

Optical Properties of Solids

LM Herz

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Contents:

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

Recommended textbooks

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

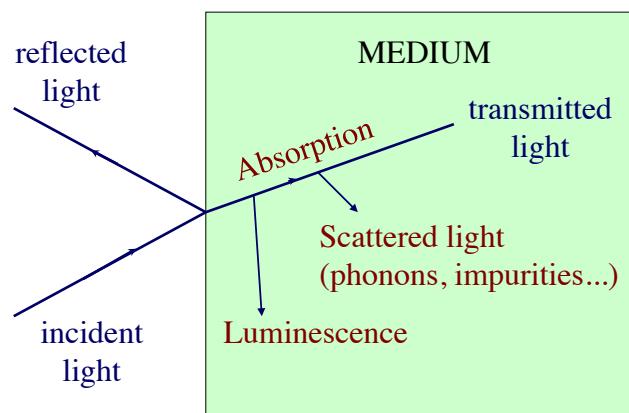
PY Yu and M Cardona, *Fundamentals of Semiconductors*,
Springer

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:

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

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

aa

$$\rho = 0 \quad (\text{no net free charge})$$

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

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

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

Linear Optics

In a linear, non-conducting medium:

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

$$\text{Solution: } \mathbf{E} = E_0 \exp [i(kz - \omega t)]$$

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

→ Define complex refractive index:

$$\tilde{n} \equiv \sqrt{\epsilon_r} \equiv n + i\kappa$$

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 ϵ_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

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

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

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:

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

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:

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

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

background

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

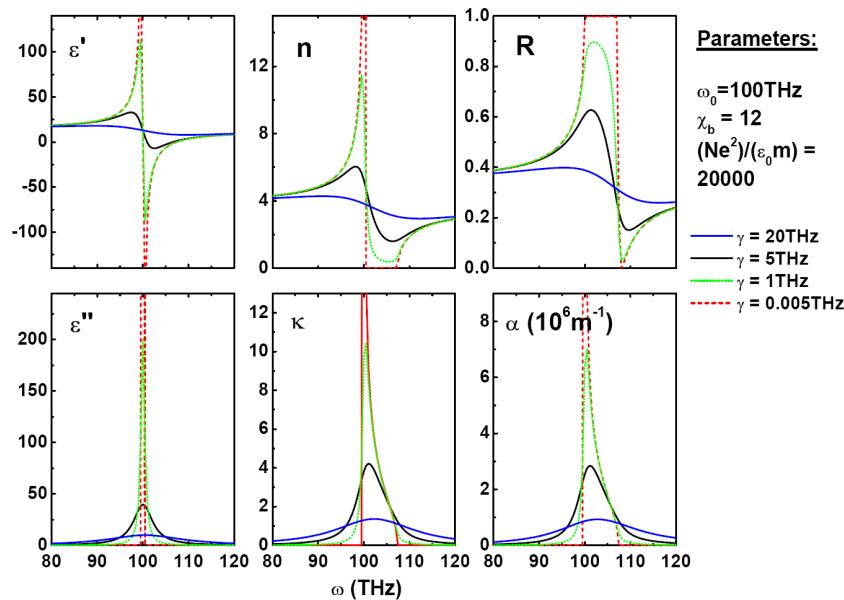
Real and imaginary part of ϵ_r

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



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

Optical constants for a classical dipole oscillator



Local field corrections

In a dense medium:

- atoms experience “local field” composed of external field \mathbf{E} and polarization from surrounding dipoles
- treat interacting dipole as being at centre of sphere surrounded by a polarized dielectric

➡ Clausius-Mossotti relationship:

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

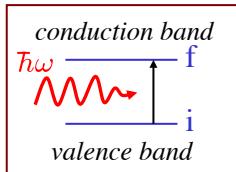
electric susceptibility per atom

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:

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

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

where $V(\mathbf{r}) = -e \underbrace{\mathbf{r} \cdot \mathbf{E}}_{\text{dipole moment}} \quad \begin{matrix} \mathbf{E} = \mathbf{E}_0 \cos(\mathbf{k} \cdot \mathbf{r}) \\ \text{E-field of incident wave} \end{matrix}$

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

Matrix element for interband transitions:

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

absorption
emission

→ deduce conditions for dipole allowed (direct) transitions.

Consider:

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

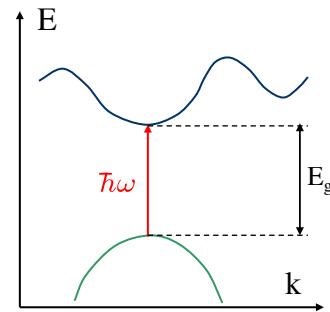
Conditions for direct interband transitions

(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: $\mathbf{k} \ll \mathbf{k}_i, \mathbf{k}_f$
 → “vertical” transitions



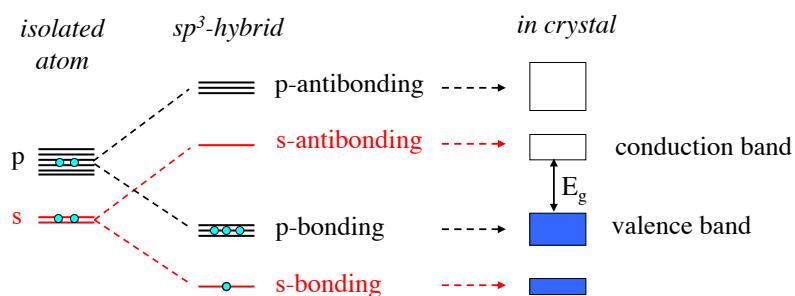
(2) parity selection rule

$$M_{if} \propto eE_0 \cdot \int u_c^*(\mathbf{r}) \mathbf{r} u_v(\mathbf{r}) d^3r$$

odd parity

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

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



→ expect to see strong absorption for these materials

(3) Dependence of transition probability on photon energy

Final state is an electron-hole pair

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

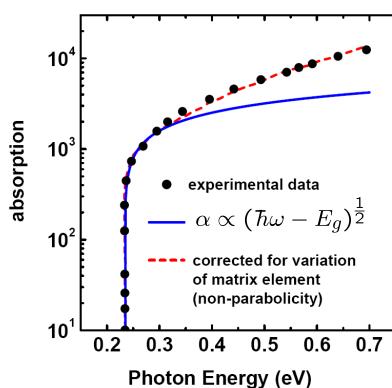
where $\mu = (\frac{1}{m_e^*} + \frac{1}{m_h^*})^{-1}$ reduced effective mass

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

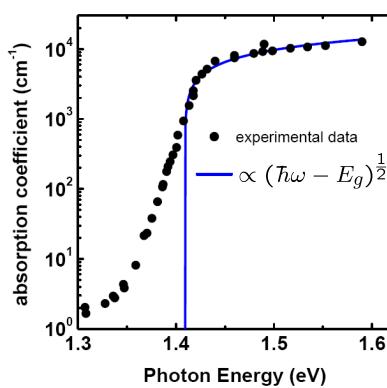
Absorption coefficient
(for direct transitions): $\alpha \propto (\hbar\omega - E_g)^{\frac{1}{2}}$

Examples for direct semiconductors

a) InSb at 5K



b) GaAs at 300K



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

Indirect interband transitions

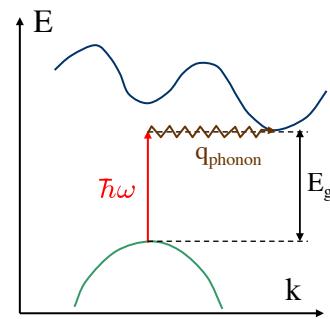
- Indirect gap: valence band maximum and conduction band minimum lie at different wavevectors, $\mathbf{k}_v^{max} \neq \mathbf{k}_c^{min}$
- direct transitions across the indirect gap forbidden, but phonon-assisted transitions may be possible.

