Optical Properties of Solids

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Contents:

I. Absorption and Reflection
II. Interband optical transitions
III. Excitons
IV. Low-dimensional systems
V. Optical response of an electron gas
VI. Optical studies of phonons
VII. Optics of anisotropic media
VIII. Non-linear optics

For lecture feedback please use the QR code above. These slides as on my web page at https://www.physics.ox.ac.uk/our-people/rtaylor/teaching

Recommended textbooks

M Fox, *Optical Properties of Solids,* Oxford University Press

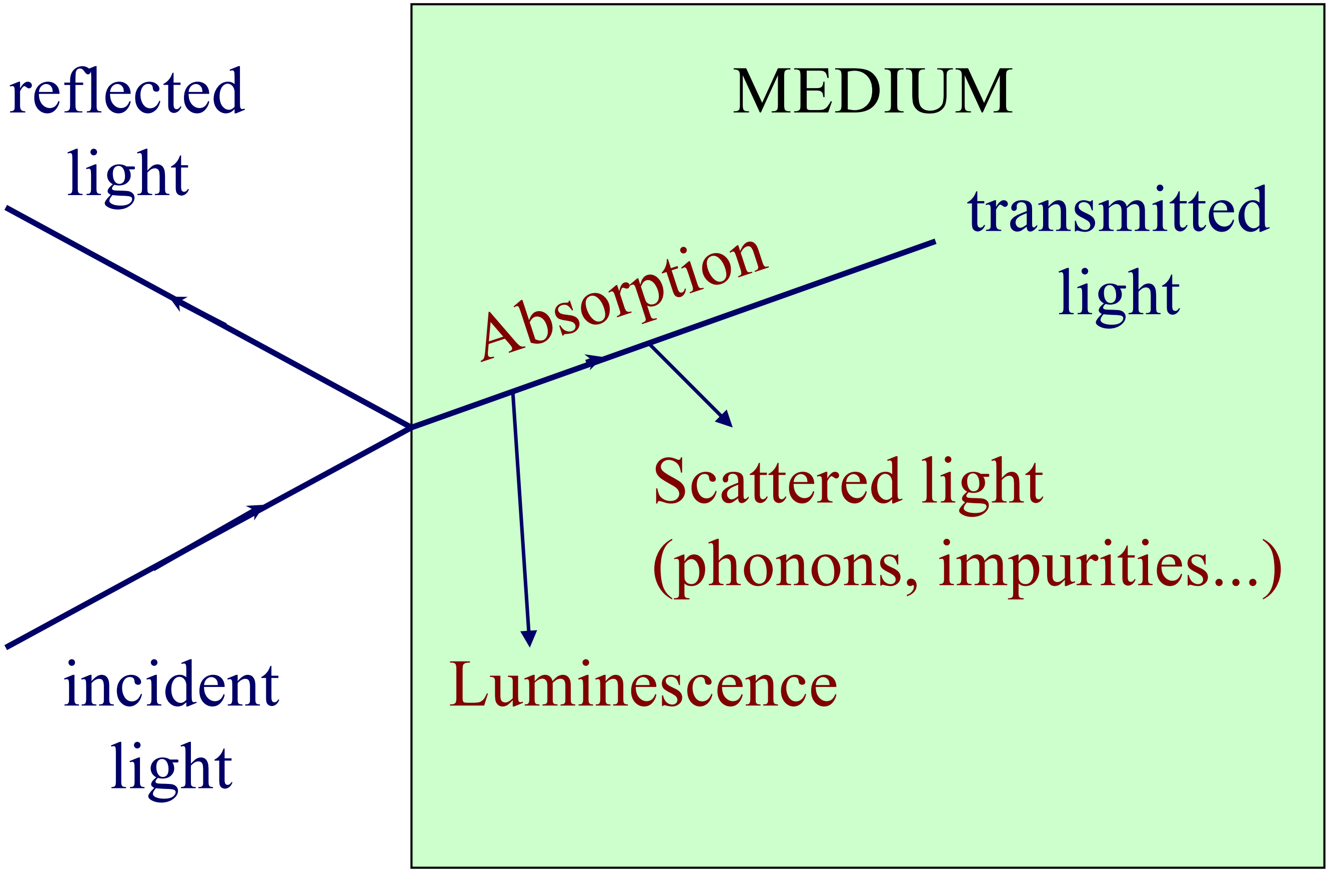
PY Yu and M Cardona, *Fundamentals of Semiconductors*, Springer

C Kittel, *Introduction to Solid State Physics*, Wiley

B Saleh, M. Teich, *Fundamentals of Photonics*, Wiley

A Yariv, *Quantum Electronics*, Wiley

Interaction of Electromagnetic Radiation with Matter



reflected light

MEDIUM

transmitted light

Absorption

Scattered light (phonons, impurities...)

incident light

Luminescence

I Absorption and Reflection

Macroscopic Electromagnetism

Maxwell' s equations:

$$\nabla \cdot \mathbf{D} = \rho \qquad \nabla \times \mathbf{H} = \mathbf{j} + \frac{d}{dt}\mathbf{D}$$

$$\nabla \cdot \mathbf{B} = 0 \qquad \nabla \times \mathbf{E} = -\frac{d}{dt}\mathbf{B}$$

$\rho = 0$ (no net free charges)

$\mathbf{B} = \mu_0 \mathbf{H}$ (non-magnetic)

$\mathbf{j} = \sigma \mathbf{E}$ (ohmic conduction)

$$\boxed{\nabla^2 \mathbf{E} = \mu_0 \, \sigma \, \frac{d}{dt}\mathbf{E} + \mu_0 \, \frac{d^2}{dt^2}\mathbf{D}}$$

Linear Optics

In a linear, non-conducting medium:

$$\nabla^2 \mathbf{E} = \epsilon_0 \, \mu_0 \, \frac{d^2}{dt^2} \left(\epsilon_r \, \mathbf{E} \right)$$

Solution: $\mathbf{E} = \mathbf{E}_0 \, \exp \left[i \left(kz - \omega t \right) \right]$

where: $k = \frac{\omega}{c} \sqrt{\epsilon_r} \equiv k' + i k''$ complex!

⇨ Define complex refractive index:

$$\boxed{\tilde{n} \equiv \sqrt{\epsilon_r} \equiv \underset{\substack{\uparrow \\ \text{refraction}}}{n} + i \underset{\substack{\uparrow \\ \text{absorption}}}{\kappa}}$$

Absorption

Intensity decay of wave:
(Beer’s law)

$$I(z) = I_0 \exp\left(-\frac{2\omega\kappa}{c} z\right)$$

Define absorption coefficient: $\alpha = \frac{2\omega\kappa}{c}$

Reflection

At normal incidence:

$$R = \left| \frac{\sqrt{\epsilon_r}-1}{\sqrt{\epsilon_r}+1} \right|^2 = \frac{(n-1)^2+\kappa^2}{(n+1)^2+\kappa^2}$$

⇨ Reflectivity *R* for a material’s surface contains information on its absorption!

Relationship between components of ñ and ε_r

$$\underbrace{\tilde{n} = n + i\,\kappa \qquad \epsilon_r = \epsilon' + i\,\epsilon''}_{\tilde{n} = \sqrt{\epsilon_r}}$$

$$\Downarrow$$

$$\boxed{\begin{aligned} \epsilon' &= n^2 - \kappa^2 \\ \epsilon'' &= 2n\kappa \end{aligned}}$$

and

$$\boxed{\begin{aligned} n &= \frac{1}{\sqrt{2}}\left(\epsilon' + (\epsilon'^{\,2} + \epsilon''^{\,2})^{\frac{1}{2}}\right)^{\frac{1}{2}} \\ \kappa &= \frac{1}{\sqrt{2}}\left(-\epsilon' + (\epsilon'^{\,2} + \epsilon''^{\,2})^{\frac{1}{2}}\right)^{\frac{1}{2}} \end{aligned}}$$

if $\kappa \ll n$ (weak absorption): $n \simeq \sqrt{\epsilon'}$ $\qquad \kappa \simeq \dfrac{\epsilon''}{2n}$

The classical dipole oscillator model

Inside a material the electric field of an EM wave may interact with:

- bound electrons (e.g. interband transitions)
- ions (lattice interactions)
- free electrons (plasma oscillations)

Equation of motion for a bound electron in 1D:

$$m\frac{d^2x}{dt^2} + m\,\gamma\,\frac{dx}{dt} + m\,\omega_0^2\,x = -e\,E$$

where $\quad E = E_0\,\exp(-i\omega t)$

⇨ stationary solutions: $x(t) = x_0 \exp(-i\omega t)$

$$= \frac{-eE}{m}\frac{1}{\omega_0^2-\omega^2-i\gamma\omega}$$

Displacement of charge causes polarisation:

$P = -N\,e\,x$ (N: oscillator density)

$$D = \epsilon_0\epsilon_r E = \epsilon_0 E + P + P_b$$

background

$$\boxed{\epsilon_r(\omega) = 1 + \underbrace{\frac{e^2N}{\epsilon_0 m}\frac{1}{(\omega_0^2-\omega^2-i\,\gamma\,\omega)}}_{\chi(\omega)} + \chi_b}$$

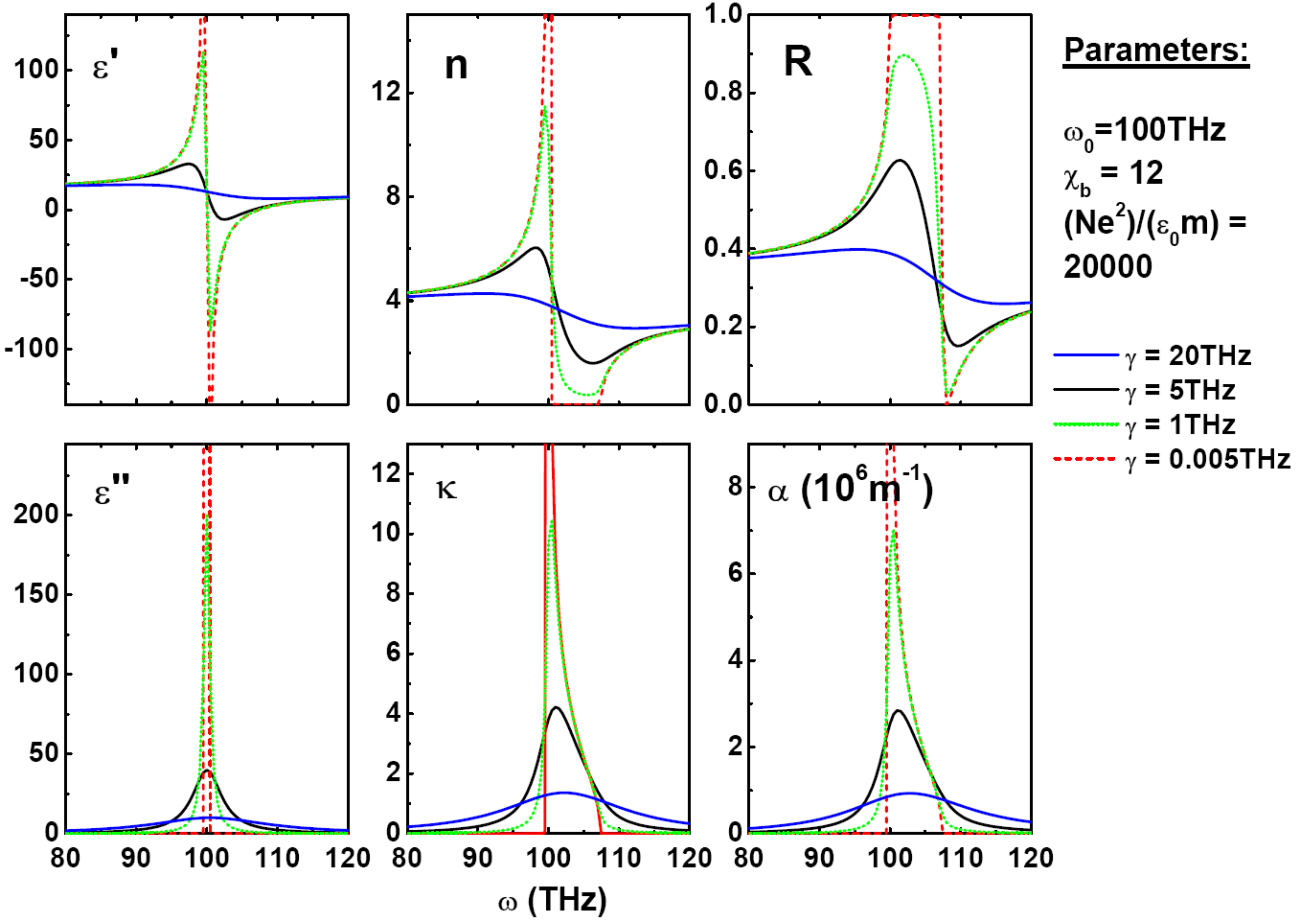
Real and imaginary part of ε_r

$$\begin{aligned}\epsilon'(\omega) &= 1 + \chi_b + \frac{Ne^2}{\epsilon_0 m}\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \\ \epsilon''(\omega) &= \frac{Ne^2}{\epsilon_0 m}\frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2}\end{aligned}$$

⇩

Can now calculate $n(\omega),\ \kappa(\omega)$ and $R(\omega),\ \alpha(\omega)$

Optical constants for a classical dipole oscillator



Parameters:

ω_0=100THz
χ_b = 12
$(Ne^2)/(\varepsilon_0 m)$ =
20000

Local field corrections

In a dense medium:

- atoms experience "local field" composed of external field **E** and polarization from surrounding dipoles
- treat interacting dipole as being at centre of sphere surrounded by a polarized dielectric

⇒ Clausius-Mossotti relationship:

$$\frac{\tilde{\chi}_a N}{3} = \frac{\epsilon_r - 1}{\epsilon_r + 2}$$

electric
susceptibility
per atom

Problems with the classical oscillator model

- no information on selection rules

  → need quantum mechanics

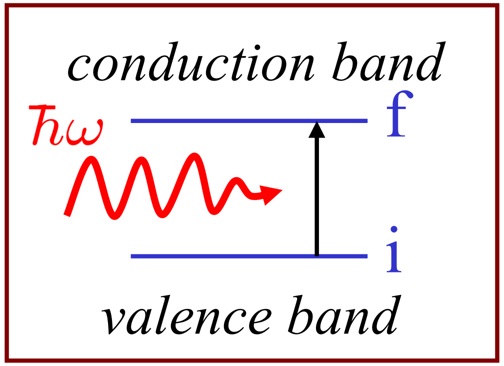
- interband transitions should depend on the density of states g(E)

- One possible modification:

"oscillator strength"
(from QM)

write: $$\epsilon_r = \underbrace{1 + \frac{e^2 N}{\epsilon_0 m}\frac{f}{\omega_0^2 - \omega^2 - i\omega\gamma}}_{\text{line shape of transition (from classical oscillator model)}}$$

II Interband optical transitions



Treat interband transitions through time-dependent perturbation theory - Fermi’s golden rule gives transition probability:

$$W_{if} = \frac{2\pi}{\hbar}|M_{if}|^2\, g(\hbar\omega) \longleftarrow \text{joint density of states}$$

with matrix element: $M_{if} = \int \psi_f^*(\mathbf{r})\, V(\mathbf{r})\, \psi_i(\mathbf{r})\, d^3r$

where $V(\mathbf{r}) = -\underbrace{e\mathbf{r}}_{\text{dipole moment}} \cdot \mathbf{E}$ $\qquad \mathbf{E} = \mathbf{E}_0 \cos(\mathbf{k}\cdot\mathbf{r})$

E-field of incident wave

$$\left.\begin{aligned} \psi_i(\mathbf{r}) &= \frac{1}{\sqrt{V_0}}\, u_v \exp\left(i\, \mathbf{k}_i \cdot \mathbf{r}\right) \\ \psi_f(\mathbf{r}) &= \frac{1}{\sqrt{V_0}}\, u_c \exp\left(i\, \mathbf{k}_f \cdot \mathbf{r}\right) \end{aligned}\right\} \text{Bloch wavefunctions}$$

Matrix element for interband transitions:

absorption

$$
\begin{aligned}
M_{if} &= \frac{1}{2V_0}\int(-e\mathbf{E}_0)\cdot\left(u_c^*(\mathbf{r})\,\mathbf{r}\,u_v(\mathbf{r})\right)\,\exp\Big(i(\mathbf{k}_i-\mathbf{k}_f\overset{\swarrow}{+}\mathbf{k})\cdot\mathbf{r}\Big)\,d^3r \\
&+ \frac{1}{2V_0}\int(-e\mathbf{E}_0)\cdot\left(u_c^*(\mathbf{r})\,\mathbf{r}\,u_v(\mathbf{r})\right)\,\exp\Big(i(\mathbf{k}_i-\mathbf{k}_f\underset{\nwarrow}{-}\mathbf{k})\cdot\mathbf{r}\Big)\,d^3r
\end{aligned}
$$

emission

⇒ deduce conditions for dipole allowed (direct) transitions.

<u>Consider:</u>

(1) wavevector conservation
(2) Parity selection rule
(3) dependence on photon energy

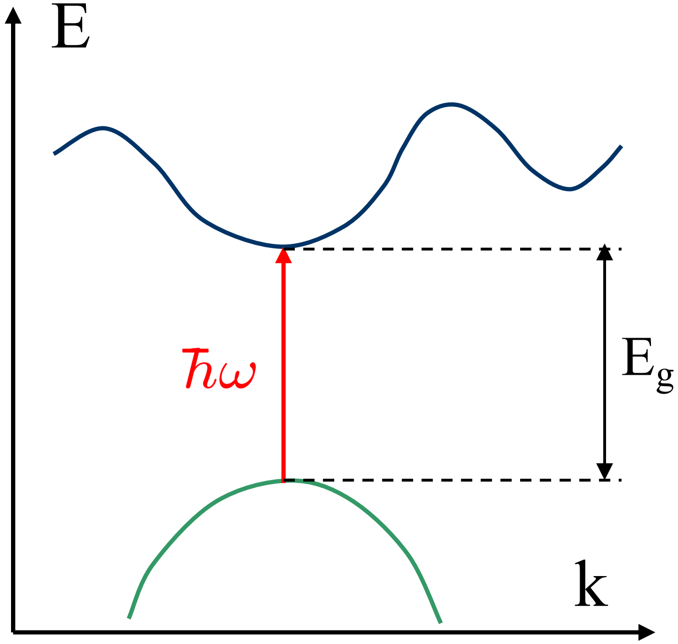
Conditions for direct interband transitions

(1) wavevector conservation

$$M_{if} \neq 0 \text{ only if } \mathbf{k}_f = \mathbf{k}_i + \underset{\text{absorption}}{\mathbf{k}} \text{ or } \mathbf{k}_f = \mathbf{k}_i \underset{\text{emission}}{-} \mathbf{k}$$

typically: $\mathbf{k} \ll \mathbf{k}_i,\ \mathbf{k}_f$

⇨ "vertical" transitions



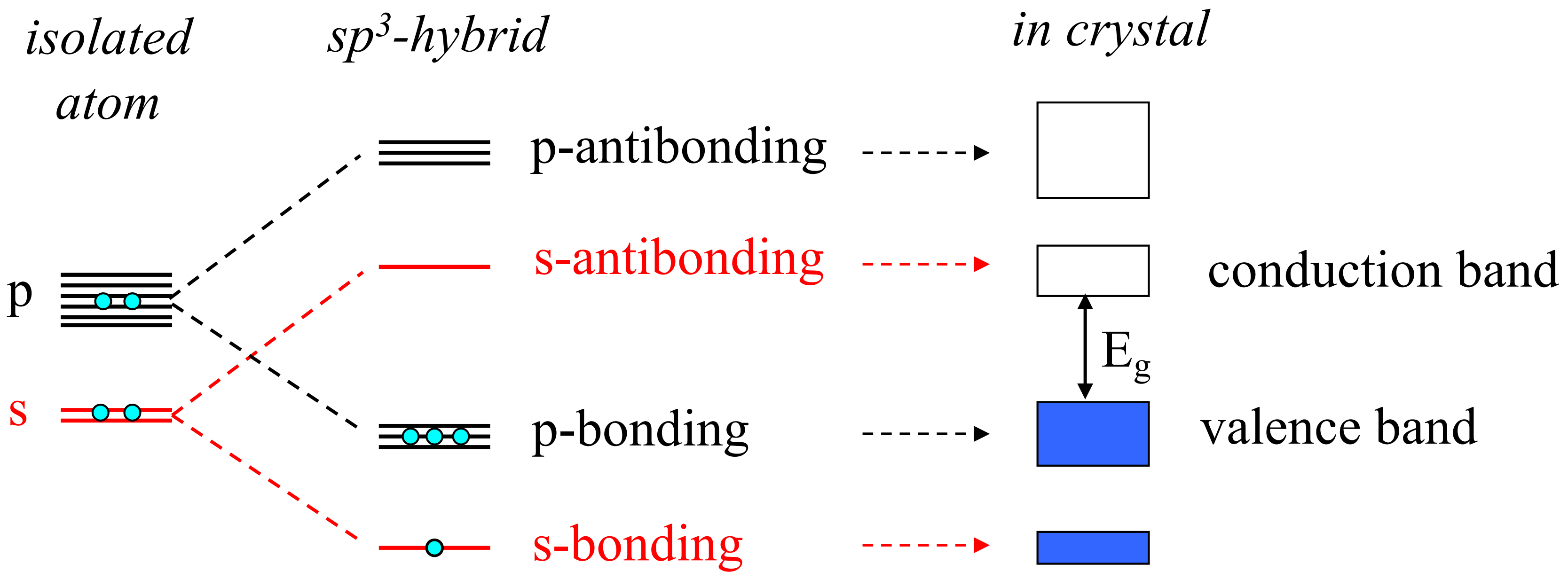
(2) parity selection rule

$$M_{if} \propto e\mathbf{E}_0 \cdot \int u_c^*(\mathbf{r})\,\mathbf{r}\,u_v(\mathbf{r})\,d^3r$$

odd parity

⇒ $M_{if} \neq 0$ only if $u_c(\mathbf{r})$ and $u_v(\mathbf{r})$ have different parity!

In a typical 4-valent system (e.g. group IV or III-V compound):



isolated atom

sp³-hybrid

in crystal

p

s

p-antibonding

s-antibonding

p-bonding

s-bonding

conduction band

E_g

valence band

⇒ expect to see strong absorption for these materials

(3) Dependence of transition probability on photon energy

Final state is an electron-hole pair

$$\Longrightarrow \quad g(\hbar\omega) = \frac{1}{2\pi^2}\left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}}(\hbar\omega - E_g)^{\frac{1}{2}}$$

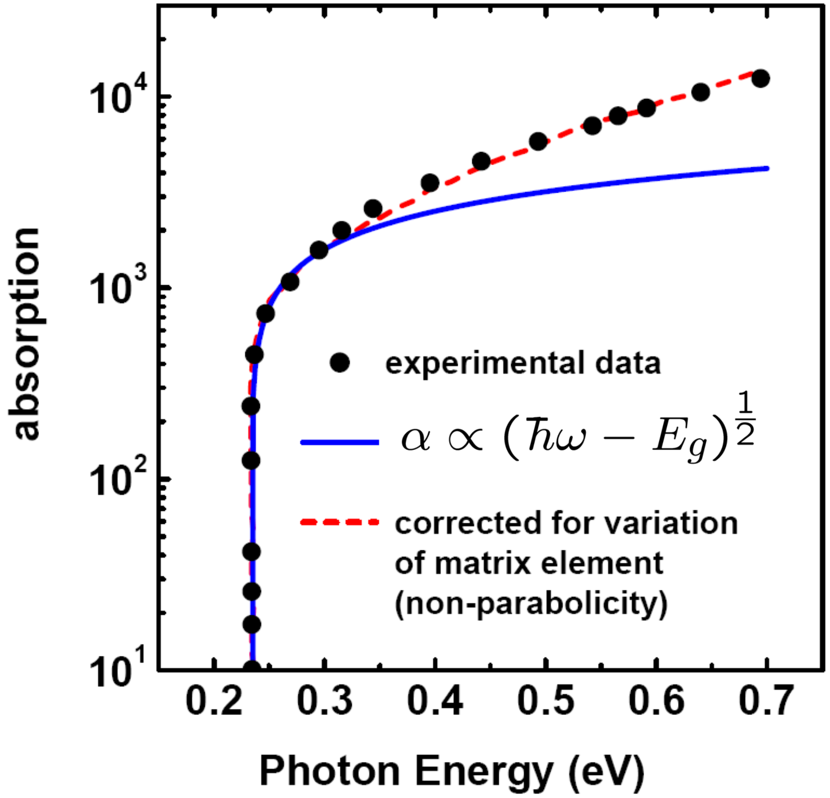
where $\mu = (\frac{1}{m_e^*} + \frac{1}{m_h^*})^{-1}$ reduced effective mass

If M_{if} is independent of the photon energy $\hbar\omega$, the joint density of states contains the dependence of the transition probability on $\hbar\omega$. For this case:

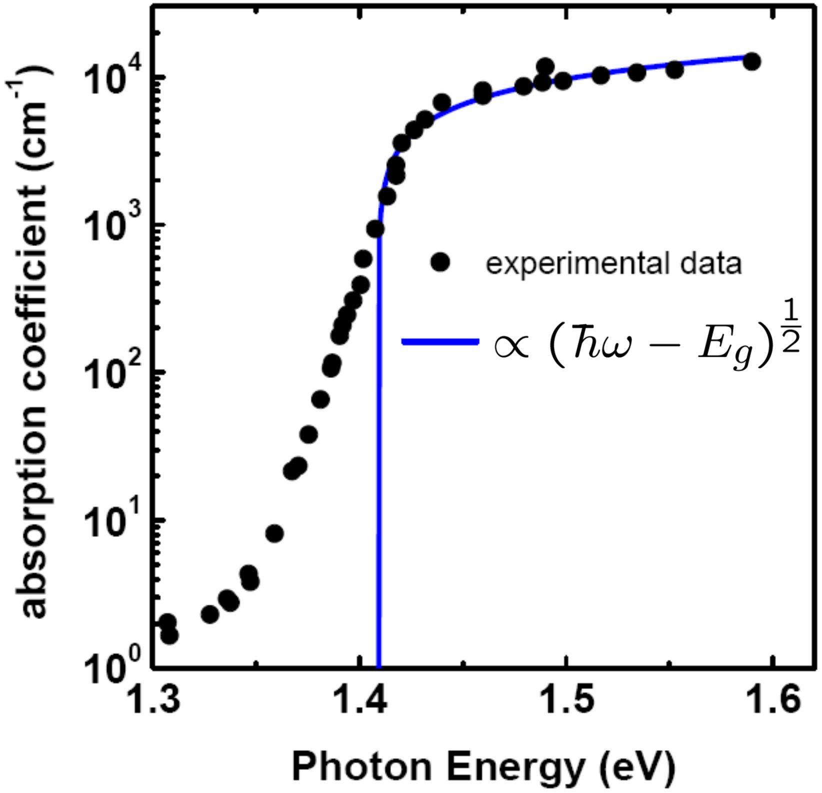
Absorption coefficient (for direct transitions): $\alpha \propto (\hbar\omega - E_g)^{\frac{1}{2}}$

Examples for direct semiconductors

a) InSb at 5K



b) GaAs at 300K



⇨ deviations from $\alpha \propto (\hbar\omega - E_g)^{\frac{1}{2}}$ e.g. due to phonon absorption or non-parabolicity of the bands.

