THE SOLID STATE

TOPIC-3
BRAGG'S EQUATION AND CALCULATION OF DENSITY OF CRYSTAL

VERY SHORT ANSWER QUESTIONS

1. Explain Bragg's equation?
Ans: Braggg's equation is given by;

$$n\lambda = 2\ d\ Sin\theta$$

where,
n = order of diffraction
λ = wave length
d = distance between the planes
Θ = angle of incident beam.

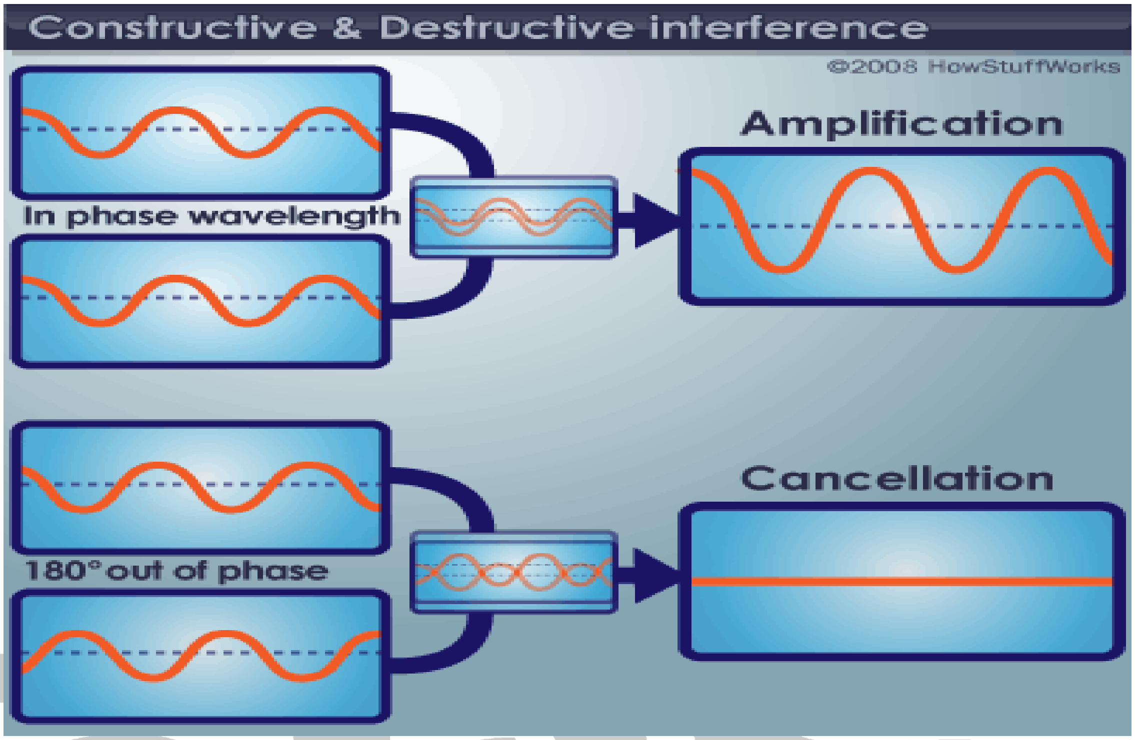
2. Which crystal structure has 12 as co-ordination number?
Ans: Crystals having hexagonal close packing (hcp) crystal has coordination number '12'.

3. The diffracted X-rays from copper sulphate crystal are allowed to fall on a photographic plate. What happens to the photgraphic plate?
Ans: The photographic plate gets bright and dark patches that result from the constructive and destructive interference of the diffracted rays.

4. **How many lattice points are there in a unit cell of a) bcc lattice; b) end centered lattice**?
Ans:
a) In bcc the lattice points are 8. They are the corners of primitive unit cell.
b) The end centered unit cell has 4 nearest lattice points to the lattice **x** and **y** in primitive unit cell.
The end centered lattice has lattice point on each of the two faces bounded by edge of length **a** and **b.**
Therefore, the number of lattice points is 10.

SHORT ANSWER QUESTIONS

1. Explain when the diffracted rays may constructive and destructive interference?
Ans:
In constructive interference,
- Two waves are in the same phase
- Mxima and minima of two waves mutually interfere with one another
- One wave reinforces the other wave.



