**Band Theory of Solids : Energy-band Structure :** A solid contains an enormous number of atoms packed closely together. Each atom, when isolated, has a discrete set of electron energy levels 1s, 2s, 2p, 3s, 3p, ..... If we imagine all the $N$ (say) atoms of the solid to be isolated from one another, then they would have completely coinciding sets of energy levels. That is, each of the energy levels of this $N$-atom system would have an $N$-fold degeneracy. The electrons fill the energy levels in each atom independently. As the atoms approach one another to form the solid, a continuously increasing interaction occurs between them which causes each of the levels to "spilt" into $N$ distinct levels. In practice, however, $N$ is very large ($\approx 10^{23}/cm^3$). Therefore, the splitted energy levels become so numerous and so close together that they form an almost continuous "energy *band*".

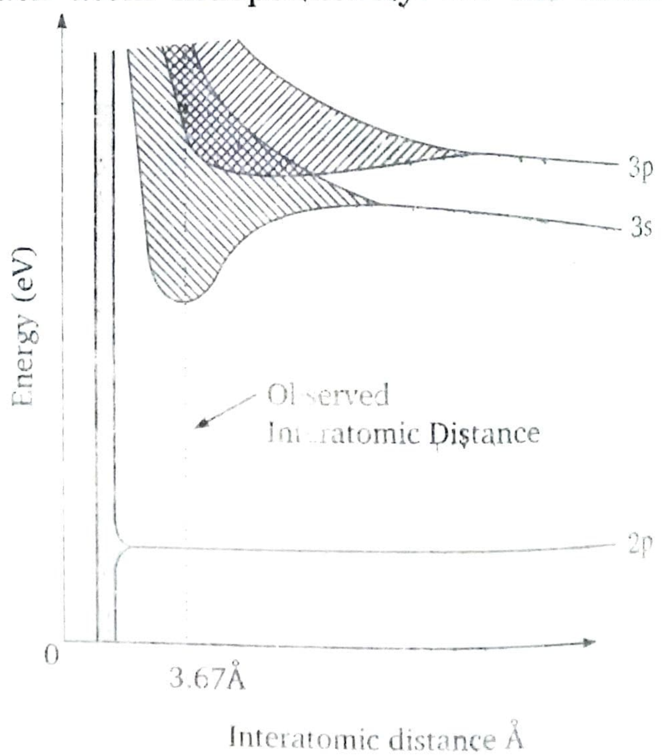


Fig. 1

The amount of splitting is different for different energy levels. In general, the lower levels are splitted less than the higher levels, the lowest levels remaining almost unsplitted. The reason is that the electrons in lower levels are the "inner" electrons of the atoms, which are not significantly influenced by the presence of nearby atoms. On the other hand, the electrons in higher levels are the "valence" electrons whose wavefunctions overlap appreciably.

Fig. 1 shows the formation of energy levels for some of the higher energy levels of isolated sodium atoms (whose ground-state configuration is ($1s^2\ 2s^2\ 2p^6\ 3s^1$) as their interatomic distance decreases. The (dashed line indicates the observed interatomic separation in solid sodium). The $3s$ level is the first "occupied" level to be splitted into a band; the $2p$ level does not begin to spilt until the interatomic distance becomes smaller than actually found in the solid sodium. (The levels 1 s and 2s do not split at all).

Now, the energy bands in a solid correspond to energy levels in an atom. An electron in a solid can have only energies that fall within these energy bands. The various energy bands in a solid may or may not overlap depending upon the structure of the solid. If they do not overlap (Fig. 2a) then the intervals between them represent energies which the electrons in the solid cannot have. These intervals are called "forbidden bands" or "energy gaps". If, however, the adjacent energy bands in a solid overlap (Fig.2b), the electrons have a continuous distribution of allowed energies.

