MTLE-6120: Advanced Electronic Properties of Materials

Optical properties of Materials

Reading:

- Kasap: 9.1 - 9.18

Maxwell's equations in free media

- Linear response of materials described very generally by $\epsilon(\omega)$ and $\mu(\omega)$
- Maxwell's equations in the absence of free charges and currents

$$\nabla \cdot (\epsilon(\omega)\vec{E}) = 0$$
$$\nabla \times \vec{E} = i\omega\vec{B}$$
$$\nabla \times \frac{\vec{B}}{\mu(\omega)} = -i\omega(\epsilon(\omega)\vec{E})$$
$$\nabla \cdot \vec{B} = 0$$

- Substitute second equation in curl of third equation:

$$\frac{\nabla \times (\nabla \times \vec{B})}{\mu(\omega)} = -i\omega\epsilon(\omega)\nabla \times \vec{E} = \omega^2\epsilon(\omega)\vec{B}$$
$$-\nabla^2\vec{B} = \omega^2\epsilon(\omega)\mu(\omega)\vec{B} \qquad \text{using } \nabla \cdot \vec{B} = 0$$

Electromagnetic waves

- Write Maxwell's equation in linear media with no free charge or current as:

$$v^2(\omega)\nabla^2\vec{B} = -\omega^2\vec{B}$$
$$v^2(\omega)\nabla^2\vec{E} = -\omega^2\vec{E}$$

where $v(\omega) \equiv 1/\sqrt{\epsilon(\omega)\mu(\omega)}$

- This is exactly the equation of a wave with speed v

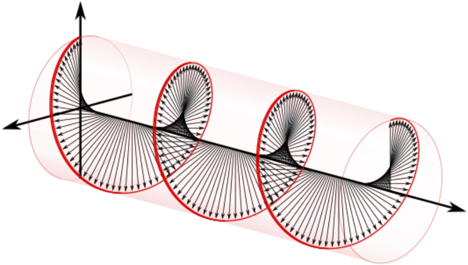
$$v^2\nabla^2 f = -\omega^2 f$$
$$v^2\nabla^2 f = \frac{\partial^2 f}{\partial t^2}$$

where f is either $\vec{E}$ or $\vec{B}$

- Solution to the wave equation with $|\vec{k}| = \omega/v$:

$$f(\vec{r}) = f e^{i\vec{k}\cdot\vec{r}}$$
$$f(\vec{r}, t) = f e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

Polarization



- EM wave propagating along x:

$$\vec{E}(\vec{r},t) = E_0 \hat{y} e^{i(kx-\omega t)} \qquad \text{or} \qquad \vec{E}(\vec{r},t) = E_0 \hat{z} e^{i(kx-\omega t)}$$

  two field directions $\Rightarrow$ two independent linear polarizations

- Linearly combine to

$$\vec{E}(\vec{r},t) = E_0 \frac{\hat{y}+i\hat{z}}{\sqrt{2}} e^{i(kx-\omega t)} \qquad \text{or} \qquad \vec{E}(\vec{r},t) = E_0 \frac{\hat{y}-i\hat{z}}{\sqrt{2}} e^{i(kx-\omega t)}$$

  $\Rightarrow$ two independent circular polarizations (left/right)

- Photons: circular polarizations have spin angular momentum $\pm\hbar$ along propagation direction (photons are spin $s=1$ particles)

Wave speed and refractive index

- Electromagnetic waves satisfy dispersion relation $\omega = v|\vec{k}|$
- EM wave velocity $v(\omega) = 1/\sqrt{\epsilon(\omega)\mu(\omega)}$
- In vacuum, $\epsilon(\omega) = \epsilon_0$ and $\mu(\omega) = \mu_0$, so that speed of light in free space

$$c = \frac{1}{\sqrt{\epsilon_0 \mu_0}}$$

- In materials, speed of light usually specified by refractive index

$$n(\omega) \equiv \frac{c}{v(\omega)} = \sqrt{\frac{\epsilon(\omega)\mu(\omega)}{\epsilon_0 \mu_0}}$$

