Optical Properties of Solids
LM Herz

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

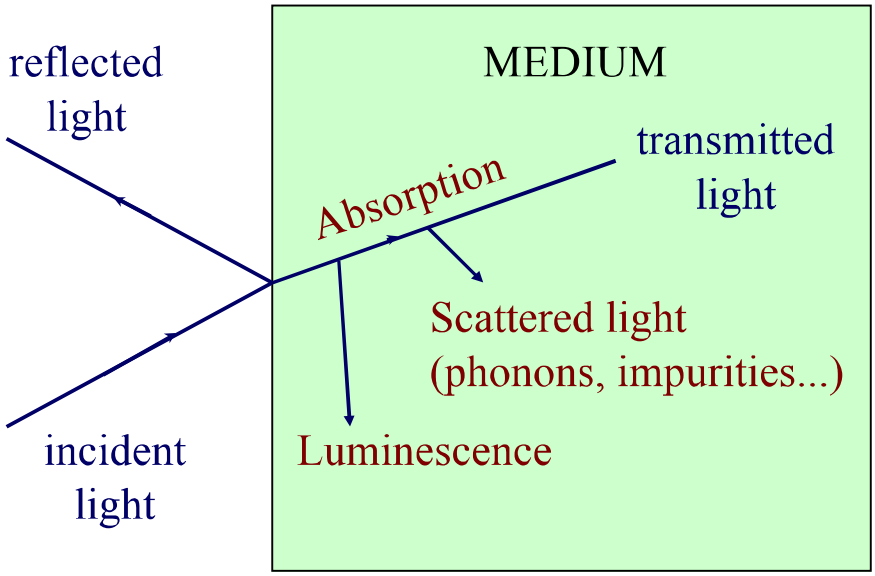
PY Yu and M Cardona, *Fundamentals of Semiconductors*, Springer

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:

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

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

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

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

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

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

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

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

⇒ Define complex refractive index:

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

n: refraction, κ: absorption

Absorption

Intensity decay of wave: (Beer's law)

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

Define absorption coefficient:

$$\alpha = \frac{2\omega\kappa}{c}$$

Reflection

At normal incidence:

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

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

Relationship between components of ñ and ε_r

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

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

$$\epsilon' = n^2 - \kappa^2$$
$$\epsilon'' = 2n\kappa$$

and

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

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:

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

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:

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

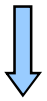
$D = \epsilon_0\epsilon_r E = \epsilon_0 E + P + P_b$ ← background

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

Real and imaginary part of ε_r

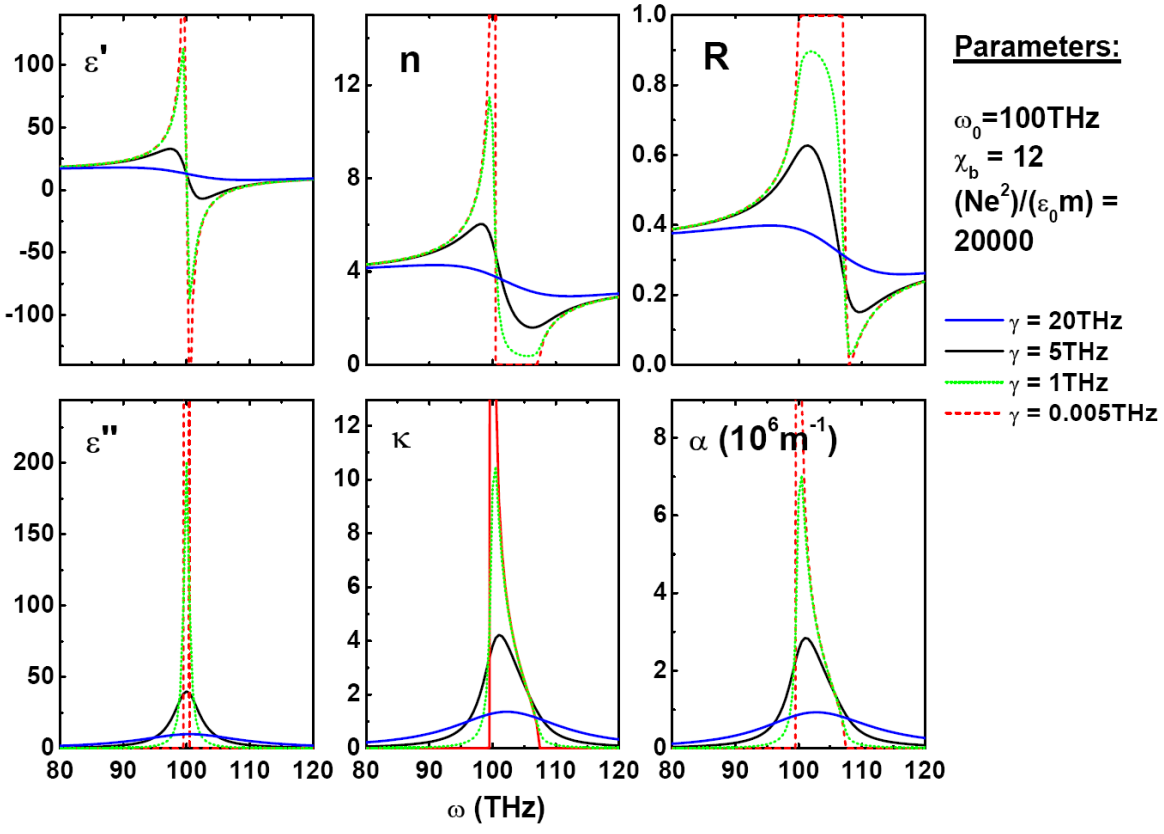
$$\epsilon'(\omega) = 1 + \chi_b + \frac{Ne^2}{\epsilon_0 m} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2}$$

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



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

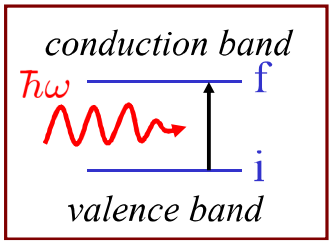
- interband transitions should depend on the density of states g(E)
- One possible modification:

"oscillator strength" (from QM)

write: $\epsilon_r = 1 + \underbrace{\frac{e^2 N}{\epsilon_0 m} \frac{f}{\omega_0^2 - \omega^2 - i\omega\gamma}}$

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:

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

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

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

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

Matrix element for interband transitions:

absorption

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

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

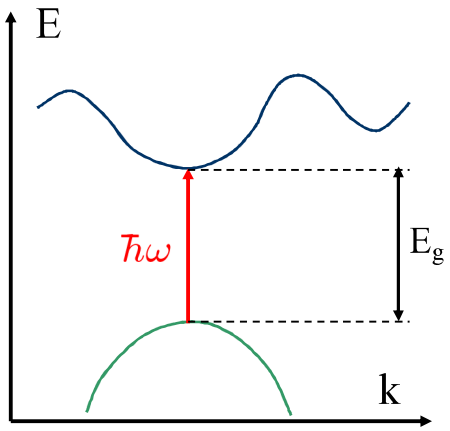
(1) wavevector conservation

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

absorption emission

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

⟹ "vertical" transitions



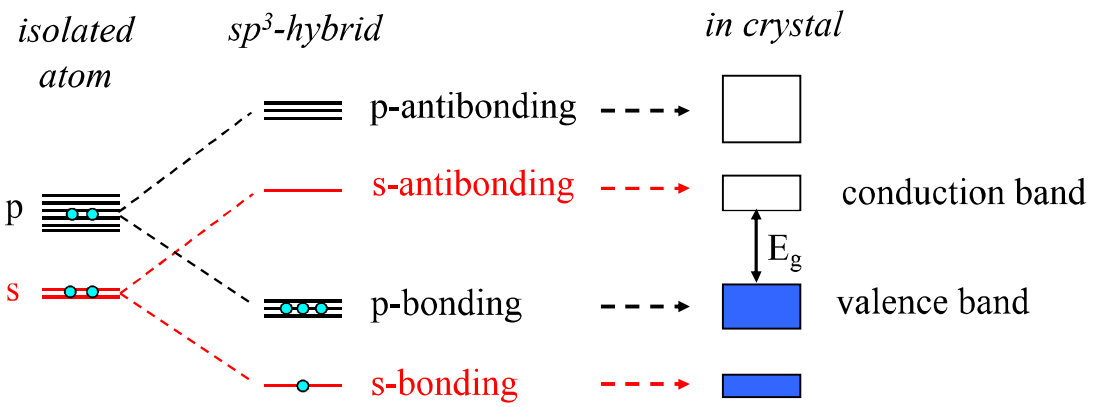
(2) parity selection rule

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

odd parity

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

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



⟹ expect to see strong absorption for these materials

(3) Dependence of transition probability on photon energy

Final state is an electron-hole pair

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

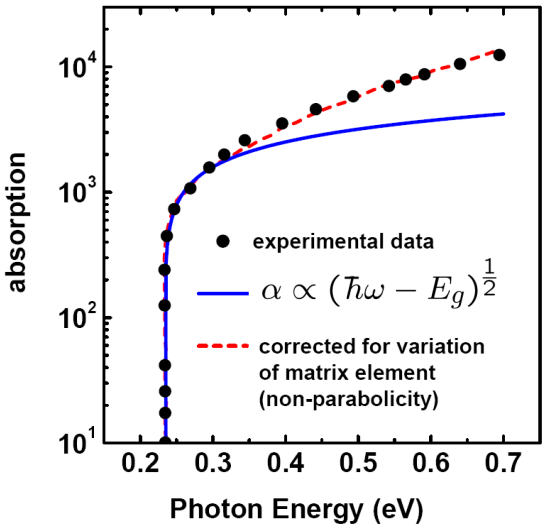
where $\mu = (\frac{1}{m_e^*} + \frac{1}{m_h^*})^{-1}$ reduced effective mass

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

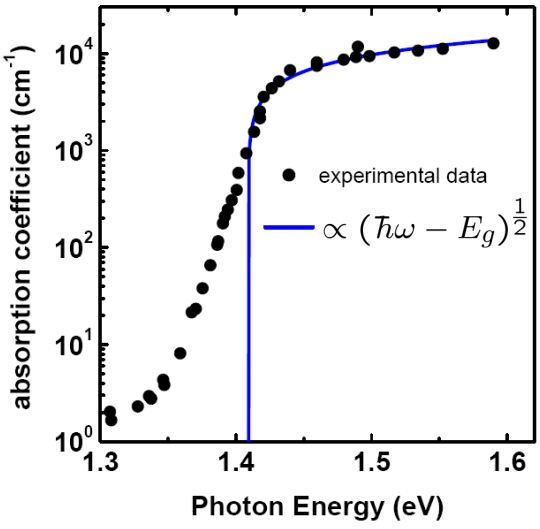
Absorption coefficient (for direct transitions):	$\alpha \propto (\hbar\omega - E_g)^{\frac{1}{2}}$

Examples for direct semiconductors

a) InSb at 5K



b) GaAs at 300K



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

Indirect interband transitions

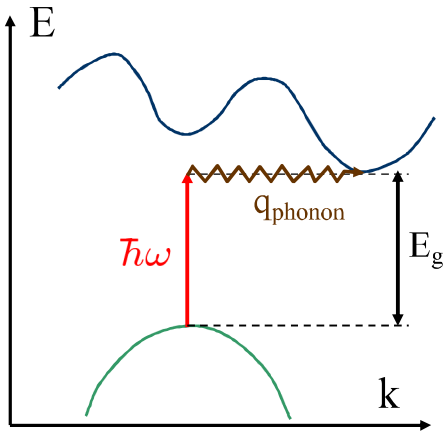
- Indirect gap: valence band maximum and conduction band minimum lie at different wavevectors, $\mathbf{k}_v^{max} \neq \mathbf{k}_c^{min}$
- direct transitions across the indirect gap forbidden, but phonon-assisted transitions may be possible.

