Solid State

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Types of Solids

The solids are of two types: Crystalline (or true) solids and amorphous (or pseudo) solids.

Crystalline Solids

- They are rigid solids having definite shape and volume and have sharp melting point because they have definite order closed packed structure.
- They have a plane of cleavage.
- They are anisotropic. (Means their electrical and mechanical properties depend on direction along which these are measured.)

Amorphous Solids (or Pseudosolids)

- They are isotropic.
- They do not have definite shape and melting point because they have short range order packing structure.
- Glass, rubber, plastic and wood are amorphous solids.

Types of Crystalline Solids on the basis of nature of bonds: There are four types – ionic solids, covalent solids, molecular solids and metallic solids. Their properties are as follows:

S. No.	Property	Ionic Solids	Covalent Solids	Molecular solids	Metallic Solids
1.	Constituent particles	Ions	Atoms	Molecules	Positive ions or ion cores and free e$^-$
2.	Type of attractive forces	Electrostatic (Coulombic)	Covalent bonds	van der Waals'	Metallic bonds
3.	Electrical conductance	Conductor (in Molten state and aq. Solution)	Insulator	Insulator	Conductor
4.	Examples	NaCl, KCl, LiF, CaO	SiO_2, SiC, C (diamond and graphite)	CO_2, I_2, P_4	Metals and alloys

Isomorphism and polymorphism

Isomorphism is the property of two or more crystalline solids having similar chemical composition to exist in the same crystalline form or structure is called isomorphism, e.g. Na_2SeO_4 and Na_2SO_4.

Polymorphism is the existence of a particular substance in more than one crystalline form is called polymorphism e.g. $CaCO_3$ exists in two crystalline form called calcite and aragonite.

Crystal Lattice or Space Lattice

It is a regular three dimensional arrangement of constituent particles (atoms, molecules or ions) in a definite orderly manner.

- In end centred unit cell particles are present at the corners as well as at the centre of any two opposite faces.
- Density of unit cell is defined as the ratio of mass per unit volume of unit cell.

$$d = \frac{z \times M}{N_0 \times V} = \frac{z \times M}{N_0 \times a^3}$$

where, d = density of unit cell

z = number of atoms/unit cell

(z = 1 for simple unit cell, z = 2 for bcc, z = 4 for fcc)

M = At. Mass of element N_0 = Avogadro number

V = volume of unit cell   a = edge length of unit cell

Types of Crystal Systems

There are total 7 types of crystal systems

(i) Cubic   (ii) Rhombic   (iii) Triclinic   (iv) Monoclinic (v) Trigonal   (vi) Hexagonal (vii) Tetragonal

Unit Cell

A solid crystal is made of many repeating units called as unit cell. The unit cell is the smallest repeating unit in three dimensional space or crystal lattice or space lattice.

Basic Types of Cubic Lattice Cells

On the basis of different arrangements of constituent particles, there are 3 basic types of cubic Body centered cubic unit cell and Face centered cubic unit cell. Comparative study of these unit cells is as follows:

S. No.	Property	Simple Cubic Unit Cell	Face Centered Cubic Unit Cell	Body Centered Cubic Unit Cell
1.	Positions occupied by constituent particles	All corners of cube	All corners of cube and center of each face	All corners of cube and centre of unit cell
2.	No. of particles/unit cell	$8 \times \frac{1}{8} = 1$	$(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$	$(8 \times \frac{1}{8}) + (1 \times 1) = 2$
3.	Percentage efficiency (Space occupied by particles)	$\frac{\pi}{6} = 52\%$	$\frac{\sqrt{2}\pi}{6} = 74\%$	$\frac{\sqrt{3}\,\pi}{8} = 68\%$
4.	Radius of particle(r)	$r = \frac{a}{2}$	$r = \frac{\sqrt{2}}{4}a$	$r = \frac{\sqrt{3}}{4}a$
5.	Nearest neighbour Distance(d)	$d = a$	$d = \frac{1}{\sqrt{2}}a$	$d = \frac{\sqrt{3}}{2}a$

(Where a = edge length)

Calculation of Number of Particles per Unit Cell

(i) Contribution of each atom at the corner = $\dfrac{1}{8}$

(ii) Contribution of each atom at the face centre = $\dfrac{1}{2}$

(iii) Contribution of each atom at the edge centre = $\dfrac{1}{4}$

(iv) Contribution of each atom at the body centre =1

Packing Fraction (or Density of Packing)

It is the ratio of volumes occupied by atoms in unit cell to the total volume of the unit cell.

