

ASSIGNMENT

UNIT - III

Ques 1) Define the terms:-

1) Lattice:- The periodic arrangement of atoms in a crystal is called a lattice.

2) Basis:- The atom or the molecules associated with a lattice point is called the basis.

3) Unit Cell:- Unit cell is that smallest geometrical shape by the repetition of which complete crystal structure can be represented.

4) Bravais Lattice:- Bravais lattice refers to the 14 different 3-dimensional configuration into which atoms can be arranged in crystals.

b) Write the essential feature of a unit cell to be called a primitive cell.

Ans A primitive cell is a type of unit cell which contains lattice points at the corners only and is a minimum volume unit.

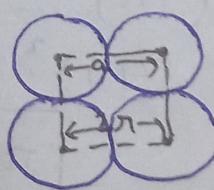
Ques 2) Deduce atomic radius, packing fraction, lattice constant for a cubic crystal (sc, bcc, fcc)

Ans I Simple Cubic Crystal

Atomic Radius:-

$$a = 2r$$

$$r = \frac{a}{2}$$



Packing fraction :- No. of atoms in unit cell
 $= 8 \times \frac{1}{8} = 1$

atomic radius = $r = \frac{a}{2}$

Volume of atom occupying unit cell = $1 \times \frac{4}{3} \pi r^3$

$$= \frac{4}{3} \pi \left(\frac{a}{2}\right)^3$$

Volume of unit cell = a^3

Packing fraction = $\frac{\frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6}$

$$f = 52\%$$

Lattice constant-

$$a = \left\{ \frac{nM}{NP} \right\}^{1/3}$$

for S.C.C, $n=1$

$$a = \left(\frac{M}{NP} \right)^{1/3}$$

II Body centred

Atomic Radius =

$$PQ = r + 2r + r = 4r$$

$$PR = RS = a$$

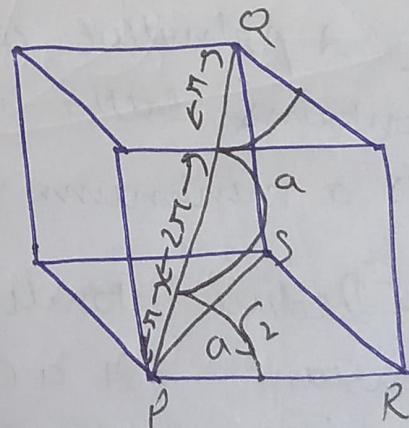
$$PS = a\sqrt{2}$$

$$PQ = \sqrt{(PS)^2 + (SQ)^2}$$

$$(4r)^2 = \sqrt{(2a)^2 + a^2}$$

$$(4r)^2 = 2a^2 + a^2$$

$$r = \frac{a\sqrt{3}}{4}$$



Packing fraction:- $n=2$

$$\text{atomic radius} = \frac{a\sqrt{3}}{4}$$

$$\text{Volume of unit cell} = a^3$$

$$\text{Volume of atoms occupying the unit cell} = 2 \times \frac{4}{3} \pi r^3$$

$$\begin{aligned} \text{Packing fraction} &= \frac{2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}}{4} a\right)^3}{a^3} \\ &= \frac{\sqrt{3}}{8} \pi = 0.68 = 68\% \end{aligned}$$

Lattice constant:-

$$n=2 \cdot \boxed{a = \left\{ \frac{2M}{NP} \right\}^{1/3}}$$

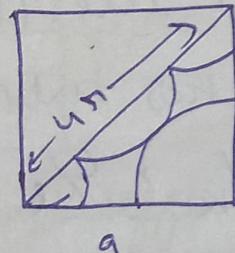
III Face Centred

Atomic radius:-

$$(4r)^2 = a^2 + a^2$$

$$4r^2 = 2a^2$$

$$\boxed{r = \frac{\sqrt{2}}{4} a \text{ or } \frac{a}{2\sqrt{2}}}$$



Packing fraction:- $n=4$

$$\text{atomic radius} = \frac{a}{2\sqrt{2}}$$

$$\text{Volume of atoms occupying unit cell} = 4 \times \frac{4}{3} \pi r^3$$

$$\text{packing fraction} = \frac{4 \times \frac{4}{3} \pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3}$$

$$\boxed{f = 74\%}$$

Lattice Constant

$$n = \frac{4}{3}$$

$$a = \left\{ \frac{4M}{NP} \right\}^{1/3}$$

Ques 3 What are Miller Indices? Deduce formula for the distance between two adjacent plane of a simple cubic lattice?

