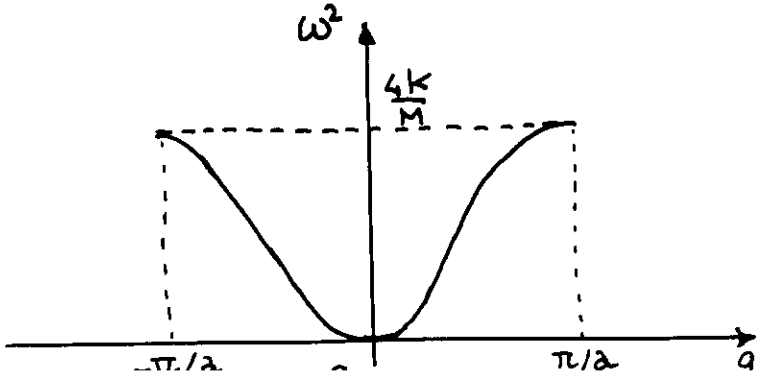
$$M\ddot{u}_l = -K(2u_l - u_{l+a} - u_{l-a})$$

Using the Bloch theorem

$$u_l \sim e_q e^{iqR^0(l) - i\omega t}$$

the dispersion relation becomes

$$\omega^2 = 4\frac{K}{M}\sin^2\frac{qa}{2}$$



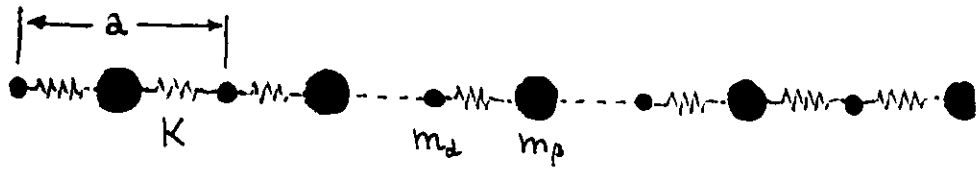
Es. FINITE unidimensional diatomic chain

N atoms of mass m_α

N atoms of mass m_β

$m_\alpha < m_\beta$

Force Costant K



$$\begin{cases} m_\alpha \frac{d^2 u_1}{dt^2} = K(u_2 - u_1) \\ m_\beta \frac{d^2 u_{2j}}{dt^2} = -K(u_{2j} - u_{2j-1}) + K(u_{2j+1} - u_{2j}) \quad 1 \le j \le N-1 \\ m_\alpha \frac{d^2 u_{2j-1}}{dt^2} = -K(u_{2j} - u_{2j-1}) + K(u_{2j+1} - u_{2j}) \quad 2 \le j \le N \\ m_\beta \frac{d^2 u_{2N}}{dt^2} = -K(u_{2N} - u_{2N-1}) \end{cases}$$

Normal Coordinates

$$u_{2j-1} = A_{2j-1} e^{-i\omega t}$$
$$u_{2j} = A_{2j} e^{-i\omega t}$$

By putting:

$$u = \frac{\omega^2 m_\alpha}{K} - 2$$

$$v = \frac{\omega^2 m_\beta}{K} - 2$$

the secular equation becomes:

$$D_{2N}(u,v) = \begin{vmatrix} u+1 & 1 & 0 & \dots & 0 & 0 & 0 \\ 1 & v & 1 & \dots & 0 & 0 & 0 \\ 0 & 1 & u & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & v & 1 & 0 \\ 0 & 0 & 0 & \dots & 1 & u & 1 \\ 0 & 0 & 0 & \dots & 0 & 1 & v+1 \end{vmatrix} = 0$$

Substituting:

$$\cos\theta = -\frac{1}{2}\sqrt{uv}$$

we obtain:

$$D_{2N} = (uv + u + v)\frac{\sin 2N\theta}{\sin\theta} = 0$$

Solutions:

Wave Modes

$$\frac{\sin 2N\theta}{\sin\theta} = 0$$

Surface Modes

$$uv + u + v = 0$$

Wave Modes

Substituting u e v in the definition of θ we obtain:

$$\omega^2 = \sigma\left[1 \pm \sqrt{\cos^2\theta + \varepsilon^2 \sin^2\theta}\,\right]$$

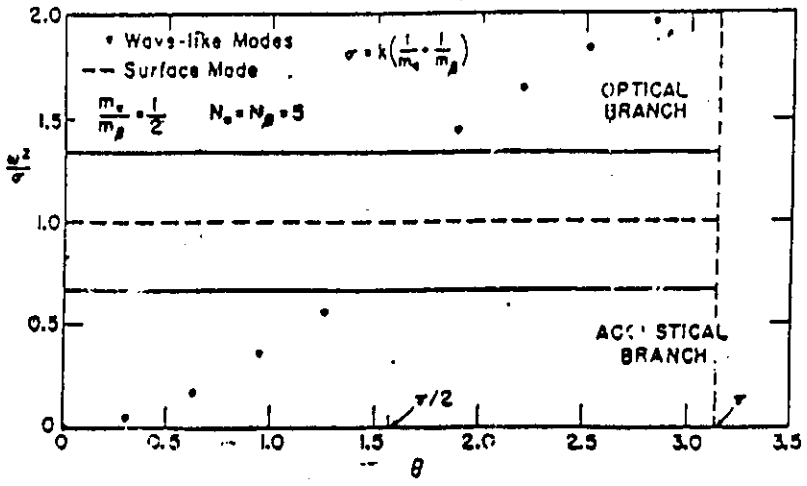
with

$$\sigma = K\left(\frac{1}{m_\alpha} + \frac{1}{m_\beta}\right)$$

$$\varepsilon = \frac{m_\beta - m_\alpha}{m_\beta - m_\alpha}$$

Only $2N - 2$ vibrational normal modes are possible with:

$$\theta = \frac{(j+2)\pi}{2N} \qquad j = 0, \dots, 2N-2$$



Surface Modes SM:

The solutions of the secular equation are:

$\omega^2 = 0$ Lattice Translation
$\omega^2 = \sigma$ Localized Mode

Localized Mode

For this kind of mode we obtain:

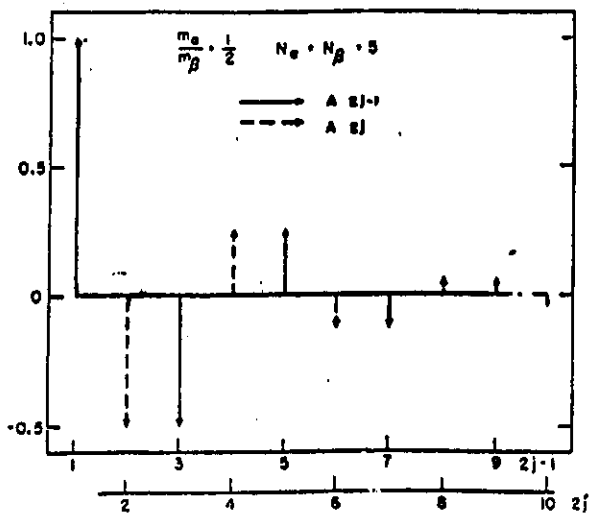
$$\theta = \frac{\pi}{2} + i \sinh^{-1} \frac{p}{2}$$

with:

$$p^2 = (m_\beta - m_\alpha)^2 / m_\alpha m_\beta$$

The maximum displacement of the atoms decreases exponetially starting from the lighter atom at the end of the chain.

