

CRYSTALLOGRAPHY

Q1. Derive Expression for Interplanar spacing.

The perpendicular distance between any two planes in a set of parallel planes is called as the interplanar distance for that set of planes. Consider a plane ABC which has a parallel plane A'B'C' placed at the origin.

Then the perpendicular distance between the plane ABC is the interplanar distance for this set of parallel planes. Let the plane ABC shown in *Figure 1* belongs to the family of planes whose miller indices are (h,k,l) and ON is normal

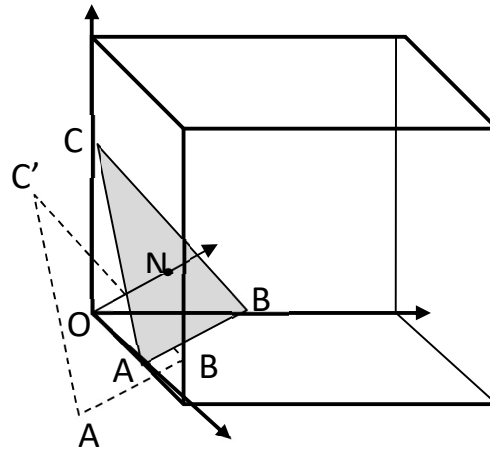


Figure 1: Interplanar Spacing

drawn to a plane A'B'C' parallel to plane ABC. Thus, ON is the interplanar distance for this family and will be represented as d_{hkl} . Let α , β , and γ be the angles normal ON makes with coordinate axes X, Y and Z respectively. For any vector 'ON' the cosine ratios of the angles that it makes with the axis are related as follows:

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \text{ -----(1)}$$

From the *Figure 1* we can find the cosine ratios as follows:

$$\cos \alpha = \frac{l(ON)}{l(OA)}, \cos \beta = \frac{l(ON)}{l(OB)}, \cos \gamma = \frac{l(ON)}{l(OC)}$$

As, $ON = d_{hkl}$, we get

$$\cos \alpha = \frac{d_{hkl}}{l(OA)}, \cos \beta = \frac{d_{hkl}}{l(OB)}, \cos \gamma = \frac{d_{hkl}}{l(OC)} \text{ -----(2)}$$

Miller Indices of a plane are by definition the reciprocals of intercepts of that plane on co-ordinate axis in terms of its lattice parameters. For the plane

ABC its intercepts on axis are OA, OB and OC respectively. Hence Miller indices can be written as:

$$h = \frac{a}{l(OA)}, k = \frac{b}{l(OB)}, l = \frac{c}{l(OC)}$$

For a cubic unit cell $a=b=c$; hence

$$h = \frac{a}{l(OA)}, k = \frac{a}{l(OB)}, l = \frac{a}{l(OC)} \text{ ----- (3)}$$

Putting OA, OB and OC from (3) into equation (2) we get

$$\cos \alpha = \frac{h d_{hkl}}{a}, \cos \beta = \frac{k d_{hkl}}{a}, \cos \gamma = \frac{l d_{hkl}}{a} \text{ ----- (4)}$$

Substituting the cosine ratio obtained in (4) into (1) we get,

$$\left(\frac{h d_{hkl}}{a}\right)^2 + \left(\frac{k d_{hkl}}{a}\right)^2 + \left(\frac{l d_{hkl}}{a}\right)^2 = 1 \text{ ----- (5)}$$

Rearranging (5) for d_{hkl} gives,

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

This is the expression for interplanar distance in any (hkl) set of atomic planes and its applicable only to cubic crystal structure.

Q2. Explain Bragg's law.

(M.U. Dec. 2013, 2015, 2016, 2017, 2018; May 2010, 2012, 2013, 2018, June 2019) [8 Marks]

A crystal acts like collection of **sets of parallel planes** that consist of atoms. Each plane in a given set has the **same distribution of atoms**. In a crystal there are several sets of planes, each set oriented in different direction. Each set is characterized by **different inter-planar spacing**. Bragg suggested that when a beam of X-rays falls on the crystal, each atom acts as the **scattering center** and emits secondary X-rays giving rise to **reflected wave-fronts** (by Huygens's theory). If in a given orientation of crystal, planes rich with atoms are facing the incident X-rays, then we get **intensity maxima at different**

angles with respect to incident direction. Thus, a very simple design of intensity spots on photographic plate will indicate atomic arrangement in the crystal plane.

