# B.Sc. (Semester - 4) Subject: Physics

## Course: US04CPHY21

## Electromagnetic Theory and Spectroscopy

## Part 2

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# UNIT - IV  X-ray and X-ray Spectra

## Topics

- **Continuous X-RAY SPECTRUM**
- **Characteristic Absorption Spectrum**
- **A close Survey of Emission Spectrum**
- **Comparison between Optical and X-ray spectra**
- **Explanation of Emission and Absorption Spectra**

Reference Book:

Elements of Spectroscopy,  S L Gupta, V Kumar, R C Sharma, (20th Edition) Pragati Prakashan

# Continuous X-RAY SPECTRUM:

# Continuous X-RAY SPECTRUM:

- The study of continuous X-ray spectrum was first made by **Duane and Hunt**.

- The continuous spectrum is generated when **low energy electrons fall on a target** under certain conditions.

- But in general the background of **continuous** spectrum always has the **characteristic** lines.
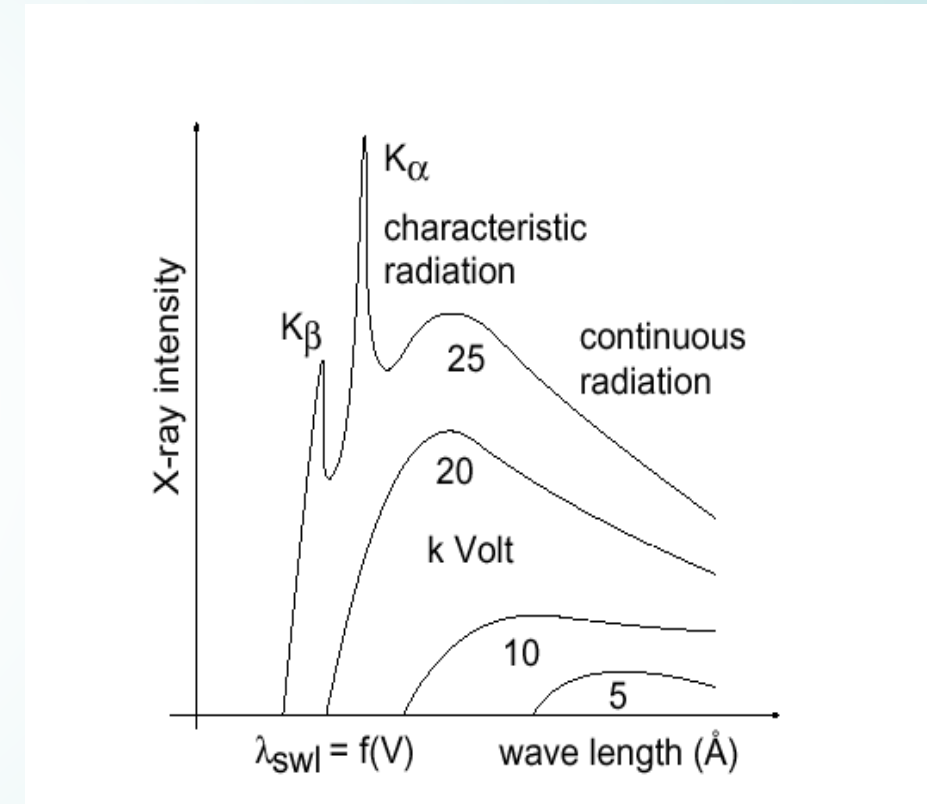
# Properties of the Spectrum

**Distribution of continuum radiation from an X-ray tube with a tungsten target.**
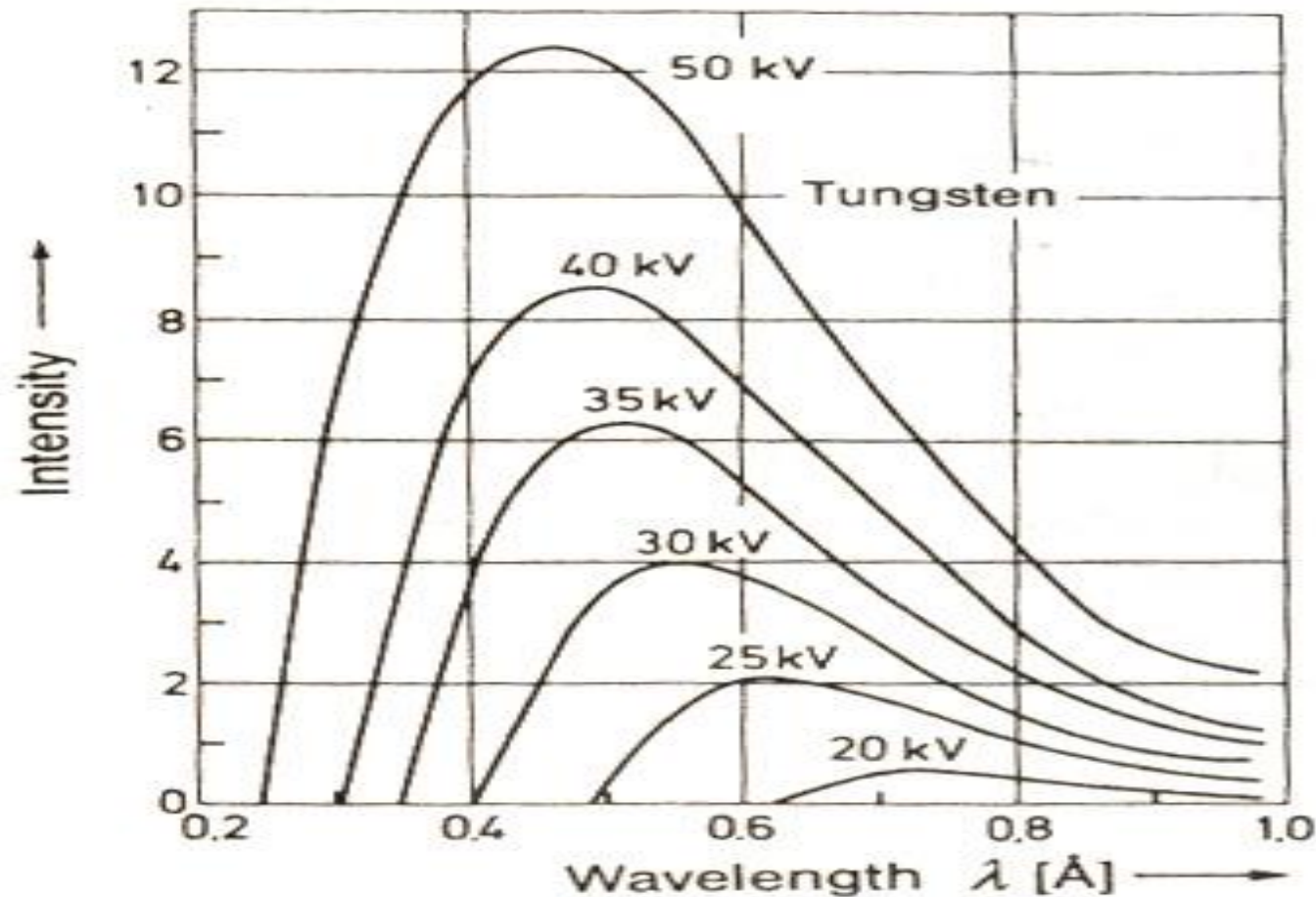
## Properties of the Spectrum

1 The striking sharp limit on short wavelength side.

2 Independent of material: the sharp limit does not depend upon the material of the target.

3 The shortest wavelength limit is the function of tube voltage.

4 Higher is the potential difference applied across the tube, shorter is the wavelength limit.

5 The intensity of the continuous spectrum increases at all wavelength as the tube voltages increases.

6 High PD, lower the wavelength at which intensity maximum.

# Properties of the Spectrum

**7 Integrated intensity, at a given voltage and current, is function of atomic number of the target element.**

**8 For a given target and tube current, integrated intensity is function of the square of the voltage applied.**

9 If we begin with longer wavelength side then the inversely rises to a maximum slowly and slowly, reaches a maximum value and then falls off rapidly to zero.

