E-Content

Topic: X-Rays and Crystal Structure

Chapter: Solid State

Physical Chemistry

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By

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X-RAYS AND CRYSTAL STRUCTURE

Crystal structures are usually determined with the help of X-rays. In addition to X-rays, other forms of radiations having similar properties-like a beam of neutrons or electrons could also be used. We know that X-rays are electromagnetic radiations of wavelengths much shorter' than either visible or ultraviolet light. In 1911, Ewall showed that whenever the wavelength of radiation is of the same order of magnitude as the size of the particle in a material, the radiation would be diffracted by the particle. In 1912, Laue suggested that since the order of the magnitude of the wavelength of X-rays and the crystal lattice distances are the same, we should expect diffraction of X-rays by crystals. When a beam of x-rays is allowed to fall on a crystal, a large number of images of different intensities are formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots are produced on a photographic plate placed in their path. On the other hand, if the diffracted waves are out of phase, dark spots are caused on the photographic plate (fig 1). From the overall diffraction pattern produced by a crystal, can arrive at the detailed information regarding the position of particles in the crystal.

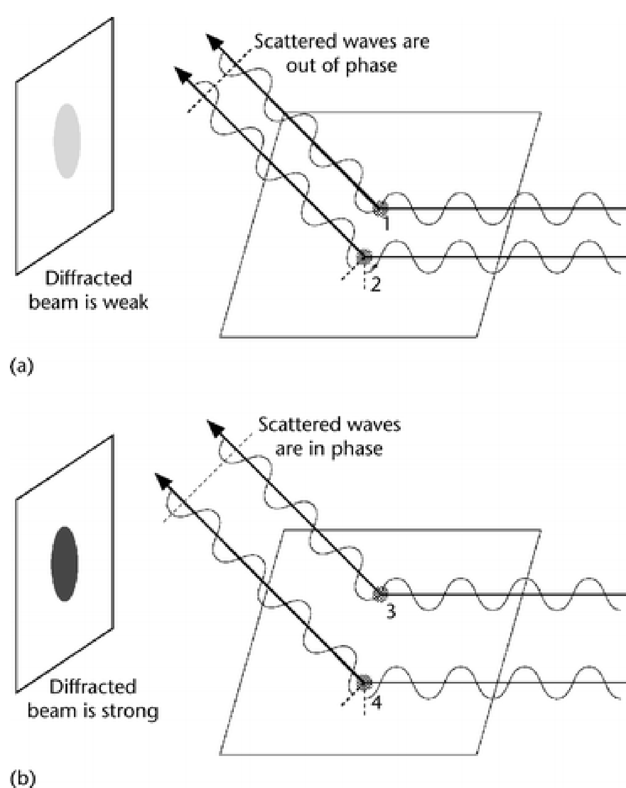

Fig. 1. Diffraction patterns produced by crystals

Bragg’s equation

Bragg’s pointed that the scattering of x-rays by crystal could be taken to be equivalent to reflection from successive planes of atoms in the crystal. However the reflection of x-rays can take place only at certain angles which are dependent on wavelength of the x-rays and the distance between the planes of the crystal. The fundamental equation which gives a simple relation between the wave length of x-rays, the interplaner distance in the crystal and the angle of reflection is known is known as Bragg’s equation.

Derivation:

Suppose a beam of x-rays incident at an angle falls on the crystal. The horizontal lines represent parallel planes in the crystal structure separated from one another by a distance d. Some of the incident rays will be reflected from uppermost plane at the same angle, while the other will be absorbed and get reflected from successive planes, as shown in Fig. 2.

