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PG AND RESEARCH DEPARTMENT OF PHYSICS

CLASS : II M.SC PHYSICS

SUBJECT CODE : GPH42

SUBJECT NAME : CRYSTAL GROWTH AND THIN FILMS

UNIT 3

Solution: Given: atomic wt. = 26.98, $\rho = 2.7 \times 10^3$ kg/m^3. Since aluminium has an fcc structure, $n = 4$.

From eq. 4, we have

$$a^3 = \frac{Mn}{\rho N} = \frac{26.98 \times 4}{2.7 \times 10^3 \times 6.023 \times 10^{26}} = 66.36 \times 10^{-30}\ \text{m}^3$$

This gives $a = 4.05$ Å

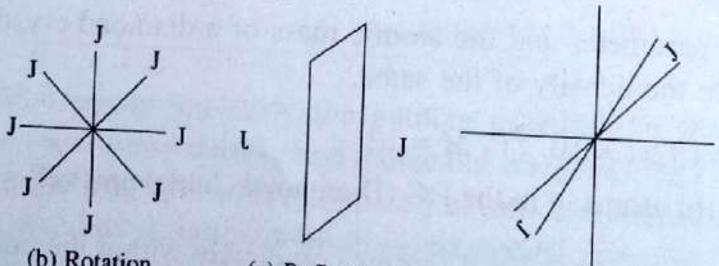
Now for fcc crystals, we know that $\sqrt{2}a = 4R = 2D$

Therefore, $$D = \frac{a}{\sqrt{2}} = 2.86\ \text{Å}$$

1.6 SYMMETRY ELEMENTS

In section 1.2, we observed that the repetition of an object (or a lattice point) by a translation leaves the environment around that object (or lattice point) unchanged. In an extended array, such as atomic pattern of a crystal, symmetries involving translation, rotation, reflection, inversion or their combinations are found to occur. The characteristic feature of these symmetries is that the translaton operation repeats an object infinite number of times, while other operations (such as rotation, reflection, inversion or their combinations) repeat it only a finite number of times (Fig. 1.13). Further, the operations like translation or proper rotation leave the 'motif' (a fundamental group of atoms or molecules) unchanged whereas the operations like reflections, inversion or improper rotation change the character of the motif from a right handed to a left handed one and vice versa. The geometrical locus about which a group of finite operations act is known as 'symmetry element'. Thus in Fig. 1.13, the line normal to the page about which a rotation takes place, the plane about which the reflection occurs and the centre about which the inversion takes place are simple examples of symmetry elements and are called, a rotation axis, a reflection or a miror plane and an inversion centre, respectively.

(a) Translation



(b) Rotation (c) Reflection (d) Inversion

Fig. 1.13 Simple symmetry operations

A crystalline solid can have the following symmetry elements:

(i) Pure translation: (T) defined by eq. 2
(ii) Proper rotation: through an angle ϕ

(iii) Reflection: across a line (in two dimensions) or a plane (in three dimensions)
(iv) Inversion: through a point
(v) Improper rotation: Rotoreflection/Rotoinversion.

However, it may be easily verified that the above symmetry elements are not all independent but are interconnected to each other. We have already discussed the translation operation and derived plane and space lattices earlier in section 1.2. In the following, we shall discuss about other symmetry elements.

Proper Rotation

The simplest way of representing the operation for proper rotation is shown in Fig. 1.13b. One can think of a line or axis passing through the centre and normal to the figure so that the J's (or in general any geometrical figure) are represented by a rotation through any angle $\phi = 2\pi/n$ about the axis of rotation, the axis is said to have n-fold symmetry. However, because of the reticular structure of crystals, only 1-, 2-, 3-, 4- and 6- fold rotational symmetries (Fig. 1.14) are possible. They are known as symmetry elements corresponding to proper rotation, consequently, it means that a crystalline solid can not possess either 5-fold or any other rotational symmetry higher than 6-folds. They are being demonstrated in Fig. 1.14e, 1.14g and 1.14h.

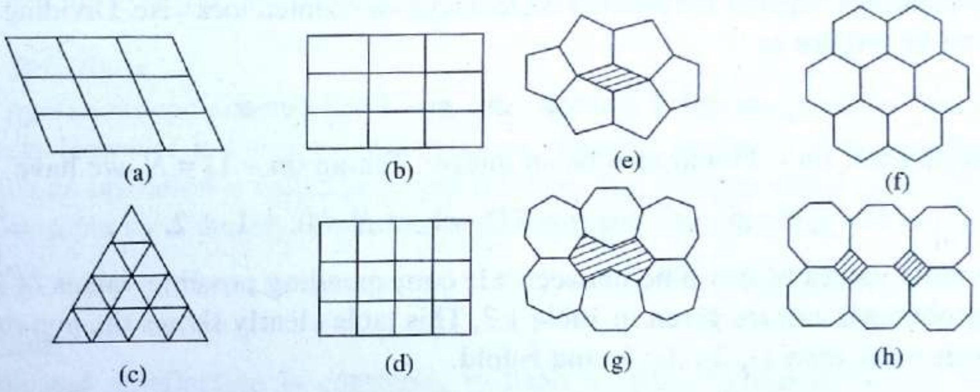


Fig. 1.14 Possible and non-existent symmetry axes

For $n = 1$ in equation $\phi = 2\pi/n$ means that the crystal must be rotated through 2π (360°) to achieve congruency. Such an axis is also called as identity axis. Every crystal possesses an infinite number of such axes. Further, $n = 2$ means the crystal is rotated through π (180°) and the axis is said to have 2-fold symmetry. Such an axis is termed as a diad axis and symbolically represented as (). In a similar way for $n = 3$, 4 and 6 the corresponding angles of rotation are 120°, 90° and 60°, respectively. They are said to have 3-fold, 4-fold and 6-fold symmetry, the axes are termed as triad, tetrad and hexad and symbolically represented as △, □ and ⬡ respectively.

In order to check the permissible rotational symmetry elements in a crystal, one may start with the fundamental requirement that all crystals must have periodic structure, that is the symmetry elements present in the crystals must conform to their translational periodicities. This is the reason why the number of symmetry elements found in crystals is limited. Now, let us consider the combination of n-fold axis of rotation A_n with a translation t as shown Fig. 1.15. As we have already seen that a rotation axis repeats the translation $\phi°$ (= $2\pi/n$) away, and hence n such rotations will bring back the object into its initial position (it is immaterial whether the rotation is clockwise or counter clockwise). Therefore, starting from the linear array as in Fig. 1.15, two such rotations will produce new lattice points p and q as shown in Fig. 1.16. Since they are equidistant from the original lattice row by construction, the two lattice points p and q must be connected by the same translation t or some integral multiple of it say mt, depending upon the magnitude of ϕ. Consequently, the allowed values of ϕ can be determined from the construction shown in Fig. 1.16. From simple geometrical consideration, we have

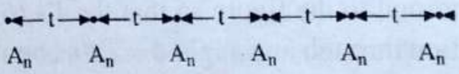


Fig. 1.15 ***n*-fold axis of rotation with a translation *t***

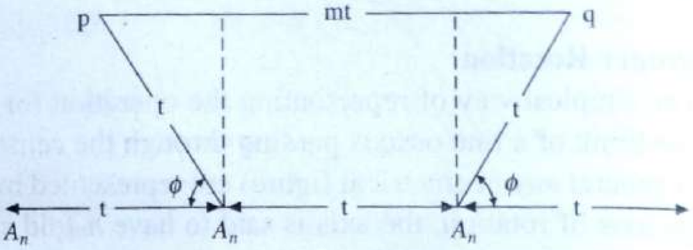


Fig. 1.16 **Two dimensional array of: (a) objects, (b) points; a plane lattice**

$$mt = t + 2t\cos\phi, \text{ where } m = 0, \pm 1, \pm 2, \ldots \qquad (5)$$

$\pm m$ is used dependineg whether the rotation is clockwise or counterclockwise. Dividing both sides by t, eq. 5 can be written as

$$m = 1 + 2\cos\phi \quad \text{or} \quad m - 1 = 2\cos\phi \qquad (6)$$

Since m is an integer, $(m - 1)$ will also be an integer. Taking $(m - 1) = N$, we have

$$N = 2\cos\phi \quad \text{or} \quad \cos\phi = N/2, \text{ where } N = 0, \pm 1, \pm 2, \ldots \qquad (7)$$

Since all possible values of $\cos\phi$ lie between ±1, corresponding possible values of N, ϕ and n can be easily obtained and are given in Table 1.3. This table clearly shows the non existence of symmetry axes other than 1-, 2-, 3-, 4- and 6-fold.

