5. Inorganic semiconductors

5.1 Crystalline materials (band structure)

Last week:

Opaque systems and powders

- Reminder on specular reflection, why scattering media behave differently
- Absorption/reflection by scattering media
- Measuring absorption spectra for powders and (some) films

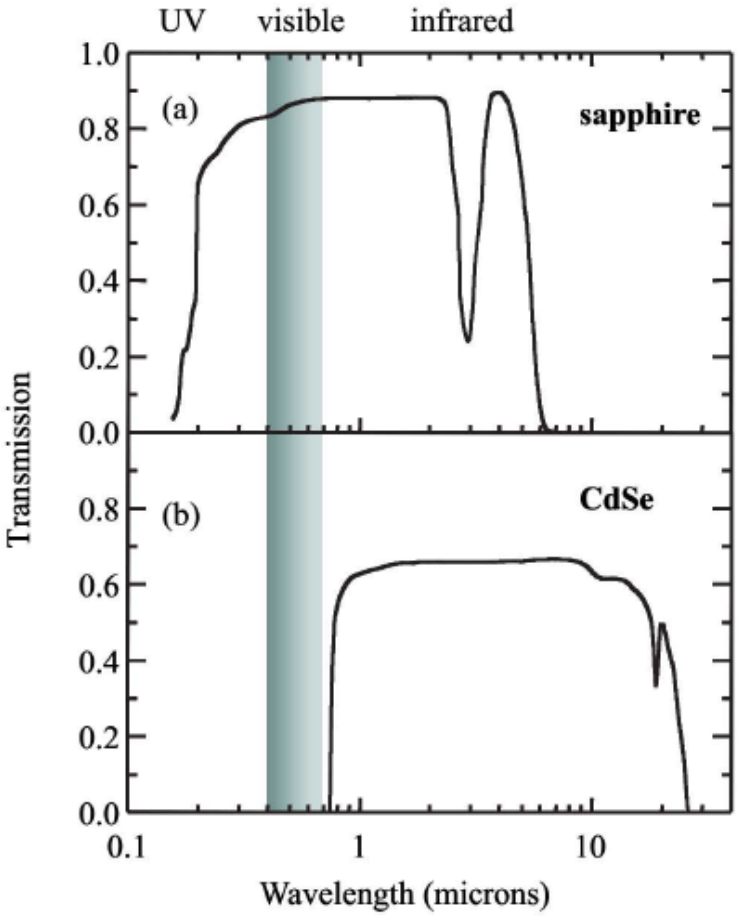
Thin films

- How to measure optical constants of films: ellipsometry
- Basic principles and experimental setup
- Ellipsometry versus conventional absorption measurements
- Data analysis

Topics of this lecture:

- Optical properties of semiconductors vs. insulators and metals
- Reminder on band structure
- Light absorption: direct vs indirect semiconductors
- Excitonic effects
- Luminescence: direct vs indirect semiconductors

Crystalline insulators and semiconductors

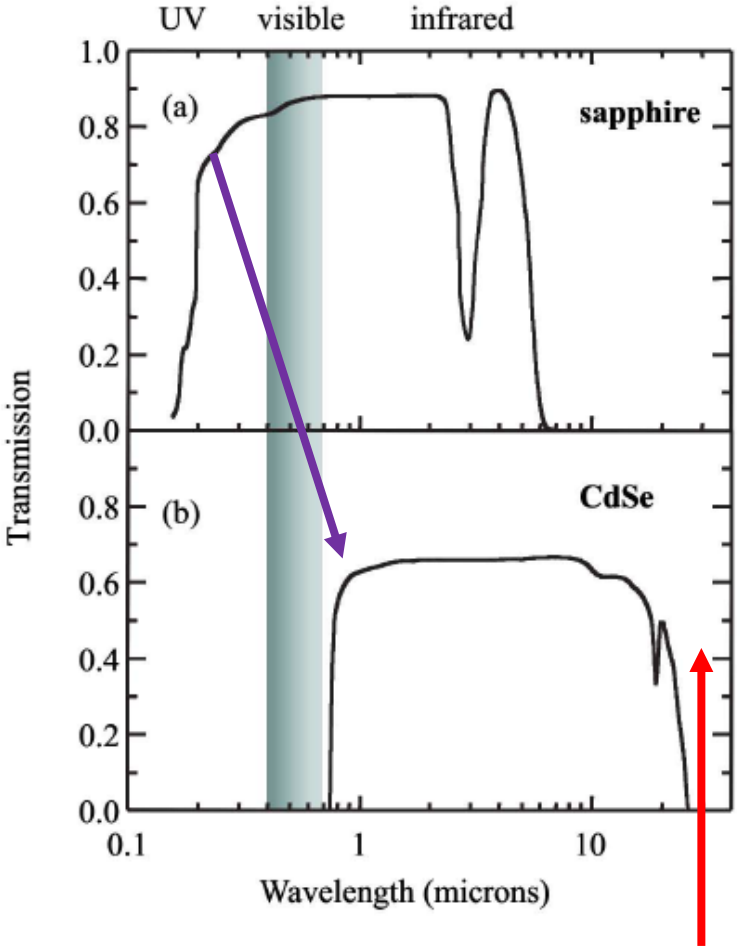


Crystalline sapphire (Al_2O_3)

- Within the transparency range the absorption coefficient is very small, and refractive index may be taken to be real with no imaginary component
- Dip in transmission in µm range caused by vibrational absorption, analogous to IR absorption due to vibrations in polar molecules
- Vibrational excitations of a crystal lattice are called ***phonon modes***
- Vibrational absorption in a solid is usually called phonon absorption or lattice absorption
- Transmission drops sharply in UV region for $\lambda < 0.2$ µm due to absorption by bound electrons: **Fundamental absorption edge**

Fox, Mark. Optical Properties of Solids (Oxford Master Series in Physics)

Crystalline insulators and semiconductors



Lattice absorption + free carriers

Cadmium selenide

- Transparency range lies outside the visible spectrum!
- No visible light is transmitted through the crystal, it has a dark metallic appearance

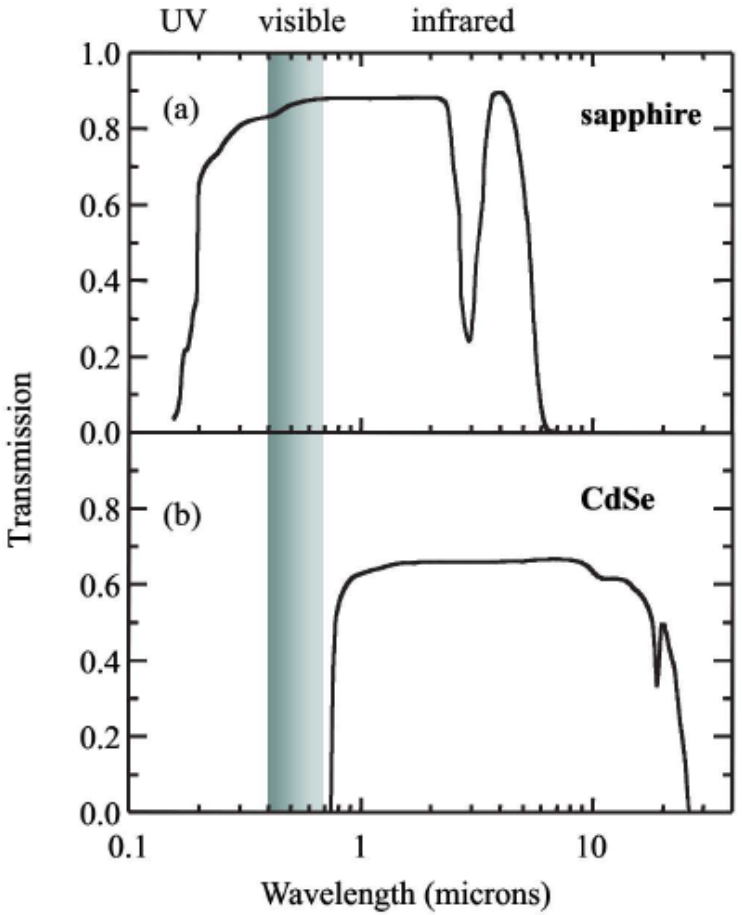
Table 1.2 Approximate transparency range, band gap wavelength λ_g, and refractive index n of a number of common semiconductors. n is measured at 10 μm. Data from Driscoll & Vaughan (1978), Kaye & Laby (1986), and Madelung (1996).

