

591-4

Relative intensities of high energy plasmon satellites in $K\alpha$ X-ray emission spectra of various fluorine compounds

K S Srivastava, Kirti Sinha, V K Rastogi*, Sharad Srivastava & K K Saxena

Physics Department, Lucknow University, Lucknow 226 007

Received 12 December 2000; accepted 26 June 2001

The K^1L^1 satellites of $K\alpha_{1,2}$ X-ray emission line of various fluorine compounds may be identified as plasmon satellites. An explanation for their origin is suggested using the Bohm and Pines theory of plasma oscillations in solids. Present calculated values for the relative intensities of the K^1L^1 satellites with respect to the main $K\alpha_{1,2}$ X-ray line agree well with the experimentally observed values of Endo *et al.*, [*Phys Rev A*, 22 (1980) 1436-1440].

1 Introduction

With improved technique in X-ray spectrography, many more lines, other than the main X-ray diagram lines, were discovered. Most of them were rather faint and were usually found close to and on the high or low-frequency side of the more intense lines; hence they were called "satellites" or "second order" lines; as they could not be readily fitted in the conventional energy level diagram, unlike the "parent" lines, they were called also "non-diagram" lines. The satellites which are found on the high-energy side of the X-ray diagram lines, often abbreviated as high-energy satellites (HES) and those on the low-energy side of the parent lines as low-energy satellites (LES).

Various theories, like charge transfer theory^{1,2}, multi-ionization theory³ and shake-up theory⁴ have been proposed from time to time, to explain the origin of high-energy satellites. But those X-ray satellites whose energy distance from the parent line is equal to plasmon energy, cannot be explained satisfactory by conventional theories¹⁻⁴ except by plasma oscillations theory.

Ferrell⁵ and Nozieres and Pines⁶ pointed out for the first time and later Srivastava *et al.*^{7,8} have shown theoretically that plasma oscillations in solids can complicate the structure of X-ray emission spectra. Nozieres and Pines⁶ and Brouers⁹ have also advanced the theory that X-ray transition in metals

could be accompanied by the excitation of one or more plasmons. In recent years it has also been shown theoretically and experimentally by several workers⁹⁻¹⁵ that the interpretation of X-ray emission spectra must include the contribution of created or annihilated core holes to the collective mode of conduction electrons. This interaction produces a structure, in the X-ray emission spectra, which is displaced from the main peak by an energy separation $\Delta E = \hbar\omega_p$ (the volume plasmon energy) or $\Delta E = \hbar\omega_s$ (the surface plasmon energy).

About twenty years back, Endo *et al.*¹⁶ have observed high-energy X-ray satellites of F $K\alpha$ main diagram line for the compounds NaF, LiF, CaF₂, Na₃AlF₆, MgF₂, AlF₃, NiF₂, PbF₂, CuF₂ and teflon. The group of satellites, i.e. α' , α_3 and α_4 is designated as K^1L^1 satellites originating from single-K and single-L hole states. They have observed relative intensities of these satellites with respect to $K\alpha$ main diagram line irradiated with photons and electrons both separately. They have said that intensity of these satellites depends upon Pauling bond ionicity or bond covalency of fluorides and ascribed these satellites as due to shake up and shake off processes ignoring totally the involvement of plasmon excitation during the process.

Therefore, in the present paper, it is thought of great interest to use plasma oscillations theory to explore the origin of high-energy X-ray satellites

*Lajpat Rai (PG) College, Sahibabad, Ghaziabad (UP)

(K^1L^1) of $K\alpha$ main emission line of various fluorine compounds.

According to plasma oscillation theory^{7,17-19}, during the X-ray emission process, the transiting valence electron excites a plasmon in the valence band. The transition energy of the main emission line is shared between the plasmon and the emitted photon which will thus be deprived of an energy equal to the plasmon energy ($\hbar\omega_p$ or $\hbar\omega_s$) used up in emitting the plasmon. Thus, this process will give rise to the emission of a low-energy X-ray plasmon satellite. On the other hand, if plasmon pre-exists, it can transfer its energy on decay, to a conduction electron which subsequently fills the core vacancy, with the emission of an X-ray photon. This emission line, due to plasmon energy gain, will possess energy higher than the parent line by an amount $\hbar\omega_p$ or $\hbar\omega_s$. This line is known as high-energy plasmon satellite.

