1

CRYSTALLOGRAPHY

§ 1. Introduction : The science of Crystallography is concerned with the enumeration and classification of all possible types of crystal structures and the determination of the actual structure of the crystalline solids. Today it includes not only regular solids but also other substances like plastics and rubber because it brings out principles of structure.

All materials are composed of atoms and molecules. What distinguishes crystals from non-crystals is the way that atoms are stacked in a regular manner in crystals. In crystals the atomic array is *periodic*, that is, a representative unit or motif is repeated at regular intervals along any and all directions in the crystal. In non-crystals the same atomic groups are arrayed more randomly. This is true for all non-crystalline materials, whether in the form of gases, liquids or solids. Before proceeding with any further discussion it is first necessary to consider the different periodic arrays that can exist in three dimensions. The study of these different possibilities and the laws that govern them is called pattern theory or *geometrical crystallography*. It should be noted that periodicity is not an exclusive property of crystals but occurs quite commonly in nature.

§ 2. Single and Polycrystalline Crystals : In single crystals the periodicity extends, throughout the material.

In polycrystalline crystals the periodicity does not extend throughout the crystal but is interrupted at grain boundaries. Grains or crystallites are smaller than the size of the pattern unit which forms the periodicity. The size of the grains in which the structure is periodic may vary from macroscopic dimensions to several Angstroms.

When the size of the grains becomes comparable with the size of the pattern unit, the periodicity of structure is completely disturbed, it is no longer a crystal, single or polycrystalline, but becomes an amorphous substance.

§ 3. Symmetry Considerations : External symmetry of crystals reveal that most of them possess geometrical symmetry.

A fundamental group of atoms or molecules known as motif can be periodically repeated in a number of permissible ways without considering its intimate details. For convenience the figure of seven will be used in the illustrations to symbolize a fundamental group of atoms or molecules in a crystal. There are four principal means for repeating such a motif in space.

1. *Translation* by an amount t as shown in fig. 1.

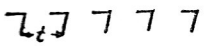

Fig. 1

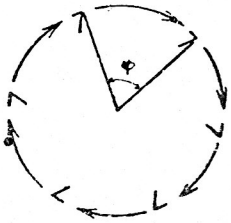

Fig. 2

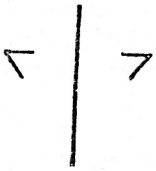

Fig. 3

Fig. 4

2. *Rotation* through an angle ϕ, as shown in fig. 2.

3. *Reflection* across a line (in two dimensions) or plane (in three dimensions) as shown in fig. 3.

4. *Inversion* through a point as shown in fig. 4.

Note that repetition by a translation or rotation leaves the motif unchanged whereas reflection or inversion changes the character of motif from right-handed to left handed one. Note also that a translation repeats the motif an infinite number of times along a given direction while the other operations repeat the motif a finite number of times.

§ 4. Periodicity in Crystals : Ideal crystals comprise of atoms arranged in a net–like arrangement known as *lattice*.

To be clear about lattice we can see that a single translation in fig. 1 produces an infinite linear array of the repeated object.

If such a linear translation t_1 is combined with another non-collinear translation t_2 then a two dimensional array is obtained as follows : The entire linear array due to translation t_1 is repeated an infinite number of times by the second translation t_2. Another way of looking at this is to say that linear array due to t_2 is repeated by t_1 which gives an imaginary character.

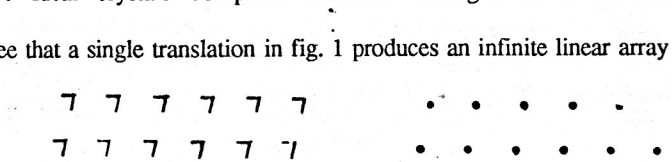

Fig. 5

Since the nature of repeated objects in fig. 5 (a) does not affect the translation periodicity, it is conventional to represent this periodicity by replacing each object in the array with a point. The resulting collection of periodic points in space is called a lattice, in this case, a two dimensional lattice or *plane lattice*. It should be remembered that a point is an imaginary, infinitesimal spot in space, and so a lattice of points is also imaginary.

It is possible to add a third translation to the plane lattice or to the lattice array of fig. 6. In each case the third translation repeats the entire plane at equal intervals t_3. This third translation produces a *space latice* or three dimensional lattice array.

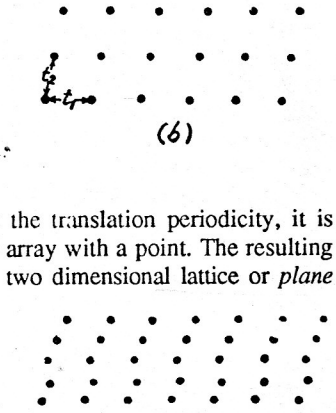

Fig. 6

A crystal structure is formed by associating with every lattice point a unit assembly known as a basis. **A basis is an assembly of atoms identical in composition, arrangement and orientation.**

All lattice points are connected by translation operator t which is defined as under :

$$t = n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \qquad \ldots(4.1)$$

where $\vec{a}$, $\vec{b}$, $\vec{c}$ are fundamental translation vectors and integers n_1, n_2 and n_3 are known as translation group of the crystals. Fig. 7 gives the diagram of a two dimensional lattice with lattice vectors a and b.

Besides geometrical arrangement of atoms a function f (r) which describes any property of a crystal must also be periodic *i.e.*,

$$f(r) = f(r + t). \qquad \ldots(4.2)$$

This indicates that atomic arrangement will look the same in every respect when viewed from any point and from another point distant r. In general

$$r' = r + n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \qquad \ldots(4.3)$$

§ 5. Unit Cell : The lattice array of a group of atoms is just a periodic repetition of a fundamental grouping. Therefore it is not necessary to consider the entire array. This is done by selecting a region of

e crystal defined by three vectors $\vec{a}, \vec{b}, \vec{c}$ translated by any egral multiple of these vectors, reproduce a similar region the crystal. This region is called a *unit cell* and these ctors as *basis vectors*. Unit cells can be defined in any of e possible ways P Q R S : P' Q' R' S', and P" Q" R" S" fig. 7. The way in which a unit cell can be chosen in a ne lattice is illustrated in fig. 7.

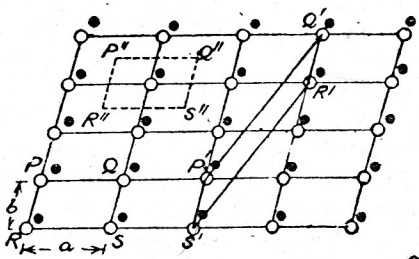

Fig. 7

array
Insight

If pairs of translations such as t_1, t_2, or t_3, t_4 are osen, they are said to define a *primitive cell*, so called cause it contains only one lattice point as can be easily en by slightly displacing the origin of the shaded cells m a lattice point, fig. 8. Thus we can now define *primitive unit cell* the smallest unit cell in volume that can be defined for a given tice and the set of linearly independent vectors that define a imitive unit cell as *primitive basis vectors*.

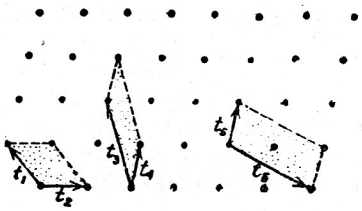

Fig. 8

If instead, translations like t_5, t_6 are chosen, the unit cell ntains more than one lattice point and it is called a *non-primitive or ultiple cell*.

The cubic unit cell for the simple cubic lattice is also a primitive it cell because it contains the irreducible minimum of one atom in ch such cell, but not for *f* c c (face-centred cubic) or b c c (body-centred cubic) structure.

In the case of a simple cubic cell there are 8 atoms at the 8 corners of the cell, each atom being shared ually among the 8 unit cells that adjoin at each corner. Therefore for the 8 corner atoms we can say that of each belongs to this particular cell making a total of one atom per unit cell.

The cubic cell for the *f* c c structure contains 8 corner atoms shared among 8 cells and 6 face centre oms each shared between two cells giving a total of $8(\frac{1}{8}) + 6(\frac{1}{2})$ or 4 atoms in the cubic cell. Therefore c c cubic cell is not a primitive cell.

The primitive cell for the *f* c c structure is a trigonal structure with $= \beta = \gamma = 60°$. Here it should be noted that this suggests that a trigonal ucture for this particular value of α possesses cubic symmetry and can reduced to *f* c c lattice.

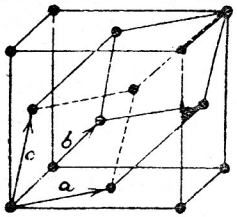

Fig. 9

Similarly it can be shown that a cubic cell for b c c structure is not a imitive cell. Since there are 8 corner atoms each shared between 8 cells d a central atom which belongs exclusively to each cubic b c c cell ving a total of $8(\frac{1}{8}) + 1 = 2$ atoms per cubic cell.

A primitive cell contains only one atom is true only in simple uctures which contain atoms of one kind only otherwise it will contain e number of atoms associated with each basis. No basis contains fewer oms than a primitive basis contains.

The volume V of a primitive cell is given by

$$V = | a \times b.c |.$$

There is another method of choosing a cell of equal volume V.

(i) First draw lines to connect a given lattice point to all nearby tice points.

(ii) At the mid-point and normal to these lines draw planes. The allest volume enclosed in this way is the new primitive cell.

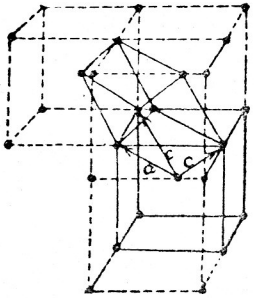

Fig. 10
b c c primitive cell.

The cell formed in this way is called *Wigner-Seitz primitive cell.*

The three directions selected for unit cell in general are non-coplanar, they are termed as crystallographic axes a, b, c and the angles between them α, β, γ as in fig. 12. Use can be made of these axes to define any other translation direction in the lattice by forming an appropriate vector sum.

For example, the translations t_1 and t_2 shown in fig. 13 can be expressed as

$$\left.\begin{aligned} t_1 &= 2a + 1b \\ t_2 &= 1a + 4b \end{aligned}\right\} \quad \ldots (5.1)$$

A translation direction in space can be represented by vector sum

$$t = ua + vb + wc. \quad \ldots (5.2)$$

Actually it is not necessary to write the entire expression in (5.2) once a, b and c have been selected, since the only thing that changes for different directions is the set of co-efficient u, v and w. It is convenient, therefore, to use the shorthand notation [u v w] to designate a translation direction in the lattice. Negative projections on any co-ordinate axis have negative indices and are indicated by a bar over the appropriate index number.

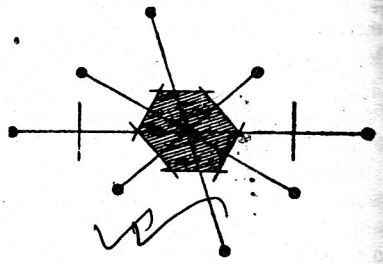

Fig. 11

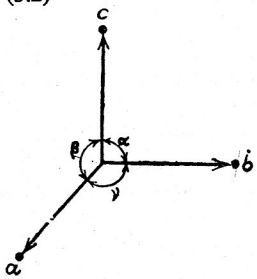

Fig. 12

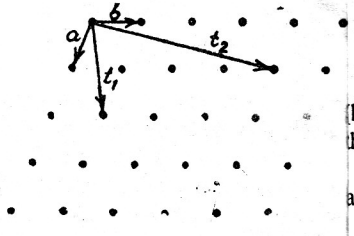

Fig. 13

§ 6. Number of atoms or lattice points per unit cell : Knowledge of the volume, density and molecular weight of the constituent atoms of the cell also leads us so have number of atoms or lattice points per unit cell.

