Module 6 : PHYSICS OF SEMICONDUCTOR DEVICES

Lecture 32 : Bonding in Solids

Objectives

In this course you will learn the following

- Bonding in solids.
- Ionic and covalent bond.
- Structure of Silicon
- Concept of effective mass.

Bonding in Solids

Crystals can be classified on the basis of bonding of atoms to form a solid. There are primarily four types of bonding in solids, viz., molecular, ionic, covalent and metallic bonds.

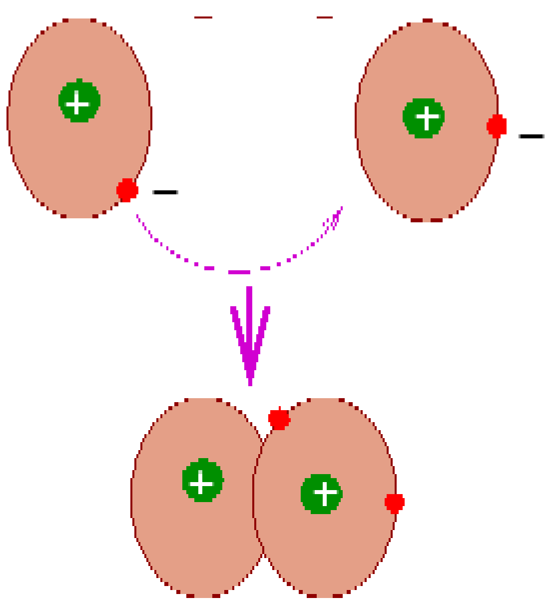
Molecular solids are formed by weak inter-molecular forces between molecules. Because of weak binding, the solids have low melting points

Metallic solids are characterized by **free electrons** which move freely through the crystal being bonded to different atoms at different times.

Ionic Bond

In ionic solids, one of the specis of atoms donates electrons to another specis so that each of the atoms may become more stable by having a noble gas (octet) configuration of electrons. For instance in sodium chloride crystal,

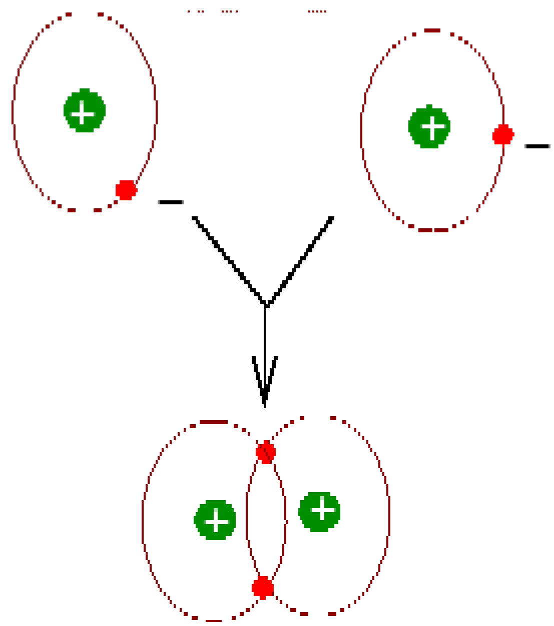
$$\mathrm{Na} + \mathrm{Cl} \rightarrow \mathrm{Na}^{+}\mathrm{Cl}^{-}$$

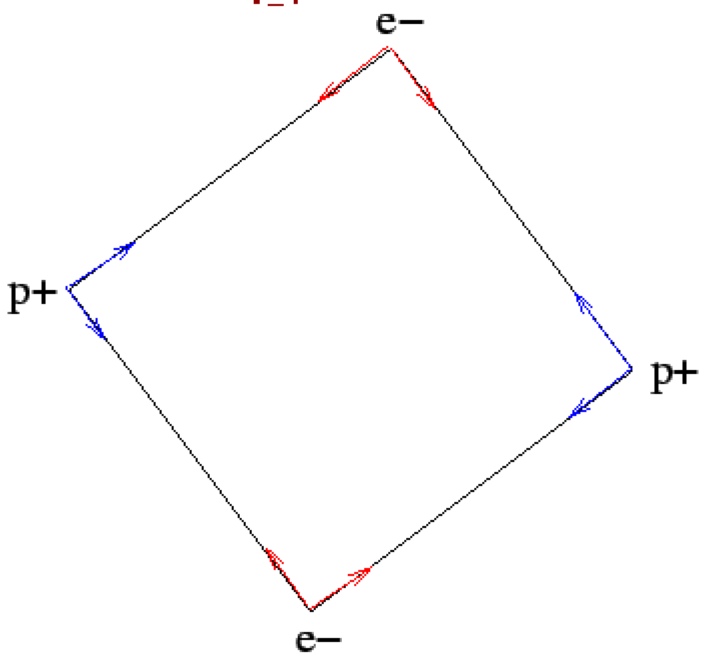


Sodium with an atomic number 11 has an electronic configuration $1s^2 2s^2 2p^6 3s^1$ while chlorine with the atomic number 17 has the configuration $1s^2 2s^2 2p^6 3s^2 3p^5$. When the atoms come together, Na gives away one electron and becomes positively ionized while Cl receives one electron and acquires a net negative charge. The negative an the positive ions are held together by electrostatic interaction. Ionic solids are hard, brittle, have high melting points and are poor electrical conductors.

