The Solid State

Solids are broadly classified into two groups —

(i) Crystalline solids

(ii) Amorphous solids.

Difference between crystalline and amorphous solids:

1. A crystalline solid has a definite geometry due to regular arrangement of particles in three-dimensional space.

   An amorphous solid doesn't have a definite geometry because it doesn't have an orderly arrangement of its particles in three-dimensional space.
2. A crystallographic solid has a sharp melting point, on the contrary an amorphous solid melts over a range of temperature.
3. An amorphous solid's properties such as electrical conductivity, thermal conductivity, mechanical strength etc. are the same in all directions. Amorphous substances are, therefore, said to be isotropic.

   Crystalline solids, on the other hand, are anisotropic, their physical properties are different in different directions.

Classification of crystalline solids based on the nature of chemical bonding and intermolecular forces present in the crystal:

(1) *Ionic crystals*: It consists of an array of positive and negative ions and are held together by the electrostatic attraction between oppositely charged ions, e.g., NaCl, $CaCl_2$, MgO and KNO_3.

(ii) *Metallic crystals*: These are composed of bonded metal atoms; some of the valence electrons are delocalised over the entire metal and held the crystal together, e.g., Na, Cu, Fe and various alloys.

(iii) *Covalent crystals*: These consist of an infinite network of atoms held together by polar or non-polar covalent bonds, no individual molecule being present, e.g., carbon in the form of graphite and diamond, Si, SiO_2 and SiC. In ionic, metallic and three-dimensional covalent crystal it is not possible to identify individual molecules, the entire crystal is a giant molecule.

(iv) *Molecular crystal*: These are composed of individual molecules, the atoms within each molecule are held together by covalent bonds. Relatively weak intermolecular forces hold the molecule together in the crystal, e.g., Ar(s), CO_2(s), H_2O(s), I_2(s) etc.

Crystal Structures

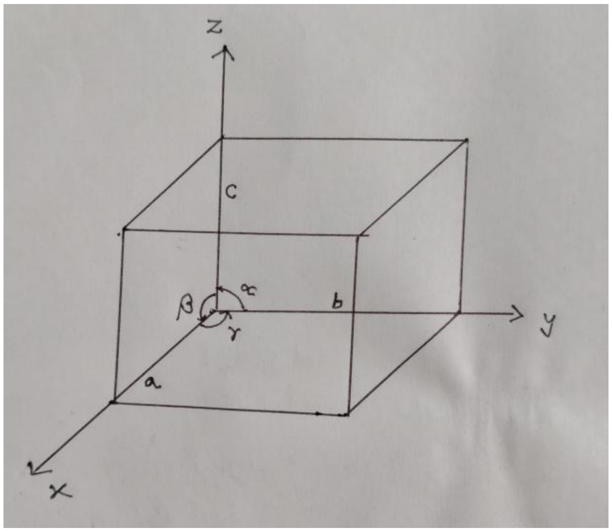
Interfacial angle: Crystals are bound by surfaces which are usually planar. These planar surfaces are called faces. The angle between any two faces in a cryptal is called interfacial angle.

Law of constancy of interfacial angles: The angles between the corresponding faces of various crystals of the same substance are constant. This law is also known as the first law of crystallography.

The basis: A crystal contains a structural unit that is repeated in three dimensions to generate the crystal structure. Such a structural unit is called the *basis* or *motif*. The basis may be a single atom or molecule or it may be a small group of atoms, molecules or ions. Each basis has the same structure. Basis has the same stoichiometric composition as the crystal. For NaCl, the basis consists of one Na^+ ion and one Cl^- ion.

The space lattice or crystal lattice: A space lattice or crystal lattice is the pattern formed by points representing the locations of the repeating structural units (basis) in three-dimensional space. Each point of the space lattice has the same environment. The crystal structure can be generated by placing a basis on each lattice points.

Unit cell: The simplest array of points from which a crystal can be created is called a unit cell. The unit cell is an imaginary parallelopiped from which the entire crystal may be constructed by purely translational repetition. The edge lengths of a unit cell are denoted by a, b, c and the angles between the edges are denoted by α, β, γ where α is the angle between the edges b and c, β is the angle between c and a and γ is the angle between a and b.



The seven crystal systems:

Unit cells are classified into seven crystal systems on the basis of rotational symmetry elements they possess. The following table lists the essential symmetries and other unit cell parameters. The essential symmetries are the symmetry elements that must be present for the unit cell to belong to a particular crystal system.

