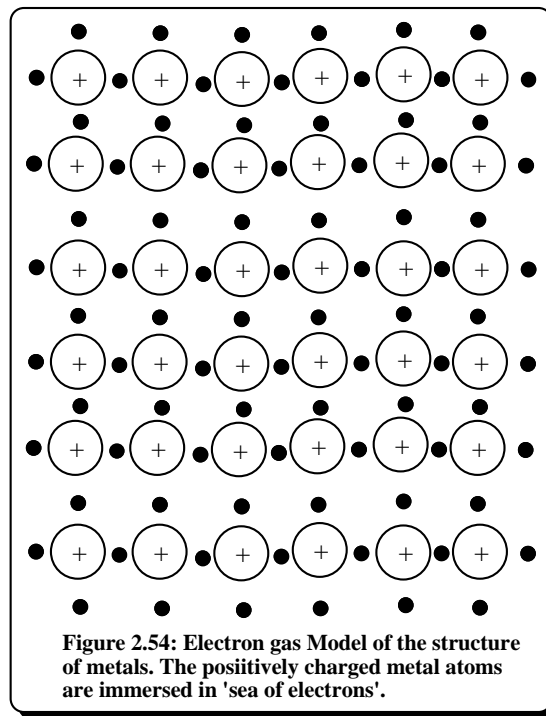# Theories of Metallic Bonding

    Three important theories have been presented to explain the different properties of the metals.

6.2.1 Electron Gas Theory: This theory was first proposed by Drude in 1900 and later on developed by Lorentzin 1916. Its main points are listed here.

According to this theory:

1. Each atom in a metal crystal loses all its valence-electrons. These electrons form an electron pool or gas.
2. The positively charged metal ions are held together by this electron pool or gas.
3. The positively charged metal ions have definite positions at measurable distances from each other in the crystal lattice.
4. The valence-electrons are not attached to any individual ions or pairs of ions but belong to the crystal as a whole, therefore, they are free to move throughout the lattice from one part of the crystal to the other as gas molecules move freely throughout their container. The number of such free electrons is not certain.

Figure 2.54: Electron gas Model of the structure of metals. The posiitively charged metal atoms are immersed in 'sea of electrons'.

In short, according to this theory, metallic solids may be supposed as a collection of positive atomic cores immersed in a fluid of mobile electrons or sea of mobile electrons. The force that binds a metal ion to the mobile electrons within its sphere of influence is known as metallic bond.
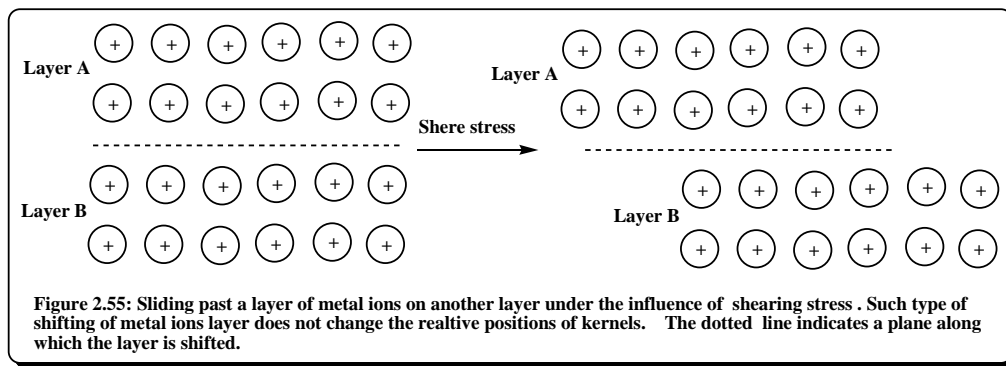
The Successes of Electron Gas Theory

The electron gas theory successfully explains the following properties of metals.

1. *Electrical Conductivity.* Electrical Conductivity of metals is due to the presence of mobile valence-electrons. These electrons are in a position to move in an electric field and thus conduct electricity through the metal.

2. *Metallic luster.* As a beam of light falls on the surface of a metal, the mobile electrons go to higher energy level. On coming back from the excited state to the ground state in one or more jumps, light of all wavelengths in the visible region is emitted.When light falls on a metal surface; it appears as if light is being reflected. The surface, therefore, emits the typical metallic luster.

