Solid States

General Properties

- Solid is that state of a matter in which constituents are firmly bound because of strong forces.
- They have definite mass, shape and volume.
- They are incompressible, rigid and have strength.
- They have close packed arrangement of particles.
- They have high density but very slow diffusion rate.
- They can only have vibrational motion as constituents have fixed positions.

Concept Ladder

Matter can exist in one of three main states : solid, liquid, or gas.
Three phases of water
Ice (solid), Water (liquid) and Steam (gas)

Types of Solids

Solids are classified into 2 types, crystalline and amorphous.

Rack your Brain

Why density of ice is lower than water?

Crystalline Solids

- In crystalline solids, constituents are arranged in a definite or proper order which repeats itself over long distances.
- They generally have definite geometry having flat faces and sharp edges.
- They have sharp melting points.
- They are considered true solids.
- They give clean cleavage with fixed cleavage planes.
- They show anisotropic behaviour which means different physical properties in different directions because of orderly arrangement of constituents.
- They are incompressible. For example, CaF_2, ZnS, diamond, quartz, NaX.
- All elements and compounds are of this type.

Concept Ladder

Isotropic : Properties of a material are identical in all directions.
Anisotropic : Properties of a material depend on the direction; for example, wood. In a piece of wood, you can see lines going in one direction; this reaction is referred to as “with the grain”.

Amorphous Solids

- In these type of solids, constituents are not arranged in a regular or orderly manner for long range.

- They do not have sharp melting points.
- They are pseudo solids.
- They show isotropic behaviour which is same as physical properties in all directions because of irregular arrangement.
- They do not give clean cleavage. They have irregular cut.

  E.g., glass, plastic, and rubber

Concept Ladder

There exists strong electrostatic force in ionic crystalline solids like NaCl because of attraction between anions and cations.

Terms related to crystalline solids

Crystal: This is a homogeneous part of solid substance which is made by regular pattern of structural units which are bonded by plane surface making definite angles with each other.

Crystal lattice or space lattice: It is regular arrangement of constituent particles (atom, ions etc.) of a crystal in 3-D space.

Face: It is plane surface of crystal.

Edge: It is formed because of intersection of two adjacent faces.

Interfacial angle: It is angle between perpendiculars of two intersecting faces.

Rack your Brain

What is interfacial angle between two adjacent faces of a cube?

Q.1 Why is glass of window panes of very old buildings found to be thicker at the bottom than at the top and why is it milky?

A.1 Glass is amorphous solid which is a supercooled liquid of high viscosity and hence possesses fluidity. Due to presence of this property it is thicker at the bottom than at the top. Milkiness of glass is due to fact that it undergoes heating during the day and cooling at night, i.e., annealing over several years. as a result, it acquires some crystalline character..

Types of crystalline solids

Nature of constituent particles and binding forces of crystalline solids are generally classified as shown in table given below.

Types of Crystalline Solids

Type of crystalline solids	Constituents particles	Nature of force	M.P. in Kelvin	Binding energy in kJ/mole	Conductivity	Example
Ionic	Cations and anions	Strong electrostatic force	Very high > 1300 K	400–4000	Conductors	NaCl, KCl, KNO_3, CaO, LiF
Covalent or network	Atoms	Covalent bonds	Extremely high > 3900 K	150–500	Insulators	Diamond, SiC, AlN, SiO_2, quartz
Molecular	Molecules	Van der Waals forces	Low < 273 K	Low < 40	Insulators	Dry ice, I_2, solid argon, P_4 , S_8, CCl_4 etc.
Metallic	Atoms	Metallic bonds	High 800 ~ 1000	80 ~ 1000	Conductors	All metals and most of the alloys

Solid angle When three or more than three edges are intersect, a solid angle is formed.

Bragg's Equation

Max von Laue identified possibility of diffraction of X-rays by crystals as order of wavelength of X-rays is compatible to inter-atomic distances present in a crystal.

- Bragg's equation gives a simple relationship between wavelength of X-rays and distance between planes in crystal and angle of reflection. The equation can be given as:

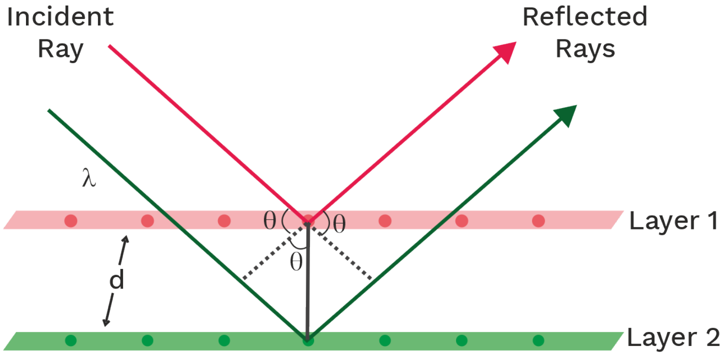
$$n\lambda = 2d \sin \theta$$

Here,
λ = Wavelength of X-rays
n = Order of reflection it is taken generally as 1.
θ = Angle of incident light
d = Distance between 2 layers of crystals

Concept Ladder

Due to their bonding, metallic solids have delocalised electrons. These free electrons can move around, therefore they can conduct electricity. But in ionic solids electrons are not free to move so they can't conduct electricity.

- For a given number of lattice planes, value of 'd' is fixed so possibility of getting maximum reflection depends only on θ. If we increase θ gradually several positions will be observed at which there will be maximum reflection.



Applications

- Bragg's observation has proved to be highly useful in determination of structures and dimensions of ionic crystalline solids.
- It also explains many properties of X-rays.
- Equation helped in construction of an X-ray spectrometer to describe crystalline structure of crystals as in case of face-centered cubic structure of NaCl.

Unit Cell

- Unit cell is the smallest unit or three-dimensional portion of the space lattice which when repeated and again in different directions gives rise to the complete space lattice.
- It has characteristics properties of a, b, c (edge distance) and α, β, γ, (angles).
- It is smallest geometrical figure which has properties of a crystal in a lattice.
- A crystal can have infinite number of unit cells.

Rack your Brain

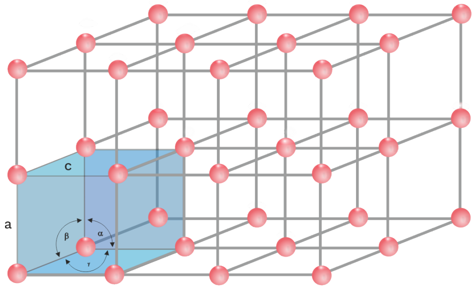
What is the shape of unit cell iof NaCl crystalline structure?

Previous Year's Questions

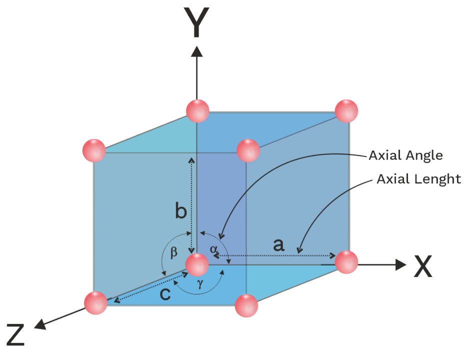
The number of carbon atoms per unit cell of diamond is

[NEET-2013]

(1) 6 (2) 1
(3) 4 (4) 8



Space lattice
and unit cell



Representation of
dimensions of a unit cell

Types of Unit Cell

They are of four types, namely, simple, face-centred, end-centred and body-centred.

Simple or primitive or basic unit cell: In this, lattice points (particles) are present only at corners.

Face-centred unit cell: In this, lattice points or particles are present not only at corners but also at centre of each face.

Body-centred unit cell: In this, particles are present at all the corners and body centre of unit cell.

End-centred unit cell: In this, particles are present at all the corners as well as at centre of 2 opposite faces .

Concept Ladder

In cube of any crystal A-atom placed at every corners and B-atom placed at every centre of face. The formula of this compound is AB_3.

Types of Symmetry in Crystals

A crystal can have centre of symmetry, axis of symmetry and plane of symmetry.

