Low energy plasmon satellite in X-ray excited Auger electron spectra of Ag,Pd,Rn,In,Sn & Sb.

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Abstract

Anomalous loss structures have been observed in the recent past by Kleiman *et al* on low energy side of main X-ray excited Auger electron spectral line $L_{2,3}$ $M_{4,5}$, M_{45} of Ag,Pd,Rn,In,Sn & Sb elements. A possible theoretical explanation and quantitative account has been estimated for this loss on the basis of surface & volume plasmon oscillations. The energy separation agree with the calculated values of surface plasmon satellites (for Ag,Pd &Rn) and volume plasmon satellites (for In,Sn & Sb). The relative intensity of these satellites have also been calculated which agrees well with the observed experimental curves of Kleiman *et al*.

Keywords: Plasmon, Satellite, Volume and surface plasmon, relative Intensity.

I.Introduction

In the recent past many multiple structures & X ray Satellites have been observed [1-7] on high as well as on low energy side of X ray $L_{2,3}$ $M_{4,5}$, M_{45} transitions of Xray excited Auger electron spectra of Ag,Pd,Rn,In,Sn & Sb by Kleiman et al [1,2]. However in their studies, they paid much attention for structure and satellite peaks on high energy side of main electron X ray spectra (XAES). They made a passing reference for the structures on low energy side without going in theoretical details. Therefore it remained as a subject of great interest to explore the possibility of a quantative explanation based on volume and surface plasmon energy transfer in low energy side of $L_{2,3}$ $M_{4,5}$, M_{45} X ray excited Auger electron spectra.

Entrance or ejection of high energy electron or X ray photon having energy higher than K-shell electron produces surface and volume oscillations in free electron cloud of solids while passing through it. The basic reasons for these oscillations lie in Coulombian potential. When a valence electron before filling the core vacancy looses a small amount of quantized energy compatible to the energy of coupled oscillation of free electron charge cloud the so called plasma, plasma oscillations are excited. This makes a time & space fluctuations of electron charge density over the surface of charged cloud as well as in bulk material in the vicinity of the track from where it passes (whose dimensions lie in Debye length).

The bulk plasma oscillations are volume oscillations corresponding to a frequency ω_p and energy $\hbar\omega_p$ while the surface plasma oscillations correspond to the frequency ω_s and energy $\hbar\omega_s$. Therefore the emitted X-ray photon can have energy lesser by an amount $\hbar\omega_p$ or $\hbar\omega_s$ as the case may be. Thus the line is shifted by this amount in low energy side producing low energy satellite.

II. Quantitative Analysis

Two types of computations have been presented here. The first one is for energy shift ΔE in low energy side of X-ray $L_{2,3}$ $M_{4,5}$, M_{45} X-ray excited Auger electron spectra of Ag, Pd, Rn, In, Sn & Sb elements. The second one is for relative intensity calculations based on transition probability.

III. Calculation of energy shift.

For the first type of calculations volume plasma oscillations have been estimated using Marton et al [7]. As such the volume plasma oscillation frequency ω_p and energy shift ΔE is given as

$$\Delta E = 2.88\left[\frac{Z\sigma}{W}\right]^{1/2} \text{eV} \qquad (1)$$

$$\& \omega_p = \frac{\Delta E}{\hbar}$$

Where Z is effective number of bulk electrons taking part in volume plasma oscillations, σ the specific gravity & W the molecular weight. Z depends over the Debye length. For the surface oscillations of plasma we follow Ritchie [8]. The energy shift and frequency of surface oscillation is given [8] as

$$\Delta E = \hbar\omega_s$$

$$= \frac{\hbar\omega_p}{\sqrt{2}}$$

$$\& \qquad \omega_s = \frac{\omega_p}{\sqrt{2}} \tag{2}$$

The calculations indicate that eq. (1) is in agreement for In,Sn & Sb while eq(2) is in close agreement for Ag,Pd ,Rn elements. Eq(1) & (2) are valid for free electrons but to the first approximation they have also been used for semiconductors and insulators too [9,10].

IV. Calculation of relative Intensity

In order to confirm that these satellite lines are arising due to plasmons, the relative intensity to these lines has also been estimated. As such the transition probability [11] $P(\omega)$ per unit time and per unit energy is given as

$$P(\omega) = |f|^2 \sum_n e^{-\alpha} \frac{\alpha^n}{n!} \delta(W - tn - \alpha\omega_p + n\omega_p) \tag{3}$$

where $\alpha = e^2 q_{\max} \big/ \pi\hbar\omega_p = .16\gamma_s$ (4)

with $\gamma_s = \left(47.11 \big/ \hbar\omega_p \right)^{2/3}$ (5)

where α is coupling factor and γ_s a dimensionless parameter [12] and f is the matrix element.

The weight factor $e^{-\alpha}\dfrac{\alpha^n}{n!}$ appearing in eq (3) represents the strength of the nth satellite (n=0 yields the main peak). The intensity also depends upon mode of excitation. In case if it is intrinsic mode of excitation when electron are not conserved the relative intensity of first peak is given by [9]

$$(\Delta E_{cal})\ i = \left[\frac{I_1}{I_2} \right] = \alpha = .16\gamma_s$$

$$= .16 \left[\frac{47.11}{\hbar\omega_p} \right]^{2/3} \tag{6}$$

$$= .16 \left(47.11 \big/ \hbar\omega_s \right)^{2/3} \tag{7}$$

Here Eq(7) is for surface plasmons.

Table 1

Elements	Effective Z	$\Delta E_p = \hbar\omega_p$	$\Delta E_{cal} = \frac{\hbar\omega_p}{\sqrt{2}} = \Delta E_p/\sqrt{2}$	ΔE_{obs}	$I_{cal} = \left(I_1/I_0\right) = .16\,\gamma_s$	I_{obs}
Ag	1	8.99eV	6.35eV	6.81eV	0.60	0.55
Pd	3	16.76eV	11.85eV	11.36eV	0.40	0.46
Rh	1	10.00eV	7.07eV	6.81eV	0.56	0.51.

Table 2

Elements	EffectiveZ	ΔE_p (cal) $=28.8\sqrt{Z\sigma/W}$	ΔE(ob)	$I_{cal}=I_1/I_0$	I_{obs}
In	2	10.28eV	10.64eV	.44	.39
Sn	2	10.11 eV	11.06 eV	.45	.41
Sb	2	11.69 eV	11.06 eV	.40	.44

V. Comparison with Experimental Results & discussions

Values of ΔE have been calculated using Eq (1)& (2). In Table 1 , ΔE is calculated for surface plasmons using $\Delta E = \frac{\hbar\omega_p}{\sqrt{2}}$. While in Table 2 the same is estimated using volume plasmons. These estimated values (ΔE_{cal}) are compared with experimental energy shift ΔE_{obs}. Both values are in close agreement with observed experimental data. For confirmation relative intensity is also calculated. In Table 1 $I_{cal}=(I_1/I_0)$ is estimated using eq(7) while in Table 2 it has been estimated using eq(6). The comparison shows that for Ag, Pd & Rh the theory of surface plasmon agrees well while for In,Sn & Sb it is volume Plasmon play the key role. The difference in theory might be due to change in atomic number and molecular weight. As the surface oscillation cover a larger surface the frequency of oscillation would be lower as compared to volume plasmon. Thus one concludes that anomalous loss peak unaccounted so far are due to surface & volume excitations in free electron plasma.

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