Defects in solids :→ Solids are formed from many small crystals however, during the process of crystallization, the defect in solids occurs due to the fast or moderate rate of formation of crystals.

Defects in general are defined as those in which there is irregularities in the arrangements of constituent particles. On the basis of irregular arrangent, the defects may be classified into two categories-

(I) Point defects (II) Line defects

Point defect can be classified into

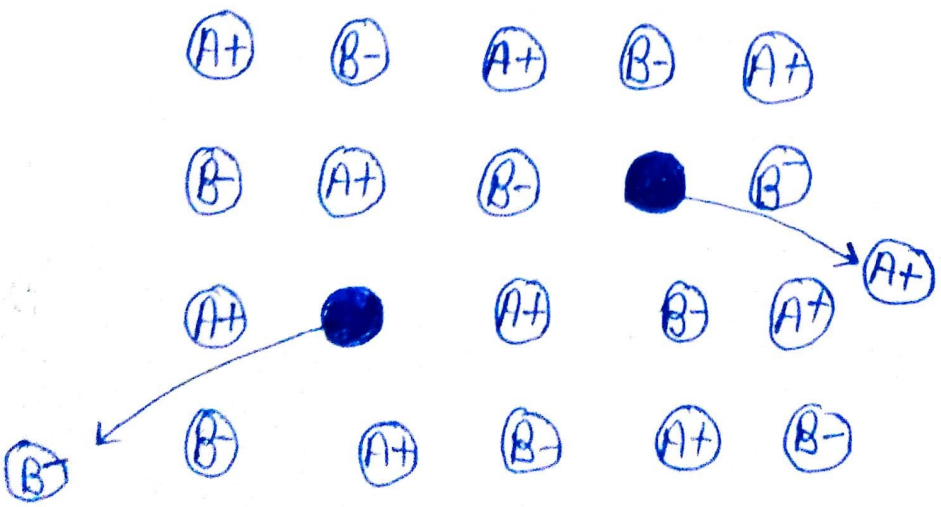
(i) Schottky defect

(ii) Frenkel defect

(iii) Vaccancy defect

(iv) Interstitial

(i) Schottky defect :→ This defect occurs due to the missing of the same number of cations and anions from the lattice site. These type of defect is shown by the substances which have high coordination number.



The substances which show Schottky defects, have the following properties:-

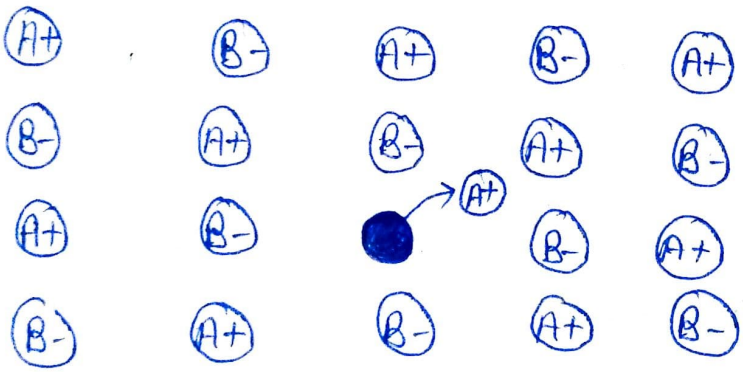
(i) High co-ordination numbers.

(ii) Small difference in size of cation & anion.

(iii) density decreases ∵ $\rho = \frac{\text{mass}\downarrow}{\text{Volum- fixed}} \Rightarrow \rho\downarrow$

(iv) Example- NaCl, KCl, CsCl.

Frenkel defect:→ In this type of defect, some cations are missing from their lattice site and occupy the interstitial site of lattice. This type of defect is shown by those substances which have low co-ordination number.



The substances which show Frenkel defects, have the following properties:-

(i) Low co-ordination number

(ii) Large difference in size of cation and anion

(iii) Exp- ZnS, AgCl, AgBr.

(iv) No change in density ∵ $\rho = \frac{\text{mass - No change}}{\text{Volume - No change}} \Rightarrow \rho$ No change

✣ Bragg's Law

Bragg's law of X-ray Diffraction: Crystal structure is explored through the diffraction of waves having a wavelength comparable with the interatomic spacing (10^{-10} m) in crystals. Radiation of longer wavelength cannot resolve the details of structure, while radiation of much shorter wavelength is diffracted through inconveniently small angles. Usually, diffraction of X-rays, neutrons and, less often, electrons is employed in the study of crystal structure. This diffraction of X-rays be crystals led to the conclusion that X-rays are electromagnetic in nature.

