

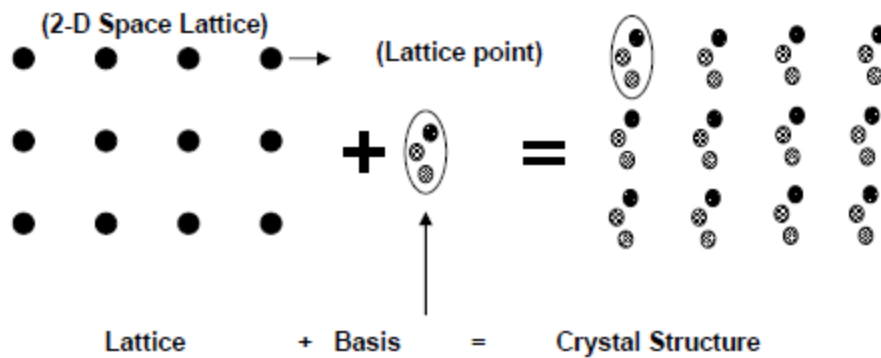
UNIT-5

CRYSTAL PHYSICS

A **Crystal** is a solid composed of atoms or other microscopic particles arranged in an orderly repetitive array. The study of crystal physics aims to interpret the macroscopic properties in terms of properties of the microscopic particles of which the solid is composed. The arrangement of atoms in a crystal is called **Crystal structure**.

Lattice points and Space Lattice

Points can be imagined in space about which atoms or molecules are located. Such points are called **Lattice points**. The totality of such points is called **Space Lattice or Crystal Lattice**. A three dimensional space lattice (**3-D space lattice**) may be defined as a finite array of lattice points in three-dimension such that each and every lattice has identical surrounding in the array.

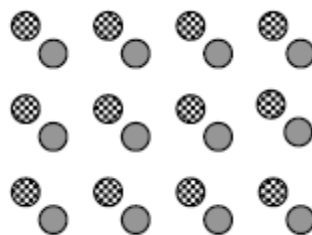






Basis

Every lattice points can be associated with one or unit assembly of atoms or molecules identical in composition called **Basis or Pattern**. The regular periodic three-dimensional arrangement of Basis is called **Crystal Structure**. Space lattice is imaginary. Crystal structure is real.

Bravais and Non-Bravais Lattice

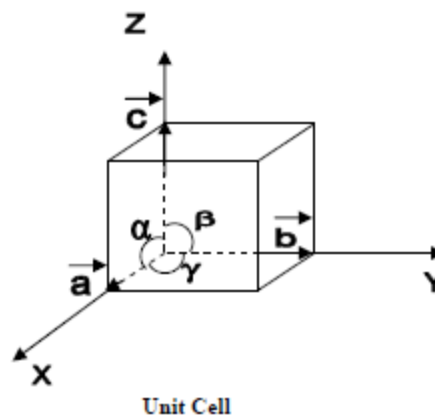
A Bravais lattice is one in which all lattice points are identical in composition. If the lattice points are not identical then the lattice is called Non-Bravais lattice.



The set of lattice points 's together constitutes a Bravais lattice. Similarly the set of lattice points 's together constitutes a Bravais lattice. But set of all lattice points 's and 's together constitute a Non-Bravais lattice. Hence a Non-Bravais lattice could be considered as the superposed pattern of two or more interpenetrating Bravais lattice.

Unit cell and Lattice parameters

In every crystal some fundamental grouping of particles is repeated. Such fundamental grouping particles is called **Unit cell**. A unit cell is chosen to represent the symmetry of the crystal. Hence the unit cell with maximum symmetry is chosen. They are building blocks of the crystal. When these unit cells are translated in three dimensions that will generate the crystal.



Each crystal lattice is described by type of unit cell. But each unit cell is described three vectors **a**, **b** and **c** when the length of the vectors and the angles (α, β, γ) between them are specified. They are nothing the intercepts of the faces and the interfacial angles. All together they constitute **Lattice parameters**.

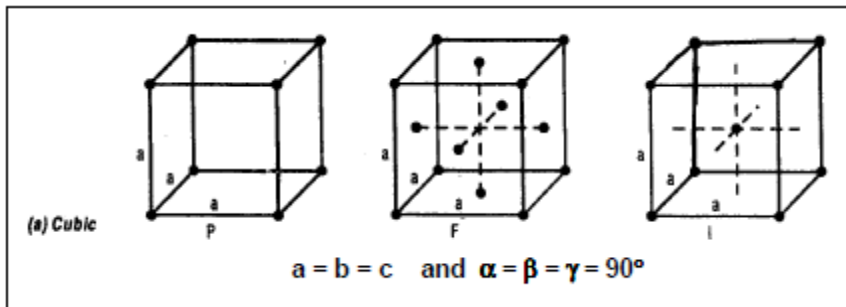
Primitive cell: Sometimes reference is made to a primitive cell. Primitive cell may be defined as a geometrical shape which, when repeated indefinitely in three dimensions, will fill all space and it consists of lattice points only at corners. It consists of only one atom per cell. Therefore may be primitive or Non-primitive.