Sl No	System	Sides	Angle	Essential symmetries
1	**Cubic**	$a=b=c$	$\alpha=\beta=\gamma=90°$	Four C_3 axes
2	**Tetragonal**	$a=b\neq c$	$\alpha=\beta=\gamma=90°$	One C_4 axis
3	**Orthorhombic**	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$	Three perpendicular C_2 axes
4	**Rhombohedral**	$a=b=c$	$\alpha=\beta=\gamma\neq 90°$	One C_7 axis
5	**Hexagonal**	$a=b\neq c$	$\alpha=\beta=90°$, $\gamma=120°$	One C_6 axis
6	**Monoclinic**	$a\neq b\neq c$	$\alpha=\gamma=90°$, $\beta\neq 90°$	One C_2 axis
7	**Triclinic**	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$	None

Bravais latices: There are only 14 distinct crystal lattices in three dimensions. These are called Bravais lattices.

- It is conventional to depict these lattices by (i) primitive unit cells, in some cases and (ii) non-primitive unit cells in others.
- Primitive unit cells (P) are those with lattice points only at the corners.
- A body-centered unit cell (I) also has a lattice point at its centre in addition to those at the corners.
- A face-centered unit cell (F) has lattice points at its corners and also at the centres of its six faces.
- A side-centered unit cell (A, B or C) has lattice points at its corners and at the centres of its opposite faces.

Problem: Calculate the number of atoms per unit cell in a (i) simple (primitive) cubic lattice (ii) face-centred cubic (*fcc*) lattice. (iii) body-centred cubic (*bcc*) lattice.

Lattice planes: The points in a space lattice may be arranged in a large number of ways in a series of parallel and equidistant planes known as lattice planes.

Law of rational indices: The intercepts of any plane along the three crystallographic axes are either equal to the ratio of the unit cell intercepts a, b, c or some integral multiples of them; i.e., *la*, *mb* and *nc* where *l*, *m* and *n* are small whole numbers.

Weiss indices: The coefficients of a, *b* and *c* in the intercepts of any plane along the three crystallographic axes are called Weiss indices.

Miller indices: The reciprocal of Weiss indices are called Miller indices. It's generally represented by (*hkl*).

Interplanar spacing: In general, the interplanar spacing ($d_{h\,k\,l}$) between the planes (*hkl*) in a cubic lattice is given by

$$\boldsymbol{d_{hkl}} = \frac{\boldsymbol{a}}{\sqrt{\boldsymbol{h^2} + \boldsymbol{k^2} + \boldsymbol{l^2}}}$$

where, *a* is the side of the cube.

Problem: The planes in a crystalline solid intercept the crystal axes at (2a, b, c); (−a, b, c); (a,2b,3c) and (−*a*, *b*, ∞). Determine the units and Miller indices for those planes.

Solution: The unit cell intercepts are *a*,*b*,*c*.

Intercepts	2a, b, c	−a, b, c	a,2b,3c	−*a*, *b*, ∞
Weiss indices	2 1 1	−1 1 1	1 2 3	−1 1 ∞
Reciprocal	½ 1 1	−1 1 1	1 ½ ⅓	−1 1 0
Clear fraction	1 2 2	−1 1 1	6 3 2	−1 1 0
Miller indices	(122)	$(\bar{1}11)$	(632)	$(\bar{1}10)$

Problem: Draw the (100), (110) and (111) planes in a simple cubic crystal.

Problem: Draw the (200), (220) and (111) planes in face-centred cubic lattice.

Problem: Calculate the interplanar spacing between two successive (i) (200) planes (ii) (220) planes and (iii) (111) planes in a face-centred cubic lattice.

Problem: Calculate the interplanar spacing between two successive (i) (100) planes (ii) (110) planes and (iii) (111) planes in a simple cubic lattice.

Solution:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}}$$

$$= a$$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}}$$

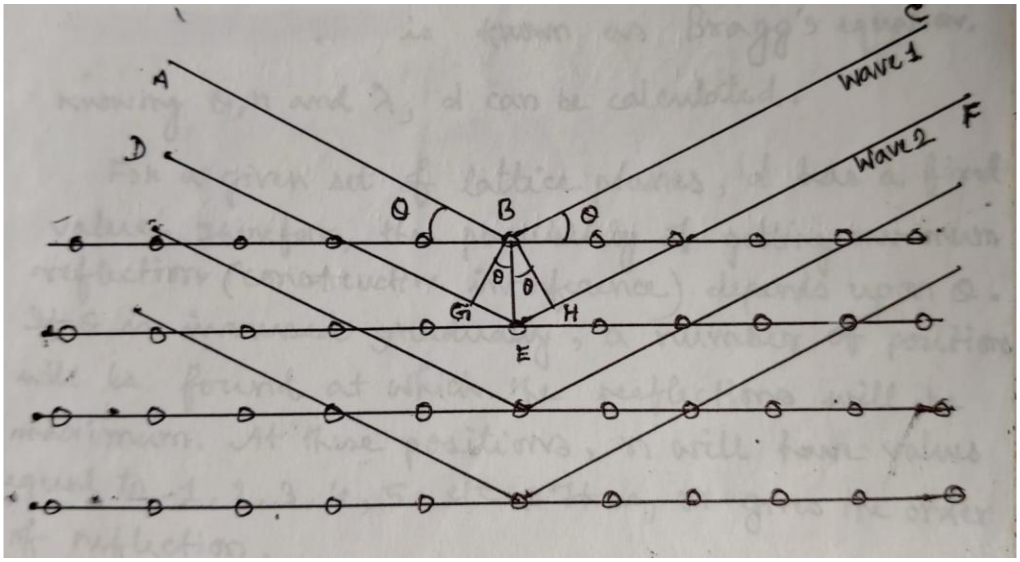
$$= \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}}$$