Refractive index: frequency dependence

- Most materials are non-magnetic $\mu \approx \mu_0$
- Therefore $n^2(\omega) \approx \epsilon_r \equiv \epsilon(\omega)/\epsilon_0$
- Several contributions to relative permittivity:

$$n^2 \approx \epsilon_r = 1 + \chi_e^{(\text{free } e^-)} + \chi_e^{(\text{bound } e^-)} + \chi_e^{(\text{ions})} + \chi_e^{(\text{dipoles})}$$

- Frequency dependence (Drude-Lorentz model):

$$n^2(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_\alpha \frac{\chi_{0\alpha}\omega_{0\alpha}^2}{\omega_{0\alpha}^2 - i\gamma_\alpha\omega - \omega^2}$$

  where α includes bound e^-, ions and dipoles
- First Drude term proportional to free carrier density:
  - Dominates for metals
  - Present to varying degrees for doped semiconductors
- Remaining terms contribute in all materials

Refractive index: wavelength dependence

- Frequency dependence (Drude-Lorentz model):

$$n^2(\omega) = 1 + \sum_\alpha \frac{\chi_{0\alpha}\omega_{0\alpha}^2}{\omega_{0\alpha}^2 - i\gamma_\alpha\omega - \omega^2}$$

(Drude term captured by setting $\chi_0\omega_0^2 \to \omega_p^2$, $\omega_0 \to 0$ and $\gamma \to 1/\tau$)

- Equivalently in terms of wavelength $\lambda = 2\pi c/\omega$:

$$n^2(\lambda) = 1 + \sum_\alpha \frac{\chi_{0\alpha}\lambda^2}{\lambda^2 - i\delta_\alpha\lambda - \lambda_{0\alpha}^2}$$

where $\lambda_0 = 2\pi c/\omega_0$ and $\delta = 2\pi c\gamma_\alpha/\omega_0^2$

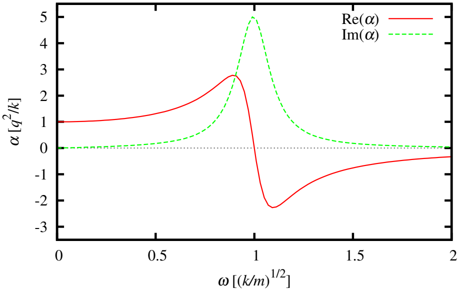
- Can use a number of α in the empirical Sellmeier relation instead:

$$n^2(\lambda) = 1 + \sum_\alpha \frac{A_\alpha\lambda^2}{\lambda^2 - i\delta_\alpha\lambda - \lambda_\alpha^2}$$

Complex refractive index

- The n^2 we have been working with so far has been implicitly complex (due to the τ and γ's)
- Customary to call complex refractive index $N = n + iK$ (where n and K are real)
- Wave speed $v = \frac{c}{N} = \frac{c}{n+iK}$ is complex
- Wave vector $k = \frac{\omega}{v} = \frac{\omega}{c}(n + iK) = k_0(n + iK)$ is complex
- What do the imaginary parts here mean?
- Wave function (fields) $\propto e^{ikx} = e^{i(nk_0)x} \cdot e^{-(Kk_0)x}$
- Wave intensity $\propto e^{-(2Kk_0)x}$ (proportional to $|\text{field}|^2$)
- $\Rightarrow$ Wave attenuates as $e^{-\alpha x}$ with absorption coefficient $\alpha = 2Kk_0$

Kramers-Kronig relations



- Real and imaginary parts of $\epsilon(\omega)$ (and hence $n(\omega)$) not independent
- Causality $\Rightarrow$ response functions (eg. $\chi(\omega)$) must be complex analytic functions ($\chi(z)$)
- Leads to the Kramers-Kronig relations:

$$\mathrm{Re}\chi(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{+\infty} \mathrm{d}\omega' \frac{\mathrm{Im}\chi(\omega)}{\omega' - \omega}, \qquad \mathrm{Im}\chi(\omega) = \frac{-1}{\pi}\mathcal{P}\int_{-\infty}^{+\infty} \mathrm{d}\omega' \frac{\mathrm{Re}\chi(\omega)}{\omega' - \omega}$$

