# 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***

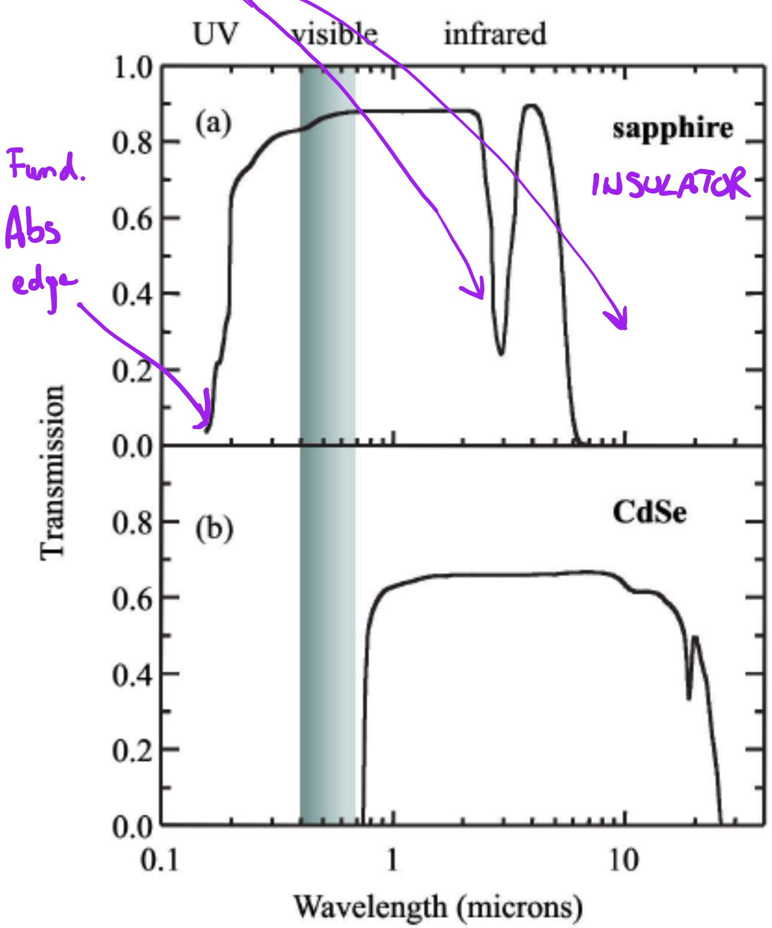
- How to measure optical constants of films: ellipsometry
- Basic principles and experimental setup
- Ellipsometry versus conventional absorption measurements
- Data analysis

## 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

Vib. absorbtion → phonon modes

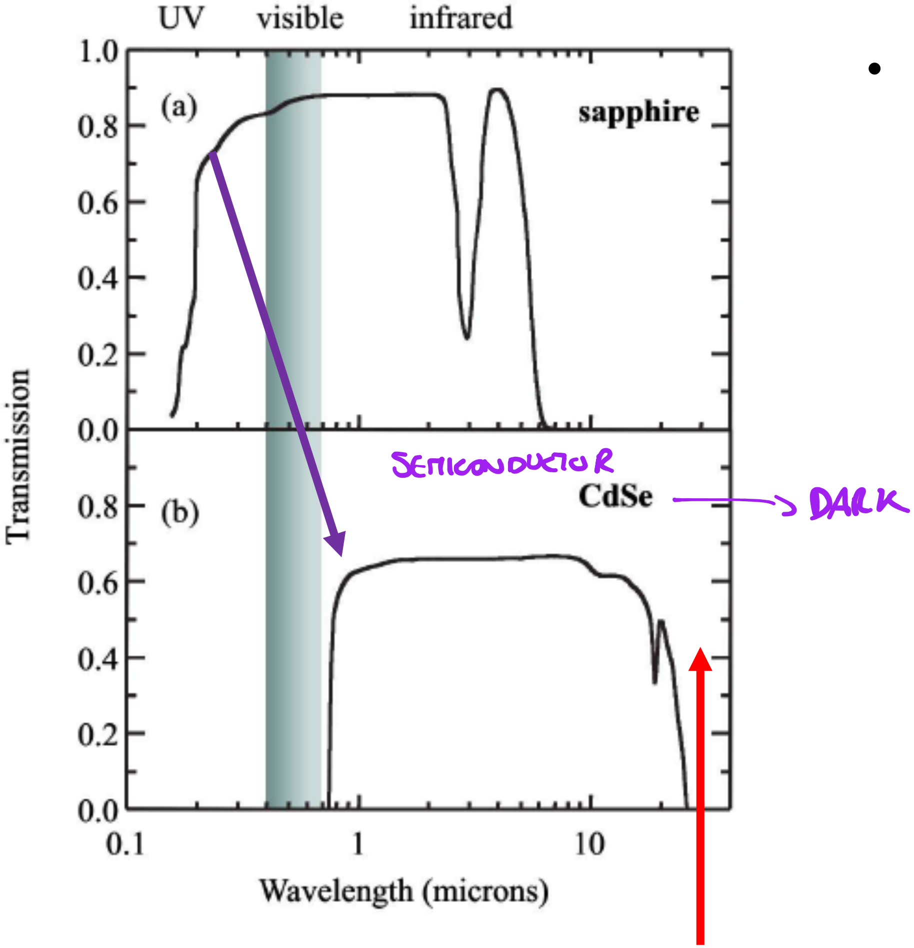


**Crystalline sapphire ($Al_2O_3$)**

- 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 λ < 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 $\lambda_g$, 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).

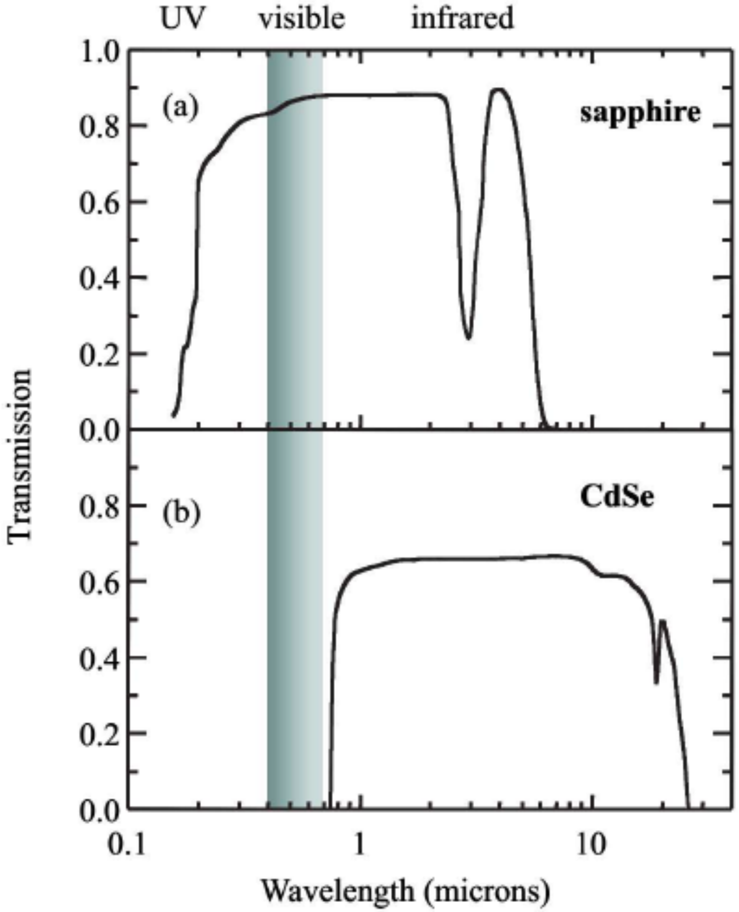
$$\vec{P} = \varepsilon_0 \chi \vec{E} = \varepsilon_0(\underbrace{\tilde{\varepsilon}}_{\tilde{n}^2}-1)\vec{E}$$

| Crystal | Range (µm) | $\lambda_g$ (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 |

