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Crystal Structure

Q. 1.1 (a) What is a crystal? Distinguish between a crystal and an amorphous solid.
(Pb.U. 2004; Meerut U. 2002; Gauhati U. 2000; P.U. 1991)

(b) Why are most solids crystalline in nature?
(P.U. 2003)

(c) Give three main differences between crystalline and amorphous solids.

(H.P.U. 2002)

Ans. (a) **Crystal.** A solid of definite shape with its atoms, ions or molecules arranged in some regular repetitive three dimensional pattern is termed as a crystal.

Crystalline solid. The crystalline state of a solid is characterised by regular and periodic arrangement of atoms or molecules.

When a crystal grows in a constant environment, the shape remains unchanged during growth. It appears as if identical building blocks are continuously added. The building blocks are atoms or group of atoms.

A periodic and regular arrangement of points in space is known as a *lattice* arrangement. In a crystalline structure, the various atoms and molecules are attached to the lattice in an identical manner. The distances between the various particles constituting a crystal are of the order of the size of these particles. The mean potential energy of every particle is more than its mean kinetic energy and their vibrations about the position of equilibrium are extremely limited. There is always internal regularity of particles, which is responsible for the symmetry of external shapes. A crystal, therefore, presents a sort of *spatial regularity* extending over a large volume i.e., a long range *order* in its structure. The various properties like thermal conductivity, compressibility, tensile strength etc., depend on the structure of the crystal or the arrangement of particles in it. The crystals have generally sharp melting points and get converted into liquid state very soon.

Amorphous solid. There are certain substances like pitch, plastics, silicate glass, in which the molecules do not form a regular spatial lattice and are in a more or less chaotic and random distribution throughout the solid, even though the distance between nearest molecules is of the same order as that of the molecules in crystalline substances. Such substances are known as '**amorphous**' i.e., *substances without any regular form or shape*. They are uncrosslinked solids. Like liquids they are isotropic in nature i.e., the value of conductivity, elasticity, tensile strength etc., remains the same, no matter in which direction it is measured within the substance. Also these substances do not have long range spatial order. They have only short range order. They can be regarded to be highly viscous, super-cooled liquids without any sharp melting points and no periodicity and regularity of the arrangement of atoms.

In a crystalline solid, the changing of long range order into short-range order takes place after breaking such bonds, whose strength is nearly the same ; while in case of amorphous substances, the strength of bonds vary. At low temperature, only the weakest bond gets ruptured. This accounts for the sharp melting points in crystals, while there is gradual softening in case of the amorphous solids.

(b) Why are most solids crystalline? Most solids are crystalline in nature due to the reason that crystalline state is a low energy state and is, therefore, preferred by most solids. The energy released during formation of an ordered structure is more than that released during the formation of disordered structure thereby making the crystalline state a low energy state.

(c) Main difference between crystalline and amorphous solids.

- (i) A crystalline solid has *spatial regularity* extending over a large volume i.e., there is a *long range order* in its structure whereas an amorphous solid has only a *short range order*.
- (ii) A crystalline solid has different properties along different directions or crystal axes, like conductivity, elasticity or tensile strength i.e., it is *anisotropic* in character whereas an amorphous solid is *isotropic* in character i.e., it has the same value of these properties no matter in which direction it is measured.
- (iii) Crystalline solids have sharp melting points whereas in amorphous solids there is a gradual softening of the material.

Q. 1.2 (a) Define crystal lattice, plane lattice, space lattice, basis, unit cell and translation vectors. (Pbi.U. 2004, 2003, 2002, 2000; Osm. U. 2004; G.N.D.U. 2002, 2001; P.U. 2000, 1999, 1997, 1994; K.U. 2001, 1996; A.U. 1995; Luck. U. 1993)

(b) What is crystal structure? State the relation between crystal structure, lattice and basis. (Pbi. U. 2002, 2000)

(c) Define a primitive cell. Distinguish between a primitive unit cell and non-primitive unit cell with the help of two dimensional diagram. Can a unit cell be primitive?

(Pbi. U. 2004, 2000; Luck. U. 2001; K.U. 2001; P.U. 2001, 2000, 1999)

(d) Define and explain translation operation. (P.U. 1999)

(e) How a Wigner Sietz unit cell is drawn? (G.N.D.U. 2001; Luck. U. 2001)

Ans. (a) Crystal lattice. In a crystalline substance, the atoms are regularly arranged.

The periodic arrangement of atoms in a crystal is called the lattice.

Plane lattice. If the arrangement of atoms is represented in a plane, it will be somewhat as shown in Fig. 1.1. Thus in two dimensions, any atom has got the same environment as any other atom. Such an array of atoms is called a *plane lattice*. In case of three dimensional picture, any atom

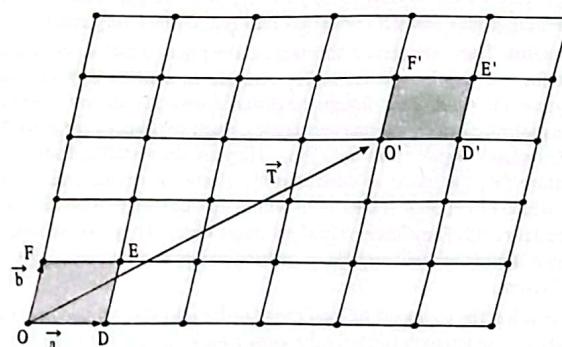


Fig. 1.1

will similarly have the same environment as any other atom and this array of atoms is called *space lattice*.

Space lattice. A space lattice is defined as an infinite array of points (atoms or molecules) in three dimensions in which every point has identical surroundings.

Basis. The structure of all crystals can be described in terms of a lattice with a group of atoms attached to each *lattice point*. The group of atoms is called the *basis (pattern or motif)*. It is repeated in space to form the structure of the crystal.

A *basis* is defined as an assembly of atoms, ions or molecules identical in composition, arrangement and orientation, which when repeated in three dimensions generates a crystal structure.

The number of atoms in a basis may be one as in many metals and inert gases, but could be as large as 1000 in many structures.

Since there are many different ways of placing atoms in a volume, the distance and orientation between atoms can take many forms.

Unit-cell. Consider a plane lattice which is a part of a two dimensional crystal, the atoms of which are arranged in a pattern as shown in Fig. 1.1. It is seen that when a parallelogram like *ODEF* is repeatedly translated by the vectors \vec{a} and \vec{b} corresponding to \overrightarrow{OD} and \overrightarrow{OF} , the pattern may be reproduced. For example, if the vector \vec{a} is translated by $4\vec{a}$ and vector \vec{b} by $3\vec{b}$ the parallelogram *ODEF* is translated and repeated as parallelogram *O'D'E'F'*.

The region *ODEF* is known as a *unit cell* and the vectors \vec{a} and \vec{b} as *basis vectors*.

Translation vectors. In two dimensions \vec{a} and \vec{b} are also the *translation vectors* of the lattice and the area of the unit cell is $|\vec{a} \times \vec{b}|$.

If we consider a space lattice, which is a part of a three dimensional crystal, then a *unit cell* is defined as that volume of the solid from which the entire crystal can be constructed by the translational repetition in three dimensions. For a three dimensional space lattice we have correspondingly *three basis vectors*, say \vec{a} , \vec{b} and \vec{c} .

In three dimensions, \vec{a} , \vec{b} and \vec{c} are the *translation vectors* of the lattice and the volume of the unit cell is $|(\vec{a} \times \vec{b}) \cdot \vec{c}|$.

A crystal may not possess a unique unit cell. Many unit cells can exist for the same structure. A cell of size $2a$, $2b$, $2c$ is as much correct as the cell of size a , b , c . For certain structures, unit cells of completely different geometry are possible. Most of the structures have smallest unit cells containing only a few atoms, but some elements like manganese have even hundreds of atoms in a unit cell.

(b) **Crystal structure.** A crystal structure is formed by the addition of a basis to every lattice point i.e., a lattice combined with a basis creates a crystal structure. Mathematically it is expressed as

$$\text{Lattice} + \text{basis} = \text{crystal structure}$$

Thus, whereas a lattice is a mathematical concept, the crystal structure is a physical concept. For *crystal translation vector* see part (d).

(c) **Primitive cell.** A primitive cell is a type of unit cell which contains only one lattice point at corners and is a minimum volume unit cell.

For example, consider the lattice points as shown in Fig 1.2. If pairs of translation vectors (T_1, T_2) and (T_3, T_4) are chosen we get a *primitive cell* because it contains 4 lattice points at its corners and each lattice point is shared by 4 cells i.e., each primitive cell has only one lattice point. If, on the other hand, we choose translation vectors (T_5, T_6) the unit cell contains more than one lattice point and is called a *non-primitive or multiple cell*.

Primitive basis vectors. If the vectors \vec{a} , \vec{b} and \vec{c} define a primitive cell of space lattice in three dimensions then \vec{a} , \vec{b} , \vec{c} are known as *primitive basis vectors*.

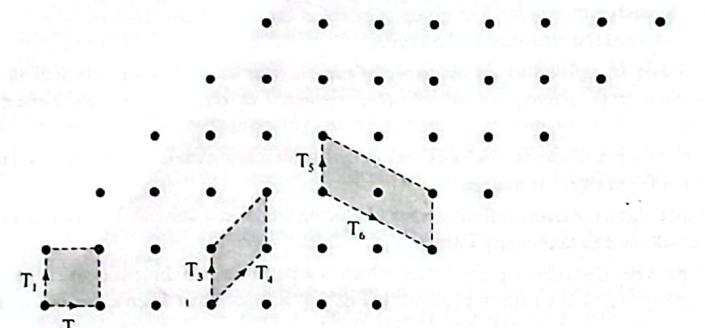


Fig. 1.2

Primitive crystal axes. The directions of the primitive basis vectors \vec{a} , \vec{b} and \vec{c} define the *primitive crystal axes*.

The volume of the primitive cell is given by

$$V = |(\vec{a} \times \vec{b}) \cdot \vec{c}| \quad \dots(i)$$

where \vec{a} , \vec{b} and \vec{c} are primitive axes vectors.

Can a unit cell be primitive? A primitive cell is a type of unit cell which contains lattice points at corners only and is a *minimum volume cell*. A unit cell is a conventional cell which may be equal to a primitive cell or a multiple of it. Thus a unit cell can be primitive. Also see Q. 1.9.

(d) Crystal translation vectors. An ideal crystal is composed of atoms arranged on a lattice defined by three fundamental or lattice translation vectors \vec{a} , \vec{b} , \vec{c} such that the atomic arrangement looks the same in every respect when viewed from any point O as when viewed from the point O' as shown in Fig. 1.1. The vector $OO' = \vec{T}$ is given by

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

where n_1 , n_2 and n_3 are arbitrary integers and T is called *Lattice or crystal translation vector*.

Translation operation. In a crystal, in addition to the geometrical arrangement of atoms a function $f(r)$ which describes any property of a crystal must also be invariant or periodic i.e.,

$$f(r) = f(r + T)$$

where T is the *translation operation* given by

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

Hence a translation operation is a kind of symmetry operation which when performed leaves the crystal invariant.

The displacement of a crystal parallel to itself by a crystal translation vector is thus a *crystal translation operation*. Translation repeats the motif infinite number of times in a given direction whereas all other operations repeat the motif only a finite number of times in a given direction.

(e) Wigner Sietz primitive cell. This is another method of choosing a cell of volume V given by relation (i).

1. First draw lines to connect a given lattice point to all nearby lattice points.
2. At the midpoints and normal to these lines draw new lines or planes. The smallest volume enclosed in this way is a new primitive cell.

It is known as Wigner Sietz primitive cell.

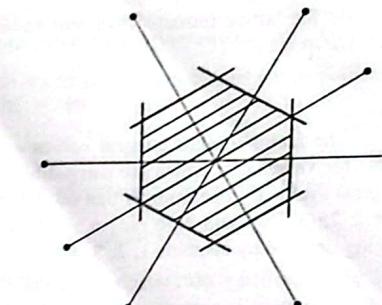


Fig. 1.3

Q. 1.3 (a) What do you mean by a symmetry operation? Explain briefly the various symmetry operations applicable to two dimensional and three dimensional lattices. What is a point operation?

(b) Prove that a crystal cannot have five fold symmetry.

(P.U. 2003, 2001; Luck. U. 1994; H.P.U. 1992)

Ans. (a) Symmetry operation. Crystal lattices can be carried into themselves by lattice translation vector \vec{T} and by various other symmetry operations.

A symmetry operation is that which transforms the crystal to itself i.e., a crystal remains invariant under a symmetry operation.

Types of symmetry operations. We shall consider a group of atoms or molecules called *motif* which can be repeated periodically in a number of permissible ways to form the crystal. For simplicity we shall represent the *motif* in a crystal by a figure of seven (7). There are four major methods of repeating the *motif* in space which are known as symmetry operations.

(i) Translation operation. The *motif* represented by a figure of seven (7) can be repeated by a translation operation as shown in Fig 1.4.

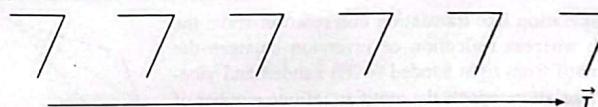


Fig. 1.4

A lattice point \vec{r} under translation operation \vec{T} gives another point \vec{r}' , which is exactly identical to \vec{r} ; i.e.,

$$\vec{r}' = \vec{r} + \vec{T}$$

Translation repeats the motif an infinite number of times.

(ii) Rotation operation. In this operation the *motif* can be rotated through an angle ϕ about an axis of rotation as shown in Fig 1.5. This operation repeats the motif a finite number of times.

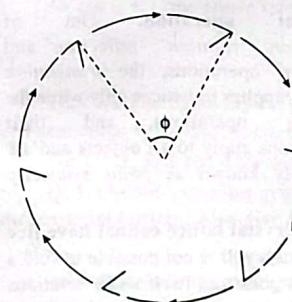


Fig. 1.5

A lattice is said to possess rotational symmetry if its rotation by an angle ϕ about an axis transforms the lattice to itself.

