Solid State Physics

Lattice

A crystal is periodic repetition of identical structural units in space. This periodic repetition is called lattice

Lattice can be defined as n dimensional array of points, each of which has identical surroundings.

Basis

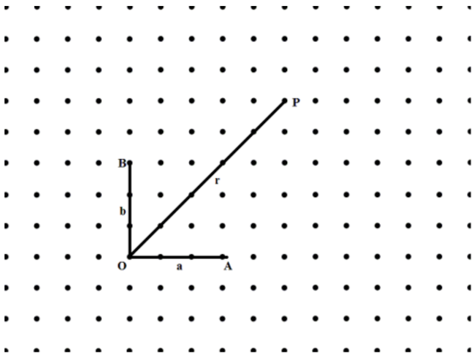
A group of atoms attached to each lattice point is called as basis; which when repeated in space forms a crystal

Translation vector

A lattice in three dimension is defined by three fundamental translation vectors $\vec{a}$, $\vec{b}$ & $\vec{c}$ such that the atomic arrangement looks the same when viewed from a point $\vec{r} = n_1\vec{a} + n_2\,\vec{b} + n_3\,\vec{c}$

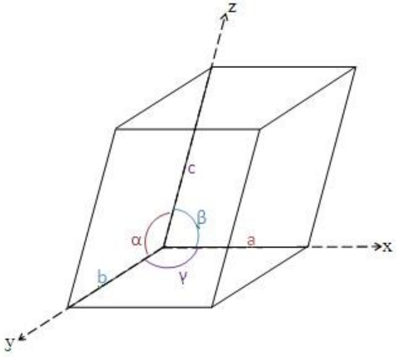
Where n_1, n_2 & n_3 are integers

In two dimension $\vec{r} = n_1\vec{a} + n_2\,\vec{b}$ is as shown in figure.



Unit cell

Unit cell is the smallest volume which when repeated in all direction gives the crystal.

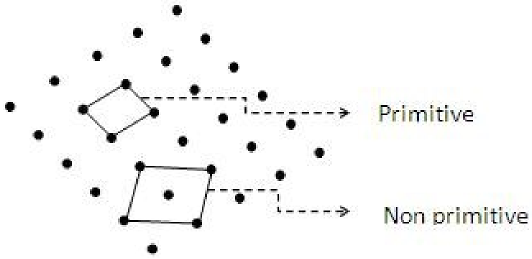


The three edges a, b, c along the axis and angle between them α, β and γ is termed as lattice parameters. In 3D it is better to consider a parallelepiped as unit cell.

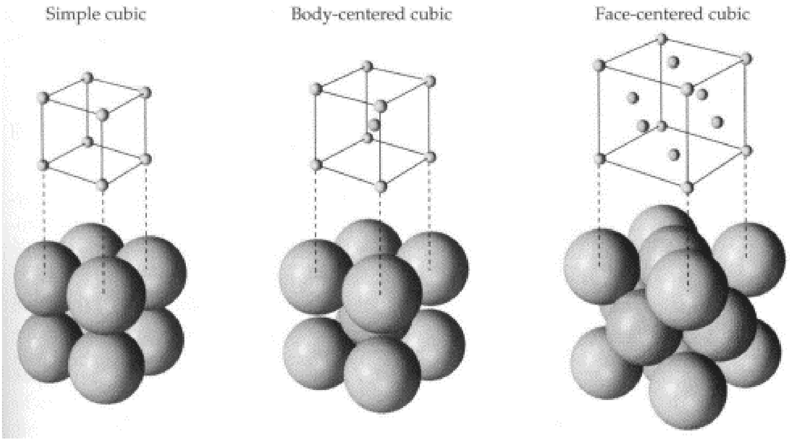
Types of unit Cell

Primitive: The unit cell having only one lattice point per unit cell in it is called primitive cell.

Non primitive : The unit cell having more than one lattice point per unit cell in it is called non primitive.



In the given figure below, simple cube is a primitive cell. Number of atoms per unit cell is one for it. Body centered cubic and face centered cubic is non primitive. No. of atoms per unit cell is 2 and 4 respectively.

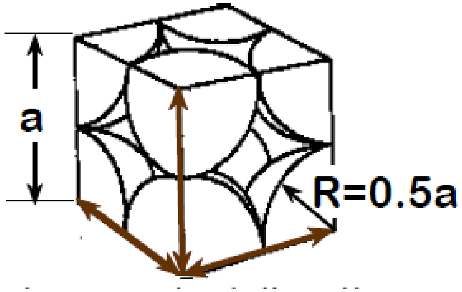


Simple Cubic Structure (SC)

Simple cube has eight corner atoms. Each corner atom contribute 1/8th to unit cell. And each atom has six nearest atom.