Packing fraction = $\dfrac{\text{volume occupied by particles of unit cell}}{\text{total volume of unit cell}}$

The density of packing gives idea about how closely the atoms are packed in a unit cell. For the primitive cubic lattices it follows the order fcc (74%) > bcc (68%) > simple cubic lattice (52%)

(a) Simple cubic unit cell:
Let the radius of atom in packing = r
Atoms are present at the corner of the cube, each of the eight atom present at the eight corners shared amongst eight unit cells. Hence number of atoms per unit cell = 8 x (1/8) = 1
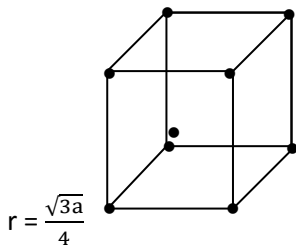Again, r = $\dfrac{a}{2}$ therefore,

P.F. = $\dfrac{\frac{4}{3}\pi r^3}{(2r)^3} = \dfrac{\pi}{6} = 0.52, \% \text{ P. F.} = 52\%$

Void fraction = 1 – packing fraction = 1 – 0.52 = 0.48

(b) Body centered cubic unit cell:
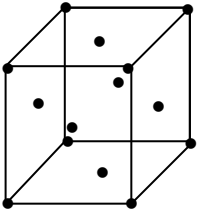Number of atoms per unit cell = 8 x (1/8) + 1 = 2

r = $\dfrac{\sqrt{3}a}{4}$

P.F. = $\dfrac{2 \times \frac{4}{3}\pi r^3}{\left(2r/\sqrt{3}\right)^3} = \dfrac{\sqrt{3}\pi}{8} = 0.68$

%P.F. = 68%; % of void = 100 – 68 = 32%

(c) Face centered cubic unit cell:
Number of atoms per unit cell = 4

$$r = \frac{\sqrt{2}}{4}a$$

$$\text{P.F.} = \frac{4 \times \frac{4}{3}\pi r^3}{\left(4r/\sqrt{2}\right)^3} = \frac{\sqrt{2}\pi}{6} = 0.74$$

%P.F. = 74%

% of void = 100 − 74 = 26%

Types of Crystalline solids:

According to attractive force which hold crystal together are generally of five types and thus crystal can be classified into five types.

Ionic Crystals:

(a) The lattices in ionic crystal consists of alternative positive and negative ions in equivalent amount arranged in an order so that the potential energy of the ions in the lattice is minimum.

(b) Such crystal are normally found in ionic compound.

e.g. $NaCl \rightarrow Na^+ + Cl^-$

Covalent Crystals:

(a) In covalent crystals, atoms at their lattice point are held together by shared pairs of electrons between them.

(b) The covalent bonding extends through out the crystals in spatial direction and has no small molecules in the conventional sense.

e.g. Diamond, Graphite

Molecular Crystals:

(a) In molecular crystals, the repeating unit is chemically identifiable atoms or molecules which do not carry a net charge.

(b) Molecular bonds are formed for those elements or compounds whose electronic configuration is such that there is little transfer of electrons between their atoms.
e.g. Noble gases.

(c) The molecules having H-atom attached on N, O or F give hydrogen bonding crystals. The existence of H-bonding in the crystal lattice is beyond doubt.

Metallic Crystals:

In metallic crystals, the lattice consists of assemblage of positive ions immerged in a sea of mobile electrons. The binding force is due to-

(a) Attraction between positive ions or ion cores of the metal and electron cloud.

(b) The mutual repulsion of free electrons.

(c) The mutual repulsion of ion cores.

Close Packing in Crystal

For sake of convenience we assume that the constitute particle in a crystals are hard sphere. The packing of these spheres take place in such a way that they occupy the maximum available space and there is minimum empty space, which leads the maximum density of crystal.

Close Packing in One Dimension

The constituent particles are arranged in one row and each sphere is touching two neighbouring spheres. Hence, coordination number is 2.