As the lattice remains invariant under a rotation of 2π , the angle 2π must be an integral multiple of ϕ i.e.,

$$n\phi = 2\pi \text{ or } \phi = \frac{2\pi}{n}.$$

The factor n takes integral values only and is known as *Multiplicity of rotation axis*. The possible values of n which are compatible with symmetry requirements are 1, 2, 3, 4 and 6. Thus, typical symmetry operation is that of rotation about an axis passing through a lattice point by 2π , $2\pi/2$, $2\pi/3$, $2\pi/4$ and $2\pi/6$ radian and by their integral multiples, the corresponding rotation axis being denoted by symbols 1, 2, 3, 4 and 6.

For $n = 6$, $\phi = 60^\circ$, which means that the lattice repeats itself with a minimum rotation of 60° . Such a rotation is shown in Fig 1.5. A rotation corresponding to the value of n is called *n-fold rotation*. A two dimensional square lattice has 4-fold rotational symmetry.

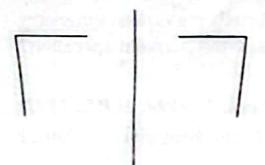


Fig. 1.6

(iii) **Reflection.** A lattice is said to possess reflection symmetry if there exists a plane (or line in two dimensions) in the lattice which divides it into two identical halves which are mirror images of each other.

Reflection across a line or plane changes the character of the lattice from *left handed* to *right handed* and vice-versa.

All the above symmetry operations are applicable to a *two dimensional lattice*.

(iv) **Inversion.** Inversion is a point operation which is applicable to *three dimensional lattice* only. The symmetry element implies that each point located at \vec{r} relative to a lattice point has an identical point located at $-\vec{r}$ relative to the same lattice point. Inversion through a point is shown in Fig 1.7. It also changes the character of the *motif* from right handed to left handed.

To sum up:-

Symmetry operation like translation and rotation leave the motif unchanged, whereas reflection or inversion changes the character of the motif from right handed to left handed and vice-versa. Further, a translation repeats the motif an infinite number of times in a given direction whereas the other operations repeat the motif a finite number of times.

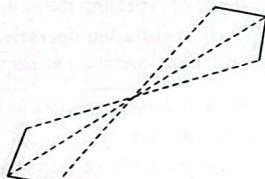


Fig. 1.7

Point operation. Out of 'translation', 'rotation', 'reflection' and 'inversion' operations, the *translation operation* applies to lattices only while the remaining operations and their combinations apply to all objects and are collectively known as *point symmetry operations*.

(b) **Crystal lattice cannot have five fold symmetry.** It is not possible to find a lattice that goes into itself under rotations like $2\pi/5$ or $2\pi/7$ or by any other symmetry operation like mirror reflection or inversion. In other words, a *crystal cannot have five fold symmetry*.

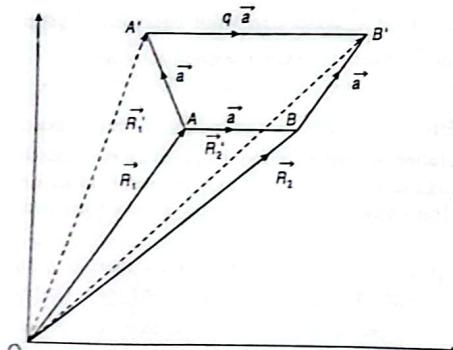


Fig. 1.8

To prove it mathematically let $AB = \vec{a}$ be a primitive translation vector and $OA = \vec{R}_1$, $OB = \vec{R}_2$ the two lattice vectors connecting the origin to A and B - the two closest lattice points of the crystal, then

$$|\vec{a}| = |\vec{R}_1 - \vec{R}_2|$$

Now consider a line perpendicular to the plane of the paper and passing through the lattice point A . Let the vector \vec{a} be rotated about this line as axis through an angle $\theta = \frac{2\pi}{n}$ in the anti-clockwise direction, so that it produces a new lattice vector $OA' = \vec{R}'_1$. Similarly, let the vector \vec{a} be rotated about an axis passing through the lattice point B and perpendicular to the plane of the paper through the same angle $\theta = \frac{2\pi}{n}$ in the clockwise direction so that it produces a new lattice vector $OB' = \vec{R}'_2$.

$$AA' = BB' = |\vec{a}|$$

and

$$\angle BAA' = \angle ABB' = \theta.$$

The quadrilateral is a trapezium with $A'B'$ parallel to AB . Further $A'B'$ must also be an integral multiple of the primitive translation vector \vec{a}

$$A'B' = q|\vec{a}|$$

where q is an integer.

Now

$$A'B' = q|\vec{a}| = |\vec{R}'_1 - \vec{R}'_2|$$

$$\begin{aligned} &= |\vec{a}| + |\vec{a}| \sin \left(\theta - \frac{\pi}{2} \right) + |\vec{a}| \sin \left(\theta - \frac{\pi}{2} \right) \\ &= |\vec{a}| + 2|\vec{a}| \sin \left(\theta - \frac{\pi}{2} \right) \\ &= |\vec{a}|[1 - 2 \cos \theta] \end{aligned}$$

∴

$$q = 1 - 2 \cos \theta \text{ or } |\cos \theta| = \frac{|1-q|}{2}$$

As $\cos \theta < 1$, the above relation can be satisfied only when $q = 3, 2, 1, 0, -1$.

or

$$\theta = \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}, \frac{2\pi}{1} \text{ or } n = 1, 2, 3, 4, 6 \text{ only.}$$

Thus we find that a crystal can have only $\overline{1}, \overline{2}, \overline{3}, \overline{4}$ and $\overline{6}$ fold axis of rotation or symmetry and cannot have *five fold symmetry*.

For $n = 2, 3, 4$ and 6 the symmetry is known as *diad*, *triad*, *tetrad* and *hexad* respectively.

Q. 1.4 What are point groups and space groups? Give their numbers for two and three dimensional lattices. Also give the characteristics of space group.

(G.N.D.U. 2004; P.U. 2000; Pbi. U. 2000)

Ans. Point groups and space groups. There are mainly four types of symmetry operations; *translation*, *rotation*, *reflection* and *inversion*. The last three operations are point operations and their combinations give certain symmetry elements which collectively determine the symmetry of space around a point. The group of such symmetry operations at a point is called a *point group*.

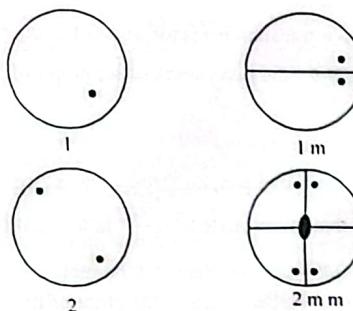


Fig. 1.9

rotation through π goes into the other point (dot). With a two-fold axis and one mirror plane there is a second mirror plane normal to the first and we have 4 equivalent points (2 m m). The point symmetry of a crystal structure as a whole is determined by the point symmetry of the lattice as well as the basis.

The group of all the symmetry elements of a crystal structure is called space group.

It determines the symmetry of the crystal structure as a whole.

Number of point groups and space groups. In two dimensional space there are 10 different point groups designated as 1, 1 m, 2, 2 mm, 3, 3 m, 4, 4 mm, 6 and 6 mm.

In three dimensional space there are a total of 32 point groups in a three dimensional lattice.

The point symmetry of crystal structure as a whole is determined by the point symmetry of the lattice as well as of the basis. In order to determine the point symmetry of a crystal it should be noted that

(i) a unit cell might show point symmetry at more than one locations inside it and (ii) the symmetry elements comprising combined point and translation operations might be existing at these locations.

There are 17 distinct space groups possible in 2 dimensions and 230 in three dimensions.

Characteristics of a space group. (a) The symmetry of a crystal structure is specified completely when the space group is known.

(b) The space group is characterised by Bravais lattice and by the location of the point group and other symmetry elements in a unit cell.

(c) The space group through its symmetry elements determines the position of equivalent points within the unit cell. .

(d) For a crystal structure specified by a particular space group, if only one point in a particular cell is occupied it is necessary that all equivalent points be occupied by identical atoms or molecules.

Q. 1.5 (a) What are Bravais lattices? Discuss Bravais lattices in two dimensions. Write down symmetry operations in which each is invariant.

(Pbi. U. 2004; K.U. 2002, 2001; M.D.U. 2001; P.U. 2000; A.U. 1995; H.P.U. 1991)

(b) Discuss seven crystal systems by giving one example of each and describe the various types of Bravais lattices in case of three dimensions with the help of neat and clear diagrams.

(Patna U. 2004; Calicut U. 2003; Meerut U. 2003, 2000;

Pbi. U. 2001; A.U. 1995, H.P.U. 1991)

(c) Why there is no face centred tetragonal space lattice?

We define a lattice point group as the collection of the symmetry operations which when applied about a lattice point leaves the lattice invariant.

In other words, in point groups all the possible symmetry elements must pass through a point.

Location of equivalent points are shown for four point groups in Fig 1.9.

The dots denote equivalent points. The point group 1 has no symmetry element, so this point has no other point equivalent to it. The point group 1 m has a mirror plane, so this point (dot) on reflection across the mirror plane becomes the second point (dot). The point group 2 has a two fold axis, so this point (dot) on rotation through π goes into the other point (dot). With a two-fold axis and one mirror plane there is a second mirror plane normal to the first and we have 4 equivalent points (2 m m). The point symmetry of a crystal structure as a whole is determined by the point symmetry of the lattice as well as the basis.

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(c) Why there is no face centred tetragonal space lattice?

Ans. (a) Bravais lattice. The group of four types of symmetry operations at a point is called 'point group', there being 10 point groups in two dimensions and 32 in three dimensions respectively. These point groups form the basis for the construction of different types of lattices known as 'Bravais lattices'.

Two dimensional lattice types. In a two dimensional lattice there is no restriction regarding the lengths of the primitives \vec{a} and \vec{b} and the angle ϕ between them. The only condition is that the lattice should be invariant under symmetry operations.

In a two dimensional case there are in all five types of lattices depending upon the relative values of $|\vec{a}|$ and $|\vec{b}|$ and ϕ . These are known as Bravais lattices in two dimensions. These are:

(i) Oblique lattice. A general lattice is known as oblique lattice and is invariant under rotation of 2π and $2\pi/2$ about any lattice point. An oblique lattice is shown in Fig. 1.10 (i) where $|\vec{a}| \neq |\vec{b}|$ and $\phi \neq 90^\circ$. The conventional unit cell is a parallelogram. Special lattices of oblique type can be invariant under rotation of $2\pi/3$, $2\pi/4$ and $2\pi/6$.

(ii) Square lattice. A square lattice is shown in Fig. 1.10 (ii). Here $|\vec{a}| = |\vec{b}|$ and $\phi = 90^\circ$. It is invariant under a rotation of $2\pi/4$. The conventional unit cell is a square.

(iii) Hexagonal lattice. A hexagonal lattice is shown in Fig. 1.10 (iii). Here $|\vec{a}| = |\vec{b}|$ and $\phi = 120^\circ$. This is invariant under a rotation of $2\pi/6$. The conventional unit cell is a 60° rhombus.

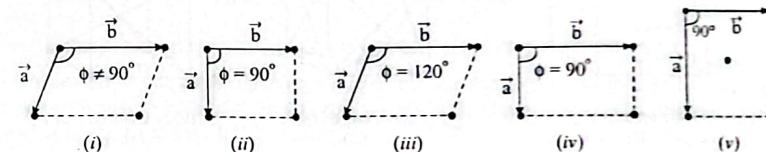


Fig. 1.10

(iv) Primitive Rectangular lattice. A primitive rectangular lattice is shown in Fig. 1.10 (iv). Here $|\vec{a}| \neq |\vec{b}|$ and $\phi = 90^\circ$. This is invariant under mirror reflection. The conventional unit cell is a rectangle.

(v) Centred rectangular lattice. A centred rectangular lattice is shown in Fig. 1.10 (v). Here $|\vec{a}| \neq |\vec{b}|$ and $\phi = 90^\circ$ but $|\vec{a}| > |\vec{b}|$. This is invariant under inversion operation. The conventional unit cell is again a rectangle.

The two dimensional Bravais lattices are given below:

	Lattice	Conventional unit cell	Crystal axes
1.	Oblique	Parallelogram	$a \neq b; \phi \neq 90^\circ$
2.	Square	Square	$a = b; \phi = 90^\circ$
3.	Hexagonal	60° Rhombus	$a = b; \phi = 120^\circ$
4.	Primitive rectangular	Rectangle	$a \neq b; \phi = 90^\circ$
5.	Centred rectangular	Rectangle	$a \neq b; \phi = 90^\circ$

Three dimensional lattice types. In three dimensional space lattices, there can be in all fourteen types (one general and 13 special). The general type is the *triclinic lattice*. All these are known as Bravais space lattices.

With these fourteen types of lattices and on the basis of primitive cell, the crystals have been classified into seven systems. Fig. 1.11 gives the convention used for the angles between primitives a , b , c , also called *lattice parameters*. Thus the angles between (a, b) , (b, c) and (c, a) are denoted by γ , α , β respectively. Different specifications for a , b and c as well as α , β and γ generate different crystal systems. There are seven crystal systems in all (i) Cubic (ii) Tetragonal (iii) Hexagonal (iv) Rhombohedral (v) Orthorhombic (vi) Monoclinic and (vii) Triclinic. The seven systems of crystals with their types of lattices, angles between the axes and relation between the length of primitives is given below.