Figure 2 shows a set of parallel atomic planes in a crystal, 'd' is the interplanar spacing for the set. Suppose an X-ray beam is incident at a glancing angle ' θ ' on the set. Let AB & A'B' represent two parallel X-

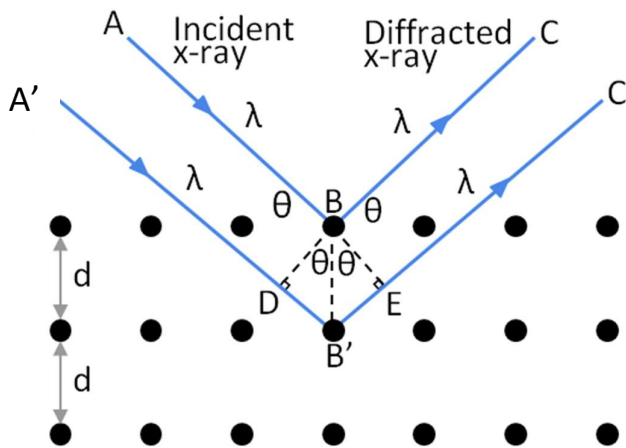


Figure 2: Xray diffraction from crystal lattice

rays which are reflected by two atoms at points B and B' in adjacent atomic layers and rays BC & B'C' represent reflected rays. Construct a perpendicular from B on the ray A'B' meeting it at D and on ray B'C' meeting it at E. We need to now calculate the path difference between two light rays, one travelling path A-B-C and other travelling path A'-B'-C'. Since before points B-D and after points B-E the light rays have traveled same distance, the physical path difference (Δ) between them is ($DB' + B'E$).

$$\therefore \Delta = DB' + B'E \text{-----(1)}$$

From geometry of *Figure 2*,

$\Delta BDB'$ is congruent to $\Delta BEB'$

$$\therefore \angle DBB' = \angle EBB' = \theta \text{-----(2a)}$$

$$\therefore DB' = B'E \text{-----(2b)}$$

Substituting (2b) in (1)

$$\therefore \Delta = 2DB' \text{-----(3)}$$

From $\Delta BDB'$, we have,

$$\sin\theta = \frac{DB'}{BB'} \text{ -----(4)}$$

$$\therefore DB' = BB' \sin\theta \text{ -----(5)}$$

But $BB' = d$ (inter-planar spacing), hence,

$$DB' = d \sin\theta \text{ -----(6)}$$

Substituting (6) in (3) we get,

$$\Delta = 2d \sin\theta \text{ -----(7)}$$

For maximum resultant intensity due constructive interference between these two rays, we must have

$$\Delta = n\lambda \text{ -----(8)}$$

where, $n = 1, 2, 3, \dots$ and λ' – wavelength of incident X – rays

Comparing (8) and (7) we get,

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

This relation is known as **Bragg's law**.

The max value of $\sin\theta$ is 1. Therefore, Bragg reflection can occur only for wavelength $\lambda < 2d$ and **d is of the order of 1\AA** . This is why we cannot use visible light which has λ of the order of 1000\AA .

Q3. Explain Bragg's X-ray Spectrometer and its use to analyses crystal structures.

(M.U. Dec. 2013, 2015, 2016, 2017, 2019; May 2010, 2012, 2013, 2018;

June 2019) [5 Marks]

Bragg devised an apparatus to investigate the **structure of single crystal** by using **X-rays**. The apparatus is used to measure **glancing angle 'θ'**. He used crystal as a **reflecting grating** and not as a transmission grating.

Experimental arrangement

of the set up is shown in *Figure 3a*,

it consists of three main parts: the **collimator**, **telescope** and the **turn table**.

