T.Y.B.Sc. Chemistry

Paper –II Inorganic Chemistry

Sem- IV

Chapter -2. Metals, Semiconductors and Superconductors

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2. Metals, Semiconductors and Superconductors

Introduction

Metal possess special physical properties. Metals are generally hard and have high melting point and boiling point. They are malleable and ductile. They are opaque and lustrous i.e they are non transparent and have high reflecting power. They possess high coordination number usually 12 or 14 or sometimes 8. Metals are good conductors of electricity and heat. The electrical conductance of metals decreases with increasing temperature. Metals have low ionization potential. There are really lose their valency electrons and form positive ions.

Nature of bonding in metals (Metallic Bonding)

The nature of bonding in metals is peculiar. The atoms in metals are believed to be held together by means of special type of bond known as **Metallic Bond.** The few electrons available for bonding must be completely delocalized. The force that binds a metal atom to a number of electrons within the square of influence is known as **Metallic Bond.**

Theories of bonding in metals

The metallic Bond should possess the following characteristics :

1. It should have the ability to bind identical metallic atoms.
2. The direction of metallic Bond should be unimportant to the properties because on destroying the direction by melting the metallic properties are still preserved.
3. It should have the ability to transfer electrons from atom to atom.

Therefore any theory of bonding in metals should explain :

1. The bonding of large number of similar atoms in pure metal.
2. The absence of directional bonds, and
3. The great mobility of electrons and hence high electrical conductivity.

There are three theories to explain the nature of metallic Bond

1. Free electron theory
2. Valence bond theory and
3. Molecular orbital or band theory

1. Free electron theory

Metals have low ionization potential values, hence they readily lose their valency electrons and form positive ions. These free electrons are said to be delocalized. This theory can explain the electrical conductivity, malleability and ductility of the metals. **It fails to explain the specific heat and magnetic properties of metals.**

2. Valence bond theory

It was introduced by Pauling. It was based on the concept of resonance. It considers that there is a resonance of electron pair bond(i.e ordinary covalent bond) between each atom and its nearest neighbours. This theory can explain many of the physical properties of the metals. **It fails to explain the metallic character in the solution state.**

3. Molecular orbital theory(Band Theory)

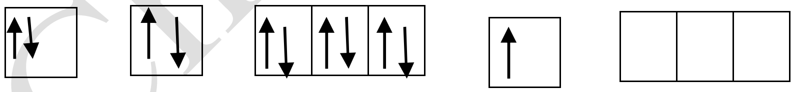
The band model

This theory is usually known as the band model. It is based onmolecular orbital concept. Molecular orbital approach to metallic bonding considers the delocalization of the 'free' electron orbitals over all the atoms in the metal crystal.

Band Theory for Sodium metal

We Shall directly apply the band theory (MO theory) to the sodium metal. Consider a crystal of metallic sodium. It has a close-packed structure with coordination number of 8. Each sodium atom possesses the arrangement of electrons in the various energy levels as follows :

Energy level	1s	2s	2p	3s	3p
Number of electrons	2	2	6	1	0



Every electron occupies a particular energy level. There is single electron in the outer (valence) energy level viz, 3s and three 3p ($3p_x$,$3p_y$,$3p_z$) orbitals are vacant. The basic necessity for the metallic properties is the the presence of empty atomic orbitals in the valence shell. In sodium metal atom 1s, 2s and 2p orbitals are filled, they inner and considered as nonbonding. We shall first consider only the valence 3s orbitals of each sodium atom.

When two sodium atoms are brought close to each other, the 3s- orbital of one atom can combined with the 3s- orbital of the other atom to form two molecular orbitals. One of the molecular orbitals will be lower energy bonding molecular orbital (BMO) and the other higher energy anti bonding molecular orbital (ABMO) as shown in figure 2.1.

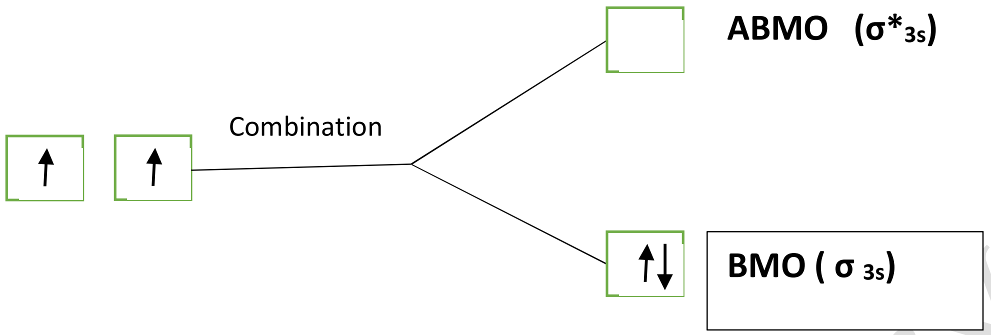


Fig. 2.1 Formation of Na_2 molecule

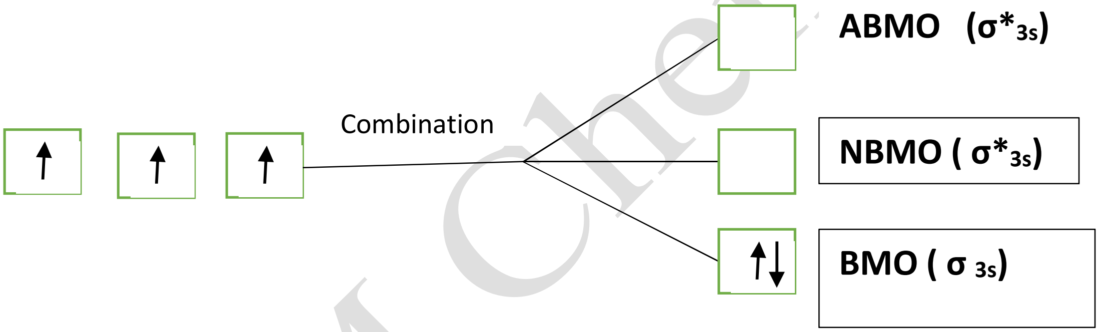


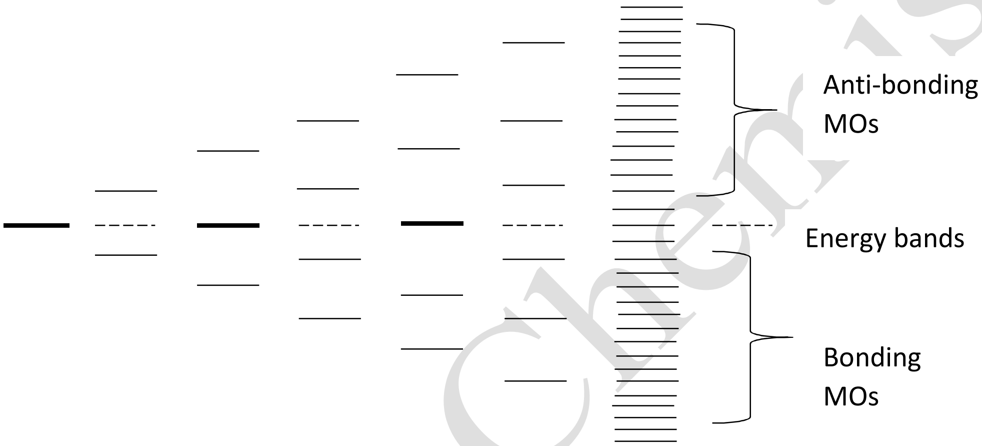
Fig. 2.2 Formation of Na_3 molecule

When three sodium atom are brought together, three molecular orbitals will be formed bonding, non-bonding and antibonding. The energy of non-bonding molecular orbital is in between that for the bonding and anti-bonding molecular orbital (figure 2.2) In this way 'n' atomic orbitals ($3s^1$) of 'n' sodium atoms will combine to form 'n' number of molecular orbitals in sodium crystal (fig 2.3). For a crystal of sodium the number of molecular orbitals produced must, by definition, be equal to the number of atoms concerned. In a crystal of sodium metal the number of molecular orbitals will be very large. The energy levels of these molecular orbitals will be so close together that they can almost be considered as continuous and form an **energy band.** Such a group of energy levels is known as **'a band'** and hence the name **'band model'**. The energy band is also called **quasicontinuous brand of levels** (i.e pseudo continuous band levels).