- Plane of symmetry (POS): It is an imaginary plane which passes from centre of crystal and divides it into two equal part. (mirror images of each other).
- Centre of symmetry: It is an imaginary point which separates surface of crystal which is at equal distances in both the directions by drawing any line through it.

Rack your Brain

What is the symmetry of PCl_5 molecule?

- A crystal generally has one centre of symmetry.
- Axis of symmetry is imaginary straight line which on rotation of crystal gives same appearance more than a single time.
- It is 2-fold, 3- fold, 4-fold and 6-fold type respectively.

Crystal Systems

There are 7 types of crystal systems and fourteen bravais lattices as given in table below

Concept Ladder

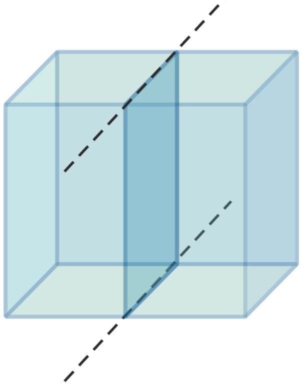
A sphere has all kinds of symmetry of point, axis and plane.

Crystal Systems and Bravais Lattices

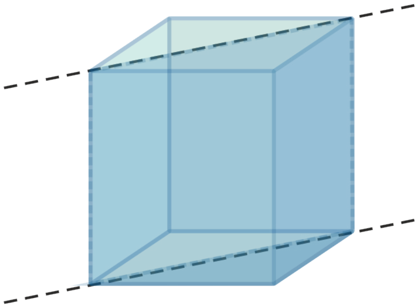
Crystal system	Bravais lattices	Parameters of unit cell		Examples
		Edge length	Axil angle	
Cubic	Primitive, Face-centred, Body centred	a = b = c	$\alpha = \beta = \gamma = 90°$	Ag, Au, Hg, Pb, diamond, NaCl, ZnS
Orthorhombic	Primitive, Face-centred, Body centred, End-centred	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90°$	K_2SO_4, KNO_2, $BaSO_4$ Rhombic Sulphur
Tetragonal	Primitive Body-centred	a = b ≠ c	$\alpha = \beta = \gamma = 90°$	TiO_2, SnO_2, $CaSO_4$
Monoclinic	Primitive End-centred	a ≠ b ≠ c	$\alpha = \beta = 90°$ $\gamma \neq 90°$	Monoclinic sulphur, $Na_2SO_4.10H_2O$, $CaSO_4.2H_2O$
Triclinic	Primitive	a ≠ b ≠ c	$\alpha \neq b \neq \gamma \neq 90°$	$CaSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3
Hexagonal	Primitive	a = b ≠ c	$\alpha = b = 90°$ $\gamma = 120°$	Zn, Mg, CdS, SiO_2 , ZnO, Graphite
Rhombohedral	Primitive	a = b = c	$\alpha = \beta = \gamma \neq 90°$	Bi, As, Sb, $CaCO_3$, HgS
	Total (14)			

Symmetry in Crystals

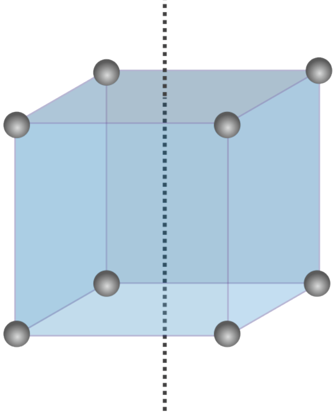
(a) Rectangular Plane of Symmetry



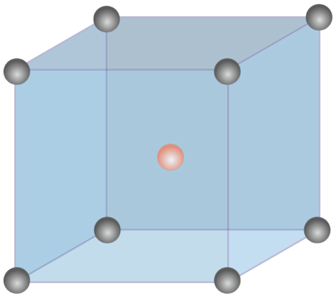
(b) Diagonal Plane of Symmetry



(c) Axis of Four Fold Symmetry



(d) Centre of Symmetry



Mathematical Analysis of Cubic System

Atomic Radius (r)

- Atomic radius: It is half the distance between two nearest neighbour atoms in crystal.
- It's expressed in terms of length of edge (a) Of unit cell of a crystal.
- In simple cubic $r = \frac{a}{2}$
- In face-centred cubic (FCC) $r = \frac{a}{\sqrt{2}}$
- In body-centred cubic (BCC) $r = \frac{\sqrt{3}a}{4}$

Previous Year's Questions

For orthorhombic system axial ratios are $a \neq b \neq c$ and the axial angles are

[AIPMT]

(1) $\alpha = \beta = \gamma \neq 90°$

(2) $\alpha = \beta = \gamma = 90°$

(3) $\alpha = \gamma = 90°, \beta \neq 90°$

(4) $\alpha \neq \beta \neq \gamma \neq 90°$

No. of Atoms Per Unit Cell/ Unit Cell Content (Z)

- It is total number of atoms contained in a unit cell.

  $$Z = \frac{n_c}{8} + \frac{n_e}{4} + \frac{n_f}{2} + \frac{n_i}{1}$$

  Where; n_c = no. of atoms at corner position
  n_e = no. of atoms at edge center
  n_f = no. of atoms at face center position
  n_i = no. of atoms present at the center

- In SCC, $Z = 8 \times \frac{1}{8} = 1$

  Every corner atom is shared by surrounding unit cells so it accounts for $\frac{1}{8}$ of an atom.

- In a FCC structure, Z = 3 + 1 = 4
  Eight(8) corner atoms contribute $\frac{1}{8}$ of an atom.
  which means only of one atom per unit cell.
  Each of 6 face-centred atoms are shared by two adjacent unit cells such that only half of one face- centred atom is contributed as its share that is,

  $$6 \times \frac{1}{2} = 3 \text{ (atoms per unit cell)}$$

  total of 4 atoms per unit cell.
- In a BCC structure, Z = 1 + 1 = 2. Each of eight corner atoms will be contributing only 1 atom per unit cell.
  Central atom has contribution of only one atom per unit cell.

Concept Ladder

A point lying at the corner of a unit cell is shared equally by eight unit cells and therefore, only one-eighth portion of each of such a point belongs to the given unit cell.

Rack your Brain

Find out the two nearest atoms in FCC and BCC crystalline structures and also find their radii?

Previous Year's Questions

The number of atoms in 100 g of a fcc crystal with density d = 10 g/cm³ and cell edge equal to 100 pm, is equal to

[AIPMT]

(1) 2×10^{25} (2) 1×10^{25}
(3) 4×10^{25} (4) 3×10^{25}

Address of an atom	Corner of Cube	Corner of Hexagonal	Edge of Cube	Face of Cube	Centre of Body	Side of Hexagonal
Contribution	$\frac{1}{8}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{2}$	1	$\frac{1}{2}$

Coordination Number (C. No.)

- It is equal to the number of nearest neighbours atom, that is, touching particles present around a species in a crystal. Its larger value shows closer packing.
- The values depend upon structure of crystal.

S.C : Coordination number is 6

FCC : Coordination number is 12

BCC : Coordination number is 8

NaCl ;	CsCl ;	ZnS ;	CaF_4 ;	Na_2O
6:6	8:8	4:4	8:4	4:8

Concept Ladder

In ionic crystal, the number of oppositely charged ions surrounding each ion is known to be its coordination.

Shape	Radius ratio	C No.
Cubic	0.732-1.000	8
Octahedral	0.414-0.732	6
Tetrahedral	0.225-0.414	4
Triangular	0.155-0.225	3

Density of Lattice Matter (d)

- Density of lattice matter is ratio of mass per unit cell to total volume of unit cell and it is given as:

$$d = \frac{Z \times \text{Atomic weight}}{N_0 \times \text{Volume of unit cell } (a^3)}$$

Here,

N_0 = Avogadro number

a^3 = Volume

Z = Number of atoms in unit cell

a = Edge length in cm

d = Density in g/ml or g/cm^3

Previous Year's Questions

A metal crystallises with a face centred cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is

[AIPMT-2012]

(1) 288 pm (2) 408 pm

(3) 144 pm (4) 204 pm

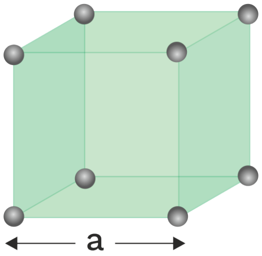
Packing Fraction

- ● It is defined as the ratio of volume occupied by spheres $\left(\frac{4}{3}\pi r^3\right)$ in a unit cell to the total volume (a^3) of that unit cell. Fraction of volume that is empty is called void fraction.

