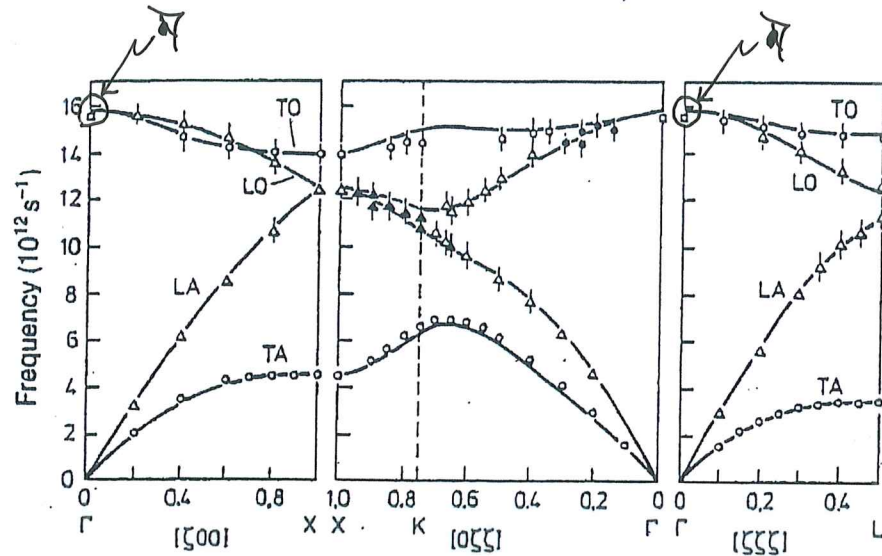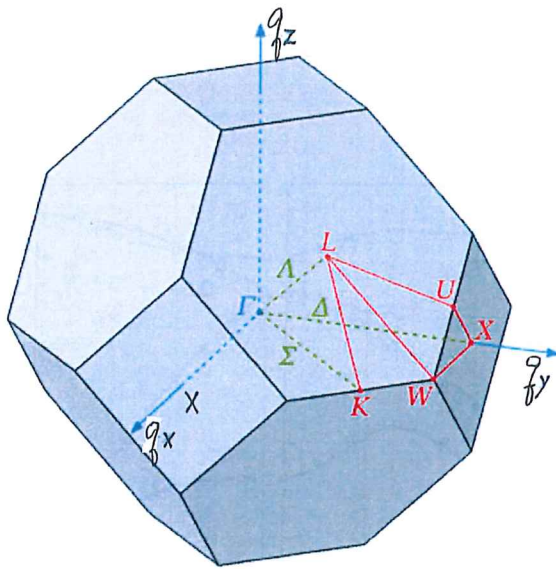# N. Optical Properties[+] of Ionic Crystals in the Infrared

["Optical Branches"? Optical here includes a wider range than visible range]

Silicon (Si) has FCC structure with a basis of 2 atoms

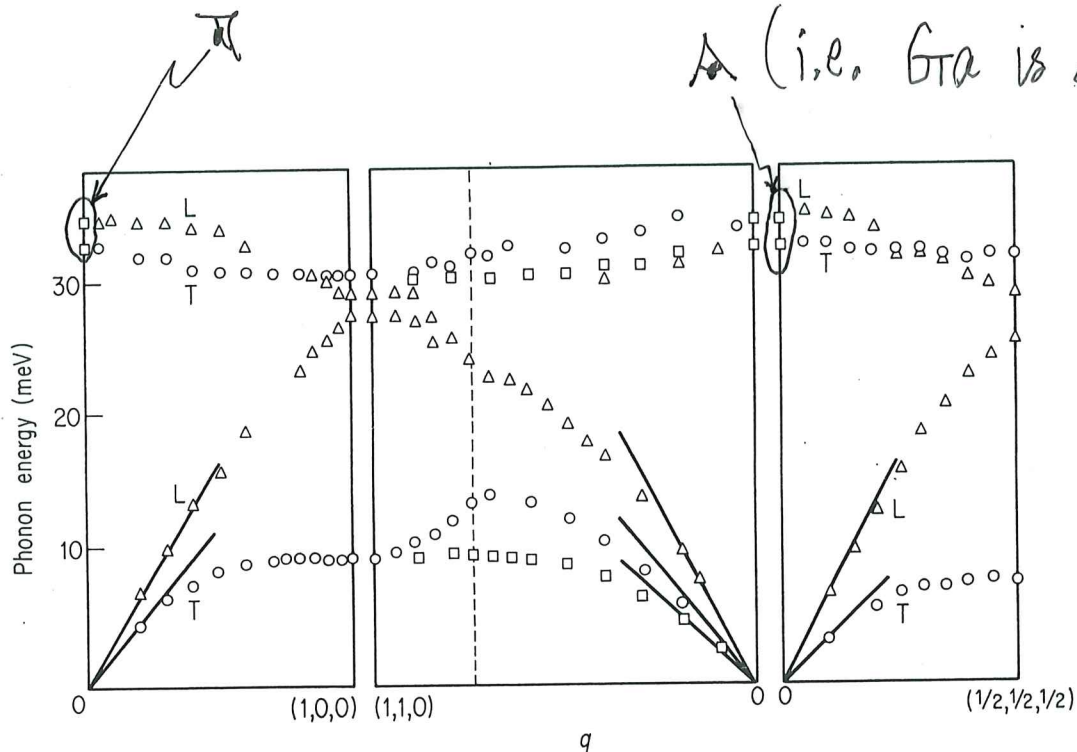$\Rightarrow$ 3 Acoustic branches + 3 optical branches

Two __identical atoms__ in Basis. At Γ (zone center), $\omega_{TO}(\vec{q}=0) = \omega_{LO}(\vec{q}=0)$

[+] Cross reference to Optical Properties

GaAs (same structure, but Ga and As are different atoms)

electron density is slightly higher on As

(i.e. Ga is a bit positive, As is a bit negative)

Vibrational spectrum of GaAs at 296 K (compare Si)

[Taken from Elliot and Gibson, "An Introduction to Solid State Physics and its Applications"]

$$\omega_{LO}(\vec{q}=0) \neq \omega_{TO}(\vec{q}=0)$$

in fact $\omega_{LO}(\vec{q})$ is higher than $\omega_{LO}(\vec{q})$ for a wide range of $\vec{q}$

$$\omega_{LO}(\vec{q}=0) > \omega_{TO}(\vec{q}=0) \qquad (86)$$

$\omega_{LO}(\vec{q}=0)$ is pushed higher relative to $\omega_{TO}(\vec{q}=0)$
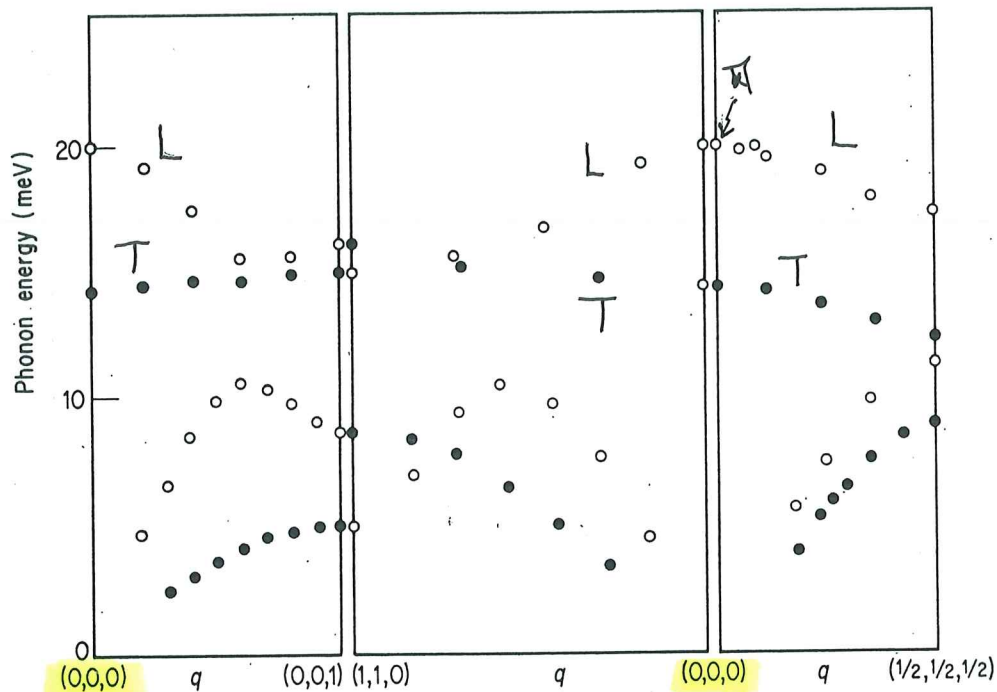
by the differently charged ions

