

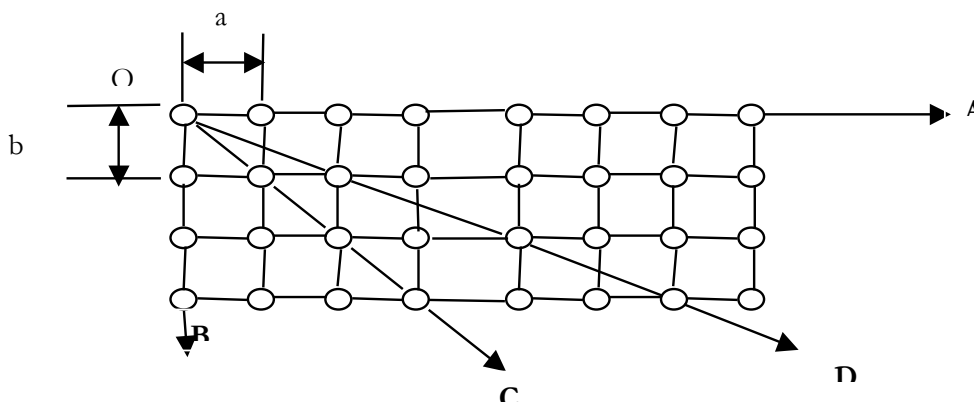
CRYSTAL STRUCTURE**UNIT-VII****VTU University Syllabus (2006-07)**

Space lattice, Bravais lattice - unit cell, primitive cell. Lattice parameters. Crystal systems. Direction and planes in a crystal. Miller indices. Expression for inter-planar spacing. Co-ordination number. Atomic packing factor. Bragg's Law. Determination of crystal structure by Bragg's x-ray spectrometer. Crystal structures of NaCl, and diamond. **(6Hours)**

In mineralogy and crystallography, a crystal structure is a unique arrangement of atoms in a crystal. A crystal structure is composed of a unit cell, a set of atoms arranged in a particular way; which is periodically repeated in three dimensions on a lattice. The spacing between unit cells in various directions is called its *lattice parameters*. The symmetry properties of the crystal are embodied in its space group. A crystal's structure and symmetry play a role in determining many of its properties, such as cleavage, electronic band structure, and optical properties.

Space Lattice

In order to describe the structure of crystals, a mathematical concept called space lattice is used and is defined as an infinite number of points in space with property that the arrangement of points about a given point is identical with that about any other point. The points are called ***lattice points or lattice sites***. By using a network of lines the lattice points may be joined. The lines are called ***lattice lines or lattice directions***. A plane containing lattice points is known as a ***lattice plane or atomic plane***.

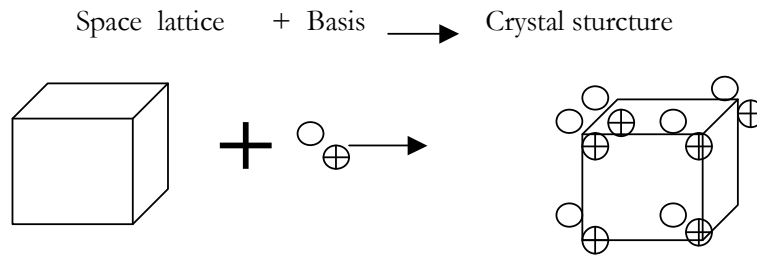


The periodic arrangement of points and identical environment around each lattice point can be understood better with the help of a two dimensional lattice, called net as shown above. It may be noted that if the distance between neighbouring points in a given direction is 'a', the distance between successive points in the same direction is 'a', and that the n^{th} point on the same line is located at a distance of 'na' from the first point. 'a' is called the periodicity in that particular direction. The arrangement of points around a given lattice point is called its environment. Thus the space lattice is a skeleton upon which crystal structure is built by placing atoms on or near the lattice points.

Crystal lattice

A Crystal lattice is a space lattice in which the lattice sites are occupied by atoms or clusters of atoms. Each lattice point is associated with the same unit of groups of atoms, **called basis**. The basis must be identical in composition, arrangement and orientation such that the crystal appears exactly the same at one point as it does at other equivalent points. When the basis is associated with each lattice sites, the crystal structure is obtained.

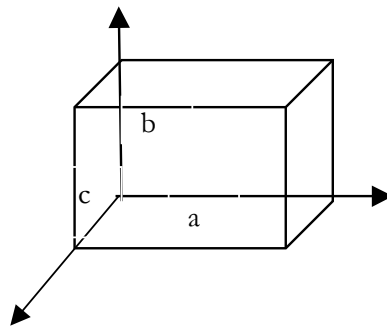
Thus



Unit cell

The unit cell is a spatial arrangement of atoms which is tiled in three-dimensional space to describe the crystal. The unit cell is given by its **lattice parameters**, the length of the cell edges (a, b, c) called **axial lengths** and the angles between them (α, β, γ); while the positions of the atoms inside the unit cell are described by the set of atomic positions (x_i, y_i, z_i) measured from a lattice point.

For each crystal structure there is a *conventional unit cell*, which is the smallest unit that has the *full symmetry* of the crystal. However, the conventional unit cell is not always the smallest possible choice. A **primitive unit cell** of a particular crystal structure is the smallest possible unit cell one can construct such that, when tiled, it completely fills space. If atoms are associated with only the corners of corresponding unit cells, such unit cells are primitive cells. However, in addition to the seven primitive cells, there exist seven nonprimitive cells, of three different types. The three types of nonprimitive cells are body centered cell, face centered cell and base centered cell. The primitive unit cell does not, however, display all the symmetries inherent in the crystal. The crystal systems are a grouping of crystal structures according to the axial system used to describe their lattice. Each crystal system consists of a set of three axes in a particular geometrical arrangement. There are seven unique crystal systems.



The Bravais lattices

When the crystal systems are combined with the various possible lattice centerings, we arrive at the Bravais lattices. They describe the geometric arrangement of the lattice points, and thereby the translational symmetry of the crystal. In three dimensions, there are 14 unique Bravais lattices which are distinct from one another in the translational symmetry they contain. All crystalline materials recognized until now (not including quasicrystals) fit in one of these arrangements. The fourteen three-dimensional lattices, classified by crystal system, are shown below. The Bravais lattices are sometimes referred to as *space lattices*.

