Surface Plasmon Excitation in 2p^{3/2} X-ray Photoemission Satellites of Nickel Dihalides

Sanjay Kumar Srivastava and Amar Bahadur Department of Physics, Kamla Nehru Institute of Physical and Social Sciences, Sultanpur, (U.P.), (INDIA) E-mail: amar.b.007@gmail.com

Received October 29, 2008; accepted November 10, 2008

ABSTRACT

The origin of $2p^{3/2}$ satellites of Nickel dihalides have been explained using plasmon theory with new approach by considering relative contribution of extrinsic and intrinsic effects. The present calculated values for the energy separation and relative intensity agree well with the experimentally observed values. Our calculation shows that satellites are due to surface plasmon excitation. We have also reviewed the existing calculations and experimental measurements.

Keywords: Surface plasmon, extrinsic and intrinsic effects, relative intensity.

1. Introduction

The phenomenon of surface plasmon has been known for a long time. The underlying principles and theories are well understood and a number of publications can be found which discuss their properties in detail. The concept of surface plasmon was first introduced by Ritchie [1] shortly after the discovery of bulk plasmon. In 1957, Ritchie published a series of papers on electron energy losses in thin films, in which he described that plasmon can also exist near the surface of metals and thus Ritchie represented first theoretical description of the surface plasmon. Gabor [2] attempted to develop the theory to describe the energy loss characteristics of electrons passing through finite metal crystals. As Ritchie [1] pointed out, Gabor mistakenly assumed electric field is always zero at the surface of the crystal, which led to unrealistic results. Rithcie [1] corrected this and applied more realistic boundary conditions to calculate the electron interactions in extremely thin films. His work resulted in the prediction of surface plasmons and consequently pioneered a whole new field of interest in surface physics. However, in Maxwell's theory it has been already shown that electromagnetic surface waves can also propagate along a metal surface or a metal film with a broad spectrum of eigen frequencies. Using this idea Ritchie [1] theoretically proved that surface plasmon simply arise as purely 2D solutions of Maxwell's equations that propagate as transverse magnetic wave along the metallo- dielectric interface and hence, calculated surface plasmon energy as-

$$\hbar\omega_{\rm s} = \hbar\omega_{\rm p}/\sqrt{2} \tag{1}$$

where ω_p = bulk plasmon frequency. This equation is valid for free electron model, but to a fairly good approximation. It can also be used for semiconductors and insulators. Ritchie's [1] prediction of surface plasmon was confirmed in a series of experiments carried out by Powell and Swan [3] who demonstrated the existence of collective electronic oscillations at the surface of Mg and Al. Shortly after, Stern and Ferrell [4] pointed out that surface electromagnetic waves at a metallic surface involve electromagnetic radiation coupled to the surface plasmons. They showed that surface plasma frequency not only depend upon bulk plasmon frequency, but also depends upon dielectric constant of second medium (ε_2) adjacent to the metal. This is due to fact that a part of restoring field of surface plasma oscillation also extends beyond the metallic boundary. Thus the surface plasmon frequency is given by equation-

$$\omega_{\rm s} = \omega_{\rm p} / \sqrt{(1 + \varepsilon_2)} \tag{2}$$

For a complete clear metal surface in a vacuum $\varepsilon_2=1$, and so above equation reduces to Ritchei equation. Since then there has been significant advancement in both theoretical and experimental investigations of collective modes in the vacuum solid interface. The renewed interest of surface plasmon has come from x-ray satellite spectra in transition metal halides. In a particular case, the collective excitation of electrons in the bulk of transition metal halides has been extensively discussed, while the surface plasmon excitation has been less frequently studied. In this paper we focus exclusively on surface plasmon excitation in Nickel halides.

2. Energy separation calculation

X-Ray photoemission spectra of core levels in many transition metal compounds show intense satellites occurring on high energy binding energy side of main line [9-11]. Such satellites have been observed in gas phase molecules as well as in solids. During the photoemission process the solid absorbs a photon and emits an electron form core level. The outgoing electron may suffer energy loss processes including before escaping out of the material. Thus, in core level energy loss spectrum of a metal or compound shows a zero loss peak centered at energy E_0 and satellite peaks centered 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.

