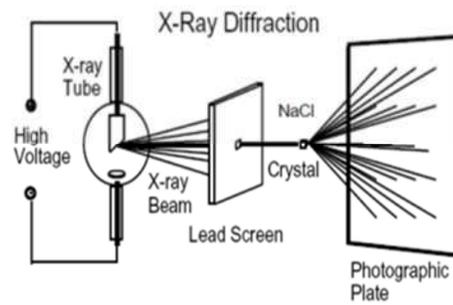


## Chapter-2

### X-ray diffraction

X - ray diffraction is one of the earliest methods for studying the structure of solids.

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction. In the process of diffraction, electromagnetic waves of a given frequency but different phases interact to produce constructive interference (bright spots on the film exposed to the light) and destructive interference (dark spots). By a careful analysis of the diffraction patterns, very accurate values of the lattice parameters (unit cell dimensions) can be inferred. A diffraction pattern is not a direct representation of the crystal lattice. Wave Interacting with a Solid Scattered beams interfere constructively in some directions, producing diffracted beams. Random arrangements cause beams to randomly interfere and no distinctive pattern is produced. Crystalline Material Regular pattern of crystalline atoms produces regular diffraction pattern. Diffraction pattern gives information on crystal structure. When the wavelength of the radiation is comparable with or smaller than the lattice constant, we may find diffracted beams in directions quite different from the incident direction. This technique had its beginnings in von Laues discovery in 1912 that crystals diffract x - rays, the manner of the diffraction revealing the structure of the crystal. At first, x-ray diffraction was used to analyze the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. The diffraction depends on the crystal structure and on the wavelength. General X-ray diffraction phase/composition identification will distinguish the major, minor, and trace compounds present in a sample. The data usually includes mineral (common) name of the substance, chemical formula, crystalline system, and reference pattern number from the ICDD International database.



## 2.1. Reciprocal lattices

The diffraction pattern is a representation of the reciprocal lattice. For every real lattice there is an equivalent reciprocal lattice, which is the inverse space of the real lattice. A two dimension (2-D) real lattice is defined by two unit cell vectors, say  $\mathbf{a}_1$  and  $\mathbf{a}_2$  inclined at an angle. The equivalent reciprocal lattice in reciprocal space is defined by two reciprocal vectors, say  $\mathbf{b}_1$  and  $\mathbf{b}_2$ .

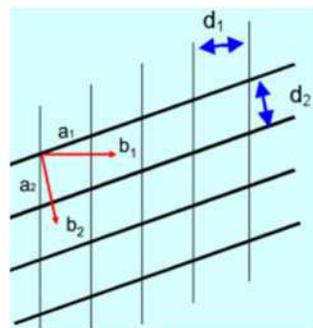
Each point in the reciprocal lattice represents a set of planes.

### *Defining the reciprocal lattice vector*

Take two sets of 2D planes: Draw directions normal: These lines define the orientation but not the length.

We use  $1/d$  to define the lengths, these are called reciprocal lattice vectors  $\mathbf{b}_1$  and  $\mathbf{b}_2$

Dimensions = 1/length



- The reciprocal vectors are defined as follows:
- $\mathbf{b}_1$  is of magnitude  $1/d_1$  where  $d_1$  is the spacing of the vertical planes, and is perpendicular to  $\mathbf{a}_1$ .

- $\mathbf{b}_2$  is of magnitude  $1/d_2$  where  $d_2$  is the spacing of the horizontal planes, and is perpendicular to  $\mathbf{a}_2$ .
- A reciprocal lattice can be built using reciprocal vectors. Both the real and reciprocal constructions show the same lattice, using different but equivalent descriptions.

The volume of the unit cell is thus given by  $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ . We can define the reciprocal lattice vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$  and  $\mathbf{b}_3$  in terms of direct lattice vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  as follows:

$$\mathbf{b}_1 = 2\pi \frac{(\mathbf{a}_2 \times \mathbf{a}_3)}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{(\mathbf{a}_3 \times \mathbf{a}_1)}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_3 = 2\pi \frac{(\mathbf{a}_1 \times \mathbf{a}_2)}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

A crystal has another characteristic periodicity arising from a periodic arrangement of its atoms. So Periodic structure always repeats itself after  $2\pi$ .

## 2.2 Diffraction of waves by crystals: Braggs law

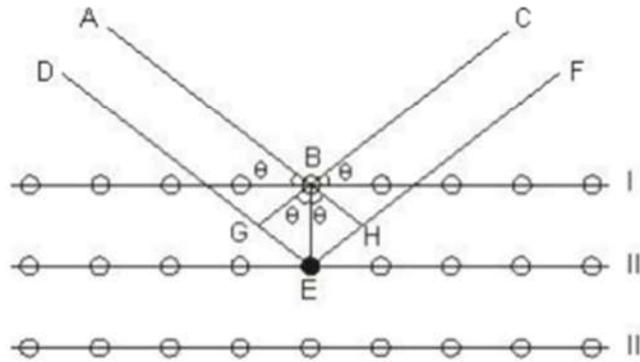
### 2.2.1 Braggs law

Diffraction from a three dimensional periodic structure such as atoms in a crystal is called Bragg Diffraction. Bragg's law is the fundamental law of x-ray crystallography. Braggs diffraction was first proposed by William Lawrence Bragg and William Henry Bragg, in the year 1913, during their experiments on crystalline solids.

