

ToppersNotes

CBSE

CLASS-XII

CHEMISTRY

SAMPLE BOOK

Sierra Innovations Pvt. Ltd.

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The Solid State

Chapter 1

- Solids are of 2 types -
1. Amorphous
 2. Crystalline

COMPARISON

Property	Crystalline Solids	Amorphous Solids
Shape	Definite characteristic geometrical shape	Irregular shape.
Melting pt.	Melt at a sharp & characteristic temperature.	Gradually softens over a range of temp.
Fracture property	When cut with a sharp edge or tool, they split into pieces and new planes are smooth.	When they are cut, they split into irregular pieces.
Heat of fusion	They have characteristic heat of fusion.	They do not have heat of fusion.
Isotropy	Anisotropic nature	Isotropic nature.
Order of arrangement	Long range order	Only short range order.
Nature	True solid	Pseudo solid.

ANISOTROPIC

They are those in which some of the physical properties like electrical resistance, R.T. show diff. properties in diff. directⁿ in the same crystal. Crystalline solids are anisotropic because they have regular arrangement of particles, so particle may differ from particles lying in other directⁿ.

ISOTROPIC

They are those in which physical prop. have same value along all directⁿ. Amorphous have no long

ordered arrangement, so these are isotropic

Ques. Some glass from an ancient monuments are found to be milky. why?

ans. amorphous solids become crystalline at ~~room~~ ^{some} temp. since glass is amorphous, its crystallisation takes place to some extent during long period which make them milky.

Ques. Glass fixed to old windows are thicker at bottom & thinner at top. why?

ans. Like liquids, amorphous solids have tendency to flow but very slowly. Hence glass flows from upper part to the down under the action of gravity, making it thicker.

Ques. Name amorphous solid used in photovoltaic cell?

ans. amorphous silicon is used to convert sunlight into electricity, so it is called photovoltaic material.

TYPES OF SOLIDS

1. Molecular solid
2. Ionic solid
3. Metallic solid
4. Covalent or Network solid

type of solid	Constituent Particles	Bonding/Attractive forces	Examples	Physical Nature	Electric conductivity	Mel
1. Molecular						
(i) Non-polar	Molecules	Dispersion or London force	$Ar, CCl_4, H_2, I_2, CO_2$	Soft	Insulator	very low
(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator in solid, conductor in liquid	low
2. Ionic	Ions	Coulombic or electrostatic force	$NaCl, MgO, ZnS, CaF_2$	Hard & brittle	Insulator in solid and conductor in liquid	High
3. Metallic Solids	+ve ions in a sea of delocalised e^-	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable & ductile	conductor in solid & liquid	Fairly high
4. Covalent or network Solids	Atoms	Covalent bonding	SiO_2 (quartz) → Hard SiC, C (diamond) → Hard AlN (graphite) → soft	Hard	Insulator (exception) conductor	Very high

LATTICE

The three dimensional arrangement of particles is called lattice. Each particle of lattices is called lattice point. The small arrangement of lattice point which on repetition generates complete lattice is called unit cell.

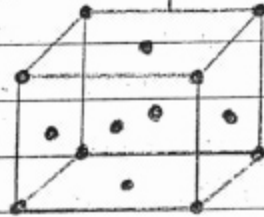
TYPES OF UNIT CELL

1. Primitive or Simple Cubic - In this unit cell, one particle is present at each corner

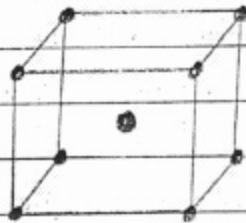


2. Centered - It is of foll. types -

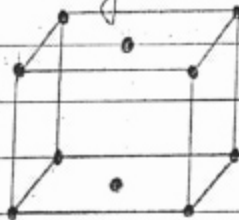
→ FACE CENTERED - One particle is present at each face along with corner particles.



