Dr. Y. Aparna,
Associate Prof., Dept. of Physics,
JNTU College of Engineering, JNTU - H,

Defects in Crystals and X-Ray Diffraction

Classify crystal defects ?

Ans: They are broadly classified into four categories, namely,

1. Point defects (zero dimensional defects)

    (i)   Vacancies

    (ii)   Interstitialcies

    (iii)   Compositional defects

    (iv)   Electronic defects

2. Line defects (one dimensional defects)

    (i)   Edge dislocation

    (ii)   Screw dislocation

3. Surface defects (two dimensional defects)

    (i)   Grain boundaries

    (ii)   Tilt boundaries

    (iii)   Twin boundaries

    (iv)   Stacking faults

4. Volume defects (three dimensional defects)

   (i)   Large voids

    (ii)   Cracks

    (iii)

Discuss about the point defects in crystals?

 Ans: **POINT DEFECTS**

Point defects are formed due to the missing of atoms or the present of foreign atoms in the crystals. The presence of point defects in a crystal increases its internal energy compared that of the perfect crystal. The effect of such defects is local and produce distortion inside the crystal structure. The presence of point defects change the electrical resistance of the crystals. Due to present of point defects, distortion or strain appears around the defect up to few atomic diameters. Hence the mechanical strength at that point gets reduced.

(i)   Vacancies:

An empty site of an atom position in a crystal is simply known as vacancy. This refers to a missing atom simply known as vacancy. This refers to a missing atom or vacant site as shown in Figure. Such defects may form either due to imperfect packing during the original crystallization or due to thermal vibrations will increase and ultimately some electrons jump out of their positions of lowest energy. It is possible that the transport of atoms occur through the lattice with the help of vacancies during the industrial processes of annealing, precipitation, sintering, surface hardening etc.
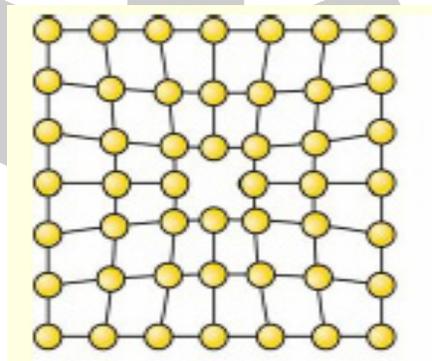
Figure

(ii)   Interstitialcies:

This defects occurs as an additional atom occupies a void space (empty space between the atoms) which causes some mechanical strain on the surrounding atoms. The amount of strain depends on the size of the interstitial atom. The atom which occupies void space is called interstitial atom as shown in Figure   such atoms may be present in the crystals which have low packing fraction. When a crystal has undergone enormous stress then some of the parent atoms get displaced from their lattice sites to voids present in the crystal. These defects can be treated as self- interstitial defects.
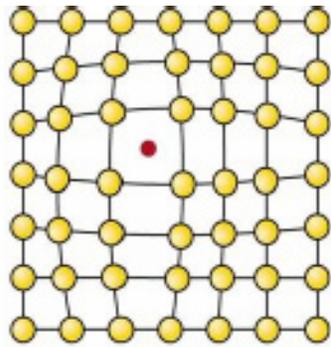
(iii)   Compositional defects:

Compositional defects arise due to presence of either unwanted impurities or purposely doped impurities during the process of crystallization. These defects play an important role in semiconductors which are specially prepared for diodes, transistors, etc. these defects are of two types, (1) Substitutional impurities and (2) Interstitial impurities. A substitutional impurity refers to a foreign atom that replaces a parent atom in the crystal lattice. This is shown in Figure. if the size of substitutional impurity is same as parent atom then the amount of strain around will be less, otherwise it will be more.

Ex: Extrinsic semiconductor of silicon which is doped with aluminium or phosphorus.

An interstitial impurity refers to a small sized foreign atom lodging the void space in the parent crystal without disturbing any of the parent atoms from their sites. It is shown in Figure.
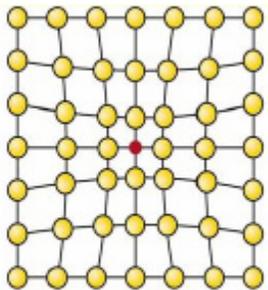
small substitutional atom
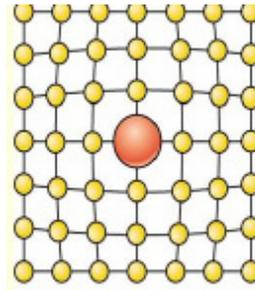
large substitutional atom

Ex: Occupying carbon atoms of atomic radius 0.777 Å in the octahedral void space of FCC iron of the atomic radius 2.250 Å.

(iv) **Electronic defects:**

Electronic defects occur as a result of errors in charge distribution in solids. By the influence of external electric field, these defects move freely within the crystal. To understand the phenomena related to electrical conductivity, the electronic defects play an important role.

Derive an expression for the number of vacancies at a given temperature ?

