UNIT - II

3. X-RAY DIFFRACTION

Directions & Planes in Crystals:

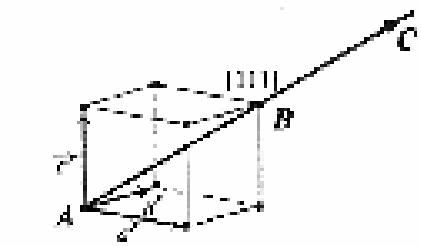
While dealing with the crystals, it is necessary to refer to crystal planes, and directions of straight lines joining the lattice points in a space lattice. For this purpose, an indexing system deviced by Miller known as Miller indices is widely used.

Directions in A Crystal:

Consider a cubic lattice in which a straight line is passing through the lattice points A, B, C etc and 1 lattice point on the line such as point A is chosen as the origin.

Then the vector R which joins A to any other point on the line such as B (position vector) can be represented by the vector eqn.

$$R = n1\ a + n2\ b + n3\ c \text{------ (1) where a, b, c are basic vectors}$$



DIRECTION OF LINE IN A LATTICE

The direction of the vector R depends on the integers n1, n2, n3 since a, b, c are constants. The common multiple is removed and n1, n2, n are re-expressed as the smallest integers bearing the same relative ratio. The direction is then specified as [n1 n2 n3].

R =a+b+c, which provides the value of 1 for each of n1, n2, n3

Thus the direction is denoted as [1 1 1].

All lines in the space lattice which are parallel to the line AB possess either same set of values for n1, n2, n3 as that of AB, or its common multiples.

Ex: 1. The direction that connects the origin and (1/3, 1/3, 2/3) point is [1 1 2].

i.e, (1/3, 1/3, 2/3)

L.C.M = 3.

(1/3x3 1/3x3 2/3x3)= [1 1 2].

2. [2 1 1] is the direction that connects the origin (0, 0, 0) and point (1, 1/2, 1/2)

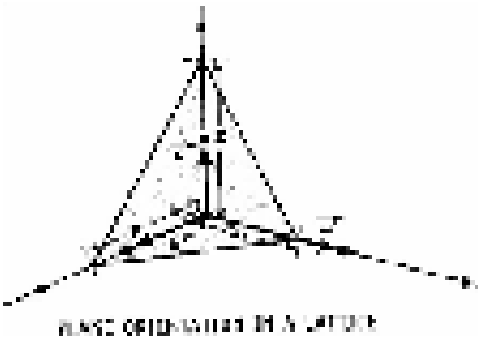
Largest Number = 2

(2/2, 1/2, 1/2) = (1, 1/2, 1/2)

Planes in Crystals (*Miller Indices)*:

It is possible for defining a system of parallel and equidistant planes which can be imagined to pass through the atoms in a space lattice, such that they include all the atoms in the crystal. Such a system of planes is called crystal planes. Many different systems of planes could be identified for a given space lattice.

The position of a crystal plane can be specified in terms of three integers called Miller indices.



Consider a crystal plane intersecting the crystal axes.
Procedure for finding Miller indices

1. Find the intercepts of the desired plane on the three coordinate axes.
   Let these be (pa, qb, rc).

2. Express the intercepts as multiples of unit cell dimensions or lattice parameters i.e. (p, q, r)

3. Take the reciprocals of these numbers i.e. 1/p: 1/q: 1/r

4. Convert these reciprocals into whole numbers by multiplying each with their LCM to get the smallest whole number.

This gives the Miller indices (h k l) of the plane.

Ex: (3a, 4b, αc)

(3, 4, α)

1/3 1/4 1/α

(4 3 0) = (h, k, l)

Def: Miller indices is a set of 3 lowest possible integers whose ratio taken in order is the same as that of the reciprocals of the intercepts of the planes on the corresponding axes in the same order.

Important features of Miller indices:

1. When a plane is parallel to any axis, the intercept of the plane on that axis is infinity. Hence its Miller index for that axis is zero.
2. When the intercept of a plane on any axis is negative, a bar is put on the corresponding Miller index.
3. All equally spaced parallel planes have the same index number (h k l)

Ex : The planes (1 1 2) and (2 2 4) are parallel to each other.

