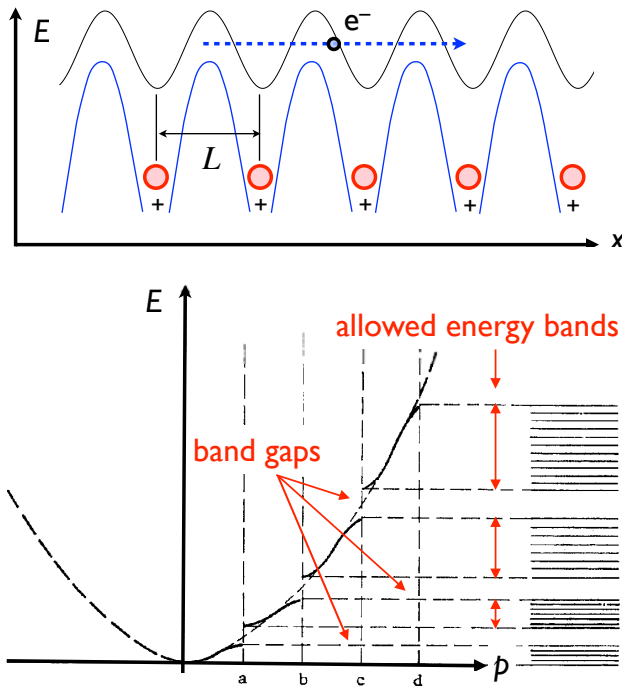## Bloch-Brilloin model

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

Solving the Schrödinger's equation in this case yields:
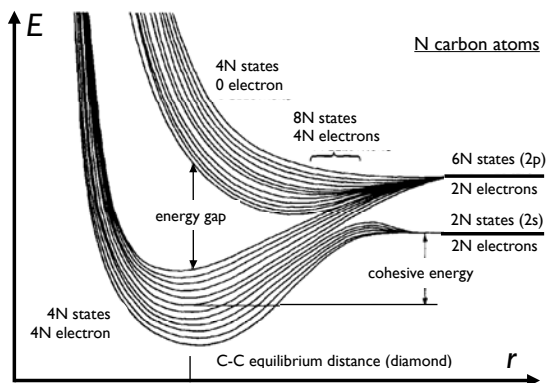
$$E_n = n^2 \cdot \frac{\hbar^2}{8m_e^* \cdot L^2}$$

with $\quad n = \pm 1, \pm 2, ...$

m_e^* is the electron effective mass, such as it satisfies (within an allowed band) de Broglie's relation :
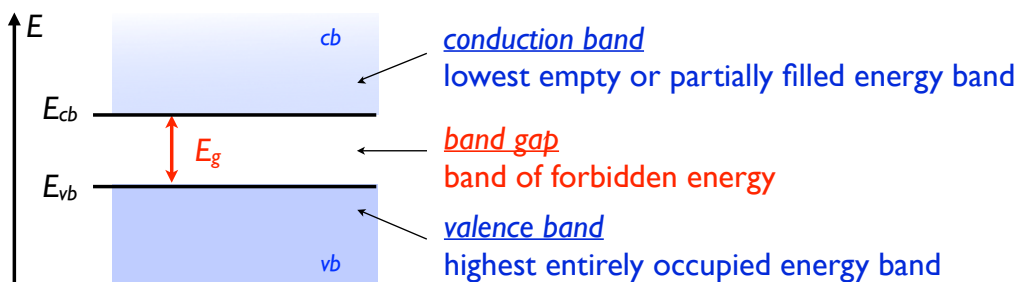
$$E = \frac{p^2}{2m_e^*} = \frac{\hbar^2 \cdot k^2}{2m_e^*}$$
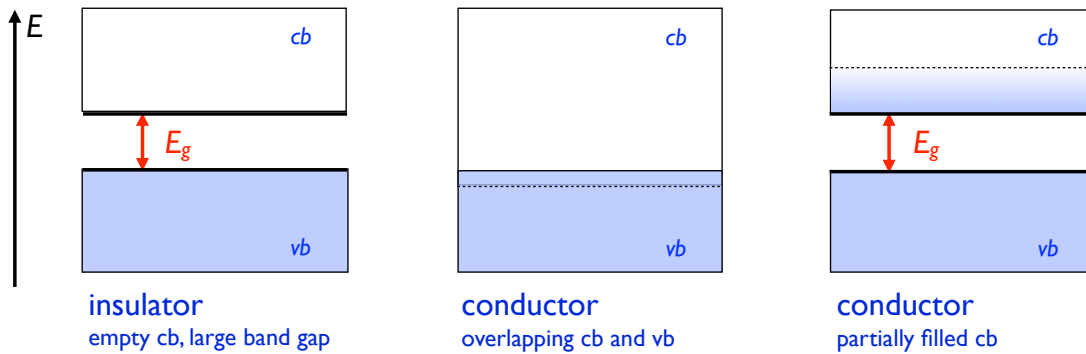
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Band theory

