US03CPHY22 UNIT - 3

CRYSTAL PHYSICS AND X – RAY DIFFRACTION

INTRODUCTION

A crystal is a solid composed of atoms or other microscopic particles arranged in an orderly periodic array in three dimensions. It may not be a complete definition, yet it is a true description.

The three general types of solids: *amorphous, polycrystalline and single crystal* are distinguished by the size of ordered regions within the materials. Order in *amorphous* solids is limited to a few molecular distances. In *polycrystalline* materials, the solid is made-up of grains which are highly ordered crystalline regions of irregular size and orientation. *Single crystals* have long-range order. Many important properties of materials are found to depend on the structure of crystals and on the electron states within the crystals. 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 study of the geometric form and other physical properties of crystalline solids by using x-rays, electron beams and neutron beams constitute the science of crystallography or crystal physics.

LATTICE POINTS AND SPACE LATTICE

The atomic arrangement in a crystal is called crystal structure. In perfect crystal, there is a regular arrangement of atoms. This periodicity in the arrangement generally varies in different directions. *It is very convenient to imagine points in space about which these atoms are located. Such points in space are called lattice points and the totality of such points forms a crystal lattice or space lattice*. *If all the atoms at the lattice points are identical, the lattice is called a "**Bravais lattice**"*. Thus, the three-dimensional space lattice may be defined as a finite array of points in three-dimensions in which every point has identical environment as any other point in the array.

Fig 1 shows two-dimensional array of points. The environment about any two points is the same and hence it represents a lattice.

Choose any arbitrary point as origin and consider the position vectors r_1 and r_2 of any two lattice points by joining them to O as shown in Fig. 1. If the difference T of the two vectors r_1 and r_2 satisfies the following Relation,

$$\vec{T} \; = \; n_1\vec{a} + \; n_2\vec{b} \qquad (1)$$

where n_1 and n_2 are integers and $\vec{a}$ and $\vec{b}$ are fundamental translation vectors characteristic of the array, then the array of points is a two-dimensional lattice.

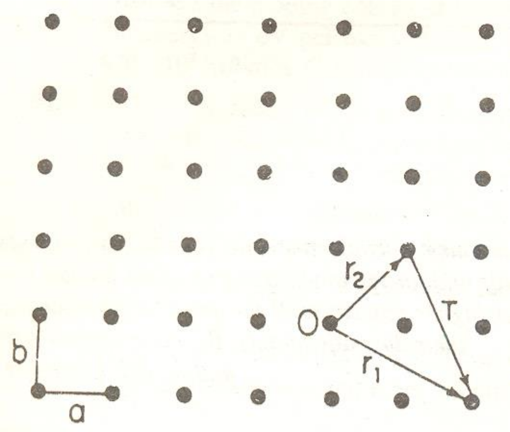


Figure 1 Two-dimensional array of points

For three dimensional lattices:

$$\vec{T} \; = \; n_1\vec{a} + \; n_2\vec{b} + \; n_3\vec{c} \qquad (2)$$

Hence it should be remembered that a crystal lattice refers to the geometry of a set of points in space whereas the structure of crystal refers to the actual ordering of its constituent ions, atoms, molecules in the space.

THE BASIS AND CRYSTAL STRUCTURE

For a lattice to represent a crystal structure, we associate every lattice point with one or more atoms called the **basis** or the **pattern**. When the basis is repeated with correct periodicity in all directions, it gives the actual crystal structure. The crystal structure is real, while the lattice is imaginary. Thus,

Basis + lattice = crystal structure

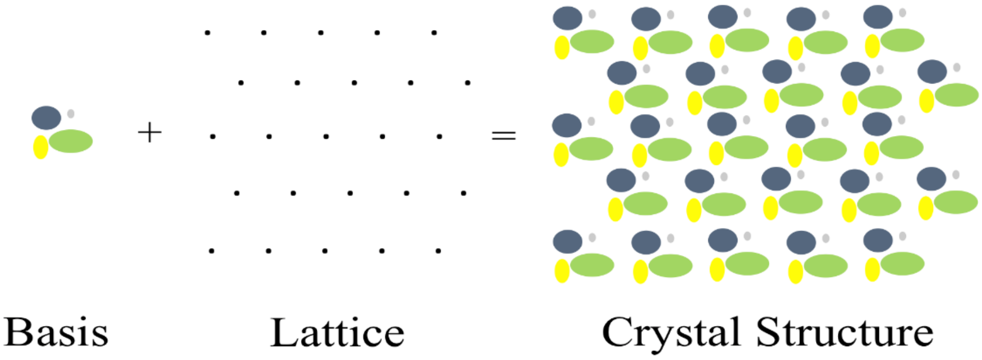


Figure 2 Basis or pattern

(Fig. 2) shows the basis or pattern representing each lattice point. It is observed from the figure that a basis consists of three different atoms. It can also be observed that the basis is identical in composition, arrangement and orientation. In crystalline solids like copper and sodium, the basis is a single atom (monoatomic), in NaCl and CsCl, the basis is diatomic whereas in crystals like CaF_2, the basis is triatomic.

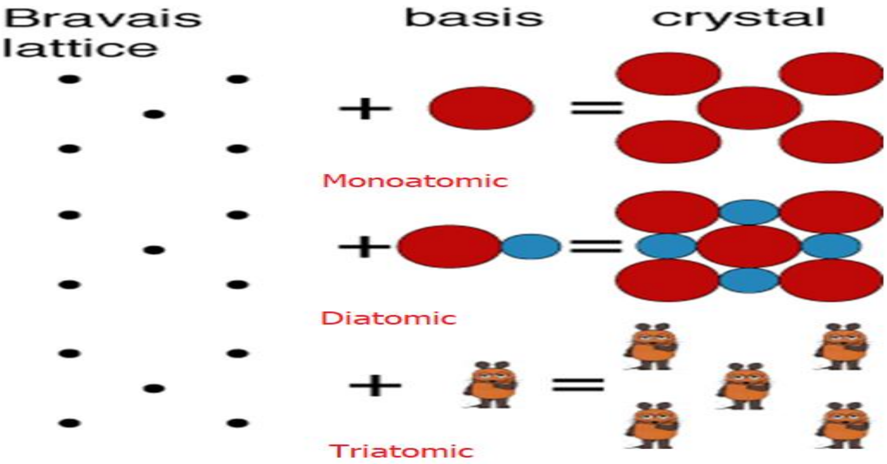


Figure 3

UNIT CELLS AND LATTICE PARAMETER

The atomic order in crystalline solids indicates that the small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, the structure us subdivided into small repeat entities called unit cell. In every crystal some fundamental grouping of particles called unit cell. Unit cell for most crystals is parallelopiped or cubes having three sets of parallel faces, a unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translation of the unit cell through integral distances along each of its edges. Thus, unit ***cell is the basic structural unit or building block of the crystal structure by virtue of its geometry and atomic position within.*** Unit cells are the building blocks of the crystal, each one is indistinguishable from next.

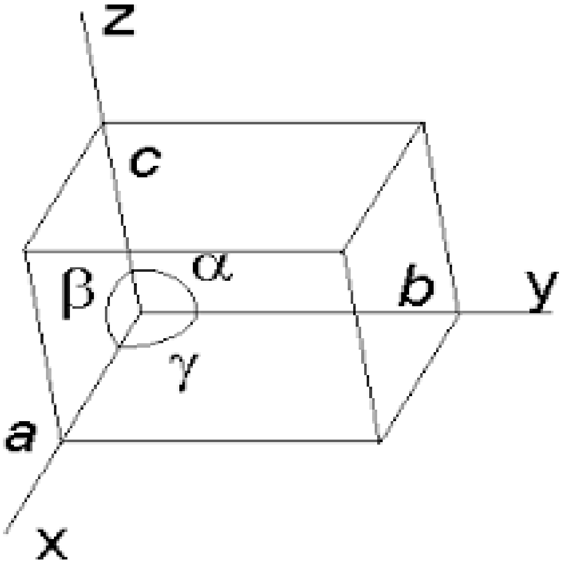


Fig 4 Lattice parameters of unit cell

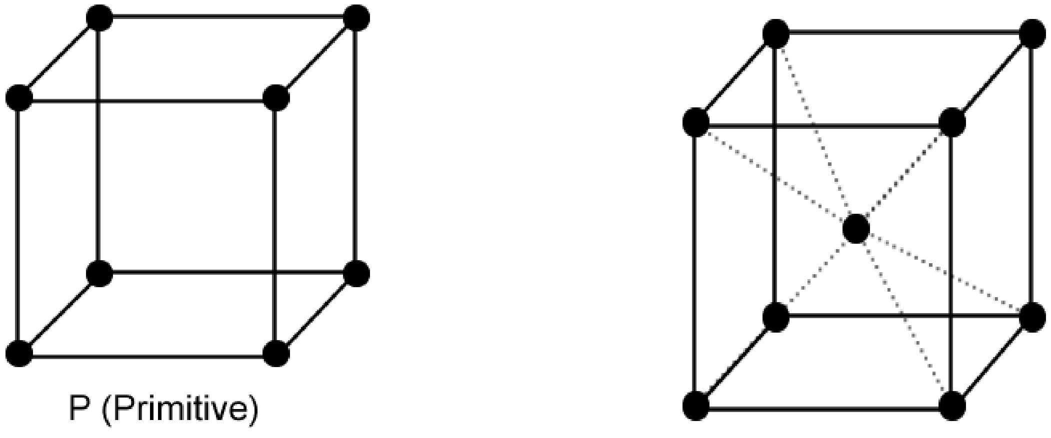
Fig 4 shows a unit cell of a three – dimensional crystal lattice. ***A space lattice is a regular distribution of points in a space, in such a manner that every point has identical surroundings.*** The lattice is made up of repetition of unit cells, and a unit cell described by three vectors, $\vec{a}$, $\vec{b}$, $\vec{c}$ where the length of the vectors and angles between them (α, β, γ) are specified.