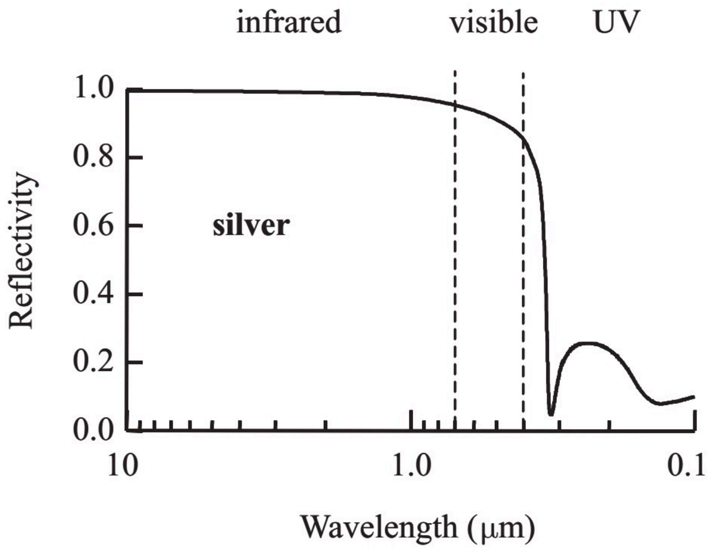
Fox, Mark. Optical Properties of Solids (Oxford Master Series in Physics)

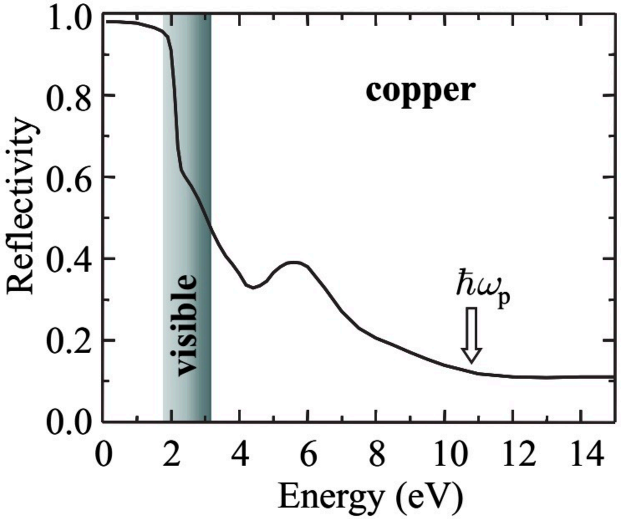
# Insulators and semiconductors vs. metals

Color mostly defined by transparency window



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

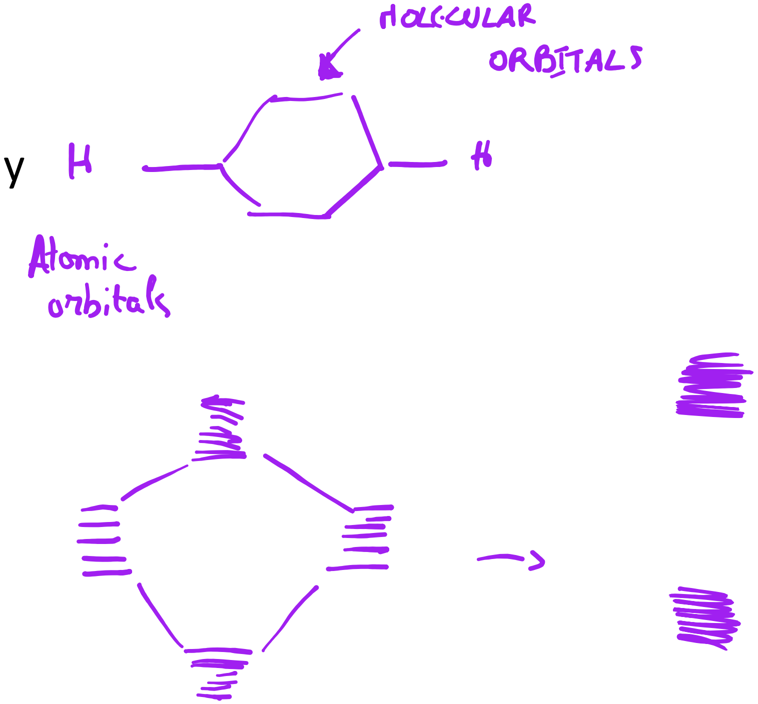




Fox, Mark. Optical Properties of Solids (Oxford Master Series in Physics)

# 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**

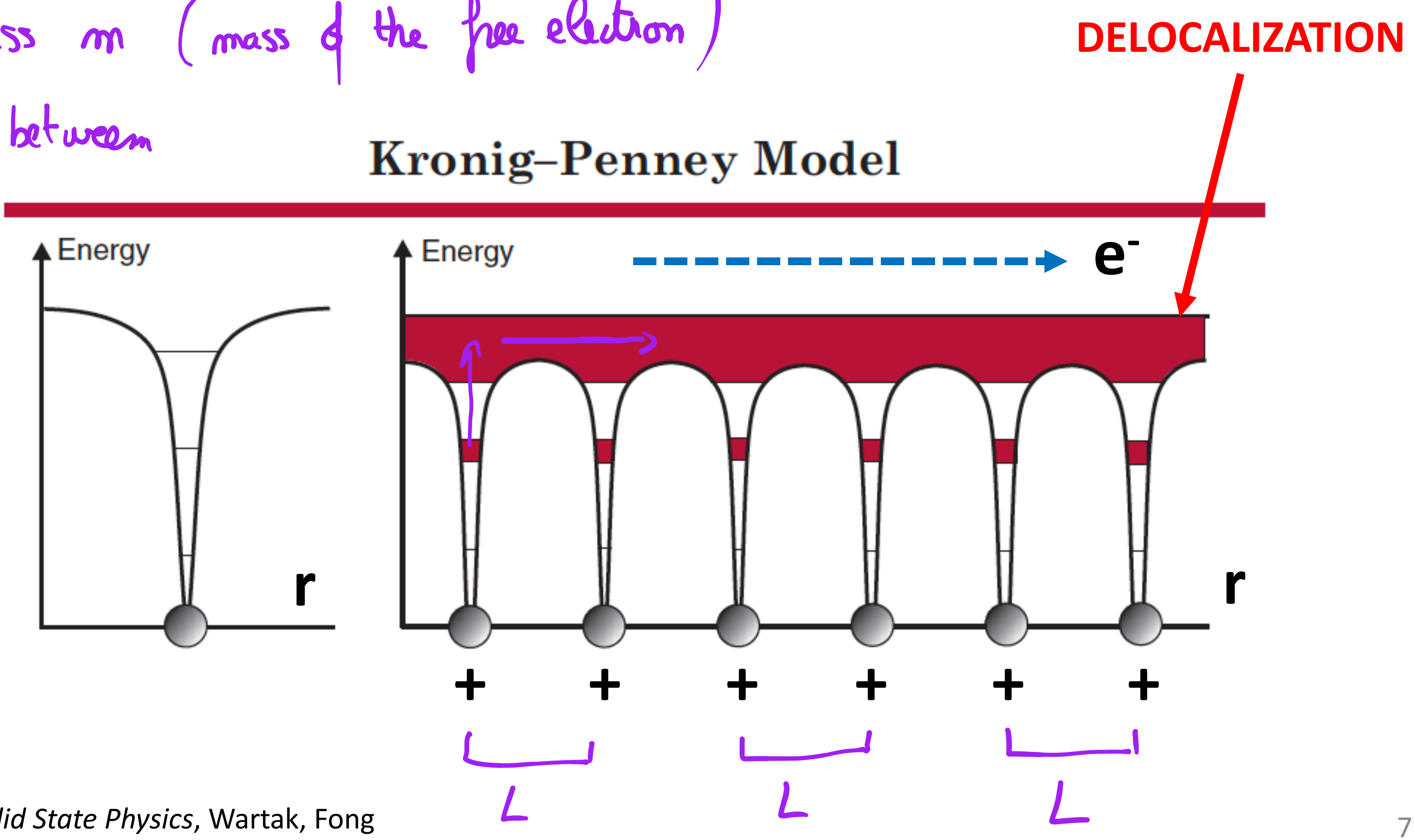
# Electronic bands

- 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

$e^-$ of mass $m$ (mass of the free electron)

