

MODULE 2 CRYSTALLOGRAPHY

1) Introduction:

The science of crystallography concerns itself with the study of geometric structure, physical properties & the classification of all types of crystal structure. The knowledge of crystal is very important for us because it has led to the band theory of solids which enables us to understand properties & function of semiconductor devices like transistors, diode, FET, IC, microprocessor, computer etc

2) Definitions & prerequisites

a) SOLIDS

Solids consist of atoms or clusters of atoms arranged in close proximity. The physical structure of a solid & its properties are closely related to the scheme of arrangement of atoms within the solids.

Depending upon the atomic arrangement solids are classified into two categories viz crystalline solids & amorphous solids.

b) Space lattice: A space lattice is defined as an array of points arranged in a regular periodic fashion in 3D space such that each point in the lattice has exactly identical surrounding. These points are called as lattice points or lattice sites. By using a network of lines the lattice points may be joined. The lines are called lattice lines. A plane containing lattice points is known as lattice plane or atomic plane.

c) Basis:

An atom or group of atom associated with the lattice sites is called the basis. The basis must be identical in composition, arrangement & orientation such that the crystal appears exactly the same at one point as it does at other equivalent points. If Basis is single atom then the crystal is said to be monoatomic eg silicon. If Basis is two, then diatomic e.g. NaCl. If more than 2 atoms polyatomic crystal e.g. proteins.

d) unit cell:

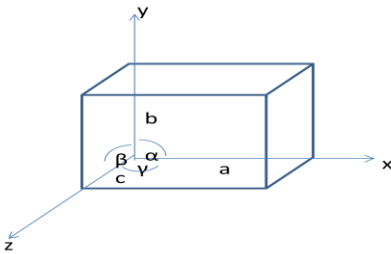
Unit cell is the smallest volume of a solid by the repetition of which entire crystal is constructed. Unit cell possesses all the structural properties of bulk crystal. The unit cell should be chosen in such a way that it conveys all the symmetry of a crystal lattice by having shortest physical size which makes mathematical calculation easy. (I.e. minimal in content of atom).

The importance of unit cell lies in the fact that all possible crystal structures can be reduced to limited basic unit cell geometries. If the atoms are located only at the corners and nowhere else then

It is Primitive unit cell. If there are additional atoms along with the corner atoms then they are called as non primitive unit cell.

e) Lattice parameters

Each unit cell is characterized by six parameters. A typical unit cell is shown below



a, b, c are lattice vectors. The length of vectors becomes measures of the three side of the unit cell. They are called axial lengths. The angle between the sides is termed as interaxial angles. a, b, c axial length and α, β, γ interaxial angles forms lattice parameters.

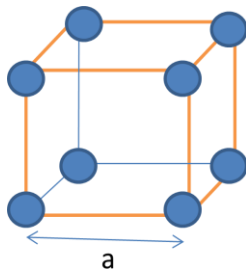
3). Cubic systems:

For a cube $a=b=c$ & $\alpha=\beta=\gamma=90^\circ$. Three space lattices are possible in cubic system. Simple cube, body centered & face centered cube.

3.1) Simple cube:

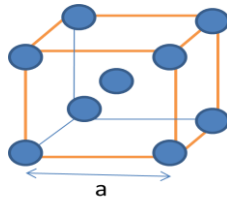
In simple cube, corner atoms touch each other I,e. atoms are arranged along the edges.

For a cube there are 8 corners so there are 8 atoms located at 8 corners of a cube all of them touching each other.



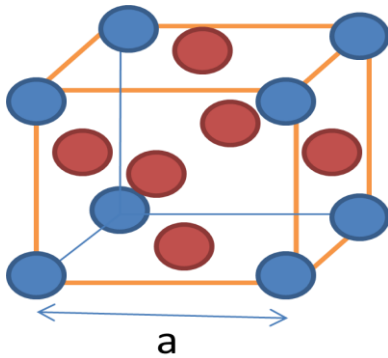
3.2) Body centered cube (BCC):

In BCC, corner atoms do not touch each other but all of them touch an atom which is located at intersection of all body diagonal. Atoms are arranged along the body diagonal.



3.3) Face centered cube (FCC):

In FCC, corner atoms do not touch each other but they touch all face center atoms. A cube has 6 faces, so 6 face atoms.