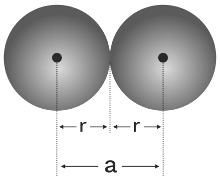
$$\text{P.F.} = \frac{Z \times \frac{4}{3}\pi r^3}{a^3}$$

- In a SCC,

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



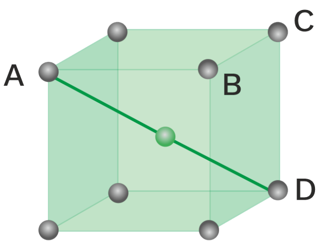
SCC



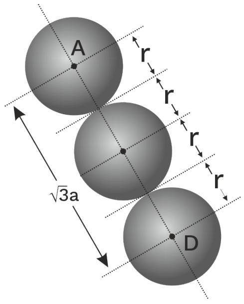
Here, a = 2r; % void = 48%

- In a body-centred cubic structure,

$$\text{P.F.} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0.68 = 68\%$$



B.C.C



Here, $a = \frac{4r}{\sqrt{3}}$; % void = 32%

Concept Ladder

A crystal may have a nubmer of planes or axis of symmetry but it possesses only one centre of symmetry.

Rack your Brain

Why the closest packed structures have high value of coordination?

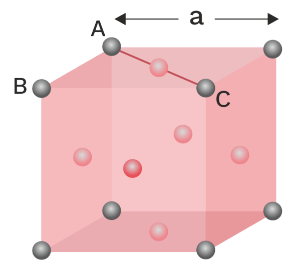
Previous Year's Questions

The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is

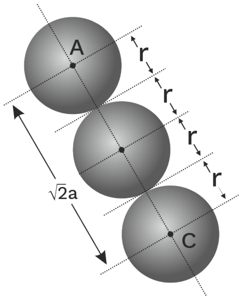
[AIPMT]

(1) face-centred cube
(2) simple cube
(3) body-centred cube
(4) none of these

- In a face-centred cubic structure,



F.C.C



$$P.F. = \frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0.74 = 74\%$$

$$\text{Here, } a = \left(\frac{4r}{\sqrt{2}}\right)^3$$

$$\%\ \text{void} = 26\%$$

Concept Ladder

- In fcc, the nearest neighbour of a corner atom is the face centred atom and thus, atom on each corner has 4 nearest neighbours.
- It also possesses four face centred atoms in planes below and above it.

Property	Primitive	FCC	BCC
Edge length	$2r = a$ $a = 2r$	$4r = \sqrt{2}\,a$ $a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\,r$	$4r = \sqrt{3}\,a$ $a = \frac{4r}{\sqrt{3}}$
Volume occupied by spheres	$1 \times \frac{4}{3}\pi r^3$	$4 \times \frac{4}{3}\pi r^3$	$2 \times \frac{4}{3}\pi r^3$
Volume of unit cell	$a^3 = 8r^3$	$a^3 = (2\sqrt{2}\,r)^3$	$a^3 = (4r / \sqrt{3})^3$
Packing fraction $\frac{\text{Vol. occupied by atoms}}{\text{Vol. of unit cell}}$	$\frac{4/3\,\pi r^3}{8r^3} = 0.524$	$\frac{4 \times 4/3\,\pi r^3}{(2\sqrt{2}\,r)^3} = 0.74$	$\frac{2 \times 4/3\,\pi r^3}{(4r/\sqrt{3})^3} = 0.68$
Percentage of free space per unit cell	47.6%	26%	32%

Interstitial Voids

Interstitial voids are spaces left after hexagonal close packing (hcp) and cubic close packing (ccp). The spaces or voids are of the following types:

Trigonal void: It is a vacant space touching three spheres that is, two-dimensional void formed when three spheres are in same plane having corners are at corners of triangle.

Tetrahedral voids: Vacant space created when each sphere of second layer rests on vacant space created by three spheres (of first layer) touching each other is called a tetrahedral void.

Octahedral voids: They are formed by combination of two triangular voids of first and second layers. They are so called because they are enclosed between six spheres, centres of which occupy corners of a regular octahedron.

Location and number of voids

(1) Tetrahedral void: They are located at body diagonals, two in each body diagonal at one fourth of the distance from each end.

Number of Tetrahedral voids = 8

(2) Octahedral voids: These are located at middle of cell edges and at centre of cubic unit cell.

Total number of Octahedral voids $= \frac{1}{4} \times 12 + 1 = 4$

Size of voids:

$$V_{oct} = 0.414 \times r$$

$$V_{tetra} = 0.214 \times r$$

$$V_{tri} = 0.115 \times r$$

where r is radius of the biggest sphere.

Concept Ladder

Voids are terms as the gaps between the constituent particles in a closed packed structure. Close packing in solids can be generally done in three ways : 1D close packing, 2D close pakcing and 3D close packing.

Rack your Brain

What is the coordination number for tetrahedral void?

Previous Year's Question

The number of octahedral void(s) per atom present in a cubic close-packed structure is

[AIPMT-2012]

(1) 1 (2) 3

(3) 2 (4) 4

Radius Ratio

Radius ratio is radius of octahedral void to radius of sphere forming close packed arrangement.

(1) For stability of ionic compounds, each cation must be surrounded by maximum no, of anions and vice-versa.

(2) The maximum no. of opposite charged ions surrounding another ion is known as coordination number. Since, ionic bonds are non- directional arrangement of ions in crystal is determined by sizes.

Ratio of radius of cation to anion is known as radius ratio, i.e.,

$$\text{Radius Ratio} = \frac{\text{Radius of the cation}(r^{+})}{\text{Radius of the anion}(r^{-})}$$

(4) If radius ratio is greater, then size of cation is larger and therefore greater is its coordination number.

(5) Relationships between radius ratio and the coordination number and structural arrangement are called radius ratio rules.

Concept Ladder

The packing density data reveals that close packing of atoms in cubic structure follow the order, FCC > BCC > SCC, i.e., more closely packed atoms are in FCC structure.

Rack your Brain

If the radius of the bromide ion is 0.182 nm, how large a cation can fit in each of the tetrahedral hole?

Q.2 The two ions A^{+} and B^{-} have radii 88 and 200 pm respectively. In the close packed crystal of compound AB, predict the coordination nubmer of A^{+}.

A.2 $$\frac{r_{+}}{r_{-}} = \frac{r(A^{+})}{r(B^{-})} = \frac{88\ \text{pm}}{200\ \text{pm}} = 0.44$$

It lies in the rage 0.414 to 0.732

Hence, the coordination number of A^{+} = 6

Packing of Constituents in Crystals

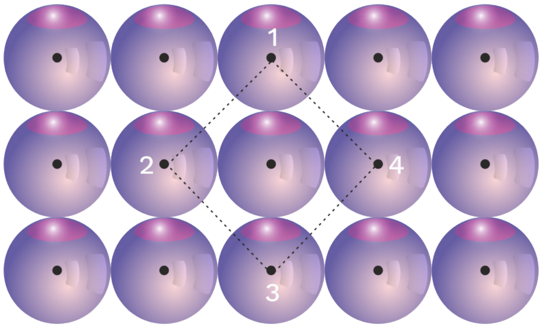
Crystal constituents can be packed in two dimensions and 3-Dimensions.

Close Packing in Two Dimensions

In this, close packing arrangement in two dimensions are as follows:

Square close packing

- In this, each sphere is in contact with four other spheres.
- Voids form a square in this type of packing.
- About 52.4% space is occupied by the spheres.



