

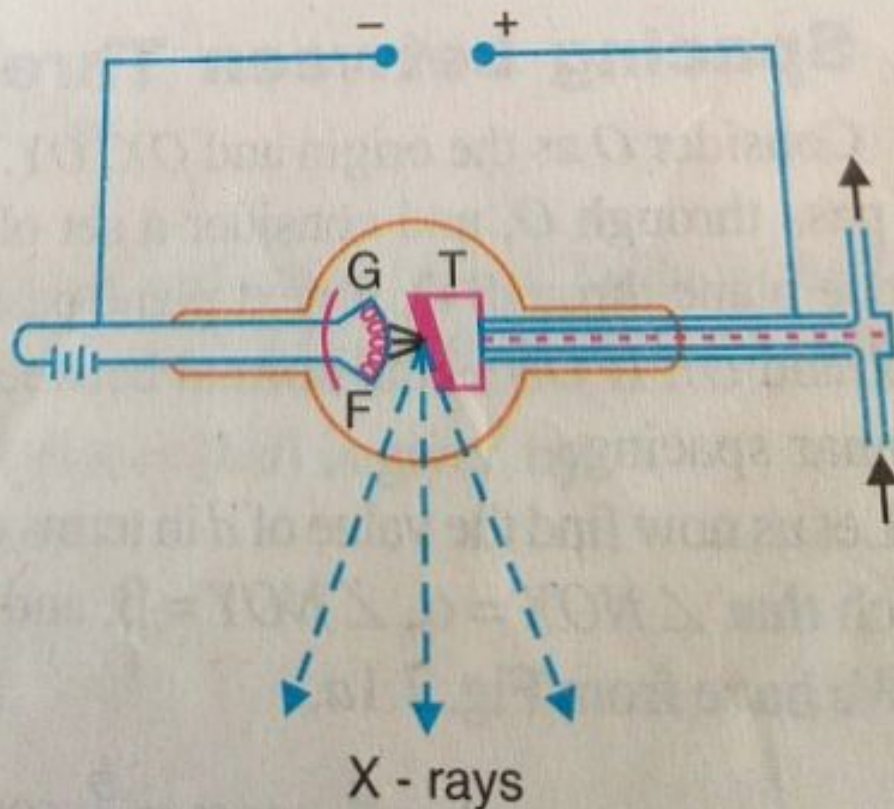
X-Rays

7.1 Introduction

X-rays were discovered by Roentgen in 1895. X-rays are electromagnetic waves of short wavelengths in the range of 10 \AA to 0.5 \AA . The longer wavelength end of the spectrum is known as the "soft X-rays" and the shorter wavelength end is known as "hard X-rays."

7.2 Production of X-rays

The Coolidge tube. X-rays are produced when fast moving electrons are suddenly stopped by a solid target. A Coolidge tube is shown in Fig. 7.1. The tube is exhausted to the best pos-



Laue diffraction pattern. The condition to be satisfied so that X-rays reflected from a set of lattice planes may produce an intense spot in the diffraction pattern may be derived. This is known as Bragg's law.

7.6 Bragg's Law

When monochromatic X-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering radiation of the same wavelength. The crystal acts as a series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different planes is an integral multiple of λ .

Derivation of Bragg's law. Consider a set of parallel planes of atom points at a spacing d between two successive planes. Let a narrow monochromatic X-ray beam of wavelength λ be incident on the first plane at a glancing angle θ (Fig. 7.6). Consider the ray PQ incident on the first plane. The corresponding reflected ray QR must also be inclined at the same angle θ to the plane. Since X-rays are much more penetrating than ordinary light, there is only partial reflection at each plane. The complete absorption takes place only after penetrating several layers. Consider two parallel rays PQR and $P'Q'R'$ in the beam, which are reflected by two atoms Q and Q' . Q' is vertically below Q . The ray $P'Q'R'$ has a longer path than the ray PQR . To compute the path-difference between the two rays, from Q draw normals QT and QS on $P'Q'$ and $Q'R'$ respectively. Then

$$\text{the path-difference} = TQ' + Q'S = d \sin \theta + d \sin \theta = 2d \sin \theta.$$

Hence the two rays will reinforce each other and produce maximum intensity, if

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

where $n = 1, 2, 3, \dots$. The integer n gives the order of the scattered beam, λ is the wavelength of the X-rays used. This equation is called *Bragg's law*.

7.7 The Bragg X-ray Spectrometer

The essential parts of a Bragg spectrometer are shown in Fig. 7.7. It is similar in construction to an optical spectrometer. It consists of three parts. (1) a source of X-rays (2) a crystal held on a circular table which is graduated and provided with vernier and (3) a detector (ionisation chamber). X-rays from an X-ray tube, limited by two narrow lead slits S_1 and S_2 , are allowed to fall upon the crystal C . The crystal is mounted on the circular table T , which can rotate

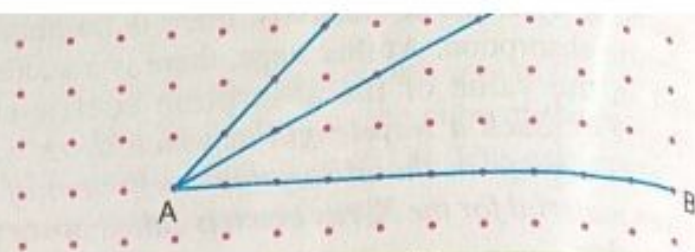


Fig. 7.5 (iii)

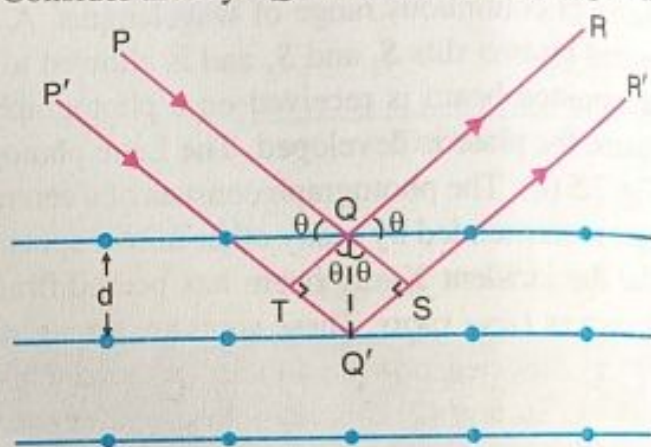


Fig. 7.6



Bragg X-ray Spectrometer.

Moseley's law: statement. The frequency of a spectral line in X-ray spectrum, varies as the square of the atomic number of the element emitting it, or $\nu \propto Z^2$. Moseley's law may be written as $\sqrt{\nu} = a(Z - b)$. Here, Z is the atomic number of the element and a and b are constants depending upon the particular line.

Explanation, according to Bohr's theory. Bohr's theory of hydrogen spectrum gives the frequency of a spectral line as

$\nu = Z^2 R c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ where R is Rydberg's constant and c the velocity of light. Considering the K_α line, we can regard it as originating from the transition of electron from second to first orbit. Now, $n_1 = 1$ and $n_2 = 2$.

So frequency of k_α line = $\nu = Z^2 R c \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} c R Z^2$

This approximately corresponds to Moseley's law.

Importance of Moseley's law. (1) According to this law, it is the atomic number and not atomic weight of an element which determines its characteristic properties, both physical and chemical. Therefore, the atoms must be arranged in the periodic table according to their atomic numbers and not according to their atomic weights. This would remove some discrepancies in the order of certain elements from the point of view of their atomic weights. For example, argon ${}_{18}\text{Ar}^{40}$ comes before potassium (${}_{19}\text{K}^{39}$), cobalt (${}_{27}\text{Co}^{58.9}$) comes before nickel (${}_{28}\text{Ni}^{58.7}$) etc. So the arrangement is correct in the order of atomic number.

(2) Moseley's work has also helped to perfect the periodic table by (i) the discovery of new elements, e.g., hafnium (72), illinium (61), masurium (43), rhenium (75), etc., and (ii) the determination of the atomic numbers of rare-earths and fixing their positions in the periodic table.

Example. The wavelength of the L_α X-ray line of platinum (atomic number 78) is 1.321 Å. An unknown substance emits L_α X-rays of wavelength 4.174 Å. Calculate the atomic number of the unknown substance. Given $b = 7.4$ for L_α lines.