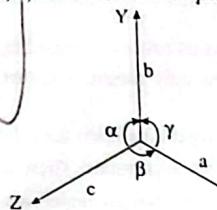


Fig. 1.11

(i) **Cubic.** The crystal axes are perpendicular to one another i.e., $\alpha = \beta = \gamma = 90^\circ$. The repetitive interval or the length of the primitives is the same along the three axes i.e., $a = b = c$. Cubic lattices may be *simple* (*sc*) or *primitive* (*P*), *face centred* (*fcc*) or (*F*) and *body centred* (*bcc*) or (*I*) as shown in Fig. 1.12 (i), (ii) and (iii).

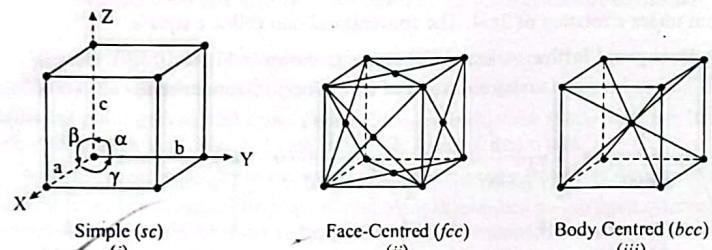


Fig. 1.12

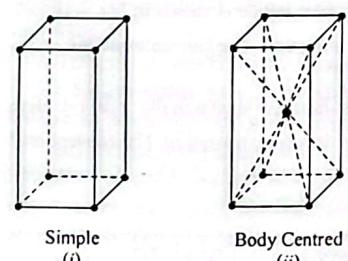


Fig. 1.13

(ii) **Tetragonal.** The crystal axes are perpendicular to one another i.e., $\alpha = \beta = \gamma = 90^\circ$. The repetitive interval or the lengths of the primitives along two axes are the same but the interval along the third axis is different i.e., $a = b \neq c$. Tetragonal lattices may be *simple* (*P*) or *body centred* (*I*) as shown in Fig. 1.13 (i) and (ii).

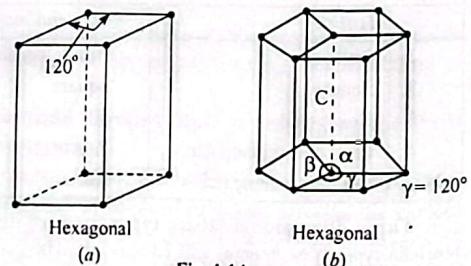


Fig. 1.14

The *hexagonal* system is so called because a simple hexagonal structure can be formed from such unit cells as shown in Fig. 1.14 (b).

(iv) **Trigonal.** (Also known as *rhombohedral*). The angle between each pair of crystal axes are the same but are not 90° i.e., $\alpha = \beta = \gamma \neq 90^\circ$. The repetitive interval (or length of primitives) is the same along all the three axes as shown in Fig. 1.15 i.e., $a = b = c$.

(v) **Orthorhombic.** The crystal axes are perpendicular to one another but the repetitive interval (or length of primitives) are different along all the three axes i.e., $\alpha = \beta = \gamma = 90^\circ$ and $a \neq b \neq c$. The orthorhombic lattices may be *simple*, *base centred* (or *end centred*), *body centred* or *face centred* as shown in Fig. 1.16 (a), (b), (c) and (d) respectively.

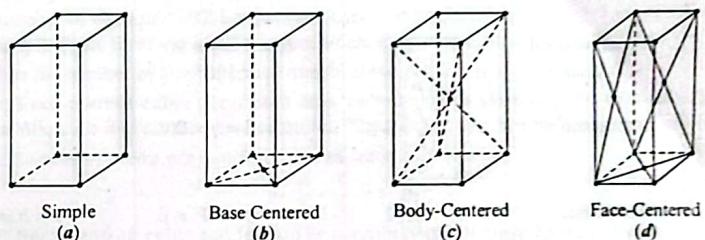


Fig. 1.16

(vi) **Monoclinic.** Out of the three crystal axes, two are not perpendicular to each other but the third is perpendicular to both of them i.e., $\alpha = \gamma = 90^\circ \neq \beta$. Monoclinic lattices may be *simple* or *base-centred* as shown in Fig. 1.17 (a) and (b).

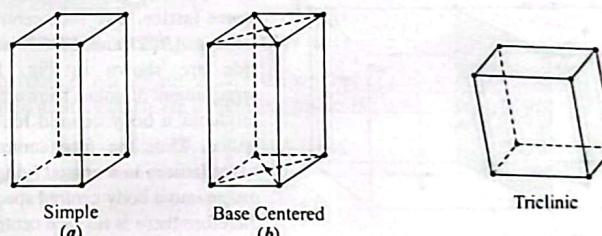


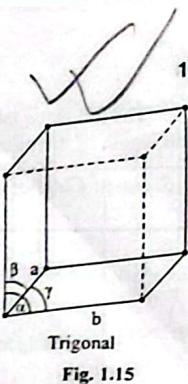
Fig. 1.17

Fig. 1.18 (a)

(vii) **Triclinic.** None of the crystal axes is perpendicular to any of the others $\alpha \neq \beta \neq \gamma$. The repetitive intervals are also different ($a \neq b \neq c$) as shown in Fig. 1.18 (a).

Example of various classes of crystals. Some examples of various classes of crystals are:—

1. Cubic (*P*) Cu, Ag, Fe; (*F*) CsCl; (*I*) Na, NaCl.
2. Tetragonal (*P*) β -Sn; (*I*) TiO₂.
3. Hexagonal (*P*) Mg, Zn, Cd.
4. Rhombohedral or Trigonal (*R*) As, Sb, Bi.
5. Orthorhombic (*P*) Ga; (*F*) Mg₂Cu; (*I*) Fe₃C (*C*) PuBr₃
6. Monoclinic (*P*) CaSO₄.2H₂O; (*C*) Li₂SO₄.H₂O
7. Triclinic (*P*) K₂Cr₂O₇; CuSO₄.5H₂O.



13

The following table gives the class of crystal, types and number of lattices, angle between axes and length of the primitives for all the 14 Bravais lattices.

S. No.	Class of crystal	Type and no. of Lattices	Angle between axes	Length of primitives
1.	Cubic	$sc(P)$ $fcc(F) \{ 3$ $bcc(I)$	$\alpha = \beta = \gamma = 90^\circ$	$a = b = c$
2.	Tetragonal	$P \} 2$ $I \} 1$	$\alpha = \beta = \gamma = 90^\circ$	$a = b \neq c$
3.	Hexagonal	$P \} 1$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	$a = b \neq c$
4.	Rhombohedral (Trigonal)	$R \} 1$	$\alpha = \beta = \gamma \neq 90^\circ$ $< 120^\circ$	$a = b = c$
5.	Orthorhombic	$P \} 1$ $F \} 1$ $I \} 1$ $C \} 1$	$\alpha = \beta = \gamma = 90^\circ$	$a \neq b \neq c$
6.	Monoclinic	$P \} 2$ $C \} 1$	$\alpha = \gamma = 90^\circ \neq \beta$	$a \neq b \neq c$
7.	Triclinic	$P \} 1$	$\alpha \neq \beta \neq \gamma$	$a \neq b \neq c$

P = Primitive; sc (simple cubic); F = fcc (Face centred); I = bcc (body centred); C = base centred; R = Rhombohedral.

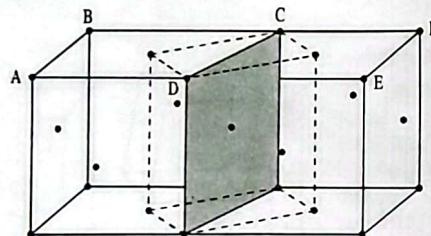


Fig. 1.18 (b)

(c) Why no face centred tetragonal space lattice. Two face centred tetragonal lattices $ABCD$ and $CDEF$ placed side by side are shown in Fig. 1.18(b). The arrangement of points shown by dotted lines produces a body centred tetragonal space lattice. Thus the face centred tetragonal space lattices in a crystal lying side by side merge into a body centred space lattice and, therefore there is no face centred tetragonal space lattice.

Q. 1.6 (a) Discuss the characteristics of a unit cell of a cubic system and explain the terms "volume of a unit cell", "atoms per unit cell", "co-ordination number", "atomic radius" and "atomic packing fraction" as applied to crystal structure. Calculate their values for a simple cubic, face centred cubic and body centred cubic cell.

(b) How many lattice points are there in the cubic unit cell of fcc structure?

(P.U. 2004, 2001, 2000, 1993; H.P.U. 2003, 2001, 1992; Meerut. U. 2000; G.N.D.U. 2004, 1997; Pbi. U. 2003, 2000; Nag. U. 2002; A.U. 1994)

Ans. (a) Characteristics of a unit cell. The characteristics of a unit cell are:

(i) Volume, (ii) Atoms per unit cell, (iii) Co-ordination number, (iv) Atomic radius and (v) Atomic packing fraction.

1. Volume of a unit cell. For cubic crystals $a = b = c$.

Hence volume of a unit cell $V = a \times b \times c = a^3$.

Crystal Structure

2. Atoms per unit cell. A study of extended cubic crystal lattice shows that every corner atom in each unit cell participates in the corner position with seven other unit cells. Therefore, each of the eight corner atoms in a cubic unit cell contributes only $1/8$ th of an atom to the unit cell. Thus:

- (i) An atom lying at the corner of a cubic unit cell is shared equally by eight unit cells and, therefore, counts for one eighth of an atom. Similarly
- (ii) An atom lying completely within a unit cell belongs wholly to that cell.
- (iii) An atom lying in the face of a unit cell belongs equally to two unit cells and, therefore, counts as one half for that particular cell.
- (iv) An atom lying on one edge of a unit cell is shared equally by four unit cells and, therefore, counts as one quarter of an atom per unit cell.

(a) Simple cubic cell (sc). As stated above, each corner atom in a cubic unit cell is shared by a total number of eight unit cells so that each corner atom contributes only $1/8$ of its effective part to a unit cell. Since there are in all 8 corner atoms their total contribution is equal to $8/8 = 1$.

Thus the number of atoms per unit simple cubic cell is *one*.

(b) Face centred cubic (fcc). Each face centred atom is shared by two unit cells. There are six faces of a cube and six face centred atoms. These are in addition to eight corner atoms.

∴ Number of atoms per unit face centred cubic cell

$$= \frac{6}{2} + \frac{8}{8} = 4.$$

(c) Body centred cubic cell (bcc). The contribution of a body centred atom is full i.e., *one*. This is in addition to eight corner atoms.

∴ Number of atoms per unit body centred cubic cell

$$= 1 + \frac{8}{8} = 2.$$

Hence we conclude that

$$\text{Total number of atoms per unit cell } N = \frac{N_c}{8} + \frac{N_f}{2} + N_i$$

where N_c = number of corner atoms, N_f = the number of face centred atoms and N_i = The number of body centred atoms (which are completely inside the cell). Thus

$$\text{For } sc \quad N = \frac{8}{8} + 0 + 0 = 1$$

$$\text{For } fcc \quad N = \frac{8}{8} + \frac{6}{2} + 0 = 4$$

$$\text{For } bcc \quad N = \frac{8}{8} + 0 + 1 = 2$$

3. Co-ordination number. In a crystal the number of nearest neighbours to an atom in a given structure is called co-ordination number. It gives an idea of the closeness of the packing of the atoms.

Consider any corner atom in a simple cubic cell. It has one close neighbour along +X axis and another along -X axis as shown in Fig. 1.12 (i). The same is true for Y and Z axes. Thus the coordination number for each corner atom is 6.

For a body centred cell the atom inside the cell has all the corner atoms as its close neighbours as shown in Fig. 1.12 (iii). Thus the coordination number for the interior atom is 8.

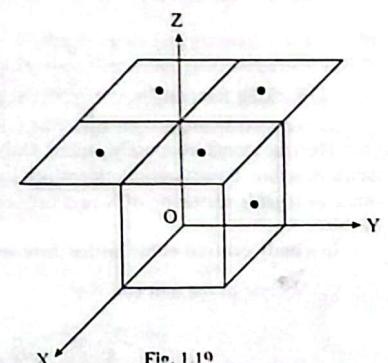


Fig. 1.10

For a *face centred cell* each corner atom is having four close neighbours in each of the three XY, YZ and ZX planes as shown in Fig. 1.19. Thus the coordination number in this case is $4 \times 3 = 12$.

4. Atomic radius. It is supposed that all the atoms in a crystal have the *same size* and are touching each other. *Thus the atomic radius is the distance between the centres of two neighbouring atoms.*

In the case of a *simple cube*, if r is the atomic radius and lattice parameter is a , then

$$a = 2r$$

or

$$r = a/2$$

In the case of a *body centred cube*, the atoms touch each other along the diagonal of the cube as shown in Fig. 1.20 and we have

$$(4r)^2 = (\sqrt{2}a)^2 + a^2$$

$$\text{or } r = \frac{\sqrt{3}}{4}a.$$

In the case of a face-centred cube as shown in Fig. 1.21, the atoms are in contact along the diagonal of the faces.

$$\therefore 4r^2 = 2a^2$$

$$\text{or } r = \frac{\sqrt{2}}{4}a = \frac{a}{2\sqrt{2}}.$$

5. Atomic packing fraction (or factor). Also known as *relative packing density* is defined as the ratio of the volume of the atoms occupying the unit cell to the volume of the unit cell relating to the structure of the crystal.

In a *simple cubic structure* the number of atoms per unit cell is *one*. The atomic radius is given by half the primitive i.e., $r = a/2$.

i.e. Volume occupied by the atom in the unit cell

$$= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \left(\frac{a}{2}\right)^3$$

Volume of the unit cell = a^3

$$\therefore \text{Packing fraction } f = \frac{\frac{4}{3}\pi \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 52\%.$$

Thus the atoms are loosely packed. Only polonium at a certain temperature is known to exhibit such a structure. Potassium chloride which has alternate ions of K and Cl also behaves like a simple lattice as regards scattering of X-rays because the two ions are almost identical.

