

Unit-1

Crystallography

Introduction:

- Solids can be broadly classified into two categories based on the arrangement of atoms or molecules as *crystalline* and *non crystalline (amorphous)*.

1. Crystalline Solids:

- In crystalline solids the atoms or molecules are arranged in a periodic manner in all three directions and further those are classified as *mono (single) crystals* and *polycrystalline* solids.
- Crystals which have different periodic arrangements in all the three directions exhibit varying physical properties with directions and they are called **anisotropic** substances.

Ex: Al, Cu, Ag, Ge, Si, Diamond etc...

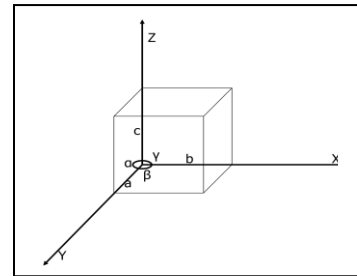
2. Non crystalline Solids:

- Non crystalline substances are also called *amorphous*. In amorphous solids the atoms or molecules arranged randomly and which have no regular structure.
- They have no directional properties and therefore they are called as *isotropic* substances.

Ex: Rubber, Glass, Wood, Plastic etc..

Definations:

- Space lattice:** A space lattice is defined as an infinite array of points in three dimensions in which every point has surroundings identical to that of every other point in the array.
 - Basis:** A group of atoms or molecules are attached to every lattice point in the space lattice called the Basis.
 - Lattice + basis = Crystal structure
 - Unit cell:** The smallest geometric structure that repetition which gives an entire crystal structure called unit cell.
 - In the fig. **a, b, c** and **α, β, γ** are called lattice parameters.
 - Note: 1. Primitives (a, b, c)** decide the **size** of the unit cell.
3. **Interfacial angles (α, β, γ)** decide the **shape** of the unit cell.

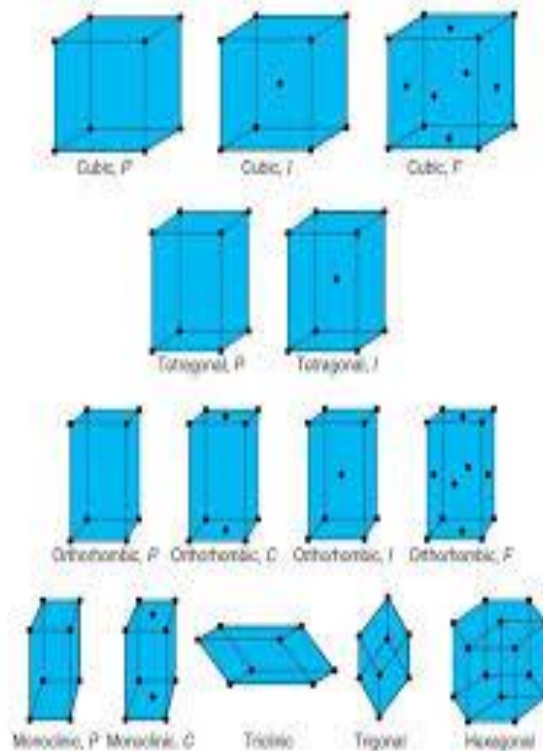


Crystal Systems and Bravais lattices:

- Based on the lattice parameter values all the crystals are classified into 7 types.

| Sl.No | Crystal system | Primitives & Angles | Bravais lattices |
|-------|----------------|-------------------------------------------------------------------|------------------|
| 1 | Cubic | $a=b=c$ & $\alpha=\beta=\gamma=90^\circ$ | P, I, F |
| 2 | Tetragonal | $a=b \neq c$ & $\alpha=\beta=\gamma=90^\circ$ | P, I |
| 3 | Orthorhombic | $a \neq b \neq c$ & $\alpha=\beta=\gamma=90^\circ$ | P, I, F, C |
| 4 | Monoclinic | $a \neq b \neq c$ & $\alpha=\beta=90^\circ \neq \gamma$ | P, C |
| 5 | Triclinic | $a \neq b \neq c$ & $\alpha \neq \beta \neq \gamma \neq 90^\circ$ | P |
| 6 | Trigonal | $a=b=c$ & $\alpha=\beta=\gamma \neq 90^\circ$ | P |
| 7 | Hexagonal | $a=b \neq c$ & $\alpha=\beta=90^\circ, \gamma=120^\circ$ | P |