(i) wavevector conservation:

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

with phonon wavevector

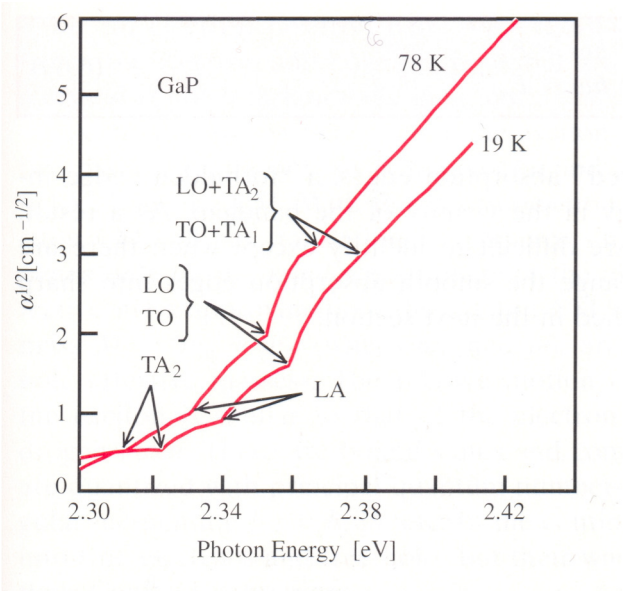
$$\mathbf{q}_{phonon} = \mathbf{k}_v^{max} - \mathbf{k}_c^{min}$$



(ii) probability for indirect transitions:

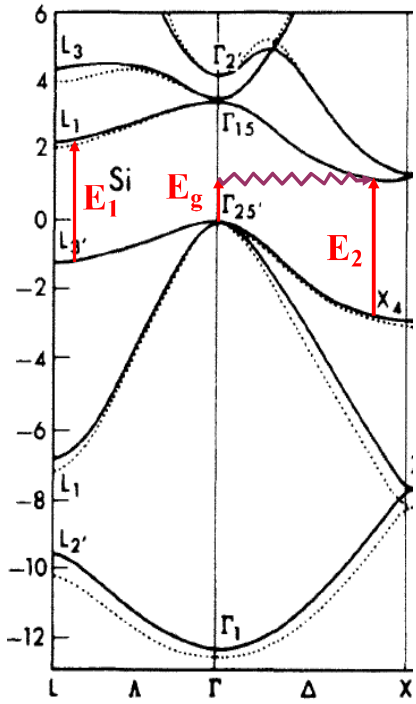
- perturbation causing indirect transitions is second order
  ⟹ optical absorption much weaker than for direct transitions!
- find absorption coefficient $\alpha \propto (\hbar\omega - E_g \pm \hbar\omega_q)^2$

phonon absorption or emission

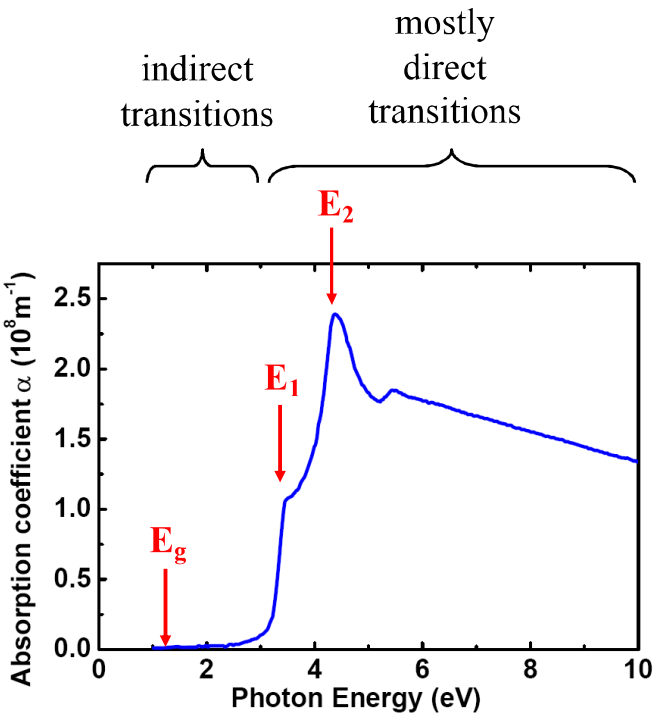


Example for an indirect semiconductor: Si

Band structure:

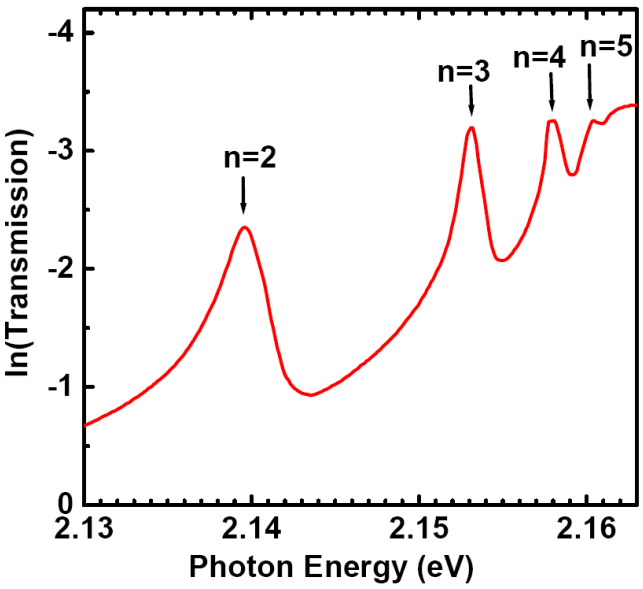


Absorption spectrum:



III Excitons

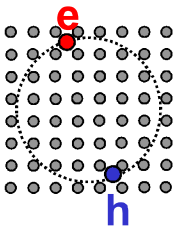
Absorption coefficient of CuO_2 at 77K:



Series of absorption peaks just below the energy gap

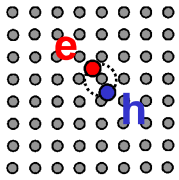
Coulomb interaction between electron and hole gives rise to "excitonic" states (bound electron-hole pairs)

Wannier-Mott Excitons



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

Frenkel Excitons



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

Weakly bound (Wannier) Excitons

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

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

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

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

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

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

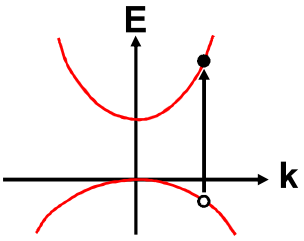
$\mu = (\frac{1}{m_e^*} + \frac{1}{m_h^*})^{-1}$ reduced mass

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

where a_0 = 0.529Å (Bohr radius)

E-k diagram for the weakly bound exciton

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



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

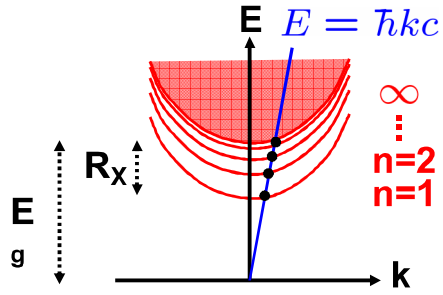
wavevector conservation:

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

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

⇒ "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:

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

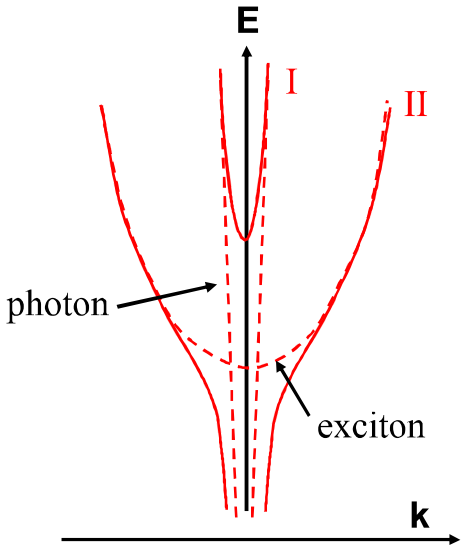
⇒ transitions where light line $E = \hbar kc$ intercepts with E_X

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

⇒ $E_X \to E_g$ for $n \to \infty$

continuum onset at band edge

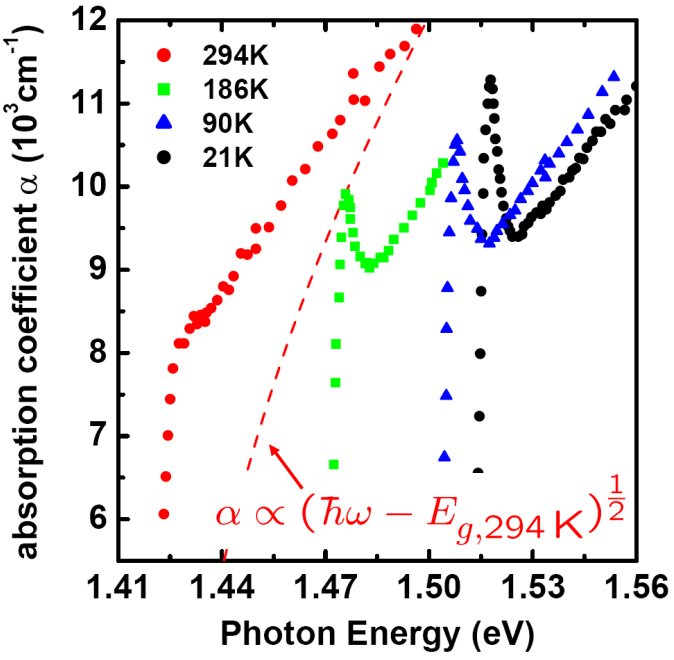
Exciton-Polariton



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

  ⟹ altered dispersion curve (2 branches)
- But: if exciton damping (phonon scattering...) is larger than exciton-photon interaction we can treat photons and excitons separately.

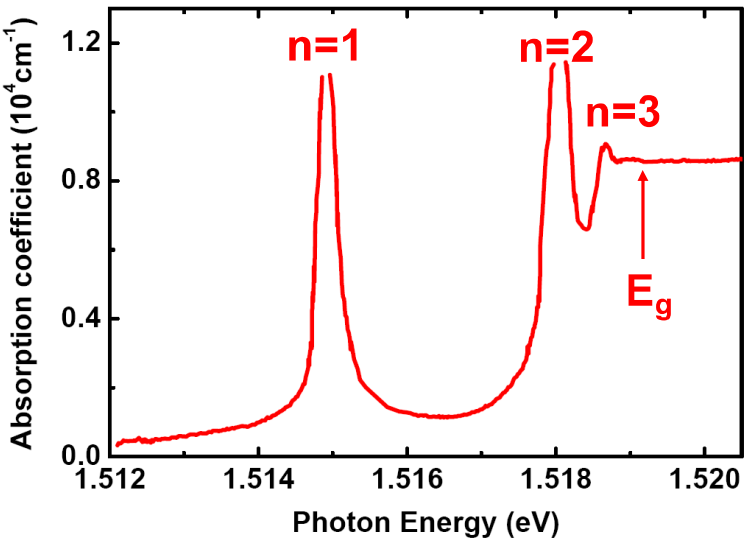
Examples for weakly bound excitons: GaAs



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

Examples for weakly bound excitons: GaAs

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



here: $m_e^* = 0.067$

$m_{hh}^* = 0.45$

$\epsilon_r = 13$

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

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

Tightly bound (Frenkel) excitons

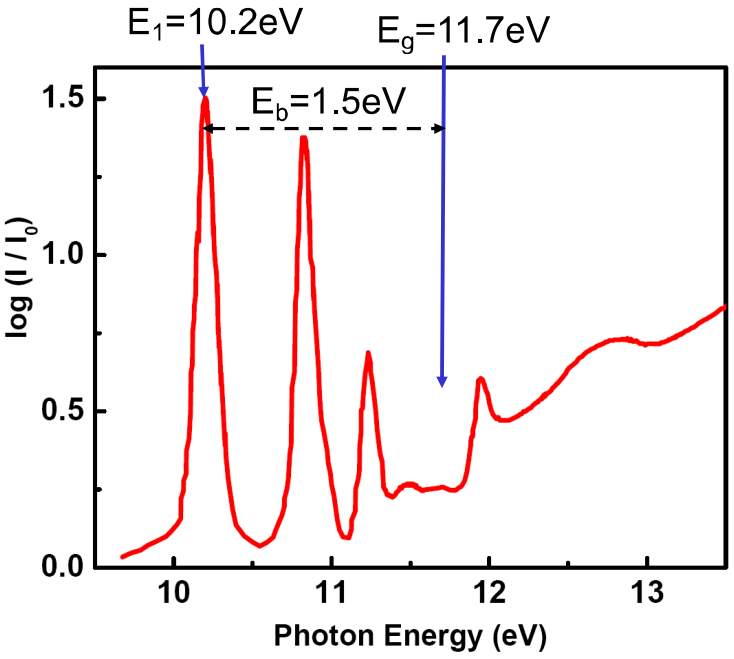
- radius of weakly-bound excitons: $a_n = \epsilon_r \frac{m_e}{\mu} n^2 a_0$
  - ⇨ model of bound e-h pair in dielectric medium breaks down when a_n is of the order of interatomic distances (Å)
  - ⇨ have tightly bound excitons for small ε_r , large μ
- tightly-bound electron-hole pair, typically located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

Transition energies for tightly bound excitons

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

Examples for tightly bound excitons: rare gas crystals

absorption spectrum of crystalline Kr at 20K:



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

⇩

close to lowest excitonic transition E_1 in crystal

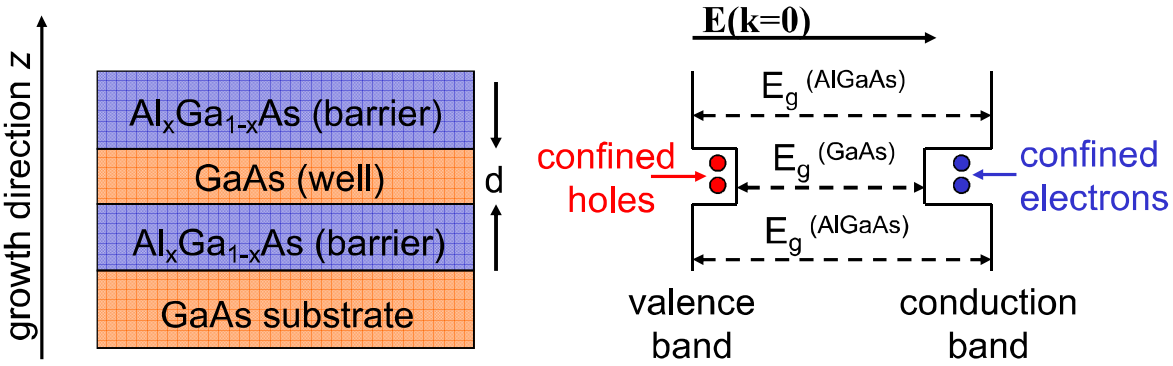
VI Low-dimensional systems

de Broglie wavelength for an electron at room temperature:

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

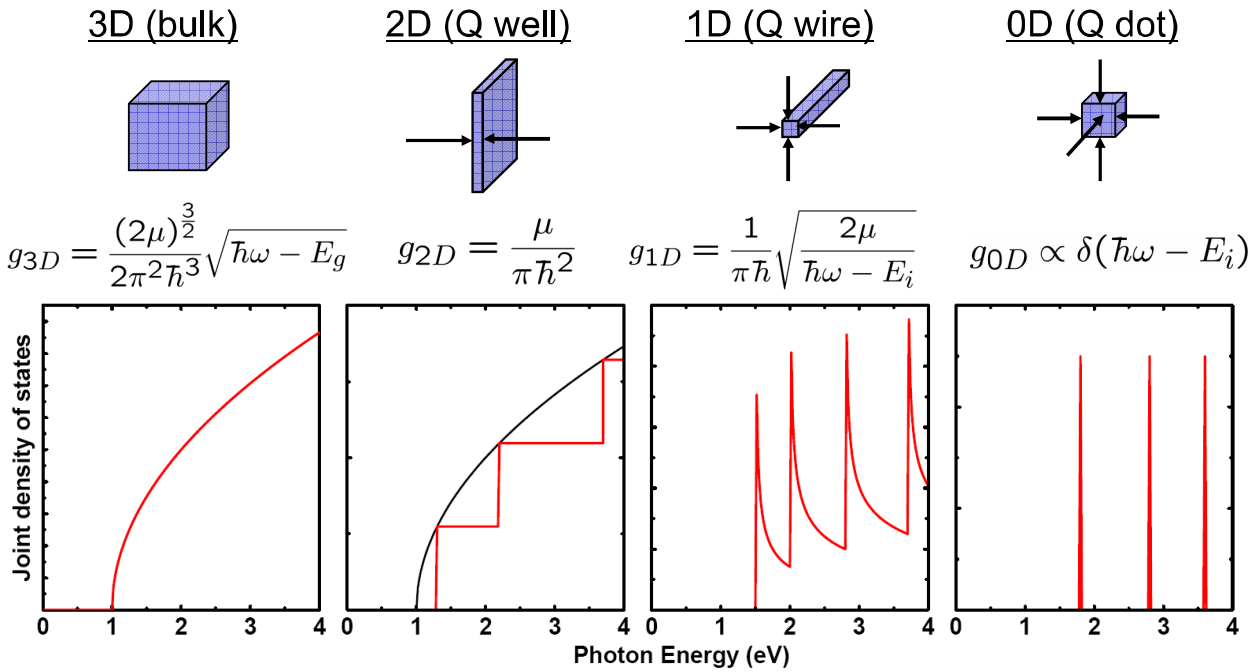
⇒ If we can make structured semiconductors on these length scales we may be able to observe quantum effects!

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

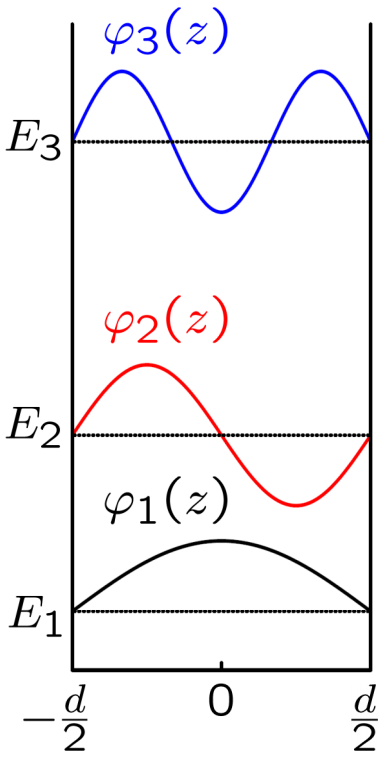


Effect of confinement on the DOS

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(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:

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

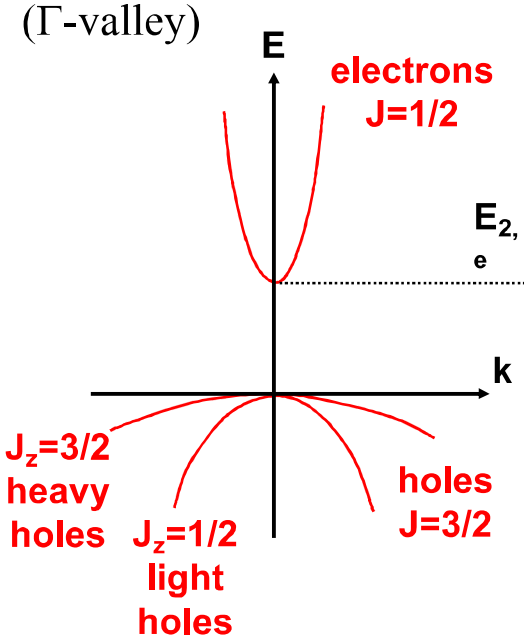
with wavevector $k_n = \frac{n\pi}{d}$

confinement energy:

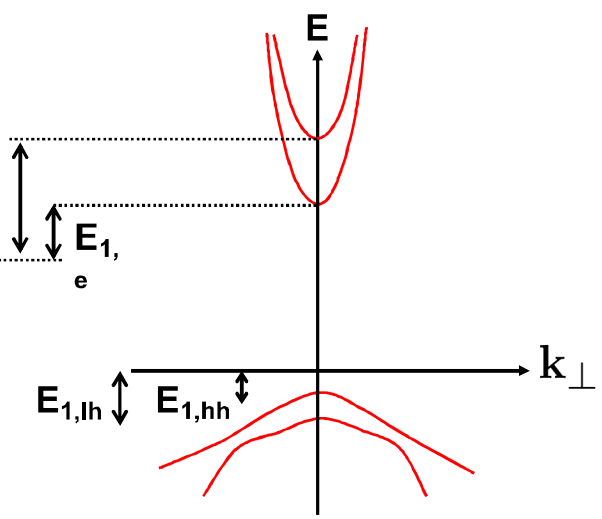
$$E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*}\left(\frac{n\pi}{d}\right)^2$$

Bandstructure modifications from confinement

bulk GaAs
(Γ-valley)



GaAs QW



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

Optical transitions in a quantum well

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

wavefunctions now:

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

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

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

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

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

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:

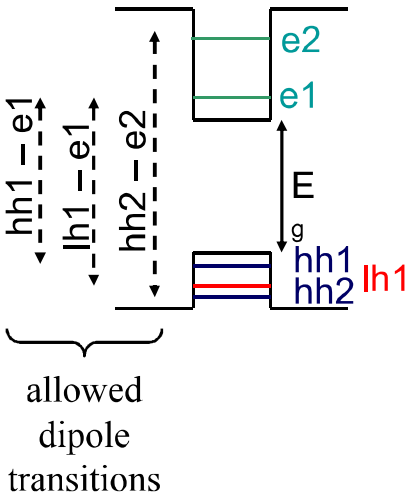
$$M_{n,n'} = \frac{2}{d}\int_{\frac{d}{2}}^{-\frac{d}{2}} \sin\left(k_n z + \frac{n\pi}{2}\right)\sin\left(k_{n'} z + \frac{n'z}{2}\right)dz$$

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

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

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

(v) energy conservation:



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

photon energy; band gap of well material; confinement energy of electron/hole; kinetic energy in plane of QW

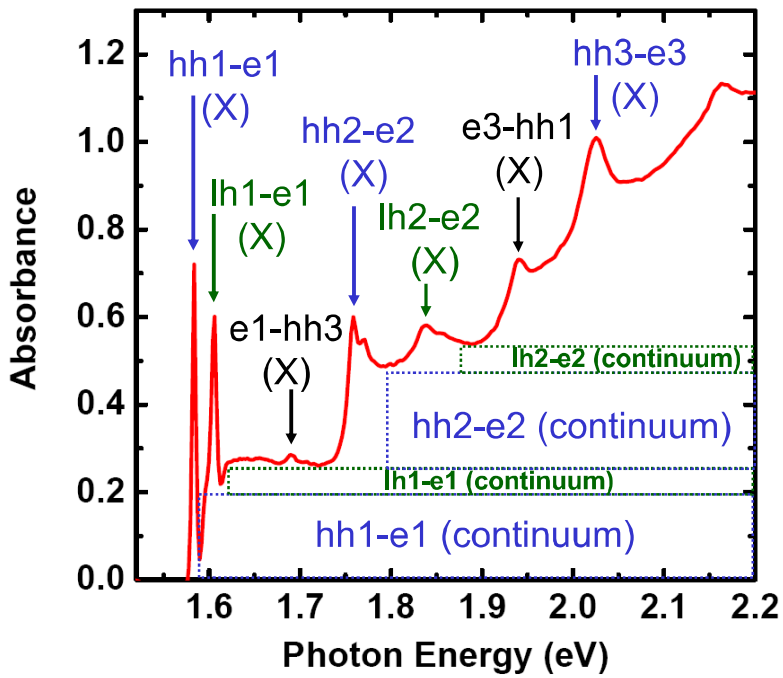
and for $\mathbf{k}_\perp = 0$ (at the band edge):

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

$$= E_g + \frac{\hbar^2\pi^2 n^2}{2d^2\mu}$$

Example: absorption of a GaAs/AlAs QW

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

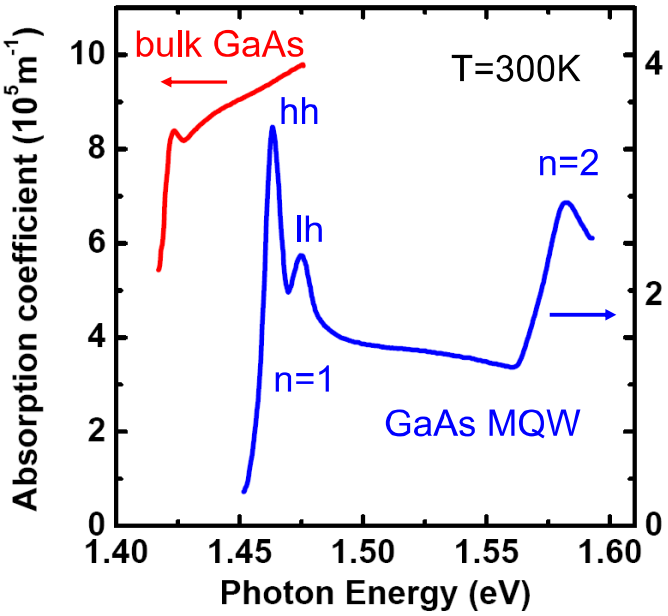


below each onset of absorption: excitonic features (X)

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

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

Influence of confinement on the exciton



Confinement brings electron and hole closer together.

⇨ enhanced exciton binding energy

⇨ increased oscillator strength

V Optical response of a free electron gas

Classic Lorentz dipole oscillator model (again):

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

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

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

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

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

⟹ real and imaginary part of the dielectric constant:

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

AC conductivity of a free electron gas

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

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

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

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

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

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

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

optical measurements of ε_r equivalent to those of AC conductivity!

