

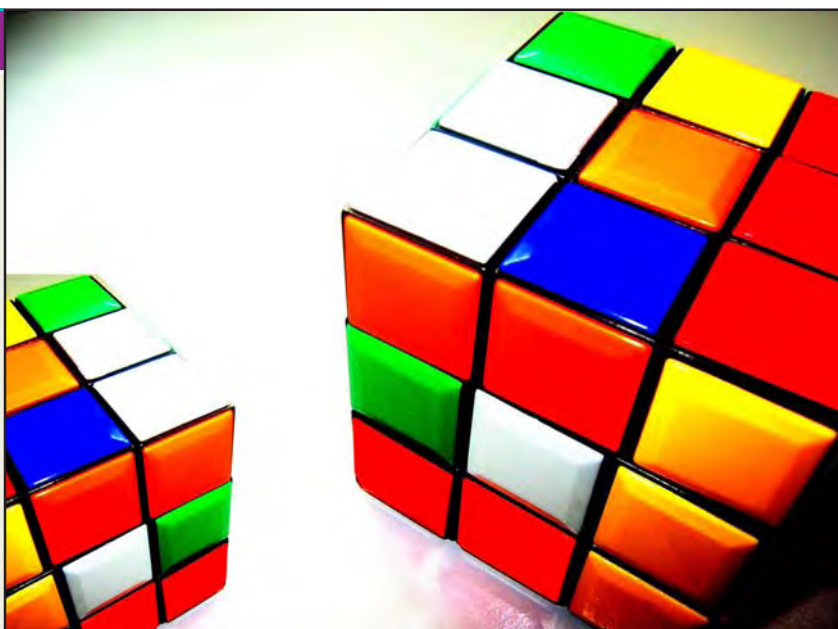
## 12

## Solid State

## CHAPTER

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**G**ases and liquids can flow and take up the shape of their container. Solids, on the other hand, have a definite volume and shape. They are rigid and lack the ability to flow.

In both gases and liquids, atoms, ions and molecules continually move. They translate randomly as well as rotate and vibrate. This determines the ability of gases and liquids to flow. In solids, atoms, ions and molecules are held together by relatively strong chemical forces-ionic bond, covalent bond, or by intermolecular van der Waals' forces. They do not translate although they vibrate to some extent in their fixed positions. This explains why solids are rigid and have definite shape.

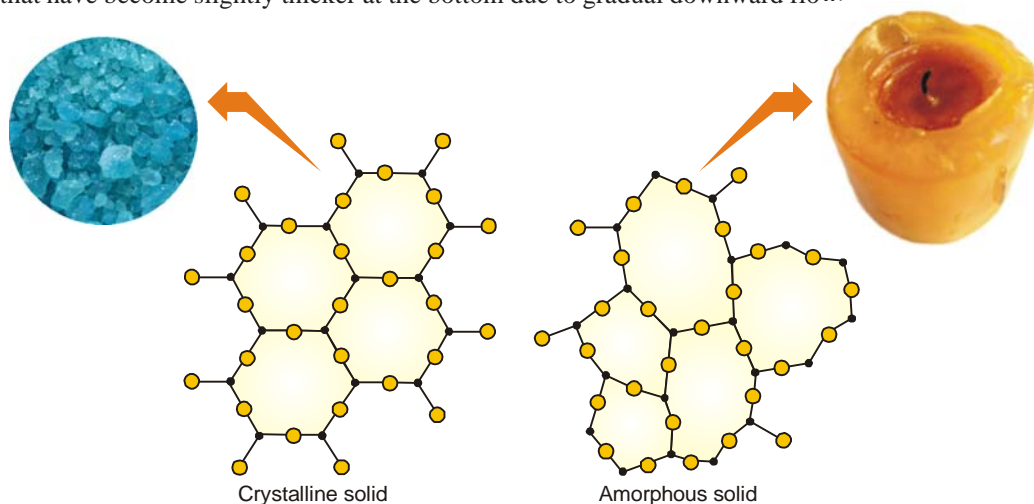
### TYPES OF SOLIDS

Broadly speaking, solids are of two types :

- (a) Crystalline solids; also called true solids
- (b) Amorphous solids

A **crystalline solid** exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensional pattern called the **crystal lattice**. Sugar and salt are crystalline solids.

An **amorphous solid** (Gr *amorphous* = no form) has atoms, molecules or ions arranged at random and lacks the ordered crystalline lattice. Examples are rubber, plastics and glass. In their disordered structure, amorphous solids resemble liquids. Thus glasses are to be regarded as super-cooled or highly viscous liquids. The liquid nature of glass is sometimes apparent in very old window panes that have become slightly thicker at the bottom due to gradual downward flow.



■ **Figure 12.1**

**Two-dimensional representation of crystalline solid and an amorphous solid. Each substance has the formula  $A_2O_3$ . A is shown by  $\bullet$  and O is shown by  $\circ$ .**

### ISOTROPY AND ANISOTROPY

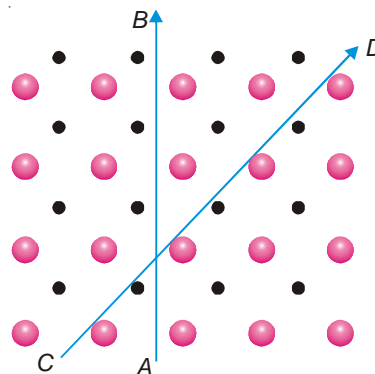
**Amorphous substances are said to be isotropic because they exhibit the same value of any property in all directions.** Thus refractive index, thermal and electrical conductivities, coefficient of thermal expansion in amorphous solids are independent of the direction along which they are measured.

**Crystalline substances, on the other hand, are anisotropic and the magnitude of a physical property varies with directions.** For example, in a crystal of silver iodide, the coefficient of thermal expansion is positive in one direction and negative in the other. Similarly, velocity of light in a crystal may vary with direction in which it is measured. Thus a ray of light passing through a Nicol prism splits up into two components, each travelling with different velocity (double refraction).

#### Explanation of Isotropy and Anisotropy

In amorphous substances, as in liquids, the arrangement of particles is random and disordered. Therefore all directions are equivalent and properties are independent of direction.

On the other hand, the particles in a crystal are arranged and well ordered. Thus the arrangement of particles may be different in different directions. This is illustrated in Fig. 12.2 in which a simple two-dimensional arrangement of two different types of particles has been shown. When a property is measured along  $AB$  and  $CD$ , the value along  $CD$  will be different from that along  $AB$ . This is so because there is only one type of particles along  $AB$  while there are two types of particles in alternate positions along  $CD$ . This explains why crystalline substances are anisotropic.



■ **Figure 12.2**

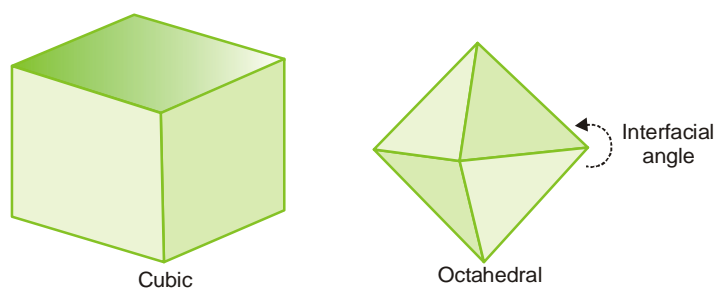
**Anisotropy in crystals is due to different arrangements of particles in different directions.**

## THE HABIT OF A CRYSTAL

The external shape is called the **habit** of the crystal. The plane surfaces of the crystal are called **faces**. The angles between the faces are referred to as the **interfacial angles**. The interfacial angles for a given crystalline substance are always the same.

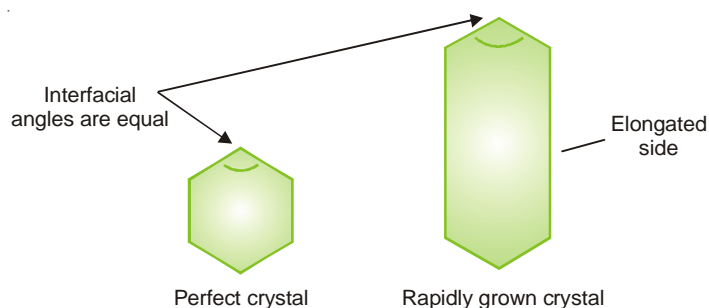
**The consistency of interfacial angles is an essential characteristic of crystalline solids.**

The habit of a crystal of a given compound depends on the rate of development of the different faces. Slow growth from a slightly super-saturated solution or a very slowly cooling solution gives large crystals. Different crystals of the same substance may not look alike. In the presence of certain impurities, different faces grow at different rates and give rise to many forms. For example, if sodium chloride is crystallised from its supersaturated solution, it forms cubic crystals. But if urea is added as impurity, it gives octahedral crystals.



■ **Figure 12.3**  
Shapes of sodium chloride crystals obtained under different conditions.

As already stated, the external appearance or size of crystals of a substance may be different. It depends on the relative development of the different faces under appropriate conditions. **But the interfacial angles are always the same.** This is illustrated diagrammatically in Fig. 12.4.



■ **Figure 12.4**  
Interfacial angles are always the same.

## SYMMETRY OF CRYSTALS

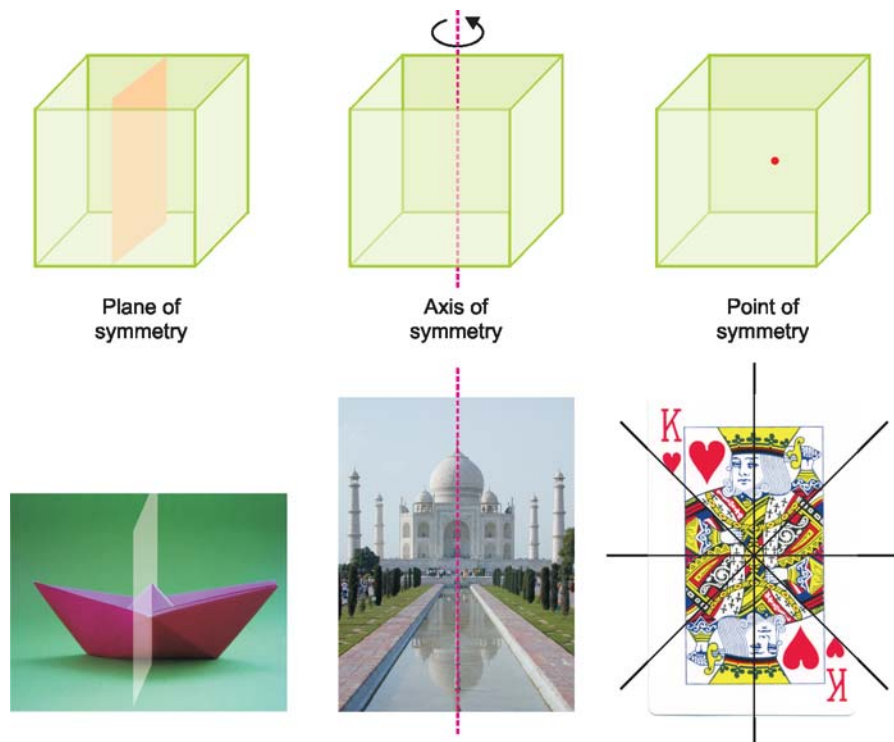
In addition to the angles, another important property of crystals is their symmetry. Symmetry in crystals may be due to a plane, a line or a point. Accordingly there are three types of symmetry elements associated with a crystal. These are called the **Elements of Symmetry**.

### (1) Plane of Symmetry

A crystal is said to have a plane of symmetry if it can be divided by an imaginary plane into two equal parts, each of which is the exact mirror image of the other.

**(2) Axis of Symmetry**

An axis of symmetry is an imaginary line drawn through the crystal such that during rotation of the crystal through  $360^\circ$ , the crystal presents exactly the same appearance more than once. If similar view appears twice, it is called an axis of two fold symmetry or **diad axis**. If it appears thrice, it is an axis of three fold symmetry or **triad axis**, and so on.



■ **Figure 12.5**  
Elements of Symmetry in a cubic crystal.

**(3) Centre of Symmetry**

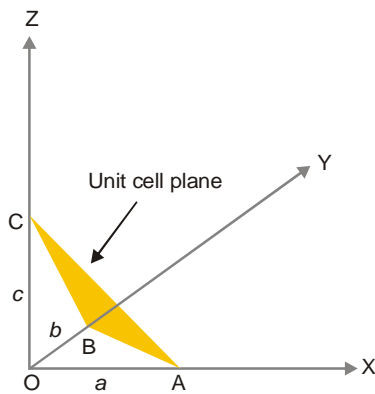
It is a point at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distances on either side. It is noteworthy that a crystal may have a number of planes of symmetry or axis of symmetry but it can have only one centre of symmetry.

