CHAPTER-3

THEORY

OF

X-RAY EMISSION

SATELLITES
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In the characteristic X-ray Spectra, Diagram as well as non Diagram lines are present. Those lines which fit in the conventional energy level diagram are called Diagram lines. & those lines which do not fit in the conventional energy level diagram are called non diagram lines. It is also known as “Satellites or Second order lines”. Satellites are generally of weak intensity lines & are found close to more intense parent line. The satellites which are observed on higher energy side are called high energy satellites (HES) whereas those are observed on lower energy side are called lower energy satellites (LES). As the sensitivity and resolving power of spectrometers were improved and increased, the observed number of faint-non diagram lines were also increased so much that they outnumbered the number of diagram lines. Therefore, it becomes of paramount importance to find out a proper explanation for the origin of these ‘non diagram’ lines or X-ray satellites. In this chapter we are going to review various theories of low and high energy satellites respectively.
3.1 **Review of theory of low energy X-ray satellites**

3.1.1 **Selikow and Krasnikow’s theory (1925)**

Selikow and Krasnikow’s [61] were the first who studied the low energy Kβ’ X-ray satellites of the parent line Kβ1,3. They interpreted first the Kβ’ and Kβ1,3 lines to be the doublet corresponding to M2 and M3 levels. However, the observed energy separation of the two lines does not coincide with that of M2 and M3 levels, hence this theory has no validity.

Selikow and Krasnikow [61] have also calculated the relative intensity of the Kβ’ satellites with respect to the main line Kβ1,3 is about 50%, which is much higher than the observation of Ekstig et al [62] and Schnopper [63].

3.1.2 **Ortner’s Theory (1925)**

In 1925 Ortner [64] assumed new M levels in the iron group and explained the Kβ’ satellites is due to M level transition. This theory has no importance because Ortner could not utilize this theory for other group elements.

3.1.3 **Coster and Druyvesteyn’s theory (1927)**

Coster and Druyvesteyn’s [65] also explained the low-energy X-ray Satellites Kβ’. They have described the Kβ’ satellites in the transition
elements to arise from the interaction between a hole and the incomplete 4d level. They have also tried to explain the L series satellites of the Lanthanides (rare earth elements) originate in a similar manner from the exchange interaction between a hole and the incomplete 4d level. This theory was also of not much use because Coster and Druyvesteyn's [65] failed to calculate the energy separation and the relative intensity, the two most important parameters of the satellites.

To explain the Kβ’ satellites in transition series and Lβ’2,15 and L γ’ satellites of rare earth element, Tsutsumi et al. [66] and Salem and Scott [67] extended the exchange interaction theory but got a very limited success.

3.1.4 **Deodhar’s Theory (1931)**

Deodhar [68] explained some of low energy satellites as arising due to single electron jumps taking place in multiply ionized atoms, supporting the basic idea of Wentzel's theory [5]. Deodher and Abidi [69] obtained a relation between δ[v/R] and Z. This relation was later on extended by Deodhar and Padalia [70] to a large number of satellites of several elements. They plotted the frequency difference between the parent and satellite lines δ[v/R] against the atomic number Z and found a straight
line. From this straight line they derived several new formulae given below

\[ \delta[v/R] = 1.5 (Z-1) \]

the range of elements covered \( Z=11 \) to \( Z=35 \) and

\[ \delta[v/R] = 0.25 (Z-4) \]

holds over the range \( Z=33 \) to \( Z=42 \) and

\[ \delta[v/R] = 0.25 (Z-3) \]

over the range of elements \( Z=44 \) to \( Z=53 \).

According to this theory, the K\( \beta' \) is due to a single transition.

\[ KL3 \rightarrow L3M1 \]

Which shows that the K\( \beta' \) satellite line is excited in those atoms in which one K and one L electrons are missing. To remove a K electron from an atom of atomic number \( Z \), the energy needed is \( E(K)_Z \) and to remove another L electron from the same atom, energy needed is approximately \( E(L)_{Z+1} \). Hence K\( \beta' \) line can only be emitted by photons having energy equal and greater than \[ E(K)_Z + E(L)_{Z+1} \].

