INDEX

SOLID STATE PHYSICS

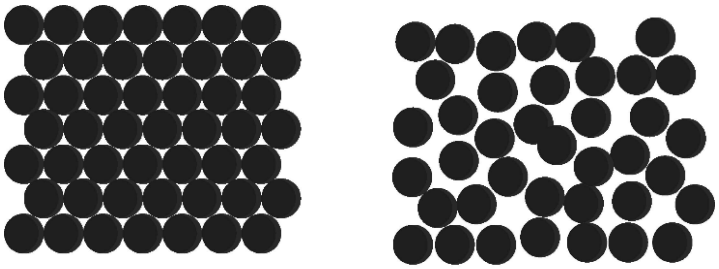
Chapter 1

Crystalline Solid

Solids are Periodic in Nature (Solids consists of some building block elements)
Solids can be classified into two parts, on the basis of their arrangement of constituent building block elements:- Crystalline Solids and Amorphous Solids

Crystalline Solid:
A crystalline solid is formed by regular repetition of its building blocks (atoms or molecules) in a three-dimensional periodic array. The examples of crystals are table salt (NaCl), diamond, snowflakes, metals, ice, ceramics etc.

Amorphous Solid:
Materials in which constituents (atoms or molecules) are not arranged in a regular manner over a long range. There is no periodicity in structure, if periodicity occurs, it must be over a short distance. The examples of crystalline solid are glass, plastic, rubber etc.

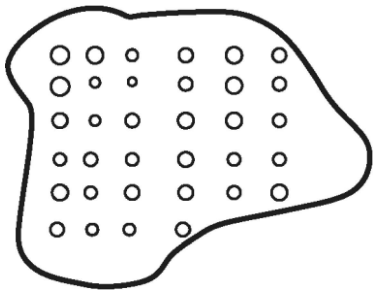


Crystalline Amorphous

Amorphous solids / non-Crystalline solids	**Crystalline solids**
Amorphous solids do not have an ordered structure	Crystalline solids have an ordered structure
Do not have a sharp melting point	Have a sharp melting point
Have no characteristic heat of fusion	Have a definite heat of fusion
Isotropic since they have the same physical properties in all directions	Anisotropic since their physical properties are different in different directions
Have covalently bonded networks Ex- Plastic, Wooden piece, Rubber, Glass.	Have covalent bonds, ionic bonds, van der Waal's bonds and metallic bonds Ex- Rock Salt, Diamond, Al, Au, Ag, etc….

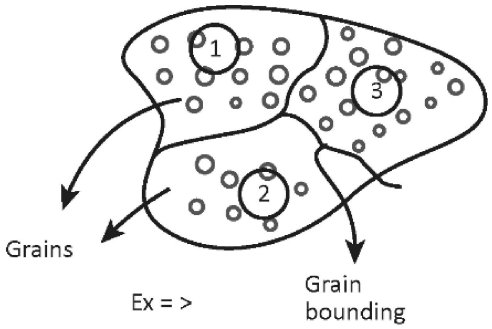
Crystalline solids can be further classified into two categories:

1. Single Crystalline Solid: -



Ex. Quartz, Gemstones etc.

2. Poly-Crystalline Solid



Ex. Rocks, Ice, all common metals etc.

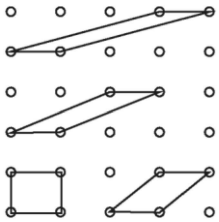
Crystal Structure:

Terms used in study of crystal structure:

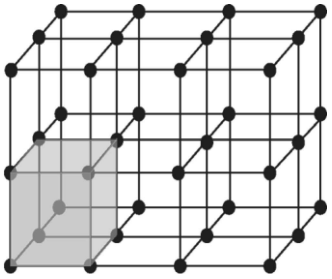
- **Lattice:** It's a regular periodic array of points in space. Every point in a lattice has an identical environment. Lattice is just a periodic pattern of fictitious points in space.
- **Basis:** It is an atom, ion or a group of atoms (2, 3, 4….) to be placed on each & every lattice point of the regular arrangements in the lattice to form crystal. For example, in NaCl crystal, NaCl molecules, a group of one Na and one Cl atoms form a basis.

  Crystal Structure = Lattice + Basic

  In an Ideal crystal → ∞ number of lattice points will be arranged periodically.



