

EXTRINSIC AND INTRINSIC PLASMON EFFECTS IN PHOTON INDUCED X- RAY SATELLITE SPECTRA OF FLUORINE COMPOUNDS

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ABSTRACT. The origin of $K_{\alpha}L^2$ satellites of five fluorine compounds have been explained using plasmon theory, with new approach by considering intrinsic and extrinsic effects simultaneously. The calculated values of energy separation and relative intensity are in excellent agreement with recently observed values by K. RAM *et al.* and better than previously calculated by T. ABERG. Here we focus the relative coupling of intrinsic and extrinsic plasmon effects.

Keywords - Surface plasmon, 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 spectroscopy [1-24]. In a pioneered theoretical investigation, BOHM and PINE [1-2] suggested that beyond Debye length electrons behave collectively and oscillate with frequency called plasma frequency $\omega_p = (4\pi n e^2 / m)^{1/2}$ where n = electron density, m = effective mass of electrons, e = charge of electron. These collective oscillations of free electron gas are called plasma oscillation. During X- ray photoemission process (XPS) the solid absorbs an incident photon and emits an electron from 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. 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*.

Recently, K. RAM *et al.* [25] have observed $K_{\alpha}L^2$ low energy satellites five fluorine compounds LiF, NaF₂, MgF₂, KF, and SrF₂ using photon impact. The theoretical values were estimated for fluorine while the experimental values are determined for compounds of fluorine as target. The energy separation and relative intensity of these satellites were also calculated by T. ABERG [26]. However, the relative intensity of satellite for LiF calculated by T. ABERG is slightly smaller than the experimental values [25]. This is due to reason that the calculations are base upon sudden approximation and neglects exchange effects between electrons. A comparison of theoretical estimates of relative intensities of $K_{\alpha}L^2$ satellites of these compounds are in slight disagreement with the experimental values. 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 explained the origin of $K_{\alpha}L^2$ satellites of fluorine compounds using plasma oscillation theory with new approach by considering intrinsic and extrinsic effects simultaneously.

Plasma oscillations are two types- Bulk plasmon and Surface plasmon [27]. Bulk plasmons are longitudinal oscillation mode of the electron gas in the solid and are given by condition $\epsilon = 0$, wher ϵ is bulk dielectric function. The collective oscillations of electron gas at 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 $\epsilon = -1$. The surface plasmons at the interface of a bulk metal and vacuum were first predicted by RITCHIE [27]. They were observed by POWELL and SWAN [6-7]. STERN and FERRELL [18] found that surface plasmons at the interface of a metal and its oxide can account for some of the perplexing peaks occurring in the inelastic scattering of fast by metal foils. In particular, surface plasmon can excite in compounds, when the dielectric constant of first medium is negative which are generally for metals, while for second medium it should be positive; which is for insulators and the electronegativity of the second medium should be large. The metal oxides are ideal examples of these types of compounds and excitation of surface plasmons are well established [22-24]. If above conditions are satisfied, then surface plasmons dominate the bulk plasmons. In oxygen compounds, the surface property is more important than the bulk one. Due to presence of oxygen at the surface, the surface energy losses dominate the bulk energy losses. This is due to fact that surface of these compounds is more electronegative and dielectric constant is also more positive than the metal and hence energy loss probability at the surface is enhanced. However the literature is silent about these energy losses in halogen compounds. The halogens (seventh group elements) are next to the oxygen (sixth group elements) and before zero group of the periodic table. Halogens are more electronegative than the oxygen and dielectric constant of halogen is more positive as compared to the oxygen. So the probability of surface energy losses in halogen compounds can not be ignored.

For the primary investigation, we calculated surface plasmon energy using formula given by RITCHIE [27] as-

$$\hbar\omega_s = \frac{\hbar\omega_p}{\sqrt{2}} \quad (1)$$

where $\hbar\omega_p = 28.8 (Z'\sigma/W)^{1/2}$ is bulk plasmon energy [3]. Here, Z' is number of electrons taking part in plasma oscillation, σ is specific gravity of compounds, and W is molecular weight of compounds. The calculated surface plasmon energy is shown in table-1.

Table 1. - Energy separation of fluorine compounds (eV).

Compounds	Z'	σ	W	Present work ($\hbar\omega_s$)	Experimental [25]
LiF	2	2.64	25.94	9.2	9.2
NaF	3	2.78	41.99	9.1	10.5
MgF ₂	3	3.184	62.31	7.9	8.6
KF	3	2.48	58.10	7.3	7.0
SrF ₂	3	4.24	125.6	6.5	6.5

INTRINSIC AND EXTRINSIC EFFECTS

Our calculated values of surface plasmon energy agree well with the observed energy separation of satellites, but in order to further confirm the involvement of surface plasmon, we also calculated the relative intensity of these satellites using plasmon theory in new light. The physics of plasma excitation in photoemission is very interesting because different processes contribute to its intensity. Plasma excitations are two types- intrinsic and extrinsic [28]. 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 had 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 can also be visualize as the interaction between localizes photohole (intrinsic) and the outgoing photoelectron (extrinsic) in which the virtual plasmon created by one is absorbed by the other. It has been observed that contribution of both intrinsic and extrinsic plasmon excitations in photoemission spectrum overlap one another, so they are not readily be 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.

