

## Unit -2 BAND THEORY OF SOLIDS

### ❖ Formation of Energy bands in solids:

In the case of single isolated atom, the electron in any orbit as shown in following figure -1 have a definite energy. As a result, they occupy discrete energy levels, as shown in figure-2.

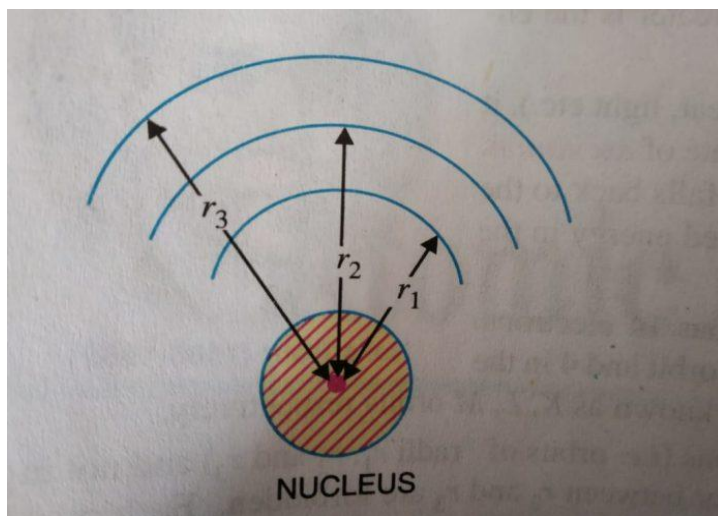


Figure-1

The Pauli exclusion principle allows each energy level to contain only two electrons.

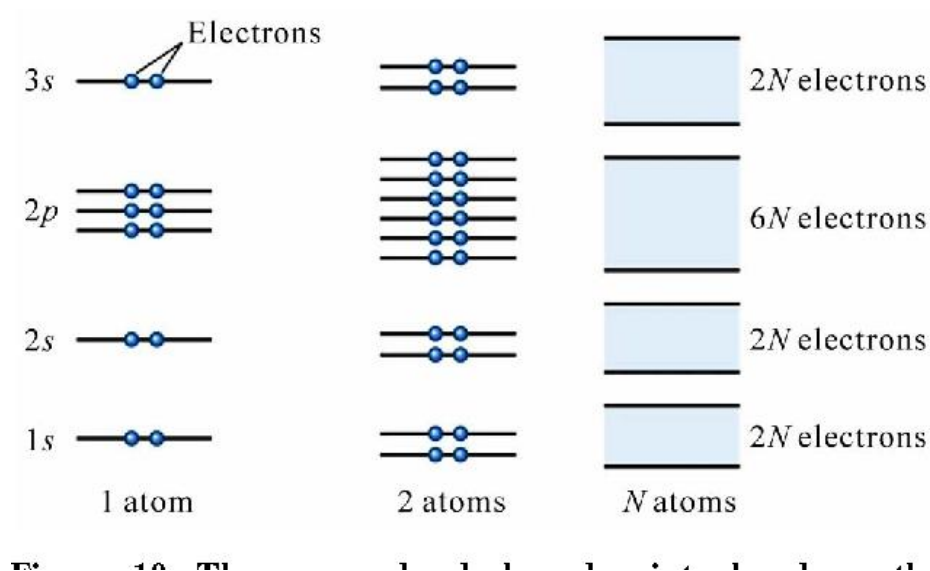


Figure -2

Let us consider the formation of bands in a solid sodium ( $z=11$ ). The Single energy level of an isolated sodium ( $Z=11$ ) based on the electron configuration  $1s^2 2s^2 2p^6 3s^1$  is shown in Figure-2.

When an another sodium atom is brought close to it, the electrons will be subjected to the effect of an additional field. As a result, each energy level is split into two as shown in figure-2.

