

The Solid State

Amorphous and Crystalline Solids & Classification of Crystalline Solids

Amorphous and Crystalline Solids

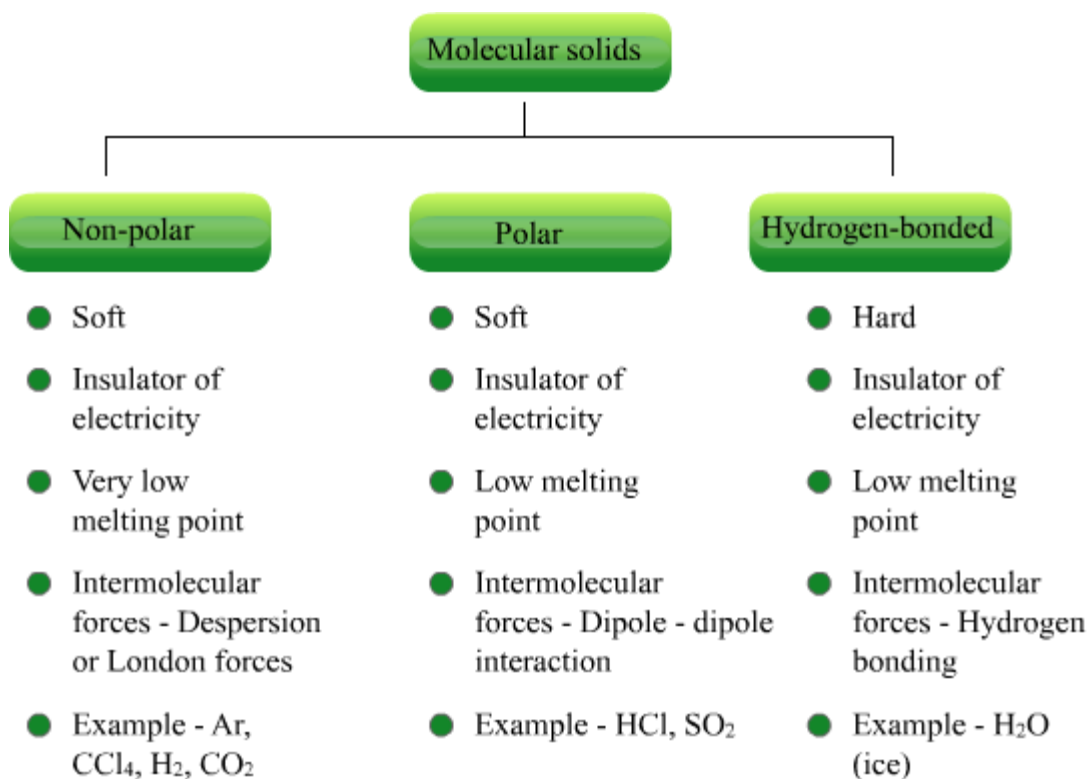
- Based on the nature of the order of arrangement of the constituent particles, solids are classified as amorphous and crystalline.
- Differences between amorphous and crystalline solids are listed in the given table.

Amorphous solids		Crystalline solids	
1	Have irregular shape	1	Have definite characteristic geometrical shape
2	Have only short-range order in the arrangement of constituent particles	2	Have long-range order in the arrangement of constituent particles
3	Gradually soften over a range of temperature	3	Have sharp and characteristic melting point
4	When cut with a sharp-edged tool, they cut into two pieces with irregular shapes	4	When cut with a sharp-edged tool, they split into two pieces with plain and smooth newly generated surfaces.
5	Do not have definite heat of fusion	5	Have definite and characteristic heat of fusion
6	Isotropic in nature	6	Anisotropic in nature

7	Pseudo solids or super-cooled liquids	7	True solids
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Classification of Crystalline Solids

- Based on the nature of intermolecular forces, crystalline solids are classified into four categories –
- Molecular solids
- Ionic solids
- Metallic solids
- Covalent solids
- Constituent particles are molecules



- Ionic solids
- Constituent particles are ions

- Hard but brittle
- Insulators of electricity in solid state, but conductors in molten state and in aqueous solution
- High melting point
- Attractive forces are Coulombic or electrostatic
- Example – NaCl, MgO, ZnS
- Metallic solids
- In metallic solids, positive ions are surrounded and are held together in a sea of delocalised electrons.
- Hard but malleable and ductile
- Conductors of electricity in solid state as well as molten state
- Fairly high melting point
- Particles are held by metallic bonding
- Example – Fe, Cu, Mg
- Covalent or network solids
- Constituent particles are atoms
- Hard (except graphite, which is soft)
- Insulators of electricity (except graphite, which is a conductor of electricity)
- Very high melting point and can decompose before melting
- Particles are held by covalent bonding
- Example – SiO₂ (quartz), SiC, diamond, graphite

Add to your knowledge

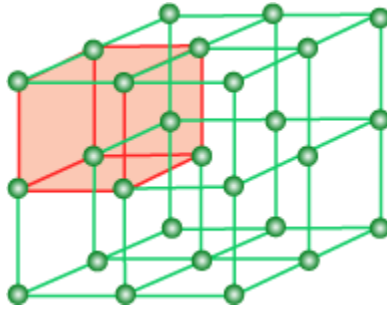
The property by virtue of which two or more crystalline solids having similar chemical composition exist in the same crystalline form is called **isomorphism**. For example: Na₃PO₄.

The property by virtue of which a particular substance exists in more than one crystalline form is called polymorphism. For example: existence of calcium carbonate in two crystalline forms called calcite and aragonite.

Crystal Lattices and Unit Cells

Crystal Lattice

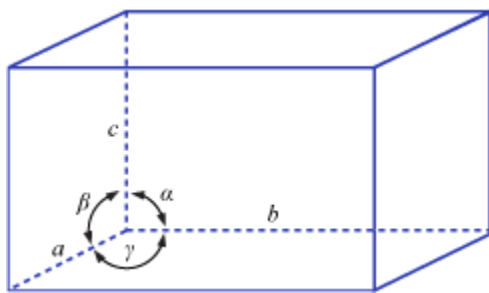
- Regular three-dimensional arrangement of points in space



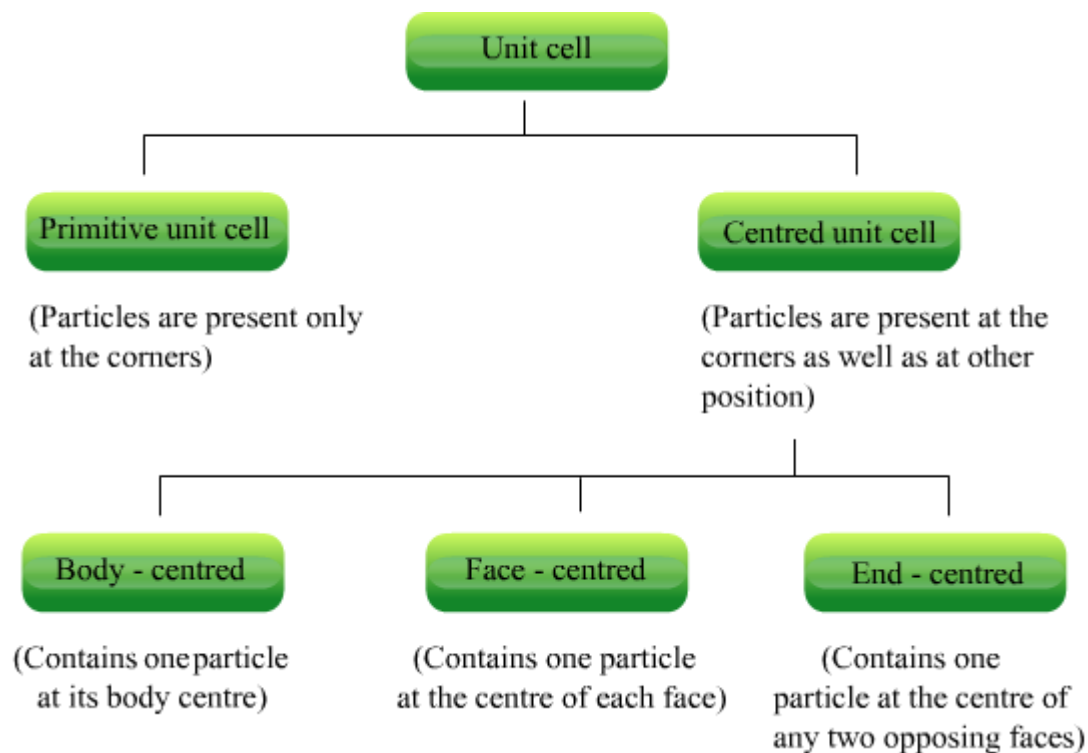
- There are 14 possible three-dimensional lattices, known as Bravais lattices.
- Characteristics of a crystal lattice:
- Each point in a lattice is called lattice point or lattice site.
- Each lattice point represents one constituent particle (atom, molecule or ion).
- Lattice points are joined by straight lines to bring out the geometry of the lattice.