$$= \frac{a}{\sqrt{3}}$$

Diffraction of X-rays by crystals: In 1912, Max von Laue predicted that if a beam of non-homogeneous X-rays were passed through a crystal, a diffraction pattern would be observed. A crystal can act like a 3-dimensional diffraction grating because the distances between particles in a crystal are of the same order of magnitude ($\approx 10^{-8}$ cm) as the wavelength of X-rays.

Bragg Equation: When X-rays are incident on a crystal face, they penetrate into the crystal and suffer reflections on striking the atoms in successive planes:



If the reflected waves from successive layers are out of phase, then due to the destructive interference, no diffraction will be observed. If the reflected waves are in phase, then due to constructive interference, diffraction patterns will be observed.

Let θ be the incident angle of monochromatic X-rays of wavelengths λ with the parallel equidistant planes of atoms with interplanar spacing equal to *d*. The waves are in phase before striking the planes. Let us consider *wave1* and *wave2*. After the reflection, the two waves will be in phase provided the extra distance travelled by *wave2* is an integral multiple of wavelength λ. From the figure,

$$AB=DG,\ BC=HF,\ GE=EH$$

$$GE=EH= d\sin\theta$$

So, extra distance travelled by *wave2* = GE+EH= $2d\sin\theta$

Thus, in order to have *wave1* and *wave2* in phase, we must have

$$2d\sin\theta = n\lambda, \qquad n = 1,2,3,\ldots\ldots\ldots.$$

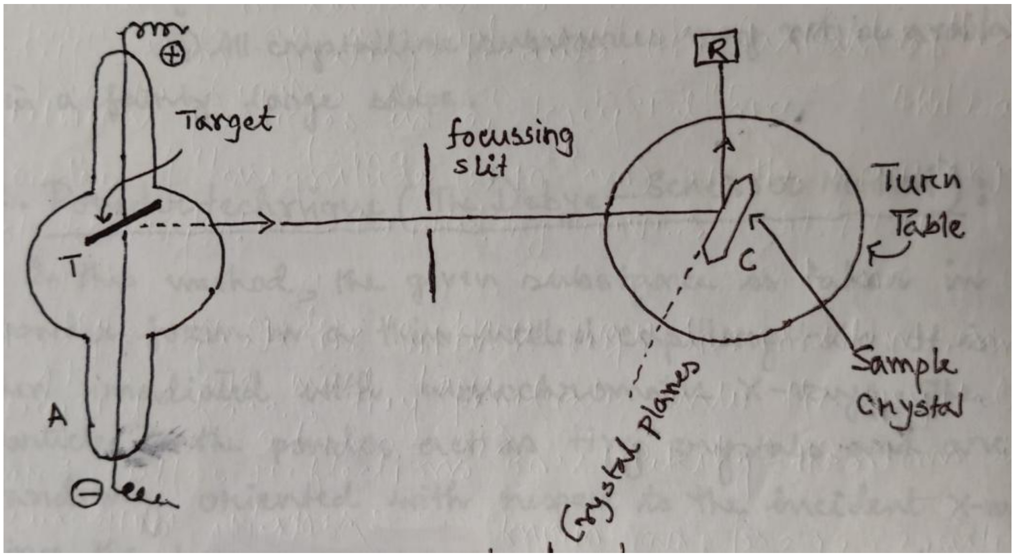
This equation is known as Bragg's equation. Knowing θ, *n* and λ, *d* can be calculated.

For a given set of lattice planes, *d* has a fixed value. Therefore, the possibility of getting maximum reflection (constructive interference) depends upon θ. If θ is increased gradually, a number of positions will be found at which the reflections will be maximum. At these positions, *n* will have values equal to 1,2,3,4,5, etc. Thus, *n* gives the order of reflection.

