Analytical Chemistry M.Sc I

QUALITATIVE ANALYSIS BY X-RAY EMISSION

The sample is excited by irradiation in the X-ray tube and subsequently recovered without any change. The abscissa in Fig. 9 has been plotted in terms of angle 2θ which can be converted into wavelength using the equation $n\lambda = 2d \sin \theta$. Identification of peaks can then be made by reference to tables for emission lines of the elements. In Fig. 9 there is one K_α line for EDDT, topaz, LiF and two K_α lines for NaCl. The qualitative information obtained from the Fig. 9 can be converted into semiquantitative data by measuring the peak heights. This measurement consists in setting the goniometer to the appropriate angle 2θ and then counting for suitable period. The concentration can be roughly estimated by the relation, $P_x \doteq P_s W_x$ where, P_x = relative line intensity measured in terms of number of counts for a fixed period. W_x = weight fraction of the element in the sample. P_s = relative intensity of the line that would be observed under identical counting conditions when W_x were unity. The value of P_s can be calculated by using a standard sample of known composition with respect to the element being determined.

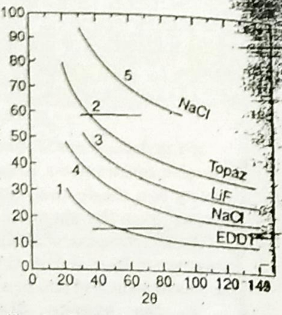

Fig. 9. X-ray dispersion curves for various crystals.

Exercise. *What is meant by enhancement effect?*

Solution. When the sample contains an element whose characteristic emission spectrum is excited by the incident beam and this spectrum in turn causes a second matrix effect which is known as **enhancement effect.** The results so obtained are greater than expected owing to this effect. Procedures like comparison standards, internal standards, dilution techniques and preparation of thin films can be adopted to eliminate this effect.

X-RAY EMISSION vs X-RAY ABSORPTION

1. X-ray emission is more versatile than X-ray absorption for general elemental analysis.
2. Speed, good precision, spectral line specificity, applicability to a wide range of elements without changing any instrumental parameter other than the Bragg angle make X-ray emission spectroscopy more useful than X-ray absorption.
3. X-ray emission methods are applicable to all elements having atomic number 11 to 92 with some limitations.
4. An unique advantage of the absorption edge method over emission is the elimination of matrix effect which is inherent in emission analysis.
5. The lower limit of detection by emission method is a function of the peak to background ratio and the number of photons counted.

X-RAY DIFFRACTION

Max Von Laue (1912) suggested that X-rays might be diffracted while passing through a crystal where it acts as a three dimensional diffraction grating and produce interference effect. He realized that the wavelength of the X-rays are comparable to the separation of lattice planes (interatomic distance is of the order of 10^{-8} cm). Laue's suggestion was confirmed immediately by **W. Friedrich and P. Knipping** and has grown since then into a

chnique of extraordinary power. **Time resolved X-ray diffraction** techniques make use synchrotron sources which can emit intense polychromatic pulses of X-ray radiation with lse widths varying from 100 ps to 200 ps. The technique in millisecond can identify a mber of structural changes that follow electronic excitation of the chromophore with a laser lse, *i.e.*, isomerization, ejection, protonation of the exposed chromophore and a number of mino acid motions.

utomated X-ray Diffractometry.

Four circle diffractometer is used for measuring single crystal diffraction patterns. The mputer linked to the diffractometer determines the unit cell dimensions and the angular ttings of the diffractometers. The computer controls the settings, moves the crystal and tector for each one in turn. At each setting, the diffraction intensity is measured and ckground intensities are assessed at slightly different settings. Computing techniques lead t only to automatic indexing but also to the automated determination of the shape, mmetry and size of the unit cell.

MILLER INDICES

Miller indices are a set of integers (h, k, l) which are used to describe a given plane in crystal. Miller indices of a face of crystal are inversely proportional to the intercepts of that ce on the various axes. If the face is parallel to an axis, the intercept is L and Miller index comes 1/α or 0. Miller indices for a plane may be obtained from **Weiss indices** (coefficients the unit length as b and c of the plane) by taking the reciprocals of the latter and ltiplying throughout by the smallest number in order to make all reciprocals as integers.

Determination of Miller Indices. *(i) Prepare a three-column table with the unit cell es at the top of the columns. (ii) Enter intercept (expressed as a multiple of a, b or c) of the anes. (iii) Invert all the numbers. (iv) Clear fractions to get h, k, l.*

ercise. *Calculate Miller indices of crystal planes which cut through the crystal axes at* 2a, 3b, c (ii) 2a, – 3b, – 3c.

Solution.

	(i) a	b	c	(ii) a	b	c
Intercepts	2	3	1	2	– 3	– 3
Reciprocals	1/2	1/3	1	1/2	– 1/8	– 1/3
Clear fractions	3	2	6	3	– 2	– 2

∴ **Miller indices are (3 2 6)**

∴ **Miller indices are** $(3\,\bar{2}\,\bar{2})$

Note. The negative sign in the Miller indices is indicated by placing a bar on the integer.

Interplanar Spacing in a Crystal System. The interplanar distance d_{hkl} in different bic lattices is given by

$$1/(d_{hkl})^2 = (h/a)^2 + (k/b)^2 + (l/c)^2 \qquad ...(9)$$

here h, k, l are the Miller indices of the planes and a, b, c are dimensions of the cell.

For a **cubic system,** $a = b = c$ **so** from the equation (9)

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2} \qquad ...(10)$$

For **tetragonal system,** $a = b \neq c$, so that

$$1/(d_{hkl})^2 = (h^2 + k^2)/a^2 + l^2/c^2 \qquad ...(11)$$

For **orthorhombic system,** $a \neq b \neq c$, thus

$$1/(d_{hkl})^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \qquad ...(12)$$

BRAGG'S CONDITION FOR DIFFRACTION

W.L. Bragg (1913) showed that scattered radiation from a crystal behaves as if the diffracted beam were reflected from a plane passing through points of the crystal lattice in a manner that makes these crystal lattice planes analogous to mirrors (Fig. 10).

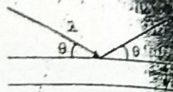

Fig. 10. Condition for diffraction.

