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Low-energy plasmon $K\beta'$ satellite in the $K\beta_{1,3}$ x-ray emission spectra of Mn, Cr, and their compounds

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Using plasma oscillations in solids' theory, the energy separation and relative intensity of the $K\beta'$ satellites of the $K\beta_{1,3}$ x-ray emission line of Mn, MnO, MnO_2, Cr, CrO_3, K_2CrO_4, and $K_2Cr_2O_7$ have been calculated. Our calculated values agree better with the experimentally observed values than the values calculated by Tsutsumi *et al.* from molecular-orbital theory. This suggests that the possible origin of the $K\beta'$ satellite may be plasmon oscillations in solids.

I. INTRODUCTION

It is well known[1-11] that plasmons are excited during x-ray or Auger-electron transitions in metals as well as in semiconductors. Some nondiagram lines which are separated by an energy distance of $\hbar\omega_p$ (ω_p is the plasmon frequency) on the low-energy side of the main line are believed due to plasmon excitations in solids. Such satellites are known as plasmon satellites and have been observed in x-ray emission spectra[12-14] as well as in Auger spectra[15-18] in a wide range of metals and semiconductors. The low-energy plasmon satellites are obtained when a valence electron or Auger electron, before filling up a vacancy in a core state, excites a plasmon and the emitted x-ray photon or Auger electron is deprived of the energy $\hbar\omega_p$, giving rise to a low-energy plasmon satellite.

Recently Tsutsumi[19-21] *et al.* have obtained low-energy $K\beta'$ satellites in the $K\beta_{1,3}$ x-ray emission spectra of Mn, MnO, MnO_2, Cr, CrO_3, K_2CrO_4, and $K_2Cr_2O_7$. Several[22-25] workers have proposed from time to time various possible explanations for the origin of the $K\beta'$ satellite. Parratt[26] and Tsutsumi[21] have reviewed the various theories for $K\beta'$ satellites but none of them is able to account satisfactorily for the energy separation and its relative intensity. Tsutsumi[19] *et al.* have tried to explain the origin of the $K\beta'$ satellites on the basis of molecular-orbital (MO) theory by considering the exchange interaction between the electrons of the incomplete $3d$ shell and the hole in the inner shell due to the emission of the x ray. However, from their data it is apparent that there is a wide disagreement between their observed and calculated values for the energy separation and relative intensity of $K\beta'$ satellites with respect to the main-line $K\beta_{1,3}$. Further, MO theory has not been able to give any satisfactory numerical value for the energy separation and relative intensity of $K\beta'$ satellites of CrO_3, K_2CrO_4, and $K_2Cr_2O_7$ compounds.

Therefore, it was thought of great interest to explain the origin of low-energy $K\beta'$ satellites by some alternative theory like plasmon oscillations in solids. The MO theory of Tsutsumi[19,20] *et al.* may also be true but our calculated values for the relative intensity and energy separation are in better agreement with the observed values than the calculated values of Tsutumi[19,20] even after Watanabe's correction[27] for Auger transitions.

Blochin[28] in 1957, tried to explain the origin of $K\beta'$ satellites by assuming that part of the energy quantum of the $K\beta_1$ line may be absorbed by a $3d$ electron giving rise to a low energy $K\beta'$ satellite. This approach was quite reasonable but Tsutsumi[21] has rejected the idea without giving any reason for it. The present theory is fairly close to the Blochin[28] theory. According to it, part of the energy quantum of the $K\beta_1$ line may be used to excite the plasmon in the valence band. Thus, the energy of the emitted quantum of the $K\beta_1$ line will be less by an energy equal to the plasmon energy, giving rise to a low-energy plasmon satellite, $K\beta'$. Low-energy satellites have been observed by several workers[11-18] in several metals and compounds and most of them have been explained on the basis of the theory of plasmon oscillations in solids. The authors have, therefore, also tried to explain the $K\beta'$ low-energy satellite using the theory of plasma oscillations. A good agreement was found between the authors' calculated values and the observed values of Tsutsumi *et al.*[19,20] for both the energy separation and the relative intensities.