4) Unit Cell Parameters:

A unit cell is characterized by 7 parameters

i) Atomic radius ii) Coordination number iii) Atomic packing fraction iv) Atoms/ cell or effective number of atoms v) Void Space vi) Density vii) Volume.

Parameters	Simple cubic	Body centered cubic	Face centered cubic
Volume	a^3	a^3	a^3
Atoms/cell	1	2	4
Atomic radius	$a/2$	$\sqrt{3} a/4$	$\sqrt{2} a/4$
CN	6	8	12
APF	52 %	68 %	74 %
Density	$a^3 \quad P = [n \times (A/N)]$	$a^3 \quad P = [n \times (A/N)]$	$a^3 \quad P = [n \times (A/N)]$

SYLLABUS

Q1. What are Miller Indices and explain the procedure to obtain Miller Indices?

ANS:

The imaginary, parallel, equidistant planes passing through the lattice points are called as crystal lattice planes. For a given lattice, we can assign sets of parallel planes oriented in any arbitrary direction. Crystal is an aggregate of atoms in 3D. so there are numerous planes in the crystal. Miller adopted a scheme to nomenclature the planes. The set of three integers used to denote particular plane or a set of parallel planes are called Miller Indices.

Procedure to find Miller Indices:

- 1) Find the Intercept made by plane on the axes
- 2) Take reciprocal of the intercept
- 3) Reduce it to smallest integer by taking LCM.
- 4) Write the value in parenthesis ()

For example

If 1, 2, 3 are intercept made by plane on axes

Reciprocal $1/1, 1/2, 1/3$

LCM = 6

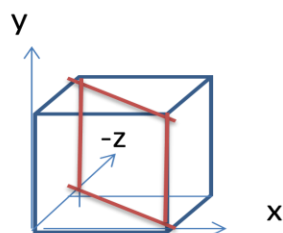
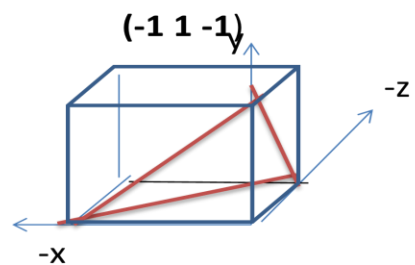
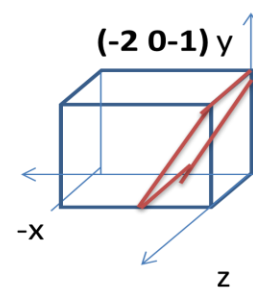
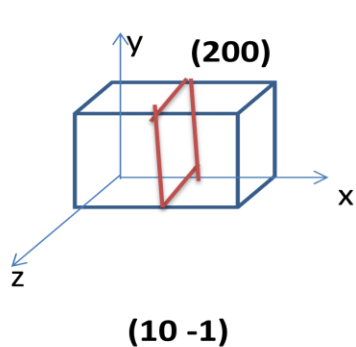
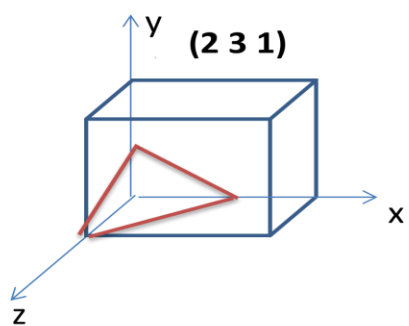
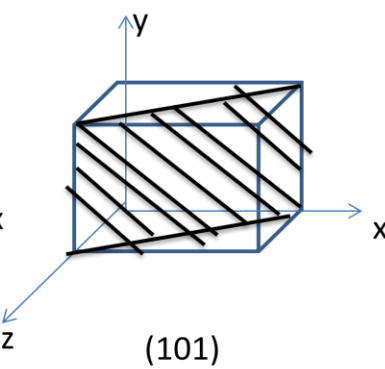
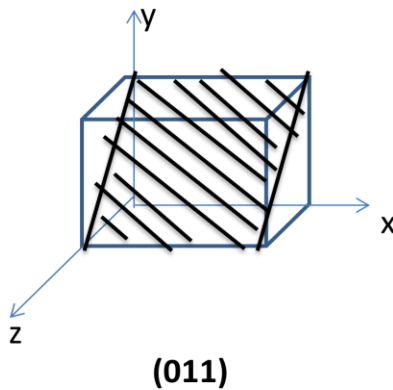
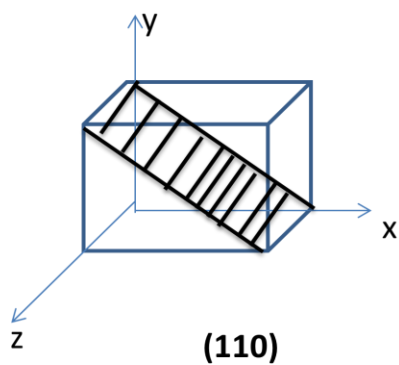
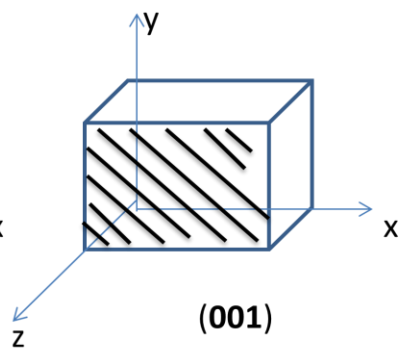
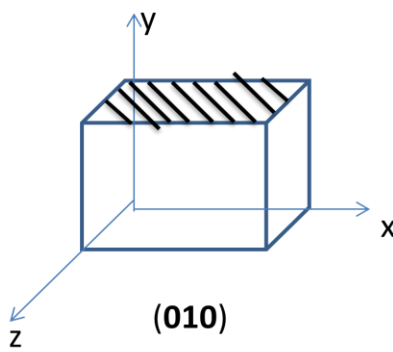
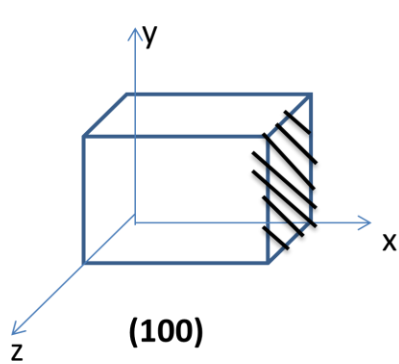
Therefore Miller Indices is (632)