Number of atoms per unit cell = 8 atoms X 1/8 = 1

Co-ordination number =6



If a is lattice constant then atomic radius, r = a/2

Atomic packing fraction = $\frac{volume\ of\ atoms}{volume\ of\ unit\ cell}$

Atomic packing fraction = $\frac{1X\,\frac{4}{3}4\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\frac{4}{3}\pi r^3}{8r^3}$

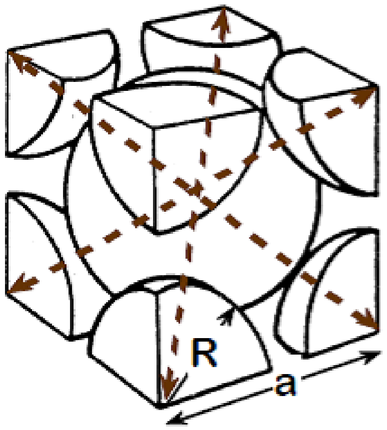
$$= \frac{\pi}{6} = 0.526 \ = 52.6\%$$

Body Centered Cubic Structure (BCC)

Body centered cube has eight corner atoms and one atom at the center. Each corner atom contribute 1/8th to unit cell. And center atom has eight nearest atom.

Number of atoms per unit cell = 8 atoms X 1/8 (corner atom)+ 1 (center atom) = 2

Co-ordination number = 8



If a is lattice constant then atomic radius, r = $\frac{\sqrt{3}a}{4}$

Atomic packing fraction = $\frac{volume\ of\ atoms}{volume\ of\ unit\ cell}$

Atomic packing fraction = $\frac{2X\,\frac{4}{3}4\pi r^3}{a^3} = \frac{\frac{8}{3}\pi\left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\frac{8}{3}\pi\frac{3\sqrt{3}}{64}a^3}{a^3}$

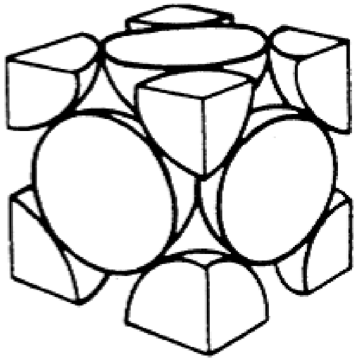
$$= \frac{\sqrt{3}}{8}\pi = 0.68\ = 68\%$$

Face Centered Cubic Structure (BCC)

Face centered cube has eight corner atoms and six atom at the center of each face. Each corner atom contribute 1/8th to unit cell and each atom at the center of the face contributes ½ to unit cell. And center atom at the center of the face has 12 nearest atom.

Number of atoms per unit cell = 8 atoms X 1/8 (corner atom) +6X 1/2 (corner atom (face center atom) = 4

Co-ordination number = 12



If a is lattice constant then atomic radius, r = $\frac{\sqrt{2}a}{4}$

Atomic packing fraction = $\frac{volume\ of\ atoms}{volume\ of\ unit\ cell}$

Atomic packing fraction = $\frac{4X\,\frac{4}{3}4\pi r^3}{a^3} = \frac{\frac{16}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3} = \frac{\frac{16}{3}\pi\frac{2\sqrt{2}}{64}a^3}{a^3}$

$$= \frac{\sqrt{2}}{6}\pi = 0.74\ = 74\%$$

The 7 Crystal Systems

The crystals can be classified according to the relationship between the lattice sides a, b, and c and angles α, β and γ.

collectively called Crystal Systems: Tricinic, Monoclinic, Orthorhombic, Tetragonal, Trigonal, Hexagonal, and Cubic.

1) Cubic crystal

In this crystal,

i) All the sides of unit cell are equal
ie. a=b=c

ii) All the sides of unit cell are at right angle to each other
ie. $\alpha = \beta = \gamma = 90°$
Ex. NaCl, KCl, etc.

2) Tetragonal crystal

In this crystal,

i) Two sides of unit cell are equal but third one is longer.
ie. a=b≠c

iii) All the sides of unit cell are at right angle to each other
ie. $\alpha = \beta = \gamma = 90°$
ex. $NiSO_4$, SnO_2, etc.

3) Orthorhombic crystal

In this crystal,

ii) All sides of unit cell are different.
ie. a≠b≠c

iv) All the sides of unit cell are at right angle to each other
ie. $\alpha = \beta = \gamma = 90°$
ex. KNO_3, $BaSO_4$, etc.

4) Rhombohedral crystal (or Trigonal)

In this crystal,

i) All the sides of unit cell are equal
ie. a=b=c

ii) All the sides of unit cell are equally inclined to each other to an angle other than $90° < 120°$
ie. $\alpha = \beta = \gamma \neq 90° < 120°$
ex. $CaSO_4$, etc.

5) Monoclinic crystal

In this crystal,

i) All sides of unit cell are different.
ie. a≠b≠c

iii) The two sides of unit cell are at right angle but third one is oblique.
ie. $\alpha = \beta = 90° \neq \gamma$
ex. Na_2SO_4, etc.

6) Triclinic crystal

In this crystal,

ii) All sides of unit cell are different.
ie. a≠b≠c

iv) All the sides are oblique to each other.
ie. $\alpha \neq \beta \neq \gamma$
ex. $K_2\,Cr_2O_7$, Cu_2SO_4etc.

