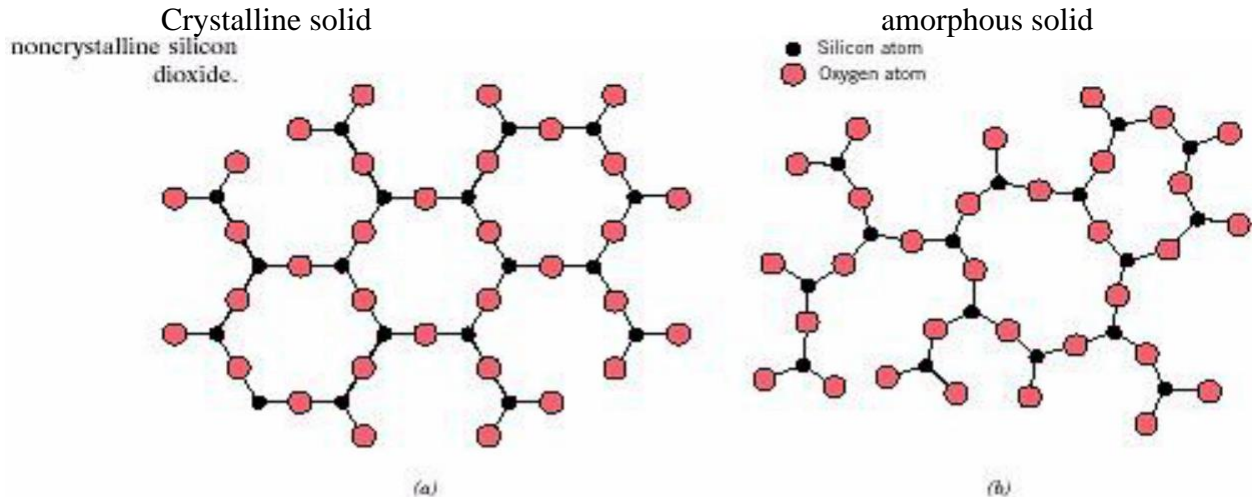


MODULE-4

CRYSTAL STRUCTURE

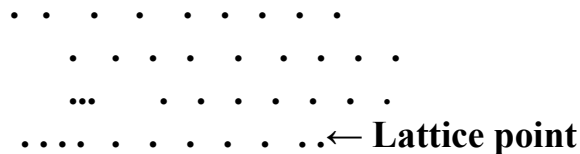
INTRODUCTION:

Matter is normally divided into three states namely solids, liquids and gases. Solids could be either amorphous or crystalline. In amorphous solids, only short range order could be found in the arrangement of the constituent atoms or molecules and hence no definite structure could be assigned to them. And they do not have a sharply defined melting point and are isotropic. In Crystalline solid is characterized by a high degree of symmetry and structural regularity in the arrangement of constituent atoms or molecules. They have a sharply defined melting point and their properties are different along different directions, i.e. they are anisotropic.



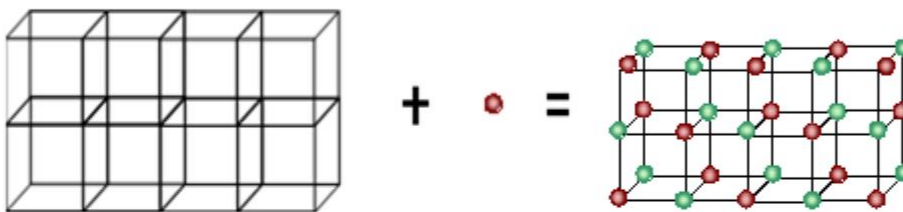
Crystal: A crystal is a solid composed of atoms molecules or ions arranged in a regular periodic array.

Lattice: The imaginary points in space about which the atoms are located are called lattice points



Basis: A group of atoms attached to every lattice point is known as basis.

Crystal structure: A crystal structure is formed when the basis is substituted in the space lattice

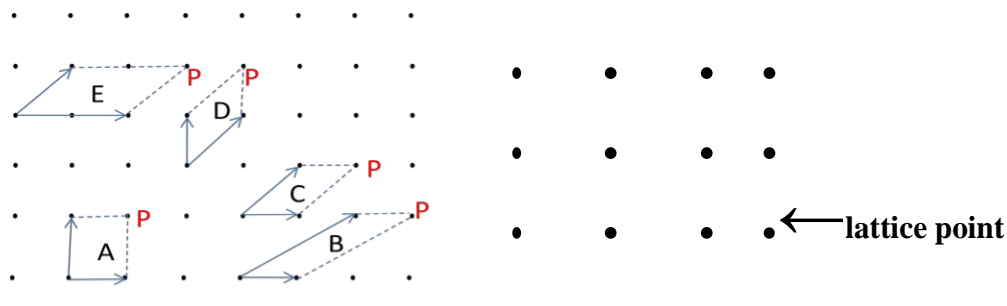


Lattice + Basis = Crystal Structure

Space lattice: A crystal consists of a three-dimensional periodic array of atoms or molecules. In order to study the crystal geometry, it is necessary to mark the intervals at which periodically. “A space lattice is a regular periodic array of points in space.”

Or

“A geometrical representation of the crystal structure in terms of lattice points is called space lattice.”



Bravais lattice: A space lattice is a regular periodic array of points in space, a particular type of space lattice is known as Bravais lattice.

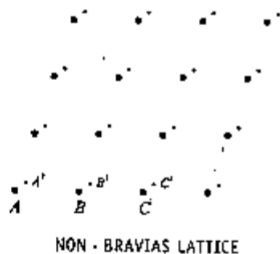
Or

if each lattice point in the crystal lattice substitutes an identical set of one or more atoms then the lattice points becomes equivalent then the lattice is called **Bravais Lattice**

In two dimensions with no restriction on the length ‘a’ and ‘b’ or on the angle γ between two lines.

On the other hand, the lattice points are non-equivalent then it is called non-Bravais lattice.

Non Bravais Lattice :



On the other hand if some of the lattice points are non-equivalent then it is said to be **Non-Bravais lattice**.

Consider the crystal lattice. The lattice points ABC etc are equivalent. Similarly another set of lattice points A^1 , B^1 and C^1 etc are equivalent which constitutes another Bravais Lattice. But the lattice prompts A & A^1 , B & B^1 etc are not equivalent. Therefore the lattice is called non Bravais Lattice. Thus a non Bravais lattice is a superposed pattern of two or more different Bravais Lattices.

Unit cell and lattice parameters:

“A parallelepiped formed by fundamental vectors a, b and c of space lattice is called **unit cell**”.

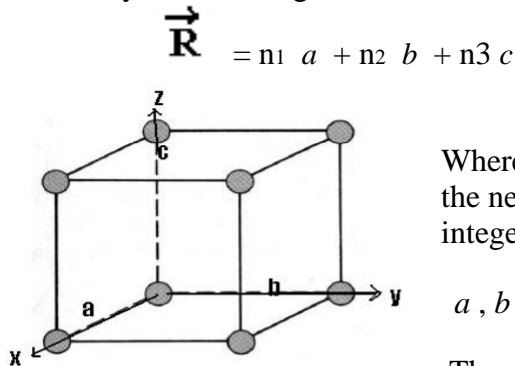
or

“The unit cell is defined as the smallest portion of the space lattice which can generate the complete crystal by repetition in three dimensions.”