Table 1.3 Allowed rotational axis in a crystal lattice

N	$\cos\phi$	ϕ	n allowed rotational axes
−2	−1	180	2
−1	−1/2	120	3
0	0	90	4
+1	+1/2	60	6
+2	+1	360 or 0	1

Example: Construct a two dimensional pentagonal and octagonal lattice.

Solution: Since each interior angle of a pentagon is 108°, which is not a quotient of 360°. So, if we try to construct a periodic array having 5-fold symmetry, we can see that the resulting pentagons do not fit together neatly and leave empty spaces in between as shown by the shaded region in Fig. 1.14e. Similarly, in an octagon each interior angle is 135°, which again is not a quotient of 360°. In this case too, the octagons cannot fill the whole space without leaving gaps

(Fig. 1.14h). Both considerations indicate that neither 5-fold nor 8-fold symmetries can exist. In fact, all symmetries higher than 6-fold are not possible.

Reflection (Mirror Plane or Symmetry Plane)

If we look at Fig. 1.13c, we find that a plane transforms left handed object into a right handed one and vice-versa. The element of symmetry in this case is known as a symmetry plane or a mirror plane and symbolically represented by the letter m. Mirror coincident figures of this type are known as enantiomorphous pairs and are related by reflection across a plane passing half way between them. If a crystal is cut along symmetry plane and put on a mirror, the image will produce the other half of the crystal.

Inversion Centre (Centre of Symmetry)

This is a symmetry operation similar to reflection, with the difference that reflection occurs in a plane of mirror, while inversion is equivalent to reflection through a point called inversion centre or centre of symmetry. In other words, the enantiomorphous pair of figures in this case is related by inversion centre lying half way between the two (Fig. 1.13d). Each point of one figure is obtained from the other by reflection through centre and is symmetrically inverted. The complete figure thus obtained is inverted completely. Thus the inversion centre or the centre of symmetry has the property of inverting all space (at present the letter J) through a point.

Improper Rotations

Symmetry operations encountered above, i.e. reflection and inversion, produce enantiomorphous sets of objects. However, it is also possible to have a rotational operation relating enantiomorphous objects. Such an operation is called improper rotation. The corresponding symmetry element is known as improper rotation axis. There exist two improper rotations, they are rotoreflection and rotoinversion.

Rotoreflection

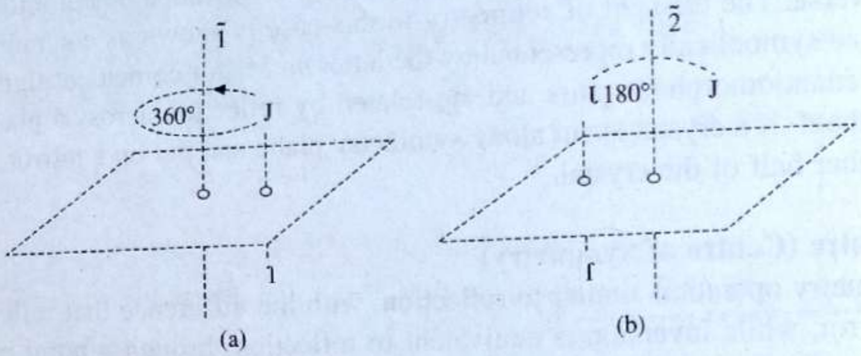
If a rotation and a reflection is combined to form a single hybrid operation, the resulting operation is called rotoreflection. The corresponding symmetry element is called rotoreflection axis. For each proper rotation axis, there exists a corresponding rotoreflection axis. To distinguish the two kinds of axes, a tilde symbolically represented as (~) is placed over the numerical symbol of the corresponding rotationa axis, e.g. $\tilde{1}$, $\tilde{2}$, $\tilde{3}$, etc. For a better understanding, let us see the following examples.

Example: Show that $\tilde{1}$ (one "tilde") is equivalent to a mirror plane.

Solution: It is a combined operation of rotation and reflection. In this case, the proper 1-fold rotation will rotate the motif representing all space (here it is taken as *J*) through an angle of 0° or 360°, i.e. leaving it unchanged. Combining this with reflecting plane perpendicular to the rotation axis to produce a configuration as shown in Fig. 1.17a, which is identical to the configuration already encountered in Fig. 1.13c. Thus, the operation $\tilde{1}$ is equivalent to a reflection through a plane (specifically a mirror plane).

Example: Show that $\tilde{2}$ is equivalent to an inversion centre.

Solution: In this case, the proper 2-fold rotation will rotate the object (through an imaginary axis) through an angle 180° and then reflected across an imaginary plane placed at right angle to the imaginary rotation axis, the resulting configuration (Fig. 1.17b), is identical to the configuration shown in Fig. 1.13d. Thus, the operation $\tilde{2}$ is equivalent to an inversion centre.



(a) (b)

Fig. 1.17 Improper rotation axes (a) $\tilde{1}$, (b) $\tilde{2}$

Rotoinversion

As we stated above that an inversion is equivalent to a reflection through a point, therefore it is possible to combine an inversion with a rotation axis to produce a rotoinversion axis in a manner similar to the formation of a rotoreflection axis. Consequently, there exist five rotoinversion axes corresponding to five proper rotation axes. Again, to distinguish these axes, both from pure rotation and rotoreflection, a bar (–) is plaed over the numerical symbol of the corresponding rotational axis, e.g. $\bar{1}, \bar{2}, \bar{3}$ etc.

When these rotoinversion axes are compared with the corresponding rotoreflection axes, they are found to be equivalent in pairs and therefore, it is sufficient to adopt only one kind to represent these symmetry operations. Table 1.4 enlists the conventional symbols used to represent the improper axes.

Table 1.4 Conventional symbol for improper axes

Rotoinversion axes	Rotoreflection axes	Conventional symbol	
$\bar{1}$	$\tilde{2}$	Centre of symmetry	$\bar{1}$
$\bar{2}$	$\tilde{1}$	Mirror Plane	m
$\bar{3}$	$\tilde{6}$	3-fold rotoinversion	$\bar{3}$
$\bar{4}$	$\tilde{4}$	4 " "	$\bar{4}$
$\bar{6}$	$\tilde{3}$	6 " "	$\bar{6}$

Example: Find the total number of symmetry elements that exist in a cube.

Solution: Looking at the Fig. 1.18, we find that there exist

(i) 2-fold axes parallel to the face diagonal and passing through the centre of the cube. There are six such axes.

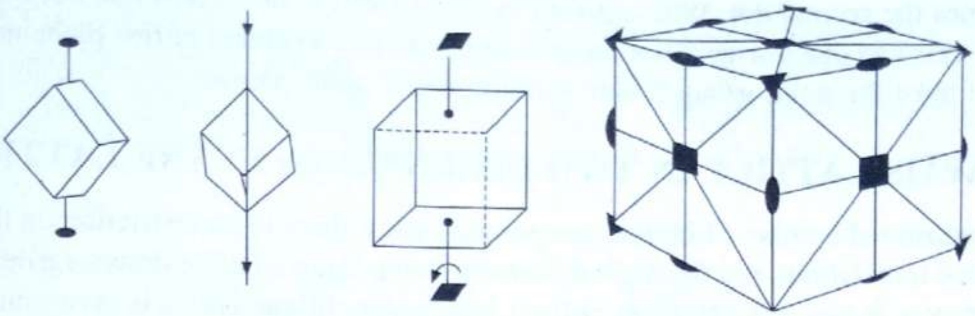


Fig. 1.18 **Showing various symmetries of a cube**

(ii) 3-fold rotoinversion axes passing through the body diagonal. There are four such axes.

(iii) 4-fold symmetry about an axis passing through the centre of two opposite faces. There are three such symmetry axes.

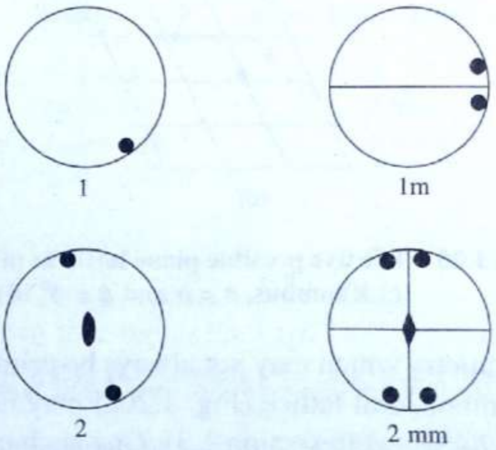
(iv) Nine mirror planes bisecting the parallel faces, and connecting diagonal edges. All of them passing through the centre of the cube.

