



SOLID STATE

Solids are rigid and have definite shapes.

- Solids have definite volume irrespective of the size or shape of the container in which they are placed.
- Solids are almost incompressible.
- Solids diffuse very slowly as compared to liquids and gases. Constituent particles are very closely packed in solids permitting very little space for their movement.
- Solids have a much higher density (mass to volume ratio) than that of gases and liquids.
- Most solids become liquids when heated. Some undergo sublimation on heating. The temperature at which a solid changes into liquid is called the melting point and the process is called as melting. Due to the varying natures of solids their melting temperatures vary considerably.

CLASSIFICATION OF SOLIDS

Solids are divided into two classes, namely crystalline and amorphous solids.

Amorphous solids: Substances that appear like solids but do not have perfectly ordered crystalline structure and no regular arrangement of constituent particles in structure is called amorphous solids.

Example: Tar, glass, plastic, rubber, butter etc.

General characteristics of Amorphous solids:

- i) Amorphous substances appear like solids but they do not have perfectly ordered crystalline structure, hence they are not real solids.
- ii) An amorphous solid does not have regular arrangement of constituent particles.
- iii) The arrangement of constituent particles like atoms or molecules has only short range order hence periodically repeating regular pattern is only over a short distance.
- iv) Regular patterns are scattered and hence the arrangement is disordered.
- v) Amorphous solids are called supercooled liquids of very high viscosity or pseudo solids.
- vi) Physical properties do not change with change in directions hence amorphous solids are isotropic in nature.
- vii) Amorphous solids behave like fluids and very slowly float under gravity.
- viii) Amorphous solids do not have sharp melting points.
- ix) When cut, they split into pieces with irregular and rough surfaces.

Crystalline solids:

A crystalline solid is a homogeneous solid in which the constituent particles (atoms, ions or molecule) are arranged in a definite repeating pattern.

Example: Diamond, Quartz, NaCl, K₂SO₄ etc.

General characteristics of Crystalline solids:

- i) A crystalline solid is a homogeneous solid in which the constituent particles (i.e. atoms, ions or molecules) are arranged in a definite repeating pattern in all dimensions.
- ii) The total intermolecular force of attraction in crystalline solid is maximum thus imparting maximum stability, the forces responsible for the stability involves ionic bonds, covalent bonds, hydrogen bonds and Van der Waal's forces.
- iii) A crystalline solid usually consist of a large number of small tiny crystals called unit cell, each having a definite characteristic geometrical shape.
- iv) Crystalline solid has regular arrangement of particles which repeats periodically over entire crystal, thus exhibiting short and long range order.



- v) Crystalline solids have sharp melting point, thus have definite heat of fusion.
- vi) Crystalline solids are true solids.
- vii) Crystalline solid on cutting gives a clean cleavage.
- viii) Crystalline solid shows different physical properties in different direction, this type of behavior is called anisotropy and the substances exhibiting this type of behavior are called anisotropic. The properties like electrical conductivity, refractive index, thermal expansion etc. have different value in different direction.
- ix) Two or more crystalline substances having same crystal structure are said to be isomorphous. Isomorphous substance contains constituent atom of same atomic ratio.

Anisotropy:

The ability of crystalline solids to change their physical properties when measured in different directions is called anisotropy.

Explanation: This property is due to different arrangement of constituents in different directions.

Different types of particles fall on the way of measurements in different directions. Hence, the composition of crystalline solids changes with directions changing their physical properties.

Isotropy:

The ability of amorphous solids to have same physical properties when measured in different directions is called isotropy.

Explanation: This property is due to no regular arrangement of particles in any direction. Hence the properties like electrical conductivity, thermal expansion are identical in all the direction.

(1) Difference between crystalline and amorphous solids

Property	Crystalline solids	Amorphous solids
Shape	<i>They have long range order.</i>	<i>They have short range order.</i>
Melting point	They have definite melting point	They do not have definite melting point
Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion
Compressibility	They are rigid and incompressible	These may not be compressed to any appreciable extent
Cutting with a sharp edged tool	They are given cleavage <i>i.e.</i> they break into two pieces with plane surfaces	They are given irregular cleavage <i>i.e.</i> they break into two pieces with irregular surface
Isotropy and Anisotropy	<i>They are anisotropic</i>	<i>They are isotropic</i>
Volume change	There is a sudden change in volume when it melts.	There is no sudden change in volume on melting.
Symmetry	These possess symmetry	These do not possess any symmetry.