10 There is a minimum potential difference at which peaks appear in intensity distribution curve. This minimum potential difference depends upon the atomic number of target element. Higher is Z higher is potential difference.

11 Heights of peaks increase with increase in the potential difference.

**12** The positions of the discrete peaks in the intensity distribution curve depend upon the **atomic number Z** and on **applied potential**.

# **Explanation of sharp wavelength limit:**

- Minimum wavelength in the X-ray Spectra **can be explain by Plank-Einstein quantum equation.**

- **Duane and Hunt -** successfully applied to X-ray

- **Maximum KE gained by electron in passing from cathode to the target is eV**

  V:     accelerating voltage

  e:     charge on electron

# Explanation of sharp wavelength limit:

- **Maximum KE gained by electron in passing from cathode to the target is e V**
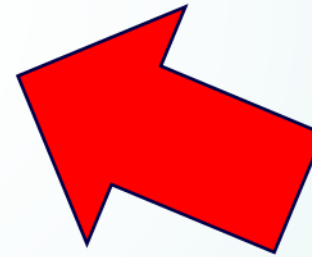
- **This energy is converted into photon**

- $$K_{max} = eV = h\,\nu_{max} = \frac{h\,c}{\lambda_{min}}$$

- **This relation is known as Duane-Hunt Law.**

**Duane-Hunt Law**

$$K_{max} = e\textbf{V} = h\,\nu_{max} = \frac{h\,c}{\lambda_{min}}$$

*The short wavelength limit is inversely proportional to potential applied across the tube terminals.*

# Inverse photoelectric effect:

➡ **Inverse photoelectric effect**

⬇

➡ **KE of an electron converted into radiant energy**

➡ **Photoelectric Effect**

⬇

➡ **Radiant energy partially converted into KE of electron.**

# **Explanation of continuous form of X-ray:**

▶ Second method to explain the continuous form of X-ray spectrum using **quantum mechanics.**

▶ The spectrum is emitted as a result of the deflection of cathode ray electrons by the strong field surrounding the nuclei of atoms of the target.

# *Bremsstrahlung radiation:*

• *X-ray produced by electrons during their deceleration.*

When electrons (charged particles) are suddenly decelerated (as in the tube), they produce X-Rays.

• The produced rays are called ***bremsstrahlung radiation*** (from German **braking radiation**).

**The bremsstrahlung process do not depend on the target material. It depends only on the accelerating voltage.**

# Characteristic Emission Spectrum

# Characteristic Emission Spectrum:

- It is called characteristic because it is **characteristic of the target element** in the energy of the photon produced.

KE of cathode electron must be sufficiently high to excite the target for particular radiations.

| Tube voltage | Series |
|---|---|
| **2500** volt | **M series** |
| **12000** volt | **L series** |
| **70000** volt | **K series** |

# Characteristic Emission Spectrum:

- Projectile electron with high enough energy to totally remove an inner-shell electron of the tungsten target.

- Characteristic x-rays are produced when outer-shell electron fills an inner-shell void.

- All tube interactions result in a loss of kinetic energy from the projectile electron.

# **Moseley Law:**

- Each group contains several lines of definite wavelengths.

- **Striking feature of the spectrum is its Regularity**

- **Moseley** found that the $K_\alpha$ frequency line in the x-ray spectra from a particular target element is **varied smoothly** with that element's atomic number $Z$.

# Moseley Law:

- **Moseley** found that the $K_\alpha$ frequency line in the x-ray spectra from a particular target element is **varied smoothly** with that element's atomic number

**Moseley Law:**

**"As one goes from lighter to heavier elements, the frequency of the corresponding lines increases in a regular fashion."**

# Moseley Law: Proof

- **The relationship between frequency of spectral line and atomic number of the spectral emitting element**

- **For any line in K series**  $$\upsilon_k = a\,(Z - b)^2$$

  - **Z-b  is effective atomic number**
  - **a  is a general constants**
  - **b  is characteristic constants of a  particular  series and is called screening constants**

# Moseley Law: Proof

- According to Bohr Theory the energy of an electron moving in an orbit with principal quantum number $n_1$ is given by

$$E_1 = -\frac{2\pi^2 m e^4 Z^2}{n_1^2 h^2} \frac{1}{(4\pi\varepsilon_0)^2}$$

- The energy of an electron moving in an orbit with principal quantum number $n_2$ is given by

$$E_2 = -\frac{2\pi^2 m e^4 Z^2}{n_2^2 h^2} \frac{1}{(4\pi\varepsilon_0)^2}$$

# Moseley Law: Proof

**Considering the effect of electrons which screen the positive charge of the nucleus, reducing thereby the value of Z to Z-b**

$$E_1 = -\frac{2\pi^2 m e^4 (Z - b_1)^2}{n_1^2 h^2} \frac{1}{(4\pi\varepsilon_0)^2}$$

$$E_2 = -\frac{2\pi^2 m e^4 (Z - b_2)^2}{n_2^2 h^2} \frac{1}{(4\pi\varepsilon_0)^2}$$

# Moseley Law: Proof

$$E_1 = -\frac{2\pi^2 m e^4 (Z-b_1)^2}{n_1^2 h^2} \frac{1}{(4\pi\varepsilon_0)^2}$$

$$E_2 = -\frac{2\pi^2 m e^4 (Z-b_2)^2}{n_2^2 h^2} \frac{1}{(4\pi\varepsilon_0)^2}$$

$$E_1 - E_2 = \frac{2\pi^2 m e^4 (Z-b_2)^2}{h^2 (4\pi\varepsilon_0)^2}$$

$$\left[ \frac{1}{n_2^2} - \frac{1}{n_1^2} \frac{(Z-b_1)^2}{(Z-b_2)^2} \right]$$

# Moseley Law: Proof

$$E_1 - E_2 = \frac{2\pi^2 \, m \, e^4 \, (Z - b_2)^2}{h^2 \, (4\pi\varepsilon_0)^2}$$

$$\left[ \frac{1}{n_2{}^2} - \frac{1}{n_1{}^2} \frac{(Z - b_1)^2}{(Z - b_2)^2} \right]$$

**If Z is high enough, then $b_1 \approx b_2 \approx b$**

$$E_1 - E_2 = \frac{2\pi^2 \, m \, e^4 \, (Z - b)^2}{h^2 \, (4\pi\varepsilon_0)^2} \left[ \frac{1}{n_2{}^2} - \frac{1}{n_1{}^2} \right]$$

# Moseley Law: Proof

$$E_1 - E_2 = \frac{2\pi^2 m e^4 (Z-b)^2}{h^2 (4\pi\varepsilon_0)^2} \left[ \frac{1}{n_2^{\,2}} - \frac{1}{n_1^{\,2}} \right]$$