In a *body centred cubic lattice* there are *two atoms per unit cell*. The atomic radius $r = \frac{\sqrt{3}}{4}a$

i.e. Volume of the unit cell = a^3

$$\therefore \text{Packing fraction } f = \frac{\frac{\sqrt{3}}{8}\pi a^3}{a^3} = \frac{\sqrt{3}}{8}\pi = 68\%.$$

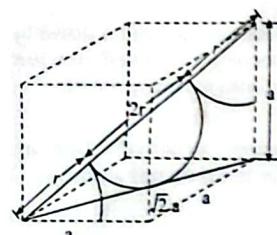


Fig. 1.20

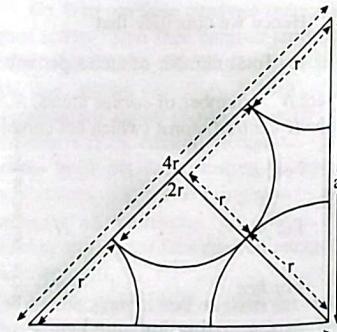


Fig. 1.21

Common substances with *bcc* lattice are barium, chromium, sodium, iron and caesium chloride. In caesium chloride, for example, each caesium ion has eight nearest neighbours of chlorine ions. The caesium ion is at the centre of the cube while chlorine ions are at the corners of the cube.

In a *face centred cubic lattice* there are *four atoms per unit cell*. The atomic radius $r = \frac{\sqrt{2}}{4}a$

$$\therefore \text{Volume occupied by the atoms in the unit cell} = 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi \frac{2^{3/2}}{4^3}a^3 = \frac{\pi}{3\sqrt{2}}a^3$$

Volume of the unit cell = a^3

$$\therefore \text{Packing fraction } f = \frac{\frac{\pi}{3\sqrt{2}}a^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 74\%$$

Common examples of this type of structure are Ni, Cu, Au, Al, Ag, Li, K etc.

(b) Number of lattice points. We have calculated the number of atoms per unit cell in a *simple cubic (sc)*, *face centred cubic (fcc)* and *body centred cubic (bcc)* cell. The same discussion is equally valid, if we use the word 'lattice point' instead of 'atom'.

Thus, a *lattice point* lying at the corner of a cubic unit cell is shared equally by *eight* such unit cells. Therefore, the contribution of a lattice point lying at the corner towards a particular cell is $\frac{1}{8}$.

A *lattice point* lying completely within a unit cell belongs wholly to the cell.

A *lattice point* lying on the face of a unit cell belongs equally to *two* unit cells and, therefore, counts as *one half* of a particular cell.

The following equation is used to calculate the effective number of lattice points N belonging to a particular cell

$$N = N_i + N_f/2 + N_c/8$$

where N_i represents the number of lattice points present completely inside the cell, N_f and N_c represent the lattice points occupying the face centre and corner positions of the cell respectively.

Using the relation the effective number of lattice points in a cubic unit cell is $\frac{8}{8} = 1$.

[Note. By the same relation the effective number of lattice points in a body centred cubic unit cell is 2 i.e., $8 \times \frac{1}{8} + 1 = 2$ and face centred cubic cell is 4 i.e., $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$]

Q. 1.7 (a) Prove that the packing fraction for a *simple cubic (sc)* structure is 0.52; for *body centred cubic (bcc)* structure is 0.68 and for a *face centred cubic (fcc)* structure is 0.74.

(Pbi.U. 2004, 1997; G.N.D.U 2003, 1997, 1995; Calicut U. 2003; P.U. 1992)

(b) If the lattice parameter for a *fcc* crystal is 2.14 Å find the radius of the particle.

(Nag. U. 2002)

Ans (a) For proof See Q 1.6 (5) **Atomic packing fraction.**

(b) For an *fcc* crystal the radius of the atom (particle)

$$r = \frac{a}{2\sqrt{2}} \text{ where } a \text{ is the lattice parameter.}$$

Here,

$$a = 2.14 \text{ Å}$$

$$\therefore r = \frac{2.14}{2\sqrt{2}} \text{ Å} = 0.76 \text{ Å.}$$

Q. 1.8 Mark the correct answer:

(i) The atomic radius for (fcc) lattice is

$$(a) \frac{a}{2} \quad (b) \frac{\sqrt{3}}{4}a \quad (c) \frac{\sqrt{2}}{4}a \quad (d) \text{none of these.}$$

(H.P.U. 1997)

(ii) Packing fraction has maximum value for

(a) fcc structure (b) hcp structure (c) sc structure (d) bcc structure. (H.P.U. 1999)

$$\text{Ans. (i) (c) The atomic radius for (fcc) lattice } r = \frac{\sqrt{2}}{4}a.$$

(ii) (a) and (b). The packing fraction for both (fcc) and (hcp) structure is 0.74 as compared to 0.52 for (sc) and 0.68 for (bcc) structure.

Q. 1.9 Define a primitive unit cell. Can a unit cell be primitive?

(P.U. 2001; Pbi. U. 2000; G.N.D.U. 1995; H.P.U. 1993; L.U. 1992)

Ans. Primitive cell. For definition see Q 1.2 primitive cell.

A unit cell may or may not be primitive. A primitive cell has only one lattice point associated with it. A simple cubic unit cell is primitive as it has only one lattice point associated with a unit cell. The body centred cubic (bcc) and (fcc) face centred cubic unit cells are not primitive as the effective number of lattice points in a (bcc) unit cell is 2 and in a (fcc) unit cell is 4.

Q. 1.10 (a) For a cubic (fcc) crystal, lattice constant

$$a = \left[\frac{4M}{\rho N} \right]^{1/3}$$

where M is the gm molecular weight of molecules at lattice points, ρ is the density of crystal and N is Avogadro's number. (A.U. 1995, 1994)

(b) A substance has fcc lattice, molecular weight 60.2 and density 6250 Kg/m³. Calculate its lattice constant 'a' (P.U. 2000)

$$\text{Ans. (a) Mass per molecule} = \frac{M}{N}$$

Let n be the number of molecules in a unit cell.

$$\therefore \text{Mass of a unit cell} = \frac{nM}{N}$$

$$\text{Density of the crystal} = \rho$$

$$\therefore \text{Volume of a unit cell} V = \frac{nM}{\rho N}$$

For a (fcc) crystal the number of lattice points (molecules) per unit cell = 4

$$\therefore \text{Volume of a unit cell} V = \frac{4M}{\rho N}$$

If a is the lattice constant, $V = a^3$

$$\therefore a = (V)^{1/3} = \left(\frac{4M}{\rho N} \right)^{1/3}$$

(b) For (fcc) lattice

$$a = \left(\frac{4M}{\rho N} \right)^{1/3}$$

Here $M = 60.2$; $\rho = 6250 \text{ Kg/m}^3$; $N = 6.02 \times 10^{26}$ per Kg mole.

$$\therefore a = \left[\frac{4 \times 60.2}{6250 \times 6.02 \times 10^{26}} \right]^{1/3} = \left[\frac{8 \times 10^{-27}}{125} \right]^{1/3}$$

$$\text{or } a = \frac{2}{5} \times 10^{-9} \text{ m} = 4 \text{ \AA}.$$

Q. 1.11(a) Describe a hexagonal close-packed structure (hcp). What is co-ordination number in (hcp)? Calculate its atomic packing fraction.

$$(b) \text{ Show that } \frac{c}{a} \text{ ratio for an ideal (hcp) structure is } \frac{\sqrt{8}}{3} = 1.633. \quad (\text{G.N.D.U., 2003, 1999; Luck. U., 1995, 1992; H.P.U. 1991, 1992})$$

Ans. (a) Hexagonal close packed structure. The most efficient packing of atoms—considered to be spheres—in a plane is obtained as shown in Fig. 1.22 with each atom touching six atoms in the plane. A second similar layer can be added by placing atoms in contact with three atoms of the bottom layer in positions marked as B or equivalently C . The third layer may have atoms placed in two ways:

(i) The atoms are placed over the holes in the first layer not occupied by the second layer i.e., if the atoms in the second layer are placed in positions marked B , those in the third layer are placed in positions marked C or vice-versa. The positions of atoms in successive layers is thus indicated as ABC , ABC . This is the face-centred cubic (fcc) structure.

The close-packed layers of the fcc structure are in the body diagonal planes as shown in Fig. 1.23 or in (111) plane. Familiar examples of elements that have face centred cubic structures are Cu, Ag, Au, Al, Pd and Pt.

(ii) The atoms are placed directly over the atoms placed in the first layer. The position of atoms in successive layers of this structure may be indicated as AB , AB , AB This leads to hexagonal close-packed (hcp) structure as shown in Fig. 1.24.

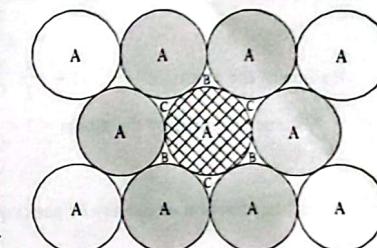


Fig. 1.22

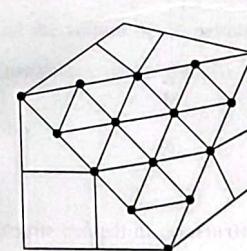


Fig. 1.23

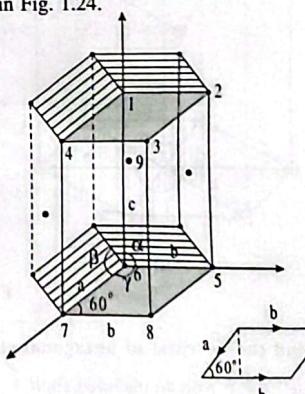


Fig. 1.24

Co-ordination number. According to the above discussion each atom touches six atoms in its plane, three atoms in the layer immediately above it and similarly three atoms in the layer immediately below it. Hence co-ordination number of hcp structure is $6 + 3 + 3 = 12$.

∴ Volume occupied by the atoms in the unit cell

$$= 8 \times \frac{4}{3} \pi r^3 = 8 \times \frac{4}{3} \pi \frac{3\sqrt{3}}{8^3} a^3 = \frac{\sqrt{3}}{16} \pi a^3$$

Volume of unit cell

$$= a^3$$

∴ Packing fraction

$$f = \frac{\frac{\sqrt{3}}{16} \pi a^3}{a^3} = \frac{\sqrt{3}}{16} \pi = 34\%$$

Thus we find that packing in diamond structure is rather loose.

(b) Distance between the two atoms = nearest neighbour distance = $\frac{\sqrt{3}}{4} a$

Here, $a = 5\text{\AA}$

$$\therefore \text{Distance between the two atoms} = \frac{\sqrt{3}}{4} \times 5\text{\AA} = \frac{1.732 \times 5}{4} = 2.16\text{\AA}$$

Q. 1.15 How many atoms are there in the primitive cell of diamond? What is the length of a primitive translation vector if the cube edge $a = 3.56\text{\AA}$. (Luck. U. 1994)

Ans. Diamond has fcc Bravais lattice with two carbon atoms in a primitive cell. The number of atoms in a conventional cube is 8.

If

$$\vec{a} = \text{cube edge, then}$$

$$\text{Primitive translation vector} = \frac{a}{\sqrt{2}} = \frac{3.56}{1.41} = 2.52\text{\AA}$$

Q. 1.16 (a) Explain the concept of Miller indices. How are they calculated? How the orientation of a plane is specified by Miller indices? Define Miller indices of a direction. State their important features. (G.N.D.U. 2003, 2001, 2000, 1996; H.P.U. 2003, 1994; P.U. 2003, 2001, 2000, 1995; Pbi. U. 1999; Meerut U. 2002, 2000; Osmania U. 2004; Nag. U. 2002; Cal. U. 2003, 1991; A.U. 1993)

(b) Why the reciprocals of intercepts of the plane are taken to find Miller indices? (H.P.U. 2001, 1999; P.U. 2000; M.D.U. 2001)

Ans. (a) Miller indices and their calculation. The position and orientation of a crystal plane are determined by any three points in the plane provided the points are not collinear. If each point lies on a crystal axis, the plane can be specified by giving the position of the points along the axes in terms of the lattice constants. For example, if the points have the coordinates $(2, 0, 0)$, $(0, 3, 0)$, $(0, 0, 1)$ relative to axis vectors from some origin as shown in Fig. 1.29, the plane may be specified by three numbers $2, 3, 1$.

However, in crystal structure analysis it is more useful to specify the orientation of a plane in accordance with the following rules.

(i) Find the intercepts of the plane on the crystal axes \vec{a} , \vec{b} and \vec{c} in terms of the lattice constant. The axes may be primitive or non-primitive.

(ii) Take the reciprocals of these numbers and then reduce to the smallest three integers having the same ratio. Denote the result as $(h k l)$ enclosed in parentheses.

The three integers h , k and l are called **Miller indices**.

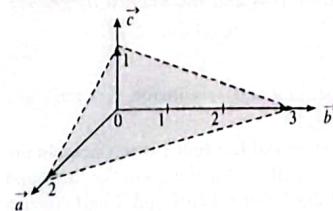


Fig 1.29

Orientation of a plane by Miller Indices. The Miller indices $(h k l)$ may denote a single plane or a set of parallel planes. If a plane cuts an axis on the negative side of the origin, the index is negative and denoted as $(h \bar{k} l)$ by placing a minus (-) sign above the corresponding index (in this case \bar{k}). For an intercept at infinity the corresponding index is zero. For the crystal plane having intercepts $2a$, $3b$ and c on the crystal axes \vec{a} , \vec{b} and \vec{c} , the reciprocals of the numbers 2, 3 and 1 are $\frac{1}{2}$, $\frac{1}{3}$ and 1. The smallest three integers having the same ratio are 3, 2 and 6. The plane is, therefore, referred to as (3 2 6) plane.