More generally, when a solid is formed by bringing  $N$  atoms together, the Pauli's principle still demands that only two electrons in the entire solid should have the same energy. Hence, in a solid the different split energy levels of electrons come together to form continuous bands on energies as shown in figure-2.

The large number of energy levels resulting from splitting of an energy level will be very closely spaced and form an energy continuum that is called **Energy Band**.

While occupying an energy band, electrons start from the lowest energy level in the band and fill the levels one after other in the ascending order of energy. When  $2N$  electrons occupy the  $N$  levels available in a band, the band is said to be **completely filled**. In case of non-availability of  $2N$  electrons, the energy band gets **Partially filled**. When there are no electrons to occupy the levels, the energy band remains **vacant**.

#### ❖ ENERGY BANDS IN SOLIDS:

In case of any solid atom, the discrete energy levels of an atom become bands during the formation of solid due to the influence of the constituent atoms. Each band consists of a large number of energy levels which correspond to a range of energy values. The energies within the bands depend on the spacing between the atoms.

***The highest occupied band is called the valence band*** below which all the lower bands are occupied fully. The valence band may even be partially filled.

***The empty band which is immediately above the valence band is called the conduction band.***

***The gap between the valence band and conduction band is called the forbidden band or the energy gap.***

The following are the important energy bands in the solids.

#### 1. Valence Band

***The electrons in the outermost orbit of an atom are known as valence electron.*** The band of energies occupied by the valence electrons is called as valence band. This band may be completely or partially filled.

#### 2. Forbidden energy gap

***The gap between the valence band and the conduction band on the energy level diagram is known as forbidden band or energy gap.*** Electrons are never found in this gap.

### 3. Conduction band

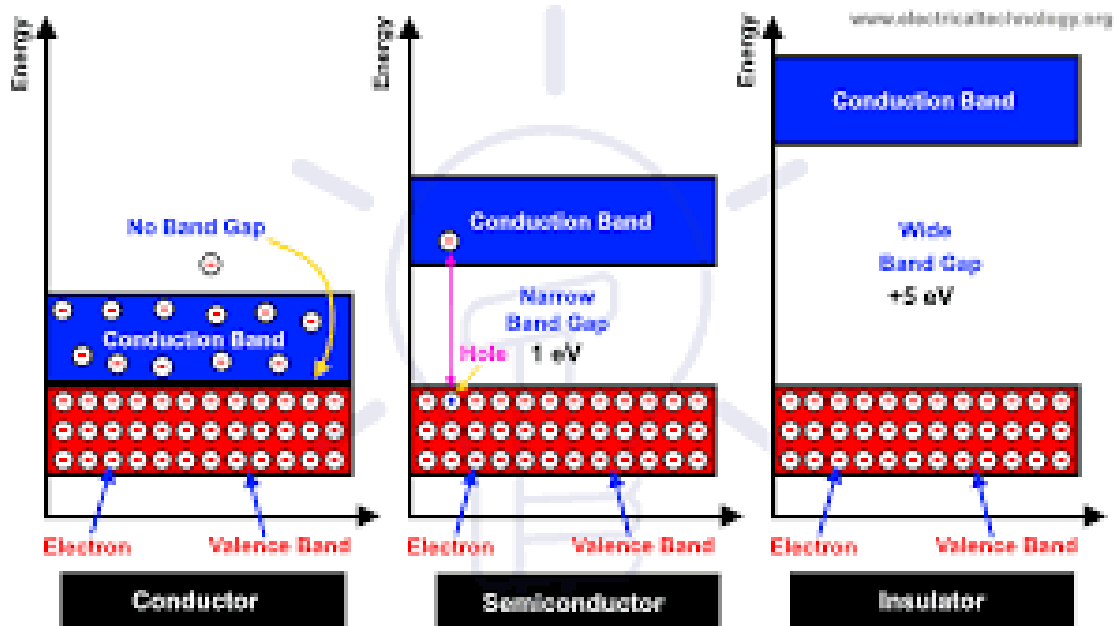
**The band of energies occupied by conduction electrons is known as conduction band.** This is the uppermost band, all electrons in the conduction band are free electrons. The conduction band is empty for insulators and partially filled for conductors.