It is the purpose of this paper to present an alternative method to the MO theory of Tsutsumi *et al.*[19,20] for calculating the energy separation and relative intensities of $K\beta'$ satellites with respect to the $K\beta_{1,3}$ emission line of Mn, Cr, and their compounds.

II. CALCULATION OF THE PLASMON ENERGY

The energy of plasma oscillation is given[29] by

$$\hbar\omega_p = 28 \cdot 8\sqrt{Z\sigma/W}\ \ \text{eV}, \quad (1)$$

where Z is the number of electrons involved in plasmon oscillations, σ is the specific gravity, and W is the molecular weight.

The above expression for the plasmon energy is valid for free electrons, but to a first approximation it can be used for semiconductors and insulators also.[30-32]

The recent[33-37] observed plasma loss values in transition elements show that the effective number of electrons involved in Mn as well as in Cr is unity. In the case of oxygen, Glasston[38] has shown that the number of unpaired electrons is two. Taking these facts into account the number of unpaired electrons taking part in plasmon oscillations in Mn, MnO, MnO_2, Cr, CrO_2, K_2CrO_4, and $K_2Cr_2O_7$ is 1, 3, 5, 1, 7, 11, and 18, respectively, and the calculated plasmon energies for the above, using Eq. (1), turn out to be 10.42, 13.85, 15.48, 10.72, 12.52, 11.33, and 11.69 eV, respectively, which is in fair agreement with the observed values of the energy separation of $K\beta'$ satellites (See Table I). The energy separation of $K\beta'$ satellites in Mn, MnO, MnO_2, and Cr, as calculated by Tsutsumi[19,20] *et al.* from MO theory, is 3.55, 10.44, 7.36, and 1.77 eV, respectively, which is far below the observed values. Thus, we can say from energy considerations alone that $K\beta'$ satellites are due to volume plasmons.

III. CALCULATION OF RELATIVE INTENSITY

Further support for the plasmon satellites can be obtained by calculating the relative intensities of $K\beta'$ with respect to $K\beta_{1,3}$ lines in Mn, MnO, MnO_2, Cr, CrO_3, K_2CrO_4, and $K_2Cr_2O_7$.

Recently several papers[39-44] have been published which draw attention to the strong plasmon satellites found accompanying core-level peaks. Langreth[40] has developed a general theory to explain the presence or absence of plasmon satellites in XPS, SXS, SXAPS, ($\hbar\omega_p$-APS), etc., experiments and he has differentiated between extrinsic and intrinsic coupling processes. An extrinsic effect is generally associated with an energy-loss process, while the intrinsic effect is important for plasmon satellites. Langreth[40] has further classified the intrinsic effect into two processes: (i) The slow electron is not conserved, e.g., in SXAPS, XPS, etc. experiments, and in this case plasmon satellites will be strong if the coupling constant is sufficiently large. (ii) Slow electrons are conserved in the transition process, e.g., in SXS, $\hbar\omega_p$-APS experiments, etc., and in this case plasmon satellites will be weak, even though the coupling constant itself may be large. Recently, Bradshaw *et al.*[43] have estimated the coupling constant for various processes.

Following Bradshaw *et al.*[43] and Langreth[40] the transition probability $P(\omega)$ per unit time and unit energy at energy ω, for the emission of a plasmon satellite, is given by

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

where[41,43] $\alpha = e^2 q_{\max}/\pi\hbar\omega_p \approx 0.12 r_s$, f is the matrix element for the process, and r_s is a dimensionless parameter and is given by[45]

$$r_s = (47.11/\hbar\omega_p)^{2/3}. \quad (3)$$

The weight factor $e^{-\alpha}\alpha^n/n!$ in Eq. (2) represents[39] the strength of the nth satellite ($n=0$ represents the main peak). Thus, the relative intensity of the first plasmon peak is given by

$$i = I_1/I_0 = \alpha \approx 0.12 r_s \quad (4)$$

The coupling parameter α can further be modified[39] by taking into account the effect of "slow-fast" interference terms which produces the cancellation when "slow" charge is conserved. The effect[39,41] of this interference term is to reduce α

TABLE I. Values of Z, σ, W, ΔE, and $\hbar\omega_p$ for Mn, Cr, and their compounds.

