

4.10.7 Bragg's Law

Consider a crystal which consists of equidistant parallel planes with the interplanar spacing ' d ' as shown in Fig. 4.19. When X-rays of wavelength (λ) fall on these crystal planes, the atoms in the planes diffract (reflect) the X-rays in all directions.

Let the X-ray PA incident at an angle ' θ ' with the plane 1 be reflected at atom A in the direction AR and another X-ray QB reflected at atom ' B ' in the direction BS . These diffracted X-rays will interfere constructively or destructively depending on the path difference between the X-rays. To calculate the path difference, two normals AC and AD are drawn from A to QB and BS .

$$\text{Path difference} = CB + BD$$

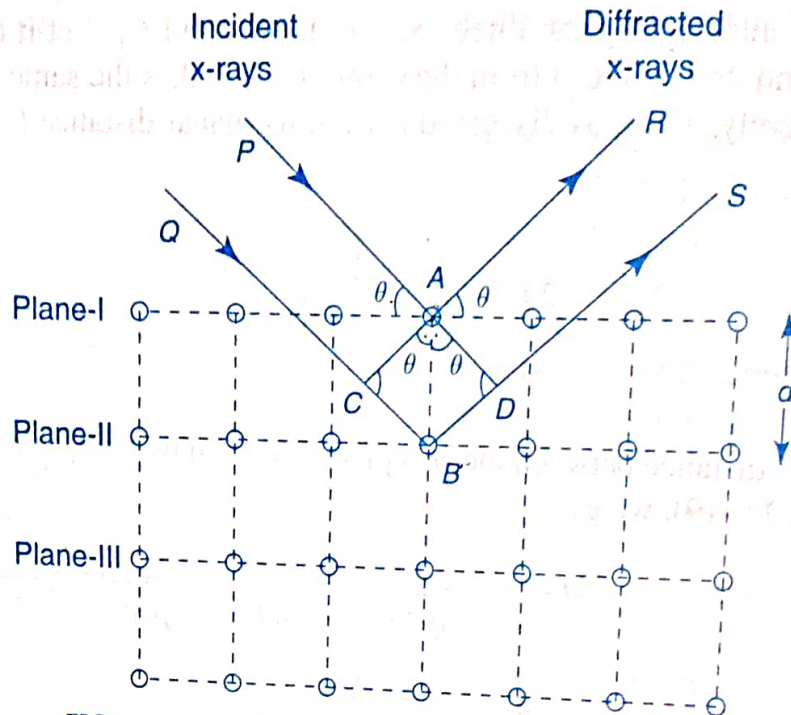


FIGURE 4.19 Diffraction of X-rays by crystal planes

$$\text{From } \triangle ACB, \sin \theta = \frac{CB}{AB}$$

$$CB = AB \sin \theta = d \sin \theta$$

$$\text{Similarly, from } \triangle ADB, BD = d \sin \theta$$

$$\therefore \text{path difference} = d \sin \theta + d \sin \theta \\ = 2d \sin \theta$$

To get maximum intensity, path difference should be equal to integral multiple of λ .
 Path difference $= n\lambda$

$$2d \sin \theta = n\lambda \quad \text{where } n=1,2,3$$

The above expression represents Bragg's law, according to which the diffracted X-rays interfere constructively when the path difference is an integral multiple of the wavelength of X-rays. Corresponding to $n = 1, 2, 3$ we obtain, first, second, third ... order diffraction spots. Since maximum possible value of θ is 1, we get

$$n\lambda = 2d$$

$$\lambda \leq 2d$$

Thus, the wavelength λ should not exceed twice the interplanar spacing for diffraction to occur.

Importance of Bragg's law

1. From Bragg's law, $2d \sin \theta = n\lambda$, we get

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

Knowing wavelengths of X-rays (λ) and the glancing angle θ , 'd' can be calculated.