Crystal systems

Based on lattice parameters crystals are classified into seven basic systems. If atoms are only at corners seven crystal systems yield seven lattices. But few more lattices could be constructed by placing atoms at face center, body center etc., Bravais showed that there are 14 such lattice exist in nature. Hence the name Bravais space lattices. Each crystal system differs from the other in lattice parameters.

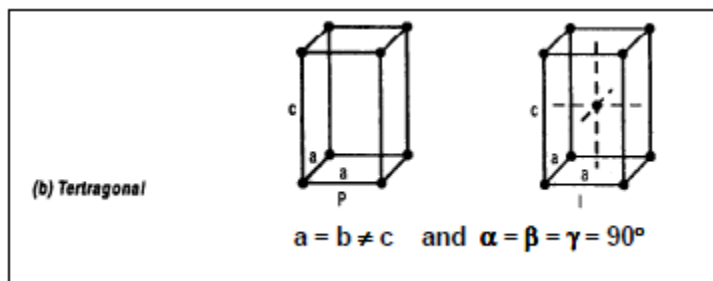
1. Cubic Crystal systems (Isometric)

(Simple or primitive, Face centered (FCC) and Body centered (BCC))



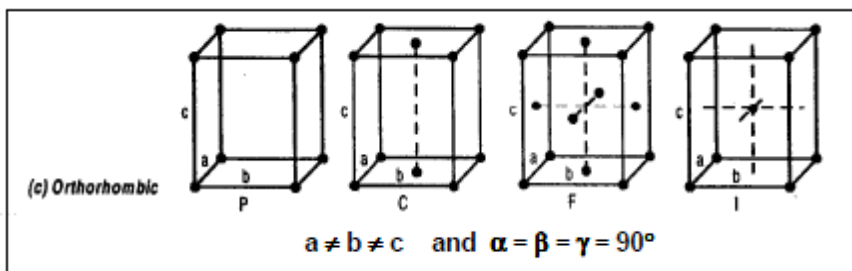
2. Tetragonal Crystal system

(Simple and Body centered)



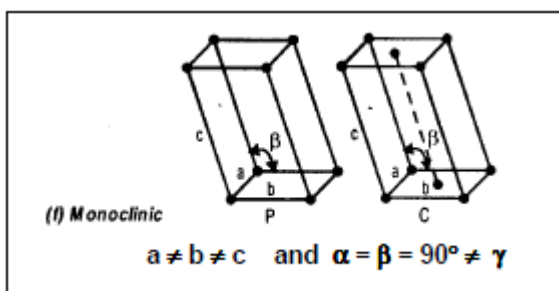
3. Orthorhombic Crystal system

(Simple, Face centered (FCC), Body centered (BCC) and Base centered)



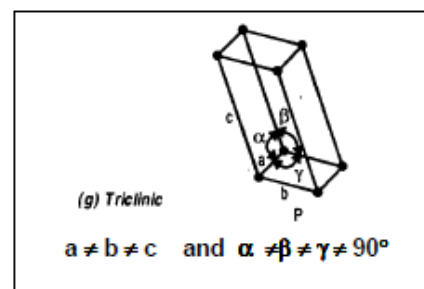
4. Monoclinic Crystal system

(Simple and Base centered)



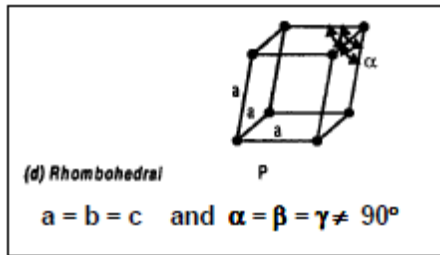
5. Triclinic Crystal system

(Simple)



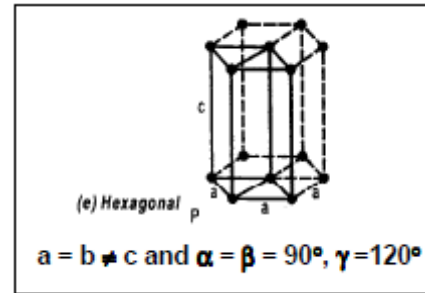
6. Trigonal Crystal system (Rhombohedral)