Covalent Bond

Atoms can also achieve stable octet configuration by sharing of electrons. For instance, in forming hydrogen molecule a pair of hydrogen atoms share two electrons.





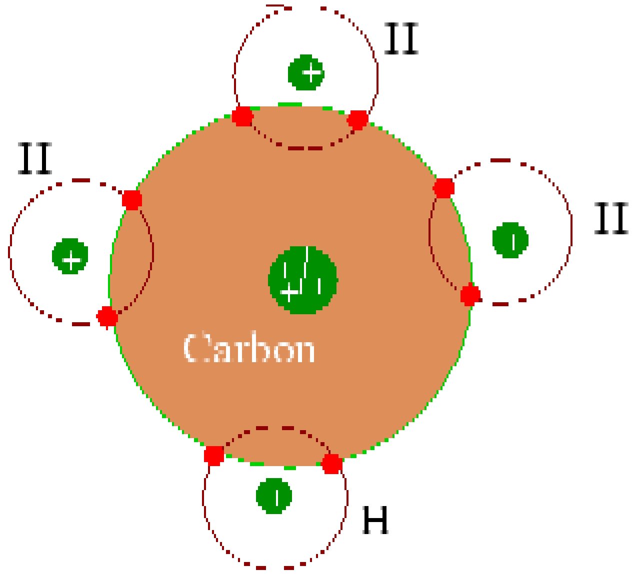
Other examples of covalent bonded crystals are diamond, graphite, quartz (SiO_2) etc. Covalently bonded crystals are very hard, have high melting point (diamond has a melting point of 3550 ^{o} C) and are poor electrical conductors. Each electron that is shared is attracted to both the nuclei.

Example-2

Draw a picture of bond formation in Methane molecule.

Solution

Methane molecule has one carbon atom with the configuration $2A - 12Bk^2$ and requires four electrons to complete octet. This is done by sharing two electrons with each of the hydrogen atom so that carbon atom and all the hydrogen atoms are in noble gas configuration.

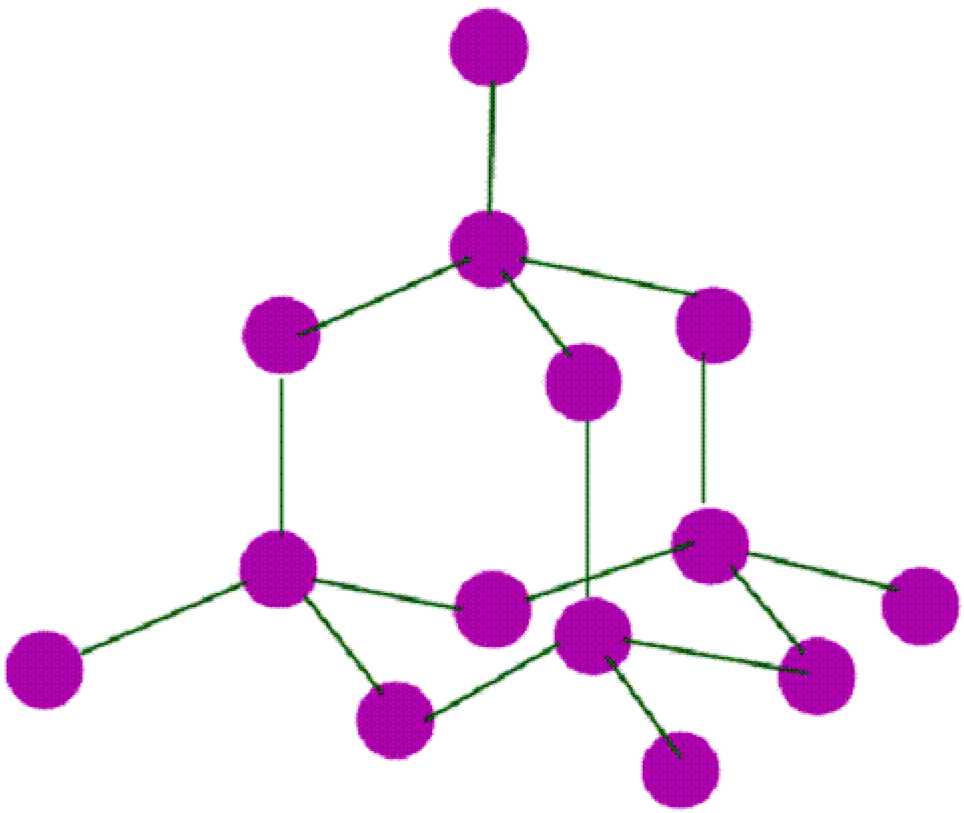


Exercise 1

Draw a picture of covalent band formation in Ammonia molecule.

