Solid State Physics

1. Diffraction of X-rays by crystal planes

The visible light rays when pass through a sharp edge of an object can form some bright regions inside the geometrical shadow of the object. This is due to the bending nature of light, called diffraction. Diffraction of visible light rays can also be produced using plane-ruled grating. This grating consists of about 6000 lines/cm; so that the spacing between any two consecutive lines in the grating is of the order of the wavelength of visible light used to produce diffraction. The wavelength of X-rays is of the order of an angstrom, so X-rays are unable to produce diffraction with plane optical grating. To produce diffraction with X-rays, the spacing between the consecutive lines of grating should be of the order of few angstroms. Practically, it is not possible to construct such a grating. In the year 1912, a German physicist Laue suggested that the three-dimensional arrangement of atoms in a crystal can serve as a three-dimensional grating for X-rays. Inside the crystal, the spacing between the crystal planes can work as the transparent regions as between lines in a ruled grating. Laue's associates Friedrich and Knipping succeeded in diffracting X-rays by passing through a thin crystal.

In 1913, W.L. Bragg and his son W.H. Bragg gave a simple interpretation of the diffraction pattern. According to Bragg, the diffraction spots produced are due to the reflection of some of the incident X-rays by various sets of parallel crystal planes. These planes are called Bragg's planes. The Bragg's interpretation is explained in the following topic.

2. Bragg's law:

W.L. Bragg and W.H. Bragg considered the X-ray diffraction as the process of reflection of X-rays by crystal planes as shown in Fig. 1. A monochromatic X-ray beam of wavelength λ is incident at an angle θ to a family of Bragg planes. Let the inter planar spacing of crystal planes is 'd '. The dots in the planes represent positions of atoms in the crystal. Every atom in the crystal is a source of scatterer of X-rays incident on it. This angle θ is called the angle of diffraction or glancing angle.

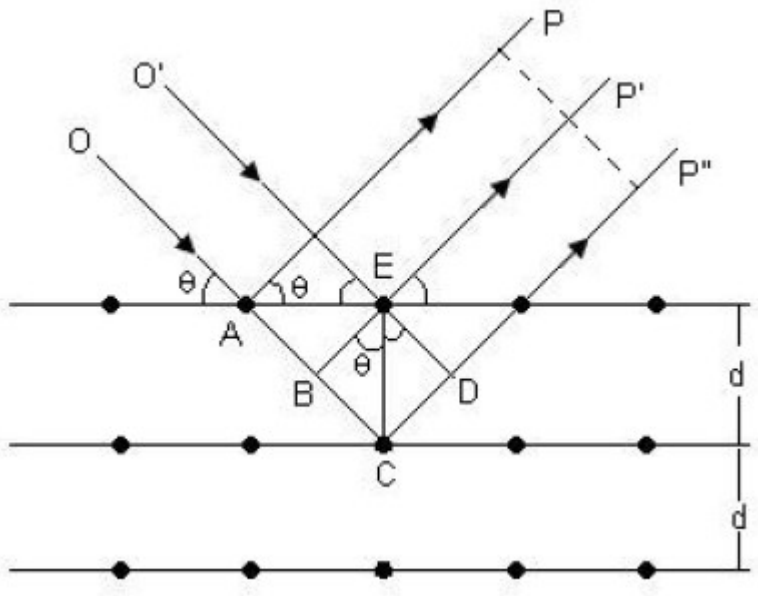

Figure 1

Consider two of the incoming x-ray OA and O′E inclined at an angle θ with the topmost plane of the crystal and are scattered in the directions AP and EP′, also at an angle θ with that plane. Since the path length of the rays OEP′ and O′AP are the same, they arrive at P and P′ respectively in phase with each other and again form a common wavefront. This is the condition for scattering in phase by single plane of the crystal.

Now, let us consider X-ray scattering from two adjacent planes $(hkl)_1$ and $(hkl)_2$ as shown in Figure.

If EB and ED are parallel to the incident and scattered wavefront respectively, the total path O′CP′′ is longer than the path OEP′ by an amount

$\Delta = BCD = BC + BD$

Now, from the right angle triangle EBC and EDC, we have

$BC = d \sin\theta = BD$

So, $\Delta = 2d \sin\theta$

If two consecutive planes scattered in phase with each other then we know that the path difference Δ must be equal to an integral multiple of wavelength, i.e. $\Delta = n\lambda$, where n = 0, 1, 2 ... gives the order of reflection. Thus the condition for constructive interference (in-phase scattering) by a set of equidistant parallel planes in a crystal is given by

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

Therefore, Bragg's law states that X-rays diffracted from different parallel planes of a crystal interfere constructively when the path difference is integral multiples of wavelength of X-rays.
From Bragg's law $n\lambda = 2d \sin\theta$, since maximum possible value for sin θ is 1,
$n\lambda/2d = 1$ or $\lambda = 2d$ when n =1.
This sets the limitation on the wavelength, i.e. in order to get the diffraction pattern by a crystal, the wavelength of X-rays should not exceed twice the inter-planar spacing.