Unit Cell

- Smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice
- Characterised by –
 - (i) Its dimensions along the three edges a , b and c
 - (ii) Angles between the edges α , β and γ

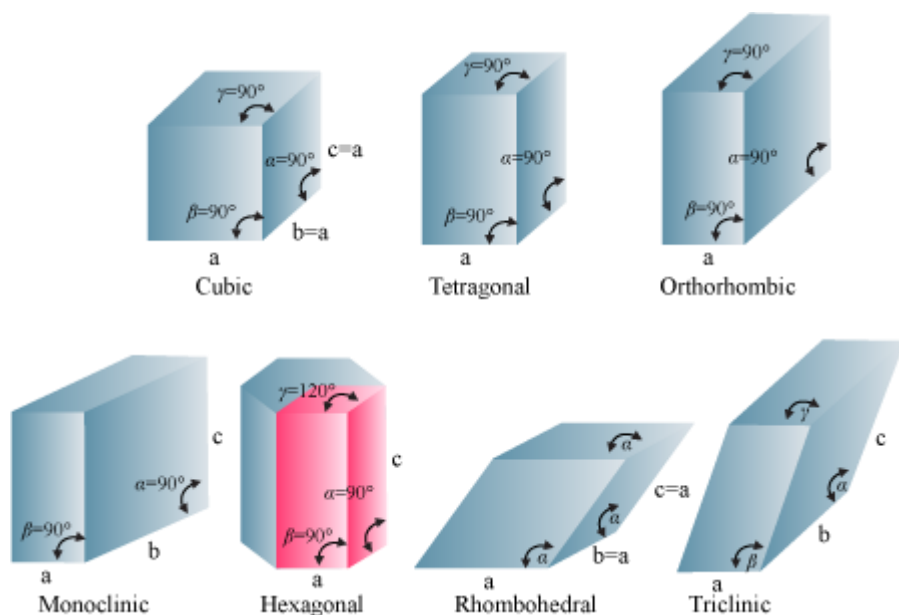


- The unit cells can be classified as follows:



Seven Crystal Systems

There are seven types of primitive unit cells, as given in the following table.



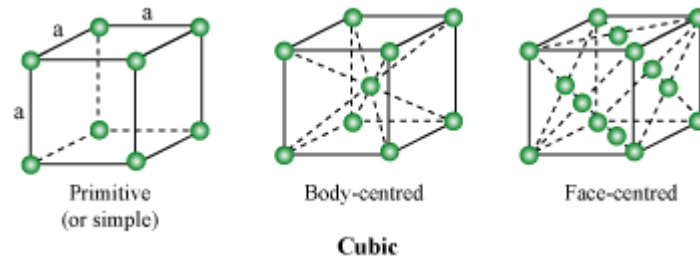
The given table lists seven primitive unit cells and their possible variations as centered unit cells.

Crystal Class	Axial Distances	Axial Angles	Possible Types of Unit Cells	Examples
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, body-centred, face-centred	KCl, NaCl
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, body-centred	SnO ₂ , TiO ₂
3. Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, body-centred, face-centred, end-centred	KNO ₃ , BaSO ₄
4. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Primitive	Mg, ZnO
5. Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive	(CaCO ₃) Calcite, HgS (Cinnabar)
6. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Primitive and end-centred	Monoclinic sulphur, Na ₂ SO ₄ ·10H ₂ O
7. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive	K ₂ Cr ₂ O ₇ , H ₃ BO ₃

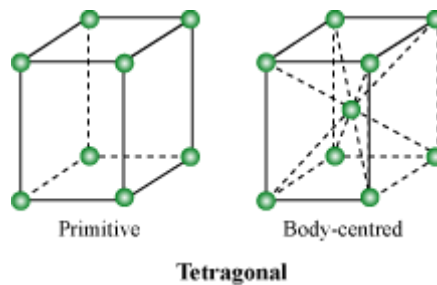
- **Unit cells of 14 types Bravais lattices:**

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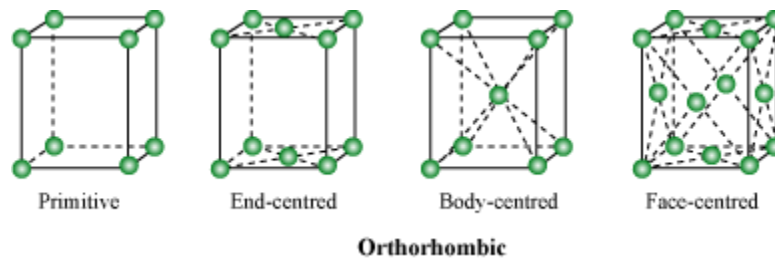
- Cubic lattices: All sides are of the same length, and the angles between the faces are 90° each



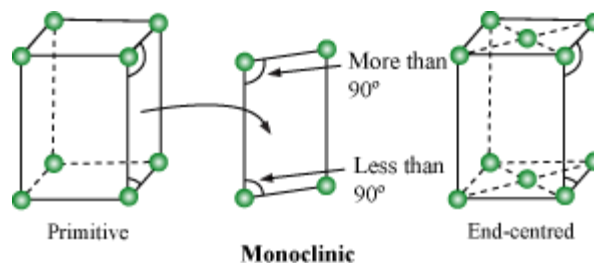
- Tetragonal lattices: One side is different in length from the other two, and the angles between the faces are 90° each



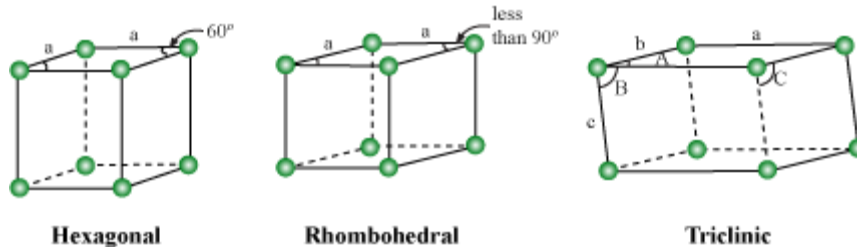
- Orthorhombic lattices: Unequal sides; angles between the faces are 90° each



- Monoclinic lattices: Unequal sides; two faces have angles not equal to 90°



- Hexagonal lattice: One side is different in length from the other two, and the marked angles on two faces are 60°
- Rhombohedral lattice: All sides are of equal length, and the marked angles on two faces are less than 90°
- Triclinic lattice: Unequal sides; unequal angles, with none equal to 90°



Questions asked in previous years' board examinations

Ques. Name the type of structure possessed by a unit cell of CsCl.

(1 mark)

–2004 CBSE Delhi

Sol: A unit cell of CsCl possesses body-centred cubic structure.

Number of Atoms in a Unit Cell

Calculation of number of atoms in a unit cell

The number of atoms in a unit cell can be calculated, by using the following approximations.

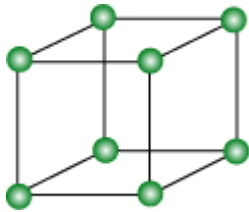
An atom at the corner is shared by 8 unit cells. Hence, an atom at the corner contributes $\frac{1}{8}$ to the unit cell.

An atom at the face is shared by 2 unit cells. Hence, an atom at the face contributes $\frac{1}{2}$ to the unit cell.

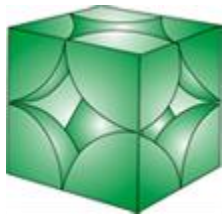
An atom within the body of a unit cell is shared by no other unit cell. Hence, an atom at the body contributes singly, i.e., 1 to the unit cell.

Primitive Cubic Unit Cell

Open structure for a primitive cubic unit cell is shown in the given figure.



Actual portions belonging to one unit cell are shown in the given figure.



Total number of atoms in one unit cell

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

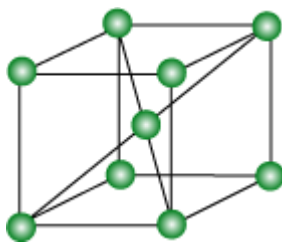
$$= 8 \times \frac{1}{8}$$

$$= 1$$

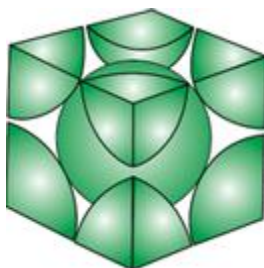
Let us see the packing in a simple cubic unit cell through this video.