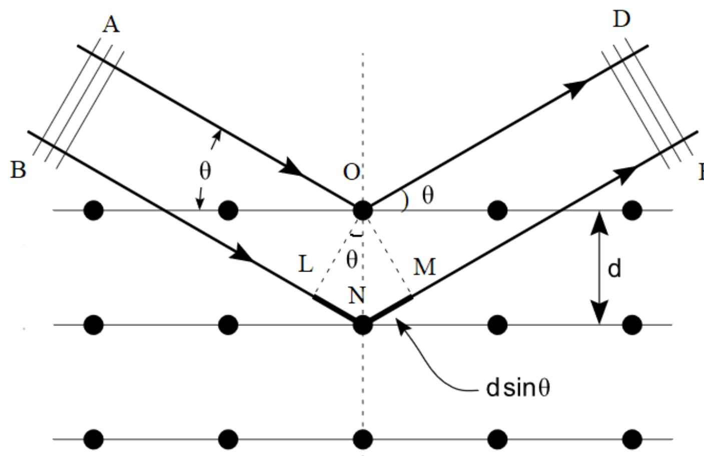

Fig. 2. X-ray diffraction by crystals

Let the planes AB and DE drawn perpendicular to the incident and reflected beams, respectively. The waves reflected from different planes will be in phase will one another only if the difference in the path length of the wave reflected from the successive planes is equal to an integral number of wavelengths. Drawing perpendicular OL and OM to the incident and reflected beams, it will be seen that the path difference in the wavelength, say δ of the wave reflected from the first two planes is given by

$$\delta = LN + NM \text{ .... } (1)$$

This should be equal to a whole number multiple of wavelength λ, i.e.

$$n\lambda = LN+NM \text{ ....(2)}$$

Since the two triangle ONL and ONM are congruent LN=NM

$$n\lambda = 2LN = 2d\sin\theta \text{ ....(3)}$$

Equation (3) is known as Bragg's equation.

For a given set of lattice planes, d has a fixed value.

Therefore possibility of getting maximum diffraction (i.e., the possibility of getting reflected waves in phase with one another) depends upon θ. If θ is increased gradually, a number of positions will be found at which the reflection will be maximum. At these positions, n will have values 1,2,3,4...etc. generally, in experiments on x-ray diffractions, any set as equal to 1. If λ in known, it is possible to determine d, the distance between atomic planes in the crystal by determining θ experimentally. Thus if d is known λ can be calculated.

EXPERIMENTAL METHODS FOR THE DETERMINATION OF CRYSTAL STRUCTURE

The X-ray diffraction techniques used in the study of crystals are of two types known as rotating crystal method and powder method. Both these techniques make use of the x-ray spectrometer. In any method of crystal structure determination, we must find out θ as well as the intensity of the diffracted beam.

Powder Method:

Power method is the simplest technique for obtaining x-ray diffraction. It was first used by P.J.W. Debye and P. Scherer. Instead of taking a single crystal having a definite orientation to the x-rays, we can take a mass of finely divided crystal with random orientation. In this method, the crystal sample is need not to be taken in large quantity but a little as one milligram of the material is sufficient for study. The power, in fact consists of many small crystals which are oriented in all possible directions. As a result of this x-rays are scattered from all set of planes (e.g., 100,110, etc.). The scattered rays are detected by using an x-ray sensitive film. A narrow beam of x-rays is allowed to fall on the powder. The diffracted x-rays strike a strip of photographic film arranged in the form of circular arc, as shown in the Fig 3.