Importance of Bragg's law:

1. Bragg's law is the essential condition to be satisfied by crystal planes in order to get diffraction pattern from a crystal.
2. It is used to calculate inter-planar spacing. Knowing the values of inter-planar spacing, lattice parameters can be determined.

1. The Laue method:- applicable for single crystals
2. The Rotating crystal method:- applicable for single crystals
3. The Powder method:- used for finely divided crystalline or polycrystalline powers

3. LAUE METHOD:

The Laue method was the first diffraction method ever used. This method is used to study the orientation of crystal and to verify crystal symmetry. A beam of white radiation, the continuous spectrum from an x-ray tube, is allowed to fall on a fixed single crystal. The Bragg angle θ is therefore fixed for every set of planes in the crystal, and each set picks out and diffracts that particular wavelength which satisfies the Bragg law for the particular values of d and involved. Each diffracted beam thus has a different wavelength. There are two variations of the Laue method, depending on the relative positions of source, crystal, and film (Fig. 2). In each, the film is flat and placed perpendicular to the incident beam. The film in the transmission Laue method (the original Laue method) is placed behind the crystal so as to record the beams diffracted in the forward direction. This method is so called because the diffracted beams are partially transmitted through the crystal. In the back-reflection Laue method the film is placed between the crystal and the x-ray source, the incident beam passing through a hole in the film, and the beams diffracted in a backward direction are recorded. In either method, the diffracted beams form an array of

spots on the film as shown in Fig. 2 for a cubic crystal. This array of spots is commonly called a pattern, more specifically, Laue pattern, but the term is not used in any strict sense and does not imply any periodic arrangement of the spots. On the contrary, the spots are seen to lie on certain curves, as shown in fig. 2 for transmitted pattern. These curves are generally ellipses or hyperbolas for transmission patterns and hyperbolas for back-reflection patterns.

The spots lying on any one curve are reflections from planes belonging to one zone. This is due to the fact that the Laue reflections from planes of a zone all lie on the surface of an imaginary cone whose axis is the zone axis. The positions of the spots on the film, for both the transmission and the back-reflection method, depend on the orientation of the crystal relative to the incident beam, and the spots themselves become distorted and smeared out if the crystal has been bent or twisted in any way. The facts account for the two main uses of the Laue methods include: the determination of crystal orientation and the assessment of crystal perfection. Therefore, the way of arrangement of spots on a film is a characteristic property of the crystal. Laue method is useful to decide the crystal symmetry and orientation of the internal arrangement of atoms/molecules in the crystal. The atomic arrangement in a crystal can be analyzed by studying the positions and intensities of spots in Laue pattern. As several wavelengths of X-rays can reflect in different orders from the same set of planes with the different order reflections superimposed on the same spot in the film, the intensity of the spots and hence the cell parameters of a crystal cannot be determined using Laue method. For transmission Laue method, the crystal should be thin. Laue method can be used to study imperfections or strains in the crystal. The presence of above defects forms streaks instead of spots in the Laue photograph.

By recording the diffraction patterns (both angles and intensities) for various crystal orientations, one can determine the shape and size of unit cell as well as arrangement of atoms inside the cell.