Taking any lattice point as the origin, all other points on the lattice can be obtained by a repeated operation of the lattice vectors $\vec{a}$, $\vec{b}$, $\vec{c}$. ***The $\vec{a}$, $\vec{b}$, $\vec{c}$ lattice vectors and interfacial angles (α, β, γ) constitutes the <u>lattice parameters</u> of the unit cell.***

The vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ and the angles α, β and γ may or may not be equal. Based on these conditions there are seven different crystal systems. If atoms are existing only at the corners of the unit cells, the seven crystal systems will give seven types of lattice. More space lattice can be constructed by placing atoms or particle at the body centers of the unit cells, or at the centers of the faces. **Bravais** showed that the total number of different space lattice types is only fourteen and hence termed as "***Bravais lattice***".

UNIT CELL VERSUS PRIMITIVE CELL

The **unit cells** and **primitive cell** may be defined as a geometrical shape which, when repeated indefinitely in three dimensions. *The primitive cell is also defined as the minimum volume unit cell having only one lattice point*. In Fig. 3 lattice point is only since one point at each corner contributes l/8th of a point to the cell. The other cell shown in Fig. 3 (b) has two lattice points and, therefore, it is non-primitive. We can also say that in a primitive cell, lattice points are located only at the corners of the cell. All the lattice points are equivalent in a primitive cell, whereas it is not so in general [Fig. 3 (b)]. But we must not forget here that the basis of all the lattice points (whether equivalent or non-equivalent) remains identical in the whole volume of the crystal.



(a) **(b)**

Figure3 (a) A primitive cell. (b) A non-primitive cell

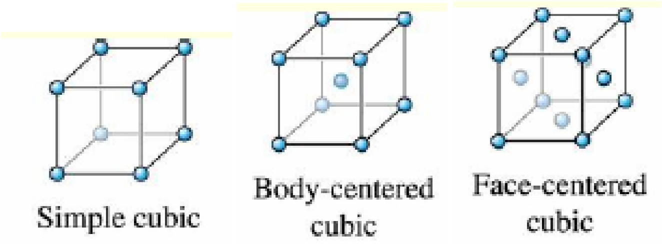
The unit cell that contains one lattice point only at the corners is known as primitive cell. The unit cell may be primitive cells but all the primitive cells need not be unit cell.

CRYSTAL SYSTEMS

There are thirty-two classes of the crystal systems based on the geometrical considerations i.e., symmetry and internal structure. But it is a common practice to divide all the crystal systems into seven groups or basic systems. These seven basic crystal systems are distinguished from one another by the angles between the three axes and the intercepts of the faces along them. The basic crystal systems are:

- cubic (Isometric)
- tetragonal
- orthorhombic
- monoclinic
- triclinic
- trigonal (rhombohedral)
- hexagonal

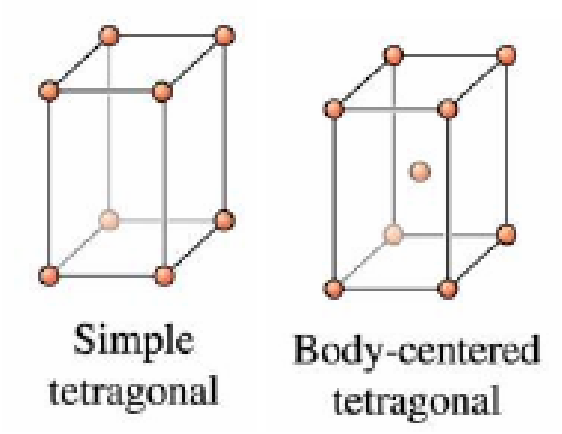
(i) CUBIC CRYSTAL SYSTEM



$a = b = c, \alpha = \beta = \gamma = 90^0$

The crystal axes are perpendicular to one another, and the repetitive interval is the same along all the three axes. Cubic lattices may be simple, body-centered or face-centered.

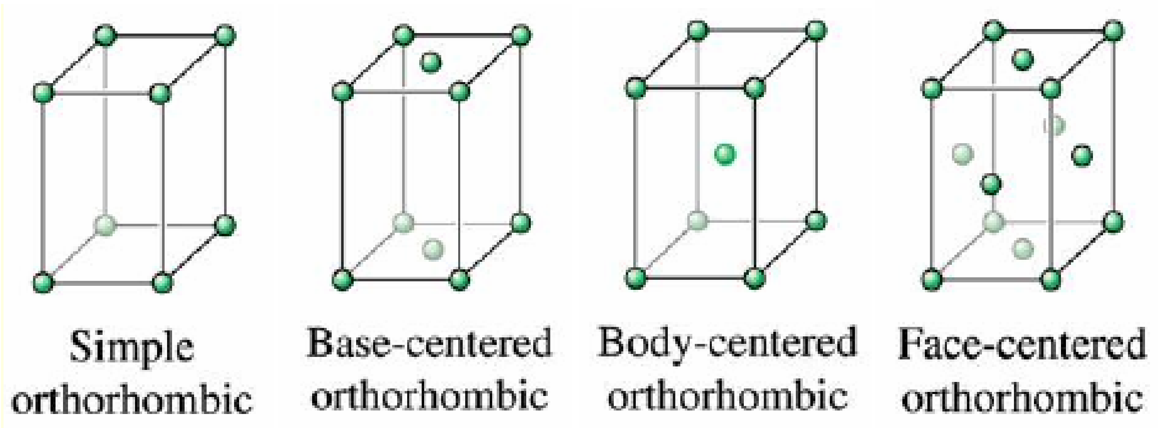
(II) TETRAGONAL CRYSTAL SYSTEM



$a = b \neq c, \alpha = \beta = \gamma = 90^0$

The crystal axes are perpendicular to one another. The repetitive intervals along two axes are the same, but the interval along the third axis is different. Tetragonal lattices may be simple or body-centered.

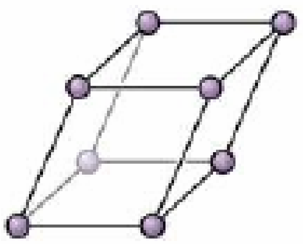
(III) ORTHORHOMBIC CRYSTAL SYSTEM



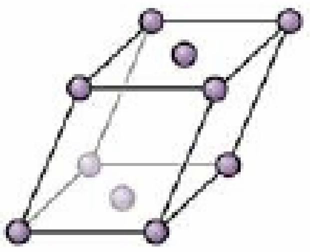
$a \neq b \neq c, \alpha = \beta = \gamma = 90^0$

The crystal axes are perpendicular to one another, but the repetitive intervals are different along all the three axes. Orthorhombic lattices may be simple, base centered, body-centered or face-centered.

(iv) MONOCLINIC CRYSTAL SYSTEM



Simple monoclinic

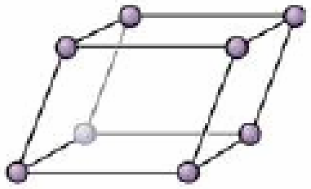


Base-centered monoclinic

$a \neq b \neq c, \alpha = \beta = 90^0 \neq \gamma$

Two of the crystal axes axe perpendicular to each other, but the third is obliquely inclined. The repetitive intervals are different along all the three axes. Monoclinic lattices may be simple or base-centered.

(v) TRICLINIC CRYSTAL SYSTEM

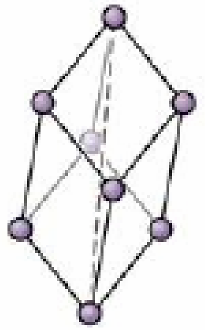


Triclinic

$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^0$

None of the crystal axes is perpendicular to any of the others, and the repetitive intervals are different along all the thee axes.

(VI) TRIGONAL (SOMETIMES CALLED RHOMBOHEDRAL) CRYSTAL SYSTEM

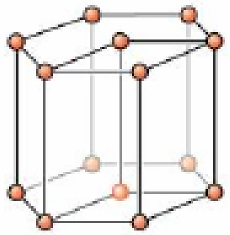


Rhombohedral

$$a = b = c, \alpha = \beta = \gamma \neq 90^0$$

The three axes are equal in length and are equally inclined to each other at an angle other than 90°.

(Vii) HEXAGONAL CRYSTAL SYSTEM



Hexagonal

$$a = b \neq c, \alpha = \beta = 90^0, and\ \gamma = 120^0$$

Two of the crystal axes are 60° apart while the third is perpendicular to both of them. The repetitive intervals are the same along the axes that are 60° apart, but the interval along the third axis is different.

The seven crystal systems (fourteen lattice types) and their properties are given in **Table 1**.

Table 1. The seven crystal systems (fourteen lattice types) in three dimensions.

Sr. No.	Crystal System	Axial length of Unit Cell	Inter axial angles	Number of Lattice in the system
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	3
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	2
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$	4
4	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^0 \neq \gamma$	2
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$	1
6	Trigonal	$a = b = c$	$\alpha = \beta = \gamma < 120^0, \neq 90^0$	1
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0, and\ \gamma = 120^0$	1

CRYSTAL SYMMETRY (SYMMETRY ELEMENTS IN CRYSTALS)

The definite ordered arrangement of the faces and edges of a crystal is known as ***crystal symmetry***. An operation that takes the crystal into itself and leaves crystal and its environment invariant is called a ***symmetry operation***.

