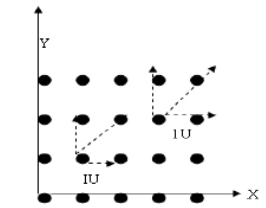
Crystal Structure

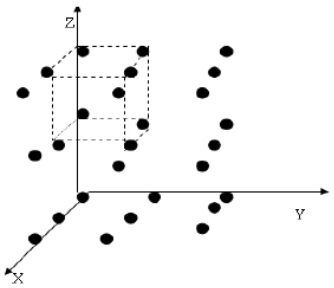
What is mean by Space lattice?

In order to study about crystal structure (ie., the atomic arrangement), it is convenient to imagine periodic arrangement of points in space about which these atoms are located. This leads to the concept of space lattice.

"A space lattice is defined as infinite array of points in space, such that the environment about each point is the same"



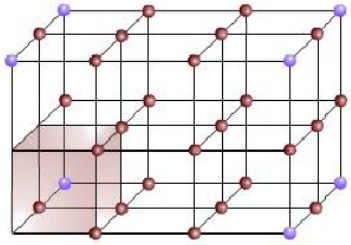
2-Dim. lattice (or) Plane lattice

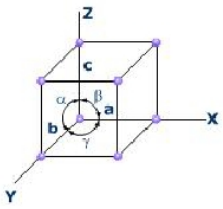


3-Dim. Lattice (or) space lattice

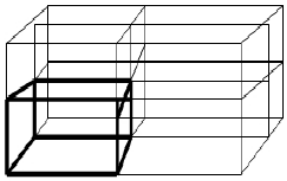
What is mean by unit cell?

unit cell is the **smallest geometric unit,** the repetition of which generates the entire crystal structure". The unit cells are also called as "Building blocks", in most of the crystals, the unit cells are **cube or parallello piped**"


Representation of space lattice and unit cell



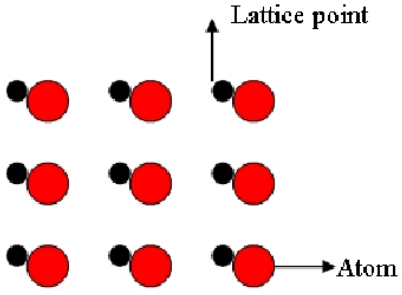
Representation of dimensions of a unit cell

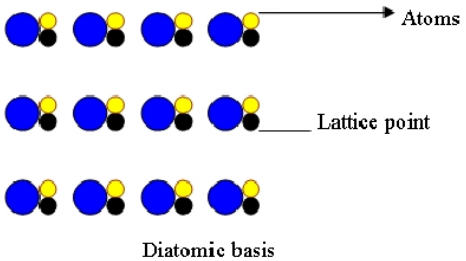


What is "Basis"?

The sets of one **or more atoms situate at each and every lattice** point is known as basis .The lattice together with basis is known as crystal structure.

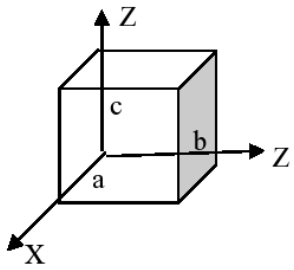
Lattice + Basis ⟶ Crystal structure





Diatomic basis

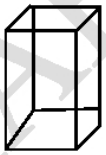
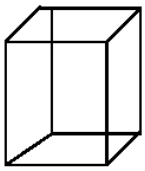
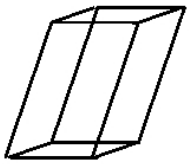
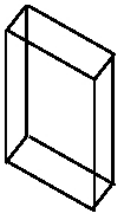
What are lattice parameters?

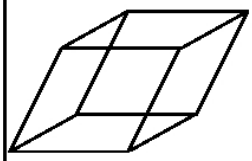
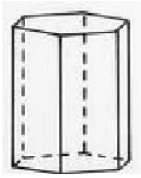


There are six lattice parameters to specify a crystal systems , they are

1. X,Y and Z are called Crystallographic axes
2. a,b and c are called primitives
3. α, β and γ are called interfacial or interaxial angles.