“The lengths of the primitive lattice translation vectors in a unit cell and the three interfacial angles in a unit cell are known as lattice parameters”. i.e. a , b , c . and α , β , and γ .

Each crystal is built up of a repetitive stacking of unit cells each identical in size shape and orientation the unit cell with basis is thus the fundamental building block of the crystal.

A unit cell is always drawn with lattice points at each corner, but there may also be lattice points at the center of some of the faces or at the body center of the cell. Although there are infinite number of ways of choosing the unit cell, but the simplest one is conventionally accepted.



Where a , b , c are the three vectors joining the origin to the nearest non-coplanar points and n_1, n_2 , and n_3 are integers.

a , b , c are the basis vectors set

The angle between a & b is α

The angle between b & c is β

The angle between c & a is γ

Primitive cell: Primitive cell is a unit cell which contains atoms only at the corners. Or

“The unit cell that contains one lattice point only at the corners is known as primitive cell”

A non primitive cell is a unit which incorporates an integral multiple of primitive cells. And it is imagined only for the sake of easy visualization of the symmetry in arrangement of points.

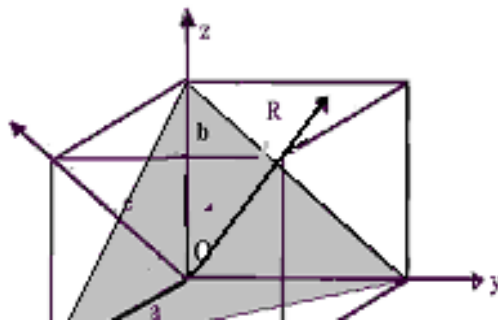
a and c are primitive cells
 b is non primitive cell

In the non primitive cell of b in addition to the four points at the corners, there is one more lattice point at the center which is not at the meeting point of the basis vectors.

Direction and Planes in a crystal lattice:

In a crystal system it is necessary to refer to planes comprising of lattice points and also to directions of straight lines on which the lattice points lie in a space lattice.

In a crystal there exist directions and planes which contain a large concentration of atoms. The crystal direction is a line joining any two points of the lattice or it is an imaginary line passing through the origin and a given lattice point in the



VTU IN POCKETS

crystal lattice.

Let us consider a simple cubic lattice. In order to specify the directions in a lattice we make use of lattice vectors. For example if we want to indicate the direction in the fig., the point can be generated starting from the origin 'O'; and move n_1 steps in the direction of a , n_2 steps in the direction of b and n_3 steps in the direction of c . The position vector \vec{OR} can be represented as

$$\vec{R} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

Where, n_1 , n_2 , & n_3 are integers and a , b , c are constants called basis vectors.

As per this vector equation, the direction vector R depends purely on the Integers n_1 , n_2 and

n_3 . since a , b , c are constants we can remove them. Then the directions are specified as $R = [n_1 n_2 n_3]$.

In a Cubic unit cell, the direction $[111]$ is resultant vector, X –axis is $[100]$ direction Y axis $[010]$ direction and Z axis is $[001]$ direction.

Crystal planes and Miller indices:

“The crystal lattice to be made up of a parallel set of equidistant planes known as crystal planes or lattice planes.”

“The reciprocal of the intercepts made by the plane on the crystallographic axes when reduced to smallest numbers.”

Or

The position of a crystal plane can be specified in terms of three integers called miller indices.

Procedure for finding Miller Indices:

1. Find the intercepts of the plane with the crystal axis along the axes x , y and z in terms of the lattice constants a , b and c respectively.

2. Express x , y , and z as fractional multiplier of respective basic vectors, then we obtain the fraction

$$\frac{x}{a}, \frac{y}{b}, \frac{z}{c}$$

3. Take the reciprocal of the fractions to obtain

$$\frac{1}{h}, \frac{1}{k}, \frac{1}{l}$$

4. Find the least common multiple [LCM] of the denominator by which multiply the above three ratios.

This operation reduces them to a set of 3 integers h, k, l called miller indices for the crystal plane.

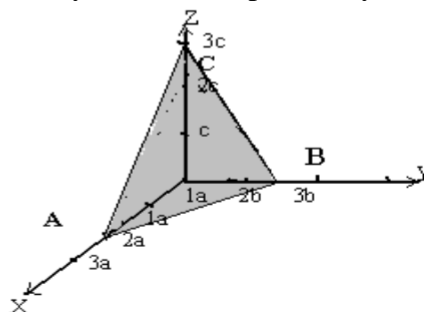
The position of the plane in the space lattice is denoted as (hkl).

Example: Consider a parallel plane ABC with intercepts 2a along X – axis, 2b on Y axis and 3c on Z axis, where a, b & c are lattice constants respectively. The intercepts of x, y, z = 2; 2; 3

Reciprocals of integers = $1/2; 1/2; 1/3$

LCM is 6; we get 3; 3; 2

The Miller indices of the Plane ABC, (h K l) = (3 3 2).



Example.

1) The intercepts of the plane is

$$X = \frac{a}{h}, Y = \frac{b}{k}, Z = \frac{c}{l}$$

2) Taking the ratio of intercepts with the basis vectors.

$$\left[\frac{a}{h}, \frac{b}{k}, \frac{c}{l} \right] = [h_1, h_2, h_3]$$

3) Taking the reciprocals of the 3 fractions.

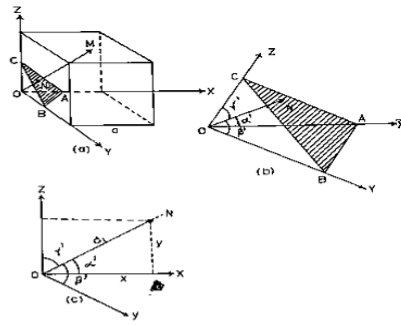
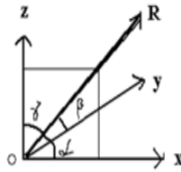
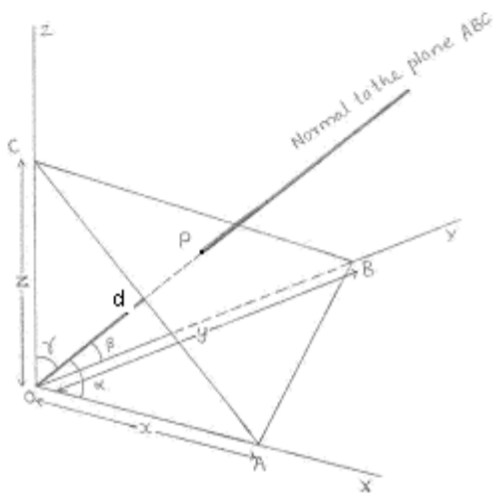
$$\left[\frac{h_1}{a}, \frac{h_2}{b}, \frac{h_3}{c} \right]$$

4) Throughout by the least common multiple by 4

$$[h_1 \times 4, h_2 \times 4, h_3 \times 4]$$

(5 6 8) which is read as five six eight.

Expression for interplanar spacing in terms of miller indices:



Interplanar distance is defined as the distance between two adjacent lattice planes is known as the interplanar distance.

Let ABC be one of the parallel planes represented by the miller indices (hkl). Its intercepts on the crystal axes are x, y and z.

Another plane parallel to this plane, passes through the origin O. if OP is drawn perpendicular from O to the plane ABC, then OP is equal to the interplanar distance denoted by d_{hkl} . Let angle made by OP with respect to the co-ordinate axes x, y and the z, be α, β, γ , let us consider the space lattice in which x, y, z are orthogonal.