2. Knowing 'd', the lattice constant 'a' of the cubic crystal can be known.

3. Knowing a , ρ (density) and M (molecular weight) of the crystal, the number of atoms (or) molecules in the unit cell can be calculated.

4. For a cubic crystal, $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

Knowing d and a , the value of $h^2 + k^2 + l^2$ can be calculated.

5. Depending on the values of $h^2 + k^2 + l^2$, we can classify the crystals as BCC, FCC, simple cubic, etc.

4.10.8 Laue Method

The Laue method is one of the X-ray diffraction techniques used for crystal structure studies. The experimental arrangement is as shown in Fig. 4.20.

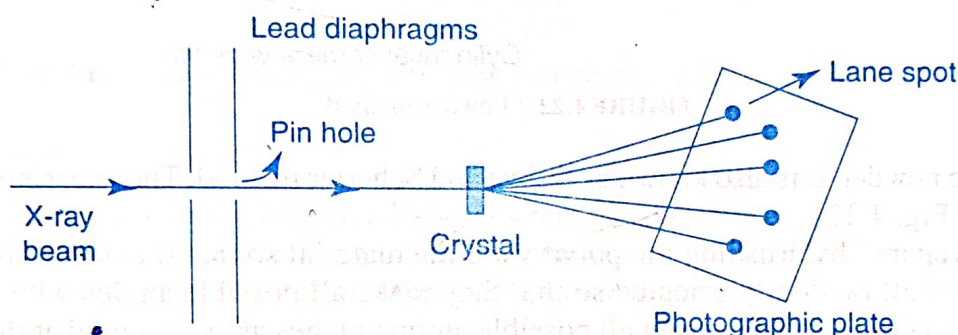


FIGURE 4.20 Laue method

The crystal whose structure has to be studied, is held stationary in a continuous X-ray beam. After passing through the pin holes of lead diaphragms, we obtain a fine beam of X-rays. These X-rays are allowed to fall on the crystal. The crystal planes in the crystal diffract the X-rays satisfying Bragg's law.

The diffracted X-rays are allowed to fall on a photographic plate. The diffraction pattern consists of a series of bright spots corresponding to interference maximum for a set of crystal planes satisfying the Bragg's equation $2d \sin \theta = n\lambda$ for a particular wavelength of the incident beam.

The distribution of spots depends on the symmetry of the crystal and its orientation with respect to X-ray beam. For a simple cubic crystal, the Laue photograph is as shown in Fig. 4.21.

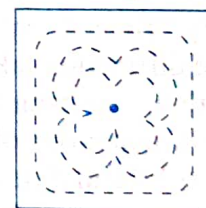


FIGURE 4.21 Laue photograph for simple cubic crystal

4.10.9 Merits and Demerits

This method is used for determination of crystal orientation and symmetry. It is also used to study crystalline imperfections (defects).

This method is not convenient for actual crystal structure determination, because several wavelengths of X-rays diffract in different order from the same plane, and they superimpose on a single Laue spot.

4.10.10 Powder Method

The powder method is an X-ray diffraction technique used to study the structure of microcrystals (tiny crystallites) in the form of powder. This method gives information regarding the size and orientations of