Previous Year's Questions

In crystals of which one of following ionic compounds would you expect maximum distance between centres of cations and anions?

[AIPMT]

(1) CsI (2) CsF

(3) LiF (4) LiI

Q.3 The edge length of a unit cell of a metal having molecular mass 75 g/mol is 5Å which crystallizes in a cubic lattice. If the density is 2 g/cc, then find the radius of the metal atom.

A.3

$$\rho = \frac{Z \times M}{a^3 \times N_0}$$

$$\text{or} \quad Z = \frac{\rho \times a^3 \times N_0}{M} = \frac{2 \times (5 \times 10^{-8})^3 \times 6.02 \times 10^{23}}{75} = 2$$

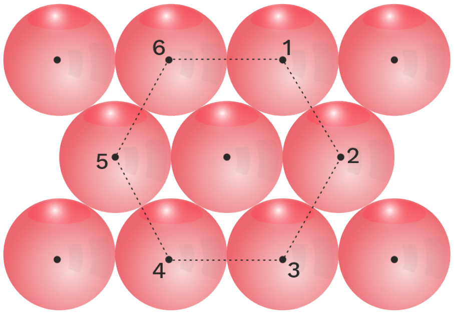
This shows that the metal has body-centred cubic lattice.

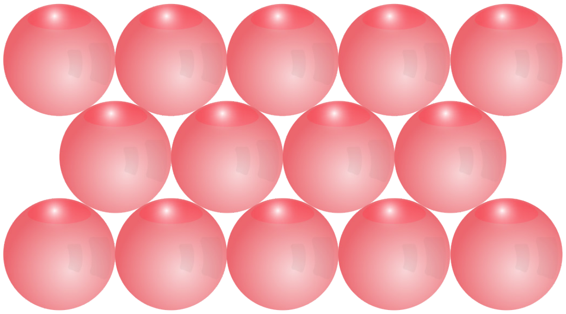
For BCC lattice,

$$r = \frac{\sqrt{3}}{4} a = \frac{1.732}{4} \times 5\text{Å} = 2.165\text{Å}$$

Hexagonal close packing

- It is more densely packed than square closed packing.
- In this, voids are triangular.
- In this, 60.4% space is occupied by spheres.





Base layer

Packing in Three Dimensions

This packing is of following three types:

Hexagonal close packing

- Atoms are present at center and at corners of two hexagons placed parallel to each other, 3 more atoms are placed in a parallel plane midway between the two planes.
- It generally has a six-fold axis of symmetry.
- In this, packing gives an arrangement of layers as AB AB, that is, odd number layers are similar and so are even number layers.

Concept Ladder

In 2D hexagonal close pakcing, their is less free space between sphere than 2D square close packing. Thus hexagonal close pakcing is denser than square close packing.

Rack your Brain

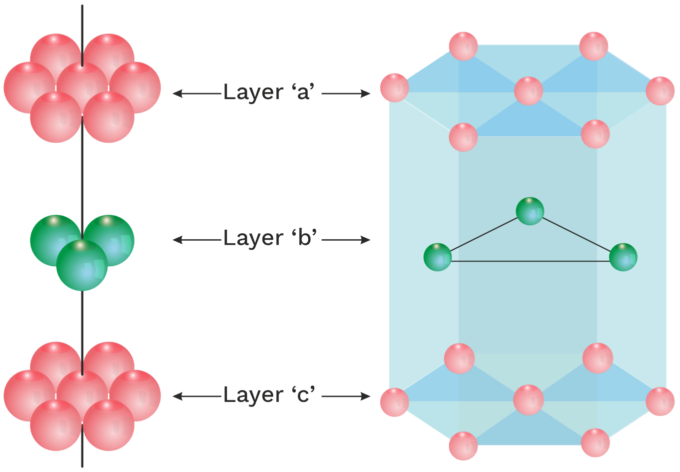
At what angle the HCP structure can be rotated so that it appears same as original one?

Previous Year's Questions

A compound is formed by cation C and anion A. The anoins form hexagnoal close packed (hcp) lattice and the cations occupy 75% of octahedral voids. The formula of the compound is

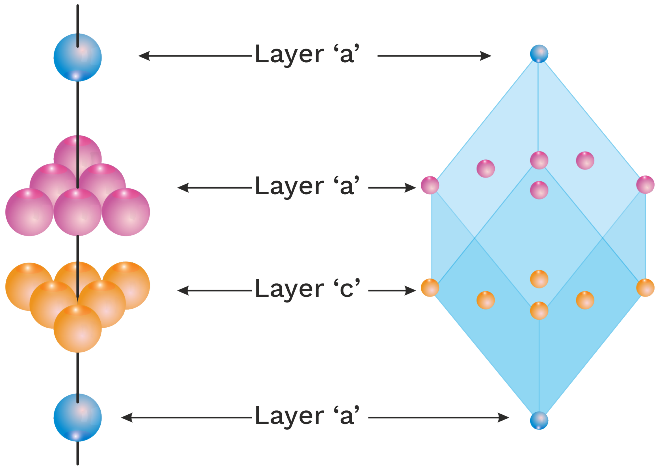
[NEET-2019]

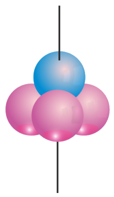
(1) C_4A_3 (2) C_2A_3
(3) C_3A_2 (4) C_3A_4



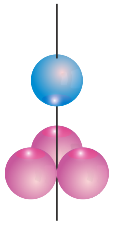
Cubic close packing

- Sphere in fourth layer will correspond to that in first layer and give rise to ABC, ABC, type of packing.
- It has 3-fold axis of symmetry which pass through the diagonal of the cube.
- Here coordination number is 12. Examples: Cu, Ag, Au, Ni, Pt

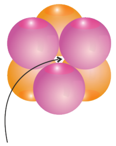




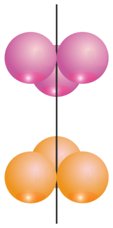
Tetrahedral void



Tetrahedral void



Octahedral void



Octahedral void

Concept Ladder

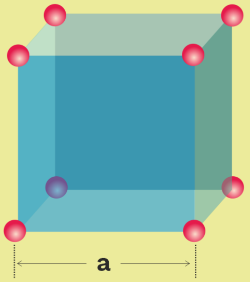
In both hexagonal close packing (hcp) and cubic close packing (ccp) the coordination number of spheres remian twelve.

Previous Year's Questions

Structure of a mixed oxide is cubic close packed (ccp). The cubic unit cell of mixed oxide is composed of oxide ions. One fourth of the tetrahedral voids are occupied by divalent metal A and the octahedral voids are occupied by a monovalent metal B. The formula of the oxide is **[AIPMT-2012]**

(1) ABO_2 (2) A_2BO_2
(3) $A_2B_3O_4$ (4) AB_2O_2

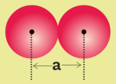
Bravais Lattice Of Crystal



Primitive cube

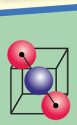
● 8 - Corner atoms $= 8 \times \frac{1}{8} = 1$

Total Number of atoms = 1



a = 2r

$$P.F. = \frac{\text{Volume of atoms}}{\text{Volume of cube}} = 0.52$$



$4r = \sqrt{3}a$

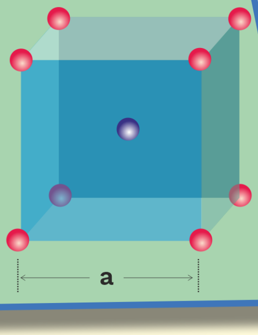
$$P.F. = \frac{\text{Volume of atoms}}{\text{Volume of cube}} = 0.68$$