Then since OP is normal to the plane x, y, z will be the hypotenuses to the 3 right angled triangles all of which have a common adjacent side OP

$$d_{hkl} = x \cos \alpha = y \cos \beta = z \cos \gamma \quad \text{----- (1)}$$

If a, b, c is the lengths of the basis vectors then as per our convention in designating the miller indices.

$$(hkl) = \left(\frac{a}{x}, \frac{b}{y}, \frac{c}{z} \right)$$

$$(X y z) = \left(\frac{1}{x}, \frac{1}{y}, \frac{1}{z} \right)$$

Using the above equation (1) we have

$$d_{hkl} = \frac{a}{h \cos \alpha} = \frac{b}{k \cos \beta} = \frac{c}{l \cos \gamma} \quad \text{----- (2)}$$

$$\text{From equation (2)} \quad \frac{1}{d_{hkl}} = \frac{h}{a} \cos \alpha$$

$$\cos \alpha = \frac{h d_{hkl}}{a}$$

Squaring both the sides

$$\cos^2 \alpha = \frac{h^2 d_{hkl}^2}{a^2} \text{ similarly for } \cos^2 \beta = \frac{k^2 d_{hkl}^2}{b^2} \text{ and } \cos^2 \gamma = \frac{l^2 d_{hkl}^2}{c^2}$$

But for orthogonal co-ordinates we know that

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \text{----- (3)}$$

From equation (2) and (3) we have

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

Then, the interplanar distance 'd' is given by

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

Where, d_{hkl} is the interplanar distance.

For cubic lattice $a=b=c$ then, $d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}}}$

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

Crystal systems:

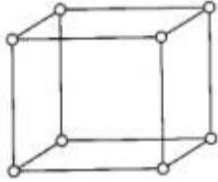
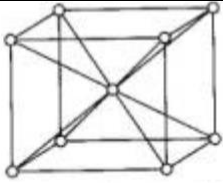
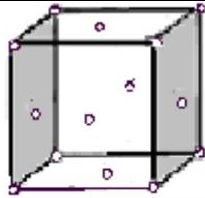
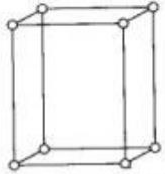
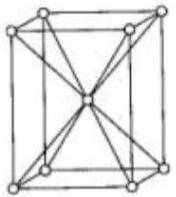
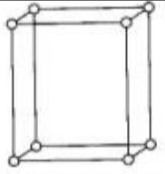
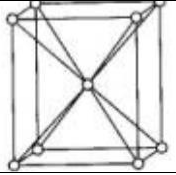
Different crystals have different arrangements of lattice points which give rise to different types of space lattices. For representing the type of distribution of lattice points in space, a co-ordinate system is needed. To serve this purpose, it requires seven different co-ordinate systems, the co-ordinate systems are called crystal systems. They are named on the basis of geometrical shape and symmetry as follows.

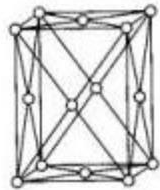
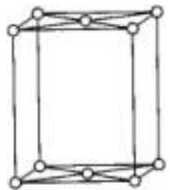
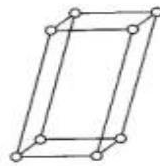

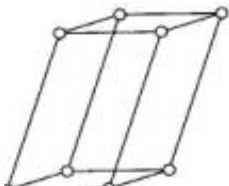
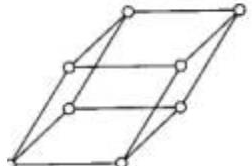
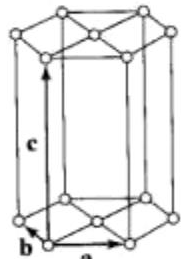
Based on the geometrical considerations these are divided into 7 groups distinguished from one another by their angles between them and intercepts of the faces along them in these basic system further divided into 14 special systems (Bravais lattice)

Crystal is broadly classified into seven types they are also called seven *crystal systems*.

- (1) Cubic
- (2) Tetragonal

- (3) Orthorhombic
 (4) Mono clinic
 (5) Triclinic
 (6) Trigonal (Rhomboheral)
 (7) Hexagonal

S.No	Crystal System	No of space lattice points	Unit cell characteristics	Bravais lattice and symbol	Unit cell geometry	Example
I	Cubic	3	$a=b=c$ (lengths) $\alpha=\beta=\gamma=90^\circ$ (Angles)	Simple cube (P) (SC)		Au, Cu, Ag, NaCl,
				Body Centered (I) (bcc)		
				Face Centered (F) (fcc)		
II	Tetragonal	2	$a=b \neq c$ $\alpha=\beta=\gamma=90^\circ$	Simple		SnO ₂ , TiO ₂ ,
				Body Centered		
III	Orthorhombic	4	$a \neq b \neq c$ $\alpha=\beta=\gamma=90^\circ$	6. Simple (P)		KNO ₃ , K ₂ SO ₄ , PbCO ₃
				7. Body Centered (I)		

				Face Centered(F) (Fcc)		
				Base Centered (C)		
IV	Monoclinic	2	a b c = 90, 90°	Simple (P)		Borax 2H ₂ O,
				Base Centered (C)		
V	Triclinic	1	a b c 90°	Simple(P)		CuSO ₄ , 5H ₂ O
VI	Trigonal, Rhombohedral	1	a=b=c = 90 <120	Simple (P)		Calcite As, sb, Quartz
VII	Hexagonal	1	a=b c = 90 =120	Simple (P)		Zn, Mg, Cd, , SiO ₂

1. Cubic: In this crystal all the three lengths of the primitives are equal and are at right angles to each other i.e., $a = b = c$, and $\alpha = \beta = \gamma = 90^\circ$

2. Tetragonal: In this crystal, the two lengths of the primitives are equal and one is different but all the interfacial angles are equal to 90, i.e., $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$.

3. Orthorhombic: In this unit cell the lengths of the primitives are different but all the interfacial angles are equal to 90° , i.e., $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$

4. Monoclinic: In this unit cell the length of the primitives are different. Two interfacial angles equal to 90° and one not equal to 90° , i.e., $a \neq b \neq c$ and $\alpha = \beta = 90^\circ \neq \gamma$.

5. Triclinic: In this Crystal all the three primitives and all the three angles are not equal, i.e. $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$.

6. Trigonal (Rhombohedral): In this crystal three lengths of the primitives are equal and all the interfacial angles are equal but not equal to 90° , i.e., $a = b = c$ and $\alpha = \beta = \gamma < 120^\circ$.

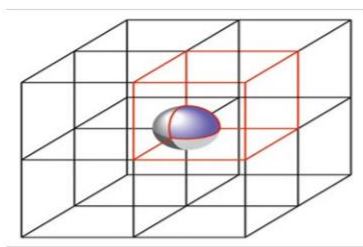
7. Hexagonal: In this crystal two lengths of the primitives are equal and one is different and two interfacial angles equals 90° and one equals 120° , i.e. $a = b \neq c$ and $\alpha = \beta = 90^\circ \neq \gamma = 120^\circ$.

The modified corners (cells), along with the primitive / unit cell are said to be Bravais lattice. If we consider all seven crystal systems, there are 14 Bravais lattice which can be classified based on body centered, base centered and face centered cell.