Crystal	Range (μm)	λ_g (μm)	n
Ge	1.8 – 23	1.8	4.00
Si	1.2 – 15	1.1	3.42
GaAs	1.0 – 20	0.87	3.16
CdTe	0.9 – 14	0.83	2.67
CdSe	0.75 – 24	0.71	2.50
ZnSe	0.45 – 20	0.44	2.41
ZnS	0.4 – 14	0.33	2.20

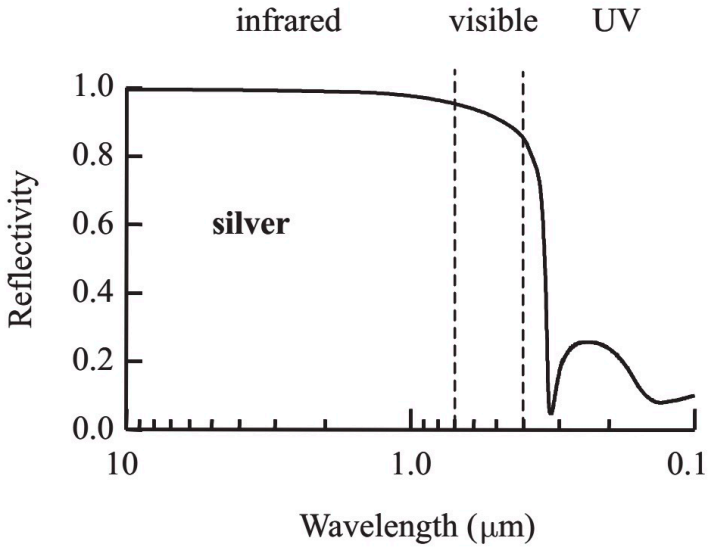
Fox, Mark. Optical Properties of Solids (Oxford Master Series in Physics)

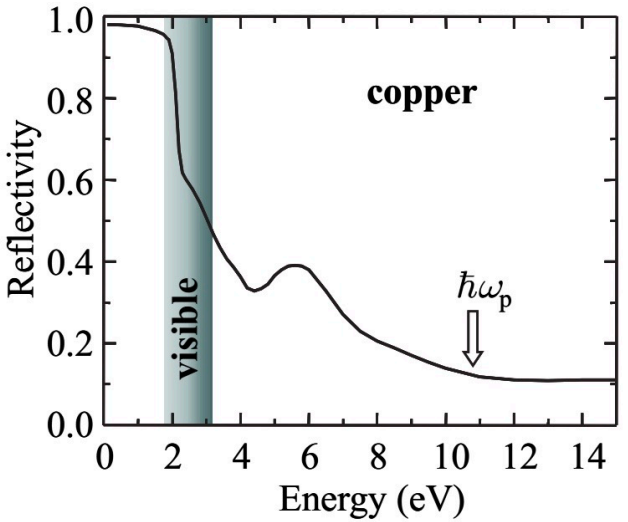
Insulators and semiconductors vs. metals

Color mostly defined by transparency window



Color mostly defined by high reflectivity and interband electronic transitions (ex: gold and copper when polished)





Fox, Mark. Optical Properties of Solids (Oxford Master Series in Physics)

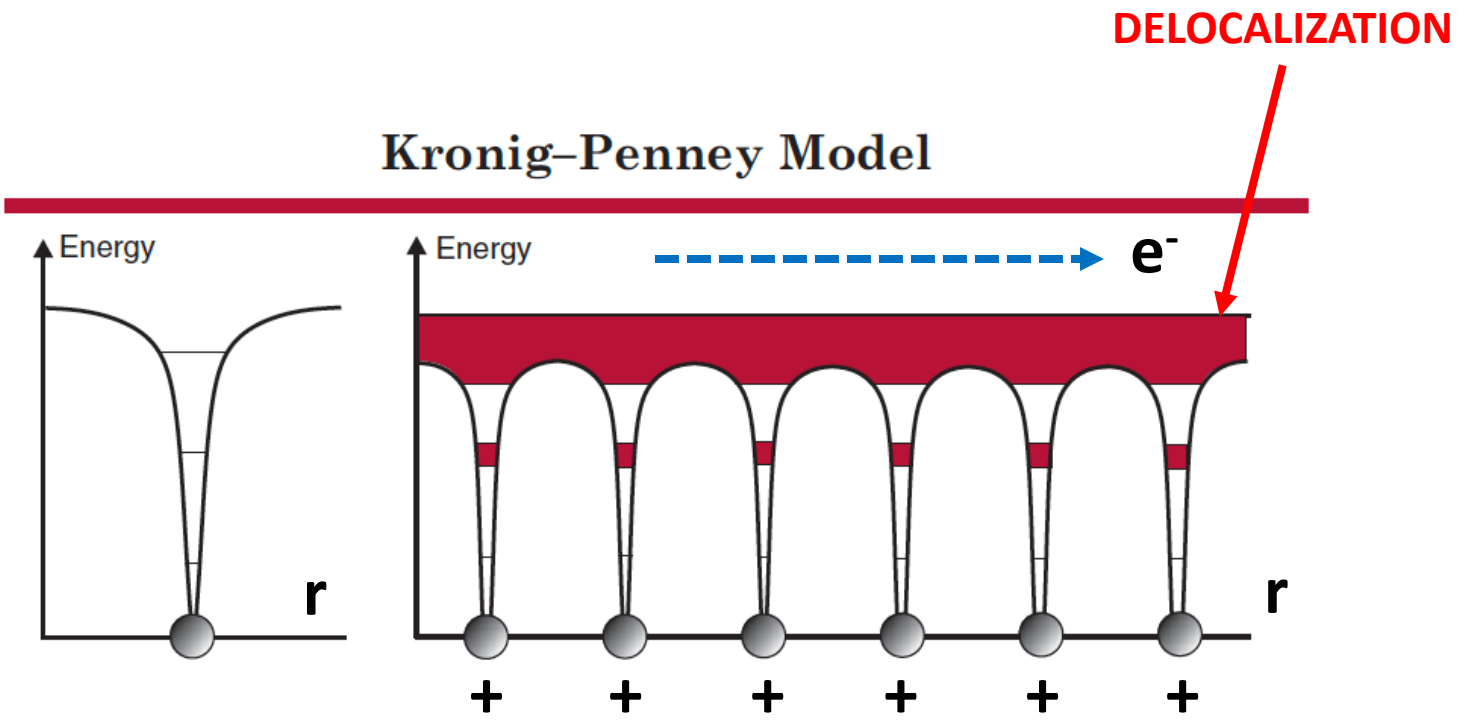
Electronic bands

Atoms in a solid are packed very close to each other, with interatomic separation approximately equal to the size of the atoms

