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X-Ray Spectra

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277

Discovery of X-rays:-

Roentgen discovered X-rays in 1895 when he was studying the fluorescence of the walls of a highly evacuated glass tube through which an electric discharge was passing. He covered the glass tube with a shield of thin black cardboard in order to facilitate the observation of the fluorescence. To his surprise he found that a paper screen coated with barium platinocyanide placed in the neighbourhood of the tube fluoresced brilliantly. The observation led Roentgen to conclude that the fluorescence of the screen is due to some type of invisible radiation emerging from the tube. He called these invisible radiations X-rays indicating their unknown nature. Roentgen later on asserted that X-rays were electromagnetic waves just like ordinary light, but of much smaller wavelength. They are produced whenever high energy electrons impinge on a solid body, but heavy elements like platinum are more efficient in this respect than light elements.

* Diffraction of X-rays:- The diffraction of X-rays carried by Laue by passing a narrow beam of X-rays through a crystal of Zinc sulphide, after passing through the crystal, the X-rays were allowed to fall on a photographic plate and a characteristic diffraction pattern consisting of a central spot corresponding to the direct X-ray beam, surrounded by a group of symmetrically situated spots was obtained. This pattern is known as Laue pattern and the spots are called Laue spots. The positions of these spots were found to change with the change in the orientation of the crystal and were different for different crystals. The range of wavelengths in the heterogeneous X-ray beam used in this experiment was calculated to be from 0.13 to 0.46 Å. This experiment proved that X-rays have wave nature.

Bragg's law:- Imagine a crystal made up of parallel equidistant planes of atoms and a beam of monochromatic X-rays from a distant source impinge on the crystal. Each atom then becomes a source of elementary scattered waves (or wavelets) which are coherent and liable to produce interference effects. The wave diffracted in a particular direction is the resultant of these waves issuing from the atoms of the crystal. X-rays besides being reflected from the surface layer of the crystal readily penetrate through it to encounter a large number of planes parallel to each other. Some of the incident radiations will be diffracted by the layer A_1A_2 as shown in figure. The remainder will penetrate still deeper. Any diffraction beam will therefore have contributions from large number of layers.

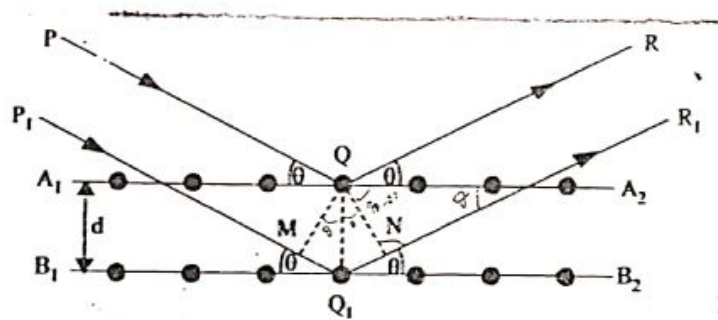


Fig. 122: Diffraction of X-rays from a face of the crystal

The first step in the analysis of a mixture is to determine the components present. This is often done by using a technique such as chromatography or spectroscopy. The results of these analyses are then used to identify the individual components and their relative concentrations.

Once the components have been identified, the next step is to determine the amount of each component in the mixture. This is often done by using a technique such as gravimetry or titrimetry. The results of these analyses are then used to calculate the composition of the mixture.

The final step in the analysis of a mixture is to determine the purity of the components. This is often done by using a technique such as chromatography or spectroscopy. The results of these analyses are then used to calculate the percentage of each component in the mixture.

In summary, the analysis of a mixture involves three main steps: identifying the components, determining the amount of each component, and determining the purity of the components. Each step is often done using a different technique, and the results of these analyses are used to calculate the composition and purity of the mixture.



It consists of three parts namely (i) a source of X-rays (ii) crystal mounted on the turn table to be rotated about vertical axis. The position of the table can be read on a circular graduated scale V and (iii) Ionization chamber I.

A beam of X-rays is made to pass through the slits S_1 and S_2 which is collimated into a fine pencil. The collimated beam then falls on the NaCl crystal placed on the turn table T. The reflected beam after passing through the another slit S_3 enters the ionization chamber I. The ionization chamber connected to the galvanometer G, measures the ionization current. In practice the turn table is geared to the ionization chamber so that the chamber turns through 2θ when crystal is turned through θ angle.

Initially the glancing angle θ for the incident beam is kept small. It is increased in small steps starting from the angle $\theta = 0$. It is observed that as the glancing angle θ increases the ionization current also increases. A graph showing the variation of current with the glancing angle θ is given in figure. No graph is obtained is called X-ray spectrum. Three peaks are observed. These peaks are the characteristics of Bragg's reflection from the crystal planes. The glancing angle called Bragg's angle θ_1, θ_2 and θ_3 corresponding to these three peaks are obtained from the graph. It is found that $\sin \theta_1 : \sin \theta_2 : \sin \theta_3 = 1 : 2 : 3$. These show that the peaks A_1, A_2 and A_3 refer to the first, second and third order reflections of the same wavelength.

From the observed value of θ and known value of n and d , the wavelength λ can be determined by using the relation $2d \sin \theta = n\lambda$.
 on the other hand if known value of wavelength λ of the X-ray beam is incident on the NaCl crystal the distance d between two neighbouring ions can be calculated from the above relation.

