

axis. A straight line is obtained of n_{sp}/c having the value at that stage is called

2.5.0 REFRACTIVE INDEX (الانكساف) (نفا)

2.5.1 Introduction:

"When a ray of light enters from one medium to the other, then it changes its direction. This property of light is called refraction."

When a ray of light travels from air or vacuum to a denser medium (دقیق واسطه) say liquid, then ray of light bends towards the normal (عمود). This is shown in the following diagram.

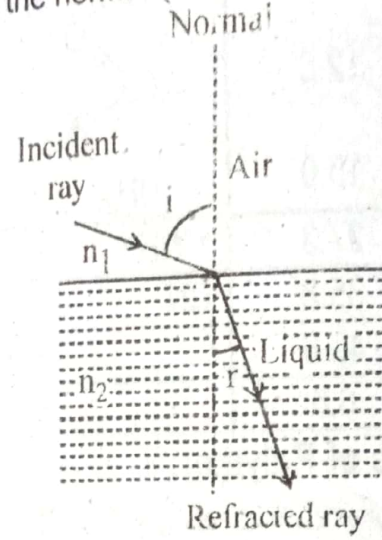


Fig. (2.12) Refraction of light.

When the angle of incidence 'i' is increased, then angle of refraction (انكساف) 'r' also increases. Anyhow, the value of r always remains smaller than 'i'. If the ray enters from denser to the rarer medium, then it bends away from the normal. The angle of incidence is less than the angle of refraction as shown in the following diagram. (2.13)

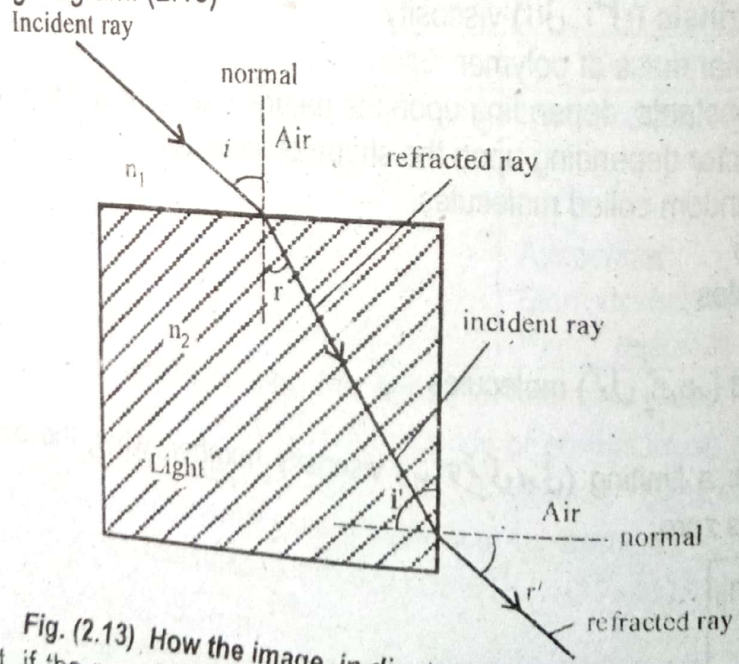


Fig. (2.13) How the image is displaced due to refraction.

It means that, if the ray of light enters into the denser medium and then emerges out on the other side of the rarer medium, then the ray is displaced. This diagram explains that a image is displaced due to refraction.

Liquids

2.5.2 Snell's Law:

87

According to this law, the ratio of sine of the angle of incidence to the sine of angle of refraction is a constant quantity.

$$n = \frac{\sin i}{\sin r} = \frac{\text{velocity in the air (medium of angle i)}}{\text{velocity in the liquid (medium of angle r)}}$$

Actually the angle of incidence is different from the angle of refraction due to the reason that the velocity of the light in the two media is different. According to the law of refraction,

$$\frac{\sin i}{\sin r} = \frac{n_2}{n_1}$$

n_1 = Refractive index of the rarer medium

n_2 = Refractive index of the denser medium.

2.5.3 Critical Angle of Refraction:

... of the standard liquid.

The value of the ϵ can help us to estimate (اندازہ لگانا) the polarity (قطبیت) of a compound and so, we can calculate the dipole moment of a compound from it.

