

CHAPTER I

X-RAY SPECTRA

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1.1 INTRODUCTION

Spectroscopy is a study of the phenomena of emission and absorption of radiations, by matter. It deals with the understanding of the structure and properties of matter by the study of the effects resulting out of the interaction of radiations with matter. Spectroscopy is subdivided into different branches such as U.V., Visible, I.R., N.M.R., E.P.R., X-ray etc., depending on the type of electromagnetic radiations involved. Among these, the X-ray spectroscopy is unique in giving information right from the inner levels of the atom to the outer-most valence and conduction bands of the solid.

Some fundamental aspects of X-ray spectroscopy are briefly dealt with in the following sections of this chapter. The details regarding these have appeared in a number of review articles (1-4) and a few text books (5-9). In the present work X-ray absorption studies have been carried out and hence more weightage is given to the X-ray absorption phenomenon.

1.2 X-RAY EMISSION SPECTRUM

1.2(a) Characteristic Spectrum

X-rays are generated when high energy electrons are suddenly stopped by matter. The radiations thus emitted give a spectrum consisting of sharp lines on a continuous background.



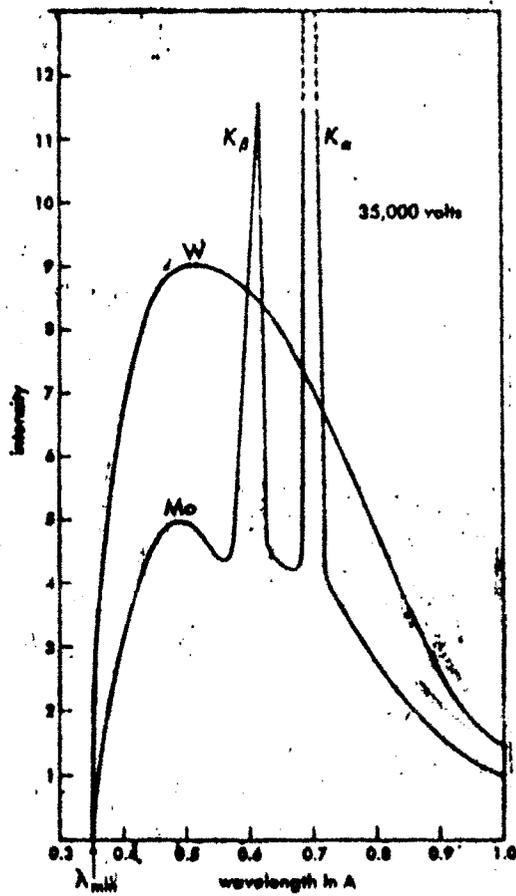


Fig.1.1 : Continuous and characteristic x-ray spectrum showing λ_{min} is independent of target material.

ground (Fig. 1.1). The sharp lines which are characteristic of the target producing X-rays constitute the characteristic spectrum. A systematic study of characteristic X-ray spectra of different elements was first made by Moseley (10). His findings are as follows :

i) Along with the back-ground radiation (the continuous spectrum) each element emits some characteristic lines, which can be grouped as K series and L series lines, known as characteristic spectrum.

ii) Unlike the optical spectrum it consists of fewer lines, similarly disposed for all elements at different wavelengths.

iii) The frequency of the emitted line can be given by a simple relation as,

$$\nu^{1/2} = K (Z - \sigma) \quad \dots \quad 1.1$$

where K and σ are constants for a particular series and Z is atomic number. The equation (1.1) is known as Moseley's law. The plot corresponding to this law is known as Moseley plot and is shown in (Fig. 1.2). Moseley himself showed that his law could be derived by applying Bohr's (11) theory.