→ BODY CENTERED - One particle is present at center of cube along with corner particles.



→ END CENTERED - One particle is present at each two opp. faces along with corner particles.



CONTRIBUTION OF PARTICLES IN UNIT CELLS

Particles at corner = $\frac{1}{8}$

Particles at edge = $\frac{1}{4}$

Particles at face = $\frac{1}{2}$

Particles at body = 1

CALCULATION OF NUMBER OF PARTICLES AT UNIT CELL (Z)

In simple unit cell

$$8 \text{ corners} \times \frac{1}{8} = 1$$

$$\text{Face centered } (8 \text{ corners} \times \frac{1}{8}) + (6 \text{ faces} \times \frac{1}{2}) = 4$$

$$\text{End centered } (8 \text{ corners} \times \frac{1}{8}) + (2 \text{ faces} \times \frac{1}{2}) = 2$$

$$\text{Body centered } (8 \text{ corners} \times \frac{1}{8}) + (1 \text{ body} \times 1) = 2$$

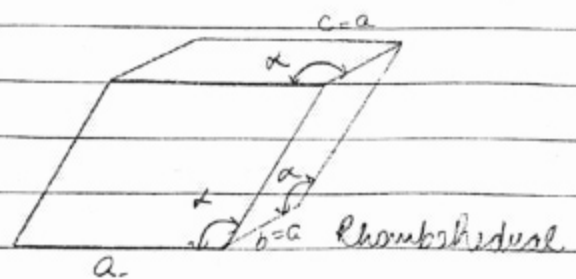
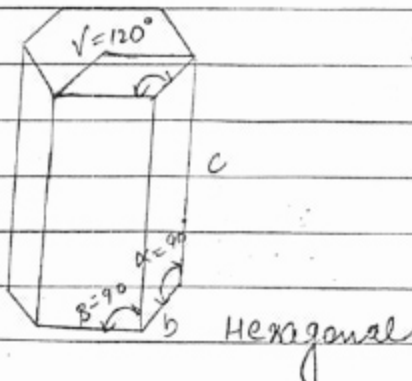
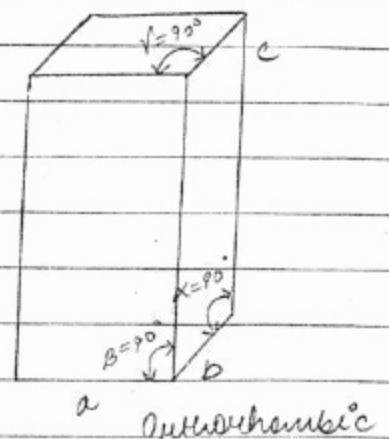
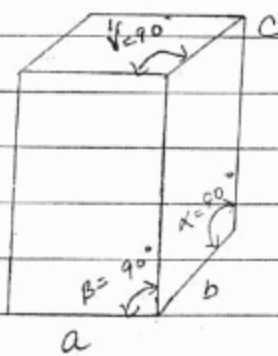
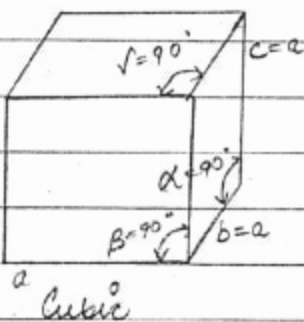
Seven types of unit cells exist namely-