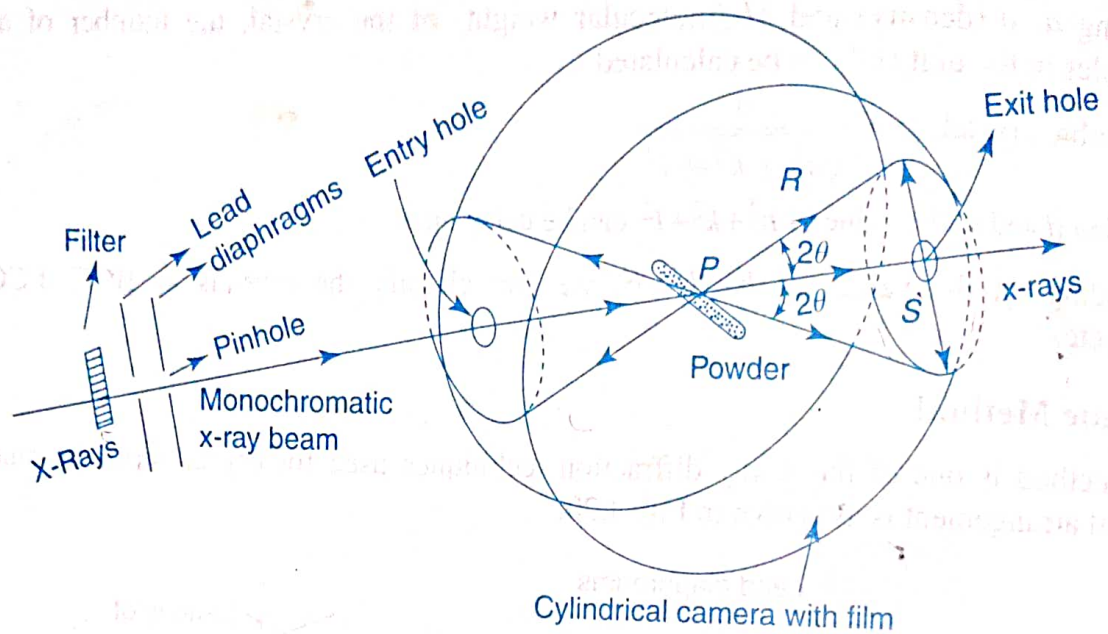


FIGURE 4.22 Powder method

the crystallites in the powder. It is also known as Debye and Scherrer method. The experimental arrangement is as shown in Fig. 4.22.

The powder is prepared by crushing the polycrystalline material so that it consists of crystallites. These crystallites are all randomly oriented so that they make all possible angles with the incident X-rays. Thus all orders of reflections from all possible atomic planes are re-ordered at the same time.

The experimental arrangement consists of a cylindrical camera, called the Debye-Scherrer camera consisting of a film in the inner portion. The finely powdered sample is filled in a thin capillary tube made of non diffracting material. The incident X-rays after passing through the filter and pin holes of lead diaphragms, produce a fine beam of monochromatic X-rays. The fine beam after passing through the entry hole falls on the capillary tube P containing the powdered crystals. Since the powder consists of randomly oriented crystallites, all possible θ and d values are available for diffraction of incident X-rays. The diffraction takes place for these values of d and θ which satisfy the Bragg's relation $2d \sin \theta = n\lambda$, where λ is constant for monochromatic X-rays. For a particular value of the angle of incidence ' θ ', various orientations of a particular set of planes are possible. The diffracted rays corresponding to fixed values of θ and d lie on the surface of a cone with its apex at the tube P and the semivertical angle 2θ . Different cones are observed for different sets of d and θ for a particular order of n and also for different combinations of θ and n for a particular value of d .

The transmitted X-rays come out through the exit hole. The diffracted X-ray cones make impressions on the film in the form of arcs on either side of the exit and entry holes with their centres coinciding with the hole. The diffraction pattern is as shown in Fig. 4.23.

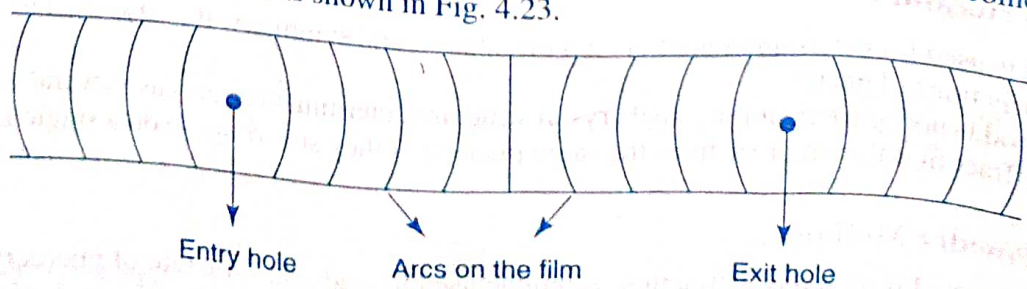


FIGURE 4.23 Diffraction pattern

The angle θ corresponding to a particular pair of arcs is related to the distance 's' between the arcs as