Sol. Moseley's law is

$$\sqrt{\nu} = a(Z - b)$$

... of the L_α line of platinum and the unknown substance ... respectively. Then

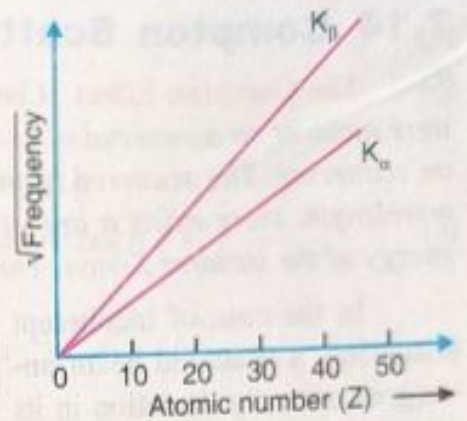


Fig. 7.18

length) be made to fall upon a material. A major part of the incident energy of X-ray photons is spent in ejecting electrons from the K -shell of the atom. The energy of the X-ray beam is thus absorbed photoelectrically, causing the ejection of the K -electrons. But if the incident radiation has a wavelength slightly longer (or the energy slightly smaller) than that required to eject the K -electrons, there is no photoelectric absorption. At this stage, there is a sudden fall in the value of the absorption coefficient (Fig. 7.4). Such a wavelength at which there is a sudden change in the absorption coefficient of a given material for the X-ray beam is called **absorption edge**.

As the wavelength is further increased, the absorption coefficient again increases. The X-ray photons now start ejecting electrons from the L -shell. There is again a sudden decrease in the value of μ at another definite wavelength $\lambda = \lambda_{L I}$. Immediately after this there are two further discontinuities at two closely lying wavelengths $\lambda_{L II}$ and $\lambda_{L III}$. In the case of ionization from the L -shell there are three absorption edges (L_I, L_{II}, L_{III}), indicating that the electrons in the L -shell can exist in three energy sub-group states.

Laue's experiment. Laue showed that if X-rays are allowed to pass through a crystal, a diffraction pattern is obtained. T is a source of X-rays. This source gives white X-rays, i.e., X-ray beam of continuous range of wavelengths. A narrow beam of X-rays from the X-ray tube is collimated by two slits S_1 and S_2 and is allowed to pass through a thin crystal of zinc blende (ZnS). The transmitted beam is received on a photographic plate P [Fig. 7.5 (i)]. After an exposure of many hours, the plate is developed. The Laue photograph obtained on the photographic plate is shown in Fig. 7.5 (ii). The photograph consists of a central spot which arises due to the direct beam. The central spot is surrounded by many other fainter spots arranged in a definite pattern around O . This indicates that the incident X-ray beam has been diffracted from the various crystal planes. These spots are known as *Laue spots*. These spots are arranged according to different geometrical patterns for different crystals, depending on their structure. This experiment proved: (1) that X-rays are electromagnetic waves and (2) that the atoms of a crystal are arranged in a regular three-dimensional lattice.

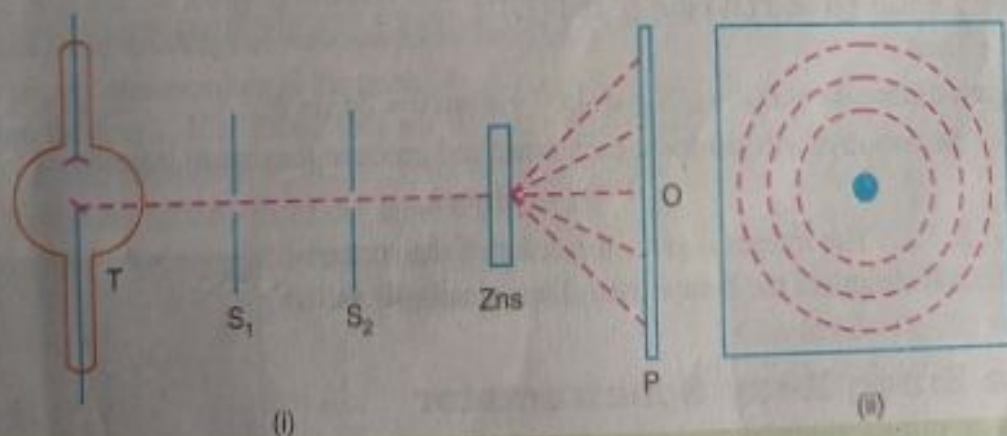


Fig. 7.5

Bragg gave a simple interpretation of the pattern. The regular repetition of atomic, ionic or molecular units in three dimensions is called the "lattice". Many planes can be imagined in the lattice, containing these atoms. Some planes will be richer in atoms than others. This can be easily seen by considering two dimensional lattice. Fig. 7.5 (iii) represents a two-dimensional lattice, indicating lines of atom distribution. Line AB contains greater concentration of atoms, line AC less and line AD

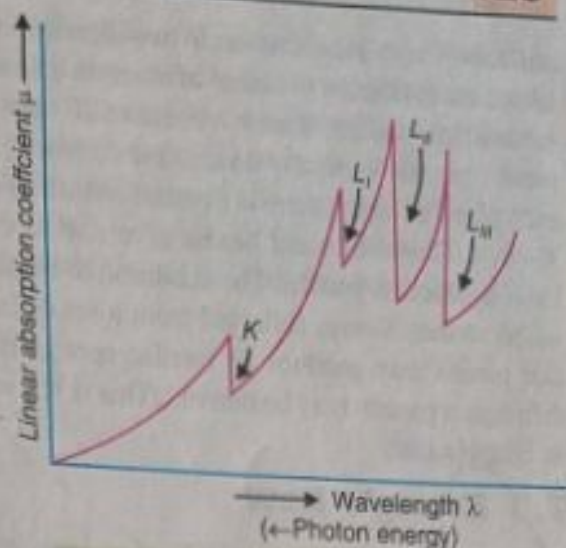


Fig. 7.4

still less. These lines of atoms in two-dimensional lattice are analogous to planes of atoms in a three-dimensional lattice. If now a beam of X-rays is incident in the vertically downward direction, at each plane of atoms there is a partial reflection of X-rays. These reflected beams give rise to the Laue diffraction pattern. The condition to be satisfied so that X-rays reflected from a set of lattice planes may produce an intense spot in the diffraction pattern may be derived. This is known as Bragg's law.

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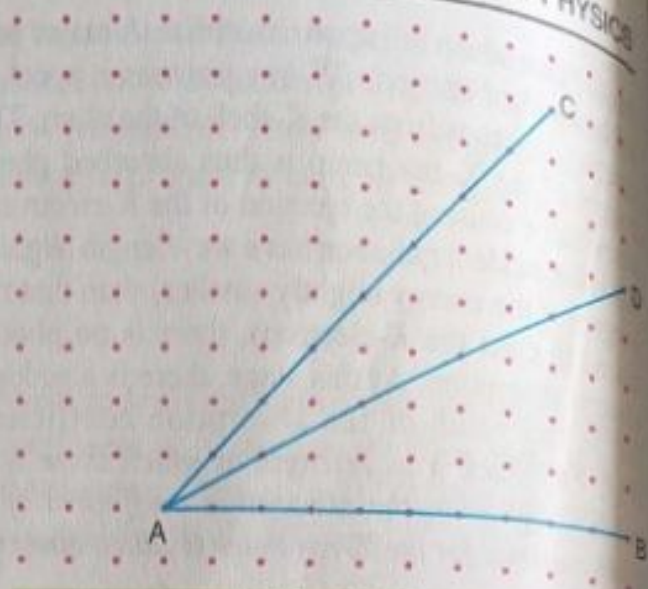


Fig. 7.5 (iii)

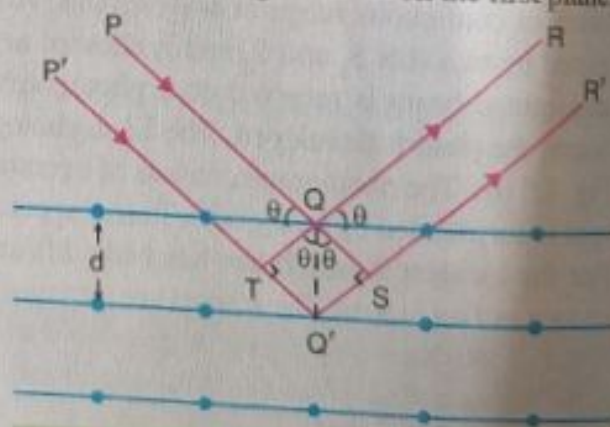


Fig. 7.6



neighbour cubes. This is illustrated by the ion indicated by an asterisk in Fig. 7.9. Hence each ion contributes only $\frac{1}{8}$ th of its mass to the cube. The unit cube is made up of 4 sodium ions and 4 chlorine ions. Hence, the mass of each cube = the mass of $\frac{1}{2}$ NaCl molecule. If M is the molecular weight of NaCl and N_A the Avogadro's No.,

$$\text{Mass of } \frac{1}{2} \text{ NaCl molecule} = M/2N_A$$

$$\therefore \rho d^3 = \frac{M}{2N_A} \text{ or } d = 3\sqrt{\frac{M}{2N_A\rho}}$$

Knowing M , N_A and ρ , d can be found.