Indirect interband transitions

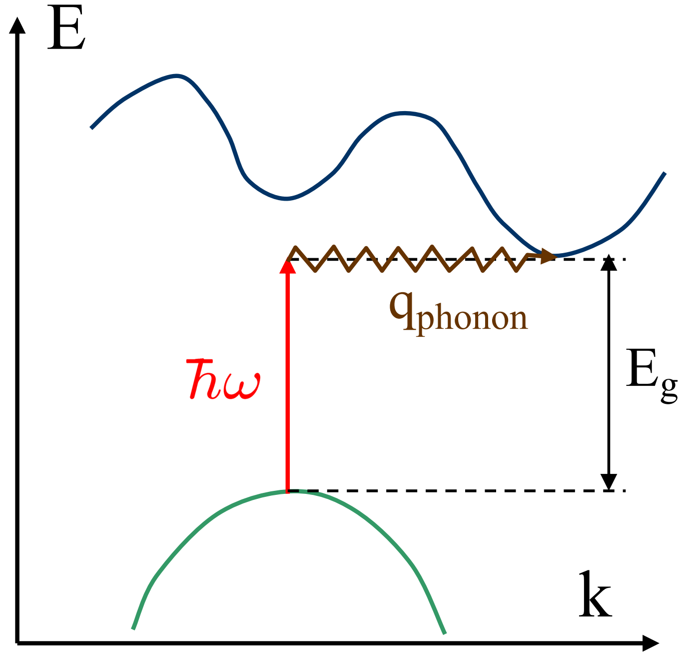
- Indirect gap: valence band maximum and conduction band minimum lie at different wavevectors, $\mathbf{k}_v^{max} \neq \mathbf{k}_c^{min}$
- direct transitions across the indirect gap forbidden, but phonon-assisted transitions may be possible.

(i) wavevector conservation:

$$\mathbf{k}_f = \mathbf{k}_i \pm \mathbf{k} \pm \mathbf{q}_{phonon}$$

with phonon wavevector

$$\mathbf{q}_{phonon} = \mathbf{k}_v^{max} - \mathbf{k}_c^{min}$$



(ii) probability for indirect transitions:

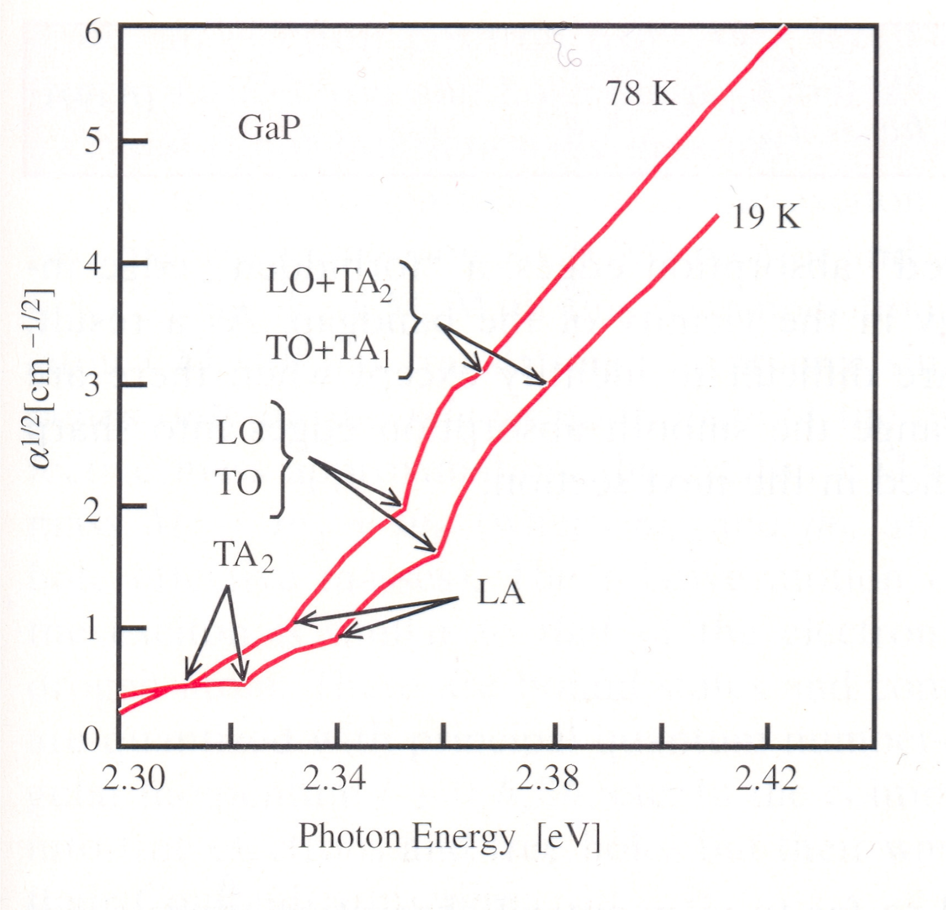
- perturbation causing indirect transitions is second order

  ⇒ optical absorption much weaker than for direct transitions!

- find absorption coefficient $\alpha \propto (\hbar\omega - E_g \pm \hbar\omega_q)^2$

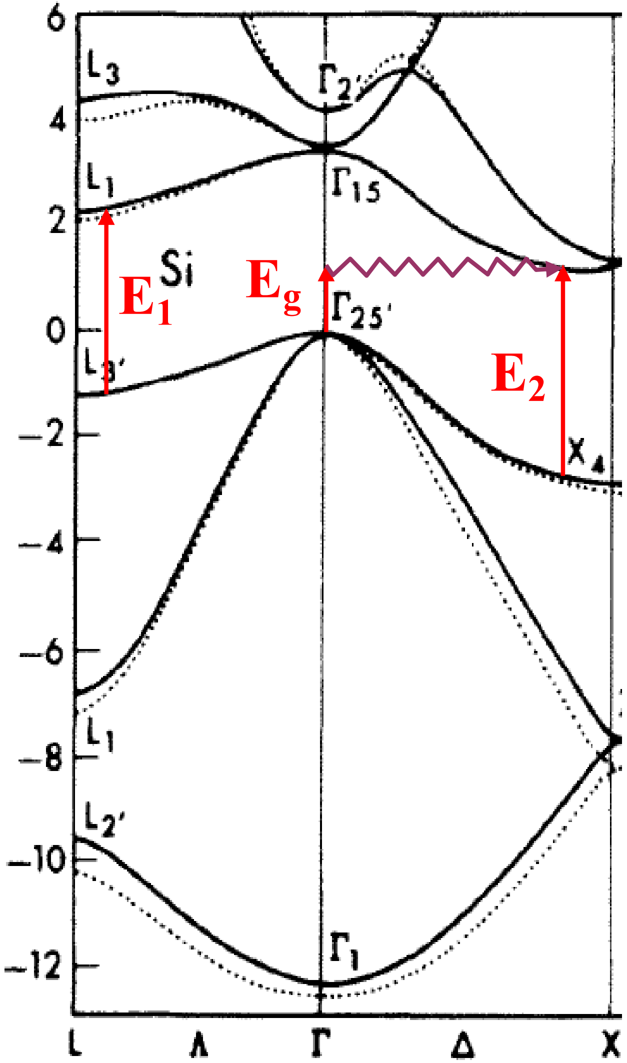
↑

phonon absorption
or emission

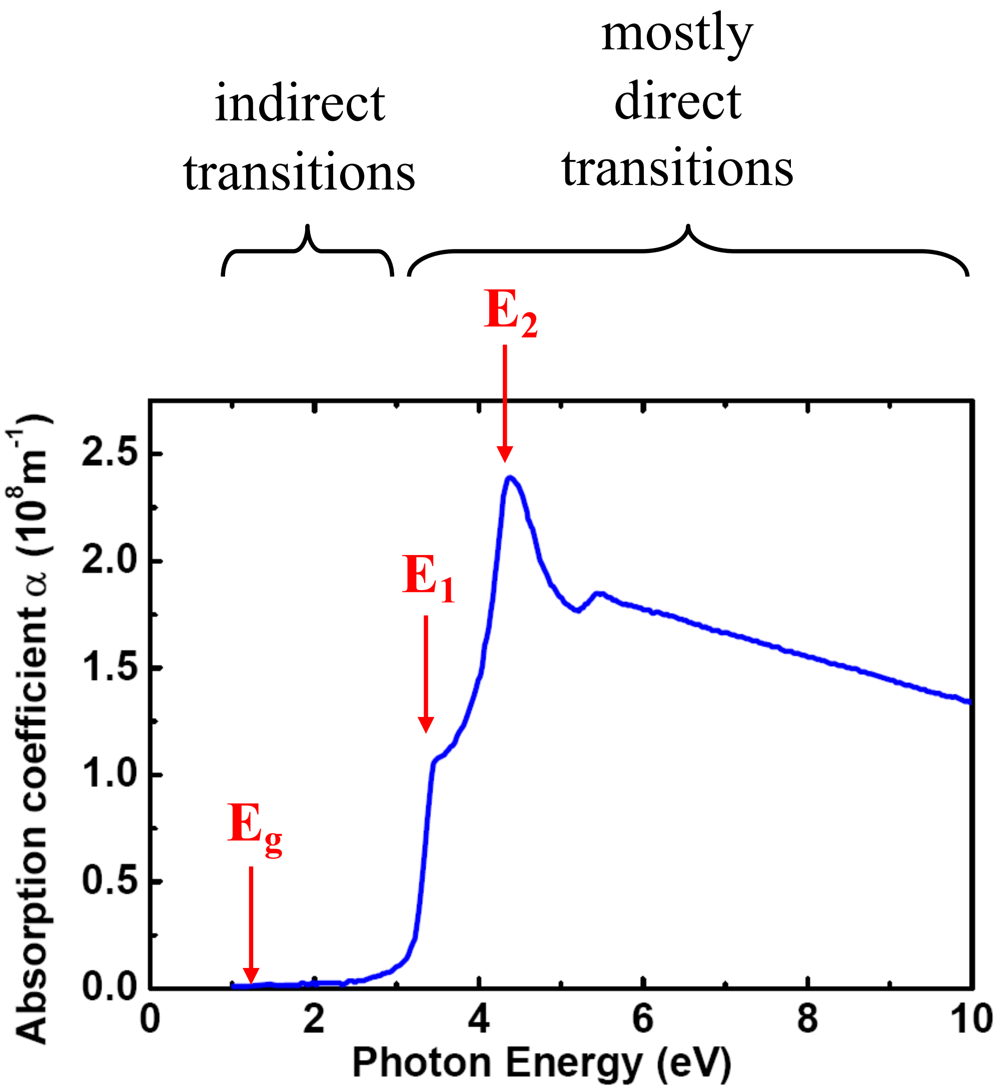


Example for an indirect semiconductor: Si

Band structure:

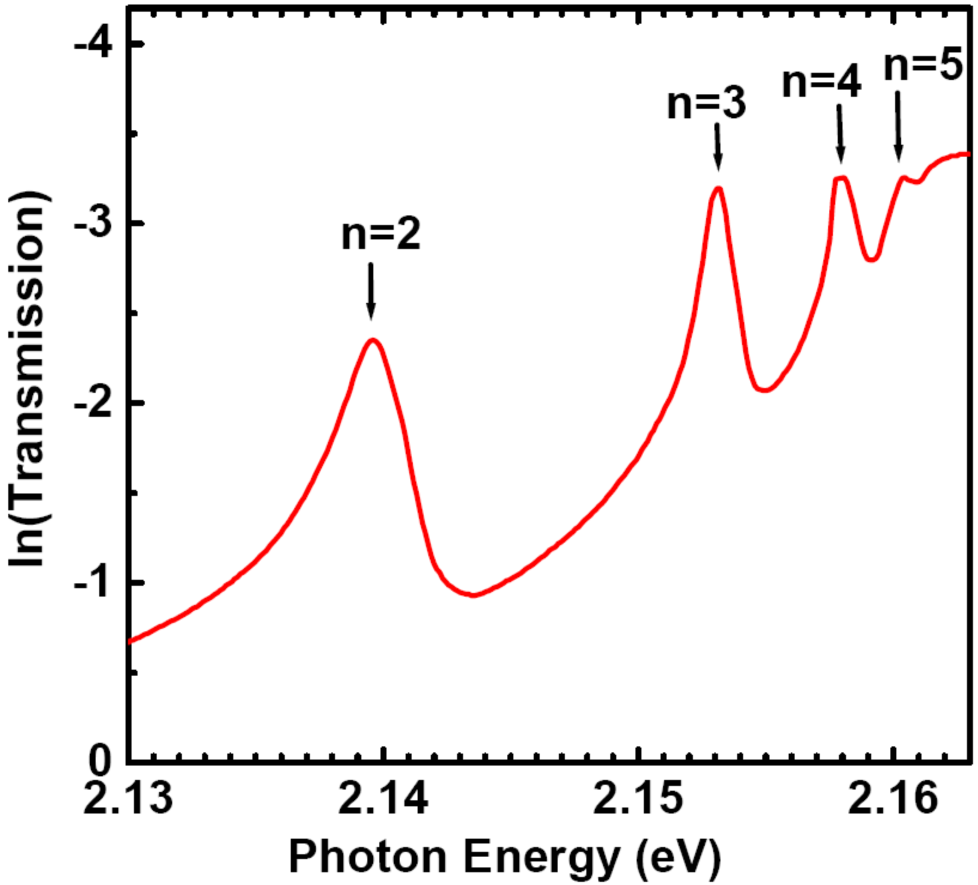


Absorption spectrum:



III Excitons

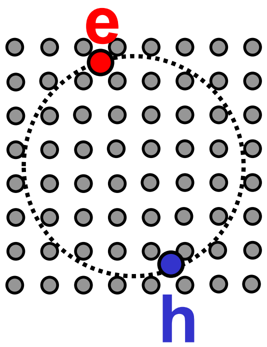
Absorption coefficient of CuO_2 at 77K:



Series of absorption peaks just below the energy gap

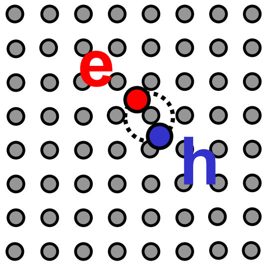
Coulomb interaction between electron and hole gives rise to “excitonic” states (bound electron-hole pairs)

Wannier-Mott Excitons



- weakly bound (free) excitons
- binding energy ~ 10meV
- common in inorganic semiconductors (e.g. GaAs, CdS, CuO_2...)
- particle moving in a medium of effective dielectric constant ε_r

Frenkel Excitons



- strongly (tightly) bound excitons
- binding energy ~ 0.1 – 1eV
- typically found in insulators and molecular crystals (e.g. rare gas crystals, alkali halides, aromatic molecular crystals)
- particle often localized on just one atomic/molecular site

Weakly bound (Wannier) Excitons

Separate exciton motion into centre-of-mass and relative motion:

CM motion: exciton momentum: $\mathbf{k}_X = \mathbf{k}_e + \mathbf{k}_h$ where $\mathbf{k}_h = -\mathbf{k}_v$

exciton mass: $m_X = m_e^* + m_h^*$

kinetic energy: $$E_{CM} = \frac{\hbar^2 k_X^2}{2m_X}$$

Relative motion: Binding energy: $$E_n = -\frac{\mu\, e^4}{8h^2\epsilon_0^2\epsilon_r^2}\frac{1}{n^2} = -\frac{R_X}{n^2}$$

where $R_X = \frac{\mu}{m_e\,\epsilon_r^2} R_y$ $\quad R_y{=}13.6\,\text{eV}$ (Rydberg)

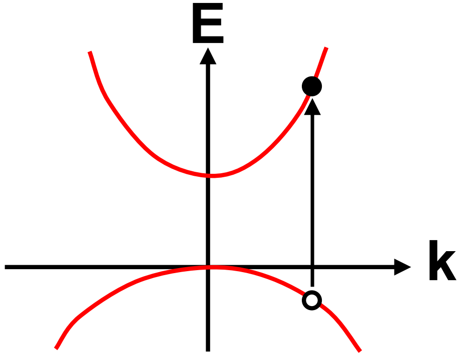
$\mu = (\frac{1}{m_e^*} + \frac{1}{m_h^*})^{-1}$ reduced mass

Exciton radius: $a_n = \epsilon_r \frac{m_e}{\mu} n^2 a_0$

where $a_0 = 0.529$Å (Bohr radius)

E-k diagram for the weakly bound exciton

(a) uncorrelated electron-hole pair
(one-electron picture)



$$E_e = E_g + \frac{\hbar^2 k_e^2}{2m_e^*}; \quad E_h = \frac{\hbar^2 k_h^2}{2m_h^*}$$

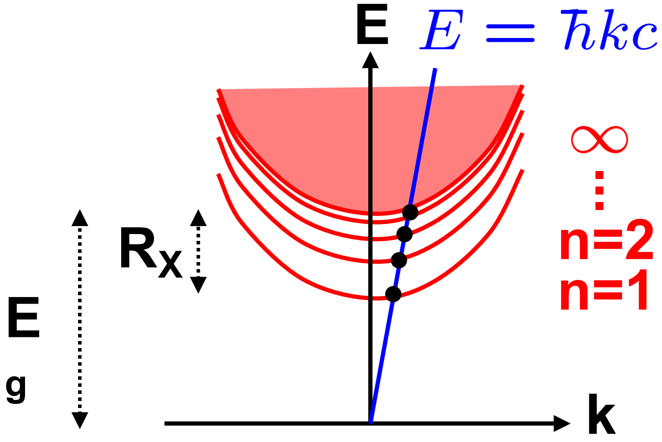
<u>wavevector conservation:</u>

$$\mathbf{k}_e - \mathbf{k}_v = \mathbf{k}_{photon}$$

$$\mathbf{k}_{photon} \approx 0$$

⇨ "vertical transitions"

(b) exciton (one-particle picture)



$$E_X = E_g + \frac{\hbar^2 k_X^2}{2m_X} - \frac{R_X}{n^2}$$

<u>wavevector conservation:</u>

$$\mathbf{k}_X = \mathbf{k}_e - \mathbf{k}_v = \mathbf{k}_{photon}$$

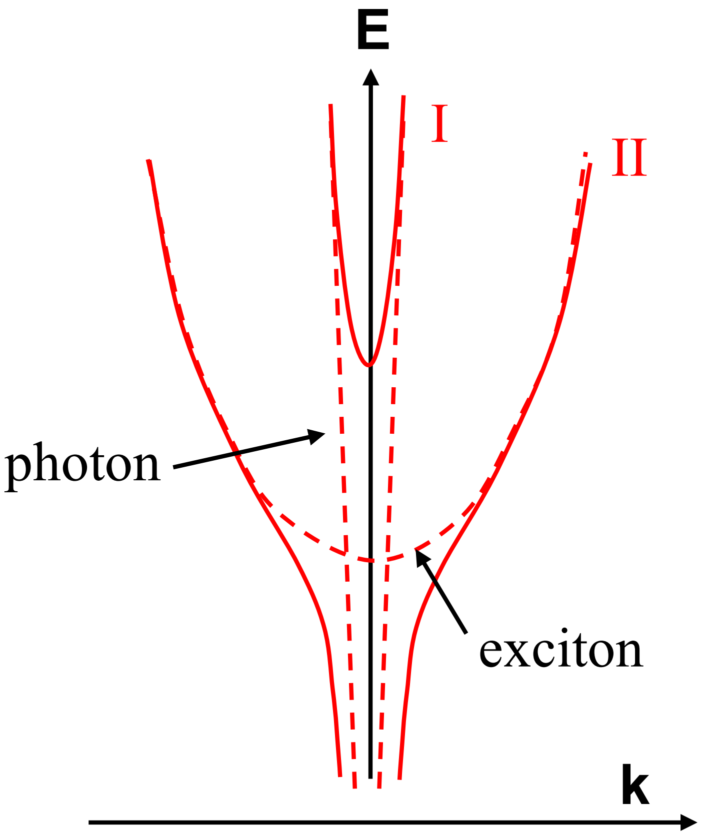
⇨ transitions where light line $E = \hbar kc$ intercepts with E_X

$$\mathbf{k}_{photon} \approx 0$$

⇨ $E_X \to E_g$ for $n \to \infty$

continuum onset at band edge

Exciton-Polariton

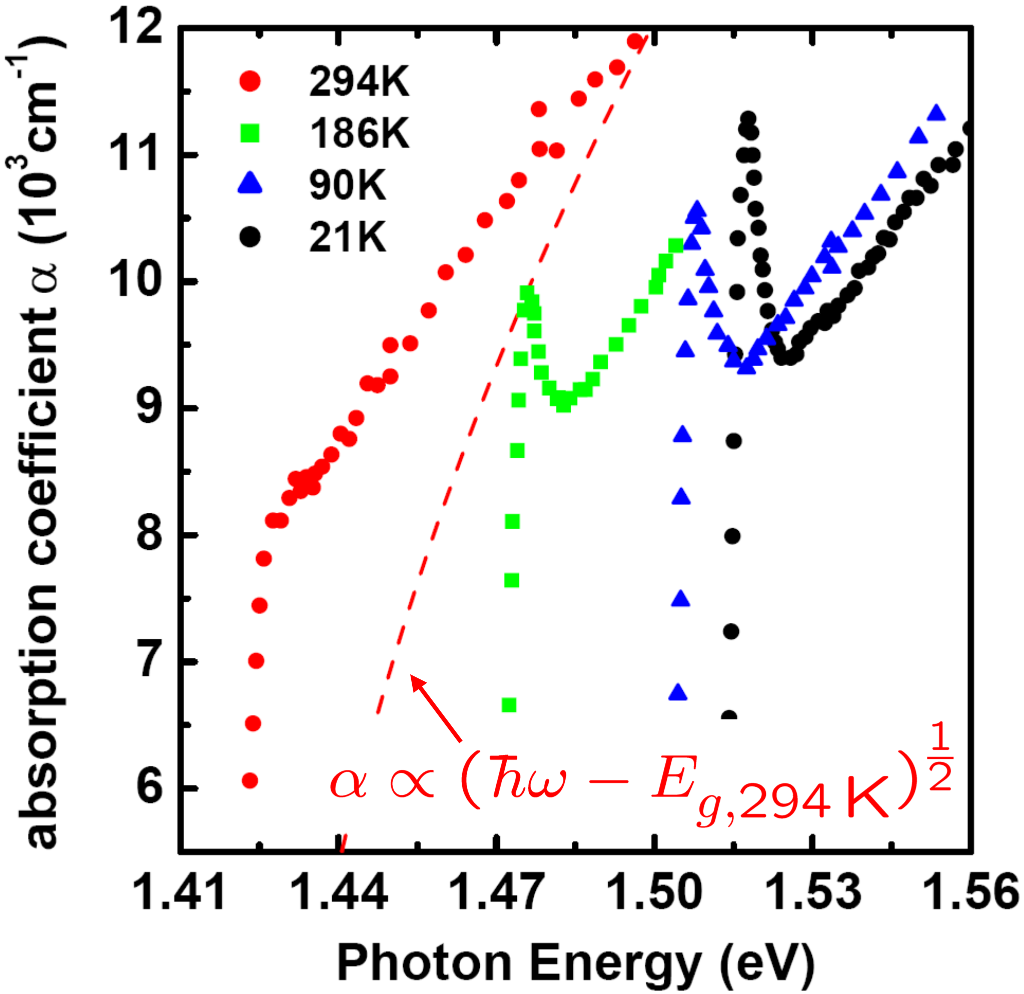


- Absorption occurs at point where photon dispersion intersects exciton dispersion curve.
- exciton-photon interaction leads to coupled EM and polarization wave (polariton) travelling in the medium

⇨ altered dispersion curve
(2 branches)

- But: if exciton damping (phonon scattering...) is larger than exciton-photon interaction we can treat photons and excitons separately.