(v) One centre of symmetry at the centre of the cube.

Thus, there are: 6-diads + 4-triads + 3-tetrads = 13 axes, 3 surface planes + 6 diagonal planes = 9 planes, and 1 centre of symmetry. Therefore, the total symmetry elements in a cube = 13 + 9 + 1 = 23.

1.7 COMBINATION OF SYMMETRY ELEMENTS (POINT GROUP)

In the preceding section, we discussed about various symmetry elements and their relationships. It was found that the symmetry elements are interlinked to each other and are not independent. In other words, a given symmetry element could be obtained from suitable combinations (if they are compatible) of other symmetry elements. Such a combination forms a group and gives rise to different symmetry points called point groups. Thus, a point group in the lattice is defined as the collection of symmetry operations which when applied about a lattice point, leave the lattice invariant. In other words, in point groups all possible symmetry elements must pass through a point. Suitable combinations of various symmetry elements give rise to thirty two (32) allowed point groups. Since crystals belonging to different crystal systems show different point group symmetries and therefore the classification of crystal systems can be easily made on the basis of point groups. A few examples illustrating the locations of equivalent positions forming groups are shown in Fig. 1.19.



1 1m 2 2 mm

Fig. 1.19 **Locations of equivalent positions for four point groups**

Here, the dots represent equivalent points. The point group 1 has no symmetry elements and hence the single isolated point has no other point equivalent to it. For 1m, there is a mirror plane, one dot on reflection across the mirror plane becomes the second dot. With a 2-fold axis 2, a rotation of π takes one dot into the other. With 2-fold axis and one mirror plane there is automatically a second mirror plane normal to the first and we have the point group 2 mm with four equivalent points.

1.8 BRAVAIS LATTICE IN TWO DIMENSIONS: PLANE LATTICE

In general, unlimited number of lattices are possible since there is no restriction on the length a, b of the lattice translations and on angle ϕ between them. Such a lattice drawn earlier in Fig. 1.9 for an arbitrary a, b, and ϕ is known as oblique lattice. An oblique lattice is invariant only under the rotation $2\pi/n$ (with $n = 1$ and 2) about any lattice point. However, this can also be made invariant under the rotation $2\pi/n$ with $n = 3, 4, 6$ or mirror reflection if some suitable restrictions are imposed on a, b and ϕ. These symmetry elements in turn put restrictions on the shape of the lattice (precisely the shape of the unit cell). The resulting latices are known as special lattices. They are obtained as follows.

We know that we need two repeat distances (noncollinear translations) a and b and an angle ϕ to form a two dimensional or plane lattice. Clearly there exist two possibilities $a = b$, or $a \neq b$. Further, the angle ϕ between the two vectors may take any value including that of $\phi = 90°$. A suitable combination of these possibilities leads to four possible planar lattices filling the plane space completely. They are represented by the square, rectangle, rhombus and parallelogram, as shown in Figs. 1.20a-d.

It is to be mentioned here that in general it is convenient to work with a cell of higher symmetry which may not always be primitive and therefore an alternative cell in place of a plane rhombohedral lattice (Fig. 1.20c) may be used because the choice of the unit cell is not unique (as discussed in section 1.3). One such cell is marked out as a centred rectangular lattice shown in Fig. 1.21. In addition to the above, plane space can also be filled by hexagonal or triangular figures. However, an equilateral triangle cannot be used as the basis of a lattice because its

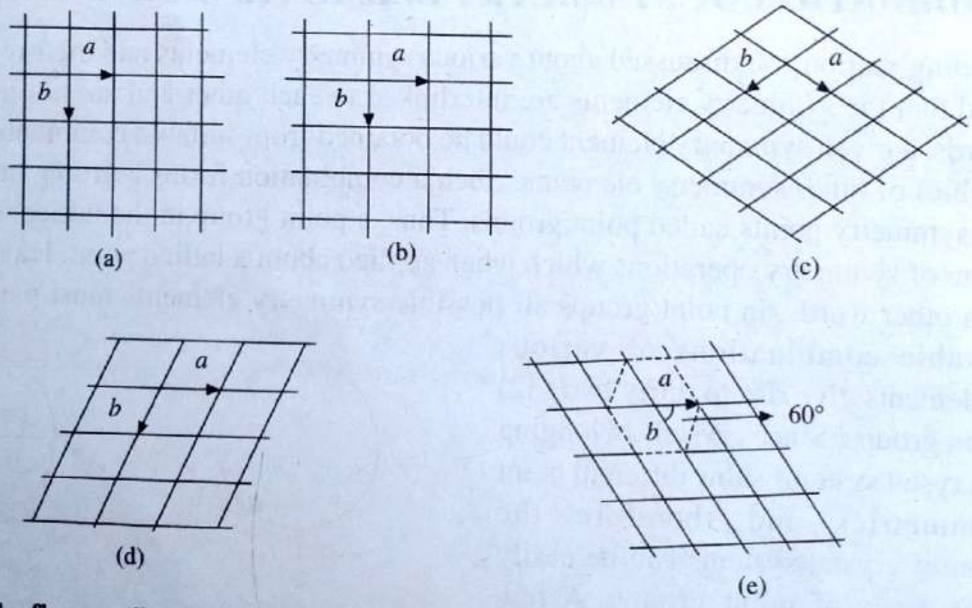


Fig. 1.20 **The five possible plane lattices: (a) Square, $a = b$ and $\phi = 90°$, (b) Rectangular, $a \neq b$ and $\phi = 90°$, (c) Rhombus, $a = b$ and $\phi = \phi°$ (d) Oblique, $a \neq b$ and $\phi = \phi°$, (e) Hexagonal, $a = b$ and $\phi = 60°$**

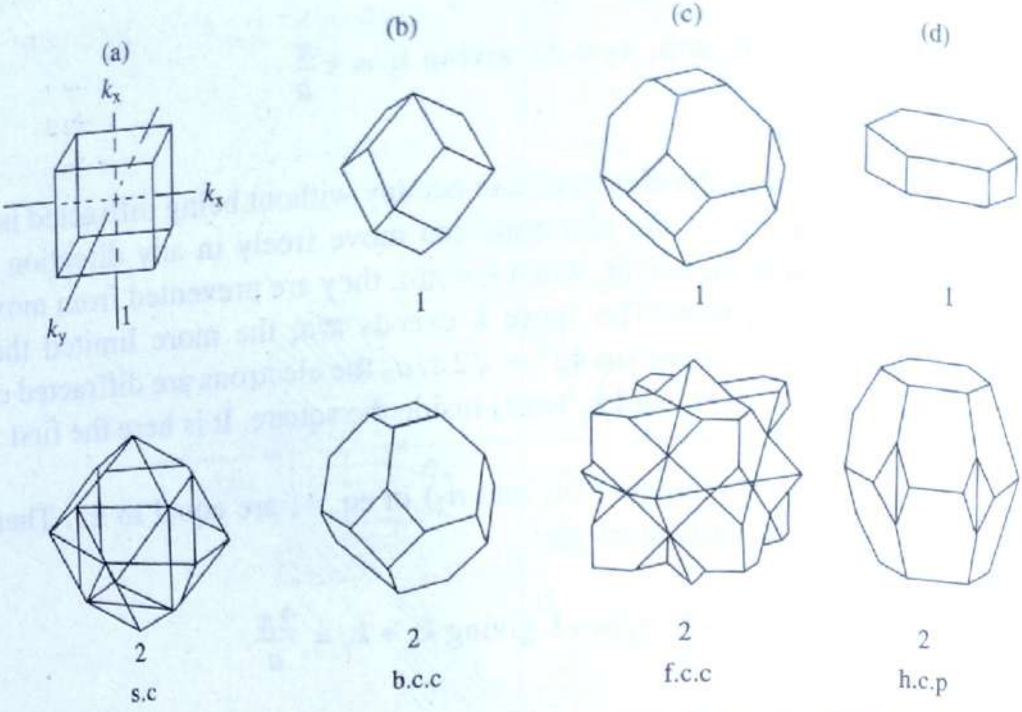


Fig. 11.10 The first and second Brillouin zones for some simple lattices

Example: Find the ratio between the kinetic energies of an electron in a two dimensional square lattice (a) when $k_x = k_y = \pi/a$ and (b) when $k_x = \pi/a$ and $k_y = 0$.

