Band structure of solids

Molecular orbital theory extended to solids is known as Band Theory

* All the atoms of a solid, if assumed isolated from one another, can have identical electronic scheme of the energy levels.
* In crystals, atoms are arranged in a regular and periodic manner. A solid crystals contains about 10^{23} atoms/cm^3.
* The electrons in the innermost shell are almost unaffected since they are tightly bound to the nucleus.
* Due to interaction of neighbouring atoms, the energy levels of the electrons in the outermost shell get modified and there will be splitting of a single level of an isolated atom into a large number of closely spaced energy levels.

The electronic structure of a lithium atom is

1s	2s	2p		
↑↓	↑			

Li_2 molecule

There are six electron arranged in Molecular orbitals.

$\sigma_{1s}^2, \sigma^{*2}_{1s}\ \sigma_{2s}^2$

* Bonding occurs because the σ_{2s} bonding MO is full & the corresponding antibonding orbitals is empty. The 2S AOs on each of the two Li atoms combine to give two MOs - one bonding and one antibonding (Fig. ⓐ)
* 3 Li atoms joined to form Li_3. Three 2S AOs combine to form 3 MOs - one bonding, one non-bonding and one anti bonding. (Fig. ⓑ).

*As the number of electrons in the cluster increases, the spacing between the energy levels of the various orbitals decreases & when there are large number of atoms, the energy levels of the orbitals are so close together that they almost form a continuum (Fig. ②).

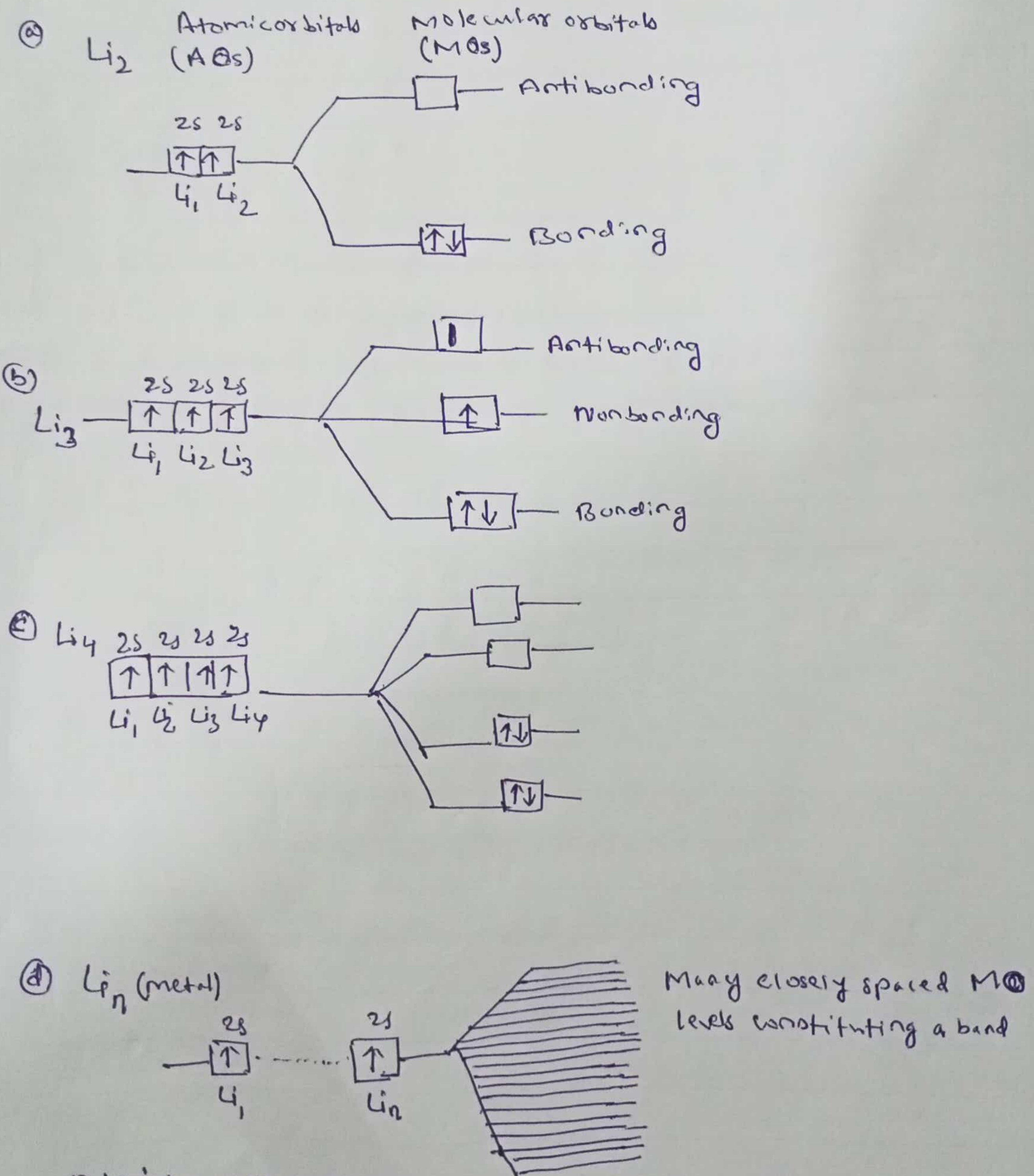
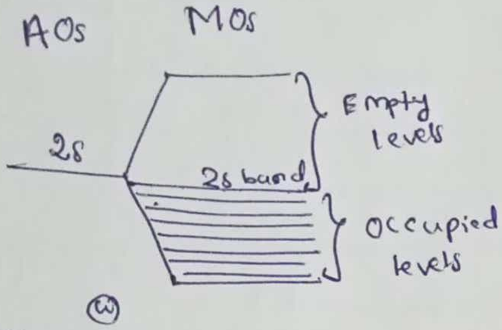