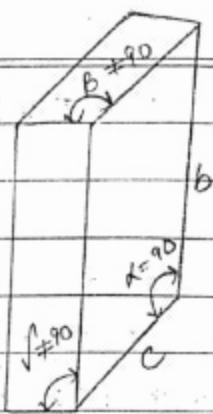
1. Cubic
2. Tetragonal
3. Orthorhombic
4. Rhombohedral
5. Monoclinic
6. Triclinic
7. Hexagonal

most symmetric \rightarrow cubic

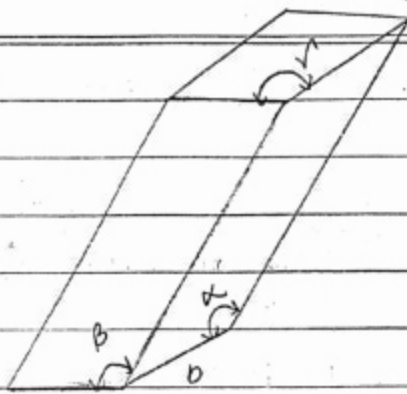
most unsymmetric \rightarrow triclinic

these 7 types of unit cells result in only 14 types lattices called Bravais lattice.





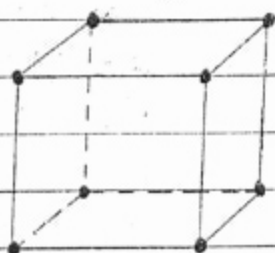
Monoclinic



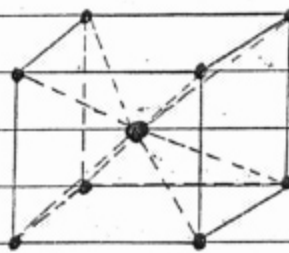
Triclinic

Seven types of unit cells

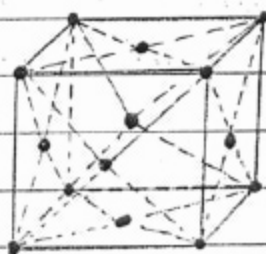
→ Unit cells of 14 types of Bravais lattice



Primitive (or simple)



body centered

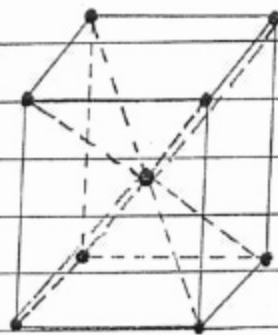


face centered

The three cubic lattices - all sides of same length
angles b/w all faces 90° .