- Outer atomic orbitals overlap and interact strongly with each other
- Energy levels split, yielding many new orbitals
- The difference in energy between them becomes very small, so the levels may be considered as forming continuous bands of energy = broadens the discrete levels of the free atoms into **bands**
- The electron states within the bands are **delocalized**
- Some intervals of energy contain no orbitals = **band gaps**

Electronic bands

- In a unidimensional approximation, electrons in a solid experience a periodic potential due to the positively charged atomic nuclei of the crystal lattice
- This situation is further simplified by considering equidistant potential wells of constant depth



Field Guide to Solid State Physics, Wartak, Fong

Electronic bands

- The mathematical treatment of the SC band structure is given by the Bloch's theorem
- The Coulomb potential in a crystalline solid is **periodic** and the wave functions of electrons inside a crystal are modulated by this periodic potential

Modulated plane wave:

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = u_{\boldsymbol{k}}(\boldsymbol{r}) \cdot \exp(i\boldsymbol{k} \cdot \boldsymbol{r})$$

This is a solution to Schrödinger's equation $\hat{H}\psi = E\psi$

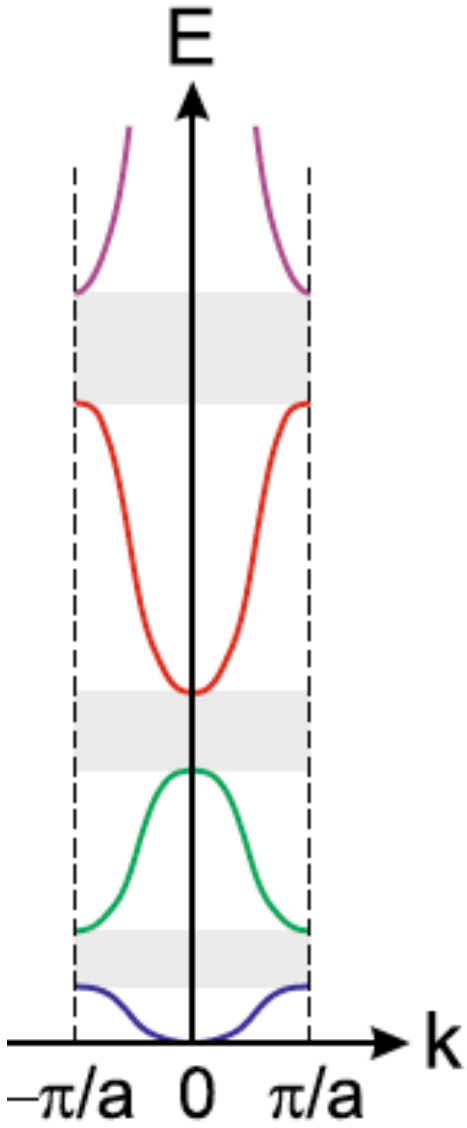
with $E = \frac{1}{2}mv^2 = \frac{1}{2}\frac{\boldsymbol{p}_{crystal}{}^2}{m} = \frac{h^2}{8\pi^2 m}\boldsymbol{k}^2 = \frac{h^2}{8mL^2}n^2$ and $\boldsymbol{k} = \frac{n\pi}{L}$

Note: Electrons in a crystal lattice have a momentum. It is defined by the associated wave vectors $\boldsymbol{k}$ of this lattice, according to $\boldsymbol{p}_{crystal} \equiv \hbar\boldsymbol{k}$

Crystal band structure

- Map of energy E against wavevector $\hbar k$:
  E($\hbar k$) = crystal band structure
- Gives the band gap and the **Brillouin** zones
- A Brillouin zone is the volume of $\hbar k$ - space containing all the values of $\hbar k$ up to π/a
  (*a* = lattice constant in one dimension)
- E($\hbar k$) reaches a maximum or a minimum within the Brillouin zone
- Bands appear parabolic due to $E = \frac{h^2}{8\pi^2 m}\hbar k^2$

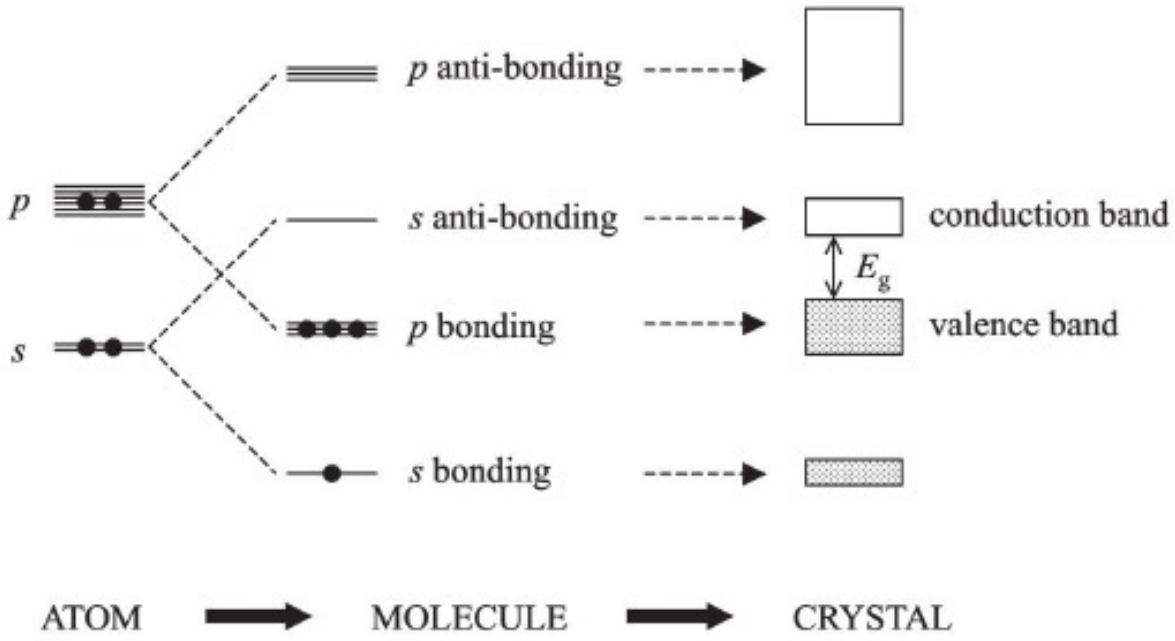
Note: This relationship is derived for **free electrons**.
In order to provide a good fit one should use the effective mass of the electron (or hole)



Brillouin zone

Grundmann, The Physics of Semiconductors

Transitions

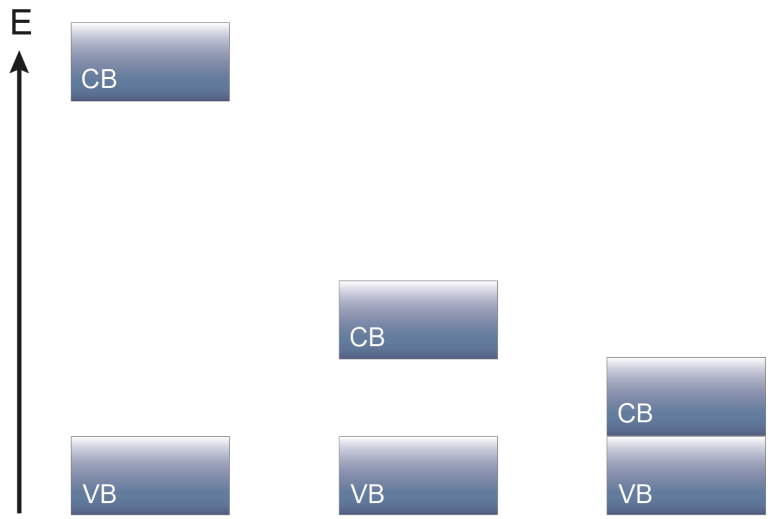


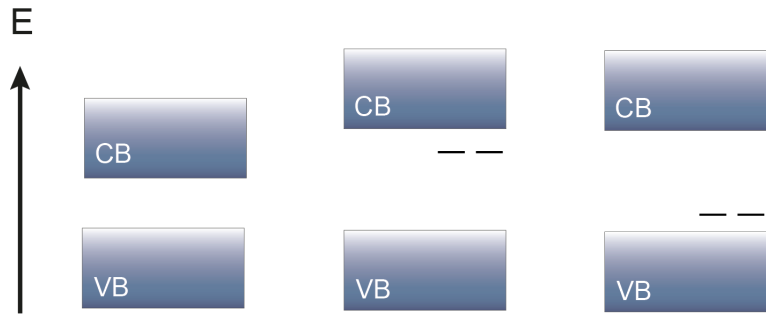
Lowest empty or partially filled energy band