Let us consider a unit cell with volume V (in cm^3), which can be calculated from unit cell dimensions. Let ρ (gm/cm^3) be the density of the crystal. Then the weight of the matter in the unit cell will be $V \times \rho$.

If n be the number of atoms or molecules per unit cell and M be the atomic (molecular) wt. of one atom or molecule. The weight of the matter in the unit cell will be given by an expression –

$$n \times M \times 1{\cdot}66 \times 10^{-24} \text{ gms.}$$

where $1{\cdot}66 \times 10^{-24}$ is the weight of a hydrogen atom in gms. used in converting molecular weight in gms.

Thus we have

$$n \times M \times 1{\cdot}66 \times 10^{-24} = V \times \rho$$

or

$$n = \frac{V \times \rho}{M \times 1{\cdot}66 \times 10^{-24}}$$

$$= \frac{V \times \rho}{M} \times 6{\cdot}023 \times 10^{23}$$

$$= \frac{V \times \rho \times N}{M}$$

where N is the Avagadro number equal to $6{\cdot}02 \times 10^{23}$.

The volume of unit cell for different lattices is as given here :

Cubic : $V = a^3$; Hexagonal : $V = abc \sin 60$; Ortho–rhombic : $V = abc$;

Rhombohedral : $V = \frac{1}{2} a^3 \sin(\alpha/2) \cos(\alpha/2)$; Tetragonal : $V = a^2c$; Monoclinic : $V = abc \sin \beta$.

§ 7. Representation of Planes : Miller Indices : It is frequently necessary to consider planes passing through a space lattice since it is the planes which are determined by X-ray diffraction. In order to make the designation uniform for a chosen plane, the following procedure has been adopted :

1. Determine the intercepts of the plane along a, b, c in terms of lattice constants. The axis may be primitive or non-primitive.
2. Invert the intercepts ; that is, write the numbers as their reciprocals.
3. If fractions result, multiply them by lowest common denominator.

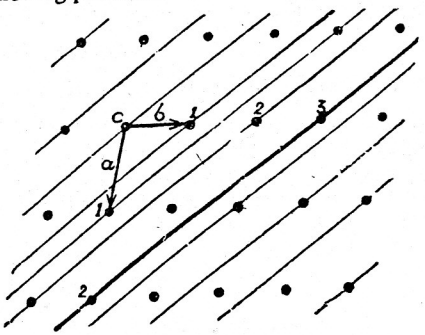

Fig. 14

For example, consider the planes drawn in fig. 14, which shows a view of a space lattice along c and a set of planes that are parallel to c so that they are also seen in edge view. Consider the plane shown by the heavy line in fig. 14, we have to tabulate as given below :

	Indexing procedure	a	b	c
1.	Determine intercepts	2	3	∞
2.	Note their reciprocals	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{\infty}=0$
3.	Clear the fractions	3	2	0

...(6.1)

The resulting integers are called *Miller indices* of a plane and are conventionally closed in parentheses [h k l]. The meaning of these indices is that a set of a parallel planes [h k l] cuts the a - axis into h parts, the b-axis into k parts and the c-axis into l parts.

Examples : The +a axis has indices [100], the –a axis [$\bar{1}$00]. The + b axis has indices [010]; the –b axis [0$\bar{1}$0]. The diagonal of a-b face has indices [110]; that of a.c face [101].

Several features should be noted about this scheme in the cubic system :

(1) Parallel planes equally spaced all have the same index numbers (h k l), analogous to the index notations for directions, where all parallel rows of atoms have the same indices [u v w].

(2) A plane parallel to one co-ordinate axis has index number 0 for that direction.

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

Examples : The cube face normal to a-axis is described by (100). Plane of this type is sketched in fig. 15 (a). Planes normal to b-axis are designated (010) and are sketched in fig. 15 (b). Planes having equal intercepts on the three axes are (111) planes, fig. 15 (c). Index numbers (110) specify planes with equal intercepts on a and b axes and parallel to c-axis, fig. 15 (d). Some planes may have one or two negative intercepts. An example is the parallel family of (100) planes, fig. 15 (e). Finally a few of the planes (112) are sketched in fig. 15 (*f*).

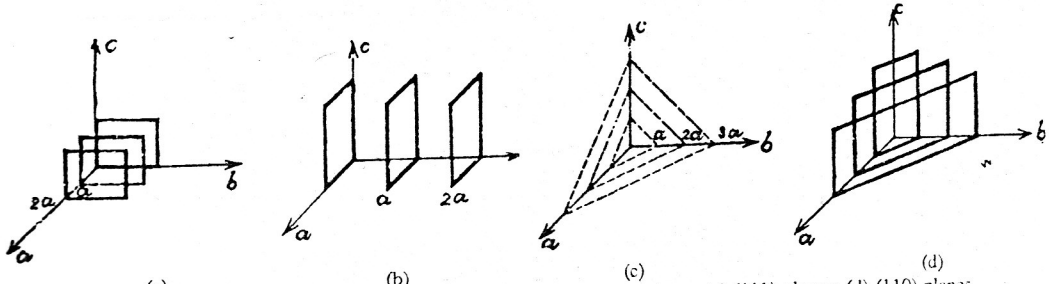

Fig. 15. Examples of important cubic crystal planes, (a) (100) planes (b) (010) planes; (c) (111) planes; (d) (110) planes

The Miller index notation is especially useful for cubic systems. Among its desirable features are these :

(1) The angle θ between two crystallographic directions $[u_1\ v_1\ w_1]$ and $[u_2\ v_2\ w_2]$ can be calculated easily. It is given by the expression

$$\cos\theta = \frac{u_1u_2 + v_1v_2 + w_1w_2}{\left(u_1^2 + v_1^2 + w_1^2\right)^{1/2} \cdot \left(u_2^2 + v_2^2 + w_2^2\right)^{1/2}} \qquad \ldots(6.2)$$

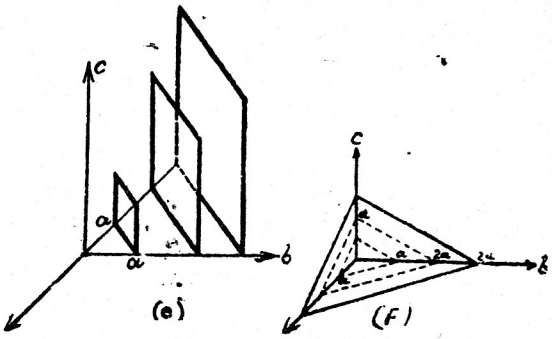

Fig. 15. Examples of important cubic crystal planes, (e) $(\bar{1}10)$ planes; (f) (112) planes.

(2) The normal to the plane with index numbers (h k l) is the direction [h k l]. This correspondence is of an enormous aid in calculating the angle between planes.

(3) The distance d between adjacent planes of index numbers (hkl) is given in terms of the cube edge a by the expression

$$d = \frac{a}{\left(h^2 + k^2 + l^2\right)^{1/2}} \qquad \ldots(6.3)$$

which can be deduced as shown in next article.

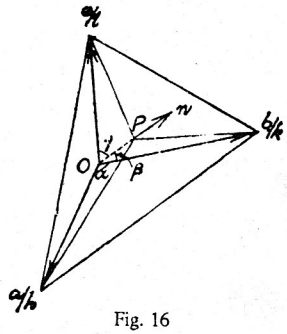

Fig. 16

§ 8. Spacing of Planes in Crystal Lattice. Any lattice point is taken as origin. Axes are taken in the abc directions. The spacing or distance between adjacent planes are found by finding perpendicular distance between this origin and the plane whose intercepts are

$$\frac{a}{h}, \frac{b}{k}, \frac{c}{l}.$$

Referring to fig. 16, we have

$$d = OP = \frac{a}{h}\cos\alpha = \frac{b}{k}\cos\beta = \frac{c}{l}\cos\gamma \qquad \ldots(7.1)$$

where α, β and γ are the angles between the normal to the plane and the a-, b-, c-axis respectively. If $\vec{n}$ is the unit vector normal to the plane, then $\vec{n} = a\cos\alpha$ etc. and $d = \frac{\vec{n}.\vec{a}}{h} = \frac{\vec{n}.\vec{b}}{k} = \frac{\vec{n}.\vec{c}}{l}$

In an orthogonal lattice taking the X co-ordinate axis along a, the Y-axis along b and Z-axis along c, the equation of (h k l) plane whose intercepts are $\frac{a}{h}, \frac{b}{k}, \frac{c}{l}$ is

$$f(x, y, z) = \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} = 1. \qquad \ldots(7.3)$$

If (x, y, z) = constant, is the equation of a surface, then ∇f is a vector normal to that surface and the unit normal n is given by

$$n = \frac{\nabla f}{|\nabla f|} = \frac{\left(\frac{h}{a}\right)i_x + \left(\frac{k}{b}\right)i_y + \left(\frac{l}{c}\right)i_z}{\sqrt{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)}} \qquad \ldots(.4)$$

and the spacing d between (h k l) planes is

$$d = \frac{n.a}{h} = \frac{1}{\sqrt{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)}} \qquad \ldots(7.5)$$

In non-orthogonal lattices the problem of finding the spacing between adjacent planes in terms of lattice spacing and angles is more complex although general expressions (7.1) and (7.2) are correct in both orthogonal and non-orthogonal systems.

Distances between parallel planes decrease as the indices increase ; thus high index reflections require X-rays of shorter wavelength.

§ 8.1. Density of Lattice Points : If the density of lattice points in a Miller plane is δ and the spacing between the planes is d given by equation (7·5), then the relation between d and δ can be represented by an expression

$$\frac{d}{\delta} = \text{constant}$$

Let (h k l) and (h'k'l') be two Miller planes, d and d' be interplanar spacings respectively. If δ and δ' are the densities of lattice points in these Miller planes, then we have

$$\frac{d}{\delta} = \frac{d'}{\delta'} = \text{constant}$$

or

$$\frac{d}{d'} = \frac{\delta}{\delta'}$$

This can be proved as hereunder.

Let unit volume be obtained in one case from m planes each of area A and in the other case from m' planes, each of area A'. Because of equality of volumes, we have –

$$mA.d = m'A'd' \qquad \ldots (i)$$

Because of equality of the number of lattice points, we have

$$mA\delta = m'A'\delta' \qquad \ldots (ii)$$

From expressions (i) and (ii), we have

$$\frac{d}{d'} = \frac{\delta}{\delta'}$$

§ 9. Symmetry Elements : As we have already discussed, it is possible to repeat an object by a rotation, a reflection or an inversion. Combinations of two such operations into a single symmetry operation are also possible. We discuss here the symmetry elements associated with three dimensional crystal point groups :

Rotation Axes. One-, two-, three-, four-, and six- fold rotation axes are permissible corresponding to rotations by 360°, 180°, 120°, 90° and 60° (see Appendix A). The rotation axes are denoted by the symbols 1, 2, 3, 4 and 6. The axes 2, 3, 4 and 6 are often referred to as diad, triad, tetrad and hexad axes respectively as shown in fig. 17.

