CRYSTALLOGRAPHY

Q 1. Discuss broad classification of solids (Short Answer question).

Solids may be broadly divided into two types.

    (1) Crystalline Solids

    (2) Amorphous Solids

<u>Crystalline Solids</u>	<u>Amorphous Solids</u>
(a) They have regular periodic arrangement of particles (atoms, ions or molecules) i.e.; they have long range order.	(a) They have no regularity or periodicity in the arrangement of particles, i.e.; they have short range order.
(b) They are anisotropic, i.e., the physical properties vary with direction.	(b) They are isotropic, i.e.; they possess the same properties in all directions.
(c) They have well defined melting and freezing points.	(c) They do not possess well defined melting and freezing points.

Q 2. Explain the term space lattice (Short Answer question).

A lattice is a regular periodic arrangement of points in space. Lattice is a geometric concept of the structure of the crystal. A three dimensional collection of points is called a space lattice provided that the environment about any particular point is in every way the same. Each atom in a crystal is replaced by a point, then we are left with an infinite array of points in space and each such point is called a lattice point.

Q 3. Explain the term Basis (Short Answer question).

The atoms, molecules or ions associated with every lattice point is called a basis. Basis is the group of atoms, molecules or ions. Crystal structure is formed only when a basis of atoms is attached identically to each lattice point.

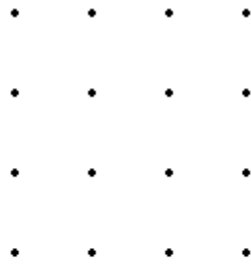   Lattice + Basis = Crystal Structure

An Illustration:

Fig 1. Space Lattice

Fig 2. Basis
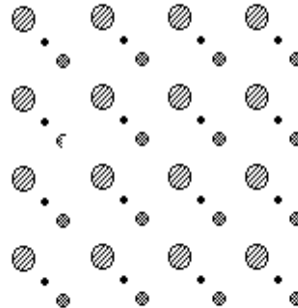

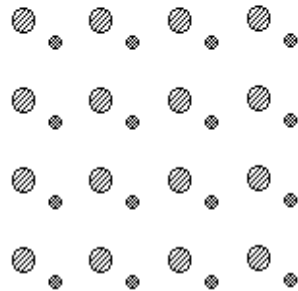Fig 3. Basis
associated with
each lattice point.

Fig 4. Crystal
         Structure

Q 4. What is a Unit cell? (Short Answer question).

Unit cell is the smallest geometric figure, the repetition of which in three dimensions will give the actual crystal structure. The fundamental elementary pattern of minimum group of atoms or molecules which exhibits all the characteristics of the crystal is called the unit cell. To know the properties of a crystal, it is only sufficient to know the properties of a unit cell of the crystal. The unit cell maybe primitive or non-primitive cell.

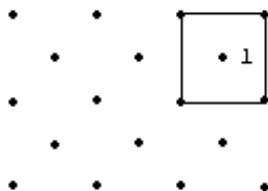**Q 5. What is a Primitive Unit cell? (Short Answer question).**

The choice of a unit cell is a matter of convenience. Usually, a cell with shortest possible size (minimum area in two dimensions or minimum volume in three dimensions) and sides is chosen as a unit cell. This is called primitive cell. Consider the following example.
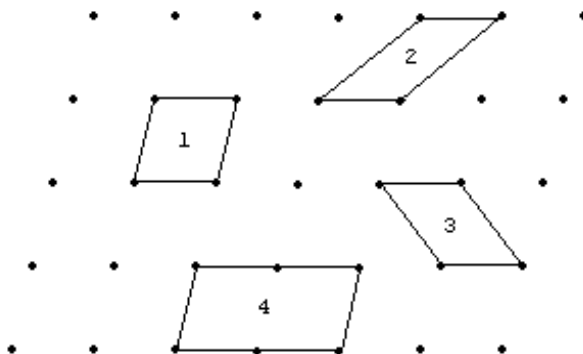
In the above figure, the parallelograms 1, 2, 3 are equal in area and any of them could be taken as the primitive unit cell. These cells contain lattice points only at the corners. Since a lattice point is shared by four unit cells, we can say that 1/4 of the lattice point is associated with this cell. The effective number of atoms belonging to the unit cell or lattice density is $\frac{1}{4} \times 4 = 1$.

