

Role of doping on band structure,

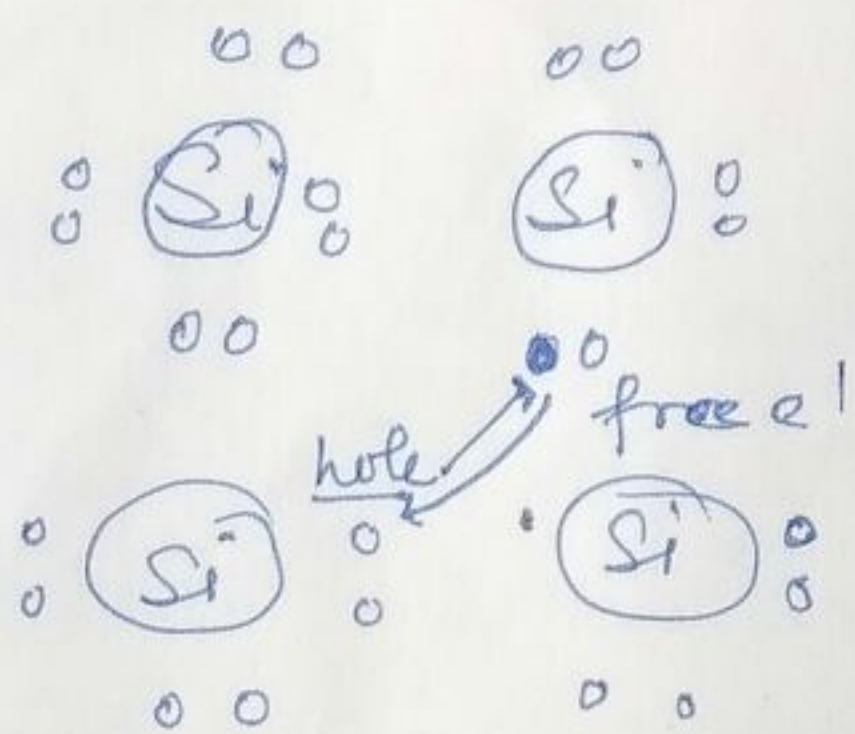
Semiconductor

Intrinsic Semiconductor \rightarrow Forbidden gap energy is about 1 eV. They are pure like Si, Ge, Se.

having 4 valance e^- , and forms 4 covalent bonds by sharing with four neighbouring atoms

— Energy gap is so small (about 1 eV) that even at ordinary temp, there are many valance e^- , which possess sufficient energy to jump across the forbidden gap to conduction band.

— when an e^- from valance band is ejected band is broken and positively charged hole is left behind. this hole can travel to adjacent atom by accepting an e^- from latter one. This involves re-establishing a new covalent bond by filling up the previous hole and creating a new hole. when electric field is applied, e^- move to anode & the +vely charged holes in valance band move to cathode. So current flows as a result of simultaneous movement of holes and e^- in opposite directions.