For NaCl, $M = 58.45 \text{ kg}$; $\rho = 2170 \text{ kg m}^{-3}$ and $N_A = 6.06 \times 10^{26}$.

$$\therefore d = 3\sqrt{\frac{58.45}{2 \times (6.06 \times 10^{26}) \times 2170}} = 2.81 \times 10^{-10} \text{ m.}$$

Example 1. The spacing between principal planes of NaCl crystal is 2.82 \AA . It is found that first order Bragg reflection occurs at an angle of 10° . What is the wavelength of X-rays?

Sol. By Bragg equation, $2d \sin \theta = n\lambda$.

Here, $d = 2.82 \times 10^{-10} \text{ m}$; $n = 1$ and $\theta = 10^\circ$. $\lambda = ?$

$$\lambda = \frac{2d \sin \theta}{n} = \frac{2 \times (2.82 \times 10^{-10}) \sin 10^\circ}{1} = 0.98 \times 10^{-10} \text{ m.}$$

Example 2. Bragg's spectrometer is set for the first order reflection to be received by the detector at glancing angle of $9^\circ 18'$. Calculate the angle through which the detector is rotated to receive the second order reflection from the same face of the crystal.

Sol. Let λ be the wavelength of X-rays. Let θ_1 and θ_2 be the glancing angles for the first and second orders. Then,

$$2d \sin \theta_1 = 1\lambda \text{ and } 2d \sin \theta_2 = 2\lambda.$$

$$\therefore \sin \theta_2 = 2 \sin \theta_1, \text{ or } \sin \theta_2 = 2 \sin 9^\circ 18' = 0.3232 \text{ or } \theta_2 = 18^\circ 48'$$

Now, $\theta_2 - \theta_1 = 9^\circ 30'$. Hence the crystal is rotated through an angle $9^\circ 30'$. The angle through which the detector is rotated is twice the angle through which the crystal is rotated. Therefore, the angle through which the detector is rotated from first order to second order = $2(\theta_2 - \theta_1) = 19^\circ$.

7.8 The Powder Crystal Method

The Laue's and Bragg's techniques for the investigation of crystal structures can be applied only if single crystals of reasonable size are available. But, in general, large crystals, without fault are difficult to obtain. Therefore, Debye and Scherrer adopted a different technique. The specimen was taken in the form of a well powdered sample of the crystal in a thin glass capsule.

The experimental arrangement is shown in Fig. 5.10. The X-rays from the source are made approximately monochromatic by the filter F . A narrow beam of these monochromatic X-rays, suitably collimated by two lead slits S_1 and S_2 , falls on the powdered speci-

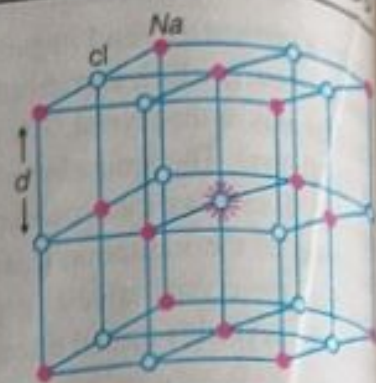


Fig. 7.9

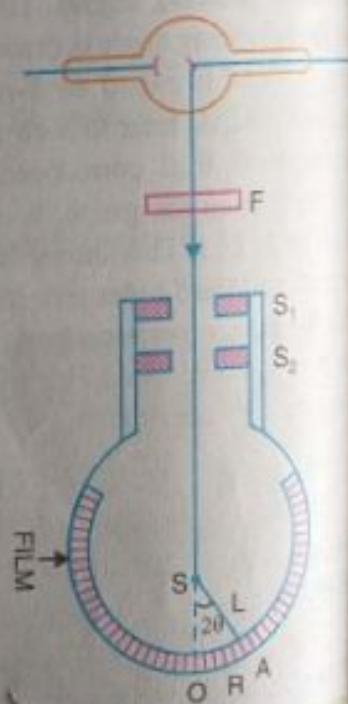


Fig. 7.10

men S . The specimen is suspended vertically on the axis of a cylindrical camera. The photographic film is mounted round the inner surface of the camera, covering nearly the whole circumference in order to receive the beams diffracted upto 180° .

The powder specimen of the crystal can be imagined to be a collection of random oriented tiny crystals, presenting all values of glancing angles to the incident beam. For a given wavelength and a given value of d , there can be only one value of θ (the glancing angle) which satisfies the equation $2d \sin \theta = n\lambda$, where $n = 1$. Such reflected beams emerge out from the specimen in all directions inclined at an angle 2θ with the direction of the incident beam, because millions of tiny crystals in the specimen are random oriented. The reflected rays will be on the surface of a cone, vertex at the specimen, base on the photographic film and having a semi-vertical angle 2θ . The traces obtained on the photographic film will be as in Fig. 7.11.



Fig. 7.11

Let L be the radius of the cylindrical camera. The direct beam strikes the film at O . Suppose a spectrum with glancing angle θ is found at A which is at a distance R from O . Then $\theta = R/2L$. Using this value of θ in the Bragg's equation and knowing the value of λ , d (spacing of the plane involved) can be calculated.

The powder method has been employed in the study of microcrystalline substances like metals, alloys, carbons, fluorescent powders and other forms where single crystals are not available.

7.9 (a) The Laue Method

A single crystal is held stationary in a beam of X-rays of continuous wavelength. The crystal selects and diffracts the discrete values of λ for which planes exist of spacing d and incidence angle θ satisfying the Bragg law. The experimental arrangement is shown in Fig. 7.12 (a). A source is used that produces a beam of X-rays over a wide range of wavelengths preferably from 0.02 nm to 0.2 nm. A pinhole arrangement produces a well-collimated beam. The dimensions of the crystal are usually less than 1 mm. Flat films are placed in front of and behind the specimen. Since λ covers a continuous range, the crystal selects that particular wavelength which satisfies Bragg's law at the present orientation. A diffracted beam emerges at the corresponding angle. The diffracted beam is then recorded as a spot on the film. But since the wavelength corresponding to a spot is not measured, one cannot determine the actual values of the interplanar spacings—only their ratios. Therefore one can determine the shape but not the absolute size of the unit cell.

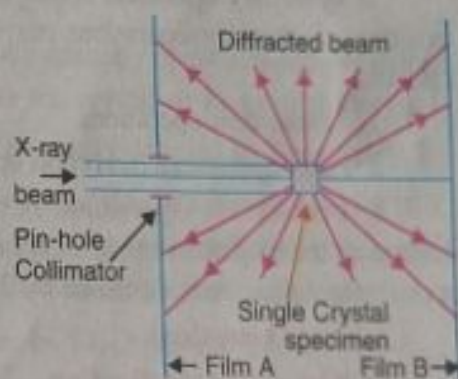


Fig. 7.12 (a)

The pattern will show the symmetry of the crystal : if a crystal has a fourfold axis of symmetry parallel to the beam, the Laue pattern will show fourfold symmetry. The Laue method is widely used to orient crystals for solid state experiments.

This method is, however, not suitable for determining the crystal structure. This is because, out of a continuous range of wavelengths, several wavelengths are reflected in different orders from a single plane, so that different orders of reflection may overlap on a single spot. This makes difficult the measurement of the reflection intensity of individual spots and hence of the missing reflections. The missing reflections would have been an important step in the determination of the crystal structure. However, the shape of the unit cell can be established from the symmetry of the pattern.

7.9(b) Rotating-Crystal Method

In this method, a single crystal is rotated about a fixed axis (usually vertical), in a beam of monoenergetic X-rays. The variation in the angle θ brings different atomic planes into position for reflection. The experimental arrangement is shown in Fig. 7.12 (b).

The crystal is usually about 1 mm in diameter and is mounted on a spindle which can be rotated. A photographic film is placed on the inner side of a cylinder concentric with the axis of rotation. The incident X-ray beam is monochromatised by a filter or by reflection from an earlier crystal. The incident beam is diffracted from a given crystal plane whenever in course of rotation

the value of θ satisfies the Bragg equation. Beams from all planes parallel to the vertical rotation axis will lie in the horizontal plane. Planes with other orientations will reflect in layers above and below the horizontal plane. However, there will be no reflected beams from a plane which always contains the incident beam during the whole rotation and from ones whose spacing is so small that $\lambda/2d > 1$. The reflected spots on the film form parallel lines. Since λ is known, the spacing d may be calculated from $2d \sin \theta = n\lambda$.

