

High Energy Triple Plasmon Satellites of Mn and its Compounds



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Abstract

The origin of high energy $K_{\beta 5}$ triple Plasmon satellites of $K_{\beta 1,3}$ main emission line of Mn and its compounds have been explained using Plasmon theory with new formulation of relative intensity by considering relative interference between intrinsic and extrinsic effects. The interference 'Plasmon-coupling' have been obtained theoretically in terms of non-diagram line to diagram X-ray line for the satellite profiles in the X-ray photoemission spectra. It is found that our results with new intensity formulation are in better agreement with experimental results.

Keywords: X-ray Satellites, Plasmon, Intrinsic and Extrinsic effects, Relative Intensity.

Introduction

Plasmons are collective oscillations which correspond to fluctuations in the density of the normal electron distribution in solid materials.

In a pioneered theoretical investigation, Bohm and Pine [1-2] suggested that electrons are not entirely free in an electron gas as concluded by Sommerfeld [3], but these are free within the Debye length. This electron gas or sea of conduction electrons refers to the bulk of material which has properties that allow the assumption of conduction electrons acting as free electron gas. Beyond Debye length they behave collectively and oscillate with frequency called plasma frequency given as –

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

Where n = electron density, m = effective mass of electrons, e = charge on electron. Both Plasmon excitations in the bulk and on the surface may be observed. Bulk Plasmons are longitudinal oscillation mode of the electron gas in the solid and are given by condition $\epsilon = 0$, where ϵ is bulk dielectric function. The collective oscillations of electron gas on the interface between metal and dielectric are known as surface Plasmons [4]. Surface Plasmons are an Oscillating sheet of charge located at the surface, although its energy is associated with bulk Property $\epsilon = -1$. The Plasmon energy can be calculated by using formula given as [5] –

$$\hbar\omega_p = 28.8 \left(\frac{Z'\sigma}{W} \right)^{1/2} \quad (2)$$

Where $\hbar\omega_p$ = bulk (volume) Plasmon energy, Z' = effective number of electrons taking part in plasma oscillations, σ = specific gravity, W = molecular weight of compounds. Surface Plasmon energy using formula given by Ritchie as [4] –

$$\hbar\omega_s = \frac{\hbar\omega_p}{\sqrt{2}} \quad (3)$$

The energy of the surface Plasmon is a factor of about 0.707 lower than that of the bulk Plasmon.

Objective of the study

In the present work, the author tries to investigate the sole cause of probability of occurrence (relative intensity) of high energy $K_{\beta 5}$ triple Plasmon satellites of $K_{\beta 1,3}$ main emission line of Mn and its compounds using the hypothesis of plasma oscillations.

Concepts and Hypothesis

X-ray photoemission spectra (XPS) from metals often include non diagram lines also known as satellites, which arise from creation of Plasmons. When a photoelectron is emitted from a solid, it is the final probability that it may excite a collective oscillation in the conduction electron gas. During X-ray photoemission process (XPS) the solid absorbs an incident photon and emits an electron from the core-level. The outgoing 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 centred at E_0 and satellite peaks 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 Satellite. However if Plasmon pre exists, 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 energy separations $E_0 + \hbar\omega_p$, $E_0 + 2\hbar\omega_p$, $E_0 + 3\hbar\omega_p$ etc. The emission line owing to this process is called High Energy Satellite.

Extrinsic and intrinsic effects

In X-ray photoemission spectra (XPS) we usually classify the Plasmon loss peaks in two Classes, intrinsic and extrinsic [6]. 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. Photoelectrons that stem from intrinsic Plasmon excitation belong to the intrinsic (primary) electron emission spectrum together with the main peak and its asymmetric tail. This 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-holes. On the other hand extrinsic Plasmon excitation is created by Coulomb interaction of conduction electrons 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 loses 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 relative importance of the two processes was studied experimentally by Pardee et al. [7]. Intrinsic process is further divided [6] 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 interference effects can also be visualized as the interaction between localized (photo-hole) and outgoing photoelectron (extrinsic) in which the virtual Plasmon created by one is absorbed by other.

Review of Literature

The problem which has received considerable attention in the recent decades is the response of conduction electrons of metals to creation of core holes in X-ray photoemission spectra (XPS). As the contributions of both intrinsic and extrinsic

Plasmon excitations in photoelectron spectrum overlap one another, so that they are not readily separable experimentally. Many theoretical studies have been performed to evaluate the contributions of the intrinsic and extrinsic processes and to understand their origin in photoemission. The missing feature of Nozieres and Pines [8] studies is that they considered only extrinsic (electron induced) loss spectra produced in a system by outside electrons without creation of a core-hole. Mahan [9-10], Lengreth [11], W. Gadzak [12], M. Šunjić and D. Šokčević [13-15] have greatly expanded on these Plasmon arguments for which core-holes are necessary adjunct (e.g. during photoemission and X-ray spectroscopy). Johansson et al. [16] predicted that plasmon losses could be taken as extrinsic process. The interpretation of this experimental behaviour has been made by Mahan with an extrinsic model of random spatial emission for bulk extrinsic plasmons [10]. Thus these authors have tried to describe the situation in which intrinsic (hole caused) losses & hole induced couplings and shifts accompany the extrinsic in the loss spectra. Unfortunately, all of this had been done by later group without consideration of possibility of collective (e.g. plasmons) versus non-local losses in a non free electron gas type environment. Šunjić and Šokčević [13-15] used a model Hamiltonian to describe the energy loss spectra of solids and thin films using plasmon theory. However, the Hamiltonian takes only electron-plasmon scattering into account and admits a simple solution only if the plasmons are dispersion less. In this concern most of authors adopted a three step model (a) photo-excitation of electrons, (b) transport of photoelectron to the surface and (c) escape through the surface, to explain the energy loss spectra (ELS) of core level. Pardee et al. [7] and D. Penn [17] further extended this model for 2p and 2s core level spectra of Al, Mg, and Na for combined relative intensity. They concluded that Plasmon structure accompanying core level X-ray photoemission in Al and Mg could be well fit by only the extrinsic Plasmon production. But the analysis used there was based on assumption that the outgoing photoelectron could be well described by classical trajectory. Pardee et al. [7] 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. K.S. Srivastava et al. [19-22] and R. Srivastava, [23] studied theoretically the involvement of Plasmons in XPS of various metals and compounds but considered only intrinsic excitations, as predicted by Bradshaw et al. [24] in which number of slow electrons is not conserved. They 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 electrons is conserved. However in calculation of relative intensity they applied approximation method and were silent for extrinsic effects. Here we conclude that