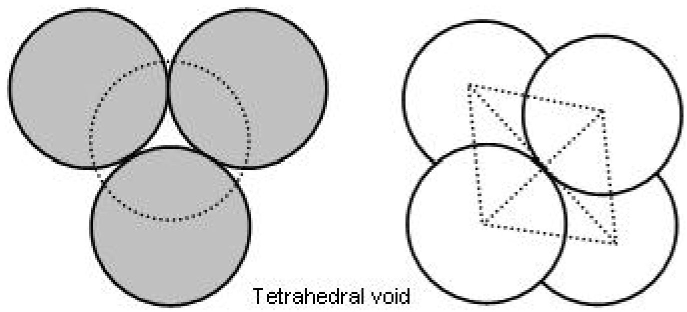
In destructive interference,

- Two waves are not in the same phase i.e. out of phase
- One wave nullifies the other

2. What is tetrahedral hole?

Tetrahedral hole

In close packing arrangement, each sphere in the second layer rests on the hollow (triangular void) in three touching spheres in the first layer. The centres of theses four spheres are at the corners of a regular tetrahedral. The vacant space between these four touching spheres is called tetrahedral void. In a close packing, the number of tetrahedral void is double the number of spheres, so there are two tetrahedral voids for each sphere



Radius of the tetrahedral void relative to the radius of the sphere is 0.225

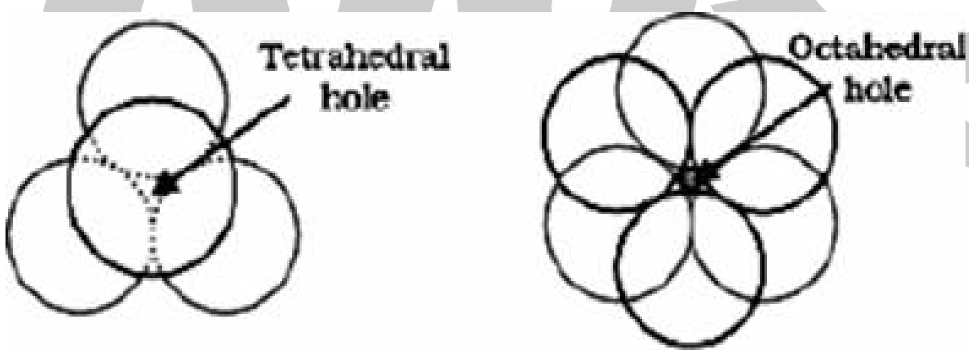
i.e. $r_{void} / r_{sphere} = 0.225$

In a multi layered close packed structure , there is a tetrahedral hole above and below each atom hence there is twice as many tetrahedral holes as there are in close packed atoms

3. What is octahedral hole?

Ans:

The interstitial void, formed by combination of two triangular voids of the first and second layer is called octahedral void because this is enclosed between six spheres centres of which occupy corners of a regular octahedron



4. Write a brief account of VBT of metal bonding?

Ans:

VBT is also called as resonance theory proposed by 'Pauling'. According to this theory;

- Metallic bond is essentially polar or non-polar covalent bond.
- The covalent bond involves resonance between a number of structures one electron and electron pair bonds
- There is a possibility of insufficient valence electrons for the formation of electron pair bonds with each atom of the metal; it is assumed that resonance takes place through out the solid metal.
- The atoms undergo hybridization.

Defects of the theory:

- This theory does not explain the conduction of heat in solids or their luster or retention of metallic properties in either the liquid or in the solution.

LONG ANSWER QUESTIONS

1. Describe Bragg's method for determining the structure of a regular crystalline solid?

The German physicist M Von Laue (1879 – 1960) in 1913 suggested the possibility of diffraction of X – Rays by crystals. The reason for this suggestion was that the wavelength of X – Rays was of about the same order as the inter atomic distances in a crystal. Then if these X – Rays was allowed to strike the crystal the rays will penetrate into the crystal and will be scattered by the electrons of the atoms or the ions of the crystal. The rays reflected from different layers of the atoms, due to wave nature will then undergo interference (constructive and destructive) to produce a diffraction pattern just as it happens in case of light passing through a grating containing a large number of closely spaced lines. In other words, crystals should act as a three dimensional grating for X – Rays. Bragg applied this fact in determining structure and dimensions of crystal.

