

## Crystal Types and Crystal Binding

Our aim is to discuss what holds the atoms of a crystal together, or in other words, how the atoms stay together to form a solid. For this, we should consider the nature of the forces acting between atoms or molecules in the solids. Just by casual thinking we may draw two general conclusions from the very existence of solids : firstly, there must act attractive forces between the atoms or molecules in a solid which keep them together and secondly, there must also be the repulsive forces between them since large external pressures are required to compress a solid to any appreciable extent. In order to understand the importance of both types of forces, let us consider the simplest system in this respect, namely a single pair of atoms which forms a stable chemical compound and consider its total potential energy when they are at distance  $r$  apart. Clearly, it is the sum of individual energies of the atoms and its interaction energy. We shall choose the zero of potential energy when the atoms are in their ground state and infinitely far apart so that they do not interact with each other i.e. we let  $U = 0$  for infinite separations of the ground state atoms. Consider now that the two atoms are brought together and ' $r$ ' is the distance between them. Clearly, if the assembly of the two atoms is to be more stable at this distance, then its potential energy must be less than zero. This means that the total potential energy must be negative and that it should be proportional to some power of the distance ' $r$ '. Now, there are essentially two interactions mentioned above : the attraction and the repulsion. The potential energy of attraction is negative because the atoms do the work of attraction. Also, this is proportional to some power of ' $r$ ' so that

$$U_{\text{attract}} = - \frac{A}{r^m} \quad \dots(1)$$

where  $A$  is the attraction constant. Clearly, at large separations this is zero, but decreases gradually at shorter distances according to the curve shown in fig. 1 (a). The potential energy of repulsion is, however, positive because external work must be done to bring the atoms together, when they repel each other. Normally, this repulsion is insignificant until the atoms are so close to each other that the outer electrons of each atom can interact. Its magnitude is also inversely proportional to some power of ' $r$ ' (but not necessarily the same power), so that

$$U_{\text{repul}} = \frac{B}{r^n}, \quad \dots(2)$$

where  $B$  is the repulsion constant. It increases more rapidly, as shown also in fig. 1 (a), than the attractive potential because the positive charges on the nuclei repel each other very strongly when  $r$  becomes small. The total potential energy is then given as

$$U = U_{\text{attract}} + U_{\text{repul}} = -\frac{A}{r^m} + \frac{B}{r^n} \quad (3)$$

and is represented in fig. 1 (a) by the solid curve. The constants  $A, B, m$  and  $n$  entering into this equation are characteristics of the molecule.

The force between the atoms can now be written

$$F = -\frac{dU}{dr} = -\frac{mA}{r^{m+1}} + \frac{B}{r^{n+1}} \quad (4)$$

This is shown plotted in fig. 1 (b). The solid curves in fig. 1 have now the following meaning : At large separations, the atoms do not interact with each other so that  $U = 0$ . As the atoms approach each

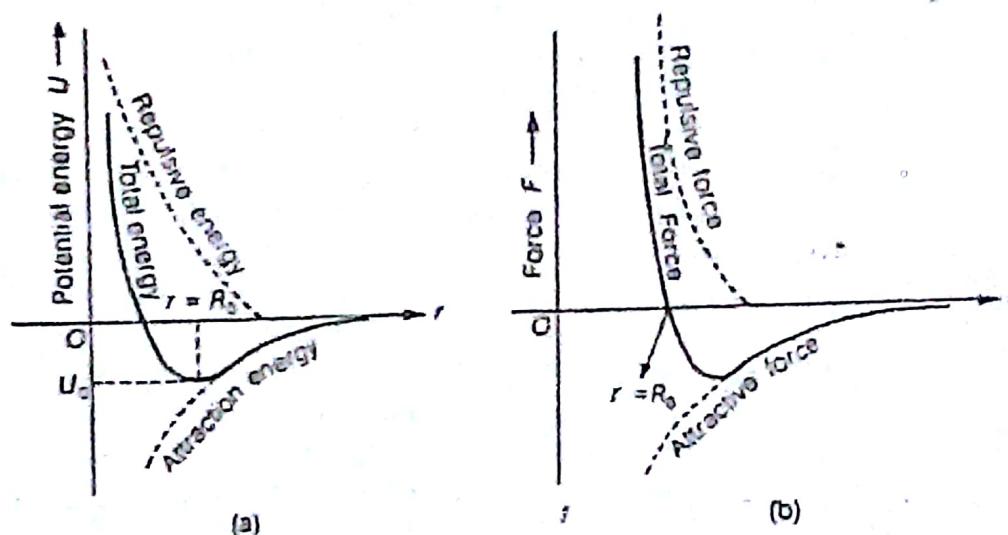


Fig. 1.

other, they experience attractive forces due to each other, primarily because of the attraction of positive and negative charges in the atoms. As the interatomic separation decreases to the order of one to two atomic diameters, the attractive forces start to become appreciable and, also, the repulsive forces come into play. The repulsive forces arise as a consequence of the Pauli exclusion principle (as will be explained later) and has the effect of increasing the potential energy ; since this increase is not consistent with the stability of the system, the further reduction in the interatomic separation is checked. At still smaller distances the energy is dominantly repulsive. It is thus now quite clear that because of the repulsive forces the atoms cannot reduce their interatomic separation in an arbitrary fashion. This result illustrates the importance of the repulsive forces : without their being, the atoms would ultimately interpenetrate into each other because of the increasing attractive forces and would occupy the same site. How fantastic result would that be ! Essentially, the equilibrium is then established only when a compromise between the attractive and repulsive forces is reached so that  $F$  is equal to zero. It is seen from the figs. 1 that the compromise occurs at  $r = R_0$ , and this situation corresponds to a minimum in the energy curve at this point. The system is thus most stable at this distance. This distance is called the equilibrium separation. It may be added that this minimum in the energy curve is possible only if  $n >> m$ . This may be shown

by employing the condition  $\left(\frac{d^2U}{dr^2}\right)_{=R_0} > 0$  which is the condition for the energy minimum. From this

we conclude that the formation of a chemical bond requires that the repulsive forces be of shorter range than the attractive ones.

The energy corresponding to  $R_0$ , denoted by  $U(R_0)$ , is called the binding energy or the cohesive energy of the molecule. Clearly, it is the energy required to remove the two atoms into an infinite separation. More generally speaking, the binding energy is the energy necessary to dissociate the solid into separated atoms, molecules, or ions as appropriate. These are of the order of one or a few electron volts in magnitude.

So far the discussion has been quite general ; to discuss the matter further, we should know the exact estimates of the two terms appearing in equation (3) and their origin in detail. This essentially requires that the detailed nature of the charge distributions in the different atoms be known, particularly that of the outer (valence) electrons. Various types of distributions can be recognised in different crystals. In some crystals, the valence electrons are transferred from one atom to another. In others, the valence electrons are shared equally between neighbouring atoms rather than being transferred from one atom to another. Another possibility is that the valence electrons are free to wander at will throughout the crystal. Crystals may even be formed by molecules which retain their electrons substantially in the same configurations as in the free molecules. Each type of distribution produces characteristic electronic and mechanical properties. Based on this distribution, the solids may be roughly classified into five major types. These are :

1. Ionic crystals such as sodium chloride (transfer of valence electrons) ;
2. Covalent crystals of which diamond a good example (sharing of valence electrons) ;
3. Metal crystals (valence electrons essentially free) ;
4. Molecular crystals such as solid nitrogen (electrons remain associated with original molecules).
5. Hydrogen-bonded crystals such as ice.

This classification is somewhat arbitrary ; many solids fall into intermediate categories, i.e. they cannot be put with precision into any one of these five classes. An example is CuO, which is partly ionic and partly covalent in character. We shall now discuss each of these crystal types turn by turn.

### Ionic Crystals

The ionic crystals are those compounds in which valence electrons are completely transferred from one atom to other; the final result being a crystal that is composed of positively and negatively charged ions. The atoms which give up electrons are called electropositive atoms and are usually metal atoms : Na, K, Ca. The atoms which acquire electrons are called electronegative atoms and are non-metallic atoms such as O, F, Cl. The NaCl crystal is a good example of this class. It may be considered as to be built up of  $\text{Na}^+$  ( $1s^2 2s^2 2p^6$ ) and  $\text{Cl}^-$  ( $1s^2 2s^2 2p^6 3s^2 3p^6$ ) ions. The source of cohesive energy that binds the crystal together is largely the coulomb electrostatic interaction between these ions. The ions arrange themselves in such a way that the coulomb attraction between ions of opposite sign is stronger than the coulomb repulsion between ions of the same sign. The magnitude of the cohesive energy is about 5–10 eV per molecule ; for NaCl its value is 7.8 eV. On account of such a strong binding, the ionic crystals are hard and have a relatively high melting point; for NaCl it is 801°C. They are quite poor electrical conductors at normal temperatures because the valence electrons are bound quite tightly to the ionic nuclei. At elevated temperatures however, the ions themselves become mobile and ionic conductivity results. They are usually transparent to visible light, while exhibiting a single characteristic optical reflection peak in the far infrared region of the spectrum. These crystals are often quite soluble in ionizing solvents such as water, the solutions being highly dissociated into free ions.

## Crystal Types and Crystal Binding

The positive and negative ions have the same electronic structure as the nearest inert gas atoms, except that they are electrically charged. In the above example  $\text{Na}^+$  have the neon electron structure and  $\text{Cl}^-$  have argon electron structure. The charge on the ions is therefore spherically distributed (with some distortion near the region of contact with neighbouring atoms, of course) and an ion is thus not unlike a small charged sphere and the packing of ions is a closest one. Because ions having like charges repel each other, a stable packing is obtained in which each ion is surrounded with ions having an opposite charge. A periodic array results in which the environment of all similar atoms is the same and the sum of all positive and negative charges adds up to zero, so that the ionic solid is electrically neutral. They usually crystallize in the relatively close-packed  $\text{NaCl}$  and  $\text{CsCl}$  structure; the structure actually depends upon the radius ratio of the two ions.

All alkali halides, alkaline oxides, etc. are the examples of ionic crystals.

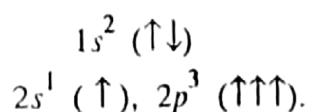
## Covalent Crystals

Covalent crystals are those crystals in which the valence electrons are shared equally between neighbouring atoms rather than being transferred from one atom to another, as is the case in ionic crystals. There is thus no net charge associated with any atom of the crystal. This occurs between atoms having lack of one or more electrons from having a closed outer shell in the following manner : Suppose two such similar or identical atoms are brought together to such an interatomic separation that the orbital of one of the unpaired electrons begin to overlap with that of one in the other atom. The original atomic charge distributions are then deformed in such a way that the unpaired electron charge of each atom is transferred into the space between them, as is illustrated for two chlorine atoms below :



Note that the two electrons lying between the two chlorine atoms belong equally to both and serve to complete the outer shells of both atoms. This is what we mean by 'sharing'. Now if the sharing electrons have antiparallel spins, the atoms attract each other and the bonding results. This is the covalent bond. Since the valence of both atoms forming this bond is the same, it is also called the valence bond.

