Shake-down Satellites on core-level regions of the XPS for Europium (III) Compounds

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Abstract— We have observed "shake-down" and "shake-up" satellites evidenced on core-level regions of the XPS binding energy data base for europium(III) compounds, in which Eu cation have various chemical environments: simple oxide Eu2O3 , Eu mixed oxides with organic oxalate, acetylacetonate [Eu(CH3COOCH3)3] or inorganic sulfate [Eu2(SO4)3] , Nitrate [Eu(NO3)3] , carbonate [Eu2(CO3)3 , Eu2(C2O4)3] ligands.

Index Terms— Surface Plasmon Satellites, Relative Intensity & Energy Separation

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INTRODUCTION

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). First Siegbahn & Stenstroem observed these satellites in the K-Spectra of element from Cr (24) to Ge (32) while coster theraeus & Richtmyer in the L-Spectra of element from Cu (29) to Sb (51) & Hajlmar, Hindberg & Hirsch in the M-Spectra of elements from Yb (70) to U (92). Several theories were proposed from time to time to explain the origin of these satellites. Out of these theories the plasmon theory is found to be the most suitable theory especially for those satellites.

Plasmon theory was first proposed by Bohm & pines which are extended by Housten, Ferrel, Noziers & Pines. According to this theory the low energy plasmon satellites are emitted when valence electron excites a plasmon during the annihilation of core hole conversely if Plasmon pre exists, its energy add up to the energy of diagram line.The radiation less reorganization of electronic

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shell of an atom is known as Auger effect. Auger satellites have also been observed by Korbar and Mehlhorn [1] Haynes et at. [2] Edward and Rudd [3]. Theoretical explanation for K series Auger spectrum was given by Burhop and Asaad [4] using intermediate coupling. Later on more refined theory, using relativistic and configuration interaction has been used by Listengarter [5] and Asaad [6]

In Auger primary spectra, one can also observe secondary electron peaks close to the primary peaks are produced by incident electrons which have undergone well energy losses. The most common source of such energy loss in the excitation of collective plasma oscillations of the electrons in the solid. This gives rise to a series of plasma peaks of decreasing magnitude spaced by energy $\hbar\omega_p$ where ω_p is the frequency of plasma oscillation.

Auger peaks are also broadened by small energy losses suffered by the escaping electrons. This gives rise to a satellite on the low energy of the Auger peak. Energy loss peaks have well defined energy with to primary energy.

The involvement of Plasmon oscillation in the X-ray emission or absorption spectra of solids has been widely studied during the last few decades and has been recognized that the electron –electron interaction has played an important role.

This Paper is devoted to Plasmon theory to explain the Energy Satellites and relative intensity of "shake-down" and "shake-up" satellites evidenced on core-level regions of the XPS binding energy data base for europium(III) compounds, in which Eu cation have various chemical environments: simple oxide Eu_2O_3 , Eu mixed

oxides with organic oxalate, acetylacetonate [$Eu(CH_3COOCH_3)_3$] or inorganic sulfate [$Eu_2(SO_4)_3$] , Nitrate [$Eu(NO_3)_3$] , carbonate [$Eu_2(CO_3)_3$, $Eu_2(C_2O_4)_3$] ligands.

According to Plasmon theory , if the valence electron , before filling the core vacancy , also excites a Plasmon ,then the energy $\hbar\omega_p$ needed for the excitation of Plasmon oscillation is taken from the transiting valence electron so that the emitted radiation will be derived off an energy $\hbar\omega_p$ and a low energy satellites will emitted whose sepration from the main X-ray line will correspond to $\hbar\omega_p$. On the other hand if the Plasmon pre exists , during the X-ray emission process , then , on its decay it can give its energy to the transiting valence electron before it annihilates the core vacancy . Thus the energy of emitted X-ray photon will be higher than the main emission line and by an amount $\hbar\omega_p$ giving rise to high energy satellite .

MATHEMATICAL CALCULATION –

In order to confirm the involvement of Plasmon in the emission of X-ray satellites the relative intensity of single Plasmon satellites must be calculated . In this process first we deal with mathematical details of canonical transformation carried out over the model Hamiltonian of the system . Thus the energy separation ΔE of the low and high energy Plasmon satellite from the corresponding main line should be equal to the quantum of Plasmon energy $\hbar\omega_p$ which is given by [10]

$$\Delta E = \hbar\omega p = 28.8 \ \sqrt{\left(\frac{Z.\sigma}{w}\right)} \text{ev} \qquad 1$$

Where Z = No.of unpaired electrons , σ = Specific gravity & ω = Molecular Weight

This equation can be derived as given below .