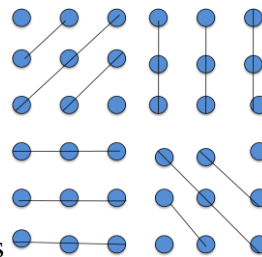
- i). Primitive Lattice(P), ii). Body Centered Lattice(I), iii). Face Centered Lattice(F) and iv). Base Centered Lattice(C).



Lattice planes and Miller indices:

Crystal planes:

- A crystal is made up of a large number of parallel equidistant planes passing through lattice points are called Lattice planes or crystal planes.

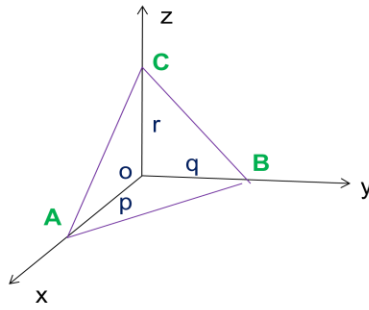


- The perpendicular distance between adjacent planes is called inter planar spacing.

Miller indices:

- “The Miller Indices are the three smallest possible integers (h k l), which have the same ratio as the reciprocals of the intercepts of the crystal plane having on the three crystallographic axes”.
- These indices are used to indicate the different sets of parallel planes in a crystal.

Procedure for finding Miller indices:



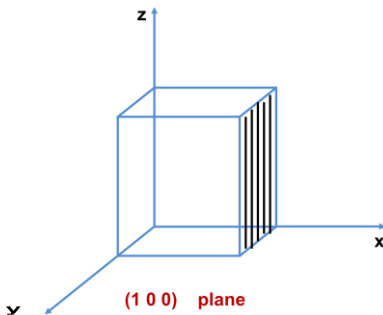
- Choose system of three coordinate axes x,y & z i.e., crystallographic axes
- Determine the intercepts p, q & r of the required plane 'ABC' on these axes i.e., OA = p, OB = q & OC = r.
- Take ratio of reciprocals of the Intercepts i.e., 1/p:1/q:1/r.
- Convert these reciprocals into integers by multiplying each one of them with their L.C.M .
- Enclose these integers in smaller parenthesis i.e., Miller indices (h k l) of the crystal.

Important features of miller indices:

- 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.
- When the intercept of a plane on any axis is negative a bar is put on the corresponding miller index.
- All equally spaced parallel planes have the same index number (h k l).
- If a plane passes through origin, it is defined in terms of a parallel plane having non-zero intercept.
- If a normal is drawn to a plane (h k l), the direction of the normal is [h k l].

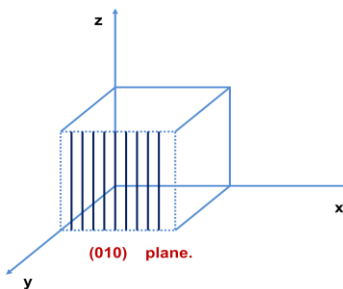
Constructions of planes:

(100) plane:



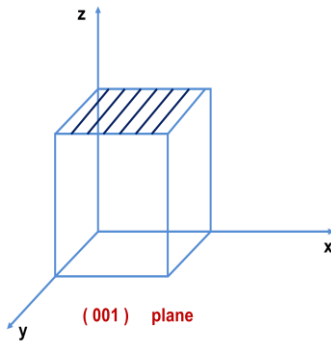
Intercepts of the Plane are = $(1, \infty, \infty)$
 Reciprocals of intercepts are = $(\frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty})$
 Miller indices : $(1,0,0)$

(010) plane:



Intercepts of the Plane are = $(\infty, 1, \infty)$
 Reciprocals of intercepts are = $(\frac{1}{\infty}, \frac{1}{1}, \frac{1}{\infty})$
 Miller indices : $(0,1,0)$