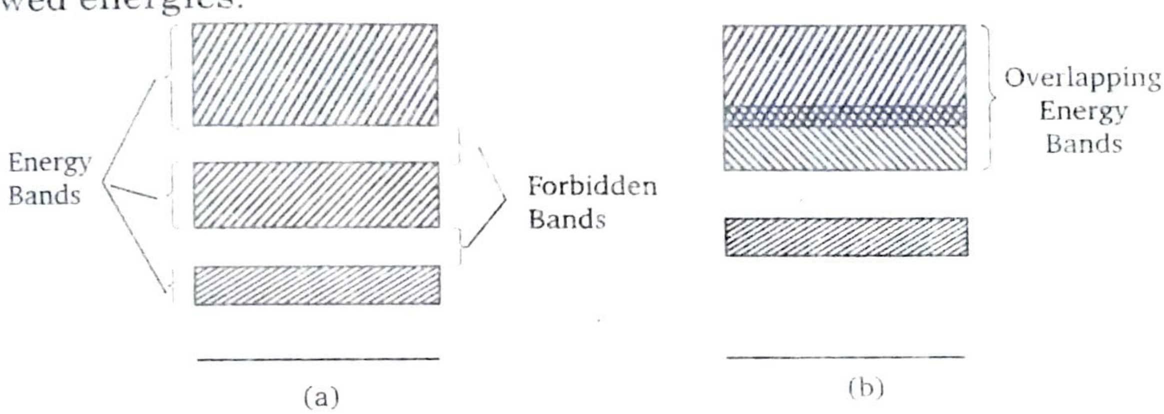



Fig. 2

**Classification of Solids on the basis of Band Structure :** The electrical properties of a solid depend upon its energy-band structure and the way in which the energy-bands are occupied by the electrons. In general, each energy band has a total of $N$ individual levels, and each level can hold $2(2l + 1)$ electrons* so that the capacity of each band is $2(2l + 1)\,N$ electrons. Thus, the that the capacity of each band is $2(2l + 1)\,N$ electrons. Thus, the $1s, 2s, 2p, 3s, \ldots$ bands can hold

* Corresponding to the two different orientations of the electron spin and the $2l + 1$ orientations of the electron orbital angular momentum.

$2N$, $2N$, $6N$, $2N$, ..... electrons respectively*. Depending on the nature of band occupation by electrons and on the width of forbidden bands, all solids can be classified as conductors, insulators and semiconductors.

**Conductors :** In the band structure of some solids, there is a *partially-filled* band above the completely-filled lower bands. Such a band is formed from partially-filled atomic levels as in case of alkali metals like sodium (Fig. 3a). A sodium atom has a single valence electron in its outer $3s$ level. Therefore, of the $N$ atoms in a solid piece of sodium, each contributes only one $3s$ electron to the solid, and so there are only $N$ (valence) electrons in the $3s$ band. The valence band** $3s$ is thus only half full.

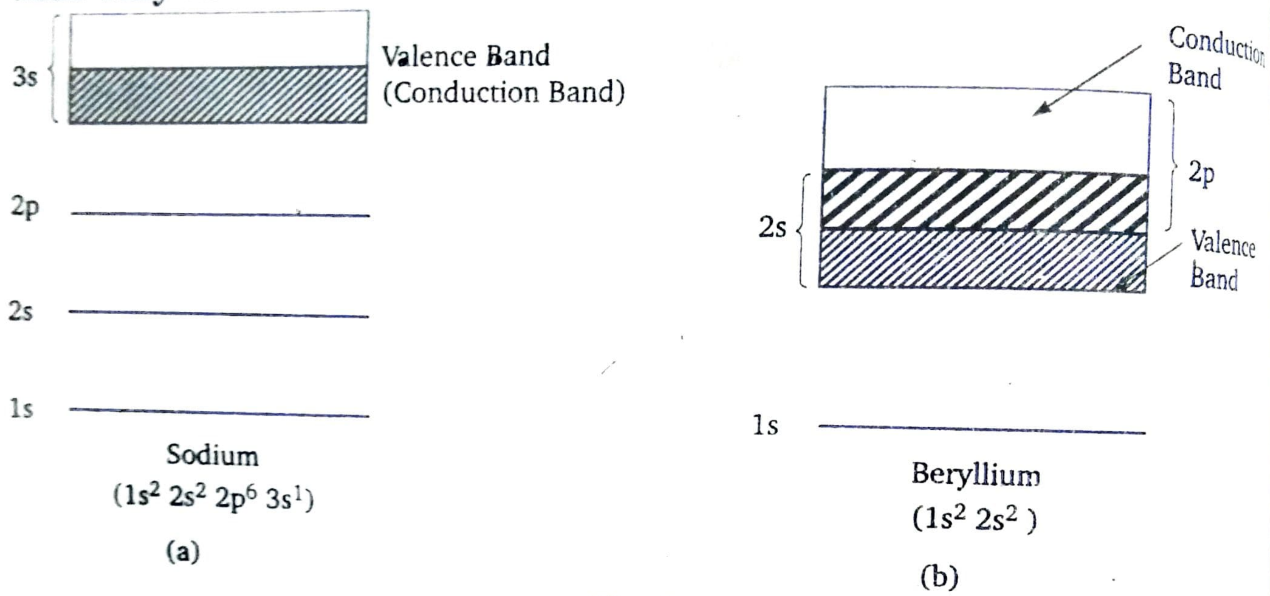



Fig. 3

A partially-filled band may also be the result of overlapping of a completely-filled band and an empty band, as in case of alkaline-earth metals, In Fig. 3*b* are shown the energy bands of beryllium in which there is an overlap of the lower energy levels of the empty $2p$ band with the upper energy levels of the completed $2s$ band. Those electrons which would occupy the highest energy levels in the $2s$ band will actually go into the lowest levels of the overlapping $2p$ band. Thus, levels at the top of the $2s$ band become unoccupied and the band is only partially-filled.