Interfacial angles	These possess interfacial angles.	These do not possess interfacial angles.
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(2) **Classification of solids** : Depending upon the nature of interparticle forces the solids are classified into four types :

Types of Solid	Constituents	Bonding	Examples	Physical Nature	M.P.	B.P.	Electrical Conductivity
Ionic	Positive and negative ions network systematically arranged	Coulombic	<i>NaCl, KCl, CaO, MgO, LiF, ZnS, BaSO₄ and K₂SO₄</i> etc.	Hard but brittle	High ($\approx 1000K$)	High ($\approx 2000K$)	Conductor (in molten state and in aqueous solution)
Covalent	Atoms connected in covalent bonds	Electron sharing	<i>SiO₂ (Quartz), SiC, C (diamond), C(graphite)</i> etc.	Hard Hard Hard	Very high ($\approx 4000K$)	Very high ($\approx 5000K$)	Insulator except graphite
Molecular	Polar or non-polar molecules	(i) Molecular interactions (intermolecular forces) (ii) Hydrogen bonding	<i>I₂, S₈, P₄, CO₂, CH₄, CCl₄</i> etc. Starch, sucrose, water, dry ice or drikold (solid <i>CO₂</i>) etc.	Soft Soft	Low ($\approx 300K$ to $600K$) Low ($\approx 400K$)	Low (≈ 450 to $800K$) Low ($\approx 373K$ to $500K$)	Insulator Insulator
Metallic	Cations in a sea of electrons	Metallic	Sodium, <i>Au, Cu</i> , magnesium, metals and alloys	Ductile malleable	High ($\approx 800K$ to $1000K$)	High ($\approx 1500K$ to $2000K$)	Conductor
Atomic	Atoms	London dispersion force	Noble gases	Soft	Very low	Very low	Poor thermal and electrical conductors

TERMS AND CONCEPTS

Space lattice or crystal lattice:

It may be defined as a regular three-dimensional arrangement of constituent particles of a solid substance in space.

The positions which are occupied by atoms, ions or molecules in the crystal lattice are called lattice points or lattice sites.



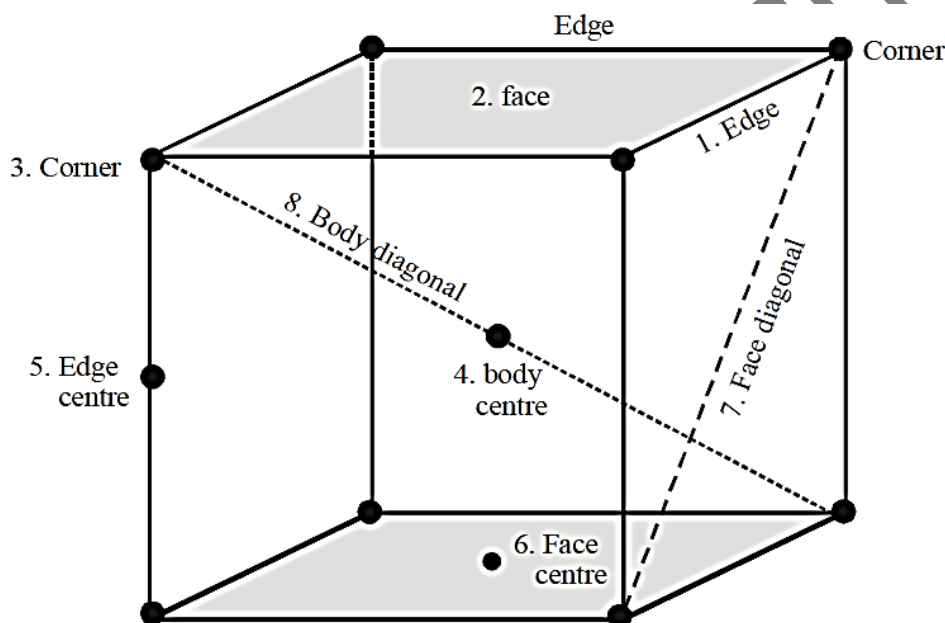
Characteristics of Crystal lattice:

1. Lattice points or lattice sites: The crystal lattice of a substance is represented by showing the position of the particle in space. These positions are represented by points and are referred to as Lattice points.
2. Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.
3. Lattice points are joined by straight lines to bring out the geometry of the molecule.