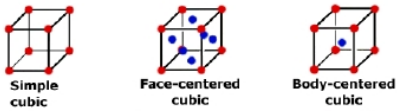
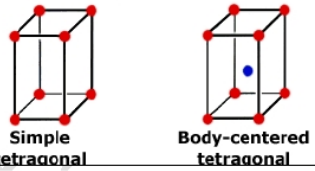
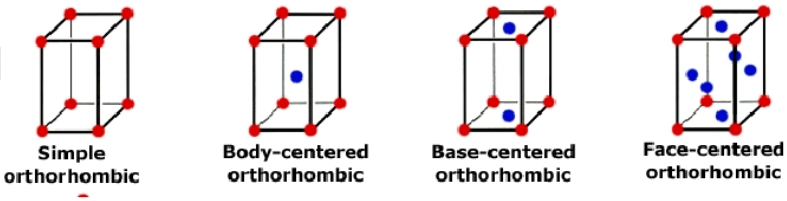
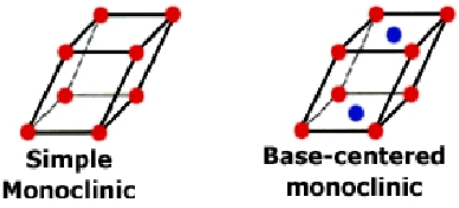
Define the seven crystal systems?

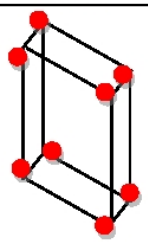
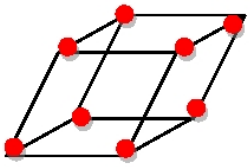
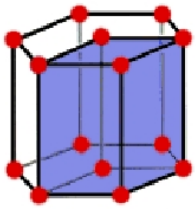
SL.NO	CRYSTAL SYSTEM	UNIT CELL	EXAMPLE
Cube	a=b=c α=β=γ=90⁰		Nacl, Cu, Au
Tetragonal	a≠b=c α=β=γ		TiO_3,Sn O
Orthorhombic	a≠b≠c α=β=γ		KnO_3,$BaSo_4$
Monoclinic	a≠b≠c α≠β=γ		$CaSo_4$,$NaSo_4$..
Triclinic	a≠b≠c α≠β≠γ		$K_2Cr_2O_7$

Rhomobedral	$a=b=c$ $\alpha=\beta=\gamma\neq 90^0$		As, Sb, Bi…..
Hexagonal	$a=b\neq c$ $\alpha=\beta=90^0$, $\gamma=120^0$		Si O_2, Zn, Mg

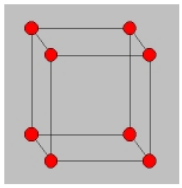
What are Bravais lattics?

Bravais showed there are 14 types of lattices possible in seven crystal systems known as of Bravais lattices.

Crystal System	No of lattices	Type of lattice	Bravais Lattices
Cube	3	P,I,F	
Tetragonal	2	P,I	
Orthorhombic	4	P,I,F,C	
Monoclinic	2	P,C	

Triclinic	1	P	
Rhomobedral	1	P	
Hexagonal	1	P	 Hexagonal

Explain about Simple Cubic Structure.



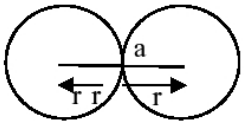
1. Atomic arrangement:
In this type of lattice the atoms will be situated only at the eight corners of the unit cell.

2. Co-ordination number:
It is nothing but the **number of equidistant nearest neighbors** that an atom has in a unit cell.
Therefore the co-ordination number of the SC structure is = 6

3. Atomic radius:

Form the figure $2r = a$

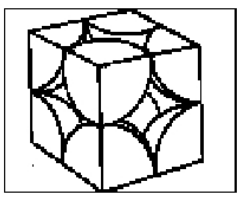
$r = a/2$



4. Effective number of atoms:

Since each atom in the unit cell is shared by 8 unitcells , the contribution of the Atom belong to the particular unit cell is Only 1/8
Therefore the effective number of atom Belong to a particular unit cell is **8 x 1/8 =1**

1 unit cell



(contains 8 x 1/8 = 1 atom)

Packing fraction:

$$P.F = \frac{\text{Volume occupied by the atoms in the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{\text{Effective number of atoms x Volume of each atom}}{\text{The volume of the unit cell}}$$

$$= \frac{1 \times \frac{4}{3} \times \pi \times \frac{a^3}{8}}{a^3} = \frac{\pi}{6} = 0.52 \text{ or } 52\%$$

Conclusion:

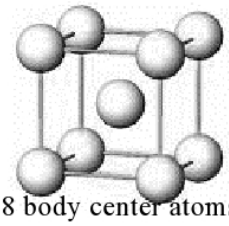
Since the atoms occupy only 52% of the volume of the unit cell, the remaining space ids left free. Therefore it is a **loosely packed structure.**

Example: Polonium

Explain about body centre cubic system.