Bragg's Law. The conditions leading to diffraction are given by **Bragg's law.** Consider the reflection of two parallel rays of the same wavelength by two adjacent planes of a lattice, as shown in Fig. 11. One ray strikes point D on the upper plane but the other ray must travel an additional distance AB before striking the plane immediately below. Similarly, the reflected rays will differ in path length by a distance BC. The net path length difference of the two rays is then

$$AB + BC = 2d \sin\theta$$

where θ is the **glancing angle.** For many glancing angles the path-length difference is not an integer number of wavelengths and the waves interfere largely destructively. However, when the path-length difference is an integer number of wavelengths ($AB + BC = n\lambda$), the reflected waves are in phase and interfere constructively. It follows that a reflection should be observed when the glancing angle satisfies **Bragg's law :**

$$n\lambda = 2d \sin\theta = 2d_{hkl} \sin\theta$$

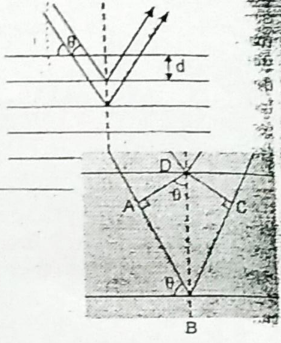

Fig. 11. Geometry of diffraction and its relation to Bragg's law. Constructive interference (reflection) occurs when $AB + BC$ is equal to an integral number of wavelengths.

d_{hkl} denotes the perpendicular distance between adjacent planes with indices hkl).

Reflections with $n = 2, 3, \ldots$ are called **second-order, third-order,** and so on. They correspond to path-length differences of 2, 3, ... wavelengths.

When $n = 1$, *i.e.*, first order diffraction, then $\lambda = 2d \sin\theta$. Since $|\sin\theta| \le 1$ for all values of θ, so Bragg's reflection can occur for wavelength $\lambda \le 2d$.

The primary use of Bragg's law is in the determination of the spacing between the layers in the lattice for, once the angle θ corresponding to a reflection has been determined, d may readily be calculated.

✓ **Exercise.** *A first order reflection from the (111) planes of a cubic crystal was observed at a glancing angle 11·2° using CuKα radiation. Calculate the length of the side of unit cell.*

Solution. According to $\lambda = 2d \sin\theta$, the (111) planes responsible for the diffraction have separation

$$d_{111} = \lambda/2 \sin\theta$$

The separation of (111) planes of a cubic-lattice of side a is given by $d_{111} = a/3^{1/2}$

$$a = \frac{3^{1/2}\lambda}{2\sin\theta} = \frac{3^{1/2} \times 154\ \text{pm}}{2\sin 11{\cdot}2^\circ} = 687\ \text{pm}.$$

Geometrical Description of Diffraction by P. Ewald. Ewald construction provides a geometrical relationship between the orientation of the crystal and the direction of the X-ray beams diffracted by it. As illustrated in Fig. 11, the **Bragg's condition** for diffraction occurs when a set of lattice planes, with defined d_{hkl} spacing, are inclined with respect to the

cident beam by an angle θ. The diffracted am (Bragg reflection) occurs at 2θ from e incident beam. The diffraction vector efined as $H = (s - s_0)/\lambda]$ is perpendicular to e lattice plánces (Fig. 12).

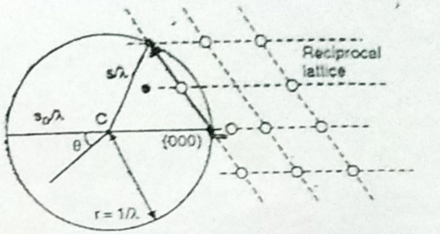

Fig. 12. Ewald sphere showing orientation of the reciprocal lattice with its origin (hkl = 000) at O.

The crystal can be physically oriented that a required reciprocal lattice point n intersect the sphere. From there, s_0 (the irection of the diffracted beam) can be educed from H. As the crystal is rotated, so s its crystal lattice and thus also the eciprocal lattice. If during the rotation of the crystal a reciprocal lattice point (hkl) touches the surface of the sphere, **Bragg's law is satisfied.** The result is a reflection in the direction s_0, with values of h, k, l corresponding both to the value of the reciprocal lattice point and for the crystal lattice planes.

X-RAY DETECTION AND MEASUREMENT

X-ray detection and measurement is accomplished by energy dispersive and wavelength dispersive spectrometer. In case of **wavelength dispersive** *X*-ray fluorescence, the diffraction property of a single analyzing crystal is used to disperse the polychromatic beam of emitted radiation from the specimen. The basic **principle** underlying this technique is the Bragg's law of diffraction ($n\lambda = 2d \sin\theta$). For wavelength's which satisfy Bragg's law, the characteristic X-rays are diffracted from the crystal through an angle of 2θ into the detector thereby allowing the measurement of just one X-ray line, and therefore one element at a time.

In the **energy dispersive X-ray fluorescence** (EDXRF), the proportional characteristics of the semiconductor detectors to produce a distribution of voltage pulses proportional to the X-ray energies emitted from the specimen are used. With these detectors X-rays of different energies emitted from a sample can be detected simultaneously whereas this characteristic is missing in the wavelength dispersive systems. EDXRF is a more accessible technique because

- *All the elements with $Z > 11$ can be quantified.*
- *It is non-destructive in nature.*
- *Specimen in any physical form can be analysed.*
- *The technique has multi-elemental capability.*
- *Elements present in a sample upto ppm can be detected readily.*

STRUCTURAL ANALYSIS OF CRYSTALS

Following diffraction methods are generally used for the determination of internal structure of crystals.

1. Laue Photographic Method. A single small crystal is placed in the path of a narrow beam of X-rays from a tungsten anticathode and the resulting diffracted beam is allowed to fall on a photographic plate. When the photographic plate is developed, a characteristic pattern, known as **Laue pattern** of spots is seen. From the

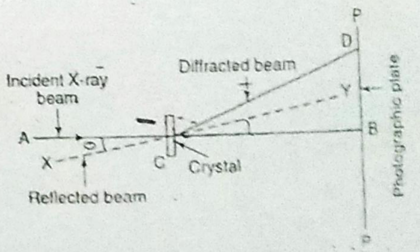

Fig. 13. Laue photographic method.

positions of the spots and the distance of the photographic plate from the cry calculated and the relative spacing between the planes is estimated. Laue patter used to orient crystals for solid state experiments and to determine the symmetry o crystal. However, the significance of reflection intensities is uncertain due to inhom nature of the incident X-rays.

2. Bragg's Method. To determine the crystal structure by Bragg's law, the X-ra allowed to fall on the crystal surface. Then the crystal is rotated and X-rays are m reflect from various lattice planes. The glancing angle for each intense reflection is rec On applying Bragg's equation ($n\lambda = 2d \sin\theta$), ratio of lattice spacing for various gro planes can be obtained. This ratio has been found to be different for different crystals. T the experimentally observed ratios are compared with the calculated ratios to identi particular structure. Hence,

(i) $d_{100} : d_{110} : d_{111} = 1 : 1/\sqrt{2} : 1/\sqrt{3}$ for simple cubic lattice.

(ii) $d_{100} : d_{110} : d_{111} = 1 : 1/\sqrt{2} : 2/\sqrt{3}$ for *fcc* crystal.

(iii) $d_{100} : d_{110} : d_{111} = 1 : 2/\sqrt{2} : 1/\sqrt{3}$ for *bcc* crystal.