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 interfere constructively.***

In Fig. 1 is shown a particular set of atomic planes in a crystal, d being the interplanar spacing. Suppose a monochromatic X-ray beam is incident at a glancing angle θ. It is scattered by the atoms like A and B in random directions. Constructive interference takes place only between those scattered waves which are reflected specularly and have a path difference of $n\lambda$, where λ is the X-ray wavelength and n is an integer. The path difference for the waves reflected from adjacent planes is

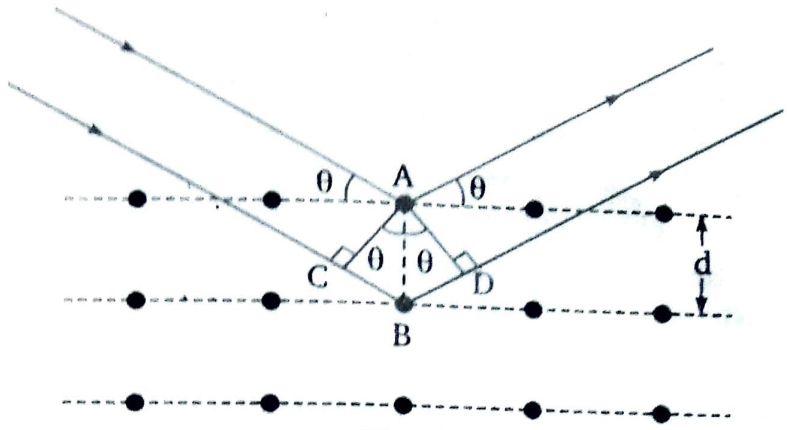


Fig. 1

$$CB + BD = d \sin\theta + d \sin\theta = 2d \sin\theta$$

For constructive interference,. we must have

$$\boxed{2d \sin\theta = n\lambda} \qquad n = 1, 2, 3, \ldots\ldots$$

This is Bragg's law. It shows that for given values of λ and d, only for certain values of θ (corresponding to $n = 1, 2, 3 \ldots\ldots$) the reflected waves add up in phase to give a strong reflected (diffracted)* beam. The images obtained in these directions are the first, second, third, ... order diffraction images.

Importance : The Bragg's law is a consequence of the periodicity of the space lattice. The arrangement of atoms (composition of the basis) associated with each lattice point determines the relative intensity of the various order n of diffraction from a given set of parallel planes.

The maximum value of sin θ is 1. Therefore, Bragg reflection can occur only for wavelengths $\lambda \leq 2d$, and d is of the order of 1 Å. This is why we cannot use visible light.

Determination of X-ray Wavelength λ : The Bragg's equation requires that θ and λ should be so related as to satisfy the equation $2d \sin\theta = n\lambda$. X-rays of wavelength λ striking a three-dimensional crystal at any angle of incidence will, in general, not be reflected. To satisfy the Bragg's equation in experiment, θ is varied until diffraction

*It is a true case of 'diffraction' because the waves penetrate into the crystal. Reflection is purely a surface phenomenon.

images appear. The value of θ is measured for a known order X-ray maximum. λ may then be calculated using equation $2d \sin \theta = n\lambda$, provided d is known.

✣ Laue Method

Laue Method : In Laue's method, a single crystal is held *stationary* in a *continuous* X-ray beam. The crystal diffracts the discrete values of λ for w[illegible] the crystal planes of spacing d and the incidence angle θ satisfy t[illegible]ragg's equation.

The experimental arrangement is shown in Fig. 5(a). A continuous (≈ 0.2 Å to 2Å) X-ray beam, well-collimated by a pinhole arrangement, is allowed to fall on the crystal. The crystal holder is adjusted to obtain proper orientation of the crystal. A flat film A is placed to receive the transmitted- diffracted beams (or a flat film B to receive the reflected-diffracted beams). The diffraction pattern is a regular one, consisting of a series of spots and is characteristic of the crystal structure. It is called the Laue pattern (Fig 5b).

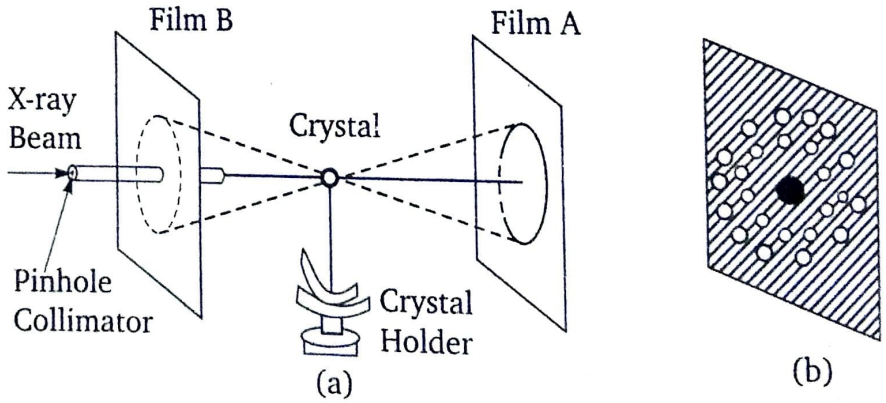


Fig. 5

Each spot in the Laue pattern corresponds to an interference maximum for a set of crystal planes satisfying the Bragg equation $2d \sin\theta = n\lambda$ for a particular wavelength selected from the (continuous) incident beam. The atomic arrangement in the crystal can, therefore be deduced from a study of the positions and intensities of the Laue spots.

The distribution of spots in the Laue pattern depends on the symmetry of the crystal and its orientation with respect to the X-ray beam. For example, if a crystal with four-fold axial symmetry is

oriented with the axis parallel to the beam, then the Laue pattern will show the four-fold symmetry, as in Fig. 5b.

Applications : The Laue method is convenient for the rapid determination of crystal orientation and symmetry which is needed for solid state experiments. It is also used to study crystalline imperfections under mechanical and thermal treatment.

Drawback : The method is, however, not used for actual crystal structure determination. This is because it is possible for several wavelengths to reflect in different orders from the same plane, so that different orders may superpose on a single spot. This would make the analysis difficult.