Unlike the ionic bond, the covalent bond is strongly directional since the bonding electron-pair is concentrated along the line joining the two atoms under consideration. (Recall that in ionic crystals the bonding electrons are in tight spherical shells and thus the ionic bond have no directionality character). It would, therefore be meaningful in this case to consider the number of bonds that an atom can form when present in the crystal. Obviously, this number is determined by the number of unpaired electrons associated with the atom. The later number is determined by  $8-N$  rule, where  $N$  is the number of the column in the periodic table containing the atom. Thus fluorine ( $1s^2 2s^2 2p^5$ ) can form one bond, oxygen ( $1s^2 2s^2 2p^4$ ) can form two bonds, nitrogen ( $1s^2 2s^2 2p^3$ ) three, and so forth. The bonds in these atoms are formed by an overlap of the  $2p$ -orbitals of the unpaired electrons. There is a difficulty in case of carbon, however : according to the  $8-N$  rule it can form four covalent bonds, even though there are only two unpaired electrons in the ground state of carbon ( $1s^2 2s^2 2p^2$ ). To resolve this difficulty, the energies of the  $2s$ - and  $2p$ -states are considered. It turns out that the energy difference between these states is very small, so that a carbon atom can distribute its electrons as follows :



That is, one of the  $2s$ -electrons is considered excited to a  $2p$ -state. We now have four unpaired electrons in the so-called  $sp^3$  hybrid state. The four orbitals of the  $sp^3$  hybrid are elliptical and are directed towards the four corners of a tetrahedron, as shown in fig. 2. Thus, each carbon atom in a diamond crystal is tetrahedrally coordinated by four other carbon atoms.

As might be expected, the covalent crystals are very strongly bound. The binding energy of carbon in diamond is 7.4 eV. On account of this, covalent crystals are usually hard, brittle materials with high melting points (3280°K for diamond). Also, because the valence electrons are localized in the bonds by fairly strong forces, electrical conductivity is normally not possible and as such these crystals are insulators at ordinary temperatures. Ionic conductivity at elevated

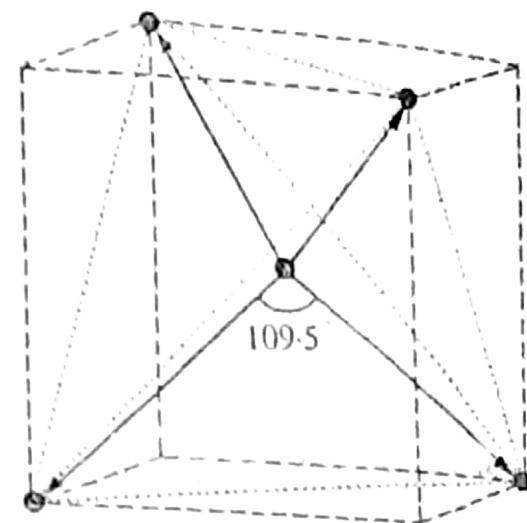


Fig. 2. Tetrahedral directions and tetrahedral coordination in a diamond crystal.

temperatures is similarly not possible. In some crystals in which the electronic binding forces are weaker than in others, a limited amount of electronic conductivity is possible at temperatures sufficiently high enough to free some of the valence electrons. They are typically semiconductors, whose electrical conductivity is also quite sensitive to the presence of small amounts of impurity atoms, and increases with rising temperatures in the sufficiently high temperature range. They are transparent to long-wavelength radiation, but opaque to shorter wavelengths, the transition being abrupt and occurring at a characteristic wavelength, usually in the visible or near-infrared region of the spectrum.

Other examples are : Si, Ge,  $\alpha$ -Sn.

## Metal Crystals

In metal crystals the valence electrons of the constituting atoms are free to move about throughout their crystal. They do not promote the formation of any permanent bond between atoms. Thus, we can picture a metal crystal as a frame-work of the positive ions (*i.e.* atoms which give up their valence electrons) plus a gas of free electrons (called a free-electron gas) permeating this framework. The crystal is held together largely by the electrostatic attraction between the negative electron gas and the positive metal ions. This model for metals, called the 'free-electron model', was first proposed by Drude at the beginning of the twentieth century to account for the high electrical and thermal conductivities of metals which are the characteristic properties of the metals, and several other properties too. Let us now understand the modern term origin of this model.

First consider the two sodium atoms ( $Z=11$ ; each atom containing one unpaired  $3s$  electron) approaching towards each other, and eventually assuming such interatomic separations that their  $3s$ -orbitals begin to overlap. If the spins of the two  $3s$ -electrons are now of opposite sense, then one electron-pair bond is formed between the two atoms. Now suppose that a third sodium atom, also having an unpaired  $3s$  electron approaches this pair. Since both the  $3s$  quantum states are already occupied, this atom must experience repulsion in accordance with the Pauli's exclusion principle. But since the energy of the unoccupied  $3p$ -states is very nearly the same as the energy of a  $3s$ -state, the third electron can go into this state without violating the Pauli's exclusion principle. Consequently it can also form an electron pair bond with either of the two other valence electrons. In this way, a very large number of atoms can thus surround a single sodium atom. Since the central atom has only one unpaired electron, this electron must take turns to form electron-pair bonds with each neighbour. Consequently, it forms less than a whole

electron-pair bond with each neighbour. The situation can be understood well with reference to solid sodium. It has b.c.c. structure, so that on the average, each sodium atom forms one-eighth of an electron-pair bond with each of its neighbours. Essentially such bonds are incomplete or unsaturated covalent bonds.

With the formation of such bonds, the valence electrons of each atom in a crystal spend only a part of the time between any two atoms, and during the rest of the time, migrate from atom to atom throughout the crystal and form bond with other atoms. Under such circumstances, the valence electrons cannot be associated with any one nucleus and hence behave in the crystal as if almost free and forming a gas penetrating the lattice of positive ion cores. We are thus having the same picture of metals as mentioned above.

Since the metallic bond is essentially a covalent bond, but without saturation, it is much less directional than the covalent bond and thus the main reason for a metal adopting a particular structure is associated with the packing efficiency. Metals are therefore closely packed. In some respects the bond resembles the ionic bond. But it is not as strong as either. The low melting point, softness, high ductility and malleability of most metals bear out this expectation. The binding energies of sodium and aluminium, for example, are 1.13 and 3.23 eV respectively. The density of electrons between atoms is much lower than is allowed by the Pauli's exclusion principle. This allows electrons to move fairly freely inside the metals without a significant increase in their energy. Further, the lack of quantum restriction on the electrons also removes any restriction on the kind of neighbour a metallic atom can have. Thus metals have the characteristics of forming alloys.

### Molecular crystals

Molecular crystals are composed of atoms or molecules which have no tendency to lose or even share their valence electrons with other molecules in the solid. These are the crystals of solidified gases such as oxygen, nitrogen, hydrogen, the inert gas solids and their materials normally occurring as gases. The binding in these crystals arises solely from dipolar forces between the atoms or molecules of the crystal. It may be noted that although such an atom or molecule is not a permanent dipole, i.e., it has no time-average dipole moment, it will in general have an instantaneous, fluctuating dipole moment in the presence of other atoms. It is primarily due to non-uniformities in the electrostatic charge distribution which are caused by the momentary shifts of the electrons and nuclei towards the opposite ends of the atom, producing so-called dipoles. This dipole moment is the source of an electrostatic dipole field which in turn may induce a dipole moment in another atom or molecule. The interaction between the original and the induced dipole moment is attractive and can serve to bind a crystal in the absence of ionic or covalent binding. Such type of binding forces (i.e. arising from fluctuating dipole interactions) are called Van der Waal's forces and are usually quite weak. In the case of inert gases these are insufficient to hold two such atoms together for any length of time at room temperature and atmospheric pressure. It is for this reason, of course, that inert gases are monatomic gases under standard conditions. They are crystals under special conditions. When in crystalline form, they are characterised by small binding energy and consequently low melting point and boiling point. They are usually poor electrical conductors.

### Hydrogen-Bonded Crystals

A neutral hydrogen atom has only one electron and is expected normally to form a covalent bond with one other hydrogen atom. However, this is not always so; under certain circumstances the hydrogen atom appears to be attracted by rather strong forces to two other atoms. This is the hydrogen bond. The other atoms involved are electronegative atoms such as oxygen, fluorine and nitrogen. It is believed that the hydrogen bond is largely ionic in character: in the extreme ionic form of the hydrogen bond, the

hydrogen atom gives up its electron to one of the other atoms with the result that there is an equal probability of finding the electron on either atom and the hydrogen ion (or the proton) then tends to draw the two anions more closely together than their normal separation in the crystal. The small size of the proton permits only two nearest neighbours, because the atoms adjacent to the proton are so close that more than two of them would clash with each other's way. Thus hydrogen bond connects only two atoms. Recent diffraction measurements have shown that the proton is not located mid-way between the two anions ; but rather occupies either of two lower-energy positions, each respectively one-third of the way along the interatomic separation.

The binding energy of a hydrogen atom in this manner is of the order of 0.1 eV, so that the hydrogen-bonded crystals are quite weak. A notable example of this type of bond occurs in ice where the water molecules are bound to each other by hydrogen bonds; see fig. 3. Also, it restrains protein molecules to their normal geometrical arrangements. Other examples include hydrogen difluoride ( $\text{HF}_2^-$ ), potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), etc.

High dielectric constant and ferroelectricity in some crystals are the properties associated with hydrogen bonds.

The following table gives the summary of these five crystal types and their properties :

### THE FIVE CRYSTAL TYPES

Type	Representative crystal of the type	Principal cause of Binding	Properties	Occurrence
Ionic Crystals	$\text{NaCl}$	Ionic bond : transfer of electrons between atoms and subsequent attraction between them.	Very strong binding, high melting point, brittle, close-packed structures; good ionic conductors, but poor electrical and thermal conductors. Transparent over wide range of electro-magnetic spectrum.	Group I-VII elements; Group I-VI compounds; Group II-VII compounds.
Covalent crystals	Diamond	Covalent bond : mutual sharing of valence electrons between atoms.	Strongly bound, hard, poor cleavability, loose-packed structures; good electronic semiconductors; transparent in infrared, opaque at higher frequencies.	Group IV elements, Group III-V compounds; Group II-VI compounds.
Metal crystals	$\text{Na, Al}$	Metallic bond : the attraction between the lattice of ion cores and the free electron gas	Moderate to strong binding, softness, ductility, malleability, low melting points, close-packed structures; very good electrical and thermal conductors; opaque to electromagnetic radiation, good reflectors.	Group I and II elements ; heavy elements ; Rare earths,

Molecular crystals	Ne or N <sub>2</sub> (Solid)	Van der Waals attraction : mutual polarization of atoms due to each other.	Weak binding, soft, flaky, lowest melting points; close-packed structures; low electrical and thermal conductivity, transparent.	Group VIII elements; Group VII elements ; Oxygen, Nitrogen, Hydrogen.
Hydrogen-bonded crystals	Ice (H <sub>2</sub> O)	Hydrogen bond : lowering of K.E. of proton by the arrangement O—H—O.	Moderately weak binding, loose structures; low electrical and thermal conductivity, transparent ; peculiar dielectric properties.	Same as above except always contain H and an electronegative element O, F, N, etc.

It must be emphasized once again that this classification is arbitrary : there are some crystals which fall into the intermediate classes. We shall mention these crystals at the appropriate places.