Fig: Development of MOs into bands in metals.

Bands → overlapping bands. eg $Be = 1s^2 2s^2 2p^0$, $Mg = 1s^2 2s^2 2p^6 3s^2 3p^0$

→ Non overlapping bands $Li = 1s^2 2s^1$, $Na = 1s^2 2s^2 2p^6 3s^1$

$Cu = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$



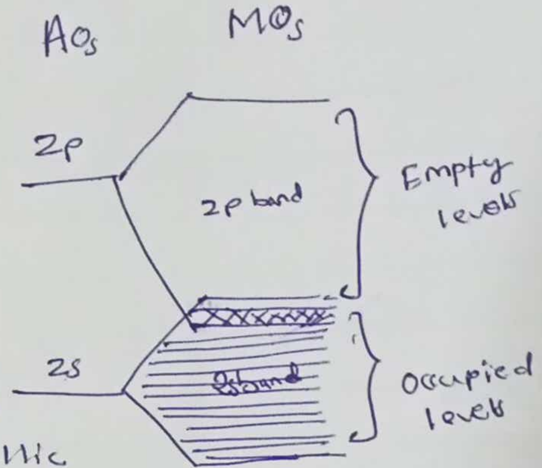


Fig: Two methods by which conduction can occur. (a) metallic molecular orbitals for Lithium showing half filled band (b) metallic molecular orbitals for beryllium showing overlapping bands.

* The band of energy levels occupied by the valence electrons is called Valence band

→ partially filled with electrons, eg $Na(3s^1)$, $Cu(3d^{10}, 4s^1)$

→ completely filled with electrons eg $Be(1s^2 2s^2)$

* The next permitted band above the valence band is called the Conduction band

→ partially filled electrons

→ completely filled electrons

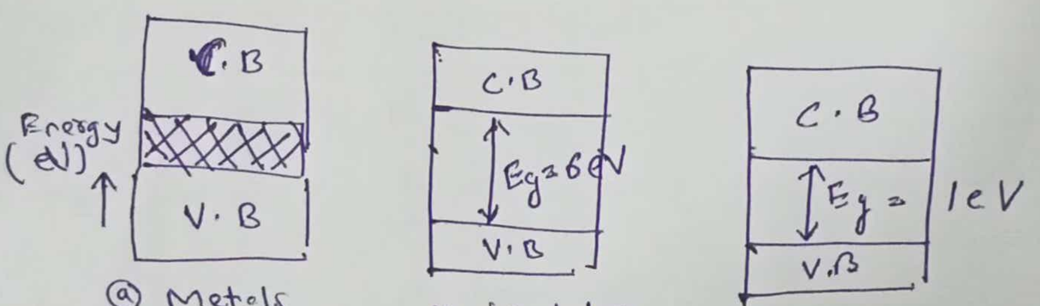
* The gap between the valence band and the conduction band is called forbidden gap. The width of the forbidden gap is called energy gap (E_g).

Classification of solids on the basis of Band Theory

On the basis of band structure of solids, solids can be classified as

- metals (or conductors)
- insulators
- semiconductors

(1) Metals: The energy gap between the valence and conduction bands. The two bands overlap with each other [Fig ⓐ]. It is very easy for a valence electron to become a free electron. So, it works as a good conductor. eg Na, Li, Be etc



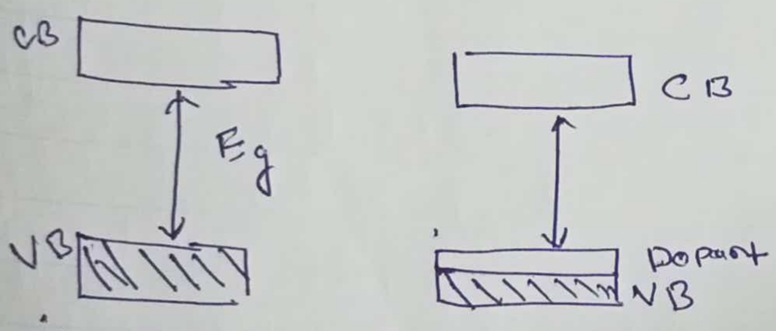
ⓐ Metals ⓑ insulators ⓒ Semiconductors

(2) Insulators: The energy gap between valence and conduction band is very large. eg diamond = 6 eV [Fig ⓑ]. It has poor electrical conductivity.