Number of atoms per unit cell:

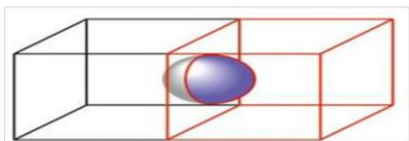
The atoms in a crystal may be shared by more than one unit cell. Ex: an atom in a simple cubic structure is shared by eight unit cells. An atom at the face centered in a cubic cell shared only two unit cells. In body centered unit cell, the atoms at the centre of the cell is not shared by the cell with other cells.

of Atoms/Unit Cell



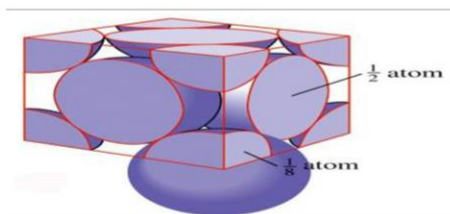
For atoms in a cubic unit cell:

- Atoms in corners are $\frac{1}{8}$ within the cell



For atoms in a cubic unit cell:

- Atoms on faces are $\frac{1}{2}$ within the cell



A face-centered cubic unit cell contains a total of 4 atoms: 1 from the corners, and 3 from the faces.

- 1) **Simple cubic (SC):** A simple cubic cell has eight atoms at each of its eight corners. As each atom at the corner is shared by eight unit cells. Only $\frac{1}{8}^{\text{th}}$ of each atom belongs one cell.

Number of atoms per unit cell = $8 \times \frac{1}{8} = 1$

- 2) **Body centered cubic (BCC):** As there are 8 corner atoms, the no of corner atoms belonging to the unit cell $8 \times \frac{1}{8} = 1$ also, there is an atom at the centre of the unit cell which is not shared with other cell

Number of atoms per unit cell = $1 + 1 = 2$

- 3) **Face centered cubic (FCC):** The number of corner atoms belonging to a unit cell is $8 \times \frac{1}{8} = 1$. Also, there is an atom at the centre of each of the six faces. Each atom at the face centered is shared by two unit cells. Hence $\frac{1}{2}$ of each face centered atom belonging to the unit cell. As there are 6 faces, the no of face centered atoms belonging to the unit cell is $\frac{1}{2} \times 6 = 3$

Number of atoms per unit cell = $1 + 3 = 4$

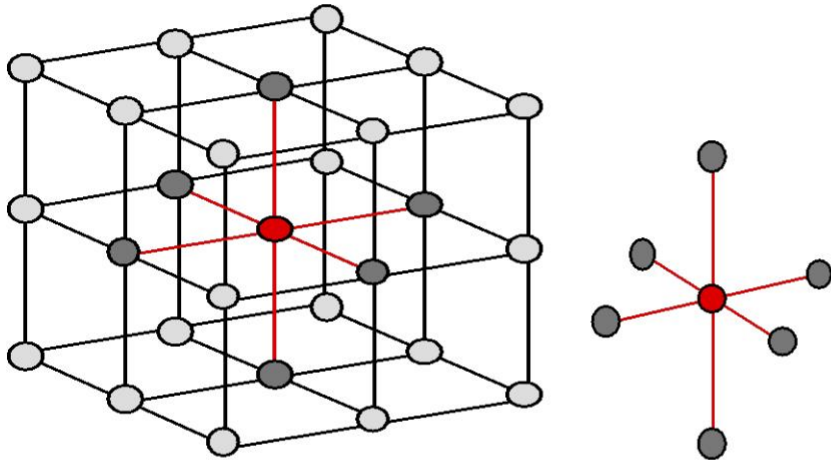
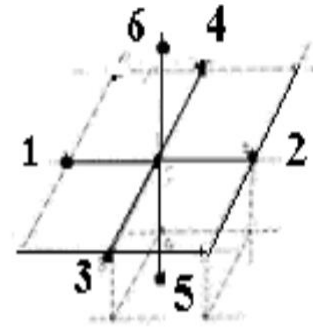
Co-ordination number: In a crystal, each atom is surrounded by a definite number of nearest equidistant neighbors.

“Co-ordination number is the number of nearest neighbors directly surrounding a given atom within a crystal”.

1) Simple cubic (SC) structure.

In a simple cubic structure, there will be one atom at each corner of the unit cell. Let us consider one corner atom at of a unit cell in the crystal lattice, and then it will have 4 nearest atoms (1, 2, 3 &4) in the horizontal plane. There are 2 more atoms nearest one is directly above (5) and the directly below (6). Except these 6 atoms, all other atoms lie at greater distance.

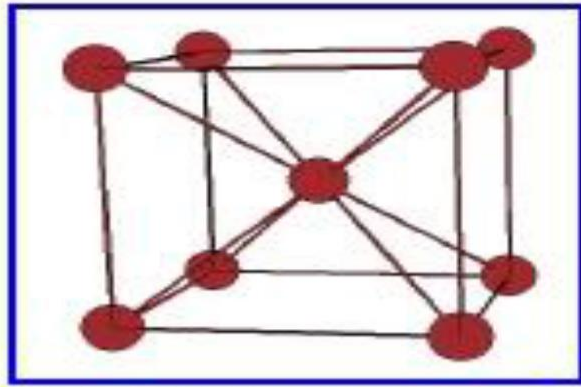
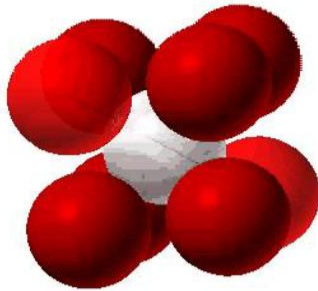
Thus the co-ordination number for an atom in the simple cubic is =6



2) Body centered cubic(BCC) structure:

In this structure, there will be one atom at the body center and eight atoms at the corners of the unit cell.

Thus for an atom at the body centre, obviously there are eight (8) nearest neighbors. Hence the co-ordination number of an atom in bcc structure =8



Body Centered Cubic
and related structures

3) Face centered cubic(FCC) structure:

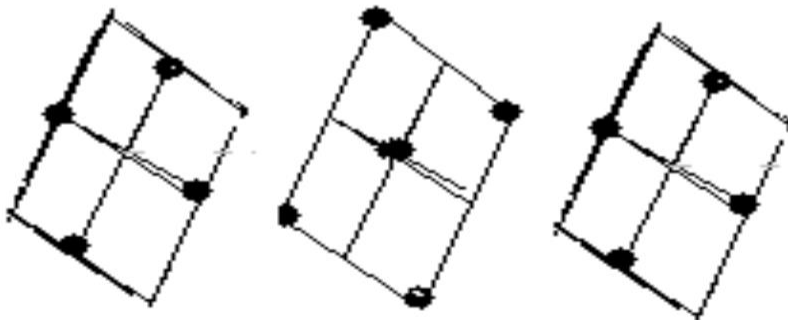
For a lattice of FCC structure, 3 consecutive planes can be taken.

It can be recognized that each atom irrespective of the 3 planes to which it belongs to lie, there are 4 such atoms in each plane.

Thus the number of nearest atoms to $3 \times 4 = 12$

Hence the co-ordination number for the FCC structure =12.

It is seen that in the 3-d lattice for FCC structure, each atom possesses the same surroundings as that shown



Relation between Atomic radius and lattice constant for cubic lattices:

1. Simple Cell Structure:

Let consider one face of the unit cell of a sc structure. We can see from the figure that there are 4 atoms at each corner of the cube. Due to symmetry, the distributions of atoms at their corners lie at the center of the square with spherical bodies touching each other.

