

# The solid state. -----Dr. Savita Desai.

## Syllabus:

### Unit 8. The solid state. [10]

#### 8.1 Introduction

Space lattice, lattice sites, Lattice planes, Unit cell.

8.2 Laws of crystallography : (i) Law of constancy of interfacial angles

(ii) Law of rational indices (iii) Law of crystal symmetry.

14

8.3 Weiss indices and Miller indices.

8.4 Cubic lattice and types of cubic lattice, planes or faces of a simple cubic system, spacing of lattice planes.

8.5 Diffraction of X-rays, Derivation of Bragg's equation.

8.6 Determination of crystal structure of NaCl and KCl on the basis of Bragg's equation.

#### 8.7 Numerical problems.

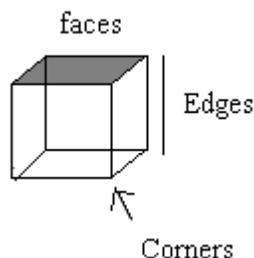
##### Introduction:

Crystallography is a branch of science which deals with the geometry, properties and structure of crystals. The study of crystals has two aspects: The examination of the external form and the elucidation of the internal structure.

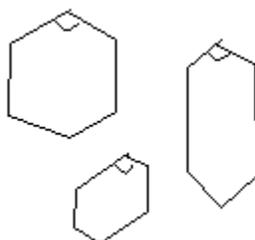
Laws of crystallography:

1. The law of constancy of interfacial angles.
2. The law of rational indices.
3. The law of crystal symmetry.

To understand these laws one must know the terms: faces, edges, corners of a crystal which can be explained by following fig.

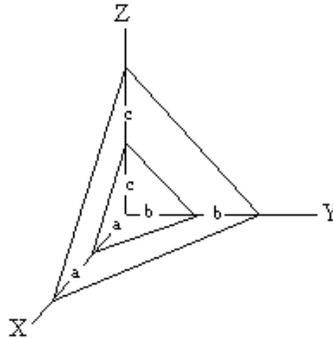


1. The law of constancy of interfacial angles: The angles between the two faces are always constant irrespective of the conditions under which crystallization occurs. The angles are measured by the use of Goniometer.



2. The law of rational indices: for any crystal, a set of three coordinate axes can so chosen that all the faces of the crystal will either intercept these axes or be

parallel to some of them. The law states that it is possible to have unit distances (a,b,c) such that the ratio of the three intercepts of any plane in the crystal is given by  $1/a$ ,  $1/b$  and  $1/c$ , where  $l$ ,  $m$  and  $n$  are simple whole numbers. This can be explained well with the following fig.



3. The law of crystal symmetry: The law states that every crystal has at least one element of symmetry.

Three elements of symmetry are:

1. The plane of symmetry: It is an imaginary plane which can divide the crystal into two equal halves.
2. The axis of symmetry: It is an imaginary line about which the crystal can be rotated through  $360^\circ$  so that it represents same appearance more than once in the complete rotation.

If the self coincidence occurs two times i.e. by rotation by  $180^\circ$ , the axis is called diad OR two fold axis.

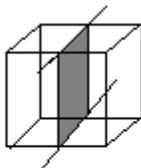
If the self coincidence occurs three times i.e. by rotation by  $120^\circ$ , the axis is called triad OR three fold axis.

If the self coincidence occurs four times i.e. by rotation by  $90^\circ$ , the axis is called tetrad OR four fold axis.

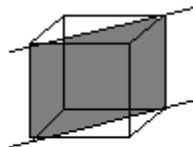
3. The Centre of symmetry: It is a point inside the crystal such that any line drawn through it will intersect the surfaces of the crystal at equal distances on either side.

A crystal can have one or more planes and axes of symmetry but never more than one centre of symmetry. E.g. the cubic crystal has 23 elements of symmetry as follows.

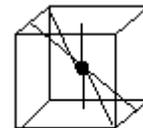
Planes of symmetry



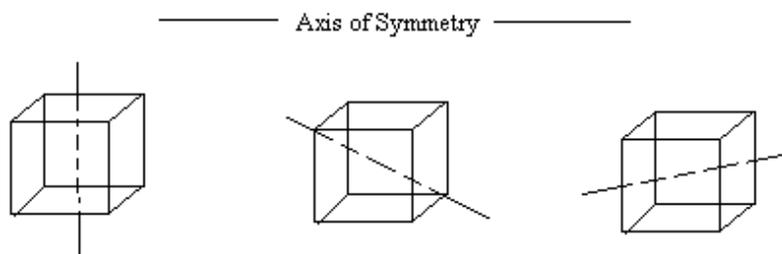
Passing thr. 2 faces  
Total face: 6  
Total planes of this type:  $6/2=3$



