



Module 2: Solid State

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Module outline:

Types of unit cell

Space lattice (only cubes)

Bragg's equation

Calculation of density of unit cell

One and two dimensional imperfections in solid

Structure and application of Graphite and Fullerenes

2.1. INTRODUCTION

Matter is anything that occupies space and has mass. From a macroscopic view of matter associated with its bulk properties, there are three main phase of it: gaseous, liquid and solid. A fourth phase, plasma exists at very high temperatures. Gaseous phase of matter generally transparent and has no definite boundaries other than those imposed by the wall of a confining vessel. Particles of a gas (atom, molecule or ions) are well separated, have no regular arrangement and move freely at high speed. Due to the large space in between their atoms (molecule or ions), gases are highly compressible.

Liquid and solids possess clearly delineated phase. Particles of a liquid are close together but have no regular arrangement, they move about and slide past each other. Liquids are relatively incompressible because there is a much less free space between the particles in liquid. Liquids and solids are often referred to as condensed phase because the particles in these phases are very closely packed.

2.2. CHARACTERISTICS OF SOLID STATE

- i. Solids are rigid and have definite shape.
- ii. Solids maintain their shape independent of the size or shape of the container in which they are placed.
- iii. Solids are nearly incompressible.
- iv. As compared to liquid and gases, solids diffuse very slowly.
- v. Solids are occupied fixed positions and can oscillate about their mean positions.

2.3. TYPES OF SOLIDS

Solids can be classified as crystalline or amorphous on the basis of the nature of order present in the arrangement of their constituent particles.

2.3.1. Crystalline Solid

A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Crystalline solids have a sharp melting point. Crystalline solids are *anisotropic* in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. Sodium chloride and quartz are typical examples of crystalline solids.

2.3.2. Amorphous Solid

An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only short range order. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Such portions are scattered and in between the arrangement is disordered. The structure of amorphous solids is similar to that of liquids. Glass, rubber and plastics are typical examples of amorphous solids.

Amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called pseudo solids or super cooled liquids. Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker. Amorphous solids are isotropic in nature. It is because there is no long range order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction.

2.4. SPACE LATTICE OR CRYSTAL LATTICE

A crystal can be imagined to be generated from the regular repetition of some basic unit of pattern such as atom, molecule, ion or a group of ions. "Space lattice may be defined as a regular three dimensional arrangement of identical points in space".

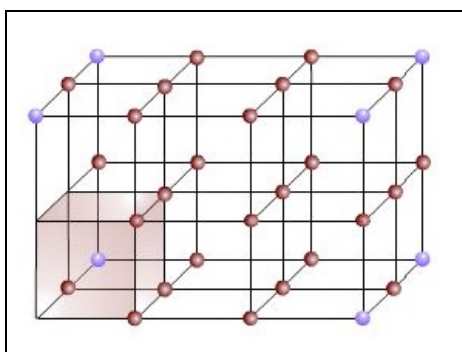


Fig. 2.1 Representation of space lattice

It may be noted here that:

1. Each lattice point has the same environment as that of any other point in the lattice.
2. The constituent particle has always to be represented by a lattice point, irrespective of whether it contains single atom or more than one atom.

2.5. UNIT CELL

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterised by:

1. its dimensions along the three edges, a , b and c . These edges may or may not be mutually perpendicular.
2. angles between the edges, α (between b and c) β (between a and c) and γ (between a and b). Thus, a unit cell is characterised by six parameters, a , b , c , α , β and γ . These parameters of a typical unit cell are shown in Fig. 2.2.

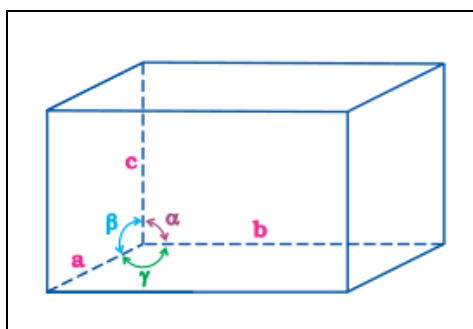


Fig. 2.2 Illustration of parameters of a unit cell

2.6. TYPES OF UNIT CELL IN CUBIC SYSTEM

There are three types of unit cell

2.6.1. Primitive or Simple Cubic Unit Cells

When constituent particles are present only on the corner positions of a unit cell, it is called as primitive or simple unit cell. [Fig.2.3(a)].

2.6.2. Body-Centred Unit Cells

Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners. [Fig.2.3(b)].

2.6.3. Face-Centred Unit Cells

Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners. [Fig.2.3(c)].