For maximum intensity reflections, the glancing angles are 5·9°, 8·4° and 5·20° for (10 (110) and (111) faces respectively.

Exercise. *Show that NaCl crystal has a fcc lattice.*

Solution. In case of NaCl crystal,

$$d_{100} + d_{110} + d_{111} = \frac{1}{\sin 5\cdot 9} : \frac{1}{\sin 8\cdot 4} : \frac{1}{\sin 5\cdot 2}$$

$$= 1/0\cdot 1028 : 1/0\cdot 146 : 1/0\cdot 0906 = 1 : 0\cdot 704 : 1\cdot 155$$

$$= 1 : 1/\sqrt{2} : 2/\sqrt{3}$$

The above value is in full agreement with the values predicted theoretically. Thus NaCl crystal has a *fcc* lattice.

3. Rotating Crystal Method. The method developed by **Schiebold (1919) and M. Polanyi (1921)**, is perhaps the most widely used method in the study of crystal structure. In this method a beam of homogeneous X-ray is allowed to penetrate a small crystal at right angles. The crystal being rotated around an axis parallel to one of the crystal axes. During the rotation of the crystal various planes come successively into suitable positions for diffraction to occur and the corresponding spots are observed on a photographic plate.

In **Fig. 14**, *A* and *B* show points on two successive lattice planes. For a diffraction maxima to occur the difference (*BR*) in the path of two diffracted rays must be equal to whole number of wavelengths *i.e.*, equal to $n\lambda$. Since the value of *n* depends on the angle θ (BAR), a series of directions of diffraction corresponding to increasing value of *n* is obtained on the photographic plate. Horizontal lines are seen for all lattice planes having the same spacing (*AB*) in the direction parallel to the axis of rotation. Such lines are referred to as **layer lines**. If the λ of incident X-rays is known and the distance from the crystal to the photographic plate and vertical distance between the layer lines is determined, it is possible to calculate θ and hence the spacing of the planes *AB*. A set of spots in a transverse direction called row lines is also observed on the photograph which is used to deduce lattice spacings and the size of the unit cell.

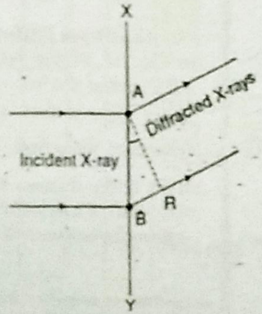

Fig. 14. Rotating crystal method.

4. Oscillating Crystal Method. In oscillation method the crystal is oscillated through ngle of 15° to 20°. But the number of reflecting positions exposed to the incident X-rays mited. The oscillations of the crystal are synchronised with the movement of the drical photographic film. The position of a spot on the plate indicates the orientation of crystal at which the spot was formed.

5. Debye and Scherrer Powder Method. Powder method was devised independently **P. Debye and P.Scherrer (1916) and A.W. Hill (1917).** It employs finely powdered les in the form of a cylinder inside a thin glass tube. A narrow beam of X-rays is allowed ll on the powder. The diffracted X-rays strike a strip of photographic film arranged in form of a circular arc (**Fig. 15**). The scattered rays from all sets of planes (*e.g.*, 100, 110) are detected by using an X-ray sensitive film.

In this method, no rotation is necessary since the dered sample already contains microcrystals nged in all possible orientations. Hence a large ber of them will have their lattice planes in correct tions for maximum X-ray reflection to occur. Thus we lighted areas in the form of arcs of lines at different ances from the incident beam. These distances can converted into scattering angles to be used in bragg ation for different planes of the crystal.

Seeman-Bohlin focussing camera is also used for tographic recording of powder diffraction. The metric arrangement of the specimen in the camera which diffraction pattern is limited to $2\theta > 90°$) is d in accurate lattice parameter measurements.

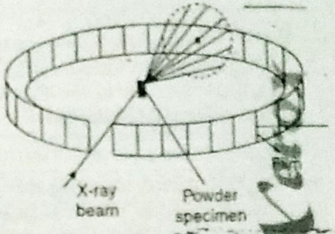

Fig. 15. The powder method for X-ray diffraction.

SIMPLE LATTICES AND X-RAY INTENSITIES

A crystal may be regarded as a *three dimensional natural grating in which atoms are nged in a definite geometrical shape with flat faces and sharp edges.* The classification of stal was mainly studied by **L. Sohncke, E. Fedoroff, A. Schonflies and W. Barlow.** *The ular repetition of identical units in a crystal is called* **unit cell.** Unit cells are classified o seven crystal systems by noting the rotational symmetry elements they possess. There e 14 distinct space lattices in three dimensions. These **Bravais lattices** may be **primitive** nit cell, (with lattice points only at the corners), body centred, face centred or a side centred it cell.

Intensity of X-rays reflected from the planes of a crystal. Since the crystals are perfect and the extent of imperfection is not known, certain assumption has been made to lculate the intensity of X-rays. A **mosaic crystal**, which is made up of a number of small rfect crystalline units inclined at small angles to each other is postulated. From the face such crystals the reflections change over a small angle. It is possible to measure the total ount of reflected radiation by turning the crystal through a small range in the region of flection. The **integrated reflection,** *R* is considered as a measure of intensity of the flected beam.

$$R = E\omega / I$$

here *E* is total reflected energy, I is total incident radiation falling on the crystal face per and ω is uniform angular velocity of rotation of the crystal. The *R* on (*hkl*) plane of a crystal r a glancing angle θ is given in terms of structure amplitude factor *F*(*hkl*).

Thus,

$$I(hkl) = \frac{I_0 e^4}{m^2 c^4} |F(hkl)|^2 \frac{\lambda^3}{2\mu \sin^2\theta} P$$

where m = mass of atom, c = velocity of light, e = electronic charge, N = number of uni per cc of crystal, λ = wavelength of X-rays, μ = absorption coefficient of the crys material of crystal, P = polarisation factor, $(1 + \cos^2 2\theta)/2$. Since the structure provides the structural information, the object of measuring the intensities of reflections is to determine the values of the corresponding structure factors. J.H. Robe (1934) gave the general method for the comparison of intensities. The crystal investigated and a standard crystal are alternately exposed to X-ray beam for identical of time and spectra is recorded on the same moving film. The blackening so produced photographic plate is then compared by photometric examination.

Factors affecting X-ray intensity. (i) Scattering power of the atoms within the plane and (ii) on the mean amplitude of the wave scattered by the particular atoms occupying the plane. The latter is known as atomic scattering factor, given by

$$f = \int_0^\infty \omega(r) \frac{\sin\phi}{\phi} dr$$

where $\omega(r)\,dr$ shows the probability of finding an electron between two shells r and $r + dr$ from the centre of the atom, and $\phi = 4\pi r (\sin\theta)/\lambda$. The value of f depends on θ and λ of the X-rays. But f is a function of $\sin\theta/\lambda$ and it decreases with the increase in $\sin\theta/\lambda$. For small glancing angles, f is almost the same as the atomic number of the element.