The Collimator of the usual Spectrometer is replaced by two or more parallel lead slits, a crystal with its cleavage face vertical is employed in place of a prism or grating and an ionisation chamber with a slit at its entrance replaces the telescope. The ionisation chamber is capable of rotating around the axis of the instrument just like the telescope in the usual Spectrometer. Sometimes the ionisation chamber is geared to the table on which the crystal is mounted so that it turns through an angle 2θ when the crystal turns through an angle θ . This automatically keeps the chamber in the position in which it will receive the beam reflected from the crystal face.

A photographic plate may be employed in place of the ionisation chamber. It is placed in a container which forms an arc around the crystal as centre. The crystal is then slowly rotated so that one set of planes after the other is at the correct angle of setting for the Bragg equation to apply. The photographic method is preferred for recording accurately the angle θ of the Bragg equation. However, for recording relative intensities of the reflected beams at diffraction maxima, the ionisation chamber method is preferred.

Experimental methods of X-ray diffraction :- Bragg's law $2d \sin \theta = n\lambda$ requires that θ and λ be matched; X-rays of wavelength λ

falling on a crystal at an arbitrary angle of incidence will not in general be reflected. To satisfy the Bragg's law, it is necessary to vary either wavelength λ or angle θ . This can be done experimentally by providing for continuous range of values of either λ or θ , usually θ is varied. The standard methods are:

1. Laué method :- A single crystal is held stationary in a beam of continuous wavelength X-ray radiation, out of these the crystal selects out and diffracts the discrete values of λ for which there exist planes of spacing d and incidence angle θ satisfying the Bragg's law.
2. Rotating crystal method :- A single crystal is rotated about a fixed axis in a beam of monochromatic X-rays. The variation in θ brings different atomic planes into position

- necessary for diffraction to take place.
3. Powder method :- A powdered sample of crystalline material is placed in a fixed position in a monochromatic X-ray beam. Among the distribution of the crystal plane orientations there will be some for which the angle of incidence satisfies the Bragg's law. The Laué method is suitable for the rapid determination of the crystal orientation and symmetry. The rotating crystal method is best suited for determination of structure, when single crystal is available. The powder method is mostly applied when single crystals are not available.

X-rays

- Electromagnetic radiations with wavelength in approximate interval from 1 \AA to 100 \AA are considered as X-rays. These can be produced by X-ray tube in which heated cathode gives electrons which are accelerated by high potential difference between cathode and metallic target (anode). Accelerated electrons strike the anticathode and X-rays are obtained from the side of tube. Classical electromagnetic theory suggests that X-rays are produced when swiftly moving electrons are stopped by a target. According to classical electrodynamics, moving charge emits radiations and sudden stopping give rise to pulse of radiations taking the form of X-rays.

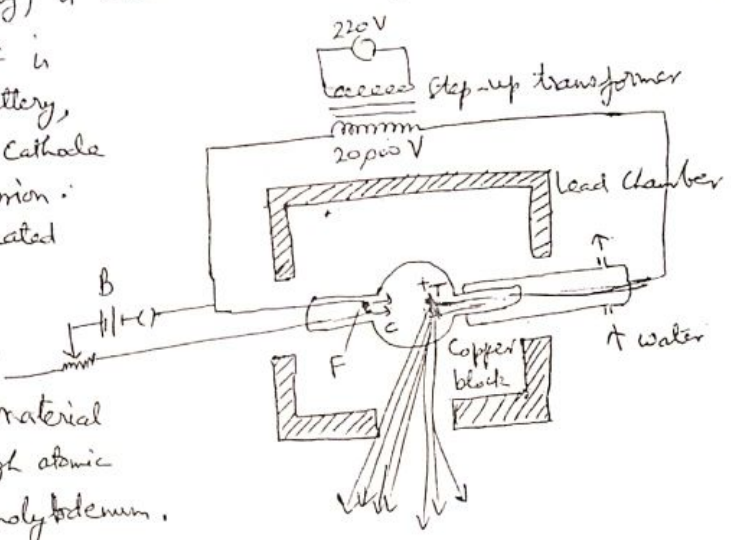
X-rays possess strong penetrating power, based on penetrating power their classification is

- (1) Soft X-rays (of low penetrating power)
- (2) Hard X-rays (of high penetrating power)

Production of X-rays :-

Coolidge tube :- X-rays are produced with the help of a Coolidge tube. It is a glass bulb inside which a high quality vacuum (of the order of 10^{-6} cm of mercury) is created. A Coolidge tube is shown in figure.

When tungsten filament F is heated by a low tension battery, electrons are emitted from cathode C due to thermionic emission. These electrons are accelerated towards target T by a high potential difference.



Target T is made of a material of high melting point and high atomic weight like tungsten or molybdenum. High energy electrons, striking the target

may produce large heat so that the target may get melted. To avoid this a continuous supply of cold water is maintained through the tube.

When high energy electrons emitted from the cathode hit the target they lose their kinetic energy either in heating the target or by emitting an X-ray photon. Hence the process of production of X-rays is a kind of inverse photo electric effect.

Both photoelectric effect and X-ray production confirm the quantum view of radiation.