Scattering ability of an atom: The atom with the greater number of electrons has the greater scattering power than the one with lesser number of electrons. It is because of this reason that the scattering ability of hydrogen atom is very small and thus whatever effect it produces is overshadowed by the effect of neighbouring atoms which contain larger number of electrons. Thus, the positions of H atoms cannot be deduced from X-ray diffraction. Similarly, from X-ray diffraction, it is not possible to distinguish between atoms which differ only by the possession of additional electron e.g. C and N are indistinguishable.

X-ray diffraction techniques:

1. **Bragg method** or **Rotating crystal technique** or **Single crystal technique:**
   This technique uses the Bragg X-ray diffractometer:



The X-rays are generated in tube A by bombarding cathode rays on a target T. Generated X-rays are passed through a series of slits and filters in order to get a sharp monochromatic beam. It is then directed to strike the face of a crystal C placed on a graduated turn-table. The crystal is rotated gradually by means of the turn-table so as to increase the glancing angle at which the X-rays are incident at the exposed face of the crystal. The intensities of the reflected rays are measured on a recording device R, such as photographic plate or an ionisation chamber. The angles for which reflections are maximum give the value of θ. The process is carried out for each plane of the crystal. The lowest angle at which the maximum reflection occurs corresponds to n=1. This is called the first order reflection. The next higher angle at which the maximum reflection occurs again, corresponds to n=2. This is the second order reflection, and so on.

Limitations:

(i) In this method one has to use a fairly large crystal with flat faces carefully oriented in a number of specific directions. This is very time consuming.

(ii) All crystalline substances may not be available in a fairly large shape.

Problem: A first order reflection from the (111) planes of a cubic crystal was observed at a glancing angle of 11.2° when Cu K_α X-rays of wavelength 154 pm were used. What is the length of the side of the unit cell?

Solution: Applying Bragg's equation: $2d_{111}\sin\theta = n\lambda$

Considering first order reflection: n=1

$$2d_{111}\sin\theta = \lambda$$

$$\Rightarrow d_{111} = \frac{\lambda}{2\sin\theta}$$

The separation of the (111) planes of a cubic lattice of side a is given by

$$d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}}$$

$$= \frac{a}{\sqrt{3}}$$

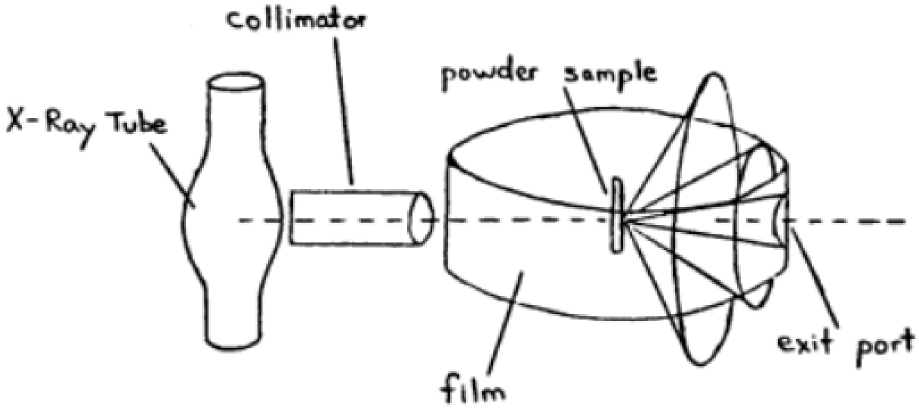
Therefore, $a = \frac{3^{1/2}\lambda}{2\sin\theta} = \frac{3^{\frac{1}{2}}(154\,pm)}{2\sin 11.2^0} = \frac{1.732\times(154\,pm)}{2\times 0.194} = 687$ pm

Problem: A certain solid crystallizes in *bcc* lattice. First order X-ray ($\lambda = 0.154\,nm$) reflection maximum from a set of (200) planes was observed at an angle of 16°6΄. Calculate the edge length of the unit cell.

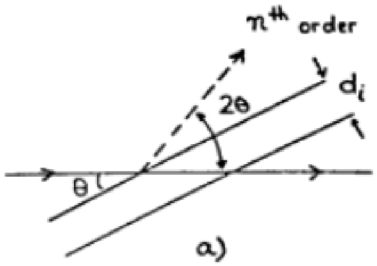
Problem: The glancing angle of a Bragg reflection from a set of crystal planes separated by 99.3 pm is 20.85°. Calculate the wavelength of the X-ray.