If the operation of rotation results in a congruent set, it is called a *proper rotation* and the rotation axis is called a *proper rotation axis*. It is also possible to have a rotational operation relating Enantiomorphous objects, that is, a right-handed motif becomes left-handed upon repetition and vice-versa. Such an

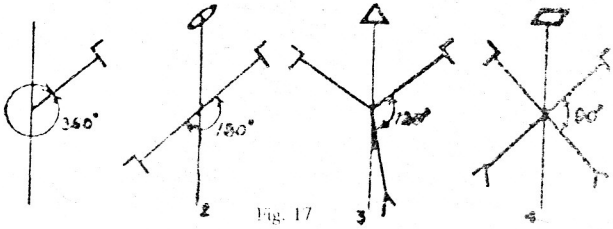

Fig. 17

operation is called an *improper rotation* and the corresponding symmetry element is called an *improper rotation axis.*

It should however be noted that a single molecule can have any degree of rotational symmetry but an infinite periodic lattice has only limited degree of rotational symmetry.

Reflection Plane. Mirror reflection is in a plane through the lattice point. A reflection plane is denoted by m.

By mirror reflection we mean that one half of the crystal reflected in such a plane passing through a lattice point reproduces the other half.

Inversion Centre. A crystal structure possesses a centre of inversion if the structure is brought into self coincidence by operation $\mathbf{r} \rightarrow -\mathbf{r}$, where r is the vector position of any arbitrary point in the crystal referred to the lattice point. An inversion centre is denoted by $\bar{1}$.

Rotation Inversion Axis. A crystal structure has a rotation inversion axis if it is brought into self coincidence, by rotation followed by inversion. Crystals can possess one-, two-, three-, four, and six-fold rotation inversion axes.

Other possible choice of symmetry operations can be shown to be equivalent to linear combination of these.

Screw Axis. The operation where a rotation, say from e to f, by an amount ϕ combined with a translation from f to g by an amount T is equivalent to a screw motion from e to g. The symmetry element that corresponds to such a motion is called *screw axis.* In a lattice an axis must be parallel to zero translation direction. Therefore after n rotations through an angle ϕ and n translations T are concluded, that is, after n translations along the screw axis the cumulative translation distance in the direction of the axis must equal some multiple of the lattice translation mt. In other words

$$nT = mt, \text{ where n and m are integers}$$

$$\therefore \quad T = \frac{mt}{n}$$

§ 10. Symmetry Groups. Whenever we talk of a group we mean a set of elements which obey a certain set of rules. The symmetry elements that can exist in a crystal such as rotations, reflections and inversion operations also form symmetry groups. They do not occur as isolated individuals. Particular of them are point groups and space groups.

§ 11. Point Groups : A point group in lattice is defined as the **collection of 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.

Consider first the way in which the various symmetry elements can combine at a point. Suppose two two-fold axes intersect at 90° to each other. The way that each repeats seven is shown in fig. 18 (a). Note that the sevens in the resulting array are related to each other in pairs by still a third two-fold axis at right angles to the first two. Thus it can be seen that a combination of two two-fold axes at 90° produces a third two-fold axis mutually oriented as shown in fig. 18 (b).

Thus it is clear that the symmetry elements can combine and form group.

The symmetry operations can be represented graphically by symbols.

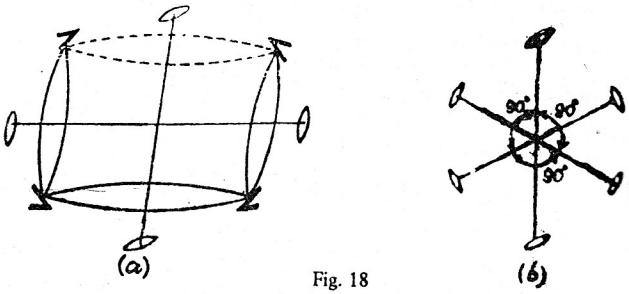

Fig. 18

The dots indicate equivalent points where the symmetry element of the points themselves is ignored as they may be single atoms or molecules.

The point group 1 has no symmetry, so here a point has no other point equivalent to it.

For 1m, there is a mirror plane, one dot on reflection across the mirror plane becomes a second dot.

With a two fold axis and one mirror plane there is automatically a second mirror plane normal to the first and we have 2mm with four equivalent points.

Similarly we can talk of the other rotations and reflections.

The various combinations of allowed rotation and reflection operations give rise to thirty two (32) allowed point groups. The restriction is brought about by translation symmetry, e.g., all point groups containing a five fold axis or any axis greater than six fold are excluded. Seven of the groups define the seven crystal systems discussed later.

Different point groups of a system give rise to crystals of different geometrical shapes, for example, the three point groups of orthorhombic system give rise to three geometrical shapes shown in fig. 20.

(a) Di-diagonal polar— In it there are two reflection planes at right angles and a two-fold axis.

(b) Diagonal holoaxial— In it there are two two - fold axes at right angles. The existence of two such axes demands the existence of a third.

(c) Di - diagonal— In it there are two two-fold axes, three reflection planes and a centre of symmetry.

Thus it would be clear that besides seven crystal systems with its lowest symmetry requirements twenty five point groups arise by associating arrangements of atoms with each lattice point and thus adding symmetry requirements each system is capable of.

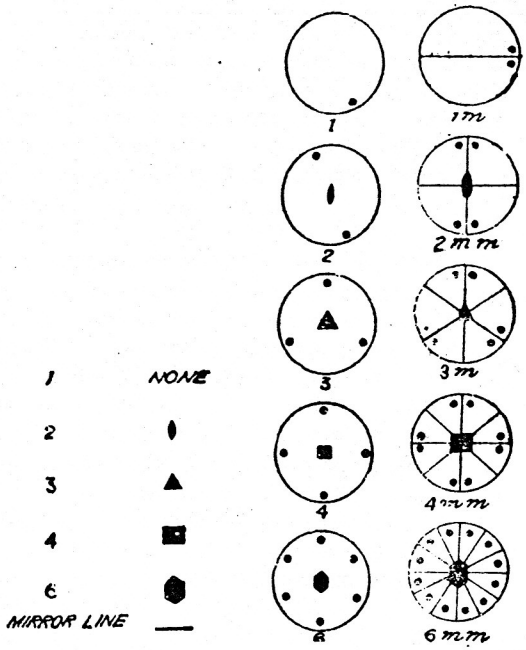

Fig. 19. The rotation is denoted by numbers and the mirror reflection by the symbol m.

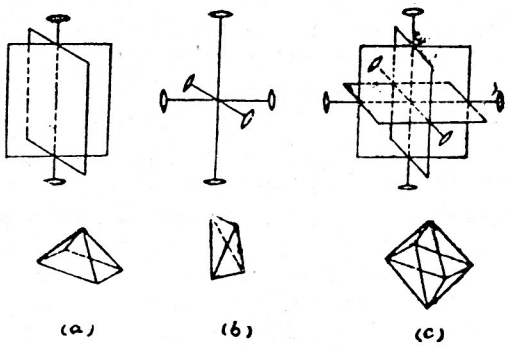

Fig. 20

If a basis of atoms is assigned to a lattice point, the lattice point group will be reduced if the atomic arrangement has a lower symmetry than the Bravais lattice itself (see next section). If the basis consists of only a single atom at the lattice point the resulting crystal structure will have the highest point group symmetry capable with the lattice system. The class having the highest possible symmetry for a system is called *holohedral* class of that system, for example, fig. 20 (c) is the holohedral class of orthorhombic system.

Classes having less than full symmetry are called *hemihedral* or *tetartohedral* (having half or a quarter of the complete set of faces). It is usual to refer to any class having less than the full symmetry of its system as hemihedral.

§ 12. Space Group. From the above it is clear that in a crystal each point has an associated point group. Therefore there is an arrangement of point groups in space. In addition to point group symmetry elements, such as rotations and reflections, there is now the possibility of *screw axis or glide plane* operations which are composed of non - primitive translations together with a rotation or reflection respectively. **The set of symmetry operations emerging from the arrangement of point groups form a group of its own known as space group.**

The nature of *glide plane* may be understood from fig. 21.

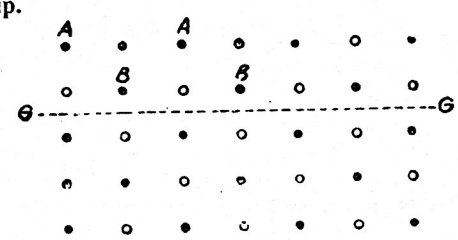

Fig. 21

The black circles B lie at the mid-points of the rectangle formed by the black circles A. All the circles A and B are similar. Let GG' be the trace of a plane perpendicular to the plane of the paper and half way between the lines of circles A and B. By reflection across this plane the black circles are brought to the positions shown by the white circles in the diagram and if they are given a translation parallel to the plane of reflection of one half the spacing AA, they coincide again with the original A and B circles. The whole figure is in effect brought into coincidence by a reflection across GG' and a translation of half the lattice spacing parallel to the plane of reflection. If now we imagine the figure extended to three dimensions so that a set of points similar to A lie at equal intervals exactly below them, the B points being supposed to lie in planes half way between the A planes, the figure can again be brought into self-coincidence by reflection across GG' and a glide parallel to the plane of half the A spacing in the plane of the paper plus the A spacing in a direction perpendicular to the plane of paper. This example illustrates the two types of glide planes.

An n - fold screw axis produces a rotation by $2\pi/n$ about the axis and a translation parallel to the axis whose amount depends on n. If we now take GG' as an axis instead of as a trace of a plane we see that a rotation of 180° about GG' together with a translation of 1/2 AA parallel to the axis brings the figure into self - coincidence. The translation for a two-fold screw axis is always half the spacing of the lattice in the direction of the axis, for a 3-fold axis it is $\frac{1}{3}$ and in the simplest cases of the 4-fold and 6-fold axes $\frac{1}{4}$ and $\frac{1}{6}$ of the spacing respectively. In all these cases except that of the two - fold axes the equivalent points are arranged spirally about the axis and we have to distinguish between right-handed and left-handed rotations.

The addition of these new kinds of symmetry elements and the fact that in a space group the planes and axes do not all pass through one point greatly increases the number of combinations of symmetry elements which are possible and the number of groups increases from 32 for the external form to 230 when the inner structure is taken into account.

As an example for the class of orthorhombic system having three 2-fold axes we shall find that instead of the one possibility of the point group there are nine ways of combining three such axes including, of course, the screw axis. They all correspond to one crystal class or in other words to one type of external symmetry. If we add a centre of symmetry to the axis so as to produce the holohedral class of the system we find that there are twenty eight (28) possible combinations of axes and symmetry centres of 28 holohedral orthorhombic space groups corresponding to only three point groups or class of external symmetry.

§ 13. Characteristics of Space Group : The symmetry of a crystal structure is specified completely when the space group is known.

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

3. The space group through its symmetry elements determines the positions of equivalent points within the unit cell.

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

(ii) Square lattice :

$|a| = |b|, \gamma = 90°$

The point operation 4 obviously requires a square lattice, fig. 24.