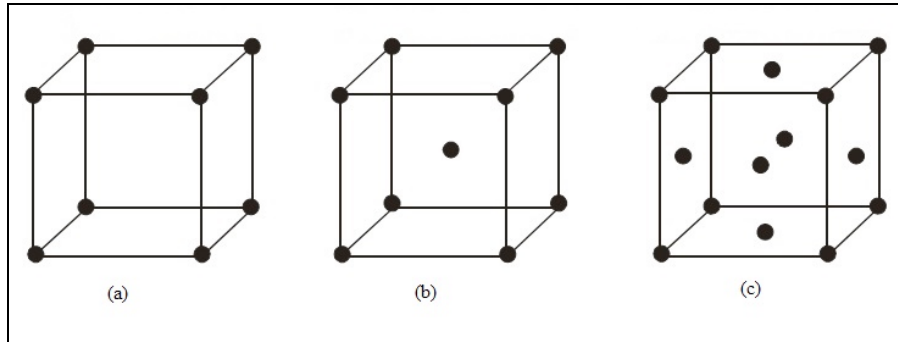


Fig. 2.3. (a) Simple cubic unit cell (b) Body centred cubic unit cell (c) Face centred cubic unit cell

2.7. NUMBER OF ATOMS IN A UNIT CELL

We shall consider three types of cubic unit cells and for simplicity assume that the constituent particle is an atom.

2.7.1. Primitive Cubic Unit Cell

Primitive cubic unit cell has atoms only at its corner. Since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is $8 \times \frac{1}{8} = 1$ atom

2.7.2. Body- Centred Cubic UnitCell

A body-centred cubic (*bcc*) unit cell has an atom at each of its corners and also one atom at its body centre. Thus in a body-centred cubic (*bcc*) unit cell:

$$(i) 8 \text{ corners} \times \frac{1}{8} \text{ per corner atom} = 8 \times \frac{1}{8} = 1 \text{ atom}$$

$$(ii) 1 \text{ body centre atom} = 1 \times 1 = 1 \text{ atom}$$

$$\therefore \text{Total number of atoms per unit cell} = 2 \text{ atoms}$$

2.7.3. Face- Centred Cubic Unit Cell

A face-centred cubic (*fcc*) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. Thus, in a face-centred cubic (*fcc*) unit cell:

$$(i) 8 \text{ corners atoms} \times \frac{1}{8} \text{ atom per unit cell} = 8 \times \frac{1}{8} = 1 \text{ atom}$$

$$(ii) 6 \text{ face-centred atoms} \times \frac{1}{2} \text{ atom per unit cell} = 6 \times \frac{1}{2} = 3 \text{ atoms}$$

$$\therefore \text{Total number of atoms per unit cell} = 4 \text{ atoms}$$

Table 2.1: Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO ₂ , TiO ₂ , CaSO ₄
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO ₃ , BaSO ₄
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Graphite, ZnO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO ₃), HgS (cinnabar)
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Monoclinic sulphur, Na ₂ SO ₄ .10H ₂ O
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , CuSO ₄ .5H ₂ O, H ₃ BO ₃

2.8. CALCULATION OF DENSITY OF UNIT CELL

From the unit cell dimensions, it is possible to calculate the volume of the unit cell. Knowing the density of the metal, we can calculate the mass of the atoms in the unit cell. The determination of the mass of a single atom gives an accurate method of determination of Avogadro constant. Suppose, edge length of a unit cell of a cubic crystal determined by X-ray diffraction is a , d the density of the solid substance and M the molar mass. In case of cubic crystal:

$$\text{Volume of a unit cell} = a^3$$

$$\text{Mass of the unit cell} = \text{number of atoms in unit cell} \times \text{mass of each atom} = z \times m$$

(Here z is the number of atoms present in one unit cell and m is the mass of a single atom)

Mass of an atom present in the unit cell:

$$m = \frac{M}{N_A} \quad (M \text{ is molar mass})$$

Therefore, density of the unit cell

$$\begin{aligned} &= \frac{\text{mass of unit cell}}{\text{volume of unit cell}} \\ &= \frac{z m}{a^3} = \frac{z M}{a^3 N_A} \quad \text{or} \quad \rho = \frac{z M}{a^3 N_A} \end{aligned}$$

Where $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

For SC, $Z = 1$

For BCC, $Z = 2$

For FCC, $Z = 4$

Note: The density of the unit cell is the same as the density of the substance. The density of the solid can always be determined by other methods. Out of the five parameters (ρ , z , M , a and N_A), if any four are known, we can determine the fifth.