But

$$E_1 - E_2 = h\,\nu_K$$

$$h\,\nu_K = \frac{2\pi^2 m e^4 (Z-b)^2}{h^2 (4\pi\varepsilon_0)^2} \left[ \frac{1}{n_2^{\,2}} - \frac{1}{n_1^{\,2}} \right]$$

$$\nu_K = \frac{2\pi^2 m e^4 (Z-b)^2}{h^3 (4\pi\varepsilon_0)^2} \left[ \frac{1}{n_2^{\,2}} - \frac{1}{n_1^{\,2}} \right]$$

# Moseley Law: Proof

$$\nu_K = \frac{2\pi^2\, m\, e^4\, (Z-b)^2}{h^3\, (4\,\pi\,\varepsilon_0)^2} \left[ \frac{1}{n_2{}^2} - \frac{1}{n_1{}^2} \right]$$

$$For\ K_\alpha\ line\ n_1 = 2\quad and\quad n_2 = 1$$

$$\nu_{K_\alpha} = \frac{2\pi^2\, m\, e^4\, (Z-b)^2}{h^2\, (4\,\pi\,\varepsilon_0)^2} \left[ \frac{1}{1^2} - \frac{1}{2^2} \right]$$

# Moseley Law: Proof

**Higher is the principal quantum number, higher is the screening constant**

**Or**

$$\upsilon_k \ \alpha \ \ (Z-b)^2$$

**This is Moseley Law**

# Moseley Law:

$$\upsilon_k \,\, \alpha \,\, (Z-b)^2$$

**For K$\alpha$ line**   $a = \dfrac{3\,R\,c}{4}$ and $b = 1$

**For L$_{\beta 1}$ line**   $a = \dfrac{5\,R\,c}{36}$ and $b = 7.4$

X-ray spectrographs of all available elements show that Moseley law holds good throughout the periodic table.

# Applications of Moseley Law

1. **Moseley's researches showed that the <span style="color:red">determining factor of the position of the element in the periodic table should *be* the atomic number and not the atomic weight.</span>**

   **Thus the law remove the discrepancy in the arrangement of the different elements in the periodic table.**

   Previously, for example,

   $_{18}A^{40}$ was placed later than $_{19}K^{39}$

   But according to this law the current arrangement must be as

   $_{18}A^{40}$ before $_{19}K^{39}$ and

   This sort of corrected arrangement finds its support also from the isotopic constitution of the elements.

# Applications of Moseley Law

- **With the help of the Moseley's law, by observing the X-ray spectra of <span style="color:red">rare earths</span> their atomic numbers were also determined.**
- The X-ray spectrum analysis and successive application of Moseley's. law also perfected the periodic table with the discovery of some new elements as **hafnium** (57), **promethium** (61), **rhenium** (75) and **technetium** (43) etc.
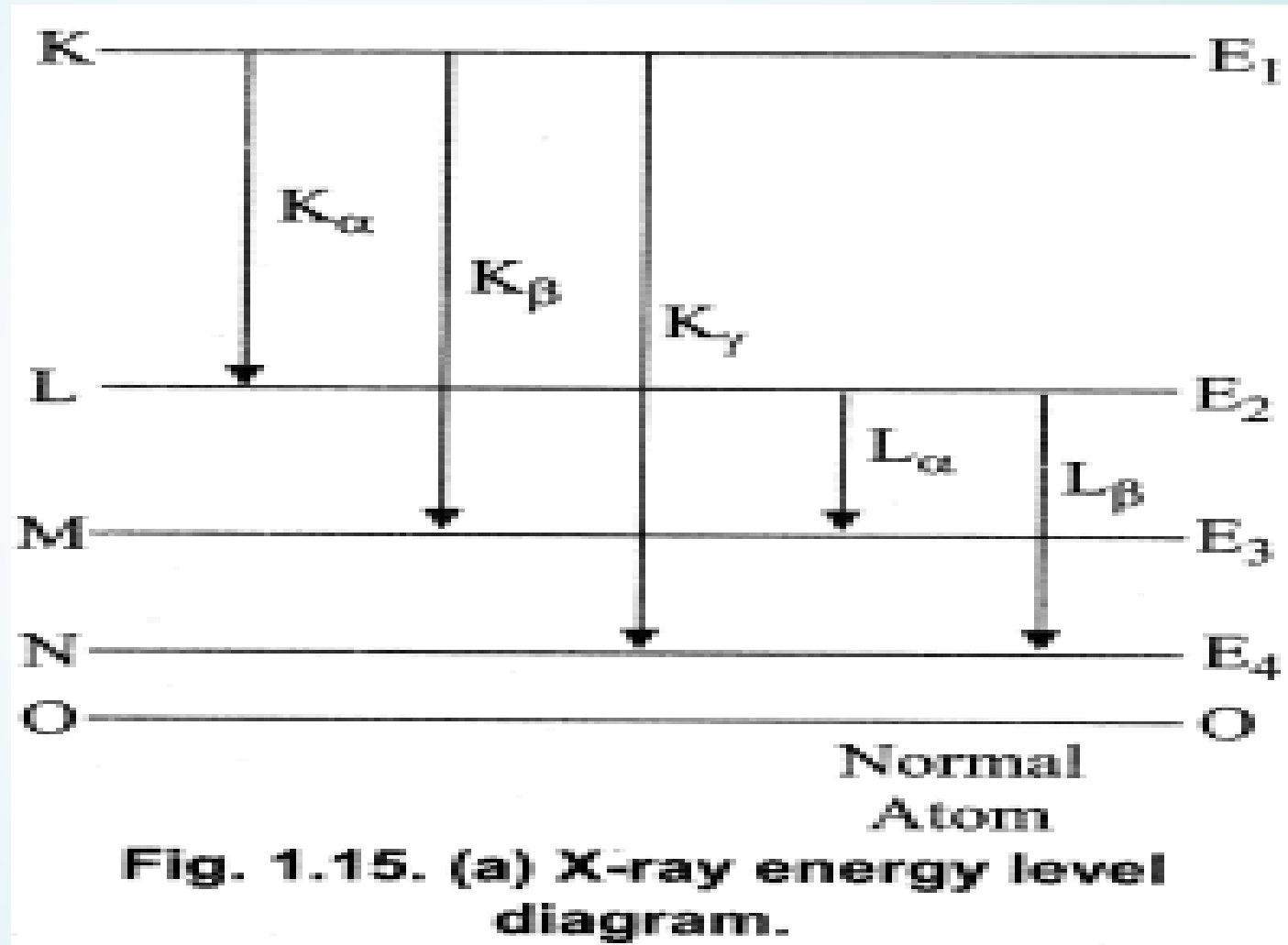
# A close Survey of Emission Spectrum:

# A close Survey of Emission Spectrum:

In the emission spectrum of an element in general, there are **Four series K, L, M, and N in the wavelength region above 0.1 A$^0$**

In heavier atoms, other series like **O and P** exist theoretically but these series lie **in the UV wavelength region.**

# A close Survey of Emission Spectrum:

All the groups and lines are shown in Fig. in an energy level diagram.



Fig. 1.15. (a) X-ray energy level diagram.

# A close Survey of Emission Spectrum:

## General Characteristics

**Each group has got the same general features with the difference that** *as we move towards higher elements, the groups are displaced towards shorter wavelength side.*

# A close Survey of Emission Spectrum:

There are **Two** absorption discontinuities in the case of **K** series.

The K series consists of two lines $\beta$ and $\alpha$,

But these lines are resolved into four lines $\gamma, \beta, \alpha_1$ and $\alpha_2$.

The lines $\gamma$ and $\beta$ further resolved into **two** lines.