JOHANSSON *et al.* [29] predicted that plasmon losses could be taken as extrinsic process. The interpretation of this experimental behavior has been made with an extrinsic model, by MAHAN [12], of random spatial emission for bulk extrinsic plasmons. This model predicts that, for a thick sample and for relatively high electron kinetic energies, the bulk

extrinsic plasmon intensity should go as $\left(1 + \frac{l}{L}\right)^{-1}$. The comparison of the experimental data was made with the theoretical calculations based on the mean free path values extracted from the calculations of TUNG and RITCHIE [19] and L. KLEINMAN [9]. TUNG and RITCHIE [19] calculated the plasmon contributions to the inverse mean free path of a fast electron whereas KLEINMAN calculated the plasmon contribution to the imaginary part of the self-energy of a fast electron from which mean free path values can be extracted [9]. CHANG and LANGRETH [10] treated the inelastic plasmon losses as a many body effects of solid surface and core-hole. They estimated that the intrinsic plasmon production associated with core-hole is quite small including the interference between core-hole and outgoing electron. ŠUNJIĆ *et al.* [14] used an electron-plasmon interaction model for fast electrons and considered the effect of localized core holes to provide qualitative description of multiple bulk and surface processes in metals. They argued that the photoemission is a many body process and thus the breakdown into the intrinsic and extrinsic effects are artificial. P.J. FEIBELMAN [11] calculated the plasmon intensities as a function of depth and θ , assuming an core-hole life time and a smooth cut off at the critical wave-vector. PENN [18] discussed three step theoretical model for electron-electron scattering and plasmon dispersion, but the interference effect was not included.

While earlier studies assumed a classical trajectory for the outgoing electron and neglected the plasmon dispersion, INGLESFIELD [13] used the golden rule formalism of photoemission and considered plasmon dispersion as well as the interference effect. INGLESFIELD studied the suppression of the plasmon intensities at low electron kinetic energy by calculating the plasmon line shapes as function of the kinetic energy and depth of the site of photoemission [13]. INGLESFIELD found that interference between extrinsic and intrinsic plasmon is suppressed in the long wavelength plasmon excitations [13]. PARDEE *et al.* [16] carried out X-ray photoemission spectroscopy studies and came to the conclusion that the intrinsic effect was almost absent using a random spatial emission model for the excitation of plasmons. This was in contradiction with theoretical results which predicted the existence of the intrinsic plasmon. SRIVASTAVA *et al.* [23-24] calculated plasmon energy of different elements and compounds. But in calculation of intensities, they considered only intrinsic excitations, as predicted by BRADSHAW [15] in which number of slow electron is not conserved. SRIVASTAVA *et al.* [23-24] 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. Although plasmon excitations in photoemission have been known for more than four decades and were studied by different groups in the late 1960 and early 1990s, yet the explanation of satellite intensity remained unresolved. Now in the present work we have tried tackle this longstanding problem and tried to incorporate both the processes. It is well known that intrinsic process is further divided into two categories- (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. The combined effect of intrinsic and extrinsic excitations was suggested by PARDEE *et al.* [16], LANGRETH *et al.* [21] as –

$$\frac{I_s}{I_m} = \alpha^n \sum_{m=0}^n \frac{\left(\frac{\beta}{\alpha}\right)^m}{m!} \quad (2)$$

where, $\beta = 0.12r_s$, $\alpha = 0.47r_s^{1/2}$ is newly introduced parameter [30-32] in the place of in the place of $\alpha = \left(1 + \frac{l}{L}\right)^{-1}$ as defined by PARDEE *et al.* [17]. Here, l = is mean free path for extrinsic plasmon excitation; L = is mean attenuation length for electrons due to processes other than plasmon excitation and $r_s = \left(\frac{47.11}{h\omega_s}\right)^{2/3}$. The first term of equation (2) is purely extrinsic, while second term is purely intrinsic. The other terms are containing the relative contributions of both extrinsic and intrinsic excitations [20]. 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 *et al.* [20] and gives better results as compared than traditional methods for calculation of the relative intensity. It is also beauty of the method that the relative intensity of higher order satellites can easily be calculated without going in much mathematical details. It is also possible to separate the relative contributions of extrinsic and intrinsic excitations in total intensity. No method is present in the literature which proves the strength of much higher satellites and separates these contributions with such accuracy.

Table 2. - Relative intensity of fluorine compounds.

Compounds	r_s	α	β	Relative intensity (%)	
				Present work ($\beta^2/2\alpha + \beta^2/2\alpha$)	Experimental [25]
LiF	2.97	0.81	0.36	9.0	8.8±0.9
NaF	3.0	0.81	0.36	9.1	-
MgF ₂	3.28	0.85	0.39	11	-
KF	3.97	0.88	0.42	11	-
SrF ₂	3.75	0.91	0.45	13	-

CONCLUSION

Our calculated surface plasmon energy of $K_\alpha L^2$ satellites are in excellent agreement with the energy separation observed by K. RAM *et al* [25]. The calculated value of relative intensity for LiF in presnt case is 9.0 which agree well with the experimental value 8.8±0.9 (see table-2). However T. ABERG [26] has calculated 8.0, which is smaller than the experimental data. The theoretical model of T. ABERG [26] based on sudden approximation and neglects the exchange effects between conduction electrons. However, in case of NaF₂, MgF₂, KF, and SrF₂ we have no experimental data to compare relative intensity, but the agreement of relative intensity of LiF with experimental one, confirms their theoretical existence. Hence the satellites originate due to surface plasmon excitations and are due to relative coupling between intrinsic and extrinsic effects.

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