Materials Physics

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Introduction:

Matter, in general, occurs in three states- solid state, liquid state and gaseous state. As we move from the solid state to gaseous state, the distance between the neighbouring atoms increases and their structures vary too. A fourth case of matter is the state of the plasma, in which the substance is ionized gas, and a fifth case in which the material appears in high-energy atomic particles. From the above, we can come to the conclusion that "the kinetic energy of the molecule or the atom is responsible for determining the state in which the substance appears."

The solids are classified on the basis of their electrical behaviour as conductors, semiconductors and insulators. The conductors are the materials which have a large number of free electrons. These free electrons are responsible for carrying current. On the other hand, the insulators have practically no free electron to conduct electric current. Between the conductors and insulators, we have semiconductors. A semiconductor behaves like an insulator at absolute zero but its conductivity increases as its temperature increases. In this unit, you will study about different states of solids. You will also study about lattice, bases, different types of lattices and crystal structures.

Crystalline and Amorphous:

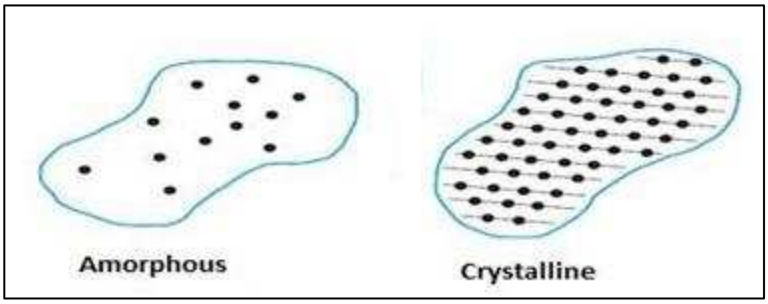
A most remarkable feature of matter in the solid state is the tendency of the constituent atoms of a great many solids to arrange themselves in an ordered periodic pattern. On the basis of the arrangements of its constituents, the solids are broadly classified into two categories- crystalline and amorphous.

A crystalline solid, commonly a crystal, is a solid material with such a regular arrangement. A crystalline solid is formed by regular and periodic repetition of identical building blocks in three dimensions. These building blocks may be a single atom or a group of atoms. These identical building blocks are called motif.

Crystals which have regularity and periodicity in the arrangement of atoms or molecules only in one dimension or two dimensions are known as semi or partially crystalline solids. Metals, in general, are crystalline in nature. On melting, these lose their crystalline structure but their electrical properties remain almost the same. Ina crystal, all the bonds have the same bond strength. The crystalline solids both organic and inorganic, therefore, melt (and solidify) at a given fixed temperature. Diamond, rock salt, sugar etc. are some examples of crystalline solids.

The amorphous solids are those in which there is no regularity and periodicity in the arrangement of atoms. All the bonds in an amorphous solid are not equally strong. When it is heated, the weak bonds are first to be broken. Thus, on heating, an amorphous solid gradually softens into a liquid. They, therefore, have no fixed melting point and freezing point. On cooling, the molten state of the amorphous solid gradually hardens into a solid at varying temperatures on account of its high viscosity or the fast rate of cooling. The disordered form, thus, retained even in the solid state of an amorphous body. Glass is the best example of an amorphous solid.

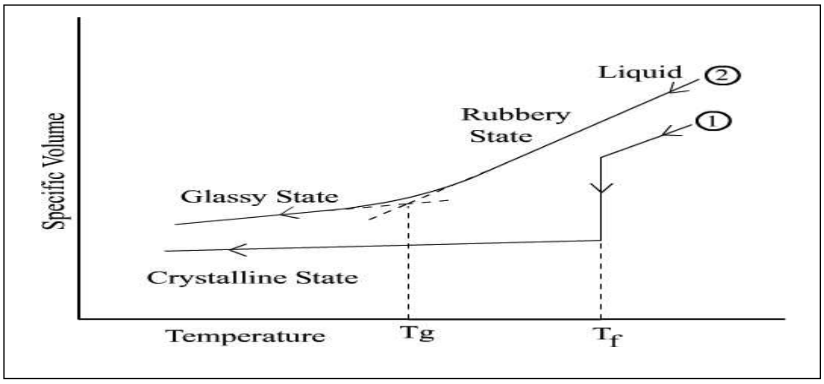
Thus, the presence of long range order is the defining property of a crystal while amorphous solids do exhibit short range order in their structures.



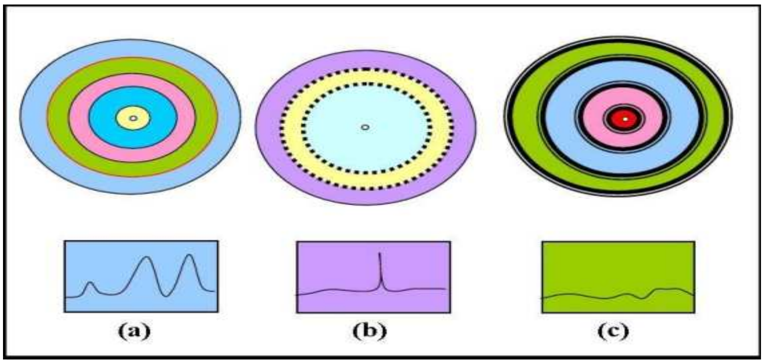
Practical distinction can be made between crystallized and non-crystallizedmaterials by many independent criteria:

1. The atoms or molecules of the crystalline solids are periodic in space, while the atoms or molecules of the amorphous solids are not periodic in space.

2\. Crystallized material crystallized suddenly and at a certain temperature constant always non-crystalline materials fused over a certain temperature range.



2\. Non-crystallized materials will be dispersed at x-ray diffraction in the form of concentric rings, while this formation will be of crystallized materials, distinct and separate spots, with identical symmetry.



(XRD) of (a) Polycrystalline (b) single crystal (c) Amorphous crystal

3. All crystallized materials are differentiated by the **anisotropic** directional properties such as refractive index, electrical and thermal conductivity, etc… of varying degrees. The non-crystallized materials are all the same as the **isotropic** properties, which does not show any effect of the direction on their properties.
4. A crystal break along certain crystallographic planes, while the broken surface is irregular in amorphous solid, because it has no crystal planes.

Crystal: A solid object that contains a number of atoms aligned geometrically and consists of very small units that are regularly repeated in the three dimensions, called **unit cell**.

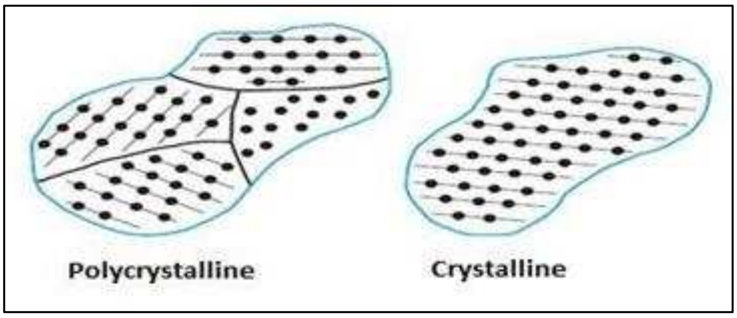
The basis of crystalline construction is repetition and there are crystals on the types:

1. Real crystals represent most of the crystals in nature and contain some defects and distortions.
2. Perfect crystals, which is a supposed crystalline, where we assume the existence of a perfect crystal free of defects and distortions for the study and there is no perfect crystal in nature and is similar to the idea of ideal gas and has the ideal crystal:

Single Crystal and Poly Crystal:

1- A single crystal: has a periodicity of three-dimensional crystal model extends through the entire crystal.

1- Poly crystal or polycrystalline crystals where the periodicity of the model does not extend throughout the crystal but ends at the limits of the crystal called **grain boundaries**.



The grains or crystallites are smaller than the size of the pattern unit which forms the periodicity. The size of the grains in which the structure is periodic may vary from macroscopic dimensions to several angstroms. When the size of the grains or crystallites becomes comparable with the size of the pattern unit, the periodicity of structure is completely disturbed; it is no longer a crystal, single or polycrystalline but becomes an amorphous substance.

Elementary Ideas About Crystal Structure:

Let us discuss some important terms in this section which play very important role in the formation of a crystal.

The Crystal Lattice and Crystal Structure

A crystal is constructed by the infinite repetition in space or identical structural units (atoms, molecules or ions). One can replace each unit by a geometrical point. The result is a patternof points having the same geometrical properties as the crystal. This geometrical pattern is the crystal lattice or simply the lattice. The points are called lattice points. Thus, the regular pattern of points which describes the three-dimensional arrangement of particles (atoms, molecules or ions) in a crystal structure is called the crystal lattice or space lattice.

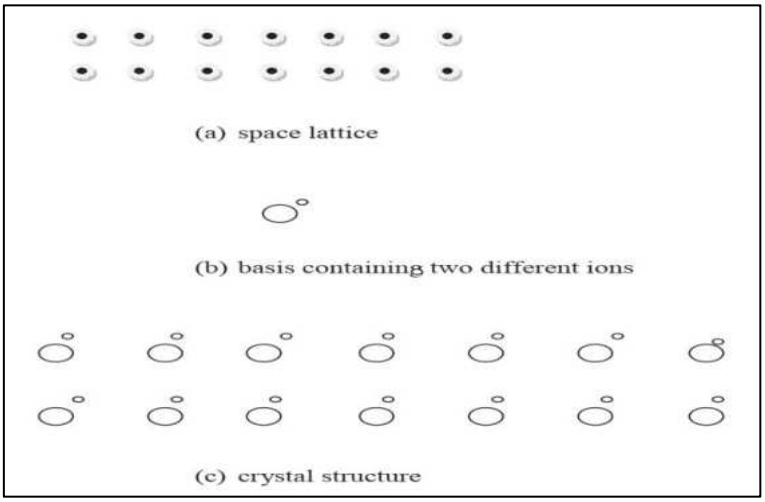
A crystal structure is formed by the addition of a basis to every lattice point

Lattice + Basis = Crystal Structure.

Basis: An atom, ion, molecule or group of atoms is called a point and each point is connected with the other points to form a specific body. The basis for each point should be:
1 - Symmetrical parts in terms of structure, arrangement and direction.
2. The number of atoms in the primary unit cell is equal to the number of base atoms.

Lattice: A group of points arranged by a specific system, not a group of atoms. for the crystalline structure, an atom or group of atoms must be attached to each of the splicing points, which is called the base.

The crystal structure is real whereas the lattice is imaginary. The simple logical relation between lattice, basis and crystal structure can be expressed as in figure below. The crystal structure is formed by the addition of the basis (b) to every lattice point of the lattice (a). By looking at (c), you can recognize the basis and then you can abstract the space lattice.



Q : What is the difference between the atomic structure and the crystal structure?

Atomic structure is the number of neutrons and protons in the nucleus of the atom and the number of electrons in electronic orbits. Crystalline structure means the formation of atoms within crystalline solids in certain formations.

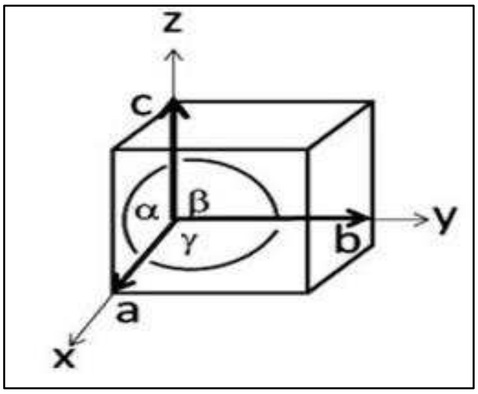
Unit Cell

The smallest portion of a space lattice which can generate the complete crystal by repeating its own dimensions in various directions is called unit cell.

A unit cell is defined by:

1. The length of its edges, these edges may or may not be mutually perpendicular. In the figure below, OA = a, OB = b and OC = c are the dimensions of the unit cell. The vectors ($\vec{a}, \overrightarrow{b}, \vec{c}$) define the axes of the crystal.

2. The angles between them. The angle between (a and b) is (γ), while the angles between (c and a) (c and b) are represented by (α) and (β) respectively. They are called interfacial angles.