Ans Miller Indices:- In a crystal, express the inclination of lattice plane w.r.t three directions, Miller gave a method according to which a crystal plane is represented by three numbers h, k, l . These numbers are called Miller Indices.

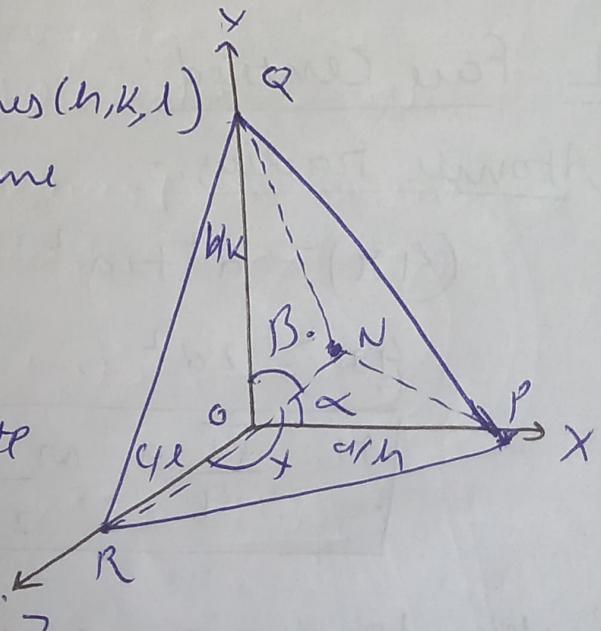
Let us consider a set planes (h, k, l)

In a unit cell. This plane

PQR makes intercepts

$\frac{a}{h}, \frac{b}{k}, \frac{c}{l}$ on the
three cartesian coordinate
axes P, Q and R resp.

(consider O as the origin).



Draw a perpendicular ON from origin to the plane $ON = d$, is the distance between adjacent plane. Normal ON makes angle α, β and γ with x, y , and z axes.

$$OP = a/m, OQ = b/k, OR = c/l$$

$$\therefore \Delta ONP, \cos\alpha = \frac{ON}{OP} \Rightarrow \cos\alpha = \frac{dh}{a}$$

$$\Delta ONQ, \cos\beta = \frac{ON}{OQ} \Rightarrow \cos\beta = \frac{dk}{b}$$

$$\Delta ORN, \cos\gamma = \frac{ON}{OR} \Rightarrow \cos\gamma = \frac{dl}{c}$$

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

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

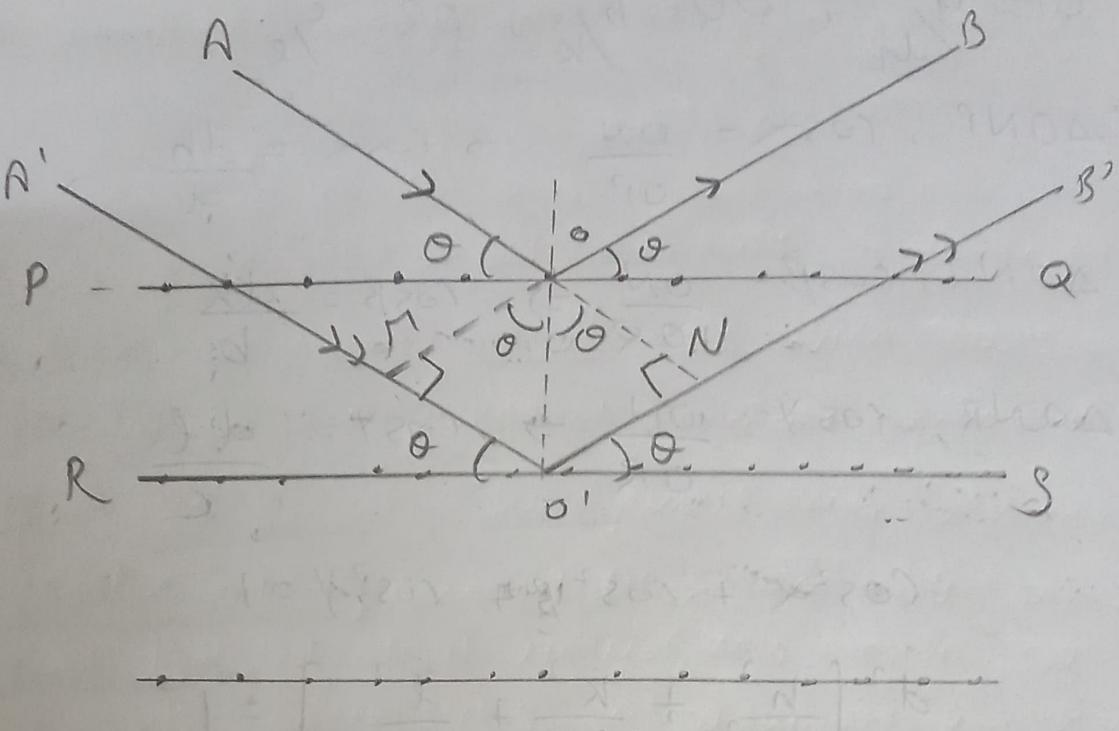
$$d = \frac{1}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{1/2}}$$