Properties of X-rays :-

$\frac{1}{\lambda} \propto \frac{1}{\Delta T}$ - 100°K

27/11

- (1) X-rays are electromagnetic waves of very short wavelength.
- (2) They show all the wave phenomena like reflection, refraction, interference, diffraction and polarisation.
- (3) X-rays propagate with velocity of light.
- (4) They blacken photographic plates.
- (5) X-rays also show photoelectric effect and Compton effect.
- (6) X-rays are highly penetrating. However lead is practically opaque to X-rays.
- (7) X-rays produce fluorescence in many substances.
- (8) X-rays are not affected by electric and magnetic fields, so they are not charged particles.
- (9) X-rays produce ionisation in gases.

Intensity of X-rays :- Intensity of X-rays is proportional to the number of electrons falling upon the target material per second. When current in the filament is increased by using low tension battery, temperature of the filament gets increased and greater number of electrons are emitted from cathode due to thermionic emission. Hence intensity of X-rays can be increased by increasing current in the filament.

Penetration of X-rays :- The penetration of X-rays depends upon their wavelength. Greater the wavelength lesser will be the frequency and therefore lesser penetration. The X-rays of lesser energy (i.e., of large wavelength and small frequency) have lesser penetration so they are called soft X-rays. However the X-rays of high frequency and small wavelength have high penetration so they are called hard X-rays.

Penetration of X-rays may be increased by increasing potential difference across the ends of Coolidge tube.

and mechanism
Origin of X-rays :- The origin of x-rays is from two entirely different mechanisms. Both the mechanisms produce different types of x-rays. When high speed electrons from an electron gun strike the target some of them penetrate into the atom and encounter with the electrons in the innermost orbits and knock out them. Let us suppose an electron from K-shell is knocked out. Thus, a vacancy is created in the K shell which is filled by electron from L, M, N, --- shells. If it is filled by a L-shell electron it is termed as K_{α} transition if by M, N, --- shell electron, then the transitions will correspond to K_{β} , K_{γ} , --- transitions. The similar process is for L-shell vacancy, the transitions will correspond to L_{α} , L_{β} , L_{γ} , --- transition. In this way the vacancy moves to outer most shell and the vacancy is filled by the free electrons available. Thus, it is possible for a single atom to emit line x-rays of different frequencies (wavelengths). The K-series is less than 0.1nm while L-series is greater than 0.1nm. It has been noticed that wavelength of L-series are approximately 10 times higher than of K-series.

There is another possibility that the incident electron don't strike with any of the orbital electrons. I- this case the high speed negatively charged electron is deflected from its path due to force of attraction of positively charged nucleus. In this process the electron loses some of its kinetic energy which appears in the form of electromagnetic radiation. This process is also known as Bremsstrahlung. Decelerating charge particles emit radiation. These radiations are called Bremsstrahlung.

Soft and Hard X-rays :- The penetrating power of x-rays depends upon .
 i) the applied potential difference between the cathode and the anticathode
 ii) the atomic weight of the material of the anticathode.

The greater the potential difference, smaller is the wavelength of x-rays, higher is their energy and more penetrating are the rays.

The x-rays having high penetrating power are known as hard-x-rays. These carry high energy.

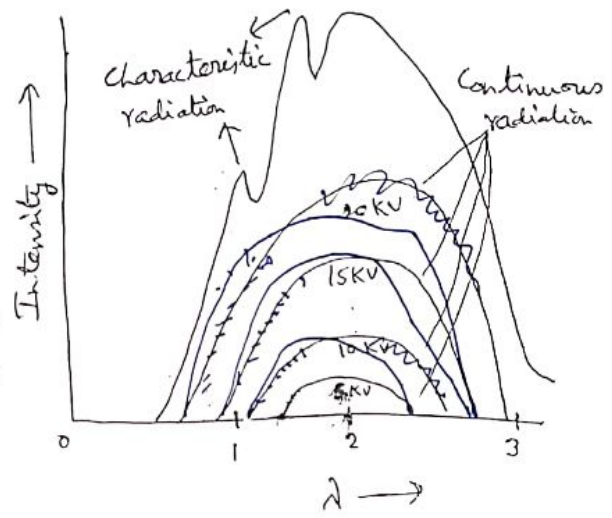
Those x-rays having low penetrating power are known as soft-x-rays. These are of longer wavelength, carry lower energy and are less penetrating.

X-ray Spectrum :- When x-rays obtained from the target of an x-ray tube operated at high voltage are analysed by Bragg spectrometer and their intensity is measured by an ionization chamber, then the graph between ionization current (i.e. intensity) and the wavelength comes out as shown in figure.

It consists of a spectrum which continuously covers a wide wavelength range (Continuous spectra) and at very high voltages, ^(the spectrum) is superimposed by sharp lines (Characteristic spectra). Thus two distinct types of spectra are seen to be present.

- (1) Continuous spectrum
- (2) Characteristic spectrum

$\lambda_c = 1.54 \text{ \AA}$
 $m\lambda = n\lambda_c$



X-ray spectrum of Molybdenum as function of the applied voltage.

Continuous X-ray spectra :-

when the radiations from the x-ray tube are analysed by Bragg's spectrometer, the spectra consists of a continuous spread of uninterrupted wavelengths having a minimum wavelength limit. If tube voltage is sufficiently high then a line spectra is also superimposed upon the continuous spectra. At sufficiently low tube voltage the pure continuous spectrum with certain wavelengths can be obtained without characteristic lines imposed there upon.