(Simple)



7. Hexagonal Crystal system

(Simple)

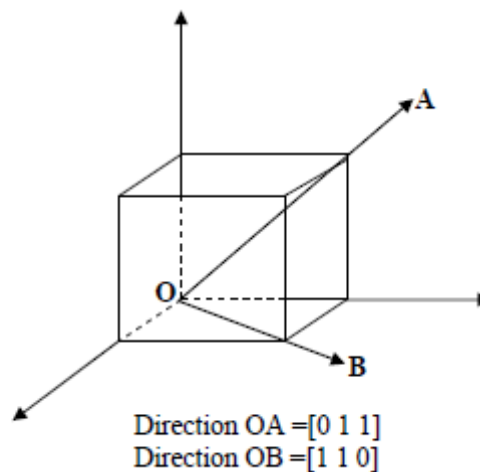
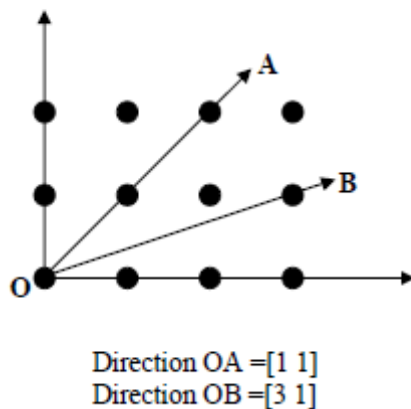


Directions and planes in a crystal

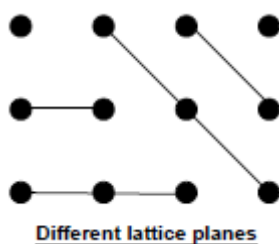
Directions: In crystals there exists directions and planes in which contain concentration of atoms. It is necessary to locate these directions and planes for crystal analysis. Arrows in two dimensions show directions.

The directions are described by giving the coordinates of the first whole numbered point ((x,y) in two dimension, (x,y,z) in three dimension) through which each of the direction passes. Directions are enclosed within square brackets.

Eg.



Planes: The crystal may be regarded as made up of an aggregate set of parallel equidistant planes, passing through the lattice points, which are known as **Lattice planes**. These lattice planes can be chosen in different ways in a crystal. The problem in designating these planes was solved by Miller who evolved a method to designate a set of parallel planes in a crystal by three numbers (**h k l**) called **Miller Indices**.



Miller indices

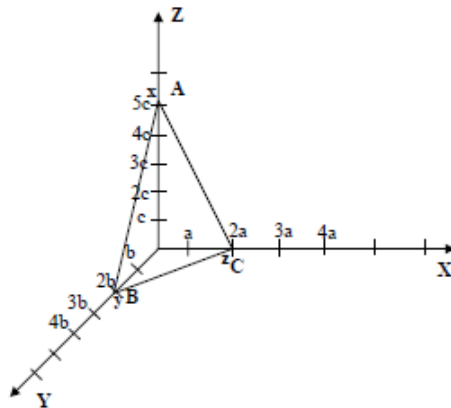
Miller Indices may be defined as the reciprocals of the intercepts made by the plane on the crystallographic axes when reduced to smallest numbers.

Steps to determine Miller Indices of given set of parallel planes:

Consider a plane ABC which is one of the planes belonging to the set of parallel planes with miller indices (h k l). Let x, y and z be the intercepts made by the plane along the three crystallographic axes X, Y and Z respectively.

1. Determine the coordinates of the intercepts made by the plane along the three crystallographic axes.
2. Express the intercepts as multiples of the unit cell dimensions or lattice parameters along the axes.
3. Determine the reciprocals of these numbers.
4. Reduce them in to the smallest set of integral numbers and enclose them in simple brackets. (No commas to be placed between indices)

Example:



1. The intercepts $x = 2a$, $y = 2b$ & $z = 5c$. Generally $x = pa$, $y = qb$ & $z = rc$.
2. The multiples of lattice parameters are

$$\frac{x}{a} = \frac{2a}{a} = 2, \frac{y}{b} = \frac{2b}{b} = 2, \frac{z}{c} = \frac{5c}{c} = 5$$

3. Taking the reciprocals

$$\frac{a}{x} = \frac{1}{2}, \frac{b}{y} = \frac{1}{2}, \frac{c}{z} = \frac{1}{5}$$

