BAND THEORY OF SOLIDS

module I (i)

The information of the band of energy levels of solids can be clearly illustrated in terms of the 'molecular orbital Theory'.

- The salient features of band theory of solids are as follows.

(1) Materials in the solid state do have very large aggregation of atoms (or ions) and are arranged in regular close-packed structures.

(2) The constituents (ions or atoms) of solids are bound together by a cohesive force and as a result, the atomic orbitals of valence e^- shells interact and overlap with each other and give rise to 'molecular orbitals'.

→ When two atomic orbitals (half-filled) overlapp, two molecular orbitals of different energy levels are formed as shown in fig.

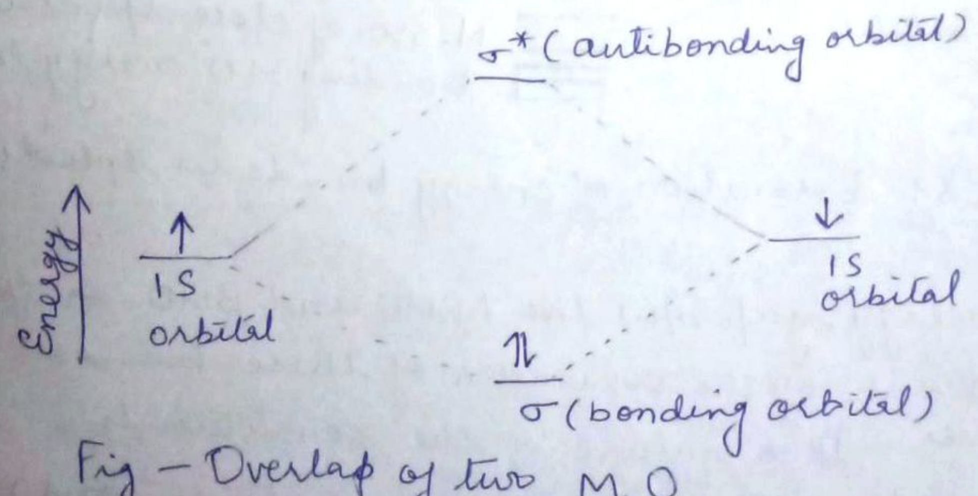


Fig – Overlap of two MO

- One of the molecular orbitals (MO) gets stabilized due to pairing up of e^- and acquires lower energy state, which is called Bonding Molecular Orbital (BMO), while the other empty molecular orbital is destabilised (higher energy) and is known as 'antibonding Molecular orbital (ABMO).

- When a 2N no. of valence atomic orbitals of constituent atoms (or ions) overlap with each other in solids, they give rise to 'N' number of closely spaced bonding molecular orbitals and as well to 'N' no. of antibonding M.O.

- For very large aggregation of atoms (or ions), a very closely spaced energy levels (σ MOs and σ^* MOs) of extremely small energy difference results in the formation of 'bands' in solids and these energy bands appear to be continuous as shown below —

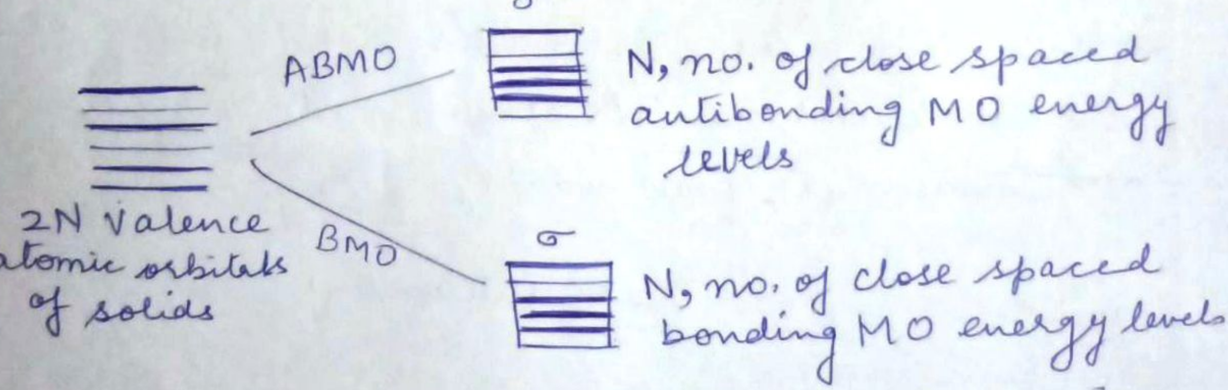


Fig- Formation of energy bands in solids

- The energy gap b/w the ABMO and BMO or the magnitude of the separation of these bands depends on ① the nature of the constituents.
② the internuclear distance of atoms (ions)
③ and the orientation of the valence e^- orbitals in a particular crystal structure.

However, in few cases, the energy bands of atoms in solid may also overlap and gives rise to a continuous half-filled energy bands.