for simple cubic crystal $a = b = c$

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

Ques 4 Derive Bragg's law of X Ray diffraction in crystal. Discuss briefly the law method of crystal structure.

Ans Suppose a beam of X rays falls on the crystal at glancing angle θ then some of these rays will be reflected from the upper plate at some angle θ . Consider the rays reflected at two consecutive plane



$$\angle MOO' = \angle NOO' = \theta$$

$$AO = A'M$$

$$BO = B'M.$$

$$\text{Path difference} = MO' + NO' - \textcircled{1}$$

Path difference is defined as an integral multiple of wavelength = $n\lambda$ — $\textcircled{2}$

$$n\lambda = MO' + NO' - \textcircled{3}$$

$$\frac{\Delta MOO'}{d \sin \theta} = \frac{MO'}{d \sin \theta}$$

$$\boxed{MO' = d \sin \theta} - \textcircled{4}$$

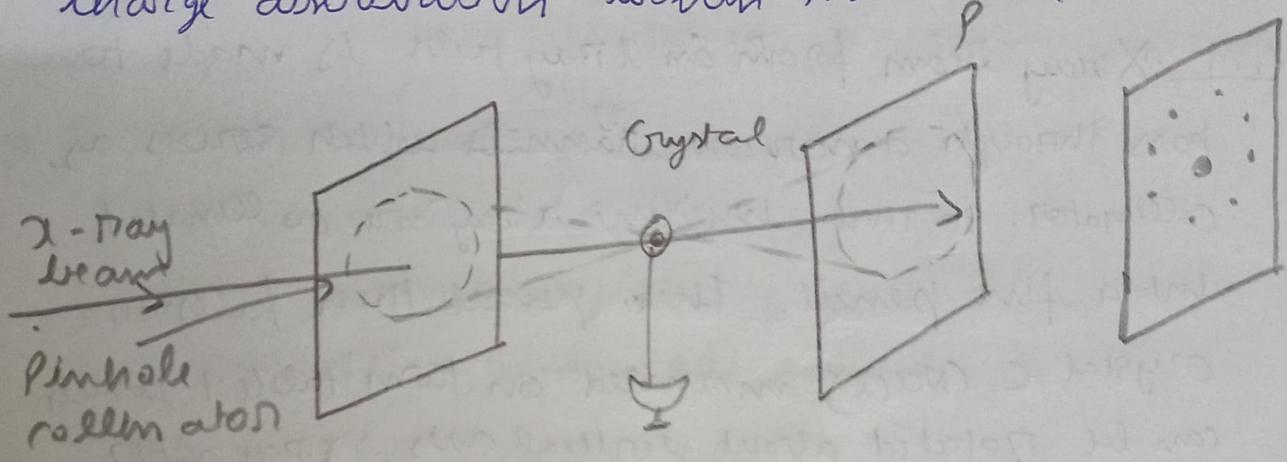
$$\text{Similarly } \boxed{NO' = d \sin \theta} - \textcircled{5}$$

Putting value of $\textcircled{4}$ and $\textcircled{5}$ in eq $\textcircled{3}$

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

$$\boxed{2 d \sin \theta = n\lambda}$$

Laue Method:- This method is used for determination of crystal structure and the details of electron charge distribution within the solid.