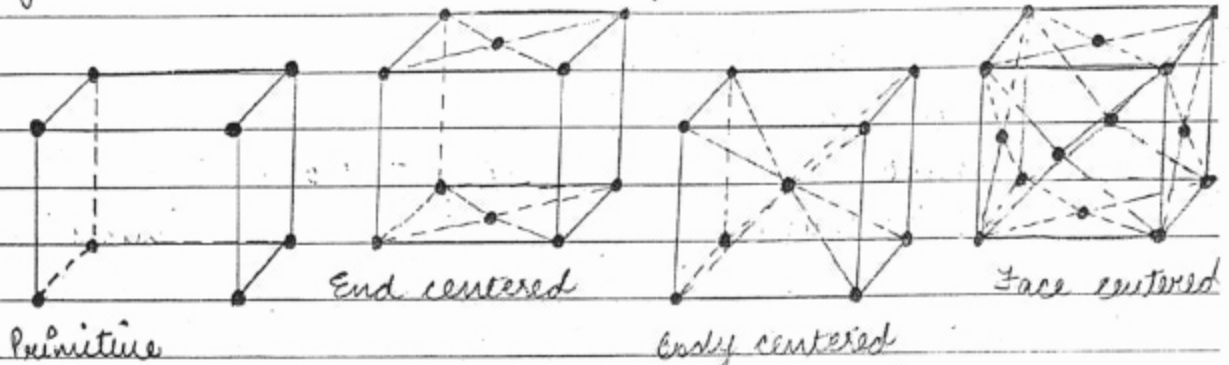


Primitive

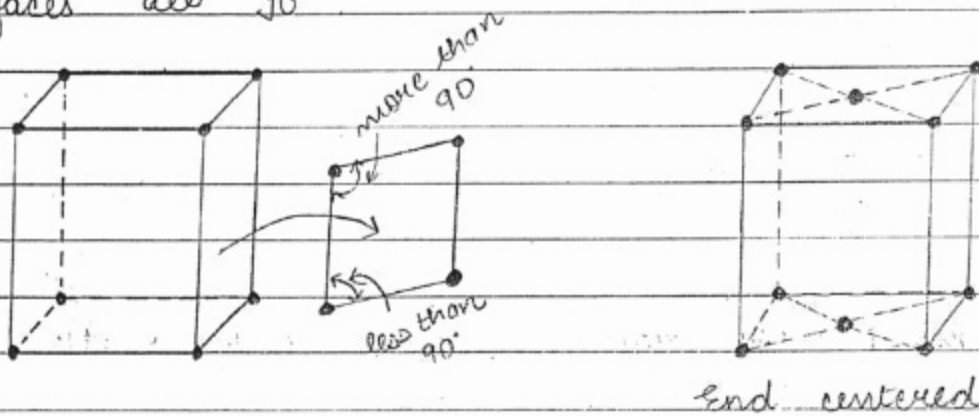


body centered

The two tetragonal lattices - one side different in length to the other two angles b/w faces 90° .



4 orthorhombic lattices = unequal sides, angles b/w faces all 90°



The two monoclinic lattices: unequal sides two faces have angles different from 90° .

CLOSE PACKING IN ONE DIMENSION

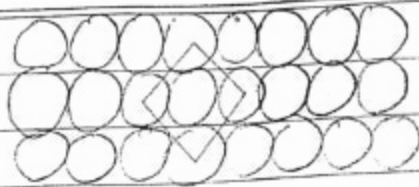
In one dimension, particles can be packed by arranging them in a row.



co-ordination no. = 2

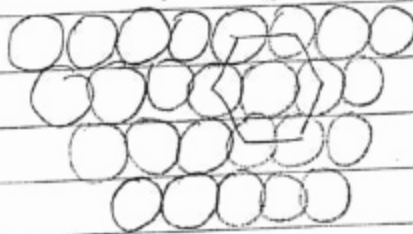
CLOSE PACKING IN TWO DIMENSION

1. Square closed packing - there is arrangement of sphere in vertical as well as horizontal rows. Efficiency is 52.4% .



co-ordination no. - 4

2. Hexagonal close packing - Spheres of IInd row are in depressions of Ist row, similarly, spheres of IIIrd row are in depressions of IInd row. Efficiency is 60.4%



co-ordination no. = 6

CLOSED PACKING IN THREE (3) DIMENSION

- (1) Square closed - Square closed packing of 2-dimension is repeated ^{packing} 1 over the other to form the lattice. In this simple cubic unit cell is present.

as layers are same, this arrangement is called 'AAA' arrangement.

- (2) Hexagonal close packing - Spheres of first layer are arranged in HCP and spheres of IInd layer lie in the depression of Ist layer.

The spheres of IIIrd layer are above IInd layer in such a manner that Ist and IIIrd layers spheres coincide.

Hence, Ist and IIIrd layers are same. Similarly, IInd & IVth layers are same.

If Ist layer is 'A', IInd is B, then third is A and packing is called ABAB..... of hexagonal closed packing. Efficiency is 74%. Coordination no. = 12
Unit cell = Hexagonal

CUBIC CLOSED PACKING

First and second layers are same, as in HCP but spheres of third layer lies over the voids, which are present in both Ist & IInd layer both. Hence, third layer is different. This is called ABC ABC closed packing or cubic closed packing. Coordination no. = 12
Efficiency = 74% Unit cell = FCC

INTERSTITIAL VOIDS

Space remained unoccupied by solid particles is called interstitial void. It is of foll. types-

