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

Course: US04CPHY21

Electromagnetic Theory and Spectroscopy

Part 3

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UNIT - IV X-ray and X-ray Spectra

Topics

- Comparison of Optical and X-ray Spectra,
- Energy levels,
- Moseley's Law,
- The Fluorescence yield and Auger Effect
- Satellites

UNIT - IV X-ray and X-ray Spectra

Reference Book:

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

Comparison between Optical and X-ray spectra

UNIT - IV X-ray and X-ray Spectra

Topics

- **Comparison between Optical and X-ray spectra**
- **ENERGY LEVELS**
- **SATELLITES**
- **THE FLUORESCENCE YIELD AND AUGER EFFECT**

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Comparison between Optical and X-ray spectra

- The *X-ray spectrum arises due to the transitions in the innermost part of the atom*, while *the optical spectrum arises due to the transition in the outermost part of the orbit*.
- Since the regions of transition in two cases are different, in X-ray emission spectrum, high frequency radiations are emitted and in the optical spectrum low frequency radiations are observed.
- The X-ray spectral lines occupy a narrow region of spectrum beyond the ultraviolet, while the optical spectrum covers a wide range.
- The spectral lines in the X-ray spectrum are classified into two groups, one of short wavelength region and the other of long wavelength region.

Comparison between Optical and X-ray spectra

- The X-ray spectrum consists of fewer lines than the optical spectrum, hence much simpler. The type of lines of a particular series is almost the same for all elements.
- The X-ray spectrum has been observed to be independent of the chemical combination and isotopic constitution of the element approximately.
- In X-ray absorption spectrum there is no selective absorption of spectral lines. In this, we have absorption bands with definite edges and critical absorption discontinuities. But in optical spectrum there is a selective absorption of lines.
- In the diagrammatical representation, the zero of the energy in the case of X-ray spectrum is taken as that of neutral atom, while in the case of optical spectrum the zero of the energy is taken as that of ionized atom.

1.16. ENERGY LEVELS

1.16. ENERGY LEVELS

- In X-ray spectra K, L, M, N etc. shells or levels correspond to the level for which principal quantum number n = 1, 2, 3, 4, respectively.
- The **zero of the energy levels** is taken that of the **normal state** of the neutral atom.
- But in the **optical spectra**, the **zero of the energy is taken that of the ionized atom.**

1.16. ENERGY LEVELS

- Let us now suppose that the neutral atom has been ionized by removing one of its strongly bound electrons in the *K* shell. The atom is now said to be in ***K* energy state**.

- If E_1 represents the amount of work done in removing one electron from *K* shell, then the energy of the atom is represented by the level above the zero-energy level at a height of E_1.

1.16. ENERGY LEVELS

- Similarly, E_2, E_3, E_4 are the amounts of work done in removing the electron from *L*, *M*, *N* ... shells, respectively; then the energy of the atom will be represented by the levels at the heights of E_2, E_3 E_4, respectively.

- Further, we suppose that the atom is in the *K* energy state, *i.e.*, one electron is missing from *K* shell.