2.7.0 DIPOLE MOMENT (دو قطبی قوتوں کا معیار اثر)

2.7.1 Introduction:

Those molecules in which the electron pair making the bonds are not equally shared are responsible (ذمہ دار) for creating the dipole (دوپولز). This is due to difference of electronegativity between two atoms. Dipole moment is the property which is associated with such type of molecules.

Definition:

Dipole moment is the product of electrical charge and the distance between the two charges.

Mathematically,

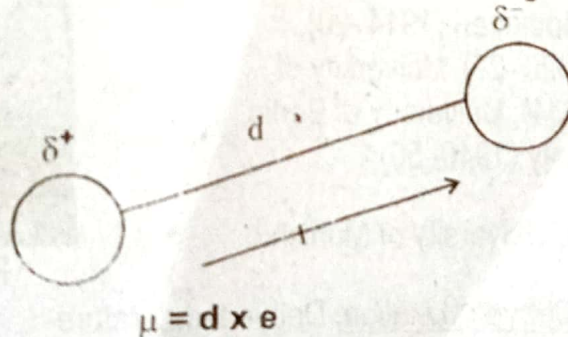
$$\mu = d \times e$$

d = Distance between two charges

e = Charge on any one of the poles.

μ = Dipole moment.

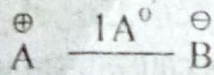
Dipole moment is a **vector quantity** (سکتی مقدار), so it is represented by an arrow. This arrow shows the direction from positive to the negative charge. The magnitude (قیمت) of the dipole moment is indicated (نشان دہی کرتا) by the length of arrow, as shown in the following diagram.



Dipole moment can help us to have the quantitative measurement of the extent to which a molecule is polar. It also helps to know the molecular configuration (مالیکیولز کے ترتیب اجزا) of the substance.

2.7.2 Units of Dipole Moment:

In order to derive the units, consider hypothetical (فرضی) molecule $A^{\oplus} - B^{\ominus}$, which has 100% ionic bond. In that case, 'A' has full positive and 'B' has full negative charge.



Suppose that the bond distance is $1A^{\ominus}$.

Since, $\mu = d \times e$

$$d = 1 \text{ \AA} = 10^{-8} \text{ cm (in C.G.S. system)}$$

$$e = 4.8 \times 10^{-10} \text{ e. s. u (in C.G.S. system)}$$

$$\mu = 10^{-8} \text{ cm} \times 4.8 \times 10^{-10} \text{ E.S.U.} = 4.8 \times 10^{-18} \text{ cm e. s. u.}$$

$$10^{-18} \text{ cm e. s. u.} = 1 \text{ Debye} = 1 \text{ D}$$

Hence, $\mu = 4.8 \text{ D}$

So, Debye is the unit of dipole moment in C. G. S. system.

electrostatic unit
of charge.

(ایسی اکائی ہے جو C.G.S. سسٹم کے مطابق ہے)

In SI system, the distance is taken in meters and charge in coulomb.

$$d = 1 \text{ \AA} = 10^{-10} \text{ m (in SI units)}$$

$$e = 1.602 \times 10^{-19} \text{ C (in SI units)}$$

$$\mu = 10^{-10} \text{ m} \times 1.602 \times 10^{-19} \text{ C} = 1.602 \times 10^{-29} \text{ mC}$$

$$\mu = 46.02 \times 10^{-30} \text{ mC}$$

mC (ایسی اکائی ہے جو S. سسٹم میں ہے)

In SI system, the unit of dipole moment is mC. Anyhow, the absolute values of both dipole moments are same for the same molecule $\overset{\oplus}{A} - \overset{\ominus}{B}$. (which is thought to be 100% ionic).

Hence, $4.8 \text{ D} = 16.02 \times 10^{-30} \text{ mC}$

$$1 \text{ D} = 3.338 \times 10^{-30} \text{ mC}$$

Debye (بڑی اکائی ہے mC سے)

With the help of this relationship, we can interconvert two types of units of dipole moment.