X-rays entering through the collimator are adjusted using slit 'S1'. These are then made to fall on a crystal 'C' which is mounted on the turn-table of the spectrometer. X-rays

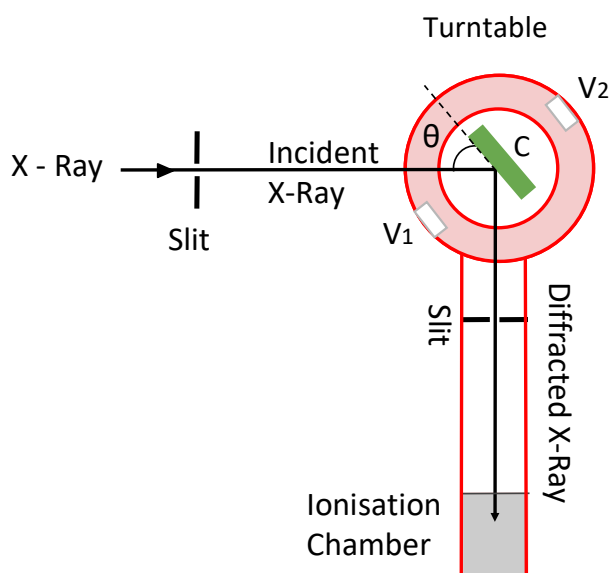


Figure 3a: Bragg's X-Ray Spectrometer

reflected from the crystal are gathered by the telescope arm which has an ionization chamber mounted at the extreme end. Production of ionization current is the indication that, diffracted X-rays have been gathered by the telescope arm successfully.

Two Vernier scales V1 and V2 are attached to turn-table placed on a circular scale, they help to measure the glancing angle ' θ ' shown in *Figure 3a*.

Working:

A strong monochromatic X-ray beam is incident on the crystal face from S1. The diffracted beam after passing through the slit S2 enters the ionization chamber mounted on the telescope arm. This arm is rotated until gas in the ionization chamber is ionized by the X-ray and ionization chamber reads ionization current. This position can be read from the Vernier. The resulting ionization current is a measure of intensity of X-rays reflected by the crystal. Then the turn-table on which the crystal is mounted is rotated through small angles, while the arm carrying the ionization current is rotated through double the angles, and the ionization current is measured each time.

The curve of intensity i.e. **ionization current** against **glancing angle 'θ'** is plotted as shown in *Figure 3b*. It is observed that for certain values of 'θ', the **intensity of ionization current increases abruptly**.

Determination of Crystal structure: -

Suppose for the particular crystal used for Bragg's spectrometer, strong reflections from the set of planes (100), (110) and (111) are obtained for angles $\theta_1, \theta_2, \theta_3$ respectively

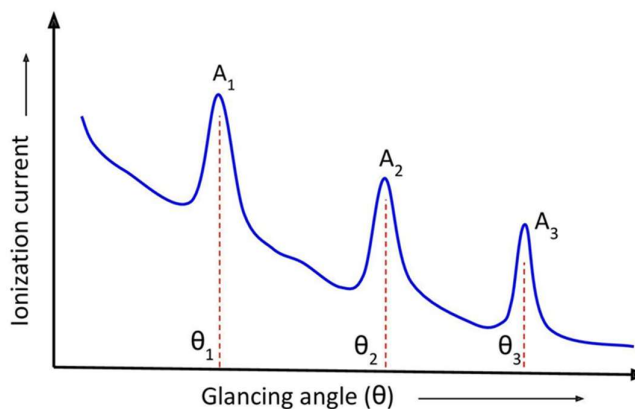


Figure 3b: Variation of Ionization current against Glancing angle

in the first order ($n=1$) reflection because they are planes rich in terms of atoms. Substituting in Bragg's equation ($2d\sin\theta=n\lambda$) we have

$$2d_{100}\sin\theta_1 = \lambda \text{ -----(1a)}$$

$$2d_{110}\sin\theta_2 = \lambda \text{ -----(1b)}$$

$$2d_{111}\sin\theta_3 = \lambda \text{ -----(1c)}$$

From the (1) we can deduce

$$d_{100} : d_{110} : d_{111} :: \frac{1}{\sin\theta_1} : \frac{1}{\sin\theta_2} : \frac{1}{\sin\theta_3} \text{ -----(2)}$$

The $\theta_1, \theta_2, \theta_3$ can be obtained from graph and hence the $\sin\theta_1, \sin\theta_2, \sin\theta_3$ can be calculated to eventually find $d_{100} : d_{110} : d_{111}$.