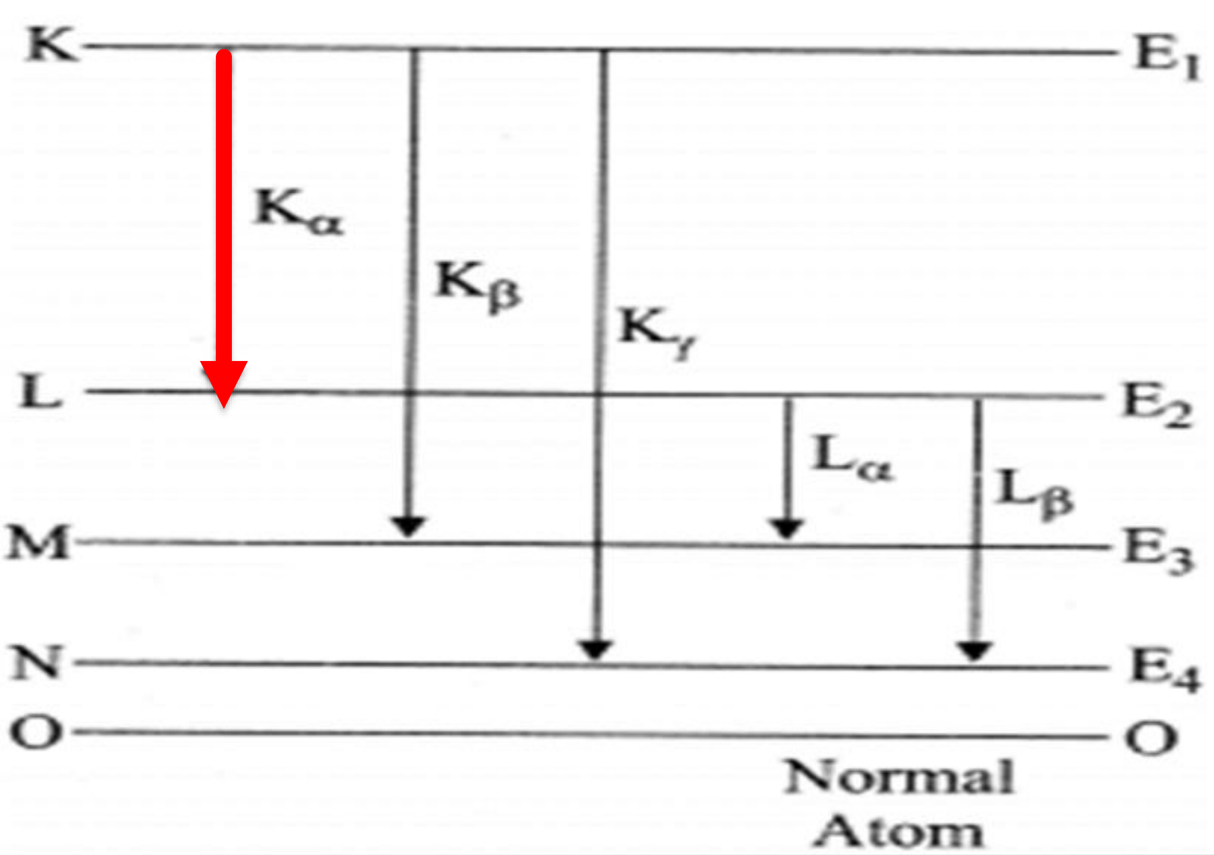
1.16. ENERGY LEVELS

- If an electron now goes from *L* shell to *K* shell, atom goes from K energy state to L energy state.

- The frequency of the radiation emitted is given by

- $\gamma_1 = \frac{E_1 - E_2}{h}$

and the corresponding line is called K_α line.



