The Polariton Concept

In vacuum:
Light propagates as pure electromagnetic (EM) wave

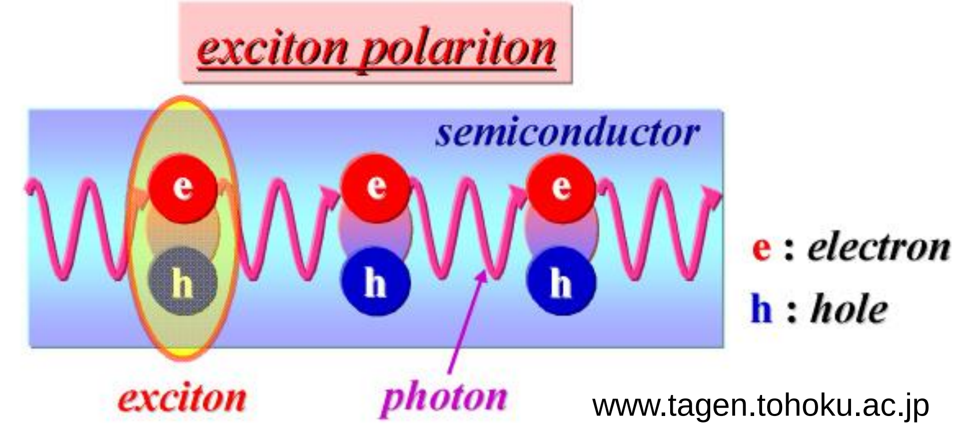
In matter:
(Strong) interaction of electromagnetic field with elementary excitations of the solid induces polarization $\boldsymbol{P}$

Examples:
- Optical phonons (lattice vibrations) in ionic crystal
- Excitons (optically generated electron-hole pairs) in semiconductors
- Plasma oscillations of free electrons in metals etc.

Oscillating light field induces polarization $\boldsymbol{P}$ in solid

↕

Oscillating polarization $\boldsymbol{P}$ generates EM wave



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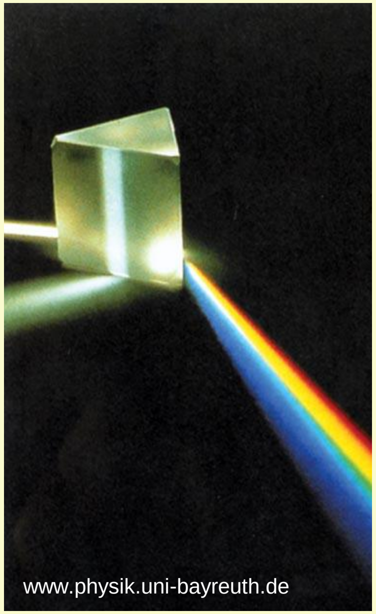
⇒ *Light propagation in a solid:*

“Mixture” between EM wave and elementary excitation
(Quantum mechanics (QM): Diagonalization of corresponding Hamiltonian)

⇒ Coupled states with *new properties, the quanta (quasi-particles) of which are called polaritons*

Example: Light in a piece of glass . . .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Photons are constantly (virtually) absorbed and reemitted by the atoms in the glass (depending on photon energy $\hbar\omega$)

⇒ Propagation of “light” (polaritons) in glass slower than the speed of light in vacuum and ω-dependent

Macroscopic description:

Refractive index $n\ (\omega) \Rightarrow$ dispersion . . .

How Do We Model Polaritons ?

Maxwell and material equations

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P}$$ ← Polarization due to external EM wave

$\boldsymbol{P}$ is generated through dipoles induced by the EM wave via

- a distortion of the atomic electron clouds (light couples to an *electronic transition*)
- lattice deformations (light couples to an *optical phonon*)
- collective *plasma oscillations* of free electrons in metals around the nuclei

For not too strong fields, i.e., the regime of “linear optics” we have

$$\boldsymbol{P} = \varepsilon_0 \chi \boldsymbol{E}$$ (Taylor expansion of “true” $\boldsymbol{P}(\boldsymbol{E})$ up to linear term)

$$\Rightarrow \quad \boldsymbol{D} = \varepsilon_0 (1+\chi) \boldsymbol{E} = \varepsilon_0 \varepsilon \, \boldsymbol{E}$$

All optical properties of solid contained in dielectric function of polaritons !!!

But how do we calculate / model $\varepsilon(\omega)$ *?*

Classical models - quantum-mechanical models

Insulators:

Lorentz model (bound electrons, ions) - interband transitions, phonons

Metals:

Drude model (free electrons) - QM: intra-band transitions
Corrections due to bound electrons

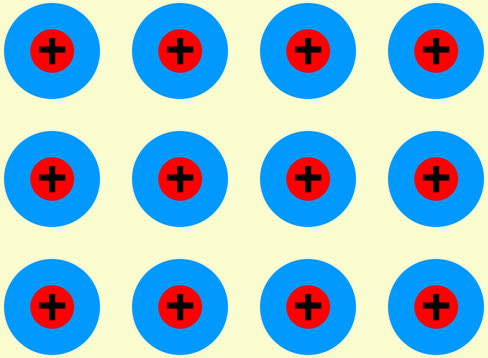
Semiconductors:

Lorentz model (interband transitions, ions),
but often also Drude contributions (intra-band transitions)
due to free charges (doping !)

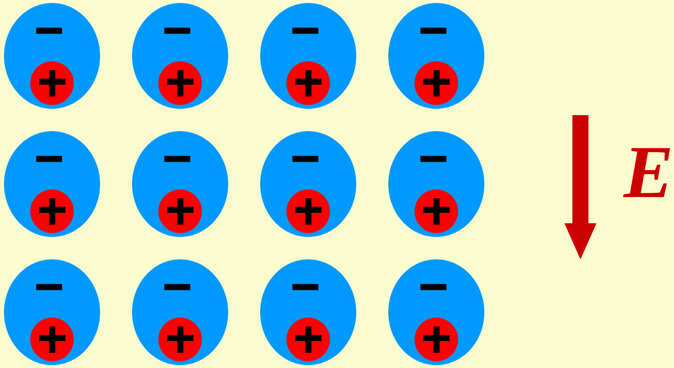
Drude-Lorentz Model (Classical Approach)

Consider polarizable "model material" with following properties:

- Medium is a homogeneous ensemble of *harmonic oscillators*
- Oscillators are *dipoles* consisting of:
  - fixed positive charges at lattice points (think, e.g., of the atom nuclei)
  - negatively charged mass m bound to it with spring constant β (think, e.g., of the polarizable electron clouds around the nuclei)
- The incident EM wave leads to forced oscillations and resulting dipole moments



Without electric field



Dipoles induced by electric field

Note 1:

This simplified classical model can be justified by QM (→ later).
Essentially, the oscillatory deformation of the electron cloud corresponds to a wavefunction that contains a mixture of two electronic eigenstates with energies E_2 and E_1.

ω_0' (or β/m) are chosen such that $E_2 - E_1 = \hbar\omega_0' = \hbar\sqrt{\frac{\beta}{m}}$

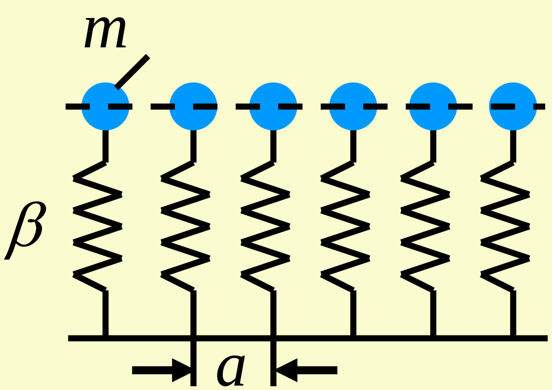
Note 2:

Although we discussed the coupling of the light field to *electronic transitions* in a solid above, the model discussed below is applicable to *any* kind of polariton (taking into account the corrections discussed later)

Initial simplifications:

- All oscillators have identical eigenfrequency $\omega_0' = \sqrt{\frac{\beta}{m}}$
- No coupling between different oscillators
- One oscillator per crystal unit cell

Dispersion Relation of Polarization Waves in our Model Solid



Lattice parameter

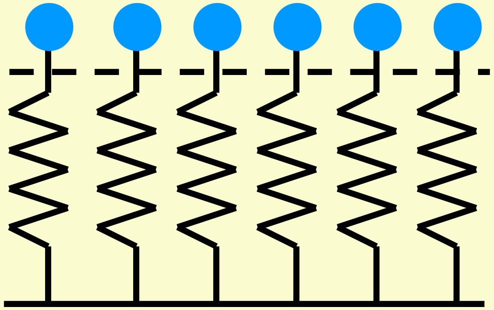
Spring model of solid

All oscillators in equilibrium

Limiting case 1:

All oscillators in phase

$\lambda = \infty \;\Rightarrow\; k = 0$

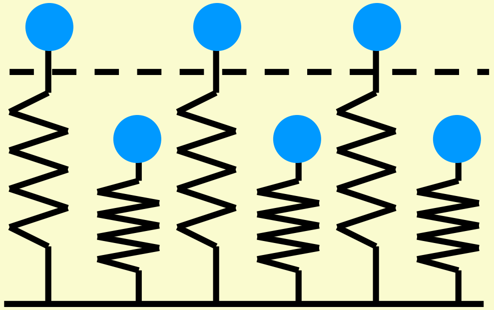


Whole ensemble oscillates with ω_0'

Limiting case 2:

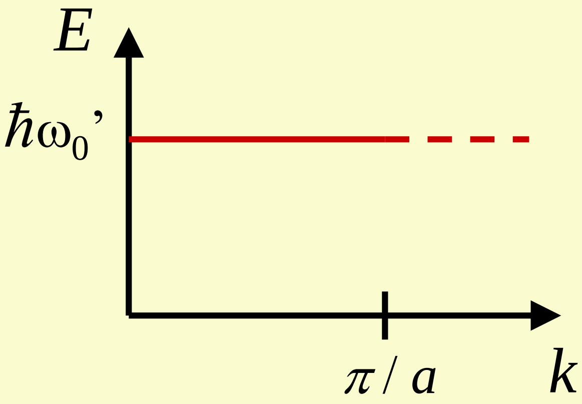
Neighboring osc. in anti-phase

$\lambda = 2a = \lambda_{\min} \;\Rightarrow\; k = \pi / a = k_{\max}$



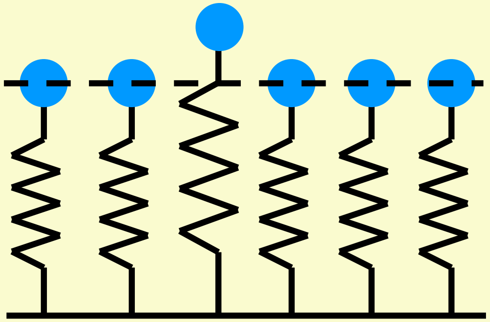
Whole ensemble oscillates with ω_0'

Same frequency ω_0' for all λ ($\infty \geq \lambda \geq 2a$) or k ($0 \leq k \leq \pi / a$) !



$\Rightarrow$ Dispersion relation: constant !

Group velocity: $v_g = \frac{d\omega}{dk} = 0$



$\Rightarrow$ A wave packet (e.g., a single excited oscillator) does not propagate, as expected for uncoupled oscillators

Now: Consider response of model solid to EM wave:

$$\boldsymbol{E} = \begin{pmatrix} E_0 \\ 0 \\ 0 \end{pmatrix} \cdot e^{i\left(k_z z - \omega t\right)}$$

- Polarization along x
- Propagation along z

Oscillator dynamics: differential equation for damped driven oscillation

$$m\frac{d^2x}{dt^2}+\gamma m\frac{dx}{dt}+\beta x=-eE_0e^{-i\omega t} \qquad (\lambda >> a_0 \text{ , i.e., all osc. are in phase})$$

Damping due to collisions with other quasi-particles, radiative damping, etc.

Response of system when EM field is switched on at $t = 0$:

$$x(t)=x_0e^{-i(\omega_0'^2-\gamma^2/4)^{1/2}t}e^{-t\gamma/2}+x_pe^{-i\omega t}$$

Damped oscillation with frequency $\left(\omega_0'^2-\gamma^2/4\right)^{1/2}$ vanishes for $t >> \gamma^{-1}$

Driven oscillation with frequency ω of external perturbation

Amplitude: $$x_p=\frac{e/m}{\omega_0'^2-\omega^2-i\omega\gamma}E_0$$

Oscillation is associated with a generated (max.) dipole moment ex_p

and a polarizability $$\hat{\alpha} := \frac{ex_p}{E_0} = \frac{e^2/m}{\omega_0'^2 - \omega^2 - i\gamma\omega}$$

(Max.) polarization density in our model solid (preliminary !):

$$P = Nex_p = N\hat{\alpha}E_0 = \frac{Ne^2/m}{\omega_0'^2 - \omega^2 - i\omega\gamma}E_0$$

⬆

Density of oscillators

(Time-dependent) dielectric displacement:

$$\boldsymbol{D} = \varepsilon\varepsilon_0\boldsymbol{E} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P} = \varepsilon_0\left(1 + \frac{Ne^2/m\varepsilon_0}{\omega_0'^2 - \omega^2 - i\omega\gamma}\right)\boldsymbol{E}$$

$$\Rightarrow \quad \varepsilon(\omega) = 1 + \frac{Ne^2/m\varepsilon_0}{\omega_0'^2 - \omega^2 - i\omega\gamma}$$

for model solid consisting of *uncoupled* oscillators with a *single fixed* resonance frequency

QM Treatment of Dielectric Function and Resulting Corrections to Model ε

Interaction of QM system with light field

Unperturbed system for $t < 0$:

$$H_0\phi_n = E_n\phi_n \quad ; \quad H_0 : \text{ Time-indep. Hamiltonian of system}$$

$$\phi_n : \quad \text{Unperturbed states}$$

At $t = 0$ the light field is switched on (⇒ small perturbation)

$$H = H_0 + \underbrace{H'(t)}_{\text{periodic perturbation}} \text{ for } t \geq 0$$

Time-dependent Schrödinger equation: $$i\hbar\frac{\partial\psi}{\partial t} = \left[H_0 + H'(t)\right]\psi$$

Ansatz for solution: $$\psi(\mathbf{r},t) = \sum_n a_n(t)\phi_n(\mathbf{r})e^{-i\frac{E_n}{\hbar}t}$$

$|a_n|^2$: Probability to find system in state n

Evaluation of $a_n(t)$:

$$i\hbar\sum_n \dot{a}_n(t)\phi_n e^{-iE_n t/\hbar} + i\hbar\sum_n a_n \cancel{\left(-i\frac{E_n}{\hbar}\right)}\phi_n e^{-iE_n t/\hbar}$$

$$= \sum_n a_n(t)\cancel{H_0\phi_n e}^{-iE_n t/\hbar} + \sum_n a_n(t)H'\phi_n e^{-iE_n t/\hbar}$$

$$\Rightarrow\ \ i\hbar\sum_n \dot{a}_n\phi_n e^{-iE_n t/\hbar} = \sum_n a_n(t)H'\phi_n e^{-iE_n t/\hbar}$$

Multiply by $\phi_m^* e^{iE_m t/\hbar}$ from left and integrate over space:

$$i\hbar\dot{a}_m = \sum_n a_n H'_{mn} e^{i(E_m - E_n)t/\hbar} \quad \text{with} \quad H'_{mn} = \int \phi_m^* H'\phi_n d^3\mathbf{r}$$

Solid initially (and essentially also later) in ground state $\Rightarrow$

For $t \cong 0$: $a_n \approx \delta_{n0} \ \Rightarrow\ i\hbar\dot{a}_m = H'_{m0} e^{i(E_m - E_0)t/\hbar} = H'_{m0} e^{i\omega_{m0} t}$ (*)

$$\omega_{m0} := (E_m - E_0)/\hbar$$

Perturbation operator: $H' = e\boldsymbol{E}_{\text{local}} \cdot \boldsymbol{r}$

Let $\boldsymbol{E}_{\text{local}} = \boldsymbol{E}_x \cos \omega t = \frac{1}{2} \boldsymbol{E}_x \left(e^{i\omega t} + e^{-i\omega t} \right)$

$$\Rightarrow \quad H' = \frac{1}{2} e E_x x \left(e^{i\omega t} + e^{-i\omega t} \right)$$

$\Rightarrow$ Matrix element $H'_{mn} = \frac{1}{2} e E_x x_{mn} \left(e^{i\omega t} + e^{-i\omega t} \right)$ with $x_{mn} = \int \phi_m^* x \phi_n d^3\boldsymbol{r}$

In (*) : $i\hbar \dot{a}_m = \frac{1}{2} e E_x x_{m0} \left(e^{i\omega t} + e^{-i\omega t} \right) e^{i\omega_{m0} t}$

Integration from $t' = 0$ to $t' = t$ $(a_m = 0$ for $t = 0$ and $m \neq 0)$

$$\hbar a_m(t) = \frac{e E_x x_{m0}}{2} \left(\frac{1 - e^{i(\omega_{m0} + \omega)t}}{\omega_{m0} + \omega} + \frac{1 - e^{i(\omega_{m0} - \omega)t}}{\omega_{m0} - \omega} \right) \qquad (**)$$

Polarization density: $P = Np$ where $p = \langle -ex \rangle = \int \psi^* (-ex) \psi \, d^3\boldsymbol{r}$

$$p = -\sum_{k,l} \int d^3\boldsymbol{r} \; a_k^* \phi_k^* e^{iE_k t/\hbar} (ex) a_l \phi_l e^{-iE_l t/\hbar}$$

Since we are solely interested in the polarization response of the system in the ground state, not in the excitation of higher states, we only keep terms containing a_0 or a_0* (~ 1) and skip small terms only containing other $a_{k,l}$, $a_{k,l}$* (~ 0)

$$\Rightarrow \quad p = -\sum_m \int d^3\boldsymbol{r}\,[a_m^*\phi_m^* e^{iE_m t/\hbar}(ex)a_0\phi_0 e^{-iE_0 t/\hbar} + a_0^*\phi_0^* e^{iE_0 t/\hbar}(ex)a_m\phi_m e^{-iE_m t/\hbar}]$$

Note: Transitions from $m = 0$ to 0 occur twice in this formula but only once above, however, they do not contribute to p anyway!

Since $a_0 \approx a_0^* \approx 1$ and $E_m - E_0 = \omega_{m0}\hbar$ we can write

$$p = -e\sum_m \left(x_{m0}a_m^* e^{i\omega_{m0}t} + x_{0m}a_m e^{-i\omega_{m0}t}\right)$$ with a_m, a_m* from (**) ⇒

$$p = \frac{e^2 E_x}{2\hbar}\sum_m |x_{m0}|^2\left(\frac{e^{-i\omega t} - e^{i\omega_{m0}t}}{\omega_{m0}+\omega} + \frac{e^{i\omega t} - e^{i\omega_{m0}t}}{\omega_{m0}-\omega} + \frac{e^{i\omega t} - e^{-i\omega_{m0}t}}{\omega_{m0}+\omega} + \frac{e^{-i\omega t} - e^{i\omega_{m0}t}}{\omega_{m0}-\omega}\right)$$

If damping (e.g., due to radiation) was included, terms with ω_{m0} would vanish for long times (steady state), see discussion of classical problem above

$$\Rightarrow \quad p \approx \frac{e^2 E_x}{2\hbar}\sum_m |x_{m0}|^2\left(\frac{1}{\omega_{m0}+\omega} + \frac{1}{\omega_{m0}-\omega}\right)\cdot 2\cos\omega t$$

“Trick” to include damping

(i.e., absorption, because energy is dissipated in damped oscillation)

$$E_m \rightarrow E_m + \frac{1}{2} i\hbar\gamma_m$$

$$\Rightarrow \quad p = \frac{e^2 E_x}{2\hbar} \sum_m |x_{m0}|^2 \left[\left(\frac{1}{\omega_{m0} + \omega + \frac{1}{2} i\gamma} + \frac{1}{\omega_{m0} - \omega - \frac{1}{2} i\gamma} \right) e^{i\omega t} \right.$$

$$\left. + \left(\frac{1}{\omega_{m0} - \omega + \frac{1}{2} i\gamma} + \frac{1}{\omega_{m0} + \omega - \frac{1}{2} i\gamma} \right) e^{-i\omega t} \right]$$

$$p = \frac{e^2 E_x}{2\hbar} \sum_m |x_{m0}|^2 \left[\frac{2\omega_{m0} e^{i\omega t}}{\omega_{m0}^2 - \omega^2 - i\omega\gamma \cancel{+ \frac{1}{4}\gamma^2}} + complex\ conjug. \right]$$

$$\gamma << \omega$$

Define oscillator strength : $f_{m0} = \frac{2m\hbar\omega_{m0}}{\hbar^2}|x_{m0}|^2$

$$\Rightarrow \quad p = \frac{e^2 E_x}{2m}\sum_m \mathrm{Re}\left[\frac{f_{m0}}{\omega_{m0}^2 - \omega^2 - i\omega\gamma}\right]$$

If we use the *complex* representation $p = p_0 e^{i\omega t}$ (p_0 complex amplitude) as in the classical discussion we can rewrite this equation simply as

$$p = \frac{e^2 E_x}{2m}\cdot\sum_m \frac{f_{m0}}{\omega_{m0}^2 - \omega^2 - i\omega\gamma}$$

$$P = Np \quad ; \quad D = \varepsilon_0 \varepsilon E = \varepsilon_0 E + P \quad \Rightarrow$$

$$\varepsilon(\omega) = 1 + \frac{Ne^2}{m\varepsilon_0} \cdot \sum_m \frac{f_{m0}}{\omega_{m0}^2 - \omega^2 - i\omega\gamma} \qquad (***)$$

Same dependence as for classical Drude-Lorentz theory but QM results in individual transitions / oscillators weighted by oscillator strengths f_{m0} !!!

Summation rule for oscillator strengths:

$$\sum_m f_{m0} = 1$$

- Classical oscillator strength is distributed over all transitions !
- f_{m0} for individual oscillator depends on transition matrix element of corresponding transition $0 \leftrightarrow m$
- Contributions of different oscillators add up in dielectric function

Why do QM and Classical Treatment yield identical results ?

- Correspondence principle of QM
- *Kramers – Kronig relations*
  - ➢ resulting from fundamental principle of causality !
  - ➢ Connection between *absorption* (related to ε_2) and *dispersion* (ε_1)

Assume sharp (δ - like) absorption resonance at $\omega = \omega_0$

$$\varepsilon_2(\omega) = A\delta(\omega - \omega_0)$$

Kramers – Kronig:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' = 1 + A \cdot \frac{2}{\pi} P \int_0^\infty \frac{\omega' \delta(\omega' - \omega_0)}{\omega'^2 - \omega^2} d\omega'$$

$$\Rightarrow \quad \varepsilon_1(\omega) = 1 + \frac{2A}{\pi} \cdot \frac{\omega_0}{\omega_0^2 - \omega^2}$$

$\Rightarrow$ Universal relationship
for dielectric function !

Local Field Correction

Assumption so far:

Electric field acting on oscillators identical to external incident field

Valid for *dilute* systems, but *solid is dense system of oscillators*

$\Rightarrow$ *Local field acting on oscillators consists of two parts:* → Kittel

- External field
- Field generated by all other dipoles

$\Rightarrow$ Lorentz field : $\boldsymbol{E}_{\mathrm{loc}} = \boldsymbol{E} + \frac{1}{3\varepsilon_0}\boldsymbol{P}$

$\Rightarrow$ Clausius-Mosotti or Lorenz-Lorentz equation → Hecht, Zajac

(for classical Drude-Lorentz model)

$$\frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+2} = \frac{N}{3\varepsilon_0}\hat{\alpha}(\omega) = \frac{1}{3}\frac{Ne^2/m\varepsilon_0}{\omega_0'^2-\omega^2-i\omega\gamma}$$

(For dilute systems with N<< : $\varepsilon \sim 1$ in denominator $\Rightarrow$ old formula)

However, for *small damping* (as often found in experiment)

ε can be rewritten in the previous form (***) using a *shifted eigenfrequency*

$\omega_0^2 = \omega_0'^2 - \frac{Ne^2}{3m\varepsilon_0}$ or – with QM correction – $\omega_0^2 = \omega_0'^2 - f'/3$

Properties of the Dielectric Function in the Drude-Lorentz Model

For the dielectric function in the Drude-Lorentz model we had (compactly written):

$$\varepsilon(\omega) = 1 + \sum_m \frac{f'_m}{\omega_{m0}^2 - \omega^2 - i\omega\gamma_{(m)}}$$

In a real solid: Many different oscillators: Phonons, electronic trans., etc.

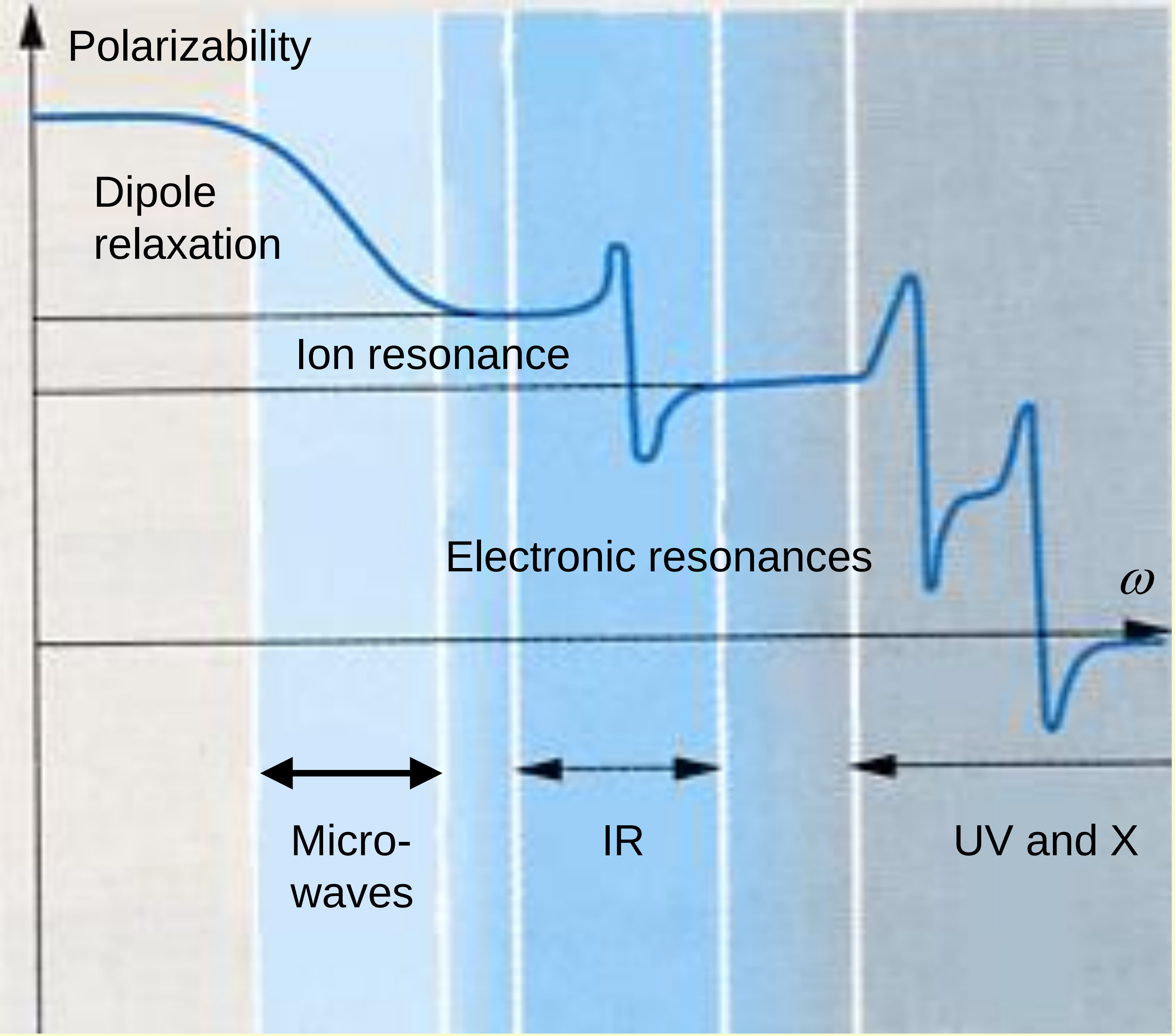
⇒ *Simplification of* $\varepsilon(\omega)$

- For $\omega >> \omega_{m0}$: contribution of oscillator $m \to 0$

  ⇒ Essentially, only oscillators with resonance frequency $\omega_{m0} > \omega$ contribute to $\varepsilon(\omega)$

  ⇒ For $\omega >>$ highest resonance (i.e., hard x-rays) : $\varepsilon \approx 1$
  (No coupling of EM field with medium, propagation as pure photon!)

- For $\omega << \omega_{m0}$: *constant* contribution f'_m / ω_{m0}^2 of oscillator m



After D. Meschede, *Gerthsen Physik*

⇒ In the vicinity of a *single* resonance m', far away from all other resonances $m \neq m'$ we can approximate

$$\varepsilon(\omega) = \varepsilon_\mathrm{b}\left(1 + \frac{f'_{m'}/\varepsilon_\mathrm{b}}{\omega_{m'0}^2 - \omega^2 - i\omega\gamma_{m'}}\right)$$

Hopfield model

ε_b : Background dielectric constant
(contains constant contributions of all higher resonances)

or, using $f_{m'} = f'_{m'}/\varepsilon_b$ as oscillator strength and skipping the index m' :

$$\varepsilon(\omega) = \varepsilon_\mathrm{b}\left(1 + \frac{f}{\omega_0^2 - \omega^2 - i\omega\gamma}\right) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

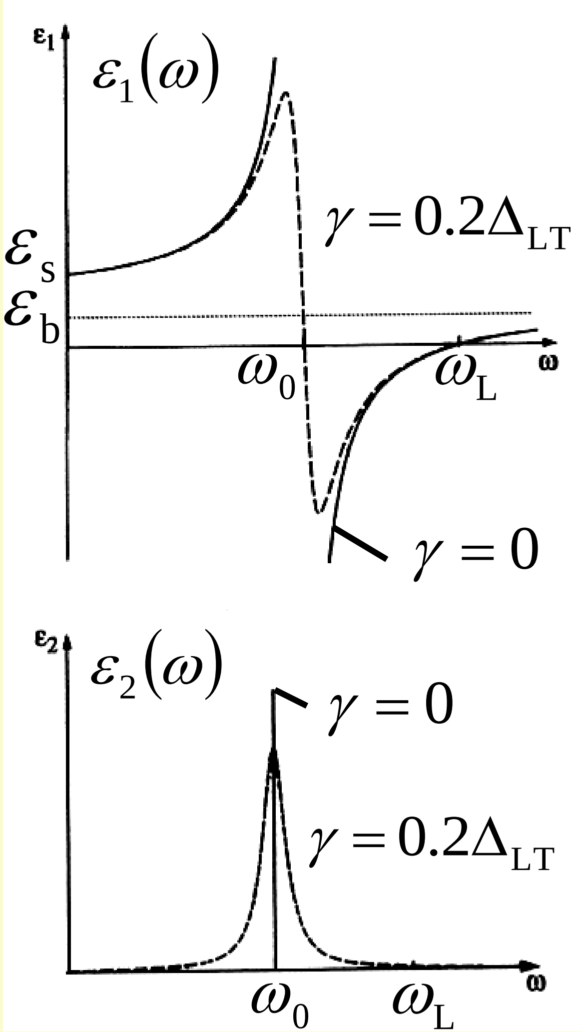
ε is complex due to the phase shift between $D(t)$ (or $P(t)$) and $E(t)$

in $D = \varepsilon_0 \varepsilon E$

(in full analogy to the phase shift between driving force and oscillation
for a driven mechanical harmonic oscillator)

Separation of the real and imaginary part yields:

$$\varepsilon(\omega)=\varepsilon_{\mathrm{b}}\left(1+\frac{\left(\omega_0^2-\omega^2\right)f}{\left(\omega_0^2-\omega^2\right)^2+\omega^2\gamma^2}\right)+i\varepsilon_{\mathrm{b}}\frac{\omega\gamma f}{\left(\omega_0^2-\omega^2\right)^2+\omega^2\gamma^2}$$



For vanishing damping $\gamma\rightarrow 0$

- Pole at ω_0 in ε_1
- δ distribution at ω_0 for ε_2

Finite (small) damping

- General broadening, defined by γ
- Slight shift of resonance frequency
- Singularity in ε_1 disappears, i.e., smooth connection of both branches (possibly even $\varepsilon_1 > 0$ for all ω)
- ε_2 broadens to Lorentzian

After C. Klingshirn, *Semiconductor Optics*

For $\omega = \omega_L$ and small damping the special case

$\mathrm{Re}\{\varepsilon(\omega_L)\} \approx \varepsilon(\omega_L) = 0$ occurs :

Generally, $\nabla \cdot \boldsymbol{D} = \varepsilon_0 \varepsilon(\omega) \nabla \cdot \boldsymbol{E} = 0 \quad ; \quad \boldsymbol{E} \sim e^{i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)}$

$\Rightarrow$ For $\omega \neq \omega_L$, i.e., $\varepsilon(\omega) \neq 0$: $\boldsymbol{k} \cdot \boldsymbol{E} = 0$ *Transverse* EM waves

$\Rightarrow$ For $\omega = \omega_L$, i.e., $\varepsilon(\omega) = 0$: $\boldsymbol{k} \cdot \boldsymbol{E}$ arbitrary *Longitudinal* mode possible

$$\boldsymbol{D} = \varepsilon_0 \varepsilon \boldsymbol{E} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} = 0 \quad \Rightarrow \quad \boldsymbol{P} = -\varepsilon_0 \boldsymbol{E}$$

$\Rightarrow$ Longitudinal pure polarization mode $(\boldsymbol{D} = \boldsymbol{B} = \boldsymbol{H} = 0)$

Important:

Since this mode is *longitudinal*, it can – under normal circumstances – *not* be excited by incident (transverse) light !!!