Ans: **CALCULATION OF NUMBER OF VACANCIES AT A GIVEN TEMPERATURE**

Almost in all crystals vacancies are present and the main cause for these defects is thermal agitation. And these vacancies are produced and destroyed constantly. Let us consider E_v is the energy required to move an atom from lattice site on the surface. Therefore the amount of energy required to produce n number of isolated vacancies can be written as

$$u = nE_v \qquad (2.17)$$

The total number of ways to move n number of atoms out of N number of atoms in a crystal on to its surface will be

$$p = \frac{N!}{(N-n)!n!} \qquad (2.18)$$

The increase in entropy due to formation of n vacancies can be written as

$$S = K_B \log P \qquad (2.19)$$

Substituting equation (2.18) in equation (2.19),

$$S = K_B \log\left\{\frac{N!}{(N-n)!n!}\right\} \qquad (2.20)$$

But, the free energy

$$F = u - TS$$

Hence,

$$F = nE_v - K_BT \log \frac{N!}{(N-n)!n!} \qquad (2.21)$$

$$F = nE_v - K_BT[\log N! - \log(N-n)! - \log n!]$$

Using Stirling is approximation, log x! = x logx – x the second term on R.H.S can be simplified as

$$F = nE_v - K_BT[N \log N - N - (N-n)\log(N-n) + (N-n) - n\log + n]$$

$$F = nE_v - K_BT[N \log N - (N-n)\log(N-n) - n\log n] \qquad (2.22)$$

At thermal equilibrium, free energy is constant and minimum with respect to n, hence,

$$\left[\frac{\delta F}{\delta n}\right]_T = 0 = E_v - K_BT\left[0 - (N-n)\frac{-(1)}{(N-n)} - (-1)\log(N-n) - n\frac{1}{n} - 1\log n\right]$$

$$E_V = K_BT[1 + \log(N-n) - 1 - \log n]$$

$$E_V = K_BT \log\left[\frac{(N-n)}{n}\right] \qquad (2.23)$$

$$\frac{N-n}{n} = \exp\left(\frac{E_V}{K_BT}\right)$$

$$n \cong (N-n)\exp\left[\frac{-E_V}{K_BT}\right] \qquad (2.24)$$

If n <<N, n can be neglected, so that

$$n \cong N \exp\left[\frac{-E_V}{K_BT}\right] \qquad (2.25)$$

If $E_V = 1eV$ and $T = 1000K$

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

$$\frac{n}{N} = 9.1 \times 10^{-6} \cong 10^{-5}$$

Hence, the equilibrium concentration of vacancies decreases with temperature.

**Discuss the Schottky defects in ionic crystals?   (April/may 2008, JNTU)**

In ionic crystals, the formation of point imperfections is subjected to the requirement that the overall electrical neutrality has to be maintained. A pair of one cation and one anion can be missed from an ionic crystal as shown in Figure. the valency of the missing pair of ions should be equal and opposite to maintain the electrical neutrality. So these are known as ion vacancies in a crystal. When vacancies are created by the movements of an anion and a cation from positions inside the crystal to positions on the surface of the crystal, a Schottky defect is said to be formed. Such defects are dominant in alkali halides.
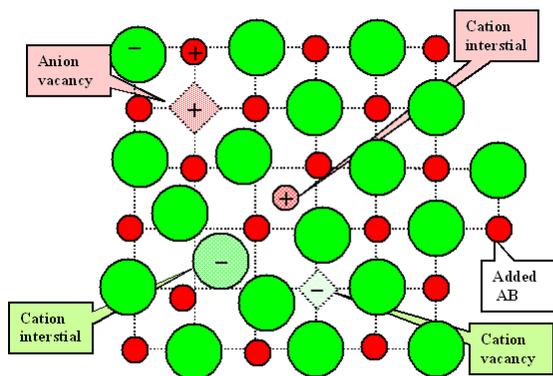
Derive an expression for the number of Schottky defects at a given temperature ?

Answer: CALCULATON OF NUMBER OF SCHOTTKY DEFECTS AT A GIVEN TEMPERATURE

In ionic crystals, the number of Schottky defects at a given temperature, can be calculated assuming an equal number of positive and negative ion vacancies are present. The formation of pairs makes it possible to keep the surface of the crystal electrostatically neutral. The Schottky defect is as shown in figure
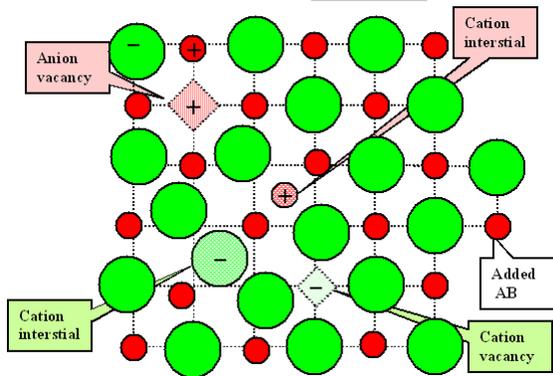
The number of pairs can be related to the total number of atoms present in the crystal on following the same procedure as adopted in pure atomic crystals.

Let us consider E_p is the energy required to move an ion pair from lattice site inside the crystal to a lattice site on the surface. Therefore the amount of energy required to produces n number of isolated ion pair vacancies will be

$$u = n E_p \tag{2.26}$$

The total number of ways that to move n numbers of ion pairs out of N numbers of ionic molecules in a crystal on to the surface will be

$$P = \left[\frac{N!}{(N-n)!\, n!} \right]^2 \tag{2.27}$$

$$S = K_B \log P$$

$$S = K_B \log \left[\frac{N!}{(N-n)!\, n!} \right]^2 \tag{2.28}$$

But, the free energy, F = u – TS (2.29)

Submitting the equations (2.26) and (2.28) in equation (2.29),

$$F = nE_p - K_B T \log \left[\frac{N!}{(N-n)!\, n!} \right]^2 \tag{2.30}$$

Where, E_p is the energy of formation of a pair of ion vacancies.

