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THE IIT - JEE SECRET

JEE MAINS AND JEE ADVANCED

PHYSICAL CHEMISTRY

VOL - III

SIERRA INNOVATIONS
Private Limited

Contents

SOLID STATE

Generally, solids are classified into two types-

1. CRYSTALLINE SOLIDS
2. AMORPHOUS SOLIDS

Crystalline Solids	Amorphous Solids
① These solids have regular arrangement of atoms/ions & molecules in 3-dimension (long range order)	① These solids do not have regular arrangement throughout. (short range order)
② They have definite geometry.	② They do not have definite geometry.
③ They have sharp MP's.	③ They have range of temp. over which it melts.
④ Smooth surface is obtained, when cut by sharp edge tool.	④ Rough surfaces are obtained, when cut by sharp edge tool.
⑤ These are True solids.	⑤ These are pseudo solids/ super cooled solids.
⑥ These solids are anisotropic. ⇓ Some phy. properties are different in different directions. eg.- Refractive index, electrical & thermal conductance.	⑥ These are isotropic ⇓ Having same phy. properties in different directions.
⑦ Examples: NaCl, Caesium chloride.	⑦ Glass, plastic, rubber

CLASSIFICATION OF CRYSTALS

On the basic of type of bonding

1. MOLECULER CRYSTAL - Constituent particles are molecules.

Molecular crystals are divided into NON-POLAR and POLAR. POLAR is divided into Dipole-dipole attraction and H-bonding.

NON-POLAR	POLAR: Dipole-dipole attraction	POLAR: H-bonding
① Molecules are held together by london Dispersion forces.		
② Examples: H_2, Cl_2, I_2 etc.	① eg- HCl, SO_2, etc.	① eg- H_2O (ice)
③ These are insulators	② insulators	② MP is low
④ Very low MP	③ low MP	③ insulators
⑤ Soft	④ Soft	④ Hardy

2. IONIC CRYSTALS -

① Constituent particles are ions & these ions are held together by electrostatic force of attraction.
② Example- NaCl, ZnS, etc.
③ These are insulators in solid state, however conduct electricity in molten/aqueous state.
④ These are hard & brittle.
⑤ High MP.

3. METALLIC CRYSTALS -

① Consists of +ve charged kernels, which are present in

the sea of Valence e^-.
② eg - Fe, Cu, Ag
③ Conductors of electricity
④ hard, Malleable & ductile
⑤ high MP.

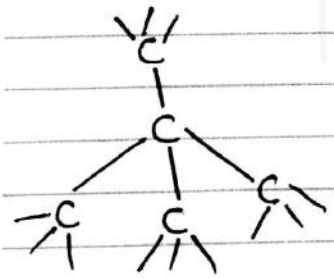
4. COVALENT CRYSTALS -

① Crystals consists of atoms, which are held together by Covalent bonds.
② These are insulators.
③ These have very high MP.
④ These are hard & brittle.

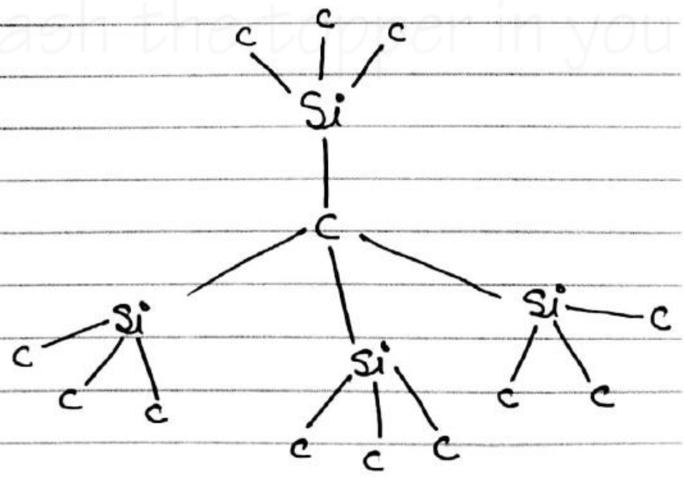
Graphite → Conductor & soft

5. Examples -

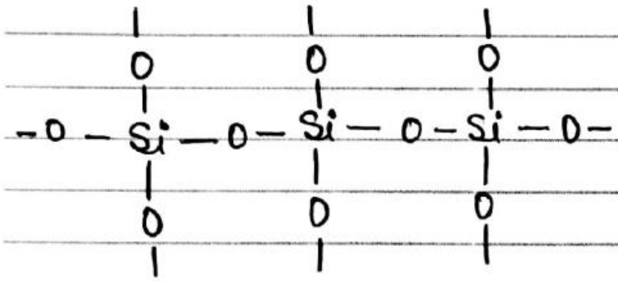
Diamond



Carborundum (SiC)