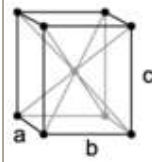
The crystal structure consists of the same group of atoms, the *basis*, positioned around each and every lattice point. This group of atoms therefore repeats indefinitely in three dimensions according to the arrangement of one of the 14 Bravais lattices. The characteristic rotation and mirror symmetries of the group of atoms, or unit cell, is described by its crystallographic point group.

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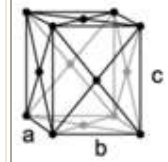
Body-centered

Face-centered

$a \neq b \neq c$



$a \neq b \neq c$



Properties of Unit Cell:-

A unit cell is characterized by an effective number of atoms, coordination number, atomic packing fraction, void space and density.

1) **Volume of Unit cell:-**

The volume of a unit cell is given by

$$V = abc \left[1 - \cos^2(\alpha) - \cos^2(\beta) - \cos^2(\gamma) + 2 \cos(\alpha) \cos(\beta) \cos(\gamma) \right]^{\frac{1}{2}}$$

For the case of Cubic Crystal, $a=b=c$ and $\alpha=\beta=\gamma=90^\circ$.

Therefore in case of simple cubic cell $V=a^3$.

2) **Effective number of atoms per unit cell (Z):-** It is the product of the contribution of number of atoms per lattice point and the number of lattice points per unit cell. A unit cell is a part of an infinite scheme, and is not an isolated entity. Therefore, the lattice points do not exclusively belong to one unit cell but each one is shared by several adjacent cells. Thus, the atom located at a lattice site contributes only a fraction of its mass and volume to one unit cell.

3) **Atomic Radius.** (r) :- The specific direction along which atoms are in contact, is identified and by applying simple geometry, the relationship between the atomic radius ' r ' and the edge length ' a ' may be computed.

4) **Nearest neighbor distance** ($2r$):-

The nearest neighbor distance in metallic structures is the distance between the centres of the atoms in contact expressed in terms of the length of the edge of the unit cell.

5) **Coordination number, CN:-**

The coordination number of an atom in a crystal is the number of nearest neighbor atoms which are simultaneously in contact with that atom. It signifies the tightness of packing of atoms in the crystal. In a Bravais lattice, all atoms have the same coordination number.

6) **Atomic Packing Fraction, APF:-**

The fraction of space occupied by atoms in a unit cell is known as atomic packing fraction. It is defined as the ratio of volume of effective number of atoms in the unit cell to the total volume of the unit cell.

Thus

$$APF = \frac{\text{(Number of atoms/unit cell) (volume of each atom)}}{\text{Volume of the unit cell.}}$$

$$APF = \frac{Zv}{V}$$

The atomic packing fraction denotes the efficiency with which the available space in a unit cell is utilized.

7) **Void Space :** The void space in the unit cell is the vacant space left unutilized in the cell. It is equal to $(1 - APF)$. It is often expressed as percentage.

Thus, Void space = $(1 - APF) * 100$

The void space is more commonly known as **interstitial space**.

8) **Density (ρ)-** As a unit cell possesses all the structural properties of a bulk crystal. The density of a unit cell must be same as that of the bulk crystal. Thus, Density $\rho = \text{Mass/Volume} = Zm/V$

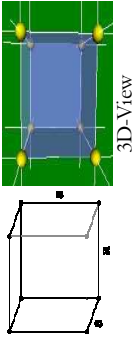
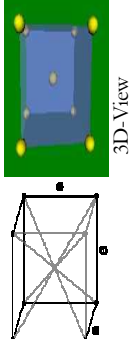
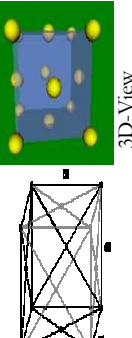
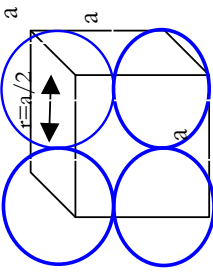
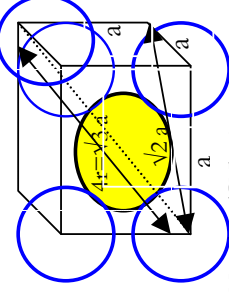
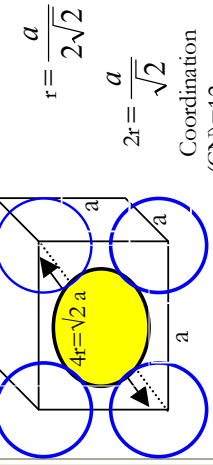
Where m is the mass of each atom, $m = M/N_a$

Where M is the molecular weight of the material and N_a is the Avogadro number

\therefore

$$\rho = \frac{ZM}{N_a V}$$

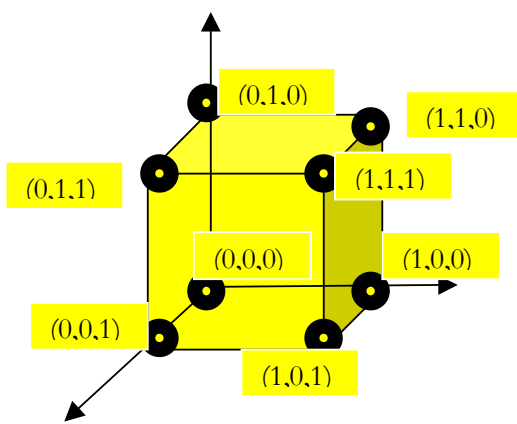
All the properties of Unit cell for the cubic structure is discussed in the table given below:-