$$4\theta(\text{radius}) = \frac{s}{R} \left[\because \text{angle} = \frac{\text{arc}}{\text{radius}} \right]$$

where R is the radius of the camera.

$$\begin{aligned} 4\theta(\text{degrees}) &= \frac{s}{R} \left(\frac{180}{\pi} \right) \\ &= \frac{57.296s}{R} \end{aligned}$$

From the above expression, θ can be calculated. Then the interplanar spacing for first-order diffraction is

$$d = \frac{\lambda}{2\sin\theta}$$

Knowing all the parameters, the crystal structure can be studied.

4.10.11 Merits

1. Using filters, we get monochromatic X-rays (λ remains constant).
2. All crystallites are exposed to X-rays and diffractions take place with all available planes.
3. Knowing all parameters, crystal structure can be studied completely.

SOLVED PROBLEMS

- ① Chromium has bcc structure. Its atomic radius is 0.1249 nm. Calculate the free volume/unit cell.

Given data

Atomic radius of chromium, $r = 0.1249$ nm

Solution

Volume of the unit cell, $V = a^3$

$$a = \frac{4r}{\sqrt{3}} \Rightarrow \frac{4}{\sqrt{3}} \times 0.1249 \text{ nm} = 0.28845 \text{ nm}$$

$$\therefore \text{volume of the unit cell } V = a^3 = (0.28845)^3 \text{ nm}^3 = 0.024 \text{ nm}^3$$

Number of atoms in a BCC unit cell = 2

$$\text{Hence, volume of atoms in the unit cell } v = \frac{4}{3} \pi r^3 \times 2 = 0.01633 \text{ nm}^3$$

$$\text{Free volume/unit cell} = V - v = 0.00767 \text{ nm}^3$$

9.8 BRAGG'S SPECTROMETER

For the structural studies of crystals, W.H. Bragg and his son W.L. Bragg devised a spectrometer in which a crystal is used as a reflection grating instead of a transmission grating. With the help of their spectrometer, interatomic separation in the crystal can be calculated.

Experimental arrangement: Experimental arrangement of Bragg's spectrometer is shown in Fig. 9.8. It consists of a source of X-rays S , slits S_1 and S_2 , and crystal C mounted on a prism table. A round scale, consisting of two vernier scales V_1 and V_2 to note down the angle, is attached with the prism table. An ionisation chamber is attached with the prism table, along with a galvanometer.