Extrinsic Semiconductors \rightarrow are Intrinsic semiconduc

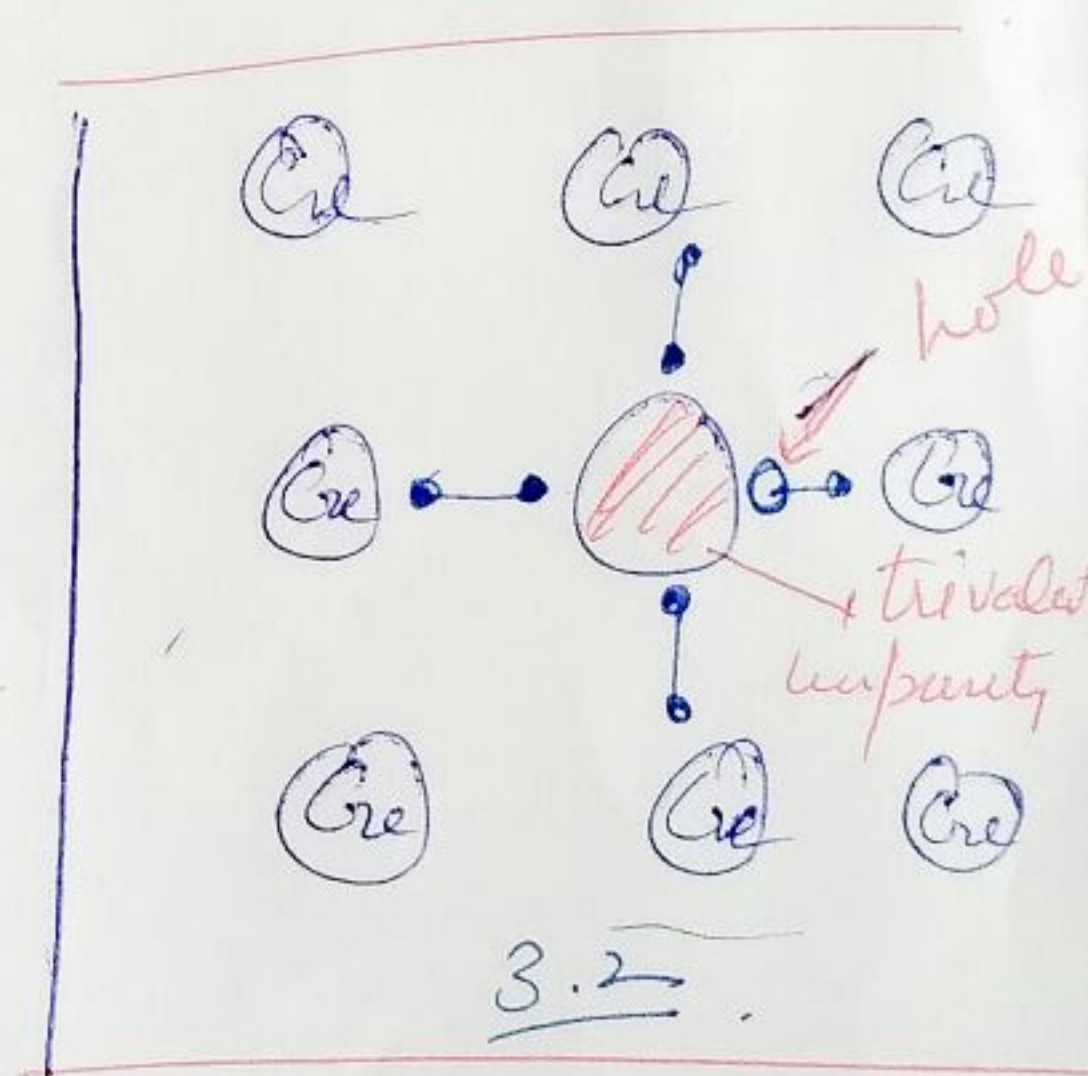
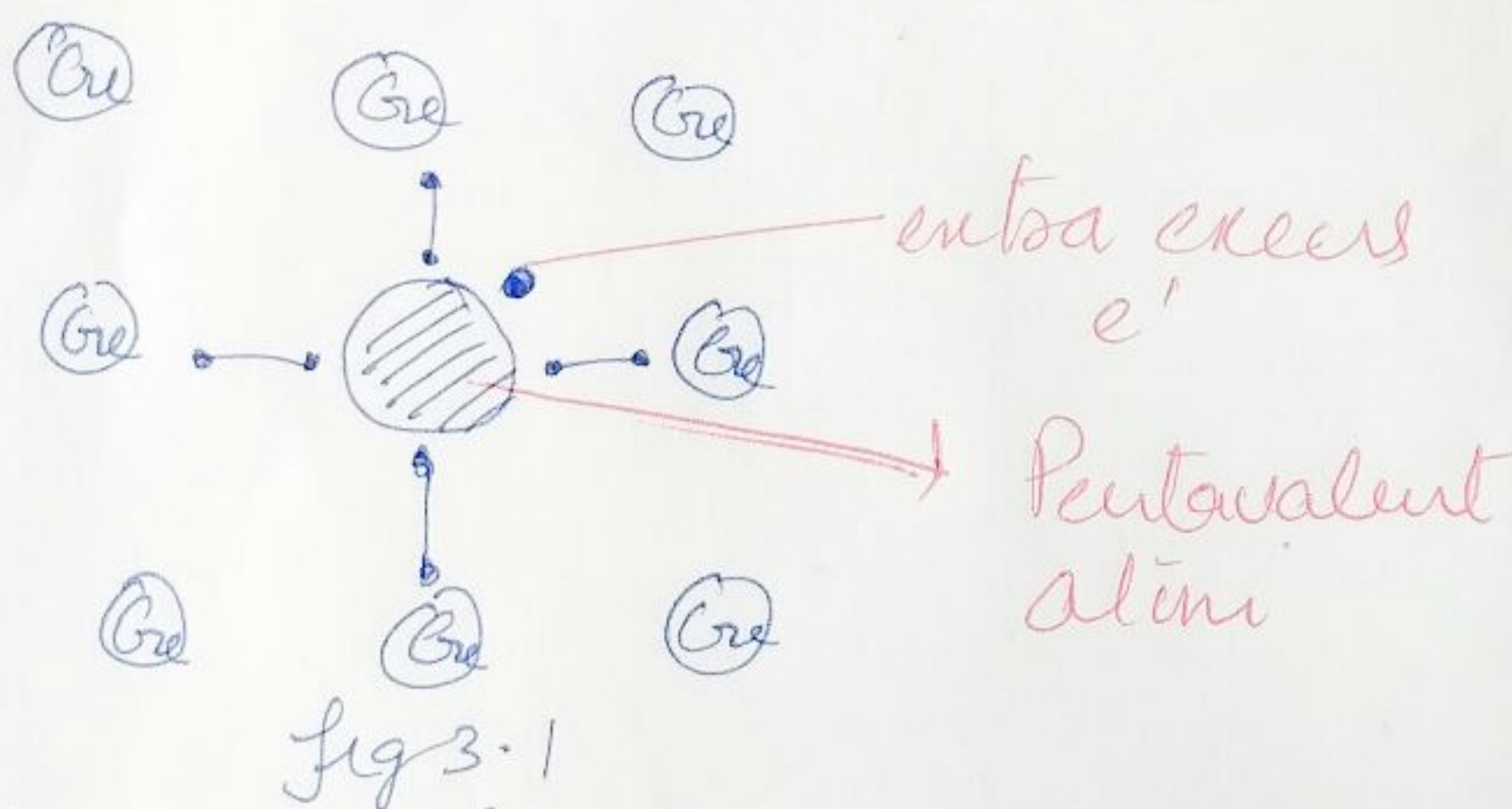
tors whose conducting properties are improved by adding extremely small amount of specific substitutional impurities (called doping agents or dopants). Doping agents reduces the energy gap (E_g) thereby allowing more e^- to flow from valance band to empty conduction band

usually one part of substance is added to 10^6 (2) part of parent element (Si, Ge etc). By doping conductivity of a semiconductor can be \uparrow ed 10,000 times.

Based on doping agent added, 2 types of Semiconductor.

n-type extrinsic :- Pentavalent impurity like P, As, Sb are added to pure semiconductor like Ge, Si. fig 3.1

Conduction process :- donor atom forms four covalent bond \bar{c} four surrounding atoms of intrinsic semiconductor but the fifth e^- remains loosely bound to donor atom. This e^- is easily excited from valance band to the conduction band when electric field E is applied. So in n-type e^- are responsible for conduction.



p-type semiconductor :- It is obtained by adding trivalent element (B, Al) to pure intrinsic semiconductor, so it contains an excess \bar{c} vely charged hole.