**MILLER INDICES**

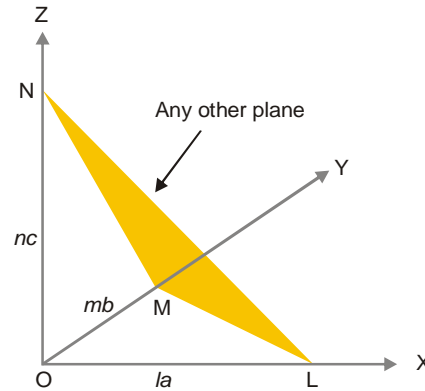
We know that crystal lattice consists of unit cells arranged in parallel planes. Thus each crystal plane lies parallel to the crystal face as also to the unit cell face. These planes cut the three axes along the three crystallographic axes (OX, OY, OZ). Haüy proposed that a given crystal plane could be described in terms of intercepts along the axes (Law of Rational intercepts). The reciprocals of these intercepts are small whole numbers. These numbers,  $h$ ,  $k$  and  $l$  are called **Miller indices** after the name of the British scientist W.H. Miller. Thus Miller indices of a plane may be defined as **the reciprocals of the intercepts which the plane makes with the axes**.

For illustration, let us consider a crystal system with the axes OX, OY and OZ. In Fig. 12.6 ABC represents a unit cell surface while LMN in Fig. 12.7 depicts another crystal plane under study. The intercepts of the unit cell plane are OA, OB and OC which have the lengths  $a$ ,  $b$  and  $c$  respectively. The intercepts of the plane under study are OL, OM and ON. These can be expressed as multiples of the

intercepts  $a, b, c$ , i.e.,  $la, mb$  and  $nc$ . Here  $l, m, n$  are either integral whole numbers or fractions of whole numbers. The reciprocals of these numbers are written together in brackets  $(h, k, l)$  to give the Miller indices of the plane under study.



■ **Figure 12.6**  
A unit cell plane intercepts the axes to give intercepts  $a, b$  and  $c$ .



■ **Figure 12.7**  
Any other plane intercepts the axes to give intercepts equal to  $la, mb$  and  $nc$ .

#### How to Find Miller Indices?

- (1) Write the intercepts as multiples of  $a, b, c$ , say,  $la, mb$  and  $nc$ .
- (2) Take reciprocals of  $l, m$ , and  $n$ ,
- (3) Clear fractions to get whole numbers  $h, k, l$ ,
- (4) Miller indices of the plane are  $(h, k, l)$ .

**SOLVED PROBLEM.** Determine the Miller indices for a plane when the intercepts along the axes are  $2a, 3b$  and  $2c$ .

#### SOLUTION

The unit cell intercepts are  $a, b, c$

The intercepts of the given plane are  $2a, 3b, 2c$

The lengths of the intercepts in terms of unit cell intercepts are 2, 3, 2

The reciprocals are  $\frac{1}{2}, \frac{1}{3}, \frac{1}{2}$

Clear fractions by multiplying with 6 which gives the whole numbers 3, 2, 3

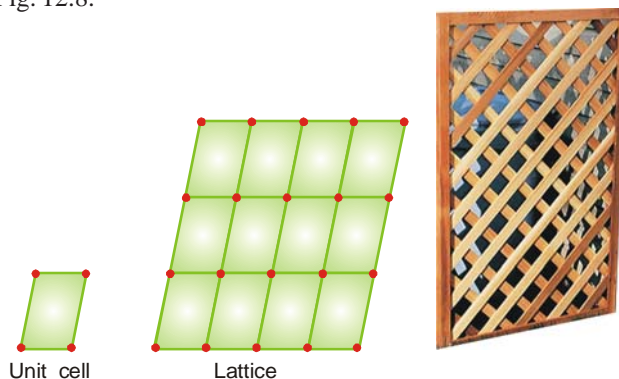
Thus the Miller indices of the given plane are  $(3, 2, 3)$ .

#### CRYSTAL STRUCTURE

The particles (atoms, ions or molecules) in crystals are highly ordered as is evident from their geometrical shapes, smooth surfaces and specific interfacial angles.

The particles in crystals are arranged in regular patterns that extend in all directions. The overall arrangement of particles in a crystal is called the **Crystal lattice, Space lattice or Simply lattice**.

To describe the structure of a crystal it is convenient to view it as being made of a large number of basic units. The simple basic unit or the building block of the crystal lattice is called the **Unit cell**. This is illustrated in Fig. 12.8.



■ **Figure 12.8**  
Two-dimensional illustration of unit cell and crystal lattice.

### How to Represent Crystal Lattice and Units Cells ?

The crystal lattice of a substance is depicted by showing the position of particles (**structural units**) in space. These positions are represented by bold dots (or circles) and are referred to as **lattice points** or **lattice sites**. The overall shape and structure of a crystal system is governed by that of the unit cell of which it is composed.

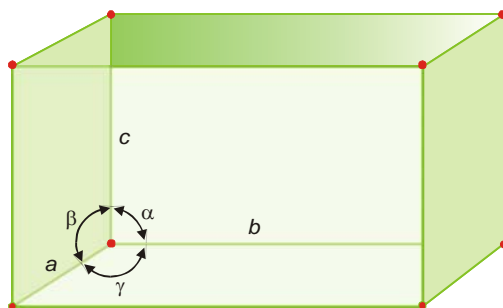
A unit cell has one atom or ion at each corner of the lattice. Also, there may be atoms or ions in faces and interior of the cell. A cell with an interior point is called the **body centered cell**. A cell which does not contain any interior points is known as the **primitive cell**. That is, a **primitive cell is a regular three-dimensional unit cell with atoms or ions located at its corners only**.

### Parameters of the Unit Cells

In 1850, August Bravais, a French mathematician observed that the crystal lattice of substances may be categorised into seven types. These are called **Bravais lattices** and the corresponding unit cells are referred to as **Bravais unit cells**. The unit cells may be characterised by the following parameters :

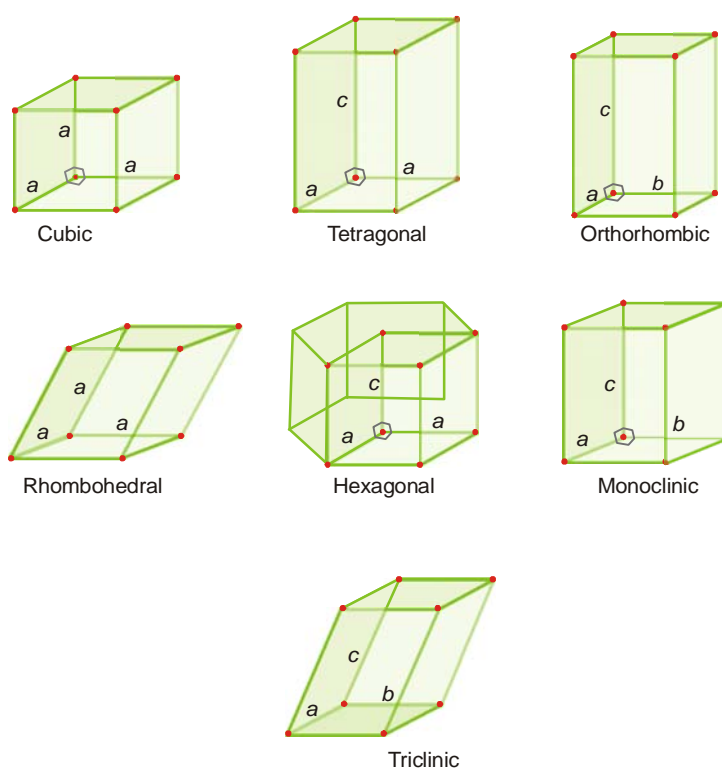
- relative lengths of the edges along the three axes ( $a$ ,  $b$ ,  $c$ ).
- the three angles between the edges ( $\alpha$ ,  $\beta$ ,  $\gamma$ ).

The parameters of a unit cell can be illustrated as in Fig. 12.9. Parameters of the seven Bravais unit cells are listed in Table 12.1.



■ **Figure 12.9**  
Illustration of parameters of a unit cell.

TABLE 12.1. THE SEVEN UNIT CELLS			
Crystal system	Relative axial length	Angles	Examples
Cubic (isometric)	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{Na}^+\text{Cl}^-$ , $\text{Cs}^+\text{Cl}^-$ , $\text{Ca}^{2+}(\text{F}^-)_2$ , $\text{Ca}^{2+}\text{O}^{2-}$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$(\text{K}^+)_2\text{PtCl}_6^{2-}$ , $\text{Pb}^{2+}\text{WO}_4^{2-}$ , $\text{NH}_4^+\text{Br}^-$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$(\text{K}^+)_2\text{SO}_4^{2-}$ , $\text{K}^+\text{NO}_3^-$ , $\text{Ba}^{2+}\text{SO}_4^{2-}$ , $\text{Ca}^{2+}\text{CO}_3^{2-}$ (aragonite)
Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	$\text{Ca}^{2+}\text{CO}_3^{2-}$ (calcite), $\text{Na}^+\text{NO}_3^-$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	AgI, SiC, HgS
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	$\text{Ca}^{2+}\text{SO}_4^{2-} \cdot 2\text{H}_2\text{O}$ , $\text{K}^+\text{ClO}_3^-$ , $(\text{K}^+)_4\text{Fe}(\text{CN})_6^{4-}$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{Cu}^{2+}\text{SO}_4^{2-} \cdot 5\text{H}_2\text{O}$ , $(\text{K}^+)_2\text{Cr}_2\text{O}_7^{2-}$



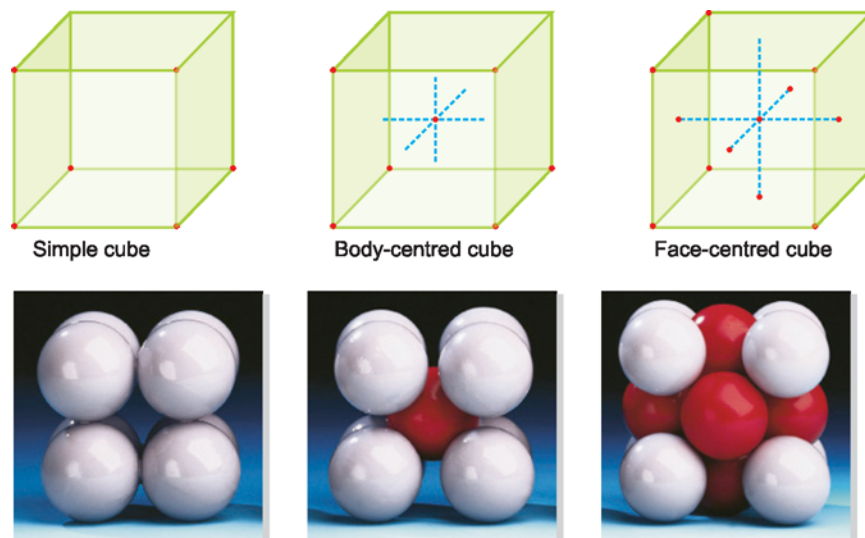
■ **Figure 12.10**

The primitive unit cells for the seven crystal systems. Where two or more of the axes are equal, the same letter is shown in each. Right angles ( $90^\circ$ ) are shown as  $\gamma$ . The heavy line indicates the hexagonal unit cell.

### CUBIC UNIT CELLS

These are the simplest unit cells. These unit cells are particularly important for two reasons. First, a number of ionic solids and metals have crystal lattices comprising cubic unit cells. Second, it

is relatively easy to make calculations with these cells because in them all the sides are equal and the cell angles are all  $90^\circ$ .



■ **Figure 12.11**  
Three cubic unit cells.

### Three types of Cubic Unit Cells

There are three types of cubic unit cells :

- (1) Simple cubic unit cell
- (2) Body-centred cubic unit cell
- (3) Face-centred cubic unit cell

A **simple cubic unit cell** is one in which the atoms or ions are occupying only the corners of the cube.

A **body-centred cubic unit cell** has one particle at the centre of the cube in addition to the particles at the corners.

A **face-centred cubic unit cell** has one particle at each of the six faces of the cube apart from the particles at the corners.

### How to Compute Atoms or Points in a Unit Cell ?

In counting the number of atoms (or points) per unit cell, we must keep in mind that atoms on corners of faces are shared with adjoining cells. Therefore the number of atoms in a cubic unit cell may be computed as follows.

(1) Eight unit cells share each corner atom. Therefore **the simple cubic unit cell contains the equivalent of one atom.**

$$\begin{aligned} \text{At each corner we have} &= 1/8 \text{ atom} \\ \text{At 8 corners we have} &= 1/8 \times 8 = 1 \text{ atom} \end{aligned}$$

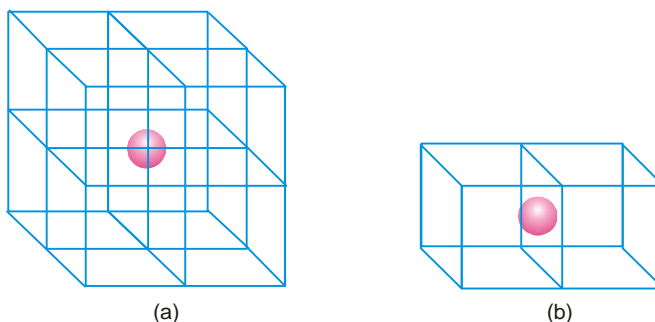
(2) Each face-centred atom is shared by two unit cells. Therefore **the face-centred unit cell contains the equivalent of four atoms.**

$$\begin{aligned} \text{At 8 corners, } 1/8 \text{ each} &= 1 \text{ atom} \\ \text{6 face-centred sites, } 1/2 \text{ each} &= 3 \text{ atoms} \\ \text{Total equivalent atoms} &= 1 + 3 = 4 \end{aligned}$$



(3) A body centred unit cell contains the equivalent of two atoms.

$$\begin{aligned} \text{At 8 corners at } 1/8 \text{ each} &= 1 \text{ atom} \\ \text{central unshared} &= 1 \text{ atom} \\ \text{Total equivalent atoms} &= 1 + 1 = 2 \end{aligned}$$



■ Figure 12.12

(a) In the simple cubic cell, each corner atom is shared by 8 cells; (b) In the face-centred cell, each atom in a face is shared by 2 cells.