W.L. Bragg and his father W.H. Bragg determined the cubic structure of NaCl using X – Rays. According to Bragg, a crystal (Composed of series of equally spaced atomic planes) could be employed not only as a transmission grating (as suggested by Laue) but also as a reflection grating. In Bragg's treatment, the X – rays strike the crystal at angle **q**, these penetrates into the crystal and are reflected by different parallel layers of particles in the crystal.

A strong reflected (constructive) beam will result only if all the reflected rays are in phase. The reflected waves by different layer planes will be in phase with one another only if the difference in the path length of the waves reflected from the successive planes is equal to an integral number of wavelengths.

2. **Derive bragg's equation for X-rays of wavelength (λ) and diffraction angle ϴ for an nth order reflection**?

It may be noted from the fig. that the beams of X – rays which are reflected from deeper layers travel more to reach the detector. Two X – Ray waves in phase are shown to be approaching the crystal. One wave is reflected from the first layer of atoms while the second wave is reflected from the second layer of atoms. The wave reflected from the second layer travels more distance before emerging from the crystal than the first wave. The extra distance travelled is equal to
LN + NM. For constructive interference to take place the extra distance travelled by the more penetrating beam must be on integral multiple of the wavelength

Path difference = LN + NM

LN = nγ (n = 1, 2, 3 ….)

Since the triangles OLN and OMN are congruent hence LN = NM

So, path difference = 2LN

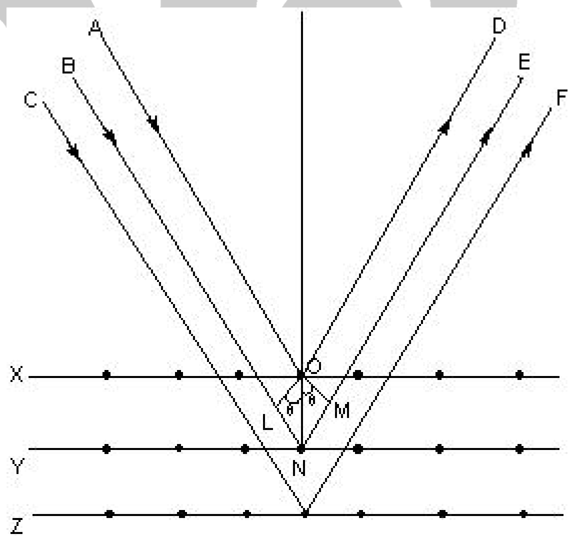
LN = d Sinq where d is the distance between two planes

So, path difference = 2d Sinθ

For constructive interference 2 d Sinq must be equal to nl

Or, **nγ = 2 d Sin**θ

This relation is called Bragg's equation. Distance between two successive planes d can be calculated form this equation. With X – Ray of definite wavelength, reflection at various angles will be observed for a given set of planes separated by a distance 'd'. These reflections correspond to n = 1, 2 , 3 and so on and are spoken of as first order, second order, third order and so on the
angle q increases as the intensity of the reflected beams weakens



X – Ray reflection from crystals

NUMERICALS

1. An X- ray beam (wavelength = 70.93 pm) was scattered by a crystalline solid. The angle (2θ) of diffraction for a second order reflection is 14.66°. Calculate the distance between parallel planes of atoms from which the scattered beam appears to have been reflected?

Formula is $n\lambda = 2d \sin\theta$

Given second order reflection, n = 2

λ = wavelength of X – ray = 70.93 pm = 70.93×10^{-12} m

d = distance between planes = ?

Given $2\theta = 14.66^0 \Rightarrow \theta = \dfrac{14.66}{2} = 7.33^0$

$\sin\theta = \sin 7.33^0 = 0.127$

$$n\lambda = 2d\sin\theta \Rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{2 \times 70.93 \times 10^{-12}}{2 \times 0.127} = 558 \times 10^{-12}\text{m}$$

∴ Distance between the planes (d) = 558×10^{-12}m = 558pm.

2. crystal when examined by the Bragg's technique using X – rays of wavelength 2.29 A° gave on X – ray reflection at an angle of 23°20'. Calculate the inter planar spacing; with another X – ray source, the reflection was observed at 15° 26'. What was the wave length of the X – rays of the second source?

Ans. Case -1 : $n\lambda = 2d\sin\theta$

n = 1

λ = 2.29 A° = 2.29×10^{-10}m

d = ?

