The Solid State

Solid is a state of matter in which the constituting particles are arranged very closely. The constituent particles can be atoms, molecules or ions.

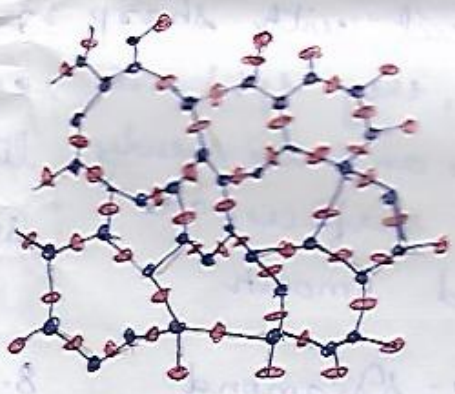
Properties of solids:

1. They have definite mass, volume and shape
2. They are compressible and rigid
3. Intermolecular distances are very short and hence the intermolecular forces are strong.
4. The constituent particles have fixed position and can oscillate about their mean positions.

Classification on the basis of nature of order in the arrangement of constituent particles

1. Crystalline solids
2. Amorphous solids

(a) Structure of crystalline quartz



(b) Structure of amorphous quartz

Distinction between crystalline and Amorphous solids

Crystalline solids	Amorphous solids
1. Have definite characteristic geometrical shape	1. Have an irregular shape.
2. Have a long range order	2. Have only short range order.
3. Have a sharp melting point	3. They gradually soften over a range of temperature
4. They are anisotropic in nature. i.e., their physical properties show different values when measured along different directions in the same crystal	4. They are isotropic in nature. i.e, their physical properties are same in all directions
5. These are true solids	5. Pseudo solids or supercooled liquids
6. have a definite and characteristic heat of fusion	6. They do not have definite heat of fusion
7. when cut with sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	7 when cut with a sharp edged tool, they cut into two pieces with irregular surfaces
8. Example - Diamond solid NaCl, crystalline quartz.	8. Example - Glass, rubber plastics

* Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity.

Types of crystalline solids

1. Molecular solids
   - Constituent particles - molecules.

   It is of 3 types

Type of solid	constituent particles	Bonding / attractive forces	Electrical conductivity	Physical nature	Melting point	Example
i) Non-polar solid	Molecules	dispersion / london forces	Insulator	soft	Very low	Ar, CCl_4 H_2, I_2 CO_2
ii) Polar solids	Molecules	dipole-dipole interactions	Insulator	soft	low	solid HC solid SC solid NH
iii) Hydrogen bonded	Molecules	Hydrogen bonding	Insulator	Hard	low	H_2O (ice)

2. Ionic solids
   - Constituent particles - Ions
   - Bonding / attractive forces - Coulombic or Electrostatic
   - Electrical conductivity - Insulators in solid state but conducts in molten state and in aqueous solutions
   - Physical nature - Hard but brittle
   - Melting point - High
   - Examples - CaF_2, ZnS, MgO, NaCl

3. Metallic solids
   - Constituent particles - positive ions in a sea of delocalized electrons

- Bonding/attractive forces : Metallic bonding
- Electrical conductivity: Conductors in solid state as well as in molten state
- Physical nature : Hard but malleable and ductile
- Melting point : Fairly high
- Examples : Fe, Cu, Ag, Mg

4. Covalent or Network solids
- Constituent particles : Atoms
- Bonding/attractive forces : Covalent bonding
- Electrical conductivity : Conductors in solid state as well as in molten state
- Physical nature : Hard but malleable and ductile
- Melting point : Fairly high
- Examples :- SiO_2 (quartz), SiC, C (diamond) C (graphite)