1. Cubic void - It is present in simple cubic structure AAA. It is surrounded by 8 spheres.
2. Tetrahedral void - In HCP, sphere in second layer is placed over 3 spheres of 1st layer. The space among these four layers touching each other is called tetrahedral void. It is surrounded by 4 spheres.
3. Octahedral void - In CCP (ABC ABC) all the voids of Ist layer are not occupied by the spheres of IInd layer of ~~the~~ layer, so there is void which is in Ist as well as IInd layer. It is surrounded by 6 particles.
No. of octahedral voids are equal to no. of spheres, but no. of tetrahedral void is double

\therefore No. of spheres = $4N$
 No. of tetrahedral voids = $8N$
 \therefore No. of tetrahedral void = $2N$
 Total voids = $3N$

POSITION OF VOIDS

In FCC tetrahedral voids are at body diagonals. Each body diagonal contains two tetrahedral voids.

As there are 4 body diagonals, so, tetrahedral voids are 8.

No. of spheres in FCC is only 4, hence, no. of tetrahedral voids is double the no. of spheres.

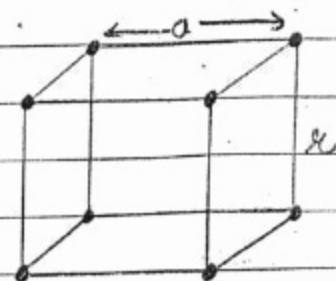
Octahedral voids are at each H also at body centre. 12H voids make three complete voids. Now including body centre voids, there are 4 voids.

In FCC, 4 spheres are there and 4 voids are present i.e. there are equal no. of voids and spheres.

CALCULATION OF EFFICIENCY OF VARIOUS UNIT CELLS

- Simple cubic - Let us consider a unit cell with edge length 'a' and radius of sphere 'r', then it will be $2r$ because all 4 corner spheres touch each other.

$$\begin{aligned}
 a &= 2r \\
 \text{Vol of unit cell} &= (\text{edge})^3 \\
 &= a^3 \\
 &= (2r)^3 = 8r^3
 \end{aligned}$$



$$\begin{aligned} \text{Vol. occupied by sphere} &= \text{Vol. of 1 sphere} \times \text{no. of spheres} \\ &= \frac{4}{3} \pi r^3 \times 1 = \frac{4}{3} \pi r^3 \end{aligned}$$

$$\begin{aligned} \text{efficiency} &= \frac{\text{vol. occupied}}{\text{Total Volume}} \times 100 = \frac{\frac{4}{3} \pi r^3}{28r^3} \times 100 \\ &= 52.4\% \end{aligned}$$

x [Let us consider a unit cell with edge length 'a' and length radius of sphere 'r' then will be 2r because all corners spheres touch each other] x

2. Body centered (BCC) - let us consider a BCC having edge 'a' and radius is r. The sphere at body centre will touch above and below corners spheres such that body diagonal consists of 4r.

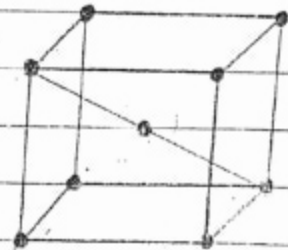
$$\text{Body diagonal} = \sqrt{3}a \quad \text{--- (1)}$$

$$\text{Body diagonal} = 4r \quad \text{--- (2)}$$

From (1) & (2)

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

$$a = \frac{4r}{\sqrt{3}} \quad \text{--- (3)}$$



$$\begin{aligned} \text{Vol. of unit cell} &= a^3 \\ &= \left(\frac{4r}{\sqrt{3}} \right)^3 = \frac{64r^3}{3\sqrt{3}} \end{aligned}$$

$$\begin{aligned} \text{Vol. occupied by sphere} &= \text{Vol. of 1 sphere} \times \text{No. of spheres} \\ &= \frac{4}{3} \pi r^3 \times 2 = \frac{8\pi r^3}{3} \end{aligned}$$

$$\text{Efficiency} = \frac{\text{Vol. occupied}}{\text{Total vol.}} \times 100$$

$$\begin{aligned} &= \frac{8\pi r^3}{3} \times 100 \\ &= \frac{8\pi r^3}{\frac{64r^3}{3\sqrt{3}}} \times 100 = 68\% \end{aligned}$$