(i) wavevector conservation:

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

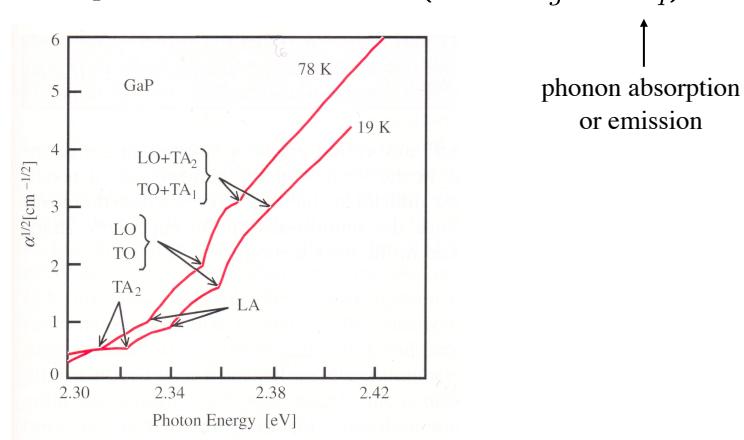
with phonon wavevector

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



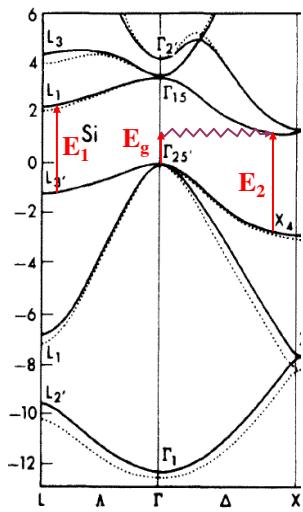
(ii) probability for indirect transitions:

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

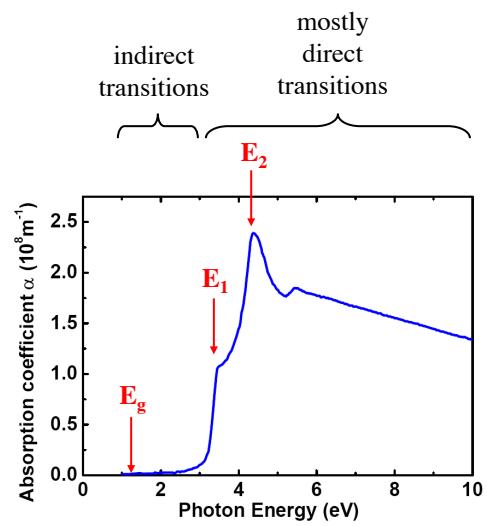


Example for an indirect semiconductor: Si

Band structure:

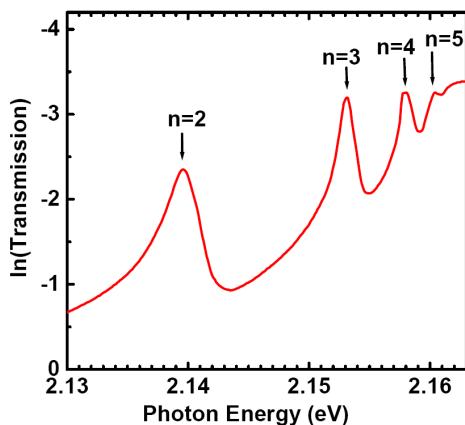


Absorption spectrum:



III Excitons

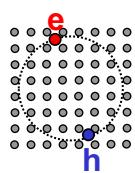
Absorption coefficient of CuO₂ at 77K:



Series of absorption peaks just below the energy gap

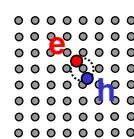
Coulomb interaction between electron and hole gives rise to “excitonic” states (bound electron-hole pairs)

Wannier-Mott Excitons



- weakly bound (free) excitons
- binding energy $\sim 10\text{meV}$
- common in inorganic semiconductors (e.g. GaAs, CdS, CuO₂...)
- particle moving in a medium of effective dielectric constant ϵ_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 $\mathbf{k}_h = -\mathbf{k}_v$

$$\text{exciton mass: } m_X = m_e^* + m_h^*$$

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

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

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

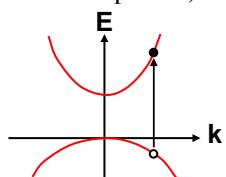
$$\mu = (\frac{1}{m_e^*} + \frac{1}{m_h^*})^{-1} \quad \text{reduced mass}$$

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

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

E-k diagram for the weakly bound exciton

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



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

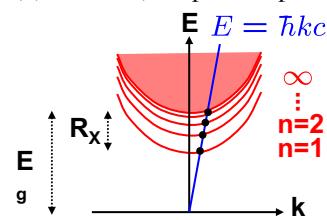
wavevector conservation:

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

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

→ “vertical transitions”

(b) exciton (one-particle picture)



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

wavevector conservation:

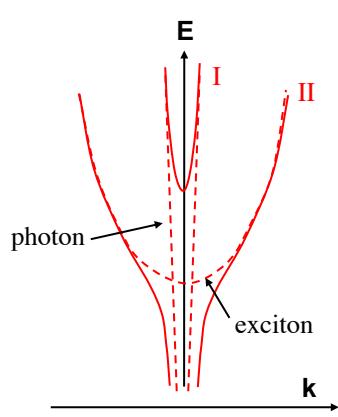
$$\mathbf{k}_X = \mathbf{k}_e - \mathbf{k}_v = \mathbf{k}_{photon}$$

→ transitions where light line $E = \hbar k c$ intercepts with E_X

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

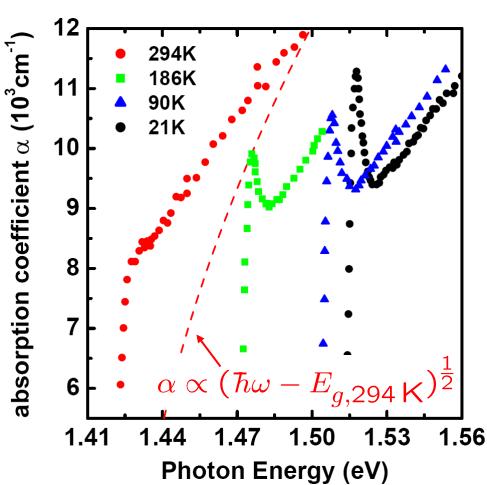
→ $E_X \rightarrow E_g$ for $n \rightarrow \infty$
continuum onset at band edge

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.

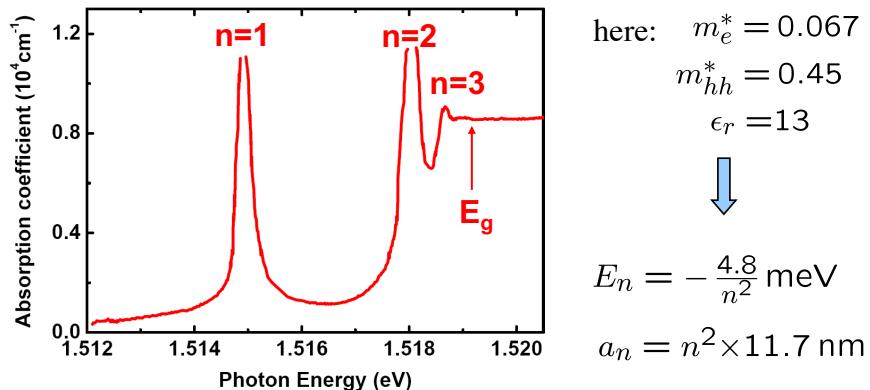
Examples for weakly bound excitons: GaAs



- 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:



Tightly bound (Frenkel) excitons

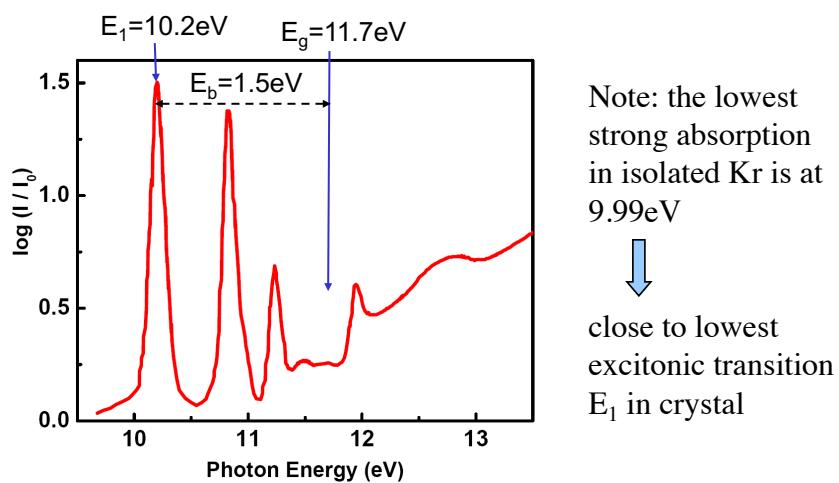
- radius of weakly-bound excitons: $a_n = \epsilon_r \frac{m_e}{\mu} n^2 a_0$
 - model of bound e-h pair in dielectric medium breaks down when a_n is of the order of interatomic distances (Å)
 - have tightly bound excitons for small ϵ_r , large μ
- tightly-bound electron-hole pair, typically located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