SCATTERING FACTORS

The scattering of X-rays is caused by the oscillations an incoming electromagnetic wave generates in the electrons of atoms, and heavy atoms give rise to stronger scattering than light atoms. This dependence on the number of electrons is expressed in terms of the **scattering factor**, f, of the element. If the scattering factor is large, then the atoms scatter X-rays strongly. The scattering factor of an atom is related to the electron density distribution in the atom, $\rho(r)$, by

$$f = 4\pi \int_0^\infty \rho(r) \frac{\sin kr}{kr} r^2\, dr \qquad k = \frac{4\pi}{\lambda}\sin\theta \qquad \ldots(13)$$

The value of f is greatest in the forward direction and smaller away from the forward direction (**Fig. 16**). The detailed analysis of the intensities of reflections must consider this dependence on direction. The scattering factor in the forward direction (at $\theta = 0$, hence $\sin\theta/\lambda = 0$) is equal to the total number of electrons in the atom.

As $\theta \to 0$, so $k \to 0$. Because $\sin x = x - \frac{1}{6}x^3 + \ldots$,

$$\lim_{x\to 0} \frac{\sin x}{x} = \lim_{x\to 0} \frac{x - \frac{1}{6}x^3 + \ldots}{x}$$

$$= \lim_{x\to 0}\left(1 - \frac{1}{6}x^2 + \ldots\right) = 1$$

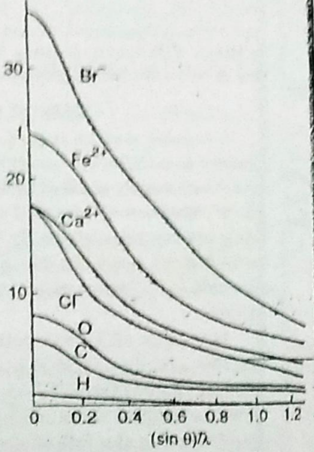

Fig. 16. The variation of the scattering factor of atoms and ions with atomic number and angle.

For forward scattering, the factor $(\sin kr)/kr$ is therefore equal to 1. Hence in the forward direction, scattering factor is

$$f = 4\pi \int_0^\infty \rho(r) r^2\, dr$$

The integral over the electron density ρ (the number of electrons in an infinitesimal region divided by the volume of the region) multiplied by the volume element $4\pi r^2\, dr$ is the total number of electrons, N_e, in the atom. So in the forward direction, $f = N_e$. For instance, the scattering factors of Na^+, K^+ and Cl^- are 10, 18 and 18, respectively.

The scattering factor is smaller in non-forward directions because $(\sin kr)/kr < 1$ for $k > 0$, so the integral is smaller than the above calculated value.

STRUCTURE FACTOR AND ITS RELATION TO ELECTRON DENSITY

If a unit cell contains several atoms with scattering factors f_j and coordinates $(x_j a, y_j b, z_j c)$, then the overall amplitude of a wave diffracted by the (hkl) planes is given by

$$F_{hkl} = \sum_j f_j e^{i\phi_{hkl}(j)} \qquad \ldots(14)$$

where

$$\phi_{hkl}(j) = 2\pi(hx_j + ky_j + lz_j)$$

The sum is over all the atoms in the unit cell. The quantity F_{hkl} is called the structure factor. Each structure factor is associated with a particular reflection from the (hkl) planes.

Fourier Synthesis of Electron Density in a Crystal. Since the electron density is a periodic function, it can be expanded by a Fourier series. The intensity of the (hkl) reflection is proportional to $|F_{hkl}|^2$, so we can calculate the structure factors experimentally by taking the square root of the corresponding intensities. From structure factors F_{hkl}, we can calculate the electron density distribution, $\rho(r)$, in the unit cell by

$$\rho(r) = \frac{1}{V} \sum_{hkl} F_{hkl}\, e^{-2\pi i(hx + ky + lz)} \qquad \ldots(15)$$

where V is the volume of the unit cell. Equation 15 is called a Fourier synthesis of the electron density.

IDENTIFICATION OF UNIT CELLS FROM SYSTEMATIC ABSENCES IN DIFFRACTION PATTERN

Consider the following phase differences to identify the unit cells from systematic absences in diffraction pattern.

(i) Phase Difference. If in the unit cell there is an A atom at the origin and a B atom at the coordinates (xa, yb, zc), where x, y and z lie in the range 0 to 1, then the phase difference, ϕ, between the hkl reflections of the A and B atoms is

$$\phi_{hkl} = 2\pi(hx + ky + lz)$$

(ii) Phase Difference for (100) Reflection. Consider diffraction from a crystal shown in **Fig. 17**. If the reflection corresponds to two waves from adjacent A planes, the phase difference of the waves is 2π. If there is a B atom at a fraction x of the distance between the two A-planes, then it gives rise to a wave with a phase difference $2\pi x$ relative to an reflection. Note that, if $x = 0$, there is no phase difference. If $x = \frac{1}{2}$, the phase difference is

If $x = 1$, the B atom lies where the lower A atom lies and the phase difference is 2π.

(iii) Phase Difference for (200) Reflection. For (200) reflection there is 2× difference between the waves from the two A layers. If B were to lie at $x = 0.5$ it would

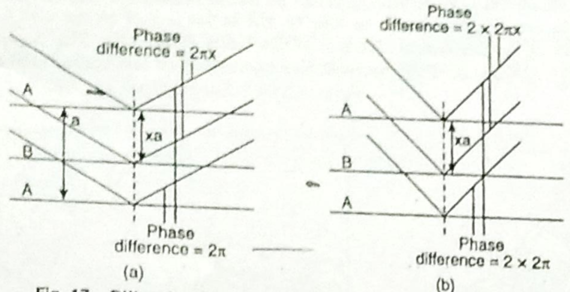

Fig. 17. Diffraction from a crystal containing two kinds of atoms.

rise to a wave that differed in phase by 2π from the wave from the upper A layer. Thus, for a general fractional position x, the phase difference for a (200) reflection is $2 \times 2\pi x$. **For a general (h00) reflection,** the phase difference is therefore $h \times 2\pi x$.

Diffraction Pattern of a Cubic System. In case of cubic unit cells with B atom at $x = y = z = 1/2$, the AB phase difference is $(h + k + l)\pi$. Therefore, all reflections for odd values of $h + k + l$ disappear because the waves are displaced in phase by π. Hence the diffraction pattern for a cubic I lattice can be obtained from that of cubic P lattice (a cubic lattice without points at the centre of its unit cells) by striking out all reflections with odd values of $h + k + l$. Recognition of these systematic absences in a powder spectrum immediately indicates a cubic I lattice (**Fig. 18**). The locations of the lines give the cell dimensions.