1.16. ENERGY LEVELS

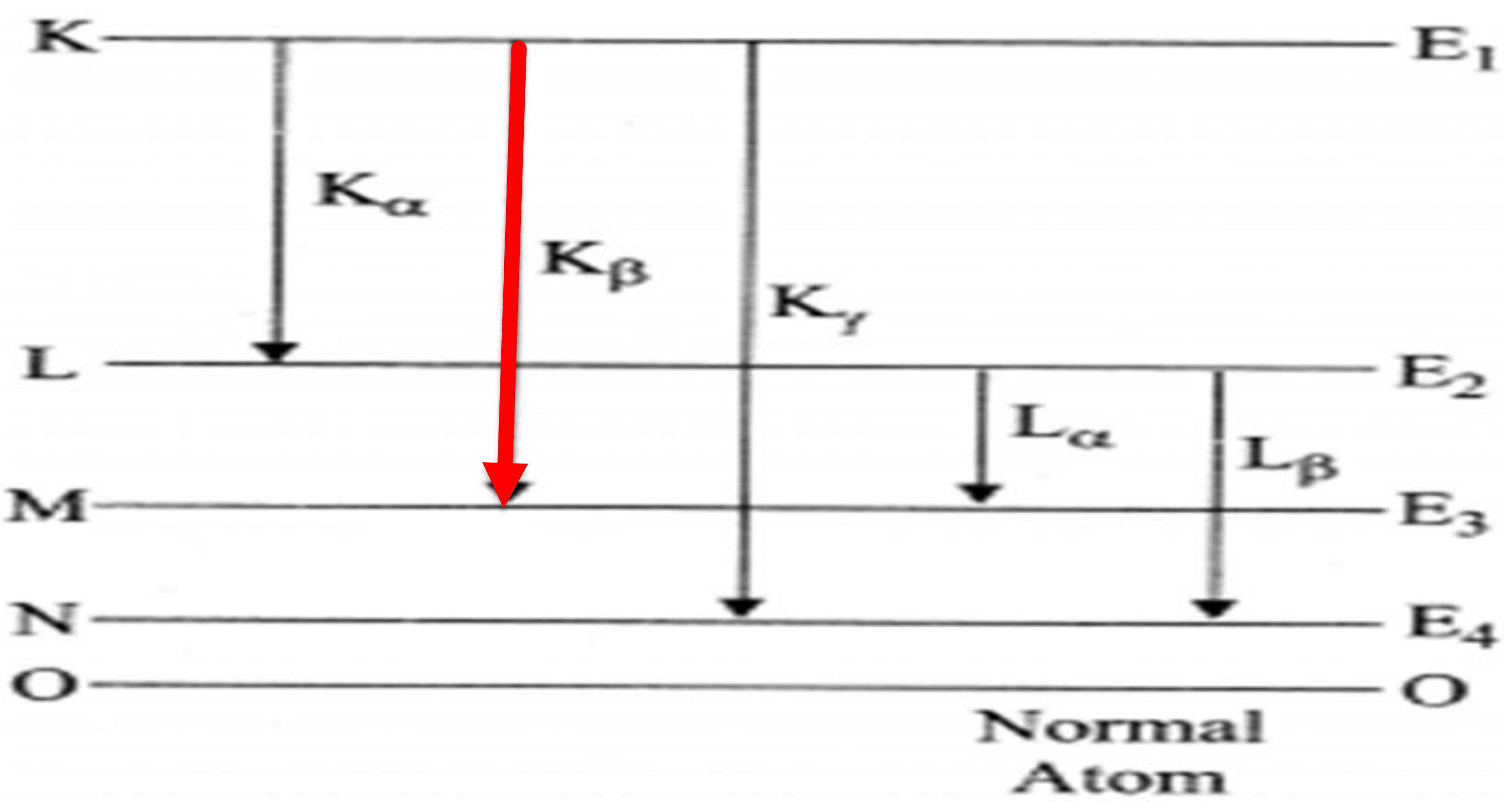


Fig. 1.15. (a) X-ray energy level diagram.

1.16. ENERGY LEVELS

- If the electron comes from *M* shell, then the line is called **K_β line** and the frequency of radiation is given by

$$\gamma_2 = \frac{E_1 - E_3}{h}$$

- In this way we have K_α, K_β, K_γ, K_δ lines i.e., ***K* series**.

- Fig. 1.15a depicts the transitions of the atomic states.

1.16. ENERGY LEVELS

- It should be noted here that the atom jumps from *K* energy state to *L* energy state and so on, while the **electron** goes in the opposite direction.

- The *K* series of spectral lines is formed when the electron directly goes to *K*-shell from *L*, *M*, *N*, ... shells.

1.16. ENERGY LEVELS

- *L* series is emitted by those atoms in which the electron directly goes to *L*-shell from *M*, *N*,... shells.

- Similarly, we have *M* series and *N* series.

1.16. ENERGY LEVELS

- The **intensity of a spectral line** is proportional to the number of atoms in which same transition takes place.

- The more probable transition is the jumping of an electron from *L* shell to *K* shell than jumping from *M* shell or *N* shell to *K* shell.

- Hence $K\alpha$ is most strong and K_δ is faint.

1.16. ENERGY LEVELS

- Further, due to the spin of the electron, *K, L, M* states are not really single but they split up into a number of levels as in the case of optical spectra,
- for example
- *L* level into **3** levels,
- *M* level into 5 levels and so on.