Salient Features of Continuous X-ray spectra :-

- (1) It has a sharply defined wavelength

$$\lambda_{\text{minimum}} = \frac{12396 \text{ \AA}}{V} ; (V = \text{tube voltage in volts})$$

λ_{minimum} is independent of the nature of target material but inversely proportional to potential difference across the tube.

- (2) The intensity of continuous spectra is nearly proportional to square of tube voltage for a given target and also to atomic number of target material when potential difference is constant i.e.

$$I \propto V^2 \text{ and } I \propto Z \text{ (at constant potential difference)}$$

- (3) There is a shift of maximum intensity position towards the short wavelength side as voltage is increased.



Mechanism or origin of production of Continuous X-ray spectra :- 282

When speedy electrons strike the target; about 99.8% electrons collide and lose their little energy and simply increase the average K.E. of atoms of targets. The remaining electrons produce X-rays by losing their most or all K.E. in a specified way in one single collision. The high velocity electron penetrates the interior of the atom and its path is deflected due to attraction force of nucleus. The electron experiences retardation in the strong field of nucleus. The energy lost during retardation

is given in the form of X-rays of continuous X-ray spectrum.

If v is the velocity of electron at the time of entrance, v' is the velocity after passage through atom. The loss of energy of electron in the passage is

$$= \frac{1}{2}mv^2 - \frac{1}{2}mv'^2$$

This loss must be equal to the energy of the X-ray photon emitted i.e.

$$\frac{1}{2}mv^2 - \frac{1}{2}mv'^2 = h\nu \quad \text{--- (1)}$$

The highest or maximum frequency of the emitted X-rays corresponds to the case when electron is completely stopped i.e. $v' = 0$ and then

$$\frac{1}{2}mv^2 = h\nu_{\max} \quad \text{--- (2)}$$

If electron is accelerated through a potential difference of V volts then

$$\frac{1}{2}mv^2 = eV \quad \text{--- (3)}$$

Then in view of equation (2)

$$h\nu_{\max} = eV \quad \text{--- (4)}$$

This relation is also known as Duane-Hartley rule, again

$$\frac{hc}{\lambda_{\min}} = eV \quad \text{as } \nu_{\max} = \frac{c}{\lambda}$$

$$\text{or } \lambda_{\min} = \frac{hc}{eV}$$

Putting the value of h, c & e we get

$$\lambda_{\min} = \frac{12396 \text{ \AA}}{V}$$

Another name given to these X-rays is Braking Radiation as these are produced by the braking (slowing down) of high velocity electrons.

Explanation of Continuous X-rays :- The emission of continuous X-rays by electrons striking the target and the short wavelength limit can be explained by quantum theory. According to this theory, emission of X-rays takes place in the form of small bundles of energy called 'photons'. The energy of each photon is $h\nu$, where ν is the frequency of X-radiation and h is Planck's constant. When a voltage V is applied across the X-ray tube, then an electron emitted by the filament will reach the target with energy eV , where e is the charge of electron. When the electron strikes an atom of the target, it loses part or whole of its energy. The lost energy is detached in the form of an X-ray photon.

For the most favourable collision in which the electron loses the whole of its energy in a single collision with the target atom, an X-ray photon of maximum energy $h\nu_{max}$ is emitted. Thus, for an accelerating voltage V the maximum X-ray photon energy is given by

$$h\nu_{max} = eV$$

Consequently, the maximum frequency of X-ray produced by electron of energy eV is

$$\boxed{\nu_{max} = \frac{eV}{h}} \quad \text{--- (1)}$$

The minimum wavelength corresponding to this maximum frequency ν_{max} is given by

$$\lambda_{min} = \frac{c}{\nu_{max}} \quad \text{--- (2)}$$

where c is the speed of light.

Substituting the value of ν_{max} from eq. (1) in eq. (2), we have

$$\boxed{\lambda_{min} = \frac{hc}{eV}} \quad \text{--- (3)}$$

Thus, the minimum wavelength limit is inversely proportional to the accelerating potential. Eq. (3) is known as Duane and Hunt relation.

Substituting $h = 6.6 \times 10^{-34} \text{ J-s}$, $c = 3 \times 10^8 \text{ m/s}$, $e = 1.6 \times 10^{-19} \text{ C}$ in the above expression and solving, we get

$$\lambda_{min} = \frac{1.2375 \times 10^{-6}}{V} \text{ m} = \frac{1237.5}{V} \text{ \AA}$$

In this expression V is in Volt.

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The electron rarely loses whole of its energy in a single collision. More usually it undergoes a sequence of collisions with atoms of the target before coming to rest, thus emitting photons of smaller and smaller energies, that is, of longer and longer wavelengths. This accounts for the production of a range of x-ray wavelengths above a definite limit.

Most of the kinetic energy of the electron beam striking the target goes simply into heat. It is only 1% or even less of the electron energy which is converted into x-rays.

Characteristic X-ray Spectra :- The characteristic X-ray spectra is line spectra which may generally be obtained experimentally at higher tube potentials and this spectra remains superimposed upon continuous emission spectra obtained by Bragg's spectrometer.

A heavy element as a target in a X-ray tube emits a X-ray spectra which consists of several series of lines.