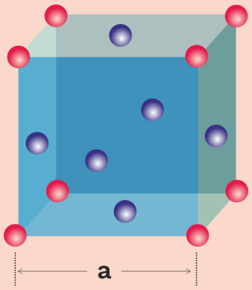
Body Centered Cube

● 8 - corner atoms $= 8 \times \frac{1}{8} = 1$

● Center atoms = 1

Total Number of atoms = 2



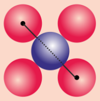


Face Centered Cube

● 8 - corner atoms $= 8 \times \frac{1}{8} = 1$

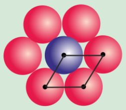
● 6 - Face atoms $= 6 \times \frac{1}{2} = 3$

Total Number of atoms = 4



$4r = \sqrt{2}a$

$$P.F. = \frac{\text{Volume of atoms}}{\text{Volume of cube}} = 0.74$$



$h = 4r\sqrt{\frac{2}{3}}$

$$P.F. = \frac{\text{Volume of atoms}}{\text{Volume of hexagonal}} = 0.74$$

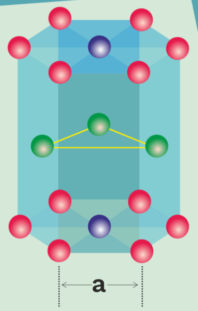
Hexagonal Close Packed

● 12 - corner atoms $= 12 \times \frac{1}{6} = 2$

● 2 - Face side atoms $= 2 \times \frac{1}{2} = 1$

● 3 - Inside atoms $= 3 \times 1 = 3$

Total Number of atoms = 6



Body-centred cubic packing

- In this, each sphere is in contact with 8 spheres: 4 in lower layer and four in upper layer.
- It is possible when spheres in first layer are slightly opened that is none of spheres is touching the other. Examples: Li, Na, K, Rb, Cs, Ba

Structure of Some Ionic Solids

Rock salt (NaCl) type

- Cl^- has a close cubic packing (ccp) type structure that is face centred cubic type (fcc).
- In this, Na^+ occupies octahedral spaces.
- Na^+ and Cl^- have coordination number 6.
- No. of formula units per unit cell are 4.
- Theoretically, $\frac{r_{Na^+}}{r_{Cl^-}}$ should be 0.414 but it is 0.525. Examples: LiX, NaX, KX, AgCl, AgBr, NH_4Cl.

CsCl type

- In this, Cl^- ions are at corners of cube and Cs^+ ions are in cubic void.
- Coordination number of both Cs^+ and Cl^- is 8.
- In this, number of formula units per unit cell is 1.
- Theoretically, $\frac{r_{Cs^+}}{r_{Cl^-}}$ should be 0.732 but it is 0.93.

  Examples: CsX, TiCl, TiBr, NH_4Cl, NH_4Br

Zinc Blend (ZnS type)

- In this, S^{2-} occupies CCP while Zn^{2+} ions occupy alternate tetrahedral voids.
- Only half of total voids are occupied.
- In this, coordination no.of both Zn^{2+} and S^{2-} is 4.
- No. of formula units in a unit cell is 4.
  Examples: ZnS, CuCl, CuBr, CuI, AgI, BeO

Concept Ladder

- Ionic solids have consituents particles as ions. These are formed by arrangement of cations and anions by strong Coulombic forces and also are hard and brittle in nature.
- Ionic solids acts as an insulator in its solid states where as they acts as conductors in its molten and aqueous states.

Rack your Brain

In NaCl type structure, the larger atoms form _______ arrangement and smaller atoms fill all ______ voids.

Fluorite structure (CaF_2 type)

- In this, Ca^{2+} occupies CCP and F^- occupies all tetrahedral voids.
- Also, coordination no. of Ca^{2+} is 8 while for F^- it is 4.
- In this, no. of formula units per unit cell is Examples: CaF_2, $BaCl_2$, BaF_2, SrF_2.

Antifluorite structure (Na_2O type)

- Here negative ions (O^{2-}) occupy ccp while cations (Na^+) occupy all the tetrahedral voids.
- Co-ordination no. of Na+ is 4 while for O^{2-} . It is 8.
- In this, no. of formula units per unit cell is 4. Examples: Na_2O, Li_2O, K_2O.

Normal spinel structure (AB_2O_4)

They have a general formula AB_2O_4.
A Bivalent Cation (Mg^{+2})
B Trivalent Cation (Al^{3+})

- $MgAl_2O_4$ is spinel crystal.
- In this, Mg^{2+} occupy tetrahedral voids while oxide ions occupy CCP. Aluminium occupies octahedral voids.
- Ferrites [$ZnFe_2O_4$] can also have structure.
- They are used in telephones, memory loops of computers as magnetic material.

Structure of Fe_3O_4 (Magnetite)

- In Fe_3O_4, Fe^{3+} and Fe^{2+}, they are present in 2:1 ratio.
- In this, oxide ions are in CCP. Fe^{2+} occupies octahedral voids where as Fe^{3+} occupies octahedral and tetrahedral voids.
- $MgFe_2O_4$ also has this kind of structure

Imperfections In Solids

- Deviation from perfectly ordered arrangement constitutes a defect or imperfection.
- The defects are also called thermodynamic defects as a number of the defects depend on temperature.

Concept Ladder

The crystal in which all the lattice points are occupied by the component particles or groups of particles is knonw as ideal crystal.
With change in temperature, molecular motion increases, which causes deviation from ordered arrangement and gives rise to a defect or imperfection in the crystal.

Rack your Brain

Coordination number of fluorine in calcium chloride is?

Previous Year's Questions

Formula of nickel oxide with metal deficiency defect in its crystal is $Ni_{0.98}O$. The crystal contains Ni^{2+} and Ni^{3+} ions. The fraction of nickel existing as Ni^{2+} ions in the crystal is **[NEET-2019]**

(1) 0.96
(2) 0.04
(3) 0.50
(4) 0.30

- Crystals may possess additional defects because of presence of impurities. Imperfection not only modifies properties of solids but also gives rise to new properties.

Electronic Imperfection

Electrons are present in fully occupied lowest energy states but at very high temperatures few electrons may occupy higher energy states depending upon the temperature.

- For example, in crystals of pure silicon or germanium some electrons are released thermally from covalent bonds at temperature above 0 K. These electrons are free to move in crystal and are responsible for electrical conductivity. This type of conduction is called as intrinsic conduction.
- Electron deficient bond formed by release of an electron is known as hole. In presence of an electric field the positive holes move in a direction opposite to that of the electrons and conduct electrically.

Previous Year's Questions

Which one of following elements silicon should be doped so as to give p-type of semiconductor?

[AIPMT]

(1) Selenium (2) Boron
(3) Germanium (4) Arsenic

Q.4 Why stoichiometric defects are also called intrinsic defects?

A.4 Stoichiometric defects are called because they do not change the stoichiometry of the crystal (Schottky defect and Frenkel defect). They are called intrinsic defects because it is due to the deviation from regular arrangement of atoms or ions within the crystal and no external substance is added..

Q.5 $CaCl_2$ will introduce Schottky defect if added to AgCl crystal. Explain.

A.5 Two silver ions will be replaced by one calcium ions to maintain electrical neutrality. So, a hole is created at the lattice site for every Ca2+ ion introduced..

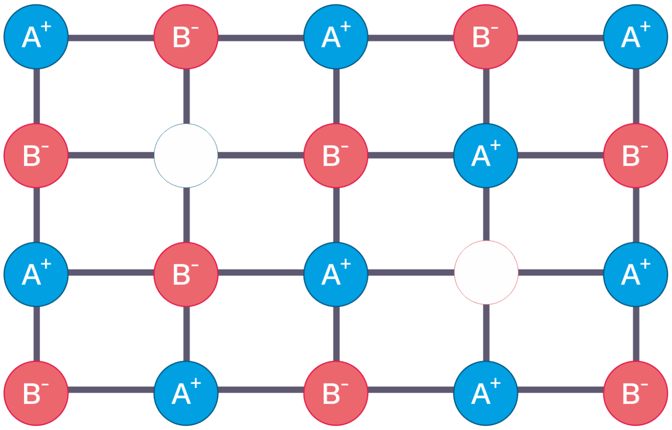
Atomic Imperfection

Compounds in which number of irregularities present in arrangement of atoms or ions are called atomic imperfections. It is of two types:

Stoichiometric defects: Compounds in which number of positive and negative ions are exactly in ratio indicated by the chemical formula are known as stoichiometric compounds for example, NaCl.