4. Reducing the reciprocals to smallest set of integral numbers by taking LCM.

$$\frac{1}{2} \times 10, \frac{1}{2} \times 10, \frac{1}{5} \times 10$$

5, 5, 2

Miller indices of the plane ABC = (h k l) = (5 5 2)

Note: a) All parallel equidistant planes have the same Miller Indices

b) If the Miller Indices have the same ratio, then the planes are parallel

c) If the plane is parallel to any of the axes, then the corresponding intercept is taken to be ∞

Expression for Interplanar spacing in terms of Miller Indices

Consider a Lattice plane ABC, which is one of the planes belonging to the set of planes with Miller indices (h k l). Let x, y and z be the intercepts made by the plane along the three crystallographic axes X, Y and Z respectively.

Let OP be the perpendicular drawn from the origin to the plane. Let α' , β' and γ' be the angles made by OP with the crystallographic axes X, Y and Z respectively. Let another consecutive plane parallel to ABC pass through the origin. Let a, b and c be the lattice parameters. OP is called interplanar spacing and is denoted by d_{hkl} .

Now from the right angled triangle OAP

$$\cos \alpha' = \frac{OP}{OA} = \frac{d_{hkl}}{x} \dots \dots \dots (1)$$

Similarly from the right angled triangle OPB

$$\cos \beta' = \frac{OP}{OB} = \frac{d_{hkl}}{y} \dots \dots \dots (2)$$

Similarly from the right angled triangle OPC

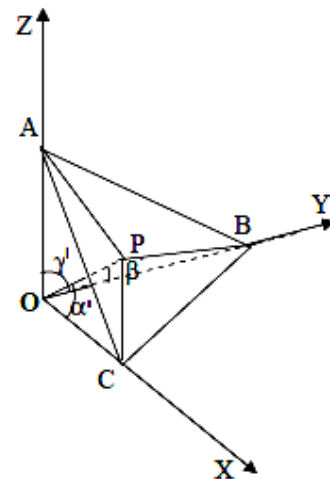
$$\cos \gamma' = \frac{OP}{OC} = \frac{d_{hkl}}{z} \dots \dots \dots (3)$$

Now the coordinates of the intercepts made by the plane ABC along the three axes are given by

$$x = n_1 a \quad y = n_2 b \quad z = n_3 c$$

$$n_1 = \frac{x}{a} \quad n_2 = \frac{y}{b} \quad n_3 = \frac{z}{c}$$

$$h = \frac{a}{x} \quad k = \frac{b}{y} \quad l = \frac{c}{z}$$



$$x = \frac{a}{h} \quad y = \frac{b}{k} \quad z = \frac{c}{l}$$

Substitute the above in the equations (1), (2) and (3)

$$(1) \Rightarrow \cos \alpha' = \frac{h}{a} d_{hkl}$$

$$(2) \Rightarrow \cos \beta' = \frac{k}{b} d_{hkl}$$

$$(3) \Rightarrow \cos \gamma' = \frac{l}{c} d_{hkl}$$

For the rectangular Cartesian coordinates system, we have

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

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

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

For the cubic lattice $a = b = c$, the interplanar spacing will be given by

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

Coordination number: It is the number of equidistant nearest neighbours that an atom has in a crystal structure.

Nearest neighbour distance: It is the distance between two neighbours in a crystal structure.

Lattice Constant: In a cubic lattice the distance between atoms remains constant along the crystallographic axes and is called Lattice Constant.

Expression for space lattice constant

Consider the case of a cubic lattice of lattice constant a . If ρ be the density of the crystal,

Volume of the unit cell = a^3

Mass of each unit cell = ρa^3 ----- (1)

But, total mass of molecule in a unit cell = no. of molecules belonging to a unit cell \times mass of each molecule.

Mass of each molecule = M / N_A

Let the number of molecules in a unit cell = n

$$\text{Total mass of molecules in a unit cell} = \frac{n M}{N_A} \text{-----(2)}$$

