ORIGIN OF HIGH AND LOW FREQUENCY *K*-EMISSION SATELLITES

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Hayasi's theory of quasi-stationary states has been used to account for the origin of high and low frequency *K*-emission satellites of ^{37}Rb, ^{39}Y, ^{40}Zr and ^{41}Nb. It has been shown that the same QSS difference gives rise to a particular satellite of either type in all the elements. The results have been compared with those of multiple ionisation theory.

1. Introduction

The subject of X-ray satellite spectra is the most intricate problem in the field of X-ray spectroscopy. The field of X-ray satellites on the experimental side does not seem to be exhausted and the theories regarding their origin do not appear to have, as yet, reached a final decisive stage. A number of reviews summarising the various aspects of the satellites have been made from time to time [1]. The multiple ionisation theory of Wentzel [2] and Druyvesteyn [3] has been most widely accepted to account for the origin of the high frequency satellites. However, in a recent review, Nigam and Mathur [4] have pointed out that about 40% of the high frequency satellites remain unexplained on the basis of multiple ionisation theory and in many cases the agreement between the calculated and experimental values of the wavelengths is not good. Further, as the frequency of a satellite calculated on the basis of multiple ionisation theory of Wentzel and Druyvesteyn always comes out to be more than that of the parent line, the theory is inherently incapable of explaining the low frequency satellites. The present paper is an attempt to explain the origin of high and low frequency satellites of ^{37}Rb, ^{39}Y, ^{40}Zr and ^{41}Nb, using Hayasi's theory of quasi stationary states [5].

2. Calculations

Hayasi's theory of extended X-ray absorption fine structure (EXAFS) [6] suggests that in the process of *K* excitation of atoms by X-irradiation of solid crystals, the specification of the final states requires a two fold axis of symmetry for the wave function. The

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propagation sphere in the reciprocal lattice must pass through two points located so that the sum of the propagation vectors vanishes. Accordingly, during the K absorption of X-rays the ejected photoelectron will endure a total reflection ($\theta = 90°$) by certain crystal planes producing a standing wave pattern in the vicinity of the parent atom. This leads to the existence of a number of energy states called quasi stationary states (QSS). According to Hayasi's theory [5], when a transition between inner atomic levels takes place together with a transition of an excited electron between two QSS, a satellite is emitted. As this process is obviously reverse of that which causes the EXAFS in the X-ray absorption spectra, the energy difference between a satellite and the parent line must be equal to the energy difference between two absorption maxima appearing in the EXAFS of the element to which the parent line belongs. As we propose to apply this theory to the low frequency satellites also, we write

$$E_{\text{satellite}} \sim E_{\text{parent line}} = \Delta E_{(\text{between two QSS})} = \Delta E_{(\text{between two EXAFS maxima}).} \quad (1)$$

The mechanism by which high and low frequency satellites are emitted is diagramatically represented in Fig. 1. Accordingly, when a transition takes place from a higher energy QSS to a lower energy QSS simultaneously with the transition corresponding to the emis-

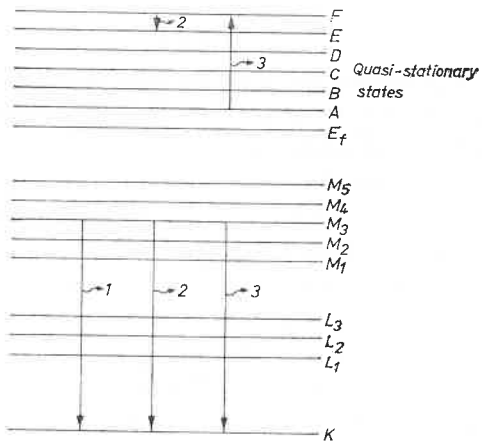

Fig. 1. Energy level diagram (not to scale) for the emission of satellites of parent $K\beta_1$ line. 1 — Parent dipole line $K\beta_1$, 2 — High frequency satellite $K\beta_7$, 3 — Low frequency satellite $K\beta_8$

sion of parent line (dipole line), a high frequency satellite is emitted. Similarly, when a transition from a lower energy QSS to higher energy QSS takes place simultaneously with the transition corresponding to the parent line, a low frequency satellite is emitted.

A necessary requirement of this theory is the knowledge of the accurate data of the EXAFS maxima of the element in metallic form. The EXAFS data for the K-absorption spectra of ^{37}Rb, ^{39}Y, ^{40}Zr and ^{41}Nb metals have been recently made available. Hence, we thought it to be of considerable interest to use Hayasi's theory to explain the high and low frequency satellites of these elements.

