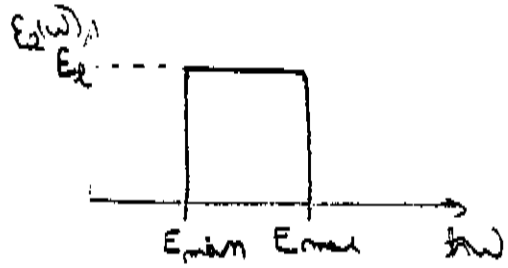
(a).

Kramers-Kronig relations: $\varepsilon_1(\omega)$ for $\varepsilon_2(\omega)$ modelled as a step function



$$\varepsilon_2(\omega) = \begin{cases} \varepsilon_\ell & \text{if } \omega_{min} < \omega < \omega_{max} \\ 0 & \text{otherwise} \end{cases}$$

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \mathcal{P} \int_0^\infty d\omega' \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} = 1 + \frac{2}{\pi} \mathcal{P} \int_{\omega_{min}}^{\omega_{max}} d\omega' \frac{\omega' \varepsilon_\ell}{\omega'^2 - \omega^2}.$$

Using

$$\int_a^b dy \frac{y}{y^2 - q^2} = \frac{1}{2} \ln \left| \frac{b^2 - q^2}{a^2 - q^2} \right| \Rightarrow \quad \varepsilon_1(\omega) = 1 + \frac{\varepsilon_\ell}{\pi} \ln \left| \frac{E_{max}^2 - \hbar^2\omega^2}{E_{min}^2 - \hbar^2\omega^2} \right|$$

$\varepsilon_1(\omega)$ exhibits structure for $\hbar\omega \simeq E_{min}$ and $\hbar\omega = E_{max}$.
This is reasonable as ε_1 and ε_2 exhibit structure in the same frequency regions. These correspond to the onset and the maximum frequency for interband absorption.

c) $\varepsilon_1(0) = 1 + \frac{2\varepsilon_\ell}{\pi} \ln\left(\frac{E_{max}}{E_{min}}\right)$

In narrow gap semiconductors $E_{min} \simeq E_c - E_v$ is very small, whereas E_{max} is not very different from that of wide gap semiconductors. Hence $\ln \frac{E_{max}}{E_{min}}$ is large and so is $\varepsilon_1(0)$.

4. cont.

(d). $$\epsilon_1(\omega) - \epsilon_1(\infty) = \frac{2}{\pi} \cdot P\int_0^{\infty} \frac{\omega' \cdot \epsilon_2(\omega')}{\omega'^2 - \omega^2} \cdot d\omega',$$

and $\epsilon_2(\omega') \to 0$ for $\omega' \gg \omega_c$,

$$\Rightarrow \epsilon_1(\omega) - \epsilon_1(\infty) = \frac{2}{\pi} \cdot P\int_0^{\omega_c} \frac{\omega' \cdot \epsilon_2(\omega')}{\omega'^2 - \omega^2} \cdot d\omega'$$

$\because$ for $\omega > \omega_c > \omega'$,

$$\Rightarrow \epsilon_1(\omega) - \epsilon_1(\infty) = \frac{2}{\pi} \cdot P\int_0^{\omega_c} \frac{\omega' \cdot \epsilon_2(\omega')}{\omega'^2 - \omega^2} \cdot d\omega' \cong \frac{2}{\pi} \cdot \int_0^{\omega_c} \frac{\omega' \epsilon_2(\omega')}{(-\omega^2)}.$$

also for high freq. limit, $\epsilon(\omega) = \epsilon_{core} - \frac{4\pi n e^2}{m\omega^2} = \epsilon_1(\infty) - \frac{4\pi n e^2}{m\omega^2}$

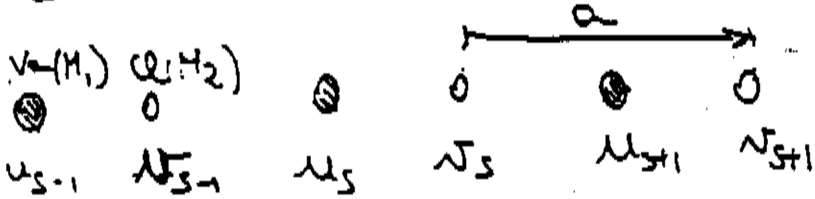
$$\Rightarrow \frac{2}{\pi} \cdot \int_0^{\omega_c} \frac{\omega' \cdot \epsilon_2(\omega')}{\cancel{+\omega^2}} d\omega' = + \frac{4\pi n e^2}{m \cancel{\omega^2}},$$

$$\Rightarrow \frac{ne^2}{m} = \frac{1}{2\pi^2} \int_0^{\omega_c} \epsilon_2(\omega') \cdot \omega' \cdot d\omega' \cong \frac{1}{2\pi^2} \int_0^{\infty} \epsilon_2(\omega')\omega' d\omega'.$$