Solution: Given: Case I: $k_x = k_y = \pi/a$ and case II: $k_x = \pi/a$ and $k_y = 0$. We know that the energy of an electron inside a BZ is given by

$$E = \frac{h^2}{8\pi^2 m} k^2$$

For case I, the energy becomes

$$E_1 = \frac{h^2}{8\pi^2 m}(k_x^2 + k_y^2) = \frac{h^2}{8\pi^2 m} \times \frac{2\pi^2}{a^2} = \frac{h^2}{4a^2 m}$$

Similarly, for case II

$$E_2 = \frac{h^2}{8\pi^2 m} \frac{\pi^2}{a^2} = \frac{h^2}{8a^2 m}$$

This gives

$$\frac{E_1}{E_2} = 2$$

11.4 SYMMETRY PROPERTIES OF THE ENERGY FUNCTION

Based on the earlier discussions and from chapter 12 it can be shown that each energy band $E_n(k)$ satisfies the following symmetry properties:

(i) Translational Symmetry: $E_n(k + G) = E_n(k)$
This indicates that $E_n(k)$ is periodic, with a period equal to the reciprocal lattice vector $(G = 2\pi/a)$.

In other words, any two points in k-space related to each other by a displacement equal to a reciprocal lattice vector, have the same energy. Let us take the case of E versus k for a square lattice as shown in Fig. 11.11a. The points P_1, P_2 and P_3 will have the same energy, because P_2 is related to P_1 by a translation equal to $-G_2$ and P_3 is related to P_1 by a translation $-G_1$, where $-G_1$ and $-G_2$ are reciprocal lattice vectors.

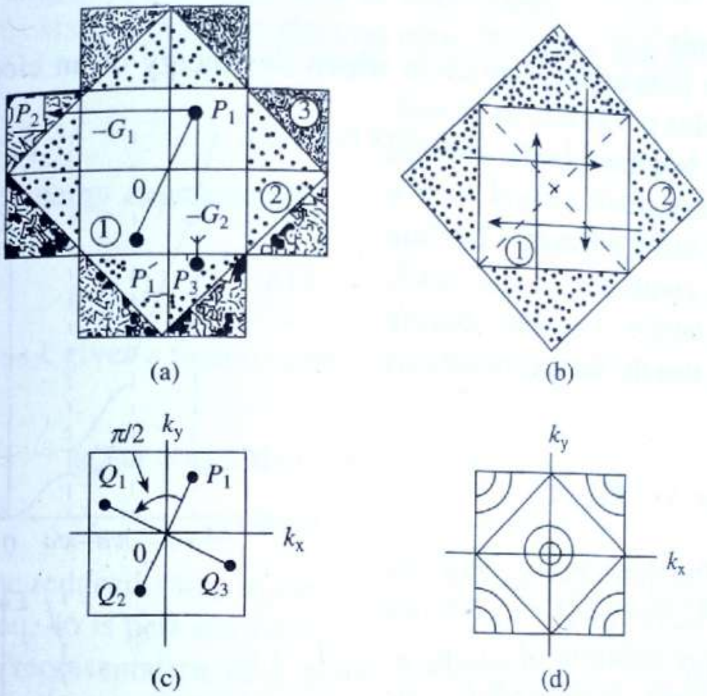


Fig. 11.11 (a) The translational symmetry of the energy $E(k)$ in k-space for a square lattice. (b) Mapping of the second zone into the first zone. (c) The rotational symmetry of the energy $E(k)$ in k-space for a square lattice

Making use of this translational symmetry, if we translate four pieces of the second zone in backward directions by the respective lattice vectors, it can be shown that the pieces just fit into the first zone as illustrated in Fig. 11.11b. This means that the first and the second zones are equivalent. The same is valid for higher-order zones. Hence, the first zone contains all necessary information of higher zones.

(ii) Inversion Symmetry: $E_n(-k) = E_n(k)$

This shows that the band is symmetric with respect to the inversion around the origin $k = 0$. Accordingly, in Fig. 11.11a, energy at the point P_1' is equal to that at P_1.

(iii) Rotational Symmetry

The energy band $E_n(k)$ has the same rotational symmetry as that of a real lattice. Thus, for a square lattice a rotation of $\pi/2$ will give rise to four equivalent energy positions. Accordingly, the value of energy at points Q_1, Q_2 and Q_3 should be the same as that of P_1 as shown in Fig. 11.11c.

11.5 EXTENDED, REDUCED AND PERIODIC ZONE SCHEME

The wave vector representation of a plane wave eigenstate is simple and unambiguous while the

so that
$$\delta_{(111)} = \frac{2}{\frac{a^2\sqrt{3}}{2}} = \frac{4}{a^2\sqrt{3}}$$

If we compare the densities calculated above for three cubic systems, we find that the planes of widest spacings (100) of sc, (110) of bcc and (111) of fcc respectively correspond to highest densities in their own category, while the (111) planes of fcc correspond to highest density of all. It is because of this, (111) planes of the fcc lattice are called the close packed planes.

Example: Give the Miller indices of the family of close packed planes and directions in sc, bcc, fcc and diamond crystal.

Solution: From above calculations of the densities and the idea of indices of directions discussed in section 1.10, we can write

	sc	bcc	fcc	Dc
Family of close packed planes	{100}	{110}	{111}	none
Family of close packed directions	<100>	$<\bar{1}11>$	$<1\bar{1}0>$	none

1.13 SOME SIMPLE AND COMMON CRYSTAL STRUCTURES

As we shall see later that many properties of solids can be explained only if the detail crystal structure of the substance is taken into account. We shall, therefore, give a brief description of some of the very common and simple crystal structures.

Out of over hundred elements in the periodic Table, only one element (polonium) is known to crystallize in the simple cubic form. The geometry of this structure is easy and is very helpful in understanding other structures. A large number of other elements are found to crystallize in the form of fcc, bcc, hcp and the derivatives of the basic cubic structures.

Simple Cubic Structure

In this structure the atoms are situated only at the corners of the cube touching each other along the edges (Fig. 1.50). This is a very open and loosely packed structure, i.e. there is much empty space in it. This structure is introduced mainly because of its simple geometry. However, as we shall see in the following that many other crystal structures bear a simple relationship to this structure.

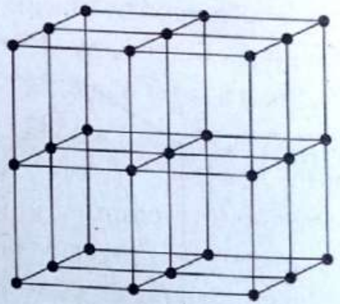


Fig. 1.50 The simple cubic structure

Body Centred Cubic Structure

As a rule, atoms tend to pack more closely and therefore if we examine the simple cubic arrangement to see how it might accommodate more atoms, the most obvious empty space is that at the centre of the cube. If this space is filled, we can obtain a body centred cubic (bcc) structure (Fig. 1.51a). It is to be noted that it can be considered as if two simple cubic structures interpenetrated along the body diagonal of one cube by half the length of the diagonal (Fig. 1.51b). Many metals are found to have bcc structure.

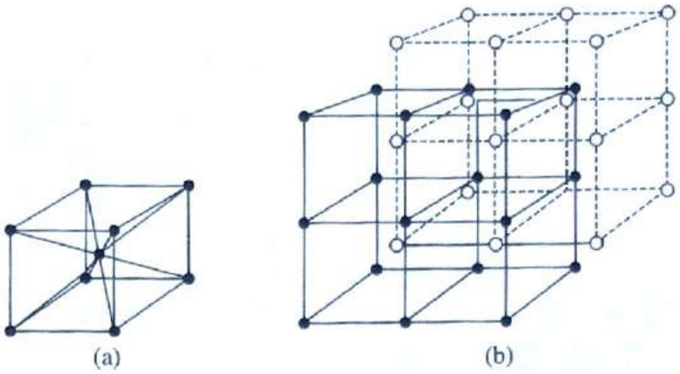


Fig. 1.51 **(a) Body centred cubic structure, (b) Body centred cubic structure may be considered to be two interpenetrated simple cubic structures**

most important is iron while some others are Cr, Mo, W and also the alkali metals Li, K, Na, Rb and Cs.

Certain simple binary compounds essentially have the bcc arrangement in which the centre of the cube is occupied by one type of atoms and the corners are occupied by the others. This is usually called cesium chloride structure.