Passing thr. 2 opposite edges  
Total edges: 12  
Total planes of this type :  $12/2=6$



Centre of symmetry



Axis passing thr. 2 opposite faces: Tetrad OR four fold axis  
 Total faces: 6  
 Total axes of this type:  $6/2=3$

Axis passing thr. 2 opposite corners: Triad OR three fold axis  
 Total corners: 8  
 Total axes of this type:  $8/2=4$

Axis passing thr. 2 opposite edges: diad OR two fold axis  
 Total edges: 12  
 Total axes of this type:  $12/2=6$

The crystal systems: A. Bravais suggested 14 simple types of arrangements of atoms in space called Bravais lattices. A combination of Bravais lattices with elements of symmetry produced 230 crystal forms. Which are grouped into 32 classes which further constitute 7 crystal systems such as cubic, tetragonal, hexagonal, orthorhombic, monoclinic, triclinic and rhombohedral.

**Crystal lattice and space lattice:** The crystal of NaCl consists of a regular arrangement of  $\text{Na}^+$  and  $\text{Cl}^-$  ions. If all the  $\text{Na}^+$  ions are represented by points and the points are joined together by imaginary lines, we get a network of  $\text{Na}^+$  ions, which is called space lattice of  $\text{Na}^+$  ions. Similarly we can have a **space lattice** of  $\text{Cl}^-$  ions. Together both space lattices form a crystal lattice. In the **crystal lattice**, the points are visualized as arranged in a number of parallel and equidistant planes called as **lattice planes**. In a crystal lattice, atoms/ions are arranged in a regular manner, by a repetition of a small unit of the crystal which has all the characteristics of the crystal such as elements of symmetry etc. This small unit is called **Unit Cell**.

**Weiss indices and Miller indices:**

The different planes present in the crystal can be represented by the intercepts made by them on x, y and z axes as (a,b,c). These intercepts are called Weiss indices.

But generally the planes are represented by the Miller indices which are obtained by reciprocals of the intercepts and expressing them in the form of smallest whole numbers.

If the plane is parallel to z plane and intercepting x and y axes at unit distances, then it has Weiss indices as  $(1,1,\infty)$  and its Miller indices are given as  $(1,1,0)$ . Miller indices are also called (h,k,l) values.

**Problem: 1.** A crystal plane intercepts the three crystallographic axes at the multiples of  $5/2$ , 3, 1. What will be the Miller indices of the plane?

Intercepts:  $5/2$ , 3, 1

Reciprocals of them:  $2/5$ ,  $1/3$ ,  $1/1$

Miller indices: 6, 5, 15. [Multiplying every number by 15.]

**Problem: 2.** A crystal plane intercepts the crystallographic axes at the following multiples of unit distances, 1, 1,  $2/3$ . What will be the Miller indices?

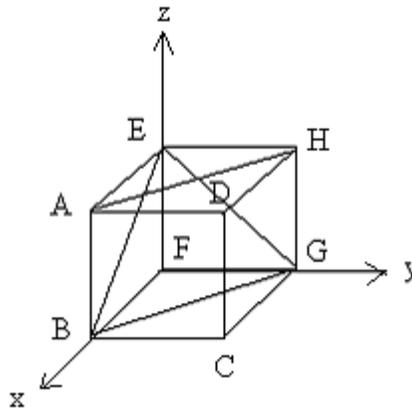
Intercepts: 1, 1,  $2/3$ .

Reciprocals: 1, 1,  $3/2$ .

Miller indices: 2, 2, 3 [multiplying every number by 2]

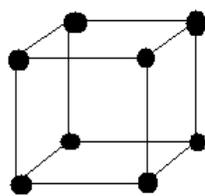
**Types of crystal planes:**

1. (1, 0, 0) plane: The plane intercepting x axis at unit distance but parallel to y and z axes is called (1, 0, 0) plane.
2. (1, 1, 0) plane: The plane intercepting x and y axes at unit distances but parallel to z axis is called (1, 1, 0) plane.
3. (1, 1, 1) plane: The plane intercepting all axes at unit distances is called (1, 1, 1) plane. These planes can be represented as follows:

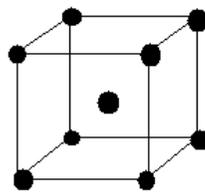


Here, in this figure, plane ABCD represents (1, 0, 0) plane.  
 plane ABGH represents (1, 1, 0) plane  
 And plane BGE represents (1, 1, 1) plane.