1) Optical branches for NaCl ← Care of 1992 TA)

(a) The longitudinal and transverse modes for a 3D lattice vibration are decoupled. Hence each of them can be treated as a 1D problem.

For NaCl considering only nearest neighbour interactions we have



$$\left.\begin{aligned} M_1 \frac{d^2 u_s}{dt^2} &= K(v_s + v_{s-1} - 2u_s) \\ M_2 \frac{d^2 v_s}{dt^2} &= K(u_{s+1} + u_s - 2v_s) \end{aligned}\right\} (1)$$

We look for a solution in the form of traveling wave:

$$u_s = u\, e^{i(ksa-\omega t)}, \quad v_s = v\, e^{i(ksa-\omega t)} \qquad (2)$$

(2) ⇒ (1):

$$\left.\begin{aligned} -\omega^2 M_1 u &= K v\left[1+e^{-ika}\right] - 2Ku \\ -\omega^2 M_2 v &= K u\left[1+e^{ika}\right] - 2Kv \end{aligned}\right\}$$

$\omega(k)$:

$$\begin{vmatrix} 2K - M_1\omega^2 & -K\left[1+e^{-ika}\right] \\ -K\left[1+e^{ika}\right] & 2K - M_2\omega^2 \end{vmatrix} = 0$$

Which gives

$$M_1 M_2 \omega^4 - 2K(M_1+M_2)\omega^2 + 2K^2(1-\cos ka) = 0.$$

For photon excitation $k \approx 0$. For the TO mode

$$\omega_t^2 = 2K\left(\frac{1}{M_1}+\frac{1}{M_2}\right)$$

$$K = \frac{\omega_t^2}{2\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}$$

where $\omega_t = \frac{2\pi c}{\lambda_t} = 3.09\ 10^{13}\ s^{-1}$

$$\underset{(Na)}{M_1} = \frac{23}{6.02\cdot 10^{23}}\ g \ ,\ \underset{(Cl)}{M_2} = \frac{35.5}{6.02\cdot 10^{23}}\ g.$$

This gives a force constant : $K = 11\ N/m$.

(b) $\varepsilon(\omega) = \underbrace{\varepsilon(\infty)}_{\text{electronic contribution}} + \underbrace{\frac{4\pi N e^2/M}{\omega_t^2-\omega^2}}_{\text{lattice contribution}}.$

$$\varepsilon(\omega_l) = \varepsilon(\infty) + \frac{4\pi N e^2/M}{\omega_t^2-\omega_l^2} = 0. \rightarrow \frac{4\pi N e^2}{M} = \varepsilon(\infty)(\omega_l^2-\omega_t^2)$$

Therefore the lattice contribution to the dielectric constant

is $\dfrac{\varepsilon(\infty)(\omega_l^2-\omega_t^2)}{\omega_t^2-\omega^2}$

-) If we assume that the force constant K is not dependent on the temperature then

$$\omega_t = \sqrt{\frac{K}{M}} \qquad \left(M = \frac{M_1 M_2}{M_1 + M_2}\right)$$

is also independent of T, and

$$\omega_e = \sqrt{\frac{4\pi N e^2/M}{\varepsilon(\infty)} + \omega_t^2}$$

does not depend on T either because $\varepsilon(\infty) \neq f(T)$ for an insulator.

Thus, $\omega_e - \omega_t$ is expected to be temperature independent.