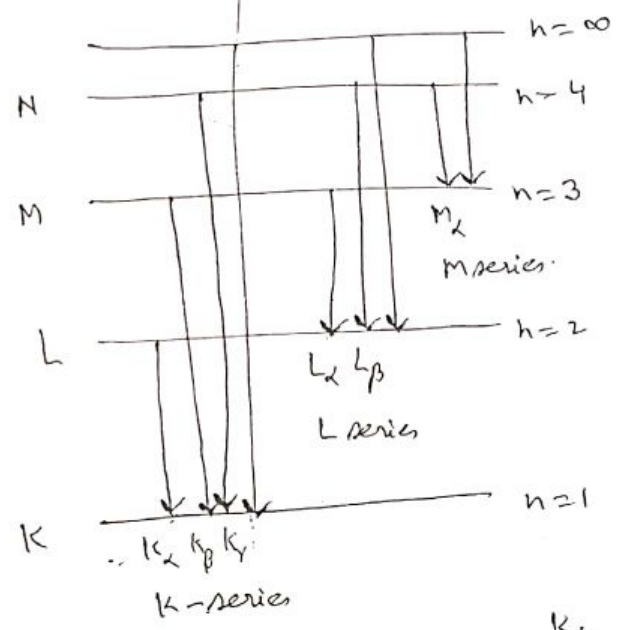
- (a) Each series converges towards high frequencies.
- (b) Each series consists only of few lines not infinitely many like optical spectra.

The characteristic X-ray spectra consists of discrete spectral line which constitute K, L, M series etc. The series located at higher frequencies are called K series, next comes L series and so on. The line spectra is characteristic of the element of which the target is made up of and is called characteristic spectra. (Unlike the continuous spectra which is characteristic of the tube voltage or the energy of impinging electron)

Mechanism For origin of characteristic X-ray Spectra :- The origin of characteristic spectrum of X-rays may be

explained due to electronic transitions within the target atom.

Suppose an electron of the incident cathode rays removes a K-electron from an atom of the target by hitting it. Now a vacancy is created in the K-shell to fill up this vacancy an electron from either of L, M or N shell or any free electron may jump into the K-shell. These possible transitions produce K_{α} , K_{β} etc. spectral lines which form K-series. Similarly if incident electron removes an L-electron from an atom of the target, L-series of characteristic spectrum will originate. The origin of M-series etc may be explained in a similar manner.



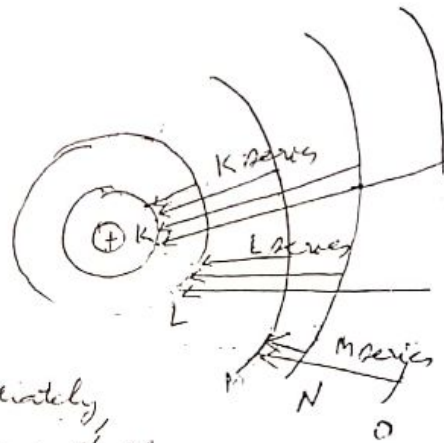
Low 'z' - characteristic spectrum such as molybdenum $Z=42$, $V < 20,000$ volts, $V > 25,000$ volt or higher, $Cu: Z=29, V > 20,000$ volts
 High 'z' - continuous spectrum, such as tungsten $Z=74$



Explanation of characteristic x-rays:- The characteristic x-rays are distinguished by their simplicity. Most elements, used as target in x-ray tube, show in their x-ray spectra, two series of lines known as K-series and L-series. Each series contains a small number of lines designated as $K_\alpha, K_\beta, \dots, L_\alpha, L_\beta, \dots$ etc. The wavelength of K-series are generally less than 1 \AA , while those of L-series are roughly ten times greater. Heavier elements ($Z > 66$) show further series known as M and N series.

According to the quantum concept, an atom consists of a central +ve charged nucleus with electrons revolving around it in orbits, or shells of definite radii. These shells are called the K, L, M, N, ... shells, K being the innermost. The maximum number of electrons which the K, L, M, N, ... shells can hold are 2, 8, 18, 32, ... The electrons in the K-shell are attracted by the positive nucleus with the greatest force, and to eject them from the atom, maximum energy is required, lesser energy is required to eject an electron from the L-shell, still lesser from M-shell, and so on.

Now, in an x-ray tube, an electron emitted from the cathode strikes the target with a tremendous velocity so that it penetrates well inside the atoms of the target. If it ejects an electron from the K-shell of the atom, a



Vacancy is created in the K-shell. Immediately, an electron from one of the outer shells, say L-shell, jumps to the K-shell emitting an x-ray photon of energy equal to the energy difference between the two shells. Similarly, if an electron from the M-shell jumps to the K-shell, x-ray photon of higher energy is emitted. The x-ray photons emitted due to the jump of electron from the L, M, N, ... shells to the K-shell give $K_\alpha, K_\beta, K_\gamma, \dots$ lines of the K-series of the spectrum.

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If the electron striking the target ejects an electron from the L-shell of the target atom, an electron from the M, N, ... shell jumps to the L-shell, so that x-ray photons of lesser energy are emitted. These photons form the L-series of the spectrum. Clearly, the frequencies of the L-series are smaller than those of the K-series. In a similar way, the formation of M-series, N-series, etc. may be explained.