Unit Cell: It is the smallest portion of a crystal lattice which, when repeated in three dimensions produces crystal lattice.

Characteristics of Unit cell: A unit cell is characterized by following parameters,

1. Edges or edge length: The intersection of two faces of crystal lattice is called as edge. The three edges denoted by a , b and c represent the dimensions (lengths) of the unit cell along three axes. These edges may or may not be mutually perpendicular.
2. Angles between the edges (or planes): There are three angles between the edges of the unit cell represented as α , β and γ . The crystal is defined with the help of these parameters of its unit cell.
 - a) The angle α is between edges b and c .
 - b) The angle β is between edges a and c .
 - c) The angle γ is between edges a and b .



A space lattice can be sub-divided into a number of small cells known as unit cells. It can be defined as the smallest block from which entire crystal can be built up by its translational repetition in three dimensions

- 1) Total number of edges in a cube = 12
- 2) Total number of faces in a cube = 6
- 3) Total number of corners in a cube = 8
- 4) Total number of body centre in a cube = 1
- 5) Total number of face diagonals in a cube = $6 \times 2 = 12$
- 6) Total number of body diagonals in a cube = 4

TYPES OF LATTICES AND TYPES OF UNIT CELL

Unit Cells are of two types: Primitive & Non-primitive.



(i) Primitive or simple Unit Cells: In a primitive unit cell, the same type of particles is present at all the corners of the unit cell.

(ii) Non-primitive or centered unit cells:

There are three types of non-primitive unit cells as follows:

(a) Face Centered: When atoms are present in all 8-corners and six face centers in a cubic unit cell then this arrangement is known as FCC.

(b) Body Centered(BCC): When atoms are present at 8 corners as well as in the body centre in a cubic unit cell then this arrangement is known as BCC.

(c) End-Centered: In addition to particles at the corners, there are particles at the centers of two opposite faces.

(2) Number of atoms per unit cell/Unit cell contents : The total number of atoms contained in the unit cell for a simple cubic called the unit cell content.

(i) Simple cubic structure (sc) : Each corner atom is shared by eight surrounding cubes. Therefore, it contributes for $\frac{1}{8}$ of an atom. $\therefore Z = 8 \times \frac{1}{8} = 1$ atom per unit cell in crystalline solid.

(ii) Face centered cubic structure (fcc) : The eight corners atoms contribute for $\frac{1}{8}$ of an atom and thus one atom per unit cell. Each of six face centred atoms is shared by two adjacent unit cells and therefore one face centred atom contribute half of its share. $\therefore Z = 6 \times \frac{1}{2} = 3$ atom per unit cell.

So, total $Z = 3 + 1 = 4$ atoms per unit cell.

(iii) Body centered cubic structure (bcc) : Eight corner atoms contribute one atom per unit cell.

Centre atom contribute one atom per unit cell. So, total $1 + 1 = 2$ atoms per unit cells.

$$Z = 8 \times \frac{1}{8} + 1 = 2$$

Cubic unit cell	n_c	n_f	n_i	Total atom in per unit cell
Simple cubic (sc)	8	0	0	1
body centered cubic (bcc)	8	0	1	2
Face centered cubic (fcc)	8	6	0	4



Unit cell	Distance between nearest neighbour (d)	Radius (r)
Simple cubic	a	$\frac{a}{2}$
Face centred cubic	$\frac{a}{\sqrt{2}}$	$\frac{a}{2\sqrt{2}}$
Body centred cubic	$\frac{\sqrt{3}}{2} a$	$\frac{\sqrt{3}}{4} a$

(1) **Close packing in crystalline solids** : In the formation of crystals, the constituent particles (atoms, ions or molecules) get closely packed together. The closely packed arrangement is that in which maximum available space is occupied. This corresponds to a state of maximum density. The closer the packing, the greater is the stability of the packed system. It is of two types :

(i) **Close packing in two dimensions** : The two possible arrangement of close packing in two dimensions.

(a) **Square close packing** : In which the spheres in the adjacent row lie just one over the other and show a horizontal as well as vertical alignment and form square. Each sphere in this arrangement is in contact with four spheres.