Low-frequency regime

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

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

(ϵ' and ϵ'' labeled)

$\Rightarrow \epsilon'' \gg \epsilon'$ 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: $\sigma_0 = 6.5\times10^7\,\Omega^{-1}\mathrm{m}^{-1}$

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

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

High-frequency regime

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

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

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

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

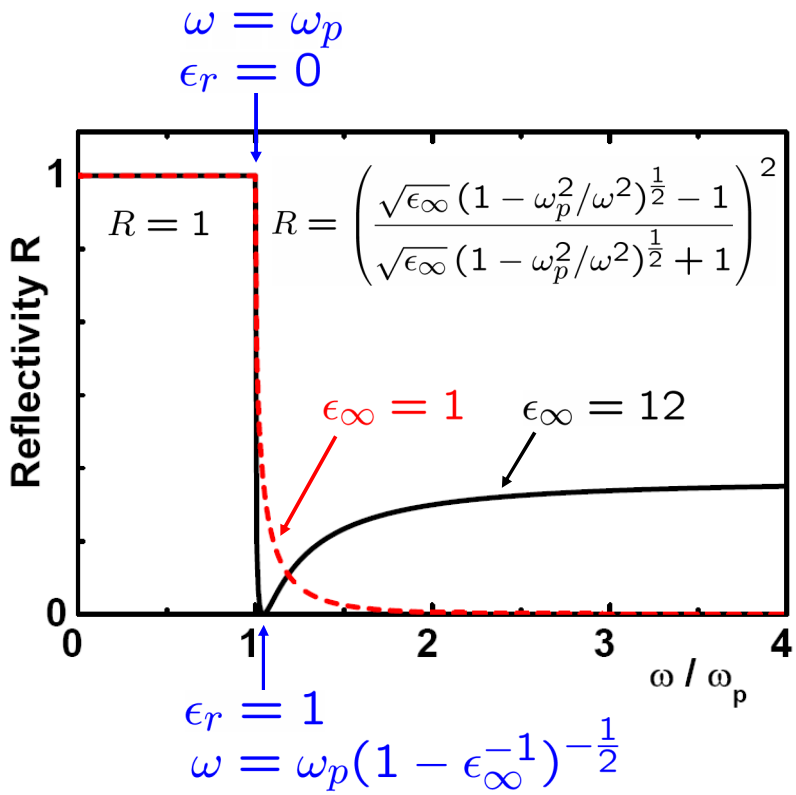
(i) $\omega < \omega_p$ $\quad \epsilon' < 0$ $\quad \tilde{n}$ largely imaginary

$R \approx 1$ wave mostly reflected

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

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

Reflectivity in the high-frequency regime



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

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

Example: Reflection from Alkali metals

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

measured at low T

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

measured UV transmission cut-off

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

Example: Reflection from transition metals

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

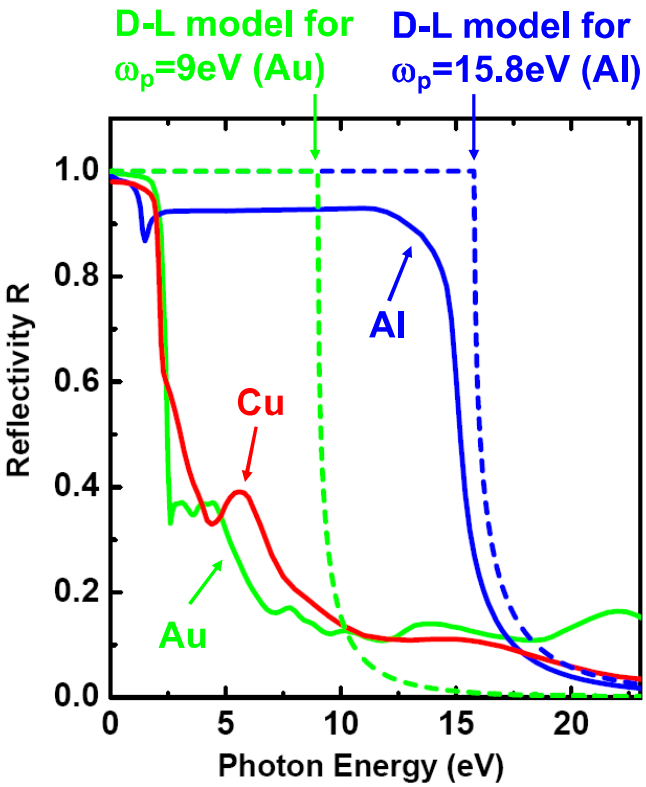
measured at low T ↑ calculated from $\omega_p = \left(\frac{Ne^2}{\epsilon_0 m}\right)^{\frac{1}{2}}$

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:



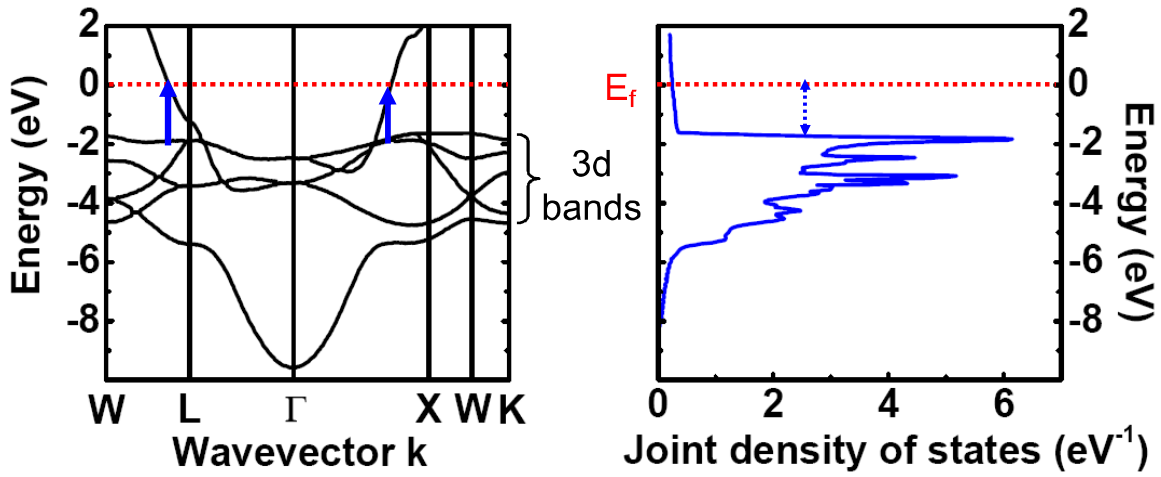
Drude-Lorentz model does not account fully for optical absorption of transition metals (especially in the visible)

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

Example: Reflection from Copper

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

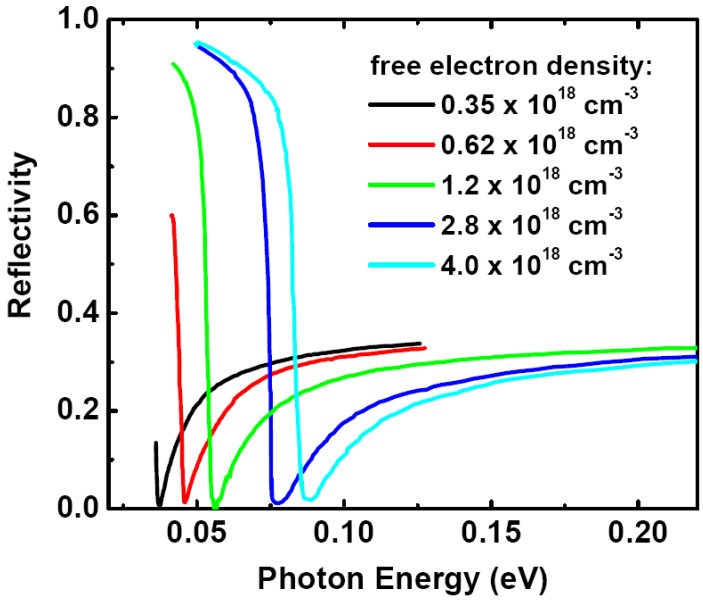
Transitions (in visible range of spectrum) between relatively dispersionless bands of tightly bound 3d electrons and half-filled band of 4s-electrons:



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

Example: Reflection from doped semiconductors

Free-carrier reflectivity of InSb:



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

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

$\Rightarrow$ 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:

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

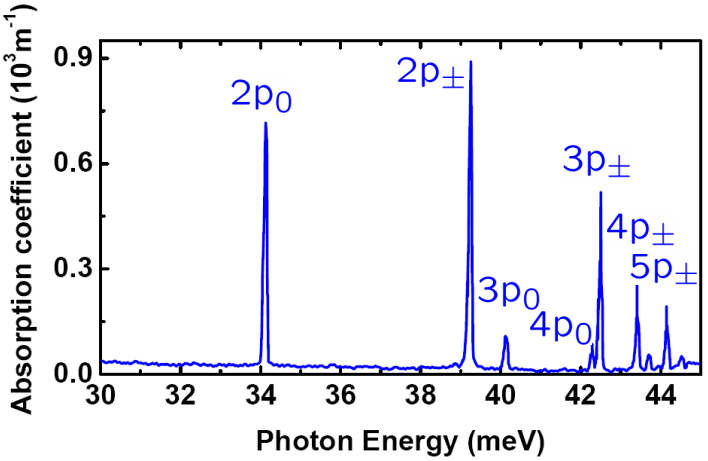
Deviations arise from:

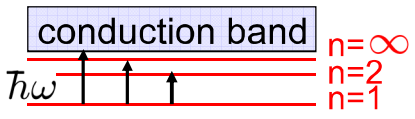
- intraband transitions involving phonon scattering
- in p-type semiconductors: intervalence band absorption
- absorption by donors bound to shallow donors or acceptors

Example: Impurity absorption in semiconductors

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

Absorption of Phospor-doped silicon at 4.2K:





valence band

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

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

Plasmons

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

What happens at this frequency?

- Polarization induced by the EM wave:

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

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

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

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

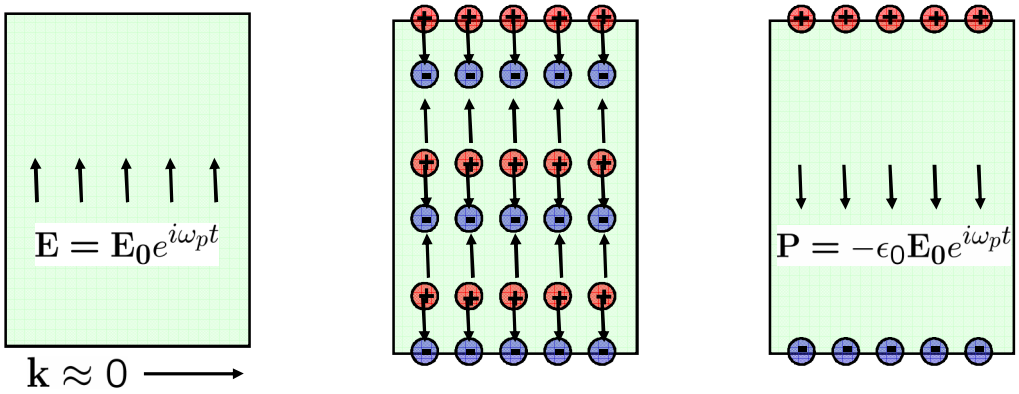
⇒ At the Plasma edge a uniform E-field in the material shifts the collective electron w.r.t the ionic lattice!

Plasma oscillations for ε_r=0:

applied EM wave

resulting charge distribution

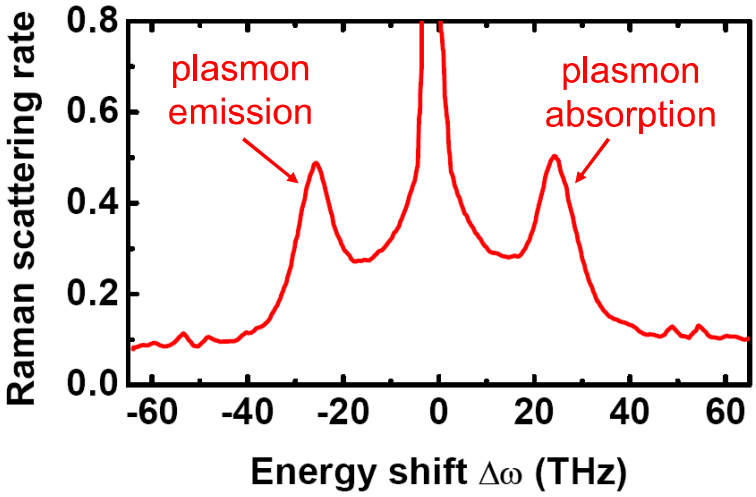
induced macroscopic polarization



- 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:

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

$\Rightarrow$ from data:

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

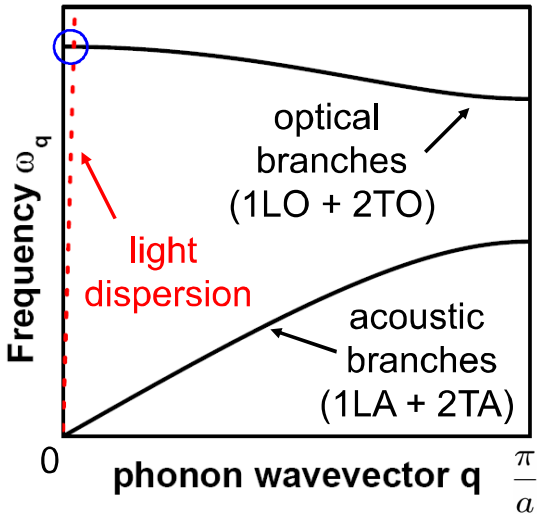
Expect from:

$$N = 1.75 \times 10^{23}\, m^{-1}$$
$$\epsilon_\infty = 10.6$$
$$m_e^* = 0.067 m_e$$