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Whenever a vacancy is created in a inner shell, say K-shell, the electron from the next higher shell, the L-shell, is most likely to jump to the K-shell emitting a line of the K-series. The vacancy left by the jumping electron in the L-shell is filled by the jump of another electron from a still higher shell, so that a line of L-series is emitted. This process continues until the vacancy reaches the outermost shell where it is filled by some free electron. Thus, the emission of K-series is always accompanied by the emission of L, ... series.

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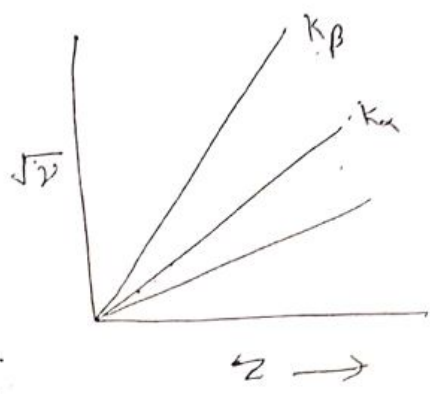
Moseley Law :- Moseley studied the X-ray line spectra of several elements and found that for a given transition (for example K_{α} or K_{β}) the frequencies of the emitted lines for different elements were proportional to the atomic number of the element, according to the relation:

$$\boxed{\sqrt{\nu} = c'(Z - \sigma)}$$

$$\sqrt{\nu} \propto Z$$

where c' and σ are constants. The constant c' depended on the characteristic line considered.

The graph between $\sqrt{\nu}$ and Z is thus a straight line for a particular spectral line as shown in figure. Thus the square root of the frequency of characteristic X-ray line is proportional in the atomic number of element which emitted it. This is Moseley law.



Derivation of Moseley law from Bohr's theory :- According to Bohr's theory for hydrogen like atoms, the energy

of an electron in n^{th} orbit is given by

$$E_n = -\frac{2\pi^2 m e^4 Z^2}{h^2 h^2} = -\frac{R h Z^2}{n^2} \quad \dots \text{--- (A)}$$

where $R = \frac{2\pi^2 m e^4}{h^3}$ is the Rydberg constant.

In hydrogen like atoms, the only electron moves in the field of positive nucleus of charge Ze , but for atoms having many electrons situated in different orbits, a certain electron finds itself in the field created by nucleus as well as by the other electrons surrounding the nucleus. Thus the nucleus is in a way screened by the presence of electrons round it. This screening effect can be accounted by replacing Z by $(Z - \sigma)$ in equation (A) σ represents the screening effect by the remaining electrons. So above equation becomes.

$$E_n = -\frac{R h (Z - \sigma)^2}{n^2} \quad \dots \text{--- (B)}$$

For a transition from $n = n_2$ to n_1 level, we get

$$\boxed{E_{n_2} - E_{n_1} = h\nu = R h (Z - \sigma)^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]}$$

or $\nu \propto (Z - \sigma)^2$ or $\sqrt{\nu} \propto (Z - \sigma)$

or $\sqrt{\nu} = c'(Z - \sigma)$

where c' is some constant, given as $c' = R h \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)^{\frac{1}{2}}$

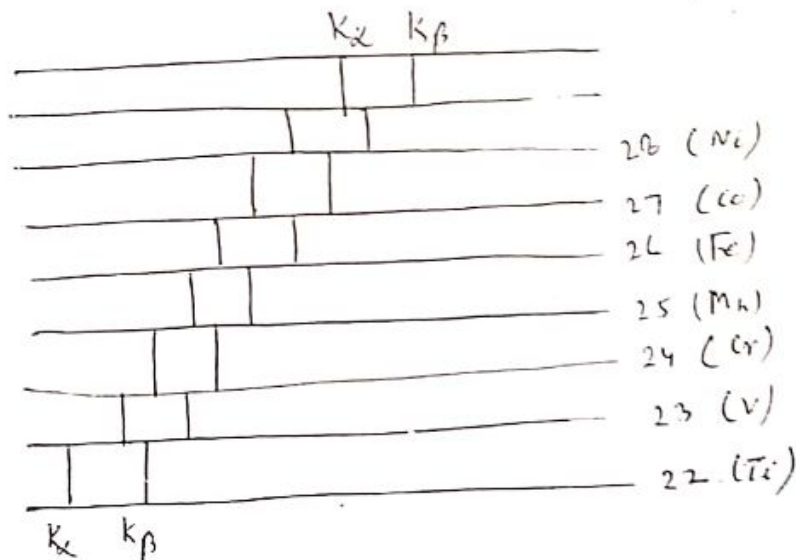
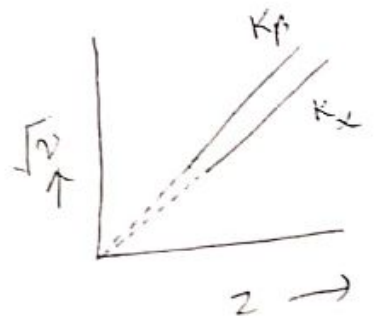
Imp For K_{α} line.
 $c' = \sqrt{\frac{3 R h}{4}} \sigma = 1$
 $c' = R h \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)^{\frac{1}{2}}$

P.T.O.