From figure, it is seen that

$a = 2r$	lattice Constant
----------	---------------------

$$R=a/2 \text{ (Atomic radius)}$$

2. Bcc Structure:

In bcc cell atoms are in contact diagonally along the body which is as shown in the figure. There are two atomic radii from the center atom and one from atomic radius from each of the corner atom too the body diagonal and its length are equal to $4r$. From figure, we get

Triangle, ABC, $AC^2 = AB^2 + BC^2$

$$AC^2 = a^2 + a^2 = 2a^2 \text{ and}$$

$$AG = r + 2r + r = 4r$$

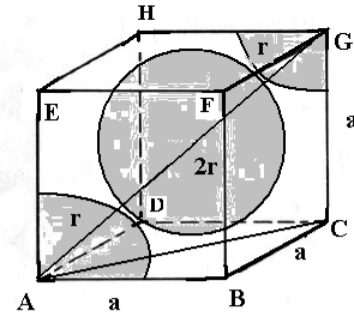
Along diagonal, $AG^2 = AC^2 + CG^2$

$$(4r)^2 = 2a^2 + a^2 = 3a^2$$

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

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

$$r = \sqrt{3}a/4 \text{ (atomic radius)}$$



3. Fcc structure:

In an FCC cell, atoms are in contact diagonally along the face of the cube which is as shown in the figure. There are four atomic radii along the face diagonal. From the geometry of the figure,

Triangle ABC,

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

$$(4r)^2 = a^2 + a^2 = 2a^2$$

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

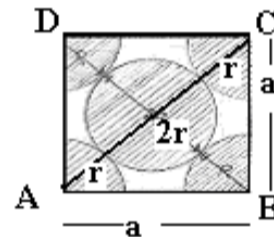
or

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

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

$$r = \frac{a\sqrt{2}}{4} = \frac{a}{2\sqrt{2}} = \frac{a}{2.828}$$

$$r = a/2.828 \text{ (Atomic radius)} \quad a = 2.828 r \text{ (lattice constant)}$$



Atomic packing factor (APF):

We have seen different kinds of crystal structure and each structure (unit cell) have different amount of matter contents. For a given space, some structures shall have more voids and some have more matter contents.

The fraction of space occupied by atoms in a unit cell is known as atomic packing factor. Packing factor is concerned to density of packing and can be evaluated by considering the actual type of crystal structure. But the atoms are perfectly spherical in shape then "**packing factor is**

the ratio of the volume occupied by the atoms in the unit cell to the total volume of the unit cell."

i.e. APF=_____

We are considering here unit cells of cubic type the lattice parameter for them is "a". it implies the edge length of the cube is a.

Total Volume of the unit cell = a^3

As the atoms are assumed to be spherical in shape,

Volume of the each atom = $\frac{4}{3} \pi R^3$

There are n atoms in a unit cell, the volume occupied by all the atoms in the unit

Cell = $n \times \frac{4}{3} \pi R^3$

Where, R is the radius of an atom.

According to definition

$$\text{APF} = \frac{n \times \frac{4}{3} \pi R^3}{a^3}$$

1. Simple Cubic Cube (Sc) lattice:

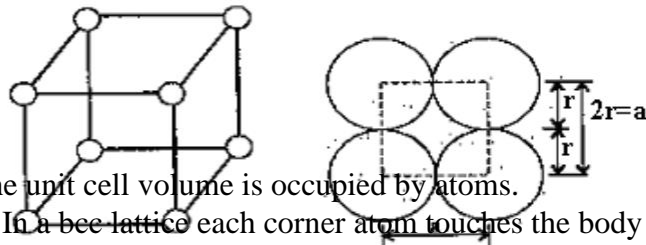
In simple cubic lattice number a atoms per unit cell, $n = 1$.

The corner atoms touch each other and lattice constant and radius of the atom can be relate as, $a = 2R$.

The volume of the atom, $v = \frac{4}{3} \pi R^3$ and volume of the unit cell,

$$\begin{aligned} \text{APF} &= \frac{n \times \frac{4}{3} \pi R^3}{a^3} \\ &= \frac{1 \times \frac{4}{3} \pi R^3}{(2R)^3} \\ &= \frac{\frac{4}{3} \pi R^3}{8 R^3} \\ &= \frac{4 \pi}{24} = \frac{\pi}{6} \approx 0.52 \end{aligned}$$

$$\text{APF} = 52\%$$



This means that, in a sc lattice, 52 % of the unit cell volume is occupied by atoms.

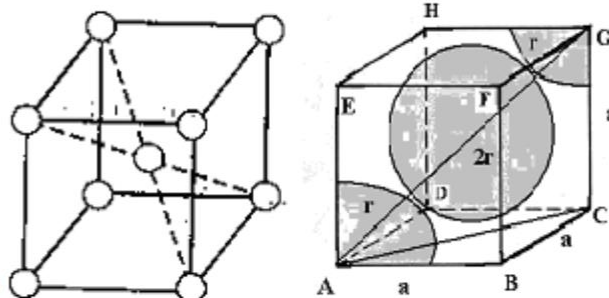
2. Body Centered Cube (Bcc) Lattice:- In a bcc lattice each corner atom touches the body centered atom and no of atoms per unit cell = $n = 2$.

$$\text{APF} = \frac{n \times \frac{4}{3} \pi R^3}{a^3}$$

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



$$= \frac{2 \cdot \frac{4}{3} R^3}{a^3} = \frac{2 \cdot \frac{4}{3} R^3}{\frac{4R^3}{\sqrt{3}}} = \frac{2}{\sqrt{3}} \times \pi R^3 = \frac{8}{\sqrt{3}} \times \pi R^3 = \frac{8}{\sqrt{3}} \times \pi R^3$$

$$= 0.21 \times 3.14$$

$$\text{APF} = 0.68.$$

$$\text{APF} = 68 \%$$

This means that, in a bcc lattice, 68 % of the unit cell volume is occupied with atoms.

3. Face Centered Cube (FCC) Lattice:

In a FCC lattice each corner atom touches the face centered atom and the no. of atoms per unit cell $n = 4$

$$a = 2\sqrt{2} R$$

$$\text{APF} = \frac{n}{a^3} \times \pi R^3$$

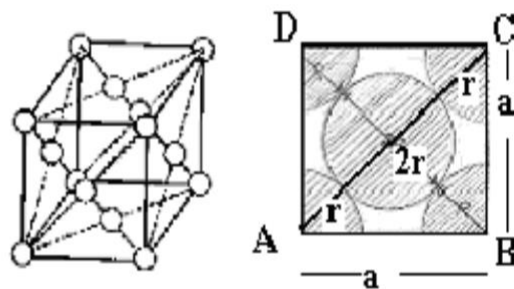
$$= \frac{4}{a^3} \times \pi R^3$$

$$= \frac{4}{(2\sqrt{2} R)^3} \times \pi R^3$$

$$= \frac{4}{16\sqrt{2}} \times \pi = \frac{1}{4\sqrt{2}} \times \pi$$

$$= 0.23 \times 3.142 = 0.74$$

$$\text{APF} = 74\%$$



This means in an FCC unit cell, 74 % of the unit cell volume is occupied by atoms. Thus the FCC unit cell is the most densely packed than bcc and SC.

