

# Crystallography

Kumkum Sanyal

Applied Physics Section  
Thadomal Shahani Engineering College.  
Bandra West, Mumbai - 400050

`kasanyal@gmail.com`

February 28, 2021

# Unit 02 : Crystallography

## Prerequisites :

(Crystal Physics → Crystallographic parameters, Unit cell, Space lattice;

Crystal structure → Simple cubic, Body-centered cubic, Face-centered cubic, Diamond structure;

X-rays → Production, Properties)

## Contents :

- Miller indices
- Interplanar Spacing
- X-ray diffraction and Bragg's law
- Determination of Crystal structure using Bragg's diffractometer

# Basic Terms and Definitions of Crystallography

- **Crystal:** A crystal is a solid in which constituent atoms, ions or molecules are arranged in a regular, periodic repetitive manner in three-dimensional space extending up to infinity.
- **Space lattice:** A three-dimensional array of dimensionless points in space, each of which has an exactly identical surrounding of neighboring points.
- **Crystallographic parameters:** The translational vectors or the basis vectors  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  together with the inter-axial angles between them  $\alpha$ ,  $\beta$ ,  $\gamma$  are known as lattice parameters.
- **Unit Cell:** The smallest repeat unit of a crystal structure in three-dimension, which shows the structural properties of the bulk crystal.

# Cubic Unit Cell

- The three lattice constants  $a, b, c$  are equal and the three inter-axial angles  $\alpha, \beta, \gamma$  are all  $90^\circ$ .
- There is one primitive cell **simple cubic (SC)** and two non-primitive cells **body-centered cubic (BCC)** and **face-centered cubic (FCC)** structures.
- Effective number of atoms ( $N_{eff}$ ): SC=1, BCC=2, FCC=4.
- Volume of the cell ( $V$ ):  $a^3$ .
- Atomic radius ( $r$ ): Half of the nearest neighbour distance;  
SC =  $\frac{a}{2}$ , BCC =  $\frac{\sqrt{3}a}{4}$ , FCC =  $\frac{a}{2\sqrt{2}}$ .
- Co-ordination number ( $n$ ): Number of nearest neighbour atoms;  
SC = 6, BCC = 8, FCC = 12.
- Atomic Packing Fraction (**apf**): Ratio of volume of atoms and volume of the cell;  
SC = 0.52, BCC = 0.68, FCC = 0.74.

# Miller Indices for Planes

- **Definition:** Miller indices for planes are defined as the reciprocal of the intercepts made by a plane on the three crystallographic axes, reduced to minimum numbers.
- Miller indices form a **notation system** in crystallography for specifying planes and directions in crystal lattices.
- A group of three numbers **(hkl)** the Miller indices indicates the orientation of a plane or a set of parallel planes of atoms in a crystal.
- The orientation of a crystal plane may be defined by considering how the plane intersects main crystallographic axes of the solid.
- The set of numbers in the Miller indices **(hkl)** therefore quantify the intercepts and thus may be used to uniquely identify the plane.

# Procedure to assign Miller Indices

- Identify the intercepts made by a plane on the three crystallographic axes  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$ .
- Express the intercepts in terms of lattice constants.
- The reciprocal of these intercepts are computed.
- Fractions are cleared by multiplying them with the LCM to get the three Miller indices (**hkl**).
- This operation of multiplication simply generates a parallel plane which is at a different distance from the origin of the particular unit cell being considered.
- Since the unit cell repeats in space, the notation actually represent a family of planes.

## Example to assign Miller Indices

- The following discussion on Miller indices will involve cubic crystal system only (all the lattice constants are equal to the cube length  $a$ ).
- If a plane intersects axes  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  (or equivalently  $\vec{X}$ ,  $\vec{Y}$ ,  $\vec{Z}$  respectively) at a distance  $1a$ ,  $2a$ ,  $3a$  respectively, then to find Miller indices, the steps involved are:
  1. Intercepts :  $1a$ ,  $2a$ ,  $3a$
  2. Numerical parameter :  $1$ ,  $2$ ,  $3$
  3. Reciprocal :  $1$ ,  $(\frac{1}{2})$ ,  $(\frac{1}{3})$
  4. LCM :  $6$
  5. Clearing of fraction :  $1 \times 6$ ,  $(\frac{1}{2}) \times 6$ ,  $(\frac{1}{3}) \times 6 = 6, 3, 2$
- These integer numbers are then parenthetically enclosed  $(632)$  and designate that specific crystallographic plane in the lattice.