Importance of Moseley Law :- (1) Moseley's work showed that the determining factor in the arrangement of elements in the periodic table should be atomic number and not the atomic weight. Thus the discrepancy in the order of placement of certain elements was removed. For example, $^{40}_{18}\text{Ar}$ (39.948) comes before $^{39}_{19}\text{K}$ (39.0983) and similarly $^{58}_{28}\text{Ni}$ (58.69) comes before $^{59}_{27}\text{Co}$ (58.93) which is correct according to their chemical properties and is justified on the basis of atomic number.

- (2) With the help of Moseley's law it became possible to predict the existence of new elements, to determine atomic numbers of rare-earths and to fix their positions in the periodic table.
- (3) Moseley's studies provided a rapid means for the analysis of the substance.

Ar → Argon
 K → Potassium
 Co → Cobalt
 Ni → Nickel



ν →
 K series

X-Ray Absorption Spectra :- The striking feature of X-ray absorption spectra is that it is different from ^{emission} absorption spectra of common elements.

In normal absorption spectra when radiations are passed through an element, some dark bands are seen on the spectrograph, and these dark bands correspond to the energy difference of two states of the element, i.e., the electron jumps from one state to another state by absorbing the energy of the incident photon.

In the case of ~~X-rays~~ continuous X-rays is passed through the substance (thin layer) and the transmitted beam is analysed by X-ray spectrograph; the absorption spectra of that substance is obtained. This is entirely different from the emission spectra of the ^{same} substance.

Salient Features :- (1) Absorption lines corresponding to $K_{\alpha}, K_{\beta}, \dots$ are not observed. (2) A continuous region of absorption bounded by a sharp edge at the limit of emission of ~~absorption spectra~~ ^{absorption spectra} K-series is observed.

- (3) The edge shifts regularly towards higher frequency side when successive elements of periodic table are used as absorbers. These edges are characteristic of the absorber element and are called "absorption edges".
- (4) For each substance the frequency of the absorption edge, ν_k , is different and is called the K-absorption limit. The frequencies above it are strongly absorbed while lower than ν_k are less absorbed.

Explanation of absence of discrete lines :- ^{absorption} the K_{α} -line in emission occurs when an electron drops from the L-shell to the K-shell. In absorption, the absence of discrete lines for example, K_{α} -absorption line will occur only if electron of K-shell, after absorbing X-ray photon from continuous beam jumps to L-shell, but L-shell is already filled, so this K_{α} -absorption line doesn't exist. Similarly other lines also don't exist.

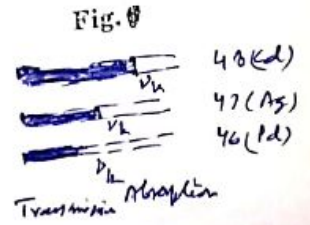
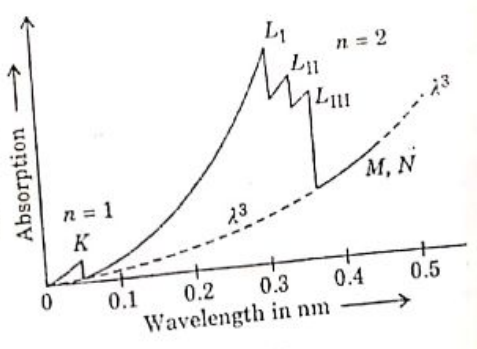
Explanation of continuous absorption bounded by a sharp edge :- The presence of absorption edge is obvious. When the atom absorbs a photon of energy higher than the binding energy of K-shell electron it goes to outer shells (infinitely) ^{why K-shell no longer exist} and the absorption edge appears. Photons which have energy less than aforesaid photon are transmitted. Thus, an absorption takes place at a frequency ν_k and continuous for all frequencies higher than ν_k , so absorption continuum appears. ^{the shift of absorption edge toward higher frequency side with increase in atomic number of the substance is quite obvious.} As the atomic number increases, binding energy of the electron also increases, i.e. more energy is required (h ν) that is why it shifts toward higher frequency side.

Explanation why absorption edge shifts with elements :-

The K-absorption edge seen in the X-ray spectra directly determines the K-energy level as, it is energy required to a free K-shell electron. It also be seen that each element has only one K-absorption edge, so the K-shell has only a single energy level.

Similarly to the K-absorption X-ray spectra, L-absorption spectra also exists, but in this case there are three absorption edges (L_I, L_{II}, L_{III}). The absorption edges indicates that there are energy levels for L-shell.

* Photons of frequency lower than ν_k would be transmitted by the absorbing element, M. ^{black part corresponds to the transmission of X-ray photons of all frequencies lower than ν_k .} At the freq ν_k absorption in the K-shell suddenly starts and thereafter continues for all frequencies higher than ν_k .



Fine Structure in X-ray levels :- The fine structure of X-ray spectra was not well explained by Kossel. Kossel explained line spectra only in terms of transitions in K, L, M, ... levels. Each line of K-series i.e. $K_{\alpha}, K_{\beta}, K_{\gamma}, \dots$ is doublet. In other words such line spectra are not singlet. The absorption edges show that K-level is single, L-level is 3-fold, M-level is 5-fold and N-level has 7 sub-levels etc. The main energy levels are split into $(2l+1)$ sublevels. These sublevels are referred to as the fine structure of X-ray levels.

