Chapter 1

The Solid State

Crystal Lattices & Unit Cells

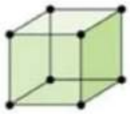
What is a Crystal?

Crystalline solid consists of a large number of small units, called **crystals**, each of which possesses a definite geometric shape bounded by plane faces. The crystals of a given substance produced under a definite set of conditions are always of the same shape.

Different crystalline solids formed from repetition of small units (unit cells)

Characteristics of Crystal Lattice

- In a crystal lattice, each atom, molecule or ions (constituent particle) is represented by a single point.
- These points are called lattice sites or lattice points.
- Lattice sites or points are together joined by a straight line in a crystal lattice.
- When we connect these straight lines we can get a three-dimensional view of the structure. This 3D arrangement is called Crystal Lattice also known as Bravais Lattices.
- Note that lattice points only represent the points at which the constituent atom/ion/molecule is present.



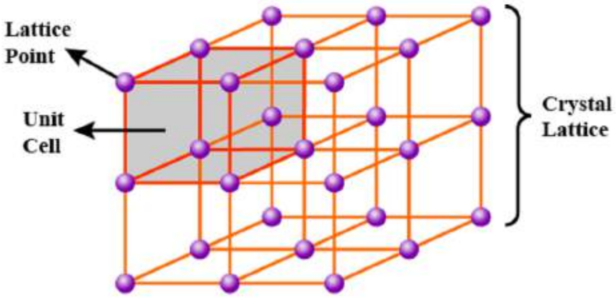
a) The black balls represent the lattice points

b) The lattice points with constituent atoms.

What is a Unit Cell?

The smallest repeating unit of a crystal lattice is called a unit cell. It is the building block of a crystal.

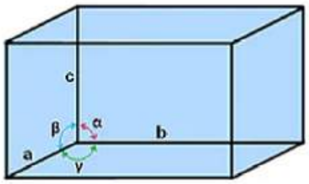
- Any amount of the solid can be constructed by simply putting as many unit cells as required.
- We would be studying certain properties of a solid which depend only on the constituents of the solid and the pattern of arrangement of these constituents.



Characteristics of Unit Cell

The following characteristics define a unit cell:

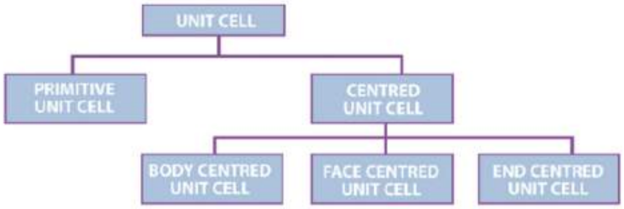
- A unit cell has three edges a, b, and c, and three angles α, β, and γ between the respective edges.
- The a, b and c may or may not be mutually perpendicular.
- The angle between edge b and c is α, a and c is β and between a and b is γ.



Parameters of a unit cell.

Parameters of a unit cell.

Types of Unit Cell



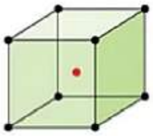
1. Primitive Unit Cells

When the constituent particles occupy only the corner positions, it is known as Primitive Unit Cells.

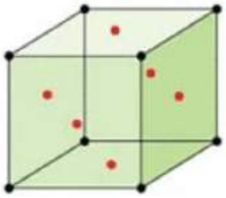
Lattice points only at the corners of the unit cell- Primit

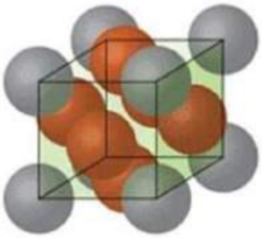
2. Centred Unit Cells

When the constituent particles occupy other positions in **addition to those at corners,** it is known as Centred Unit Cell.
There are 3 types of Centred Unit Cells:
(i) Body Centred: When the constituent particle at the centre of the body, along with the one's present at the corners, it is known as Body Centred Unit cell.

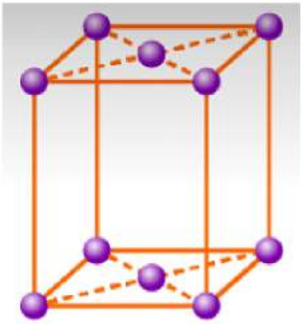


(ii) Face Centred: When the constituent particle present at the centre of each face, along with the one's present at the corners is known as the Face Centred Unit cell.





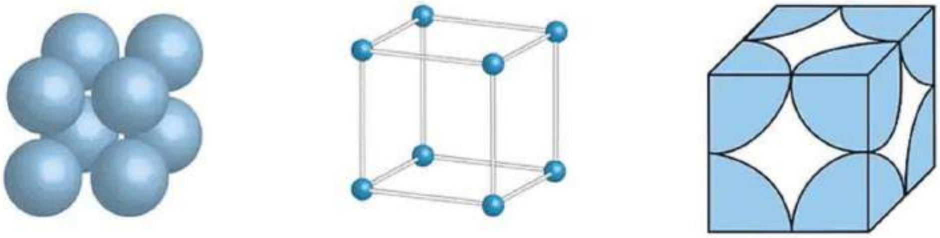
(iii) End Centred: When the constituent particle present at the centre of two opposite faces, along with one's present at the corners, it is known as an End Centred Unit cell.



Number of Atoms & Packing Fraction in a Unit Cell

1. Simple Cubic (SC) Unit Cell

- A simple cubic unit cell consists of eight corner atoms. In a simple cubic unit cell, a corner atom touches with another corner atom.



Simple cubic unit cell of a crystal lattice

- **Number of Atoms in a Simple Cubic Unit Cell**
  A simple cubic unit cell consists of 8 corner atoms. Each and every corner atom is shared by eight adjacent unit cells. Therefore, one corner atom contributes 1/8th of its parts to one unit cell. Since there are eight corner atoms in a unit cell, the total number of atoms is $(1/8) * 8=1$. Therefore, the number of atoms in a simple cubic unit cell is one.

- **Atomic Radius**
  In a simple cubic lattice, a corner atom touches with another corner atom. Therefore, 2r=a. So, the atomic radius of an atom in a simple cubic unit cell is a/2.
- **Coordination Number**
  Consider a corner atom in a simple cubic unit cell. It has four nearest neighbours in its own plane. In a lower plane, it has one more nearest neighbour and in an upper plane, it has one more nearest neighbour. Therefore, the total number of the nearest neighbour is six.
- **Packing Density**
  <u>The packing density of a simple cubic unit cell is calculated as follows:</u>
  The unit cell Number of atoms

  $$= \frac{1 \times \frac{4}{3}\pi r^3}{a^3}$$

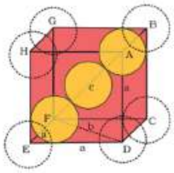
  p
  Substituting, r=a/2, we get,

  $$Packaging\ density = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 \frac{1}{a^3} = \frac{\pi}{6} = 0.52$$

  The packing density of a simple cubic unit cell is **0.52**. It means, 52% of the volume of the unit cell is occupied by atoms and the remaining 48% volume is vacant.

2. Body-Centred Cubic Unit Cell

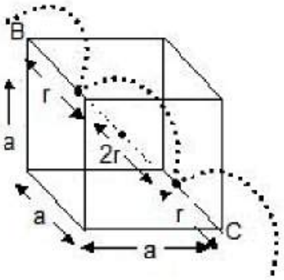
- A Body-Centered unit cell is a unit cell in which the same atoms are present at all the corners and also at the **centre of the unit cell** and are not present anywhere else.
- This unit cell is created by placing four atoms that are not touching each other.



Body-centred cubic unit cell

- Then we place an atom on top of these four. Again, four spheres eclipsing the first layer are placed on top of this.
- The effective number of atoms in a Body-Centered Cubic Unit Cell is 2 (One from all the corners and one at the centre of the unit cell).

- Moreover, since in BCC the body-centred atom touches the top four and the bottom four atoms, the length of the body diagonal **($\sqrt{3}a$) is equal to 4r**.

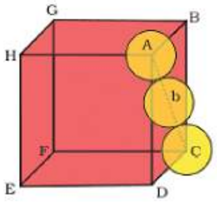


The packing fraction in this case is = $\dfrac{2\times\frac{4}{3}\pi r^3}{(\frac{4r}{\sqrt{3}})^3} \approx 0.68$

VF ≈ 0.32

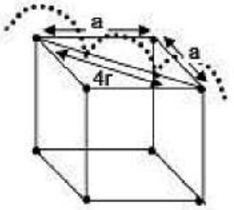
3. Face Centered Cubic (FCC) Unit Cell

- In an fcc unit cell, the same atoms are present at all the **corners of the cube** and are also present at the **centre of each square face** and are not present anywhere else.
- The effective number of atoms in fcc is 4 (one from all the corners, 3 from all the face centres since each face-centred atom is shared by two cubes).



Face centered cubic unit cell

- Since, here each face-centred atom touches the four corner atoms, the face diagonal of the cube $(\sqrt{2a})$ is equal to 4r.

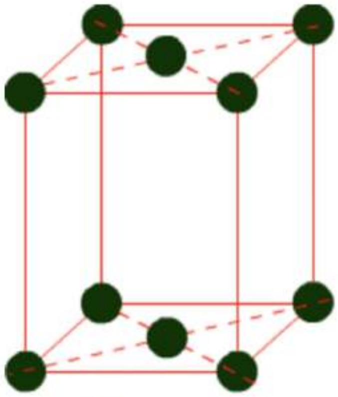


$$\text{packing fraction} = \frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} \approx 0.74$$

$\text{VF} \approx 0.26$

4. End Centered Cubic (FCC) Unit Cell

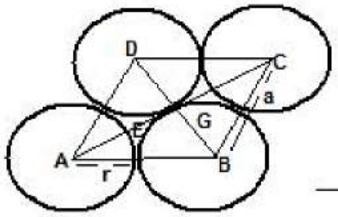
A unit cell with a single constituent particle of atom, molecules, or ions located in the centre of the opposite faces, apart from that present in the corners. Two atoms are present in end centred cubic unit cell.

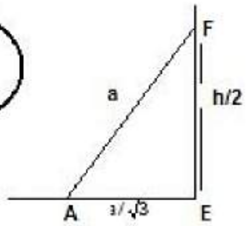


End Centered

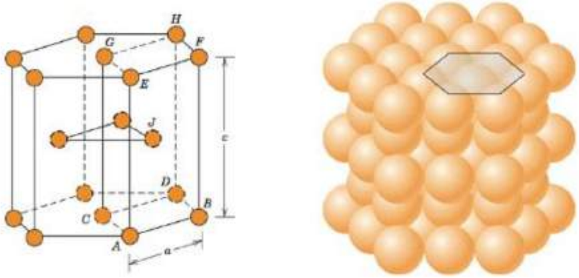
5. Hexagonal Primitive Unit Cell

Each corner atom would be common to 6 other unit cells, therefore their contribution to one unit cell would be **1/6**. Therefore, the total number of atoms present per unit cell effectively is **6**.