Born
Citizenship
March 24, 1884, Maastricht, Netherlands

$$\mu = 0.0128 \sqrt{(P_m - P_i) T D}$$

2.7.11 Applications of Dipole Moment Measurements:

Dipole moment is one of the excellent (بہترین) constitutive property (والی) for liquids and solids. A few important applications are mentioned.

(i) **Comparison of Relative Polarities:**

The greater the electronegativity difference between two bonded atoms, greater the polarities (پولز بننے کا عمل) and greater the values of dipole moments. The μ -values decrease from HCl to HI for halogen acids, because their polarities go on decreasing down the group.

(ii) **Percentage of Ionic Character:**

The polar covalent compounds are not 100 % covalent. They have certain % age of ionic character in them. This can be calculated by the following formula.

$$\% \text{age ionic character} = \frac{\text{observed dipole moment}}{\text{diple moment of 100\% ionic bond}} \times 100$$

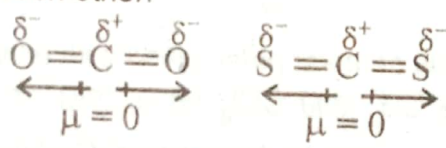
The dipole moment of 100% ionic character is calculated from the actual bond length and the charge of electron or proton.

(iii) **Shape of Molecules:**

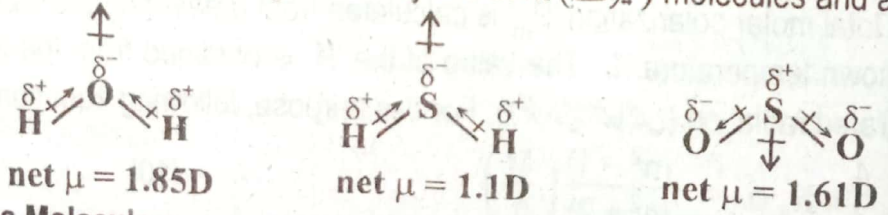
Dipole moment is vector quantity (سمتی مقدار). Every bond in a compound has almost a constant value of bond moment (بانڈ کے اندر کسی قوت کا کسی شے سے متاثر ہو کر گھمانا). The net values of the bond moments give us information about the shapes of the molecules.

(a) **Triatomic Molecules:**

Linear (سیدھے) triatomic molecules like CO₂ and CS₂ have zero dipole moments because their bond moments cancel the effect of each other.

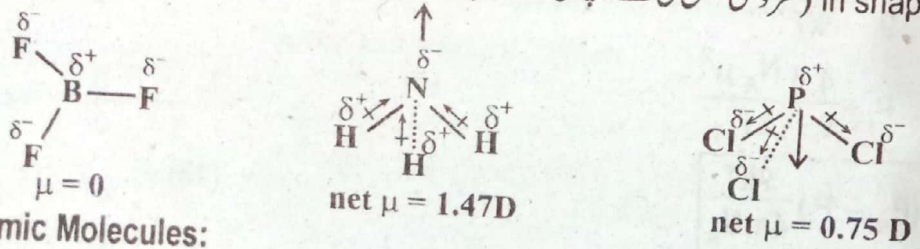


Triatomic non-linear (جو سیدھے نہ ہوں) molecules like H₂O, H₂S and SO₂ etc. have net dipole moments as shown by the following diagram. They are bent (نیڑھے) molecules and are V-shaped.



(b) **Tetratomic Molecules:**

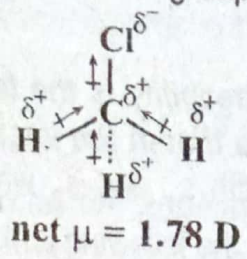
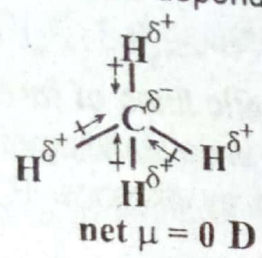
The molecules like BF₃, AlF₃ etc. are planar triangular (ایک سطح پر تینوں بانڈز برابر فاصلے پر) and have zero μ values. Anyhow, the compounds like NH₃, NF₃, PCl₃, PF₃ etc. have net dipole moments as shown in the following diagram. They are pyramidal (مخروطی شکل کی شے کا چوٹی دار ڈھیر) in shape.