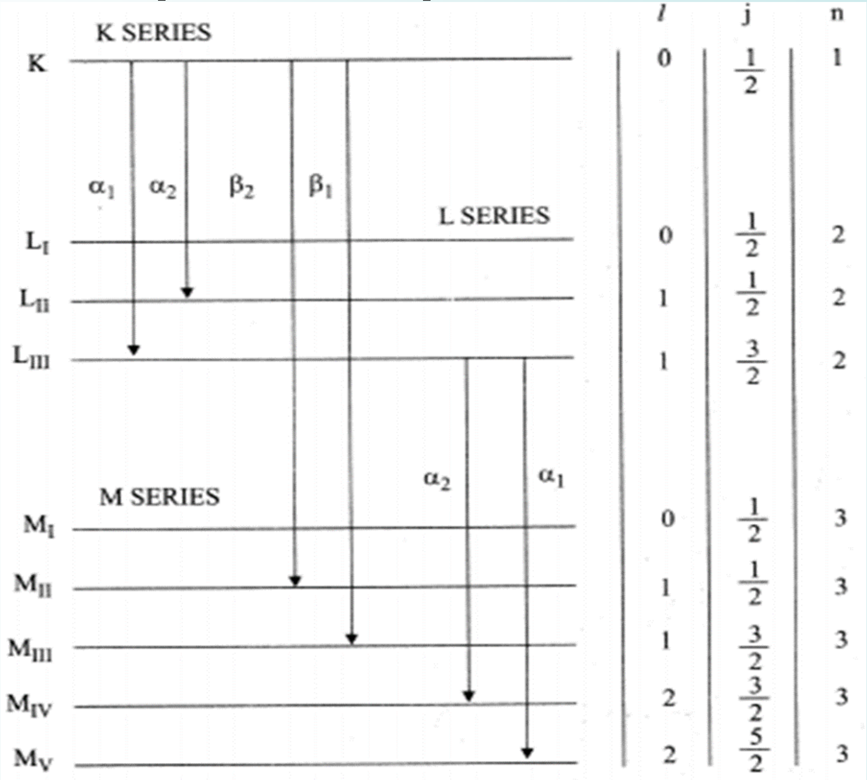
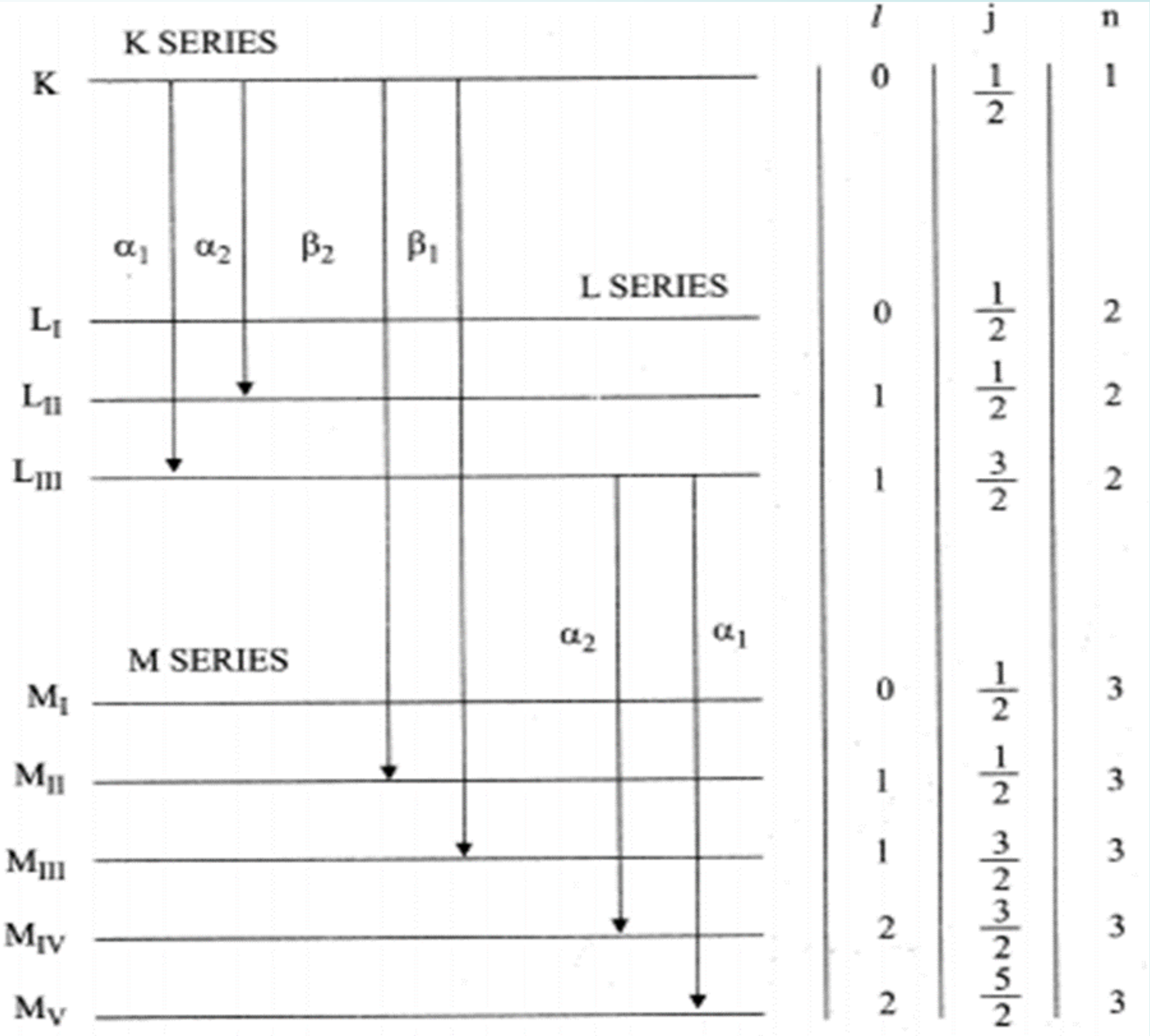


Fig. 1.15. (b) structure of X-ray levels.

1.16. ENERGY LEVELS

- So, the lines, which are emitted due to the transitions between different terms of *L* state and a single term of *K* state, are called $K_{\alpha 1}$, $K_{\alpha 2}$ etc..; if from the different terms of *M* state to *K* state, then corresponding lines are called $K_{\beta 1}$, $K_{\beta 2}$ and so on.



