Diffraction of X-rays by Crystals

It is known that when light falls on an object, which is of the same size as the wavelength of light, it is diffracted. W.H Bragg and W.L.Bragg discovered that a crystal could behave as a threedimensional diffraction grating to x-rays. Thus they used x-ray for the purpose of studying the internal structure of crystals.

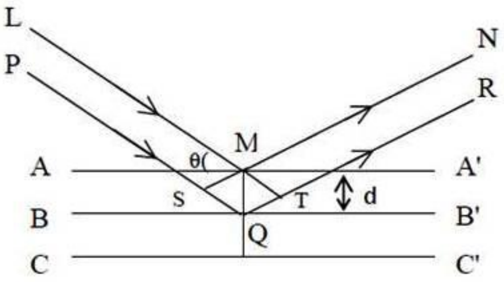
Bragg Equation The following equation is the mathematical statement of Bragg's law of x-ray diffraction

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

Where λ = the wavelength of the x-rays used; d = the interplanar distance;

n = the order of reflection; and θ = the angle of incidence.

Derivation: A beam of x-rays incident on the atoms, which constitute a plane, is diffracted in such a way as to cause either interference or reinforcement of the beam diffracted from the first or the outer plane. The whole beam behaved as if it had been reflected from the surface of the crystal. The crystal behaves as transmission grating because it contains a series of equally spaced atomic planes.



When x-rays are incident on a crystal face they penetrate into the crystal and scattered by the atoms or ions.

Consider a set of parallel and equidistant planes AA', BB', etc. in the crystal as shown in Fig.

These planes characterize the arrangement of the atoms or ions in the crystal. A parallel beam of monochromatic x-ray of wavelength λ strikes these planes at an angle of incidentθ.

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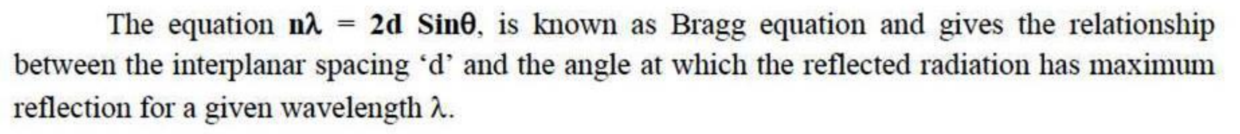
Bragg's equation Derivation:

Some of the rays will be reflected by atoms from the upper layer AA', with angle of reflection being equal to the angle of incident. When the rays reflected from the successive layers are in phase, constructive interference will occur and a bright diffraction spot would be obtained from these planes.

The condition for the constructive interference is that the path difference between the reflected rays from successive planes must be an integral multiple of wavelength.

The path difference for LMN and PQR is equal to SQ + QT, where MS and MT are perpendiculars drawn from M to PQ & QR respectively



The equation **$n\lambda = 2d\ Sin\theta$**, is known as Bragg equation and gives the relationship between the interplanar spacing 'd' and the angle at which the reflected radiation has maximum reflection for a given wavelength λ.

If $n = 1$, the order of reflection is one. If $n = 2$, the order of reflection is two and so on.

Diffraction of X-rays by Crystals

Experimental Methods of Crystal Analysis: X-ray cryatallography is used to study the crystals. Thhis is also known as Single Crystal Method

The basic classes of crystal defects are:

1. Point defects (Zero-dimensional defects)

2. Line defects (One-dimensional defects)

3. Surface defects (Two-dimensional defects)

4. Volume defects (Three-dimensional defects)

In general, point defects occur in metallic and ionic crystals.

Point defects are of following types:

(1) Vacancies

(2) Interstitial defects (Impurity)

(3) Substitutional defects

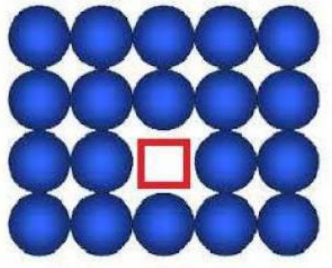
(4) Frenkel's defect (Stoichiometric defect)

(5) Schottky's defect (Stoichiometric defect)

I. Vacancies

Vacancies are simplest point defects in a crystal which refers to a missing atom at its site.

Definition: The defects due to the missing atoms at their lattice sites are called vacancies.



Vacancy (missing atom)

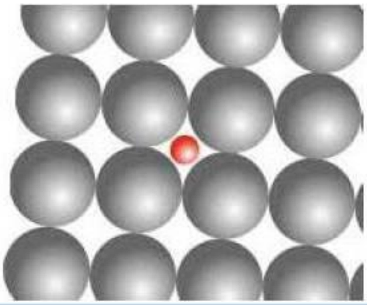
- Vacancy defects are mainly due to the imperfect packing during the formation of crystal or due to thermal vibrations of atoms at high temperature.
- At high temperature atoms are frequently and regularly change their positions leaving empty lattice sites behind their positions.

2. Interstitial defects (Impurity)

Definition: When an impurity atom tries to settle in the interstitial space between the parent atoms of the crystal without displacing, then such a defect is known as interstitial defect.

- Interstitial impurities are much smaller than the atoms in the bulk matrix.
- The formation of interstitial impurity defect is shown figure.

Formation of interstitial impurity defect is shown figure.



The number of vacancies per unit volume of the crystal depends upon temperature.

- In most cases, diffusion (mass transport by atomic motion) can only occur because of vacancies.