- Absorption at ω_0 affects n at all ω

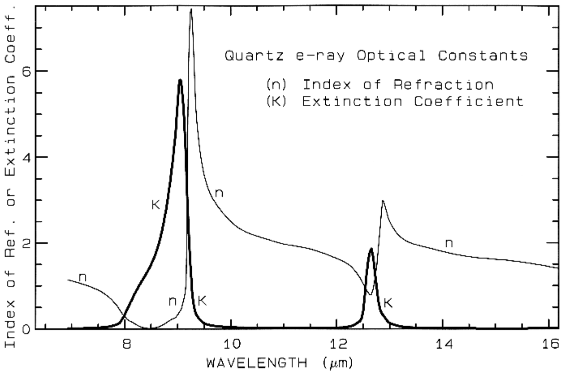
Absorption mechanisms

Every polarizability term has a corresponding absorption mechanism:

- Free electrons: resistive loss in Drude term
- Bound electrons: absorption excites electronic transitions
- Ions: absorption excites phonons
- Dipoles: absorption excites molecular rotations

- Simple model so far (Lorentz) assumed single resonant frequency ω_0
- Each of the above processes have a band of absorption frequencies instead

Lattice absorption: Restrahlen band



- Optical phonons in ionic crystals: charge oscillations $\Rightarrow$ interact with EM (hence the name 'optical' phonons)
- High DOS for transverse and longitudinal optical phonons
- Absorption peaks at corresponding wavelengths: Restrahlen band
- Typically in the mid-infrared part of the spectrum

Electronic absorption: bound model

- Simple model for inuslators so far: electrons bound by springs
- In reality: electrons delocalized in insulators / semiconductors too
- Only no net current in completely filled (or empty) bands
- Low frequency response is effectively like bound electrons (because $v_d = 0$)
- Bound model obtained response of form:

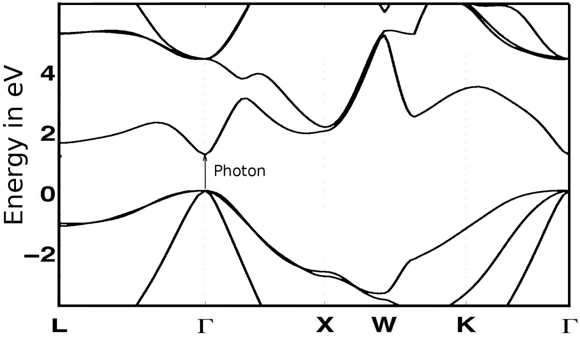
$$\chi(\omega) = \frac{\chi_0 \omega_0^2}{\omega_0^2 - i\gamma\omega - \omega^2}$$

- Interpretation of behavior near $\omega \sim \omega_0$ needs revision
- Energy absorbed from light must be taken up by the electrons
- How can you increase the electronic energy of insulators?
- Move an electron from the valence to conduction band (leave hole behind)
- What is the minimum frequency that can do this? $\hbar\omega = E_g$
- Effectively ω_0 now corresponds to $E_g/\hbar$