Connection between transverse and longitudinal eigenfrequency

We had : $\varepsilon(\omega) = \varepsilon_\mathrm{b}\left(1 + \frac{f}{\omega_0^2 - \omega^2 - i\omega\gamma}\right)$

$\varepsilon(\omega_\mathrm{L}) = 0 \;,\; \gamma \approx 0 \;\Rightarrow\; \omega_\mathrm{L}^2 = \omega_0^2 + f$ Longitudinal eigenfrequency

For weak damping : $\omega_\mathrm{T}^2 = \omega_0^2$ Transverse eigenfrequency

$\Rightarrow \quad \omega_\mathrm{L}^2 = \omega_\mathrm{T}^2 + f$ (†)

Static dielectric constant : $\varepsilon_\mathrm{s} = \varepsilon(0) = \varepsilon_\mathrm{b}\left(1 + \frac{\omega_\mathrm{L}^2 - \omega_\mathrm{T}^2}{\omega_\mathrm{T}^2}\right)$

$\Rightarrow \quad \frac{\varepsilon_\mathrm{s}}{\varepsilon_\mathrm{b}} = \frac{\omega_\mathrm{L}^2}{\omega_\mathrm{T}^2}$ Lyddane-Sachs-Teller relation (††)

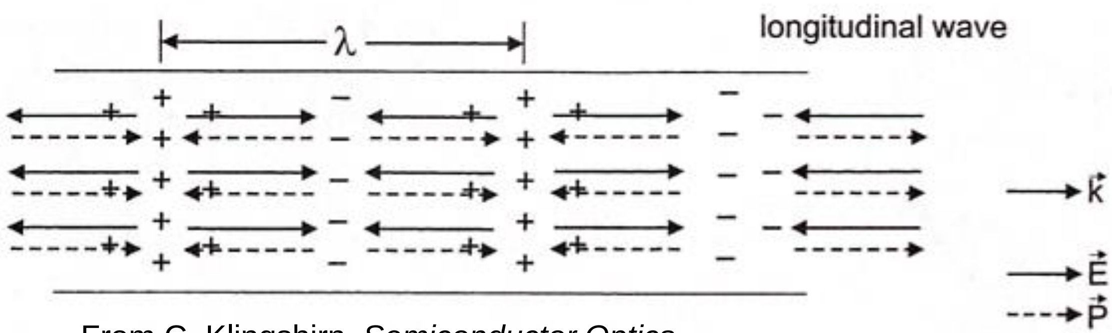
Consequences of (†) *and* (††) :

- An oscillator coupling to the EM field (i.e., with finite oscillator strength) implies a finite longitudinal-transverse splitting

$$\Delta_{\mathrm{LT}} = \hbar\left(\omega_{\mathrm{L}} - \omega_{\mathrm{T}}\right)$$

  and vice versa

- Δ_{LT} grows with oscillator strength. The term “small damping” can be quantified as $\gamma < \hbar^{-1}\Delta_{\mathrm{LT}}$
- For $f > 0$, we always have $\omega_{\mathrm{L}} > \omega_{\mathrm{T}}$



From C. Klingshirn, *Semiconductor Optics*

Physical reason:
Longitudinal polarization wave produces longitudinal electric field acting as additional restoring force

- For $f > 0$ we always have $\varepsilon_{\mathrm{s}} > \varepsilon_{\mathrm{b}}$ (difference growing with f) . Note, that ε_{b} for a resonance ω_{0m} is (essentially) identical with ε_{s} for the next-higher resonance ω_{0m+1}

Optical Properties of Solids in the Lorentz Model : n, κ, R

Lorentz Model :

- Electrons harmonically bound with oscillator frequency ω_0
- No free electrons (i.e., no metals, doped semiconductors)

Note: Still approximation of uncoupled oscillators, i.e., $\omega_0(\mathbf{k}) = const.$

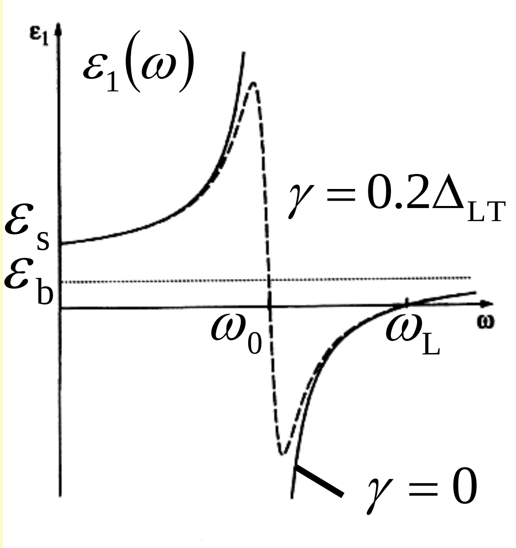
We had: $(n + i\kappa)^2 = \tilde{n}^2 = \varepsilon = \varepsilon_1 + i\varepsilon_2$

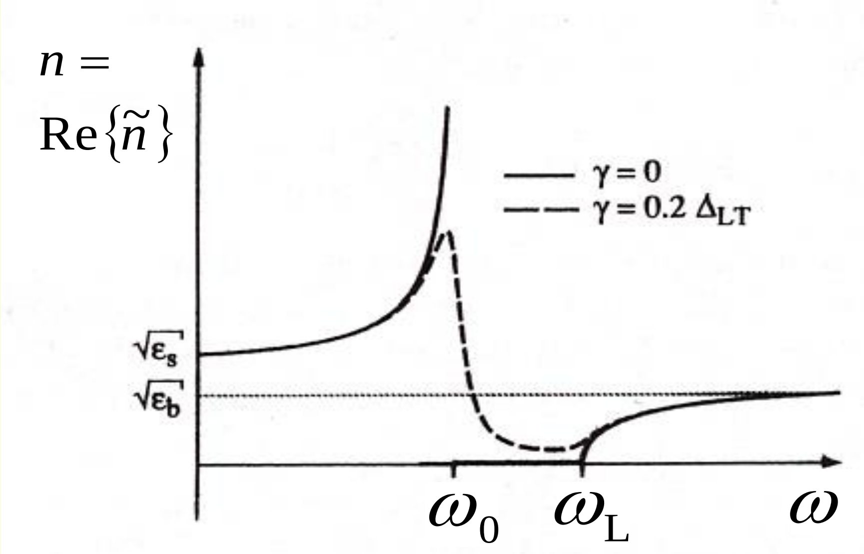
$$n = \left\{ \frac{1}{2} \left[\left(\varepsilon_1^2 + \varepsilon_2^2 \right)^{1/2} + \varepsilon_1 \right] \right\}^{1/2}$$

$$\kappa = \left\{ \frac{1}{2} \left[\left(\varepsilon_1^2 + \varepsilon_2^2 \right)^{1/2} - \varepsilon_1 \right] \right\}^{1/2}$$

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

Refractive index below the resonance



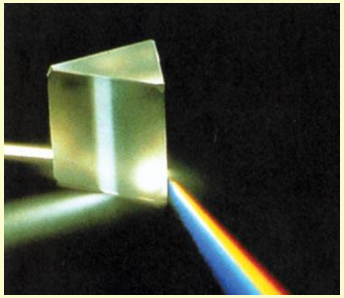


After C. Klingshirn, *Semiconductor Optics*

For $\gamma = 0$: ε *real* and $> 0 \;\Rightarrow\; n = \sqrt{\varepsilon}$

$\Rightarrow$ Below the resonance, $n(\omega)$ increases, i.e., $n(\lambda)$ decreases when the resonance is approached $\Rightarrow$ "Normal dispersion"

$\Rightarrow$ Qualitatively the same behavior for finite damping

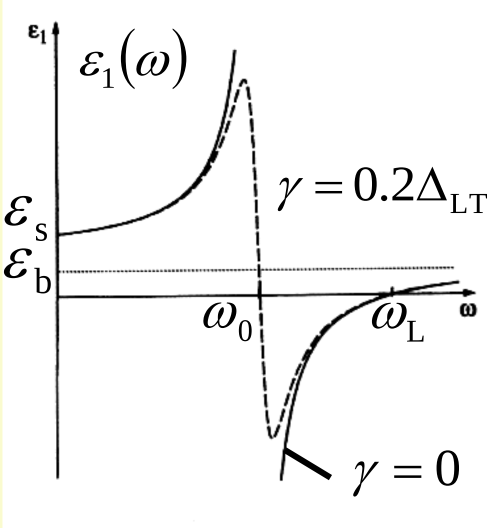


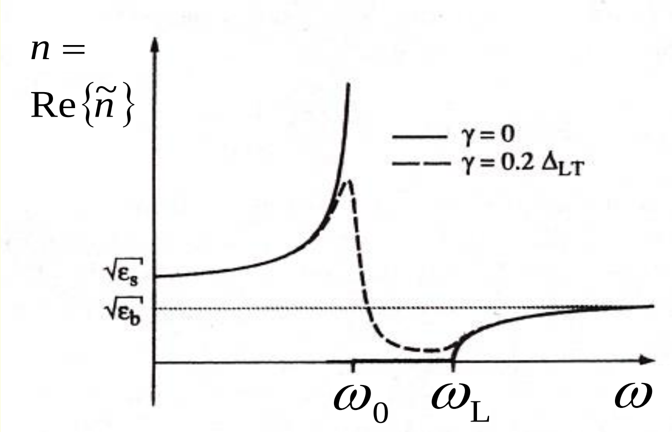
Example:

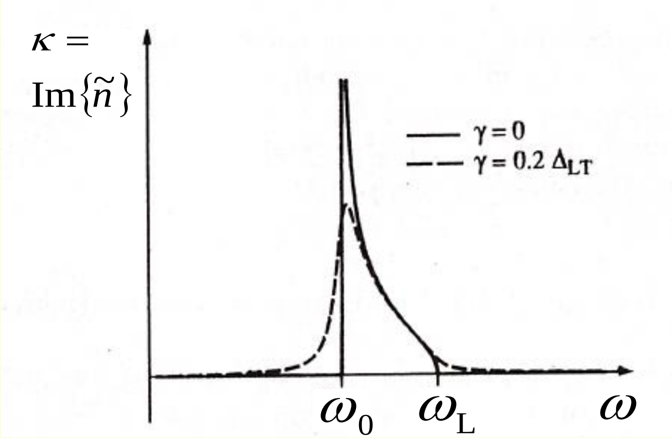
In a piece of glass, n increases with ω in the visible due to the electronic resonances (transitions) in the UV. This explains why blue light is refracted stronger than red.

Refractive index between ω_0 and ω_L

For $\omega_0 < \omega < \omega_L$ and $\gamma = 0$:







After C. Klingshirn, *Semiconductor Optics*

ε real and < 0 $\Rightarrow$ $\tilde{n} = \sqrt{\varepsilon} = i\kappa$

purely imag. $\Rightarrow$

- $n = 0$
- κ starts with singularity and drops towards ω_L

$\Rightarrow$ No spatially oscillating propagating mode (exponent. decaying amplitude)

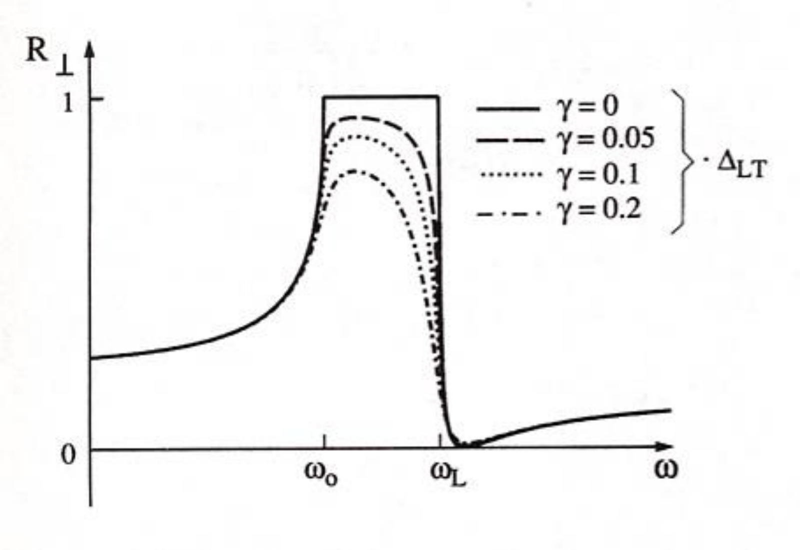
$\Rightarrow$ For *finite* γ: Small n but large κ: Light can penetrate but is strongly damped

Yes, but where does the light end up … ???

Reflectivity: "Reststrahlen" band

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

For $\omega_0 < \omega < \omega_\mathrm{L}$ and $\gamma = 0$: $n = 0 \;\Rightarrow\; R = 1$

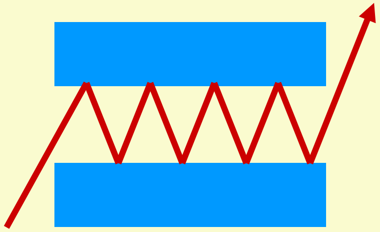


- *Total reflection* ("Reststrahlen" band), no transmission ("stop band") !!!
- *No absorption* despite finite κ !!! (Dissipation of energy would require damping, i.e., γ > 0 !!!)
- Drop in R for finite γ due to absorption and transmission

Further properties of R :

- For $\omega << \omega_0$: $R = \left(\varepsilon_\mathrm{s}^{1/2} - 1\right)^2 / \left(\varepsilon_\mathrm{s}^{1/2} + 1\right)^2$
- For $\omega >> \omega_0$ *lower* refl.: $R = \left(\varepsilon_\mathrm{b}^{1/2} - 1\right)^2 / \left(\varepsilon_\mathrm{b}^{1/2} + 1\right)^2$
- R = 0 for $n(\omega)$ = 1 just above ω_L (for no damping)
- Large $\kappa \Rightarrow R \rightarrow 1$!

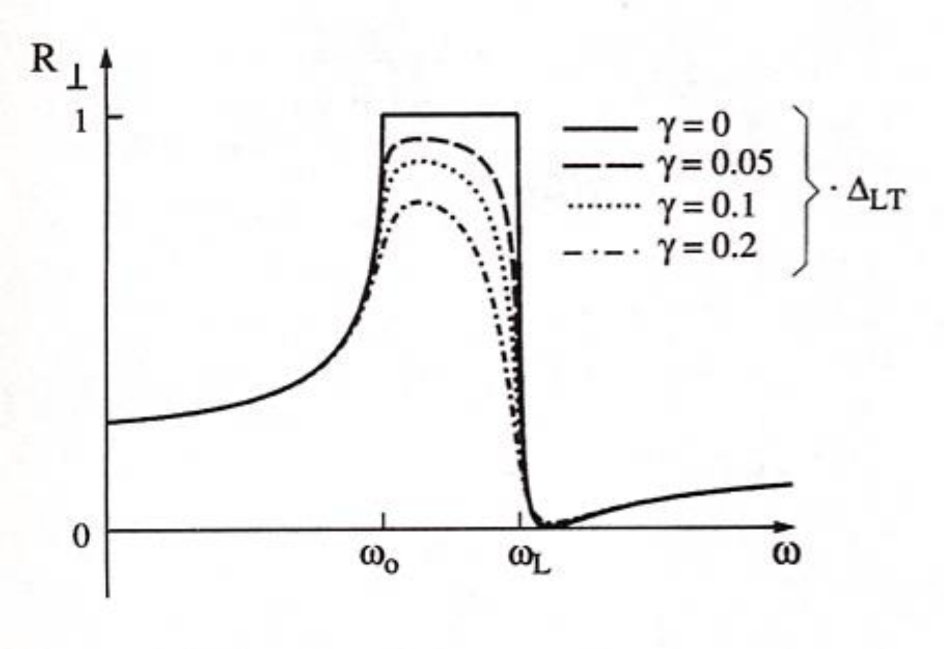
Arrangement to measure the "Reststrahlen" band of a solid

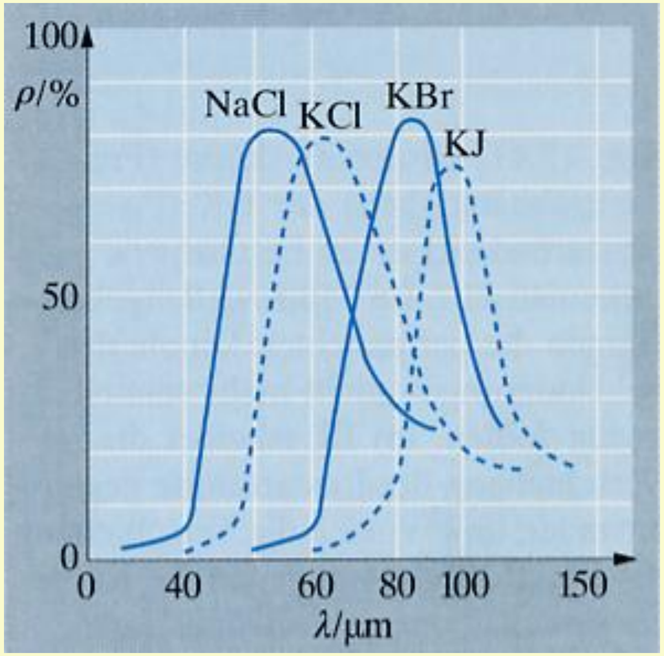


"Rest" spectrum

"White" light

Comparison with experiment: Phononic “Restrahlen” band





Degree of reflectivity for some alkali halides in the infrared

From: D. Meschede, *Gerthsen Physik*

Reflection at crystals of finite thickness

Close to 100% reflectivity at interface air – crystal

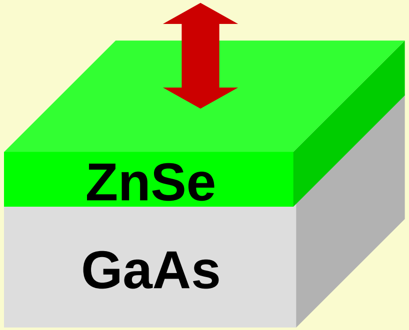
↕

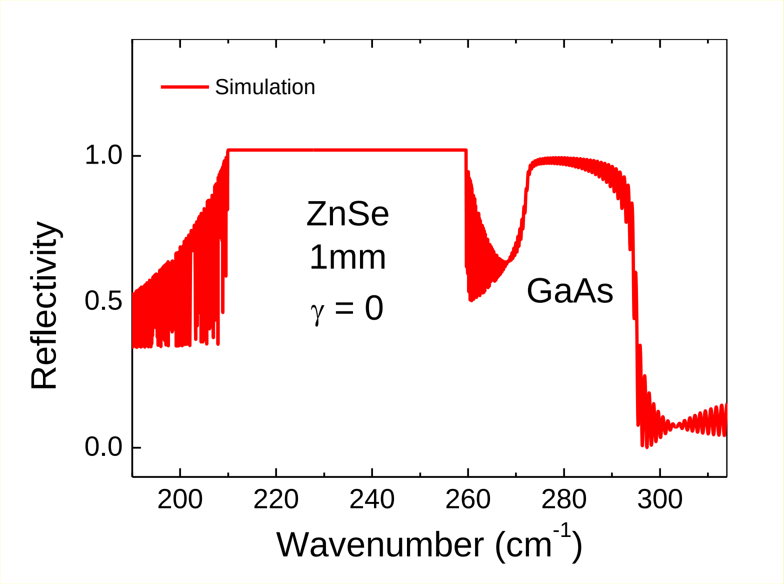
Evanescent wave penetrates into crystal

→ *„Where“ is the light reflected ?*

What happens for thin samples (< penetration depth) ?

Example: Reflection at a thin ZnSe layer on a thick GaAs substrate





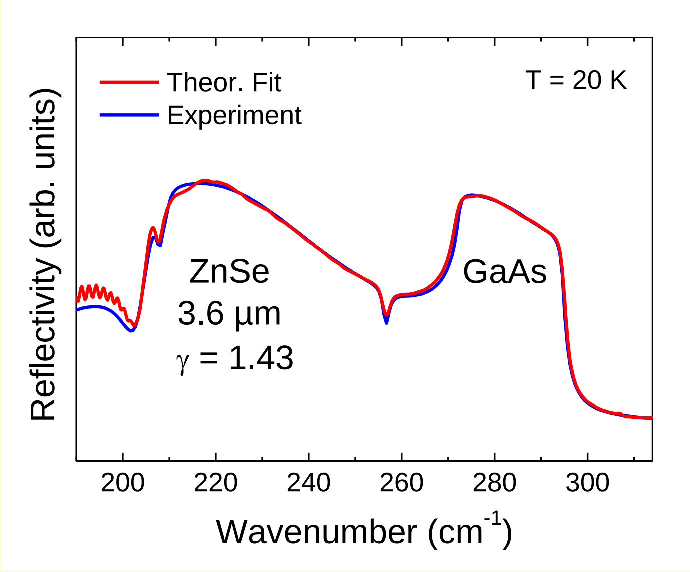
- Reststrahlen bands for both materials
- Reflections at all interfaces

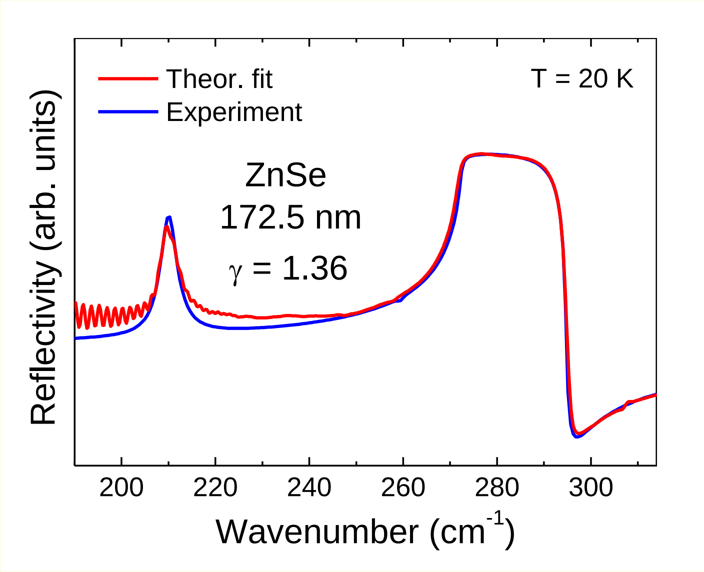
  ⇒ Oscillations due to Fabry-Pérot interference fringes

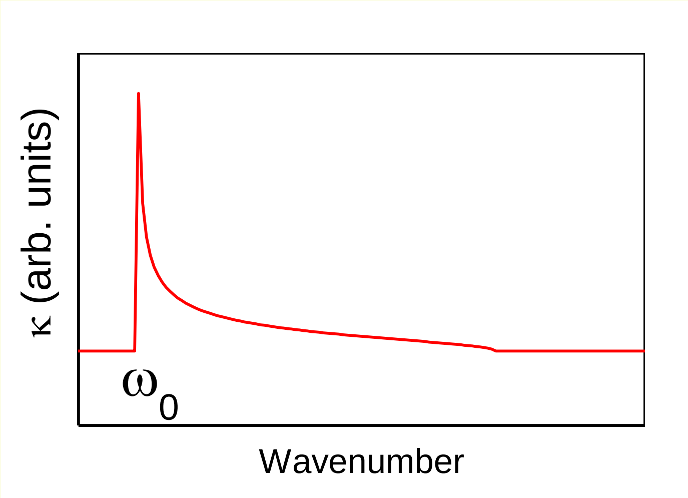
What happens to the Reststrahlen band for thicknesses < penetration depth ?

What happens to the Reststrahlen band ???

Light is partly transmitted !







⇒ Reststrahlen band *breaks down*, except for ω close to ω_0 :

Absolute value of ε_1 large

⇒ κ large ⇒ small penetration depth

⇒ Despite „reflection at surface“ the volume behind is required to form the Reststrahlen band !

Spectra from: K.C. Agarwal,…, and M. Hetterich, PRB **73**, 045211 (2006).

Polariton Equation and Dispersion

Wave propagation in solid with $\mu \approx 1$:

$$\Delta \boldsymbol{E} = \frac{1}{c_{\mathrm{solid}}^2} \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = \mu_0 \varepsilon \varepsilon_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} \quad ; \quad \boldsymbol{E} = \boldsymbol{E}_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)}$$

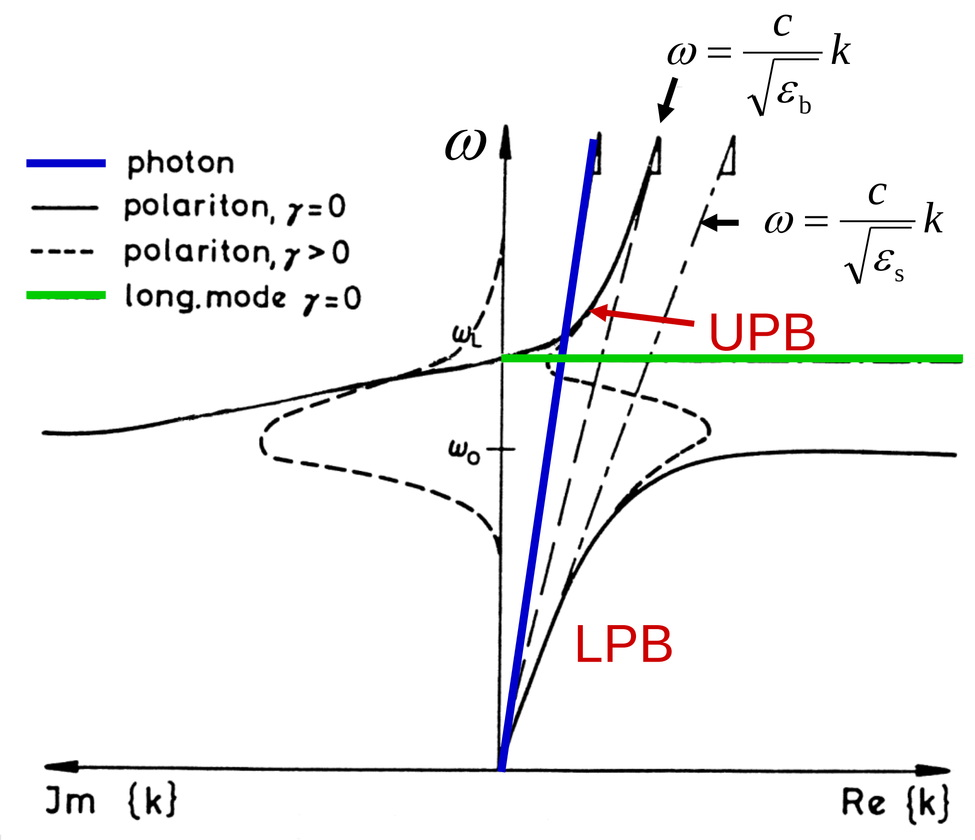
$$\Rightarrow \quad \Delta \boldsymbol{E} = -k^2 \boldsymbol{E} \quad \text{and} \quad \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = -\omega^2 \boldsymbol{E}$$

$\Rightarrow$ Polariton equation $\dfrac{c^2 k^2}{\omega^2} = \varepsilon(\omega)$ with $c^2 = \dfrac{1}{\varepsilon_0 \mu_0}$

For a single resonance ω_0 and *uncoupled* oscillators $(\omega_0(\boldsymbol{k}) = const.)$:

$$\frac{c^2 k^2}{\omega^2} = \varepsilon_{\mathrm{b}} \left(1 + \frac{f}{\omega_0^2 - \omega^2 - i\gamma\omega} \right)$$

Implicit representation of *polariton dispersion* $E(\boldsymbol{k})$



Photon dispersion +

oscillator dispersion +

anticrossing between the two

⇒ Polariton dispersion with upper (UPB) and lower (LPB) polariton branch

- *For ω far away from resonance:*
  - *"Photon-like"* dispersion with refractive index $n = \varepsilon_b^{1/2}$ (UPB) / $n = \varepsilon_s^{1/2}$ (LPB)
  - Propagating modes with weak damping
- *Close to resonance:*
  - Flat *"oscillator-like"* dispersion
  - Splitting into UPB and LPB due to anticrossing for $\gamma = 0$
  - Strong damping (*k complex* !) and absorption for $\gamma > 0$
  - No coupling to light field for longitudinal branch

Coupled Oscillators and Polaritons with Spatial Dispersion

Simplification so far: Uncoupled osc. with *fixed* resonance frequency ω_0

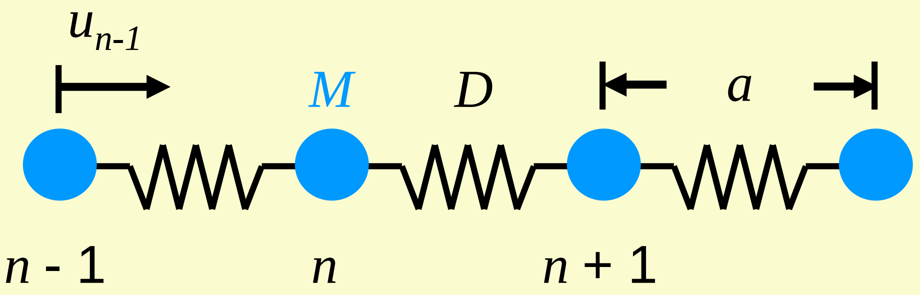
In a real solid: Oscillators are typically coupled !!!

⇒ Excitation can propagate through solid as a polarization wave with wave vector k

⇒ Spatial dispersion $\omega_0(k)$ of resonance frequency, since

group velocity $v_g = \frac{d\omega}{dk} \neq 0$ (energy transport possible !)

Example: Phonons (lattice vibrations)



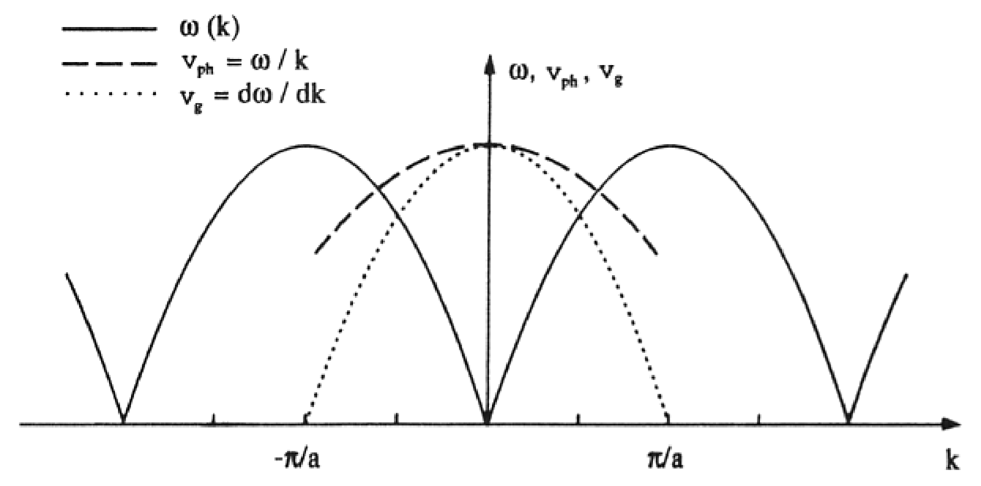
Simplified linear chain model:
masses M (atoms),
coupled by springs (interaction)

Equations of motion: $$M\ddot{u}_n = D\left[\left(u_{n+1} - u_n\right) - \left(u_n - u_{n-1}\right)\right]$$

Ansatz for wave through chain: $u_n = u_n^0 e^{i(kna-\omega t)}$

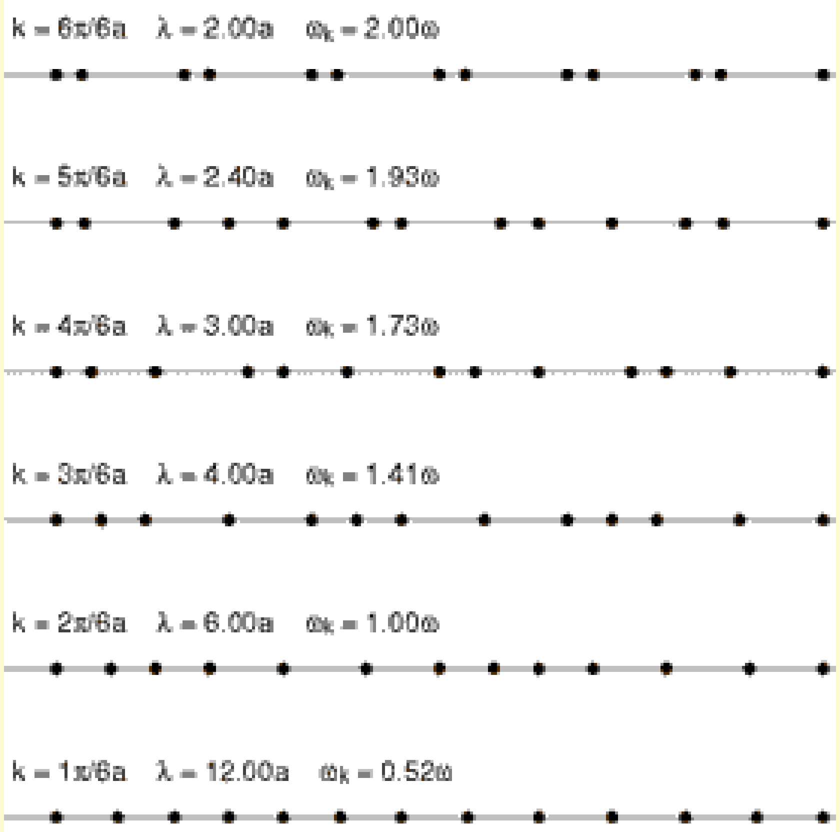
$$\Rightarrow \quad \omega(k) = \sqrt{\frac{4D}{M}} \left| \sin \frac{ka}{2} \right| \neq const. \quad !!!$$

Dispersion relation



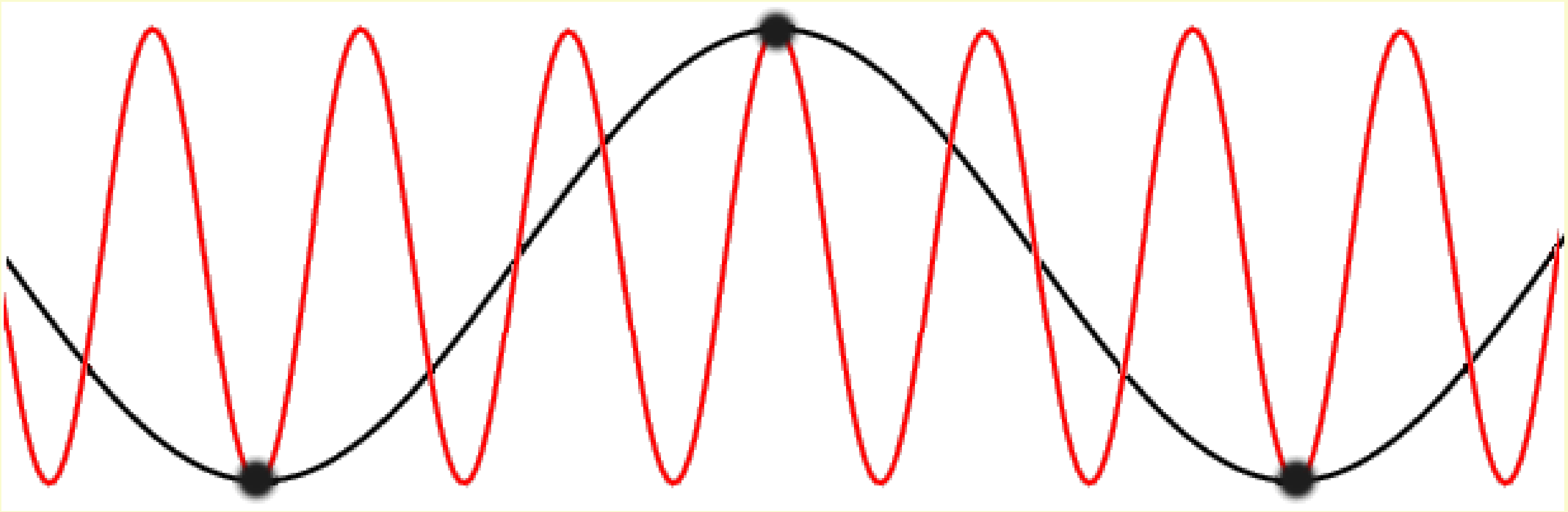
C. Klingshirn, *Semiconductor Optics*

Modes for different k



From Wikipedia

- $v_g = 0$ (standing wave) at border of Brillouin zones
- Repetition of modes / $\omega(k)$ for higher k ! Physical origin ?



Wikipedia

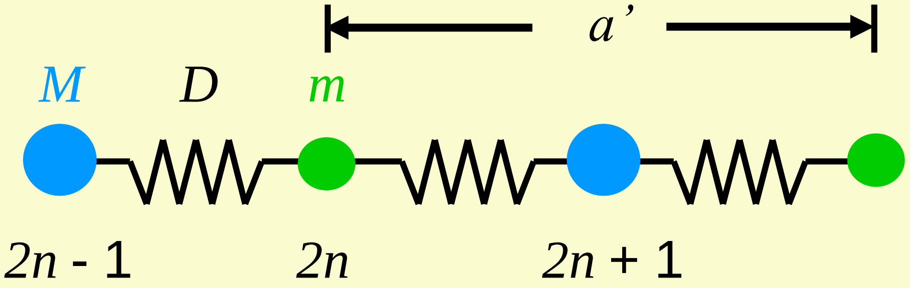
- Shortest physical wavelength (highest k) : Neighboring atoms in antiphase

$$\lambda_{\min} = 2a \quad \Rightarrow \quad k_{\max} = \frac{2\pi}{\lambda_{\min}} = \frac{\pi}{a}$$ (border of 1st Brillouin zone)

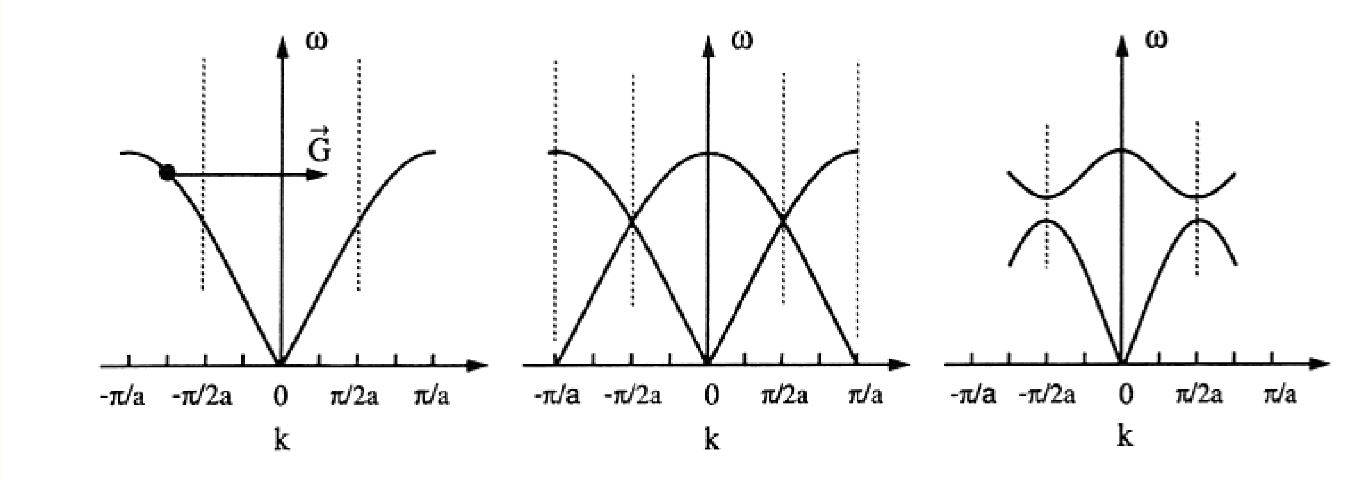
- Shorter wavelength (higher k) : Identical to state shifted into 1st Brillouin zone (BZ) by reciprocal lattice vector G

Most solids have more than one atom per unit cell. What happens then?

→ Linear chain model with two different masses M and m per unit cell



Size of unit cell doubles !



C. Klingshirn, *Semiconductor Optics*

⇒ Reciprocal unit cell halves

⇒ Fold dispersion relation outside 1st BZ back into the first zone

⇒ Splitting at zone borders due to unequal masses

⇒ Two phonon branches (in 1D: *n* for *n* atoms per unit cell)

Equations of motion: $$m\frac{\partial^2 u_{2n}}{\partial t^2} = D\left(u_{2n+1} - 2u_{2n} + u_{2n-1}\right)$$

$$M\frac{\partial^2 u_{2n+1}}{\partial t^2} = D\left(u_{2n+2} - 2u_{2n+1} + u_{2n}\right)$$

ansatz : $u_{2n} = u_{2n,0}\exp\{i[2na'k - \omega t]\}$

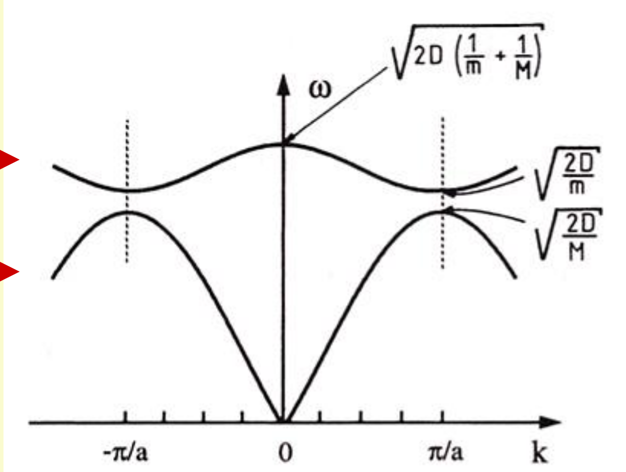
$$u_{2n+1} = u_{2n+1,0}\exp\{i[(2n+1)a'k - \omega t]\}$$

$$\Rightarrow \omega^2 = D\left(\frac{1}{m}+\frac{1}{M}\right) \pm D\left[\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4}{Mm}\sin^2\frac{ka'}{2}\right]^{1/2}$$

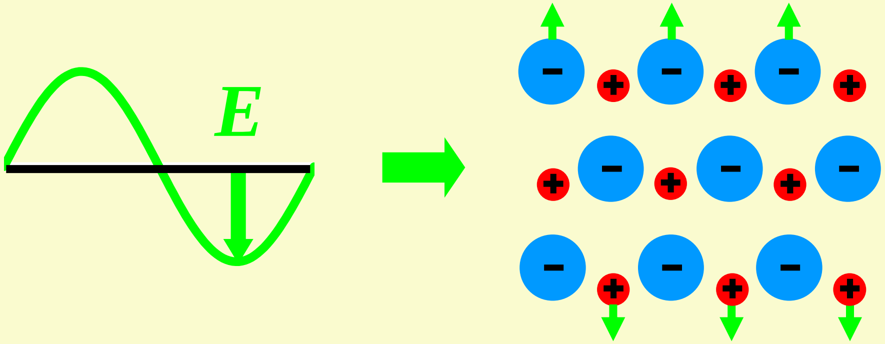
Two phonon branches :

Optical branch →

Acoustic branch →



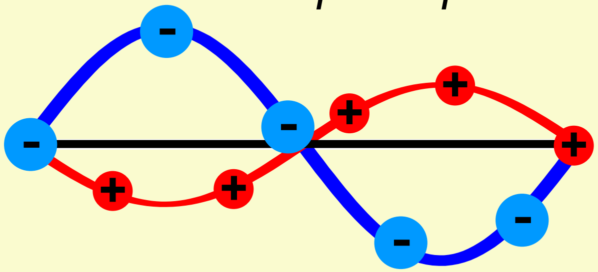
Which phonons couple to the electromagnetic field?