(c) **Pentatomic Molecules:**

Pentatomic molecules having symmetrical (ایک جیسا پن) structure like CH₄, SiH₄, CCl₄ etc. have net dipole moments zero, because they are perfectly tetrahedral (چار پہلوؤں والی ٹھوس چیز) molecules as

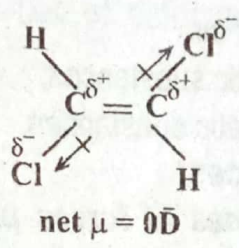
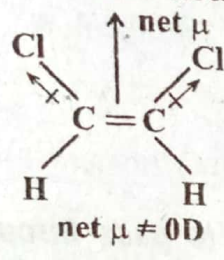
shown below. Anyhow, if one of the atoms attached with the central atom is substituted then the dipole moment is developed and its value depends upon the nature and size of group.



(iv) **Comparison of Cis and Trans Geometrical Isomers:**

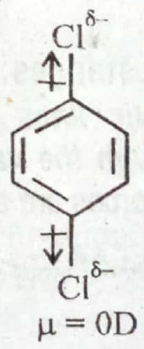
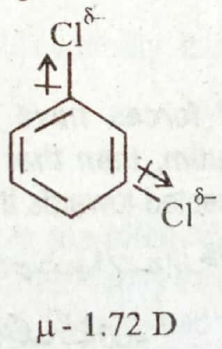
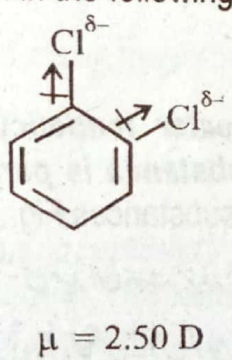
Due to restricted rotation (پابندی کی وجہ سے کم گھومنا) of the double bond or cyclic structure of a compound geometrical isomers are developed. In case of cis isomer, there is a certain value of dipole moment but the bond moments cancel the effect of each other in trans-isomer.

Following diagram makes the idea clear.



(v) **Comparison of o, m, p Isomers:**

The dipole moment of benzene is zero, because it is regular hexagonal (چھ سائڈز والی) symmetrical molecule. The bond moments cancel the effect of each other and they are directed towards the center as shown in the following diagram.



In the case of disubstituted p-derivative the net μ is zero in many cases. But it is non zero in the case of o-and m-derivatives. Anyhow, the net dipole moment of o-derivatives should be greater than those of m-isomers.

- (i) Each lattice point has the same environment (گرد و پیش) as that of any other point in the lattice.
- (ii) A constituent particle is to be represented by lattice point, irrespective (قطع نظر) of the (حقیقت) and whether it contains the single atom or more than one atoms.

3.1.2 Unit Cell:

Smallest 3-D part of crystal lattice

When we picturize (تصور کشی کرنا) a crystal lattice as shown in the above diagram (3.1), then it is possible to select a group of lattice points. This group of lattice points repeated again and again is called the unit cell. The whole lattice can be generated by translation or stacking (اکٹھا جوڑنا) of these unit cells.

So, unit cell is a three dimensional group of lattice points which generate the whole lattice by translation or stacking Fig. (3.2)

3.1.3 Types of Unit Cells:

Unit cell can be divided into four types.

(i) Simple unit cell:

This type of unit cell is produced, when the particles are present only at the corners of the unit cell (یونٹ سیل کے کونے).

(ii) Face centred unit cell:

When the particles are located at the centre of each face in addition to the corners, then it is called face centred unit cell.

(iii) End face centred unit cell: *constituent particles at 2 opposite faces*

When the particles are located at the centers of the end face (ہر سائیڈ کے سنٹر میں) in addition to the corners, then it gives end face centred unit cell.

(iv) Body centred unit cell:

When the particles are present at the centre of the cell in addition to the corners, then it is called body centred unit cell.

The following set of diagrams (3.3) show these four types of unit cell.