LATTICE POINTS IN 2D



LATTICE POINTS IN 3D

Ex⇒ In 2D:-

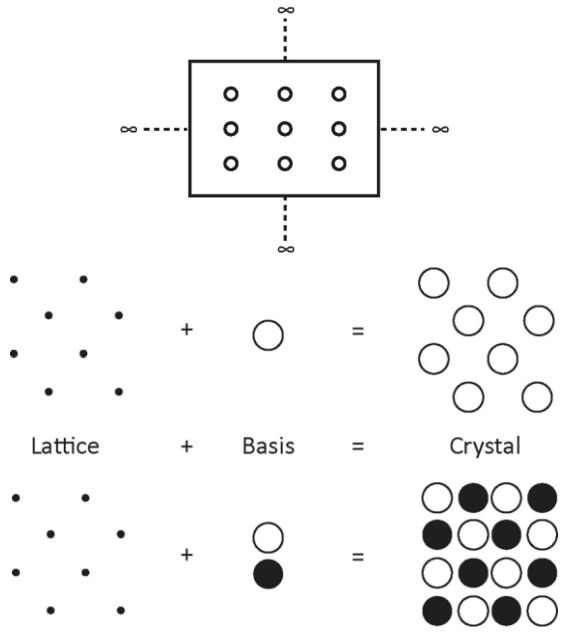
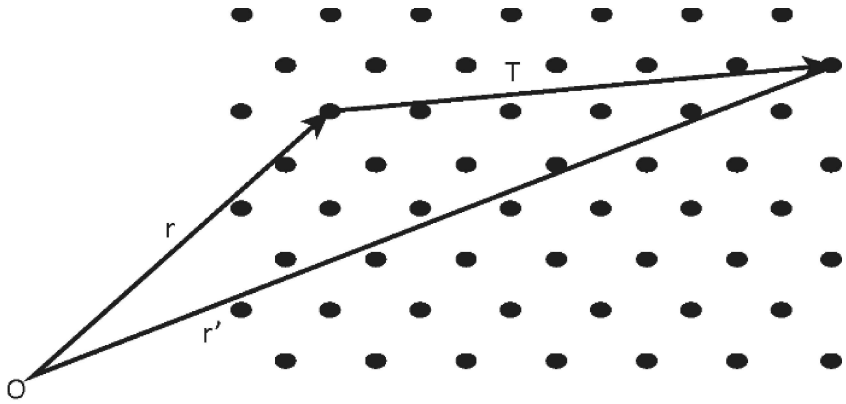


Figure: crystal as combination of lattice and basis

Lattice Translational Vector:- $(\vec{a}, \vec{b}, \vec{c})$

Say we define the lattice by 3 fundamental vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ or $\vec{a}, \vec{b}, \vec{c}$ such that the atomic arrangement looks exactly the same for $\vec{r}$ as that form $\vec{r}_1 = \vec{r} + u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$where $u_1, u_2, u_3 \rightarrow$ are integers and $\vec{T} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$



$\vec{T} \rightarrow$ Lattice Translational Vector or Lattice Translational operator.

Some important points while describing the crystal structure: -

1. Choice of more than & Lattice is always possible.
2. Hence, more than 1 translational vector can always be defined (depends on lattice).
3. Basis can only be identified once the lattice & the axis has been chosen.
   Ex. $C_sCl \rightarrow$ Simple Cubic

Unit Cell: It is advantageous to divide the crystal into little entities because such a small group of atoms or molecules is a well-defined arrangement. These small cells are called unit cells. The building blocks for the formation of the crystal structure are the unit cells.

Formation of a Unit Cell: - By connecting some lattice points, which will repeat over & over, again & again all over the lattice.
Shape of a unit cell is not unique, we according to our convenience choose the shape of the unit cell.
In general, to avoid the structural & mathematical correlation issues, for our convenience we choose the smallest possible unit cell.

A unit cell can be completely described by three lattice vectors

Primitive Unit Cell:-

1. Minimum volume cell $(\vec{a}_1(\vec{a}_2 \times \vec{a}_3))$
2. Must serve as a building block of the crystal structure.
3. Total constituent of lattice points must be = 1

Non-Primitive Unit Cell: - All the unit cells that are not Primitive.

Weigner Seitz Cell:- Always a Primitive Cell The area bounded by perpendicular bisectors of lines connecting the nearest neighbors is a practical technique to select a primitive cell or unit cell in a crystal, among other options. The Wigner Seitz cell is a specific sort of unit cell that describes the symmetry of the cell in 3D. A unit cell with exactly one lattice point is a primitive cell, such as a Wigner-Seitz cell. Another way of drawing a Primitive cell.