1.2(b) Continuous Spectrum

The important feature of the continuous spectrum which forms the back-ground for the X-ray emission lines is that it

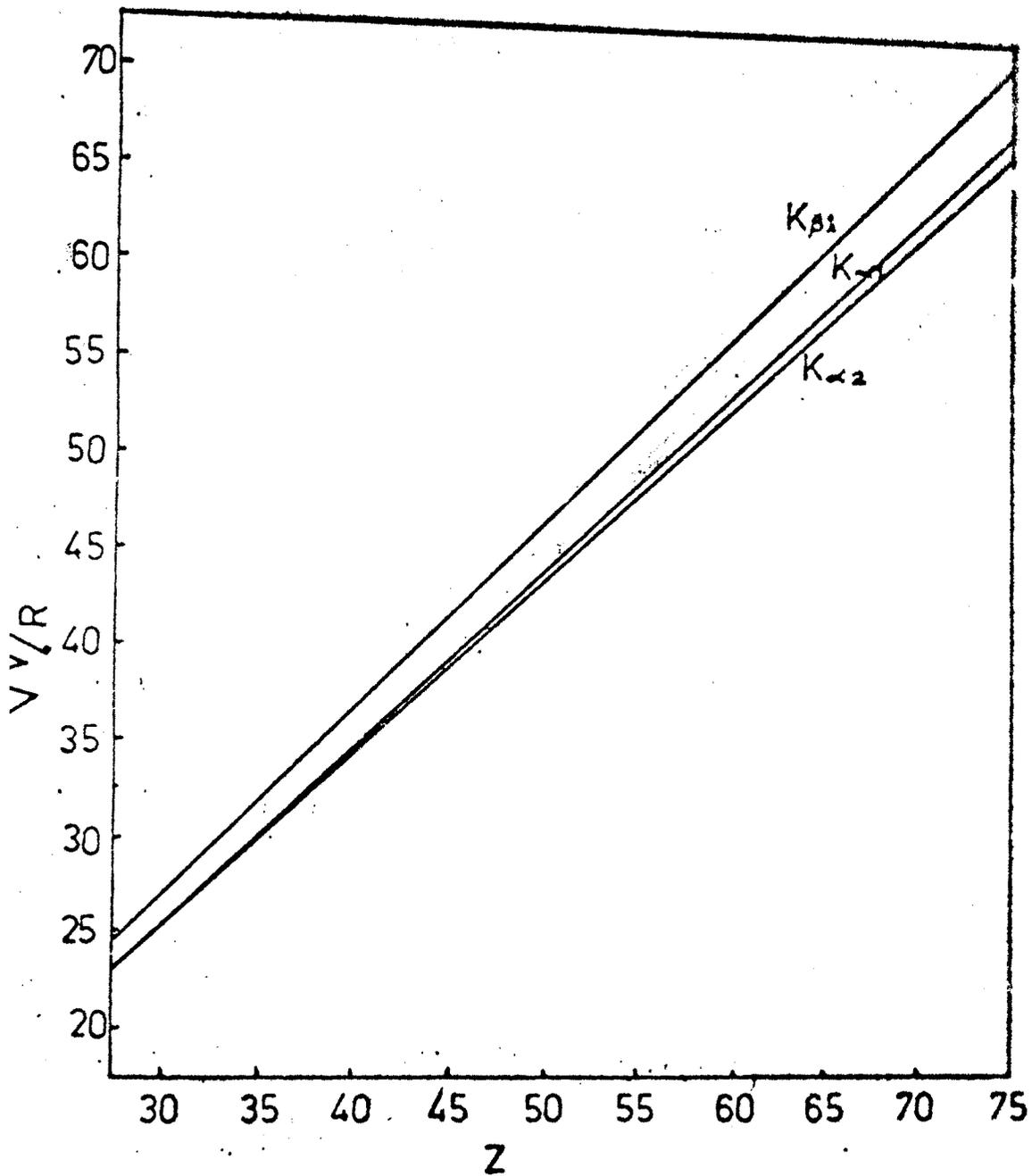


Fig.12 : Moseley diagrams for the lines $K\alpha_1$, $K\alpha_2$ and $K\beta_1$ for elements with atomic number Z from 29 to 75

is sharply limited on the short wavelength side and is independent of the target material (Fig. 1.1) and depends only on the potential difference applied to the tubes. Duane and Hunt (12) have shown the following relation between the potential applied to the tube and the short wavelength limit.

$$h \nu_{\max} = eV = hc/\lambda_{\min} \quad \dots \quad 1.2$$

where,

V = voltage across the tube,

e = charge on the electron,

λ_{\min} = short wavelength limit, and

c = speed of light.