Band gap:
band of forbidden energy

Highest entirely occupied energy band

Electric conduction in solids

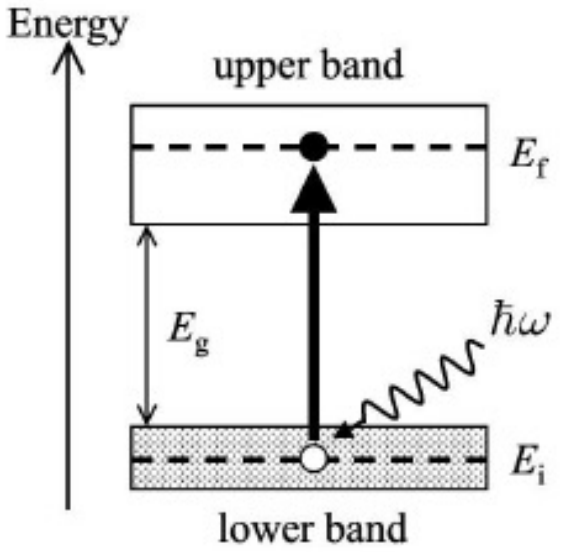




So far we have not provided anything else than thermal energy.
What happens when there is energy from an electromagnetic wave?

Optical transitions

- Optical transitions can occur between the electronic bands if they are allowed by the selection rules
- This ‘interband’ absorption is possible over a continuous range of photon energies determined by the lower and upper energy limits of the bands (≠ free atoms)
- Absorption edge is caused by the onset of optical transitions across the fundamental band gap of the material
- Opposite process = interband luminescence



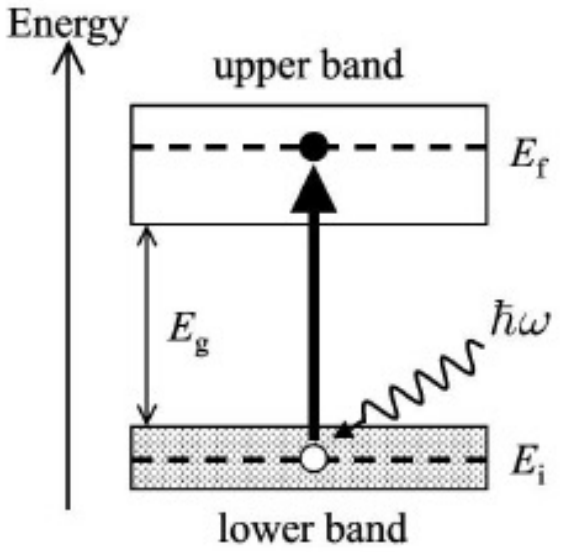
The photo-conduction of the semiconductor under band-gap irradiation is due to both e_{cb}^- and h_{vb}^+

Optical transitions

Energy conservation: $E_f = E_i + \hbar\omega$

Momentum conservation: $\hbar\boldsymbol{k_f} = \hbar\boldsymbol{k_i} + \hbar\boldsymbol{k_{photon}}$

But…The wave vector of a photon is very small…
What does this imply??



The photo-conduction of the semiconductor under band-gap irradiation is due to both e_{cb}^- and h_{vb}^+

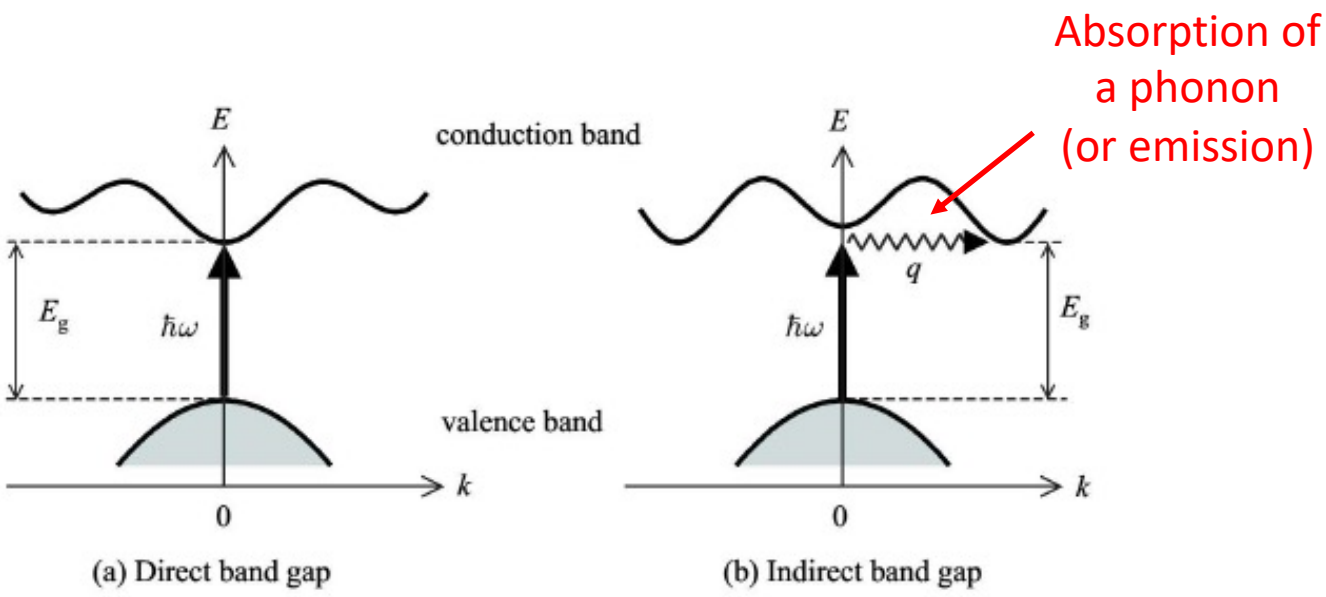
Example of optical transition:
TiO_2 is a solid with ionic character, we can see it as constituted of Ti^{4+} ions and O^{2-} ions

Ti: $3d^2\ 4s^2$ → Ti^{4+} : $3d^0$ → empty conduction band
O: $2p^4$ → O^{2-} : $2p^6$ → entirely occupied valence band

Photons of energy $\hbar\omega$ > ~3.2 eV can give a transition 2p(O)→ 3d(Ti)