Miller Indices are three smallest integers that bears the same ratio as the reciprocal of the intercepts .

$$h : k : l = 1/u : 1/v : 1/w.$$

- When a plane is parallel to any of the axes its intercept is infinity and miller indices is zero.
- When a plane cuts any axes at its negative part, then MI is distinguished by putting bar on it.
- Parallel planes have same Miller indices.

Q2. Draw the following planes: (100),(010), (001),(-100),(0-10),(00-1),(110),(101),(011),(231),(200),
(-20-1),(10-1),(-11-1)



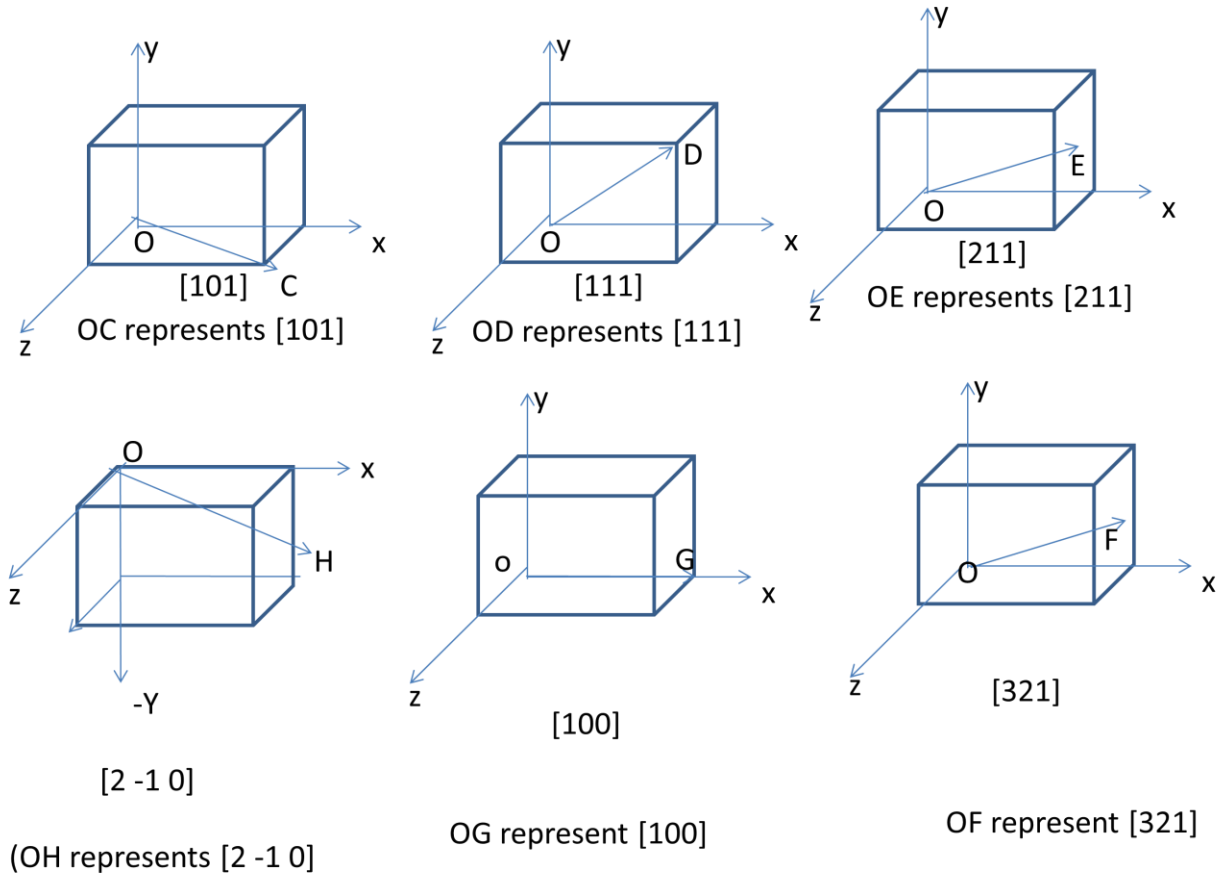
Q3. What is **Crystal lattice direction**.