Atomic arrangement:

In this case in addition to eight corner atoms, one atom will be situated exactly at the center of the unit cell.



Co-ordination number:

The coordination number for BCC structure is **eight.** For the corner atoms the 8 body center atoms in the surrounding unit cells are the equidistant nearest neighbors

Atomic radius:

From the figure

In the triangle ACD

$DC^2 = DA^2 + AC^2$

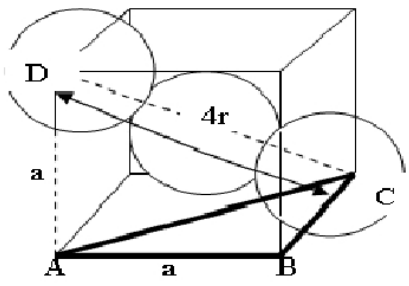
$(4r)^2 = a^2 + AC^2$ ---------- (1)

In the triangle ABC

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

$= a^2 + a^2$

$= 2a^2$ ---------- (2)



by sub. (2) in (1)

$16 r^2 = a^2 + 2a^2$

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

Effective no of atoms:

i) Corner atoms = 8 x 1/8 = 1

ii) Body center atom = 1

2

Packing fraction:

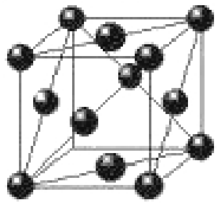
$$P.F = 2 \times 4/3 \times \pi \times \frac{3\sqrt{3}\,a^3}{64\,a^3} = \frac{\sqrt{3}\,\pi}{8} = 0.68 \text{ or } 68\%$$

Conclusion:

Since only 68% of the volume is occupied by the atoms, it is a **loosely packed structure**.

Examples: Fe, Cr, Na …….

Explain about face Centre cubic system.



Atomic arrangement:

In this case in addition to the 8 corner atoms, six faces consisting of center atoms.

Co-ordination number:

The co-ordination number for FCC Structure is equal to 12

Atomic radius:

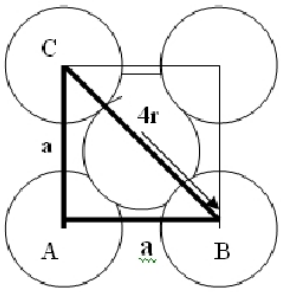
From the figure

In the triangle ABC,

$CB^2 = CA^2 + AB^2$

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

$r^2 = a^2/8 = a/(2\sqrt{2})$



The effective number of atoms

i) corner atoms $= 8 \times 1/8 = 1$

ii) FC atoms $= 6 \times ½ = 3$

4

Packing fraction:

$$\text{Packing Fraction} = \frac{4 \times \frac{4}{3}\pi\left(\frac{a^3}{8 \times 2 \times \sqrt{2}}\right)}{a^3} = \frac{\pi}{3\sqrt{2}} = 74\%$$

Conclusion:

It is a closed packed structure

Example:

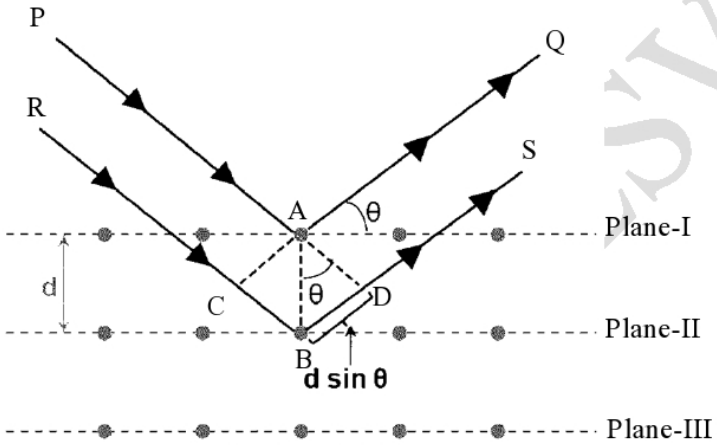
Aluminum, copper, nickel, gamma iron, gold, and silver

