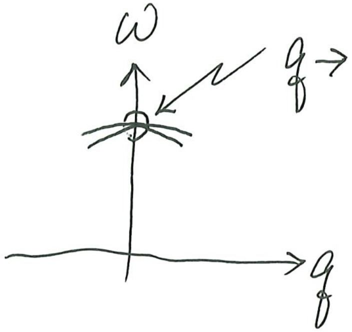
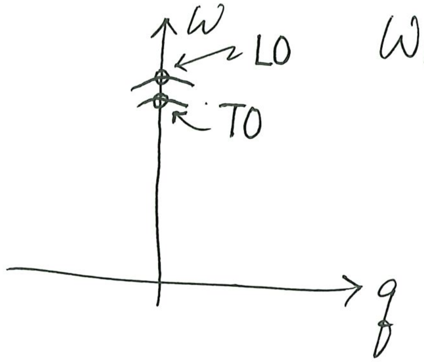
# L. Optical Branches in Crystals of Ionic Character and Lattice Optical Properties in the Infrared (IR)

## Motivation #1

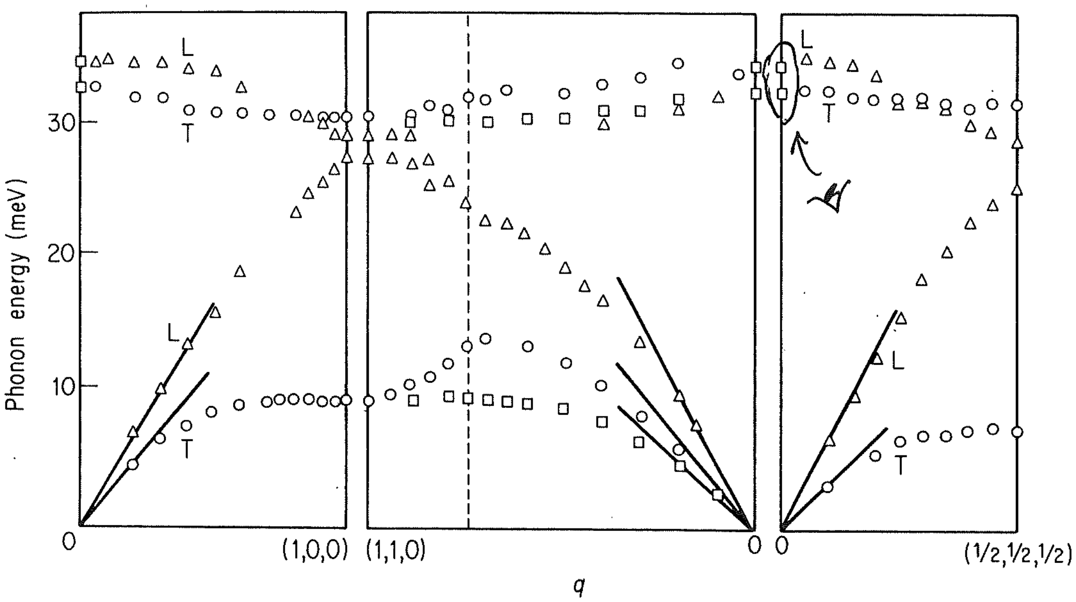
- Si, Ge



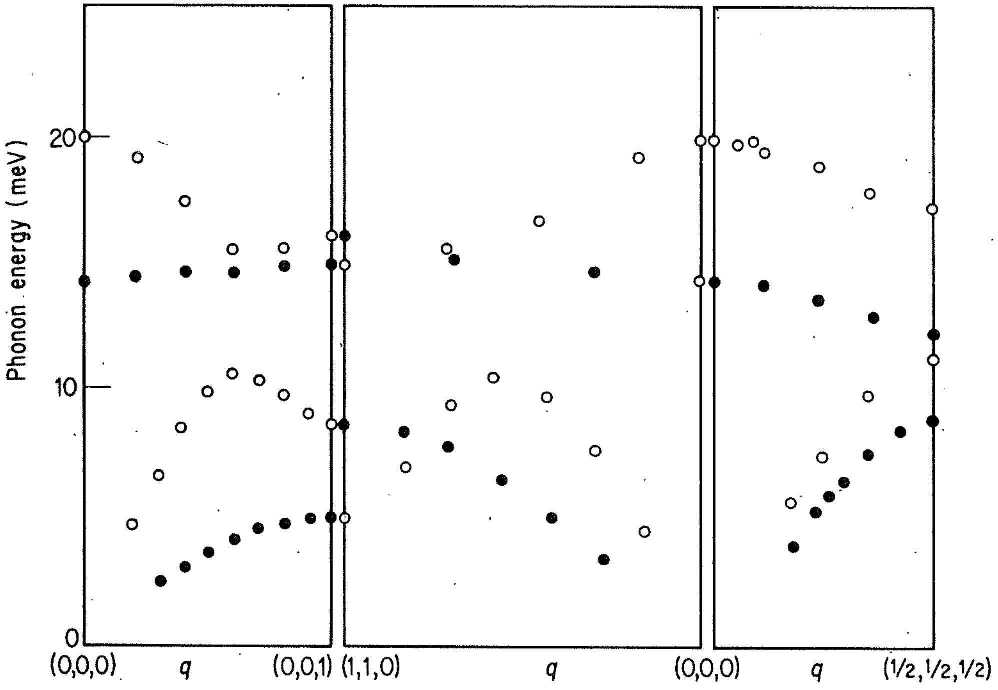
- Ionic crystals (KBr, GaAs)



$\omega_L$ and $\omega_T$ split! Why?



Spectrum of <u>GaAs</u> at room temperature



KBr

Splitting of optical branches at $\vec{q}=0$ is more apparent

# Motivation #2

- Why those branches are called "Optical branches"?
- Light interacts strongly with transverse optical branch in ionic crystals
  - strongly reflective in IR and also strong absorption
  - Physics of two coupled oscillators

phonon (oscillator)
photon (oscillator)

} could strongly mix into something very different from phonon and photon when coupling is strong "polariton"

- How the dispersion relation of light $\omega(k)$ in ionic crystals being modified by coupling with optical phonons?

## Motivation #3

- A quick look at some optical properties of solids
- A sense of dielectric function

## Be aware of sources of confusion

- "$\omega_L$" (the $q \to 0$, LO frequency) appears a special frequency in discussing $\varepsilon(\omega)$
- That special frequency turns out to be $\omega_L$
- The formulation is that of 2 atoms per unit cell now with an applied $\mathcal{E}$ field [think it as: springs + $\mathcal{E}$-field ⇒ driven (forced oscillators)]

## (a) Quick introduction on Dielectric Function

$$\underset{\text{electric displacement}}{D} = \overset{\text{dielectric constant}}{\varepsilon}\, \underset{\text{electric field}}{\mathcal{E}} = \varepsilon_r \varepsilon_0 \mathcal{E} = \varepsilon_0 \mathcal{E} + \underset{\substack{\text{Polarization} \\ \text{(electric dipole moment} \\ \text{per unit volume)}}}{P} \qquad (40)$$

assumed all parallel to each other (not tensorial $\varepsilon$)

$\varepsilon_r$ = relative dielectric constant

(OR formally relative permittivity)

$\varepsilon_r(\omega)$ is our focus [thus ignored non-locality in space]

[retained non-locality in time, and thus causality]

Depending on choices, one could take a real $\varepsilon$ and a real $\sigma$ (and a real $\mu$ (magnetism))

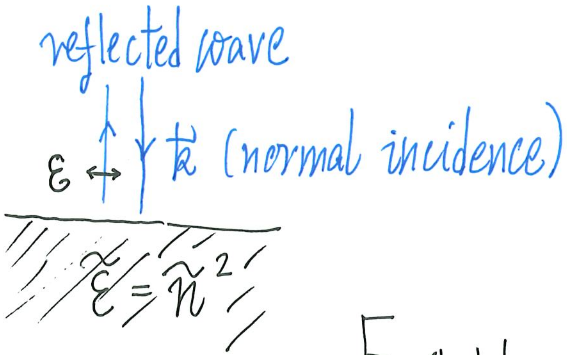
OR a complex $\tilde{\sigma}$ OR a complex $\tilde{\varepsilon}$