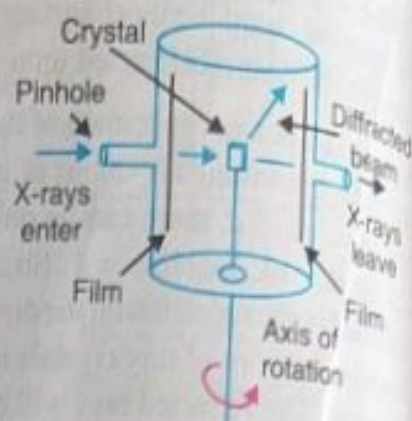


Fig. 7.12 (b)

7.10. Symmetry Operations

A symmetry operation is one which leaves the crystal invariant. Symmetry operations may be grouped into three classes:

1. Translation operations
2. Point operations
3. Hybrid operations

1. Translation Operation. A translation operation is defined as the displacement of a crystal parallel to itself by a crystal translation vector defined by $T = n_1a + n_2b$.

2. Point Operations

(i) **The mirror reflection.** In this operation, the reflection of a structure at a mirror plane m passing through a lattice point leaves the crystal unchanged. Fig. 7.13 (a) shows two mirror planes in a two-dimensional crystal.

(ii) **Inversion:** A crystal structure has an inversion symmetry if for every lattice point of position vector r , there is a corresponding lattice point at the position $-r$ [Fig. 7.13 (b)]. The origin about which the position vector r is chosen is called the *centre of inversion* and is represented by i .

(iii) **Rotation:** A structure is said to possess rotational symmetry about an axis if rotation of the structure about this axis by an angle ϕ gives an unchanged configuration of the original structure. The angle ϕ which satisfies this condition is given by

$$\phi = \frac{2\pi}{n}; n = 1, 2, 3, \dots$$

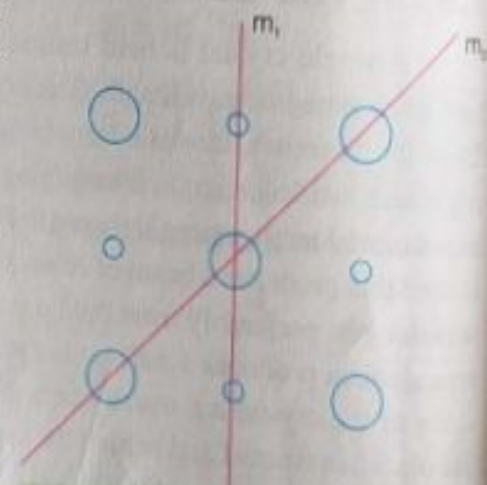


Fig. 7.13 (a)

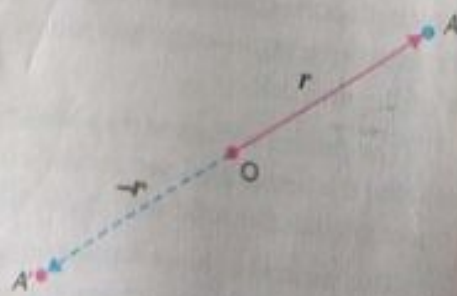


Fig. 7.13 (b)

DEFECTS IN CRYSTALS

77.11 Introduction

In an *ideal crystal*, the atomic arrangement is perfectly regular and continuous throughout. Thus an ideal crystal is a perfect one in all respects.

Real crystals usually contain several types of imperfections, such as substitutional and interstitial atoms, as well as vacancies or holes. Dislocations and surface defects are also usually present in crystals. The mechanical, electrical and magnetic properties of engineering crystalline solids, particularly metals and alloys, are profoundly affected by the imperfections in the crystals.

The properties of solids such as, strength of crystals, luminescence, colour of crystals, diffusion, crystal growth, plasticity etc., cannot be explained on the basis perfect periodicity concept. Such properties are greatly affected by the lattice defects or atomic imperfections arising due to irregularities of atomic arrays in crystals. These properties are called defect or structure sensitive properties.

The term imperfection or defect is used to describe any deviation from the perfect periodic array of atoms in the crystals.

77.12 Classification of Crystal Imperfections (or Defects)

Crystalline imperfections can be classified on the basis of their geometry under the following four main divisions.

1. POINT DEFECTS (zero dimensional defects)

(a) Vacancies	(b) Interstitialcies
(c) Impurities	(d) Electronic defects
2. LINE DEFECTS (one dimensional defects)

(a) Edge dislocation	(b) Screw dislocation
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3. SURFACE DEFECTS (two dimensional defects)

(a) Grain boundaries	(b) Tilt boundaries
(c) Twin boundaries	(d) Stacking faults
(e) Ferromagnetic domain walls	
4. VOLUME DEFECTS (three dimensional defects)

(a) Large voids	(b) Cracks
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77.13 Point Defects

Point imperfections are also called zero dimensional imperfections. They are imperfect point-like regions in the crystal. One or two atomic diameters is the typical size of a point imperfection. In a crystal lattice, point defect is one which is completely local in its effect, e.g., a vacant lattice site.

The introduction of point defect into a crystal increases its internal energy as compared to that of the perfect crystal.

(i) If the point defect is a vacancy, then there is no bonding. Hence the value of the mechanical strength at that point is reduced.

(ii) If an impurity atom is present instead of the original atom, in the lattice, there must be some strain due to the different size of the impurity atom.

*The number of defects at equilibrium at a certain temperature can be determined from the following equation :

$$n_d = N e^{-E_d/kT}$$

is the number of defects

total number of atomic sites per cubic metre or per mole,
 E_d is the energy of activation necessary to form the defect,
 k is the Boltzmann constant, and
 T is the absolute temperature.

77.13.1 Vacancies

An empty site of an atom in a crystal is called vacancy.

A vacancy implies an unoccupied atom position within a crystal lattice (Fig. 77.23).

The atoms surrounding a vacancy tend to be closer together, thereby distorting the lattice planes.

Vacancies may occur as a result of imperfect packing during the original crystallization or they may arise from **thermal vibrations** of atoms at elevated temperatures, because as thermal energy is increased there is a higher probability that individual atoms will jump out of their position of lowest energy.

It may be shown by thermodynamic reasoning that lattice vacancies are a stable feature of metals at all temperatures above absolute zero.

The everyday industrial processes of annealing, homogenization, precipitation, sintering, surface hardening, oxidation and creep, all involve to varying degrees, the transport of atoms through the lattice with the help of vacancies.

Vacancies exist in a certain proportion in a crystal in thermal equilibrium, leading to an increase in the randomness of the structure.

Schottky defect. Schottky defect is closely related to vacancies. It is formed when an atom or an ion is removed from a normal lattice site and replaced in an average position on the surface of the crystal (Fig. 77.24). In other words, when vacancies are created by movements of atoms from positions inside the crystal to positions on the surface of the crystal, a *Schottky defect* is said to have been formed.

Schottky defects in ionic crystals

In ionic crystals, formation of point imperfections is subject to the requirement that the overall electrical neutrality is maintained. A pair of one cation and one anion can be missing from an ionic crystal as shown in Fig. 77.25.