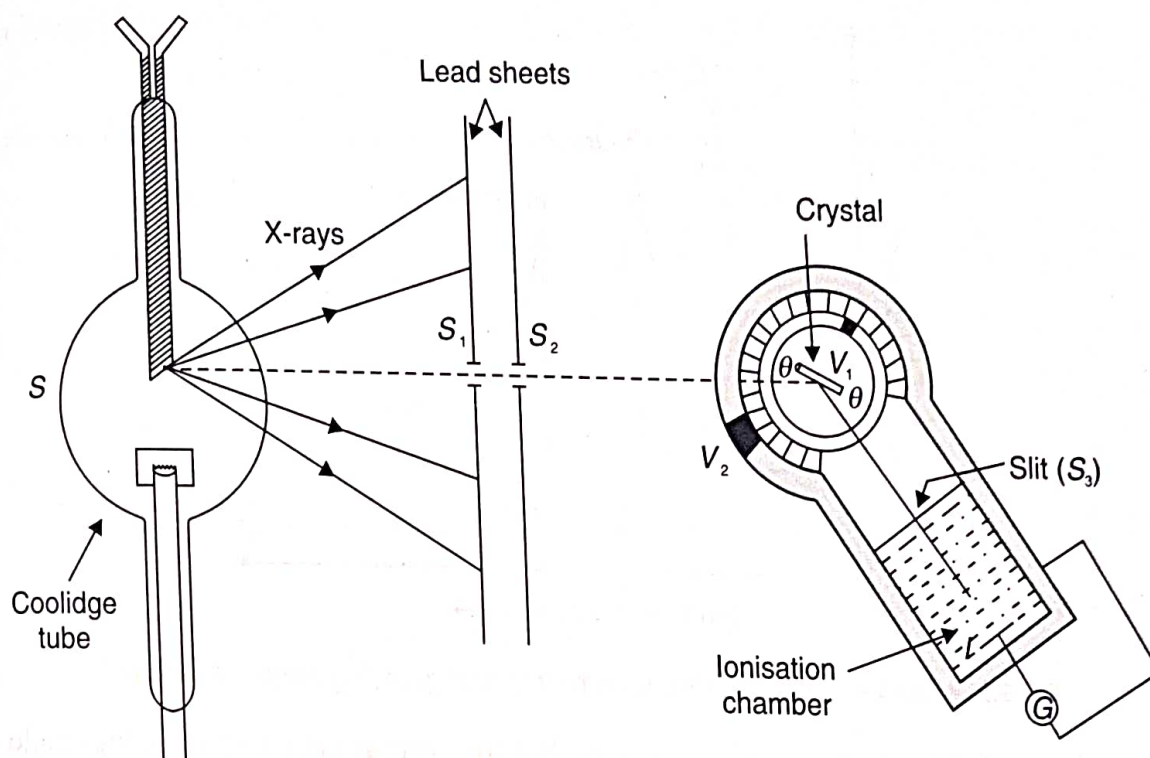


FIG. 9.8 Bragg's spectrometer

Working: X-rays from the Coolidge tube are passed through slits S_1 and S_2 to obtain a fine pencil of beam. Now, this narrow beam is allowed to fall on the crystal C mounted on the prism table, capable of rotating about a vertical axis passing through the centre of the prism table. The X-ray beam after reflection from the crystal face enters the ionisation chamber I through slit S_3 . The ionisation chamber I is filled with ethyl bromide and is capable of rotating with the prism table or crystal. The reading of second vernier scale gives the position of the ionisation chamber. The position of crystal and ionisation chamber is arranged in such a way that a rotation by angle θ in the position of crystal produces the rotation of 2θ in the position of ionisation chamber. Due to this arrangement, the X-ray beam reflected from the surface of the crystal is always received in the ionisation chamber. The intensity of X-rays in terms of ionisation current is observed for different values of glancing angle. The resulting ionisation current is observed through a galvanometer.

The graph plotted between the ionisation current I and glancing angle θ for the sodium chloride crystal is shown in Fig. 9.9.