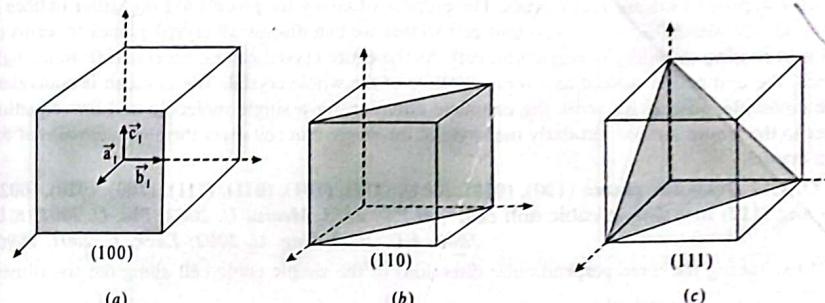


Fig 1.30

The six faces of a cubical crystal are (100) , (010) , (001) , $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$. From a crystallographic point of view many planes in a lattice are equivalent i.e., a plane with given Miller indices can be shifted about in the lattice simply by a choice of the position and orientation of the unit cell. The indices of such equivalent planes are enclosed in braces {} instead of in parenthesis (). For example, all the six cube faces are crystallographically equivalent because the unit cell can be rotated in various directions and still appear the same. The six equivalent faces are collectively designated as $\{100\}$.

The faces (100) , (110) and (111) of a cubic crystal are shown in Fig. 1.30 (a), (b) and (c) respectively. The plane shown in Fig. 1.31 is (200) plane. It is parallel to (100) and $(\bar{1}00)$

plane. Its intercepts on crystal axes \vec{a} , \vec{b} and \vec{c} are $\frac{1}{2}a$, ∞ and ∞ respectively.

Miller indices of a direction. The *indices of a direction* in a crystal are expressed as the set of the smallest integers which have the same ratio as the components of a vector in the desired direction referred to the axes vectors. The integers are written between square brackets as $[h k l]$.

The \vec{a} axis is the $[100]$ direction, the $-\vec{b}$ axis is $[0\bar{1}0]$ direction. In a cubic crystal if we take the origin at one of the corners and the axes parallel to the edges, the body diagonal would be represented as $[111]$. Similarly the \vec{a} axis is $[100]$ direction, the \vec{b} axis $[010]$ direction and the \vec{c} axis $[001]$ direction. In a cubic crystal the direction $[h k l]$ is always perpendicular to a plane $(h k l)$ having the same indices.

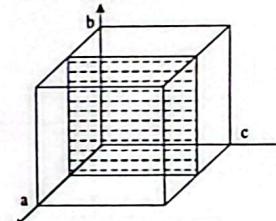


Fig 1.31

Important features. (i) If a plane is parallel to a co-ordinate axis, then the intercept of this plane is *infinity* and hence its Miller index is zero.

(ii) A plane passing through the origin is defined in terms of a parallel plane having non-zero intercept.

(iii) Parallel planes equally spaced have the same index numbers.

(iv) It is the ratio of the indices which is important and determines a plane. For example, (2 4 6) and (1 2 3) represent the same plane.

(v) The direction $[h k l]$ is perpendicular to the plane $(h k l)$. [For proof see Q 1.23].

(b) **Purpose of taking reciprocals.** The purpose of taking reciprocals to find Miller indices is to bring all the planes inside a single unit cell so that we can discuss all crystal planes in terms of the planes passing through the single unit cell. As the entire crystal can be generated from a single unit cell, the unit cell is studied as a representative of the whole crystal. The unit cell is equivalent to the molecule. Just as we write the chemical equation for a single molecule and this equation applies to the whole sample, similarly the study of the single unit cell gives the characteristics of the whole crystal.

Q. 1.17 Draw the planes (100), (010), (001), (110), (101), (011), (111), (200), (020), (002), (201) and (112) in a simple cubic unit cell. (H.P.U. 2003; Meerut U. 2002; P.U. 2001; K.U. 2002; P.U. 2004; Nag. U. 2002; Luck. U. 2001, 1996)

Ans. Taking the three perpendicular directions of the simple cubic cell along the co-ordinate axes \vec{x} , \vec{y} and \vec{z} respectively, we have

(i) (100) plane. The (100) plane lies in the $y-z$ plane and has an intercept 1 along the x -axis. Fig. 1.32 (i)

(ii) (010) plane. The (010) plane lies in the $x-z$ plane and has an intercept 1 along the y -axis. Fig. 1.32 (ii)

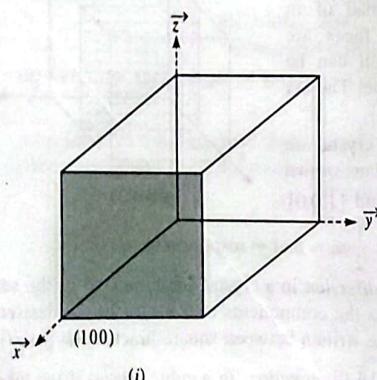
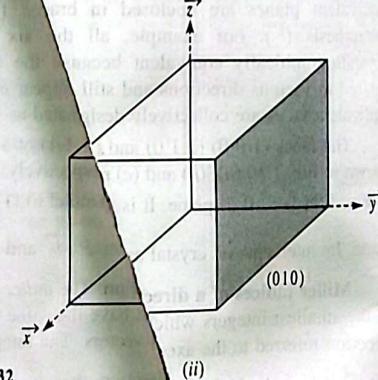


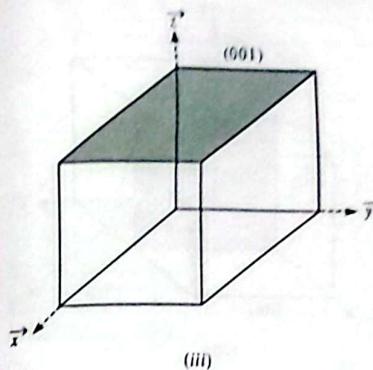
Fig 1.32 (i)



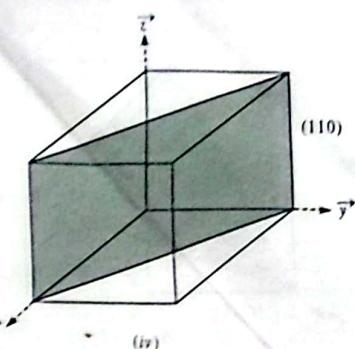
(ii)

(iii) (001) plane. The (001) plane lies in the $x-y$ plane and has an intercept 1 along the z -axis. Fig. 1.32 (iii)

(iv) (110) plane. The (110) plane is parallel to z -axis and has an intercept 1 on x -axis as well as y -axis. Fig. 1.32 (iv)



(iii)

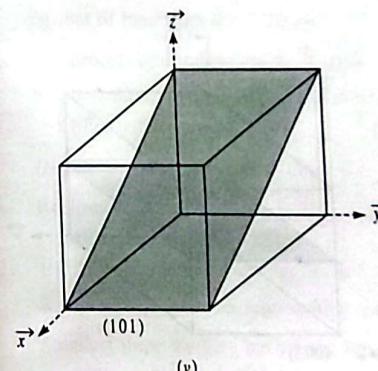


(iv)

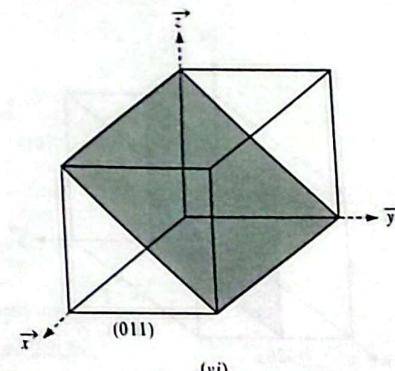
Fig 1.32

(v) (101) plane. The (101) plane is parallel to y -axis and has an intercept 1 on x -axis as well as on z -axis. Fig. 1.32 (v)

(vi) (011) plane. The (011) plane is parallel to x -axis and has an intercept 1 on y -axis as well as on z -axis. Fig. 1.32 (vi)



(v)



(vi)

Fig 1.32

(vii) (111) plane. The (111) plane has intercept 1 along each of the three axis x , y and z . Fig. 1.32 (vii)

(viii) (200) plane. The (200) plane has intercept $\frac{1}{2}$ on the x -axis and lies in the $y-z$ plane. Fig. 1.32 (viii)

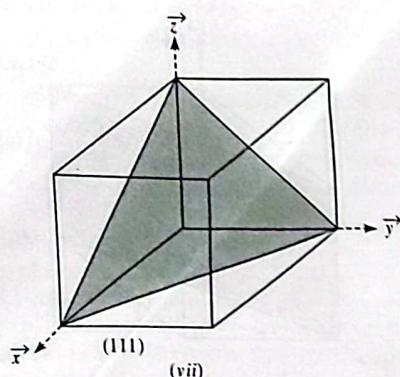
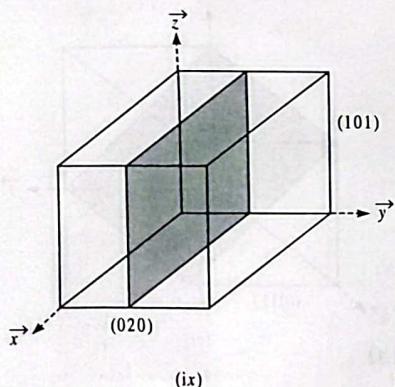


Fig. 1.32

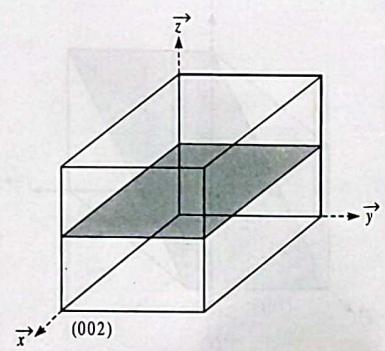
(ix) (020) plane. The (020) plane has intercept $\frac{1}{2}$ on the y-axis and lies in the x-z plane. Fig. 1.32 (ix)

(x) (002) plane. The (002) plane has intercept $\frac{1}{2}$ on the z-axis and lies in the x-y plane. Fig. 1.32 (x)



(ix)

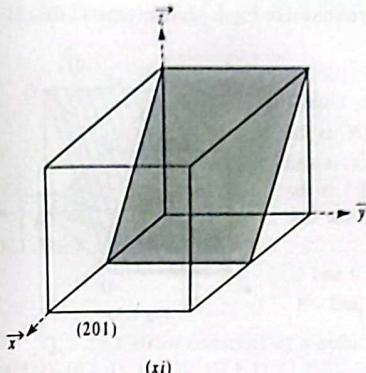
Fig. 1.32



(x)

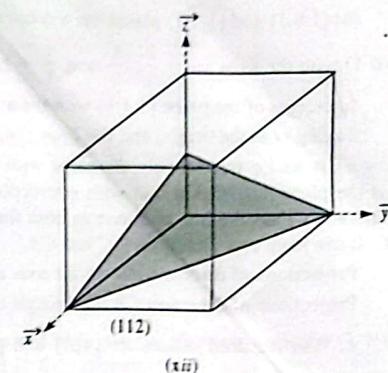
(xi) (201) plane. The (201) plane has intercept $\frac{1}{2}$ on the x-axis, is parallel to y-axis and has an intercept 1 on the z-axis. Fig. 1.32 (xi)

(xii) (112) plane. The (112) plane has intercept 1 each on x-axis and y-axis and intercept $\frac{1}{2}$ on the z-axis. Fig. 1.32 (xii)



(xi)

Fig. 1.32



(xii)

Q. 1.18 Find the Miller indices for planes in each of the following sets which intercept \vec{a} , \vec{b} , and \vec{c} at (i) $3a, 3b, 2c$; (ii) $a, 2b, \infty$; (iii) $a, b/2, c$; (iv) $3a, 2b, 2c$. (P.U. 2003, 1991)

Ans. (i) Set of intercepts = $3a, 3b, 2c$

Reciprocal of numbers representing the intercepts are $\frac{1}{3}, \frac{1}{3}, \frac{1}{2}$.

Smallest three integers having the same ratio are 2, 2, 3.

\therefore Miller indices are = (2 2 3)

(ii) Set of intercepts are $a, 2b, \infty$.

Reciprocals of numbers are 1, $\frac{1}{2}, 0$.

Smallest three integers having the same ratio 2, 1, 0.

\therefore Miller indices are = (2 1 0)

(iii) Set of intercepts = $a, \frac{b}{2}, c$

Reciprocal of numbers are 1, 2, 1.

\therefore Miller indices are = (1 2 1)

(iv) Sets of intercepts are $3a, 2b, 2c$.

Reciprocal of numbers representing the intercepts are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$.

Smallest three integers having the same ratio are 2, 3, 3.

\therefore Miller indices are (2 3 3).

Q. 1.19 (a) Explain the meaning of (3 2 2) and (1 1 1) planes. (A. U. 1993)

(b) Draw (1 0 1) and (1 1 1) planes in a cubic unit cell. Determine the Miller indices of the directions which are common to both the planes. (Luck. U. 1993)

Ans. (a) (3 2 2) plane has Miller indices 3, 2, 2. Its intercepts on \vec{a} , \vec{b} and \vec{c} axes are $\frac{1}{3}, \frac{1}{2}$

and $\frac{1}{2}$. Taking the whole numbers, the intercepts are 2, 3, 3 i.e., $2a, 3b$ and $3c$.

(1 1 1) plane has Miller indices 1, 1, 1. Its intercepts on \vec{a} , \vec{b} and \vec{c} axes are 1, 1, and 1 i.e., a, b and c .