Energy bands can also be understood by considering mutual interactions of electronic wave functions of atoms constituting the solid. When a large number of atoms are brought together, 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. Some intervals of energy contain no orbitals, no matter how many atoms are aggregated, forming band gaps.

conduction band
lowest empty or partially filled energy band

band gap
band of forbidden energy

valence band
highest entirely occupied energy band

Electric conduction in solids

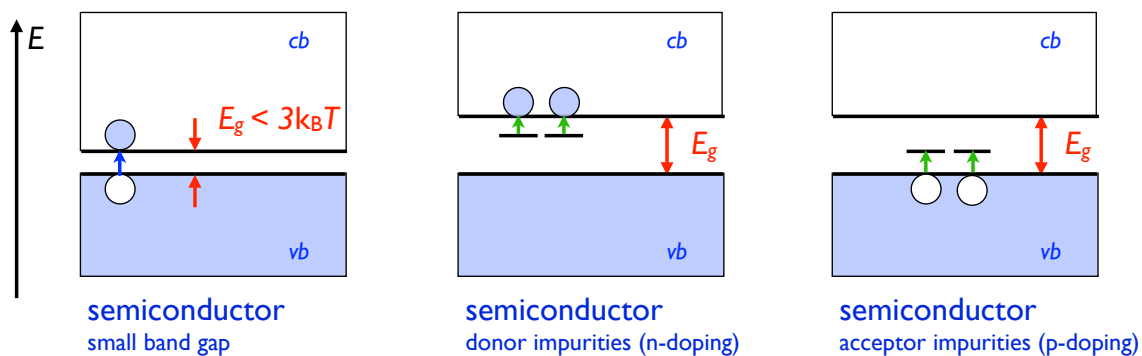| insulator	conductor	conductor
empty cb, large band gap	overlapping cb and vb	partially filled cb

Insulators' conduction band is totally empty, while their valence band is entirely occupied. Electrons, then, may not contribute to the electrical conductivity of the material, because no energy level is available for them to acquire kinetic energy and to move.

Conductors, or metals are characterized by a partially filled conduction band. Electrons, when subjected to an electric field, may acquire some kinetic energy. The specific electrical conductivity s is given by the product of the density n of charge carriers and their mobility μ:

$$s = |q| \cdot n \cdot \mu \quad \left[\Omega^{-1} \cdot m^{-1} \right]$$

Semiconductors

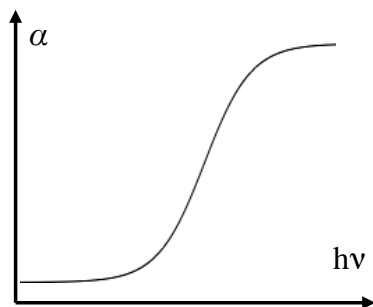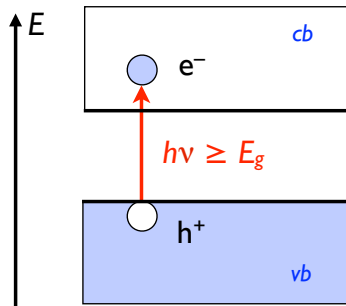| semiconductor	semiconductor	semiconductor
small band gap	donor impurities (n-doping)	acceptor impurities (p-doping)

Semiconductors are insulators for which a conduction can however be obtained under some conditions. If $E_g < 3\ k_BT$, for instance, electrons can jump thermally across the band gap and be promoted from the valence band to the conduction band. Both conduction band electrons and valence band holes charge carriers contribute then to the conduction.

Charge carriers can also be produced by chemical doping of the solid. Donor impurities yield n-doping (e_{cb}^- carriers). Acceptor impurities produce holes in the valence band (h_{vb}^+ carriers) and p-doping. In semiconductors, the density of charge carriers n is always rather small.

Intrinsic light absorption

The promotion of an electron from the fully occupied valence band to the conduction band can also be achieved by **intrinsic light absorption** of photons of energy $h\nu \geq E_g$. The photo-conduction of the semiconductor under band-gap irradiation is due to both e_{cb}^- and h_{vb}^+ charge carriers.

