

## Optical Properties of Solids

LM Herz

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  - IV. Low-dimensional systems
  - V. Optical response of an electron gas
  - VI. Optical studies of phonons
  - VII. Optics of anisotropic media
  - VIII. Non-linear optics

### Recommended textbooks

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

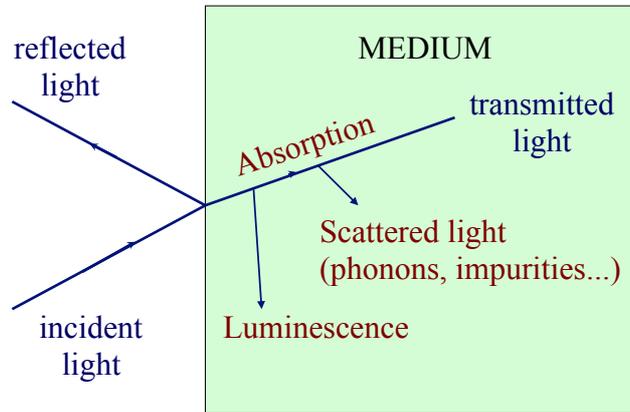
PY Yu and M Cardona, *Fundamentals of Semiconductors*, Springer

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

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

A Yariv, *Quantum Electronics*, Wiley

Interaction of Electromagnetic Radiation with Matter



## I Absorption and Reflection

### Macroscopic Electromagnetism

Maxwell's equations:

$$\begin{aligned} \nabla \cdot \mathbf{D} &= \rho & \nabla \times \mathbf{H} &= \mathbf{j} + \frac{d}{dt} \mathbf{D} \\ \nabla \cdot \mathbf{B} &= 0 & \nabla \times \mathbf{E} &= -\frac{d}{dt} \mathbf{B} \end{aligned}$$



$$\begin{aligned} \rho &= 0 & (\text{no net free charges}) \\ \mathbf{B} &= \mu_0 \mathbf{H} & (\text{non-magnetic}) \\ \mathbf{j} &= \sigma \mathbf{E} & (\text{ohmic conduction}) \end{aligned}$$

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

### Linear Optics

In a linear, non-conducting medium:

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

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

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

→ Define complex refractive index:

$$\tilde{n} \equiv \sqrt{\epsilon_r} \equiv n + ik$$


  
 refraction    absorption

## Absorption

Intensity decay of wave:  $I(z) = I_0 \exp\left(-\frac{2\omega\kappa}{c}z\right)$   
(Beer's law)

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

## Reflection

At normal incidence:

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



Reflectivity  $R$  for a material's surface contains information on its absorption!

## Relationship between components of $\tilde{n}$ and $\epsilon_r$

$$\tilde{n} = n + i\kappa \quad \epsilon_r = \epsilon' + i\epsilon''$$



$$\tilde{n} = \sqrt{\epsilon_r}$$



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

and

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

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

## The classical dipole oscillator model

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

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

Equation of motion for a bound electron in 1D:

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

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

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

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

Displacement of charge causes polarisation:

$$P = -N e x \quad (N: \text{oscillator density})$$

$$D = \epsilon_0 \epsilon_r E = \epsilon_0 E + P + \underbrace{P_b}_{\text{background}}$$

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

$\underbrace{\hspace{15em}}_{\chi(\omega)}$

Real and imaginary part of  $\epsilon_r$

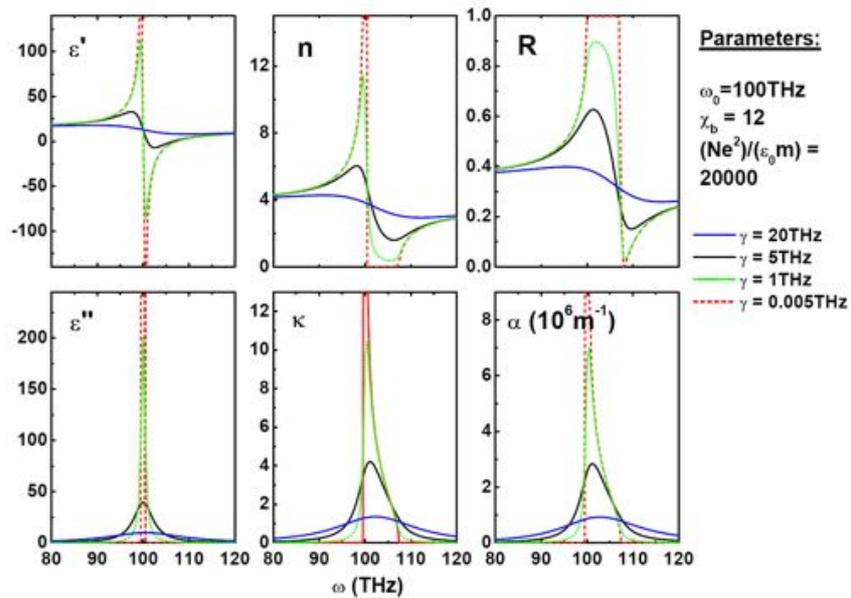
$$\epsilon'(\omega) = 1 + \chi_b + \frac{Ne^2}{\epsilon_0 m} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2}$$

$$\epsilon''(\omega) = \frac{Ne^2}{\epsilon_0 m} \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2}$$



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

Optical constants for a classical dipole oscillator



## Local field corrections

In a dense medium:

- atoms experience “local field” composed of external field  $E$  and polarization from surrounding dipoles
  - treat interacting dipole as being at centre of sphere surrounded by a polarized dielectric
- ⇒ Clausius-Mossotti relationship:

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

electric susceptibility per atom

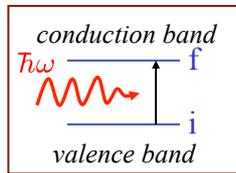
## Problems with the classical oscillator model

- no information on selection rules
  - ⇒ need quantum mechanics
- interband transitions should depend on the density of states  $g(E)$
- One possible modification: “oscillator strength” (from QM)

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



## II Interband optical transitions



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

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

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

where  $V(\mathbf{r}) = -\underbrace{e\mathbf{r}}_{\text{dipole moment}} \cdot \underbrace{\mathbf{E}}_{\text{E-field of incident wave}} = E_0 \cos(\mathbf{k} \cdot \mathbf{r})$

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

Matrix element for interband transitions:

$$M_{if} = \frac{1}{2V_0} \int (-e\mathbf{E}_0) \cdot (u_c^*(\mathbf{r}) \mathbf{r} u_v(\mathbf{r})) \exp(i(\mathbf{k}_i - \mathbf{k}_f + \mathbf{k}) \cdot \mathbf{r}) d^3r \quad \leftarrow \text{absorption}$$

$$+ \frac{1}{2V_0} \int (-e\mathbf{E}_0) \cdot (u_c^*(\mathbf{r}) \mathbf{r} u_v(\mathbf{r})) \exp(i(\mathbf{k}_i - \mathbf{k}_f - \mathbf{k}) \cdot \mathbf{r}) d^3r \quad \leftarrow \text{emission}$$

⇒ deduce conditions for dipole allowed (direct) transitions.

Consider:

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

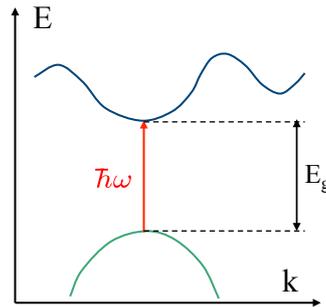
Conditions for direct interband transitions

**(1) wavevector conservation**

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

↑ absorption      ↑ emission

typically:  $\mathbf{k} \ll \mathbf{k}_i, \mathbf{k}_f$   
 $\Rightarrow$  “vertical” transitions



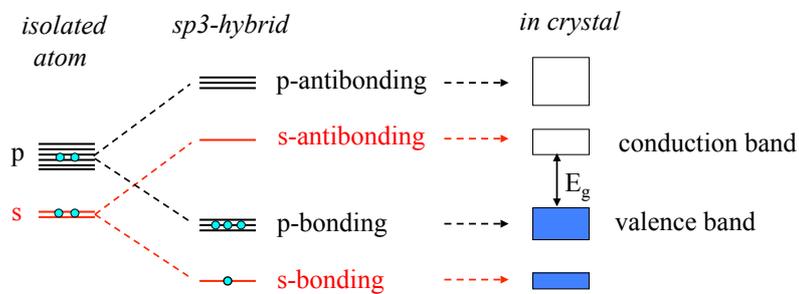
**(2) parity selection rule**

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

↑ odd parity

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

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



### (3) Dependence of transition probability on photon energy

Final state is an electron-hole pair

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

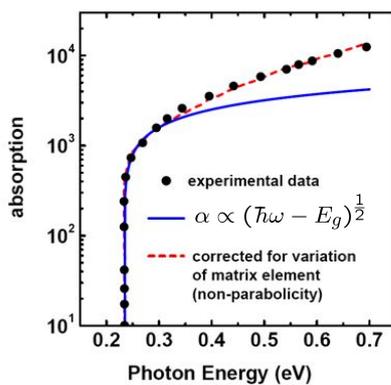
where  $\mu = \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)^{-1}$  reduced effective mass

