APPLICATION OF PLASMA OSCILLATIONS THEORY TO $K\beta'$ SATELLITE OF SOME CHROMIUM COMPOUNDS

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ABSTRACT

The energy separation and relative intensity of $K\beta'$ satellite of $K\beta_1$ X-ray emission line of $CrCl_2$, $Cr_2(SO_4)_3$ and Cr_2O_3 have been calculated using the theory of plasma oscillations in solids. This theory gives better fit with the experimentally observed values than the molecular orbital theory or exchange interaction theory.

INTRODUCTION

X-RAY satellites or non-diagram lines on the high energy side of parent emission lines are well known in X-ray emission spectroscopy. There are a number of theories[1–3] concerning the origin of these satellites and most of the high energy X-ray satellites have been explained. But there are some non-diagram lines which are found on the low energy side of the main X-ray emission line. There exists no satisfactory theory[3–9] which can give the correct energy separation and relative intensity of these low energy satellites.

Recently Tsutsumi *et al.*[6–8] have studied the low energy $K\beta'$ satellites in the $K\beta_1$ X-ray emission spectra of Mn, Cr and their compounds.

According to Tsutsumi *et al.*[6–8] the origin of the $K\beta'$ satellite is due to the exchange interaction between the electrons in the incompete $3d$ shell of elements in the first transition series and the hole in the $3p$ shell owing to the emission of the $K\beta_1$ line. The energy separation ($\triangle E$) between $K\beta'$ and $K\beta_1$ lines is given by

$$\triangle E = J(2S + 1) \tag{1}$$

and intensity ratio of the $K\beta'$ to $K\beta_1$ lines is given by

$$\frac{I'}{I} = \frac{S}{(S + 1)} \tag{2}$$

where J is the exchange integral[10] and S is the total spin of the $3d$ electrons. J can be expressed in terms of Hartree-Fock Slater integral[10] G^1 and G^3 as

$$J = \left[\frac{2}{15} G^1(3p, 3d) + \frac{3}{35} G^3(3p, 3d)\right] \tag{3}$$

The values of G^1 and G^3 have been computed by Mann[11]. Salem *et al.*[12] have also explained their origin on similar lines. According to them the exchange interaction between the $3d$ and $3p$ electrons in these elements causes some of the electrons in the $3p$ state to move to lower energy levels. Transitions from these levels appear as emission bands at the low energy side of the $K\beta_1$ line. However, from their data it appears 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 $K\beta_{1,3}$. It was therefore, thought of interest to explain the origin of the low energy satellite using plasmon oscillations in solids theory, which can give better values for the energy separation and relative intensity of satellites.

PLASMON THEORY

Blochin[9] in 1957 tried to explain the origin of $K\beta'$ satellites by assuming that part of the quantum energy 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[8] had rejected the idea without giving any reason for it. The present plasma oscillations in solids theory are fairly close to the Blochin[9] theory. In the X-ray emission process of $K\beta_1$ line if the valence electron while filling up the core level vacancy excites a plasmon in the valence band the energy of the emitted quantum of the $K\beta_1$ line will be less by an energy equal to the plasmon energy ($\hbar\omega_p$), giving rise to a weak line at an energy distance of $\hbar\omega_p$ from the main peak. This weak line is known as low energy plasmon satellite $K\beta'$. The quantized energy of plasmon oscillations is given by Marton *et al.*[13]

$$\hbar\omega_p = 28{\cdot}8 \sqrt{\frac{Z\sigma}{W}} \text{ eV} \tag{4}$$

where Z is the effective number of electrons taking part in plasma oscillations, σ is the specific gravity and W is the molecular weight.

Equation (4) is true for free electron model but to a fairly good approximation can also be used for semiconductors and insulators. According to Kittel[14], plasma oscillation in a dielectric is physically the same as in a metal. This fact can be substantiated from the work of Raether[15], Philipp and Ehrenreich[16], who have

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TABLE I

Value of Z, σ, W $\hbar\omega_p$ and r_s for $CrCl_2$, $Cr_2(SO_4)_3$ and Cr_2O_3