Transition energies for tightly bound excitons

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

Examples for tightly bound excitons: rare gas crystals

absorption spectrum of crystalline Kr at 20K:



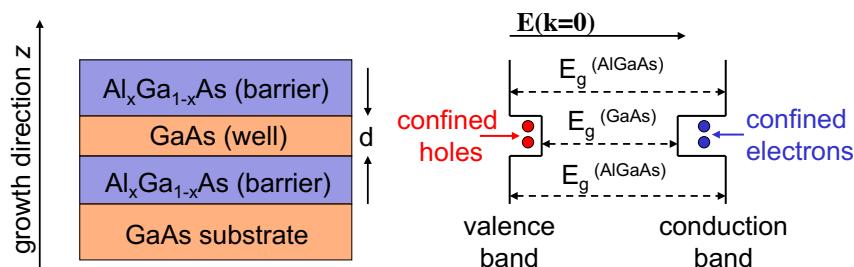
VI Low-dimensional systems

de Broglie wavelength for an electron at room temperature:

$$\lambda = \frac{h}{p} \approx \frac{h}{\sqrt{m_e k T}} \approx 10 \text{ nm}$$

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

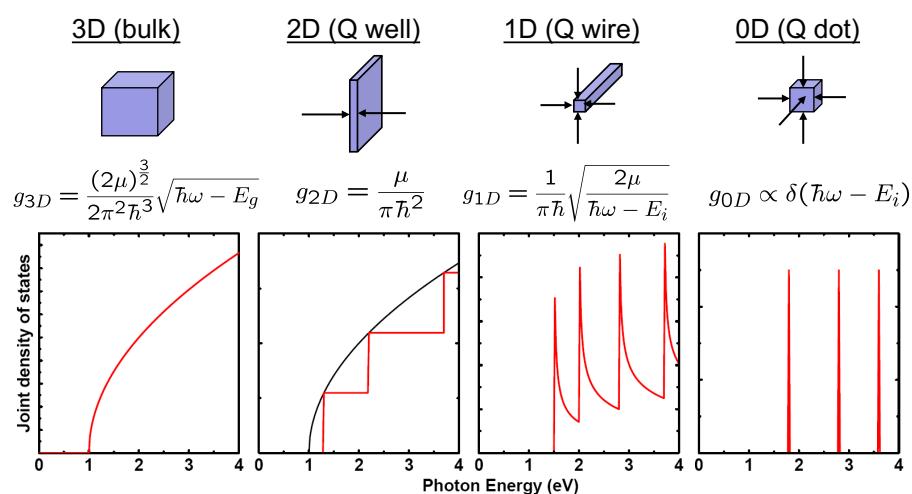
Possible using e.g. *molecular beam epitaxy* (MBE) or *metal-organic chemical vapour deposition* (MOCVD)



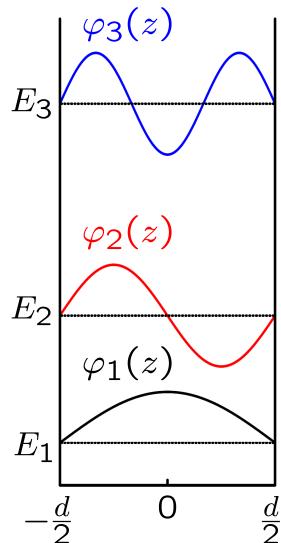
Effect of confinement on the DOS

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(ħω) (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:

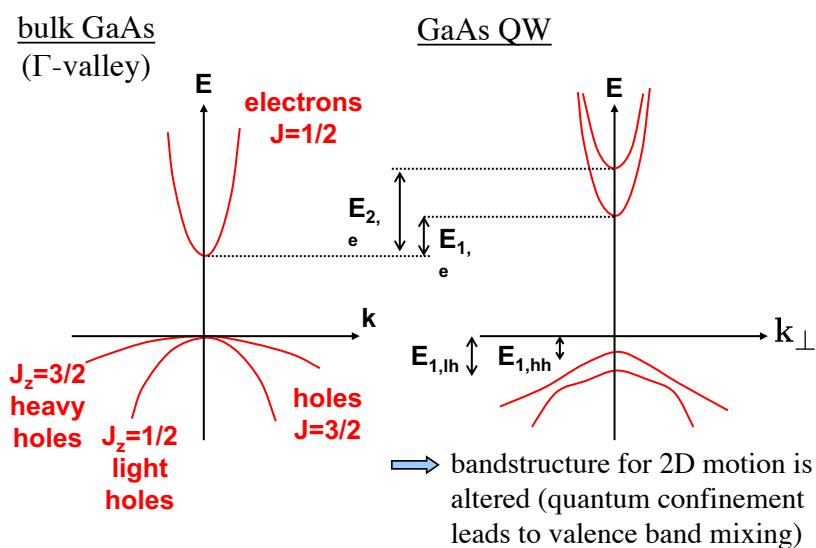
$$\varphi_n(z) = \sqrt{\frac{2}{d}} \sin\left(k_n z + \frac{n\pi}{2}\right)$$

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



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:

$$\psi_i(\mathbf{r}) = \underbrace{\frac{1}{\sqrt{V_0}} u_v(\mathbf{r}) \exp(i \mathbf{k}_{\perp,v} \cdot \mathbf{r}_{\perp})}_{\text{valence/conduction band Bloch function}} \varphi_{n,v}(z)$$

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

- $$\begin{aligned} & \text{(i) } \varphi(z) \text{ changes slowly over a unit cell (compared to } u_c, u_v) \\ & \text{(ii) } M_{if} \approx 0 \text{ unless } \mathbf{k}_{\perp,v} = \mathbf{k}_{\perp,c} \pm \mathbf{k}_{photon} (\text{k-conservation}) \\ \implies M_{if} & \propto e \mathbf{E}_0 \cdot \underbrace{\int u_c^*(\mathbf{r}) \mathbf{r} u_v(\mathbf{r}) d^3 r}_{M_{CV}} \times \underbrace{\int \varphi_{n,c}^*(z) \varphi_{n',v}(z) dz}_{M_{n,n'}} \\ & \text{dipole transition criteria (as before)} \qquad \qquad \qquad \text{electron-hole spatial overlap in well} \end{aligned}$$

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

$\left. \begin{array}{l} \\ \\ \end{array} \right\}$ as before

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

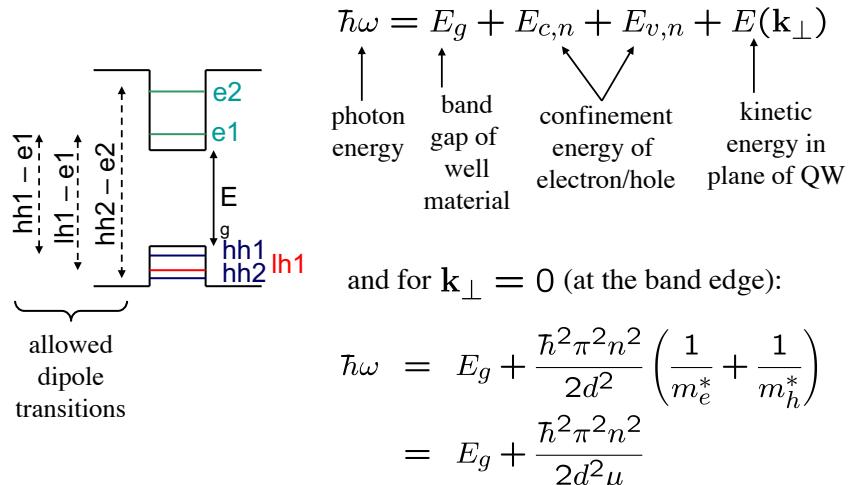
$$M_{n,n'} = \frac{2}{d} \int_{\frac{d}{2}}^{-\frac{d}{2}} \sin\left(k_n z + \frac{n\pi}{2}\right) \sin\left(k_{n'} z + \frac{n'z}{2}\right) dz$$