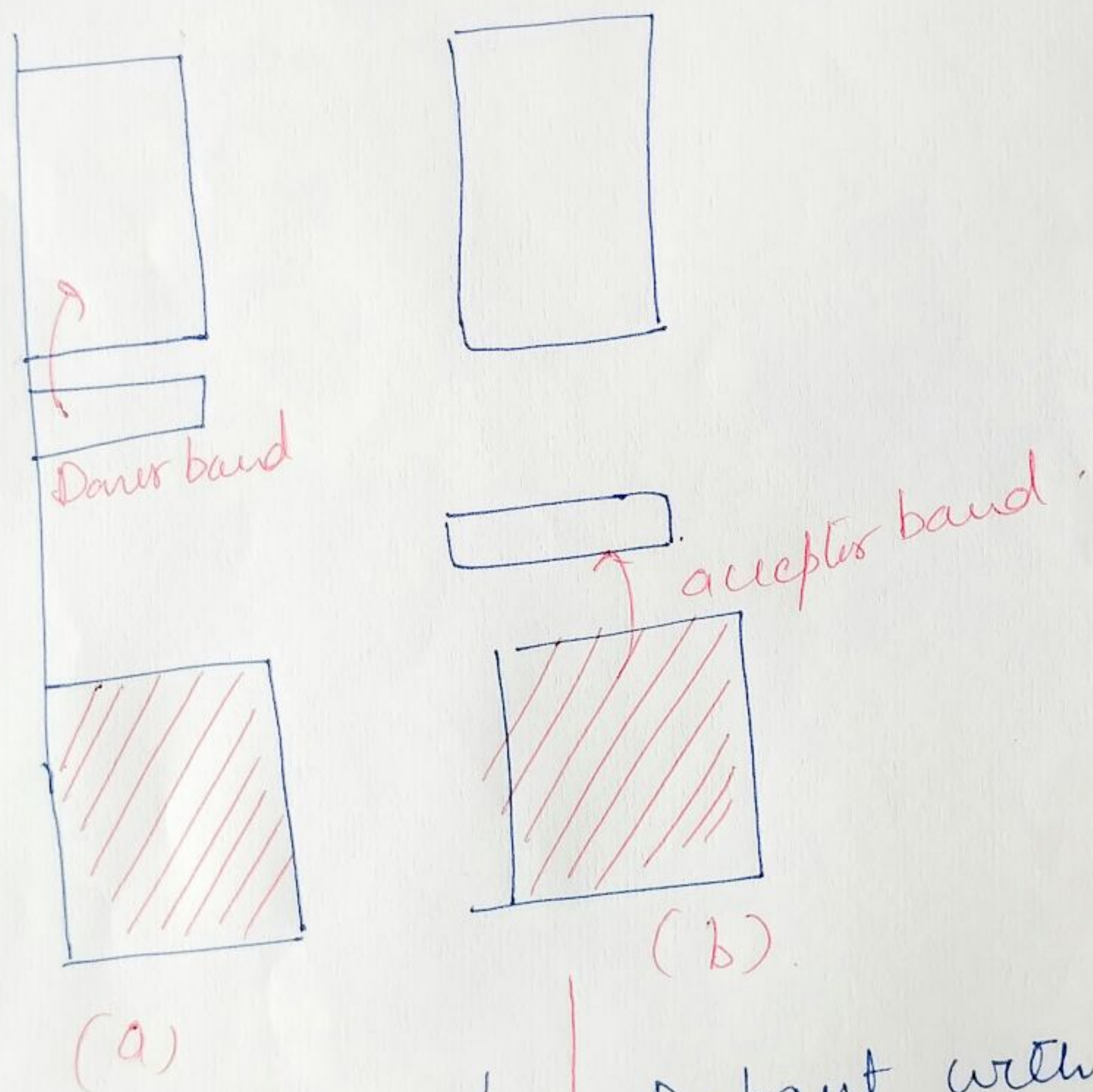
Conduction process: All the $3e^-$ valance electrons present in doping agent form 3 covalent bonds with 3 of four atoms of Ge thereby leaving one of the four Ge atoms incomplete. This gives rise to positive hole which conduct current. In this conduction process hole travels to adjacent atom by acquiring e^- and forming a new bond. So \bar{c} vely charged holes are carriers during conduction.

n type

p type

- 1) Pentavalent impurity + Si/Ge
- 2) Has excess e^-
- 3) Conduction is due to free e^-

- Tetravalent impurity + Si/Ge
- Has excess holes
- Conduction is due to electron-holes



Dopant with more e^- than its host atom (Si) forms narrow band that can supply e^- to conduction band

Dopant with fewer e^- than its host atom forms narrow band that can accept e^- from valence band

Band theory of Solids

Effect of temperature on conductivity. The conductivity of the metal decreases with rise in temperature. This is because with the rise in temperature the positively charged kernels also start vibrating which interferes with the movement of electrons. As a result, conductivity decreases.

In metals, the electrons are the charge carriers. In molten ionic compounds, the charge is carried by the ions. Further, the electrons are smaller than ions and hence are more mobile. It is because of this reason that the electrical conductivity of metals is much higher than the electrical conductivity of ionic liquids.

(ii) **Thermal conductivity.** Thermal conductivity of the metals is also due to mobile electrons. On heating a part of the metal, the kinetic energy of the electrons in that region increases. The energetic electrons move rapidly to the cooler parts and transfer their excess kinetic energy to other electrons in the cooler part of the metal. Thus the heat is conducted throughout the metal.

(iii) **Metallic lustre.** The bright metallic lustre is due to the delocalised mobile electrons. When light falls on the surface of a metal, the most loosely bound electrons absorb photon of a radiant energy of visible light. Consequently, the electrons start vibrating at a frequency equal to that of the incident light. The vibrating electrons emit electromagnetic radiations in the form of light. Thus it appears as if light is being reflected from metal surface and the surface gains a shiny appearance which is known as metallic lustre.

(iv) **Malleability and ductility.** Since the metallic bond is non-directional, metals can be drawn into wires or beaten into sheets. This is because the kernels can slip over each other when a shearing force is applied.

(v) **Hardness.** Metals are generally hard. The hardness depends upon the strength of metallic bond which in turn depends upon the following two factors:

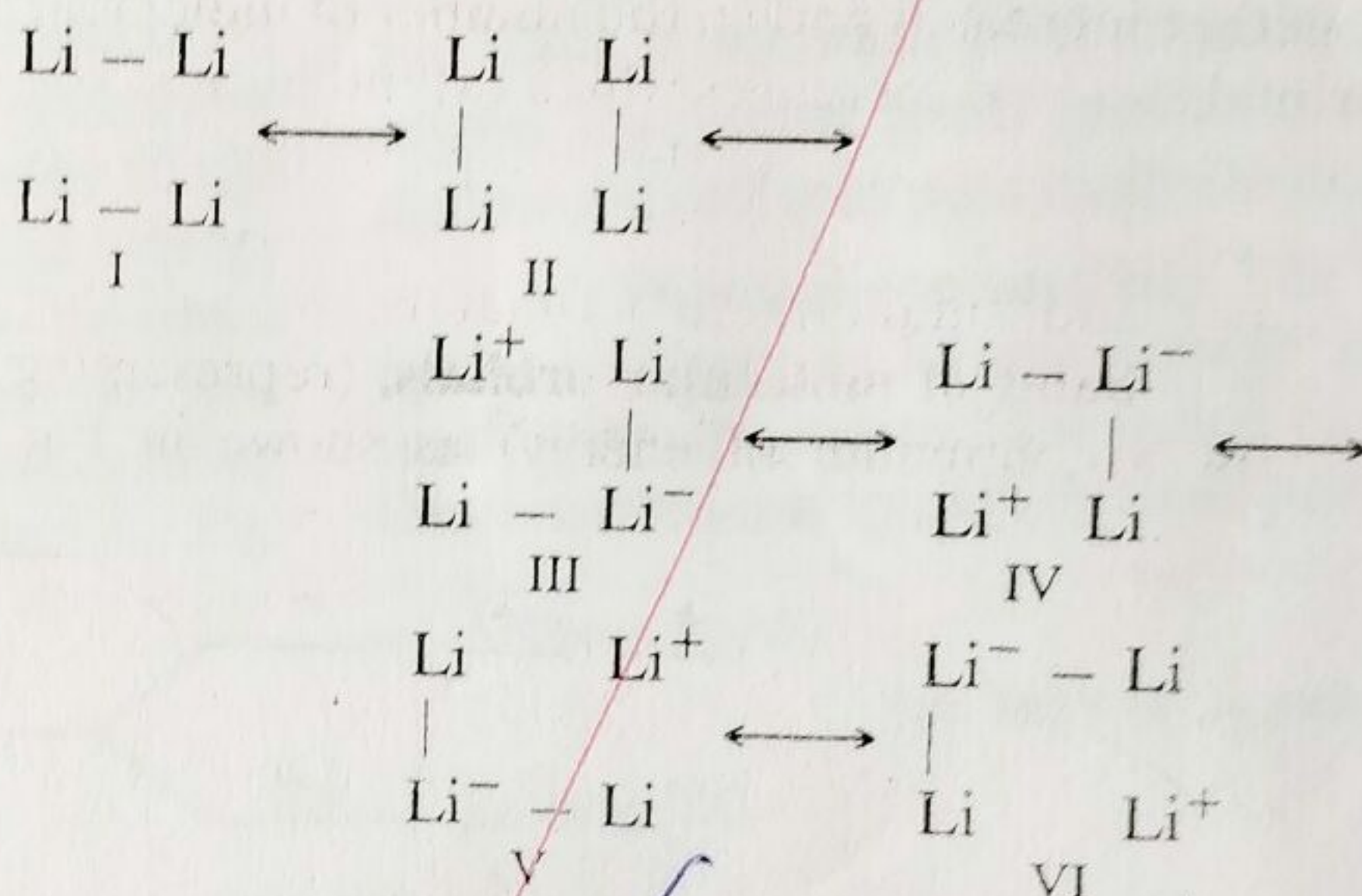
(a) **Number of valence electrons.** Greater the number of valence electrons, greater is the attraction between the kernels and hence stronger is the bond.

(b) **Size of the kernels.** Smaller the size of the kernels, greater is the attraction on the valence electrons and hence stronger is the bond.

Alkali metals are soft because they have only one valence electron and large-sized kernels. As a result, the metallic bond in them is weak.

(2) Valence Bond Model or Resonance Model.

Taking the example of lithium metal, in the lattice each lithium atom is surrounded by eight nearest neighbours and six next nearest neighbours. As Li atom has only one valence electron, it can form only one normal covalent bond with another Li atom. The only way in which Li atom can bond all its neighbouring Li atoms can be explained by postulating that the covalent bond resonates among all the neighbouring Li atoms and the actual structure is a resonance hybrid of all these structures. Taking the example of four Li atoms, the resonating structures may be represented as follows:



The actual bonding includes all the atoms of the crystal and is three-dimensional.

In structures III, IV, V and VI, ionic forms have been shown. In these structures, Li carrying negative charge is bonded to other Li atoms. This means that more than one valence orbital of each Li atom is involved in the metallic bonding. It is assumed that the vacant $2p$ orbital, which is not much higher in energy than $2s$, is used. This orbital is called the **metallic orbital**.

As a result of resonance, the crystal is stabilized.

(3) **Band Model (Band Theory of Metallic bonding) – Molecular Orbital Approach.** According to molecular orbital approach, when two atomic orbitals of nearly same energy and same symmetry but belonging to two different atoms (e.g. two H-atoms) combine or overlap, they form two molecular orbitals, one with lower energy than the combining atomic orbitals and is called the **bonding molecular orbital** and the other with energy higher than the combining atomic orbitals and is called **antibonding molecular orbital**.

Now let us apply this theory to the bonding between metal atoms, taking the example of lithium. When two Li atoms come close together, their $2s$ orbitals overlap (because they have same energy *i.e.* they are degenerate when they are far apart and also have the same symmetry). As a result, two molecular orbitals will be formed *i.e.* their degeneracy is split into two levels (Fig. 1.2.22 (a)). The $2s$ electron of each Li atom will be in the lower energy bonding molecular orbital. If more than two atoms come close together, more than two atomic orbitals overlap and hence the number of molecular orbitals formed is also more. As the number of Li atoms coming close together increases, the number of atomic orbitals combining together increases and so the number of molecular orbitals formed increases which extend over all the Li atoms. However, as this happens, the energy difference between the molecular orbitals becomes smaller and smaller and ultimately, we say that there is **band of molecular orbitals**, (representing almost a continuum of energy) as shown in Fig.

1.2.22(e). As each Li atom contributes one level to the band, therefore, number of levels in the band is equal to the number of atoms.

Each level of the band can accommodate two electrons of opposite spin. If N atoms contribute N levels to a band, the band is capable of holding $2N$ electrons. Since N Li atoms have a total of N valence electrons, this means that half of the levels would be vacant.

This model helps to explain the properties of lithium as follows :

(i) **Electrical conductivity.** When an electric current is applied, electrons move into vacant levels in the band. Since each level extends over the entire crystal, the vacant levels provide a route by which electric current may pass easily through the metal.

(ii) **Thermal conductivity.** The electrons take up heat energy as kinetic energy and since their motion is unrestricted for going to vacant levels they transfer energy rapidly to all parts of the metal.