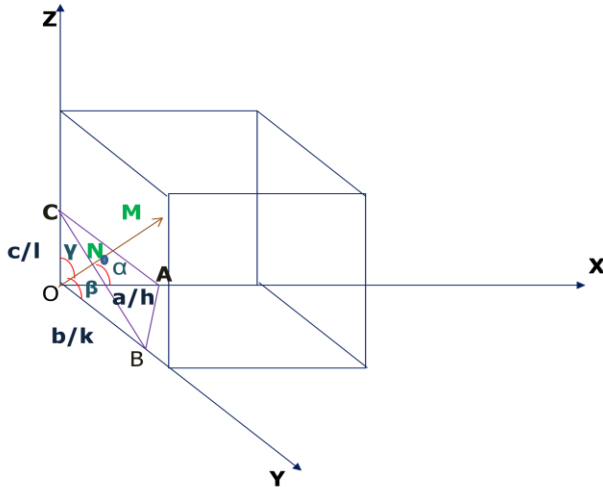
(001) plane:



Intercepts of the Plane are = $(\infty, \infty, 1)$
 Reciprocals of intercepts are = $(\frac{1}{\infty}, \frac{1}{\infty}, \frac{1}{1})$
 Miller indices : $(0, 0, 1)$

Inter planner spacing of orthogonal crystal system:

- ‘The distance ‘d’ between a series of planes in a crystal is known as the ‘d’ spacing or inter planar spacing’.
- Let (h, k, l) be the miller indices of the plane ABC.
- Let $ON=d$ be a normal to the plane passing through the origin ‘0’. Let this ON make angles α, β and γ with x, y and z axes respectively.
- Imagine the reference plane passing through the origin “o” and the next plane cutting the intercepts $a/h, b/k$ and c/l on x, y and z axes.



Let the direction cosines of ON be $\cos\alpha, \cos\beta$ & $\cos\gamma$

$$\therefore \cos\alpha = \frac{ON}{OA} = \frac{d}{a/h} = \frac{dh}{a}$$

$$\cos\beta = \frac{ON}{OB} = \frac{d}{b/k} = \frac{dk}{b}$$

$$\cos\gamma = \frac{ON}{OC} = \frac{d}{c/l} = \frac{dl}{c}$$

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

- But law of direction cosines

$$\left[\frac{d}{a/h}\right]^2 + \left[\frac{d}{b/k}\right]^2 + \left[\frac{d}{c/l}\right]^2 = 1$$

$$d^2 \left\{ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right\} = 1$$

$$ON = d_{hkl} = \frac{1}{\left[\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \right]^{\frac{1}{2}}} \quad \text{--- (1)}$$

- Therefore, the spacing between the adjacent planes $d_{hkl} = OM-ON$

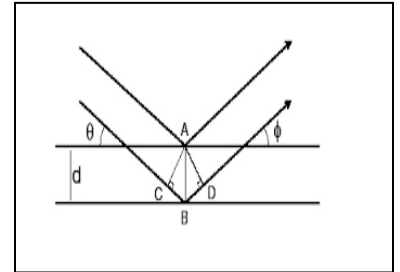
$$d_{hkl} = \frac{1}{\left[\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \right]^{\frac{1}{2}}}$$

Note: The inter planar spacing of Simple Cubic Structure $a=b=c$

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

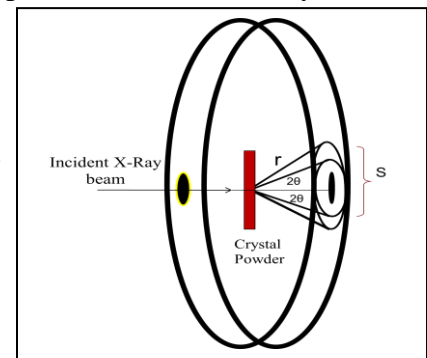
Bragg's law:

- Bragg's law states that, the path difference between the two reflected rays by the crystal planes should be an integral multiple of wavelength of incident x-rays for producing maxima or constructive interference.
- When a monochromatic light of wavelength λ is incident on a surface of the film the light gets diffracted in all directions. The diffracted rays in some directions interfere constructively and form the fringes when the path difference is equal to $n\lambda$.
- From the fig. $d \sin\theta = CB$ & $d \sin\theta = BD$
- The path difference between these two rays is $CB + BD = 2d \sin\theta$.
- Bragg's law $2d \sin\theta = n\lambda$. Where $n = 1, 2, 3, \dots$ first, second ...order etc.