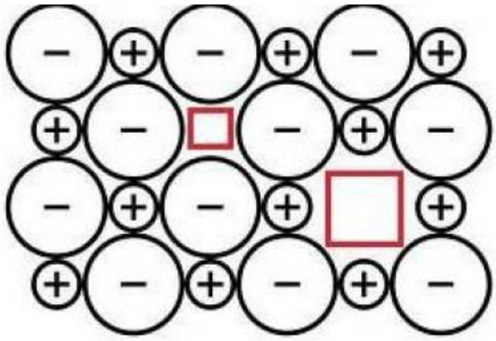
- In case of ionic crystals, there are two types of point defects related to vacancies.

They are: (A) Schottky defects

(B) Frenkel defects

3. Schottky defects

- It is a special case of vacancy defects in ionic crystals.
- Definition: When a pair of vacancies are produced at one positive ion site and one negative ion site due to the absence of positive and negative ions, this type of defect is called the Schottky defect.
- In ionic crystals, there are two types of possible vacancies, namely cation (+ve ion) vacancies and anion (−ve ion) vacancies
- When a +ve ion from the interior of the lattice moves out of the crystal to its surface, then a +ve vacancy is formed at its site.
- The formation of +ve ion vacancy results in excess negative charge inside the crystal.
- To maintain charge neutrality, a −ve ion moves to the crystal surface creating a −ve ion vacancy at its site.



4. Frenkel defects

It is special case of vacancy and interstitial defects in ionic crystals.

Definition: When an ion displaced from a regular location in the crystal lattice to an interstitial location in the crystal lattice , then this type of defect is called the Frenkel defect.

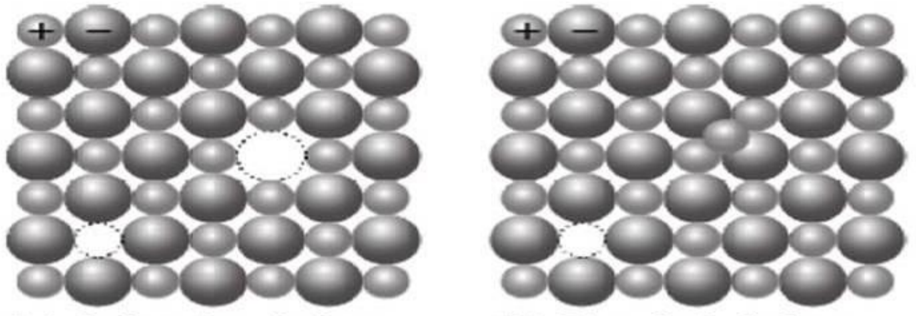
Consider the periodic distribution of +ve and −ve ions in an ionic crystal.

- When a +ve ion leave its site and settles in the interstitial position then it creates a vacancy in its position.

Thus, a vacancy and interstitial defects are created. This pair of defects is known as Frankel defect.

In case of Frankel defect also charge neutrality is maintained.

- AgBr, AgCl, ZnS etc., exhibits Frankel defects
- The formation of Frankel defects is described in the following figure.



(a) Schottky defect (b) Frenkel defect

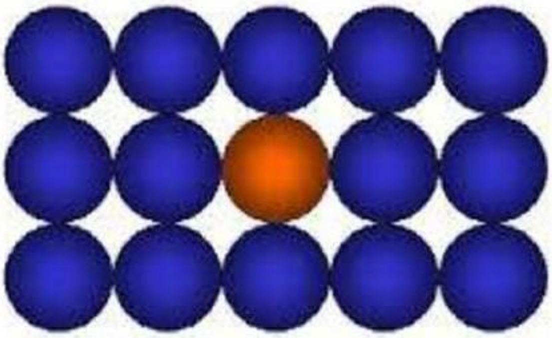
5. Substitutional defects

Definition: When an impurity atom occupies the one of the positions of the parent atoms of the crystal, then such a defect is known as substitutional defect.

- A substitutional impurity atom is an atom of a different type than the bulk atoms.
- Usually, substitutional atoms are close in size (within approximately 15%) to the bulk atom.

The formation of substitutional impurity defect is shown figure.

- Example: Zinc atoms are substitutional impurity atoms that are added to Copper to make Brass.



COLOUR CENTERS

Color centers are point defects or point defect clusters associated with trapped electrons or holes in normally transparent materials.

These centers cause the solid to become colored when the electronic ground state of the defect is excited to higher energy states by the absorption of visible light.

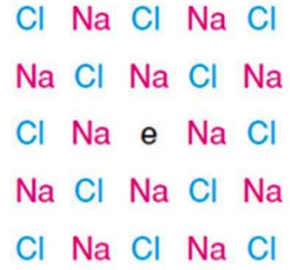
Its name comes from the German word "Farbe" which means colour and F centres are also named as "Farbzentren".

These centres are generally generated by heating a crystal in an excess of alkali vapour or by irradiating the crystal by x-rays.

If NaCl crystal is heated in an atmosphere of Na vapours, excess alkali atons (i.e. Na) are then added to the crystal. Each of the excess atoms absorbed from the vapour may then ionise to a positive ion i.e. Na^+ and an electron. Corresponding to the total umber of Na^+ ions, an equal number of negative vacancies will be created to keep the crystal electrically neutral. The extra electrons from the ionised Na atoms are injected into the conduction band where they do ot remain for a long time and are soon captured by the negative ion vacancies. Since the negative ion vacancy represents a net posiitve charge within the crystal, it attracts the electron to itself. Thus negative ion vacabcy captures an excess electron. This vacancy with trapped electron is called F-centre. These electrons are responsible for absorption of particular wavelength and reflect the complimentary colour.

Eg. NaCl -------- Yellow

KCl----------Violet ; CsCl---------Pink



Cl	Na	Cl	Na	Cl
Na	Cl	Na	Cl	Na
Cl	Na	e	Na	Cl
Na	Cl	Na	Cl	Na
Cl	Na	Cl	Na	Cl