Light is a transverse el. magn. wave

⇒ Only transverse phonons couple to the light field

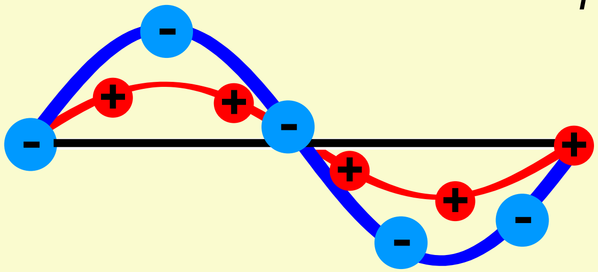
Optical phonons



High dipole moment

⇒ Strong interaction with light field

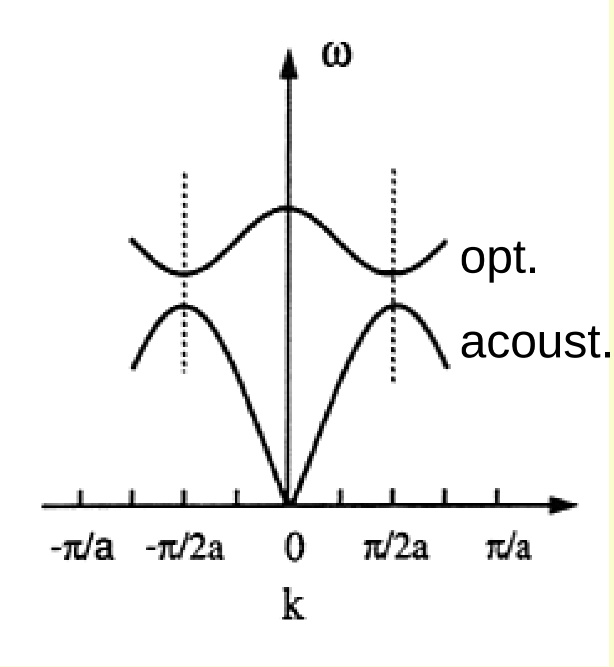
Acoustic phonons



Low dipole moment (0 for equal masses)

⇒ Only weak interaction with light field

⇒ Mainly transverse optical (TO) phonons couple to the light field



After C. Klingshirn, *Semiconductor Optics*

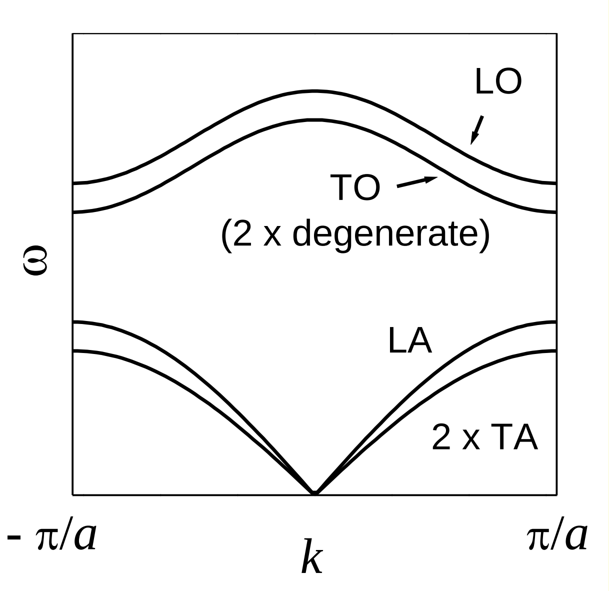
For crystal with n atoms per unit cell :

3 n branches (= number of degrees of freedom)

- 3 n – 3 optical branches
- 3 acoustic branches

Coupling to the light field

if character of oscillation is transverse



- Coupling to light field implies
  LO – TO splitting (see above),
  even for $k \to 0$!!!

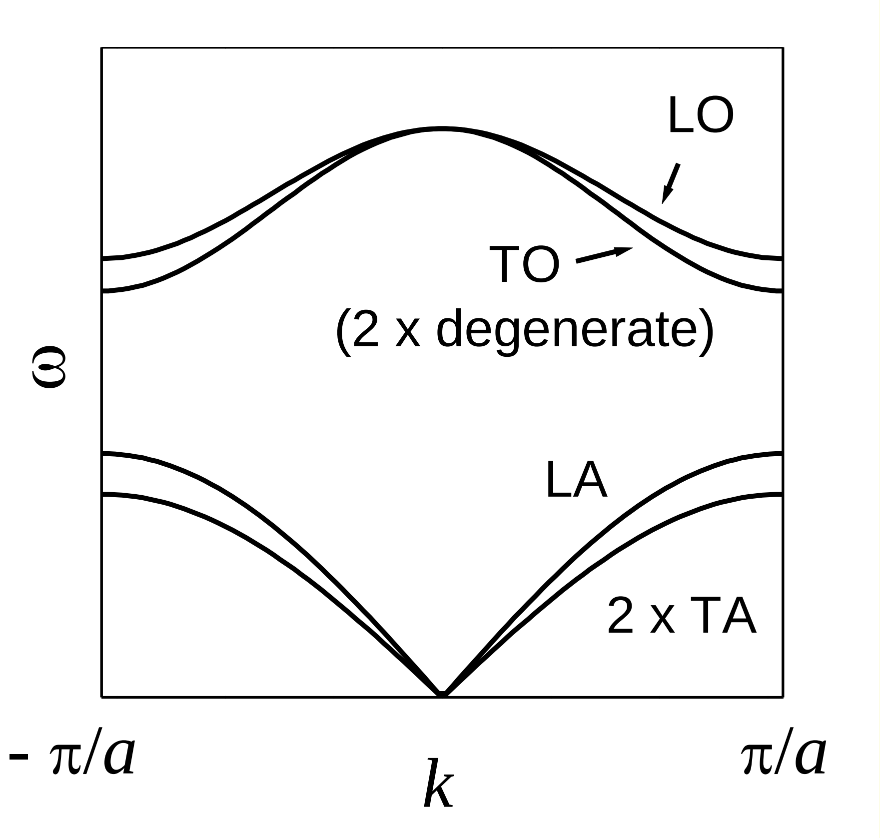
  (where the coupling takes place, see below)

- Longitudinal phonons at higher energy than transverse phonons

Crystals with perfectly covalent binding

Examples: Si, Ge

No dipole moment $\Rightarrow$ No LO – TO splitting for $k \to 0$!!!



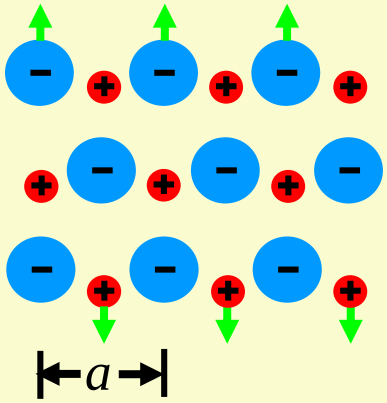
However :

Light still propagates as a polariton !

(electronic contributions to ε)

Which part of the dispersion relation is relevant?

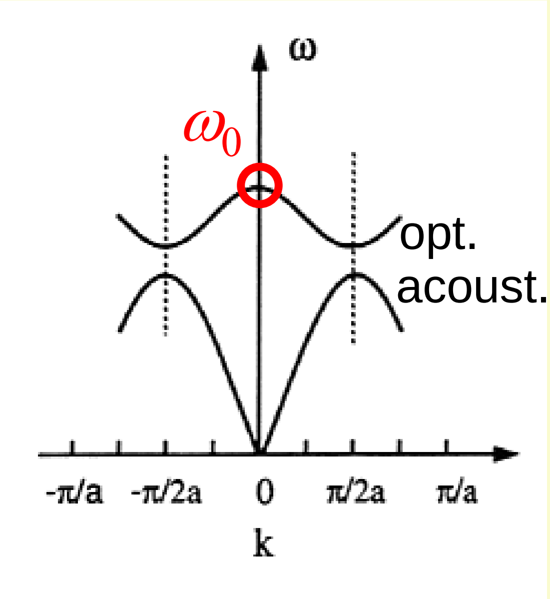
Important : In the spectral range of phonon resonances usually $\lambda_{\text{Light}} >> a$



$\Rightarrow$ (Neighboring) equal ions oscillate in phase !

$\Rightarrow$ Important for optical properties:
$\omega_0 = \omega\,(k = 0)$!

$\Rightarrow$ **Dispersionless oscillator picture adequate despite spatial dispersion !**

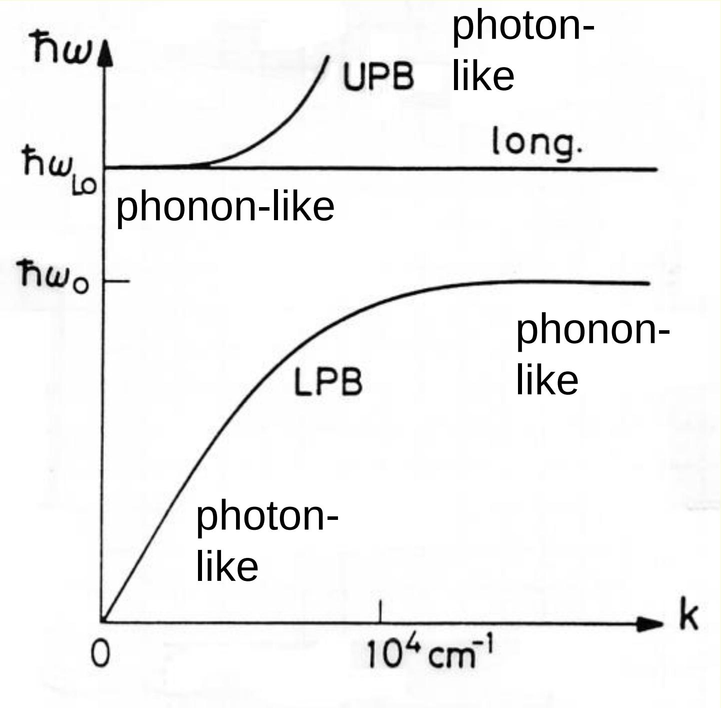


After C. Klingshirn, *Semiconductor Optics*

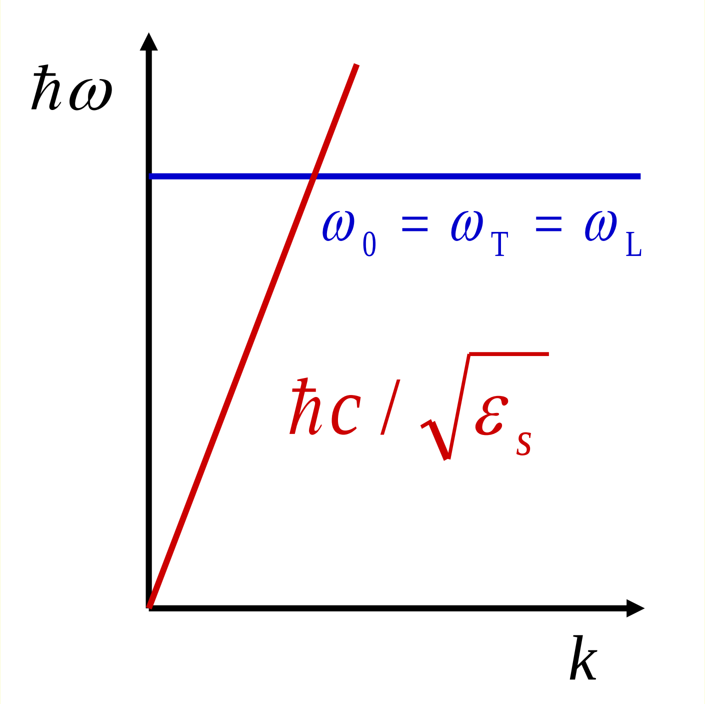
Phonon polariton dispersion

Phonon dispersion ~ constant (scale !). Photon dispersion linear.

Polar crystals (NaCl, ZnSe, GaAs)



Covalent crystals (Si, Ge)



- LO – TO splitting only for polar crystals
- In covalent crystals, polariton dispersion degenerates to straight line
- Longitudinal phonon does not couple to light field $\Rightarrow$ No polariton formation

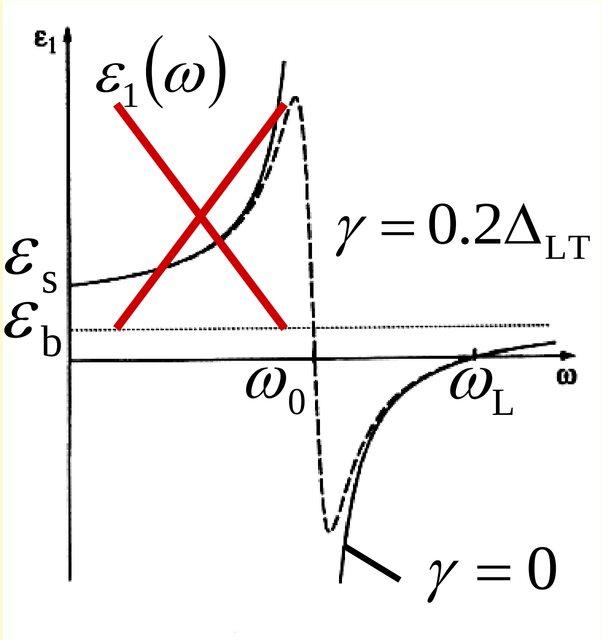
Optical Properties of Metals
(and Doped Semiconductors)

Free electrons (restoring force = 0) !

⇒ Drude model : Lorentz model with $\omega_0 = 0$

⇒ Only high-energy branch of dispersion relation !

$$\Rightarrow \quad \varepsilon(\omega) = \varepsilon_{\mathrm{b}}\left(1 + \frac{Ne^2/m\varepsilon_0}{-\omega^2 - i\omega\gamma}\right)$$



Damping for metals :

Mainly electron – electron scattering with

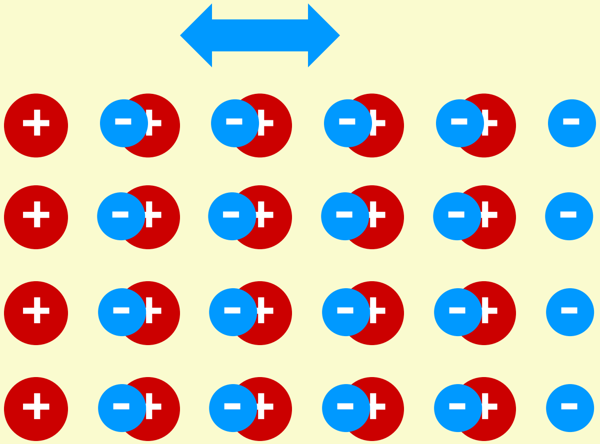
$\gamma \approx 10^{-14}$ s (T = 300 K) $\Rightarrow \hbar\gamma = \hbar / \tau \approx$ 65 meV

Longitudinal mode for $\gamma = 0$:

$$\varepsilon(\omega) = 0 = \varepsilon(\omega_{\mathrm{L}}) \quad \Rightarrow \quad \omega^2 = \frac{Ne^2}{m\varepsilon_0} = \omega_{\mathrm{L}}^2 = \omega_{\mathrm{P}}^2$$

ω_{P} : plasma frequency

Longitudinal mode at ω_P: Collective plasma oscillation (electrons)



Restoring force for plasma oscillation :
space charges at surfaces

$\Rightarrow$ All electrons oscillate in phase: Plasmon at $k = 0$

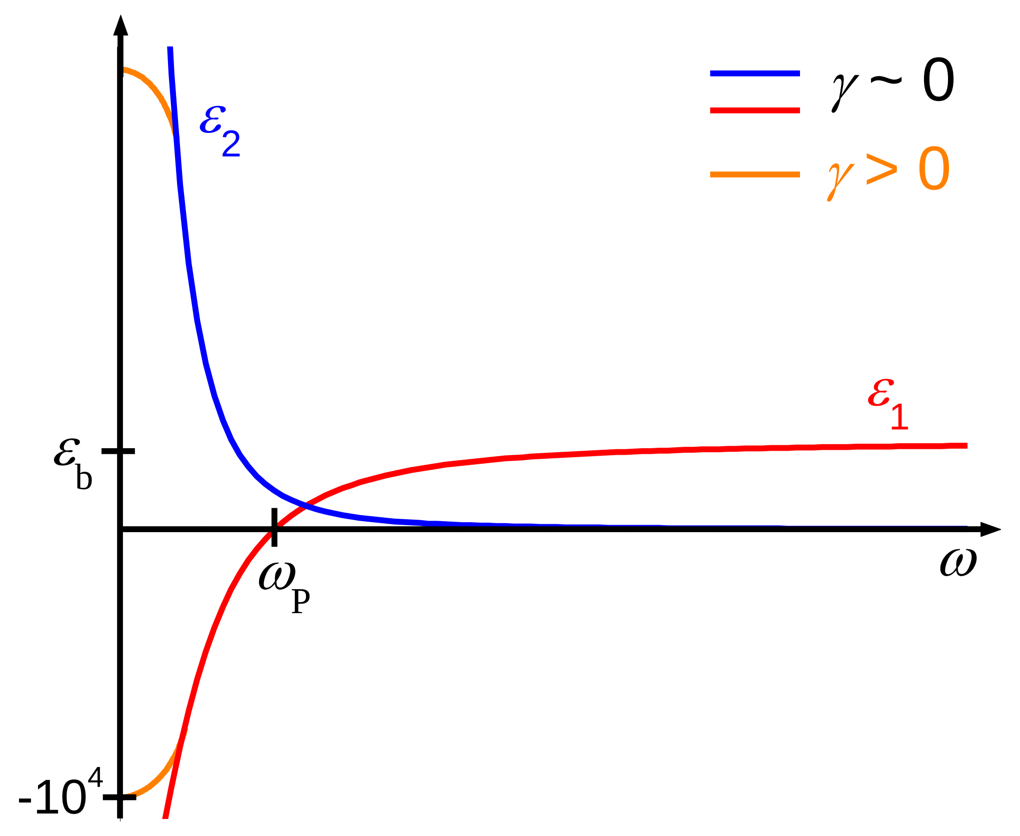
Important :

The plasma oscillation itself does NOT couple to the light field, not even for $k = 0$ (see discussion above)

Nevertheless ω_P important quantity for optical properties
(related to fact that difference between longitudinal / transverse oscillation becomes meaningless for $k = 0$)

Free electron gas : Real and imaginary part of ε

$$\varepsilon(\omega) = \varepsilon_\mathrm{b}\left(1 - \frac{\omega_\mathrm{P}^2}{\omega^2+\gamma^2}\right) + i\varepsilon_\mathrm{b}\,\frac{\gamma\omega_\mathrm{P}^2}{\omega\left(\omega^2+\gamma^2\right)}$$



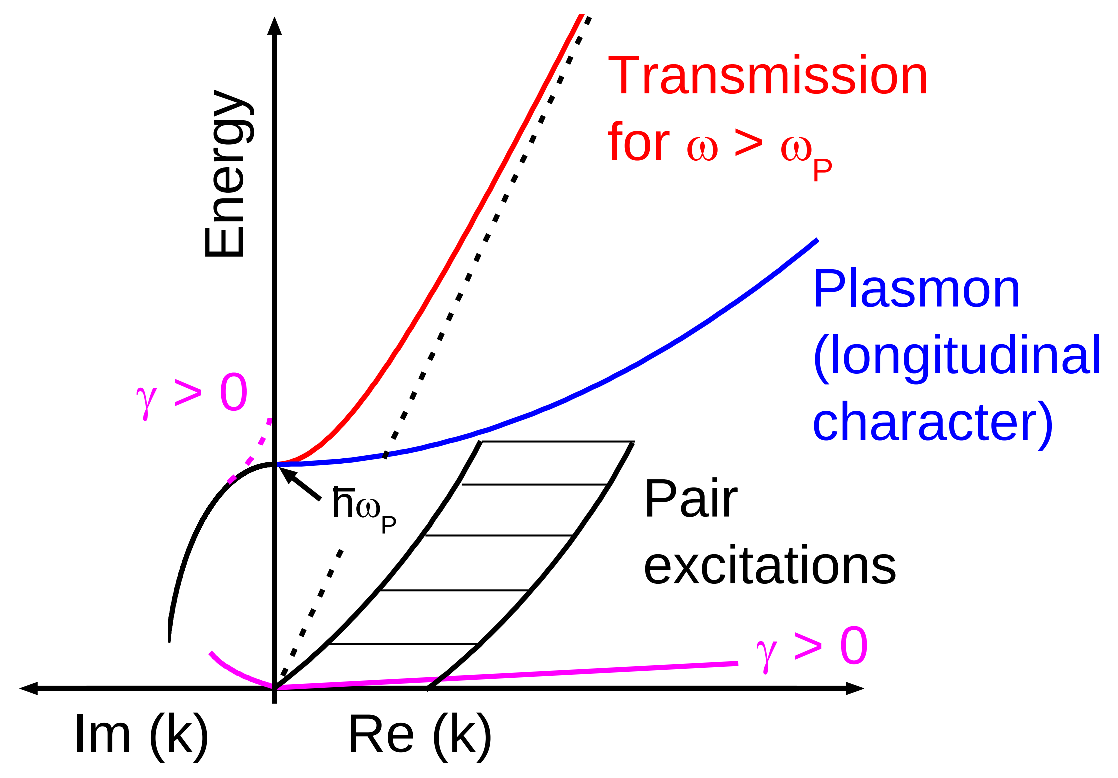
Polariton dispersion for the free electron gas

$$\frac{c^2k^2}{\omega^2} = \varepsilon(\omega) = \varepsilon_\mathrm{b}\left(1-\frac{\omega_\mathrm{P}^2}{\omega^2+i\omega\gamma}\right) \Rightarrow \frac{c^2k^2}{\varepsilon_\mathrm{b}} = \omega^2 - \frac{\omega^2\omega_\mathrm{P}^2}{\omega^2+i\omega\gamma} = \omega^2 - \frac{\omega\omega_\mathrm{P}^2}{\omega+\mathrm{i}\gamma}$$

For $\gamma = 0$: $$\frac{c^2k^2}{\varepsilon_\mathrm{b}} = \omega^2 - \omega_\mathrm{P}^2$$

No lower polariton branch (LPB) !

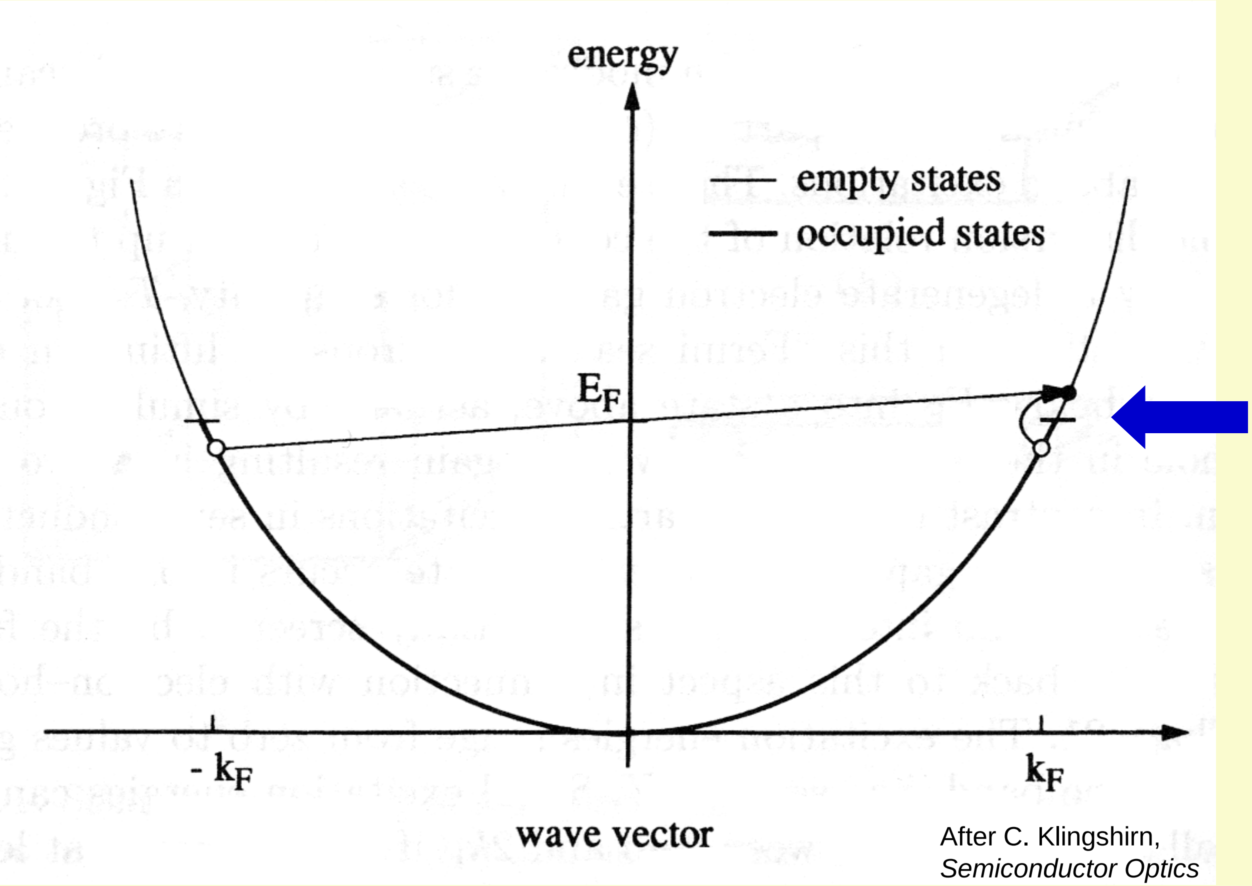
$\gamma > 0$: LPB but strongly damped !



Plasmon excitations:

- Longitudinal exc. ⇒ e – e interaction but e – photon interaction *not influenced*
- Degeneracy with polariton dispersion at $k = 0$!
- Strongly damped for large k due to *pair excitation continuum* (intraband excitations)

Intraband pair excitations in metals



After C. Klingshirn, *Semiconductor Optics*

Fermi edge

Excitation of electron above Fermi level and remaining hole ⇒

- *Continuum* of *two-particle* excitations within *one* band
  ↔ Exciton in semiconductors (discussed later)
- High energy only for large k ⇒ Not important for optical properties

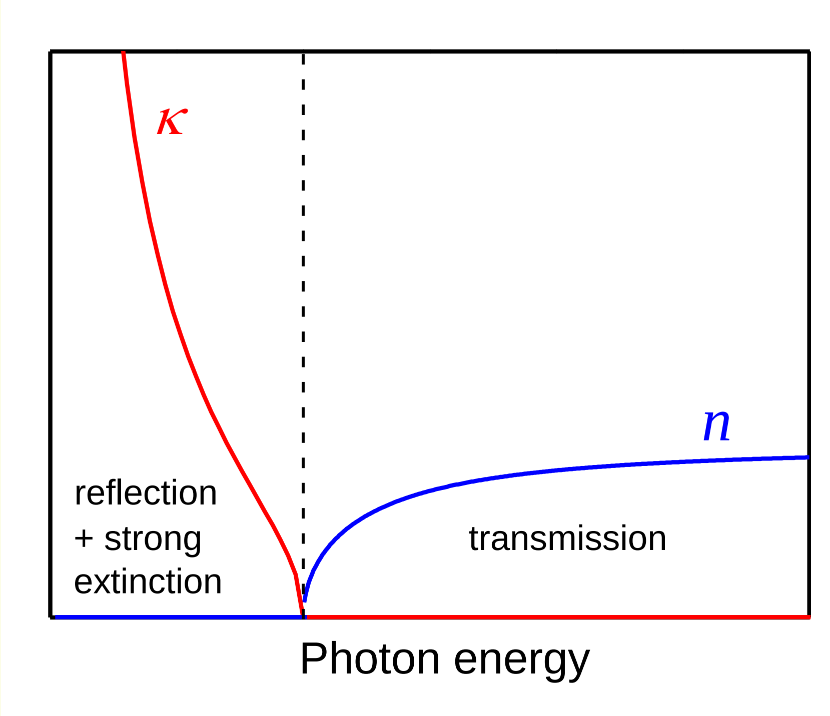
Optical constants of the free electron gas

$$\varepsilon(\omega) = \varepsilon_b\left(1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}\right) \qquad \omega \approx \omega_p \gg \gamma \;\Rightarrow\; \varepsilon_2 \approx 0$$

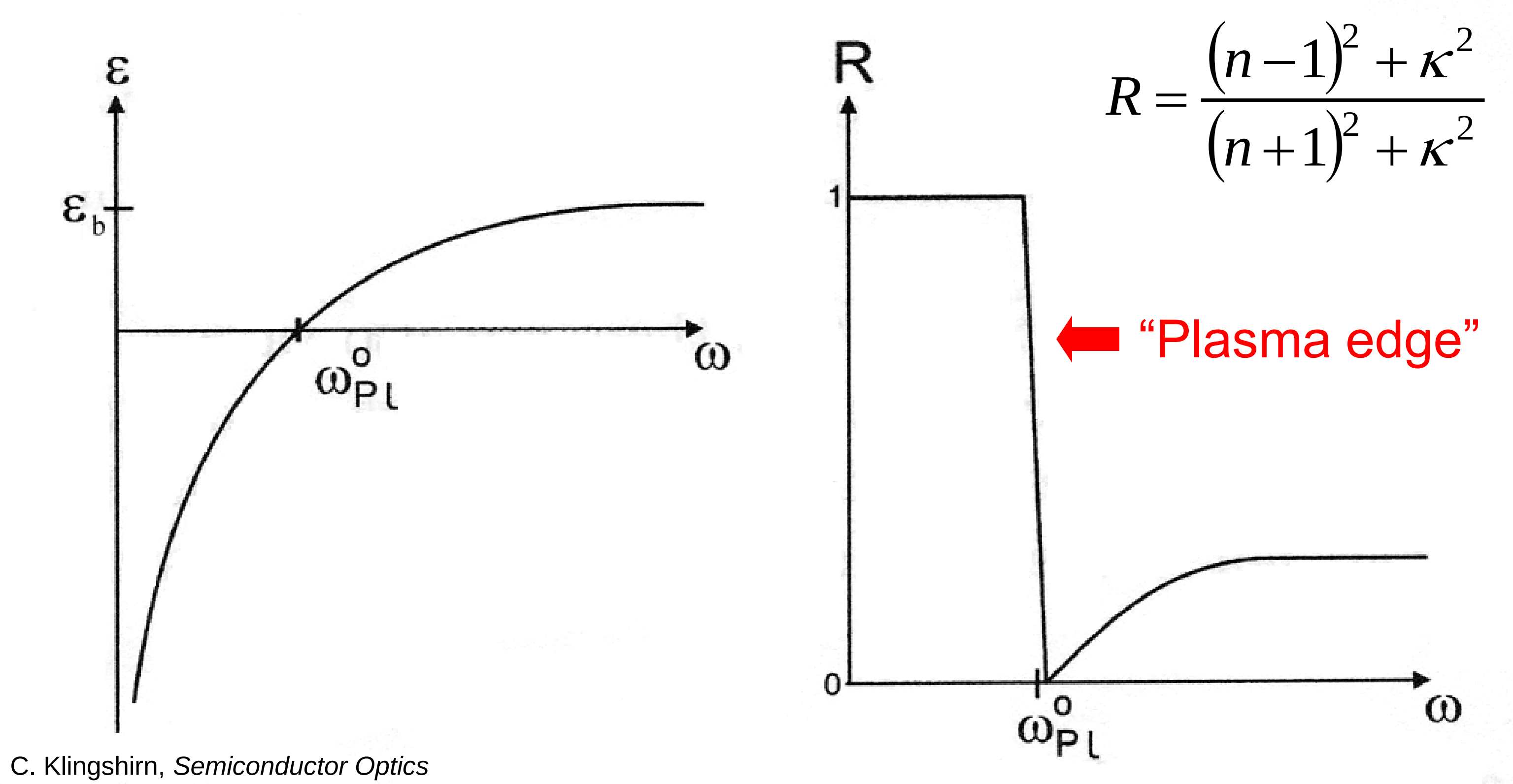
$$\varepsilon_1 + i\cancel{\varepsilon_2} = (n + i\kappa)^2 \;\Rightarrow$$

$$\omega > \omega_p: \qquad n^2 = \varepsilon_b\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

$$\omega < \omega_p: \qquad -\kappa^2 = \varepsilon_b\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$



Reflection coefficient



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

“Plasma edge”

C. Klingshirn, *Semiconductor Optics*

Free electron gas model describes optical properties of some “simple” metals reasonably well.

Example: Al ($3s^2 3p^2$)

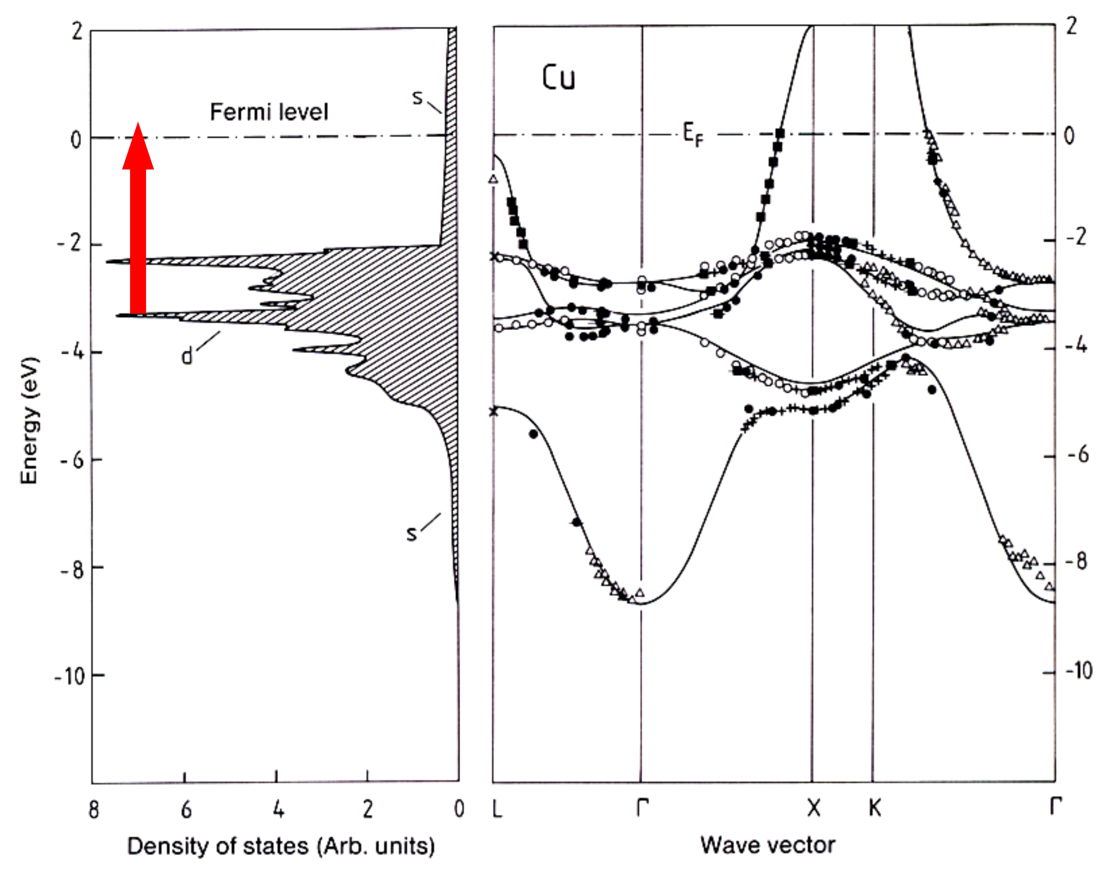
Fails for many “real” metals, e.g., Cu ($3d^{10}4s$) or Ag($4d^{10}5s$). Why?