3. ***Thermal Conductivity.*** This property is also due to the presence of mobile electrons. When one part of a metal is heated, the electrons in that part acquire a large amount of kinetic energy. These electrons are free and move rapidly through the crystal and conduct heat to the other parts of the metal. This process is repeated and results in quicker heat transfer to the other end of the metal.

5. ***Malleability and Ductility***. The free and delocalized electrons in a metal crystal surround each kernel (i.e. metal ion, say M^+) symmetrically, therefore, the binding forces holding M^+ ions and valence-electrons are non-directional. It means that the force of attraction between M^+ ions and the valence-electrons is uniform in all directions and there are no localized bonds. Therefore the bonds holding the crystal lattice in metals are not rigid like covalent solids such as ice. This indicates that a layer of kernel can easily be shifted along a plane (indicated by dotted lines in Figure 2.55) from one lattice site to the other one, when a

Figure 2.55: Sliding past a layer of metal ions on another layer under the influence of shearing stress . Such type of shifting of metal ions layer does not change the realtive positions of kernels. The dotted line indicates a plane along which the layer is shifted.

shearing stress is applied on a metallic crystal. In the final state of the shifting process the relative positions of kernels remain the same as they were before shifting because delocalized electrons are available everywhere. Hence we see that within the crystal each kernel has the same position with respect to its neighbors before and after shifting process and electron gas surrounds the kernel symmetrically in both the positions. The nearest neighbors can be changed easily and new metal bonds may be formed readily. The ease with which new metal bonds may be formed by moving the metal ions form one lattice site to another is responsible for the facts that metals can be beaten into their sheets (i.e. are malleable) and can be drawn into wires (i.e., are ductile) by very little expenditure of energy.

6. ***High elasticity***. The positively charge metal ions can change position without breaking the metallic crystal shows that under a stress the structure is temporarily changed and attains the original position on removing the stress. The fact explains the high elasticity of metals
7.
The Limitations of Electron Gas Theory
1. This theory does not give satisfactory explanation of the experimental observation that electrical and thermal conductivity of metals decreases with rise of temperature.
2. Paramagnetic behavior of metals cannot be explained by this theory.
3. This theory does not explain the specific heats of metals.
4. Accordingly to the experimental data, obtained during the study of the photo-effect, electron emission, and metal atomization, not less than 2 eV of energy should be spent to break off

the electron from the atom in the solid metal. These data completely exclude the possibility of the free electrons in the form of electron gas existence in the metal.

6.2.2 Valence Bond Theory or Resonance Mode

Pauling proposed Valence bond or resonance model to explain the nature of metallic bonds. According to this approach the metallic bonding is essentially covalent in origin and metallic structure involves resonance of electron-pair bonds between each atom and its nearest neighbors. This theory assumes the formation of large number of covalent bonds due to resonance between two each atom and its neighbors. For example a large number of resonance structures can be written for the metals and over all stable character of the metallic structure is due the resonance hybrid of all the resonating structures.

Let us take the example of potassium (K). Three resonance structures of K are given in figure 2.34. The resonance structures can be written only if empty orbitals are available for hybridization. The structure (3) in figure 2.34 makes use of two sp hybrid orbitals to form two covalent bonds.

Figure2.56: Structure of potassium metal according to VBT

The ground state electronic configuration of K_{19} ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$) shows that by losing one electron from $4s^1$, $4s$, $3d$ and $4p$ orbitals become vacant. These unoccupied orbitals are called metallic orbitals according to Pauling. These orbitals form metallic bonds and characterize the metal having these bonds. Carbon is nonmetal because it has no vacant orbital after undergoing sp^3 hybridization.

Figure 2.57: Electronic cinfiguration of K_{19}

According to valence bond theory, the strength of metallic bond depends on the number of valence electrons contributed by the metal atoms. The number of electrons contributed by metals in fourth period (K, Ca, Sc, Ti, V and Cr) is 1, 2, 3, 4, 5 and 6 in going from left to right in the periodic table. The same trend in metallic bond strength is reflected in their melting points and hardness in going from left to right in the periodic table.