Q 6. What is a Non-Primitive Unit cell? (Short Answer question).

Sometimes it is convenient to use a cell of larger area and thus containing more than one lattice density (The effective number of atoms belonging to the unit cell). The cells of this type are known as non-primitive unit cells. Consider the following example.


The rectangle 1 is a non-primitive unit cell. The reason for choosing a non-primitive unit cell is that it satisfies the symmetry elements better.

Q 7. Explain lattice parameters of a unit cell (Short Answer question).

The lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane are called crystallographic axes. Naturally the three translational vectors a, b and c lie along the crystallographic axes. In the figure, a unit cell is shown with three crystallographic axes x, y and z. The intercepts a, b and c define the dimensions of a unit cell and are known as its primitives.

The angles between the three crystallographic axes are known as interfacial angles. The angle between b and c is α, the angle between c and a is β, and that between a and b is γ. The primitives a, b and c and interfacial angles α, β and γ are the basic lattice parameters because they determine the form and actual size of the unit cell.
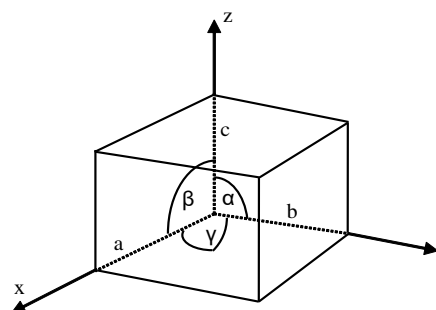
Q 8. Discuss Bravais lattices and crystal systems with the help of illustrations.

A three dimensional space lattice is generated by repeated translations of three non-coplanar vectors a, b and c. One would expect that many lattices can be generated in three dimensions with different primitive and non-primitive cells. However, Bravais showed that there are only fourteen different ways of arranging identical points in three dimensional space, satisfying the condition of periodicity, so that they are in every way equivalent in their surroundings. These fourteen types of arrangements are called Bravais lattices. There are seven primitive cells and seven non-primitive cells. With the 14 types of lattices and on the basis of primitive cell, crystals are grouped into 7 systems. They are cubic, tetragonal, orthorhombic, monoclinic, triclinic, hexagonal and rhombohedral (trigonal).
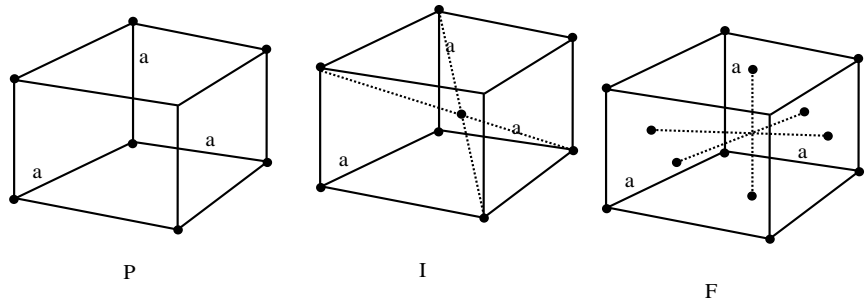
Crystal system	Unit cell axes	Angles	Bravais lattice
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	Simple Body centered Face centered
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	Simple Body centered

Orthorhombic	a ≠ b ≠ c	α = β = γ = 90⁰	Simple
			Base centered
			Body centered
			Face centered
Monoclinic	a ≠ b ≠ c	α = γ = 90⁰ ≠ β	Simple
			Base centered
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90⁰	Simple
Trigonal	a = b = c	α = β = γ ≠ 90⁰	Simple
Hexagonal	a = b ≠ c	α = β = 90⁰ γ = 120⁰	Simple

Cubic System:

In this system, $a = b = c$ and $\alpha = \beta = \gamma = 90^0$. Cubic lattice has three possible types of arrangements, simple cubic, body centered and face centered. Simple cubic has lattice points at all 8 corners of the unit cell. Body centered cubic has lattice points at all 8 corners of the unit cell and one lattice point at the center of the body. Face centered cubic has lattice points at all 8 corners of the unit cell and one lattice point each at the center of six faces of the cube.