We have studied that the K_{α} transition corresponds to an electron jump from L-shell to K-shell, but now we have seen that L-shell is three fold, so apparently there are three possible transitions. Now the selection rule comes into the picture. According to it the only possible transitions are for $\Delta l = \pm 1$ and $\Delta j = 0$ or ± 1 , i.e., l changes by ± 1 and j changes by 0 or ± 1 . The selection rule disallows the transition from $L_I (2^2s_{1/2})$ to K-shell. The possible transitions are from L_{III} and $L_{II} (2^2p_{3/2}, 2^2p_{1/2})$ to K-shell. These transitions give rise to K_{α_1} and K_{α_2} lines respectively.

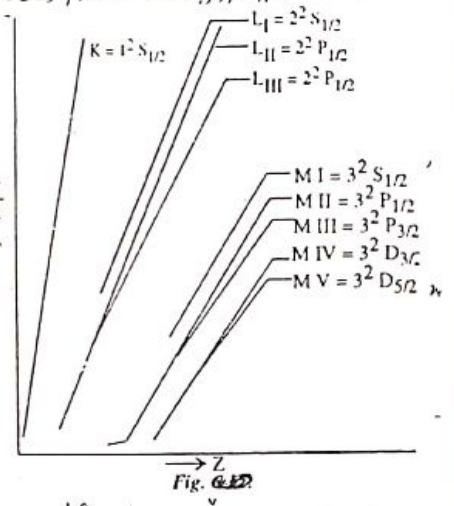
The electron in the L-shell move in a field which is approximately coulombian field, the two K-electrons behave very much as if they have combined with the nucleus. The screening of the nucleus by the two K-electrons effectively reduces the charge in the nucleus by about two. Therefore neglecting, for the moment the fine structure of energy levels, the energy for the L-level should be given by the hydrogen-like formula

$$T = \frac{R}{n^2} Z_{eff}^2 = R \frac{(Z-\sigma)^2}{n^2}$$

where σ is the screening constant and has the value equal to about $\frac{1}{2}R$ is the Rydberg constant, T is the term value.

In a similar way the energy for the m-level should be given but in this case the electrons in the m-shell are screened from the nucleus and two-K shell electrons resulting in an effect nucleus by about 10. This type of screening is termed as internal screening.

Apart from this internal screening effect a correction, known as also be applied. This screening effect is due to presence of outer shell electron is carried to infinity. Generally this screening effect is small in comparison to the main energy.



Spin-Relativity doublets (Regular doublets) :- When $\sqrt{\frac{T}{R}}$ of the X-ray levels against atomic number (Z) is plotted, we get a graph as shown

in above. The near straightness of the curves may be explained by a hydrogen like term value relation ($T = \frac{R(Z-\sigma)^2}{n^2}$).

It is seen that the separation of the $\sqrt{\frac{T}{R}}$ values for successive levels are of two kinds. The separation $L_I - L_{II}, M_{II}, M_{III} - M_{IV}$ etc are independent of Z , but the separation between $L_{II} - L_{III}, M_{III} - M_{IV}, M_{IV} - M_V$ etc increase rapidly with Z . The former are called screening doublets where as later are called spin-relativity doublets. The two levels of screening doublets have same J but different L while those belonging to spin-relativity doublets have identical L but different J having same S .

Q: An X-ray tube operates at 20 kV. Calculate maximum speed of electron striking at anticathode and shortest wavelength of X-ray produced.

A:- Accelerating potential = 20 kV = 20×10^3 Volts

If v_{max} is maximum speed of electron then

$$\frac{1}{2} m v_{max}^2 = eV$$

$$v_{max} = \sqrt{\frac{2eV}{m}} = \sqrt{\frac{2 \times 1.6 \times 10^{-19} \times 20 \times 10^3}{9.1 \times 10^{-31}}}$$

$$= 2.38 \times 10^8$$

$$\text{Again } \lambda_{min} = \frac{12400}{V} \text{ \AA} = \frac{12400}{20 \times 10^3} = \frac{1.24}{2} = 0.62 \text{ \AA} \quad \text{Ans}$$

Q:- Minimum wavelength recorded in an X-ray continuous spectrum of 50 kV tube is 24.7×10^{-12} m. Calculate the value of Planck's constant.

A:- for continuous X-rays

$$\lambda_{min} = \frac{hc}{eV}$$

Given $V = 50 \times 10^3$ V, $\lambda_{min} = 24.7 \times 10^{-12}$ m, $e = 1.6 \times 10^{-19}$ C, $c = 3 \times 10^8$ m/s

$$\text{So } h = \frac{eV\lambda_{min}}{c} = \frac{1.6 \times 10^{-19} \times 24.7 \times 10^{-12} \times 50 \times 10^3}{3 \times 10^8}$$

$$= 6.566 \times 10^{-34} \text{ J.s} \quad \underline{\underline{\text{Ans}}}$$

Q:- The shortest wavelength produced by an X-ray tube is 0.1 \AA . What accelerating potential does it employ?

Ans:- we know

$$\lambda_{min} = 0.1 = \frac{12400}{V} \text{ \AA} = \frac{12400}{V}$$

$$V = \frac{12400}{0.1} \text{ Volts} = 124000 = 124 \text{ kV} \quad \text{Ans}$$