[there is a $\mu$ [magnetic permeability] that doesn't concern our present discussion]

Often, take $\varepsilon_r$ as a complex quantity $\tilde{\varepsilon}_r$

$$\tilde{n} = \text{complex refractive index} = \underset{\uparrow\ \text{refractive index}}{n} + i\underset{\nwarrow\ \text{extinction coefficient}}{K} \qquad (41)$$

$$\tilde{\varepsilon}_r = \tilde{n}^2 = (n+iK)^2 \quad (42) \quad \left\{ \begin{array}{l} \varepsilon_{r,1} + i\varepsilon_{r,2} = n^2 - K^2 + 2inK \\ \Rightarrow \boxed{\begin{array}{l} \varepsilon_{r1} = n^2 - K^2 \\ \varepsilon_{r2} = 2nK \end{array}} \begin{array}{l} (\text{real part of } \tilde{\varepsilon}_r) \\ (\text{imaginary part of } \tilde{\varepsilon}_r) \end{array} \end{array} \right. \quad (43)$$



$$\frac{E_{\text{reflected}}}{E_{\text{incident}}} = \underset{\uparrow\ \text{complex reflectivity amplitude } \tilde{r}(\omega)}{\tilde{r}} = \frac{1-\tilde{n}}{1+\tilde{n}} \qquad (44)\ (\text{normal incidence})^{+}$$

$$R = \text{Reflectivity} = \tilde{r}^{*}\tilde{r} = \left|\frac{1-\tilde{n}}{1+\tilde{n}}\right|^2 = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \qquad (45)$$

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[+] Experimentally, $R(\omega)$ is often measured over as wide a range of $\omega$ as possible, then the Kramers-Kronig relation can be used to obtain the complex $\tilde{r}(\omega) = \rho(\omega)e^{i\theta(\omega)}$, then everything follows.

$$\tilde{n} = n + \underbrace{iK}_{\nwarrow} \qquad (41)$$

$\underbrace{\mathcal{E}\text{-field attenuates}}$ as wave propagates

$$e^{-K\frac{\omega}{c}z} \Rightarrow \underbrace{I}_{\text{intensity}} \sim e^{-\left(2\frac{\omega}{c}K\right)z} \qquad (\because I \propto |\mathcal{E}|^2)$$

extinction coefficient

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

absorption coefficient

$$= 2kK = \frac{4\pi}{\lambda}\cdot K \qquad (46)$$

$\lambda \leftarrow$ wavelength of light in vacuum

We will find an expression for $\varepsilon_r(\omega)$ including the effects of $\underbrace{\text{ionic polarization}}$ and electronic polarization (47)

related to lattice vibrations

and apply $\varepsilon_r(\omega)$ to study light propagation in ionic crystals

Aside:

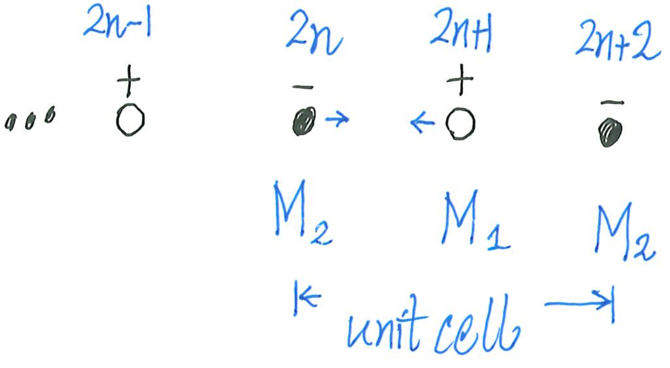
- See in Eq. (43) that $\overset{\text{real}}{\varepsilon_1}$ and $\overset{\text{imaginary}}{\varepsilon_2}$ are not independent of each other
- $n$ and $K$ form another pair
- $\tilde{r} \Rightarrow \left(\sqrt{R}\, e^{i\theta(\omega)}\right)$ and $R$ and $\theta$ form another pair

$(\varepsilon_1, \varepsilon_2)$ ; $(n, K)$ ; $(R, \theta)$ are related by the Kramers - Kronig relation that reflects casuality

e.g. knowing $\varepsilon_2(\omega)$ for ALL $\omega$'s $\Rightarrow$ knowing $\varepsilon_1$

## (b) Back to 2 atoms per unit cell: forced oscillations

Picture:



cations: $+e^*$

anions: $-e^*$

$e^*$ (a parameter, not necessarily $e$)

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

$\mathcal{E}$ = an alternating electric field

Equations of motion†:

spring constant (short-range restoring force)

$$M_1 \frac{\partial^2 u_{2n+1}}{\partial t^2} = -K\left(2u_{2n+1} - u_{2n} - u_{2n+2}\right) + e^*\mathcal{E} \qquad (48a)$$

$$M_2 \frac{\partial^2 u_{2n}}{\partial t^2} = -K\left(2u_{2n} - u_{2n-1} - u_{2n+1}\right) - e^*\mathcal{E} \qquad (48b)$$

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† Did the spring forces terms in Sec. C [free oscillations]. Now with $\mathcal{E}$ [forced oscillations]

- Take $\mathcal{E}$ to be a propagating plane wave

$$\mathcal{E} = \mathcal{E}_0 \, e^{ikz - i\omega t}$$

$\omega$ enters here as the angular frequency of the driving term

- take $\lambda \gg a$, so $\underbrace{k \to 0}$

easier case, then all $M_1$ atoms have displacement $u_+$ \
all $M_2$ atoms have displacement $u_-$ } doesn't matter where they are

$$u_+ = \underbrace{u_{0+}}_{\text{amplitude of } +e^* \text{ ions}} e^{-i\omega t} \quad ; \quad u_- = \underbrace{u_{0-}}_{\text{amplitude of } -e^* \text{ ion}} e^{-i\omega t} \qquad (49)$$

Solving for $u_{0+}$ and $u_{0-}$ in terms of $(M_1, M_2, K, \omega, \mathcal{E}_0)$ using $\overbrace{\text{Eqs. of motion}}^{\text{Eq. (48)}}$:

$$u_{0+} = \frac{e^*}{M_1} \frac{1}{(\omega_T^2 - \omega^2)} \mathcal{E}_0$$

$$u_{0-} = -\frac{e^*}{M_2} \frac{1}{(\omega_T^2 - \omega^2)} \mathcal{E}_0 \qquad (50)$$

where $\omega_T^2 = \frac{2K}{\underset{\substack{\uparrow \\ \text{reduced mass}}}{\mu}} = 2K\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \qquad (51)$

- $\omega_T^2$ came out as we solve the equations for $u_{0+}$ and $u_{0-}$ (see Eq. (51))
- Saw $\omega_T = \sqrt{\dfrac{2K}{\mu}}$ as the $q=0$ optical branch frequency (sometimes $\omega_{TO}$)

(labelled "T" because it is the TO $q=0$ frequency)

- Next, we want to get $\varepsilon_r(\omega)$

$$\varepsilon_r \varepsilon_0 \mathcal{E} = \varepsilon_0 \mathcal{E} + P \quad (40)$$

$$\Rightarrow \varepsilon_r = 1 + \frac{P}{\varepsilon_0 \mathcal{E}} \leftarrow \text{need to consider Polarization}$$

Ionic Polarization

$n$ = # unit cells / Volume

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

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

$$= \frac{n e^{*2}}{\mu}\cdot\frac{2}{(\omega_T^2-\omega^2)}\mathcal{E}_0 = \frac{n e^{*2}}{\mu\omega_T^2}\cdot\left(\frac{2}{1-\frac{\omega^2}{\omega_T^2}}\right)\mathcal{E}_0 \quad (52)$$

"per unit volume" in it ($\because n$)

[c.f. EM: $P_{ionic} = \chi_{ionic}\varepsilon_0\mathcal{E}$, we got $\chi_{ionic}$]

$P_{el}$ = <u>electronic polarization</u> (from electrons in atomic shells)

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

$$\boxed{\varepsilon_r(\omega) = 1 + \frac{P_{el}}{\varepsilon_0 \mathcal{E}} + \frac{2ne^{*2}}{\varepsilon_0 \omega_T^2 \mu} \cdot \frac{1}{1 - \frac{\omega^2}{\omega_T^2}}} \quad (53)$$