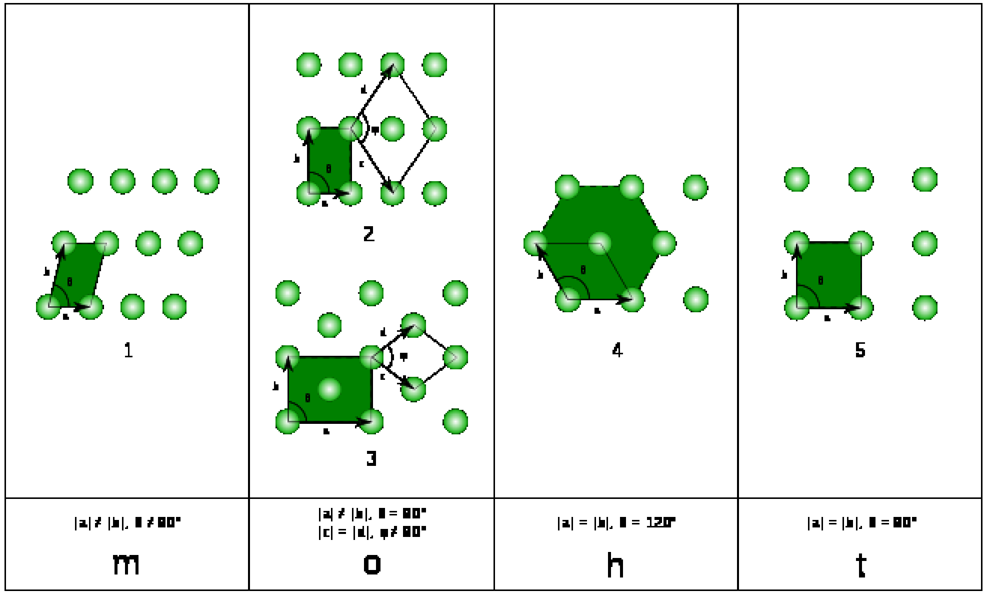
7) Hexagonal crystal

In this crystal,

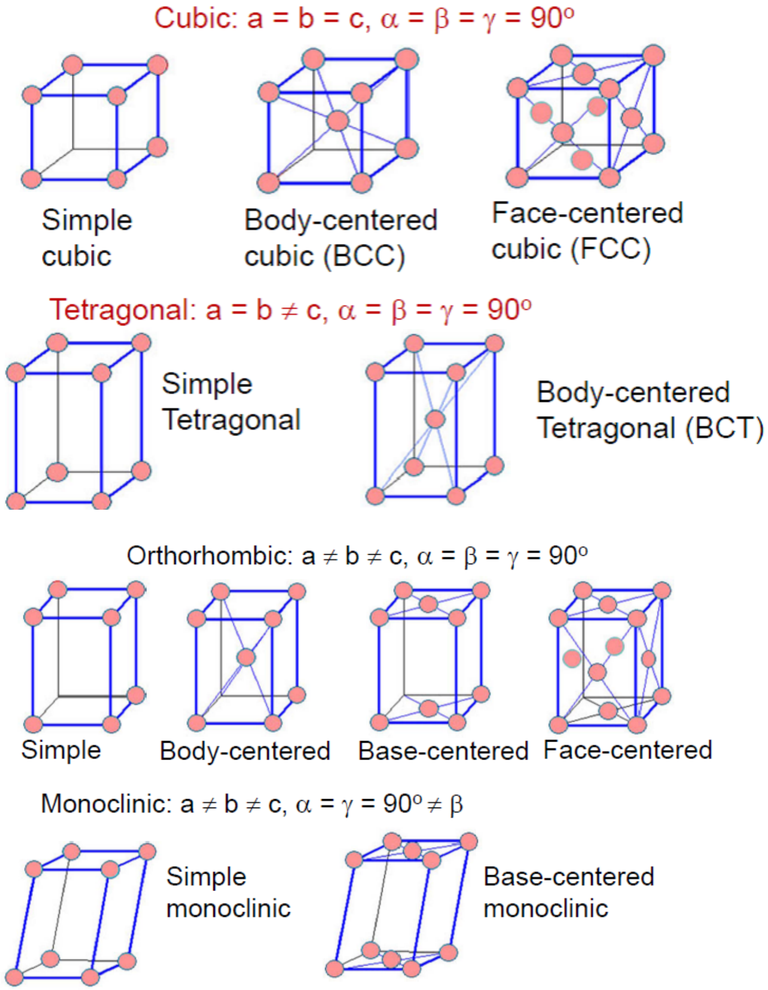
i) Two sides of unit cell are equal but third one is longer.
ie. a=b≠c

v) The two sides of unit cell are at right angle but third one is 120°.
ie. $\alpha = \beta = 90° \quad \gamma = 120°$
ex. SiO_2, AgI etc.

Bravais Lattice in Two dimension-Plane lattice



1 – oblique, 2 – rectangular, 3 – centered rectangular, 4 – hexagonal, and 5 – square.

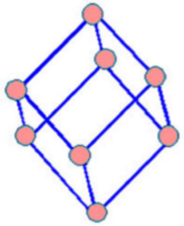


Bravais Lattice in Three dimension-Space lattice

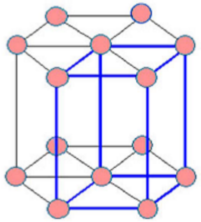
Based on the lattice parameters a, b, c, α, β and γ and applying the restrictions as above, only 7 types of crystals are possible in three dimensions.