– A 'band' is a group of infinitesimal energy levels in a solid.

Types of Energy Bands –

The composition, electronic configuration of constituents and the structure of crystals/Solids give rise to two kinds of energy band models

(1) Overlapping Energy bands – For a particular crystal type, the higher energy band of the solid overlaps the lower energy band to some extent.

– Beryllium (Be) and Magnesium (Mg) are metals because the empty np^0 energy band overlaps the lower filled ns^2 energy bands in both the cases,

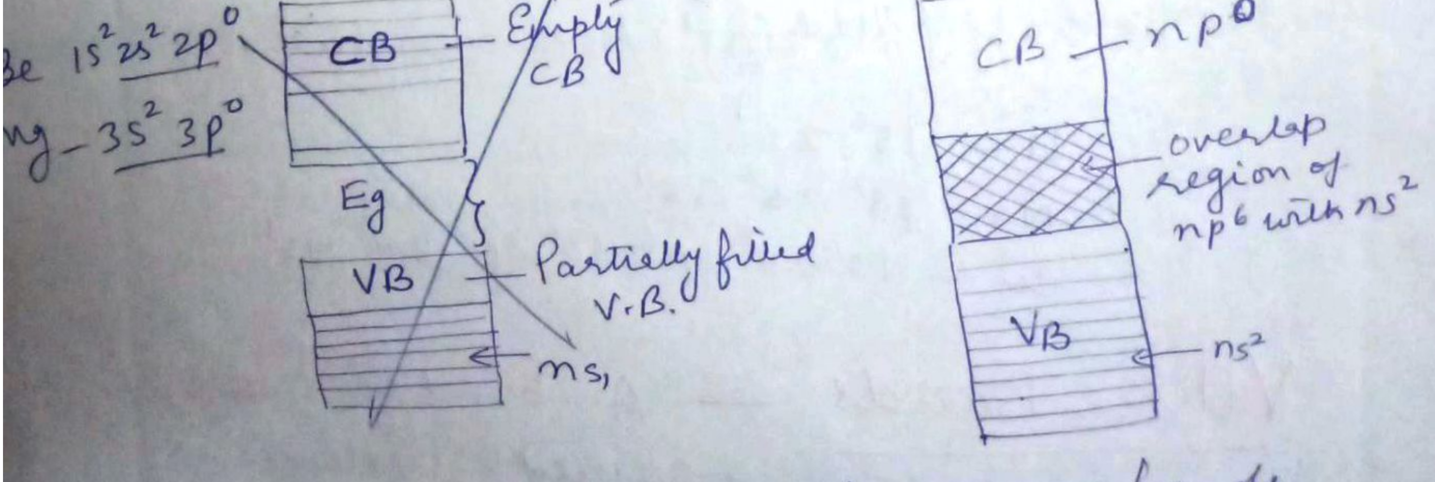


Fig – Overlapping energy bands

CB – Conduction Band
VB – Valence Band
E_g – Forbidden Energy gap.

② <u>Non-overlapping energy bands</u> – In many solids, the higher empty energy band does not overlap the lower filled (or half-filled) energy level band, and there is an energy gap b/w the two bands of energy levels. This energy gap is known as '<u>forbidden</u> energy gap'.

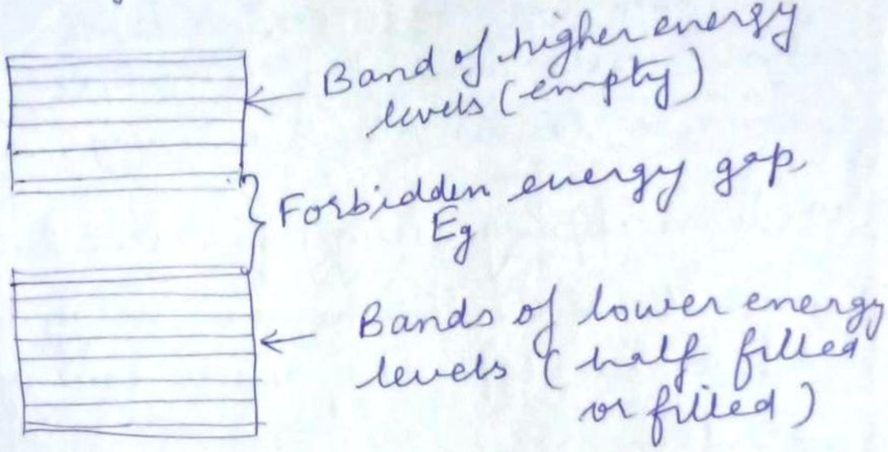


Fig – Non-overlapping energy bands

→ The energy level bands of Li, Na and Cu metals ~~are~~ shown ~~in fig.~~ that They are good conductors due to half filled (ns^1) lower energy band.