### Calculation of Mass of the Unit Cell

Mass of the unit cell can be calculated from the number of atoms in the unit cells. For this multiply the mass of one atom by the number of atoms in the unit cell.

$$\text{Thus the mass of one atom} = \frac{\text{molar mass of the substance}}{\text{Avogadro's number}}$$

**SOLVED PROBLEM 1.** The unit cell of metallic gold is face-centred cubic.

- (a) How many atoms occupy the gold unit cell ?  
 (b) What is the mass of a gold unit cell ?

#### SOLUTION

eight corners at  $1/8$  atom each = 1 atom  
 six faces at  $1/2$  atom each = 3 atoms  
 $\therefore$  4 atoms occupy the gold unit cell.

$$\begin{aligned} \text{Mass of gold atom} &= \frac{\text{molar mass}}{\text{Avogadro's number}} \\ &= \frac{197 \text{ g/mol}}{6.022 \times 10^{23} \text{ Au atoms/mol}} \times \frac{1}{4} = 8.178 \times 10^{-23} \text{ g} \end{aligned}$$

**SOLVED PROBLEM 2.** By X-ray diffraction it is found that nickel crystals are face-centred cubic. The edge of the unit cell is  $3.52 \text{ \AA}$ . The atomic mass of nickel is 58.7 and its density is  $8.94 \text{ g/cm}^3$ . Calculate Avogadro's number from the data.

#### SOLUTION

Number of atoms in nickel unit cell = 4

Let Avogadro's number =  $N$

$$\text{Thus the mass of one Ni atom} = \frac{58.7}{N}$$

$$\text{the mass of one unit cell} = 4 \left( \frac{58.7}{N} \right) \text{ g}$$

the volume of one unit cell =  $(3.52 \times 10^{-8})^3 \text{ cm}^3$

the density of nickel cell =  $\frac{4(58.7/N) \text{ g}}{(3.52 \times 10^{-8})^3 \text{ cm}^3} = 8.94 \text{ g/cm}^3$  (given)

$\therefore$

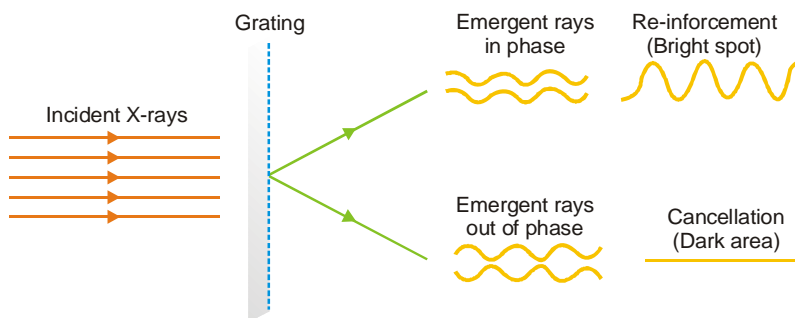
$$N = 6.02 \times 10^{23}$$

### What is Coordination Number of a Crystal Lattice ?

The coordination number of a crystal structure is the number of particles (ions, atoms or molecules) immediately adjacent to each particle in the lattice. It is characteristic of a given space lattice and is determined by inspection of the model. In a simple cubic lattice *e.g.*, NaCl, each particle is surrounded by six other particles and so the coordination number is six. It will be observed that the coordination numbers for body-centred and face-centred cubic lattice are 8 and 12 respectively.

### X-RAY CRYSTALLOGRAPHY

A crystal lattice is considered to be made up of regular layers or planes of atoms equal distance apart. Since the wavelength of X-rays is comparable to the interatomic distances, Laue (1912) suggested that crystal can act as grating to X-rays. Thus when a beam of X-rays is allowed to fall on a crystal, a large number of images of different intensities are formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots are produced on a photographic plate placed in their path. On the other hand, if the diffracted waves are out of phase, dark spots are caused on the photographic plate. From the overall diffraction patterns produced by a crystal, we can arrive at the detailed information regarding the position of particles in the crystal. **The study of crystal structure with the help of X-rays is called X-ray crystallography.**



■ **Figure 12.13**  
Diffraction patterns produced by crystals.

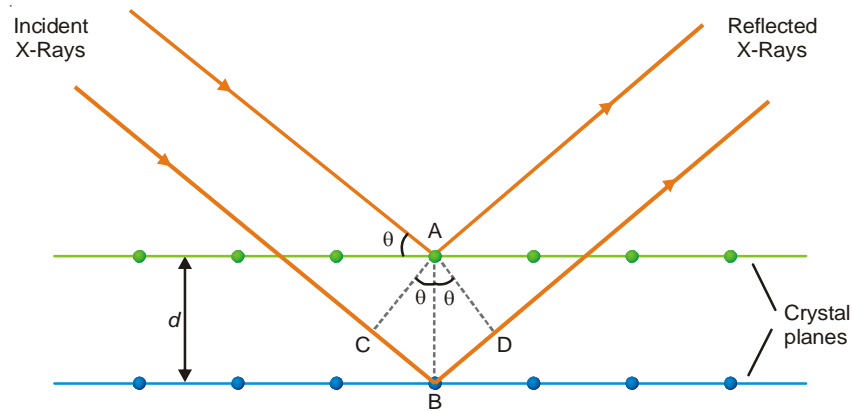
### BRAGG'S EQUATION

In 1913 the father-and-son, W.L. Bragg and W.H. Bragg worked out a mathematical relation to determine interatomic distances from X-ray diffraction patterns. This relation is called the **Bragg equation**. They showed that :

- (1) **the X-ray diffracted from atoms in crystal planes obey the laws of reflection.**
- (2) **the two rays reflected by successive planes will be in phase if the extra distance travelled by the second ray is an integral number of wavelengths.**

### DERIVATION OF BRAGG EQUATION

Fig. 12.14 shows a beam of X-rays falling on the crystal surface. Two successive atomic planes of the crystal are shown separated by a distance  $d$ . Let the X-rays of wavelength  $\lambda$  strike the first plane at an angle  $\theta$ . Some of the rays will be reflected at the same angle. Some of the rays will



■ **Figure 12.14**  
Reflection of X-Rays from two different planes of a crystal.

penetrate and get reflected from the second plane. These rays will reinforce those reflected from the first plane if the extra distance travelled by them ( $CB + BD$ ) is equal to integral number,  $n$ , of wavelengths. That is,

$$n\lambda = CB + BD \quad \dots(i)$$

Geometry shows that

$$CB = BD = AB \sin \theta \quad \dots(ii)$$

From (i) and (ii) it follows that

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

or

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

This is known as the **Bragg equation**. The reflection corresponding to  $n = 1$  (for a given series of planes) is called the first order reflection. The reflection corresponding to  $n = 2$  is the second order reflection and so on.

Bragg equation is used chiefly for determination of the spacing between the crystal planes. For X-rays of specific wave length, the angle  $\theta$  can be measured with the help of **Bragg X-ray spectrometer**. The interplanar distance can then be calculated with the help of Bragg equation.

**SOLVED PROBLEM.** Find the interplanar distance in a crystal in which a series of planes produce a first order reflection from a copper X-ray tube ( $\lambda = 1.539 \text{ \AA}$ ) at an angle of  $22.5^\circ\text{C}$ .

**SOLUTION**

From Bragg equation

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

We have

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

Hence

$$\begin{aligned} d &= \frac{1.539 \text{ \AA}}{2 \sin (22.5)} \\ &= \frac{1.539 \text{ \AA}}{2(0.383)} = 2.01 \text{ \AA} \end{aligned}$$

**SOLVED PROBLEM.** Diffraction angle  $2\theta$  equal to  $16.8^\circ$  for a crystal having inter planar distance in the crystal is  $0.400\text{ nm}$  when second order diffraction was observed. Calculate the wavelength of X-rays used.

**SOLUTION.** Here

$$n = 2; d = 0.400\text{ nm} = 0.4 \times 10^{-9}\text{ m}$$

$$2\theta = 16.8^\circ \text{ or } \theta = 8.4^\circ$$

Using Bragg's equation

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

Substituting the values, we get

$$2 \times \lambda = 2 \times 0.4 \times 10^{-9} \times \sin 8.4$$

$$\text{or } \lambda = \frac{2 \times 0.4 \times 10^{-9} \times 0.146}{2}$$

$$\text{or } \lambda = 0.0584 \times 10^{-9}\text{ m}$$

$$\text{or } \lambda = 0.584 \times 10^{-10}\text{ m}$$

$$\text{or } \lambda = \mathbf{0.584 \text{ \AA}}$$

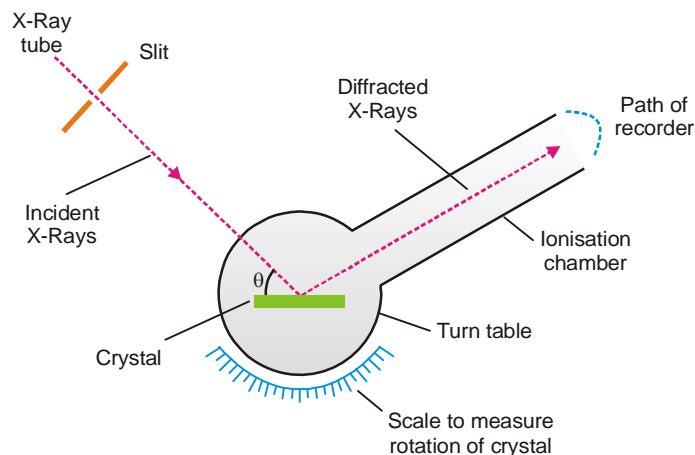
### MEASUREMENT OF DIFFRACTION ANGLE

The measurement of diffraction angle,  $\theta$ , required for Bragg equation can be done in two ways.

- (1) The rotating crystal method (Braggs, 1913)
- (2) The powder method (Debye and Scherrer, 1916)

#### (1) The Rotating Crystal Method

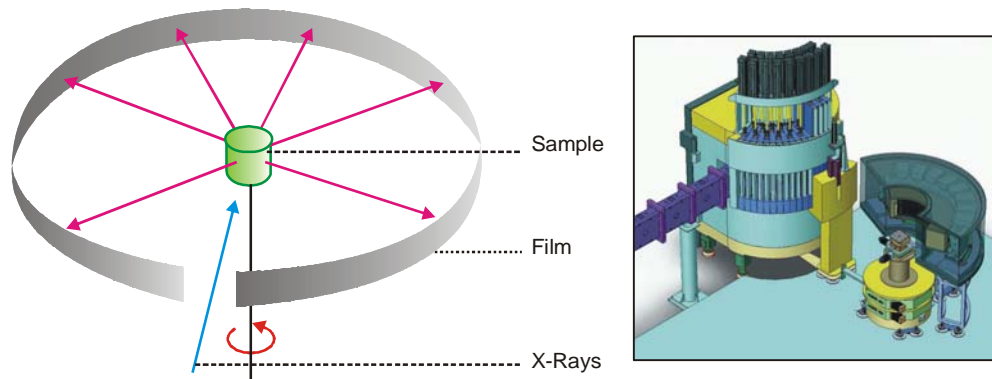
The apparatus used by Bragg is shown in Fig. 12.15. A beam of X-rays of known wave length falls on a face of the crystal mounted on a graduated **turn table**. The diffracted rays pass into the ionisation chamber of the **recorder**. Here they ionise the air and a current flows between the chamber wall and an electrode inserted in it which is connected to an electrometer. The electrometer reading is proportional to the intensity of X-rays. As the recorder along with the crystal is rotated, the angles of maximum intensity are noted on the scale. Thus values of  $\theta$  for  $n = 1, 2, 3$ , etc. are used to calculate the distance  $d$  between the lattice planes parallel to the face of the crystal.



■ **Figure 12.15**  
Rotating crystal method to determine the angle of diffraction  $\theta$ .