Optical properties of real metals

Problem: Further contributions to the dielectric function

In particular: Direct electronic interband transitions

e.g., d (quasi-bound states) → conduction band ($E > E_F$), $\hbar\omega < \hbar\omega_p$



Remarks:

- d band relatively small
  ⇒ relatively sharp contribution to ε (similar to single resonance)
- E-dep. density of states in target band important for contribution to ε

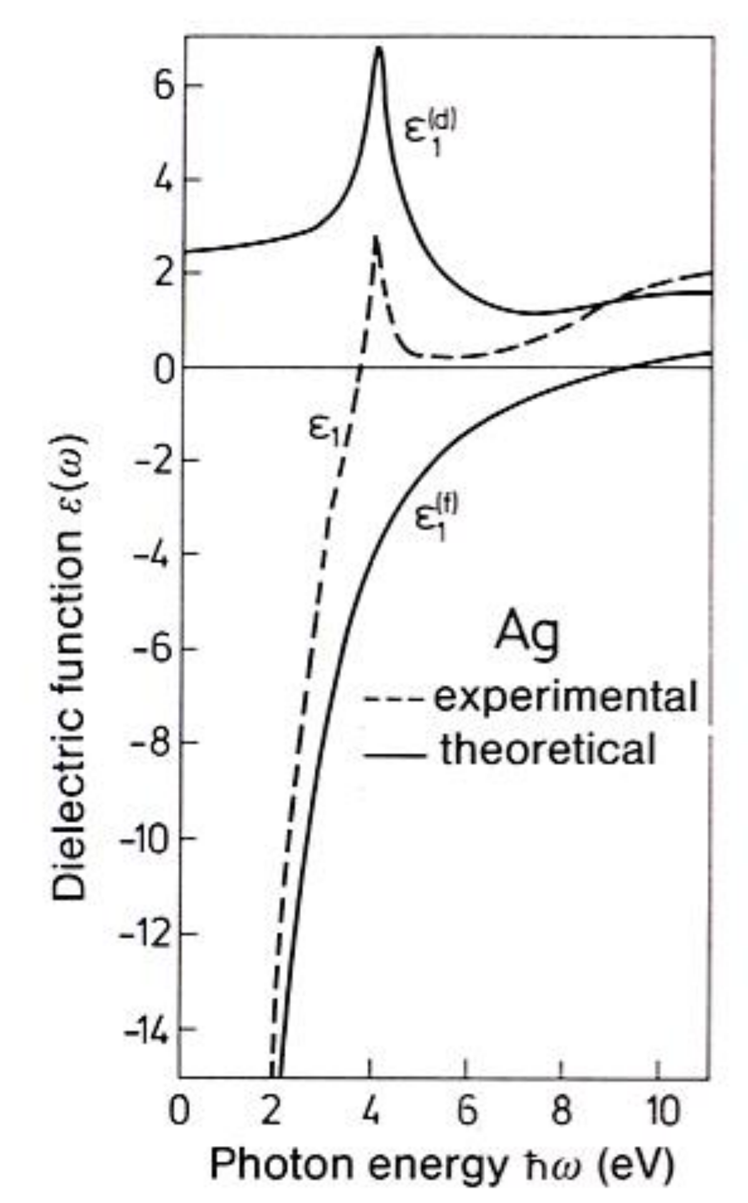
⇒ Plasma + band – band models:

$$\varepsilon(\omega) = \varepsilon^{f}(\omega) + \varepsilon^{d}(\omega)$$

f : free s electrons (Drude)
d : quasi-localized d electrons (Lorentz)

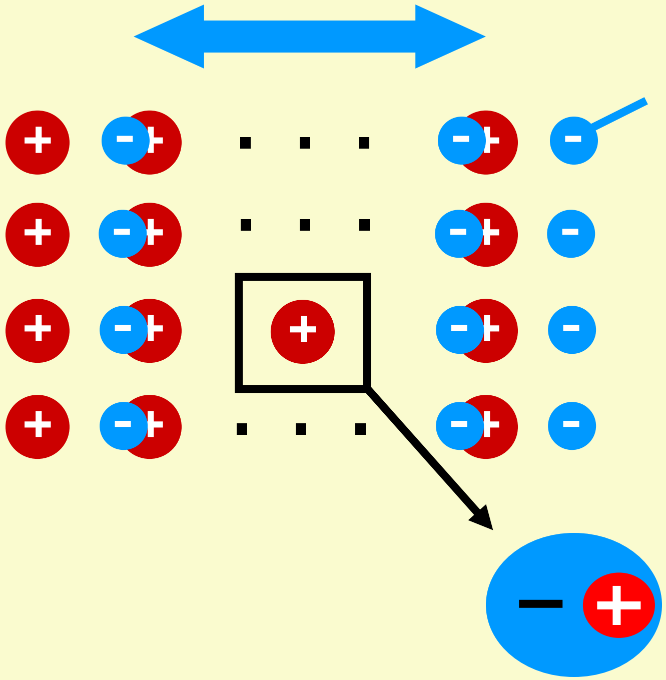
⇒ "Effective ω_p" strongly shifted due to additional contribution of direct transitions to ε

⇒ *"Screened" plasma frequency*



From Ibach, Lüth, *Solid-State Physics*

Intuitive picture



Plasma oscillation of free s electrons

- Quasi-bound d electrons are polarized by oscillating electric field
- *Below resonance frequency* (transition energy $E_{d-CB} \ / \ \hbar$):

  Polarization phase opposite to free electron polarization
  $\Rightarrow$ Effective plasma frequency (plasma edge) shifts to lower frequency

⇒ Plasma + band – band models:

$$\varepsilon(\omega) = \varepsilon^{f}(\omega) + \varepsilon^{d}(\omega)$$

f : free s electrons (Drude)
d : quasi-localized d electrons (Lorentz)

⇒ “Effective ω_p” strongly shifted due to additional contribution of direct transitions to ε'

⇒ *“Screened” plasma frequency*

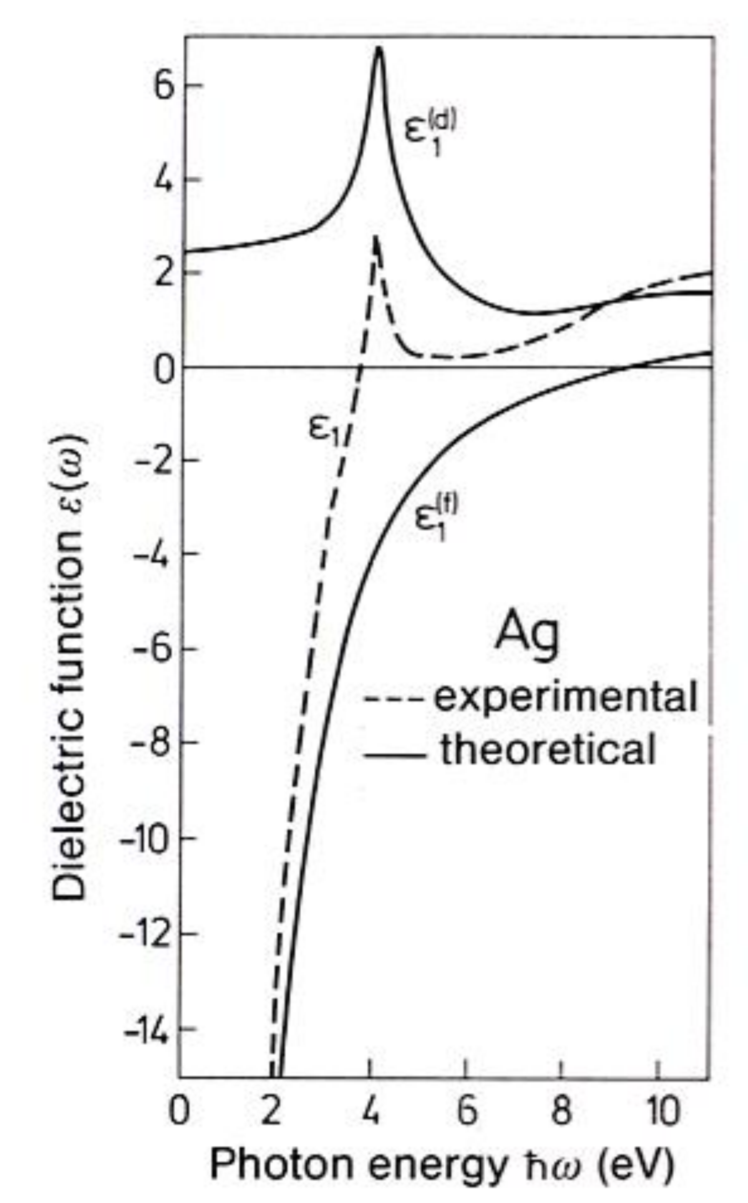
Important example: Cu

$\hbar\omega_p \approx 2$ eV

⇒ Reflectivity in yellow-green region lower than for red light

⇒ Explains redish color

Further literature:
Wooten; Ibach, Lüth; Kalt, Klingshirn

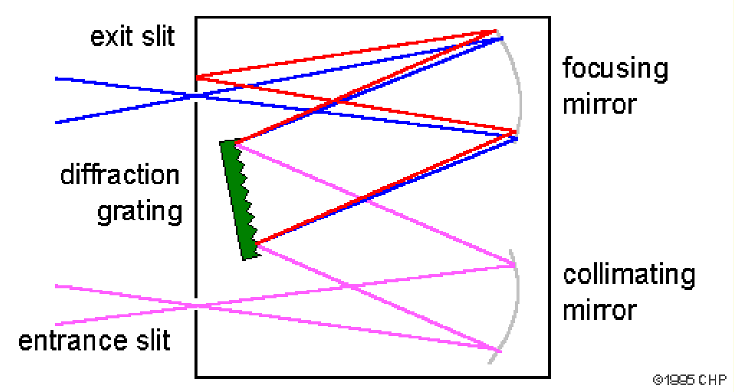


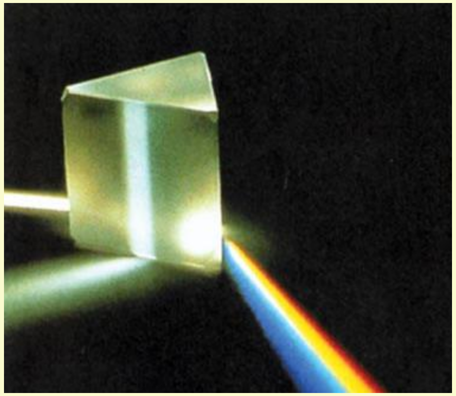
From Ibach, Lüth, *Solid-State Physics*

Optical spectroscopy in the IR (phonons etc.)

Spectroscopy in the visible and NIR :

Dispersive spectroscopic techniques: Grating or prism monochromators





In the infrared (e.g. phonons):

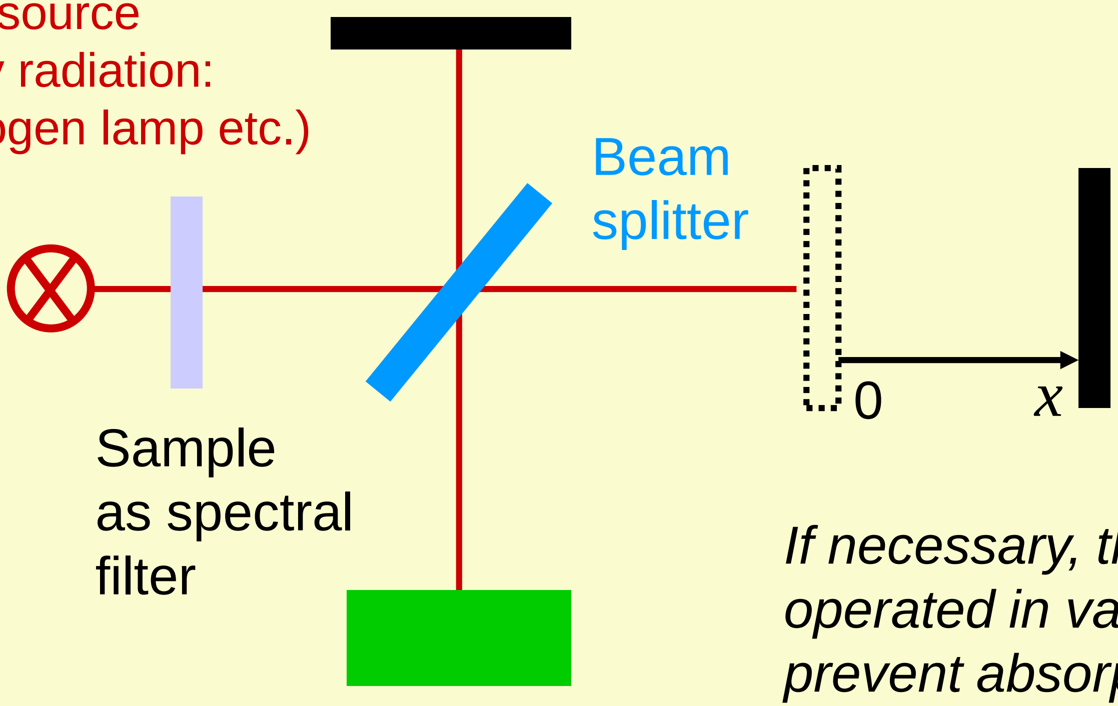
- Problem with conventional optics (lenses etc.) : *absorption* (Reststrahlen bands !)
- Wide spectral range has to be covered ⇒ *dispersion*

⇒ Use mirrors (no dispersion) and *interferometric spectroscopy*

⇒ Fourier Transform Infrared (FTIR) Spectroscopy

Principle of FTIR spectroscopy: Michelson interferometer

Example : Absorption measurement



Mirror (fixed)

White light source
(black body radiation:
globar, halogen lamp etc.)

Beam
splitter

Mirror
(moveable)

Sample
as spectral
filter

Detector

If necessary, the set-up is operated in vacuum to prevent absorption in air / water vapor

Two-beam interference at detector !

Measure resulting light intensity as a function of mirror position x

⇒ Interferogram function $I(x)$

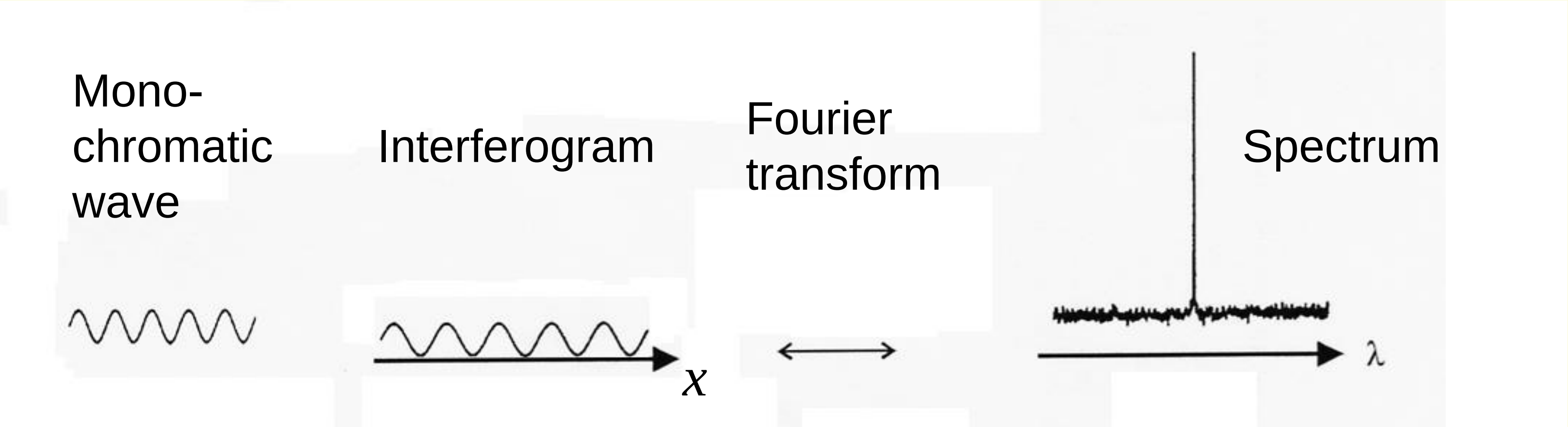
Analysis of interferogram function

- Interference between the two split components of one wavelength:

  $\Rightarrow$ $I(x)$ oscillating (cos-like) :
  Constructive or destructive interference,
  depending on optical path difference

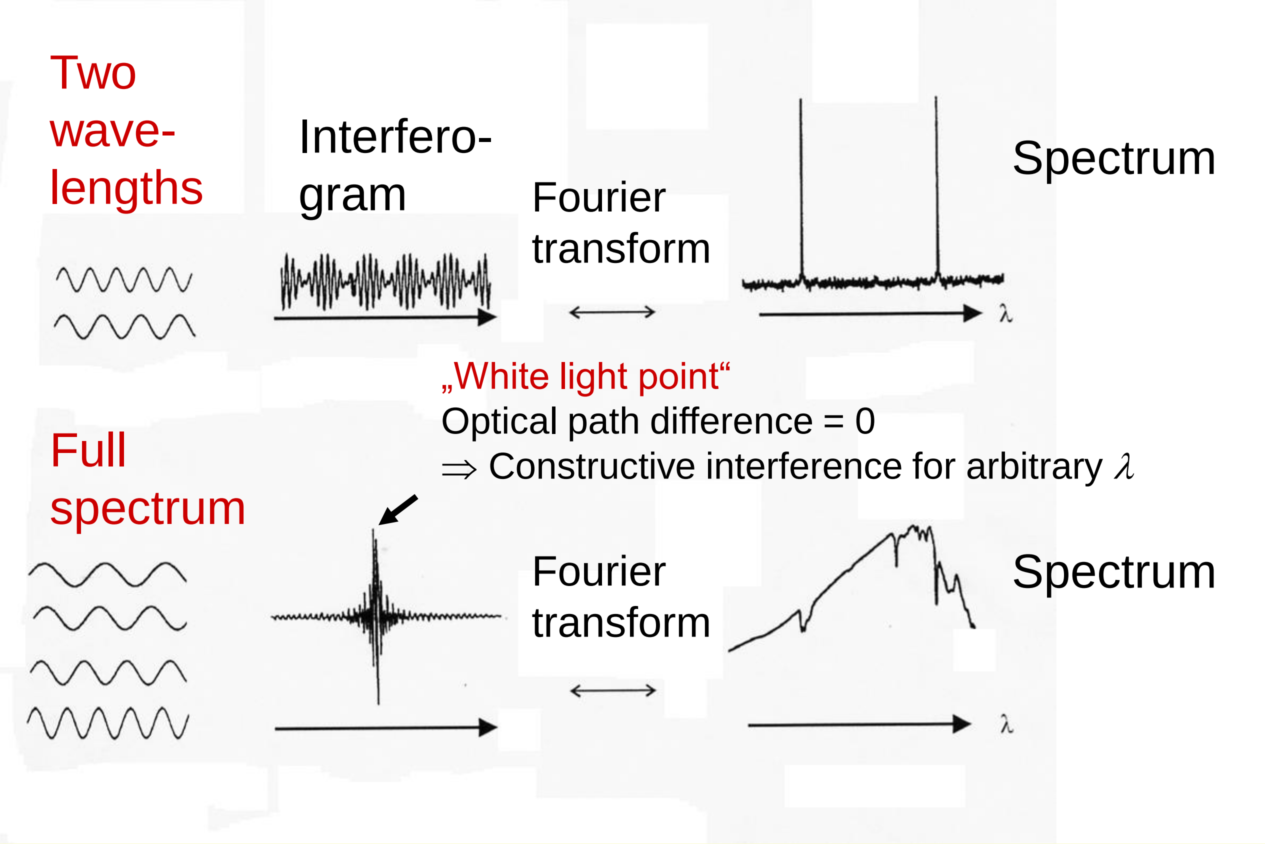
- Frequency of oscillation depends on wavelength

  $\Rightarrow$ Spectrum obtained by *Fourier transformation of* $I(x)$



Several wavelengths simultaneously

- Waves with different wavelengths are incoherent
  ⇒ *Intensities* sum up at detector ⇒ Constant offset / background
- Total $I(x)$: Incoherent background + osc. 2-beam interf. of each λ with itself



Two wave-lengths

Interfero-gram

Fourier transform

Spectrum

„White light point“
Optical path difference = 0
⇒ Constructive interference for arbitrary λ

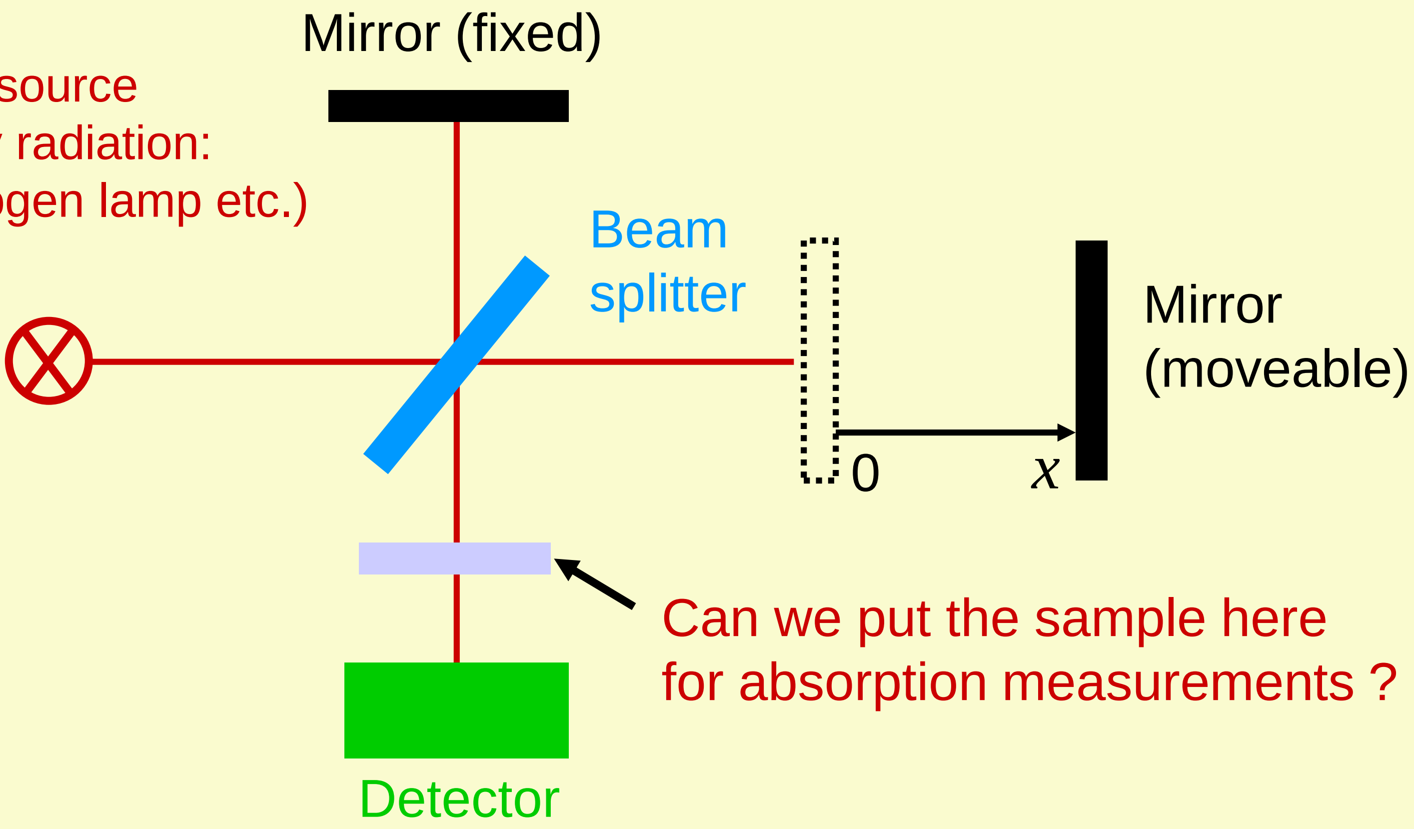
Full spectrum

Fourier transform

Spectrum

⇒ Spectrum can still be obtained by Fourier transformation of $I(x)$

Where do we put the sample ?



Mirror (fixed)

White light source
(black body radiation:
globar, halogen lamp etc.)

Beam
splitter

Mirror
(moveable)

0

x

Can we put the sample here
for absorption measurements ?

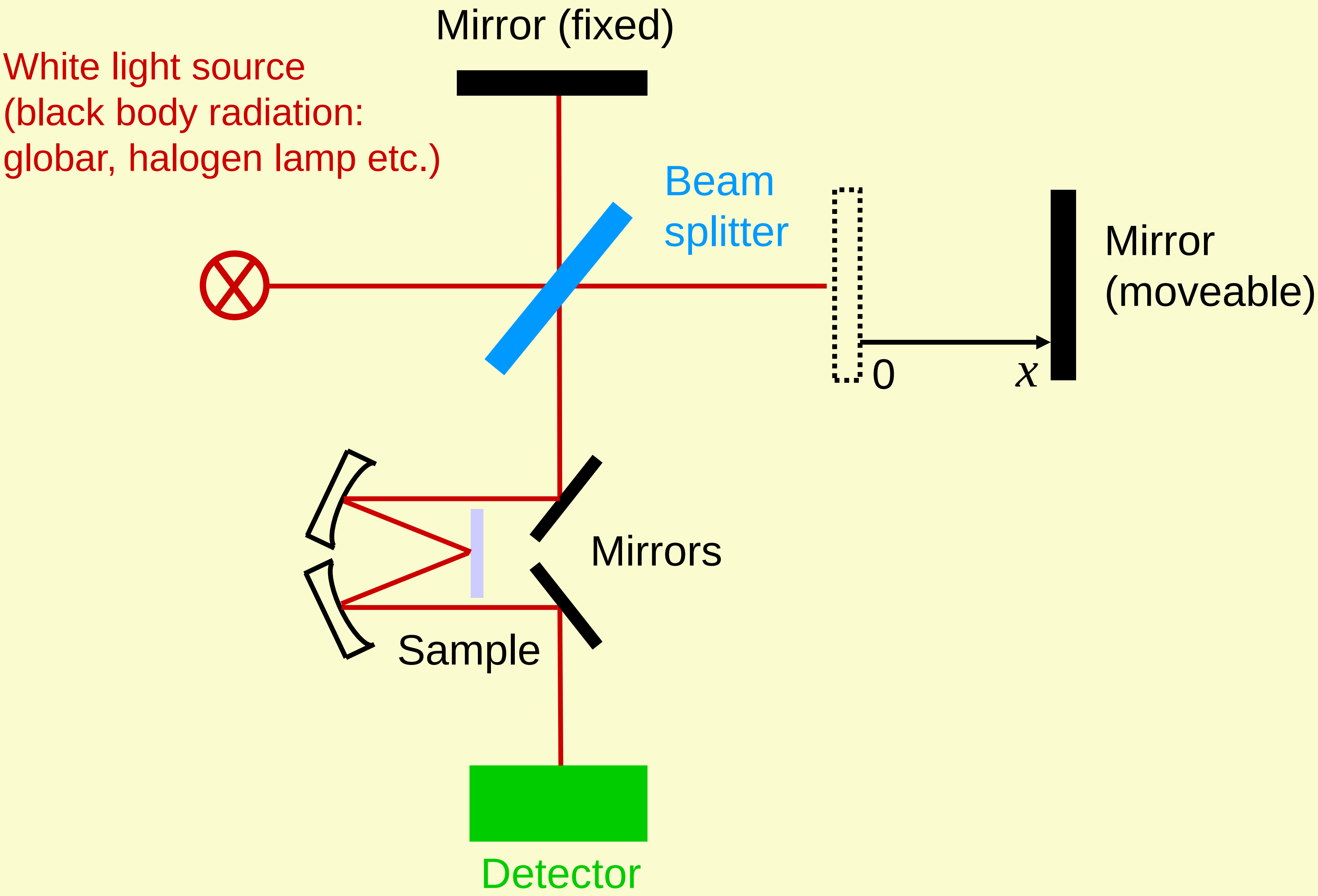
Detector

Yes we can and usually do ! (Make it clear to yourself why this is possible !)

Advantages :

- Measurement takes place *outside* of actual interferometer
- No disturbance of light path in interferometer due to sample

FTIR set-up for reflectivity measurements



Advantages of FTIR spectroscopy

Throughput (energy) advantage :

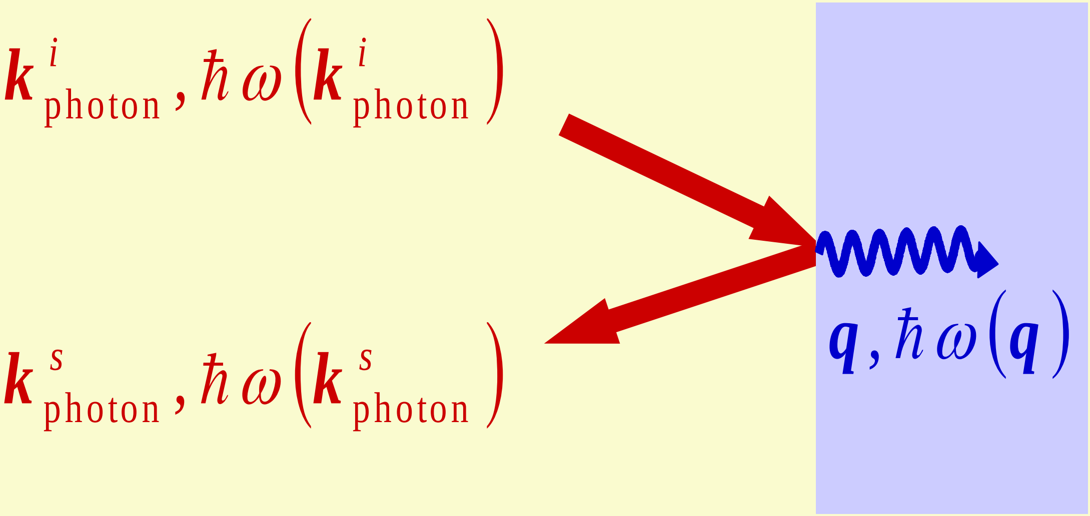
During the whole measurement time, the complete intensity falls onto the detector and is used

Multiplex advantage :

The complete spectral range is measured simultaneously, not wavelength by wavelength

Raman spectroscopy

Inelastic scattering of photons (visible, NIR, UV) in a medium with simultaneous generation or annihilation of elementary excitations (e.g., phonons, plasmons)



$$\boldsymbol{k}^{i}_{\text{photon}}, \hbar\omega\left(\boldsymbol{k}^{i}_{\text{photon}}\right)$$

$$\boldsymbol{k}^{s}_{\text{photon}}, \hbar\omega\left(\boldsymbol{k}^{s}_{\text{photon}}\right)$$

$$\boldsymbol{q}, \hbar\omega\left(\boldsymbol{q}\right)$$

Mechanism :

- *Spatial* and *temporal* modulation of dielectric function induced by elementary excitation (e.g. phonon) leads to scattering
- QM : Virtual excitation of intermediate (electronic) state and following emission of photon with simultaneous generation or annihilation of a further elementary excitation

Stokes and Anti-Stokes lines

Energy conservation :

Generation of elementary excitation: Stokes scattering

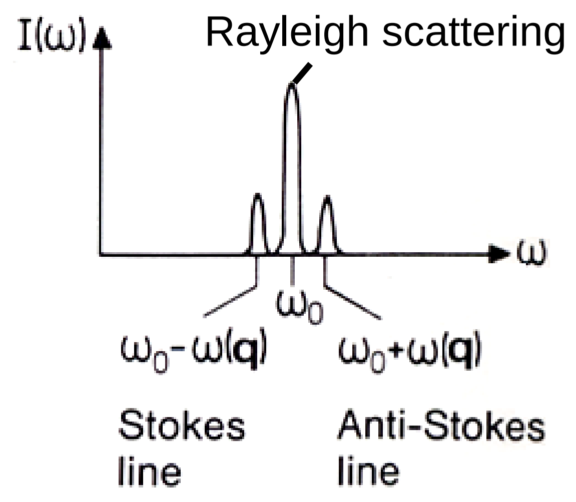
$$\hbar\omega\left(\boldsymbol{k}^{i}_{\text{photon}}\right)=\hbar\omega\left(\boldsymbol{k}^{s}_{\text{photon}}\right)+\hbar\omega\left(\boldsymbol{q}\right)$$

Photon energy of scattered light reduced by energy of created excitation

Annihilation of elementary excitation: Anti-Stokes scattering

$$\hbar\omega\left(\boldsymbol{k}^{i}_{\text{photon}}\right)=\hbar\omega\left(\boldsymbol{k}^{s}_{\text{photon}}\right)-\hbar\omega\left(\boldsymbol{q}\right)$$

Photon energy of scattered light increased by energy of destroyed excitation



In addition : *Elastic* Rayleigh scattering

Problem :

Raman scattering very weak and spectrally close to much stronger Rayleigh peak

⇒ Use double / triple monochromator

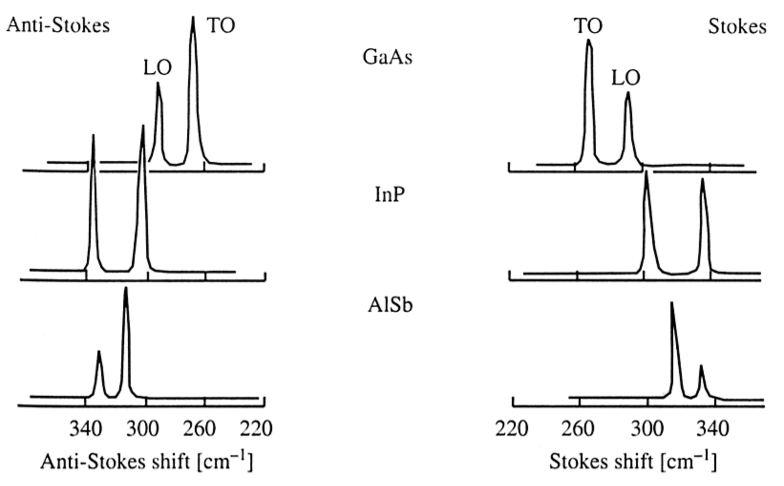
⇒ Use resonant Raman scattering to increase signal (e.g., photon energy of incident light ~ band gap)

For phonons :

Anti-Stokes process requires presence of phonons
⇒ Increase with rising temperature

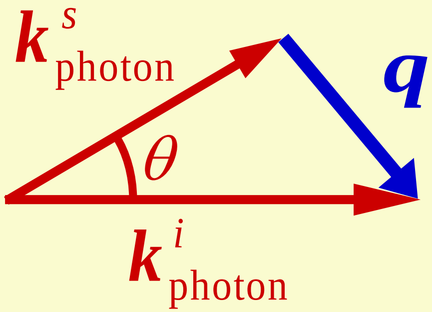
Practical applications

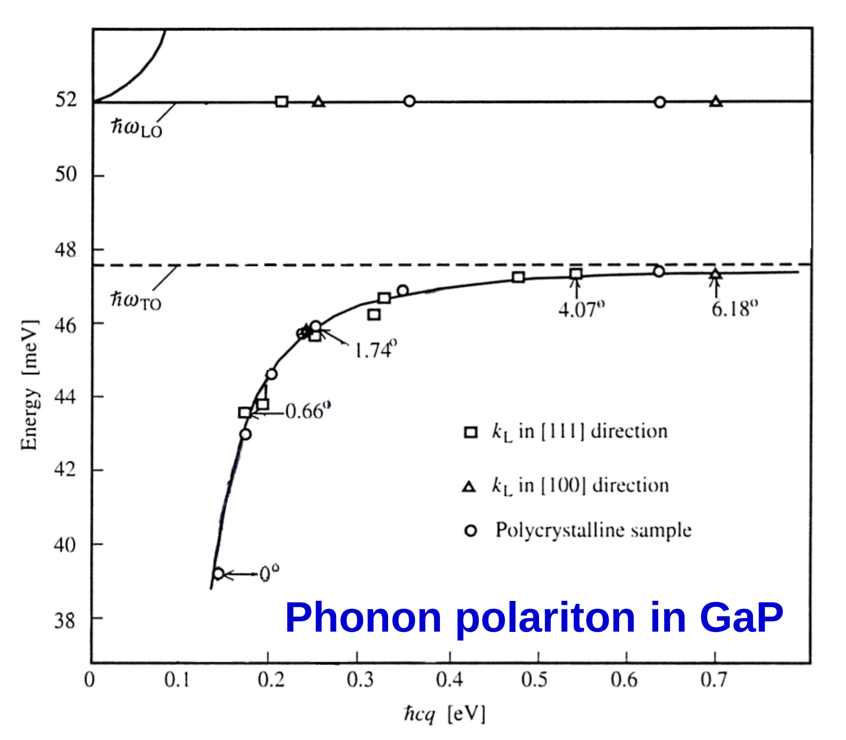
- Use intensity ratio of phononic Stokes / Antistokes lines (and their thermal shift) to measure T-distribution in optoelectronic devices (e.g., laser diodes). Even measurement of inner parts of the structures possible by selecting phonon lines of corresponding materials
- Measurement of longitudinal excitations (e.g., LO phonons) possible ! (Because they lead to a periodic modification of the dielectric function.)
- Identification of excitation (e.g., LO, TO phonon) via selection rules (from group theory)



Further advantages and applications

- Low energy excitations (e.g., phonons) can be measured using visible / NIR / UV light, which is easier to handle than FIR etc.
- Apart from energy also k conservation
  $\Rightarrow$ Dispersion relation of excitation can be measured, e.g., by variation of the angle θ between incident and scattered light





Phonon polariton in GaP

From Yu, Cardona

Note : Since the k vectors for (visible) light are small, Raman spectroscopy can only probe the dispersion relation around the center of the Brillouin zone !

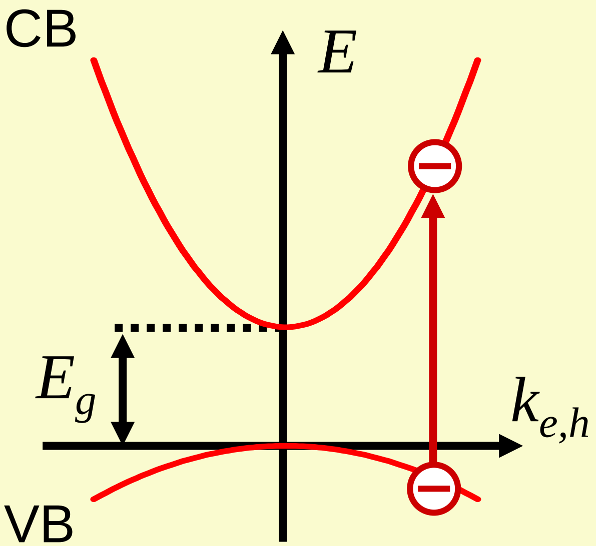
Band-to-Band Transitions in Semiconductors (and Insulators)

So far:
Optical properties induced by excitations in solid with
discrete resonances $\omega_0^i(k)$ (which nevertheless possess a dispersion !)

Examples:
phonons, excitons (discussed in detail later on)

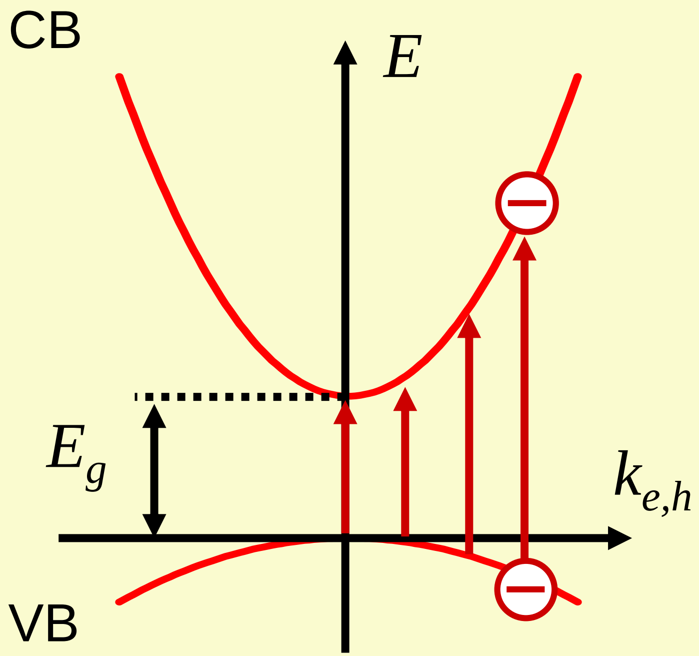
Typical situation in a semiconductor / insulator:

Optical properties (e.g. absorption) in visible / near infrared dominated by band-to-band transitions*
(transition energies in eV regime)



* in particular at room-temperature, where excitonic effects are less important, see discussion later-on

Example: Optical absorption in bulk semiconductor



Absorption due to electronic transitions from valence band (VB) to conduction band (CB)

Photon momentum ≈ 0

$\Rightarrow$ Momentum conservation implies "vertical" transitions (i.e., $\Delta \mathbf{k} \sim 0$) in band diagram

Important:

Continuum of possible electronic transitions with $\Delta \mathbf{k} \sim 0$ for energies > E_g

$\Rightarrow$ *No* absorption for $E_{\text{Photon}} < E_g$, *continuous* absorption for $E_{\text{Photon}} > E_g$

How do we calculate the absorption spectrum etc. for this case?