(d) Now we have:

$$\varepsilon(\omega) = A + \frac{B_1}{\omega^2 - \omega_{t_1}^2} + \frac{B_2}{\omega^2 - \omega_{t_2}^2} \qquad \text{(2 optical branches)}$$

- $\varepsilon(\infty) = A$.
- $\varepsilon(0) = \varepsilon(\infty) - \frac{B_1}{\omega_{t_1}^2} - \frac{B_2}{\omega_{t_2}^2}$
- $\varepsilon(\omega_e) = 0 = \varepsilon(\infty) + \frac{B_1}{\omega_e^2 - \omega_{t_1}^2} + \frac{B_2}{\omega_e^2 - \omega_{t_2}^2}$

The last equation can be rewritten as

$$\omega_e^4 + \left[\frac{B_1}{\varepsilon(\infty)} + \frac{B_2}{\varepsilon(\infty)} - (\omega_{t_1}^2 + \omega_{t_2}^2)\right]\omega_e^2 +$$

$$+ \frac{1}{\varepsilon(\infty)}\left(\varepsilon(\infty)\,\omega_{t_1}^2\,\omega_{t_2}^2 - B_1\,\omega_{t_2}^2 - B_2\,\omega_{t_1}^2\right) = 0.$$

This is a quadratic equation in ω_ℓ^2, which has two roots: $\omega_{\ell_1}^2$ and $\omega_{\ell_2}^2$.

For a generic quadratic equation $x^2+bx+c=0$ we have

$$x_{1,2} = \frac{-b \pm \sqrt{b^2-4c}}{2} \Rightarrow x_1 \cdot x_2 = \frac{b^2-(b^2-4c)}{4} = c$$

Therefore,

$$\omega_{\ell_1}^2 \omega_{\ell_2}^2 = \frac{1}{\varepsilon(\infty)}\left(\varepsilon(\infty)\omega_{t_1}^2 \omega_{t_2}^2 - B_1 \omega_{t_2}^2 - B_2 \omega_{t_1}^2\right)$$

or

$$\frac{\omega_{\ell_1}^2 \omega_{\ell_2}^2}{\omega_{t_1}^2 \omega_{t_2}^2} = \frac{1}{\varepsilon(\infty)}\left(\varepsilon(\infty) - \frac{B_1}{\omega_{t_1}^2} - \frac{B_2}{\omega_{t_2}^2}\right) = \frac{\varepsilon(0)}{\varepsilon(\infty)}$$

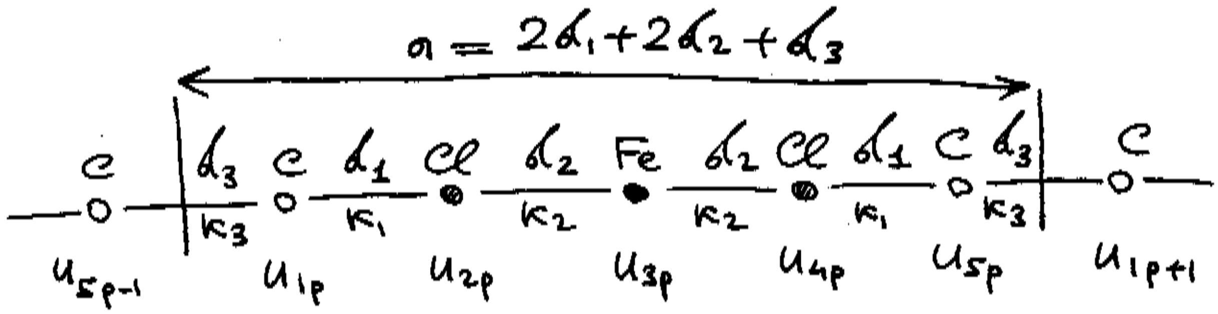
That is,

$$\boxed{\frac{\omega_{\ell_1}^2 \omega_{\ell_2}^2}{\omega_{t_1}^2 \omega_{t_2}^2} = \frac{\varepsilon(0)}{\varepsilon(\infty)}}$$

which can be generalized for p optical branches to

$$\prod_{j=1}^{p}\left(\frac{\omega_{\ell,j}}{\omega_{t,j}}\right)^2 = \frac{\varepsilon(0)}{\varepsilon(\infty)}$$