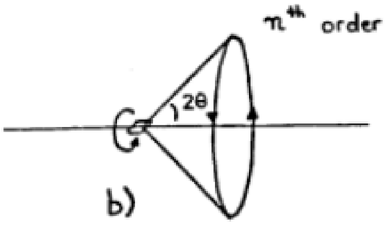
2. Powder technique (The Debye-Scherrer Method):

In this method, the given substance is taken in powder form in a thin-walled capillary tube. It is then irradiated with monochromatic X-rays. The particles in the powder act as tiny crystals and are randomly oriented with respect to the incident X-rays. Since, the powder contains a very large number of particles, it is possible that some particles will have their (100) planes correctly oriented so that the Bragg equation is satisfied. Some others will have their (110) planes properly oriented, while there may be some with their (111) planes properly oriented and so on. Thus, the powder provides all types of lattice planes for the reflection of X-rays. The diffracted X-rays strike a strip of photographic film arranged in the form of a circular arc.

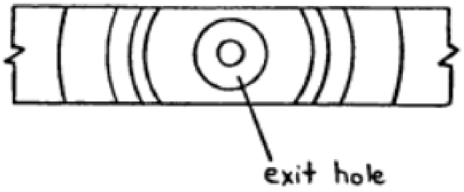


Let us consider a set of parallel planes making an angle θ with the incident beam of X-rays as shown:





Since, in the powder, a large number of crystals with all types of orientations are available, the diffracted beam will travel over the surface of a cone and they will leave impressions on the film.



Diffraction Pattern on Film After Exposure

Diffraction pattern of a cubic system:

While dealing with X-ray diffraction, it is more convenient to express higher order reflections in terms of the first order reflection from planes of higher (*hkl*):

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

$$\Rightarrow \lambda = 2\left(\frac{d}{n}\right)\sin\theta$$

$$\Rightarrow \lambda = 2d_{hkl}\sin\theta_{hkl} \qquad \text{………………………(1)}$$

For a cubic crystal spacing between the *(hkl)* planes is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \qquad \text{………………………(2)}$$

From (1) and (2),

$$\lambda = 2\times\frac{a}{\sqrt{h^2+k^2+l^2}}\sin\theta_{hkl}$$

$$\Rightarrow \sin\theta_{hkl} = \frac{\lambda}{2a}\times\sqrt{h^2+k^2+l^2}$$

$$\Rightarrow \sin^2\theta_{hkl} = \frac{\lambda^2}{4a^2}\times(h^2+k^2+l^2)$$

$$\Rightarrow \sin^2\theta_{hkl} = K(h^2+k^2+l^2) \qquad \text{……………………(3)}$$

where $K = \frac{\lambda^2}{4a^2}$

K is a constant for a given cubic crystal and for a given wave length λ of X-rays.

Theoretical prediction of diffraction pattern:

1. **Primitive cubic lattice:**

   Using equations

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

and $$\sin^2 \theta_{hkl} = K(h^2 + k^2 + l^2)$$

by assigning consecutive integral values (0, 1, 2, ⋯) to *hkl*, we can calculate a series of values d_{hkl} and $\sin^2 \theta_{hkl}$:

hkl	100	110	111	200	210	211	220	221 300	310	311	222	320
d_{hkl}	a	$\frac{a}{\sqrt{2}}$	$\frac{a}{\sqrt{3}}$	$\frac{a}{2}$	$\frac{a}{\sqrt{5}}$	$\frac{a}{\sqrt{6}}$	$\frac{a}{2\sqrt{2}}$	$\frac{a}{3}$	$\frac{a}{\sqrt{10}}$	$\frac{a}{\sqrt{11}}$	$\frac{a}{\sqrt{12}}$	$\frac{a}{\sqrt{13}}$
$\sin^2 \theta$	K	2K	3K	4K	5K	6K	8K	9K	10K	11K	12K	13K

$\sin^2 \theta$ can't be 7K because there is no way in which the integer 7 can be written in the form $(h^2 + k^2 + l^2)$. This is also true of 15, 23, 28, etc. Thus, diffraction pattern lines will be observed as shown below:

100	110	111	200	210	211		220	221 300	310	311	222	320	321		400
1K	2K	3K	4K	5K	6K	7K	8K	9K	10K	11K	12K	13K	14K	15K	16K
|	|	|	|	|	|		|	|	|	|	|	|	|		|

Diffraction pattern for a primitive cubic lattice consists of a set of equally spaced six lines followed by an extinction and then another series of seven lines with the 15th missing.