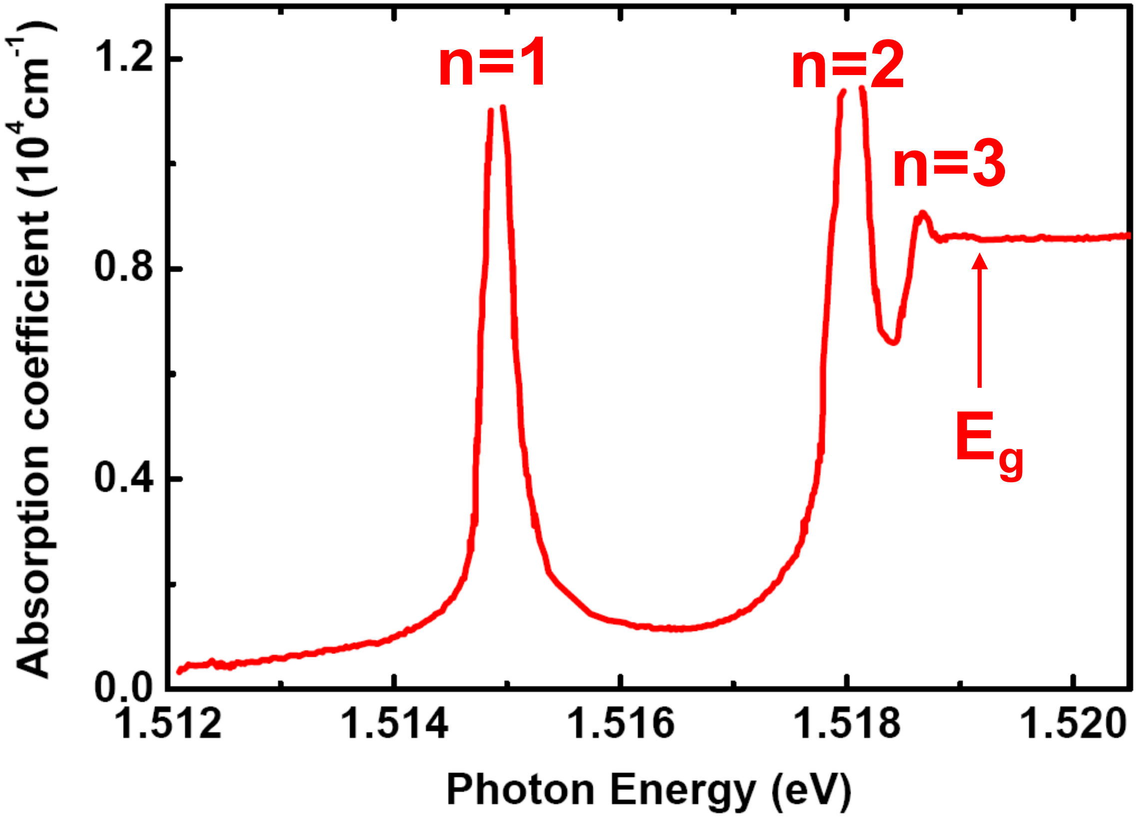
Examples for weakly bound excitons: GaAs



- sub-gap excitonic absorption features
- exciton dissociation through collisions with LO phonons becomes more likely at higher T → exciton lifetime shortened and transition line broadened
- Coulomb interactions increase the absorption *both above and below* the gap

Examples for weakly bound excitons: GaAs

At low temperature (here: 1.2K) and in ultra pure material, the small line width allows observation of higher excitonic transitions:



here: $m_e^* = 0.067$

$m_{hh}^* = 0.45$

$\epsilon_r = 13$

$\Downarrow$

$$E_n = -\frac{4.8}{n^2}\,\mathrm{meV}$$

$$a_n = n^2 \times 11.7\,\mathrm{nm}$$

Tightly bound (Frenkel) excitons

- radius of weakly-bound excitons: $a_n = \epsilon_r \frac{m_e}{\mu} n^2 a_0$

  ⇨ model of bound e-h pair in dielectric medium breaks down when a_n is of the order of interatomic distances (Å)

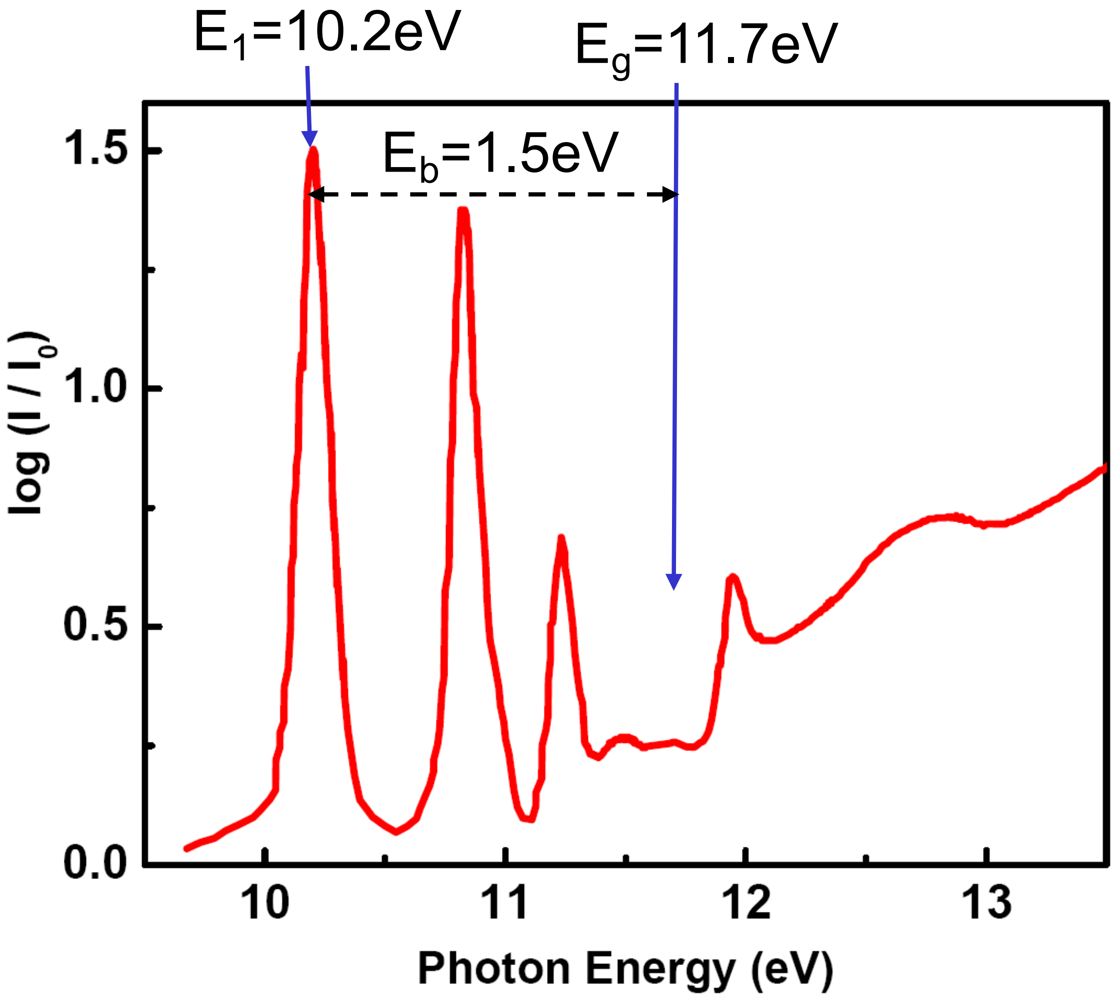
  ⇨ have tightly bound excitons for small ε_r , large μ
- tightly-bound electron-hole pair, typically located on same unit (atom or molecule) of the crystal (but the whole exciton may transfer through the crystal)
- large binding energies (0.1 – 1eV) → excitons persist at room temperature.

Transition energies for tightly bound excitons

- transition energies often correspond to those found in the isolated atom or molecule that the crystal is composed of
- theoretical calculations may be based e.g. on tight-binding or quantum-chemical methods
- often need to include effects of strong coupling between excitons and the crystal lattice (polaronic contributions)

Examples for tightly bound excitons: rare gas crystals

absorption spectrum of crystalline Kr at 20K:



Note: the lowest strong absorption in isolated Kr is at 9.99eV

⇩

close to lowest excitonic transition E_1 in crystal

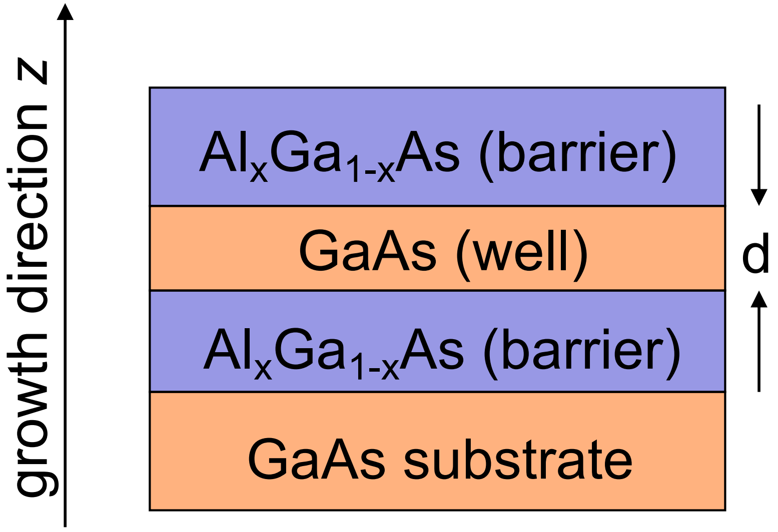
IV Low-dimensional systems

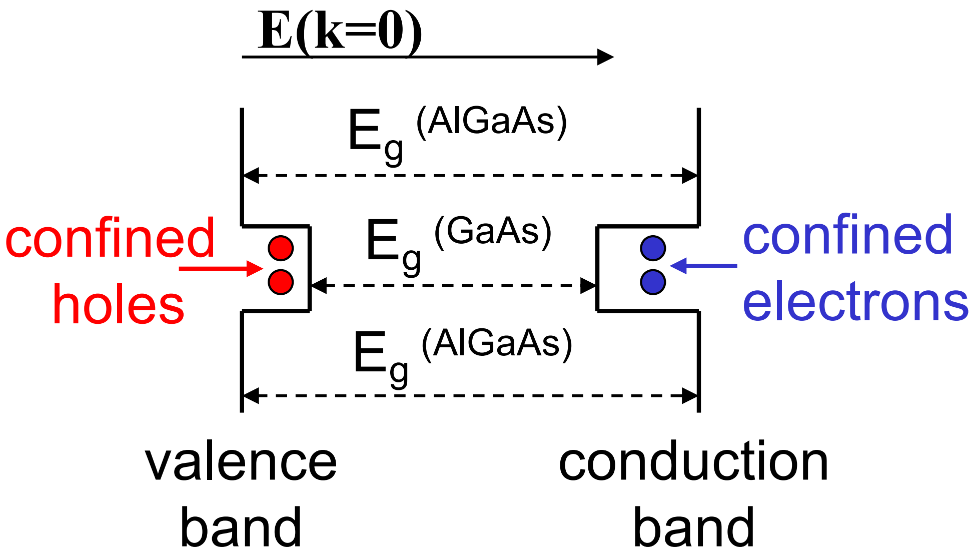
de Broglie wavelength for an electron at room temperature:

$$\lambda = \frac{h}{p} \approx \frac{h}{\sqrt{m_e kT}} \approx 10\,\mathrm{nm}$$

⇨ If we can make structured semiconductors on these length scales we may be able to observe quantum effects!

Possible using e.g. *molecular beam epitaxy* (MBE) or *metal-organic chemical vapour deposition* (MOCVD)





Effect of confinement on the DOS

Confinement in a particular direction results in discrete energy states, but free movement in other directions gives rise to continuum.

→ Joint density of states g(ħω) (for direct CB-VB transitions):

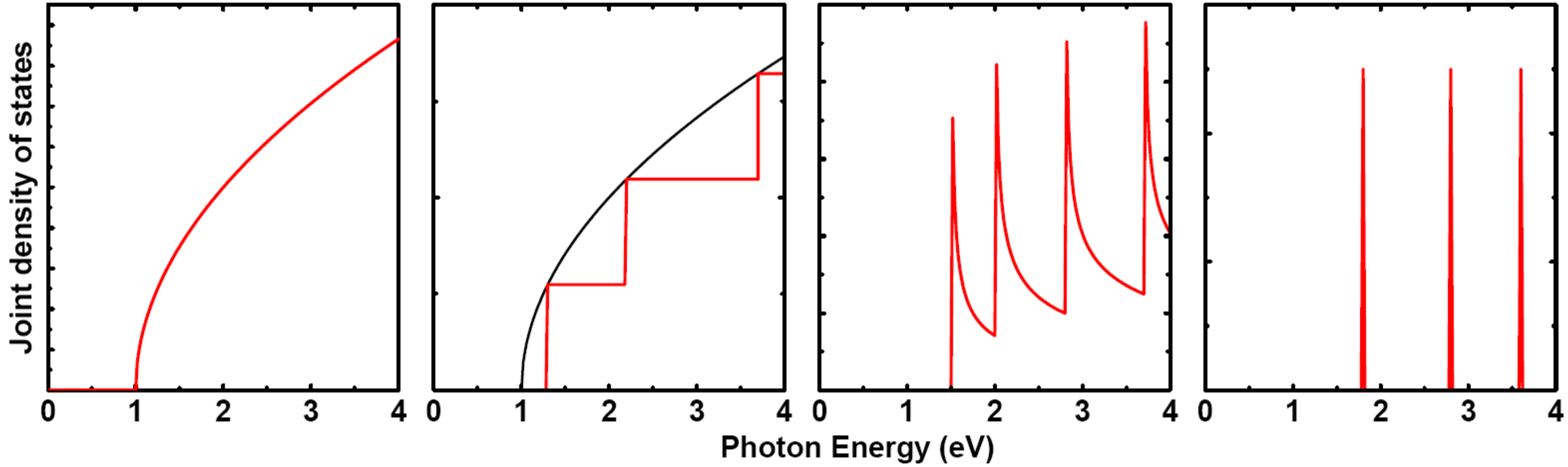
3D (bulk) | 2D (Q well) | 1D (Q wire) | 0D (Q dot)

$$g_{3D} = \frac{(2\mu)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{\hbar\omega - E_g}$$

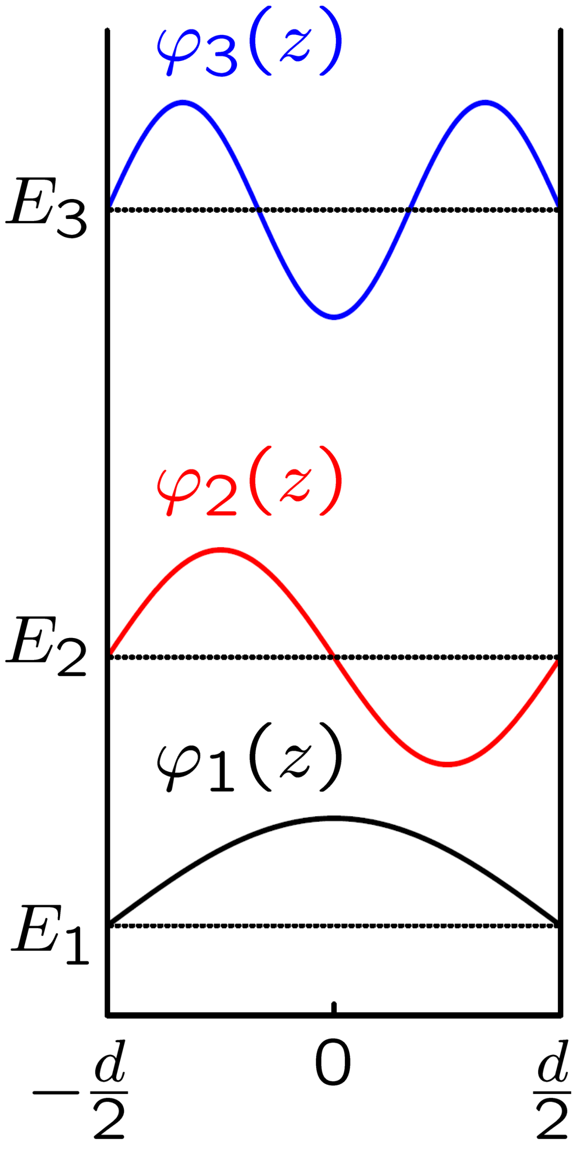
$$g_{2D} = \frac{\mu}{\pi\hbar^2}$$

$$g_{1D} = \frac{1}{\pi\hbar}\sqrt{\frac{2\mu}{\hbar\omega - E_i}}$$

$$g_{0D} \propto \delta(\hbar\omega - E_i)$$



Quantum well with infinite potential barriers



Schrödinger' s eqn inside the well:

$$-\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2}\varphi(z) = E\,\varphi(z)$$

outside the well: $\varphi(z) = 0$

⇩

wavefunction along z:

$$\varphi_n(z) = \sqrt{\frac{2}{d}}\,\sin\left(k_n z + \frac{n\pi}{2}\right)$$

with wavevector $k_n = \frac{n\pi}{d}$

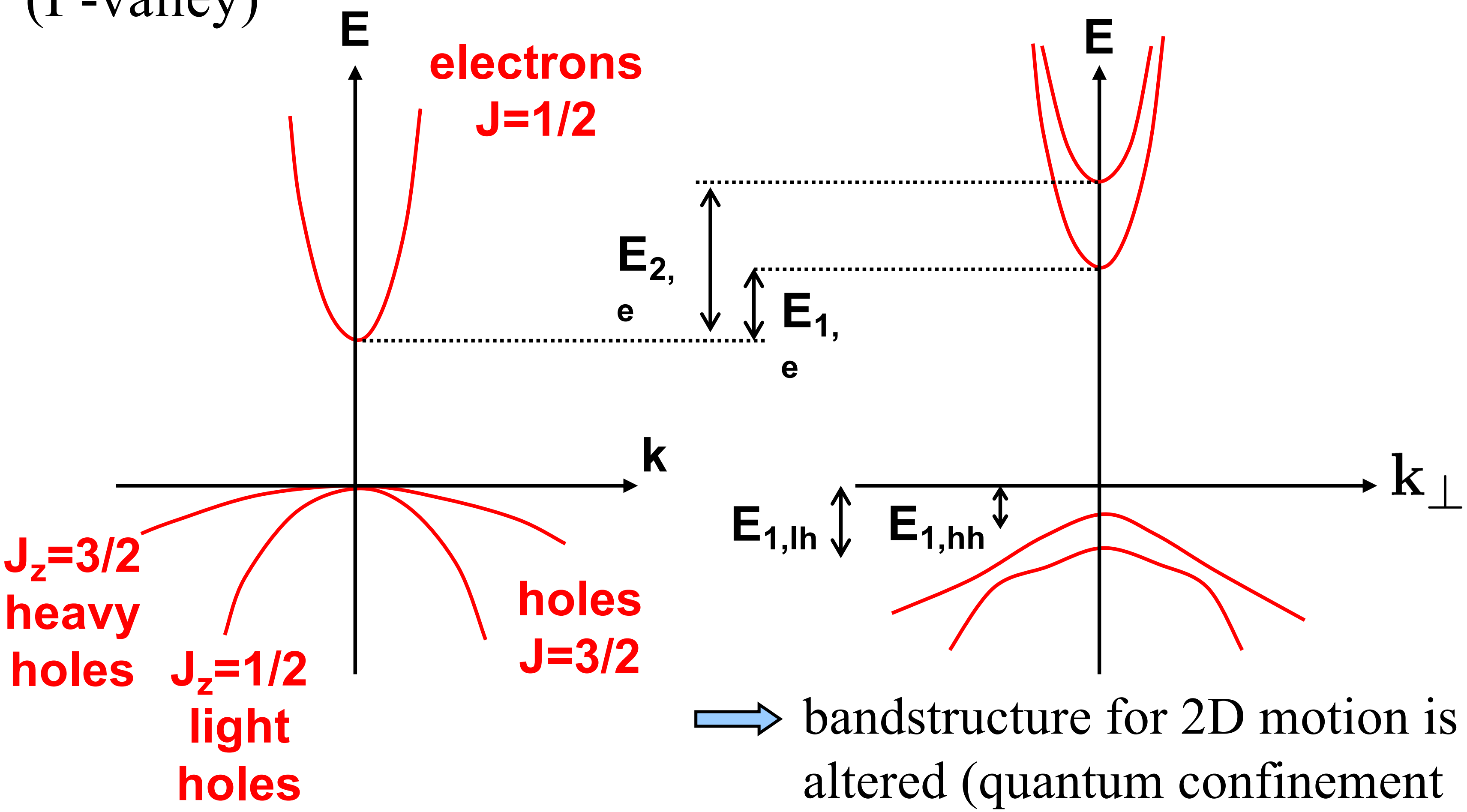
confinement energy:

$$E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*}\left(\frac{n\pi}{d}\right)^2$$

Bandstructure modifications from confinement

bulk GaAs
(Γ-valley)

GaAs QW



⇒ bandstructure for 2D motion is altered (quantum confinement leads to valence band mixing)

Optical transitions in a quantum well

as before, matrix element: $M_{if} = \int \psi_f^*(\mathbf{r})\,(-e\mathbf{r}\cdot\mathbf{E})\,\psi_i(\mathbf{r})\,d^3r$

wavefunctions now:

$$\psi_i(\mathbf{r}) = \frac{1}{\sqrt{V_0}}\,u_v(\mathbf{r})\exp\left(i\,\mathbf{k}_{\perp,v}\cdot\mathbf{r}_\perp\right)\varphi_{n,v}(z)$$

$$\psi_f(\mathbf{r}) = \underbrace{\frac{1}{\sqrt{V_0}}\,u_c(\mathbf{r})\exp\left(i\,\mathbf{k}_{\perp,c}\cdot\mathbf{r}_\perp\right)}_{\substack{\text{valence/conduction band} \\ \text{Bloch function}}}\underbrace{\varphi_{n,c}(z)}_{\substack{\text{hole/electron} \\ \text{wavefunction along z}}}$$

(i) $\varphi(z)$ changes slowly over a unit cell (compared to u_c, u_v)

(ii) $M_{if} \approx 0$ unless $\mathbf{k}_{\perp,v} = \mathbf{k}_{\perp,c} \pm \mathbf{k}_{photon}$ (***k***-conservation)

⇨ $$M_{if} \propto \underbrace{e\mathbf{E}_0\cdot\int u_c^*(\mathbf{r})\,\mathbf{r}\,u_v(\mathbf{r})\,d^3r}_{\substack{M_{CV} \\ \text{dipole transition criteria (as before)}}} \times \underbrace{\int \varphi_{n,c}^*(z)\,\varphi_{n',v}(z)\,dz}_{\substack{M_{n,n'} \\ \text{electron-hole spatial overlap in well}}}$$

Selection rules for optical transitions in a QW

(i) wavevector conservation: $\mathbf{k}_{\perp,v} = \mathbf{k}_{\perp,c} \pm \mathbf{k}_{photon}$

(ii) parity selection rule: $u_c(\mathbf{r})$ and $u_v(\mathbf{r})$ must differ in parity

as before

(iii)
$$M_{n,n'} = \int \varphi^*_{n,c}(z)\,\varphi_{n',v}(z)\,dz$$

need sufficient spatial overlap between electron and hole wavefunctions along the z-direction. For an infinite quantum well:

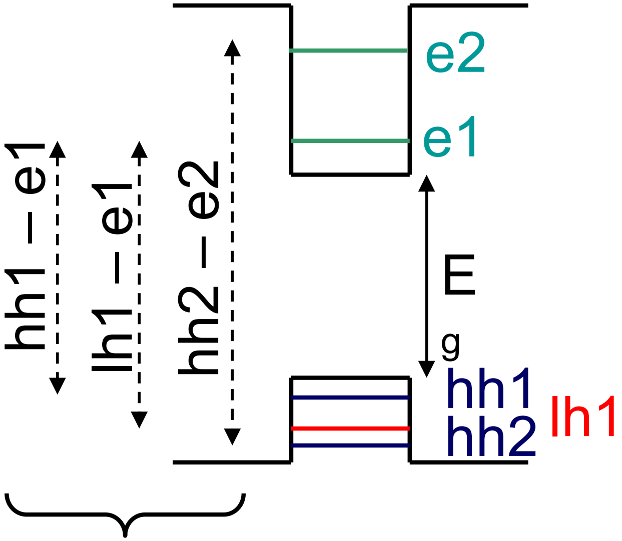
$$M_{n,n'} = \frac{2}{d}\int_{\frac{d}{2}}^{-\frac{d}{2}} \sin\left(k_n z + \frac{n\pi}{2}\right)\,\sin\left(k_{n'} z + \frac{n' z}{2}\right)\,dz$$

$$\boxed{M_{n,n'} = 0 \quad \text{unless} \quad n' = n}$$

N.B.: expect some deviation in finite quantum wells!

(iv) $M_{n,n'} = 0$ unless $\varphi_{n,c}(z)$ and $\varphi_{n',v}(z)$ have equal parity

(v) energy conservation:



allowed
dipole
transitions

$$\hbar\omega = E_g + E_{c,n} + E_{v,n} + E(\mathbf{k}_\perp)$$

photon energy

band gap of well material

confinement energy of electron/hole

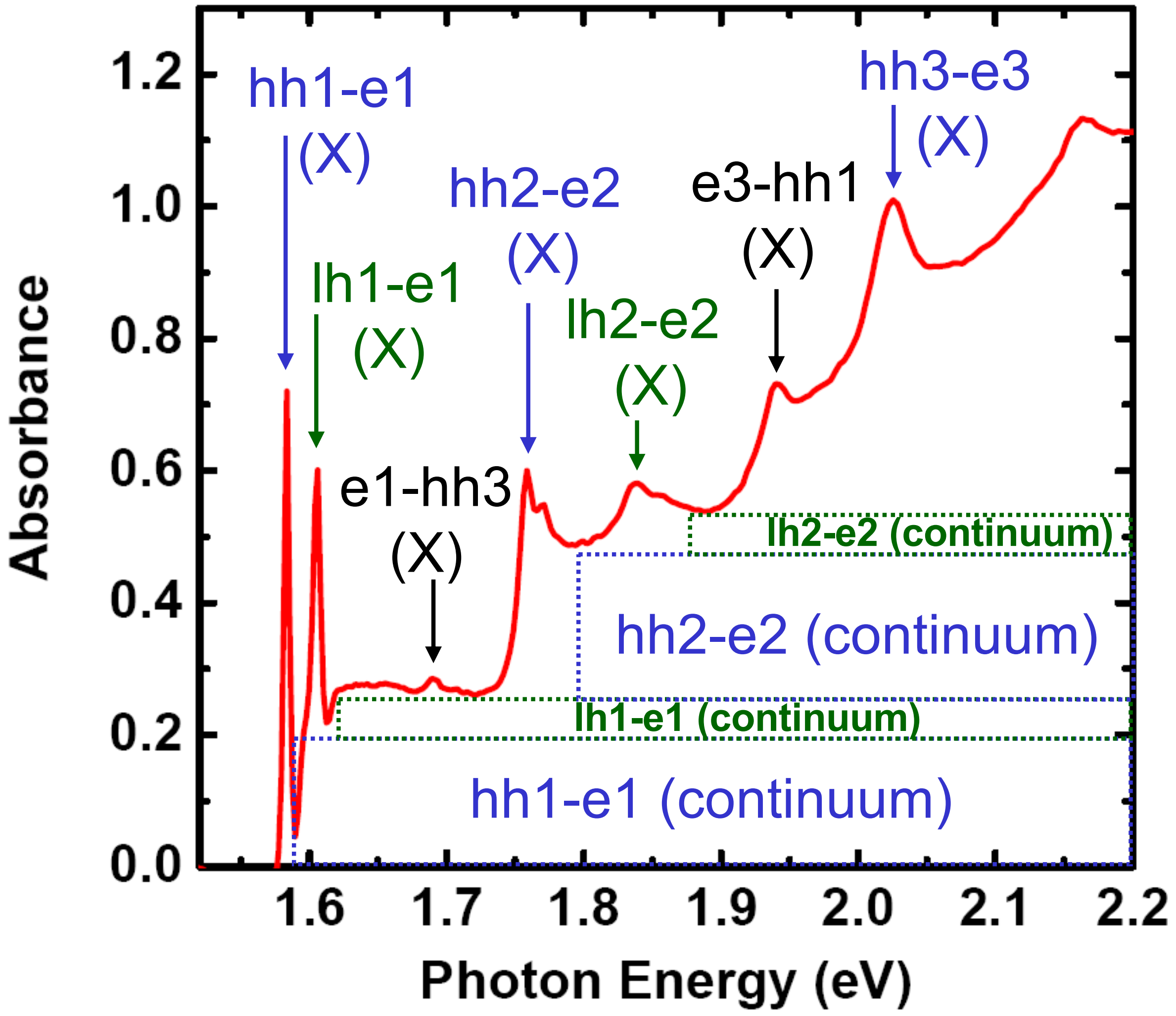
kinetic energy in plane of QW

and for $\mathbf{k}_\perp = 0$ (at the band edge):

$$\begin{aligned}\hbar\omega &= E_g + \frac{\hbar^2\pi^2 n^2}{2d^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)\\ &= E_g + \frac{\hbar^2\pi^2 n^2}{2d^2\mu}\end{aligned}$$

Example: absorption of a GaAs/AlAs QW

Absorption of GaAs/AlAs MQW (d=76Å) at 4K:

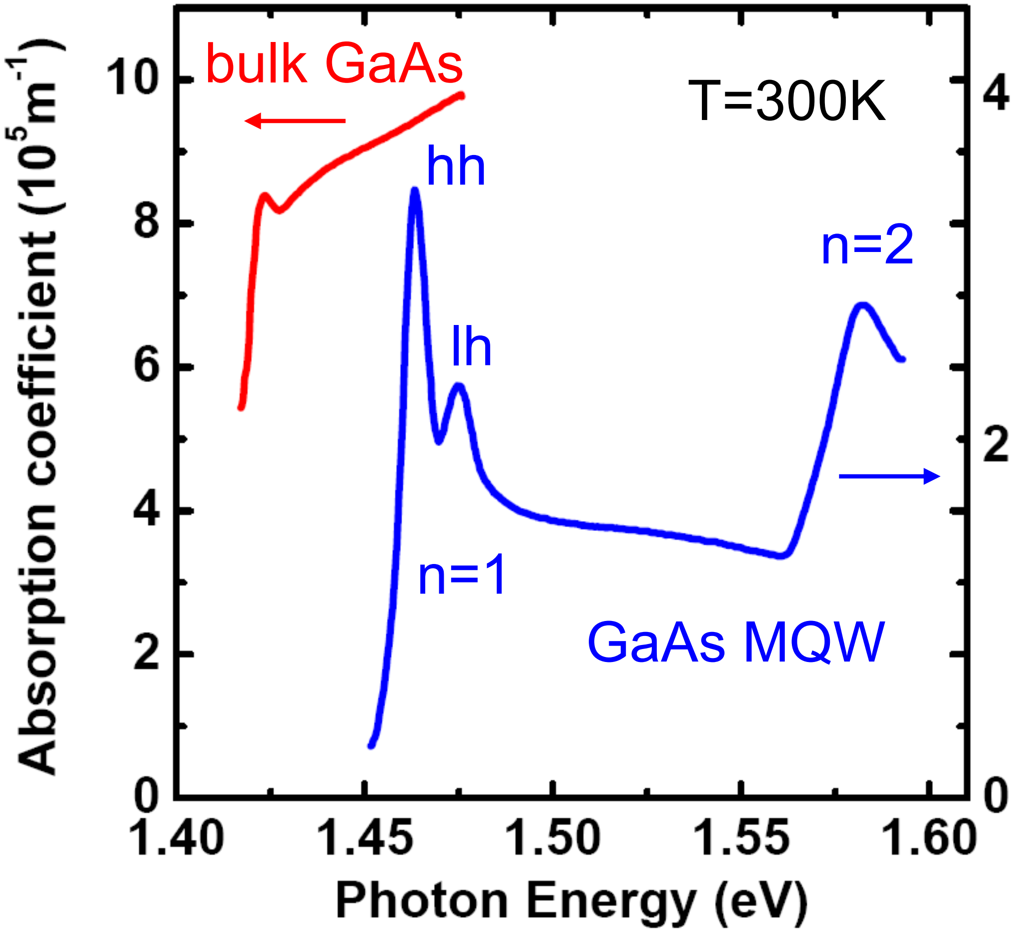


below each onset of absorption: excitonic features (X)

above onset: flat absorption, since 2D joint density of states independent of $\hbar\omega$

deviation from $\Delta n=0$, in particular at high E

Influence of confinement on the exciton



Confinement brings electron and hole closer together.