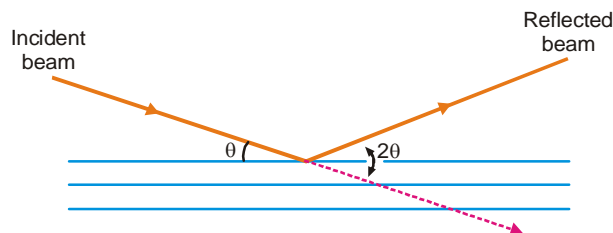
## (2) The Powder Method

The rotating crystal method could only be used if a single undistorted crystal is available. To overcome this limitation, the powder method was devised. In this method the crystalline material contained in a capillary tube is placed in the camera containing a film strip (Fig. 12.16). The sample is rotated by means of a motor. The X-rays pass through the gap between the ends of the film.



■ **Figure 12.16**  
The Powder method.

The powdered sample contains small crystals arranged in all orientations. Some of these will reflect X-rays from each lattice plane at the same time. The reflected X-rays will make an angle  $2\theta$  with the original direction. Hence on the photo are obtained lines of constant  $\theta$ . From the geometry of the camera,  $\theta$  can be calculated for different crystal planes.



■ **Figure 12.17**  
Angle made by the reflected beam with incident beam.

## CLASSIFICATION OF CRYSTALS ON THE BASIS OF BONDS

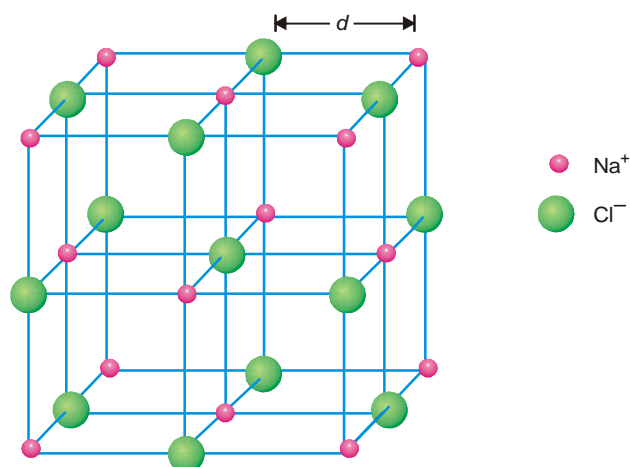
Crystals can also be classified on the basis of the bonds that hold the ions, molecules or atoms together in the crystal lattice. Thus we have :

- (a) Ionic crystals
- (b) Molecular crystals
- (c) Network covalent crystals
- (d) Metallic crystals

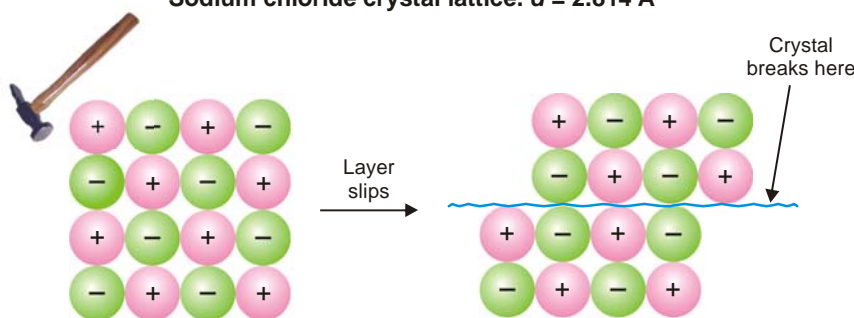
### IONIC CRYSTALS

In an ionic crystal the lattice is made of positive and negative ions. These are held together by ionic bonds – the strong electrostatic attractions between oppositely charged ions. Consequently, the cations and anions attract one another and pack together in an arrangement so that the attractive forces maximise. The sodium chloride lattice shown in Fig. 12.18 is an example. Each ion is surrounded by neighbours of opposite charge and there are no separate molecules. Since the ions are fixed in their lattice sites, typical ionic solids are hard and rigid with high melting points. In spite of

their hardness, ionic solids are brittle. They shatter easily by hammering (Fig. 12.19). By hammering, a layer of ions slips away from their oppositely charged neighbours and brings them closer to ions of like charge. The increase of electrostatic repulsions along the displaced plane causes the crystal to break.



■ **Figure 12.18**  
Sodium chloride crystal lattice.  $d = 2.814 \text{ \AA}$



■ **Figure 12.19**  
An ionic crystal is brittle and breaks by hammering.

Ionic solids are non-conducting because the ions are in fixed positions. However, in the fused state the ions are allowed freedom of movement so that it becomes possible for them to conduct electricity.

### Sodium Chloride Crystal

The ionic lattice of NaCl is shown in Fig. 12.18. Each sodium ion is surrounded by six chloride ions and each chloride ion is clustered by six sodium ions. The co-ordination number for this crystal lattice is six as required by simple cubic type. In this cubic system, the planes can be passed through the atoms having Miller indices (100), (110) or (111) and the relative spacings for the unit cell of a face-centred cubic lattice are  $\frac{a}{2}$ ,  $\frac{a}{2\sqrt{2}}$  and  $\frac{a}{\sqrt{3}}$  while it is  $a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}}$  for simple cubic and  $\frac{a}{2} : \frac{a}{\sqrt{2}} : \frac{a}{2\sqrt{3}}$  for body-centred cubic lattice. For face-centred cubic lattice,

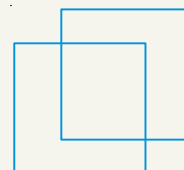
$$\begin{aligned} d_{100} : d_{110} : d_{111} &= \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}} \\ &= 1 : 0.707 : 1.154 \end{aligned} \quad \dots(i)$$

## HOW TO DRAW STRUCTURE OF NaCl ?

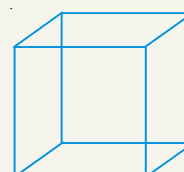
Draw a perfect square.



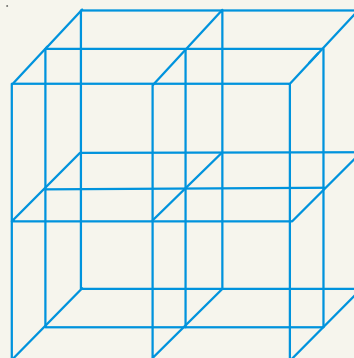
Now draw an identical square behind this one and offset a bit. You might have to practice a bit to get the placement of the two squares right. If you get it wrong, the ions get all tangled up with each other in your final diagram.



Turn this into a perfect cube by joining the squares together.

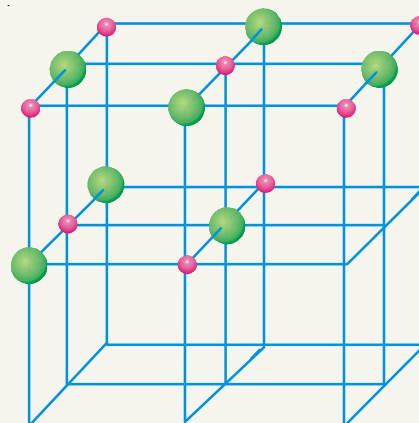


Now the tricky bit! Subdivide this big cube into 8 small cubes by joining the mid point of each edge to the mid point of the edge opposite it. To complete the process you will also have to join the mid point of each face (easily found once you've joined the edges) to the mid point of the opposite face.



Now all you have to do is put the ions in. Use different colours or different sizes for the two different ions, and don't forget a key. It doesn't matter whether you end up with a sodium ion or a chloride ion in the centre of the cube – all that matters is that they alternate in all three dimensions.

You should be able to draw a perfectly adequate free-hand sketch of this in under two minutes – less than one minute if you're not too fussy!



In the case of sodium chloride the *first order* reflections from (100), (110) and (111) faces using *K* line from palladium anti-cathode are  $5.9^\circ$ ,  $8.4^\circ$  and  $5.2^\circ$  respectively. From Bragg equation  $n\lambda = 2d \sin \theta$ , we have

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

Since  $n = 1$  and  $\lambda$  is the same in each case, the ratio of the spacings parallel to the three principal planes are

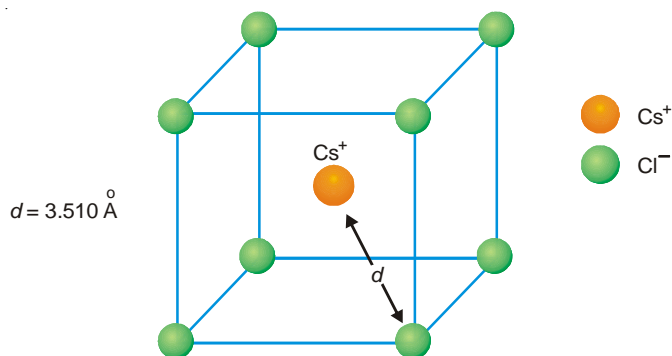
$$\begin{aligned} d_{100} : d_{110} : d_{111} &= \frac{1}{\sin 5.9^\circ} : \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ} \\ &= 9.731 : 6.844 : 11.04 \\ &= 1 : 0.704 : 1.136 \quad \dots(ii) \end{aligned}$$

This ratio is almost identical with the ratio required in the case of a face-centred cubic lattice as shown in (i).

X-ray diffraction studies reveal that unlike sodium chloride, potassium chloride has a simple cubic lattice. The edge length of the unit cell is  $3.1465 \text{ \AA}$ .

### Cesium Chloride Crystal

Cesium chloride, CsCl, has a body-centred cubic structure. In its crystal lattice, each  $\text{Cs}^+$  ion is surrounded by 8  $\text{Cl}^-$  ions and its coordination number is eight. The value of  $d$  (Fig. 12.20) as determined by Bragg spectrometer is  $3.510 \text{ \AA}$ .



■ **Figure 12.20**  
Cesium chloride crystal lattice.

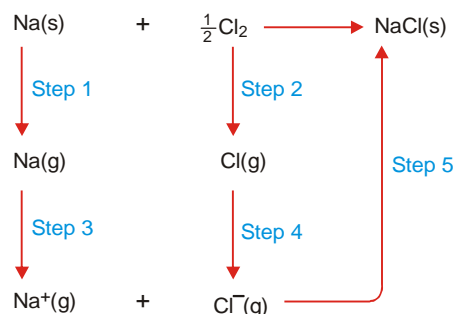
Let us assume that the ions are hard spheres. Further, the anions are in contact with cations *i.e.*, ions are as closely packed as possible.  $\text{Cs}^+\text{Cl}^-$  is, therefore,  $r_+ + r_-$ , where  $r_+$  and  $r_-$  represent radius of cations and the anions respectively. The radius ratio  $r_+/r_-$  has been determined to be 1.37. The radius ratio for sodium chloride structure is 2.44. Knowing the radius ratio of a particular crystal, we can say whether it has CsCl or NaCl structure.

### Lattice Energy of an Ionic Crystal (Born-Haber Cycle)

The positive and negative ion in an ionic crystal are held together by electrostatic forces. The bond energy is expressed in terms of the **lattice energy** which may be defined as :

**the change in enthalpy (heat change) that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions.**





■ **Figure 12.21**  
A Born-Haber cycle for the formation of NaCl crystal from its elements.

The lattice energy of NaCl, for example, is the change in enthalpy,  $\Delta H^\circ$ , when  $\text{Na}^+$  and  $\text{Cl}^-$  ions in the gas phase come together to form 1 mole of NaCl crystal.

### Determination of Lattice Energy

The lattice energy of an ionic crystal can be found by applying Hess's law. The formation of an ionic solid from its elements can be thought of as occurring directly in one step or indirectly as the sum of the series of steps. Let us illustrate by taking example of NaCl.

**Enthalpy change for direct formation.** The enthalpy change for the direct formation of sodium chloride from sodium metal and chlorine is  $-411$  kJ.



**Enthalpy change by indirect steps.** The direct enthalpy change of NaCl stated above is equal to enthalpy changes of five steps by which the formation of NaCl can be accomplished.

**Step 1.** Conversion of sodium metal to gaseous atoms (sublimation).



**Step 2.** Dissociation of chlorine molecules to chlorine atoms. The enthalpy of dissociation is 121 kJ per mole of chlorine.



**Step 3.** Conversion of gaseous sodium to sodium ions by losing electrons. The enthalpy of ionisation is the ionisation energy, 495 kJ/per mole of sodium atoms.



**Step 4.** Chlorine atoms gain an electrons to form chloride ions. The energy released is the electron affinity of chlorine  $-348$  kJ.



**Step 5.** Sodium and chloride ions get together and form the crystal lattice. The energy released in this process is the negative of lattice energy.



The lattice energy can be calculated by equating the enthalpy of formation of NaCl,  $-411$  kJ, to the sum of the enthalpy changes for the five steps.

$$\Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ = -411 \text{ kJ}$$

$$108 \text{ kJ} + 121 \text{ kJ} + 495 \text{ kJ} - 348 \text{ kJ} - \text{lattice energy} = -411 \text{ kJ}$$

By solving this equation we get

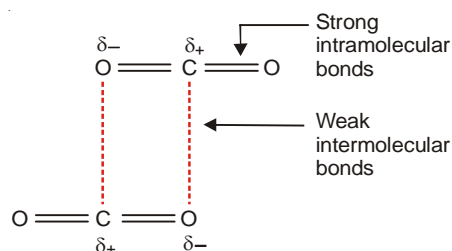
$$\text{Lattice energy} = +787 \text{ kJ mol}^{-1}$$

The cycle of changes shown in Fig. 12.21, is called the **Born-Haber Cycle** after Max Born and Fritz Haber, who devised this method of calculating lattice energies.