Optical excitation of electrons

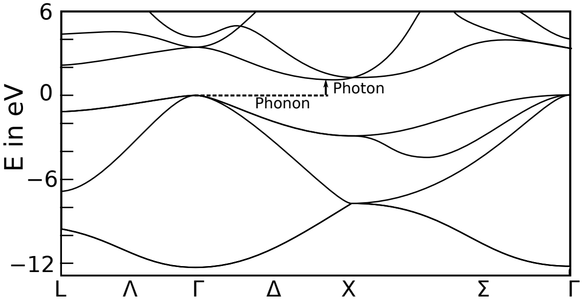
- Light excites electron in valence band (initial energy $E_i < 0$) to conduction band (final energy $E_j > E_g$)
- Energy conservation: $E_i + \hbar\omega = E_j \Rightarrow \omega = (E_j - E_i)/\hbar > E_g/\hbar$
- Momentum conservation $\hbar k_i + \hbar\omega/c = \hbar k_j \Rightarrow k_j - k_i = \omega/c = 2\pi/\lambda$
- Typical $E_g \sim 1 - 10$ eV with $\lambda \sim 100$ nm - 1 μm (NIR, visible, UV)
- Typical $k_i, k_j \sim 2\pi/a$ with $a < 1$ nm
- $\Rightarrow$ photon momentum is negligible in electronic processes
- Effectively $k_i = k_j$ (vertical transitions) for optical absorption

Direct absorption



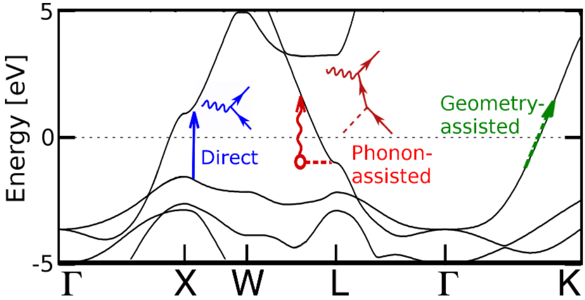
- Direct band-gap semiconductors (eg. GaAs): VBM and CBM at same k
- Possible to have $E_j - E_i = E_g$ with $k_i = k_j$
- Direct absorption: light produces electron-hole pair
- Allowed here for $\omega \geq E_g/\hbar$

Indirect absorption



- Indirect band-gap semiconductors (eg. Si): VBM and CBM at different k
- Not possible to have $E_j - E_i = E_g$ with $k_i = k_j$
- Indirect absorption: light produces electron-hole pair $\pm$ phonon
- Conservation: $E_j - E_i \pm \hbar\omega_{\rm ph} = \hbar\omega$, $k_j \pm k_{\rm ph} = k_i$
- Negligible energy in phonon, negligible momentum in photon
- Direct absorption becomes possible above interband threshold E_t

Absorption in metals (plasmon decay)

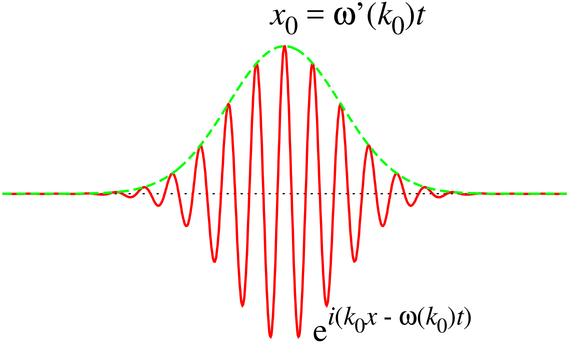


- Direct interband transitions from d-bands to Fermi level
- Indirect transitions possible in two ways:
  - Get momentum from phonons (lattice vibrations)
  - Geometry effect in nanostructures: uncertainty principle / momentum from surface
- Additionally resistive losses at all frequencies (dominates at low frequency)

Excitons

- Photons absorbed to produce electron-hole pairs for $\hbar\omega \geq E_g$
- This assumes electrons and holes don't interact with each other
- Instead they attract with potential $V(r) \sim -e^2/(r\epsilon_r)$
- Corresponding binding energy $E_b = \frac{m_{\text{eff}}}{m\epsilon_r^2}$ Ryd (typically $\sim 0.01 - 0.1$ eV) (similar to the donor/acceptor level estimate)
- Here $m_{\text{eff}} \sim m_e^* m_h^*/(m_e^* + m_h^*)$ is reduced mass of electron-hole pair
- Exciton: bound pair of electron and hole
- Can absorb photons when $\hbar\omega \geq E_g - E_b$ (slightly smaller than band gap)