Explain about Braggs Law:

According to Bragg, when a monochromatic X-ray beam of suitable wavelength is allowed to fall on a crystal, then **each atom** inside the crystal acts as a **source of scattering,** the reflected rays from the crystal produces **constructive interference only when the path between them is integral multiple of the wavelength used.**

Proof:

Let us consider a ray $\overrightarrow{PA}$ incident at an atom "A", after reflection moves in the direction $\overrightarrow{AR}$. Another ray $\overrightarrow{QB}$ incident at an atom "B" after reflection moves in the direction $\overrightarrow{BS}$ as shown below.



Let "θ" be the angle of incident and angle of reflection called "Glancing angle". Acc. to Bragg, these two rays interfere constructively only when the path difference between them is integral multiple of wavelength "λ".

Ie

$$\text{Path difference} = n\lambda$$

The path difference = CB+BD

= d sin θ + d sin θ

= 2d sin θ

Acc. to Braggs Law

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

When n = 1,2,3……..

$$Sin\theta = \frac{n\lambda}{2d}$$

When n=1

$Sin\theta_1 = \frac{\lambda}{2d}$ 1st order diffraction)

n =2

$Sin\theta_2 = \frac{2\lambda}{2d}$ 2nd order diffraction)

Note:

In the triangle ABC

$\sin\theta = \frac{CB}{AB} = \frac{CB}{d} =$ d sinθ

In the triangle BCD

$sin\theta = \frac{BD}{AB} = \frac{BD}{d} =$ d sinθ

X- Ray diffraction methods:

Powder crystal method:

Principle:

In this case a monochromatic X-ray beam of wavelength "λ"("λ" is constant) is allowed to fall on thousands of randomly oriented micro crystals (ie., "θ" is a variable) which are existing in the form of powder. Of that larger number of crystals, the crystals which oriented in such a way that their "θ" value satisfies Braggs relation can produce diffraction.

Experimental setup:

Source:

A monochromatic X-Ray beam of wave length (K_α- Line) is used as the source. Zirconium filters are used for this purpose.

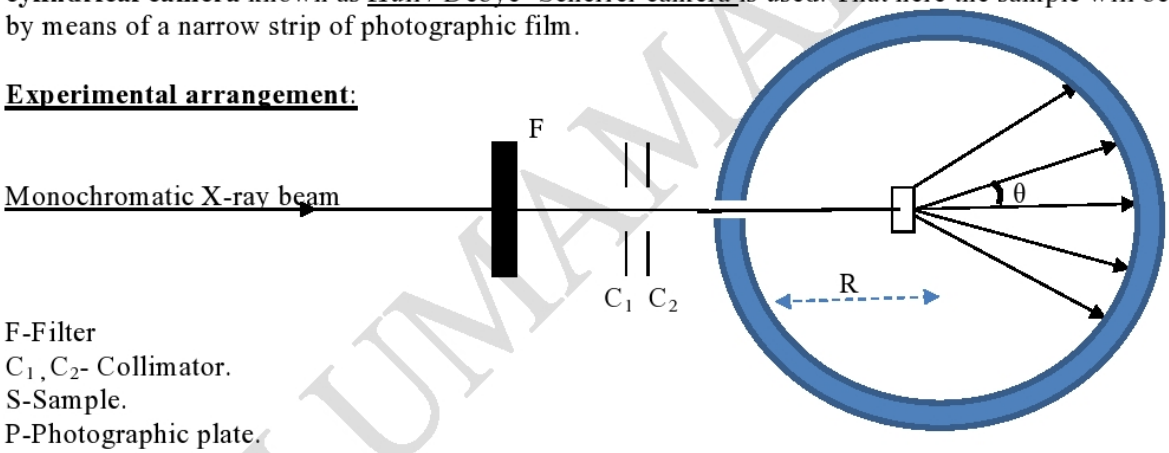
Sample:

Here the sample used is a finely grinded polycrystalline material. The grain size is of the order of 1 to 3 micrometer. The sample is taken in a capillary tube of diameter 0.3 to 0.5 mm.

Hull / Debye- Scherrer camera:

Since the sample in this case in the form of powder , flat cameras cannot be used. A special type of **cylindrical camera** known as Hull / Debye- Scherrer camera is used. That here the sample will be surrounded by means of a narrow strip of photographic film.