Body-Centred Cubic Unit Cell

Open structure for a body-centred cubic unit cell is shown in the given figure.



Actual portions belonging to one unit cell are shown in the given figure.



Total number of atoms in one unit cell

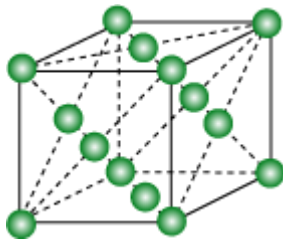
$$= 8 \text{ corners} \times \frac{1}{8} \text{ per corner atom} + 1 \text{ body-centre atom}$$

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

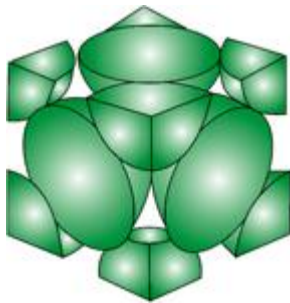
$$= 2$$

Face-Centred Cubic Unit Cell

Open structure for a face-centred cubic unit cell is shown in given figure.



Actual portions of atoms belonging to one unit cell are shown in the given figure.



Total number of atoms in one unit cell

$$= 8 \text{ corner atoms} \times \frac{1}{8} \text{ atom per unit cell} + 6 \text{ face-centred atoms} \times \frac{1}{2} \text{ atom per unit cell}$$

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2}$$

$$= 4$$

Now, let us visualise the packing in face-centred cubic lattice through this video.

Questions asked in previous years' board examinations

Ques. What is the total number of atoms per unit cell in a face-centred cubic (fcc) structure?

(1 mark)

–2008 CBSE Delhi

Sol: The total number of atoms per unit cell in a face-centred cubic (fcc) structure is 4 (8 corner

atoms $\times \frac{1}{8}$ atom per unit cell + 6 face-centred atoms $\times \frac{1}{2}$ atom per unit cell)

Ques. What is the number of atoms per unit cell in a body-centred cubic structure?

(1 mark)

–2007 CBSE Delhi

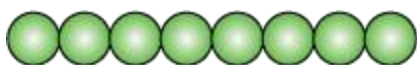
Sol: The number of atoms per unit cell in a body-centred cubic structure is 2 (8 corner atoms $\times \frac{1}{8}$ atom per unit cell + 1 body-centre atom).

Closed-Packed Structures

Coordination number – The number of nearest neighbours of an atom

Close-Packing in One dimension

- Only one way of arrangement, i.e., the particles are arranged in a row, touching each other

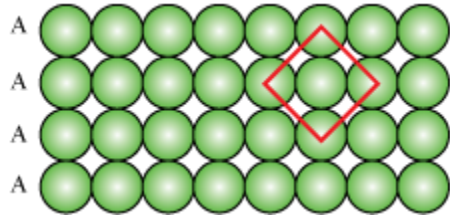


- Coordination number = 2

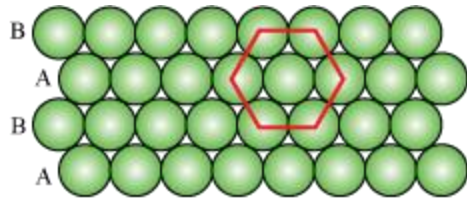
Close-Packing in Two Dimensions

- Square close-packing in two dimensions

- AAA type arrangement



- The particles in the second row are exactly above those in the first row.
- Coordination number = 4
- Hexagonal close-packing in two dimensions
- ABAB type arrangement

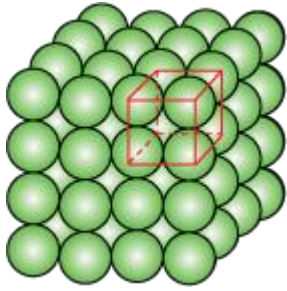


- The particles in the second row are fitted in the depressions of the first row. The particles in the third row are aligned with those in the first row.
- More efficient packing than square close-packing
- Coordination number = 6

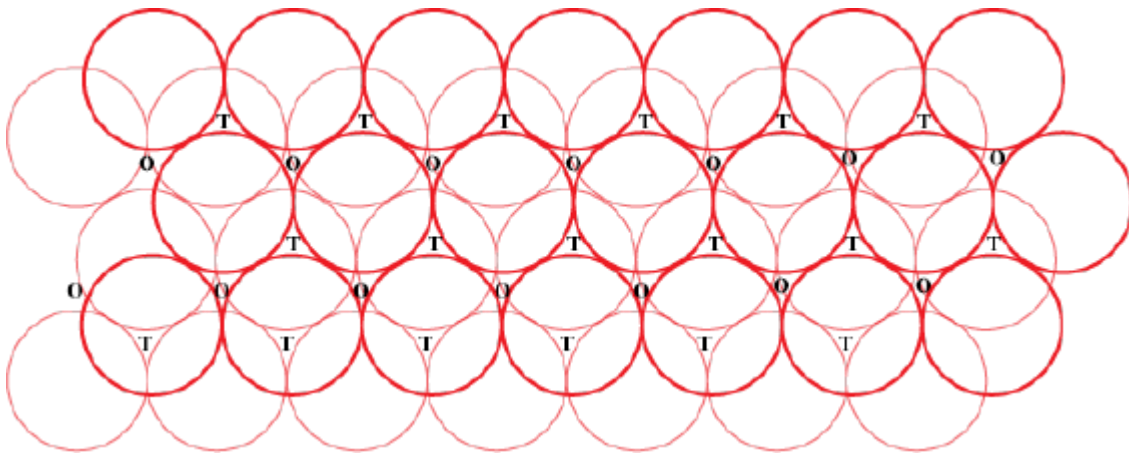
Close-Packing in Three Dimensions

Three-dimensional close-packing is obtained by stacking two-dimensional layers (square close-packed or hexagonal close-packed) one above the other.

- By stacking two-dimensional square close-packed layers
- The particles in the second layer are exactly above those in the first layer.
- AAA type pattern
- The lattice generated is simple cubic lattice, and its unit cell is primitive cubic unit cell.



- Coordination number = 6
- By stacking two-dimensional hexagonal close-packed layers
- Placing the second layer over the first layer
- The two layers are differently aligned.
- Tetrahedral void is formed when a particle in the second layer is above a void of the first layer.
- Octahedral void is formed when a void of the second layer is above the void of the first layer.

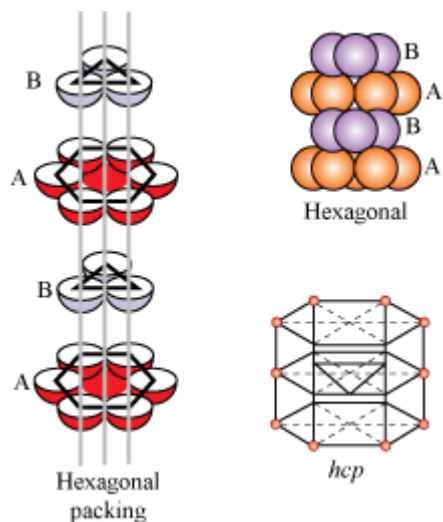


Here, T = Tetrahedral void, O = Octahedral void

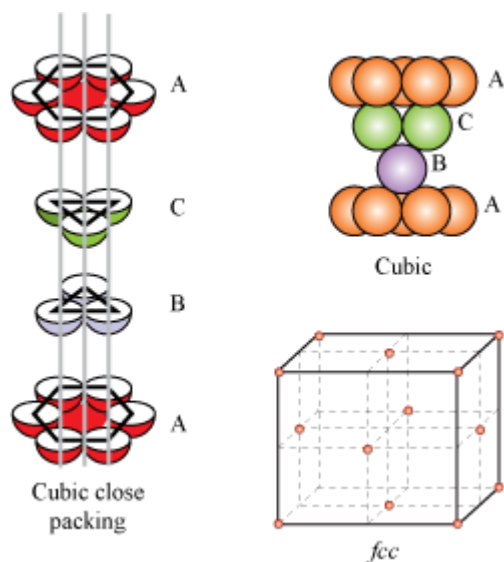
Number of octahedral voids = Number of close-packed particles

Number of tetrahedral voids = $2 \times$ Number of close-packed particles

- Placing the third layer over the second layer: There are two ways –
- Covering tetrahedral voids: ABAB ... pattern. The particles in the third layer are exactly aligned with those in the first layer. It results in a hexagonal close-packed (*hcp*) structure. Example: Arrangement of atoms in metals like Mg and Zn



- Covering octahedral voids: ABCABC ... octahedral voids. The particles in the third layer are not aligned either with those in the first layer or with those in the second layer, but with those in the fourth layer aligned with those in the first layer. This arrangement is called 'C' type. It results in cubic close-packed (*ccp*) or face-centred cubic (*fcc*) structure. Example: Arrangement of atoms in metals like Cu and Ag



- Coordination number in both *hcp* and *ccp* structures is 12.
- Both *hcp* and *ccp* structures are highly efficient in packing (packing efficiency = 74%)

Questions asked in previous years' board examinations

Ques. What is the coordination number of each type of ions in a rock-salt type crystal structure?