<u>Example</u>:

Titanium dioxide TiO_2 is a solid with a rather ionic character. It can be seen as being constituted of Ti^{4+} and O^{2-} ions.

Ti $3d^2\,4s^2$ $\longrightarrow$ Ti^{4+} $3d^0$ $\longrightarrow$ empty conduction band

O $2p^4$ $\longrightarrow$ O^{2-} $2p^6$ $\longrightarrow$ entirely occupied valence band.

Photons of energy $h\nu \geq E_g$ = 3.2 eV ($\lambda \leq$ 380 nm) are absorbed, yielding a transition $2p(O) \longrightarrow 3d(Ti)$.
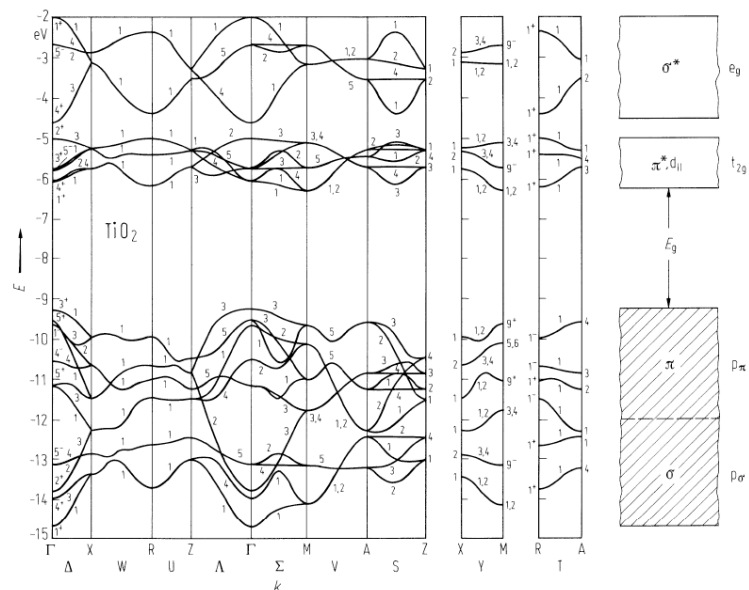
Band structure

Band structure in the *reciprocal space* is a compact and elegant way to represent all electronic states in a periodic system. In such a representation, bands appear ideally as a series of de Broglie's parabolas $E = f(k)$:

$$E = \frac{p^2}{2m_e^*} = \frac{\hbar^2 \cdot k^2}{2m_e^*}$$

where k is the wave vector of a charge carrier and p its momentum: $k = 2\pi \cdot p\,/\,h$
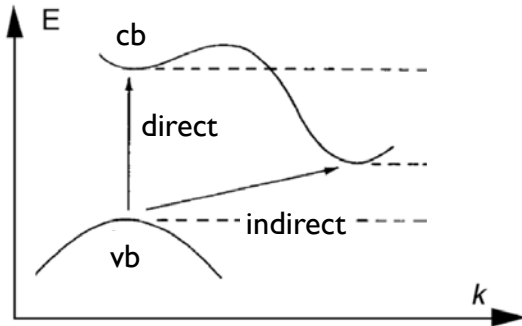
However, because m_e^* is not the same in all directions of the 3D space, a complex structure is observed rather than simple parabolas.

Band structure of TiO₂ rutile. Left: Energy vs. wave vector along symmetry lines in the Brillouin zone. Right: schematic of energy bands.
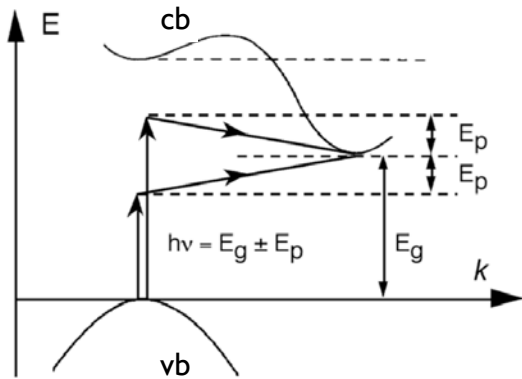
Direct *vs* indirect transitions

Since photons do not carry any mechanical momentum, k should remain unchanged during an electronic transition if no vibration is coupled to it. A transition following the Frank-Condon principle (k constant) is called a ***direct transition***.

