What is Bragg's Law and why is it Important?

- Bragg’s law refers to a simple equation derived by English physicists Sir W. H. Bragg and his son Sir W. L. Bragg in 1913.

- This equation explains why the faces of crystals appear to reflect (diffract) X-ray beams at certain angles of incidence $\theta$.

- This observation is an example of X-ray wave interference, known as X-ray diffraction (XRD).

- Bragg’s law can easily be derived by considering the conditions necessary to make the phases of the beams coincide when the incident angle = reflecting angle (Figure 1)

- The second incident beam $b$ continues to the next layer where it is scattered by atom C

- The second beam must travel the extra distance $BC + CD$ if the two beams $a & b$ are to continue travelling adjacent and parallel

- This extra distance must be an integral ($n$) multiple of the wavelength for the phases of the two beams to be the same
Figure 1: Derivation of Bragg's Law

- \( n\lambda = BC + CD \), the distance \( BC = d \sin \theta \)
- Since \( BC = CD \), we have: \( n\lambda = 2BC \)
- Then after substitution gives Bragg's Law

\[
n\lambda = 2d \sin \theta
\]

- \( d \): lattice interplanar spacing of the crystal
- \( \theta \): x-ray incidence angle (Bragg angle)
- \( \lambda \): wavelength of the characteristic x-rays
• The process of diffraction is described in terms of incident and diffracted (reflected) rays, each making an angle $\theta$ with a fixed crystal plane.

• Reflection occurs from planes set at an angle $\theta$ with respect to the incident beam and generates a reflected beam at an angle $2\theta$ from the incident beam.

• The possible “$d$” spacing defined by the miller indices, $h$, $k$, $l$ are determined by the shape of the unit cell.

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- Rewriting Bragg’s law:

$$\sin \theta = \frac{\lambda}{2d}$$

- Thus, the possible $2\theta$ values where we can have reflections are determined by the unit cell dimensions.

- The intensities of the reflections depend on what kind of atoms and their location in the unit cell.
• Diffraction only occurs when the Bragg condition is satisfied.

• In order to be sure of satisfying Bragg’ law, either $\lambda$ or $\theta$ must be continuously varied during the experiment.

• The ways in which these parameters are varied distinguish the two main diffraction methods:

  - **Laue Method**: $\lambda$ is varied and $\theta$ is fixed
  - **Powder Method**: $\lambda$ is fixed and $\theta$ is varied

**LAUE METHOD**

• In this method, continuous radiation is used

• This radiation falls on a stationary crystal. The crystal diffracts the X-ray beam and produces a pattern of spots which conform exactly with the internal symmetry of the crystal

• The Laue method can be used in two ways:
  - **Transmission method (Figure 2a)**
  - **Back-reflection method (Figure 2b)**

• Depending on the relative position of the X-ray source, the crystal and the photographic film (to detect the diffracted X-rays)
In the Laue method, the crystal is fixed in a position relative to the X-ray beam, thus, not only is the value for $d$ fixed, but the value of $\theta$ is also fixed. The diffracted beam is produced by diffraction from the planes which belong to a particular zone axis (ZA) of the crystal. The beam in each set all lie on the surface of an imaginary cone: the axis of this cone is the zone axis (Figure 3). When this beam intersects with the plane of the photographic film it produces spots (Figure 4).
Figure 3: Location of Laue spots (a) on ellipses in transmission method and (b) on hyperbolas in back-reflection method. (C: crystal, F: film, Z.A: zone axis)

Figure 4: Laue diffraction patterns (a) Transmission method and (b) Back-reflection method.
• For transmission patterns the curves are generally *ellipses or hyperbolas* (Figure 3a). For back reflection patterns they are usually *hyperbolas* (Figure 3b)

• The spots which lie on any one curve are reflections from planes which belong to one zone

• Each diffracted beam in the *Laue* method has a different wavelength

• The *Laue* method is used mainly for the determination of crystal orientation and assessment of crystal quality because the positions of the spots on the film depend on the orientation of the crystal with respect to the incident beam.