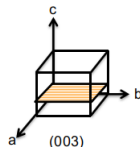
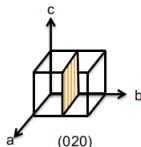
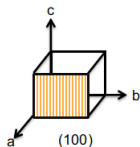
# Features of Miller Indices

- In general, if  $(a, b, c)$  are the three lattice constants along the three crystallographic axes and  $(hkl)$  are the Miller indices of a particular plane, then the corresponding intercepts are  $(\frac{a}{h}, \frac{b}{k}, \frac{c}{l})$  respectively along the three axes.
- If a plane is parallel to an axis, the corresponding intercept is taken to be at infinity so that the reciprocal comes as zero.
- If an intercept is negative, the corresponding index will have a bar on top of it. Example :  $(\bar{h}kl)$  denotes x-intercept to be negative.
- All equally spaced parallel planes with a particular orientation have same index number  $(hkl)$ .
- A plane passing through the origin is defined in terms of a parallel plane having non-zero intercept.



# Miller Indices of Specific Planes

1. **Surface planes** : characterised by the fact that these planes are parallel to two axes while having only one definite intercept. Therefore two zeros will appear in the  $(hkl)$  format. Example  $(100)$ ,  $(020)$ ,  $(003)$ .

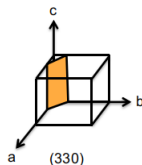
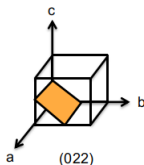
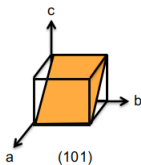


*To draw surface plane in an unit cube :*

- Define the coordinate system along with the origin .
- Mark the intercept on the axis.
- Move from that point parallel to the two specified axes till the end of the cube.
- Join smoothly to make a surface plane.

## Specific Planes (contd.)

2. **Diagonal planes** : characterised by the fact that these planes are parallel to one axis and having two definite intercepts. Therefore only one zero will appear in the  $(hkl)$  format. Example  $(101)$ ,  $(022)$ ,  $(330)$ .

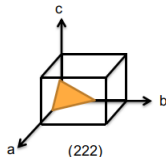
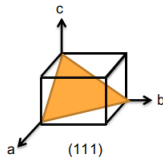


*To draw diagonal plane in an unit cube :*

- Define the coordinate system along with the origin.
- Mark the intercepts on the axes.
- Join them with a line.
- Move parallel to the specified axis from both the ends of that line till the end of the cube.
- Join the two new points to get the diagonal plane.

## Specific Planes (contd.)

3. **Triangular Planes** : characterised by the fact that all the three intercepts on the three axes are finite. Therefore all the three digits will appear in the  $(hkl)$  format. Example:  $(111)$ ,  $(222)$ .

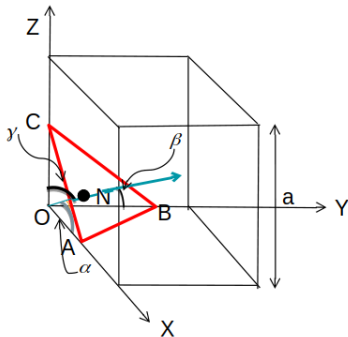


*To draw triangular plane in an unit cube :*

- Define the coordinate system in the cube along with the origin.
- Mark the three intercepts on the three axes.
- Join them to form a triangle in the cube.

# Interplanar Spacing $d_{hkl}$

**Interplanar Spacing :** The perpendicular distance  $d$  between two parallel consecutive planes denoted by Miller indices  $(hkl)$ .