Close Packing in Two Dimension

It is of two types:

(i) Square close packing in 2-D

It has spheres of adjacent rows one over the other, having a vertical as well as horizontal alignment in form of a square. Hence, Coordination number is 4.

Space occupied = 52.4%

(ii) Hexagonal close packing in 2-D

It has spheres of every second row placed in depression between spheres of the first row. The spheres of third row are vertically aligned with those of the first row. Hence, Coordination number is 6.

Space occupied = 60.4%

Close Packing in Three Dimension

It involves the arrangement of sphere in two different ways.

(i) AB AB....arrangement gives hexagonal close packing (hcp).

(ii) ABC ABC....arrangement gives cubical close packing or face centred cubic.

Hence,

Coordination number = 12

Space occupied = 74%

Determination of Structure of Crystal (Bragg's Equation)

The structure of crystal is determined by X-ray analysis.

$n\lambda = 2d\sin\theta$

Where, d= diffraction order (1,2,3.....)

λ = wavelength of incident X-ray

θ= angle of diffraction

- **Coordination number** is the number of spheres (atoms) in contact with the sphere (atom) under consideration or the number of nearest neighbours. The value of coordination number depends on the structure of unit cell. Coordination number for simple cubic lattice = 6, for fcc = 12 and

- for bcc = 8.

- **Radius ratio** is the ratio of radius of cation (r^+) to that of anion (r^-) in the crystal.

Radius ratio = $\dfrac{radius\ of\ cation}{radius\ of\ anion} = \dfrac{r^+}{r^-}$

S. No.	Radius ratio(r^+/r^-)	Coordination No.	Arrangement of particles
1.	0.155 – 0.225	3	Triangular planar
2.	0.225 – 0.414	4	Tetrahedral
3.	0.414 – 0.732	6	Octahedral
4.	0.732 – 1.0	8	Body centered cubic

- **Voids or holes** are interstitial spaces which exist between constituent particles in a crystal lattice. Voids are of two types tetrahedral voids and octahedral voids. Tetrahedral void is a simple triangular space surrounded by four spheres while an octahedral void is a double triangular void surrounded by six spheres. In close packing for 'n' spheres, number of tetrahedral voids is 2n and octahedral voids are n.

Structure of Simple Ionic Compounds

The structures of simple ionic compounds can be classified in 3 categories AB type (Example NaCl, CsCl, ZnS), AB_2 type (Example CaF_2), and A_2B type (Example Na_2O). Comparative study of some basic structure of ionic crystals is as follows:

S. No.	Property	NaCl type	CsCl type	ZnS type	CaF_2 type (Fluorite Structure)	Na_2O type (anti-fluorite Structure)
1.	Constituent ions	Na^+ and Cl^-	Cs^+ and Cl^-	Zn^{2+} and S^{2-}	Ca^{2+} and F^-	$2Na^+$ and O^{2-}
2.	Position of cation	Octahedral voids	Centre of unit cell	Alternate tetrahedral voids	fcc or ccp	All tetrahedral sites
3.	Position of anion	fcc	Corners of unit cell	fcc	All tetrahedral sites	fcc or ccp
4.	No. of formula units/cell	4	1	4		
5.	Coordination No.	6:6	8:8	4:4	8:4	4:8
6.	Examples	Halides of Li, Na, K, Rb, AgF, AgBr, NH_4Cl	CsCl, CsBr, Csl, TiCl, TiCN	ZnS, CuCl, CuBr, Cul, AgI	CaF_2, BeF_2, SrF_2, $BaCl_2$	Na_2O, K_2O, Na_2S, Li_2O

Imperfections in Crystals

Deviation in pattern of arrangement of constituent particles in crystal is called crystal defect. It is cause due to change in temperature or pressure or addition of some foreign particles.

Crystal Defects: The defects are basically irregularities in the arrangement of constituent particles. Broadly the defects are of two types, namely, point defects and line defects. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in

a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects.

Types of Point defects.

Point defects can be classified into three types:

(a) Stoichiometric defects   (b) Impurity defects and   (c) Non-stoichiometric defects.