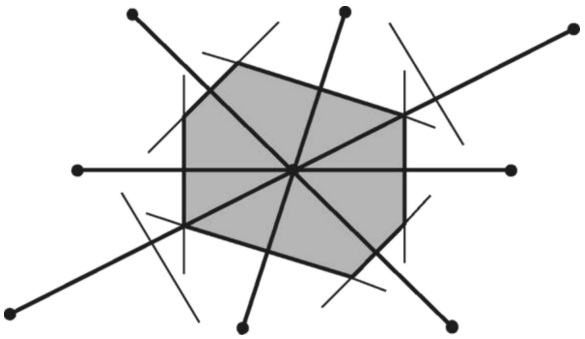
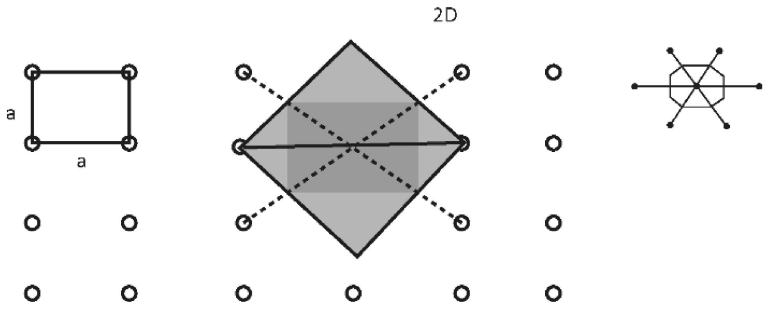


Figure: WEIGNER SEITZ CELL



1. Choose any 1 lattice point.
2. Connect the line drawn between all the nearest lattice point.
3. Draw a new ⊥ line in the middle of these lines.
4. The smallest volume enclosed this way is the Wigner-Seitz cell.

a_1, a_2, a_3

Symmetry Operations (Closely related with group theory): -

An operation, which transforms the crystal into itself & the crystal remains invariant under the symmetry operation.

1. Translational
2. Rotational
3. Reflection
4. Inversion

1. **Translation Symmetry:** When a lattice point is subject to a lattice translation operation, another point is produced that is a perfect duplicate of the original point.

2. **Rotational Symmetry:** When a crystal is rotated via a point at an angle, the lattice changes into another lattice that looks identical to the original.

   $\phi_n^\circ = \frac{360^\circ}{n}$ → order of rotational symmetry or n-fold symmetry

   $$n = 1, 2, 3, 4, 6$$

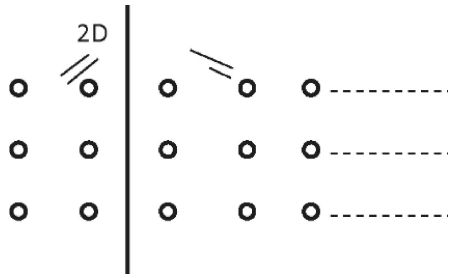
   ϕ_n° =The angle by which we need to rotate about the geometric center to get the symmetry.

   5-fold symmetry doesn't exist in lattices, but that can be found in nature.

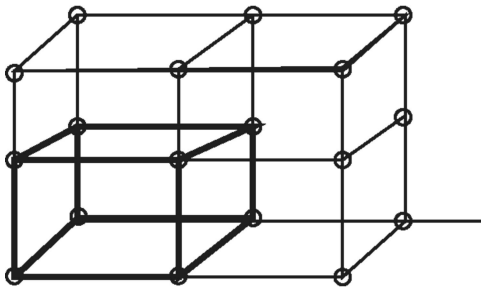
   Reason:-

   1. Won't be able to get symmetry after translating it.
   2. Leaves some vacant space.

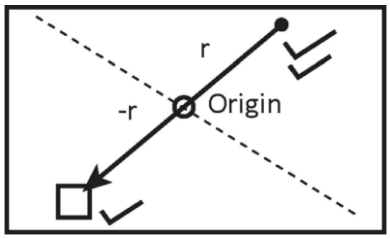
3. **Reflection Symmetry:** - In 2D about a line
(Mirror Image)



In 3D:- about a plane



4. **Inversion Symmetry**: - Translation + Reflection
A symmetry operation known as inversion is only applicable to three-dimensional lattice structures. If we choose a point in this symmetry as the center of symmetry and use the lattice vector r to locate all of the points, then -r (sign inversion) results in the same lattice.