ANS:

A line normal to a plane is taken as its direction. This line gives an idea about the orientation of the plane. If (hkl) are miller indices then direction are [hkl] written in square bracket.

How to draw direction.

Draw the cubic unit cell, choose appropriate origin and axes. If you have an integer greater than one, divide entire values by the highest index. Assume the above numbers as coordinates of a point. Locate this point in the unit cell. Join this point with the origin to get required direction. Indicate it by an arrow.

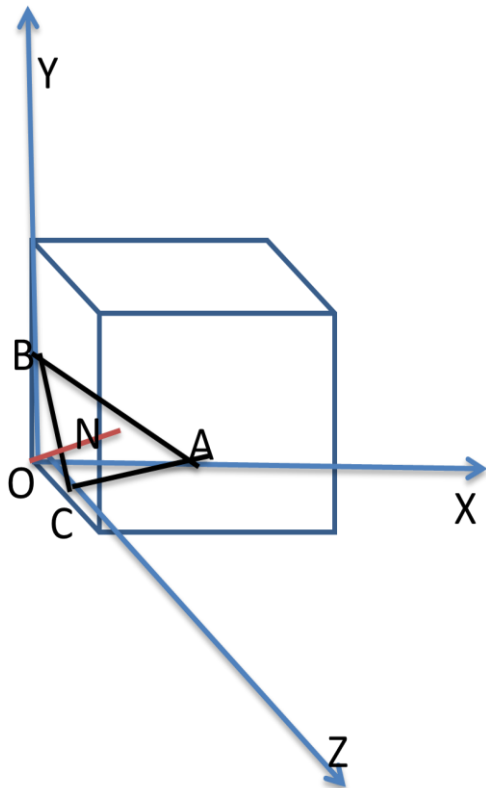


Q4. Derive an Expression for Interplanar distance in a cubic unit cell?

ANS:

Consider a cube of side 'a'. Consider a plane ABC making intercept u, v, w on x, y, z axes respectively and having miller indices (hkl) .