Wave packets



- Velocity so far is phase velocity $v(\omega) = \frac{\omega}{k} = \frac{c}{n(\omega)}$
- Wavepackets travel with group velocity $v_g = \frac{\partial\omega}{\partial k}$
- Same concept for all waves; only difference: dispersion relation $\omega(k)$

Group velocity and group index

- Group velocity

$$\begin{aligned} v_g = \frac{\partial \omega}{\partial k} &= \frac{1}{\partial k/\partial \omega} \\ &= \frac{1}{\partial(\omega n(\omega)/c)/\partial \omega} \\ &= \frac{c}{n(\omega) + \omega n'(\omega)} \\ &= \frac{c}{n(\lambda) - \lambda n'(\lambda)} \end{aligned}$$

since $\omega \propto \lambda^{-1}$

- Correspondingly group index:

$$\begin{aligned} n_g \equiv c/v_g &= n(\omega) + \omega n'(\omega) \\ &= n(\lambda) - \lambda n'(\lambda) \end{aligned}$$

- For a non-dispersive medium (constant n), $v_g = v$ and $n_g = n$

Optical energy density and power flux

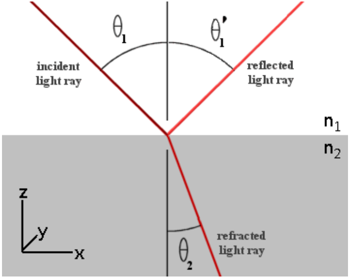
- Energy density in electric field $= \frac{\epsilon E^2}{2}$
- Energy density in magnetic field $= \frac{B^2}{2\mu}$
- Maxwell's equation $\nabla \times \vec{E} = -\partial \vec{B}/\partial t \Rightarrow |\vec{E}| = v|\vec{B}| = \frac{|\vec{B}|}{\sqrt{\epsilon\mu}}$
- Therefore energy densities in $\vec{E}$ and $\vec{B}$ are equal
- Net energy density $= \epsilon E^2$
- Wave moves with velocity v, so power flux is $v\epsilon E^2$ $= v^2\epsilon EB = \frac{1}{\mu}EB = EH$
- More generally, power flux given by Poynting vector $\vec{E} \times \vec{H}$

Interface between media

- In material with index n_1, light incident towards interface with n_2
- Wavevectors: incident $\vec{k}_1$, reflected $\vec{k}_1'$ and transmitted $\vec{k}_2$
- At boundary, $\vec{E}_{\|}, D_{\perp}$ and $\vec{B}$ continuous (non-magnetic)
- Frequencies: common ω for all three (phases match for all t)
- Phase of fields must match at all x and y
- y-matching implies all three wavevectors in same plane
- x-matching implies that for all x:

$$e^{ik_1 \sin\theta_1 x} = e^{ik_1 \sin\theta_1' x} = e^{ik_2 \sin\theta_2 x}$$

$$\Rightarrow k_1 \sin\theta_1 = k_1 \sin\theta_1'$$



- Therefore $\theta_1 = \theta_1'$ and

$$\frac{\sin\theta_2}{\sin\theta_1} = \frac{k_1}{k_2} = \frac{\omega/v_1}{\omega/v_2} = \frac{c/v_1}{c/v_2} = \frac{n_1}{n_2}$$

(Snell's law)

Fresnel's equations: E in plane ($\|$)

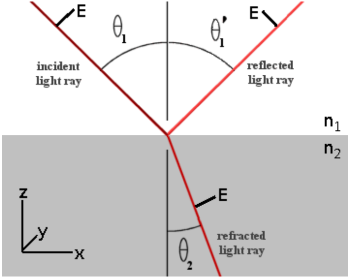
- Matching conditions:

$$\epsilon_1 (E_1 \sin\theta_1 + E_1' \sin\theta_1') = \epsilon_2 E_2 \sin\theta_2 \qquad \text{(Normal)}$$
$$E_1 \cos\theta_1 - E_1' \cos\theta_1' = E_2 \cos\theta_2 \qquad \text{(Tangential)}$$