P   I   F

Tetragonal System:

In tetragonal crystals, $a = b \neq c$ and $\alpha = \beta = \gamma = 90^0$. Tetragonal lattice has two possible types of arrangements, simple and body centered. Simple has lattice po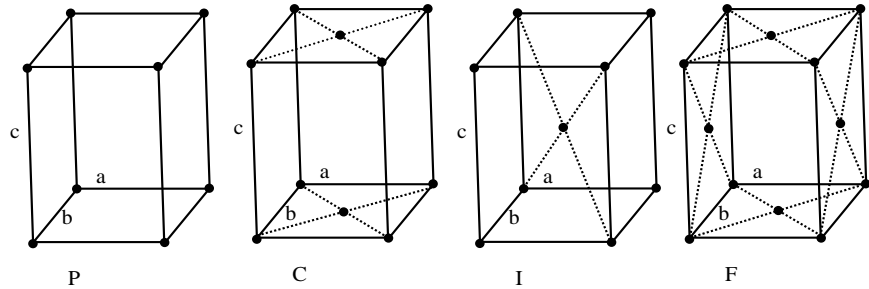ints at all 8 corners of the unit cell. Body centered cubic has lattice points at all 8 corners of the unit cell and one lattice point at the center of the body.


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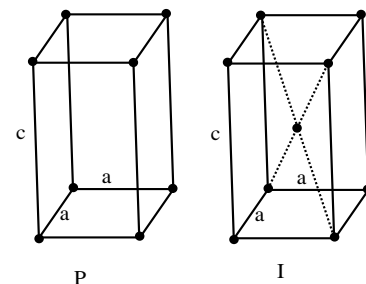
Orthorhombic System:

The geometrical configuration is a ≠ b ≠ c and α = β = γ = 90^0

There are four different types in this category, namely, simple, base centered, body centered and face centered.


Monoclinic System:

In this system, the three axes have repetition intervals of unequal lengths. Two of them are not perpendicular to the third one. The geometrical configuration is a ≠ b ≠ c and α = γ = 90^0 ≠ β. Monoclinic lattices are either simple or base centered.
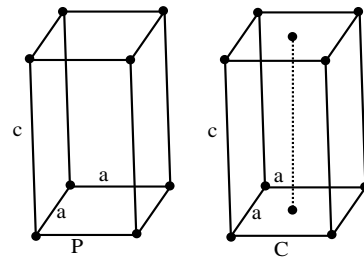

Triclinic system:

None of the axes are either equal to or perpendicular to any of the other. The geometrical configuration is a ≠ b ≠ c and α ≠ β ≠ γ ≠ 90^0 .There is only one structure of its type.
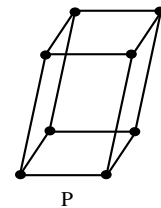

Trigonal system:

All the three axes have repetition intervals of equal length, and they are oriented to each other at equal angles, but other than 90^0. The geometrical configuration is a = b = c and α = β = γ ≠ 90^0
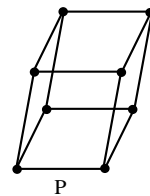
Hexagonal system:

Two of the axes have repetition interval of equal length, between which there is an angle of 120^0. The third axis is oriented 90^0 to the former two axes. The geometrical configuration is a = b ≠ c and α = β = 90^0 γ = 120^0.