The quantum theory provides an adequate explanation of this Duane-Hunt law.

1.3 MECHANISM OF X-RAY EMISSION AND ABSORPTION

When high energetic focussed electron beam is incident on the target atom, the electron from the inner level, say K level of the target atom is knocked out creating a vacancy, at the K level. In order to fill this vacancy, an electron from higher level jumps down releasing an amount of energy corresponding to the energy difference in the energy levels between which the transition takes place. The emission lines appear on the spectrogram at definite positions corresponding to the frequencies given by the relation,

$$E_K - E_L = h\nu \quad (\text{or higher levels})$$

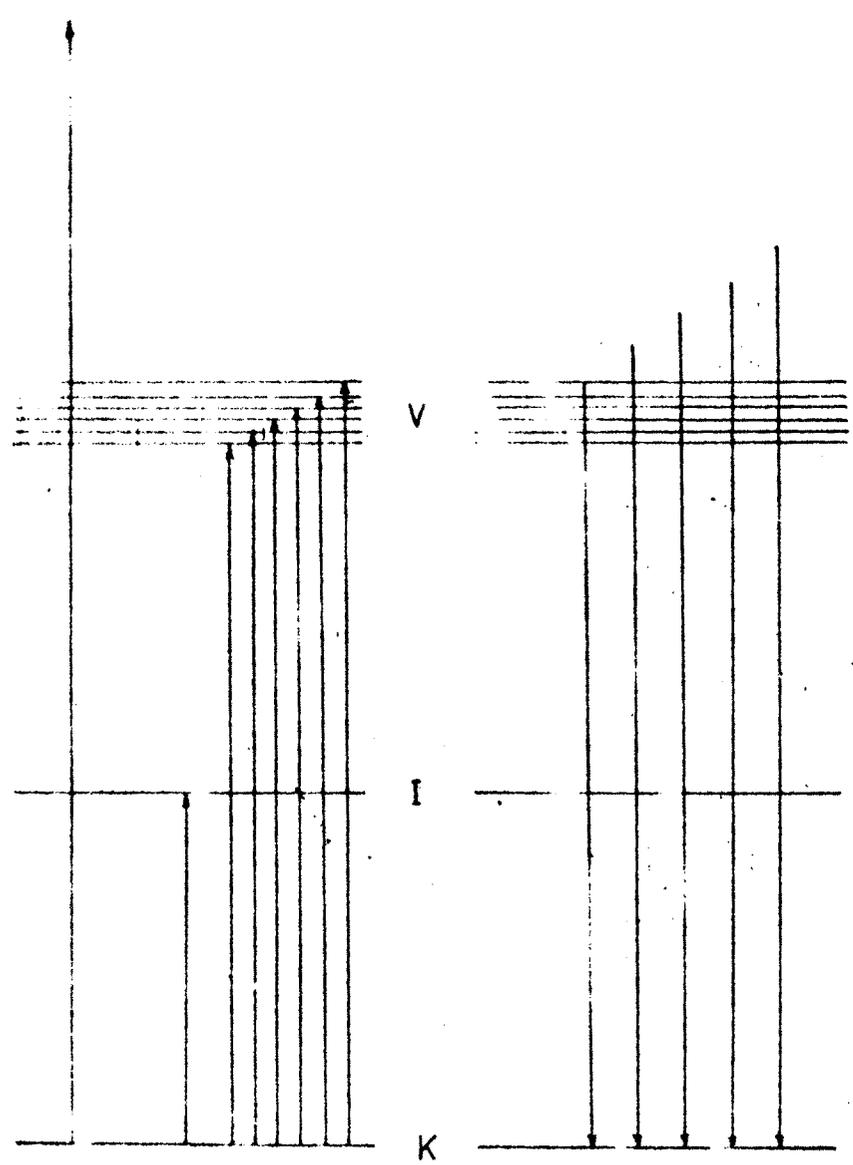


Fig.13a : (Emission)