2.9. BRAGG'S LAW

In 1913, W.L. Bragg and W.H. Bragg discovered a mathematical relation to determine inter atomic distances from X-rays diffraction patterns, known as Bragg's equation.

The structure of crystals at the level of ions, atoms and molecules can be revealed by their interaction with X rays. X rays are electromagnetic radiations of short wavelength and this wavelength is comparable with the spacing of atoms in crystals.

Derivation

The horizontal line in Fig. 2.4 represents parallel planes in the crystal structure separated by a distance 'd'. When the X-rays of wavelength ' λ ' strike the first plane at angle θ , some of the rays will be reflected at the same angle while some of the rays will penetrate and get reflected from the successive (second) plane also at the same angle θ . These rays will reinforce those reflected from the first plane if the extra distance travelled by them is equal to integral number 'n' of wavelength.

\therefore Extra distance = $n\lambda$

Drawing OA and OB perpendiculars to the incident and reflected beams, then the waves will be in phase provided the difference of path lengths of waves reflected by first two planes will be integral multiple of wavelength.

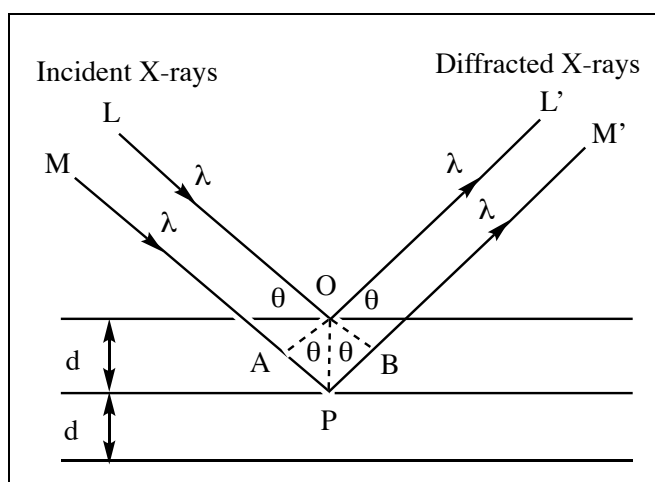


Fig. 2.4. X-rays reflections from a crystal

Path length of $MPM' >$ Path length of LOL' by $AP + BP$ (Extra distance)

$$\therefore \text{Path difference} = AP + BP = n\lambda \quad (1)$$

$$\angle AOP = \angle BOP = \theta$$

$$\text{In } \Delta AOP, \sin \theta = \frac{AP}{OP} = \frac{AP}{d}$$

$$\therefore \therefore AP = d \sin \theta \quad (2)$$

$$\text{In } \Delta BOP, \sin \theta = \frac{BP}{OP} = \frac{BP}{d}$$

$$\therefore BP = d \sin \theta \quad (3)$$

$$\therefore AP + BP = d \sin \theta + d \sin \theta = 2 d \sin \theta$$

$$\therefore n\lambda = 2 d \sin \theta \quad (4)$$

The equation (4) is called Bragg's equation

Where, n = order of reflection

(if $n = 1$ = first order of reflection, $n = 2$ = second order of reflection)

λ = wavelength of X-rays

d = interplanar distance

θ = angle

Example 2.1. Calculate the density of a BCC crystal. The side of cube is 4\AA and $M = 60$ (Avogadro's number = 6.023×10^{23})

Solution. Density of crystal is given as:-

$$\text{Density } (\rho) = \frac{z M}{a^3 N_A}$$

Given $Z = 2$ (for BCC crystal)

$$M = 60$$

$$a = 4\text{\AA} = 4 \times 10^{-8} \text{ cm}$$

$$N_A = 6.023 \times 10^{23}$$

Therefore,

$$\text{Density } (\rho) = \frac{2 \times 60}{(4 \times 10^{-8})^3 \times 6.03 \times 10^{23}} = 3.11 \text{ g/cm}^3$$

Example 2.2. An edge of cubic cell of NaCl crystal is 6.5×10^{-8} cm. Assuming, that four molecules of NaCl are associated per unit cell, calculate its density. $N_A = 6.023 \times 10^{23}$.