Key Result

Then, write $\varepsilon_r(\omega)$ into a form that carries <u>measurable quantities</u>

(i) $\omega = 0$, static $\varepsilon_r$ ($\varepsilon_r(0)$)

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

$$\varepsilon_r(0) = 1 + \frac{P_{el}}{\varepsilon_0 \mathcal{E}} + \frac{2ne^{*2}}{\varepsilon_0 \omega_T^2 \mu} \quad (54)$$

↑ static dielectric function

(ii) $\omega \to \infty$, ions can't follow (not contributing)

$$\varepsilon_r(\underset{\substack{\uparrow \\ \text{high frequency}}}{\infty}) = 1 + \frac{P_{el}}{\varepsilon_0 \mathcal{E}} \qquad (55)$$

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

$$\varepsilon_r(\omega) = \underbrace{1 + \frac{P_{el}}{\varepsilon_0 \mathcal{E}}}_{\varepsilon_r(\infty)} + \underbrace{\frac{2ne^{*2}}{\varepsilon_0 \omega_T^2 \mu}}_{\varepsilon_r(0)-\varepsilon_r(\infty)} \cdot \frac{1}{1-\frac{\omega^2}{\omega_T^2}} \qquad (53)$$

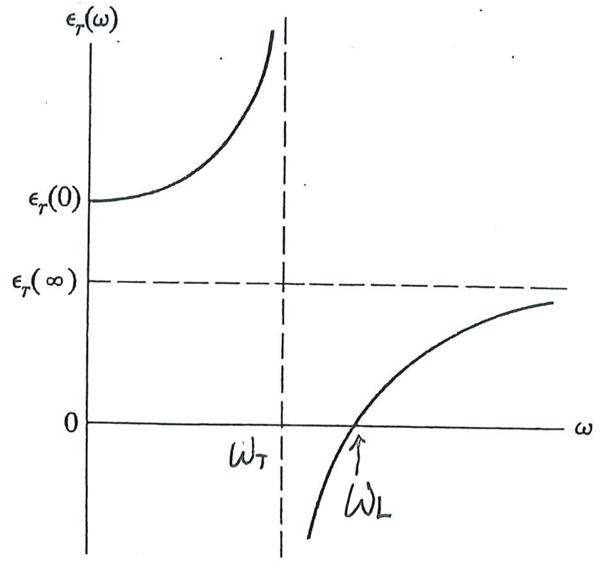
The Ionic Polarization term is of the typical Lorentz Oscillator form

$$\Rightarrow \boxed{\varepsilon_r(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 - \frac{\omega^2}{\omega_T^2}}} \qquad (54)$$

Key Result

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

$$\varepsilon_r(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 - \frac{\omega^2}{\omega_T^2}} \qquad (54)$$



$\varepsilon_r > 0$ propagating

$\varepsilon_r < 0$ range (be careful)

highly reflective

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

Call the frequency at which $\varepsilon_r = 0$ the frequency $\omega = \omega_L$

i.e. $\varepsilon_r(\omega_L) = 0$ (55)

(defines $\omega_L$)

(i) a symbol

(ii) turns out to be LO branch $q \to 0$ frequency

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

$\varepsilon_r(\omega) = \tilde{n}^2 \Rightarrow \tilde{n}$ purely imaginary in this range

$$\tilde{n} = \underbrace{n}_{0} + i\underbrace{\kappa}_{\neq 0} \leftarrow$$ "kappa" [extinction coefficient]

From Eq.(45): $R = \dfrac{(n-1)^2+\kappa^2}{(n+1)^2+\kappa^2} = 1$ (total reflection)[†]

$\kappa \neq 0 \Rightarrow$ attenuation

(can't propagate through thick samples)

$$\underset{\substack{\uparrow \\ \text{absorption}}}{\alpha_{ab}} = 2\left(\frac{\omega}{c}\right)\underbrace{\kappa}_{\neq 0}$$

(thus explained observed behavior in IR for ionic crystals)

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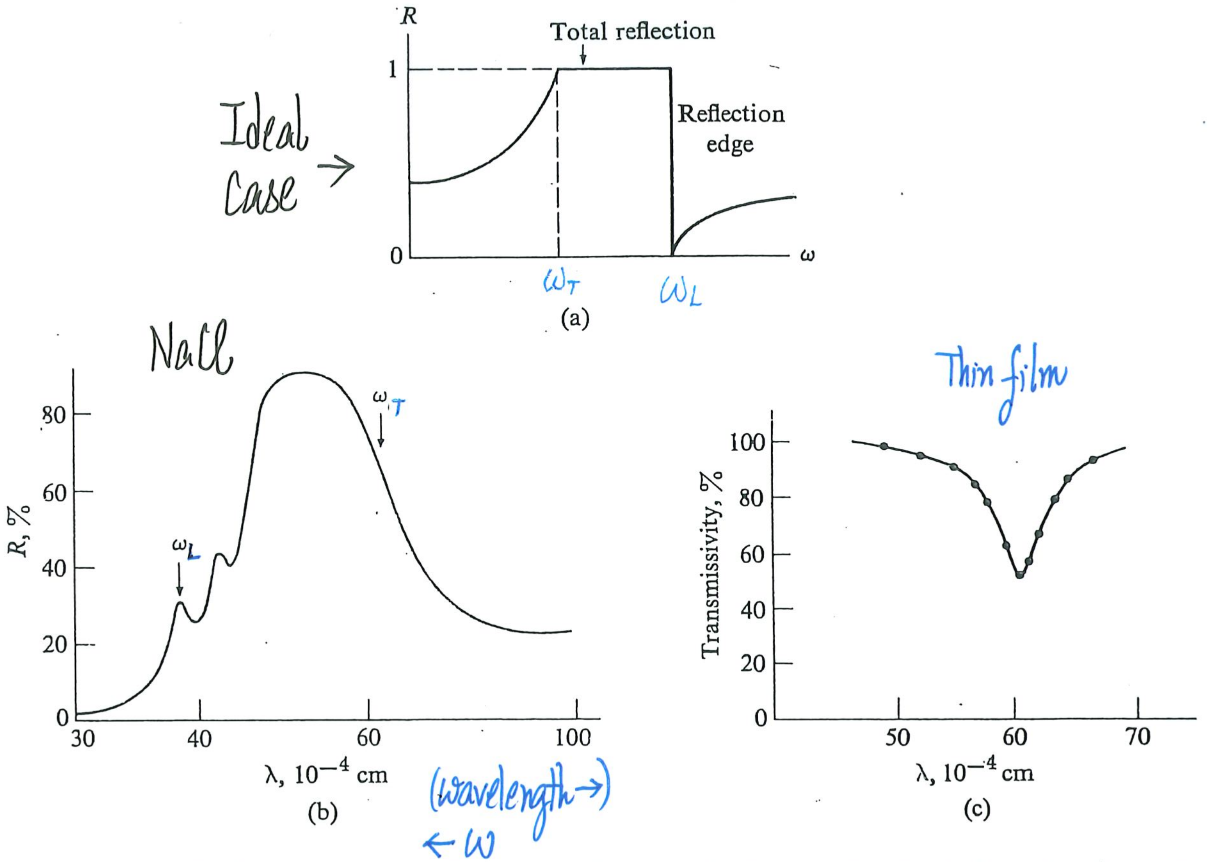
[†] For those who have the experience of working with metals, it is the same physics for $\omega < \omega_p$ [the plasma frequency], only that the frequencies are in visible range. Here, it is in IR.