### CALCULATIONS OF BINDING ENERGIES

#### Ionic Crystals

We shall treat a crystal of NaCl. We let  $U_{ij}$  be the potential energy of interaction between ions  $i$  and  $j$  of the crystal. The total energy of interaction between the ion  $i$  and all other ions of the crystal will then be

$$U_i = \sum_j U_{ij}, \quad (6)$$

where the summation includes all ions except  $j = i$ , because there cannot be any binding interaction between the ion  $i$  and itself. Now, according to the general discussion introduced in the beginning,  $U_{ij}$  is

the sum of two terms : one the coulomb energy of interaction  $\pm \frac{e^2}{r_{ij}}$ , where  $r_{ij}$  is the distance between ions  $i$  and  $j$ ; and the other resulting from a repulsive force which becomes appreciable only at very small inter-ionic separations. We now inject here a short explanation of the latter interaction. When the inter-ionic separations are very small, the electron shells of neighbouring ions have a tendency to overlap which means that the electrons from one atom try to occupy, in part, the states of the other atom which are already occupied. The Pauli exclusion principle, however, resists this tendency of overlapping as it prohibits multiple occupancy. This action of the exclusion principle is equivalent to a repulsive interaction. We know that if the repulsive force were not present, the crystal would always have a net coulomb attractive energy, and the ions would then attempt to occupy the same space leading to collapse of the lattice to essentially zero volume ! The repulsive force, therefore, compensates for the effects of the singular coulomb force at small distances and ensures the stability of the crystal. The energy of interaction between ions  $i$  and  $j$  due to this force is usually taken as  $\frac{A}{r_{ij}^n}$ , where  $A$  is a constant of proportionality. It

will turn out later that the exponent  $n$  is a reasonably large number and thus the repulsive interaction is indeed very small at large distances, becoming appreciable only at quite small inter-ionic spacings. We may now write the total energy of interaction between the two ions  $i$  and  $j$  as the sum of the two terms :

$$U_{ij} = \frac{A}{r_{ij}^n} \pm \frac{e^2}{r_{ij}}.$$

**What is Crystallography ? — Space Lattice — Crystal Lattice and Unit Cell — Lattice Parameters of Unit Cell — The Seven Crystal Systems — Bravais' Lattices — Symmetry Elements of a Crystalline Solid — Space Lattices of Cubic System — Calculations of Unit Cell — Crystal Structures of Commercially Important Materials — Coordination Number — Atomic Radius — Number of Atoms per Unit Cell — Density of Packing — Important Plane Systems in a Cubic Crystal — Directions, Planes and Miller Indices — Unit Face and Axial Units — Miller Indices — Miller Indices of Cubic Crystal Planes — Procedure for Finding Miller Indices — Relation Between Interplanar Spacing  $d$  and Cube Edge  $a$  — Important Features of Miller Indices — Crystal Plane and its Normal — Highlights — Can You Answer This ?**

## 4.1. What is Crystallography ?

The study of the geometric form and other physical properties of crystalline solids by using X-rays, electron beams and neutron beams etc. constitutes the science of crystallography.

Crystalline solids are those in which the atoms or molecules are arranged in a very regular and orderly fashion in a three-dimensional pattern. Each atom or molecule is fixed at a definite point in space at a definite distance from and in a definite angular orientation to all others surrounding it. This internal spatial symmetry of atomic or molecular orientation is an essential feature of crystalline state. The angular arrangement of the space positions of the atoms in a crystal is called space lattice or lattice array.

## 4.2. Space Lattice

A space lattice may be defined as an infinite array of points in three dimensions in which every point has surroundings or environments identical to that of every other point in the array.

As an example, let us consider a finite two-dimensional squares array of points shown in Fig. 4.1. If we locate ourselves at any lattice point and look around in the plane of the paper, the scenery is the same irrespective of where we are. Consider the immediate surroundings of a point like A. If we look due North or due East from this point, we see another point at a distance of 1 unit; along North-East, we see the nearest point at a distance of  $\sqrt{2}$  units and along North-North-East, the nearest point is at a distance of  $\sqrt{5}$  units. The environments or surrounding scenery would remain unchanged if we shift our position to another point like B in the array.

Since this would be true for every point in the array, this array when extended infinitely satisfies the definition given above and can be called a two-dimensional square lattice.

The space lattice may be defined in a more rigorous mathematical way as under :

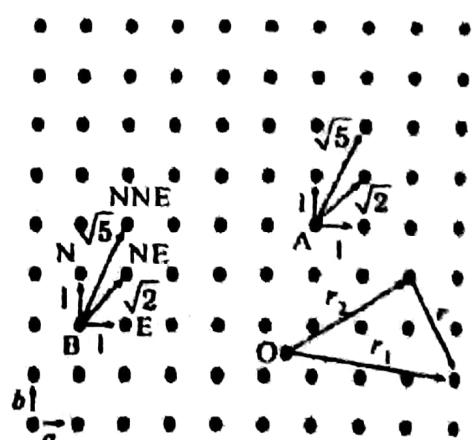


Fig. 4.1

Choose any arbitrary point  $O$  as origin and let vectors  $r_1$  and  $r_2$  join any two lattice points to this origin. The difference  $T$  of the vectors should satisfy the following relation

$$T = n_1 a + n_2 b$$

where  $a$  and  $b$  are the fundamental translation vectors characteristic of the array and  $n_1$  and  $n_2$  are integers. When the above relation is true for all values of  $r_1$  and  $r_2$ , the array of points is a two-dimensional lattice.

Similarly, in a 3-dimensional lattice,  $T = n_1 a + n_2 b + n_3 c$ .

#### 4.3. Crystal Lattice and Unit Cell

The entire lattice structure of a crystal is found to consist of identical blocks or unit cells. The unit cell is the smallest block or geometric figure from which the crystal is built up by repetition in three-dimensions. The unit cell is a parallelepiped by moving which in the direction of each of the coordinate axis  $x$ ,  $y$  and  $z$ , arranged parallel to edges of the figure, the crystal lattice can be constructed. As seen, this process resembles brick laying. It is also known as fundamental elementary pattern because it is repeated again and again to form the lattice structure of a crystal.

In general, a unit cell may be defined as that volume of a solid from which the entire crystal can be constructed by translational repetition in three-dimensions (Fig. 4.2). In fact, unit cell is the smallest part of a crystal having all the structural properties of the given lattice.

If each atom in a lattice is replaced by a point, then each such point is called a *lattice point* and the arrangement of the points is referred to as the (three-dimensional) lattice array. The length of the side of a unit cell is the distance between atoms of the same kind. In the case of pure metals whose crystals have simple cubic structure [Fig. 4.3 (a)], it is equal to the basic distance ' $a$ ' only. However, in the case of crystals of chemical compounds like the cubic crystal of sodium chloride ( $\text{NaCl}$ ), it is twice the distance ' $d$ ' between two adjacent atoms as shown in Fig. 4.3 (b).

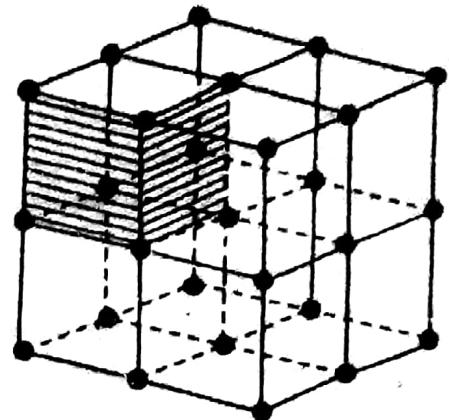


Fig. 4.2

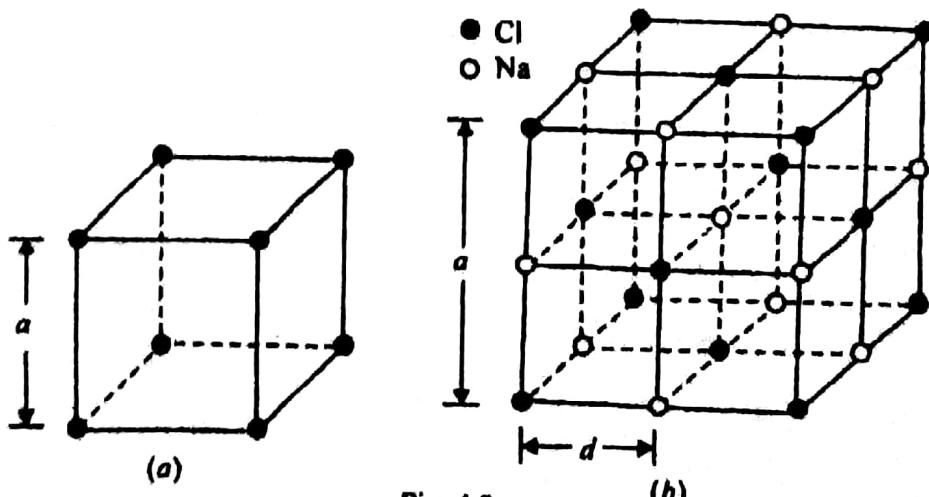


Fig. 4.3

#### 4.4. Lattice Parameters of a Unit Cell

The three sides of a unit cell which are called the  (crystallographic axes) are chosen to have directions such that they pass regularly through the lattice points associated with like-atoms. An arbitrary arrangement of crystallographic axes, marked  $X$ ,  $Y$  and  $Z$ , defining a unit cell is shown

in Fig. 4.4. The angles between the three axes are called *interfacial angles*. The intercepts  $a$ ,  $b$  and  $c$  define the dimensions of a unit cell and are known as its *primitives* or *characteristic intercepts* on the axes. The primitives and interfacial angles constitute the *lattice parameters* of the unit cell. These are also called the geometrical constants of a given crystal substance.

If we know the linear dimensions  $a$ ,  $b$  and  $c$  and also the interfacial angles  $\alpha$ ,  $\beta$  and  $\gamma$ , we know the form and actual size of the unit cell. But if we do not know actual values of primitives but only their ratio and the values of interaxial angles, then we can only determine the form of the unit cell and not its actual size.

In a space lattice, all lattice points may be included in a set of parallel and equally-spaced planes known as *lattice planes*. These planes give the orientations of the possible faces of a crystal of the substance in question. In theory, there are 320 such lattices or space groups divided into 32 crystal classes. These can be arranged in 7 crystal systems which are characterised by three symmetry elements : (i) the plane of symmetry (ii) the axes of symmetry and (iii) the centre of symmetry.

#### 4.5. The Seven Crystal Systems

As stated above, there are seven crystal systems corresponding to seven distinct types of unit cells (or subunits). These unit cells are all parallelepipeds whose shapes are determined by the lengths of the three sides  $a$ ,  $b$ ,  $c$  and the values of the three interfacial angles  $\alpha$ ,  $\beta$ , and  $\gamma$ .