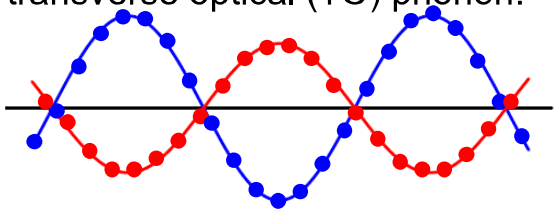
$$\Rightarrow \quad \omega_p = \left(\frac{Ne^2}{\epsilon_\infty \epsilon_0 m}\right)^{\frac{1}{2}} = 28\mathrm{THz}$$

VI Optical studies of phonons

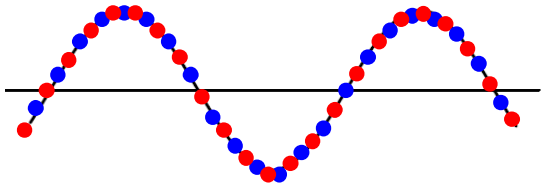
Dispersion relation for a diatomic linear chain:



transverse optical (TO) phonon:



transverse acoustic (TA) phonon:

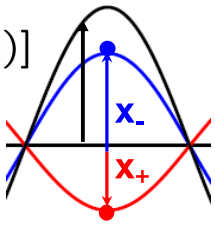


EM radiation is a transverse wave with wavevector $k \ll \pi/a$ and can thus interact directly *only with TO modes in polar crystals near the centre of the Brillouin zone.*

Harmonic oscillator model for the ionic crystal lattice

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

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



Equations of motion:

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

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

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

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

Add damping term to account for finite phonon lifetime:

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

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 (ϵ_s) and the high-frequency (ϵ_∞) limits of the dielectric constant:

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

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

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

Lattice response in the low-damping limit

Long phonon lifetimes: $\gamma \approx 0$

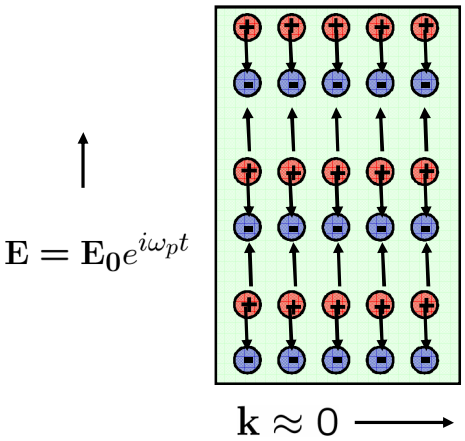
$$\Longrightarrow \quad \epsilon_r(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \frac{\omega_{TO}^2}{(\omega_{TO}^2 - \omega^2)}$$

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

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

What happens at ε_r=0 ?

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



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

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

The Lyddane-Sachs-Teller relationship

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

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

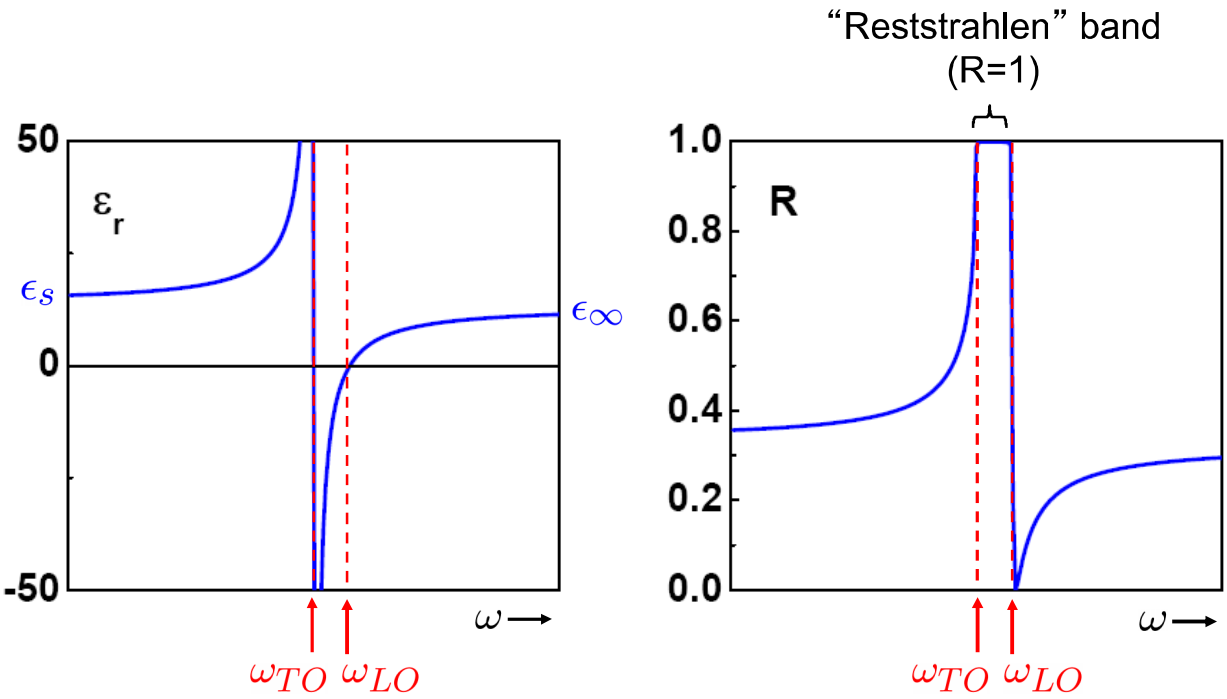
Lyddane-Sachs-Teller relationship

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

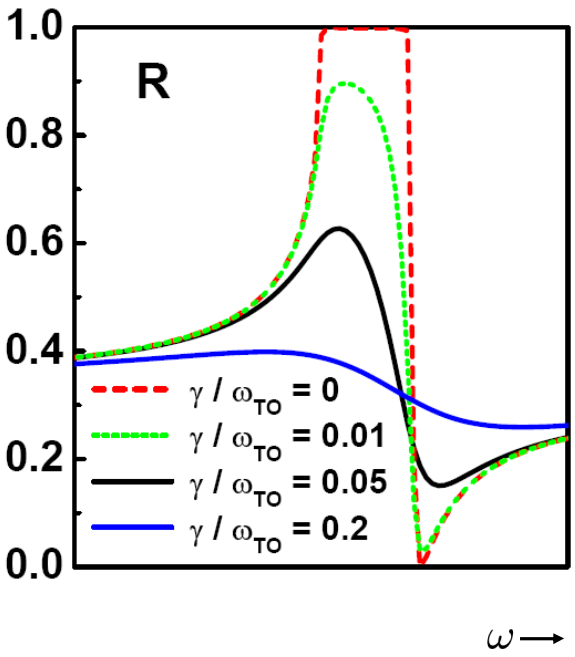
→ In non-polar crystals, $\epsilon_s = \epsilon_\infty$ and the LO and TO phonon modes are degenerate (at the Brillouin zone centre)

Dielectric constant and Reflectivity for undamped lattice



Influence of damping

Lattice Reflectivity:



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

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

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

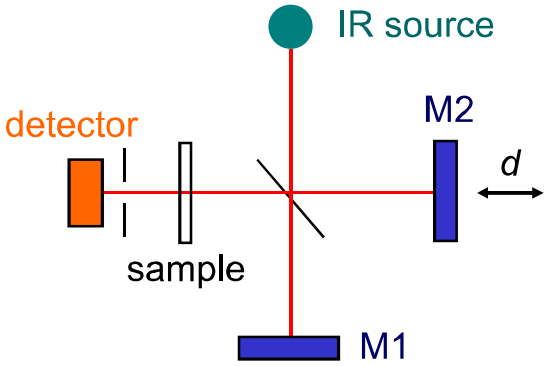
→ Reststrahlen band no longer fully reflective

→ general broadening of features

Measurements of IR reflectivity

Fourier transform infrared spectroscopy (FTIR):

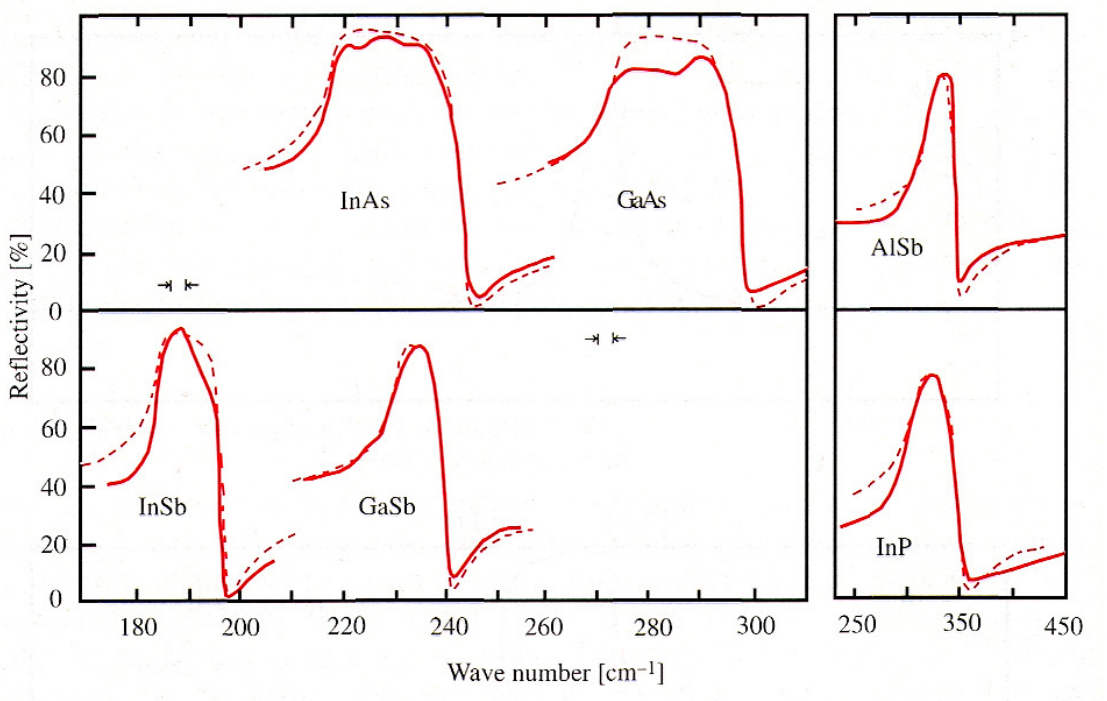
- measure interference pattern *I(d)* as a function of mirror displacement *d*
- *I(d)* gives Fourier transform of sample transmission *T(ν)* multiplied with system response *S(ν)*:



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

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

Example: reflection spectra for zinc-blende-type lattices



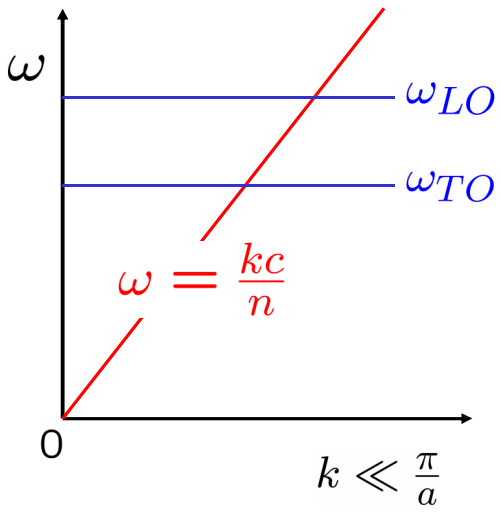
measured at 4.2K

measured at RT

Phonon-Polaritons

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

If no coupling occurred:



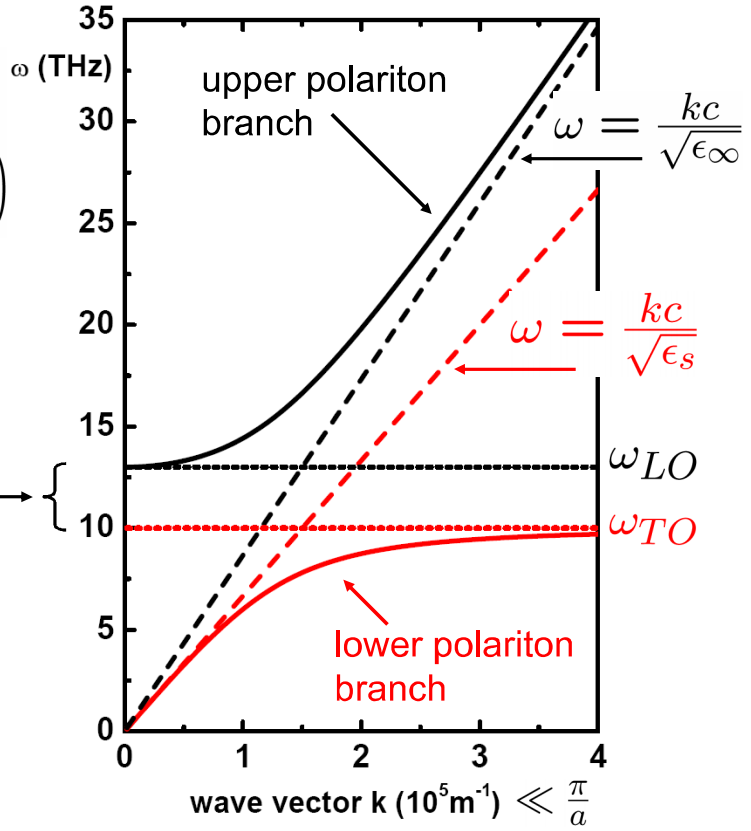
- But: coupling between TO phonon and EM wave leads to modified dispersion
- resulting wave is mixed mode with characteristics of TO polarization and EM wave
- LO phonon dispersion remains unchanged as it does not couple to the EM wave