(1 mark)

–2008 CBSE Delhi

Sol: In rock salt or common salt, every Na^+ ion is surrounded by 6 Cl^- ions and each Cl^- ion is surrounded by 6 Na^+ ions. Thus, the coordination number of each type of ion in rock salt is 6.

Ques. What is the maximum possible coordination number of an atom in an *hcp* crystal structure of an element?

(1 mark)

–2005 CBSE Delhi

Sol: The maximum possible coordination number of an atom in an *hcp* crystal structure of an element is 12.

Formula of a Compound and Number of Voids Filled

- Number of octahedral voids = Number of close-packed particles

Number of tetrahedral voids = $2 \times$ Number of close-packed particles

- In ionic solids, the bigger ions (usually anions) form the close-packed structure and the smaller ions (usually cations) occupy the voids.
- If the latter ion is small enough, then it occupies the tetrahedral void, and if bigger, then it occupies the octahedral void.
- Not all the voids are occupied. Only a fraction of the octahedral or tetrahedral voids are occupied.
- The fraction of the octahedral or tetrahedral voids that are occupied depends on the chemical formula of the compound.

Example

A compound is formed by two elements X and Y. The atoms of element X form *hcp* lattice and those of element Y occupy $\frac{1}{4}$ th of the tetrahedral voids. What is the formula of the compound formed?

Solution:

It is known that the number of tetrahedral voids formed is equal to twice the number of atoms of element X.

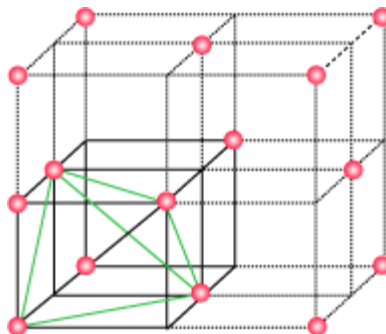
It is given that only $\frac{1}{4}$ th of the tetrahedral voids are occupied by the atoms of element Y.

$$\begin{aligned}\text{Therefore, ratio of the number of atoms of X and Y} &= 1 : 2 \times \left(\frac{1}{4}\right) \\ &= 2 : 1\end{aligned}$$

Hence, the formula of the compound formed is X_2Y .

Locating Tetrahedral Voids

- A unit cell of *ccp* or *fcc* lattice is divided into eight small cubes. Then, each small cube has 4 atoms at alternate corners. When these are joined to each other, a regular tetrahedron is formed.

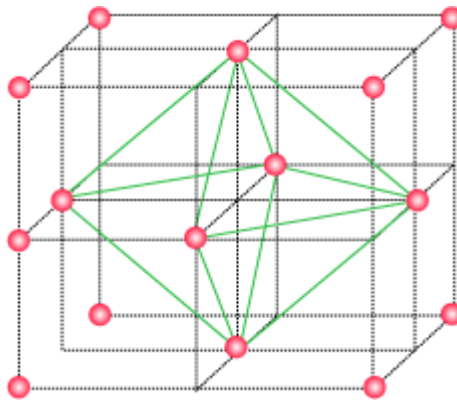


- This implies that one tetrahedral void is present in each small cube. Therefore, a total of eight tetrahedral voids are present in one unit cell.

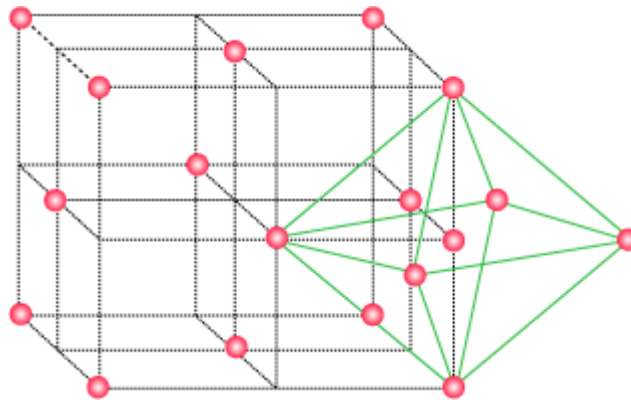
- Since each unit cell of *ccp* structure has 4 atoms, the number of tetrahedral voids is twice the number of atoms.

Locating Octahedral Voids

- When the six atoms of the face centres are joined, an octahedron is generated. This implies that the unit cell has one octahedral void at the body centre.



- Besides the body centre, there is one octahedral void at the centre of each of the 12 edges. But only $\frac{1}{4}$ th of each of these voids belongs to the unit cell.



- Now, the total number of octahedral voids in a cubic loose-packed structure

$$\begin{aligned}
 &= 1 + 12 \times \frac{1}{4} \\
 &= 1 + 3 \\
 &= 4
 \end{aligned}$$

This means that in *ccp* structure, the number of octahedral voids is equal to the number of atoms in each unit cell.

Now, let us see the stacking of two layers and the formation of the two types of voids by means of this video.

Add to your knowledge

In NaCl, the Na^+ ions occupy all the octahedral voids. In ZnS, Zn^{2+} are in alternate tetrahedral voids. In CaF_2 , F^- ions occupy all the tetrahedral voids.

In Fe_3O_4 , if Fe^{2+} ions are replaced by divalent cations such as Mg^{2+} and Zn^{2+} , then the compounds obtained are called ferrites.

Questions asked in previous years' board examinations

Ques. A cubic solid is made of two elements X and Y. Atoms Y are at the corners of the cube and X at the body centre. What is the formula of the compound?

(1 mark)

–2006 CBSE Delhi

Sol: The atom at the body centre makes a contribution of 1 to the unit cell, while the atom at the corner makes a contribution of $\frac{1}{8}$ to the unit cell.

Thus, number of atoms Y per unit cell

= Number of atoms $\times$ Contribution per unit cell

= 8 (at the corners) $\times \frac{1}{8}$ atoms per unit cell

= 1

Thus, number of atoms X per unit cell

= Number of atoms $\times$ contribution per unit cell

= 1 (at the body centre) $\times 1$

$$= 1$$

Thus, the formula of the given compound is XY.

Packing Efficiency & Calculations Involving Unit Cell Dimensions

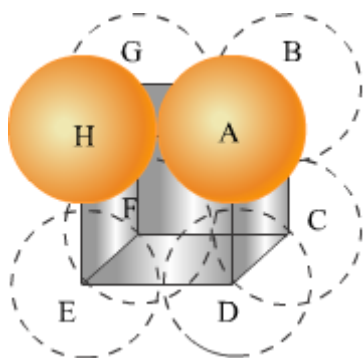
Packing Efficiency

- Percentage of total space filled by particles

Calculations of Packing Efficiency in Different Types of Structures

- **Simple cubic lattice**

In a simple cubic lattice, the particles are located only at the corners of the cube and touch each other along the edge.



Let the edge length of the cube be ' a ' and the radius of each particle be r .

Then, we can write:

$$a = 2r$$

Now, volume of the cubic unit cell = a^3

$$= (2r)^3$$

$$= 8r^3$$

The number of particles present per simple cubic unit cell is 1.

Therefore, volume of the occupied unit cell $= \frac{4}{3}\pi r^3$

Hence, packing efficiency $= \frac{\text{Volume of one particle}}{\text{Volume of cubic unit cell}} \times 100\%$

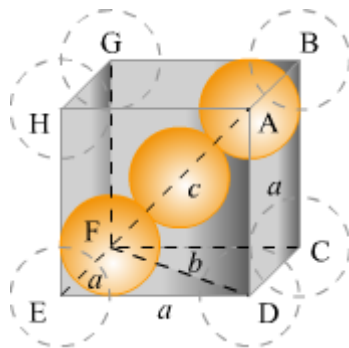
$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\%$$

$$= \frac{1}{6}\pi \times 100\%$$

$$= \frac{1}{6} \times \frac{22}{7} \times 100\%$$

$$= 52.4\%$$

- **Body-centred cubic structures**



It can be observed from the above figure that the atom at the centre is in contact with the other two atoms diagonally arranged.