In a similar way, it might be possible that 1s, 2s and 2p orbitals combine to form 1s, 2s and 2p energy bands respectively in a crystal of sodium metal.

The formation of energy band in a crystal takes place only when

1. there are large number of atoms,
2. the atoms are sufficiently close to each other,
3. the combining atomic orbitals possesses matching symmetry,
4. that make orbitals are of the same energy and have sufficient overlap,
5. the interaction between atomic orbital is strong,
6. the energy band covers all atoms and belongs to the the whole crystali i.e complete delocalisation.



No. of combining atoms 1 2 3 4……n Molecular orbitals

Fig. 2.3 : The combination of 'n' atomic orbitals to form n-molecular orbitals in an energy band

Sodium exists in the vapour state as free atoms. There are no energy bands. The electrons occupy atomic orbitals with separate and distinct energy levels. As a sodium atoms are brought closer and closer the interactions between the various atomic orbitals increases so that the 'width' of the resulting band also increases.

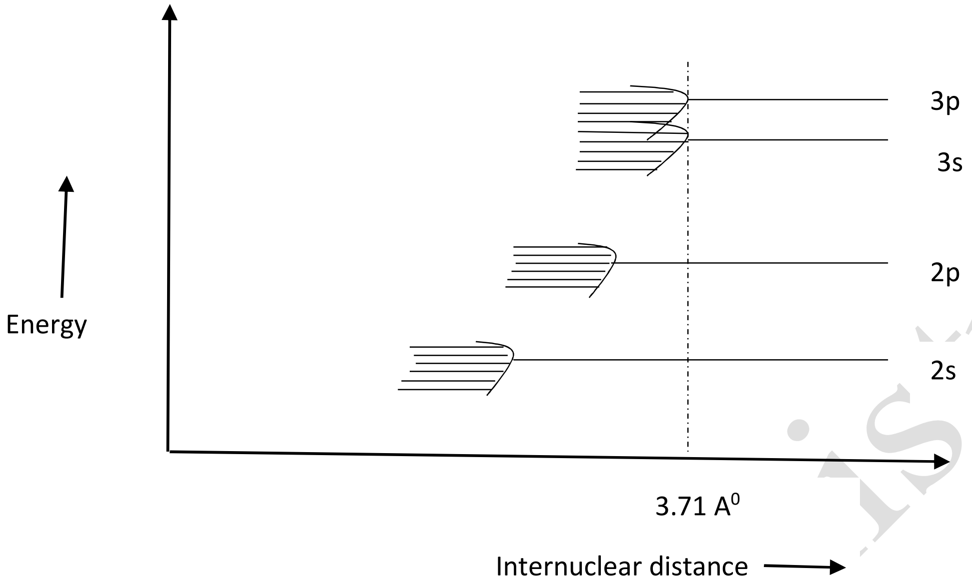


Fig.2.4 : The broadening of energy bands with the decrease in interatomic distance and overlap of 3s and 3p bands in a sodium crystal

The potential energy diagram of each energy state will now appear as in figure 2.4. The equilibrium position is indicated by the dotted line. This increase in width of energy band with the decrease in the the inter atomic distance is shown for the 2s, 2p,3s and 3p levels in sodium crystal in figure 2.4. It is at 3.71 A^0.

It should be noted that the lower energy orbitals (2s, 2p) interact to form the energy bands at smaller interatomic distance while the higher energy orbitals (3s, 3p) interact to form the energy bands at the greater distances. The equilibrium position is indicated by the dotted line. This is 3.71A^0 for Sodium crystal at which 3s and 3p energy bands overlap with each other.

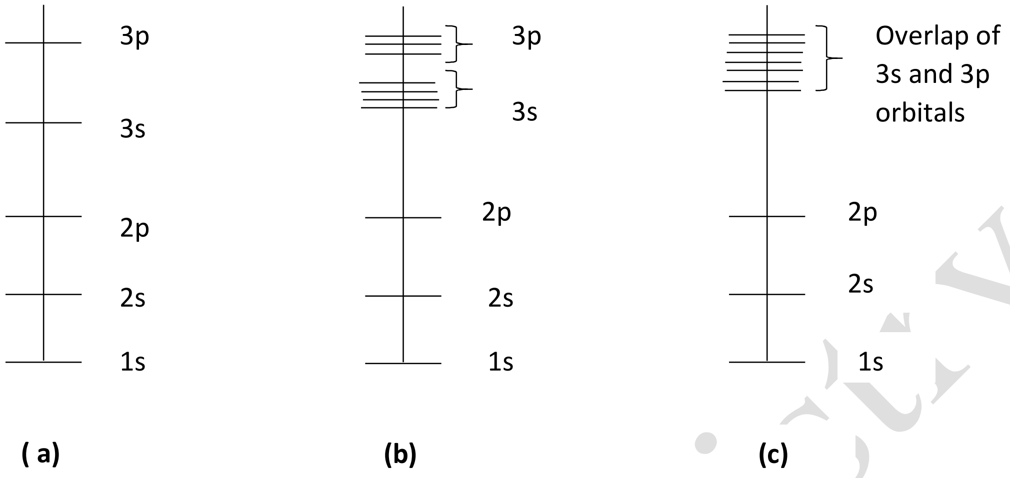


Fig.2.5 : (a) shows the discrete energy level in a free sodium atom (b) shows the development of 3s and 3p bands when the sodium atoms come close together (c) shows the overlap of the 3s and 3p bands when the atoms reach equilibrium position in the crystal.

The situation can also be summarized, diagrammatically, as shown in figure 2.5. The energy bands are absent for the free sodium atom in the vapour state and the energy levels are diagrammatically indicated by the line as shown in figure 2.5 (a). This is because the sodium atom are not close. Thus the electrons occupy atomic orbitals with separate and distinct energy levels.

The energy bands are formed when the sodium atoms are brought closer and closer as shown in figure 2.5 (b). Therefore an energy level which is diagrammatically indicated by a line in an isolated atoms, has to be represented as a band in a metallic crystal. figure 2.5(c) shows the overlap of 3s and 3p bands when the atoms reach the equilibrium position in crystal.

Filling of electrons in the 3S band of sodium metal

In general when there is overlap of **n** orbitals in **n** atoms in a solid structure, **n** molecular orbitals will be obtained. Each **MO** in a band can accommodate two electrons.