These solids show following types of defects:

(a) Schottky defect: Schottky defect is created when same number of negative and positive ions are missing from respective positions leaving behind a pair of holes.



- Schottky defect more common in ionic compounds with high coordination number and where size of negative and positive ions is almost equal.
- This defect decreases density of crystals but maintain neutrality e.g., NaCl, CsCl, KCl, KBr. In case of NaCl, there is nearly 10^6 Schottky pairs per cm^3 at room temperature.

Concept Ladder

In Schottky defect the density of crystal decreases. The crystal begins to conduct electricity to small extent by ionic mechanism.

Rack your Brain

Explain why ZnO becomes yellow on heating.

Previous Year's Questions

The correct statement regarding defects in crystalline solids is **[NEET-2015]**

(1) Frenkel defects decrease the density of crystalline solids

(2) Frenkel defect is a dislocation defect

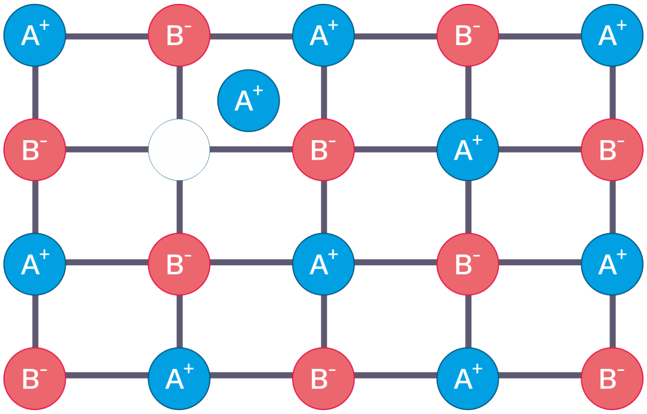
(3) Frenkel defect is found in halides of alkaline metals

(4) Schottky defects have no effect on the density of crystalline solids.

(b) **Interstitial defect:** Interstitial defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystal.

(c) **Frenkel defect:** Frenkel defect is created when an ion leaves its correct lattice site and occupies an interstitial site. This defect is common in ionic compounds which have low coordination number and in which there is large difference in size between negative and positive ions. Due to this defect, neutrality density remains same but dielectric constant of the medium increases.

For example, ZnS, AgCl, AgBr, AgI etc.



Non-stoichiometric defect: In Non-stoichiometric defect many compounds in which ratio of positive and negative ions differs from what is required by the ideal formula of the compound. Such compounds are called non-stoichiometric compounds, for example, VOx . In this type of compounds, a balance of positive and negative charges is always maintained by having extra electrons or extra positive charge.

Concept Ladder

Generally, cations are smaller than anions, hence it is more common to find the cations occupying the interstitial sites.

Rack your Brain

State whether the density of solid remains same or not for Frenkel defect.

Previous Year's Questions

The appearance of colour in solid alkali metal halides is generaly due to

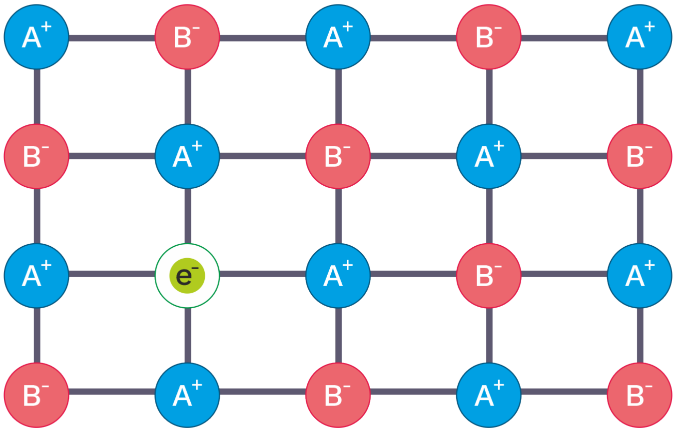
[AIPMT]

(1) interstitial positions
(2) F-centres
(3) Schottky defect
(4) Frenkel defect

These defects are explained below:

(a) Metal excess defects due to anion vacancies

- Compound may have excess metal ions if a negative (–ve) ion is absent from its lattice site, leaving a hole which is engaged by an electron to maintain electrical neutrality.
- Holes occupied by electrons are called F-centres and are responsible for colour of compounds, examples are,
  1. Excess of Na in NaCl makes crystal appear yellow.
  2. Excess of Li in LiCl makes it pink.
  3. Excess of K in KCl makes it violet.
- Greater the number of F-centres, greater will be intensity of colour. This kind of defect is found in crystal which is likely to possess Schottky defect.



(b) Metal excess defects

- This defect occurs if an extra positive ion is present in an interstitial site.
- Electrical neutrality is sustained by presence of an extra electron in interstitial site.

Concept Ladder

Defects due to interstitial cations is shown by crystals which are likely to exhibit Frenkel defect. An excess positive ion is located in the interstitial sites.

Rack your Brain

Write some difference between stiochiometric and non-stiochiometric defects.

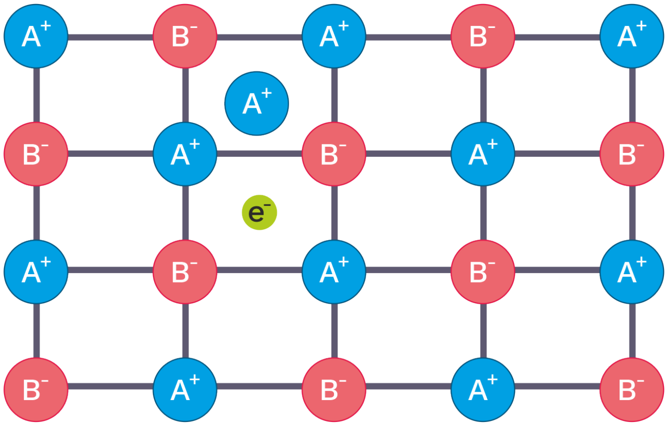
Previous Year's Questions

Ionic solids, with Schottky defects, contain in their structure

[AIPMT]

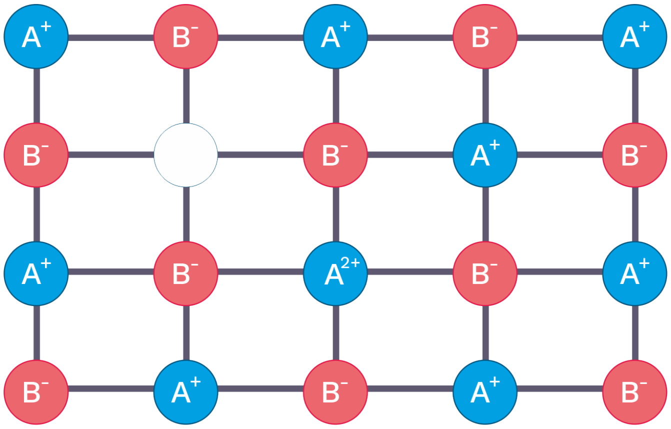
(1) cation vacancies only
(2) cation vacancies and interstitial cations
(3) equal number of cation and anion vacancies
(4) anion vacancies and interstitial anions.

- The type of defect is shown by crystals which are likely to show Frenkel defects, for example, yellow colour of Zn.



(c) Metal deficiency due to cation vacancies

- Non-stoichiometric compounds can have metal deficiency due to absence of a metal ion from their lattice site.
- The charge is balanced by an adjacent ion having high positive charge.
- These type of defect is generally shown by compounds of transition metals, for example, FeO, FeS and NiO.



Concept Ladder

When extra positive ions occupy interstitial site to maintain electrical neutrality, some extra electron occupy some other interstitial sites.

Rack your Brain

What will be the colour of KCl crystal mixed in the atmosphere K?