From $\triangle FED$, we have

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

$$\Rightarrow b^2 = 2a^2$$

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

From $\triangle AFD$, we have

$$\begin{aligned}
 c^2 &= a^2 + b^2 \\
 \Rightarrow c^2 &= a^2 + 2a^2 \quad (\text{Since } b^2 = 2a^2) \\
 \Rightarrow c^2 &= 3a^2 \\
 \Rightarrow c &= \sqrt{3}a
 \end{aligned}$$

Let the radius of the atom be r .

Length of the body diagonal, $c = 4r$

$$\begin{aligned}
 \Rightarrow \sqrt{3}a &= 4r \\
 \Rightarrow a &= \frac{4r}{\sqrt{3}}
 \end{aligned}$$

$$\text{or, } r = \frac{\sqrt{3}a}{4}$$

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

Volume of the cube,

A body-centred cubic lattice contains 2 atoms.

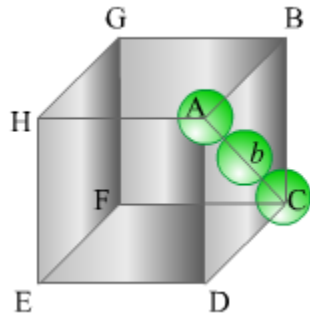
$$\begin{aligned}
 \text{So, volume of the occupied cubic lattice} &= 2 \times \frac{4}{3} \pi r^3 \\
 &= \frac{8}{3} \pi r^3
 \end{aligned}$$

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

$$\begin{aligned}
 &= \frac{\frac{8}{3} \pi r^3}{\left(\frac{4}{\sqrt{3}} r \right)^3} \times 100 \% \\
 &= \frac{\frac{8}{3} \pi r^3}{\frac{64}{3\sqrt{3}} r^3} \times 100 \% \\
 &= 68 \%
 \end{aligned}$$

- **hcp and ccp Structures**

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



From $\triangle ABC$, we have

$$AC^2 = BC^2 + AB^2$$

$$\Rightarrow b^2 = a^2 + a^2$$

$$\Rightarrow b^2 = 2a^2$$

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

Let r be the radius of the atom.

Now, from the figure, it can be observed that:

$$b = 4r$$

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

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

Now, volume of the cube, $a^3 = (2\sqrt{2}r)^3$

We know that the number of atoms per unit cell is 4.

So, volume of the occupied unit cell $= 4 \times \frac{4}{3} \pi r^3$

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

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

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

$$= 74\%$$

- Thus, *ccp* and *hcp* structures have maximum packing efficiency.

Calculations Involving Unit Cell Dimensions

In a cubic crystal, let

a = Edge length of the unit cell

d = Density of the solid substance

M = Molar mass of the substance

Then, volume of the unit cell $= a^3$

Again, let

z = Number of atoms present in one unit cell

m = Mass of each atom

Now, mass of the unit cell = Number of atoms in the unit cell $\times$ Mass of each atom

$$= z \times m$$

$$\text{But, mass of an atom, } m = \frac{M}{N_A}$$

Therefore, density of the unit cell,

$$d = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$\Rightarrow d = \frac{z \cdot m}{a^3}$$

$$\Rightarrow d = \frac{z \cdot M}{a^3 \cdot N_A}$$

Let us calculate the density of an element crystallising in face-centred cubic lattice.

Questions asked in previous years' board examinations

Ques. The density of copper metal is 8.95 g cm^{-3} . If the radius of copper atom is 127.8 pm , is the copper unit cell a simple cubic, a body-centred cubic or a face centred cubic structure? (Given: At. Mass of Cu = 63.54 g mol^{-1} and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

(3 marks)

–2010 CBSE Delhi

$$d = \frac{z \times M}{a^3 \times N_A} \quad \dots(i)$$

Sol: We know that density,

For SCC: $z = 1$ and $a = 2r$

For BCC: $z = 2$ and $a = \frac{4}{\sqrt{3}}r$

For FCC: $z = 4$ and $a = \frac{4}{\sqrt{2}}r$

Substituting the values of z and a in equation (i) we can calculate the value of density.

It is given that $M = 63.54 \text{ g mol}^{-1}$

$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

$r = 127.8 \times 10^{-10} \text{ cm}$

$$\text{so } d = \frac{z \times 63.54}{a^3 \times 6.02 \times 10^{23}} = \frac{z \times 10.55 \times 10^{-23}}{a^3}$$

$$\begin{aligned} \text{For SCC: } d &= \frac{(1) \times 10.55 \times 10^{-23}}{(2 \times 127.8 \times 10^{-10})^3} \\ &= \frac{10.55}{1.67} = 6.31 \text{ g/cm}^3 \end{aligned}$$

$$\begin{aligned} \text{For BCC: } d &= \frac{(2) \times 10.55 \times 10^{-23}}{\left(\frac{4}{\sqrt{3}} \times 127.8 \times 10^{-10}\right)^3} \\ &= \frac{21.10}{2.57} = 8.2 \text{ g/cm}^3 \end{aligned}$$

$$\begin{aligned} \text{For FCC: } d &= \frac{4 \times 10.55 \times 10^{-23}}{\left(\frac{4}{\sqrt{2}} \times 127.8 \times 10^{-10}\right)^3} \\ &= \frac{42.2}{4.73} = 8.92 \text{ g/cm}^3 \end{aligned}$$

The given value of density is 8.95 g/cm^3 . Hence, from the given data, we can conclude that copper unit cell is face centred cubic or fcc.

Ques. Iron has a body-centred cubic unit cell with a cell edge of 286.65 pm . The density of iron is 7.87 g cm^{-3} . Use this information to calculate Avogadro's number.

(At. Mass of Fe = 56 g mol^{-1})

(3 marks)

–2009 CBSE Delhi

Sol: In a body-centred cubic unit cell, number of atoms present = 2

At mass of iron = 56 g mol^{-1}

Density of iron = 7.87 g cm^{-3}

Mass of iron = $7.87 \times \text{Volume}$

Volume in BCC = $(a)^3$

= $(286.65)^3 \text{ pm}$

$$= 2.34 \times 10^{-23} \text{ cm}$$

$$\text{Mass} = 7.87 \times 2.34 \times 10^{-23} \text{ g}$$

$$\text{Avogadro's number} = \frac{\text{No. of atoms} \times \text{Molar mass}}{\text{Given mass}}$$

$$= \frac{2 \times 56}{7.87 \times 2.34 \times 10^{-23}}$$

$$\therefore \text{Avogadro's number} = 6.022 \times 10^{23}$$

Ques. An element has a body-centred cubic structure with a cell edge of 288 pm. The density of the element is 7.2 g cm^{-3} . Calculate the number of atoms present in 208 g of the element.

(3 marks)

–2006 CBSE Delhi

Sol: Cell edge (a) = 288 pm

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

$$= (288 \text{ pm})^3$$

$$= (288 \times 10^{-10} \text{ cm})^3$$

$$= 2.389 \times 10^{-23} \text{ cm}^3$$

$$\text{Volume of 208 g of the element} = \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{208 \text{ g}}{7.2 \text{ g cm}^{-3}}$$

$$= 28.89 \text{ cm}^3$$

$$\text{Number of unit cells} = \frac{\text{Total volume}}{\text{Volume of a unit cell}}$$

$$= \frac{28.89 \text{ cm}^3}{2.389 \times 10^{-23} \text{ cm}^3}$$

$$= 12.09 \times 10^{23}$$

In a bcc structure, the number of atoms per unit cell = 2

$$\therefore \text{Number of atoms in 208 g of the given element} = 2 \times 12.09 \times 10^{23}$$

$$= 24.18 \times 10^{23}$$

Ques. Aluminium metal forms a cubic close-packed crystal structure. Its atomic radius is $125 \times 10^{-12} \text{ m}$.

(a) Calculate the length of the side of the unit cell.

(b) How many such unit cells are there in 1.00 m^3 of aluminium?

(3 marks)

–2005 CBSE Delhi

Sol:

(a) For a cubic close-packed crystal structure,

$$\text{Radius of an atom, } r = \frac{a}{2\sqrt{2}}$$

Where, $a \rightarrow$ Edge length

$$\text{Therefore, } a = 2\sqrt{2}r$$

$$= 2\sqrt{2} \times 125 \times 10^{-12}$$

$$= 354 \times 10^{-12} \text{ m}$$

Hence, the length of the side of the unit cell is $354 \times 10^{-12} \text{ m}$.

(b) Volume of the unit cell = a^3

$$= (354 \times 10^{-12} \text{ m})^3$$

$$= 4.436 \times 10^{-29} \text{ m}^3$$

Therefore, the number of unit cells in 1.00 m^3 of aluminium = $\frac{1}{4.436 \times 10^{-29} \text{ m}^3}$

$$= 2.25 \times 10^{28}$$

Ques. Calculate the density of silver which crystallises in the face-centred cubic structure. The distance between the nearest silver atoms in this structure is 287 pm.