# **A close Survey of Emission Spectrum:**

## *K* series <u>12 or more lines</u>

It is noted that for the lightest elements as many as <u>12 or more lines</u> may appear in the *K* series instead of the usual **four** or **five**.

**Wentzel** claimed that these lines are due to **multiple ionization of atoms.**

# A close Survey of Emission Spectrum:

Further, the experimental results also showed that *the wavelength of K$\gamma$ emission line is only a fraction of a per cent longer than that of the K absorption limit.*

This observation helps in identifying whether there are additional lines between K$\gamma$ and the limit.

# A close Survey of Emission Spectrum:

*L* series <u>20 or more lines</u>

The *L* group contains **three** overlapping series designated as $L_I$, $L_{II}$ and $L_{III}$.

The three series of the group, in turn, contain many lines. More than **20** lines have been identified for **Uranium** in $\alpha$, $\beta$ and $\gamma$ groups.

# A close Survey of Emission Spectrum:

- ***M* series <u>Many lines</u>**

- **The *M* group contains five series designated as $M_I$, $M_{II}$, $M_{III}$, $M_{IV}$ and $M_V$ and these series in turn contains many lines.**

- **Similarly, *N* group contains 7 series designated as $N_I$ ... $N_{VII}$, each series containing in turn a number of lines.**

- **Thus, we observe that the higher groups show some complexity.**

# Characteristic Absorption Spectrum

# Characteristic Absorption Spectrum:

- To study the X-ray absorption spectrum of an **element** the continuous spectrum of X-ray is used.

- It is then allowed to fall upon suitable absorber and then results are analyzed.

- *When a beam of X-rays is passed through a thin layer of matter, its intensity or power is generally diminished as a consequence of absorption and scattering.*

# Characteristic Absorption Spectrum:



X-ray absorption spectra for lead and silver.
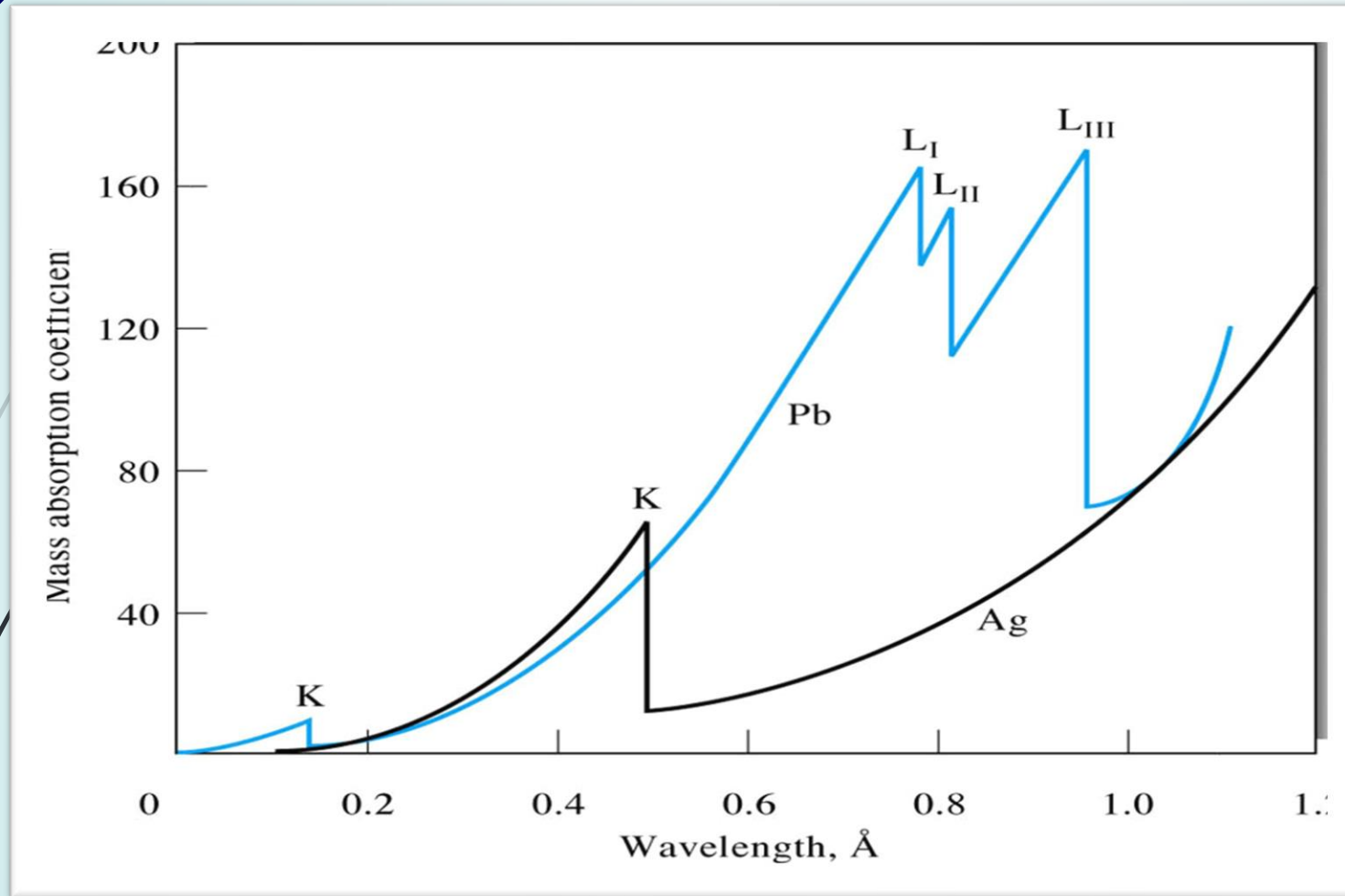
The results of a typical experiment using thin foil of **lead** and **Ag** as absorbing materials are shown in Fig.
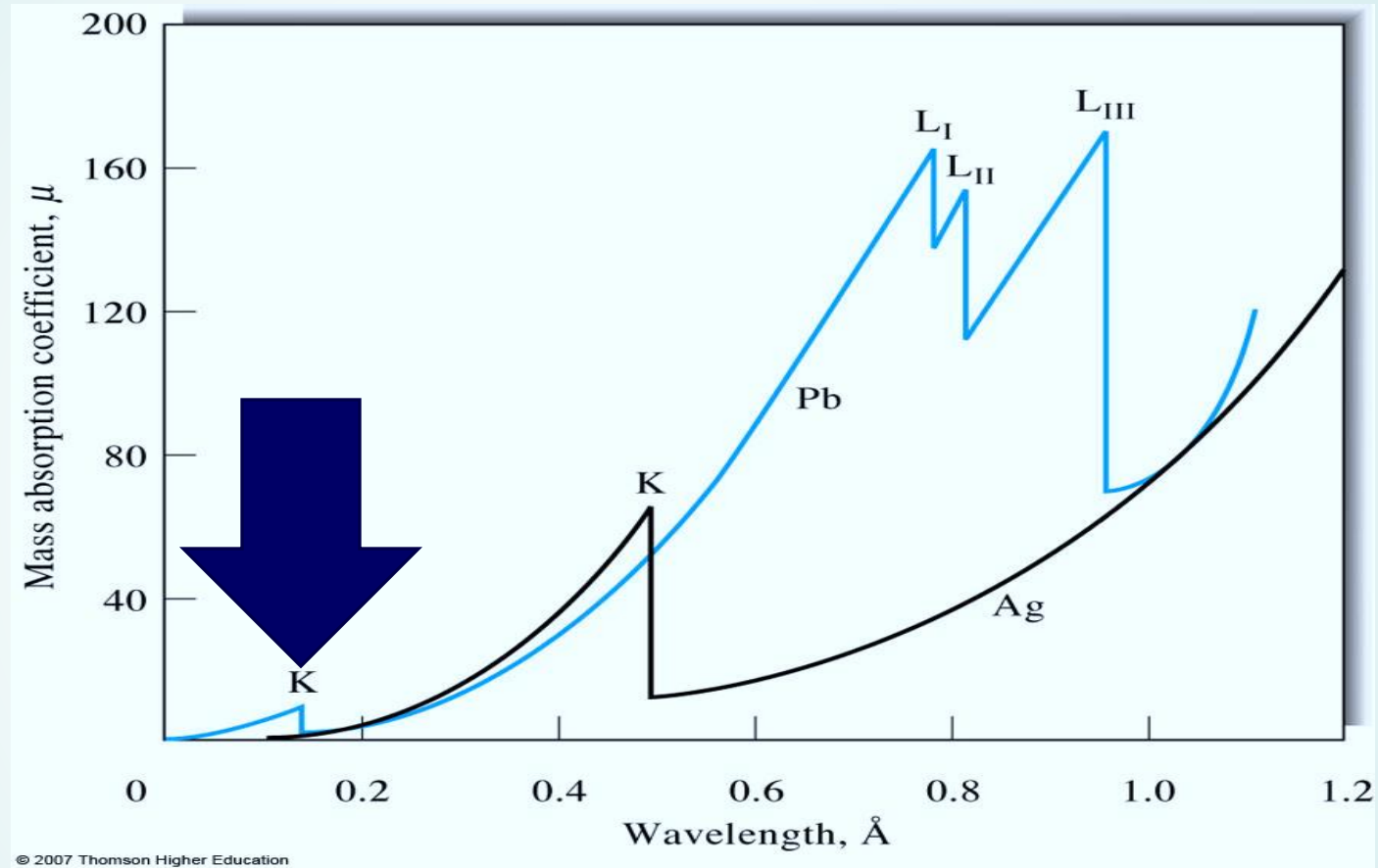
# Characteristic Absorption Spectrum:

- **Explanation for the characteristic spectrum**

- $\mu$ - *Absorption coefficient*

- $\mu/\rho$ *is a ratio of absorption coefficient of the material and its density.*

# Characteristic Absorption Spectrum:

Mass Absorption coefficient µ/$\rho$ is

1.  It is **characteristic of the  Element**.

2.  It represents the **fraction of energy removed from a beam of X-radiations of <u>unit cross-section</u> by <u>one gram</u> of substance.**

3.  It **increases with** $\lambda^3$.

# **Characteristic Absorption Spectrum:**



When the position K with wavelength $\lambda_K$ is reached, the mass absorption coefficient drops suddenly. **[k-absorption limit]**

# **Characteristic Absorption Spectrum:**
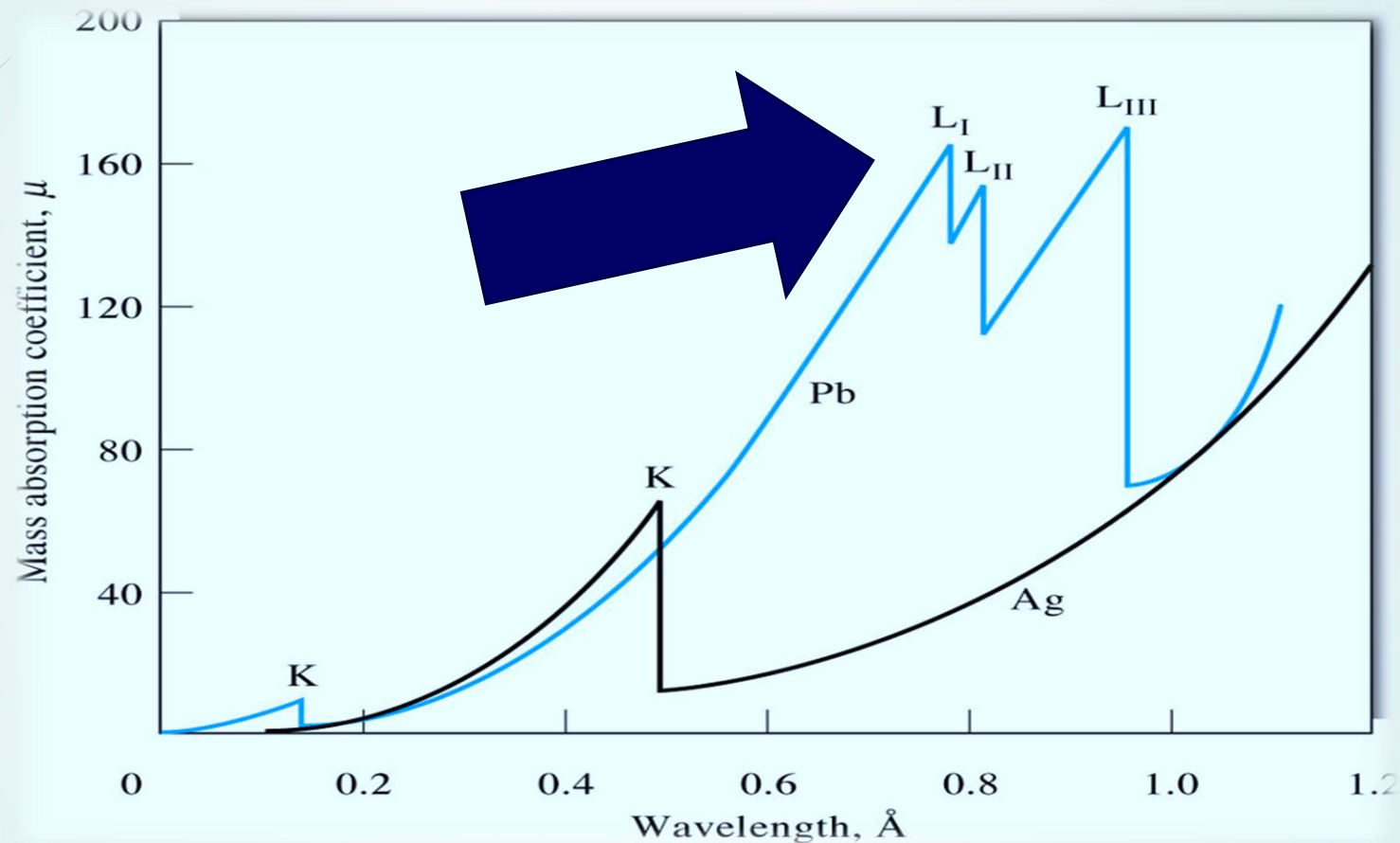


The value of $\mu/\rho$ again increases giving rise to three absorption limits known as $L_I$ , $L_{II}$ and $L_{III}$   **$L_I$ $L_{II}$ and $L_{III}$ absorption limit**

# Characteristic Absorption Spectrum:

There are *FIVE* absorption discontinuities in the case of *M* series

There are *SEVEN* absorption discontinuities in the case of *N* series

There are *NINE* absorption discontinuities in the case of *O* series

*The wavelengths of absorption discontinuities are characteristics of the chemical element.*