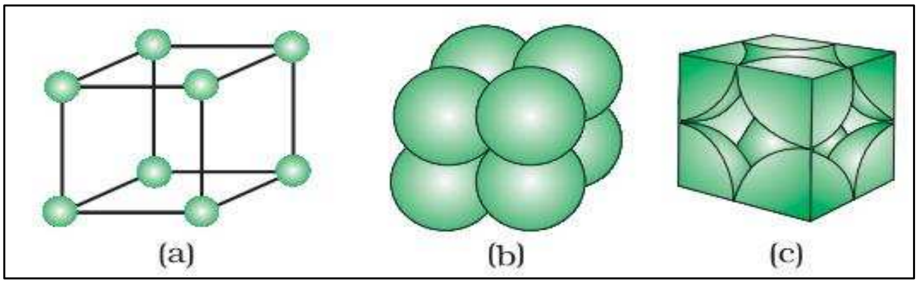


It is, however, traditional to choose a unit cell with minimum volume. A unit cell is thus a minimum volume cell which when repeated systematically in all the three directions gives the whole arrangement of atoms in the crystal.

Type of Unit Cell:

1. Primitive or Simple Cubic (SC) Unit Cell (P):

There is one lattice point at each of the eight corners of the unit cell. This type of cell is called primitive or simple cubic cell (P) of the system. Each atom at a corner is shared between eight adjacent unit cells, four unit cells in the same layer and four unit cells of the upper (or lower) layer. Therefore, only ($1/8^{th}$) of an atom (or molecule or ion) actually belongs to a particular unit cell. The arrangement of particles is easier to follow in open structures. The total number of atoms in one unit cell is: **1/8 * 8 = 1 atom.**



2. Non Primitive Unit Cell:

A unit cell that contains additional lattice points, either on a face of the unit cell or within the unit cell.

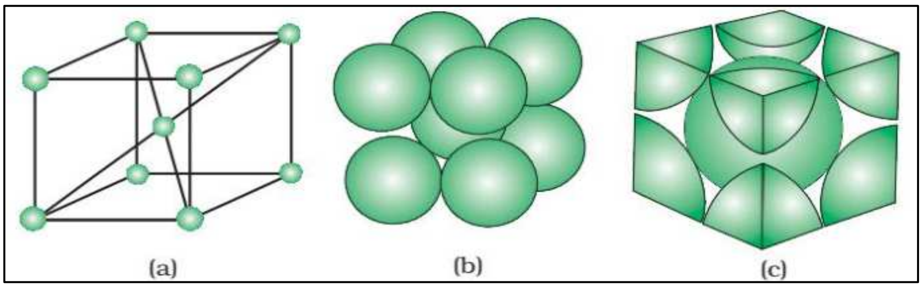
1. Body-Centred Cubic Unit Cell (BCC) (I):

A body-centred cubic (bcc) unit cell has an atom at each of its corners and also one atom at its body center. It can be seen that the atom at the body center wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:

(i) 8 corners × 1/8 per corner atom = 8 * 1/8 = 1 atom

(ii) 1 body centre atom = 1 × 1 = 1 atom

∴ Total number of atoms per unit cell = 2 atoms.

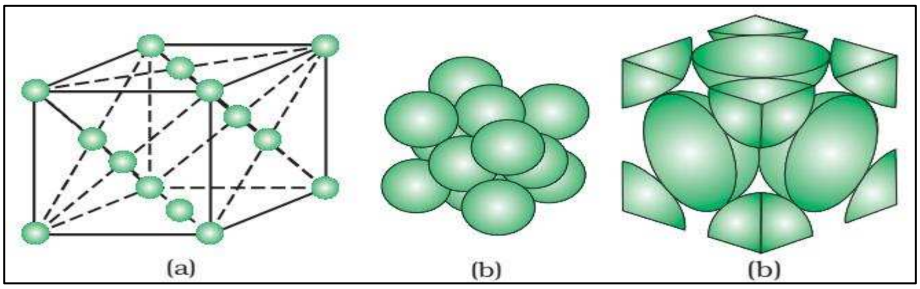


The BCC structure is commonly found for the elements at the lighter end of all the rows of the periodic table, from the alkali metals (Li, Na, K, Rb, Cs) through to the start of the transition metals (V, Cr, Fe, Nb, Mo, Ba, Ta, W).

2. Face-Centred Cubic Unit Cell (FCC) (F):

A face-centred cubic (fcc) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. It can be seen in figure below that each atom located at the face-centre is shared between two adjacent unit cells and only (1/2) of each atom belongs to a unit cell. Thus, in a face-centred cubic (fcc) unit cell:

(i) 8 corners atoms × 1/8 atom per unit cell = 8 * 1/8 = 1 atom
(ii) 6 face-centred atoms × 1/2 atom per unit cell = 6 × 1/2 = 3 atoms
∴ Total number of atoms per unit cell = 4 atoms.



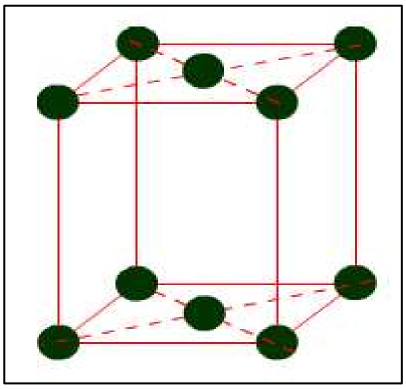
The FCC structure is adopted by a large number (~20) of metals, including the heavier end of the transition metals (Ni, Rh, Pd, Ir, Pt), the noble metals (Cu, Ag, Au), and some of the rare gases (Ne, Ar, Kr, Xe).

In addition, many compounds and alloys are based on the cubic structure. two examples of general interest are NaCl and CsCl, and these compounds have given their names to these generic types of structure.

3. **Base or End-Centred Cubic Unit Cell (C):**

Which denoted by (C). The unit cell in this type contains two atom, from the eight corner atoms which it shares with the other cells, and one from the two surface atoms it shares with other cell.

(i) 8 corners atoms × 1/8 atom per unit cell = 8 * 1/8 = 1 atom
(ii) 2 base or end-centred atoms × 1/2 atom per unit cell = 2 × 1/2 = 1 atoms
∴ Total number of atoms per unit cell = 2 atoms.

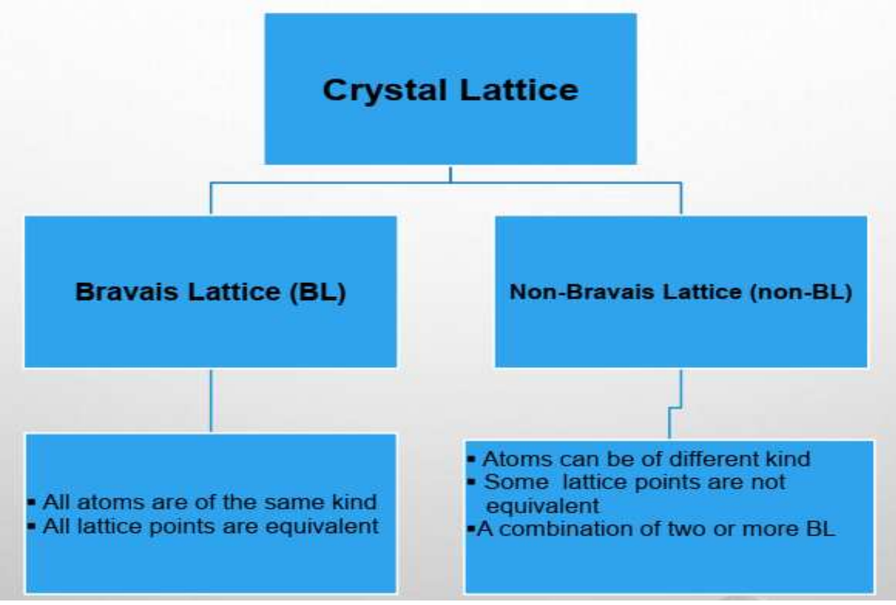


Bravais Lattice and Non Bravais Lattice:

In a solid crystalline material, the atoms or molecules are arranged regularly and periodically in all three dimensions.

The atomic arrangement in a crystal is called crystal structure. If each such atom or unit of atoms in a crystal is replaced by a point in space, then the resultant points in space are called space lattice. Each point in a space lattice is called a lattice point and each atom or unit of atoms is called basis or pattern.

If the surroundings of each lattice point is same or if the atom or all the atoms at lattice points are identical or equivalent; (every atoms in crystal have the same type), then such a lattice is called Bravais lattice. On the other hand, if the atom or a lattice points are not same or not equivalent; which a mixture of two lattice or more of bravais lattice add to each other at constant position with each other, then it is said to be a non-Bravais lattice.



Crystal Lattice

Bravais Lattice (BL)

- All atoms are of the same kind
- All lattice points are equivalent

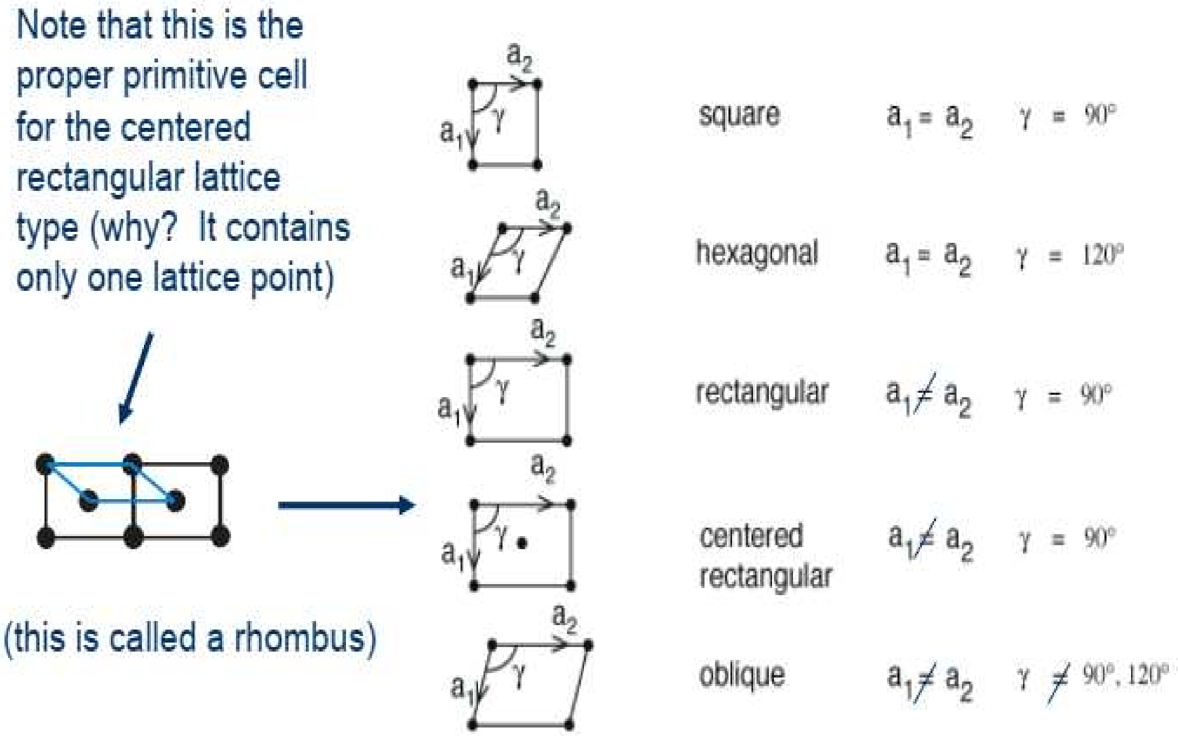
Non-Bravais Lattice (non-BL)

- Atoms can be of different kind
- Some lattice points are not equivalent
- A combination of two or more BL

In 1948, Bravais showed that there are one bravais lattice in one dimension, five Bravais lattices in two dimensions and fourteen in three dimensions.

a. One Dimensional bravais lattice.

b. Two Dimensional bravais lattice.