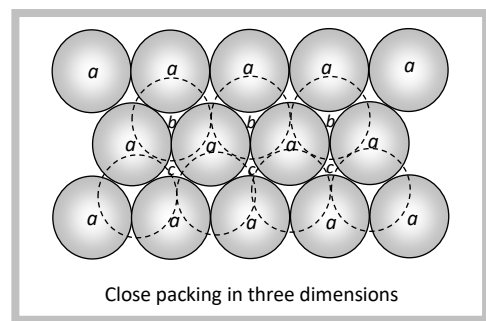
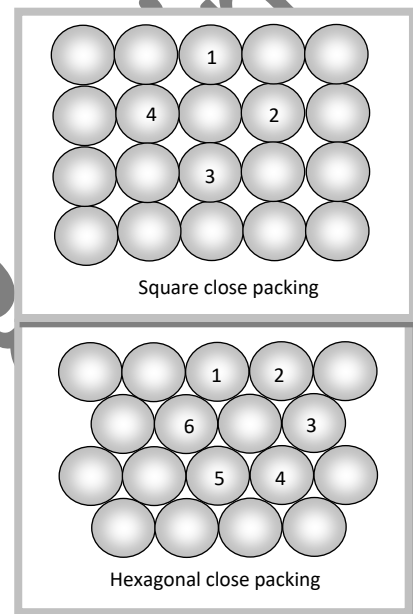
(b) **Hexagonal close packing** : In which the spheres in every second row are seated in the depression between the spheres of first row. The spheres in the third row are vertically aligned with spheres in first row. The similar pattern is noticed throughout the crystal structure. Each sphere in this arrangement is in contact with six other spheres.

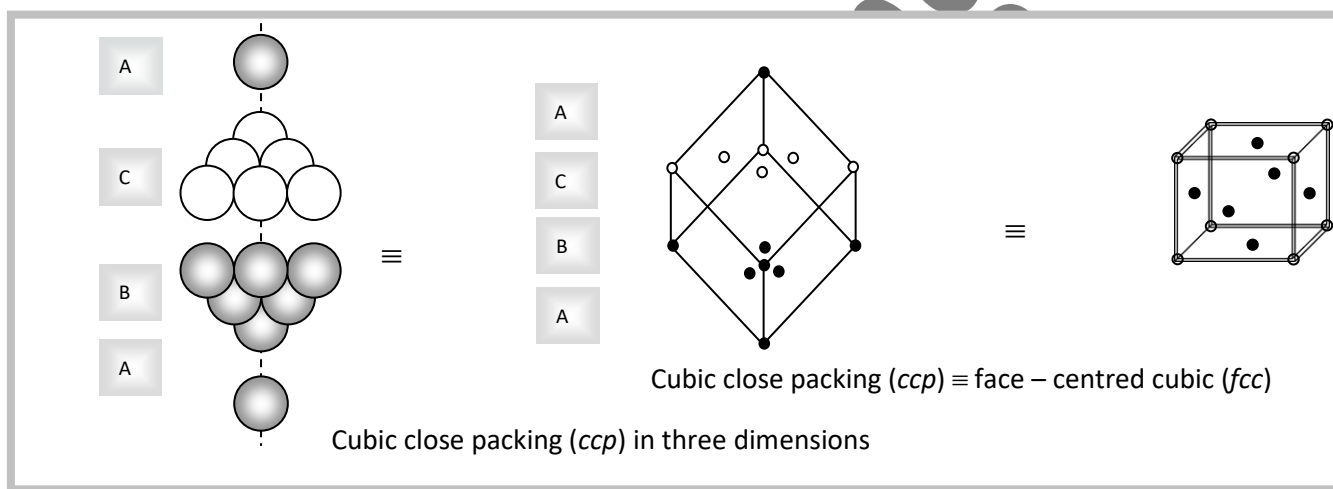
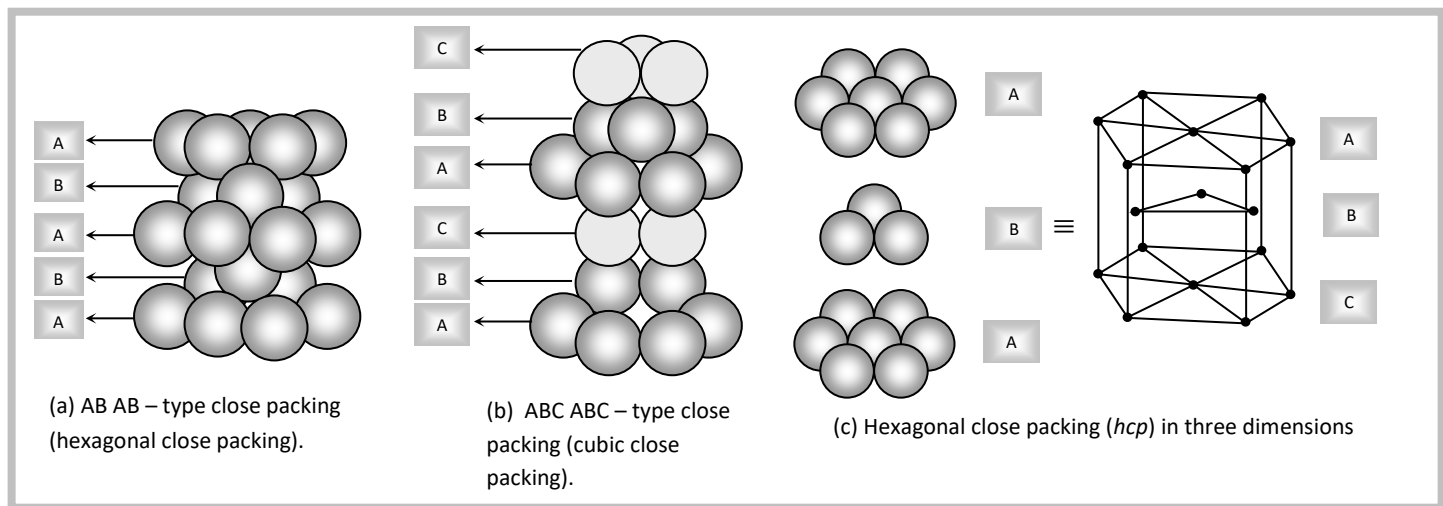
(ii) **Close packing in three dimensions** : In order to develop three dimensional close packing, let us retain the hexagonal close packing in the first layer. For close packing each spheres in the second layer rests in the hollow at the centre of three touching spheres in the layer as shown in figure. The spheres in the first layer are shown by solid lines while those in second layer are shown by broken lines. **It may be noted that only half the triangular voids in the first layer are occupied by spheres in the second layer (i.e., either b or c).** The unoccupied hollows or voids in the first layer are indicated by (c) in figure.