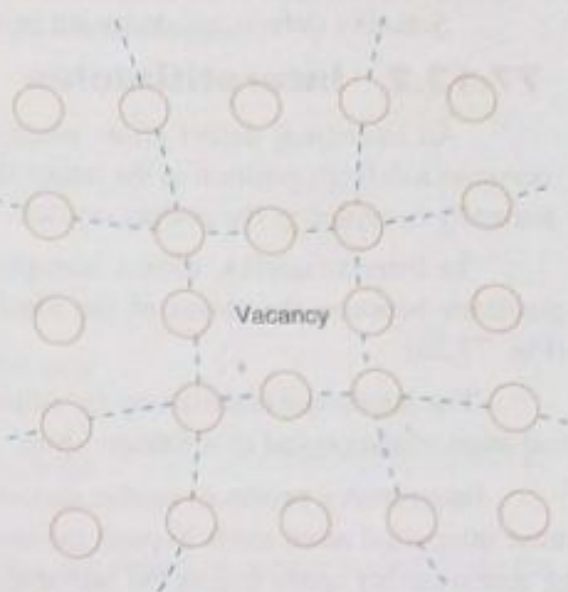


Fig. 77.23

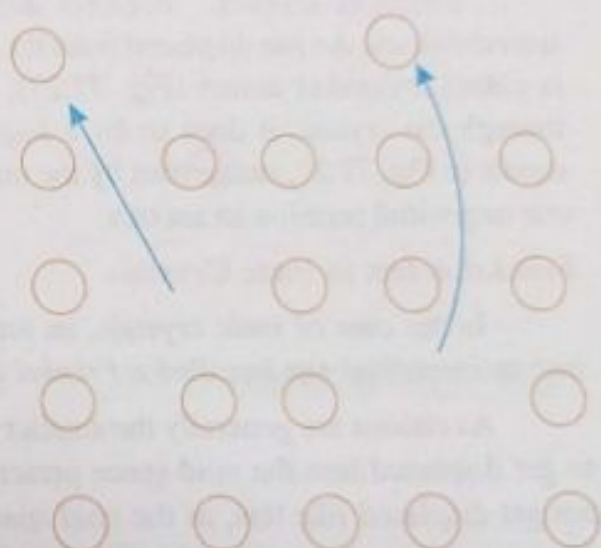


Fig. 77.24

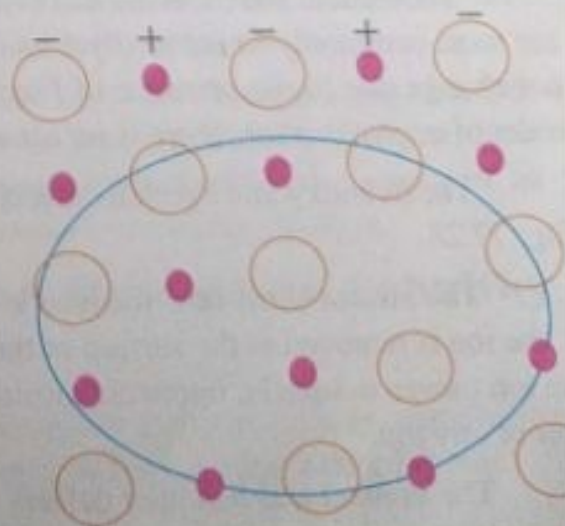


Fig. 77.25

When vacancies are created by movements of one anion and one cation from positions inside the crystal to positions on the surface of the crystal, a Schottky defect is said to have been formed.

The valency of the missing pair of ions should be equal to maintain the electrical neutrality. So these are normally generated in equal numbers of anion and cation vacancies in a crystal.

Schottky defects are dominant in alkali halides.

77.13.2 Interstitialcies

An interstitial defect arises when an atom occupies a definite position in the lattice that is not normally occupied in the perfect crystal.

In interstitialcies, atoms occupy vacant positions between the atoms of the ideal crystal (Fig. 77.26).

The interstitial (atom) may be either a normal atom of the crystal or a foreign atom.

Interstitialcy produces atomic distortion because interstitial atom tends to push the surrounding atoms farther apart, unless the interstitial atom is smaller than the rest of the atoms in the crystal.

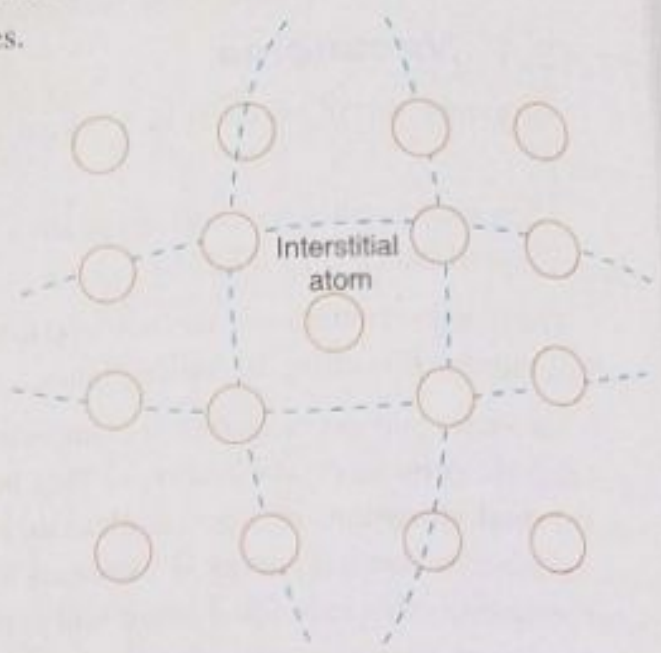


Fig. 77.26

Frenkel Defect. Frenkel defect is closely related to interstitialcies. An ion displaced from the lattice into an interstitial site is called a Frenkel defect (Fig. 77.27). When the defect migrates through the crystal, it does so by a sequence of jumps of the kind shown in Fig. 77.27, rather than by the migration of a single ion from one interstitial position to another.

Frenkel defect in Ionic Crystals

In the case of ionic crystals, an ion displaced from the lattice into an interstitial site is called a Frenkel defect.

As cations are generally the smaller ions, it is possible for them to get displaced into the void space present in the lattice. Anions do not get displaced like this, as the void space is just too small for their size. A Frenkel imperfection does not change the overall electrical neutrality of the crystal.

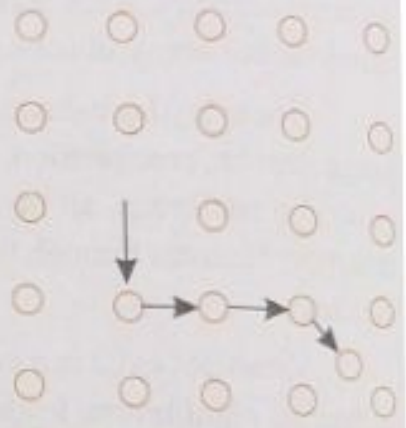


Fig. 77.27

Theoretical and experimental evidence shows that Frenkel defects are most commonly found in silver halides. The density of crystal does not change due to the presence of Frenkel defects because, to the first order of approximation, there is no net change of volume of the crystal.

The Schottky and Frenkel defects in an ionic crystal are shown in Fig. 77.28.

The arrows show how the ions are displaced. In Schottky defect S, the ion is removed to the surface of the crystal. In a Frenkel defect F, the ion moves to such an interstitial position which is not a normal position of any ion.

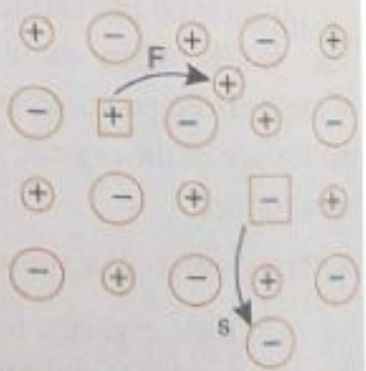


Fig. 77.28

The Frenkel and Schottky defects together are called 'Intrinsic defects'.

77.13.3 Impurities

Impurities give rise to compositional defects. Impurities may be small particles (such as slag inclusions in metals) embedded in the structure, or foreign (metal) atoms in the lattice. Foreign atoms generally have atomic radii and electronic structures differing from those of the host atoms and therefore act as centres of distortion. Impurities may considerably distort the lattice.

There are two types of impurity defects.

(i) **Substitutional impurity.** A substitutional impurity refers to a foreign atom that substitutes for or replaces a parent atom in the lattice (Fig. 77.29).

Examples. 1. In ionic solids (e.g., in NaCl), the substitution of Na^+ by Li^+ produces a substitutional impurity.

2. In semiconductor technology, aluminium and phosphorus doped in silicon are substitutional impurities in the crystal.

A controlled addition of impurity to a very pure crystal is the basis of producing many electronic devices.

3. During the production of brass alloy, the zinc atoms are doped in copper lattice. Here the zinc atoms are called substitutional impurities.

(ii) **Interstitial impurity**

An interstitial impurity is a small sized atom occupying the void space in the parent crystal, without dislodging any of the parent atoms from their sites (Fig. 77.30).

An atom can enter the interstitial or void space only when it is substantially smaller than the parent atom.

Example. In FCC iron, the atomic radius of iron atom is 0.225 nm. Carbon atoms with atomic radius 0.0777 nm can occupy the octahedral void spaces in FCC lattice as interstitial impurities.



Fig. 77.29



Fig. 77.30

77.13.4 Electronic Defects

Electronic defects are the result of errors in charge distribution in solids.

These defects are free to move in the crystal under the influence of an electrical field. This accounts for some electronic conductivity of certain solids and their increased reactivity.

Example. In zinc oxide (ZnO), the zinc ions occupy interstitials. This leads to a large number of positive charges at interstitials. Suppose in some places zinc ions are missing. Then, at these places, there is a gain of negative charges due to loss of positive charges. Thus a vacancy or an interstitial impurity may produce an excess or deficiency of positive or negative charges.

77.14 To Derive an Expression for the Number of Schottky Defects at a given Temperature

Fig. 77.31 shows two kinds of Schottky defects most commonly found in crystals, namely, the individual positive and negative vacancy, presumed to form near each other, and a coupled pair.

If $E_v = 1\text{eV}$ and $T = 1000\text{K}$, then

$$\frac{n}{N} = e^{-11.6} = 10^{-5}$$

The equilibrium concentration of vacancies decreases as the temperature decreases.

77.17 Line Defects

Line defects are called dislocations. These are one-dimensional imperfections in the geometrical sense. A *dislocation* may be defined as a disturbed region between two substantially perfect parts of a crystal (Fig. 77.33).

Dislocation is a line defect in a crystal structure whereby a part-plane of atoms is displaced from its symmetrically stable positions in the array. It is surrounded within the structure by an extensive elastic strain field and its associated stresses.