- **Point Group:-** Symmetry operations performed about a point or a line are called point group symmetry operations
Combination of -
Rotation → about a point
Reflection → about a line in - 2D or about a in plane - 3D
Inversion → about a point
Number of Point Group elements: In 2D – 10 & In 3D – 32
In 2D - 10
In 3D – 32

- **Space Group: -** symmetry operations performed by translation vectors called space symmetry operations.
Combination of Point group & Translation Symmetry operation (i.e. moving in space)
In 2D - 17
In 3D – 230
A total of 230 space groups make up the crystal system as a whole, and 32 point groups describe all symmetry operations involving a fixed point in space.

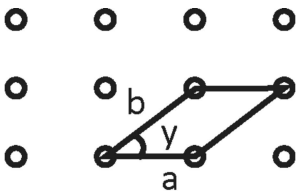
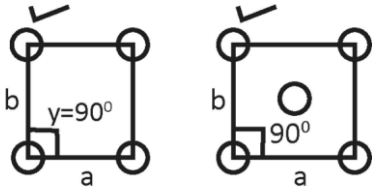
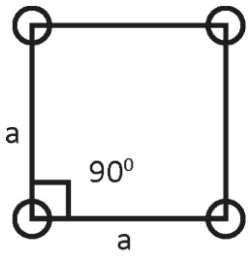
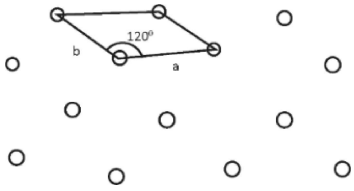
- **Bravais Lattice:-**
All the possible lattices that follow all the point group symmetry operations.

- **Crystal System:-** According to certain specifications about the lengths of the edges & the angle between them, the Bravais lattices are grouped into certain systems called crystal systems.

In 2D:- Bravais Lattices - 5
Crystal System - 4

In 3D:- Bravais Lattices – 14
Crystal System – 7

In 2D:

Crystal System	Bravais Lattice	Parameters of the conventional cell
Oblique	 Primitive	$a \neq b$ $\gamma \neq 90$
Rectangular	 Rectangular Primitive Rectangular Primitive	$a \neq b$ & $\gamma = 90°$
Square	 Primitive	$a = b$ $\gamma = 90°$
Hexagonal	Primitive 	$a = b$ $\gamma = 120°$

In 3D:

Crystal system	Bravais Lattice	Lattice Symbols	Parameters of Conventional unit all	Examples
1. Cubic	Simple	P	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Cu, Al, CsCl, NaCl.
2. Tetragonal	Simple Body-centered	P I	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	S_nO_2 T_iO_2
3. Orthorhombic	Simple Body centred face centred end centered	P I F C	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	KNO_3, $BoSO_4$, G_a,
4. Trigonal Rhombohedral	Simple	P	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	$CaCO_3, H_\theta S$, Sb, B_i
5. Hexagonal	Simple	P	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\&\gamma = 120^\circ$	$Z_nO, m_g\ Cd$
6. Monoclinic	Simple End Centred	P C	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	$CoSO_4, 24_2O$
7. Triclinic	Simple	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	$K_2Cr_2O_9$, $H_3B\ O_3$

Note: Cubic crystal system is a 1 atom basis system.

For cubic system: Body diagonal distance $= \sqrt{3}a$

& For Face diagonal → $\sqrt{2}a$

Simple Cubic Structure: -

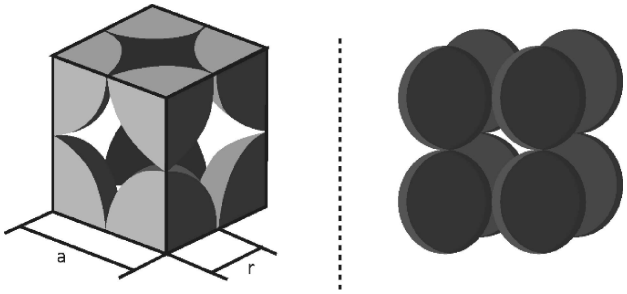
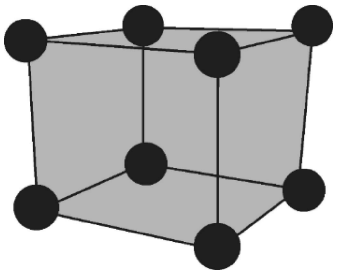