The Laue method of crystal structure is a technique used to determine the arrangement of atoms within a crystal. It involves analyzing the angles and intensities of X-ray diffraction patterns produced when X-rays are directed at a crystal.

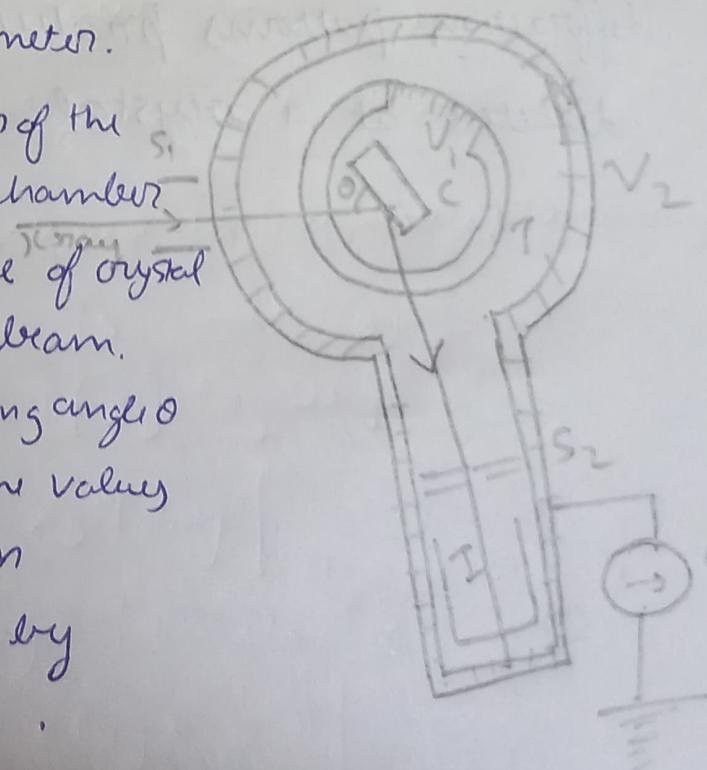
Ques 5 Describe Bragg's Spectrometer and explain with the help of an example how it is used to study the crystal structure.

An X-ray beam from an X-ray tube is made to pass through a narrow channel which serves as collimator, so that incident x-ray are collimated into a fine pencil. This pencil then falls on a crystal C (NaCl) mounted on turn table 1 which can be rotated about vertical axis. X-ray after passing through the slit S_2 enters the ionisation chamber I, which is mounted on a special movable arm about the same axis of the crystal. The position of chamber can be read by a second vernier V_2 . The x-rays entering the chamber ionise the gas causing a current to flow between the two electrodes which can be measured by galvanometer.

For each small rotation of the crystal the ionisation chamber is rotated twice the rate of crystal to receive the reflected beam.

It is observed that glancing angle θ is varied. By observing the values of θ at various orders n λ/d can be determined by

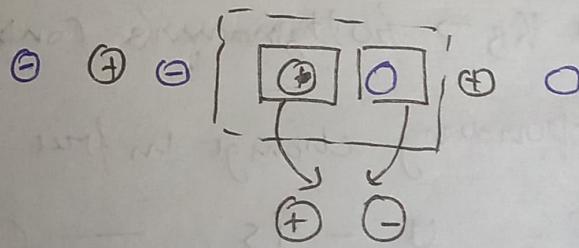
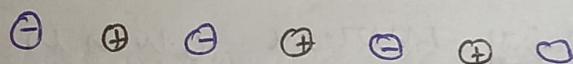
$$2ds \sin \theta = nd$$



Ques What are Schottky and Frenkel defects ?
Obtain an expression for concentration of Schottky defects in crystal.

Ans SCHOTTKY DEFECTS

- In ionic crystal if there is vacancy in +ve ion site then charge neutrality of crystal may be achieved by creating a vacancy in neighbouring -ve ion site such a pair vacant site is called Schottky defects.
- Cation and anion are shifted to surface i.e. volume increase and hence density decrease.



Eg NaCl

Concentration of Schottky defect in a crystal :-

Consider a pure crystal made up of equal no. of opposite charged ions.

Let $n \rightarrow$ No. of Schottky defects.