Direct and indirect band gap

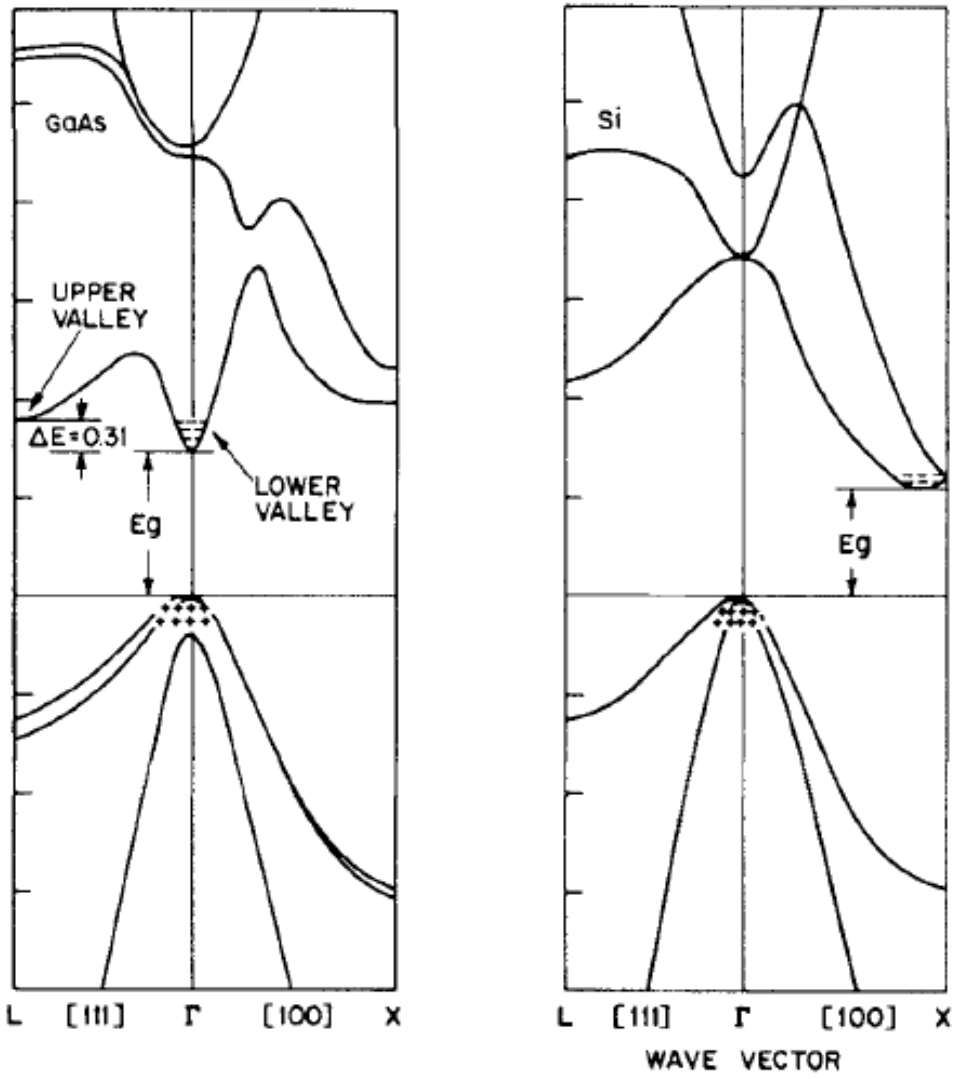
- The distinction concerns the relative positions of the conduction band minimum and the valence band maximum in the Brillouin zone
- Direct gap material: both occur at the center of the Brillouin zone where $\hbar k = 0$
- Indirect gap material: the CB minimum does not occur at $\hbar k = 0$, but rather at some other value of $\hbar k$ which is usually at the zone edge or close to it
- Indirect band gap: It is not possible to make this jump by absorption of a photon alone, transition must involve a phonon to conserve momentum



Direct and indirect band gap

GaAs: direct gap at 1.42 eV

Silicon: indirect gap at 1.12 eV



Transition rate and density of states

- Transition rate for **direct** absorption can be calculated with Fermi's golden rule:

- Because electronic states and the phonon modes have a continuous range of energies, one can define a density of states = number of available states:

$$\text{Number of states in the range } E \rightarrow (E + dE) = g(E)dE$$

- Knowing $g(E)$ is is needed for calculating absorption and emission spectra

- Occupation changes with temperature!

- Absorption strength is usually very high because of the very large density of absorbing atoms in the solid

- This is a very different case than molecular systems! → Produce sizeable optical effects in very thin samples, good for optoelectronic devices

Optical absorption in direct SCs

- Simple method for determining direct/indirect bandgap: absorption spectroscopy
- For a **direct** band gap, the absorption coefficient $\propto$ is related to the light frequency by:

$$\propto \sim \sqrt{h\upsilon - E_g}$$

This approximation is only valid for
$h\upsilon \sim E_g$
and near $\hbar$ = 0 !

Direct transitions:

- For $h\upsilon > E_g$, $\propto$ shows a steep rise with photon energy up to 10^4 -10^6 cm^{-1}
- For $h\upsilon < E_g$, $\propto$ = 0 or close to (trap states could contribute)

Plots of $\propto$ and $\propto^2$:

Optical absorption in indirect SCs

- For a indirect band gap, one needs to consider the phonon energy E_p:

$$\propto \sim \frac{\left(h\upsilon - E_g + E_p\right)^2}{\exp\left(\frac{E_p}{kT}\right) - 1} + \frac{\left(h\upsilon - E_g - E_p\right)^2}{1 - \exp\left(-\frac{E_p}{kT}\right)}$$

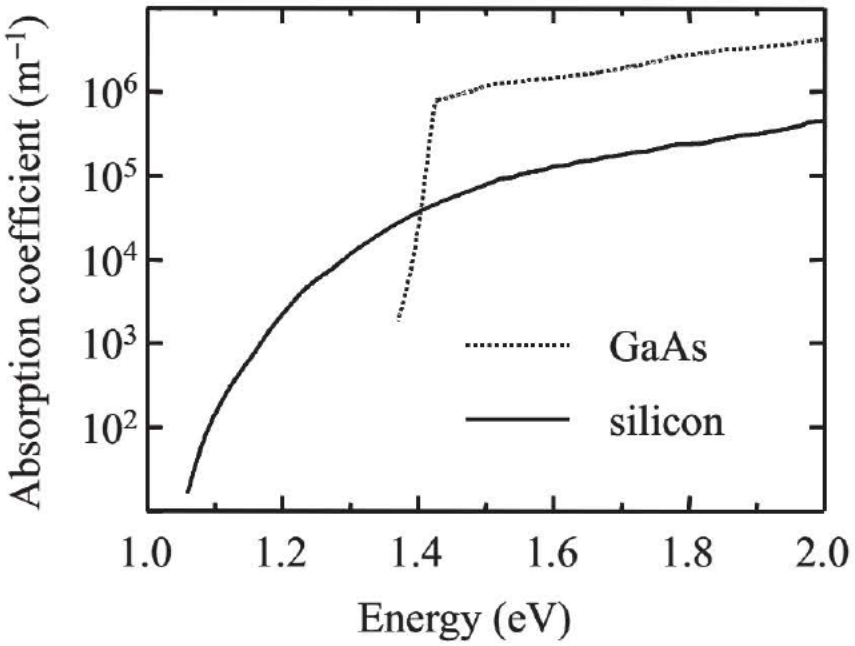
- Transitions are less probable → absorption coefficients are usually lower…
- What is the shape of $\propto (h\upsilon)$ vs $(h\upsilon)$?