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

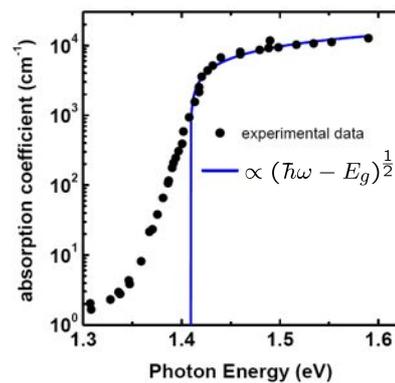
Absorption coefficient  
(for direct transitions):  $\alpha \propto (\hbar\omega - E_g)^{\frac{1}{2}}$

#### Examples for direct semiconductors

a) InSb at 5K



b) GaAs at 300K



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

## Indirect interband transitions

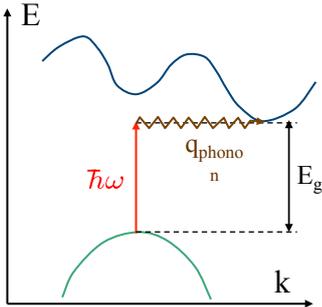
- Indirect gap: valence band maximum and conduction band minimum lie at different wavevectors,  $k_v^{max} \neq k_c^{min}$
- direct transitions across the indirect gap forbidden, but phonon-assisted transitions may be possible.

**(i) wavevector conservation:**

$$k_f = k_i \pm k \pm q_{phonon}$$

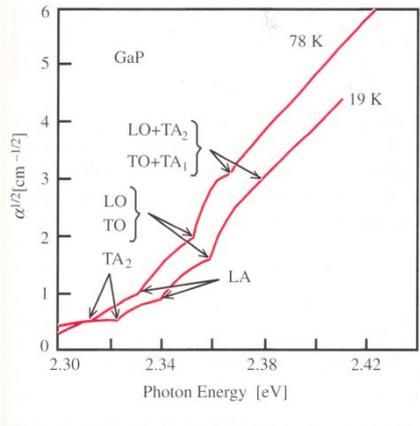
with phonon wavevector

$$q_{phonon} = k_v^{max} - k_c^{min}$$



**(ii) probability for indirect transitions:**

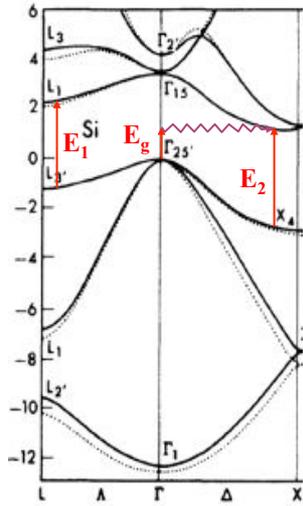
- perturbation causing indirect transitions is second order  
 $\Rightarrow$  optical absorption much weaker than for direct transitions!
- find absorption coefficient  $\alpha \propto (\hbar\omega - E_g \pm \hbar\omega_q)^2$



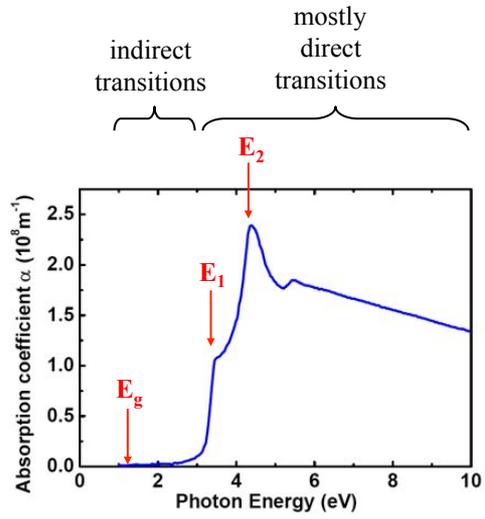
↑  
phonon absorption  
or emission

Example for an indirect semiconductor: Si

Band structure:



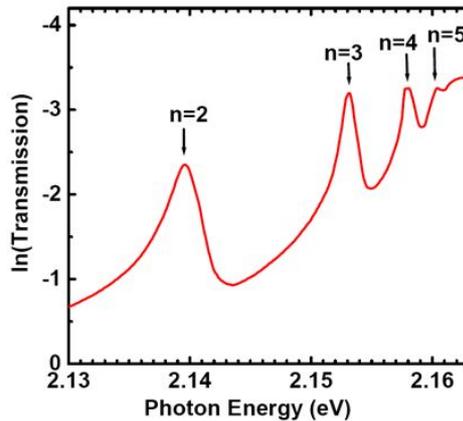
Absorption spectrum:





## III Excitons

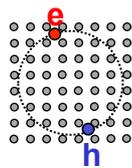
Absorption coefficient of  $\text{CuO}_2$  at 77K:



Series of absorption peaks just below the energy gap

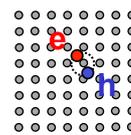
Coulomb interaction between electron and hole gives rise to “excitonic” states (bound electron-hole pairs)

### Wannier-Mott Excitons



- weakly bound (free) excitons
- binding energy  $\sim 10\text{meV}$
- common in inorganic semiconductors (e.g. GaAs, CdS,  $\text{CuO}_2$ ...)
- particle moving in a medium of effective dielectric constant  $\epsilon_r$

### Frenkel Excitons



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

## Weakly bound (Wannier) Excitons

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

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

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

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

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

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

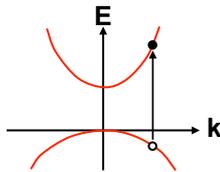
$\mu = \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)^{-1}$  reduced mass

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

where  $a_0 = 0.529 \text{ \AA}$  (Bohr radius)

## E-k diagram for the weakly bound exciton

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



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

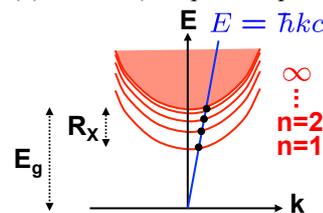
wavevector conservation:

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

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

⇒ “vertical transitions”

(b) exciton (one-particle picture)



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

wavevector conservation:

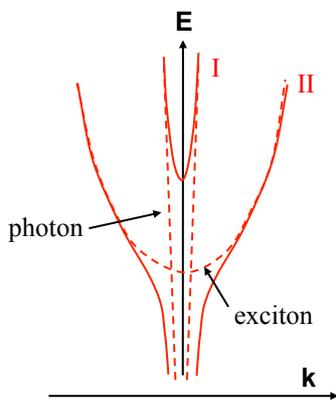
$$\mathbf{k}_X = \mathbf{k}_e - \mathbf{k}_v = \mathbf{k}_{\text{photon}}$$

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

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

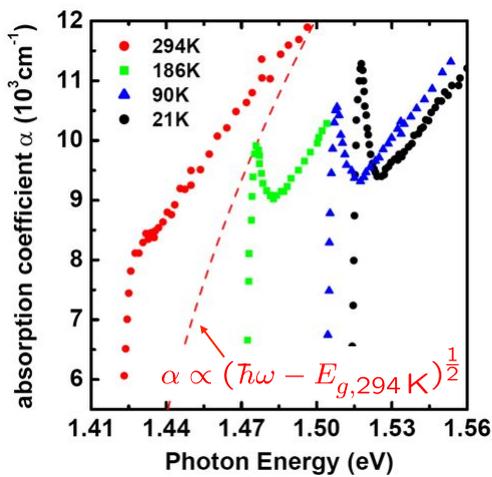
⇒  $E_X \rightarrow E_g$  for  $n \rightarrow \infty$   
continuum onset at band edge

## Exciton-Polariton



- Absorption occurs at point where photon dispersion intersects exciton dispersion curve.
- exciton-photon interaction leads to coupled EM and polarization wave (polariton) travelling in the medium
  - ⇒ altered dispersion curve (2 branches)
- But: if exciton damping (phonon scattering...) is larger than exciton-photon interaction we can treat photons and excitons separately.