3. Face centered (FCC) - let us consider FCC has edge length 'a' and radius 'r'. Here, face centered particles will touch 4 corner particles but corner particles will not touch each other. Hence, face diagonals will consist of 4r

$$\text{Face diagonal} = \sqrt{2}a \quad \text{--- (1)}$$

$$\text{Face diagonal} = 4r \quad \text{--- (2)}$$

From (1) & (2)

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

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

$$\text{Vol. of unit cell} = a^3$$

$$= \left(\frac{4r}{\sqrt{2}}\right)^3 = \frac{64r^3}{2\sqrt{2}}$$

$$\begin{aligned} \text{Vol. occupied by sphere} &= \text{Vol. of 1 sphere} \times \text{No. of spheres} \\ &= \frac{4}{3}\pi r^3 \times 4 = \frac{16}{3}\pi r^3 \end{aligned}$$

$$\text{Efficiency} = \frac{\text{Vol. occupied}}{\text{Total vol.}} \times 100$$

$$= \frac{\frac{16\pi r^3}{3}}{\frac{64r^3}{2\sqrt{2}}} = \frac{16 \times 2\sqrt{2} \times \pi}{3 \times 64} = \frac{\pi}{3\sqrt{2}}$$

RELATION B/W EDGE OF CUBE, RADIUS OF SPHERE & DISTANCE B/W NEAREST NEIGHBOUR

1. Simple cube = In this all four corner spheres are in contact with each other, so the edge will be twice the radius of sphere.
Edge = a = 2r \therefore a = 2r

The two spheres of corner are in contact with each other, hence the distance between their centres is $2r$.
 So, the face diagonal = $4r$.

2. Face centered (FCC) = In this face sphere touches corner, touch each other so the distance is 4 times the radius. If edge length is a , then diagonal is $\sqrt{2}a$.

$$\text{Face diagonal} = \sqrt{2}a$$

$$\text{--- } 4r \text{ ---} = 4r$$

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

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

$$\begin{aligned} \text{Nearest neighbour} = d &= \frac{1}{2} \times \text{diagonal} \\ &= \frac{1}{2} \times \sqrt{2}a = \frac{\sqrt{2}a}{2} \end{aligned}$$

$$\text{Moreover} = d = 2r$$

3. Body centered (BCC) = In this body sphere touches corner sphere, hence, body sphere and corner spheres will be nearest neighbour.

$$\text{Body diagonal} = \sqrt{3}a$$

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

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

$$\text{Nearest neighbour} = d = \frac{1}{2} \times \text{body diagonal}$$

$$= \frac{1}{2} \times \sqrt{3}a = \frac{\sqrt{3}a}{2}$$

$$\text{Moreover} = d = 2r$$

It is the ratio of radius of void to the radius of sphere. In ionic compound it is ratio of



radius of sphere and radius

radius of void = radius of sphere

radius of sphere

Triangular void - It is surrounded by 3 spheres, hence its co-ordination no. is 3. Its radius ratio is 0.155. If the size of the void increases, the spheres will slightly separate from each other, thus the spheres touching each other will move nearer to in contact with each other and structure will open a bit, further increment in size will allow four spheres to surround a void and hence, it will result in tetrahedral voids.

5. Tetrahedral voids - It is surrounded by 4 spheres, hence, its co-ordination no. is 4. Radius ratio is 0.225. If size of tetrahedral void increases, it leads to opening of structure & results in octahedral void.