Solution. Density of crystal is given as:-

$$\text{Density } (\rho) = \frac{z M}{a^3 N_A}$$

Given $Z = 4$

$$M = 58.5 \text{ (For NaCl)}$$

$$a = 6.5 \times 10^{-8} \text{ cm}$$

$$N_A = 6.023 \times 10^{23}$$

Therefore,

$$\text{Density } (\rho) = \frac{2 \times 58.5}{(6.5 \times 10^{-8})^3 \times 6.03 \times 10^{23}} = 1.415 \text{ g/cm}^3$$

Example 2.3. A body centred cubic element of density 10.3 g/cm^3 has a edge length of 314 pm. Calculate the atomic mass of the element. $N_A = 6.023 \times 10^{23}$

Solution. Density of crystal is given as:-

$$\text{Density } (\rho) = \frac{z M}{a^3 N_A}$$

Given $Z = 2$ (for BCC crystal)

$$M = ? \quad a = 314 \times 10^{-10} \text{ cm}, \quad N_A = 6.023 \times 10^{23}, \quad \rho = 10.3 \text{ g/cm}^3$$

Therefore,

$$\text{Density } (\rho) = \frac{2 \times M}{(314 \times 10^{-8})^3 \times 6.03 \times 10^{23}}$$

$$M = \frac{(314 \times 10^{-8})^3 \times 6.03 \times 10^{23}}{2}$$

$$M = 96.03$$

Example 2.4. A metal has an FCC crystal structure. The length of unit cell is 404 pm. What is the molar mass of atom, if the density of metal is 2.72 g/cm^3 and $N_A = 6.023 \times 10^{23}$

Solution. Density of crystal is given as:-

$$\text{Density } (\rho) = \frac{z M}{a^3 N_A}$$

Given $Z = 4$ (for FCC crystal)

$$M = ?$$

$$a = 404 \times 10^{-10} \text{ cm}$$

$$N_A = 6.023 \times 10^{23}$$

$$\rho = 2.72 \text{ g/cm}^3$$

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Therefore,

$$\text{Density } (\rho) = \frac{4 \times M}{(404 \times 10^{-8})^3 \times 6.03 \times 10^{23}}$$

$$M = \frac{(404 \times 10^{-8})^3 \times 6.03 \times 10^{23} \times 2.72}{4}$$

$$M = 27$$

Example 2.5. Calculate the density of silver which crystallizes in a face centred cubic lattice with edge length 0.4086 nm (Atomic wt. of Ag = 107.88) $N_A = 6.023 \times 10^{23}$

Solution. Density of crystal is given as:

$$\text{Density } (\rho) = \frac{z M}{a^3 N_A}$$

Given $Z = 4$ (for FCC crystal)
 $M = 107.88$
 $a = 0.4086 \text{ nm} = 0.4086 \times 10^{-7} \text{ cm}$
 $N_A = 6.023 \times 10^{23}$

Therefore,

$$\text{Density } (\rho) = \frac{4 \times 107.88}{(0.404 \times 10^{-7})^3 \times 6.03 \times 10^{23}} = 10.50 \text{ g/cm}^3$$

Example 2.6. A unit cell of sodium chloride has four formula units. The edge length of unit cell is 0.0564 nm. What is the density of NaCl crystal?

Solution. Density of crystal is given as:-

$$\text{Density } (\rho) = \frac{z M}{a^3 N_A}$$

Given $Z = 4$
 $M = 58.5$ (For NaCl)
 $a = 0.0564 \text{ nm} = 0.0564 \times 10^{-7} \text{ cm}$
 $N_A = 6.023 \times 10^{23}$

Therefore,

$$\text{Density } (\rho) = \frac{4 \times 58.5}{(0.0564 \times 10^{-7})^3 \times 6.03 \times 10^{23}} = 21.66 \text{ g/cm}^3$$

Example 2.7. When an electron in an excited molybdenum atom falls from the L to K shell, an X-ray is emitted. These X-rays are diffracted at angle of 7.75° by planes with a separation of 2.64 \AA . What is the difference in energy between the K shell and L shell in molybdenum, assuming a first order diffraction?

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

$$\lambda = \frac{2d \sin \theta}{n} = \frac{2 \times 2.64 \times 10^{-10} \times \sin 7.75}{1} = 0.7120 \times 10^{-10} \text{ m}$$

$$E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{0.7120 \times 10^{-10}} = 27.89 \times 10^{-16} \text{ J}$$

Example 2.8. The diffraction of barium with X-radiation of wavelength 2.2 \AA gives a first order reflection at 30° . What is the distance between the diffracted planes?

Solution. $n = 1, \lambda = 2.29 \text{ \AA}, \sin \theta = \sin 30^\circ, d = ?$

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

$$1 \times 2.29 = 2 \times d \times \sin 30^\circ$$

$$d = \frac{1 \times 2.29}{2 \times \sin 30^\circ} = 2.29 \text{ \AA}$$

2.10. IMPERFECTIONS IN SOLIDS

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects. The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, point defects and line defects. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects.