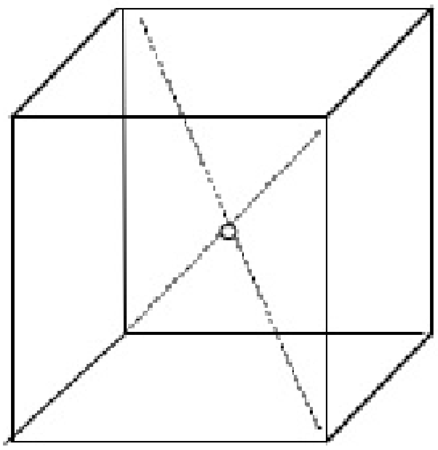
Symmetry operations performed about a point or a line are called ***point group symmetry operations*** and symmetry operations performed by translations as well as rotation are called ***space group symmetry operations***. Crystals exhibits both types of symmetries independently and in compatible combinations. A symmetry operation is performed on body which leaves it unchanged or invariant. After performing an operation on the body, if the body becomes indistinguishable from the initial configuration, the body is said to possess symmetry element compare to the particular operation. The different types of the point group symmetry elements exhibited by the crystals are

- ***Centre of symmetry or Inversion Centre.***
- ***Reflection symmetry.***
- ***Rotation symmetry.***

THE TWENTY – THREE SYMMETRY ELEMENTS IN A CUBIC CRYSTAL

The features of the many crystals are a certain regularity in the arrangement of faces. Another feature is frequent occurrence of similar faces in parallel pairs on opposite sides of the crystal.

A cube possesses three such points of parallel and opposite faces. Hence a cube is said to show a centre of symmetry, i.e., the body centre of the cube is a centre of symmetry. This centre lies at equal distances from various symmetrical Positions. Centre of symmetry is also known as ***inversion centre.***



A crystal will possess an inversion centre if for e very lattice point given by the position vector $\vec{r}$, there will be a corresponding lattice point at position $-\vec{r}$

Thus, inversion is a symmetry operation in a crystal equivalent to reflection through a point as shown in above figure.

The second kind of the symmetry element in crystal is a plane of symmetry or reflection symmetry. A crystal is said to possess reflection symmetry about a plane if it is left unchanged in every way after being reflected by a plane. Regular crystals may be bilaterally symmetrical about several plane cutting them in different directions. These may have several planes of symmetry. It's not only divides crystal into two equal portions, but these two portions must be so situated that they are mirror images each other with respect to the plane. The two symmetry elements, centre of inversion and plane of reflection. The three planes of symmetry in a cube are shown in Fig. A and Six diagonal planes of symmetry in a cube are shown in Fig B

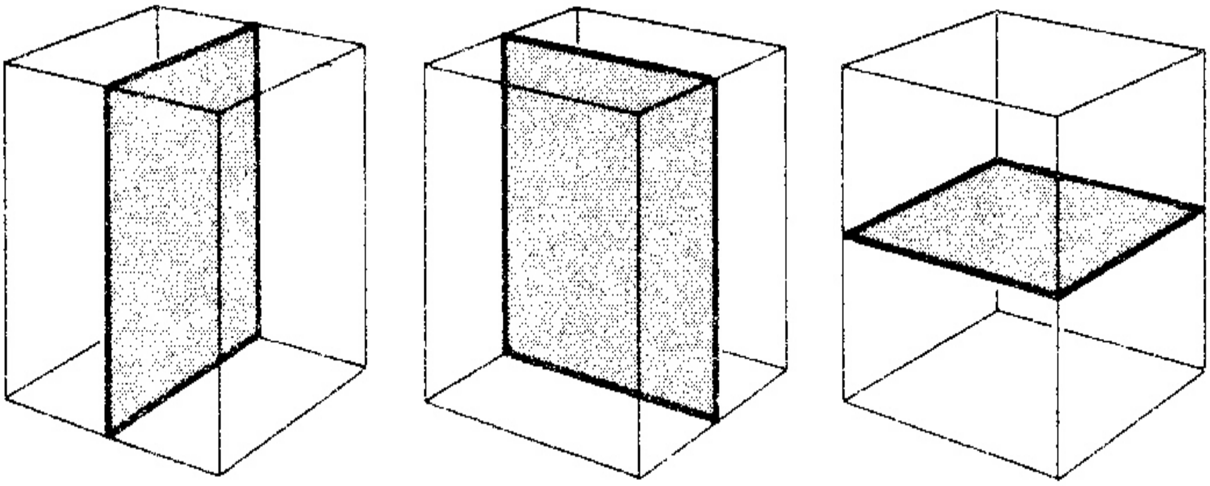


Fig A The three planes of symmetry parallel to the faces of the cube

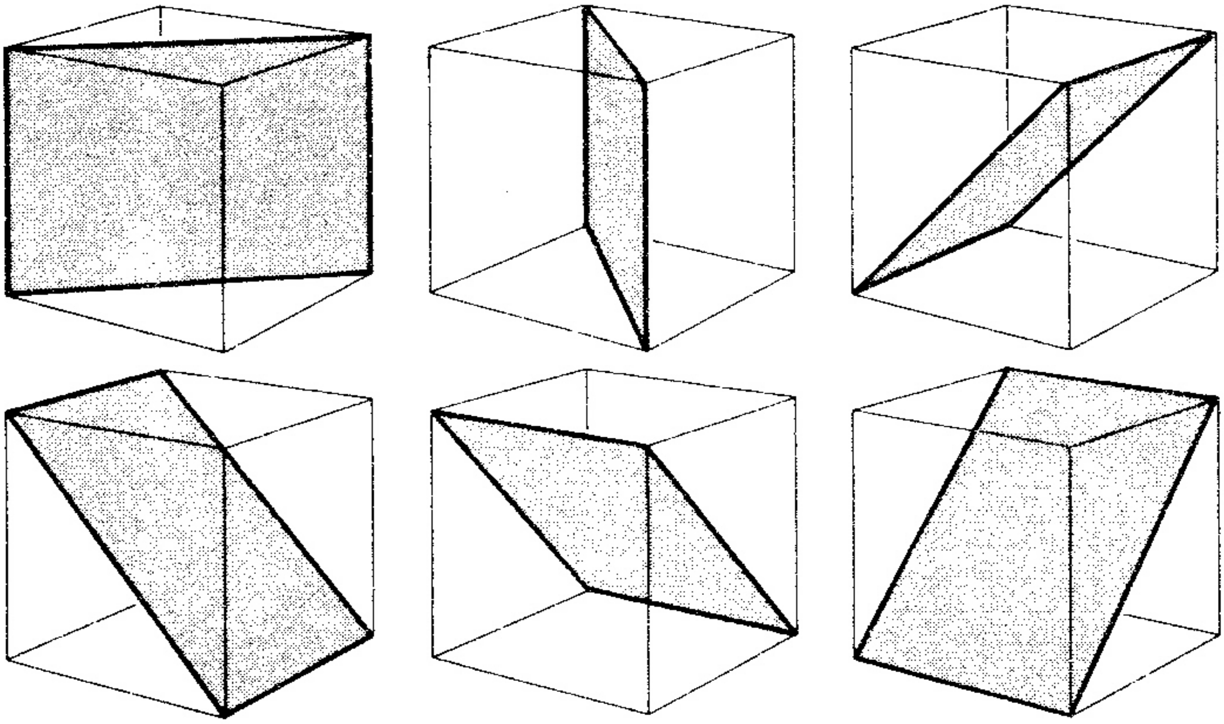


Fig. B Six Diagonal planes of symmetry in a cube.

A body is said possess rotational symmetry about an axis if after rotation of the body, about this axis by some angle Φ_n, the body appears as it did prior to rotation. The axis of symmetry may thus define as a line such that the crystal assumes a similar position for every rotation of $\left[\frac{360}{n}\right]^0$. The value of n decides the fold of the axis. Only one, two, three, four and six - fold rotation axes of symmetry alone are possible in a single crystal lattice.

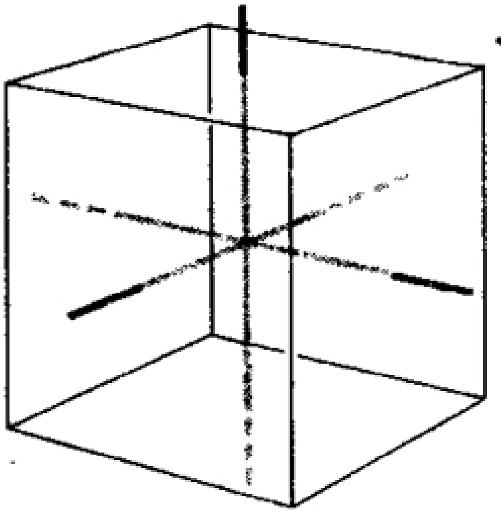


Fig. c three tetrad axis of cubes.

If a cube is rotated about a line perpendicular to one of its faces at its midpoint, it will turn into invariant position every 90^0, four times during complete 360^0 revolution; the axis is four – fold symmetry, a tetrad axis, and a cube clearly possess three such axes, one normal to each of the three pairs of the parallel faces as shown in Fig. c.

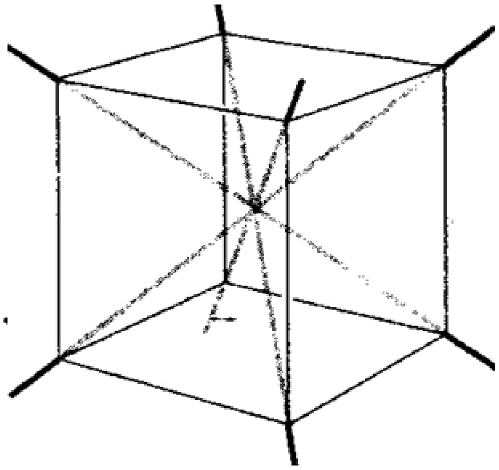


Fig d four triad axes of a cube

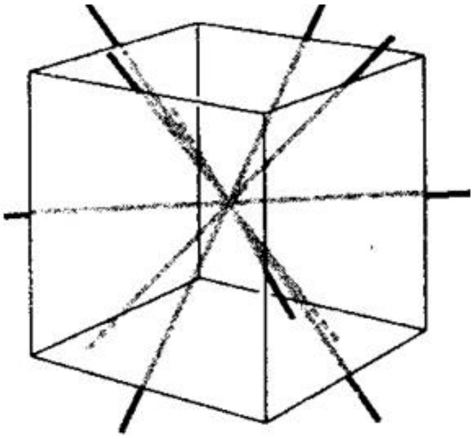


Fig e six diad axes of a cube

When cube is rotated about solid diagonal through 120^0 to get symmetry position, and such a line, of which there are four, is therefore triad axis is shown in

Fig d. a line joining the mid points of a pair of opposite edges proves to be a diad axis, and there are six of such axes present in a cube as shown in Fig. e.