2. **Body-centred cubic lattices:**

In bcc lattice, (200) planes lie halfway between adjacent (100) planes. The X-rays scattered at the Bragg angle for reflection from the (100) planes will be out of phase with those scattered by the (200) planes. As a result, destructive interference will occur, and the diffraction line corresponding to the (100) planes will be absent. On the other hand, at the Bragg angle for reflections from the (200) planes, all scattered X-rays will be in phase and thus a strong diffraction line will be observed. This way, it can be shown for *bcc* lattice that all diffraction lines for which (h + k + l) is an odd integer must be absent:

hkl	100	110	111	200	210	211	220	221 300	310	311	222	320
d_{hkl}		$\frac{a}{\sqrt{2}}$	$\frac{a}{\sqrt{3}}$	$\frac{a}{2}$		$\frac{a}{\sqrt{6}}$	$\frac{a}{2\sqrt{2}}$		$\frac{a}{\sqrt{10}}$		$\frac{a}{\sqrt{12}}$	
$\sin^2\theta$		2K	2K	4K		6K	8K		10K		12K	
lines		|	|	|		|	|		|		|	

3) Face centred cubic lattice:

In *fcc* lattice, only half the atoms lie in the (100) and the (110) planes. Thus, it is expected that the diffraction from these planes will be absent. On the other hand, all atoms lie in (111), (200) and (220) planes and thus the corresponding diffraction lines will be observed. In general, for *fcc* lattice, the strong diffraction lines are observed only from those planes for which the values of *h*, *k*, and *l* are either all even or all odd.

hkl	100	110	111	200	210	211	220	221 300	310	311	222	320
d_{hkl}			$\frac{a}{\sqrt{3}}$	$\frac{a}{2}$			$\frac{a}{2\sqrt{2}}$			$\frac{a}{\sqrt{11}}$	$\frac{a}{\sqrt{12}}$	
$\sin^2\theta$			3K	4K			8K			11K	12K	
lines			|	|			|			|	|	

The difference between the three diffraction patterns clearly help in distinguishing between the three types of cubic lattices. In the X-ray diffraction studies, the crystallographer searches for missing reflections. It should be noted that the spacing between the lines of a primitive cubic system is equal to *K* and there are gaps after the 6th, 14th and 22nd, etc., lines. On the other hand, the spacing between lines of a body-centred cubic system is equal to 2*K*. Thus, the number of lines obtained in the diffraction pattern can help in distinguishing between these systems. After identification of the lattice type, it is possible to assign each line with the correct values of the Miller indices h, k, l. From the measurement of θ for any one of these lines, the edge length **a** of the cube can be computed from:

$$a = \frac{\lambda}{2\sin^2\theta_{hkl}}\left(h^2 + k^2 + l^2\right)^{1/2}$$

If the indexing of the lines has been done correctly, the same value of **a** will be obtained from all values of $\sin\theta_{hkl}$.

Defects in Crystals

Hypothetically, solids are assumed to be perfect. In reality, all crystals contain defects, or imperfections of structure or composition. Defects in solids influence properties such as mechanical strength, electrical conductivity, corrosion, and chemical reactivity.

Types of defects: There are of two types —

1. **Point defects**: These defects occur at single sites. Point defects are random errors on a periodic lattice. Point defects may arise in two ways:
    - (i) they arise due to the absence of an atom at its usual site (a vacancy defect)
    - (ii) due to the presence of an atom at a site that is not ordinarily occupied (an interstitial defect).
2. **Extended defects** (line defects): Extended defects are ordered in one, two, or three dimensions. Extended defects involve various inequalities in the stretching of planes.

Defects are also classified as —

(a) **Intrinsic defects** — These defects occur due to thermodynamic reasons.

All solids have a thermodynamic tendency to acquire point defects because defects introduce disorder into an otherwise perfect structure and hence increase its entropy. The Gibbs free energy ($G = H - TS$), of a solid with defects has contributions from the enthalpy and entropy of the sample. Defects contribute a negative term (through entropy) to the Gibbs free energy of the solid. The formation of defects is usually endothermic (H is higher in the presence of defects). Process of formation of defects are spontaneous when the system's free energy becomes negative. It is found that Gibbs free energy of the crystal $G=H-TS$ has a minimum at a nonzero defect concentration, and hence the defect formation is spontaneous. Moreover, as the temperature is varied, the minimum in Gibbs free energy moves to higher defect concentrations, and so more defects are present at equilibrium at higher temperatures than at low.

(b) **Extrinsic defects** — These defects are not required by thermodynamics and can often be controlled by purification or by changing the synthetic conditions.

Intrinsic Point Defects:

In the 1950s, two solid-state physicists — Schottky in Germany and Frenkel in Russia — identified two specific types of point defects in solids.

(a) Schottky defect: A Schottky defect is a vacancy in an otherwise perfect lattice. That is, it is a point defect in which an atom or ion is missing from its normal site in the lattice. The overall stoichiometry of a solid is not usually affected by the presence of Schottky defects because there are equal numbers of vacancies at *cation* and anion sites so as to preserve charge balance. The creation of a Schottky defect is accompanied by the creation of an equivalent number of new lattice sites or removal of the ions to the gas phase from the lattice. Some *d*-metal complexes, sulfides, and hydrides have very high concentrations of Schottky defects. Schottky defects are commonly encountered when

(i) the metal ions can readily assume more than one oxidation state,
(ii) co-ordination number is high
(iii) ions (cations and anions) are almost of similar sizes.