They are triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic.

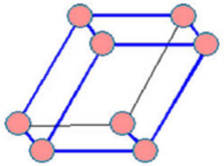
Seven different crystals are again represents 14 Bravais lattice.



Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90^{o}$



Hexagonal
$a = b \neq c$
$\alpha = \beta = 90^{o}\ \gamma = 120^{o}$



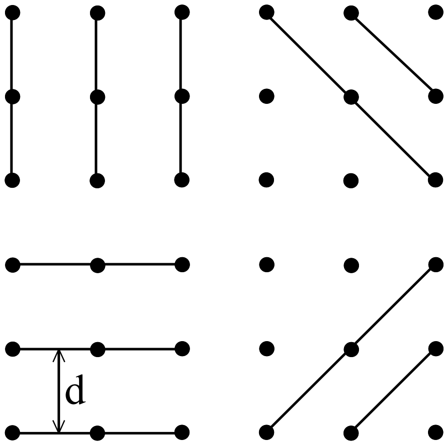
Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^{o}$

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.

For a given lattice, the lattice planes can be chosen in a different number of ways.

DIFFERENT LATTICE PLANES



The orientation of planes or faces in a crystal can be described in terms of their intercepts on the three axes. Miller introduced a system to designate a plane in a crystal ie. a set of three numbers to specify a plane in a crystal. This set of three numbers is known as '**Miller Indices**' of the concerned plane.

Miller indices is defined as the reciprocals of the intercepts made by the plane on the three axes.

Procedure for finding Miller Indices

Step 1: Determine the intercepts of the plane along the axes X,Y and Z in terms of the lattice constants a,b and c.

Step 2: Determine the reciprocals of these numbers.

Step 3: Find the least common denominator (*lcd*) and multiply each by this *lcd*.

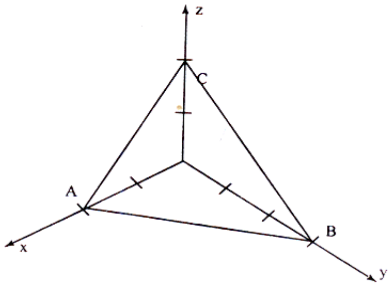
Step 4: The result is written in parenthesis. This is called the `Miller Indices' of the plane in the form (h k l).

Note:- 1) If a plane cuts an axis on the negative side of the origin, corresponding index is negative.

2) A plane which is parallel to any one of the co-ordinate axes has an intercept of infinity (∞). Therefore the Miller index for that axis is zero; i.e. for an intercept at infinity, the corresponding index is zero.

ILLUSTRATION

1)



Plane ABC has intercepts of 2 units along X-axis, 3 units along Y-axis and 2 units along Z-axis.

DETERMINATION OF 'MILLER INDICES'

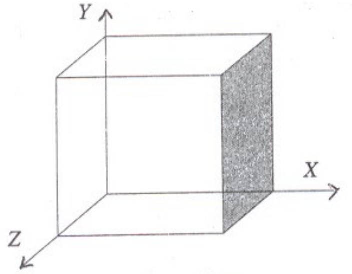
Step 1: The intercepts are 2,3 and 2 on the three axes.

Step 2: The reciprocals are 1/2, 1/3 and 1/2.

Step 3: The least common denominator is '6'. Multiplying each reciprocal by lcd, we get, 3,2 and 3.

Step 4: Hence Miller indices for the plane ABC is (3 2 3)

2)



a. (100) plane

(1 0 0) plane

Plane parallel to Y and Z axes

In the above plane, the intercept along X axis is 1 unit. The plane is parallel to Y and Z axes. So, the intercepts along Y and Z axes are '∞'.

Step 1: Now the intercepts are 1, ∞ and ∞.

Step 2 : The reciprocals of the intercepts are = 1/1, 1/∞ and 1/∞.

Step 3 : Therefore the Miller indices for the above plane is (1 0 0).

3. **Miller indices for the plane with intercepts 2a,- 3b and 4c the along the crystallographic axes.**

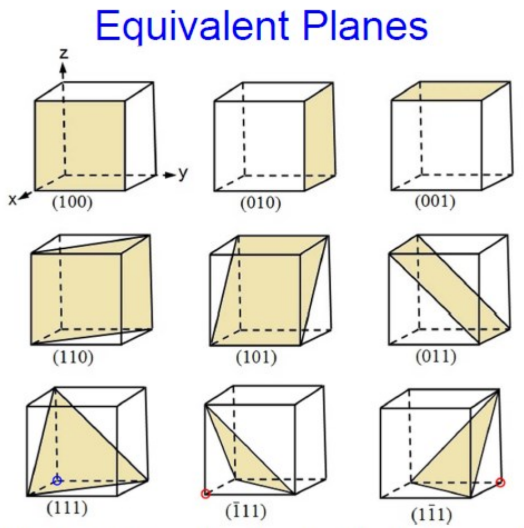
Step 1: The intercepts are 2, -3 and 4 along the 3 axes