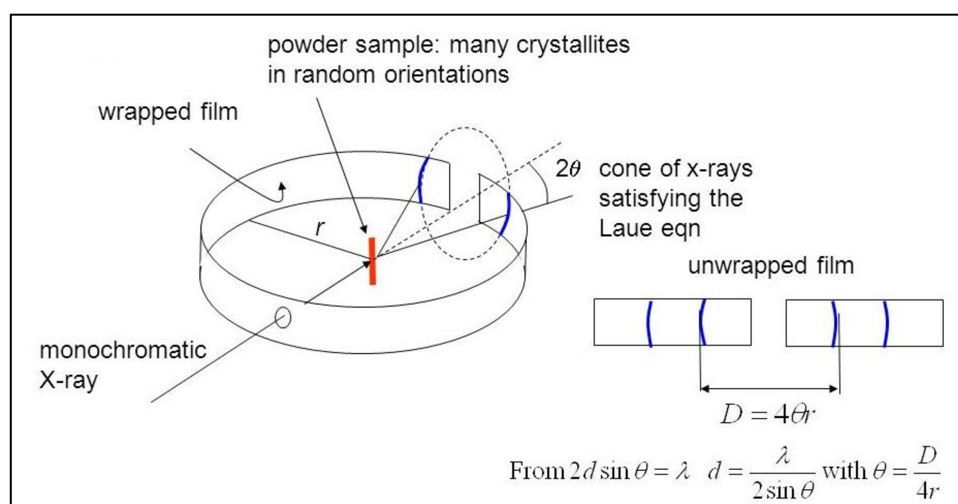

Fig. 3. Powder method

In this method no rotation is necessary since the powder sample already contains microcrystal arranged in all possible orientations. Hence, a large number of them will have their lattice planes in correct positions for maximum x-ray reflection to occur. As a result of this we get lighted areas in the form of arcs of lines at different distances from the incident been as shown.

These distances can be converted into scattering angles to be used in the Bragg's equation for different planes of crystals. Using powder method, the interplanar spacing can be found out since both λ and θ are known. The X-ray powder pattern for sodium chloride is shown in Fig. 4.

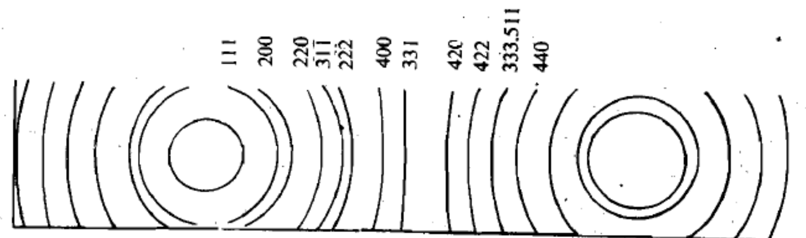

Fig. 4. X-ray diffraction pattern for sodium chloride.

Rotating crystal method

X-ray generated in the tube T are passed through a slit so as to obtain a narrow beam which is then allowed to strike a single crystal C mounted on the turn table (Fig. 5). The crystal is rotated gradually by means of the turn table so as to increase the glancing angle at which x-rays are incident at the exposed phase of the crystal. The intensities of the refracted rays are measured on a recording device R. The recording device may be either a photographic plate or an ionisation chamber. The angle 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 maximum reflection occurs corresponds to n=1. This is called first order reflection. The next higher angle at which maximum reflection occurs again, corresponds to n=2. This is second order reflection, and so on.

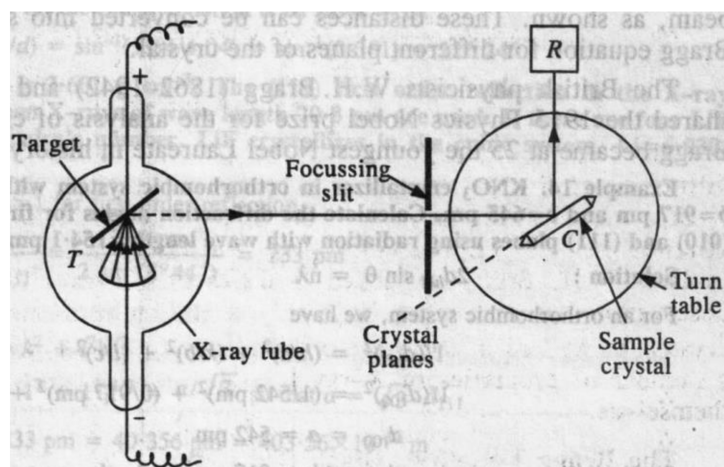

Fig. 5. Rotating crystal method