(iii) Hexagonal lattice :

$|a| = |b|, \gamma = 120°$

This is invariant under a rotation $2\pi/6$ about an axis through a lattice point and normal to the plane, fig. 25.

(iv) For mirror reflection m, if primitive translation vectors $\vec{a}, \vec{b}$ are written in terms of the unit vectors $\vec{i}, \vec{j}$ along the x, y-axes.

$$\vec{a} = a_x\vec{i} + a_y\vec{j}$$
$$\vec{b} = b_x\vec{i} + b_y\vec{j} \qquad \ldots(15.1)$$

If the primitive vectors are mirrored in the x-axis we have after reflection operation.

$$\vec{a'} = a_x\vec{i} - a_y\vec{j}$$
$$\vec{b'} = b_x\vec{i} - b_y\vec{j} \qquad \ldots(15.2)$$

Since $\vec{a'}, \vec{b'}$ are lattice vectors, one possible choice of a, b to achieve this is

$$\vec{a} = a\vec{i}$$
$$\vec{b} = b\vec{j} \qquad \ldots(15.3)$$

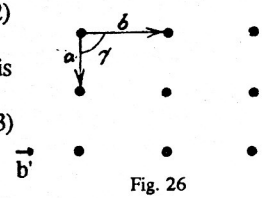

Fig. 26

the resulting lattice is rectangular.

$|a| \neq |b|, \gamma = 90°.$

(v) There is another possibility also. As $\vec{b'}$ is a lattice vector then

$$\vec{b'} = \vec{a} - \vec{b}. \qquad \ldots(15.4)$$

Using (15.1) and (15.2)

$$b_x' = a_x - b_x = b_x$$
$$b_y' = a_y - b_y = -b_y \qquad \ldots(15.5)$$

We have a solution if $a_y = 0$, $a_x = 2b_x$, thus another possible choice of primitive translation vector is

$$\vec{a} = a\vec{i}$$
$$\vec{b} = \frac{1}{2}a\vec{i} + b_y\vec{j} \qquad \ldots(15.6)$$

This gives centred-rectangular lattice. Both the primitive cell and the rectangular unit cell for centred-rectangular lattice are shown in fig. 27.

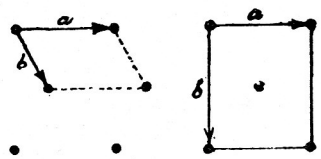

Fig. 27

Summary :

Lattice	Conventional unit cell	Correspond-ing axis	System	Point group symmetry about lattice points
1. Oblique	Parallelogram	$a \neq b, \gamma \neq 90°$	oblique	1, 2
2. Square	Square	$a = b, \gamma = 90°$	Square	4, 4*mm*
3. Hexagonal 60°	Rhombus	$a = b, \gamma = 120°$	Hexagonal	3, 3*m*, 6*mm*
4. Primitive Rectangular	Rectangle	$a \neq b, \gamma = 90°$	Rectangle	1*m*, 2*mm*
5. Centred Rectangular				

§ 14. Determination of the Space Group : Space group is determined from characteristic absent spectra.

As an example let us consider a structure based on a simple orthorhombic space lattice with each point of which is associated a crystal unit. The existence of a lattice of this sort is shown by the fact that spectra of all general types occur. Suppose now that perpendicular to 100 face of the lattice a 2-fold screw axis is added. The existence of such an axis necessitates the existence of other units of structure derived from those already present by a rotation of 180° about the axis and a translation parallel to it of half the 'a' spacing. A set of planes is thus formed half-way between the (100) planes of the lattice, fig. 22. The spacing 'a' is halved and the spectra 100, 300,..... corresponding to the space lattice vanish. In general a 2-fold screw axis must halve the spacing of the lattice in a direction parallel to itself. In a similar way glide planes of symmetry produce characteristic halvings. A glide plane parallel to (100) with a glide of b/2 must halve the b or (010) spacing. If the glide is b/2 + c/2 both the b and c or (010) and (001) spacings are halved. Glide plane and screw axis are always parallel to special directions in the lattice with the result that spectra with some indices are zero which are affected by them and it is this fact which makes it important to consider the general spectra in determining the space lattice.

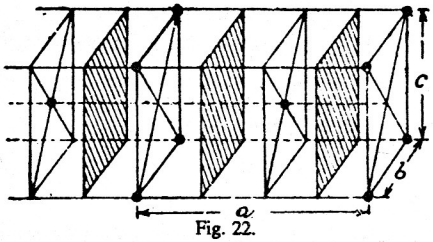

Fig. 22.

A good collection is found in International Crystal Tables of Niggli, Arttriry and Yardley.

§ 15. Classification of Crystals : Crystals occurring in nature reflect the symmetry of their internal atomic arrangements in the symmetry relating their terminal faces. Though, of course there are deviations from ideal crystals both at the surface where the periodicity condition obviously breaks down and also due to dislocations, impurities and other imperfections in the interior, yet still the symmetry can be used to classify crystals.

There are various ways of positioning structureless points in space such that all points have identical surroundings. These are known as *Bravais lattices.* Thus there are five Bravais lattices in two dimensions and fourteen Bravais lattices in three dimensions.

§ 16. Bravais Lattice in Two Dimensions : The various combinations of allowed rotation and reflection operations are found to give rise to 10 different two dimensional point groups permissible in a crystal indicated below :

1, 2 1m, 2mm, 4mm, 3, 3m, 6mm.

The first refers to the rotation about the point and the point group 4 contains 4-fold rotations. The second position refers to a mirror line normal to the x-axis and it refers also to other mirror lines related to this by a rotation operation. The third refers to the presence of other mirror lines related among themselves by symmetry but not covered up in the first set of mirror lines.

The requirement that a lattice should be invariant under a rotation operation $2\pi/n$ where n = 1, 2, 3, 4 or 6 or under the mirror operation places restriction on the primitive translation vector a, b.

(i) Oblique lattice :

$|a| \neq |b|$; $\gamma \neq 90°$

The general oblique lattice is invariant under the point operations 1 and 2 without further restriction, fig. 23.

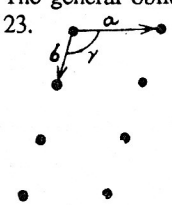

Fig. 23

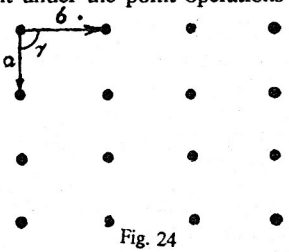

Fig. 24

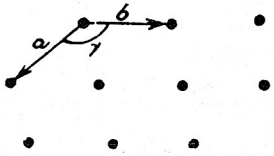

Fig. 25

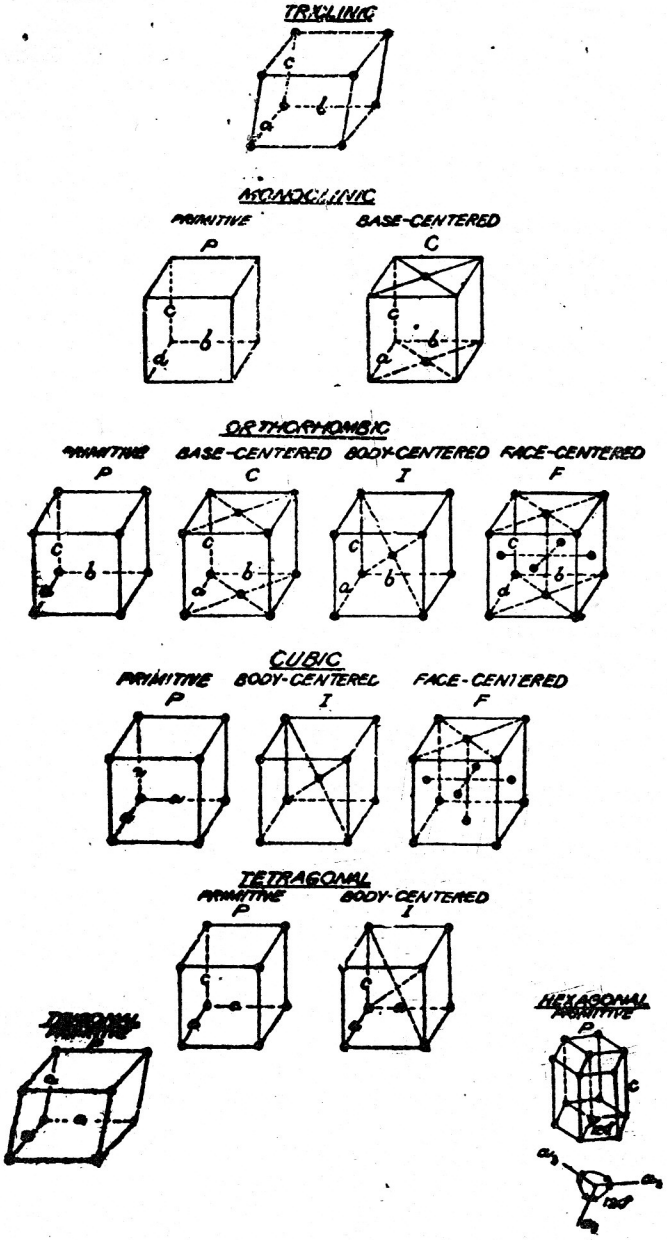
TRICLINIC
MONOCLINIC
PRIMITIVE
P
BASE-CENTERED
C
ORTHORHOMBIC
PRIMITIVE
P
BASE-CENTERED
C
BODY-CENTERED
I
FACE-CENTERED
F
CUBIC
PRIMITIVE
P
BODY-CENTERED
I
FACE-CENTERED
F
TETRAGONAL
PRIMITIVE
P
BODY-CENTERED
I
HEXAGONAL
PRIMITIVE
P

Fig. 28

The Seven Crystal Systems

System	*Characteristic Symmetry elements*	*Bravais Lattices*	*Unit ceil Characteristics*	*Number of Lattice in system*
TRICLINIC	None	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	1
MONOCLINIC	One 2-fold rotation axis $2/m$	P C	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$	2
ORTHORHOMBIC	Three mutually perpendicular 2-fold rotation axes $m\ m\ m$	P C I F	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	4
TETRAGONAL	One 4-fold rotation axis or a 4-fold rotation-inversion axis $4/mm$	P C	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	2
CUBIC	Four 3-fold rotation axes (cube diagonals) $m\ 3m$	P I F	$a = b = c$ $\alpha = \beta = \gamma = 90°$	3
HEXAGONAL	One 6-fold rotation axis $6/m\ m\ m$	P	$a = b \neq c$ $\alpha = 120°$ $\beta = \gamma = 90°$	1
TRIGONAL (Rhombohedral)	One 3-fold rotation axis $\bar{3}\ m$	P	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	1

Lattice Symbols

P— Primitive— It has atoms only at the corners of the parallelopipedon.

C— Base-centred— It has extra atoms at the centres of the base.

I—Body- centred— From German Innenzentriete.

F—Face-centred.

§ 17. Bravais Lattice in Three Dimensions : There are fourteen ways of arranging points in space lattices such that all the lattice points have exactly the same surroundings. Therefore there are 14 Bravais lattices in three dimensions. Each of these 14 Bravais lattices belongs to one of the seven crystal systems which are characterised by the groups of symmetry elements associated with the lattice points. For example, there are three Bravais lattices belonging to the cubic system, each of which has the same collection of symmetry elements at the lattice points.