Now, suppose an electric field is applied across a piece of solid sodium (or beryllium). Then, electrons in the partially-filled valence band easily acquire additional energy to move to the higher unoccupied energy levels *within the same band*, without crossing any energy gap. The additional energy is in the form of kinetic energy, and the moving electrons constitute an electric current. Sodium (or beryllium) metal is

* The bands formed by $1s$, $2s$, $2p$, ... atomic energy levels, each $N$ in number, are called $1s$, $2s$, $2p$, .... bands.

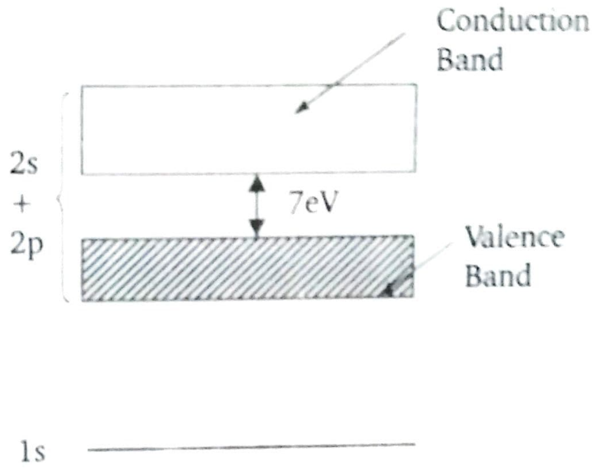
** The band formed from the atomic energy levels containing valence electrons is called valence band.

therefore a good conductor of electricity. Thus, a ***partially-filled valence energy-band is a feature of conductors.***

An empty band into which electrons can pass is termed as 'conduction band'. In conductors, the valence band itself is the conduction band.

**Insulators :** In the band structure of some solids, the valence band (containing the outer electrons of the atoms) is completely filled, while the next higher band separated by an energy gap of a few electron-volts is completely empty. Such a solid is an "insulator". Diamond and sodium chloride are typical examples of insulators.

Fig.(4) shows the energy bands of diamond. There is an energy band completely filled with electrons (the valence band), and above it is an empty band (the conduction band) separated by a gap of 7eV*. (The bands below the valence band are also completely filled). At least 7eV of energy must be provided to an electron in the diamond crystal in order to enter the conduction band where it can move freely. With $kT = 0.025\,\text{eV}$ at room temperature, valence electrons do not have enough thermal energy to cross the 7-eV gap.




Diamond

($1s^2\ 2s^2\ 2p^2$)

Fig. 4

Now, if an electric field be applied, the electrons in the valence band would not accept energy to move within the band because there are no unoccupied levels in this band. They can, however, move to the higher empty band provided they get energy of about 7 eV to cross the gap. Since the electric field *cannot* give this amount of energy**, the

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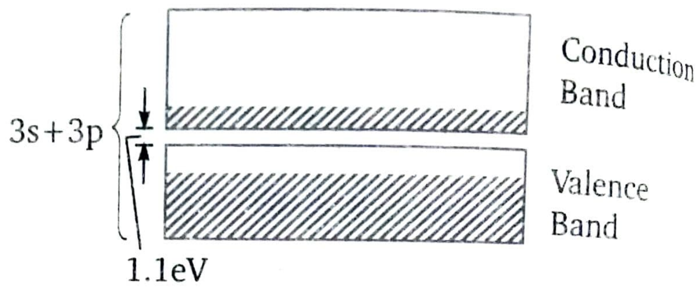
* In the formation of diamond crystal, the bands $2s$ and $2p$ first completely overlap to form a single band of capacity $2N + 6N = 8N$ electrons. As the atoms approach still closer, the band divides inot two bands, separated by 7eV, each with a capacity of $4N$ electrons. Since diamond atom has 4 valence electrons (two $2s$ and two $2p$), the lower (valence) band is completely filled and the upper (conduction) band is completely empty.

** An electron moving through a crystal undergoes frequent collisions with crystal imperfections and so loses much of the energy it gains from the applied elecric field. An electric field of over $10^8$ V/m is required for an electron to gain 7 eV in a path length of $10^{-8}$ m. This is over $10^{10}$ times greater than the field needed to cause a flow of current in sodium.

electrons do not acquire a directional motion. Diamond is, therefore, an insulator.