$\underline{SiO_2}$



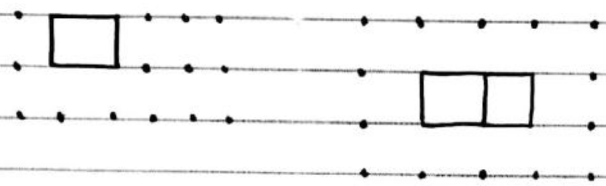
TERMS RELATED WITH CRYSTAL STRUCTURE

1. BASIRS - Basis is single atom/molecule/ion or group of atoms/molecules/ions, which are repeated in 3-dimension to generate a crystal structure.

2. SPACE LATTICE / LATTICE - If we place points at the location of basis, then a set of points is obtained, which form the lattice, i.e regular 3-D arrangement of points in a space is known as lattice.
Each point in the lattice is known as lattice points.

3. UNIT CELL - A space lattice of a crystal can be divided into identical parallelopipes by joining the points through st lines. Each such parallelopipe is known as unit cell.
i.e unit cell is the smallest repeating unit, which

can generate the complete lattice.



⇒ unit cell is characterised by two parameters -
① Geometry
② Position of atoms.

Depending on position of atoms, types of unit cell -

① SIMPLE / PRIMITIVE - In this type of unit cell, atoms are present at the corner of unit cell.

② BODY CENTERED - In addition to corners, atoms are present at the center of unit cell.

③ FACE CENTERED - In addition to corners, atoms is present at the center of each face.

④ END CENTERED - In addition to corners - atom is present at the centers of two opp. faces.

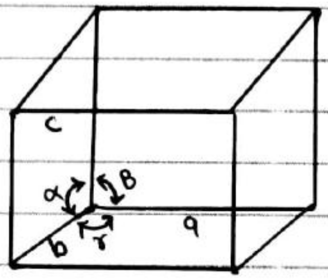
Depending upon edge length (a, b, c) and interfacial angles (α, β, γ), 7 independent geometries are possible -

These independent geometries are known as 7 basic crystal systems -

Types of unit cells

①

eg - NaCl

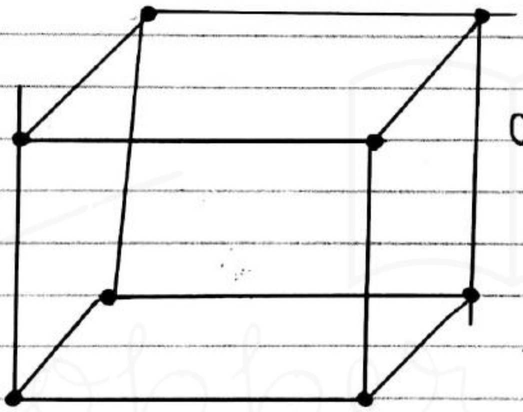


Simple Cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$

① Primitive
② Face centered
③ Body centered

②

eg - Rhombic Sulphur

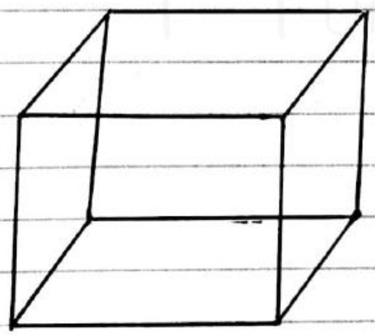


Ortho rhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

① Primitive
② Face centered
③ Body centered
④ End centered

③

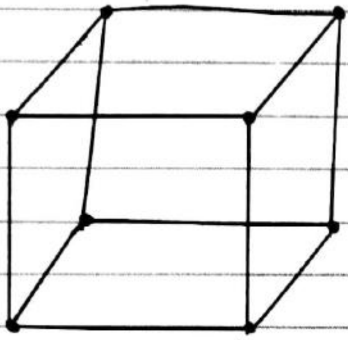
eg - white Tin



Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

① Primitive
② Body centered

④

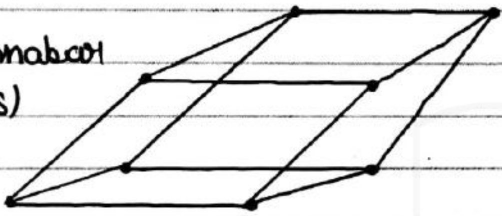


Monoclinic
~~Tetragonal~~
$a = b \neq c$
$\alpha = \gamma = 90^\circ$
$\beta \neq 90^\circ$