# **Characteristic Absorption Spectrum:**

- The rays with the **wavelength shorter** than that of a given discontinuity are **absorbed** by the element to a markedly greater extent than rays with the wavelength larger than this critical value.
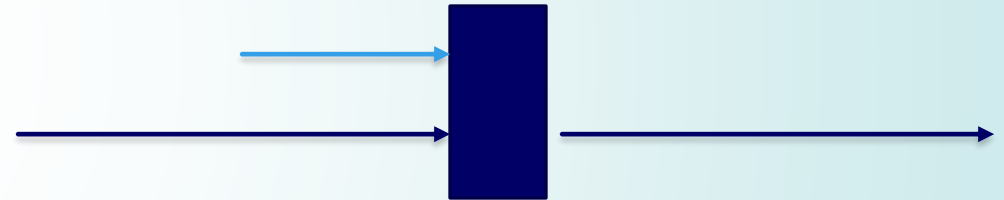
- In other words, *an absorbing material is relatively opaque to X-rays of wavelengths upto a characteristic value and is transparent to larger rays.*
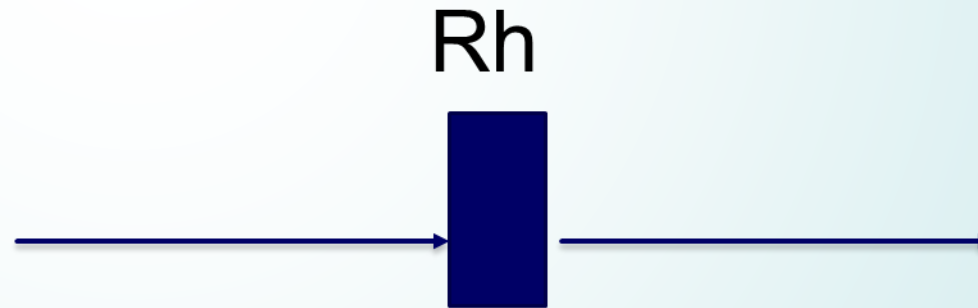
# Characteristic Absorption Spectrum:

- Another aspect of X-ray absorption is the fact that **X-radiations are not selectively absorbed**, i.e., the element does not absorb its characteristic X-ray lines.

# Characteristic Absorption Spectrum:

- As an example, we take the case of $K_\alpha$, line of Rh which has the wavelength $\lambda = 0.613\ A^0$.

- When Rh is placed in the path of these monochromatic radiations, they are not absorbed.

Rh

$\lambda_{K_\alpha} = 0.613\ A^0$

# Characteristic Absorption Spectrum:

- *The absorption coefficient for Rh in this region is a monoatomic function of wavelength with no usual features.*

- The above mentioned fact is in contrast to behaviour of sodium vapour which is opaque for D-lines.
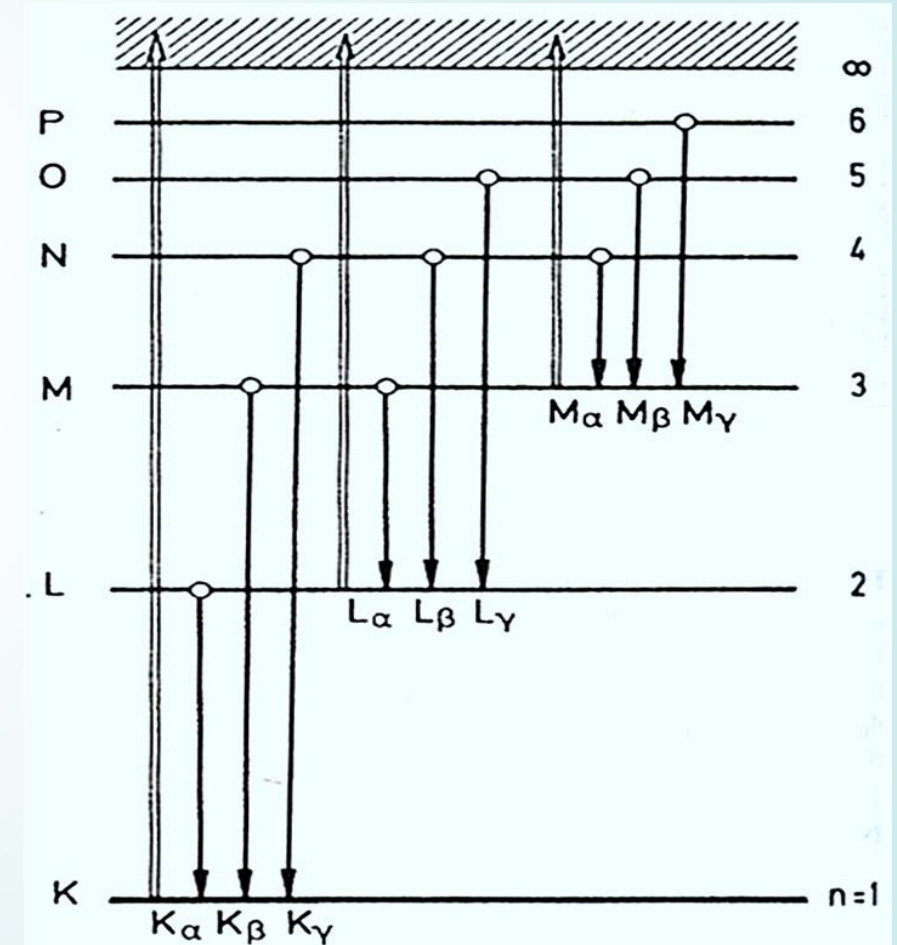
# Explanation of Emission and Absorption Spectra

# Explanation of Emission and Absorption Spectra:

- The general features of X-ray spectra may be explained on the basis of the work put forward by

- Moseley and enlarged by Kossel.

- Their work finds support from Bohr theory.

- The existence of individual, widely separated spectral series leads to the fundamental conception that

- *a number of electron groups are present in the atom which differ from each other in respect of the energy and distance between electrons and nucleus.*

# Explanation of Emission and Absorption Spectra:

- The aggregate of electrons with quantum number

- n = 1 forms K level,
- n = 2 form L level,
- n = 3, M level and so on.

# Explanation of Emission and Absorption Spectra:

- As in the case of optical spectra, the X-ray emission spectrum may be thought as due to the transition of electrons from an upper level to a lower energy level.

- Now since X-rays have much higher energies than optical rays, it means in this case large change of energy takes place.