Note that this is the proper primitive cell for the centered rectangular lattice type (why? It contains only one lattice point)

(this is called a rhombus)

c. Three Dimensional bravais

Lattice	Number and types of bravais lattice	Edge Length	Angles between faces	Examples
Cubic	3 (P, I, F)	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Au, Cu, Ag, NaCl, KCl, Zinc blende, diamond andZnS
Tetragonal	2(P, I)	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2, TiO_2 and $CaSO_4$.
Orthorhombic	4 (P, C, I, F)	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic Sulphur, $BaSO_4$, KNO_3, K_2SO_4 ,$CaCo_3$ and $SnSO_4$
Monoclinic	2 (P,C)	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	monoclinic Sulphur, $Na_2SO_4.10H_2O$, $CaSO_4 .2H_2O$ (gypsum) and Na_3AlF_6 (cryolite)
Hexagonal	1 (P)	$a = b \neq c$	$\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$	Graphite,Mg, ZnO and CdS
Rhombohedral or Trigonal	1 (P)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$, $< 120^\circ$	As, Bi, Sb, $CaCO_3$(Calcite) and HgS (cinnabar),
Triclinic	1(P)	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$	H_3PO_3 , $CuSO_4.5\ H_2O$, $K_2Cr_2O_7$ and $CuSO_4.5H_2O$

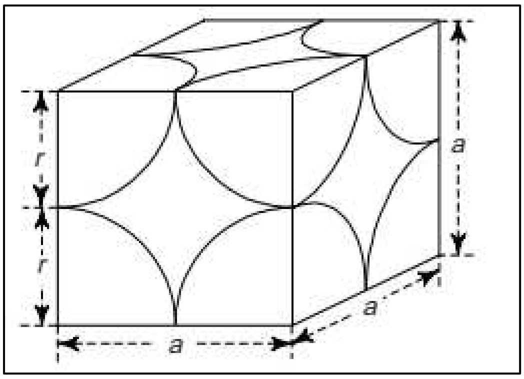
Here (P) means Primitive (simple), (C) means Base Centred, (I) means Body Centred, (F) means Face Centred.

Relation Between atomic radius and lattice constant:

Atomic radius is defined as half the distance between the nearest neighbours in the crystal structure of a pure element. This is denoted by (r) and expressed in terms of the cube edge element (a). One can calculate the atomic radius by assuming that atoms are spheres in contact in a crystal. The relation between atomic radius and the lattice constant is obtained by considering the shape of atoms to be spherical which is Calculated in various crystal structures as illustrated below:

1. Primitive or Simple Cubic (SC) Unit Cell:

In a simple cubic lattice the atoms are located only on the corners of the cube. The particles touch each other along the edge.



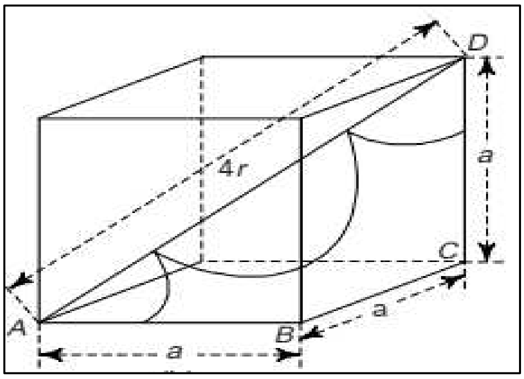
Thus, the edge length or side of the cube ‘a’, and the radius of each particle, (r) are related as

$a = 2r \qquad r = a / 2$

Area $a^2 = 4r^2$

2. Body-Centred Cubic Unit Cell (BCC):

From figure below, it is clear that the atom at the center will be in touch with the other two atoms diagonally arranged. The diagonal in this case is (4r). Also:



$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$
$$AD^2 = AC^2 + CD^2 = 2a^2 + a^2 = 3a^2$$
$$(4r)^2 = 3a^2$$

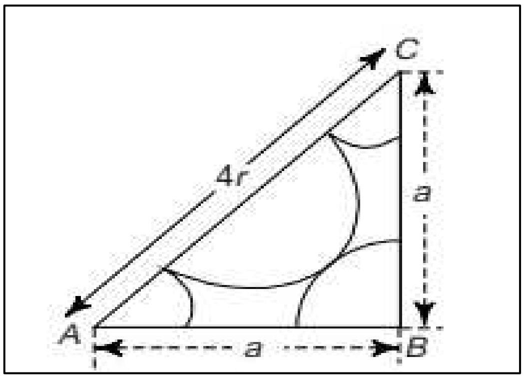
$$a = \frac{4r}{\sqrt{3}} \text{ and } 2r = \frac{a\sqrt{3}}{2}$$

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

$$a^2 = \frac{16r^2}{3}$$

3. Face-Centred Cubic Unit Cell (FCC):

Atoms within this structure touch along the diagonal of any face of the cube, as in figure below. The diagonal has a length of (4r).



$$AC^2 = AB^2 + BC^2$$
$$(4r)^2 = a^2 + a^2$$

$$r^2 = \frac{2a^2}{16}$$

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

$$= a^2 = 8r^2$$

Example: Iron at (200 ºC) is (BCC) with atoms of atomic radius (0.124 nm). Calculate the lattice constant (a) for the cube edge of the iron unit cell.

$\sqrt{3}a = 4R$ Where R is the radius of the iron atom.

Therefore $a = \frac{4R}{\sqrt{3}} = \frac{4(0.124\ nm)}{\sqrt{3}} = 0.2864$ nm

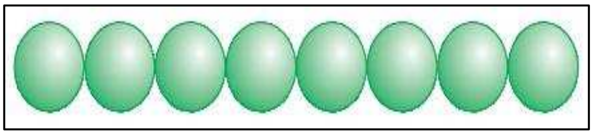
Coordination Number:

The coordination number is the number of atoms touching a particular atom, or the number of nearest neighbors for that particular atom.

Because the Bravais lattice is periodic, all points have the same number of nearest neighbours or coordination number. It is a property of the lattice.

1. **In One Dimension:**

There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row and touching each other.



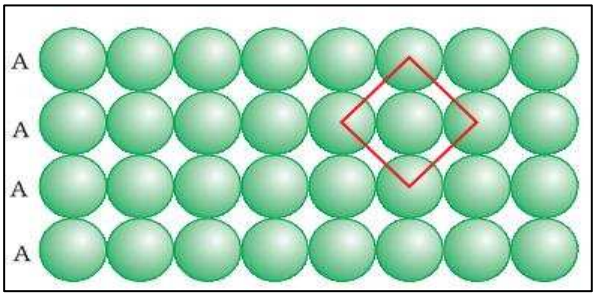
In this arrangement, each sphere is in contact with two of its neighbours. The number of nearest neighbours of a particle is called its coordination number. Thus, in one dimensional close packed arrangement, the coordination number is (2).

2. **In Two Dimensions:**

Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways.

a. **Square close-packed:**

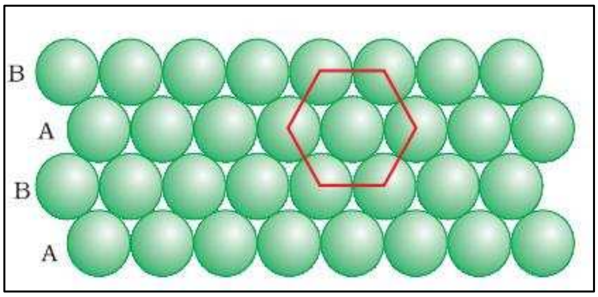
The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as ‘A’ type row, the second row being exactly the same as the first one, is also of ‘A’ type.



In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two dimensional coordination number is (4). Also, if the centres of these (4) immediate neighbouring spheres are joined, a square is formed. Hence this packing is called square close packing in two dimensions.

b. Hexagonal close-packed:

The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type.

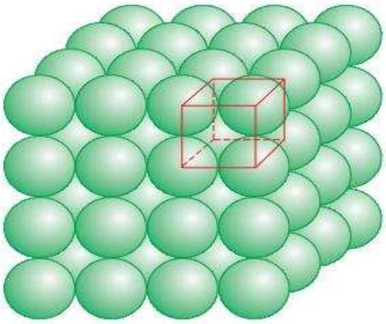


When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of (ABAB) type. In this arrangement there is less free space and this packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two dimensional coordination number is 6. The centres of these six spheres are at the corners of a regular hexagon, hence this packing is called two dimensional hexagonal closepacking. It can be seen in Figure that in this layer there are some voids (empty spaces). These are triangular in shape. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards.

3. In Three Dimensions:

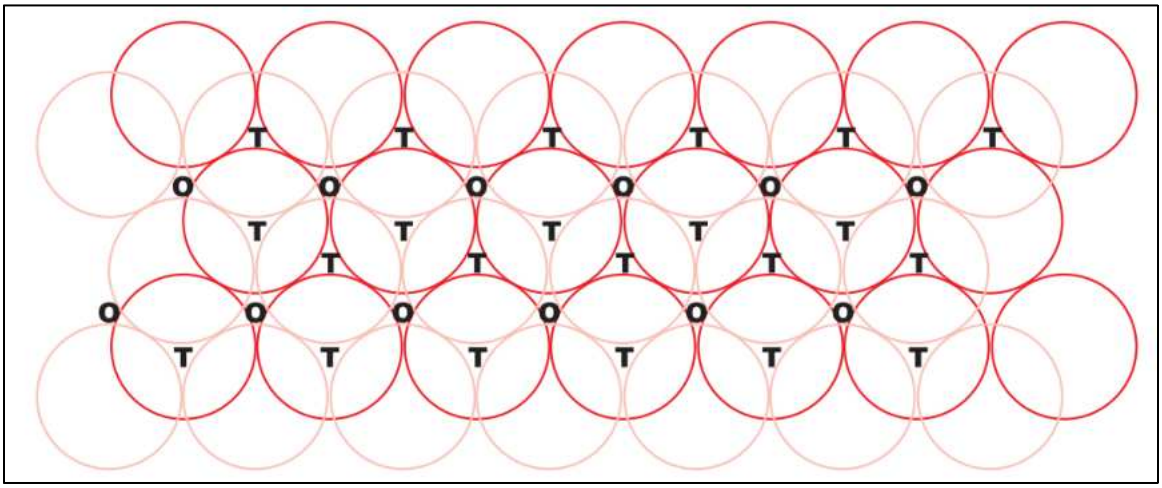
All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other. Three-dimensional packing can be obtained by square close packing and hexagonal close packing

a. Three-dimensional close packing from two-dimensional square close packing: The second layer and all further layers are arranged in such a way that they are horizontal and vertically aligned with each other. Hence, if we call the first layer as the 'A' type, then the lattice will be the (AAA) type. This will give simple cubic lattice, and its unit cell will be a primitive cubic unit cell.

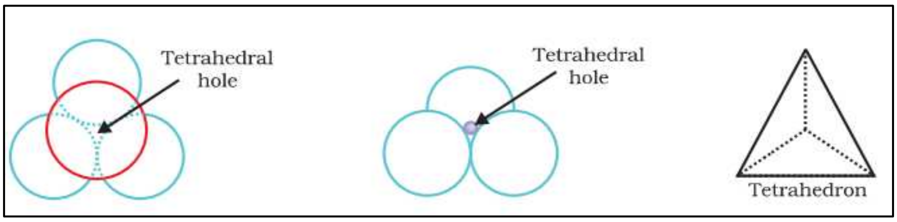


b. Three dimensional close packing from two dimensional hexagonal close packed layers: Three dimensional close packed structure can be generated by placing layers one over the other.

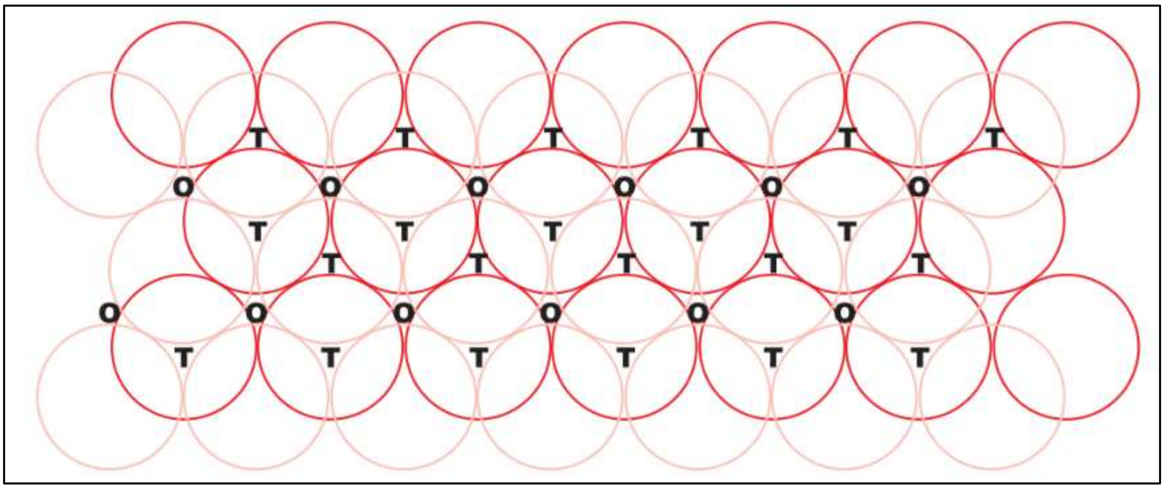
1. Placing second layer over the first layer; Let us take a two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are aligned differently, let us call the second layer as (B).