(3) Semiconductor: The conductivity is much greater than an insulator but much smaller than metal. The energy gap is of the order of 1eV as shown in [fig ⓒ]. Ge, $E_g = 0.72$ eV Si, $E_g = 1.1$ eV. At $0°C$, the V.B is filled & CB is empty. Hence they are insulators at low temperature. However, at room temperature, the thermal energy is sufficient to lift electrons from VB to CB.

Intrinsic and Extrinsic semiconductors

* When the conductivity of a semiconductor is determined by the thermally generated carriers (electrons), the semiconductor is termed as a pure or intrinsic semiconductor. eg Ge & Si
* Intrinsic semiconductors are having small energy gap between the filled VB & empty CB [Fig.], hence sufficient to promote an electron from VB to CB, resulting in conductivity. As the temperature increases the conductivity of semiconductors increases.
* The intrinsic or pure semiconductors have less conductivity. Its conductivity is increases by adding some suitable impurity called doping agent, such semiconductors are called as extrinsic semiconductors. [Fig.]



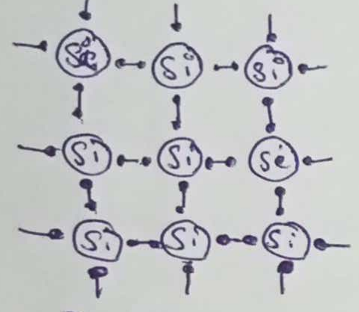
(i) Intrinsic Extrinsic

Role of Doping on Band Structures: The process of deliberately adding the impurity to a semiconductor to increase its conductivity is called doping. The impurity atoms are called as dopants and the semiconductor containing the impurity atoms is called a doped or an impurity or extrinsic semiconductor.

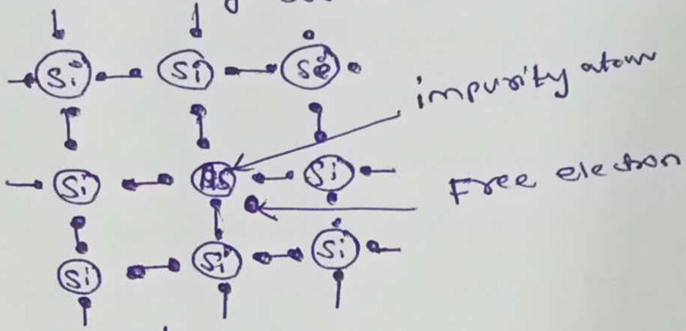
- N or Donor type semiconductor eg, P, As, Sb
- P or Acceptor type semiconductor. eg B, Ga, In, Al

N-type semiconductor

When a pentavalent impurity atom of group V is introduced to the semiconductor, the resulting extrinsic semiconductor is called N-type semiconductor. eg As added to Si, four of its five valence electrons form covalent with the neighbouring four Si atoms while the fifth electrons remains loosely bound to its nucleus as shown in Fig.



Intrinsic – Si crystal



As/Si crystal

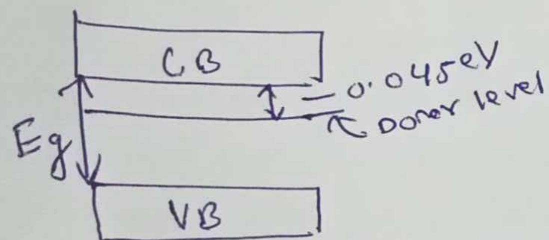
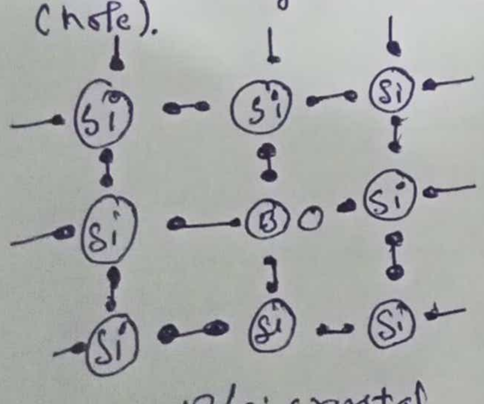


Fig: Energy level diagram of N-type

P-type semiconductor

When a trivalent impurity of group III is added to a semiconductor, the resulting semiconductor is called a p-type semiconductor. eg Boron added to Si, three valence electrons of boron atoms forms a covalent bonds with three neighbouring Si atoms while fourth bond remains deficient of electron (hole).



B/Si crystal

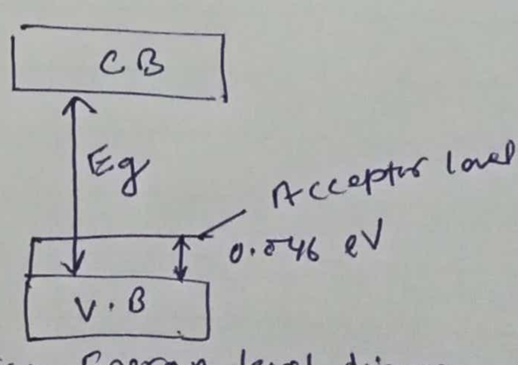


Fig: Energy level diagram of p-type