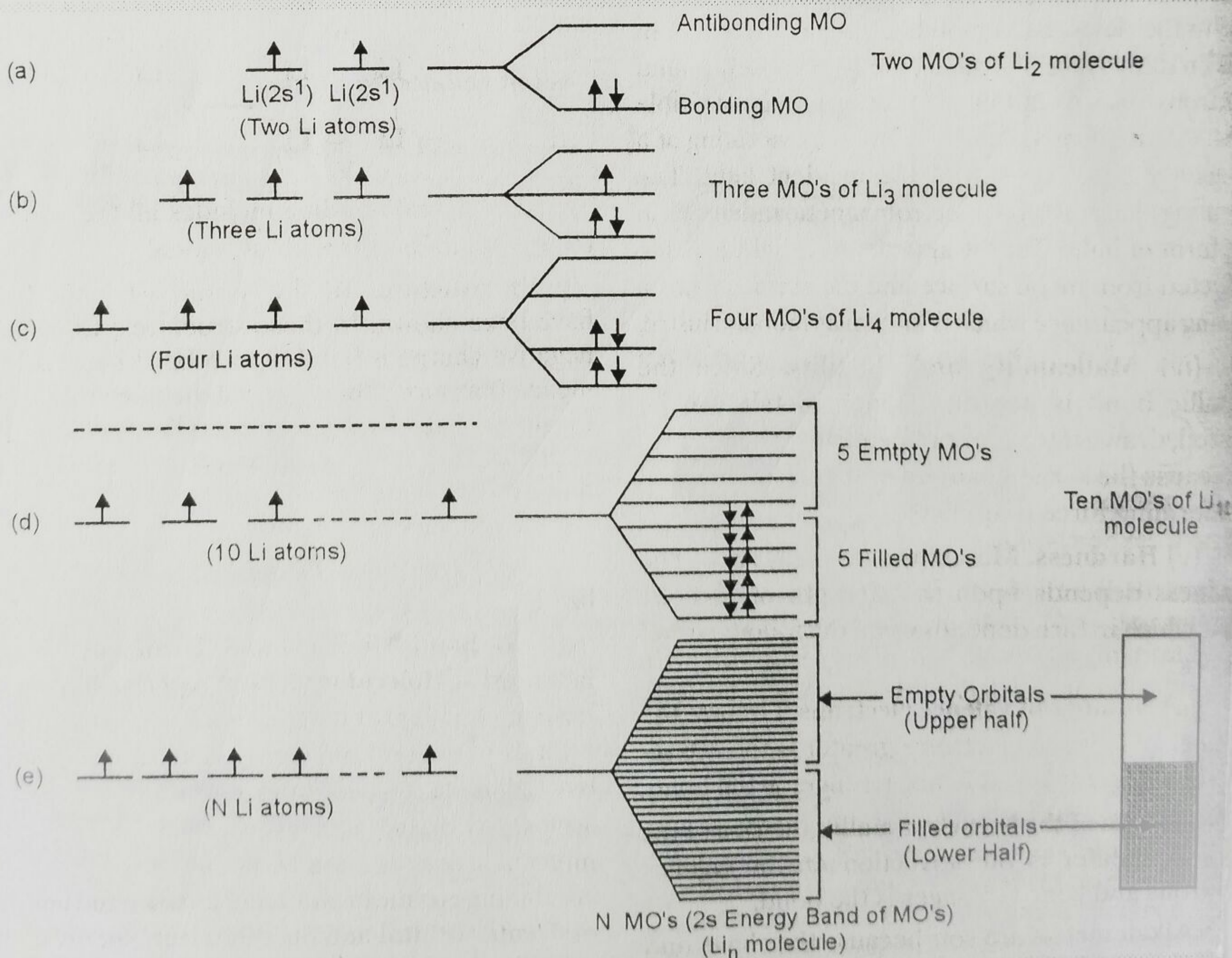


FIGURE 1.2.22. $2s$ orbitals of Li atoms combining to form molecular orbitals

(iii) **Lustre.** As the levels in the band are very close together, the transference of an electron to a higher level of the band requires addition of very little energy. Thus they can absorb light of a wide range of wavelengths. When electrons fall back to lower energy levels, light is radiated. This gives rise to the shining appearance.

A difficulty arises when we apply the band theory to beryllium, the next metal in the periodic table. Beryllium has double the number of valence electrons than lithium. Therefore, the 2s orbital band will be filled and it is well known that a filled orbital band does not allow the conduction of electricity. But the electrical conductivity of beryllium is greater than that of lithium. This difficulty

has been overcome by suggesting that the 2s orbitals are not the only atomic orbitals which overlap to form a band. The 2p orbitals which are only slightly higher in energy may also overlap to form empty band. Thus, we can differentiate between two types of orbital bands. The band which holds the valence electrons is called **valence band** and the other band which is slightly higher in energy and is formed by the overlap of valence atomic orbitals is called the **conduction band** because it helps to explain the conduction of electricity in case of metals like beryllium as well as other alkaline earth metals.

In case of these metals, the 2s orbital band and the 2p orbital bands are so close that they partially overlap as shown in Fig. 1.2.23.