(3 marks)

–2004 CBSE Delhi

Sol: Given, molar mass of Ag, $M = 107.87 \text{ g mol}^{-1}$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

In case of fcc lattice, number of atoms per unit cell, $z = 4$

Distance between two nearest Ag atoms = 287 pm

$$\Rightarrow \frac{\text{Face diagonal}}{2} = 287 \text{ pm}$$

$$\Rightarrow \frac{\sqrt{2}a}{2} = 287 \text{ pm}$$

$$\Rightarrow a = 287 \times \sqrt{2} \text{ pm}$$

$$\Rightarrow a = 287 \times 1.414 \text{ pm}$$

$$\Rightarrow a = 405.818 \text{ pm}$$

Thus, edge length = 406 pm (approx)

$$= 406 \times 10^{-12} \text{ m}$$

Therefore, density of silver is given by

$$\begin{aligned}
 d &= \frac{z.M}{a^3.N_A} \\
 &= \frac{4 \times 107.87 \text{ g mol}^{-1}}{(406 \times 10^{-12} \text{ m})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})} \\
 &= 1.07 \times 10^7 \text{ g m}^{-3} \\
 &= 1.07 \times 10^4 \text{ kg m}^{-3}
 \end{aligned}$$

Imperfections in Solids

Defects

- Irregularities or deviations from the ideal arrangement of constituent particles

Two types:

- Point defects – Irregularities in the arrangement of constituent particles around a point or an atom in a crystalline substance.
- Line defects – Irregularities in the arrangement of constituent particles in entire rows of lattice points.
- These irregularities are called crystal defects.

Types of Point Defects

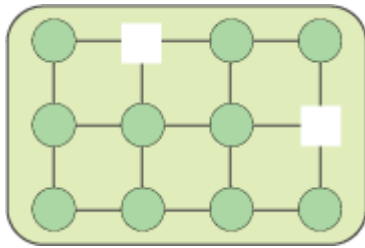
Three types:

- Stoichiometric defects
- Impurity defect
- Non-stoichiometric defects

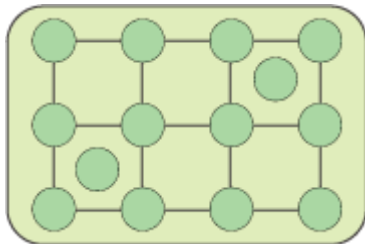
Stoichiometric Defects

- Do not disturb stoichiometry of the solid
- Also called intrinsic or thermodynamic defects

- Two types –
 - (i) Vacancy defect
 - (ii) Interstitial defect
- **Vacancy defect**
- When some of the lattice sites are vacant
- Shown by non-ionic solids
- Created when a substance is heated
- Results in the decrease in density of the substance

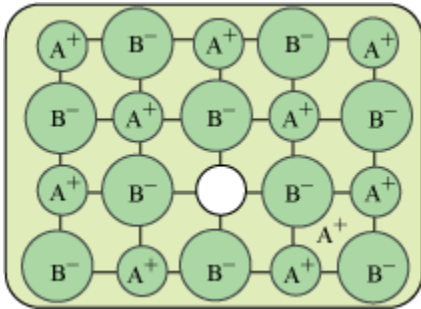


- **Interstitial defect**
- Shown by non-ionic solids
- Created when some constituent particles (atoms or molecules) occupy an interstitial site of the crystal.

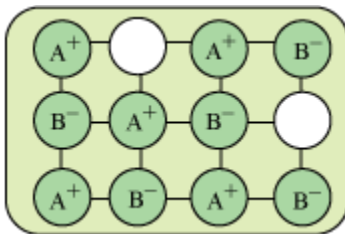


- Ionic solids show these two defects as Frenkel defect and Schottky defect.
- **Frenkel defect**
- Shown by ionic solids containing large differences in the sizes of ions
- Created when the smaller ion (usually cation) is dislocated from its normal site to an interstitial site
- Creates a vacancy defect as well as an interstitial defect

- Also known as dislocation defect
- Ionic solids such as AgCl, AgBr, AgI and ZnS show this type of defect.

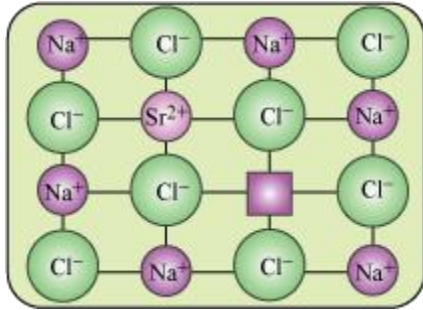


- **Schottky defect**
- Basically a vacancy defect shown by ionic solids
- An equal number of cations and anions are missing to maintain electrical neutrality
- Results in the decrease in the density of the substance
- Significant number of Schottky defect is present in ionic solids. For example, in NaCl, there are approximately 10^6 Schottky pairs per cm^3 , at room temperature.
- Shown by ionic substances containing similar-sized cations and anions; for example, NaCl, KCl CsCl, AgBr



Impurity Defect

- Point defect due to the presence of foreign atoms
- For example, if molten NaCl containing a little amount of SrCl_2 is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} ions. Each Sr^{2+} ion replaces two Na^+ ions, occupying the site of one ion, leaving the other site vacant. The cationic vacancies thus produced are equal in number to those of Sr^{2+} ions.



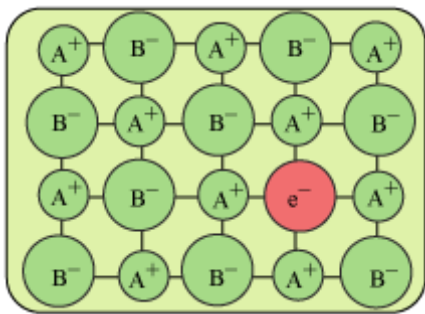
- Solid solution of CdCl_2 and AgCl also shows this defect

Non-Stoichiometric Defects

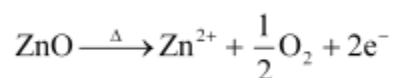
- Result in non-stoichiometric ratio of the constituent elements
- Two types –
- Metal excess defect
- Metal deficiency defect

Metal excess defect

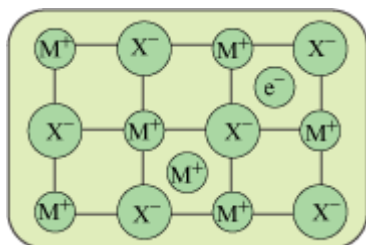
- Metal excess defect due to anionic vacancies:
- Alkali metals like NaCl and KCl show this type of defect.
- When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse from the crystal to its surface and combine with Na atoms, forming NaCl . During this process, the Na atoms on the surface of the crystal lose electrons. These released electrons diffuse into the crystal and occupy the vacant anionic sites, creating F-centres.
- When the ionic sites of a crystal are occupied by unpaired electrons, the ionic sites are called F-centres.



- Metal excess defect due to the presence of extra cations at interstitial sites:
- When white zinc oxide is heated, it loses oxygen and turns yellow.



Then, zinc becomes excess in the crystal, leading the formula of the oxide to Zn_{1+x}O . The excess Zn^{2+} ions move to the interstitial sites, and the electrons move to the neighbouring interstitial sites.



Metal deficiency defect

- Arises when a solid contains lesser number of cations compared to the stoichiometric proportion.
- For example, FeO is mostly found with a composition of $\text{Fe}_{0.95}\text{O}$. In crystals of FeO, some Fe^{2+} ions are missing, and the loss of positive charge is made up by the presence of the required number of Fe^{3+} ions.

Questions asked in previous years' board examinations

Ques. Which point defect in crystals of a solid decreases the density of the solid?

(1 mark)

–2010 CBSE Delhi

Sol: Vacancy defect decreases the density of a substance. Vacancy defect in ionic solids is known as Schottky defect.

Ques. Which point defect in crystals does not affect the density of the relevant solid?

(1 mark)

2009 CBSE Delhi

Sol: Frenkel defect in crystals does not affect the density of the relevant solid.

Ques. Which point defect in its crystal units alters the density of a solid?

(1 mark)

2008 CBSE Delhi

Sol: Schottky defect in crystals units alters the density of a solid.

Ques. How would you account for the following?

- (i) Frenkel defects are not found in alkali metal halides.
- (ii) Schottky defects lower the density of related solids.
- (iii) Impurity doped silicon is a semiconductor.