- enhanced exciton binding energy
- increased oscillator strength

V Optical response of a free electron gas

Classic Lorentz dipole oscillator model (again):

$$m\frac{d^2x}{dt^2} + m\,\gamma\,\frac{dx}{dt} + \xcancel{m\,\omega_0^2\,x} = -e\,E_0\,\exp(-i\omega t)$$

solutions are as before, but with $\omega_0 = 0$ (no retaining force!)

⇨ dielectric constant: $\epsilon_r(\omega) = \epsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right)$

with plasma frequency $\omega_p = \left(\frac{Ne^2}{\epsilon_\infty \epsilon_0 m}\right)^{\frac{1}{2}}$

and background dielectric constant $\epsilon_\infty = 1 + \chi_b$

⇨ real and imaginary part of the dielectric constant:

$$\epsilon'(\omega) = \epsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2 + \gamma^2}\right) \qquad \epsilon''(\omega) = \epsilon_\infty \frac{\gamma}{\omega}\frac{\omega_p^2}{\omega^2 + \gamma^2}$$

AC conductivity of a free electron gas

Can re-write equation of motion as: $$\frac{d\mathbf{p}}{dt} = -\frac{\mathbf{p}}{\tau} - e\mathbf{E}_0 \exp(-i\omega t)$$

⇨ electron with momentum p is accelerated by field but looses momentum at rate $\gamma = \tau^{-1}$

obtain electron velocity: $$\mathbf{v} = -\frac{e\tau}{m}\frac{1}{1-i\omega\tau}\mathbf{E}(t)$$

and using $\mathbf{j} = -Ne\mathbf{v} = \sigma\mathbf{E}$

⇨ AC conductivity $$\sigma(\omega) = \frac{\sigma_0}{1-i\omega\tau}$$

where $\sigma_0 = \frac{Ne^2\tau}{m} = \omega_p^2\,\epsilon_0\,\epsilon_\infty\,\tau$ (DC conductivity)

and $$\epsilon_r(\omega) = \epsilon_\infty + \frac{i}{\epsilon_0\,\omega}\sigma(\omega)$$

optical measurements of ε_r equivalent to those of AC conductivity!

Low-frequency regime

At low frequency of the EM wave, or $\omega \ll \gamma$

$$\epsilon_r(\omega) = \epsilon_\infty \left(1 - \frac{\omega_p^2/\omega^2}{1 + i\frac{\gamma}{\omega}} \right) \approx \underbrace{\epsilon_\infty}_{\epsilon'} + i\underbrace{\frac{\epsilon_\infty \, \omega_p^2}{\gamma \, \omega}}_{\epsilon''}$$

$\Longrightarrow$ $\epsilon'' \gg \epsilon'$ and one may approximate:

$$\kappa \approx \sqrt{\frac{\epsilon''}{2}} = \sqrt{\frac{\sigma_0}{2\epsilon_0\omega}} \quad \Longrightarrow \quad \alpha = \frac{2\omega\kappa}{c} = \sqrt{2\sigma_0\omega\mu_0}$$

Skin depth (distance from surface at which incident power has fallen to 1/e):

$$\boxed{\delta = \frac{2}{\alpha} = \left(\frac{2}{\sigma_0\omega\mu_0} \right)^{\frac{1}{2}}}$$

For Cu at 300K: $\sigma_0 = 6.5\times10^7\ \Omega^{-1}\mathrm{m}^{-1}$

$\Longrightarrow$ $\delta = 8.8\,\mathrm{mm}$ @ $\nu = 50\,\mathrm{Hz}$

$\delta = 6.2\,\mu\mathrm{m}$ @ $\nu = 100\,\mathrm{MHz}$

High-frequency regime

In a typical metal: $N \approx 10^{28} - 10^{29}$ m^{-3}, $\sigma_0 \approx 10^{7}\,\Omega^{-1}\mathrm{m}^{-1}$

⇒ Drude model predicts: $\gamma \approx 10^{14}$ s^{-1}

At optical frequencies: $\omega \gg \gamma$ (weak damping)

$$\epsilon_r \approx \epsilon' \approx \epsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2}\right) \quad \text{and} \quad \epsilon'' \approx \epsilon_\infty \frac{\gamma}{\omega} \frac{\omega_p^2}{\omega^2} \ll \epsilon'$$

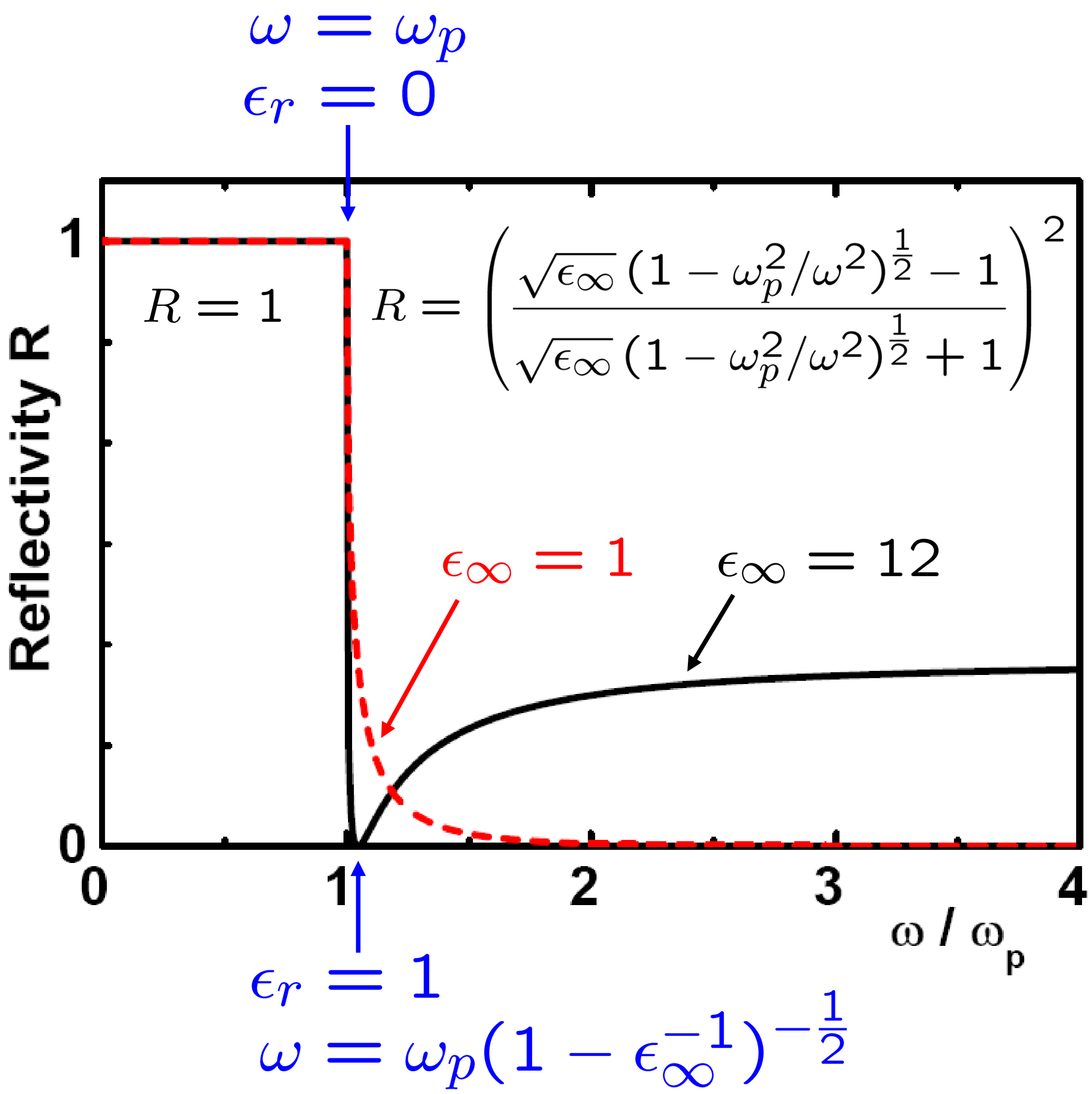
(i) $\omega < \omega_p$ $\quad \epsilon' < 0$ $\quad \tilde{n}$ largely imaginary

$R \approx 1$ wave mostly reflected

(ii) $\omega > \omega_p$ $\quad \epsilon' > 0$ $\quad \tilde{n}$ largely real

$R < 1$ wave partly transmitted,
weak absorption ($\alpha \propto \epsilon''$)

Reflectivity in the high-frequency regime



$\omega = \omega_p$
$\epsilon_r = 0$

$R = 1$

$$R = \left(\frac{\sqrt{\epsilon_\infty}\,(1 - \omega_p^2/\omega^2)^{\frac{1}{2}} - 1}{\sqrt{\epsilon_\infty}\,(1 - \omega_p^2/\omega^2)^{\frac{1}{2}} + 1} \right)^2$$

$\epsilon_\infty = 1$

$\epsilon_\infty = 12$

$\epsilon_r = 1$
$\omega = \omega_p(1 - \epsilon_\infty^{-1})^{-\frac{1}{2}}$

doped semiconductors:
large background dielectic constant ($\epsilon_\infty \approx 10 - 15$) from higher-energy interband transitions

most metals:
$\epsilon_\infty \approx 1$ (if no strong optical transitions at higher photon energy)

Example: Reflection from Alkali metals

Metal	**N** **(10^{28}m^{-3})**	**$\omega_p/2\pi$** **(10^{15}Hz)**	**λ_p** **(nm)**	**λ_{UV}** **(nm)**
Li	4.70	1.95	154	205
Na	2.65	1.46	205	210
K	1.40	1.06	282	315
Rb	1.15	0.96	312	360
Cs	0.91	0.86	350	440

measured at low T

calculated from

$$\omega_p = \left(\frac{Ne^2}{\epsilon_0 m}\right)^{\frac{1}{2}}$$

measured UV transmission cut-off

- high reflectivity up to UV wavelengths
- good agreement between measurement and Drude-Lorentz model

Example: Reflection from transition metals

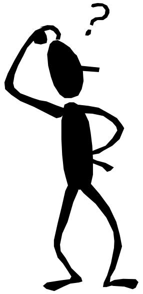
Metal	N $(10^{28}\mathrm{m}^{-3})$	$\omega_p/2\pi$ $(10^{15}\mathrm{Hz})$	λ_p (nm)
Cu	8.47	2.61	115
Ag	5.86	2.17	138
Au	5.90	2.18	138

measured at low T

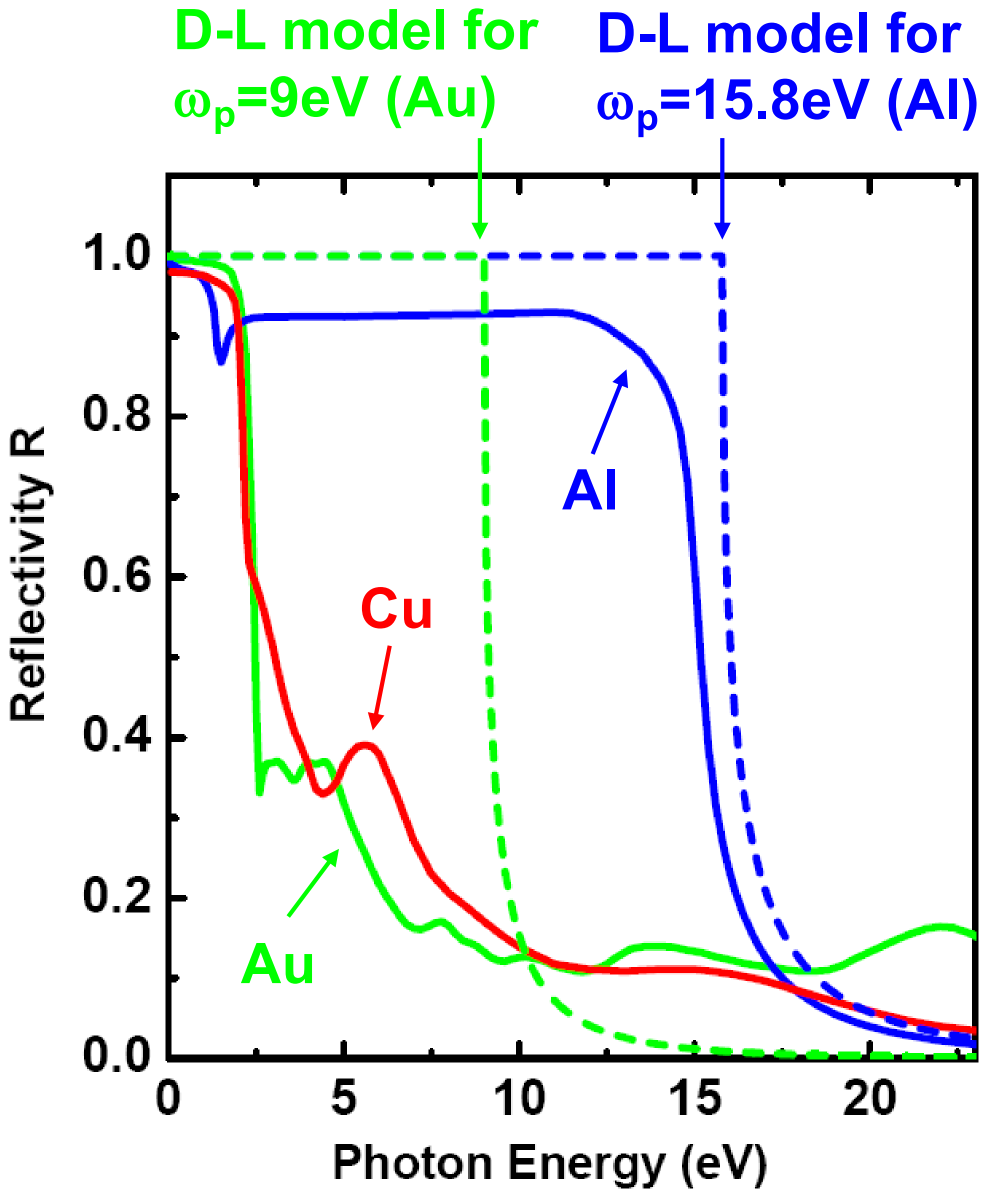
calculated from $\omega_p = \left(\frac{Ne^2}{\epsilon_0 m}\right)^{\frac{1}{2}}$

These transition metals should be fully reflective up to deep UV

But we know: Gold appears yellow, Copper red



Reflection of light from Au, Cu and Al:



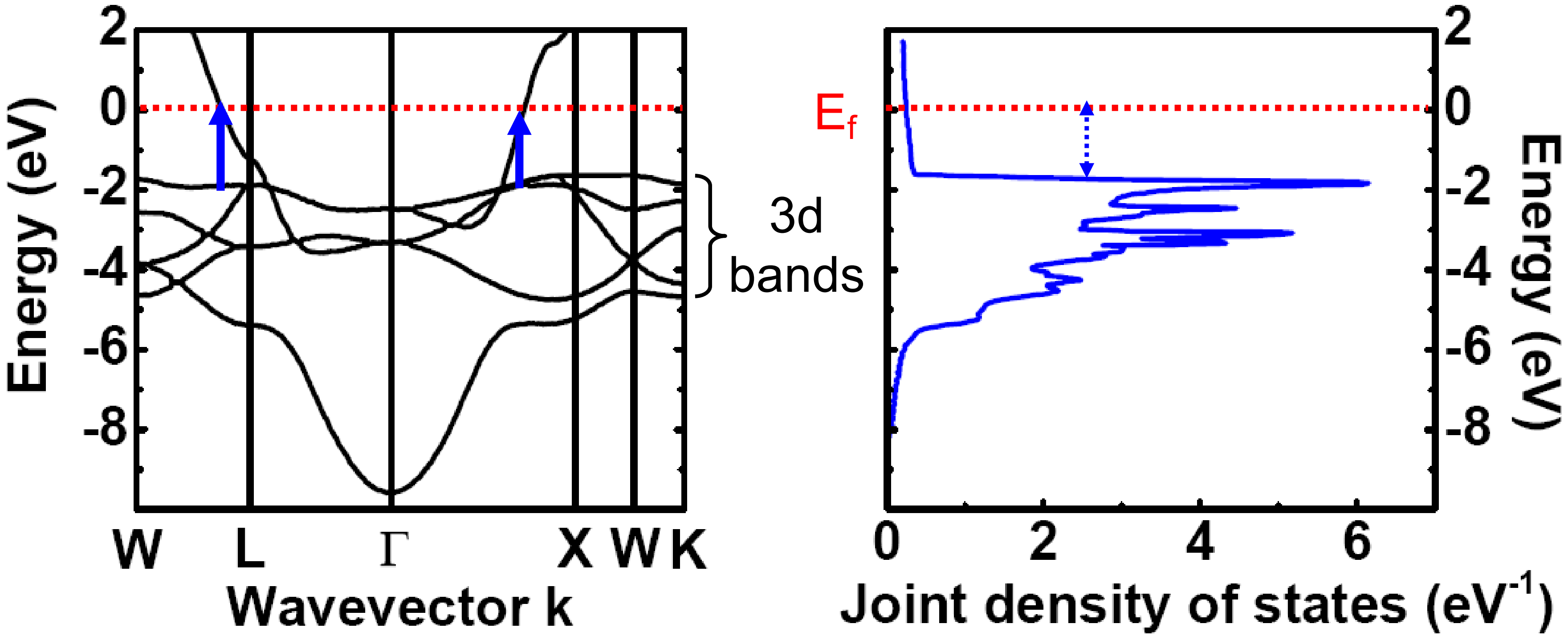
Drude-Lorentz model does not account fully for optical absorption of transition metals (especially in the visible)

⇨ need to consider bandstructure (damping has weak effect at these frequencies)

Example: Reflection from Copper

Electronic configuration of Cu: [Ar] $3d^{10}\,4s^{1}$

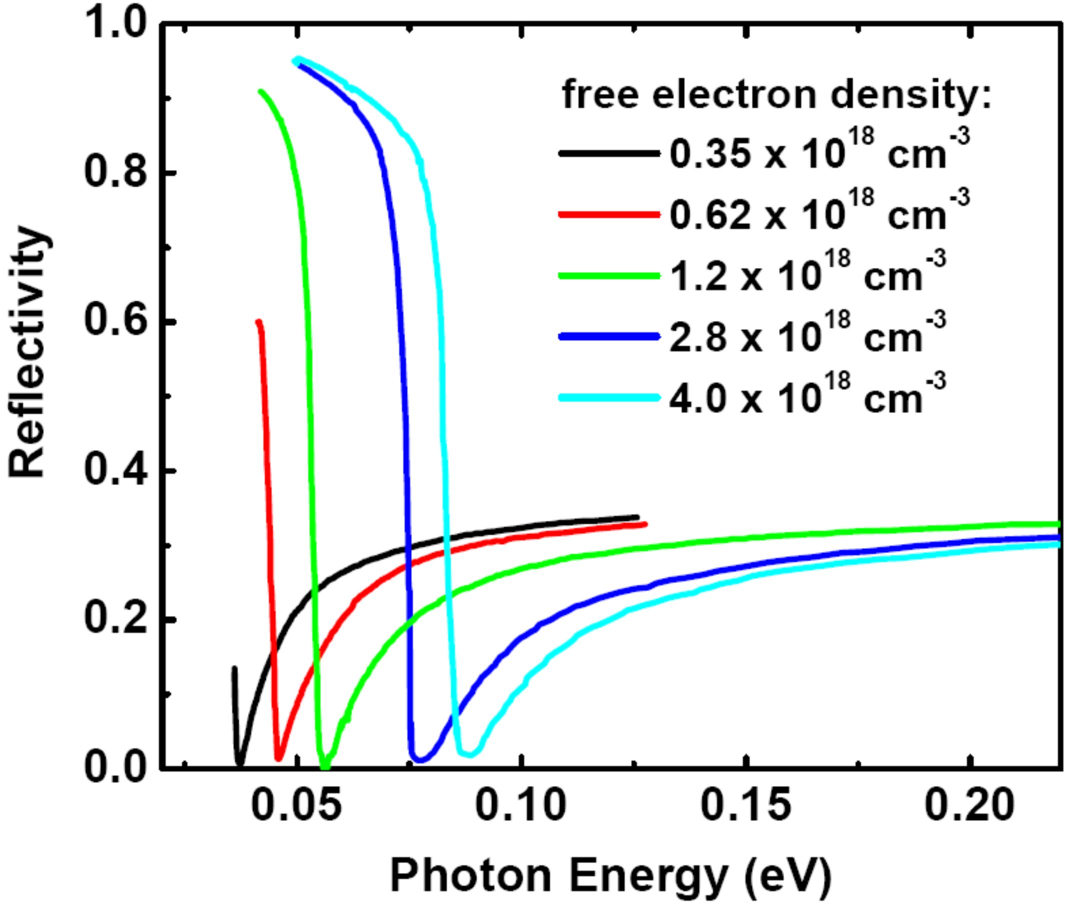
Transitions (in visible range of spectrum) between relatively dispersionless bands of tightly bound 3d electrons and half-filled band of 4s-electrons:



strong interband absorption for $\hbar\omega \geq 2\,eV$ → copper appears red !