The energy-separation (ΔE_p) of the low or high-energy volume plasmon satellite from the main emission line is given by Marton *et al*²⁰.

$$\Delta E_p = \hbar\omega_p = 28.8 \left(\frac{Z\sigma}{W} \right)^{1/2} \text{ eV} \quad \dots(1)$$

This equation represents the oscillation of volume density of electrons. But at the surface or boundary of the solid, oscillation of surface electron density gives rise to surface plasma oscillation. Ritchie²¹ showed the existence of surface plasmon using dielectric theory of loss and after some mathematical rigours gave formula for surface plasmon energy with minor modification in Eq.(1) due to Marton as:

$$\begin{aligned} \Delta E_s &= \hbar\omega_s \\ &= \frac{1}{\sqrt{2}} |\hbar\omega_p| \\ &= \frac{1}{\sqrt{2}} \left[28.8 \left(\frac{Z\sigma}{W} \right)^{1/2} \right] \text{ eV} \quad \dots(2) \end{aligned}$$

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

In order to calculate energy-separation ΔE_p or ΔE_s , the values of Z , σ and W for each compound should be known. Z can be calculated for any compound by writing down the outermost electronic configuration of each element in ground and excited states and making use of Hund's rule.

For example, take the compound Na_3AlF_6 . The electronic configuration of Na, Al and F in ground states is given by: ($3s^1$), ($3s^2.3p^1$) and ($2s^2.2p^5$), respectively. In the excited state the electronic configuration becomes ($3s^1$), ($3s^1, 3p^2$), ($2s^2.2p^5$) for Na, Al and F, respectively. Now, the distribution of electrons in the orbitals of any sub-energy level is done by Hund's rule. According to which, "As far as possible, the number of unpaired electrons in the orbitals of a given sub-energy level is a maximum and the unpaired electrons have parallel spins". Thus the number of unpaired electrons, i.e. $Z=1,3,1$ and Na, Al and F respectively. Therefore, the effective number of unpaired electrons taking part in plasma oscillations for compound $\text{Na}_3\text{AlF}_6=3\times 1+3+6\times 1=12$. With the help of values of Z , σ and W , the plasmon energies are calculated for various fluorides which are given in Table 1.

Table 1 — Energy-separation of K^1L^1 — surface plasmon satellites

S. No.	Compound	Z	σ	W	Surface Plasmon Energy E_s (calc.) $= \hbar\omega_s$ $= \frac{1}{\sqrt{2}} \hbar\omega_p $ $= 28.8$ $[(Z\sigma/2W)^{1/2}]$ [In eV]
1	NaF	2	2.558	41.99	7.11
2	LiF	2	2.635	25.94	9.18
3	CaF ₂	4	3.18	78.08	8.22
4	Na ₃ AlF ₆	12	2.90	209.94	8.29
5	MgF ₂	4	3.15	62.30	9.16
6	AlF ₃	6	2.882	83.98	9.24
7	NiF ₂	3	4.63	96.69	7.72
8	PbF ₂	6	8.24	245.20	9.14
9	CuF ₂	3	8.23	101.54	7.20

Further confirmation of the origin of K^1L^1 satellites can be made by calculating intensity relative to the $K\alpha_{1,2}$ line. The relative intensity of plasmon satellites depends on as to how the excitation of plasmon takes place.

Langreth^{22,24} and Chang & Langreth²⁵ have developed a general theory to examine the excitation of plasmon in soft X-ray spectroscopy (SXS), X-ray photoelectron spectroscopy (XPS), soft X-ray appearance potential spectroscopy (SXAPS), etc. experiments and differentiated between extrinsic and intrinsic coupling processes. An extrinsic effect is generally associated with an energy-loss process while an intrinsic effect is important for plasmon satellites. They have further classified the intrinsic effect into two categories: (1) processes in which the number of slow electrons is not conserved, e.g. in SXAPS and XPS, etc. experiments and in this case plasmon satellites will be strong if the coupling constant is sufficiently large, and (2) processes in which the number of slow electrons is conserved, e.g. in SXS experiments and in this case plasmon satellites will be weak even though the coupling constant itself, may be large.

Following Langreth²³ and Bradshaw *et al.*¹⁰ the transition probability $P(\omega)$ per unit time per unit energy range at an energy $\hbar\omega_p$ for the emission of a plasmon satellite in non-conserved case is given by:

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

where, f = matrix element for the process, α = dimensionless coupling constant between plasmon and electron and is given by^{22,25}

$$\alpha = \left[\frac{e^2 q_{max}^2}{\pi \hbar \omega_p} \right] \approx 0.12 r_s \dots(4)$$

where q_{max} is the plasmon cut-off wave vector and r_s is dimensionless parameter given by:

$$r_s = \left[\frac{47.11}{\hbar \omega_p} \right]^{2/3} ; \text{ for a volume plasmon satellite} \\ = \left[\frac{47.11}{\hbar \omega_s} \right]^{2/3} ; \text{ for a surface plasmon satellite} \dots(5)$$

The weight factor $e^{-\alpha} \alpha^n / n!$ in Eq. (3) represents²² the strength of the n th satellite ($n = 0$, represents the main line). Thus, the relative intensity of the first plasmon peak to the main peak in fluorescent excitation is given by:

$$i = \frac{I_1}{I_0} = \alpha = 0.12 r_s \dots(6)$$

The calculated values of i for various fluorine compounds are given in Table 2 and the results have also been compared there with those of Endo *et al.*¹⁶. This comparison shows that our calculated values are in fair agreement with the experimental values of Endo *et al.*¹⁶ for tabled fluorine compounds.