Using Stirling approximation, log x! = x log x –x,

$$\log \left[\frac{N!}{(N-n)!\, n!} \right]^2 = 2 \left[N \log N - N - (N-n) \log(N-n) + (N-n) - n \log n + n) \right]$$

$$\log \left[\frac{N!}{(N-n)!\, n!} \right]^2 = 2 \left[N \log N - (N-n) \log(N-n) - n \log n \right]$$

Substituting this value in equation (2.30),

$$F = nE_p - 2K_BT[N \log N - (N-n) \log(N-n) - n \log n]$$ (2.31)

At thermal equilibrium, free energy is constant and minimum with respect to n, hence,

$$\left[\frac{\delta F}{\delta n}\right]_T = 0 = E_p - 2K_BT[0 + \log(N-n) + 1 - \log n - 1]$$

$$E_p = 2K_B T \log\left[\frac{N-n}{n}\right]$$

$$\frac{E_p}{2K_BT} = \log\left[\frac{N-n}{n}\right]$$

$$\left[\frac{N-n}{n}\right] = \exp\left(\frac{E_p}{2K_BT}\right)$$

$$n = (N-n) \exp\left(\frac{-E_p}{2K_BT}\right)$$ (2.32)

If, n<<N then n can be neglected,

$$n = N \exp\left(\frac{-E_p}{2K_BT}\right)$$

$$\frac{n}{N} = \exp\left(\frac{-E_p}{2K_BT}\right)$$ (2.33)

In NaCl crystal, $E_p = 2.02$ eV at room temperature, therefore,

$$\frac{n}{N} = \exp\left(\frac{-2.02}{2 \times 0.025}\right)$$

$$\frac{n}{N} = e^{-40.4}$$

$$\frac{n}{N} = 2.8 \times 10^{-18}$$

Discuss about the Frenkel defects in crystal and derive an expression for the number of Frenkel defects at a given temperature ?

Ans: Frenkel defects:

In ionic crystals, an ion may be displaced from the regular lattice into an interstitial site or void space. If it is so, then the vacancy and an interstitial defect will be formed. These two defects together known as Frenkel defect. It is shown in Fig. 2.37. As cations are generally the similar ions, it is possible for them to get displaced 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 imperfections in silver halides and calcium fluoride are of the Frenkel type. Frenkel and Schottky defects together are called intrinsic defects. The Frenkel defect is as shown in figure:
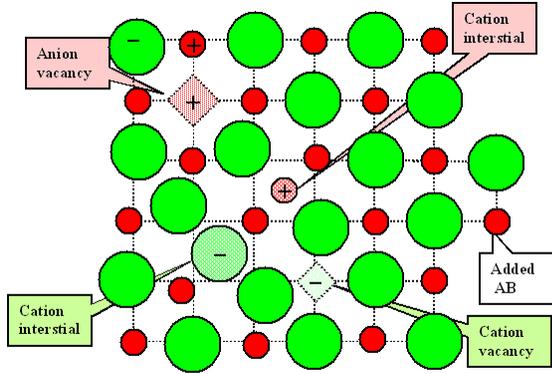
CALCULATION OF NUMBER OF FERNKEL DEFECTS AT GIVEN TEMPARATURE

Let us consider E_i is the energy required to move an atom from lattice site inside the crystal to a lattice site on the surface. Therefore the amount of energy required to produce n number of isolated vacancies,

$$u = nE \qquad (2.34)$$

the total number of ways to move n numbers of ions out of N number of ionic molecules in a crystal on to the surface will be

$$P = \frac{N!}{(N-n)!\,n!} \times \frac{N_i!}{(N_i-n)!\,n!} \qquad (2.35)$$

Where N_i is the number of interstitial ions. The corresponding increase in entropy due to the creation of Frenkel defects is given by

$$S = K_B T \, \log\left\{ \left[\frac{N!}{(N-n)!\,n!} \right] \times \left[\frac{N_i!}{(N_i-n)!\,n!} \right] \right\} \qquad (2.36)$$

But, free energy, $F = u - TS$ (2.37)

Substituting equations (2.34) and (2.36) in equation (2.37),

$$F = nE_i - K_BT \; \log\left\{\left[\frac{N!}{(N-n)! \; n!}\right] \times \left[\frac{N_i!}{(N_i-n)! \; n!}\right]\right\}$$ (2.38)

Consider, $\log\left\{\left[\frac{N!}{(N-n)! \; n!}\right] \times \left[\frac{N_i!}{(N_i-n)! \; n!}\right]\right\} = \log\frac{N!}{(N-n)! \; n!} \times \frac{N_i!}{(N_i-n)! \; n!}$

Using Stirling's approximation, $\log x! = x \log x - x$

$$\cong N \log N + N_i \log N_i - (N-n)\log(N-n) - (N_i-n)\log(N_i-n) - 2n \log n$$

Substituting this values in equation (2.38)

$$F = nE_i - K_BT \; [N \log N + N_i \log N_i - (N-n)\log(N-n) - (N_i-n)\log(N_i-n) - 2n \log n]$$

At equilibrium, the free energy is constant and minimum with respect to n, hence

$$\left[\frac{\delta F}{\delta n}\right]_T = 0 = E_i = K_BT \; \log\left[\frac{(N-n)(N_i-n)}{n^2}\right]$$

$$E_i = K_BT \; \log\left[\frac{(N-n)(N_i-n)}{n^2}\right]$$

Taking $N \gg n$ and $N_i \gg n$,

$$\cong K_BT \; \log\left[\frac{NN_i}{n^2}\right]$$

$$E_i = K_BT \; [\log(NN_i) - 2 \log n]$$ (2.39)

$$\log n = \frac{1}{2}\log(NN_i) - \frac{E_i}{2K_BT}$$ (2.40)

Hence, it is concluded that number of Frenkel defects, n is proportional to $(NN_i)^{\frac{1}{2}}$.

What are line defects and explain in detail?