Example: Reflection from doped semiconductors

Free-carrier reflectivity of InSb:



$$R = 0 \quad \text{for}$$

$$\omega = \omega_p (1 - \epsilon_\infty^{-1})^{-\frac{1}{2}}$$

$$\text{where} \quad \omega_p = \left(\frac{N e^2}{\epsilon_\infty \epsilon_0 m_e^*} \right)^{\frac{1}{2}}$$

⇨ Can determine effective mass of majority carriers from free carrier absorption

Example: Free-carrier absorption in semiconductors

For free carriers in the weak absorption regime ($\epsilon'' \ll \epsilon'$):

$$\kappa \approx \frac{\epsilon''}{2n} \Longrightarrow \text{predict:} \quad \alpha = \frac{2\omega}{c}\kappa = \frac{Ne^2}{m^* \epsilon_0} \frac{\gamma}{cn} \frac{1}{\omega^2} \propto \omega^{-2}$$

But experiments on n-type samples show:

$$\alpha \propto \omega^{-\beta} \quad \text{where} \quad \beta \approx 2 - 3$$

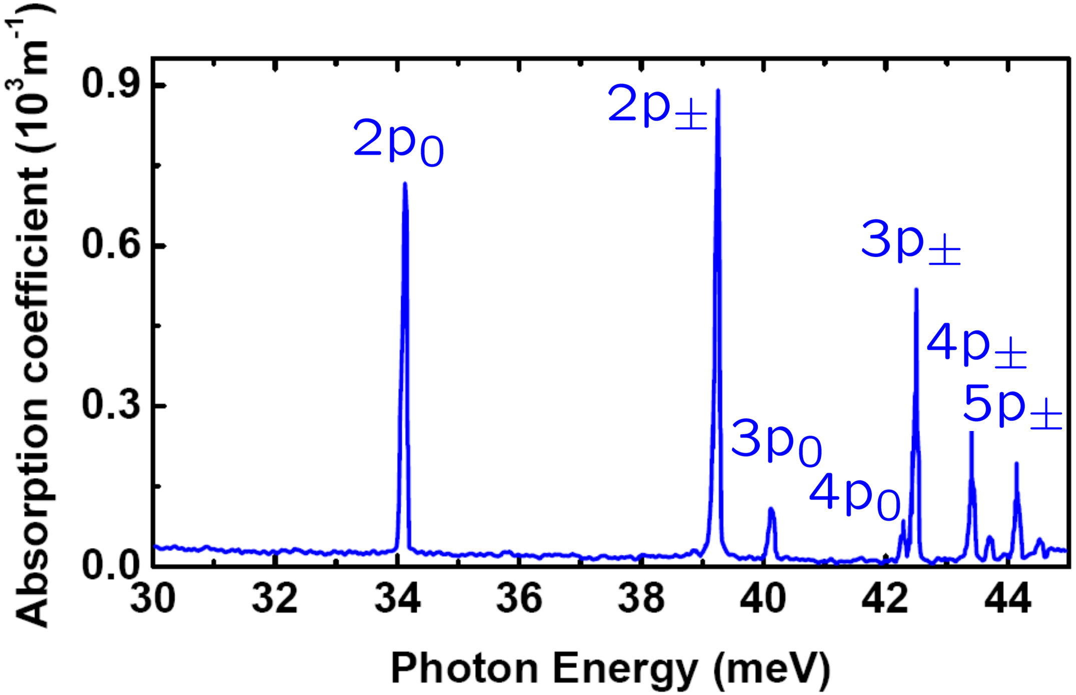
Deviations arise from:

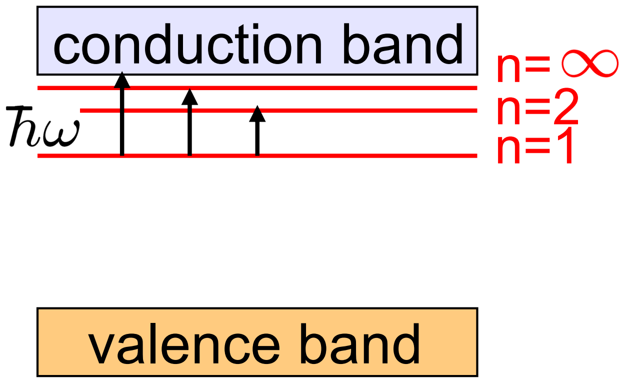
- intraband transitions involving phonon scattering
- in p-type semiconductors: intervalence band absorption
- absorption by donors bound to shallow donors or acceptors

Example: Impurity absorption in semiconductors

In doped semiconductors the electron (hole) and the ionized impurity are attracted by Coulomb interaction ⇨ hydrogenic system

Absorption of Phospor-doped silicon at 4.2K:





$$\hbar\omega = \frac{m_e^*}{m_0}\frac{R_y}{\epsilon_r^2}\left(1 - \frac{1}{n^2}\right)$$

⇨ Observe Lyman series for transitions from 1s level of Phosphor to p levels, whose degeneracy is lifted as a result of the anisotropic effective mass of the CB in Si

Plasmons

At the plasma edge ($\omega = \omega_p$): $\epsilon_r \approx \epsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2}\right) = 0$

What happens at this frequency?

- Polarization induced by the EM wave:

$$\mathbf{P} = (\epsilon_r - 1)\epsilon_0 \mathbf{E} = -\epsilon_0 \mathbf{E}$$

where $\mathbf{E} = \mathbf{E}_0 \exp[-i(\omega_p t - kz)]$

⇒ **P** is equal and opposite to incident field

- Wavevector $k = \frac{\omega_p}{c}\sqrt{\epsilon_r} \rightarrow 0$

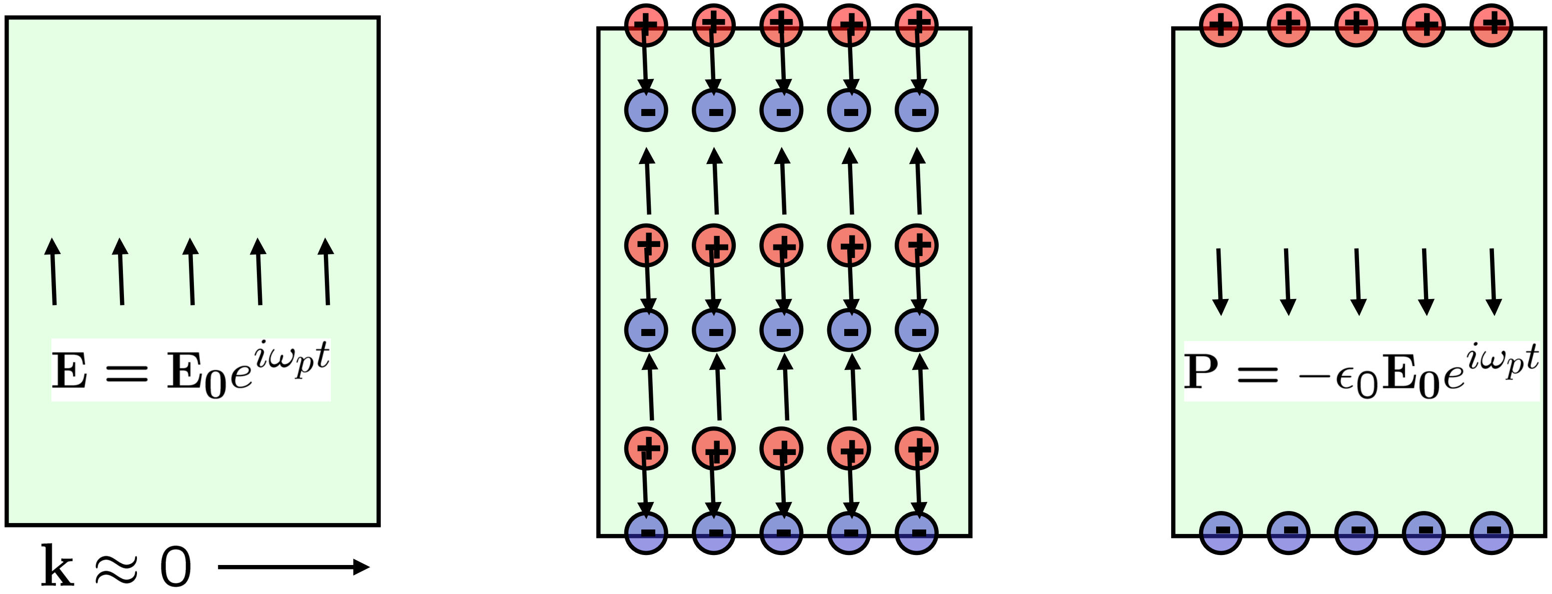
⇒ At the Plasma edge a uniform E-field in the material shifts the collective electron w.r.t the ionic lattice!

Plasma oscillations for $\varepsilon_r=0$:

applied EM wave

resulting charge distribution

induced macroscopic polarization



$\mathbf{E} = \mathbf{E_0} e^{i\omega_p t}$

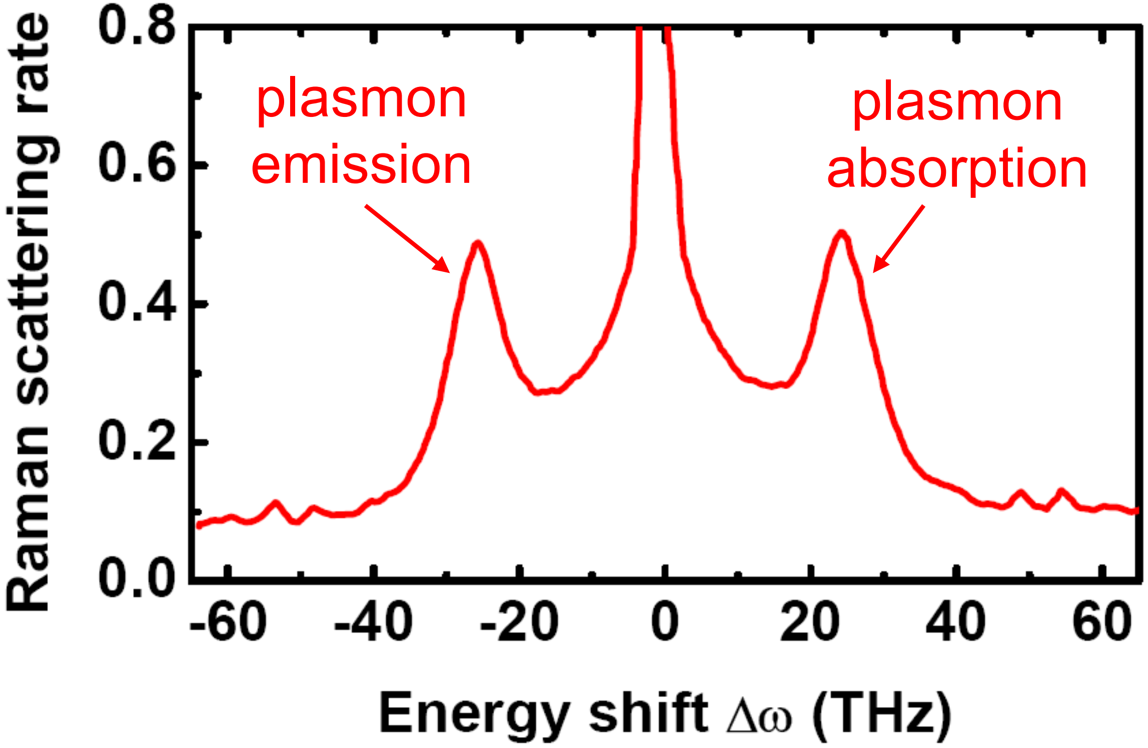
$\mathbf{k} \approx 0$

$\mathbf{P} = -\epsilon_0 \mathbf{E_0} e^{i\omega_p t}$

- For a (*transverse*) wavevector $\mathbf{k} \to 0$, the resulting charge distribution corresponds to a *longitudinal* oscillation of the electron gas with frequency ω_p!
- The quantum of such collective longitudinal plasma oscillations is termed a *plasmon*.

Example: Plasmons in n-type GaAs

Light scattered from n-type GaAs at 300K:



Energy conservation:

$$\omega_{out} = \omega_{in} \pm \omega_p$$

⇨ from data:

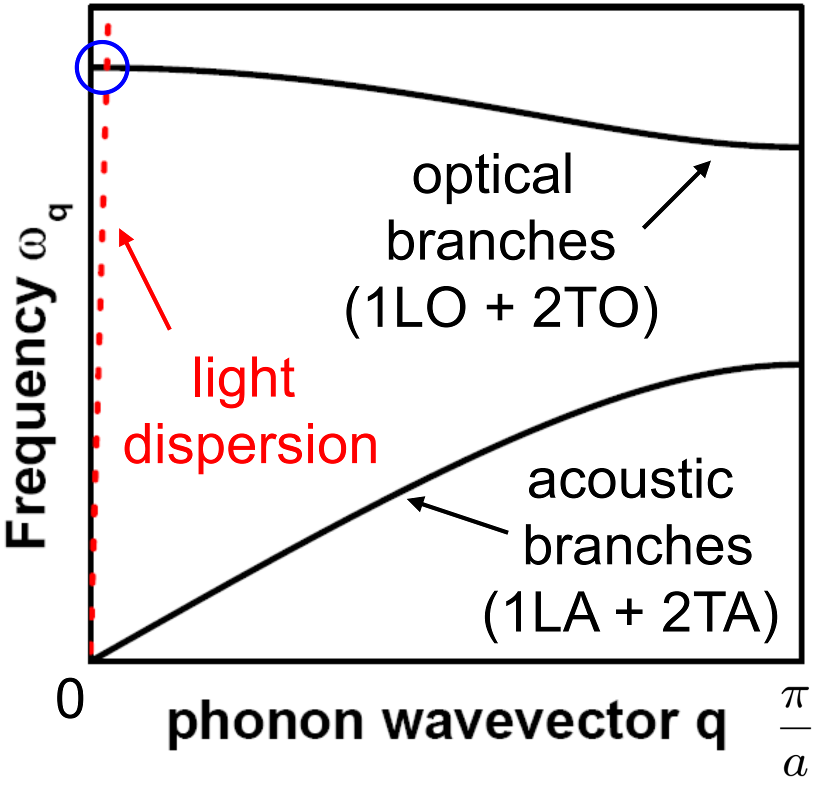
$$\omega_p = 25\,\mathrm{THz}$$

Expect from:

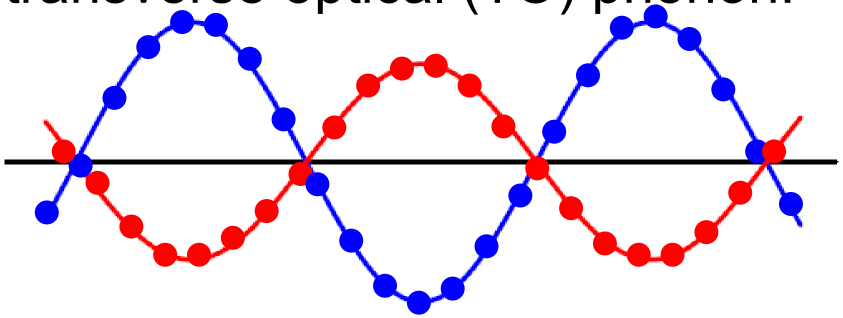
$$\left.\begin{array}{r}N = 1.75 \times 10^{23}\, m^{-1} \\ \epsilon_\infty = 10.6 \\ m_e^* = 0.067 m_e\end{array}\right\} \Rightarrow \begin{array}{rcl}\omega_p & = & \left(\dfrac{Ne^2}{\epsilon_\infty \epsilon_0 m}\right)^{\frac{1}{2}} \\ & = & 28\mathrm{THz}\end{array}$$

VI Optical studies of phonons

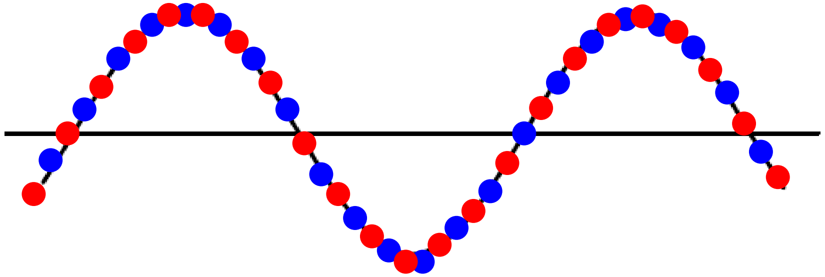
Dispersion relation for a diatomic linear chain:



transverse optical (TO) phonon:



transverse acoustic (TA) phonon:

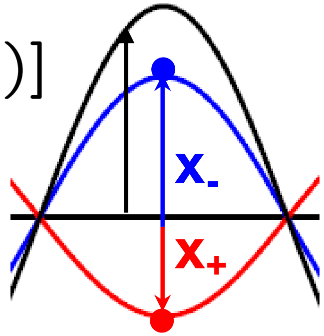


EM radiation is a transverse wave with wavevector $k \ll \pi/a$ and can thus interact directly *only with TO modes in polar crystals near the centre of the Brillouin zone.*

Harmonic oscillator model for the ionic crystal lattice

Diatomic linear chain under the influence of an external electric field:

$$E = E_0 \exp[i(kz - \omega t)]$$



Equations of motion:

$$\left.\begin{aligned} m_+ \frac{d^2 x_+}{dt^2} + C\,(x_+ - x_-) &= Q\,E(t) \\ m_- \frac{d^2 x_-}{dt^2} + C\,(x_- - x_+) &= -Q\,E(t) \end{aligned}\right\} \quad \mu \frac{d^2 x}{dt^2} + \mu\,\omega_{TO}^2\,x = Q\,E(t)$$

where $\omega_{TO} = \sqrt{\frac{C}{\mu}}$ frequency of TO mode near centre of Brillouin zone (with effective spring constant C)

$$\mu = \left(\frac{1}{m_+} + \frac{1}{m_-}\right)^{-1}$$ reduced mass

$$x = x_+ - x_-$$ relative displacement of positive and negative ions

Add damping term to account for finite phonon lifetime:

$$\boxed{\mu\,\frac{d^2x}{dt^2}+\mu\,\gamma\,\frac{dx}{dt}+\mu\,\omega_{TO}^2\,x=Q\,E(t)}$$

Displacement of ions induces polarization $P = NQx$

⇨ Dielectric constant (as before):

$$\epsilon_r(\omega)=1+\chi_b+\frac{Q^2N}{\epsilon_0\mu}\,\frac{1}{(\omega_{TO}^2-\omega^2-i\,\gamma\,\omega)}$$

Rewrite this result in terms of the static (ϵ_s) and the high-frequency (ϵ_∞) limits of the dielectric constant:

$$\epsilon_s\equiv\epsilon_r(0)=1+\chi_b+\frac{Q^2N}{\epsilon_0\,\mu\,\omega_{TO}^2}$$

$$\epsilon_\infty\equiv\epsilon_r(\infty)=1+\chi_b$$

⇨

$$\boxed{\epsilon_r(\omega)=\epsilon_\infty+(\epsilon_s-\epsilon_\infty)\frac{\omega_{TO}^2}{(\omega_{TO}^2-\omega^2-i\,\gamma\,\omega)}}$$

Lattice response in the low-damping limit

Long phonon lifetimes: $\gamma \approx 0$

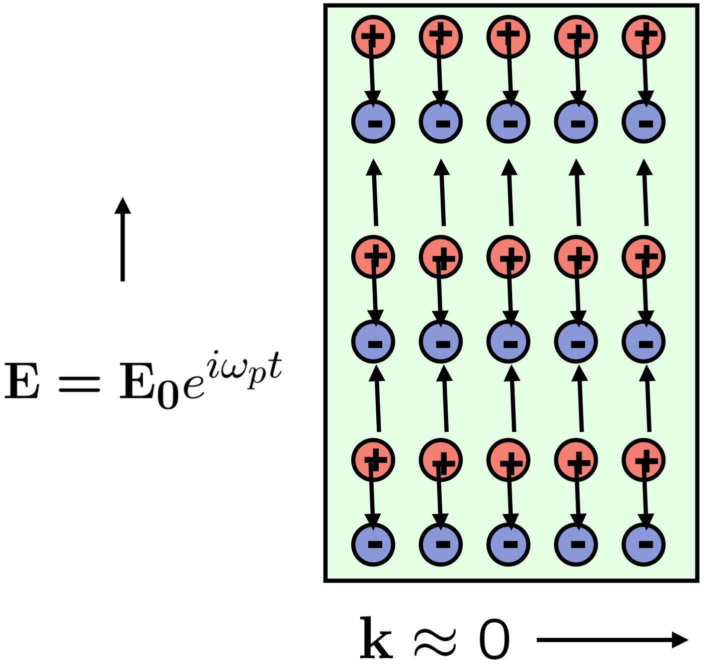
$$\Longrightarrow \quad \epsilon_r(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)\frac{\omega_{TO}^2}{(\omega_{TO}^2 - \omega^2)}$$

Consider Gauss’ s law. In the absence of free charge: $\nabla \cdot \mathbf{D} = 0$

$$\nabla \cdot (\epsilon_r \epsilon_0 \mathbf{E}) = 0 \quad \Longrightarrow \quad \begin{cases} \mathbf{k} \cdot \mathbf{E} = 0 & \text{wave must be transverse } (\, \mathbf{k} \perp \mathbf{E} \,) \\ \quad or & \\ \epsilon_r = 0 & \text{longitudinal wave possible } (\, \mathbf{k} \parallel \mathbf{E} \,) \end{cases}$$

What happens at ε_r=0 ?

Again: Wavevector of EM wave in medium: $$k = \frac{\omega_p}{c}\sqrt{\epsilon_r} \rightarrow 0$$



→ all ions of same charge shift by the same amount throughout the medium

→ result can be seen as a *transverse* wave ($\mathbf{k} \perp \mathbf{E}$) with $\boldsymbol{k} \approx 0$ or as a *longitudinal* wave ($\mathbf{k} \parallel \mathbf{E}$) in orthogonal direction.

The Lyddane-Sachs-Teller relationship

At ε_r=0 the induced polarization corresponds to a longitudinal wave, i.e. $\varepsilon_r(\omega_{LO})$=0

$$\boxed{\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\epsilon_s}{\epsilon_\infty}}$$

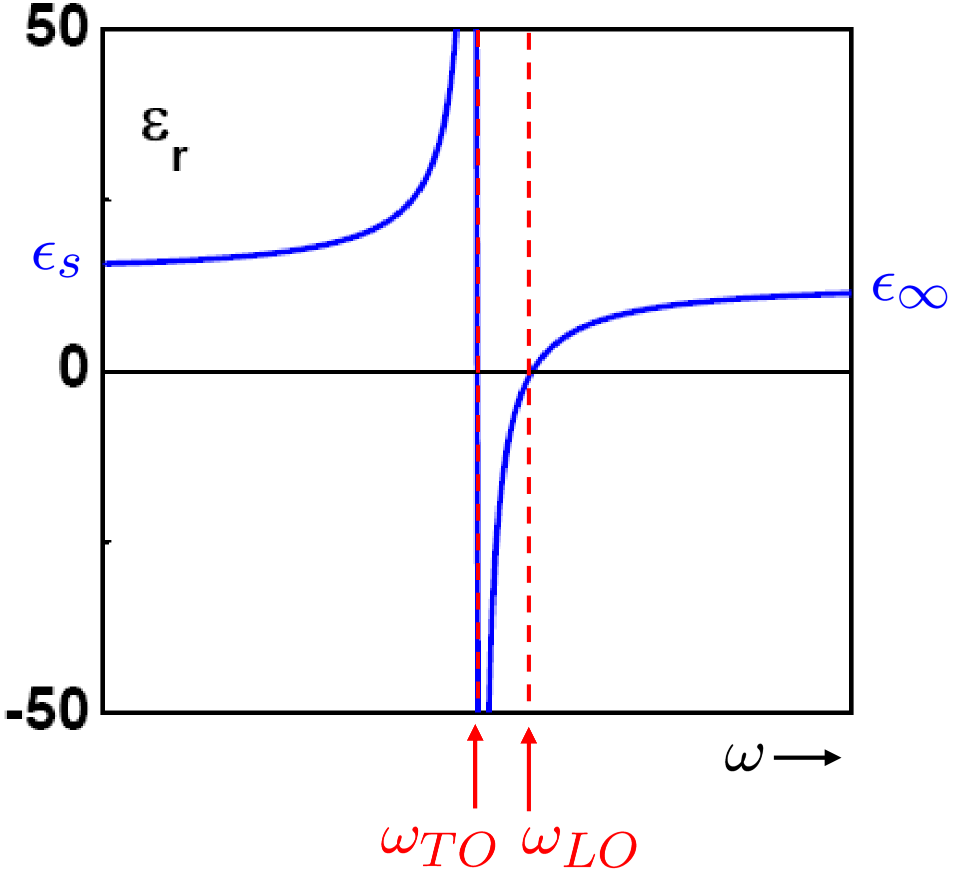
Lyddane-Sachs-Teller relationship

And from $\epsilon_s = \epsilon_\infty + \dfrac{Q^2 N}{\epsilon_0 \, \mu \, \omega_{TO}^2}$ follows: $\omega_{LO} \geq \omega_{TO}$

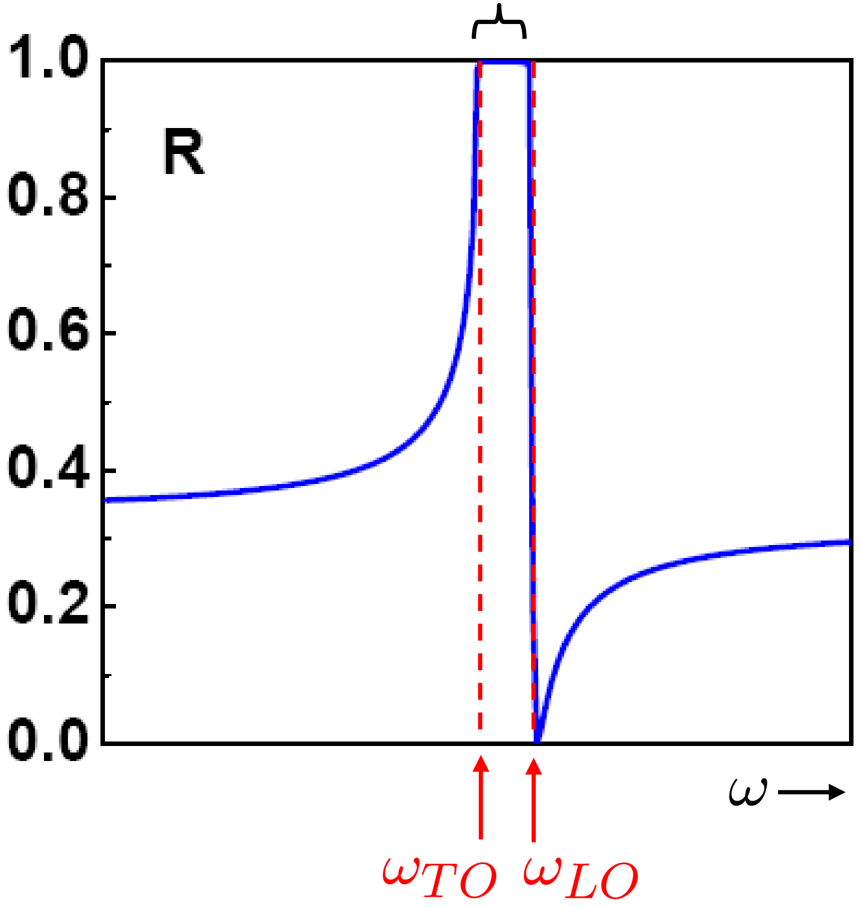
→ In polar crystals the LO phonon frequency is always higher than the TO phonon frequency

→ In non-polar crystals, $\epsilon_s = \epsilon_\infty$ and the LO and TO phonon modes are degenerate (at the Brillouin zone centre)