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

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

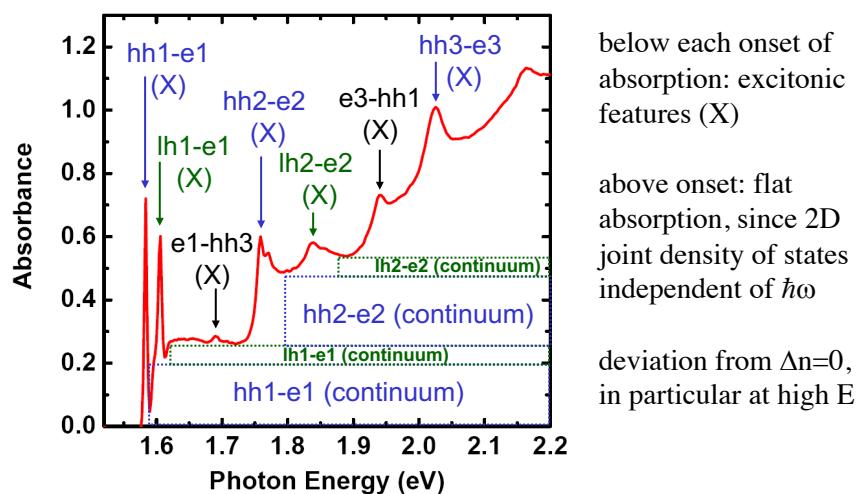
- (iv) $M_{n,n'} = 0$ unless $\varphi_{n,c}(z)$ and $\varphi_{n',v}(z)$ have equal parity

(v) energy conservation:

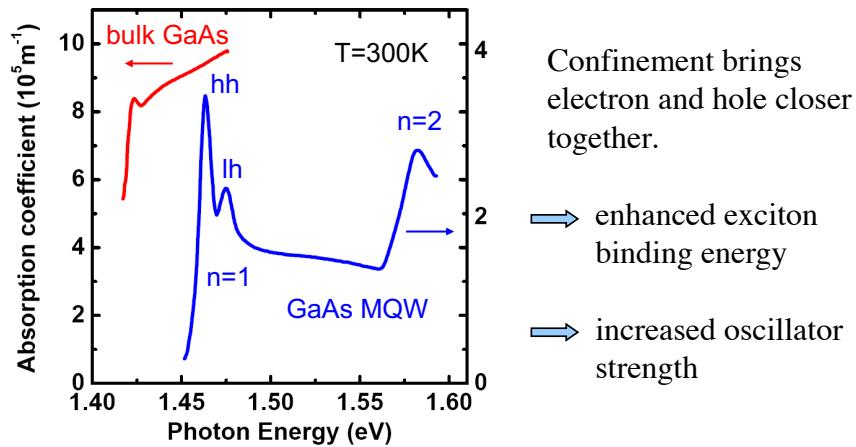


Example: absorption of a GaAs/AlAs QW

Absorption of GaAs/AlAs MQW ($d=76\text{\AA}$) at 4K:



Influence of confinement on the exciton



V Optical response of a free electron gas

Classic Lorentz dipole oscillator model (again):

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

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

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

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

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

→ real and imaginary part of the dielectric constant:

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

AC conductivity of a free electron gas

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

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

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

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

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

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

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

optical measurements of ϵ_r equivalent to those of AC conductivity!

Low-frequency regime

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

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

ϵ' ϵ''

$\Rightarrow \epsilon'' \gg \epsilon'$ 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: $\sigma_0 = 6.5 \times 10^7 \Omega^{-1} m^{-1}$
 $\Rightarrow \delta = 8.8 \text{ mm} @ \nu = 50 \text{ Hz}$
 $\delta = 6.2 \mu\text{m} @ \nu = 100 \text{ MHz}$

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)

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

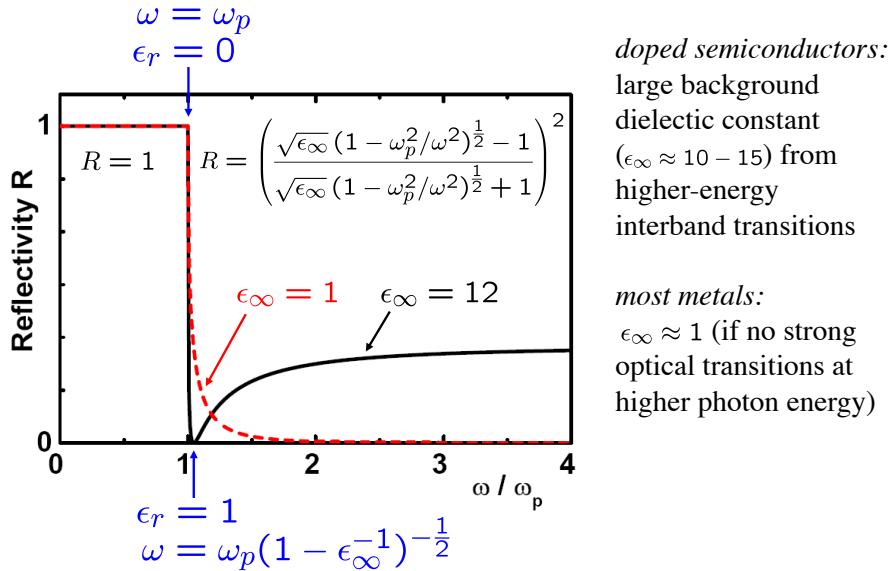
(i) $\omega < \omega_p$ $\epsilon' < 0$ \tilde{n} largely imaginary

$R \approx 1$ wave mostly reflected

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

$R < 1$ wave partly transmitted,
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)	λ_p (nm)	λ_{UV} (nm)
Li	4.70	1.95	154	205
Na	2.65	1.46	205	210
K	1.40	1.06	282	315
Rb	1.15	0.96	312	360
Cs	0.91	0.86	350	440

\uparrow measured at low T $\underbrace{\quad}_{\omega_p = \left(\frac{Ne^2}{\epsilon_0 m} \right)^{1/2}}$ calculated from \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}m^{-3})	$\omega_p/2\pi$ (10^{15}Hz)	λ_p (nm)
Cu	8.47	2.61	115
Ag	5.86	2.17	138
Au	5.90	2.18	138

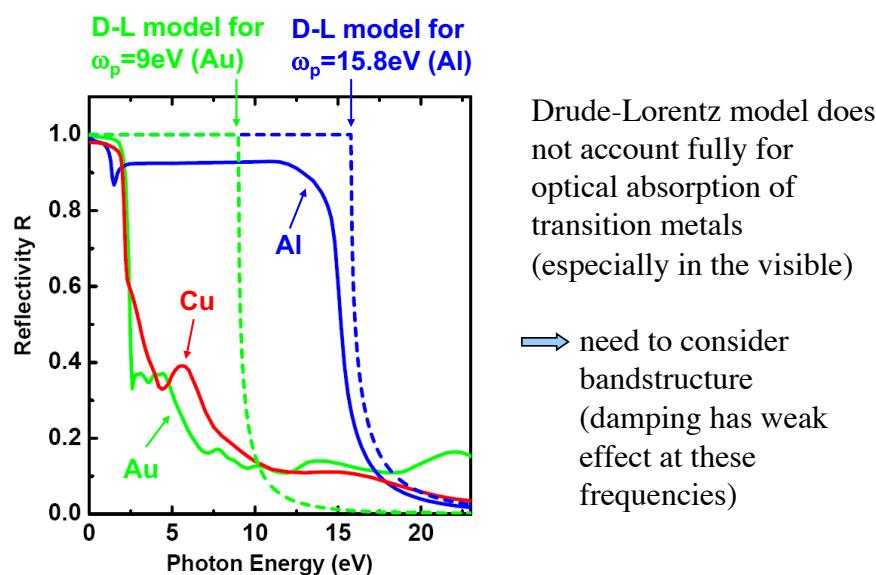
↑ measured at low T calculated from $\omega_p = \left(\frac{Ne^2}{\epsilon_0 m} \right)^{\frac{1}{2}}$

These transition metals should be fully reflective up to deep UV

But we know: Gold appears yellow, Copper red



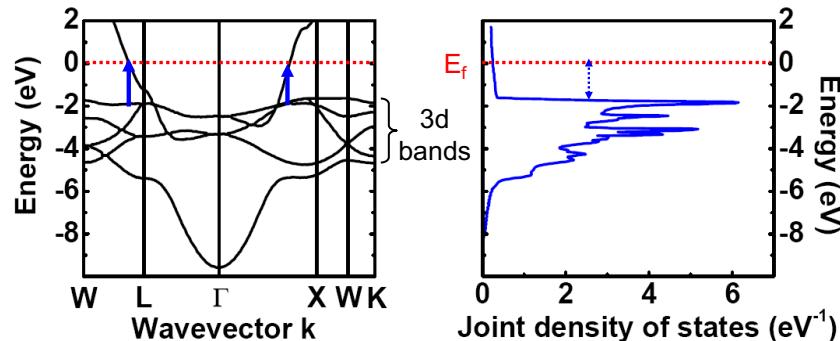
Reflection of light from Au, Cu and Al:



Example: Reflection from Copper

Electronic configuration of Cu: [Ar] 3d¹⁰ 4s¹

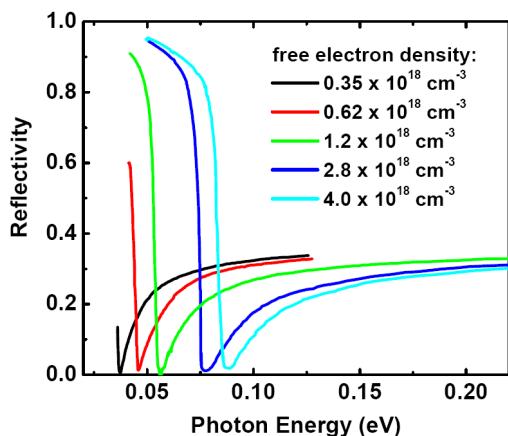
Transitions (in visible range of spectrum) between relatively dispersionless bands of tightly bound 3d electrons and half-filled band of 4s-electrons:



strong interband absorption for $\hbar\omega \geq 2 \text{ eV}$ → 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 ($\epsilon'' \ll \epsilon'$):

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

But experiments on n-type samples show:

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

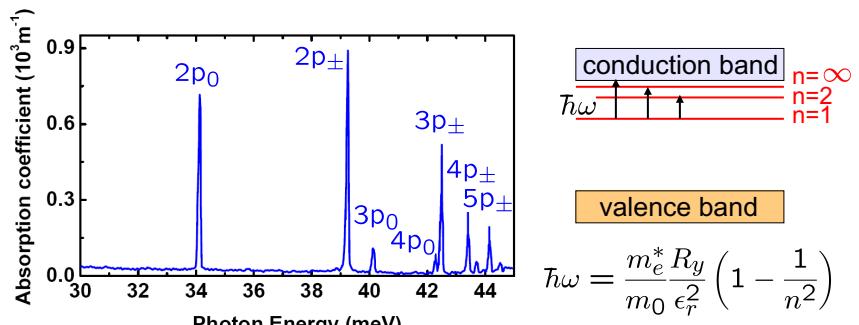
Deviations arise from:

- 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 \Rightarrow hydrogenic system

Absorption of Phosphor-doped silicon at 4.2K:



\Rightarrow 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 $\mathbf{E} = E_0 \exp[-i(\omega_p t - kz)]$

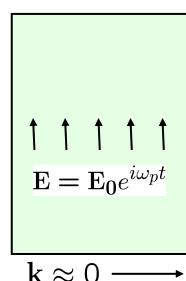
➡ \mathbf{P} is equal and opposite to incident field

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

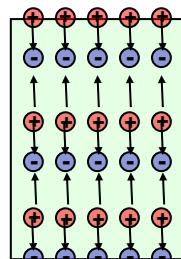
➡ At the Plasma edge a uniform E-field in the material shifts the collective electron w.r.t the ionic lattice!

Plasma oscillations for $\epsilon_r=0$:

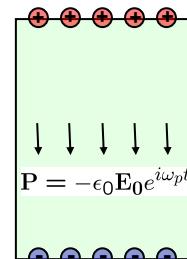
applied EM wave



resulting charge distribution



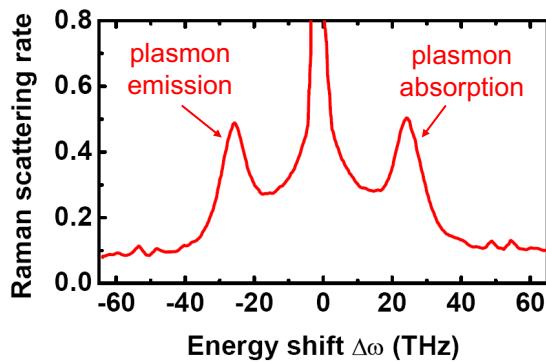
induced macroscopic polarization



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

Example: Plasmons in n-type GaAs

Light scattered from n-type GaAs at 300K:



Energy conservation:

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

→ from data:

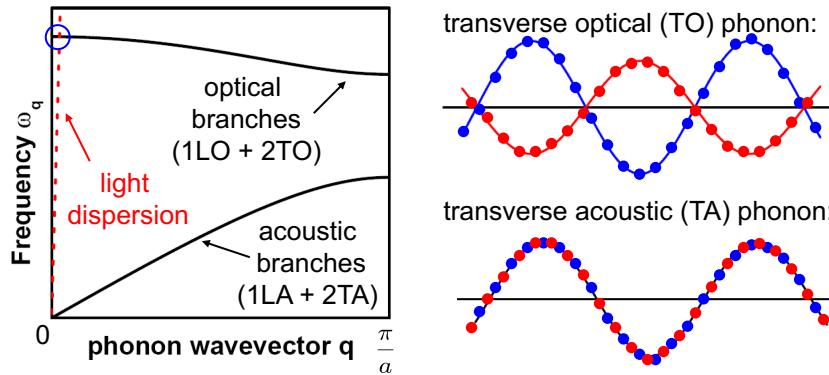
$$\omega_p = 25 \text{ THz}$$

Expect $N = 1.75 \times 10^{23} \text{ m}^{-3}$ }
 from: $\epsilon_\infty = 10.6$ }
 $m_e^* = 0.067m_e$ }

→
$$\omega_p = \left(\frac{Ne^2}{\epsilon_\infty \epsilon_0 m} \right)^{\frac{1}{2}} = 28 \text{ THz}$$

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

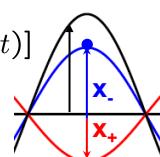
Diatomeric linear chain under the influence of an external electric field:

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

Equations of motion:

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

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



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

$$x = x_+ - x_- \quad \text{relative displacement of positive and negative ions}$$

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 $P = NQx$

\Rightarrow 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 (ϵ_s) and the high-frequency (ϵ_∞) 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: $\gamma \approx 0$

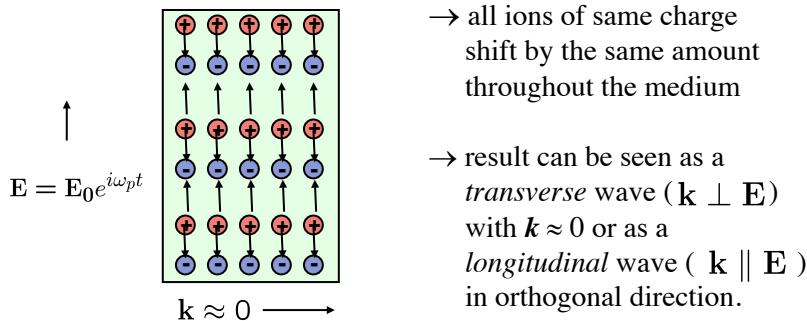
$$\Rightarrow \epsilon_r(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \frac{\omega_{TO}^2}{(\omega_{TO}^2 - \omega^2)}$$

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

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

What happens at $\epsilon_r=0$?

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



The Lyddane-Sachs-Teller relationship

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

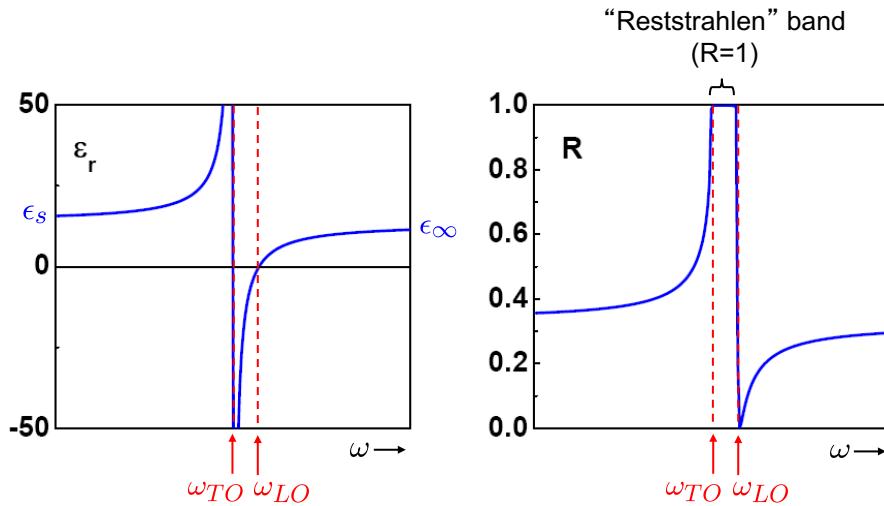
$$\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\epsilon_s}{\epsilon_\infty}$$