However, Tsutsumi et al. [66] have shown experimentally that in the transition metals and their compounds, K\( \beta' \) line is emitted by photons of
energy lower than \([E(K)z + E(L)z+1]\). They have also observed that the intensity ratios of \(K\beta_1\) and \(K\beta'\) lines were the same whether excitation energy was less than \([E(K)z + E(L)z+1]\) or more, Hence Tsutsumi et al's [66] observation disapproved Deodhar's theory and suggested that the single ionization process is more appropriate one for production of low energy satellites.

3.1.5 Sawada's Theory (1932)-

M Swada [71] working on the same line as deodhar, attributed the satellites line \(K\beta'\) to the transition

\[
KL_{2,3} \rightarrow L_1M_{4,5}
\]

Which demands not only doubly ionized states but also two transition. Sawada's theory [71] was disapproved by the recent experiment performed by Schnopper [63].

3.1.6 Hulubei's Theory (1947)-

In a Systematic study of elements As\((Z=33)\) to Br\((Z=35)\) and Rb\((Z=37)\) to Mo\((Z=42)\). Hulubei [73] found a line \(\alpha s\) on the low energy side of the X-ray emission line \(\alpha 1\alpha 2\). Later on \(\alpha s'\) and \(\alpha s''\) were also discovered by Groven and Morlet [72]. For the origin of low energy satellites, Hulubei [73] suggested two mechanism—
(1) **Partial Auger effect** :-

A part of the energy of the main line is used up to ionize an outer shell. The rest of energy is radiated out as the low energy satellites. According to this theory the energy difference between the parent and satellite lines should be greater than the ionization energy of the external shell. But Groven and Morlet [72] found experimentally that this was not the case. Hence we may rule out the validity of this mechanism.

(2) According to the second mechanism, a radiative forbidden transition takes place which has an energy less than that of an allowed transition. For example, a forbidden transition from K level to L₁ level results in the excitation of low energy satellites.

With the help of the self-consistent Hartee-field method, the value of energy separation of satellite from the parent line was calculated by Groven and Morlet [72] for the elements Zn (Z=30) to As (Z=33), and found an agreement with the observed value only in the order of magnitude. Hence we may rule out the validity of this hypothesis also.

3.1.7 **Blochin's Theory (1957)** -

M.A. Blochin's [74] has established a theory of two electron transition for the origin of Kβ' satellite in the transition elements. A single transition takes place from higher level to the K-level emitting the
parent line and simultaneously another transition takes place from the 3d level to the conduction band. Now in order to excite a 3d electron to the conduction band, the required amount of energy is absorbed from the first transition. So that the emitted radiation loses some energy and the remaining energy is emitted as the low energy satellites Kβ'.

Blochin’s [74] hypothesis was rejected by Tsutsumi et. Al. [66] without assigning any reason. The defect in the Blochin’s theory [74] is that it does not tell us as how much energy the 3d electron will take and whether this corresponds to the energy difference of Kβ' satellite with Kβ1,3—line or not. The answer to this question is provided by plasmon oscillations in solid theory. Therefore, the author has correlated this theory with the plasmon theory of Bohm and Pines [37] and consider it to be a quite reasonable approach. From this theory we have obtained much better results than from any other theory.

3.1.8 Parratt’s Theory -

L.G. Parratt’s [75] explained the low energy satellite from excited valence electron configuration states, assuming that the electron interaction would not give enough splitting to explain the observed features which are the alternative to the exchange interaction theory of Coster and Druyvesteyn [65].
He explained some of the X-ray satellites and the fine structure in X-ray absorption spectra of solids by two methods—

1. **Bound ejected electron excitation state (B.E.E. States)**

   The core electron is a bound electron when it is ejected from its orbit, instead of going out of the atom it may stop either innum. This state can be any unoccupied orbital or in continuum. This ejected electron will have slightly different energy states. As a result of this transition the conventional X-ray energy levels show splitting into several discrete levels and continuum. This state can be achieved by absorption of X-ray photons and rarely by electron bombardment.