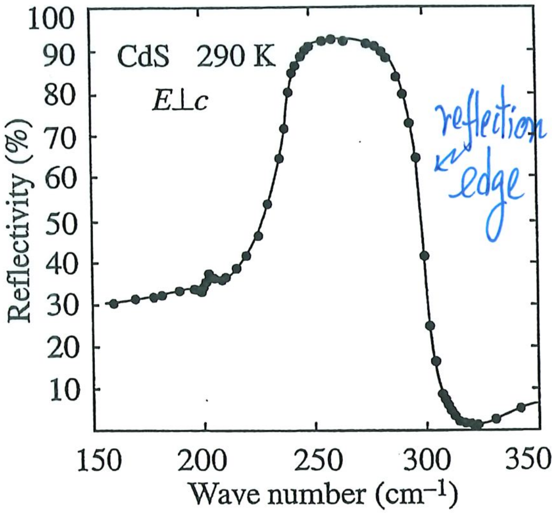


(a) Reflectivity versus frequency for an ideal crystal. (b) Infrared reflectivity versus wavelength for NaCl at room temperature. The frequencies $\omega_t$ and $\omega_l$ correspond to $\lambda = 61$ and $38 \times 10^{-4}$ cm, respectively. (c) Infrared transmissivity versus wavelength for an NaCl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

As $\omega$ goes from $\omega < \omega_L$ $(\varepsilon < 0)$ to $\omega > \omega_L$ $(\varepsilon > 0)$, R changes behavior qualitatively (reflection edge)

$\alpha = 2k \cdot \underset{\substack{\uparrow \\ K \text{ very big at } \omega \sim \omega_T}}{K}$

Also observed
in semiconductors
CdS



Reflectivity versus wave number for CdS at 290 K

Features rounded off in real materials [damping terms in Eq. of motion]

- We included only driving force in the equations of motion
- But excluded damping terms (phonons scattered off something)
- But damping ⇒ damped forced oscillators

$$\underset{\substack{\uparrow\\ \text{real part}}}{\varepsilon_{r1}(\omega)} = \varepsilon(\infty) + \frac{(\varepsilon(0)-\varepsilon(\infty))\,\omega_T^2\,(\omega_T^2-\omega^2)}{(\omega_T^2-\omega^2)^2+\omega^2\Gamma^2} \;;\; \underset{\substack{\uparrow\\ \text{imaginary part}}}{\varepsilon_{r2}(\omega)} = \frac{(\varepsilon(0)-\varepsilon(\infty))\,\overset{\swarrow\text{damping}}{\Gamma}\,\omega\,\omega_T^2}{(\omega_T^2-\omega^2)^2+\omega^2\Gamma^2} \qquad (56)$$

Defined $\omega_L$ by $\varepsilon_r(\omega_L) = 0$

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

$$\Rightarrow \boxed{\omega_L = \left(\frac{\varepsilon_r(0)}{\varepsilon_r(\infty)}\right)^{1/2} \cdot \omega_T} \qquad (57)$$

more contributions

$$\varepsilon_r(0) > \varepsilon_r(\infty)$$

electronic only

$$\Rightarrow \omega_L > \omega_T$$

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

This is the splitting of the $q=0$ optical modes[+]!

The formula is called the $\underbrace{\text{LST}}_{\text{Lyddane-Sachs-Teller}}$ relation.

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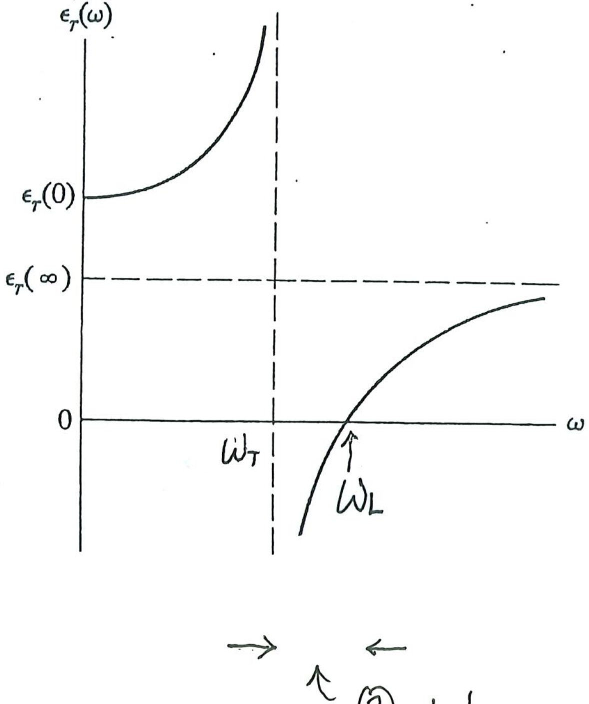
[+] Up to here, $\omega_L$ is just where the reflection edge appears. Its role in $\omega(\vec{q})$ is not clear.

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

has the following meaning at this point

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



② determines how much $\omega_L$ is bigger than $\omega_T$ and so the range for $\varepsilon_r < 0$

But $\omega_L$ has another physical meaning...

Read ① then ②

## Significance of $\omega_L$

- $\omega_L$ (OR $\omega_{LO}$) is the longitudinal optical phonon frequency

  ($\omega_T$ (OR $\omega_{TO}$) is the transverse optical phonon frequency) → appeared as resonance in the forced oscillation treatment

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

$$\therefore \quad \underbrace{\varepsilon_r(\omega)}_{= 0\,?} \; \underbrace{\vec{\nabla}\cdot\vec{\mathcal{E}}}_{= 0\,?} = 0 \qquad (58)$$

true for transverse or longitudinal

[which one?]

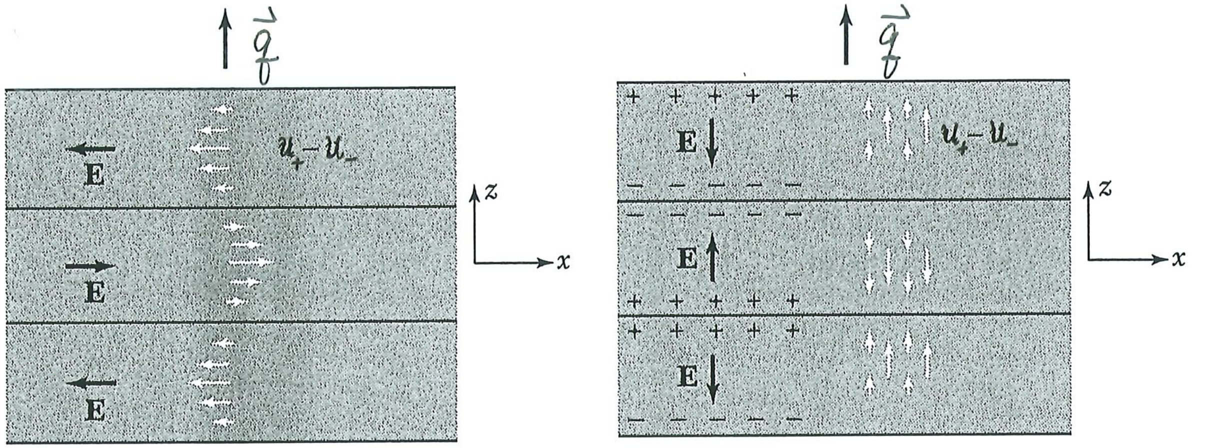
longitudinal! → requires $\varepsilon_r(\omega) = 0$

transverse → Transverse case

$$\vec{\nabla}\cdot\vec{D} = 0 \Rightarrow \vec{\nabla}\cdot\vec{\mathcal{E}} = \overbrace{-\frac{1}{\varepsilon_0}\vec{\nabla}\cdot\vec{P}}^{\text{ions oscillate } \vec{q}\cdot\vec{P} = 0}$$

for transverse case

Taken from Kittel's book



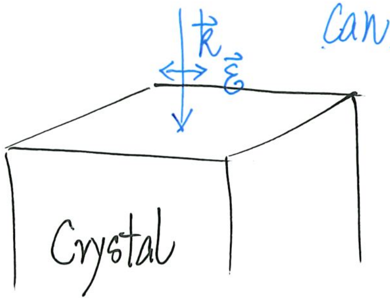
TO phonon

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 $\epsilon(\omega) = 0$.