In a core level electron energy loss spectrum both bulk and surface plasmon losses are observed. The excitation of surface plasmon is well known in oxides of transition metal compounds [12-13]. Since halogens are very nearer to oxygen in the periodic table and more electronegative than it, hence the possibility of surface plasmon excitation in halogens can not be ignored. In the present work $2p^{3/2}$ satellites of Nickel dihalides are examined for the excitation of surface plasmon by calculating their energy separation and relative intensity. Satellites of these compounds are earlier observed by J. Zaanen et.al. [14] experimentally and they explained their origin using charge transfer model. Later, Kozo Okada et. al. [15] has also reanalyzed these satellites using cluster model approach making some modifications in the previous model but discrepancy in explaining the relative intensity of these satellites could not be removed. In order to remove this discrepancy and to calculate the relative intensity we have applied plasmon theory but, applying some modified terms which prove superiority over old plasmon

method [12-13, 16]. First we calculated the energy separation of satellites from main line using formula given by Marton [17] as-

$$\hbar\omega_{\mathbf{p}} = 28.8 \left(Z'\sigma/W \right)^{1/2} \tag{3}$$

where Z' = effective number of electrons taking part in plasma oscillation, $\sigma =$ specific gravity of compounds, W = molecular weight of compounds. This equation is valid for free electron model, but to a fairly good approximation, it can also be used for semiconductors and insulators. Since at the surface a more localized oscillation can occur with frequency ω_s and also depending upon conditions and the energy of corresponding peak, surface plasmon may also be seen. The surface plasmon energy is calculated using equation (1) given by Ritchei [1]. The present calculated values of surface plasmon energy in table-1 are in better agreement with experimentally observed [14] values.

3. Relative intensity calculation

From energy separation alone, the satellites can be regarded as being due to excitation of surface plasmon but in order to further confirm the involvement of surface plasmon, we also calculated the relative intensity (I_s/I_m) of these satellites using plasmon theory in new light. There are two types of plasmon excitationintrinsic and extrinsic [19]. A sudden change in potential due to creation of core hole results intrinsic plasmon excitation (slow electron process). On the other hand, extrinsic plasmon excitation results from Coulomb interaction of the conduction electrons with the photoelectron traversing through the solid from the photoemission site to the surface (fast electron process). Besides this an interference effect can also be visualized as the interaction between the localized photo-hole (intrinsic) and the out going photoelectron (extrinsic) in which the virtual plasmon created by one is absorbed by the other. It has been observed that the contributions of both intrinsic and extrinsic plasmon excitations in photoelectron spectrum overlap one another, so that they are not readily separable experimentally. Also the question whether the photoemission satellites 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. Now in the present paper we have made new attempt to tackle this longstanding problem by incorporating both the processes i.e. the relative

contribution of extrinsic $p \frac{I_s}{I_m} = \alpha^n \sum_{m=0}^n \frac{(\beta/\alpha)^m}{m!}$ process as well as intrinsic process.

We have calculated relative intensity in both the cases with new modification in the light of Bradshaw [20] and Lengreth [21] work, which explains that not only intrinsic process but extrinsic process and their relative contributions [22-23] may also contribute in relative intensities and applied Hartee– Fock model to calculate the relative intensity of satellites using formula with improved parameter as

$$\frac{I_s}{I_m} = \alpha^n \sum_{m=0}^n \frac{\left(\beta/\alpha\right)^m}{m!} \tag{4}$$

where $\beta=0.12r_s$ which is purely intrinsic, $r_s = (47.11/ \hbar \omega_s)^{2/3}$ is dimensionless parameter[24-25] and $\alpha = 0.47r_s^{1/2}$ in the place of $\alpha = (1 + l/L)^{-1}$ used by Pardee [26].

This equation (4) contains a series of terms, which include both extrinsic and intrinsic excitation contributions [18-20] along with their relative coupling terms. The first term 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 [27-29] with other terms is able to give the relative intensity. It is the type of excitation, which decides which and how many terms will be used. Equation (4) also includes both the categories mentioned by Bradshaw [20] and gives better results as compared to that and than traditional methods for calculation of the relative intensity. Earlier workers [12-13, 16, 27] have successfully explained many satellites up to certain extent by using various terms of same formula alone. But, using various terms or their combination of this equation (4) we are able to calculate not only the relative intensity of existing satellites, but also it is possible to predict those satellites which are yet to be discovered. It is also the 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 can give the strength of much higher satellites and can separate these contributions with such accuracy.