$N \rightarrow$ Total no. of ions in the crystal

$E_p \rightarrow$ Energy required to create a pair of vacancy site.

i. Increase in energy associated with vacant site.

$$= nE_p = U$$

Total no. of ways in which an anion or cation vacancy may be created

$$= \frac{N!}{(N-n)! n!}$$

Total no. of ways in which n pairs of cation anion vacancies may be created.

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

$$2 \left(\frac{N!}{(N-n)! n!} \right)^2 - \textcircled{1}$$

\therefore Entropy increase which is given by

$$S = K_B \log \omega - \textcircled{2}$$

where $K_B \rightarrow$ Boltzmann's constant.

\therefore Corresponding change in free energy is given by

$$F = U - TS - \textcircled{3}$$

$$= U - T [K_B \log \omega]$$

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

using Stirling's formula

$$\boxed{\log x! = x \log x - x}$$

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

$$F = nE_p - 2k_B T \left[N \log N - N(N-n) \log(N-n) + N - N - n \log n + n \right]$$

$$F = nE_p - 2k_B T \left[N \log N - (N-n) \log(N-n) - n \log n \right]$$

$$F = nE_p - 2k_B T \left(N \log N - N \log(N-n) + n \log(N-n) \right)$$

$$\left(\frac{\partial F}{\partial n} \right) = E_p - 2k_B T \left\{ -\frac{N}{(N-n)} (-1) + \frac{n}{(N-n)} (-1) + \log(N-n) \times 1 - n \times \frac{1}{n} (-1) \right\}$$