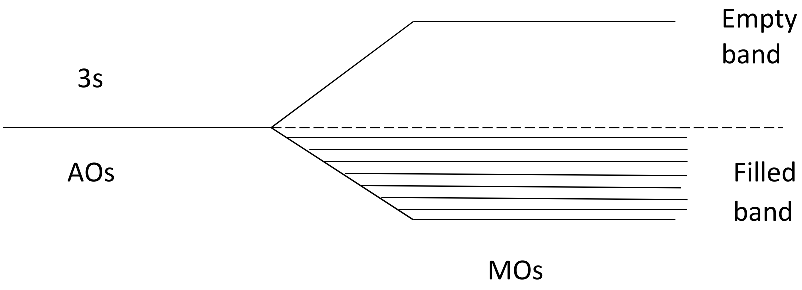


Fig.2.6: MOs of sodium metal showing half filled 3s band

In case of sodium metal, there are **n** valence electrons of **n** sodium atoms. Hence there are **n** energy levels. The maximum number of electrons that can be filled in each molecular orbital (energy level) are two. Thus **n** electrons of **n** atomic orbitals will be filled in n/2 number of bonding molecular orbitals only (figure 2.6). **Therefore, 3s bands in the sodium metal is half filled.**

Electronic energy bands

According to Molecular orbital theory, the formation of many molecular energy levels take place in the metal having **'n'** atoms. These closely spaced molecular orbital energy levels form the energy band for each type of orbital.

We Shall now consider the filling of these energy levels by the electrons. Following important points explain this distribution of electrons.

1. The inner electrons of the metal are filled in localised orbitals and not in the bands. The valence electrons are filled in the delocalised energy bands.
2. The valence orbitals and the higher energy empty orbitals merge (mix together) into the energy bands. These bands are delocalised (extended) throughout the crystal structure of the metal.
3. As for the free atom the distribution of electrons takes place in the molecular orbitals or the energy level bands.
4. **n(E) curve:** It gives the way in which the electrons are distributed in the energy band, within the various possible energy levels or States. The complete distribution of electrons between the range of energy levels in an energy band, is given by a curve called as n(E) curve, where 'n' represents number of electrons in each energy band and E stands for the energy of the band. The n(E)/dE give the number of electrons per unit volume of

material with energies between E and (E+dE). The energy distribution of the electrons in a band is given by plotting a n(E) versus E. The energy curve can be pictured as figure 2.7.

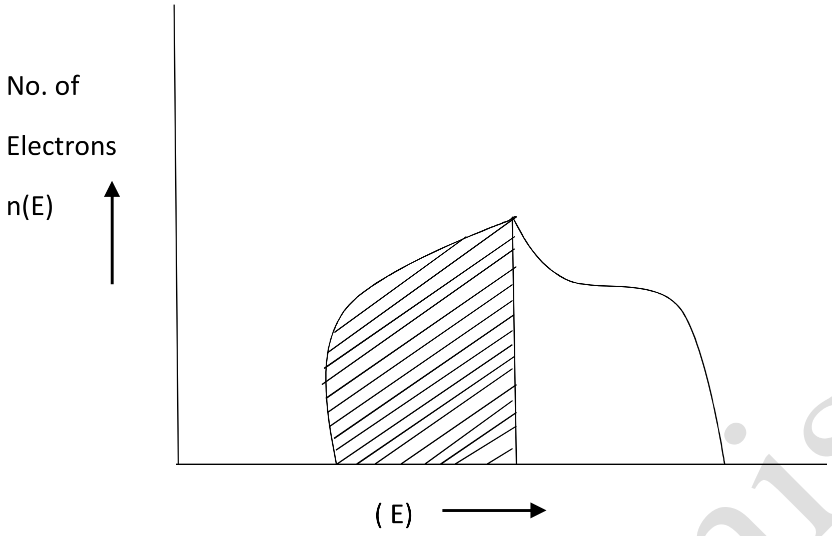


Fig. 2.7 : Energy band, shaded portion shows the half filled band

Here the energy is plotted horizontally (in previous figures energy is plotted vertically) and the vertical region under the curve (envelop) indicates the number of electrons that can be accommodated at each value of the energy. Shaded area in the curve represents the filled band.

Typical n(E) curve for or metal

We shall now study the typical n (E) for metal at absolute zero and at normal temperature. Figure 2.8(a) shows a typical n(E) curve for a metal at normal temperature. The characteristics of this curve are,

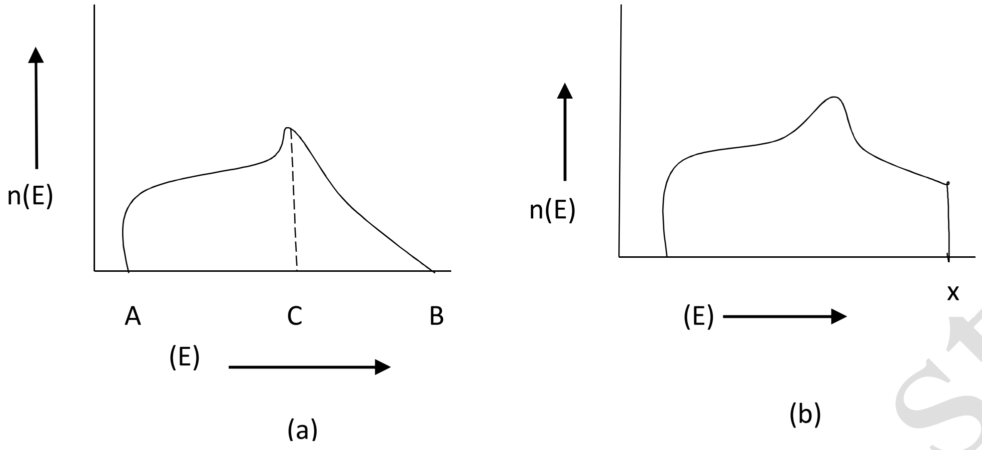


Fig.2.8 : Typical n(E) curves at (a) normal temperature (b) absolute zero

1. This curve represents and energy band for a particular energy level.
2. The area under the curve is proportional to the total number of electrons in the particular band.
3. The curve shows that C is the most favoured energy by electrons.
4. The breadth of energy band is equal to energy difference between A and B.
5. The breath of the **energy band varies from the metal to metal** but it is in the range of 1 to 10 electron volt.
6. The change in temperature changes the feeling of the electrons in the available energy levels or States within the band. It also change is the shape of the curve.

Figure 2.8 (b) shows a typical n(E) curve for a metal at absolute zero temperature. The characteristics of this curve are

i. At absolute zero, it is that assumed that the available electrons occupy all the lowest levels within a band and the energy levels higher than X are vacant i.e. there are no electrons beyond X. Therefore the boundary of the n(E) curve will be at X.

ii. As the temperature is decreased, the electrons occupy lower energy levels and hence higher energy levels remain vacant.

Thus with the decreasing temperature the right hand side of n(E) curve becomes more and more vertical. At absolute zero temperature the curve becomes completely vertical as shown by X.

iii. At higher temperature the thermal energy will be excite at least some electrons into energy level higher than X i.e. beyond X. Thus, with increasing temperature the electrons will occupy the energy levels beyond X and the vertical boundary of the n(E) curve will disappear and the curve will become more and more diffuse. Hence the n(E) curve will be similar to that shown in figure 2.8 (a) .