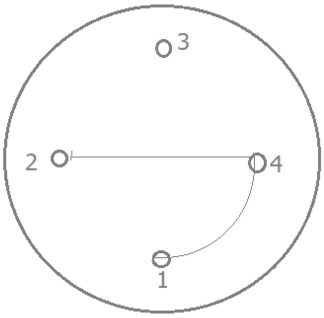
The total number of crystallographic symmetry elements of the cubic system are thus given by one centre of symmetry, three straight planes, six diagonal planes, three tetrad axis, four triad axis and six diad axis.

COMMBINATION OF SYMMETRY ELEMENTS

The different symmetry elements can also be combined if they are compatible. The different combinations give rise to different symmetry points in the crystal. All crystal system does not possess the same symmetry operations, the different crystal system exhibits different symmetries. It is found that there are 32 compatible combinations of the above three-point group symmetry element, called simply point groups. Crystals belonging to different crystal systems can be classified on the basis of point groups.

ROTATION – INVERSION AXIS

A crystal structure is said to possess rotation – inversion axis if it is brought in to self – coincidence by rotation followed by an inversion about the lattice point through which the rotation axis possesses.



Stereogram to show the operation of 4 – fold roto – inversion axis.

Consider an axis normal to the circle passing through the centre, operating on pole 1 to rotate it through 90^0 to the position 4 followed by the inversion to the position 2; the compound operation is then repeated until the original position again reached. Thus, from position 2 the pole is rotated a further 90^0 and inverted to position 3; rotated further 90^0 and inverted to position 4; rotated a further 90^0 and inverted to resume position 1.

This operation includes an n -fold rotation followed by an inversion. Its common representation is $\bar{n}$, where n = 1, 2, 3, 4, 6. Thus a roto inversion composed of a 3-fold rotation and an inversion is depicted as $\bar{3}$. Crystal can possess 1-, 2-, 3-, 4- and 6- fold rotation – inversion axes, represented by $\bar{1}, \bar{2}, \bar{3}, \bar{4}, and\ \bar{6}$.

TRANSLATION SYMMETRY ELEMENTS

(i) GLIDE PLANE

When a mirror plane is combined with a simultaneous translation operation in a crystal, one gets a glide plane. The glide plane in a crystal is always parallel to the mirror plane. The different glide planes, their symbols and their translations parallel to the different axes and planes are shown in following table.

TYPES OF GLIDE	SYMBOL	TRANSLATION COMPOUND
Axial glide	a	a/2
Axial glide	b	b/2
Axial glide	c	c/2
Diagonal glide	n	$\left(\frac{a}{2}+\frac{b}{2}\right), \left(\frac{b}{2}+\frac{c}{2}\right)$ or $\left(\frac{c}{2}+\frac{a}{2}\right)$
Diamond glide	d	$\left(\frac{a}{4}+\frac{b}{4}\right), \left(\frac{a}{4}+\frac{b}{4}\right)\ or\ \left(\frac{a}{4}+\frac{b}{4}\right)$

(ii) SCREW AXIS

When rotation and inversion are combined, it produces hybrid roto inversion axis. It is possible to combine a proper rotation with translation parallel to the rotation axis will give new symmetry element called screw axis.

A screw axis is usually represented by the symbol ‘n_m’. this is performed by a rotation of $\left[\frac{2\pi}{n}\right]$ and translation of $\left[\frac{m}{n}\right]$ times the translation vector parallel to the rotation axis. the screw axis 4_2 is performed as, rotate the point through 90^0 about the symmetry axis and translate the point by $\frac{2}{4} = \frac{1}{2}$ times the translation vector parallel to the rotation axis. Apply the operation successively until the cycle is complete. The eleven screw axes possible in the crystal lattice are shown in the figure.

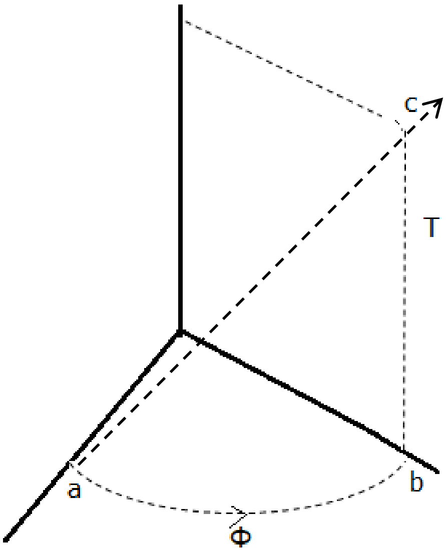


Fig. Screw axis

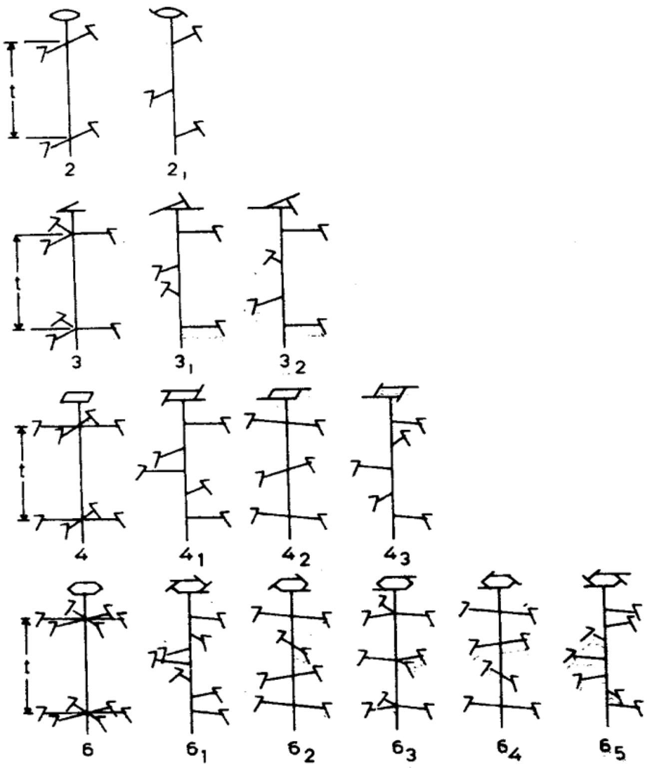


Figure The eleven possible screw axes

SPACE GROUPS

The information about a crystal structure is complete only when its point group and space group both are known. ***In a crystal, point group symmetry operations can also be combined with translation symmetry elements, such***

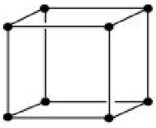
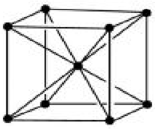
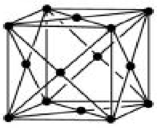
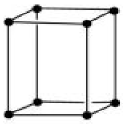
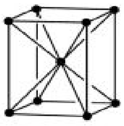
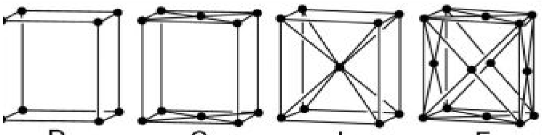
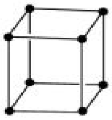
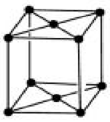
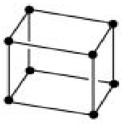
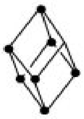
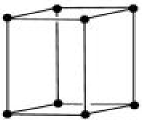
combinations are called space groups. There are **230 space groups** in three dimensions exhibited by crystals. The study of symmetry elements of the different crystals enables one of the classify the crystal and their properties based on different symmetries.

<table>
<tr><th colspan="2">Crystal family
Crystal system</th><th>space groups</th><th>Bravais lattices</th><th>Lattice system</th></tr>
<tr><td colspan="2">Triclinic</td><td>2</td><td>1</td><td>Triclinic</td></tr>
<tr><td colspan="2">Monoclinic</td><td>13</td><td>2</td><td>Monoclinic</td></tr>
<tr><td colspan="2">Orthorhombic</td><td>59</td><td>4</td><td>Orthorhombic</td></tr>
<tr><td colspan="2">Tetragonal</td><td>68</td><td>2</td><td>Tetragonal</td></tr>
<tr><td rowspan="3">Hexagonal</td><td rowspan="2">Trigonal</td><td>7</td><td>1</td><td>Rhombohedral</td></tr>
<tr><td>18</td><td rowspan="2">1</td><td rowspan="2">Hexagonal</td></tr>
<tr><td>Hexagonal</td><td>27</td></tr>
<tr><td colspan="2">Cubic</td><td>36</td><td>3</td><td>Cubic</td></tr>
<tr><td>Total: 6</td><td>7</td><td>230</td><td>14</td><td>7</td></tr>
</table>

THE BRAVAIS SPACE LATTICES

There are many numbers of ways in which actual crystal may be built up and atoms joined together resulting in many crystal structures. Each of the structure consist of some fundamental pattern repeated at each point of a space lattice. The scheme of repetitions pf a space lattice is very limited while the possible crustal structures are unlimited. The Bravais shows that there are only 14 different arrays or networks of lattice in which points can be arranged in space so that each point has identical surroundings. These are known as ***Bravais space lattice.***

To specify a given arrangement of points in a space lattice of atoms in a structure, a set of coordinate axes with an origin at one of the lattice points is chosen. Cubic crystals, are referred as cubic set of axes. Seven different systems used in crystallography possess certain characteristics like equality of angles and equality of lengths. These seven crystallographic axes generate the 14 space lattices. Most of the common metals and some important alkali halides have cubic structure. In cubic crystals, atoms are packed in cubic pattern with three different types of repetition; Simple Cubic (SC), Body Centred Cubic (BCC) and Face Centred Cubic (FCC). The 14 space lattices are shown below

 Cubic P  Cubic I  Cubic F	Cubic Structure $a = b = c;\ \alpha = \beta = \gamma = 90^\circ$
 Tetragonal P  Tetragonal I	Tetragonal cubic structure $a = b \neq c;\ \alpha = \beta = \gamma = 90^\circ$
 P C I F Orthorhombic	Orthorhombic crystal structre $a \neq b \neq c;\ \alpha = \beta = \gamma = 90^\circ$
 Monoclinic P  Monoclinic C	Monoclinic crystal strucre $a \neq b \neq c;\ \alpha = \gamma = 90^\circ \neq \beta$
 Triclinic P	Triclinic crystal structure $a \neq b \neq c;\ \alpha \neq \beta \neq \gamma \neq 90^\circ$
 Trigonal R (rhombohedral)	Trigonal crystal structure $a = b = c;\ \alpha = \beta = \gamma \neq 90^\circ$
 Trigonal and hexagonal C (or P)	Hexagonal crystal stucture $a_1 = a_2 = a_3 \neq c;$ $\alpha = \beta = 90^\circ,\ \gamma = 120^\circ$

METALLIC CRYSTAL STRUCTURES

Since atomic bonding in this group of materials is metallic, within the hard sphere model for the representation of a crystal structure, each sphere represents an ion core. Three relatively simple crystal structures are found for most of the common metals: body centered cubic, face centered cubic and hexagonal close packed. An important characteristic of most of the metals is that they are crystalline; i.e., the atoms are arranged in some regular repeatable pattern indefinitely in space.