TABLE I

Comparison between the observed and the calculated energies (in eV) for the EXAFS maxima in the K-absorption spectra of ^{37}Rb, ^{39}Y, ^{40}Zr and ^{41}Nb

EXAFS maxima	^{37}Rb			^{39}Y			^{40}Zr			^{41}Nb		
	Reflecting plane	Energy of the QSS, calculated with the help of Eq. (2), from K-edge	Experimental energy position of the EXAFS maxima from the K-edge [9]	Reflecting plane	Energy of the QSS, calculated with the help of Eq. (3), from the K-edge	Experimental energy position of the EXAFS maxima from the K-edge [7]	Reflecting plane	Energy of the QSS, calculated with the help of Eq. (3), from the K-edge	Experimental energy position of the EXAFS maxima from K-edge [9]	Reflecting plane	Energy of the QSS, calculated with the help of Eq. (2), from the K-edge	Experimental energy position of the EXAFS maxima from K-edge [8]
A	(311)	12.7	12.5	(110)	11.27	11.1	(112)	20.0	23.2	(200)	13.77	16.21
B	(422)	27.7	27.2	(203)	25.31	22.0	(220)	57.4	54.8	(310)	34.42	34.42
C	(620)	46.2	47.7	(212)	30.88	31.6	–	–	–	(400)	55.07	55.15
D	(644)	78.5	80.0	(302)	38.39	40.6	(410)	100.5	100.4	(521)	103.26	96.33
E	(860)	115.4	115.8	(221)	46.51	46.4	(600)	172.3	161.9	(620)	137.68	138.50
F	(884)	166.2	165.7	(312)	53.43	53.9	(440)	229.8	230.7	(444)	165.22	166.15
G				(402)	64.70	66.6				(730)	199.64	196.27
H				(322)	75.98	75.9						
I				(412)	83.49	86.7						
J				(502)	98.53	97.0						

Notes: Lattice parameters used in the calculations have been taken from Taylor and Kagle [11]: Rubidium – f.c.c., $a = 5.70$ Å, Yttrium – h.c.p., $a = 3.6474$ Å, $c = 5.73006$ Å, Zirconium – h.c.p., $a = 3.232$ Å, $c = 5.14756$ Å, Niobium – b.c.c., $a = 3.3007$ Å.

Experimental and calculated wavelengths (in X.U.) of the

S. No.	Satellite	Parent line of the satellite	Transitions between two QSS assigned on the basis of Hayasi's theory (present work)	Transitions assigned on the basis of multiple ionisation theory [4]	^{37}Rb		
					Experimental value [10]	Hayasi's theory (present work)	Multiple ionisation theory*
	High frequency satellites						
1	α_3	α_1	(D−B)	$KL_2 \rightarrow L_2L_3$	–	–	–
2	α'_3	α_1	(E−D)	$KL_1^2 \rightarrow L_1^2L_3$	920.8	921.17	922.41
3	α_4	α_1	(F−E)	$KL_3 \rightarrow L_3^2$	919.9	920.21	915.02
4	β_7	β_1	(F−E)	$KM_3 \rightarrow M_3^2$	824.2	824.21	825.77
5	β_6	β_1	(E−B)	$KL_3 \rightarrow L_3M_3$	821.7	822.09	821.72
6	β_8	β_1	(F−A)	$KL_1 \rightarrow L_1M_3$	817.6	818.58	820.84
7	$\beta''_{II}(\beta_{II})$	β_2	(D−A)	–	811.8	811.15	–
	Low frequency satellites						
8	α_s	α_2	(D−F)	–	933.6	933.76	–
9	β_s	β_1	(A−F)	–	834.8	835.51	–
10	$\beta_0(\eta)$	β_1	(D−F)	–	831.8	831.72	–

* Values calculated by us using energy level values of Bearden and Burr [16].

The data for the EXAFS maxima occurring at the K — absorption edge of metallic yttrium and niobium have been reported by Bhide and Bhat [7] and Bhide and Bahl [8], respectively, and for metallic rubidium and zirconium by Johri and Agarwal [9]. Their data are collected in Table I and these have been used for present calculations. In the case of ^{40}Zr we have, however, redesignated the maxima C, D and E as D, E and F respectively. The experimental values of the wavelengths of the K-satellites and the parent lines have been taken from the recently published X-ray wavelength tables of Cauchois and Senemaud [10] and are given in Table II.

The eigenvalues of the p-QSS have been also calculated by us on the basis of Hayasi's theory [6] as follows.

According to Hayasi [5], the energy (in eV) of the QSS for a cubic crystal is given by

$$E_{hkl} = 150[(h^2+k^2+1^2)/4a^2], \tag{2}$$

where (h, k, l) are Miller's indices of the reflecting planes and a is the length of the unit cell of the cube.