Optical absorption in indirect SCs

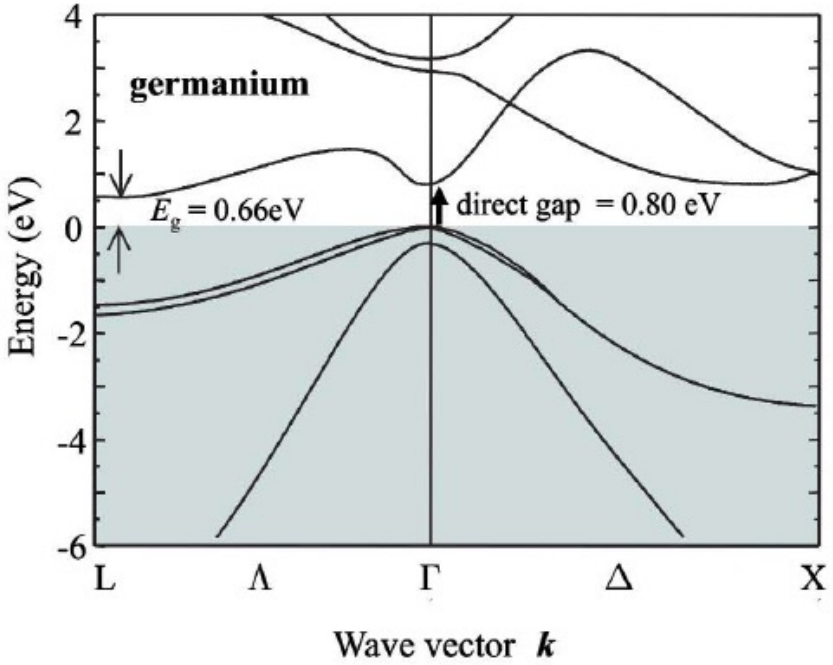
Direct vs. indirect transitions: Indirect transitions are less probable

Example: GaAs: direct gap at 1.42 eV
Silicon: indirect gap at 1.12 eV

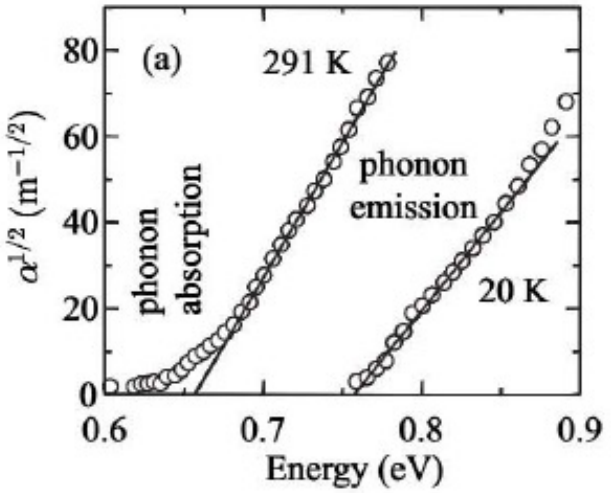
!! Log scale !!



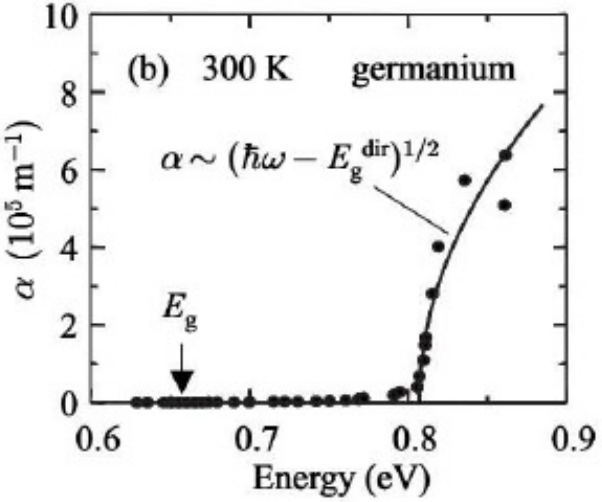
Phonons absorption/emission



Indirect absorption near the band gap



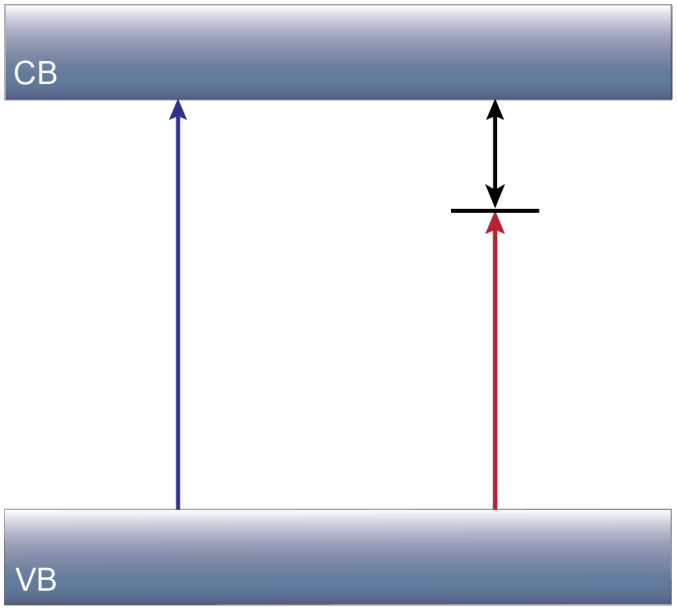
Direct absorption at higher E



Excitonic effects

Exciton

- Electron-hole pair where charge carriers are bound together by Coulombic interaction
- ***Neutral entity*** - can move easily in a material and carries excitation energy
- Simplest picture: exciton may be understood as a small hydrogenic system



Exciton bond energy E_x [meV]

Si	14.7	CdS	29	KCl	400
Ge	4	CdSe	15	KBr	400
GaAs	4.2	BaO	56	AgCl	30
GaP	3.5	InP	4	AgBr	20

$k_B T$ ≈ 25 meV at RT

- Stable excitons will only be formed if the attractive potential is sufficient to protect the exciton against collisions with phonons!
- In other words, $E_x > k_B T$

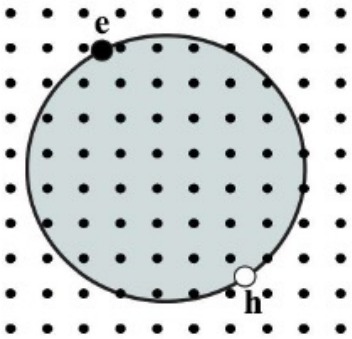
Wannier and Frenkel excitons

Wannier–Mott excitons: Free excitons

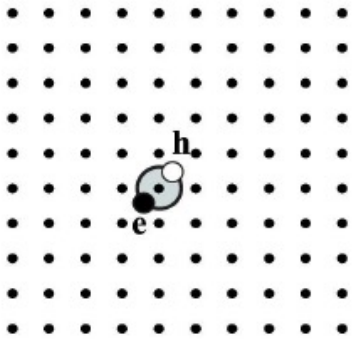
- Mainly observed in semiconductors
- Large radius that encompasses many atoms
- They are delocalized states that can move freely throughout the crystal
- Small binding energies due to their large radius, with typical values of around 0.01 eV
- Are observed clearly only at cryogenic temperatures in many materials

Frenkel excitons : Tightly bound excitons

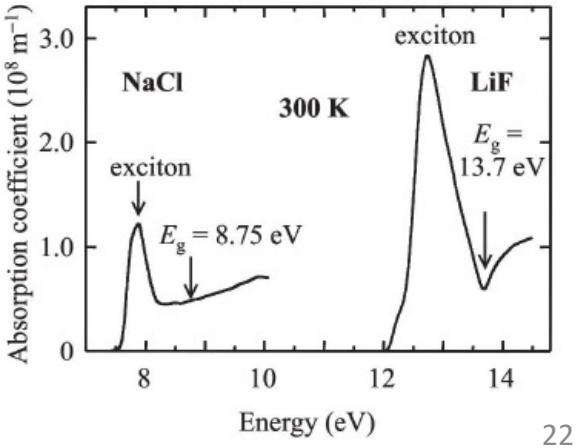
- Found in insulators and molecular crystals
- Much less mobile than free excitons
- Move through the crystal by hopping from one atom site to another
- Larger binding energies of the order 0.1–1 eV, which makes them stable at RT