There are two basic types of dislocations :

1. Edge dislocation, and
2. Screw dislocation

77.17.1 Edge Dislocation

Fig. 77.34 (a) shows a perfect crystal.

The top sketch shows a three dimensional view of a perfect crystal.

The bottom sketch shows the arrangement of atoms on its front face.

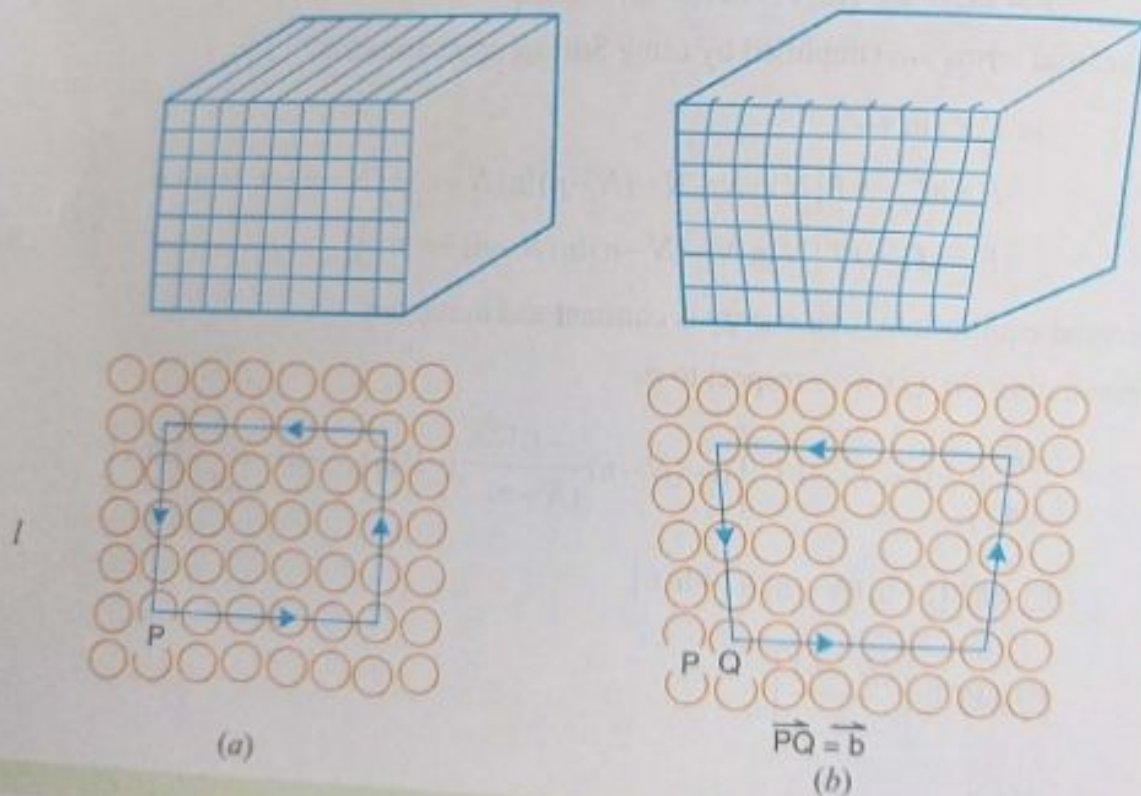


Fig. 77.34

Fig. 77.34 (b) shows an imperfect crystal.

The top sketch shows a three dimensional view of an imperfect crystal with an edge dislocation.

The bottom sketch shows the arrangement of atoms on its front face. The atoms above the edge of the extra plane are squeezed together and are in a state of compression. The bond lengths have been compressed to smaller than the equilibrium value. Just below the edge of the extraplane, the atoms are pulled apart and are in a state of tension. Here the bond lengths have been stretched to above the normal values. This distorted configuration extends all along the edge into the crystal.

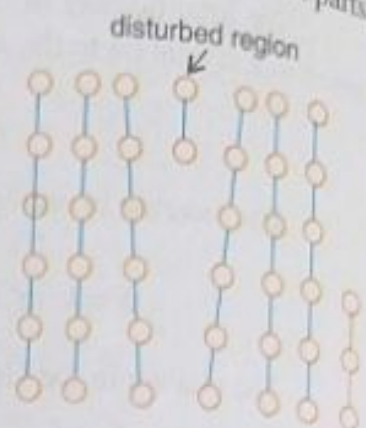


Fig. 77.33

There is an extra energy due to the distortion in the region immediately surrounding the edge of the incomplete plane. As the region of maximum distortion is centred around the edge of the incomplete plane, this distortion represents a line imperfection and is called an *edge dislocation*.

The vector $\vec{b} = \vec{PQ}$ connecting the end point Q with the starting point P is the Burgers vector of the dislocation.

Edge dislocation can be classified as *positive edge dislocation* and *negative edge dislocation*.

An edge dislocation involves an extra row of atoms, either above (positive sign) or below (negative sign) the slip plane (Fig. 77.35).

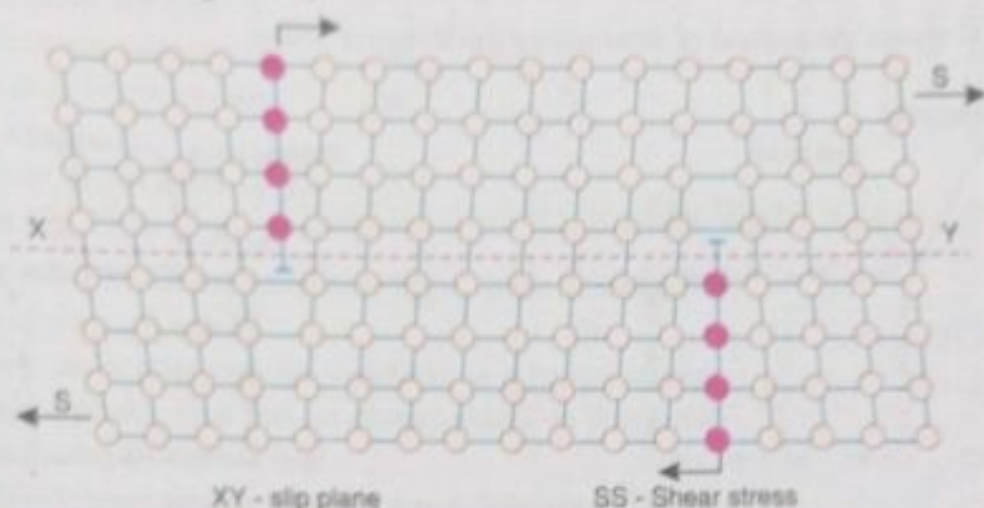


Fig. 77.35

The horizontal line XY is called the slip plane.

(i) Positive dislocation

If an extra plane of atoms is above the line XY , the edge dislocation is said to be positive. It is denoted by the symbol \perp .

(ii) Negative dislocation

If an extra plane of atoms is below the line XY , the dislocation is said to be negative. It is denoted by the symbol \top .

77.17.2 Movement of \perp and \top Dislocations Under Shear Stress \rightleftharpoons

The presence of an extra plane of atoms means that adjacent atoms are displaced elastically. Consequently, from both sides elastic forces are exerted on the dislocation. These forces balance out, so that it is easy to move the dislocation from one position to another.

Under a shear stress sense \rightleftharpoons a positive dislocation (\perp) moves to the right and a negative dislocation (\top) to the left (Fig. 77.35).

Slip caused by the movement of edge dislocation

Fig. 77.36 shows how edge dislocation (D) gets glided along the slip plane under the action of shear stress (S) and how the slip is caused by the movement of an edge dislocation.

As the dislocation glides out of the crystal completely, it produces a *slip step* of one atom width at the edge of the crystal.



Fig. 77.36

The edge dislocation is particularly useful in explaining working.

77.17.3 Burger's Vector

The Burger's vector indicates how much and in what direction the lattice above the slip plane appears to have been shifted with respect to the lattice below the slip plane. The Burger's vector is perpendicular to the edge dislocation.

Burger's Vector marks the magnitude and direction of the strain component of dislocation.

Method of determining Burger's Vector for Edge Dislocation

Fig. 77.37 shows the method of determining the Burger's Vector.