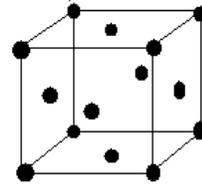
The distance between the two adjacent 100 planes is represented as  $d_{100}$ . Similarly we have  $d_{110}$  and  $d_{111}$ . The ratio of these three distances is characteristic of the internal structure of the crystal. *E.g.* a crystal with external appearance of a cube can be one of the three types as follows.



Simple cube



Body centered cube



face centered cube

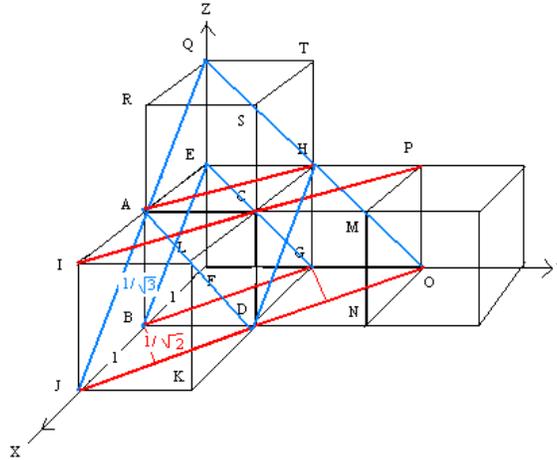
1. **Simple cube:** The ions are situated at the corners of the cube. Thus the unit cell of the cube contains one lattice point (or 8 corner points each shared among 8 cubes:  $8 \times 1/8 = 1$ ).
2. **Body centered cube:** The ions are situated at the corners of the cube as well as there is one ion at the center of the cube. Thus the unit cell of the cube contains two lattice points (or 8 corner points each shared among 8 cubes:  $8 \times 1/8 = 1$  plus one solely of the unit cell).
3. **Face centered cube:** The ions are situated at the corners of the cube as well as the centers of each faces. Thus the cube contains four lattice points (or 8 corner

points each shared among 8 cubes:  $8 \times 1/8 = 1$  plus six shared by two faces of the adjacent unit cells:  $6 \times 1/2 = 3$ ).

The distinction between the different types of the cube can be made from the ratios  $d_{100} : d_{110} : d_{111}$  as follows:

	$d_{100} : d_{110} : d_{111}$
1. <b>Simple cube:</b>	1 : $1/\sqrt{2}$ : $1/\sqrt{3}$
2. <b>Body centered cube:</b>	1 : $\sqrt{2}$ : $1/\sqrt{3}$
3. <b>Face centered cube:</b>	1 : $1/\sqrt{2}$ : $2/\sqrt{3}$

This can be understood from the following figure:



The figure exhibits 100 planes as ABCD, EFGH and IJKL. Which are unit distances apart. The 110 planes as ABGH, IJOP passing through C and D are  $1/\sqrt{2}$  distance apart and 111 planes as BGE and JOQ passing through A, D, H are  $1/\sqrt{3}$  distance apart.

If the interplaner distances could be measured and compared with the ratios for the different kinds of cubes, then one can easily confirm the type of the cube. This is possible due to X-ray diffraction studies.

The distance can be calculated from the following formula: if 100 plane intercepts x axis at distance a then,

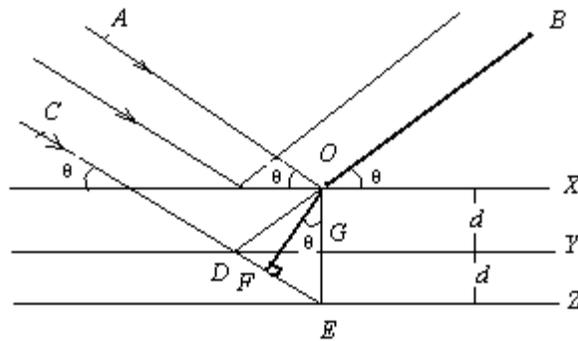
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Thus,  $d_{100} = a/\sqrt{1} = a$ ,  $d_{110} = a/\sqrt{2}$ ,  $d_{111} = a/\sqrt{3}$ .