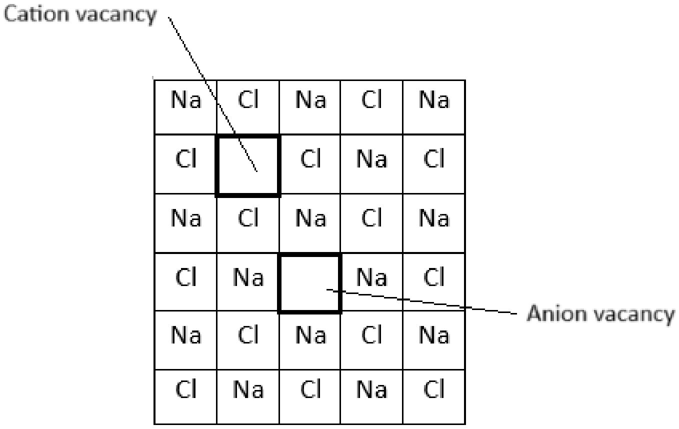


Fig.: Schottky defect

Some examples of solids showing Schottky defects are NaCl, KCl, KBr, CsCl and AgBr

(b) Frenkel Defects: A Frenkel defect is a point defect in which an atom or ion has been displaced into an interstitial site, e.g., in AgCl having rock-salt structure, a small number of Ag^+ ions reside in normally unoccupied tetrahedral sites. The stoichiometry of the compound is unchanged when a Frenkel defect forms. Frenkel defects are most often encountered

(i) in the more open structures (such as wurtzite and sphalerite) where the coordination numbers are low
(ii) anions are much larger in size than cations so that the open structure provides sites that can accommodate interstitial atoms.
(iii) Some examples of solids showing Schottky defects are NaCl, KCl, KBr, CsCl and AgBr

Some examples of solids showing Frenkel defects are AgCl, AgBr, AgI and ZnS.

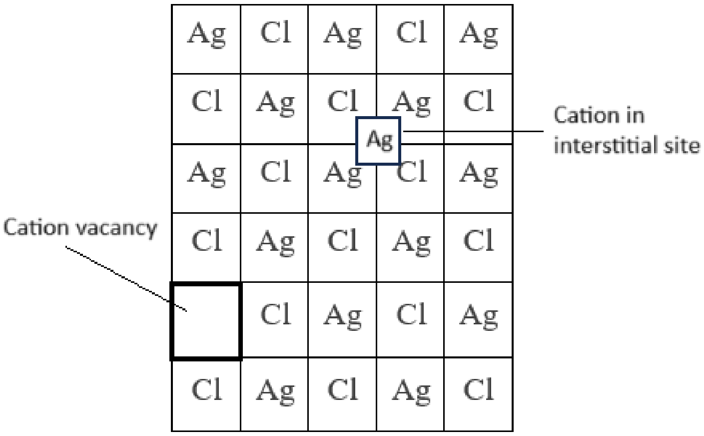


Fig.: Frenkel defect

Consequences of Schottky and Frenkel defects:

- A consequence of these defects is that a crystalline solid that has defects may conduct electricity to a small extent. Electrical conductivity in a chemically pure, stoichiometric semiconductor is called 'intrinsic semiconduction'. This occurs by an ionic mechanism. An ion moves to a 'hole' from its own lattice site; a new hole is thus created. In this way a 'hole' migrates across a crystal. This is equivalent to moving a charge in the opposite direction. Crystals with Frenkel defects have only one type of hole, but crystals containing Schottky defects have holes from both positive and negative ions, and conduction may arise by using either one type of hole or both types.
- Defects, when present in large numbers, may affect the density of a solid. Significant number of Schottky defects, as vacancies, will lead to a decrease in density. Frenkel defects have little effect on density as they involve displaced atoms or ions, leaving the number of species in the unit cell unchanged.

Q. What type of intrinsic defect would you expect to find in (a) MgO and (b) CdTe?

Answers: The type of defect that is formed depends on factors such as the coordination numbers and the level of covalency in the bonding, with high coordination numbers and ionic bonding favoring Schottky defect and low coordination and partial covalency in the bonding favoring Frenkel defects. (a) MgO has the rock-salt structure and ionic bonding in this compound generally favors Schottky defects. (b) CdTe adopts the wurtzite structure with 4:4 coordination favoring Frenkel defects.