In the figure, ABCD is the base of the hexagonal unit cell AD=AB=a. The sphere in the next layer has its centre F vertically above E and it touches the three spheres whose centres are A, B, and D.



Hexagonal close-packing

$$AE = \frac{2}{3} \times \frac{\sqrt{3}}{2} a = \frac{a}{\sqrt{3}} = \frac{2r}{\sqrt{3}}$$

Hence,

$$FE = \frac{h}{2} = \sqrt{(2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2}$$

The height of the unit cell (h) = $4r\sqrt{\frac{2}{3}}$

The area of the base is equal to the area of six equilateral triangles, = $6 \times \frac{\sqrt{3}}{4}(2r)^2$.

The volume of the unit cell = $6 \times \frac{\sqrt{3}}{4}(2r)^2 \times 4r\sqrt{\frac{2}{3}}$.

Therefore,

$$PF = \frac{6 \times \frac{4}{3}\pi r^3}{6 \times \frac{\sqrt{3}}{4}(2r)^2 \times 4r\sqrt{\frac{2}{3}}} = 0.74,$$

VF ≈ 0.26

The Density of Crystal Lattice

The density of crystal lattice is the same as the density of the unit cell which is calculated as:

$$\rho = \frac{mass\ \ of\ \ unit\ \ cell}{volume\ \ of\ \ unit\ \ cell}$$

$$= \frac{\text{number of effective atoms} \times \text{massnumber}}{\text{volume of unit cell} \times \text{Avogadro number}}$$

$$\rho = \frac{z \times M}{a^3 \times N_A}$$

Here,
Z = no. of atoms present in one unit cell
m = mass of a single atom
Mass of an atom present in the unit cell = m/NA

Bravais Lattices

Bravais (1848) showed from geometrical considerations that there are only seven shapes in which unit cells can exist.

These are

- Cubic
- Orthorhombic
- Rhombohedral
- Hexagonal
- Tetragonal
- Monoclinic
- Triclinic

Moreover, he also showed that there are basically four types of unit cells depending on the manner in which they are arranged in a given shape. These are:

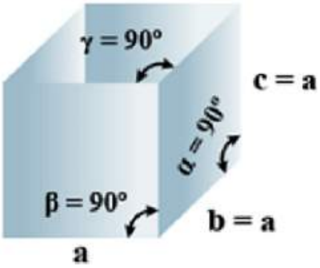
- **Primitive Unit cell**
- **Body-Centred**
- **Face Centred**
- **End Centred**

He also went on to postulate that out of the possible twentyeight unit cells (i.e. seven shapes, four types in each shape = 28 possible unit cells), only fourteen actually would exist. These he postulated based only on symmetry considerations. These fourteenunit cells that actually exist are called **Bravais Lattices**.

Seven Crystal Systems

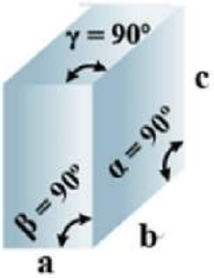
The seven crystal systems are given below:

A. Cubic



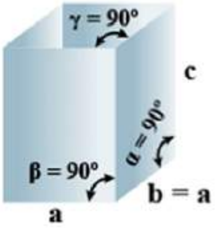
- Bravais Lattices
  Primitive, face Centered, Body Centered = 3
- Parameters of Unit Cell
  (i) **Intercepts**: a=b=c
  (ii) **Crystal angle**: $\alpha = \beta = \gamma = 90^{\circ}$
  Example: Pb, Hg, Ag, Au, Diamond, NaCl, ZnS

B. Orthorhombic



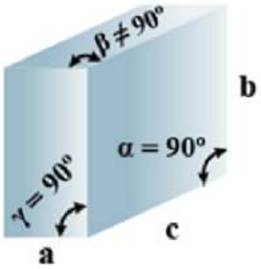
- Bravais Lattices:
  Primitive, Face Centered, Body-Centered, End Centered = 4
- Parameters of Unit Cell:
  (i) **Intercepts**: $a \neq b \neq c$
  (ii) **Crystal angle**: $\alpha = \beta = \gamma = 90^{\circ}$
  Example: KNO_2, K_2SO_4

C. Tetragonal



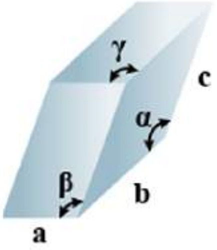
- Bravais Lattices:
  Primitive, Body-Centered =2
- Parameters of Unit Cell:
  (i) **Intercepts**: a = b≠ c
  (ii) **Crystal angle**: $\alpha = \beta = \gamma = 90^{\circ}$
  Example: TiO_2, SnO_2

D. Monoclinic



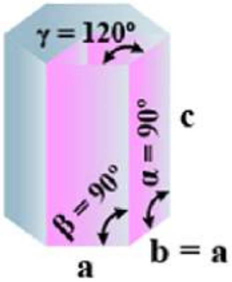
- Bravais Lattices
  Primitive, End Centered =2
- Parameters of Unit Cell
  (i) **Intercepts**: a ≠ b≠ c
  (ii) **Crystal angle**: $\alpha = \ \gamma = 90^{\circ}$
  Example: $CaSO_4.2H_2O$

E. Triclinic



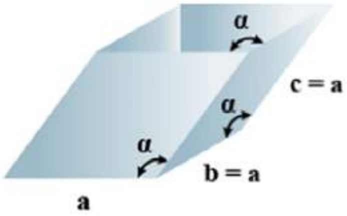
- Bravais Lattices
  Primitive = 1
- Parameters of Unit Cell
  (i) Intercepts: $a \neq b \neq c$
  (ii) Crystal angle: $\alpha \neq \beta \neq \gamma$
  Example: K_2Cr_2O7, $CaSO_4 \, 5H_2O$

F. Hexagonal



- Bravais Lattices
  Primitive = 1
- Parameters of Unit Cell
  (i) Intercepts: $a = b \neq c$
  (ii) Crystal angle: $\alpha = \beta = 90^\circ \, \gamma = 120^\circ$
  Example: Mg, SiO_2, Zn, Cd

G. Rhombohedral



- Bravais Lattices:
  Primitive = 1
- Parameters of Unit Cell
  (i) Intercepts: $a = b = c$
  (ii) Crystal angle: $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$
  Example: As, Sb, Bi, $CaCO_3$

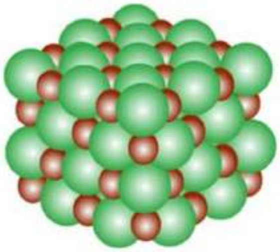
The table given below can be used to summarize types of lattice formation.

Lattice	Types	Edge Length	Angles between faces	Examples
Cubic	Primitive, Body-centred, Face-centred	a = b = c	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Copper and ZnS
Tetragonal	Primitive, Body-centred	a = b ≠ c	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2, TiO_2 and $CaSO_4$
Orthorhombic	Primitive, Body-centred, Face-centred, End- centred	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90^\circ$	Rhombic Sulphur, $BaSO_4$ and KNO_3
Hexagonal	Primitive	a = b ≠ c	$\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$	Graphite, ZnO and CdS
Rhombohedral	Primitive	a = b = c	$\alpha = \beta = \gamma \neq 90^\circ$	$CaCO_3$ (Calcite) and HgS (cinnabar)
Monoclinic	Primitive End-centred	a ≠ b ≠ c	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Sulphur
Triclinic	Primitive	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	H_3PO_3, $CuSO_4.5\ H_2O$

Characteristics & Classification of Solids

What is a Solid?

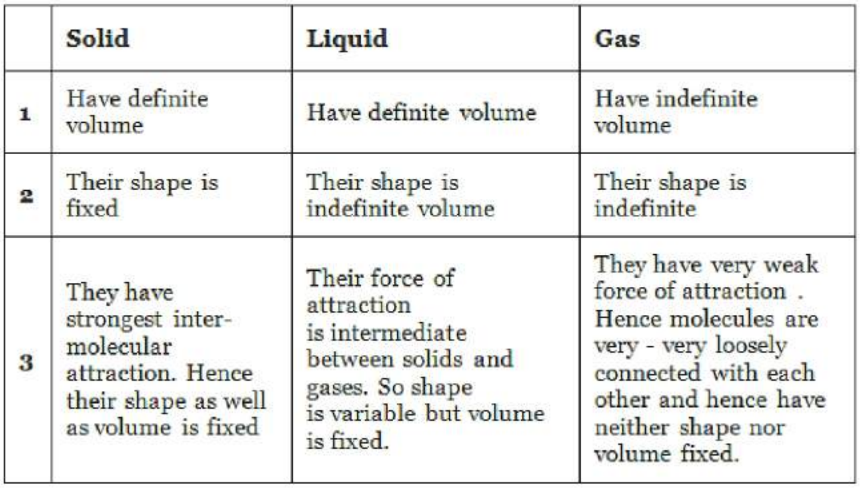
A matter is said to be solid when its constituent particles (atoms, molecules, or ions) are closely packed.



Solid State

A **solid** is also defined as that form of matter which possesses **rigidity** and hence possesses a **definite shape** and a **definite volume**. Unlike gases and liquids, whose fluidity is determined by the relative free motion of their molecules, in solids, on the contrary, molecules or atoms or ions are not free to move but can oscillate around their fixed positions due to **strong** intermolecular or inter-atomic, or inter-ionic forces. This confers rigidity and long-range order in solids.

We shall find that the explanation of these macroscopic properties in terms of the atomic theory involves the idea of lattice: a permanent ordered arrangement of atoms held together by forces of considerable magnitude.

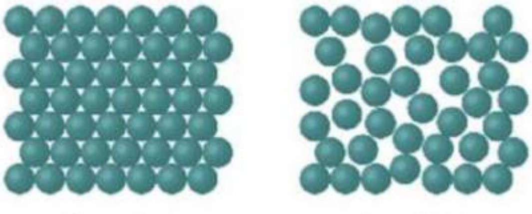


	Solid	Liquid	Gas
1	Have definite volume	Have definite volume	Have indefinite volume
2	Their shape is fixed	Their shape is indefinite volume	Their shape is indefinite
3	They have strongest inter-molecular attraction. Hence their shape as well as volume is fixed	Their force of attraction is intermediate between solids and gases. So shape is variable but volume is fixed.	They have very weak force of attraction . Hence molecules are very - very loosely connected with each other and hence have neither shape nor volume fixed.

