X-ray Satellites spectra in core level 2p peaks of transition metal oxides

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Abstract- We have used Plasmon theory to explain the Energy Satellites and relative intensity of transition metal oxides based on their core level peaks. In the photoelectron spectrum, these regions are usually complicated and therefore the choice of the analysis methods can significantly affect the quantification results. In this work, we studied the chemical state quantification of iron and chromium oxides the analysis was based on the 2p region of the photoelectron spectrum and estimated values are in agreement with the calculated values of M. Aronniemi *, J. Sainio, J. Lahtinen

Keywords; X-Ray emission spectra ,X-ray Plasmon Satellite , Iron oxide; Chromium oxide

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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 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

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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 transition metal oxides (iron and chromium oxides) based on their core level 2p peaks and estimated values are in agreement with the calculated values of M. Aronniemi *, J. Sainio, J. Lahtinen.

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 .

M. Aronniemi, J. Sainio, J. Lahtinen have observed low and high energy satellite peaks in transition metal oxides (iron and chromium oxides) . A close approximation of their tables shows that some satellites are at a distance of $\hbar\omega_p$ (Plasmon energy) from the main emission line . This observation forced us to think that these might be due to Plasmons emission and absorption .

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 taking part in plasma oscillation

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

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

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

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

And The Surface Plasmon Energy

$$E_s = E_p / \sqrt{2} \qquad 4$$

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 of non conserved slow electron The relative intensity of the X-ray plasmon satellites $K\alpha'$ has been calculated by calculating the transition probability p(w) per unit time per unit energy range at energy $\hbar\omega_p$ for the emission of a plasmon satellites and is given by [23]

$$p(\omega) = |f|^2\, \Sigma\, e^{-\alpha} (\alpha^n/n!)\, \Delta\, (\omega - \Sigma - \alpha\omega_p + n\omega_p\ ) \qquad 5$$

where α the coupling parmeter is given by

$$\alpha = (e^2 q_{max} / \pi\hbar\omega_p) = 0.12\, r_s \qquad 6$$

And $|\,f\,|$ is the matrix element for the process ,q_{max} is the cutt off wave vector and r_s is a dimensionless parameter given by

$$r_s = (\,47.11 / \hbar\omega_p)^{2/3} \qquad 7$$

Thus the relative intensity of the first plasmon peak to the main peak is given by

$$i_1 = (i_1 / i_0)$$

$$= [(e^{-\alpha} \alpha^1 / 1!) / (e^{-\alpha}\alpha^0 / 0!)]$$

$$= \alpha$$

$$=0.12 r_s \qquad 8$$

The coupling constant α can be further modified by taking account the effect of slow fast binterference terms which produce the cancellation when when the slow charge is conserved . The effect of the interference is to be modified α to a new coupling constant [30]

$$\alpha' = \alpha - (e^2 / hv) F$$

$$= \alpha - 0.1$$

$$=0.12 r_s - 0.1 \qquad 9$$

Using equation 1.5 and 1.6 the modified relative intensity will be

$$i = 0.12\, r_s - 0.1 \qquad 10$$

Using the equation (10), the author has for the first time, calculated the relative intensity **of** transition metal oxides (iron and chromium oxides). Our calculated and estimated values are in agreement with the calculated values of M. Aronniemi, J. Sainio, J. Lahtinen.

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Energy sepration ΔE Of transition metal oxides on their core level 2p peaks

S.No.	COMPOUNDS	Z	w	Sp.Gravity	Exper. Value [14]	Author Value
1	Fe_2O_3	3	159.69	5.2	8.7	9.00
2	Fe_3O_4	2	231.53	5	5.7	5.99
3	Cr_2O_3	3	151.99	5.22	9.8	9.24
4	CrO_3	2	99.99	4.88	9.1	9.00

Relative Intensity of transition metal oxides on their core level 2p peaks

S.No.	COMPOUNDS	Author intensity	Exp. Intensity [14]
1	Fe_2O_3	0.36	0.55
2	Fe_3O_4	0.47	0.52
3	Cr_2O_3	0.36	0.40
4	CrO_3	0.36	0.28