(a) Stoichiometric Defects:

(i) Schottky Defect: In Schottky defect a pair of vacancies or holes exist in the crystal lattice due to the absence of one positive and one negative ions from the lattice site and occupying a position on the surface. It is a common defect in ionic compounds of high C.N., where both cations and anions are of the same size, e.g., KCl, NaCl, KBr, etc. Due to this defect density of crystal decreases, it begins to conduct electricity to a smaller extent (ionic mechanism) and the stability of the crystal is lowered .

(ii) Frenkel Defect: This defect arises when some of the ions of the lattice occupy interstitial sites leaving lattices sites vacant. This defect is generally found in ionic crystals where anion is much larger in size than the cation. Examples: AgBr, ZnS. Density does not change. Electrical conductivity to small extent is observed and no change in overall chemical composition takes place. The stability of the crystal is lowered.
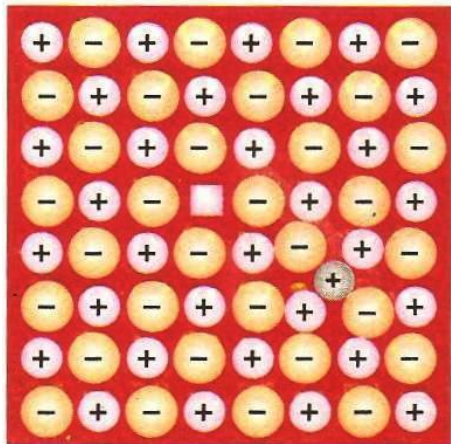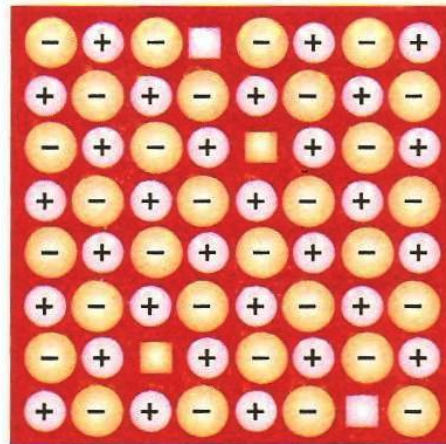

Frenkel defects   *Schottky defects*

(b) Impurity defects: These arise only because of the presence of impurities.

When an impurity is added in ionic solids, the defect is introduced in the crystal. This can be done by adding an ion which possesses different charge to host ions. Interstitials or vacancies are created. For example, addition of $CdCl_2$ to AgCl or $SrCl_2$ to NaCl gives rise to solid solutions wherein the divalent cation Ca^{2+} or Sr^{2+} occupy

Ag^+ and Na^+ site and produce simultaneously equal number of cation vacancies (equal to number of divalent cation added).

Thus, movement of ions leads to increase in conductivity.
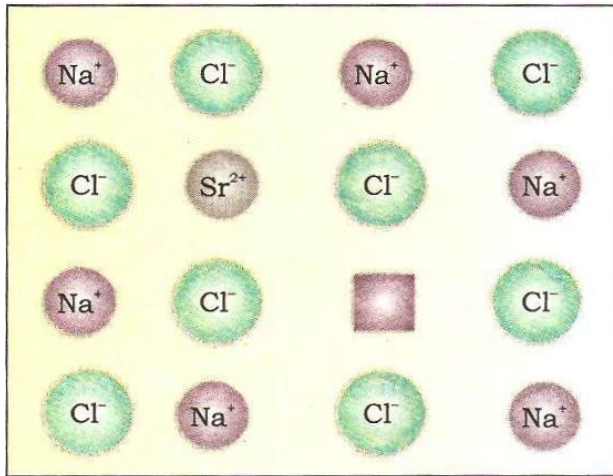
Introduction of cation vacancy in NaCl by substitution of Na⁺ by Sr²⁺.

(c) **Non-stoichiometric defects:** In such defects there is a change in over all chemical composition. The crystal stays neutral although either there is excess of positive or negative particles.

There are of two types:

(i) Metal excess defect   (ii)Metal deficiency defect

(i) **Metal excess defect:** (a) Metal excess defect due to anionic vacancies:

A negative ion from the crystal may be missing from its site leaving an anion vacancy which is occupied by the electron originally associated with the anion. Electrons trapped in anion vacancies are called F-centres. They impart colour. Examples, sodium chloride imparts yellow colour, LiCl imparts pink and KCl imparts violet due to metal excess defect.