Experimental arrangement:



F-Filter
C_1 , C_2- Collimator.
S-Sample.
P-Photographic plate.

Procedure:

The sample is irradiated with monochromatic beam of X-rays, then among the very large number of micro crystals, the crystals which are oriented in such a way that their " θ " value satisfies Braggs relation can able to produce diffraction.

In this case the diffracted rays will be emerging in the form of cone whose semi vertical angle is equal to "2θ ", for each sets of planes there will be a cone of reflected rays.

Result:

From the above method we can calculate "θ" value

$$\theta = \frac{S}{4R}$$

"S" –Diameter of the ring under consideration, "R"- Radius of the camera

Laue method

Principle:

In this case the crystal is kept stationary(ie., θ is constant). A heterogeneous (or) a white X-ray is allowed to fall in the crystal which is kept stationary (ie., λ is variable).Each sets of planes select only a particular wavelength from the source and diffracts only that particular wavelength in order to satisfy Braggs relation.

Experimental set up:

Source:

A Heterogeneous or a white X-Ray of wavelength in the range 0.2 to 2 A^0 is used as a source.

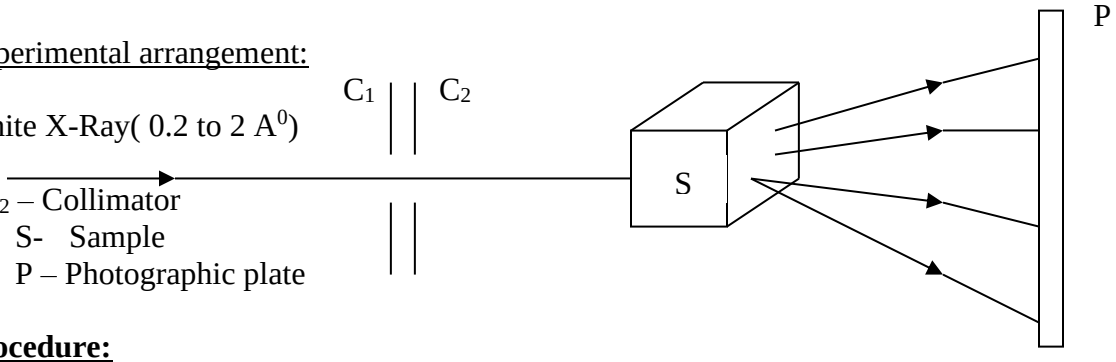
Collimator:

A pinhole arrangement in the lead diaphragm acts as collimator, which is used to collimate the X-Rays in order to get sharp diffraction pattern.

Sample:

The sample used here is a crystal (Zn S).

Experimental arrangement:



Procedure:

Transmission Laue Method:

The X-ray (White X-ray which is coming from the sample penetrates the crystal and gets scattered from different diffraction planes, each sets of diffraction plane selects only a particular wave length and diffracts it in order to satisfy Braggs relation.

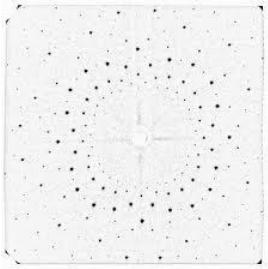
The diffraction pattern consists of a central bright spot and sets of spots arranged symmetrically around the central spot.

The diffraction pattern will be elliptical in shape in the case of transmission Laue method.

Result:

From the method we can calculate " θ" using the expression

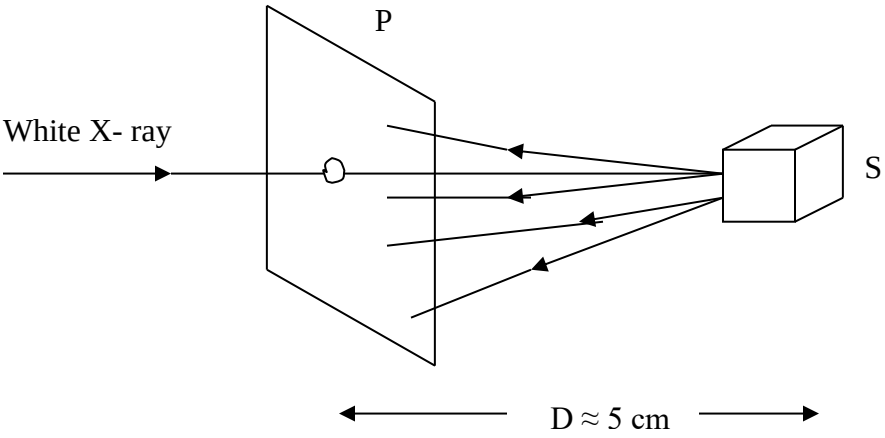
$$\tan 2\theta = \frac{r_1}{D}$$



'r_1' is thedistance between the central bright spot and the spot under consideration.
'D' is the distance between the sample and the photographic plate.(nearly equal to 5 cm).