(b) $(1\ 0\ 1)$ and $(1\ 1\ 1)$ planes for a cubic unit cell are shown in Fig 1.33. Intercepts of the plane $(1\ 0\ 1)$ with the axes are $= \frac{1}{1}, \frac{1}{0}$ and $\frac{1}{1} = 1, \infty$ and 1

Intercepts of the plane $(1\ 1\ 1)$ with the axes are $= 1, 1$ and 1

Taking O as the origin, and the lines OA , OB and OC as the axes \vec{a} , \vec{b} and \vec{c} respectively, the plane with intercepts $1, \infty$ and 1 is the plane $ADGC$ and that with intercepts $1, 1$ and 1 is the plane ABC . Thus the line common to both the planes is the line AC . It can have two directions AC and CA .

Projections of direction AC on the axis are $= -1, 0$ and 1

Projections of direction CA on the axis are $= 1, 0$ and -1

\therefore The required indices are $[1\bar{0}1]$ and $[10\bar{1}]$.

Q. 1.20 Derive the expression for the interplanar spacing between two parallel planes with Miller indices $(h\ k\ l)$ and show that for a simple cubic lattice of lattice constant a .

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

(P.U. 2004, 2000, 1995, 1994; G.N.D.U. 2003, 2001; H.P.U. 2003, 1992; Meerut U. 2002, 1999; Nag. U. 2002; Luck. U. 2001; Bang. U. 2001; Pbi. U. 1999; A.U. 1994, 1993)

Ans. Spacing of planes in crystal lattices. Consider a simple unit cell in which the crystal axes \vec{a} , \vec{b} , \vec{c} are orthogonal. Suppose these coincide with co-ordinate axes X , Y , Z respectively with O as origin taken at a lattice point.

Now consider a set of planes defined by Miller indices $(h\ k\ l)$. One such plane ABC will have:

intercepts $\frac{a}{h}$, $\frac{b}{k}$ and $\frac{c}{l}$ on the $X(\vec{a})$, $Y(\vec{b})$ and $Z(\vec{c})$ axes respectively.

Draw ON perpendicular from O on the plane ABC and let $ON = d$, then $d = ON$ is the length of the normal from the origin to the plane and represents the distance between adjacent planes or *interplanar spacing* between parallel planes.

Let ON make angles α , β and γ with $X(\vec{a})$, $Y(\vec{b})$ and $Z(\vec{c})$ axes respectively, then according to the law of direction cosines,

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \quad \dots(i)$$

Also $\angle ONA = \angle ONB = \angle ONC = 90^\circ$

Now $\triangle AON$ is a right angled triangle with $\angle AON = \alpha$ and $\angle ONA = 90^\circ$

$$\therefore \frac{ON}{OA} = \cos \alpha \text{ or } ON = OA \cos \alpha$$

or

$$d = \frac{a}{h} \cos \alpha \text{ or } \cos \alpha = d \left(\frac{h}{a} \right)$$

Similarly

$$\cos \beta = d \left(\frac{k}{b} \right) \text{ and } \cos \gamma = d \left(\frac{l}{c} \right)$$

Substituting the values of $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ in (i), we have

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

or

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

For a cubical crystal $a = b = c$.

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

Q. 1.21 Lattice constant of a cubic lattice is a . Calculate the spacing between $(2\ 1\ 1)$, $(1\ 1\ 2)$, $(0\ 0\ 1)$, $(1\ 1\ 0)$, $(0\ 1\ 1)$, $(1\ 0\ 0)$, $(1\ 1\ 1)$ and $(1\ 0\ 1)$ planes.

(Meerut U. 2003; P.U. 1999, 1997)

Ans. The spacing d of plane $(h\ k\ l)$ in a simple cubic lattice of side a is

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

For $(2\ 1\ 1)$ plane

$$d_{211} = \frac{a}{\left(2^2 + 1^2 + 1^2 \right)^{1/2}} = \frac{a}{\sqrt{6}}$$

For $(1\ 1\ 2)$ plane

$$d_{112} = \frac{a}{\sqrt{1^2 + 1^2 + 2^2}} = \frac{a}{\sqrt{6}}$$

For $(0\ 0\ 1)$ plane

$$d_{001} = \frac{a}{\left(0 + 0 + 1^2 \right)^{1/2}} = a$$

For $(1\ 1\ 0)$ plane

$$d_{110} = \frac{a}{\left(1^2 + 1^2 + 0 \right)^{1/2}} = \frac{a}{\sqrt{2}}$$

For $(0\ 1\ 1)$ plane

$$d_{011} = \frac{a}{\sqrt{0 + 1^2 + 1^2}} = \frac{a}{\sqrt{2}}$$

For $(1\ 0\ 0)$ plane

$$d_{100} = \frac{a}{\left(1^2 + 0 + 0 \right)^{1/2}} = a$$

For $(1\ 1\ 1)$ plane

$$d_{111} = \frac{a}{\left(1^2 + 1^2 + 1^2 \right)^{1/2}} = \frac{a}{\sqrt{3}}$$

For $(1\ 0\ 1)$ plane

$$d_{101} = \frac{a}{\left(1^2 + 0 + 1^2 \right)^{1/2}} = \frac{a}{\sqrt{2}}$$

Q. 1.22 (a) Calculate the separation between lattice planes in a simple cubic, face centred cubic (fcc) and body centred cubic (bcc) lattice.

(Meerut U. 2002, 2001)

(b) For a cubic lattice calculate the distance of $(1\ 2\ 3)$ and $(2\ 3\ 4)$ planes from a plane passing through the origin.

(H.P.U. 1993)

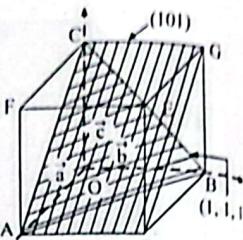


Fig 1.33

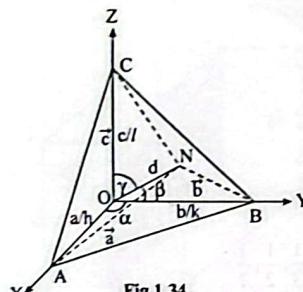


Fig 1.34

Ans. Simple cubic lattice (sc). A simple cubic lattice has (1 0 0), (1 1 0) and (1 1 1) planes. The (1 0 0) planes cut the X-axis and are parallel to Y and Z-axis.

$$d_{100} = \frac{a}{[1^2 + 0 + 0]^{1/2}} = a$$

The (1 1 0) planes cut obliquely across X and Y-axis but are parallel to Z-axis.

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

The (1 1 1) planes cut obliquely across the three axes.

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

Face centred cubic lattice. In fcc lattice there is one unit situated at each corner and one unit at the centre of each of the six faces. Thus an additional (1 0 0) plane arises half way between the (1 0 0) planes. These additional planes pass through the centre of the front and back face. As the distance between (1 0 0) planes of a simple cubic lattice is a , the distance between (100) planes of the fcc lattice is $\frac{a}{2}$,

$$d_{100} = \frac{1}{2}a$$

Similarly, there arises an additional set of (1 1 0) planes parallel to the first set midway between the planes of simple cubic lattice.

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

The (1 1 1) planes of simple cubic lattice pass through the centre of all the faces of fcc lattice and hence no new planes arise in this case.

$$d_{111} = \frac{a}{\sqrt{3}}$$

Body centred cubic lattice. In bcc lattice one unit is situated at each corner and one at the centre of the cube. An additional (1 0 0) plane arises half way between (1 0 0) planes of a simple cubic lattice.

$$d_{100} = \frac{1}{2}a$$

The (1 1 0) plane is the same as in a simple cubic lattice.

$$d_{110} = \frac{a}{\sqrt{2}}$$

The (1 1 1) plane of a bcc lattice lies midway between the (1 1 1) planes of a simple cubic lattice.

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

(b) The spacing d of plane $(h k l)$ in a simple cubic lattice is

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

(i) For (1 2 3) plane

$$d_{123} = \frac{a}{[1^2 + 2^2 + 3^2]^{1/2}} = \frac{a}{\sqrt{14}}$$

(ii) For (2 3 4) plane

$$d_{234} = \frac{a}{(2^2 + 3^2 + 4^2)^{1/2}} = \frac{a}{\sqrt{29}}$$

Q. 1.23 Show that for a crystal of cubic symmetry the direction $[h, k, l]$ is perpendicular to the plane (h, k, l) . (P.U. 2004; G.N.D.U. 2000; Pbl. U. 2002, 2001, 1997; H.P.U. 1994, 1993)

Ans. If \vec{a} , \vec{b} and \vec{c} are the cubic axes, then the intercepts of the plane (h, k, l) on these axes are

$$\vec{r}_1 = \frac{\vec{a}}{h}, \vec{r}_2 = \frac{\vec{b}}{k} \text{ and } \vec{r}_3 = \frac{\vec{c}}{l}$$

Therefore, the vectors $\vec{r}_1 - \vec{r}_2$ and $\vec{r}_1 - \vec{r}_3$ lie in the (h, k, l) plane.

$$\text{Now } \vec{r}_1 - \vec{r}_2 = \frac{\vec{a}}{h} - \frac{\vec{b}}{k} \text{ and } \vec{r}_1 - \vec{r}_3 = \frac{\vec{a}}{h} - \frac{\vec{c}}{l}$$

The vector $h\vec{a} + k\vec{b} + l\vec{c}$ represents $[h, k, l]$. It is perpendicular to $\vec{r}_1 - \vec{r}_2$ as well as $\vec{r}_1 - \vec{r}_3$ because the scalar product

$$\begin{aligned} & (\vec{r}_1 - \vec{r}_2) \cdot (h\vec{a} + k\vec{b} + l\vec{c}) \\ &= \left(\frac{\vec{a}}{h} - \frac{\vec{b}}{k} \right) \cdot (h\vec{a} + k\vec{b} + l\vec{c}) \\ &= \vec{a} \cdot \vec{a} - \vec{b} \cdot \vec{b} = 0 \end{aligned}$$

Since in a cubic crystal $a = b = c$.

$$\text{Similarly } (\vec{r}_1 - \vec{r}_3) \cdot (h\vec{a} + k\vec{b} + l\vec{c}) = 0.$$

Thus, direction $[h, k, l]$ is perpendicular to the plane (h, k, l) .

Q. 1.24 Find the Miller indices of a set of parallel planes which make intercepts in the ratio of $2a : 3b$ on the X and Y axis and are parallel to Z-axis; \vec{a} , \vec{b} , \vec{c} being primitive vectors of the lattice. Also calculate the interplanar distance d of the planes taking the lattice to be a cube with $a = b = c = 3\text{\AA}$. (P.U. 2001; H.P.U. 2000; Pbl. U. 1999)

Ans. Intercept on the X-axis = $2a$

Intercept on the Y-axis = $3b$

Intercept on the Z-axis = ∞

As the set of planes is parallel to Z-axis.

The reciprocals of the numbers $2, 3$ and ∞ are $\frac{1}{2}, \frac{1}{3}, \frac{1}{\infty}$ or zero.

The smallest three integers having the same ratio are $3, 2, 0$.

\therefore Miller indices $(h k l) = (3 2 0)$

Lattice constant $a = b = c = 3\text{\AA}$

$$\therefore \text{Interplanar distance } d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{3\text{\AA}}{\sqrt{3^2 + 2^2 + 0^2}} = \frac{3}{\sqrt{13}} \text{\AA.}$$

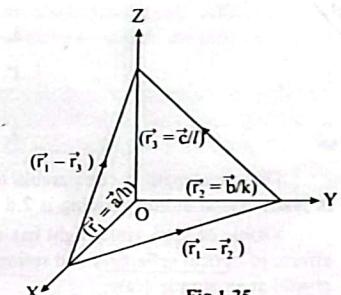


Fig 1.35

2

Crystal Diffraction and Reciprocal Lattice

- (Q. 2.1) (a) Why X-rays are used for crystal structure analysis? (H.P.U. 1997, 1999)
 (b) Why γ -rays are not used to study crystal structure? (G.N.D.U. 1999)
 (c) Why a crystal diffracts X-rays? (M.D.U. 2001)

Ans. (a) Reason for using X-rays for crystal structure. X-rays are used for producing diffraction effect in crystals due to the fact that wavelength of X-rays is comparable to the interatomic distances in actual crystals.

For example, X-rays produced by acceleration of electrons through a potential difference have a wavelength given by

$$eV = hv = \frac{hc}{\lambda}$$

or

$$\lambda = \frac{hc}{eV}$$

for

$V = 10$ kV, we have

$$\lambda = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{1.6 \times 10^{-19} \times 10^4} = 1.24 \times 10^{-10} \text{ m} = 1.24 \text{ \AA}$$

The wavelength is comparable to the inter atomic spacing of an actual crystal. For example in NaCl crystal atomic spacing is $2.8 \times 10^{-10} \text{ m} = 2.8 \text{ \AA}$.

Visible or ultra violet light has a larger wavelength. Hence these waves give rise to familiar effects of optical reflection and refraction. These rays, therefore, cannot be used for exploring the crystal at an atomic scale.

On the other hand, radiations of wavelength shorter than that of X-rays i.e., γ -rays are diffracted through very small angles which cannot be conveniently measured.

It is only X-rays which are scattered elastically without change of wavelength by the charged particles of the atom.

(b) **Why γ -rays are not used?** Gamma rays are not used to study crystal structure as the wavelength of γ -rays is much smaller than that of X-rays and, therefore, the γ -rays are diffracted through very small angles which cannot be conveniently measured.

(c) **Why a crystal diffracts X-rays?** A crystal diffracts X-rays because X-rays are scattered elastically without change of wavelength by the charged particles of the atoms in the crystal as explained below:-

When an atom is exposed to a monochromatic beam of X-rays, the atomic electrons start vibrating with a frequency equal to that of the incident beam under the effect of the electric field vector of the radiation. These electrons, therefore, undergo acceleration and the accelerated electrons emit secondary radiations of the same frequency as that of the incident X-rays. The secondary X-rays spread out in all directions. If the wavelength of original X-rays is quite large compared to the atomic dimensions, all the radiations emitted by the electrons shall be in phase with one another.