(3 marks)

2008 CBSE Delhi

Sol: (i) Frenkel defects are shown by ionic solids having large differences in the sizes of ions. Solids such as ZnS, AgCl show these defects due to the small size of Zn^{2+} and Ag^+ ions, and the large size of anions. Alkali metals are not so small so as to show these defects. Hence, Frenkel defects are not found in alkali metal halides.

(ii) Schottky defects are basically vacancy defects in ionic solids. In these defects, lattice sites become vacant. As a result, the density of the substance decreases.

(iii) Silicon is an intrinsic semi-conductor in which conductivity is very low. To increase its conductivity, silicon is doped with an appropriate amount of suitable impurity. When doped with electron-rich impurities such as P or As, *n*-type semi-conductor is obtained, and when doped with electron-deficient impurities, *p*-type semi-conductor is obtained. In *n*-type semiconductor, negatively charged electron is responsible for increasing conductivity, and in *p*-type semiconductor, electron hole is responsible for increasing conductivity.

Ques. What are the types of lattice imperfections found in crystals?

(1 mark)

2004 CBSE Delhi

Sol: Two types of lattice imperfections are found in crystals.

- (i) Point defects (irregularities in arrangement around a point or an atom)
- (ii) Line defects (irregularities in arrangement in entire rows of lattice points)

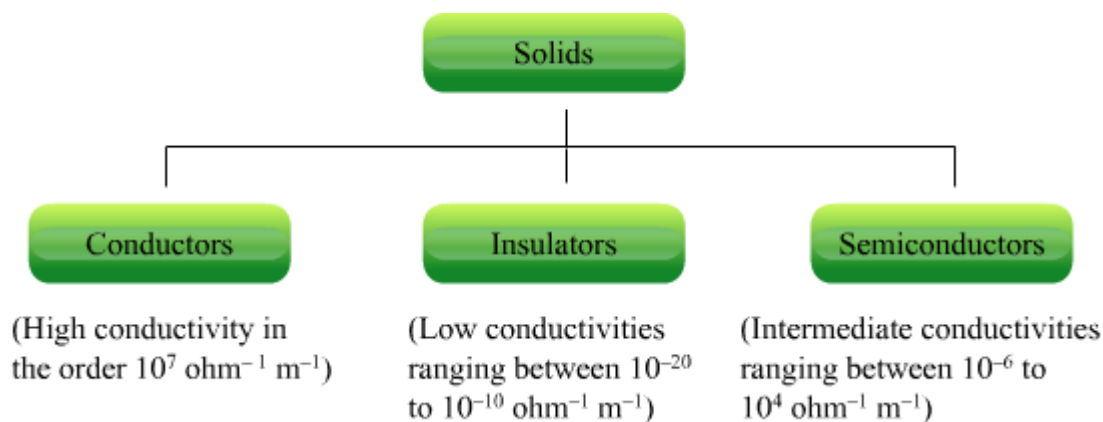
Ques. Explain interstitial defect with examples.

(3 marks)

2004 CBSE Delhi

Sol: Interstitial defect is shown by non-ionic solids. This type of defect is created when some constituent particles (atoms or molecules) occupy an interstitial site of the crystal. The density of a substance increases because of this defect.

Electrical Properties

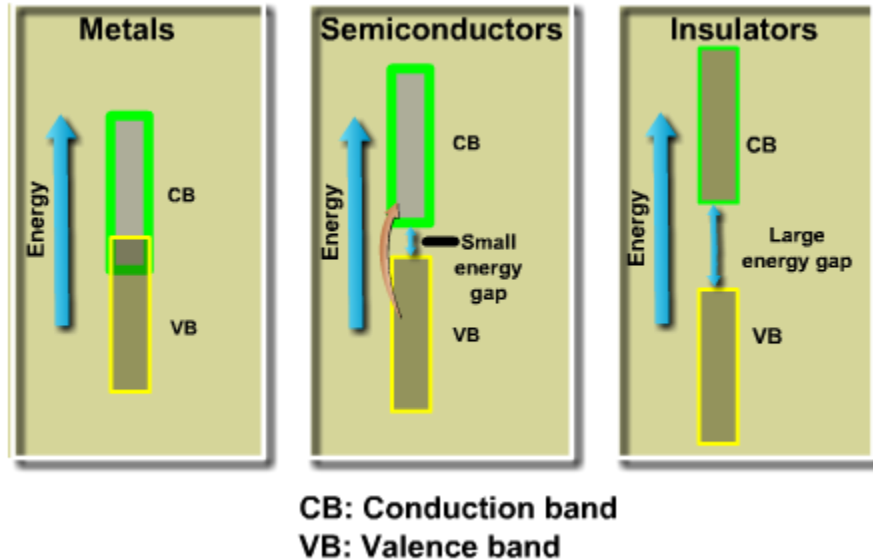


Conduction of Electricity in Metals

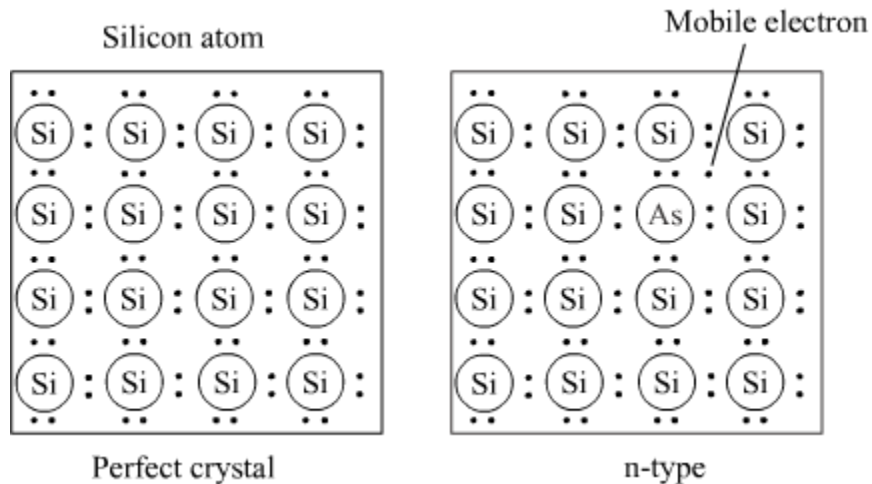
- Metals conduct electricity in molten state.
- The conductivity of metals depends upon the number of valence electrons.
- In metals, the valence shell is partially filled, so this valence band overlaps with a higher energy unoccupied conduction band so that electrons can flow easily under an applied electric field.
- In the case of insulators, the gap between filled valence shell and the next higher unoccupied band is large so that electrons cannot jump from the valence band to the conduction band.

Conduction of Electricity in Semiconductors

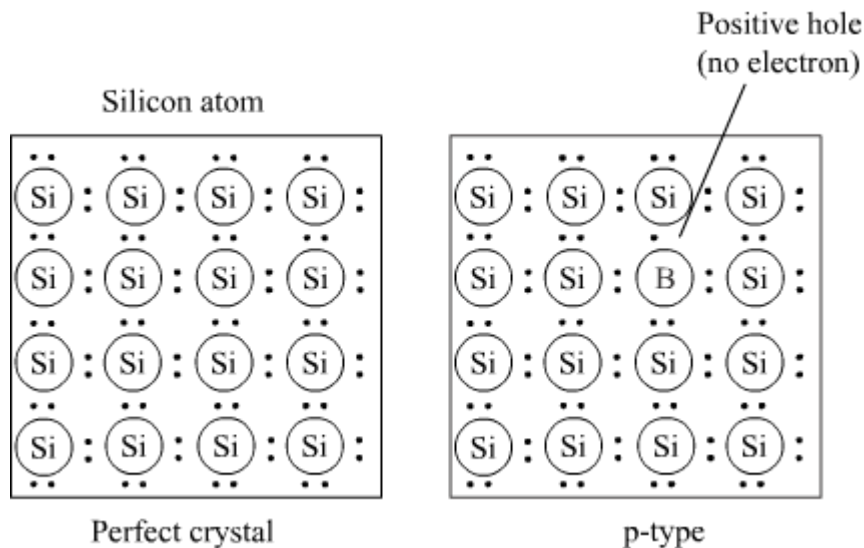
- The gap between the valence band and conduction band is so small that some electrons may jump to the conduction band.