To identify (i) primitive, (ii) body centred and (iii) face centred cubic lattices from systematic absences in diffraction pattern.

For a cubic system, interplanar distance d_{hkl} is given by

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2} \qquad \text{...(16)}$$

Combining this equation with Bragg equation,

$$\lambda = 2d_{hkl} \sin \theta_{hkl}, \text{ we get}$$

$$\lambda = 2a \sin \theta_{hkl}/(h^2 + k^2 + l^2)^{1/2} \qquad \text{...(17)}$$

$$\therefore \sin^2 \theta_{hkl} = (\lambda^2/4a^2)(h^2 + k^2 + l^2) = K(h^2 + k^2 + l^2) \qquad \text{...(18)}$$

where $K = \lambda^2/4a^2$. K has a constant value for a given cubic crystal and a given wavelength.

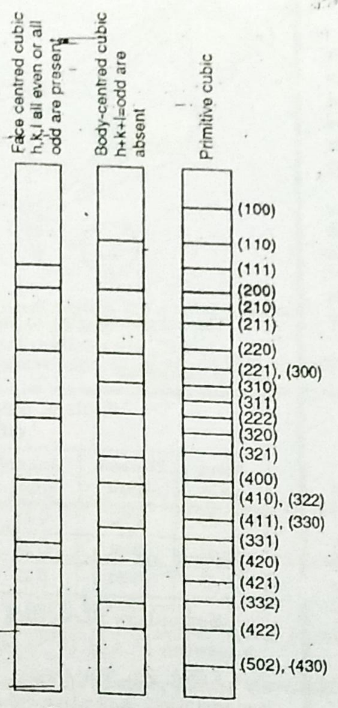

Fig. 18. The powder diffraction patterns and the systematic absences of three versions of a cubic cell.

redicting diffraction pattern of lattices.

(i) Primitive cubic lattice. Applying equations 16 and 18 and integral values 0, 1, 2, ...) for the Miller indices, we can construct Table 3. Since the integer 7 (or 15) can ot be written in the form $h^2 + k^2 + l^2$ hence $\sin^2 \theta$ cannot be equal to 7 K (or 15 K). The ffraction pattern for a primitive cubic lattice will thus consist of a set of equally spaced six nes followed by an extinction (gap) and then another series of lines.

Table 3. Interplanar distances and angles for which diffraction lines are observed for a primitive cubic lattice.

hkl	100	110	111	200	210	211	220	300 221	310	311	222
d_{hkl}	a	$a/\sqrt{2}$	$a/\sqrt{3}$	$a/\sqrt{4}$	$a/\sqrt{5}$	$a/\sqrt{6}$	$a/\sqrt{8}$	$a/\sqrt{9}$	$a/\sqrt{10}$	$a/\sqrt{11}$	$a/\sqrt{12}$
$\sin^2 \theta_{hkl}$	K	2 K	3 K	4 K	5 K	6 K	8 K	9 K	10 K	11 K	12 K

(ii) Body centred cubic lattice. Use eqs. 16 and 18 and integral for h, k, l to construct Table 4. All diffraction lines for which $(h + k + l)$ is an odd integer are missing.

Table 4. Interplanar distances and angles for body centred cubic lattice.

hkl	100	110	111	200	210	211	220	300, 221	310	311	222
d_{hkl}		$a/\sqrt{2}$		$a/\sqrt{4}$		$a/\sqrt{6}$	$a/\sqrt{8}$		$a/\sqrt{10}$		$a/\sqrt{12}$
$\sin^2 \theta_{hkl}$		2 K		4 K		6 K	8 K		10 K		12 K

(iii) Face centred cubic lattice. Here diffraction lines are observed only from those planes for which the values of h, k, l are either **all odd** or **all even.**

Table 5. Interplanar distances and angles for face centred cubic lattice.

hkl	100	110	111	200	210	211	220	300 221	310	311	222
d_{hkl}			$a/\sqrt{3}$	$a/\sqrt{4}$			$a/\sqrt{8}$			$a/\sqrt{11}$	$a/\sqrt{12}$
$\sin^2 \theta_{hkl}$			3 K	4 K			8 K			11 K	12 K

In diffraction patterns, missing reflections help in distinguishing three types of cubic lattices. In case of primitive cubic system, the spacing between the lines is equal to K (with a gap after 6, 14, 22 etc., lines) while in *bcc* system, the spacing between lines is equal to 2 K. Thus the two systems can be identified. Assign each line with the correct values of the Miller indices h, k, l. From the measurement of any one of these lines, we can determine the value of a, the length of the edge of the cube, by using the equation

$$a = (\lambda/2 \sin \theta_{hkl})(h^2 + k^2 + l^2)^{1/2}$$

If the lines are indexed correctly, the same value of a is obtained from all the values of $\sin \theta_{hkl}$.

PHASE PROBLEM

Since the observed intensity I_{hkl} is proportional to the square modulus $|F_{hkl}|^2$, so it is not certain to use either $+|F_{hkl}|$ or $-|F_{hkl}|$ in the sum in equation 15. This problem is more severe for **non-centrosymmetric unit cells** because, if we write F_{hkl} as the complex number $|F_{hkl}|e^{i\alpha}$, where α is the phase of F_{hkl} and $|F_{hkl}|$ is its magnitude, then the intensity can determine $|F_{hkl}|$ but tells nothing of its phase, which may lie anywhere from 0 to 2π. This ambiguity is known as **phase problem.**

Methods to Overcome the Phase Problem.

1. **Patterson Synthesis.** This technique is employed for determining rel orientations of pairs of atoms in a given crystal structure. Instead of the struc factors F_{hkl}, the values of $|F_{hkl}|^2$, which can be obtained without ambiguity fro the intensities, are used in an expression that resembles equation 15.

$$P(r) = \frac{1}{V} \sum_{hkl} |F_{hkl}|^2 e^{-2\pi i} (hx + ky + lz) \qquad ...(19)$$

Patterson equation is manifested in the form of a map of **vector separation** of atoms in the unit cell. If atom *A* is at the coordinates (x_A, y_A, z_A) and atom *B* is at $(x_B\, y_B\, z_B)$, then there will be a peak at $(x_A - x_B, y_A - y_B, z_A - z_B)$ in the Patterson map. There will also be a peak at the negative of these coordinates, because there is a vector from *B* to *A* as well as a vector from *A* to *B*. *The height of the peak in the map is proportional to the product of the atomic number* $Z_A\, Z_B$.