The ratio of d_{100}, d_{110} and d_{111} for SC, BCC and FCC is previously known which is as follows,

$$\text{SC } d_{100} : d_{110} : d_{111} \text{ ----> } 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} \text{ -----(3a)}$$

$$\text{BCC } d_{100} : d_{110} : d_{111} \text{ ----> } 1 : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} \text{ -----(3b)}$$

$$\text{FCC } d_{100} : d_{110} : d_{111} \text{ ----> } 1 : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}} \text{ -----(3c)}$$

By comparing (2) with (3), one can determine the crystal structure as to whether it is SC, BCC or FCC.

Q4. Define Miller Indices.

(M.U. Dec. 2009, 2013) [5 Marks]

Miller Indices of a particular atomic plane are **reciprocals of intercepts** of that plane on co-ordinate axis (The intercepts are measured in terms dimensions of the unit cell). Miller indices is a way of labelling the planes. They are represented as an **ordered triplet (h, k, l)** where h corresponds to reciprocal of x intercept, while k corresponds to reciprocal of y intercept and k corresponds to reciprocal of z intercept. Miller indices for a set of parallel planes are the same. Simplest examples are;

Consider the given plane ABC shown in a **unit cell**

(A=1, B=1 and C=1), hence its intercepts are:

x-intercept = 1

y-intercept = 1

z-intercept = 1

Miller Indices are the reciprocals of intercepts

Miller Indices (h, k, l) = $(\frac{1}{1}, \frac{1}{1}, \frac{1}{1}) = (1, 1, 1)$

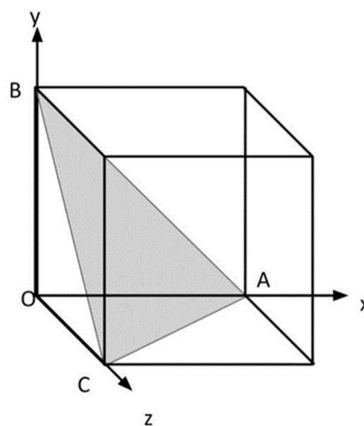


Figure 4a: Plane (111)

Sometimes planes can be **parallel to one of the axes** here in the *Figure 4b* its parallel to the y axis in this case, the intercepts are:

x-intercept = 1

y-intercept = ∞

z-intercept = 1

Miller Indices are the reciprocals of intercepts

Miller Indices $(h, k, l) = \left(\frac{1}{1}, \frac{1}{\infty}, \frac{1}{1}\right) = (1, 0, 1)$

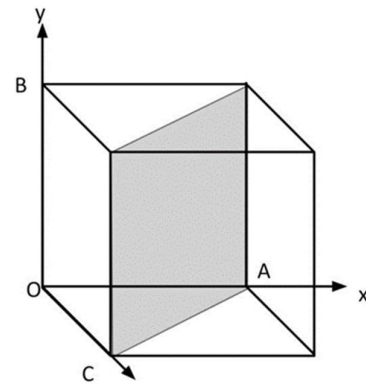


Figure 4b: (101)

Sometimes planes can be **parallel to the xy, yz or xz planes**, the plane shown in the *Figure 4c* is parallel to the yz plane in this case, the intercepts are:

x-intercept = 1

y-intercept = ∞

z-intercept = ∞

Miller Indices are the reciprocals of intercepts

Miller Indices $(h, k, l) = \left(\frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty}\right) = (1, 0, 0)$

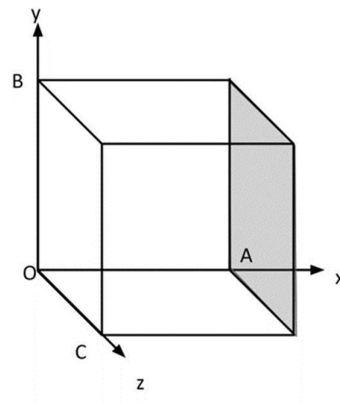


Figure 4c: (111)