# Explanation of Emission and Absorption Spectra:

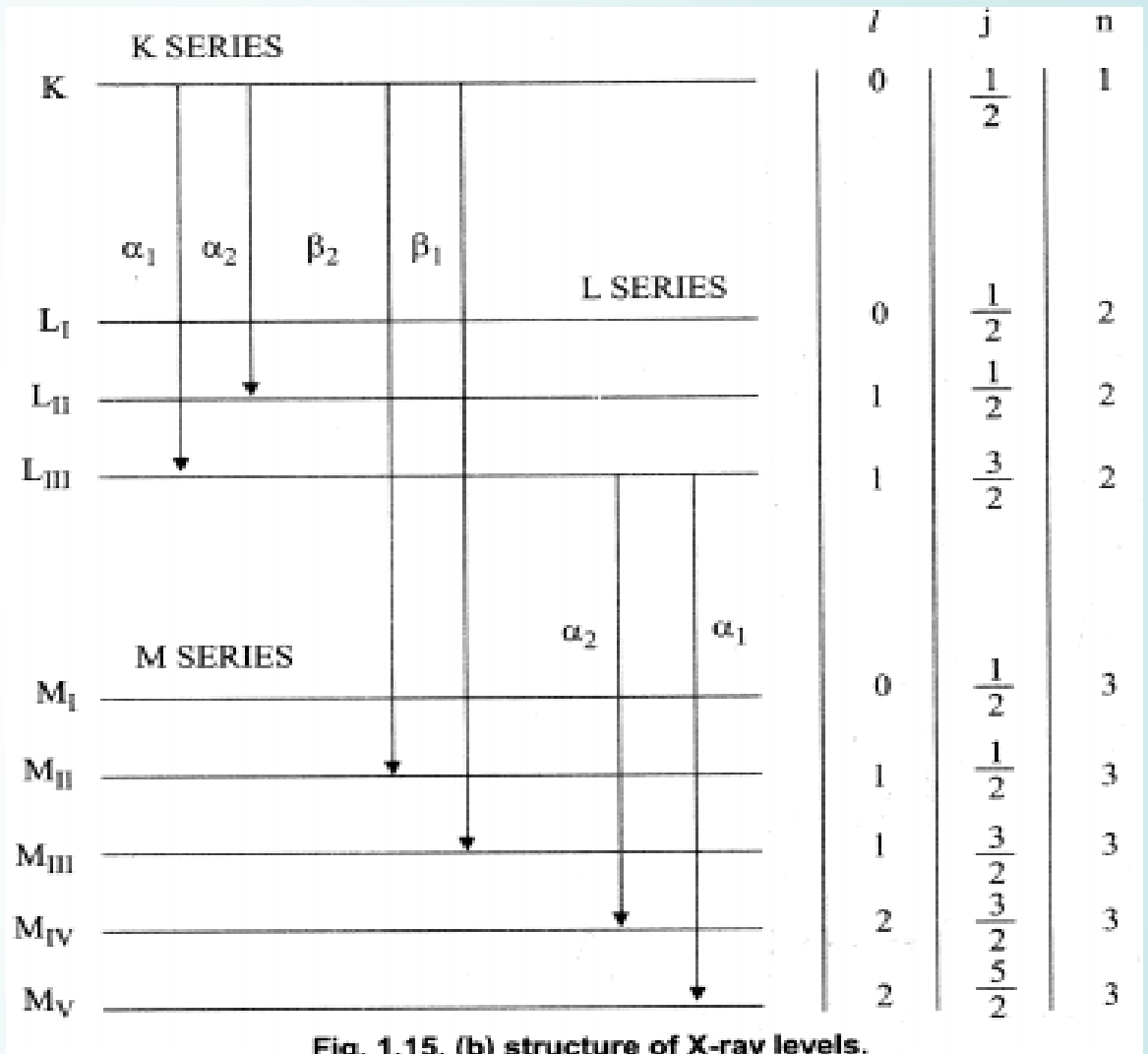- *Therefore, X-ray spectra are attributed <span style="color:red">to the transitions of inner electrons of an atom</span> since these electrons are bound to the nucleus with much larger energies than the surface electrons to which optical spectra are attributed.*
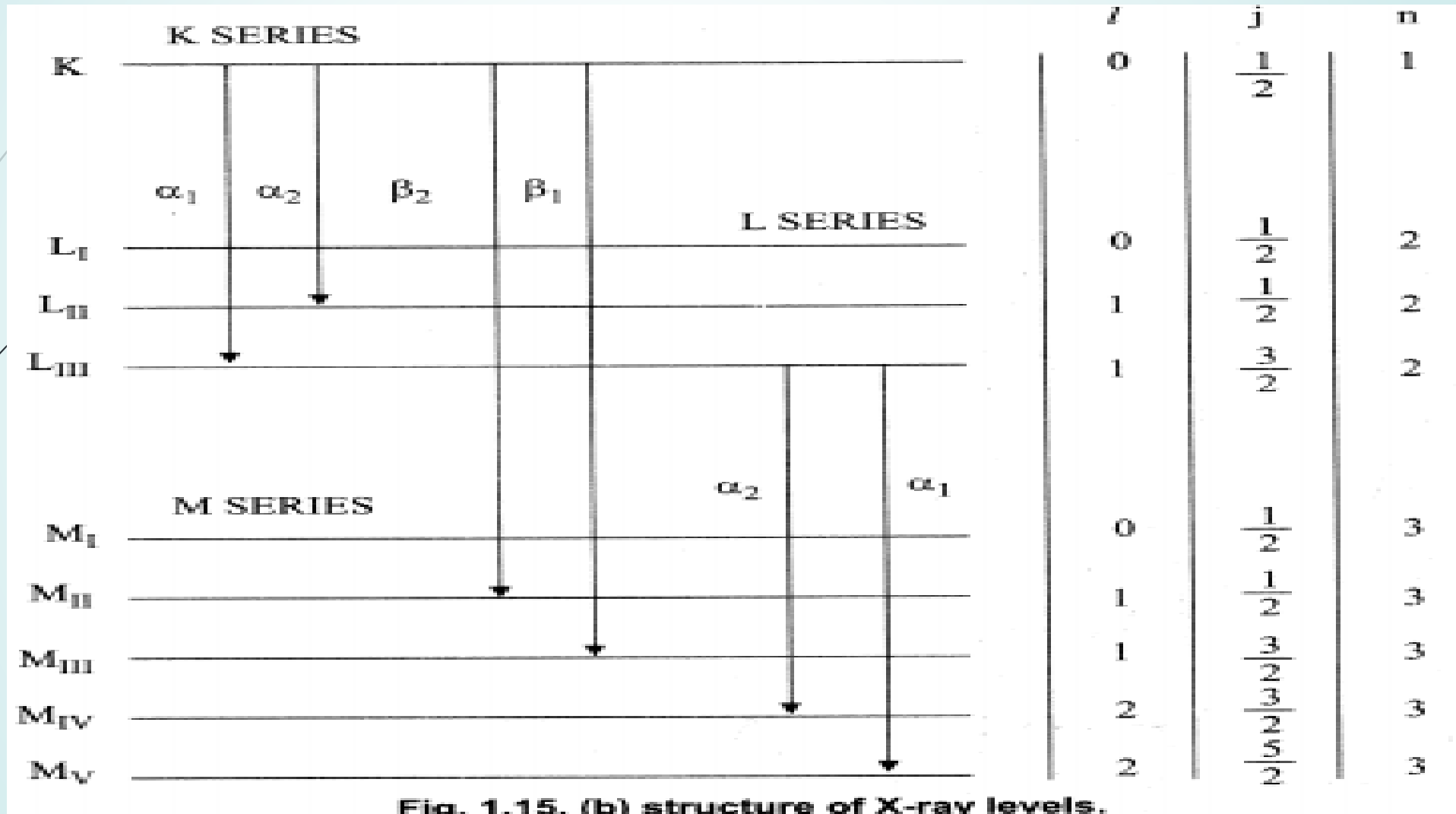
# Explanation of Emission and Absorption Spectra:

- As the *K* series contains lines of *higher frequencies*, this is associated with the innermost electrons.

- Thus *K* series arises from the transition of an electron from outer levels (say *L, M, N etc.* ) to K level.

- *L series arises from* the transition of an electron from higher levels (say *M, N, Q* etc.) to *L* level and so on.

- Similar explanation holds good for other series.

- Now different lines of a series arise due to the transition of electrons from different levels to a single level.

# Explanation of Emission and Absorption Spectra:

- **fine structure of spectral lines**

- **As there is energy difference between different sublevels of a level, therefore we get fine structure of spectral lines.** For example, $\alpha_1$, $\alpha_2$, $\beta_1$, $\beta_2$ etc. (see Fig. ).