Lyddane-Sachs-Teller
 relationship

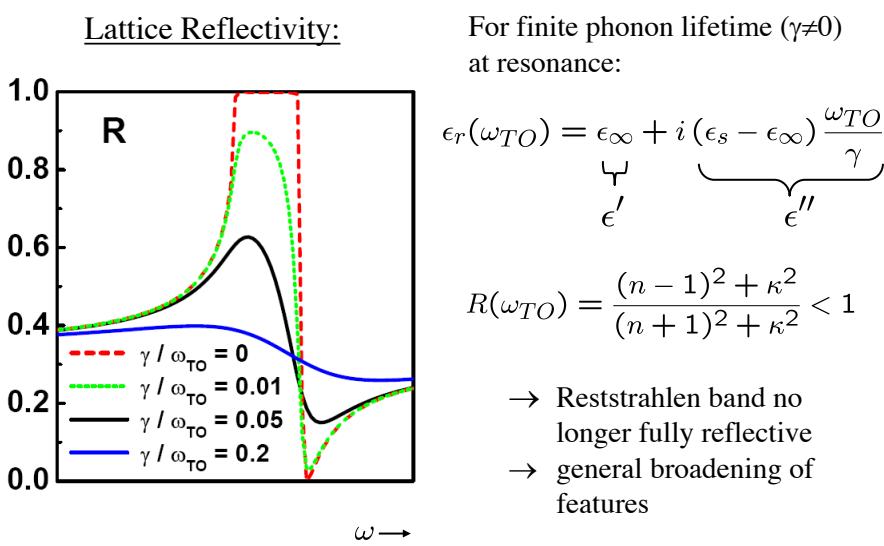
And from $\epsilon_s = \epsilon_\infty + \frac{Q^2 N}{\epsilon_0 \mu \omega_{TO}^2}$ follows: $\omega_{LO} \geq \omega_{TO}$

- 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



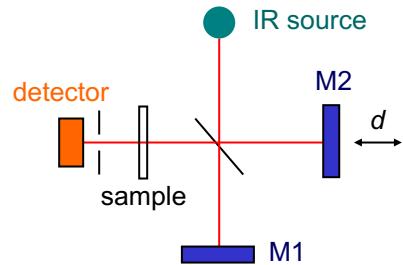
Influence of damping



Measurements of IR reflectivity

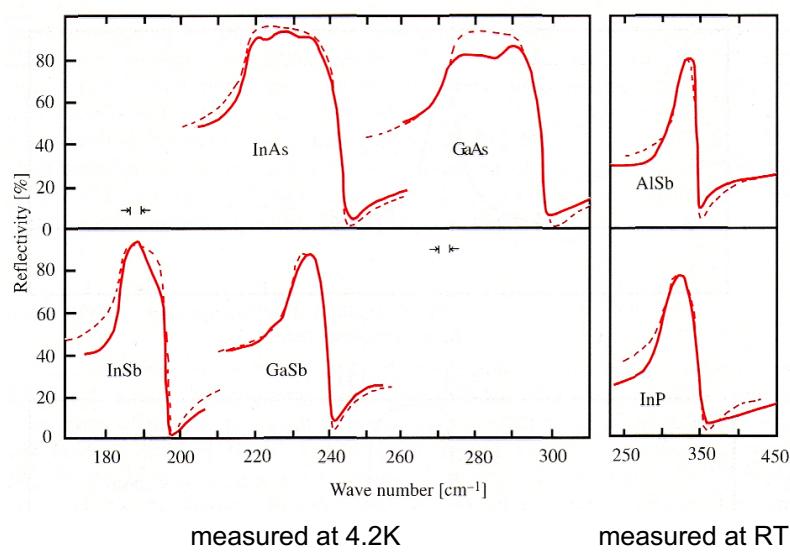
Fourier transform infrared spectroscopy (FTIR):

- 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 $S(\nu)$:



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

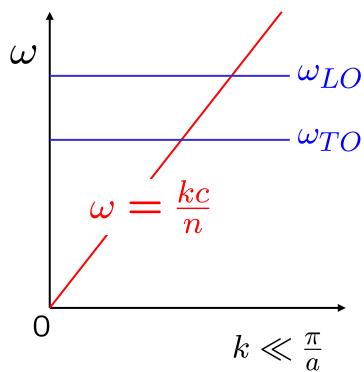
Example: reflection spectra for zinc-blende-type lattices



Phonon-Polaritons

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

If no coupling occurred:



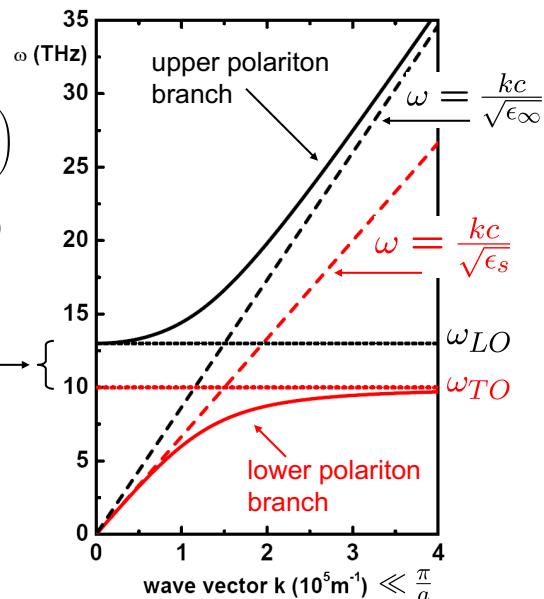
- But: coupling between TO phonon and EM wave leads to modified dispersion
- resulting wave is mixed mode with characteristics of TO polarization and EM wave
- LO phonon dispersion remains unchanged as it does not couple to the EM wave

Phonon-Polariton dispersion:

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

→ two branches for $\omega(k)$

Reststrahlen band
(perfect reflection,
no mode can propagate)



Inelastic Light Scattering

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

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

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

let $\mathbf{E} = E_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$ light wave with frequency ω

$\mathbf{u} = u_0 \cos(\mathbf{q} \cdot \mathbf{r} - \omega_q t)$ lattice wave with frequency ω_q



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

where

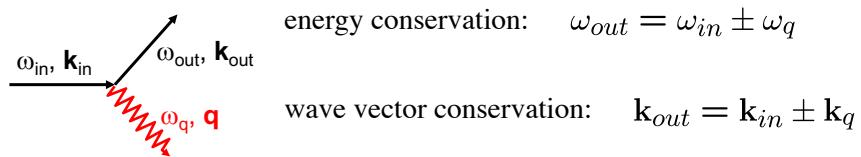
$\mathbf{P}_0 = \epsilon_0 \chi(\omega) \mathbf{E}_0 \cos \omega t$ unscattered polarization wave

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

$\underbrace{}_{\text{Stokes scattering}}$

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:

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

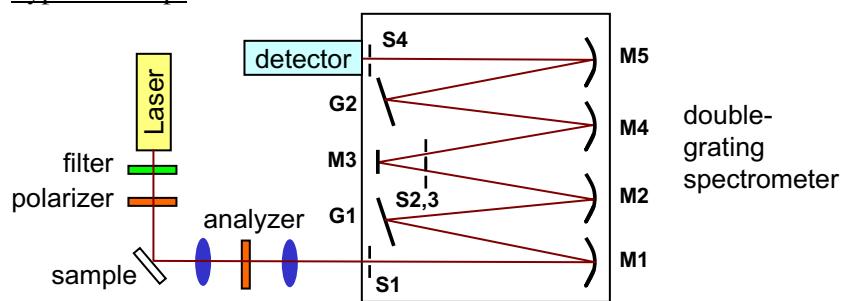
→ Inelastic light scattering probes phonons with small wave vector