N.B. This localized mode does not exist using the ciclic boundary conditions.



LATTICE DYNAMICS IN THE HARMONIC APPROXIMATION

Born Von Karman model:

$$\Phi^{(2)} = \Phi_C^{(2)} + \Phi_A^{(2)}$$

where $\Phi_C^{(2)}$ is related to two-body central forces and $\Phi_A^{(2)}$ is related to three body angular forces.

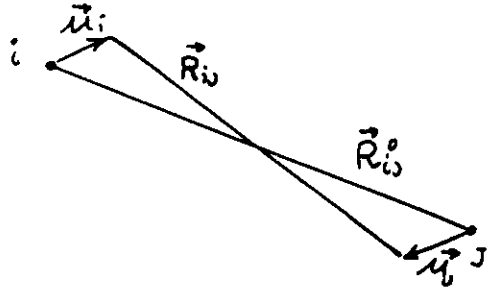
The force constants related to $\Phi_C^{(2)}$ are:

$$\alpha_i = \frac{1}{r} \frac{\partial \Phi_C^{(2)}}{\partial r}\bigg|_{r=r_i} \qquad \text{tangential force constants}$$

$$\beta_i = \frac{\partial^2 \Phi_C^{(2)}}{\partial r^2}\bigg|_{r=r_i} \qquad \text{radial force constants}$$

The force constants related to $\Phi_A^{(2)}$ are:

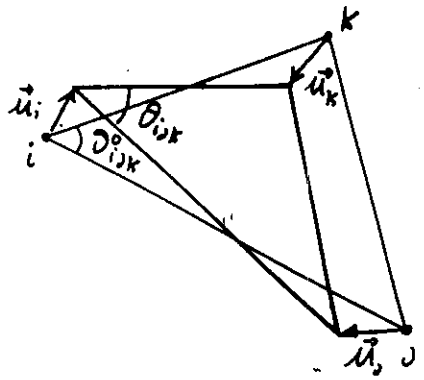
$$\delta_i = \frac{1}{3a^2} \frac{\partial^2 \Phi_A^{(2)}}{\partial \cos^2 \vartheta_{ijk}}\bigg|_{\vartheta_{ijk} = \vartheta_{ijk}^{(0)}} \qquad \text{angular force constants}$$



R°_{ij} : equilibrium distance

α_{ij} is related to bending forces

β_{ij} is related to stretching forces



S_{ijk} is related to angle variations.

The α's, the β's and the δ's are determined with a weighted least square fitting procedure, that takes into account of the experimental errors, to the:

- available experimental bulk phonon frequencies at low temperature.
- second order elastic constants.

To determine the range of the interactions we evaluate the mean square deviation:

$$\chi^2 = \frac{1}{N}\sum_{\vec{Q},j}\frac{\left[\omega^2{}_{\exp}(\vec{Q},j)-\omega^2{}_{th}(\vec{Q},j)\right]^2}{\omega^2{}_{\exp}(\vec{Q},j)}$$

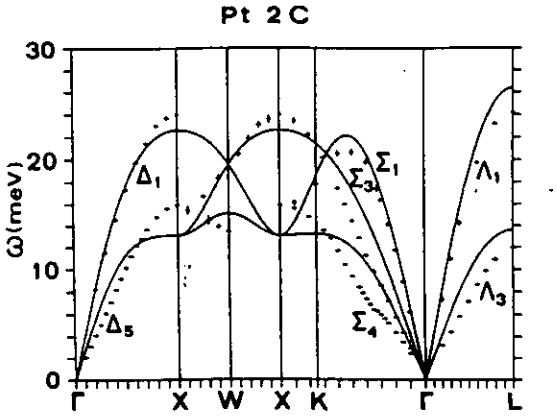
The minimum of the χ^2 is achieved for:

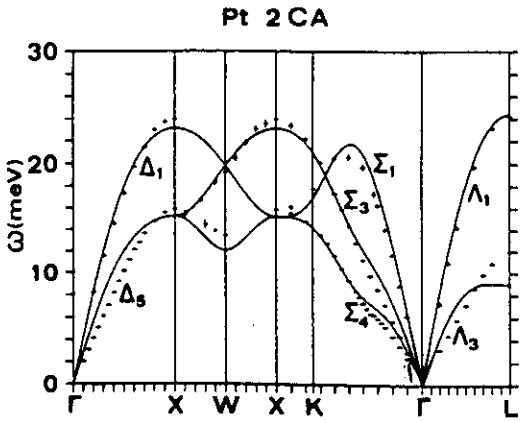
- central interactions extending up to:

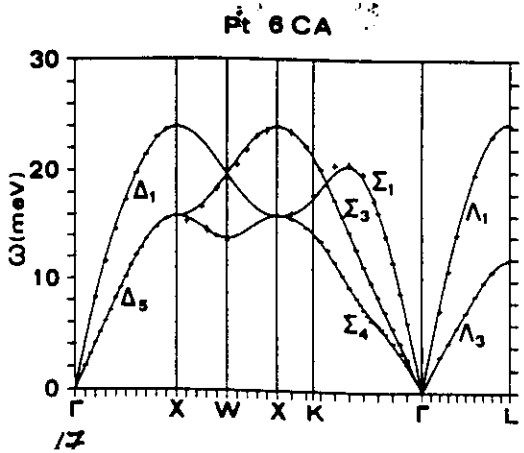
  10 *n.n.*

- angular interactions extending up to:

  2 *n.n*







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The total potential Φ up to second order in $\vec{u}$ should fulfill the stress free condition:

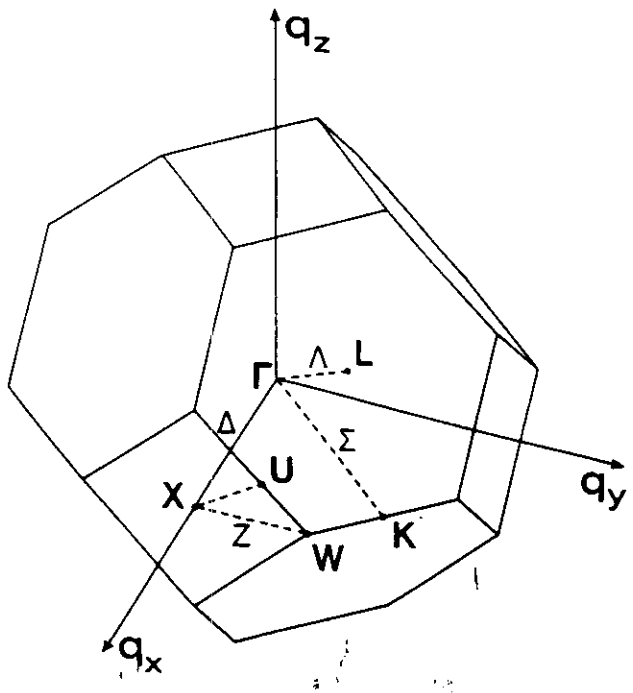
$$\left.\frac{d\Phi}{d\Omega}\right|_{\Omega=\Omega_0} = 0$$

For the central part this condition gives:

$$\sum_i \alpha_i r_i^2 = 0$$

The angular part fulfill the relation:

$$c_{12} - c_{44} = -18\delta_1 - 8\delta_2$$



DENSITY FUNCTIONAL THEORY

- The ground state energy is a functional of the electronic charge $\rho(\vec{r})$
- If the charge density is varied, the energy attains its minimum for the corrected charge density
- The variational principle leads to a single particle effective Schroedinger equation (the Kohn-Sham equation) that must be solved selfconsistently.