QM treatment using perturbation theory

Hamilton operator for electron in electromagnetic field:

$$H = \frac{\left(\frac{\hbar}{i}\nabla - e\boldsymbol{A}\right)^2}{2m}$$

$\boldsymbol{A}$: Vector potential

$$\boldsymbol{B} = \nabla \times \boldsymbol{A} \quad ; \quad \boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t}$$

H contains terms

$\sim -\frac{\hbar^2}{2m}\Delta \quad \rightarrow$ Unperturbed Hamiltonian H_0

$\sim \nabla \cdot \boldsymbol{A} = 0$ Cancels in appropriate gauge

$\sim \boldsymbol{A}^2 \quad \rightarrow$ small for weak fields,
typically negligible for linear optics

$\sim \boldsymbol{A} \cdot \nabla \quad \rightarrow \quad H' = \frac{e\hbar}{mi}\boldsymbol{A} \cdot \nabla$ perturbation

$$\Rightarrow (H_0 + H')\psi = i\hbar\frac{\partial \psi}{\partial t}$$

Transition matrix element in Fermi's Golden Rule:

$$H'_{fi} = \int \psi_f {}^* H' \psi_i d^3\boldsymbol{r}$$

Electronic wavefunctions: Bloch states for VB and CB:

$$\psi_i = \frac{1}{\sqrt{\Omega}} e^{i\boldsymbol{kr}} u_{VB}(\boldsymbol{r},\boldsymbol{k}) \qquad \psi_f = \frac{1}{\sqrt{\Omega}} e^{i\boldsymbol{kr}} u_{CB}(\boldsymbol{r},\boldsymbol{k})$$

Ω: crystal volume

Vector potential: $$\boldsymbol{A} = \frac{1}{2} A_0 \boldsymbol{a_0} \left(\underbrace{e^{i(\boldsymbol{qr}-\omega t)}}_{\text{Absorption}} + \underbrace{e^{-i(\boldsymbol{qr}-\omega t)}}_{\text{Stimulated emission}} \right)$$

$\boldsymbol{q}$: photon wavevector (small) $\boldsymbol{a_0}$: unit vector polarization

Insert everything in H' :

- Fermi's Golden Rule ⇒ Energy and momentum conservation (→ identification of absorption and emission term)
- $\boldsymbol{q}$ ~ 0, i.e., $\boldsymbol{k_f} = \boldsymbol{k_i}$ ("vert." trans.)
- Lattice periodicity: $\int d^3\boldsymbol{r} \rightarrow \sum_{n=1}^{N} \int_{cell} d^3\boldsymbol{r}$ N: Number of unit cells

$$\Rightarrow H'_{fi} = -\frac{ie\hbar A_0}{2mV_{cell}} \int_{cell} d^3\boldsymbol{r}\, u^*_{CB}(\boldsymbol{k})\left[\boldsymbol{a_0}\cdot\nabla u_{VB}(\boldsymbol{k}) + i\boldsymbol{a_0}\cdot\boldsymbol{k}\, u_{VB}(\boldsymbol{k})\right]$$

may be zero (“forbidden transition”), e.g., for symmetry reasons:

= 0 (periodic part of Bloch functions orthogonal)

$$\Gamma_f \not\in \Gamma_{H'} \otimes \Gamma_i$$

Now: Assume allowed transition

$$\Rightarrow H'_{fi} = -\frac{ie\hbar A_0}{2mV_{cell}} \int_{cell} d^3\boldsymbol{r}\, u^*_{CB}(\boldsymbol{k})\boldsymbol{a_0}\cdot\nabla u_{VB}(\boldsymbol{k}) \underset{\boldsymbol{p}=-i\hbar\nabla}{=} \frac{eA_0}{2m}\boldsymbol{a_0}\cdot\boldsymbol{p_{fi}}(\boldsymbol{k})$$

Matrix element of momentum operator

$\Rightarrow$ Transition rate (Fermi):

$$P_{fi} = \frac{2\pi}{\hbar}\left|H'_{fi}\right|^2 \delta\left(E_{fi} - \hbar\omega\right) = \frac{\pi e^2 A_0^2}{2m^2\hbar}\left|\boldsymbol{a_0}\cdot\boldsymbol{p_{fi}}\right|^2 \delta\left(E_{fi} - \hbar\omega\right)$$

Total transition rate W_{fi} :

→ *Integrate over all possible* $\mathbf{k}$ *values* (i.e., over constant energy surface)

Density of states in k *space:*

(counting of wavefunctions satisfying periodic boundary conditions, see, e.g., *Kittel*)

spin

crystal volume

$$\frac{2L^3}{(2\pi)^3} = \frac{L^3}{4\pi^3} \quad \text{or} \quad \frac{1}{4\pi^3} \quad \text{per volume}$$

$$W_{fi}(\hbar\omega) = \frac{\pi e^2 A_0^2}{2m^2\hbar} \int \frac{d^3\mathbf{k}}{4\pi^3} \left|\boldsymbol{a_0} \cdot \boldsymbol{p_{fi}}\right|^2 \delta\left(E_{fi} - \hbar\omega\right)$$

Using $\boldsymbol{E} = -\dot{\boldsymbol{A}} = i\omega\boldsymbol{A} \quad \Rightarrow \quad E_0^2 = \omega^2 A_0^2 \quad \Rightarrow \quad A_0^2 = \dfrac{2I}{v_g \varepsilon_1 \varepsilon_0 \omega^2}$

with $I = \dfrac{1}{2} v_g \varepsilon_1 \varepsilon_0 E_0^2$

$$\Rightarrow \quad W_{fi} = \frac{e^2 I}{v_g \varepsilon_0 \varepsilon_1 4\pi^2 m^2 \omega^2} \int d^3\mathbf{k} \left|\boldsymbol{a_0} \cdot \boldsymbol{p_{fi}}(\mathbf{k})\right|^2 \delta\left(E_{fi}(\mathbf{k}) - \hbar\omega\right)$$

Aim: Determine absorption etc. as a function of photon energy / wavelength

Problem: Formula still explicitly depends on $\mathbf{k}$: $E_{fi}(\mathbf{k})$, $p_{fi}(\mathbf{k})$

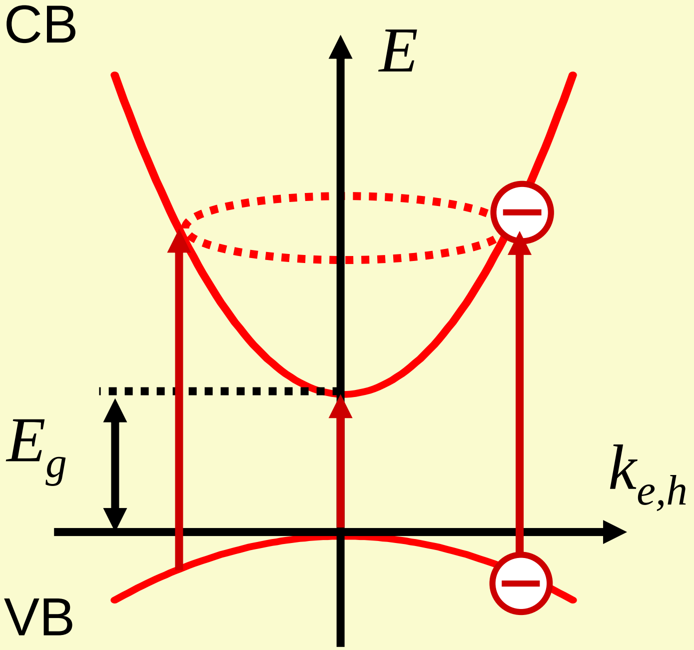
Note: There are many different $\mathbf{k}$ for each transition energy which we often do not know / are not interested in

⇒ Make specific assumptions on *dispersion of CB and VB*:

- Bands are parabolic (good approx. near band gap)
- Isotropic effective mass (or suitable average)

$$E_f = E_{\text{CB}} = \frac{\hbar^2 k^2}{2m_e} + E_g$$

$$E_i = E_{\text{VB}} = -\frac{\hbar^2 k^2}{2m_h}$$



⇒ Assume *constant transition probability* for all $\mathbf{k}$ (mean value, good approx. near band gap)

$$\left\langle \left| \mathbf{a_0} \cdot \mathbf{p}_{fi}(\mathbf{k}) \right|^2 \right\rangle \sim 3 \left\langle p_{fi}^2 \right\rangle$$ (at least for spherical symmetry)

$$\Rightarrow \quad W_{fi}(\hbar\omega) = \frac{3e^2 I \langle p_{fi}^2 \rangle}{v_g \varepsilon_0 \varepsilon_1 4\pi^2 m^2 \omega^2} \underbrace{\int d^3\mathbf{k}\, \delta\left(E_{fi}(\mathbf{k}) - \hbar\omega\right)}$$

Change to $\int dE_{fi}$

Spherical symmetry $\Rightarrow$ Use polar coordinates in k space

$$d^3\mathbf{k} = 4\pi k^2 dk = 4\pi k^2 (E_{fi}) \frac{dk(E_{fi})}{dE_{fi}} \cdot dE_{fi}$$

k^2 from $E_{\mathrm{CB}} - E_{\mathrm{VB}}$ using $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h} \quad \Rightarrow \quad k^2 = \frac{2\mu(E_{fi} - E_g)}{\hbar^2}$

$$\frac{dk}{dE_{fi}} = \frac{1}{2} \frac{\sqrt{2\mu}}{\hbar} (E_{fi} - E_g)^{-1/2} \Rightarrow \quad W_{fi}(\hbar\omega) = \frac{3e^2 I (2\mu)^{3/2} \langle p_{fi}^2 \rangle}{2\pi m^2 \hbar^3 v_g \varepsilon_0 \varepsilon_1 \omega^2} (\hbar\omega - E_g)^{1/2}$$

→ Concept of “Joint” (contains CB and VB) Density of States (DOS), see below

$\sim \sqrt{\hbar\omega - E_g}$ for *parabolic* bands (square root in analogy to DOS for single bands)

Calculation of absorption coefficient

$$\alpha_{fi} = \frac{\text{Absorbed energy per unit volume and time}}{\text{incident intensity}}$$

$$= \frac{\text{transition rate per unit volume x energy } \hbar\omega_{fi} \text{ per transition}}{\text{energy density x energy velocity}}$$

$$\Rightarrow \quad \alpha_{fi} = \alpha\left(\hbar\omega_{fi}\right) = \frac{W_{fi} \cdot \hbar\omega_{fi}}{\varepsilon_1\varepsilon_0\left\langle E^2\right\rangle v_g}$$

Numerator and denominator ~ number of photons / unit volume

$\Rightarrow$ Restriction to one photon / unit volume:

$\tilde{W}_{fi}$: W_{fi} for one photon per unit volume; $\varepsilon_1\varepsilon_0\left\langle E^2\right\rangle = \hbar\omega$

Assume weak absorption: $\varepsilon_2 \sim 0;\quad n = \sqrt{\varepsilon_1}$ and use $v_g = c/n$

$$\Rightarrow \quad \alpha\left(\hbar\omega_{fi}\right) = \frac{\varepsilon_1\tilde{W}_{fi}}{nc}$$ Connection between QM calculation and experiment

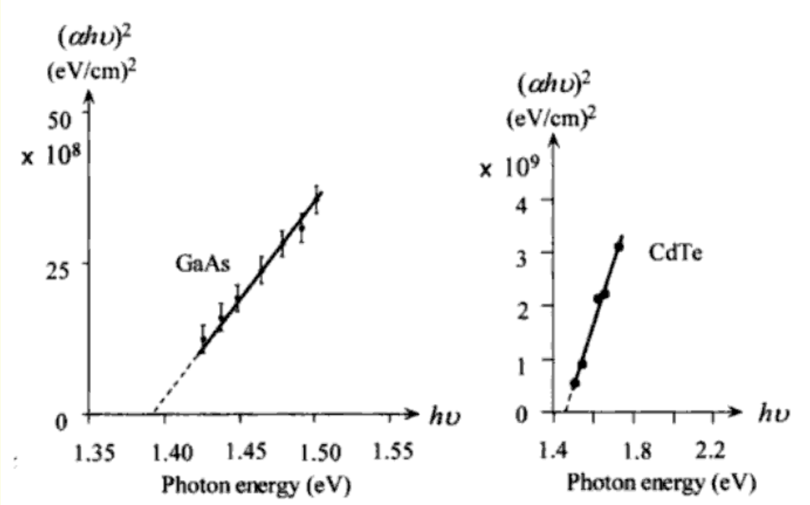
⇒ For band–band transitions:

$$\alpha = \frac{3e^2\langle f\rangle(2\mu)^{3/2}}{4\pi n c\varepsilon_0 m\hbar^2}\left(\hbar\omega - E_g\right)^{1/2} \sim \langle f\rangle\left(\hbar\omega - E_g\right)^{1/2}$$

Since oscillator strength $\langle f\rangle = \frac{2\langle p_{fi}\rangle^2}{m\hbar\omega}$ considered as ~ const./ω :

$$\alpha \sim \frac{\left(\hbar\omega - E_g\right)^{1/2}}{\omega}$$ for *direct* semiconductor (CB + VB at k = 0)

⇒ Lineshape of absorption spectrum essentially given by *energy-dependence of joint density of states*



From: *Photo-Excited Processes, Diagnostics and Applications*, ed. A. Peled, Kluwer

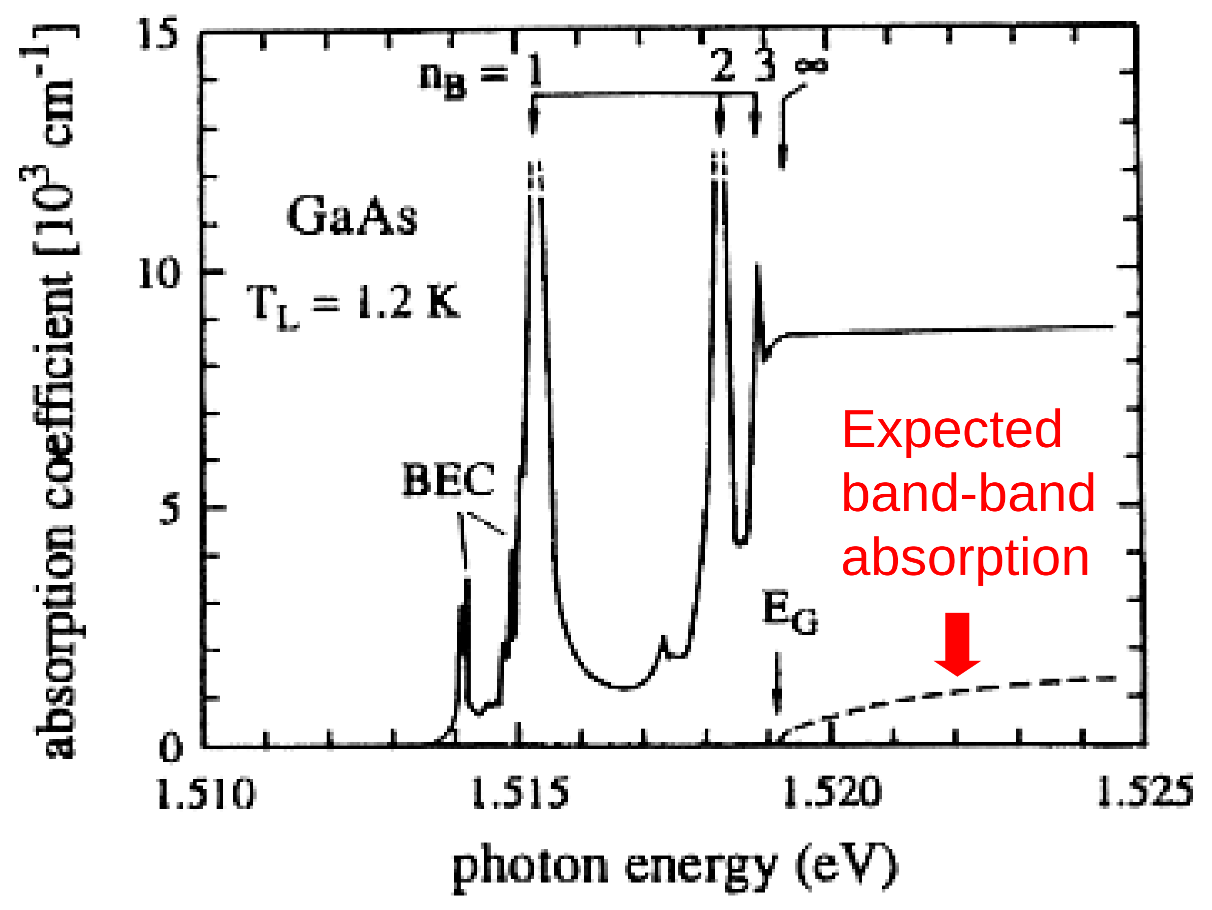
Examples:

Absorption spectra of p-GaAs and CdTe single crystals

⇒ *Reasonable agreement with expected behavior at room-temperature*

Note:

- Different behavior for *indirect* semiconductors
- Generally strong deviation from expected behavior at low temperature due to *excitonic effects* → later



Expected band-band absorption

Joint DOS and van Hove singularities in ε

Now: Consider *all* frequencies (not only close to band gap)

Total transition rate: $\tilde{W}_{fi} = \frac{e^2}{\varepsilon_0 \varepsilon_1 4\pi^2 m^2 \omega} \int d^3\boldsymbol{k} \left| \boldsymbol{a_0} \cdot \boldsymbol{p_{fi}} \right|^2 \delta\left(E_{fi} - \hbar\omega\right)$

$\alpha_{fi} = \frac{\varepsilon_1 \tilde{W}_{fi}}{nc} = \frac{2\omega}{c}\kappa$ and $\varepsilon_2 = 2n\kappa$

$$\Rightarrow \quad \varepsilon_2(\omega) = \frac{e^2}{4\pi^2 \varepsilon_0 m_0^2 \omega^2} \int d^3\boldsymbol{k} \left| \boldsymbol{a_0} \cdot \boldsymbol{p_{fi}} \right|^2 \delta\left(E_{fi} - \hbar\omega\right)$$

E.g., for VB → CB:

$$E_{fi} = E_f - E_i = E_{CB}(\boldsymbol{k}) - E_{VB}(\boldsymbol{k}) = E_{VB-CB}(\boldsymbol{k})$$

“Optical energy band”

Define Joint Density of States (JDOS) to achieve $\int d^3\boldsymbol{k} \;\rightarrow\; \int dE$

Area element in constant energy surface

$$\rho(E_{fi})dE = \frac{1}{4\pi^3}\int \frac{dS}{\left|\nabla_{\boldsymbol{k}} E_{fi}(\boldsymbol{k})\right|_{E_{fi}=\hbar\omega}}\, dE = 2J_{fi}\,dE \qquad (*)$$

spin

- Analogous to single band DOS but combines CB and VB properties
- Sums up all possible transitions with same transition energy E_{fi} but at different k

$$\Rightarrow \quad \varepsilon_2(\omega) = \frac{2\pi e^2}{\varepsilon_0 m_0^2 \omega^2}\left|\boldsymbol{a}_0 \cdot \boldsymbol{p}_{fi}\right|^2 \cdot J_{fi}$$

Pronounced features in $\varepsilon_2(\omega)$ and J_{fi} for points in k space where:

$\nabla_{\boldsymbol{k}} E_{fi} = 0$ since denominator in (*) = 0 $\Rightarrow$ Critical points,
van Hove singularities

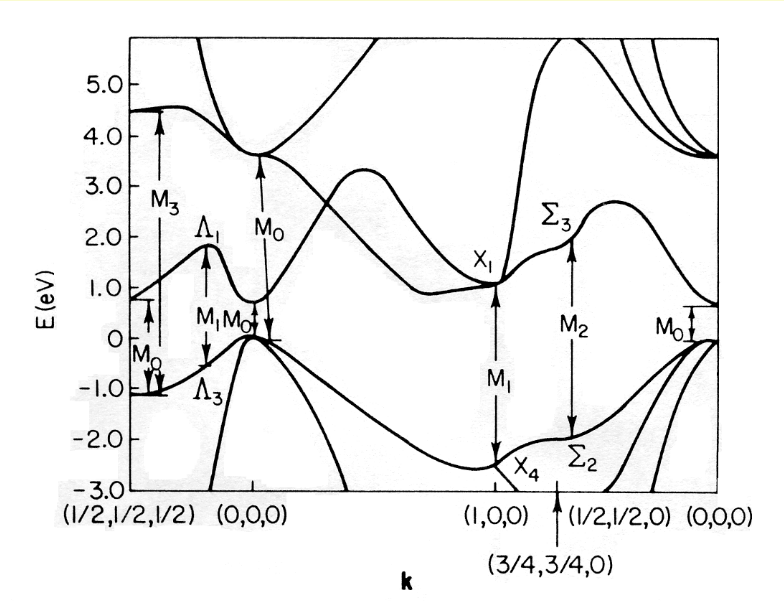
Intuitive explanation: Transition energy E_{fi} hardly changes with k

$\Rightarrow$ Many states contribute to given E_{fi} within small energy interval dE

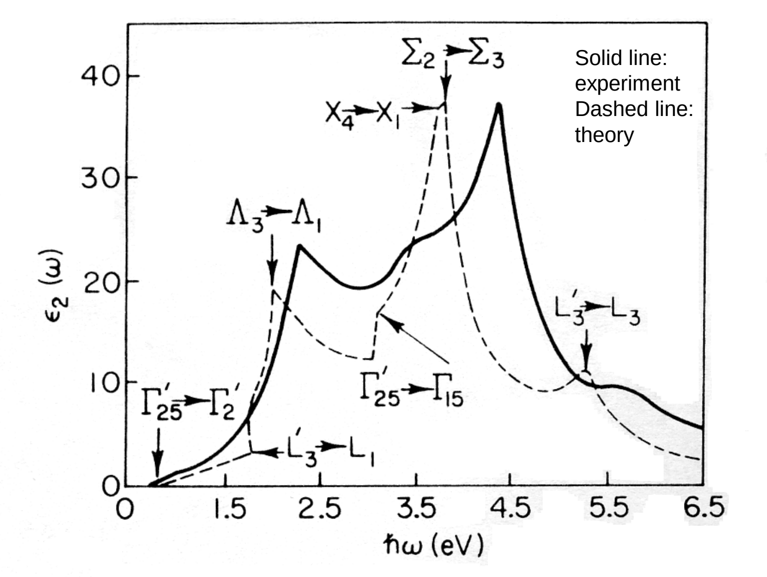
$\Rightarrow$ (Integrable) singularity in JDOS

Exploration of critical points in ε_2 (van Hove singularities) useful for band structure analysis

Example: Different types of critical points M_i in the band structure of Ge



J.C. Phillips et al., Proc. ICPS (1962)



Solid line: experiment
Dashed line: theory

D. Brust et al., PRL **9**, 94 (1962)

- Critical points of *single electronic* bands often at points of high symmetry in Brillouin zone (e.g., Γ, X)
- For *optical* bands *two possibilities:*

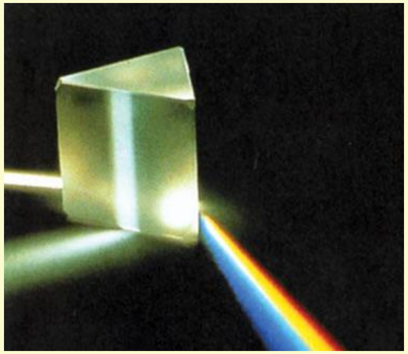
$\nabla_{\boldsymbol{k}} E(\boldsymbol{k}) = 0$ for *both* bands concerned (e.g., VB and CB) or

$\nabla_{\boldsymbol{k}} E_f(\boldsymbol{k}) - \nabla_{\boldsymbol{k}} E_i(\boldsymbol{k}) = 0$ but *gradient ≠ 0 for individual bands !*

Measurement of optical functions

For $\hbar\omega < E_g$: Semiconductor / insulator *transparent* $\Rightarrow$

Measurement of refractive index n is easy: *Transmission measurements*



- Measurement of refraction angle, Snell‘s law
- Fabry–Pérot interference fringes in transmission (or reflection) of thin films spectrum (see above)
- …

- For $\hbar\omega > E_g$: High absorption $\Rightarrow$ Very thin samples required
- Often layer on substrate (in many cases not transparent)

$\Rightarrow$ Use reflectivity spectrum

Potential problems that have to be taken into account:

Surface properties of sample can strongly influence spectra:

- Roughness ($\Rightarrow$ scattering)
- Oxidation ($\Rightarrow$ additional surface layer)
- Contamination

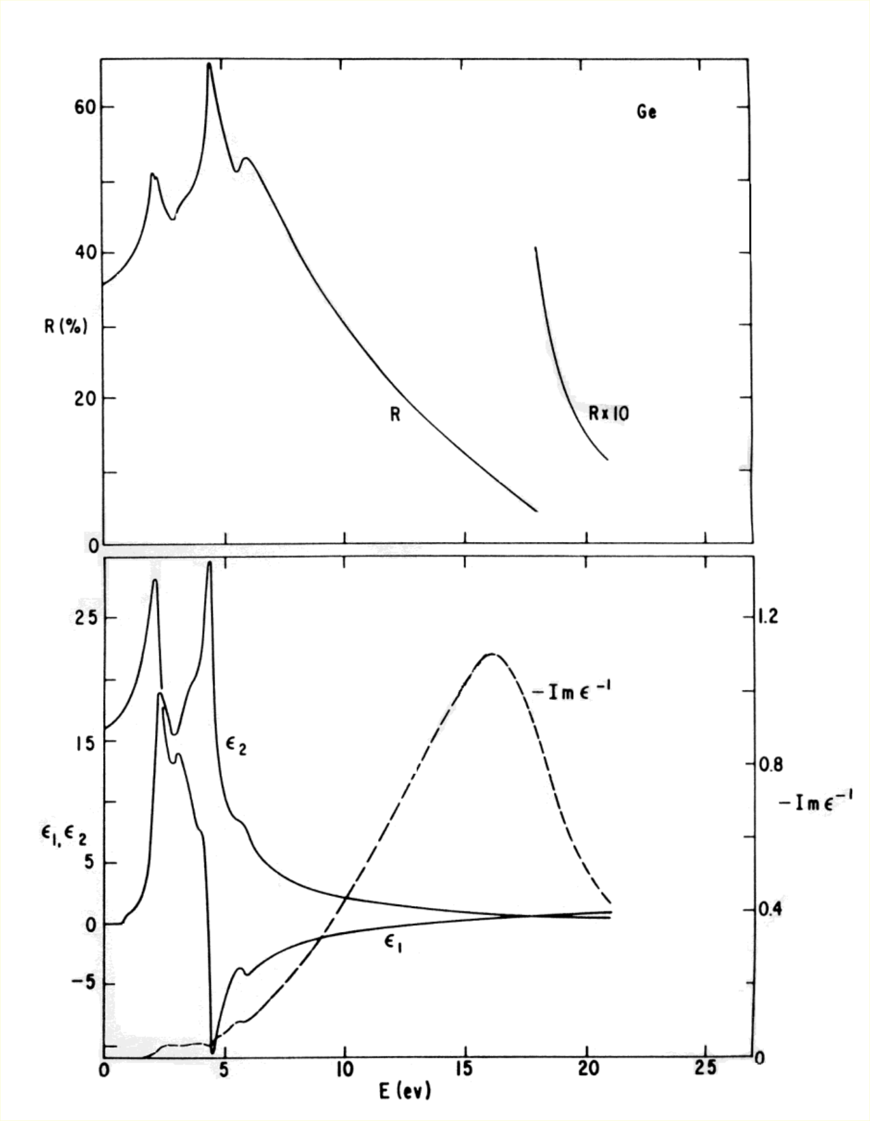
Methods:

1) *Reflectivity with perpendicular incidence over large spectral range*

- *Broad band light source:*
  Tungsten halogen lamp (NIR, VIS), globar (IR), gas discharge (UV, e.g., Xe), etc.
- *Spectral dispersion:*
  Grating (or prism) monochromator / FTIR spectrometer
- *Detection:*
  CCD camera or
  single channel detector
  (e.g., photodiode)

Measure reflectivity $R(\omega)$

$\Rightarrow$ $\alpha(\omega)$ or $\varepsilon(\omega)$ via
Kramers–Kronig relations



Example: Critical points of Ge

ε and corresponding

reflectivity spectrum R

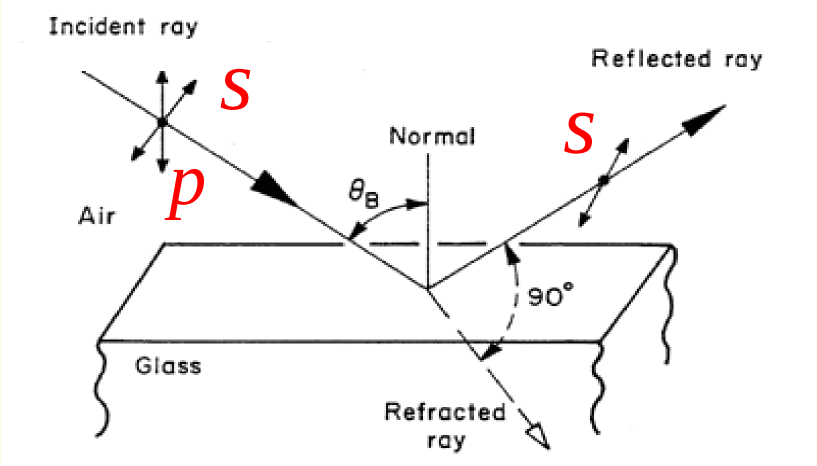
2) *Reflectivity with arbitrary incidence angle*

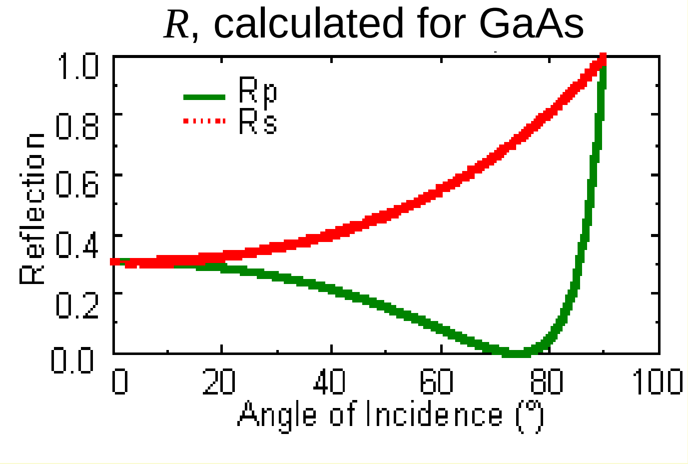
Polarization of incident light has to be considered!

Measure: $R_s = |r_s|^2$ Electric field perpendicular (german: *„**s**enkrecht“*) to plane of incidence

$R_p = |r_p|^2$ Electric field in plane of incidence

⇒ More complicated set-up than for 1)




R, calculated for GaAs

Advantage: More experimental data

⇒ Improved uniqueness of interpretation

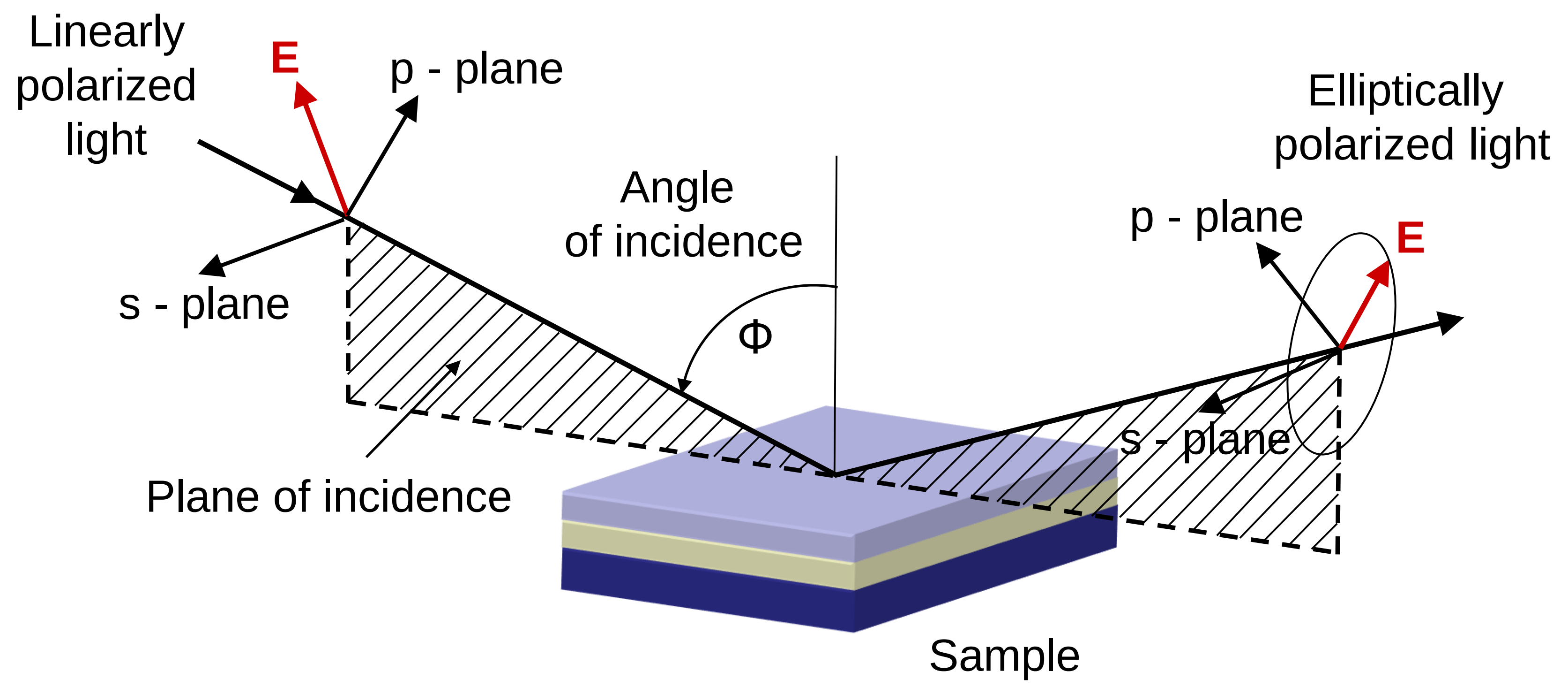
⇒ Higher accuracy possible, e.g., R_p must be zero for *Brewster angle* θ_B

3) *Ellipsometry: Preferred method to evaluate diel. fu. of multilayer structures*

Use light source with either circular or linear (neither *s* nor *p* !) polarization

⇒ Measure polarization state of reflected light for different angles of incidence on sample

(often measurements around Brewster angle to improve sensitivity, see above)



In general, reflected light is elliptically polarized

(different phase shifts for *s* and *p* polarization, e.g., for metals)

$$r_s = |r_s| \exp(i\delta_s) \quad ; \qquad r_p = |r_p| \exp(i\delta_p)$$

Measure ellipsometric parameters Ψ and Δ : $\rho = \dfrac{r_p}{r_s} = \tan\Psi \cdot e^{i\Delta}$

$$\tan\Psi = \frac{|r_p|}{|r_s|} \quad ; \qquad \Delta = \delta_p - \delta_s$$

Depend on photon energy, angle of incidence Φ, and layer properties:

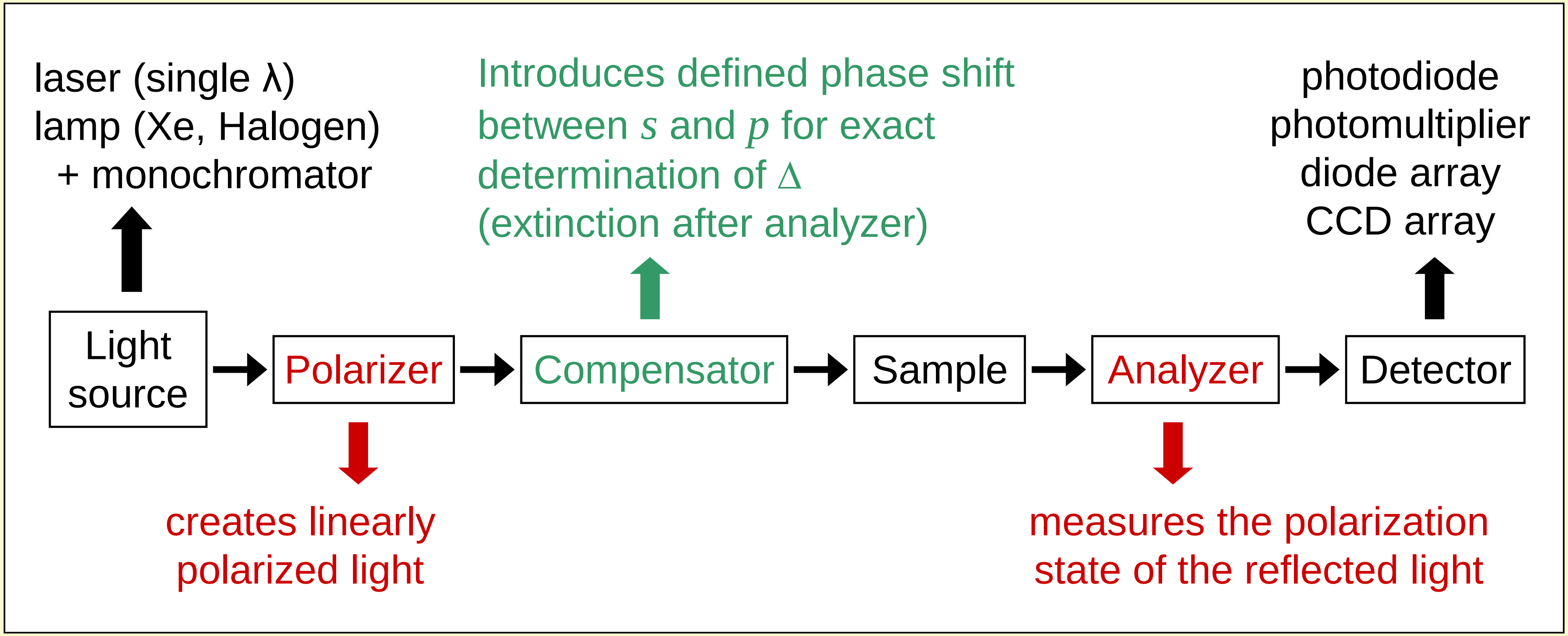
- Layer sequence
- Layer thicknesses and dielectric functions
- Surface / interface roughness etc.