Heavy atoms dominate the scattering because their **scattering factors** are large and their locations may be deduced easily. The sign of F_{hkl} can now be calculated from the locations of the heavy atoms in the unit cell, and to a high probability the phase calculated for them will be the same as the phase for the entire unit cell. Because a structure factor of a centrosymmetric cell has the form

$$F = (\pm) f_{heavy} + (\pm) f_{light} + (\pm) f_{light} + \cdots$$

where f_{heavy} is the scattering factor of the heavy atom and f_{light} that of light atoms. The phase of f_{light} are more or less random if the atoms are distributed throughout the unit cell. Hence the net effect of the f_{light} is to change *F* only slightly from f_{heavy}. Thus *F* will have the same sign as that calculated from the location of the heavy atom. This phase can then be combined with the observed $|F|$ (from the reflection intensity) to perform a Fourier synthesis of the full electron density in the unit cell, and hence to locate the light atoms as well as the heavy atoms.

2. **Direct Methods.** Direct methods, developed by **H. Hauptman and J. Karle**, are based on the possibility of treating the atoms in a unit cell as being virtually randomly distributed and then to use statistical techniques to compute the probabilities that the phases have a particular value. It is possible to deduce relations between some structure factors and sums (and sums of squares) of others, which have the effect of constraining the phases to particular values (with high probability, so long as the structure factors are large). The Sayre **probability** relation has the form

$$\text{sign of } F_{h+h', k+k', l+l'} \text{ is probably equal to (sign of } F_{hkl}) \times (\text{sign of } F_{h'k'l'}) \qquad ...(20)$$

For example, if F_{122} and F_{232} are both large and negative, then it is highly likely that F_{354}, provided it is large, will be positive.

PROCEDURE FOR X-RAY STRUCTURE ANALYSIS

The analysis of diffraction pattern produced by crystal involves study of Bragg's law, scattering factors, structure factors and their relation to electron density described earliar.

Structure Refinement. In the final stages of the determination of a crystal structure, the parameters describing the structure (atom positions) are adjusted systematically to give the best fit between the observed intensities and those calculated from the model of the structure deduced from the diffraction pattern. Modern computers provide accurate structural information (like position of all the atoms in unit cell, bond lengths, bond angles, vibrational amplitudes of the atoms) from X-ray diffraction data.

RAMACHANDRAN DIAGRAM OF PROTEIN

Ramachandran diagram (Fig. 19) provides better understanding of three dimensional **structure of protein.** A protein consists of polypeptide chains. The backbone atoms of the **polypeptide are** C_i^α, C'_i and N_i in Fig. 19. C_i^α is the α-*C* of amino acid *i*, C'_i is the carbonyl **carbon** and N_i is the amide nitrogen of the same amino acid. The peptide bond is between C'_i and $N_i + 1$, that is, bond between the carbonyl *C* of one amino acid and the amide *N* of the next.

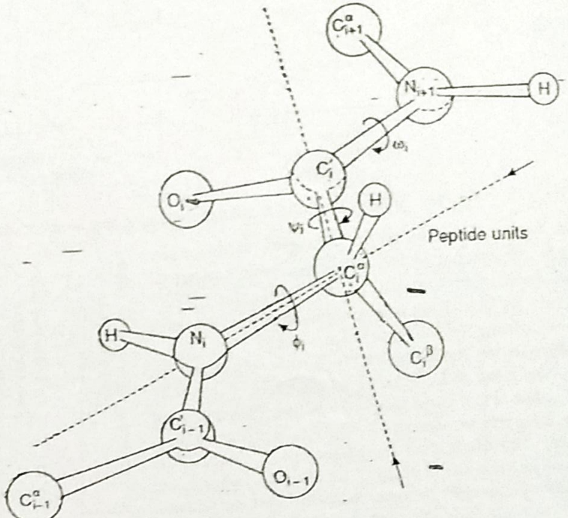

Fig. 19. Ramachandran diagram.

The torsion angles in Ramachandran diagram are ϕ,ψ and ω. ϕ is close to 180° since C'_{i-1} and C'_i are nearly trans to each other. If ϕ is turned clockwise in the direction of arrow C_i will disappear.

Table 6. Smallest nucleus-nucleus distance (in nm) for different atom-pairs in polypeptides.

Atom pair	Normal limit	Inner limit	Atom pair	Normal limit	Inner limit	Atom pair	Normal limit	Inner limit
C—C	0·28	0·27	C—O	0·28	0·27	C—N	0·29	0·28
C—H	0·24	0·22	O—O	0·28	0·27	O—N	0·27	0·26
O—H	0·24	0·22	N—N	0·27	0·26	N—H	0·24	0·22

Secondary Structure of Polypeptide. It can be determined by three torsion angl ϕ between N_i and C_i^β, ψ between C_i^α-and C'_i and ω for the peptide bond between C'_i ar $N_i + 1$ (Fig. 20). The torsion angle is zero when the neighbouring backbone atoms are in c conformation. A positive value corresponds to a twist of the torsion angle in the same way the arrows point in Fig. 19. When the backbone atoms are in trans, the torsion angl + 180° or − 180°. Sometimes dihedral angle (which is torsion angle + 180° that $\phi_{dihedral} = \phi_{torsion} + 180°$) is used instead of torsion angle.

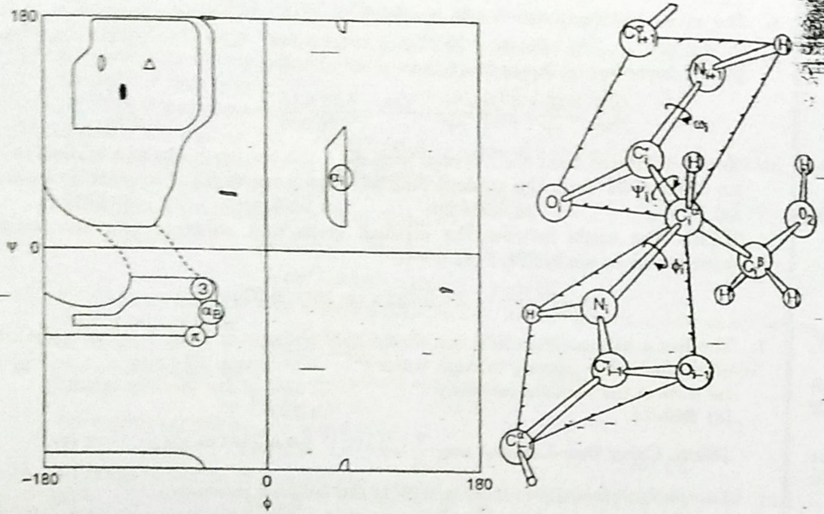

Fig. 20. Different secondary structure areas in a Ramachandran diagram. For α-helix, ϕ = 57° and ψ = −47° and for a β-strand ϕ = −139° and ψ = +135°.

The **peptide bond** has partial double bond character and is in trans form as this conformation is more favourable. Thus, angle ω is fixed and the area betwen two consecutive α-C can be regarded as rigid and planar peptide unit.