KBr $(K \to K^+$, $Br \to Br^-$ almost) (fcc direct lattice)

(more ionic character)

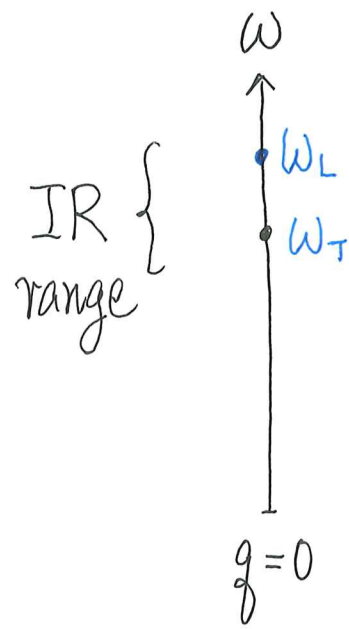$$\omega_{LO}(\vec{q}=0) > \omega_{TO}(\vec{q}=0) \qquad (86)$$
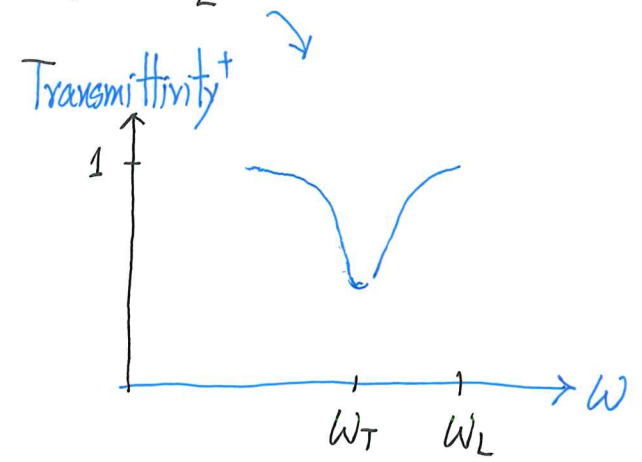
where ionic character is apparent

"Phenomenon 1"

Vibrational spectrum in KBr at 90 K

ω

IR range $\{$

$\bullet\ \omega_L$

$\bullet\ \omega_T$

$q = 0$

Consequences

$\Longrightarrow$ Call $\omega_L(\vec{q}=0) = \omega_L$

$\Longrightarrow$ Call $\omega_T(\vec{q}=0) = \omega_T$

rotate. axis

$\xrightarrow{\hspace{3cm}} \omega$

$\underset{\omega_T}{\times} \quad \underset{\omega_L}{\times}$

"Phenomenon 2"

Reflectivity

(100%) 1

$\xleftarrow{}$ highly reflective

$\omega_T \quad \omega_L \xrightarrow{} \omega$

Transmittivity[+]

1

$\omega_T \quad \omega_L \xrightarrow{} \omega$
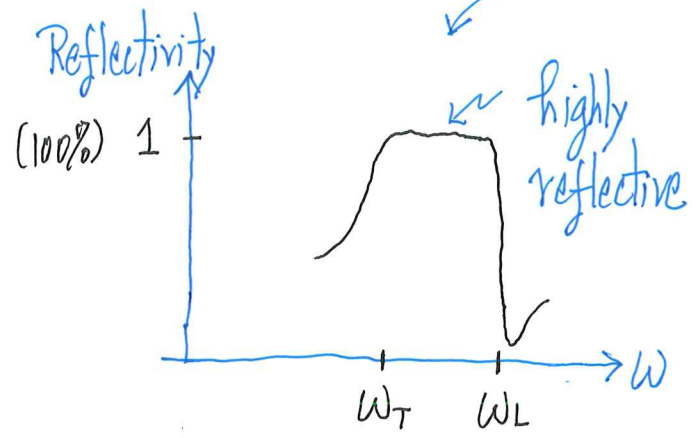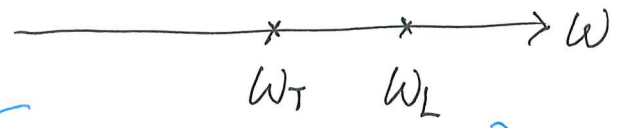
Ionic crystals in IR,

a range around and between ω_T and ω_L that the material becomes highly reflective and absorptive (87)

[+] A drop in transmittivity signals an increase in absorption

(a) <u>Optical Properties</u> of <u>Solids</u> (embedded in <u>Electromagnetism</u> Course)

- There are many approaches.

- Dielectric function ε (usually $\varepsilon(\omega)$ as given by the Lorentz oscillator model)

displacement → $D = \varepsilon \underset{\nwarrow \text{electric field}}{\varepsilon}$ (vector signs <u>omitted</u>)
field

      <u>permittivity</u> (but often called the <u>dielectric function</u>[+])

need this $= \varepsilon_0 \varepsilon + P$ (88a)
for doing EM   permittivity   Polarization = $\dfrac{\text{electric dipole moment}}{\text{Volume}}$ ← this is how
in a <u>material</u>   of vacuum   a material
(SSP!)   or relative permittivity   responds to
          $= \varepsilon_0 \varepsilon_r \varepsilon$ (88b)   an electric field
                                [optical mode at $\vec{q}=0$,
   dielectric "constant" (dielectric function)   ions move out of phase]

[+] The name is carried over from the era of using the Gaussian units in EM theory.

Depending on choice (taste), one could work with a real ε and a real σ OR a complex $\tilde{\varepsilon}$ OR a complex $\tilde{\sigma}$ Conductivity (dissipative)

[in any case, two real quantities for studying Optical Properties of solids]

We focus on $\tilde{\varepsilon}_r(w)$ and take it as possibly complex.

$$\tilde{\varepsilon}_r = \tilde{n}^2 \quad \text{where } \tilde{n} = \text{complex refractive index}$$

$$= (n + iK)^2 \qquad = n + iK$$

$$= \varepsilon_{r1} + i\varepsilon_{r2} \qquad (89)$$

refractive index   extinction coefficient

real part   imaginary part

$\frac{c}{n}$ is speed of light in matter

$$\therefore \boxed{\varepsilon_{r1} = n^2 - K^2 \; ; \; \varepsilon_{r2} = 2nK \qquad (90)}$$

$$\boxed{[\text{can write } n, K \text{ in terms of } \varepsilon_{r1} \text{ and } \varepsilon_{r2}]}$$

Normal Incidence $\rightleftarrows$ | $\widetilde{\mathcal{E}_r} = \widetilde{n}^2$
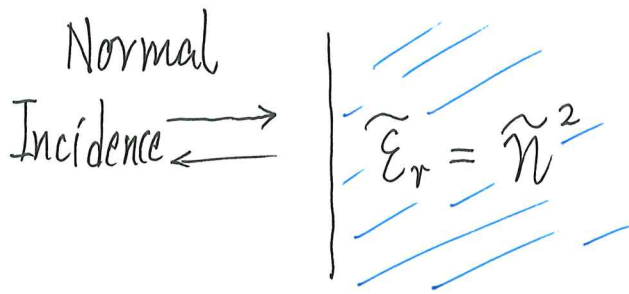
$$\frac{\mathcal{E}_{reflected}}{\mathcal{E}_{incident}} = \widetilde{\gamma} = \frac{1-\widetilde{n}}{1+\widetilde{n}} \qquad (91)^{+}$$

$$R = \text{Reflectivity (normal incidence)} = \widetilde{\gamma}^{*}\widetilde{\gamma} = \left|\frac{1-\widetilde{n}}{1+\widetilde{n}}\right|^2 = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \qquad (92)$$

Experimentally, R is measured over a wide range of ω. If we have $R(\omega)$ for __all__ ω, everything follows because there is causality.

__Strategy:__ Get $\widetilde{\mathcal{E}_r}$ (or simply $\mathcal{E}_r$), then know n and K, then know R.

 understood that it could be complex

$^{+}$ Griffiths, "Introduction to electrodynamics" (3rd edition), Ch.9 has a related discussion.
$\widetilde{\gamma} = \frac{\widetilde{n}-1}{\widetilde{n}+1}$ also works.