Drop a perpendicular from the origin into the plane. ON = perpendicular distance. Let it be represented by d' . ON makes angle α, β, γ with x, y & z axes respectively.



$$U = OA/a, v = OB/a, w = OC/a$$

$$OA = a.u, \quad OB = a.v, \quad OC = a.w$$

$$\text{We know, } h:k:l = 1/u:1/v:1/w$$

$$\text{Therefore, } OA = a/h, \quad OB = a/k, \quad OC = a/l$$

Join NA, NB & NC

In triangle ONA, ONB, ONC

$$\cos \alpha = ON / OA = d / (a/h) = dh/a$$

$$\cos \beta = ON / OB = d / (a/k) = dk/a$$

$$\cos \gamma = ON / OC = d / (a/l) = dl/a$$

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

$$(dh/a)^2 + (dk/a)^2 + (dl/a)^2 = 1$$

$$\text{Therefore, } d^2/a^2 (h^2 + k^2 + l^2) = 1$$

$$\text{I.e. } d = a/\sqrt{h^2 + k^2 + l^2}$$

Q5. Explain the Importance of planes & direction in crystal

ANS:

The atoms of a crystalline solid are arranged in certain order. The atomic densities changes if approached from different orientation of the crystal. For a given crystal, there are certain planes which are rich in atomic densities. Due to these different atomic densities along different orientation of the crystal, many important properties such as rate of chemical reactions, heat transfer, amount of magnetization, drift velocity of charge carriers etc differ along different directions. Thus, crystal is said to be anisotropic I.e. direction dependent. This anisotropy has led to the concept of planes and directions.

X Rays

1. Introduction:

When a potential difference of a few thousand volts is applied between the electrodes of a discharge tube and pressure in the tube is gradually reduced, walls of the tube opposite to cathode begin to glow with a greenish fluorescence. This is due to invisible rays coming out of cathode so they are called as cathode rays. These rays are used to produce X rays.

Prof Roentgen was performing an experiment to investigate the properties of cathode rays. During one such experiment, he observed that a fluorescent screen kept inadvertently near the tube was glowing when a discharge tube is in operation. He covered the discharge tube completely by black paper and placed a thick wooden screen between discharge tube and the fluorescent screen in order to prevent light passing from the tube to screen. Still when the tube was on the screen was glowing. Therefore, he concluded that some invisible, unknown highly penetrating rays must be emitted by the walls of discharge tube on which cathode rays were incident. These rays are called as x rays. Basically X rays are produced when a beam of high speed electrons strikes a target.

Q6. What are X rays and state the Properties of x rays:

1. X rays are electromagnetic radiation of very short wavelength 1 \AA .
2. They are not deflected by electric or magnetic field
3. They produce fluorescence when they fall upon surface coated with fluorescent materials
4. They cause ionization in gases through which they pass
5. They show diffraction effect.
6. They exhibit particle properties.
7. They have high penetration power.

Q7. Explain the statement " crystal acts as a 3D diffraction grating"? or why the x rays are preferred to study crystalline solids?

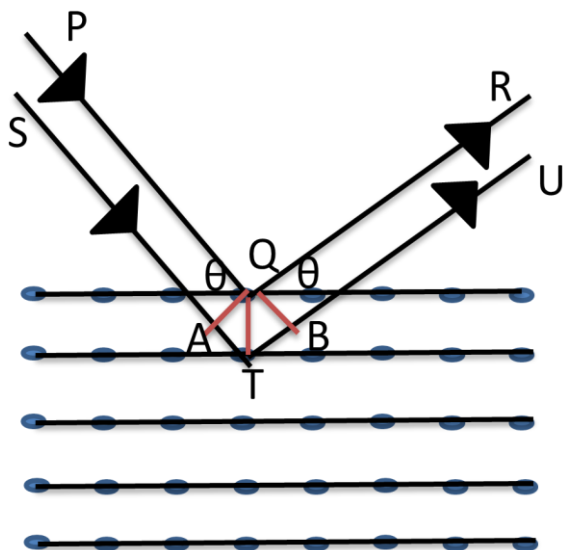
ANS:

Even after the discovery of x rays their physical nature was a great problem to scientist. Some scientist thought them to be high speed particles like cathode rays but more penetrating whereas others regarded them as electromagnetic waves of extremely high frequency.

To test the wave nature, attempts were made to produce interference as well as diffraction effects similar to those observed with light waves. Hence it was soon realized that to produce same order of diffraction with a transmission grating the X ray would require 40 millions ruling per cm and this is beyond practical possibility. Then 1912, Max Von Laue suggested the use of natural crystal as a closely spaced 3D grating. Since the structure of a crystal consists of a 3D array of regularly spaced atoms, Laue reasoned that the equally spaced layers of atoms would act like a diffraction grating.

Q8. Derive Bragg's Law .

Let us consider a set of parallel lattice planes of a crystal separated by distance 'd' apart. Suppose narrow beam of X ray of wavelength λ be incident upon these plane at an angle ' θ ' as shown in the figure



The beam will be reflected in all direction by atoms of various atomic planes. Since refractive index of matter of crystal is nearly equal to unity, practically there is no bending of x rays entering or leaving the crystal.