SELECTED TIPS

- Von Laue method consists of in passing a broad-band beam of X-rays into a single crystal and recording the diffraction pattern photographically.
- The intensity of the secondary X-rays is directly proportional to the amount of element present.
- White radiation is obtained from a tungsten target at about 60,000 volts.
- The emission behaviour of molybdenum is typical among all the elements having atomic number greater than 23.
- Elements having atomic number less that 23 produce only K-series (lower wavelength group).
- The relative intensity of the diffraction pattern of a component in a mixture is directly proportional to the concentration and inversely proportional to the mean absorption coefficient of the mixture.

NUMERICALS

1. *The first maxima for Bragg diffraction of X-rays from KCl crystal(d = 0·314 nm) appears at 14°. Calculate the energy of incident X-rays.*

Solution. Given, d = 0·314 nm, 2θ = 14° ⇒ θ = 7°, $n = 1$.

From Bragg's law, $2d \sin\theta = n\lambda$

$$\lambda = 2 \times 0{\cdot}314 \times 10^{-9}. \quad \sin 7° = 0{\cdot}0765 \times 10^{-9}\ \text{m}$$

Photon energy is given by, $E = hc/\lambda$

$$= \frac{6{\cdot}62 \times 10^{-34} \times 3 \times 10^{8}}{0{\cdot}07653 \times 10^{-9}} = 2{\cdot}59 \times 10^{-15}\ \text{J} = \mathbf{41{\cdot}5\ keV.}$$

2. *Determine atomic spacing in a NaCl crystal having cubic lattice. The density of NaCl is $2{\cdot}16 \times 10^3$ kg/m^3 and the average masses of Na and Cl atoms are $3{\cdot}82 \times 10^{-26}$ kg and $5{\cdot}89 \times 10^{-26}$ kg.*

Solution. The molecular mass of NaCl is $= \dfrac{9{\cdot}71 \times 10^{-26}}{1{\cdot}66 \times 10^{-27}} = 58{\cdot}7\ \text{g mole}^{-1}$

Density, $\rho = 2{\cdot}16 \times 10^3\ \text{kg/m}^3$

Now, $\dfrac{\text{No. of molecules}}{\text{Volume}} = \dfrac{N_A \rho}{M}$

where N_A is the Avogadro's number (molecules/mole), M is the molecular mass.

$$\therefore \quad \frac{N_A \rho}{M} = \frac{6{\cdot}023 \times 10^{23} \times 2{\cdot}16 \times 10^{3}}{58{\cdot}7 \times 10^{-3}} = 2{\cdot}2 \times 10^{28}\ \text{molecules/m}^3 = 4{\cdot}4 \times 10^{28}\ \text{atoms/m}^3.$$

Therefore volume of each atom is $1/4{\cdot}4 \times 10^{28}$ m^3. NaCl has a cubic unit cell so atoms are equidistant and separated by distance, D.

$$D = (4{\cdot}4 \times 10^{-28})^{-1/3} = 2{\cdot}82 \times 10^{-10}\ \text{m} = 0{\cdot}282\ \text{nm}.$$

3. *The utilized reflecting plane of LiF crystal has a d value of 2·014 Å. Calculate the wavelength of second order diffracted line which has a value of 50·1°.*

Solution. $n\lambda = 2d \sin\theta$ or $\lambda = 2d \sin\theta/n$

$$= 2 \times 2{\cdot}014 \times \sin 50{\cdot}1/2 = 2{\cdot}014 \times 0{\cdot}767/1$$

$$= 1{\cdot}545\ \text{Å} \quad \text{or} \quad \mathbf{0{\cdot}1545\ nm.}$$

4. *Calculate the distance, d in rock salt, if its density is 2·18 g/cc and molecular weigh 58·5.*

Ans. Rock salt (NaCl) belongs to fcc and there are four atoms in a unit cell.

$$a = [\text{Mol. wt.} \times \text{No. of atoms}/N \times d]^{1/3}$$

$$a = \left[\frac{58{\cdot}5 \times 4}{6{\cdot}02 \times 10^{23} \times 2{\cdot}18}\right]^{1/3} = 5{\cdot}63 \times 10^{-8}\ \text{cm}$$

For fcc lattice $d = a/2 = 2{\cdot}815 \times 10^{-8}$ cm

$$= \mathbf{2{\cdot}815\ Å = 0{\cdot}2815\ nm.}$$

SHORT ANSWER QUESTIONS

1. *Deduce Bragg's equation and find the distance between successive lattice pla[illegible] crystal.*

Ans. In the Bragg's equation, $n\lambda = 2d\sin\theta$, n is an integer and d is a fixed value [illegible] given set of lattice planes. If θ, the angle which the rays make with the plane of cry[illegible] is regularly increased, a number of positions corresponding to n = 1, 2, 3 etc. will [illegible] found at which the reflections will be maximum, i.e., $\theta = \sin^{-1} 1(\lambda/2d)$, $\theta = \sin^{-1} 2(\lambda/2d)$, $\theta = \sin^{-1} 3(\lambda/2d)$ and $\theta = \sin^{-1} n(\lambda/nd)$.

The reflection corresponding to n = 1 is called the **first order reflection**, th[illegible] corresponding to n = 2 is **second order reflection** and so on. If the glancing angles [illegible] are measured for various orders of n, of maximum intensity, the distance d between successive lattice planes in the crystal can be calculated, if λ is known.

2. *How the lattice spacing d is connected to cell edge ?*

Ans. (i) $d = \frac{a\sqrt{3}}{3}$ for simple cubic lattice.

(ii) $d = \frac{a}{2}$ for fcc crystal lattice.

(iii) $d = \frac{a\sqrt{3}}{2}$ for bcc crystal lattice. Here a can be calculated by using the following relation :

$$a = \left[\frac{\text{Mol. wt.} \times \text{No. of atoms in unit cell}}{\text{Avogadro's number} \times \text{Density}}\right]^{1/3}$$

AgCl has fcc unit cell whereas CsCl has bcc. Which Miller indices are permitted in their diffraction pattern?

Ans. In AgCl (fcc), only allowed reflections are those in which all indices are even or all odd. Since a = b = c, so only four peaks are observed corresponding to 200, 220, 111, 222. In CsCl (bcc), only allowed reflections are those in which h + k + l is equal to even.

A powder diffraction pattern of lead was obtained with Cu-K_α radiation (λ = 0·1539 nm). Find d value of the interplanar distance which produces a first order line at sin θ = 0·8210.

Ans. 0·09355 nm.