Fig. 1.15. (b) structure of X-ray levels.

# Explanation of Emission and Absorption Spectra :



Fig. 1.15. (b) structure of X-ray levels.

# Fine structure of the x-ray spectra:

- *The x-ray transitions indicated by Greek letters, $K_\alpha$, $K_\beta$, $L_\alpha$, $L_\beta$, start from terms with different principal quantum numbers n.*

- *The fine structure of the x-ray spectra is the occurrence of several components in a given transition, because of the splitting of the energy terms resulting from the **spin-orbit coupling of the electrons in inner shells.***

- *Similarly to the spectra of alkali atoms, the x-ray spectra can be understood as one-electron (or one-hole) spectra. A missing electron (or a hole) in a full shell is equivalent to a single electron in an empty shell.*

# Explanation of Emission and Absorption Spectra:

- In the above discussion, we have spoken of the transfer of electrons (one or two) from higher levels to K level.

- But K shell is already full; how can such an addition take place?

- The answer is that first a vacancy is created in K shell by the removal of one of the K electrons.

# Explanation of Emission and Absorption Spectra:

- Furthermore, ejecting electrons from the K shell cannot stop in L shell, if L shell is already full.

- Thus to create a vacancy in K shell, it is essential that the energy of cathode electrons impinging on the element must have sufficient energy to raise the ejected K electron's energy; above that corresponding to outermost completed shell, either deposit it in an incomplete shell or remove it to infinity.

# Explanation of Emission and Absorption Spectra:

- Now suppose a vacancy exists in K shell; the transference of L electron gives rise to K$\alpha$ radiation.
- This creates a vacancy in L shell and consequently the transference of an electron to the vacancy in L shell gives rise to L series.
- Thus, singly ionized atoms give rise to different series of X-ray spectrum. For fine structure the same arguments hold good as we have given for K series.

# **Explanation of Emission and Absorption Spectra:**

- X-ray spectra are **independent of chemical combination** and **do not exhibit periodicity** as in the case of optical spectra.

# Explanation of Emission and Absorption Spectra:

- As we have said, X-ray spectra appear due to the changes in inner levels of the atom and the electrons in these levels show <span style="color:red">a greater order</span> and <span style="color:red">regularity,</span> and the arrangement does not vary in a haphazard or even a periodic manner from element to element.

## Explanation of Emission and Absorption Spectra:

- The arrangement remains the same; the only varying factor is the pull of the nucleus which increases as the atomic number of the element increases.

- The X-ray spectra do not show the dependence over chemical combination and periodicity, because these are concerned with outer electrons.

## Explanation of Emission and Absorption Spectra:

- Let us now switch over to the case of **absorption** which is not the exact reversal of emission and **does not show selective absorption of radiations.**

- Taking the case of K$\alpha$ radiation, if this radiation is to be absorbed, there must be a vacancy in L shell which is usually not present in the elements of atomic number greater than 10.

## Explanation of Emission and Absorption Spectra:

- Hence the energy of the radiation (if it is sufficient) can only eject the electron out of the atom or can put it in an incomplete shell, ruling out thereby the probability of absorption of $K\alpha$ radiation. Hence absorption is not the exact reversal of emission.

## Explanation of Emission and Absorption Spectra:

- To explain the absorption discontinuities, we assume that $E_k = h\nu_k$ represents the energy required to remove an electron from K shell.

- Now if the frequency $\nu$ of the radiation is equal to or greater than $\nu_k$ it can eject the electron; the amount $h\nu_k$ is utilized in ejection and balance is imparted as kinetic energy to the electron.

# Explanation of Emission and Absorption Spectra:

- If the wavelength is progressively increased making $v$ less than $v_k$, the electron can not be ejected and it will show a sudden drop of absorption.

## Explanation of Emission and Absorption Spectra:

- Thus, first absorption discontinuity takes place towards the longer wavelength than $\lambda_k$.

- As the wavelength is further increased, similar discontinuities will occur every time the value of $\lambda$ just equals that required for the ejection of an electron from the three sub-groups of the L shell, 5 sub-groups of the M shell and so on.

## Explanation of Emission and Absorption Spectra:

- Further, that the energy required to remove a *K* electron from the atom is greater than the energy change involved in the production of emission lines of the *K* series, explains the fact that ***the critical absorption wavelengths are shorter than the wavelengths of emission lines***.

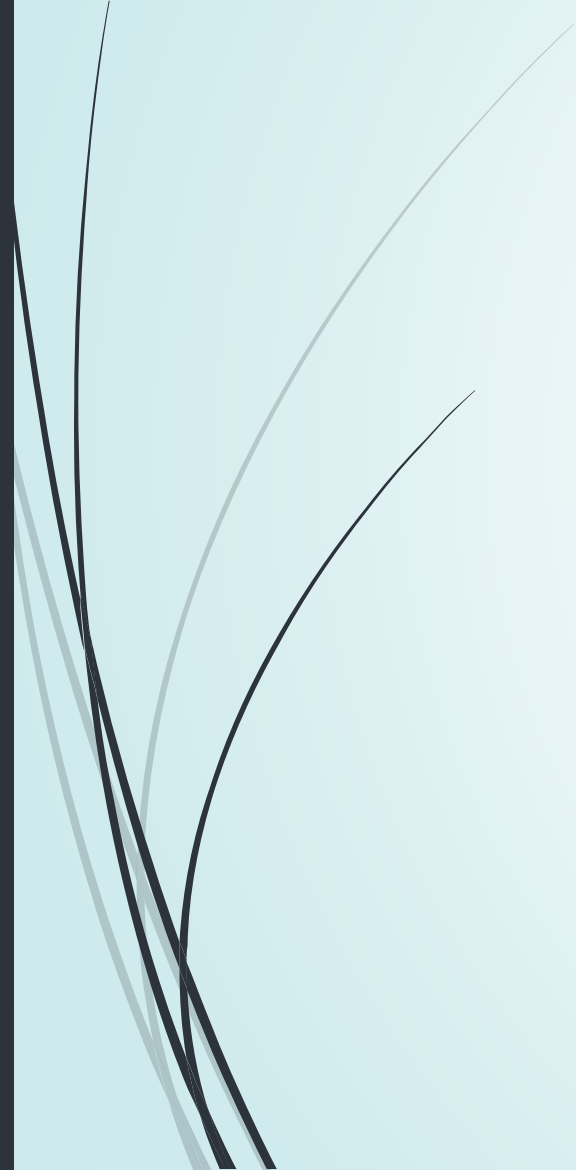# Explanation of Emission and Absorption Spectra:

- The ***appearance of fringes*** in the neighbourhood of discontinuities takes place when the electron is put in some incomplete shell making thereby some lines to appear.

- In some cases, these fringes appear due to the multiple ionization of atoms.

## Explanation of Emission and Absorption Spectra:

- As mentioned earlier - $K\alpha_1$ line arises from the transition of an electron from $L_{III}$ level to a vacancy in $K$ shell and $K\alpha_2$ arises due to the transition of an electron from $L_{II}$ level to a vacancy in $K$ shell.

- As there are four $L_{III}$ electrons and two $L_{II}$ electrons, the probability of first transition is twice that of second.

- Hence the ratio of intensities of $\alpha_1$ and $\alpha_2$ lines is 2:1 which is in close agreement with experimental facts.

## Explanation of Emission and Absorption Spectra:

- Similar probability rule holds good for other lines. Therefore, the intensity of the lines depends upon the probability of the transitions.

- Thus all the facts of X-ray spectra are explained.

Thanks…..