3a)



$$\Delta V = \sum_p \Big[\frac{K_1}{2}(u_{1p}-u_{2p})^2 + \frac{K_2}{2}(u_{2p}-u_{3p})^2 + \frac{K_2}{2}(u_{3p}-u_{4p})^2 + \frac{K_1}{2}(u_{4p}-u_{5p})^2 + \frac{K_3}{2}(u_{5p}-u_{1p+1})^2 \Big]$$

$$\begin{cases} M_C \dfrac{\partial^2 u_{1p}}{\partial t^2} + K_1(u_{1p}-u_{2p}) + K_3(u_{1p}-u_{5p-1}) = 0 \\ M_{Cl} \dfrac{\partial^2 u_{2p}}{\partial t^2} + K_1(u_{2p}-u_{1p}) + K_2(u_{2p}-u_{3p}) = 0 \\ M_{Fe} \dfrac{\partial^2 u_{3p}}{\partial t^2} + K_2(u_{3p}-u_{2p}) + K_2(u_{3p}-u_{4p}) = 0 \\ M_{Cl} \dfrac{\partial^2 u_{4p}}{\partial t^2} + K_2(u_{4p}-u_{3p}) + K_1(u_{4p}-u_{5p}) = 0 \\ M_C \dfrac{\partial^2 u_{5p}}{\partial t^2} + K_1(u_{5p}-u_{4p}) + K_3(u_{5p}-u_{1p+1}) = 0 \end{cases}$$

$$u_{jp} = c_j e^{ikpa - i\omega t}$$

$$\begin{pmatrix} (K_1+K_3-M_C\omega^2) & -K_1 & 0 & 0 & -K_3 e^{-ika} \\ -K_1 & (K_1+K_2-M_{Cl}\omega^2) & -K_2 & 0 & 0 \\ 0 & -K_2 & (2K_2-M_{Fe}\omega^2) & -K_2 & 0 \\ 0 & 0 & -K_2 & (K_1+K_2-M_{Cl}\omega^2) & -K_1 \\ -K_3 e^{ika} & 0 & 0 & -K_1 & (K_1+K_3-M_C\omega^2) \end{pmatrix}$$

3a (continued)

det $= 0$ (for $k=0$ for simplicity)

$$\Downarrow$$

$$\omega^2\left[(M_c\omega^2-2k_3)(M_{ce}\omega^2-k_2)-k_1((M_c+M_{ce})\omega^2-k_2-2k_3)\right]$$
$$\times\left[M_c\omega^2(M_{ce}M_{Fe}\omega^2-k_2(2M_{ce}+M_{Fe}))-k_1((M_c+M_{ce})M_{Fe}\omega^2 - k_2(2M_c+2M_{ce}+M_{Fe}))\right]=0$$

5 modes: 1 acoustic & 4 optical

① $\omega=0$ (acoustic for $k=0$)

②,③ $$\omega^2=\frac{1}{M_cM_{ce}}\left[k_1M_c+k_2M_c+k_1M_{ce}+2k_3M_{ce}\pm\sqrt{(k_1M_c+k_2M_c+k_1M_{ce}+2k_3M_{ce})^2-4M_cM_{ce}(k_1k_2+2k_1k_3+2k_2k_3)}\right]$$

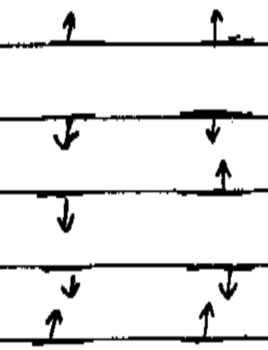
④,⑤ $$\omega^2=\frac{1}{2M_cM_{ce}M_{Fe}}\left[2k_2M_cM_{ce}+k_1M_cM_{Fe}+k_2M_cM_{Fe}+k_1M_{ce}M_{Fe}\pm\sqrt{(2k_2M_cM_{ce}+k_1M_cM_{Fe}+k_2M_cM_{Fe}+k_1M_{ce}M_{Fe})^2-4k_1k_2M_cM_{ce}M_{Fe}(2M_c+2M_{ce}+M_{Fe})}\right]$$

corresponding eigenvectors $\vec{e}=\begin{pmatrix}e_1\\e_2\\e_3\\e_4\\e_5\end{pmatrix}$ have the following form:

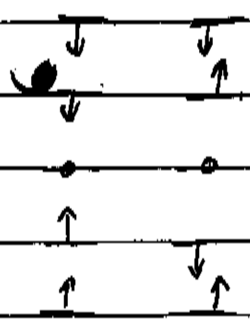
$$\vec{e}_1=\begin{pmatrix}\delta\\\delta\\\delta\\\delta\\\delta\end{pmatrix},\quad \vec{e}_{2,3}=\begin{pmatrix}-\delta\\\pm\delta\\0\\\mp\delta\\\delta\end{pmatrix},\quad \vec{e}_{4,5}=\begin{pmatrix}\delta\\-\Delta_\pm\\\pm C\Delta_\pm\\-\Delta_\pm\\\delta\end{pmatrix}$$

since ω_1 is acoustic and $\omega_{2,3}$ does not depend on M_{Fe}

The odd modes are excited by electromagnetic radiation at their respective mode frequencies (IR active).



c) The even modes are Raman active.



d) The modes at zone center $(q=0)$ are excited by electromagnetic radiation and Raman scattering.