Substance	Z	σ	W	Energy Separation (△E)		
				Authors ($\hbar\omega_p$) cal. eV	Tsutsumi *et al.*, 1968	
					Observed eV	Calculated eV
$CrCl_2$	7	2·75	122·92	11·40	13·4	6·46
$Cr_2(SO_4)_3$	32	3·012	392·22	14·28	12·5	5·88
Cr_2O_3	8	5·21	152·02	15·08	12·8	5·88

shown after taking into account of band structure of solids that the plasma frequency for a dielectric is

$$\omega_{pd}^2 = \frac{\omega_p^2}{(1 - \delta\epsilon_0)} \tag{5}$$

where $\delta\epsilon_0$ is a very small quantity and can be neglected to a first approximation. Philipp and Ehrenreich[16] have shown that calculated values of $\hbar\omega_p$ and $\hbar\omega_{pd}$ are in fair agreement with the observed values of plasmon energy for dielectrics.

The recent[17–20] observed plasma loss values in transition elements show that the effective number of electrons taking part in plasma oscillations is one. In Cr, ($3d^5$, $4s^1$), the *d* electrons are tightly bound so only the $4s^1$ electron takes part in plasmon oscillations. Thus the value of *Z* is one for Cr. This fact has also been shown theoretically by the author[20] recently. In case of oxygen, Glasstone[21] has shown that the number of unpaired electrons is two, similarly in case of sulphur and chlorine the value of *Z* is 2 and 3 respectively. Thus taking the values of *Z*, σ and *W* from Table I, equation (4) gives the calculated values for plasmon energies for $CrCl_2$, $Cr_2(SO_4)_3$ and Cr_2O_3 as 11·40 eV, 14·28 eV and 15·08 eV respectively which are fairly close to the experimentally observed[8] values of the energy separation of $K\beta'$ satellites $K\beta_1$ line (See Table I). The difference of about 2 eV in the calculated and observed values may be partly due to rough estimation of the effective number of *Z* and $\hbar\omega_p$ and partly due to the experimental error. The plasmon satellites have been identified in most of the cases by energy separation alone. Thus from energy consideration the $K\beta'$ satellite in the above mentioned compounds may be regarded as due to creation of volume plasmons.

COMPARISON OF INTENSITIES

Further confirmation for the origin of $K\beta'$ satellites can be made by calculating the relative intensity of $K\beta'$ to $K\beta_{1,3}$ line. Recently several papers[22–24] have been published drawing attention to the strong plasmon satellites accompanying the main lines.

Langreth[22–24] has developed a general theory to explain the presence or absence of plasmon satellites in SXS, XPS, XSAPS, etc., experiments and differentiated between extrinsic and intrinsic coupling processes. An extrinsic effect is generally associated with energy loss process while intrinsic effect is important for plasmon satellites. He has further classified the intrinsic effect into two processes. (1) In which the slow electron is not conserved, *e.g.*, in SXAPS and XPS, etc., experiments and in which case plasmon satellites will be strong if the coupling constant is sufficiently large, (2) When the slow electrons are conserved in the transition process, *e.g.*, in SXS experiment and in this case plasmon satellites will be weak even though the coupling constant itself may be high.

Following Langreth[23] the transition probability $P(\omega)$ per unit time per unit energy at an energy $\hbar\omega$, for the emission of a plasmon satellite is given by

$$P(\omega) = |f|^2 \sum_n e^{-a} \frac{a^n}{n!} \delta(\omega - \epsilon_k - a\omega_p + n\omega_p) \tag{6}$$

where *a*, the coupling parameter, is given by[23–25]

$$a = \frac{e^2 q_{max}}{\pi\hbar\omega_p} \approx 0{\cdot}166\, r_s \tag{7}$$

f is the matrix element for the process, q_{max} is the plasmon out of wave vector and r_s is dimensionless parameter and is given by[25]

$$r_s = \left(\frac{47{\cdot}11}{\hbar\omega_p}\right)^{2/3}. \tag{8}$$

The weight factor $e^{-a}\, a^n/n!$ in equation (6) represents[22] the strength of the *n*th satellite ($n = 0$, represents the main peak). Thus the relative intensity of the first