Differentiation between Solid, Liquid and Gas

Thus the extremes of molecular behaviour occur in gases and solids. In the former, we have molecular chaos and vanishing inter-molecular forces, and in the latter, we have an ordered arrangement in which the interatomic forces are large.

Types of Solidsa) Crystalline solids: In a single crystal the regularity of arrangement of the pattern extends throughout the solid and all points are completely equivalent. **b) Amorphous solids**: An amorphous solid differs from a crystalline substance in being without any shape of its own and has completely random particle arrangement, i.e. no regular arrangement.
Example: Glass, Plastic



Crystalline Amorphous

Types of Solids

Distinction Between Crystalline and Amorphous Solids

S.No.	Crystalline solids	Amorphous solids
1.	These have definite and regular arrangement of the constituent particles in space.	These doesn't have any regular arrangement of the constituent particles in space.
2.	These are true solids.	These are super cooled liquids or pseudo solids.
3.	These have long order in arrangement of the particles.	These have short order in arrangement of particles.
4.	These are anisotropic in nature, i.e. their physical properties are different in different directions.	These are isotropic in nature i.e. their physical properties are same in all the directions.
5.	They have sharp melting points.	They melt over a certain range of temperature.
6.	They undergo a clean cleavage when cut.	They undergo irregular cleavage when cut.
7.	They have a definite and characteristic heat of fusion.	They do not have definite heat of fusion.

Classification of Crystalline Solids

Molecular Solids

Those solids which consists of small molecules are called molecular solids.

- **Non - polar molecular solids:**
  electronegativity sequence
  $(F > O > N \approx Cl > Br > S > C\text{-}H)$
  The solids which have zero dipole moment are called non-polar molecular solids. The molecules are held together by weak Van Der Waals forces Hence they are either gas or liquids at room temperature. They are poor conductor of electricity due to their non-polar nature.
- **Polar molecular solids:**
  Those solids which have non-zero dipole moments are called polar molecular solids.
  Polar molecular solids have dipole - dipole interaction, which is slightly stronger than Van Der Waals force and hence they have larger melting and boiling points than the non - polar molecular solids.

Example: Solid CO_2, Solid NH_3

They are generally liquids or gases at room temperature.

- **Hydrogen bonded molecular solids:**

  Those molecular solids which are bonded with each other by hydrogen bonds are called hydrogen bonded molecular solids.

  Example: Ice

  They are non-conductor of electricity.

  Generally they are liquid at room temperature or soft solids.

Ionic Solids

All those solids whose constituent particles are ions are called ionic solids,
Example: NaCl, CsBr, AgBr, CsCl

Metallic Solids:

- All those solids which are bonded by metallic bonds are called metallic solids.
- Inner core electrons are immobile.
- Metallic solids show a great electrical conductivity due to availability of large number of free electrons whose movements constitute electric current.
- Metallic solids are malleable and ductile.
- Metallic solids have luster.
- Metallic solids have good thermal conductivity.

What are metallic solids?

In these solids, the constituent particles in metallic solids are metal atoms which have valence electrons to be given/lost, therefore ending up being positively charged. The sea of electrons available is spread all through the crystal and can easily move about. The attractive force between positively charged ions and the sea of electrons is the cause for metallic bond formation. This is the force holding the metal ions together. Metallic solids have a regular structure with high melting and boiling points. Because of the sea of electrons, they have high thermal and metallic conductivity. All metals and alloys are metallic solids.

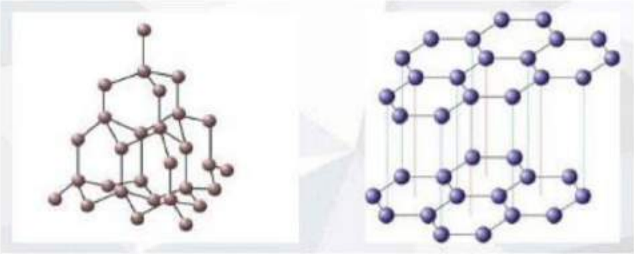
Covalent Solids or Networked Solids

Whenever an electric field is applied, electrons move between the layers.

- Graphite is a good conductor of electricity due to the availability of free electrons.

- Networked solids are hard and brittle.

Carbon-Carbon bond has got partial double bond character in graphite.

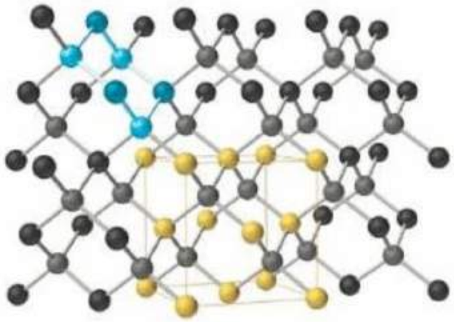


Covalent Network Solids

- Two layers in graphite are attached to each other by weak Van Der Waals force.
- Graphite can be used as a lubricant at high temperatures.

Diamonds

The structure of diamond is shown at the right in a "ball-and-stick" format. The balls represent the carbon atoms and the sticks represent a covalent bond. Be aware that in the "ball-and-stick" representation the size of the balls does not accurately represent the size of carbon atoms. In addition, a single stick is drawn to represent a covalent bond irrespective of whether the bond is a single, double, or triple bond or requires resonance structures to represent. In the diamond structure, all bonds are single covalent bonds (σ bonds). The "space-filling" format is an alternate representation that displays atoms as spheres with a radius equal to the van der Waals radius, thus providing a better sense of the size of the atoms.

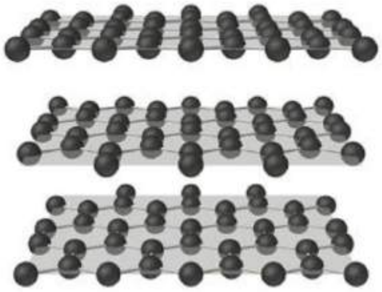


Rotating Model of Diamond Cubic.

Notice that diamond is a network solid. The entire solid is an "endless" repetition of carbon atoms bonded to each other by covalent bonds. (In the display at the right, the structure is truncated to fit in the display area.)

Graphite

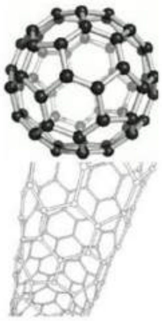
The most stable form of carbon is graphite. Graphite consists of sheets of carbon atoms covalently bonded together. These sheets are then stacked to form graphite. The figure shows a ball-and-stick representation of graphite with sheets that extended "indefinitely" in the xy plane, but the structure has been truncated for display purposes. Graphite may also be regarded as a network solid, even though there is no bonding in the z-direction. Each layer, however, is an "endless" bonded network of carbon atoms.



Rotating Graphite Structure.

Fullerenes

Until the mid-1980s, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_6O molecules in interstellar dust in 1985 added a third form to this list. The existence of C_6O, which resembles a soccer ball, had been hypothesized by theoreticians for many years. In the late 1980s, synthetic methods were developed for the synthesis of C_6O, and the ready availability of this form of carbon led to extensive research into its properties.

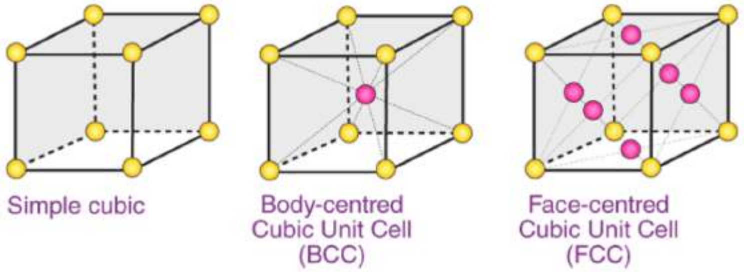


Examples of Fullerene: A Buckyball and an Extended Bucktube.

Number of Atoms in a Unit Cell

Introduction to Number of Atoms in a Unit Cell

That a crystal lattice comprises of several unit cells. In a unit cell, every constituent particle (atom, molecule or ion) has a specific and fixed position called lattice site. We can calculate a number of atoms/molecules and ions in a unit cell easily by analyzing the nature and position of constituent particles in unit cells.



(a) Primitive Cubic Unit Cell

In the primitive cubic unit cell, the atoms are only located on the corners. That means 8 atoms are located on 8 corners of the lattice. Each atom located on the corner contributes 1/8th of the original volume of the cell. So since there are total 8 atoms in a primitive cubic
unit cell, the total number of atoms in the primitive cubic unit cell.

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

So there is only 1 atom in a primitive cubic unit cell.

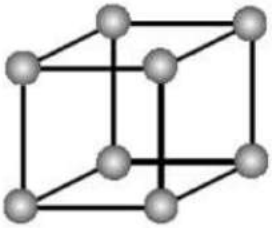


Image 2: The corners get only 1/8th part of atom

(b) Body- centred Cubic Unit Cell

In a body-centred unit cell, 8 atoms are located on the 8 corners and 1 atom is present at the center of the structure. So total atoms in the body-centred unit cell will be:

Since 8 atoms are present at the corners, each will contribute 1/8th of the original volume of the cell. Thus in the body-centred cubic unit cell:

- There are 8 corners and 1 corner shares 1/8th volume of the entire cell, so
  $8 \times \frac{1}{8} = 1$ atom
- Also, the atom at the centre is wholly present at the centre of the cell and can't be shared
  $1 \times 1 = 1$ atom
  So there are total 2 atoms present in a body centred unit cell.

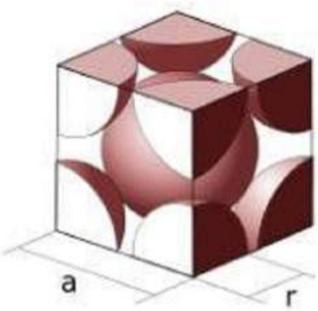


Image 3: **Atoms in body-centrd unit cell**

(c) Face-centred Cubic Unit Cell

In face-centred cubic unit cell atoms are present on 8 corners and center of all the faces. Also, each atom located on the centre of the unit cell is shared by two adjacent unit cells. There fore only half atom belongs to a single unit cell.