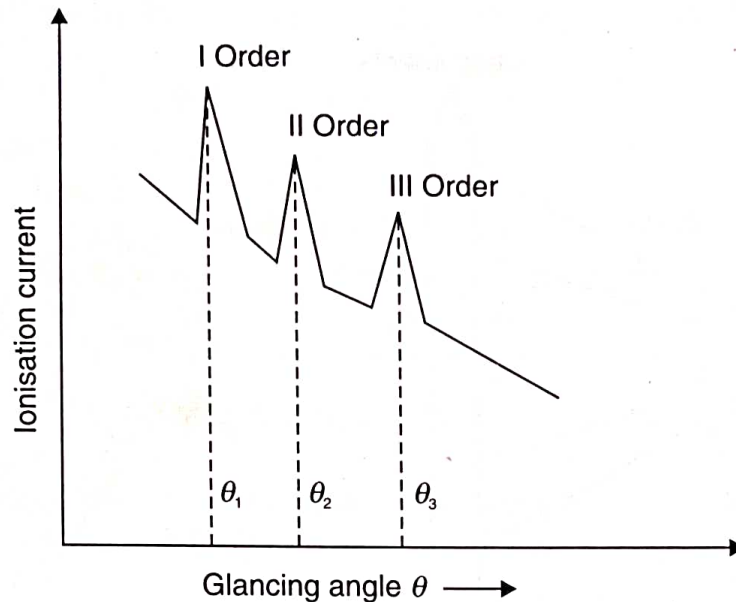


FIG. 9.9 Plot between ionisation current (I) and glancing angle (θ) for NaCl

Analysis: It is clear from the graph (Fig. 9.9) that for certain values of glancing angle θ , the ionisation current I increases abruptly. The number of peaks in the curve corresponds to those glancing angles which satisfy Bragg's equation, i.e.,

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

For

$$n = 1, \lambda = 2d \sin \theta_1$$

$$n = 2, 2\lambda = 2d \sin \theta_2$$

$$n = 3, 3\lambda = 2d \sin \theta_3$$

Hence, $\sin \theta_1 : \sin \theta_2 : \sin \theta_3 = 1 : 2 : 3$. Thus, out of θ , λ , and d , if two are known, the value of the third one can be calculated. From the experimental observations, the following facts have been established:

- (i) As the order of spectrum increases, the intensity of the reflected X-rays decreases.
- (ii) The ionisation current does not fall to zero for any value of glancing angle θ , but it does attain a maximum value for certain glancing angles. It indicates that there is continuous spectrum over which the characteristic line spectrum is superimposed.

9.3 X-RAY SPECTRA

When the intensities of different wavelengths of X-rays coming out from any source are plotted with wavelength, in general, two types of spectra, continuous and characteristic spectra, are obtained.

9.3.1 Continuous X-Ray Spectra

Continuous X-ray spectra consist of radiations of all possible wavelengths within a certain range. The intensity versus wavelength curve for different value of accelerating voltage is found as shown in Fig. 9.2.

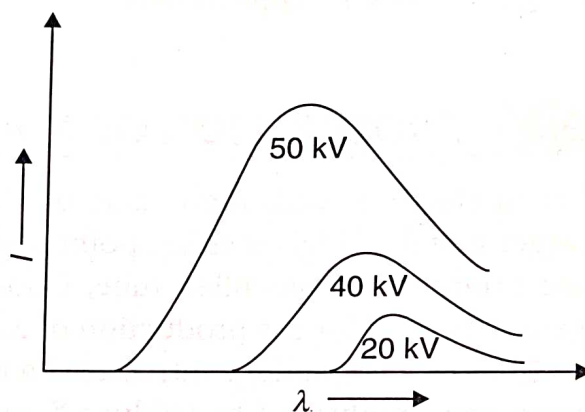


FIG. 9.2 Continuous X-ray spectra

The total intensity of continuous X-ray radiations for a given target is proportional to V^2 . The minimum wavelength λ_{\min} is independent of the nature of the target and is directly related to accelerating potential (V) as

$$Ve = h\nu_{\max} = \frac{hc}{\lambda_{\min}} \quad (7.1)$$

Origin of continuous X-ray spectra: As it is discussed in preceding sections that when high-velocity electrons hit a suitable target, X-rays are produced. As the target atom is of large atomic weight, the positive charge of the nucleus is completely shielded by the surrounding electrons (Fig. 9.3).

When incoming electron reaches near to the target atom, it experiences a strong repulsive coulomb force and is suddenly slowed down and also suffer deflection in path. During retardation the electron emits a pulse of electromagnetic radiation of energy $h\nu$. Due to different losses in velocity of the incident electrons, radiations of all possible wavelengths are emitted which give a continuous spectrum of X-rays. The continuous radiation is also termed as *bremsstrahlung radiations* or *braking radiations*.