TABLE II

Values of r_s and relative intensities

Substance	r_s	Relative Intensity (i)		
		Authors Value	Tsutsumi *et al.* (1968)	
		Calculated	Observed	Calculated
$CrCl_2$	2·57	0·43	0·47	0·67
$Cr_2(SO_4)_3$	2·21	0·37	0·37	0·60
Cr_2O_3	2·13	0·35	0·39	0·60

plasmon peak in fluorescence excitation is given by

$$i = \frac{I_1}{I_0} = a = 0{\cdot}166\, r_s. \qquad (9)$$

Thus using equations (8) and (9), the relative intensities of the $K\beta'$ plasmon satellites with respect to the main line $K\beta_{1,3}$ in $CrCl_2$, $Cr_2(SO_4)_3$ and Cr_2O_3 come out to be 0·43, 0·37 and 0·35 respectively. Thus the calculated values are in fair agreement with observed values 0·47, 0·37 and 0·39 reported by Tsutsumi *et al.*[8] (See Table II). The differences in the calculated and observed values of the relative intensities are small and can be accounted as due to the approximation made in the values of a and r_s.

CONCLUSION

Thus we can assume the $K\beta'$ satellites in $CrCl_2$, $Cr_2(SO_4)_3$ and Cr_2O_3 as due to volume plasmon creation.

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1. Hirsh, F. R., *Rev. Mod. Phys.*, 1942, **14**, 15.
2. Edwards, S. J., *Contemp. Phys.*, 1970, **11**, 195.
3. Deodhar, G. B., *Proc. Natl. Acad. Sci. India*, 1962, **32**, 320.
   Parratt, L. G., *Rev. Mod. Phys.*, 1959, **31**, 616.
5. Watson, J. M., Dimond, R. K. and Fabian, D. J., in *Soft X-Ray Band Spectra and Electronic Structure of Metal and Materials*, ed. D. J. Fabian, Academic Press, New York, 1968, p. 45.
6. Tsutsumi, K., *J. Phys. Soc. Japan*, 1959, **14**, 1696.
7. —, Nakamori, H. and Ichikawa, K., *Phys. Rev.*, 1976, B13, 929.
8. — and —, *J. Phys. Soc. Japan*, 1968, **25**, 1418.
9. Blochin, M. A., *Physik der Rontgen Strahlen*, Veb-Verlag Technik, Berlin, 1957, p. 343
10. Condon, E. U. and Shortley, G. H., *The Theory of Atomic Spectra*, Cambridge University Press, London, 1957, p. 117, 174.
11. Mann, J. B., *Los Alamos Report* 1967, No. LA3690 unpublished.
12. Salem, S. I., Hockrey, G. M. and Lee, L. P., *Phys. Rev.*, 1976, **A13**, 330.
13. Marton, L., Leder, L. B. and Mendlowitz, H., in *Advances in Electronics and Electron Physics*, ed. L. Marton, Academic Press, New York, 1955, 7, 183, 225.
14. Kittel, C., *Introduction to Solid State Paysics*, 4th Edition (1971), (Second Wiley Eastern Reprint, New Delhi, 1974), p. 227
15. Raether, H., *Ergebnisse der exacten Naturwissenchaften*, 1965, **38**, 84.
16. Philipp, H. R. and Ehrenreich, H., *Phys. Rev.*, 1963, **129**, 1550.
17. Vehse, R. C. and Arakawa, B. T., *Ibid.*, 1960, **180**, 695.
18. Feuerbacher, B., Fitton, B., *Phys. Rev. Lett.*, 1970, **24**, 499.
19. Borovskii, I. B. and Shmidt, V. V., *Soviet Phys. Dokl.*, 1959, **4**, 855.
20. Srivastava, K. S., *J. of Electron Spectroscopy and Related Phenomena*, 1980, **20**, 319.
21. Glasstone, S., *Theoretical Chemistry*, D. Van Nostrand Co. Inc., New York, 1964, p. 97.
22. Langreth, D. C., *Nobel Symposia*, 1973, **24**, 210. *Collective Properties of Physical Systems*, Academic Press, 1974.
23. Langreth, D. C., *Phys. Rev.* 1970, **B1**, 471; *Phys. Rev. Lett.*, 1971, **26**, 1229.
24. Chang, J. J. and Langreth, D. C., *Ibid.*, 1972, **5**, 3512.
25. Rooke, G. A., in *Soft X-Ray Band Spectra and Electronic Structure of Metals and Materials*, Ed. D. J. Fabian, Academic Press, New Yk,or 1968, p. 6.