$L$ = distance between nuclei



*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:

$$\psi_k(\boldsymbol{r}) = \underbrace{u_k(\boldsymbol{r})}_{\text{Function with periodicity of the lattice}} \cdot \underbrace{\exp(i\boldsymbol{k}\cdot\boldsymbol{r})}_{\text{Plane wave with wavevector } k}$$

$k = \dfrac{n\pi}{L}$ Change in phase per unit length $L$

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

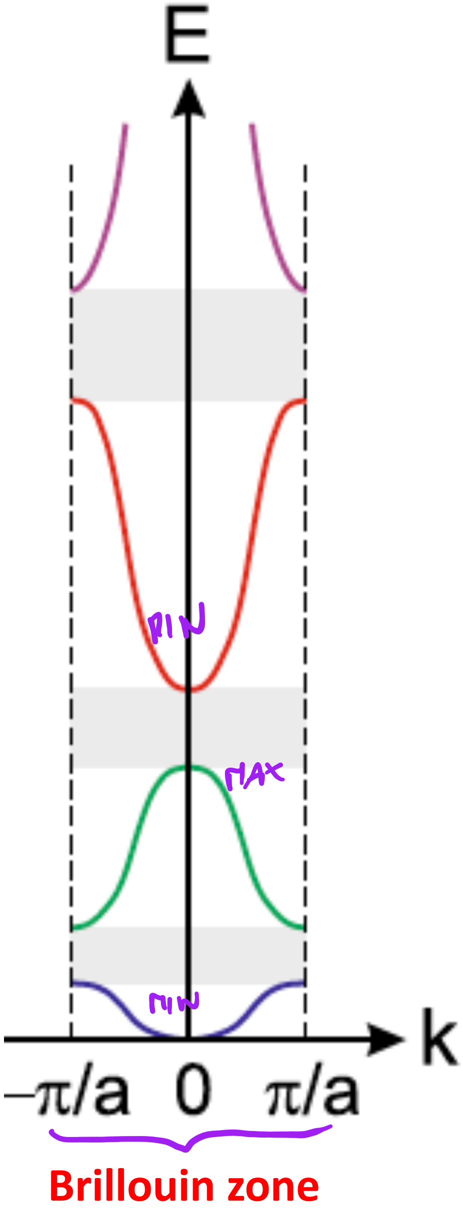
with $E = \frac{1}{2}mv^2 = \frac{1}{2}\frac{\boldsymbol{p}_{crystal}{}^2}{m} = \frac{h^2}{8\pi^2 m}\boxed{k^2} = \frac{h^2}{8mL^2}\underline{n^2}$ and $k = \frac{n\pi}{L}$

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

# Crystal band structure

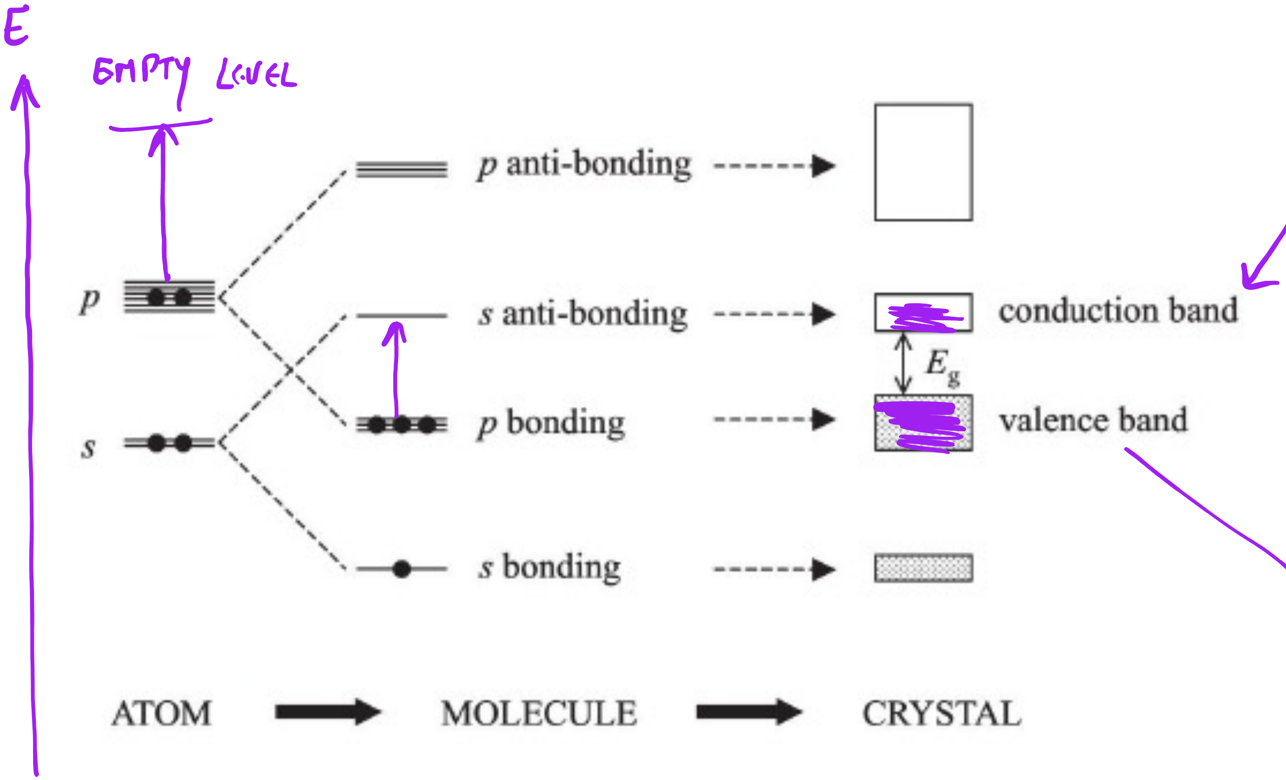
- Map of energy E against wavevector $k$:
  **E($k$)** = crystal band structure
- Gives the band gap and the **Brillouin** zones
- A Brillouin zone is the volume of $k$ - space containing all the values of $k$ up to $\pi/a$
  (*a* = lattice constant in one dimension)
- E($k$) reaches a maximum or a minimum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