### ❖ Classification of solids into Conductors(Metals), Semiconductors and Insulators on the basis of Band Theory

#### Conductors:

Conductors are characterized by high electrical conductivity. These are the solids in which plenty of free electrons are available for electrical conduction. Example silver, copper, iron, aluminum etc. In general, the resistivity of conductors lies in the range of  $10^{-9}\Omega\text{m}$  at room temperature.

In a conductor the conduction band and the valence band overlap each other as shown in figure so that the electrons can readily pass into the conduction band, i.e. the electrons can readily move under the influence of applied field.



**Figure: Schematic representation of band structure of solids**

#### Semiconductors:

These are the solids whose electrical properties lie in between those of conductors and insulators.

The resistivity of semiconductors lies between  $10^{-4}\Omega\text{m}$  to  $10^3\Omega\text{m}$  at room temperature.

In terms of energy bands semiconductors can be defined as those materials which have almost an empty conduction band and almost filled valence band with a very narrow energy gap separating the two bands = 1 eV.

The forbidden energy gap for germanium is 0.7eV and for silicon 1.1 eV.

### **Insulators:**

In an insulator the energy gap between valence band and conduction band is very large and approximately equal to 5 eV or more as shown in the figure. Therefore, a very high energy is required to push the electrons to the conduction band. For these reasons the electrical conductivity of the insulator is extremely small and may be regarded as nil under ordinary condition.

The resistivity of insulators lies between  $10^3$  to  $10^7 \Omega m$  at room temperature.

### **❖ Fermi Distribution Function**

The Fermi distribution function, also called the fermi function gives the probability of occupancy of energy levels by fermions in terms of fermi energy, temperature and Boltzmann constant.

Fermions are half integer spin particles like electrons which obey Pauli exclusion principle.

Consider a system of electrons in thermal equilibrium at a temperature T K. The probability  $f(E)$  of an electron occupying a particular energy level (state) E is given by

$$f(E) = \frac{1}{1 + e^{\frac{E - E_F}{K_B T}}} \dots (1)$$

Where  $f(E)$  is the fermi function,  $E_F$  is the fermi energy,

$K_B$  is the Boltzmann constant, T is the absolute temperature

For a filled energy level,  $F(E) = 1$  and for an unfilled level  $f(E) = 0$ .

The dependence of fermi function under different conditions of temperature and the effect on occupancy of energy levels are as follows.

### **Case : At T = 0K**

At absolute zero temperature, the electrons occupy the lowest energy level first, followed by the next higher ones as per Pauli's exclusion principle. i.e. A pair of electrons, one with spin up and the other with spin down occupy the lowest level. The next pair of electrons occupy the

next higher level and so on, till all the electrons of the metal are accommodated as shown in figure.

The uppermost filled energy level is referred as fermi level and the energy of the electrons in the fermi level at absolute zero degree is called the fermi energy.