Dielectric constant and Reflectivity for undamped lattice

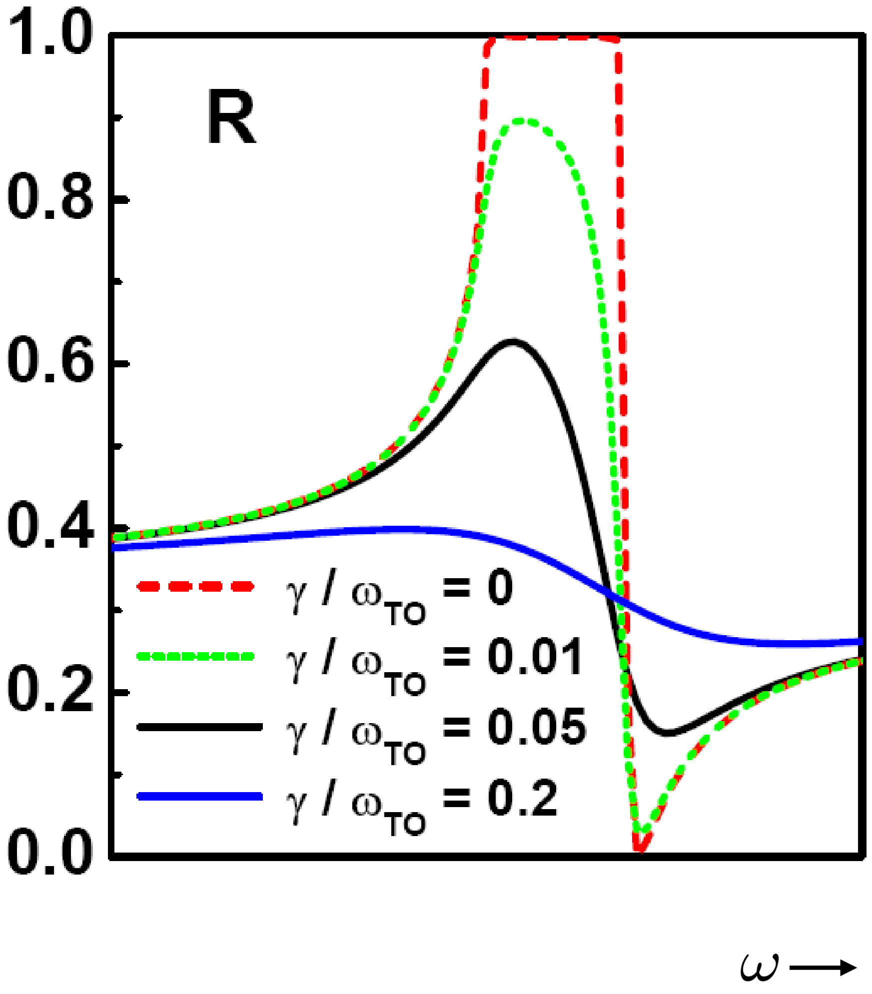


"Reststrahlen" band (R=1)



Influence of damping

Lattice Reflectivity:



For finite phonon lifetime ($\gamma \neq 0$) at resonance:

$$\epsilon_r(\omega_{TO}) = \underbrace{\epsilon_\infty}_{\epsilon'} + \underbrace{i\,(\epsilon_s - \epsilon_\infty)\,\frac{\omega_{TO}}{\gamma}}_{\epsilon''}$$

$$R(\omega_{TO}) = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} < 1$$

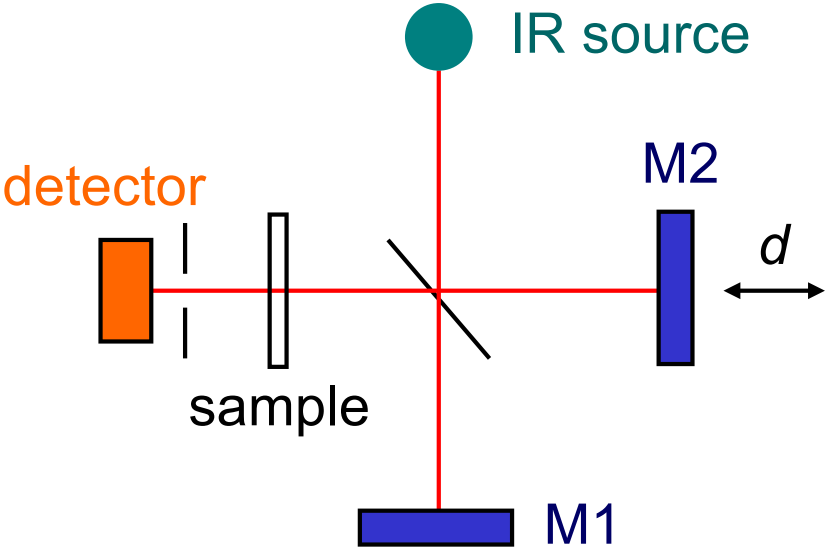
→ Reststrahlen band no longer fully reflective

→ general broadening of features

Measurements of IR reflectivity

Fourier transform infrared spectroscopy (FTIR):

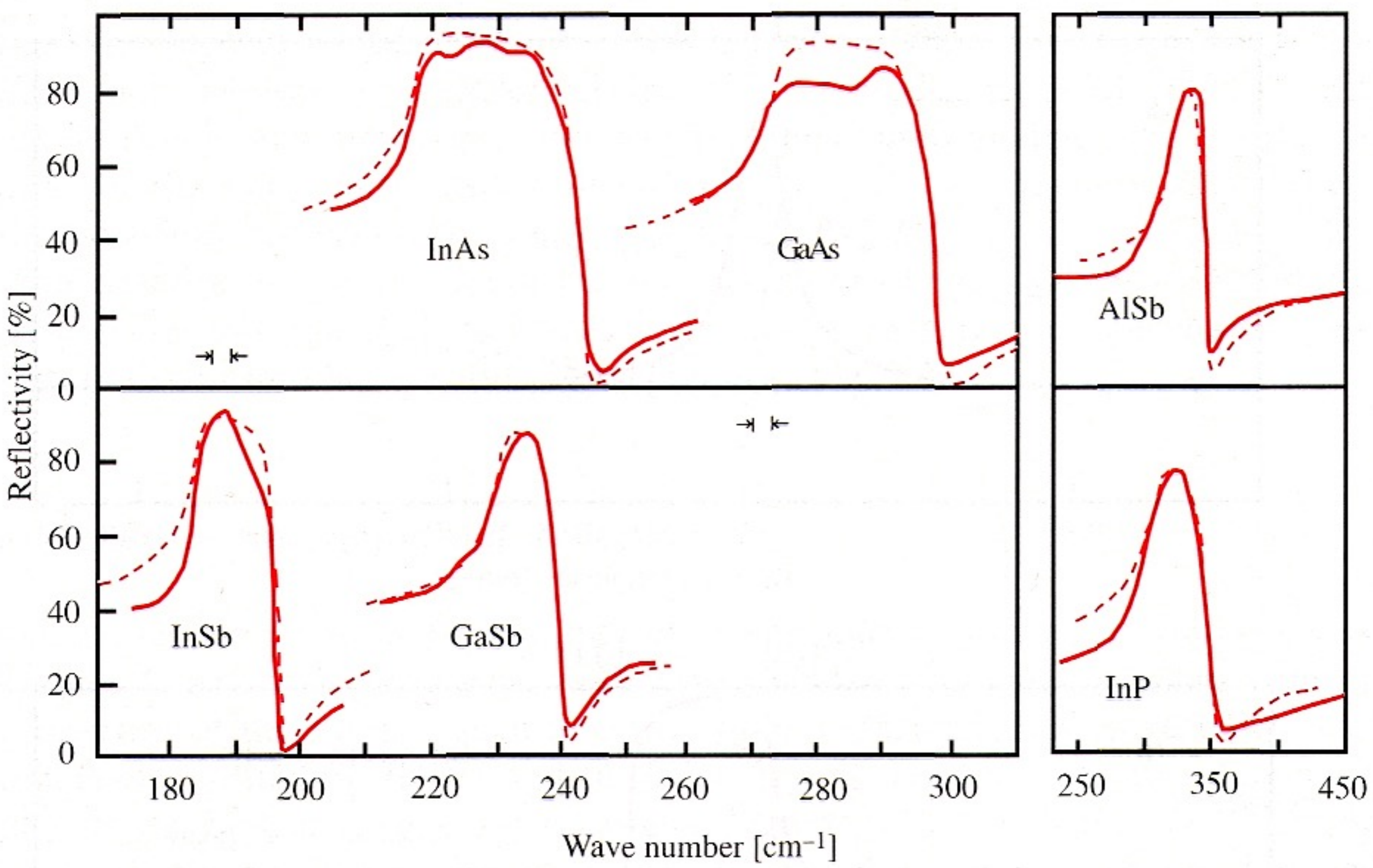
- measure interference pattern *I(d)* as a function of mirror displacement *d*
- *I(d)* gives Fourier transform of sample transmission *T(ν)* multiplied with system response *S(ν)*:



$$I(d) = \int S(\nu)\,T(\nu)\,[1+\cos(\frac{2\pi\nu d}{c})]d\nu$$

$$= \frac{1}{2}I(0) + \int S(\nu)\,T(\nu)\,\cos(\frac{2\pi\nu d}{c})d\nu$$

Example: reflection spectra for zinc-blende-type lattices



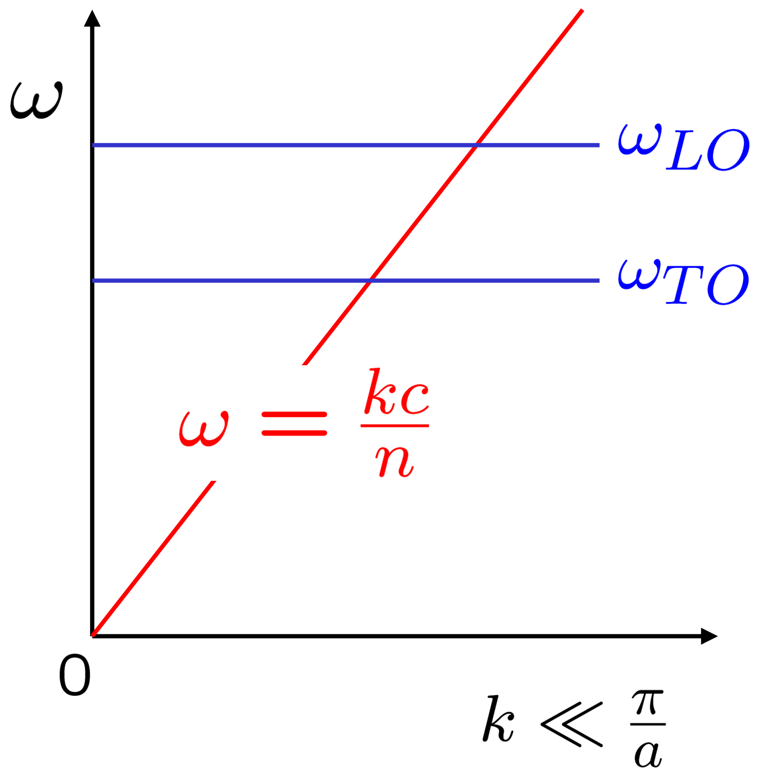
measured at 4.2K

measured at RT

Phonon-Polaritons

Examine more closely the dispersion relations for phonons and the EM wave near the Brillouin zone centre:

If no coupling occurred:



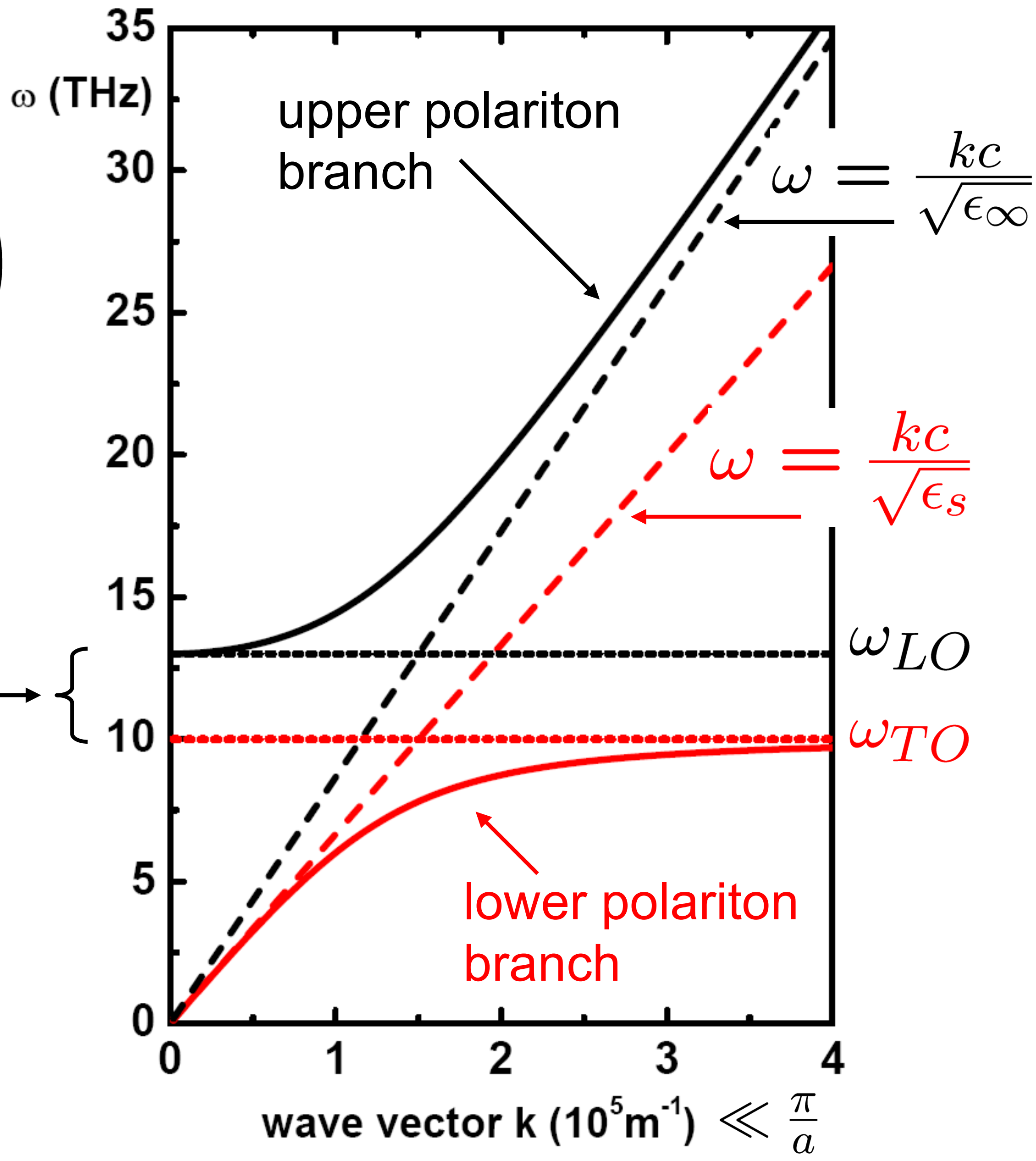
- But: coupling between TO phonon and EM wave leads to modified dispersion
- resulting wave is mixed mode with characteristics of TO polarization and EM wave
- LO phonon dispersion remains unchanged as it does not couple to the EM wave

Phonon-Polariton dispersion:

$$\begin{aligned} k^2 &= \frac{\omega^2}{c^2}\epsilon_r \\ &= \frac{\omega^2}{c^2}\epsilon_\infty \left(\frac{\omega_{LO}^2 - \omega^2}{\omega_{TO}^2 - \omega^2}\right) \end{aligned}$$

→ two branches for ω(k)

Reststrahlen band
(perfect reflection,
no mode can propagate)



Inelastic Light Scattering

- Scattering of light may be caused by fluctuations of the dielectric susceptibility χ of a medium
- time-dependent variation of χ may be caused by elementary excitations, e.g. phonons or plasmons
- scattering from optical phonons is called *Raman scattering* and that from acoustic phonons *Brillouin scattering*
- if u(r,t) is the displacement (of charge) associated with the excitation, the susceptibility can be expressed in terms of a Taylor series:

$$\chi(\omega,\mathbf{u}) = \chi(\omega) + \left(\frac{\partial\chi}{\partial\mathbf{u}}\right)_{\mathbf{u}_0}\mathbf{u} + \frac{1}{2}\left(\frac{\partial^2\chi}{\partial\mathbf{u}^2}\right)_{\mathbf{u}_0}\mathbf{u}^2 + \ldots$$

Polarization in the medium: $\mathbf{P} = \epsilon_0 \, \chi \, \mathbf{E}$

let $\mathbf{E} = \mathbf{E}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega \, t)$ light wave with frequency ω

$\mathbf{u} = \mathbf{u}_0 \cos(\mathbf{q} \cdot \mathbf{r} - \omega_q t)$ lattice wave with frequency ω_q

⇓

$$\mathbf{P} = \epsilon_0 \left(\chi(\omega) + \left(\frac{\partial \chi}{\partial \mathbf{u}} \right)_{\mathbf{u}_0} \mathbf{u} \right) \mathbf{E}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) = \mathbf{P}_0 + P_{ind}$$

where

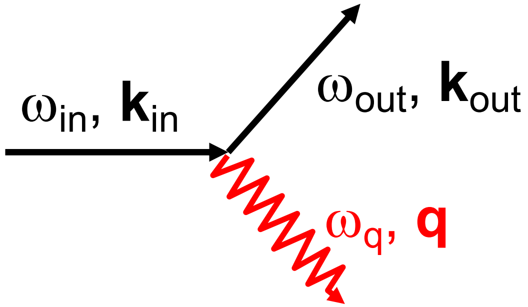
$\mathbf{P}_0 = \epsilon_0 \, \chi(\omega) \, \mathbf{E}_0 \cos \omega t$ unscattered polarization wave

$$\mathbf{P}_{ind} = \frac{1}{2} \epsilon_0 \left(\frac{\partial \chi}{\partial \mathbf{u}} \right)_{\mathbf{u}_0} \mathbf{u}_0 \mathbf{E}_0 \times$$

$$\times \ \{ \underbrace{\cos[(\mathbf{k} + \mathbf{q}) \cdot \mathbf{r} - (\omega + \omega_q) t]}_{\text{Anti-Stokes scattering}} + \underbrace{\cos[(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r} - (\omega - \omega_q) t]}_{\text{Stokes scattering}} \}$$

Energy & momentum conservation for inelastic scattering

Scattering process:



energy conservation: $\omega_{out} = \omega_{in} \pm \omega_q$

wave vector conservation: $\mathbf{k}_{out} = \mathbf{k}_{in} \pm \mathbf{k}_q$

Anti-Stokes scattering requires absorption of a phonon and therefore sufficiently high temperature. In general the ratio of Anti-Stokes to Stokes scattering intensities is given by:

$$\frac{I_{Anti-Stokes}}{I_{Stokes}} = \exp\left(-\frac{\hbar\omega_q}{k_B T}\right)$$

Maximum momentum transfer in backscattering geometry, where:

$$\pm q = k_{out} + k_{in} = \frac{n}{c}(2\omega_{in} \pm \omega_q) \approx 10^7 m^{-1} \ll \frac{\pi}{a}$$

⇨ Inelastic light scattering probes phonons with small wave vector

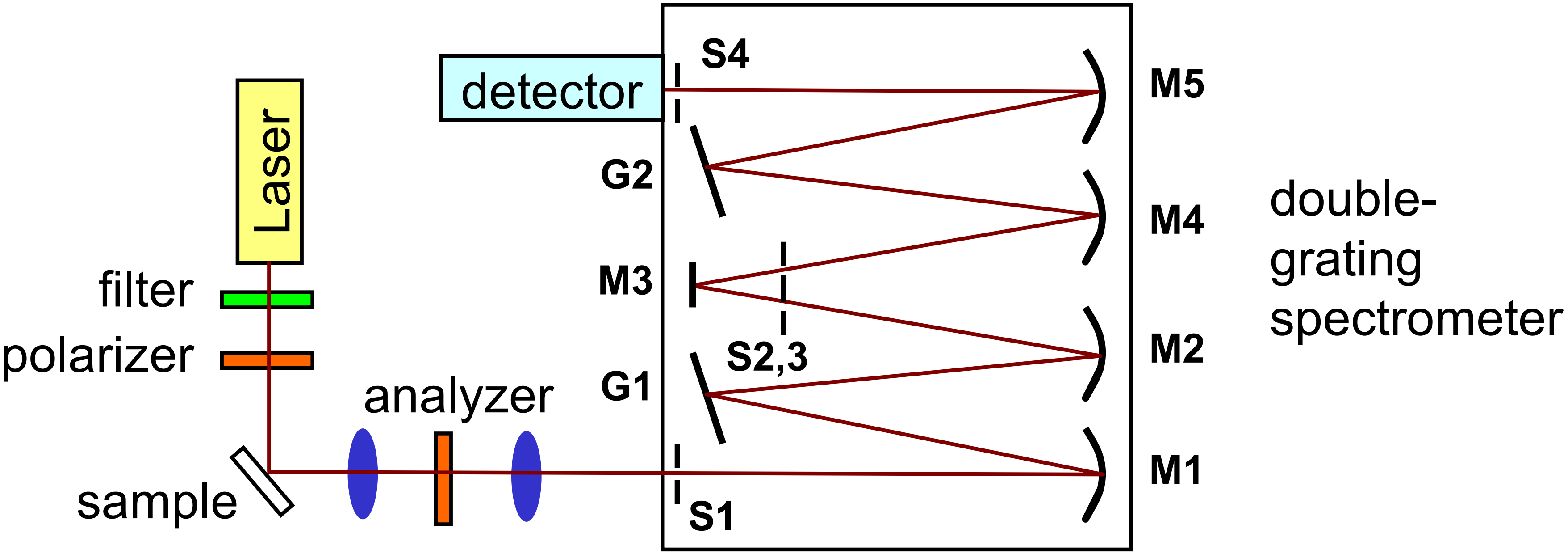
Raman spectroscopy: Experimental details

Require detection of optical phonons within typical frequency range $1\text{cm}^{-1} < \omega_p < 3000\text{cm}^{-1}$

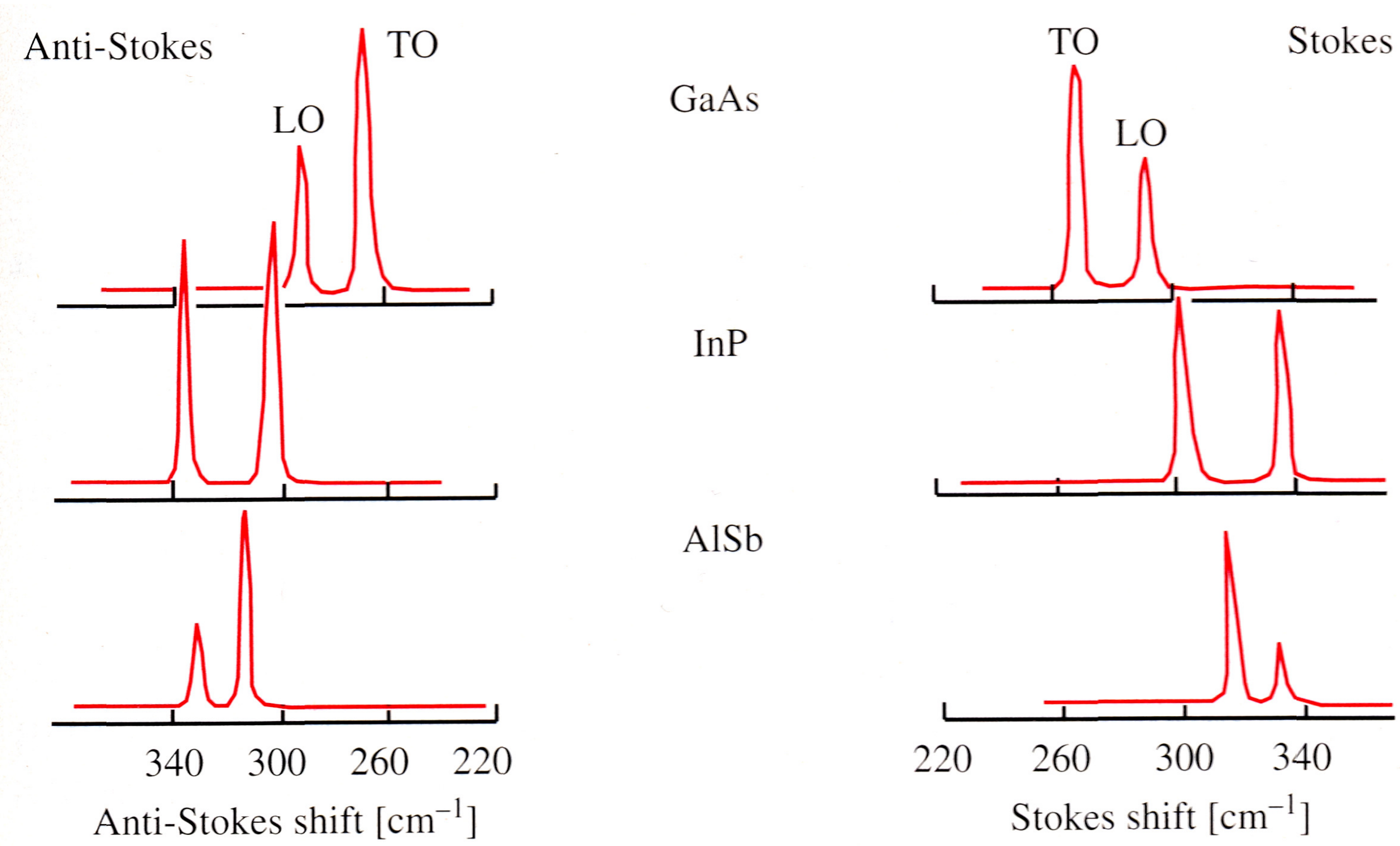
→ need excitation source (laser) with sufficiently narrow bandwidth

→ need detection system with high dispersion and ability to suppress elastically scattered light

Typical set-up:



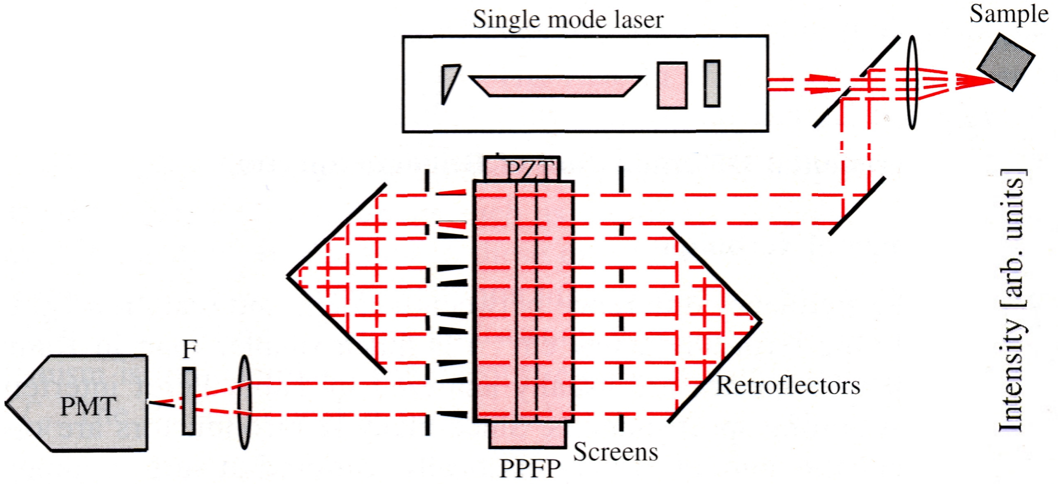
Raman spectra for zinc-blende-type semiconductors



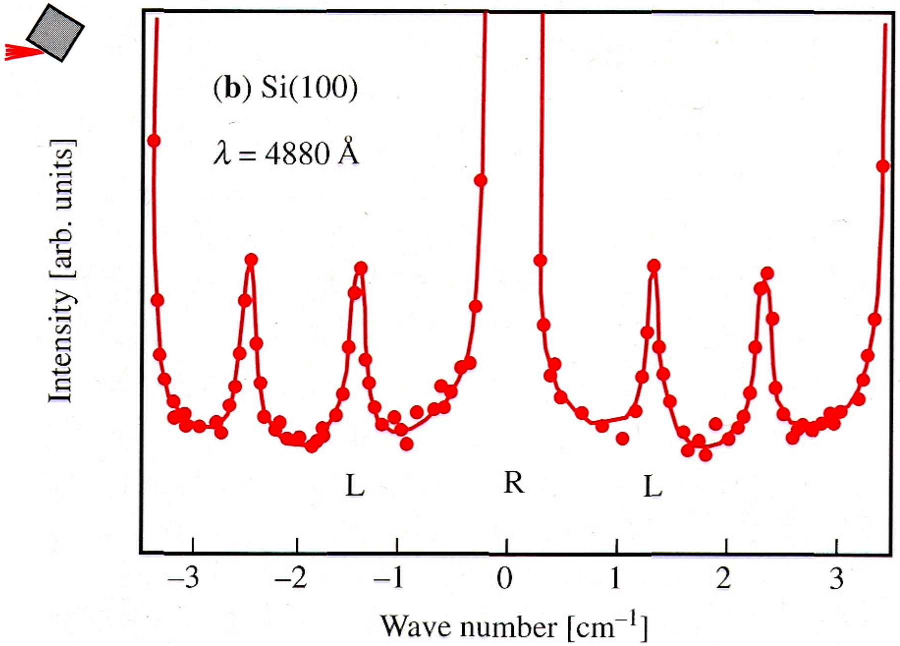
Brillouin scattering: Experimental details

Require detection of acoustic phonons near the centre of the Brillouin zone where $\omega_q = v_{ac}q$ → need to be able to measure shifts of only a few cm^{-1} !