Normal incidence (IR range)

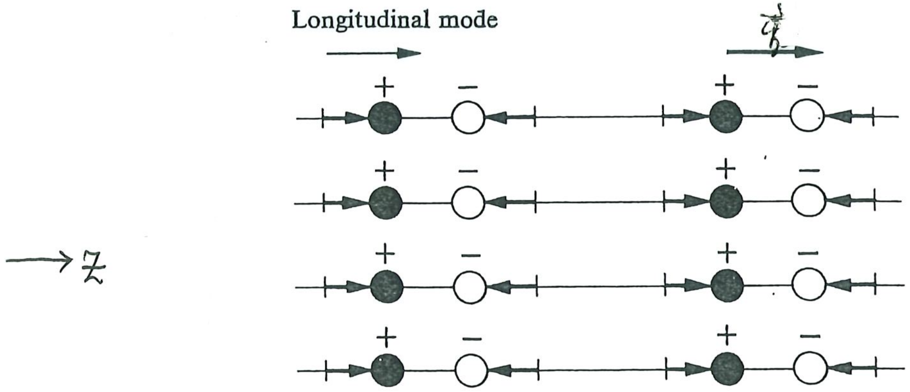
can only couple to TO phonons



Requires $\varepsilon(\omega) = 0$

thus $\omega_L$ is related to LO phonon mode

# Longitudinal Mode



Bunching of charges in the longitudinal mode.

Still has

$$\underbrace{\varepsilon_r(\omega)}\;\overbrace{\vec{\nabla}\cdot\vec{\mathcal{E}}} = 0$$

picks up $\underbrace{\vec{\nabla}\cdot\vec{\mathcal{E}}^{L}}_{\neq 0}$

requires

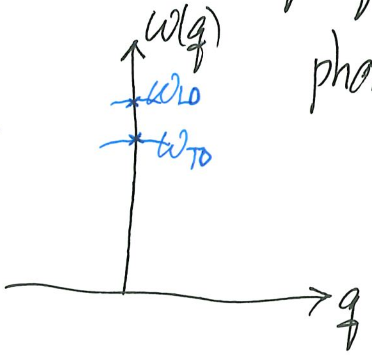
$$\boxed{\varepsilon_r(\omega) = 0 \text{ to support longitudinal mode}}$$

to satisfy the equation

∴ $\varepsilon_r(\omega_L) = 0$ obtained from $\varepsilon_r(\omega)$ gives the LO frequency

∴ $\omega_{LO} = \left(\dfrac{\varepsilon(0)}{\varepsilon(\infty)}\right)^{1/2}\omega_{TO} > \omega_{TO}$ ⇒

(LST relation again)



phonon dispersion

## Aside

- For vector field $\vec{\mathcal{E}}$ related to physical phenomena (not necessarily electric field)

Can decompose $\vec{\mathcal{E}}$ into two parts

$$\vec{\mathcal{E}} = \vec{\mathcal{E}}^{L} + \vec{\mathcal{E}}^{T} \qquad (59)$$

(without referring to a 3rd vector such as $\vec{k}$ or $\vec{q}$)

where $\vec{\mathcal{E}}^{L}$ has the property $\vec{\nabla} \times \vec{\mathcal{E}}^{L} = 0$ (called longitudinal part)

$\vec{\mathcal{E}}^{T}$ has the property $\vec{\nabla} \cdot \vec{\mathcal{E}}^{T} = 0$ (called transverse part)

Using this decomposition, we have

$$\vec{\nabla} \cdot \vec{\mathcal{E}} = \vec{\nabla} \cdot \left( \vec{\mathcal{E}}^{L} + \vec{\mathcal{E}}^{T} \right) = \vec{\nabla} \cdot \vec{\mathcal{E}}^{L}$$

$$\vec{\nabla} \times \vec{\mathcal{E}}^{T} = \vec{\nabla} \times \left( \vec{\mathcal{E}}^{L} + \vec{\mathcal{E}}^{T} \right) = \vec{\nabla} \times \vec{\mathcal{E}}^{T}$$

Useful in formal treatment of EM and Optical Properties of Solids

Semiconductors

(From Balkanski and Wallis)

Optical mode parameters of heteropolar semiconductors

| Semiconductor | $\epsilon_\infty$ | $\epsilon_s$ | $\omega_{TO}$ cm$^{-1}$ | $\omega_{LO}$ 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 |

↑

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

Ionic Crystals

Infrared Lattice Data for Ionic Crystals

|  | $\epsilon_r(0)$ | $\epsilon_r(\infty)$ | $\omega_T$, $10^{13}$ rad/s | $\omega_L$, $10^{13}$ 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 |

From Omar, "Elementary Solid State Physics"

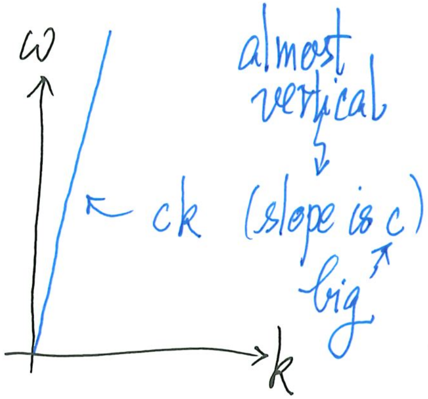
## (c) Coupling of Light and TO phonon modes: Polariton

**Question:** Influence of (Transverse) Optical Phonons on a Transverse Electromagnetic wave propagating in the crystal?

**Answer:**

Light in vacuum: $\omega^2 = c^2 k^2$

OR $\omega = ck$ gives $\omega(k)$



Light in a medium: $\omega^2 = \dfrac{c^2}{\varepsilon_r(\omega)} k^2$

OR $$\omega = \frac{c}{\sqrt{\varepsilon_r(\omega)}}\, k \quad (60)$$ dispersion relation $\omega(k)$ is modified by the medium's $\varepsilon_r(\omega)$

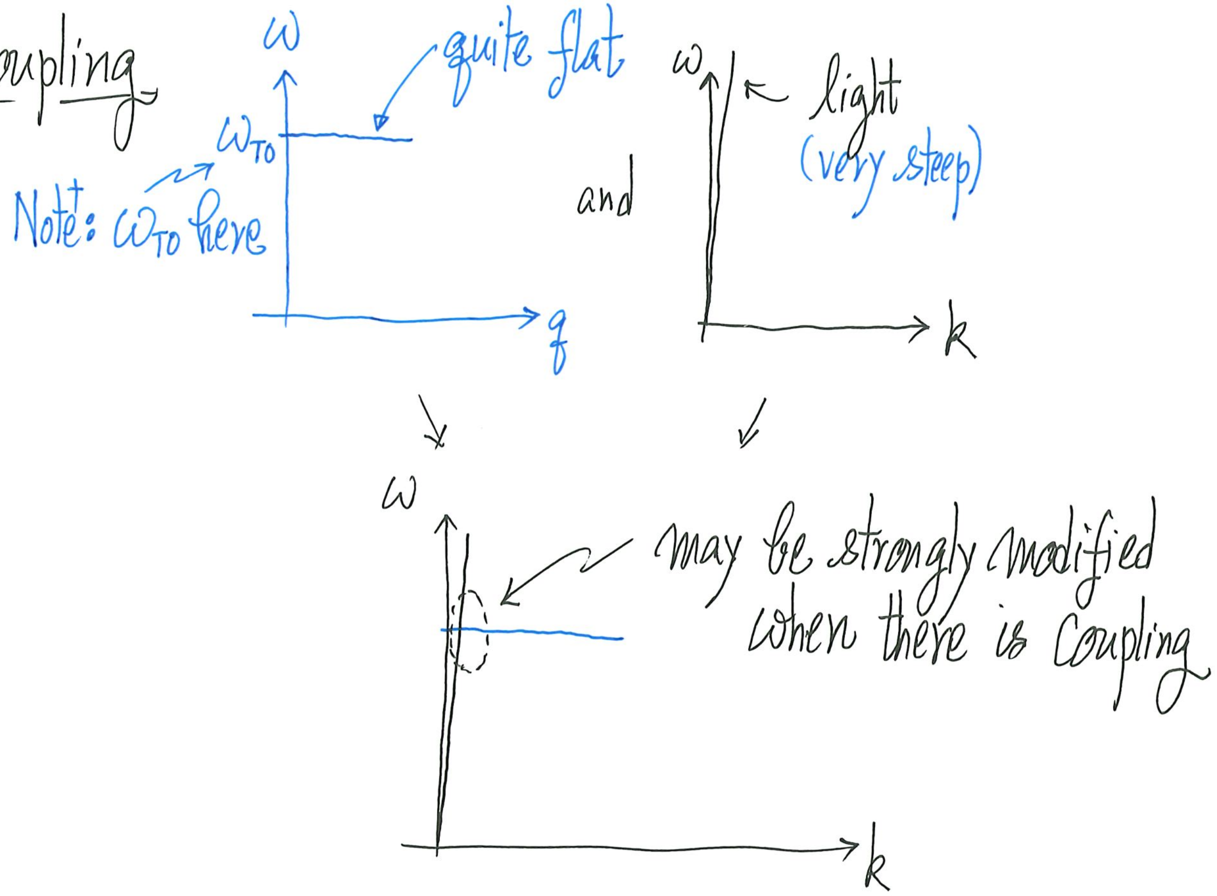
From Eq. (54): $$\varepsilon_r(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 - \frac{\omega^2}{\omega_T^2}}$$