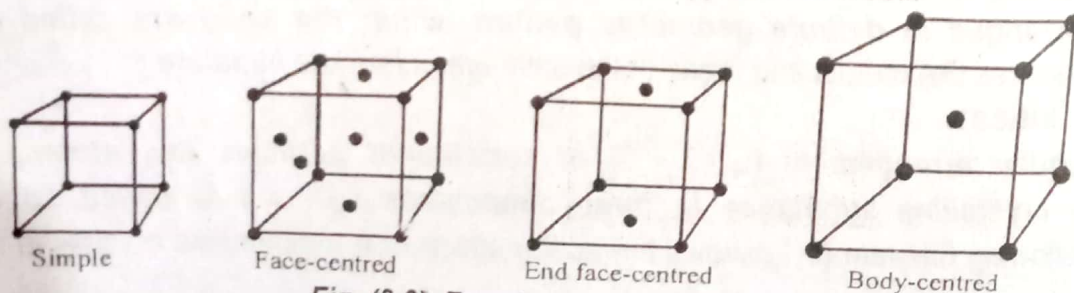


Fig. (3.3) Four types of unit cells.

3.1.4. Crystal Systems (قلموں کا نظام اشکال):

Each unit cell is a parallelepiped (مستطیل نما), whose interfacial angles (سائیڈز کے درمیانی زاویے) may or may not be 90° . The three lengths a , b , c and three interfacial angles are called unit cell dimensions. The relationship between the values of the angles and between the lengths of the axes give us seven types of crystal systems as shown in the following Table (3.1).

Table (3.1): The Seven Crystal Systems and Fourteen Bravais Lattices

Systems	Bravais lattices	unit cell characteristics	characteristic symmetry elements	examples
Cubic	3 simple, body-centred, face-centred	three axes at right angles: all equal $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	four 3-fold rotation axes (along cubic diagonals)	NaCl, ZnS, FeS ₂ , KCl, Diamond, Au, Hg, Ag, Pb,
Tetragonal	2 simple, body-centred	three axes at right angles: two are equal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	one 4-fold rotation axis	SnO ₂ , TiO ₂ , Sn, KH ₂ PO ₄
Orthorhombic	4 simple, body-centred, face-centred, end-centred.	three axes at right angles: but all unequal $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	three mutually orthogonal 2-fold rotation axes	KNO ₃ , PbCO ₃ , BaSO ₄ , rhombic sulphur
Monoclinic	2 simple, end-centred	three axes, all unequal, two axes at right angles, third is inclined to these at an angle other than 90° $a \neq b \neq c$ $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	one 2-fold rotation axis	CaSO ₄ .2H ₂ O, Na ₂ SO ₄ .10H ₂ O, Na ₂ B ₄ O ₇ .10H ₂ O, monoclinic sulphur
Triclinic	1 simple	three axes not at right angles: All unequal. $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	none	CuSO ₄ .5H ₂ O, K ₂ Cr ₂ O ₇ , H ₃ BO ₃
Hexagonal	1 simple	two equal axes in one plane with included angle 120°; 3rd axis at rt. \angle to these; unequal $a = b \neq c$ $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	one 3-fold rotation axis	ice, graphite, HgS, Mg, Zn, Cd
Rhombohedral or Trigonal	1 simple,	three equally inclined axes, not at rt. \angle ; All equal $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$	one 3-fold rotation axis	NaNO ₃ , Bi, Sb, As, ICl

$$V = (4.12)^3 \times 10^{-30} \text{ m}^3$$

$$Z = 1$$

$$N_A = ?$$

On substituting the values into following equation we get,

$$N_A = \frac{Z.M}{P.V}$$

$$N_A = \frac{1 \times 158.5 \times 10^{-3}}{3.97 \times 10^3 \times (4.12)^3 \times 10^{-30}}$$

$$= \boxed{6.023 \times 10^{23} \text{ molecules mol}^{-1}} \text{ Ans.}$$

3.2.4 Structure of NaCl:

It has face centred cubic (ایسا کیوب جس کے پہلو کے سنٹر میں ذرے ہوں) lattice and each ion is surrounded by six oppositely charged ion. The co-ordination number of Na^{\oplus} and Cl^{\ominus} each is 6. There are four units of Na^{\oplus} and Cl^{\ominus} ions in a unit cell. The structure is shown in Fig. (3.10)