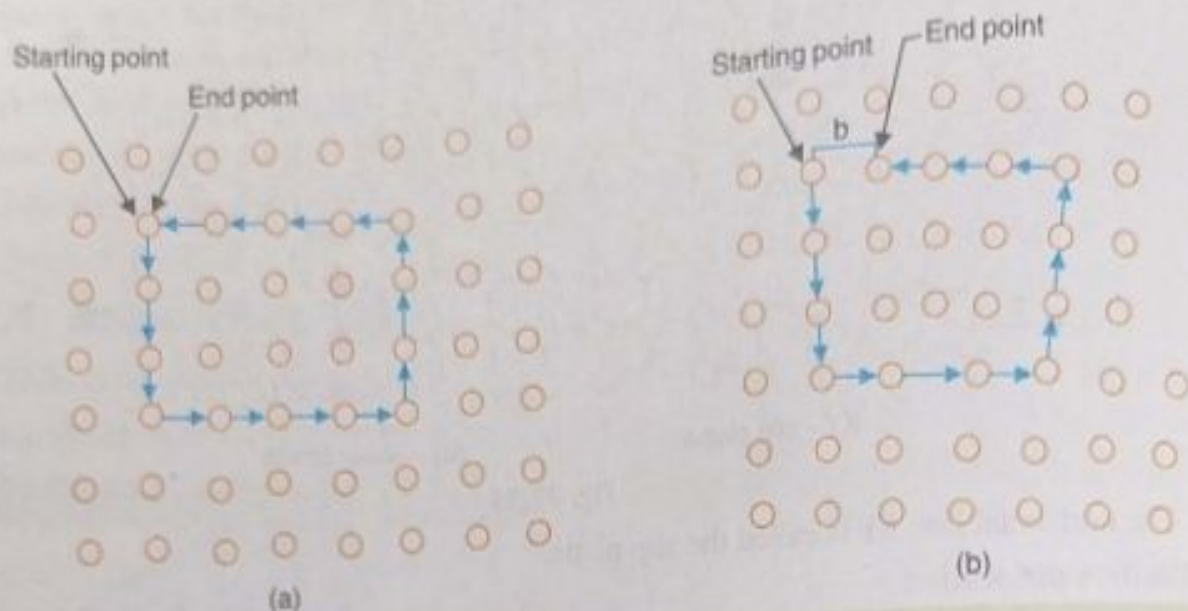


Fig. 77.37

The Burger's circuit is formed by proceeding through the undisturbed region surrounding a dislocation in steps which are integral multiples of a lattice translation. The loop is completed by going an equal number of translations in a positive sense and negative sense in a plane normal to the dislocation line.

(i) The Burger's loop closes upon itself if it does not enclose a dislocation [Fig. 77.37 (a)].

(ii) The Burger's circuit surrounding an edge dislocation is shown in Fig. 77.37 (b). The end point does not coincide with the starting point.

Therefore, the vector \vec{b} connecting the end point with the starting point is the Burger's Vector of the dislocation.

77.17.4 Screw Dislocation

Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of the crystal, forming a spiral ramp around the dislocation line.

Fig. 77.38 shows what happens when one part of the crystal is displaced relative to the rest of the crystal and the displacement terminates within the crystal.

The row of atoms marking the termination of the displacement is the screw dislocation. EF indicates the dislocation line.

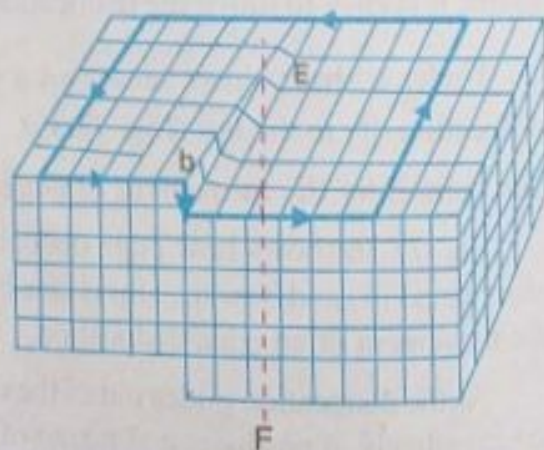


Fig. 77.38

line or atoms in the same plane. The Burger's vector lies parallel to the dislocation line along the axis of a direction of the screw dislocation. The screw dislocation may be thought of as produced by cutting the crystal partway through with a knife and shearing it parallel to the edge of the cut by one atom spacing. A screw dislocation transforms successive atom planes into the surface of a helix.

A screw dislocation is sketched in Fig. 77.39.

A part $ABEF$ of the slip plane has slipped in the direction parallel to the dislocation line EF .

A screw dislocation may be visualized as a helical arrangement of lattice planes, such that we change planes on going completely around the dislocation line.

Fig. 77.40 shows another view of a screw dislocation. The broken vertical line that marks the dislocation is surrounded by strained material.

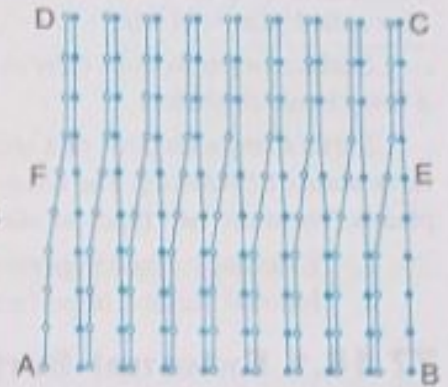
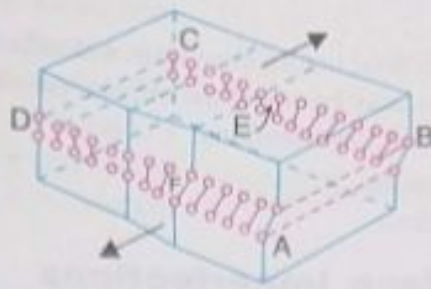


Fig. 77.39

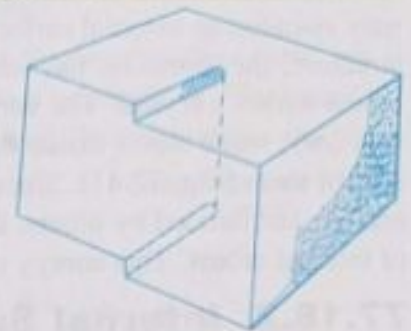




Fig. 77.40

77.17.5 Differences between Edge Dislocation and Screw Dislocation

The following Table gives the differences between edge dislocation and screw dislocation.

Edge Dislocation	Screw Dislocation
1. An edge of an atomic plane is formed internal to the crystal.	Only a distortion of the lattice cells in the immediate vicinity is produced.
2. The Burger's vector of an edge dislocation is perpendicular to the dislocation line and lies in the slip plane.	The Burger's vector of a screw dislocation is parallel to the dislocation line.
3. An edge dislocation moves (in its slip plane) in the direction of the Burger's vector (slip direction).	A screw dislocation moves (in the slip plane) in a direction perpendicular to the Burger's vector (slip direction).
4. An edge dislocation involves an extra row of atoms either above (positive sign) or below (negative sign) the slip plane. Symbols : \perp (or) \top .	In the screw dislocation, the distortion follows a helical or screw path. The pitch of the screw may be left-handed or right-handed. Symbols :  or  .
5. The forces required to form and to move an edge dislocation are smaller in their values.	The forces required to form and move a screw dislocation are somewhat greater than those required to initiate an edge dislocation.
6. Speed of movement of an edge dislocation is greater than that of a screw dislocation.	Speed of movement of a screw dislocation is less than that of an edge dislocation.
7. The edge dislocation is particularly useful in explaining slip in plastic flow during mechanical working.	Screw dislocation is especially useful in explaining crystal growth as well as slip in plastic deformation.

77.18 Surface Defects

In a surface defect, the crystalline irregularity extends in two dimensions. Surface defects are also called plane defects.

Surface imperfections refer to regions of distortions that lie about a surface having a thickness of a few atomic diameters.

Surface imperfections of a structural nature arise from a change in the stacking of atomic planes on or across a boundary. The change may be one of the orientations or of the stacking sequence of the planes. There are two types of surface imperfections.

1. External surface imperfections.
2. Internal surface imperfections.

77.18.1 External Surface Imperfections

The external surface of a crystal is an imperfection in itself, as the atomic bonds do not extend beyond the surface. Although we may visualise an external surface as simply a terminus of the crystal structure, the atoms on the surface cannot be compared with the atoms within a crystal. The surface atoms have neighbours on one side only, while atoms inside the crystal have neighbours on either side of them (Fig. 77.41). Since the external surface atoms are not entirely surrounded by others, they possess higher energy than that of internal atoms. This energy of the surface atom, for most metals, is of the order 1J/m^2 .



Fig. 77.41

77.18.2 Internal Surface Imperfections

Internal surface imperfections arise from a change in the stacking of atomic planes across a boundary. The change may be one of the orientation or of the stacking sequence of the planes.

The important internal surface imperfections are given below :

- (i) Grain boundaries
- (ii) Tilt boundaries and twist boundaries
- (iii) Twin boundaries
- (iv) Stacking faults and
- (v) Ferromagnetic domain walls.