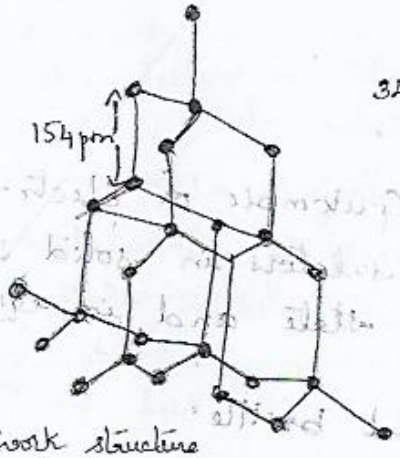
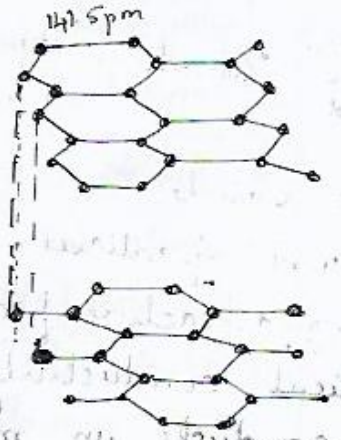


Fig. Network structure of diamond



Structure of graphite

- Crystal lattice :- A regularly ordered arrangement of constituent particles in three dimensions is called crystal lattice

• Lattice points or lattice sites: The fixed positions on which the constituent particles are present are called lattice points or lattice sites. The group of lattice points which when repeated over and over again in 3 dimensions gives the complete crystal lattice.

• Unit cell: It is defined as the smallest repeating unit in space lattice which when repeated over and over again generates the complete crystal lattice. The crystal can consist of an infinite number of unit cells.

Parameters which characterize a unit cell:

1. ile dimensions along the three edges, a, b and c. These edges may or may not be mutually perpendicular
2. angles between the edges, α, β and γ

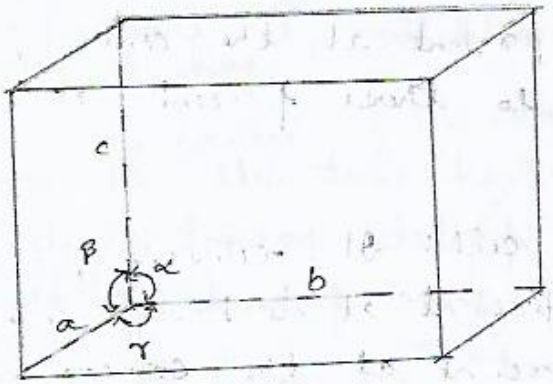


Illustration of parameters of a unit cell

• Seven crystal systems

1. Cubic $\alpha = \beta = \gamma = 90^\circ$, $a = b = c$
2. Tetragonal $\alpha = \beta = \gamma = 90^\circ$, $a = b \neq c$
3. Orthorhombic $\alpha = \beta = \gamma = 90^\circ$, $a \neq b \neq c$
4. Monoclinic $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$, $a \neq b \neq c$
5. Hexagonal $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; $a = b \neq c$
6. Rhombohedral or trigonal $\alpha = \beta = \gamma \neq 90^\circ$, $a = b = c$
7. Triclinic $\alpha \neq \beta \neq \gamma \neq 90^\circ$, $a \neq b \neq c$

• Types of unit cells

1. Primitive or simple unit cells have constituent particles only at its corners
2. Centred unit cells are those unit cells in which one or more constituent particles are present at positions in addition to those present at the corners.

• Types of centered unit cells:

1. Face centered unit cell: It consists of one constituent particle present at the centre of each face in addition to those present at the corners.
2. Body centered unit cell: It consists of a one constituent particle present at its body centre in addition to those present at the corners
3. End centered unit cell: It consists of one constituent particle present at the centre of any

two opposite faces in addition to those present at the corners.

• Number of particles at different lattice positions:

→ If an atom is present at its corner, it is shared by eight adjacent unit cell. Therefore only $\frac{1}{8}$th of an atom actually belongs to a particular unit cell.

→ If an atom is present at the body centre, it is not shared by any other unit cell. So that one atom completely belongs to the same unit cell.