Compounds	Ζ'	σ	W	Present work $\hbar\omega_s$	Experimental [14]
NiF ₂	2	4.72	96.71	6.4	5.5
NiCl ₂	3	3.55	129.62	5.8	5.5
NiBr ₂	3	5.10	218.53	5.4	5.0
NiI ₂	3	5.22	312.5	4.6	4.4

Table-1: Energy separation of Nickel Compounds (eV)

Table-2:	Relative	intensity	Nickel	compounds
----------	----------	-----------	--------	-----------

			Relative intensity		
Compounds	r _s	α	Intensity assignment	Present work	Experimental [14]
NiF ₂ NiCl ₂ NiBr ₂ NiI ₂	3.79 4.02 4.24 4.24	0.92 0.94 0.97 1.02	$ \begin{array}{c} \beta - 0.1 \\ \beta \\ \beta \\ \beta^2 / 2\alpha + \beta^3 / 6\alpha^2 \end{array} $	0.36 0.48 0.51 0.20	0.33 0.51 0.48 0.29

4. Conclusion

The energy separation of $2p^{3/2}$ satellites from main line of Nickel dihalides observed by J.Zaanen et.al. [14] are found to be in excellent agreement with our calculated

values. Now for the calculation of relative intensity compounds are treated microscopically [30-32]. 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. The calculated values of relative intensity from the present theory also agree well with the observed values [14]. Hence the $2p^{3/2}$ satellites of Nickel dihalides are due to surface plasmon excitation and new formulation approach is also verified.

Acknowledgement. We would like to thank Prof. K.S.Srivastava (Physics Department, Lucknow University, Lucknow U.P.) and Dr.A.K.Srivastava (Physics Department, Kamla Nehru Institute of Physical and Social Sciences, Sultanpur, U.P.) for his constant guidance and valuable suggestions.

REFERENCES

- 1. Ritchie R.H., Plasmon loss by fast electrons in thin films. *Phys. Rev.* 106 (1957) 874-881.
- D. Gabor, Collective oscillations and characteristic electron energy loss. *Phil. Mag.* 1 (1956) 1-18.
- C.J. Powell and J.B. Swan, Origin of characteristic electron energy loss of Aluminum. *Phys. Rev.* 115 (1959) 896-875.
- 4. E.A. Stern and R.A. Ferrell, Surface plasma oscillations of a degenerate electron gas. *Phys. Rev.* B 120 (1960) 130-136.
- 5. D. Pines and D.Bohm, A collective description of electron interaction: II Collective vs. individual particle aspects of the electron. *Phys. Rev.* 85 (1952) 338-353.
- 6. D. Pines and D.Bohm, A collective description of electron interaction: III Columb interactions in degenerate gas. *Phys. Rev.* 92 (1953) 609-625.
- 7. D. Pines, *Elementary excitations in solids*, Benjamin New York (1964) 771-774.
- 8. D. Pines, *Solid State Phys. and Advanced Research and applications*, edited by F. Seltz etc. (1955), 1, 367-370.
- 9. B.Wallbank, J. S. H. Q. Perera, D. C. Frost and C. A. McDowell, x-ray photoelectron spectroscopy of titanium tetra halide vapors. *Jour. of Chem. Phys.* 69 (1978) 5405-5410.
- Isao Ikemoto, K. Ishii, H. Kuroda, and J. M. Thomas, Satellite phenomenon in the xray photoelectron spectra of some titanium compounds. *Chem. Phys. Lett.* 28 (1974) 55-59.
- D.C.Frost, C.A. Mc Dowell, I.S. Woolsey, Evidence for multiple splitting of 2p photoelectron lines of transition metal complexes. *Chem. Phys. Lett.* 17 (1972) 320-323.
- 12. K.S.Srivastava, K.Sinha, A.K.Srivastava, Sameer Sinha, S.K.Shukla, M.N.Sharma, D.K.Singh, S.K.Srivastava, High energy K_{α} ' plasmon satellites in x- ray emission spectra of scandium and titanium compounds. *Ind. Jour. of Pure and Applied Phys.* 34 (1996) 190-192.
- K.S.Srivastava, Shiv Singh, A.K.Srivastava, R.S.Nayal, A.Chaubey, and P. Gupta, Electron electron interaction in transition metal x-ray emission spectra. *Phys. Rev.* A 25 (1982) 2838-2844.
- J. Zaanen, C.Westra and G.A.Sawatzky, Determination of electronic structure of transition metal compounds: 2p x-ray photoemission spectroscopy of nickel dihalides. *Phys. Rev.* B 33 (1986) 8060-8073.