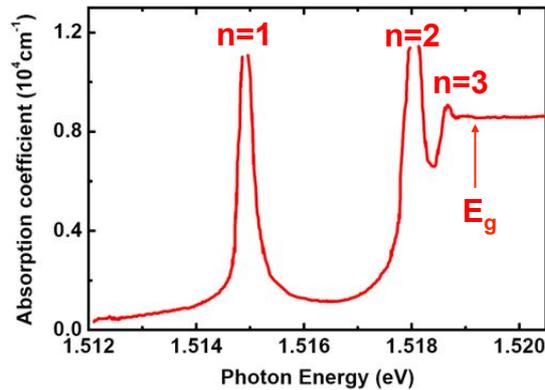
## Examples for weakly bound excitons: GaAs



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

## Examples for weakly bound excitons: GaAs

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



here:  $m_e^* = 0.067$

$m_{hh}^* = 0.45$

$\epsilon_r = 13$



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

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

## Tightly bound (Frenkel) excitons

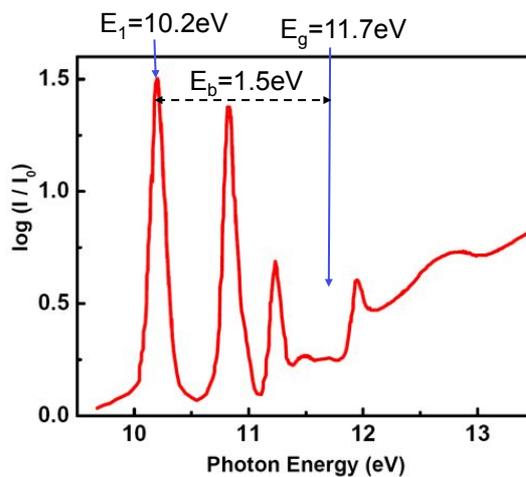
- radius of weakly-bound excitons:  $a_n = \epsilon_r \frac{m_e}{\mu} n^2 a_0$ 
  - ⇒ model of bound e-h pair in dielectric medium breaks down when  $a_n$  is of the order of interatomic distances ( $\text{\AA}$ )
  - ⇒ have tightly bound excitons for small  $\epsilon_r$ , large  $\mu$
- tightly-bound electron-hole pair, typically located on same unit (atom or molecule) of the crystal (but the whole exciton may transfer through the crystal)
- large binding energies (0.1 – 1eV) → excitons persist at room temperature.

## Transition energies for tightly bound excitons

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

## Examples for tightly bound excitons: rare gas crystals

absorption spectrum of crystalline Kr at 20K:



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



close to lowest excitonic transition  $E_1$  in crystal

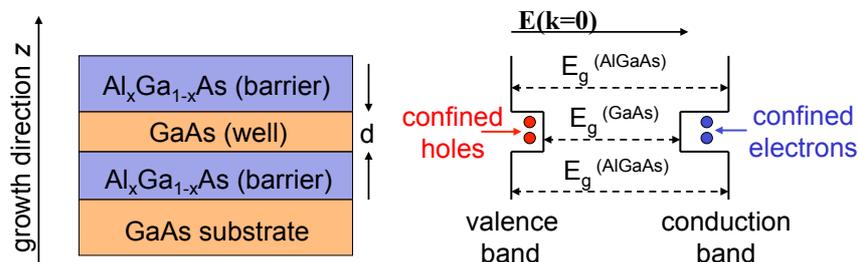


## VI Low-dimensional systems

de Broglie wavelength for an electron at room temperature:  $\lambda = \frac{h}{p} \approx \frac{h}{\sqrt{m_e kT}} \approx 10 \text{ nm}$

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

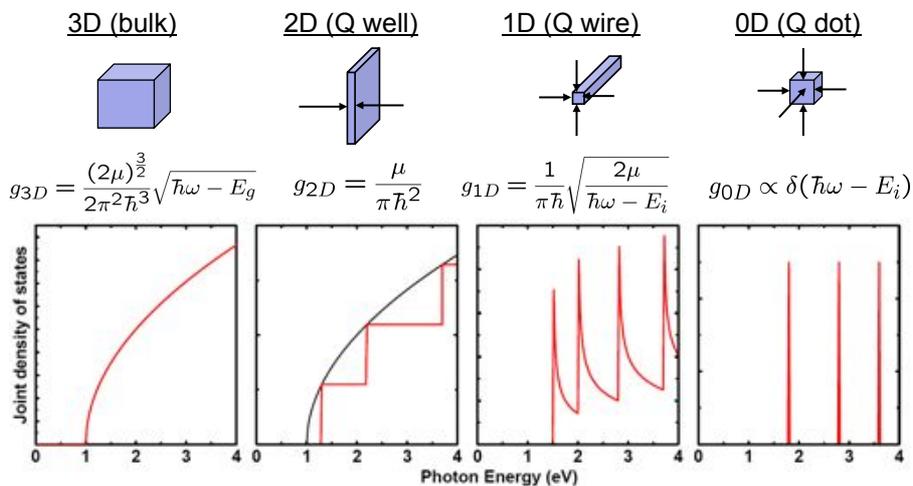
Possible using e.g. *molecular beam epitaxy* (MBE) or *metal-organic chemical vapour deposition* (MOCVD)



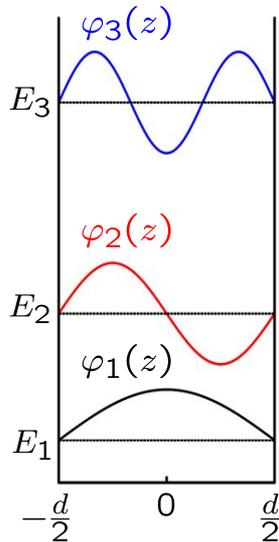
### Effect of confinement on the DOS

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

→ Joint density of states  $g(\hbar\omega)$  (for direct CB-VB transitions):



## Quantum well with infinite potential barriers



Schrödinger's eqn inside the well:

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

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



wavefunction along z:

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

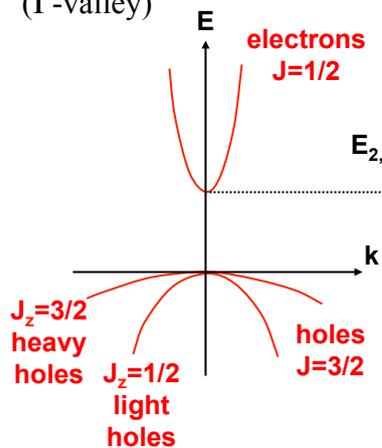
with wavevector  $k_n = \frac{n\pi}{d}$

confinement energy:

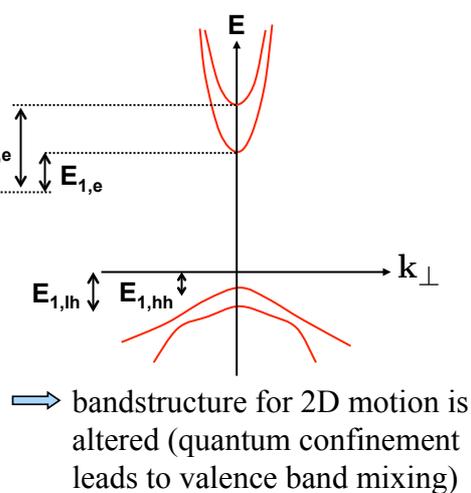
$$E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*} \left(\frac{n\pi}{d}\right)^2$$

## Bandstructure modifications from confinement

bulk GaAs  
( $\Gamma$ -valley)



GaAs QW



## Optical transitions in a quantum well

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

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

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

- (i)  $\varphi(z)$  changes slowly over a unit cell (compared to  $u_c, u_v$ )
- (ii)  $M_{if} \approx 0$  unless  $\mathbf{k}_{\perp,v} = \mathbf{k}_{\perp,c} \pm \mathbf{k}_{photon}$  ( $\mathbf{k}$ -conservation)

$$\Rightarrow M_{if} \propto e\mathbf{E}_0 \cdot \underbrace{\int u_c^*(\mathbf{r}) \mathbf{r} u_v(\mathbf{r}) d^3r}_{M_{CV}} \times \underbrace{\int \varphi_{n,c}^*(z) \varphi_{n',v}(z) dz}_{M_{n,n'}}$$

dipole transition criteria (as before)      electron-hole spatial overlap in well

## Selection rules for optical transitions in a QW

- (i) wavevector conservation:  $\mathbf{k}_{\perp,v} = \mathbf{k}_{\perp,c} \pm \mathbf{k}_{photon}$
- (ii) parity selection rule:  $u_c(\mathbf{r})$  and  $u_v(\mathbf{r})$  must differ in parity } as before
- (iii)  $M_{n,n'} = \int \varphi_{n,c}^*(z) \varphi_{n',v}(z) dz$

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

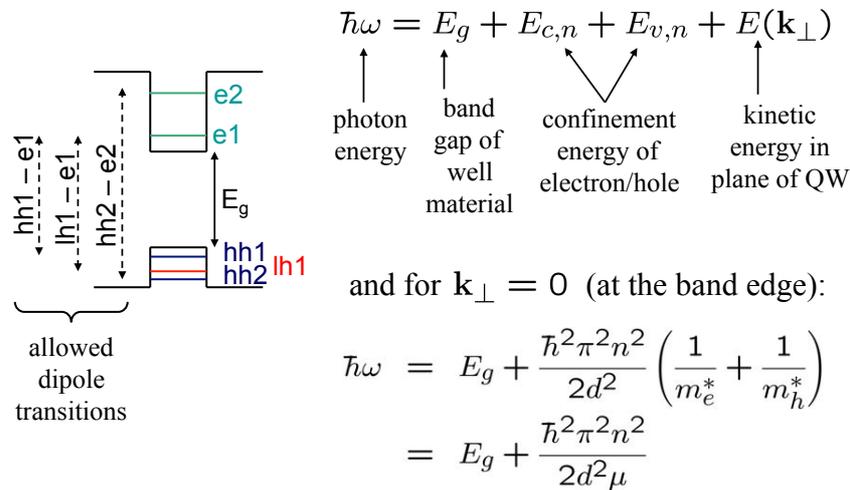
$$M_{n,n'} = \frac{2}{d} \int_{\frac{d}{2}}^{-\frac{d}{2}} \sin\left(k_n z + \frac{n\pi}{2}\right) \sin\left(k_{n'} z + \frac{n'\pi}{2}\right) dz$$