→ included ionic Polarization

→ couples to Transverse EM waves

Expect light (photon) and optical vibrations (phonons) to couple strongly under situation conditions (c.f. $\begin{pmatrix}\varepsilon_a & \Delta \\ \Delta & \varepsilon_b\end{pmatrix}$ problem)

No coupling



quite flat

light (very steep)

Note†: $\omega_{TO}$ here

may be strongly modified when there is coupling

---

† It is the TO modes coupled to EM waves. This point is stressed here because <u>the Result</u> of coupling leads to the appearance of $\omega_L$ in the answer!

Dispersion of Light in a crystal described by $\varepsilon_r(\omega)$ is:

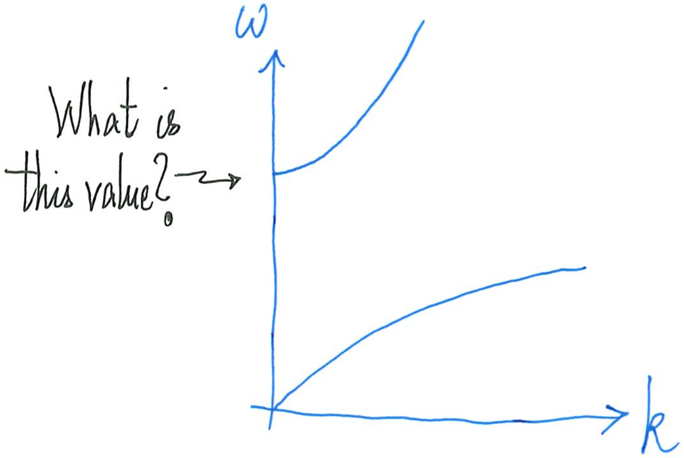
$$\omega^2\,\varepsilon_r(\omega) = c^2 k^2$$

(to solve for $\omega(k)$)

$$\Rightarrow \underbrace{\omega^2\left[\varepsilon_r(\infty) + \frac{\varepsilon_r(0)-\varepsilon_r(\infty)}{1-\frac{\omega^2}{\omega_T^2}}\right] = c^2 k^2}_{} \qquad (61)$$

(see $\omega^4$ term, $\omega^2$ term, $\omega^0$ term $\Rightarrow$ <u>quadratic equation</u> for $\omega^2(k)$)

- quadratic in $\omega^2$
- Solve for $\underbrace{\text{Two branches of } \omega(k)}_{\text{how light propagates in ionic crystals (e.g. GaAs)}}$



after solving for $\omega(k)$ from Eq.(61)

(strongly modified from  !)

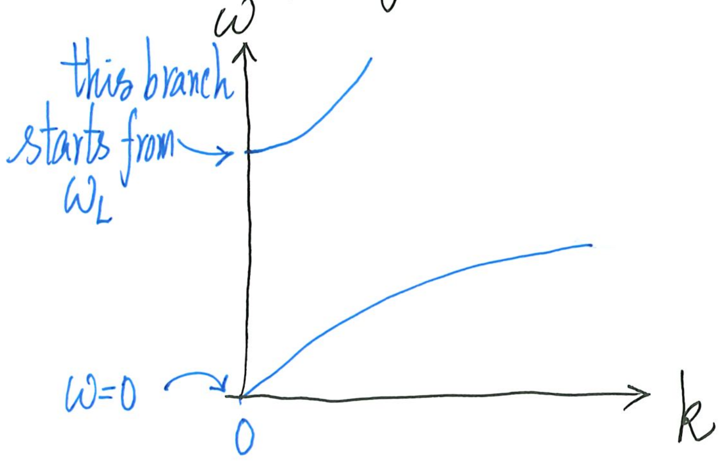
What are values of $\omega$ at $k=0$?

$$\omega_{k=0}^2\left[\varepsilon_r(\infty)+\frac{\varepsilon_r(0)-\varepsilon_r(\infty)}{1-\frac{\omega_{k=0}^2}{\omega_T^2}}\right]=0 \quad \Rightarrow \omega_{k=0}=0 \text{ is a solution}$$

$$\Rightarrow \quad \cancel{\varepsilon_r(\infty)}-\varepsilon_r(\infty)\frac{\omega_{k=0}^2}{\omega_T^2}+\varepsilon_r(0)-\cancel{\varepsilon_r(\infty)}=0 \quad \text{gives \underline{another} solution}$$

$$\Rightarrow \quad \frac{\omega_{k=0}}{\omega_T^2}=\left(\frac{\varepsilon_r(0)}{\varepsilon_r(\infty)}\right)^{1/2} \quad \text{is the value of } \omega \text{ at } k=0$$

Comparing with LST relation, $\omega_{k=0}=\omega_L$ (or $\omega_{LO}$) (62) (longitudinal$^+$ optical mode freq. at $q=0$)



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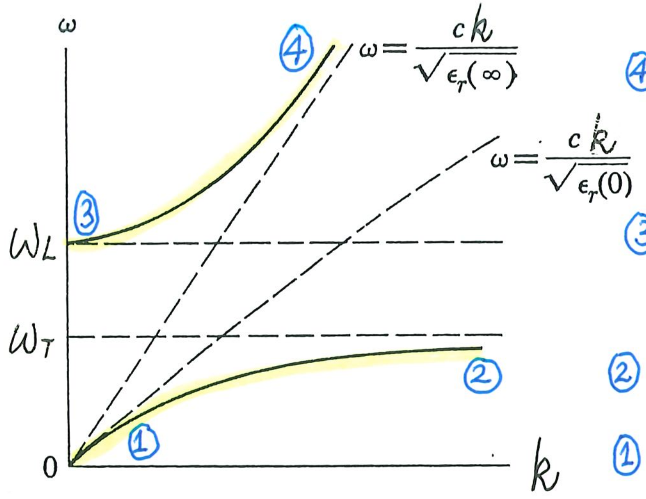
$^+$Be very sure that LO mode is NOT involved in this photon-phonon coupling!

These are called the Dispersion Relations of Polariton

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

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



The TO mode involves in coupling

④ photon-like

③ phonon-like

② phonon-like

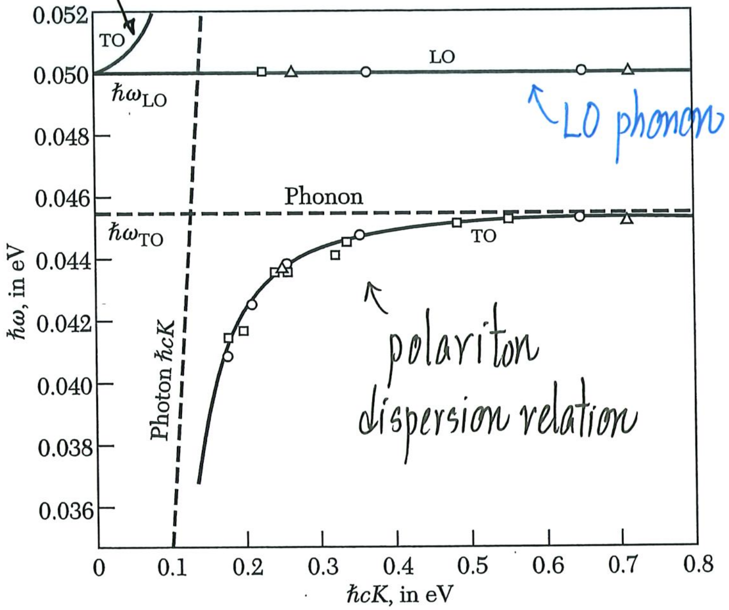
① photon-like

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

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

where coupling is strong: resulting modes are neither photon-like nor phonon-like, but picked up strong mixing of the two characters