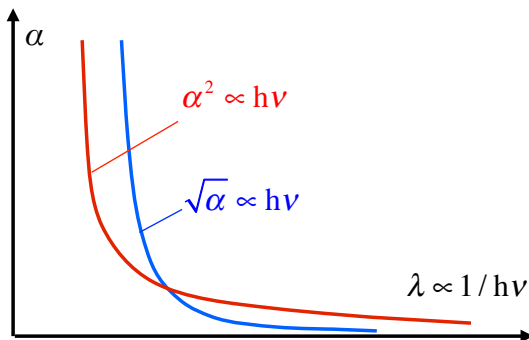$$h\nu = E_g \qquad \Delta k = 0$$

An ***indirect transition*** implies a vibration of the solid lattice is coupled to the electronic movement. The change of the momentum is brought by absorption of a phonon of energy E_p ($\Delta k > 0$) or released during the emission of a phonon in the solid ($\Delta k > 0$).
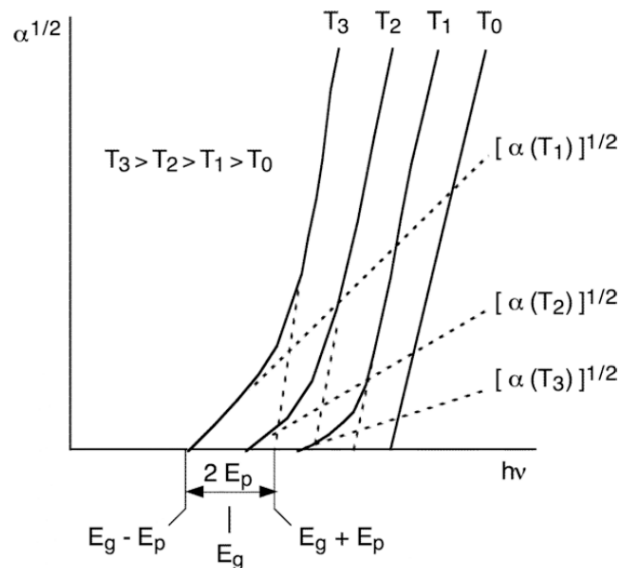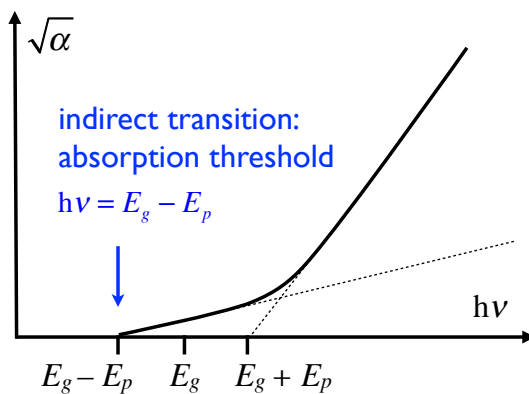
$$h\nu = E_g \pm E_p \qquad \Delta k = \pm\, k_p$$

Gärtner's relations

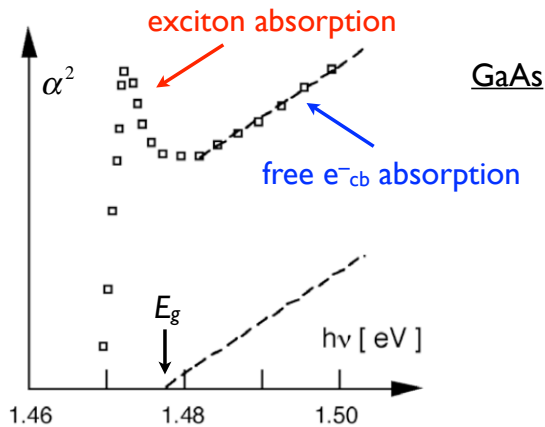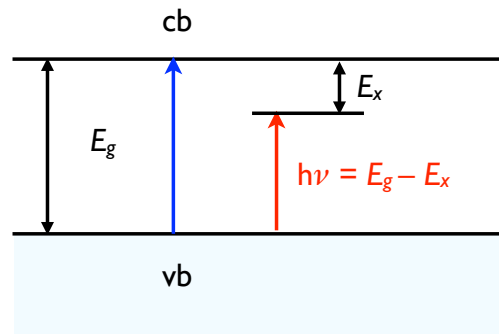direct transition: $\quad \alpha \propto \sqrt{h\nu - E_g}$

indirect transition: $\quad \alpha \propto \left(h\nu - E_g\right)^2$

Excitonic absorption

An ***exciton*** is an electron-hole pair in which charge carriers are bound together by Coulombic interaction. The exciton is a neutral entity which can move easily in an insulator and carry excitation energy.

exciton absorption

free e$^-_{cb}$ absorption

$\underline{GaAs}$

Exciton bond energy E_x [meV]