- Electrical conductivity of semiconductors increases with increase in temperature.
- Substances like Si, Ge show this type of behaviour, and are called intrinsic semiconductors.
- Doping – Process of adding an appropriate amount of suitable impurity to increase conductivity
- Doping is done with either electron-rich or electron-deficient impurity as compared to the intrinsic semiconductor Si or Ge.
- There are two types of semiconductors:
 - n – type semiconductor
 - p – type semiconductor
- n – type semiconductor
 - Conductivity increases due to negatively charged electrons
- Generated due to the doping of the crystal of a group 14 element such as Si or Ge, with a group 15 element such as P or As



- p – type semiconductor
- Conductivity increases as a result of electron hole
- Generated due to the doping of the crystal of a group 14 element such as Si or Ge, with a group 13 element such as B, Al or Ga



- Applications of n – type and p – type semiconductors
- In making a diode, which is used as a rectifier
- In making transistors, which are used for detecting or amplifying radio or audio signals
- In making a solar cell, which is a photo diode used for converting light energy into electrical energy

- A large number of compounds (solid) have been prepared by the combination of groups 13 and 15 or 12 and 16 to stimulate average valence of four as in Si or Ge.
- Examples of compounds of groups 13 – 15 are InSb, AlP, GaAs
- Examples of compounds of groups 12 – 16 are ZnS, CdS, CdSe, HgTe
- Some transition metal oxides like TiO, CrO₂, ReO₃ behave like metals.
- For example, ReO₃ resembles metallic copper in its conductivity and appearance
- Some oxides like VO, VO₂, VO₃, TiO₃ show metallic or insulating properties depending on temperature.

Do you know?

Polyacetylene, an organic compound shows conductivity when exposed to iodine vapours.

Questions asked in previous years' board examinations

Ques. What is semiconductor? Describe the two main types of semiconductors and explain mechanisms for their conduction.

(3 marks)

–2008 CBSE Delhi

Sol: Solids having intermediate conductivities (from 10^{-6} to $10^4 \Omega^{-1} \text{ m}^{-1}$) are called semiconductors. Germanium and silicon are two examples of semi-conductors. These substances act as insulators at low temperatures and as conductors at high temperatures. There are two types of semiconductors:

***n*-type semiconductor:**

When the crystal of a semiconductor is doped with group-15 elements (P, As, Sb or Bi), only four of the five valence electrons of the doped atoms participate in forming covalent bonds with the atoms of the semiconductors. The fifth electron is free to conduct

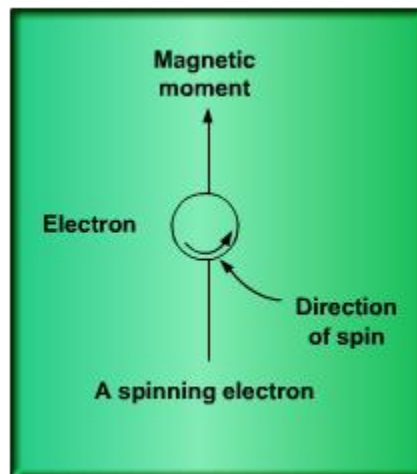
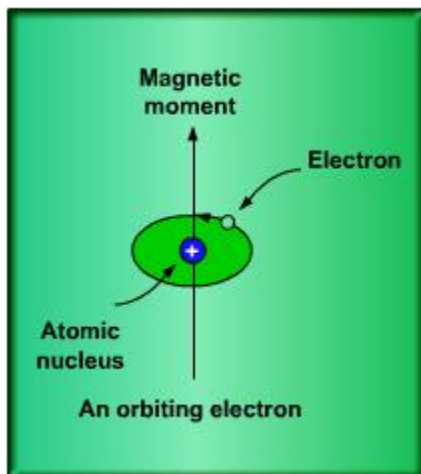
electricity. As these crystals contain extra electrons, these are known as *n*-type semiconductors.

***p*-type semiconductor:**

When the crystal of a semiconductor is doped with group-13 elements (Al, Ga or In), only three covalent bonds are formed by the atoms of the doped atoms as they contain three valence electrons. A hole is created at the place where the electron is absent. The presence of such holes increases the conductivity of the semiconductor as the neighbouring electrons can move into these holes, thereby creating newer holes. As these crystals contain lesser electrons than un-doped crystals, they are known as *p*-type semiconductors.

Magnetic Properties

- Each electron in an atom behaves like a tiny magnet.
- The magnetic moment of an electron originates from its two types of motion.
- Orbital motion around the nucleus
- Spin around its own axis
- Thus, an electron has a permanent spin and an orbital magnetic moment associated with it.
- An orbiting electron
- A spinning electron



- Based on magnetic properties, substances are classified into five categories –

- Paramagnetic
- Diamagnetic
- Ferromagnetic
- Ferrimagnetic
- Anti-ferromagnetic

Paramagnetism

- The substances that are attracted by a magnetic field are called paramagnetic substances.
- Some examples of paramagnetic substances are O_2 , Cu^{2+} , Fe^{3+} and Cr^{3+} .
- Paramagnetic substances get magnetised in a magnetic field in the same direction, but lose magnetism when the magnetic field is removed.
- To undergo paramagnetism, a substance must have one or more unpaired electrons. This is because the unpaired electrons are attracted by a magnetic field, thereby causing paramagnetism.

Diamagnetism

- The substances which are weakly repelled by magnetic field are said to have diamagnetism.
- Example – H_2O , $NaCl$, C_6H_6
- Diamagnetic substances are weakly magnetised in a magnetic field in opposite direction.
- In diamagnetic substances, all the electrons are paired.
- Magnetic characters of these substances are lost due to the cancellation of moments by the pairing of electrons.

Ferromagnetism

- The substances that are strongly attracted by a magnetic field are called ferromagnetic substances.
- Ferromagnetic substances can be permanently magnetised even in the absence of a magnetic field.
- Some examples of ferromagnetic substances are iron, cobalt, nickel, gadolinium and CrO_2 .
- In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains, and each domain acts as a tiny magnet. In an un-magnetised piece of a

ferromagnetic substance, the domains are randomly oriented, so their magnetic moments get cancelled. However, when the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field. As a result, a strong magnetic effect is produced. This ordering of domains persists even after the removal of the magnetic field. Thus, the ferromagnetic substance becomes a permanent magnet.

- Schematic alignment of magnetic moments in ferromagnetic substances is as follows:



Ferrimagnetism

- The substances in which the magnetic moments of the domains are aligned in parallel and anti-parallel directions, in unequal numbers, are said to have ferrimagnetism.
- Examples include Fe_3O_4 (magnetite), ferrites such as MgFe_2O_4 and ZnFe_2O_4 .
- Ferrimagnetic substances are weakly attracted by a magnetic field as compared to ferromagnetic substances.
- On heating, these substances become paramagnetic.
- Schematic alignment of magnetic moments in ferrimagnetic substances is as follows:



Anti-ferromagnetism

- Antiferromagnetic substances have domain structures similar to ferromagnetic substances, but are oppositely oriented.
- The oppositely oriented domains cancel out each other's magnetic moments.
- Schematic alignment of magnetic moments in anti-ferromagnetic substances is as follows:



Do you know?

When a substance offers no resistance to the flow of electric current, it is said to be

superconducting. This phenomenon was first discovered by Kammerlingh Onnes.

Questions asked in previous years' board examinations

Ques. What type of substances exhibits antiferromagnetism?

(1 mark)

–2008 CBSE Delhi

Sol: Antiferromagnetism is exhibited by substances which have domain structure similar to ferromagnetic substances, but are oppositely oriented (thereby cancelling out each other's magnetic moment), e.g., MnO.

Ques. Explain each of the following with a suitable example:

(i) Paramagnetism

(ii) Piezoelectric effect

(3 marks)

–2007 CBSE Delhi

Sol: (i) *Paramagnetism:*

The phenomenon due to which a substance gets attracted towards a magnetic field is called paramagnetism. The substances attracted by a magnetic field are called paramagnetic substances. Some examples of paramagnetic substances are O_2 , Cu^{2+} , Fe^{3+} and Cr^{3+} .

Paramagnetic substances get magnetised in a magnetic field in the same direction, but lose magnetism when the magnetic field is removed. To undergo paramagnetism, a substance must have one or more unpaired electrons. This is because the unpaired electrons are attracted by a magnetic field, thereby causing paramagnetism.

(ii) *Piezoelectric effect:*

The production of electricity due to the displacement of ions, on the application of mechanical stress, or the production of mechanical stress and/or strain due to atomic displacement, on the application of an electric field is known as piezoelectric effect.

Piezoelectric materials are used in transducers – devices that convert electrical energy into mechanical stress/strain or vice-versa. Some piezoelectric materials are lead-zirconate (PbZrO_3), ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), quartz, etc.

Ques. What makes alkali metal halides sometimes coloured, which are otherwise colourless?

(1 mark)

–2004 CBSE Delhi

Alkali metal halides have anionic sites occupied by unpaired electrons. These are called F-centres, and impart colour to the crystals of alkali metal halides. For example, the excess of lithium in LiCl makes it pink.