⇒ Pseudodielectric function (multilayer structure as effective medium) :

$$\langle\varepsilon\rangle = \sin^2\phi + \sin^2\phi \tan^2\phi \left(\frac{1-\rho}{1+\rho}\right)^2$$

Dielectric function / thicknesses of *individual* layers through fit procedure based on (extended) Drude–Lorentz-type models and transfer matrix methods to treat multilayers

Experimental set-up


laser (single λ)
lamp (Xe, Halogen)
+ monochromator

Introduces defined phase shift between s and p for exact determination of Δ (extinction after analyzer)

photodiode
photomultiplier
diode array
CCD array

Light source → Polarizer → Compensator → Sample → Analyzer → Detector

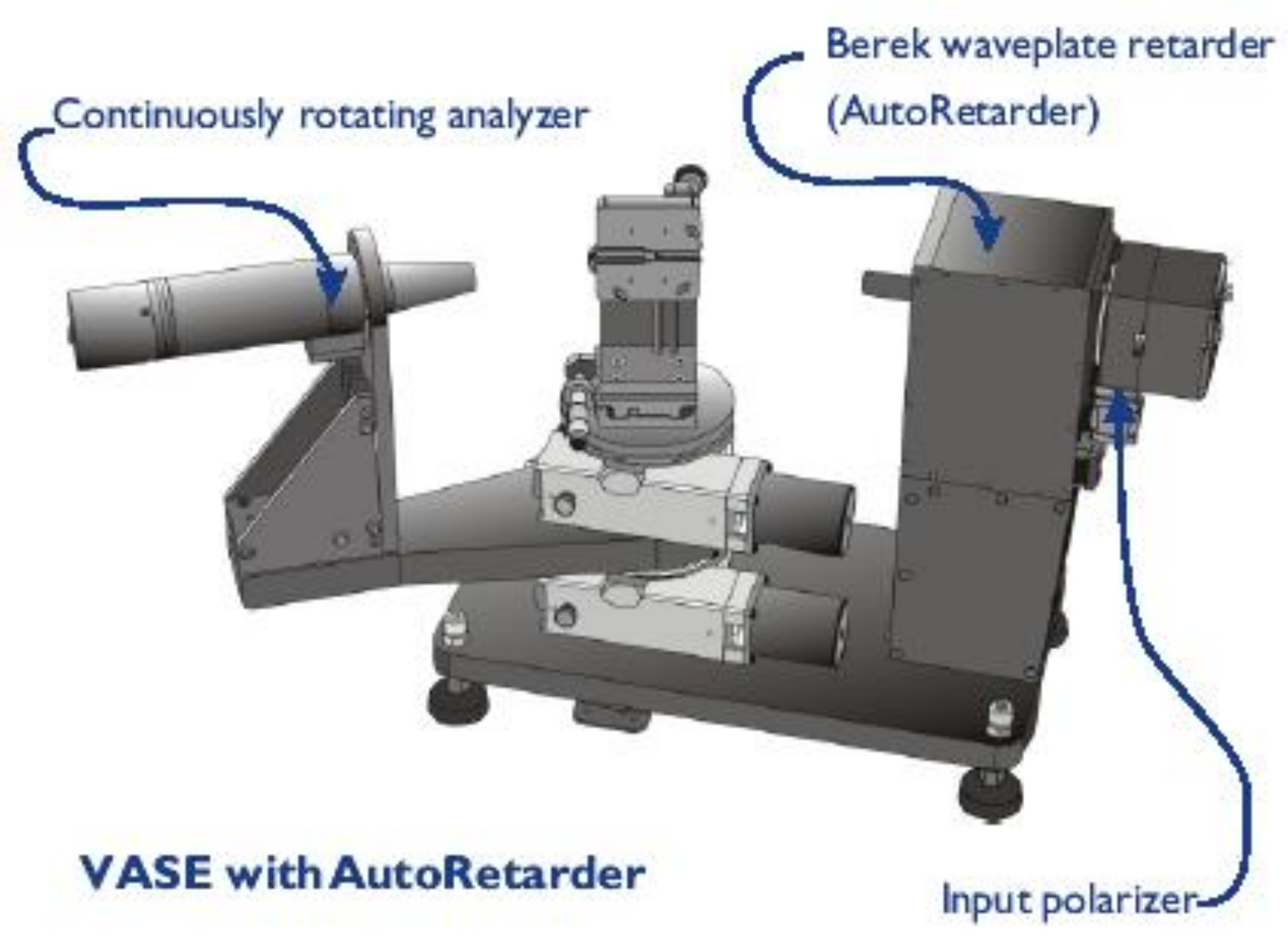
creates linearly polarized light

measures the polarization state of the reflected light

Light sources:

- *Single* λ : Simple characterization
  (e.g., thickness determination of epitaxial layer with known ε)
- Broad-band light source + monochromator: Spectroscopic Ellipsometry: Investigation of dielectric function, complicated multilayer systems

Experimental set-up



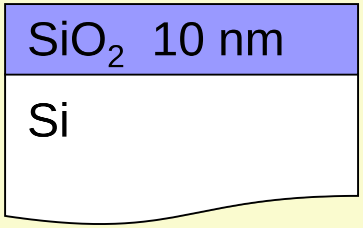
Advantages of ellipsometry:

Only ratios between s and p polarization measured ⇒

- Many (insufficiently well known) instrumental quantities (e.g., spectral intensity distribution of light source, spectral detector sensitivity, etc.) *cancel out !*
- No reference sample with known reflectivity for calibration needed ↔ conventional reflectivity
- For simple layers of a fixed material on a substrate with known properties, both ε and layer thicknesses can be determined simultaneously through a multi-sample fit with coupled parameters to the measured data.

⇒ High sensitivity and accuracy !

Example: Ellipsometry versus Reflectometry for oxide layer on Si



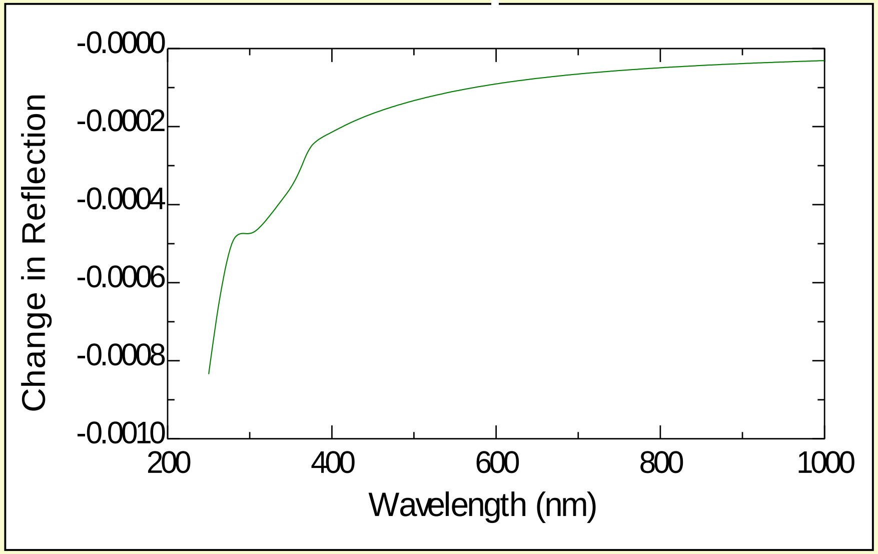
SiO_2 10 nm

Si

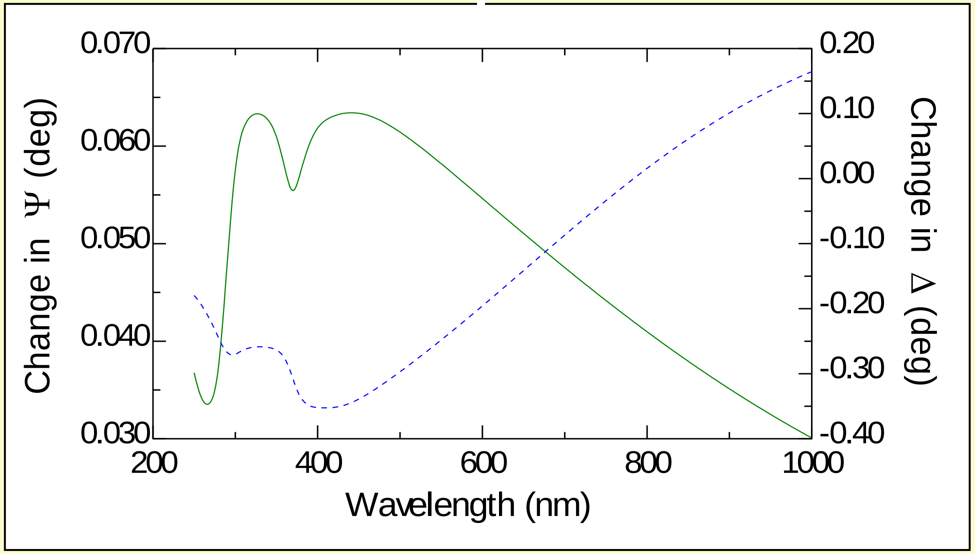
The thickness of SiO_2 layer changes by 0.1 nm

Calculated change in:

Reflection



Ellipsometry parameters



Sensitivity of typical

Reflectometer ~ 0.1%

Ellipsometer < 0.02°(ψ), 0.1°(Δ)

⇒ In contrast to reflectometry, even minimal changes can be detected !

4) *Modulation spectroscopy: Sensitive detection of critical points*

Consider joint density of states J / dielectric function ε:

- *Spectrally broad background* due to contributions of transitions ("oscillators") outside the energy range of interest (essentially at higher energies)

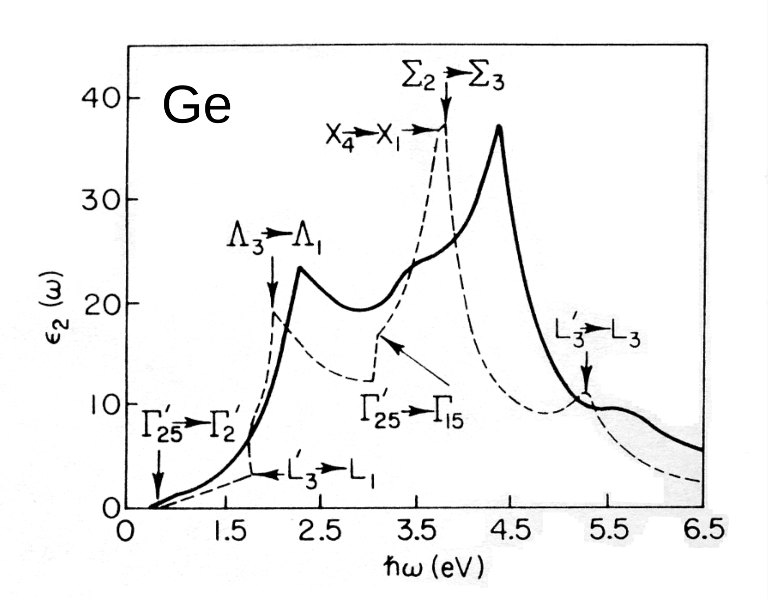
  ⇒ Not relevant for determination of critical points

- *Sharp features* due to transitions in relevant energy range, e.g., due to critical points / van Hove singularities in the band structure, quantized transitions in quantum structures, etc.

Idea: Measure ***derivative*** *of* J / ε !

⇒ Strong features at critical points etc.

⇒ Suppression of uninteresting background



D. Brust et al., PRL **9**, 94 (1962)

Approach:

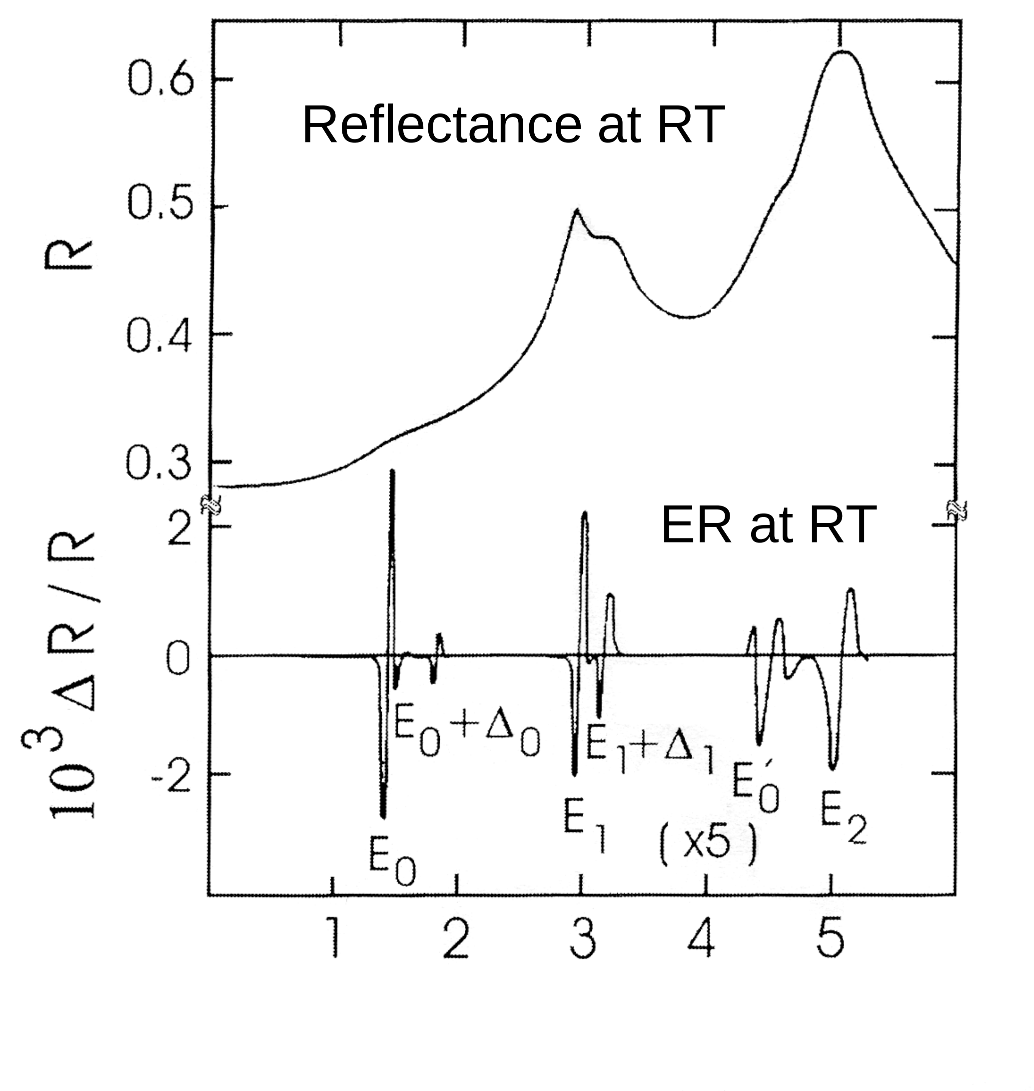
- Modulate transition energy / oscillator strength / damping periodically
- Measure change in optical function, e.g., reflectivity, phase-synchronously

Using *lock-in techniques*, relative changes as low as ~10^{-5} can be measured!

Common techniques:

- *Electroreflectance (ER):*
  Modulation due to applied AC electric field,
  e.g., (quantum-confined) Stark and Franz–Keldysh effect
- *Photoreflectance (PR):*
  Photo-generated charge carriers lead to screening of built-in electric fields (e.g., bend bending at surface due to Fermi level pinning)
  $\Rightarrow$ Results similar to ER ($\rightarrow$ later)
- *Piezoreflectance:*
  Strain / pressure-induced band structure variations
- *Thermoreflectance:*
  Thermally induced band structure modifications
- …

Example: Electroreflectance of GaAs at room-temperature



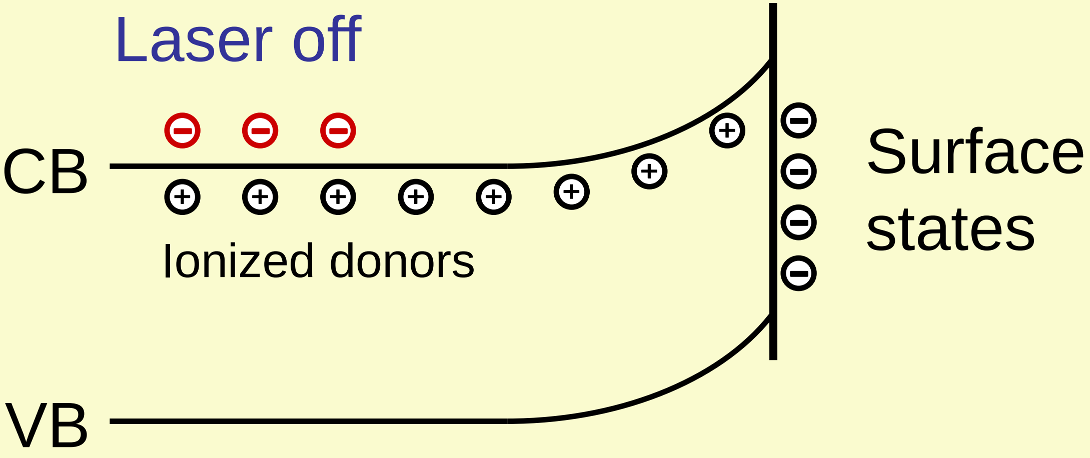
⇒ Sharp, derivative-like features at different critical points despite broadening at room-temperature

⇒ Much more pronounced features than in corresponding reflectance spectrum

Photoreflectance spectroscopy: Modulation mechanism

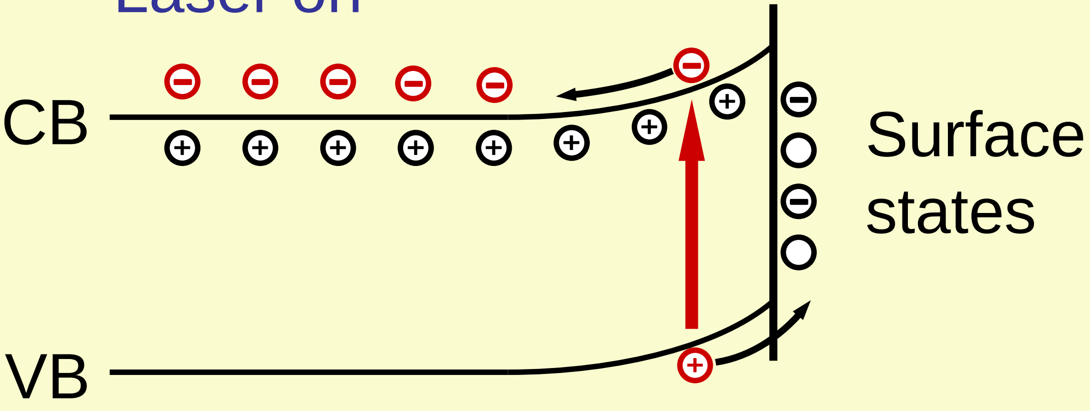
Band bending due to Fermi level pinning at surface states.
⇒ Built-in electric field

Laser off



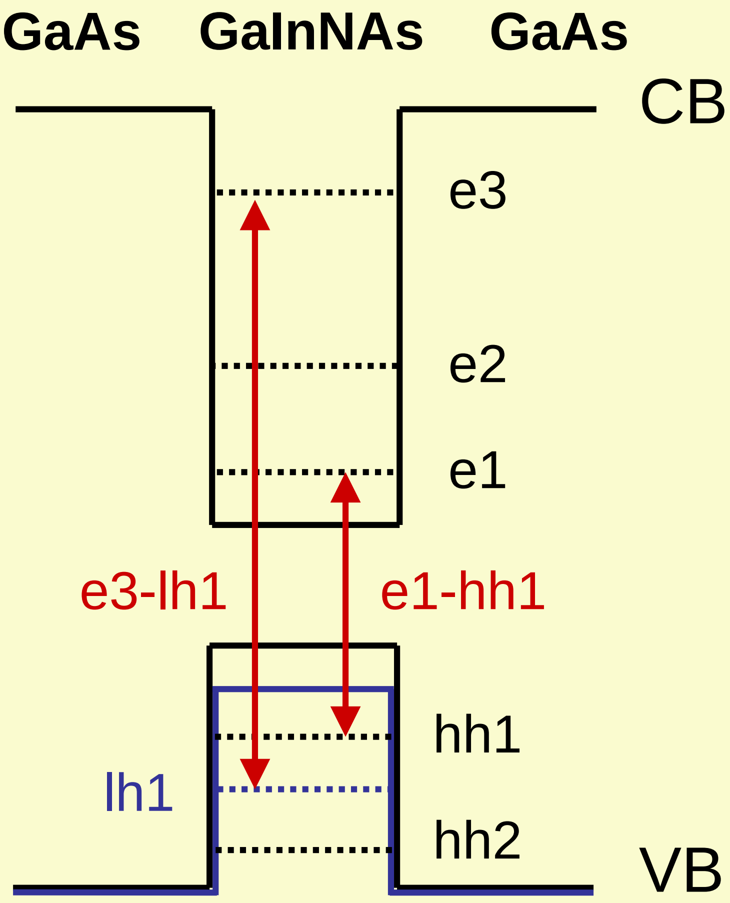
Electron-hole pairs generated by the modulating laser lead to a screening of the built-in electric field.
⇒ Electromodulation

Laser on

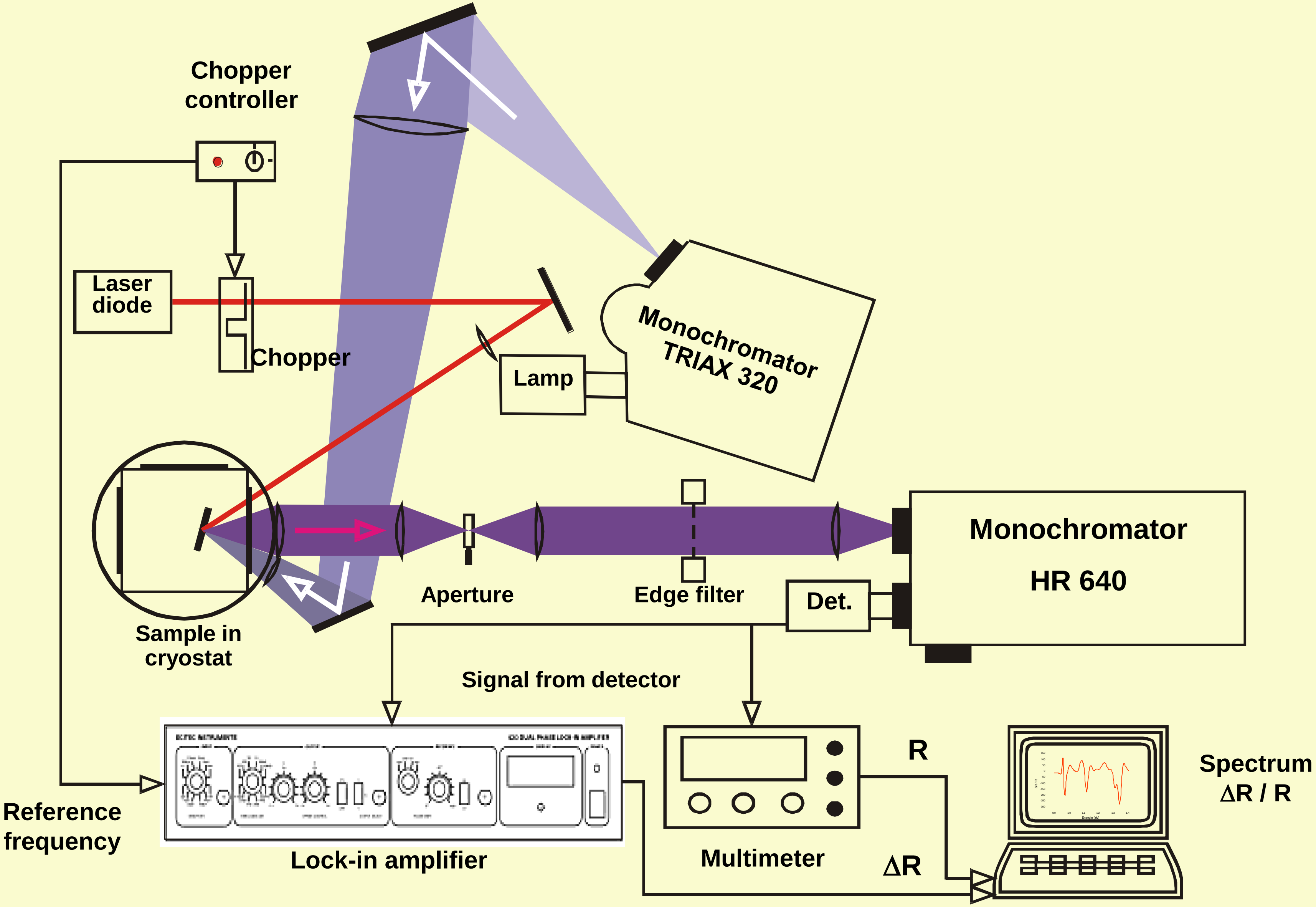


Example 2: Electronic transitions in $Ga_{1-x}In_xAs_{0.983}N_{0.017}$ (6.2 nm) QWs

Measure transitions to investigate band alignment of quantum well etc.

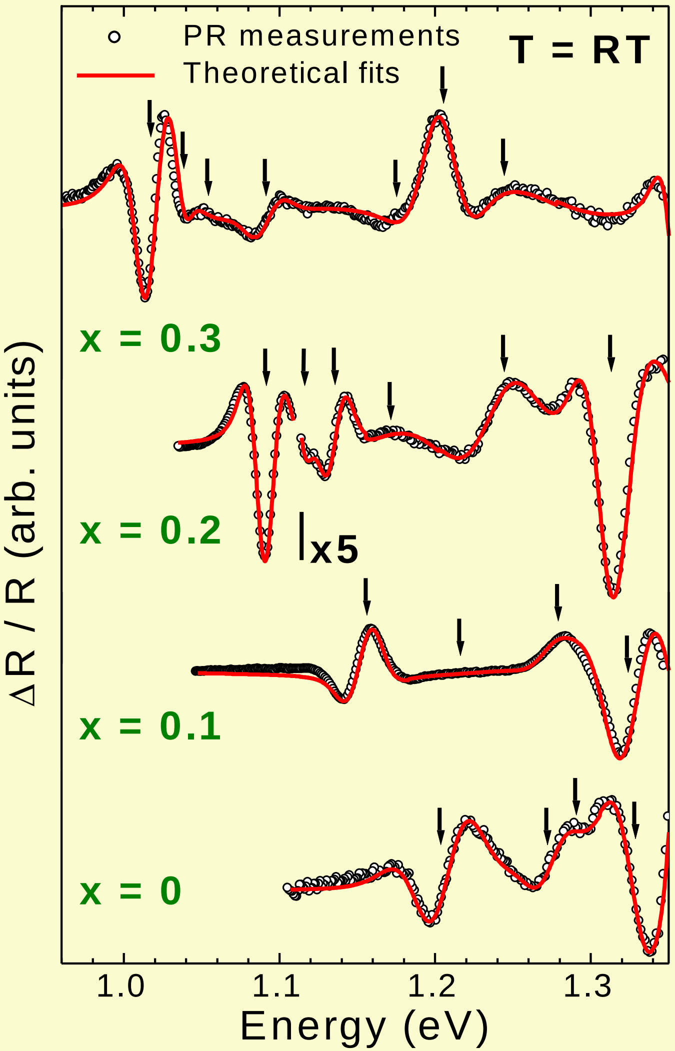


Photoreflectance: set-up



- Expected line shapes for different transitions well-known
- Practically no influence of broad background due to other contributions to ε

$\Rightarrow$ Exact transition energies from multi-oscillator fit to measured spectra



- Arrows correspond to individual oscillators (electronic transitions)
- Even very weak ("quasi-forbidden") transitions can be seen
- Good quantitative agreement between measurement and fit
- Band alignment and CB structure can be deduced from transition energies

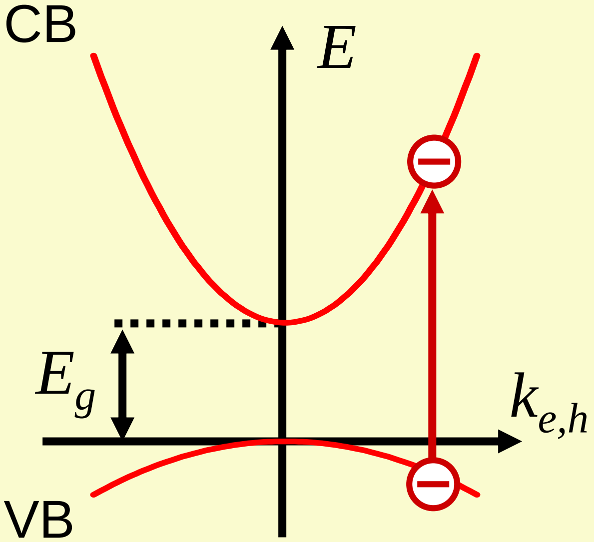
M. Hetterich *et al.*, J. Appl. Phys. **94**, 1810 (2003).

Optical Properties of Solids Near the Bandgap: Excitons

Initial simplifying assumptions about band structure:

- Isotropic, parabolic and non-degenerate (apart from spin) bands
- CB maximum and VB minimum at Γ point ($k = 0$)

$$E_{\mathrm{CB}} = \frac{\hbar^2 k^2}{2m_e} + E_g \qquad E_{\mathrm{VB}} = -\frac{\hbar^2 k^2}{2m_h}$$



Optical transition via photon absorption

Electron picture:

Excitation of electron from VB to CB

- k conserved, since $k_{\mathrm{Photon}} << k_e, k_h$
- spin of excited electron conserved ($\Delta s = 0$ in electric dipole transition)
- Negative charge in CB, total charge remaining in VB positive

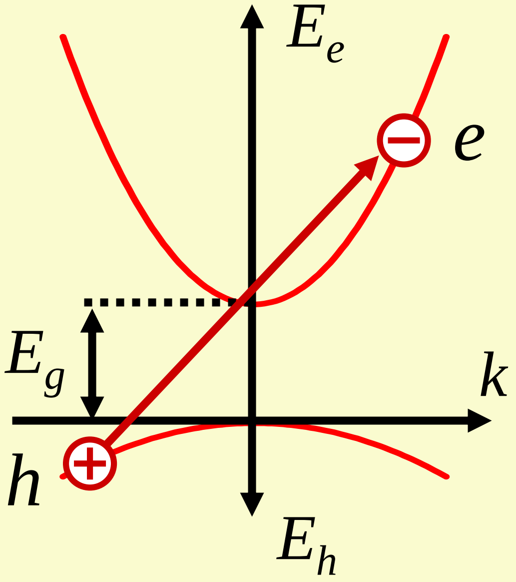
Introduce hole as quasi-particle to describe (excited *many-particle*) VB state

Hole picture: Generation of electron–hole pair

Properties of fully occupied VB before transition:

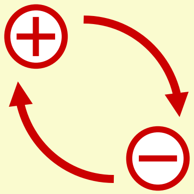
- neutral
- total k = 0
- total spin = 0
- *negative* dispersion

Hole is *missing* electron ⇒ *h and e–h pair properties:*



- Hole is *positively charged* quasi-particle with *positive dispersion (effective mass)*
- $k_h = -k_e \Rightarrow$ Total e–h pair $K = k_e + k_h = 0$
- spin(h) = – spin(e)
  ⇒ Total e–h pair spin = 0

Coulomb interaction between *negative CB electron* and *positive VB hole*



⇒ Formation of excitons: *bound electron–hole pair states*
(similar to hydrogen atom or positronium)

Photon energies required to excite excitonic states:

$$E_{\text{photon}} = E_g - Ry^* \cdot \frac{1}{n_B^2}$$

E_g : Band gap at $k = 0$

Ry^* : Excitonic Rydberg energy (exciton binding energy)

n_B^2 : Principal quantum number: $n_B = 1, 2, \ldots$

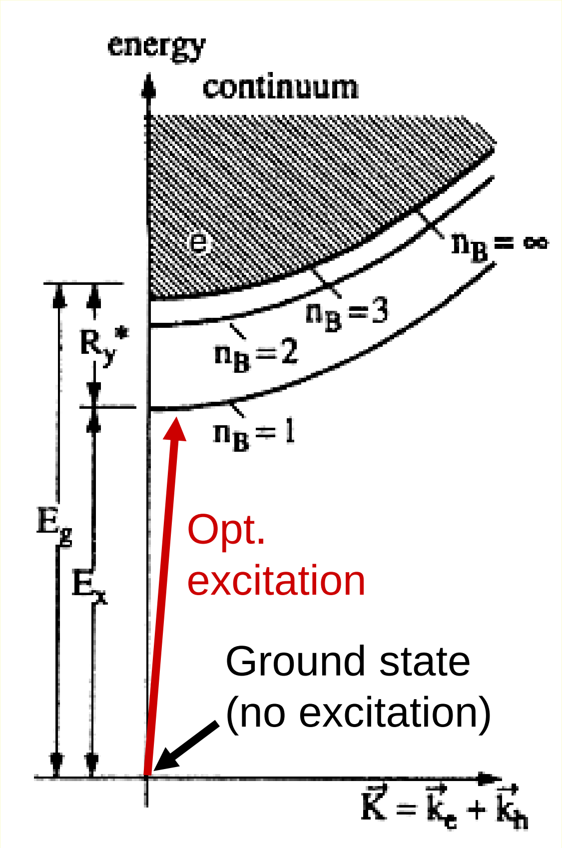
Compared to E_g, required photon energy reduced by exciton binding energy

⇒ Excitons are the lowest electronic excitations
in an ideal semiconductor / insulator at $T = 0$

⇒ Discrete states ($n_B = 1, 2, \ldots$) in spectra for excitation below band gap

⇒ Exciton continuum (unbound electron–hole pairs) above E_g

Exciton dispersion



Opt. excitation

Ground state (no excitation)

After: C. Klingshirn, Semiconductor Optics

Bound e–h pair can *move* through solid

Total exciton mass (translation): $M = m_e + m_h$

⇒ Kinetic energy due to center of mass movement

$$E_{\text{kin}} = \frac{\hbar^2 \boldsymbol{K}^2}{2M}$$

⇒ exciton dispersion relation

$$E_x(n_B, \boldsymbol{K}) = E_g - Ry^* \cdot \frac{1}{n_B^2} + \frac{\hbar^2 \boldsymbol{K}^2}{2M}$$

Important note:

Excitons are *two-particle* ($e + h$) excitations (or even multi-particle, depending on approx. used). Therefore, it is *incorrect* to draw them into a conventional (one-particle approx.) band diagram (CB + VB), as is often done in textbooks !!!

Only *singlet* excitons (total spin zero) with $K \sim 0$ couple to the light field

⇒ *Discrete peaks below* E_g in spectra (see disc. above + below for further details)

Exciton binding energy

For hydrogen atom: $Ry = \frac{m_0 e^4}{2(4\pi\varepsilon_0\hbar)^2} = 13.6\,\mathrm{eV}$

In solid :

$$m_0 \rightarrow \mu = \frac{m_e m_h}{m_e + m_h}$$

Reduced effective mass

(can be << m_0 for semiconductors

⇒ lowers binding energy)

$$\varepsilon_0 \rightarrow \varepsilon_0 \varepsilon_1$$

Coulomb interaction between electron and hole partly screened due to dielectric constant ε_1

- Covalent semiconductors: ~ ε_s
- Polar semiconductors: Polaron correction ($\varepsilon_1 > \varepsilon_s$) since Ry^* close to phonon resonance

⇒ Binding energy decreases

Typical values: 0.5 meV $\leq Ry^* \leq$ 100 meV (in alkali halides several 100 meV)

Exciton binding energies for different materials

Material	Ry^* (meV)	E_g (eV) at $T = 0$ K
CdS	28	2.582
CdSe	15	1.840
GaAs	4.2	1.520
InP	4.0	1.42
InSb	0.4	0.24

- Binding energy often lower than thermal energy at room temperature (~ 25 meV)

  ⇒ Often thermal dissociation at room temperature

  ⇒ Excitonic effects more pronounced at low temperatures

- Ry^* grows with E_g :

  $\boldsymbol{k} \cdot \boldsymbol{p}$ theory:
  Smaller interaction between CB and VB ⇒ larger masses ⇒ stronger binding

  Intuitive explanation:
  If electrons are more strongly bound to individual atoms / ions

  ⇒ *Larger band gap*, but also

  ⇒ *Higher effective mass* (due to lower tunneling probability) and
  smaller ε_1 (since polarizability is low),
  leading to increased Ry^*

Importance of excitonic effects increases with bandgap of material

Exciton Bohr radius

In analogy with the hydrogen atom for n_B = 1:

$$a_B = \frac{4\pi\varepsilon_0\varepsilon_1\hbar^2}{\mu e^2} = 0.529\ \text{Å} \cdot \frac{m_0\varepsilon_1}{\mu} \quad \Rightarrow\ 5\ \text{Å} \le a_B \le 200\ \text{Å}$$

⇒ Two types of excitons:

Wannier excitons:

- Large Bohr radius and low binding energy
- Often found in semiconductors
- Electron and hole move over many unit cells (in GaAs ~10000)
  ⇒ Effective mass approximation applicable

Frenkel excitons:

- Small Bohr radius comparable with crystal lattice constant and high binding energy
- Often found in insulators, e.g., alkali halides, and in organic materials
- Effective mass approximation *not* applicable

Quantum mechanics: Exciton wavefunction

In general: expansion in one-particle Bloch functions for electron and hole:

$$\Psi_x = \sum_{\boldsymbol{k}_e,\boldsymbol{k}_h} A(\boldsymbol{k}_e,\boldsymbol{k}_h)\left[\psi_e(\boldsymbol{r}_e,\boldsymbol{k}_e)\cdot\psi_h(\boldsymbol{r}_h,\boldsymbol{k}_h)\right]$$

Here: Electron and hole wavefunctions chosen as wavepackets localized at certain sites $\boldsymbol{r}$: Wannier functions

$$w_{e,h} = \sum_{\boldsymbol{k}} a_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r})$$

Expansion coefficients only significantly different from zero if

$|\boldsymbol{k}_e|, |\boldsymbol{k}_h| \leq 1/a_B$ since electron and hole are “localized” around the excitonic center of mass within a_B

$$\Rightarrow \Psi_x = \Omega^{-1/2}\phi^{n,\boldsymbol{K}}(\boldsymbol{r}_e,\boldsymbol{r}_h)\cdot w_e(\boldsymbol{r}_e)w_h(\boldsymbol{r}_h)$$

The envelope function ϕ results from the Schrödinger equation

$$\left\{-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{\hbar^2}{2m_h}\nabla_h^2-\frac{e^2}{4\pi\varepsilon_0\varepsilon_1\left|\boldsymbol{r}_e-\boldsymbol{r}_h\right|}\right\}\phi^{n,\boldsymbol{K}}\left(\boldsymbol{r}_e,\boldsymbol{r}_h\right)=E'\phi^{n,\boldsymbol{K}}\left(\boldsymbol{r}_e,\boldsymbol{r}_h\right)$$

with $E'=E-E_g$

Coordinate transformation: $\boldsymbol{r}=\boldsymbol{r}_e-\boldsymbol{r}_h$ *Relative coordinate*

$$\boldsymbol{R}=\frac{m_e\boldsymbol{r}_e+m_h\boldsymbol{r}_h}{m_e+m_h}$$ *Center of mass coordinate*

$$\left\{-\frac{\hbar^2}{2\mu}\nabla_{\boldsymbol{r}}^2-\frac{\hbar^2}{2M}\nabla_{\boldsymbol{R}}^2-\frac{e^2}{4\pi\varepsilon_0\varepsilon_1\boldsymbol{r}}\right\}\phi^{n,\boldsymbol{K}}\left(\boldsymbol{r},\boldsymbol{R}\right)=E'\phi^{n,\boldsymbol{K}}\left(\boldsymbol{r},\boldsymbol{R}\right)$$

Separation (product ansatz) $\Rightarrow$

Eigenfunctions: $\phi^{n,\boldsymbol{K}}\left(\boldsymbol{r},\boldsymbol{R}\right)=\frac{1}{\Omega^{1/2}}e^{i\boldsymbol{K}\cdot\boldsymbol{R}}\psi^{n}\left(\boldsymbol{r}\right)$; $\boldsymbol{K}=\boldsymbol{k}_e+\boldsymbol{k}_h$

↑

Center of mass movement

$\psi^{n}(\boldsymbol{r})$ is the solution of

$$\left\{-\frac{\hbar^{2}}{2\mu}\nabla_{\boldsymbol{r}}^{2}-\frac{e^{2}}{4\pi\varepsilon_{0}\varepsilon_{1}\boldsymbol{r}}\right\}\psi^{n}(\boldsymbol{r})=E_{n}'\psi^{n}(\boldsymbol{r})$$

with $E_{n}'=-Ry^{*}\cdot\dfrac{1}{n_{B}^{2}}$

and $E'=E'_{n}+\dfrac{\hbar^{2}K^{2}}{2M}$

$\psi^{n}(\boldsymbol{r})$ is a modified hydrogen wavefunction $(m_0 \rightarrow \mu,\ \varepsilon_0 \rightarrow \varepsilon_0\varepsilon_1)$

E.g., ground state wavefunction: $\psi^{1}(\boldsymbol{r})=\dfrac{1}{\left(\pi a_{B}^{3}\right)^{1/2}}e^{-r/a_{B}}$

Which excitonic states couple to the light field ?