(I) SIMPLE CUBIC STRUCTURE (SC)

The simplest and easiest structure to describe is the simple cubic crystal structure. Fig. shows the unit cell of a simple cubic structure. In a simple cubic lattice, there is one lattice point at each of the eight corners of the unit cell.

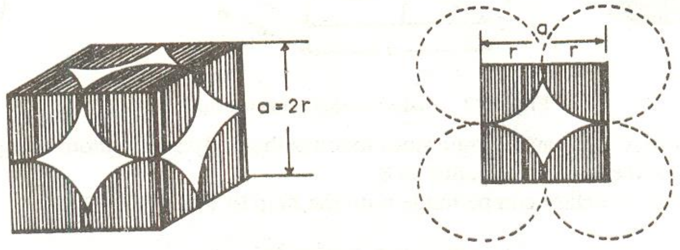


Figure Simple Cubic (SC) Structure.

If we take an atom at one corner as the centre, it is observed that this atom is surrounded by six equidistant nearest neighbours and hence the coordination number of a simple cubic lattice is **six**. In this structure, each corner atom is shared by eight-unit cells. Hence the share of each corner atom to a unit cell is one-eighth of an atom. In this way the total number of atoms in one-unit cell will be $\frac{1}{8} \times 8 = 1$atom. In other words, the effective number of lattice points in a simple cubic cell is one. In this structure the atoms touch each other along the edges. Hence the nearest neighbour distance, $2r = a$. We note in SC structure that:

Coordination number, $N = 6$

Nearest neighbour distance, $2\ r = a$

Lattice constant, $a = 2\ r$

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

Number of lattice points, $= 1$

Volume of all the atoms in a unit cell, $v = 1 \times \frac{4}{3}\ \pi\ r^3$

Volume of unit cell, $V = a^3 = (2\ r)^3$

Hence the packing factor (PF) or density of packing of this structure is:

$$PF = \frac{v}{V} = \frac{Volume\ of\ atoms\ in\ a\ unit\ cell}{Volume\ of\ primitive\ cell}$$

$$PF = \frac{v}{V} = \frac{\frac{4}{3}\pi\ r^3}{a^3} = \frac{4}{3}\ \frac{\pi\ r^3}{(2\ r)^3} = \frac{\pi}{6} = 0.53 \quad or \quad 52\%$$

Only one element polonium at a certain temperature region exhibits this structure. SC structure is a loosely packed structure.

Some important crystal structure terms are:

Coordination number (N): The coordination number is defined as the number of equidistant nearest neighbours that an atom has in the given structure. Greater is the coordination number, the more closely packed up will be the structure.

Nearest neighbour distance ($2r$): The distance between the centres of two nearest neighbouring atoms is called nearest neighbour distance. It will be $2r$ where, r is the radius of the atom.

Atomic radius (r): Atomic radius is defined as half the distance between nearest neighbours in a crystal of pure element.

Atomic packing factor: The fraction of the space occupied by atoms in a unit cell is known as ***atomic packing factor (APF)***; or simply packing factor; i.e., it is the ratio of the volume of the atoms occupying the unit cell to the volume of the unit cell relating to that structure.

(ii) BODY CENTERED CUBIC STRUCTURE (BCC)

Elements, that exhibit this structure are Li, Na, K, Rb and Cs. In this structure, in a unit cell, there are 8 atoms at the eight corners and another atom at the body centre.

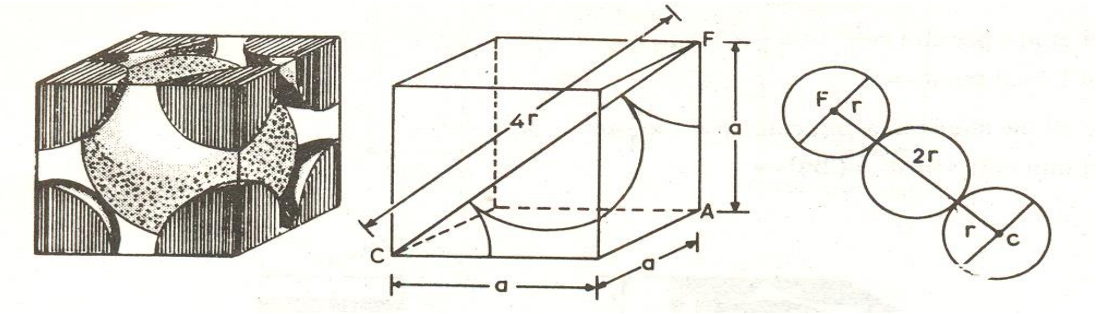


Figure Body centered cubic structure.

As the body centre is contained entirely within the unit cell and is not shared by any surrounding unit cell, the number of atoms per unit cell in a bcc structure is $n = \frac{1}{8} \times 8 + 1 = 2$. The corner atoms do not touch each other, but each corner atom touches the body centre atom along the body diagonal. Hence, the coordination number of this structure is 8.

The calculation of the lattice constant can be made with the help of above figure.

$$(AC)^2 = a^2 + a^2 = 2\,a^2 \qquad (1)$$

$$(FC)^2 = (AC)^2 + (AF)^2 \qquad (2)$$

$$(FC)^2 = 2\,a^2 + a^2 = 3\,a^2 \qquad (3)$$

$$(4\,r)^2 = 3\,a^2 \qquad (4)$$

$$a^2 = \frac{(4\,r)^2}{3} \quad \Rightarrow \quad a = \frac{4\,r}{\sqrt{3}} \qquad (5)$$

now the packing factor

$$PF = \frac{v}{V} = \frac{2\times\frac{4}{3}\,\pi\,r^3}{a^3} = \frac{8}{3}\frac{\pi\,r^3}{\left(\frac{4\,r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\,\pi}{8} = 0.68 \quad or \quad 68\% \tag{6}$$

bcc structure is a closely packed structure.

Closest packing: In metallic crystals in which all the atoms are identical, there are two forms of closest packing: Face Centered Cubic (FCC) and hexagonal close packed (hcp).

A closest packing is a way of arranging equi-dimensional objects in space so that the available space is filled efficiently. Such an arrangement is achieved when each object is in contact with the maximum number of like objects.

(iii) FACE CENTERED CUBIC STRUCTURE (FCC)

In the case of FCC lattice, there are eight atoms at the eight corners of the unit cell and six atoms at the Centre's of six faces. Considering the atom at the face centre as origin, it can be observed that this face is common to two-unit cells and there are twelve points surrounding it situated at a distance equal to half the face diagonal of the unit cell.

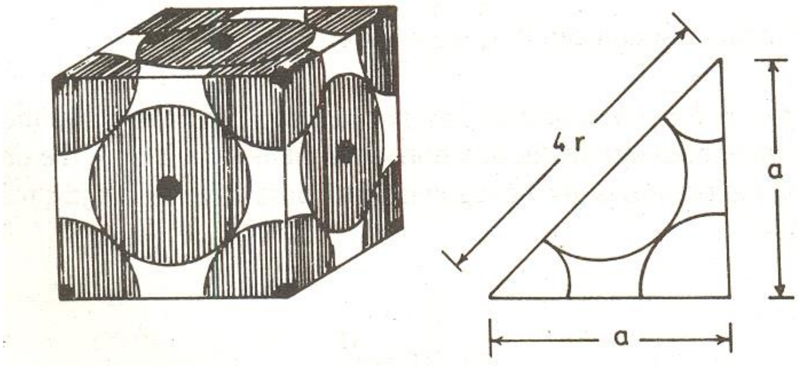


Figure Face centered cubic structure

Thus, the coordination number of FCC lattice is twelve. The atoms touch each other along the face diagonal. Each corner atom is shared by 8 surrounding unit cells and each of the face Centred atom is shared by 2 surrounding unit cells. Thus, the total number of atoms in FCC structure is $n = \left(\frac{1}{8} \times 8 + 6 \times \frac{1}{2}\right) = 4.$

Atomic packing factor of FCC structure is,

$$PF = \frac{v}{V} = \frac{4 \times \frac{4}{3}\,\pi\, r^3}{a^3} = \frac{16}{3}\,\frac{\pi\, r^3}{\left(\frac{4\,r}{\sqrt{2}}\right)^3} = \frac{\sqrt{2}\,\pi}{6} = 0.74 \quad or \quad 74\% \qquad (7)$$

Copper, aluminum, lead and silver have this structure.

(iv) HEXAGONAL CLOSE PACKED STRUCTURE (HCP)

The specific hexagonal structure formed by magnesium is shown in Fig. The unit cell contains one atom at each corner, one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell. Each atom touches three atoms in the layer below its plane, six atoms in its own plane, and three atoms in the layer above. Hence the coordination number of this structure is 12. Further the atoms touch each other along the edge of the hexagon.