Figure: Cube side length 'a' & atomic radii 'r' of Simple Cubic Structure



1. Effective no. of atoms (Z or n_{eff}) within the unit cell: - $8 \times \frac{1}{8} = 1$
2. No of 1st nearest neighbour (Coordination no.) & it's distance: 6 at 'a'
3. No of 2nd nearest neighbour & it's distance: - 12 at '$\sqrt{2}\ a$'
4. 3rd nearest neighbour & it's distance: - 8 at '$\sqrt{3}\ a$'
5. Relation between 'a' & 'r' (where 'a' is the Edge length of unit cell or lattice parameter or cell constant & 'r' is the radius of the atom) $a = 2r$
6. Volume of unit cell:- a^3

7. Atomic Density:- $\frac{1}{a^3}$
8. Atomic Packing fraction = $\frac{(Volume\ occupied\ by\ the\ atoms\ within\ unit\ cell)}{Volume\ of\ the\ unit\ cell}$

$= \frac{\left(\frac{4}{3}\pi r^3\right) \times n_{eff}}{a^3} = \frac{\frac{4}{3}\pi r^3 \times 1}{8\, r^3}$

$= \frac{\pi}{6} \approx \frac{3.14}{6} \approx 0.523$

$\approx 52\%$

$\Rightarrow 48\%\ empty/void\ space$

Body Centered Cubic Structure (Bcc):-

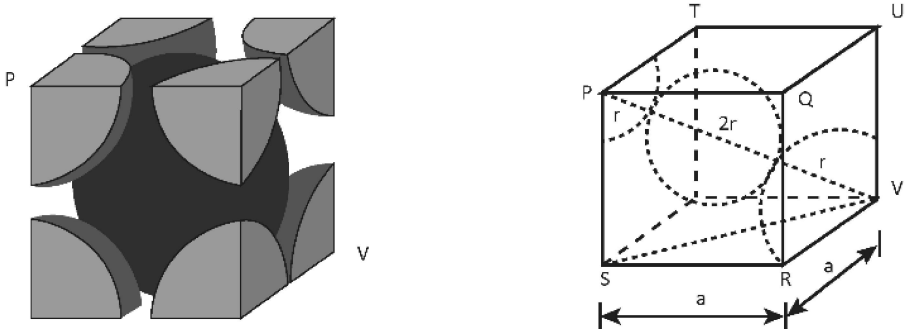


Figure: Body centered structure

Conventional structure of BCC

1. Co-ordination no.:- 8 at $\frac{\sqrt{3}a}{2}$ distance.
2. 2nd $Nearest\ neighbour\ \&\ it's\ distance: -6\ at$ 'a'
3. 3rd Nearest neighbour & it's distance:- 12 at '$\sqrt{2}a$'
4. n_{eff} or $Z = \left(\frac{1}{8} \times 8\right) + (1 \times 1) = 2$
5. Volume of unit cell:- a^3
6. Volume of Primitive unit cell: in BCC $in\ a^3 volume\ \rightarrow 2$ or lattice points.

   $\therefore in\ \left(\frac{a^3}{2}\right) \rightarrow 1$ lattice point or atom (since, Cubic system is 1 atom basis)
7. Atomic density:- $\frac{2}{a^3}$
8. Relation between 'a' & 'r'.

   $\sqrt{3}a = 4r$

   $a = \frac{4}{\sqrt{3}}r$ or $r = \frac{\sqrt{3}}{4}a$
9. Atomic Packing fraction = $\frac{(Volume\ occupied\ by\ the\ atoms\ within\ unit\ cell)}{Volume\ of\ the\ unit\ cell} = \frac{\left(\frac{4}{8}\pi r^3\right)\times 2}{a^3} \approx 0.68$

   $\approx 68\%$

   Ex. $\Rightarrow$ Monovalent metals like:- N_a, K, Li etc.