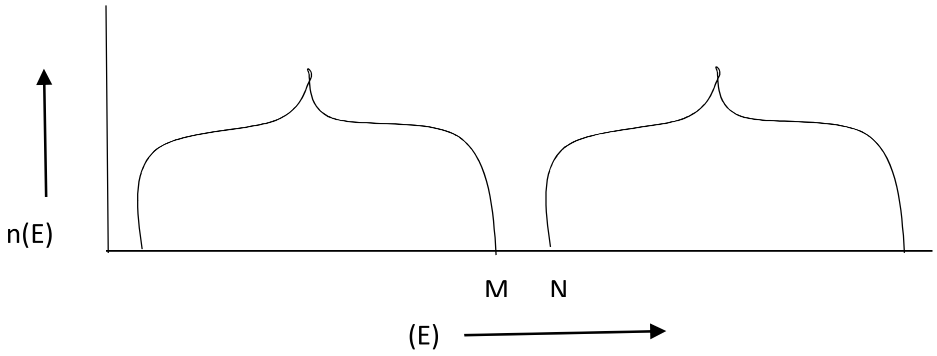


Fig.2.9: Two n(E) curves for two energy bands. It shows an energy gap between the two curves.

Energy curves for the bands : Soft x-ray spectra show that every energy band possesses n(E) curve. Thus metal possesses more than one n(E) curves as shown in figure 2.9.

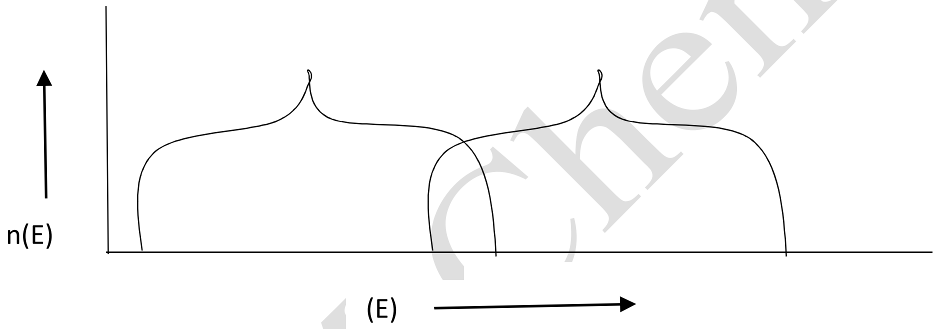


Fig.2.10 : Two n(E) curves overlap

The energy gap between the two n(E) curves is indicated by M and N. These gaps may be narrow or broad. In some metals when two n (E) curves overlap then there are no energy gaps, as shown in figure 2.10.

N (E) curves

It is important to know the number of energy levels in a given band. This is given by N(E) curves. N(E) curves also give the density of energy states (levels). The density of the energy state is the number of states per unit volume of the crystal in the energy range E and E +dE. Thus N(E) is defined in such a way that N(E) gives the number of energy states having energy between E and (E +dE).

Characteristics of N(E) curve :

1. N represents the total number of energy levels in each energy band and E stands for the energy of the band.
2. The number of N(E) curves in a metal depends on the s, p, d energy levels e.g. sodium atom possesses separate energy bands for 1s,2s,2p,3s and 3p energy levels.
3. Similar to N(E) curve, the N(E) curves are separated by an energy gap e.g. N(E) for 3s is separated from N(E) for 3p etc.
4. The two N(E) curves may overlap e.g. N(E) for 3s overlaps with N(E) of 3p.
5. The shape of a N(E) curve is very important in determining the electrical conductivity property of the metals.

Comparison of the energy curves

There are two types of energy curve a n (E) curve and b any curve.

1. n (E) versus E (energy) gives the energy distribution of the electrons in a band, i.e. it gives **the total number of electrons** in the energy band, whereas N(E) curve gives the **total number of energy state.** Each energy state can accommodate two electrons
2. n (E) curves are used to show the existing distribution of electrons between the various possible energy levels in a band, n(E) curves cannot indicate the actual levels or states that exist in a band. This is because all the lavels in the given band are not filled by the electrons and the spectral band does not indicate the empty levels in the band whereas N(E) curve indicates the actual levels that exist in the band.
3. The area under the n(E) curve gives the total number of electrons while that under n(E) curve gives the total number of energy states in the energy band.
4. Although the vertical scale has to be adjusted to make sure that the area under the n(E) curve is double than that under N(E) , the shape of both the curves is similar at absolute zero. This is because all these n/2 energy levels are filled completely.
5. The N(E) curve will extend beyond n(E) curve at higher temperature. This is because at absolute zero temperature, the available electrons will occupy only the lowest state but at higher temperature the electrons will be distributed differently between the available states and will not occupy all the available energy states in a band i.e. some levels will remain vacant.
6. The relationship between n(E) and N(E) curve can be shown to some extent by shading the area under N(E) curve which represents the electron states that would be fully occupied at absolute zero.

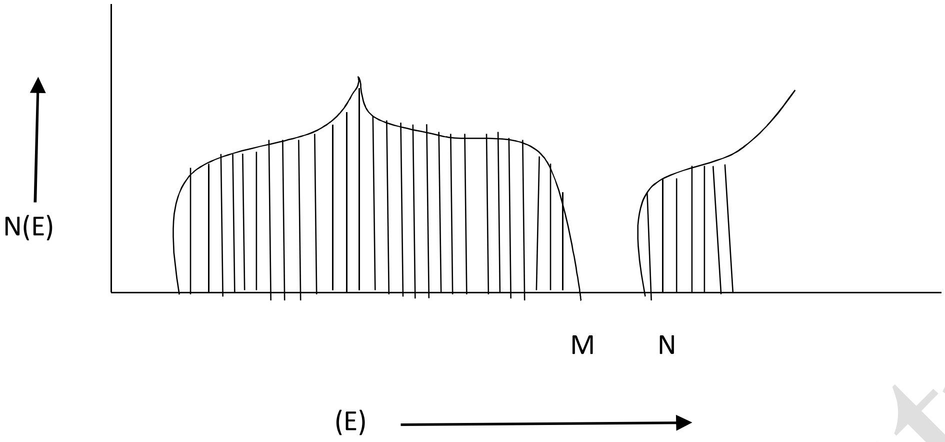


Fig. 2.11 : Two energy curves separated by an energy gap MN. The shaded portion shows the energy states which would be occupied at absolute zero.

For example, figure 2.11 shows a typical N(E) curve with the shaded portion, representing the state which would be occupied at absolute zero. There are not sufficient electrons available to filll completely the available levels.

Electrical conductivity of metals

According to band theory, electrical conductivity of metal depends upon the presence of following type of energy bands within their crystal structure.

1. The filld energy band overlaps with the vacant energy band.
2. The field energy band overlaps with the incompletely filld energy band.
3. Incompletely filled bands.
4. The energy gap between the filld band and the vacant band should be so small that the electrons from the filld energy band can be very easily promoted at ordinary temperature to vacant energy band. The filld band is usually called the **valence band** and the vacant or empty band is called the **conduction band.**

Electrical conductivity of Univalent metals

Univalent metals possess a single electron in their valence shell, i.e. **ns^1 configuration**. For example lithium, sodium, Potassium, silver, Gold etc. Univalent metals are generally very good conductors of electricity which is due to the presence of large number of vacant states in the energy bands.