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1.16. ENERGY LEVELS

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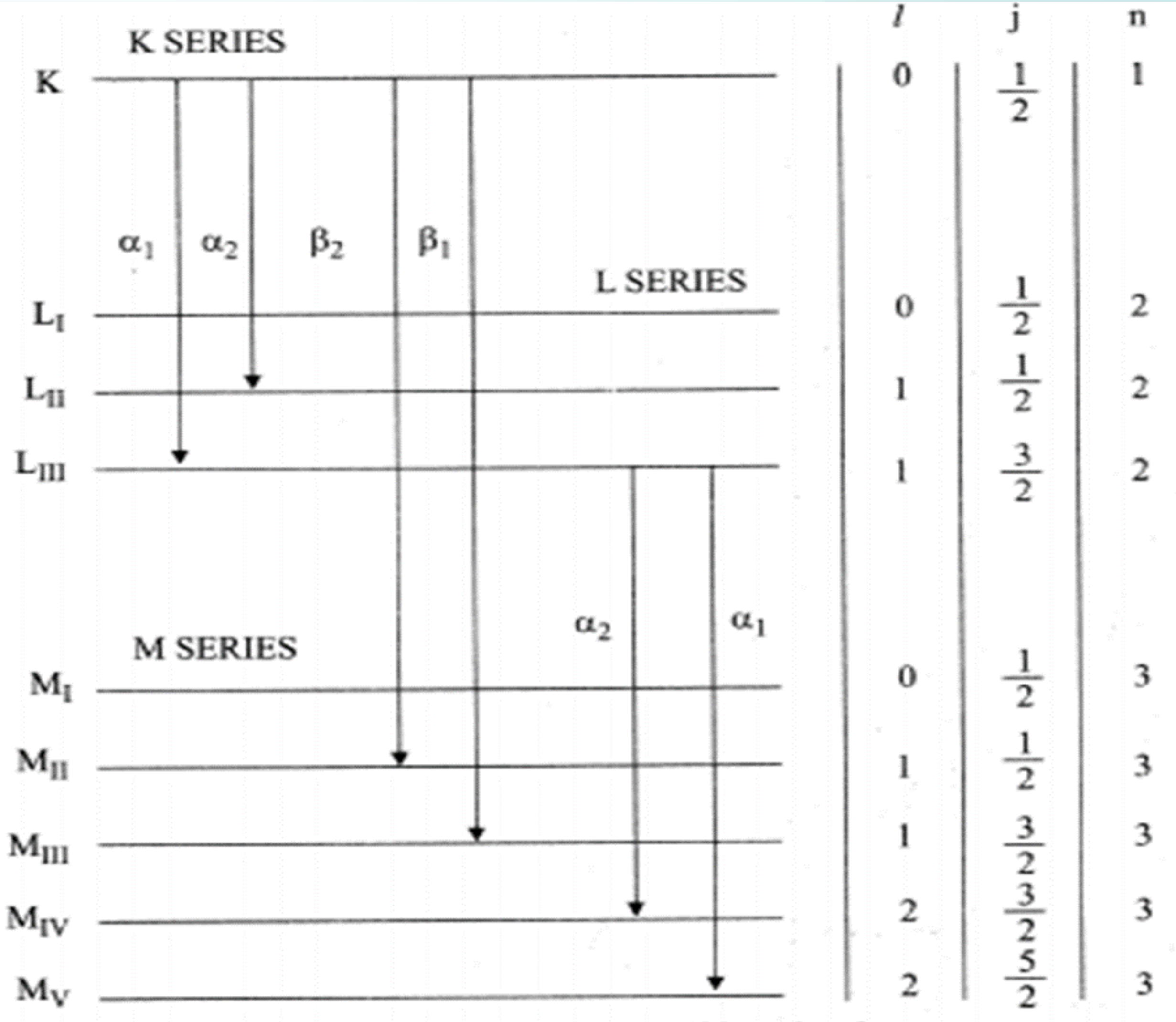


Fig. 1.15. (b) structure of X-ray levels.

1.16. ENERGY LEVELS

- Again, the transitions between different levels are governed by the **selection rules**

$$\Delta l = \pm 1 \text{ and } \Delta j = 0, \pm 1$$

- The transitions with *$\Delta n = 0$* are rarely observed in X-ray spectra, while such transitions are common in optical spectra.

1.22. SATELLITES

1.22. SATELLITES

- **What is satellites?**
- **Moseley** and his contemporaries observed the X-ray spectral lines which were intense and **easily resolvable.**

- These lines, as we know, are due to transitions between states of ***single ionization*** and can be easily fitted on an energy level diagram, and, therefore, are known as ***first order lines*** or ***diagram lines***.

1.22. SATELLITES

- **What is satellites?**

- Later on, with the improved resolving power of the instruments many more lines were discovered which could not be fitted into energy level diagram.

- Hence the new lines are known as ***second order lines*** or ***nondiagram lines*** or ***satellites***.

1.22. SATELLITES

- General Observations:
- The majority of such lines are faint.
- These lines are found close to and on the short wavelength side of more intense diagram lines.
- It is observed that most of the first order lines are accompanied by satellite lines, the number of which far exceeds the main lines.

1.22. SATELLITES

- On account of low intensity of such lines their characteristics are **difficult to be analyzed**.

- The careful investigations have brought the following points to light:

(i) The **excitation potential** of certain satellites is greater than that of corresponding parent lines.

1.22. SATELLITES

(ii) The **five satellites** can be excited by the side of $L_{\alpha 1}$ line of M_o by raising the excitation potential.

Their **appearance** corresponds to singly, doubly, trebly etc. ionized atoms.

The intensity of ionisation can be increased by increasing the excitation potential.

1.22. SATELLITES

(iii) The intensity of ***K* satellite lines** is found to decrease in a continuous manner with increasing atomic number of radiating materials.

The intensity of **L_{α} satellites** decreases abruptly as the atomic number increases from **47 to 50**; it again increases abruptly at about **75**.

The L_{α} satellites are absent between the atomic numbers **50 to 75**.