- The plane ABC described by  $(hkl)$  has intercepts OA, OB, OC on the three axes. ON is the normal drawn to ABC from origin O.
- Assume that a parallel plane passes through O. Thus ON is the required interplanar spacing  $d$ .
- Let the three axes OX, OY, OZ make angles  $\alpha$ ,  $\beta$ , and  $\gamma$  respectively with ON.
- If  $a$  is the cube length then the intercepts are  $OA = a/h$ ;  $OB = a/k$ ;  $OC = a/l$ .
- $\cos \alpha = ON/OA$ ;  $\cos \beta = ON/OB$ ;  $\cos \gamma = ON/OC$ .
- Use the identity  $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$

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

# Features of Interplanar Spacing

## Simple Cubic System

- The interplanar spacing for **surface planes** designated by **(100)** will be  $d_{100} = 1a$
- The spacing for **diagonal planes** designated by **(110)** will be  $d_{110} = \frac{a}{\sqrt{2}}$
- The spacing for **triangular planes** designated by **(111)** will be  $d_{111} = \frac{a}{\sqrt{3}}$ .
- The **reciprocal spacing** is the inverse of interplanar spacing i.e.  $1/d_{hkl}$

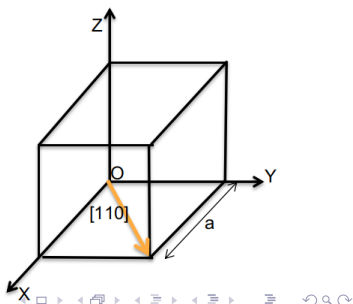
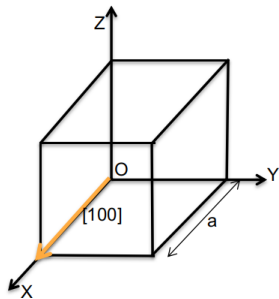
$$\begin{aligned}\text{Ratio of Spacing} - d_{100} : d_{110} : d_{111} &= 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} \\ \text{Ratio of Reciprocal Spacing} - \frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} &= 1 : \sqrt{2} : \sqrt{3}\end{aligned}$$

# Miller Indices for Direction

- A line joining any two lattice points defines a crystallographic direction.
- If one end of the line is at the origin then the vector components of the lattice site of the other end are defined to be the indices of direction.
- Since the vector components are multiples of lattice constants, therefore the linear coefficients attached to the lattice constants give the required indices.
- These coefficients, after reducing to minimum numbers (where 1 is the only common multiplier) are then enclosed within square brackets to give Miller indices for direction  $[hkl]$ .

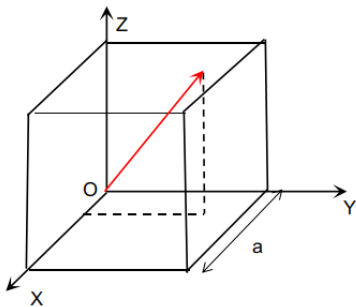
## Features of Indices for direction

- If any of the components is negative, the corresponding index will have an overhead bar, example:  $[1\bar{2}3]$  indicating Y-component to be negative.
- Double zero in the  $[hkl]$  format denotes a direction along the axis, example:  $[100]$  indicates direction along X axis.
- Single zero in the  $[hkl]$  format gives a direction on a two-dimensional plane, example:  $[110]$  indicates a direction on the XY plane.



# Drawing of Crystallographic Direction

Take the example of Miller indices  $[123]$  to show the direction in a cubic unit cell. Here  $[123]$  denotes a line whose one end is at the origin with coordinates  $(0,0,0)$  and the other end has the coordinates  $(1a,2a,3a)$ ;  $a$  is the lattice constant.



1. Here the linear coefficients are 1,2,3.
2. Divide all of them by the highest digit i.e. (3).
3. The new coefficients are  $(\frac{1}{3})$ ,  $(\frac{2}{3})$ , 1.
4. Thus the new co-ordinates become  $(\frac{1}{3})a$ ,  $(\frac{2}{3})a$ ,  $1a$ .
5. The division only reduces the length of the vector not it's direction.
6. In an unit cell locate the point with coordinates  $(\frac{1}{3})a$ ,  $(\frac{2}{3})a$ ,  $1a$ .
7. Join it with the origin  $(0,0,0)$  to show the required direction.



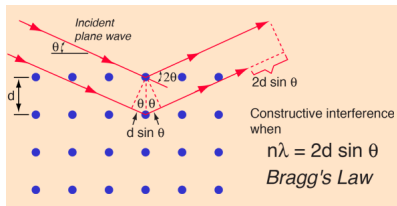
# Diffraction Basics

- X-rays are high energy electromagnetic radiation with wavelength in the range from  $1\text{\AA}$  to  $100\text{\AA}$ .
- X-rays being electromagnetic waves undergo diffraction phenomenon.
- In physical optics, satisfactory result is obtained whenever the spacing of the adjacent lines on the diffraction grating is of the same order of magnitude as the wavelength of light used.
- In X-rays this criterion is satisfied by using crystals with their regular lattices acting as a kind of three dimensional grating.
- The spacing between adjacent layers of atoms is comparable with the wavelength of the X-rays.