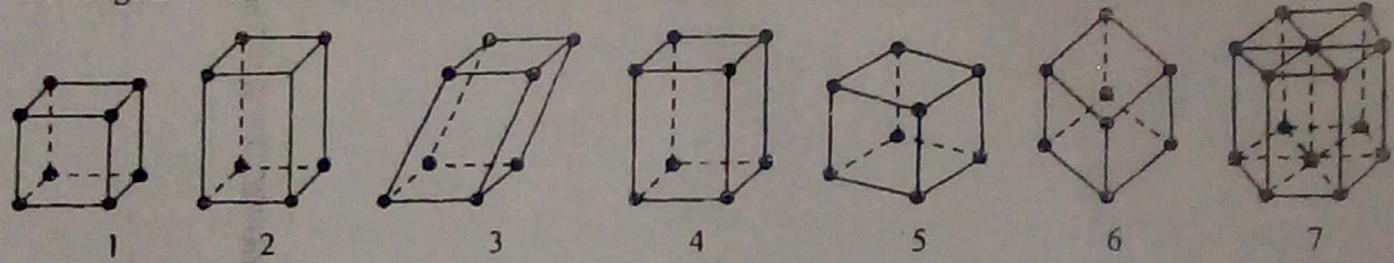


Fig. 4.5 (a)

The names of the seven crystal systems are :

(1) Cubic (2) Monoclinic (3) Triclinic (4) Tetragonal (5) Orthorhombic (6) Rhombohedral (Trigonal) and (7) Hexagonal.

The shapes of their unit cells are shown in Fig. 4.5 (a) and their lattice parameters are summarised in Table No. 4.1.

Table No. 4.1  
The Crystal Systems

S. No.	Name of system	Relation between primitives	Interfacial angles	Example
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{NaCl}, \text{CaF}_2, \text{NaClO}_4$
2.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	$\text{Na}_2\text{SO}_4, \text{FeSO}_4$
3.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4, \text{K}_2\text{Cr}_2\text{O}_7$
4.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{NiSO}_4, \text{SnO}_2$
5.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{KNO}_3, \text{BaSO}_4, \text{MgSO}_4$
6.	Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	$\text{CaSO}_4$
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	$\text{SiO}_2, \text{AgI}$

Following points are worth noting regarding the different structures given above.

- (a) In simple *cubic* structure :
  - (i) the three crystal axes are at right angles
  - (ii) the repetitive intervals along the three axes are equal.
- (b) In a simple *monoclinic* arrangement :
  - (i) one of the axes is at right angles to the other two but
  - (ii) the other two axes are not at right angles to each other and
  - (iii) repetitive interval along each axis is different.
- (c) The characteristic features of *triclinic* structure is a complete lack of symmetry i.e.
  - (i) no two of the three axes are at right angles to each other
  - (ii) repetitive interval along each axis is different.
- (d) A simple *tetragonal* structure has the following features :
  - (i) the three crystal axes are at right angles to each other
  - (ii) the repetitive intervals along two of the axes are equal
  - (iii) the interval in the third direction is different from that in the other two.
- (e) *Orthorhombic* structure has the following features :
  - (i) the three crystal axes are at right angles
  - (ii) the repetitive interval along each axis is different.
- (f) In *rhombohedral* structure :
  - (i) the three axes are equally inclined to each other at angles other than a right angle
  - (ii) the intervals along the three axes are different.
- (g) In *hexagonal* arrangement :
  - (i) there are three axes in one plane  $120^\circ$  from each other and a fourth axis normal to this plane
  - (ii) the repetition intervals along the three coplanar axes are equal but the interval along the fourth axis is unique.

It will be seen that cubic system possesses the greatest symmetry whereas triclinic system has the least.

#### 4.6. Bravais' Lattices

According to Bravais who introduced the space lattice idea as early as 1880, there are 14 possible types of space lattices in these seven systems of crystals : one triclinic, two monoclinic, four orthorhombic, two tetragonal, one hexagonal, one rhombohedral and three cubic as illustrated in Fig. 4.5 (b). In fact, it has been proved mathematically that there are only fourteen independent ways of arranging points in three-dimensional space such that each arrangement conforms to the definition of a space lattice.

The cubic system which is the simplest and also most common will be considered in detail.

#### 4.7. Symmetry Elements of a Crystalline Solid

The main symmetry elements of a crystalline solid are : (i) axes of symmetry (ii) planes of symmetry and (iii) centre of symmetry.

Consider a simple geometrical solid body such as a cube. Since it has a certain regularity in the arrangement of its faces, it is called a symmetrical solid. In fact, a description of symmetries present in a solid is a way of describing this regularity of arrangement of its faces.

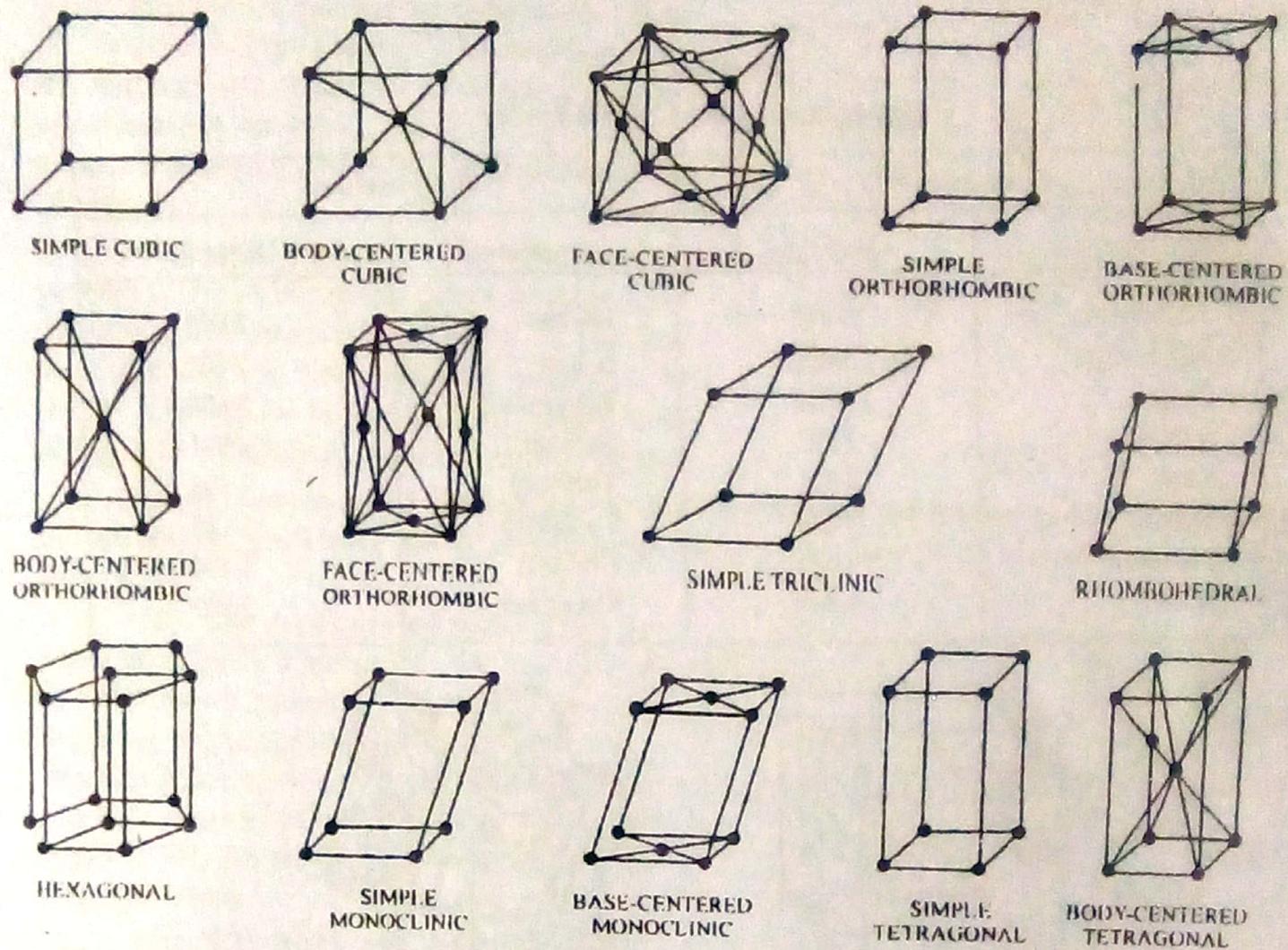


Fig. 4.5 (b)

As shown in Fig. 4.6, when a cube is laid flat on a table its four side faces become vertical. The intersections of these four faces are four vertical lines which are parallel to each other. It is obvious that if one of the intersection edges is made vertical, then the four faces automatically become vertical planes. This fact leads one to the conclusion that these faces are related to each other in some way. These four faces are said to constitute a *zone* and any direction parallel to the intersection edges is called the *zone axis*.

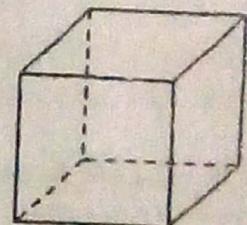


Fig. 4.6

#### (a) Axis of Symmetry

As shown in Fig. 4.7 (a), if a cube is rotated about a vertical axis (parallel to intersection edges and passing through the centre of the horizontal face), then in one complete revolution of  $360^\circ$ , there are found to be four positions of the cube which are coincident with its original position. In fact, when the cube is rotated through  $90^\circ$ , it is not possible to distinguish it from its original position. In other words, each rotation of  $90^\circ$  brings the cube into self-coincidence or in a congruent position.

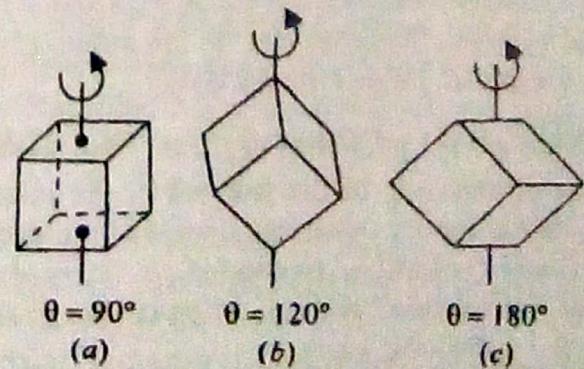


Fig. 4.7

Some elements as well compounds possess FCC lattice whereas many others crystallise into BCC lattice. These are listed in Table No. 4.2 which also gives the value of primitive  $a$  in angstrom units ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ).