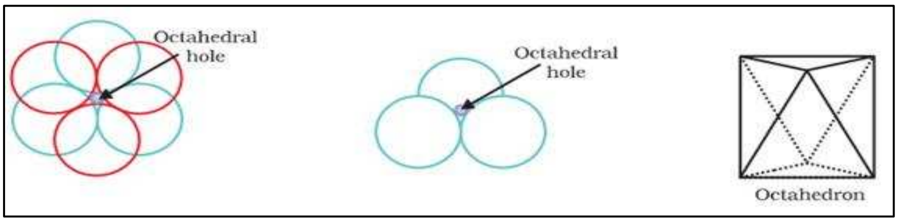
It can be observed from figure that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called tetrahedral voids because a tetrahedron is formed when the centres of these four spheres are joined. They have been marked as ‘T’ in above figure. One such void has been shown separately in figure below.



At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as ‘O’ in figure below.

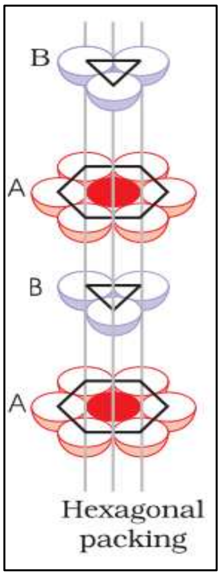


Such voids are surrounded by six spheres and are called octahedral voids. One such void has been shown separately in figure below.

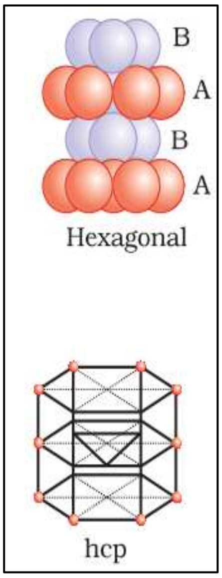


The number of these two types of voids depend upon the number of close packed spheres.

2. Placing third layer over the second layer; When third layer is placed over the second, there are two possibilities.
   a. Covering Tetrahedral Voids: Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as (ABAB ....) pattern. This structure is called hexagonal close packed (hcp) structure. This sort of arrangement of atoms is found in many metals like magnesium and zinc.



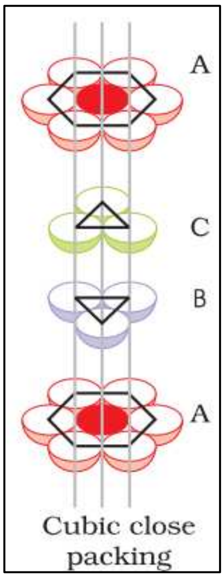
Hexagonal packing



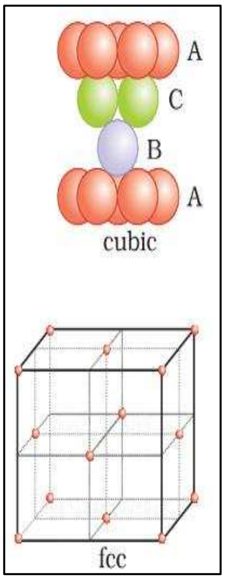
Hexagonal

hcp

   b. Covering Octahedral Voids: The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called 'C' type. Only when fourth layer is placed, its spheres are aligned with those of the first layer. This pattern of layers is often written as (ABCABC). This structure is called cubic close packed (ccp) or face-centred cubic (fcc) structure. Metals such as copper and silver crystallise in this structure.



Cubic close packing



fcc

Thus, the coordination number is 12 in either of these two structures.

Note:

- **A simple cubic has coordination number 6; a bodycentered cubic lattice, 8; and a face-centered cubic lattice,12.**
- **In crystals with directional bonds, the coordination number is lower than that of crystals with a nondirectional bond.**

Packing Fraction, Atomic Packing Factor, Filling Factor, Packing Efficiency or relative density of packing (RDP):

This is defined as the ratio of total volume of atoms in a unit cell to the total volume of the unit cell.

$$\text{Packing Fraction (P.F.)} = \frac{\text{Ratio of the volume of the atoms per unit cell}}{\text{Total volume occupied by the unit cell}}$$

Volume of the atom is the ratio of the volume per unit cell to the volume of the unit cell. Now let us calculate the packing fraction for all the structures.

(a) Simple Cubic (SC)

You know, for SC atoms per unit cell = 1

Volume of one atom = $4/3\ \pi\ r^3$

Atomic radius $r = a/2$, where a is the edge of the cube.

Therefore, packing fraction (P.F.) = $\frac{1\times\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \pi/6 = 0.52 = 52\%$

(b) Hexagonal Close Packed (HCP)

Atoms per unit cell = 2

Volume of one atom = $4/3\ \pi\ r^3$

Atomic radius $r = a/2$

Therefore, packing fraction (P.F.) = $\frac{2\times\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{\frac{1}{2}\sqrt{3}a^2c} = 0.74 = 74\%$ (with $c/a = \sqrt{8/3}$)

H.W: How you can get it the above value ----- (0.74)

(c) Face Centred Cubic (FCC)

Atoms per unit cell = 4

Volume of 4 atoms = $4 \times (4/3\ \pi\ r^3)$

Radius of atoms $r = \frac{\sqrt{2}}{4}a$

Therefore, packing fraction (P.F.) = $\frac{4\times\frac{4}{3}\pi\left(\sqrt{2}\frac{a}{4}\right)^3}{a^3} = \pi\sqrt{2}\ /6 = 0.74 = 74\%$

(d) Body Centred Cubic

In this structure, atoms per unit cell = 2

Volume of 2 atoms = $2 \times (4/3\ \pi\ r^3)$

Radius of atom $r = \frac{\sqrt{3}}{4}a$

Therefore, packing fraction (P.F.) = $\frac{2\times\frac{4}{3}\pi\left(\sqrt{3}\frac{a}{4}\right)^3}{a^3} = \pi\sqrt{3}\ /8 = 0.68 = 68\%$

Miller Indices:

The crystal lattice may be regarded as made up of an infinite set of parallel equidistant planes passing through the lattice points which are known as lattice planes.

Every plane have direction and location inside crystal, and many of physical properties depend on lattice planes and it's direction inside crystal structure. The orientation of a plane in a lattice is specified by Miller indices.

There are several methods to represent the crystalline planes:

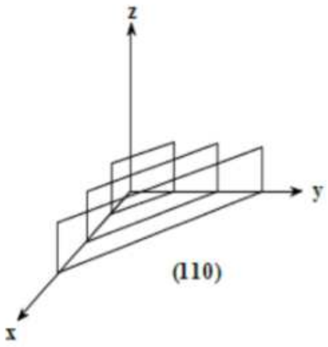
1. Intercepts method.
2. Miller method (Miller indices are used to specify directions and planes in lattices or in crystals).

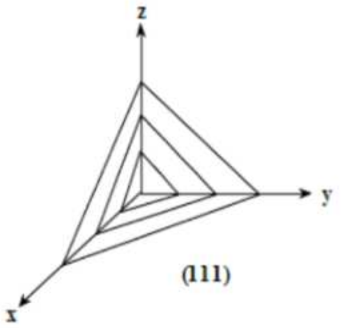
Procedure for finding Miller indices:

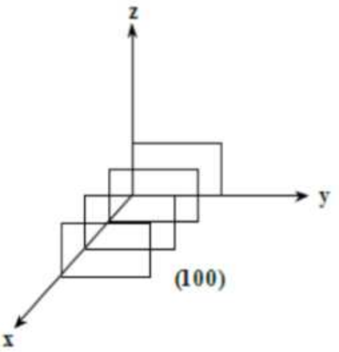
1. Choose the plane which is not pass through origin point (0,0,0).
2. Find the intercepts of the plane along the co-ordinate axes X, Y and Z.
3. Take reciprocal of these intercepts.
4. Reduce the reciprocals into whole numbers using least common multipliers (LCM).
5. Write these integers within Crescent parentheses (hkl), to get index of the plane or Miller indices of the plane.
6. The directions of miller indices can be express as square brackets [hkl].
7. Family and direction of crystallographic planes can be express as curly brackets {hkl} and triangular brackets <hkl>, respectively.
8. Negative values are expressed with a bar over the number ($\bar{h}\bar{k}\bar{l}$).
9. For example, if the plane intercepts x, y and z in points 1, 3, and 1, the index of this plane will be (313).

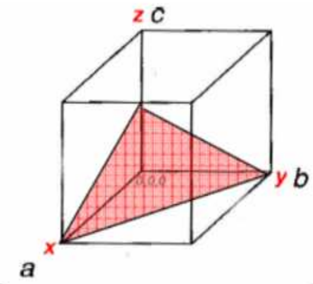
- **Notes:**
  1. The Miller indices denote a single plane or a set of parallel planes.
  2. Miller indices may all be positive or negative or mixed numbers, but they are always integers.
  3. If a Miller index is zero, the plane is parallel to that axis.
  4. The smaller a Miller index, the more nearly parallel the plane is to the axis.
  5. The larger a Miller index, the more nearly perpendicular a plane is to that axis.
  6. Multiplying or dividing a Miller index by a constant has no effect on the orientation of the plane.
  7. Miller indices are almost always small.
  8. Plane passing through the origin has non zero intercepts.
  9. The Miller indices not only describe a particular level but also the set of levels corresponding to it. For example, level (622) is the same as level (311) and level (442) is the same level (221), level (246), is the same as the plane (123).
  10. A direction and its multiple are identical; [100] is the same direction as [200].

11. If the plane cuts a coordinate in the negative direction of the axis, then it is written to the Miller parameter corresponding to the signal negative $\bar{h}$, $\bar{k}$ or l.

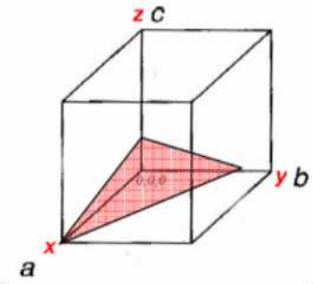




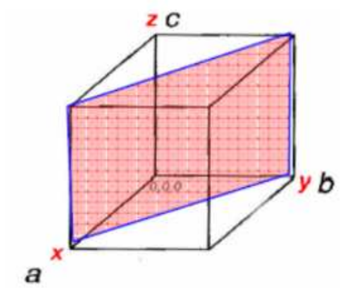




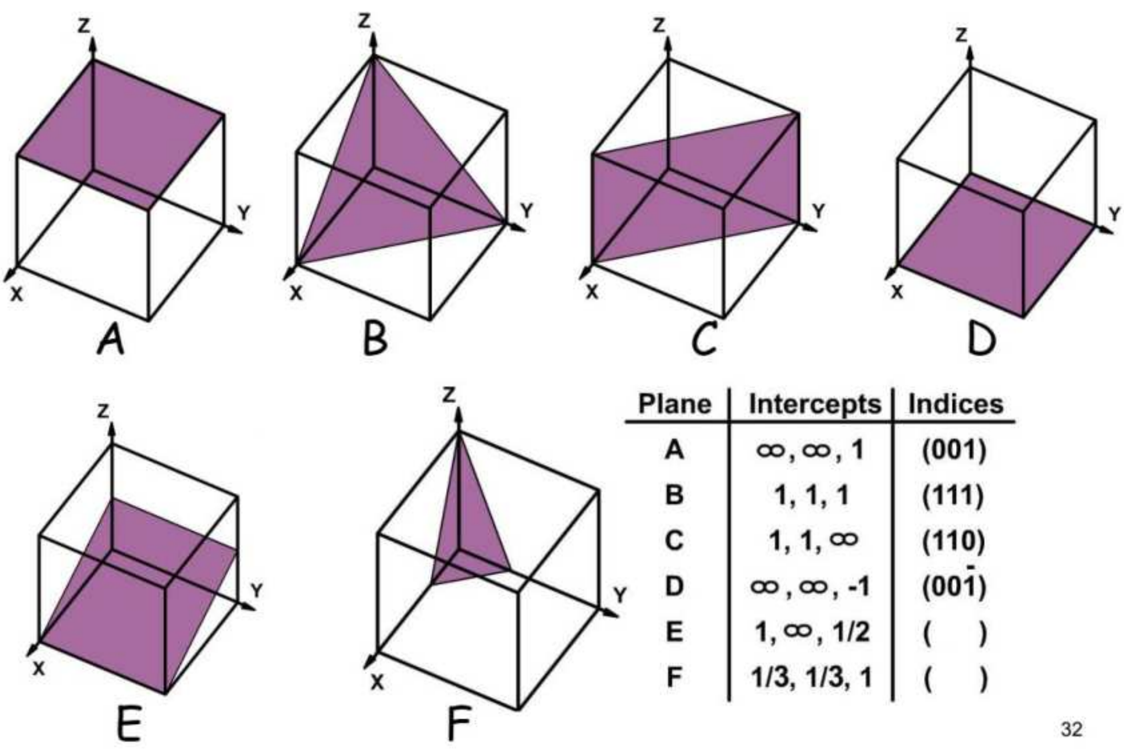
	x (a)	y (b)	z (c)
Intercept on axes	1	1	½
Reciprocal	1	1	2
Integer Clear	1	1	2
Miller Indices	(112)		