Thus in Face-centred cubic unit cell

- There are 8 atoms present on 8 corners, therefore, each corner will get 1/8 part of atom

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

- There are six faces and each face gets 1/2 part of atom then

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

Total atoms present in a face-centred unit cell = 1 + 3 = 4 atoms

(d) End-centred Cubic Unit Cell

In end-centred cubic unit cell, 8 atoms are located on 8 corners of the cube and 1

atom each is present on two opposite faces of the cube.
Therefore in end-centred cubic unit cell

- There are 8 atoms present on 8 corners, therefore each atom contributes 1/8th portion of the cell

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

- There are 2 atoms located at the center of the cell and each atom contributes 1/2 portion of the cell

  $$2 \times \frac{1}{2} = 1 \text{ atom}$$

  Total atoms present in a end-centred cubic unit cell $= 1 + 1 = 2$ atoms

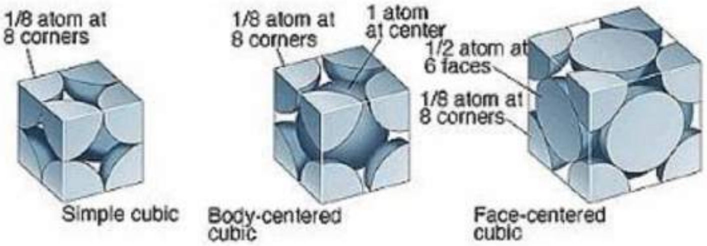
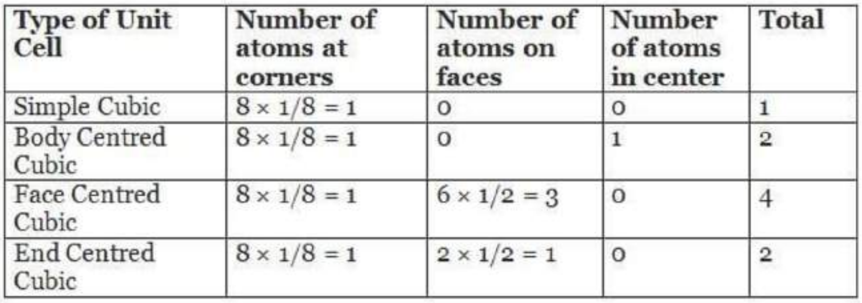
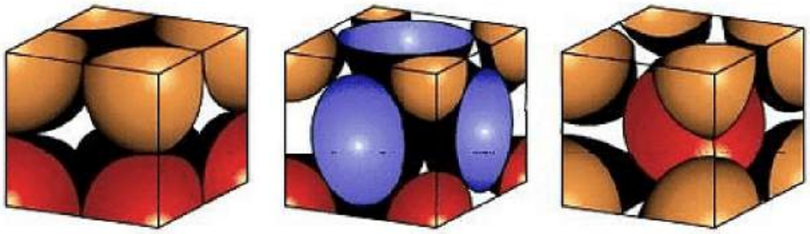


Image 4: Contribution of Atom in different unit cells

The table given below summarizes a total number of atoms present in a unit cell.



Type of Unit Cell	Number of atoms at corners	Number of atoms on faces	Number of atoms in center	Total
Simple Cubic	$8 \times 1/8 = 1$	0	0	1
Body Centred Cubic	$8 \times 1/8 = 1$	0	1	2
Face Centred Cubic	$8 \times 1/8 = 1$	$6 \times 1/2 = 3$	0	4
End Centred Cubic	$8 \times 1/8 = 1$	$2 \times 1/2 = 1$	0	2



(a) Simple cubic (b) Face centred cubic (c) Body centred cubic

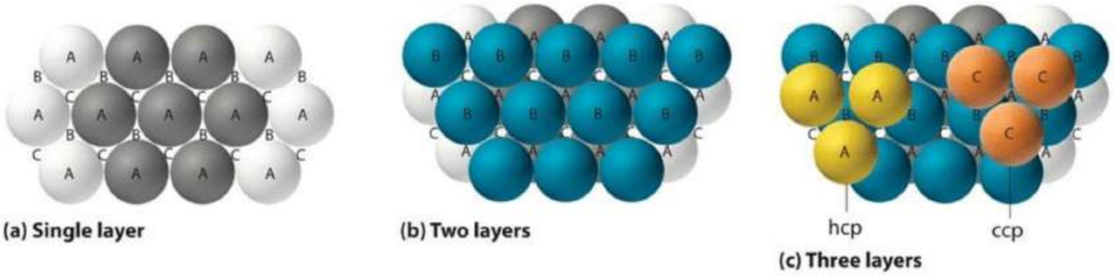
Three dimensional view showing the number of atoms per unit cell

Image 5: Types of unit cells

Close Packed Structures

What are Close Packed Structures?

In order to analyze the close packing of constituent particles (ions, molecules or atoms) in a lattice, we get into the assumption that constituent particles (ions, molecules or atoms) are hard spheres of identical shape.



(a) Single layer (b) Two layers (c) Three layers

Image 1: Different Types of Layers form closed packed structures

What is Close Packing?

The packing of constituent particles inside lattice in such a way that they occupy maximum available space in the lattice is known as Close Packing.
Close Packing is done in three ways, namely:
(a) One Dimensional Close Packing
(b) Two Dimensional Close Packing
(c) Three Dimensional Close Packing

(a) One Dimensional Close Packing

In one dimension close packing, the spheres are arranged in a row touching each other. In one-dimensional close packing, each sphere is in direct contact with two of its neighbor spheres. The number of nearest spheres to a particle in a lattice is called Coordination Number. Since there are two spheres in direct contact with the one sphere, the coordination number of one-dimensional close packing is 2.

(b) Two Dimensional Close Packing

Two-dimensional close packing is done by stacking rows of hard spheres one above the other. This can be done in two ways:

- AAA type
- ABA type

AAA Type

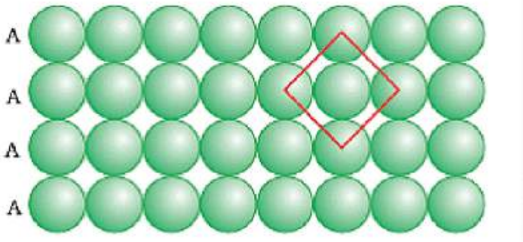


Image 2: AA type packing

The packing in which one sphere touches two spheres placed in two different rows one above and one below is called AAA type close packing. The coordination number of AAA type two-dimensional close packing is 4. The AAA type is formed by placing one-dimensional row directly one above the other in both horizontal and vertical directions. It is also called two-dimensional square close packing as the rows of spheres when arranged in vertical and horizontal alignments form a square.

AB Type

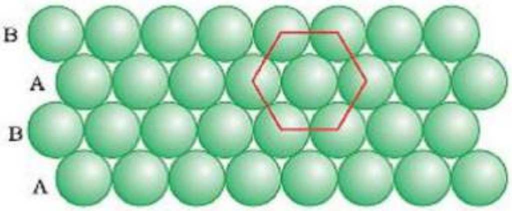


Image 3: AB Type Packing

The packing in which the spheres in the second row are located in the depressions of the first row. The ABA type close packing is formed by placing one-dimensional row let's say B type over the A type close packing and this series continues to form a two dimensional hexagonal. The coordination number of ABA Type packing is 6 as each sphere is in direct contact with 6 other spheres.

In ABA type close-packing we find triangular empty spaces called voids. These are of two types:

- Apex of triangle pointing upwards
- Apex of triangle pointing downwards

(c) Three Dimensional Close Packing

The formation of real lattices and structures take place through three-dimensional close packing. They are formed by stacking two-dimensional layers of spheres one above the other. This can be done by two ways:

- Three-dimensional close packing from two dimensional square close packed layers

- Three-dimensional close packing from two dimensional hexagonal close packed layers

Three-dimensional close packing from two-dimensional close packed layers

Formation of three-dimensional close packing can be done by placing the second square closed packing exactly above the first one. In this close packing, the spheres are aligned properly in horizontally and vertically. Similarly, by placing more layers one above the other, we can obtain a simple cubic lattice. The unit cell of the simple cubic lattice is called the primitive cubic unit cell.

Three-dimensional close packing from two dimensional hexagonal close-packed layers

Three-dimensional close packing can be formed with the help of two-dimensional hexagonal packed layers in two ways:
- Stacking the second layer over the first layer
- Stacking the third layer over the second layer

Stacking the second layer over the first layer

Suppose we take two hexagonal close packed layer 'A' and place it over the second layer B (as both layers have different alignment of spheres) such that spheres of the second layer are placed in the depressions of the first layer. We observe that a tetrahedral void is formed when a sphere of the second layer is right above the void (empty space) of the first layer. Adding further we notice octahedral voids at the points where the triangular voids of the second layer are placed right triangular voids of the first one in such a way that triangular space doesn't overlap. Octahedral voids are bordered by six spheres.

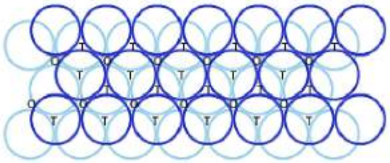


Image 4: Types of voids in three-dimensional closed packing

If there are 'N' closed spheres, then:
- Number of Octahedral Voids equals to "N"
- Number of Tetrahedral Voids equals to "2N"

Stacking the third layer over the second layer

There are two possible ways of placing the third layer over the second layer:

(1) By Covering Tetrahedral Voids

(2) By Covering Octahedral Voids

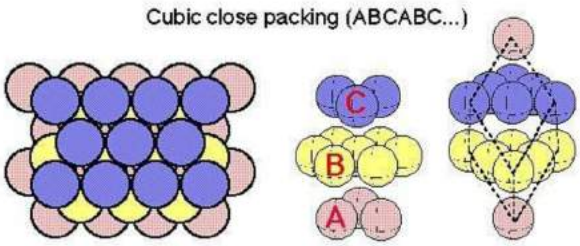
(1) Covering Tetrahedral Voids

In this kind of three-dimensional packing, the spheres of the third layer are aligned right above the spheres of the first layer. If we name the first layer as A and second layer as B, then the pattern will be ABAB… so far and so forth. The structure formed is also called hexagonal close-packed structure also known as HCP.

(2) Covering Octahedral Voids

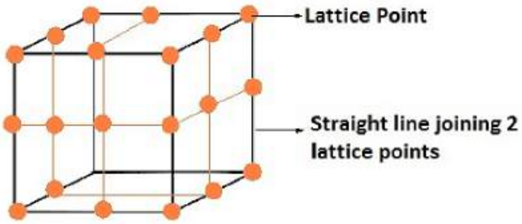
In this kind of packing the third layer, spheres are not placed with either of the second layer or first layer. If we name the first layer as A, second as B and then the third layer will be C (as it is now a different layer) then the pattern will be ABCABC… The structure formed is also called cubic closed packed (ccp) or face-centred packed cubic structure (fcc). For Example metals like copper and iron crystallize in the structure.

The coordination number in both cases will be 12 as each sphere in the structure is in direct contact with 12 other spheres. The packing is highly efficient and around 74% of the crystal is completely occupied.



ABC Type of Close Packing

The formula of a Compound and Number of Voids Filled



The number of octahedral voids present in a lattice = The number of close-packed particles.