One may think that there should be other possible Bravais lattices. For example, no face-centred tetragonal arrangement is included in the fourteen Bravais lattices. The reason for this is that such a face centred tetragonal structure is equivalent to a body-centred tetragonal lattice in which the side of the base of the unit cell is $1/\sqrt{2}$ times what it is for the face-centred arrangement. On the same lines it can be argued that other Bravais lattices are not possible.

§ 18. Different Crystal Structures : We discuss briefly the crystal structures of many materials which are relatively simple. Examples of several types of structures are described briefly in the following paragraphs. To a close approximation we may record each atom as a sphere of definite radius and crystals are considered to be formed on the principle that such spheres are packed in the most stable and economical manner.

§ 18.1. Hexagonal Close-packed Structure : The hexagonal close-packed structure, one of the common crystal types is made by stacking close packed planes in a simple sequence. There are two ways of arranging equivalent spheres to minimise the interstitial volume. One way leads to a structure with cubic symmetry and it is the face centred cubic and the other hexagonal symmetry and is called the hexagonal close-packed structure, fig. 29.

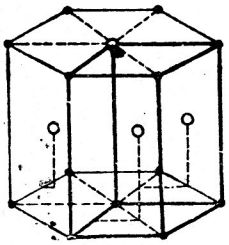

Fig. 29

Spheres may be arranged in a single closest-packed layer by placing each sphere in contact with six others. A second similar layer may be placed on top of this by placing each sphere in contact with three spheres of the bottom layer. A third layer can be added in two ways, in the cubic structure the spheres in the third layer are placed over the holes in the first layer not occupied by second layer ; in the hexagonal structure the spheres in the third layer are placed directly over the spheres of first layer and the packing may be said ABABAB... The two possibilities are shown is fig. 30.

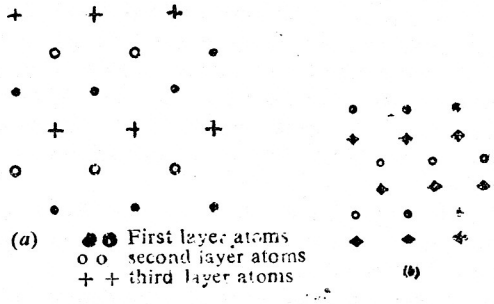

Fig. 30. It shows modes of superposition of close packed layers of spheres in (a) cubic closepacking and (b) hexagonal close packing.

The c/a ratio for hexagonal closest packing of spheres is 1.633 and the fraction of total volume filled is 0.74 as proved below :—

ABCD is the base of hexagonal unit cell AD = AB = a. The sphere in the next layer has its centre F vertically above E and it touches the three spheres whose centres are A, B and D.

AE is $\frac{2}{3}$ of median AG.

$$\therefore \quad AE = \frac{2}{3} \times \frac{\sqrt{3}}{2} a = \frac{a}{\sqrt{3}}$$

$$\text{Hence} \quad FE = \frac{c}{2} = \sqrt{\left(a^2 - \frac{a^2}{3}\right)} = \frac{a\sqrt{2}}{\sqrt{3}}$$

$$\therefore \quad \frac{c}{2} = \frac{2\sqrt{2}}{\sqrt{3}} = 1.633$$

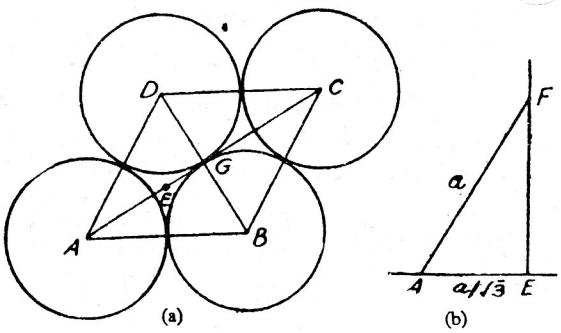

Fig. 31.

Packing Fraction *i.e.* Fraction of total volume filled

$$= \frac{\text{Volume occupied by atoms}}{\text{Volume of the unit cell}}$$

$$= \frac{2 . \frac{4}{3}\pi R^3}{\frac{1}{2} \sqrt{3} a^2 c}$$

Since in ideal case of closest packing a = 2R,

$\therefore$ Packing Fraction = 0.74.

By convention we refer to crystals as hcp even if actual c/a ratio departs somewhat from theoretical value for example for zinc c/a = 1.85 and for magnesium c/a = 1.62.

Hexagonal closed-packed structure is of Be, Mg, Zn, Cd, Ru and O.

18.2. The Face-centred Cubic or Cubic Close-packed Structure : The above close packing of cubic symmetry leads to face-centred cube. Here also the fraction of the total volume filled is 0.74. In this case the first two planes go in the AB sequence ; the third, however is displaced relative to both A and B into positions C. A fourth plane has the A position and the repetition cycle ABCABC..... is established. A unit cell of this crystal structure is shown in fig. 32 (a).

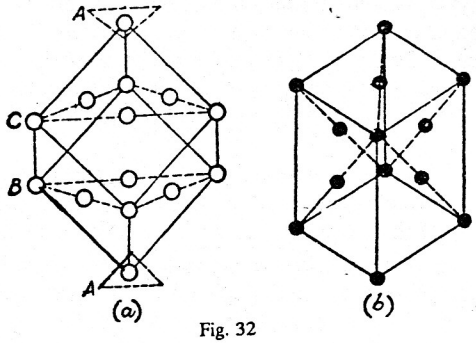

Fig. 32

This cell is not the smallest possible cell, but it does have one convenient feature ; the cell is a cube. An atom occupies each corner of the cube and the centre of each face ; hence the name face-centred cube (*fcc*). This structure is symmetrical with respect to rotation by 90° about any one of the cube edges. The more conventional way to draw this cube is pictured in fig. 32 (b). The face-centred cubic structure is also close-packed, each atom having 12 nearest neighbours.

12 is the maximum value of the coordination number in a structure of identical atoms. In other words no structure with coordination number greater than 12 is possible. Packing fraction in this case is also 0.74 as proved below.

The atoms are in contact along the diagonal of the faces. Let R be the radius of sphere, then diagonal of the face

$$= 2R + R + R = 4R.$$

Number of spheres in one unit cell $= \frac{6}{2} + 8 \times \frac{1}{8} = 4$

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

or $$(4R)^2 = a^2 + a^2 = 2a^2$$

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

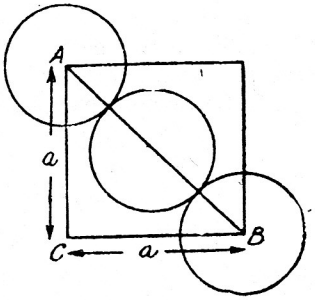

Fig. 33

Hence volume of the cube $= \left(\frac{4}{\sqrt{2}} R\right)^3$

$$\text{Packing fraction} = \frac{\text{Complete volume of spheres}}{\text{Volume of cube}}$$

$$= \frac{4\left(\frac{4}{3}\pi R^3\right)}{\left(\frac{4}{\sqrt{2}} R\right)^3} = \frac{\pi}{3\sqrt{2}} = \frac{\pi\sqrt{2}}{6}$$

$$= 0.74.$$

Since fraction of the total volume filled is the same in h.c.p. and f.c.c. structures hence these are the closest packed structures.

The atoms are in contact along the diagonal of the faces. Elements having face-centred cubic structure are Cu, Ag, Au, Ca, Al, Pb and Pt.

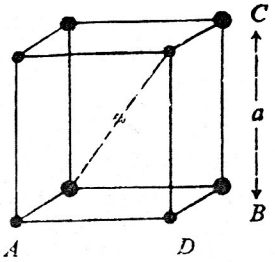

Fig. 34. Position of atom centres on b c c lattice.

18.3. Body Centred Cubic Structure : All metallic elements do not crystallize in close -packed structure. Li, Na, K, Cr,

Mo, W and ordinary modifications of Fe as well as a number of others have a body-centred cubic structure. The body-centred cubic is sketched in fig. 34. This unit cell is cubic with an atom at each corner and an atom in the centre of the cube. This structure is not close-packed since each atom has only eight neighbours. Note that atoms are in contact along body diagonals.

Here 8 spheres are attached at each corner of the cube and one atom at the centre of the body.

Number of spheres in one unit cell $= 8 \times \frac{1}{8} + 1 = 2$

Say BC = a

Now from triangle ABD

$$AB^2 = a^2 + a^2 \text{ or } AB = \sqrt{2}a$$

If R is the radius of sphere, AC = 2R + R + R = 4R for closer packing

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

or $$(4R)^2 = a^2 + (\sqrt{2}\,.\,a)^2$$

or $$16R^2 = a^2 + 2a^2 = 3a^2$$

or $$a = \frac{4R}{\sqrt{3}}$$

$$\therefore \text{ Volume of the cube} = \left(\frac{4R}{\sqrt{3}}\right)^3$$

$$\text{Packing fraction} = \frac{\text{Volume of spheres}}{\text{Volume of cube}}$$

$$= \frac{2\,\frac{4}{3}\pi R^3}{3\left(\frac{4R}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}}{8}\pi$$

$$= 0.68.$$

Hence this structure is not so close packed as hcp or *f*. c. c.

18.4. Simple Cubic Structure : Another possible structure is the simple cubic arrangement of the atoms. The unit cube of this structure has atoms only at the corners of the cube, and the atoms therefore touch along cube edges, fig. 35. This structure is loosely packed ; each atom has only six neighbours.

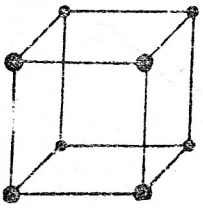

Fig. 35. Positions of atom corners on sc lattice.

Only one element Po (in a certain temperature region) exhibits this crystal structure. The simple cubic structure is introduced mainly because its simple geometry simplifies later semi-quantitative calculations and discussions.

Many other cubic unit cells bear a simple relationship to the simple cubic cell. Some can be reduced to sets of interpenetrating simple cubic sub-lattice. A body-centred cubic lattice can be considered to contain two identical simple lattices. One consists of the corner atoms, the other of the centre atoms. Face-centred cubic lattices can be considered to contain four identical simple cubic lattices properly disposed with respect to one another.

Other Cubic Structures : Many of the elements solidify in one of the structures just described, but several of the elements, for example, *As, Sb, Bi, S, Se, Te, I* and *Mn* and many compounds have other structures. Some of these structures are derivatives or combinations of one of the basic cubic structures just described, in which one lattice is interpenetrated by another. A few of these structures are described below.

The closeness of packing of the atoms in any given structure can be inferred by the number of nearest neighbours that surround each atom. This number is called the *co-ordination number*. It can range from a

maximum of twelve in close-packed structures to four in diamond and Zinc Blende where structures are relatively open.

§ 18.5 Diamond Structure. The diamond structure is a combination of two inter-penetrating face-centred cubic sublattices. The unit cell is sketched in fig. 36.

One sub-lattice has its origin at the point 0, 0, 0, the other at a point one quarter of the way along the body diagonal (at the point a/4, a/4, a/4). The diamond cubic structure is loosely packed, since each atom has only four nearest neighbours.