Most metallic elements form cubic or hexagonal crystals. No metals form simple cubic crystals; instead they are found in fcc or bcc structures.
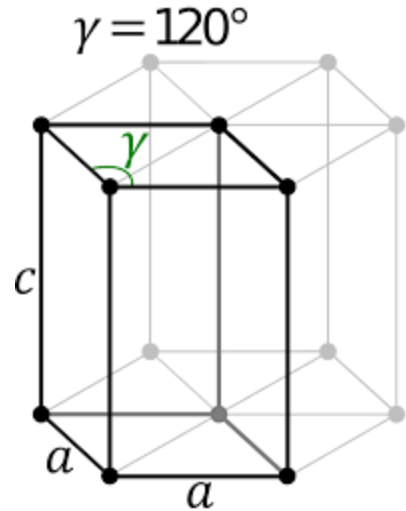
Q 9. Define nearest neighbor distance, atomic radius in a crystal? (Short Answer question).

The distance between the centres of two nearest neighboring atoms is called nearest neighbor distance. If r is the radius of the atom, nearest neighbor distance is 2r. Atomic radius is defined as half the distance between the nearest neighboring atoms in a crystal.

Q 10. Define coordination number and atomic packing factor in a crystal? (Short Answer question).

Coordination number is defined as the number of equidistant nearest neighbors that an atom has in a given structure. More closely packed structure has greater coordination number.
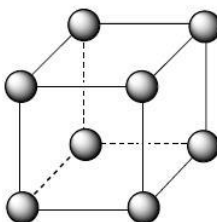
Atomic packing factor is the ratio of volume occupied by the atoms in a unit cell to the total volume of the unit cell. It is also called packing fraction.
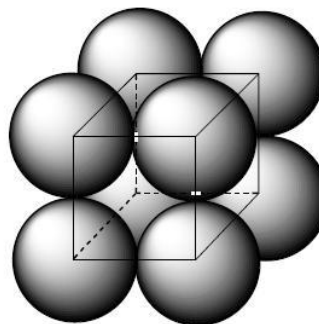
$$Packing\ factor = \frac{v}{V}$$

Q 11. Calculate nearest neighbor distance, atomic radius, coordination number and atomic packing factor in simple cubic structure?
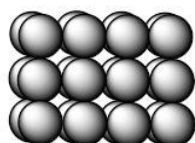
Figure 3a:
Square Array Layering

Figure 3b:
Simple Cubic

Figure 3c:
Space Filling Simple Cubic

The atoms touch along cube edges.

Nearest neighbor distance = 2r

Lattice constant, a = 2r

Atomic radius, $r = \frac{a}{2}$

Each corner atom touches four atoms in its horizontal plane and two atoms, one above it & another below it i.e., each atom is surrounded by six equidistant nearest neighbours. Hence the coordination number = 6. Each corner atom contributes $\frac{1}{8}$th to the unit cell and since there are eight corner atoms, the effective number of atoms belonging to the unit cell is $\frac{1}{8} \times 8 = 1$. Hence in this case, the unit cell is a primitive cell.

$$Packing\ factor = \frac{volume\ of\ all\ atoms\ in\ the\ unit\ cell}{volume\ of\ the\ unit\ cell} = \frac{1 \times \frac{4}{3} \times \pi\,r^3}{a^3} = \frac{4\pi\,r^3}{3(2\,r)^3} = \frac{\pi}{6} = 0.52$$