On the other hand, if the incident X-rays have the same order of wave length as that of the atomic dimensions, then the radiations emitted by the electrons are, in general, out of phase with one another. These radiations may, therefore, undergo constructive or destructive interference producing maxima or minima in certain directions i.e., under go diffraction phenomenon.

Q. 2.2 (a) Derive Bragg's law of crystal diffraction

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

and give its significance. Discuss briefly the method of crystal structure determination.

(Patna U. 2004; Meerut U. 2003; Pbl. U. 2003, 2000; K.U. 2001, 2000, 1996; Luck. U. 2001; Bang. U. 1994; Osm. U. 2004; A.U. 1994; H.P.U. 1993)

(Pbl. U. 2004)

(b) (i) What is Bragg's equation?

(ii) What is Bragg's law? (P.U. 2004; Meerut U. 2003, 2002; Bang. U. 2000)

(c) How does Bragg reflection differ from ordinary reflection? (Pbl. U. 2000)

Ans. Bragg's law – derivation W.L. Bragg discovered that X-rays can be regularly reflected by the cleavage planes of the crystals when the rays are incident on their surface nearly at glancing angle. The cleavage planes are successive atomic planes in the crystal. X-rays that penetrate more deeply into the crystal are reflected from the lower planes and thus several beams of X-rays reflected from various planes are obtained. The intensity of the reflected beam at certain angles will be maximum, where the two reflected waves from two different planes have a path-difference equal to an integral multiple of the wavelength of X-rays, while at some other angles, the intensity will be minimum.

Consider parallel lattice planes equidistant from one another in a crystal structure, separated by a distance d . Suppose a beam of X-rays AB of wavelength λ is incident on a layer of atoms in one cleavage plane P of a crystal at a glancing angle θ at B and after reflection goes along BC . The ray DE incident on cleavage plane Q after reflection goes along EF . Draw BG perpendicular on DE and BH perpendicular on EF , then BG is the incident wave front and BH the reflected wave front.

Path difference between the two wave fronts

$$= GE + EH$$

Now in $\triangle BGE$

$$GE = BE \sin \theta = d \sin \theta$$

and in $\triangle BEH$, $EH = BE \sin \theta = d \sin \theta$

\therefore Path-difference

$$GE + EH = 2d \sin \theta$$

If this path-difference is an integral multiple of wavelength λ , constructive interference will take place between the reflected beams. Thus the intensity will be maximum if

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

where $n = 1, 2, 3, \dots$

For $n = 1$, we get the first order spectrum and for $n = 2$, we get the second order spectrum and so on. This phenomenon is similar to that of the optical diffraction with diffraction grating with only this difference that here various parallel planes of the crystal act as lines in the grating.

The above equation $2d \sin \theta = n\lambda$ is Bragg's equation and represents *Bragg's law*.

Significance. The interpretation of Bragg's law gives that the diffraction intensities can be stronger only at certain values of θ for specific values of λ and d . Therefore, a knowledge of experimentally observed diffraction angles and wavelength of X-rays can provide the information

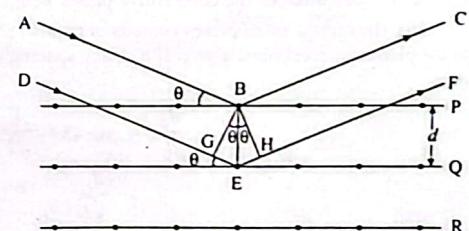


Fig. 2.1

about the inter planar spacing of the crystal. Thus, the space, shape and orientation of the unit cell can be determined from any diffraction experiment using monochromatic X-rays. This will be clear from the example of crystal structure determination given below.

Determination of crystal structure. To find the structure of a crystal, the *lattice constant d* is determined by using different planes of the crystal as reflecting surface for the same known wavelength of X-rays. Expressing the lattice constants as ratios with one of them taken as unity, it is seen that the ratios depend upon the way in which the atoms are arranged in the crystal. Thus the structure of the crystal is analysed.

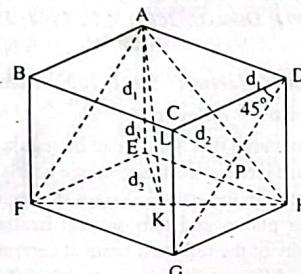
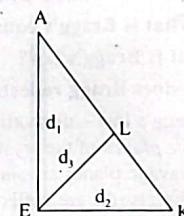


Fig. 2.2



For example, consider a crystal of cubic system. In such a crystal, the atoms are situated at definite places in relation to a system of co-ordinates or **lattice**. Suppose there is an atom at each corner of cube as at *A*, *B*, *C* etc., as shown in Fig. 2.2, the structure being repeated throughout the substance of the crystal. It is found that three sets of planes rich in atoms exist.

(i) The first set of planes such as *ABFE*, *CDHG*, *ADHE*, *BCGF* and *ABCD*, *EFGH* are alike. Let the distance between the consecutive planes be *d*₁. These are known as (100) planes.

(ii) The second set of planes consists of parallel planes like *ADGF*, inclined at an angle of 45° to the planes, as mentioned above. If *d*₂ is the spacing between these planes, as represented by *CP*, then

$$\frac{d_2}{d_1} = \sin 45 = \frac{1}{\sqrt{2}}$$

$$\therefore d_2 = \frac{d_1}{\sqrt{2}}$$

These are known as (110) planes.

(iii) The third set of planes consists of planes like *AFH*. To find the spacing between these planes, draw *EK* perpendicular to *FH* and join *AK* to complete the right-angled triangle *AEK* shown separately. From *E* draw *EL* perpendicular to *AK*; then *EL* = *d*₃ measures the spacing between these planes. Now

In $\triangle AEK$,

$$AE = d_1, EK = d_2 \text{ and } AK = \sqrt{d_1^2 + d_2^2}$$

Also

$$\sin A = \frac{d_3}{d_1} = \frac{d_2}{\sqrt{d_1^2 + d_2^2}}$$

or

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

These are known as (111) planes.

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

Using a crystal of KCl, Bragg found the following values of θ for reflection from the faces *ABCD*, *ADGF* and *AFH* respectively.

$$\theta_1 = 5.22^\circ, \theta_2 = 7.30^\circ, \text{ and } \theta_3 = 9.05^\circ$$

For the first order spectrum

$$\frac{1}{d} = \frac{2 \sin \theta}{\lambda}$$

$$\therefore \frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = \sin 5.22 : \sin 7.30 : \sin 9.05 \\ = 0.0910 : 0.1272 : 0.1570 \\ = 1 : 1.40 : 1.73$$

These ratios, within the limits of experimental error, are

$$1 : \sqrt{2} : \sqrt{3}$$

Hence we conclude that KCl has a cubic crystal structure. Similarly other forms can be investigated.

(b) (i) **Bragg's equation.** When X-rays of wavelength λ are incident on a crystal surface making an angle θ with the surface of the crystal, these suffer reflection and constructive interference takes place between the beams reflected from two consecutive lattice planes of the crystal separated by a distance *d*, then the relation

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

where *n* is the order of the diffraction spectrum maxima, is known as **Bragg's equation**.

(ii) **Bragg's law.** The law represented by Bragg's equation

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

is known as **Bragg's law**.

(c) **Difference between Bragg reflection and ordinary reflection.** In ordinary reflection all the reflected waves are in phase and there are no maxima and minima. The phenomenon of Bragg reflection is similar to that of diffraction of light from a diffraction grating with only this difference that in Bragg reflection various parallel planes of the crystal serve the same purpose as the ruled lines on the grating which produce opacities and transparencies.

Q. 2.3 State and prove Bragg's law of X-ray diffraction and verify it for NaCl crystal from the following data

$$\text{Bragg angles } 11.8^\circ, 23.5^\circ, 36^\circ$$

(A.U. 1995)

Ans. For statement and proof of Bragg's law See Q 2.2.

Verification of Bragg's law for NaCl crystal. The NaCl crystals are cubic and every elementary cube has eight ions at its corners, four of sodium and four of chlorine, which form four molecules of sodium chloride. Every elementary cube is surrounded on all sides by other such cubes, as shown in Fig. 2.3. Thus each ion of sodium chloride is shared between the two cubes and each elementary cube contains half a molecule of sodium chloride.

$$\therefore \text{The mass of elementary cube} = \frac{M}{2N}$$

where *M* is the molecular weight of NaCl and *N* is the Avogadro's number.

$$\therefore \text{Mass of elementary cube} = \frac{23 + 35.5}{2 \times 6.06 \times 10^{26}} \text{ kg.}$$

As each side of the elementary cube is equal to d , the volume of the elementary cube

$$d^3 = \frac{\text{Mass}}{\text{Density}}$$

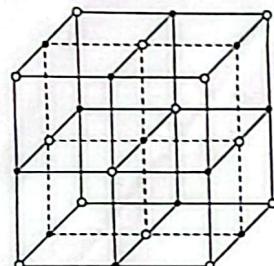


Fig. 2.3

or

Now density of NaCl is $2.17 \times 10^3 \text{ kg/m}^3$.

$$\therefore \text{Volume } d^3 = \left[\frac{58.5}{2 \times 6.06 \times 10^{26} \times 2.17 \times 10^3} \right]$$

$$\text{or } d = \left[\frac{58.5}{2 \times 6.06 \times 10^{26} \times 2.17 \times 10^3} \right]^{1/3} \\ = 2.814 \times 10^{-10} \text{ m}$$

According to Bragg's law $2d \sin \theta = n\lambda$

$$\therefore \text{For the first order diffraction } n = 1, \\ \therefore \lambda = 2d \sin \theta$$

$$\lambda = 2 \times 2.814 \times 10^{-10} \times \sin 11.8^\circ \\ = 5.628 \times 0.2 \times 10^{-10} \\ = 1.12 \times 10^{-10} \text{ m} = 1.12 \text{ \AA}$$

For the second order diffraction $n = 2$,

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

$$\lambda = d \sin \theta = 2.814 \times 10^{-10} \times \sin 23.5^\circ \\ = 1.12 \times 10^{-10} \text{ m} = 1.12 \text{ \AA}$$

For the third order diffraction $n = 3$, $3\lambda = 2d \sin \theta$

$$\text{or } \lambda = \frac{2}{3} d \sin \theta = \frac{2}{3} \times 2.814 \times 10^{-10} \times \sin 36^\circ \\ = 1.12 \times 10^{-10} \text{ m} = 1.12 \text{ \AA}$$

Thus we find that for values of $\theta = 11.8^\circ, 23.5^\circ$ and 36° for first, second and third order spectrum $2d \sin \theta = n\lambda$.

Hence diffraction from a NaCl crystal verifies Bragg's law.

Exercise. Calculate the lattice constant a for NaCl crystal with density $\rho = 2189 \text{ kg/m}^3$. Avogadro's number $N = 6.02 \times 10^{26}/\text{kg mole}$. (Meerut U. 2003)

Hint. Molecular weight of NaCl = $23 + 35.5 = 58.5$

$$\therefore \text{Lattice constant } a = \left[\frac{58.5}{2 \times 6.02 \times 10^{26} \times 2189} \right]^{1/3} \\ = 2.81 \times 10^{-10} \text{ m} = 2.81 \text{ \AA}$$

Q. 2.4 The spacing between successive (1 0 0) planes in NaCl is 2.82 \AA . X-rays incident on the surface of the crystal is found to give rise to first order Bragg reflection at glancing angle 8.8° . Calculate the wavelength of X-rays. (H.P.U. 1996)

Ans. According to Bragg's law $2d \sin \theta = n\lambda$.

Here

$$d = 2.82 \text{ \AA} = 2.82 \times 10^{-10} \text{ m}, \theta = 8.8^\circ$$

$$\sin \theta = 0.153, n = 1$$

$$\therefore 2 \times 2.82 \times 10^{-10} \times 0.153 = \lambda$$

or

$$\lambda = 0.863 \times 10^{-10} \text{ m} \\ = 0.863 \text{ \AA.}$$

Exercise 1. Calculate the glancing angle on the cube face (100) of a rock salt crystal ($a = 2.814 \text{ \AA}$) corresponding to second order reflection of X-rays of wavelength 0.710 \AA . (M.D.U. 2001)

Hint. $2d \sin \theta = n\lambda; d = a = 2.814 \times 10^{-10} \text{ m}$ for cube face (100); $n = 2; \lambda = 0.710 \times 10^{-10} \text{ m}$

$$\therefore \sin \theta = \frac{2 \times 0.710 \times 10^{-10}}{2 \times 2.814 \times 10^{-10}} = 0.2523 \\ \theta = 14.6^\circ.$$

Exercise 2. X-rays of wavelength 1.5 \AA make a glancing angle of 16° in the first order when diffracted from NaCl crystal. Find the lattice constant of NaCl. (Osmania U. 2004)

Hint. $2d \sin \theta = n\lambda; \lambda = 1.5 \times 10^{-10} \text{ m}; n = 1; \theta = 16^\circ$

$$\therefore \sin \theta = 0.2756$$

$$\therefore d = \frac{n\lambda}{2 \sin \theta} = \frac{1 \times 1.5 \times 10^{-10}}{2 \times 0.2756} = 2.72 \times 10^{-10} \text{ m} = 2.72 \text{ \AA.}$$

Exercise 3. Calculate the glancing angle on the plane (110) of a cubic rock salt crystal ($a = 2.81 \text{ \AA}$) corresponding to second order diffraction maxima of wavelength 0.71 \AA . (Bang. U. 2001)

Hint. $a = 2.81 \text{ \AA}$

$$\therefore \text{Spacing for (110) plane, } d = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}} = \frac{2.81}{\sqrt{2}} = 1.993 \text{ \AA}$$

Now, $2d \sin \theta = n\lambda; \lambda = 0.71 \times 10^{-10} \text{ m}; n = 2$

$$\therefore \sin \theta = \frac{n\lambda}{2d} = \frac{2 \times 0.71 \times 10^{-10}}{2 \times 1.993 \times 10^{-10}} = 0.3562 \text{ or } \theta = 20.87^\circ.$$

Q. 2.5 The molecular weight of rock salt (a simple cubic) crystal is $58.5 \text{ kg per kilo-mole}$ and its density is $2.16 \times 10^3 \text{ kg/m}^3$. Taking Avogadro's number = 6.02×10^{26} , calculate the grating space d_{100} of rock salt.