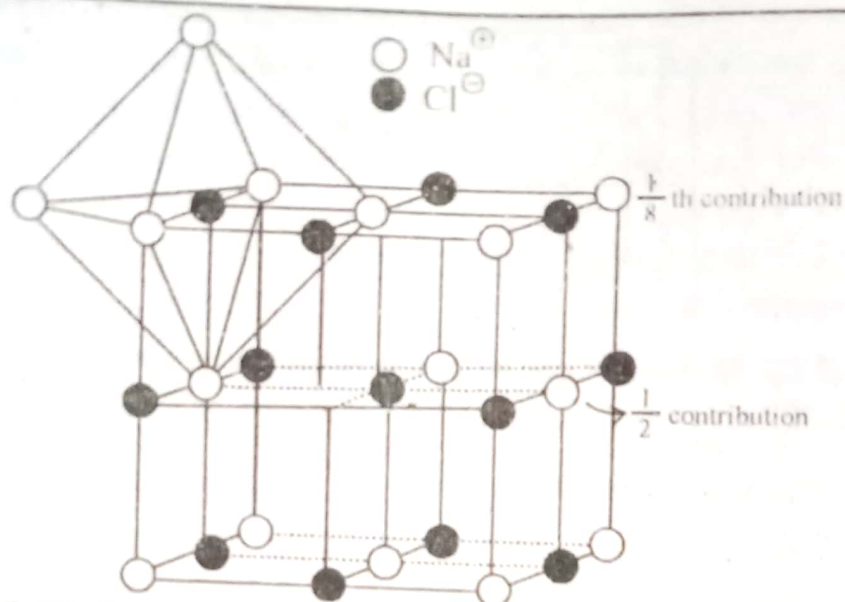


Fig. (3.10) Structure of unit cell of sodium chloride and contribution of each ion into the unit cell. Co-ordination number of each ion is 6.

The other ionic compounds like NaBr, NaI, AgCl, MgO also have sodium chloride structure.

		0.709	Zr	0.100
	$K\alpha_2$	0.713		
	$K\beta$	0.632		

3.4.2 Diffraction of X-rays:

X-ray tube provides electromagnetic radiations with wavelengths of about atomic dimensions (ایٹم کے سائز کی). In most of the cases we can think that a typical atom might behave like a hard sphere of about 2\AA diameter (قطر). The characteristic X-rays which are obtained from copper may be used for X-ray crystallography. The wavelength of such rays are 1.5418\AA . When these X-rays are passed through a crystal, they are diffracted. They form an interference pattern like that of visible light, which is diffracted (انکسار) by grating. The spacing in the gratings are comparable to its wavelength.

X-rays are electromagnetic radiations (بھی برقی مقناطیسی لہریں ہیں). Electric and magnetic fields are propagating perpendicular (یہ دونوں میدان باہمی ایک دوسرے کے عموداً ہیں) to each other. They are also perpendicular to the direction of propagation. The scattering (بکھرتا) of X-rays is due to the reason that the interaction between the electrical field of X-rays takes place with the negatively charged electrons in the crystal structure (X-rays کا برقی میدان ایٹمز کے گرد گھومنے والے الیکٹران کے منفی چارج سے الجھتا ہے). This scattering power of an atom is proportional to the atomic number or the number of the electrons of the atom. The crystal acts as three dimensional diffraction grating towards X-rays. So, a diffraction pattern is obtained when X-rays pass through the crystal.

نیو کلیس میں پروٹان کی تعداد اور تمام الیکٹران جو ان کے گرد گھوم رہے ہیں۔ X-rays کی لہریں لہائی ان پر انحصار کرتی ہے۔

3.4.3 Bragg's Equation:

Bragg has given a simple account of diffraction (انکسار) from a three dimensional crystal structure. The complex phenomenon of X-ray diffraction is reduced theoretically to simple geometrical problems looking as if we are studying the reflection of X-rays from crystal planes.