→ If an atom is present at the centre of the face, it is shared by two unit cells. So only half of the atom actually belongs to the unit cell.

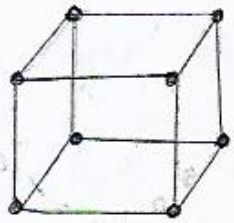
→ If an atom is present at the edge centre, it is shared by four unit cells. So only 1/4 of an atom belongs to the unit cell.

• Number of atoms in different unit cells

1. Primitive unit cell:

It has 8 atoms on its corners.

8 corners × $\frac{1}{8}$ per corner atom = $8 \times \frac{1}{8}$ = 1 atom



2. Body

2. Body - centred cubic unit cell :-

A bcc unit cell has an atom at each of its corners and also one atom at its body centre.

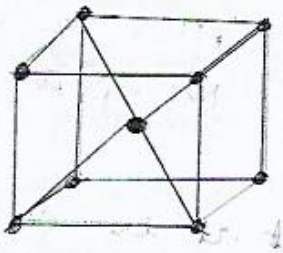
In a bcc unit cell:

(i) 8 corners $\times \frac{1}{8}$ per corner atom $= 8 \times \frac{1}{8} = 1$ atom

(ii) 1 body centre atom $= 1 \times 1$

$\therefore$ Total number of atoms/unit cell = 2 atoms

3



body centered cubic unit cell open structure

3. Face - centred cubic unit cell :

A FCC unit cell has atoms at all the corners and at the centre of all the faces of the cube.

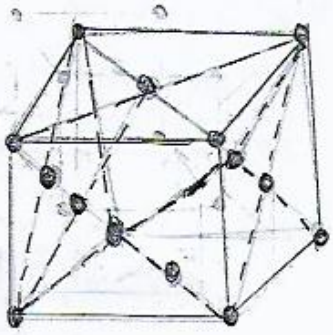
In a fcc unit cell :

(i) 8 corner atoms $\times \frac{1}{8}$ atom per unit cell $= 8 \times \frac{1}{8} = 1$ atom

(ii) 6 face - centred atoms $\times \frac{1}{2}$ atom per unit cell,

$= 6 \times \frac{1}{2} = 3$ atoms

$\therefore$ Total number of atoms per unit cell = 4 atoms



open chain structure of face centred cubic unit cell

Close packed structures :

In solids, the constituent particles are closely packed leaving the minimum vacant space.

- Coordination number :- It is the number of nearest neighbours of a particle.

Let us consider the constituent particles as identical hard spheres and build up the three dimensional structure in three steps

(a) Close packing in one dimension

- This is to arrange the hard spheres in a row and touching each other. In this arrangement, each sphere is in contact with two of its neighbour So the coordination number is two

b) Close packing in two dimensions: It is generated by stacking the rows of close packed spheres in two ways :

(i) Square close packing (ii) Hexagonal close packing

c) Close packing in three dimensions: They can be obtained by stacking the two dimensional layers one above the other. It can be obtained in two ways :

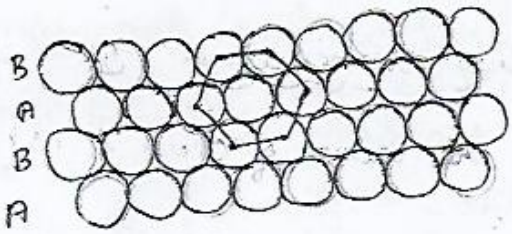
(i) square close packed layers (ii) Hexagonal close packed layers.