Using this value of lattice constant, calculate the wavelength of X-rays in second order, if angle of diffraction $\theta = 26^\circ$. (A.U. 1995, 1994; CalU. 1992, 1991; Bang. U. 1992)

Ans. Mass of one kilo-mole of NaCl = 58.5 kg

Number of molecules in one kilo-mole = 6.02×10^{26}

$$\therefore \text{Mass of one NaCl molecule} = \frac{58.5}{6.02 \times 10^{26}} = 9.72 \times 10^{-26} \text{ kg}$$

Density of NaCl crystal = $2.16 \times 10^3 \text{ kg/m}^3$

$$\text{Volume of one NaCl molecule} = \frac{9.72 \times 10^{-26}}{2.16 \times 10^3} = 4.5 \times 10^{-29} \text{ m}^3$$

As there are two atoms per NaCl molecule, the volume per atom

$$= \frac{4.5 \times 10^{-29}}{2} = 2.25 \times 10^{-29} \text{ m}^3$$

If d is the atomic spacing for NaCl crystal, then volume per atom = d^3

$$\therefore d^3 = 2.25 \times 10^{-29}$$

or

$$d = [2.25 \times 10^{-10}]^{1/2} = 2.82 \times 10^{-10} \text{ m} = 2.82 \text{ \AA}$$

$$\therefore d_{100} = 2.82 \text{ \AA}$$

According to Bragg's law $2d \sin \theta = n\lambda$.

Here

$$d = 2.82 \times 10^{-10} \text{ m}, \theta = 26^\circ \text{ or } \sin \theta = 0.4383$$

and

$$n = 2$$

$$2\lambda = 2 \times 2.82 \times 10^{-10} \times 0.4383$$

or

$$\lambda = 2.82 \times 0.4383 \times 10^{-10}$$

$$= 1.24 \times 10^{-10} \text{ m} = 1.24 \text{ \AA}.$$

Q. 2.6 (a) If X-rays of wavelength 0.5 \AA are diffracted at an angle of 5° in the first order, what is the spacing between the adjacent planes of the crystal? At what angle will second maximum occur?
(Bang. U. 1991)

(b) The Bragg angle for first order reflection from (111) plane in a crystal is 60° . Calculate the interatomic spacing if X-rays of wavelength $1.8 \times 10^{-10} \text{ m}$ are used.
(P.U. 2004; M.D.U. 2003; K.U. 2001, 1991)

Ans. (a) According to Bragg's law $2d \sin \theta = n\lambda$.

Here

$$\lambda = 0.5 \text{ \AA} = 0.5 \times 10^{-10} \text{ m}; \theta = 5^\circ$$

∴

$$\sin \theta = 0.0871$$

$$n = 1$$

∴

$$2d \times 0.0871 = 0.5 \times 10^{-10}$$

or

$$d = \frac{0.5 \times 10^{-10}}{0.1742}$$

$$= 2.87 \times 10^{-10} \text{ m} = 2.87 \text{ \AA}$$

For second order maximum, let θ' be the angle of Bragg reflection, then

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

or

$$\sin \theta' = \frac{\lambda}{d} = \frac{0.5 \times 10^{-10}}{2.87 \times 10^{-10}} = 0.1742$$

$$\therefore \theta' = 10.03^\circ$$

(b) According to Bragg's law $2d \sin \theta = n\lambda$.

Here

$$\theta = 60^\circ \therefore \sin \theta = \sin 60 = 0.866, \lambda = 1.8 \times 10^{-10} \text{ m}; n = 1$$

∴

$$2d \times 0.866 = 1.8 \times 10^{-10}$$

or

$$d = \frac{1.8 \times 10^{-10}}{1.732} = 1.039 \times 10^{-10} \text{ m}$$

This gives us d_{111}

or

$$d_{111} = 1.039 \times 10^{-10} \text{ m}$$

If the interatomic spacing for a simple cubic lattice

$$d_{100} = a, \text{ then } d_{111} = \frac{a}{\sqrt{3}}$$

∴

$$\begin{aligned} a &= d_{100} = d_{111} \times \sqrt{3} \\ &= 1.039 \times 1.732 \times 10^{-10} \text{ m} \\ &= 1.8 \times 10^{-10} \text{ m.} \end{aligned}$$

Q. 2.7 (a) Calculate the Bragg angle for X-rays having wavelength 1.54 \AA in different orders 1, 2, 3, if the interplanar distance is 2.67 \AA .
(A.U. 1994)

(b) A certain crystal reflects monochromatic X-rays strongly when Bragg glancing angle (first order) is 15° . What are the glancing angles for second and third order spectrum?
(H.P.U. 1993)

Ans. (a) According to Bragg's law $2d \sin \theta = n\lambda$.Here $\lambda = 1.54 \text{ \AA} = 1.54 \times 10^{-10} \text{ m}; d = 2.67 \text{ \AA} = 2.67 \times 10^{-10} \text{ m}$ 1st order, $n = 1; 2d \sin \theta_1 = 1\lambda$

$$\text{or } \sin \theta_1 = \frac{\lambda}{2d} = \frac{1.54 \times 10^{-10}}{2 \times 2.67 \times 10^{-10}} = 0.2884$$

$$\therefore \theta_1 = 16.76^\circ$$

Second order, $n = 2; 2d \sin \theta_2 = 2\lambda$

$$\text{or } \sin \theta_2 = \frac{2\lambda}{2d} = \frac{\lambda}{d} = \frac{1.54 \times 10^{-10}}{2.67 \times 10^{-10}} = 0.5768$$

$$\therefore \theta_2 = 35.22^\circ$$

Third order, $n = 3; 2d \sin \theta_3 = 3\lambda$

$$\text{or } \sin \theta_3 = \frac{3\lambda}{2d} = \frac{3}{2} \times \frac{1.54 \times 10^{-10}}{2.67 \times 10^{-10}} = 0.8652$$

$$\therefore \theta_3 = 59.9^\circ.$$

(b) According to Bragg's law

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

For the first order, $2d \sin \theta = 1\lambda$

$$\text{or } \sin \theta_1 = \frac{\lambda}{2d}$$

For the 2nd order, $2d \sin \theta_2 = 2\lambda$

$$\therefore \sin \theta_2 = \frac{2\lambda}{2d}$$

For the 3rd order, $2d \sin \theta_3 = 3\lambda$

$$\therefore \sin \theta_3 = \frac{3\lambda}{2d}$$

Now $\theta_1 = 15^\circ \therefore \sin \theta_1 = 0.2588$

$$\text{Hence } \frac{\lambda}{2d} = 0.2588$$

$$\text{Now } \sin \theta_2 = \frac{2\lambda}{2d}$$

$$= 2 \times 0.2588 = 0.5176$$

$$\therefore \theta_2 = 31.17^\circ$$

$$\text{Again } \sin \theta_3 = \frac{3\lambda}{2d}$$

$$= 3 \times 0.2588 = 0.7764$$

$$\therefore \theta_3 = 50.93^\circ.$$

Q. 2.8 A monochromatic beam of X-rays of wavelength 1.24 \AA is reflected by cubic crystal of KCl. Determine the inter planar distances for (100), (110) and (111) planes. Given density of KCl = 1980 kg/m^3 and molecular weight $M = 74.5 \text{ kg}$. Avogadro's number $N = 6.023 \times 10^{26} \text{ kg mole}^{-1}$.
(Bang. U. 1994)

Ans. For a cubic crystal, we have

$$a^3 = \frac{nM}{N\rho}$$

where a is the lattice constant, n the number of molecule in a unit cell, M the molecular weight, N Avogadro's number and ρ the density.

For KCl cubic crystal $n = 4$

$$\therefore a^3 = \frac{4 \times 74.5}{6.023 \times 10^{26} \times 1.98 \times 10^3} = 25 \times 10^{-29}$$

or

$$a = [250 \times 10^{-30}]^{1/3} = 6.3 \times 10^{-10} \text{ m}$$

Now

$$d_{100} = \frac{a}{\sqrt{i^2 + 0^2 + 0^2}} = a = 6.3 \times 10^{-10} \text{ m}$$

$$d_{110} = \frac{a}{\sqrt{i^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}} = \frac{6.3}{\sqrt{2}} \times 10^{-10} = 4.45 \times 10^{-10} \text{ m}$$

$$d_{111} = \frac{a}{\sqrt{i^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}} = \frac{6.3}{\sqrt{3}} \times 10^{-10} = 3.63 \times 10^{-10} \text{ m.}$$

Q. 2.9 From the following data calculate the wavelength of neutron beam and its speed. Spacing between successive (100) planes = 3.84 \AA ; grazing angle 30° ; order of Bragg reflection = 1.
(H.P.U. 1999, 1995, 1994)

Ans. According to Bragg's relation

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

Here

$$d = 3.84 \text{ \AA} = 3.84 \times 10^{-10} \text{ m}, \theta = 30^\circ; \sin 30 = \frac{1}{2}; n = 1$$

∴

$$2 \times 3.84 \times 10^{-10} \times \frac{1}{2} = 1 \times \lambda$$

or

$$\lambda = 3.84 \times 10^{-10} \text{ m} = 3.84 \text{ \AA.}$$

According to de-Broglie relation

$$\lambda = \frac{h}{p} = \frac{h}{mv} \text{ where } h \text{ is Planck's constant having a value } 6.62 \times 10^{-34} \text{ Js and neutron mass } m \\ = 1.67 \times 10^{-27} \text{ kg}$$

∴

$$v = \frac{h}{m\lambda} = \frac{6.62 \times 10^{-34}}{1.67 \times 10^{-27} \times 3.84 \times 10^{-10}} \\ = 1.03 \times 10^3 \text{ ms}^{-1}$$

Q. 2.10 Derive Laue's equations of diffraction of X-rays and obtain Bragg's diffraction condition from them.

(G.N.D.U. 2004, 2003, 2002, 2001, 1999, 1996; H.P.U. 2003, 2001, 1996; P.U. 2003, 2001, 1995; Pbi. U. 2002; Meerut U. 2001; Cal. U. 2001; M.D.U. 1999; Luck. U. 1992)

Ans. Laue's equations. Laue's diffraction equations give the conditions under which X-rays scattered from different atoms of a crystal combine to form a diffracted beam. For this purpose we

study the X-ray diffraction pattern produced by identical scattering centres located at the *lattice points* of a three dimensional crystal lattice. Let P_1 and P_2 be two such lattice points separated by a vector \vec{r} . Suppose a parallel beam of X-rays is incident on P_1P_2 along the direction of unit vector \hat{i} . The scattered beam is also parallel and let it be in any arbitrary direction given by unit vector \hat{s} . Draw P_1A perpendicular to the incident wave direction and P_2B perpendicular to the scattered wave direction, then P_1A is incident and P_2B the scattered wave front. The path difference between the two scattered waves – one scattered from P_2 and the other scattered from P_1 is given by

$$P_2A - P_1B = \vec{r} \cdot \hat{i} - \vec{r} \cdot \hat{s} = \vec{r} \cdot (\hat{i} - \hat{s}) = \vec{r} \cdot \vec{S}$$

where $\vec{S} = (\hat{i} - \hat{s})$ is a vector in the direction of the normal to the reflecting plane.

If θ is the angle that the incident beam makes with the reflecting plane, then the angle that the scattered (reflected) beam makes with the reflecting plane is also equal to θ and the angle between the unit vectors \hat{i} and \hat{s} is 2θ as shown in Fig. 2.4.

$$\therefore |\vec{S}| = 2 \sin \theta \quad [\because \hat{i} \text{ and } \hat{s} \text{ are unit vectors}]$$

The phase difference between the waves scattered at the lattice points P_1 and P_2 is given by

$$\phi = \frac{2\pi}{\lambda} (\vec{r} \cdot \vec{S})$$

The intensity of the diffracted beam is a *maximum* in the direction in which ϕ is an integral multiple of 2π .

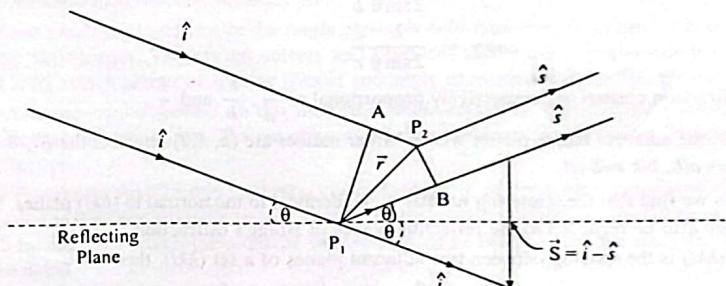


Fig. 2.4

If \vec{a} , \vec{b} and \vec{c} are the primitive lattice vectors of the point P_2 with respect to the point P_1 , then

$$\vec{r} = \vec{a} + \vec{b} + \vec{c}$$

and the above condition can be put in the form of three separate conditions i.e.,

$$\phi_a = \frac{2\pi}{\lambda} (\vec{a} \cdot \vec{S}) = 2\pi h \quad \dots(i)$$

$$\phi_b = \frac{2\pi}{\lambda} (\vec{b} \cdot \vec{S}) = 2\pi k \quad \dots(ii)$$

and

$$\phi_c = \frac{2\pi}{\lambda} (\vec{c} \cdot \vec{S}) = 2\pi l \quad \dots(iii)$$

where h, k, l are integers and ϕ_a, ϕ_b and ϕ_c are phase differences between the waves scattered from the two ends of the primitive lattice vectors \vec{a} , \vec{b} and \vec{c} respectively.