2. **Valence electron configuration (V.E.C.)**

   The Coulomb field is changed when the hole is produced in the inner shell of the atom. This affects the motion of atomic electrons. The inner electrons quickly adjusts in new orbital while the outer electron take some time in adjustment. The time allowed for outer electrons was of the order of $10^{-6}$ sec. which is also the life time of inner vacancy. After the lapse of this interval, the valence electrons occupy new orbital's while other electrons have gone to unoccupied excitation orbital. In the light of above mechanism, satellite originates when the transition
takes place between the new levels of atom. The many K-levels and many L₁, L₂ and L₃ levels in X-ray diagram lines are the result of above theory. The energy of system is decided by new arrangement of valance electrons as well as ejected electron. Kβ₁,3 diagram lines in K X-ray emission spectrum of solid manganese is produced when K-vacancy is filled by the unadjusted 4s electron in the new coulomb field while Kβ’ satellite is due to ejected 4s electron transition. Since then inner electrons are strongly bound. The X-ray quantum emitted is of lower energy, hence Kβ’ is the low energy satellite.

3.1.9 Exchange Interaction Theory -

According to salem et al [67], the exchange interaction between the 3d and 3p electrons splits both levels, causing some of the electrons splits both levels, causing some of the electrons in the 3p state to move to lower energy levels, transition from these levels appears as the Kβ’ emission satellite on the low energy side of the Kβ’ emission satellite on the low energy side of the Kβ₁,3 line. The energy difference between Kβ₁,3 and Kβ’ lines would then correspond to the difference between the exchange energy of (S + 1/2) and (S – ½) states. The exchange interaction of the state having a total spin (S+s) is given by [76,77] as

\[ \Delta E = (E)_{\text{parent}} - (E)_{\text{satellites}} + J/2(1 + 4 S.s) \] 3.3
Where $J$ is the exchange integral, $S$ is the total spin vector of the incomplete 3d shell, and $s$, the spin of the 3p shell having one vacancy, will be $\frac{1}{2}$. Hence equation 1 become

$$\Delta E = J/2 \left(1+2S\right) \quad \text{(3.4)}$$

In the above procedure, the interaction potential has been taken as $1/r12$, while Tsutsumi et al took it as $2/r12$. Hence formula for the energy separation will be

$$\Delta E = J \left(2S + 1\right)$$

For the transition metals, Salem et al [17] have calculated the values of the exchange integral $J$ in terms of Hartee-Fock Slater [78] integral $G^1$ and $G^3$ as

$$J = \frac{2}{15} G^1 \left(3p, 3d\right) + \frac{3}{15} G^3 \left(3p, 3d\right) \quad \text{(3.5)}$$

This expression is slightly in error. The Srivastava et al [17] has given the correct expression as

$$J = \frac{2}{15} G^1 \left(3p, 3d\right) + \frac{3}{35} G^3 \left(3p, 3d\right) \quad \text{(3.6)}$$

Putting the value of $J$ from eqn. 5 in eqn. 3 we get

$$\Delta E = (2S + 1) \left|\frac{2}{15} G^1 \left(3p, 3d\right) + \frac{3}{35} G^3 \left(3p, 3d\right)\right| \quad \text{(3.7)}$$
The value of $G^1$ and $G^3$ have been computed by mann [80]. The magnitude of the energy difference $\Delta E$ between the exchange interaction for $(S + 1/2)$ and for $(S-1/2)$ States is given by

$$\Delta E = J/2 [(S+1/2)(S + 1/2 + 1) - (S-1/2)(S-1/2 +1)]$$

$$= J/2 (2S + 1) \quad 3.8$$

The relative intensity $I'/I$ of the $K\beta_{1,3}$ lines is estimated from the ratio of the multiplicity of each state, that is

$$i = I'/I = \frac{[2(S-1/2)+1]}{[2 (S+1/2) +1]} = S/S+1 \quad 3.9$$

But the above eqns.2.44 and 2.45 are not true for oxides and plasmon theory gives better result so this theory is rejected by Srivastava et al [17].