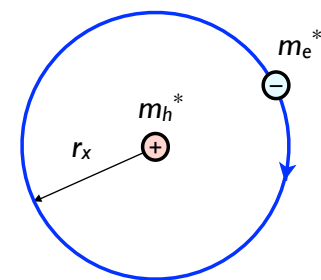|					
Si	14.7	CdS	29	KCl	400
Ge	4	CdSe	15	KBr	400
GaAs	4.2	BaO	56	AgCl	30
GaP	3.5	InP	4	AgBr	20

Size and bond energy of an exciton

<u>Bohr's planetary model (hydrogen atom)</u>

$$r_H = \frac{n^2 \cdot \hbar^2 \cdot \varepsilon_0}{\mu \cdot e^2} = n^2 \cdot 0.56 \text{Å} \qquad \text{with} \quad 1/\mu = 1/m_e + 1/m_p \simeq 1/m_e$$

$$r_x = \frac{\hbar^2 \cdot \varepsilon \cdot \varepsilon_0}{m^* \cdot e^2} = \varepsilon \cdot \frac{m_e^*}{m^*} \cdot r_H \qquad \text{with} \quad 1/m^* = 1/m_e^* + 1/m_h^*$$

$$E_x = \frac{m^* \cdot e^2}{2m_e \cdot \varepsilon^2 \cdot r_H} = \frac{m^*}{m_e \cdot \varepsilon^2} \cdot 13.6 \ [eV]$$

for comparison: ε (H$_2$O) = 87

Exciton radius r_x and bond energy E_x [meV]

	E_g / eV	m_e^*/m_e	m_h^*/m_h	ε / -	r_x / Å	E_x / meV
CdS	2.6	0.19	0.8	5.7	20.8	64
ZnO	3.2	0.24	0.45	3.7	13.2	155
TiO$_2$	3.2	30	4	184	37.8	1.1

Quantum size effect

$$\Delta E_g = \frac{\hbar^2}{8r^2} \cdot \frac{m_e}{m^*} - \frac{e^2}{\varepsilon \cdot r}$$
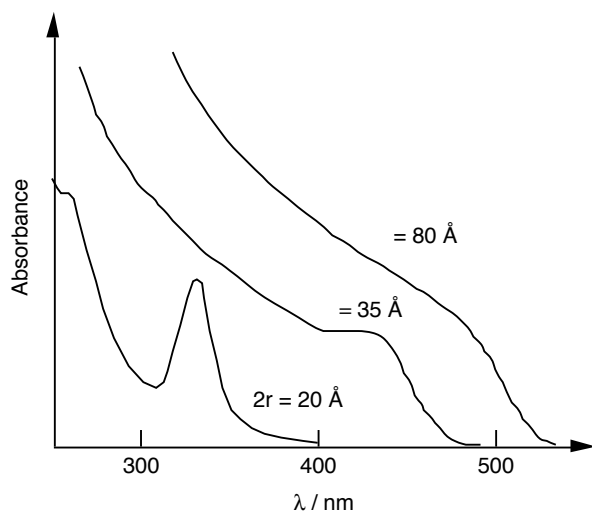
Confinement of electrons in particles whose size is comparable or smaller than that of the exciton in the bulk material leads to an increase of the excitation energy E_g.

As a result, the bandgap increases and the absorption threshold shifts to the blue when particle size is decreased.

This **quantum size effect**, which is a direct evidence of the "particle in a box" concept, allows to adjust the color of colloidal particles of wide bandgap semiconductors.

Left: Absorption spectra of aqueous colloidal suspensions of CdS particles. Particle diameter is reduced from 80 Å to 20 Å, causing an important hypsochromic shift.

Quantum dots

Quantum dots (QDs) are semiconducting nanoparticles in which excitons are confined in all three spatial dimensions.

Quantum confinement affects the absorption and emission of photons from the dot. Thus, the absorption edge of a material can be tuned by control of the particle size.

Quantum dots are particularly significant for optical applications (bio-imaging, diode lasers, LEDs, solar cells, ...) due to their high extinction coefficients.

Similar to a molecule, a quantum dot has both a quantized energy spectrum and a quantized density of electronic states near the edge of the band gap.

particle diameter

20 Å   74 Å
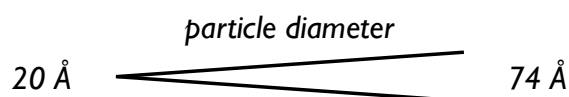
Solutions of monodisperse CdSe nanocrystals with increasing diameter (from left to right). Photoemission (fluorescence) wavelengths are indicative of the respective bandgap energies.