- The number of tetrahedral voids produced is twice this number.
- In ionic solids, the bigger ions i.e. anions forms close-packed structure and the smaller ions i.e. cations occupy the voids.
- If the latter ion is small then tetrahedral voids are occupied, if bigger, then octahedral voids are occupied.
- In a compound, the fraction of octahedral or tetrahedral voids that are occupied depends upon the chemical formula of the compound.
- Close packed structures have both tetrahedral and octahedral voids.

Calculations Involving Unit Cells Dimensions

With the help of geometry and attributes of unit cells, we can easily evaluate the volume of the unit cell. With the volume and mass of atoms, we can also evaluate the density of the unit cell. A crystal lattice is represented in terms of unit cells; we can determine the density of crystal lattices by evaluating the density of unit cells.
Volume Density
Formula volume density of metal:

ρ_v = mass per unit cell/Volume per unit cell

The density of Unit Cell

A unit cell is a three-dimensional structure occupying one, two or more atoms. With the help of the dimensions of unit cells, we can evaluate the density of the unit cell. To do so let's consider a unit cell of edge length 'a', therefore the volume of the cell will be 'a3'. Also, density is defined as the ratio of the mass of the unit cell and volume of the unit cell.

The density of Unit Cell = mass of unit cell/Volume of unit cell......(1)

Mass of unit cell varies with number of atoms "n" and mass of a single atom "m". Mathematically mass of unit cell is the product of number of atoms "n" and mass of one atom "m" i.e.

Mass of Unit Cell = n × m
Also from quantitative aspect of atoms, mass of one atom can be written in terms of Avogadro Number (NA) and molar mass of atom (M), that is,

$$\text{Mass of 1 atom} = \frac{M}{N_A}$$

Volume of Unit Cell = a^3
Placing the required values in equation 1 we get

$$\text{Density of Unit Cell} = \frac{n \times m}{a^3}$$

$$= \frac{n \times M}{a^3 \times N_A}$$

Therefore if we know molar mass of atom "M", number of atoms "n", the edge length of unit cell "a" we can evaluate the density of unit cell.

Example 1
The density of a face-centred unit cell is 6.23 g cm^{-3}. Given the atomic mass of a single atom is 60, evaluate the edge length of the unit cell. (Take value of $N_A = 6.022 \times 10^{23}$)
As the unit cell is a face-centred unit cell, a number of atoms will be 4. We have $n = 4$, $M = 60$, $N_A = 6.022 \times 10^{23}$ and $d = 6.23$ g cm^{-3}
We know that

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

$$6.23 = \frac{n \times M}{a^3 \times N_A} = \frac{4 \times 60}{a^3 \times 6.022 \times 10^{23}}$$

After evaluating we get the value of edge length of the cube to be 4×10^{-8} cm.

Example 2

KBr or potassium bromide has density 2.75 g cm^{-3}. The edge length of its unit cell is 654 pm. Prove that KBr depicts face-centred cubic structure.
We have edge length of unit cell = 654 pm = 6.54×10^{-8} cm
Therefore volume of the cell = $(6.54 \times 10^{-8})^3$ cm^3
Molar Mass of Potassium Bromide (KBr) is 119 g/mol
Density of KBr = 2.75 g cm^{-3}

We know that

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

$$2.75 = \frac{n \times M}{a^3 \times N_A}$$

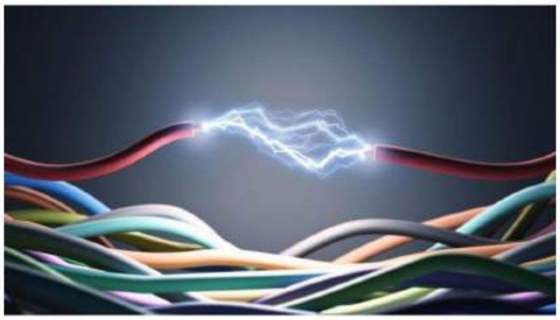
$$2.75 = \frac{n \times 119}{(6.54 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$$

Evaluating we get value of n to be $3.09 \approx 4$
Since a number of atoms is 4 we can clearly say that KBr is a face-centred cubic structure.

Electrical Properties: Conductors, Insulators & Semiconductors

What is Electrical Conductivity?

The electrical properties of solids are measured in terms of conductivity.
Conductivity may be defined as
The ease with which electric current can pass through a given substance. All solids do not conduct electricity in equal amounts. Some of them have high conductivity, whereas some of them do not conduct electricity at all.



- The electrical conductivity of solids is due to the motion of electrons or positive holes. The conductivity due to the motion of electron or positive holes is called electronic conductivity. The electrical conductivity may be due to the motion of ions. The conductivity due to the motion of ions is called **ionic conductivity**. Conductivity due to electrons is called **n-type conductivity** while that due to holes is called **p-type conductivity.**
- In metals, electrical conductivity is due to the motion of electrons and the electrical conductivity increases with the increase in the electrons available for conduction, the electrical conductivity increases.

- Pure ionic solids ions are not available for conduction hence in the pure solid state they are insulators. Due to the presence of defects in the crystal electrical conductivity increases.
- Solids exhibit a varying range of electrical conductivities, extending of magnitude ranging from 10–20 to 107 ohm^{-1} m^{-1}. Solids can be classified into three types on the basis of their conductivities. The difference in conductivities of conductors, insulators and semiconductors can be explained on the basis of band theory.

Electrical Conductivity on the Basis of Energy Bands

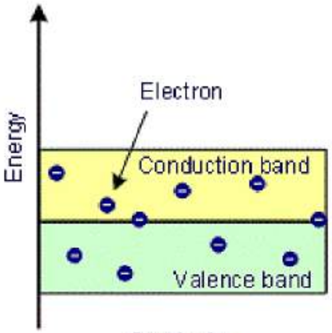
- The group of discrete but closely spaced energy levels for the orbital electrons in a particular orbit is called the **energy band.**
- Inside the crystal, each electron has a unique position and no two electrons see exactly the same pattern of surrounding charges. Because of this, each electron will have a different energy level. These different energy levels with continuous energy variation form what are called energy bands.
- The energy band which includes the energy levels of the valence electrons is called the valence band. The energy band above the valence band is called the conduction band. With no external energy, all the valence electrons will reside in the valence band.

On the basis of conduction of electricity, solids can be broadly divided into three categories:

1. Conductors
2. Insulators
3. Semiconductors

Conductors

- The solids with conductivities ranging between 104 to 107 ohm^{-1} m^{-1} are called conductors.
- Metals that have conductivities in the order of 107 ohm^{-1} m^{-1} are good conductors.
- In conductors, the lowest level in the conduction band happens to be lower than the highest level of the valence band and hence the conduction band and the valence band overlap. Hence the electron in the valence band can migrate very easily into the conduction band. Thus at room temperature, a large number of electrons are available for conduction.



Conductor

Examples: Copper, Aluminium, Silver, Gold, All metals

Characteristics of Conductors

- The substances which conduct electricity through them to a greater extent are called conductors.
- In conductors, the conduction band and valence band overlap with each other or the gap between them is very small.
- There are free electrons in the conduction band.
- Due to an increase in temperature conductance decreases.
- There is no effect of the addition of impurities on the conductivity of conductors.
- Their conductivity ranges between 10^4 to 10^7 ohm^{-1} m^{-1}.

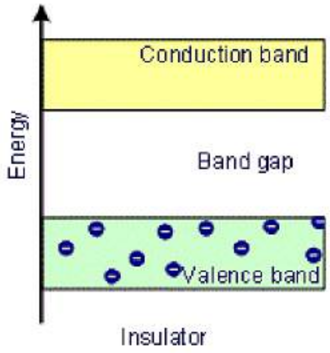
Conduction in Metallic Solids

- A metal conductor conducts electricity through the movement of free electrons. Metals conduct electricity in a solid as well as a molten state. The conduction of electricity is due to the transfer of electrons and not due to the transfer of matter.
- The conductivity of metals depends upon the number of valence electrons available per atom. It is nearly independent of the presence of impurity and lattice defects.
- Conductivity decreases with the increase in temperature. It can be explained as follows: **$M \rightarrow M^{n+}$kernel + ne^- free electrons**
  The kernels are fixed. Due to an increase in temperature, the amplitude of vibration of kernels increases. Hence the obstruction to the flow of electrons increases.

Insulators

- These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1} m^{-1}.

- The conduction band and valence band are widely spaced. Thus forbidden energy gap between the valence band and conduction band is large (greater than 3 eV). Hence the electron in the valence band cannot migrate into the conduction band. Hence no electrons are available for conduction. But at a higher temperature, some of the electrons from the valence band may gain external energy to cross the gap between the conduction band and the valence band. Then these electrons will move into the conduction band. At the same time, they will create vacant energy levels in the valence band where other valence electrons can move. Thus the process creates the possibility of conduction due to electrons in the conduction band as well as due to vacancies in the valence band.



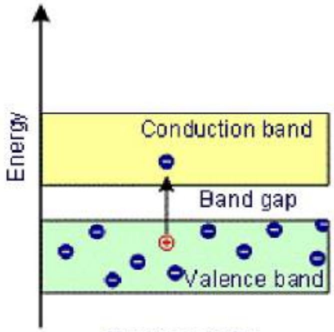
Variation of Energy in Insulators
Examples: Glass, wood, paper, plastic, mica.

Characteristics of Insulators

- In Insulators the conduction band and valence band are widely separated.
- There are no free electrons in the conduction band.
- There is an energy gap between the conduction band and valence band which is more than 3 eV.
- There is no effect of the change of temperature on the conductivity of insulators.
- There is no effect of the addition of impurities on the conductivity of the insulator.
- They have very low conductivities ranging between 10^{-20} to 10^{-10}ohm^{-1}m^{-1}.

Semiconductors

- These are the solids with conductivities in the intermediate range from 10^{-6} to 10^{4} ohm^{-1} m^{-1}.
- The forbidden energy gap between the valence band and conduction band is less than 3 eV. Thus energy gap between the valence band and conduction band is small. At absolute zero, no electrons are available for conduction.
- As the temperature increases, many electrons from the valence band may gain external energy to cross the gap between the conduction band and the valence band. Then these electrons will move into the conduction band. At the same time, they will create vacant energy levels in the valence band where other valence electrons can move. Thus the process creates the possibility of conduction due to electrons in the conduction band as well as due to vacancies in the valence band.