**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)



Grundmann, The Physics of Semiconductors

# Transitions



Lowest empty or partially filled energy band

Band gap:
band of forbidden energy

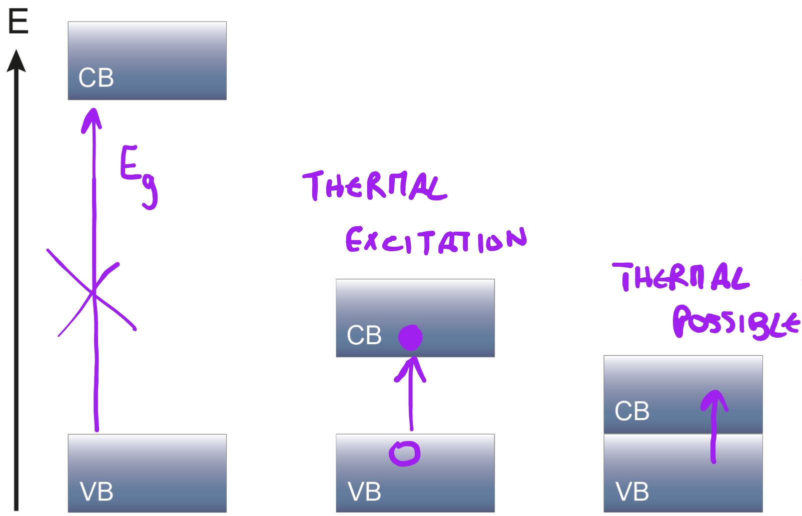
Highest entirely occupied energy band

# Electric conduction in solids

$k_BT \sim 25$ meV

THERMAL EXCITATION

THERMAL EXCITATION POSSIBLE



INSULATOR

$E_g \gg 3k_BT$

$E_g \sim 5-6$ eV

SEMICONDUCTOR

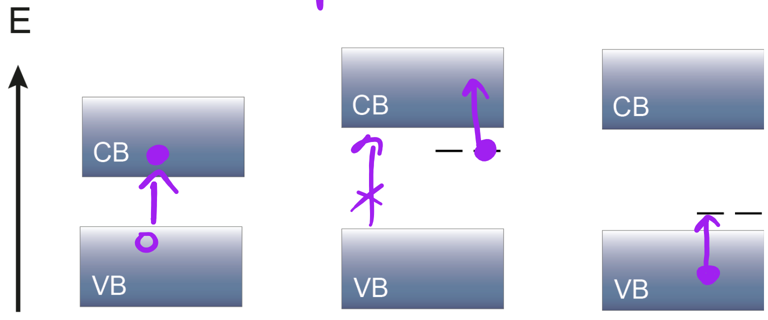
- $k_BT < E_g < 3k_BT$
- $E_g > 3k_BT$

⇒ NO TRANSITION

METALS

No $E_g$

Thermal excitation possible



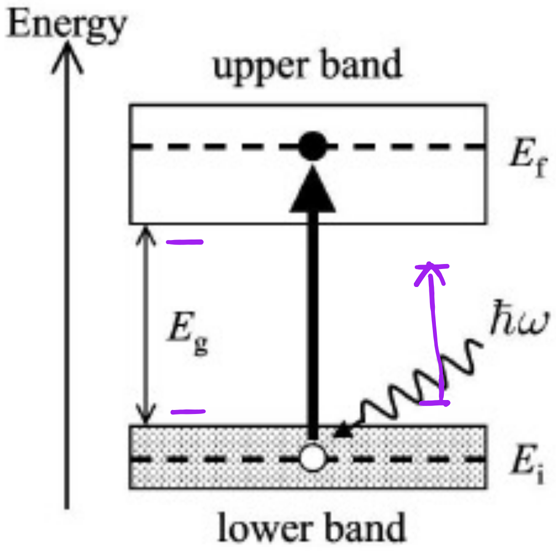
$k_BT < E_g < 3k_BT$

$E_g > 3k_BT$

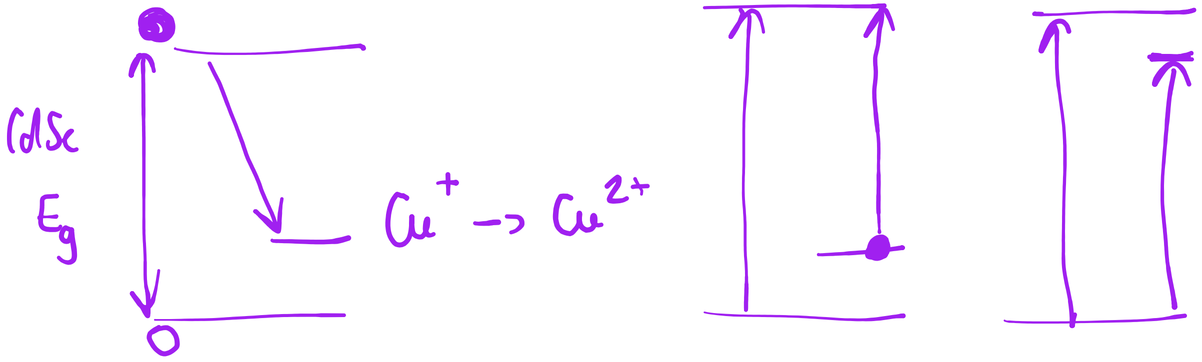
So far we have not provided anything else than thermal energy.
What happens when there is energy from an electromagnetic wave?

# 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:** $E_f = E_i + \hbar\omega$

↘ light

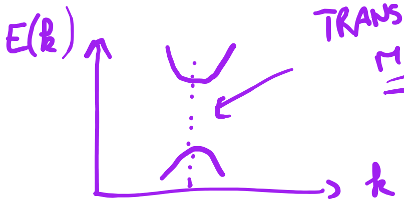
**Momentum conservation:** $\hbar \boldsymbol{k}_f = \hbar \boldsymbol{k}_i + \hbar \boldsymbol{k}_{photon}$

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

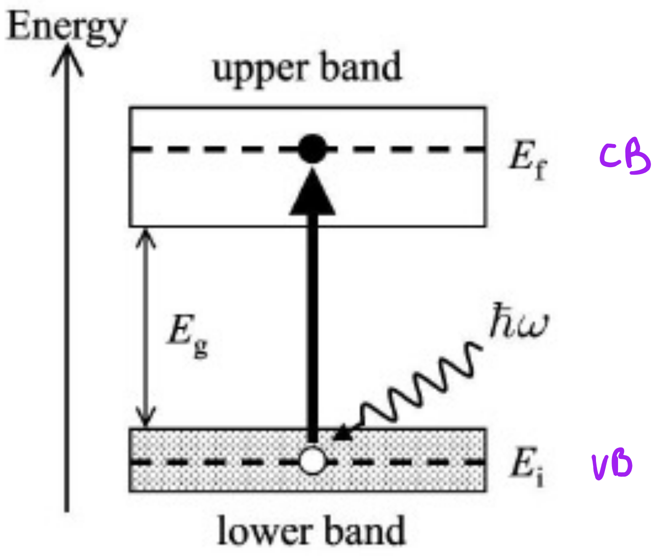
$k_{photon} = \frac{2\pi}{\lambda}$ $\quad k_{electron\ (lattice)} = \frac{n\pi}{L}$

$L \ll \lambda_{visible}$ $\quad k_{photon} \ll k_{electron}$

$\Rightarrow \hbar k_f = \hbar k_i$



TRANSITION MUST BE VERTICAL



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

**Example of optical transition:**

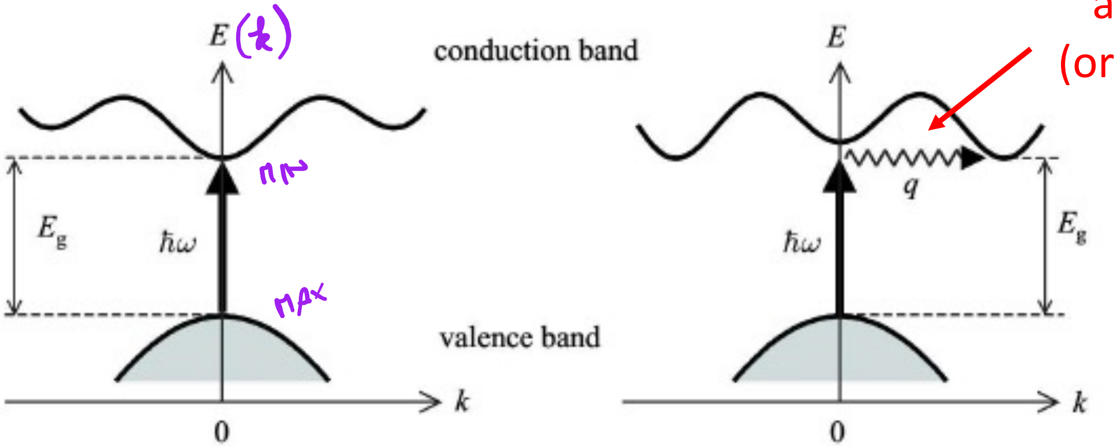
$TiO_2$ is a solid with ionic character, we can see it as constituted of $Ti^{4+}$ ions and $O^{2-}$ ions