3.2 - Review of theory of High energy X-ray satellites-

3.2.1 Wentzel's Theory (1921) –

The first theoretical attempt, to explain the origin of high energy satellites was made by wentzl [5] in 1921. Wentzel made a systematic study of the K series X-ray satellites $K\alpha'$, $K\alpha_3$, $K\alpha_4$, $K\alpha_5$, $K\alpha_6$. These satellites have been observed on the high energy side of the parent X-ray diagram line $K\alpha_{1,2}$. He explained these satellites on the basis of single
electron jumps from one state to the other in multiple ionized atoms. The vacancy other than the transiting electron is known as 'spectator'. It is well known fact that X-ray diagram lines are emitted from those atoms which have a single core vacancy. Wentzel's hypothesis requires if any how, two core vacancy are created and atom becomes doubly ionized, then the electrostatic attraction of the nucleus on the remaining electrons is slightly increases. Due to this the energy levels of the atoms are slightly changed. If an outer shell electron now makes a transition from these changed levels takes place to the core vacancy level the emitted X-ray line will have different energy. This emitted X-ray line is called in X-ray satellite of parent line. The same process will takes place if more than two vacancies are produced giving rise to the emission of several other satellites. This is the theory of Wentzel of single electron jump in multiple ionized atoms.

Wentzl assigned $K^1$ or $L^1$ to the state arising from the absence of one K or L electron, $K^2$ or $L^2$ to the state arising from the absence of two K or L vacancies and so on.

Hence he gave the following assignments to the initial and final states to the various satellites of the $K\alpha_{1,2}$ line as –
<table>
<thead>
<tr>
<th>Satellite</th>
<th>Initial State</th>
<th>Final State</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K\alpha'_1$</td>
<td>$K^1M^1$</td>
<td>$L^1M^1$</td>
</tr>
<tr>
<td>$K\alpha_3$</td>
<td>$K^1L^1$</td>
<td>$L''$</td>
</tr>
<tr>
<td>$K\alpha_4$</td>
<td>$K''$</td>
<td>$K^1L^1$</td>
</tr>
<tr>
<td>$K\alpha_5$</td>
<td>$K^1M''$</td>
<td>$L'''$</td>
</tr>
<tr>
<td>$K\alpha_6$</td>
<td>$K''M^1$</td>
<td>$K^1L''$</td>
</tr>
</tbody>
</table>

There are three possible methods by which an atom can be made doubly ionized

(1)– An atom in the target loses an inner electron by an impact from the cathode ray electrons. Subsequently and before this inner loss is replaced, the atom is again struck and another inner electron is removed.

(2)- In one encounter with a cathode ray electron, two inner electrons are removed. So cathode ray electron have sufficient energy to remove two orbital electrons from the target atom.

(3)- A single ionized atom, by the process discovered by Auger [81], ejects a second electron [82] instead of emitting photon corresponding to an X-ray diagram line. Out of these two process, Wentzel preferred the
first one for creation of multiple vacancies in an atom because of the following reasons.

The life time [75] of core vacancy is very small nearly of the order of $10^{-16}$ sec. and the electron density of the cathode ray is also very small as compared to that of atoms in the target material. Hence the probability that a core hole will exits till a second cathode electron strikes the same target atom, is very small. This small probability will give very low intense satellite, where as experimental intensity is found much higher so that second process was rejected by Wentzl [5].

He also rejected the third process because he observed that the quantum energy of none of the X-ray lines was sufficient to eject a second K-electron.

3.2.2 **Duyvesteyn’s modification to Wentzel theory**

Duyvesteyn [6] has slightly modified the wentzel theory. He suggested that it is not necessary to assume both the vacancies to be in the same (m,l) shell. He also gave the following assignments to the high energy K-series X-ray satellites.

The well known satellite Kβ''' has been assigned by Duyvesteyn to the transition KL → LM. This last notation indicates that in initial state are one K and one L electron is missing from the atom and that the transition
of an M electron into vacant K shell leaves the atom in a final state with one L and one M electron missing.