Fig.13b : (Absorption)

Fig 13 : Energy level diagram showing the mechanism of x ray emission and absorption

In the absorption process, the high energy photon is incident on the absorbing atom. A part of the photon energy is absorbed to release a bound electron from certain level and the rest of it is transferred to the photo-electron as its kinetic energy. Evidently, the minimum energy absorbed by the atom corresponds to the work done in removing the electron, say from K level to the first available vacant level. X-ray photons with energy less than this certain minimum are not absorbed and all those with energy above this critical value are absorbed. The absorption coefficient increases suddenly in this minimum energy region, giving rise to a discontinuity in the absorption coefficient, which is known as "absorption edge".

If we consider the energy of an electron configuration of a system in which there is only one electron vacancy to form an ordinary X-ray state, then the emission and absorption processes can be shown schematically as in Fig. 1.3(a) and Fig. 1.3(b). The outer levels have been shown broader than the inner levels because the outer levels are influenced by the inter-atomic interactions in the solid. The inner levels are not appreciably affected by these interactions and they remain more or less discrete. The transitions such as $K \longrightarrow I$ or $K \longrightarrow V$ gives rise to the emission of radiation of energy $E_1 - E_2 = h\nu$, as shown in Fig. 1.3(a), while, the transitions from the different stages in the empty conduction band to the inner states, as shown in Fig. 1.3(b), occur in the absorption process.

1.4 SHAPE AND POSITION OF THE ABSORPTION DISCONTINUITY

The observed shape of an absorption edge is not like a sharp cut off and therefore the determination of critical energy at which the absorption begins is rather difficult. Applying the quantum mechanical radiation theory of Weisskopf and Wigner (13) to the specific problem of X-ray absorption and assuming that the absorption curve is a result of a series of absorption lines on high energy side of the limit, Richtmeyer, Barnes and Ramberg (14) showed that the absorption coefficient is a function of frequency at an absorption edge of a metal which is given by,

$$\mu(\gamma) = C \left[1/2 - 1/\pi \cdot \tan^{-1} \left(\frac{\gamma_0 - \gamma}{\Gamma/2} \right) \right] \quad \dots \quad 1.3$$

where, Γ is width of the K excited states and γ_0 is the frequency corresponding to cut off. This relation shows that at $\gamma = \gamma_0$, $\mu(\gamma) = 1/2$ i.e. the absorption falls to 1/2. By adjusting the parameters Γ and C, one can match the curves following above equation with the experimental curves upto the inflection point, which is the position of the first vacant level in the Fermi distribution.

The importance of the above stated formula can not be understood because of the lack of the knowledge of the transition probabilities. However, it is found that in most of the metals, an arc tan curve can be fitted (15) to the observed absorption curve. The position of the inflection point on the arc tan curve, thus, would be used to determine the energy of the Fermi level in metals. For semi-conductors and insulators,

the mid-point of the absorption jump is taken as corresponding to the absorption limit in solids, as the theoretical calculations have not been possible.

1.5 FINE STRUCTURE IN X-RAY ABSORPTION SPECTRUM

It is observed that absorption coefficient does not increase monotonically but shows uneven variations with wavelength upto a critical absorption limit and then suddenly decreases. These uneven variations which extend upto few hundred electron-volts on the high energy side of the main absorption edge, constitute the fine structure. The absorption spectrum is usually separated, for the purpose of calculation, into three groups : main edge structure (such as K_1 , K_2), near edge (Kossel) structure to within 20 ev on the high energy side of the main edge and extended fine (Kronig) structure upto about 500 ev or more on the high energy side of the Kossel structure. Extended fine structure (EFS) is also called the extended X-ray absorption fine structure (EXAFS). Various theories (16) have been put forward to explain the observed fine structure, which will be dealt with, in more detail in chapter IV.