DATA ON CUBIC LATTICE					
Sl. No.	Type of lattice	Coordination Number	No. of atoms/unit cell	Relation B/W. a and r	APF %
1	SC	6	1	$a = 2R$	52.4
2	Bcc	8	2	$a = 4R/\sqrt{3}$	68
3	Fcc	12	4	$a = 2\sqrt{2} R$	74

Structure of Diamond:

- 1) In diamond structure each carbon atom linked to four other by covalent bond.
- 2) Diamond exhibits FCC crystal structure which is a combination of two inter-penetrating FCC sub lattices, one of which is displaced from the other by one fourth of the length of the unit cell.
- 3) Hence a unit cell of diamond contains 18 carbon atoms.
- 4) one each at the eight corners, (C) (00000000)
- 5) one each at the face centers (F) ($1/2, 1/2, 1/2$)
- 6) And four atoms in the interior tetrahedral positions (D) ($3/4, 1/4, 3/4, 1/4$)

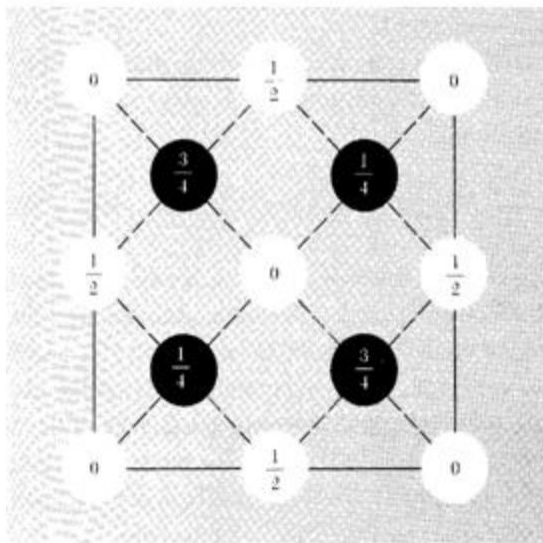


Figure 24 Atomic positions in the cubic cell of the diamond

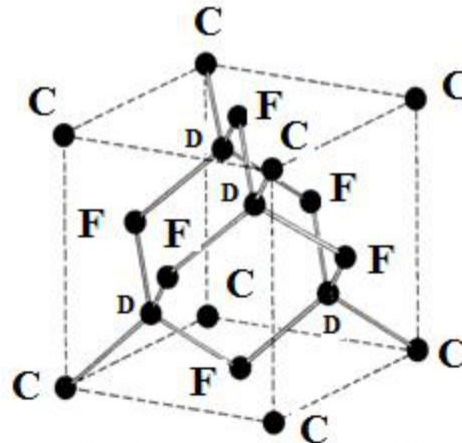
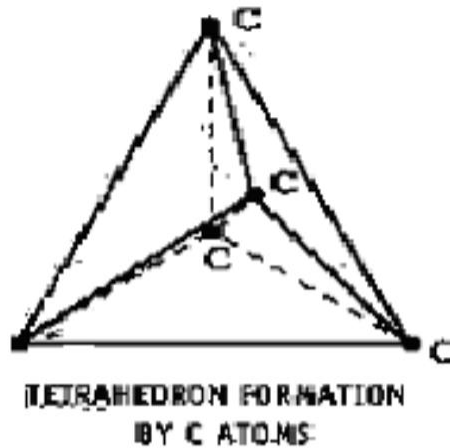
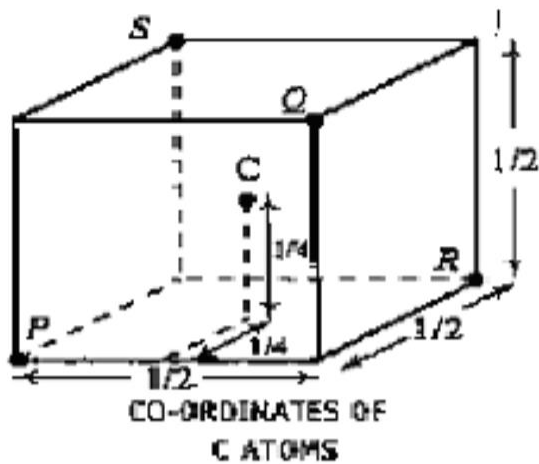


Figure 25 Crystal structure of diamond,



8). Consider a part of the unit cell. Then the coordination of the carbon atoms at the positions PQR and S can be expressed inter length of the cube edge given as $000, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, 0\frac{1}{2}\frac{1}{2}$ respectively. The coordinates of the central carbon atom are $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$.

9) The number of atoms per unit cell $n = 8$.

10) Each atom has **four** nearest neighbors. Therefore the coordination number is 4.

11) The nearest neighboring distances $2R = \sqrt{4}a$

12) The lattice parameter $a = \sqrt[3]{4}a$

13) The distance between two carbon atoms or lattice constant is $a = 3.567 \text{ \AA}$.

14) The length of each bond is 0.154 nm and the angle between the bonds is 109.5° .

$$15) \text{ Atomic packing factor} = \text{APF} = \frac{n \cdot \frac{4}{3} \pi R^3}{V_{\text{unit cell}}} = \frac{8 \cdot \frac{4}{3} \pi R^3}{(3.567 \times 10^{-10})^3} = 0.34 \text{ or } 34\%$$

16) The importance of this structure will become evident when we study semiconductors, carbon, silicon, germanium all crystals lie in diamond structure.

$$17) \text{ Density of Diamond is } \rho = \frac{nA}{N_A V} = \frac{8(12.01 \times 10^{-3})}{(6.023 \times 10^{23})(3.567 \times 10^{-10})^3} = 3.514 \times 10^3 \text{ kg/m}^3$$

Atomic weight of carbon is $A = 12.01 \text{ amu}$. & Lattice constant $a = 3.567 \text{ \AA}$

Volume of the unit cell $V = a^3 = (3.567 \times 10^{-10})^3$ & the Avogadro number is $N_A = (6.023 \times 10^{23})$

Pervoskites:

Pervoskites as class of compounds came into prominence in the year 1986. A type of oxide compounds were found to exhibit superconductivity, that too at temperature higher than the metallic superconductor.

Pervoskites crystal structure:

Pervoskites is the common name for all oxides with the formula ABO_3 where A & B are two different kinds of metals.

Ex:

$CaTiO_3$ (calcium Titan ate)

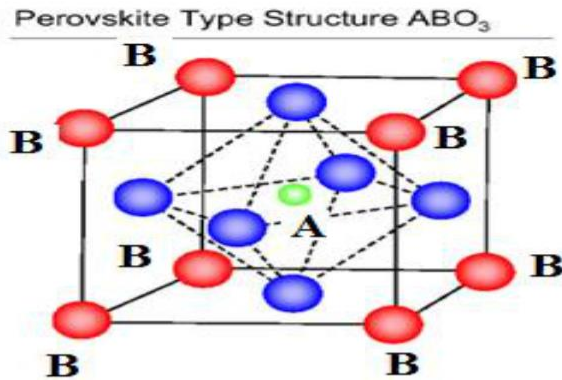
$BaTiO_3$ (Barium Titan ate)

$YBa_2Cu_3O_7$ (yttrium Barium copper oxygen)

One type of metal atoms B, are at the eight corners of the unit cell and

One atom of other type of metal A at the center.

The oxygen atoms lie at the centre of the six square faces as shown in the fig.



