Original Contribution

EXTRINSIC AND INTRINSIC PLASMON EFFECTS IN $2P_{1/2}$ X-RAY PHOTOEMISSION SATELLITES OF SCANDIUM AND TITANIUM COMPOUNDS

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ABSTRACT

The origin of high energy x-ray satellites of $2p_{1/2}$ main line in compounds of scandium and titanium has been explained using plasmon theory with a new approach by considering relative coupling of extrinsic and intrinsic plasmon effects. The present calculation of relative intensity shows superiority over the method of calculation of K.S. Srivastava et.al. We also review existing calculations and measurements.

Key words: plasmon, satellites, extrinsic and intrinsic effects, relative intensity.

INTRODUCTION

The origin of collective oscillations of free electron gas in solids is well known since early days of X- ray photoemission. In a pioneered theoretical investigation, Bohm and Pines [1-2] suggested that beyond Debye length, electrons in a solid behaves collectively and oscillate with frequency called plasma frequency $\omega_p = (4\pi ne^2/m)^{1/2}$ where n = electron density, m = effective mass of electrons, e = charge of electron. These collective oscillations of free electron gas are called plasma oscillation. Generally speaking; this electron gas or sea of conduction electrons refers to the bulk of material which has properties that allow the assumption of condition electrons acting as a free electron gas. During X- ray photoemission process (XPS) the solid absorbs an incident photon and emits an electron form the core level. The out going electron may suffer energy losses before escaping out of the material. This energy loss process is quantized and quantum of energy is called plasmon. Thus, the energy loss spectrum (ELS) shows zero loss peak centered at E_0 and satellite peak at $E_0 -\hbar\omega_p$, $E_0 -2\hbar\omega_p$, $E_0 -3\hbar\omega_p$ etc., where $\hbar\omega_p$ is plasmon energy.

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The emission line owing to this process is called *Low Energy Satellites*. However, if plasma pre- exist, then during X- ray photoemission process it can transfer its energy to the transiting photoelectron before escaping out of the material. Thus, the energy of emitted photoelectron will be higher than the energy of main peak E_0 by an amount equal to the plasmon energy and satellites are observed at an energy separation $E_0 +\hbar\omega_p$, $E_0 +2\hbar\omega_p$, $E_0 +3\hbar\omega_p$ etc. The emission line owing to this process is called *High Energy Satellites*. Plasmon theory has been proved very successful in explaining the origin of all low and high energy satellites which are found at an energy separation of $\hbar\omega_p$ (plasmon energy) from the main emission X- ray line. High energy satellites $2P_{1/2}$ and $2P_{3/2}$ main lines of Sc and Ti compounds were observed by de. Boer et.al. [3]. They proposed an anion polarization model for their origin and calculated the relative intensity using the formula as- $I/I_0 = Ep/\Delta E$, where E_p = Polarization energy and ΔE = observed energy separation. But this equation gives the same relative intensity satellites of both $2P_{1/2}$ and $2P_{3/2}$ main line, which is experimentally incorrect. Again the energy separation, the important parameter of satellites, for neither $2P_{1/2}$ nor $2P_{1/2}$ satellites could be calculated from anion polarization theory. Srivastava et. al. [4-5] applied plasmon

theory calculated better results as compared to de. Boer et. al. [3], but with limited success. In relative intensity calculation Srivastava et.al. [5] applied approximation method, which is limited to intrinsic case, where the number of slow electrons is not conserved. These satellites were also observed by several workers [6-10] and they tried to explain their origin, but much confusion exists in their interpretation. The most persistent explanation is charge transfer [11] from a ligand p to metal 3d level, just as in the other first row transition metal compounds, but this explanation is not supported, because the energy separation of satellite is larger than expected from optical transition energies and molecular calculations. Furthermore, for the charge transfer satellites, the energy separation is expected to decrease in the series CaO, ScO_2 and TiO_2; e.g. instead of the observed increase. Moreover, a study of the X- ray photoemission spectra of titanium compounds revealed the existence of weaker satellites at smaller distances in accordance with optical charge transfer excitations [9-10,12-13]. An argument that the main satellites reflect transfer from outer p to metal 4s, p- orbital's [7, 14-15] is supported by the appearance of the same kind of transition about the same energy in the optical spectra [16-18] and a similar energy separation predicted by molecular calculation [7, 14-15,19]although the calculated spectral intensity is too small. However, the molecular orbital calculations appear to be inadequate to explain the observed main satellite intensity which is much larger than the predicted value. Although, the origin of these satellites can be explained by different theoretical models, but plasmon excitation model is most suitable model for all the satellites, which are observed in plasmon energy range (4ev to 20eV). In the present paper we have applied plasma oscillation theory but with a new approach by considering intrinsic and extrinsic effects simultaneously.