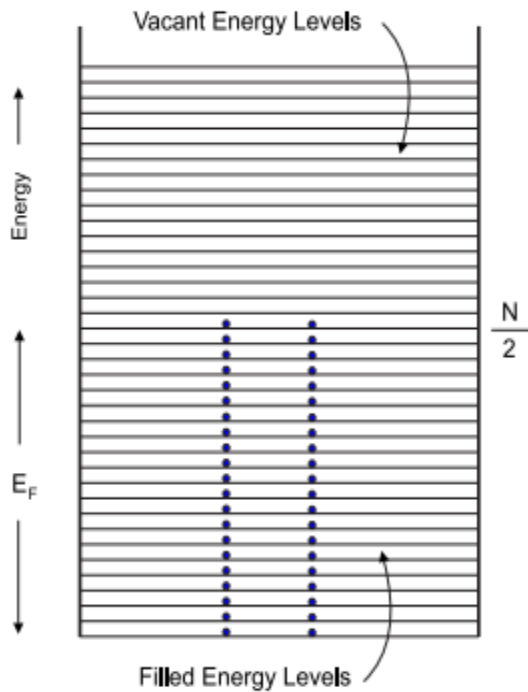
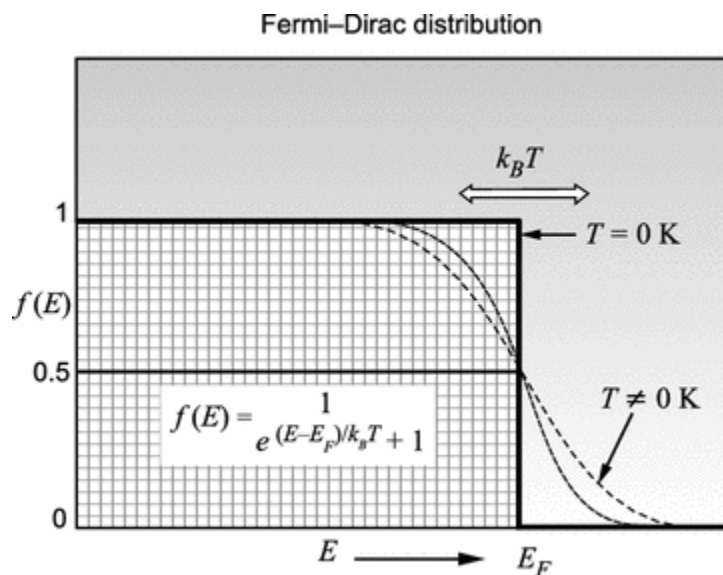


Figure 3.3: Distribution of Electrons at  $T = 0K$



Thus, at a temperature of absolute zero, all the energy levels lying above the fermi level are empty and those lying below are completely filled. Hence, fermi level helps to distinguish between an occupied and an unoccupied state.

### Special cases: Probability occupation

#### (a) At $T = 0\text{K}$ for $E < E_f$

For energy levels  $E$  lying below  $E_f$ , the term  $(E - E_f)$  takes a negative value. Hence, the argument for  $(E - E_f)/K_B T$  in the exponential function becomes  $-\alpha$ . Therefore,

$$f(E) = \frac{1}{1 + e^{-\infty}}$$

$$f(E) = \frac{1}{1 + 0} = 1$$

$F(E) = 1$  implies that, all the energy levels below  $E_f$  are occupied by electrons.

#### (b) At $T = 0\text{K}$ for $E > E_f$

For energy levels above  $E_f$ , the term  $(E - E_f)$  takes a positive value. Hence, the argument  $(E - E_f)/K_B T$  in the exponential function becomes  $\alpha$ . Therefore,