Bragg's diffraction occurs when electromagnetic radiation, or subatomic particle, waves have wavelengths that are comparable to atomic spacing in a crystal lattice. This is a simple and elegant law which is central to the analysis of diffraction data. This law relates the angle  $\theta$  (at which there is a maximum in diffracted intensity) to the wavelength of  $\lambda$  X-rays and the inter-layer distance  $d$  between the planes of atoms/ ions / molecules in the lattice.

**Derivation of Braggs Law:** Consider a crystal in which atoms are arranged in a periodic manner with interatomic spacing  $d$ . A narrow beam of monochromatic X-Ray of wavelength  $\lambda$  is allowed to fall on a crystal at a glancing angle  $\theta$ . The crystal

acts as a diffracting grating with atoms as the opaque part and the spacing between them as the transparent part.



Let AB and DE be the incident rays and BC and EF be the corresponding reflected rays the path difference between the rays ABC and DEF is  $(GE+EH)$  therefore the path difference is given by

$$\Delta = GE + EH = d \sin \theta + d \sin \theta = 2d \sin \theta$$

The diffracted beams are found when the reflections from parallel planes of atoms interfere constructively.

Constructive interference takes place only when the path difference is equal to  $n\lambda$  that is when the following condition satisfied

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

This is the Bragg law, which can be satisfied only for wavelength  $\lambda \leq 2d$ . Where  $n$ ,  $\lambda$ ,  $d$  and  $\theta$  is an integer, the wavelength of the x-rays, the distance between adjacent planes in the lattice and the incident angle of the x-ray beam respectively.

### 2.3 Brillouin zones in one and two dimensions

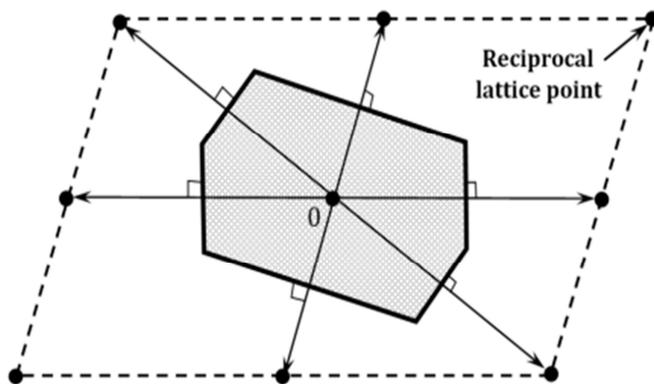
**Brillouin Zone** is a Wigner-Seitz cell in reciprocal lattice. **Wigner-Seitz cell**: smallest possible primitive cell, which consist of one lattice point and all the surrounding space closer to it than to any other point.

The construction of the W-S cell in the reciprocal lattice delivers the first Brillouin zone (important for diffraction). We can define Brillouin zones as being zones delimited by

Wigner-Seitz cells in a reciprocal lattice. The construction of **Brillouin Zone** is the same for both two and three dimensional lattices. The following procedure is adopted.

1. For a given lattice point, draw lines to connect this point to all nearby lattice points.
2. Draw new lines or planes at the midpoint of each of the previous lines. The smallest area (in two dimensions) or volume (in three dimensions) enclosed in this way gives the first **Brillouin Zone** (the wigner-Seitz primitive unit cell in reciprocal lattice). The concept of Brillouin zone is particularly important in the consideration of the electronic structure of solids.

Figure 1 shows the construction of the first Brillouin zone for a two-dimensional reciprocal lattice.



As shown in Figure 1 the first Brillouin zone is obtained by first drawing a number of reciprocal lattice vectors from the center reciprocal lattice point, say  $(0, 0, 0)$ , to all its nearest-neighboring reciprocal lattice points, and then drawing the bisecting lines perpendicular to each of these reciprocal lattice vectors. The smallest area enclosed by these bisecting lines gives the first Brillouin zone, or the unit cell of this 2-D reciprocal lattice. The first Brillouin zone for a three-dimensional crystal lattice can be constructed in a similar way to that of a 2-D reciprocal lattice.

The importance of the first Brillouin zone can be best illustrated by considering the wave function of an electron wave packet in a crystalline solid, which is described by the wave vector  $\mathbf{k}$  in momentum (or the reciprocal lattice) space. In a periodic crystal, it can be shown using translational operation that for any given wave vector  $\mathbf{k}'$  of the electron wave packet in the