There are two alternative ways in which species in third layer can be arranged over the second layer,

(a) **Hexagonal close packing** : The third layer lies vertically above the first and the spheres in third layer rest in one set of hollows on the top of the second layer. This arrangement is called **ABAB** type and 74% of the available space is occupied by spheres. This arrangement is found in *Be, Mg, Zn, Cd, Sc, Y, Ti, Zr*.

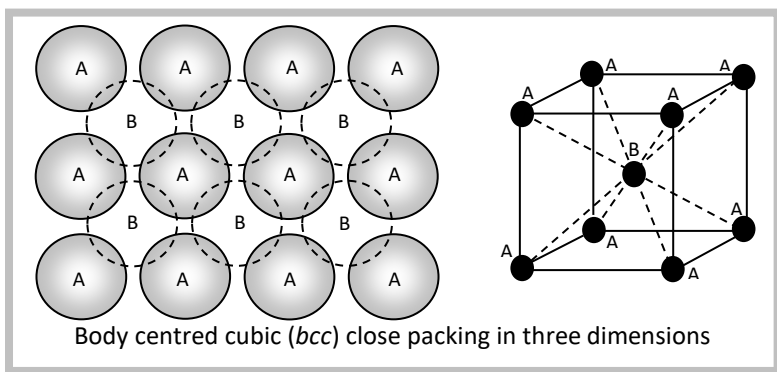
(b) **Cubic close packing** : The third layer is different from the first and the spheres in the third layer lie on the other set of hollows marked 'C' in the first layer. This arrangement is called **ABCABC.....** type and in this also 74% of the available space is occupied by spheres. The cubic close packing has face centred cubic (*fcc*) unit cell.





This arrangement is found in *Cu, Ag, Au, Ni, Pt, Pd, Co, Rh, Ca, Sr*.

(c) **Body centred cubic (bcc)** : This arrangement of spheres (or atoms) is not exactly close packed. This structure can be obtained if spheres in the first layer (A) of close packing are slightly opened up. As a result none of these spheres are in contact with each other. The second layer of spheres (B) can be placed on top of the first layer so that each sphere of the second layer is in contact with four spheres of the layer below it. Successive building of the third will be exactly like the first layer. If this pattern of building layers is repeated infinitely we get an arrangement as shown in figure. This arrangement is found in *Li, Na, K, Rb, Ba, Cs, V, Nb, Cr, Mo, Fe*.