**Semiconductors :** Certain solids have the basic crystal structure of an insulator, but with a much smaller energy gap (of the order of an electron-volt) between the valence band and the conduction band. Such solids are known as semiconductors.' Silicon and germanium, having energy gaps, of 1.1 eV and 0.7 eV respectively, are typical examples of semiconductors.

Fig. (5) shows the energy bands of silicon. At room temperature, a *few* of its electrons in the valence band have sufficient kinetic energy of thermal motion to cross the narrow energy gap (forbidden band) and enter the conduction band above it. Hence, when an electric field is applied, the few electrons present in the conduction band acquire additional energy to move to the unoccupied levels within the same band. Similarly, a few of the many electrons present in the valence band move to the few available unoccupied levels in the same band. Hence there is a *limited* flow of current across the crystal. Thus, silicon has an electrical conductivity intermediate between those of conductors and insulators, and is therefore a semiconductor.




Silicon

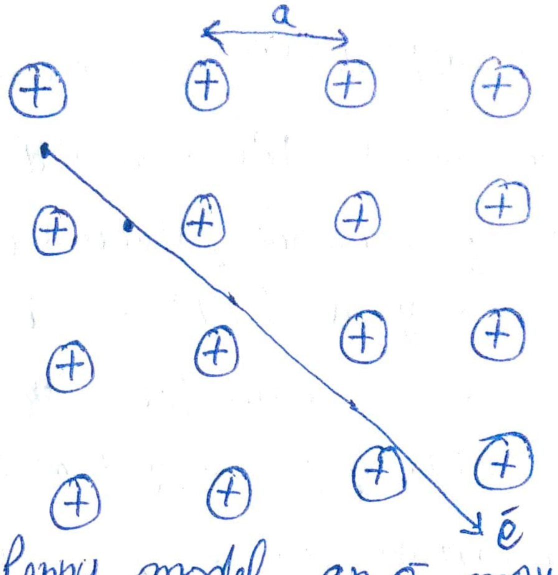
($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$)

**Fig. 5**

Kronig-Penny Model :→ According to the Free electron model of metal, the conduction electrons move freely in a region of constant potential (or zero) without interacting with the crystal lattice. The free electron model explains the certain properties of metals such as conductivity, specific heat, paramagnetism etc but it fails to explain satisfactorily the properties of solids like conductor, semiconductor, insulator separately. So it needs to be modified.

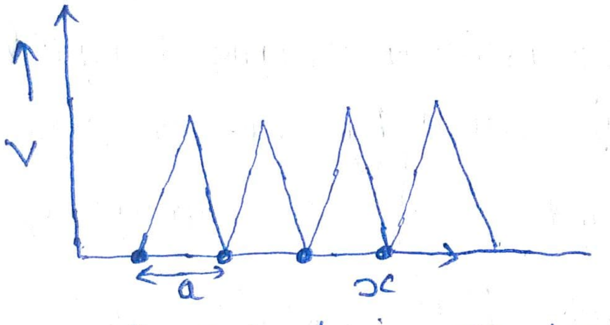
In general, an electron in a solid moves in a region of periodically varying potential (with the periodicity of lattice) caused by the ion-cores situated at the lattice points, plus the average effect of all the other free electrons. This results in the diffraction of electrons by lattice. When the de-Broglie wavelength $\left(\lambda = \frac{h}{p}\right)$ correspond to the periodicity in the spacing of ions, then the Bragg's reflection occurs there due to interaction of electrons with lattice. This limits the electron to certain ranges of momenta and correspondingly to certain ranges of energy (energy bands).

Inside a real crystal, there is an infinite array of lattice points & there is a periodic arrangement of +vely charged ions through which the $e^-$ move. The potential of $\bar{e}$ near or at the +ve ion site is zero & is max exactly in between the position of ion sites.

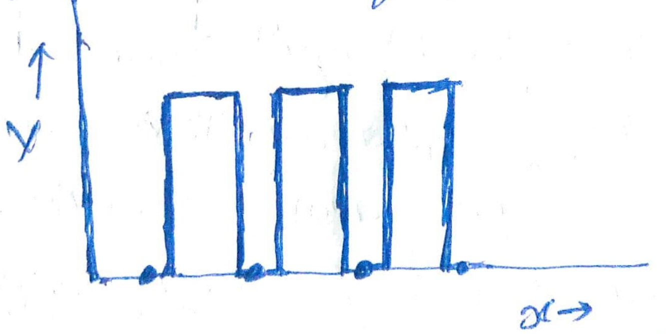



According to Kronning - Penny model an ē moves in a periodic potential produced by +ve ions.