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

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

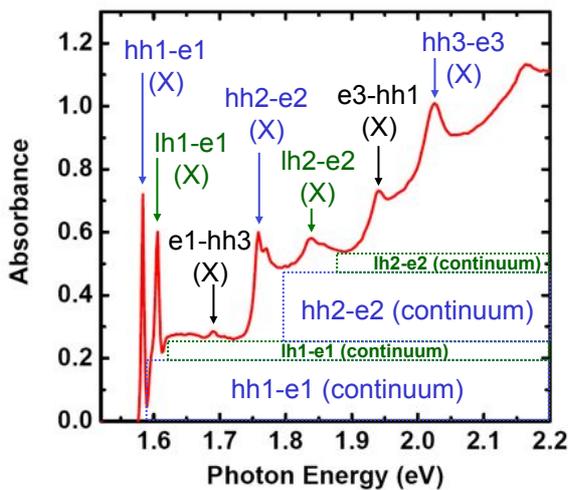
- (iv)  $M_{n,n'} = 0$  unless  $\varphi_{n,c}(z)$  and  $\varphi_{n',v}(z)$  have equal parity

(v) energy conservation:



Example: absorption of a GaAs/AlAs QW

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

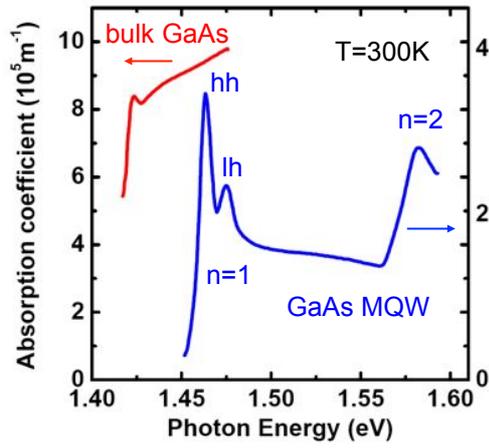


below each onset of absorption: excitonic features (X)

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

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

## Influence of confinement on the exciton



Confinement brings electron and hole closer together.

⇒ enhanced exciton binding energy

⇒ increased oscillator strength



## V Optical response of a free electron gas

Classic Lorentz dipole oscillator model (again):

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

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

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

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

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

$\Rightarrow$  real and imaginary part of the dielectric constant:

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

## AC conductivity of a free electron gas

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

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

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

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

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

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

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

optical measurements of  $\epsilon_r$  equivalent to those of AC conductivity!

## Low-frequency regime

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

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

$\swarrow \epsilon'$                        $\nwarrow \epsilon''$

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

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

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

$\delta = \frac{2}{\alpha} = \left( \frac{2}{\sigma_0\omega\mu_0} \right)^{\frac{1}{2}}$	For Cu at 300K: $\sigma_0 = 6.5 \times 10^7 \Omega^{-1}\text{m}^{-1}$ $\Rightarrow \delta = 8.8\text{mm} @ \nu = 50\text{Hz}$ $\delta = 6.2\mu\text{m} @ \nu = 100\text{MHz}$
--	---

## High-frequency regime

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

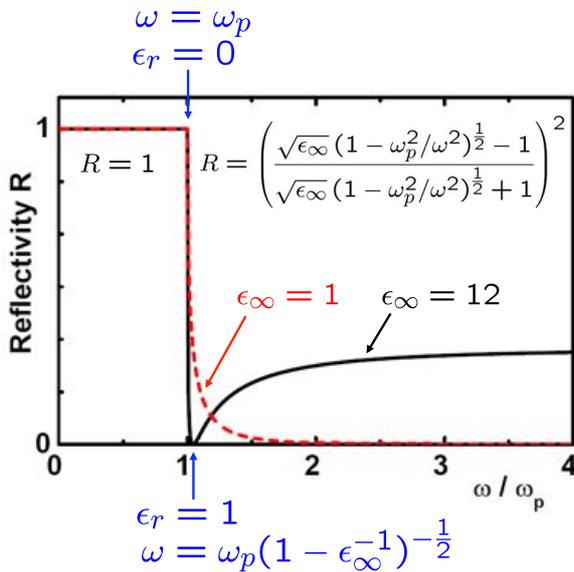
$\Rightarrow$  Drude model predicts:  $\gamma \approx 10^{14} \text{ s}^{-1}$

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

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

- |      |                     |                 |   |
|------|---------------------|-----------------|---|
| (i)  | $\omega < \omega_p$ | $\epsilon' < 0$ | $\tilde{n}$ largely imaginary<br>$R \approx 1$ wave mostly reflected  |
| (ii) | $\omega > \omega_p$ | $\epsilon' > 0$ | $\tilde{n}$ largely real<br>$R < 1$ wave partly transmitted,<br>weak absorption ( $\alpha \propto \epsilon''$ ) |

Reflectivity in the high-frequency regime



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

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

Example: Reflection from Alkali metals

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

$\uparrow$  measured at low T       $\underbrace{\hspace{10em}}_{\text{calculated from } \omega_p = \left(\frac{Ne^2}{\epsilon_0 m}\right)^{\frac{1}{2}}}$        $\uparrow$  measured UV transmission cut-off

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

### Example: Reflection from transition metals

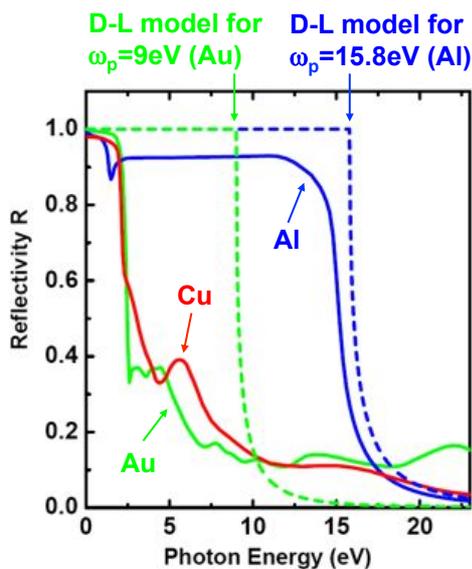
Metal	N ( $10^{28}\text{m}^{-3}$ )	$\omega_p/2\pi$ ( $10^{15}\text{Hz}$ )	$\lambda_p$ (nm)
Cu	8.47	2.61	115
Ag	5.86	2.17	138
Au	5.90	2.18	138

↑ measured at low T      calculated from  $\omega_p = \left(\frac{Ne^2}{\epsilon_0 m}\right)^{\frac{1}{2}}$

These transition metals should be fully reflective up to deep UV  
But we know: Gold appears yellow, Copper red



### Reflection of light from Au, Cu and Al:



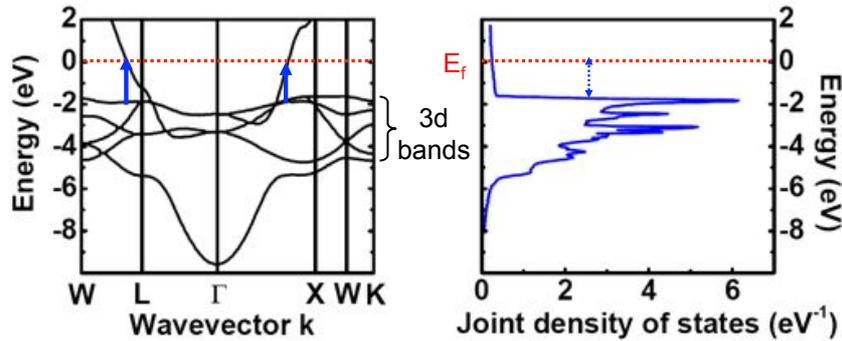
Drude-Lorentz model does not account fully for optical absorption of transition metals (especially in the visible)

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

### Example: Reflection from Copper

Electronic configuration of Cu: [Ar] 3d<sup>10</sup> 4s<sup>1</sup>

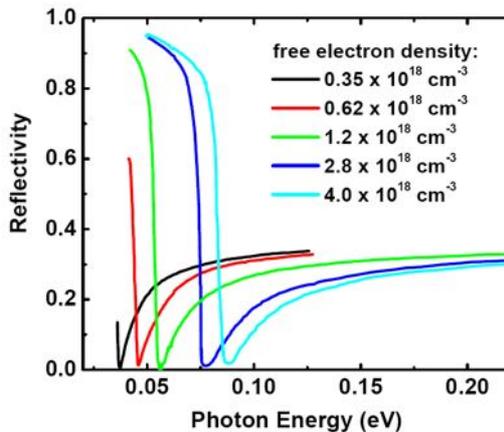
Transitions (in visible range of spectrum) between relatively dispersionless bands of tightly bound 3d electrons and half-filled band of 4s-electrons:



strong interband absorption for  $\hbar\omega \geq 2 \text{ eV} \rightarrow$  copper appears red !