LINE DEFECTS :

   Line defects are known as one- dimensional defects. The effect of these defects appear along a line in the crystal geometry. These defects are also called dislocations. These dislocations occur generally due to presence of incomplete atomic planes which arise due to growth accidents, thermal stress etc. the

Slip plane
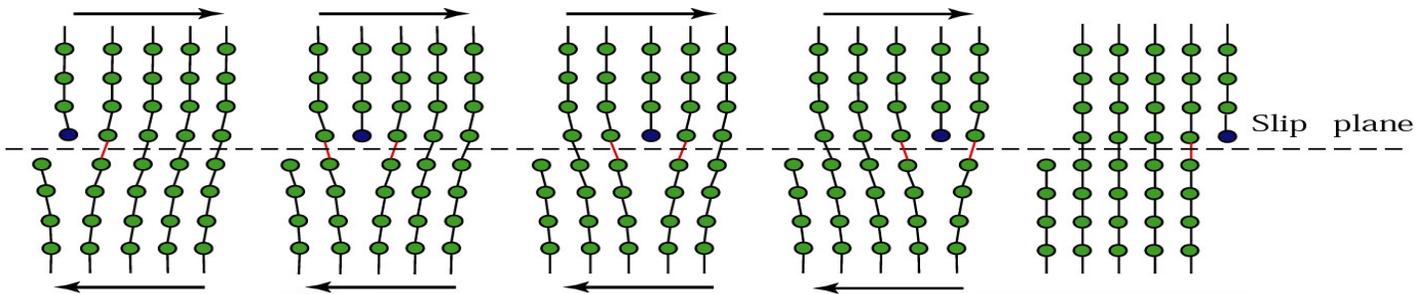
   presence of dislocations in the crystal decrease its mechanical strength. Therefore it can be said that few of the crystals are structure sensitive as the mechanical properties are dependent on the line defects.

LINE DEFECTS (ONE – DIMENSIONAL DEFECTS)

   In general, dislocations are classified into two categories.

        i.   Edge dislocation

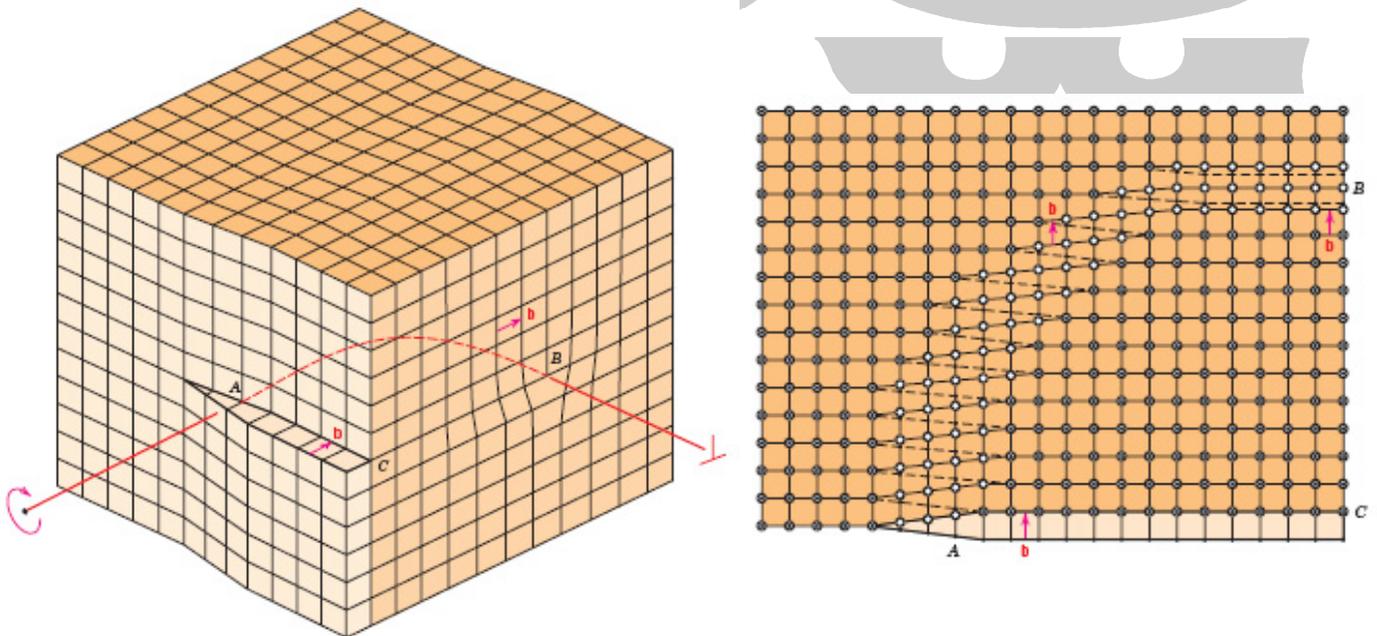   ii.   Screw dislocation

i)   Edge dislocation

   A three dimensional view of a perfect crystal is shown in Fig. 2.38. it is an aggregate of vertical planes parallel to each other and side faces, suppose one of the vertical planes does not extend from top to the bottom of the crystal i.e., ends partway with in the crystal as shown in Figure , a dislocation is said to be present.

   In a perfect crystal all the atoms are present at equilibrium positions, therefore distance between any two adjacent atoms any where in the crystal will be equal to equilibrium value. In an edge dislocated crystal, just above the edge of incomplete plane, the atoms are squeezed and are in a state of compression. The distance between neighboring atoms will be lesser than the equilibrium value. Just below the edge of the incomplete plane, the atoms are pulled apart and are in a state of tension.

The distance between neighboring atoms will be greater than the equilibrium values. The plane in between the above mentioned regions is known as slip plane. The distortion extends along the edge into all the crystal. The maximum distortion appears around the edge of the incomplete plane.