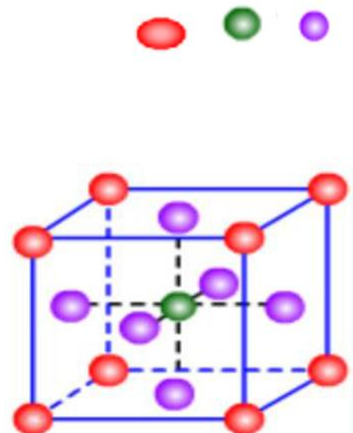
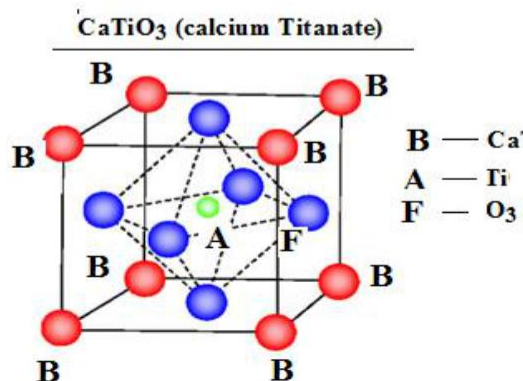
In this fig there is one "A" type atom at the centre. Hence the no of atoms /unit cell =1 There are 8 corner atoms of "B" type. Therefore total share of all the corner atoms/unit cell = $8 \times \frac{1}{8} = 1$ There are 6 face centered atoms of oxygen, therefore total share of all the oxygen atoms/unit cell = $6 \times \frac{1}{2} = 3$

Hence the no of oxygen atoms /unit cell =3

All together per unit cell, the combination results in ABO_3

Ex: $CaTiO_3$ (calcium Titanate)

$BaTiO_3$



There are 8 corner atoms of Ca^{2+} (RED COLOUR)

Therefore, Total share of all the corner atoms/unit cell = $8 \times \frac{1}{8} = 1$

Hence, the number of Ca^{2+} atoms/unit cell = 1

In this fig, there is one Ti atom at the centre, (GREEN COLOUR) hence the Number of atoms/unit cell = 1

There are 6 face centered atoms of oxygen. (BLUE COLOUR)

Therefore,

Total share of cell of the oxygen atoms/unit cell = $6 \times \frac{1}{2} = 3$ Hence,

The Number of oxygen atom/unit cell = 3

All together atoms per unit is the combination results in CaTiO_3

Polymorphism and Allotropy:

When a material has more than one crystal structure it is known as Polymorphism. Or the phenomenon in which a solid chemical compound exists in more than one crystalline form is known as polymorphism.

When an elemental solid exists in more than one crystalline form, the phenomenon is known as allotropy and different crystalline forms are known as allotropes. For ex: diamond and graphite are the allotropic forms of carbon.

X-RAYS

X – Rays are electromagnetic radiations of wave lengths between 1 \AA to 100 \AA . X-rays were first discovered by Roentgen in 1895. X-rays are produced when high speed electrons strikes a target material. X-ray carries very high photon energy and hence they have high penetration power than ordinary light. It has many more applications in medical and research field.

Bragg's Law:

A simplified way of looking at the process by a crystal was proposed by W.L. Bragg. He suggested that through the crystal a set of equidistant parallel crystal planes in which the atoms are arranged in regular interval, a parallel plane is represented.

Suppose a parallel beam of X-rays is incident in a direction of making a glancing angle with the surface of the plane. Each atom acts as a scattering centre of X-rays & sends out spherical wave fronts. Since the X-rays are highly penetrating radiations. It is necessary to consider the rays scattered not only from a single layer but from several layer.

Let us consider two parallel rays PQR and ABC which are scattered or reflected by two atoms at Q and B. in adjacent layers. The path difference between PQR and ABC is (BM + BN). The condition that the scattered wave fronts be in the same phase is that the path difference between scattered wave from one layer and that from the next be an integral multiple of wavelength ().

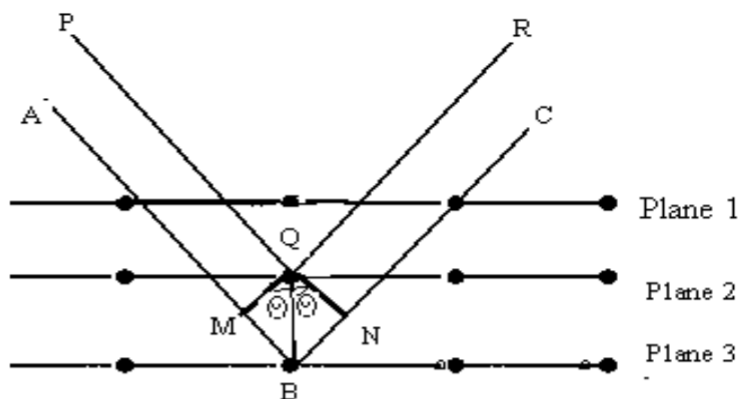
From figure, angle BQM = θ , BQN = θ and BQ = d

In the $\triangle BQM$ and $\triangle BQN$
 $\sin \theta = MB/BQ$
 $MB = d \sin \theta$

Path difference = BM + BN
 $= d \sin \theta + d \sin \theta$
 $= 2d \sin \theta$

Therefore two rays will reinforce with each other and produce maximum intensity. i.e. Path difference = $n\lambda$,

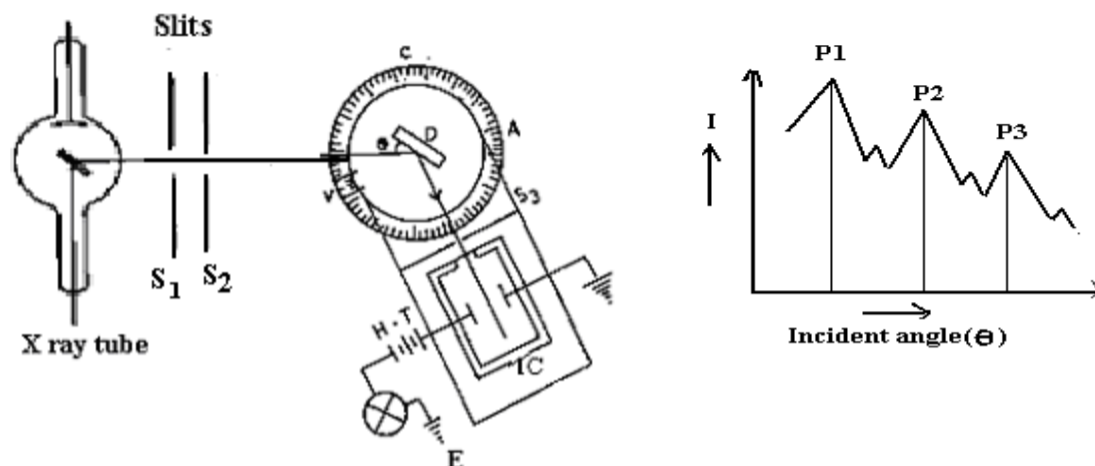
i.e. $2d \sin \theta = n\lambda$



Where n is an integer (n = 1, 2, 3 ----), d is the interplanar spacing distance & θ is the angle of incident radiation.

Bragg's X ray Spectrometer:

Bragg's X-ray spectrometer consists of a X-ray tube which produces x-rays. Electrons produced by a filament F as shown in fig. The accelerated through large potential difference of the order of several kilovolts and made incident on a tungsten or molybdenum target. The X-rays are collimated by two slits S1 and S2 the collimated X-rays are made incident on a crystal D mounted on a rotating turn table which is provided with a graduated circular scale to measure the angular displacement of the crystal.