Face Centered cubic (FCC):-

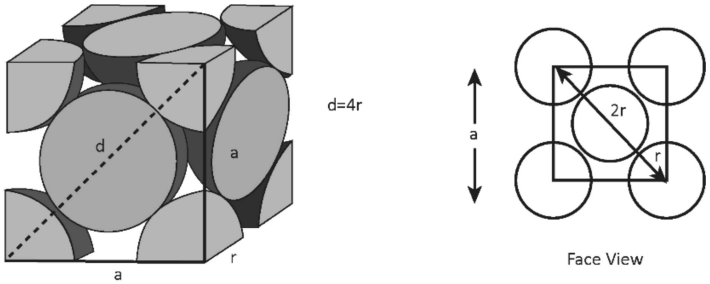


Figure: Face centered cubic structure

1. n_{eff} or $Z = \left(\frac{1}{8} \times 8\right) + \left(6 \times \frac{1}{2}\right) = 1 + 3 = 4$
2. Relation between 'a' & 'r'.
   $\frac{\sqrt{2}a}{2} or \frac{a}{\sqrt{2}} = 2r \quad \Rightarrow r = \frac{1}{2\sqrt{2}}a$ or $a = 2\sqrt{2}r$
3. No of 1st nearest neighbour (Co-ordination no.) & it's distance.- 12 at $\frac{a}{\sqrt{2}}$ distance
4. 2nd Nearest neighbour & it's distance:- 6 at 'a'
5. Atomic Density:- $\frac{4}{a^3}$
6. Atomic Packing fraction = $\frac{(Volume\ occupied\ by\ the\ atoms\ within\ unit\ cell)}{Volume\ of\ the\ unit\ cell}$:- $\frac{\left(\frac{4}{3}\pi r^3\right)\times 4}{a^3} \approx 74\%$

   Ex. ⇒ Conducting metals like:- Cu, Au, Ag. Etc.

   FCC do have the maximum APF in 3D, so is also known as the Closed packed structure
   While Simple Cubic & Body centred Cubic are known as Loosely Packed Structure ($\because$ $their$ A.P.F.< 74%)

Hexagonal Closed Packed Structure:- (HCP)

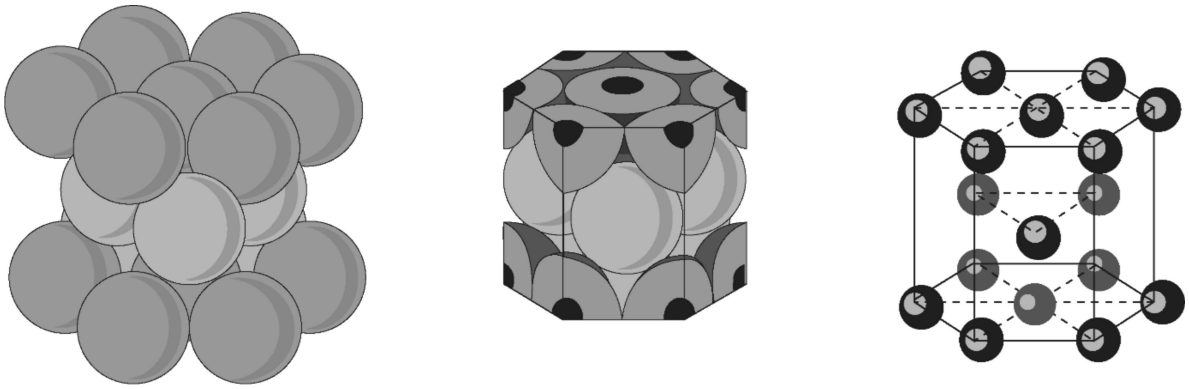
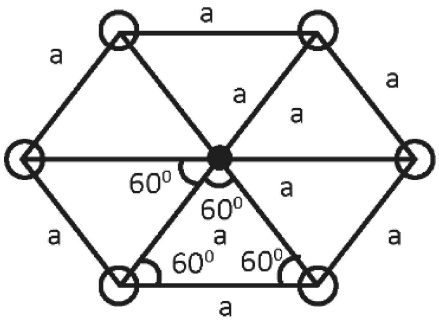


Figure: Conventional Cell of HCP structure.

A plane (Hexagonal)
B Plane (triangular)
A Plane (Hexagonal).



Regular hexagon is made up of 6 equilateral triangles.

Area of this regular hexagon $= 6 \times \left(\frac{\sqrt{3}}{4}a^2\right) = \frac{3\sqrt{3}}{2}a^2$

In this structure: - There is one triangular 2D unit cell in the middle of 2 hexagonal 2D unit cell or vice-versa
In Hexagonal closed packed structure, there are 12 atoms at corners, 2 at face centre & 3 atoms fully inside

No. of effective atoms: -

$n_{eff}\ or\ Z\ = (n_{inside} \times 1) + \left(n_{face} \times \frac{1}{2}\right) + \left(n_{corner} \times \frac{1}{6}\right)$