Thus, $a = 2\,r$.

The top layer contains seven atoms. Each corner atom is shared by 6 surrounding hexagon cells and the centre atom is shared by 2 surrounding cells. The three atoms within the body of the cell are fully contributing to the cell. Thus, the total number of atoms in a unit cell is $n = \left(\frac{3}{2} + \frac{3}{2} + 3\right) = 6$.

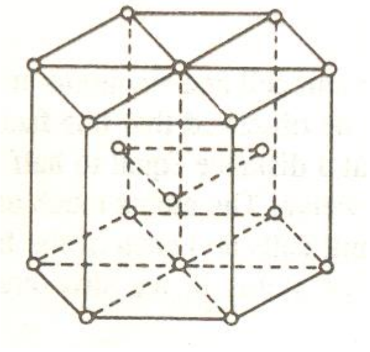


Figure Ideal hexagonal close packed structure

Calculation of c/a ratio for an ideal hexagonal close packed structure: Let ‘c’ be the height of the unit cell and ‘a’ be its edge. The three body atoms lie in a horizontal plane at c/2 from the orthocenters of alternate equilateral triangles at the top or base of the hexagonal cell. These three atoms just rest on the three atoms at the corners of the triangles.

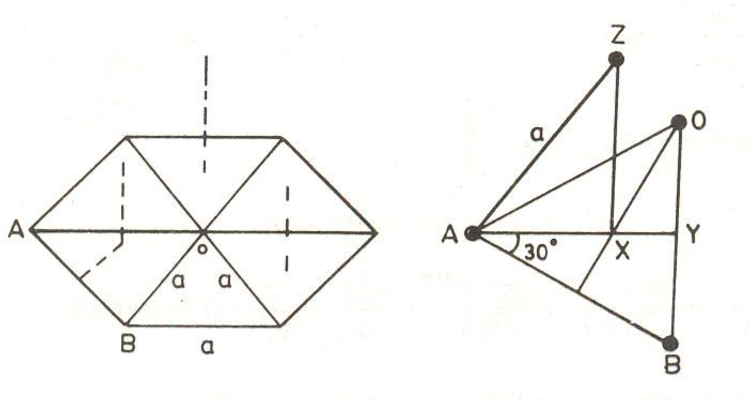


Figure Bottom layer of hcp structure

In the triangle ABY

$$\cos 30^\circ = \frac{AY}{AB} \quad \Rightarrow \quad AY = a \cos 30^\circ = \frac{a\sqrt{3}}{2} \tag{8}$$

$$(AZ)^2 = (AX)^2 + (ZX)^2 \tag{9}$$

In triangle AXZ

$$AX = \frac{2}{3} AY = \frac{2}{3}\,\frac{a\sqrt{3}}{2} = \frac{a}{\sqrt{3}}; \quad ZX = \frac{c}{2} \tag{10}$$

Substituting this in equation (19):

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4} \quad \Rightarrow \quad \frac{c^2}{4} = a^2 - \frac{a^2}{3} \quad \Rightarrow \quad \frac{c^2}{a^2} = \frac{8}{3} \quad or \quad \frac{c}{a} = \left[\frac{8}{3}\right]^{\frac{1}{2}} \tag{11}$$

Volume of the unit cell:

Area of the base = six times the area of the triangle AOB

Area of the triangle, $AOB = \frac{1}{2}\ (BO)\ (AY) = \frac{1}{2}\ a\ \frac{a\sqrt{3}}{2}$

Thus, area of the base $= 6 \times \frac{1}{2}\ a\ \frac{a\sqrt{3}}{2} = \frac{3}{2}\sqrt{3}\ a^2$

Volume of the cell, $V = \frac{3}{2}\sqrt{3}\ a^2\ c$

Volume of all the atoms in a unit cell, $v = 6 \times \frac{4}{3}\pi r^3 = \frac{24}{3}\pi \left[\frac{a}{2}\right]^3 = \pi a^3$

Hence, the packing factor

$$PF = \frac{v}{V} = \frac{6\times\frac{4}{3}\pi r^3}{\frac{3}{2}\sqrt{3}\,a^2 c} = \frac{\frac{24}{3}\pi\left(\frac{a}{2}\right)^3}{\frac{3}{2}\sqrt{3}\,a^2 c} = \frac{2\pi}{3\sqrt{3}}\left(\frac{a}{c}\right) = \frac{2\pi}{3\sqrt{3}}\left(\frac{3}{8}\right)^{\frac{1}{3}} = \frac{\sqrt{2}\,\pi}{6} = 0.74 \quad or \quad 74\% \tag{12}$$

Magnesium, Zinc, and Cadmium have hcp structure

Table Comparison of cell properties of some crystal structure.

Sr. No.	Crystal Specifications	Sc	bcc	fcc	hcp	Diamond
1	Coordination Number	$N = 6$	$N = 8$	$N = 12$	$N = 12$	$N = 4$
2	Nearest Neighbour distance	$2\ r = a$	$2\ r = \frac{a\ \sqrt{3}}{2}$	$2\ r = \frac{a\ \sqrt{2}}{2}$	$2\ r = a$	$2r = \frac{a\sqrt{3}}{4}$
3	Lattice Constant	$a = 2\ r$	$a = \frac{4\ r}{\sqrt{3}}$	$a = \frac{4\ r}{\sqrt{2}}$	$a = 2\ r$	$a = \frac{8r}{\sqrt{3}}$
4	Number of atoms per unit cell	$n = \frac{1}{8} \times 8 = 1$	$n = \frac{1}{8} \times 8 + 1$ $= 2$	$n = \frac{1}{8} \times 8 + 3$ $= 4$	$n = 6$	$n = 8$
5	Number of lattice points	$= 1$	$= 2$	$= 4$	$= 6$	= 8
6	Volume of all the atoms in a unit cell	v $= 1 \times \frac{4}{3}\ \pi\ r^3$	$v = 2 \times \frac{4}{3}\ \pi\ r^3$	$v = 4 \times \frac{4}{3}\ \pi\ r^3$	$v = 6 \times \frac{4}{3}\ \pi\ r^3$	$v = 8\ \times \frac{4}{3}\pi r^3$
7	Volume of unit cell	$V = a^3$ $= (2\ r)^3$	$V = a^3$ $= \left(\frac{4\ r}{\sqrt{3}}\right)^3$	$V = a^3$ $= \left(\frac{4\ r}{\sqrt{2}}\right)^3$	$V = a^3$ $= (2\ r)^3$	$V = a^3$ $= \left(\frac{8r}{\sqrt{3}}\right)^3$
8	Number of atoms per unit volume	$\frac{1}{a^3}$	$\frac{2}{a^3}$	$\frac{4}{a^3}$	$\frac{4}{\sqrt{3}\ a^2\ c}$	$\frac{8}{a^3}$
9	Atomic radius	$\frac{a}{2}$	$\frac{a\ \sqrt{3}}{4}$	$\frac{a\ \sqrt{2}}{4}$	$\frac{a}{2}$	$\frac{a\sqrt{3}}{8}$
10	Atomic Packing Fraction (APF)	$\frac{\pi}{6} = 0.52$	$\frac{\sqrt{3}\ \pi}{8} = 0.68$	$\frac{\sqrt{2}\ \pi}{6} = 0.74$	$\frac{\sqrt{2}\ \pi}{6} = 0.74$	$\frac{\text{л}\sqrt{3}}{16}$ = 0,34
11	Examples	Polonium	Sodium, Lithium, Chromium	Aluminum, Copper, Silver	Magnesium, Zinc, Cadmium	Germanium, Silicon, Carbon

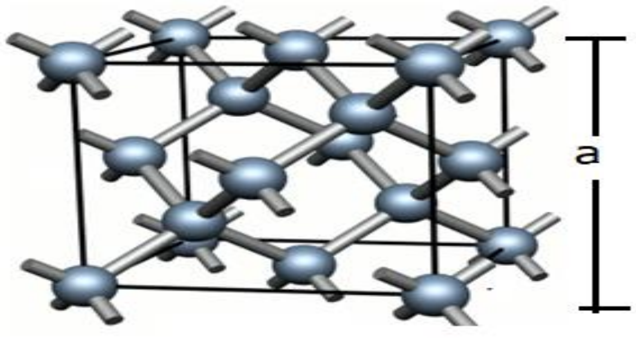
RELATIONSHIP BETWEEN THE DENSITY OF CRYSTAL MATERIAL AND LATTICE CONSTANT IN A CUBIC LATTICE:

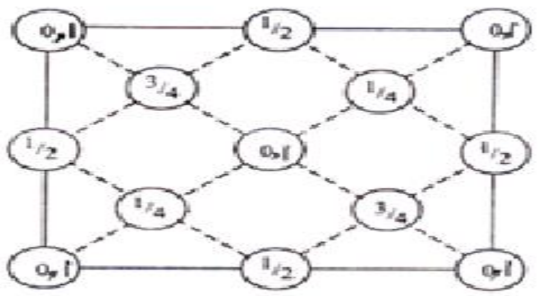
Consider a cubic crystal of lattice constant a. the number of atoms pe unit cell be n and ρ be the density of the crystal material. The atomic weight of the material is M_A. let N_A be the Avogadro's number. Thus, $\left[\frac{M_A}{\rho}\right]$ m^3 of the material will contain N_A atoms. Hence n atoms in a unit cell will occupy a volume $\left[\frac{M_A n}{\rho N_A}\right]$, Thus, $a^3 = \frac{M_A n}{\rho N_A};\ or\ \rho = \frac{M_A n}{N_A a^3}\ ;or\ a = \left[\frac{M_A n}{\rho N_A}\right]^{1/3}$

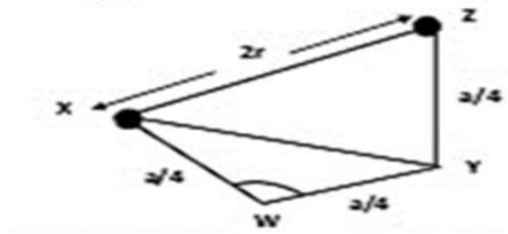
OTHER CUBIC STRUCTURES:

i) DIAMOND CUBIC STRUCTURE

The diamond lattice can be considered to be formed by interpenetrating two FCC lattices along the body diagonal by (1/4)th cube edge. One sublattice has origin at point (0,0,0,) and the other at a point quarter of the way along the body diagonal at the point (a/4, a/4, a/4). The basic diamond lattice and the atomic positions in the cubic cell of diamond projected on cube face are shown in figure.