(2) Comparison of *hcp*, *ccp* and *bcc*



Property	Hexagonal close packed (<i>hcp</i>)	Cubic close packed (<i>ccp</i>)	Body centred cubic (<i>bcc</i>)
Arrangement of packing	Close packed	Close packed	Not close packed
Type of packing	AB AB AB A.....	ABC ABC A....	AB AB AB A.....
Available space occupied	74%	74%	68%
Coordination number	12	12	8
Malleability and ductility	Less malleable, hard and brittle	Malleable and ductile	

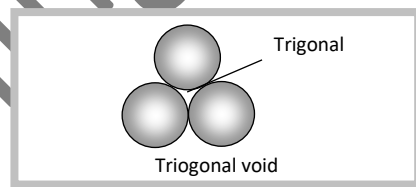
(3) **Interstitial sites in close packed structures** : Even in the close packing of spheres, there is left some empty space between the spheres. This empty space in the crystal lattice is called site or void or hole. Voids are of following types

(i) **Trigonal void** : This site is formed when three spheres lie at the vertices of an equilateral triangle. Size of the trigonal site is given by the following relation.

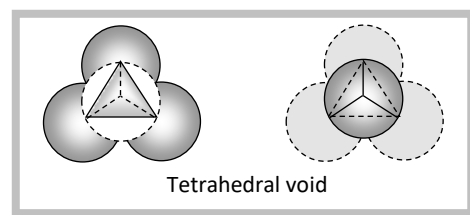
$$r = 0.155 R$$

where, r = Radius of the spherical trigonal site

R = Radius of closely packed spheres



(ii) **Tetrahedral void** : A tetrahedral void is developed when triangular voids (made by three spheres in one layer touching each other) have contact with one sphere either in the upper layer or in the lower layer. This type of void is surrounded by four spheres and the centres of these spheres lie at the apices of a regular tetrahedron, hence the name tetrahedral site for this void.

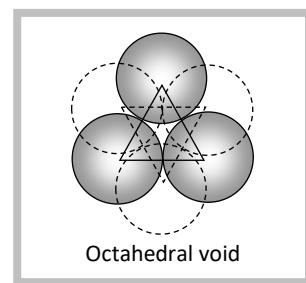


In a close packed structure, there are two tetrahedral voids associated with each sphere because every void has four spheres around it and there are eight voids around each sphere. **So the number of tetrahedral voids is double the number of spheres in the crystal structure.** The maximum radius of the atoms which can fit in the tetrahedral voids relative to the radius of the sphere is calculated to be 0.225: 1. *i.e.*.

$$\frac{r}{R} = 0.225$$

where r is the radius of the tetrahedral void or atom occupying tetrahedral void and R is the radius of spheres forming tetrahedral void.

(a) **Octahedral void** : This type of void is surrounded by six closely packed spheres, *i.e.* it is formed by six spheres. Out of six spheres, four are placed in the same plane touching each other, one sphere is placed from above and the other from below the plane of these spheres. These six spheres surrounding the octahedral void are present at the vertices of regular octahedron. **Therefore, the number of octahedral voids is equal to the number of spheres.** The ratio of the radius (r) of the atom or ion which can exactly



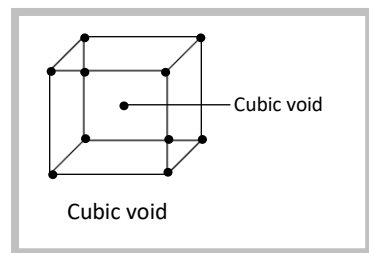


fit in the octahedral void formed by spheres of radius R has been calculated to be 0.414, i.e.

$$\frac{r}{R} = 0.414$$

(b) **Cubic void** : This type of void is formed between 8 closely packed spheres which occupy all the eight corner of cube i.e. this site is surrounded by eight spheres which touch each other. Here radius ratio is calculated to be 0.732, i.e.

$$\frac{r}{R} = 0.732$$



Thus, the decreasing order of the size of the various voids is

Cubic > Octahedral > Tetrahedral > Trigonal

Important Tips

At the limiting value of radius ratio r^+ / r^- , the forces of attraction & repulsion are equal.