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

At equilibrium free energy is constant

$$\left(\frac{\partial F}{\partial n} \right)_T = 0$$

$$E_p - 2k_B T \left[\log \left(\frac{N-n}{n} \right) \right] = 0$$

$$\frac{E_p}{2k_B T} = n \log \left(\frac{N-n}{n} \right)$$

$$\frac{N-n}{N} = \exp \left(\frac{E_p}{2k_B T} \right)$$

As no. of vacancy pair is much smaller than total no. of ions in crystal

$$N \gg n$$

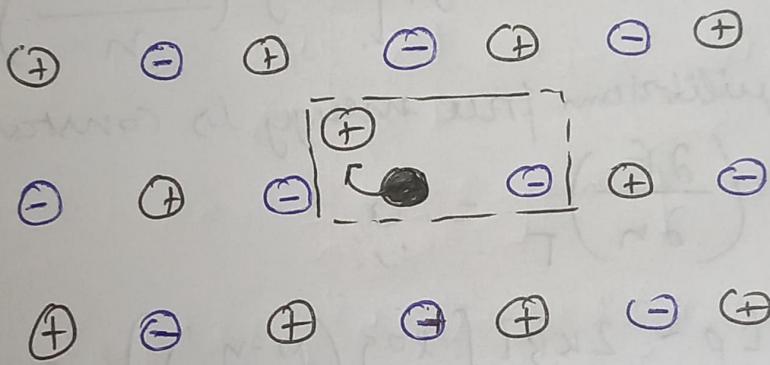
$$(N-n) \approx N$$

$$\frac{N}{n} = \exp \left[-\frac{E_p}{2k_B T} \right]$$

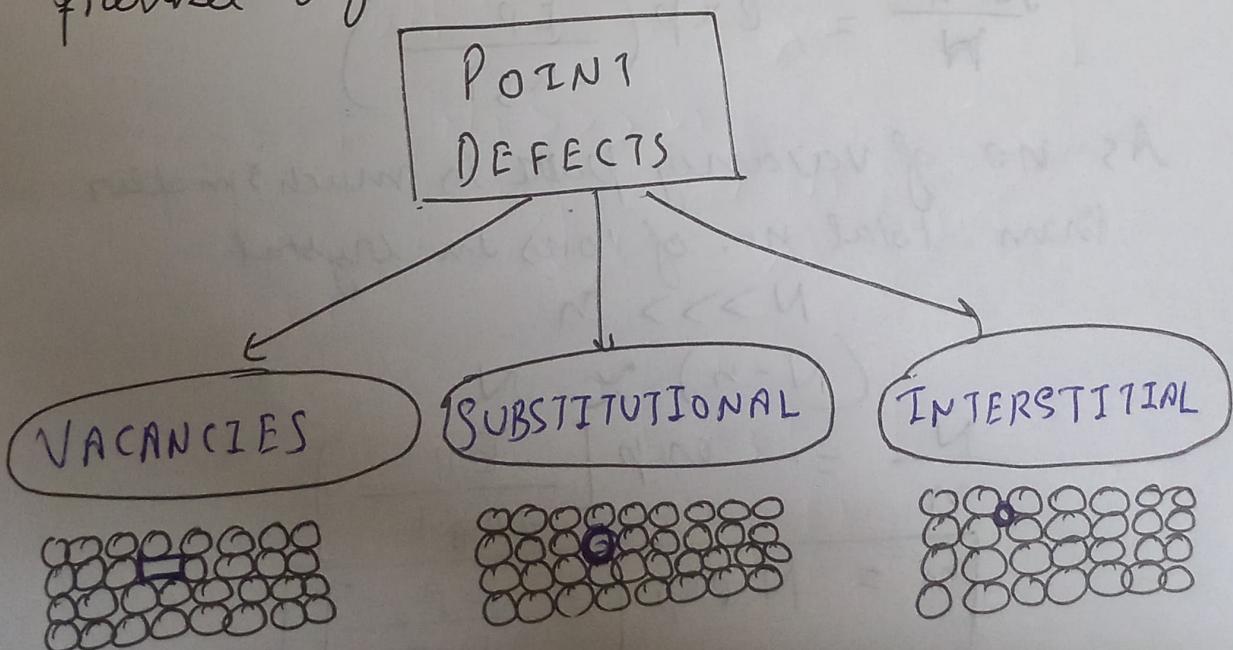
$$n = N \exp \left[-\frac{E_p}{2k_B T} \right]$$

* FRENKEL DEFECT

- In non-metallic crystal if an ion is displaced from its regular site to an interstitial site the defect is called Frenkel Defect.
- As cation is smaller in size it is possible to get displaced into interstitial space.
- This defect does not change electrical neutrality of crystal
- Density remains same.



Ques 7 Discuss all the point defects in solids.
Derive an expression for concentration of
frenkel defect in crystal.



I Vacancy:- A missing atom or vacant atomic site in a crystal. This may be arises due to imperfect packing during the original crystallisation or thermal vibration of atom.

II Substitutional:- A foreign atom replaces a parent atom in the crystal. Penta or trivalent impurity atom doped in pure SiC.

III Interstitial:- In crystal in which packing fraction is low, an extra small sized atom can enter the interstitial space in the parent crystal without disturbing the regularity position atom.

Concentration of Frenkel Defects

$E_i \rightarrow$ energy required to displace an atom

$N_i \rightarrow$ Number of interstitial atoms

$N \rightarrow$ Number of atoms

$n \rightarrow$ Frenkel defects

The total no. of ways in which frenkel defect

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

\therefore change in free energy

$$\begin{aligned} F &= U - TS \\ &= nE_i - T k_B \log \left[\left(\frac{N!}{(N-n)! \cdot n!} \right)^2 \times \frac{N_i!}{(N_i - n)! \cdot n!} \right] \end{aligned}$$

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

$$= nE_i - K_B T \left[N \log N - (N-n) \log (N-n) - n \log n + N_i \log N_i - (N_i-n) \log (N_i-n) - n \log n \right]$$

$$= nE_i - K_B T \left[N \log N - (N-n) \log (N-n) + N_i \log N_i - (N_i-n) \log (N_i-n) - 2n \log n \right]$$

$$\begin{aligned} \frac{\partial F}{\partial n} &= E_i - K_B T \left[0 - \frac{(N-n)}{(N-n)} (-1) - \log (N-n) (-1) + 0 - \frac{(N_i-n)}{(N_i-n)} (-1) - \log (N_i-n) (-1) - 2n \times \frac{1}{n} - 2 \log n \right] \end{aligned}$$