Phonon-Polariton dispersion:

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

→ two branches for ω(k)

Reststrahlen band (perfect reflection, no mode can propagate)



Inelastic Light Scattering

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

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

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

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

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

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

where

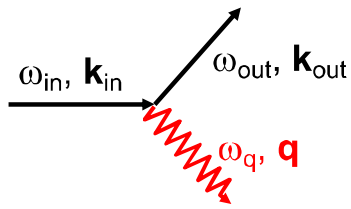
$\mathbf{P}_0 = \epsilon_0 \chi(\omega)\, \mathbf{E}_0 \cos \omega t$ unscattered polarization wave

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

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

Energy & momentum conservation for inelastic scattering

Scattering process:



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

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

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

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

Maximum momentum transfer in backscattering geometry, where:

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

⟹ Inelastic light scattering probes phonons with small wave vector

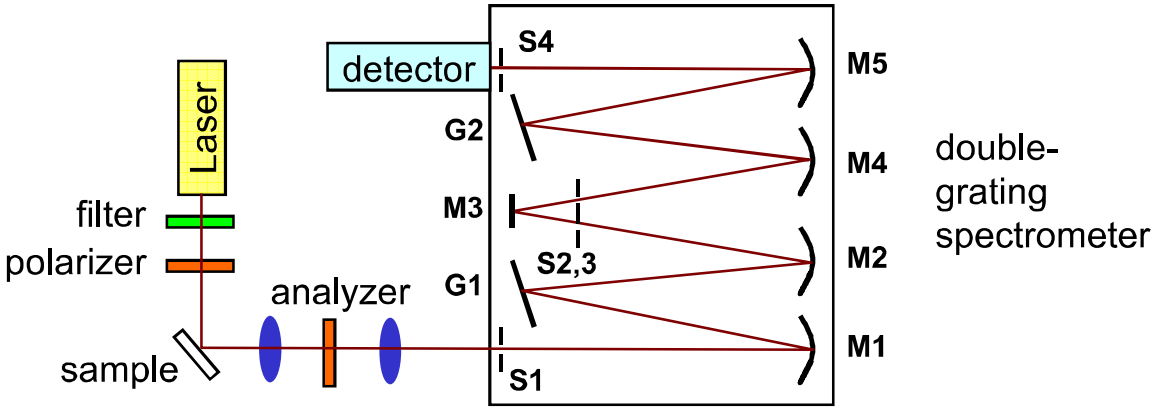
Raman spectroscopy: Experimental details

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

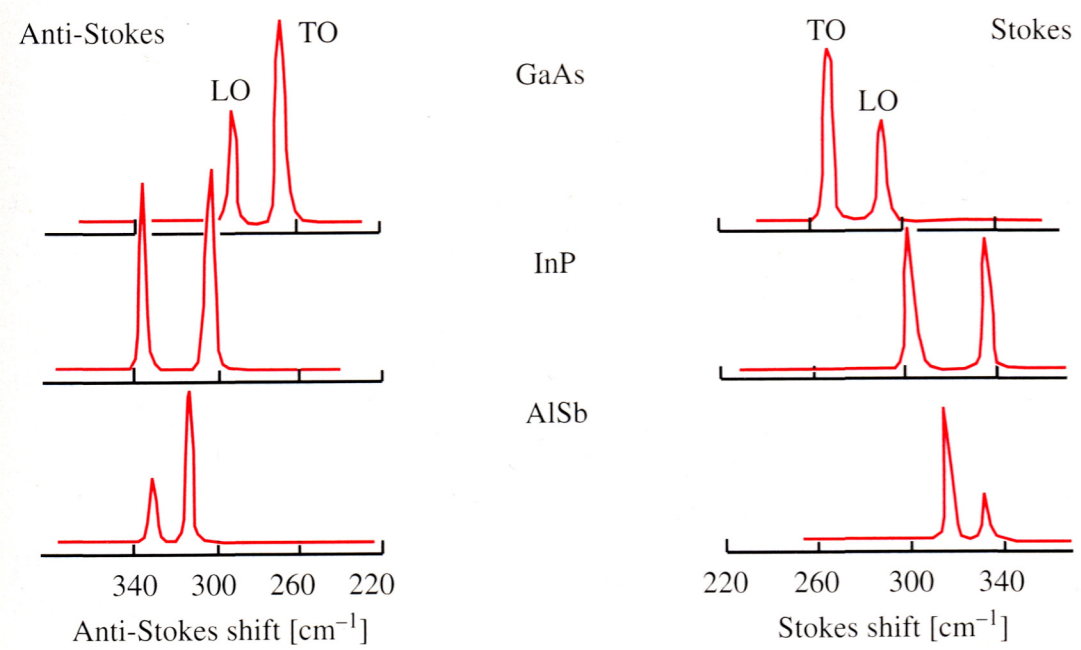
→ need excitation source (laser) with sufficiently narrow bandwidth

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

Typical set-up:



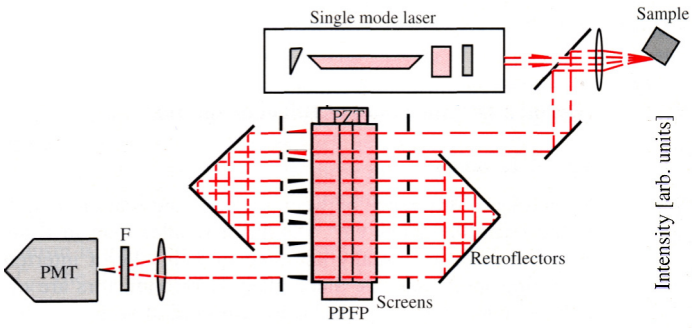
Raman spectra for zinc-blende-type semiconductors



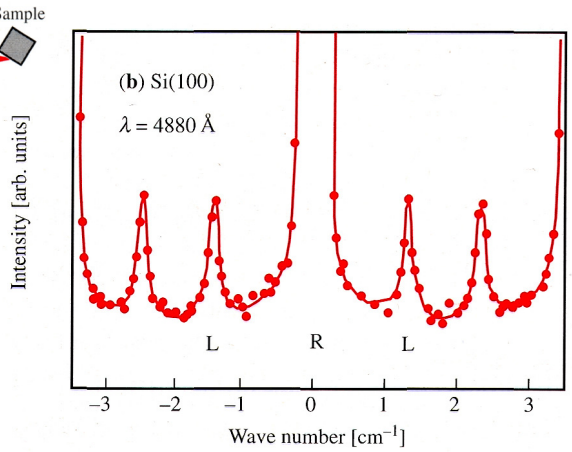
Brillouin scattering: Experimental details

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

<u>Set-up based on a Multipass Interferometer:</u>



<u>Brillouin spectrum for Si(100):</u>



Phonon lifetimes

Experimental evidence for finite phonon lifetimes from

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

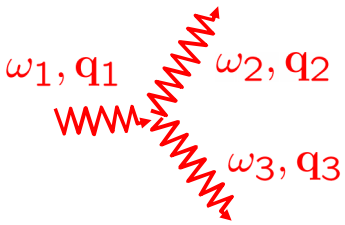
ii. Raman scattering: non-zero width of Raman line
$\Gamma = \frac{\hbar}{\tau_{phonon}}$

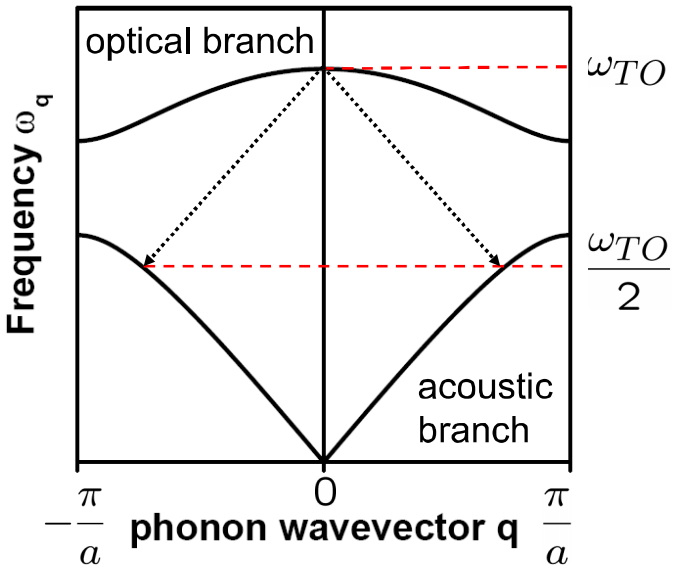
Data suggests phonon lifetimes of 1-10ps in typical inorganic semiconductors.

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

$$U(x) = C_2 x^2 + C_3 x^3 + C_4 x^4 + \ldots$$

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

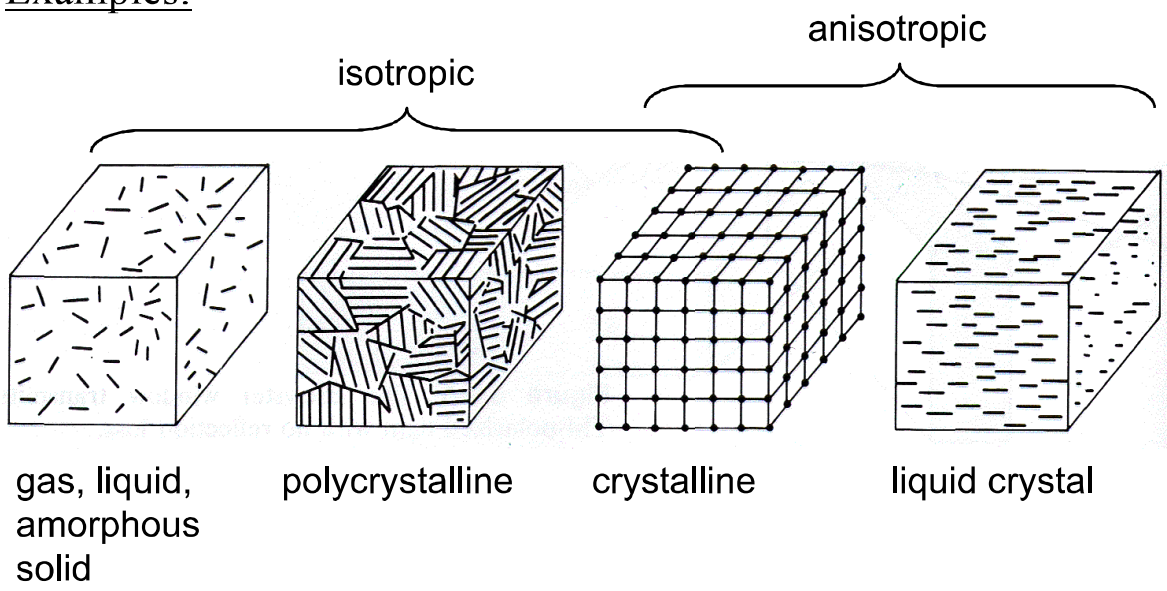




VII Optics of anisotropic media

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:

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

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

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

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

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

Propagation of plane waves in an isotropic medium

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

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

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

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

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

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

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

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

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): $\epsilon_1 = \epsilon_2 = n_o^2 \qquad \epsilon_3 = n_e^2$

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

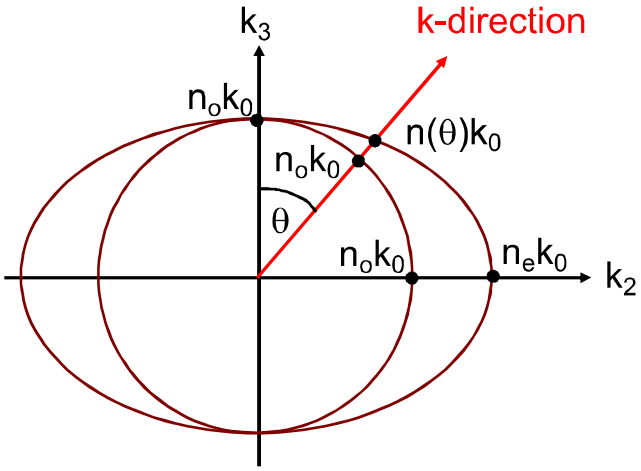
Two solutions:

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

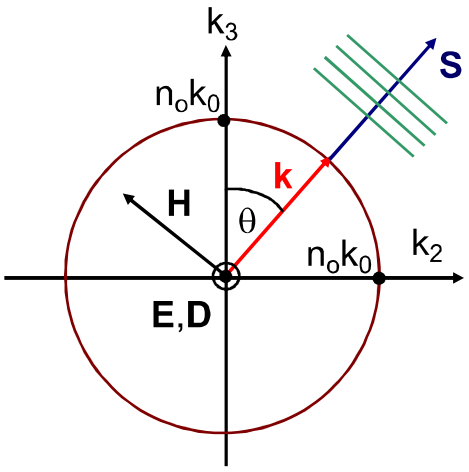
(ii) ellipsoid of revolution

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

for *extraordinary* ray
(polarized in k-z plane)

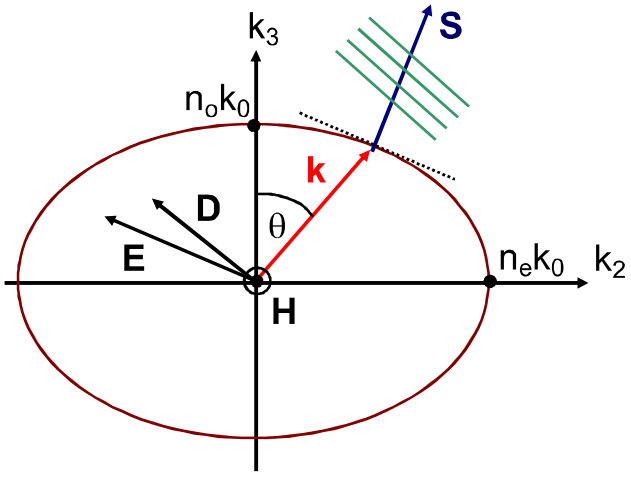


Ordinary *vs* extraordinary rays in uniaxial crystals



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

$$n = n_o$$



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

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

Comments on wave propagation in uniaxial crystals

1) Faraday's & Ampere's law for plane waves in dielectrics:
$\mathbf{k} \times \mathbf{H} = -\omega \mathbf{D}$ ⟹ **D** is normal to both **k** and **H**
$\mathbf{k} \times \mathbf{E} = \omega \mu_0 \mathbf{H}$ ⟹ **H** is normal to both **k** and **E**
N.B.: this does *not* imply **E** ⊥ **k**!

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

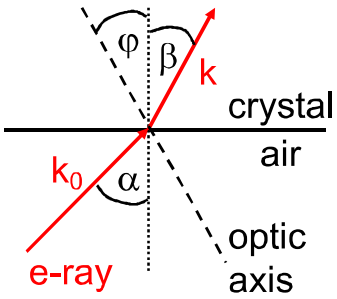
3) The phase velocity ***v*** is in the direction of **k** with
$v = \omega/k = \omega/(nk_0)$

4) As usual, the group velocity is
⟹ $\boldsymbol{v}_g$ is normal to the k-surface! $\mathbf{v}_g = \nabla_{\mathbf{k}} \omega(\mathbf{k})$

5) The pointing vector $\mathbf{S} = \frac{1}{2} \mathbf{E} \times \mathbf{H}^*$ is normal to **E** and **H**
Can show: $\Delta\mathbf{k} \cdot \mathbf{S} = 0$ for small $\Delta\mathbf{k}$ ⟹ **S** normal to **k**-surface

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

Refraction at the surface of a uniaxial crystal

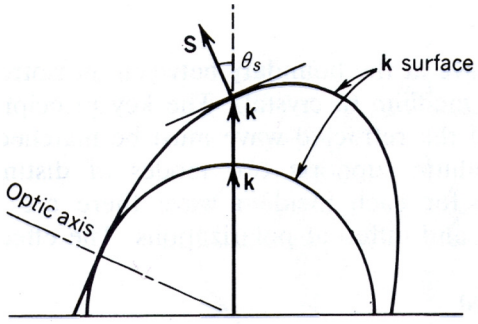


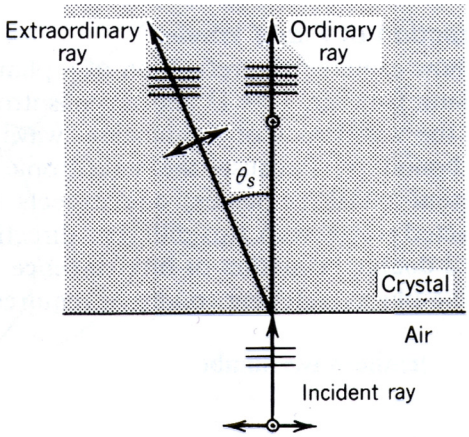
phase matching condition: $k_0 \sin\alpha = k \sin\beta$

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

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

Example: Double refraction at normal incidence:





VIII Non-linear Optics

Linear optics:

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

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

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

But:

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

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

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

Possible with tightly focused laser beams!

The non-linear susceptibility tensor

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

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

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

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

⇒ Second-order non-linear polarization components:

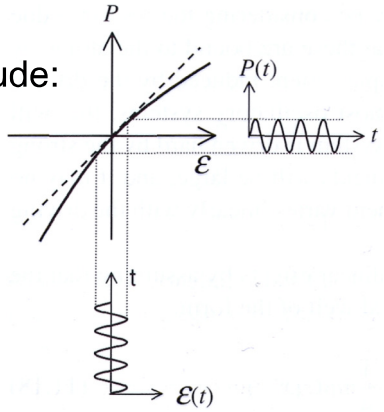
$$P_i^{(2)} = \epsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k$$

⇒ Third-order non-linear polarization components:

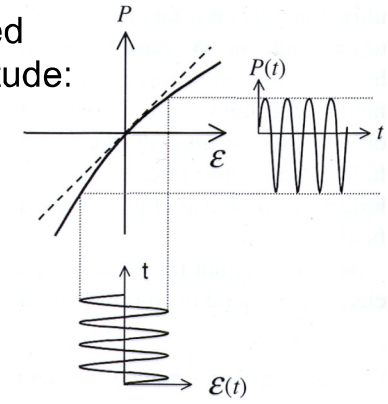
$$P_i^{(3)} = \epsilon_0 \sum_{j,k,l} \chi_{ijkl}^{(3)} E_j E_k E_l$$

Non-linear medium response to sinusoidal driving field

low applied field amplitude:



high applied field amplitude:



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

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

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

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

Second-order nonlinearities (NL)

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

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

Equation of motion:

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

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

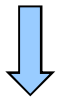
Assume $x_2 \ll x_1 \rightarrow x^2 \approx x_1^2 \exp(i2\omega t)$

Obtain displacement amplitudes: ⇒

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

Calculating the induced polarization:

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



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

linear susceptibility, as before

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

second-order non-linear susceptibility

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

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

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

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

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

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

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

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

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

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

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

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

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

Presume two waves are travelling in the medium, with

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

The induced polarization is:

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

sum-frequency generation — difference-frequency generation

Feynman diagrams for second-order nonlinear frequency mixing:



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:

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

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

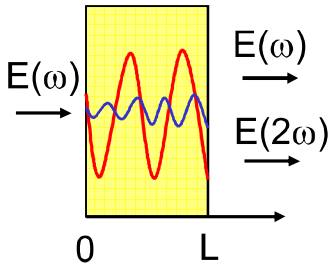
$$\frac{d^2}{dz^2} \hat{E}_i^{2\omega}(z) \ll k_{2\omega} \frac{d}{dz} \hat{E}_i^{2\omega}(z)$$

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

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

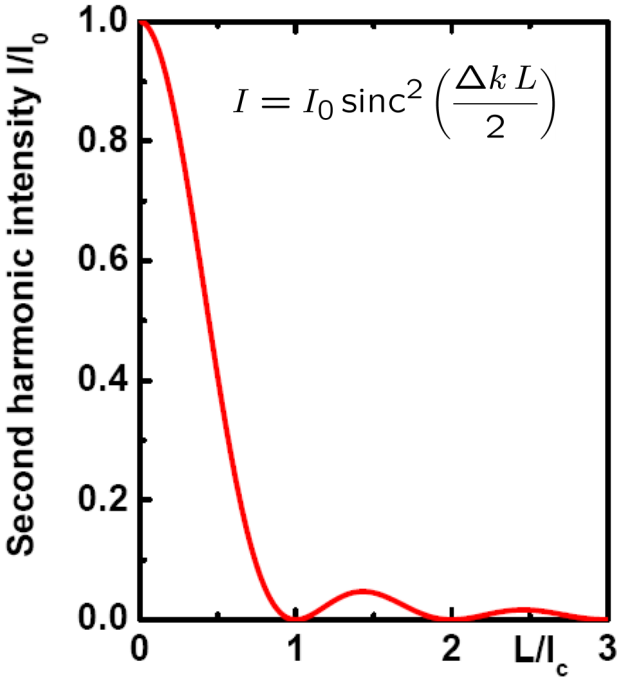
The second-harmonic field at length L for arbitrary Δk is:

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

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

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

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



First intensity minimum at:

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

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

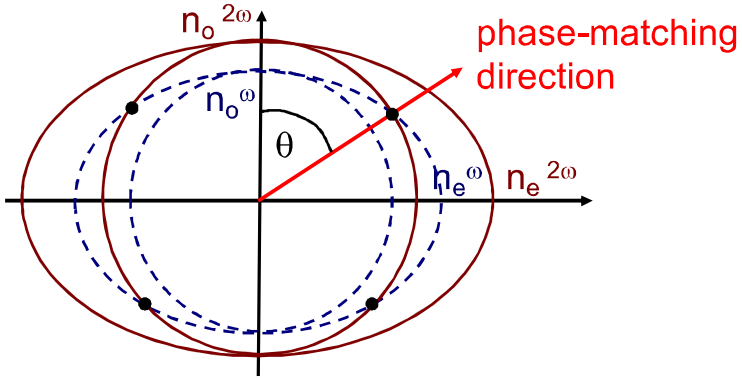
Example: Sapphire

$$n_o(2.806\mathrm{eV}) = 1.780$$
$$n_o(1.403\mathrm{eV}) = 1.757$$
$$\Rightarrow \quad l_c = 19\mu\mathrm{m}$$

→ 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 ⊥ to plane) with

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

Third-order nonlinearities

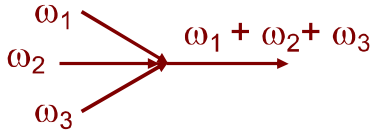
Third-order effects become important in centrosymmetric (e.g. isotropic media) where $\chi^{(2)}_{ijk} = 0$

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

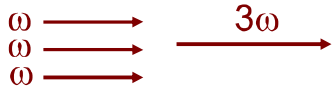
$$P_i^{(3)} = \epsilon_0 \sum_{j,k,l} \chi^{(3)}_{ijkl}\, \hat{E}_j\, \hat{E}_k\, \hat{E}_l\, \cos(\omega_1 t)\, \cos(\omega_2 t)\, \cos(\omega_3 t)$$

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

(a) four-wave mixing



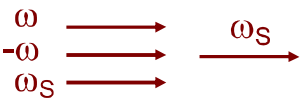
(b) frequency tripling



(c) Optical Kerr effect



(d) stimulated Raman scattering



3rd order NL: The optical Kerr effect

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

⇒ no phase mismatch

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

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

Refractive index:

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

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

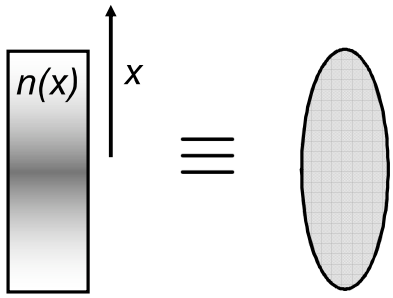
I: light intensity

⇒ Refractive index varies with light intensity!

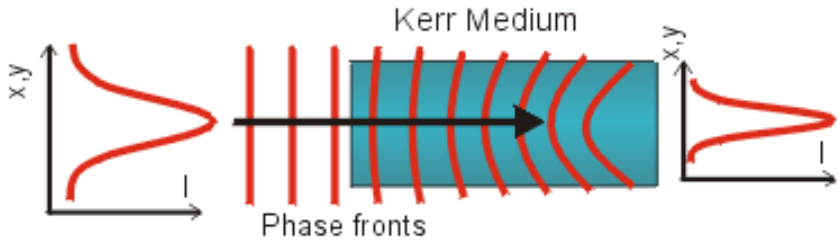
Example: Kerr lensing

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

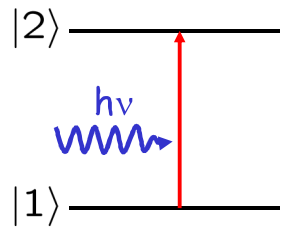
Laser beam with spatially varying profile (e.g. Gaussian beam) experiences in the medium a higher refractive index at the centre of the beam than the outside → medium acts as a lens!