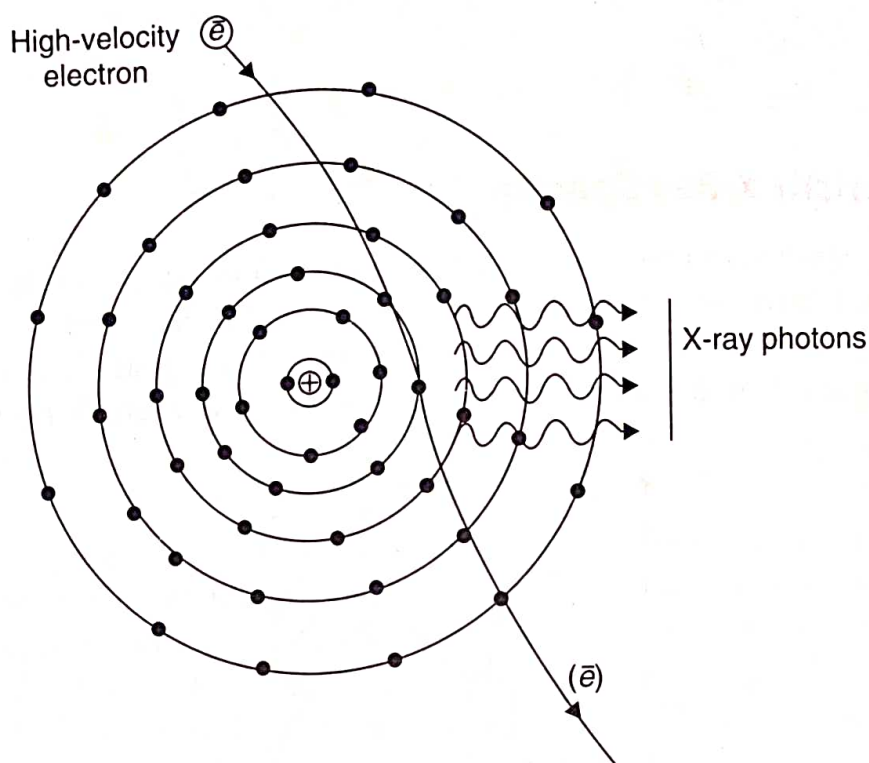


FIG. 9.3 Interaction of high-velocity electron with target atom to produce continuous X-ray spectra

In order to calculate the wavelength of emitted X-ray photon, let us consider an electron whose charge is e , accelerated by a potential V . This electron will gain on energy eV , which must be equal to its kinetic energy. Thus,

$$\frac{1}{2} m v^2 = eV$$

or
$$v = \sqrt{\left(\frac{2eV}{m}\right)} \quad (7.2)$$

where v is the velocity of striking electron of mass m .

If the entire energy of electron is converted into the energy of X-rays, then

$$\frac{1}{2} m v^2 = eV = h\nu$$

or
$$\nu = \frac{eV}{h} \quad (7.3)$$

ν is the maximum value of frequency of X-ray photon. We know that

$$c = \nu\lambda$$

Hence,
$$\lambda_{\min} = \frac{c}{\nu_{\max}} = \frac{hc}{eV} \quad (7.4)$$

9.3.2 Characteristic X-Ray Spectra

Characteristic X-ray spectra consist of a few peaks superimposed on the continuous spectrum. The number of peaks and their corresponding wavelengths are the characteristic of material used as target. These peaks generally occur in groups and are named as K peaks, L peaks, and so on from the shorter wavelength side to the longer wavelength side. Characteristic X-ray spectra is shown in Fig. 9.4.