The edge dislocation runs from front to back through the crystal. The incomplete crystal plane may begin from top or bottom and ends in midway as shown in Fig. 2.40 (a & b). in the first case the dislocation (PQ) is said to be positive and is represented by the symbol ⊥. In the later case it (P'Q') is said to be positive and represented by the symbol ⊤.

In the above symbols, i.e., ⊤ or ⊥, the horizontal lines represent slip plane and the vertical lines represent incomplete plane.

ii)   Screw dislocation

When the part of the crystal is displaced relative to another part, a spiral ramp forms around the dislocation line. It means crystal is not breaking up into two parts. The displacement is terminated with in the crystal as shown in Figure in the figure, ABCD is the slip plane. The left portion of slipped plane is not sheared the line AD represents dislocation line. The term screw is to represent that one part of the crystal is moving in spiral manner about the dislocation line.

Dislocation line

Burgers vector b

(a)

(b)
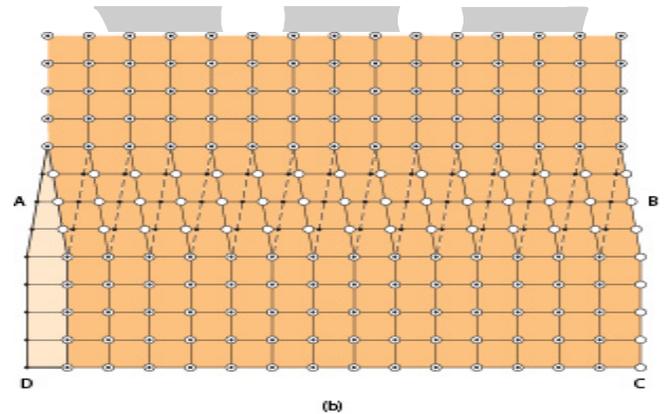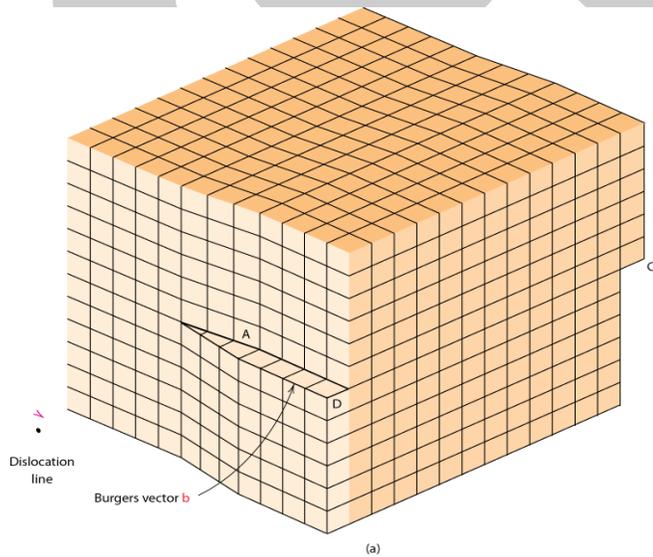
If spiral motion of one part of the crystal is in clockwise direction then the dislocation is right handed, on the other hand spiral motion is in anticlockwise direction then the dislocation is left handed.

Write a short note on Burger's vector?

Ans: BURGER'S VECTOR

The magnitude and direction of the dislocation can be understood from the concept of Burger's vector.

Let us consider a starting point P in a crystal and move X-times the atomic distance in the positive X- direction and move Y- times the atomic distance in the positive Y- direction and then move X-times the atomic distance in the negative Y-direction. After this process the starting and ending point will be same (P). this happens in the case of an ideal crystal. It is shown in Figure 1 and Fig. 2. This circuit is known as a Burger's vector.
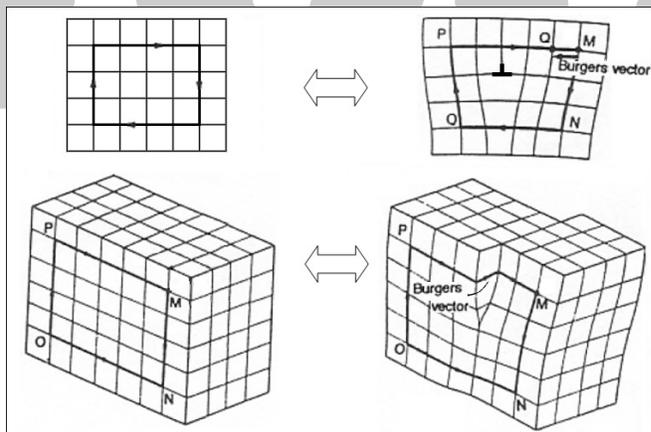
Figure

In the case of dislocated crystal, if the starting point is P, then ending point will be Q. It means to reach the initial point P, there is an extra distance b as shown in Fig. 3 and Fig. 4 The connecting vector between the starting point and ending point is known as Burger's vector of the dislocation. This given direction and magnitude of the dislocation. The Burger's vector is perpendicular to the edge dislocation andis parallel to the screw dislocation.

Distinguish between edge and screw dislocations ?