Inelastic neutron scattering probes the entire phonon branch because the deBroglie wave can have various values of wavevector.

4. Suppose we know the electronic and phonon energies of the solid: $H_{el}\Psi_{el} = E_{n,k}\Psi_{el}$

$$H_{ph}\Psi_{ph} = E_{\{\bar{q},j_{\bar{q}}\}}\Psi_{ph} \qquad j_{\bar{q}} = \text{occupation number}$$

We can treat the electron phonon interaction as perturbation:

$$H = H_{el} + H_{ph} + H_{el\text{-}ph} = H_0 + H_1$$

The form of $H_{el\text{-}ph}$ is derived in Appendix B. For our purpose

$$H_1 = H_{el\text{-}ph} = \sum_{\bar{q}} \hat{a}_{\bar{q}}\, c_{\bar{q}} + \hat{a}^+_{\bar{q}}\, c^*_{\bar{q}}$$

where $\hat{a}_{\bar{q}}$ & $\hat{a}^+_{\bar{q}}$ are the corresponding annilation and creation operators for phonon of wave vector $\bar{q}$, and $c_{\bar{q}}$ is independent of atomic displacements, and $c_{\bar{q}} \cdot c^*_{\bar{q}} = |c_{\bar{q}}|^2$

$$\Delta E^{(1)} = \langle \Psi_{el}\cdot\Psi_{ph} | H_1 | \Psi_{el}\cdot\Psi_{ph} \rangle = 0$$

$$\Delta E^{(2)} = \sum_{n',k',\{\bar{q},j\}'} \frac{|\langle \Psi_{el}(n',k')\,\Psi_{ph}\{\bar{q},j_{\bar{q}}\}' | H_1 | \Psi_{el}(n,k)\,\Psi_{ph}(\bar{q},j_q)\rangle|^2}{E_f - E_i}$$

but only terms for which all $\{\bar{q},j_q\}$ are equal but for one phonon $j_n' = j_n \pm 1$ contribute to the sum.

$$\Delta E^{(2)} = \sum_{q_n} a_{n,k,\{q,j_q\}}(j_n+1) + \sum_{q_n} a_{n,k,\{\bar{q},j_q\}}\, j_n$$

$$= \sum_{q_n} a_{n,k\{q,j_q\}}(2j_n+1)$$

The temperature dependence is from j_n only: $j_n = \dfrac{1}{e^{\hbar\omega_n/kT}-1}$

$$\Delta E(T) = \sum_{\omega_n} a_{n,k\{q,j_q\}}\left(\frac{2}{e^{\hbar\omega_n/kT}-1} + 1\right) = A\left(\frac{2}{e^{\hbar\Omega/kT}-1} + 1\right)$$

where A and Ω are weighted average values.

(b) At $kT \gg \hbar\Omega$, $e^{\hbar\Omega/kT} \sim 1 + \frac{\hbar\Omega}{kT}$

$$\Delta E_g(T) \approx A\left(\frac{2kT}{\hbar\Omega} + 1\right) \approx \frac{2AkT}{\hbar\Omega}$$

(c) Extrapolation: $\Delta E_g(T)\Big|_{T=0} = 0$

$$E_g(T) - E_g(0)\Big|_{T\to 0} = A\left(\frac{2}{\exp(\infty)-1} + 1\right) = A$$

A = renormalization energy $\sim -40\,\text{meV}$

(d) · $\Omega \sim \sqrt{\frac{K}{M}}$ $A \sim \frac{1}{M}$

As $M \Uparrow$, $\Omega \Downarrow$, $\left(\frac{2}{\exp^{\hbar\Omega/kT}-1} + 1\right) \Uparrow$

But as $M \Uparrow$, $|A| \Downarrow$

~~[illegible]~~ Following the linear approximation $\Delta E_g(T) \sim \frac{T}{\sqrt{M}}$

Since A is negative, $E_g(T)$ increases with M