The total energy of the interacting system of ions and electrons is given by:

$$E = \sum_i f_i \varepsilon_i - \frac{1}{2}\int n(\vec{r})\mathcal{V}_{coul}(\vec{r})d^3r - \int n(\vec{r})\left[\mu_{xc}(\vec{r}) - \varepsilon_{xc}(\vec{r})\right] + \mathcal{V}_{ion-ion}$$

where f_i is the Fermi occupation function and $\mathcal{V}_{ion-ion}$ is the ion-ion Coulomb interaction.
Expanding the total energy in terms of the ion displacements $\vec{u}(l\kappa)$, we obtain:

$$E_1 = \sum_{l\kappa\alpha} \Phi_\alpha(l\kappa)u_\alpha(l\kappa) = 0$$

$$E_2 = \frac{1}{2}\sum_{l\kappa\alpha}\sum_{l'\kappa'\alpha'} \Phi_{\alpha\beta}(l\kappa, l'\kappa')u_\alpha(l\kappa)u_{\alpha'}(l'\kappa')$$

We can now write:

$$E_2 = E_2^{el} + E_2^{ion}$$

E_2^{el} represent the electron contribution.

E_2^{ion} represent the ion-ion Coulomb interaction.

The latter term can be evaluated by using the Ewald technique.

The Kohn-Sham equation is:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \varphi(\vec{r}) + \mu_{xc}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i$$

In the Local Density Approximation (LDA):

$$\mu_{xc} = \frac{d[n(\vec{r})\varepsilon_{xc}]}{d[n(\vec{r})]}$$

where:

$$n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$$

is the electron density function.

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c$$

is the exchange and correlation energy for the non-interacting electron gas.
Usually the exchange term is taken in the Slater form:

$$\varepsilon_x = -e^2\left(\frac{3}{\pi}\right)^{1/3} n(\vec{r})^{1/3}$$

while the correlation term is assumed to have the Wigner form:

$$\varepsilon_c = -e^2\frac{0.056n(\vec{r})^{1/3}}{0.079 + a_B n(\vec{r})^{1/3}}$$

where a_B is the Bohr radius.

$$\varphi(\vec{r}) = \mathcal{V}_{el-ion}(\vec{r}) + \int n(\vec{r}\,')\mathcal{V}_{coul}(|\vec{r} - \vec{r}\,'|)d^3r'$$

$\mathcal{V}_{el-ion}$ represents the electron-ion interaction which is described by a pseudopotential.
The wavefunctions ψ_i are obtained by solving selfconsistently the Kohn-Sham equation.

By using the Hellmann-Feynman theorem the electronic part $\Phi^{el}_{\alpha\beta}$ of the force constants tensor can be written in the form:

$$\Phi^{el}_{\alpha\beta} = \int \frac{d\mathcal{V}_P[\vec{r} - \vec{R}(l\kappa)]}{dr_\alpha} \chi(\vec{r}, \vec{r}\,') \frac{d\mathcal{V}_P[\vec{r}\,' - \vec{R}(l'\kappa')]}{dr_\beta} d^3r d^3r\,'$$

wehre $\mathcal{V}_P$ is the bare pseudopotential that describes the electron-ion interation.

The density response function $\chi(\vec{r}, \vec{r}\,')$ of the interacting electron gas obeys the integral equation:

$$\chi(\vec{r}, \vec{r}\,') = \chi^0(\vec{r}, \vec{r}\,') + \int \chi^0(\vec{r}, \vec{r}_1)\mathcal{V}(\vec{r}_1, \vec{r}_2)\chi(\vec{r}\,', \vec{r}_2) d^3r_1 d^3r_2$$

where $\mathcal{V}(\vec{r}_1, \vec{r}_2) = \mathcal{V}_{coul}(\vec{r}_1, \vec{r}_2) + \mu_{xc}(\vec{r}_1)\delta(\vec{r}_1 - \vec{r}_2)$

χ^0 is the density response funtion of the non interacting electron gas and is given by:

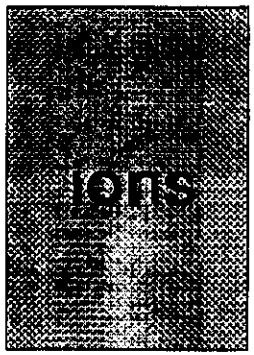
$$\chi^0(\vec{r}, \vec{r}\,') = \sum_{ij} \frac{f_i - f_j}{\varepsilon_i - \varepsilon_j} \psi_i^*(\vec{r})\psi_j(\vec{r})\psi_j^*(\vec{r}\,')\psi_i(\vec{r}\,')$$

We have at hand two approximations:

- Perturbative calculations carried out to second order in the pseudopotential by EGUILUZ et al.

In this case χ is the response function for interacting electrons embedded in an uniform background.

For a slab:



$$\mathcal{V}_{ion-el} = -\frac{2e^2}{\Omega} \int_{Slab} \frac{d^3r'}{|\vec{r} - \vec{r}'|}$$

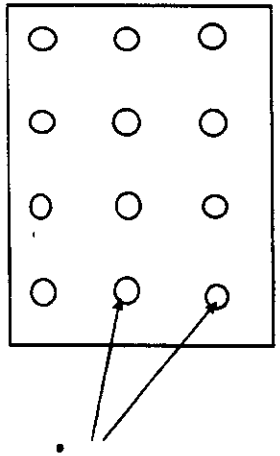
$$\psi_{\vec{K},j} = e^{-i\vec{K}\cdot\vec{R}} \sum_{l=0}^{\infty} a_{l,j} \sin(l\pi z / d)$$

where j labels the eigenstates for a given $\vec{K}$.

- Non perturbative screening calculations performed by QUONG et al.

In this case the response fonction χ is evaluated selfconsistently by considering the electrons embedded in the ion lattice.

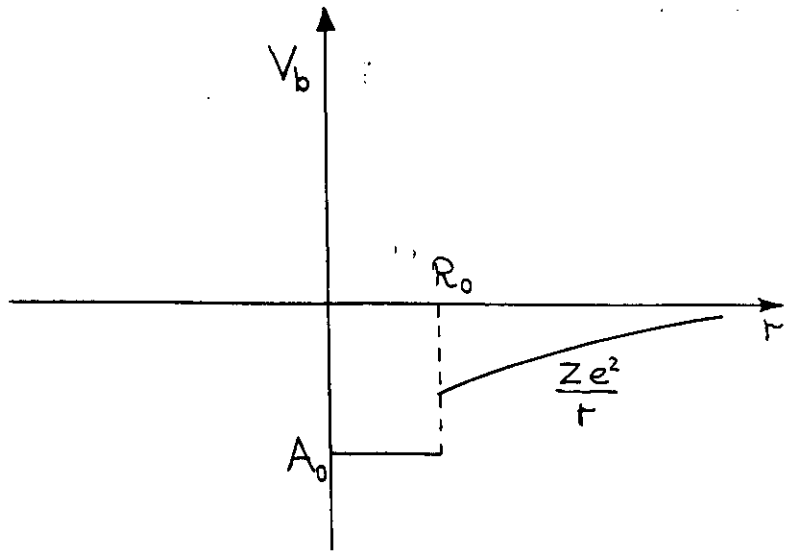
For a slab:



$$V_{ion-el} = \sum_{l\kappa} V_p(\vec{r} - \vec{R}(l\kappa))$$

$$\psi_{\vec{K},j} = \sum_{\vec{G}} \sum_{m=1}^{\infty} c^m{}_{\vec{K},j} e^{-i(\vec{K}+\vec{G})\cdot\vec{R}} \sin(m\pi z/d)$$

BARE PSEUDOPOTENTIAL



The two parameters A_0 and R_0 are determined by imposing the two conditions:

- $p = 0$
- least square fit of the bulk phonon frequencies.