Plasma oscillations are two types- Bulk plasmon and Surface plasmon. Bulk plasmons are longitudinal oscillation mode of the electron gas in the solid and are given by condition $\varepsilon = 0$, where ε is bulk dielectric function. The collective oscillations of electron gas on the interface between a metal and dielectric are known as surface plasmons. Surface plasmons are an oscillating sheet of charge located at the surface, although its energy is associated by bulk property $\varepsilon = -1$. The plasmon energy can be calculated by using formula given by Marton et.al. [20] as:

$$\hbar\omega_p = 28.8 \ (Z'\sigma/W)^{1/2} \qquad (1)$$

Where Z'= effective number of electrons taking part in plasma oscillation, σ = specific gravity, W = molecular weight of compounds. The surface plasmon energy can be calculated using formula given by Ritchie [21] as-

$$\hbar\omega_S = \hbar\omega_p \ /\sqrt{2} \qquad (2)$$

The calculated values of plasmon energy are shown in **Table 1**. A comparison has been also made in the tables for calculated values in present case with the experimental values [3]. It can be observed from the energy separation table that plasmon energy (energy separation of satellites) compare well with the experimental estimates. From energy separation calculation, the satellites can be regarded as due to plasmon excitation.

Table 1: Energy separation calculation (eV)

Compound	Z'	σ	W	Energy separation Present work		Exptl. by de. Boer et.al. [3]
				$(\hbar\omega_p)$	$(\hbar\omega_s)$	
ScF3	6	6.5	101.96	11.0		12.3
TiF4	8	2.79	123.89	12.3		13.4
*K2TiF6		-	-	-		7.3
*ScI3	6	-	425.67	-		7.4
TiI4	8	4.30	555.50	7.2		7.3
ScBr3	6	3.91	284.85	8.3		8.6
TiBr4	8	2.60	367.54	6.9		8.7
ScCl3	6	2.39	151.54	8.9		9.6
TiCl4	8	2.06	189.7	8.5		9.6
Sc2O3	12	3.86	138.20	-	11.8	11.2
TiO2	8	4.86	79.90	-	13.3	13.4

*Could not be calculated due to non- availability of constants.

EXTRINSIC AND INTRINSIC PLASMON EFFECTS

The physics of plasma excitation in photoemission is very interesting because different processes contribute to its intensity. The sudden change in the potential due to formation of a core hole attracts the conduction electrons to screen the core- hole resulting, in the *intrinsic plasmon* excitation. Plasma excitations are two types- intrinsic and extrinsic. Intrinsic plasmon is caused by the coupling of positive core- holes, created by ejection of core electrons from their orbitals, with the collective electron oscillation of the conduction electron gas simultaneously with the photoemission process at the location of initial photon- electron interaction. As a result the photoelectron is ejected with less energy $\hbar\omega_p$ or $\hbar\omega_s$ (or multiple of this energy) depending on the place of interaction, i.e. the bulk or surface region than it would have if coupling had not occurred. Photoelectrons that stem from intrinsic plasmon excitation belong to the intrinsic (primary) electron emission spectrum together with the main peak, and its asymmetric tail which is caused by an intrinsic process too, namely the reduction of kinetic energy of the photo- emitted electrons due to scattering of conduction electrons by positive core- hole.

On the other hand extrinsic plasmon excitation is created by Coulomb interaction of conduction electron traversing through solid from the photoemission site to the surface. An extrinsic plasmon energy loss process occurs by the coupling of the electric field of photoelectron on its way through the solid with that of free electrons in the solid. The photoelectron thereby losses the energy $\hbar\omega_p$ or $\hbar\omega_s$ (or multiple of this energy), depending on whether the interaction takes place in the bulk or surface of the sample. This process happens after and away from the location of the initial photoemission process. The interference effect [22] can also be visualize as the interaction between localized (photo-hole) and outgoing photoelectron (extrinsic) in which the virtual plasmon created by one is absorbed by other. It has been observed that the contributions of both intrinsic and extrinsic plasmon excitations in photoemission spectrum overlap one another, so they are not be readily separable experimentally. Also the question whether the photoemission satellite spectra seen are intrinsic or extrinsic in nature has aroused much controversy. Thus, in order to analyze the spectrum a more detailed qualitative analysis is needed. Many theoretical studies have been performed to evaluate the contribution of the intrinsic and extrinsic processes and to understand their origin in photoemission.