- Square close packing :- Here the spheres of the second row are placed exactly above those of first row. This way the spheres are aligned horizontally

as well as vertically. The arrangement is AAA type. The Coordination number is 4.

square close packing

- Hexagonal close packing: Here the spheres of second row are placed above the first one in a staggered manner in such a way that its spheres fit in the depressions of first row. The arrangement is ABAB type. The coordination number is 6.



hexagonal close packing of spheres in two dimensions

- Three dimensional close packing from two dimensional square close packed layers:-

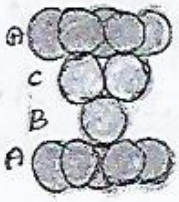
Here the spheres of the upper layer are placed exactly over the first layer such that the spheres of layers are perfectly aligned horizontally and vertically. It has a AAAA type pattern. The lattice is simple cubic lattice

6 Three dimensional close packing from two dimensional close packed layers. There are two steps involved as:

1. Placing the second layer over the first layer
2. Placing the third layer over the second layer.

- Covering the octahedral voids: Here the octahedral voids of second layer may be covered by spheres of third layer. It gives rise to ABCABCABC type pattern. The 3-dimensional structure is called cubic close packed structure or face centered cubic structure. The coordination number is 12. Example Cu, Ag.

Hexagonal arrangement



Cubical arrangement

- Types of voids

Octahedral void :- It is formed at the centre when six spheres are joined in the form of an octahedron

(diagram is drawn) in previous page.

- Formula of a Compound and number of voids filled:

In hcp or ccp arrangement, the octahedral and tetrahedral voids are present. The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral void is twice the number of octahedral voids.

For ex.

If the number of close packed particles = n

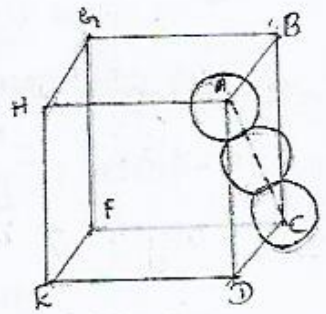
Number of particles present in octahedral voids = n

Then, number of particles present in tetrahedral void = 2n.

Packing efficiency :- It is the percentage of total space filled by the particles.

Packing efficiency in hcp and ccp structures :

Let the unit cell edge length be 'a' and face diagonal AC = b



In Δ ABC

$$AC^2 = b^2 = BC^2 + AB^2$$
$$= a^2 + a^2 = 2a^2$$
$$b^2 = 2a^2$$
$$b = \sqrt{2}a$$

If 'r' is radius of the sphere, then

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

Each unit cell in ccp structure, has 4 spheres.
Total volume of 4 spheres is $4 \times \frac{4}{3}\pi r^3$ and volume of the cube is a^3 or $(2\sqrt{2}r)^3$

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by 4 spheres in unit cell} \times 100}{\text{Total volume of unit cell}}$$

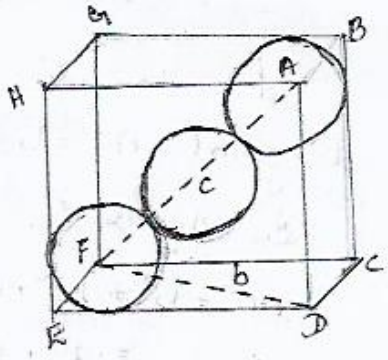
$$= \frac{4 \times \left(\frac{4}{3}\right)\pi r^3 \times 100}{(2\sqrt{2}r)^3} \%$$

$$= \frac{\frac{16}{3}\pi r^3 \times 100}{16\sqrt{2}r^3} \%$$

$$= 74\%$$

Packing efficiency in Body centred cubic structure

In BCC atom at the centre will be in touch with the other two diagonally arranged.



In Δ EFD

$$b^2 = a^2 + a^2 = 2a^2$$

$$b = \sqrt{2}a$$

Now in Δ AFD

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3}a$$

The length of body diagonal $AC = c = 4r$

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

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

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

In BCC, total number of atoms is 2 and their volume is $2 \times \frac{4}{3}\pi r^3$

$$P.E = \frac{\text{vol occupied by two spheres in unit cell} \times 100}{\text{Total vol of unit cell}} \%$$

$$= \frac{2 \times \frac{4}{3}\pi r^3 \times 100}{\left[\frac{4}{\sqrt{3}r}\right]^3} \%$$

$$= \frac{8/3\,\pi r^3 \times 100}{\frac{64}{3\sqrt{3}r^3}} \%$$

$$= 68\ \%$$

Efficiency of packing in Simple cubic lattice

In simple cubic lattice the atoms are located only on the corners of the cube. The particles touch each other along the edge.