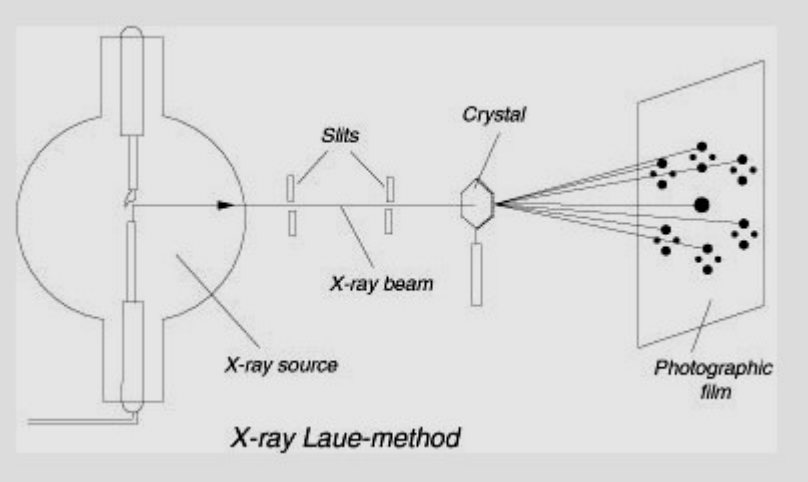

Figure 2

4. Powder diffraction Method

X-ray powder method is usually carried for polycrystalline materials. The powder photograph is obtained in the following way. The given polycrystalline material is ground to fine powder and this powder can be taken either in a capillary tube made up of non-diffracting material or is just struck on a hair with small quantity of binding material and fixed at the centre of cylindrical Debye-Scherrer camera as shown in Fig. 3.

A stripe of X-ray photographic film is arranged along the inner periphery of the camera. A beam of monochromatic X-rays is passed through the collimator to obtain a narrow fine beam of X-rays. This beam falls on the polycrystalline specimen and gets diffracted. The specimen contains very large number of small crystallites oriented in random directions. So, all possible diffraction planes will be available for Bragg reflection to take place. Such reflections will take place from many sets of parallel planes lying at different angles to the incident X-ray beam. Also, each set of planes gives not only first-order reflections but also of higher orders as well. Since all orientations are equally likely, the reflected rays will form a cone whose axis lies along the direction of the incident beam and whose semi-vertical angle is equal to twice the glancing angle (θ), for that particular set of planes. For each set of planes and for each order, there will be such a cone of reflected X-rays. There intersections with a photographic film sets with its plane normal to the incident beam, form a series of concentric circular rings. In this case, a part of the reflected cone is recorded on the film and it is a pair of arcs, the resulting pattern is shown in Fig. 3. Diameter of these rings or corresponding arcs is recorded on the film, and using this the glancing

angle and interplanar spacing of the crystalline substance can be determined. Figure 3 shows the film mounted in the camera and the X-ray powder pattern obtained. The film on spread-out is shown in Fig 3. The distance between any two corresponding arcs on the film is indicated by the symbol S. In case of cylindrical camera, the diffraction angle θ is proportional to S.