The fractions denote height about the base in units of cube edge. The point at 0 and ½ are on the FCC lattice, those at ¼ and ¾ are on a similar lattice displaced among the body diagonals by ¼ of the cube edge. The packing factor of this structure is

$$(XY)^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 = \left(\frac{a}{8}\right)^2$$

$$(XZ)^2 = (XY)^2 + (YZ)^2 = \left(\frac{a}{8}\right)^2 + \left(\frac{a}{16}\right)^2 = \left(\frac{3a}{16}\right)^2$$

But, XZ = 2r

Therefore, $(2r)^2 = \frac{3a^2}{16}$

The nearest neighbour distance

$$2r = \frac{\sqrt{3}a}{4}$$

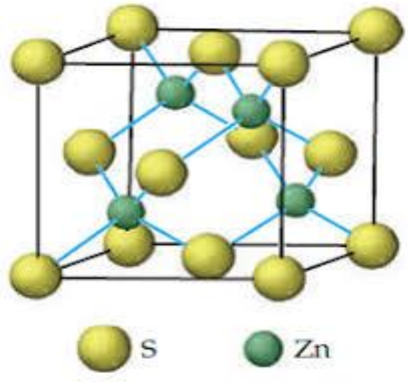
Lattice constant, $a = \frac{8r}{\sqrt{3}}$

Packing factor = $\frac{v}{V} = \frac{8X\frac{4}{3}\pi r^3}{a^3} = \frac{32}{3}\frac{\pi r^3 3\sqrt{3}}{(8r)^3} = \frac{\pi\sqrt{3}}{16} = 0.34 \; or \; 34\%$

Thus, it is a loosely packed structure.

ii) CUBIC ZINC SULPHIDE OR ZINC BLENDE STRUCTURE

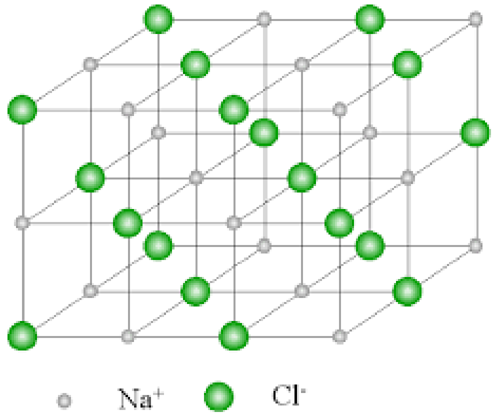
Zinc blende structure is almost identical to diamond structure except that the two interpenetrating FCC sublattices are of different atoms and displaced from each other by one quarter of the body diagonal.



The cubic zinc sulphide structure results when zinc atoms are placed on one FCC lattice and S atoms on the other FCC lattice as shown in figure. The conventional cell of this structure is a cube. There are four molecules per conventional cell. For each atom, there are four equally distant atoms of opposite kind arranged at a regular tetrahedron. The compounds which have cubic zinc sulphide CdS.

iii) SODIUM CLORIDE STRUCTURE

in sodium chloride, sodium loses its outer electron and acquires ion excess of positive charge while the chloride atom accepts one electron from sodium and becomes a negative ion. Now, due to the electrostatic forces between the excess charges, the two ions attract each other. Further, due to the strong forces of repulsion as their outer electron shells come into close proximity, the two ions cannot approach each other to within less than certain distance. When attraction and repulsion balance, equilibrium is obtained. The Bravais lattice is Face Centred Cube with basis of one Na ion and one Cl ion separated by one – half the body diagonal pf the unit cell. There are four molecules of NaCl in a unit cell, with ions in the positions:

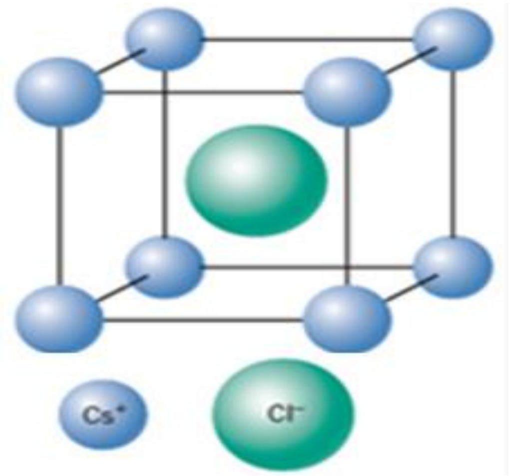


$$Na\colon\ \frac{1}{2}\frac{1}{2}\frac{1}{2}\ ;00\frac{1}{2}\ ;0\frac{1}{2}0\ ;\ \frac{1}{2}00$$

$$Cl:000;\ \frac{1}{2}\frac{1}{2}0\ ;\ \frac{1}{2}0\frac{1}{2}\ ;0\frac{1}{2}\frac{1}{2}$$

In this structure, each ion is surrounded by six nearest neighbours of the opposite kind. The coordination number is six. There are twelve next nearest neighbours of the same kind as the reference ion. Representative crystals having NaCl structure are KCl, KBr, MgO, AgBr, etc.

iv) CAESIUM CHLORIDE STRUCTURE



The space lattice is simple cubic. The basis has one Cs^+ ion at 0 0 0 and one Cl^- at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Each ion is the centre of a cube of ions of the opposite kind, the coordination number is thus eight. The lattice points of CsCl are two interpenetrating simple cubic lattices, the corner of one substance is the bcc of the other. One sublattice is occupied by Cs^+ ions and the other Cl^- ions. CsCl, RbCl and LiHg, are some materials crystallizing in this structure.

DIRECTION PLNES AND, MILLER INDICES

In a crystal there exists directions and planes which contain a large concentration of atoms. It is necessary to locate these directions and planes for crystal analysis. In Fig., two directions are shown by arrows in two dimensions.

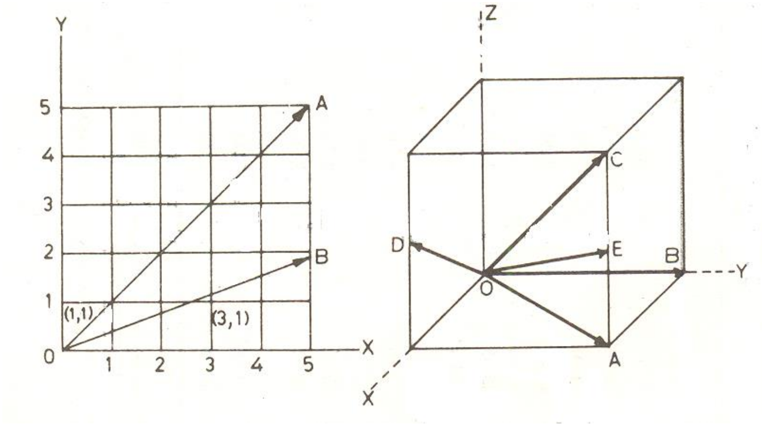
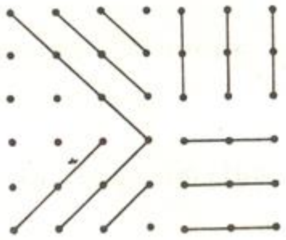


Figure Crystal directions.

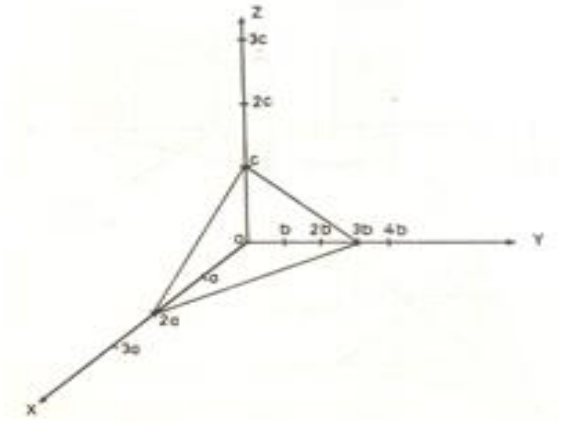
These directions pass through the origin 0 and end at A and B respectively. The directions described by giving the coordinates of the first whole numbered point (x, y) through which each of the directions passes. For direction OA, it is (1, 1) and for OB it is (3, 1). In three-dimensions, the directions are described by the coordinates of the first whole numbered point (x, y, z). Generally, square brackets are used to indicate a direction. A few directions are

OA [1 10]; OB [0 1 0]; OC [1 1 1]; OD [1 0 2]; OE [1 1 2]



(a) Different crystal planes

The crystal lattice may be regarded as made-up or an aggregate of a 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 different ways as shown in figure. The problem is that how to designate these planes in a crystal. Miller evolved a method to designate a set of parallel planes in a crystal by three numbers (h k l) known as **Miller indices**.



The steps in the determination of ***Miller indices*** of a set of parallel planes are illustrated with the aid of Figure.