The absorption coefficient α_{ab}

EM wave attenuates as it propagates

Vacuum: $\quad c k \overset{\nwarrow\ \text{EM wave wave vector}}{=} \omega$

$$\boxed{\text{Matter}: \quad k\frac{c}{\tilde{n}} = \omega}$$

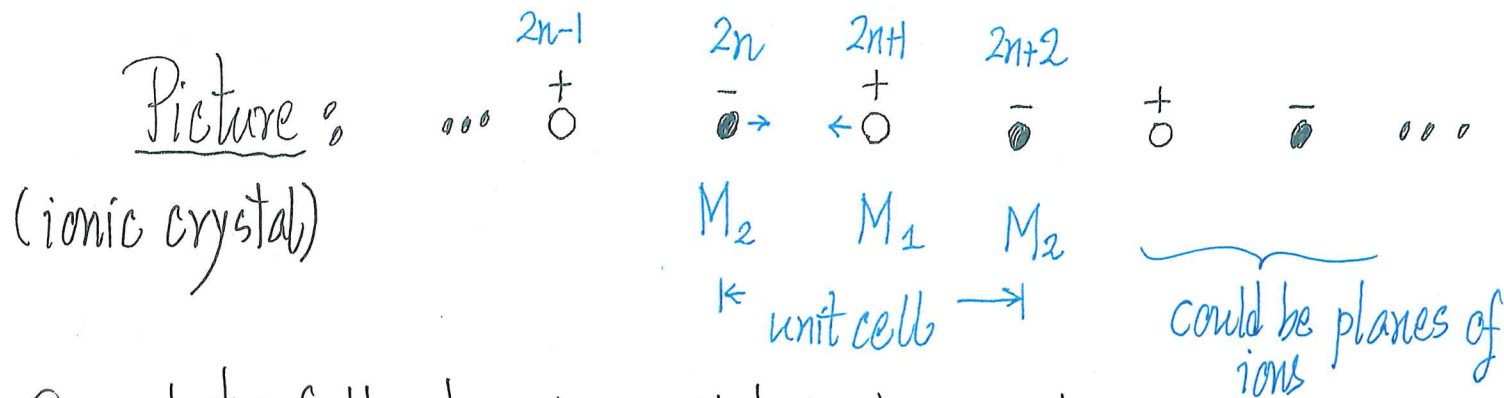$$k = \tilde{n}\frac{\omega}{c} = n\frac{\omega}{c} + iK\frac{\omega}{c} \quad \text{in Matter} \quad \text{(i.e. } k \text{ becomes complex)}$$

$$\mathcal{E}_0 e^{ikx} e^{-i\omega t} = \mathcal{E}_0 e^{in\frac{\omega}{c}x} e^{-i\omega t} \cdot \underbrace{e^{-K\frac{\omega}{c}x}}_{} \quad \leftarrow \text{attenuating as wave propagates}$$

$$I = \text{Intensity} \propto e^{-2K\frac{\omega}{c}x} = e^{-\alpha_{ab}\cdot x}$$

$$\alpha_{ab} = 2\left(\frac{\omega}{c}\right)\cdot K \quad \overset{\nwarrow \text{ extinction coefficient}}{}$$

$$= 2k\cdot K \quad (\text{unit: }1/\text{length}) \quad (93)$$

Strategy:
Get $\tilde{\varepsilon}_r$, then n and K, then know α_{ab}.

(b) <u>Back to 2 atoms per unit cell</u> : <u>forced oscillations</u>

<u>Picture</u> :

... $\overset{+}{\underset{2n-1}{O}}$ $\overset{-}{\underset{2n}{⊘}}\rightarrow$ $\leftarrow\overset{+}{\underset{2n+1}{O}}$ $\overset{-}{\underset{2n+2}{⊘}}$ $\overset{+}{O}$ $\overset{-}{⊘}$ ...

(ionic crystal)

M_2 M_1 M_2

$\underset{\longleftarrow \text{unit cell} \longrightarrow}{}$

could be planes of ions

Cations: $+e^*$

anions: $-e^*$

e^* (a parameter, not necessarily e)

($\because$ electron transfer may not be complete)

$\mathcal{E}$ = electric field set up by oscillating charges when ions vibrate

Equations of motion[+] :

spring constant (short-range restoring force)

$$M_1 \frac{\partial^2 u_{2n+1}}{\partial t^2} = -K\left(2u_{2n+1} - u_{2n} - u_{2n+2}\right) + e^*\mathcal{E}$$

(94)

$$M_2 \frac{\partial^2 u_{2n}}{\partial t^2} = -K\left(2u_{2n} - u_{2n-1} - u_{2n+1}\right) - e^*\mathcal{E}$$

[+] 1st term on RHS is restoring force, 2nd term is driving force, so it is a forced oscillator problem.

Take $q \to 0$ $(\lambda \gg a)$ [easier], then all $+e^*$ ions have same displacement $u_+(t)$ and all $-e^*$ ions have same displacement $u_-(t)$

$$u_+(t) = u_{0+} e^{-i\omega t} \quad , \quad u_-(t) = u_{0-} e^{-i\omega t}$$

$\underbrace{\phantom{u_{0+}}}$ for $+e^*$ ions $\qquad$ $\underbrace{\phantom{u_{0-}}}$ for $-e^*$ ions

It follows that $\mathcal{E} = \mathcal{E}_0 e^{-i\omega t}$.

Substituting into Eq. (94) and solving u_{0+} and u_{0-} (in terms of $M_1, M_2, K, \omega, \mathcal{E}_0$):

$$u_{0+} = \frac{e^*}{M_1} \left[\frac{1}{2K\left(\frac{1}{M_1} + \frac{1}{M_2}\right) - \omega^2} \right] \mathcal{E}_0 = \frac{e^*}{M_1} \left[\frac{1}{\omega_T^2 - \omega^2} \right] \mathcal{E}_0 \qquad \text{(Ex.)}$$

$$u_{0-} = -\frac{e^*}{M_2} \frac{1}{\left[2K\left(\frac{1}{M_1} + \frac{1}{M_2}\right) - \omega^2 \right]} \mathcal{E}_0 = \frac{-e^*}{M_2} \left[\frac{1}{\omega_T^2 - \omega^2} \right] \mathcal{E}_0$$

(95)

We called

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

- anticipating it is $W_T(\vec{q}=0)$
- Saw $\sqrt{\frac{2K}{\mu}}$ in diatomic chain problem without e^* and thus $\mathcal{E}$
- expected (EM) $\vec{\nabla} \cdot \vec{\mathcal{E}} = 0$ and so $\vec{q} \cdot \vec{\mathcal{E}} = 0$ and thus transverse displacement u_T is not affected by the forced term

Next, we want to get $\mathcal{E}_r(\omega)$

$$D = \mathcal{E}_0 \mathcal{E}_r \mathcal{E} = \mathcal{E}_0 \mathcal{E} + P$$

$$\mathcal{E}_r = 1 + \frac{P}{\mathcal{E}_0 \mathcal{E}} \quad \leftarrow \text{matter}$$

vacuum

this is "epsilon-zero" (permittivity of vacuum)

There are many charges that can contribute to Polarization

• In IR range (our interest), the ionic polarization is important.

There are electrons (e.g. polarizability α of an atom (c.f. Applied QM)), their contributions are there, and they survive even at high frequencies when the (massive) ions cannot follow/ respond.

Ionic Polarization

n = # unit cells / Volume

electric dipole moment due to ionic vibrations per unit cell = $e^* (u_{0+} - u_{0-})$

$$P_{ionic} = n e^* (u_{0+} - u_{0-}) = n e^{*2} \left[\frac{1}{M_1} \frac{1}{(\omega_T^2 - \omega^2)} + \frac{1}{M_2} \frac{1}{(\omega_T^2 - \omega^2)} \right] \mathcal{E}_0$$

$$= \frac{n e^{*2}}{\mu} \cdot \frac{2}{(\omega_T^2 - \omega^2)} \mathcal{E}_0 = \frac{n e^{*2}}{\mu \omega_T^2} \cdot \left(\frac{2}{1 - \frac{\omega^2}{\omega_T^2}} \right) \mathcal{E}_0$$

P_{el} = __electronic polarization__ (from electrons in atomic shells)

The relative dielectric function [how an ionic crystal responds to $\mathcal{E}$] is:

$$\mathcal{E}_r(\omega) = 1 + \frac{P_{el}}{\varepsilon_0 \mathcal{E}_0} + \frac{2n e^{*2}}{\varepsilon_0 \omega_T^2 \mu} \cdot \frac{1}{1 - \frac{\omega^2}{\omega_T^2}} \qquad (96)^{+}$$

Then, write $\mathcal{E}_r(\omega)$ into a form that carries measurable quantities

(i) $\underline{\omega = 0}$, __static__ $\mathcal{E}_r$ ($\mathcal{E}_r(0)$)

both electrons (P_{el} part) and ionic (P_{ionic}) part can follow

__static__
__dielectric__
__constant__ $\rightsquigarrow$ $\mathcal{E}_r(0) = 1 + \frac{P_{el}}{\varepsilon_0 \mathcal{E}_0} + \frac{2n e^{*2}}{\varepsilon_0 \omega_T^2 \mu}$

$^{+}$ Done! We can use $\mathcal{E}_r(\omega)$ to get n and κ, thus reflectivity $R(\omega)$ and absorption coefficient $\alpha_{ab}(\omega)$

(ii) $\underline{\omega \to \infty}$, ions can't follow (not contributing), only electronic P_{el}.

$$\varepsilon_r(\infty) = 1 + \frac{P_{el}}{\varepsilon_0 \varepsilon} \qquad \text{(smaller than } \varepsilon_r(0))$$

Expression of $\varepsilon_r(\omega)$ (for general ω) becomes:

$$\varepsilon_r(\omega) = \underbrace{1 + \frac{P_{el}}{\varepsilon_0 \varepsilon}}_{\varepsilon_r(\infty)} + \underbrace{\frac{2n e^{*2}}{\varepsilon_0 \omega_T^2 \mu}}_{\varepsilon_r(0) - \varepsilon_r(\infty)} \cdot \frac{1}{1 - \frac{\omega^2}{\omega_T^2}}$$

$$\Rightarrow \boxed{\varepsilon_r(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 - \frac{\omega^2}{\omega_T^2}}} \qquad (97)^+$$

- $\varepsilon_r(0)$, $\varepsilon_r(\infty)$ are measurable
- ω_T has special features

$^+$ We don't see an imaginary part of $\varepsilon_r(\omega)$ because we haven't included a damping term.