$$f(E) = \frac{1}{1 + e^{\infty}}$$

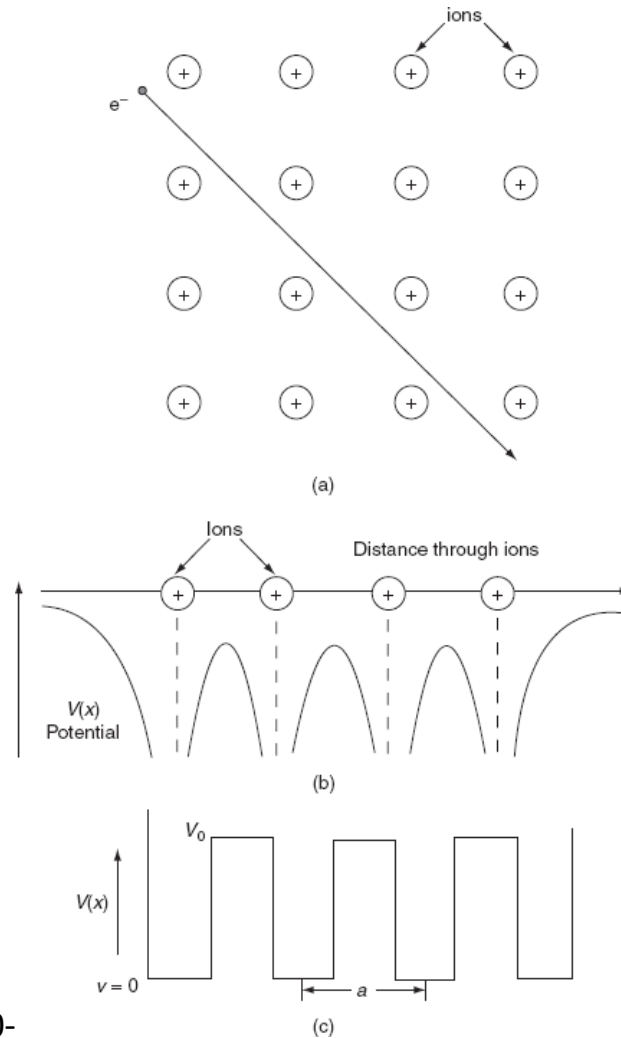
$$f(E) = \frac{1}{1 + \alpha} = 0$$

$F(E) = 0$  implies that all the energy levels above  $E_f$  are vacant, i.e. there is no chance of an electron occupying an energy level above  $E_f$ .

### THE KRONIG-PENNY MODEL:

In order to find the allowed energies of electrons in solids, we have to apply Schrodinger wave equation for an electron in a crystal lattice. Kronig-Penny suggested a simplified model consisting of an infinite row of rectangular potential wells separated by barriers of width  $b$ .

This one dimensional representation of periodic lattice is known as Kronig-Penny Model and is shown in below figure.



0-0-

Each well has width  $a$  and depth  $V_0$ .

The period of potential is  $(a + b)$ . In regions where  $0 < x < a$  the potential energy is assumed to be zero (i.e.  $V=0$ ) and in regions such as  $-b < x < 0$ , it is  $V=V_0$ .

**Bloch Theorem:**

The Schrodinger equation for two regions can be written as:

Schrodinger equation ( $E < V_0$ )

$$\begin{array}{ll} \text{Region I} & \frac{\partial^2 \phi_I(x)}{\partial x^2} + \alpha^2 \phi_I(x) = 0 \quad \alpha^2 = \frac{2mE}{\hbar^2} \\ \text{Region II} & \frac{\partial^2 \phi_{II}(x)}{\partial x^2} - \beta^2 \phi_{II}(x) = 0 \quad \beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \end{array} \quad \dots\dots(1)$$

**Region –I** where  $0 < x < a$ ,  $V = 0$

**Region – II** Where  $-b < x < 0$ ,  $V = V_0$ .

Solution of these equation can be written using Bloach Function represented as product of a free particle wave function and a periodic function  $u(x)$ . Thus,

$$\psi(x) = e^{ikx} u(x). \quad \dots\dots(2)$$

$$\text{With } u(x) = u(x+a) \quad \dots\dots(3)$$

By substituting these Bloach functions into Schrodinger equation and solve it, we get following expression.

$$\left( \frac{mV_0 ba}{\hbar^2} \right) \frac{\sin(\alpha a)}{\alpha a} + \cos(\alpha a) = \cos(ka)$$

$$\boxed{P' \frac{\sin(\alpha a)}{\alpha a} + \cos(\alpha a) = \cos(ka)}$$

$$P' = \frac{mV_0 ba}{\hbar^2}$$

Gives relation between  $k$ ,  $E$ (from  $\alpha$ ) and  $V_0$  .....(4)

### E-K DIAGRAM:

The solution of Bloach function is given by above equation (4). This relation is a trigonometric function; only certain values are possible.