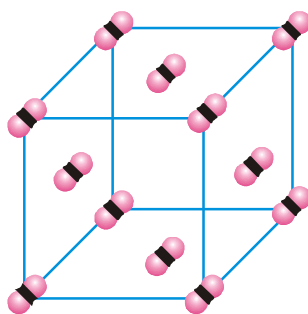
### MOLECULAR CRYSTALS

In molecular crystals, molecules are the structural units. These are held together by van der Waals' forces. As in case of ionic crystals, the molecules are packed together in a tightly packed pattern because the forces of attraction are non-directional. When this type of crystal melts, it is only the weak van der Waals forces that must be overcome. Therefore molecular solids have low melting points. Most organic substances are molecular solids.

**Crystal lattice of dry CO<sub>2</sub>.** Dry ice, or frozen carbon dioxide, is the best example of a molecular solid. The van der Waals' forces holding the CO<sub>2</sub> molecules together are weak enough so that dry ice passes from solid state to gaseous state at  $-78^\circ\text{C}$ .



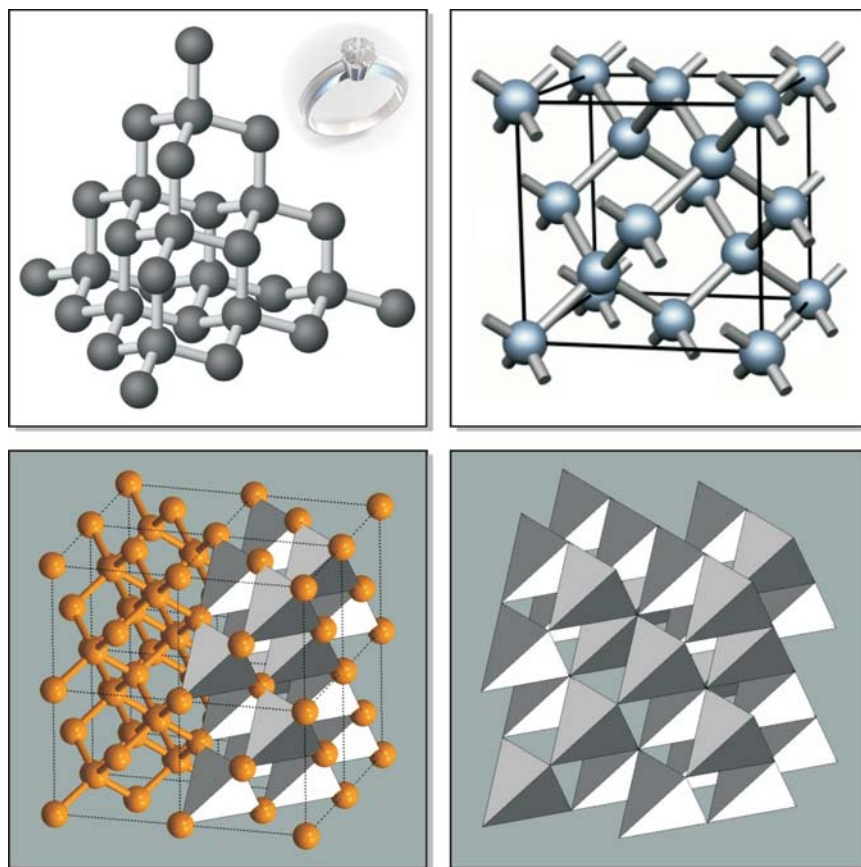
The pattern in which CO<sub>2</sub> molecules are arranged in the crystal lattice is shown in Fig. 12.22.



■ **Figure 12.22**  
Arrangement of CO<sub>2</sub> molecules in the crystal lattice.

### NETWORK COVALENT CRYSTALS

In this type of crystals atoms occupy the lattice sites. These atoms are bonded to one another by covalent bonds. The atoms interlocked by a network of covalent bonds produce a crystal which is considered to be a single giant molecule. Such a solid is called a **network covalent solid** or simply **covalent solid**. Since the atoms are bound by strong covalent bonds, these crystals are very hard and have very high melting points.



■ **Figure 12.23**  
Crystal structure of diamond.

**Structure of Diamond.** Diamond offers the best example of a network covalent solid. It consists of carbon atoms bonded to one another in a three-dimensional pattern to form the crystal. However, each carbon is  $sp^3$  hybridised and is bonded to four neighbouring carbon atoms arranged towards the corners of a tetrahedron. The diamond crystal made of carbon atoms joined by a network of strong covalent bonds is the hardest substance known and has an extremely high melting point ( $3550^\circ\text{C}$ ). Since the bonds between two carbons cannot be distorted to any great extent, the diamond crystal cannot be distorted but is rather brittle and gives way in the face of a shearing force.

### METALLIC CRYSTALS

The crystals of metals consist of atoms present at the lattice sites. The atoms are arranged in different patterns, often in layers placed one above the other. The atoms in a metal crystal are viewed to be held together by a metallic bond. The valence electrons of the metal atoms are considered to be delocalised leaving positive metal ions. The freed electrons move throughout the vacant spaces between the ions. The electrostatic attractions between the metal ions and the electron cloud constitute the metallic bond. **Thus a metal crystal may be described as having positive ions at the lattice positions surrounded by mobile electrons throughout the crystal.**

The **electron sea model** explains well the properties of metals. The mobile electrons in the crystal structure make metals excellent conductors of heat and electricity. On application of force, say with a hammer, metals can be deformed. The metal ions in the crystal change positions without making

## BUCKMINSTERFULLERENE



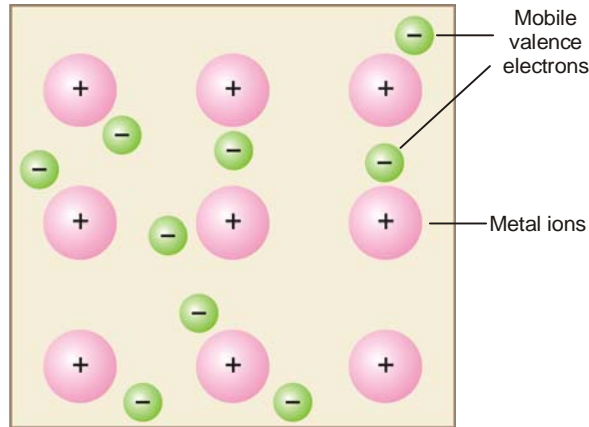
Buckminsterfullerene molecules consist of 60 carbon atoms linked together to form an almost spherical ball with the chemical formula  $C_{60}$ . The bonds between atoms form a pattern of joined hexagons and pentagons that is similar to the panels on a soccer ball. The allotrope was given its name because its structure resembles the elaborate geometrical structures invented by American architect Buckminster Fuller. The individual molecules have become known as **buckyballs**.

For many years it was believed that the element carbon occurred as only three allotropes: diamond, graphite, and amorphous carbon. In each of these allotropes, the carbon atoms are linked together in a different arrangement, giving the form of the element different properties. In 1985, however, a new family of allotropes was discovered. Of these allotropes, which are called fullerenes, buckminsterfullerene has become the most famous. Other fullerenes have more carbon atoms, and their shapes resemble elongated versions of the original, football-shaped buckminsterfullerene. Once buckminsterfullerene could be produced in large amounts, a solid form, fullerite, was also produced. In this transparent yellow solid, the molecules are stacked together in a close-packed arrangement like a pile of cannon balls. Tubular versions of fullerenes are also available in solid form.

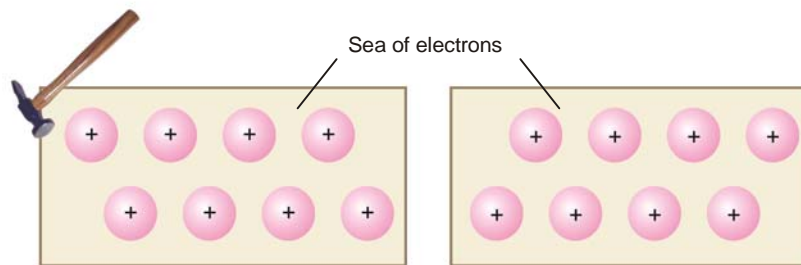
The original method of preparation of buckminsterfullerene was to produce it in a molecular beam, and only very small quantities could be made. However, it was soon found that the molecules were produced in large numbers in an electric arc between two carbon electrodes in a helium atmosphere. Scientists now believe that buckminsterfullerene is likely to be formed in sooty flames, and there is a possibility that it is abundant in the universe, particularly near red-giant stars.

The versatility of fullerene molecules has led to a great deal of research exploring their properties. One potentially useful property is that atoms of different elements can be placed inside the molecular cage formed by the carbon atoms, producing a “shrink wrapped” version of these elements. When metal atoms are introduced into fullerene tubes, the resulting material is like a one-dimensional insulated wire. Another important property is that certain compounds of buckminsterfullerene (notably  $K_3C_{60}$ ) are superconducting at low temperatures. Compounds made by adding thallium and rubidium ions (electrically charged atoms) to fullerenes become superconducting at  $-228^\circ\text{C}$  ( $-378^\circ\text{F}$ ). This temperature is relatively high compared to the cooling required by other superconducting materials. Derivatives of buckminsterfullerene have been found to be biologically active and have been used to attack cancer. It is believed that the molecules can enter the active sites of enzymes and block their action.

material difference in the environments. The attractive force between ions and the electron cloud remains the same. The crystal, therefore, does not break.



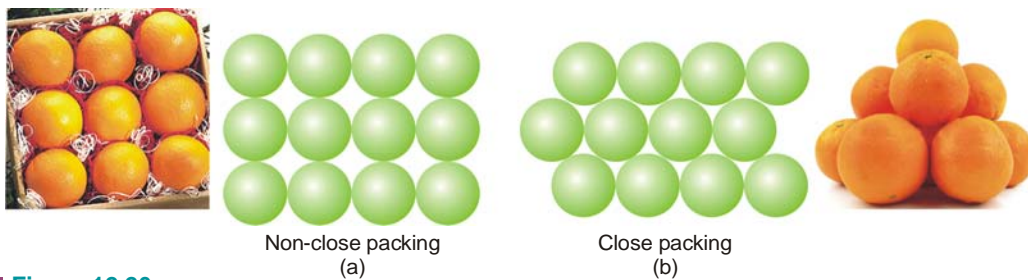
■ **Figure 12.24**  
A representation of a metallic crystal structure.



■ **Figure 12.25**  
On application of force positive kernels of metallic atoms can be moved within the sea of electrons without materially changing the environments. That is why metals can be worked into sheets or foils without cracking.

**STRUCTURE OF METAL CRYSTALS**

The individual atoms in a metallic crystal lattice can be thought of as hard spheres. The spherical atoms are packed together in the lattice very efficiently in geometrical arrangements so as to leave minimum interspaces. A layer of uniform spheres can be arranged either as in Fig. 12.26(a) or (b). Clearly the second of the patterns uses space more efficiently. Here the spheres fit into the hollows between the adjacent spheres. Thus the vacant spaces (voids) between the spheres are smaller than in the first pattern. The metallic crystals are of the second type *i.e.*, close packing.



■ **Figure 12.26**  
Two packing patterns of spheres.

As clear from Fig. 12.26(b), each sphere in a closely packed layer is in contact with four others. Thus each ball touches six other at the corners of a hexagon. Three dimensional metallic crystals consist of closely packed layers stacked one over the other. The spheres forming the second layer fill the holes or voids in the first layer and the spheres of the third layer fill the voids in the second layer. Depending upon the geometrical arrangements of spheres in the three layers, the close-packed metallic crystals are of two types :

- (a) Hexagonal close-packed (hcp)
- (b) Cubic close-packed (ccp)

### Hexagonal Close-Packed Structure

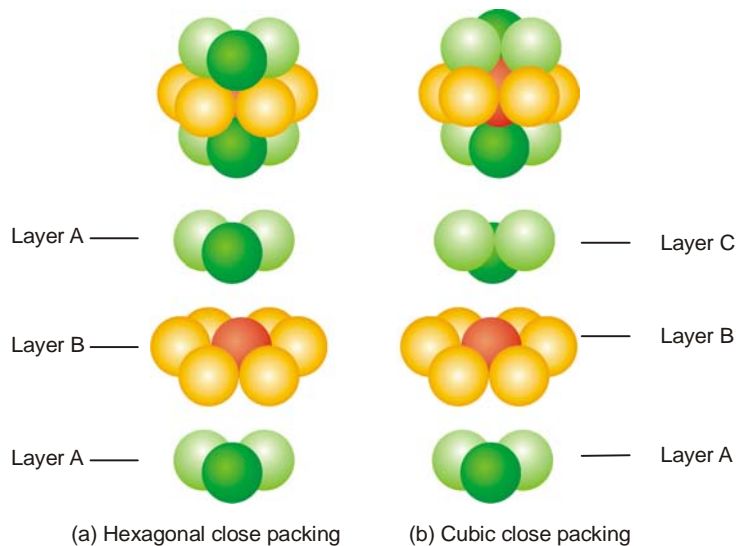
The hexagonal close-packed structure of metallic crystals is shown in Fig. 12.27. It consists of three layers of spherical atoms packed one over the another. The bottom layer (A) and the top layer (A) have three spheres in similar orientation. The middle layer (B) consists of six spherical atoms. The three spheres in the top and the bottom layer fit into the same voids on either side of the middle layer. It is noteworthy that each sphere in the structure is in contact with 12 neighbouring spheres, six in its own layer, three in the layer above and three in the layer below. Thus the coordination number of the close-packed structure is 12. In the overall close-packed structure, the layers repeat in the manner ABABAB.