Table 2 — Relative-intensity of high-energy surface plasmon satellites (K^1L^1)

S. No.	Compound	$r_s = \left(\frac{47.11}{\hbar \omega_s} \right)^{2/3}$	Relative Intensity	
			Calc. value of authors [$i=0.12r_s$]	Experimental Value of Endo <i>et al.</i> (Ref.16)
1	NaF	3.53	0.423	0.493
2	LiF	2.98	0.357	0.424
3	CaF ₂	3.20	0.384	0.392
4	Na ₃ AlF ₆	3.18	0.382	0.414
5	MgF ₂	2.98	0.358	0.375
6	AlF ₃	2.96	0.355	0.332
7	NiF ₂	3.34	0.401	0.326
8	PbF ₂	2.98	0.358	0.294
9	CuF ₂	3.50	0.420	0.293

Therefore, one can conclude that the K^1L^1 satellites of F $K\alpha$ emission line in these fluorides may be due to plasmon gain process.

Acknowledgement

The authors are thankful to the University Grants Commission, New Delhi for financial assistance.

References

- 1 Kawai J, Nihei Y, Fujinami M, Higashi Y, Fukushima S & Gohshi Y, *Solid State Commun.* 70 (1989), 567.
- 2 Kawai J, Maeda K, Sasa Y, Takami M & Uda M, *RIKEN Accel Prog Rep.* 24 (1990) 50.
- 3 Kawai J & Gohshi Y, *Spectrochimica Acta B.* 41 (1986) 256.
- 4 Kawai J, *Nucl Instrum Meth Phys B.* 75 (1993) 3.

- 5 Ferrell R. *Rev Mod Phys*, 28 (1956) 308.
- 6 Nozieres P & Pines D. *Phys Rev*, 113 (1959) 1254.
- 7 Srivastava K S, Singh Shiv, Srivastava A K, Nayal R S, Chaubey Amita & Gupta Pratibha. *Phys Rev A*, 25 (1982) 2838.
- 8 Srivastava K S, Srivastava R L, Harsh O K & Kumar V. *Phys Rev B*, 19 (1979) 4336.
- 9 Brouers F. *Phys Status Solidi*, 22 (1967) 213.
- 10 Bradshaw A M, Cederbaum S L, Domeke W & Krause V. *J Phys C, Solid State Phys*, 7 (1974) 4503.
- 11 Rooke G A. *Phys Lett*, 3 (1963) 234.
- 12 Watson L H, Dimond R K & Fabian D J, in *Soft X-ray B and spectra and the electronic structure of metals and materials*, (Ed) D J Fabian, (Academic Press, New York), 1968, p. 45; p. 57.
- 13 Houston J E & Park R L. *Solid State Commun*, 10 (1972) 91; *J Vacuum Sci*, 9 (1972) 579.
- 14 Glick A J & Longe P. *Phys Rev Lett*, 15 (1965) 589.
- 15 Srivastava K S, Srivastava R L, Harsh O K & Kumar V. *J Phys Chem Solids*, 40 (1979) 489.
- 16 Endo H, Uda M & Maeda K. *Phys Rev A*, 22 (1980) 1436.
- 17 Bohm D & Pines D. *Phys Rev*, 82 (1951) 625.
- 18 Bohm D & Pines D. *Phys Rev*, 85 (1952) 338.
- 19 Bohm D & Pines D. *Phys Rev*, 92 (1953) 609; 626.
- 20 Marton L, Leder L B & Mendlowitz H. *Advances in Electronics and Electron Physics*, Vol. 1. (Ed) L Marton, (Academic Press, New York), 7 (1955) 225.
- 21 Ritchie R H. *Phys Rev*, 106 (1957) 874.
- 22 Langreth D C. *Phys Rev B*, 1 (1970) 471.
- 23 Langreth D C. *Phys Rev Lett*, 26 (1971) 1229.
- 24 Langreth D C. *Noble Symp*, 24 (1973) 210; *Collective properties of physical systems* (Academic Press, New York), 1974.
- 25 Chang J J & Langreth D C. *Phys Rev B*, 5 (1972) 3512.