$\theta = 23^o20' \Rightarrow \sin\theta = \sin 23^o20' = 0.393$

$$n\lambda = 2d\sin\theta \Rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 2.29 \times 10^{-10}m}{2 \times 0.393} = 2.92 \times 10^{-10}m$$

$\therefore$ Inter planar spacing (d) = 2.92×10^{-10}m = 2.92 A^o

Case -II

n = 1

λ = ?

d = 2.92×10^{-10}m (calculated in case – 1)

$\theta = 15^o\,26' \Rightarrow \sin\theta = \sin 15^o\,26' = 0.267$

$$n\lambda = 2d\sin\theta \Rightarrow \lambda = \frac{2d\sin\theta}{n} = \frac{2 \times 2.92 \times 10^{-10} \times 0.267}{1} = 1.55 \times 10^{-10}m$$

$\therefore$ Wave length of X – rays (λ) = 1.55×10^{-10}m = 1.55 A^o

3. X – rays of wavelength 5460 A^o are incident on a grating with 5700 lines per cm. Find the angles of reflection for the 1st and 2nd order diffraction maximum?

Ans. Case -1

Wave length of X – rays (λ) = 5460 A^o = 5460×10^{-8} cm

Inter planar spacing (d) = $\frac{1cm}{5700}$

n = 1, angle of reflection (θ_1) = ?

$n\lambda$ $\qquad$ $1 \times 5460 \times 10^{-8}$

$$\therefore n\lambda = 2d \sin\theta_1 \Rightarrow \sin\theta_1 = \frac{\quad}{2d} = \frac{\quad}{2 \times \frac{1}{5700}} = 0.155$$

$\sin\theta_1 = 0.155$

$\theta_1 = 8.95^o$

$\therefore$ Angle of reflection (θ_1) for 1st order diffraction = 8.95^o

Case –II: $\lambda = 5460\ A^o = 5460 \times 10^{-8}$ cm

$$d = \frac{1}{5700} \text{ cm}$$

$n = 2$

Angle of reflection (θ_2) = ?

$$\therefore n\lambda = 2d \sin\theta_2 \Rightarrow \sin\theta_2 = \frac{n\lambda}{2d} = \frac{1 \times 5460 \times 10^{-8}}{2 \times \frac{1}{5700}} = 0.3115$$

$\sin\theta_2 = 0.3115$

$\therefore \theta_2 = 18.15$

$\therefore$ Angle of reflection (θ_2) for 2nd order diffraction = 18.15^o

4. The inter planar distance in a crystal used for X – ray diffraction is 0.2 nm. The angle of incidence (θ) of x – rays is 9.0^0. If the diffraction is of first order, find the wavelength of the X p rays. ?

Sol. Given: $d = 0.2$ nm $= 0.2 \times 10^{-9}$ m

$n = 1$ (given as first order)

$\lambda = ?$

$\theta = 9.0^o$ => $\sin\theta = \sin 9.0^o = 0.156$

Bragg's equation is => $n\lambda = 2d\sin\theta$

$$\Rightarrow \lambda = \frac{2d\sin\theta}{n} = \frac{0.2 \times 0.2 \times 10^{-9} \times 0.156}{1}$$

$$\Rightarrow \lambda = 0.0625 \times 10^{-9}\,m$$

$$= 0.0625 \times 10^{-9} \times 10^{-10}\,A^o$$

$$= 0.0625 \times 10 A^o$$

$$= 0.625\,A^o$$

$\therefore$ Wavelength of the X – rays = $0.625\,A^o$

5. Silicon crystallizes in face centered cubic lattice. At 22.5^{o}C, a single crystal of very pure 'Si' has the following characteristics Mol. wt = 28.09; unit cell length = 5.43 A^0,
Z = 8 (Total no. of constituent particles per unit cell). Find the density of the crystal?

Sol. Given:

$M = 28.09$

$Z = 8$

$A = 5.43\,A^o = 5.43 \times 10^{-8}\,cm$

Formula

$$\text{Density of the crystal (P)} = \frac{Z\,M}{N_o a^3}$$

Where N_o = Avogadro's number = 6.023×10^{-23}

ZM 8 x 28.09

$$\therefore P = \frac{}{N_o a3} = \frac{}{6.023 \times 10^{23} \times (5.43 \times 10^{-8})^3 \text{ cm}^3}$$

$$= \frac{224.72}{6.023 \times (5.43)^3 \times 10^{23} \times 10^{-24}}$$

$$= \frac{224.72}{6.023 \times 160} \times 10$$

$$= 2.33 \text{ g / cm}^3$$

$\therefore$ Density of given crystal = 2.33 g / cc

6. Elementary Silver crystallizes in a face centered cubic lattice with unit cell length 0.4086nm. Calculate the density and hence the atomic radius of 'Ag'? (At.wt. of Ag = 107.88)