Extrinsic Point defects:

Impurity defects:

Extrinsic defects are defects introduced into a solid as a result of doping with an impurity atom. Extrinsic defects are inevitable because perfect purity is unattainable in practice in crystals of any significant size. Extrinsic defects are commonly seen in naturally occurring minerals. The incorporation of low levels of Cr into Al_2O_3 structure produces the gemstone *Ruby*, whereas replacement of some Al by Fe and Ti results in the blue gemstone *Sapphire*. The substituting species normally has a similar atomic or ionic radius to the species which it replaces. Cr^{3+} in ruby has a similar ionic radius to Al.

Impurities can also be introduced into a solid intentionally by doping one material with another. A dopant is a small level of an element that replaces another in a structure; e.g., introduction of As into Si to modify the latter's semiconducting properties. In the ionic substance ZrO_2, the introduction of Ca^{2+} dopant ions in place of Zr^{4+} ions is accompanied by the formation of an O^{2-} ion vacancy to maintain charge neutrality. The induced vacancies allow oxide ions to migrate through the structure, increasing the ionic conductivity of the solid.

Metal excess defects:

This may occur in two different ways:

(a) **F-Centres**: A negative ion may be absent from its lattice site, leaving a 'hole' which is occupied by an electron, thereby maintaining the electrical balance. When compounds such as NaCl, KCl, LiH or δ-TiO are heated with excess of their constituent metal vapours, or treated with high energy radiation, they become deficient in the negative ions and their formulae may be represented by $AX_{1-\delta}$ where δ is a small fraction. For example, when crystal of NaCl are heated in an atmosphere of sodium vapour, the excess of sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by the loss of electrons by sodium atoms to form Na^+ ions. The electrons, thus produced by the ionisation of the sodium atoms diffuse into the crystal and get trapped at the anion vacancies. The electrons trapped in anion vacancies are referred to as *F-centres*. They impart yellow colours to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. The material resulting from exposure to Na vapour may be considered nonstoichiometric compound, $Na_{1+\delta}$ Cl.

(b) **Interstitial ions and electrons:** Metal excess defects also occur when an extra positive ion occupies an interstitial position in the lattice, and electrical neutrality is maintained by the inclusion of an interstitial electron. Their composition may be expressed by a general formula $A_{1+\delta}$ X. Examples include ZnO, CdO, Fe_2O_3 and Cr_2O_3.

ZnO is white in colour at room temperature. On heating it loses oxygen reversibly at high temperatures and turns yellow in colour:

$$ZnO \overset{\Delta}{\rightarrow} Zn^{2+} + \frac{1}{2} O_2 + 2e^-$$

The excess Zn^{2+} ions are trapped in interstitial sites and equal number of electrons are trapped in the neighborhood to balance the electrical charge. These extra electrons can be subsequently excited by absorption of visible light which imparts a yellow colour to the oxide when hot. These electrons give rise to enhanced electrical conductivity.

Metal deficiency defects: Metal deficiency defect can occur due to **absence of positive ions.** If a positive ion is absent from its lattice site, the charges can be balanced by an adjacent metal ion having an extra positive charge. e.g., FeO, NiO, δ-TiO, FeS and CuI.

In case of iron pyrites (FeS), if an Fe^{2+} is missing from its lattice site, then there must be two Fe^{3+} ions somewhere in the lattice to balance electrical charges. Therefore, the crystal contains Fe^{2+} and Fe^{3+} ions. Iron pyrite is an example of a non-stoichiometric compound with metal deficiency, which can be represented by $Fe_{1-\delta}$ S. Crystals with metal deficiency defects are semiconductors. Let us suppose that the lattice contains A^+ and A^{2+} metal ions. If an electron 'hops' from an A^+ ion to A^{2+}, the original A^+ becomes a new A^{2+}. There has been an apparent movement of A^{2+} with a series of similar 'hops', an excess electron may be transferred in one direction across the structure, and at the same time the positive hole migrates in the opposite direction across the structure. This is called *p*-type semiconduction.

Questions:

- State the law of constancy of interfacial angle.
- State the law of rational indices.
- Derive the Bragg equation for the diffraction of X-rays by crystals.
- Discuss the Bragg method or Rotating crystal technique or Single crystal technique for the determination of crystal structure.
- Discuss the Powder technique (The Debye-Scherrer Method) for the determination of crystal structure.
- Theoretically predict the X-diffraction pattern of a
    - (i) primitive cubic lattice
    - (ii) body-centred cubic lattice
    - (iii) face-centred cubic lattice
- What are Schottky defects? In what type of solids Schottky defects are encountered? Write consequences of Schottky defect.
- What are Frenkel defects? In what type of solids Frenkel defects are encountered? Write consequences of Frenkel defects.
- Write differences between Schottky defect and Frenkel defects.