# 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.

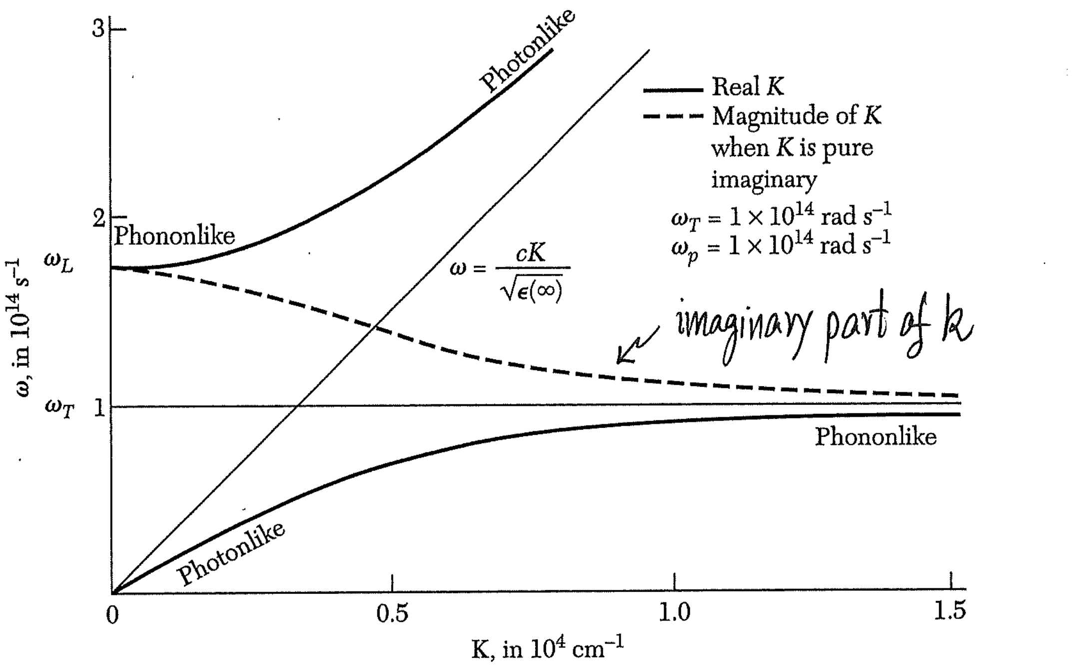
What we discussed is real stuff!

There are no modes for $\underbrace{\omega_T < \omega < \omega_L}_{\text{already knew that by behavior of } \varepsilon_r(\omega)}$

$$\omega^2 \left[ \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 - \frac{\omega^2}{\omega_T^2}} \right] = c^2 k^2 \qquad (61)$$

What if we plug in a value within $\omega_T < \omega < \omega_L$ and solve for $k$?

- No propagation $\Rightarrow$ $k$ is purely imaginary (recall $n = 0$, $\kappa \neq 0$)
- Eq. (61) gives $\underbrace{i|k|}_{\text{will depend on } \omega \, [\omega_T < \omega < \omega_L]}$ for $\omega$ inside "gap"



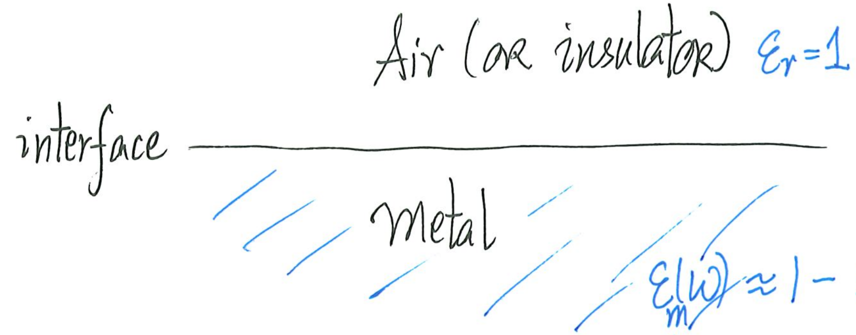
imaginary part of k

Coupled modes of photons and transverse optical phonons in an ionic crystal. The fine horizontal line represents oscillators of frequency $\omega_T$ 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 $\omega_T$. 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 $\omega_L$ and $\omega_T$: 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 $\omega_T$ than near $\omega_L$. 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.

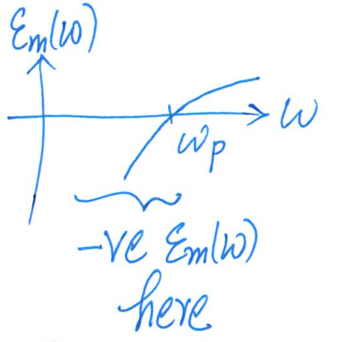
[Taken from Kittel's book]

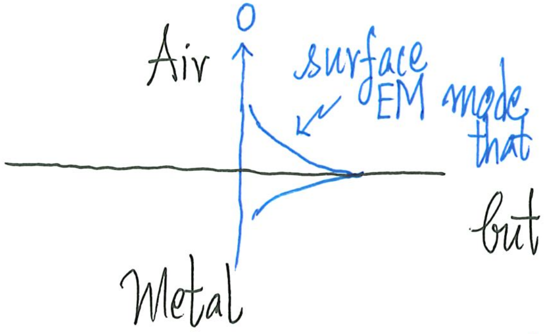
## Remarks

1/. Interesting, the same idea works for something called Surface Plasma Oscillations or Surface Plasmon or Surface Plasmon Polariton (SPP)



$$\underset{\substack{\uparrow\\ \text{metal}}}{\varepsilon_m(\omega)} \approx 1 - \frac{\omega_p^2}{\omega^2}$$

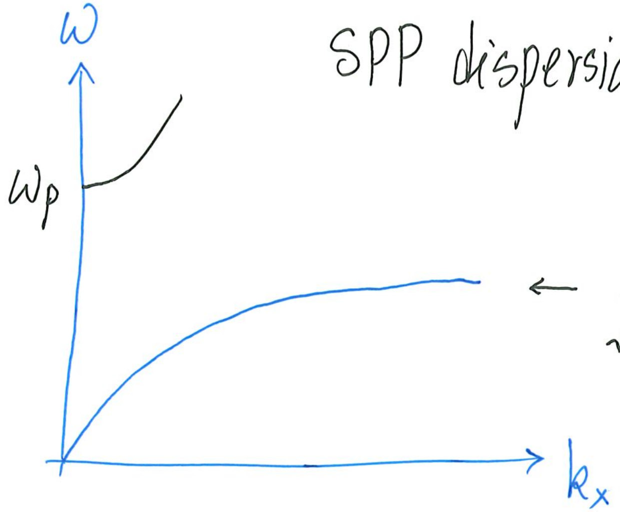




that decays ($\varepsilon$-field) to zero away from interface but it can propagate along the interface

$$\underset{\substack{\nearrow\\ \text{wave vector along}\\ \text{interface}}}{k_x^2} = \frac{\omega^2}{c^2}\,\frac{\varepsilon_{air}\left(1 - \frac{\omega_p^2}{\omega^2}\right)}{\left(\varepsilon_{air} + 1 - \frac{\omega_p^2}{\omega^2}\right)} \Rightarrow \omega(k_x)$$