1.22. SATELLITES

(iv) If, somehow or the other, it is possible to avoid multiple ionisation, the satellites are found to be absent.

1.22. SATELLITES

- The explanation of satellites was put forward by ***Wentzel*** and ***Druyvesteyn*** on the principle of ***multiple ionization of the inner electrons*.**

- It is found in the case of *K* satellites that the energy of excitation is equal to the energy required to eject a *K* electron and in addition an *L* electron from the atom.

1.22. SATELLITES

- Hence the initial state for the emission of *K* satellite is a state of double ionisation.

- In this case the atom has an electronic vacancy both in *K* shell and *L* shell. Such a state of an atom is designated as *KL* atomic state.

1.22. SATELLITES

- In a similar fashion, other states of double ionisation are designated as *KK*, *KM*, *LL*, *LM* etc.

- An atom in *KL* atomic state may undergo a **radiative transition** as

- $KL \rightarrow KM$ (an electron jumping from *M* shell to *L* shell) or

- $KL \rightarrow LL$ (an electron dropping from *L* shell to *K* shell).

1.22. SATELLITES

- The estimates of atomic energy indicate that the change in energy in the transition ***KL → LL*** is greater than that which takes place in the transition ***K→L*** (the transition which gives rise to $K\alpha$ line).

- Hence the former transition gives rise to satellites on the short wavelength side of $K\alpha$ line.

1.22. SATELLITES

- Similarly, the transition $KL \rightarrow LM$ gives rise to satellites on short wavelength side of $K\alpha$ line.

- If now we assume that a cathode ray electron ejects two electrons at once from the atom, the probability of this ejection decreases with increasing atomic number of radiating material. This is found to be the case for K series.

1.22. SATELLITES

- The anomalous behaviour outlined in point (iii) above was explained by ***Coster*** and ***Kroning*** using Auger effect in this connection.

- They suggested that L_{α} satellites are produced when in an atom L_{III} M_{IV} and L_{II} M_{V} state exist as initial states.

1.22. SATELLITES

- These initial states in an atom are produced by Auger transitions from L_I state.

- The transitions $L_I \rightarrow L_{III}\ M_{IV}$ and $L_I \rightarrow L_{III}\ M_V$ occur only if the energy of L_I state is greater than the energy of doubly ionised states $L_{III}\ M_{IV}$ and $L_{III}\ M_V$.

1.22. SATELLITES

- This is true only for elements having atomic number less than 50 and greater than 75. This explains the anomalous behaviour of L_l satellites.

The Fluorescence Yield and Auger Effect

X-ray Fluorescence

- **If an atom is in excited state, it goes to unexcited state with the emission of radiant energy.**
- **But beside this possibility there is *another possibility* which finds support from the fact that the number of *K* photons emitted appear to be less than the *K* vacancies in the metal.**

X-ray Fluorescence

$$\text{Fluorescence yield } E_K = \left(\frac{n_p}{n_e}\right)_K$$

where

n_e is the number of electrons ejected from *K* shell of same element and, as a result, n_p photons are emitted.

- The fluorescence yield of a state represents the *fraction of the excitations of the state which lead directly to the emission of a photon.*

- The fluorescence yield increases with increasing atomic number.

The Auger effect

*The Auger effect was discovered by P. Auger in **1923**.*

After an electron has been removed from an inner shell, the excess energy can be released either in the form of an x-ray quantum, or non-radiative return to the ground state with the emission of an electron from a shell farther out (Auger effect).

The Auger effect

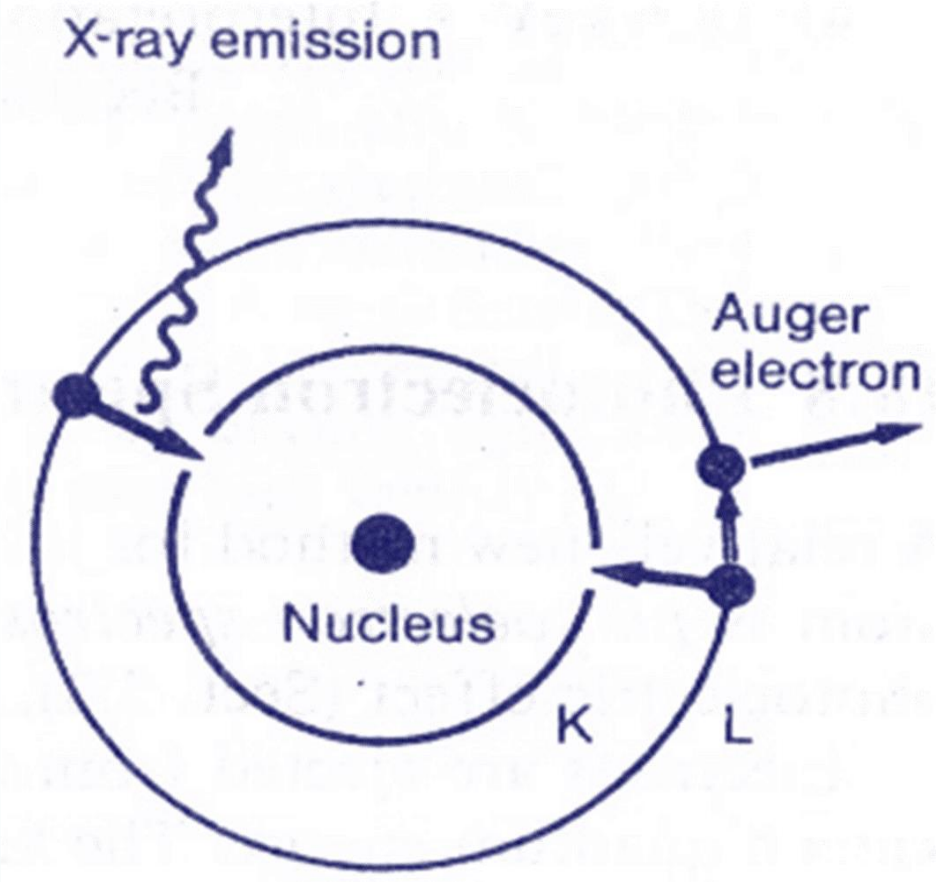
- To account for the number of vacancies present and photons emitted, Auger, in 1925, studied the ejection of X-rays from Argon using a Wilson cloud chamber.