### Example: Reflection from doped semiconductors

Free-carrier reflectivity of InSb:



$$R = 0 \text{ for } \omega = \omega_p (1 - \epsilon_\infty^{-1})^{-\frac{1}{2}}$$

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

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

### Example: Free-carrier absorption in semiconductors

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

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

But experiments on n-type samples show:

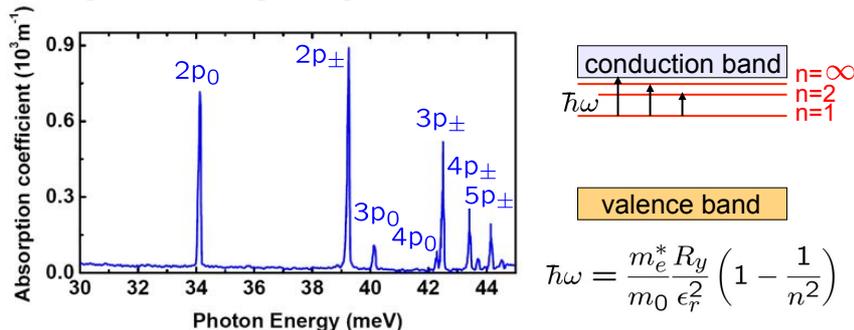
$$\alpha \propto \omega^{-\beta} \quad \text{where} \quad \beta \approx 2 - 3$$

Deviations arise from:

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

### Example: Impurity absorption in semiconductors

In doped semiconductors the electron (hole) and the ionized impurity are attracted by Coulomb interaction  $\implies$  hydrogenic system  
Absorption of Phosphor-doped silicon at 4.2K:



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

# Plasmons

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

What happens at this frequency?

- Polarization induced by the EM wave:

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

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

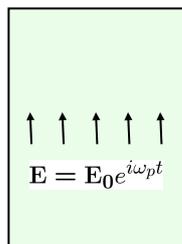
⇒  $\mathbf{P}$  is equal and opposite to incident field

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

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

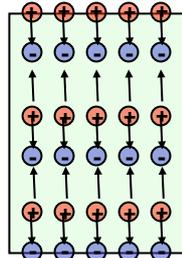
Plasma oscillations for  $\epsilon_r=0$ :

applied EM wave

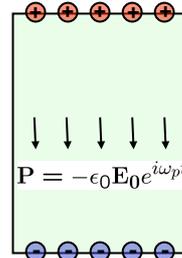


$k \approx 0 \rightarrow$

resulting charge distribution



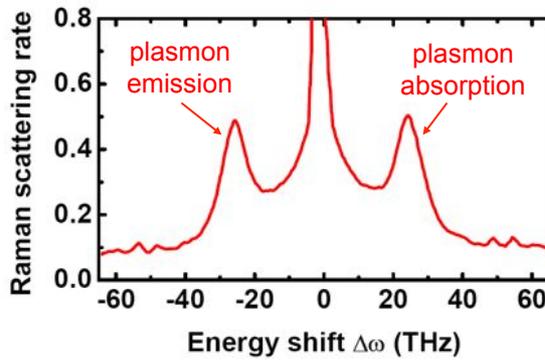
induced macroscopic polarization



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

### Example: Plasmons in n-type GaAs

Light scattered from n-type GaAs at 300K:



Energy conservation:

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

⇒ from data:

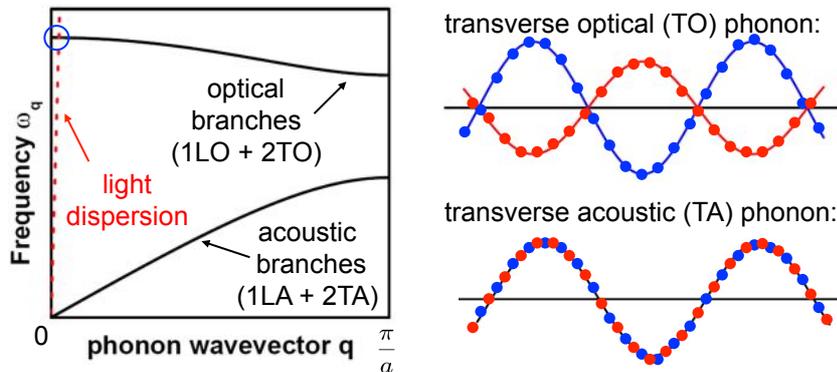
$$\omega_p = 25 \text{ THz}$$

Expect from:

$$\left. \begin{array}{l} N = 1.75 \times 10^{23} \text{ m}^{-3} \\ \epsilon_{\infty} = 10.6 \\ m_e^* = 0.067 m_e \end{array} \right\} \Rightarrow \omega_p = \left( \frac{Ne^2}{\epsilon_{\infty} \epsilon_0 m} \right)^{\frac{1}{2}} = 28 \text{ THz}$$

## VI Optical studies of phonons

Dispersion relation for a diatomic linear chain:



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

### Harmonic oscillator model for the ionic crystal lattice

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

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

Equations of motion:

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

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

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

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

Add damping term to account for finite phonon lifetime:

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

Displacement of ions induces polarization  $P = NQx$

⇒ Dielectric constant (as before):

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

Rewrite this result in terms of the static ( $\epsilon_s$ ) and the high-frequency ( $\epsilon_\infty$ ) limits of the dielectric constant:

$$\begin{aligned} \epsilon_s &\equiv \epsilon_r(0) = 1 + \chi_b + \frac{Q^2 N}{\epsilon_0 \mu \omega_{TO}^2} \\ \epsilon_\infty &\equiv \epsilon_r(\infty) = 1 + \chi_b \end{aligned}$$

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

### Lattice response in the low-damping limit

Long phonon lifetimes:  $\gamma \approx 0$

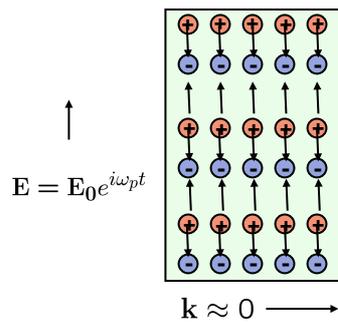
$$\Rightarrow \epsilon_r(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \frac{\omega_{TO}^2}{(\omega_{TO}^2 - \omega^2)}$$

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

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

### What happens at $\epsilon_r=0$ ?

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



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

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

### The Lyddane-Sachs-Teller relationship

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

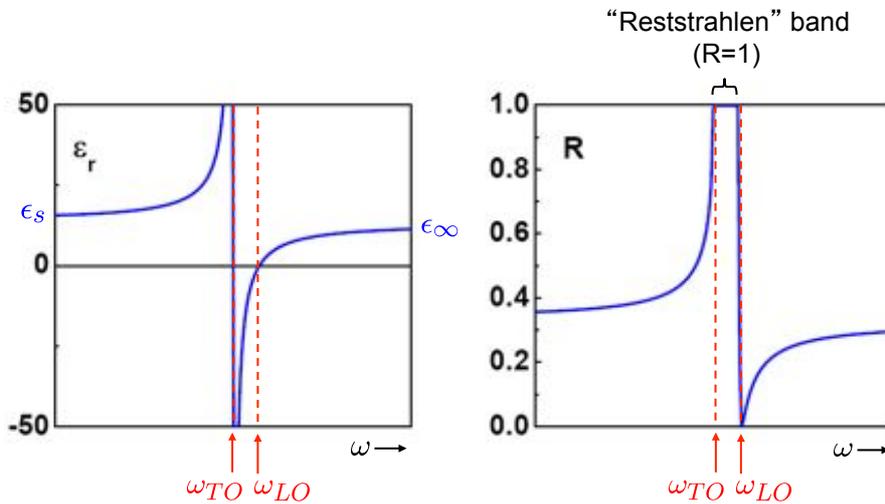
$$\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\epsilon_s}{\epsilon_\infty}$$

Lyddane-Sachs-Teller relationship

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

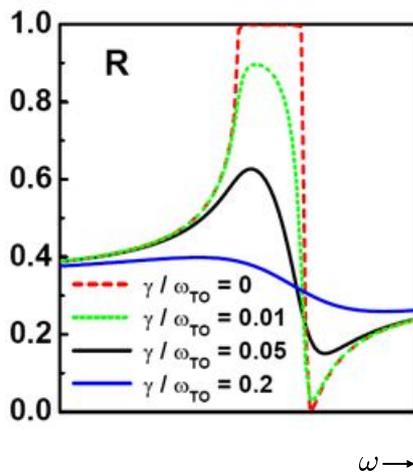
- In polar crystals the LO phonon frequency is always higher than the TO phonon frequency
- In non-polar crystals,  $\epsilon_s = \epsilon_\infty$  and the LO and TO phonon modes are degenerate (at the Brillouin zone centre)