2.11. TYPES OF IMPERFECTIONS

Imperfections in crystalline solids are normally classified according to their dimension as follows:

1. Point imperfections (Zero dimensional defects)
2. Line imperfections (one dimensional defects)
3. Plane or surface imperfections (Two dimensional defects)
4. Volume imperfections (three dimensional defects)

2.12. POINT IMPERFECTIONS (ZERO DIMENSIONAL DEFECTS)

Point imperfections can be classified into three types: stoichiometric defects, impurity defects and non-stoichiometric defects.

2.12.1. Stoichiometric Defects

These are the **point defects** that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects. Basically these are of two types, vacancy defects and interstitial defects.

(i) Vacancy Defect: When some of the lattice sites are vacant, the crystal is said to have vacancy defect (Fig. 2.5). This results in decrease in density of the substance. This defect can also develop when a substance is heated.

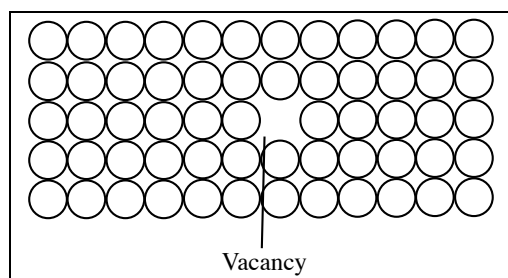


Fig. 2.5. Vacancy Defect

(ii) Interstitial Defect: When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect (Fig. 2.6).

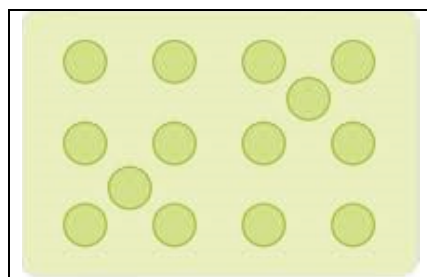


Fig. 2.6. Interstitial Defect

This defect increases the density of the substance. Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as Frenkel and Schottky defects.

(a) Frenkel Defect: This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 2.7). It creates a vacancy defect at its original site and an interstitial defect at its new location. Frenkel defect is also called dislocation defect. It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.

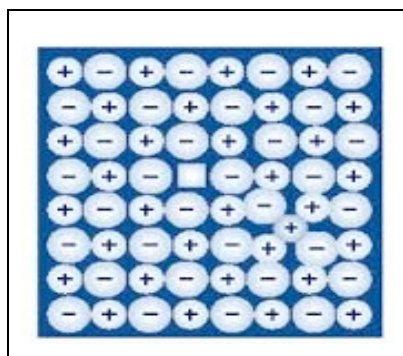


Fig. 2.7. Frenkel Defect

(b) Schottky Defect: It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (Fig. 2.8). Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

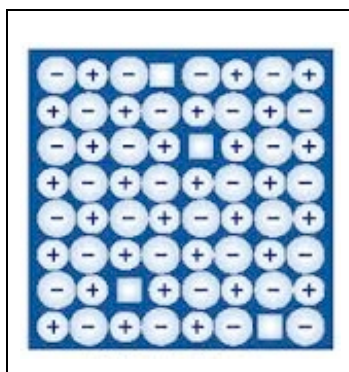
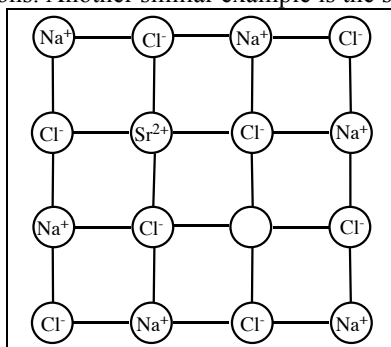


Fig. 2.8. Schottky Defect

2.12.2. Impurity Defects

If molten NaCl containing a little amount of SrCl_2 is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} (Fig.2.9). Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of CdCl_2 and AgCl .

Fig. 2.9. Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}

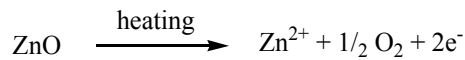
2.12.3. Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of nonstoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) Metal Excess Defect. Metal excess defect due to anionic vacancies: Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig. 2.10). As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called F-centres (from

the German word *Farbenzenter* for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

Metal excess defect due to the presence of extra cations at interstitial sites: Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.