Ans: DIFFERENCES BETWEEN EDGE DISLOCATION AND SCREW DISLOCATION

Sl. No.	Edge dislocation	Screw dislocation
1	In edge dislocation, an edge of atomic plane is formed internal to the crystal.	In screw dislocation, only distortion of the lattice cell in the immediate vicinity is proved.
2	It is perpendicular to its Burger's vector.	It is parallel to Burger's vector.
3	It moves in the direction of the Burger vector	It moves in a direction perpendicular to the Burger's vector.
4	If the incomplete plane is above the slip plane then it is known as positive edge dislocation and is represented by the symbol ⊥.	If the spiral motion of the dislocation is in clock-wise direction then it is known as right handed screw dislocation.
5	If the incomplete plane is below the slip plane then it is known as negative edge dislocation and is represented by the symbol ⊤.	If the spiral motion of the dislocation is in anti – clock wise direction then it is known as left handed screw dislocation.
6	The amount of force required to form and move an edge dislocation is less.	The amount of force required to form and move a screw dislocation is more.
7	Speed of movement of an edge dislocation is lesser.	Speed of movement of a screw dislocation is greater.

X-Ray Diffraction:

X-rays are part of electromagnetic radiation with wavelengths between about $0.02A^0$ and $100A^0$. They are part of the electromagnetic spectrum which includes electromagnetic radiation called visible light. Because X-rays have wavelengths similar to the size of atoms, they are useful to explore within the crystals.

The energy of X-rays, like all electromagnetic radiation, is inversely proportional to their wavelength as given by the Einstein equation:
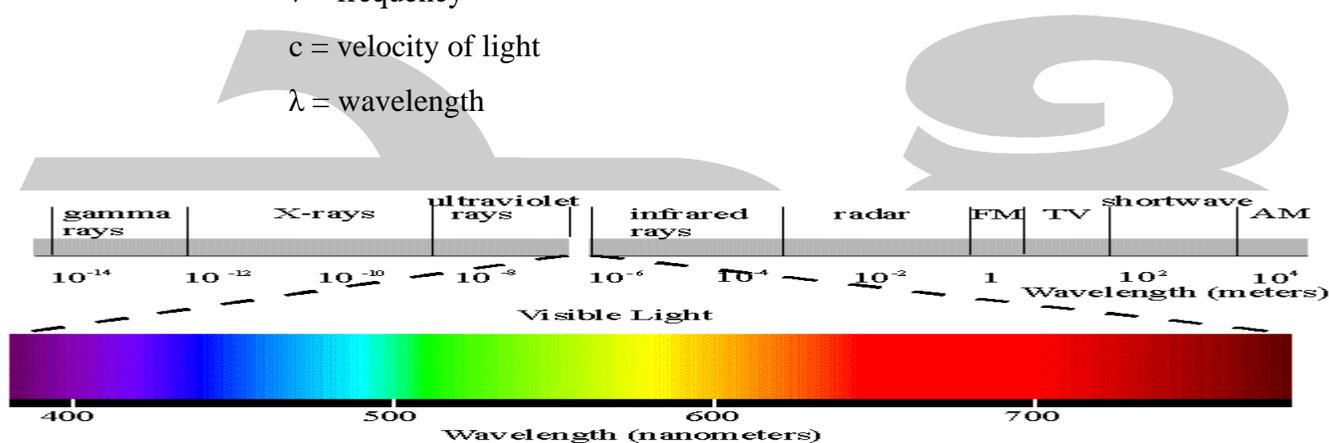
$$E = h\nu = hc/\lambda$$

Where, E= energy

h = Planck's constant

ν = frequency

c = velocity of light

λ = wavelength


Since X-rays have smaller wavelength than visible light , they have higher energy. Due presence of higher energy ,X-rays can penetrate matter more easily than visible light.

Bragg's Law:

W.L. Bragg, observed X-ray diffraction when X-rays are incident on the crystal surface nearly at Bragg's angles. Bragg's angle or glancing angle means the angle between incident ray and crystal plane at which diffraction occurs.

W.L. Bragg presented an explanation of the observed diffracted beams from a crystal. He supposed that the incident waves undergo specular (mirror-like) reflection at the various parallel planes of atoms in the crystal, with each plane reflecting only a small fraction of the radiation. The diffracted beams are found only when the reflections from the various planes of atoms interface constructively.
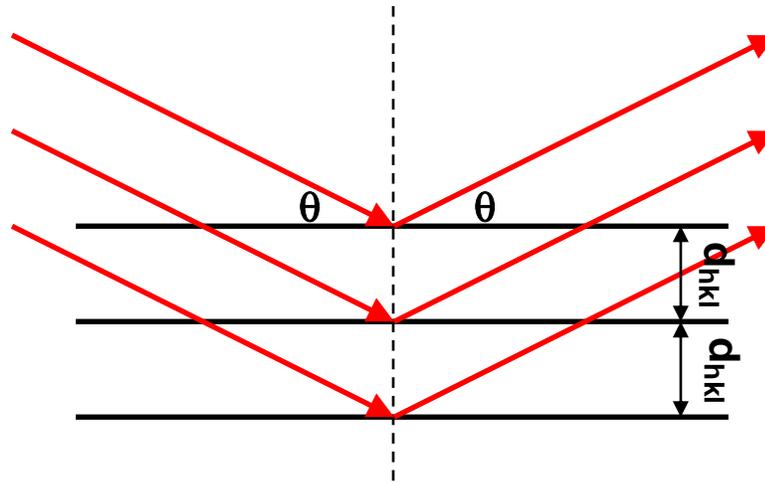
Application of X-rays:

a. XRD analysis provides

- Analysis of solid and liquid samples.
- Reflection, transmission or capillary geometry in-situ high temperature & reactive environment.
- Orientation / texture data
- Grazing incidence
- Reflectometry
- Kratky Small Angle X-ray Scattering(SAXS)

b. XRD analysis applications include

- Nano-materials: phase composition, crystallite size and shape, lattice distortions and faulting, composition variations, orientation, in-situ development.
- Catalysts: for nano-materials, with monitoring of structure throughout manufacturing and use to develop structure-property relationships.
- New materials development
- Polymers & Composites: Crystalline form, crystallinity, crystalline perfection, orientation.
- Pharmaceuticals & Organics: Polymorphs, crystallinity, and orientation are important to performance and can be followed by XRD, including in-situ studies. XRD qualified to GMP standards.