- He found certain electrons are emitted without radiant energy, *i.e., there* are certain radiation less transitions; this is known as *Auger* (pronounced as OH-ZHAY) *effect.*

The Auger effect

In the process of *K* capture, in nuclear phenomena vacancy is created in K-shell.

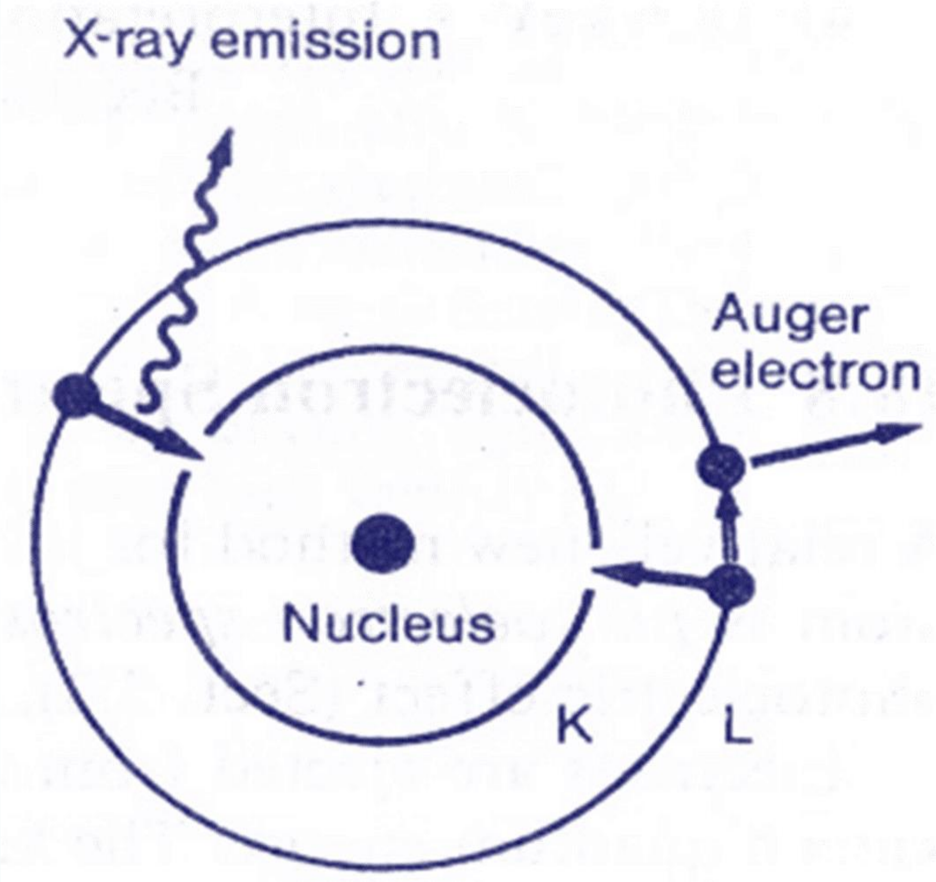
This vacancy is filled in by the electrons of *L*, *M*, ... shells etc., and subsequently, X-rays are emitted.



The Auger effect

Sometimes the X-rays eject an orbital electron with no energy left in the form of e. m. radiation.

This effect is known as Auger effect and the electrons which are emitted without fluorescence are known as *Auger electrons.*



The Auger effect

He noted the following points:

(1) The Auger electrons originate at the same point from which the photoelectron track originates.

(2) The length of Auger track is independent of the frequency of incident X-rays, whereas the length of photoelectron track increases with the frequency.