We need to consider only those reflecting planes for which structure factor F has the maximum value i.e., $4f$ where f is the atomic scattering power, all the atoms being identical. It can be seen that the planes which give $F = 4f$ should have even values for $(h+k)$, $(h+l)$ and $(k+l)$ and such planes allow the existence of QSS [12]. Using Eq. (2), the energy

TABLE II

K-emission satellites of ^{37}Rb, ^{39}Y, ^{40}Zr and ^{41}Nb

^{39}Y			^{40}Zr			^{41}Nb		
Experimental value [10]	Hayasi's theory (present work)	Multiple ionisation theory*	Experimental value [10]	Hayasi's theory (present work)	Multiple ionisation theory*	Experimental value [10]	Hayasi's theory (present work)	Multiple ionisation theory*
–	–	–	782.0	782.03	783.80	–	–	–
824.5	826.80	825.59	781.6	781.25	782.59	742.1	742.76	743.34
823.7	826.70	819.33	781.16	780.89	776.99	741.69	743.41	738.0
736.7	738.86	737.85	697.9	697.56	699.02	662.2	663.39	663.33
734.7	738.11	733.87	695.9	696.06	695.75	660.5	660.69	659.73
730.0	737.30	733.53	691.0	692.15	695.05	655.4	659.07	659.47
724.6	725.87	–	685.6	685.55	–	649.7	650.05	–
837.9	832.06	–	795.3	795.31	–	755.7	752.07	–
747.7	741.08	–	709.0	708.60	–	672.7	669.77	–
744.2	739.77	–	705.1	705.48	–	669.2	666.88	–

values of p-QSS for the f.c.c. ^{37}Rb and b.c.c. ^{41}Nb have been calculated and are given in Table I. The values of lattice parameters for these metals are also given in Table I.

At room temperature yttrium and zirconium crystallise in h.c.p. structure and for this structure Eq. (2) can be suitably modified and written as

$$E_{hkl} = (50/a^2)(h^2+k^2+hk)+37.5l^2/c^2. \tag{3}$$

Here again we need to consider reflections from only those planes for which crystal structure factor does not vanish [12]. Our calculated values of the p-QSS for ^{39}Y and ^{40}Zr are given in Table I.

Comparing the calculated energy eigen values of the p-QSS with the experimentally observed values of the energy corresponding to the EXAFS maxima (Table I), it is clear that the agreement is indeed good. This also shows the validity of using the observed values of EXAFS maxima for the energies of QSS in calculating the wavelengths of the *K*-satellites with the help of Eq. (1). Though the values of p-QSS were also calculated by Bhide and Bhat [7] and Bhide and Bahl [8] for yttrium and niobium, respectively, they have used the values of lattice constants as given by Wyckoff [13] while we have used constants given in a later publication of Taylor and Kagle [11]. It can be seen that our designation of reflecting planes gives better agreement with experiment.

3. *Assignment of transitions to satellites*

We have assigned the K_α satellites α_3, α_3' and α_4 to electron jumps between the QSS (D–B), (E–D) and (F–E), respectively, the jumps occurring simultaneously with the transition between inner atomic energy levels which gives rise to the parent line $K\alpha_1$. The $K\beta$ satellites β_7, β_6 and β_8 have been attributed to EXAFS maxima differences (F–E), (E–B) and (F–A), respectively, with the parent line $K\beta_1$. The satellite $\beta_{II}''(\beta_{II})$ is found to correspond to the maxima difference (D–A) with the parent line $K\beta_2$. Here, for all the satellites (except $\beta_{II}''(\beta_{II})$) the parent lines used by us are the same as those assigned by Nigam and Mathur [4] on the basis of multiple ionisation theory. However, these authors have not assigned any parent line to the satellite $\beta_{II}''(\beta_{II})$. The parent line assigned to the satellite $\beta_{II}''(\beta_{II})$ by us is the same as that reported by Deodhar [14].

Among the low frequency satellites, the $K\alpha$ satellite α_s has been attributed to the electron jump between the QSS(D–F), the jump occurring simultaneously with the transition responsible for the parent $K\alpha_2$ line. Other low frequency satellites β_s and $\beta_0(\eta)$ have been found to correspond to the QSS differences (A–F) and (D–F), respectively, with parent line $K\beta_1$. An inspection of Table II shows that the wavelengths calculated by us on the basis of Hayasi's theory are in good agreement with the experimental values in both types of satellites.

4. *Discussions*

The occurrence of high frequency K-satellites has also been explained by Nigam and Mathur [4] on the basis of multiple ionisation theory of Wentzel and Druyvesteyn. For calculations they have used the energy level values of Sandström [15], instead of the more recent and accurate values given by Bearden and Burr [16]. Hence, we have calculated the wavelengths for the transitions assigned by them using the energy level values of Bearden and Burr [16]. It can be seen from Table II that for high frequency satellites, the agreement between calculated and experimental values is, in most of the cases, better with Hayasi's theory in comparison to the multiple ionisation theory.