1. A negative ion may be missing from the lattice site which is occupied by an extra electrons.

(b) Metal excess defect due to the presence of extra cations at interstitial sites:

Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\triangle} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$
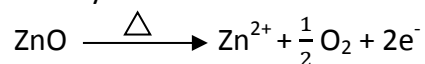
Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.
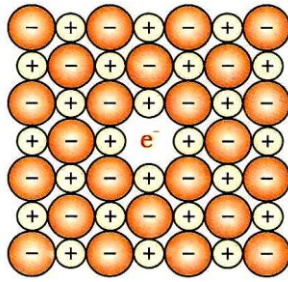
An F-centre in a crystal

(ii) Metal deficiency defect: There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compare to the stoichiometric composition. Example, $Fe_{0.95}O$.

1. One of the positive particles may be missing from its lattice sites.

The extra negative charge may be balanced if the nearby positive particle acquires an extra positive charge. Such crystals are also semiconductors. Examples: FeO, FeS, NiO, etc.

Interstitials: Atoms or ions which occupy normally vacant interstitials (voids) in a crystal are called *interstitials.*

Vacancy: When one of the constituent particles is missing from the crystal lattice, this unoccupied position is called *vacancy.*

Interstitial Position: When one of the constituent particles is missing from the crystal lattice but occupies a position meant for another particle this called *interstitial position.*

F-centres: When alkali metal halides are heated in an atmosphere of alkali metal vapour, anion vacancies are created. When the metal atoms deposit on the surface of alkali metal halide crystal, halide ion diffuses into the surface and combine with the metal atoms. The alkali metals ionize to produce electron which diffuse into crystal and combine with a negative ion vacancy. Electrons trapped in anion vacancies are called *F-centres*. These centres give rise to interesting properties.

Excess of K^+ ions in KCl   Crystals appear violet

Excess of Li^+ ions in LiCl   Crystals appear pink

ZnO becomes yellow on heating

NaCl becomes yellow in excess of sodium vapour

13-15 compounds: When the solid state materials are produced by combination of elements of groups 13 and 15, the compounds thus obtained are called 13-15 compounds. For example, InSb, AlP, GaAs, etc.

12-16 Compounds: Combination of elements of groups 12 and 16 yield some solid compounds which are referred to as 12-16 compounds. For example, ZnS, CdS, CdSe, HgTe, etc.

Magnetic Properties: Solids can be classified on the basis of their magnetic properties.

(a) Diamagnetic. Weakly repelled by the external magnetic field. Example: TiO_2, V_2O_3, NaCl, benzene, etc.

Reason: This substance has fully-filled orbitals. Magnetic moment of an electron with spin in one direction is cancelled by that of other electron with spin in opposite direction.

(b) Paramagnetic. (i) Weakly attracted by the external magnetic field. (ii) Paramagnetism is a temporary effect and the substance loses its magnetism in the absence of external magnetic field.

Example: TiO, VO_2, CuO, O_2, Cu^{2+} +, Fe^{3+}, etc.

Reason: It (atom/ion/molecule) contains unpaired electrons.

(c) Ferromagnetic. (i) Strongly attracted by the external field. (ii) Exhibits magnetism, even in the absence of magnetic field. (iii) These substances can be permanently magnetized. Example : Fe, Ni, Co, CrO_2.

Reason: It arises due to spontaneous alignment of magnetic moments in the same direction.

(d) Antiferromagnetic. Zero net magnetic moment, but expected to possess paramagnetism because of the presence of unpaired electrons.

Example : MnO, Mn_2O_3, MnO_4, V_2O_3, Fe_2O_3, FeO, CoO, Co_3O_4, NiO

Reason : Because of the presence of equal number of magnetic moments in opposite direction, the resulting magnetic moment is zero.

Ferrimagnetic: Small net magnetic moment, but expected to possess large magnetism on the basis of the unpaired electrons.

Reason: Due to the unequal number of magnetic moments of opposite direction, the net or resulting magnetic moment is small.

(e) Curie-Temperature: The temperature at which a ferromagnetic substance loses its ferromagnetism and attains paramagnetism only is called curic-temperature.