The force constants of the Born Von Karman model compare very well with the pseudopotential calculations performed both for the bulk and for the surface.

The central interactions needed to reproduce the Friedel oscillations present in the pseudopotential calculations extend at least up to 10 n.n.

BULK

First Nearest Neighbours:

pseudopotential

$$\begin{pmatrix} \frac{1}{2}(\beta_1+\alpha_1) & \frac{1}{2}(\beta_1-\alpha_1) & 0 \\ \frac{1}{2}(\beta_1-\alpha_1) & \frac{1}{2}(\beta_1+\alpha_1) & 0 \\ 0 & 0 & \alpha_1 \end{pmatrix}$$

semiempirical

$$\begin{pmatrix} \frac{1}{2}(\beta_1+\alpha_1)+\boxed{3\delta_1+2\delta_2} & \frac{1}{2}(\beta_1-\alpha_1)+\boxed{\frac{3}{2}\delta_1} & 0 \\ \frac{1}{2}(\beta_1-\alpha_1)+\boxed{\frac{3}{2}\delta_1} & \frac{1}{2}(\beta_1+\alpha_1)+\boxed{3\delta_1+2\delta_2} & 0 \\ 0 & 0 & \alpha_1+\boxed{3\delta_1} \end{pmatrix}$$

Second Nearest Neighbours:

pseudopotential semiempirical

$$\begin{pmatrix} \beta_2 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_2 \end{pmatrix} \quad \begin{pmatrix} \beta_2 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_2 \end{pmatrix}$$

BULK

First Nearest Neighbours:

pseudopotential

$$\begin{pmatrix} 10162 & 11419 & 0 \\ 11419 & 10162 & 0 \\ 0 & 0 & -1254 \end{pmatrix}$$

semiempirical

$$\begin{pmatrix} 10378 & 10886 & 0 \\ 10886 & 10378 & 0 \\ 0 & 0 & -2247 \end{pmatrix}$$

Second Nearest Neighbours:

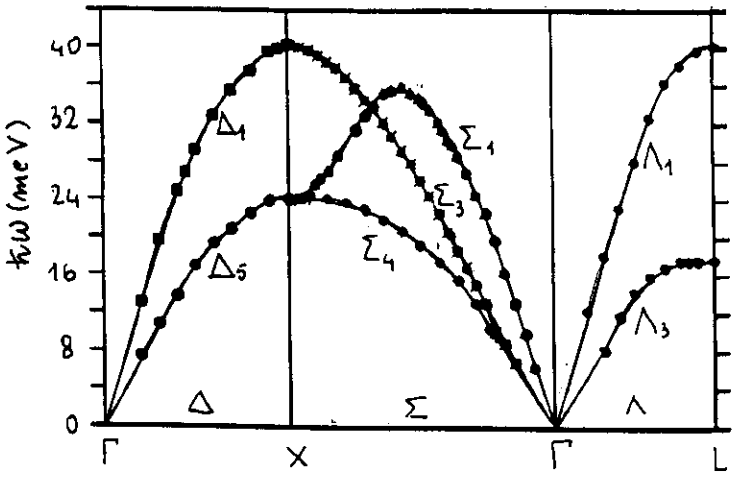
pseudopotential

$$\begin{pmatrix} 2591 & 0 & 0 \\ 0 & -163 & 0 \\ 0 & 0 & -163 \end{pmatrix}$$

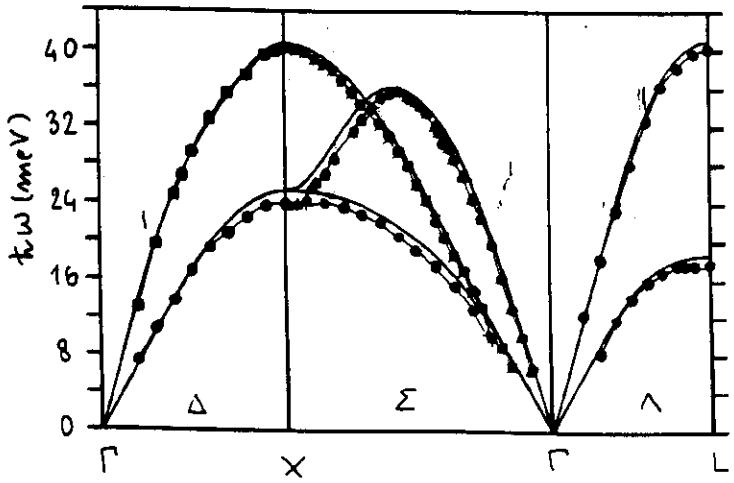
semiempirical

$$\begin{pmatrix} 2686 & 0 & 0 \\ 0 & 198 & 0 \\ 0 & 0 & 198 \end{pmatrix}$$

SEMIEMPIRICAL MODEL



PSEUDOPOTENTIAL MODEL



EMBEDDED ATOM THEORY

The total energy for a given distribution of atoms can be written as:

$$E = \sum_{l\kappa} \Big[\frac{1}{2} \sum_{l'\kappa'} \Phi(|\vec{R}_{l\kappa} - \vec{R}_{l'\kappa'}|) + F(n_{l\kappa}) \Big]$$

$\Phi(|\vec{R}_{l\kappa} - \vec{R}_{l'\kappa'}|)$ is a two body short range central potential.

$F(n_{l\kappa})$ is a non linear function of $n_{l\kappa}$ and represents the many body interactions present in the solid.

$n_{l\kappa}$ is the electronic charge at the site $\vec{R}_{l\kappa}$.

$$n_{l\kappa} = \sum_{l'\kappa'} \rho(|\vec{R}_{l\kappa} - \vec{R}_{l'\kappa'}|)$$

The force constants tensor $\Phi_{\alpha\beta}$ can be written as:

$$\Phi_{\alpha\beta}(l\kappa, l'\kappa') = \Sigma_{\alpha\beta} + \Omega_{\alpha\beta} + \Gamma_{\alpha\beta}$$

where:

$$\Sigma_{\alpha\beta} = -\Big\{ \alpha(l\kappa, l'\kappa')\delta_{\alpha\beta} + [\beta(l\kappa, l'\kappa') - \alpha(l\kappa, l'\kappa')] \frac{R_\alpha(l\kappa, l'\kappa') R_\beta(l\kappa, l'\kappa')}{R^2(l\kappa, l'\kappa')} \Big\}$$

$$\Omega_{\alpha\beta} = -\Big\{ \frac{\partial F}{\partial n_{l\kappa}} + \frac{\partial F}{\partial n_{l'\kappa'}} \Big\} \Big\{ \alpha'(l\kappa, l'\kappa')\delta_{\alpha\beta} + [\beta'(l\kappa, l'\kappa') - \alpha'(l\kappa, l'\kappa')] \frac{R_\alpha(l\kappa, l'\kappa') R_\beta(l\kappa, l'\kappa')}{R^2(l\kappa, l'\kappa')} \Big\}$$

$\Gamma_{\alpha\beta}$ = genuine many body term related to $\frac{\partial^2 F}{\partial n_{l\kappa}^2}$.