Number of spheres in one unit cell = 8.

Now the diagonal is 8R where R is radius of sphere. In diagonal there are three full spheres and two half spheres.

If 'a' is a side of the cube then diagonal will be $\sqrt{3}$ a.

$$\therefore \qquad 8R = \sqrt{3}\,a. \qquad i.e. \qquad a = \frac{8R}{\sqrt{3}}$$

$$\text{Volume of the cube} = \left(\frac{8R}{\sqrt{3}}\right)^3$$

$$\therefore \text{ Packing fraction} = \frac{\text{Complete Volume of spheres}}{\text{Total Volume of cube}}$$

$$= \frac{8 \times \frac{4}{3}\pi R^3}{\left(8R/\sqrt{3}\right)^3} = \frac{\sqrt{3}}{16}\pi = 0.34.$$

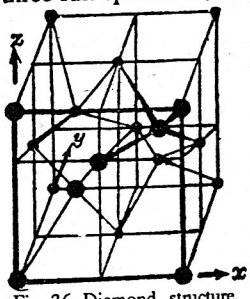

Fig. 36. Diamond structure.

Obviously diamond structure is loosely packed.

If an atom is imagined to be at the centre of the regular tetrahadron, then its neighbours are on the four corners. Ge, Si and C, (in the diamond phase) crystallise with diamond structure.

§ 18.6. Zinc Blende Structure. A new structure occurs if the two face centred cubic sublattices are occupied by different elements. The resultant structure termed the Zinc Blende is sketched in fig. 37. Important compounds which have this structure are the semiconductors InSb, GaAs, ZnS (for which it is named), CuCl and many others.

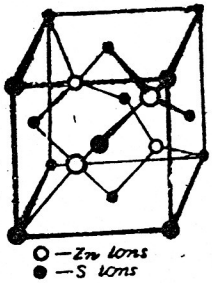

Fig. 37. Zinc Blende structure.

§ 18.7. Sodium Chloride Structure. Rock salt, NaCl is another combination structure. The compound has the unit cell as sketched in fig. 38.

In sodium chloride, sodium atom loses its outer electron and so acquires an excess of positive charge while the Cl atom has acquired the electron lost by the Na atom into its structure completing the M electron group and at the same time acquiring an excess of negative charge. Two such ions will attract one another because of the electrostatic forces between their excess charges. But they cannot approach to within less than a certain distance owing to strong forces of repulsion which must set in when their outer electron shells come into close proximity. When the centres of the two ions come within a certain distance of one another, attraction and repulsion balance and they can approach no closer and it is in this sense we must think of them as possessing a definite radius.

The Bravais lattice is face-centred cube, the basis consists of one Na atom and one Cl atom separated by one-half the body diagonal of a unit cube.

Therefore it can be considered as two face-centred cube sub-lattices, one of Na ions having its origin at the point 0, 0, 0, the other of Cl ions having its origin mid-way along a cube edge say, at point a/2, 0, 0.

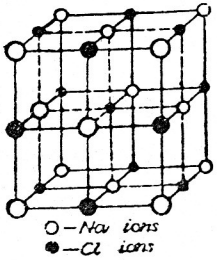

Fig. 38. NaCl crystal structure.

There are four units of NaCl in each unit cube with atoms in positions

Na	0 0 0	$\frac{1}{2}\ \frac{1}{2}\ 0$,	$\frac{1}{2}\ 0\ \frac{1}{2}$,	$0\ \frac{1}{2}\ \frac{1}{2}$.
Cl	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$,	$0\ 0\ \frac{1}{2}$,	$0\ \frac{1}{2}\ 0$,	$\frac{1}{2}\ 0\ 0$.

Each atom has as nearest neighbours six atoms of the opposite kind.

The lattice is simple cubic if the difference between Na and Cl ion positions is ignored.

General Considerations in the Formation of Compounds. In order to reduce the electrostatic energy to a minimum each ion will so far as possible surround itself with ions of opposite sign. The co-ordination number is eight which is the highest possible for a crystal with equal number of the two kinds of ions. For example, for a crystal of type AX unless the ratio of the radius of A to that of X is greater than 0.73, the X ions will touch one another along the cube edges, the A ions will settle inside the cubes of AX ions. If the ratio of the radii becomes less than 0.73, the crystals tend to have the rock salt types of lattice in which each ion is surrounded by only six of the opposite sign.

The alkali halides provide an interesting example. Of these CsI, CsBr and CsCl in which the radii of the two ions are nearly equal have a co-ordination number of eight but all others have a rock salt structure with a co-ordination number of six. Most of the oxides and sulphides and some of selenides of the bivalent metals also have a rock salt structure. If the ratio of ionic radii is less than 0.41 the larger ions come into contact without touching the smaller ions even in the rock salt structure. Geometrical stability can again be allowed if the co-ordination number is four. This gives the zinc blende (cubic) or wurtzite (hexagonal) structure in which each ion lies at the centre of a regular tetrahedron of ions of the opposite kind.

CuCl, CuBr, CuI, BeS, ZnS, ZnSe, have zinc blende structure while BeO and ZnO have wurtzite (hexagonal) structure.

If one ion is small and the other large and easily polarizable, the polarizable forces become considerable and modify the structure considerably. CdI_2 is an interesting example of this. The crystal is composed of sheets consisting of two layers of the large polarized iodine ions held together by the small cadmium ions between them. Each sheet is very rigid but adjacent sheets are only tightly held together and the crystal has a perfect cleavage.

§ 18.8. Cesium Chloride Structure : Another combination of cubic structure is that of CsCl. The lattice points of this compound are two interpenetrating simple cubic lattices ; the corner of one sub-lattice is the body-centre of the other. One of the sub-lattices is occupied by Cs ions, the other by Cl ions. The resultant structure termed the cesium chloride structure is sketched in fig. 39.

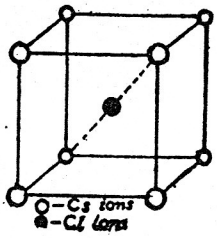

Fig.39. CsCl crystal structure.

These examples are only a few of the types of structures observed. Many of the remainder are also simple, but some are extremely complicated. With a few exceptions, each solid considered has one of the structures just described.

§ 19. Liquid Crystals : Some crystalline substances convert from the solid to the liquid phase during heating, not instantly but first passing into a thermodynamically stable transitional state in which the substances still retain the anisotropy of properties such as dielectric,optical, magnetic and others, inherent in a crystal, although they simultaneously acquire the properties specific to liquids- fluidity, ability to form droplets etc. The substances exhibiting such an intermediate, mesomorphic, phase are known as **liquid crystals.** The interest in these crystals continuously grows because they are useful in various display applications.

The temperature of transition from the solid phase to mesophase (liquid crystalline phase) is called the melting (or solidification) point T_s, and the temperature at which the liquid crystals convert to the isotropic transparent liquid is called the transparency temperature T_t. For different liquid crystals, the temperatures T_s and T_t and the temperature interval $\Delta T = T_t - T_s$ in which the liquid crystalline phase exists, vary within wide limits.

All liquid crystals are organic materials composed of rigid, moderately large rod-like molecules typically 1 to 3 m.m. in length and 0.3 to 1.0 m.m. across. At the end of molecules there are clusters of atoms exhibiting high polarizability. The ordered arrangement of molecules in the liquid crystalline state is provided by relatively weak Vander - Waals forces.

Depending upon magnitude of these forces, following three types of mesophase originate—

(i) smectic
(ii) nematic
(iii) cholesteric

Smectic mesophase : The most ordered smectic crystals have a layer structure : molecules align themselves in parallel layers gliding one relative to the other, thereby promoting fluidity. The long axes of molecules line up either perpendicular to the planes of layers, fig. (40a) or form a certain angle ø with the normal to these planes, fig (40b). The value of this angle ø depends on the temperature of liquid crystal and can be altered strongly by an externally applied field.

Nematic mesophase : In a nematic mesophase, the molecules also have their axes parallel to each other, but the location of their centres of gravity is as irregular as in conventional liquids, fig (40- c). The entire nematic liquid crystal consists of small regions, each having its molecules aligned parallel to a unique axis, but this axis generally varies in direction in different regions of the crystal. This feature accounts for a high optical inhomogenity of the crystals, which appears opaque in the transmitted and reflected light.

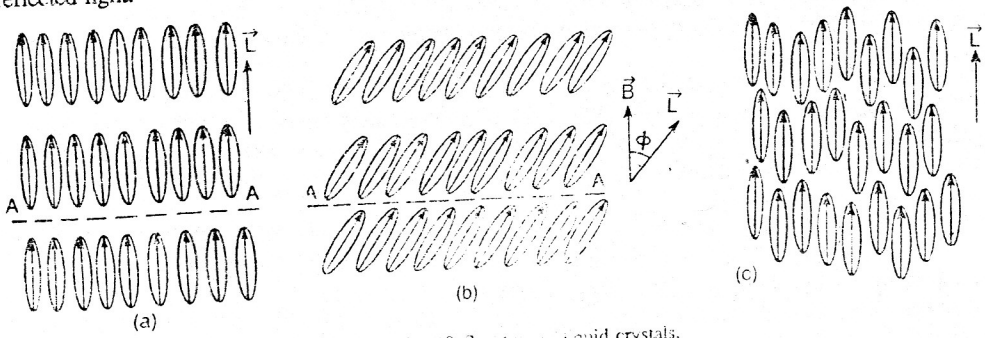

Fig. 40. Structure of liquid crystals.
(a) Smectic, axis $\vec{L}$ of molecules is normal to layer plane; AA is shear plane
(b) Smectic, axis $\vec{L}$ of molecules is at an angle ø to the normal to the layer plane. (c) Nematic.

An externally applied field orients the molecules of all regions in the same direction, and the liquid crystals become transparent. Placing a thin layer of the nematic liquid between two plate electrodes enables aligning the molecules both parallel, fig (41- a) and normal, fig (41-b), to the planes of the connecting plates. The first type of alignment is said to be planar and the second **hemotropic**. The latter structure, unlike the former, has no effect on the polarization of light transmitted through the cell at a right angle to the layer of the liquid crystal. Special treatment of the surfaces of plate electrodes or requistie chemical aligning agents introduced in the liquid give the desired orientation of molecules. An electric field produced between the plates and various other factors can change this orientation and this alters the optical properties of the liquid crystal.

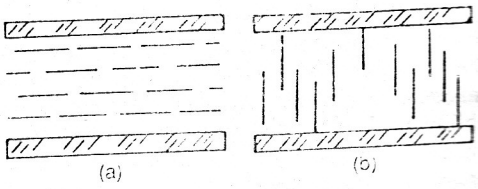

Fig. 41. Planar (a) and hemotropic (b) alignment of a liquid crystal.

Cholesteric mesophase : A cholesteric mesophase has its structure twisted about the helical axis lying perpendicular to the orientation of molecules, fig (42).

In going from one plane to the other, the vector L, called the **director,** turns by a certain angle and its end describes a helix with a pitch (structure period) of about 0.2 to 20 μm. The periodicity of the structure along the helical axis results in Bragg reflection of light at a wavelength equal to the pitch divided by the refractive index of the liquid crystal. Since it displays high optical activity, the cholesteric fluid causes the plane of polarization of light to turn through extremely large angles, of the order of 6,000 to 7,000 °/m.m. Whereas in such an optically active crystal as quartz, the angle of turn of the light polarization plane is 15.5°/m.m.