Remark : <u>Lorentz Oscillator model</u> of <u>$\mathcal{E}_r(\omega)$</u>

For those who did Griffiths,"Introduction to Electrodynamics", Ch.9[+], you saw

$$\tilde{\mathcal{E}}_r(\omega) = 1 + \frac{N q^2}{m \mathcal{E}_0} \frac{1}{\omega_0^2 - \omega^2 - i \gamma \omega}$$

"$-M\gamma \frac{du}{dt}$" term
in Eq. of motion

complex damping

$$\tilde{\mathcal{E}}_r(0) = 1 + \frac{N q^2}{m \mathcal{E}_0} \frac{1}{\omega_0^2}$$

$$\tilde{\mathcal{E}}_r(\infty) = 1$$

$$\therefore \quad \tilde{\mathcal{E}}_r(\omega) = \tilde{\mathcal{E}}_r(\infty) + \frac{\tilde{\mathcal{E}}_r(0) - \tilde{\mathcal{E}}_r(\infty)}{\left[1 - \frac{\omega^2}{\omega_0^2} - \frac{i \gamma \omega}{\omega_0^2} \right]}$$

just as in Eq. (97)

[+] Section on Dispersion and absorption (frequency dependence of permittivity)

$$\mathcal{E}_r(\omega) = \mathcal{E}_r(\infty) + \frac{\mathcal{E}_r(0) - \mathcal{E}_r(\infty)}{1 - \frac{\omega^2}{\omega_T^2}} \qquad (97)$$

"must have" physical sense

$\mathcal{E}_r > 0$
propagating
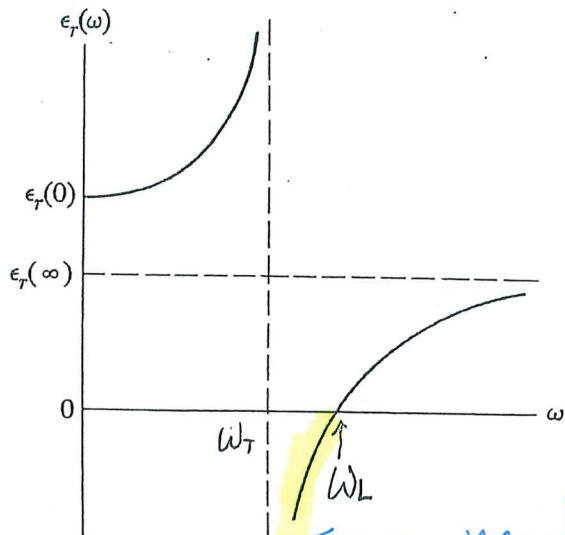
$\mathcal{E}_r < 0$ range
(be careful)

highly reflective

(98)

negative $\mathcal{E}_r(\omega)$ within $\omega_T < \omega < \omega_L$

Dielectric function $\epsilon_r(\omega)$ versus frequency. The function is singular at the transverse frequency ω_T and vanishes at the longitudinal frequency ω_L.

Call the frequency at which $\mathcal{E}_r = 0$ the frequency $\omega = \omega_L$
i.e. $\mathcal{E}_r(\omega_L) = 0$

(i) a symbol

(ii) turns out to be $\omega_{LO} (\vec{q} = 0)$

$\therefore \ \varepsilon_r(\omega) < 0$ in the range $\omega_T < \omega < \omega_L$

real, $\leadsto \varepsilon_r(\omega) = \tilde{n}^2 \ \Rightarrow \ \tilde{n}$ _purely imaginary_
but negative

$$\tilde{n} = \underbrace{n}_{\not{0}} + i\underbrace{K}_{\neq 0} \leftsquigarrow \text{"kappa" [extinction coefficient]}$$
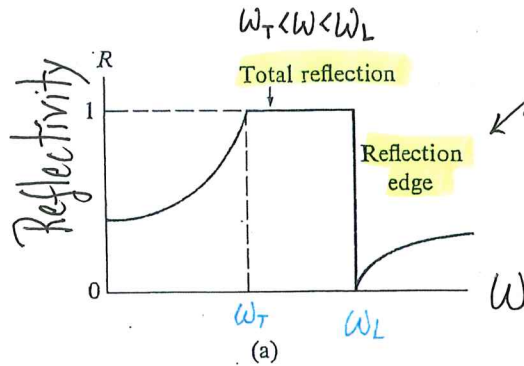
$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} = 1 \quad (\text{total reflection})^\dagger$$
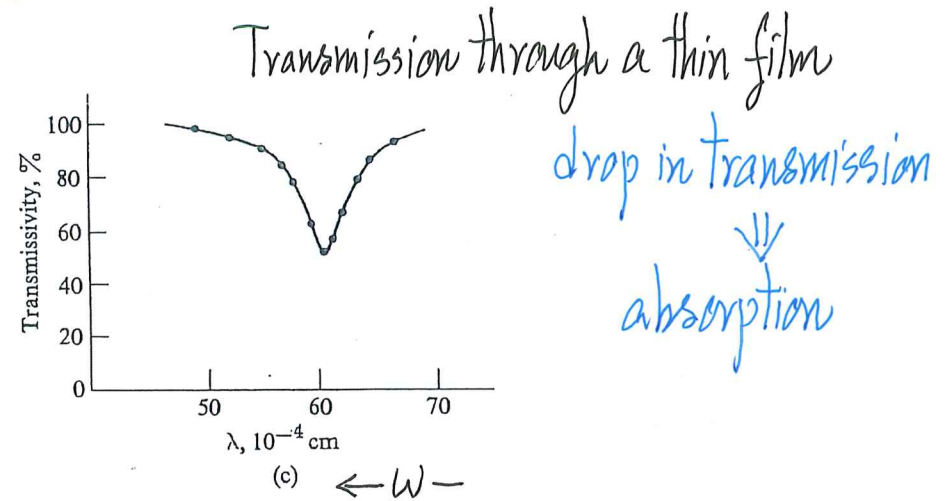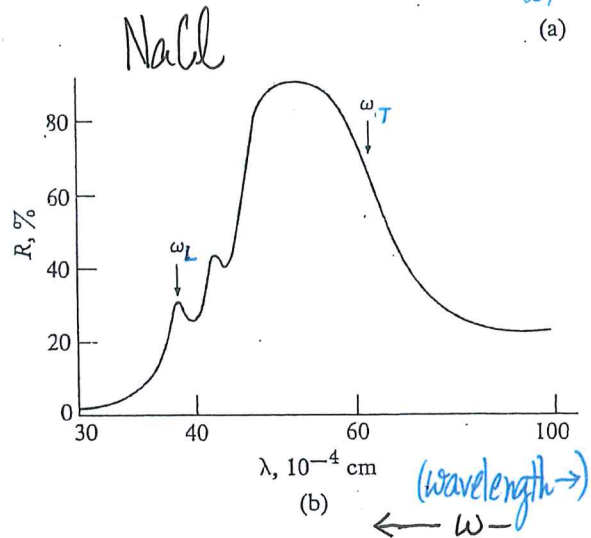
$K \neq 0 \Rightarrow$ attenuation

$$\alpha_{ab} = 2\left(\frac{\omega}{c}\right)\underbrace{K}_{\neq 0}$$

absorption enhances as ω passes ω_T

(thus explained observed behavior in IR for ionic crystals)

$\dagger$ For those who have the experience of working with metals, it is the same physics for $\omega < \omega_p$ [the plasma frequency], only that the frequencies are in visible range. Here, it is in IR.