1.6 CHEMICAL EFFECTS

By studying the K-absorption spectra of phosphorous in various allotropic modifications Bergengren (17) for the first time demonstrated that chemical combination affects the X-ray

spectra. A similar type of study was carried out by Lindh (18) on chlorine, phosphorous and sulphur compounds. He established that not only the shape of the absorption curve but also the position on the wavelength scale gets changed. It was first shown by Beeman and Bearden (19) that the wavelength of an absorption edge is influenced by the valence state of the absorbing atom and that the fine structure of the edge could be explained making use of optical term values. The chemical shift as big as $24.4 \times U$ has been measured for sulphur edge in sulphur compounds (20). Kunzl (21) has given an empirical rule correlating the frequency shift of the absorption edge with valency of the absorbing atom as,

$$\frac{\Delta \nu}{R} \propto n \quad \dots \quad 1.4$$

where R is the Rydberg constant and n is the valency. Agarwal and Verma (22) proposed an empirical rule correlating the observed chemical shift with the valency and the type of bonding. It is reported by Sapre and Mande (23) that the negative or positive chemical shift depends upon whether the charge on the ion is negative or positive and the magnitude of the shift depends upon the effective ionic charge on the absorbing atom.

It has been shown by a number of workers (24, 25, 26) that the fine structure associated with an edge is the characteristic of the chemical bonding of the absorbing atom. Van Nordstrand's classification of K-absorption curves into four groups has been found useful in making deductions about bonding

and co-ordination of the absorbing atom. Seka and Hanson (27) and later Heinz (28), on the basis of molecular orbital theory have explained fine structure of many transition metal complexes.

1.6(a) Bonding effects

Formation of chemical compounds is accompanied with rearrangement of valence electrons, that determines the nature of the chemical bond. As a result of this, outer as well as inner electronic levels of atom are perturbed. So X-ray spectroscopic study can give information about the nature of chemical bond between the bonded atoms.

The electronic structure of the materials determine their properties and bonding can be viewed to be connected to the electronic structure. That is how information regarding the electronic structure of the materials can be obtained from X-ray spectra. Several investigators have used X-ray spectra to deduce information regarding bonding in transition metal compounds (25, 26, 29, 30). However, it may be mentioned that unless the wavefunctions of the atoms in solid state are known precisely, it would not be possible to correlate quantitatively the observed spectra with chemical bonding.

1.7 SPECIAL FEATURES OF X-RAY ABSORPTION SPECTROSCOPY

i) It is less sensitive to the impurities but very sensitive to the chemical state of the element under study.

ii) It is a direct method to study unoccupied levels in solids. All types of solids can be studied.

iii) The method is non-destructive.

iv) A wide energy range is covered in the same spectrum which supplies information about shapes, widths, positions of the energy bands.

1.8 ORIENTATION OF THE WORK

A tremendous amount of work has been carried out both experimental and theoretical in the field of X-ray spectroscopic research. Much of the work is restricted to study the chemical effects in X-ray spectra. Transition metal elements of the first long period are the most widely studied because of the various valence states these elements can exhibit due to incomplete three d shell and secondly because their K-edges lie in relatively accessible region of wavelength. Cobalt like other transition metal elements shows different valencies in different states of aggregation such as inter-metallic compounds, alloys, complexes etc.

Behaviour of cobalt, when in complexes is typical from the view point of understanding the cobalt K-edge spectrum on the one hand and the electronic structure of cobalt on the other. Such correlations are necessary in order to understand the co-ordinate bond physico-chemically. A variety of stable complexes are formed by cobalt having valency two and three

with different monodentate and multidentate ligands. The environment of cobalt atom in a complex can be changed by the gradual replacement of ligands. Further, the octahedral Co(III) complexes of the type $[M(AA)_2(B)_2]X$ show geometric isomerism. These factors will influence the X-ray absorption process and hence the X-ray absorption spectrum. Therefore following studies were undertaken on Co(III) complexes.

- 1) Preparation of Co(III) complexes with monodentate and bidentate (chelate) ligands.
- 2) Preparation of cis-trans isomers of Co(III) complexes.
- 3) The effects of gradual replacement of mono/bidentate ligands on X-ray K-absorption spectra of Co(III) complexes.
- 4) The diagnosis of cis-trans isomerism with the help of X-ray K-absorption spectra.

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