Edge length of cube = a

radius of each particle = r

The volume of cubic unit cell = $a^3 = (2r)^3 = 8r^3$

Simple cubic unit cell has only 1 atom

Vol. of occupied space = $4/3 \pi r^3$

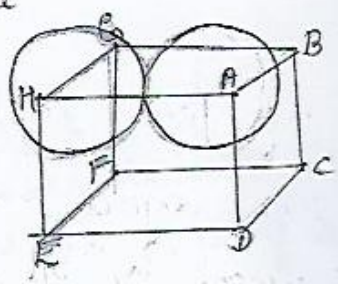
$$P.E = \frac{\text{Vol of one atom} \times 100\%}{\text{Volume of cubic unit cell}}$$

$$= \frac{4/3 \pi r^3 \times 100}{8r^3}$$

$$= \frac{\pi}{6} \times 100$$

$$= 52.36\%$$

$$= 52.4\%$$



Note: CCP and hcp structures have maximum packing efficiency.

Calculations involving Unit cell dimensions

If edge length of unit cell of cubic crystal is 'a'
density of solid substance is 'd'
Molar mass is M.

Then,

Vol of unit cell = a^3

Mass of unit cell = number of atoms in unit cell × mass of each atom

$= Z \times m$

Mass of an atom in unit cell = $m = \frac{M}{N_A}$

∴ density of unit cell = $\frac{\text{mass of unit cell}}{\text{vol of unit cell}}$

$= \frac{Zm}{a^3} = \frac{ZM}{a^3 N_A}$

$$d = \frac{ZM}{a^3 N_A}$$

Imperfections in solids :-

The defects are basically irregularities in the arrangement of constituent particles. It is of 2 types

1. Point defects 2. Line defects.

Point defects :- These are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance

Line defects :- These are the irregularities or deviations from ideal arrangement in entire rows of lattice points.

Different types of point defects :-

(i) stoichiometric defects (ii) impurity defects
(iii) non-stoichiometric defects.

(a) Stochiometric defects :- These point defects do not disturb the stoichiometry of the solid. This is also called intrinsic/ thermodynamic defects

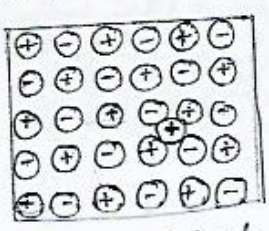
(i) Vacancy defect :- when some of the lattice sites are vacant, the crystal is said to have vacancy defect. This defect decreases the density of substance.

(ii) Interstitial defect :- when some constituent particle occupy an interstitial site, it is said to have interstitial defect. This defect increases the density of the substance.

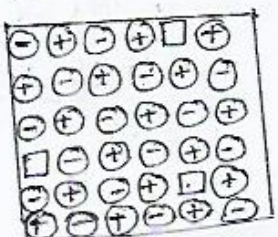
In ionic solids these defects are termed as Frenkel and Schottky defect.

Frenkel defect :- → Smaller ion (cation) is dislocated from its normal site to an interstitial site
→ It is also called dislocation defect.
→ Shown in solids where there is a large difference in size of ions. Eg. ZnS, AgCl, AgBr, AgI
→ no change in density

Schottky defect :-
→ There is a missing of equal number of cations and anions
→ decreases the density of substance.
→ shown by solid in which cation and anion are of almost similar sizes.
→ Eg. NaCl, KCl, CsCl and AgBr