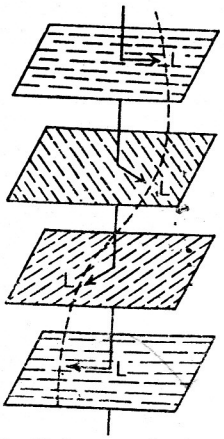

Fig. 42. Structure of a cholesteric mesophase

An external field applied to the cholesteric fluid can change the pitch of the helix, turn the helical axis, and convert the fluid to the nematic type. Therefore, the transmission of light by the system consisting of the layer of the cholesteric liquid placed between two polarizers will change with the applied potential difference. This is the principle that underlies operation of various displays, liquid crystal digital indicators applied in some types of electronic watches, clocks, microcalculators etc. Since the pitch of the helix sharply varies with temperature, the wavelength of the wave experiencing Bragg reflection and the colour of the liquid crystal vary accordingly. This makes it possible to employ cholesteric liquids for visual detection of hot spots in microcircuits, for observation of images in infra red rays etc.

The electro-optic effect of polarization plane rotation can also be induced in nematic liquid crystals with a positive anisotropy i.e. the liquid for which the difference between the dielectric constants (relative permittivities) is $\Delta \varepsilon = \varepsilon_{11} - \varepsilon_{\perp} > 0$, where ε_{11} is the dielectric constant of the liquid in the direction of the axes of molecules, and $\varepsilon_{\perp}$ is the dielectric constant of this liquid in the direction perpendicular to the axes. The appropriate treatment of the surface of plates with the liquid crystal placed in between can give the desired twisted texture of the layer causing the polarization plane of the incident light to rotate, the rotation being easily controllable by a driving field, fig (43a). This twisting of the texture was known as **twist effect.** If we place a cell between polarizers and apply potential difference to the plates, the torque produced on the molecules turns them in the field direction and disrupts the helix completely, fig (43b); the cell positioned between crossed polarizers becomes dark, and that between parallel polarizers becomes optically clear.

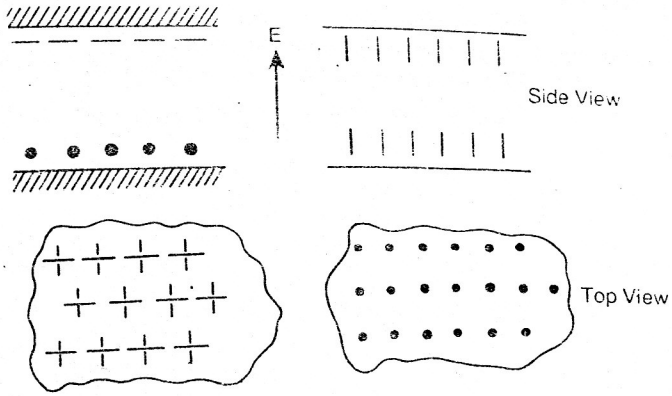

Fig. 43. Twisted texture of the layer (a) and disruption of the helix (b).

This effect produces high contrast at a low threshold voltage, 0.9 to 1.5 V, and thus holds promise for use in information displays.

The electro-optic effect of the dynamic scattering of light in nematics of negative dielectic anisotropy serves the same purpose. The essence of this effect consists in the following. The liquid crystal used

contains a strongly dissociative organic substance added in small quantities as an ionic dopant to lower the resistivity of the liquid to 10^6 - 10^9 Ω cm. The potential difference applied to the layer of the liquid crystal causes the molecules to align perpendicular to the field because $\Delta \varepsilon = \varepsilon_{11} - \varepsilon_{\perp} < 0$. The flow of ions producing the conduction current tries to disrupt this orientation. At a cetain critical field, the fluid motion becomes ,turbulent. The turbulent state causes a high optical inhomogenity of the crystal and light scattering, so that the crystal appears opaque.

Liquid crystalline cells consume less power, are cheap and easy to manufacture in any size and shape and a variety of colours. But these cells also present some disadvantages, namely, they operate in a limited temperature range, have comparatively large response times, short life etc. During the last ten years many drawbacks of liquid crystals have been over -come and possibilities have been explored for the use of liquid crystals not only in displays but also in other systems.

PROBLEMS

1. *Calculate the number of atoms per unit cell for a face centred cubic (fcc) lattice of copper crystal. Given a = 3·60 Å, atomic weight of copper = 63·6 and density of copper = 8·86.*

We know that

$$n = \frac{V \cdot \rho}{M} \times 6{\cdot}023 \times 10^{23}$$

$$= \frac{\left(3{\cdot}60 \times 10^{-8}\right)^3 \times 8{\cdot}86 \times 6{\cdot}023 \times 10^{23}}{63{\cdot}6}$$

$$= 3{\cdot}96 \cong 4.$$

As n must be a whole number; we have made it 4. Hence, a fcc lattice of copper contains 4 atoms per unit cell.

2. *Calculate the lattice constant for a rock salt crystal (density equal to 2·18 gm/cm³). Given that the crystal has fcc lattice and molecular weight = 58·5.*

For a f.c.c. lattice the number of atoms per unit cell is 4 and $V = a^3$

$$n = \frac{(V.\rho)}{M} \times 6{\cdot}023 \times 10^{23}$$

$$= \frac{a^3 \times \rho}{M} \times 6{\cdot}023 \times 10^{23}$$

or

$$a^3 = \frac{n \times M}{\rho \times 6{\cdot}023 \times 10^{23}} = \frac{4 \times 58{\cdot}5}{2{\cdot}18 \times 6{\cdot}023 \times 10^{23}}$$

or

$$a = \left[\frac{4 \times 58{\cdot}5}{2{\cdot}18 \times 6{\cdot}023 \times 10^{23}}\right]^{1/3}$$

or

$$a = 5{\cdot}63\text{Å}.$$

3. *Show that spacing d of plane (hkl) in a simple cubic lattice of side a is*

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

Given that d is the normal distance of plane from the origin

$$hx + ky + lz = a$$

The direction cosines of the normal to this plane are

$$d + \left(\frac{a}{h}\right) = \frac{dh}{a}, \text{ etc.}$$

Since the sum of the squares of the direction cosines of the normal to the plane is 1, we get

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

or $h^2d^2+k^2d^2+l^2d^2=a^2$ or $d^2(h^2+k^2+l^2)=a^2$

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

4. *The lattice constant of a cubic lattice is a. Calculate the spacing between (0 1 1), (1 0 1) and (1 1 2) planes.*

We know that spacing d_{hkl} is given by an expression

$$d=\frac{1}{\sqrt{\frac{h^2d^2}{a^2}+\frac{k^2d^2}{a^2}+\frac{l^2d^2}{a^2}}}$$

In the case of cubic lattice a = b = c, hence we have

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

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

$$d_{101}=\frac{a}{\sqrt{1^2+0^2+1^2}}=\frac{a}{\sqrt{2}}$$

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

5. *Compare the density of lattice planes in (1 3 2) plane with that in (1 0 0) planes for a cubic P lattice.*

$$\frac{\delta_{132}}{\delta_{100}}=\frac{d_{132}}{d_{100}}=\frac{a}{\sqrt{1^2+3^2+2^2}}\div\frac{a}{\sqrt{1^2+0^2+0^2}}$$

$$=\frac{a}{\sqrt{14}}\times\frac{1}{a}=\frac{1}{\sqrt{14}}$$

6. *Draw a plane lattice and indicate two kinds of double cells and one triple cell in that lattice.*

A cell containing lattice points within the cell in addition to the one shared at the corners is called a **multiple cell.** Several kinds of multiple cells are possible namely double cells, triple cells etc. depending on whether they contain two, three or more lattice points, counting all the corner points together as one point and adding one for each point contained in the interior of the cell.

Two double cells are represented by vectors t_5, t_6 and t_7, t_8. One triple cell is represented by vectors t_9 and t_{10}.

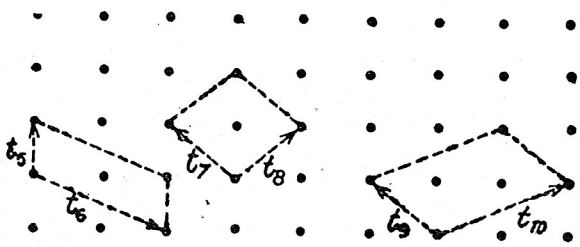

Fig. 44.

7. Draw planes of structures of the face-centred cubic, body centred cubic, hexagonal close packed and diamond structures indicating the heights of atoms as a fraction of a unit cell height and marking the unit cell sides.

Planes are shown in fig. 45.

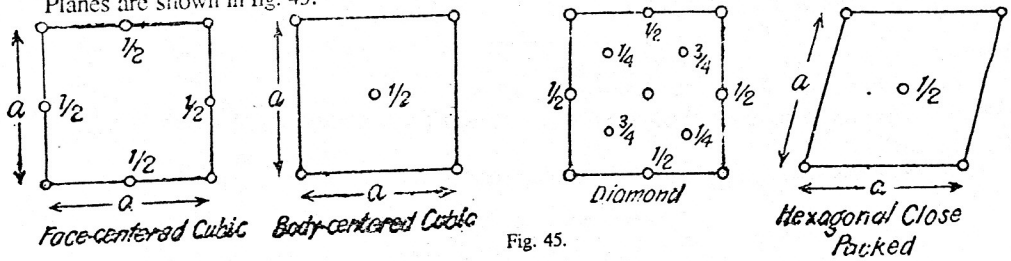

Fig. 45.

8. Show that a face-centered tetragonal lattice does not exist.

Draw two unit cells with the bases in the same plane and then draw new tetragonal unit cell of half the volume.

The new unit cell turns out to be a body centred tetragonal lattice.

Therefore face-centred tetragonal lattice does not exist.

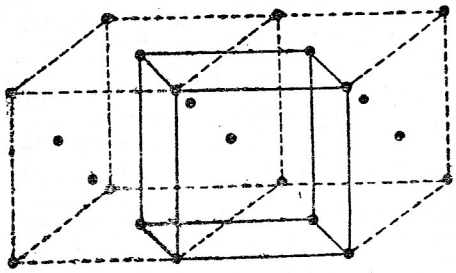

Fig. 46.

9. Topaz an orthorombic semi-precious gem has a ratio of a : b : c of 0.529 : 1 : 0 .477.

Find the Miller indices of faces whose intercepts are as follows.

0.264 : 1 : 0.238
1.057 : 1 : 0.954
0.529 : ∞ : 0.159

The intercepts in terms of the unit axial dimensions are as follows.

$$\frac{1}{2} : 1 : \frac{1}{2}$$
$$2 : 1 : 2$$
$$1 : \infty : \frac{1}{3}$$

Taking the reciprocals of this number and reducing to the smallest set of whole numbers, the following Miller indices are obtained

(2 1 2)
(1 2 1)
(1 0 3)

10. Prove that the direction [h, k, l] is the normal to the plane (h, k, l) for a cubic lattice.

Let OC be the direction of [h, k, l].

Let ABC be the plane of (h, k, l).

Let x_0, y_0, z_0 be the intercepts of the planes with x, y, z axes.