| Characteristics of Unit Cubic Lattice of volume a^3 | | |
|---|--|---|
| <p>Simple cubic (sc)</p>  <p>3D-View</p> | <p>Body-centered cubic (bcc)</p>  <p>3D-View</p> | <p>Face-centered cubic (fcc)</p>  <p>3D-View</p> |
| 1. Effective Number of atoms per unit cell (z) | | |
| <p>$Z = \frac{1}{8} (\text{atom/lattice}) 8 (\text{lattice/unitcell})$ $\therefore Z = 1$</p> | <p>$Z = (1 \text{ body center Atom /unit cell}) + \frac{1}{8} (\text{atom/lattice}) 8 (\text{lattice/unitcell})$ $\therefore Z = 1 + 1 = 2$</p> | <p>$Z = (1/2 \text{ atoms / Face}) \cdot (6 \text{ Faces /unit cell}) + \frac{1}{8} (\text{atom/lattice}) 8 (\text{lattice/unitcell})$ $\therefore Z = 3 + 1 = 4$</p> |
| <p>2). Atomic Radius, r & 3). Nearest neighbour distance, $2r$,</p>  <p>$r = a/2$ $2r = a$</p> <p>Coordination Number (CN) = 6</p> |  <p>$r = \frac{\sqrt{3}}{4} a$ $2r = \frac{\sqrt{3}}{2} a$</p> <p>Coordination Number (CN) = 8</p> |  <p>$r = \frac{a}{2\sqrt{2}}$ $2r = \frac{a}{\sqrt{2}}$</p> <p>Coordination Number (CN) = 12</p> |
| <p>Atomic Packing Fraction (APF) = $\frac{zV}{V}$ and Void Space = $(1 - \text{APF}) \cdot 100$, Where v is Volume of an atom and V is the volume of unit cell; is the molecular weight and N_A is the Avogadro Number</p> | | |
| <p>APF = $\frac{\pi}{6} = 0.52$ Void Space = 48% Density $\rho = \frac{M}{N_A a^3}$</p> | <p>APF = $\frac{\pi\sqrt{3}}{8} = 0.68$ Void Space = 32% Density $\rho = \frac{2M}{N_A a^3}$</p> | <p>APF = $\frac{\pi}{3\sqrt{2}} = 0.74$ Void Space = 26% Density $\rho = \frac{4M}{N_A a^3}$</p> |

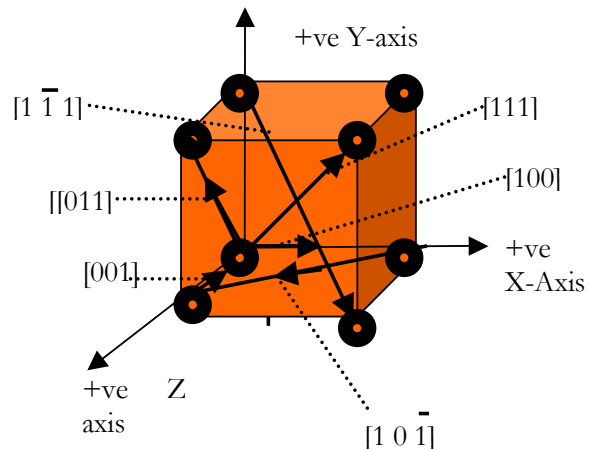
Classification of crystals by symmetry

The defining property of a crystal is its inherent symmetry, by which we mean that under certain *operations* the crystal remains unchanged. For example, rotating the crystal 180 degrees about a certain axis may result in an atomic configuration which is identical to the original configuration. The crystal is then said to have a two-fold rotational symmetry about this axis. In addition to rotational symmetries like this, a crystal may have symmetries in the form of mirror planes and translational symmetries, and also the so-called *compound symmetries* which are a combination of translation and rotation/mirror symmetries. A full classification of a crystal is achieved when all of these inherent symmetries of the crystal are identified.

Atomic Positions and the Directions in Cubic Unit cell are as below:-



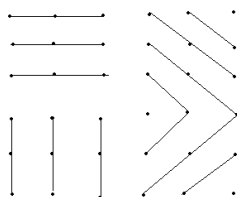
Representation of Atomic positions/Lattice sites



Representation of indices of directions/lattice lines

Lattice planes and Miller indices

The crystal lattice may be regarded as made up of 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 a different number of ways for example is shown below.



The problem is that how to designate a plane in the crystal. With reference to the axes of the “Unit Cell”, each set of planes has a particular orientation. In order to specify the orientation, one employs the so called Miller indices; these are defined as follows: Suppose a particular plane of a given set has intercepts pa , qb , rc with the crystal axes. The Miller indices of the set of planes are then given by three numbers h,k,l such that

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

with the condition that h,k and l are the smallest integers satisfying the above equation i.e., h,k and l have no common factor >1 .

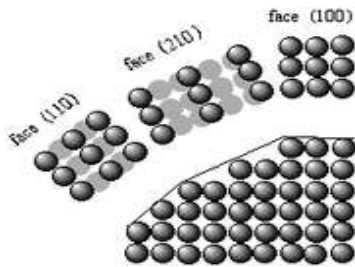
The rules for finding Miller indices are as follows:

- 1) First determine the intercepts of plane on the three coordinate axes.
- 2) Secondly take the reciprocals of these intercepts.
- 3) Lastly, reduce the reciprocals into whole numbers. This can be done by multiplying each reciprocal by a number obtained after taking LCM of denominator.

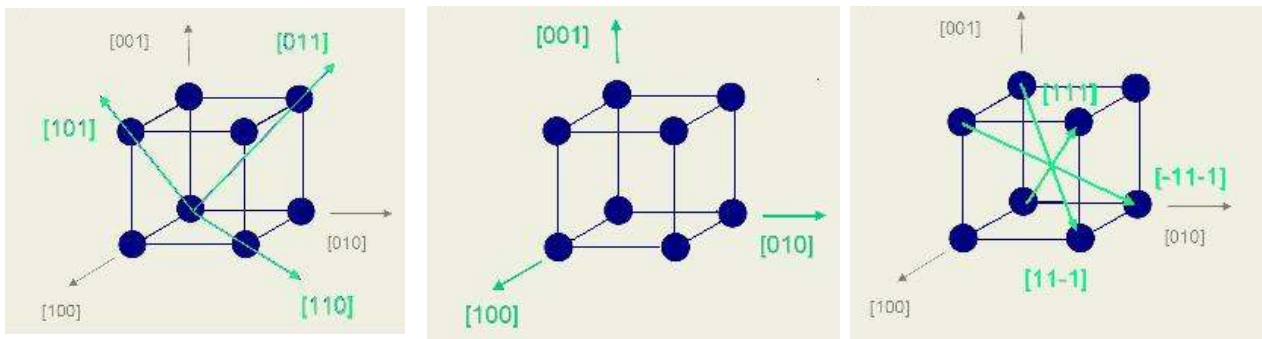
Let us consider the Miller indices in particular case where the plane cuts the intercepts of 2,3,4 units along the three axes.