① Primitive
② ~~Body~~ centered
End

⑤

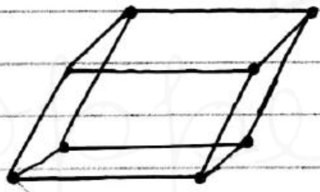
eg- cinnabar (HgS)



Rhombohedral / Trigonal
$a = b = c$
$\alpha = \beta = \gamma \neq 90^\circ$

① Primitive

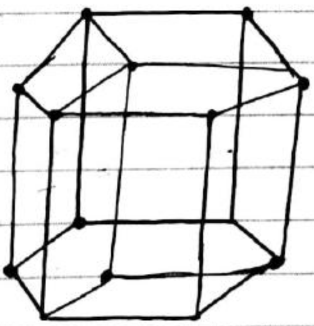
⑥



Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^\circ$

① Primitive

⑦



Hexagonal primitive
$a = b \neq c$
$\alpha = \beta = 90^\circ$
$\gamma = 120^\circ$

① Primitive

⇒ Bravis performed symmetry operations on 7 crystal systems & then he observed that only 14 arrangement of atoms are possible in 7 crystal systems.

These 14 lattices are known as Bravis lattices.

CLOSE PACKING OF SAME TYPES OF ATOMS OR SPHERES-

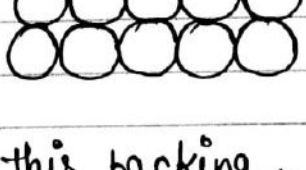
1. IN 1-DIMENSION -

In this packing, an atom is in contact with two other atoms, Therefore, co-ordination No. in 1-D close packing is 2.
↓
(No. of nearest neighboures)

2. IN 2-DIMENSIONAL-

To form two dimensional packed structures, close packed structures of one dimension are packed in rows.

Ⓐ Square closed packing in 2-D-



In this packing, atoms of 2nd row are present above the atoms of first row in such a way, that both rows are certically as wellas horizontally aligned and therefore this type of arrangement is known as AA type arrangement.

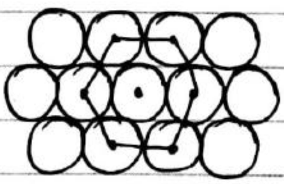
In this type of arrangement, CN=4, i.e an atom is surrounded by 4 neighboures & center of these 4 atoms are present at the Corner of a square. Therefore, it is known as square closed packing in 2D.

Ⓑ Hexagonal closed Packing in 2-D -

In this type of packing, atoms of 2[nd] row are present in depression of 1[st] row and atoms of 3[rd] row are present in the depressions of 2[nd] row & so on.

Therefore, 1[st] layer is vertically aligned with 3[rd] layer & 2[nd] layer is vertically aligned with 4[th] layer & so on.

Hence, this type of arrangement is known as ABAB type arrangement.



CN = 6

* This packing is more efficient than squre closed packing

in 2D.

⇒ CN = 6, ie an atom is in contact with 6 neighboures.

⇒ centeres of these 6 neighboures are present at the corners of the hexagon & therefore this packing is known as hexagonal closed packing in 2D.

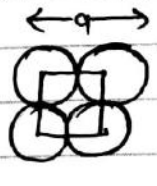
⇒ There are 2 types of triangular voids present, one pointing upwards & other pointing downwards.

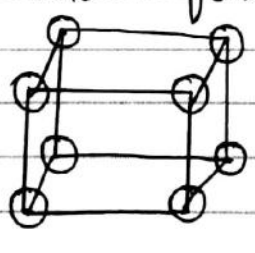
3. In 3-DIMENSION -

All real structures are 3-dimensional & these can be generated by packing two dimensional layers one above the other.

① Simple Cubic Unit cell -

In case of simple cubic unit cell, two-dimensional square closed packed layers arrange one above the other in such a way that all layers are vertically as well as horizontally aligned. Finally, it results into formation of simple cubic unit cell.





This type of packing is known as AA type square closed packing in 3D.

characteristics -

① Effective no. of atoms per unit cell (z)

$z = 8 \times \frac{1}{8} = ①$

corners → 8; $\frac{1}{8}$ → each atom is shared b/w 8 cubes.

② Atoms present along edges are in contact of each other.
i.e $\boxed{a = 2r}$ → radius of one atom
a → edge length

③ Packing fraction / efficiency -

void fraction = 1 - Packing fr.