previous workers have either used intrinsic or extrinsic processes separately or neglected their relative interference effects in calculation of relative intensity of satellites in X- ray photoemission spectra. We have extended our Plasmon model S.K.Srivastava et.al. [25-27] to calculate the relative intensity of X- ray photoemission satellites of various metals and compounds by considering intrinsic, extrinsic and their relative interference effects. In the present work the experimental data was taken from reference [28].

Research Design Calculations Energy separation

For the primary investigation we calculated Plasmon energy of high energy $K_{\beta 5}$ triple Plasmon satellites of $K_{\beta 1,3}$ main emission line of Mn and its compounds observed in X- ray photoemission spectra of Mn and its compounds. The bulk Plasmon energy is calculated by using equation (2).

Table-1: Energy separation of high energy triple Plasmon $K_{\beta 5}$ satellites of Mn and its compounds.(28)

Compounds	Z'	σ	w	Energy separation (eV) ($\hbar\omega_p$)	Triple Plasmon Energy in present work(eV) $3\hbar\omega_p$	Observed energy separation of $K_{\beta 5}$ From $K_{\beta 1,3}$	Calculated by Tsutsumi Nakamory
Mn	2	7.2	54.94	14.74	44.22	44.75	27.06
MnO	2	3.7	70.93	13.16	39.48	40.42	-----
MnO ₂	4	5.026	86.93	13.85	41.55	42.32	-----
K ₂ MnO ₄	-----	-----	-----	15.71	47.13	47.13	-----
KMnO ₄	-----	-----	-----	15.07	45.21	45.22	-----

The energy separation calculated by this method is in good agreement with experimentally observed energy separations of satellites.

Relative intensity

For calculation of relative intensity we used Plasmon model with modified parameters which includes intrinsic, extrinsic and their relative interference terms. In principle, the extent of intrinsic and extrinsic Plasmon production can be determined from intensity variation of successive Plasmon peaks in X- ray photoemission spectra (XPS) as [7] –

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

Where α is a measure of probability of intrinsic excitation given by $\alpha = 0.12r_s$ and β is a extrinsic Plasmon creation probability. The parameter $\beta=0.47r_s^{1/2}$ is newly introduced parameter [25-26] in

the place of $\beta = \left(1 + \frac{l}{L}\right)^{-1}$ as defined by Pardee et.al.[7]. The parameter, $r_s^b = \left(\frac{47.11}{\hbar\omega_p}\right)^{2/3}$ for bulk Plasmons and $r_s^s = \left(\frac{47.11}{\hbar\omega_s}\right)^{2/3}$ for surface Plasmons is a dimensionless parameter. Using this new parameter β along with α in equation (4), we calculated the relative intensity (Is/Im) of satellites using new formulation and presented them simultaneously with experimental values (table 2). The first term of equation (4) is purely extrinsic while second term is purely intrinsic. The other terms are containing the relative contributions of both extrinsic and intrinsic. The speciality 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 to traditional methods for calculation of the relative intensity.

Table-2: Relative intensity of high energy $K_{\beta 5}$ triple Plasmon satellites Mn and its compounds.(28)

Compounds	$r_s = \left(\frac{47.11}{\hbar\omega_p}\right)^{2/3}$	$\alpha = .12r_s$	$\beta = 0.47r_s^{1/2}$	Relative Intensity in the present work $\neq \beta\alpha^2/2$	Relative Intensity observed experimentally by Tsutsumi	Relative Intensity Cal. by Tsutsumi
Mn	2.170	0.2604	0.6924	0.023	0.020
MnO	2.340	0.2808	0.7190	0.028	0.011
MnO ₂	2.262	0.2714	0.7069	0.026	0.019
K ₂ MnO ₄	2.079	0.2495	0.6777	0.021	0.023
KMnO ₄	2.138	0.2566	0.6872	0.022	0.021

Conclusion

The relative intensities of high energy $K_{\beta 5}$ triple Plasmon satellites Mn and its compounds [28] are presented vis a vis along with relative intensity calculated in the present work using new formulation (eqn 4).It is clear from table2 that the calculated values of relative intensities of high energy $K_{\beta 5}$ triple Plasmon satellites Mn and its compounds in the present work compare well with the experimentally observed values however Tsutsumi et.al. [28] could not calculate the relative intensities. In addition to this we have calculated a number of results in our previous work [29-31].In the light of above supporting

results (25-27, 29-31) in the favour of new formulation for the relative intensity and the origin of satellites, it may be established that not only intrinsic Plasmon process but also the extrinsic Plasmon process and their simultaneous relative contributions are important and must be taken into account in the calculation of relative intensity of Plasmon satellites.

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