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

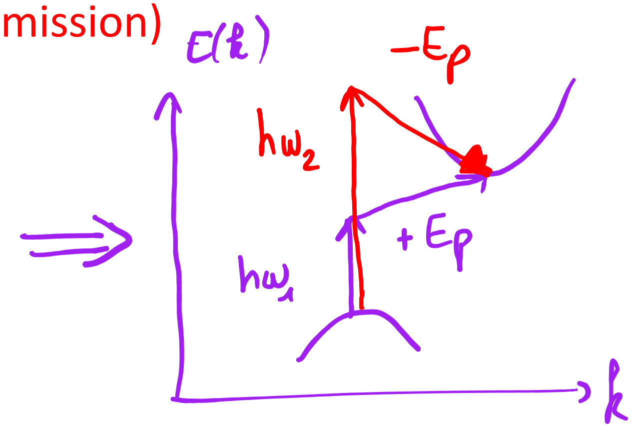
- The distinction concerns the relative positions of the conduction band minimum and the valence band maximum in the Brillouin zone
- Direct gap material: both occur at the center of the Brillouin zone where $k$= 0
- Indirect gap material: the CB minimum does not occur at $k$= 0, but rather at some other value of $k$ 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



(a) Direct band gap

(b) Indirect band gap

Absorption of
a phonon
(or emission)



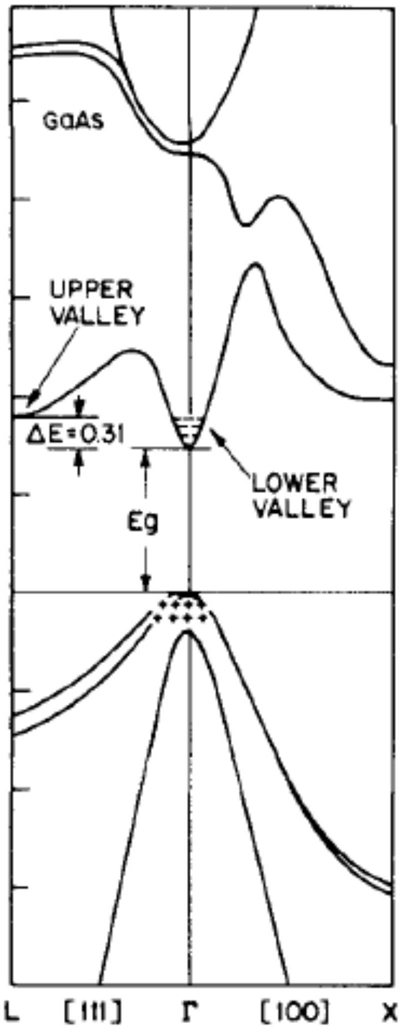
# Direct and indirect band gap

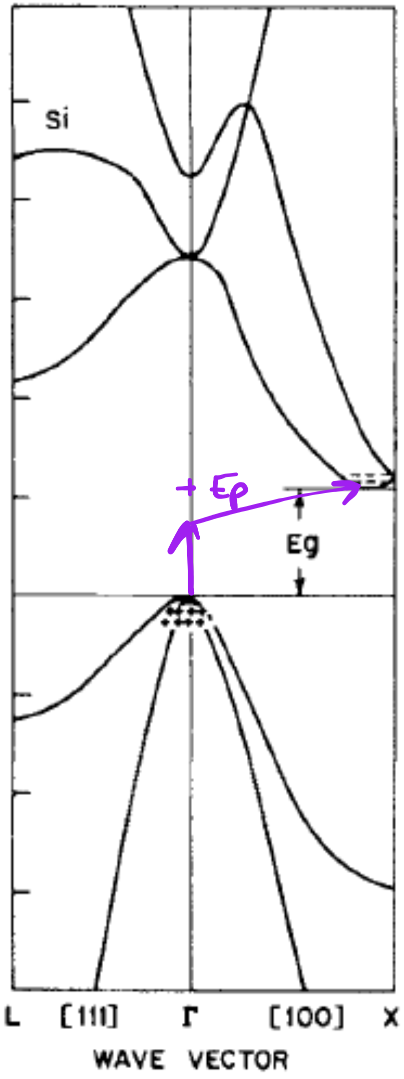
GaAs: direct gap at 1.42 eV

Silicon: indirect gap at 1.12 eV

$\hbar k_i = \hbar k_f$

VERTICAL TRANSITION





Semiconductor Electrochemistry, Memming

# Transition rate and density of states

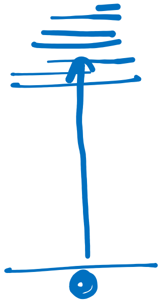
- Transition rate for **direct** absorption can be calculated with Fermi's golden rule:

$$W_{VB \to CB} = \frac{2\pi}{\hbar} |M|^2 \cdot g(h\nu) \longrightarrow \text{Density of available states}$$

Probability of transition/unit time

MATRIX ELEMENT (related to the transition dipole moment)

- 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 ∝ is related to the light frequency by:

↳ $cm^{-1}$

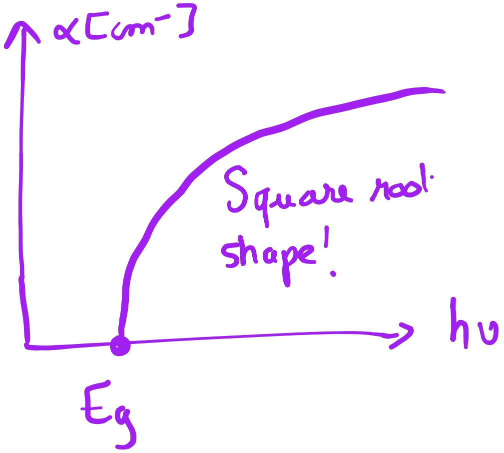
$$\boxed{\propto \sim \sqrt{h\upsilon - E_g}}$$

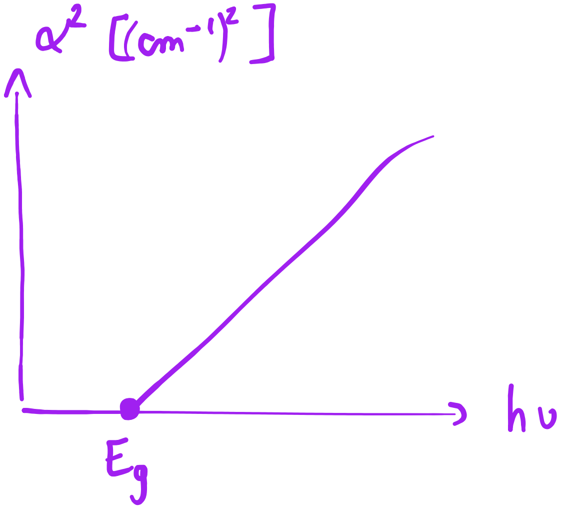
**This approximation is only valid for**
**$h\upsilon \sim E_g$**
**and near $k$ = 0 !**

**Direct transitions:**

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

**Plots of ∝ and $\propto^2$ :**



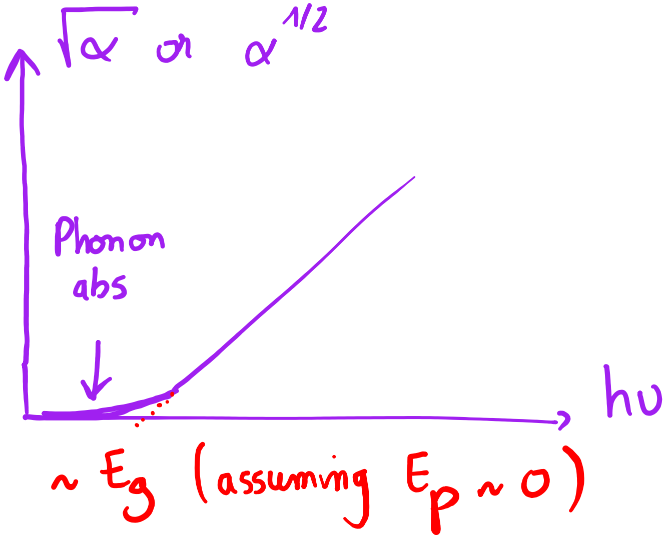


# Optical absorption in indirect SCs

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

$$\propto \sim \frac{(h\upsilon - E_g + \overset{\text{Abs}}{E_p})^{\boxed{2}}}{\underbrace{\exp\left(\frac{E_p}{kT}\right)}_{\text{BOLTZMANN FACTOR} \rightarrow \text{DEPENDS ON } T\,!} - 1} + \frac{(h\upsilon - E_g - \overset{\text{Emission}}{E_p})^{\boxed{2}}}{1 - \exp\left(-\frac{E_p}{kT}\right)}$$