- 1) Intercepts are 2,3,4
- 2) Reciprocal of these are $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$
- 3) LCM of denominators i.e., 2,3,4 is 12, Hence multiplying by 12, we have 6,4,3.

Thus Miller indices of this plane is (643).

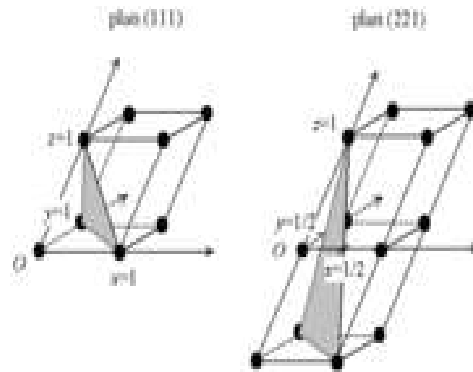
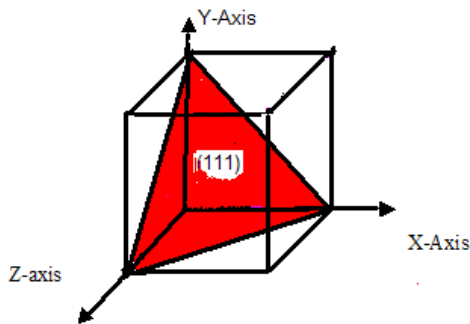
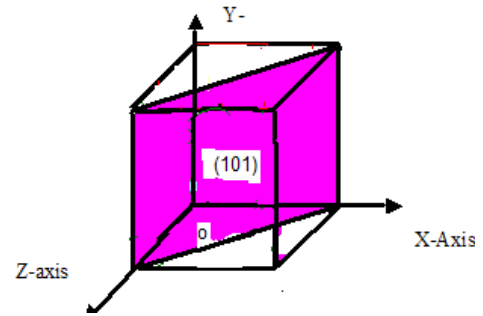
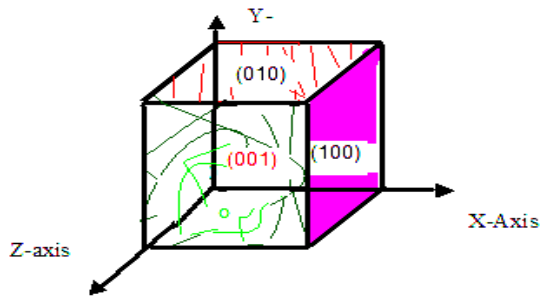


Picture of Dense Crystallographic planes.



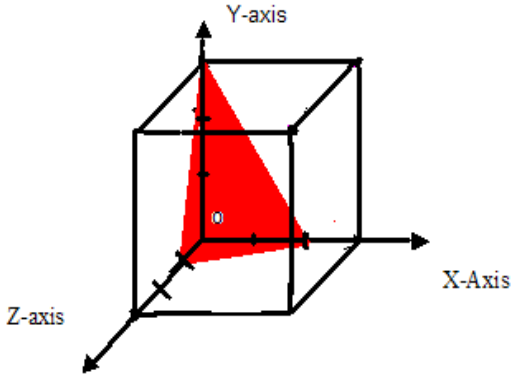
The three **Principal Miller Index Planes** (100), (110) and (111) in a cubic lattice are as below. The Miller indices for the plane (100) has the shaded plane intercepts of $1, \infty, \infty$ for the X Y and Z axes respectively. The reciprocals of the intercepts are $1, 0, 0$. The Miller indices for this plane is (100). The plane with intercepts $1, 1, \infty$ whose reciprocals are $1, 1, 0$ and the Miller indices are (110). For the intercepts $1, 1, 1$ which give Miller indices (111). When the indices are shown enclosed by braces, such as $\{h,k,l\}$, they refer to planes which in the crystal are equivalent even through their Miller indices may differ. For example, in a cubic lattice all cube faces are equivalent; in order to specify this group of

planes, one writes $\{100\}$, which includes the planes (100), (010), (001), (1 0 0), (0 1 0), (0 0 1).

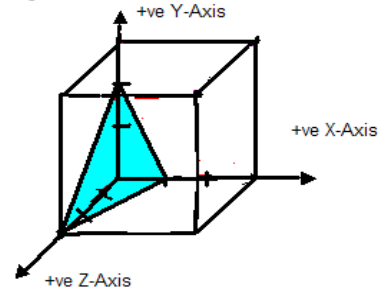


For the Unit cells of unit axial lengths, the Miller indices planes are calculated after finding its Planar intersections along each axis. The reciprocals of the planar intercepts with smallest set of integers is a Miller indices. The Planar intersections will be the fractions. Miller indices planes are shaded, along with that the plane must be drawn such that it intercepts the X,Y and Z axes at distances of 1 for 1 miller indices value, 0.5 distance for 2 miller indices value and 0.33 for 3 miller indices value and so on. Few of the Miller indices planes are shown below.

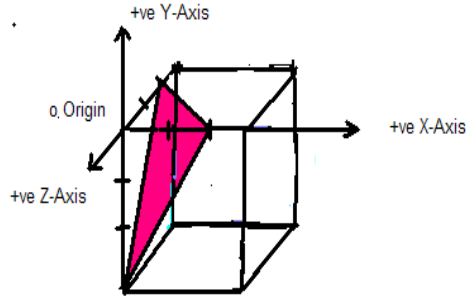
Miller indices (213) planar intersection 2,3,1 Along X at 0.5 along y at 1 along z at 0.33



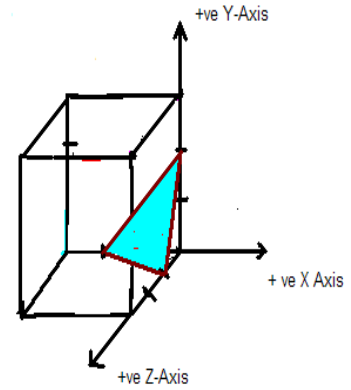
Miller indices (3 2 1) Planar Intersection 1,2,3 Along X at 0.33 Along Y at 0.5 along z at 1 unit distance.