**Table No. 4.2**  
**Elements of Cubic Crystal System**

<i>Face-centred</i>		<i>Body-centred</i>	
<i>element</i>	<i>a</i> (in Å)	<i>element</i>	<i>a</i> (in Å)
Aluminium	4.049	Barium	5.025
Copper	3.615	$\alpha$ -iron	2.867
Gold	4.079	Rubidium	5.630
$\gamma$ -iron	3.591	Sodium	4.291
Lead	4.951	Titanium	3.306
Nickel	3.524	Tungsten	3.115
Platinum	4.086	Uranium	3.474
Silver	4.086	Zirconium	3.620

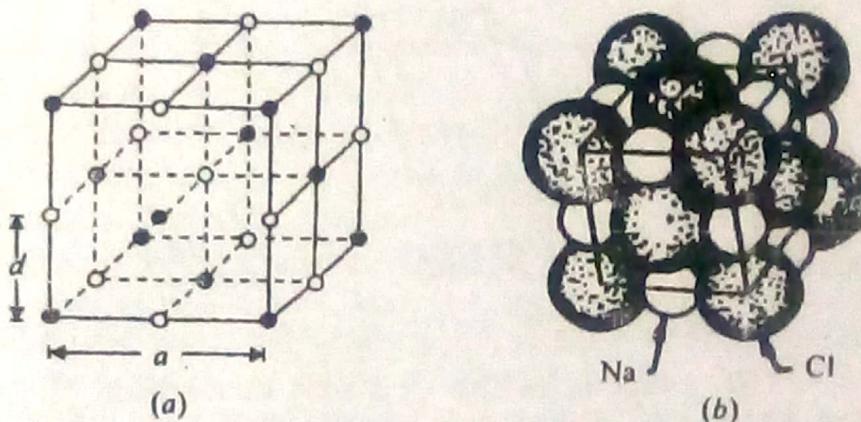


Fig. 4.11

Fig. 4.11 (a) shows the cubical crystal lattice of common salt (NaCl) which is a compound of two elements i.e. sodium and chlorine. Here, Na and Cl each forms an FCC pattern and the two patterns alternate in three dimensions. As seen, an FCC structure of chlorine penetrates a similar structure of sodium. The above-mentioned three types of lattices i.e. SC, BCC and FCC are sometimes represented by the symbols *P*, *I* and *F* respectively. Not all such lattices are possible in all crystal systems. For example, in the cubic system, we have *P*, *I* and *F* whereas triclinic and hexagonal systems have *P* lattice only.

#### 4.9. Calculations of Dimensions of Unit Cell

The dimensions of the unit cell or the interatomic distance in a crystal lattice can be computed from the knowledge of (i) molecular weight of the crystalline compound (ii) Avogadro's number  $N$  (iii) density of the material and (iv) its crystalline form. As an example, consider the following cases :

(i) *Body-centred Cubic (BCC) Lattice*. The example of such lattice is afforded by  $\alpha$ -iron crystal whose each unit cell (Fig. 4.12) consists of 8 corner iron atoms and one atom at the body centre. The

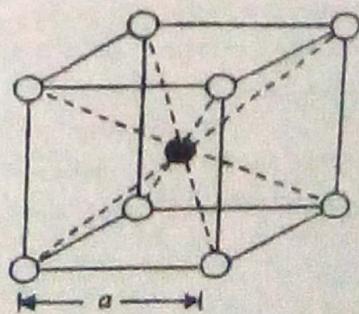


Fig. 4.12

atom at the body centre belongs entirely to the unit cell. However, each of the other 8 corner atoms is shared by 9 adjacent unit cells so that each contributes one-eighth of an atom to the cell under consideration. Hence, total number of iron atoms associated with each unit cell =  $1 + (8/8) = 2$ . For iron, density is  $7.86 \text{ g/cm}^3$ , atomic weight =  $55.85$ , hence

$$a^3 \times 7.86 = 2 \times 55.85 / 6.02 \times 10^{23}$$

$$a = 2.87 \times 10^{-8} \text{ cm} = 2.87 \text{ \AA}$$

Alternatively, we could use the formula

$$a^3 \rho = n \cdot 1/N$$

where  $A$  = atomic weight.

(ii) *Face-centred Cubic (FCC) Lattice*. The common example is the crystal of sodium chloride ( $\text{NaCl}$ ). It can be proved that each unit cell in sodium chloride has four sodium  $\text{Na}^+$  atoms (strictly, ions) and four  $\text{Cl}^-$  atoms associated with it. As shown in Fig. 4.13, the sodium atom in the centre belongs entirely to the cell shown. Each of the other twelve sodium atoms is shared with three adjacent unit cells so that each contributes one-fourth of an atom to the cell under consideration. Hence, total number of Na atoms in each unit cell is

$$= 1 + \frac{1}{4} (12) = 4.$$

Now, consider chlorine atoms. There are (i) 8 corner atoms and (ii) 6 face atoms i.e. one in each face. As proved below, out of the fourteen chlorine atoms, only four are associated with the unit cell. It is easy to visualize that each one of the corner chlorine atoms is shared by 8 adjacent unit cells so that each contributes one-eighth of an atom to the cell under consideration (Art. 4.13). Hence, number of corner atoms per unit cell is  $= 8/8 = 1$ .

Now, take the face-centred chlorine atoms. Each of these atoms is shared by two adjacent unit cells. Hence, each contributes one-half of an atom to the cell under consideration. Number of face-centred chlorine atoms associated with each unit cell  $= 6/2 = 3$ . Hence, total number of chlorine atoms belonging to each unit cell of  $\text{NaCl}$  is  $= 1 + 3 = 4$ . Taken together, it means that there are 4 molecules of  $\text{NaCl}$  per unit cell.

$$\text{Molecular weight of } \text{NaCl} = 23 + 35.5 = 58.5$$

$$\text{Mass of each molecule} = 58.5 / 6.02 \times 10^{23} \text{ gram}$$

$$\text{Mass of 4 molecules} = 4 \times 58.5 / 6.02 \times 10^{23} \text{ gram}$$

If ' $a$ ' cm is the length of the edge of the unit cell, then its volume is  $a^3$  and since density of  $\text{NaCl}$  is  $2.18 \text{ g/cm}^3$ , mass of each unit cell  $= a^3 \times 2.18 \text{ gram}$ .

$$a^3 \times 2.18 = 4 \times 58.5 / 6.02 \times 10^{23}$$

$$a = 5.63 \times 10^{-8} \text{ cm} = 5.63 \text{ \AA}$$

As will be seen from Fig. 4.3 (b), this is the distance between two adjacent atoms of the same kind i.e. chlorine atoms in this case. Obviously, the distance between two adjacent atoms i.e. Na and Cl atoms is half of the above value i.e.  $d = 5.63/2 = 2.815 \text{ \AA}$

Alternatively, we could use the relation

$$a^3 \rho = n M/N$$

where  $\rho$  = density of crystal;  $M$  = molecular weight of crystal material;  $n$  = No. of molecules/unit cell;  $N$  = Avogadro's number.

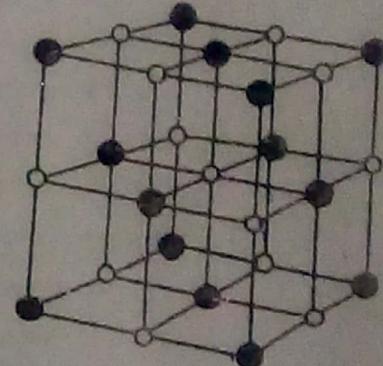


Fig. 4.13

**Example 4.1.** Classify the following unit cells into proper system:

$$(i) a = 10.3 \text{ \AA}, b = 9.47 \text{ \AA}, c = 5.2 \text{ \AA}$$

$$\alpha = 41^\circ, \beta = 83^\circ \text{ and } \gamma = 93^\circ$$

$$(ii) a = b = 10.73 \text{ \AA}, c = 14.3 \text{ \AA}$$

$$\alpha = \beta = 90^\circ \text{ and } \gamma = 120^\circ$$

**Solution.** (i) Here,  $a \neq b \neq c$  i.e. the three primitives are unequal. Also, no two axes are at right angles to each other. In other words, there is complete lack of symmetry which is characteristic of triclinic structure (Table No. 4.1). Hence, this unit cell belongs to the triclinic crystal system (Art. 4.5).

(ii) Here,  $a = b \neq c$  and  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$ . As seen, from Table No. 4.1, this unit cell belongs to hexagonal crystal system.

**Example 4.2.** NaCl crystals have f.c.c. structure. The density of sodium chloride is  $2180 \text{ kg/m}^3$ . Calculate the distance between two adjacent atoms. Given that the atomic weight of sodium = 23 and that of chlorine = 35.5. Take  $N = 6.02 \times 10^{23}$  per kg-mol.

**Solution.** We will use the formula :  $a^3 \rho = nM/N$

Now,

$$M = (23 + 35.5) = 58.5, n = 4$$

$$\therefore a^3 \times 2180 = 4 \times 58.5 / 6.02 \times 10^{23}$$

$$\therefore a = 5.63 \times 10^{-10} \text{ m} = 5.63 \text{ \AA}.$$

— Art. 4-9

This is the lattice constant i.e. distance between adjacent atoms of the same kind. The distance between adjacent atoms i.e. between sodium and chlorine atoms is

$$d = a/2 = 5.63/2 = 2.815 \text{ \AA}$$

**Example 4.3.** If density of NaCl is  $2.163 \text{ g/cm}^3$  and its molecular weight 58.45, find the spacing between planes parallel to the cubic lattice faces of the NaCl crystal. Given that Avogadro's number is  $6.02 \times 10^{23}$  molecules/g-mol.

**Solution.** Since Avogadro's number represents the number of molecules in one gram-molecular-wt. of the substance, it means that there are  $6.02 \times 10^{23}$  molecules in 58.45 gram of NaCl.

$$\text{No. of molecules/gram} = 6.02 \times 10^{23} / 58.45 = 1.03 \times 10^{22}$$

$$\text{No. of molecules/cm}^3 = 1.03 \times 10^{22} \times 2.163 = 2.23 \times 10^{22}$$

Since there are two atoms in a molecule,

$$\text{No. of atoms/cm}^3 = 2 \times 2.23 \times 10^{22} = 4.46 \times 10^{22}$$

Since, NaCl crystal lattice consists of a multitude of cubes with atoms at the corners, there will be  $(4.46 \times 10^{22})^{1/3} = 3.54 \times 10^7$  atoms in a row 1 cm long. The spacing between atoms and hence between rows or planes is

$$d = 1/3.54 \times 10^7 = 2.83 \times 10^{-8} \text{ cm} = 2.83 \text{ \AA}$$

#### 4.10. Crystal Structures of Commercially Important Materials

Many materials of commercial importance have relatively simple crystal structures. Some of these are described below :

(i) **The hexagonal close-packed (hcp) structure.** This structure is built up by stacking close-packed planes in a simple sequence. The method of stacking can be understood with the

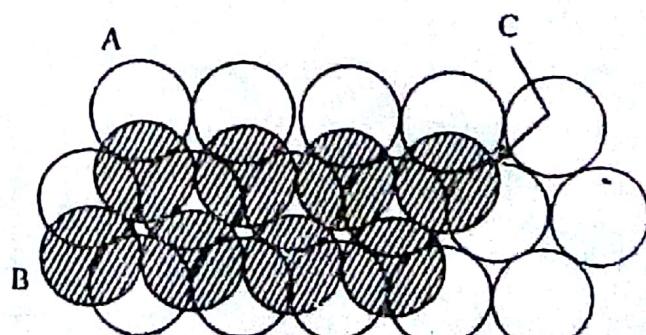


Fig. 4.14

help of Fig. 4.14 which shows two close-packed planes lying one above the other. It is seen that each atom of one plane rests in a depression against three atoms of the other. Also plane *B* has two possible positions : the one as indicated and the other given by position *C*. For either choice, important choice is that for the third plane which also has two choices. Let the first two planes have the sequence *AB*. Then the third plane may be added over the second in position *A*. In that case, the atoms of plane 3 would be directly above those of plane 1.

Alternatively, plane 3 may be stacked in position *C* (Fig. 4.14) so that atoms of plane 3 are directly above interstices of plane 1. The hcp structure has the first stacking sequence of *ABAB* .... as shown in Fig. 4.15 (b). Heavy lines in Fig. 4.15 (a) show the unit cell of hcp crystal.