The Auger effect

He noted the following points:

(3) The **direction of ejection** of Auger-electron is random and independent of the direction taken by photoelectron.

(4) **The length of the Auger track is independent of its direction and the direction of photoelectron.**

The Auger effect

He noted the following points:

(5) All photoelectron sources do not show Auger electron track.

(6) The length of the Auger-track increases with the increase in the atomic number of irradiated gas.

The Auger effect

- The above points suggest that Auger electron and photoelectron come from the same source and the two events are sequential and not simultaneous; when a *K* electron is ejected there exists a vacancy in *K* shell of an atom.

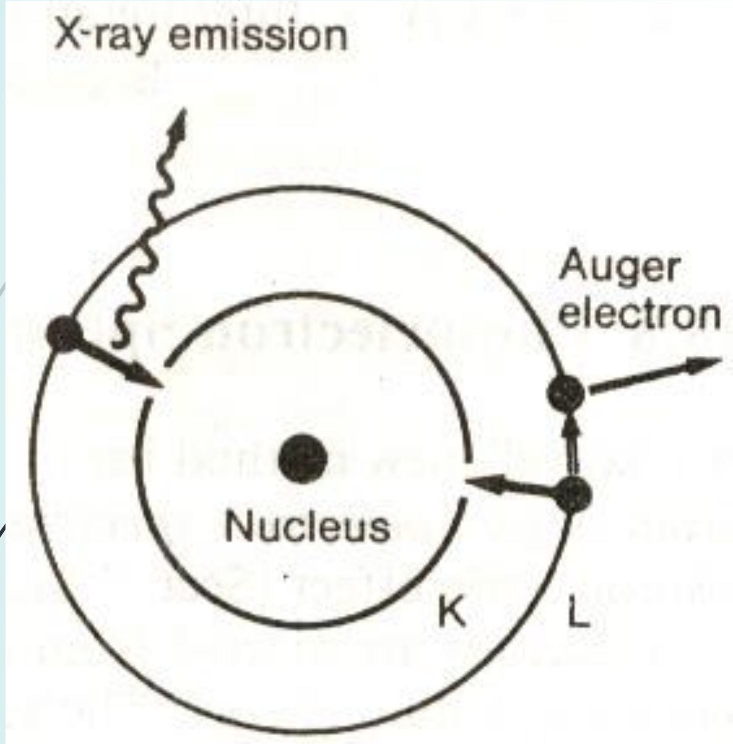
The Auger effect

- Most probably this vacancy is filled by the emission of K_α **radiation** creating thereby a vacancy in *L* shell.

- But it is also possible that the energy of K_α radiation may **eject another *L* electron** making thereby the atom **doubly ionized**.

- The process is termed as *auto-ionization* or *non-radiative transition*.

The Auger effect



Auger electron emission competes with x-ray emission.

The kinetic energy of the Auger electron:

$$E_{kin} = h\nu_{K_\alpha} - E_L = (E_K - E_L) - E_L$$

The Auger effect

Theory

If kinetic energy of Auger electron is $\frac{1}{2}mv^2$, then we can write

$$\frac{1}{2}m\,v^2 = h\nu_\alpha - (E_{LL} - E_L)$$

where $h\nu_\alpha$ is the energy of K_α radiation,

The Auger effect

Theory

$$\frac{1}{2}\, m\, v^2 = h\nu_\alpha - (E_{LL} - E_L)$$

E_{LL} is the energy of the atom when the **two electrons** are missing from *L* shell,

E_L is the energy when **one L electron is missing**.

Thus $E_{LL} — E_L$ is the energy required to remove second *L* electron.

But $h\nu_\alpha = E_K - E_L$.

The Auger effect

Hence,

$$\frac{1}{2}\, m\, v^2 = (EK - EL) - (E_{LL} - E_L)$$

If $E_{LL} \approx 2E_L$, we have

$$\frac{1}{2}\, m\, v^2 = EK - 2\, EL$$

Thus, ***the energy of Auger electron is independent of frequency of incident X-radiations***.

The Auger effect

- Further, as the difference $(E_{LL} — E_L)$ is greater than the energy required by first electron
- *and*
- to a good approximation this is equal to the energy required to remove the electron from the atom with atomic number, (Z + 1), the energy of Auger electron, thus depends upon the **ejecting atom only** .

The Auger effect

If the above discussed process is followed, the two vacancies created may be filled in by the transitions of two M - electrons from *M* shell to *L* shell and the radiant energy thus emitted may be absorbed to produce two more Auger electrons from the same atom.

These are called *secondary Auger electrons* and their energies will be less than Primary Auger electrons.

The Auger effect

- Similarly tertiary Auger electrons are produced. It should also be noted that Auger transitions need not essentially leave the atom with two vacancies in the same shell.

- Auger effect offers a means to measure the intensity of satellites.

- It is also used to analyze the fluorescence yield and it confirms the discontinuous shell structure of the atom.

Thanks…..