Photon momentum small

$\Rightarrow$ Only excitons with K ~ 0 couple to the light field (see above)

Further selection rules from group theory (see later)

Excitonic wavefunction: $\Psi_x \sim w_e \cdot w_h \cdot \phi^{n,l,m}$

Symmetry of total wavefunction: $\Gamma_x = \Gamma_e \otimes \Gamma_h \otimes \Gamma_{env}$

Transition matrix element ≠ 0 if direct product with symmetry of dipole operator contains Γ_1

$\Rightarrow$ Only excitons with *s-like envelope functions* (symmetry Γ_1) couple to light field

Example: Materials with wurtzite crystal structure (C_{6V})

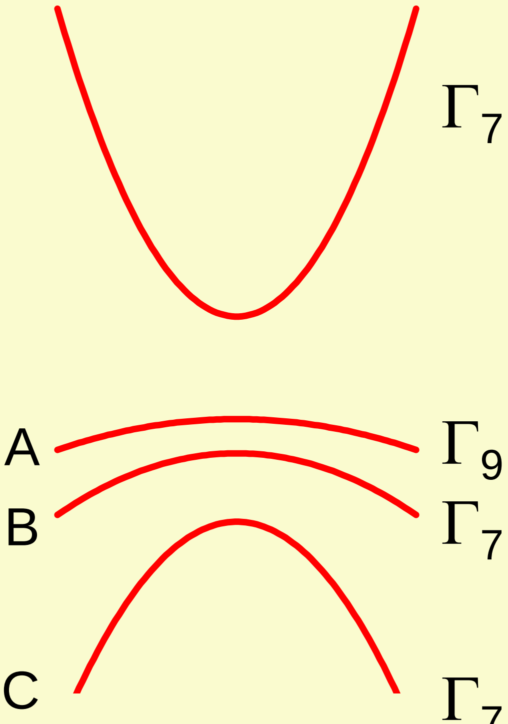
Hexagonal crystal structure with symmetry axis $\boldsymbol{c}$, e.g., CdS, ZnO, GaN, …

Single 2x degenerate CB, derived from atomic s-states

$L = 0$, $s = \pm 1/2 \Rightarrow J = 1/2$, $M_J = \pm 1/2$

Three 2x degenerate VBs, since derived from atomic p-states:

$$L = 1, s = \pm 1/2 \Rightarrow \begin{cases} J = 3/2,\ M_J = \pm 3/2, \pm 1/2 & \text{(2 x 2x)} \\ J = 1/2,\ M_J = \pm 1/2 & \text{(2x)} \end{cases}$$



For A exciton (Γ_9 VB) in 1s state

(i.e., $n_B = 1$ and s-like envelope function)

$$\Gamma_x = \Gamma_7 \otimes \Gamma_9 \otimes \Gamma_1 = \Gamma_5 \oplus \Gamma_6$$

$\Rightarrow$ Two types of excitons: Γ_5, Γ_6

Γ_5: Total spin = 0: “singlet”

Γ_6: Total spin = 1: “triplet”

Coupling to light field:

$\boldsymbol{E} \parallel \boldsymbol{c}:\quad \Gamma_5 \otimes \Gamma_1 = \Gamma_5$ no

$\boldsymbol{E} \perp \boldsymbol{c}:\quad \Gamma_5 \otimes \Gamma_5 = \underline{\Gamma_1} \oplus \Gamma_2 \oplus \Gamma_6$ yes

Couples to light field for $\boldsymbol{E} \perp \boldsymbol{c}$:

Singlet ist “bright” exciton !

$\Gamma_6 \otimes \Gamma_1 = \Gamma_6$ no

$\Gamma_6 \otimes \Gamma_5 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$ no

Does not couple to light field

Triplett is “dark” exciton !

For B and C (Γ_7 VB) 1s excitons: $\Gamma_7 \otimes \Gamma_7 \otimes \Gamma_1 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5$

	Γ_1	Γ_2	Γ_5
	Singlet (m_L= 0)	Triplet	Singlet (m_L= ±1)
Couples for	$\boldsymbol{E} \parallel \boldsymbol{c}$		$\boldsymbol{E} \perp \boldsymbol{c}$

- Result consistent with intuitive discussion for electron–hole pairs above, that only excitons with total spin zero can be created by light
- The occurrence of “bright” singlet and “dark” triplet states is a general feature of excitons in any material
- Singlet and triplet states are energetically split by the spin-dependent exchange interaction between electron and hole (~100 µeV)
- Coupling to light field for wurtzite structure:
  B and C exciton: *always*, A exciton: *only for* $\boldsymbol{E} \perp \boldsymbol{c}$ → later

Oscillator strength of excitonic transitions

Strength of optical transition given by:

$$\left|\left\langle f\right|H_{\text{exciton-Photon}}\left|0\right\rangle\right|^2 \sim \left|\phi^{n,l,m}(\boldsymbol{r}=0)\right|^2\left|H_{\text{dipole}}^{\text{VB-CB}}\right|^2 \sim \frac{1}{n_B^3}$$

Final excitonic state

Vacuum state (no exc.)

Probability to find electron and hole at same site

Dipole transition matrix element between VB and CB Bloch functions (~ const.)

- Proportional to overlap of electron and hole wavefunction
- Only ≠ 0 for s excitons ($\phi^{n,l,m}(\boldsymbol{r}=0)=0$ for p, d, f, etc. states)
- $\left|\phi^{n,l,m}(\boldsymbol{r}=0)\right|^2 \sim 1/n_B^3 \Rightarrow$ Strongest transition: 1s exciton

Exciton polaritons

For the exciton dispersion we had: $E_x(n_B, \boldsymbol{K}) = E_g - Ry^* \cdot \frac{1}{n_B^2} + \frac{\hbar^2 \boldsymbol{K}^2}{2M}$

$\Rightarrow$ For $n_B = 1$ (strongest transition, others analogously):

$$\omega_{n_B=1} = \omega_0 + \frac{\hbar \boldsymbol{K}^2}{2M} \quad \text{with} \quad \hbar\omega_0 = E_g - Ry^*$$

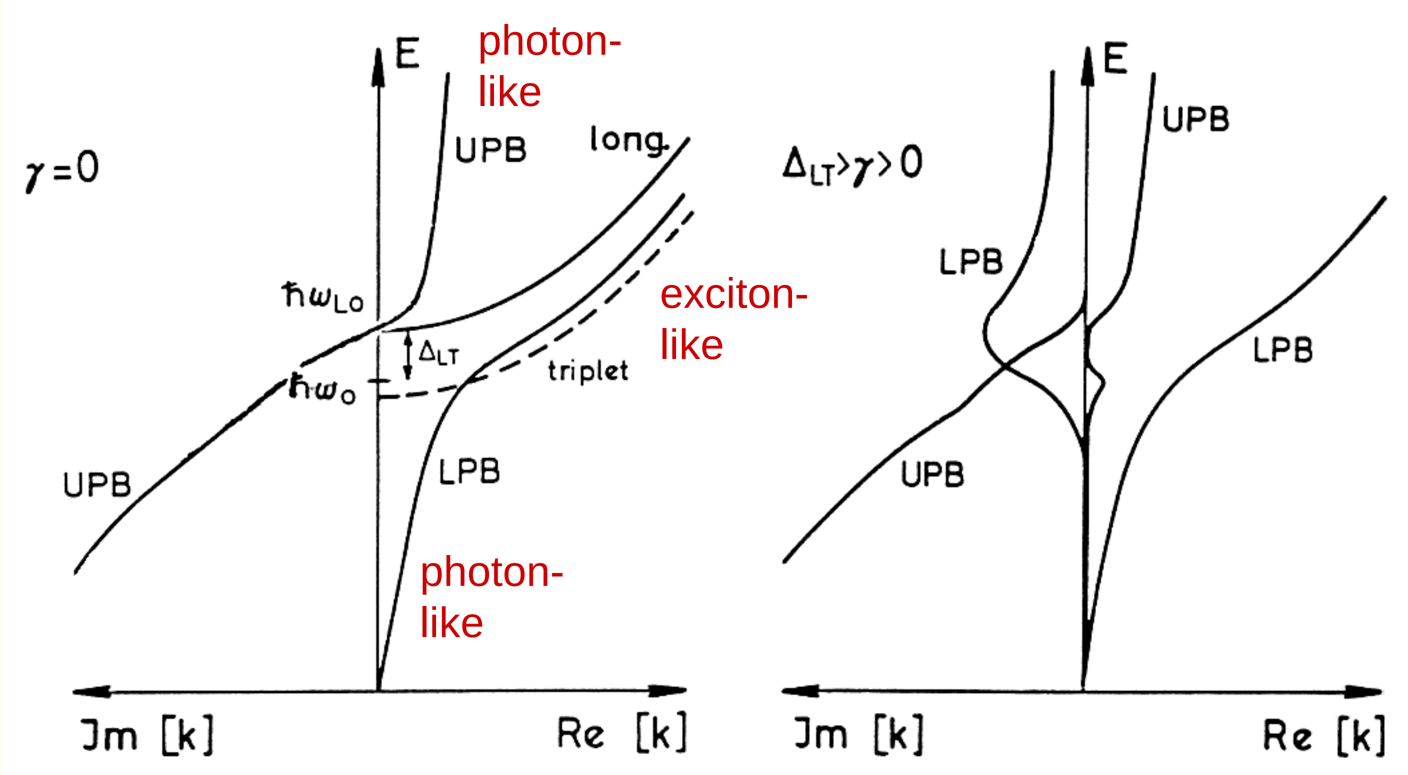
Dielectric function for 1s exciton: $\varepsilon(\omega, \boldsymbol{K}) = \varepsilon_b \left[1 + \frac{f}{\left(\omega_0 + \frac{\hbar \boldsymbol{K}^2}{2M}\right)^2 - \omega^2 - i\omega\gamma} \right]$

$\Rightarrow$ Excitons are oscillators with strong spatial dispersion !
(like phonon polaritons, but more important)

Approximation (neglect terms ~ k^4) : $\left(\omega_0 + \frac{\hbar \boldsymbol{K}^2}{2M}\right)^2 \approx \omega_0^2 + \frac{\hbar \boldsymbol{K}^2 \omega_0}{M}$

⇒ Exciton polariton dispersion

$$\frac{c^2\boldsymbol{K}^2}{\omega^2} = \varepsilon(\omega,\boldsymbol{K}) = \varepsilon_b\left[1+\frac{f}{\omega_0^2+\frac{\hbar\boldsymbol{K}^2\omega_0}{M}-\omega^2-i\omega\gamma}\right]$$



After:
C. Klingshirn

LPB : purely real

UPB : purely real for $\omega > \omega_{L0}$

LPB and UPB *over whole spectral region*

LPB : damped around and above resonance

UPB: small real K for $\omega < \omega_{L0}$,
but strongly damped

Consequences of spatial dispersion:

ω_T, ω_L are $\boldsymbol{K}$ - dependent! (In reality also $f = f(\boldsymbol{K})$)

For $\gamma = 0$:

$$\varepsilon(\omega_\mathrm{T}, \boldsymbol{K}) = \infty \;\Rightarrow\; \omega_\mathrm{T}^2(\boldsymbol{K}) = \left(\omega_0 + \frac{\hbar \boldsymbol{K}^2}{2M}\right)^2$$

$$\varepsilon(\omega_\mathrm{L}, \boldsymbol{K}) = 0 \;\Rightarrow\; \omega_\mathrm{L}^2(\boldsymbol{K}) = f + \left(\omega_0 + \frac{\hbar \boldsymbol{K}^2}{2M}\right)^2$$

⇒ No longer forbidden gap between ω_T and ω_L

⇒ Propagating mode(s) for each frequency ω

⇒ Reflectivity strongly reduced ($0.2 < R_\mathrm{max} < 0.6$), even for $\gamma = 0$.
No strict “Reststrahlen” band

⇒ For $\omega > \omega_{\mathrm{L}0}$: 2 propagating modes: LPB, UPB (with damping always)

→ Additional boundary conditions (“ABC”) required to derive intensity of individual modes, reflectivity, transmittivity etc.

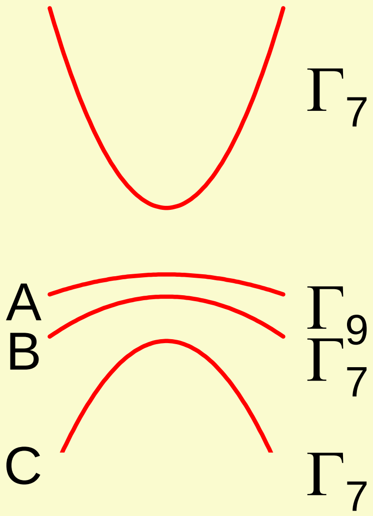
Linear spectroscopy of excitons: Reflectivity

Example: Low-temperature (T ~ 4 K) reflectivity of CdS (wurtzite crystal structure)

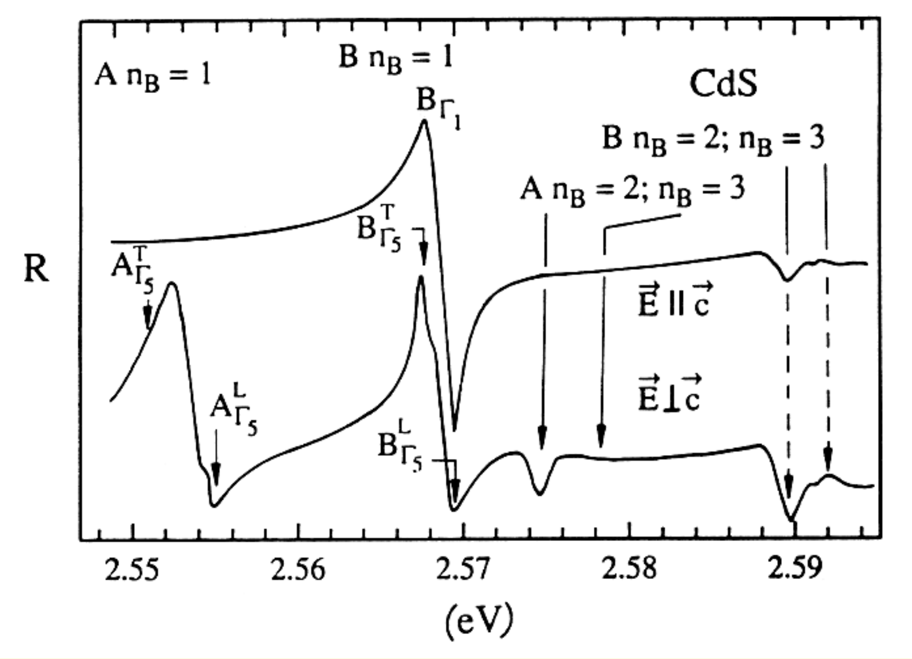
- Resonances due to A, B and C excitons at low temperatures (hardly visible at room-temperature due to thermal ionization of excitons)
- Can be modeled through Lorentz oscillators → energetic pos. of exciton transitions
- No pronounced "Reststrahlen" band

As expected (see discussion above):

- Strongest feature due to 1s exciton ($n_B = 1$), 2s and 3s excitons also visible
- Polarization dependence: A exciton couples only for $\boldsymbol{E} \perp \boldsymbol{c}$

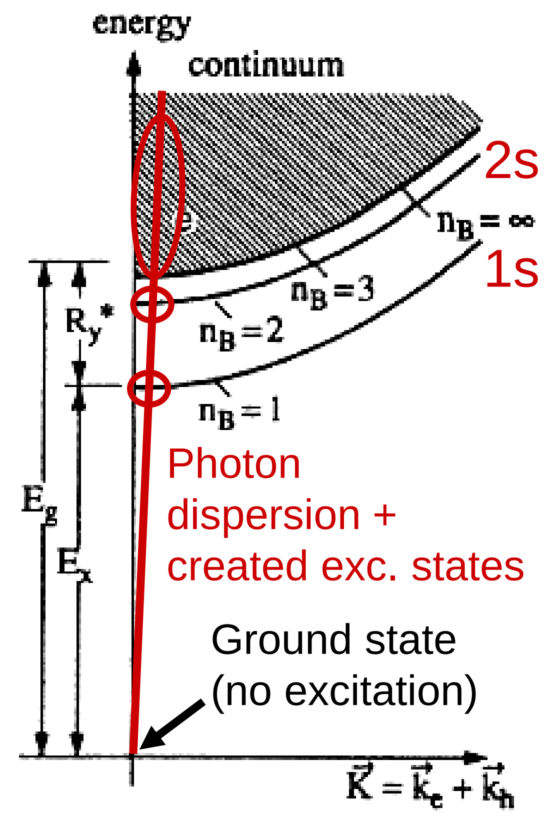


T: transverse
L: longitudinal



Linear spectroscopy of excitons: Absorption

Often: “Weak coupling”, i.e., polariton picture not required

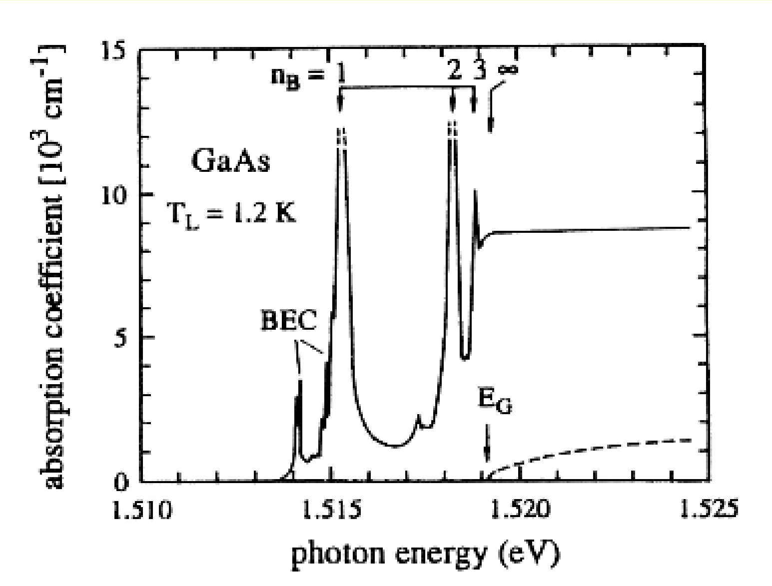


2s

1s

Photon dispersion + created exc. states

Ground state (no excitation)



BEC:
Bound exciton complexes (defects, impurities)

Low T : Sharp excitonic abs. peaks (1s, 2s, …) *below* E_g

RT : Broadened + weak: thermal exciton ionization

Absorption *above* E_g :

Osc. strength

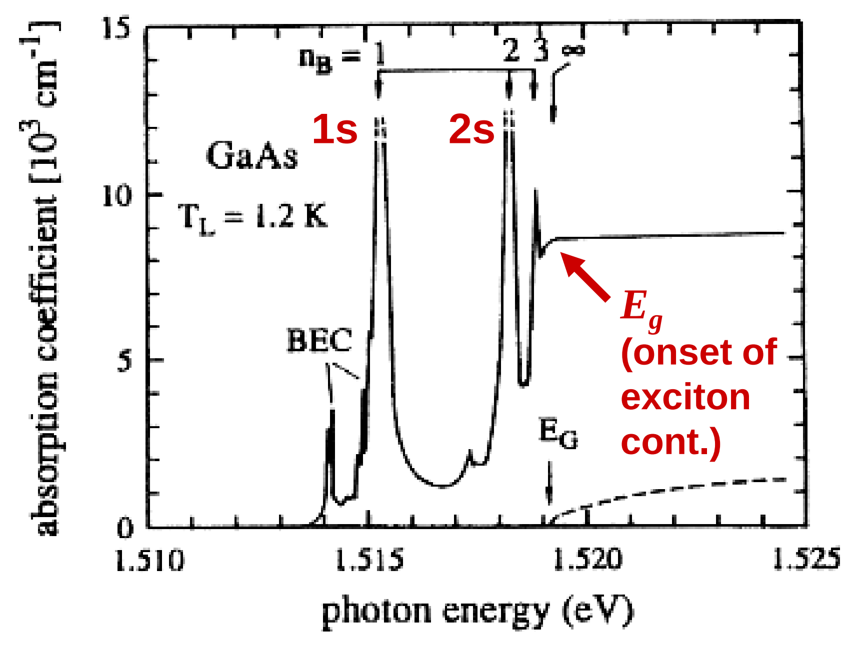
- One-particle model (no excitonic effects): $\alpha \sim f_{VB-CB}\sqrt{\hbar\omega - E_g}$ ← *Square root: Density of states*
- With excitons: Sommerfeld / Coulomb enhancement of α above E_g

Reason: Despite states unbound, position of electron and hole *correlated*

$\Rightarrow$ Higher absorption due to increased wavefunction overlap

$\Rightarrow$ $\alpha \sim$ *const.* near E_g (energy dependence of Sommerfeld enhancement)

Example: Low-temperature absorption of GaAs



- Strongest peak: 1s exciton ($n_B = 1$)
- Higher s excitons also visible, but weaker, as expected
- *Zincblende* crystal structure

  ⇒ No A and B exciton, instead two energetically degenerate (“heavy-hole” and “light-hole”) excitons

Determination of exciton binding energy

Binding energy ~ $1 / n_B^2 \Rightarrow$

$$E_x(n_B=1) - E_x(n_B=2) = Ry^*\cdot\frac{1}{1} - Ry^*\cdot\frac{1}{4} = \frac{3}{4}Ry^* = 3.15 \pm 0.15\,\mathrm{meV}$$

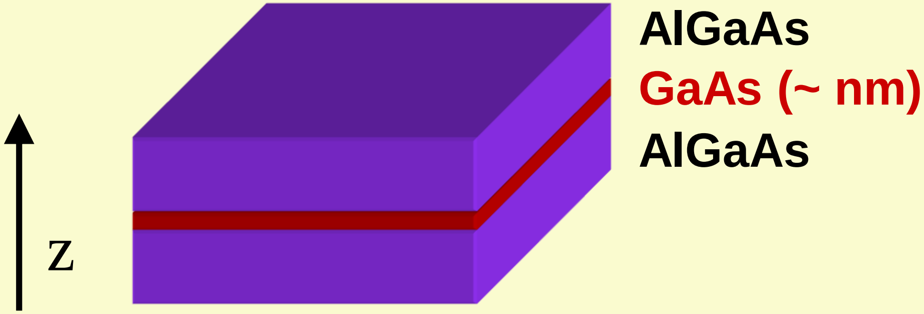
$$\Rightarrow\ Ry^* = 4.2\,\mathrm{meV}$$

⇒ *Wannier* exciton, as expected for typical semiconductor (E_g ~ 1.5 eV)

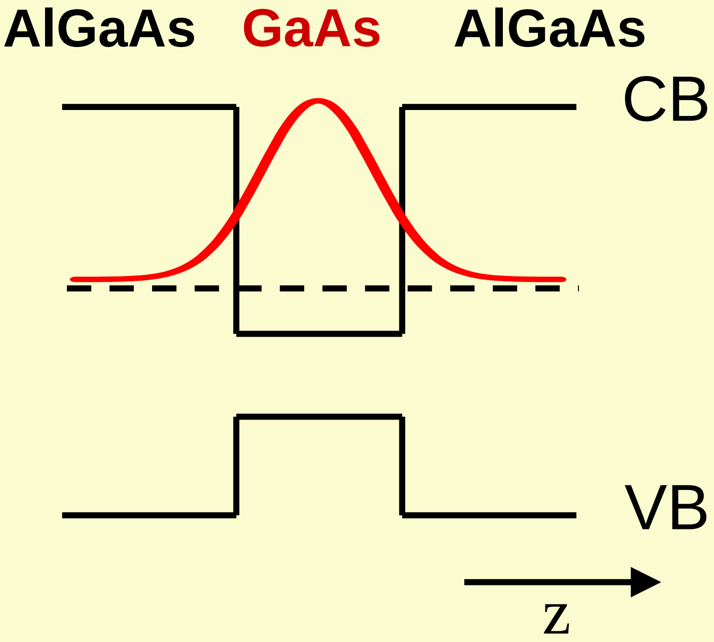
Influence of dimensionality on exciton binding energy

So far: Excitons in three dimensions

Now: Quantum well structures



Thin (~ nm) semiconductor layer, embedded in matrix material with larger band gap



Spatial band structure

⇒ Electrons and holes confined in thin quantum well layer (formation of quantized states: “Particle in a box”)

⇒ Electron and hole movement restricted to *two-dimensional* plane (quantum well layer)

Schrödinger equation for exciton in two dimensions

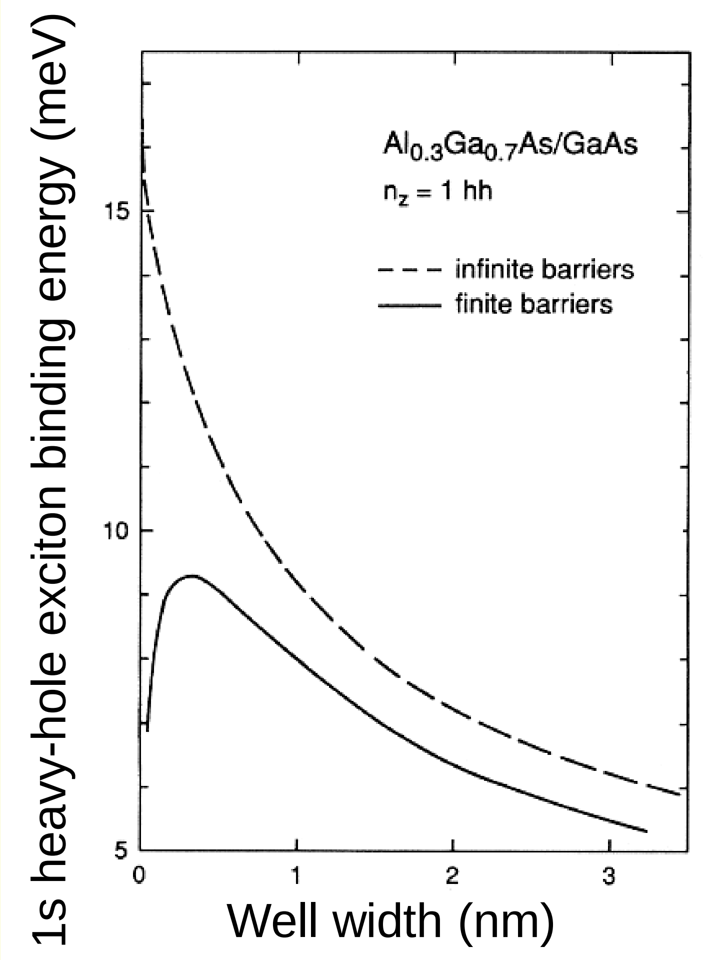
⇒ Exciton binding energy: $E_n' = -Ry^*(3D) \cdot \frac{1}{\left(n_B - \frac{1}{2}\right)^2}$

⇒ For 1s exciton: *Binding energy enhanced by a factor of 4 !*

⇒ Excitonic effects clearly visible even at *room-temperature !*

For real quantum well structures:

Finite well thickness and *finite* confinement energy ⇒



With decreasing well width:

- Increasing exciton binding energy (transition from 3D to 2D case)
- No true 2D exciton

  ⇒ 1s binding energy always < 4 $Ry^*(3D)$
- If quantum well layer extremely narrow:

  Exciton wavefunction penetrates into matrix material

  ⇒ 3D case recovered

  ⇒ Exciton binding energy decreases

After: C. Klingshirn, Semiconductor Optics

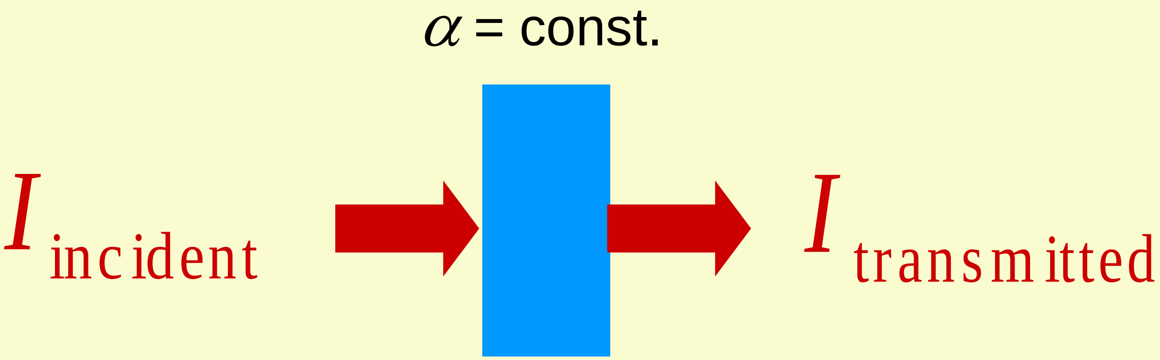
Nonlinear optics and high-excitation effects

So far:

Optical properties (ε, absorption etc.) of solid: Constant material parameters

⇒ Response of material to light field proportional to incident intensity

Example: Absorption

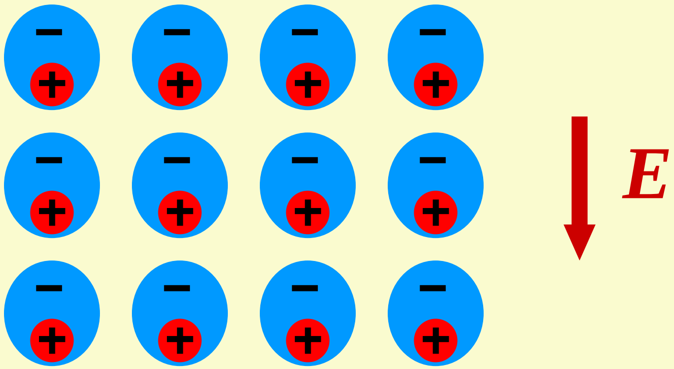


$I_{\text{transmitted}} \sim I_{\text{incident}}$ ⇒ “Linear” optics

In reality:

Response of material to incident light field is nonlinear!

In particular for polarization $\boldsymbol{P}$ induced by incident electromagnetic field:



$$\boldsymbol{P} = \varepsilon_0 \chi(\omega) \boldsymbol{E}$$

is only valid for *weak* electric fields $\boldsymbol{E}$

(Note that χ can be a tensor (represented by a matrix), i.e., $\boldsymbol{P}$ is not necessarily parallel to $\boldsymbol{E}$.)

In reality: $\boldsymbol{P}(\boldsymbol{E})$ is nonlinear $\Rightarrow$ Expansion in Taylor series:

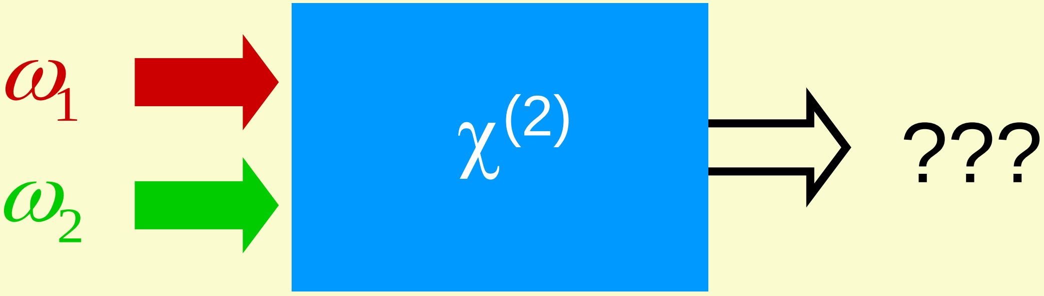
Initial simplifying assumption: Scalar P and E $\Rightarrow$

$$\frac{1}{\varepsilon_0} P(E) = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots$$

Result of nonlinear terms: Qualitatively new effects!

Example: Effects of $\chi^{(2)}$ in a "nonlinear crystal"

Two incident light fields with different frequencies



For a given position:

$$E_1(t) \sim \cos(\omega_1 t) \sim e^{i\omega_1 t} + e^{-i\omega_1 t}$$

$$E_2(t) \sim \cos(\omega_2 t) \sim e^{i\omega_2 t} + e^{-i\omega_2 t}$$

$$\frac{1}{\varepsilon_0} P(E) = \chi^{(1)} E + \chi^{(2)} E^2$$

$\chi^{(1)}$: *Nothing special:*

- Optical properties *independent of light intensity*
- Usual *linear optics* for ω_1 and ω_2 *independently!*

$\chi^{(2)}$: $P \sim E^2 \sim (E_1 + E_2)^2 \quad \Rightarrow$

$$P \sim E^2 \sim \left[\left(e^{i\omega_1 t} + e^{-i\omega_1 t}\right) + \left(e^{i\omega_2 t} + e^{-i\omega_2 t}\right)\right]^2$$

$$\Rightarrow \quad P \sim \underbrace{\left(e^{i\omega_1 t} + e^{-i\omega_1 t}\right)^2}_{P_{\mathrm{I}}(\omega_1)} + \underbrace{\left(e^{i\omega_2 t} + e^{-i\omega_2 t}\right)^2}_{P_{\mathrm{I}}(\omega_2)} + 2\underbrace{\left(e^{i\omega_1 t} + e^{-i\omega_1 t}\right)\left(e^{i\omega_2 t} + e^{-i\omega_2 t}\right)}_{P_{\mathrm{II}}(\omega_1,\omega_2)}$$

$$\underline{P_{\mathrm{I}}(\omega_{1,2})} = \left(e^{i\omega_{1,2} t} + e^{-i\omega_{1,2} t}\right)^2 = e^{i2\omega_{1,2} t} + e^{-i2\omega_{1,2} t} + 2 = \underline{2\cos 2\omega_{1,2} t + 2}$$

$> 0 \Rightarrow$ “Rectification”

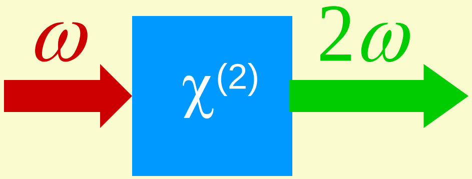
- Light induces constant contribution to polarization
  (i.e., a voltage drop over the crystal)
  Small effect, since $\chi^{(2)}$ usually small
- *Frequency doubling:* Generation of light with $2\omega_{1,2}$
  $\Rightarrow$ *“Second-Harmonic Generation”*

Application:

Used in laser systems to convert light to shorter wavelengths, that are difficult to generate directly

Example:

Nd:YAG laser:
λ = 1064 nm (near IR)



Green output
λ = 532 nm

- Usually $\chi^{(2)}$ is *small*
  - $\Rightarrow$ For efficient frequency up-conversion high intensities required
  - $\Rightarrow$ Pulsed laser sources
- Third-harmonic (3ω) generation etc. also possible

$$P_{\mathrm{II}}(\omega_1,\omega_2) \sim \left(e^{i\omega_1 t} + e^{-i\omega_1 t}\right)\left(e^{i\omega_2 t} + e^{-i\omega_2 t}\right)$$

Mixed term: Contains *both* ω_1 *and* ω_2

⇒ Nonlinearity induces *interaction* between different light waves

⇒ $\chi(\omega) \rightarrow \chi(\omega_1,\ \omega_2)$

$$P_{\mathrm{II}}(\omega_1,\omega_2) \sim e^{i(\omega_1+\omega_2)t} + e^{-i(\omega_1+\omega_2)t} + e^{i(\omega_1-\omega_2)t} + e^{-i(\omega_1-\omega_2)t}$$

$$\Rightarrow \underline{P_{\mathrm{II}}(\omega_1,\omega_2)} \sim \cos\underline{(\omega_1+\omega_2)}t + \cos\underline{(\omega_1-\omega_2)}t$$

⇒ **Sum frequency** generation (**up-conversion**) and
difference frequency generation (**down-conversion**)

Second-harmonic generation:

⇒ Special case for $\omega_1 = \omega_2$ (“interaction of light wave with itself”)

⇒ Sum frequency = $2\omega_{1,2}$, difference frequency = 0

Application of up-conversion:
(Time-resolved) detection of weak signals at wavelengths, where no suitable detectors exist

Conclusion:

Interaction of two waves with frequencies ω_1, ω_2
in second-order nonlinear optical medium

$\Rightarrow$ Generation of sum frequency $\omega_3 = \omega_1 + \omega_2$ and diff. frequency $\omega_4 = \omega_1 - \omega_2$

However, once generated, also interaction between, e.g., ω_3 and

- $\omega_1 \;\Rightarrow\; \omega_2 = \omega_3 - \omega_1$
- $\omega_2 \;\Rightarrow\; \omega_1 = \omega_3 - \omega_2$

$\Rightarrow$ *Mutual coupling*, where each pair of waves interacts
and contributes to third wave

$\Rightarrow$ “Three-wave mixing” (incoming and outgoing waves)

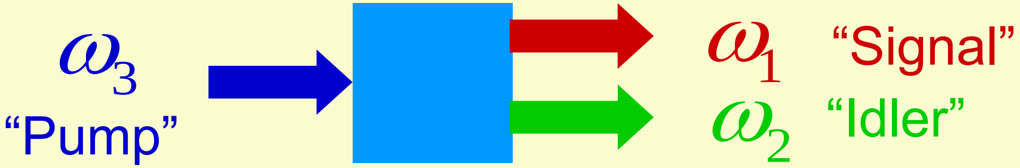
Classical view of three-wave mixing

Light field itself *modulates optical properties*
(Lorentz oscillator parameters) of solid

$P = \varepsilon_0 \chi(E) E$ $\Rightarrow$ Three-wave mixing: *Parametric* interaction

Further important parametric processes

Optical parametric generation (OPG, reversed sum frequency generation):


ω_3 "Pump"

ω_1 "Signal"

ω_2 "Idler"

High-energy photons "split" into two low-energy photons

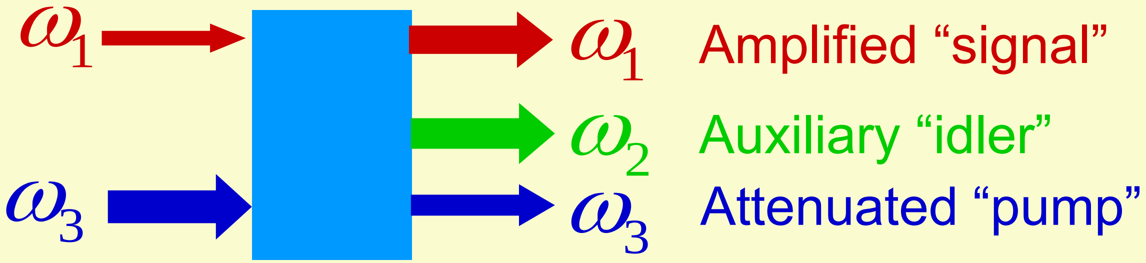
$$\hbar\omega_3 = \hbar\omega_1 + \hbar\omega_2$$

Restrictions due to phase matching (see below)

Optical parametric amplifier (OPA): Like OPG but amplification of existing ω_1

"Signal"

"Pump"
provides energy
to amplify ω_1
Rest: "idler"


ω_1 → ω_1 Amplified "signal"

ω_2 Auxiliary "idler"

ω_3 → ω_3 Attenuated "pump"

With proper feedback (resonator): Optical Parametric Oscillator (OPO)

- Only pump wave supplied
- Initial signal by OPG

Applications of OPAs and OPOs:

- Coherent light amplification
- Tunable light sources at frequencies, where no suitable lasers are available (e.g, in the UV)

General formalism

- $\boldsymbol{P}$ and $\boldsymbol{E}$ are *vectors* with components P_m and E_n
- The $\boldsymbol{\chi}^{(i)}$ are *tensors* of rank $i+1$ with components $\chi^{(i)}{}_{mn\ldots}$
- $\boldsymbol{P}$ and $\boldsymbol{\chi}^{(i)}$ are written as *complex* quantities, as in linear optics

$$
\begin{aligned}
\Rightarrow \frac{1}{\varepsilon_0} P_m(\omega_i) = & \sum_{n} \chi^{(1)}_{mn}(\omega_j) E_n(\omega_j) \delta_{\omega_i,\omega_j} + \\
& + \sum_{n,p} \chi^{(2)}_{mnp}(\omega_j,\omega_k) E_n(\omega_j) E_p(\omega_k) \delta_{\omega_i,\omega_j+\omega_k} \\
& + \sum_{n,p,q} \chi^{(3)}_{mnpq}(\omega_j,\omega_k,\omega_l) E_n(\omega_j) E_p(\omega_k) E_q(\omega_l) \delta_{\omega_i,\omega_j+\omega_k+\omega_l} \\
& + \ldots
\end{aligned}
$$

Real part of $\boldsymbol{\chi}^{(i)}$: *Passive* processes

("linear" *dispersion* due to $\boldsymbol{\chi}^{(1)}$, sum / difference frequency generation, four-wave mixing, intensity-dependent refractive index etc.)