- 15. Kozo Okada, Akio Kotani, Multiple splitting in nickel 2p x-ray photoemission spectra of nickel dihalides. *Jour. of Phys. Soc. of Japan*, 60 (1991) 772-775.
- 16. Rajeev Srivastava, High energy plsmon satellites in compounds of various elements. *Vijnan Perishad Anusandhan Patrika*, 50 (2007) 73-76.
- 17. Marton. L in *Advanced in electronic and electron phys.* edited by L. Marton (Academic Press New York) (1955), 7, 225.
- 18. Ritche R. H. and Jacob Neufield, Passage of charged particles through plasma. *Phy. Rev.* 98 (1955) 1632-1642.
- 19. Hufner, Photoelectron Spectroscopy Springer, Berlin (1995) 472-475.
- 20. A. M. Bradshaw, S.L. Caderbawm, Omecka W. D. & Kawa .U, Plasmon coupling to core hole excitations in carbon. *Jour. Phys. C, Solid State Phys.*7 (1974) 4503-4512.
- 21. D.C. Langreth, *In Collective properties of physical systems*, edited by B.Lundquist and S.Lundquist, Academic Press New York, (1974) 458- 461.
- 22. Brad P Payne, Andrew P, Grosvenor, Mark C. Biesinger, Brad A. Kobe, N. Stewart McIntyre, Structure of growth of oxides on poly crystalline nickel surfaces. *Surface and Interface Analysis.* 39 (2007) 582-592.
- 23. S.K. Srivastava, Amar Bahadur, Pankaj Singh, Surface plasmon satellites in 2p core level spectra of heavy transition metal dihalides. *Ultrascience*, 20 (2008) 315-318.
- 24. G.A. Rooke, Plasmon satellites in soft x-ray emission spectra. *Physics Letters*. 3 (1963) 234-236.
- 25. D.C. Lengreth, Born-oppenheimer principle in reverse: electrons, photons and plasmons in solid. *Phys. Rev. Lett.* 26 (1971) 1229-1233.
- W.J. Pardee, G.D. Mahan, D.E. Eastman, R.A.Pollak, L.Ley, F.R. Mcfeely, S.P. Kowalczyk and D.A.Shirley, Analysis of surface and bulk plasmon contributions to x-ray photoemission spectra. *Phys. Rev*. B 11 (1975) 3614-3616.
- 27. Xia J, O Connor K.M, Kachroo R.K, Liang G.C, Theopold U, Schmidt O, Harsh O.K, Surface plasmon satellites in the x-ray emission spectra of magnesium. *Journal of Phys. and Chem. of Solids*, 58 (1997) 1433-1437.
- 28. S.K. Srivastava, Amar Bahadur, Pankaj Singh, Surface plasmon satellites in 3s photoemission spectra of Mn and Fe insulating compounds. *Material Science; An Indian Journal.* 4 (2008) 119-121.
- 29. S.K. Srivastava, Amar Bahadur, Pankaj Singh, Bulk plasmon satellites in auger spectra of transition metals. *Material Science; An Indian Journal.* 4 (2008) 117-118.
- Andrew P. Grosvenor, Mark C. Biesinger, Roger St.C. Smartand N. Stewart McIntyre, New interpretation of XPS spectra of nickel metal and oxides. *Surface Science*, 600 (2006) 1771-1779.
- Z. Berényi, L. Kövér, S. Tougaard, F. Yubero, J. Tóth, I. Cserny and D. Varga, Contribution of intrinsic and extrinsic excitations in KLL auger spectra induced from Ge films. *Journal of Electron Spectroscopy and Related Phenomena*, 135 (2004) 177-182.
- 32. C. Deton, J.L. Gervasoni, R.O. Barrachina, N.R. A Rista, *Phys. Rev.* A 57 (1997)4498-4511.