$$= 52\ \%$$

Q 12. Calculate nearest neighbor distance, atomic radius, coordination number and atomic packing factor in body centred cubic structure?
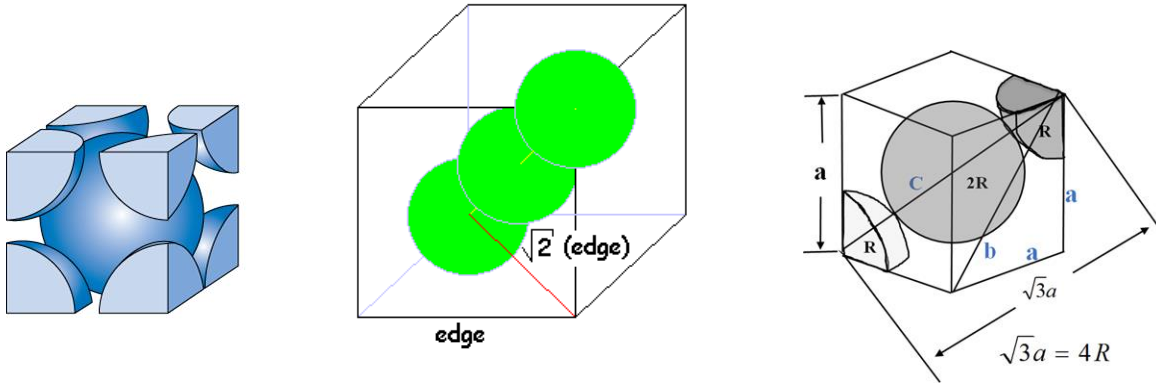
BCC structure has one at the centre of the cube and one atom at each corner. The corner atoms do not touch each other. But each corner atom touches the central atom. Since the atom at the centre touches all the eight corner atoms, the coordination number = 8. The distance between the points at the end of the body diagonal points of the cube is 4r.

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

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

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

In a unit cell, in addition to the centre atom, each corner atom contributes $\frac{1}{8}$th to the unit cell. Hence number of atom belonging to the unit cell is $1 + \left(\frac{1}{8} \times 8\right) = 2$.
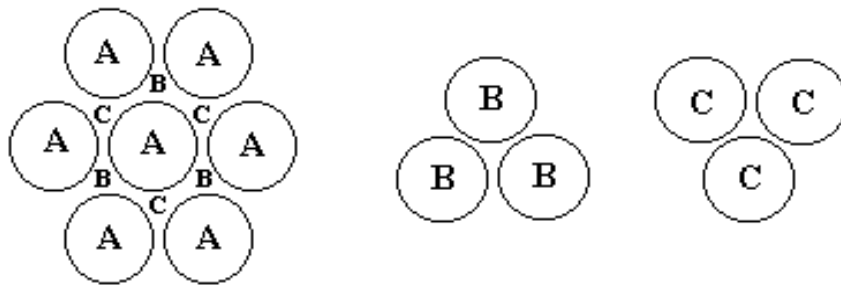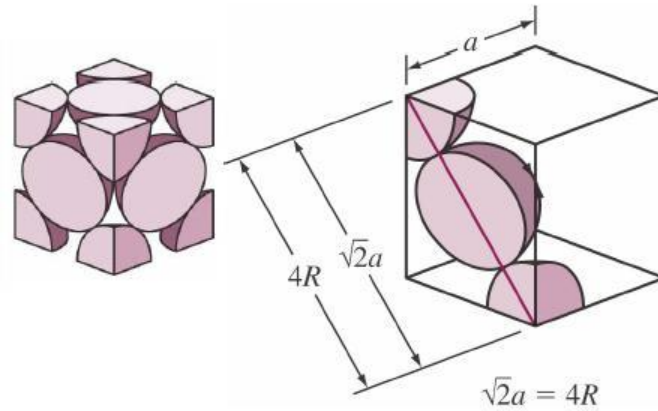
Atomic radius, $r = \frac{\sqrt{3}}{4}\, a$

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

$$packing\ factor = \frac{Volume\ of\ all\ atoms\ in\ the\ unit\ cell}{Volume\ of\ the\ unit\ cell} = \frac{2 \times \frac{4}{3} \times \pi r^3}{a^3} = \frac{8\pi\, r^3}{3\left(\frac{4}{\sqrt{3}}r\right)^3} = \frac{\sqrt{3}}{8}\pi$$

$$= 0.68 = 68\%$$

Q 13. Calculate nearest neighbor distance, atomic radius, coordination number and atomic packing factor in face centred cubic structure?

$$\sqrt{2}a = 4R$$

FCC is one of the forms of closest packing. Spheres may be arranged in a single closest packed layer by placing each sphere in contact with six others. A second similar layer is added by placing each sphere in contact with three other spheres of the bottom layer. The spheres in the third layer are placed over the holes in the first layer not occupied by the second layer. We say that packing in the FCC structure is ABCABC----, the atoms touch each other along the face diagonal.