Consider a ray PQ reflected in the direction QR from first plane and another ray ST reflected in the direction TU from the second plane. Drop perpendicular QA and QB on the incident and reflected rays respectively. The path difference between these two rays will be (AT + TB). The two reflected rays will be in phase or out of phase will depend upon this [path difference. When the path difference (AT + TB) is a integral multiple of wavelength λ , then the two rays will reinforce each other and produce an intense spot.

Thus, condition for reinforcement is $(AT + TB) = n\lambda$

$$AT = TB = d \sin\theta$$

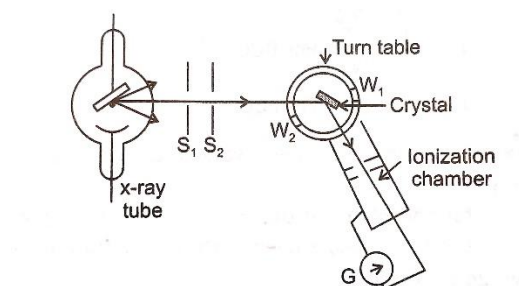
Therefore, $2d\sin\theta = n\lambda$, $n = 1,2,3,4,\dots$ first, second , third order etc

This equation is known as Bragg's Law.

Q9. Explain Bragg's Spectrometer for the investigation of crystal structure?

The schematic diagram of Bragg's x ray spectrometer is as shown in figure.

Diagram



A well collimated monochromatic x ray beam from the target of an x ray tube after passing through slits S_1 and S_2 is incident on the face of crystal. The crystal is mounted on a turn table T with a Vernier which moves on a graduated scale. The glancing angle is therefore can be measured. The rays reflected from crystal after passing through slits S_3 pass into an ionization chamber. The ionization chamber and the turn table so linked together that when turntable rotates through an angle ' θ ', then ionization chamber rotates through ' 2θ '. In this way the beam is always reflected into the ionization chamber whatever its glancing angle is at crystal surface.

The ionization current produced by reflected x ray can be measured by sensible electrometer E . The intensity of reflected beam is max at certain settings of crystal w.r.t incident beam. These maxima occur at those settings where Braggs law $2d\sin\theta = n\lambda$ is satisfied. The ionization current is measured for different value of θ . For certain value of θ , intensity of ionization current is increased. As order of spectra increases intensity decreases. Knowing order and glancing angle from the spectrometer and the wavelength of the incident x ray, interplanar spacing can be determined and hence crystal can be investigated.

Investigation of crystal structure using Bragg's Law:

From the study of crystallography, for a cubic crystal the type of unit cell is given by following ratios:

$$d_{100} : d_{110} : d_{111} :: 1 : 1/\sqrt{2} : 1/\sqrt{3} \quad \text{for simple cubic}$$

$$d_{100} : d_{110} : d_{111} :: 1 : 1/\sqrt{2} : 2/\sqrt{3} \quad \text{for face centered cubic}$$

$$d_{100} : d_{110} : d_{111} :: 1 : 2/\sqrt{2} : 1/\sqrt{3} \quad \text{for body centered cubic}$$

some crystal is cut with their reflecting surface parallel to (100) , (110) and (111) planes and are used in Bragg's x ray spectrometer one after the other for reflecting a monochromatic beam of x rays of wavelength λ . For first order spectrum experimentally found values of θ are

$$\theta_1 = 5^\circ 23', \theta_2 = 7^\circ 37', \theta_3 = 9^\circ 23'.$$

From Bragg's law we have $2d\sin\theta = n\lambda$

$$\text{Therefore, } 2d_{100}\sin\theta_1 = \lambda \quad 2d_{110}\sin\theta_2 = \lambda \quad 2d_{111}\sin\theta_3 = \lambda$$

$$\begin{aligned} d_{100} : d_{110} : d_{111} &= 1/\sin\theta_1 : 1/\sin\theta_2 : 1/\sin\theta_3 \\ &= 1/5^\circ 23' : 1/7^\circ 37' : 1/9^\circ 23' \end{aligned}$$

$$d_{100} : d_{110} : d_{111} :: 1 : 1/\sqrt{2} : 1/\sqrt{3}$$

This result is expected for simple cubic crystal. Therefore given crystal belongs simple cubic.