- Solve for E_1' and E_2:

$$r_\| \equiv \frac{E_1'}{E_1} = \frac{\frac{\epsilon_2 \sin\theta_2}{\epsilon_1 \sin\theta_1}\cos\theta_1 - \cos\theta_2}{\frac{\epsilon_2 \sin\theta_2}{\epsilon_1 \sin\theta_1'}\cos\theta_1' + \cos\theta_2}$$
$$\Rightarrow \qquad r_\| = \frac{n^2\cos\theta_1 - \sqrt{n^2 - \sin^2\theta_1}}{n^2\cos\theta_1 + \sqrt{n^2 - \sin^2\theta_1}}$$
$$t_\| = \frac{2n\cos\theta_1}{n^2\cos\theta_1 + \sqrt{n^2 - \sin^2\theta_1}}$$

where $n = n_2/n_1$



Fresnel's equations: E normal to plane ($\perp$)

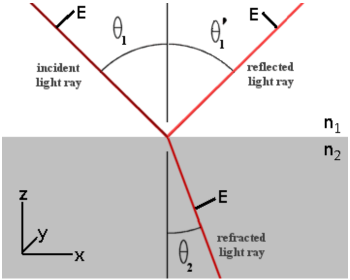
- Matching conditions:

$$\frac{1}{v_1}(E_1 \cos\theta_1 - E_1' \cos\theta_1') = \frac{1}{v_2} E_2 \cos\theta_2 \qquad (B \text{ tangential})$$
$$E_1 + E_1' = E_2 \qquad (E \text{ Tangential})$$

- Solve for E_1' and E_2:

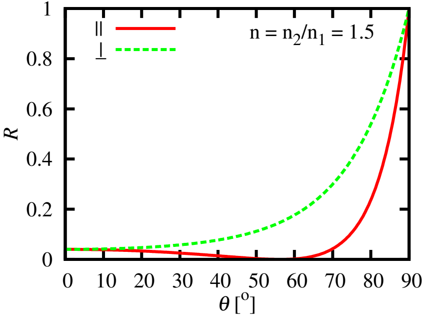
$$\Rightarrow \qquad r_\perp = \frac{\cos\theta_1 - \sqrt{n^2 - \sin^2\theta_1}}{\cos\theta_1 + \sqrt{n^2 - \sin^2\theta_1}}$$
$$t_\perp = \frac{2\cos\theta_1}{\cos\theta_1 + \sqrt{n^2 - \sin^2\theta_1}}$$

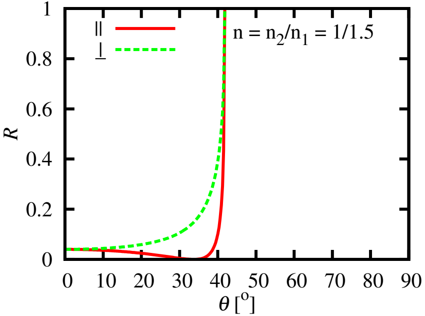
where $n = n_2/n_1$



Reflection and transmission coefficients

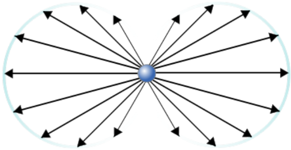
- Power flow $= v\epsilon|E|^2 = (c/n)n^2|E|^2 \propto n|E|^2$
- Therefore, $R = |r|^2$ and $T = n|t|^2$ (for each of $\parallel$ and $\perp$)