Coordination number = 12

$$(4r)^2 = a^2 + a^2, (4r)^2 = 2a^2, a^2 = 8r^2$$

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

Lattice constant = $a = \dfrac{4r}{\sqrt{2}}$

Nearest neighbor distance $= 2r = \dfrac{a\sqrt{2}}{2}$

Number of atoms per unit cell $= \dfrac{1}{8} \times 8 + 6 \times \dfrac{1}{2} = 1 + 3 = 4$

Volume of the atoms in a unit cell $= v = 4 \times \dfrac{4}{3}\pi r^3$

Volume of the unit cell $== a^3 = (\dfrac{4r}{\sqrt{2}})^3 = V$

Atomic packing factor $= \dfrac{v}{V} = \dfrac{4 \times \dfrac{4}{3}\pi r^3}{(\dfrac{4r}{\sqrt{2}})^3} = 0.74 = 74\%$

Q 14. What is the importance of Miller indices? (Short Answer question).

A crystal lattice may be considered as an aggregate of a set of parallel, equally spaced planes passing through the lattice points. The planes are called lattice planes, and the perpendicular distance between adjacent planes is called interplanar spacing. A given space lattice may have an infinite sets of lattice planes, each having its characteristic interplanar spacing. Out of these, only those, which have high density of lattice points are significant and show diffraction of x-rays. They are known as Bragg planes or cleavage planes. Miller evolved a method to designate a set of parallel planes in a crystal by three numbers (h k l) known as Miller indices.

Q 15. What are Miller indices? How are they obtained? (Short Answer question).

Miller indices is a set of 3 lowest possible integers whose ratio taken in order is the same as that of the reciprocals of the intercepts of the planes on the corresponding axes in the same order.

Procedure for finding Miller indices:

1. Find the intercepts of the desired plane on the three coordinate axes. Let these be pa, qb, rc.
2. Express the intercepts as multiples of the unit cell dimensions or lattice parameters p, q, r.

3. Take the ratio of these numbers $\frac{1}{p}, \frac{1}{q}, \frac{1}{r}$

4. Convert these reciprocals into whole numbers by multiplying each with their LCM to get the smallest whole number.

   This gives the Miller indices (h k l) of the plane. The following figure illustrates some important crystal planes in a cubic crystal.
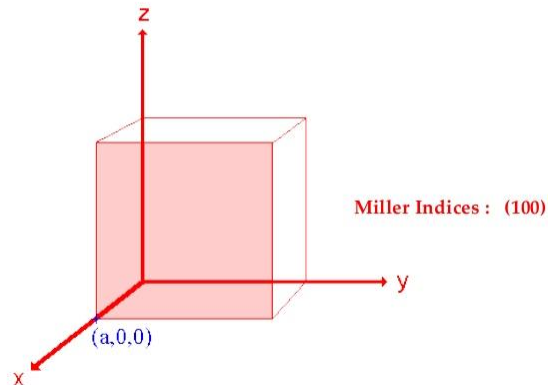

The plane cuts x-axis at a, y-axis at ∞ and z-axis at ∞. The coordinates of the intercepts of the plane are (a, ∞, ∞). As the multiples of the unit cell, the intercepts are $(1, \infty, \infty)$. Reciprocals of the intercepts are $\frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty}$ $i.e., 1, 0, 0$. Hence the Miller indices are $(1\ 0\ 0)$.
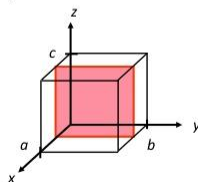
Some other illustrations:

Crystallographic Planes

example		a	b	c
1.	Intercepts	1	1	∞
2.	Reciprocals	1/1	1/1	1/∞
		1	1	0
3.	Reduction	1	1	0
4.	Miller Indices	(110)		
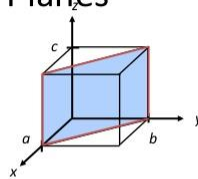
example		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(200)		