Back reflection method:

The experimental setup for the black reflection method is shown below.



From this method the" θ" value is calculated using the expression

$$\tan(180- 2\theta) = \frac{r_2}{D}$$

" r_2" is the distance between the central bright spot and the spot under consideration.
" D" is the distance between the sample and the photographic plate.

The diffraction pattern in this case is **Hyperbola** in shape.

Miller Indices

Miller indices are nothing but 3 smallest integers used to represent the crystal planes. The Miller indices are 3 small integers; they are the reciprocals of the intercepts along the 3 co-ordinate axes.

Procedure to find Miller indices:

Step 1: Find the intercepts of the plane along the 3 co-ordinate axes in terms of cell dimensions a, b & c .

For example
Intercept on X- axis= p a
Intercept on Y- axis= q b
Intercept on Z- axis= r c

Where p,q &r are the intercepts of the plane along 3 axes.

Step 2: Take the reciprocals of the intercepts

For example

$$\frac{1}{p},\frac{1}{q},\frac{1}{r}$$

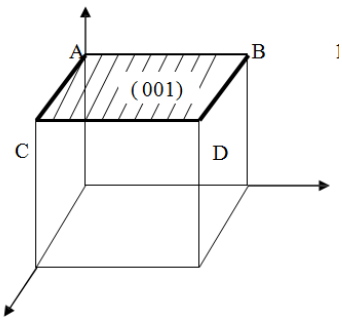
Step 3: Reduce the reciprocals into smallest integer values by tacking LCM

$$\frac{qr}{pqr},\frac{pr}{pqr},\frac{pq}{pqr}$$

Step 4: Enclose them inside the parenthesis without commas (h k l)

1) For the plane ABCD

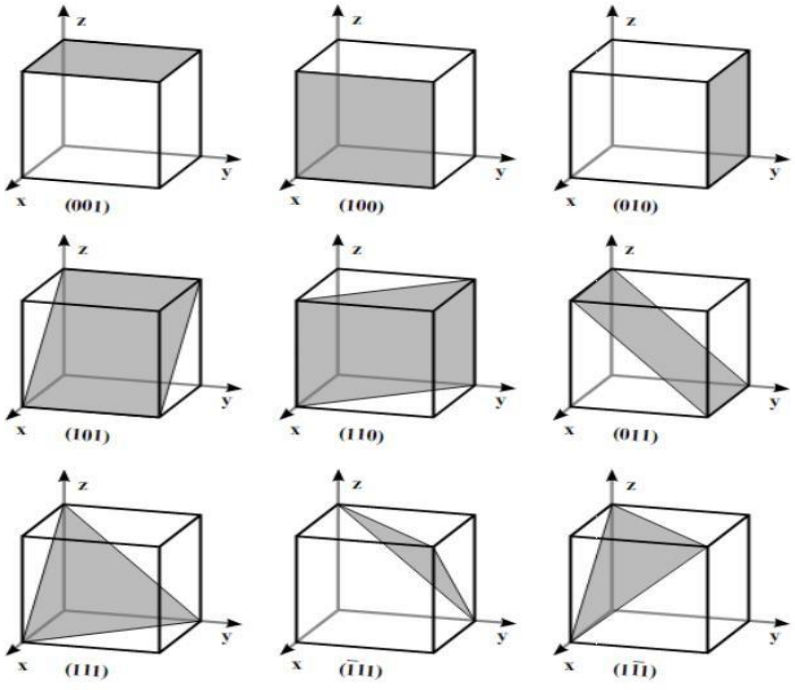
The intercept along X-axis is= ∞ a
The intercept along Y-axis is= ∞ b
The intercept along Z-axis is= 1 c



2) The reciprocals of the intercepts

$$\frac{1}{\infty},\frac{1}{\infty},\frac{1}{1}$$

3) The plane is (0 0 1)