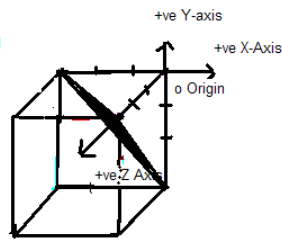
Miller indices (2 $\bar{1}$ 2) Planar Intersection 2, $\bar{1}$, 2 Along X axis at 0.5 along Y at 1 along Z at 0.5 distance



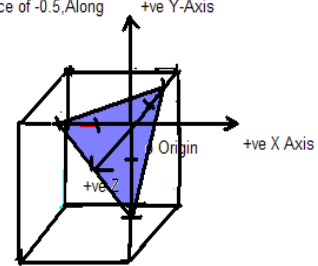
Miller Indices ($\bar{2}$ 2 3) Planar intercepts -2, 2, 1 Along X at -0.5 distance Along Y at 0.5 Along Z at 0.33 distance



Miller indices ($\bar{1}$ $\bar{1}$ 1) Planar Intersection -1, -1, 1 Along X at a distance of -1 Along Y -1 along Z 1

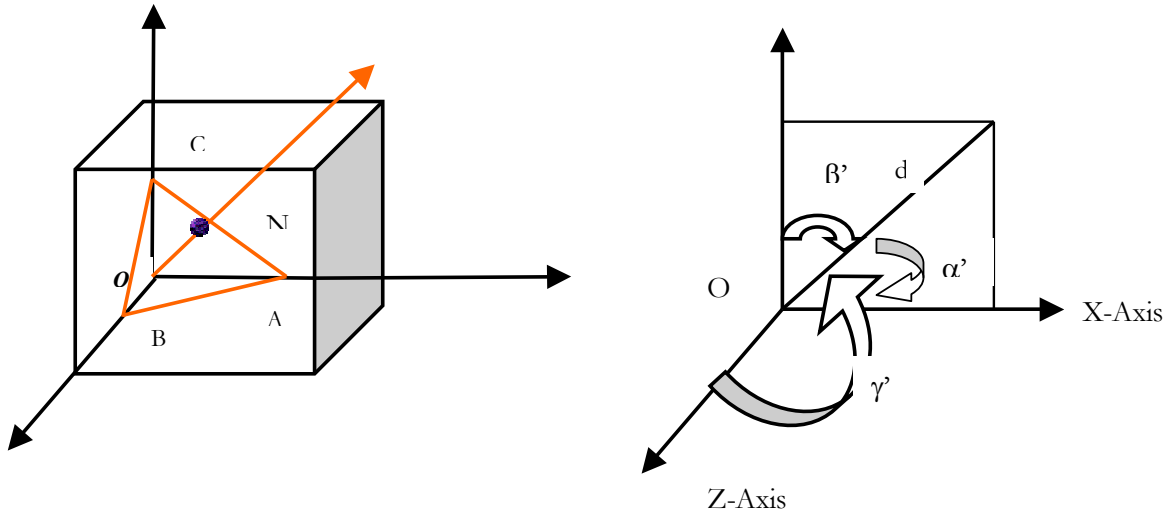


Miller Indices ($\bar{2}$ $\bar{2}$ $\bar{2}$) Planar Intersection -2, -2, -2 Along X axis at a distance of -0.5, Along Y -0.5 and along Z -0.5



Expression for inter-planar spacing

Consider the case of plane ABC of a cubic crystal as shown in Fig. . This plane belongs to a family of planes whose Miller indices are hkl because Miller indices represent a set of planes. Here ON is the perpendicular drawn from the origin to this plane. The distance ON represents the interplaner spacing d of the family of planes. Let α' , β' and γ' be the angles between coordinate axes X,Y,Z and ON respectively.



The intercepts of the plane on the three axes are

$$OA=a/h ; OB=a/k; OC=a/l \quad \text{-----(1)}$$

where 'a' is the length of the cube edge. Then from figure, we have

$$\cos \alpha' = \frac{d}{OA} \quad \cos \beta' = \frac{d}{OB} \quad \cos \gamma' = \frac{d}{OC} \quad \text{-----(2)}$$

From the figure $ON = [(x)^2 + (y)^2 + (z)^2]^{\frac{1}{2}}$

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

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

substituting the values of $\cos \alpha'$, $\cos \beta'$ and $\cos \gamma'$ in equation (2), we get

$$\left(\frac{d}{OA}\right)^2 + \left(\frac{d}{OB}\right)^2 + \left(\frac{d}{OC}\right)^2 = 1$$

or $\left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{a}\right)^2 + \left(\frac{dl}{a}\right)^2 = 1$

or
$$\frac{d^2}{a^2}(h^2 + k^2 + l^2) = 1$$

or

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

This is the relation between interplaner spacing 'd' and the edge of the cube 'a'. It should be noted that this formula is applicable only to primitive lattices in cubic, orthorhombic and tetragonal systems.

Separation Between Lattice planes in simple, face centred and body centred lattices

In case of simple cubic lattice, the (100) planes cut the X-axis and are parallel to Y and Z axis. The (110) planes cut obliquely across the X and y axis but they are parallel to Z axis. Similarly the (111) plane cut obliquely across the three axes.