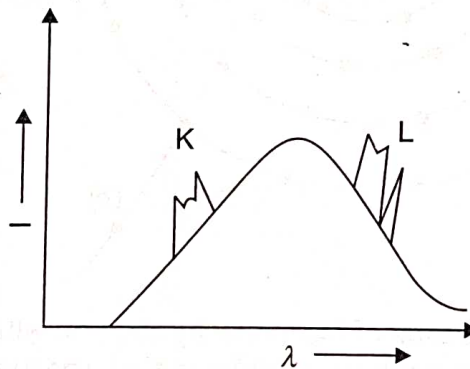


Fig. 9.4 Characteristic X-ray spectra

Origin of characteristic X-rays spectra: Sometimes it happens that the incident high-velocity electron penetrates through the outer shells of the target atom and strikes with an electron in the inner shell (Fig. 9.5). The collision is so strong that an electron from the inner shell is knocked out. Definitely a vacancy is created and to fill it, an electron from higher energy state jumps into this vacancy. The difference in energy is emitted as X-rays photon of energy $\Delta E = h\nu$. This process further creates a vacancy in higher state which is again filled up by an other electron jumping from the next higher state.

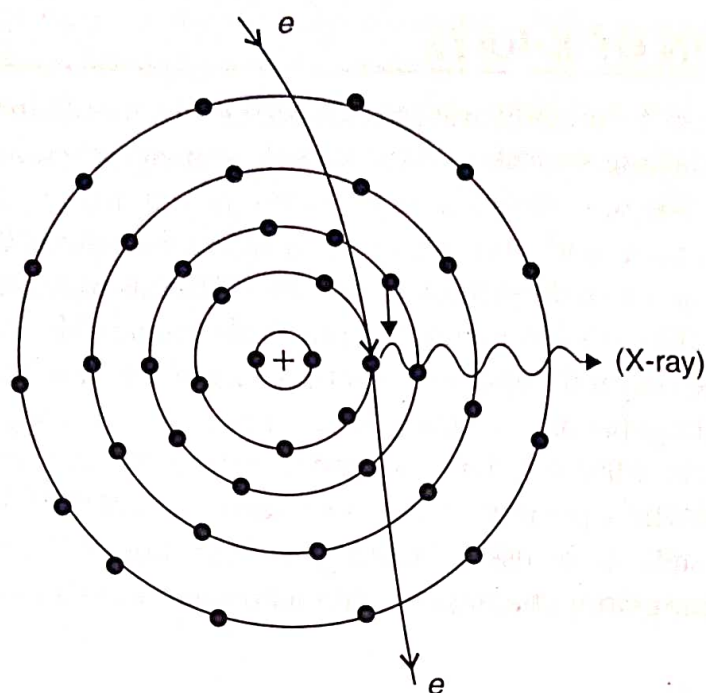


FIG. 9.5 Origin of characteristic X-ray spectra

In this way, another photon of X-ray is emitted out with slightly less energy. The process goes on till the highest shell is reached. Thus, we get a series of lines giving characteristic spectra electrons which after striking the target produce X-rays. Since most of the kinetic energy of electrons is absorbed by the target metal in the form of heat, a cooling system is required to maintain the temperature. The intensity of X-rays (the number of electrons emitted per second) is controlled by filament battery, and the quality (penetrating power) of X-rays is controlled by the high-tension battery.

9.4 IMPORTANT PROPERTIES OF X-RAYS

Some important properties of X-rays are as follows:

- (i) X-rays are electromagnetic radiations like light. Thus, they possess all the properties of electromagnetic radiations and exhibit phenomena such as reflection, refraction, diffraction, and interference.
- (ii) X-rays have very short range of wavelength, lying between 0.01 \AA and 10 \AA .
- (iii) X-rays are absorbed by the material.
- (iv) X-rays are not deviated by either electric or magnetic field.
- (v) X-rays ionise the gas through which they pass.
- (vi) X-rays can penetrate the solid materials.
- (vii) X-rays affect photographic plate.
- (viii) Secondary radiations arise when X-rays strike a metal.
- (ix) X-rays have harmful effects on human tissues. Therefore, a continuous exposure to these rays must be avoided.
- (x) X-rays cause fluorescence.