Different planes of a crystal

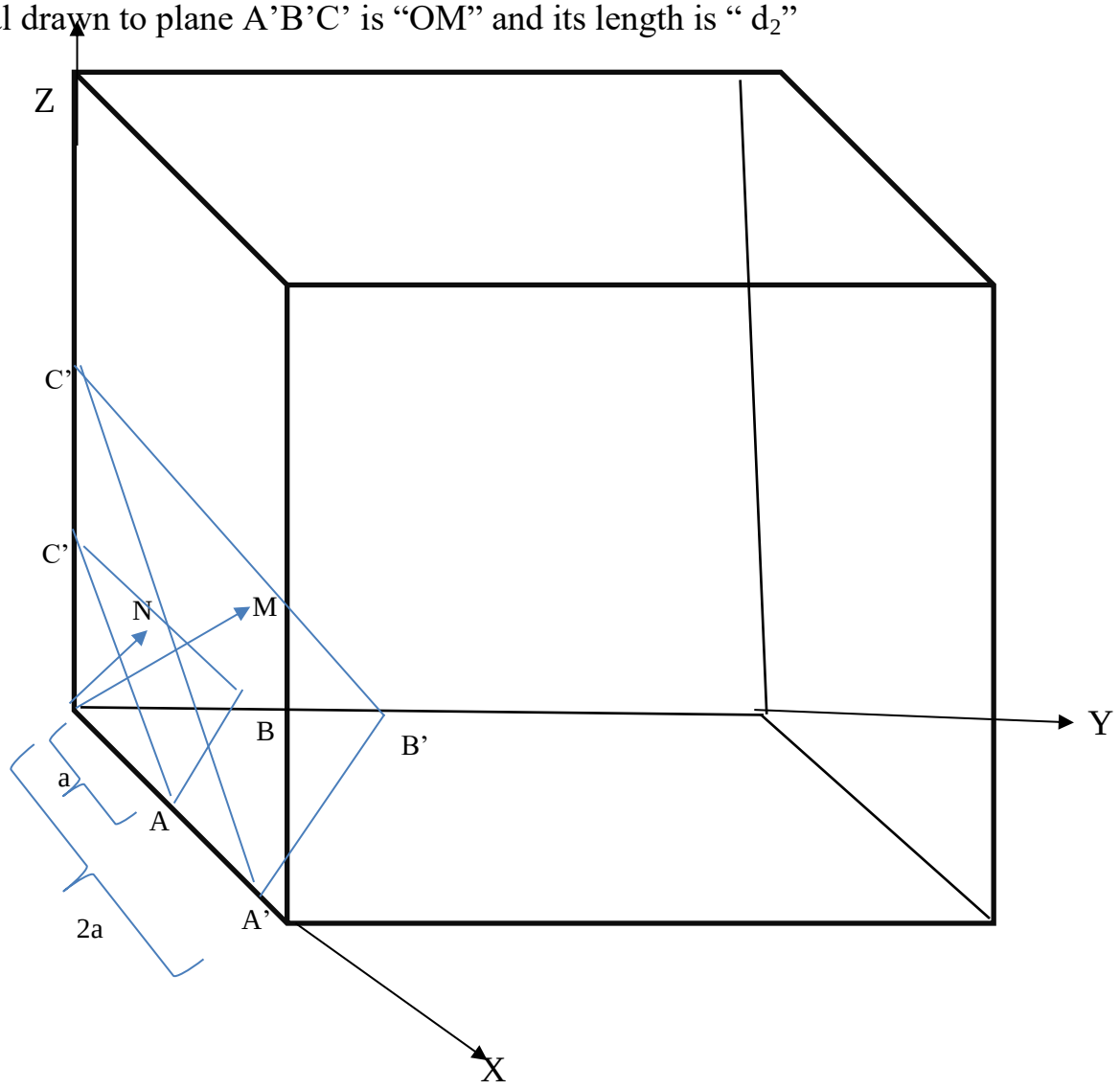
Interplanar distance (or) 'd' spacing in cubic lattice

Definition: The distance between any two successive planes is called "d" spacing or interplanar distance.

Let us consider a cubic lattice of length "a" with a plane ABC and cubic lattice with length "2a" has a plane A′ B′ C′.