In the previous expressions:

$$\vec{R}(l\kappa, l'\kappa') = \vec{R}(l\kappa) - \vec{R}(l'\kappa')$$

$$\alpha(l\kappa, l'\kappa') = \frac{1}{R} \frac{\partial \Phi}{\partial R}\Big|_{R=|\vec{R}(l\kappa, l'\kappa')|}$$

$$\beta(l\kappa, l'\kappa') = \frac{\partial^2 \Phi}{\partial R^2}\Big|_{R=|\vec{R}(l\kappa, l'\kappa')|}$$

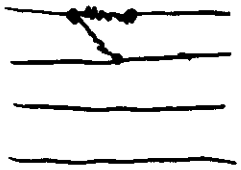
$$\alpha'(l\kappa, l'\kappa') = \frac{1}{R} \frac{\partial \rho}{\partial R}\Big|_{R=|\vec{R}(l\kappa, l'\kappa')|}$$

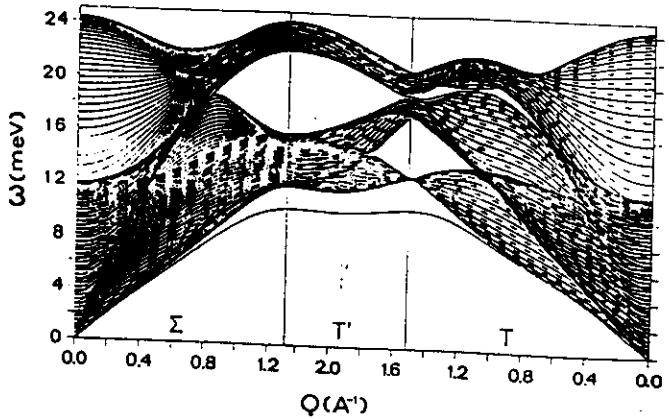
$$\beta'(l\kappa, l'\kappa') = \frac{\partial^2 \rho}{\partial R^2}\Big|_{R=|\vec{R}(l\kappa, l'\kappa')|}$$

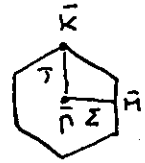
THE SLAB DYNAMICAL PROBLEM CAN BE WRITTEN IN THE FORM:

$$\left[D_{\alpha\beta;ll'} - \omega^2 \delta_{\alpha\beta}\delta_{ll'}\right] e_{\beta l'} = 0$$

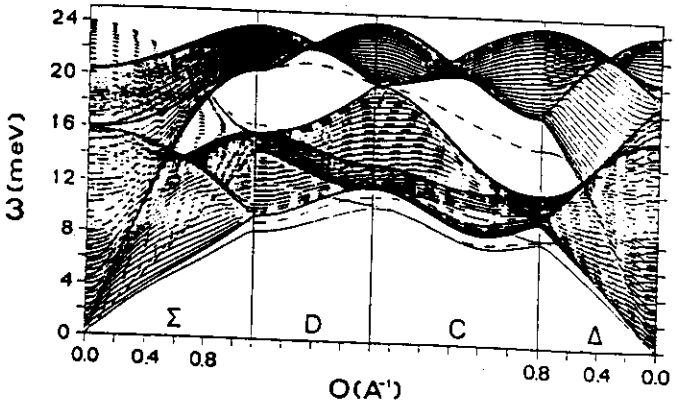
THE EIGENVALUES ω^2 AND EIGENVECTORS (POLARIZATIONS) $e_{\beta l'}$ ARE CALCULATED BY A DIRECT DIAGONALIZATION OF THE LARGE DYNAMICAL MATRIX $D_{\alpha\beta;ll'}$
THE FIRST THREE COMPONENTS OF $e_{\beta l'}$ REPRESENT THE LOCALIZATION OF THE MODES ONTO THE SURFACE PLANE.

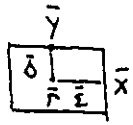




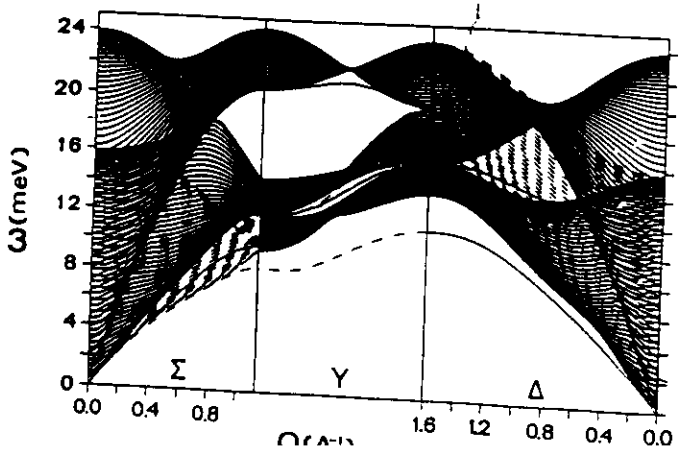


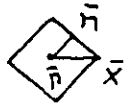
Pt(110)





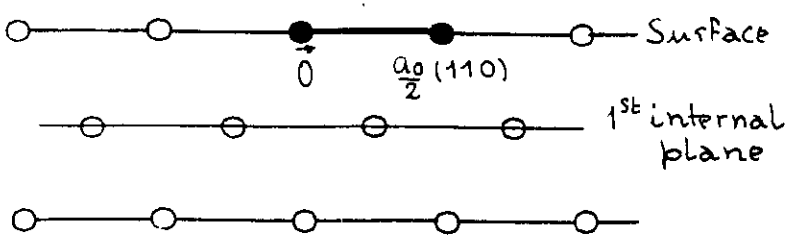
Pt(001)





(001) SURFACE

TWO ATOMS IN THE SURFACE PLANE



First Nearest Neighbours:

pseudopotential

$$\begin{pmatrix} 9999 & 10884 & 1011 \\ 10884 & 9999 & 1011 \\ -1011 & -1011 & -521 \end{pmatrix}$$

semiempirical

$$\begin{pmatrix} 11638 & 11518 & 1890 \\ 11518 & 11638 & 1890 \\ -1890 & -1890 & -987 \end{pmatrix}$$

Second Nearest Neighbours:

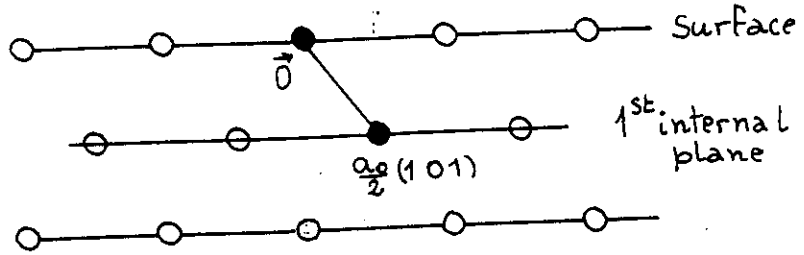
pseudopotential

$$\begin{pmatrix} 1941 & 0 & 170 \\ 0 & -240 & 0 \\ -167 & 0 & -104 \end{pmatrix}$$

semiempirical

$$\begin{pmatrix} 2686 & 0 & -120 \\ 0 & 198 & 0 \\ 120 & 0 & 198 \end{pmatrix}$$

ONE ATOM IN THE SURFACE PLANE AND ONE ATOM IN THE FIRST INTERNAL PLANE



First Nearest Neighbours:

pseudopotential

$$\begin{pmatrix} 10464 & 0 & 13333 \\ 0 & -938 & 0 \\ 11312 & 0 & 9950 \end{pmatrix}$$

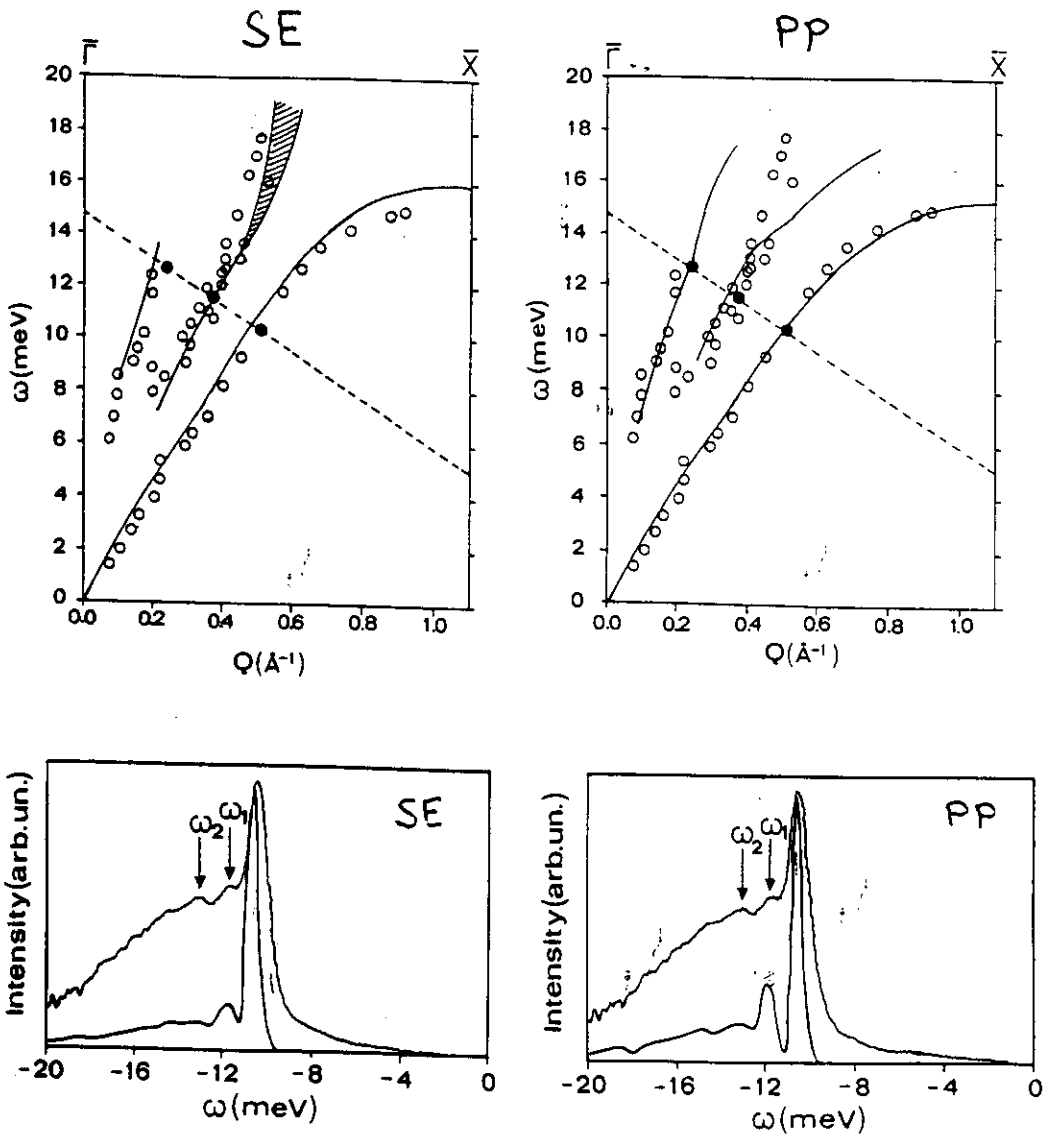
semiempirical

$$\begin{pmatrix} 10259 & 0 & 13285 \\ 0 & -2247 & 0 \\ 13765 & 0 & 10259 \end{pmatrix}$$

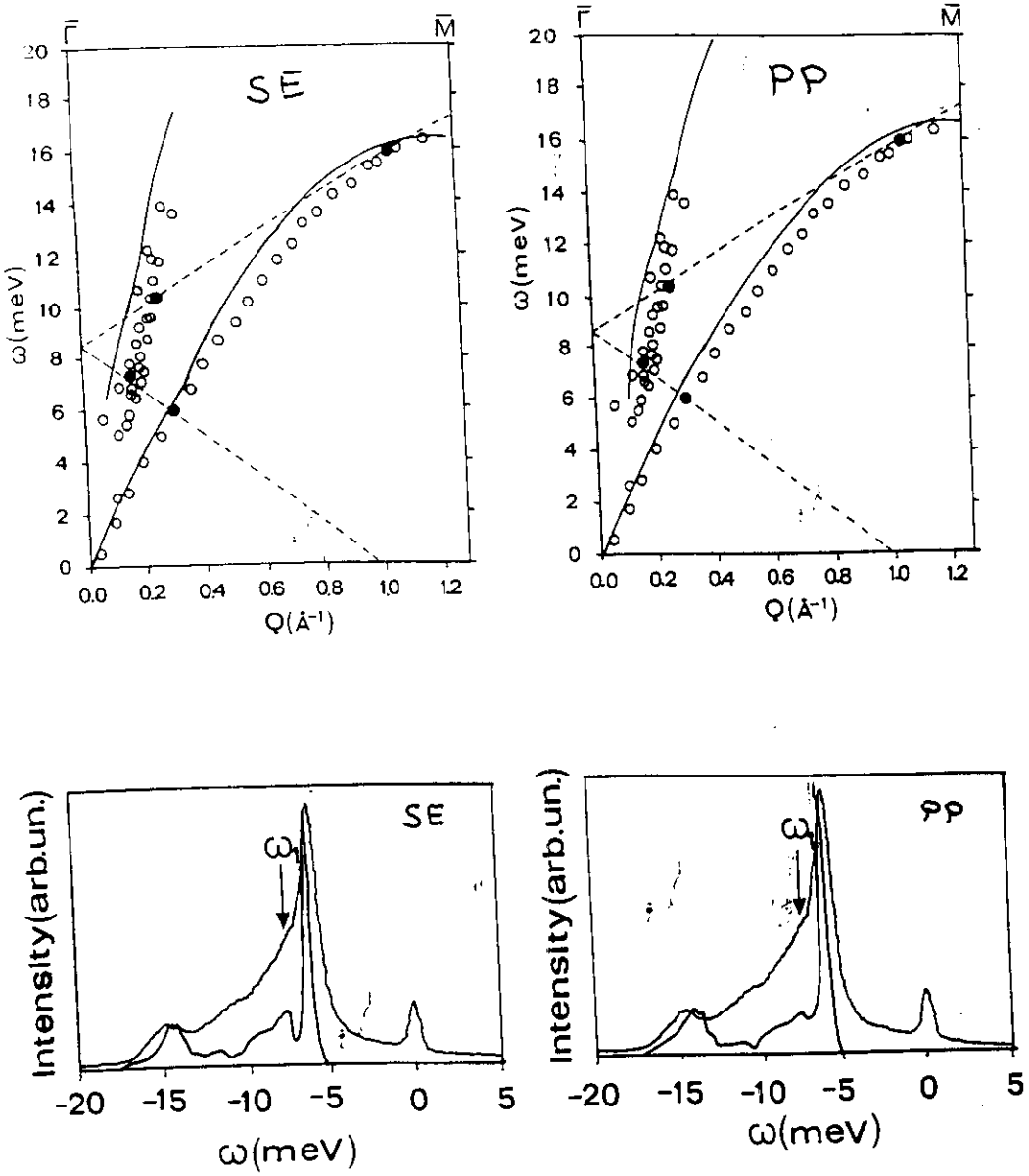
Radial force constants β for Al in dyne/cm