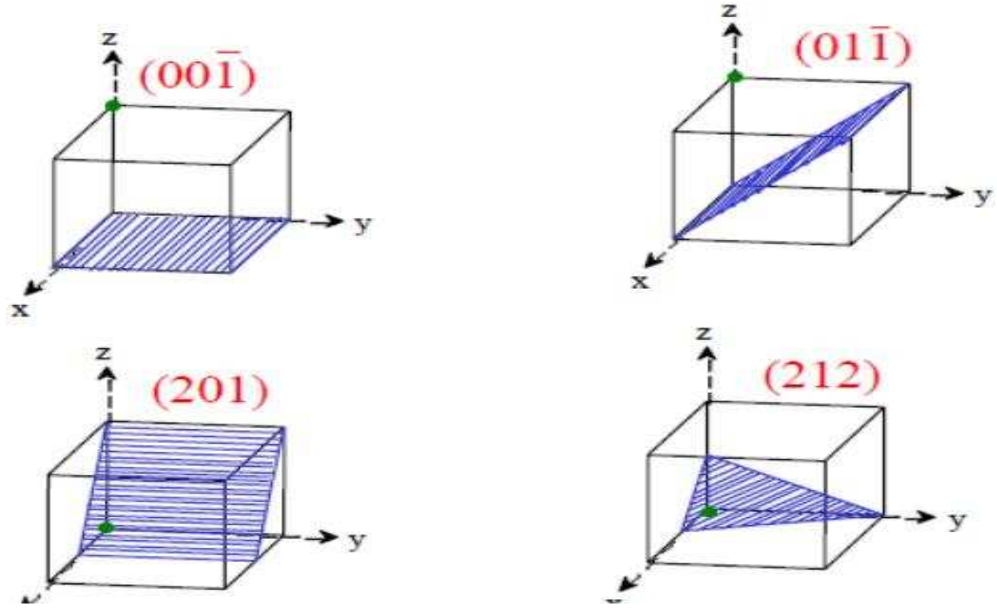
	x (a)	y (b)	z (c)
Intercept on axes	1	¾	¼
Reciprocal	1	4/3	4
Integer Clear	3	4	12
Miller Indices	(3 4 12)		

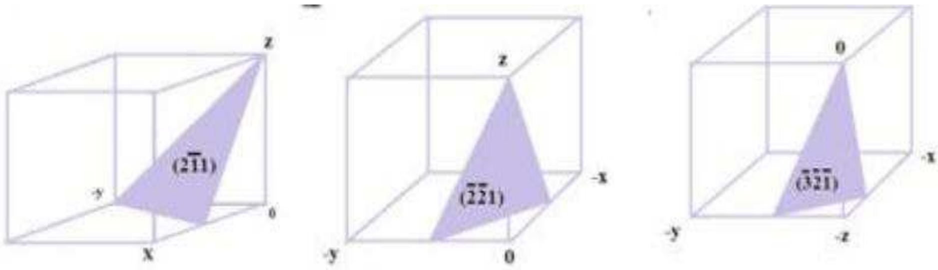


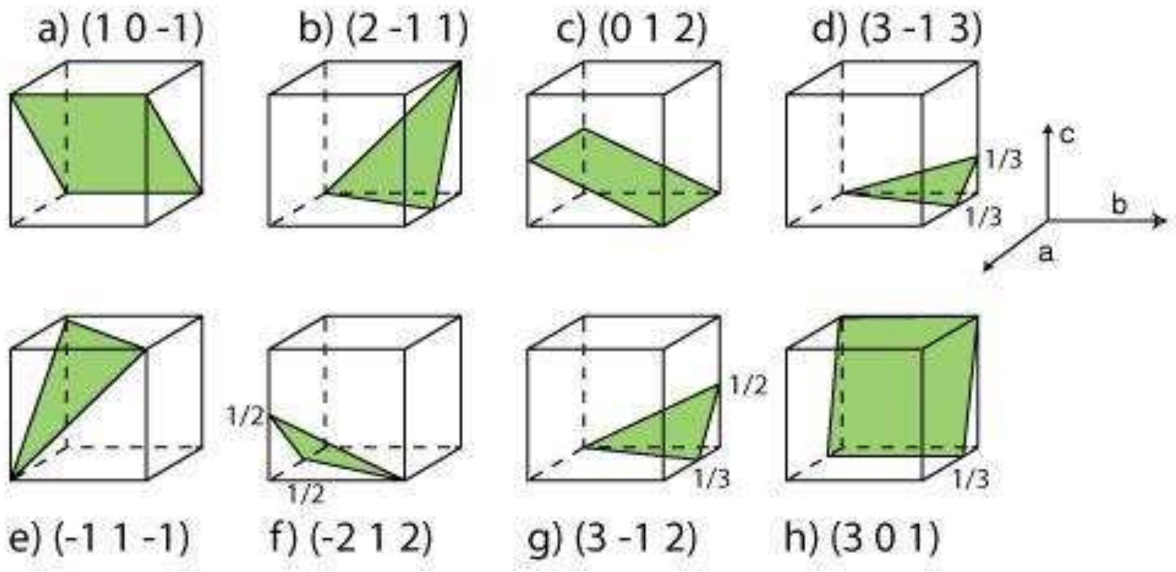
	x (a)	y (b)	z (c)
Intercept on axes	1	1	∞
Reciprocal	1/1	1/1	1/∞ = 0
Integer Clear	1	1	0
Miller Indices	(110)		



Plane	Intercepts	Indices
A	∞, ∞, 1	(001)
B	1, 1, 1	(111)
C	1, 1, ∞	(110)
D	∞, ∞, -1	$(00\bar{1})$
E	1, ∞, 1/2	( )
F	1/3, 1/3, 1	( )



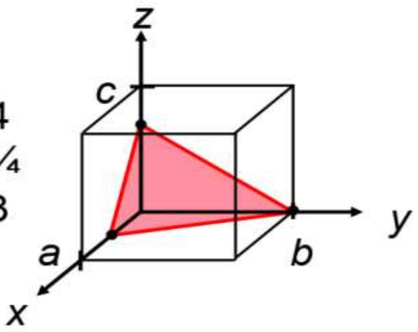


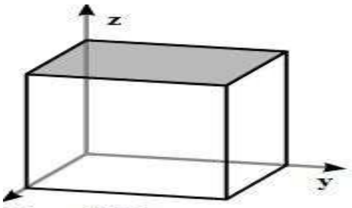


<u>example</u>

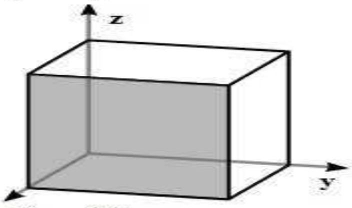
	a	b	c
Intercepts	1/2	1	3/4
Reciprocals	1/½	1/1	1/¾
	2	1	4/3
Reduction	6	3	4

Miller Indices (634)

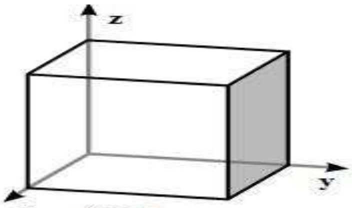




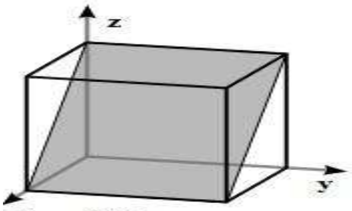
(001)



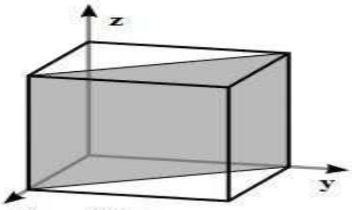
(100)



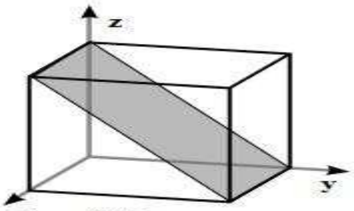
(010)



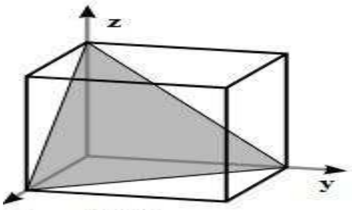
(101)



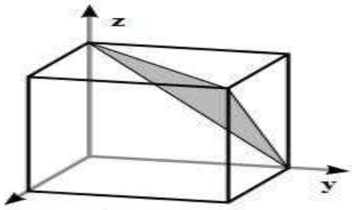
(110)



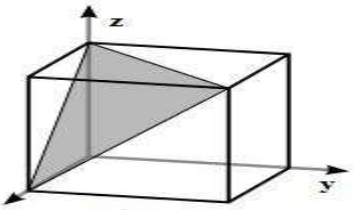
(011)



(111)



$(\bar{1}11)$



$(1\bar{1}\bar{1})$

Ex: Determine the Miller Indices of a plane which is parallel to x-axis and cuts intercepts of 2 and $\frac{1}{2}$, respectively along y and z axes.

Solution:

i) Intercepts	∞	2b	$\frac{1}{2}c$
ii) Division by unit translation	$\frac{\infty}{a}=\infty$	$\frac{2b}{b}=2$	$\frac{3c}{2c}=\frac{1}{2}$
iii) Reciprocals	$\frac{1}{\alpha}$	$\frac{1}{2}$	2
iv) After clearing fraction	0	1	4

Therefore the required Miller indices of the plane (014)

Ex: Determine the M. I. of a plane theat makes intercepts of 2Å, 3 Å, 4 Å on the co-ordinate axes of an orthorhombic crystal with a:b:c = 4:3:2

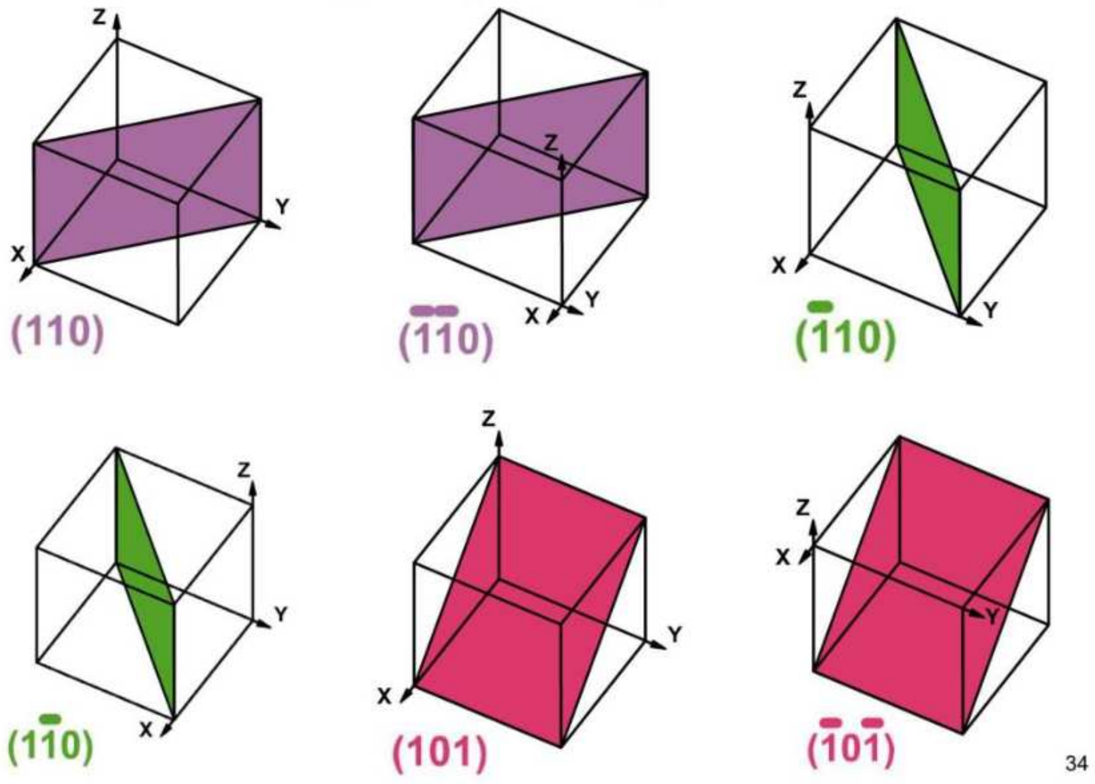
Solution:

Here the unit translations are a = 4, b = 3 and c = 2 following the same procedure

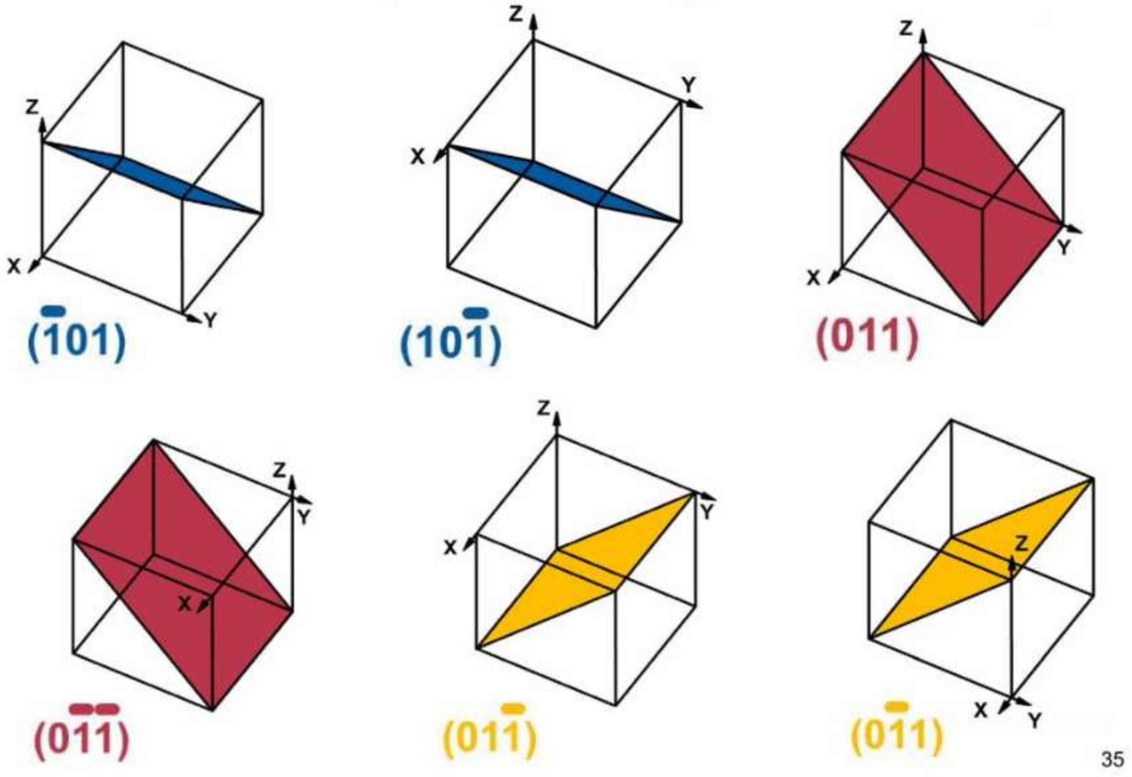
i) Intercepts	2	3	4
ii) Division by unit translation	$\frac{2}{4}=\frac{1}{2}$	$\frac{3}{3}=1$	$\frac{4}{2}=2$
iii) Reciprocals	2	1	$\frac{1}{2}$
iv) After clearing fraction	4	2	1

Therefore the Miller indices of the plan is (421)

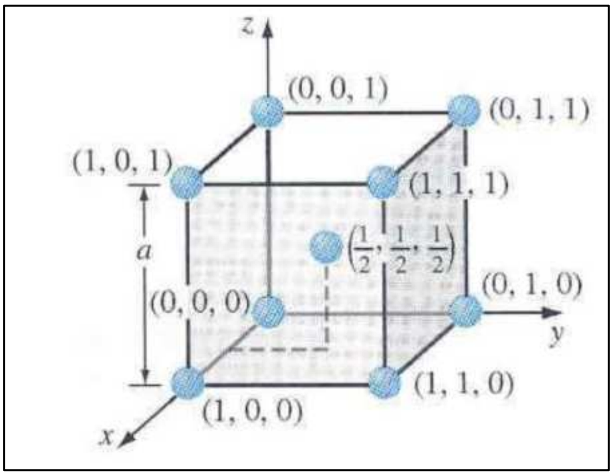
{110} Family

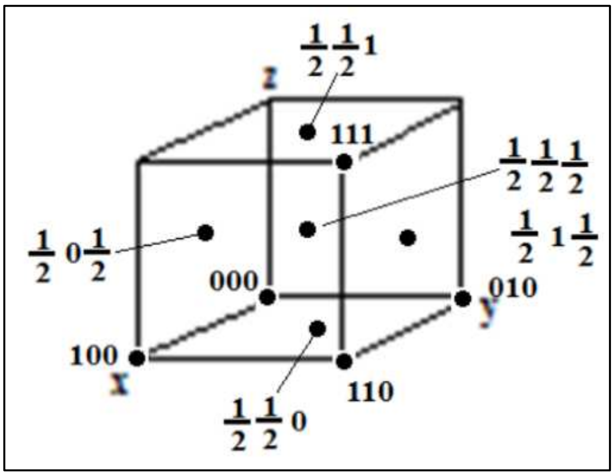


{110} Family



Atoms positions:



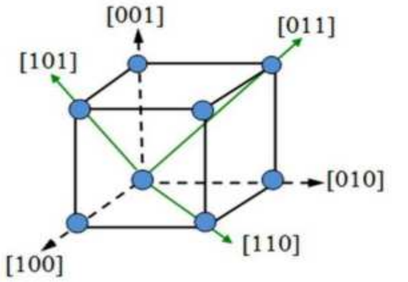


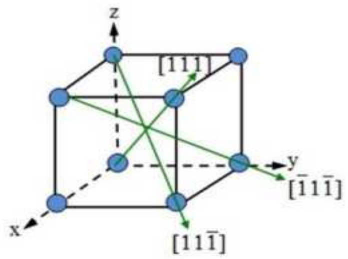
Crystal Directions and Planes:

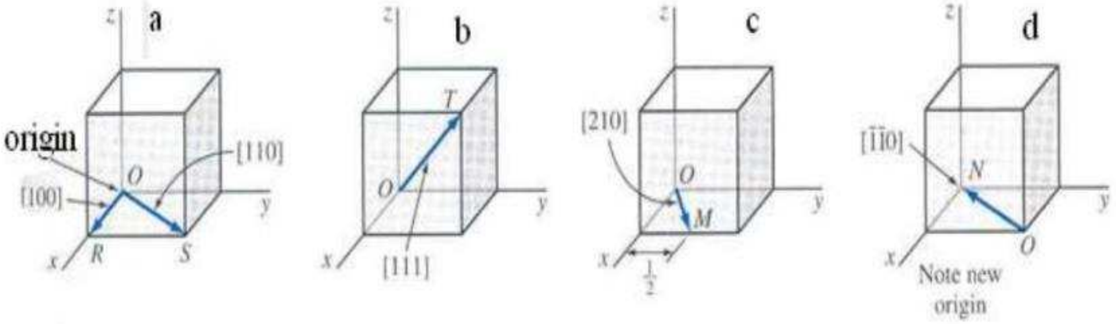
The crystalline solids display anisotropic properties, i.e. properties like refractive index, conductivity, mechanical properties depend upon the direction of studies because of presence of different concentration of atoms along the different directions. A complete description of the crystal structure can be obtained from the study of atomic positions in a unit cell. The directions and planes in the crystalline solids are specified by Miller indices.

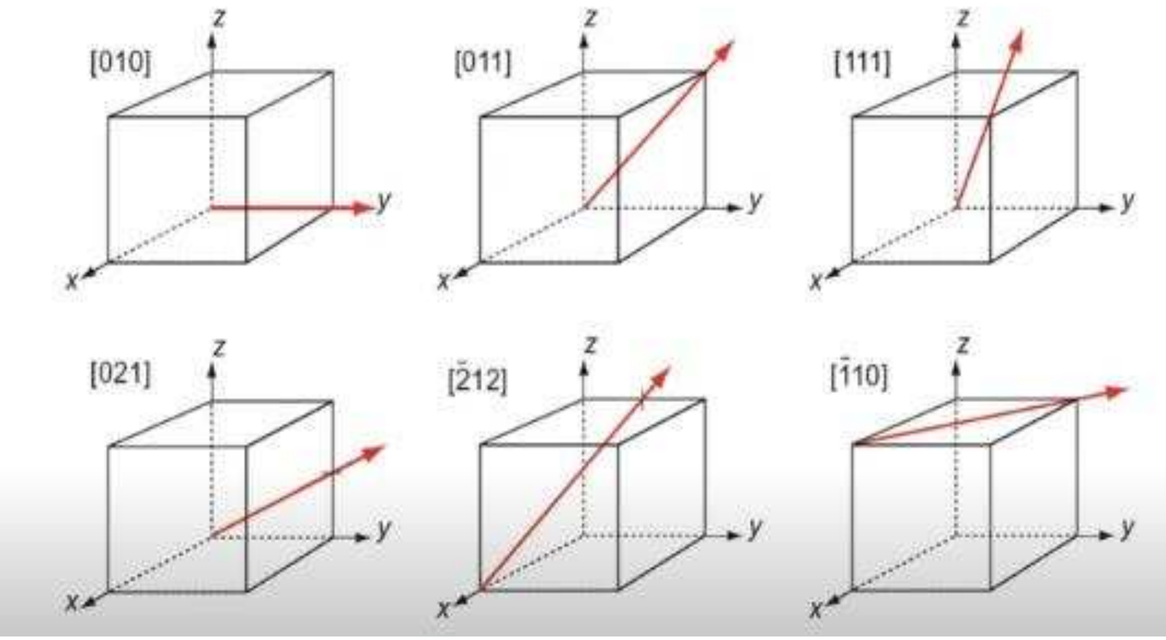
To direction of a line in the crystal can be determined as follows:

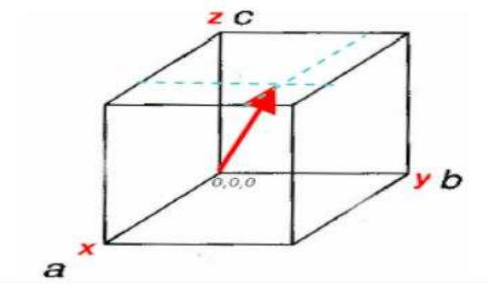
1. Take the point as origin from where the line starts.
2. Determine the coordinates of the ends of the line (or subtract the coordinates of the two ends of line (Head – Tail) and find its projection lengths on (x, y and z) axis in terms of the unit vectors (a, b and c).
3. Convert fractions, if any, in to integers and reduce to lowest term.
4. Enclose in square brackets [hkl].

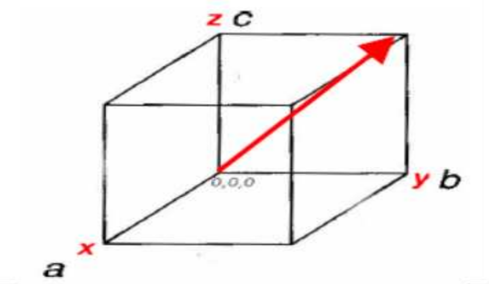


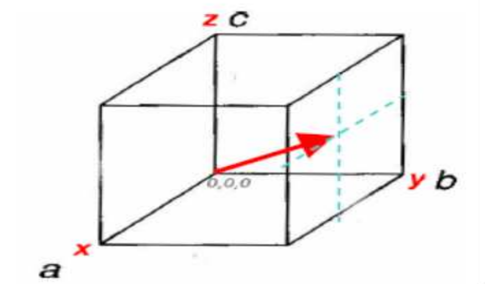


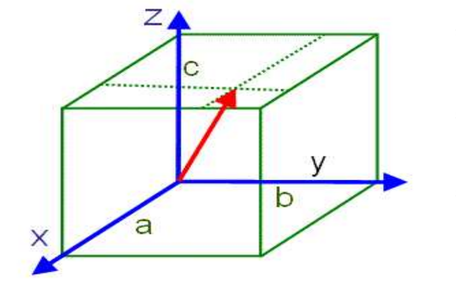




		x (a)	y (b)	z (c)
	Point Coordinates	¾	¾	1
	Clear Fractions	3	3	4
	Crystal Direction	[334]		

		x (a)	y (b)	z (c)
	Point Coordinates	0	1	1
	Clear Fractions	0	1	1
	Crystal Direction	[011]		

		x (a)	y (b)	z (c)
	Point Coordinates	½	1	½
	Clear Fractions	1	2	1
	Crystal Direction	[121]		

		x(a)	y(b)	z(c)
	Point coordinates	4/5	3/5	1
	Clear fractions	4	3	5
	Crystal direction	[435]		

Density of Crystal:

The theoretical density of a material can be calculated using the properties of the crystal structure. The general formula is

$$Density\ of\ the\ crystal\ (\rho) = \frac{Mass\ of\ unit\ cell}{Volume\ of\ unit\ cell} \qquad \ldots\ldots\ (1)$$

$$Density\ of\ the\ crystal\ (\rho) = \frac{number\ of\ atoms\ in\ unit\ cell \times mass\ of\ each\ atom}{a^3} = \frac{n \times m}{a^3} \qquad \ldots\ldots\ (2)$$

$$m = \frac{M}{N_A} \qquad \ldots\ldots\ (3)$$

Where;

M : molar mass, atomic mass or atomic weight (g/mol).