M is the molecular weight and N_A is the Avogadro's number

Compare (1) and (2) we get,

$$\rho a^3 = \left(\frac{n M}{N_A} \right)$$

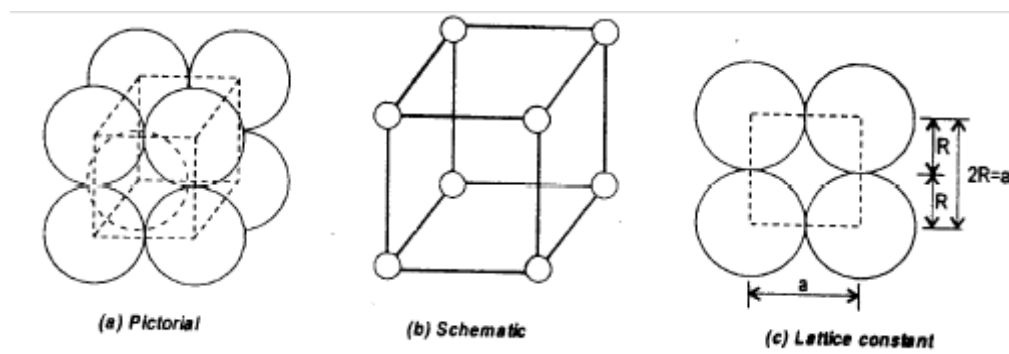
$$a = \left(\frac{n M}{\rho N_A} \right)^{1/3}$$

Atomic packing factor (APF)

It is the fraction of space occupied by atoms in a unit cell. It is defined as the ratio of volume occupied by atoms in unit cell to the volume of the unit cell. If the number of atoms per unit cell is ' n ' and if V_a the volume of atoms in the unit is cell and V is the volume of the unit cell then the Atomic packing factor is given by

$$APF = \frac{n \times V_a}{V}$$

Simple Cubic (SC) Structure



In simple cubic structure each atom consists of 6 equidistant nearest neighbors. Hence its coordination number is 6

Eight unit cells share each atom at the corner. Hence only $1/8^{\text{th}}$ of the volume of atom lies in each cell. Since the atoms are present only at corners, the number of atoms per unit cell is given by

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

We know that the APF is given by

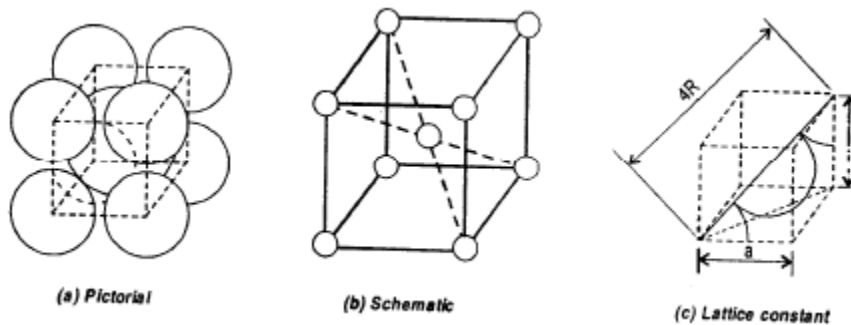
$$APF = \frac{n \times V_a}{V} \Rightarrow APF = \frac{1 \times \frac{4\pi R^3}{3}}{a^3}$$

In this structure the atoms touch each other along the sides of the cube. Therefore $a = 2R$, where R is the radius of each atom.

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

$APF = 0.5235$ Hence atoms occupy 52.35% of the volume of the unit cell.

Body Centered Cubic (BCC) Structure



Each atom has 8 equidistant nearest neighbours. Hence the co-ordination number is 8

Since there are eight atoms at corners and 1 atom at the body center, the number of atoms per unit cell is given by

$$n = 1 + \frac{1}{8} \times 8 = 2 \text{ atoms}$$

Also in this structure the atoms touch each other along the body diagonal. Therefore

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

$$16R^2 = 3a^2$$

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

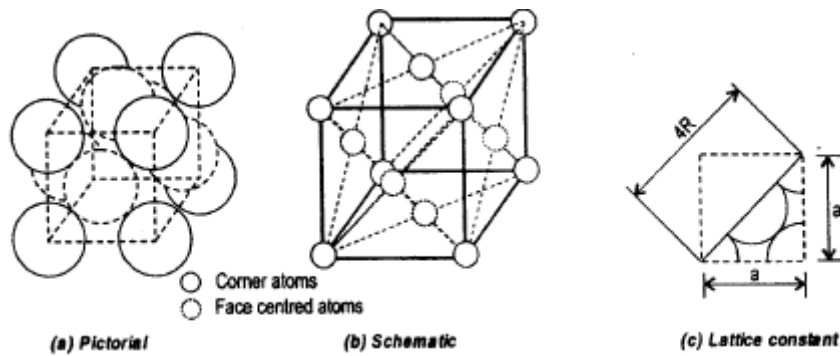
Now the APF is given by

$$APF = \frac{n \times V_a}{V} \Rightarrow APF = \frac{2 \times \frac{4\pi R^3}{3}}{a^3}$$

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

$APF = 0.6802$ Hence atoms occupy 68.02% of the unit cell

Face Centered Cubic (FCC) Structure



In FCC structure in addition to atoms at corners, atoms are present at face centers.