Set-up based on a Multipass Interferometer:



Brillouin spectrum for Si(100):



Phonon lifetimes

<u>Experimental evidence</u> for finite phonon lifetimes from

i. Reflectivity measurements: R<1 in Reststrahlen band
$\rightarrow \gamma = \tau_{phonon}^{-1} \neq 0$

ii. Raman scattering: non-zero width of Raman line

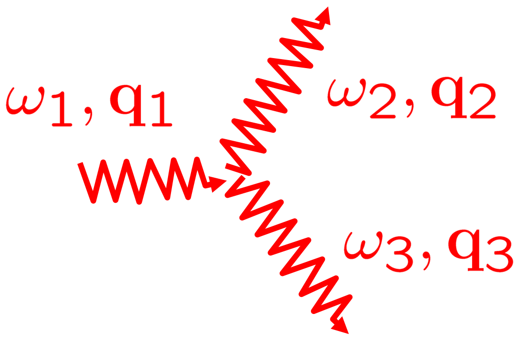
$$\Gamma = \frac{\hbar}{\tau_{phonon}}$$

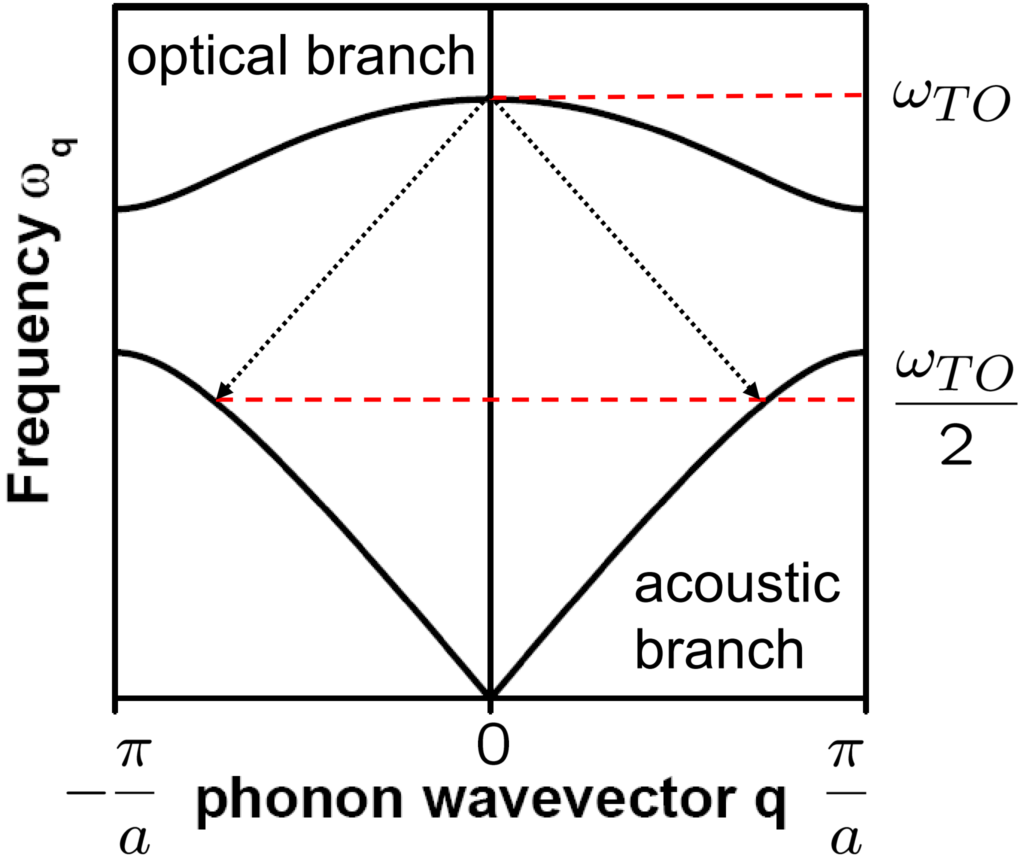
Data suggests phonon lifetimes of 1-10ps in typical inorganic semiconductors.

Origin of short phonon lifetimes: anharmonic potential experienced by the atoms:

$$U(x) = C_2x^2 + C_3x^3 + C_4x^4 + \dots$$

Anharmonic terms make possible higher-order processes, e.g. *phonon-phonon scattering:*

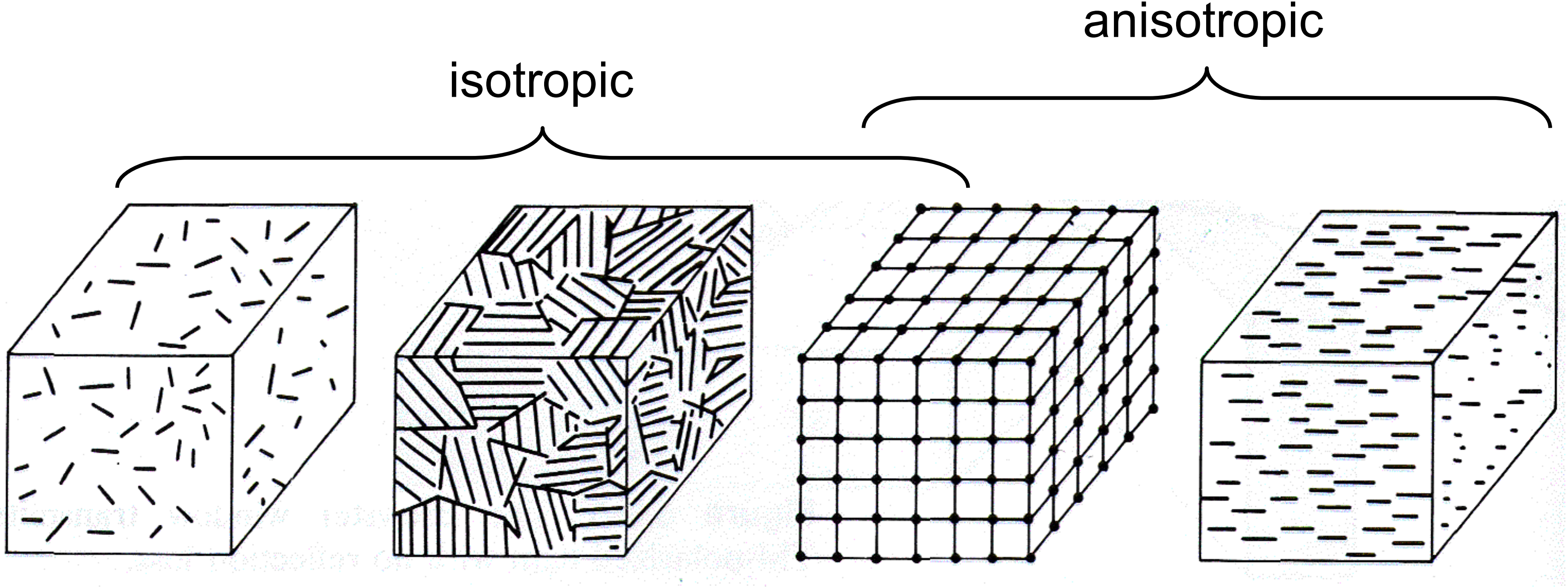




VII Optics of anisotropic media

A medium is *anisotropic* if its macroscopic optical properties depend on direction

Examples:



anisotropic

isotropic

gas, liquid,
amorphous
solid

polycrystalline

crystalline

liquid crystal

ε_r and χ in an anisotropic medium

Polarizability now depends on direction in which E-field is applied
→ relative electric permittivity ε_r and susceptibility χ now tensors:

$$\mathbf{D} = \epsilon_0 \epsilon_\mathbf{r} \mathbf{E} \quad \text{or} \quad \begin{pmatrix} D_1 \\ D_2 \\ D_3 \end{pmatrix} = \epsilon_0 \begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix}$$

→ **D** and **E** no longer necessarily point into the same direction!

But can always find coordinate system for which off-diagonal elements vanish, in which case:

$$\epsilon_\mathbf{r} = \begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix} = \begin{pmatrix} n_1^2 & 0 & 0 \\ 0 & n_2^2 & 0 \\ 0 & 0 & n_3^2 \end{pmatrix}$$

In the directions of these principal crystal axes **E** and **D** are parallel.

Propagation of plane waves in an isotropic medium

Ampere’s and Faraday’s law for plane waves:

$$\left.\begin{aligned}\mathbf{k}\times\mathbf{H} &= -\omega\,\mathbf{D}\\ \mathbf{k}\times\mathbf{E} &= \omega\,\mathbf{B}\end{aligned}\right\}\xrightarrow[\mathbf{D}=\epsilon_0\epsilon_\mathbf{r}\mathbf{E}]{\mathbf{B}=\mu_0\mathbf{H}}\ \mathbf{k}\times\mathbf{k}\times\mathbf{E} = -k_0^2\epsilon_\mathbf{r}\,\mathbf{E}$$

where $k_0 = \omega/c$is the wavevector in free space.

Choosing a coordinate system along the crystal’s principal axes yields:

$$\begin{pmatrix} k_0^2\epsilon_1 - k_2^2 - k_3^2 & k_1k_2 & k_1k_3 \\ k_1k_2 & k_0^2\epsilon_2 - k_1^2 - k_3^2 & k_2k_3 \\ k_1k_3 & k_2k_3 & k_0^2\epsilon_3 - k_1^2 - k_2^2 \end{pmatrix}\begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix} = 0$$

⇨ homogeneous matrix equation, require $\det(\cdots) = 0$

Solving the matrix equation ($\mathsf{det}(\cdots) = 0$) yields:

$$\begin{aligned}
&(k_0^2\epsilon_1 - k^2)(k_0^2\epsilon_2 - k^2)(k_0^2\epsilon_3 - k^2) \\
+ \quad & k_1^2\,(k_0^2\epsilon_2 - k^2)(k_0^2\epsilon_3 - k^2) \\
+ \quad & k_2^2\,(k_0^2\epsilon_1 - k^2)(k_0^2\epsilon_3 - k^2) \\
+ \quad & k_3^2\,(k_0^2\epsilon_1 - k^2)(k_0^2\epsilon_2 - k^2) = 0
\end{aligned}$$

This provides a dispersion relationship $\omega(k_1, k_2, k_3) = c\,k_0$

⇨ Can obtain the refractive index from the ratio of phase velocities in vacuo and inside medium:

$$n = \frac{c}{v} = \frac{\omega/k_0}{\omega/k} = \frac{k}{k_0} = \frac{1}{k_0}\sqrt{k_1^2 + k_2^2 + k_3^2}$$

Propagation of plane waves in uniaxial crystals

In uniaxial crystals (optic axis along z): $\epsilon_1 = \epsilon_2 = n_o^2 \qquad \epsilon_3 = n_e^2$

$$\Rightarrow \quad (k_0^2 n_o^2 - k^2)\left[\frac{k_1^2 + k_2^2}{n_e^2} + \frac{k_3^2}{n_o^2} - k_0^2\right] = 0$$

<u>Two solutions:</u>

(i) Sphere: $k = n_o\, k_0$

for *ordinary* ray

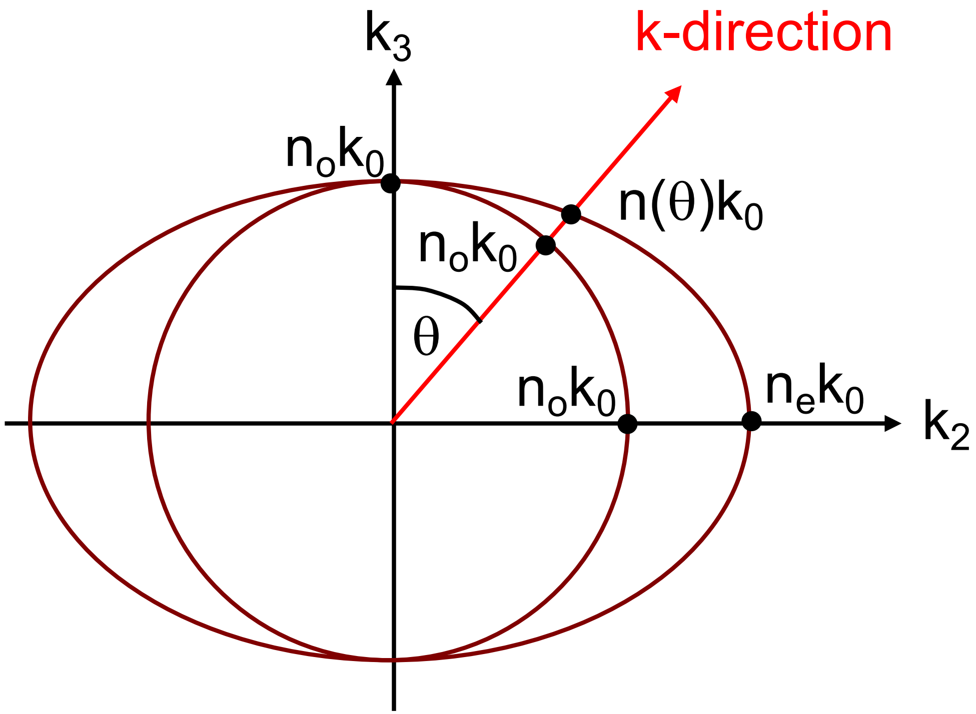
(polarized ⊥ to k-z plane)

(ii) ellipsoid of revolution

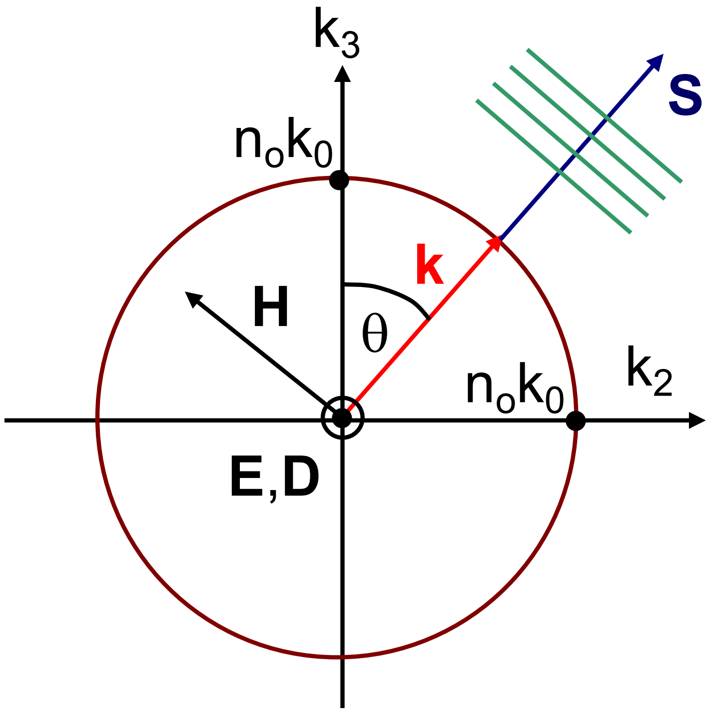
$$\frac{k_1^2 + k_2^2}{n_e^2} + \frac{k_3^2}{n_o^2} = k_0^2$$

for *extraordinary* ray

(polarized in k-z plane)

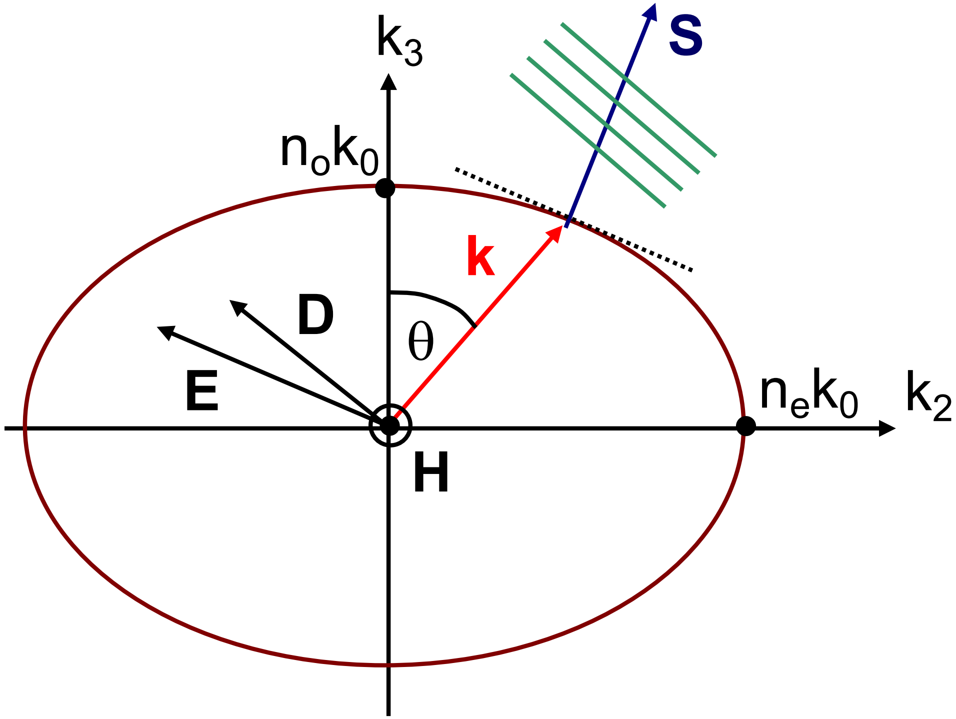


Ordinary *vs* extraordinary rays in uniaxial crystals



(a) ordinary ray:
E, **D** polarized ⊥ to plane containing k and the optic axis;
Refractive index:

$$n = n_o$$



(b) extraordinary ray:
E, **D** polarized in plane containing k and the optic axis

$$\frac{1}{n^2(\theta)} = \frac{\sin^2\theta}{n_e^2} + \frac{\cos^2\theta}{n_o^2}$$

Comments on wave propagation in uniaxial crystals

1) Faraday’ s & Ampere’ s law for plane waves in dielectrics:

$\mathbf{k} \times \mathbf{H} = -\omega\,\mathbf{D}$ ⟹ **D** is normal to both **k** and **H**

$\mathbf{k} \times \mathbf{E} = \omega\,\mu_0 \mathbf{H}$ ⟹ **H** is normal to both **k** and **E**

N.B.: this does *not* imply **E** ⊥ **k**!

2) All fields are of the form $\mathbf{A} = \mathbf{A}_0 \exp[-i(\mathbf{k}\cdot\mathbf{r} - \omega t)]$

⟹ wavefronts are ⊥ to **k**.

3) The phase velocity ***v*** is in the direction of **k** with

$$v = \omega/k = \omega/(n k_0)$$

4) As usual, the group velocity is

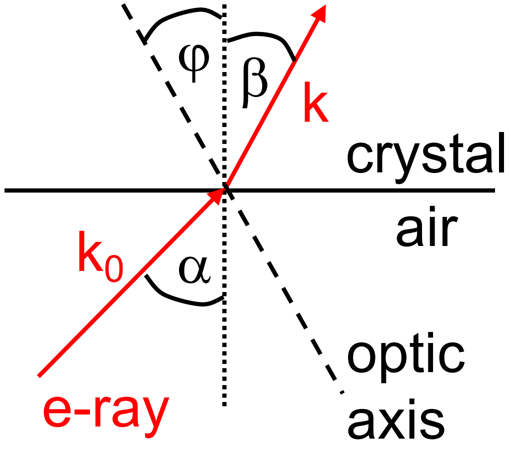
⟹ $\boldsymbol{v}_\mathrm{g}$ is normal to the k-surface! $\mathbf{v}_g = \nabla_{\mathbf{k}} \omega(\mathbf{k})$

5) The pointing vector $\mathbf{S} = \frac{1}{2}\mathbf{E} \times \mathbf{H}^*$ is normal to **E** and **H**

Can show: $\Delta\mathbf{k} \cdot \mathbf{S} = 0$ for small **Δk** ⟹ **S** normal to **k**-surface

6) From (5) and (1) follows that **E** is parallel to the **k**-surface.

Refraction at the surface of a uniaxial crystal

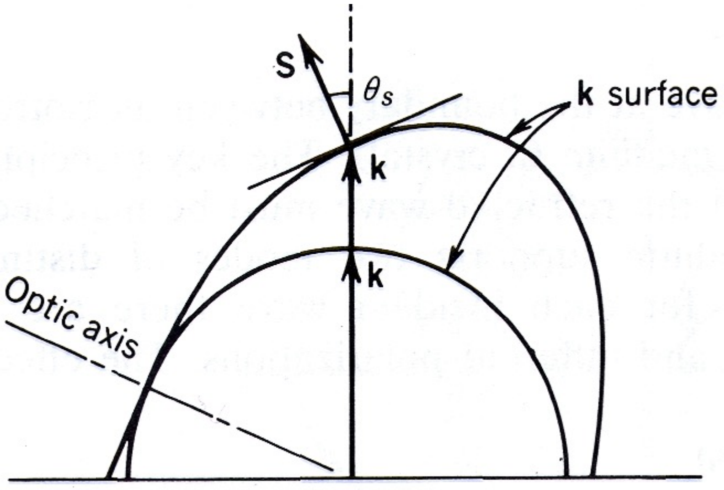


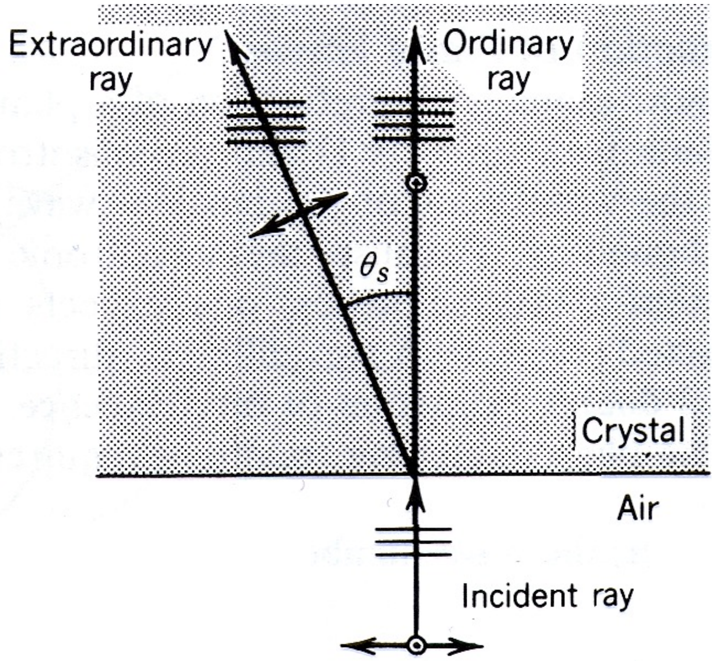
phase matching condition: $k_0 \sin\alpha = k \sin\beta$

⇨ $\sin\alpha = n(\beta + \varphi)\sin\beta$

N.B.: Snell' s law holds for the directions of **k** in the media, but this is not necessarily the direction of ray propagation!

Example: Double refraction at normal incidence:





VIII Non-linear Optics

Linear optics:

Polarization depends linearly on the electric field: $\mathbf{P} = \epsilon_0 \chi \mathbf{E}$

Electrons experience harmonic retaining potential $U(x) = \frac{1}{2} m \omega_0^2 x^2$

⇨ refractive index *n*, absorption coefficient *α*, reflectivity *R* independent of incident EM wave's intensity

But:

If E-fields become comparable to those binding electrons in the atom, anharmonic (non-linear) effects become significant.

For an H-atom: $|\mathbf{E}| \approx \frac{e}{4\pi\epsilon_0 a_B^2} \approx 5 \times 10^{11}\,\mathrm{Vm}^{-1}$

⇨ need EM wave intensity $I = \frac{1}{2} c \epsilon_0 n E^2 \approx 10^{19}\, Wm^{-2}$

Possible with tightly focused laser beams!