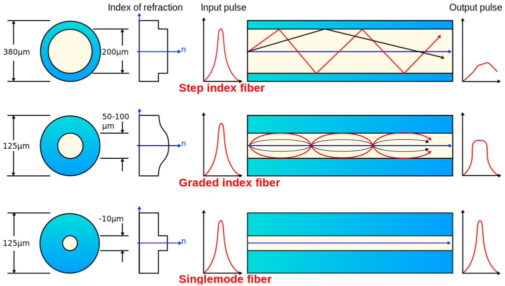
- $R_\perp$ increases monotonically with incidence angle
- $R_\parallel$ goes through zero at Brewster angle $\theta_B = \tan^{-1} n$
- $R = 1$ beyond $\theta_c = \sin^{-1} n$ when $n < 1$ (total internal reflection)
- Structures on wavelength scale: interference effects
  eg. anti-reflective coatings (see section 9.7)

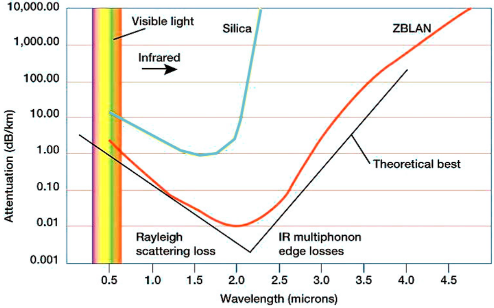
Scattering



- Index change due to impurity, defect or particles (in a suspension / composite)
- Scattered light output in all directions (cannot separate reflected / transmitted)
- Contributes to attenuation α (along with absorption)
- Rayleigh scattering: scatterer size $\ll \lambda$ (wave limit)
- Scatterng cross section $\propto \lambda^{-4}$
- Angular distribution $\propto (1 + \cos^2 \theta)$
- Mie theory: general case of spherical particles $<, \sim, > \lambda$
- Used to determine particle sizes from diffraction measurements
- Scatter size $\gg \lambda$ (particle limit)
- Scattering cross section $\sim \pi r^2$ (constant in λ)
- Why is the sky blue, but clouds white/grey?

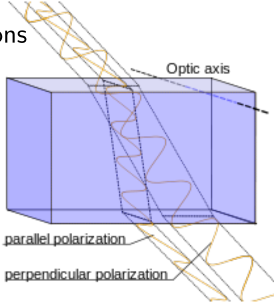
Optical fibers



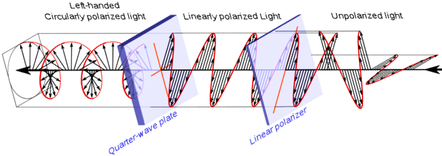


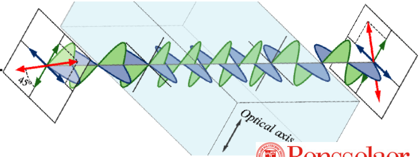
- Higher n core surrounded by lower n sheath
- Channel light using total internal reflection
- Pulse shape distortion due to angle distribution
- Rectify / minimize using graded index / single mode fibers
- Attenuation: scattering at low λ, lattice absorption at high λ
- Alternate glasses like heavy metal fluorides (expensive) eg. ZBLAN (Zr-Ba-La-Al-Na-F)

Anisotropic media



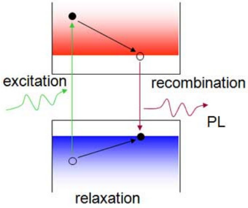
- In crystals, $n^2 = \epsilon$ is a tensor
- In general, values n_1, n_2, n_3 along principal directions
- Isotropic: $n_1 = n_2 = n_3$ eg. cubic
- Uniaxial: $n_1 = n_2 \neq n_3$ eg. tetragonal, hexagonal
- Biaxial: $n_1 \neq n_2 \neq n_3$ eg. orthorhombic, triclinic
- Optic axis: direction along which $n_\perp$ is isotropic
- Uniaxial: single optic axis (direction 3 above)
- Biaxial: two optic axes (not along 1, 2 or 3)
- Consequence: two polarizations have different n for same direction
- Refracted waves in different directions (birefringence)
- Commonly used material: calcite (rhombohedral)
- Polarizers, half-wave and quarter-wave plates (Read 9.15 - 9.17)