The right hand side of equation (4) is cosine function and can take values only between -1 and +1. Therefore, left side of the function is restricted to vary between limits. Hence certain values of  $\alpha$  are allowed. It means that the energy  $E$  is restricted to lie within certain range.

This concept is best understood by drawing the plot of energy  $E$  as a function of the wave function ( $k$ ).

To understand the nature of solution initially consider the special case for which  $V_0 = 0$  or  $P = 0$ .

$$\cos \alpha a = \cos ka \quad \text{therefore,} \quad \alpha = k = p/\hbar \quad \text{.....(5)}$$

Therefore for free electrons,

$$E = p^2/2m = \hbar^2 k^2/2m \quad \text{.....(6)}$$

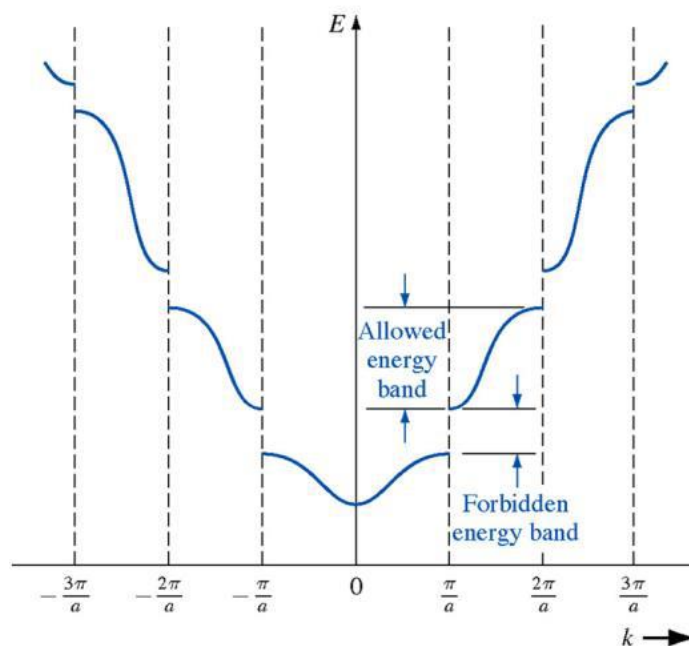
Which represents the parabolic relation as represented in following figure.