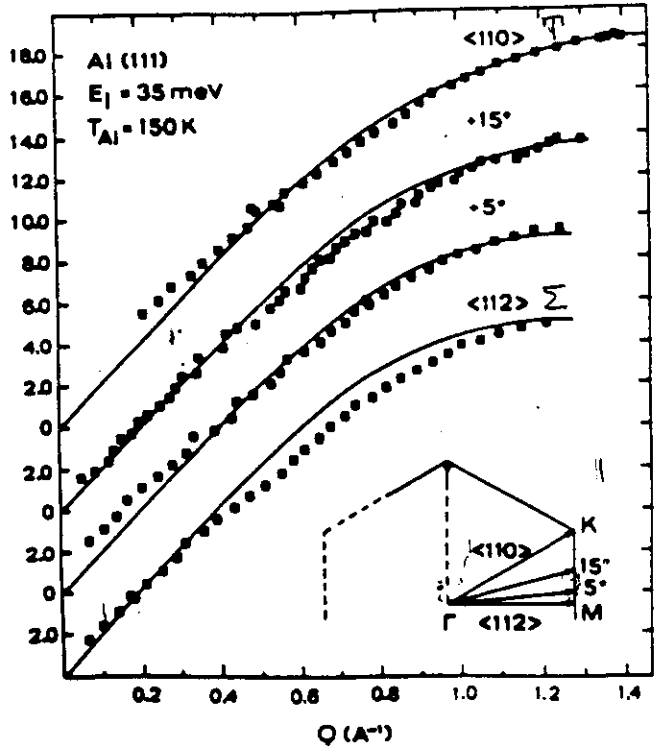
Neighbor	Non perturbative	Perturbative	Born Von Karman
1	20900	21700	24600
2	2140	2600	2680
3	-680	-860	-640
4	650	240	250
5	310	580	30
6	-430	-310	-360
7	160	90	120
8	230	160	200
9	-100	-120	120
10	-60	-96	-380

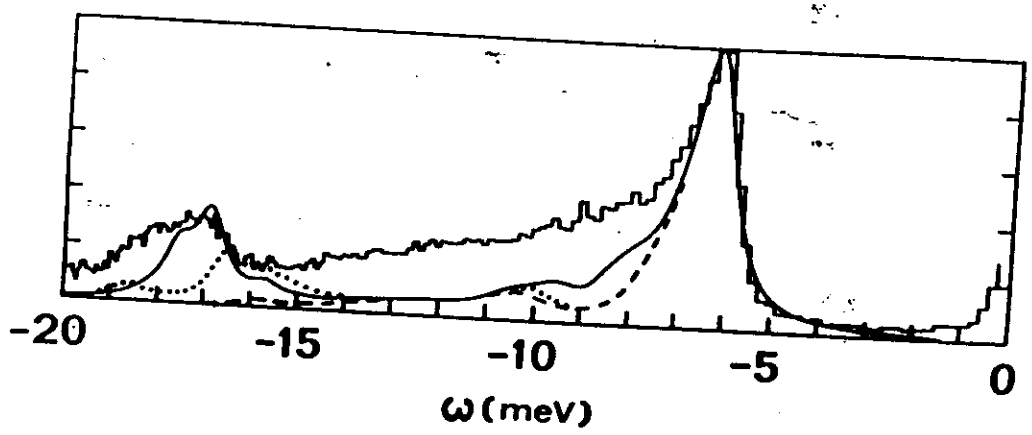
Al (100) $\langle 1\bar{1}0 \rangle \bar{\Sigma}$