Each atom consists of 12 equidistant nearest neighbours. Hence the co-ordination number is 12

The number of atoms per unit cell is

$$n = \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 4 \text{ atoms}$$

In this structure atoms touch each other along the face diagonal. Therefore

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

$$16R^2 = 2a^2 \text{ Where R is atomic radius}$$

$$a = \frac{4R}{\sqrt{2}} \text{ or } a = 2\sqrt{2}R$$

The APF is given by

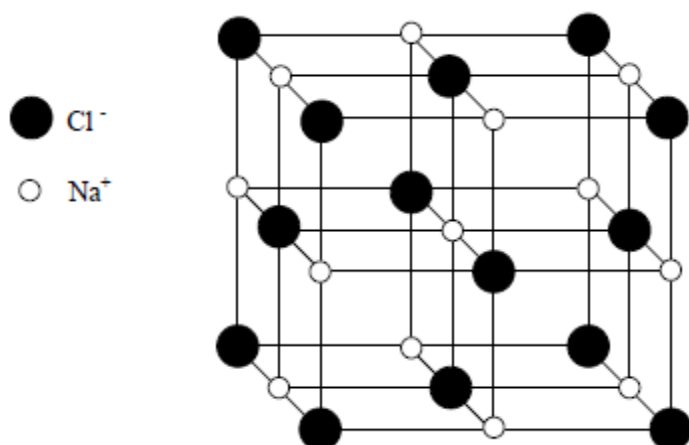
$$APF = \frac{n \times V_a}{V} \Rightarrow APF = \frac{4 \times \frac{4\pi R^3}{3}}{a^3}$$

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

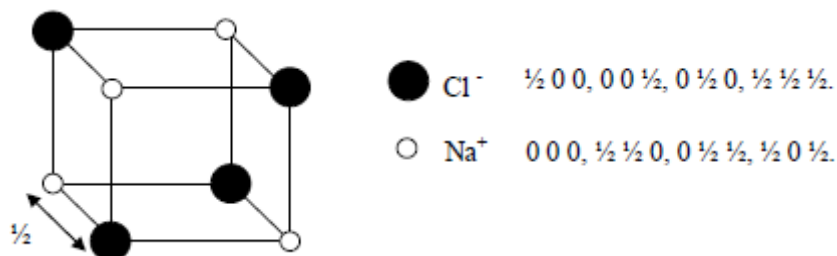
$$APF = 0.6802 \text{ Hence atoms occupy 68.02\% of the volume of the unit cell.}$$

Crystal Structure of Sodium Chloride (NaCl)

NaCl is an ionic compound. Hence both Na and Cl are in ionic state. The molecule is under equilibrium because the attractive force due to ions is balanced by repulsive force due to electron clouds.



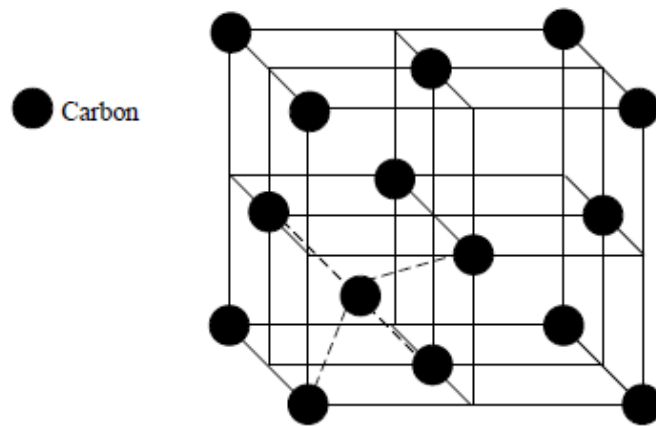
The Bravais lattice of NaCl is FCC with the basis containing one Na ion and one Cl ion. The bond length is 2.81\AA . For each atom there are 6 equidistant nearest neighbors of opposite kind. Hence the coordination number is 6. There are 12 next nearest neighbors of the same kind. The conventional cell which consists of four molecules of NaCl is as shown in the figure. The coordinates of the ions in the conventional cell are as given below. (taking Na ion as origin)



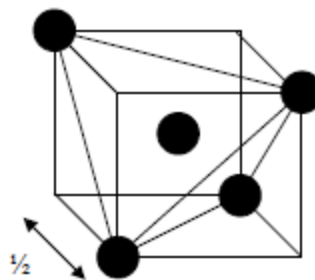
This structure could be considered as the superposed pattern of two interpenetrating Bravais lattices each made of one type of ion.