<table>
<thead>
<tr>
<th>Main Line</th>
<th>Satellite Line</th>
<th>Initial State</th>
<th>Final State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kα₁,₂</td>
<td>Kα'</td>
<td>K'L''</td>
<td>L''''''</td>
</tr>
<tr>
<td>Kα₁,₂</td>
<td>Kα₃,₄</td>
<td>K'L''''</td>
<td>L''''''</td>
</tr>
<tr>
<td>Kα₁,₂</td>
<td>Kα₅,₆</td>
<td>K'L''''''</td>
<td>L''''''</td>
</tr>
<tr>
<td>Kβ₁</td>
<td>Kβ'''</td>
<td>K'L''</td>
<td>L'M''</td>
</tr>
</tbody>
</table>

Let \((E_k)z\) be the energy required to remove one K electron from a target atom of atomic number \(Z\), then the energy required to remove one L electron from the same atom in which already one K electron is missing, is \((E_L)_{Z+1}\). This is because of electrostatic force, which is increased by one unit due to the vacancy created by missed K electron and hence the net charge on the nucleus will be \((Z+1)\). Thus the energy required to remove both K and L electrons will be given by

\[
(E_{KL})_Z = (E_K)_Z + (E_L)_{Z+1}
\]

Similarly

\[
(E_{LM})_Z = (E_L)_Z + (E_M)_{Z+1}
\]

The energy of the parent line \(K\beta_1\) written as \(K--- M\).
\[(h\nu)_\beta = (E_K)_Z - (E_M)_Z \]  

From Duyvesteyn's table the energy of the satellite can be written as

\[(h\nu)_{\beta''} = (E_{KL})_Z - (E_{LM})_Z \]  

Now the difference in energy between the satellites \((KL - LM)_Z\) and the parent line will be

\[(h\nu)_{\beta''} - (h\nu)_{\beta I} = [(E_{KL})_Z - (E_{LM})_Z] - [(E_K)_Z - (E_M)_Z] \]  

From equation 2.48 and 2.49 we have

\[(h\nu)_{\beta''} - (h\nu)_{\beta I} = [(E_L)_{Z+1} - (E_L)_Z] - [(E_M)_{Z+1} - (E_M)_Z] \]  

The calculated value \([(h\nu)_{\beta''} - (h\nu)_{\beta I}]\) agrees fairly well with the observed values of same element. But there are some more satellites in K, L and M spectra which cannot be explained by this theory.

Briand [83] has observed, in radio active substances, some hyper satellites which occur far away from the parent line. He has explained these satellites on the basis that double vacancies in the same initial level can exist.

3.2.3 **Ritchmyer Theory (1929)**

Ritchmyer [84] in 1929 suggested an alternative theory to the Wentzel-Duyvesteyn [5,6] theory based on the ideas that double electron
jumps which can take place in multiple ionized atoms. He considered two vacancies in the atoms, one in an inner (K or L) shell ‘1’ and another in an outer shell ‘0’. The inner shell vacancy when filled by an electron from a higher shell (L or M) leads to emission of the main emission line having energy $\hnu_1$, and the resulting radiation will be a high energy satellite having energy.

$$\hnu_s = \hnu_1 + \hnu_0 \quad 3.16$$

The energy $\hnu_0$ is very small and the emitted radiation is a soft X-ray line.

Since all X-ray lines obey the Moseley’s law that is

$$\sqrt{\nu_0} \propto Z \quad 3.17$$

But

$$\sqrt{\nu_0} = \sqrt{(\nu_s - \nu_1)} \propto Z \quad 3.18$$

Since $\nu_s$ is the frequency of the satellite and $\nu_1$ is the frequency of the parent line. Therefore difference between the satellite line and parent line is given by

$$\Delta \nu = (\nu_s - \nu_1)$$

Substituting this in equation 16. We get
This equation is similar to the Moseley law so that analogy of Ritchmyer has called it 'semi Moseley's law'. In some case equation 3.19 is valid. Another advantage of Ritchmyer's theory is that it can determine the frequency of parent line from the data of its satellite line.

However, Idei [85] considering the same data found that the frequency difference itself and not its square root is directly proportional to the atomic number, which casts some doubt on the validity of Ritchmyer's theory.