(a) Free exciton

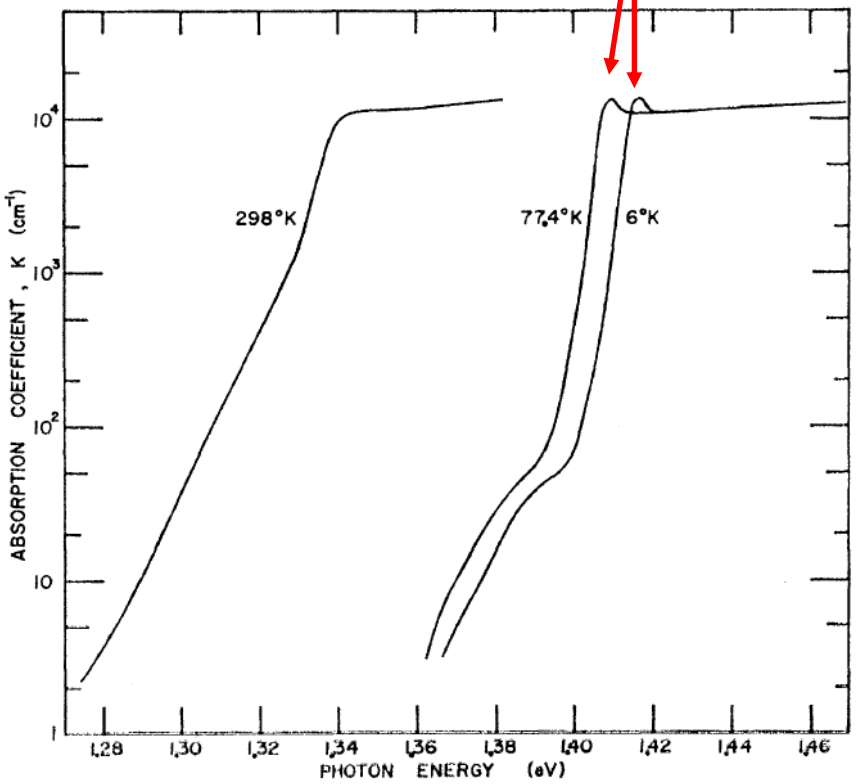


(b) Tightly bound exciton

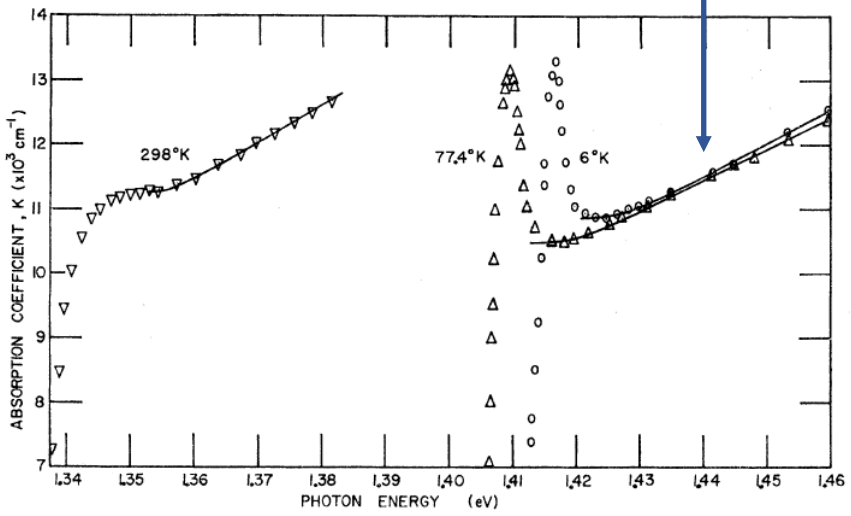


Example of InP

Exciton absorption



Free e^-_{CB} absorption



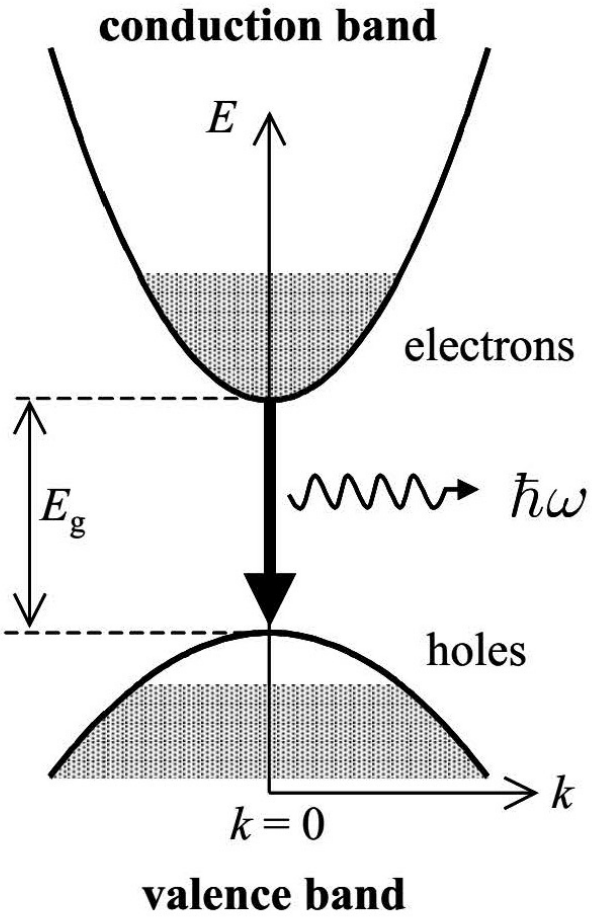
Turner et al., *Phys. Rev.*, **1964**, A1467

Luminescence: Direct bandgap

- Interband luminescence in a SC occurs when an electron that has been excited into the CB drops back to the VB by emission of a photon
- Simultaneously reduces the number of e^-_{CB} and h^+_{VB} by one
- Reverse process of interband absorption, which is equivalent to the creation of an e^-/h^+ pair

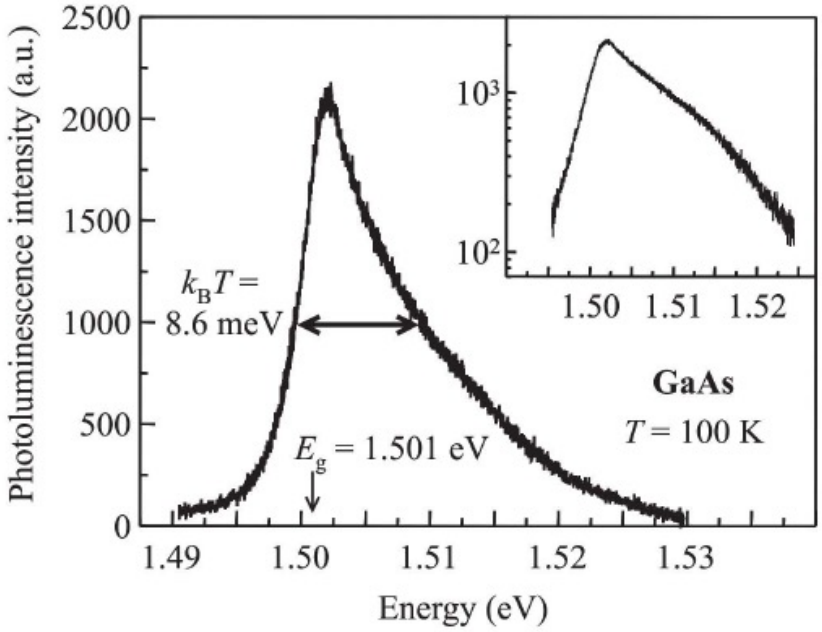
Photoluminescence: Re-emission of light after absorption of a photon of higher energy