The valence electron configuration of sodium is $3s^1$. This forms 3s band which partially overlaps with the empty 3p band. This overlap of bands provides greater number of levels for the free movement of electrons. In sodium crystal, n sodium atoms possess 'n' valence electrons in 3s band. There are 'n; labels in 3s band.

Each level can accommodate two electrons with opposite spins. Thus electrons will be filled in only n/2 levels, i.e. only half of the 3s band is filled by the electrons and the other half remains vacant. Moreover half filled 3s band overlaps with the vacant 3p band. As a result electrons can move from filld energy levels to empty energy levels giving rise to conductivity. This is shown in figure 2.12 in terms of N(E) curve.

Electrical conductivity of divalent metals

Divalent metals possesses two valence electrons i.e. **ns^2 configuration**. For example beryllium, magnesium, calcium, Strontium, barium etc.

Consider the magnesium metal having 3s^2 configuration. Magnesium metal contains n atoms having 2n valence electrons. There are in n levels in 3s and each level contains two electrons. Thus all n levels of 3s band are completely filled and we expect magnesium as non conductor. But filld 3s band partially overlaps with empty 3p band. As a result electrons can move from field energy levels two empty energy levels giving rise to conductivity. This is shown in figure 2.13. It is a typical N(E) curve for divalent metal.

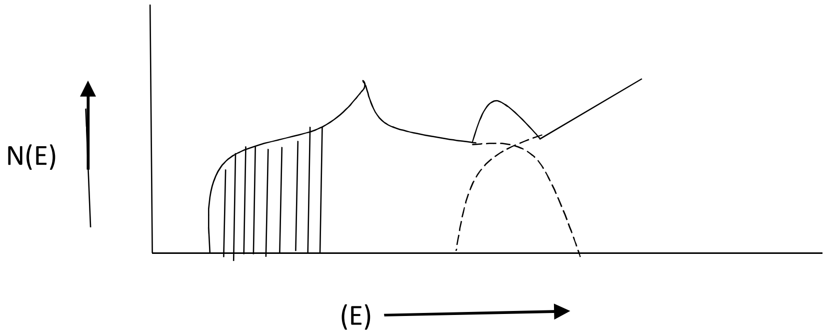


Fig.2.12 Typical N(E) curve for univalent metal. The 3s band is half filled.

The 3s band partially overlaps with 3p band

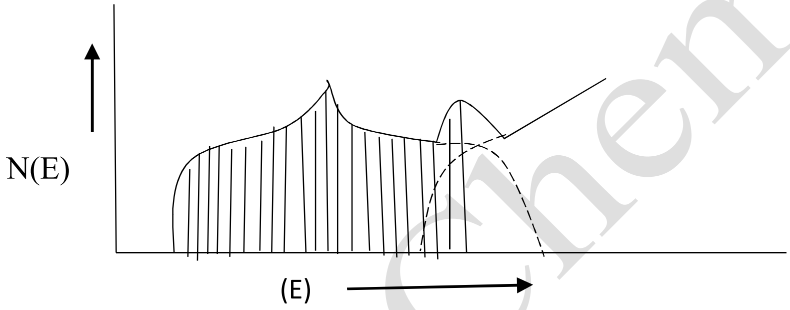


Fig. 2.13 : N(E) curves for divalent metals with overlapping 3s and 3p bands. Compare the electrons in the bands with those of univalent and divalent metals.

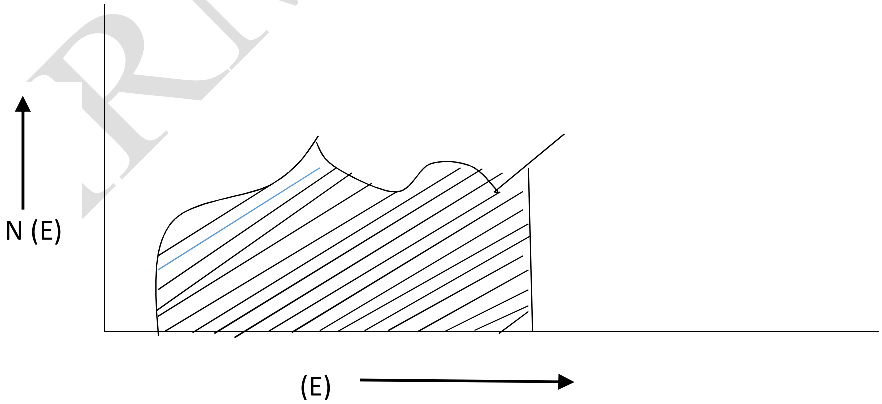


Fig.2.14 : Typical N (E) curve for a trivalent metal. Overlap of 3s band with 3p band. There are double the number of electrons than univalent metals.

Electrical conductivity of trivalent metals

The most common example of trivalent metal is aluminium. Its configuration is $3s^2,3p^1$. The 3p orbital is incompletely filled. The aluminium metal contains filld 3s energy band and incompletely filld 3p band. There is a partial overlap of 3p band with 3s band. As a result electrons can move from filld energy levels to empty energy levels giving rise to conductivity. This is shown in figure 2.14. It is a typical curve, for a trivalent metal.

Relationship between number of Valence Electrons and electrical conductivity of metals

There is no direct relation between the electrical conductivity of metal and the number of valence electrons they contain. This can be illustrated with the example of alkali metals, alkaline earth metals and the trivalent aluminium metal. The alkali metals possess a single valence electron i.e. the lowest number of valence electrons but they have the highest electrical conductivity. Similarly Copper and gold having single valence electron possess the highest conductivity. The highest conductivity is due to the presence of very large number of empty states in the 3s and 3p bands. Thus the electrical conductivity decreases from alkali to alkaline earth metals to trivalent aluminium. This is because as the number of valence electron increases the available empty States decreases.

Insulators

Diamond is an insulator (non conductor). Diamond and graphite are the allotropes of carbon. In diamonds, each carbon atom possesses four valence electrons. Carbon has valency configuration $2s^2,2p^2$. In diamond it has configuration to $2s^1,2p^3$ due to sp^3 hybridization. Due to bonding, both the 2s and 2p bands are completely filled. Moreover the gap between the filld band and the next higher empty band is very large. As a result, electrons cannot move from filld energy level to empty energy levels and cannot give rise to conductivity. This is shown in figure 2.15. It is a typical N(E) curve for an insulator.

Effect of temperature and impurity on conductivity

Conductivity decreases with increase in resistance. The resistance increases with increase in temperature and the presence of an impurity in the metal. Thus both increase in temperature and the addition of impurity decrease the electrical conductivity of metal.

1. Effect of temperature

As, greater the number of states in the energy band, greater is the free movement of electrons and hence higher should be conductivity. Generally material expands on heating and hence more spaces available. Thus we expect increase in conductivity of the metal with increase in the temperature due to passage of electrons into incompletely filled or vacant energy band. The usual observation is that conductivity decreases with increase in temperature. This is because heating produces vibrations of the atoms. The atomic vibrations increase with increase in temperature which creates disturbances in regular arrangement of the atoms in the crystal structure of the metal. i.e. lattice becomes a irregular. The vibrating atoms can create a vibrating field which scatters the electrons into different energy states. This scattering of electrons decreases the free motion of the electrons and hence decrease the conductivity.