Close Packed Structures

If the atoms are considered as hard spheres then the most efficient packing of these atoms in a plane is the close packed arrangement as shown in Fig. 1.52. There are two simple ways in which such planes can be stacked on top of one another to form a three dimensional structure. They are hexagonal close packed (hcp) structure (Fig. 1.53) and the face centred cubic (fcc) structure or equivalently the cubic close packed (ccp) structure.

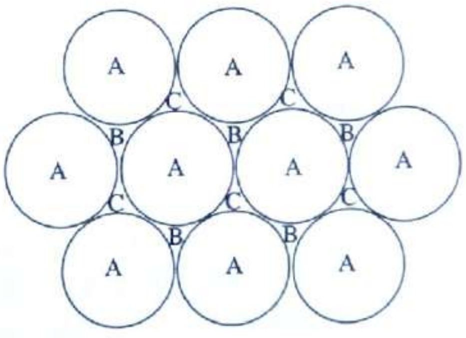


Fig. 1.52 **Close packed array of spheres. Note the three different possible positions, A, B and C for the successive layers**

In a single close packed layer, the spheres (atoms) may be arranged by placing each sphere in contact with six others, say all at positions A (Fig. 1.52). Such a layer can either be the basal plane of hcp structure or the (111) plane of the fcc structure. A second similar layer can be placed above the A layer either in the space marked B or in those marked C. Let us suppose that the second layer is a B layer. Where can the third succeeding layer be placed? There are two possible arrangements each of which is an important representative structure.

Hexagonal Close Packed Structures

Simplest arrangement for the third layer to be placed is the layer position A, i.e., immediately above the atoms in the first layer, and the fourth layer to be placed at B and so on. This gives a stacking of the type ABABAB . . . (or equivalently as ACACAC . . .) as shown in Fig. 1.53b. It has a hexagonal primitive cell in which the basis contains two atoms, one at the origin, 0 0 0 and

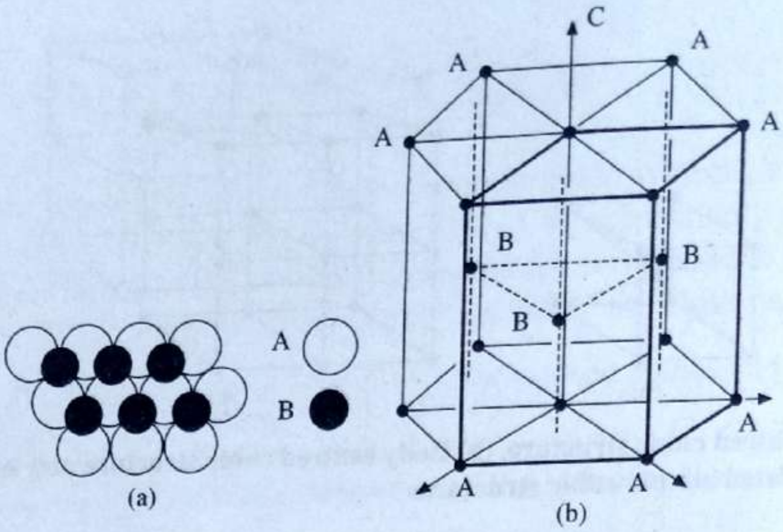


Fig. 1.53 **Hexagonal close packing. (a) The stacking sequence of layers ABABA . . . (b) The three dimensional arrangement of atoms which shows the hexagonal pattern more clearly**

the other at 2/3 1/3 1/2 as shown in Fig. 1.54. Many metals such as Mg, Zn, Cd, Ti, Ni, etc. have hcp structure.

Face Centered Cubic Structure

There is another way in which successive close packed planes of the type shown in Fig. 1.52 can be stacked. The first two layers remain in positions A and B as before, but the third layer instead of reverting to the A positions as in hcp arrangement, can be placed on the C positions. The fourth layer is then put on the A positions which are immediately above the atoms in the lowest plane. This gives a stacking of the type ABC ABC . . . , with the pattern repeating at every third layer and is called the face centred cubic structure (Fig. 1.55a).

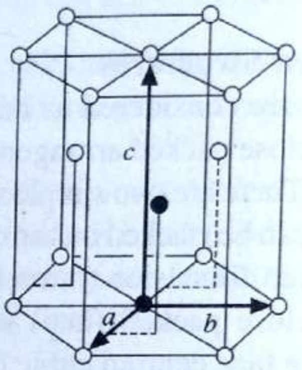


Fig. 1.54 **The hexagonal primitive cell. The two atoms of one basis are shown as solid in the figure. One atom of the basis is at the origin, 000; the other atom is at $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{2}$, which means at $T = \frac{2}{3}a + \frac{1}{3}b + \frac{1}{2}c$**

At first sight there seems to be nothing cubic in it. This is because the close packed layers which have been discussed above do not correspond to the ordinary faces of a cube. A face centred cubic unit cell drawn with conventional cube axes is shown in Fig. 1.55b. As its name implies the structure is the same as the ordinary simple cubic (Fig. 1.50) with the addition of an extra atom at the centre of each cube face. The close packed layers are the body diagonal planes of the cube and one of these is shown in Fig. 1.55c. The fcc structure has in all four equivalent close packed planes as compared to hcp which has only one (basal plane). However, the actual fraction of space filled in fcc and hcp is the same (detail calculation is given in chapter 3). Table 1.11 provides a simple comparison between the two close packed arrangements.

Face centred cubic structures are typical of many metallic elements e.g., Cu, Ag, Au, Al, Ni, Pd and Pt.

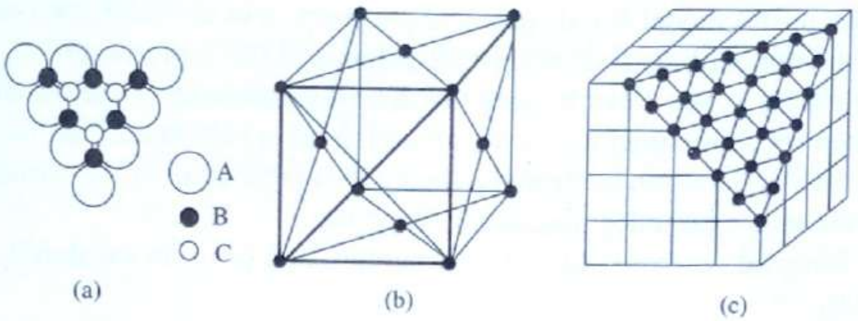


Fig. 1.55 **The face centred cubic structure. (a) Stacking sequence of layers ABCABCA . . . (b) Unit cell based on a cube. (c) Close packed planes of (a) are the body diagonal planes**

Table 1.11 Comparision between two close packed arrangements

Lattice Type	Equivalent Structure	Efficiency	# of possible polytypes	Close Packed planes	Close Packed directions
HCP	2H	74%	Theoretically Infinite	{0001}	$\langle 11\bar{2}0\rangle$
FCC	3C	74%	Only one (3C)	{111}	<110>

Other Cubic Structures

We saw above that many metallic elements solidify in one of the structures described above. However, there are several other elements, e.g. As, Sb, Bi, S, Se, Te, I and Mn and many compounds, e.g. InSb, GaAs and GaP which are found to have other structures. Some of these structures are derivatives of the cubic structures and are briefly discussed in the following.

Diamond Structure

The crystal structure of diamond can be derived from the fcc lattice although the structure itself is not a close packed one. Formally it may be described as being built up from two interpenetrating fcc lattics which are displaced with respect to one another along the body diagonal of the cube by one quarter of the length of the diagonal (Fig. 1.56a). While this definition accurately describes the position of the atoms, it is not very useful when one actually visualizes the

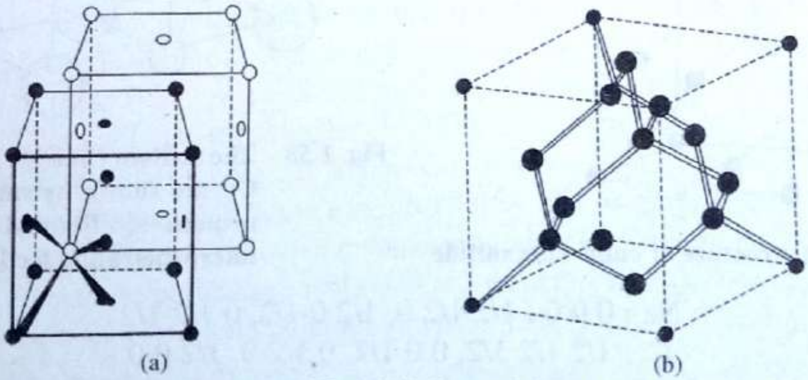


Fig. 1.56 **The diamond lattice showing (a) How it is formed from two interpenetrating fcc lattices. (b) The tetrahedral arrangement of atoms**

structure. A more useful model for all practical purposes is to consider each atom to be at the centre of a tetrahedron with its four nearest neighbours at the four corners of that tetrahedron (Fig. 1.56b). From Fig. 1.56a it can be seen that if the central atom of the tetrahedron is on one fcc sublattice then the four corner atoms are all on the other sublattice. Further, since all atoms are equivalent, each of them can be treated as being the centre atom of the tetrahedron, although it would require a rather extended diagram to show this.