Step 2: The reciprocals are

Step 3: The least common denominator is 12. Multiplying each reciprocal by lcd, we get 6 -4 and 3

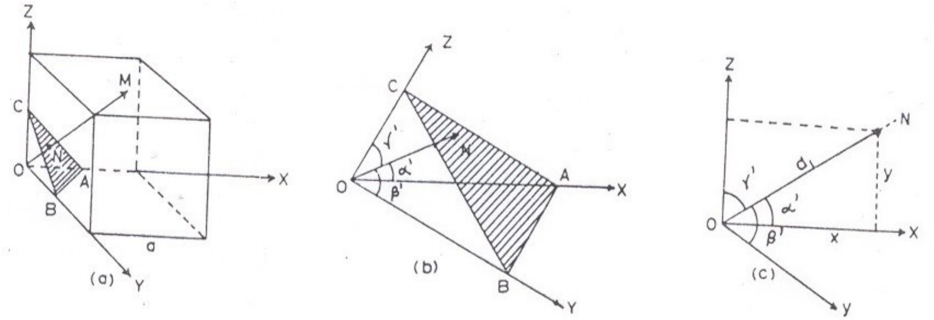
Step 4: Hence the Miller indices for the plane is (6 $\bar{4}$ 3)

MILLER INDICES OF SOME IMPORTANT PLANES



Note the shift of origin from blue to red circle for the negative indices

SEPARATION BETWEEN LATTICE PLANES (Inter planar distance)



Consider a crystal of side a, b and c be the length of sides along X, Y and Z axis respectively and a plane ABC, whose Miller indices are (h k l)

Let ON = d_1 , be the perpendicular distance of the plane ABC from the origin.

Let α′, β′ and γ' (different from the interfacial anglesα, β and γ) be the angles between co- ordinate axes X,Y,Z and ON respectively.

The intercepts of the plane on the three axes are,

$$OA = \frac{a}{h}\ , OB = \frac{b}{k} \text{and } OC = \frac{c}{l} \quad \text{........(1)}$$

From the figure, (a), we have,

$$\cos\alpha' = \frac{d_1}{OA}, \cos\beta' = \frac{d_1}{OB} \ \&\ \cos\gamma' = \frac{d_1}{OC} \quad \text{.....(2)}$$

From equation 1 and 2, we get,

$$\cos\alpha' = d_1\frac{h}{a}, \cos\beta' = d_1\frac{k}{b} \ \&\ \cos\gamma' = d_1\frac{l}{c} \quad \text{.....(3)}$$

From the property of direction of cosines,

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

From equation 2 and 3, we get,

$$d_1^2\left[\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2\right] = 1$$

i.e. $d_1^2 = \frac{1}{\left[\left(\frac{h}{a}\right)^2+\left(\frac{k}{b}\right)^2+\left(\frac{l}{c}\right)^2\right]}$

$$d_1 = \sqrt{\frac{1}{\left[\left(\frac{h}{a}\right)^2+\left(\frac{k}{b}\right)^2+\left(\frac{l}{c}\right)^2\right]}} = \sqrt{\left(\frac{a}{h}\right)^2+\left(\frac{b}{k}\right)^2+\left(\frac{c}{l}\right)^2}$$

i.e. the perpendicular distance between the origin and the 1st plane ABC is,

$$d_1 = ON = \sqrt{\left(\frac{a}{h}\right)^2+\left(\frac{b}{k}\right)^2+\left(\frac{c}{l}\right)^2} \qquad \text{....(4)}$$

Now, let us consider the next parallel plane A'B'C'. Let OM=d_2 be the perpendicular distance of this 2nd plane from the origin.

The intercepts of this plane along the three axes are

$OA' = \frac{2a}{h}$, $OB' = \frac{2b}{k}$ and $OC' = \frac{2c}{l}$

Then d_2 becomes

$$d_2 = OM = 2\sqrt{\left(\frac{a}{h}\right)^2+\left(\frac{b}{k}\right)^2+\left(\frac{c}{l}\right)^2} \qquad \text{.........(5)}$$

Hence spacing between two consecutive planes (ie. ABC and A'B'C')

$$d = d_2 - d_1 = 2\sqrt{\left(\frac{a}{h}\right)^2+\left(\frac{b}{k}\right)^2+\left(\frac{c}{l}\right)^2} - \sqrt{\left(\frac{a}{h}\right)^2+\left(\frac{b}{k}\right)^2+\left(\frac{c}{l}\right)^2}$$

$$d = \sqrt{\left(\frac{a}{h}\right)^2+\left(\frac{b}{k}\right)^2+\left(\frac{c}{l}\right)^2} \qquad \text{....}(6)$$