(i) Determine the coordinates of the intercepts made by the plane along the three crystallographic axes (x, y, z axes)

$$\begin{array}{ccc} x & y & z \\ 2a & 3b & c \\ pa & qb & rc \end{array}$$

Where $p = 2$, $q = 3$ and $r = 1$

(ii) Express the intercepts as multiples of the unit cell dimensions, or lattice parameters along the axes,

$$\frac{2a}{a} \qquad \frac{3b}{b} \qquad \frac{c}{c}$$

$$2 \qquad 3 \qquad 1$$

(iii) Determine the reciprocal of these numbers

$$\frac{1}{2} \qquad \frac{1}{3} \qquad \frac{1}{1}$$

(iv) Reduce these reciprocals to the smallest set of integral numbers and enclose them in brackets:

$$6\times\frac{1}{2} \qquad 6\times\frac{1}{3} \qquad 6\times\frac{1}{1}$$

$$(3\ 2\ 6)$$

In general, it is denoted by (h k l). We also notice that:

$$\frac{1}{p}:\frac{1}{q}:\frac{1}{r}=h:k:l$$

$$\frac{1}{2}:\frac{1}{3}:\frac{1}{1}=3:2:6$$

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

IMPORTANT FEATURES OF MILLER INDICES OF CRYSTAL PLANES

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

(ii) A plane parallel to one of the coordinate axes has an intercept of infinity.

(iii) If the Miller indices of two planes have the same ratio (i.e., 844 and 422 or 211), then the planes are parallel to each other.

(iv) 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.

IMPORTANT PLANES AND DIRECTIONS IN A CUBIC CRYSTAL

In figure a, the plane cuts the Y–axis at ∞ and Z–axis ∞. Therefore, the coordinates of the intercepts of the plane are ∞. That is ∞, 1 and ∞ are the intercept as the multiples of the unit cell dimensions. Take the reciprocals, $\frac{1}{\infty}, 1, and\ \frac{1}{\infty}$, or 0, 1, 0. Hence (0 1 0) are the miller indices of the plane and, (0 1 0) plane is perpendicular to [0 1 0] direction, (1 1 0) and (1 1 1) planes are shown in figure b and in figure c. Also figure b and figure c shows [1 1 0] and [1 1 1] directions respectively.

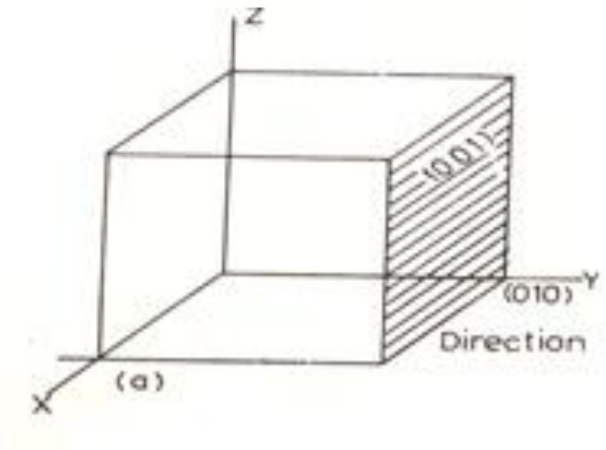
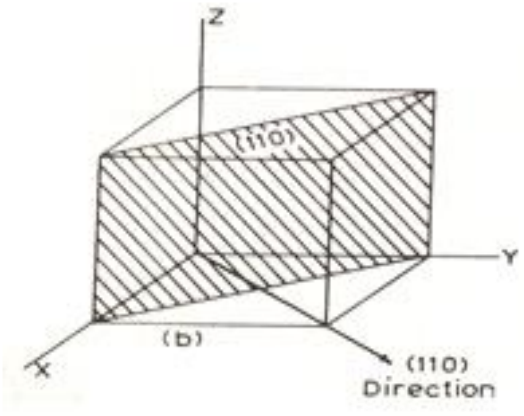


Figure a



Type equation here.

Figure b

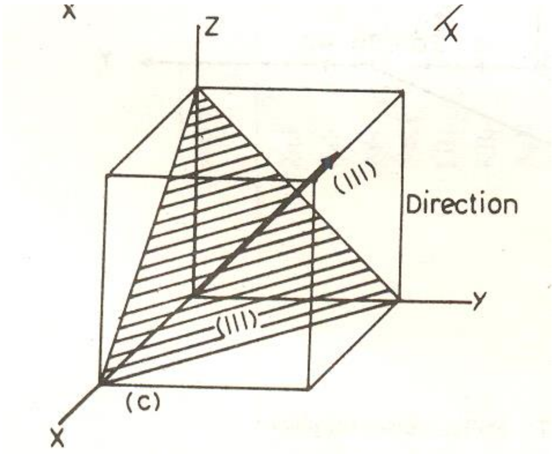
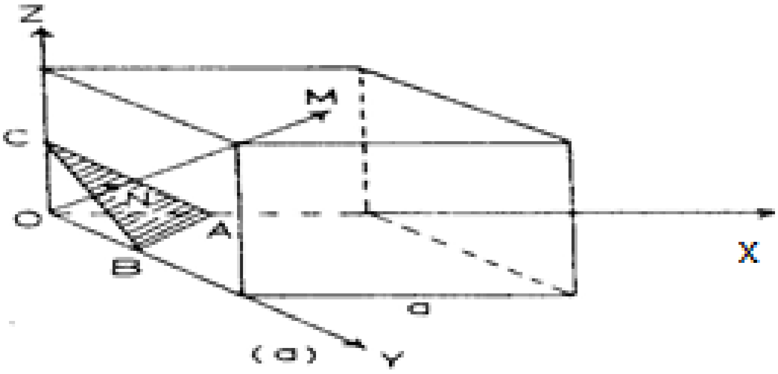


Figure c Planes and directions in a cubic system

SEPARATION BETWEEN LATTICE PLANES IN A CUBIC CRYSTAL

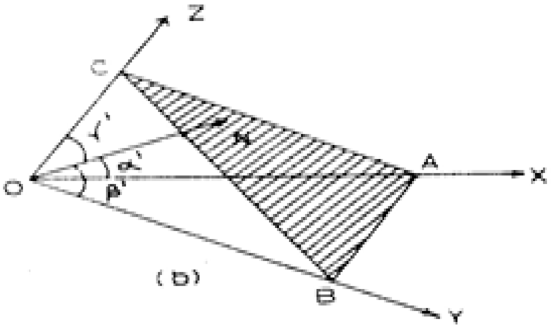
The cube edge is a. Let $(h\ k\ l)$ be the *Miller indices* of the plane$A\ B\ C$. This plane belongs to a family of planes whose miller indices are $(h\ k\ l)$ because *Miller indices* represent a set of planes. Let $ON = d_1$ be the perpendicular distance of the plane $A\ B\ C$ from the origin. Let $\alpha',\ \beta'$and γ' (different from the interfacial angles $\alpha,\ \beta$and γ) be the angles between coordinates axes $X,\ Y,\ Z$respectively and ON. The intercept of the plane on the three axes are

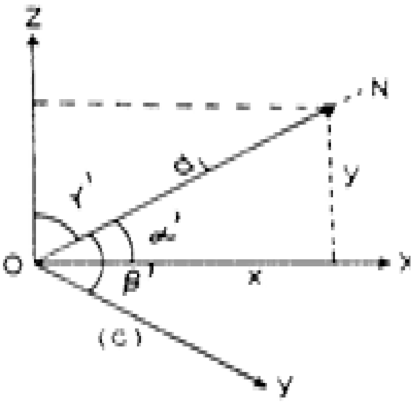
$OA = \frac{a}{h},\quad OB = \frac{a}{k}$, and $OC = \frac{a}{l}$



From fig (a) we have

$\cos\alpha' = \frac{d_1}{OA},\quad \cos\beta' = \frac{d_1}{OB}$, and $\cos\gamma' = \frac{d_1}{OC}$





From fig (b) we have,

$$(ON)^2 = x^2 + y^2 + z^2 = d_1^2 = d_1^2(\cos^2\alpha') + d_1^2(\cos^2\beta') + d_1^2(\cos^2\gamma')$$

$$(ON)^2 = d_1^2 = d_1^2[(\cos^2\alpha') + (\cos^2\beta') + (\cos^2\gamma')]$$

$$d_1 = d_1[(\cos^2\alpha') + (\cos^2\beta') + (\cos^2\gamma')]^{\frac{1}{2}}$$

But, $cos^2\alpha^{'} + cos^2\beta^{'} + cos^2\gamma^{'} = 1$

Substituting value of cosα’, cosβ’and cosγ’ in above equation we get,

$$\left[\frac{d_1}{OA}\right]^2 + \left[\frac{d_1}{OB}\right]^2 + \left[\frac{d_1}{OC}\right]^2 = \left[\frac{d_1h}{a}\right]^2 + \left[\frac{d_1k}{a}\right]^2 + \left[\frac{d_1l}{a}\right]^2 = \frac{d_1^2}{a^2}(h^2 + k^2 + l^2) = 1$$

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

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

Let $OM = d_2$be the perpendicular distance of the next plane PQR parallel to ABC, the intercept of this plane on the three crystallographic axes are,

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

$cos\,\alpha' = \frac{d_2}{OA}$, $cos\,\beta' = \frac{d_2}{OB}$, and $cos\,\gamma^{'} = \frac{d_2}{OC}$ X

$$(OM)^2 = d_1^2 = d_2^2(cos^2\alpha^{'}) + d_2^2(cos^2\beta^{'}) + d_2^2(cos^2\gamma^{'})$$

$$d_2^2 = d_2^2[(cos^2\alpha^{'}) + (cos^2\beta^{'}) + (cos^2\gamma^{'})]$$

$$d_2 = d_2[(cos^2\alpha^{'}) + (cos^2\beta^{'}) + (cos^2\gamma^{'})]^{\frac{1}{2}}$$

But, $cos^2\alpha^{'} + cos^2\beta^{'} + cos^2\gamma^{'} = 1$

Substituting this in equation X we get,

$$\left[\frac{d_2h}{2a}\right]^2 + \left[\frac{d_2k}{2a}\right]^2 + \left[\frac{d_2l}{2a}\right]^2 = \frac{d_2^2}{4a^2}(h^2 + k^2 + l^2) = 1$$

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

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

Thus, the inter planner spacing between two adjacent parallel planes of Miller indices $(h\ k\ l)$ is given by,

$$d = d_2 - d_1 = \frac{a}{\sqrt{h^2+k^2+l^2}}$$