Now there is excess of zinc in the crystal and its formula becomes Zn_{1+x}O . The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

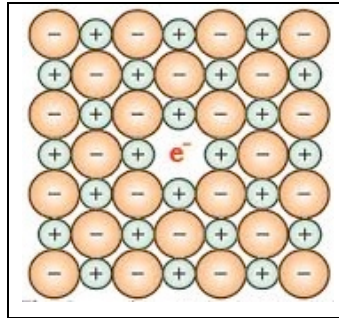


Fig. 2.10. An F-centre in a crystal

(ii) Metal Deficiency Defect There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of $\text{Fe}_{0.95}\text{O}$. It may actually range from $\text{Fe}_{0.93}\text{O}$ to $\text{Fe}_{0.96}\text{O}$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

2.13. LINE IMPERFECTIONS (ONE DIMENSIONAL DEFECTS)

In **linear defects** groups of atoms are in irregular positions. Linear defects are commonly called dislocations. Any deviation from perfectly periodic arrangement of atoms along a line is called the line imperfection. In this case, the distortion is centered only along a line and therefore the imperfection can be considered as the boundary between two regions of a surface which are perfect themselves but are out of register with each other. The line imperfection acting as boundary between the slipped and un-slipped region, lies in the slip plane and is called a dislocation. Dislocations are generated and move when a stress is applied. The strength and ductility of metals are controlled by dislocations.

To extreme types of dislocations are distinguish as

1. Edge dislocations and
2. Screw dislocations.

2.13.1. Edge Dislocations

The inter-atomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. As shown in the set of images, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position in image (b) and finally image (c). In the process of slipping one plane at a time the dislocation propagates across the crystal. The movement of the dislocation across the plane eventually causes the top half of the crystal to move with respect to the bottom half. However, only a small fraction of the bonds are broken at any given time. Movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

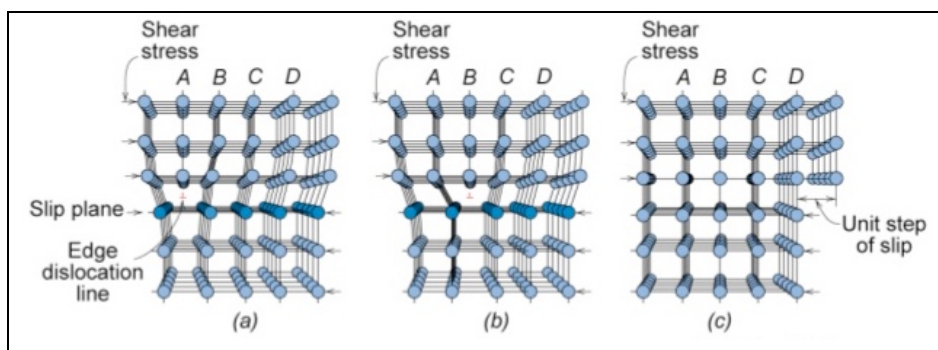


Fig. 2.11. Edge dislocations

2.13.2. Screw Dislocations

The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end so that the metal begins to rip. In this way, the screw dislocation will move upward in the image, which is perpendicular to direction of the stress.

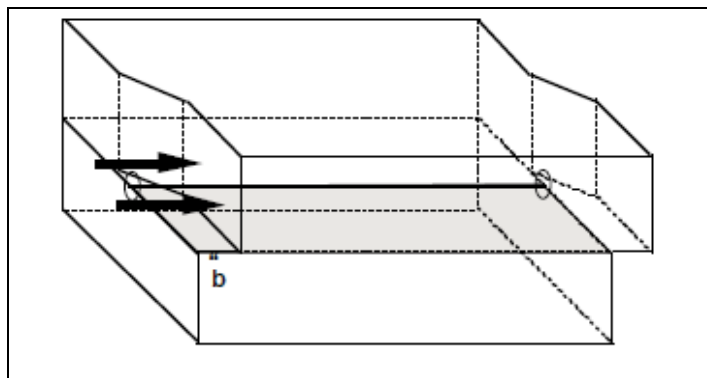


Fig. 2.12. Screw dislocations

2.14. PLANE IMPERFECTIONS (TWO DIMENSIONAL DEFECTS)

When the irregularities extend along surfaces i.e. along lattice plane, the defect is known as plane defect or plane imperfections. These are two dimensional imperfections. They include:

2.14.1. Grain Boundaries

Solid generally consists of a number of crystallites or grains ranging from nanometers to millimeters in size across. Their orientations are usually rotated with respect to neighboring grains. The interface between grains is called grain boundary. As they, limit the length and motions of dislocations, the strength of a material depends directly on the grain boundary surface area.