Electroluminescence: Emission of light caused by running an electrical current through the material



Direct bandgap:
Absorption is high → luminescence is high! With short radiative lifetimes (ns)

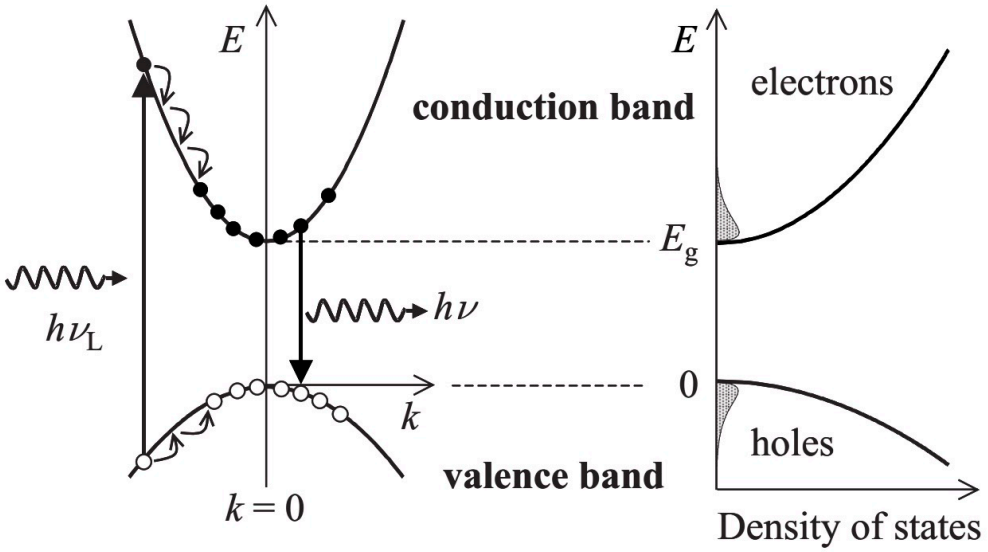
Luminescence: Direct Bandgap



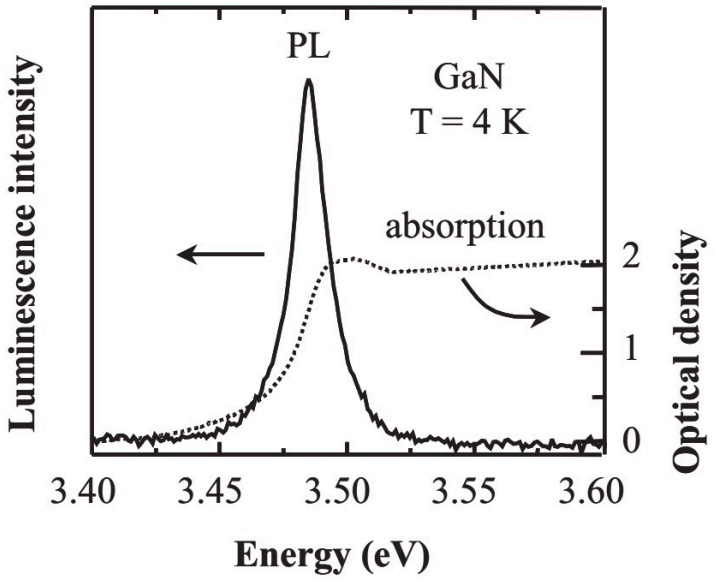
$$I(h\upsilon) \sim \sqrt{h\upsilon - E_g}\exp(-\frac{h\upsilon - E_g}{k_B T})$$

- Luminescence spectrum rises sharply at E_g and falls off exponentially
- Exponential decay due to Boltzmann factor: Describes e- and h^+ distributions in bands
- Expect a sharply-peaked spectrum of width $\sim k_B T$ starting at E_g

Additional considerations on PL



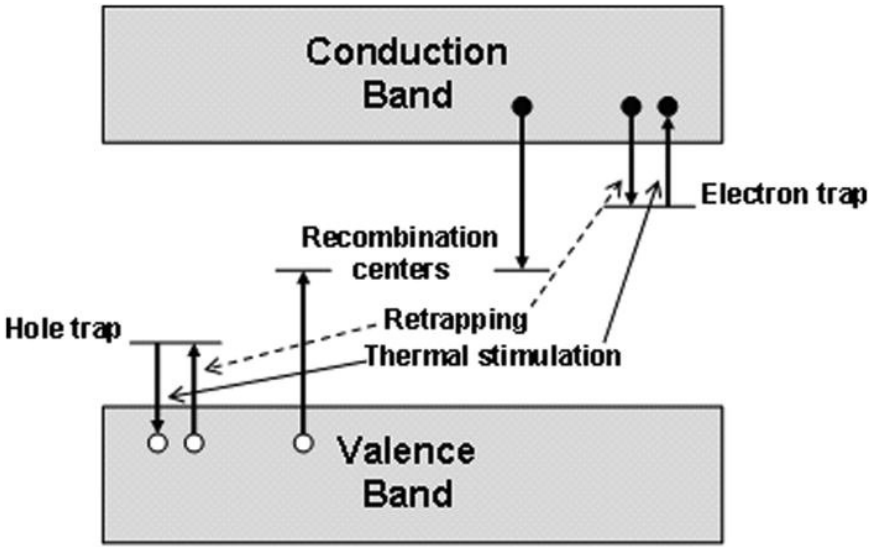
M. Fox, Optical Properties of Solids



- Because of rapid relaxation of e-/h^+ to the bottom/top of their respective bands, PL will occur close to the bandgap

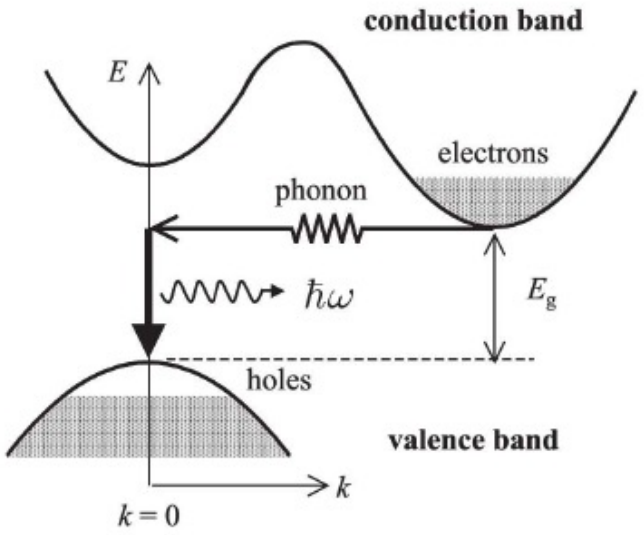
→Characteristic ***narrow*** shape of PL bands
≠ large absorption bands

- But…There can always be trap states!



J. Appl. Phys.. 2012;111(6). doi:10.1063/1.3693581

Luminescence: Indirect bandgap



- The requirement of emitting both a phonon and a photon during the transition makes it a second-order process, with a relatively small transition probability
- Radiative lifetime is therefore much longer than for direct transitions!
- Competition with non-radiative recombination…

- Indirect gap materials are generally bad light emitters
- Two important semiconductors, crystalline silicon and germanium, have indirect band gap and are not used as light emitters…

…But they are good for separating charges!!!