3.2.4-Ray-Langer Wolfe Theory (1931)-

Wentzel's interpretation of the K series X-ray satellite neglects the multiplicity of the levels. Ray [86] first took into account the level multiplicity, in the production of X-ray satellites and gave them optical spectroscopic notation.

Langer [87] utilized the optical spectroscopic interpretation of satellites introduced firmly by Ray He attributed the origin of the five satellites Kα', Kα3, Kα4, Kα5 and Kα6 of the parent X-ray line Kα1,2 to one or other of the following two transition.

1. From state 1s 2s to state 2s 2p^5

2. From state 1s 2p^5 to state 2p^4
Using Russell – Saunders (L-S) coupling is 2s gives rise to two multiplets 1s and 3s. 1s2p$^5$ give rise to four multiplet term 1s, 3s, 1p and 3p, while the state 2p4 gives rise to three multiplet terms 1s, 1d and 3p. Five possible transitions between these multiplet states give rise to the five ka satellites Wolfe (93) in 1933. Made some modifications in Langer’s (92) assignment of transitions to the various satellites and showed very good agreement between the calculated and observed values of $\mu/R$ for the ka satellites. The various assignment of these satellites are as follows:

<table>
<thead>
<tr>
<th>Satellite</th>
<th>Langer’s Assignment</th>
<th>Wolf’s Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K\alpha^*$</td>
<td>1s2s – 2s2p$^5$</td>
<td>1s2p$^5$ – 2p$^4$</td>
</tr>
<tr>
<td></td>
<td>1s – 1p</td>
<td>1p – 1s</td>
</tr>
<tr>
<td>$K\alpha_3$</td>
<td>1s2p$^5$ – 2p$^4$</td>
<td>1s2s – 2s2p$^5$</td>
</tr>
<tr>
<td></td>
<td>3p – 3p</td>
<td>3s – 3p</td>
</tr>
<tr>
<td>$K\alpha_4$</td>
<td>1s2s – 2s2p$^5$</td>
<td>1s2s – 2s2p$^5$</td>
</tr>
<tr>
<td></td>
<td>3s – 1s</td>
<td>1s – 1p</td>
</tr>
<tr>
<td>$K\alpha_5$</td>
<td>1s2p$^5$ – 2p$^4$</td>
<td>1s2p$^5$ – 2p$^4$</td>
</tr>
<tr>
<td></td>
<td>1p – 1s</td>
<td>3p – 3p</td>
</tr>
<tr>
<td>$K\alpha_6$</td>
<td>$1s2p^5 - 2p^4$</td>
<td>$1s2p^5 - 2p^4$</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>$1p - 1\text{D}$</td>
<td>$1p - 1\text{D}$</td>
<td></td>
</tr>
</tbody>
</table>

Using Slater’s [89] method of computing interaction energy, Wolfe [88] has calculated the frequencies of these satellites to substantiate his assignment. The calculations were carried out for potassium and it was found that the interchange of electron spins contributed more towards the energy than the spin – orbit interaction energy, which justifies use of the use of Russell – Saunders coupling. Moreover, according to Wolfe’s assignment, the $k\alpha_3$ and $k\alpha_5$ satellites involve transitions between triplet states and should be diffuse which agrees with experiment. Also, the initial configuration 1s 2s of $k\alpha_3$ and $k\alpha_4$ lines, is different from that of the other lines, which explains their greater intensity.

3.2.5 Coster’s and Kronig’s Theory:-

Wentzel’s theory of doubly ionized atoms was very successful in explaining K- series satellites but he was unable to give any satisfactory result for explaining the L and M series satellites. In the Wentzel’s theory, we assume that double ionization takes place due to a single energetically sufficient cathode electron impact, the intensity of the
satellite relation to parent line should increases continuously with increase in atomic number, but it is not true for the L and M ones. Coster [90,91] noted that Lα1 and Lβ2 satellites show their maximum intensity relative to their parent lines at Z = 45, then intensity decreases and at Z = 52 it totally vanishes. After that it re-appears at Z = 74 [95,96]. This baffling paradox was solved by Coster and Kronig [97]. They pointed out that the radiation less auger process of producing double vacancy, which was rejected by Wentzel for the K series satellites due to the reason that the energy needed to eject an L or M electron is comparatively much smaller than that for a K series electrons. Therefore, when an L or M vacancy is being filled by an outer electron of the same sub – level the resulting radiation has got sufficient energy to eject second M or N electron; thus creating two vacancies.