This effect of temperature on conductivity may also be explained in terms of Molecular orbital theory. In a highly regular arrangement of the atoms in the metal crystal lattice the molecular orbitals are spread completely over all the atoms. The electrons in these molecular orbitals are delocalised and highly mobile. If irregularities are created in the the crystal lattice then delocalisation of electrons decreases i.e. localisation of bands increases with increase in temperature which results in decreasing conductivity.

2. Effect of impurity

The regular order of arrangement of the atoms and the regular filld in the crystal lattice of a metal is also disturbed by the addition of small quantity of an impurity e.g. the conductivity of Copper metal decreases by the addition of Manganese to it. Thus manganese atoms disturb the regular arrangement of the copper atoms and produce a defect in The crystal structure of copper.

Binding energy in metals

Binding energy refers to the strength of the bond or the energy required to break a bond i.e. bond energy. We shall Mainly compare the bond energies in metallic crystals with those of covalent compounds. For covalent compounds the bond energy is the measure of the energy required to split (break) a covalent bond. While for metals the bond energy (heat of dissociation) is the measure of the energy required to break down the binding forces in the metal to produce free atoms.

Metallic band is weaker than covalent bond because-

1. The interatomic distance in the metal crystal is greater than that in diatomic molecules.
2. In metals, each atom is bonded to 8 to 12 neighbouring atoms and there is a shortage of electrons for Bond formation, while covalent bond contains electron pair between the two adjacent atoms.
3. Metals contain aggregate of atoms while covalent compounds contain discrete molecules. Thogh a metallic bond is weaker than a covalent bond, the net strength of the metallic bonds is large due to the very large number of non-directional bonds. In other words the weakness of metallic bond is compensated by the presence of large number of bonds, widely spread throughout the crystal. In general metallic bond is non- directional and weak whereas covalent bond is directional and strong. This is the reason why the energy required to vaporize a mole of metal

(e.g copper) to free the atoms is smaller than the energy required to vapourise a mole of covalent substance (e.g. graphite).

Semiconductors

Materials (elements) which may be insulator (non-conductors) under normal conditions but which become conductors when the temperature is increased or when certain impurities are added. These materials are called as **semiconductors.**

Definition : **"A material whose electrical conductivity is less than that of a metal but greater than that of an insulator is called a semiconductor".** The group four elements mainly Silicon (Si) and Germanium (Ge) in their pure state are important semiconductors. These are the materials whose electrical properties lie in between those of insulator and good conductors. There are mainly two types of semiconductors.

1. Intrinsic semiconductor
2. Extrinsic semiconductors

1. Intrinsic semiconductors

These are the materials which are insulators at absolute zero but become conductors of electricity at high temperature e.g. graphite.

In terms of energy bands, they possess filled bands and there is very small energy gap between the filled and empty band. When temperature is increased their electrons of filled band get thermal energy and some of them are promoted into the next higher empty band. This results in the conductivity of the material. This is shown in figure 2.16. The most important point of this is that the conductivity of an intrinsic semiconductors increases with increase in temperature. This is due to the increase in the number of excited electrons with increase in temperature.

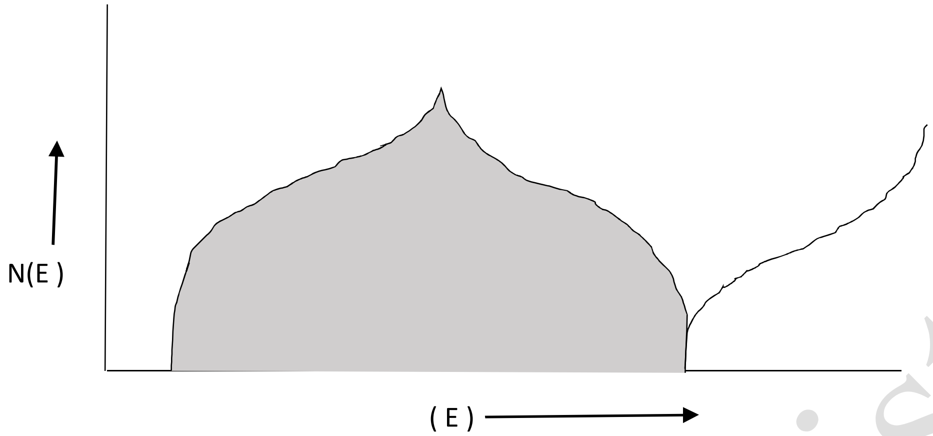


Fig. 2.16 : Typical N (E) curve for intrinsic semiconductors. It has a very small gap between the filled and empty bands,

2. Extrinsic semiconductor

Some elements, which are normally insulators can be made semiconductors when small amount of impurity is added to them. Such elements are called **extrinsic** or **impurity semiconductors**. Thus the conductivity of same element can be improved by adding small amount of impurity, that is, a small proportion of atoms of the other elements which have Valence Electrons less or more than the parent element itself. The extrinsic semiconductors are divided into the two types depending upon the nature of the impurity added.

1. n- type extrinsic semiconductors
2. P- type extrinsic semiconductors

1. n-type semiconductors

In n-type semiconductors the impurity provides and excess of electrons. Here and impurity atom to be added has more valence electrons than the parent insulator or a semiconductor atom, e.g. **Phosphorus, arsenic or antimony** (all containing five valence electrons ns^2 np^3) atoms are added to pure Silicon or Germanium (both containing four valence electrons ns^2 np^2). Each P or As or Sb atom forms 4 covalent bonds with the surrounding for Silicon or Germanium atoms, by using its four valence electrons and fifth electron is left unused as shown in figure 2.17 Thus there is an extra electron per atom at the lattice points occupied by Phosphorus or arsenic or antimony atoms compared to the lattice points occupied by Silicon or Germanium atoms .

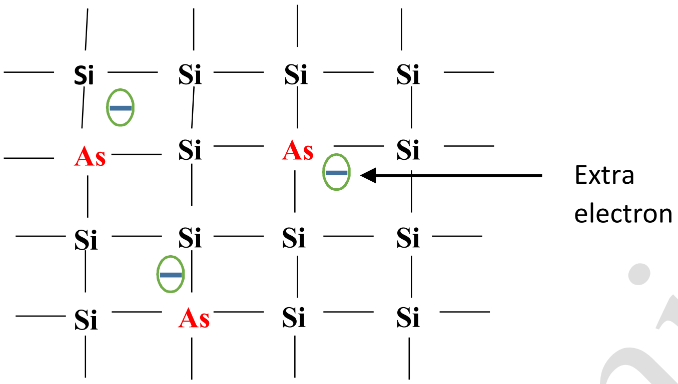


Fig. 2.17 : Schematic drawing of n-type silicon

According to band theory filled energy band of impurity lies in between filled and next empty energy band of parent metal. The extra electrons of impurity can easily be excited to the empty bands by the application of heat or electric field (figure 2.18). Crystals of pure elements of silicon or Germanium shows increased conductivity due to the presence of extra electrons obtained from the donor impurity atoms and hence the name n-type semiconductors. **It is also said that Si or Ge are doped with P or As or Sb which possess n-type semiconductivity.**

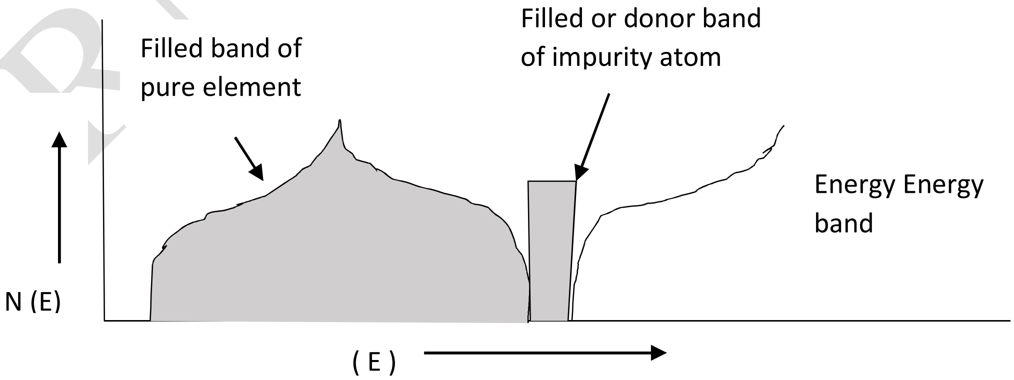


Fig. 2.18 : It shows n-type semiconductor. The filled band of impurity lies just below an empty band of pure element.