Separation Between successive (h k l) Planes:

Let (h k l) be the Miller indices of the plane ABC.

Let OP=d_{hkl} be the normal to the plane ABC passing through the origin O.

Let OP make angles α, β, γ with X, Y & Z axes respectively.

Then cos α =d / OA = d / x = d / (a / h)

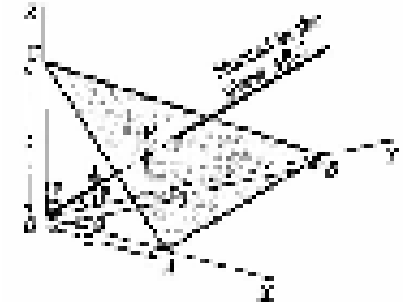


Fig. Interplanar Spacing.

Cos β =d /OB = d / y = d / (b / k)

Cos γ =d /OC = d/z =d/(c/l)

(Since convention in designing Miller indices x=a/h, y=b/k, z=c/l)

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

Hence $d^2 / (a / h)^2 + d^2 / (b/k)^2 + d^2 / (c/l)^2 = 1$

➔ $(d\,h / a)^2 + (d\,k / b)^2 + (d\,l / c)^2 = 1$

➔ $d_{(h\,k\,l)} = OP = 1 / \sqrt{(h^2/a^2 + k^2/b^2 + l^2/c^2)}$.

Therefore for cubic structure, a=b=c,

$$d_{(h\,k\,l)} = a / \sqrt{(h^2 + k^2 + l^2)}$$

Let the next plane be parallel to ABC be at a distance OQ from the origin. Then its intercepts are 2a / h, 2a / k, 2a / l.

Therefore $OQ = 2d = 2a / \sqrt{(h^2 + k^2 + l^2)}$

Hence the spacing between adjacent planes = OQ - OP = PQ.

i.e. $d = a / \sqrt{(h^2 + k^2 + l^2)}$

Expression for Space Lattice Constant 'a' For a Cubic Lattice:

Density p = (total mass of molecules belonging to unit cell) / (volume of unit cell)

Total mass of molecule belonging to unit cell = nM / N_A

Where n-number of molecules belonging to unit cell
M-Molecular weight
N_A -Avagadro Number

Volume of cube = a^3

Therefore $p = nM / a^3 N_A$

Or $a^3 = nM / p N_A$

Lattice Constant for Cubic Lattice $a = (nM / p N_A)^{1/3}$.

Diffraction of X- Rays by Crystal Planes:

X-Rays are electromagnetic waves like ordinary light, therefore, they should exhibit interference and diffraction .Diffraction occurs when waves pass across an object whose dimensions are of the order of their own wavelengths. The wavelength of X-rays is of the order of 0.1nm or 10 -8 cm so that ordinary devices such as ruled diffraction gratings do not produce observable effects with X-rays. Laue suggested that a crystal which consisted of a 3-dimensional array of regularly spaced atoms could serve the purpose of a grating. The crystal differs from ordinary grating in the sence that the diffracting centers in the crystal are not in one plane. Hence the crystal acts as a space grating rather than a plane grating. There are 3 main X-ray diffraction methods by which the crystal structure can be analysed.

(1) Laue Method – for single crystal

(2) Powder Method- for finely divided crystalline or polycrystalline powder

(3) Rotating crystal Method - for single crystal

Bragg's Law:

It states that the X-rays reflected from different parallel planes of a crystal interfere constructively when the path difference is integral multiple of wavelength of X-rays.

Consider a crystal made up of equidistant parallel planes of atoms with the interplanar spacing d.

Let wave front of a monochromatic X-ray beam of wavelength ג fall at an angle θ on these atomic planes. Each atom scatters the X-rays in all directions.

In certain directions these scattered radiations are in phase ie they interfere constructively while in all other directions, there is destructive interference.

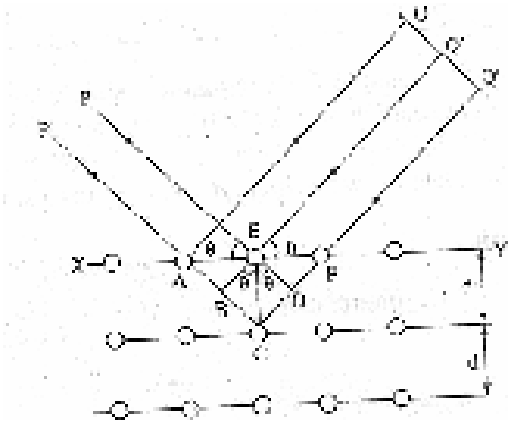


Figure 1 X-Ray Scattering by Crystal.