Coster and Kronig [97] noticed that between Z=45 to Z=52 the transition energy L1→L3 is greater than the ionization energy of the M4,5 level. Hence energy of transition L1→L3 can be used up in ejecting an electron from the M4,5 level and L1→L3 becomes radiation less and between Z=52 to Z=74 transition energy is less than the ionization energy of M4,5 level, so here the transition L1→L3 is radiative and double vacancy is produced according to Wentzel’s theory of single electron
impacts Ritchmyer et al [95,96] and Hirsh [93,94] have given a proof of Coster and Kronig theory.

Thus Coster- Kronig theory utilizing the Auger effect was very satisfactory in the high energy x-ray satellites. It becomes more satisfactory as we pass from K to L, M, N, etc. satellites. After its establishment, this theory eclipsed all the other pre-existing theories explaining L, M etc. satellites.

3.2.6 Hayasi’s theory (1961):-

The formation of quasi stationary state has been suggested by Hayasi [98]. During x-ray absorption the ejected K or L electron of the element is reflected by crystal planes and occupies the position in the vicinity of its atom. Close to this atom, a standing wave pattern is set up. Thus several allowed energy levels are formed. The name ‘quasi’ stationary state has been given to these levels. The secondary structure close to the X-ray absorption edge is the result of the transition of inner electron to quasi stationary state.

In 1961, Hayasi’s [99] used this mechanism to explain the various X-ray satellites which are emitted when there are simultaneous transitions in inner energy level and in quasi stationary states. As this process is the
reverse of the process causing secondary structure in X-ray absorption spectra, the energy difference between the satellite and the parent band is given by the energy difference between the two absorption maxima in the corresponding absorption spectra. In support of the above correlation, quite sufficient number of example are found in the literature but the existence of quasi-stationary state is still not fully justified.

3.2.7 – Kakuschadze’s Theory (1961) –

Kakuschadze [100,101] observed that the intensity of the certain X-ray satellites in the iron series, was due to electron phonon interaction. From this relative intensity is temperature dependent. This theory is suitable for the transition metal and their alloys where 3d and 4s energy band overlap. According to Kakuschadze [100] the number of electron passing from s level to d level is same as the electron passing from d level to s level at 0°K. But at higher temperature the number of electron going to s-levels is more than that going to d level. This cause a separate electron layer ΔE to be formed high in the 4s zone, while the Fermi level in the 3d zone is decreased by an amount of energy ΔE. High energy satellites can be attributed to the inner electron transition occurring simultaneously with the outer electron transition from 4s layer.
to 3d band. The transition of electron from 4s to 3d band can yield quanta of energy between 0 and $(\Delta E + \delta E)$.

This will then be energy separation of the satellite and parent band. Kakuschadza has calculated the energy separation of high energy satellite of calcium between 0.3 to 0.6 rydberg. He also calculated the probability of simultaneous outer layer transition, inner transition and found the result varying from unity in Hydrogen, to $10^{-2}$ for Ge. Kakuschadze further confirmed his hypothesis by observing that satellites are more radially obtained when the transition probability is near unity. $\alpha'$ Satellites in Oxygen to Aluminium and $\alpha''$ Satellites in oxygen to aluminium and $\alpha'''$ satellites in Si to V gave a good agreement with this theory.

In his earlier paper [100] Kakuschadze has explained that the distribution of electrons in 3d and 4s bands is effected by electrons interaction and thermal vibration of lattice. This argument was tested by Schorling [102]. Schorling found that the relative intensity of the satellites was not much influenced by the temperature and therefore temperature effect could be neglected.
3.2.8 **Menshikov’s Theory (1962)**

Menshikov [120] suggested that the incident electron beam, on the anode in X-ray tube is not mono energetic. The electrons of the beam are influenced by frequent oscillations. During collision process, K or L shell is ionized. Therefore, when K or L ionization take place in atoms which have already been excited by interaction with such electrons, the emitted radiation has more energy than in the normal case. Satellites may arise due this process is the high energy X-ray Satellites. This theory failed due to lack of experimental evidence. Moreover, satellites in the fluorescent spectra, can not be given by this hypothesis.