This structure is called close-packed because it possesses the maximum density of packing of hard spheres. Each atom has 12 nearest neighbours. In other words, coordination number is 12 (Art. 4.10).

(ii) **The face-centred cubic (fcc) or cubic close-packed structure.** The unit cell of this structure is shown in Fig. 4.16. It has the stacking sequence of *ABCABC* .... This structure is also close-packed because each atom has 12 nearest neighbours. As shown in Fig. 4.16 (b), the atoms are in contact with the diagonal atoms.

(iii) **The body centred cubic (bcc) structure.** The unit cell of such a structure is sketched in Fig. 4.12. It has one atom at each corner and one atom at the centre of the cube. Such a structure is not formed of close-packed planes as the above two since each atom has only eight nearest neighbours. However, the atoms are in contact along body diagonals.

(iv) **The simple cubic (sc) structure.** As shown in Fig. 4.10 (a), the unit cell of this structure has atoms only at the corners of the cube. Consequently, these atoms touch along cube edges. This structure is loosely-packed because each atom has only six nearest neighbours. Only one element i.e. polonium (Po) exhibits this structure (in a certain temperature region).

Many crystal structures are a variation of this simple structure. In fact, many of them consist of sets of interpenetrating simple cubic sub-lattices. For example, *BCC* lattice can be considered to consist of two identical *SC* lattices, one consisting of corner atoms and the other of the centre atoms. Similarly, an *FCC* lattice can be considered to contain four identical *SC* lattices properly disposed with respect to each other.

(v) **Other structures.** Although many elements solidify in one of the structures described above, several other elements and all compounds possess other structures. Some of these structures are derivates from or combination of the basic structures described above.

(a) **Diamond cubic structure.** Germanium (Ge), silicon (Si) and carbon (C) possess this structure which is a combination of two interpenetrating *FCC* sub-lattices. As seen from the unit

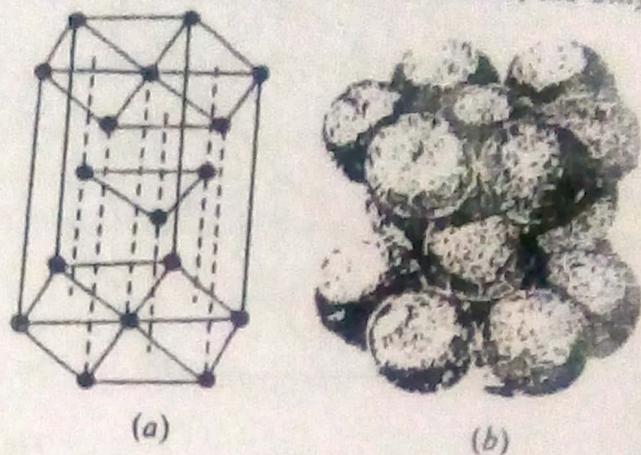


Fig. 4.15

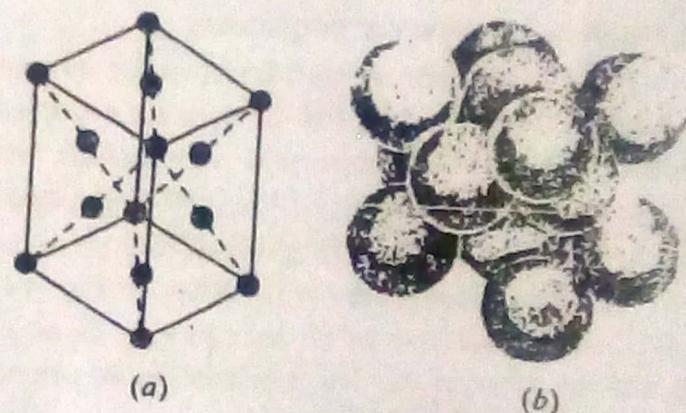


Fig. 4.16

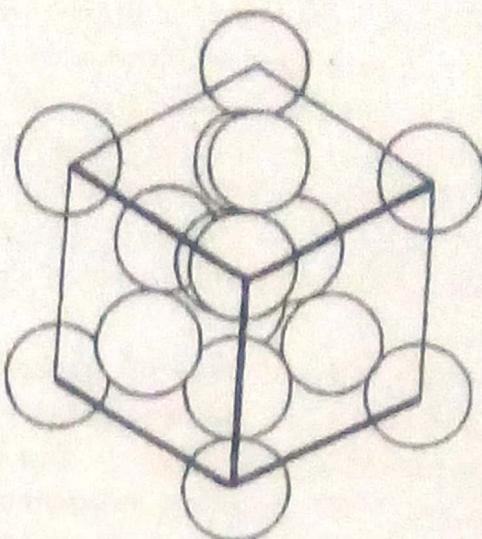
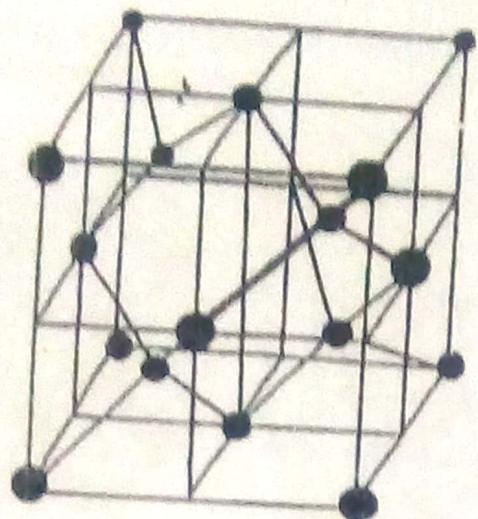


Fig. 4.17

cell of Fig. 4.17 (a), one sub-lattice has its origin at  $(0, 0, 0)$  and the other at a point one quarter of the way along the body diagonal i.e. at the  $(a/4, a/4, a/4)$  point. This structure is loosely-packed since each atom has only four *nearest* neighbours.

(b) Zinc blende or sphalerite cubic structure. This structure (Fig. 4.18) results if the two sub-lattices are occupied by two different elements. Some of the important compounds which possess this structure are : semiconductors like InSb and GaAs; also ZnS (after which it is named), CuCl and many others.

(c) NaCl structure. It is shown in Fig. 4.11 and consists of two FCC sublattices, one of Cl ions having its origin at the  $(0, 0, 0)$  point and the other of the Na ions having its origin midway along a cube-edge, say, at  $(a/2, 0, 0)$  point.

### 4.11. Coordination Number

By coordination number, it is meant the number of *nearest* neighbours which an atom has in the unit cell of any crystal structure.

Following cases would be considered :

#### (i) sc structure [Fig. 4.10 (a)]

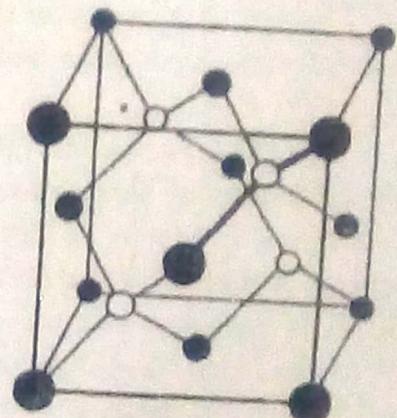
In this case, the coordination number is *six*. It is so because each corner atom is linked with seven other unit cells that can be imagined to be built around the unit cell containing the atom. In that case, each corner atom has four neighbours in the same plane, one vertically above and one immediately below, giving a total of six *nearest* neighbouring atoms.

#### (ii) bcc structure [Fig. 4.10 (b)]

Its coordination number is *eight*. It should be noted that in this case, the *nearest* neighbours of any corner atom are the body-centred atoms (and not the other corner atoms). Since, there are eight surrounding unit cells for any corner atom, their eight body-centred atoms form the *nearest* neighbours for any corner atom.

#### (iii) fcc structure [Fig. 4.10 (c)]

The coordination number of such a structure is *twelve*. In this case, the *nearest* neighbours of any corner atom are the face-centred atoms of the surrounding unit cells. Any corner atom has four such atoms in its own plane, four in a plane above it and four in a plane below it.



Zn atoms ○  
S atoms ●  
Fig. 4.18

#### 4.12. Atomic Radius

It is defined as *half the distance between nearest neighbours in a crystal of a pure element*. Usually, it is expressed in terms of the cube edge  $a$ . It must be remembered that *any two nearest neighbouring atoms touch each other*.

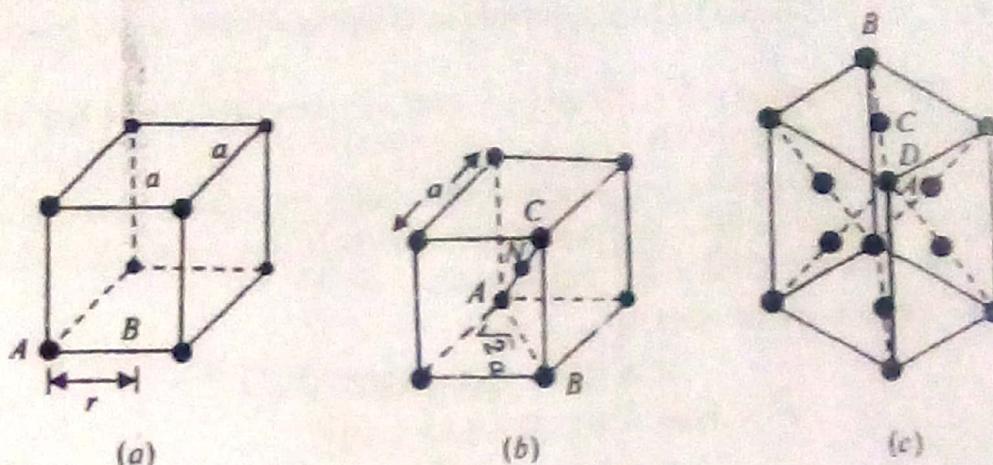


Fig. 4.19

- (i) **SC structure.** By definition,  $AB$  represents the atomic radius. It is obvious from Fig. 4.19 (a) and 4.20 (b) that  $r = a/2$ .

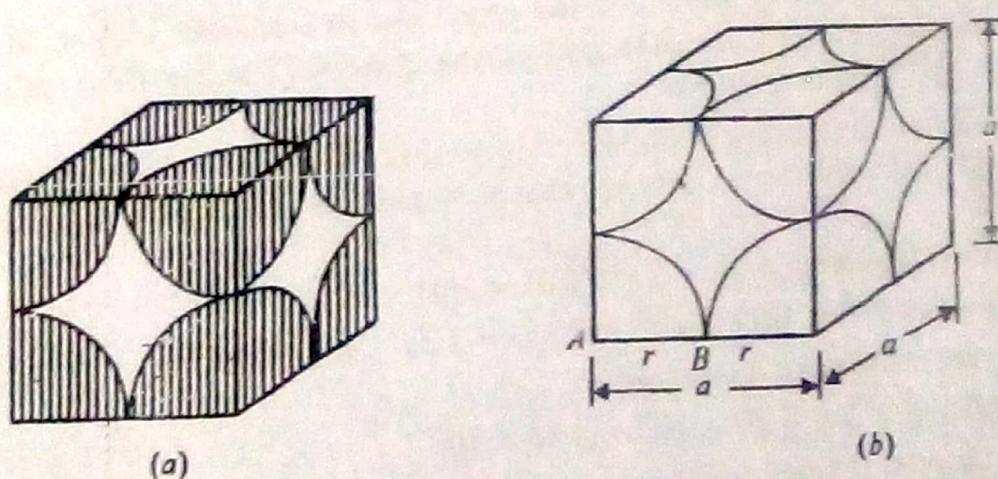


Fig. 4.20

- (ii) **BCC structure.** As seen from Fig. 4.19 (b), atoms  $C$  and  $N$  are the nearest neighbours. By definition  $r = CN/2$ .