77.18.3 Grain Boundaries

Most of the engineering materials are polycrystalline in nature. Grain boundaries are those surface imperfections which separate crystals or grains of different orientation in a polycrystalline aggregation during nucleation or crystallisation. During solidification or during recrystallization of polycrystalline crystals, new crystals are randomly oriented with respect to one another. They grow by the addition of atoms from the adjacent regions and eventually impinge on each other. When two crystals impinge in this manner, the atoms that are caught in between the two crystals



Grain Boundaries.

are being pulled by each of the two crystals to join its own configuration. They can join neither crystal due to the opposing forces. Therefore, they take up a compromise position. The thickness of this region is only a few atomic diameters, because the opposing forces from neighbouring crystals are felt by the intervening atoms only at such short distances. The boundary region is called a crystal boundary or a grain boundary. The crystal orientation changes sharply at the grain boundary (Fig. 77.42).

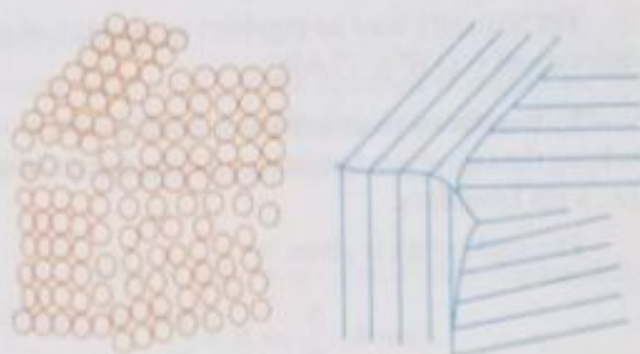


Fig. 77.42

Definition. Grain boundaries are those planar imperfections in polycrystalline materials that separate crystals (grains) of different orientation.

A grain boundary is formed when two growing grain surfaces meet.

For example if we take a piece of iron or copper, it is not in a single crystalline form, but it consists of many small interlocking crystals or grains having random orientations. The boundary between these interlocking crystals must have a structure common to both the orientations and structures of the adjacent crystals. Therefore, the grain boundary forms a discontinuity in the periodicity of the lattice of crystallite or grain. This type of lattice imperfection is called *grain boundary*. The crystal orientation changes sharply at the grain boundary (Fig. 77.42).

The grain boundary has a definite thickness of 2 to 10 or more atomic distances. A grain boundary thickness of a few atoms has been confirmed by the field ion micrography. Boundaries between grains in commercial metals are often wider, because impurities commonly concentrate at the grain boundaries during solidification.

In grain boundaries, the atomic packing is imperfect. At the grain boundary between two adjacent grains, there is a transition zone which is not aligned with either grain (Fig. 77.43).

Most atoms at the boundaries are located in highly strained and distorted positions and their free energy is higher than that of the atoms in the regular, undisturbed part of the crystal lattice.

High angle Grain Boundary. If the misorientation angle (θ), between the grains is greater than $10^\circ - 15^\circ$, the resultant grain boundaries are called *High-angle grain boundaries*. These imperfections in the grain boundary enable the microscopist to see them, for in a transparent crystalline material they may scatter light and in opaque material they can be etched chemically.

Low angle Grain Boundary. Low angle grain boundaries have angular misorientation of the order of few degrees but less than 10° .

77.18.4 Tilt Boundaries

Tilt boundaries is another surface imperfection. This is called low-angle boundary as the orientation difference between two neighbouring crystals is less than 10° .

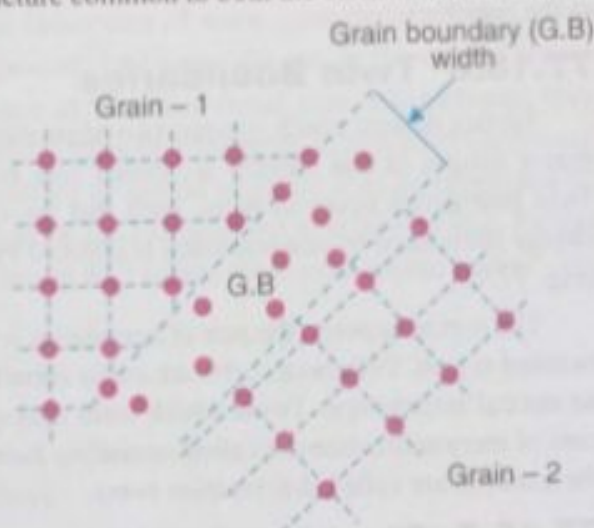


Fig. 77.43

Tilt boundary may be regarded as an array of edge dislocations (\perp) (Fig. 77.44).

By rotation of an axis in the boundary it is possible to bring the axis of two bordering grains into coincidence, i.e., a tilt boundary.

The angle of tilt is given by

$$\tan \theta = \frac{b}{D} \text{ or } \theta = \frac{b}{D}$$

(because in tilt boundary, the degree of misorientation of the grain boundary or angle of tilt, i.e., θ is less than 10°).

D is the dislocation spacing and b is the length of Burger's vector.

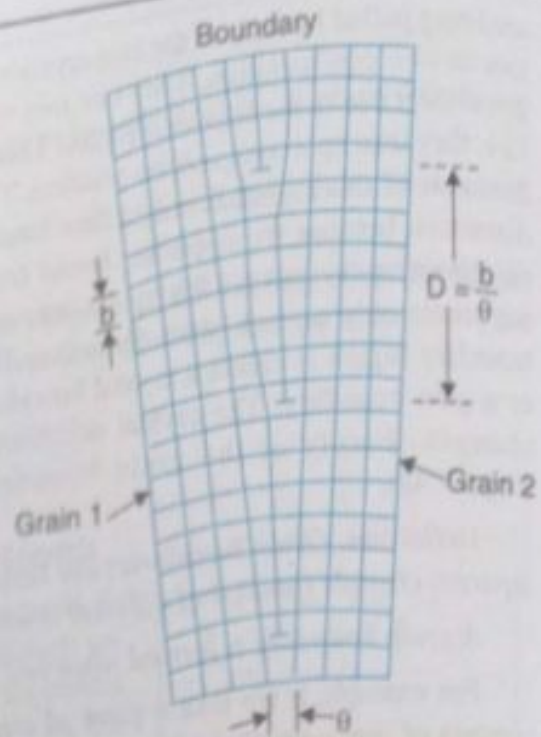


Fig. 77.44

77.18.5 Twist Boundaries

Twist boundaries are the second class of low angle boundaries resulting from the set of screw dislocations. In a twist boundary, the rotation is about an axis normal to the boundary.

77.18.6 Twin Boundaries

Surface defects which separate two orientations that are mirror images of one another are called twin boundaries. Twin boundaries occur in pairs, such that the orientation change introduced by one boundary is restored by the other (Fig. 77.45).

The region between the pair of boundaries is called the twinned region. Twin boundaries are easily identified under an optical microscope. Twins which form during the process of recrystallization are called annealing twins. Twins which form during plastic deformation of the material are called deformation twins.

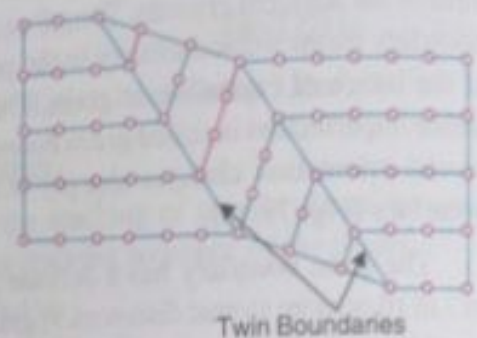


Fig. 77.45

77.18.7 Stacking Faults

A stacking fault is a surface imperfection that results from the stacking of one atomic plane out of sequence on another, while the lattice on either side of the fault is perfect. The stacking fault is a discrepancy in the packing sequence of the layers of atoms (although all the lattice sites are occupied).

It is usually produced during the growth of the crystals and plastic deformation of crystals.

Example : In the case of close packed FCC structure the stacking sequence can be written as ABC, ABC.....In that sequence it is possible in one atom layer 'A', the atoms are not positioned properly in a small region and hence deviates from the sequence, relative to the atoms of the layers above and below giving a defect, since now there is a sequence ofBCBC.....which belongs to HCP structure instead ofABC ABC.....

Fig. 77.46 shows the stacking fault in a FCC metal. So one may conclude that stacking fault may arise when there is only small dissimilarity (electrostatically) between the stacking sequences of close-packed planes in FCC and HCP metals.

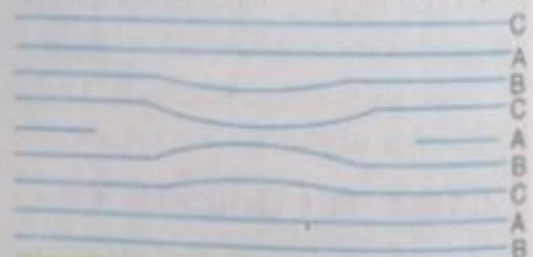


Fig. 77.46