Apart from diamond (carbon), silicon, germanium, and grey tin crystallize in the form of diamond structure.

Zinc Blende Structure

If the two interpenetrating lattices (as considered for the formation of diamond structure) are of two different elements, the atoms on different sublattices are no longer equivalent. However, they still produce a similar tetrahedral arrangement. This is then called the zinc blende (ZnS) structure (Fig. 1.57). Thus zinc blende has equal number of zinc and sulfur ions distributed on a diamond lattice so that each has four of the opposite kind as nearest neighbours. It is typical of the 3–5 semiconducting crystals such as InSb, GaAs, GaP.

Sodium Chloride Structure

Sodium chloride (NaCl) consists of equal number of sodium and chlorine ions placed at alternate points of a simple cubic lattice (Fig. 1.58) in such a way that each ion has six of the other kind of ions as nearest neighbours. This structure can be described as a face centred cubic lattice with a basis consisting of a sodium ion and a chlorine ion separated by one half the body diagonal of a unit cube. There are four units of NaCl in each cube, with ions in the positions:

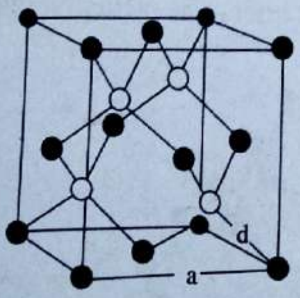


Fig. 1.57 Crystal structure of cubic zinc sulfide

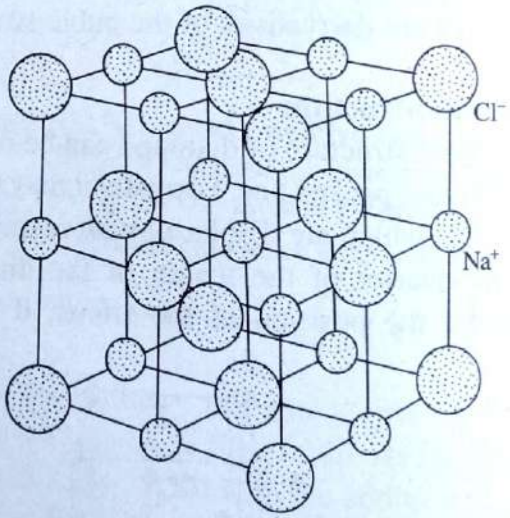


Fig. 1.58 The sodium chloride structure. Na^+ and Cl^- are shown by small and big circles respectively. Big and small circles from interpenetrating fcc lattice

Na : 0 0 0 , 1/2 1/2 0, 1/2 0 1/2, 0 1/2 1/2
Cl : 1/2 1/2 1/2, 0 0 1/2, 0 1/2 0, 1/2 0 0

Large number of compounds including other alkali halides crystallize in this form and are said to have rock salt structure.

Cesium Chloride Structure

Like sodium chloride, cesium chloride (CsCl) also consists of equal number of cesium and chlorine ions. However, in this case, one type of ions are situated at the body centred positions (Fig. 1.59) so that each ion has eight other ions as nearest neighbour. The translational symmetry of this structure is the same as that of simple cubic lattice and therefore cesium chloride structure can be described as a simple cubic lattice with a basis consisting of a cesium ion at the origin (000) and a chlorine ion at the cube centre (1/2 1/2 1/2). The cesium chloride structure is shared by cesium bromide and cesium iodide.

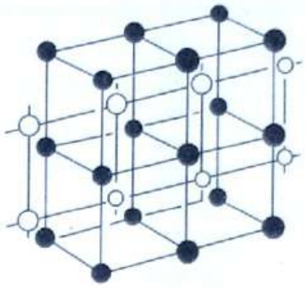


Fig. 1.59 **The cesium chloride structure • and O represents two different ions which form interpenetrating simple cubic lattice**

In Table 1.12, we enlist for convenience the most common crystal structures and the lattice constants of various elements.

Table 1.12 Crystal structures and lattice parameters

Element	Symbol	Crystal structure	Lattice Parameters	
			a (Å)	*c* (Å)
Actinium	Ac	fcc	5.31	
Aluminium	Al	fcc	4.05	
Americium	Am	hex		
Antimony	Sb	rhomb.		
Argon	Ar	fcc	5.31	
Arsenic	As	rhomb.		
Astatine	At			
Barium	Ba	bcc	5.02	
Berkelium	Bk			
Beryllium	Be	hcp	2.27	3.59
Bismuth	Bi	rhomb.		
Boron	B	rhomb.		
Bromine	Br	complex		
Cadmium	Cd	hcp	2.98	5.62
Calcium	Ca	fcc	5.58	
Californium	Cf			
Carbon	C	diamond	3.567	
Cerium	Ce	fcc	5.16	
Cesium	Cs	bcc	6.045	
Chlorine	Cl	complex		
Chromium	Cr	bcc	2.88	
Cobalt	Co	hcp	2.51	4.07
Copper	Cu	fcc	3.61	
Curium	Cm			

(Contd.)

$$a^2 \sin^2 60° = h^2 + \frac{a^2}{9} \sin^2 60°$$

or

$$\frac{h}{a} = \frac{\sqrt{2}}{\sqrt{3}} = 0.8165 \tag{9}$$

or

so that,

$$\frac{c}{a} = \frac{nh}{a} = 0.8165 \times n \tag{10}$$

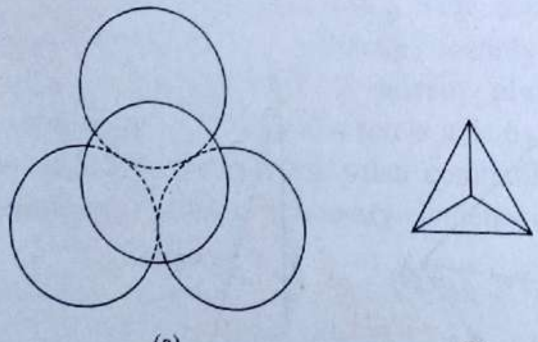
The ratio c/a is known as axial ratio, for an ideal close packed structure its value must be an integral multiple of 0.8165.

In cubic close packing, we know the layers...*ABC*... are stacked along [111] direction (body diagonal) of the unit cell. Therefore, the body diagonal of the cubic unit cell must be equal to $3h$. If the side of the cube is a_c then the body diagonal will be $\sqrt{3}a_c$ (which is equal to $3h$). Therefore, $a_c = \sqrt{3}h = \sqrt{2}a$ from eq. 9, where $a = 2R$ = the diameter of the sphere. Thus, the lattice parameter of an fcc unit cell is $\sqrt{2}$ times the diameter of the sphere.

3.6 VOIDS IN CLOSE PACKING

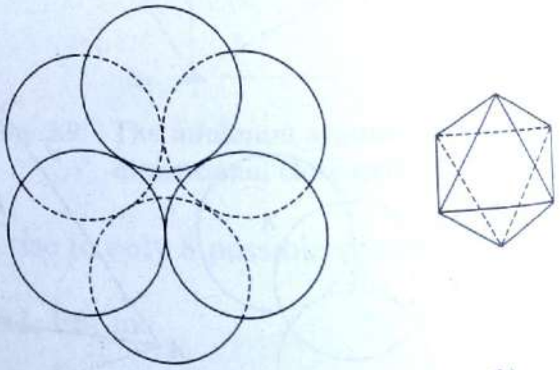
Classification of Voids

There are two kinds of voids that occur in close packing. If the triangular void in a close packed layer has a sphere directly above it, the resulting void will have four spheres around it as shown in Fig. 3.11a. These spheres are arranged on the corners of a regular tetrahedron (Fig. 3.11b), such a void is called tetrahedral void. On the other hand, if a triangular void pointing up in one close packed layer is covered by a triangular void pointing down in the next layer, the resulting void will be surrounded by six spheres (Fig. 3.12a). These spheres are arranged on the corners of an octahedron, such a void is known as an octahedral void and is shown in Fig. 3.12b. Thus in three dimensions, where the possible close packed sequences are theoretically infinite, there are two kinds of possible voids.