Electrical Properties : Solids are classified into three groups:

Conductors, Semiconductors and Insulators.

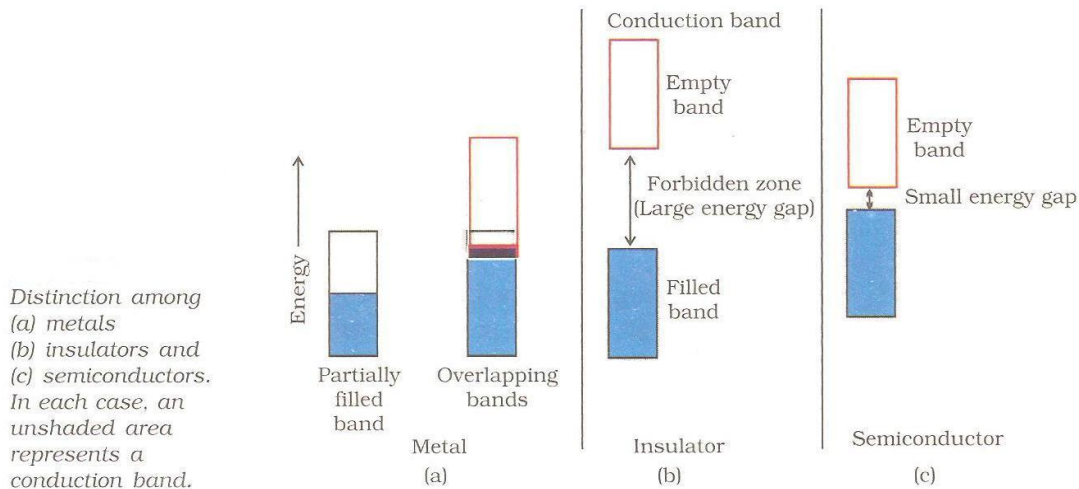(i) *Conductors*: These generally include metals. Their conductivity is of the order of 10^7 (ohm m)$^{-1.}$

(ii) *Semiconductors*: Those solids which have intermediate conductivities ranging from 10^{-6} to 10^4 (ohm m)$^{-1}$ are classified as semiconductors. There is a rise in conductivity value as the temperature rises. Pure substances, like silicon and germanium, show conducting behaviour. The value of conductivity for these elements is too low at low temperatures. Doping is done to improve their conducting behaviour. As the temperature rises large number of valence electrons from the valence band jump to conduction band.

(iii) *Insulators:* These are solids which have very low conductivity values ranging from 10^{-10} to 10^{-20} (ohm m)$^{-1}$. These are called insulators.

(iv) **Causes of Conductance in Solids:** In most of the solids and also in insulators conduction takes place due to migration of electrons under the influence of electric field. However, in ionic solids, it is the ions that are responsible for the conducting behaviour due to their movement. The number of electrons available to participate in the conduction process determines the magnitude of electrical conductivity.

In metals, conductivity strongly depends upon the number of valence electrons available in an atom. A band is formed due to closeness of molecular orbitals which are formed from atomic orbitals.

If conduction band is not completely full or it lies very close to a higher unoccupied band, then electrons can jump from valence band to conduction band and some conductivity is observed.

According to Band theory in case of metals or conductors conduction band and valence band are overlapping each other and electrons can flow from one band to other readily. Hence they are good conductors of electricity. In case of insulator there is a large energy gap between conduction band and valence band which is known as *Forbidden Zone.* Thus, electrons cannot jump the gap hence, they do not conduct electricity. In case of semi conductor the gap is jumpable and conductivity lying between conductor and insulator.

Distinction among (a) metals (b) insulators and (c) semiconductors. In each case, an unshaded area represents a conduction band.

(i) **Doping:** It is a process by which impurity is introduced in semiconductors to enhance its conductivity value.