$\omega_T < \omega < \omega_L$

(a)

sudden drop in R as $\omega \gtrsim \omega_L$

(Theoretical Calculation)

NaCl

(wavelength →)

← ω —

(b)

Transmission through a thin film

drop in transmission

$\Downarrow$

absorption

(c) ← ω —

(a) Reflectivity versus frequency for an ideal crystal. (b) Infrared reflectivity versus wavelength for NaCl at room temperature. The frequencies ω_t and ω_l correspond to $\lambda = 61$ and 38×10^{-4} cm, respectively. (c) Infrared transmissivity versus wavelength for an NaCl thin film (of thickness 0.17×10^{-4} cm). Dip is at frequency ω_T

Appreciation: Apply simple physics (various subjects) to understand optical (IR) properties of ionic crystals

Also observed
in semiconductors

$\underbrace{CdS}$

Ⅱ - Ⅵ compound

(ionicity)
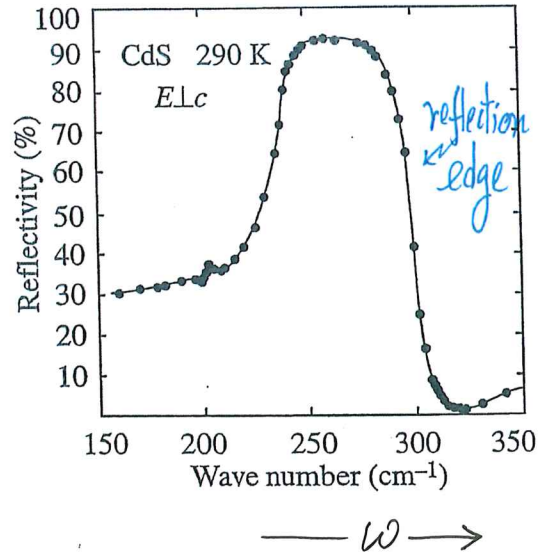
Reflectivity versus wave number for CdS
at 290 K
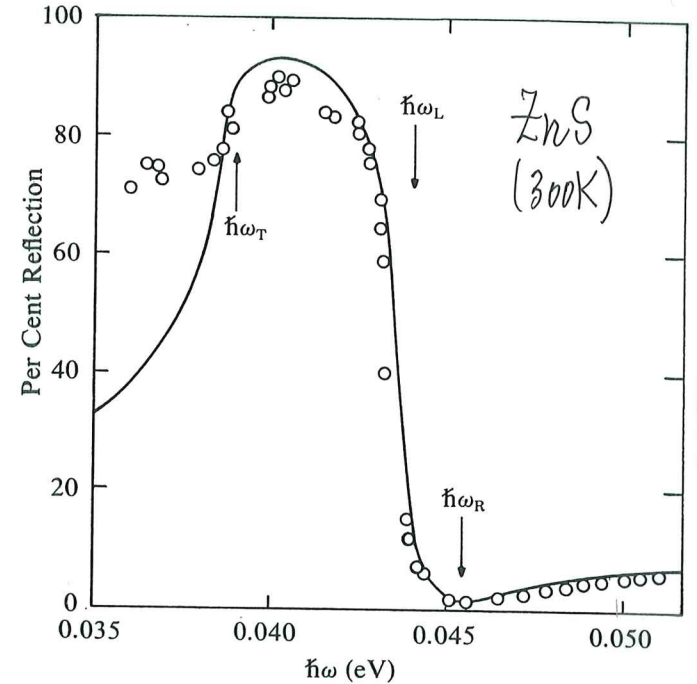
⸿ We included only driving force in the equations of motion

⸿ But excluded damping terms (phonons scattered off something)

⸿ With damping $\Rightarrow$ damped forced oscillators $\Rightarrow \widetilde{\varepsilon}_r(\omega)$

$$\varepsilon_{r1}(\omega) = \varepsilon(\infty) + \frac{(\varepsilon(0)-\varepsilon(\infty))\,\omega_T^2\,(\omega_T^2-\omega^2)}{(\omega_T^2-\omega^2)^2 + \omega^2\Gamma^2} \;;\; \varepsilon_{r2}(\omega) = \frac{(\varepsilon(0)-\varepsilon(\infty))\,\Gamma\,\omega\,\omega_T^2}{(\omega_T^2-\omega^2)^2 + \omega^2\Gamma^2} \quad \text{(Optional)}$$
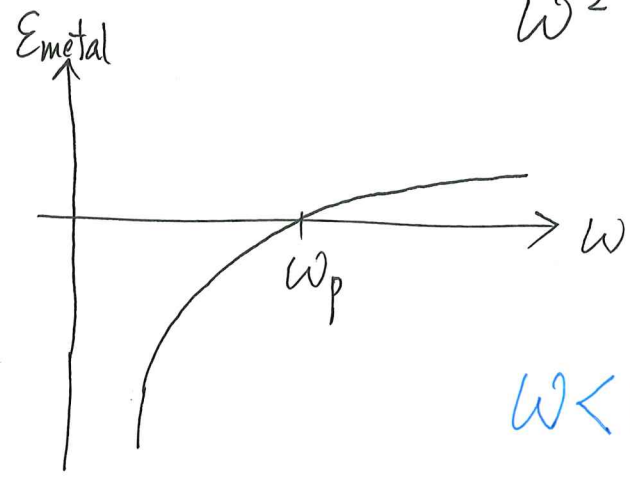
real part   imaginary part

Remark: Buy one get one free (metals)

$$\varepsilon_{metal}(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} \qquad (99)$$

ω_p = plasma frequency = $\dfrac{n e^2}{\varepsilon_0 m_e}$

electrons per volume

mass of electron

(typically in UV)

$\omega < \omega_p$; $\underline{\varepsilon_{metal} < 0}$

$\Rightarrow$ highly reflective (in visible range)

e.g. Copper was used as mirrors

For ω in UV, some metals become transparent (to UV range)

Defined ω_L by $\varepsilon_r(\omega_L) = 0$ (last ω where $R = 1$)

$$\therefore \quad 0 = \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 - \dfrac{\omega_L^2}{\omega_T^2}}$$

$$\Rightarrow \boxed{\omega_L = \left(\frac{\varepsilon_r(0)}{\varepsilon_r(\infty)}\right)^{1/2} \cdot \omega_T} \qquad (100)$$

more contributions
↙
$\varepsilon_r(0) > \varepsilon_r(\infty)$ (both measureable)

$\Rightarrow \boxed{\omega_L > \omega_T \text{ in a definite way}}$

$[\omega_L \neq \omega_T$ when there is ionic polarization$]$

This is the splitting of the $q = 0$ optical modes⁺!
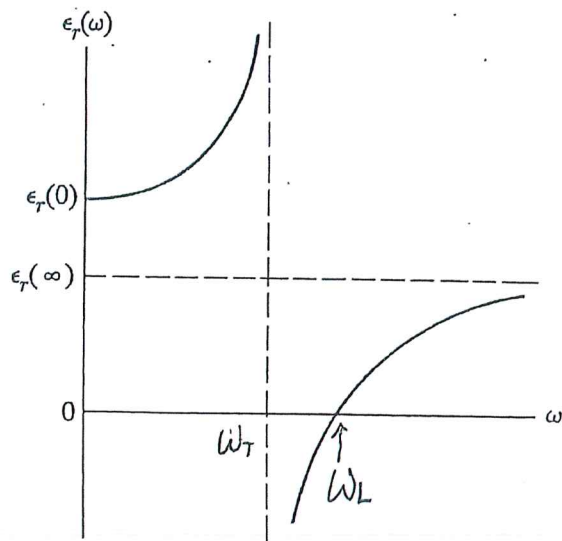
The formula is called the LST relation

Lyddane-Sachs-Teller

⁺ Up to here, ω_L is just where the reflection edge appears. Its role in $\omega(\vec{q})$ is not clear, yet.

$$W_L = \left(\frac{\varepsilon_r(0)}{\varepsilon_r(\infty)} \right)^{1/2} \cdot W_T \qquad (\text{LST relation})$$

has the following meaning at this point

① how
$\varepsilon_r(0)$ and
$\varepsilon_r(\omega)$
differ

But W_L has another
physical meaning...

② determines how much
W_L is bigger than W_T
and so the range for which $\varepsilon_r < 0$

Read ① then ②

$\underline{\text{Significance of } \omega_L}$

- ω_L (OR ω_{LO}) is the longitudinal optical phonon frequency

  (ω_T (OR ω_{TO}) is the transverse optical phonon frequency) $\rightarrow$ appeared as resonance in the forced oscillation treatment

- No net charge $\quad \vec{\nabla} \cdot \hat{\vec{D}} = 0 \quad$ (EM)

  $$\therefore \quad \varepsilon_r(\omega) \; \vec{\nabla} \cdot \vec{\hat{\mathcal{E}}} = 0 \quad (101) \quad \text{true for transverse or longitudinal}$$

  $\underbrace{\qquad}_{\substack{\text{"}0\text{"} \\ ?}} \qquad \underbrace{\qquad}_{\substack{\text{"}0\text{"} \\ ?}} \qquad$ [which one?]