Table 2.5: Melting points and electronic configuration of metals of 4th period

	K	Ca	Sc	Ti	V	Cr
Electronic configuration	$3d°4s^1$	$3d° 4s^2$	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^4 4s^2$
No. of electrons contributed for bonding	1	2	3	4	5	6
Melting points (°C)	63.7	843	1795	1750	2190	2176

6.2.3 Molecular Orbital Theory (Band Theory)

Molecular orbital theory is a comprehensive model of metallic bonding given by Felix Black in 1928 and it is also known as Band Theory. Following are the essential features of this theory.

➢ When two atoms come close to each other the orbitals combine according to LCAOs (linear combination of atomic orbitals) manner and give rise to two molecular orbitals known as bonding molecular orbital (σ MOs) and antibonding molecular orbitals (σ* MOs).

➢ For example two lithium atoms combine in the gas phase to form the dilithium molecule, the two 2*s* atomic orbitals interact to form σ 2*s* and σ*2*s* molecular orbitals. Similarly four atomic orbitals (four 2*s*) of four Li atoms interact to form four molecular orbitals as shown in figure 2.58.
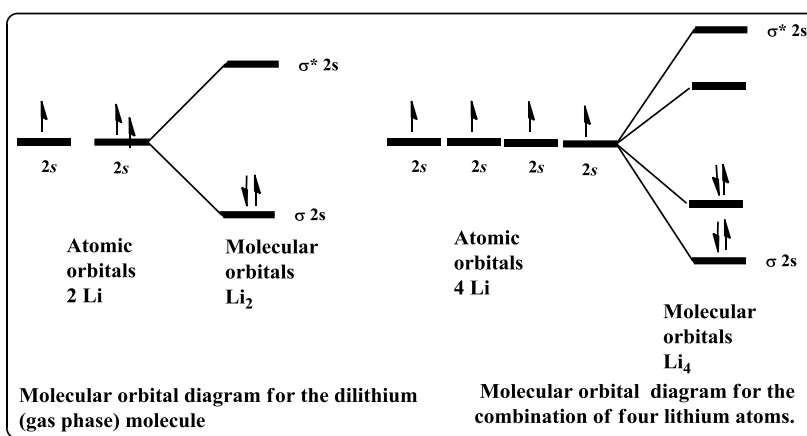
Figure 2.58: formation of molecular orbitals of lithium atoms

➢ In a large metal crystal, the orbitals of *n* atoms, where *n* is some enormous number, are mixed. These orbitals interact throughout the three dimensions of the metal crystal, in the same manners and give rise to ½ *n* σ2*s*, bonding molecular orbitals and ½ *n* σ*2*s*, antibonding molecular orbitals. The large number of energy levels are very closely spaced and spacing of levels becomes so close that they essentially constitute a continuum. This continuum is referred to as a band. For lithium, the band derived from the 2*s* atomic orbitals will be half filled. That is, the σ 2*s* part of the band will be filled and the σ*2*s* part will be empty (Figure 2.59)
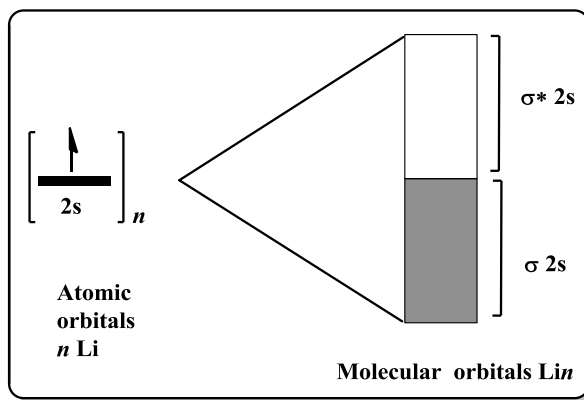
Figure 2.59: Band formation from 2*s* orbitals of Li

➢ Band Theory can also be applied to Beryllium. The electron configuration of Be, [He] $2s^2$ shows that both the σ $2s$ and σ* $2s$ molecular orbitals will be fully occupied. It means that the band derived from overlap of the $2s$ atomic orbitals will be completely filled and beryllium would not be able exhibit metallic properties because there is no space in the band in which the electrons can move freely. However, the empty $2p$ band overlaps with the $2s$ band and enables   the electrons to "roam" through the metal structure as shown in figure 2.60.