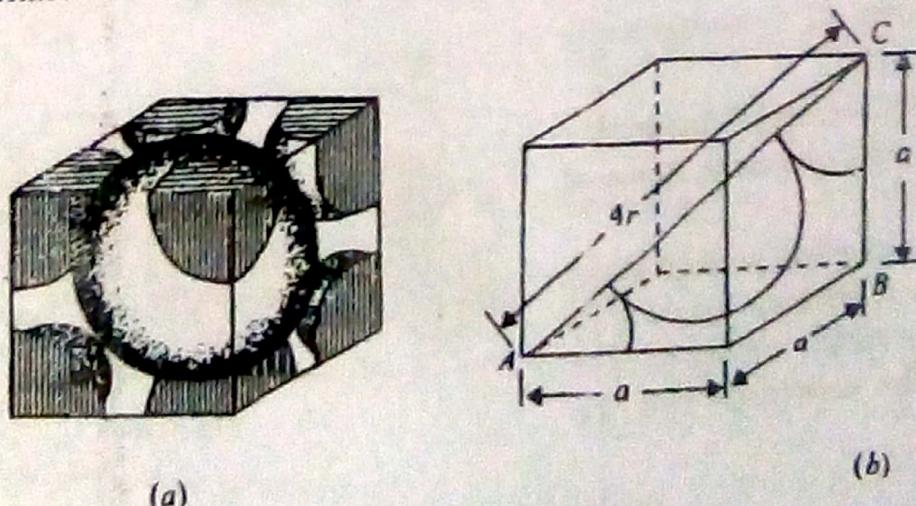


Fig. 4.21

Now

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$$

$$r = CN/2 = AC/4 = \sqrt{3}a/4$$

$$\text{Conversely, } a = 4r/\sqrt{3}$$

A more detailed view is shown in Fig. 4.21 (b) where solid diagonal  $AC$  equals four times the radius of a single atom.

### (iii) FCC structure

Here, as seen from Fig. 4.19 (c), atoms  $A$  and  $C$  are the nearest neighbours.

Hence,

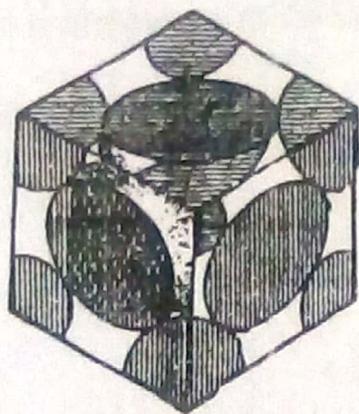
$$r = AD = AC/2 = AB/4$$

Now,

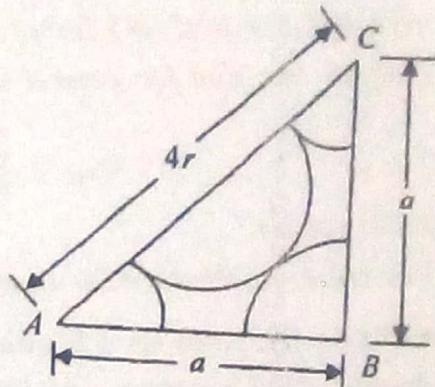
$$AB = \sqrt{2}a \quad \therefore r = \sqrt{2}a/4$$

Conversely,

$$a = 4r/\sqrt{2}$$



(a)



(b)

Fig. 4.22

Fig. 4.22 (b) shows more detailed view of the same. Here, surface diagonal  $AC$  equals four times atomic radii.

The lattice constant or side of a cubic unit cell as well its face and body diagonals in terms of atomic radius are tabulated as under.

Table No. 4.3

	SC	BCC	FCC
Side	$2r$	$4r/\sqrt{3}$	$4r/\sqrt{2}$
Face diagonal	$\sqrt{2}(2r)$	$\sqrt{\frac{2}{3}}(4r)$	$4r$
Body diagonal	$\sqrt{3}(2r)$	$4r$	$\sqrt{\frac{3}{2}}(4r)$

**Example 4.4.** Copper has FCC structure and the atomic radius is 1.278 A.U. Calculate its density. Atomic weight of copper = 63.54.

**Solution.** As seen from Art. 4.12 (iii), the lattice constant for FCC structure is given by

$$a = 4r/\sqrt{2} = 4 \times 1.278/\sqrt{2} = 3.61 \text{ A.U.}$$

$$\text{Volume of unit cell} = a^3 = (3.61 \times 10^{-8})^3 \text{ cm}^3 \\ = 47 \times 10^{-24} \text{ cm}^3$$

If its density is  $\rho$ , then mass of unit cell  
 $= \rho \times 47 \times 10^{-24} \text{ gram}$

Now, let us find the mass of the same unit cell in a different way.

Each unit cell of FCC structure contains 4 atoms. Obviously, their mass would represent the mass of the cell. Since  $6.02 \times 10^{23}$  atoms have a mass of 63.54 gram, 4 atoms will have a mass  
 $= 4 \times 63.54 / 6.02 \times 10^{23} = 4.22 \times 10^{-23} \text{ gram}$

Equating the two masses, we get

$$\rho \times 47 \times 10^{-24} = 4.22 \times 10^{-23}; \rho = 8.98 \text{ g/cm}^3.$$

### Alternate Solution

We could use the following formula

$$a^3 \rho = nA/N$$

where

$A$  = atomic weight

$$(3.61 \times 10^{-8})^3 \rho = 4 \times 63.54 / 6.02 \times 10^{23}$$

∴

$$\rho = 8.98 \text{ g/m}^3.$$

### 4.13. Number of Atoms per Unit Cell

#### (I) Simple Cube

Since each corner atom is shared by *eight* surrounding cubes, share of each cube comes to one-eighth of an atom (Fig. 4.23). As there are eight corner atoms in all, each cube has  $8 \times 1/8 = 1$  atom.

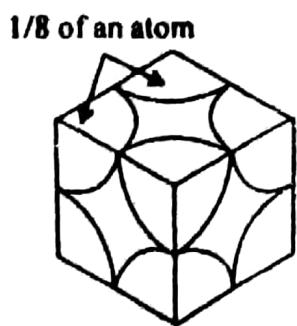


Fig. 4.23

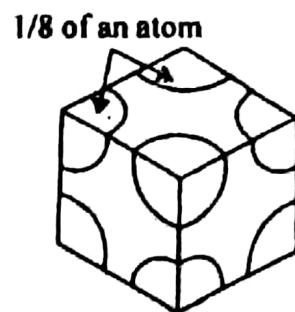


Fig. 4.24

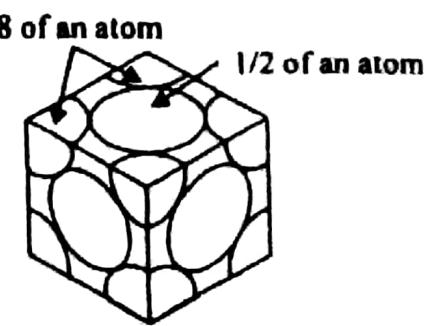


Fig. 4.25

#### (II) Body-centred Cube

It has *eight* corner atoms and one centre atom (Fig. 4.24). The number of atoms which belong to this cube are

- (a) one centre atom and
- (b)  $8 \times 1/8 = 1$  corner atom.

Hence, number of atoms per cube =  $1 + 1 = 2$ .

#### (III) Face-centred Cube (Fig. 4.25)

It has *six* face-centred and *eight* corner atoms. Each of the 6 face-centred atoms is shared by the two adjoining cubes. Hence, a total of  $6/2 = 3$  such atoms belong to the cube. As before, one corner atom comes to the share of this cube. Hence, total number of atoms per cube is  $(3 + 1) = 4$ .

#### 4.14. Density of Packing

The relative density of packing is defined as the fraction of volume occupied by spherical atoms as compared to the total available volume of the structure.

##### (i) Simple Cube

As shown earlier, this cube has one atom.

$$\text{Volume of one atom} = \frac{4}{3} \pi r^3$$

$$\text{Now, atomic radius } r = \frac{a}{2}$$

$$\therefore \text{Volume of the atom, } v = \frac{4}{3} \pi \left( \frac{a}{2} \right)^3 = \frac{\pi a^3}{6}$$

$$\text{Volume of the cube, } V = a^3$$

$$\therefore \text{relative density of packing is } = \frac{v}{V} = \frac{\pi a^3 / 6}{a^3} = \frac{\pi}{6}$$

##### (ii) Body-centred Cube

In this case, number of atoms per cube is 2 (Art. 4.13)

Volume occupied by two atoms is

$$v = 2 \times \frac{4}{3} \pi r^3$$

$$\text{Now } r = \sqrt{3}a/4$$

$$\therefore v = 2 \times \frac{4}{3} \pi \left( \frac{\sqrt{3} \cdot a}{4} \right)^3 = \frac{\sqrt{3} \pi}{8} \cdot a^3$$

$$\text{Volume of the cube, } V = a^3$$

$$\therefore \frac{v}{V} = \frac{\sqrt{3} \cdot \pi}{8} \times \frac{a^3}{a^3} = \frac{\sqrt{3} \cdot \pi}{8}$$

$$\therefore \text{relative density of packing} = \frac{\sqrt{3} \cdot \pi}{8}$$

##### (iii) Face-centred Cube

As shown in Art. 4.13, in this case, there are 4 atoms per cube.

$\therefore$  volume occupied by four atom is

$$v = 4 \times \frac{4}{3} \pi r^3$$

$$\text{Now, } r = \sqrt{2} \cdot a/4$$

$$\therefore v = 4 \times \frac{4}{3} \cdot \pi \left( \frac{\sqrt{2} \cdot a}{4} \right)^3 = \frac{\sqrt{2} \cdot \pi}{6} \cdot a^3$$

$$V = a^3$$

$$\therefore \frac{v}{V} = \frac{\sqrt{2} \cdot \pi}{6} \cdot \frac{a^3}{a^3} = \frac{\sqrt{2} \cdot \pi}{6}$$

$$\therefore \text{relative density of packing} = \frac{\sqrt{2} \cdot \pi}{6}$$

Some of the details of elementary cubic structure are summarised below in Table No. 4.4.

Table No. 4.4

	SC	BCC	FCC
Coordination number	6	8	12
Atomic radius ( $r$ )	$\frac{a}{2}$	$\frac{\sqrt{3} \cdot a}{4}$	$\frac{\sqrt{2} \cdot a}{4}$
Face diagonal	1	2	4
Body diagonal	$\frac{\pi}{6}$	$\frac{\sqrt{3}\pi}{8}$	$\frac{\sqrt{2}\pi}{6}$

**Example 4.5.** (a) With reference to crystals, state what you understand by the terms (i) unit cell (ii) coordination number and (iii) factor.