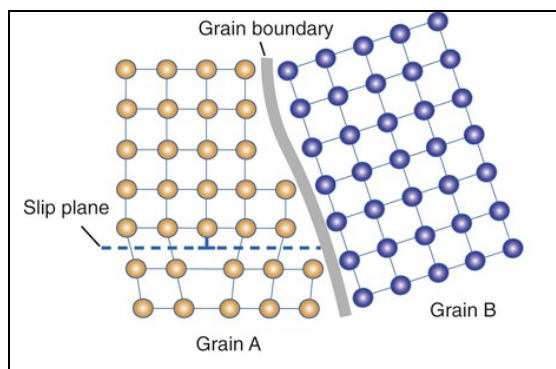


Fig. 2.13. Grain Boundaries

2.14.2. Twin Boundary

Twin boundaries occur in pairs such that the orientation change introduced by one boundary is restored by the other. The region between the pair of boundaries is called the twinned region. Twins which forms during the process of recrystallization are called annealing twins, whereas deformation twins form during plastic deformation. Twinning occurs on a definite crystallographic plane and in a specific direction, both of which depend on the crystal structure. Annealing twins are typically found in metals that have FCC crystal structure (and low stacking fault energy), while deformation twins are observed in BCC and HCP metals. Annealing twins are usually broader and with straighter sides than mechanical twins. Twins do not extend beyond a grain boundary.

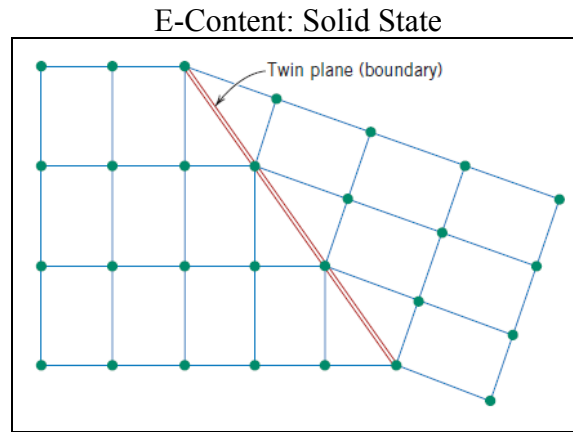


Fig. 2.14. Twin Boundaries

2.14.3. Stacking Faults

These are produced as result of a change in the stacking sequence over a few atomic spacing. It is a one or two layer interruption in the stacking sequence of atom planes.

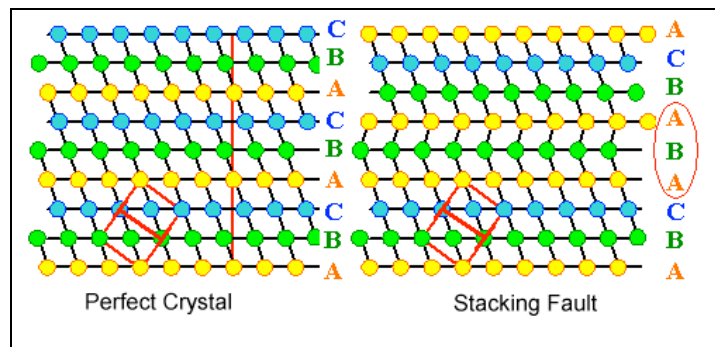


Fig. 2.15. Stacking Faults

2.15. GRAPHITE

Graphite has layered structure (Fig.2.16). Layers are held by van der Waals forces and distance between two layers is 3.40 Å. Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 1.42 Å. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation with bond angle 120° and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant and graphite is used for making lead of pencils.

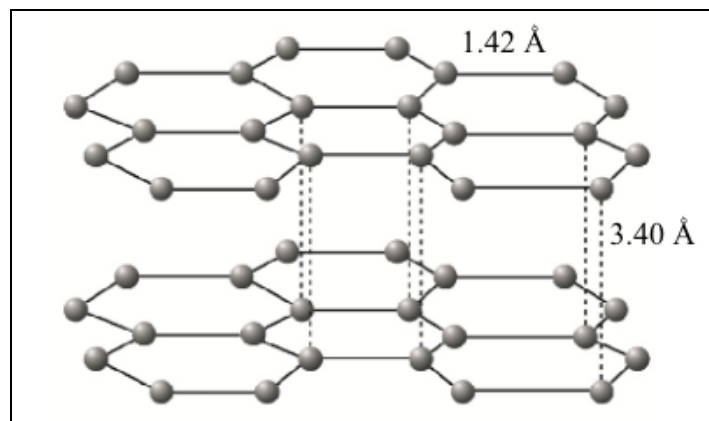


Fig: 2.16. The structure of graphite

2.16. FULLERENE

A third form of pure carbon was discovered while scientists were conducting experiments designed to understand how long-chain molecules are formed in outer space. R. E. Smalley, R. F. Curl, Jr., and H. W. Kroto, the discoverers of this new form of carbon, shared the 1996 Nobel Prize in chemistry for their discovery. They named this new form buckminsterfullerene (often shortened