Applications of Molecular Orbital Theory (Band Theory)

The band theory can explain that why some substances are electrical conductors, some are not, and some are semiconductors. In the metals, bands overlap and allow a free movement of electrons. In nonmetals, bands are widely separated, so no electron movement can occur (Figure 2.38a). These elements are called insulators. In a few elements, the bands are close enough to allow only a small amount of electron excitation in an upper unoccupied band (Figure 2.61b). These elements are known as intrinsic semiconductors.
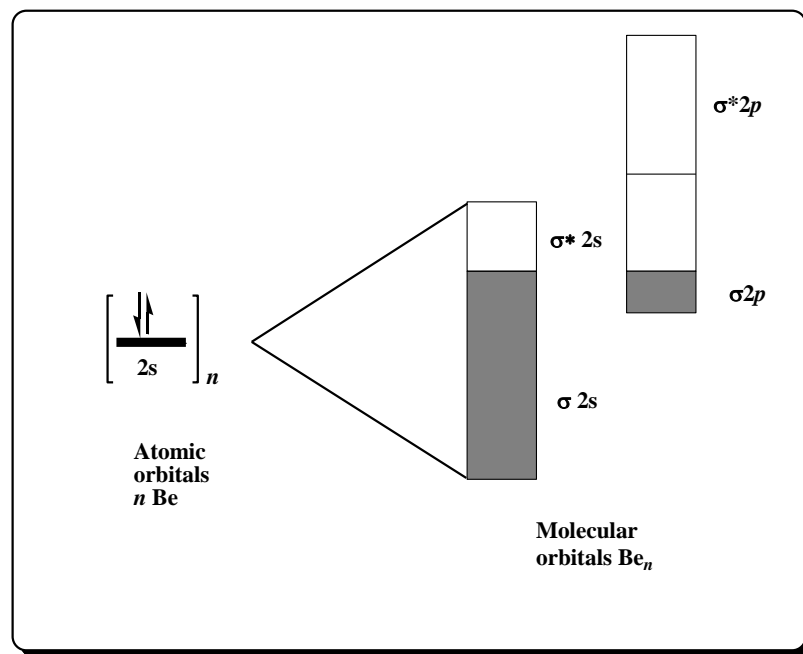

Figure 2.60: Bands derived from the frontier orbitals ($2s$ and $2p$) of beryllium

By using the band theory, semiconductors with specific properties have been synthesized by taking an element with a wide band gap and "doping" it with some other element, as impurity. The element added as impurity has an energy level between that of the filled and empty energy levels of the main component (Figure 2.61. This impurity band can be accessed by the electrons

in the filled band and imparts some conductivity to the non-conductors. In this way the electrical properties of semiconductors can be modified as per requirements.
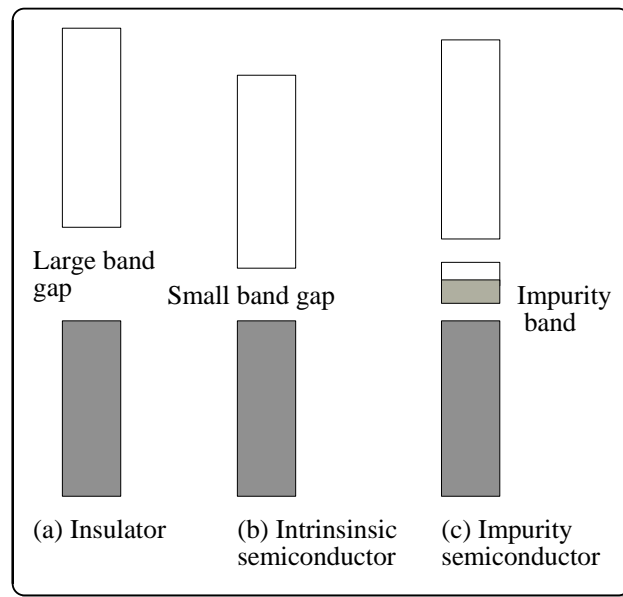

Large band gap

Small band gap

Impurity band

(a) Insulator

(b) Intrinsinsic semiconductor

(c) Impurity semiconductor

Figure 2.61: Band structure of (a) a nonmetal,
(b) an intrinsic semiconductor, (c) an impurity semiconductor