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:

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

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

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

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

Optical Properties of Solids: Problem Set
Michaelmas Term 2021

1. **Reflection and absorption of EM radiation.** Light with angular frequency $\omega = 7.2 \times 10^{12}\,\mathrm{rad\,s^{-1}}$ is incident on a sample of thickness $20\,\mu$m with index of refraction $n = 11.7$ and extinction coefficient $\kappa = 8.5$.

   (a) What is the speed of the wave in the sample?

   (b) What is the wavelength of the wave before and after entering the sample?

   (c) What fraction of light entering the sample is present in the beam just before exiting?

   (d) What are the real and imaginary parts of the dielectric constant ϵ' and ϵ'' at this frequency?

2. **Absorption coefficient of AlAs.** Explain the difference between direct and indirect optical transitions in a semiconductor. Why is it difficult to make light-emitting devices out of indirect gap material?

   Figure 1 shows data for the absorption coefficient α of of the III-V semiconductor AlAs at 300 K. What can you deduce from the data about the band structure of AlAs?

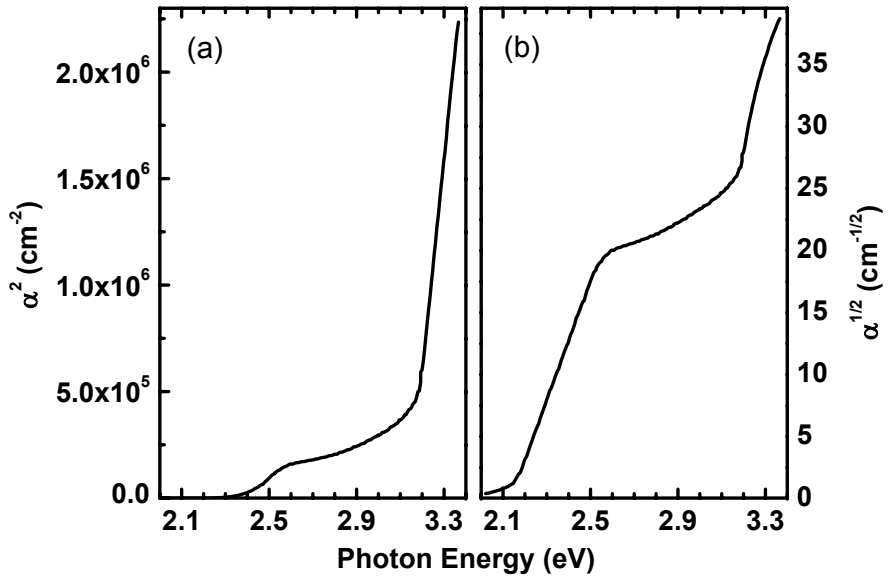


Figure 1: Absorption of AlAs at 300 K. For ease of analysis α is given both in terms of (a) α^2 and (b) $\sqrt{\alpha}$.

3. **Excitons in cuprous oxide.** Estimate the exciton binding energy of Cu_2O from the absorption spectrum shown in Figure 2.

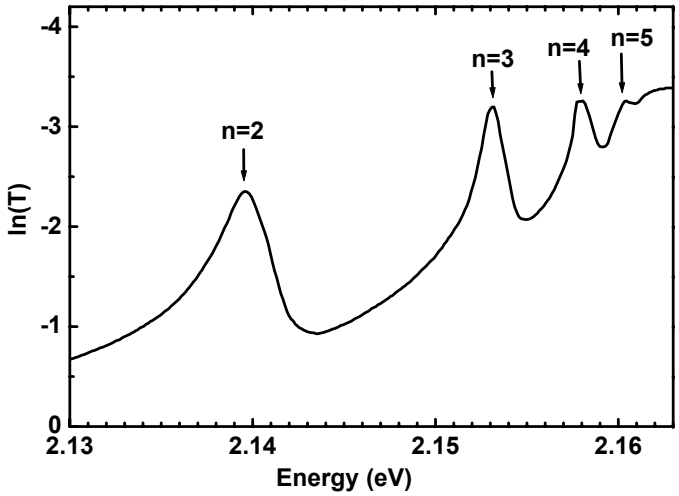


Figure 2: Absorption spectrum of Cu_2O at 77 K. (T is the fraction of light transmitted.)

Given that $\epsilon_\infty \approx 10$ obtain an estimate of the electron-hole reduced mass. The n=1 exciton transition is "forbidden" by symmetry in this material; suggest an alternative optical probe.

4. **Absorption in a GaAs/AlAs heterostructure.** Figure 3 shows the absorption spectrum of a sample containing a number of identical GaAs/AlAs quantum wells, measured at 4 K using the photoluminescence excitation (PLE) technique.

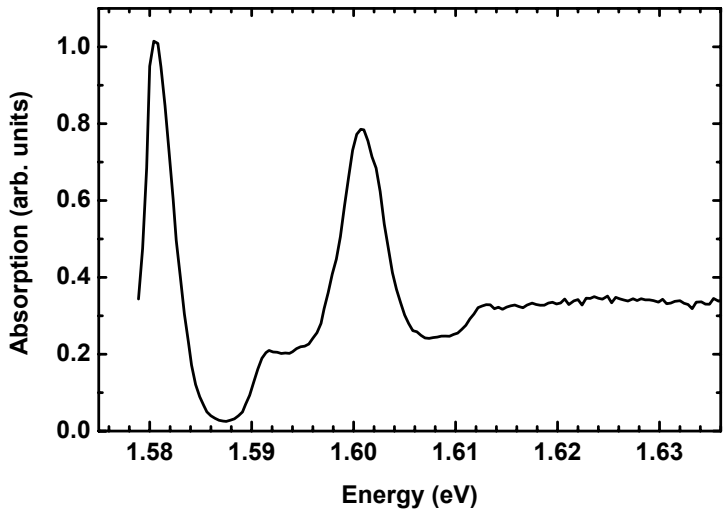


Figure 3: Absorption spectrum (PLE Intensity) of a GaAs/AlAs quantum well at 4K.

(a) Account for the shape of the absorption spectrum.

(b) Estimate the width of the quantum wells by assuming that the wells behave like perfectly confined two-dimensional systems. Would you expect the true well width to be larger or smaller than the answer you have calculated?

(c) Deduce the binding energies of the heavy and light hole excitons and comment on the values you obtain.

(d) What values would you expect for the binding energies in the limit of very wide and very narrow quantum wells?

GaAs data: $E_g(4\,K) = 1.519\,\text{eV}$; effective masses: electrons: $m_e^* = 0.07$; heavy holes: $m_{hh}^* = 0.45$ $m_{lh}^* = 0.085$.

5. **Free electon absorption in InSb.** Figure 4 shows data for the reflectivity of n-type indium antimonide as a function of photon energy.

(a) Explain the general shape of the curves and comment in particular on how and why the sharp drop in relectivity correlates with the free carrier density.

(b) Using the given data, estimate the value of the dielectic constant in the high-frequency limit, ϵ_∞. For each free-carrier density, determine the effective electron mass of InSb. Comment on the result you obtain.

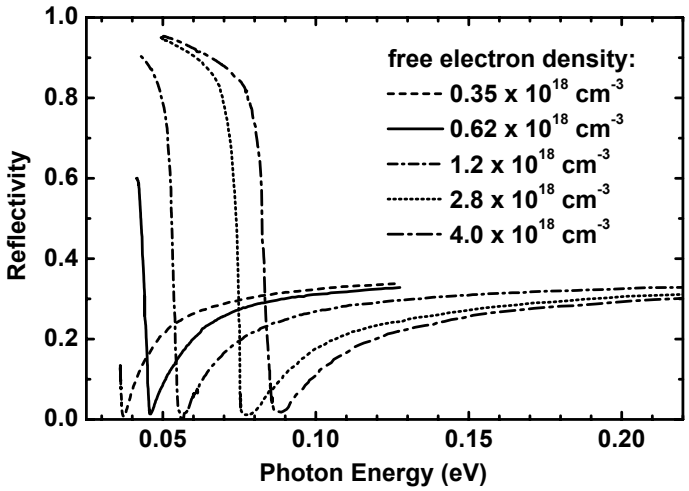


Figure 4: Reflectivity of n-type InSb for a range of free-electron densities.

6. **IR reflectivity of an ionic solid.** A linear chain of ions is often used to model the dielectric properties of an ionic solid. Here, the ions have masses m_1 and m_2 and charges $+q$ and $-q$, respectively, and they are subject to an interionic restoring force $-kx$, where k is a constant and x is the separation of an ion from its neighbour. Using such a model, show that the relative permittivity ϵ_r of the solid in the near infrared is of the form:

$$\epsilon_r(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)\,\frac{\bar{\omega}^2}{\bar{\omega}^2 - \omega^2} \tag{1}$$

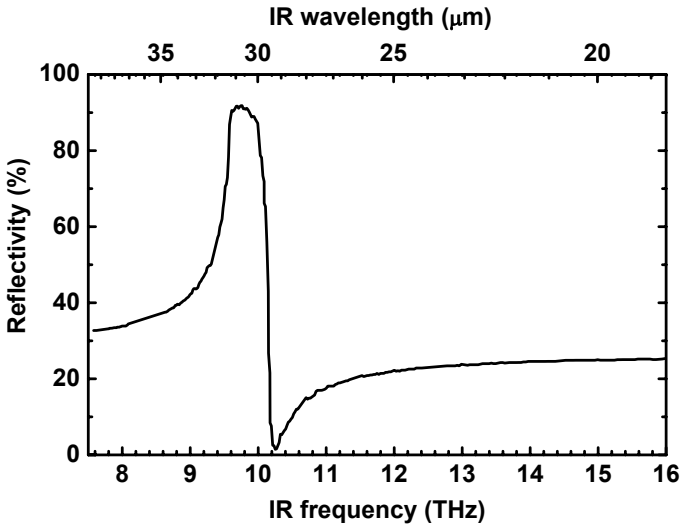


Figure 5: Infrared reflectivity of AlSb.

where ϵ_s and ϵ_∞ are relative permittivities at zero and very high (optical) frequencies, respectively. Derive an expression relating ϵ_s, ϵ_∞, $\bar{\omega}$ and ω_0, where ω_0 is the angular frequency at which $\epsilon_r = 0$. Show that $\bar{\omega}$ and ω_0 are equal to the angular frequencies of the transverse and longitudinal optic phonon modes, respectively, close to the Brillouin zone centre.

Figure 5 shows the reflectivity at normal incidence of a crystal of AlSb in the infrared. Account briefly for the descrepancies between the reflectivity predicted by your model and the experimental data shown in the figure. Using your model estimate the frequencies of the transverse and longitudinal optic phonons close to the Brillouin zone centre, and the permittivities ϵ_s and ϵ_∞. Hence estimate the value of the constant k for AlSb. Describe how you would estimate the lifetime of transverse optical phonons in AlSb using the data in the figure.

[The molar masses of Al and Sb are 27 g and 122 g, respectively.]

7. **Nonlinear Optics.**

   (a) A nonlinear substance is subjected to an applied optical-frequency field **E**, whose cartesian components are E_i (i=1, 2, 3). The polarization of the substance is given by

   $$P_i = \epsilon_0 \sum_j \chi_{ij}\, E_j + \epsilon_0 \sum_{jk} \chi^{(2)}_{ijk}\, E_j\, E_k + \epsilon_0 \sum_{jkl} \chi^{(3)}_{jkl}\, E_j\, E_k\, E_l + \cdots \qquad (2)$$

   Explain qualitatively the origin of the given terms that contribute to **P**. How does the crystal symmetry affect the nonlinear properties of solids? Explain why $\chi^{(2)}$ is found to be zero in centrosymmetric crystals.

   (b) Describe how the phase matching condition for second-harmonic generation may be fulfilled in a uniaxial crystal. Show that for a positive uniaxial crystal (i.e. $n_e > n_o$) with $\chi^{(2)} \neq 0$ second-harmonic generation may occur if the fundamental travels at

an angle θ with respect to the optic axis, where

$$\sin^2\theta = \frac{(n_o^\omega)^{-2} - (n_o^{2\omega})^{-2}}{(n_o^\omega)^{-2} - (n_e^\omega)^{-2}} \tag{3}$$

(c) The nonlinear optical coefficient tensor of a crystal from the orthorhombic crystal class is given by

$$\mathbf{d} = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix} \tag{4}$$

A laser beam is incident on the crystal. The beam travels in the xy plane, and is polarized with its electric field in the xy plane. Show that a second harmonic beam is produced which is polarized along the z axis. Show also that the magnitude of the second harmonic beam is a maximum if the incoming beam travels at 45° to the x axis.

(d) Explain how the $\chi^{(3)}$ terms of the nonlinear polarization give rise to an intensity-dependent refractive index in isotropic media. Describe why this effect may lead to self-focussing of intense laser beams in the medium.