# SPP dispersion relation

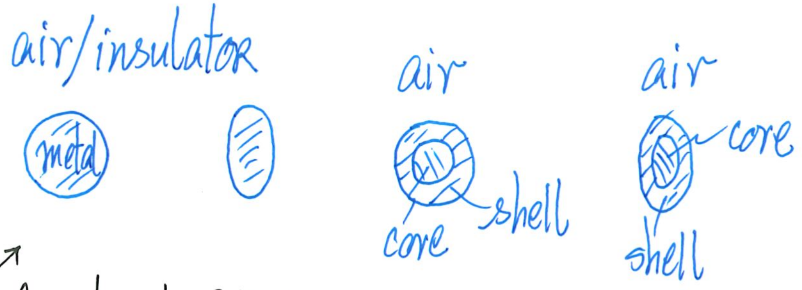


← $\frac{\omega_p}{\sqrt{\varepsilon_{air}+1}} = \frac{\omega_p}{\sqrt{2}}$

↕ $\frac{\omega_p}{\sqrt{2}} < \omega < \omega_p$ (no modes)

Further development :

<u>LSSP</u>

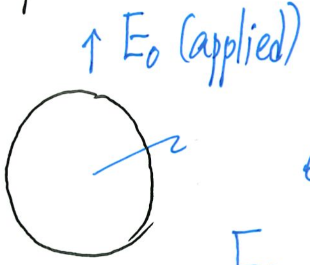


nanoparticles

↗ <u>localized</u> SPP
(very hot area)

→ different physics here

Nanophotonics



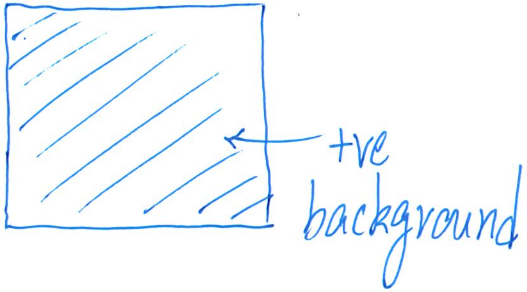
electrons collective motion

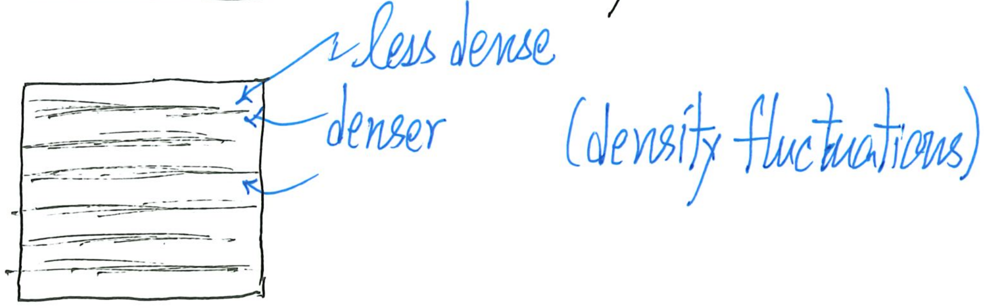
$$E_{inside} = \frac{3}{\varepsilon_{metal}+2} E_0$$

Resonance when $\underbrace{\varepsilon_{metal}}_{\text{can be negative}} + 2 \approx 0$ or $\omega \approx \frac{\omega_p}{\sqrt{3}}$

"Plasma": Neutral overall, charged entities (+ve & -ve), at least one type can move

Simplest Picture: Positive Background fixed and smeared out (Jellium)





background and electron fluctuations will work to return the electron density to uniform (pull-back)

(Coulomb interaction in work)

→ overshoot → full back → overshoot → ...

plasma oscillation (quanta is "plasmon")

# Nanoparticles [Gold particles]

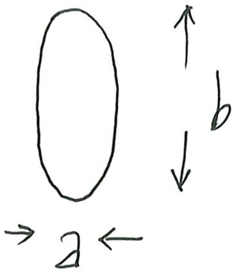
spherical

$$\frac{\omega_p^{(\text{bulk Au})}}{\sqrt{3}}$$

↑ related to shape

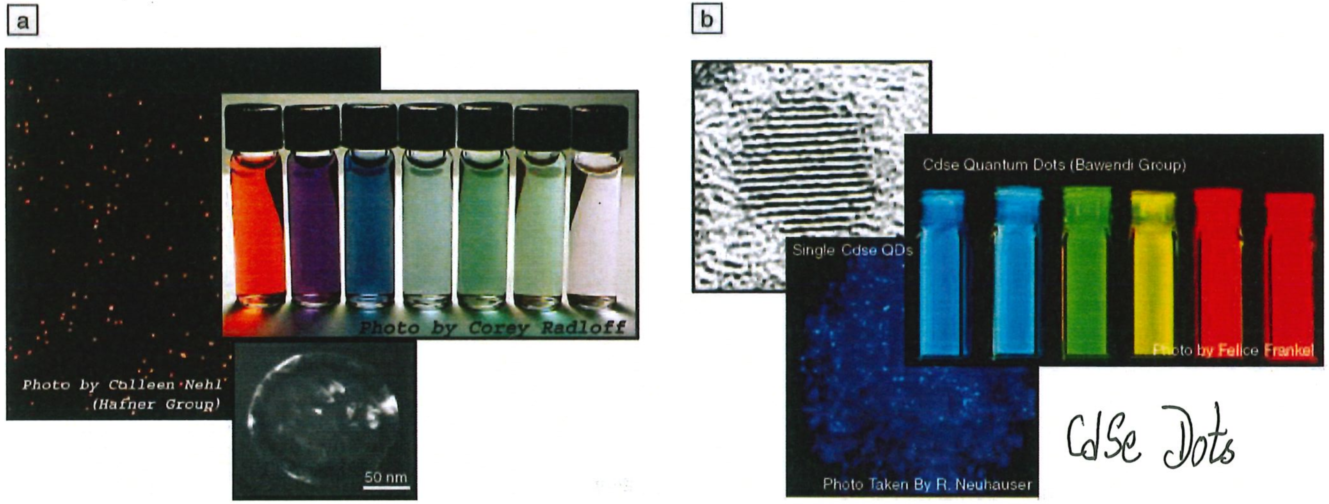
shell

tunable resonance



⇒ two characteristic oscillation frequencies

Same Material but different sizes ⇒ different colors



CdSe Dots

*Figure 3. (a) Nanoshells are tunable plasmonic nanoparticles. Micrographs show a field of many nanoshells (large micrograph) and one nanoshell (small micrograph). Vials show nanoshells in solution. (b) Semiconductor quantum dots are tunable excitonic nanoparticles (courtesy of the Bawendi group). A field of quantum dots is displayed in the bottom image; an individual quantum dot is shown in the upper-left micrograph. Vials of quantum dots are also shown. Comparing single nanoshells to single quantum dots, nanoshells typically have a $10^6$ larger absorption cross section, nominally five times the physical cross section of the nanoparticle.*

From
N. Halas,
MRS Bulletin,
Vol. 30, p. 362
(2005)

2/. What are these "...ons" (polaritons)?

This is typical of coupling between oscillators

Polarization of the ion lattice $\underbrace{\text{[TO-phonons]}}_{\text{"some polarization quanta"}}$

couples to

Photons

Roughly (just a picture): photon part $\left(\sum_k \hbar \overbrace{ck}^{\omega} (a_k^\dagger a_k + \frac{1}{2})\right)$ (oscillator physics)

phonon part $\left(\sum_{k\,(\text{OR } q)} (\text{phonon energy})(b_k^\dagger b_k + \frac{1}{2})\right)$

then they interact through $(-\vec{\mathcal{E}}\cdot\vec{P})$ term

$\sim (a_k - a_{-k}^\dagger) \quad (b_k + b_{-k}^\dagger)$

⇒ interaction terms are quadratic, e.g. $a_k^\dagger b_k$, $a_k b_k^\dagger$, ...

$\therefore$ $H = H_{phonon(TO)} + H_{photon} + H_{int}$

is quadratic in the operators

$\Rightarrow$ form linear combinations of the operators

AND $H$ can be diagonalized

The new operators correspond to the creation and annihilation of a new quanta of elementary excitations (independent ones, called polaritons) with $\omega(k)$ given by the two branches

## Refs

- Kittel, Introduction to Solid State Physics { Chapters on
  - Plasmons, Polaritons, polarons
  - Optical Processes
  - Dielectrics
- Balkanski and Wallis, Ch. 7 and Ch. 10 (Sec. 10.1, 10.5)
- Omar, "Elementary Solid State Physics"
- Madelung, "Introduction to Solid State Theory" Sec 6.1, Sec. 3.3