N_A : Avogadro's number (6.023×10^{23} atoms/mol).

$$\rho = \frac{n \times M}{a^3 \times N_A} \qquad \ldots\ldots\ (4)$$

Q: Calculate a value for the density of FCC platinum in grams per cubic centimeter from its lattice constant a of 0.39239 nm and its atomic mass of 195.09 g/mol.

First calculate the mass per unit cell based on the atomic mass and the number of atoms per unit cell of the FCC structure,

$$\text{mass/unit cell} = \frac{(4\ \text{atoms/unit cell})(195.09\ \text{g/mol})}{6.023 \times 10^{23}\ \text{atoms/mol}} = 1.296 \times 10^{-21}\,\text{g/unit cell}$$

The density is then found as,

$$\rho_\upsilon = \frac{\text{mass/unit cell}}{\text{volume/unit cell}} = \frac{\text{mass/unit cell}}{\text{a}^3} = \frac{1.296 \times 10^{-21}\ \text{g/unit cell}}{[(0.39239 \times 10^{-9}\ \text{m})^3]/\ \text{unit cell}}$$

$$= 21{,}445{,}113\ \text{g/m}^3 \left(\frac{\text{m}}{100\ \text{cm}}\right)^3 = \mathbf{21.45\ g/cm^3}$$

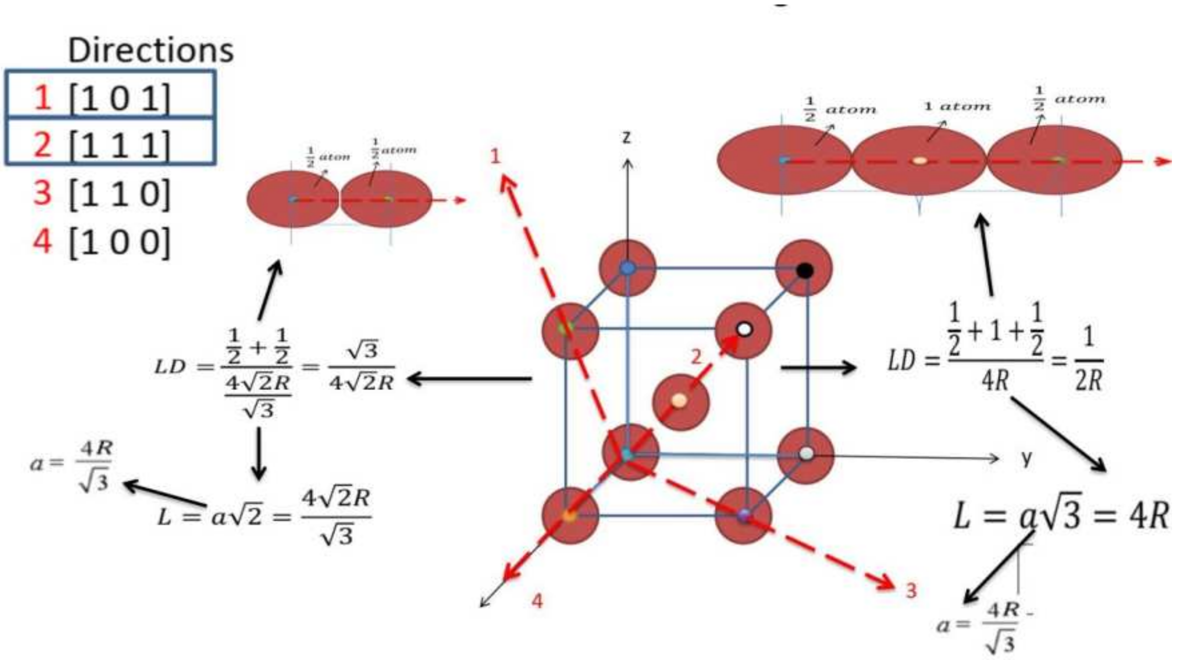
Linear density and Planar Density:

Linear density (LD):

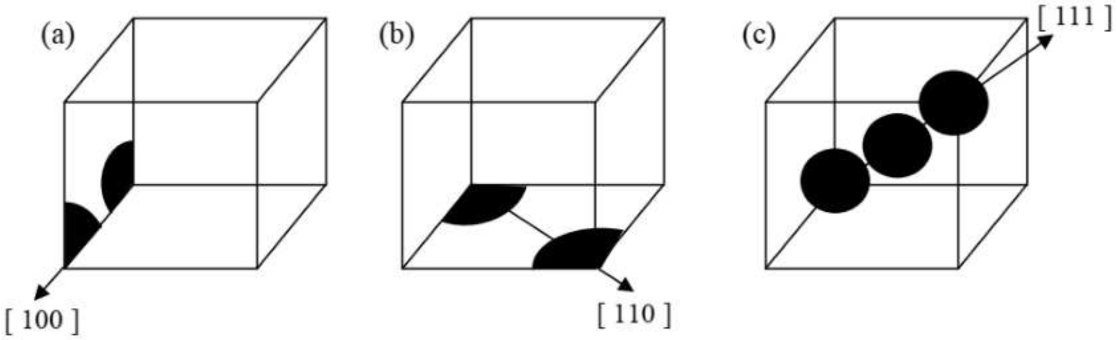
It is defined as the number of atoms per unit length whose centers lie on the direction vector for a specific crystallographic direction.

$$\text{Linear density } (LD) = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$$

- The unit of linear density are reciprocal length (m^{-1} or nm^{-1}).
- For a particular material, equivalent directions have identical linear densities.
- With regard to the numbers of atoms, it is necessary to take into account the sharing of atoms with adjacent unit cells.



Q: Calculate the linear atomic density in atoms per millimeter for the following directions in (BCC) vanadium, which has a lattice constant of 0.3039 nm: (a) [100], (b) [110], (c) [111]?



In general, the linear atomic density is derived from:

$$\rho_l = \frac{\text{no. of atomic diam. intersected by selected length of direction line}}{\text{selected length of line}}$$

(a) For the [100] direction of BCC vanadium,

$$\rho_l = \frac{\text{no. atom dia.}}{\text{a}} = \frac{1 \text{ atom}}{(0.3039 \text{ nm})(10^{-9} \text{ m/nm})(10^{3} \text{ mm/m})} = \mathbf{3.29 \times 10^{6} \text{ mm}}$$

(b) For the [110] direction of BCC vanadium,

$$\rho_l = \frac{\text{no. atom dia.}}{\sqrt{2}a} = \frac{1\text{ atom}}{\sqrt{2}(0.3039\text{ nm})(10^{-6}\text{ mm/nm})} = \mathbf{2.33 \times 10^6\ mm}$$

(c) For the [111] direction of BCC vanadium,

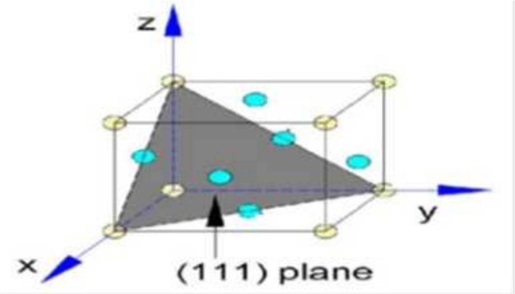
$$\rho_l = \frac{\text{no. atom dia.}}{\sqrt{3}a} = \frac{2\text{ atoms}}{\sqrt{3}(0.3039\text{ nm})(10^{-6}\text{ mm/nm})} = \mathbf{3.80 \times 10^6\ mm}$$

Planar density (PD):

It is taken as the number of atoms per unit area that are centered on a particular crystallographic plane.

$$\text{Planar density }({}_P D) = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$$

- The units for planar density are reciprocal area (m^{-2} or nm^{-2}).
- Slip occurs on the most densely packed crystallographic planes and, in those planes, along directions having the greatest atomic packing.



$$\textit{Aera of the Plane } (111):\ S = \frac{\text{height} \times \text{width}}{2} = \frac{a\sqrt{2}}{2} \times h$$

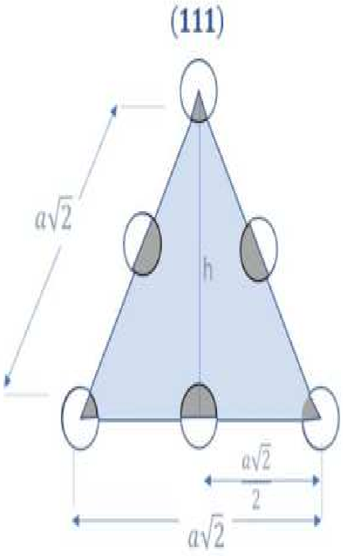
$$\textit{How to find heigth}:\ \left(a\sqrt{2}\right)^2 = h^2 + \left(\frac{a\sqrt{2}}{2}\right)^2 \rightarrow h^2 = 2a^2 - \frac{2a^2}{4} = \frac{3a^2}{2} \quad \text{thus } h = a\sqrt{\frac{3}{2}}$$

$$S = \frac{a\sqrt{2} \times a\sqrt{\frac{3}{2}}}{2} = \frac{a^2\sqrt{3}}{2} \quad S = \frac{\sqrt{3}}{2} \times \left(2\sqrt{2}R\right)^2 \rightarrow \boxed{S = 4R^2\sqrt{3}}$$

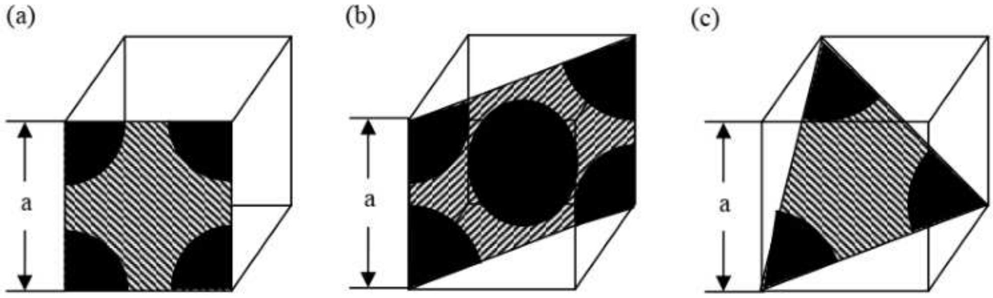
$$\textit{number of atoms in the } (111) \textit{ plane}: \left(3 \times \frac{1}{6} + 3 \times \frac{1}{2}\right)$$

$$\text{Surface of each of them } s = \pi r^2$$

$$\textit{Planar Density}^{(111)} = \frac{(3 \times \frac{1}{6} + 3 \times \frac{1}{2}) \times \pi r^2}{\textit{area of the } (111) \textit{ plane}} = \frac{\pi}{2\sqrt{3}} = \boxed{0.906}$$



Q: Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in BCC chromium, which has a lattice constant of 0.28846 nm: (a) (100), (b) (110), (c) (111).



To calculate the density, the planar area and the number of atoms contained in that area must first be determined.