6. Octahedral void - It is surrounded by 6 spheres hence, co-ordination no. is 6. Radius ratio is 0.414

7. Cubic void - Surrounded by 8 spheres, so co-ordination no. is 8. Radius ratio is 0.732

Type of void	radius ratio
Triangular	0.155 - 0.225
Tetrahedral	0.225 - 0.414
Octahedral	0.414 - 0.732
Cubic	0.732 - 0.999

Arrangement	Void	Co-ordination Number
Plane triangular	Triangular	3
CCP & HCP	Tetrahedral	4
CCP	Octahedral	6
Cubic	Cubic	8

CALCULATION OF RADIUS RATIO IN OCTAHEDRAL

Octahedral void is surrounded by 4 spheres in a plane. If 'r' is the radius of void & 'R' is radius of sphere and 'a' is side of squares formed by joining the centres of 4 spheres surrounding the void, then we have

$$\text{side} = a$$

$$\text{side} = 2R$$

$$a = 2R \text{ --- (1)}$$

$$\text{Diagonal} = \sqrt{2}a$$

$$\text{Diagonal} = 2R + 2r$$

$$\sqrt{2}a = 2R + 2r \text{ --- (2)}$$

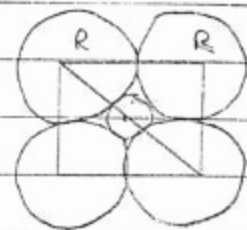
Divide eqⁿ (1) by (2)

$$\frac{\sqrt{2}a}{a} = \frac{2R + 2r}{2R}$$

$$\sqrt{2} = \frac{R+r}{R}$$

$$\sqrt{2}R - R = r \quad \sqrt{2} = 1 + \frac{r}{R}$$

$$\frac{r}{R} = \sqrt{2} - 1 = 1.414 - 1 = 0.414$$



CALCULATION OF RADIUS RATIO OF TETRAHEDRAL VOID

Let us consider tetrahedral void such that all its four spheres be at corners of cube.

Edge = a

$$\text{Face diagonal} = \sqrt{2}a$$

$$\text{---"---} = 2R \quad \text{---(1)}$$

$$\sqrt{2}a = 2R \quad \text{---(1)}$$

$$\text{Body diagonal} = \sqrt{3}a$$

$$\frac{1}{2} \text{ Body diagonal} = \frac{\sqrt{3}a}{2}$$

$$\frac{1}{2} \text{ Body diagonal} = R+r$$

$$\frac{\sqrt{3}a}{2} = R+r \quad \text{---(2)}$$

Divide (2)/(1)

$$\frac{\frac{\sqrt{3}a}{2}}{\sqrt{2}a} = \frac{R+r}{2R}$$

$$\frac{\sqrt{3}}{2\sqrt{2}} = \frac{R+r}{2R}$$

$$\frac{\sqrt{3}}{\sqrt{2}} = 1 + \frac{r}{R}$$

$$\frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{r}{R}$$

$$\frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{r}{R}$$

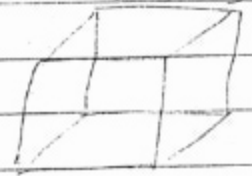
$$\frac{r}{R} = 0.225$$

DERIVATION OF DENSITY OF UNIT CELLS

Let us consider a unit cell having edge ' a ' picometre (pm) and mass of 1 particle be ' M ' amu (So, its molar mass becomes M gram)

Derivation of density

$$\begin{aligned} \text{Edge} &= a \text{ pm} \\ &= a \times 10^{-10} \text{ cm} \end{aligned}$$



$$\begin{aligned} \text{Volume} &= (\text{edge})^3 \\ &= (a \times 10^{-10})^3 = a^3 \times 10^{-30} \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} 1 \text{ mole particle weights } &M \text{ g} \\ 1 \text{ particle weighs } &= \left(\frac{M}{N_A} \right) \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Mass of unit cell} &= \left(\text{Mass of 1 particle} \right) \times \left(\text{No. of particles} \right) \\ &= \frac{M}{N_A} \times 2 = \frac{2M}{N_A} \end{aligned}$$

$$\text{density} = \frac{\text{Mass}}{\text{Vol.}} = \frac{2M}{N_A} \div \frac{a^3 \times 10^{-30}}{1} = \frac{2M}{N_A \times 10^{-30} \times a^3}$$