If the turn table is rotated by an angle θ , the diffracted beam rotates by an angle 2θ , the intensity of diffracted beam is recorded by an ionization chamber connected to an electrometer E.

When the crystal is rotated, peaks of ionization current are observed when Bragg's condition is satisfied at that particular angle.

By Bragg's Law, we have $2d \sin \theta = n \lambda$.

The peaks P₁, P₂ & P₃ correspond to first, second and third order reflections. If θ_1 , θ_2 and θ_3 are the angles of incidence for the different orders of reflection with $n = 1, 2$ and 3 respectively for a given wavelength then we can write.

$$2d \sin \theta_1 = \lambda$$

$$2d \sin \theta_2 = 2\lambda$$

$$2d \sin \theta_3 = 3\lambda$$

$$2d \sin \theta_1 : 2d \sin \theta_2 : 2d \sin \theta_3 = \lambda : 2\lambda : 3\lambda$$

$$\sin \theta_1 : \sin \theta_2 : \sin \theta_3 = 1 : 2 : 3$$

The above equation can be used to verify the accuracy of the measurements.

Using Bragg's equation, if the distance 'd' between the successive planes in the crystal is known then the wavelength of X rays can be determined and if λ is known then d can be determined.

The value of interplanar spacing's calculated from this experiment is used to determine the crystal structure.

Determination of crystal structure:

One gets different values of d depending upon the particular set of parallel planes that satisfy Bragg reflection as θ is changed. By taking the ratios of the different values of d obtained. It is possible to decide the particular crystal system to which the experiment crystal belongs.

Let us consider the case of a cubic crystal the interplanar spacing for (100) planes for d_1 , and that for (110) & (111) planes are d_2 & d_3 . the geometry of the planes in a cubic crystal

$$\text{For cubic crystal, } d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$d_1 : d_2 : d_3 = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

$\therefore \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$ it indicates that the crystal structure of the cubic.

Knowing a and θ , the values of Θ can be compared. These values of Θ are compared with those obtained values from the Bragg's spectrometer reading. A perfect match between computed and observed value establishes the validity of Bragg's law.

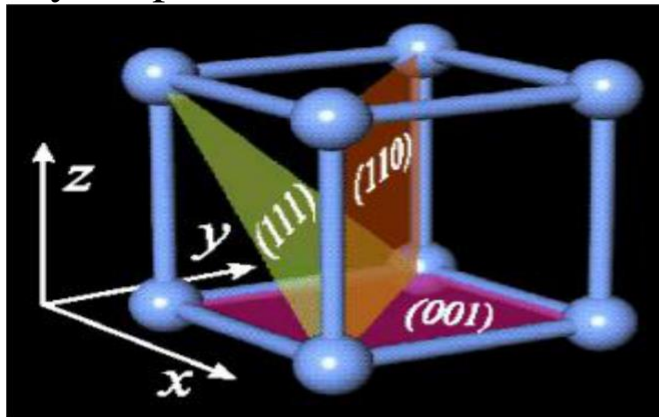
Similarly for FCC , $d_1 : d_2 : d_3 = 1 : \frac{1}{a} : \frac{1}{a}$ and

BCC, $d_1 : d_2 : d_3 = 1 : \frac{1}{a} : \frac{1}{a}$

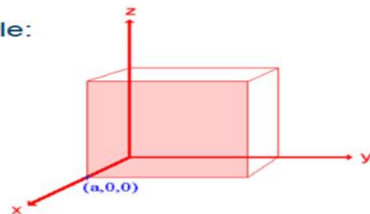
Applications of X-rays:

1. Scientific research
2. Industrial and Engineering
3. Medical uses

Crystal planes



An example:

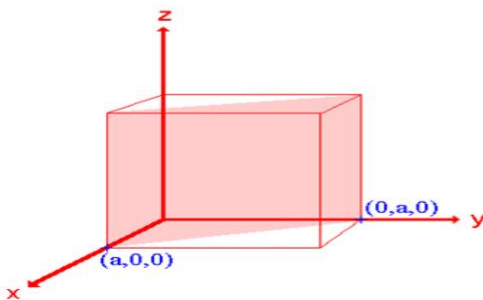


Intercepts: a, ∞, ∞

Reciprocals: $a/a, a/\infty, a/\infty$
 $= 1, 0, 0$

Miller index for this plane : $(1\ 0\ 0)$

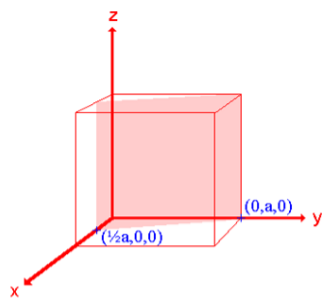
(note: this is the normal vector for this plane)



Intercepts: a, a, ∞

Reciprocals: $a/a, a/a, a/\infty$
 $= 1, 1, 0$

Miller index for this plane : $(1\ 1\ 0)$



Intercepts: $1/2a$, a , ∞
 Reciprocals: $2a/a$, a/a , a/∞
 $= 2, 1, 0$
 Miller index for this plane : $(2\ 1\ 0)$

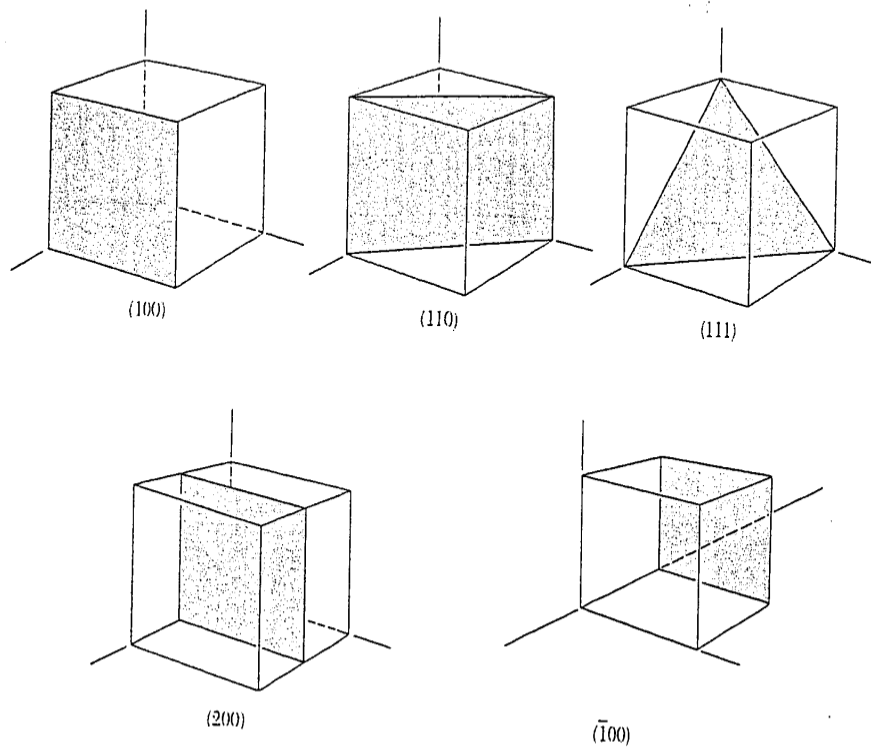


Figure 16 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to $(\bar{1}00)$.