  $\underbrace{\qquad\qquad}_{\text{longitudinal!}} \qquad \underbrace{\qquad\qquad}_{\text{transverse}}$

  longitudinal! requires $\varepsilon_r(\omega) = 0$

  transverse $\rightarrow$ Transverse case

  $$\vec{\nabla} \cdot \hat{\vec{D}} = 0 \implies \vec{\nabla} \cdot \vec{\hat{\mathcal{E}}} = -\frac{1}{\varepsilon_0} \vec{\nabla} \cdot \vec{P} \quad \text{for Transverse case}$$

  $\vec{q} \perp \vec{P}$

  $\underbrace{\text{ions oscillate}}$

  $\vec{q} \cdot \vec{P} = 0$

Taken from
Kittel's book
"Introduction to Solid
State Physics", Ch.14

TO phonon   LO phonon
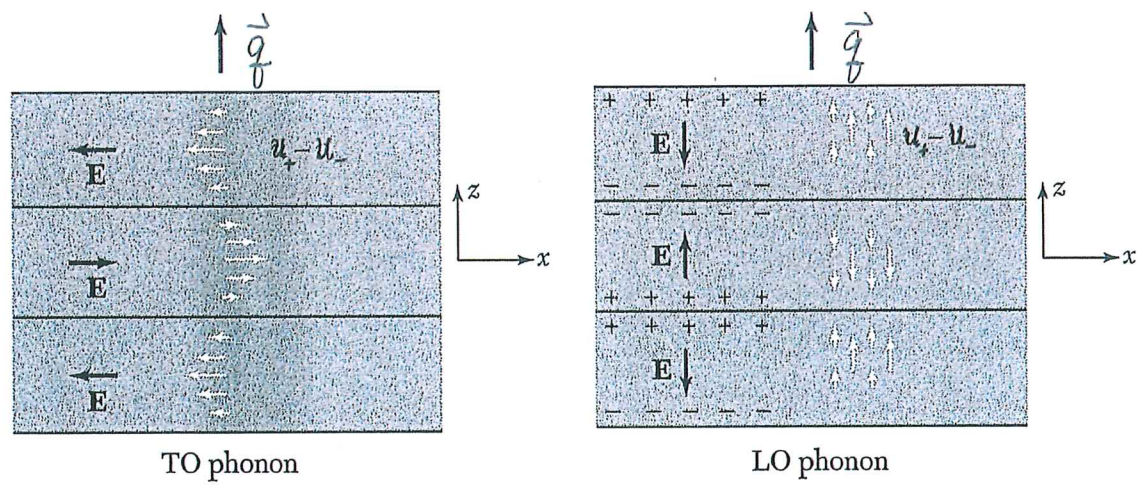
Relative displacements of the positive and negative ions at one instant of time for a wave in an optical mode traveling along the z axis. The planes of nodes (zero displacement) are shown; for long wavelength phonons the nodal planes are separated by many planes of atoms. In the transverse optical phonon mode the particle displacement is perpendicular to the wavevector $\vec{q}$; the macroscopic electric field in an infinite medium will lie only in the $\pm x$ direction for the mode shown, and by the symmetry of the problem $\partial E_x/\partial x = 0$. It follows that div $\mathbf{E} = 0$ for a TO phonon. In the longitudinal optical phonon mode the particle displacements and hence the dielectric polarization $\mathbf{P}$ are parallel to the wavevector. The macroscopic electric field $\mathbf{E}$ satisfies $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = 0$ in CGS or $\epsilon_0\mathbf{E} + \mathbf{P} = 0$ in SI; by symmetry $\mathbf{E}$ and $\mathbf{P}$ are parallel to the z axis, and $\partial E_z/\partial z \neq 0$. Thus div $\mathbf{E} \neq 0$ for an LO phonon, and $\epsilon(\omega)$ div $\mathbf{E}$ is zero only if $\epsilon(\omega) = 0$.
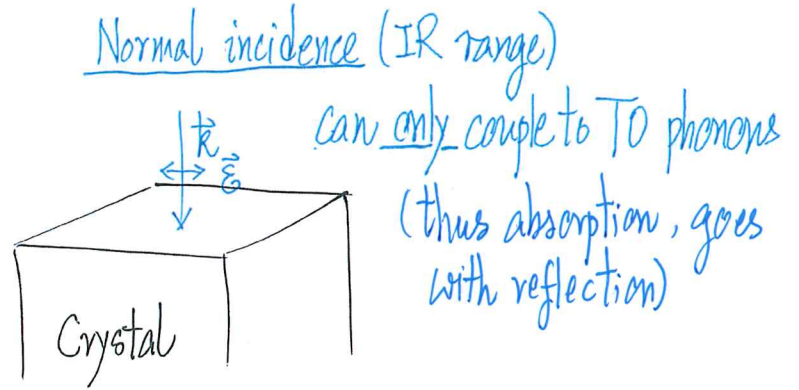
Longitudinal optical phonon

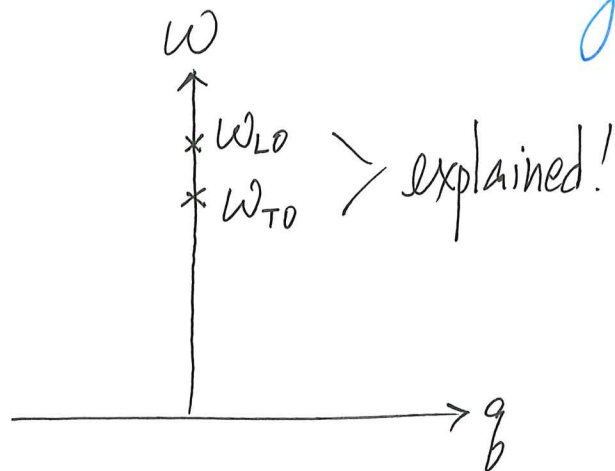Requires $\varepsilon(\omega) = 0$

thus ω_L is related to LO phonon mode

Normal incidence (IR range)

Can only couple to TO phonons
(thus absorption, goes with reflection)

Crystal

$$\varepsilon_r(\omega) \; \overrightarrow{\nabla} \cdot \overrightarrow{\varepsilon} = 0$$

$\neq 0$ for longitudinal optical mode

requires $\varepsilon_r(\omega) = 0$ to support LO mode

found $\varepsilon(\omega_{LO}) = 0$ for $\omega_{LO} = \left(\dfrac{\varepsilon_r(0)}{\varepsilon_r(\infty)} \right)^{1/2} \cdot \omega_{TO}$

recognize/identify it as $\omega_{LO}(\vec{q} = 0)$

we started off with $\overrightarrow{q} = 0$

ω

$\ast \, \omega_{LO}$

$\ast \, \omega_{TO}$ $\Big\rangle$ explained!

$\rightarrow q$

Optical mode parameters of heteropolar semiconductors

Semiconductor	ϵ_∞	ϵ_s	ω_{TO} cm^{-1}	ω_{LO} cm^{-1}	e_T^*/e
AlP	7.56	9.83	440	501	2.28
AlAs	9	11	361	404	2.3
AlSb	10.2	11.6	319	340	1.93
GaP	8.5	10.7	367	403	2.04
GaAs	10.9	12.9	269	292	2.16
GaSb	14.4	16.1	230	243	2.15
InP	9.6	12.4	304	345	2.55
InAs	12.3	14.9	219	241	2.53
InSb	15.6	17.7	185	197	2.42
ZnS	5.1	8.7	271	352	2.15
ZnSe	5.9	8.8	207	253	2.03
ZnTe	7.3	9.9	177	206	2.00
CdTe	7.3	10.8	140	170	2.35
HgTe	14.0	20.1	116	139	2.96

$$\uparrow$$
$$\mathcal{E}_s = \mathcal{E}(0)$$

From Omar, "Elementary Solid State Physics"

Semiconductors

(From Balkanski and Wallis, "Semiconductor Physics and Applications")