Though Hayasi's theory has been used by several authors to explain the origin of satellites, the main objection against it has been that the number of QSS differences greatly exceeds the number of satellites, so that some correspondence is inevitable [1]. This objection has been raised, perhaps because Hayasi's theory has been applied only in a few scattered cases of ^{12}Mg, ^{13}Al, ^{39}Y, ^{47}Ag and ^{48}Cd [5, 17–23]. It seems that no attempt has been made to correlate the results of one element with another in the past till we, recently, applied Hayasi's theory to the rare earth series and showed that the same QSS difference gives rise to a particular satellite in all the elements [24]. This observation is further substantiated in the present paper. It can be seen from Table II that the same QSS difference gives rise to a particular satellite in all the elements. Hence, the assignment of transitions is not arbitrary in our case.

Rai and Rai [17] have also applied Hayasi's theory to explain the high frequency K satellites of yttrium. However, they have not applied the theory to low frequency satellites

and also their assignment of transitions between the QSS seems to be arbitrary. They have also changed the parent lines of some $K\beta$ satellites. The transitions between the QSS assigned by us are not arbitrary because the same transitions have been assigned by us in all the elements under study as already mentioned above.

As already pointed out in the introduction the low frequency satellites cannot be explained on the basis of multiple ionisation theory. However, in recent years attempts have been made to explain the origin of some of the low frequency satellites on the basis of multiple ionisation theory. But a careful examination shows that in such cases either the parent line has been altered or the agreement between the experiment and theory is not good. For example Deodhar and Rai [25] have attributed the satellite $L\gamma_{10}$ to the transition $L_1M_3 \rightarrow M_3N_1$ with L_1N_1 as the parent line. Now, $L\gamma_{10}$ is a low frequency satellite of $L\gamma_2$ line while Deodhar and Rai have treated it to be high frequency satellite of the forbidden transition L_1N_1. According to them if initially an atom is in the doubly ionised state L_1M_3 then a transition from N_1 to L_1 state will leave the atom in the doubly ionised state M_3N_1 and give rise to the satellite $L\gamma_{10}$. As the emission rate of L_1N_1 is only about 10^{-5} times that of $L\gamma_2$ line [26], it is very doubtful that electron jump from a N_1 to a L_1 level (in doubly ionised state of the atom) will be able to give rise to an intense satellite like $L\gamma_{10}$.

The other examples are the assignments of Nigam and Mathur [4] in the case of $L\gamma_9$ and $L\beta_{14}$ satellites. In the case of the former these authors have changed the parent line from $L\gamma_1$ to $L\gamma_5$, thus treating $L\gamma_9$ as the high frequency satellite of $L\gamma_5$ line instead of it being the low frequency satellite of $L\gamma_1$. In the case of other satellite $L\beta_{14}$, the agreement between experiment and theory is shown to be poor. Various other mechanisms have been proposed to explain the low frequency satellites, by Hulubei [27], Utriainen et al. [28] and Sawada et al. [29]. The mechanism proposed by Hulubei is based on the conception of radiationless forbidden transitions and has been tested only in the case of Zn and As by Groven and Morlet [30]. Utriainen et al. have interpreted some low frequency $K\alpha$ and $K\beta$ satellites in terms of the radiative Auger effect. Sawada et al. have attributed the low frequency $K\eta$ satellites to $(1s)^{-1}\ (2p)^{-1}\ {}^{1,3}P \rightarrow (2s)^{-1}(3s)^{-1}\ {}^{1,3}S$ transitions. This implies strong configuration mixing between the $(2p)^{-2}$ and$(2s)^{-1}(3s)^{-1}$ configurations and the result of this transition is a doublet structure contrary to the observations. In the present paper we have attempted to use Hayasi's theory to explain the low frequency satellites and it is seen that the agreement between the calculated and experimental results is good.

We would like to mention here that we very much wanted to correlate the intensities or transition probabilities of the EXAFS maxima with those of the satellites so as to give our assignment of the satellites a theoretical basis. But, due to lack of availability of such data it has not been possible to attempt such a correlation at present. We also very much wished to include in our study other elements of the second transition series but sufficient EXAFS data for these is also not available. It is encouraging to note that very recently, it has become possible to obtain accurate EXAFS data using synchrotron radiation [31] and it is hoped that in the near future accurate EXAFS data will become available for most of the metals. It may then become possible to apply the presently proposed mechanism

to a number of other cases and to test this unified theory of the low and high frequency satellites.

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