(b) Show that for bcc and fcc crystal structures, the lattice constants are given by

$$a_{bcc} = \frac{4r}{\sqrt{3}} \text{ and } a_{fcc} = \frac{4r}{\sqrt{2}}$$

where  $r$  is the atomic radius.

**Solution.** For solution please refer to Art. 4.3, 4.10, 4.11 and 4.12.

#### 4.15. Important Plane Systems in a Cubic Crystal

In a cubic crystal, there are three sets of planes which are very rich in atoms. Consequently, Bragg reflections (i.e. X-ray reflections) from these planes are more intense than from others. These three sets of planes which have different spacings are shown in Fig. 4.26.

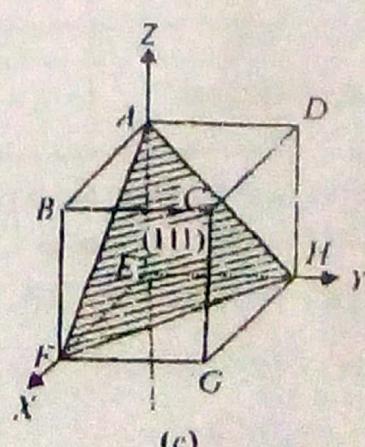
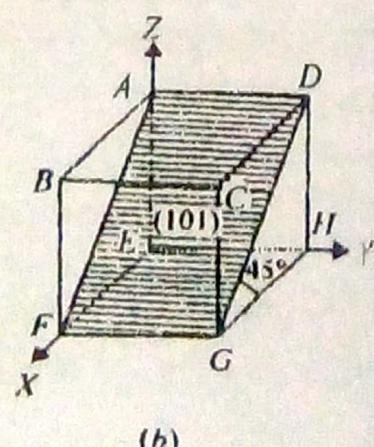
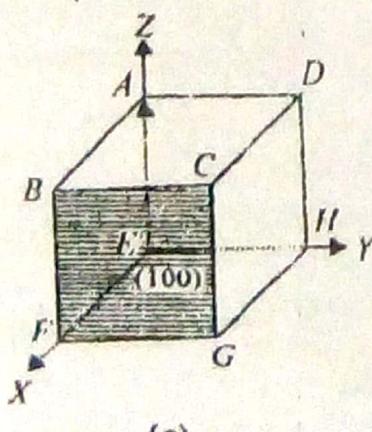
(i) The first set of planes consists of surface planes of the cube and those parallel to them such as  $BFGC$ ,  $AEHD$ ,  $ABCD$ ,  $EFGH$  etc. [Fig. 4.26 (a)]. Let the distance between consecutive parallel surface planes be  $d_1$ .

(ii) The second set of planes consists of parallel planes like  $AFGD$  which are inclined at an angle of  $45^\circ$  to the planes mentioned above [Fig. 4.26 (b)]. Their spacing, as shown in Fig. 4.27, is  $d_2$ .

(iii) The third set of planes consists of those planes which are parallel to the plane  $AFH$  [Fig. 4.26 (c)]. Let the spacing of such planes be  $d_3$  as shown in Fig. 4.27.

##### (a) Spacing of planes

The knowledge of spacing of these three sets of planes is essential for identifying different types of crystals. It is so because for each basic crystal structure, a definite ratio exists between the spacings of planes which are rich in atoms.



Consider the case of a simple cubic crystal with atoms at the corners of the cube as shown in Fig. 4.26 (a). The spacing of face planes like  $ABCD$  and  $EFGH$  is  $d_1$ .

The spacing of planes like  $AFGH$  which are inclined at  $45^\circ$  to the first set of planes is  $d_2 = d_1/\sqrt{2}$ .

The triangle  $AFH$  represents the third set of planes whose spacing  $d_3$  may be found by drawing the triangle  $AEK$  in true shape as in Fig. 4.27 (b).

In Fig. 4.27 (a),  $EK$  is perpendicular to  $FH$  and  $EL = d_3$  is perpendicular to  $AK$ .

From the two similar triangles  $ELK$  and  $AEK$  of Fig. 4.27 (b), we have

$$\frac{EL}{EK} = \frac{AE}{AK}$$

or

$$\frac{d_3}{d_2} = \frac{d_1}{\sqrt{(d_1^2 + d_2^2)}}$$

or

$$d_3 = \frac{d_1 d_2}{\sqrt{(d_1^2 + d_2^2)}}$$

Now, putting

$$d_2 = d_1/\sqrt{2}, \text{ we get}$$

$$d_3 = \frac{d_1^2}{\sqrt{2} \cdot \sqrt{(d_1^2 + \frac{1}{2} d_1^2)}} = \frac{d_1}{\sqrt{3}}$$

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

Similarly, it can be shown that for a body-centred lattice structure

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

Also, for face-centred lattice structure

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

By experimenting with reflection of monochromatic X-rays from different crystals, Bragg not only verified the above ratios but also used them to recognise whether the crystal was simple, cubic or a body-centred type.

#### 4.16. Directions, Planes and Miller Indices

One basic necessity in crystal analysis is the ability to describe relative orientations of lines and planes. It can be achieved with the help of a suitable frame of reference. Latitude and longitude serve this function on a map whereas X- and Y-axes are used on the graph paper (Fig. 4.28). In Fig. 4.28, two directions have been shown by arrows starting from the origin and ending at points A and B. These

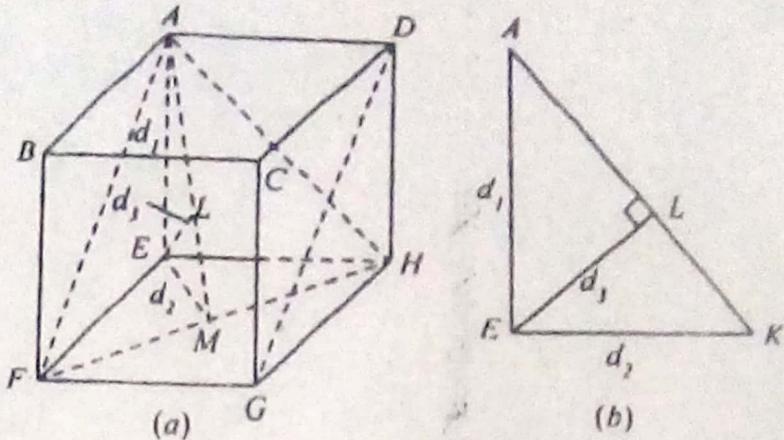


Fig. 4.27

## Crystallography

directions can be satisfactorily described by giving the coordinates of the first whole-numbered point ( $x, y$ ) through which each passes. For direction  $OA$ , it is  $(2, 1)$  and for  $OB$ , it is  $(1, 1)$ .

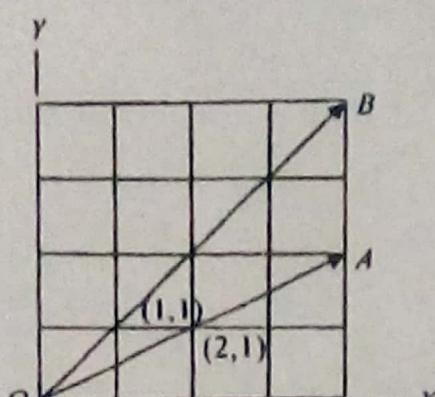


Fig. 4.28

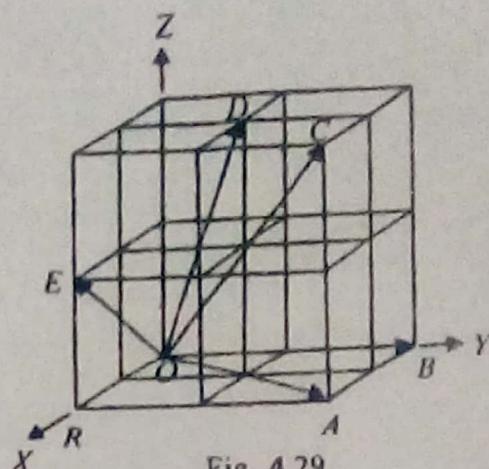


Fig. 4.29

Three-dimensional graph paper of Fig. 4.29 can be used for describing a direction in space. As before, these directions are described by giving the coordinates of the first whole-numbered point ( $x, y, z$ ) through which they pass. The directions of various lines of Fig. 4.29 are as under :

$OA [110]$	$OR [100]$
$OB [010]$	$OD [\frac{1}{2}, \frac{1}{2}, 1] \text{ or } [112]$
$OC [111]$	$OE [1, 0, \frac{1}{2}] \text{ or } [201]$

The square brackets are used to indicate a *direction*. Commas are unnecessary but the digits are read as "one one zero" and not "one hundred and ten". The digits in square brackets indicate the indices of that direction. In general, the indices of a direction are written as  $[uvw]$ . A negative index is indicated by a bar over the digit.

For example, +X-axis has indices of  $[100]$  whereas -X-axis has  $[100]$  indices. Similarly, +Y-axis has indices  $[010]$  and the -Y-axis  $[010]$ . Positive Z-axis has indices  $[001]$  whereas -Z-axis has  $[001]$ .

### 4.17. Unit Face and Axial Units

In Fig. 4.30, let  $OX$ ,  $OY$  and  $OZ$  be taken as the reference axes. The faces  $a_1, b_1, c_1$  and  $a_2, b_2, c_6$  make certain intercepts or segments on these axes. The first face or plane intercepts segments of  $oa_1, ob_1$ , and  $oc_1$ , and the second -  $oa_2, ob_2$ , and  $oc_6$ . These segments represent the respective linear parameters of the two faces.

It is seen that the first face intercepts one spacing along each axis whereas second face intercepts two, three and six spacings along the respective axes. The first face is called *unit face* which may be defined as the face which makes one intercept on each axis.

Obviously, the unit face produces three values which are related to each other as  $1 : 1 : 1$ . The second face produces three values of  $2a, 3b$  and  $6c$  which are related to each other as  $2 : 3 : 6$ . These figures of 1, 2, 3, 6 represent the numerical parameters of the faces and must always be whole numbers.

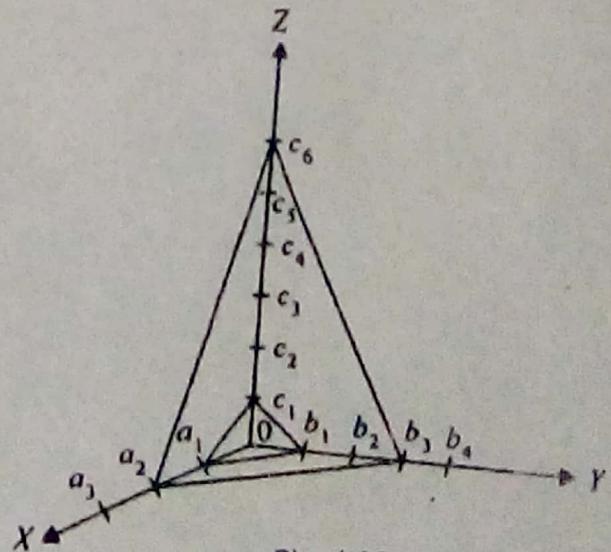


Fig. 4.30