For Simple cube a = b = c ; let it be a

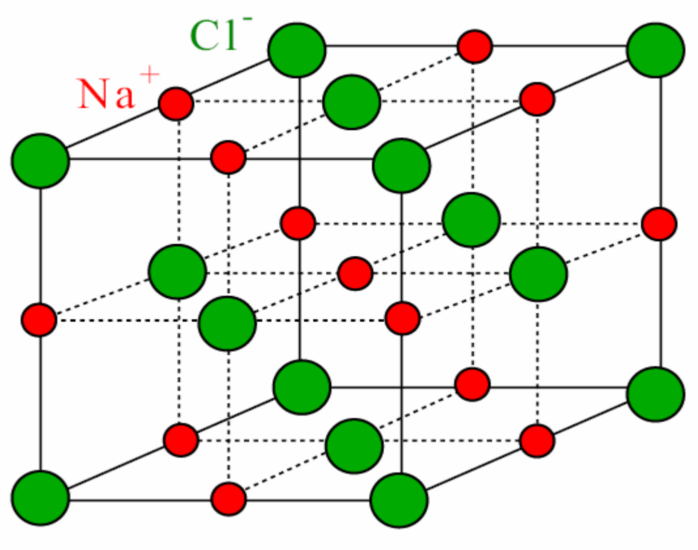
Then d for simple cube is,

$$d = \sqrt{\left(\frac{a}{h}\right)^2+\left(\frac{a}{k}\right)^2+\left(\frac{a}{l}\right)^2} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Special cases:

1) Simple cube: $d_{100}: d_{110}: d_{111} = 1: \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$
2) Body centered cube : $d_{100}: d_{110}: d_{111} = 1: \frac{2}{\sqrt{2}} : \frac{1}{\sqrt{3}}$
3) Face centered cube : $d_{100}: d_{110}: d_{111} = 1: \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

NaCl structure



NaCl has FCC structure with Na^+ and Cl^- ions as basis. The Na^+ ions are situated at corners as well as at the center of the faces of cube. Cl^- ions are relatively placed at ½ of the edge of unit cell along each axis.

NaCl crystal is formed by interpenetration of two BCC sub lattices of Na^+ and Cl^- ions exactly at the half of the edge of the lattice along each axis.

If the Cl^- ions occupy corners of the unit cell, one corner is taken as the origin and the coordinates of ions are expressed in fractions of the edge length of the cube. The coordinates of Cl^- ions are 000, ½0½, 0½½, ½ ½ 0.

In the same system the coordinates of the four Na ions are ½½½ , ½00, 0½0, 00½

No of atoms per unit cell: The unit cell of NaCl contains four sodium and four chlorine ions. Therefore the unit cell contains 4 NaCl molecules.

The Each unit cell has 8 corner Cl^- atoms contributing 1/8th to the unit cell. And 6 face centered atoms contributing ½ to the unit cell.

No of Cl^- atoms per unit cell = (1/8 x 8 corner atoms)

+ (1/2 x 6 face atoms)

= 4

The Each unit cell has 12 edge center Na^+ atoms contributing 1/4th to the unit cell. And 1 body center atom.

No of Na^+ atoms per unit cell = (1/4 x 12 edge center atoms)

+ (1 body center atoms)

= 4

Coordination number: Each Na^+ ion has 6 nearest Cl^- ions and each Cl^- has 6 nearest Na^+ ions.

The coordination number for opposite kind of ions is 6 with distance ($d=a/2$)

The coordination number for same kind of ions is 12 with distance ($d= a/\sqrt{2}$)

Note: KCl has same structure instead of sodium Na potassium K atom and KCl is simple cube(from Bragg's law)

X- Ray diffraction

X-ray has wavelength of order 0.1 to 1A^o . Ordinary grating with 6 X 10^5 lines per metre can not produce X-ray diffraction. For X- ray diffraction to take place 4000 million lines per metre grating is required which is impossible.

Laue suggested that crystal can be used to produce diffraction of X- ray. This diffraction pattern consists of a central spot and a series of spots arranged in a definite pattern around the central spot. This pattern is known as Laue's pattern.

The diffraction depends on the crystal structure and on the wavelength.When the wavelength of the radiation is comparable with or smaller than the lattice constant, one can find diffracted beams in directions quite different from the incident radiation.

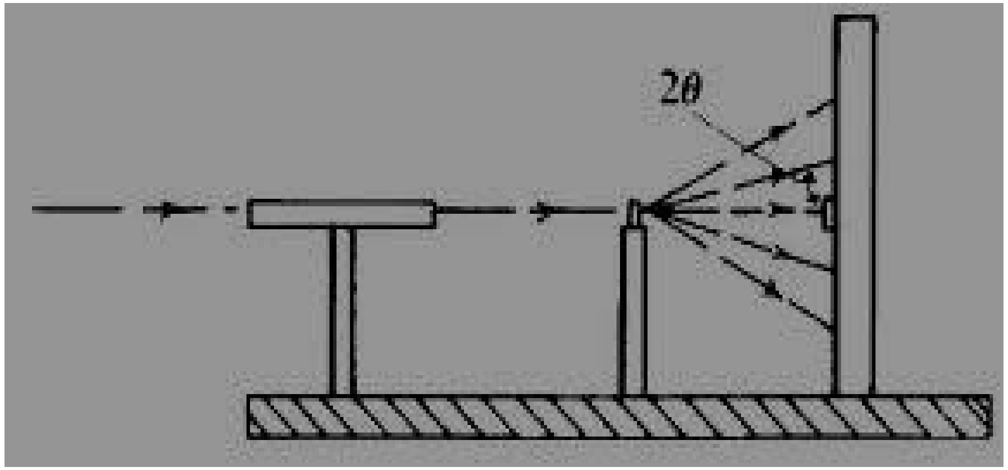
The structure of a crystal can be determined by studying the diffraction pattern of a beam of radiation incident on the crystal.