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

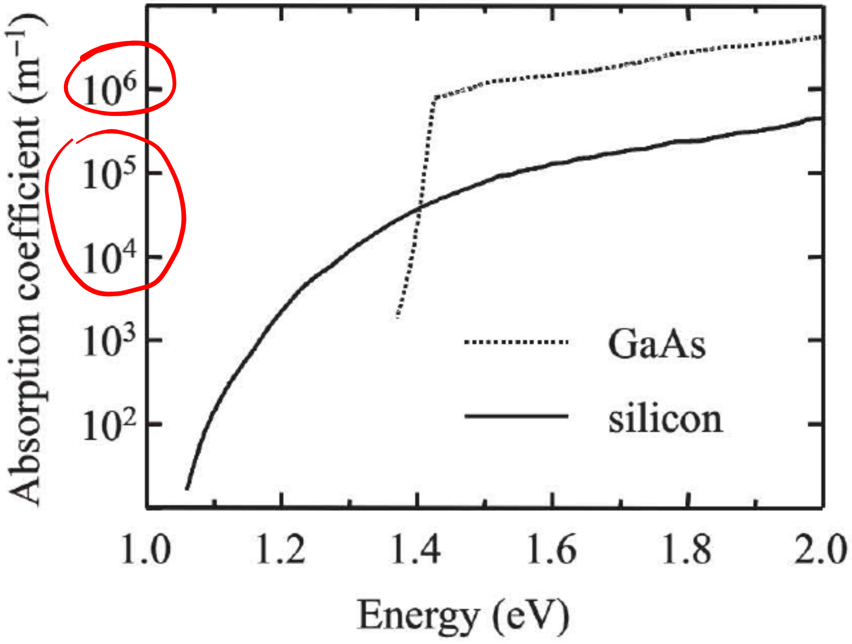


# Optical absorption in indirect SCs

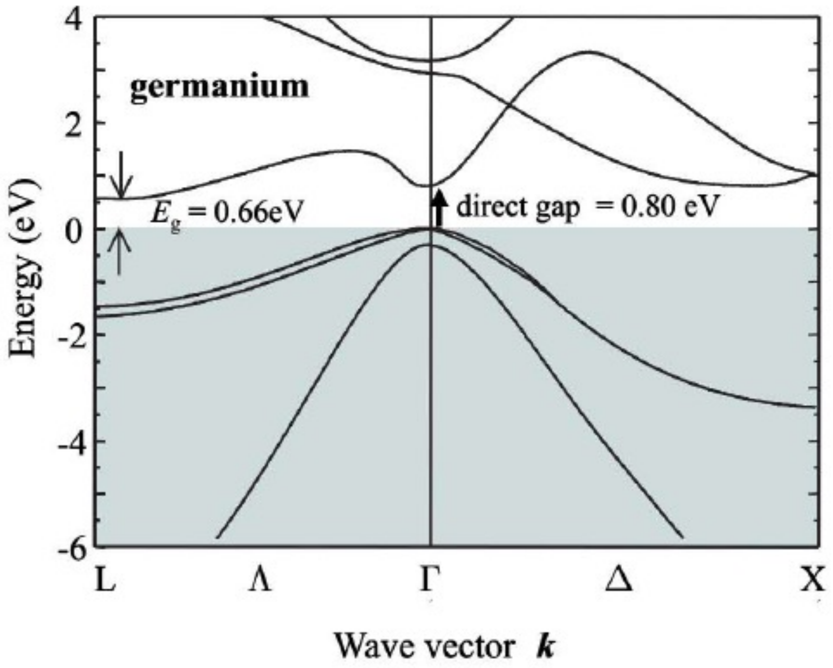
**Direct vs. indirect transitions:** Indirect transitions are less probable

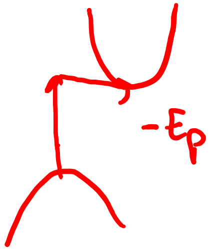
**Example:** GaAs: direct gap at 1.42 eV
Silicon: indirect gap at 1.12 eV

**!! Log scale !!**



# Phonons absorption/emission



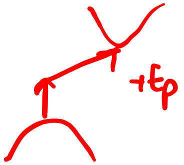


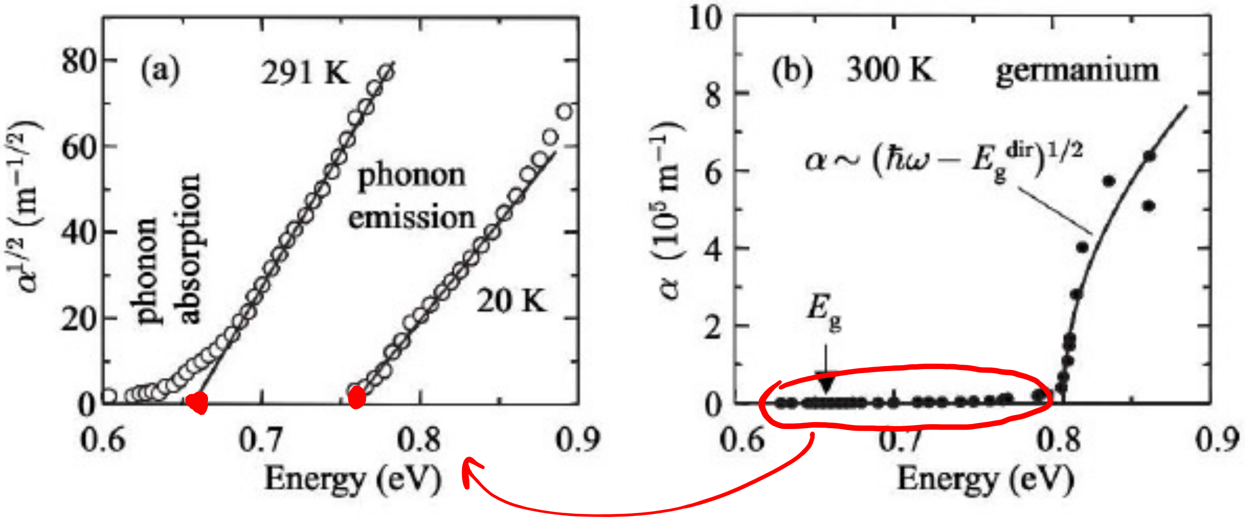
Indirect absorption near the band gap

Direct absorption at higher E

INDIRECT

$\alpha^{1/2}$ vs $h\nu$

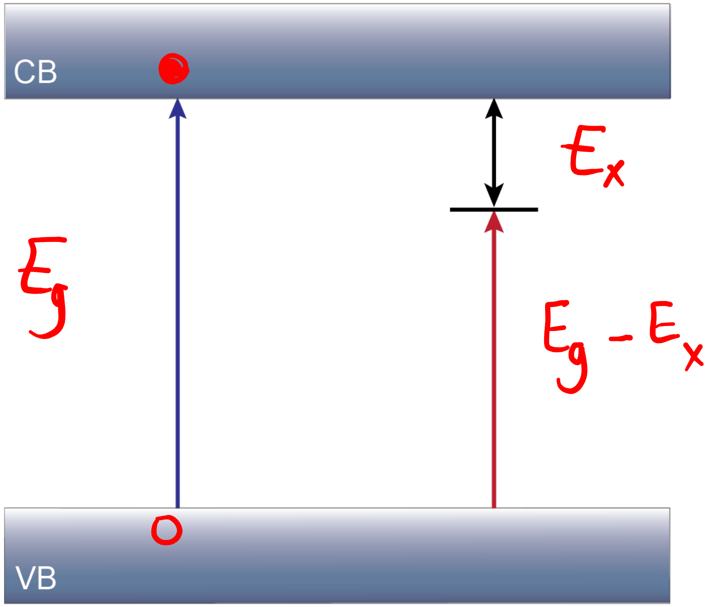




# Excitonic effects

**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 |

**$k_B T \approx 25$ 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

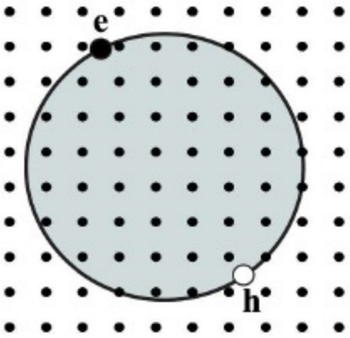
**Wannier–Mott excitons:** Free excitons