Miller indices are $\frac{1}{x_0}, \frac{1}{y_0}, \frac{1}{z_0}$

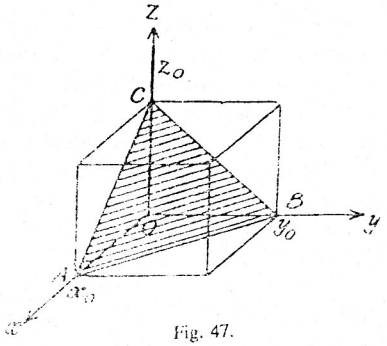

Fig. 47.

and reduced indices become $\frac{g}{x_0}, \frac{g}{y_0}, \frac{g}{z_0}$

where g is an integer.

For cubic lattice h = k = l or $x_0 = y_0 = z_0 = \alpha$

And the direction $\overrightarrow{OP} = \left(i\frac{g}{\alpha} + j\frac{g}{\alpha} + k\frac{g}{\alpha} \right)$

$$\overrightarrow{OA} + \overrightarrow{OB} = \overrightarrow{OR}$$

$$\overrightarrow{AB} = \overrightarrow{OB} - \overrightarrow{OA} = \left(j\frac{g}{\alpha} - i\frac{g}{\alpha} \right)$$

$$\overrightarrow{OP}.\ \overrightarrow{AB} = \frac{-g^2}{\alpha^2} + \frac{g^2}{\alpha^2} = 0$$

Similarly we may prove

$$\overrightarrow{OP}.\ \overrightarrow{BC} = 0$$

$$\overrightarrow{OP}.\ \overrightarrow{CO} = 0$$

Hence dot product of $\overrightarrow{OP}$ with $\overrightarrow{AB}$, $\overrightarrow{BC}$ and $\overrightarrow{CA}$ is zero.

Hence OP is normal to $\overrightarrow{AB}$, $\overrightarrow{BC}$ or $\overrightarrow{CA}$.

Hence [h, k, l] is normal to plane (h, k, l).

11. Iron is b.c.c. below 910° C and is f.c.c. above 910°C. The atomic radius of an atom is the same in both structures. Calculate the ratio of the densities of bulk iron in the two structures at 910°C.

Packing Fraction i.e. density in b.c.c. case $= \frac{\pi\sqrt{3}}{8}$

Packing Fraction i.e. density in f.c.c. case $= \frac{\pi}{3\sqrt{2}}$

For above derivation see text pages 17 and 16.

Hence ratio of densities $= \frac{\pi\sqrt{3}}{8} \times \frac{3\sqrt{2}}{\pi} = \frac{3\sqrt{6}}{8} = 0.92.$

12. Show that the Packing Fraction in the case of Simple Lattice is 52.

In the simple cubic structure there are eight spheres at eight corners and also each sphere is common for eight cubes. Thus the number of spheres in one unit cell

$$= 8 \times \frac{1}{8} = 1.$$

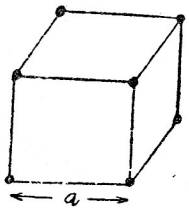

Fig. 48

∴ Volume of all spheres in unit cell

$$= 1 \times \frac{4}{3}\pi R^3$$

where R is radius of sphere.

For closesr packing a = 2R

Volume of cube = $(2R)^3$

$$\therefore \quad \text{Packing Fraction} = \frac{\text{Complete volume of spheres}}{\text{Total volume of cube}} = \frac{1 \times \frac{4}{3}\pi R^3}{(2R)^3} = \frac{\pi}{6} = 0{\cdot}52.$$

Note. From Packing Fractions dealt in text and in problem here it is clear that h.c.p. and f.c.c. are the closest packed structures.

13. Calculate the packing fraction in crystals for (i) sc, (ii) f.c.c. and (iii) hcp structures, treating the atoms as spherical.

We know that packing fraction in crystals is defined as the ratio of the volume of atoms in a unit cell and the volume of the unit cell.

(i) If atomic diameter is d, the volume occupied by the atoms in sc structure will be

$$\frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{4}{3}\pi\frac{d^3}{8} = \frac{\pi}{6}d^3$$

The parameter of the unit cell in this case will be a = d.

Hence the volume of unit cell will be d^3

∴ Packing fraction for sc structure

$$= \frac{\text{Vol. of the atoms in a unit cell}}{\text{Vol. of unit cell}} = \frac{\pi\, d^3/6}{d^3} = \frac{\pi}{6}.$$

(ii) Refer to § 17·2

(iii) Refer to § 17·1.

14. What will be the density of planes (100), (111), (110) and (210) in a cubic lattice (P) ?

Given $a = 2{\cdot}5 \times 10^{-8}$ cms.

The inter-planer spacings for these planes will be given by

$$d_{100} = a/\sqrt{(1^2 + 0^2 + 0^2)} = a$$
$$d_{110} = a/\sqrt{(1^2 + 1^2 + 0^2)} = a/\sqrt{2}$$
$$d_{111} = a/\sqrt{(1^2 + 1^2 + 1^2)} = a/\sqrt{3}$$
$$d_{210} = a/\sqrt{(2^2 + 1^2 + 0^2)} = a/\sqrt{5}$$

The volume of simple cubic lattice is a^3. Hence

$$\delta_{100} = \frac{d}{a^3} = \frac{1}{a^2} = \frac{1}{\left(2{\cdot}5 \times 10^{-8}\right)^3}$$

$$= 16 \times 10^{12} \text{ atoms per cm}^2.$$

$$\delta_{110} = \frac{a}{\sqrt{2}\,a^3} = \frac{1}{\sqrt{2}\,a^2} = \frac{16}{\sqrt{2}} \times 10^{12} \text{ atoms per cm}^2$$

$$\delta_{111} = \frac{a}{\sqrt{3}\,a^3} = \frac{1}{\sqrt{3}\,a^2} = \frac{16}{\sqrt{3}} \times 10^{12} \text{ atoms per cm}^2$$

$$\delta_{210} = \frac{a}{\sqrt{5}\,a^3} = \frac{1}{\sqrt{5}\,a^2} = \frac{16}{\sqrt{5}} \times 10^{12} \text{ atoms per cm}^2$$

15. If unit cells have following characteristics–

(i) a = 10·8Å, b = 9·47Å, c = 5·2Å

$\alpha = 41°$, $\beta = 83°$ and $\gamma = 93°$

(ii) a = b = 10·73Å, c = 14·3Å

$\alpha = \beta = 90°$ and $\gamma = 120°$,

identify to which crystal system do these unit cells belong ?

(i) Since $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$, this shows that the three primitives are unequal and there is a complete lack of symmetry. This is a characteristic of Triclinic structure.

Hence the unit cell belongs to a Triclinic system.

(ii) In this case the given data reveals that $a = b \neq c$, $\alpha = \beta = 90°$ and $\gamma = 120°$.
This is the characteristic of hexagonal structure.
Hence the unit cell belongs to hexagonal system.

16. The orthorhombic crystal has axial units in the ratio of 0·424 : 1 : 0·367. Find the Miller indices of a crystal face whose intercepts are in the ratio 0·212 : 1 : 0·183.

The axial units are

$$a : b : c :: 0{\cdot}424 : 1 : 0{\cdot}367$$

$$pa = 0{\cdot}212$$

or $$p \times 0{\cdot}424 = 0{\cdot}212$$

$$\therefore \quad p = \frac{0{\cdot}212}{0{\cdot}424} = \frac{1}{2}$$

Similarly $qb = 1$ or $q \times 1 = 1$ $\therefore$ $q = 1$

and $$rc = 0{\cdot}183$$

$$r \times 0{\cdot}367 = 0{\cdot}183$$

$$\therefore \quad r = \frac{0{\cdot}183}{0{\cdot}367} = \frac{1}{2}$$

Hence parameters of the plane is $\frac{1}{2}, 1, \frac{1}{2}$

$$\text{Miller indices} = \left(\frac{1}{1/2} : \frac{1}{1} : \frac{1}{1/2}\right)$$
$$= (2\ 1\ 2)$$

17. The primitives of a crystal are 1·2Å, 1·8Å and 2Å along whose Miller indices (2 3 1) cut intercept 1·2Å along x–axis. What will be the lengths of intercept along y and z axes ?

Given that $h : k : l = 2 : 3 : 1$

We have

$$\frac{1}{p} : \frac{1}{q} : \frac{1}{r} = h : k : l = 2 : 3 : 1$$

$$\therefore \quad p : q : r = \frac{1}{2} : \frac{1}{3} : \frac{1}{1}$$
$$= 3 : 2 : 6$$

Now $$pa : qb : rc = (3 \times 1{\cdot}2) : (2 \times 1{\cdot}8) : (6 \times 2)$$
$$= 3{\cdot}6 : 3{\cdot}6 : 12$$

If l_x, l_y and l_z be the lengths of intercepts on x, y and z axes respectively, then

$$l_x : l_y : l_z = 3{\cdot}6 : 3{\cdot}6 : 12$$

Since $$l_x = 1{\cdot}2\text{Å}$$

Hence $$l_y = \frac{3{\cdot}6}{3{\cdot}6} \times 1{\cdot}2\ \text{Å} = 1{\cdot}2\ \text{Å}$$

and $$l_z = \frac{12}{3{\cdot}6} \times 1{\cdot}2\ \text{Å} = 4\ \text{Å}$$

Thus the length of intercepts along y and z axes are 1·2Å and 4Å respectively.

18. Calculate the length of intercepts made by Miller indices (1 1 1) and (1 2 3) in a $BaCl_2$ crystal with primitive translation vectors t_1 = 6·69Å; t_2 = 10·86Å and t_3 = 7·15Å if both the planes make intercepts 7·15Å along z axis.

19. Show that for a cubic lattice the distance between the successive planes of Miller indices (hkl) is given by an expression

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

Find the interplaner spacings for lattice planes of Miller indices (3 2 1), (2 1 0) and (1, 1, 1) for a cubic lattice with a = 5·62Å.

20. A substance with f.c.c. lattice has density 6250 kg/m³ and molecular weight 60·2. Calculate the lattice constant a. Given Avogadro Number 6·02 × 10²⁶ (kg mole⁻¹).

We know that number of molecules per unit cell is given by an expression,

$$n = \frac{V \times \rho \times N}{M}$$

or

$$\rho = \frac{n \times M}{V \times N}$$

But density

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{m}{a \times a \times a}$$

$\therefore$

$$\rho a^3 = \frac{n \times M}{N}$$

or

$$a^3 = \frac{n \times M}{N \cdot \rho}$$

or

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

In this case of f.c.c. lattice, n = 4, M = 60·2, N = 6·02 × 10²⁶ and ρ = 6250

$\therefore$

$$a = \left(\frac{4 \times 60{\cdot}2}{6{\cdot}02 \times 10^{26} \times 6250}\right)^{1/3}$$

$$= 4 \times 10^{-10}\ \text{m}$$

or

$$a = 4\text{Å}$$

21. Show from symmetry considerations that a base-centred cubic lattice does not exist.

22. Many metals can occur with both the body - centered cubic and the face-centred cubic structures and it is observed that the transition from one structure to the other involves only an insignificant volume change. Assuming no volume change, find the ratio D_{fc}/D_{bc}, where D_{fc} and D_{bc} are the closest distances of approach of metal atoms in the two structures.

[1.029]