Li – $1s^2 2s^1$
Na – $1s^2 2s^2 3s^1$
Cu – $1s^2 2s^2 2p^6 3s^2 3p^2 3d^{10} 4s^1$

Valence Bands

— A band of stabilized lower energy levels occupied by valence e^- of the solid is called the <u>Valence band</u> (VB) and it is the highest filled state of a band.

- The VB of a solid may be either
  (1) Partially filled or

electronic configuration of the constituent in the solid.

(1) The 'valence band' of Solids, especially in Be($1s^2 2s^2$) and Mg($1s^2 2s^2 2p^6 3s^2$) is <u>completely filled</u> with ns^2 e^-.

(2) The valence shells of Na ($1s^2 2s^2 2p^6 3s^1$), Al ($1s^2 2s^2 2p^6 3s^2 3p^1$) and Cu ($1s^2 2d^{10} 4s^1$) are <u>partially filled</u> and, therefore, the valence band (VB) of these solids are partially filled with e^-.

<u>Conduction Band</u> – A band of energy levels above the valence band in solids is called 'conduction band' (CB). The conduction band is generally empty at absolute 0 K for solid

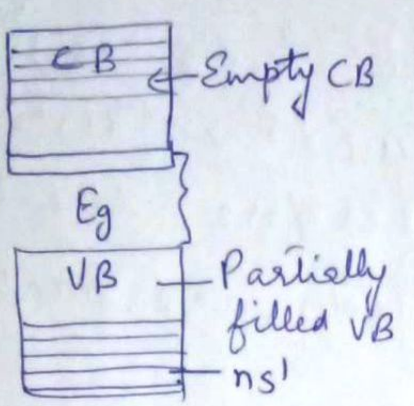
– At higher temp., CB is occupied by e^-. The e^- occupying this band are called conduction (free or delocalised) e^-.

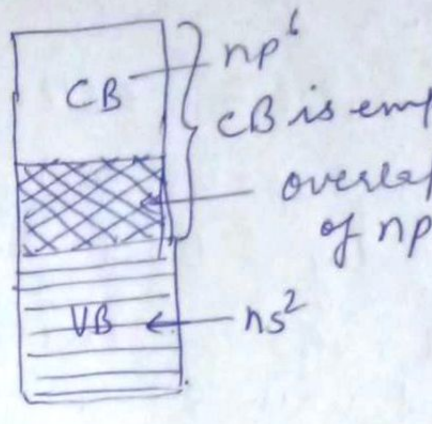
<u>Forbidden Energy Gap</u> – An energy gap exists between the valence band and CB in solids of particular types. This energy gap Eg (eV) is called the 'forbidden energy gap'.

APPLICATION OF BAND THEORY TO SOLIDS

(1) <u>Conductors</u> – Many solid substances are good conductors of electricity. This particular behaviour of solids can be explained in terms of 'band theory of solids'.

A material is a good conductor if it possess either a partially filled VB or an empty CB overlaps with filled VB.





- In metals such as Na, Li etc the valence band (VB) is partially filled with their valence e^-, ns^1.
- When these partially filled e^- of the VB acquire sufficient energy, they are promoted to the higher energy levels of the same VB and thus, the e^- are free to conduct electricity. Such solids behaves as good conductors.

→ Be and Mg (metals) have a completely filled VB with ns^2 valence e^-. The metallic property of Be and Mg are due to the overlap of empty np^0 energy band (CB) with the completely filled VB (ns^2 e^-).

- A slight thermal excitation promotes these free e^- to move into different higher energy levels of the overlapped bands. Thus Be and Mg exhibit metallic conduction.

Insulator –

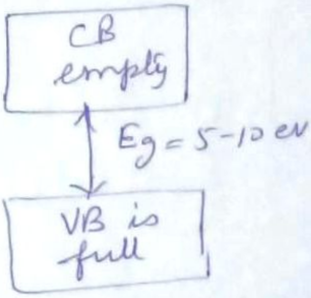
Generally if the solids have very high value of electrical resistivities, which is greater than 10^{10} ohm cm at room temp., then such materials are ~~classif~~ classified as insulator.

– In terms of band theory of solids, the insulators are described in terms of the following–

(1) VB is completely filled with valence $\bar{e}$.

(2) CB is completely empty.

(3) The forbidden energy gap, E_g b/w VB & CB is very large eg 5–10 eV



Semiconductors –

– Electrical conductivity of solid semiconductors is in b/w those of insulators and conductors. The electrical conductivity of these solids ranges between 1 and 10^{-8} ohm^{-1} cm^{-1} at room temp.

– A solid is a semiconductor, if it satisfies the following characteristics in terms of band theory of solids.

(1) Almost filled VB,

(2) Empty CB, and

(3) A very narrow energy gap, E_g, of the order 1–2 eV.

– All semiconductors are insulators at 0K.

- As the temp. is raised above $0°C$, thermal agitation will lift a predictable no. of e^- from VB to a higher band, CB, if $E_g \sim 1.0$ eV.
- The electrical conductivity of semiconductors increases with the rise in temp.