If d_{100} represents the perpendicular distance between successive (100) planes, then

$$d_{100} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a$$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

Hence

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

Or

$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \sqrt{3}$$

For Face Centered Cubic lattice, the (100), (110) and (111) planes will have the additional planes arise half the way between these planes.

$$d_{100} = \frac{1}{2}(d_{100})_{\text{simple lattice}} \quad d_{110} = \frac{1}{2}(d_{110})_{\text{simple lattice}} \quad d_{111} = (d_{111})_{\text{simple lattice}}$$

The ratio of the basic interplaner distance will be as

$$d_{100} : d_{110} : d_{111} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}}$$

or
$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \frac{\sqrt{3}}{2}$$

For Body Centered Cubic lattice, the (100), (110) and (111) planes will also have the additional planes arise half the way between these planes.

$$d_{100} = \frac{1}{2}(d_{100})_{\text{simple lattice}} \quad d_{110} = \frac{1}{2}(d_{110})_{\text{simple lattice}} \quad d_{111} = \frac{1}{2}(d_{111})_{\text{simple lattice}}$$

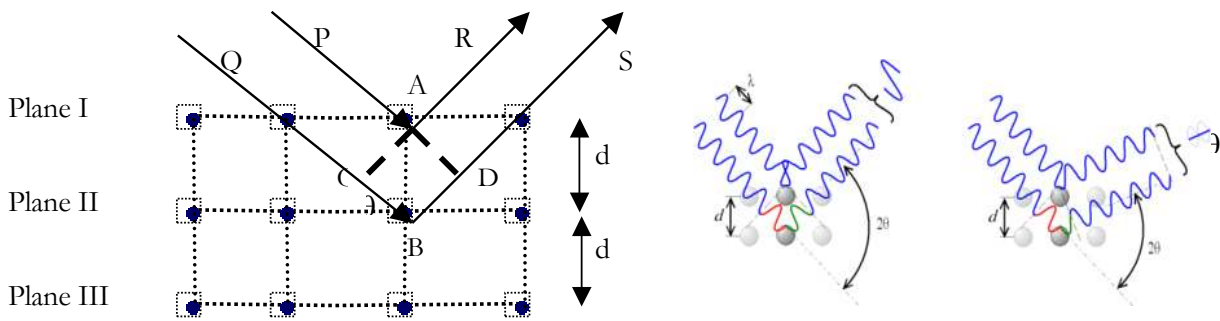
The ratio of the basic interplaner distance will be as

$$d_{100} : d_{110} : d_{111} = \frac{a}{2} : \frac{a}{\sqrt{2}} : \frac{a}{2\sqrt{3}} = 1 : \frac{2}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

or
$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \frac{\sqrt{2}}{2} : \sqrt{3}$$

Bragg's Law

Let us consider a set of parallel lattice planes of a crystal separated by a distance 'd' apart. Suppose a narrow beam of X-rays of wavelength 'λ' be incident upon these planes at an angle 'θ' as shown in the below figure.



According to the 2θ deviation, the phase shift causes constructive or destructive interferences

The beam will be reflected in all directions by the atoms of various atomic planes. Because the refractive index of the matter of the crystal is very nearly equal to unity hence there is practically no bending of the rays entering or leaving the crystal.

Consider ray PA reflected at atom A in the direction AR from plane 1 and another ray QB reflected at another atom B in the direction BS. Now from the atom A, draw two perpendiculars AC and AD on the incident ray QB and reflected ray BS respectively. The path difference between these two rays is (CB+BD). The two reflected rays will be in phase or out of phase will depend upon this path difference. When the path difference (CB+BD) is a whole wavelength λ, or multiple of whole wavelength nλ, then the two rays will reinforce each other and produce an intense spot. Thus the condition of reinforcement is

$$CB+BD = n\lambda$$

From the above figure, $CB=BD = d \sin \theta$

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

where $n = 1, 2, 3, \dots$ etc., for first order, second order, third order..etc., maximum respectively. This relation is known as Bragg's law.

Different directions in which intense reflections will be produced can be obtained by giving different values to θ i.e.,

For first maxima, $\sin\theta_1 = \lambda/2d$

For second maxima, $\sin\theta_2 = 2\lambda/2d$

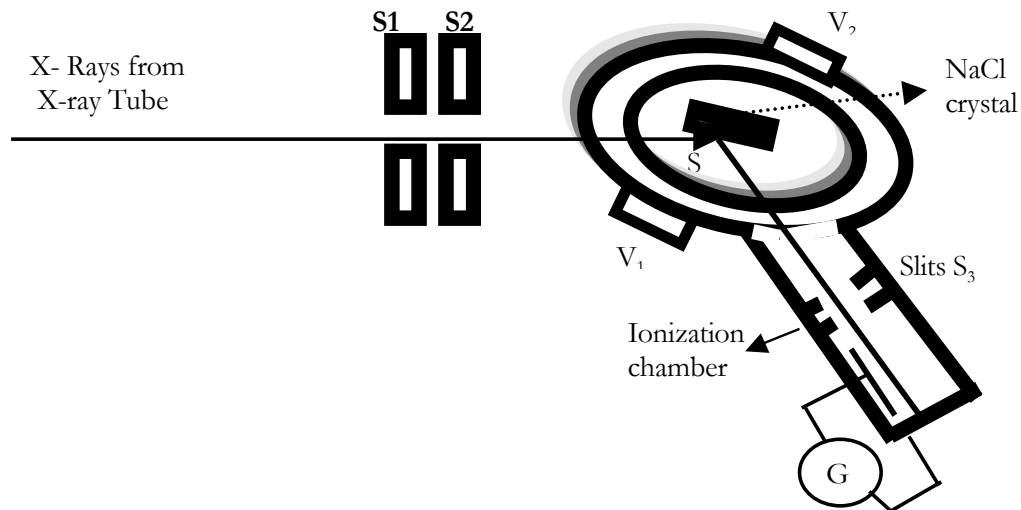
For third maxima, $\sin\theta_3 = 3\lambda/2d$ etc.,

It should be remembered that the intensities go on decreasing as the order of the spectrum increases. Theory of Bragg's diffraction: - When a beam of monochromatic X-rays falls on a crystal, each atom becomes a source of scattering radiations. It has already been mentioned that in a crystal there are certain planes which are particularly rich in atoms. The combined scattering of X-rays from these planes can be looked upon as reflections from these planes. Generally the Bragg scattering is regarded as Bragg reflection and hence are known as Bragg planes. At certain glancing angles, reflections from these sets of parallel planes are in phase with each other and hence they reinforce each other to produce maximum intensity. For other angles, the reflections from different planes are out of phase and hence they reinforce to produce either zero or extremely feeble intensity.