Consider the X-rays PE and P'A are inclined at an angle θ with the top of the crystal plane XY. They are scattered along AQ and EQ' at an angle θ w.r.t plane XY. Consider another incoming beam P'C is scattered along CQ"

Let normal EB & ED be drawn to AC &CF . if EB & ED are parallel incident and reflected wave fronts then the path difference between the incident and reflected waves is given by

$$\Delta = BC + CD \quad \text{----------(1)}$$

In Δ ABC , $\sin\theta = BC / EC = BC / d$

$$\text{i e } BC = d \sin\theta$$

Similarly, in Δ DEC , $CD = d \sin\theta$

Hence path difference $\Delta = 2d \sin\theta$

If the 2 consecutive planes scatter waves in phase with each other , then the path difference must be an integral multiple of wavelength.

i e $\Delta = n\lambda$ where n = 0 ,1 , 2 , 3 ,…….is the order of reflection

Thus the condition for in phase scattering by the planes in a crystal is given by

$$2d \sin\theta = n\lambda \quad \text{…….(2)}$$

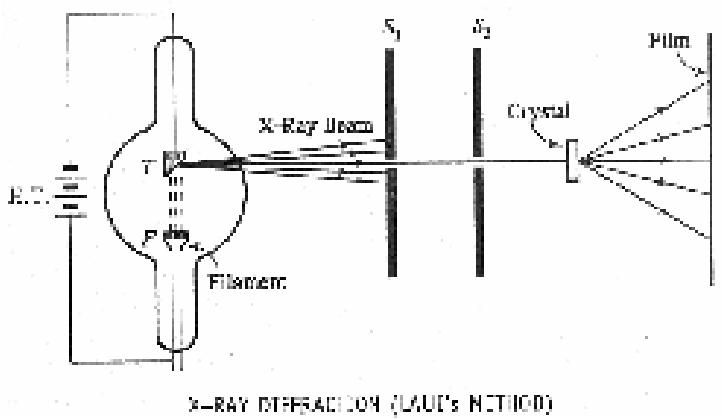
This condition is known as Bragg's Law .

The maximum possible value for θ is 1 .

$$n\,d / 2\,d \leq 1$$

the wavelength λ should not exceed twice the inter planar spacing for diffraction to occur.

Laue Method : S_1 & S_2 are 2 lead screens in which 2 pin holes act as slits . X-ray beam from an X –ray tube is allowed to pass through these 2 slits S_1 & S_2 . the beam transmitted through S_2 will be a narrow pencil of X – rays . the beam proceeds further to fall on a single crystal such that Zinc blended (ZnS) which is mounted suitably on a support . the single crystal acts as a 3 – dimensional diffraction grating to the incident beam. Thus, the beam undergoes diffraction in the crystal and then falls on the photographic film. The diffracted waves undergo constructive interference in certain directions, and fall on the photographic film with reinforced intensity. In all other directions, the interference will be destructive and the photographic film remains unaffected.
The resultant interference pattern due to diffraction through the crystal as a whole will be recorded on the photographic film (which requires many hours of exposure to the incident beam). When the film is developed, it reveals a pattern of fine spots, known as Laue spots.

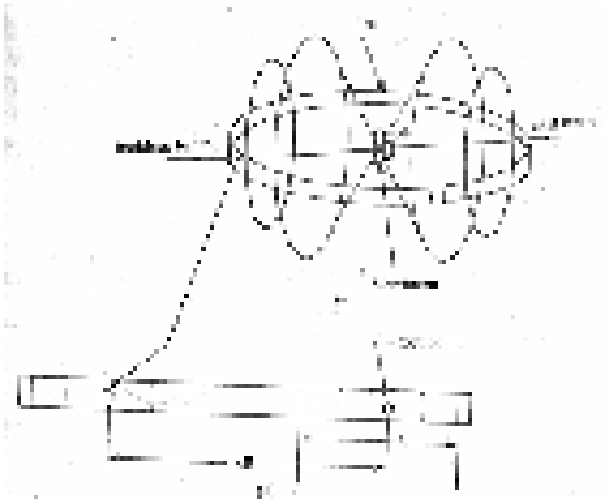


X–RAY DIFFRACTION (LAUE's METHOD)