Luminescence

- Reverse of electronic absorption: electron de-excitation emits light (de-excitation includes electron-hole recombination in semiconductors)
- Electrons in excited states for multiple reasons:
  - Optical excitation: photoluminescence (PL)
  - Electronic excitation: cathodoluminescence
  - Thermal excitation: thermoluminescence

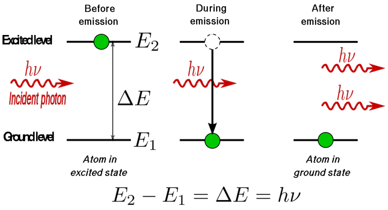


- Includes fluorescence and phosphorescence (slowed by forbidden transitions)
- Phosphors: materials used for their luminescence
- Example: Cr^{3+} in corundum Al_2O_3 emits in red (ruby)
- Traps / dopants in semiconductors: radiative recombination
- Applications:
  - Defunct display technologies (CRT)
  - Down-conversion: white LEDs generate red components from blue
  - Time-resolved PL: analysis of trap levels and lifetimes

Stimulated emission

- Consider two level system with populations N_1 and N_2
- Incident light with intensity I: absorb to excite $1 \rightarrow 2$

$$-\dot{N}_1 = \dot{N}_2 = B_{12} I N_1$$



- Emission in presence of light:

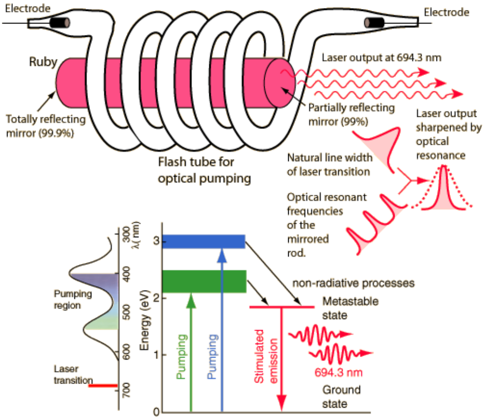
$$\dot{N}_1 = -\dot{N}_2 = \underbrace{A N_2}_{\text{spontaneous}} + \underbrace{B_{21} I N_2}_{\text{stimulated}}$$

- Einstein's theorem: $B_1 2 = B_2 1$ for detailed balance / microscopic reversibility
- Basically, matrix element for forward and reverse process
- Net result:

$$\dot{N}_1 = -\dot{N}_2 = A N_2 + B I (N_2 - N_1)$$

- Important: stimulated emission in same quantum state as incident (Bosonic effect)

Lasers



- Basic idea: a synchronized photoluminescence using stimulated emission
- Population inversion $(N_2 > N_1)$ by optical pumping
- Need long-lived metastable state to hold N_2 (small A)
- Resonant cavity: light reflects back and forth
- Stimulated emission enhances intensity (amplification)
- Light output through slightly transmitting mirror
- Coherence: light with single wavelength and phase (line narrowing)

Electro- and magneto-optic effects

- Nonlinearity of ϵ and hence n with respect to $\vec{E}$

$$n(\vec{E}) = n_0 + \underbrace{\vec{a}_1 \cdot \vec{E}}_{\text{Pockel}} + \underbrace{\vec{E} \cdot \bar{a}_2 \cdot \vec{E}}_{\text{Kerr}} + \cdots$$

- Kerr effect: present in all materials to varying degrees
- Pockel's effect: present only in materials that are non-centosymmetric (symmetry breaking needed to give $\vec{a}_1$ a direction)
- Note: n must be tensorial for such materials
- Similarly, magneto-optic effect: nonlinearity in $\vec{B}$
- Faraday rotation: magnetic field along propagation direction rotates polarization
- Relative permeability of iron $\sim 2 \times 10^5 \Rightarrow n = \sqrt{\epsilon\mu} \sim 450$
- Relative permeability of ferrite $\sim 640 \Rightarrow n = \sqrt{\epsilon\mu} \sim 25$
- Much higher than any dielectric: why are these not used in optics?