Crystal Structure of Diamond (Allotropic form of Carbon)

Diamond is an allotropic form of carbon. The Bravais lattice is an FCC similar to ZnS. There are 18 Carbon atoms in the unit cell, 8 at corners, 6 at face centres and 4 at intermediate tetrahedral positions. The unit cell is as shown in the fig.



The Co-ordinates of the atoms in conventional cell are
 $\frac{1}{4} \frac{1}{4} \frac{1}{4}, \frac{1}{2} 0 0, 0 \frac{1}{2} 0, 0 0 \frac{1}{2}, \frac{1}{2} \frac{1}{2} \frac{1}{2}$



In the unit cell, each carbon atom bonds to four other atoms in the form of a tetrahedron. Since each atom has four equidistant nearest neighbours the coordination number is 4. This structure could be considered as the superposed pattern of two interpenetrating Bravais FCC lattices each made of carbon with one displaced from the other along $\frac{1}{4}^{\text{th}}$ of the body diagonal. The inter atomic distance is 1.54 \AA and the lattice constant is 3.56 \AA .

X- Ray Diffraction

We know that, for the diffraction to take place, the width between two lines of the grating must be comparable with the dimension of the wavelength of the wave.

In the case of optical diffraction gratings, there will be about 15,000 lines per inch, which are distributed uniformly in a plane. The light passing through the grating undergoes diffraction and produces a diffraction spectrum.

In the case of X-rays, wavelength is of the order of 10^{-8}cm . An optical grating will be ineffective to cause diffraction of X-rays, since, wavelength is less than slit width.

But, we know that, the dimensions of atoms are of the order of 10^{-8}cm and the atoms are distributed uniformly in a crystal. Therefore a crystal provides an excellent facility to diffract the X-rays.

Bragg's Diffraction Theory:

When a beam of X-rays falls on a crystal, each atom becomes a source of scattering radiations. It has already been mentioned that in a crystal there are certain planes which are particularly rich in atoms. The combined scattering of X-rays from these planes can be looked upon as reflections from these planes. Generally, the Bragg scattering is known as Bragg reflection and the planes are known as Bragg planes. At certain glancing angles, reflection from these planes are in phase with each other and hence they reinforce each other to produce maximum intensity. For other angles, the reflections from different planes are out of phase and hence they reinforce to produce zero intensity.

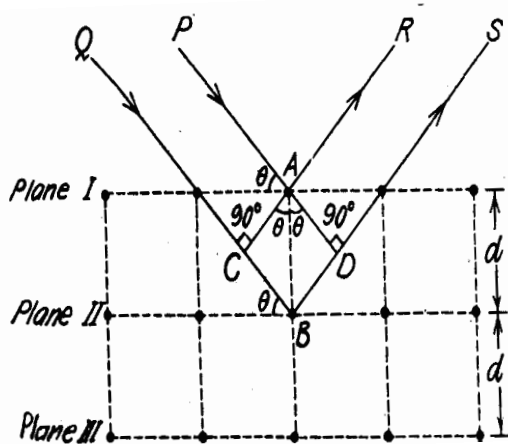
Bragg's Law:

Consider a set of parallel lattice planes of a crystal separated by a distance 'd' apart. Suppose a narrow beam of X-rays of wavelength λ be incident upon these planes at an angle θ called glancing angle as shown in figure. The beam will be reflected in all directions by the atoms of various atomic planes.

Consider a ray PA reflected at atom A in the direction AR from plane 1 and another ray QB reflected at another atom B in the direction of BS from plane 2. The atom B in the plane 2 lies immediately below the atom A.

Draw two perpendiculars AC and AD from the atom on the incident ray QB and reflected ray BS respectively.

From the figure, it is observed that the ray QBS travels more distance than the ray PAR. The two reflected rays will be in phase or out of phase will depend upon this path difference. We know that the two rays will reinforce when the path difference is equal to $n\lambda$ (bright fringe)



Hence, the path difference between the two rays = $CB + BD$

From the ΔABC $CB = AB \sin \theta$

From the ΔABD $BD = AB \sin \theta$

Therefore, the Path difference $= 2 AB \sin \theta$

But AB is the interplanar spacing and is 'equal to 'd'