The distribution spots follow a particular way of arrangement that is the characteristic of the specimen used in the form of crystal to diffract the beam. The Laue spot photograph obtained by diffracting the beam at several orientations of the crystal to the incident beam are used for determining the symmetry and orientations of the internal arrangement of atoms, molecules in the crystal lattice . it is also used to study the imperfections in the crystal .

POWDER METHOD (Debye – Scherrer Method):

This method is widely used for experimental determination of crystal structures. A monochromatic X- ray beam is incident on randomly oriented crystals in powder form. In this we used a camera called Debye – Scherrer camera. It consists of a cylindrical cassette, with a strip of photographic film positioned around the circular periphery of cassette. The powder specimen is placed at the centre, either pasted on a thin fibre of glass or filled in a capillary glass tube. The X- ra
y beam enters through a small hole in the camera and falls on the powder specimen. Some part of the beam is diffracted by the powder while the remaining passes out through the exit port.



Since large no. of crystals is randomly oriented in the powder, set of planes which make an angle θ with the incident beam can have a no. of possible orientations. Hence reflected radiation lies on the surface of a cone whose apex is at the point of contact of the radiation with the specimen. If all the crystal planes of interplanar spacing d reflect at the same bragg angle θ, all reflections from a family lie on the same cone.

After taking n=1 in the Bragg's law

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

There are still a no of combinations of d and θ, which satisfies Bragg's law. Hence many cones of reflection are emitted by the powder specimen. In the powder camera a part of each cone is recorded by the film strip.

The full opening angle of the diffracted cone 4θ is determined by measuring the distance S between two corresponding arcs on the photographic film about the exit point direction beam. The distance S on the film between two diffraction lines corresponding to a particular plane is related to bragg's angle by the equation

$$4\theta = (S / R) \text{ radians} \quad \text{(or)}$$

$$4\theta = (S / R) \times (180 / \Pi) \text{ degrees} \quad \text{where R- radius of the camera}$$

A list of θ values can be thus be obtained from measured values of S. Since the wavelength 'λ' is known, substitution of λ gives a list of spacing'd'.

Each spacing is the distance between neighbouring plane (h k l). From the ratio of interplanar spacing, the type of lattice can be identified.

Questions

1. Explain the various types of bonding in crystals. Illustrate with examples.
2. Distinguish between ionic and covalent bonding in solids.
3. Obtain a relation between potential energy and inter atomic spacing of a molecule.
4. Derive an expression for cohesive energy of a solid.
5. Obtain an equation for total binding energy of sodium chloride crystal.
6. Differentiate between crystalline and amorphous solids.
7. Explain the terms i) Basis ii) Space lattice iii) Unit cell
8. Explain with neat diagram the following crystal structures.
   i) simple cubic structure(SC)
   ii) body centered cubic structure(BCC)
   iii) face centered cubic structure (FCC)
9. What do you understand by packing density? Show that packing density for simple lattice, body centered lattice and face centered lattice is $\prod/6$, $\sqrt{3}\prod/8$, $\sqrt{2}\prod/6$ respectively
10. Show that FCC is the most closely packed of the three cubic structures.
11. a) For a crystal having $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^0$, what is the crystal system?
    b) For a crystal having $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^0$, what is the crystal system?
    c) Can you specify the Bravais lattices for parts (a) and (b) explain.
12. Explain the special features of the three types of lattices of cubic crystals?
13. What are ionic crystals? Explain the formation of an ionic crystal and obtain an expression for its cohesive energy?
14. What is a Bravais lattice? What are the different space lattices in the cubic system?
15. What are the miller indices? How they obtained?
16. Derive the expression for the interplannar spacing between two adjacent planes of miller indices (h k l) in a cubic lattice of edge length ‘a ‘.
17. Derive bragg’s law
18. Describe Laue’s method of determination of crystal structure.
19. Explain the power method of crystal structure analysis.