## Dielectric constant and Reflectivity for undamped lattice



## Influence of damping

### Lattice Reflectivity:



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

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

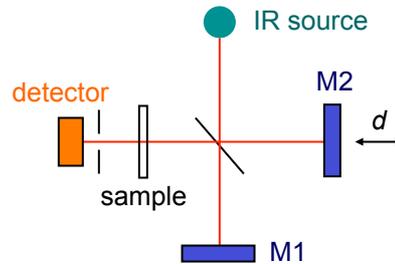
$$R(\omega_{TO}) = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} < 1$$

- Reststrahlen band no longer fully reflective
- general broadening of features

## Measurements of IR reflectivity

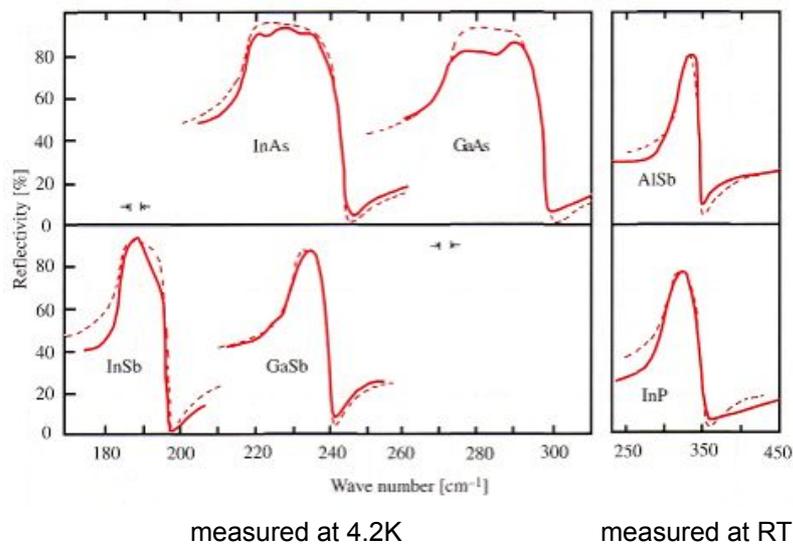
Fourier transform infrared spectroscopy (FTIR):

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



$$\begin{aligned}
 I(d) &= \int S(\nu) T(\nu) \left[1 + \cos\left(\frac{2\pi\nu d}{c}\right)\right] d\nu \\
 &= \frac{1}{2} I(0) + \int S(\nu) T(\nu) \cos\left(\frac{2\pi\nu d}{c}\right) d\nu
 \end{aligned}$$

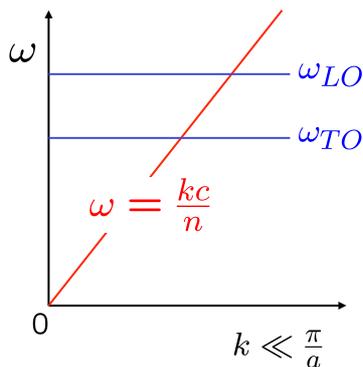
## Example: reflection spectra for zinc-blende-type lattices



## Phonon-Polaritons

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

If no coupling occurred:



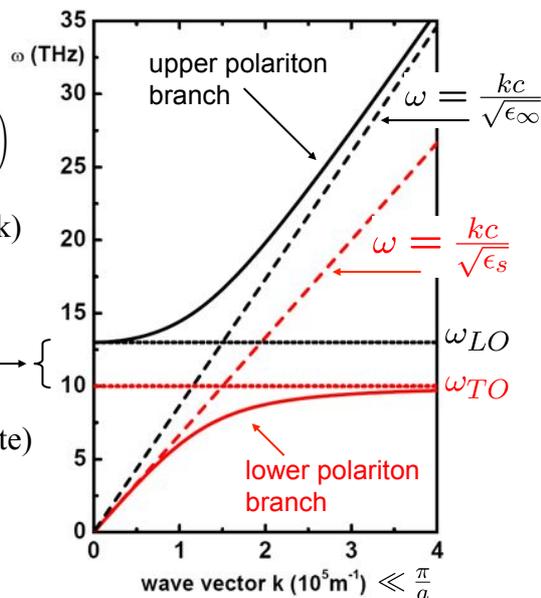
- But: coupling between TO phonon and EM wave leads to modified dispersion
- resulting wave is mixed mode with characteristics of TO polarization and EM wave
- LO phonon dispersion remains unchanged as it does not couple to the EM wave

### Phonon-Polariton dispersion:

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

→ two branches for  $\omega(k)$

Reststrahlen band (perfect reflection, no mode can propagate)



## Inelastic Light Scattering

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

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

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

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

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



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

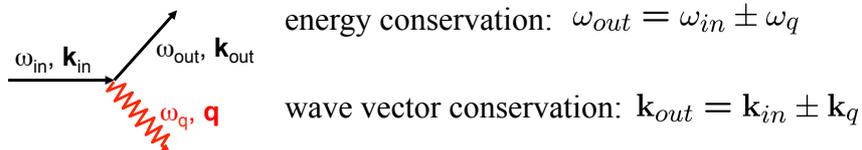
where

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

$$\begin{aligned} \mathbf{P}_{ind} = & \frac{1}{2} \epsilon_0 \left( \frac{\partial \chi}{\partial \mathbf{u}} \right)_{\mathbf{u}_0} \mathbf{u}_0 \mathbf{E}_0 \times \\ & \times \left\{ \underbrace{\cos[(\mathbf{k} + \mathbf{q}) \cdot \mathbf{r} - (\omega + \omega_q)t]}_{\text{Anti-Stokes scattering}} + \underbrace{\cos[(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r} - (\omega - \omega_q)t]}_{\text{Stokes scattering}} \right\} \end{aligned}$$

## Energy & momentum conservation for inelastic scattering

Scattering process:



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

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

Maximum momentum transfer in backscattering geometry, where:

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

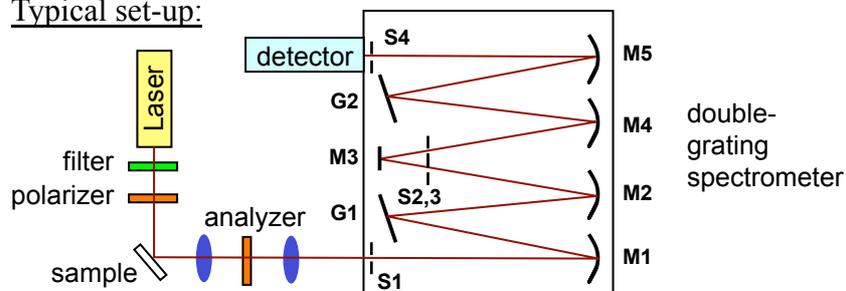
⇒ Inelastic light scattering probes phonons with small wave vector

## Raman spectroscopy: Experimental details

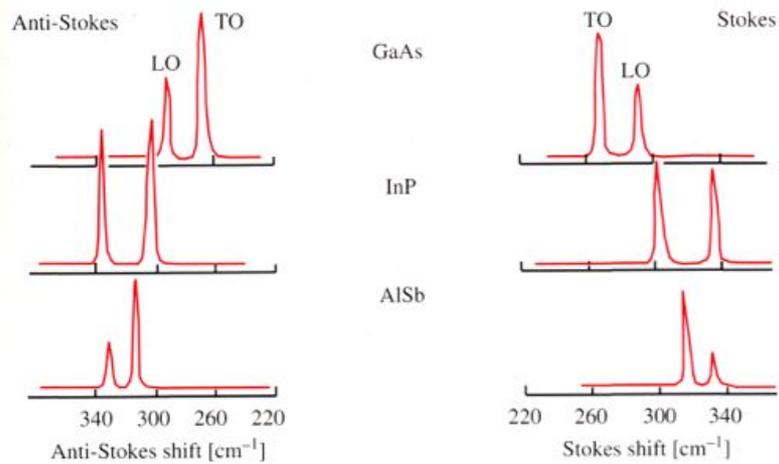
Require detection of optical phonons within typical frequency range  $1\text{cm}^{-1} < \omega_p < 3000\text{cm}^{-1}$

- need excitation source (laser) with sufficiently narrow bandwidth
- need detection system with high dispersion and ability to suppress elastically scattered light

Typical set-up:



## Raman spectra for zinc-blende-type semiconductors

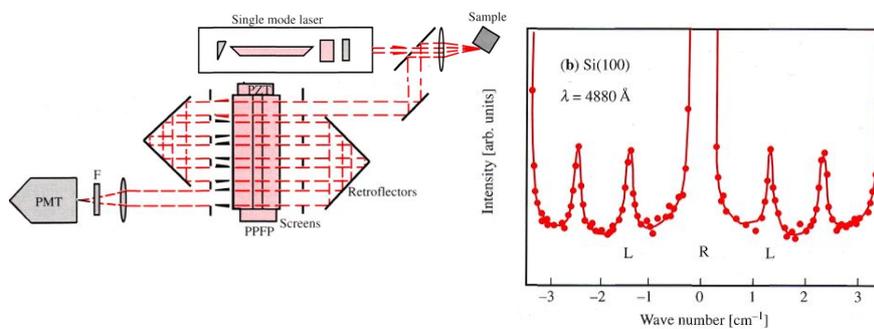


## Brillouin scattering: Experimental details

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

Set-up based on a Multipass Interferometer:

Brillouin spectrum for Si(100):



## Phonon lifetimes

Experimental evidence for finite phonon lifetimes from

i. Reflectivity measurements:  $R < 1$  in Reststrahlen band

$$\rightarrow \gamma = \tau_{\text{phonon}}^{-1} \neq 0$$

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

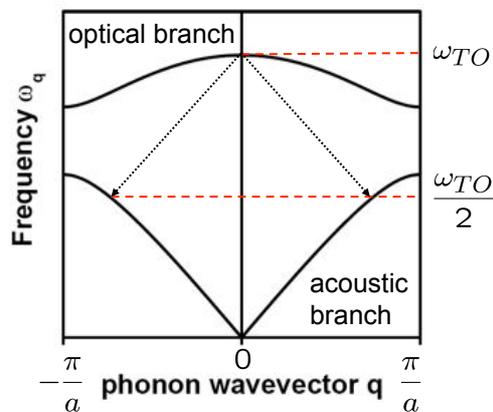
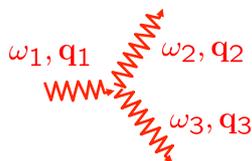
$$\Gamma = \frac{\hbar}{\tau_{\text{phonon}}}$$

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

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

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

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





## Propagation of plane waves in an isotropic medium

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

$$\left. \begin{array}{l} \mathbf{k} \times \mathbf{H} = -\omega \mathbf{D} \\ \mathbf{k} \times \mathbf{E} = \omega \mathbf{B} \end{array} \right\} \begin{array}{l} \mathbf{B} = \mu_0 \mathbf{H} \\ \mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E} \end{array} \rightarrow \mathbf{k} \times \mathbf{k} \times \mathbf{E} = -k_0^2 \epsilon_r \mathbf{E}$$

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

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

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

⇒ homogeneous matrix equation, require  $\det(\dots) = 0$

Solving the matrix equation ( $\det(\dots) = 0$ ) yields:

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

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

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

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

## Propagation of plane waves in uniaxial crystals

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

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

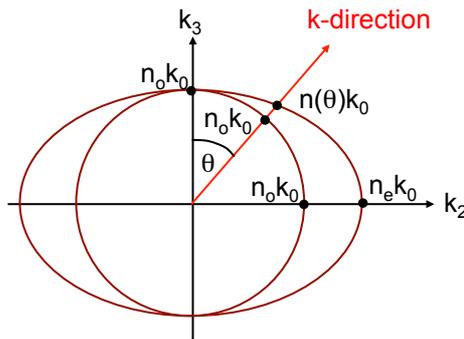
Two solutions:

(i) Sphere:  $k = n_o k_0$   
for ordinary ray  
(polarized  $\perp$  to k-z plane)

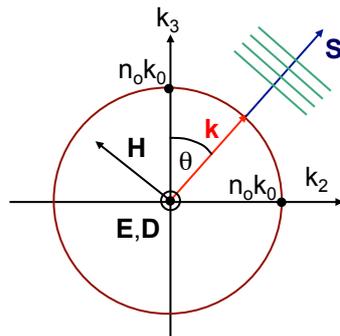
(ii) ellipsoid of revolution

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

for extraordinary ray  
(polarized in k-z plane)

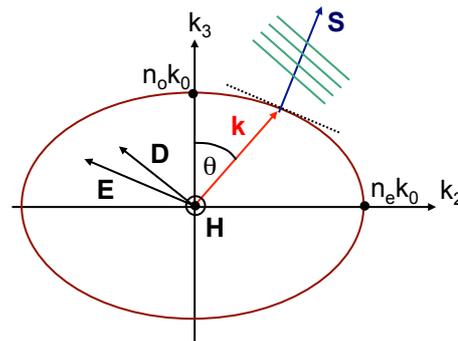


## Ordinary vs extraordinary rays in uniaxial crystals



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

$$n = n_o$$



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

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

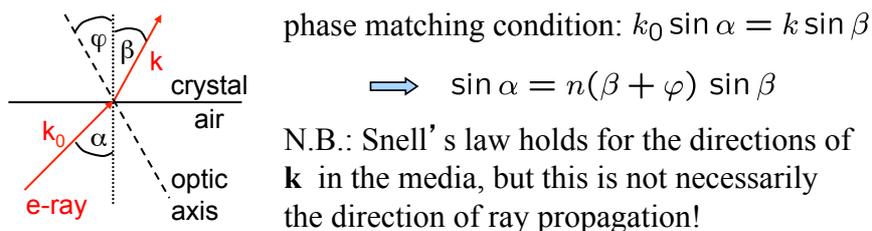
## Comments on wave propagation in uniaxial crystals

- 1) Faraday's & Ampere's law for plane waves in dielectrics:  
 $\mathbf{k} \times \mathbf{H} = -\omega \mathbf{D} \implies \mathbf{D}$  is normal to both  $\mathbf{k}$  and  $\mathbf{H}$   
 $\mathbf{k} \times \mathbf{E} = \omega \mu_0 \mathbf{H} \implies \mathbf{H}$  is normal to both  $\mathbf{k}$  and  $\mathbf{E}$   
 N.B.: this does *not* imply  $\mathbf{A} = \mathbf{A}_0 \exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$
- 2)  $\mathbf{E}$  fields are of the form  
 wavefronts are  $\perp$  to  $\mathbf{k}$ .
- 3)  $v = \omega/k = \omega/(nk_0)$  in the direction of  $\mathbf{k}$  with  

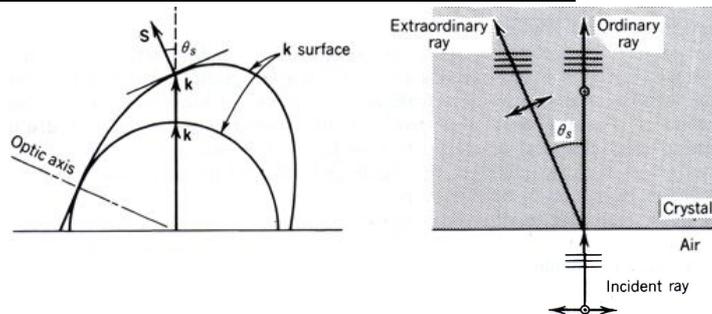
$$\mathbf{v}_g = \nabla_{\mathbf{k}} \omega(\mathbf{k})$$
- 4)  $\mathbf{S}$  usual, the group velocity is  

$$\mathbf{v}_g \text{ is normal to } \mathbf{S} = \frac{1}{2} \hat{\mathbf{E}} \times \hat{\mathbf{H}}^*$$
- 5) The point in  $\Delta \mathbf{k} \cdot \mathbf{S} = 0$  is normal to  $\mathbf{E}$  and  $\mathbf{H}$   
 Can show: for small  $\Delta \mathbf{k}$   $\mathbf{S}$  normal to  $\mathbf{k}$ -surface
- 6) From (5) and (1) follows that  $\mathbf{E}$  is parallel to the  $\mathbf{k}$ -surface.

## Refraction at the surface of a uniaxial crystal



Example: Double refraction at normal incidence:



## VIII Non-linear Optics

### Linear optics:

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

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

⇒ refractive index  $n$ , absorption coefficient  $\alpha$ , reflectivity  $R$  independent of incident EM wave's intensity

### But:

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

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

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

Possible with tightly focused laser beams!