Ionic Crystals

Infrared Lattice Data for Ionic Crystals

	$\epsilon_r(0)$	$\epsilon_r(\infty)$	$\omega_{TO}\,10^{13}$ rad/s	$\omega_{LO}\,10^{13}$ rad/s	e^*/e
LiF	8.9	1.9	5.8	12	0.87
NaF	5.3	1.75	4.4	7.8	0.93
NaCl	5.62	2.25	3.08	5.0	0.74
NaBr	5.99	2.62	2.55	3.9	0.69
KCl	4.68	2.13	2.71	4.0	0.80
KBr	4.78	2.33	2.18		0.76
KI	4.94	2.69	1.91	2.64	0.69
RbCl	5	2.19	2.24		0.84
RbBr	5	2.33	1.69		0.82
AgCl	12.3	4.04	1.94	3.4	0.78
AgBr	13.1	4.62	1.51	2.5	0.73
CsCl	7.20	2.60	1.87	3.1	0.85
CsBr	6.51	2.87	1.39		0.78

(c) <u>Property of Light in Ionic Crystal of $\varepsilon_r(\omega)$: Polariton</u>

[when two oscillators are strongly coupled, the "new oscillators" do not resemble the original ones] (e.g. $\chi_{1S,H}^{(L)} \pm \chi_{1S,H}^{(R)}$ $\to$ bonding molecular orbital
$\to$ anti-bonding molecular orbital

$\underset{\substack{\text{atomic state} \\ \text{of left atom}}}{\uparrow} \quad \underset{\substack{\text{atomic state} \\ \text{of right atom}}}{\uparrow}$

$\therefore$ when "1-on" meets with "2-ons" $\Rightarrow$ "another-ons" (if couple strongly)

<u>Question</u>: How does light's dispersion relation behave in a medium of $\varepsilon_r(\omega)$?
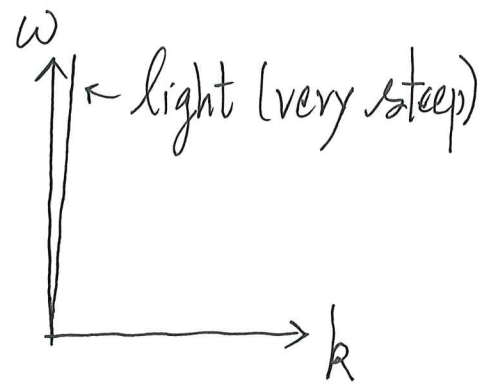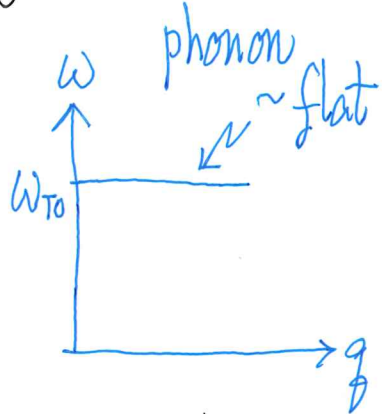
<u>Easy</u>: $\omega^2 = c^2 k^2$ in vacuum

$\omega^2 = \dfrac{c^2}{\varepsilon_r(\omega)} k^2$ in a medium of $\varepsilon_r(\omega)$ (102)   Done!

$\underbrace{\phantom{\dfrac{c^2}{\varepsilon_r(\omega)}}}$
gives $\omega(k)$

What do we expect?

- Light (transverse, _photon_) can couple with TO (transverse optical) _phonon_

- Coupling is strong when their energy and momentum are close to each other
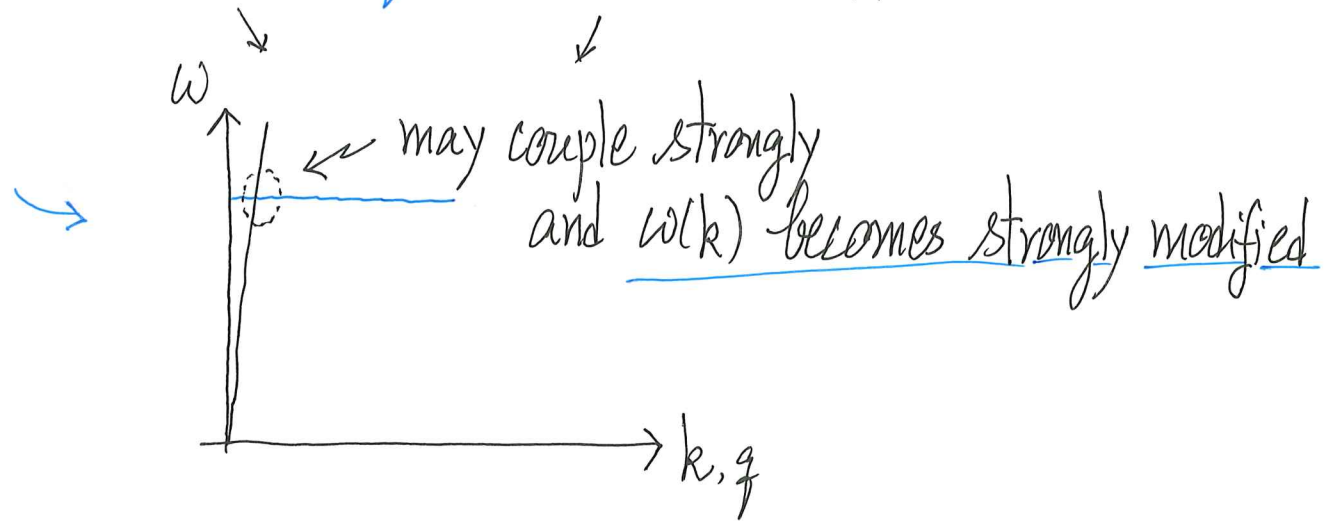
No coupling (assumed)

Recall
2×2 matrix

$$\begin{pmatrix} \omega_1 & \Delta \\ \Delta & \omega_2 \end{pmatrix}$$

$\varepsilon_r = 1$
(uncoupled)

← may couple strongly
and $\omega(k)$ becomes strongly modified

Dispersion of Light in a crystal described by $\varepsilon_r(\omega)$ is:
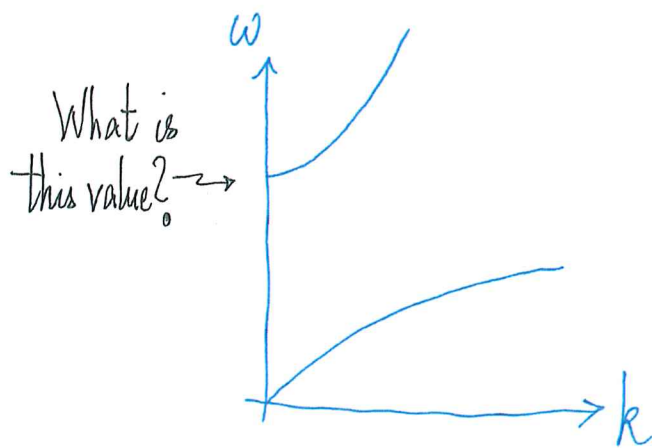
$$\omega^2 \, \varepsilon_r(\omega) = c^2 k^2 \qquad \text{(to solve for } \omega(k))$$

$$\Rightarrow \omega^2 \left[\varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 - \frac{\omega^2}{\omega_T^2}} \right] = c^2 k^2 \qquad (103)$$

(see ω^4 term, ω^2 term, ω^0 term
$\Rightarrow$ quadratic equation for $\omega^2(k)$)

• quadratic in ω^2 (two values of ω^2 for each k)

• Solve for Two branches of $\omega(k)$

how light propagates in ionic crystals

What is this value? →

after solving for $\omega(k)$ from Eq. (103)
← (strongly modified from !)

What are values of ω at $k=0$?

Plug $k=0$ in (103) : $\omega_{k=0}^2 \left[\mathcal{E}_r(\infty) + \dfrac{\mathcal{E}_r(0) - \mathcal{E}_r(\infty)}{1 - \dfrac{\omega_{k=0}^2}{\omega_T^2}} \right] = 0$ $\qquad \Rightarrow \omega_{k=0} = 0$ is a solution

$$\Rightarrow \quad \cancel{\mathcal{E}_r(\infty)} - \mathcal{E}_r(\infty) \dfrac{\omega_{k=0}^2}{\omega_T^2} + \mathcal{E}_r(0) - \cancel{\mathcal{E}_r(\infty)} = 0 \qquad \text{gives \underline{another} solution}$$

$$\Rightarrow \quad \dfrac{\omega_{k=0}}{\omega_T^2} = \left(\dfrac{\mathcal{E}_r(0)}{\mathcal{E}_r(\infty)} \right)^{1/2} \qquad \text{is the value of } \omega \text{ at } k=0$$

Comparing with LST relation, $\omega_{k=0} = \omega_L$ (or ω_{LO}) $\begin{pmatrix} \text{longitudinal}^+ \text{ optical mode} \\ \text{freq. at } q = 0 \end{pmatrix}$