(a) The area intersected by the (1 0 0) plane inside the cubic unit cell is a^2 while the number of atoms contained is: (4 corners)× (¼ atom per corner) = 1 atom. The density is

$$\rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}}$$

$$= \frac{1\text{ atom}}{(0.28846\times10^{-9}\text{ m})^2} = (1.202\times10^{19}\text{atoms/m}^2)\left(\frac{\text{m}}{1000\text{ mm}}\right)^2$$

$$= \mathbf{1.202\times10^{13}\ atoms/mm^2}$$

(b) For the more densely packed (1 1 0) plane, there are:

1 atom at center + (4 corners) × (¼ atom per corner) = 2 atoms

And the area is given as $(\sqrt{2}a)(a) = \sqrt{2}a^2$. The density is thus,

$$\rho_p = \frac{2\text{ atoms}}{\sqrt{2}(0.28846\times10^{-9}\text{ m})^2} = (1.699\times10^{19}\text{atoms/m}^2)(10^{-6}\text{ m}^2/\text{mm}^2)$$

$$= \mathbf{1.699\times10^{13}\ atoms/mm^2}$$

(c) The triangular (1 1 1) plane contains: (3 corners) × ($^1/_6$ atom per corner) = ½ atom.

The area is equal to $= \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)\left(\frac{\sqrt{3}}{2}a\right) = \frac{\sqrt{6}}{4}a^2$. The density is thus,

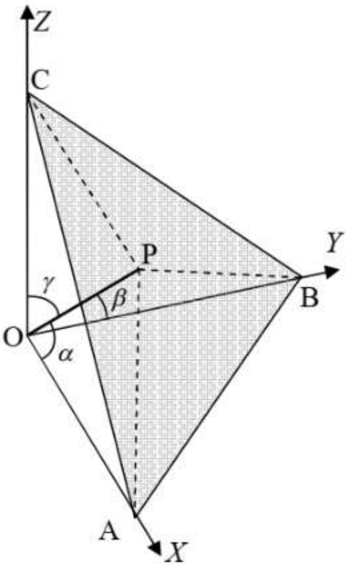
$$\rho_p = \frac{1/2\text{ atom}}{\frac{\sqrt{6}}{4}(0.28846\times10^{-9}\text{ m})^2} = (9.813\times10^{18}\text{atoms/m}^2)(10^{-6}\text{ m}^2/\text{mm}^2)$$

$$= \mathbf{9.813\times10^{12}\ atoms/mm^2}$$

Q / Show that the perpendicular distance between two adjacent planes of a set (hkl) in a cubic lattice of lattice constant a is: $\mathbf{d_{hkl} = a\sqrt{h^2+k^2+l^2}}$ for cubic structure.

Relation between interplanar spacing and Miller indices:

Let us consider three mutually perpendicular coordinate axis, OX, OY, and Oz and assume that a plane (hkl) parallel to the plane passing through the origin makes intercepts a/h, b/k and c/l on the three axes at A. B and C respectively as shown in figure.



Let OP = d_{hkl}, the interplaner spacing be normal to the plane drawn from the origin and makes angle α, β, and γ with the three axes respectively.

Therefore, $OA=\frac{a}{h}, OB=\frac{b}{k}, OC=\frac{c}{l}$

From ΔOPA we get, $\cos\alpha=\frac{OP}{OA}=\frac{d_{hkl}}{a/h}$

Similarly, from ΔOPB we get $\cos\beta=\frac{OP}{OB}=\frac{d_{hkl}}{b/k}$

and from ΔOPC we get $\cos\gamma=\frac{OP}{OC}=\frac{d_{hkl}}{c/l}$

But, for a rectangular coordinate system, using directional cosine we have

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1 \qquad (1)$$

Substituting the values of cosα, cosβ and cosγ in Eq.1 we get,

$$d_{hkl}^2\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)=1$$

$$\therefore d_{hkl}=\frac{1}{\sqrt{h^2/a^2+k^2/b^2+l^2/c^2}} \qquad (2)$$

This is the general formula and is applicable to the primitive lattice of orthorhombic, tetragonal and cubic systems.

i) Orthorhombic system: $a \neq b \neq c$

$$d_{hkl}\frac{1}{\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)}$$

ii) Cubic system: $a = b = c$

$$\therefore \qquad d_{hkl}=\frac{a}{\sqrt{h^2+k^2+l^2}}$$

ii) Tetragonal system: $a = b \neq c$

$$\therefore \qquad d_{hkl}=\frac{1}{\sqrt{\left(\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right)}}$$

Q: Find the perpendicular distance between the two planes indicated by the Miller indices (1 2 1) and (2 1 2) in a unit cell of a cubic lattice with a lattice constant parameter ‘a’.

$$d_1 = \frac{a}{\sqrt{h_1^2 + k_1^2 + l_1^2}} = \frac{a}{\sqrt{1^2 + 2^2 + 1^2}} = \frac{a}{\sqrt{6}}$$

$$d_2 = \frac{a}{\sqrt{h_2^2 + k_2^2 + l_2^2}} = \frac{a}{\sqrt{2^2 + 1^2 + 2^2}} = \frac{a}{\sqrt{9}} = \frac{a}{3}$$

The perpendicular distance between the planes (1 2 1) and (2 1 2) are;

$$d = d_1 - d_2 = \frac{a}{\sqrt{6}} - \frac{a}{3} = \frac{3a - \sqrt{6}a}{3\sqrt{6}} = \frac{a(3 - \sqrt{6})}{3\sqrt{6}} = 0.0749\ a$$

Some special crystal structures:

Diamond unit cell

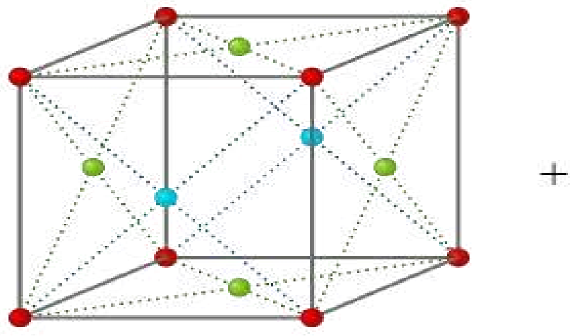
Diamond crystallizes in cubic crystal structure. In diamond unit cell all the atoms are carbon. The diamond unit cell consists of two interpenetrating (FCC) unit cells. The diamond lattice may be considered as two identical atoms at (000, ¼, ¼, ¼) positions associated with each point of the (FCC) lattice. The unit cell has eight corner atoms, six face centered atoms and four atoms on the body diagonals, which are located at the following coordinates:

$$(000),(100),(010),(110),(001),(101),(011),(111)$$

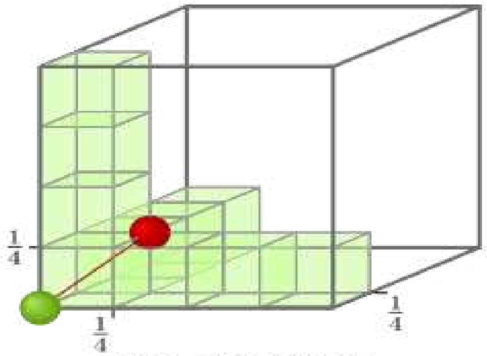
$$\left(\frac{1}{2}0\frac{1}{2}\right),\left(\frac{1}{2}\frac{1}{2}0\right),\left(0\frac{1}{2}\frac{1}{2}\right),\left(1\frac{1}{2}\frac{1}{2}\right),\left(\frac{1}{2}1\frac{1}{2}\right),\left(\frac{1}{2}\frac{1}{2}1\right)$$

$$\left(\frac{1}{4}\frac{1}{4}\frac{1}{4}\right),\left(\frac{1}{4}\frac{3}{4}\frac{3}{4}\right),\left(\frac{3}{4}\frac{1}{4}\frac{3}{4}\right),\left(\frac{3}{4}\frac{3}{4}\frac{1}{4}\right)$$

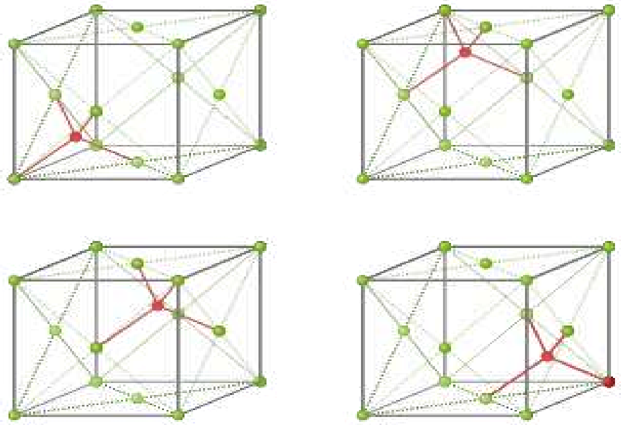
The body diagonal atom lies at a distance of one fourth of the body diagonal. The body diagonal atoms are tetrahedrally bonded with corner atoms and hence touch with the corner atoms. The diamond unit cell is shown in figure below.

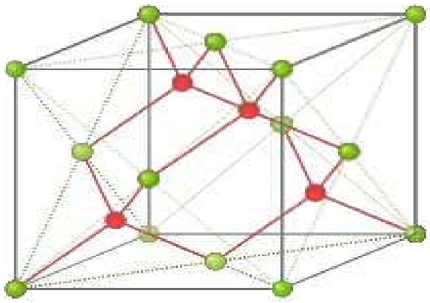


fcc structure



two-atomic basis





diamond structure

Diamond is one of the hardest materials. The high value of hardness of diamond is due to its crystal structure and the strong interatomic covalent bonds. Some of the elements that crystallize in diamond unitmcell are C, Si, Ge and gray tin.

Number of atoms in a unit cell:

There are eight corner atoms. Each and every corner atoms are shared by eight adjacent unit cells. Therefore, one corner atom contributes($1/8^{th}$) of its parts to one unit cell. Since there are eight corner atoms, the number of atoms contributed by the corner atom is [8*1/8 = 1].

There are six face centered atoms. Each and every face centered atom is shared by two adjacent unit cells. So, a face centered atom contributes(1/2) of its parts to one unit cell. Therefore, the total number of atoms contributed by the face centered atoms is [6*1/2 = 3].

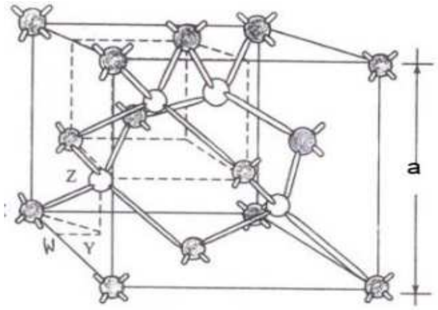
The body diagonal atoms lies within the unit cell. There are four body diagonal atoms.

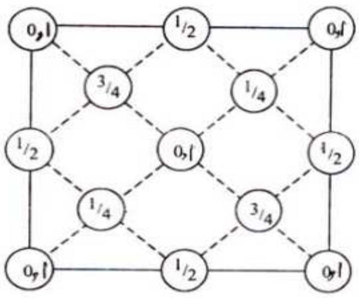
Therefore, the total number of atoms in a diamond unit cell is [1+3+4=8].

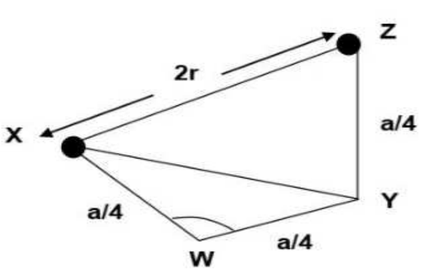
Atomic radius

The atoms that lie along the body diagonal of the unit cell are tetrahedrally bonded with corner atoms and hence touch with the corner atoms. The body diagonal atom lies at a distance of one fourth of the body diagonal.

From the figure below,in the triangle (WXY);







$(XY)^2 = (XW)^2 + (WY)^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 = \frac{a^2}{8}$

Also in the triangle (XYZ);

$(XZ)^2 = (XY)^2 + (YZ)^2 = \frac{a^2}{8} + \left(\frac{a}{4}\right)^2 = \frac{3a^2}{16}$

But XZ = 2r

$(2r)^2 = \frac{3a^2}{16}$

$r^2 = \frac{3a^2}{64}$

$r = \frac{\sqrt{3}}{8}\, a$

Atomic packing factor (APF) or Packing density (PD):

The packing density of a diamond unit cell is calculated as follows:

$$PD = \frac{Number\ of\ atoms\ per\ unit\ cell \times Volume\ of\ one\ atom}{Volume\ of\ the\ unit\ cell}$$

$$PD = \frac{8 \times \frac{4}{3}\pi r^3}{a^3} = \frac{8 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}}{8}a\right)^3}{a^3} = \frac{\sqrt{3}}{16}\pi = 0.34$$