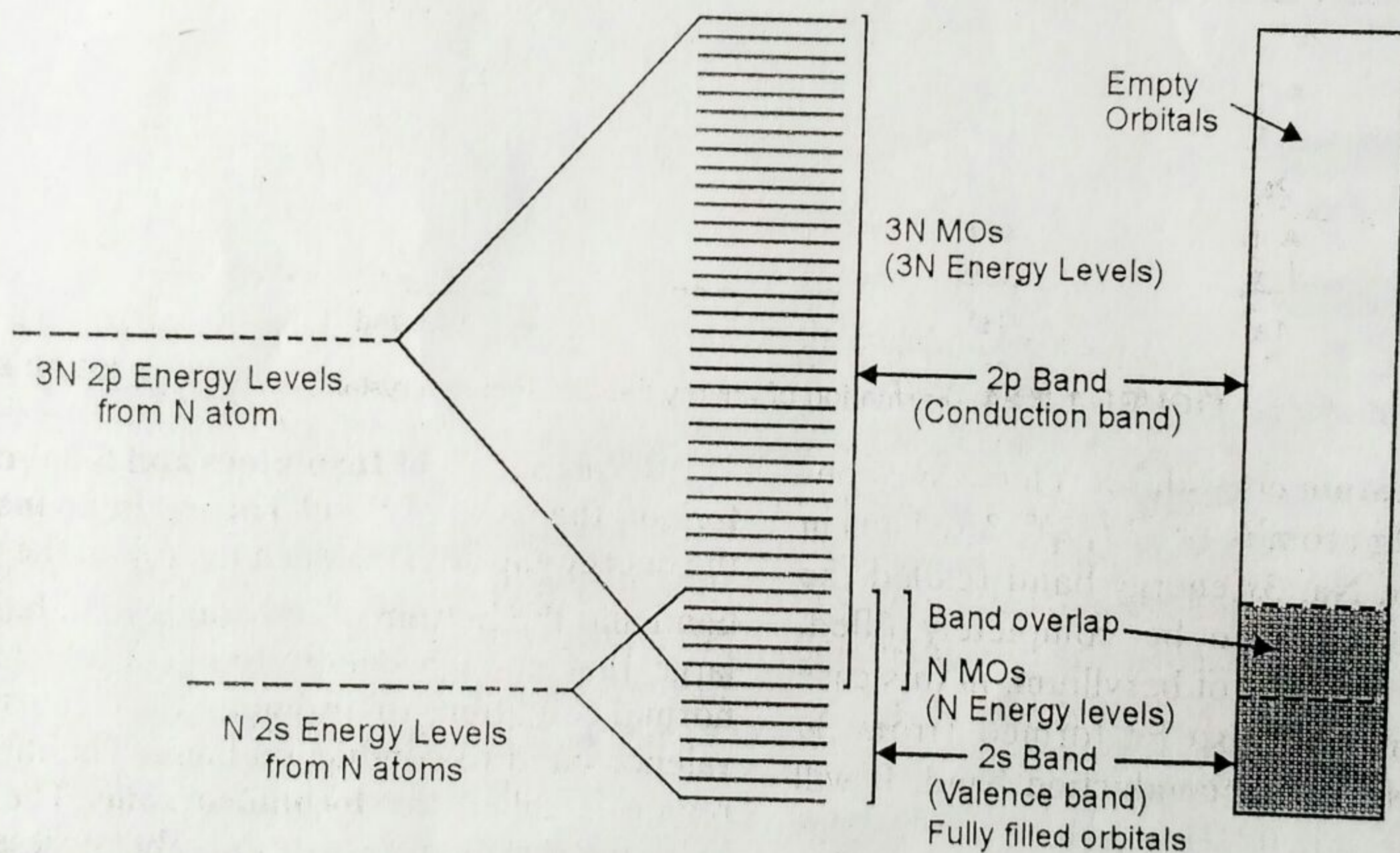


FIGURE 1.2.23. Overlap of 2s energy band (valence band) and 2p energy band (conduction band) of Beryllium.

In fact, the conduction band from 2p orbitals is formed even in case of lithium. Since each lithium atom contributes one 2s orbital and three 2p orbitals, the band resulting from the combination of N atoms would consist of 4N levels which can hold upto 8N electrons. Hence lithium band is only 1/8th filled.

All metals have either an unfilled valence band or overlap between the valence band and the conduction band. In general, substances are electrical conductors if there are more valence orbitals than valence electrons. The only element that has more valence orbitals than valence electrons but does not have metallic properties is boron.

Two more examples to illustrate band theory of metallic bonding are explained below :

(1) **Sodium crystal.** The electronic configuration of Na atom is $1s^2, 2s^2, 2p^6, 3s^1$. Now let us suppose that in the crystal, N atoms of Na are present. Thus as shown in Fig. 1.2.24.,

N 1s orbitals will combine to form 1s band
 N 2s orbitals will combine to form 2s band
 N 2p orbitals will combine to form 2p band
 and N 3s orbitals will combine to form 3s band.

1s energy band will have N energy levels which can accommodate 2N electrons. As there are 2N 1s-electrons, 1s band will be completely filled. Similarly, 2s and 2p bands will also be completely filled. However in the 3s band, there are 2N energy levels but only N 3s-electrons to be filled. Hence **3s band is only half-filled**. This helps to explain the high electrical conductance of sodium. Diagrammatically, the energy bands of sodium may be represented as follows :

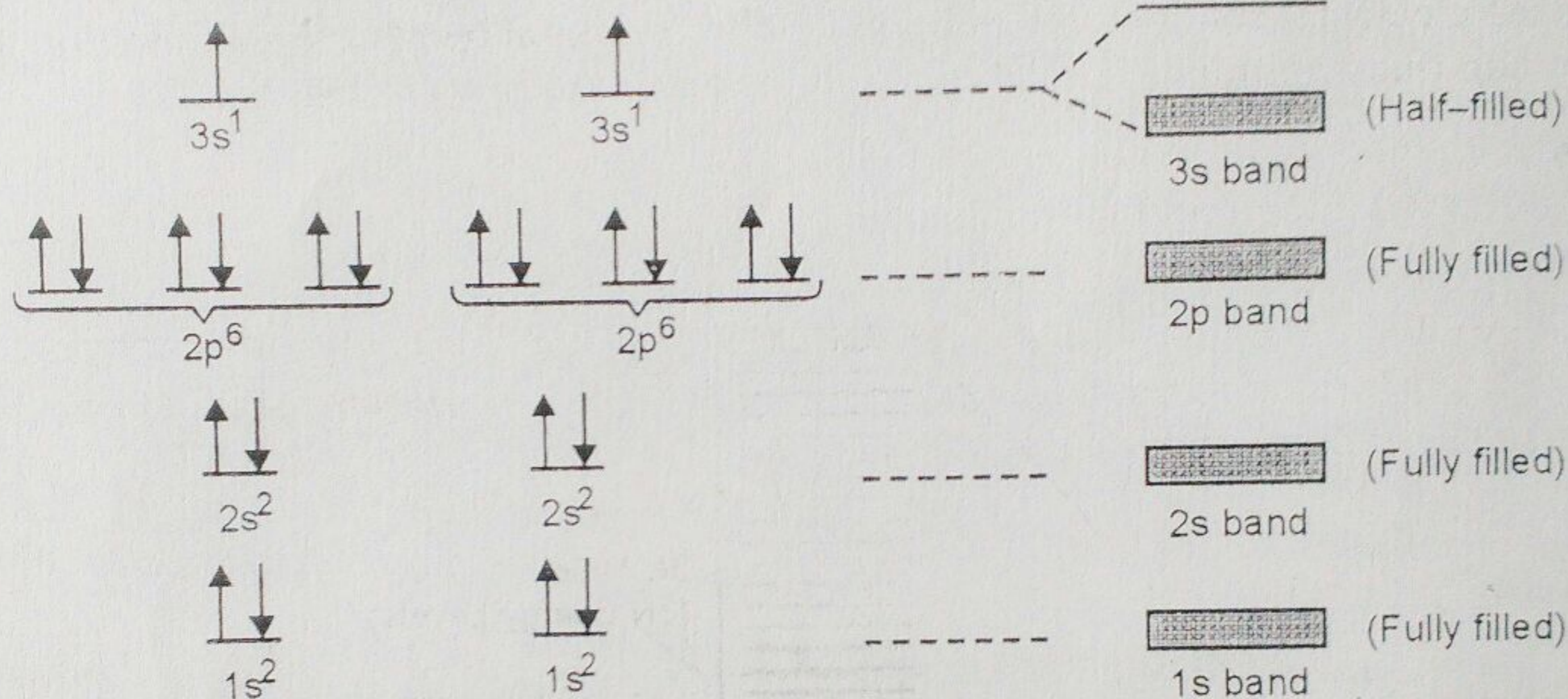


FIGURE 1.2.24. Formation of energy band in sodium crystal.