(a) (b)

Fig. 3.11 (a) A tetrahedral void (b) Projection of centre of spheres



(a) (b)

Fig. 3.12 (a) An octahedral void (b) Projection of centre of spheres

The number of these voids in a three dimensional close packing of sphere is surrounded by three *B* voids and three *C* voids (Fig. 3.7). When the next layer is placed on the top of this, three voids of one kind are occupied and the other three are not. Thus first three become tetrahedral voids and the other three become octahedral voids. Similarly, the close packed layer below the *A* layer gives rise to three tetrahedral and three octahedral voids. Further, the reference sphere also covers a triangular void in layer above it and another in the layer below it. There are thus two more tetrahedral voids. Each sphere is therefore surrounded by 3 + 3 + 2 = 8 tetrahedral voids and 3 + 3 = 6 octahedral voids. Since the total number of spheres and voids in a close packing is very large and difficult to calculate. However, it is possible to find the average number of voids of each kind belonging to a sphere.

As we know that each octahedral void is surrounded by six spheres and each sphere in turn is surrounded by six voids, therefore, the number of octahedral voids belonging to a sphere is given by the ratio,

$$\frac{\text{Number of octahedral voids around a sphere}}{\text{Number of spheres around an octahedral void}} = \frac{6}{6} = 1$$

Similarly, each tetrahedral void is surrounded by four spheres and each sphere is surrounded by eight tetrahedral voids. Therefore, the number of tetrahedral voids belonging to a sphere is given by the ratio,

$$\frac{\text{Number of tetrahedral voids around a sphere}}{\text{Number of spheres around a tetrahedral void}} = \frac{8}{4} = 2$$

This follows that:

(i) There are as many octahedral voids as there are spheres, and (ii) There are twice as many tetrahedral voids as there are spheres.

3.7 SIZE AND COORDINATION OF THE VOIDS

In Two Dimensions

Referring to the close packed arrangement of equal spheres in a plane as shown in Fig. 3.7, we find that one particular void (*B* or *C* type) is surrounded by three spheres and hence its coordination number is 3. The size of the planar void can be determined simply by measuring the radius of the sphere that would just fit into the void. Consider one such arrangement as shown in Fig. 3.13. Let *r* be the radius of the central sphere which just fits into the void and *R* be the radius of the coordinating spheres. From the simple construction in Fig. 3.13, we have

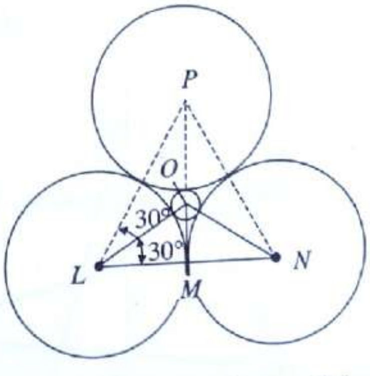


Fig. 3.13 A planar void

$$\frac{LM}{LO} = \frac{R}{R+r} = \cos 30^\circ$$

or

$$r = \frac{R}{\cos 30^\circ} - R = \frac{2}{\sqrt{3}}R - R = 1.155R - R \qquad (11)$$

or

$$r = 0.155\,R$$

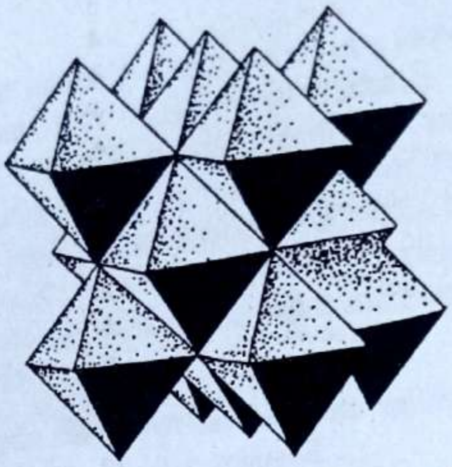


Fig. 3.22 **An octahedral representation of cubic close packing**

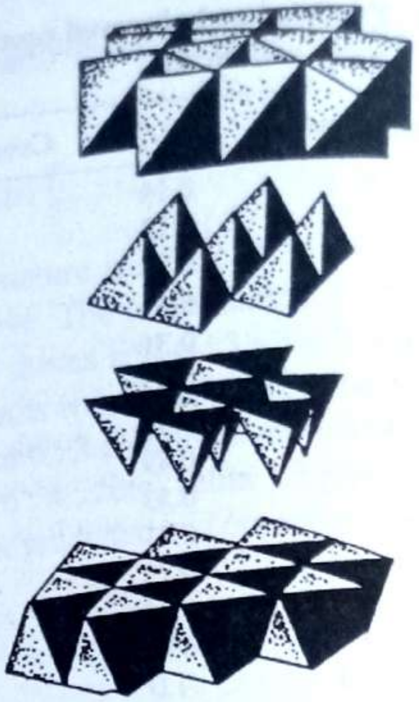


Fig. 3.23 **An exploded view of a hexagonal close packing**

scheme shown above. This kind of representation was first employed by Pauling, who showed that definite rules govern the packing of such polyhedra. These rules are called Pauling's rule and are discussed below.

3.11 PAULING'S RULE

In section 3.9, we discussed the effect of radius ratio on coordination numbers and vice-versa. In fact, a definite relationship between the ionic sizes and the coordination numbers of ions have been found to hold in many compounds occurring in nature. Thus certain cation-anion combinations always form similar arrangements which persist with little change from one compound to another. Therefore, one can think of many such compounds as being composed of coordination polyhedra of anions surrounding a cation at their centres. For example, the largest single group of naturally occurring compounds are silicates, having structures that are based on packing arrangements of SiO_4 polyhedra. Based on the observation of such packing arrangements, Pauling postulated a set of rules that determine the nature of possible arrangements. Although these rules apply strictly to ionic compounds only, they can be applied to other compounds also with slight modifications. Notable exceptions are metals and organic compounds. Pauling's rules are as follows:

1. A coordination polyhedra of anion is formed about each cation. The cation-anion distance is determined by the sum of the respective radii, and the coordination number is determined by the radius ratio.
2. In a stable structure, the total strength of the valency bonds that reach an anion in a coordination polyhedron, from all neighbouring cations, is equal to the total charge of the anion.
3. The polyhedra in a structure tend not to share edges, and in particular not faces, common to two polyhedra. If edges are shared, the shared edges are shortened.

4. Since sharing of polyhedron elements decreases the stability of a structure, cations with high valency and small coordination numbers tend not to share polyhedron elements with each other.
5. The number of essentially different kinds of atoms in a structure tend to be small. This is so called rule of parsimony.

The polyhedra which result from connecting the centres of the anions surrounding a central cation are called anion polyhedra, or in the more general case of atoms (instead of ions), it is called simply coordination polyhedra. The limiting case, i.e., the close packing of equal spheres (equal size atoms) has been discussed in the previous section. The coordination polyhedra for hcp and fcc arrangements are shown in Fig. 3.24. The coordination polyhedron for both bcc packing and cubic coordination is simply a cube. However it should be remembered that, by convention, the description, bcc is reserved when all atoms are of equal size.