(Hint : Nitrogen has 7 electrons with electronic configuration $k = 0$).

Silicon, which is one of the prominent elemental semiconductors is in the same group as carbon in the periodic table and like carbon, it has four valence electrons. These electrons form covalent bonds. Crystalline silicon has the same structure as diamond. The structure of diamond consists of two interpenetrating face centered cubic lattices which are displaced along the body diagonal by one fourth the distance.



Effective Mass

For a free electron moving under the action of an external force F_{ext} the equation of motion is given by

$$m\frac{dv}{dt} = F_{ext}$$

Identifying $\hbar k$ as the momentum of the particle, we have

$$E = \frac{\hbar^2 k^2}{2m}$$

We may, therefore, express the mass of the particle in terms of the second derivative of the energy with respect to the wavenumber k

$$m^{-1} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}$$

The velocity of the particle can be expressed as

$$v = \frac{\hbar k}{m} = \frac{1}{\hbar}\frac{dE}{dk}$$

When an electron moves in a lattice (i.e. in a periodic potential), in addition to the external forces, it is subjected to forces within the lattice. These foreces are generally quite large. We may write the equation of motion for the electron in the lattices as

$$m\frac{dv}{dt} = F_{ext} + F_{lattice}(A)$$

One can define the **effective mass** of the electron in a lattice to be mass of a particle, which, when subjected to an external force F_{ext} would give an acceleration dv/dt defined by eqn. (A), i.e.,

$$m^*\frac{dv}{dt} = F_{ext}$$

Using the expression for v above, we can write

$$\frac{dv}{dt} = \frac{1}{\hbar}\frac{d}{dt}\frac{dE}{dk} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}$$

$$= \frac{1}{\hbar^2}\frac{d^2E}{dk^2}\frac{d}{dt}(\hbar k)$$

$$= \frac{1}{\hbar^2}\frac{d^2E}{dk^2}\cdot F_{ext}$$

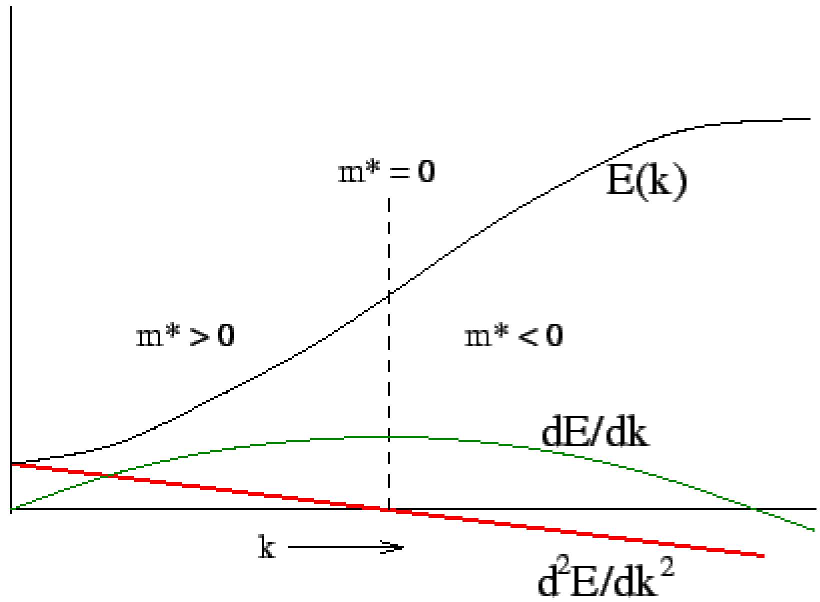
The effective mass m^* is given by

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}$$

For a band with anisotropy, (i.e., where $E-k$ relationship is not spherically symmetric), the effective mass is direction dependent

$$\frac{1}{m_{ij}^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j}$$

Note that unlike real mass, the effective mass can even be negative as it is proportional to the curvature of the band.



Example-3

Calculate the effective mass for a simple cubic lattice whose band structure is given by

$$E(k) = E_0(\cos k_x a + \cos k_y a + \cos k_z a)$$

at the point (0,0,0) of the k-space.