$\boxed{\text{Void fr} = 1 - 0.5236}$

$$\text{Pack. eff} = \frac{\text{Volm occupied by atoms}}{\text{Volm occupied by unit cell}} \times 100$$

$$= \frac{2 \times \frac{4}{3}\pi r^3}{a^3} \times 1000$$

$$= \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} \times 100 = 52.36\,\%$$

molecular mass = M
mass of atom = M amu

$1\,amu = \frac{1}{N_A}\,gm$
$= 1.67 \times 10^{-21}\,gm$

④ Density of Unit cell-

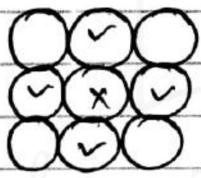
$$\text{Density} = \frac{\text{mass of unit cell}}{\text{Volm of unit cell}} = \frac{z \times \frac{M}{N_A}}{a^3} \ \text{gm cm}^{-3}$$

$N_A \longrightarrow M\,gm$

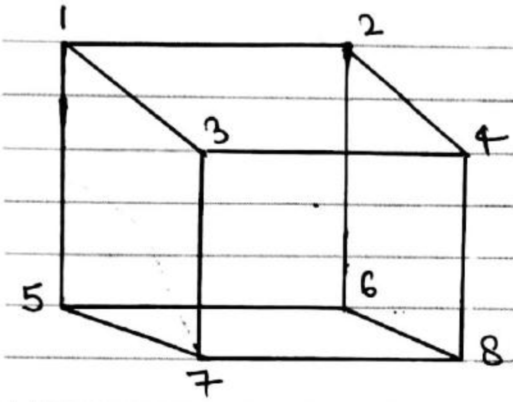
$1 \longrightarrow \frac{M}{N_A}\,gm$

$z \longrightarrow z \times \frac{M}{N_A}\,gm$

⑤ Co-ordination no. = 6 incase of simple cubic unit cell.



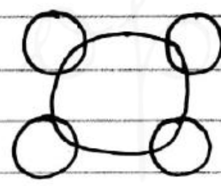
	no.	distance		
Nearest neighbour	6 (CN)	a	along edges	3, 5, 8
Next nearest neighbour	12	$\sqrt{2}a$	along face diag.	6, 4, 1
Next to next nearest neigh-bour	8	$\sqrt{3}a$	along body diag.	2

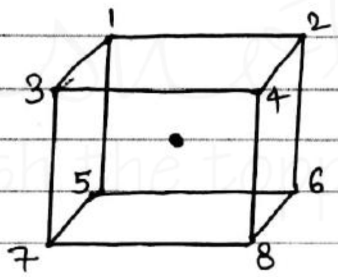


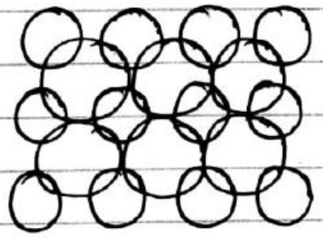
② Body centered Unit cell- (BCC)

In this type of unit we, atoms of 1st, 3rd & 2nd, 4th are vertically aligned. Therefore, this type of packing is known as ABAB type square closed packing.

It results into the formation of body centered unit cell. (BCC)







characteristics -

① Eff. no. of atoms per unit cell (z)

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

② Atoms present along body diagnal are in contact with each other, therefore $\sqrt{3}a = 4r$

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

③ Packing efficiency -

$$\text{Pack. eff} = \frac{z \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

$$= \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4}{\sqrt{3}} r\right)^3} \times 100 \qquad = 68.02\ \%$$

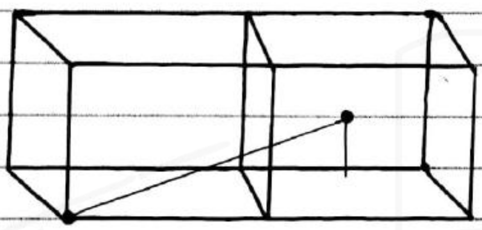
④ Density -

$$D = \frac{z \times \frac{M}{N_A}}{a^3} \text{ gm cm}^{-3}$$

⑤ Co-ordi no. - ⑧ in Body centered cubic unit cell.

Nearest neighbours	8	$\frac{\sqrt{3}a}{2}$	body diag

next nearest	6	a	edge
next-next	12	$\sqrt{2}a$	Face diag.
next-next next	24 (6x4) faces	$\frac{\sqrt{11}a}{2}$	



$$= \sqrt{\frac{9a^2}{4}+\frac{a^2}{4}+\frac{a^2}{4}} = \frac{\sqrt{11}a}{2}$$

③ Closed pack Structures

It is generated from hexagonal closed packing in 2D. It results into the formation of two types of closed packed structure-

① HCP (Hexagonal closed packed structure)
② CCP (cubic closed pack structure)

⇒ Atoms in first layer are in contact of 6 other atoms in the same layer and in this way, two types