Powder (Debye – Scherer) Method:

- The Powder method is applicable to finely divided crystalline powder. It is used for accurate determination of lattice parameters in crystals.
- The powdered specimen is kept inside the capillary tube.
- A narrow pencil of monochromatic X-Ray is diffracted from the powder and recorded by the Photographic film as a series of lines of varying curvature.
- The diffracted and reflected beams (cones) leave impressions on the photographic film in the form of arcs.
- The full opening angle of the diffraction cone ' 4θ ' is determined by measuring the distance ' S ' between two corresponding arcs. $4\theta = S/r$ then $\theta = S/4r$.

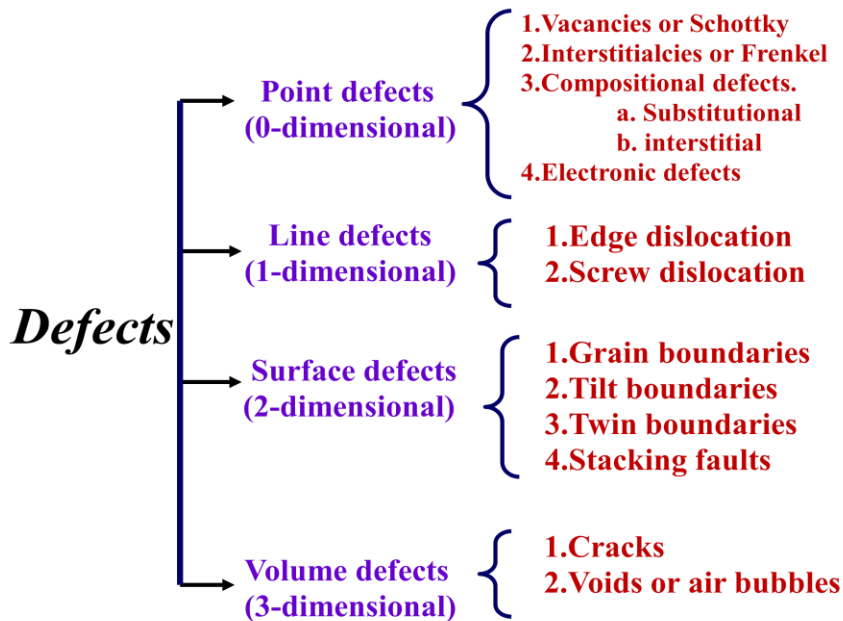


Applications of Powder Method

- Study of d-spacing.
- Study of mixtures.
- Study of alloys.
- Stress determination in metals.
- Determination of particle size.

Crystal Defects

- In an ideal crystal, the atomic arrangement is perfectly regular and continuous but real crystals never perfect.
- Real crystals always contain a considerable density defects and imperfections that affect their physical, chemical, mechanical and electronic properties.
- Crystalline imperfections can be classified on the basis of their geometry under four main divisions namely.



Point Defects:

- Point imperfections are also called zero dimensional imperfections.

Vacancy:

- A Vacancy refers to an atomic site from where the atom is missing.

Compositional defects:

- Substitution impurity is a point imperfection and it refers to a foreign atom that substitutes or replaces a parent atom in the crystal.

Electronic defects: Errors in charge distribution in solids are called electronic defects.

Frenkel Defect:

- An atom leaves the regular site and occupies interstitial position. Such defects are called Frenkel defects.

Schottky defect:

- A pair of one cat-ion and one an-ion can be missing from an ionic crystal as shown in a figure. Such a pair of vacant ion sites is called Schottky defect.

Calculation of number Schottky defects at a given temperature:

- In ionic crystals, the number of Schottky defects at a given temperature, can be calculated assuming an equal number of positive and negative ion vacancies are present.