Al(111) $\langle 11\bar{2}\rangle$ $\bar{\Sigma}$



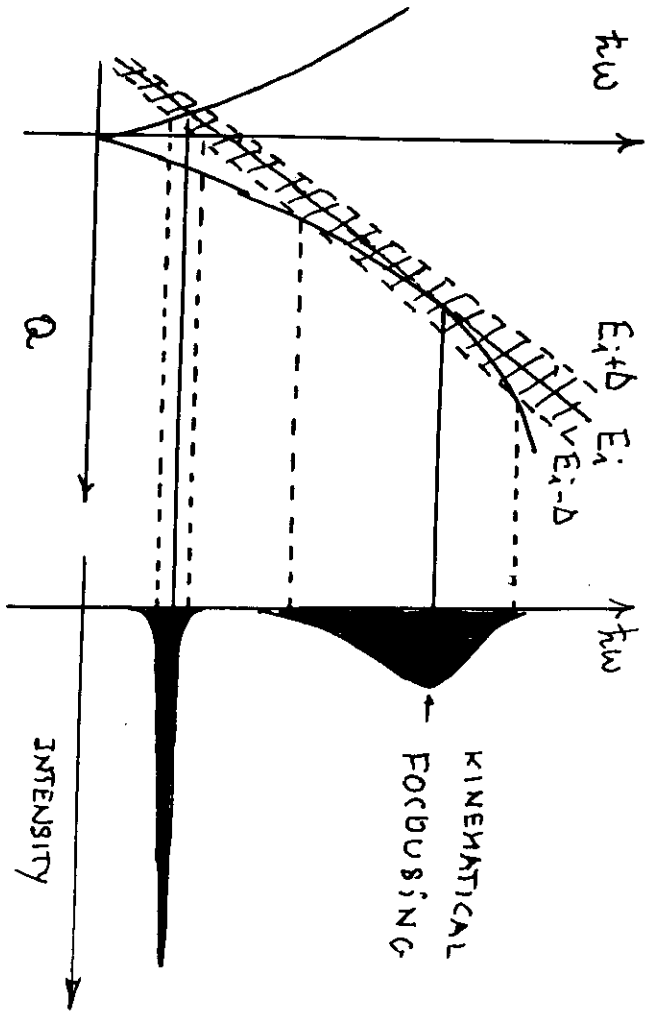




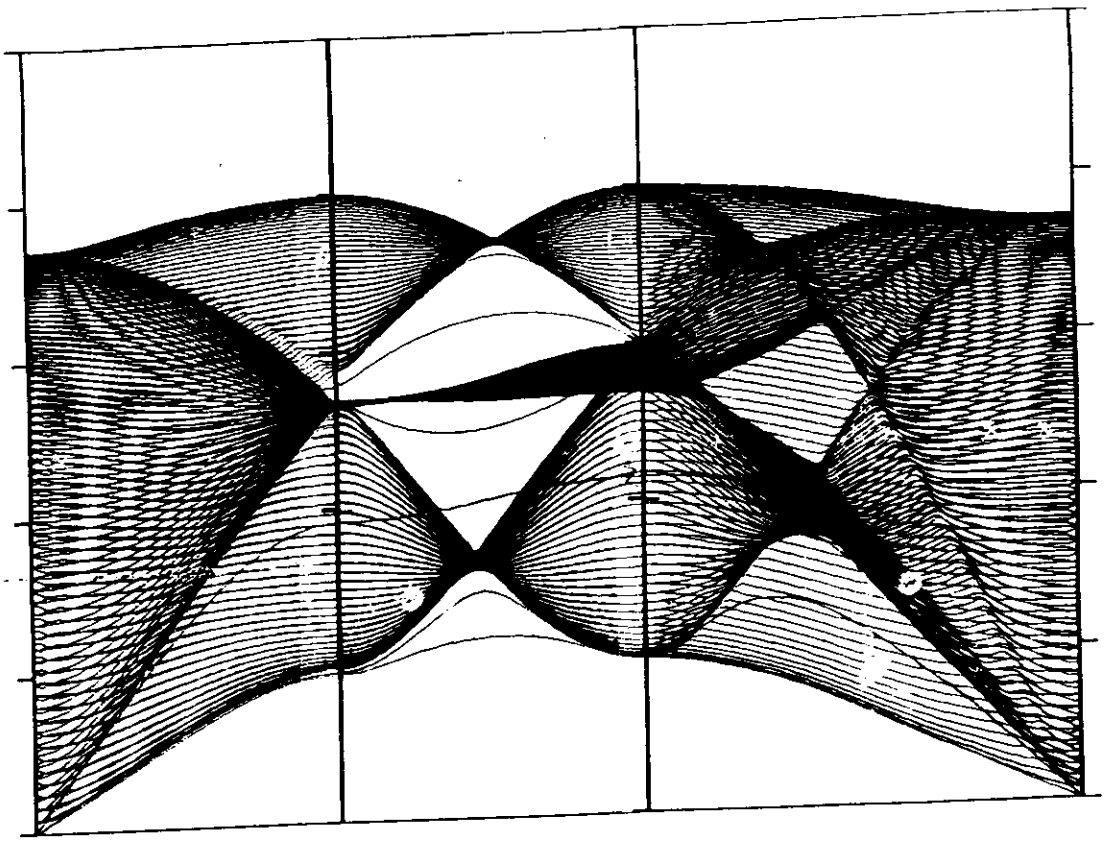
$\beta_\perp^S = 1.015\,\beta_\perp^B$

$\beta_\perp^S = 1.070\,\beta_\perp^B$

$\beta_\perp^S = 0.970\,\beta_\perp^B$



Na (001) SE



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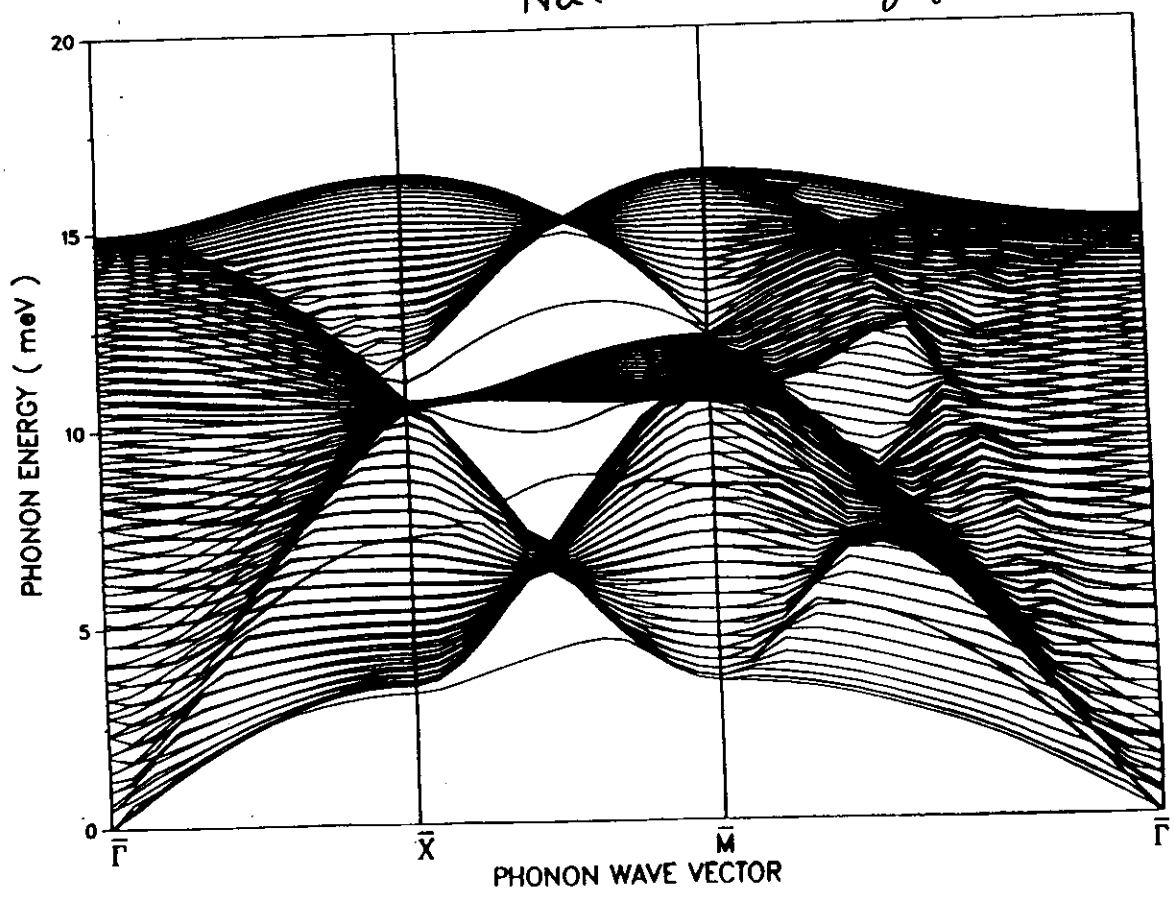
Na (001) Quong (2nd order)



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