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Plane intercepts axes at $3\bar{a}, 2\bar{b}, 2\bar{c}$

Reciprocal numbers are: $\dfrac{1}{3}, \dfrac{1}{2}, \dfrac{1}{2}$

Indices of the plane (Miller): (2,3,3)

Indices of the direction: [2,3,3]

(200) (100) (110) (111) ($\bar{1}$00)
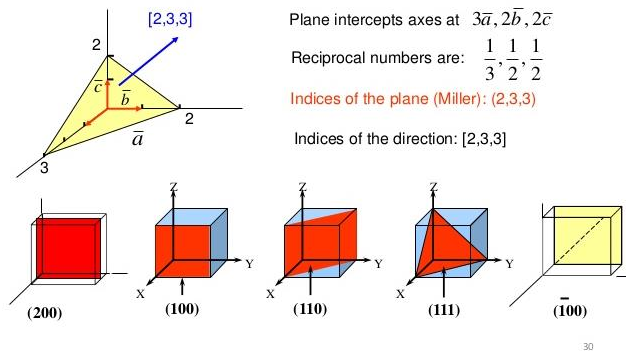
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Q 16. What are the Important features of Miller indices? (Short Answer question).

1) All the parallel equidistant planes have the same Miller indices. Thus Miller indices define a set of parallel planes.

2) A plane parallel to one of the coordinate axes will have an intercept at infinity.

3) If the Miller indices of two planes have the same ratio, i.e., (8 4 4) and (4 2 2) or (2 1 1), then the planes are parallel to each other.

4) If (h k l) are the Miller indices of a plane, then the plane cuts the axes into h, k and l equal segments respectively.

5) If a normal is drawn to a plane (h k l), the direction of the normal is [h k l].

6) If a, b, c are the lattice parameters along crystallographic axes, then for a plane with Miller indices (h k l), the intercepts would be at $\dfrac{a}{h}, \dfrac{b}{k}, \dfrac{c}{l}$.

Q 17. Show that in a cubic crystal the spacing between consecutive parallel planes of Miller indices (h k l) is given by $d_{h\,k\,l} = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$.

Let ABC be one of the parallel planes represented by the Miller indices (h k l). 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 $d_{h\,k\,l}$. Let the angle made by OP with respect to the coordinate axes X, Y and Z be α, β and γ. Let us consider the space lattice in which X, Y and Z are orthogonal. Then, since OP is
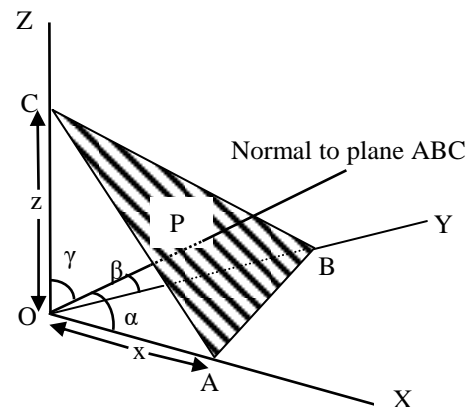
normal to the plane, x, y and z will be the hypotenuses to the 3 right angled triangles all of which have the common adjacent side OP.

$$d_{h\,k\,l} = x \cos \alpha = y \cos \beta = z \cos \gamma$$

If a, b and c are the lengths of the basis vectors, then we have

$$(h\,k\,l) = \left[\frac{a}{x}, \frac{b}{y}, \frac{c}{z}\right] \ or \ (x\,y\,z) = \left[\frac{a}{h}, \frac{b}{k}, \frac{c}{l}\right]$$

$$d_{h\,k\,l} = \frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma$$

But for orthogonal coordinates $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$

Then one can have, $d_{h\,k\,l}^2 = \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right] = 1$

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

In the case of cubic structure, $a = b = c$

$$d_{h\,k\,l} = \frac{1}{\sqrt{\dfrac{h^2 + k^2 + l^2}{a^2}}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$