3.2.9 **Sachenko’s and Demekhin’s Theory (1966)**

In case of β decay, a rapid change in nuclear charge take place. This cause a rapid change in their energy states. In such process, some electrons become free and the probability [121,122] for an inner and outer electrons becoming free has been proportional to $1/Z^2$ and unity respectively. This auto ionization process can be produced of a transition from a state $\psi_k^0$ of the unperturbed Hamiltonian to the state $\psi_n^0$ of the perturbed one is given by

$$W_{kn} = |\langle \psi_k^0 | \psi_n^0 \rangle|^2$$
Using this theory, Sachenko and Demekhin [123] calculated the probability, for KL ionization of the potassium atom and dependence on atomic number of probabilities of various double ionized states. This idea was originally used in Nuclear Physics by Midgal [122]. Later on Sachenko and Demekhin [123] used this idea for high energy X-ray satellites. From this, the dependence of relative intensity of satellite on atomic number was determined and result was compared with the experimental values of Parratt the agreement was found good upto \( Z=24 \), but above \( Z=24 \), the agreement was poor. The reason for this disagreement was attributed as due to approximation taken in the calculation of probability of non radiative transition. According to these authors, the theory is applicable only when the atom is in free state.

Using this theory, Sawada and Aberg [124] have calculated the intensities of the K-satellites and ionization probability for the ions \( F^- \), \( Na^+ \), \( Cl^- \), \( K^+ \) etc respectively. From these calculation relative intensities have been estimated from KL satellites to \( K\beta_{1,2} \) line and KM satellites to \( Ka_{1,3} \) line. The calculated values have been compared with other theories and observed values. The good agreement shows the effectiveness of this theory.
3.3 - **Plasmon theory of low and high energy X-ray satellites**

Houston [57] and Park [56] and Mahan have pointed out that the interpretation of X-ray emission and absorption experiments must take into account the interaction between suddenly created or annihilated core holes with collective modes of conduction electrons. Thus interaction produces a structure which is displaced from the principal one by the energy \( \hbar \omega_p \), the plasmon energy and is given by [125]

\[
\hbar \omega_p = 28.8 \left( \frac{Z \sigma}{\omega} \right)^{1/2} \text{ ev}
\]

Where \( Z \) is the effective number of electrons taking part in plasmon oscillation, \( \sigma \) is the specific gravity, and \( \omega \) is the molecular weight.

When plasmons are excited during X-ray or Auger electron transition, it will give rise to low energy X-ray satellites. These low energy plasmon satellites are obtained when a valence electron before filling up the vacancy in the inner shell excite a plasmon. The energy of the emitted X-ray photon will be less by an amount \( \hbar \omega_p \) which has been used up in exciting the plasmon.

It has also been shown by several workers that plasmon decay can give its energy to valence or Auger electrons giving rise to a satellite at
an energy distance of $\hbar \omega_p$ on the high energy side of the main X-ray or Auger peak. Such satellites are called high energy plasmon satellites.

The relative intensity of plasmon satellites is different in different processes. It depends upon how the plasmon satellites are excited. There are two processes, one is known as extrinsic process, in which the excitation of plasmon occurs during the transport of electron through the solid and the other is known as intrinsic process, in which the excitation of plasmon takes simultaneously with creation of hole. In the present research work we are confirmed only in the intrinsic process.

Brandshaw et al have further divided intrinsic process into two classes: one where the number of slow electrons is conserved and the other where the number of slow electrons is not conserved. Electrons are termed "Slow" when bound in a core state, or when having a low kinetic energy, just above Fermi level. In the Process where the no. of slow electron are conserved the plasmon satellites will be weak but where the no. of slow electron is not conserved The plasmon satellites will be strong.