But in calculation of intensities Srivastava et. al. [5], considered only intrinsic excitations, as predicted by Bradshaw [23] in which number of slow electron is not conserved. Srivastava et.al. [5] pointed out that the difference in relative intensity between experimental and calculated estimates may be due to involvement of second intrinsic category, where the number of slow electron is conserved. However, they were silent for extrinsic effects. Now in the present paper we have tried tackle this longstanding problem and tried to incorporate both the processes, i.e. the relative contribution of extrinsic process as well as intrinsic process. Intrinsic process is further divided into two categories [23]. (i) When number of slow electrons is conserved; plasmon satellites are weak and (ii) when number of electrons is not conserved; plasmon satellites are strong. We calculated relative intensity in both the cases with new modification in the light of Bradshaw [23] and Lengreth [24] 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 Pardee et.al. [25] as –

$$\frac{I_s}{I_m} = \alpha^n \sum_{m=0}^{n} \frac{\left(\beta/\alpha\right)^m}{m!} \qquad (3)$$

where, $\beta = 0.12 r_s$, $\alpha = 0.47 r_s^{\frac{1}{2}}$ in the place of $\alpha = \left(1 + \frac{l}{L}\right)^{-1}$ as defined by Pardee et. al. [25]. Here, $l =$ is mean free path for extrinsic plasmon excitation; $L =$ is mean attenuation length for electrons due to processes other than plasmon excitation.

The parameter, $r_s^b = \left(\frac{47.11}{\hbar\omega_p}\right)^{2/3}$ for bulk plasmons and for surface plasmons $r_s^s = \left(\frac{47.11}{\hbar\omega_s}\right)^{2/3}$, is a dimensionless parameter.

Using this new value of α along with β in equation (3), we calculated the relative intensity of satellites, shown in **Table 2** simultaneously with experimental [3] and theoretical values [5]. The first term of equation (3) 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 [23] and gives better results as compared than traditional methods for calculation of the relative intensity.

Table 2: Relative intensity of High energy satellites of Scandium and Titanium compounds

Compound	r_s	α	β	Intensity assignments	Rel. intensity in present work	Rel. intensity by de.Boer et.al [3]		Calc. by Srivastava et.al. [5]
						Expt.	Calc.	
ScF_3	2.63	0.32	0.76	$\beta + \dfrac{\beta^2}{2\alpha}$	0.35	0.35	0.25	0.29
TiF_4	2.43	0.29	0.73	$\beta + \dfrac{\beta^2}{2\alpha}$	0.35	0.43	0.17	0.29
*K_2TiF_6	2.23	0.27	0.70	$\beta + \dfrac{\beta^2}{2\alpha}$	0.32	0.30	0.19	0.27
*ScI_3	3.39	0.41	0.87	$\beta + \dfrac{\beta^2}{2\alpha} + \dfrac{\beta^3}{6\alpha^2}$	0.11	0.10	0.30	0.41
TiI_4	3.45	0.41	0.87	$\beta + \dfrac{\beta^2}{2\alpha} + \dfrac{\beta^3}{6\alpha^2}$	0.11	0.25	0.44	0.41
$ScBr_3$	3.14	0.38	0.83	β	0.38	0.30	0.25	0.38
$TiBr_4$	3.57	0.43	0.89	$\dfrac{\beta^3}{6\alpha^2}$	0.02	0.04	0.34	0.43
$ScCl_3$	3.0	0.36	0.81	$\beta + \dfrac{\beta^3}{6\alpha^2}$	0.37	0.40	0.22	0.36
$TiCl_4$	3.09	0.37	0.83	$\beta + \dfrac{\beta^3}{6\alpha^2}$	0.38	0.41	0.30	0.37
Sc_2O_3	2.49	0.29	0.74	$\beta + \dfrac{\beta^2}{2\alpha} + \dfrac{\beta^3}{6\alpha^2}$	0.37	0.40	0.29	0.30
TiO_2	2.30	0.28	0.71	$\beta + \dfrac{\beta^2}{2\alpha} + \dfrac{\beta^3}{6\alpha^2}$	0.34	0.40	0.30	0.28

CONCLUSION

Our calculated values of plasmon energies agree well with the experimental energy separation. Now for the calculation of relative intensity compounds are treated microscopically [26-27]. When treated in this way, the satellites of different compounds slightly differ in assignment from one another in natural way as types of halides differ. But for the similar type of halides the contributions of extrinsic and intrinsic plasmon coupling processes are the same. There is only difference between $ScBr_3$ and $TiBr_4$ in showing low intensity. This might be due to any other reason. The lower value of relative intensity for $TiBr_4$ could neither be accurately calculated by de Boer et.al. [3] nor by Srivastava et.al. [4-5] with the help of previous methods. So, the calculated value in the present work is the only available nearest theoretical value. The comparison of the relative intensity among experimentally observed values and the calculated values by different workers prove superiority of present work earlier works. So, it can be established that the satellites of $2p_{1/2}$ - line are due to plasmon gain processes and the consideration of relative contributions of both extrinsic and intrinsic effect plays an important

role in the calculation of relative strength of satellites.

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