Let us consider a crystal having three planes '11" '22" and '33"'. These planes are successive (یکے بعد دیگرے). A beam of X-rays of wavelength ' λ ' is incident (پڑتی ہے) on these planes at an angle ' θ '. A part of the beam 'BC' is reflected from the point 'B'. On the other hands, some rays like 'A'B'C' penetrate (گھس جاتا) into crystal and are reflected by the atoms present in the lower planes '22" and '33"'. The diagram is as follows. Fig. (3.24).

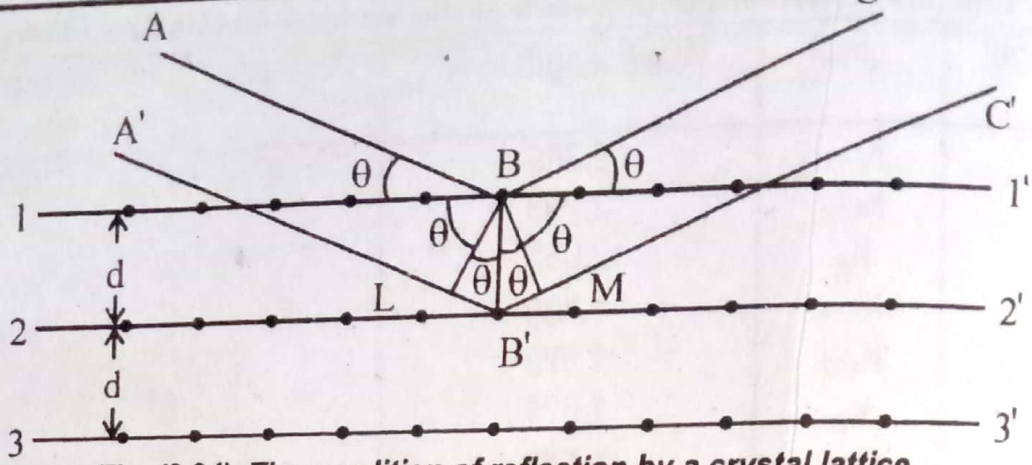


Fig. (3.24) The condition of reflection by a crystal lattice.

The ray $A'B'C'$ has to travel a longer distance in order to emerge out (باہر نکلنا) of crystal. BL' and BM' are the perpendiculars on $A'B'C'$ ray. The reflected (منعکس شدہ) beams BC' and $B'C'$ undergo interference (داخل اندازی) with each other. If these reflected rays are in phase then they reinforce (ایک دوسرے کے لئے تقویت کا باعث بننا) each other and the intensity of the reflected ray is maximum. When we say that rays are in phase with each other, then it means that the crest falls over the crest and trough over the trough.

If the reflected rays are out of phase, then the intensity (شدت) of reflected beam is very low. When a photographic plate is placed to receive the reflected rays, then the diffraction pattern is obtained.

It is clear that, the reflected rays BC' and $B'C'$ can do the constructive (تعمیری) interference (داخل اندازی), if the path difference ($LB' + MB'$) is the integral multiple of wavelength of X-rays (x-rays کی لہر کی لمبائی کا سادہ حاصل ضرب).

From the right angled triangle, LBB' , the length LB' is perpendicular and BB' is hypotenuse

$$\text{So, } \frac{LB'}{BB'} = \sin \theta$$

$$LB' = BB' \sin \theta$$

From the right angled triangle MBB' , the length MB' is perpendicular and BB' is hypotenuse.

$$\text{So, } \frac{MB'}{BB'} = \sin \theta$$

$$\text{Hence, } MB' = BB' \sin \theta$$

$$BB' = d \quad (\text{inter planar distance})$$

$$MB' = d \sin \theta$$

Path difference,

$$LB' + MB' = d \sin \theta + d \sin \theta$$

$$\text{Path difference} = 2d \sin \theta$$

The path difference is integral multiple of wavelength. Let that integral multiple is 'n'. So,

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

..... (1)

By gradually increasing the value of angle ' θ ', a number of positions are observed corresponding to $n = 1, 2, 3, 4, \dots$ etc. At these positions, the reflected beam will have maximum intensity. For other values of ' θ ' lying in between, those values of n , the intensity of reflected beam will be less than maximum. So, a diffraction pattern maxima corresponding to $n = 1, 2, 3, \dots$ etc. are obtained.