Semiconductor

Examples: Silicon, Germanium

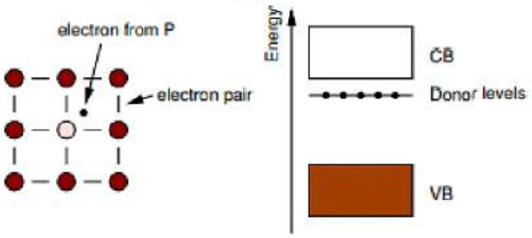
Characteristics of Semiconductors

- In semiconductors, the conduction band and valence band are very close to each other or the forbidden energy gap between them is very small.
- The electrons of the valence bond can easily be excited to the conduction band.
- There is an energy gap between the conduction band and the valence band which is less than 3 eV.
- Due to an increase in temperature conductance increases.
- There is an effect of the addition of impurities on the conductivity of semiconductors.
- Their conductivity ranges from 10^{-6} to 10^{4} ohm^{-1} m^{-1}.

Conduction of Electricity in Semiconductors

1. **Electron-Rich Impurities**: This involves substituting Si by neighbouring elements that contribute excess electrons. For example, small amounts of P or As can substitute Si.
Since P/As have 5 valence electrons, they behave like Si plus an extra electron. This extra electron contributes to electrical conductivity, and with a sufficiently large number of such dopant atoms, the material can display metallic conductivity. With smaller amounts, one has an extrinsic n-type semiconductor. Rather than n and p being equal, the n electrons from the donor usually totally outweigh the intrinsic n and p-type carriers so that: $\sigma \sim n|e|\mu_e$
The donor levels created by substituting Si by P or As lie just below the bottom of the conduction band. Thermal energy is usually sufficient to promote the donor electrons into the conduction band.

2.



N-type doping

3. **Electron-Deficit Impurities:** This involves substituting Si by a neighbouring atom that has one less electron than Si, for example, by B or Al. The substituent atom then creates a "hole" around it, that can hop from one site to another. The hopping of a hole in one direction corresponds to the hopping of an electron in the opposite direction. Once again, the dominant conduction process is because of the dopant.

$\sigma \sim \rho|e|\mu_h$

T dependence of the carrier concentration The expression:

$$\rho = \rho_0 \exp(\frac{E_g}{2k_{\mathrm{B}}T})$$

can be inverted and written in terms of the

$$\sigma = \sigma_0 \exp(\frac{-E_g}{2k_{\mathrm{B}}T})$$

conductivity

Now $\sigma = n|e|\mu_e$ or $\sigma = p|e|\mu_h$. It is known that the mobility μ is effectively temperature-independent so we can express the carrier concentration in terms

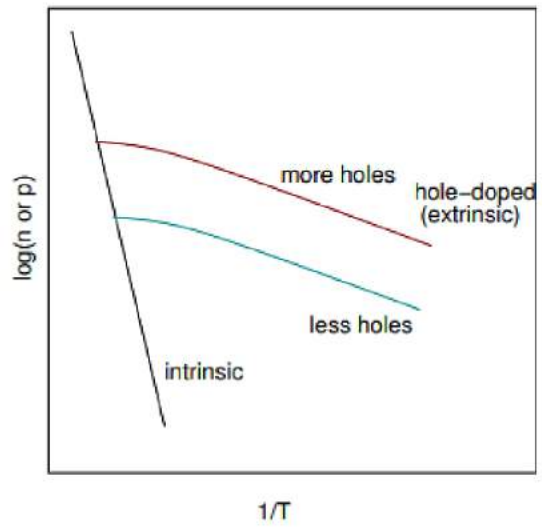
$$n = n_0 \exp(\frac{-E_g}{2k_{\mathrm{B}}T}) \quad \text{or} \quad \log n = \log n_0 - \frac{-E_g}{2k_{\mathrm{B}}T}$$

of temperature:

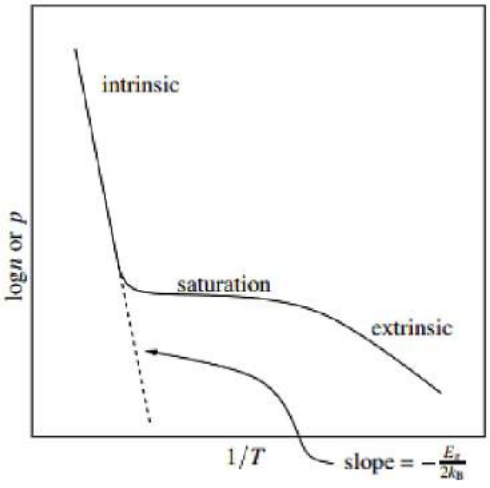
For an electron-doped semiconductor and for a hole-doped

$$p = p_0 \exp(\frac{-E_g}{2k_{\mathrm{B}}T}) \quad \text{or} \quad \log p = \log p_0 - \frac{-E_g}{2k_{\mathrm{B}}T}$$

semiconductor:



The plot above shows a typical variation of the logarithm of the carrier concentration with inverse temperature. At high temperatures (small 1/T) the data follows the usual activated behaviour of an intrinsic semiconductor. At lower temperatures (larger 1/T) extrinsic behaviour dominates.



Initially, lowering the temperature results in saturation of the acceptor levels or exhaustion of the donor levels. Only at still lower temperatures does the extrinsic behaviour take over.

Imperfections in Solids

Stoichiometric Defects

The compounds in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called stoichiometric defects. These are of following types,

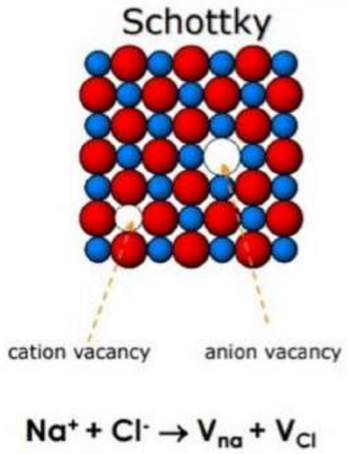
(a) Interstitial defect: This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystals.

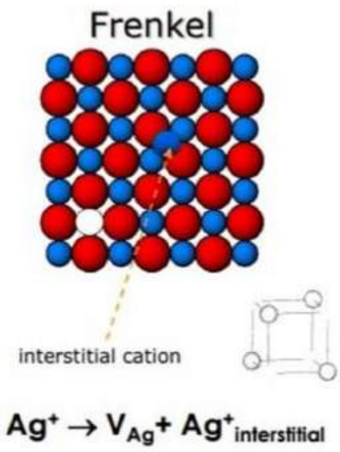
(b) Schottky defect: This type of defect when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This type of defect occurs in highly ionic compounds which have high co-ordination number and cations and anions of similar sizes.

Example: NaCl, KCl, CsCl and KBr etc.

(c) Frenkel defect: This type of defect arises when an ion is missing from its lattice site and occupies an interstitial position. The crystal as a whole remains electrically neutral because the number of anions and cations remain same. Since cations are usually smaller than anions, they occupy interstitial sites. This type of defect occurs in the compounds which have low co-ordination number and cations and anions of different sizes.

Example: ZnS, AgCl and AgI etc.
Frenkel defect are not found in pure alkali metal halides because the cations due to larger size cannot get into the interstitial sites. In **AgBr both Schottky and Frenkel defects occur simultaneously.**





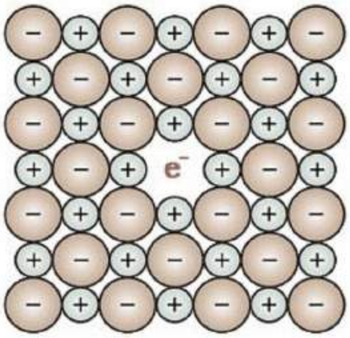
Non-Stoichiometric Defects:

Nonstoichiometric inorganic solids contain the constituent elements in a non-stoichiometric ratio due to defects in their crystal structures.

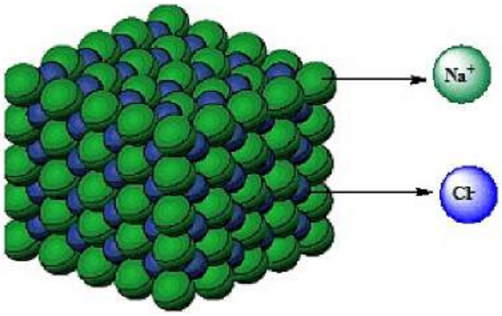
These defects are of two types:

(i) metal excess defect and
(ii) metal deficiency defect.

(i) Metal Excess Defect.



⇒ Metal excess defect due to anionic vacancies.
⇒ This type of defect is exhibited by alkali halides like NaCl and KCl.
⇒ Application of heat to NaCl in an atmosphere of sodium vapour results in deposition of the sodium atoms on the surface of the crystal.
⇒ The sodium atoms lose electron to form Na^+.
⇒ The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl.



⇒ The released electrons diffuse into the crystal and occupy anionic sites.
⇒ The anionic sites occupied by unpaired electrons are called F-centres that imparts yellow colour to the crystals of NaCl due to the excitation of the electrons on absorption of energy from the visible light falling on the crystals.
⇒ Excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet.
⇒ Metal excess defect due to the presence of extra cations at interstitial sites:
⇒ Heating Zinc oxide that exists in white colour at room temperature loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + 1/2\ O_2 + 2e^-$$

⇒ This results in excess of zinc in the crystal and its formula becomes Zn1+xO.
⇒ The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

Metal Deficiency Defect:

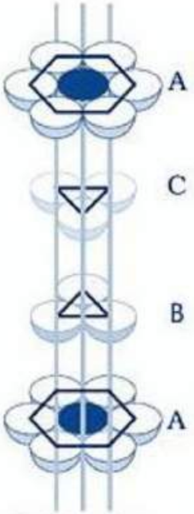
⇒ Many solids possess less amount of the metal as compared to the stoichiometric proportion.
⇒ For example, FeO is mostly found with a composition ranging from $Fe_{93}O$ to $Fe_{0.96}O$.

⇒ In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+}.

Packing Efficiency & Imperfections in Solids

Close Packing of Spheres

Atoms are space-filling entities and structures can be described as resulting from the packing of spheres. The most efficient, called Closest Packing, can be achieved in two ways, one of which is called **Hexagonal Close Packing** (Hexagonal Primitive) and the other, Cubic Close Packing (ccp or fcc). Hexagonal close-packing can be built up as follows:
Place a sphere on a flat surface. Surround it with six equal spheres as close as possible in the same plane. Looking down on the plane. Let us call this layer as the A layer.
Now form over the first layer a second layer of equally bunched spheres, so as to nestle into the voids. It will be clearly seen that once a sphere is placed over a void, it blocks the void which is adjacent to that void. Let us call this layer as the B layer.
Now, it can be clearly seen that there are two types of voids created by the B layer of spheres.
If a sphere is placed on the x - type of voids, it would resemble the A layer of spheres in the sense that it eclipses the spheres of the A layer. This arrangement (i.e., ABAB……) is called the **hexagonal close packing (hcp) or hexagonal primitive.** On the other hand, if the spheres were to be placed on the y - type of voids, it would neither eclipse the A layer nor the B layer of spheres. This would clearly be a unique layer. Let us call this layer as the C layer. This arrangement (i.e, ABCABC...) is called the **Cubic Close Packing (fcc).**



cubic close packing

Exercise 1: It can be seen now that both fcc and Hexagonal Primitive Structure have the same packing fraction. Moreover, this is also the highest packing fraction of all the possible unit cells with one type of atom with empty voids. Can you explain this?