Beam diffraction takes place only in certain specific directions, much as light is diffracted by a grating. By measuring the directions of the diffraction and the corresponding intensities, one obtains information concerning the crystal structure responsible for diffraction.

LAUE METHOD

The Laue method is one of the x-ray diffraction techniques used for crystal structure studies.

The experimental arrangement is as in fig.



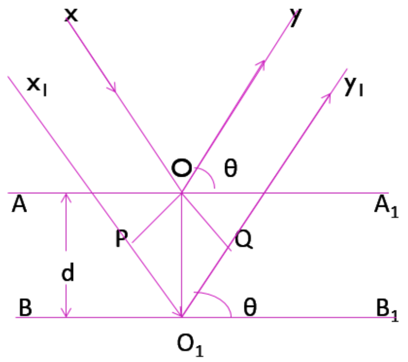
The crystal whose structure has to be studied is held stationary in a continuous x-ray beam.

After passing through the pin holes of lead diaphragm a fine beam of x-rays is obtained

These x-rays are allowed to fall on the crystal. The crystal planes in the crystal diffract the x – rays satisfying Bragg's law. The diffracted x-rays are allowed to fall on a photographic plate.

The diffraction pattern consists of a series of bright spots corresponding to interference, satisfying the Braggs Law, for a particular wavelength of incident X-rays.

Bragg's Law



If 'd' is the inter planar spacing in a crystal,

λ is the wave length of the Incident x-rays

n is the order of diffraction spots

θ is glancing angle,

Then 2d sinθ = nλ

This Eq^n is known as Bragg's law.

Proof :- Consider a set of parallel planes of crystal in which spacing between successive planes is d. If a narrow beam of X-ray of wavelength λ be incident on the planes with glancing angle θ.

Let AA_1 and BB_1 are two consecutive planes and XO and X_1O_1 are the two light rays , reflected at O and O_1 along OY and OY_1, such that

$YOA_1 = Y1O_1B_1 = \theta$

OP and Oq are perpendicular lines drawn from O on X1O1. Then path difference between two beams reflected at two consecutive planes is $\Delta = PO_1 + O_1Q$

From Δle OPO_1

$$\sin POO_1 = \sin\theta = \frac{PO_1}{OO_1} = \frac{PO_1}{d}$$

$$PO_1 = d\sin\theta$$

From Δle OQO_1

$$\sin QOO_1 = \sin\theta = \frac{QO_1}{OO_1} = \frac{QO_1}{d}$$

$$QO_1 = d\sin\theta$$

$\therefore \Delta = PO_1 + O_1Q = d\sin\theta + d\sin\theta = 2d\sin\theta$

If path difference is integral multiple O

Importance of Bragg's law:

1. From Bragg's law the inter planar distance can be calculated
2. The lattice constant 'a' can be calculated from the value of d
3. Knowing ρ and M(molecular weight) of the crystal and the number of atoms N in unit cell, a can be calculated. By the formula $a = \left(\frac{M}{2N\rho}\right)^{1/3}$
4. Knowing d and a, $[h^2 + k^2 + l^2]$ can be calculated
5. Depending on the values of $h^2 + k^2 + l^2$ we can classify the crystal structure .

Bragg's X-ray spectrometer

Bragg's spectrometer used to determine the wavelength of X–rays is shown in Fig. Bragg's spectrometer is similar in construction to an ordinary optical spectrometer.

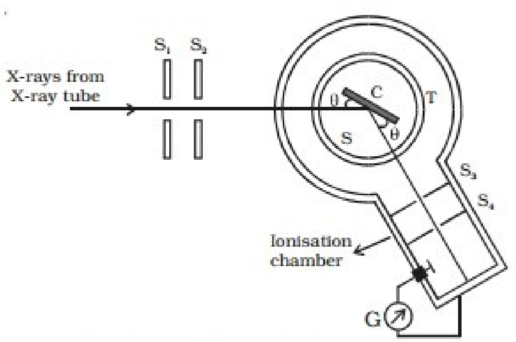


Fig Bragg's spectrometer

X–rays from an X-ray tube are made to pass through two fine slits S_1 and S_2 . This fine X-ray beam is then made to fall upon the crystal 'C' mounted on the spectrometer table. This table is capable of rotation about a vertical axis and its rotation can be read on a circular graduated scale S.

The reflected beam after passing through the slits S_3 and S_4 enters the ionization chamber. The X-rays entering the ionization chamber ionize the gas which causes a current to flow between the electrodes and the current can be measured by galvanometer G. The ionization current is a measure of the intensity of X-rays reflected by the crystal.

Verification of Bragg's law

The ionization current is measured for different values of glancing angle θ. A graph is drawn between the glancing angle θ and ionization current (Fig.).