Effect of temperature on n type semiconductor

The conductivity of n-type semiconductor increases with the increase in temperature. This is because the electrons of the impurity atoms possess higher energy than the energy of filled band of the pure elements. The tendency of passing these electrons into the higher band increases with increasing temperature. We know that the number of extra electrons depends upon the number of impurity atoms. Thus if only a small amount of impurity is added to the pure element then the number of extra electrons will be less. This results into the promotion of less number of electrons to the higher energy empty bands and hence the increase in conductivity is limited. If there is a large increase in temperature, then the conductivity decreases. This is due to increase in atomic vibrations and electron scattering.

2. p-type semiconductor

In a p-type semiconductor the impurity provides an excess of holes. Here ‘p’ stands for the positive holes in pure elements. These are obtained when an impurity atom to be added has less number of valence electrons than the parent atoms e.g. **gallium or indium** (both containing 3 Valence Electrons ns^2,np^1)atoms are added to pure Silicon or Germanium (containing 4 Valence Electrons ns^2 np^2). In this case three valence electrons of each gallium or indium atom form three covalent bonds with three silicon for Germanium atoms and the fourth Silicon or Germanium atom is linked with gallium or Indian atom by an incomplete bond containing only 1 electron (from Silicon or Germanium) figure 2.19

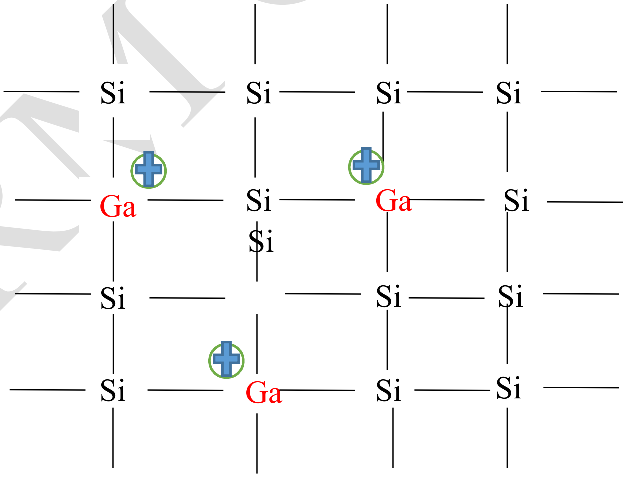


Fig.2.19 : Schematic diagram of p-type silicon

Thus in this band is there is an electron deficiency in the lattice. This creates a positive hole in the valence band of silicon or Germanium. The number of positive holes in Silicon or

Germanium are equal to the number of gallium or Indian atoms. Positive holes are the places where electrons are missing as shown in figure 2.20

The electron from neighbouring atom moves into the positive holes which appears to migrate. The conductivity is due to the movement of positive holes and hence the name p-type semiconductor

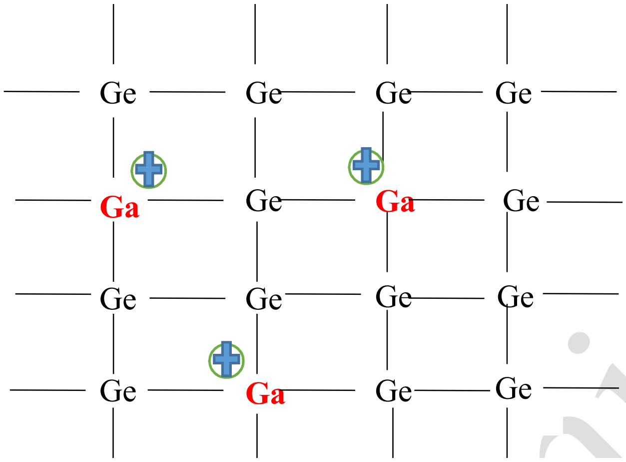


Fig.2.20 : Schematic diagram of p-type germanium

According to band theory and in terms of N(E) curve it can be explained as follows - The impurity of gallium contains an empty energy bands just above the filled band of pure Silicon or Germanium elements. The electrons from the filled band of silicon or Germanium are excited into the empty level of gallium.

Silicon and Germanium show increased conductivity due to the positive holes created gallium atoms and hence the name p-type semiconductor. It is shown in figure 2.21

Effect of temperature on p-type semiconductor

Similar to n-type, the conductivity of p-type semiconductor increases with increase in temperature. It is also important in deciding the conductivity of the element.

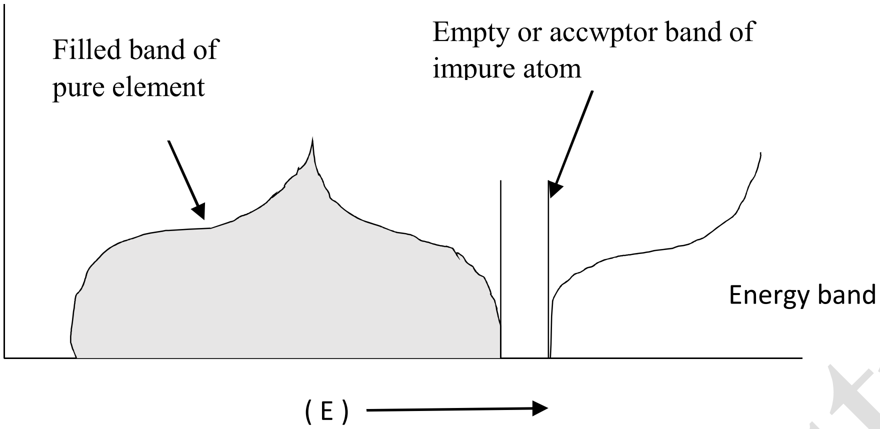


Fig. 2.21 : The empty band of the impurity lies just above the completely filled band of pure element. It is a p-type semiconductor.

Applications of semiconductors

1. **In the preparation of thermistors and photocells:** Thermistors are used to control temperature in heating devices. Photocell are used for long distance signaling and automation.
2. They are used in making **thermocouples** which are used to produce electricity.
3. **In rectification of an A.C. current** : Semiconductors are used to convert an alternating current into direct current by p-n junction diodes.
4. **In transistors** : transistors are used in the entire field of electronics, p-n-p or n-p-n junctions can serve as a device of amplification and hence semiconductors are used in transistors.
5. Semiconductors are used to control current intensity and voltage.
6. They are used to convert heat energy to electrical energy.
7. In some chemical reactions semiconductors are used as catalysts.
8. In television set etc.