Octahedral and Tetrahedral Voids

The close packing system involves two kinds of voids - tetrahedral voids and octahedral voids. The former has four spheres adjacent to it while the latter has six spheres adjacent to it. These voids are only found in either fcc or Hexagonal Primitive unit cells. Let us first consider an fcc unit cell. Not all the atoms of the unit cell are shown (for convenience). Let us assume that there is an atom (different from the one that forms the fcc) at the center of an edge.
Let it be big enough to touch one of the corner atoms of the fcc. In that case, it can be easily understood that it would also touch six other atoms (as shown) at the same distance. Such voids in an fcc unit cell in which if we place an atom it would be in contact with six spheres at equal distance (in the form of an octahedron) are called octahedral voids.
On calculation, it can be found out that an fcc unit cell has four octahedral voids effectively.

The number of effective octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell.

Let us again consider an fcc unit cell. If we assume that one of its corners is an origin, we can locate a point having coordinates (¼,¼,¼). If we place an atom (different from the ones that form the fcc) at this point and if it is big enough to touch the corner atom, then it would also touch three other atoms which are at the face centers of all those faces which meet at that corner. Moreover, it would touch all these atoms at the corners of a regular tetrahedron. Such voids are called tetrahedral voids.
Since there are eight corners, there are eight tetrahedral voids in a fcc unit cell. We can see the tetrahedral voids in another way. Let us assume that eight cubes of the same size make a bigger cube. Then the centers of these eight small cubes would behave as tetrahedral voids for the bigger cube (if it were face-centered). **The number of tetrahedral voids is double the number of octahedral voids.** Therefore, the number of tetrahedral voids in hcp is 12.

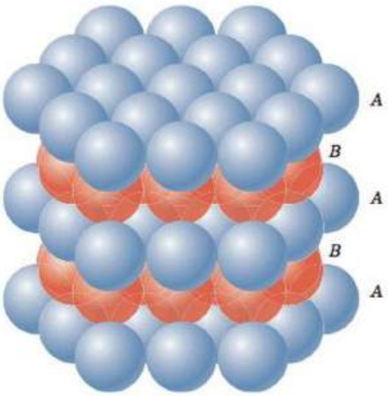


Fig: Hexagonal closed packing.

Radius Ratio Rules

The structure of many ionic solids can be accounted for by considering the relative sizes of the positive and negative ions, and their relative numbers. Simple geometric calculations allow us to work out, as to how many ions of a given size can be in contact with a smaller ion. Thus, we can predict the coordination number from the relative sizes of the ions.

Coordination Number 3

The smaller positive ion of radius r^+ is in contact with three larger negative ions of radii r^-. It can be seen that $AB = BC = AC = 2r^-$, $BD = r^- + r^+$. Further, the angle ABC is 60^o, and the angle DBE is 30^o.
By trigonometry $\text{Cos } 30^o = (BE / BD)$. $BD = (BE/\text{Cos } 30^o)$, $r^+ + r^- = r^- /\text{Cos } 30^o =$ $(r^- / 0.866) = r^{-}\ \acute{}\ 1.155$, $r^+ = (1.155\ r^-) - r^- = 0.155\ r^-$,
Hence $(r^+ / r^-) = 0.155$.

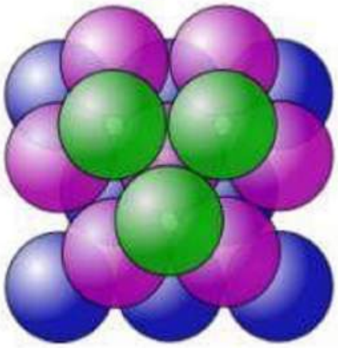


Fig: Cubic close packing.

Coordination Number 4 (Tetrahedron)

Angle ABC is the tetrahedral angle of 109° 28' and hence the angle ABD is half of this, that is 54°44'. In the triangle ABD, Sin ABD = 0.8164 = AD/AB =.

Taking reciprocals, $\frac{r^+ + r^-}{r^-} = \frac{1}{0.8164} = 1.225$, rearranging, we get, $\frac{r^+}{r^-} = 0.225$.

Coordination Number 6 (Octahedron) or 4 (Square Planar)

A cross-section through an octahedral site is shown in the adjacent figure and the smaller positive ion (of radius r^+) touches six larger negative ions (of radius r^-). (Note that only four negative ions are shown in this section and one is above and one below the plane of the paper). It is obvious that $AB = r^+ + r^-$ and $BD = r^-$. The angle ABC is 45° in the triangle ABD. cos ABD = 0.7071

$$= (BD/AB) = r\frac{r^-}{r^+ + r^-}$$

Rearranging, we get, $r^+/r = 0.414$

Limiting radius ratio $r^+/r^- = x$	**Co - ordination number**	**Shape**	**Example**
$x < 0.155$	2	Linear	BeF_2
$0.155 \le x < 0.225$	3	Planar Triangle	$AlCl_3$
$0.225 \le x < 0.414$	4	Tetrahedron	ZnS
$0.414 \le x < 0.732$	4	Square planar	$PtCl_4^{2-}$
$0.414 \le x < 0.732$	6	Octahedron	NaCl
$0.732 \le x < 0.999$	8	Body centered cubic	CsCl

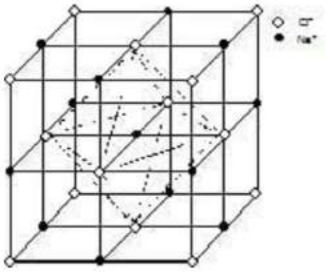
Exercise 2: The radius of a calcium ion is 94 pm and of an oxide ion is 146 pm. Predict the crystal structure of calcium oxide.

Classification of Ionic Structures

In the following structures, a black circle would denote a cation and a white circle would denote an anion In any solid of the type A_xB_y, the ratio of the coordination number of A to that of B would be y: x.

Rock Salt Structure

Cl^- is forming an fcc unit cell in which Na^+ is in the octahedral voids. The coordination number of Na^+ is 6 and therefore that of Cl^- would also be 6. Moreover, there are 4 Na^+ ions and 4 Cl^- ions per unit cell. The formula is Na_4Cl_4 i.e,NaCl. The other substances having this kind of a structure are halides of all alkali metals except cesium halides and oxides of all alkaline earth metals except beryllium oxide.



Unit cell structure of NaCl

Zinc Blende Structure

Sulfide ions are face centered and Zinc is present in alternate tetrahedral voids. Formula is Zn_4S_4, i.e, ZnS. Coordination number of Zn is 4 and that of sulfide is also 4. Other substance that exists in this kind of a structure is BeO.

Fluorite Structures

Calcium ions are face-centered and fluoride ions are present in all the tetrahedral voids. There are four calcium ions and eight fluoride ions per unit cell. Ther efore the formula is Ca_4F_8, (i.e, CaF_2). The coordination number of fluoride ions is four (tetrahedral voids) and thus the coordination number of calcium ions is eight. Other substances which exist in this kind of structure are UO_2, and ThO_2.

Anti-Fluorite Structure

Oxide ions are face-centered and lithium ions are present in all the tetrahedral voids. There are four oxide ions and eight lithium ions per unit cell. As it can be seen, this unit cell is just the reverse of Fluorite structure, in the sense that, the positions of cations and anions is interchanged. Other substances which exist in this kind of a structure are Na_2O, K_2O and Rb_2O.

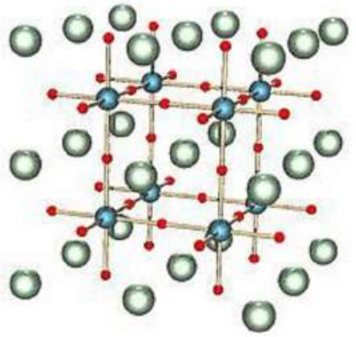
Cesium Halide Structure

Chloride ions are primitive cubic while the cesium ion occupies the center of the unit cell. There is one chloride ion and one cesium ion per unit cell. Ther efore the formula is CsCl. The coordination number of cesium is eight and that of chloride ions is also eight. Other substances which exist in this kind of a structure are all halides of cesium.

Corundum Structure

The general formula of compounds crystallizing in corundum structure is A_2O_3. The closest packing is that of anions (oxide) in hexagonal primitive lattice and two-thirds of the octahedral voids are filled with trivalent cations. Examples are Fe_2O_3, Al_2O_3 and Cr_2O_3.

Perovskite Structure



Perovskite Structure

The general formula is ABO_3. One of the cations is bivalent and tetravalent. Example: $CaTiO_3$, $BaTiO_3$. The bivalent ions are present in primitive cubic lattice with oxide ions on the centers of all the six square faces. The tetravalent cation is in the center of the unit cell occupying octahedral void.

Spinel and Inverse Spinel Structure

Spinel is a mineral ($MgAl_2O_4$). Generally they can be represented as $M^{2+}M_2{}^{3+}O_4$, where M^{2+} is present in one-eighth of tetrahedral voids in a FCC lattice of oxide ions and M^{3+} ions are present in half of the octahedral voids. M^{2+} is usually Mg, Fe, Co, Ni, Zn and Mn; M^{3+} is generally Al, Fe, Mn, Cr and Rh. Examples are $ZnAl_2O_4$, Fe_3O_4, $FeCr_2O_4$ etc.

Many substances of the type $M^{4+}M_2^{2+}O_4$ also have this structure. In an inverse spinel the ccp is of oxide ions, M^{2+} is in one-eight of the tetrahedral voids while M^{3+} would be in one-eight of the tetrahedral voids and one-fourth of the octahedral voids.

Exercise 3: The unit cell of silver iodide (AgI) has 4 iodine atoms in it. How many silver atoms must be there in the unit cell?

Exercise 4: The coordination number of the barium ions, Ba^{2+}, in barium chloride (BaF_2) is 8. What must be the coordination number of the fluoride ions, F^-.