From the classical consideration , we get the frequency of Plasmon oscillation as

$$\omega p = \left(\frac{4\pi n e^2}{m}\right)^{1/2} \qquad 2$$

Hence the amount of energy given to Plasmon becomes

$$E_p = \hbar\omega_p = \hbar \ \left(\frac{4\pi n c^2}{m}\right)^{1/2}$$

In this equation we can write $n = \frac{L\sigma Z}{w}$

Where σ , Z and W are defined above and L is the Avogadro number .By putting the numerical value of constant , we get the Plasmon energy as

$$\Delta E = \hbar\omega p = 28.8 \ \sqrt{\left(\frac{Z.\sigma}{w}\right)} \text{ev} \qquad 3$$

Our calculated values of ΔE have been compared with the Scrocco's experimental value. And We have also calculated the relative intensity of plasmon satellites, which is different in different processes. If the excitation of plasmon occurs during the transport of the electron through the solid, it is known as extrinsic process of plasmon excitation. The plasmon can also be excited by another method known as intrinsic process. In this process, excitation of plasmon takes place simultaneously with creation of a hole. Bradshaw et al have further divided core hole excitation into two classes,

1 - Where the number of slow electrons are conserved.

2 - Where the number of slow electrons are not conserved

The Author has calculated relative intensity in both the cases with new modification in the light of Bradshaw [12] and Lengreth [13] work, which explains that not only intrinsic process but extrinsic process and their relative contribution may also contribute in relative intensities. The combined effect of intrinsic and extrinsic plasmon excitation intensity variation was suggested by Lengreth as**:**

$$i = \frac{Is}{Im} = \alpha^n \sum_{m=0}^{n} \frac{\left(\frac{\beta}{\alpha}\right)^m}{m!} \qquad 4$$

The value of β is taken as $\beta = 0.12r_s$ which is purely intrinsic, $r_s = (47.11/\hbar w_s)^{2/3}$ is dimensionless parameter and $\alpha = 0.47\ r_s^{1/2}$ in the place of $\alpha = (1+l/L)^{-1}$ used by Pardee et. al.(14) . The equation (3) contains a series of terms. The first term of the equation is purely extrinsic, while second term is purely intrinsic. The other terms are containing the relative contributions of both extrinsic and intrinsic. The specialty of this formula is that each term alone or simultaneously with other terms is able to give the relative intensity. This formula also includes both the categories mentioned by Bradshaw and gives better results as compared than traditional methods for calculation of the relative intensity. Using the values of α, β and rs in equation (4)

Using the equation (4), the author has for the first time, calculated the relative intensity of Shake down satellites in Europium (III) compounds and Our calculated and estimated values are in agreement with the calculated values of F. Mercier & its associate   [15,16] (2005)

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Table -1 Energy sepration ΔE of Eu4d photoelectron peak, of its associated shake-down Kα Satellite

S.No.	Compounds	Z	σ	ω	Author's Calculated Plasmon Energy Separation (ΔE_s)	Experimental value of Energy Separation Ref. [133,134]
1	Eu_2O_3	2	351.93	7.40	5.91	6.4
2	$Eu(CH_3COOCH_3)_3$	3	374.2	7.89	7.24	7.1
3	$Eu_2(C_2O_4)_3$	3	567.99	11.98	7.24	7.1
4	$Eu_2(CO_3)_3$	3	483.95	10.21	7.24	7.4
5	$Eu_2(SO_4)_3$	4	592.12	12.49	8.36	9
6	$Eu(NO_3)_3$	5	592.12	12.49	9.35	10.2
7	EuF_3	4	208.96	4.41	8.36	9.9
8	$EuCl_3$	5	258.32	5.45	9.35	9.60

Table – 2 Relative Intensity of Eu4d photoelectron peak, of its associated shake-down Kα Satellite

S.No.	Compounds	ΔE_s	R_s	Alpha (α)	Beta (β)	Author Calculated Relative Intensity	Experimental value of Relative Intensity Ref.	Intensity assignment
1	Eu_2O_3	4.18	5.03	1.054	0.6035	0.2785903	0.24	$\beta-0.1-\beta^2/2\alpha-\beta^3/6\alpha^2$
2	$Eu(CH_3COOCH_3)_3$	5.12	4.39	0.984	0.5267	0.2650213	0.29	$\beta-0.1-\beta^2/2\alpha-\beta^3/6\alpha^2$
3	$Eu_2(C_2O_4)_3$	5.12	4.39	0.984	0.5267	1.3770302	1.43	$2*(\beta+\beta^2/2\alpha+\beta^3/6\alpha^2)$
4	$Eu_2(CO_3)_3$	5.12	4.39	0.984	0.5267	0.1650213	0.19	$\beta-0.2-\beta^2/2\alpha-\beta^3/6\alpha^2$
5	$Eu_2(SO_4)_3$	5.91	3.99	0.938	0.4786	0.1503615	0.13	$\beta-0.2-\beta^2/2\alpha-\beta^3/6\alpha^2$
6	$Eu(NO_3)_3$	6.61	3.7	0.904	0.4442	0.1371624	0.11	$\beta-0.2-\beta^2/2\alpha-\beta^3/6\alpha^2$
7	EuF_3	5.91	3.99	0.938	0.4786	0.1503615	0.19	$\beta-0.2-\beta^2/2\alpha-\beta^3/6\alpha^2$
8	$EuCl_3$	6.61	3.7	0.904	0.4442	0.2371624	0.27	$\beta-0.1-\beta^2/2\alpha-\beta^3/6\alpha^2$