The non-linear susceptibility tensor

For a medium in which $\mathbf{P} \parallel \mathbf{E}$ we may in general write:

$$\begin{aligned} P = \epsilon_0 \chi^{NL} E &= \epsilon_0 (\chi E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots) \\ &= \underbrace{P^{(1)}}_{\text{linear}} + \underbrace{P^{(2)} + P^{(3)} + \cdots}_{\text{non-linear part}} \end{aligned}$$

$$\epsilon_r^{NL} = 1 + \chi + \chi^{(2)} E + \chi^{(3)} E^2 + \cdots \quad \text{now power-dependent!}$$

In an anisotropic medium, non-linear response will depend on directions of E-fields wrt the crystal:

⇨ Second-order non-linear polarization components:

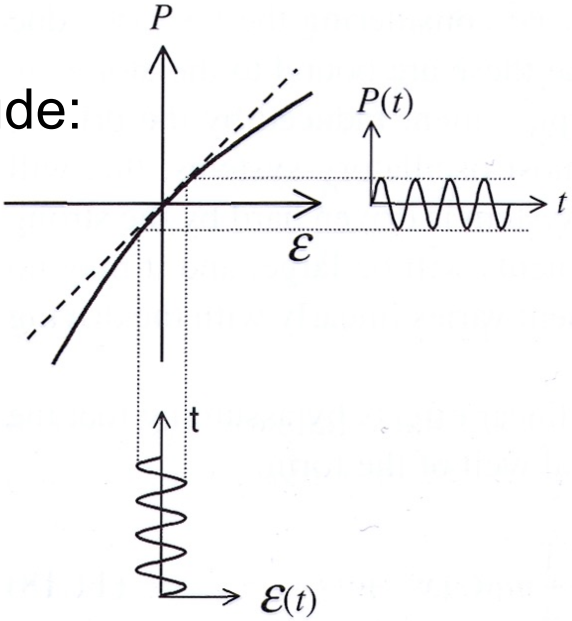
$$P_i^{(2)} = \epsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k$$

⇨ Third-order non-linear polarization components:

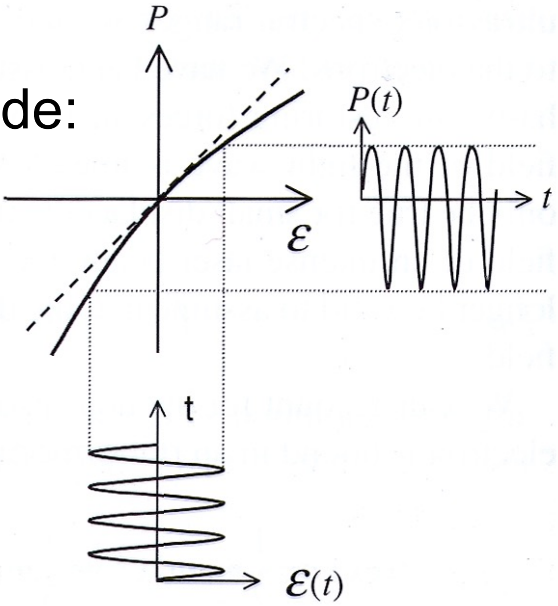
$$P_i^{(3)} = \epsilon_0 \sum_{j,k,l} \chi_{ijkl}^{(3)} E_j E_k E_l$$

Non-linear medium response to sinusoidal driving field

low applied
field amplitude:



high applied
field amplitude:



If $\mathbf{P} \parallel \mathbf{E}$ and the applied field $E = E_0 \sin \omega t$, then:

$$P = \epsilon_0 \chi E_0 \sin \omega t + \epsilon_0 \chi^{(2)} E_0^2 \sin^2 \omega t + \epsilon_0 \chi^{(3)} E_0^3 \sin^3 \omega t + \cdots$$

$$\begin{aligned} P = \epsilon_0 \chi E_0 \sin \omega t \quad &+ \quad \frac{1}{2} \epsilon_0 \chi^{(2)} E_0^2 (1 - \cos 2\omega t) \\ &- \quad \frac{1}{4} \epsilon_0 \chi^{(3)} E_0^3 (3 \sin \omega t - \sin 3\omega t) + \cdots \end{aligned}$$

⇒ second-order nonlinearity: rectification and frequency doubling
third-order nonlinearity: frequency tripling

Second-order nonlinearities (NL)

Treatment of non-resonant 2nd order NL within oscillator model:

Assume anharmonic potential: $U(x) = \frac{1}{2} m\,\omega_0^2 x^2 + \frac{1}{3} m\, C_3\, x^3 + \cdots$

Equation of motion:

$$m \frac{d^2 x}{dt^2} + m\,\gamma \frac{dx}{dt} + m\,\omega_0^2\, x + m C_3 x^2 = -e\, E_0 \exp(i\omega t)$$

Use trial solution: $x(t) = x_1 \exp(i\omega t) + x_2 \exp(i2\omega t)$

Assume $x_2 \ll x_1 \quad \rightarrow \quad x^2 \approx x_1^2 \exp(i2\omega t)$

Obtain displacement amplitudes: ⇨

$$\begin{cases} x_1 = -\dfrac{eE_0}{m} \dfrac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \\[2ex] x_2 = -C_3\, x_1^2 \dfrac{1}{\omega_0^2 - (2\omega)^2 + i2\omega\gamma} \end{cases}$$

Calculating the induced polarization:

$$\begin{aligned} P &= -N e\, x \\ &= -N e\, x_1 \exp(i\omega t) - N e\, x_2 \exp(i2\omega t) \\ &= \epsilon_0\, \chi E + \epsilon_0\, \chi^{(2)} E^2 \end{aligned}$$

$$\Downarrow$$

$$\chi = \frac{Ne^2}{m\epsilon_0} \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma}$$

linear susceptibility, as before

$$\chi^{(2)} = C_3 \frac{Ne^3}{m^2\epsilon_0} \frac{1}{(\omega_0^2 - \omega^2 + i\omega\gamma)^2\,(\omega_0^2 - (2\omega)^2 + i2\omega\gamma)}$$

second-order non-linear susceptibility

Can re-write the second-order non-linear susceptibility as:

$$\chi^{(2)} = C_3 \frac{m\epsilon_0^2}{N^2 e^3} [\chi(\omega)]^2 \chi(2\omega)$$

→ materials with large *linear* susceptibilty also have a large *non-linear* susceptibility

→ in a centrosymmetric medium, *U(x) = U(-x)* and therefore $C_3 = 0$ and $\chi^{(2)}=0$

⇨ second-order nonlinearities only occur in media that lack inversion symmetry!

(This may also be shown directly from the definition of P(2) - see question sheet.)

The second-order non-linear coefficient tensor d_{ij}

$$P_i^{(2)} = \epsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k \quad \Longrightarrow \quad 27 \text{ components in } \chi^{(2)}_{ijk}$$

But some of these components must be the same (e.g. $\chi^{(2)}_{xyz} E_y E_z = \chi^{(2)}_{xzy} E_z E_y$, so $\chi^{(2)}_{xyz} = \chi^{(2)}_{xzy}$ because ordering of fields is arbitrary)

⇒ Second-order response can be described by the simpler tensor d_{ij}, i.e.

$$\begin{pmatrix} P_x^{(2)} \\ P_y^{(2)} \\ P_z^{(2)} \end{pmatrix} = \epsilon_0 \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2\,E_y\,E_z \\ 2\,E_z\,E_x \\ 2\,E_x\,E_y \end{pmatrix}$$

In many cases crystal symmetry requires that most of the components of d_{ij} vanish.

2^{nd} order NL: Frequency (three-wave) mixing

Presume two waves are travelling in the medium, with

$$E_{1,j}(t) = \hat{E}_{1,j}\cos\omega_1 t \qquad E_{2,k}(t) = \hat{E}_{2,k}\cos\omega_2 t$$

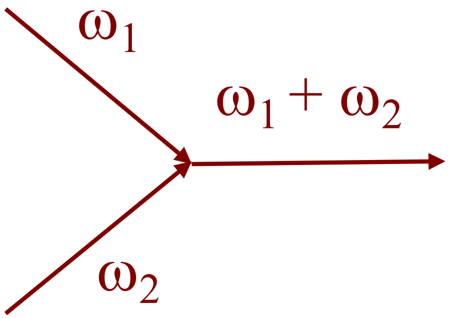
The induced polarization is:

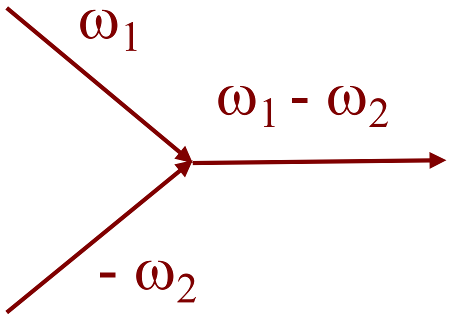
$$\begin{aligned} P_i^{(2)}(t) &= \epsilon_0 \sum_{j,k} \chi_{ijk}\,\hat{E}_{1,j}\,\hat{E}_{2,k}\,\cos\omega_1 t\,\cos\omega_2 t \\ &= \epsilon_0 \sum_{j,k} \chi_{ijk}\,\hat{E}_{1,j}\,\hat{E}_{2,k}\,\frac{1}{2}\left[\cos(\omega_1+\omega_2)t + \cos(\omega_1-\omega_2)t\right] \end{aligned}$$

sum-frequency generation

difference-frequency generation

Feynman diagrams for second-order nonlinear frequency mixing:





2^{nd} order NL: Frequency doubling

Consider the generation of second harmonics in more detail:

Maxwell's equations:

$$\nabla \times \mathbf{E} = -\frac{d}{dt}(\mu_0 \mathbf{H})$$

$$\nabla \times \mathbf{H} = \frac{d}{dt}\mathbf{D} = \frac{d}{dt}(\epsilon_0 \mathbf{E} + \underbrace{\epsilon_0 \chi \mathbf{E} + \mathbf{P}^{(2)}}_{\mathbf{P}})$$

⇨ Wave equation:

$$\nabla^2 \mathbf{E} = \epsilon_0 \, \mu_0 \, (1 + \chi) \, \frac{d^2}{dt^2} \mathbf{E} + \mu_0 \, \frac{d^2}{dt^2} \mathbf{P}^{(2)}$$

Consider propagation of second-harmonic wave in z-direction:

$$E_i^{2\omega}(z,t) = \hat{E}_i^{2\omega}(z) \exp[i(2\omega t - k_{2\omega} z)]$$

Let this wave be generated from two fundamental waves:

$$E_j^{\omega}(z,t) = \hat{E}_j^{\omega}(z) \exp[i(\omega t - k_{\omega} z)]$$

$$E_k^{\omega}(z,t) = \hat{E}_k^{\omega}(z) \exp[i(\omega t - k_{\omega} z)]$$

⇨ Obtain specific wave equation:

$$\begin{aligned}\frac{d^2}{dz^2}\,E_i^{2\omega}(z,t) &= \epsilon_0\,\mu_0[1+\chi(2\omega)]\,\frac{d^2}{dt^2}\,E_i^{2\omega}(z,t)\\ &+ \epsilon_0\,\mu_0\,\frac{d^2}{dt^2}\sum_{j,k}\chi_{ijk}^{(2)}\,E_j^{\omega}(z,t)\,E_k^{\omega}(z,t)\end{aligned}$$

Assume that the variation of the complex field amplitude is small (slowly varying envelope approximation):

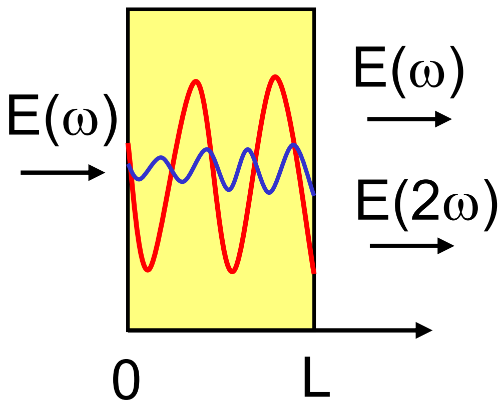
$$\frac{d^2}{dz^2}\,\widehat{E}_i^{2\omega}(z) \ll k_{2\omega}\,\frac{d}{dz}\,\widehat{E}_i^{2\omega}(z)$$

Obtain DE for increase of the second harmonic along the direction of propagation:

$$\frac{d}{dz}\,\widehat{E}_i^{2\omega}(z) = -i\,\frac{\omega}{c\,n_{2\omega}}\sum_{j,k}\chi_{ijk}^{(2)}\,\widehat{E}_j^{\omega}(z)\,\widehat{E}_k^{\omega}(z)\,\mathrm{exp}(i\,\Delta k\,z)$$

where $\Delta k = k_{2\omega} - 2k_{\omega}$ is the phase mismatch between fundamental and second harmonic wave

2nd order NL: Phase matching conditions



For efficient frequency conversion, we need the fundamental wave and the higher harmonic to be in phase throughout the crystal, i.e.

$\Delta k = 0$ where

$$\Delta k = k_{2\omega - 2k_\omega} = \frac{2\omega}{c}(n_{2\omega} - n_\omega)$$

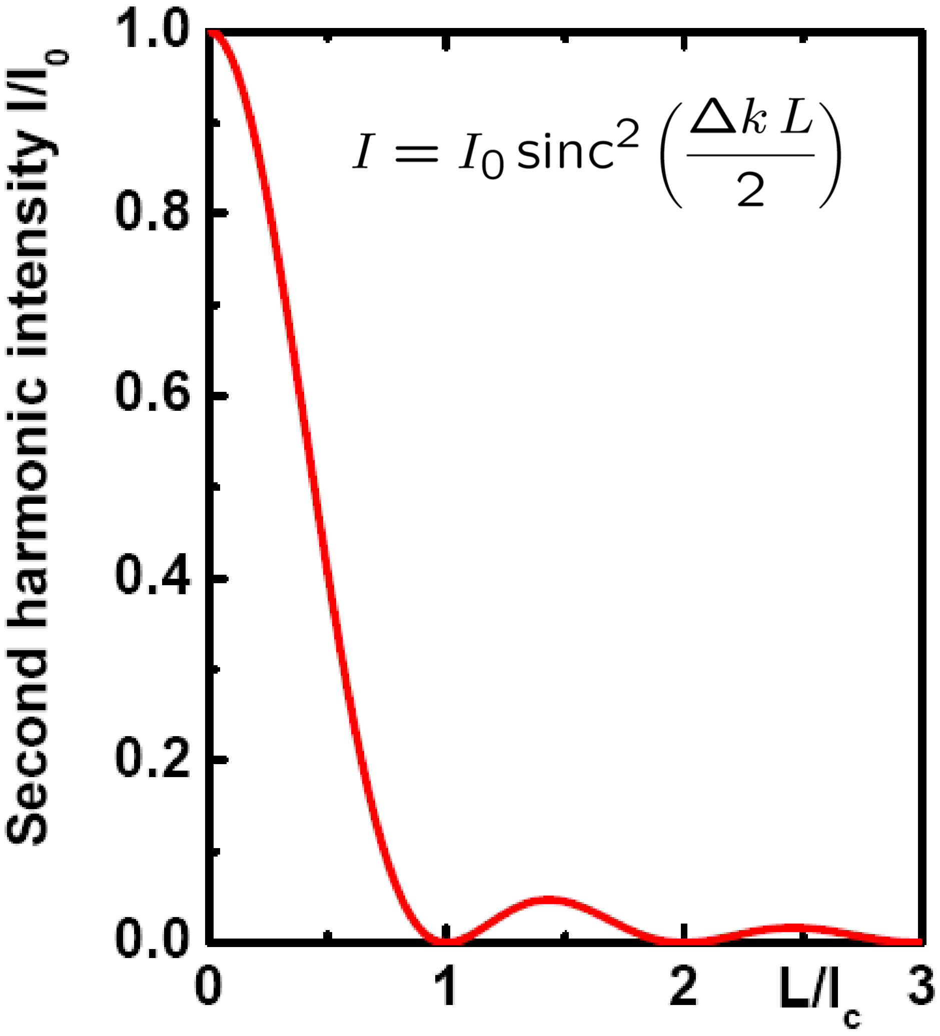
The second-harmonic field at length L for arbitrary Δk is:

$$\hat{E}_i^{2\omega}(L) = \int_0^L -i\,\frac{\omega}{c\,n_{2\omega}} \sum_{j,k} \chi_{ijk}^{(2)}\, \hat{E}_j^{\omega}(z)\, \hat{E}_k^{\omega}(z)\, \exp(i\,\Delta k\, z)\, dz$$

For constant fundamental wave amplitudes (thin crystal) the second harmonic intensity is then given by:

$$|\hat{E}_i^{2\omega}(L)|^2 = \frac{\omega^2 L^2}{c^2\, n_{2\omega}^2} \left(\sum_{j,k} \chi_{ijk}^{(2)}\, \hat{E}_j^{\omega}\, \hat{E}_k^{\omega} \right)^2 \mathrm{sinc}^2\left(\frac{\Delta k\, L}{2}\right)$$

Second-harmonic intensity after propagation through crystal of length L without phase matching



First intensity minimum at:

$$L = \frac{2\pi}{\Delta k} = \frac{\lambda_0}{2(n_{2\omega} - n_\omega)} \equiv l_c$$

But: dispersion in media means that in general: $n_{2\omega} \neq n_\omega$

Example: Sapphire

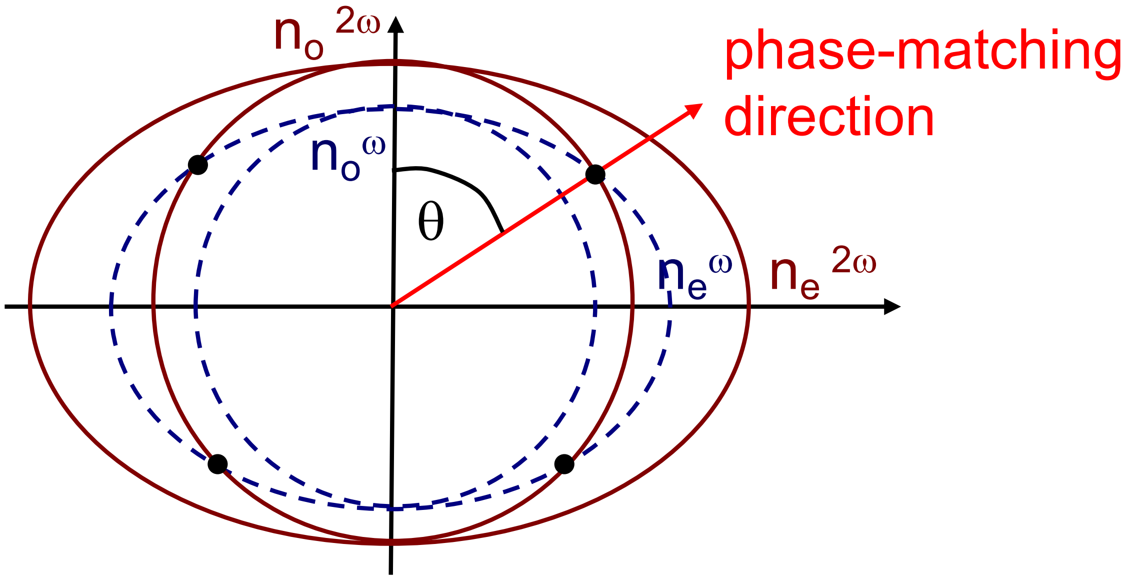
$$n_o(2.806\mathrm{eV}) = 1.780$$
$$n_o(1.403\mathrm{eV}) = 1.757$$

⇨ $l_c = 19\mu\mathrm{m}$

→ need too thin a crystal to achieve efficient 2nd harmonics generation

2^{nd} order NL: Phase matching in a uniaxial crystal

In general, in the birefringent medium, $n_{2\omega} \neq n_\omega$ since the refractive index now depends on the direction of propagation and wave polarization wrt the optic axis, for some geometries we may have $n_{2\omega} = n_\omega$ → phase matching!



Here, phase matching occurs for the fundamental travelling as extraordinary (polarization in plane) and the 2nd harmonic as ordinary (polarization ⊥ to plane) with

$$\frac{1}{(n_o^{2\omega})^2} = \frac{\sin^2\theta}{(n_e^{\omega})^2} + \frac{\cos^2\theta}{(n_o^{\omega})^2}$$

Third-order nonlinearities

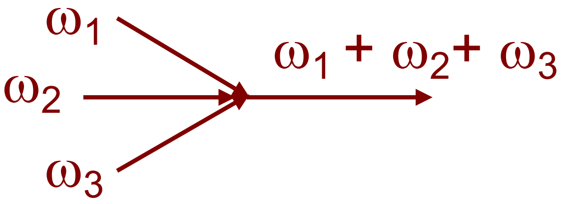
Third-order effects become important in centrosymmetric (e.g. isotropic media) where $\chi^{(2)}_{ijk} = 0$

For three waves with frequencies $\omega_1, \omega_2, \omega_3$ the third-order nonlinear polarization is

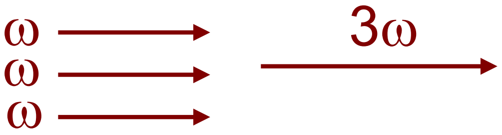
$$P_i^{(3)} = \epsilon_0 \sum_{j,k,l} \chi^{(3)}_{ijkl}\, \hat{E}_j\, \hat{E}_k\, \hat{E}_l\, \cos(\omega_1 t)\, \cos(\omega_2 t)\, \cos(\omega_3 t)$$

generates a wave with $\omega_4 = \pm\omega_1 \pm \omega_2 \pm \omega_3$.:

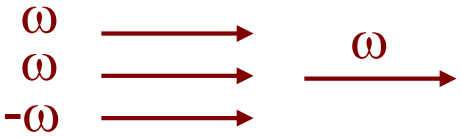
(a) four-wave mixing



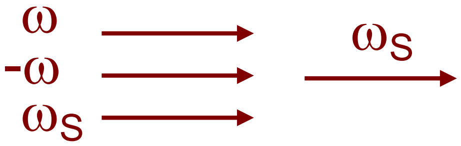
(b) frequency tripling



(c) Optical Kerr effect



(d) stimulated Raman scattering



3rd order NL: The optical Kerr effect

Optical Kerr effect: $\omega_1 = \omega_2 = +\omega$ and $\omega_3 = -\omega$

⇒ no phase mismatch

$$P^{(3)} = \epsilon_0 \chi^{(3)} E_0^3 \cos^3 \omega t = \epsilon_0 \chi^{(3)} E_0^3 \left(\tfrac{3}{4} \cos \omega t + \tfrac{1}{4} \cos 3\omega t \right)$$

In an isotropic medium ($\chi^{(2)}=0$):

$$\epsilon_r^{NL} = \underbrace{1 + \chi}_{\epsilon_r} + \underbrace{\frac{3}{4}\chi^{(3)} E^2}_{\Delta\epsilon}$$

Refractive index:

$$n = (\epsilon_r + \Delta\epsilon)^{\frac{1}{2}} \approx \sqrt{\epsilon_r} + \frac{\Delta\epsilon}{2\sqrt{\epsilon_r}}$$

$$\begin{aligned} n &= n_0 + \frac{3}{4}\frac{\chi^{(3)}}{2n_0} E^2 \\ &= n_0 + n_2 I \end{aligned}$$

where $n_2 = \frac{3}{4}\frac{\chi^{(3)}}{n_0^2 \, c \, \epsilon_0}$

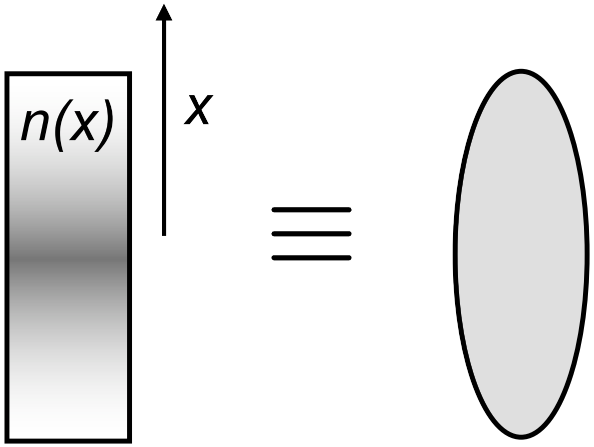
light intensity

⇒ Refractive index varies with light intensity!

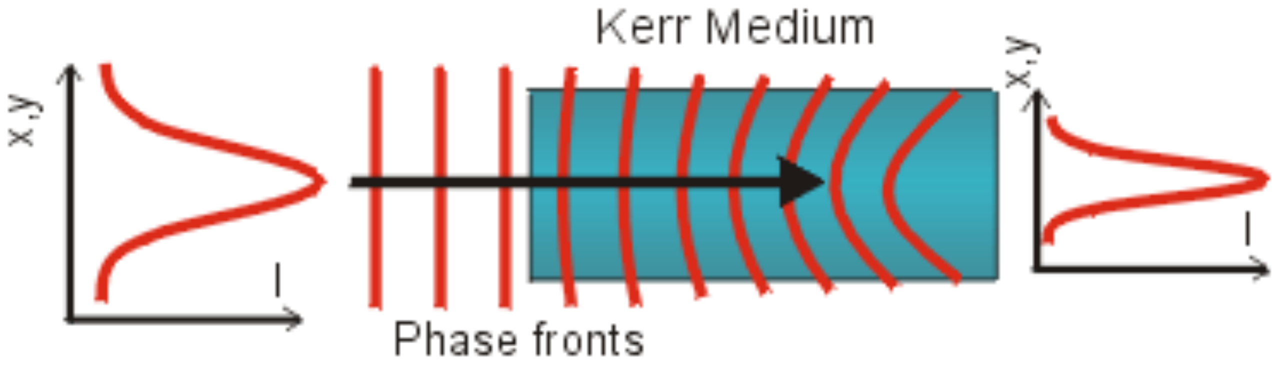
Example: Kerr lensing

Optical Kerr effect: $n = n_0 + n_2 I$ at high intensity I

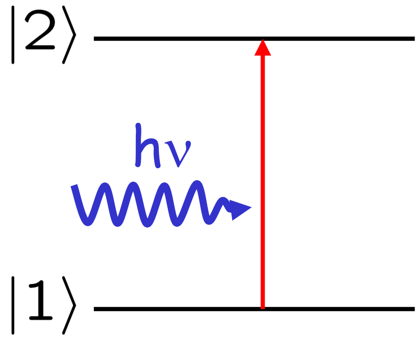
Laser beam with spatially varying profile (e.g. Gaussian beam) experiences in the medium a higher refractive index at the centre of the beam than the outside → medium acts as a lens!



Propagation of an intense gaussian beam through a Kerr medium:



3^{rd} order NL: Resonant nonlinearities



Consider medium with optical transition at resonance with incident wave of Intensity I

⇒ find that absorption decreases as higher state become more populated:

Absorption coefficient $$\alpha = \frac{\alpha_0}{1+\frac{I}{I_S}} \approx \alpha_0 - \alpha_0 \frac{I}{I_S} \quad \text{for} \quad I \ll I_S$$

$$\begin{aligned} \epsilon_r = \epsilon' + i\epsilon'' \quad &\approx \quad n^2 + i2n\kappa && \text{for } \kappa \ll n \\ &= \quad n^2 + i\frac{cn}{\omega}\alpha && \text{(weak absorption)} \end{aligned}$$

$$\epsilon_r = n^2 + i\frac{cn}{\omega}\alpha_0 - i\frac{cn}{\omega}\alpha_0\frac{I}{I_S} \longleftarrow \propto E^2$$

Can view saturable absorption as a third-order optical nonlinearity!

And finally, please fill in the feedback!

For lecture feedback please use the QR code above. These slides as on my web page at https://www.physics.ox.ac.uk/our-people/rtaylor/teaching