Bragg's law can be utilized to analyze different types of crystal structures.

Bragg's X-ray spectrometer

The schematic arrangement of Bragg's spectrometer is shown in the following figure.



X-rays from tube are narrowed to obtain a fine pencil of beam by passing them through slits S_1 and S_2 provided in lead screens. The beam is now allowed to fall on a crystal C (usually of NaCl with 100 face) mounted on a circular turn table of spectrometer. This turn table is capable of rotation about a vertical axis passing through its center. The rotation can be read on a circular graduated scale S with the help of vernier V_1 . The reflected beam then passes through slits S_3 and enters the ionization chamber. Ionization chamber is simply a container for gas or vapour with two electrodes. The ionization chamber is mounted on a special movable arm about the same axis of crystal. The position of ionization chamber can be read by a second vernier V_2 . The turn table and ionization chamber are linked together in a such a way that when the turn table rotates through an angle θ , the ionization chamber turn through 2θ . In this way, the beam is always reflected into the ionization chamber whatever may be the glancing angle at the surface of the crystal. The X-rays entering the ionization chamber ionise the gas which causes a current to flow between two electrodes which can be measured by galvanometer G .

The ionization current is measured for different values of glancing angle θ and the ionization current. For certain values of glancing angle θ , the intensity of ionization current increases abruptly. We know from the Bragg's equation that

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

and we get $\sin\theta_1 : \sin\theta_2 : \sin\theta_3 = 1 : 2 : 3$.

From the graph of glancing angle θ and ionization current, the glancing angles $\theta_1, \theta_2, \theta_3$ or first, second and third order reflections are measured. It can be seen that $\sin\theta_1 : \sin\theta_2 : \sin\theta_3 = 1 : 2 : 3$. This shows that the assumption that X-rays get reflected like ordinary light is justified. Here we have assumed that the X-rays beam is monochromatic.

From the observed value of θ and known values of d and n , the wavelength λ of X-rays can be calculated by using Bragg's equation i.e., $2d\sin\theta = n\lambda$.

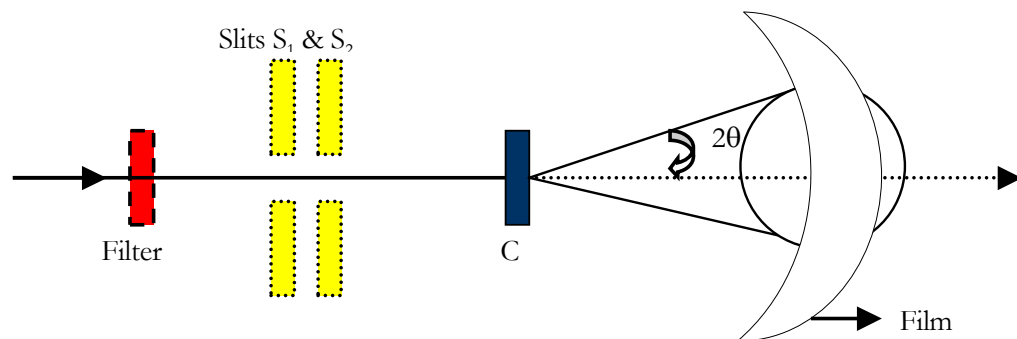
Facts observed are:-

- 1) As the order of spectrum increases, the intensity of the reflected X-rays decreases.
- 2) the ionisation current does not fall to zero for any value of glancing angle θ . It is maximum for certain angles. This shows the existence of a continuous spectrum over which the characteristic line spectrum is superposed.

Determination of crystal structure by Bragg's X-ray spectrometer

The Bragg's spectrometer can be used to diffract X-rays by using a single crystal free from distortion. There are variety of materials also e.g., metals, alloys, powder etc. which are available in micro-crystalline nature. Actually only few substances are available in the form of a large single crystal. Powder crystal method is a standard technique to study the structure of micro-crystal (substances which are available in the form of very small crystals or in powder form). This method gives information regarding the size of crystals, presence of impurities, distortion, preferred orientation of crystals etc.

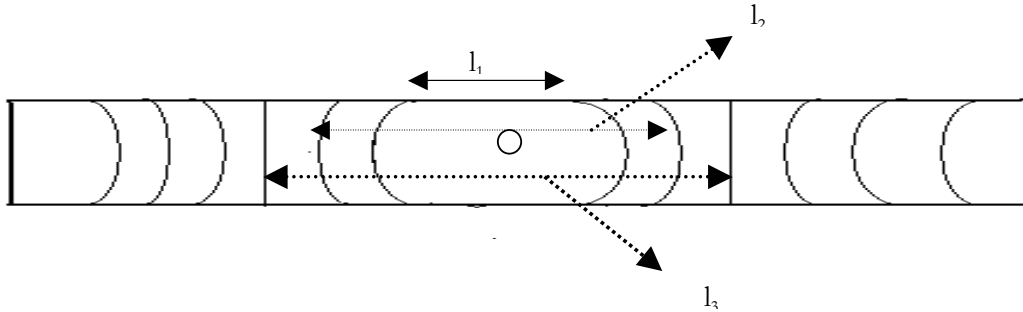
The experimental arrangement of powder method is shown in the following figure. X-rays from X-rays tube are allowed to pass through a filter F which absorbs all wavelengths except one. In this way a monochromatic beam of X-rays is obtained. The beam is collimated by passing it through two fine slits S1 and S2 cut in two lead plates. This fine pencil of X-rays is made to fall on the powdered specimen C. the specimen is located at the center of drum shaped cassette with photographic film at the inner circumference.



The basic principle underlying this powder technique is that in the powder, millions of micro crystals have all possible random orientations. Among these very large number of micro-crystal there will always exist some crystals whose lattice planes are so oriented to satisfy the Bragg's relation $n\lambda = 2d \sin\theta$. Reflection therefore takes place at these planes. For this value of θ , the beam appears at the corresponding 2θ , deviation. As the parallel lattice planes with a given spacing d and same value of n and θ occur in all position around the axis of the incident beam, the reflected rays produce a cone with semi-vertical angle 2θ . For various sets of d and n , various cones of rays are obtained.