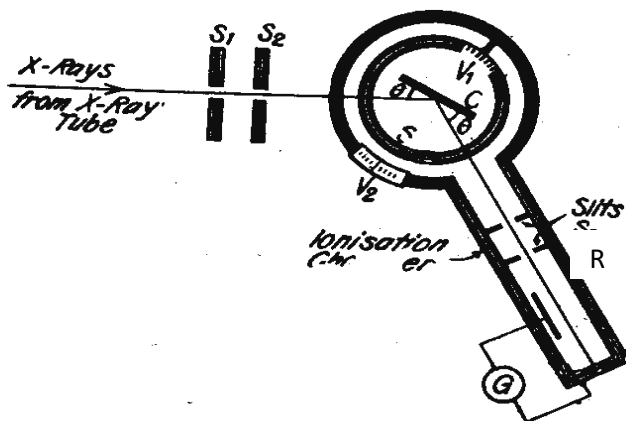
$$\therefore \text{Path difference} = 2d \sin \theta$$

For constructive interference, path difference $= n\lambda$, where $n = 1, 2, 3, \dots$

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

The above equation is called Bragg's Law and θ is called the glancing angle.

Bragg's X-ray spectrometer:



Construction: The X-rays from X-ray tube are passed through the two slits S_1 and S_2 and the narrow beam of X-rays are obtained.

Then it is made to fall on a crystal C at a glancing angle θ which is mounted on the circular turn table of the spectrometer.

The turn table rotates about its vertical axis passing through the center. The rotation can be read on the vernier scale V_1

The reflected beam then passes through slits S_3 and enters the ionization chamber, which is mounted on the arm R. It is capable of rotation about same axis as the turn table. The ionization chamber contains a gas with electrodes.

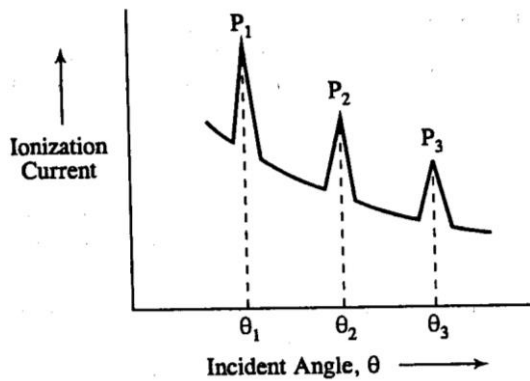
The position of the ionization chamber can be read by vernier V_2 .

The turn table and ionization chamber are linked together in such a way that, when the turn table rotates an angle θ , the ionization chamber turns through an angle 2θ . Thus irrespective of the glancing angle, the reflected beam is always enters in to the ionization chamber.

On entering into the ionization chamber, the reflected X-rays ionize the gas, which in turn will produce ionization current and can be measured by galvanometer.

Working: Let us consider a monochromatic X-ray beam. The crystal is placed on the turn table. The turn table is adjusted so that the glancing angle is almost zero.

The glancing angle θ is increased by rotating the turn table step by step. And for each step, the ionization current is measured from the galvanometer.



Plot the graph ionization current versus glancing angle.

The intensity of ionization current increases For certain values of θ . Because, when the reflected rays from the crystal reinforce, the intensity of X-rays entering the ionization chamber increases causing a rise in the ionization current. Reinforcement occurs when Bragg's law is obeyed.

The rise in current occurs more than once as θ is varied because law is satisfied for various values of n , i.e.

$$2d \sin \theta_1 = \lambda \quad n=1, \text{ this is for the first order spectrum}$$

$$2d \sin \theta_2 = 2\lambda \quad n=2, \text{ this is for the first order spectrum}$$

$$2d \sin \theta_3 = 3\lambda \quad n=3, \text{ this is for the first order spectrum}$$

Thus it is found that $\sin \theta_1 : \sin \theta_2 : \sin \theta_3 = 1 : 2 : 3$

This helps in assessing the accuracy of measurements of $\theta_1, \theta_2, \theta_3$.

From the graph:

- i) The intensity of the reflected X-rays beam decreases as the order of the spectrum increases.
- ii) The fact that the ionization current never reaches zero shows that X-rays spectrum is a continuous.
- iii) The positions of the peaks depend on the nature of the target material and the reflecting surfaces of the crystal.

Determination of d:

One can measure the interplanar spacing d , through the relation $2d \sin \theta = n\lambda$, using the measured value of θ from the above graph, provided n the order and λ the wavelength of the incident X-ray are known.

Determination of λ :

If the glancing angle θ is determined experimentally as described above for the known order spectrum (preferably first order) and if the interplanar spacing d of the crystal for any given plane is found, the wavelength λ of the X-ray can be calculated by Bragg's equation

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