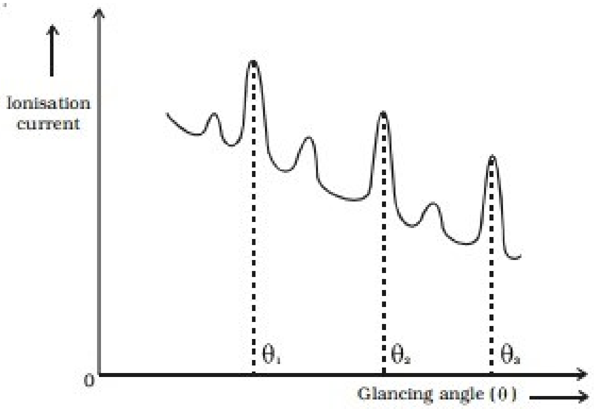


Fig Plot of glancing angle and ionisation current

- For certain values of glancing angle, the ionization current increases abruptly. The first peak corresponds to first order, the second peak to second order and so on.
- From the graph, the glancing angles for different orders of reflection can be measured.
- From Bragg's law

$2d\ \sin\theta_1 = 1\lambda\,, 2d\ \sin\theta_2 = 2\lambda\,, 2d\ \sin\theta_3 = 3\lambda \ldots \ldots$

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

Bragg's law and crystal structure

a) KCl stucture

For (100) , (110) and (111) planes the glancing angles are found to be $5^0 23'$, $7^0 37'$ and $9^0 25'$ respectively

By Bragg's law (2d sinθ = nλ)

The ratios of d for 100) , (110) and (111) planes are found to be

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

Hence KCl belongs to simple cubic.

a) NaCl stucture

For (100) , (110) and (111) planes the glancing angles are found to be $5^0$23' , $7^0$37' and 5^0 respectively

By Bragg's law (2d sinθ = nλ)

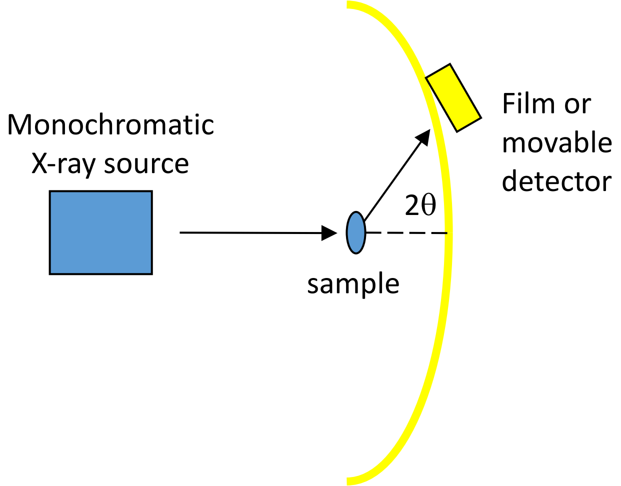
The ratios of d for 100) , (110) and (111) planes are found to be

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

Hence NaCl belongs to Face centre cubic.

Powder Crystal Method

The powder method is an X-ray diffraction technique used to study the structure of micro crystals in the form of powder. The experimental arrangement is as in the figure.



It consists of a cylindrical camera, consisting of a film in the inner portion.

The powder is prepared by crushing the polycrystalline material so that it consists of crystallites.The finely powdered crystal is filled in a capillary tube and held stationary.

Around the powder specimen a photograph film is set circularly so as to record the diffraction at any possible angle ϴ.

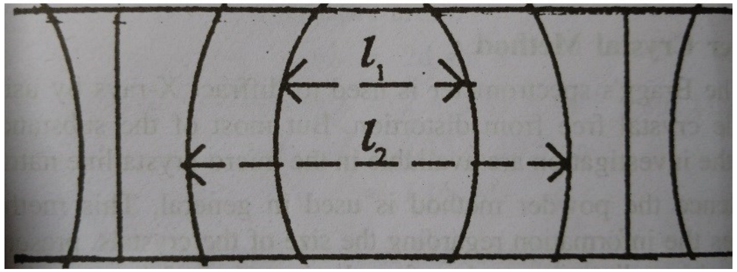
Procedure:

A fine beam of monochromatic x-rays are send through the powdered crystal. The x-rays are diffracted from individual micro crystals which orient with planes making Bragg's angle ϴ with the beam For different values of ϴ and d.

The diffracted rays corresponding to fixed values of ϴ and d, lie on the surface of a cone with its apex at the tube p and the semi vertical angle 2ϴ.

Different cones are observed for different sets of ϴ and d, for a particular order of n.

The diffracted X-ray cones make impressions on the film in the form of arcs. It is noted that arcs are reversed when angle of diffreaction exceeds 90°



Let l_1, l_2, l_3 be the distances between symmetric lines and D is diameter of the cylindrical film

Then $\theta_1 = \frac{90^\circ}{\pi D}\, l_1$, $\theta_2 = \frac{90^\circ}{\pi D}\, l_2$, $\theta_3 = \frac{90^\circ}{\pi D}\, l_3$