- ☞ The most malleable metals (Cu, Ag, Au) have cubic close packing.
- ☞ Cubic close packing has fcc (face centred cubic) unit cell
- ☞ Number of octahedral voids = Number of atoms present in the closed packed arrangement.
- ☞ Number of tetrahedral voids = $2 \times$ Number of octahedral voids = $2 \times$ Number of atoms.

PACKING EFFICIENCY

Packing efficiency is the % of total space occupied by particles.

Packing efficiency (P. E.) of simple unit cell

$$P.E. = \frac{\text{Volume occupied by atoms present in unit cell}}{\text{Volume of unit cell}} = \frac{n \times \frac{4}{3} \pi r^3}{V} \quad \left[\because \text{Volume of atom} = \frac{4}{3} \pi r^3 \right]$$

$$\text{For SCC : } P.E. = \frac{1 \times \frac{4}{3} \times \pi \times \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 0.524 \text{ or } 52.4\% \quad [\because r = \frac{a}{2} \text{ and } V = a^3, n = 1]$$

Packing efficiency of Body centred cubic (b.c.c.) cell :

$$P.E. = \frac{n \times \frac{4}{3} \pi r^3}{V} = \frac{2 \times \frac{4}{3} \times \pi \left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \quad [\because n = 2, r = \frac{\sqrt{3}a}{4}, V = a^3]$$



In B.C.C. 68% of total volume is occupied by atoms or ions.

Packing efficiency of Face centred cubic (f.c.c.) cell

$$P.E. = \frac{n \times \frac{4}{3} \pi r^3}{V} = \frac{4 \times \frac{4}{3} \pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\% \quad [\because n=4, r=\frac{a}{2\sqrt{2}}, V=a^3]$$

i.e. In FCC, 74% of total volume is occupied by atoms.

S. No.	Crystal Structure	Brief description	Examples	Co-ordination number	Number of formula units per unit cell
1.	Type AB Rock salt (NaCl) type	It has fcc arrangement in which Cl^- ions occupy the corners and face centres of a cube while Na^+ ions are present at the body and edge of centres.	Halides of Li, Na, K, Rb, AgF, AgBr, NH_4Cl , NH_4Br , NH_4I etc.	$Na^+ = 6$ $Cl^- = 6$	4
2.	Zinc blende (ZnS) type	It has ccp arrangement in which S^{2-} ions form fcc and each Zn^{2+} ion is surrounded tetrahedrally by four S^{2-} ions and vice versa.	$CuCl$, $CuBr$, CuI , AgI , BeS	$Zn^{2+} = 4$ $S^{2-} = 4$	4
3.	Type AB_2 Fluorite (CaF_2) type	It has arrangement in which Ca^{2+} ions form fcc with each Ca^{2+} ions surrounded by 8 F^- ions and each F^- ions by 4 Ca^{2+} ions.	BaF_2 , $BaCl_2$, SrF_2 $SrCl_2$, CdF_2 , PbF_2	$Ca^{2+} = 8$ $F^- = 4$	4
4.	Antifluorite type	Here negative ions form the ccp arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion by 8 positive ions	Na_2O	$Na^+ = 4$ $O^{2-} = 8$	4
5.	Caesium chloride ($CsCl$) type	It has the bcc arrangement with Cs^+ at the body centre and Cl^- ions at the corners of a cube or vice versa.	$CsCl$, $CsBr$, CsI , $CsCN$, $TlCl$, $TlBr$, TlI and $TlCN$	$Cs^+ = 8$ $Cl^- = 8$	1



$$\star \text{ Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\star \text{ Mass of unit cell} = \frac{Z \times M}{N_a}$$

$$\star \text{ Volume of unit cell} = a^3$$

$$\star \text{ Density of unit cell} = \left(\frac{Z \times M}{N_a} \right) / a^3$$

$$\star \text{ Density of unit cell} = \frac{Z \times M}{N_a \times a^3}$$

1 mole of gold = 197 g = 6.02×10^{23}

Hence, No. of atoms present in 1 g of gold = $\frac{6.02 \times 10^{23}}{197}$

As face – centered cubic unit cell contains 4 atoms,

therefore, number of unit cells present = $\frac{6.02 \times 10^{23}}{197 \times 4} = 7.64 \times 10^{20}$

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