The potential varies periodically with the same period as lattice.




To solve the Schrodinger equation using the above potential form, is difficult, so Kronnig - Penney changed this form of potential as follows:-




This periodic arrangement of potential wells and potential barriers is most probably very close to reality.

Now we will solve Schrodinger equation to find the energy of electron in the crystal lattice.

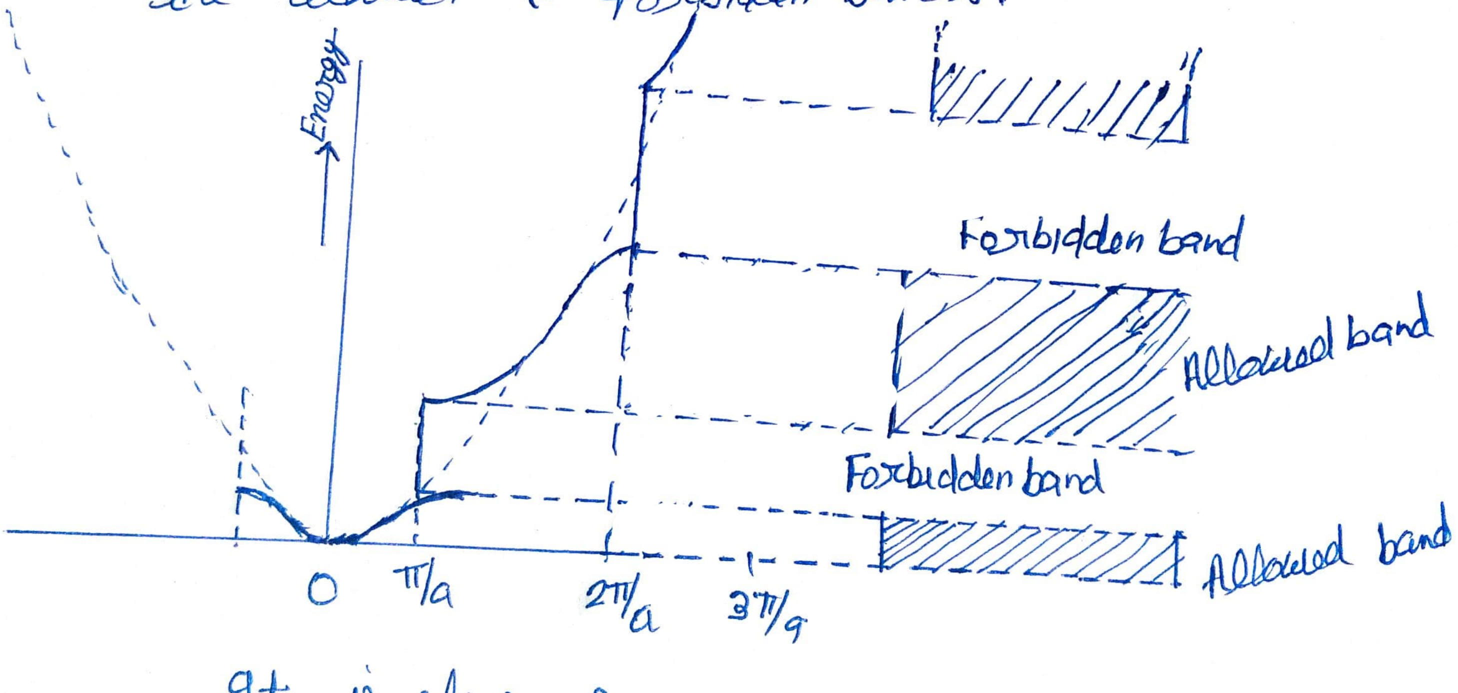
On solving the Schroedinger equation, we get the energy of electron, which is moving in periodic potential,

$$E = \frac{h^2 k^2}{8\pi^2 m}$$

where $k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm\frac{3\pi}{a}$

i.e energy is not continuous, but discontinuity occurs at $k = \pm\pi/a, \pm\frac{2\pi}{a}, \pm 3\pi/a$ ---

Now we plot a graph b/w $E$ & $k$ to show the allowed & forbidden bands.




It is clear from the above graph that the energy of $\bar{e}$ is continuous in crystal lattice but discontinuity occurs at $k = \pm\pi/a, \pm 2\pi/a, \pm 3\pi/a$ so the regions in which energy is continous, are known as allowed energy bands but the regions in which energ is discontinous are known as forbidden bands.