Frenkel defects

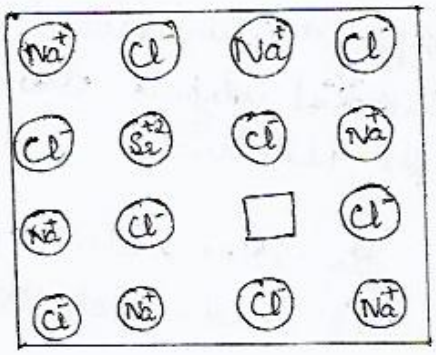


Schottky defects

(b) Impurity defects :-

If molten NaCl containing little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{+2}. Each Sr^{+2} replaces two Na^+ ions, the cationic vacancies are equal in number to that of Sr^{+2} ions

Eg. solid solution of $CdCl_2$ and AgCl.



Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{+2}

(c) Non-stoichiometric defects :-

These defects do not disturb the stoichiometry of crystalline substance.

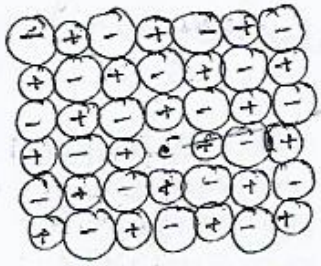
These defects are of two types

(i) metal excess defect (ii) metal deficiency defect

(i) Metal excess defect :-

a) Metal excess defect due to anionic vacancies :-

When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atom are



F-centre

An F-centre in a crystal

deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions. The released electron diffuse into the crystal and occupy anionic sites. As a result the crystal now has an excess of sodium.

→ The anionic sites occupied by unpaired electrons are called F- centres (Farbenzentr for colour centre).

→ They impart yellow colour to the crystals of NaCl.

→ Another Eg. Excess of Li makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac)

(ii) Metal excess defect due to presence of extra cations at interstitial sites.

Eg. Zn oxide is white in colour at room temp. On heating it loses oxygen and turns yellow

$$ZnO \xrightarrow{\Delta} Zn^{+2} + \frac{1}{2}O_2 + 2e^-$$

There is excess of Zn in crystal and formula becomes $Zn_{1+x}O$. The excess of Zn^{+2} moves to interstitial sites and electrons to neighbouring interstitial sites.

b) Metal deficiency defect.

Many solids contain less amount of the metal as compared to stoichiometric proportion. Eg. FeO with composition of $Fe_{0.95}O$

Electrical Properties :-

Solids can be classified into three types on the basis of their conductivities.

(i) Conductors :- The solids with conductivities ranging between $10^4 - 10^7$ $ohm^{-1}m^{-1}$ are called conductors. Metals have conductivities in order of 10^7 $ohm^{-1}m^{-1}$ are good conductors.

(ii) Insulators :- they have low conductivities ranging between $10^{-20} - 10^{-10}$ $ohm^{-1}m^{-1}$

(iii) Semiconductors :- These have conductivities in intermediate range from 10^{-6} to 10^4 $ohm^{-1}m^{-1}$

Conduction of electricity in metals :-

Metallic conductors conduct electricity through movement of electrons.

- They conduct electricity in solid as well as in molten state
- The conductivity depends on the number of valance electrons available per atom

The conduction in metals is explained according to Valence band theory, which says

→ The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to form band

→ If this band is partially filled or it overlaps with high energy unoccupied conduction band, then electrons flow easily under applied electric field then metal shows conductivity

→ If the gap between filled valence band and next higher unoccupied band is large, electrons cannot jump into it, such substances will have very small conductivity and they behave as insulators.

Conduction of electricity in Semi Conductors

In case of semiconductors, gap between the valence band and conduction band is small, therefore some electrons may jump to conduction band and show conductivity.

→ Electrical conductivity of semiconductors increase with rise in temperature as more electrons may jump to conduction band

Ex. Silicon and germanium

→ The conductivity of the intrinsic semiconductors is too low to be of practical use. Their conductivity can be increased by adding appropriate amount of suitable impurity which is called doping