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**POWDER METHOD**

• In this method, *characteristic X-ray radiation* of fixed wavelength (monochromatic) is used

• The material to be studied is in the form of a very fine powder, each particle of the powder is a very small crystal

• In this method, we take a monochromatic X-radiation of one fixed wavelength and place the crystal (powder material to be studied) in front of the beam (Figure 5a).

• If one plane is set at exactly the correct value of $\theta$ for diffraction, then we observe one and only one reflected (diffracted) beam from that crystal.
Imagine now, still holding the crystal fixed at the angle \( \theta \), we rotate the crystal around the direction of the incident X-ray beam so that the plane causing a reflection is still set at the angle \( \theta \) relative to the X-ray beam.

The reflected beam will describe a cone as shown in Figure 5b. The axis of this cone coincides with the axis of the incident beam.

In the powder material the crystals are not rotated. However, there are so many randomly oriented crystals that there will be some with \((hkl)\) planes which make the right Bragg angle with the incident beam.
• We will have many reflected beams each giving one observable point.

• Imagine when these many crystals are rotated about the axis of the incident X-ray beam, we will have many cones traced out by these reflected beams.

• Since there are millions of crystals in the powder material, there will be many crystals in that powder which will be in a position to diffract the incident beam and there will be enough of them to get the effect of a continuous point reflections which will be lying along the arc of the cone.

• A separate cone is formed for each set of differently spaced lattice planes.

• This is the basis of the powder or Debye-Sherrer method which is the most common technique used in X-ray crystallography.

• The incident beam is in the plane of the circle.

• The cones of diffracted radiation interact with the film in lines which are generally curved except at $2\theta = 90^\circ$ in which case they are straight.
• Figure 6a shows schematically three cones and Figure 6b shows what the film looks like when it is unrolled and laid out flat.

• From the measured position of a given diffraction line on the film, \( \theta \) can be calculated; since \( \lambda \) is fixed and known, the interplanar spacing \( d \) of the reflecting planes which produced the line can be calculated.

Figure 6: Debye-Sherrer powder method: (a) relation of film to specimen and incident beam, (b) appearance of film when laid out flat
What is a powder Camera-(Debye Sherrer Camera)?

- A powder camera (Figure 7) consists of a metal cylinder at the centre of which is the sample.
- The powdered material (which has a diameter of about 0.3 mm) is often glued onto a glass rod, or placed into a thin glass tube.
- The sample must be placed accurately on the axis of the cylinder and must be rotated about its axis so that the randomness of the particles of powder shall be as great as possible.

Figure 7: Schematic of Debye-Sherrer camera, with cover plate removed
• A strip of X-ray film is placed accurately inside the cylinder (on its perimeter).

• Punched into one side of the film is a hole for the beam collimator and punched

• The appearance of the diffraction pattern on the film strip after development depends on the way the film is placed in the camera.

• There are three mounting in common use, which differ in the position of the free ends of the film relative to the incident beam (Figure 8)
Determination of Accurate Lattice Parameters From Powder Photographs

- The pattern of lines on a photograph represents possible values of the Bragg angles $\theta$ which satisfy the Bragg law for diffraction.

- We need to derive the values of $\theta$ from the powder photograph.

- The lattice parameter, "a" can be calculated using an appropriate formula (which depends on the type of unit cell)

- The way in which $\theta$ is measured depends on the method of film mounting as illustrated in Figure 8

In the method shown in Figure 8c, we find the Bragg angle $\theta$ for any pair of lines by measuring the distance $S$ between the centre of the exit hole and the diffraction line

- The angle between a pair of lines (two lines) originating from the same cone is $= 4\theta$. Thus:

$$\frac{S}{2\pi R} = \frac{4\theta}{360}$$

- $R$ is the camera radius.
- Typical cameras have $R = 28.65$ mm (5.73 cm); this gives $2\pi R = 180$.
- The measured value of $S$ is therefore given by:

$$S = 2\theta$$