Solution

Because of symmetry, we have m_{ij}^* is the same for all i and j for $i \neq j$. Thus $m_{xy}^* = m_{yz}^* = m_{zx}^*$

$$\begin{aligned}\frac{1}{m_{xy}^*} &= \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_x \partial k_y} \\ &= \frac{1}{\hbar^2}E_0(-a\sin(k_x a) - a\sin(k_y a)) \\ &= 0 \text{ for } (0,0,0)\end{aligned}$$

On the other hand $m_{xx}^* = m_{yy}^* = m_{zz}^*$ is given by

$$\begin{aligned}\frac{1}{m_{xx}^*} &= \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_x^2} \\ &= \frac{1}{\hbar^2}E_0(-a\cos(k_x a)) \\ &= -\frac{E_0 a^2}{\hbar^2} \text{ for } (0,0,0)\end{aligned}$$

Example-4

The $E-k$ relationship near the conduction band of GaAS is given by

$$E = E_c + Ak^2 - Bk^4$$

where $A, B > 0$. How does it affect the effective mass of electrons near the conduction band minimum ?

Solution

We have

$$\frac{dE}{dk} = 2Ak - 4Bk^3$$

$$\frac{d^2E}{dk^2} = 2A - 12Bk^2$$

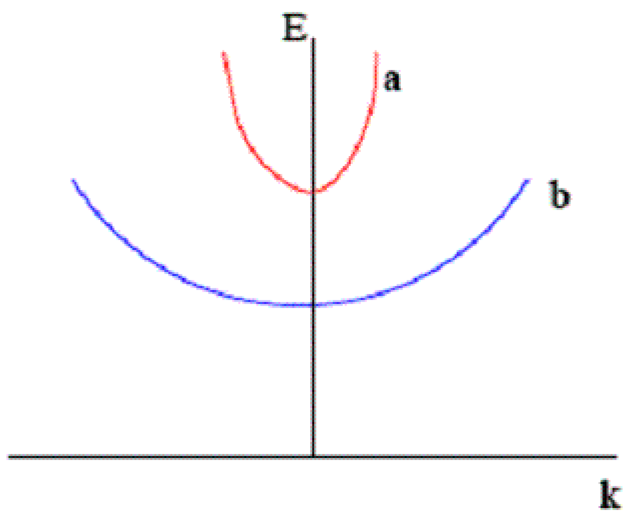
Thus

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2} = 2A - 12Bk^2$$

For values of k removed from $k = 0$, m^* increases with k.

Exercise 2

Which one of the bands has higher effective mass near $k = 0$?



Exercise 3

The energy of an electron in the valence band of a certain one dimensional semiconductor may be written as

$$E = E_0(1 - \cos(ka))$$

where E_0 and a are constants. Sketch the variation of the energy and of the effective mass of the electron as functions of k. Calculate the effective mass at $k = 0$ and at given that $a = 3$

$k = \pi/a$

Åand $E_0 = 0.75$ eV.

(Ans. 1.02×10^{-30} kg)

Exercise 4

Electrons in a two dimensional square lattice are in a band whose structure is given by

$$E(k) = E_0 - 2t(\cos(k_x a) + \cos(k_y a))$$

where E_0, t and a are constants. Analyze the behaviour of electrons near the centre (0,0) and at the edges ($\pm\pi/a, \pm\pi/a$) of the Brillouin zone and show that near these points, the structure may be approximated as $E(k) \sim \text{constant } + \frac{\hbar^2 k^2}{2m^*}$

where m^* is the effective mass. Determine the value of the effective mass at $k = 0$.

(Ans. 3.83×10^{-31} kg)

Exercise 5

The $E - k$ relationship for the conduction band of Ge is given by

$$E = E_c + \frac{\hbar^2}{2m_l^*}k_x^2 + \frac{\hbar^2}{2m_t^*}(k_y^2 + k_z^2)$$

where E_c is the energy of the bottom of the conduction band. The *longitudinal effective mass* m_l^* is 1.6 times the free electron mass while the *transverse effective mass* m_t^* is 0.082 times the free electron mass. Show that the energy surface is an ellipsoid of revolution with the major and minor axes being respectively $\sqrt{(2m_l/\hbar^2)(E - E_c)}$ and $\sqrt{(2m_t/\hbar^2)(E - E_c)}$.

Recap

In this course you have learnt the following

- Atoms combine to form solids through different types of bonds such as ionic, covalent, molecular and metallic bonds.
- In ionic solids, atoms give out and receive electrons so that each atom completes octet configuration.

- Semiconductors such as silicon and germanium are bonded covalently. In such bonding the atoms share electrons so that each one completes octet.

- The effect of lattice potential on an otherwise free electron can be taken into account by defining an effective mass. Effective mass is proportional to the curvature of the band.