LAUE'S METHOD:

The Laue's method, a single crystal is held stationary in a continuous X-ray beam. The crystal diffracts the discrete values of λ for which the crystal planes of spacing d and the incidence angle θ satisfy the Bragg's law.

The Laue method is mainly used to determine the orientation of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal.

The diffracted beams form arrays of spots, that lie on curves on the film. The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of *d* and   involved. Each curve therefore corresponds to a different wavelength. The spots lying on any one curve are reflections from planes belonging to one zone. Laue reflections from planes of the same zone all lie on the surface of an imaginary cone whose axis is the zone axis.

Experimental

There are two practical variants of the Laue method, the back-reflection and the transmission Laue method. You can study these below:

Back-reflection Laue

In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.

One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.
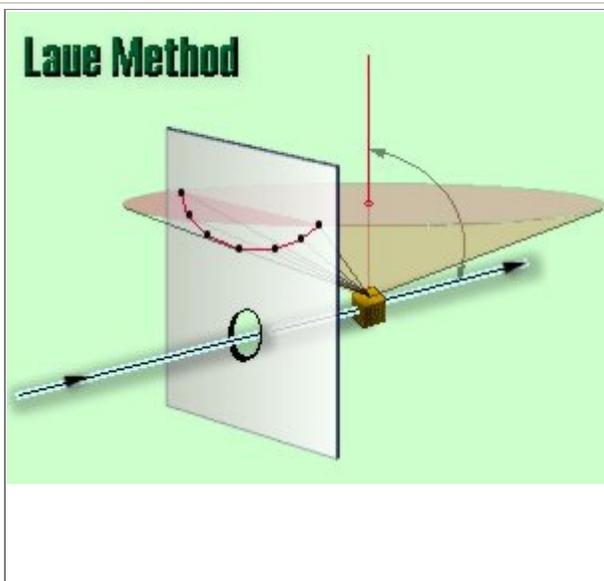
Transmission Laue

In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal.

One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.
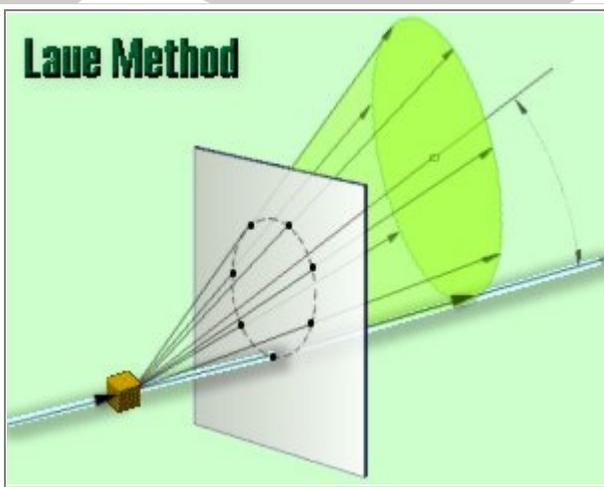
Crystal orientation is determined from the position of the spots. Each spot can be indexed, i.e. attributed to a particular plane, using special charts. The Greninger chart is used for back-reflection patterns and the Leonhardt chart for transmission patterns.

The Laue technique can also be used to assess crystal perfection from the size and shape of the spots. If the crystal has been bent or twisted in anyway, the spots become distorted and smeared out.

POWDER METHOD (Debye and Scherrer Method):

The Powder method was developed by Debye and Scherrer in Germany and by Hill in America simultaneously. This method is used to study the structure of the crystals which can not be obtained in the form of perfect crystals of appreciable size. Therefore, the sample used is in the form of a fine powder containing a large number of tiny crystallities with random orientations.

The X-ray Powder Method

In practice, this would be a time consuming operation to reorient the crystal, measure the angle θ, and determine the d-spacing for all atomic planes. A faster way is to use a method called the *powder method*. In this method, a mineral is ground up to a fine powder. In the powder, are thousands of grains that have random orientations. With random orientations we might expect most of the different atomic planes to lie parallel to the surface in some of the grains. Thus, by scanning through an angle θ of incident X-ray beams form 0 to 90°, we would expect to find all angles where diffraction has occurred, and each of these angles would be associated with a different atomic spacing.
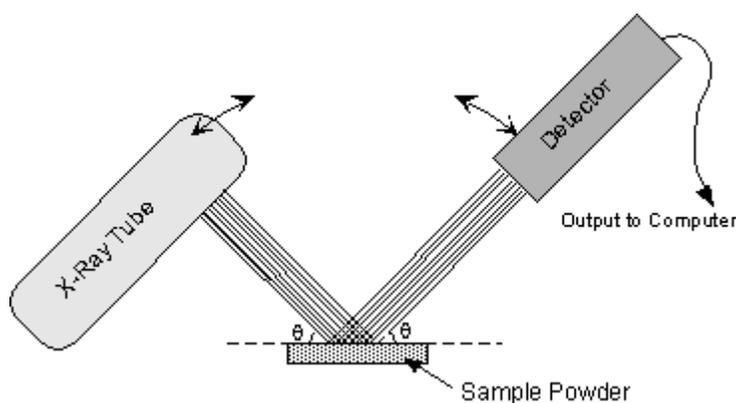
The instrument used to do this is an x-ray powder diffractometer. It consists of an X-ray tube capable of producing a beam of monochromatic X-rays that can be rotated to produce angles from 0 to 90°. A powdered mineral sample is placed on a sample stage so that it can be irradiated by the X-ray tube. To

detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube, and it too is allowed to rotate to produce angles from 0 to 90°.