- 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

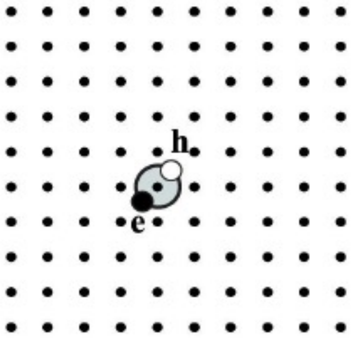
**Frenkel excitons :** Tightly bound excitons

- 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

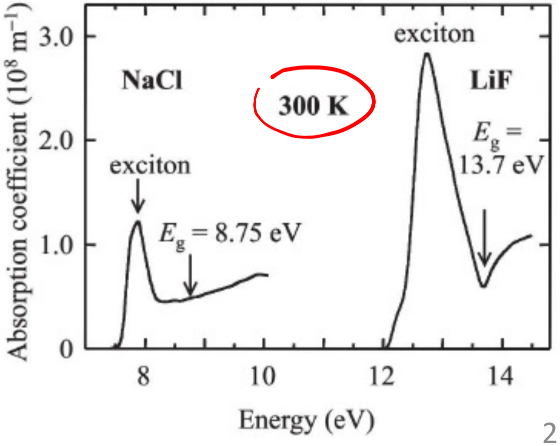
At RT, Tightly bound excitons !



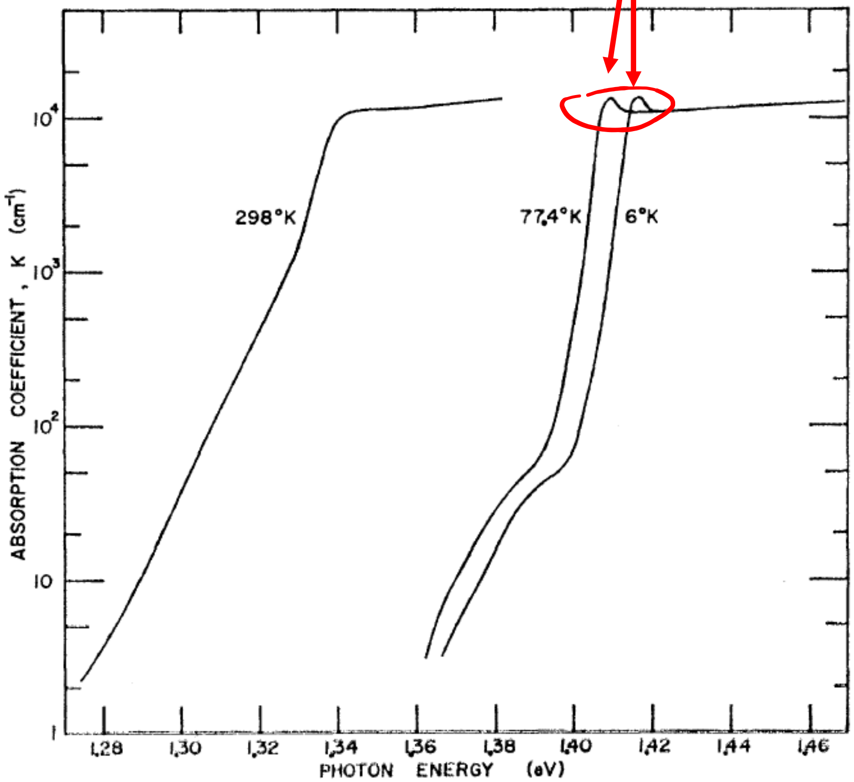
(a) Free exciton



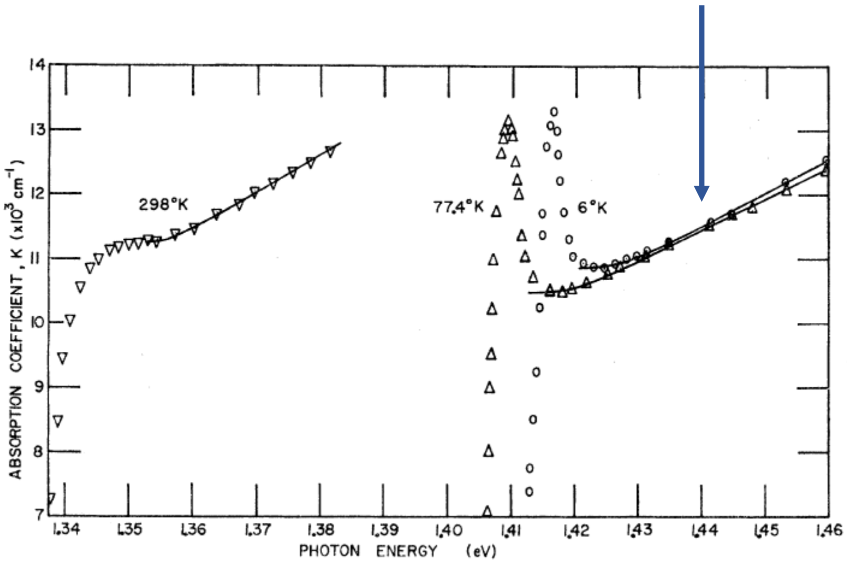
(b) Tightly bound exciton



# Example of InP



Exciton absorption



Free e-$_{CB}$ absorption

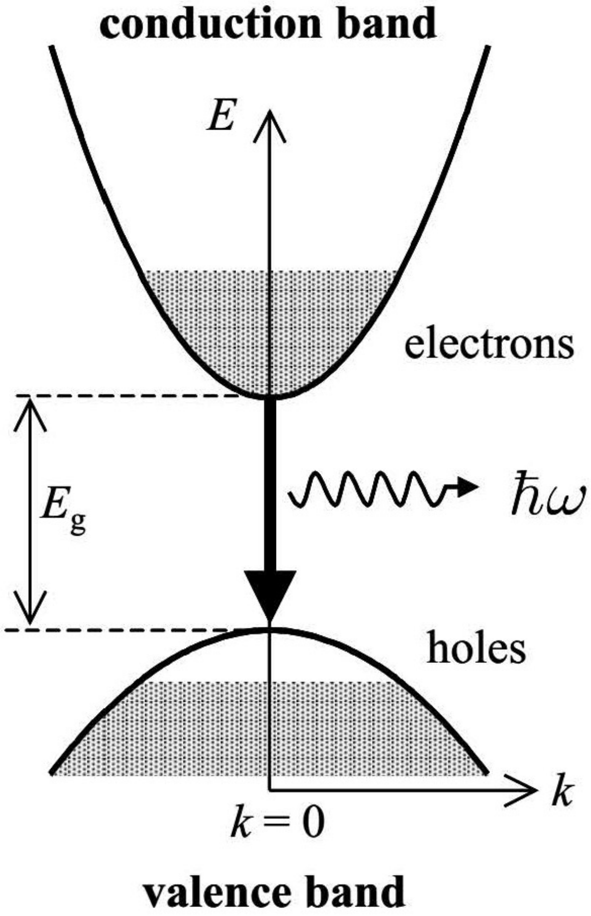
Turner et al., *Phys. Rev.*, **1964**, A1467

# 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

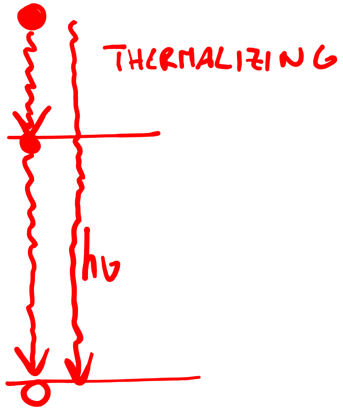
**Electroluminescence:** Emission of light caused by running an electrical current through the material