The examples of metals having hexagonal close-packed structures are Ba, Co, Mg and Zn.

### Cubic Close-Packed Structure

The cubic close-packed (ccp) pattern of a metallic crystal is illustrated in Fig. 12.27. Its coordination number is also 12. Like the hcp structure, it consists of three layers of spherical atoms lying over one another. There are three spheres in the top layer (C), six in the middle layer (B), and three in the bottom layer (A). However, the overall ccp differs in structure from the hcp structure in respect of the orientation of the three spheres in the top layer. In hcp structure both the top and the bottom layers have the same orientation. But in ccp structure, they are oriented in opposite directions. Therefore, the three spheres in the top layer do not lie exactly on the spheres in the bottom layers. In ccp structure, the layers are repeated in the order ABCABCABC. By turning the whole crystal you can see that the ccp structure is just the face-centred cubic structure.

Many metals including Ag, Au, Ca, Co, Cu, Ni, crystallise in ccp structures.



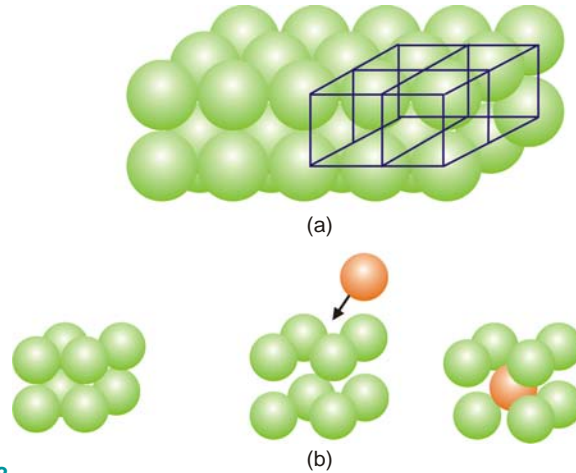
■ **Figure 12.27**  
Hexagonal and cubic close packed structures.

### Body-Centred Cubic Structure

About one-third of the metals pack in a body-centred cubic structure in which the coordination number is only 8. Each atom touches four atoms in the layer above and four atoms in the layer below.

When a square-packed layer (non-close packed) is packed on another layer (Fig. 12.28), a simple cubic pattern of spherical atoms results. The large holes remaining in the middle of each cube on slight expansion can accommodate another sphere to form a body-centred cube.

Li, Na and K crystallise in body-centred cubic structures.



■ **Figure 12.28**  
**(a) Layers of non-close spheres stacked one on the other. (b) Fifth atom when inserted in a simple cubic structure forms a body-centred cubic pattern.**

### CRYSTAL DEFECTS

So far in our discussion of crystalline substances, we have assumed them to be **perfect crystals**. A perfect crystal is one in which all the atoms or ions are lined up in a precise geometric pattern. But crystals are never actually perfect. The **real crystals** that we find in nature or prepare in the laboratory always contain imperfections in the formation of the crystal lattice. These crystal defects can profoundly affect the physical and chemical properties of a solid.

The common crystal defects are :

- (a) Vacancy defect
- (b) Interstitial defect
- (c) Impurity defects

These defects pertaining to lattice sites or points are called **Point defects**.

#### Vacancy Defect

When a crystal site is rendered vacant by removal of a structural unit in the lattice, the defect is referred to as the **vacancy defect**. In an ionic crystal, a cation and anion may leave the lattice to cause two vacancies. Such a defect which involves a cation and an anion vacancy in the crystal lattice is called a **Schottky defect**. This defect is found in the crystals of sodium chloride and cesium chloride (CsCl).

#### Interstitial Defect

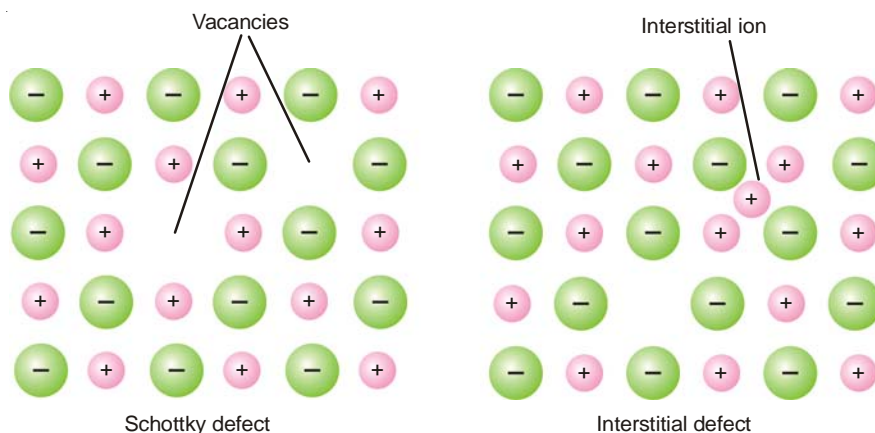
Here, an ion leaves its regular site to occupy a position in the space between the lattice sites (interstitial position). This causes a defect known as **Interstitial defect or Frenkel defect**. As shown in Fig. 12.29, ordinarily the cation moves as it is smaller than the anion and can easily fit into the

vacant spaces in the lattice. Thus in AgCl crystal,  $\text{Ag}^+$  ion occupies an interstitial position leaving a vacancy (or hole) at the original site.

### Impurity Defect

These defects arise due to the incorporation of foreign atoms or ions in regular lattice sites or interstitial sites.

When foreign particles are substituted for normal lattice particles, it is called **substitution impurity**.



■ **Figure 12.29**

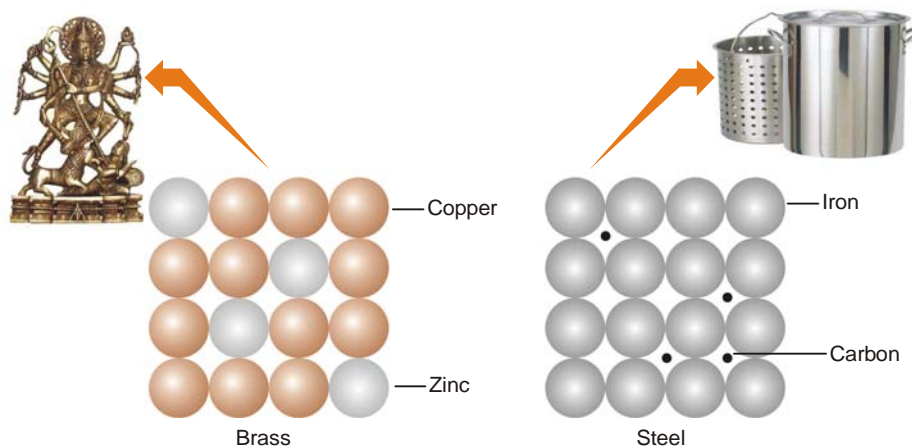
**Two common types of defects in ionic crystals.**

When foreign particles are trapped in vacant interstitial spaces, it is called **interstitial impurity**. Both types of impurities can have drastic effect on the properties of solids.

### METAL ALLOYS

Other elements can be introduced into a metallic crystal to produce substances called **alloys**. Alloys are of two types.

(1) **a substitutional alloy** in which the host metal atoms are replaced by other metal atoms of similar size. For example, in brass (an alloy of copper and zinc) about one-third of the copper atoms have been substituted by zinc atoms.



■ **Figure 12.30**

**Structure of alloys; brass and steel.**

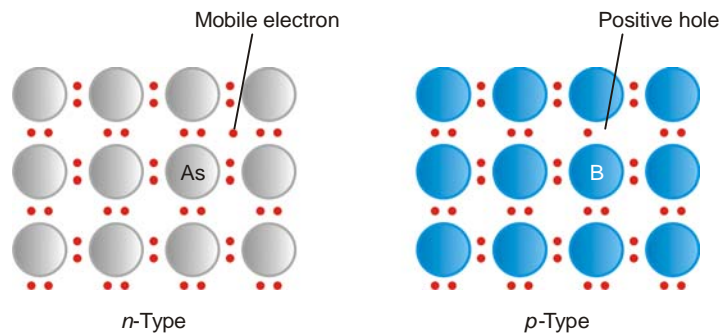


(2) **an interstitial alloy** in which some of the interstices (holes) in close-packed metal structure are occupied by small atoms. For example, steel is an alloy of iron and carbon. It contains carbon atoms in the holes of an iron crystal. The presence of interstitial atoms changes the properties of the host metal. Thus pure iron is relatively soft, malleable and ductile. The introduction of the carbon atoms forms the directional carbon-iron bonds (C–Fe). This makes the relative movement of spherical iron atoms rather difficult and the resulting steel is harder, stronger and less ductile compared to pure iron.

### SEMICONDUCTORS

Typical metals are good conductors of electricity while elements like silicon and germanium are nonconductors at ordinary temperature. However, they exhibit appreciable conductivity upon addition of impurities as arsenic and boron. The resulting materials are called **semiconductors** (poor conductors). The increase of conductivity upon addition of arsenic and boron can be easily explained.

In silicon and germanium crystals, each atom is covalently bonded to four neighbours so that all its four valence electrons are tied down. Thus in the pure state these elements are nonconductors. Suppose an atom of arsenic is introduced in place of silicon or germanium in the crystal lattice. Arsenic has five valence electrons, four of which will be utilised in the formation of covalent bonds and the remaining electron is free to move through the lattice. This leads to enhanced conductivity.



■ **Figure 12.31**  
Semiconductors derived from Silicon. *n*-Type semiconductor has As atom impurity and a mobile electron; *p*-Type conductor has B atom and positive hole.

Now let a boron atom be introduced in place of silicon atom in the crystal lattice. A boron atom has only three valence electrons. It can form only three of the four bonds required for a perfect lattice. Thus it is surrounded by seven electrons (one of Si) rather than eight. In this sense, there is produced an electron vacancy or a 'positive hole' in the lattice. Another electron from the bond of the adjacent Si atom moves into this hole, completing the four bonds on the B atom. This electron also leaves a hole at its original site. In this way electrons move from atom to atom through the crystal structure and the holes move in the opposite direction. Therefore the conductivity of the material improves.

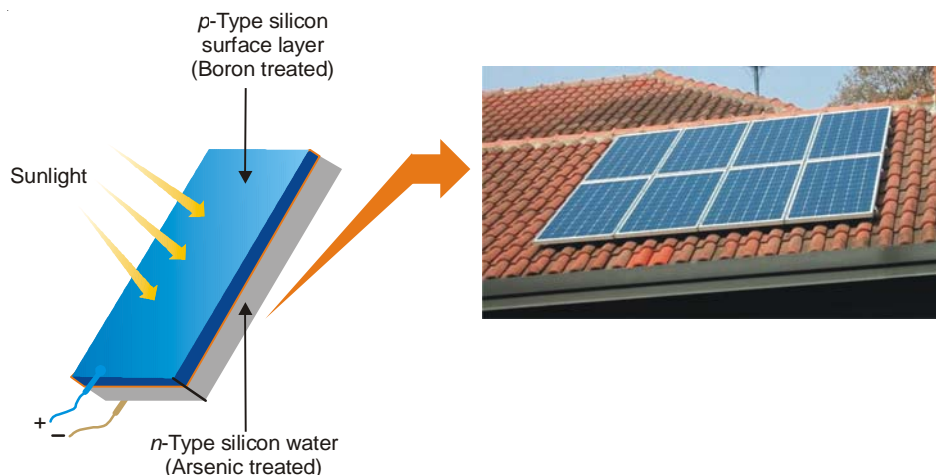
Semiconductors which exhibit conductivity due to the flow of excess negative electrons, are called ***n*-type semiconductors** (*n* for negative).

Semiconductors which exhibit conductivity due to the positive holes, are called ***p*-type semiconductors** (*p* for positive).

Semiconductors find application in modern devices as rectifiers, transistors and solar cells.

**SOLAR CELL**

**It is a device to convert light energy into electrical energy.** It is made of a thin wafer of silicon containing a tiny amount of arsenic (*n*-type semiconductor). A thin layer of silicon containing a trace of boron is placed on the surface of the wafer. Thus a junction, called the *p-n* junction, exists between the *p*-type silicon and *n*-type silicon. When the cell is exposed to sunlight, energy from sunlight excites electrons from *n*-type silicon to the holes of the *p*-type silicon. From the *p*-type silicon, the electrons flow through the external circuit as an electric current.