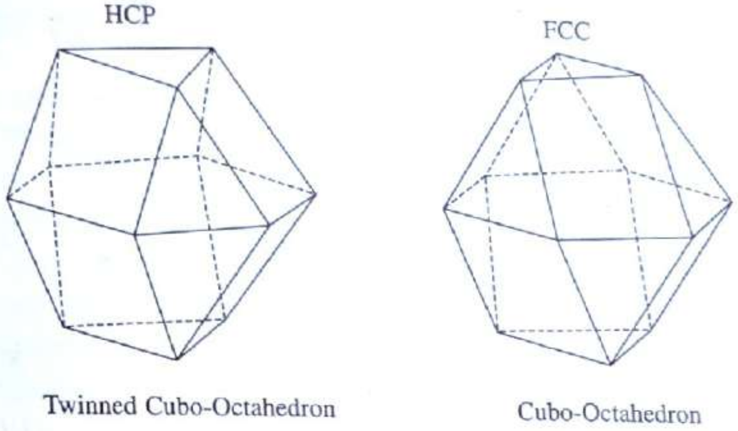


Fig. 3.24 Coordination polyhedra for hcp and fcc packing

3.12 APPLICATION OF PAULING'S RULE TO ACTUAL STRUCTURES

Let us apply the above rules to ionic structures. It is possible to gauge the ionic nature of a structure by the extent to which Pauling's rules are satisfied. Rule 1 is simply a concise statement of the radius ratio effect already discussed. Rule 2 can be equivalently stated as: In a stable structure, local charge neutrality must be maintained. In ionic crystals, we observe that the anions are surrounded by the cations and vice-versa. In this situation, it is necessary to estimate the amount of positive charge that is effectively associated with each cation-anion bond. For a cation M^{m+} surrounded by n anions, X^{x-}, the electrostatic bond strength (e.b.s.) of the cation-anion bond is defined as

$$e.b.s = \frac{m}{n} \tag{17}$$

Further, for each anion, the sum of the electrostatic bond strengths of the surrounding cations must balance the negative charge on the anion, i.e.

$$x = \Sigma \frac{m}{n} \tag{18}$$

Semicrystalline (Polycrystalline) Solids

A solid consisting of many crystallites grown together in the form of an interlocking mass, oriented randomly and separated by well defined boundaries is said to be a polycrystalline solid (Fig. 1.4). In general, the grains in such a solid are not related in shape to the crystal structure, the surface being random in shape rather than well defined crystal planes. A great majority of solids occurring in nature such as rock, sand, metals, salts, etc. are of polycrystalline structure. However, they can be grown as a single crystal under suitable conditions. Due to random distribution of crystallites, a polycrystalline solid is isotropic, i.e. its properties are same, on an average in all directions.

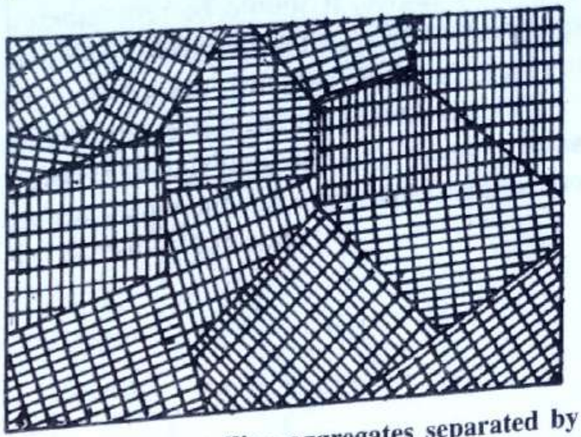


Fig. 1.4 Polycrystalline aggregates separated by well defined boundaries

Noncrystalline (Amorphous) Solids

A class of solids showing neither reticular nor granular structure is termed as noncrystalline or amorphous solid. In other words, an amorphous solid is the opposite extreme of a single crystal. Glass and plastic are common examples of this class. Other common substances include, resin, pitch, sugar candy, etc. A typical feature of these substances is that they have no definite melting points. As their temperature is raised, they gradually become soft, their viscosity drops, and begin to behave like ordinary viscous liquids. Observations reveal that an amorphous body may get crystallized with the passage of time. For instance, crystals of sugar are formed in sugar candy after a certain time has passed. In exactly the same way, glass "ages" i.e. polycrystalline grains are formed in it. When this happens, the glass loses its transparency and becomes brittle.

1.2 PERIODICITY IN CRYSTALS

Space Lattice and Translation Vectors

The property that distinguishes crystals from other solids is that the constituent particles (atoms, ions or molecules) in crystals are arranged in a three dimensional periodic manner. In order to describe the periodicity in crystals, in 1848 Bravais introduced the concept of space lattice. To understand the concept clearly, let us consider the translation of an object (symbolized by the letter J) to a finite distance (say a) and then repeated systematically along three crystallographic directions, x, y and z to obtain three dimensional space lattice. Since a translation operation repeats an object infinite number of times in one direction, therefore using such an operation a one dimensional periodic array (infinite linear array) of J's can be obtained (Fig. 1.5a). Further, since the nature of the repeated object in Fig. 1.5a does not affect the translational periodicity,

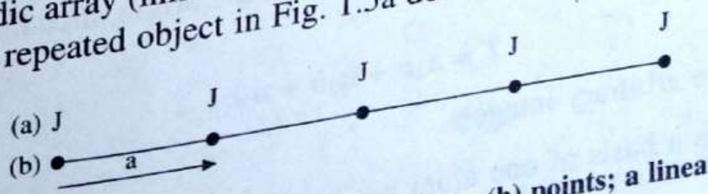


Fig. 1.5 One dimensional array of: (a) objects, (b) points; a linear lattice

Polymorphism

Two possible polymorphs of ZnS shown in Figs. 3.31 and 3.32 have been found to occur in nature. The hexagonal polymorph is the mineral wurtzite, and the cubic one is called the sphalarite or zinc blende. Polymorphism is exhibited by a number of substances.

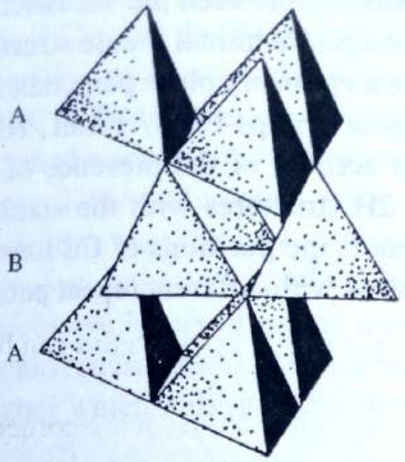


Fig. 3.31 Packing of zinc tetrahedra in α-ZnS (wurtzite)

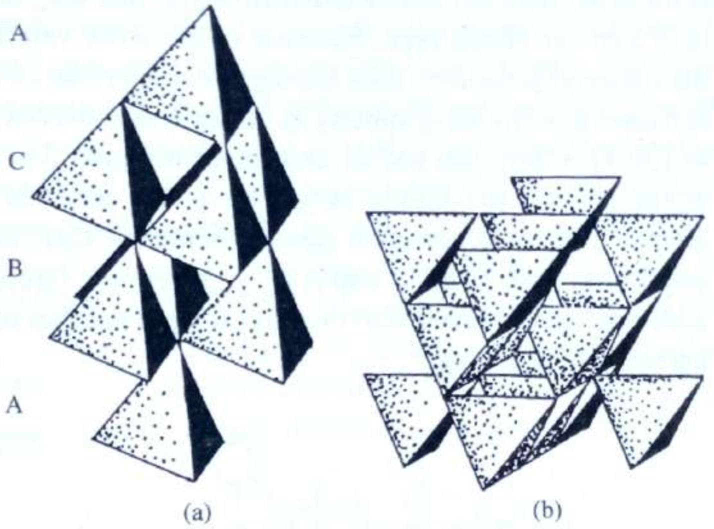


Fig. 3.32 Packing of zinc tetrahedra in β-ZnS (sphalerite). (a) [111] vertical (b) [001] vertical

Any substance in general, can exist in the solid, liquid, or the gaseous state, depending on the conditions of temperature and pressure. Similarly, a chemical substance grown from solution, melt or vapour can crystallize in more than one possible structural modifications, depending on the conditions of temperature and pressure prevailing at the time of growth. This phenomenon of the same chemical substance crystallizing in more than one structure (crystallographic modifications) is known as polymorphism. The different modifications are called the polymorphs or polymorphic modifications of that substance. They can be obtained from solid state phase transformations also. Polymorphism therefore includes every possible difference in the crystalline structures of a substance of constant chemical composition, except homogeneous deformations.

Since the different modifications have the same chemical composition they have similar chemical properties; but their physical properties, like density, specific heat, conductivity, melting point, and optical behaviour, which depend on the arrangement of atoms in the structure may be widely different.

Atomic Packings in AB_2 (or MX_2 – type) Compounds

Cadmium Iodide Structure

Cadmium iodide is known to be an ionic compound, the ionic radii of Cd and I being 0.97Å and 2.16Å, respectively. The structure consists of a close packing of the I ions with the Cd ions distributed among the voids. The radius ratio $r_{Cd}/r_I = 0.45$ permits the Cd ions to occupy the octahedral voids, the composition then requires a 6 : 3 coordination of Cd and I ions. Since there are only half as many Cd ions as I ions in the structure, only one-half of the total voids are occupied. The Cd ions form close packed layers, occupying alternate layers of octahedral voids