The normal drawn to plane ABC is "ON" and its length is "d_1"

The normal drawn to plane A'B'C' is "OM" and its length is " d_2"



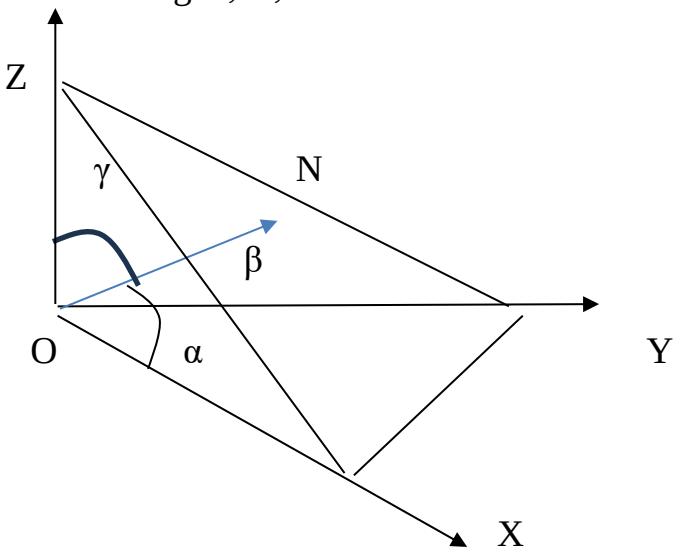
The intercept of the plane ABC , along

X- axis is OA = $\frac{a}{h}$

Y- axis is OB = $\frac{a}{k}$

Y- axis is OB = $\frac{a}{l}$

The angle made by the plane ABC along X, Y, Z is



$$\cos\alpha = \frac{ON}{OA} = \frac{d_1}{a/h} = \frac{d_1 h}{a}$$

$$\cos\beta = \frac{ON}{OB} = \frac{d_1}{a/k} = \frac{d_1 k}{a}$$

$$\cos\gamma = \frac{ON}{OC} = \frac{d_1}{a/l} = \frac{d_1 l}{a}$$

$$\therefore \cos\alpha : \cos\beta : \cos\gamma = \frac{d_1 h}{a} : \frac{d_1 k}{a} : \frac{d_1 l}{a}$$

From the law of directions of cosines we can write $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

$$\therefore \left(\frac{d_1 h}{a}\right)^2 + \left(\frac{d_1 k}{a}\right)^2 + \left(\frac{d_1 l}{a}\right)^2 = 1$$

Or $$\frac{d_1}{a^2}\left(h^2 + k^2 + l^2\right) = 1$$

Therefore, $$d_1^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

$$d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Let the next plane parallel to ABC be at a distance OM from the Origin. Then its intercepts

are $$OA' : OB' : OC' = \frac{2a}{h} : \frac{2a}{k} : \frac{2a}{l}$$

$$\cos\alpha' = \frac{OM}{OA'} = \frac{d_2}{2a/h} = \frac{d_2 h}{2a}$$

$$\cos\beta' = \frac{OM}{OB} = \frac{d_2}{2a/k} = \frac{d_2 k}{2a}$$

$$\cos\gamma' = \frac{OM}{OC} = \frac{d_2}{2a/l} = \frac{d_2 l}{2a}$$

$$\therefore \cos\alpha' : \cos\beta' : \cos\gamma' = \frac{d_2 h}{2a} : \frac{d_2 k}{2a} : \frac{d_2 l}{2a}$$

$$\therefore \left(\frac{d_2 h}{2a}\right)^2 + \left(\frac{d_2 k}{2a}\right)^2 + \left(\frac{d_2 l}{2a}\right)^2 = 1$$

$$\frac{d_2^2 h^2}{4a^2} + \frac{d_2^2 k^2}{4a^2} + \frac{d_2^2 l^2}{4a^2} = 1$$

$$\frac{d_2^2}{4a^2}\left(h^2 + k^2 + l^2\right) = 1$$

$$d_2^2 = \frac{4a^2}{\left(h^2 + k^2 + l^2\right)}$$

$$d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}}$$

Interplanar distance d:

We know interplanar distance is the distance between two successive planes. Since ‘d’ is the distance between the two planes ABC and A’B’C’, we can write the interplanar distance ‘d’ as

$d = d_2 - d_1$

Interplanar distance

$$d = \frac{2a}{\sqrt{h^2 + k^2 + l^2}} - \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

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