Any deviation from well ordered arrangement of lattice is called defects. There are foll.:-

1. Electronic defect
2. Atomic defect

1. Electronic defect - Electrons remain normally in lowest energy state but due to ↑ in temp., it can leave its normal site which creates a hole of vacancy. Electrons & holes are collectively responsible for e^- imperfection. CONSEQUENCE → It does not effect density of solid but ↑ electrical conductivity. eg - silicon shows high conductivity at higher temperature.

2. Atomic Impurity - In this, atoms or ions are not at their normal site.

These are either missing or occupy interstitial site. These are of two types:-

(i) Line defect - when there is irregularity or deviation in whole row, its called line defect.

(ii) Point defect - when there is imperfections around an atom, it is called point defect. These are of 3 types -

→ Stoichiometric

→ Non-stoichiometric

→ Impure.

→ STOICHIOMETRIC

Those ~~effect~~ defects which do not effect the stoichiometry of compound i.e. no. of atoms of or ions are acc. to their chemical formulae, are called stoichiometric defect. Also called intrinsic or thermodynamic effect. It is of foll. types:-

(i) Vacancy defect - when some particles are absent from their lattice site they create lattice effect. These are called created due to heat. It decreases the density of solid.

(ii) Interstitial defect - when some particles occupy, interstitial site, they create interstitial effect. They increases the density of solid.

NOTE: Vacancy and interstitial spaces are exhibited by non-ionic solids.

SCHOTTKY DEFECT

- Equal no. of anions & cations are missing from their site.
- Electric neutrality is maintained.
- Generally, those compounds in which cations & anions have similar size, show this defect.
- Generally those comp. compds having ions with high coordination no. show this defect, eg NaCl, KCl, AgBr

CONSEQUENCE

- Due to missing of ions, it results in ↓ in density because volume remains same but mass ↓ as ions are missing.
- Electrical conductivity ↑ as at vacant spaces allows shifting of ions. Stability of lattice ↓ due to vacancy. If large no. of vacancies are present, lattice may collapse.

FRENKEL / DISLOCATION DEFECT

- In this defect, generally cation dislocates from its normal site and occupy interstitial site.
- Ions having low co-ordination number, show this type of defects.
- Generally compounds having different sized sites of cation and anion show this defect.
- Density is not affected as ions are not missing but only change in their location.
- Stability of crystal ↓ due to creation of vacancy.
- Dielectric constant of substance ↑ due to closeness of ions.
- alkali halides do not show this defect because of size of ion are almost same in these compds.

→ Compounds showing this defect are AgBr , AgCl and ZnS .

NOTE: AgBr shows both Schottky as well as Frenkel defect.

→ NON - STOICHIOMETRIC DEFECT

In this defect, no. of ions are not in accordance with stoichiometry. eg FeO is not stoichiometric & have formula $\text{Fe}_{0.93-0.96}\text{O}$
These defects are of foll. types :-

1. Metal excess Defect - In this cations are more than expected from formula. These are of two types -

i) Due to anion vacancy - In this defect, anions are missing from their site and to maintain electrical neutrality e^- are present. The e^- are unpaired & helps in electrical conductivity. The type of conductivity is called 'n' type conductivity as e^- are -ve.

→ The site occupied by e^- is called F-centered & it is responsible for colour of compound.

Eg → when KCl is heated in potassium vapour, some potassium atoms get deposited on KCl surface. Cl^- ions from lattice diffuse towards K and combine to form KCl . Potassium atoms loses e^- to become K^+ these e^- diffuse into the lattice & is responsible for colour & conductivity KCl becomes violet.

Similarly, KCl when heated in lithium vapours become pink.