$$\alpha^2 = \frac{2mE}{\hbar^2}$$

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

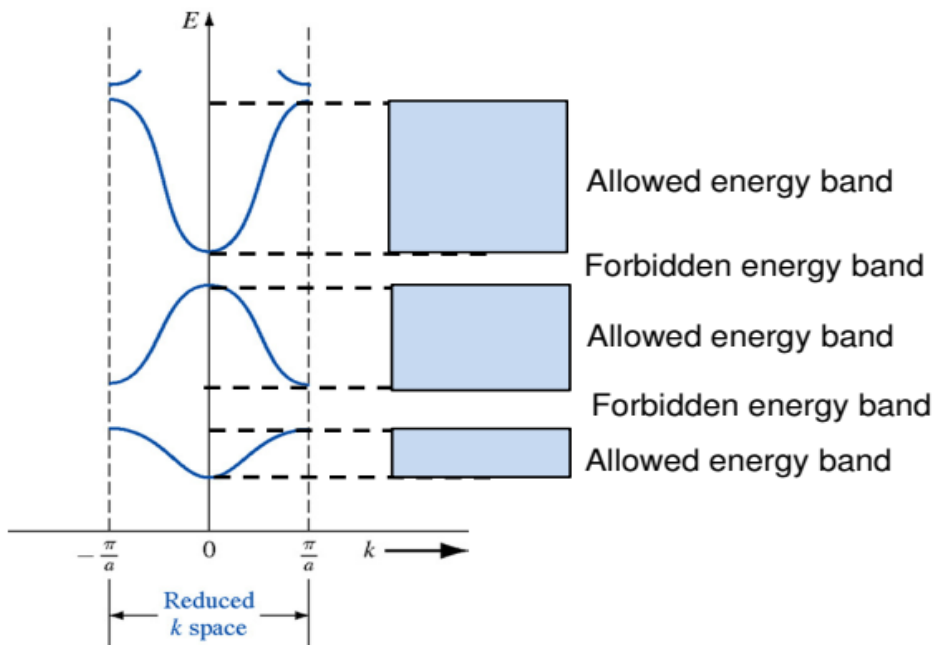
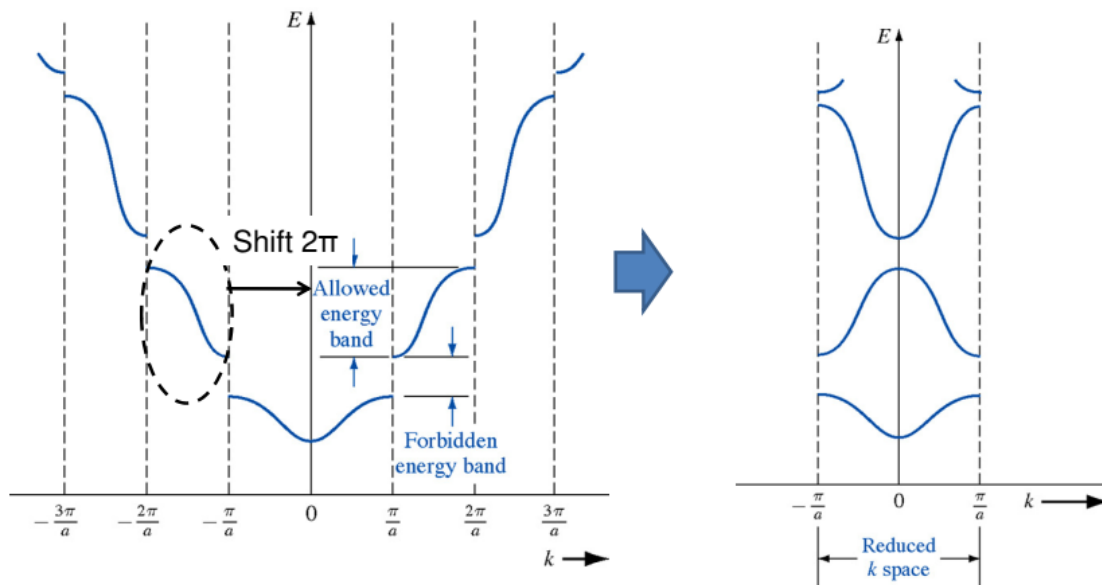
Plot E-k →

Discontinuity of E



Right side

$$f(\alpha a) = \cos(ka) = \cos(ka + 2n\pi) = \cos(ka - 2n\pi)$$



First Brillouin zone

### Conclusions:

1. Energy spectrum of electrons consist of a number of allowed energy bands separated by forbidden regions.
2. Width of allowed energy bands increases with increasing value of E (value of  $\alpha$ ).

3.Width of a particular allowed band decreases with increasing binding energy of electron (i.e. the value of  $P$ , which depends on  $V_0$ ).

### Concept of Effective Mass of electrons:

We generally assume that the mass of an electron in a solid is the same as the mass of a free electron. However, experimentally measured values indicate that in some solids the electron mass is larger while for others it is slightly smaller than the free electron mass.

The experimentally determined electron mass is called the **effective mass  $m^*$** .

The cause for the deviation of the effective mass from the free electron mass is due to the interactions between the drifting electrons and the atoms in a solid.

It has been found that the effective mass is inversely proportional to the curvature of an allowed energy band. It means that the effective mass depends on the location of an electron in the allowed energy band (Following Figure).