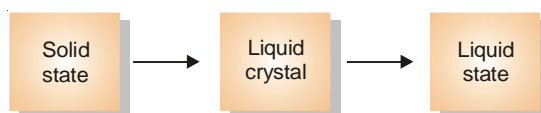


■ **Figure 12.32**  
A solar cell.

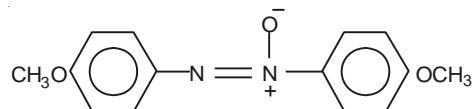
The voltage of the solar cell is not large. Therefore a series of such cells are used to power communication devices in satellites and space crafts which have to remain in space for long periods.

**WHAT ARE LIQUID CRYSTALS ?**

Some organic solids having long rod-like molecules do not melt to give the liquid substance directly. They, instead, pass through an intermediate state called the **liquid crystal state**, often referred to as the **liquid crystal**. Thus the liquid crystal state is intermediate between the liquid state and the solid state.



One such substance that forms liquid crystal is



*p*-Ozoxyanisole

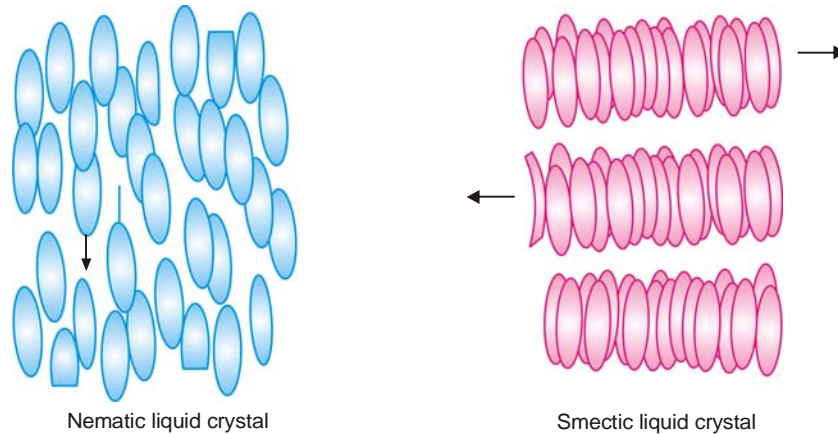
**The liquid crystals have a structure between that of a liquid and that of a crystalline solid.** In a liquid the molecules have a random arrangement and they are able to move past each other. In a solid crystal the molecules have an ordered arrangement and are in fixed positions. In a liquid crystals, however, molecules are arranged parallel to each other and can flow like a liquid. **Thus the liquid crystals have the fluidity of a liquid and optical properties of solid crystals.**

### Types of Liquid Crystals

According to their molecular arrangement, the liquid crystals are classified into three types.

**Nematic liquid crystals.** They have molecules parallel to each other like soda straws but they are free to slide or roll individually.

**Smectic liquid crystals.** The molecules in this type of crystal are also parallel but these are arranged in layers. The layers can slide past each other.



■ **Figure 12.33**  
Nematic and Smectic liquid crystals.

**Cholesteric liquid crystals.** As in nematic crystals, in this type of crystal the molecules are parallel but arranged in layers. The molecules in successive layers are slightly rotated with respect to the layers above and below so as to form a spiral structure.

### APPLICATIONS OF LIQUID CRYSTALS

On account of their remarkable optical and electrical properties, liquid crystals find several practical applications. Some of these are shown in Fig.12.34.



■ **Figure 12.34**  
The technical application of liquid crystals in flat panel displays for desktop and notebook-computers or in the displays of cellular phones has become an indispensable part of modern information and communication technologies.

### Number Displays

When a thin layer of nematic liquid crystal is placed between two electrodes and an electric field

is applied, the polar molecules are pulled out of alignment. This causes the crystal to be opaque. Transparency returns when electrical signal is removed. This property is used in the number displays of digital watches, electronic calculators, and other instruments.

### Monitoring Body Temperature

Like the solid crystals, liquid crystals can diffract light. Only one of the wavelengths of white light is reflected by the crystal which appears coloured. As the temperature changes, the distance between the layers of molecules also changes. Therefore the colour of the reflected light changes correspondingly. These cholesteric liquid crystal undergoes a series of colour changes with temperature. These crystals are used in indicator tapes to monitor body temperature or to spot areas of overheating in mechanical systems.

## EXAMINATION QUESTIONS

- Define or explain the following terms :
 

(a) Molecular solid	(b) Ionic solid
(c) Covalent network solid	(d) Metallic solid
(e) Crystalline solid	(f) Amorphous solid
(g) Isotropy	(h) Anisotropy
(i) Crystal lattice	(j) Unit cell
(k) Cubic unit cells	(l) Body centred cubic unit cell
(m) Face centred cubic unit cell	(n) Bragg's equation
- Aluminium forms face-centred cubic crystals. The density of Al is  $2.70 \text{ g/cm}^3$ . Calculate the length of the side of the unit cell of Al. (At. wt. of Al = 27)  
**Answer.**  $4.053 \times 10^{-8} \text{ cm}$
- (a) Describe the theory of Bragg's method of crystal analysis.  
 (b) Differentiate between the cubic close packing and hexagonal close packing of spheres.
- How is Avogadro's number determined from X-ray diffraction of crystals? Explain.
- Gold has a face-centred cubic structure with a unit length  $4.07 \text{ \AA}$ , a density of  $19.3 \text{ g cm}^{-3}$ . Calculate the Avogadro's number from the data (At. wt. of Au = 197).  
**Answer.**  $6.056 \times 10^{23}$
- (a) Derive the relation  $n\lambda = 2d \sin \theta$  in crystallography.  
 (b) Draw diagrams to represent (i) F.C.C. lattice, (ii) B.C.C. lattice.
- Polonium crystallises in a simple cubic unit cell. It has atomic mass = 209 and density =  $91.5 \text{ kg m}^{-3}$ . What is the edge length of its unit cell?  
**Answer.**  $15.597 \times 10^{-8} \text{ cm}$
- (a) Write a short note on Bravis Lattices.  
 (b) Calculate the angle at which first order diffraction will occur in an X-ray diffractometer when X-rays of wavelength  $1.54 \text{ \AA}$  are diffracted by the atoms of a crystal, given that the interplanar distance is  $4.04 \text{ \AA}$ .  
**Answer.**  $10.987^\circ$
- (a) What do you understand by the packing efficiency of a crystal?  
 (b) Explain the terms point groups and space groups.  
 (c) The ionic radii of Cs is 169 pm and Br is 195 pm. What kind of unit cell would be expected for CsBr crystal? Calculate the unit cell dimensions and the density of CsBr crystal (At. wt. of Cs = 133; Br = 80)  
**Answer.** (c)  $390 \times 10^{-10} \text{ cm}$ ;  $5.96 \text{ g cm}^{-3}$

10. Derive a relationship between the interplanar spacing of a crystal and the wavelength of X-ray diffracted by it. (Delhi BSc, 2000)
11. Differentiate between isomorphism and polymorphism. (Delhi BSc, 2001)
12. (a) Discuss Bragg's equation. Describe briefly the experimental set up used to record rotating crystal X-ray diffraction photograph. What are the limitations of this method?  
 (b) What is the minimum number of molecules per unit cell in a crystal having body centred cubic crystal lattice?  
 (c) Why radiation of wavelength about  $1.0 \text{ \AA}$  is used to determine crystal structure by X-ray diffraction method? (Jamia Millia BSc, 2001)
13. The face centred cubic lattice has closer packing than body centred cubic lattice. Why? (Delhi BSc, 2002)
14. (a) Enumerate various elements of symmetry of a cubic type of unit cell.  
 (b) What is the law of rational indices? (Delhi BSc, 2002)
15. (a) Identify the crystal system to which some solids having the following dimensions for their unit cell belong. Give examples of the solid.  
 (i)  $a \neq b \neq c$      $\alpha \neq \beta \neq \gamma \neq 90^\circ$     (ii)  $a \neq b \neq c$      $\alpha = \beta = \gamma = 90^\circ$   
 (b) What are various types of crystals? (MD Rohtak BSc, 2002)
16. Calculate Miller indices of a crystal plane which is cut through the crystal axes  $2a$ ,  $-3b$ ,  $-c$ .  
**Answer.**  $3, -2, -6$  (Guru Nanak Dev BSc, 2002)
17. (a) Explain the following with examples.  
 (i) Primitive unit cell and non-primitive unit cell.  
 (ii) Plane of symmetry and axis of symmetry.  
 (b) Define and explain the law of constancy of interfacial angles and the law of rational indices. (MD Rohtak BSc, 2002)
18. For a FCC crystal  $d_{100} = 2.8 \times 10^{-10} \text{ m}$ . Calculate  $d_{110}$ ,  $d_{111}$  for the crystal.  
**Answer.**  $1.9799 \times 10^{-10} \text{ m}$ ;  $1.6166 \times 10^{-10} \text{ m}$  (Nagpur, BSc, 2002)
19. Calculate the angle at which second order diffraction will appear in a X-ray spectrophotometer when X-rays of wavelength  $1.5 \text{ \AA}$  are used and interplanar distance is  $4.04 \text{ \AA}$ .  
**Answer.**  $21.795^\circ$  (Guru Nanak Dev BSc, 2002)
20. Explain what is meant by ionic crystal, molecular crystal and covalent crystal. Give examples. (Jammu BSc, 2002)
21. Calculate the wavelength of X-ray which shows a second order Bragg refraction angle of  $14^\circ$  from the 100 plane of KCl. The density of KCl is  $1.9849 \text{ g cm}^{-3}$  and there are four atoms in the unit cell.  
**Answer.**  $5.67 \times 10^{-8} \text{ cm}$  (Vidyasagar BSc, 2002)
22. Tabulate all possible crystal systems alongwith geometrical characteristics of their lattices. (Guru Nanak Dev BSc, 2002)
23. What is meant by unit cell of crystal? Sketch the unit cell of simple body centred and face centred cubic space lattice and calculate the number of atoms per unit cell in these systems. (Nagpur BSc, 2003)
24. (a) Discuss various elements of symmetry of a cubic crystal lattice.  
 (b) What are different Bravia lattice types of a cubic crystal? (Vidyasagar BSc, 2003)
25. What do you understand by  
 (i) axis of four fold symmetry and  
 (ii) axis of three fold symmetry.  
 How many such axes are present in cubic crystals? (Nagpur BSc, 2003)
26. A certain solid X having atomic mass 30, crystallizes in the fcc arrangement. Its density is  $3.0 \text{ g cm}^{-3}$ . What is the unit cell length? ( $N = 6.023 \times 10^{23}$ )  
**Answer.**  $4.049 \text{ \AA}$  (Sambalpur BSc, 2003)