- Let us consider 'E_s' is the energy required to move an ion Pair from lattice site inside the crystal to a lattice site on the surface.
- Therefore the amount of energy required to produce 'n' number of isolated ion pair vacancies will be
- The total number of ways that to move 'n' numbers of ion pairs out of 'N' number of ionic molecules in a crystal on to the surface will be

$$P = \left[\frac{N!}{(N-n)!n!} \right]^2$$

$$S = K_B \log P \Rightarrow S = K_B \log \left[\frac{N!}{(N-n)!n!} \right]^2 \Rightarrow S = 2K_B \log \left[\frac{N!}{(N-n)!n!} \right]$$

- The free energy

$$F = U - TS$$

$$F = nE_p - 2K_B T \log \left[\frac{N!}{(N-n)!n!} \right]$$

Using sterling approximation $\log x! = x \log x - x$

$$\log \left[\frac{N!}{(N-n)!n!} \right] = [N \log N - N - (N-n) \log(N-n) + (N-n) - n \log n + n]$$

$$\log \left[\frac{N!}{(N-n)!n!} \right] = [N \log N - (N-n) \log(N-n) - n \log n]$$

$$F = nE_p - 2K_B T [N \log N - (N-n) \log(N-n) - n \log n]$$

- At thermal equilibrium, free energy is constant and minimum with respect to 'n', hence

$$\left[\frac{dF}{dn} \right]_T = 0$$

$$E_p = 2K_B T \log \left[\frac{N-n}{n} \right] \Rightarrow \frac{E_p}{2K_B T} = \log \left[\frac{N-n}{n} \right] \Rightarrow n = (N-n) \exp \left\{ \frac{-E_p}{2K_B T} \right\}$$

$$\text{if } n \ll N \Rightarrow n \cong N \exp \left\{ \frac{-E_p}{2K_B T} \right\}$$

Calculation of number of Frenkel Defects at given temperature:

- In ionic crystal an ion may be displaced from the regular lattice into an interstitial site or void space. If it is so, then a vacancy and an interstitial defect will be formed.
- Let us consider E_i is the energy required to move an atom from lattice site inside the crystal to a lattice site on the surface.
- The amount of energy required to produce 'n' number of isolated vacancies... $U = nE_i$
- The total number of ways to move n numbers of ions out of N number ionic molecules in a crystal on to the surface will be,

$$p = \left[\frac{N!}{(N-n)!n!} \right] \left[\frac{N_i!}{(N_i-n)!n!} \right]$$

$$\text{entropy} = K_B \log p$$

$$S = K_B \log \left\{ \left[\frac{N!}{(N-n)!n!} \right] \left[\frac{N_i!}{(N_i-n)!n!} \right] \right\}$$

$$\text{freeenergy} = U - TS$$

$$F = nE_i - K_B T \log \left\{ \left[\frac{N!}{(N-n)!n!} \right] \left[\frac{N_i!}{(N_i-n)!n!} \right] \right\}$$

$$\log\left\{\left[\frac{N!}{(N-n)!n!}\right]\left[\frac{N_i!}{(N_i-n)!n!}\right]\right\}$$

$$= N \log N + N_i \log N_i - (N-n) \log(N-n) - (N_i-n) \log(N_i-n) - 2n \log n$$

$$F = nE_i - K_B T \{N \log N + N_i \log N_i - (N-n) \log(N-n) - (N_i-n) \log(N_i-n) - 2n \log n\}$$

- At equilibrium, the free energy is constant and minimum with respect to n, hence

$$\left[\frac{dF}{dn}\right]_T = 0$$

$$E_i = K_B T \log\left\{\frac{(N-n)(N_i-n)}{n^2}\right\}$$

$$N \gg n, N_i \gg n \Rightarrow n \cong K_B T \log\left\{\frac{NN_i}{n^2}\right\}$$

$$\log\left\{\frac{NN_i}{n^2}\right\} = \frac{E_i}{K_B T}$$

$$\frac{NN_i}{n^2} = \exp\left\{\frac{E_i}{K_B T}\right\} \Rightarrow \frac{n^2}{NN_i} = \exp\left\{-\frac{E_i}{K_B T}\right\} \Rightarrow n^2 = NN_i \exp\left\{-\frac{E_i}{K_B T}\right\}$$

$$\therefore n \cong (NN_i)^{\frac{1}{2}} \exp\left\{\frac{-E_i}{2K_B T}\right\}$$