After a scan of the sample the X-ray intensity can be plotted against the angle θ (usually reported as 2θ because of the way older diffractometers were made) to produce a chart, like the one shown here. The angle 2θ for each diffraction peak can then be converted to d-spacing, using the Bragg equation. The instrument used to rotate both the X-ray tube and the detector is called a goniometer. The goniometer keeps track of the angle θ, and sends this information to a computer, while the detector records the rate of X-rays coming out the other side of the sample (in units of counts/sec) and sends this information to the computer.
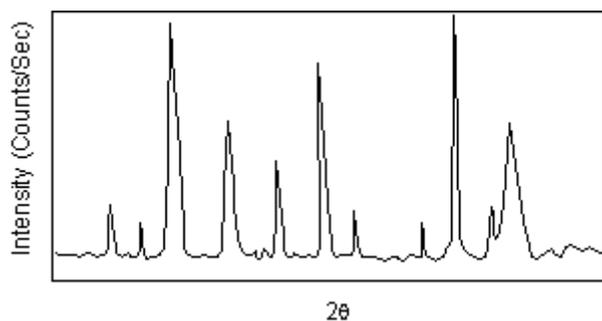
One can then work out the crystal structure and associate each of the diffraction peaks with a different atomic plane in terms of the Miller Index for that plane (hkl). A group known as the Joint Committee on Powder Diffraction Standards (JCPDS) has collected data such as this on thousands of crystalline substances. This data can be obtained as the JCPDS Powder Diffraction File. Since every compound with the same crystal structure will produce an identical powder diffraction pattern, the pattern serves as kind of a "fingerprint" for the substance, and thus comparing an unknown mineral to those in the Powder Diffraction file enables easy identification of the unknown. We will see how this is done in our laboratory demonstration.

PROBLEMS:

1. Electrons are accelerated by 8.54 V and are reflected by a crystal. The first reflection maximum occurs when the glancing angle is 56^0. estimate the spacing of the crystal.

Given data: Accelerated Voltage V= 854 V

                Glancing angle $\theta = 56^0$

                Inter planar spacing d =?

                Diffraction order, n = 1

Principle: i. $\qquad \lambda = \dfrac{h}{\sqrt{2meV}}$ and

       ii. $d = \dfrac{n\lambda}{s \sin \theta}$

solution: $\qquad \lambda = \dfrac{h}{\sqrt{2meV}}$

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} kg \times 1.6 \times 10^{-19} c \times 854V}}$$

$$\lambda = \frac{6.625 \times 10^{-34}}{157.6974 \times 10^{-25}}$$

$$\lambda = 0.0420 \times 10^{-9} m$$

$$\lambda = 0.0420 \times 10^{-10} m = 0.42 \overset{0}{A}$$

$$\lambda = \frac{0.420 \times 10^{-10} m}{2 \times \sin 56}$$

$$d = 0.253 \ \overset{0}{A}$$

2. The concentration of Schottky defects in an ionic crystal 1 in 10^{10} at a temperature of 300K. Estimate the average separation in terms of the lattice spacings between the defects at 300K and calculate the value of the concentration to be expected at 1000K.

Given data: $T_1 = 300K$

$T_2 = 1000K$

Principle: $n = Ne^{\frac{-E_v}{2K_BT}}$

Solution: $\dfrac{n}{N} = \dfrac{1}{10^{10}} = e^{\frac{-Ev}{2K_BT}}$

At 300K, $K_BT = 0.025$ eV

$\dfrac{n}{N} = \dfrac{1}{10^{10}} = e^{\frac{-Ev}{2\times0.025}}$

$e^{\frac{-Ev}{0.05}} = \dfrac{1}{10^{10}}$

$e^{\frac{-Ev}{0.05}} = 10^{10}$

$\dfrac{E_v}{0.05} = 10 \log_e 10 = 23$

$E_v = 23 \times 0.05 = 1.2$ eV

$E_v = 1.2$ eV

At 300K. $\dfrac{n}{N} = \dfrac{1}{10^{10}}$

$n = \dfrac{10^{29}}{10^{10}} = 10^{19}$

i.e. ine metre^3 may contain 10^{19} defects

hence, 1 metre will contain $(10^{19})^{1/3} = 2.15 \times 10^6$ defects

or

$$n = \left(\frac{1}{2.15 \times 10^6}\right) = 0.46 \times 10^{-6} \text{ m will be required.}$$

3. The density of Schottky defects in a certain sample of Nacl is $5 \times 10^{11}/m^3$ at 25^0 c. If the interionic $(Na^+ - cl^-)$ distance is $2.82A^0$, what is the energy required to create one schottky defect.

Given data: Density of Schottky defects $\rho = 5 \times 10^{11}/m^3$ distance r $= 2.82A^0$

Principle: $n = N \exp(-E/2K_BT)$

Solution: The unit cell NaCl contains four ion – pairs and its volume is

$(2 \times 2.82)^3 \times 10^{-30} = 1.794 \times 10^{-28} \text{ m}^3$

One meter cube of an ideal crystal contains $\dfrac{4}{1.794 \times 10^{-28}} = 2.23 \times 10^{28}$

Ion pairs

$$n = N \exp\left(-\frac{E}{2K_BT}\right)$$

$$n = 2.303 \log_{10}\left(-\frac{N}{n}\right) = \frac{E_a}{2K_BT}$$

E $= 2.303 (16.65)(2) \times (8.625 \times 10^{-5})(298)$

E $= 1.97$ eV