MULTIPLE CHOICE QUESTIONS

X-rays are produced following photoelectric process while continuous X-rays are produced as a result of

(a) Bremsstrahlung process (b) Diffraction

(c) Interference (d) Duane Hunt process

2. The absorption of X-rays in a material is governed by

(a) Bragg's law (b) Beer Lambert's law

(c) Stephan's law (d) All

3. An X-ray tube produces a continuous spectrum of radiation with its short wavelength at 0·63 Å. The maximum energy of a photon is

(a) 19·5 eV (b) 19·2 eV (c) 19·8 eV (d) 19·5 eV

[**Hint.** $E = \frac{hc}{\lambda} = \frac{6\cdot626 \times 10^{-34} \times 3 \times 10^{8}}{0\cdot63 \times 10^{-10}\,\text{m}}$

$= 3\cdot15 \times 10^{-15}\,\text{J} = 3\cdot15 \times 10^{-15}/1\cdot6 \times 10^{-19} = 19\cdot8\,\text{keV}$]

4. The wavelength of K_α X-rays is 0·76 Å. The atomic number of anode material of X-ray tube is

(a) 40 (b) 32 (c) 21 (d) 72

[**Hint.** $\frac{1}{\lambda} = R_H \cdot Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

For K_α line, $n_1 = 1$, $n_2 = 2$

$$\therefore \frac{1}{0\cdot76 \times 10^{-10}} = 1\cdot097 \times 10^{7} \times Z^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right), Z = 40]$$

5. The minimum X-ray wavelength produced for an X-ray machine operated at 30 kV is

(a) 4·2 m (b) $4\cdot1 \times 10^{-11}$ m (c) 5·5 m (d) $5\cdot4 \times 10^{-10}$ m

[**Hint.** According to Duane Hunt rule

$$\lambda_{min} = \frac{hc}{eV} = \frac{1\cdot24 \times 10^{-6}\,\text{V m}}{V} = \frac{1\cdot24 \times 10^{-6}}{30{,}000} = 4\cdot1 \times 10^{-11}\,\text{m}]$$

6. X-rays scattered from NaCl crystal with d = 0·282 nm gives rise to a maxima (n = 1) at an angle of 20° from the incident direction. The wavelength of incident X-rays is

(a) 10 nm (b) 0·098 nm (c) 0·98 nm (d) 0·65 nm

[**Hint.** The angle between the incident beam and scattered rays for constructive interference is always 2θ. Here θ = 10°.

$$\lambda = \frac{2d\sin\theta}{n} = 2 \times 0\cdot282 \times \sin 10^\circ = 0\cdot098\,\text{nm}]$$

7. The linear attenuation coefficient for 2·0 MeV photons in water is 4·9 m⁻¹. The intensity of photons after passing through water column of length 10 cm is

(a) 61% of the incident intensity (b) 33% of the incident intensity

(c) 90% (d) 25%

[**Hint.** Using Beer-Lambert law, $\frac{I}{I_0} = e^{-\mu x} = e^{-(4\cdot9\,\text{m}^{-1})(0\cdot1\,\text{m})} = 0\cdot61$

i.e., photon intensity reduces to 61% of the incident intensity]

8. X-rays scattered from a crystal have a first order diffraction peak at θ = 15°. At what angle will the second order peak will appear?

(a) 30° (b) 21° (c) 31·17° (d) 35·0°

[**Hint.** For first order maxima, $2d\sin\theta = n\lambda$ or $d = \lambda/2\sin 15^\circ$

For n = 2, $\sin\theta = n\lambda/d = 0\cdot5175$, θ = 31·17°]

9. The mass absorption coefficient is contributed by absorption coefficients corresponding to

(a) Photoelectric process (b) Elastic scattering

(c) Inelastic scattering (d) All

10. The elastic scattering of the photons by bound atomic electrons is termed as

(a) Rayleigh scattering (b) Coherent scattering

(c) Both (a) and (b) (d) Incoherent scattering

11. The short wavelength region of 62 kV X-ray tube is

(a) 0·2 nm (b) 0·02 nm (c) 0·6 nm (d) 0·05 nm

[**Hint.** λ_{min} = 12400/V = 12400/62000 = 0·2 Å = 0·02 nm]

12. The parameters of an orthorhombic unit cell are $a = 50$ pm, $b = 100$ pm, $c = 150$ pm. spacing between (123) planes is

(a) 25 pm (b) 15 pm (c) 29 pm (d) 50 pm

[**Hint.** Interplanar distance d_{hkl} is given by

$$1/(d_{hkl})^2 = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$$

On solving $1/d_{123} = \sqrt{3}/50$ pm so that $d_{123} = 50 \text{ pm}/\sqrt{3} = \mathbf{29\ pm}$].

13. The hkl all-odd reflections are less intense than the hkl all-even. The hkl all-odd have zero intensity corresponding to the systematic absences of

(a) Cubic P unit cells (b) Cubic I unit cells

(c) Primitive centred cubic lattice (d) None

14. X-rays of wavelength 1·54 Å are diffracted by atoms of a crystal. The angle at which first order reflection will occur ($d = 4{\cdot}04$ Å) is

(a) 22° (b) 10°59′ (c) 15°60′ (d) 30°

[**Hint.** Bragg's equation for $n = 1$ is $2d \sin\theta = \lambda$

$$\theta = \sin^{-1}(\lambda / 2d) = \sin^{-1}(1{\cdot}54\ \text{A°}/8{\cdot}08\ \text{Å})$$

$$= \sin^{-1}(0{\cdot}191) = 10°59′].$$

15. If reflections from the crystal planes 100, 110, 210, 211 are absent in diffraction pattern, the crystal lattice is

~~(a) Simple cubic~~ (b) bcc (c) fcc (d) Hexagonal

16. The crystal plane for which interplanar spacing $d_{hkl} = a/\sqrt{12}$ is

(a) 110 (b) 111 (c) 221 (d) 222

17. For a cubic crystal d_{100}/a is equal to

(a) 1 (b) 1/2 (c) 1/4 (d) 1/8

18. No Bragg reflection of X-rays from a crystal will be observed if d_{hkl} is smaller than

(a) λ (b) $\lambda/2$ (c) $\lambda/3$ (d) $\lambda/4$

19. For a first order Bragg reflection, $d_{hkl}/\lambda = 1/2$ and for second order $d_{hkl}/\lambda = 1$. The Bragg (glancing) angle of incidence in first and second order reflection is

(a) 90° (b) 30° (c) 60° (d) 45°

20. The smallest interplanar spacing in a crystal which will give nth order Bragg reflection is

(a) $d_{hkl} = n$ (b) $d_{hkl} = n/2$ (c) $d_{hkl} = n/3$ (d) $d_{hkl} = n/4$.

ANSWERS

1. (a) **2.** (b) **3.** (c) **4.** (a) **5.** (b) **6.** (b) **7.** (a) **8.** (c) **9.** (d) **10.** (c)

11. (b) **12.** (c) **13.** (a) **14.** (b) **15.** (c) **16.** (d) **17.** (a) **18.** (b) **19.** (a) **20.** (b)

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