## The non-linear susceptibility tensor

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

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

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

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

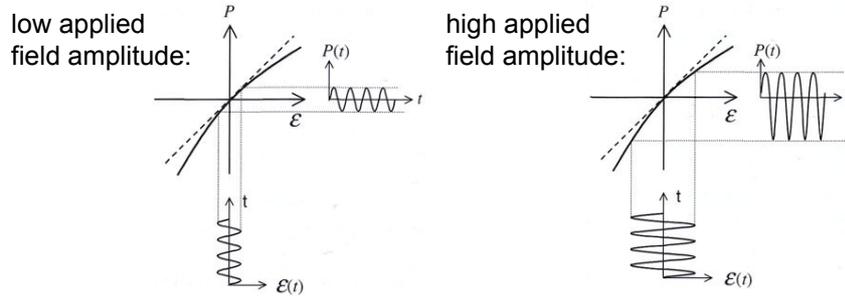
⇒ Second-order non-linear polarization components:

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

⇒ Third-order non-linear polarization components:

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

## Non-linear medium response to sinusoidal driving field



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

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

$$P = \epsilon_0 \chi E_0 \sin \omega t + \frac{1}{2} \epsilon_0 \chi^{(2)} E_0^2 (1 - \cos 2\omega t) - \frac{1}{4} \epsilon_0 \chi^{(3)} E_0^3 (3 \sin \omega t - \sin 3\omega t) + \dots$$

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

## Second-order nonlinearities (NL)

Treatment of non-resonant 2<sup>nd</sup> order NL within oscillator model:

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

Equation of motion:

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

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

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

Obtain displacement amplitudes: ⇒ 
$$\begin{cases} x_1 = -\frac{eE_0}{m} \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \\ x_2 = -C_3 x_1^2 \frac{1}{\omega_0^2 - (2\omega)^2 + i2\omega\gamma} \end{cases}$$

Calculating the induced polarization:

$$\begin{aligned}
 P &= -Nex \\
 &= -Nex_1 \exp(i\omega t) - Nex_2 \exp(i2\omega t) \\
 &= \epsilon_0 \chi E + \epsilon_0 \chi^{(2)} E^2
 \end{aligned}$$



$$\begin{aligned}
 \chi &= \frac{Ne^2}{m\epsilon_0} \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \quad \text{linear susceptibility, as before} \\
 \chi^{(2)} &= C_3 \frac{Ne^3}{m^2\epsilon_0} \frac{1}{(\omega_0^2 - \omega^2 + i\omega\gamma)^2 (\omega_0^2 - (2\omega)^2 + i2\omega\gamma)} \\
 &\quad \text{second-order non-linear susceptibility}
 \end{aligned}$$

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

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

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

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

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

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

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

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

But some of these components must be the same

(e.g.  $\chi_{xyz}^{(2)} E_y E_z = \chi_{xzy}^{(2)} E_z E_y$ , so  $\chi_{xyz}^{(2)} = \chi_{xzy}^{(2)}$  because ordering of fields is arbitrary)

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

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

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

2<sup>nd</sup> order NL: Frequency (three-wave) mixing

Presume two waves are travelling in the medium, with

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

The induced polarization is:

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

sum-frequency generation
difference-frequency generation

Feynman diagrams for second-order nonlinear frequency mixing:



## 2<sup>nd</sup> order NL: Frequency doubling

Consider the generation of second harmonics in more detail:

Maxwell's equations:

$$\begin{aligned} \nabla \times \mathbf{E} &= -\frac{d}{dt}(\mu_0 \mathbf{H}) \\ \nabla \times \mathbf{H} &= \frac{d}{dt} \mathbf{D} = \frac{d}{dt}(\epsilon_0 \mathbf{E} + \underbrace{\epsilon_0 \chi \mathbf{E} + \mathbf{P}^{(2)}}_{\mathbf{P}}) \end{aligned}$$

⇒ Wave equation:

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

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

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

Let this wave be generated from two fundamental waves:

$$\begin{aligned} E_j^\omega(z, t) &= \hat{E}_j^\omega(z) \exp[i(\omega t - k_\omega z)] \\ E_k^\omega(z, t) &= \hat{E}_k^\omega(z) \exp[i(\omega t - k_\omega z)] \end{aligned}$$

⇒ Obtain specific wave equation:

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

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

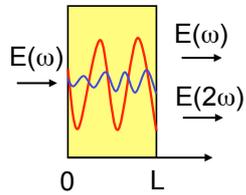
$$\frac{d^2}{dz^2} \hat{E}_i^{2\omega}(z) \ll k_{2\omega} \frac{d}{dz} \hat{E}_i^{2\omega}(z)$$

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

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

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

2<sup>nd</sup> order NL: Phase matching conditions



For efficient frequency conversion, we need the fundamental wave and the higher harmonic to be in phase throughout the crystal, i.e.  $\Delta k = 0$  where

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

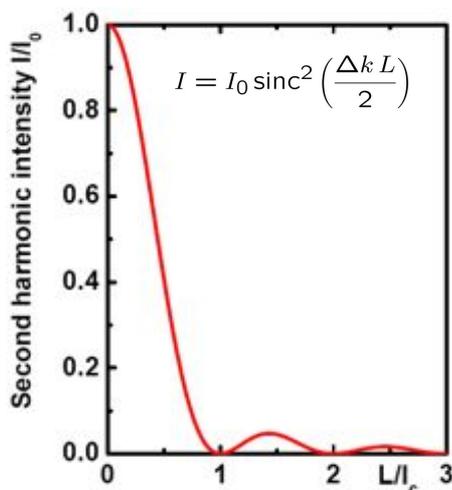
The second-harmonic field at length L for arbitrary  $\Delta k$  is:

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

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

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

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



First intensity minimum at:

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

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

Example: Sapphire

$$n_o(2.806\text{eV}) = 1.780$$

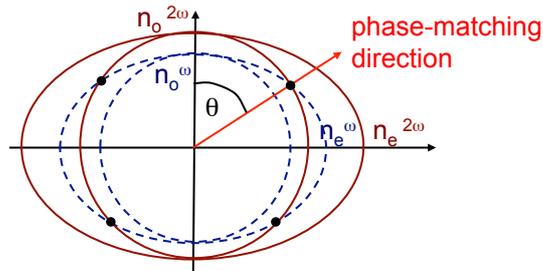
$$n_o(1.403\text{eV}) = 1.757$$

$$\Rightarrow l_c = 19\mu\text{m}$$

→ need too thin a crystal to achieve efficient 2<sup>nd</sup> harmonics generation

## 2<sup>nd</sup> order NL: Phase matching in a uniaxial crystal

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



Here, phase matching occurs for the fundamental travelling as extraordinary (polarization in plane) and the 2<sup>nd</sup> harmonic as ordinary (polarization  $\perp$  to plane) with  $\frac{1}{(n_o^{2\omega})^2} = \frac{\sin^2 \theta}{(n_e^\omega)^2} + \frac{\cos^2 \theta}{(n_o^\omega)^2}$

## Third-order nonlinearities

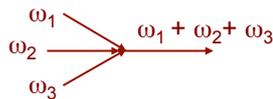
Third-order effects become important in centrosymmetric (e.g. isotropic media) where  $\chi_{ijk}^{(2)} = 0$

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

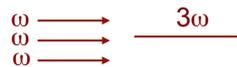
$$P_i^{(3)} = \epsilon_0 \sum_{j,k,l} \chi_{ijkl}^{(3)} \hat{E}_j \hat{E}_k \hat{E}_l \cos(\omega_1 t) \cos(\omega_2 t) \cos(\omega_3 t)$$

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

(a) four-wave mixing



(b) frequency tripling



(c) Optical Kerr effect



(d) stimulated Raman scattering



3<sup>rd</sup> order NL: The optical Kerr effect

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

⇒ no phase mismatch

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

In an isotropic medium ( $\chi^{(2)}=0$ ):  $\epsilon_r^{NL} = \underbrace{1 + \chi}_{\epsilon_r} + \underbrace{\frac{3}{4} \chi^{(3)} E^2}_{\Delta \epsilon}$

Refractive index:

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

$$n = n_0 + \frac{3 \chi^{(3)}}{4 \cdot 2 n_0} E^2$$

$$= n_0 + n_2 I \quad \text{where} \quad n_2 = \frac{3 \chi^{(3)}}{4 n_0^2 c \epsilon_0}$$

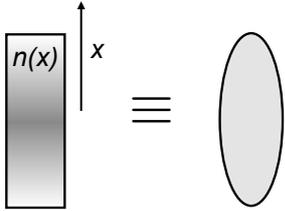
↙  
light intensity

⇒ Refractive index varies with light intensity!

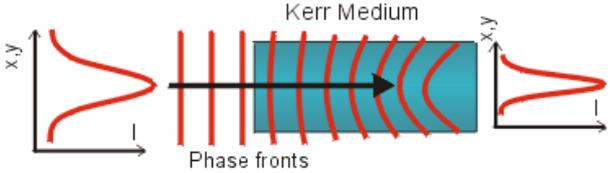
Example: Kerr lensing

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

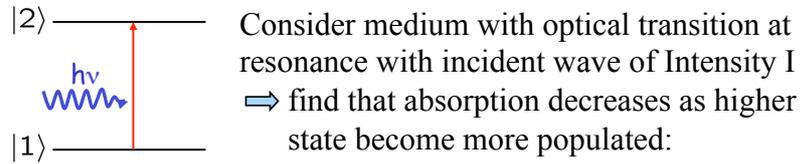
Laser beam with spatially varying profile (e.g. Gaussian beam) experiences in the medium a higher refractive index at the centre of the beam than the outside → medium acts as a lens!



Propagation of an intense gaussian beam through a Kerr medium:



### 3<sup>rd</sup> order NL: Resonant nonlinearities



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

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

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

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