Imaginary part of $\boldsymbol{\chi}^{(i)}$: *Active* processes

("linear" *absorption* due to $\boldsymbol{\chi}^{(1)}$, nonlinear absorption, e.g., two photon absorption and saturable absorption, see below)

When can nonlinear processes occur ???

- *Typically, nonlinear effects are small*

$\Rightarrow$ Use materials with high $\chi^{(n)}$, $n = 2, 3, \ldots$ (see below for examples)

$\Rightarrow P \sim E^n$ ($n = 2, 3, \ldots$) $\Rightarrow$ Use high intensities such as (pulsed) lasers

E.g., for frequency doubling: $P \sim E^2 \Rightarrow I_{out} \sim I_{in}^2$ (make it clear to you why!)

- *Frequency matching (often = energy conservation, but not always!)*

E.g., for three-wave mixing (see above): $(\hbar)\omega_3 = (\hbar)\omega_1 + (\hbar)\omega_2$

$\Rightarrow$ Factor $\delta_{\omega_i,\omega_j+\omega_k+\ldots}$ in general formula for $P_m(\omega_i)$

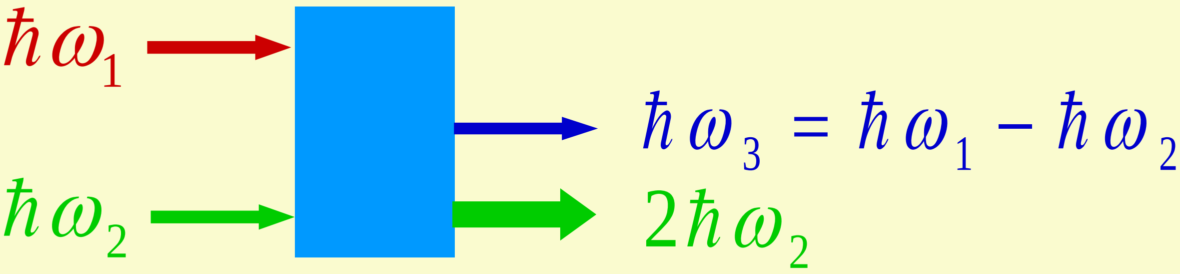
$$\delta_{\omega_i,\omega_j} = \begin{cases} 1 & \text{for } \omega_i = \omega_j \\ 0 & \text{for } \omega_i \neq \omega_j \end{cases}$$

Can often be interpreted as (photon) energy conservation

But: $\omega_{j,k,\ldots}$ can also be *negative!*

Example: Generation of photons with *difference* frequency: $\omega_3 = \omega_1 - \omega_2$

How about energy conservation in the photon picture … ???



For each photon generated at frequency ω_3, one photon at frequency ω_1 is destroyed but one *additional* photon at ω_2 is *created !!!*

⇒ Parametric amplification process (see above)

Note: This is an example where frequency matching is not identical to energy conservation!

When can nonlinear processes occur ???

- *Phase matching / conservation of photon momentum*

Discussion so far: Fields $E_i(t) \sim \cos(\omega_i t)$ at given position $\boldsymbol{r}$

But actually: *Waves* $E_i(t, \boldsymbol{r}) \sim \cos(\omega_i t - \boldsymbol{k} \cdot \boldsymbol{r})$

Light generated by nonlinear effects at *different positions* must contribute to corresponding total wave field with correct phase in order to generate a macroscopic wave!

For three-wave mixing we must have (higher orders analogously):

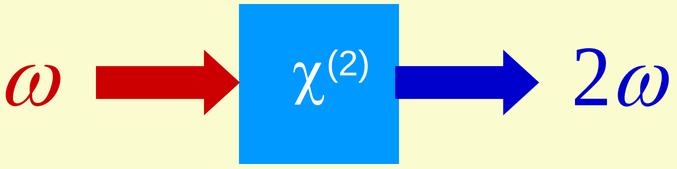
$$\boldsymbol{k}_3 = \boldsymbol{k}_1 + \boldsymbol{k}_2$$

(→ Calculation above with full wave)

Can (but does not have to) be interpreted as

conservation of total photon momentum

Example: Second-harmonic generation (SHG)



$\omega \rightarrow \boxed{\chi^{(2)}} \rightarrow 2\omega$

$\omega_1 = \omega_2 = \omega$ $\qquad \omega_3 = 2\omega$

If all three waves travel in the same direction: Scalar equations for momenta

$k_1 = k_2 = k$ $\qquad k_3 = 2k$

$$k = \frac{\omega}{c} \quad \Rightarrow \quad \frac{\omega_3}{c_0} n(\omega_3) = 2\frac{\omega_{1,2}}{c_0} n(\omega_{1,2})$$

⇒ for *non-dispersive* media (n = const.): $\omega_3 = 2\omega_{1,2}$

⇒ Would be trivially fulfilled due to frequency matching

Real crystals: *Dispersion*, i.e., refractive index *frequency-dependent* !

⇒ Waves with ω and 2ω travel with *different phase velocities*

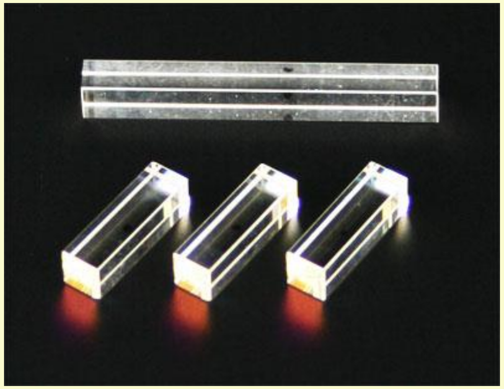
⇒ Photons with 2ω generated at different positions
are generally *not* in phase ⇒ No efficient SHG ! (Make that clear to you!)

To achieve phase matching we must have:

$$\frac{\omega_3}{c_0} n(\omega_3) = 2\frac{\omega_{1,2}}{c_0} n(\omega_{1,2}) \quad \Rightarrow \quad \frac{2\omega}{c_0} n(2\omega) = 2\frac{\omega}{c_0} n(\omega)$$

$$\Rightarrow \quad n(2\omega) = n(\omega)$$

- Can be achieved using different polarization directions for ω and 2ω in a birefringent crystal
- Fine-tuning of refractive indices often via *crystal temperature*
- Suitable materials with strong nonlinearities and low absorption at all involved frequencies



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- β-BaB_2O_4 (BBO)
- $KTiOPO_3$ (KTP)
- LiB_3O_5 (LBO)
- …

When can nonlinear processes occur ???

- *Selection rules due to crystal symmetries*

Example: For crystals with inversion symmetry: $\boldsymbol{P}(-\boldsymbol{E}) = -\boldsymbol{P}(\boldsymbol{E})$

$$\frac{1}{\varepsilon_0}\boldsymbol{P}(-\boldsymbol{E}) = -\chi^{(1)}\boldsymbol{E} + \chi^{(2)}\boldsymbol{E}\boldsymbol{E} - \chi^{(3)}\boldsymbol{E}\boldsymbol{E}\boldsymbol{E} + \ldots$$

$$\parallel$$

$$-\frac{1}{\varepsilon_0}\boldsymbol{P}(\boldsymbol{E}) = -\chi^{(1)}\boldsymbol{E} - \chi^{(2)}\boldsymbol{E}\boldsymbol{E} - \chi^{(3)}\boldsymbol{E}\boldsymbol{E}\boldsymbol{E} - \ldots$$

$$\Rightarrow \quad \chi^{(2)}\boldsymbol{E}\boldsymbol{E} = -\chi^{(2)}\boldsymbol{E}\boldsymbol{E} \qquad \Rightarrow \quad \chi^{(2)} = 0$$

⇒ *Non-centrosymmetric crystals* required for $\chi^{(2)}$ processes (SHG etc.)

Question: Is glass (amorphous) a possible candidate ???

Active processes (imaginary part of susceptibility)

Example: Two-photon absorption (TPA)

First: *Linear* (one-photon) absorption ($\chi^{(1)}$) from state(s) i to f with energy difference E_{fi}

polarization

Interaction with electromagnetic field: $\boldsymbol{A}(\boldsymbol{r},t) = A_0 \boldsymbol{a}_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}$

Probability for absorption process:

Fermi´s Golden Rule $\Rightarrow$ $$P_{fi} = \frac{\pi}{2\hbar}\left(\frac{eA_0}{m}\right)^2 \left|\langle\psi_f|\boldsymbol{a}_0\cdot\boldsymbol{p}|\psi_i\rangle\right|^2 \delta(E_{fi}-\hbar\omega)$$

$$A_0^2 = \frac{8\pi}{\varepsilon_0 c n \omega^2} I$$ I : Light intensity

Absorption from total transition probability at relevant wavelength
Summation over all bands and integration over k-space

$$W_{fi} = \sum_{\mathrm{CB,VB}} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} P_{fi} \ldots$$

Absorption coefficient: $-\alpha I = \frac{dI}{dz} = \hbar\omega W_{fi}$

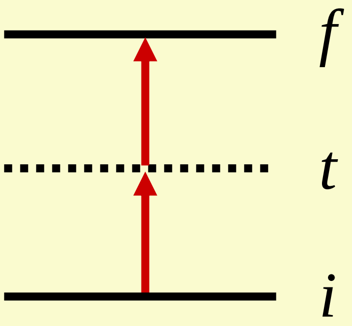
P_{fi} and $W_{fi} \sim A_0^2 \sim I$ Absorption probability proportional to probability to find *one photon* at certain position

$\Rightarrow \quad \alpha = const.$

Now: Degenerate two-photon absorption: *Second-order* perturbation theory

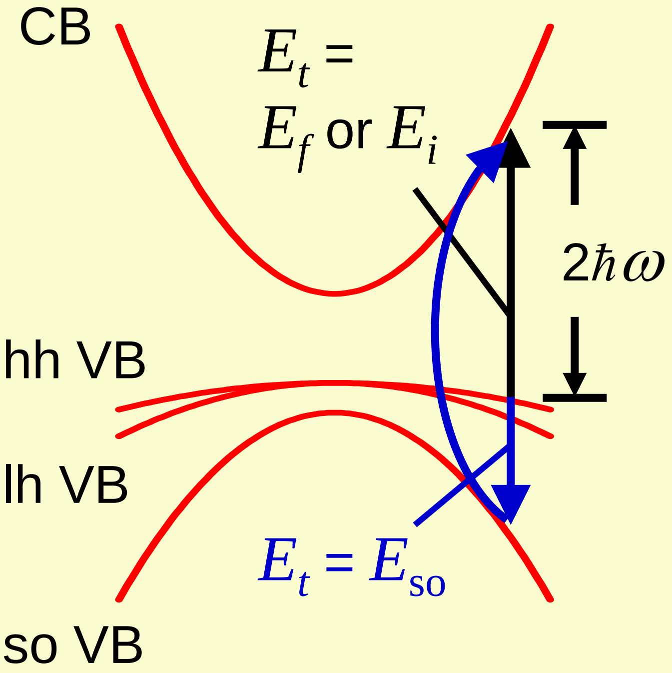
$$\Rightarrow \; P_{fi} = \frac{\pi}{2\hbar}\left(\frac{eA_0}{m}\right)^4 \left| \sum_t \frac{\langle \psi_f | \mathbf{a}_0 \cdot \mathbf{p} | \psi_t \rangle \langle \psi_t | \mathbf{a}_0 \cdot \mathbf{p} | \psi_i \rangle}{E_t - E_i - \hbar\omega} \right|^2 \delta\left(E_f - E_i - 2\hbar\omega\right)$$

- $P_{fi} \sim I^2$ $\Rightarrow$ *Nonlinear* absorption, grows with intensity !!!
- Absorption probability proportional to probability to find *two photons* at certain position
- *Nondegenerate* TPA also exists: 2 photons with different frequencies



TPA: principle

TPA in typical
III-V semiconductor
with zincblende
crystal structure
(GaAs, InSb, …)



- Absorption via *virtual* intermediate (transitional) state *t*
- In general transition energy $i \rightarrow t \quad \neq \ni\omega$!
  (Excitation of virtual intermediate state at “wrong” energy:
  Intuitive picture: Possible within limits of Heisenberg uncertainty relation!)
- Summation over all *t* to get total transition probability
- Strong resonant enhancement of TPA, if $\ni\omega$ corresponds to “correct” energy of *t* (e.g., for biexcitons, see below)

$\Rightarrow$ Coefficient for TPA: $-\dfrac{dI}{dz} = \alpha I + \beta I^2 \;\Rightarrow\; \beta = \dfrac{2\hbar\omega}{I^2} W_{fi}$

β in semiconductors: 10^{-3} … 10 cm^{-1}/MW

Solution of differential equation: $I(z) = \dfrac{1}{\frac{1}{I_0} e^{\alpha z} - \left(1 - e^{\alpha z}\right)\beta / \alpha}$

- $\beta = 0$ (linear absorption) $\Rightarrow$ $I(z) = I_0 e^{-\alpha z}$ *Beer's law*
- $\alpha = 0$, $\beta \neq 0$ (pure TPA, e.g., for $\hbar\omega$ below and 2 $\hbar\omega$ above band gap) $\Rightarrow$

$$I(z) = \frac{1}{\frac{1}{I_0} + \beta z}$$

For $I_0 \to \infty$: $I(z) = \dfrac{1}{\beta z} = const.$

Optical limiting: Max. intensity transmitted through slab of thickness z is independent of I_0 !

How strong is TPA? An estimation …

$\beta \sim 10^{-7}$ cm/W for $I = 10^{6}$ W/cm^2

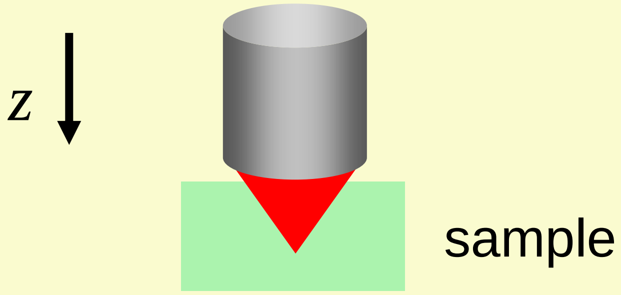
$$-\frac{dI}{dz} = \alpha I + \beta I^{2} = \underbrace{\left(\alpha + \beta I\right)}_{\text{effective absorption}} I$$

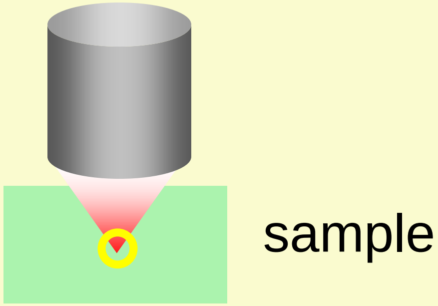
Compare $\beta I \sim 10^{-1}$ cm^{-1} with $\alpha \sim 10^{4} - 10^{5}$ cm^{-1} close to E_g in semiconductor

⇒ β only important in *transparent region* ($\alpha \sim 0$) !

Important application of TPA: Two-photon fluorescence microscopy

Spatially resolved fluorescence image of sample (often biological) obtained by scanning microscope objective with laser excitation / detection (confocal)





Single-photon absorption

Absorption and fluorescence in *whole* irradiated region

⇒ Bad spatial resolution, in particular along z

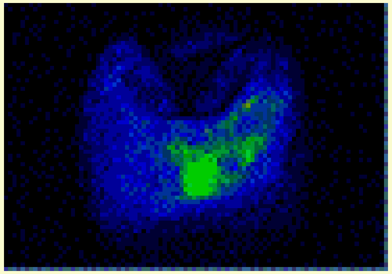
⇒ Inner parts of samples hidden

Two-photon absorption

Absorption and fluorescence *only in focus*, where laser intensity is high !

⇒ High 3D resolution !

⇒ Inner parts of sample accessible !



Two-photon image of a carious tooth.
Carious area shown in green

www.photonics.ac.uk

High excitation effects in semiconductors

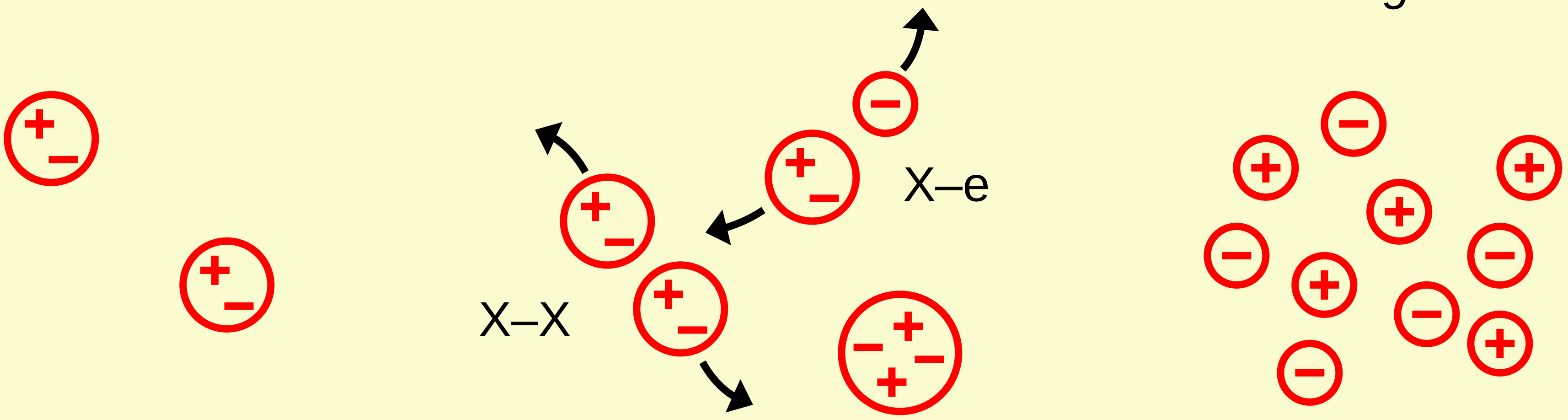
Optical excitation of semiconductors generates electron–hole pairs

Excitation / e–h pair density

Low

Medium

High



X–e

X–X

Independent excitons (low T) / free e–h pairs (high T)

biexciton

electron–hole plasma

Linear optics

Nonlinear optics

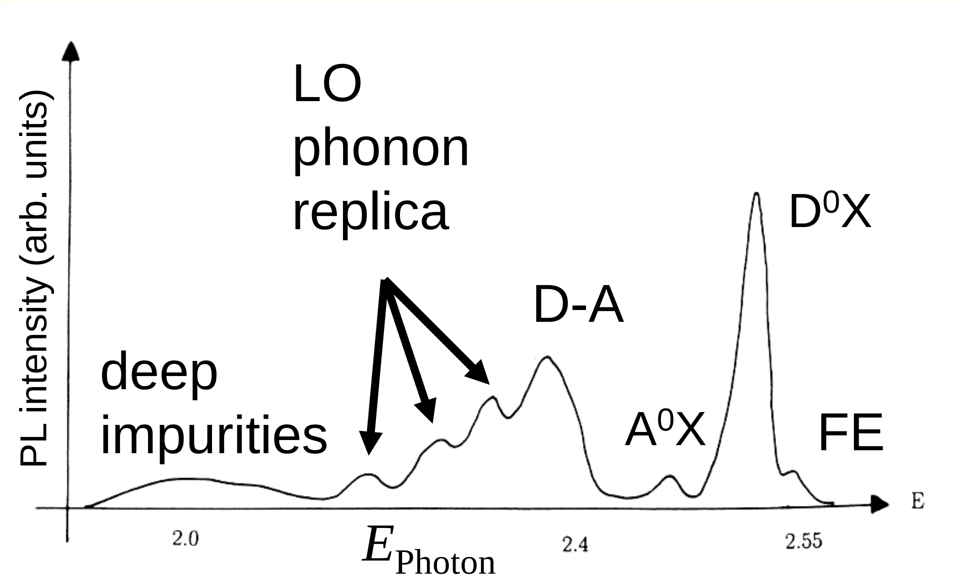
Photoluminescence (PL)

Spectrum of emitted photons due to optically excited e–h pairs,
typically measured at low temperatures

At low densities:

Distance of excitons *large* compared to exciton Bohr radius ⇒

- PL due to *independent* excitons
  (free (FE) and / or bound to (neutral) donors (D^0X), acceptors (A^0X), etc.)
- Phonon “replica” if opt. recombination with simultaneous generation of LO phonon(s)
- PL due to donor–acceptor (D–A) pair transitions, deep impurities etc.

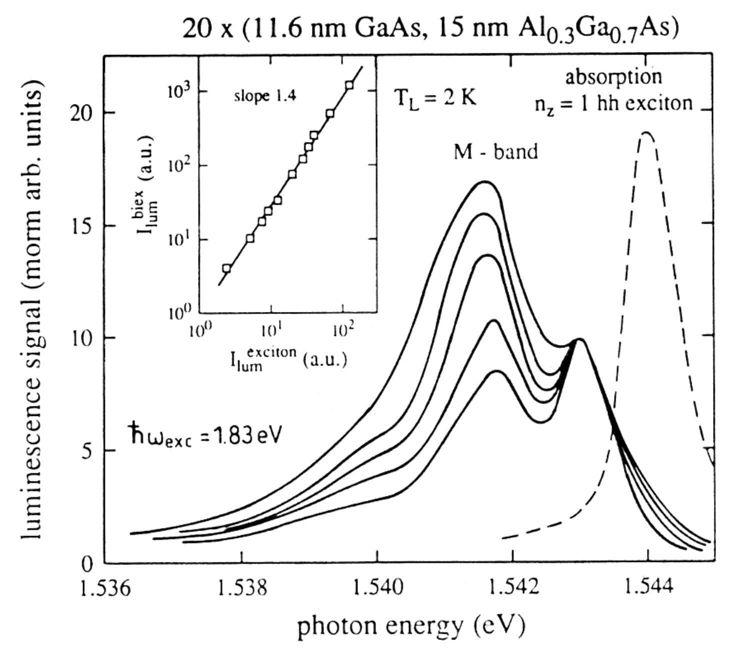


Low-temperature PL (T ~ 4 K) of CdS in low-density regime

At medium densities:

Distance of excitons no longer large compared to exciton Bohr radius
⇒ *Interaction, excitons no longer independent*

- Formation of biexcitons:
  - Excitonic molecule, i.e., two excitons bound to each other (similar to hydrogen molecule)
  - Dispersion: $E_{\mathrm{biexciton}}(\boldsymbol{K}) = 2E_X(n_B = 1, \boldsymbol{K} = 0) - E_{\mathrm{biexc.}}^{\mathrm{bind}} + \frac{\hbar^2 \boldsymbol{K}^2}{4M}$



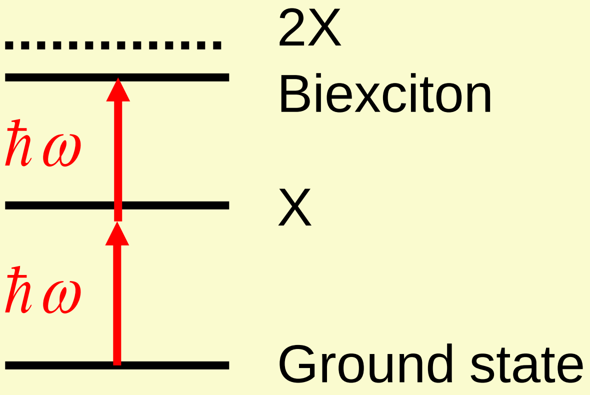
M : *single* exciton mass

⇒ *New emission band below* free exciton due to biexcitons: M band

⇒ Grows superlinearly with excitation intensity

C. Klingshirn, Semiconductor Optics

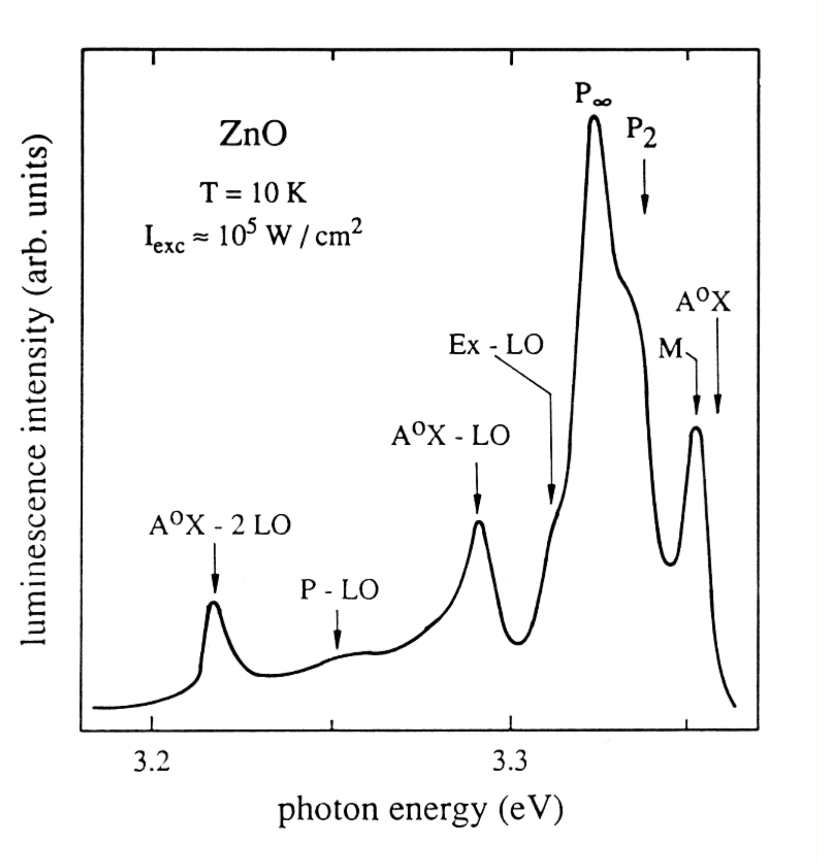
Resonant two-photon absorption for biexcitons



⇒ Single exciton state X serves as nearly resonant intermediate state t close to $E_{\text{biexciton}}$ / 2

⇒ Example for very efficient two-photon absorption !

- Exciton–exciton (X–X) scattering:
  - Optical recombination of exciton with simultaneous excitation of existing second exciton to state n_B ⇒ P_{n_B} bands
  - Same with excitation to exciton *continuum* ⇒ P_∞ band
- Exciton–electron/hole (X–e/h) scattering:
  - Same as X–X but excitation of free electron/hole (if present)
- LO phonon replica



At high densities:

- Screening of Coulomb interaction between electron and hole!

Stability of exciton?

Consider exciton in sea of free carriers (electrons and holes) with density n_P

Screening of Coulomb potential $\Rightarrow$ Yukawa potential

$$\frac{1}{4\pi\varepsilon_0\varepsilon}\frac{e^2}{|\boldsymbol{r}_e-\boldsymbol{r}_h|} \quad\rightarrow\quad \frac{1}{4\pi\varepsilon_0\underset{\uparrow}{\varepsilon(n_P)}}\frac{e^2}{|\boldsymbol{r}_e-\boldsymbol{r}_h|}\underline{\exp\left[-\frac{|\boldsymbol{r}_e-\boldsymbol{r}_h|}{l}\right]}$$

Influence of plasmons /
plasmon–phonon
mixed states

$l\,(n_B)$: Screening *length*

- Reduced e–h interaction $\Rightarrow$ Exciton binding energy *decreases* with growing n_P
- If $n_P > n_c$ (*Mott density*): $l < l_c = a_B / 1.19$ (critical screening length)

  $\Rightarrow$ No longer bound state for Yukawa potential (at least in 3D)

  $\Rightarrow$ Mott transition: Formation of electron–hole plasma (EHP),
  i.e., high-density plasma consisting of free electrons and holes
  (common in, e.g., the optically active layer of laser diodes)

- Band-gap renormalization due to exchange and correlation effects

⇒ Band-gap decreases monotonically with increasing n_P

Exchange interaction:

For random distribution of electrons and holes:

Sum of all Coulomb energies for given electron (hole) would cancel out

In reality:

Pauli principle / exchange interaction between
identical charge carriers with *parallel* spin

⇒ Larger average distance for electrons (holes) with *parallel* spin

⇒ Reduction of *repulsive*, i.e., *positive* Coulomb energy contributions

⇒ *Lower total energy* of considered electron (hole)

Correlation:

Despite EHP, electrons and holes are not *randomly distributed:*

Higher probability to find electron close to a hole due to Coulomb interaction
(→ discussion of Sommerfeld enhancement in absorption above)

⇒ Increase of *attractive*, i.e., *negative* Coulomb energy contributions

⇒ *Lower total energy* of electron / hole

- Burstein–Moss shift

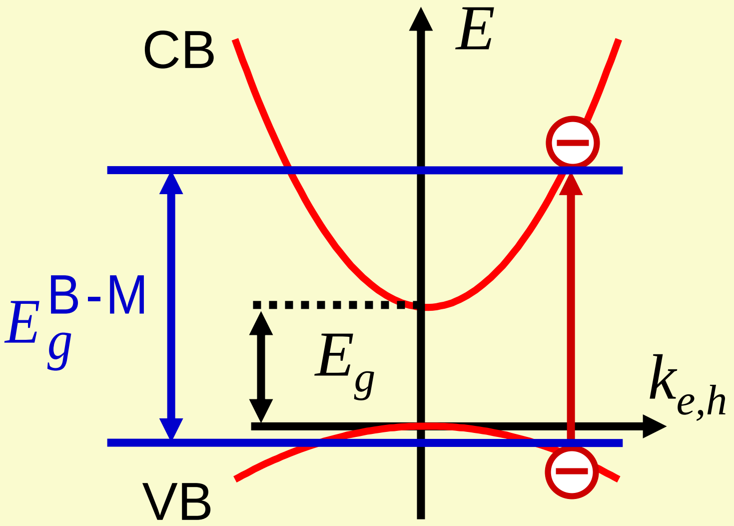
Electrons and holes are *fermions* (spin ½)

⇒ Each conduction / valence band state can only be occupied *once* (Pauli principle)

⇒ High carrier densities lead to band filling

⇒ Absorption close to band edge blocked due to already filled CB / empty VB (i.e., filled by holes) states

⇒ *Burstein–Moss shift:*
Blue-shift of absorption edge for highly excited semiconductors
(similar effect for high doping levels)



Due to band filling,
absorption is blocked for

$$E_{\text{Photon}} < E_g^{\text{B-M}}$$

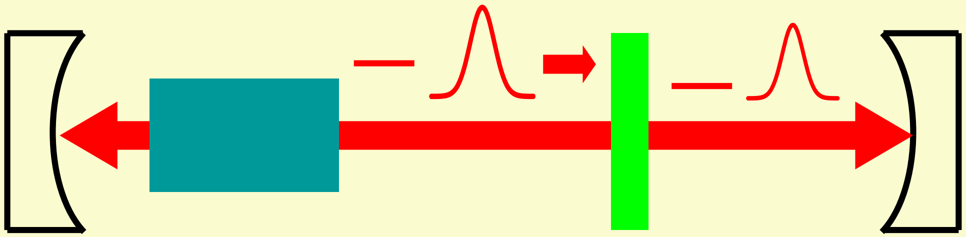
Note: Burstein–Moss shift and band-gap renormalization partly cancel each other!

Application:

Burstein–Moss shift: Absorption near band-gap *drops* with light *intensity*

⇒ *Saturable absorber*

⇒ Used to realize (ps-) pulsed lasers based on “passive mode-locking”

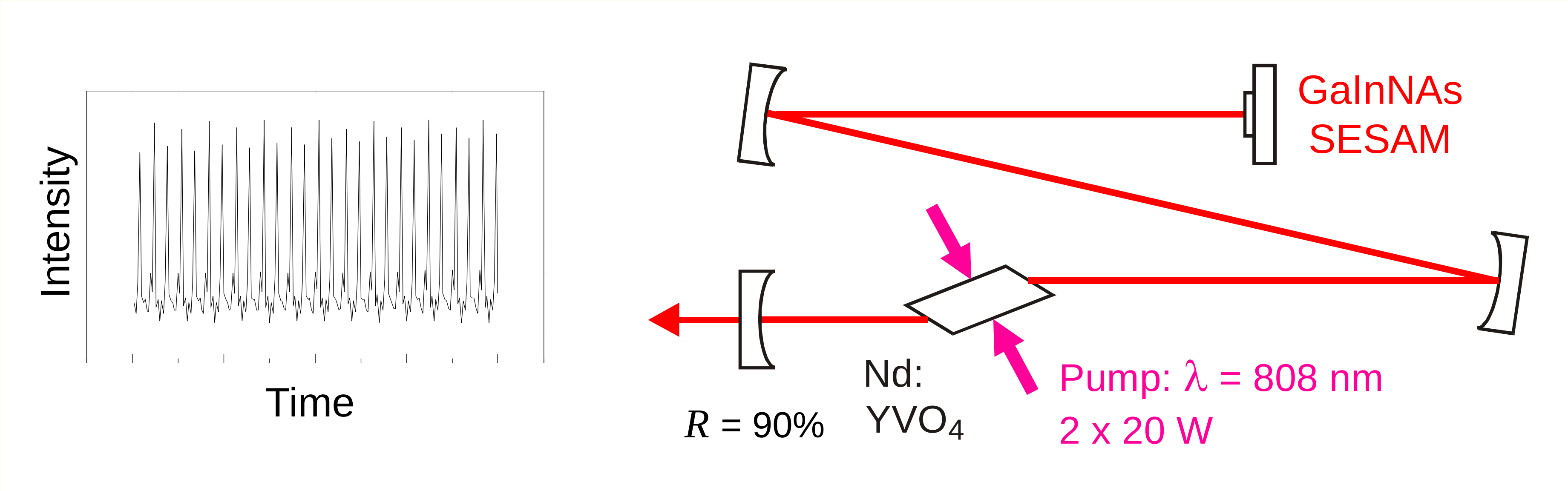


Saturable absorber: Lower absorption for higher intensity

- ⇒ *Temporally peaked intensity fluctuations are amplified*
- ⇒ Continuous operation *instable*
- ⇒ Pulse circulating in cavity generated
- ⇒ *Pulsed output*

Example: Mode-locked Nd:YVO$_4$ laser with GaInNAs SESAM

SESAM : SEmiconductor Saturable Absorber Mirror



- 40-ps pulses, rep. rate: 133 MHz
- Output power: 3.8 W
- λ = 1342 nm

With optimized GaInAs/GaAsP SESAM:

- 21-ps pulses, rep. rate: 90 MHz
- 20 W (diffraction-limited beam)
- λ = 1064 nm

G. Vysniauskas, M. Hetterich et al., Proc. CLEO 2001, Baltimore, paper CWA3 (2001).
*D. Burns, M. Hetterich et al., J. Opt. Soc. Am. B **17**, 919 (2000).*