Imperfections in a Crystal

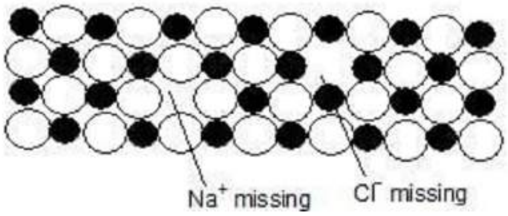
The discovery of imperfections in an otherwise ideally perfect crystal is one of the most fascinating aspects of solid state science. An ideally perfect crystal is one which has the same unit cell and contains the same lattice points throughout the crystal. The term **imperfection** or **defect** is generally used to describe any deviation of the ideally perfect crystal from the periodic arrangement of its constituents.

Point Defect

If the deviation occurs because of missing atoms, displaced atoms or extra atoms, the imperfection is named as a **point defect.** Such defects can be the result of imperfect packing during the original crystallisation or they may arise from thermal vibrations of atoms at elevated temperatures because with increase in thermal energy there is increased probability of individual atoms jumping out of their positions of lowest energy.

The most common point defects are the **Schottky defect** and the **Frenkel defect**. Comparatively less common point defects are the **metal excess defect** and **metal deficiency defects**. All these defects have been discussed below in some detail.

Schottky Defects: The defects arise if some of the lattice points in a crystal are unoccupied. The points which are unoccupied are called lattice vacancies. The existence of two vacancies, one due to a missing Na^+ ion and the other due to a missing Cl ion in a crystal of NaCl, is shown in figure 16. The crystal, as a whole remains neutral because the number of missing positive and negative ions are the same.



Schottky defects appear generally in ionic crystals in which the positive and the negative ions do not differ much in size. Sodium chloride and cesium chloride furnish good examples of ionic crystals in which Schottky defects occurs.

Frenkel Defects:

These defects arise when an ion occupies an interstitial position between the lattice points. This is shown in figure for the crystal of AgBr.

Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+
Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-
Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+
Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-

Frenkel Defects in a Crystal

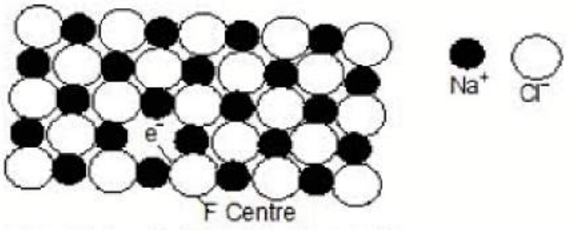
As can be seen, one of the Ag^+ ions occupies a position in the interstitial space rather than its own appropriate site in the lattice. A vacancy is thus created in the lattice as shown. It may be noted again that the crystal remains neutral since the number of positive ions is the same as the number of negative ions. The presence of Ag^+ ions in the interstitial space of AgBr crystal is responsible for the formation of a photographic image on the exposure of AgBr crystals (i.e., photographic plate) to light.

ZnS is another crystal in which Frenkel defects appear. Zn^{2+} ions are entrapped in the interstitial space leaving vacancies in the lattice.

Frenkel defects appear in crystals in which the negative ions are much larger than the positive ions. Like Schottky defects, the Frenkel defects are also responsible for the conduction of electricity in crystals and also for the phenomenon of diffusion in solids.

Metal Excess Defects (The Colour Centres) It has been observed that if a crystal of NaCl is heated in sodium vapour, it acquires a yellow colour.

This yellow colour is due to the formation of a non-stoichiometric compound of sodium chloride in which there is a slight excess of sodium ions. What happens in this case is that some sodium metal gets doped into sodium chloride crystal which, due to the crystal energy, gets ionised into Na^+ and Cl^-. This electron occupies a site that would otherwise be filled by a chloride ion, as illustrated in the figure.



F-centre in a Sodium chloride crystal

There is evidently an excess of metal ions although the crystal as a whole is neutral. A little reflection would show that there are six Na$^+$ sites adjacent to the vacant site occupied by the electron. The extra electron in thus shared between all the six Na$^+$ ions which implies that this electron is not localised at the vacant Cl site. On the other hand, this electron is similar to the delocalised p electrons present in molecules containing conjugated double bonds.
Light is absorbed when this delocalised electron makes an easy transition from its ground state to an excited state. As a result, the non-stoichiometric form of sodium chloride **appears coloured**. Because of this, the sites occupied by the extra electrons are known as **colour centers**. These are also called **F-centres**. This name comes from the German word **Farbe** meaning **colour**. The non-stoichiometric sodium chloride may be represented by the formula $Na_{(1+d)}Cl$ where d is the excess sodium metal doped in the crystal because of its exposure to sodium vapour.
Another common example of metal excess defects is the formation of a magenta coloured non-stoichiometric compound of potassium chloride by exposing the crystals of KCl to K metal vapour. The coloured compound contains an excess of K$^+$ ions, the vacant Cl sites being filled by electrons obtained by the ionization of the excess K metal-doped into the crystal.

Metal Deficiency Defects.

In certain cases, one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring two charges instead of one. There is evidently, a deficiency of the metal ions, although the crystal as a whole is neutral.
This type of defect is generally found amongst the compounds of transition metals which can exhibit variable valency. Crystals of FeO, FeS and NiO show this type of defects. The existence of metal deficiency defects in the crystal of FeO is illustrated.

Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}
O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}
Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	▨	O^{2-}	Fe^{2+}	O^{2-}
O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{+3}	O^{2-}	Fe^{+3}	O^{2-}	Fe^{2+}
Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}

Figure 19

It is evident from the above discussion that all types of point defects result in the creation of vacancies or`holes' in the lattice of the crystals. The presence of holes lowers the density as well as the lattice energy or the stability of the crystals. The presence of too many holes may cause a partial collapse of the lattice.

Magnetic Properties of Solids

Magnetic properties:

The macroscopic magnetic properties of material are consequence of magnetic moments associated with the individual electron. Each electron in an atom has magnetic moment due to two reasons. The first one is due to the orbital motion around the nucleus, and the second is due to the spin of electron around its own axis. A moving electron may be considered to be a small current loop, generating a small magnetic field, and having a magnetic moment along its axis of rotation.
The other type of magnetic moment originates from electron spin which is directed along the spin axis. Each electron in an atom may be thought of as being a small magnet having permanent orbital and spin magnetic moments. ***The fundamental*** **magnetic moment is Bohr Magneton, m_s equal to 9.27×10^{-24} Am^2** . *For each electron in an atom, the* **spin magnetic moment is $\pm m_B$** (depending upon the two possibilities of the spin). The contribution of the orbital magnetic moment is equal to m_i m_B, where m_i is the magnetic quantum number of the electron.
Based on the behaviour in the external magnetic field, the substances are divided different categories.

(i) Diamagnetic substances:

Substances which are weakly repelled by the external magnetic field are called diamagnetic substances,

Example: TiO_2, NaCl, Benzene.

(ii) Paramagnetic substances: Substances which are attracted by the external magnetic field are called paramagnetic substances,

Example: O_2, Cu^{2+}, Fe^{3+}.

(iii) Ferromagnetic substances: Substances which show permanent magnetism even in the absence of the magnetic field are called ferromagnetic substances.

Example: Fe, Ni, Co, CrO_2.

(iv) Ferrimagnetic Substances: Substances which are expected to possess large magnetism on the basis of the unpaired electrons but actually have small net magnetic moment are called ferrimagnetic substances.

Example: Fe_3O_4.

(v) Anti-ferromagnetic substances: Substances which are expected to posses paramagnetic behaviour, ferromagnetism on the basis of unpaired electron but actually they possess zero not magnetic moment are called anti-ferromagnetic substances.

Example: MnO_2

Note: Ferromagnetic, Anti-ferromagnetic and Ferrimagnetic solids change into paramagnetic at some temperature. It may be further pointed out here that each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This is known as **Curie Temperature.**

Dielectric Properties:

Insulators do not conduct electricity because the electrons present in them are held tightly to the individual atoms or ions and are not free to move. however, when electric field is applied, polarization takes place because nuclei are attracted to one side and the electron cloud to the other side. Thus dipoles are formed. In addition to these dipoles, there may also be permanent dipoles in the crystal. These dipoles may align themselves in an ordered manner so that such crystals have a net dipole moment.
Such polar crystals show the following interesting properties:

(i) Piezoelectricity or Pressure - electricity: When mechanical stress is applied on such crystals so as to deform them, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric crystals. A few examples of piezoelectric crystals include Titanates of Barium and Lead, Lead zirconate ($PbZrO_3$), Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and Quarts. These crystals are used as pick-ups in record players where they produce electrical signals by application of pressure. They are also used in microphones, ultrasonic generators and sonar detectors.

(ii) Ferroelectricity: In some of the piezoelectric crystals, the dipoles are permanently polarized even in the absence of the electric field. However, on applying, electric field, the direction of polarization changes, this phenomenon is called ferroelectricity due to analogy with ferromagnetism. Some examples of the ferroelectric solids are barium titanate ($BaTiO_3$), Sodium potassium tartarate (Rochelle salt) and Potassium dihydrogen phosphate (KH_2PO_4)

Note: All ferroelectric solids are piezoelectric but the reverse is not true.

(iii) Anti-ferroelectricity: In some crystals, the dipoles align themselves in such a way that alternately, they point up and down so that the crystal does not posses any net dipole moment. Such crystals are said to be anti-ferroelectric. A typical example of such crystals is Lead zirconate ($PbZrO_3$)

Superconductivity:

A substance is said to be superconducting when it offers no resistance to the flow of electricity.

Isomorphism:

The property shown by crystals of different chemical substances which exhibit the same crystalline form is known as isomorphism.
Such substances have similar chemical formula,

Example: $Na_2HPO_4 . 12H_2O$ and $Na_3ASO_4 . 12H_2O$
Chemically substances having same type of formulae are not necessarily Isomorphous.

Magnetic Properties of Crystals

Properties	**Information**	**Magnetic Alignment**	**Example**	**Application**
1. Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	⥮⥮⥮⥮⥮	Benzene NaCl, TiO_2, V_2O_5, etc.	Insulators
2. Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetized.	↖↙→↑↘↗	O_2, VO, CuO, TiO	Electronic devices
3. Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic permanently magnetized. On heating to a temperature called Curie Point, these solids change to paramagnetic solid.	↑↑↑↑↑↑↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio, video tapes.
4. Antiferro-magnetic	In these solids change electrons align themselves in such a way that resultant magnetic moment is zero.	⇅ ⇅ ⇅ ⇅	Cr_2O_3, CoO, Co_3O_4, Fe_2O_3 MnO, MnO_2	Used in the instruments of magnetic susceptibility measurement
5. Ferrimagnetic	unpaired electrons align themselves in such way that there is a net magnetic moment.	⇅↓ ↑ ↓⇵ ↓↓ OR ↑↑ ↓↓↓ ↑↑ ↓↓↓ ↑↑ and so on	Fe_3O_4, ferrites	