Raman spectroscopy: Experimental details

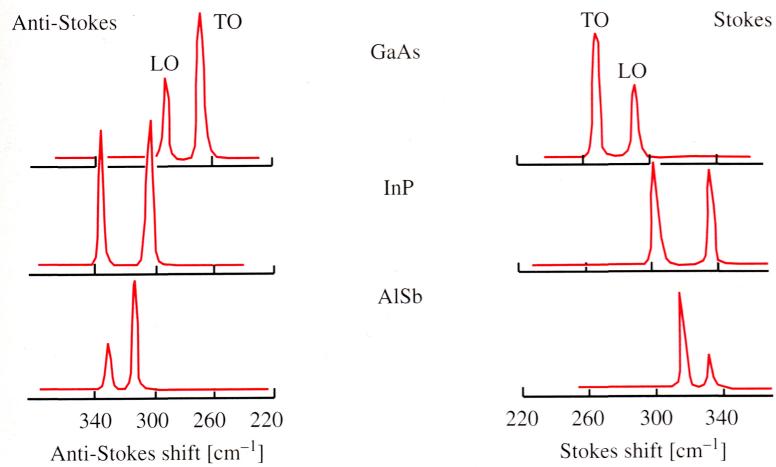
Require detection of optical phonons within typical frequency range
 $1\text{cm}^{-1} < \omega_p < 3000\text{cm}^{-1}$

- 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

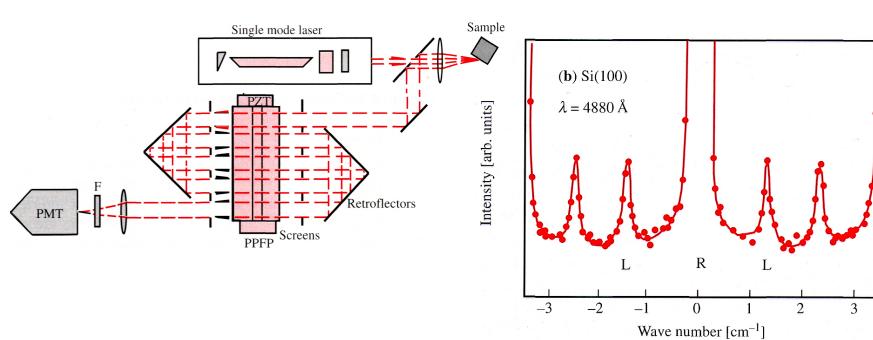


Brillouin scattering: Experimental details

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

Set-up based on a Multipass Interferometer:

Brillouin spectrum for Si(100):



Phonon lifetimes

Experimental evidence for finite phonon lifetimes from

- i. Reflectivity measurements: $R < 1$ in Reststrahlen band
 $\rightarrow \gamma = \tau_{phonon}^{-1} \neq 0$
- ii. Raman scattering: non-zero width of Raman line

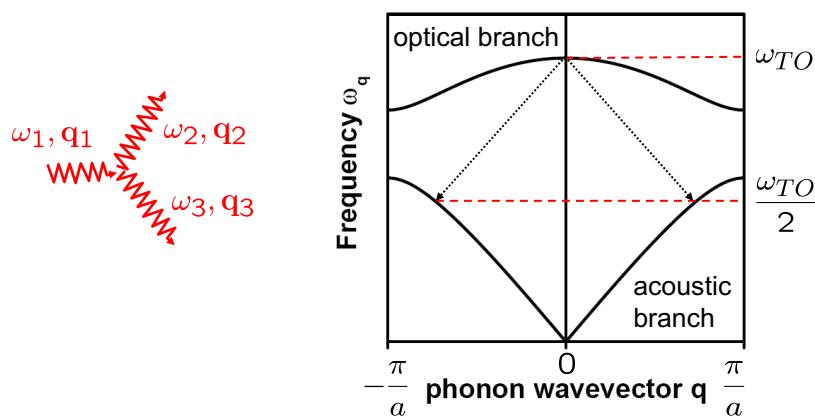
$$\Gamma = \frac{\hbar}{\tau_{phonon}}$$

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

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

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

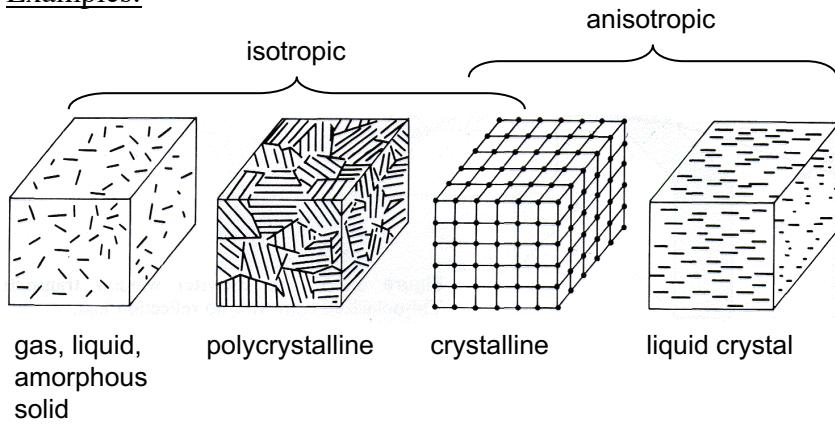
Anharmonic terms make possible higher-order processes, e.g.
phonon-phonon scattering:



VII Optics of anisotropic media

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

Examples:



ϵ_r and χ in an anisotropic medium

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

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

→ \mathbf{D} and \mathbf{E} no longer necessarily point into the same direction!

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

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

In the directions of these principal crystal axes \mathbf{E} and \mathbf{D} are parallel.

Propagation of plane waves in an isotropic medium

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

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

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 $\det(\cdot \cdot \cdot) = 0$

Solving the matrix equation ($\det(\cdot \cdot \cdot) = 0$) 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): $\epsilon_1 = \epsilon_2 = n_o^2$ $\epsilon_3 = n_e^2$

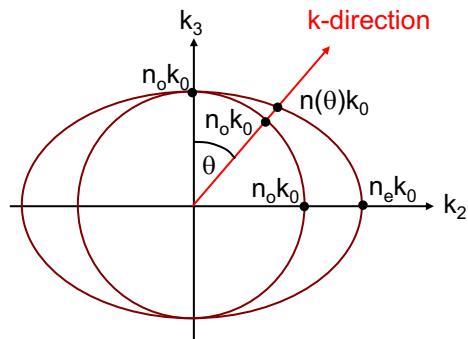
$$\Rightarrow (k_0^2 n_o^2 - k^2) \left[\frac{k_1^2 + k_2^2}{n_e^2} + \frac{k_3^2}{n_o^2} - k_0^2 \right] = 0$$

Two solutions:

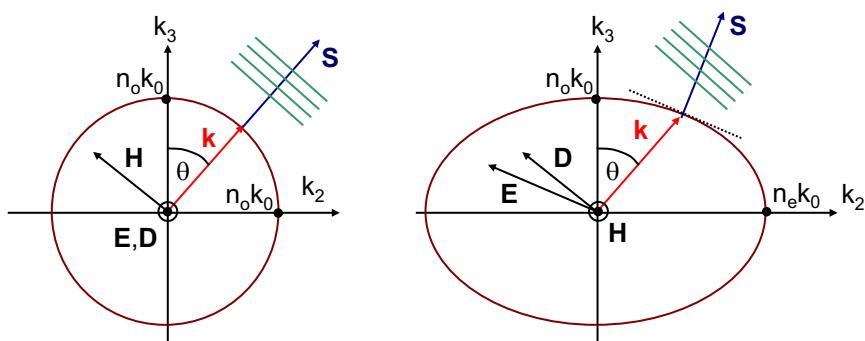
- (i) Sphere: $k = n_o k_0$
for *ordinary ray*
(polarized \perp to k-z plane)
- (ii) ellipsoid of revolution

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

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:

$$n = n_o$$

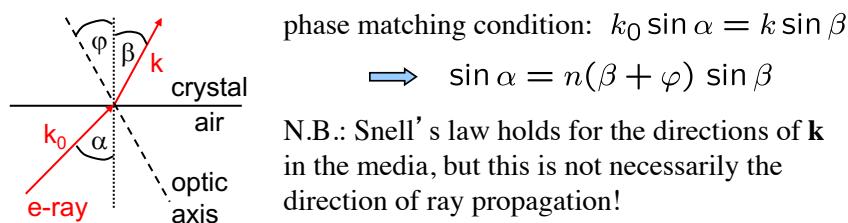
(b) extraordinary ray:
E, D polarized in plane
containing **k** and the optic axis

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

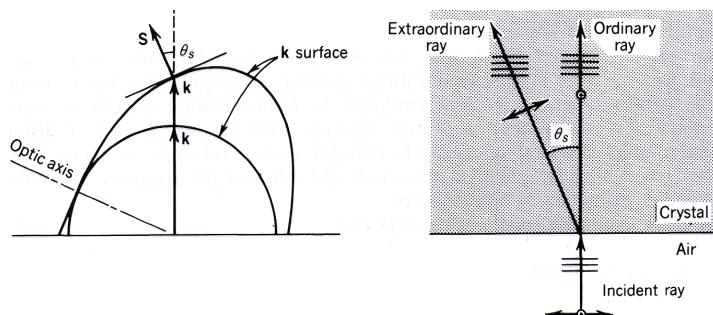
Comments on wave propagation in uniaxial crystals