(2) **Magnesium crystal.** The electronic configuration of Mg atom is $1s^2, 2s^2, 2p^6, 3s^2$. Thus in this case unlike Na, 3s energy band (called the valence band) will also be completely filled. However as in the case of beryllium, in this case 3p energy band will also be formed (from 3p atomic orbitals), called conduction band. It will overlap with the 3s band. Hence there is no energy gap between the valence band and the conduction band (Fig. 1.2.25). That is why Mg is an excellent conductor.

Explanation of Insulators and Semi-conductors on the basis of Band Theory. In an insulator the energy gap (E_g) between the top of the valence band and the bottom of the conduction band is so large that enough energy is not available under normal conditions to promote the electrons from valence band to conduction band. The interband region is called the **forbidden zone**. The energy level diagram of an insulator may be represented as shown in Fig. 1.2.26 (a).

In a **semi-conductor**, the energy gap between the valence band and the conduction band is smaller than in insulators (Fig. 1.2.26b). The thermal energy available under ordinary conditions is sufficient to excite some electrons from valence band to conduction band and thus a small amount of current can flow through them.

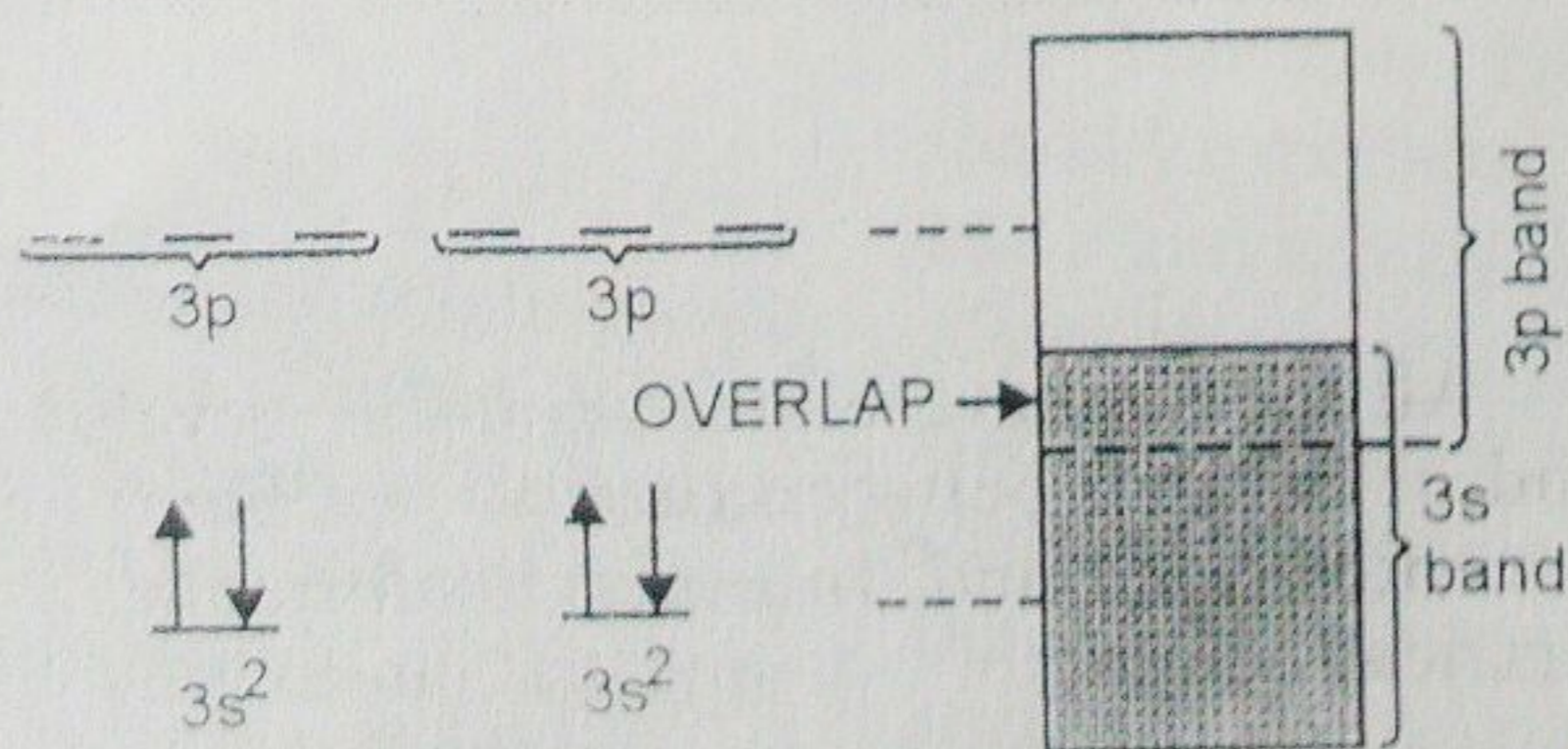


FIGURE 1.2.25. Formation of energy bands in Mg crystal. (1s, 2s, 2p bands are same as shown in Fig. 1.2.24 for Na)

For example, the energy gap values in kJ mol^{-1} for some elements of the carbon family are under :

- Diamond = 511, Silicon = 111, Germanium = 63, Tin (grey) = 8, Tin (white) = 0, Lead = 0

Thus diamond with large energy gap is an insulator whereas silicon and germanium with small energy gap are semiconductors and tin (grey) with very small energy gap and tin (white) and lead with no energy gap are metals. Also note that the value of the energy gap is decreasing down the group. Thus we may present different cases as follows :