(104)

this branch starts at $\rightarrow$ ω_L
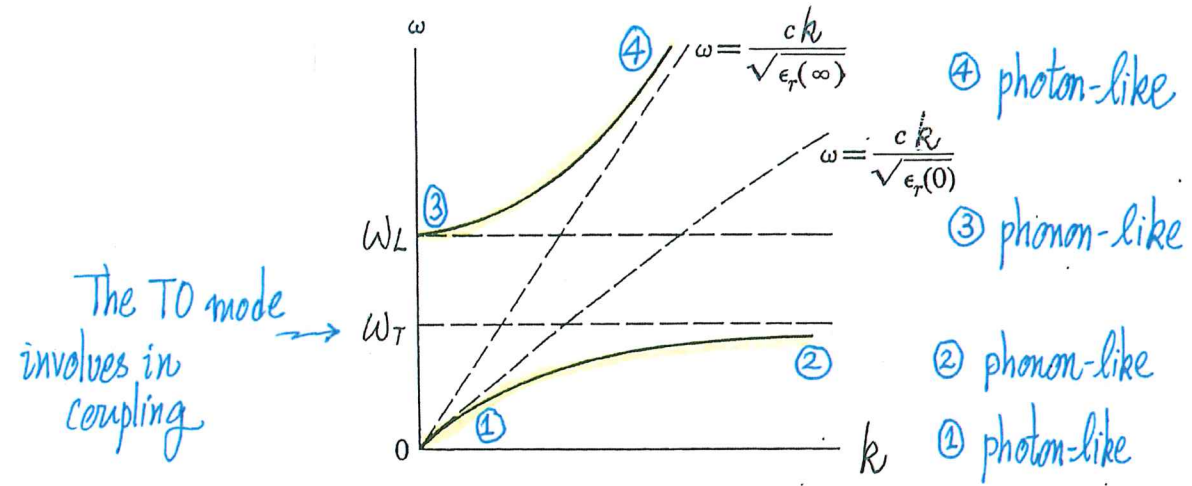
$\omega = 0$
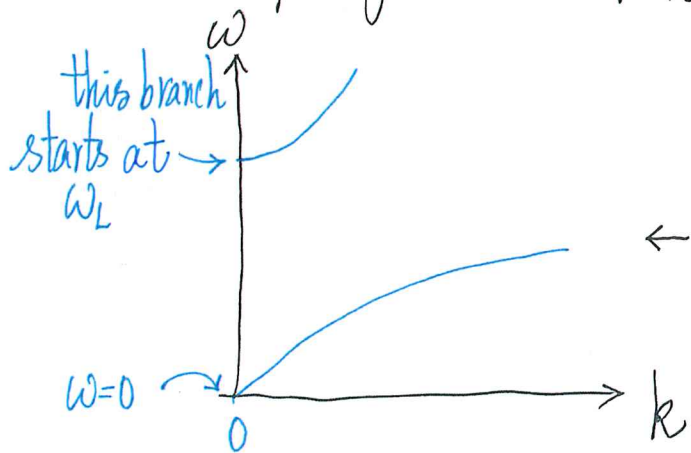
$\leftarrow$ What is this frequency?

+Be very sure that LO mode is NOT involved in this photon - phonon coupling!

These are called the <u>Dispersion Relations of Polariton</u>

Plotting out $\omega(k)$ from Eq. (61)

name given to the resulting entity due to photon (oscillator) – phonon (oscillator) coupling

④ photon-like

③ phonon-like

② phonon-like

① photon-like

The TO mode involves in coupling

All slopes (group velocity) less than c, as it should be

$$\omega = \frac{ck}{\sqrt{\epsilon_r(\infty)}}$$

$$\omega = \frac{ck}{\sqrt{\epsilon_r(0)}}$$

Dispersion curves for the polariton.   Dashed curves represent free modes, while solid curves describe interacting modes—the polariton.

[Taken from Omar, " Elementary Solid State Physics]

where coupling is strong : resulting modes are <u>neither</u> photon-like <u>nor</u> phonon-like, but picked up <u>strong mixing</u> of the two characters
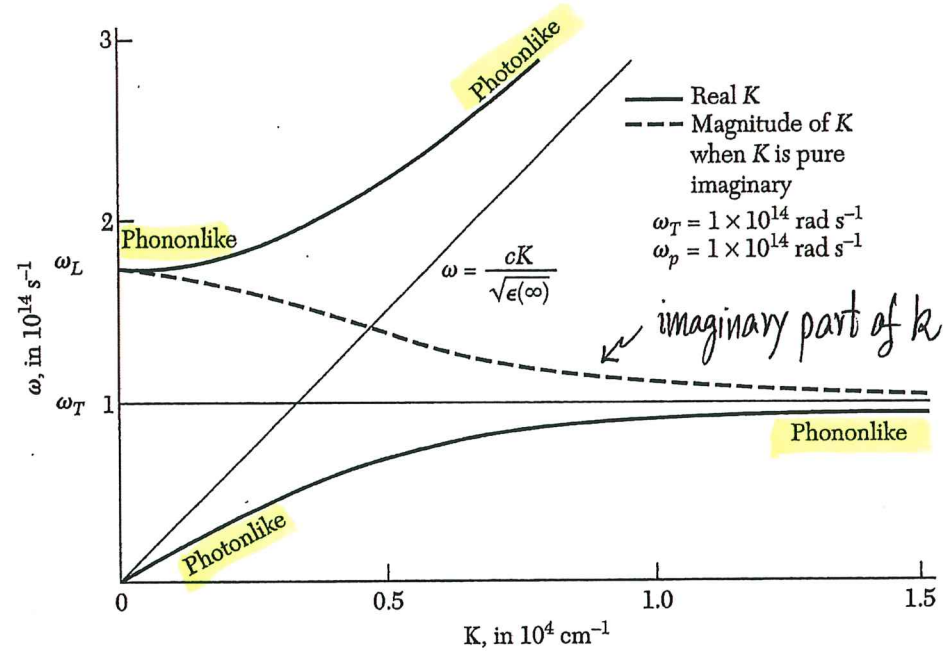
Coupled modes of photons and transverse optical phonons in an ionic crystal. The fine horizontal line represents oscillators of frequency ω_T in the absence of coupling to the electromagnetic field, and the fine line labeled $\omega = cK/\sqrt{\epsilon(\infty)}$ corresponds to electromagnetic waves in the crystal, but uncoupled to the lattice oscillators ω_T. The heavy lines are the dispersion relations in the presence of coupling between the lattice oscillators and the electromagnetic wave. One effect of the coupling is to create the frequency gap between ω_L and ω_T: within this gap the wavevector is pure imaginary of magnitude given by the broken line in the figure. In the gap the wave attenuates as $\exp(-|K|x)$, and we see from the plot that the attenuation is much stronger near ω_T than near ω_L. The character of the branches varies with K; there is a region of mixed electric-mechanical aspects near the nominal crossover. Note, finally, it is intuitively obvious that the group velocity of light in the medium is always $<c$, because the slope $\partial\omega/\partial K$ for the actual dispersion relations (heavy lines) is everywhere less than the slope c for the uncoupled photon in free space.

[Taken from Kittel, "Introduction to Solid State Physics", Ch.14]

polariton
dispersion
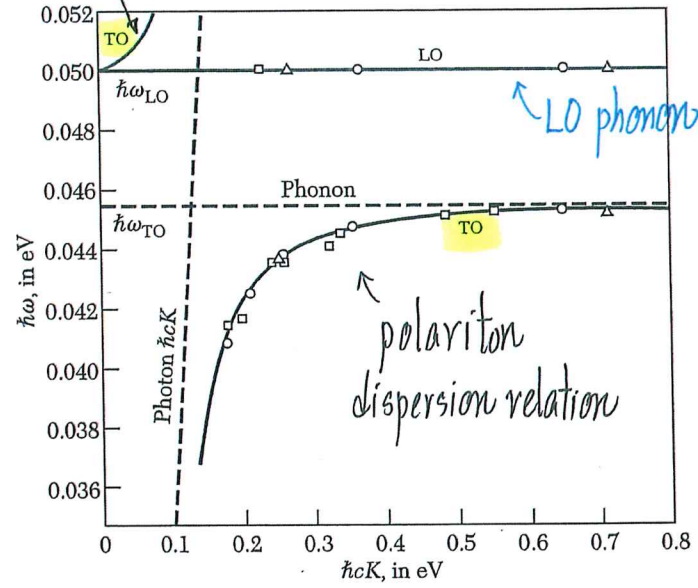
GaP (observed)

A plot of the observed energies and wavevectors of the polaritons and of the LO phonons in GaP. The theoretical dispersion curves are shown by the solid lines. The dispersion curves for the uncoupled phonons and photons are shown by the short, dashed lines.

What we discussed is real stuff!

For those interested in Optical Properties, see M. Fox, "Optical Properties of Solids".