# X-Ray Diffraction

- Each atom in a crystal can scatter electromagnetic waves.
- An atom in a constant external electric field becomes polarised, thereby giving rise to an electric dipole.
- An oscillating dipole is created when the constant field changes to an alternating field.
- The oscillating dipole will then radiate electromagnetic waves of same frequency as that of the external field.
- The atoms in the crystal thus absorb the incident plane waves and give out secondary spherical waves with same frequency in all directions.
- In certain directions the scattered waves will interfere constructively giving diffraction maxima.

# Derivation of Bragg's Law



- X-rays are incident on the parallel atomic planes ( $hkl$ ) making an angle  $\theta$  with the atomic plane.
- X-rays are monochromatic waves with wavelength  $\lambda$ .
- Constructive interference for the outgoing radiation will occur only when the path difference between the two diffracted rays is an integral multiple of wavelength  $\lambda$ .
- The path difference is equal to  $2d_{hkl} \sin \theta$ .
- Therefore for maximum intensity Bragg's law gives  $2d_{hkl} \sin \theta = n\lambda$   $n = 1, 2, 3, \dots$
- Here  $n \rightarrow$  order of diffraction,  $\theta \rightarrow$  glancing angle or Bragg angle.
- The total angle by which the incident ray is deflected is  $2\theta$ .

# Bragg's Spectrometer

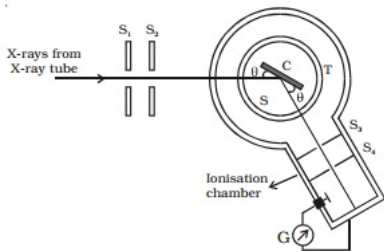


Fig Bragg's spectrometer

- The slits  $S_1, S_2$  collimate the X-ray beam into fine pencil.
- $C$  is the crystal sample mounted on a turn table  $T$ .
- The table can rotate around a vertical axis.
- The circular scale  $S$  on the table gives the angle of rotation.
- The slits  $S_3, S_4$  allow only the reflected X-ray beam to enter the ionization chamber(I.C).
- $G$  the galvanometer measures the current generated in the chamber.
- The ionization current is a measure of the intensity of X-rays reflected by the crystal.

## Spectrometer Contd.

The ionization chamber is so coupled with the turn table that the angle of rotation of the chamber is twice that of the crystal.

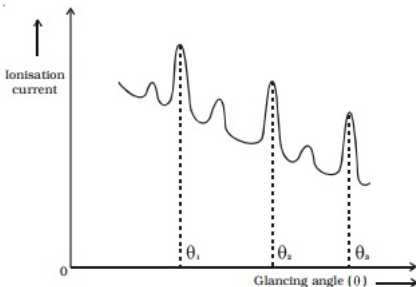


Fig Plot of glancing angle and ionisation current

- The turn table is rotated till a sharp increase in the ionization current (the peak) is detected.
- The corresponding glancing angle is noted from the scale on the turn table.
- The first peak corresponds to first order ( $n = 1$ ), second peak to second order ( $n = 2$ ) and so on.
- Knowing the angle  $\theta$  and the spacing  $d$ , one can find the wavelength of X-rays.

# Structure Determination

- The interplanar spacing  $d$  can be obtained for an unknown sample using the  $\theta$  value from the graph and the known wavelength  $\lambda$  of the X-ray.
- Thus  $d$  is obtained for different orientation of the sample namely (100), (110), (111) planes.
- Let  $\theta_1$ ,  $\theta_1'$  and  $\theta_1''$  be the corresponding first order glancing angles.
- Therefore  $d_{(100)} = \frac{\lambda}{2 \sin \theta_1}$ ,  $d_{(110)} = \frac{\lambda}{2 \sin \theta_1'}$ ,  $d_{(111)} = \frac{\lambda}{2 \sin \theta_1''}$
- Hence  $\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = \sin \theta_1 : \sin \theta_1' : \sin \theta_1''$
- If the ratio of reciprocal spacing follows the value as  $1 : \sqrt{2} : \sqrt{3}$  then the sample has a **SC** structure.
- Bragg's law specifies the diffraction condition for primitive cells such as simple cubic (SC) structure.