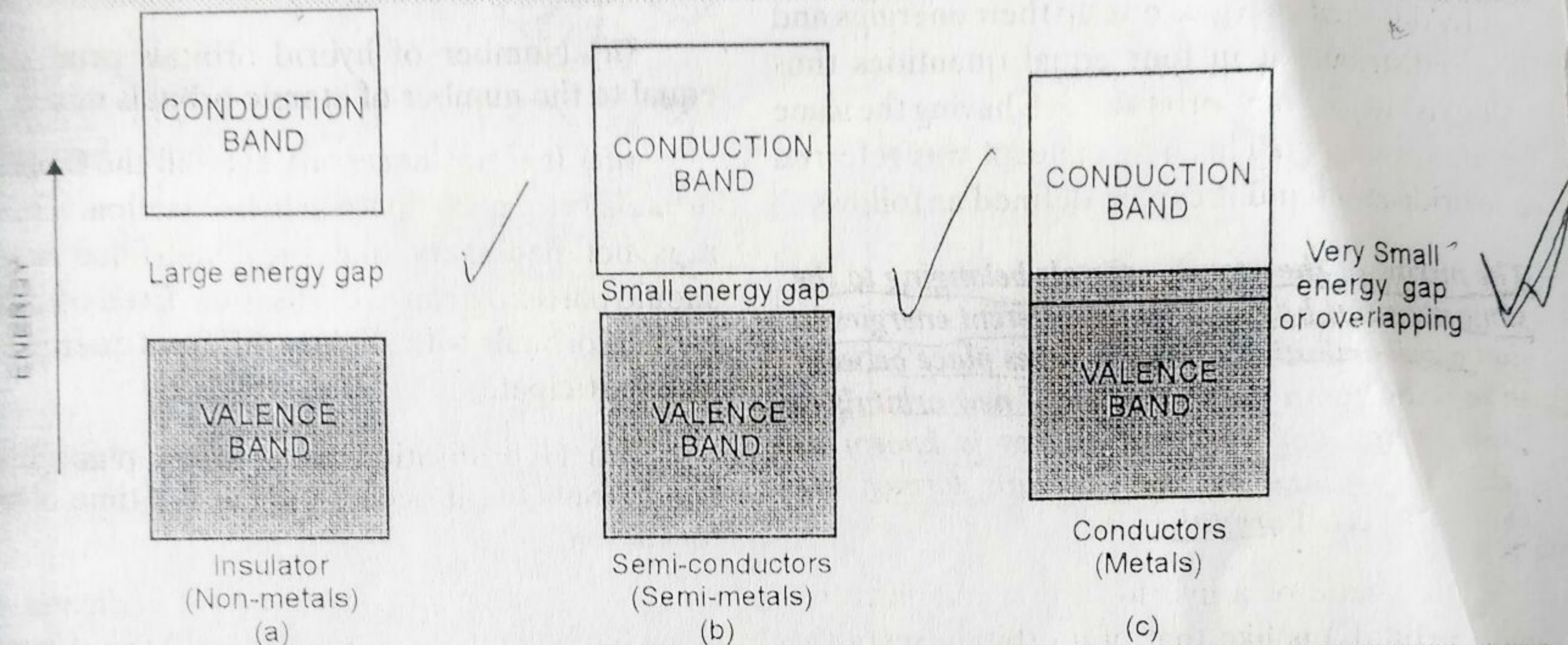


FIGURE 1.2.26. Representation of energy gaps of insulators, semiconductors and metals (Li is an exception which has valence band only that is half-filled).

Hybridisation

The concept of 'hybridisation' has already discussed in Class XI. This is briefly reviewed as under :

According to valence bond theory, a covalent bond is formed by the overlap of half-filled atomic orbitals. Thus the covalency of an element should be equal to the number of half-filled atomic orbitals present. However, on the basis of this concept, the formation of many compounds such as those of boron, boron and beryllium cannot be explained. Let us have a look at this problem.

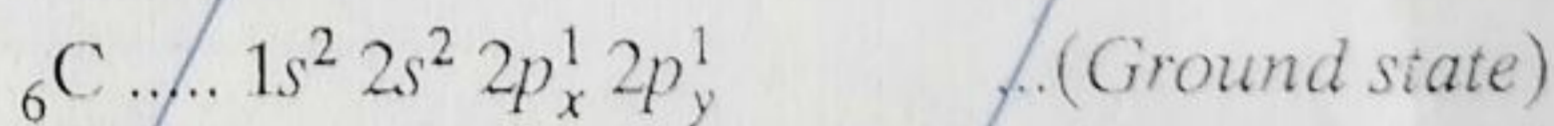
The electronic configuration of beryllium, boron and carbon in the ground state are as follows :

Element	Atomic Number	Electronic Configuration
Be	4	$1s^2 2s^2$
B	5	$1s^2 2s^2 2p_x^1$
C	6	$1s^2 2s^2 2p_x^1 2p_y^1$

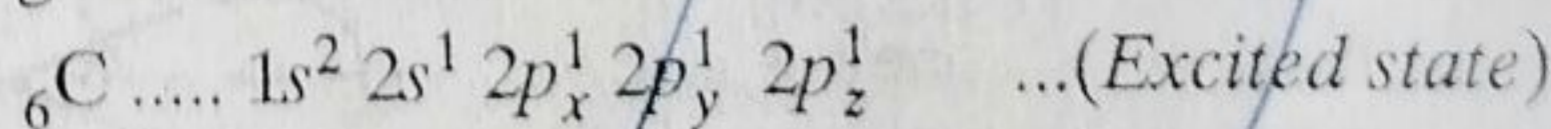
On having a look at these configurations, we conclude that Be, B and C should possess valencies of 0, 1 and 2 respectively as Be has no half-filled atomic orbital, boron has one and carbon has two. But Be forms compounds of the type BeF_2 , BeH_2 etc. in which it has a covalency of two,

B forms BF_3 , BH_3 , etc. in which its covalency is three and C forms CH_4 , CCl_4 , CO_2 etc. in which its covalency is four.

To overcome the above problem, it was suggested that one electron from the 2s orbital jumps to the empty 2p orbital without consuming excessive energy. Let us, for example, consider the case of carbon. Its atomic number is 6. So its configuration in the ground state is



Thus it has two unpaired electrons in the ground state. So it should form two bonds only. But actually carbon shows a covalency of four. To explain this, it is suggested that an electron from 2s orbital jumps to an empty 2p orbital so that the configuration of carbon in the excited state is



Thus now carbon has four unpaired electrons thereby explaining tetravalent nature of carbon. Its one s and three p orbitals can overlap the orbitals of reacting atoms, forming four covalent bonds. But covalent bond formed by 2s orbital of carbon should differ in energy from the bonds obtained by the three p orbitals. However, experimental data clearly show that all the four bonds of carbon are