Non-stoichiometry and Semiconductivity: -

Compounds in which constituent ions cation and anion are not in exactly same ratio as indicated by chemical formula search compounds are called as non stoichiometric crystals. e.g. FeO, ZnO,NiO etc.

for example the ideal composition in compounds like FeO should be Fe_1O_1 but generally the composition is $Fe_{0.95}O$ i.e. $Fe_{1-\delta}O$, were δ is a small fraction. Similarly for ZnO the composition was found to be $Zn_{1+\delta}O$. Thus $Fe_{1-\delta}O$ possesses less number of Fe^{2+} ions in the oxide (O^{2-}) ions while $Zn_{1+\delta}O$ possess slightly - more number of zinc ions than oxide ions. Thus these compounds are non-stoichiometric and possess defects in their crystal structure. The non-stoichiometric compounds possess variable composition and the number of positive and negative ions present are less or more than those expected of of positive or negative charges. But overall, the Crystal is neutral. In these compounds, the excess of positive charge is balanced by the presence of extra electron and the excess of negative charge is balanced by the presence of extra positive charge.

This results into a regular crystal structure containing defects .These non-stoichiometric defects may exist in the crystal along with the **Schottky and Frenkel defects**. There are mainly two types of non- stoichiometric defects. This division is based upon whether there is an excess of metal (cation) or deficiency of the metal (cation).

Where there is an excess of metal, the compound is formulated as $Na_{1+\delta}Cl$ or $Zn_{1+\delta}O$. In such compounds, the non-metal ion leaves the electrons behind and goes out of the crystal lattice as neutral atom. The electrons occupy an interstitial position or lattice position in the crystal lattice. These electrons freely move in the crystal and give rise to conduction. So Such crystal is called n-type semiconductor.

When there is a deficiency of metal, the compound is formulated as $Fe_{1-\delta}O$, $Ni_{1-\delta}O$. This type of defect is shown by those compounds which show variable oxidation state of a metal. In such compounds, a positive ion is absent from its normal lattice site. To secure the charge balance, adjacent cation gets oxidized to the higher oxidation state. In this crystal an electron transfer takes place from say $Fe^{2+}$to Fe^{3+} or Ni^{2+} to Ni^{3+}. This makes the F^{3+} or Ni^{3+} ion appear to move through the crystal lattice. Since the charge carriers are positive centres, such a crystal is called p-type semiconductor.

	Conductor	**Semiconductor**	**Insulator**
Valence electron	Metals having 1/2 electron	Nonmetal s4 electron	Nonmetals – more than 4 electron
Energy gap bet^n V.B. and C.B.	Absent or very small	Very small	Very large
Valence band	Half-filled / partially filled	Completely filled	Completely filled
Temperature.	High conductivity at R.T., at high temp conductivity is decreases.	Insulator at low temp, conductor at high at high temp	No conductivity by change in temp
Impurity	Conductivity decreases with addition of impurity.	Conductivity increases with addition of impurity.	No change in Conductivity

Super conductivity:

The scientist Lord Kelvin in 1848 first proposed that there is an absolute zero temperature i.e. limit to coldness. This absolute zero is known as *Kelvin.* The Van-deer-Walls have done further study about absolute zero in 1873. The K. Onnes in 1911 firstly liquefies Helium at 4.2 °k temperature at atmospheric pressure. He was awarded Noble Prize in 1913 for investigation of properties of matter at low temperate.

Definition of superconductivity:

A substance that has no electrical resistance below certain characteristic temperature, (T_c) called as the *Critical Temperature.*

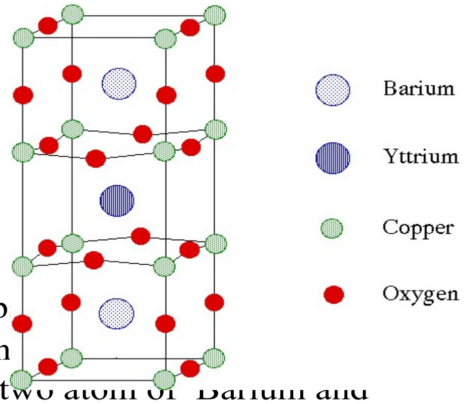
Properties:

The superconductor is the absence of electrical resistance. The zero electric resistance below temperature called the Critical Temperature (T_c). There are two types of semiconductors.

Type – I: The super conductors, which includes magnetic field completely, until critical field (H_c) is reached, show loss of superconductivity.

Type – II: The superconductor, which includes high temperature material, show gradual magnetic field penetration above lower critical field (H_{c1}) and gradual loss of superconductivity. This lost completely above an upper critical field (H_{c2}).

Structure of superconductors: -



In 1986, Bednorz and Muller found that La_2CuO_4 in which Lanthanum is partially replaced by Barium shows superconductivity around 3°k. The oxide La–Ba–Cu–O is metallic and probably magnetic. Thus it is unlikely material for superconductor. In 1987, several group compound of the type $YBa_2Cu_3O_7$ become super conductin compound is also called as '123' (i.e. one atom of Yttrium, two atom of Barium and three atoms of Copper).

Synthesis and processing:

Method –1:

The precursor metal oxides are directly sintered or calcined in air or O_2. It is then annealed in air or O_2.

$$\frac{1}{2}\ Y_2O_3 + 2BaCO_3 + 3CuO \xrightarrow{\quad} 950 - 960°C$$

$$YBa_2Cu_3O_{6.5} + 2CO_2 \xrightarrow{\quad}$$

$$YBa_2Cu_3O_{6.5} + 0.2O_2 \quad 400 - 500°C \quad YBa_2Cu_3O_{6.9}$$

After heating this mixture at 960°C, material is then cooled to 500°C in the stream of O_2 for several hours and then cooled slowly to room temp.

Method –2: - Sol-Gel method –

The sol-gel method is used for the preparation of 123 compounds. First dispersion of various metal compounds is converted into homogeneous gel by adding organic solvent such as alcohol. The gel is then decomposed at low temperature to get expected oxide. The material prepared by this method is very fine particle size material which further need annealing or heating under suitable condition to get desired oxygen stoichiometry and characteristic material.

Applications:

1) Magnets – used in High field magnet, NMR, medical diagnostic, refining bymagnetic separation, magnetic shielding.
2) Energy related – production by magnetic fusion and magneto-hydrodynamics, energy storage and electrical power transmission.
3) Transportation – high speed trains, ship drive system.
4) Electronics – bolometer, electromagnetic shielding.
5) Computers and information technology – semiconductor-superconductor hybrid, active super conducting element, voltage standard, Opto-electronics.

Low temperature Super conductors (Liquid Helium):

The applications based on low temperature liquid helium super conductors are

1) High field magnet, electronics and radio frequency devices.
2) NMR spectrometers,
3) NMR imaging which is better than CATSCAN.
4) Useful in high Q – cavities.
5) Used in Josephson junction – used in digital computers in detectors for high frequency electromagnetic radiation, used in SQUID (Superconducting Quantum Interference Devices.)

High temperature Superconductors:

The applications banned on high temperature Superconductors are –

1) For low current applications - LASER ablation, election beam evaporators
2) In SQUIDS – used in medical diagnostics i. e. checking the heart and the brain, under sea communication, submarine detection, etc.

References

A Text book of Inorganic Chemistry by Manali Publication.