# Non-Primitive Cells

- Combine Bragg's law and interplanar spacing to get
$$\sin^2 \theta = \frac{n^2 \lambda^2}{4a^2} (h^2 + k^2 + l^2)$$
- In non-primitive cubic cells some of the diffractions predicted by Bragg's law do not occur.
- There are some selection rules for Miller indices of different planes in non-primitive cubic cells leading to allowed reflections from them.
- Conditions on Miller indices ( $hkl$ ) for allowed reflections:

BCC Lattice :  $(h + k + l) \rightarrow \text{even}$   
FCC Lattice :  $(hkl) \rightarrow \text{all odd or all even}$

## Non-Primitive Cells contd.

- Let  $\theta_1$  and  $\theta_2$  be the two angles for which diffraction maximum occurs from two corresponding planes ( $h_1k_1l_1$ ) and ( $h_2k_2l_2$ ) respectively.
- Then 
$$\frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{(h_1^2 + k_1^2 + l_1^2)}{(h_2^2 + k_2^2 + l_2^2)}$$
- The first two permissible sets of (hkl) values for BCC lattice are (110) and (200).
- In case of FCC these values are (111) and (200).
- Therefore: 
$$\frac{\sin^2 \theta_1}{\sin^2 \theta_2} = \frac{1}{2} = 0.5 \text{ for BCC and}$$
$$= \frac{3}{4} = 0.75 \text{ for FCC .}$$
- The first two diffraction angles can be obtained from the spectrometer data.
- The ratio then will give the idea about the structure.



# Numerical Exercises - 1

1. Determine the Miller indices of a plane parallel to the Z axis and cut intercepts of 2 and  $2/3$  units along X and Y axes, respectively.
2. Deduce the Miller indices of a set of parallel planes which make intercepts in the ratio of  $b:2c$  on the Y and Z axis and parallel to X axis.
3. Draw the following planes and directions in an unit cube:  
a)  $(\bar{1}02)$ ,  $(\bar{2}3\bar{1})$ ,  $(\bar{2}10)$ ,  $(23\bar{2})$  and  
b)  $[2\bar{2}1]$ ,  $[401]$ ,  $[12\bar{3}]$ ,  $[023]$ .
4. Silver has FCC structure and its atomic radius is  $1.414\text{\AA}$ . Find the interplanar spacing for (200) and (111) planes.
5. Calculate the interplanar spacing for (231) plane of a FCC structure whose atomic radius is  $0.175\text{nm}$ .

## Numerical Exercises - 2

6. For a cubic lattice, calculate the distance of (123) and (234) planes from a plane passing through the origin.
7. Monochromatic X-ray beam of wavelength  $5.8189\text{\AA}$  is diffracted by a cubic crystal of lattice constant  $3\text{\AA}$  at a glancing angle  $75.86^\circ$ . Find the Miller indices of the planes for first order diffraction.
8. The smallest angle of Bragg scattering in potassium chloride (KCl) is  $28.4^\circ$  for  $0.30\text{nm}$  X-rays. Find the distance between atomic planes of potassium chloride.
9. A crystal is mounted on a X-ray spectrometer. X-rays are incident at the glancing angles  $5^\circ 28'$ ,  $12^\circ 1'$  and  $18^\circ 12'$  for three reflections. Show that these are successive reflections from the same plane. Also find the spacing.  
Given  $\lambda = 0.586\text{\AA}$ .

## Numerical Exercises - 3

10. The X-rays of wavelength 154.2pm produce reflections from (200) and (111) planes of Cu which has FCC structure and density of 8.935gm/cm<sup>3</sup>. At what angles the diffracted intensity be maximum?
11. Calcite crystals contain scattering planes separated by 0.3nm. What is the angular separation between the first and second order diffraction maxima when X-rays of 0.130nm wavelength are used?
12. The following diffractometer data (expressed as  $2\theta$ ) were generated from a specimen: 14.10°, 19.98°, 24.57°, 28.41°, 31.85°, 34.98°, 37.89°, 40.61°. Determine the crystal structure and the lattice constant. Wavelength used is  $\lambda = 0.574\text{\AA}$ .