Sol. Given:

a = 0.4086nm

$= 0.4086 \times 10^{-9}$ m

M = 107.88

We have,

$N_o = 6.023 \times 10^{23}$

Z = 4(for f.c.c.)

$$\therefore \text{Density } (P) = \frac{Z\,M}{N_o\,a3}$$

$$P = \frac{4 \times 107.88 \times 10^{-3} \text{ kg}}{6.023 \times 10^{23} \times (0.4086 \times 10^{-9})^3 \text{ m}^3}$$

$$= \frac{4315}{0.4108}$$

$$= 10503 \text{ (or) } 1.0503 \times 10^4 \text{ kg/ m}^3$$

$\therefore$ Density of given metal = 1.0503×10^4 kg/ m^3

For f.c.c. lattice, radius of metal atom = $\frac{a}{2\sqrt{2}}$

Given, a = 0.4086nm = 4.086 A°

$$\text{Radius of metal atom} = \frac{a}{2\sqrt{2}} = \frac{4.086}{2\sqrt{2}}$$

$$= \frac{4.086}{2.828}$$

$$= 1.444 \text{ A}^o$$

7. X – rays of wavelength equal to 0.134 nm gave a first order diffraction from the surface of a crystal. The ‘θ’ value was found to be 10.5°. Calculate the distance between the planes in the crystal?

Sol. Given:

λ = 0.134nm

n = 1 (for first order)

$\theta = 10.5^o \Rightarrow \sin\theta = \sin 10.5^o = 0.182$

d = ?

Bragg’s equation $n\lambda = 2d \sin\theta$

$$\Rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 0.134}{2 \times 0.182}$$

$$= 0.36\text{nm}$$

$\therefore$ Distance between the planes of crystal = 0.36nm.

8. Aluminium crystallizes with an fcc lattice. If the closest approach of aluminium atoms in the crystal is 0.4054 nm, find the density of aluminium ?(At. wt. of Al = 26.98).

Sol. Given:

Closest approach distance = 0.4054nm

$$\therefore \text{Radius } (r) = \frac{0.4054}{2} = 0.2027\text{nm}$$

We have $r = \frac{a}{2\sqrt{2}}$ (for fcc)

$$\Rightarrow 0.2027 = \frac{a}{2\sqrt{2}}$$

$$\Rightarrow \text{Unit cell length } (a) = 0.2027 \times 2\sqrt{2}$$

$$= 0.2027 \times 2.828$$

$$= 0.573\text{nm}$$

$$= 0.573 \times 10^{-9}\text{ m}$$

We have Density (p) = $\frac{Z\,M}{N_o\,a3}$

$Z = 4$ (for fcc), $M = 26.98$, $N_o = 6.023 \times 10^{23}$

$a = 0.573 \times 10^{-9}$m (calculated)

$$\therefore p = \frac{4 \times 26.98}{6.023 \times 10^{23} \times (0.573 \times 10^{-9})^3 \, m^3} = 95.318 \times -10^4 \, g / m^3$$

$\therefore$ Density of the given metal is $= 95.318 \times -10^4 \, g / m^3$

Solutions:

The crystalline sodium has body centered cubic unit cell with a = 0.424nm at 298 k. Calculate the density of sodium metal.

Ans.

The density of sodium (ρ) $= \dfrac{Z\,M}{N_o\,a^3}$

For body centered cubic substance z = 2

Molar mass (M) of sodium = 23g

$= 23 \times 10^{-3}$ kg

Unit cell length (a) = 0.424 nm

$= 0.424 \times 10^{-9}$ m

Avogadro's number (N_o) $= 6.023 \times 10^{23}$

$\therefore \rho = \dfrac{ZM}{N_o\,a^3}$ = density of the unit cell

$$= \frac{2\,(23 \times 10^{-3} \text{ kg mol}^{-1})}{6.023 \times 10^{23} \times (0.424 \times 10^{-9})^3 \, m^3}$$

$= 1002 \text{ kg m}^{-3}$

$= 1.002 \times 10^3 \text{ kgm}^{-3}$