**Diffraction of X-rays:** When light passes through a small space whose dimension is comparable with the wavelength of light, the light gets scattered and produces diffused luminous spot composed of concentric light and dark rings. This is called diffraction. The wavelength of the x-rays is comparable with the distance between the planes in the crystal. Scientist Laue observed that a crystal may be used as a diffraction grating for the x-rays and obtained a diffraction pattern on the photographic plate. Though this method is not used due to difficulties in the interpretation, the crystallographic study still includes the use of x-rays. This is based on Bragg's equation [ $n\lambda = 2d \sin\theta$ ]

**Bragg's equation:** Every plane is able to scatter the X-rays depending upon the number of atoms or ions present in them, because, every atom is able to scatter the X-rays depending upon the number of external electrons. The nature of the diffraction is determined by the spacing between the successive parallel planes. The concentric bright, luminous spot is due to reinforcement of the reflected rays ( i.e. enhancement of intensity by different rays reflecting in the same direction and angle) W. H. Bragg and W. L. Bragg observed the diffraction pattern and concluded that the reinforcement of the rays is possible only when **the excess distance traveled by the two rays is the integral multiple of the wavelength** of the incident radiation.

This can be understood from the following figure.



Suppose, X, Y and Z are the three successive parallel planes, separated by a distance d. A and C are the two parallel beams striking the planes X,Y and Z at an angle of incidence  $\theta$ . The part of first beam is reflected by the first plane X, at point O and the beam travels a path AOB. While part of the second beam is reflected by the plane Y, at point D with the same angle of reflection  $\theta$ . Hence the beam reinforces the first reflected beam, traveling the path CDOB. This excess distance traveled by the second beam should be integral multiple of the wavelength of the rays.

$$\therefore CDOB-AOB=n\lambda \text{-----}[1]$$

The second beam strikes the third plane Z at point E, where, EO is perpendicular to X, Y and Z. If a perpendicular is drawn from point O on the line DE, angle EOF is also  $\theta$ . From the geometry of the diagram one can also observe that, plane Y is dividing the angle ODE into two congruent angles ODG and EDG having DG common.

$$\text{Hence, } l(DO)=l(DE)$$

As well as,  $CDOB-AOB=CDO-AO$

As,  $CDO=CDE$  and  $AO=CF$ , The excess distance traveled by the second ray is equal to EF.

$$\therefore EF= n\lambda \text{-----}[2]$$

If the angle EOF is  $\theta$ , then,  $\sin \theta = \frac{EF}{OE}$ . But, OE is distance between the first and third plane i. e.  $2d$ .

Hence,  $\sin \theta = \frac{EF}{2d}$ .

$$\therefore EF= 2d \sin \theta \text{-----}[3]$$

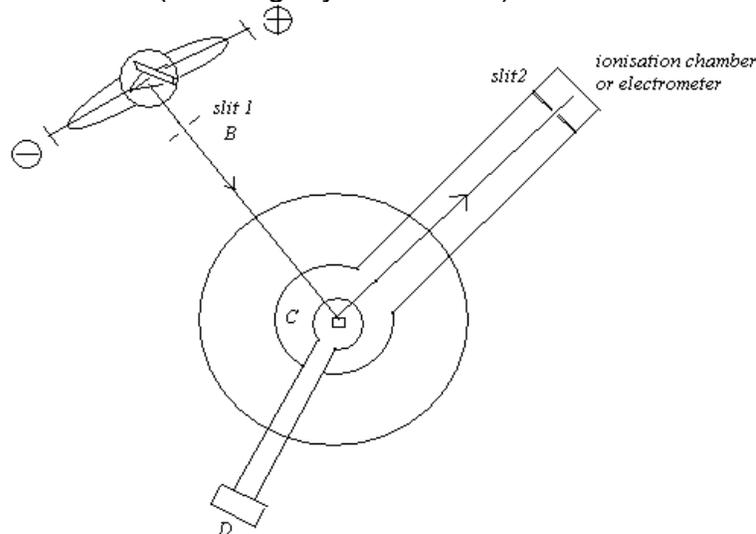
From equations 2 and 3,

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

Hence for maximum reflection, the condition is governed by this equation which is called Bragg's equation.  $n$  gives order of reflection as 1,2,3,4 etc.

The intensity decreases with increasing values of  $n$ .

Bragg's X-ray spectrometer: (Rotating crystal method)



A beam of X-rays of definite wavelength coming from the anticathode A of an X-ray tube passes through a slit B and then falls upon the face of crystal mounted on a turntable, the rays reflected by the crystal pass through the another slit into the ionization chamber or electrometer, where, the intensity of the reflected beam can be determined from the gas  $\text{CH}_3\text{Br}$  OR  $\text{SO}_2$  ionized in the ionization chamber / the intensity of current produced in the electrometer. By determining the intensities at different angles and comparing the intensities, one can know the angle of maximum reflection  $\theta$ . If wavelength of the rays is known, one can calculate  $d$ . Thus the distances are measured and compared to get the ratio  $d_{100} : d_{110} : d_{111}$ . This further helps in confirmation of the crystal form.