The scattered X-rays are incident on the photographic film. The intersections of the different cones of the photographic film are series of concentric circular rings. Radial of these rings can be used to find glancing angle. Now the interplaner spacing of the crystalline substances can be calculated.

The pattern recorded on the photographic film is shown below. When the film is laid flat. Due to the narrow width of film. Only parts of circular rings are registered on it. The curvature of arcs reverses when the angle of diffraction 90° .



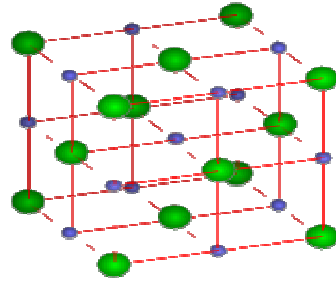
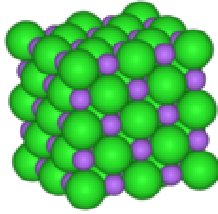
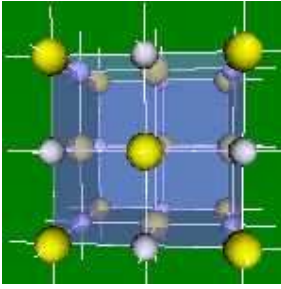
Let l_1, l_2, l_3 etc be the distances between symmetrical lines or stretched paragraph and D , the diameter of cylindrical film. The

$$\frac{h}{\pi D} = \frac{4 \theta_1}{360^\circ} \quad \text{or} \quad \theta_1 = \frac{90^\circ}{\pi D} l_1$$

similarly,

$$\theta_2 = \frac{90^\circ}{\pi D} l_2 \quad \theta_3 = \frac{90^\circ}{\pi D} l_3$$

Using these values of θ in Bragg's formula, interplaner spacing d can be calculated.

Crystal structures of NaCl

3D Views and crystal structure of NaCl crystal. Each atom has six nearest neighbors, with octahedral geometry.

Sodium chloride, also known as **common salt**, **table salt**, or halite, is a chemical compound with the formula NaCl. Sodium chloride is the salt most responsible for the salinity of the ocean and of the extracellular fluid of many multicellular organisms. As the main ingredient in edible salt, it is commonly used as a condiment and food preservative.

The type of Bravais lattice is determined by considering only one kind of atoms shows that NaCl shows the Face centered Cubic structure. NaCl is an ionic compound. Hence the atoms of Na and Cl remain in ionic state in the lattice. In the lattice they occupy alternate positions. The symmetry of arrangement is such that ions of either type could be imagined to occupy the corner positions and the face center positions, with the ions of the opposite type occupying the alternate positions in between. It makes the ion of one type to have six ions of other type as its nearest neighbors. The shortest distance between ions of same type in the NaCl crystal is 5.62 \AA . By considering corner Na ion as the origin the coordinates are expressed in fraction of the edge-length of the cube. Then 4 Na atoms will have the coordinate value 000 ; $\frac{1}{2} 0 \frac{1}{2}$; $0 \frac{1}{2} \frac{1}{2}$; $\frac{1}{2} \frac{1}{2} 0$. In the same coordinate system, the coordinates of the four Cl ions is $\frac{1}{2} 0 0$; $0 0 \frac{1}{2}$; $0 \frac{1}{2} 0$, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$. The crystal structure of many ionic crystals are identical to that of NaCl. KCl, PbS, MnO and AgBr also possess the same structure.

For NaCl the interatomic distance can be calculated using the formula, $a = \frac{zM}{\rho N_A}$

Where $Z=4$, $N_A = 6.02 \times 10^{26} / \text{K Mole}$; Atomic Weight of Na=23

Atomic Weight of Cl= 35.45

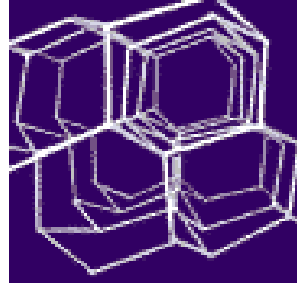
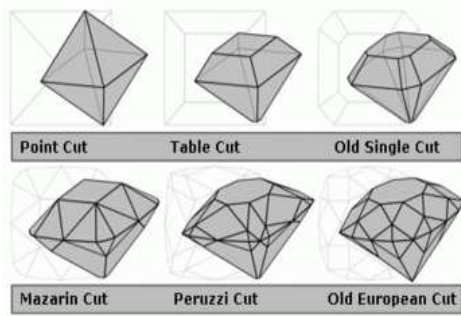
\therefore Molecular Weight of NaCl, $M= 23 + 35.45= 58.45$

Density of NaCl = 2180 Kg/m^3

$\therefore a= 5.627 \times 10^{-10} \text{ m}$.

Since Na and Cl atoms are alternated at equal intervals.

Interatomic distance= $a/2= 2.813 \text{ \AA}$.

Crystal Structure of Diamond*Some Sample pictures of Diamond cuts**Diamond Structure*

In Diamond each carbon atom will be at the center of a tetrahedron, with four carbon atoms as its nearest neighbors located at four corners of the same tetrahedron as shown in the above figure. The 4 atoms are at diagonally opposite points in the respective planes. With this arrangement, two carbon atoms one at the center of the tetrahedron and the other at the corner, form the basis. The bonding is of covalent type. The lattice constant $a = 3.56 \text{ \AA}$, and the bond length is 0.356 nm , with bond angles 109.5° .

Considering a corner of the cube by expressing the coordinates in terms of the edge length of the cube, the position of each of the C atoms can be evaluated. The coordinates of the central C atom are

$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ The coordinates of C atoms at the other positions of unit cell are $0, 0, \frac{1}{2}$, $\frac{1}{2}, 0, \frac{1}{2}$, $\frac{1}{2}, \frac{1}{2}, 0$, $0, \frac{1}{2}, \frac{1}{2}$.

The Semiconductors Ge and Si crystallize in this structure.

Questions Bank

Numericals