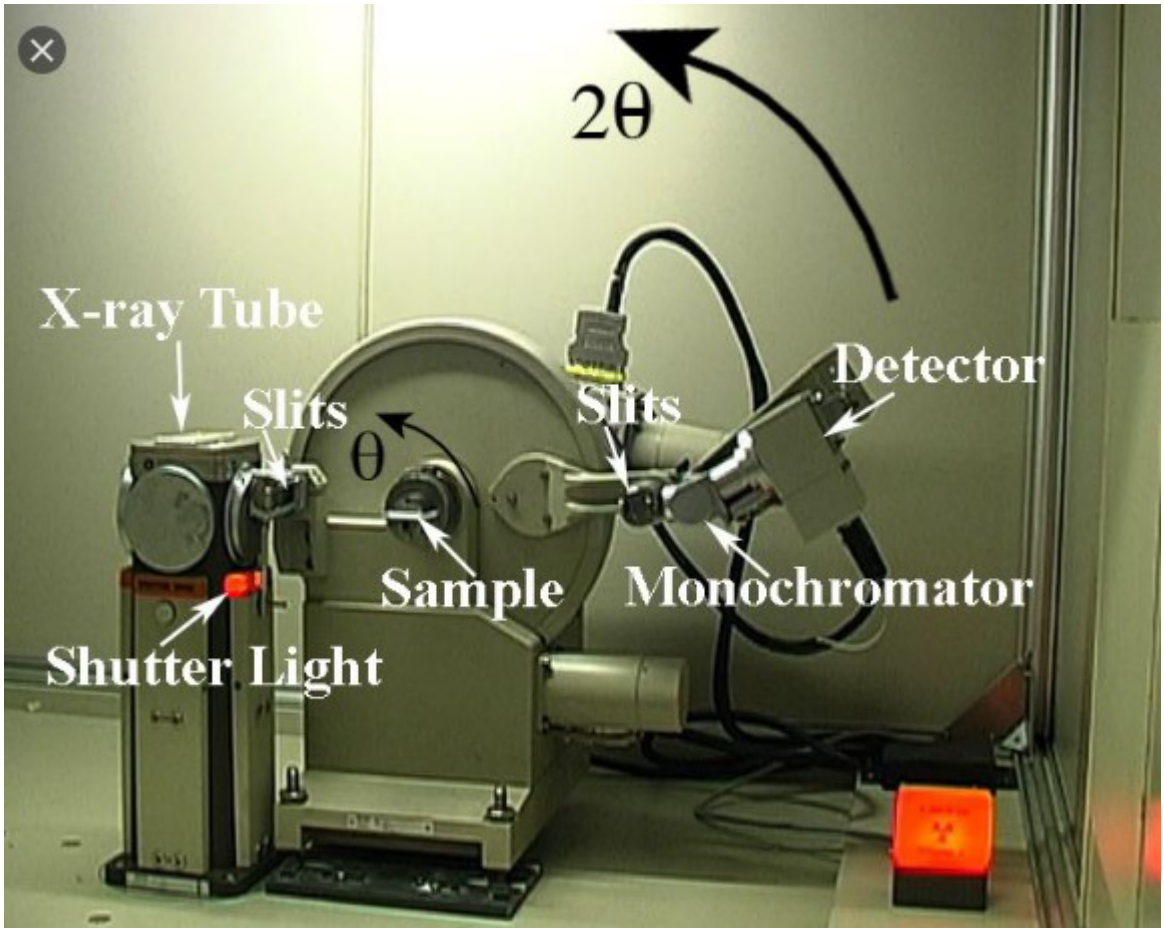

Figure 3

5. Applications of XRD

XRD is a non destructive technique. Some of the uses of x-ray diffraction are;

1. Differentiation between crystalline and amorphous materials;
2. Determination of the structure of crystalline materials;
3. Determination of electron distribution within the atoms, and throughout the unit cell;
4. Determination of the orientation of single crystals;
5. Determination of the texture of poly-grained materials;
6. Measurement of strain and small grain size…..etc

Advantages and disadvantages of X-rays

Advantages;

1. X-ray is the cheapest, the most convenient and widely used method.

2. X-rays are not absorbed very much by air, so the specimen need not be in an evacuated chamber.

Disadvantage;

1. They do not interact very strongly with lighter elements.

• Crystal structures

• Crystal Directions, Crystal Planes, Miller Indices, X-ray diffraction

List of Questions:

1. Describe seven crystal systems with diagrams.
2. Obtain the relations between the edge of the unit cell and atomic radius for the BCC and FCC lattices.
3. What are Bravais lattices?
4. Describe FCC crystal structure.
5. Define crystal lattice, unit cell, lattice parameter and coordination number.
6. Explain the unit cell and lattice parameters. What is a primitive cell and how does it differ from unit cell.
7. Explain the terms: (i) basis, (ii) space lattice, (iii) lattice parameters and (iv) unit cell.
8. Describe BCC structure, with suitable example.
9. Describe in detail, the seven crystal systems with diagrams.
10. Tabulate the characteristics of the unit cells of different crystal systems.
11. Illustrate Bravais lattices.
12. Illustrate simple cubic, FCC and BCC crystal structures.
13. What is space lattice? Find the packing fraction for BCC and FCC crystals.
14. Classify various lattice types in the crystal system.
15. What is a Bravais lattice? What are the different space lattices in the cubic system?
16. Describe FCC crystal structure.
17. Obtain an expression for the packing factor of FCC structure.
18. Define crystal lattice, unit cell, lattice parameter and coordination number.
19. Explain the unit cell and lattice parameters. What is a primitive cell and how does it differ from unit cell.
20. Describe the crystal structure of CsCl.
21. Consider a body centred cubic lattice of identical atoms having radius ‘R’ compute (i) the number of atoms per unit cell (ii) The coordination number and (iii) the packing fraction
22. Explain the terms: (i) basis, (ii) space lattice, (iii) lattice parameters and (iv) unit cell.
23. Describe BCC structure, with suitable example.
24. Describe in detail, the seven crystal systems with diagrams.
25. Tabulate the characteristics of the unit cells of different crystal systems.

26. Illustrate Bravais lattices.
27. What is space lattice? Find the packing fraction for BCC and FCC crystals.
28. Classify various lattice types in the crystal system.
29. Describe in detail the structure of ZnS.
30. What is a Bravais lattice? What are the different space lattices in the cubic system?
31. Deduce the expression for the inter planar distance in terms of Miller indices for a cubic structure.
32. Sketch the following planes of a cubic unit cell: (001), (120) and (211).
33. Define Miller indices. Sketch the following atomic planes in a simple cubic structure (010), (110) and (111).
34. How can the interplanar spacing of a set of Miller planes be calculated in terms of Lattice parameters?
35. What is Bragg's law? Explain.
36. What are Miller Indices? Draw (111) and (110) planes in a cubic lattice.
37. Draw the (112) and (120) planes and the [112] and [120] directions of a simple cubic crystal.
38. Sketch the following planes of a cubic unit cell: (001), (120) and (211).