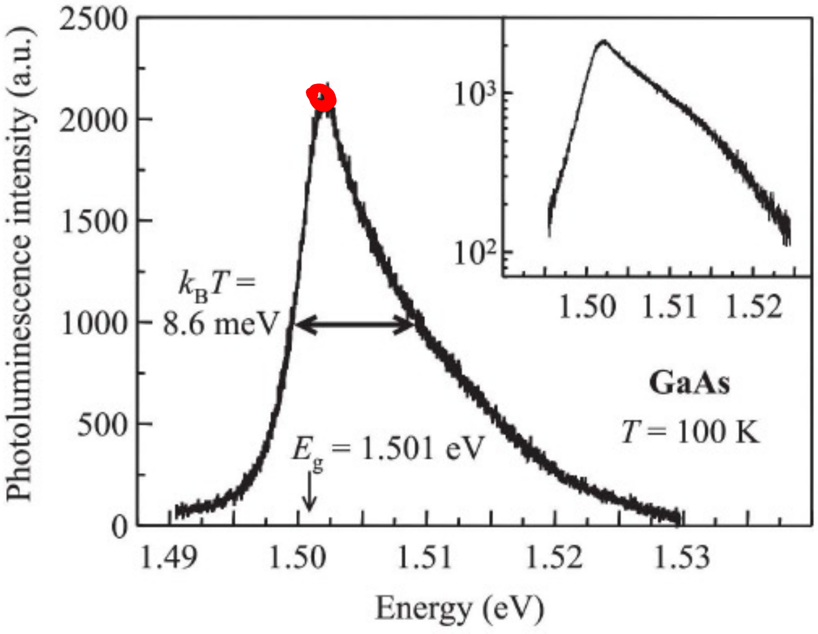


**Direct bandgap:**

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

# Luminescence: Direct Bandgap

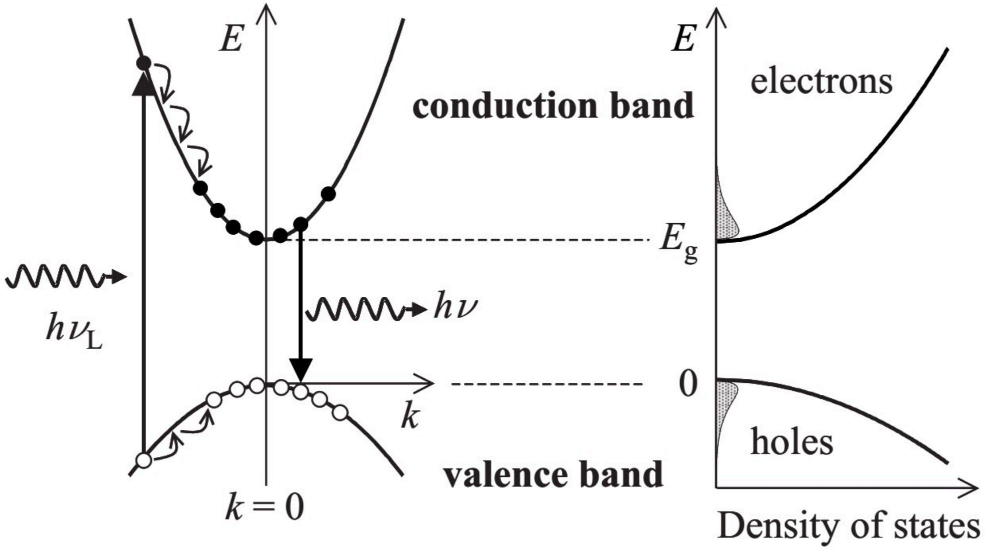




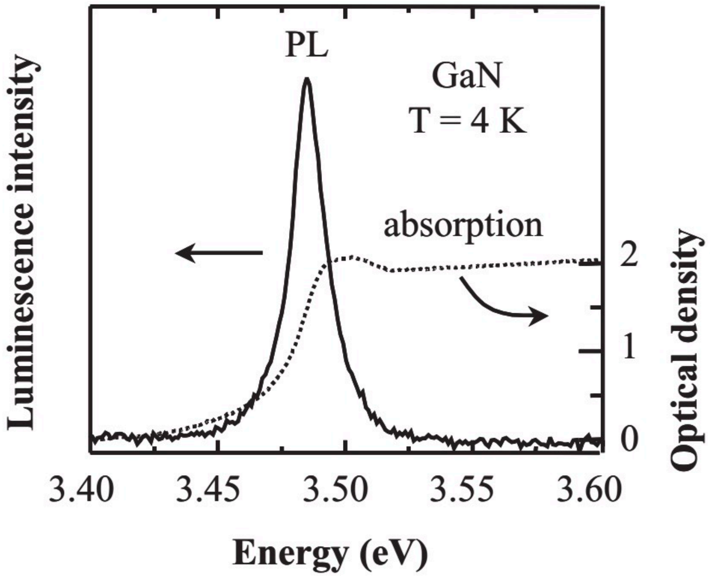
$$I(h\upsilon) \sim \sqrt{h\upsilon - E_g}\underbrace{\exp(-\frac{h\upsilon - E_g}{k_BT})}_{\text{T factor}}$$

- 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 $\sim k_BT$ starting at $E_g$

# Additional considerations on PL



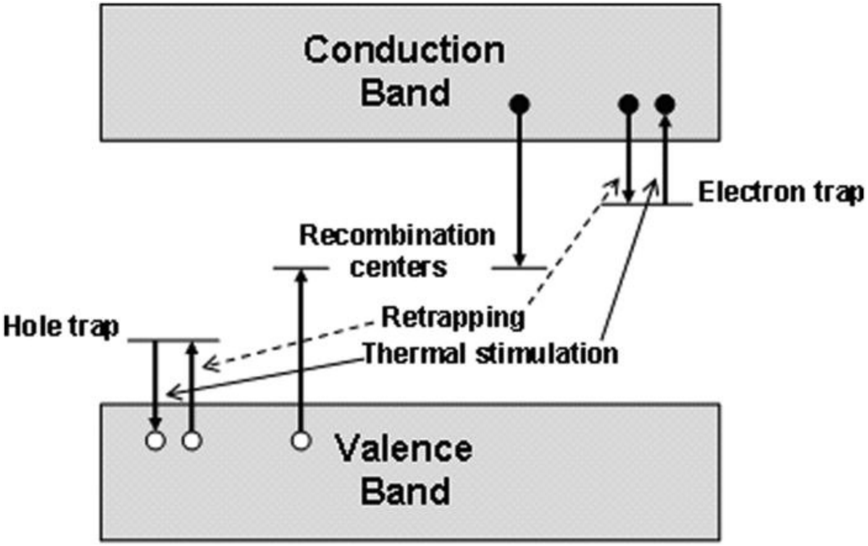
M. Fox, Optical Properties of Solids



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

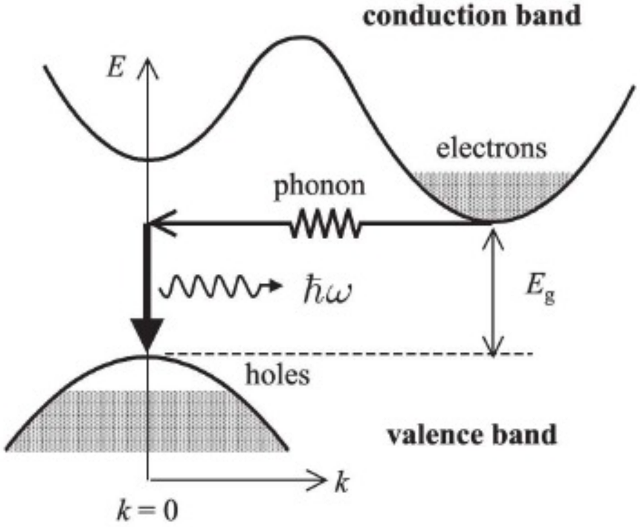
→Characteristic ***narrow*** shape of PL bands
≠ large absorption bands

- 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!!!**