Previous Year's Questions

If NaCl is doped with 10^{-4} mole % of $SrCl_2$. Calculate the concentration of cation vacancies? ($N_A = 6.02 \times 10^{23}$ mol^{-1})

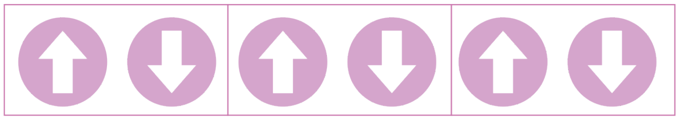
[AIPMT]

(1) 6.02×10^{16} mol^{-1}
(2) 6.02×10^{17} mol^{-1}
(3) 6.02×10^{14} mol^{-1}
(4) 6.02×10^{15} mol^{-1}

Magnetic Properties of Solids

Diamagnetic substances:

They are weakly repelled by magnetic field and do not have any unpaired electron, i.e., all paired electrons.

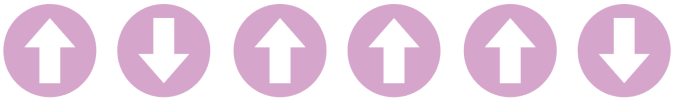


For example, NaCl, Zn, Cd, Cu^+ , TiO_2.

- They act as electrical insulators.

Paramagnetic substances:

They are attracted by magnetic field and have unpaired electrons. They lose magnetism in absence of magnetic field.



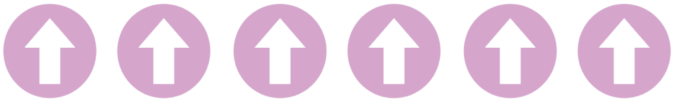
For example,

1. Metal oxides like CuO, VO_2 etc.
2. Transition metals for example, Cr, Mn, Ni, Co, Fe etc.

Ferromagnetic substances:

They are attracted by magnetic field and show permanent magnetism even in absence of magnetic field. Some examples are, Fe, Co, Ni, CrO_2 (used in the audio and video tapes) Fe_3O_4 etc.

- Ferromagnetism arises because of spontaneous alignment of magnetic moments in same direction.



- When we go above curie point/curie temperature ferromagnetism doesn't exist.

Concept Ladder

The temperature at which a feromagnetic substance loses its ferromagnetism and attains paramagnetism only is known as Curie temperature. For Iron the Curie temperature is 1033K and Ni it is 629K.

Rack your Brain

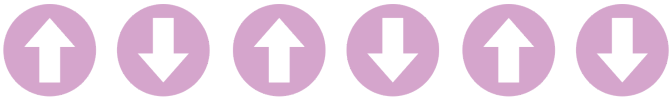
Mention some application based on ferromagnetic and anti-ferromagnetic substances.

Concept Ladder

A material is diamagnetic if it tends to move out of a magnetic field and paramagnetic if it tends to move into a magnetic field.

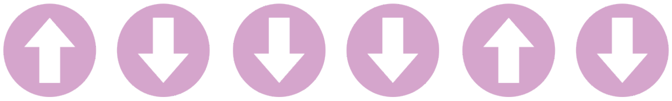
Anti-ferromagnetic substances:

They are expected to possess paramagnetism or ferromagnetism on basis of unpaired electrons but in real have zero net magnetic moment, some examples are, MnO, MnO_2, Mn_2O_3, FeO, Fe_2O_3. Anti-ferromagnetism occurs when number of parallel magnetic moments is equal to number of anti-parallel magnetic moments. This results in a net zero magnetic moment.



Ferrimagnetic substances:

In case of ferrimagnetic substances, there are unequal number of parallel and anti-parallel magnetic moments which lead to net magnetic moment, for example, Fe_3O_4, ferrites.



Ferrimagnetic, anti-ferromagnetic and ferromagnetic solids change into paramagnetic substance at a particular temperature. For example, ferrimagnetic Fe_3O_4 on heating to 850 K becomes paramagnetic. This is because of alignment of spins in one direction on heating.

Curie Temperature

The ferromagnetic substance has a characteristic temperature above which no ferromagnetism is seen. It is known as curie temperature.

Concept Ladder

Solids are classified into three groups viz – conductors, semiconductors and insulators. Conductivity of metal ranges from 10^{-7} – 10^4 ohm m, for semi conductor from 10^{-6} – 10^4 ohm m and for insulators from 10^{-10} – 10^{-20} ohm m.

Rack your Brain

Name the process of introducing an impurity into semi-conductors to enhance their conductivity.

Previous Year's Questions

If we mix a pentavalent impurity in a crystal lattice of germanium, what type of semiconductor formation will occur?

[AIPMT]

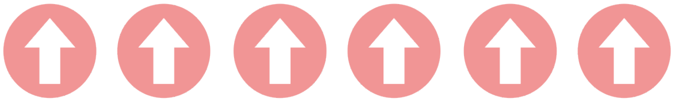
(1) n-type semiconductor
(2) p-type conductor
(3) Both (1) and (2)
(4) None of these

Electrical Properties of Solids

Piezoelectricity: It is electricity produced when mechanical force is applied on polar crystals due to displacement of ions. A piezoelectric crystal acts like a mechanical electrical transducer. They are used in record players.

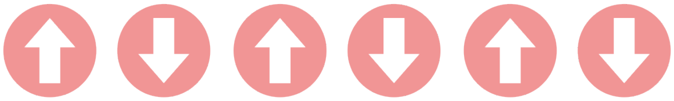
Pyroelectricity: It is the electricity produced when some polar crystals are heated. e.g., $LiNbO_3$.

Ferroelectricity: In few piezoelectric crystals, dipoles are permanently polarized even in absence of electric field. However, on applying electric field, direction of polarization changes. The phenomenon is known as ferroelectricity due to analogy with ferromagnetism.



Barium titanate, sodium potassium tartrate (Rochelle salt) and potassium dihydrogen phosphate are some of polar crystals which exhibit ferroelectricity.

Anti-ferroelectricity: In few crystals, dipoles align in such a way that they alternately point up and down in a manner that crystal does not possess any net dipole moment, for example, lead zirconate.



Superconductivity: Superconductivity defined when it offers no resistance to flow of electricity. There are no substances which are having super conductance at room temperature.

Concept Ladder

- Diode is used as a rectifier which is formed by combinaiton of n-type and p-type semiconductors.
- Transistors can be 'npn' or 'pnp' type which are formed by making sandwitch of a layer of p-type semiconductor between two n-type semiconductors (i.e., npn).

Previous Year's Questions

On doping Ge metal with a little of In or Ga, one gets

[AIPMT]

(1) p-type semiconductor
(2) n-type semiconductor
(3) insulator
(4) rectifier

- Superconductors: They are widely used in building super magnets, electronic power transmission, etc.
  Examples: $YBa_2Cu_3O_7$, Nb_3 Ge alloy, La1.25 Ba0.15 CuO_4 , $(TMTSF)_2$ PF_6 (TMTSF stands for tetra methyl tetra Selena fulvalene).
- Kammerlingh Onnes observed this phenomenon at 4K in mercury.

Semiconductors: They are electronic conductors which have electrical conductivity in range of 10^{4-} 10^{7} Ω^{-1} cms, for example, Sn, Ge, Si (grey only), SiC, Cu_2O.

- Pure substances which are semiconductors which are known as intrinsic semiconductors, for example, Si, Ge.
- In case of semiconductors, if conductivity is due to impurities, they are known as extrinsic semiconductors.
- ● Addition of impurities in to a semiconductor is known as doping. Example includes, when phosphorous and arsenic (5th group element) are doped in silica (4th group element) n-type of conductance is seen.
  When a group 3rd element (for example, Ga) is Doped, p-type of conductance is observed..

Definition

The type of semiconductor formed by doping of impurities to any substance is known as extensive semiconductors.

Rack your Brain

What are the group numbers of elements which form semiconducters substances?

Q.6 Despite long-range order in the arrangement of particles why are the crystals usually not perfect?

A.6 Crystallization process will be faster so that particle may not get enough time to arrange in perfect order. That is why crystals have the long- range arrangement of particles but not perfect..