to fullerene) because it reminded them of the geodesic domes popularized by R. Buckminster Fuller, an American architect and philosopher. The substance is nicknamed “buckyball.”

Consisting of a hollow cluster of 60 carbons, fullerene is the most symmetrical large molecule known. Fullerene has only sp^2 hybridized carbons, but instead of being arranged in layers, the carbons are arranged in rings, forming a hollow cluster of 60 carbons that fit together like the seams of a soccer ball. Each molecule has 32 interlocking rings (20 hexagons and 12 pentagons). The bond length in pentagon is 1.45 Å while in hexagon it is 1.40 Å. At first glance, fullerene would appear to be aromatic because of its benzene-like rings. However, it does not undergo electrophilic substitution reactions; instead, it undergoes electrophilic addition reactions like an alkene. Fullerene’s lack of aromaticity is apparently caused by the curvature of the ball, which prevents the molecule from fulfilling the first criterion for aromaticity that it must be planar.

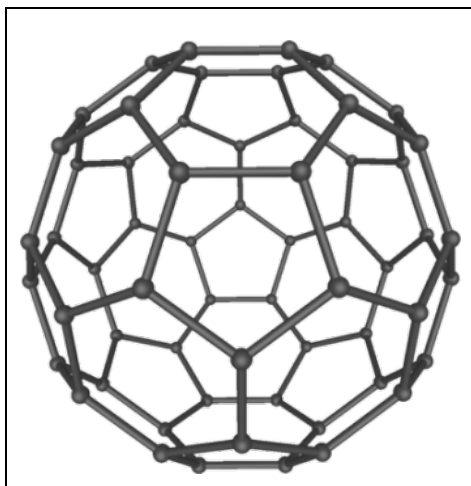


Fig.2.17. The structure of C_{60} , Buckminsterfullerene

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C^n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above.

Buckyballs have extraordinary chemical and physical properties. They are exceedingly rugged and are capable of surviving the extreme temperatures of outer space. Because they are essentially hollow cages, they can be manipulated to make materials never before known. For example, when a buckyball is “doped” by inserting potassium or cesium into its cavity, it becomes an excellent organic superconductor. These molecules are presently being studied for use in many other applications, such as new polymers and catalysts and new drug delivery systems. The discovery of buckyballs is a strong reminder of the technological advances that can be achieved as a result of conducting basic research.

Scientists have even turned their attention to buckyballs in their quest for a cure for AIDS. An enzyme that is required for HIV to reproduce exhibits a nonpolar pocket in its three-dimensional structure. If this pocket is blocked, the production of the virus ceases. Because buckyballs are nonpolar and have approximately the same diameter as the pocket of the enzyme, they are being considered as possible blockers. The first step in pursuing this possibility was to equip the buckyball with polar side chains to make it water soluble so that it could flow through the bloodstream. Scientists have now modified the side chains so that they bind to the enzyme. It’s still a long way from a cure for AIDS, but this represents one example of the many and varied approaches that scientists are taking to find a cure for this disease.

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EXERCISE

1. The density of NaCl is 2.163 g/cc. Calculate the edge of its cubic cell. Assuming that four molecules of NaCl are associated per unit cell.
2. Derive Bragg's equation. When an electron in an excited molybdenum atom falls from the L to the K shell, an x-rays is emitted. These X-rays are diffracted at angle of 7.75° by planes with a separation of 2.64 Å. What are the difference in energy between the K shell and L shell in molybdenum, assuming a first order diffraction? (Given that $h = 6.62 \times 10^{-34}$).
3. With the help of neat diagram describe the structure of graphite. Discuss its electrical and lubricant properties.
4. Describe the preparation, structure and applications of fullerenes.
5. Derive Bragg's equation for diffraction of X – rays by crystals.
6. Calculate the number of atoms per unit cells in SC, BCC and FCC.
7. Derive the expression for the density (d) of a cubic crystal.
8. Discuss the properties and applications of fullerenes.
9. What is a Schottky defect?
10. What are F-centres?