(ii) **n-type semiconductor**: When a silicon or germanium crystal is doped with group 15 element like P or As, the dopant atom forms four covalent bonds like a Si or Ge atom but the fifth electron, not used in bonding, becomes delocalised and contribute its share towards electrical conduction. Thus silicon or germanium doped P or As is called n-type semiconductor, n indicative of negative since it is the electron that conducts electricity.

p-type semiconductor: When silicon or germanium is doped with group 13 element like B or Al. The dopant is present only with three. Valence electrons. An electron vacancy or a hole is created at the place of missing fourth electron. Here, this hole moves through the crystal like a positive charge giving rise to electrical conductivity. Thus Si or Ge doped with B or Al is called *p* type of semi conductor, (*P* stands for positive hole)

Fig. 1.30: Creation of n-type and p-type semiconductors by doping groups 13 and 15 elements.
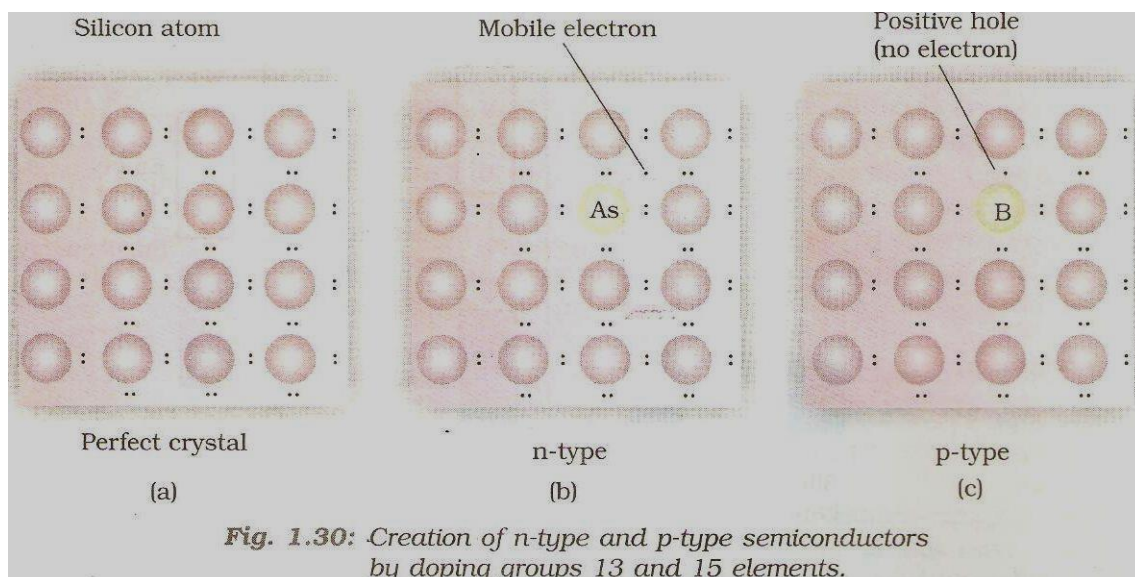
(v) **Diode:** When n-type and p-type conductors are combined, what results is known as diode.
These diodes are used as rectifiers

(vi) **Transistors:** These are used to detect or amplify radio or audio signals. They consist of *pnp* or *npn* sandwich semiconductors.

(vii) **Photo-diode:** These are diodes which are capable of converting light energy into electrical energy and are used in solar cells.

Structure of Some Ionic Solids

(a) **NaCl (fcc) :** Cl^- in ccp, Na^+ occupy all the octahedral voids.

   Coordination number 6:6 and

   $\frac{r_+}{r_-} = 0.52$

   Number of formula units per unit cell = 4

(b) **CsCl (bcc) :** Cl^- in cubic arrangement Cs^+ ion occupy cubic voids.

   Coordination number 8 : 8 and

   Number of formula units per unit cell = 1

(c) **ZnS (Zinc blende) :** form fcc lattice and in alternate tetrahedral voids, coordination number 4 : 4 and

   Number of formula units per unit cell = 4

(d) **ZnS (Wurtzite) :** S^{2-} form hcp structure and in alternate tetrahedral voids, coordination number 4 : 4 and

   Number of formula units per unit cell = 4

(e) **CaF$_2$ (Fluorite) :** ions in ccp and ion occupy all tetrahedral voids, coordination number

   8 : 4 and

   $\frac{r_+}{r_-} = 0.73$

   Number of formula units per unit cell = 4

(f) **Na$_2$O (Antifluorite structure) :** O^{2-} ions in ccp and Na^+ ions occupy ally tetrahedral voids, coordination number 4 : 8