27. Calculate the angle at which first order diffraction will occur in X-ray diffractometer when X-rays of wavelength  $1.54 \text{ \AA}$  are diffracted by the atoms of crystal, given the interplanar distance is  $4.04 \text{ \AA}$ .  
**Answer.**  $10.9874 \text{ \AA}$  (Delhi BSc, 2003)
28. A crystal plane has intercepts of 3, 4 and 2 units with x, y and z axes respectively. Calculate its Miller Indices.  
**Answer.** 4, 3, 6 (Vidyasagar BSc, 2003)
29. Lithium borohydride crystallizes as an orthorhombic system with four molecules per unit cell. The unit cell dimensions are  $a = 6.81 \text{ \AA}$ ,  $b = 4.43 \text{ \AA}$  and  $c = 7.2 \text{ \AA}$ . If the molar mass of  $\text{LiBH}_4$  is  $21.76 \text{ g mol}^{-1}$ , Calculate the density of crystal.  
**Answer.**  $0.668 \text{ g cm}^{-3}$  (Guru Nanak Dev BSc, 2003)
30. A body centred cubic element of density  $10.3 \text{ g cm}^{-3}$  has a cell edge of  $314 \text{ pm}$ . Calculate the atomic mass of the element (Avogadro's number =  $6.023 \times 10^{23}$ )  
**Answer.**  $96.0304 \text{ g}$  (Delhi BSc, 2003)
31. (a) Discuss powder method of crystal analysis?  
 (b) Potassium crystallizes with a body-centred cubic lattice and has a density of  $0.856 \text{ g cm}^{-3}$ . Calculate the length of side of the unit cell 'a' and the distance between 200, 110 and 222 planes.  
**Answer.**  $4.192 \times 10^{-8} \text{ cm}$ ;  $2.096 \times 10^{-8} \text{ cm}$ ;  $2.964 \times 10^{-8} \text{ cm}$ ;  $1.195 \times 10^{-7} \text{ cm}$  (Jamia Millia BSc, 2003)
32. The density of Lithium metal is  $0.53 \text{ g cm}^{-3}$  and the separation of 100 planes of metal is  $350 \text{ pm}$ . Determine whether the lattice is fcc or bcc. (molar mass of Lithium =  $6.941 \text{ g mol}^{-1}$ )  
**Answer.** bcc (Kolkata BSc, 2002)
33. Fe(II) oxide crystal has a cubic structure and each edge of the unit cell is  $5.0 \text{ \AA}$ . Taking density of the oxide as  $4.0 \text{ g cm}^{-3}$ , calculate the number of  $\text{Fe}^{2+}$  and  $\text{O}^{2-}$  ions present in each unit cell.  
**Answer.** 4 (Kalyani BSc, 2003)
34. Derive the law of constancy of interfacial angles and law of symmetry. (Agra BSc, 2004)
35. Differentiate between crystalline and amorphous solid. What are Miller indices? Draw (110) plane in a face centred cubic lattice. Write a note on point defects in ionic crystal. (Patna BSc, 2004)
36. Discuss X-ray diffraction in elucidating structures of crystals and powders. (Jiwaji BSc, 2004)
37. Derive Bragg's equation for the diffraction of X-rays by crystal lattice. (Madras BSc, 2004)
38. Define unit cell and crystal lattice. (Kerala BSc, 2004)
39. Calculate the co-ordinate number in an atom is  
 (a) A body centred cubic  
 (b) A face centred cubic unit cell (Burdwan BSc, 2004)
40. Calculate the value of Avogadro's number from the data : Density of NaCl =  $2.165 \text{ g cm}^{-3}$  ; Distance between  $\text{Na}^+$  and  $\text{Cl}^-$  in NaCl structure =  $281 \text{ pm}$ .  
**Answer.**  $6.089 \times 10^{23}$  (Sambalpur BSc, 2005)
41. Sodium chloride crystallises in face-centred cubic ( fcc ) structure. Its density is  $2.165 \text{ g cm}^{-3}$ . If the distance between  $\text{Na}^+$  and its nearest  $\text{Cl}^-$  is  $281 \text{ pm}$ , find out the Avogadro's number (  $\text{Na} = 23 \text{ g mol}^{-1}$  ;  $\text{Cl} = 35.44 \text{ g mol}^{-1}$  )  
**Answer.**  $6.08 \times 10^{23} \text{ mol}^{-1}$  (Baroda BSc, 2005)
42. Copper crystal has fcc cubic lattice structure. Its density is  $8.93 \text{ g cm}^{-3}$ . What is the length of the unit cell? (  $N_o = 6.023 \times 10^{23}$  ; Atomic mass of Cu =  $63.5$  )  
**Answer.**  $3.614 \times 10^{-8} \text{ cm}^{-3}$  (Jiwaji BSc, 2005)
43. A unit cell of sodium chloride has four formula unit. The edge length of the unit cell is  $0.564 \text{ nm}$ . What is the density of sodium chloride ?  
**Answer.**  $2.1656 \text{ g cm}^{-3}$  (Kanpur BSc, 2006)
44. A body centred cubic element of density  $10.3 \text{ g cm}^{-3}$  has a cell edge of  $314 \text{ pm}$ . Calculate the atomic mass of element. ( Avogadro's constant =  $6.023 \times 10^{23}$  )  
**Answer.**  $94 \text{ amu}$  (Madurai BSc, 2006)

45. Sodium chloride crystal has fcc structure. Its density is  $2.163 \times 10^3 \text{ kgm}^{-2}$ . Calculate the edge of the unit cell cube. ( $M_{\text{NaCl}} = 58.45 \times 10^{-3} \text{ kg mol}^{-1}$ ;  $N_o = 6.023 \times 10^{23} \text{ mol}^{-1}$ )
- Answer.**  $5.640 \times 10^{-8} \text{ cm}$  (Delhi BSc, 2006)

### MULTIPLE CHOICE QUESTIONS

- Which is not true about the solid state?
  - they have definite shape and volume
  - they have high density and low compressibility
  - they have high attractive forces among molecules
  - they have high vapour pressure

**Answer.** (d)
- The melting point is that temperature at which
  - solid and liquid forms of the substance do not co-exist at equilibrium
  - solid and liquid forms of the substance have same vapour pressure
  - vapour pressure is equal to one atmospheric pressure
  - none of the above

**Answer.** (b)
- Amorphous solids do not have
 

(a) sharp melting point	(b) characteristic geometrical shapes
(c) regularity of the structure	(d) all of these

**Answer.** (d)
- A crystalline solid has
 

(a) definite geometrical shape	(b) flat faces
(c) sharp edges	(d) all of these

**Answer.** (d)
- Amorphous substances are isotropic because
  - they have same value of any property in all directions
  - they have different values of physical properties in different directions
  - they have definite geometrical shape
  - none of the above

**Answer.** (a)
- The elements of symmetry are
 

(a) plane of symmetry	(b) axis of symmetry
(c) centre of symmetry	(d) all of these

**Answer.** (d)
- The amorphous solid among the following is
 

(a) table salt	(b) diamond
(c) plastic	(d) graphite

**Answer.** (c)
- A crystalline solid does not have one of the following properties. It is
 

(a) anisotropy	(b) sharp melting points
(c) isotropy	(d) definite and regular geometry

**Answer.** (c)
- For tetragonal crystal system, which of the following is not true
 

(a) $a = b \neq c$	(b) $\alpha = \beta = \gamma = 90^\circ$
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- (c)  $a \neq b \neq c$  (d) none of these

**Answer.** (c)

10. For a orthorhombic crystal system, which is incorrect?

- (a)  $a \neq b \neq c$  (b)  $\alpha = \beta = \gamma = 90^\circ$   
 (c)  $a = b \neq c$  (d) none of these

**Answer.** (a)

11.  $\text{Na}^+\text{Cl}^-$ ,  $\text{Cs}^+\text{Cl}^-$  are the example of

- (a) cubic crystal system (b) tetragonal crystal system  
 (c) orthorhombic crystal system (d) rhombohedral crystal system

**Answer.** (a)

12. The total number of atoms in a body centred cubic unit cell is

- (a) 1 (b) 2  
 (c) 3 (d) 4

**Answer.** (b)

13. If there are 4 atoms in unit cell in a cubic system, it is an example of

- (a) simple cubic unit cell (b) body centred cubic unit cell  
 (c) face centred cubic unit cell (d) none of these

**Answer.** (c)

14. Which is incorrect for a hexagonal crystal system?

- (a)  $a = b = c$  (b)  $a = b \neq c$   
 (c)  $\alpha = \beta = 90^\circ, \gamma = 120^\circ$  (d) none of these

**Answer.** (a)

15. The co-ordination number of  $\text{Na}^+$  in  $\text{Na}^+\text{Cl}^-$  crystal is

- (a) 2 (b) 4  
 (c) 6 (d) 8

**Answer.** (c)

16. The co-ordination number of body centred cubic lattice is

- (a) 2 (b) 4  
 (c) 6 (d) 8

**Answer.** (d)

17. The Bragg's equation for diffraction of X-rays is

- (a)  $n\lambda = 2d^2 \sin \theta$  (b)  $n\lambda = 2d \sin \theta$   
 (c)  $n\lambda = 2d \sin^2 \theta$  (d)  $n\lambda = d \sin \theta$

**Answer.** (b)

18. In Bragg's equation  $n\lambda = 2d \sin \theta$ , 'n' represents

- (a) the number of moles (b) the principal quantum number  
 (c) the Avogadro's number (d) the order of reflection

**Answer.** (d)

19. The change in enthalpy that occurs when one mole of a solid crystalline substance is formed from the gaseous ions

- (a) lattice energy (b) ionic energy  
 (c) Born-Haber cycle (d) crystalline energy

**Answer.** (a)

20. In cubic close packed (ccp) pattern of a metallic crystal, the co-ordination number is

- (a) 12 (b) 8  
 (c) 6 (d) 4

**Answer.** (a)



21. In an ionic crystal, a cation and an anion leave the lattice to cause two vacancies. This defect is called  
 (a) Schottky defect (b) Frenkel defect  
 (c) interstitial defect (d) none of these

**Answer.** (a)

22. Which of the following defects is generally found in sodium chloride and cesium chloride?  
 (a) Frenkel defect (b) interstitial defect  
 (c) Schottky defect (d) none of these

**Answer.** (c)

23. In a solid lattice, a cation has left a lattice site and is present in interstitial position, the lattice defect is  
 (a) Schottky defect (b) Frenkel defect  
 (c) vacancy defect (d) interstitial defect

**Answer.** (b)

24. In Frenkel defect,  
 (a) some of the lattice sites are vacant  
 (b) an ion occupies interstitial position  
 (c) some of the cations are replaced by foreign ions  
 (d) none of the above

**Answer.** (b)

25. A device used to convert light energy into electrical energy is called  
 (a) a semiconductor (b) a solar cell  
 (c) an irreversible cell (d) an electrochemical cell

**Answer.** (b)

26. For an ionic crystal of formula AX, the radius ratio lies between 0.732 and 0.414. Its co-ordination number is  
 (a) 4 (b) 6  
 (c) 8 (d) 12

**Answer.** (b)

27. The radius ratio in an ionic crystal lies between 0.732–1.000, the co-ordination number is  
 (a) 3 (b) 4  
 (c) 6 (d) 8

**Answer.** (d)

28. The permitted co-ordination number in an ionic crystal is 6, the arrangement of anions around the cation will be  
 (a) plane triangular (b) tetrahedral  
 (c) octahedral (d) body centred cubic

**Answer.** (c)

29. A solid AB has the NaCl structure. If radius of the cation is 120 pm, the minimum value of radius of the anion B<sup>-</sup> will be

- (a)  $\frac{0.414}{120}$  (b)  $\frac{120}{0.414}$   
 (c)  $\frac{0.732}{120}$  (d)  $\frac{120}{0.732}$

**Answer.** (d)

30. The number of atoms per unit cell in a simple cubic, fcc and bcc are  
 (a) 1, 2, 4 (b) 1, 4, 2  
 (c) 4, 2, 1 (d) 2, 4, 1

**Answer.** (b)

31. In a crystal, the atoms are located at the positions where potential energy is  
(a) maximum (b) zero  
(c) minimum (d) infinite  
**Answer.** (c)
32. Potassium crystallises in a *bcc* structure. The co-ordination number of potassium in potassium metal is  
(a) 2 (b) 4  
(c) 6 (d) 8  
**Answer.** (d)
33. In an ionic crystal of general formula AX, the co-ordination number is six. The value of radius ratio is in the range  
(a) 0.155 – 0.215 (b) 0.215 – 0.414  
(c) 0.414 – 0.732 (d) 0.732 – 1  
**Answer.** (c)
34. The number of atoms in a unit cell of a cube is  
(a) 0 (b) 1  
(c) 2 (d) 3  
**Answer.** (c)
35. The number of atoms in a unit cell of a face centred cube is  
(a) 2 (b) 4  
(c) 6 (d) 8  
**Answer.** (b)
36. NaCl is an example of  
(a) covalent solid (b) metallic solid  
(c) ionic solid (d) molecular solid  
**Answer.** (c)
37. Which of the following defects results in the decrease of density of crystal  
(a) Schottky defect (b) Frenkel defect  
(c) interstitial defect (d) impurity defect  
**Answer.** (a)
38. Which of the following is a non-crystalline solid?  
(a) rubber (b) ZnS  
(c) HgS (d) PbI  
**Answer.** (a)
39. Particles of quartz are packed by  
(a) ionic bonds (b) van der Waal's forces  
(c) hydrogen bonds (d) covalent bonds  
**Answer.** (d)
40. LiF is an example of  
(a) molecular crystal (b) covalent crystal  
(c) ionic crystal (d) metallic crystal  
**Answer.** (c)
41. In silicon crystal each atom is covalently bonded to \_\_\_\_\_ neighbours.  
(a) 2 (b) 4  
(c) 6 (d) 8  
**Answer.** (b)

42. Silicon is an example of  
(a) non-conductor (b) good conductor  
(c) semi conductor (d) metallic conductor  
**Answer.** (c)
43. Semiconductors which exhibit conductivity due to the flow of excess negative electrons are called  
(a) *n*-type conductor (b) *p*-type conductor  
(c) good conductors (d) none of these  
**Answer.** (a)
44. In *p*-type semiconductors, the conductivity is due to  
(a) negative holes (b) positive holes  
(c) mobile electrons (d) valence electrons  
**Answer.** (b)
45. Super conductors are substances which  
(a) conduct electricity in liquid crystal state (b) conduct electricity at low temperatures  
(c) conduct electricity at high temperatures (d) offer no resistance to the flow of current  
**Answer.** (d)
46. The liquid crystals have  
(a) properties of super cooled liquid  
(b) properties of amorphous solids  
(c) the fluidity of a liquid and optical properties of a solid  
(d) none of these  
**Answer.** (c)
47. Silicon and Germanium in the pure state are  
(a) non-conductors (b) good conductors  
(c) metallic conductors (d) metal complexes  
**Answer.** (a)
48. *p*-Ozoxyanisole is an example of  
(a) semi conductor (b) super conductor  
(c) liquid crystal (d) none of these  
**Answer.** (c)
49. When an arsenic atom is introduced in place of silicon in a crystal lattice, the conductivity  
(a) increases  
(b) decreases  
(c) remains the same  
(d) sometimes increases and sometimes decreases  
**Answer.** (a)
50. The voltage of a solar cell is  
(a) very high (b) high  
(c) not very large (d) none of these  
**Answer.** (c)