Sample No.	Substance	Z	σ	W	Energy separation: Tsutsumi *et al.* $(\Delta E)_{cal}$ (eV)	$(\Delta E)_{obs}$ (eV)	Authors $(\hbar\omega_p)_{cal}$ (eV)
1	Mn	1	7.20	54.99	3.55	9.02	10.42
2	MnO	3	5.46	70.93	10.44	15.18	13.85
3	MnO_2	5	5.026	86.93	7.36	14.72	15.48
4	Cr	1	7.20	52.01	1.77	8.3	10.72
5	CrO_3	7	2.70	100.01	···	10.3	12.52
6	K_2CrO_4	11	2.732	194.20	···	10.3	11.33
7	$K_2Cr_2O_7$	18	2.69	294.21	···	10.5	11.69

TABLE II. Intensity ratio $K\beta'/K\beta_{1,3}$ and r_s for Mn, Cr, and their compounds.

			Intensity ratio I_1/I_0		
			Tsutsumi *et al.*		
Sample No.	Substance	r_s	Calculated	Observed	Authors
1	Mn	2.73	0.34	0.11	0.22
2	MnO	2.26	0.71	0.19	0.17
3	MnO_2	2.10	0.60	0.14	0.15
4	Cr	2.68	0.23	0.26	0.22
5	CrO_3	2.41	...	0.22	0.19
6	K_2CrO_4	2.58	...	0.16	0.20
7	$K_2Cr_2O_7$	2.53	...	0.13	0.20

by an amount $(e^2/\hbar v)F$, i.e.,

$$\alpha' = \alpha - (e^2/\hbar v)F, \quad (5)$$

where F is a slowly varying function of velocity of magnitude one. The value of $e^2/\hbar v$ has been calculated[39,41] to be the order of 0.1 for incident energy of the order of keV and so α' is given by

$$\alpha' = \alpha - e^2/\hbar v = \alpha - 0.1,$$

$$\alpha' = \alpha - 0.1 = 0.12 r_s - 0.1. \quad (6)$$

Thus, using Eqs. (3)–(6) we have the intensity of the $K\beta'$ satellite,

$$i = I_1/I_0 = \alpha' = \alpha - 0.1 = 0.12 r_s - 0.1. \quad (7)$$

Thus, the calculated values of i for Mn, MnO, MnO_2, Cr, CrO_3, K_2CrO_4, and $K_2Cr_2O_7$ are 0.22, 0.17, 0.15, 0.22, 0.19, 0.21, and 0.20, respectively. These intensities calculated by plasmon-oscillations theory are more close to the observed values for $K\beta'$ satellites than those calculated by MO theory[19,20] (see Table II).

Thus, we can assign $K\beta'$ satellites in Mn, MnO, MnO_2, Cr, CrO_3, K_2CrO_4, and $K_2Cr_2O_7$ as due to volume-plasmon creation. Recently, Singh[46,47] has also estimated the value of the relative intensities of the $K\beta'$ plasmon satellites of Mn, MnO, and MnO_2. He has used a very high value of β, i.e.,

$$\beta = (4/q\pi)^{1/3} r_s = 0.52 r_s. \quad (8)$$

This value of β is valid[48] only at $T = 0$, where all plasmons are frozen. Thus, his estimation for the relative intensities of the $K\beta'$ satellites is not acceptable.

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