Q.7 Why is FeO (s) not formed in stoichiometric composition?

A.7 The composition of Fe^{2+} and O^{2-} ions is not 1:1 it is 0.95:1. This is obtained if and only if a small number of Fe^{2+} ions are replaced by two-third of Fe^{3+} in OH sites..

Q.8 Gold crystallizes in an FCC unit cell. What is the edge length of unit cell (r = 0.144 mm)?

A.8 r = 0.144 nm

$$a = 2\sqrt{2}\,r$$
$$= 2 \times 1.414 \times 0.144 \text{ nm}$$
$$= 0.407 \text{ nm}$$

Q.9 Analysis shows that a metal oxide's empirical formula is M0.98O1.00. Calcu late the percentage of M2+ and M3+ ions in the crystal.

A.9 Let the M2+ ion in crystal be x

M3+ = 0.98 – x

Since, total charge on compound must be zero,

So, 2x + 3(0.98 – x) – z = 0

Or $x = 0.94$

$$\% \text{ of } M^{2+} - \frac{0.94}{0.98} \times 100 = 97.9\%$$
$$\% \text{ of } M^{3+} = 100 - 97.9 = 2.1\%$$

Q.10 Explain how electrical neutrality is maintained in compounds showing Frenkel and Schottky defect.

A.10 The compound showing Frenkel defect, ions just get displaced within lattice, while in compounds showing Schottky defect,have equal number of cations and anions are removed from lattice. So it's electrical neutrality is maintained in both cases..

Q.11 The electrical conductivity of a metal decreases with rise in temperature while that of a semi-conductor increases. Explain.

A.11 In metals with increase of temperature, kernels electrons start vibrating at faster rate and thus offer resistance to own of electrons. Then conductivity of metals decreases.

In case of semi-conductors (14th group elements), with increase of temperature, more electrons can shift from valence band to conduction band. Then conductivity of semiconductors increases.

Q.12 What type of substances would make better permanent magnets – ferromagnetic or ferromagnetic ? Why ?

A.12 Ferromagnetic substances make better permanent magnets. This is because metal ions of a ferromagnetic substance are grouped into small regions known as domains. Each domain acts as small magnet and get oriented in direction of magnetic field in which it is placed. This persists even in absence of magnetic field.

Q.13 In a crystalline solid, the atoms A and B are arranged as follows :
(a) Atoms A are arranged in ccp array.
(b) Atoms B occupy all the octahedral voids and half of the tetrahedral voids.
What is the formula of the compound ?

A.13 No. of A (ccp) = 4

$$\text{No. of B} = \text{octahedral voids} + \frac{\text{Tetrahedral}}{2}$$

$$= 4 + \frac{8}{2}$$

$$= 8$$

A : B so, formula of the compound is AB_2
4 : 8
1 : 2
AB_2

Q.14 A unit cell consists of a cube in which X atoms are at the corners and Y atoms are at the face centres. If two atoms are missing from two corners of the unit cell, what is the formula of the compound?

A.14 Total contribution of 'X' atoms from 6 corners $= \frac{1}{8} \times 6 = \frac{3}{4}$

Number of atoms of Y from face centres = 3

$\therefore$ x : y = $\frac{3}{4}$: 3 = 3 : 12 or 1 : 4

Hence, formula is XY_4.

Q.15 Calculate the number (n) of atoms contained within (a) simple cubic cell (b) a body centred cubic cell (c) a face centred cubic cell.

A.15 (a) The simple cubic jnit cell has 8 atoms at eight corners. Each aotm is shared by 8 unit cells.

$$\therefore \qquad n = 8 \times \frac{1}{8} = 1$$

(b) The body centred cubic (BCC) cell consists of 8 atoms at the corners and one atom at centre.

$$\therefore \qquad n = \left(8 \times \frac{1}{8}\right) + 1 = 2$$

(c) The face centred cubic (FCC) unit cell consists of 8 atoms at the eight corners and one atom at all faces. This atom at the face is shared by two unit cells.

$$\therefore \qquad n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$$

Q.16 Calculate number of atoms in a cubic unit cell having one atom on each corner and tow atoms on each body diagonal.

A.16 There are total 4 body diagonals and there are 2 atoms at each body diagonal.
Hence nubmer of atoms from 4 diagonals = 8
Number of atoms from 8 corners = 1
$\therefore$ Total number of atoms in this unit cell = 8 + 1 = 9

Q.17 In compound atoms of element Y forms ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. What is the formula of the compound ?

A.17 No. of Y atoms per unit cell in ccp lattice = 4

No. of tetrahedral voids = 2 × 4 = 8

No. of tetrahedral voids occupied by X = 2/3 × 8 = 16/3

Therefore, Formula of the compound = $X_{16/3}Y_4$

$= X_{16}Y_{12}$

$= X_4Y_3$

Q.18 Potassium crystallizes in a body centred cubic lattice. How many unti cells are present in 2g potassium? (At. mass of K = 39)

A.18 A bcc unit cell has 2 atoms per unit cell

$$\therefore \text{ Mole of potassium } = \frac{2}{39}$$

$$\text{Number of atoms of K } = \frac{2 \times 6.022 \times 10^{23}}{39}$$

$$\text{Number of unit cells } = \frac{2 \times 6.022 \times 10^{23}}{39 \times 2} = 1.54 \times 10^{22}$$

Q.19 A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 241.5 pm, what should be the ideal radius of the cation? Can a cation C^+ having radius of 50 pm be fitted into the tetrahedral hole of the crystal A^+B^-?

A.19 As A+B- has NaCl structure, A+ ions will be present in octahedral voids.

Ideal radius of cation will be equal to radius of the octahedral void becuase in that case, it will touch the anions and arrangement will be close packed. Hence,

Radius of octahedral void = r_{A}^{+} = 0.414 × r_{B}^{-} = 0.141 × 241.5 pm = 100.0 pm

Radius of tetrahedral void = 0.225 × r_{B}^{-} = 0.225 × 241.5 pm = 54.3 pm

As radius of cation C^+(50 pm) is smaller than size of tetrahedral void and can be placed into tetrahedral voids (but not exactly fitted into it).

Summary

- In NaCl, there are nearly 10^6 Schottky pairs per cm^3 at room temperature (As in 1 cm^3 there are nearly 10^{22} ions so there is one schottky defect per 10^{16} ions.)
- Combination of ‘p’ and ‘n’ type semiconductors are used to make electronic components e.g., Diode.
- On increasing temperature of CsCl structure the coordination number changes from 8–8 to 6–6. While on increasing pressure in NaCl structure Co No increases from 6–6 to 8–8.
- The production of frenkel or schottky defects is an endothermic process.
- He has HCP structure while rest of inert gases have C.C.P structure.
- The most unsymmetrical crystal system is Tri clinic as $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$.
- At the highest temperature at which super conductivity was called as 23 K in case of alloys of Niobium.
- **d–spacing:** It is a distance between two parallel planes in a cubic lattice.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Here, a = edge length
h, k, l = miller indices of plane.

- **Atomic Radius → and Edge Length (a)**

In a simple cubic unit cell $r = \frac{a}{2}$

In face-centred cubic cell (FCC) $r = \frac{a}{\sqrt{2}}$

In body-centred cubic cell (BCC) $r = \frac{\sqrt{3}\,a}{4}$

- ● **No. of Atoms in a Unit Cell/ Unit Cell Content (Z)**

$$Z = \frac{n_c}{3} + \frac{n_f}{2} + \frac{n_i}{1}$$

Here $n_c = 3$, $n_f = 6$, $n_i = 1$

- **Density of Lattice Matter (d)**

$$d = \frac{Z \times \text{Atomic weight}}{N_0 \times \text{Volume of unit cell } (a^3)}$$

Here d = Density
Z = Number of atoms
N_0 = Avogadro number
a^3 = Volume
a = Edge length

- **Packing Fraction**

$$P.F = \frac{Z \times \frac{4}{3}\pi r^3}{a^3}$$

- **Bragg's Equation**

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