$$= E_i - K_B T \left[1 + \log (N-n) + 1 + \log (N_i-n) - 2 - 2 \log n \right]$$

$$= E_i - K_B T \left[\log (N-n) + \log (N_i-n) - 2 \log n \right]$$

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

As $N \gg n, N_i \gg n$

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

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

$$NN_i = n^2 \exp \left(\frac{E_i}{K_B T} \right) \text{ or}$$

$$n^2 = N N_i \exp \left[\frac{-E_i}{K_B T} \right]$$

$$n = \sqrt{N N_i} \exp \left[-\frac{E_i}{2 K_B T} \right]$$

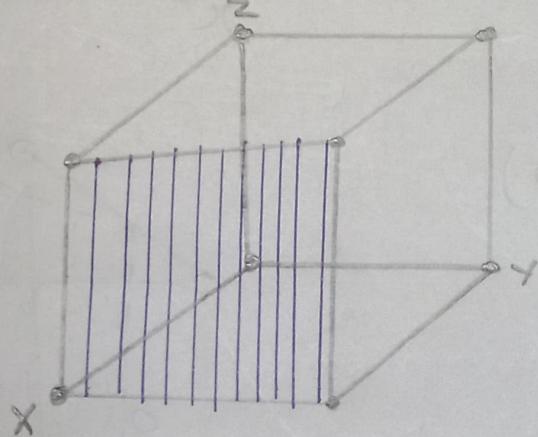
→ No. of objects increases exponentially with temperature.

Ques 8 a) Why x-rays are used in crystal diffraction studies?

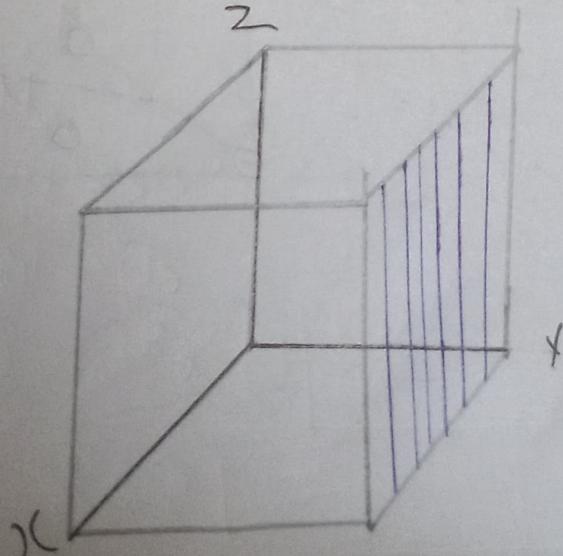
Ans As the wavelength of x-rays are of same order as of interatomic spacing in crystals, it can be used to provide the imagery of crystal structure.

b) Draw (100)(010)(001)(111)(220)(020) planes in cubic unit cell.

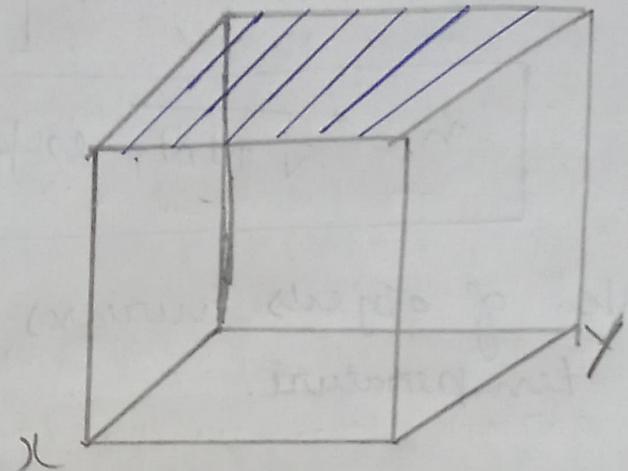
1) (1 0 0)



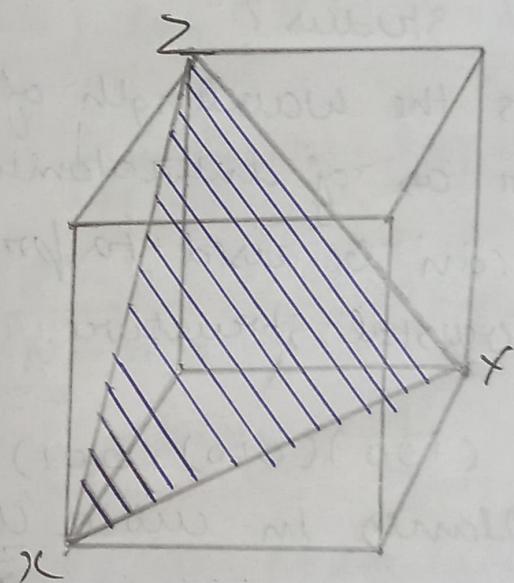
2) (010)



37(001)



47(111)



(5) (220)