- 1) Faraday's & Ampere's law for plane waves in dielectrics:
 $\mathbf{k} \times \mathbf{H} = -\omega \mathbf{D}$ $\rightarrow \mathbf{D}$ is normal to both \mathbf{k} and \mathbf{H}
 $\mathbf{k} \times \mathbf{E} = \omega \mu_0 \mathbf{H}$ $\rightarrow \mathbf{H}$ is normal to both \mathbf{k} and \mathbf{E}
 N.B.: this does *not* imply $\mathbf{E} \perp \mathbf{k}$!
- 2) All fields are of the form $\mathbf{A} = \mathbf{A}_0 \exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$
 \rightarrow wavefronts are \perp to \mathbf{k} .
- 3) The phase velocity v is in the direction of \mathbf{k} with
 $v = \omega/k = \omega/(nk_0)$
- 4) As usual, the group velocity is
 $\rightarrow \mathbf{v}_g$ is normal to the \mathbf{k} -surface! $\mathbf{v}_g = \nabla_{\mathbf{k}}\omega(\mathbf{k})$
- 5) The pointing vector $\mathbf{S} = \frac{1}{2}\mathbf{E} \times \mathbf{H}^*$ is normal to \mathbf{E} and \mathbf{H}
 Can show: $\Delta\mathbf{k} \cdot \mathbf{S} = 0$ for small $\Delta\mathbf{k}$ $\rightarrow \mathbf{S}$ 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 $U(x) = \frac{1}{2} m \omega_0^2 x^2$
 \Rightarrow refractive index n , absorption coefficient α , reflectivity R
 independent of incident EM wave's intensity

But:

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

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

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

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

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

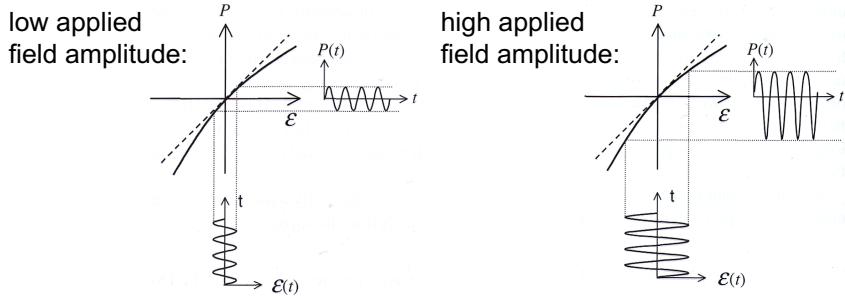
\Rightarrow Second-order non-linear polarization components:

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

\Rightarrow 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:

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

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

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

Second-order nonlinearities (NL)

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

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

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:

$$\rightarrow \begin{cases} x_1 = -\frac{e E_0}{m} \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \\ x_2 = -C_3 x_1^2 \frac{1}{\omega_0^2 - (2\omega)^2 + i2\omega\gamma} \end{cases}$$

Calculating the induced polarization:

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



$$\chi = \frac{Ne^2}{m\epsilon_0} \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \quad \text{linear susceptibility, as before}$$

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

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.

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

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

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

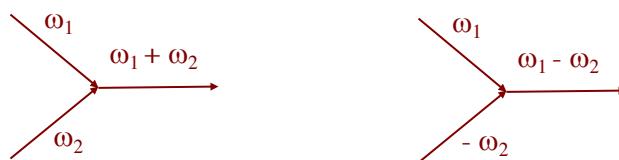
Presume two waves are travelling in the medium, with

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

The induced polarization is:

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

Feynman diagrams for second-order nonlinear frequency mixing:



2nd order NL: Frequency doubling

Consider the generation of second harmonics in more detail:

Maxwell's equations:

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

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

⇒ Wave equation:

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

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

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

Let this wave be generated from two fundamental waves:

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

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

⇒ Obtain specific wave equation:

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

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

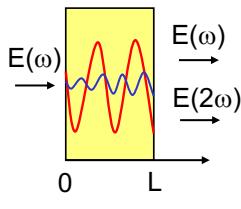
$$\frac{d^2}{dz^2} \hat{E}_i^{2\omega}(z) \ll k_{2\omega} \frac{d}{dz} \hat{E}_i^{2\omega}(z)$$

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

2nd order NL: Phase matching conditions



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

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

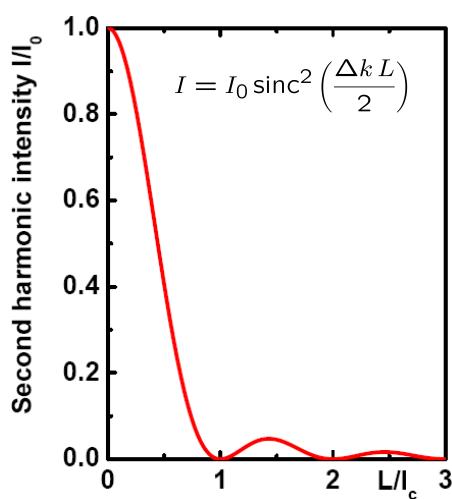
The second-harmonic field at length L for arbitrary Δk is:

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

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

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

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: $n_{2\omega} \neq n_\omega$

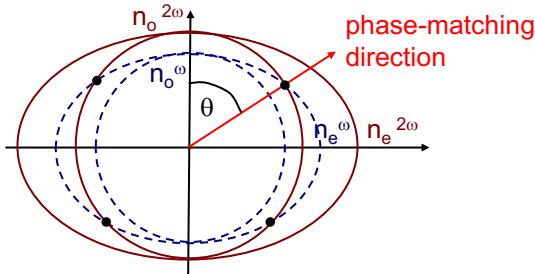
Example: Sapphire

$$\begin{aligned} n_o(2.806\text{eV}) &= 1.780 \\ n_o(1.403\text{eV}) &= 1.757 \end{aligned}$$

$\rightarrow l_c = 19\mu\text{m}$
 \rightarrow need too thin a crystal to achieve efficient 2nd harmonics generation

2nd order NL: Phase matching in a uniaxial crystal

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



Here, phase matching occurs for the fundamental travelling as extraordinary (polarization in plane) and the 2nd 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

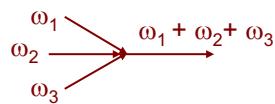
Third-order effects become important in centrosymmetric (e.g. isotropic media) where $\chi_{ijk}^{(2)} = 0$

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 $\omega_4 = \pm \omega_1 \pm \omega_2 \pm \omega_3$:

(a) four-wave mixing



(b) frequency tripling



(c) Optical Kerr effect



(d) stimulated Raman scattering



3rd order NL: The optical Kerr effect

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

➡ no phase mismatch

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

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

Refractive index:

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

$$\begin{aligned} n &= n_0 + \frac{3\chi^{(3)}}{42n_0} E^2 \\ &= n_0 + n_2 I \quad \text{where} \quad n_2 = \frac{3}{4} \frac{\chi^{(3)}}{n_0^2 c \epsilon_0} \end{aligned}$$

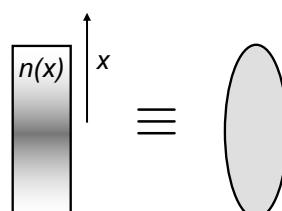
light intensity

➡ Refractive index varies with light intensity!

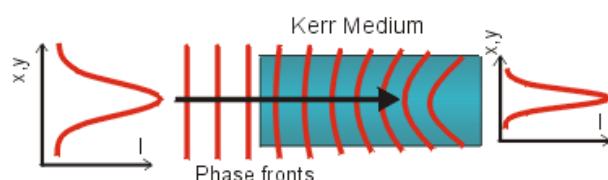
Example: Kerr lensing

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

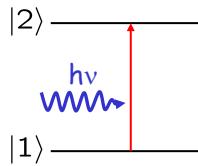
Laser beam with spatially varying profile (e.g. Gaussian beam) experiences in the medium a higher refractive index at the centre of the beam than the outside → medium acts as a lens!



Propagation of an intense gaussian beam through a Kerr medium:



3rd order NL: Resonant nonlinearities



Consider medium with optical transition at resonance with incident wave of Intensity I
 → find that absorption decreases as higher state become more populated:

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

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

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

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