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

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The $K\ell'$ satellites of $K\alpha\ell$ 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 $K\ell'$ satellites with respect to the main $K\alpha\ell$ 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, multi-ionization theory and shake-up theory 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 theories except by plasma oscillations theory.

Ferrell and Nozieres and Pines pointed out for the first time that later Srivastava et al. have shown theoretically that plasma oscillations in solids can complicate the structure of X-ray emission spectra. Nozieres and Pines and Brouers 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 workers 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. have observed high-energy X-ray satellites of F $K\ell$ main diagram line for the compounds NaF, LiF, CaF$_2$, NaAlF$_3$, MgF$_2$, AlF$_3$, NiF$_2$, Pbf$_3$, CuF$_2$ and teflon. The group of satellites, i.e. $\alpha'$, $\alpha_1$ and $\alpha_2$ is designated as $K\ell'$ 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.
(K'LI') of Kα main emission line of various fluorine compounds.

According to plasma oscillation theory\cite{17-20}, 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 ($h\omega_p$ or $h\omega_e$) 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 $h\omega_p$ or $h\omega_e$. This line is known as high-energy plasmon satellite.

The energy-separation ($\Delta E_p$) of the low or high-energy volume plasmon satellite from the main emission line is given by Marton et al\cite{10}:

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

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. Ritchie\cite{13} 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:

$$\Delta E_s = h\omega_s = \frac{1}{\sqrt{2}} \left[ h\omega_p \right]$$

$$\Delta E_s = \frac{1}{\sqrt{2}} \left[ 28.8 \left(\frac{Z\sigma}{W}\right)^{1/2} \right] \text{eV} \quad \text{(2)}$$

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

In order to calculate energy-separation $\Delta E_p$ or $\Delta E_s$, the values of $Z$, $\sigma$ 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 NaAlF₄. The electronic configuration of Na, Al and F in ground states is given by: $(3s^1)$, $(3s^2,3p^1)$ and $(2s^2,2p^3)$ respectively. In the excited state the electronic configuration becomes $(3s^1)$, $(3s^1, 3p^1), (2s^2, 2p^3)$ 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 NaAlF₄ is $3+3+6\times1=12$. With the help of values of $Z$, $\sigma$ and $W$, the plasmon energies are calculated for various fluorides which are given in Table 1.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>$Z$</th>
<th>$\sigma$</th>
<th>$W$</th>
<th>Surface Plasmon Energy $E_s$ (calc.) $= h\omega_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaF</td>
<td>2</td>
<td>2.558</td>
<td>41.99</td>
<td>7.11</td>
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<tr>
<td>2</td>
<td>LiF</td>
<td>2</td>
<td>2.635</td>
<td>25.94</td>
<td>9.18</td>
</tr>
<tr>
<td>3</td>
<td>CaF₂</td>
<td>4</td>
<td>3.18</td>
<td>78.08</td>
<td>8.22</td>
</tr>
<tr>
<td>4</td>
<td>NaAlF₄</td>
<td>12</td>
<td>2.90</td>
<td>209.94</td>
<td>8.29</td>
</tr>
<tr>
<td>5</td>
<td>MgF₂</td>
<td>4</td>
<td>3.15</td>
<td>62.30</td>
<td>9.16</td>
</tr>
<tr>
<td>6</td>
<td>AlF₃</td>
<td>6</td>
<td>2.882</td>
<td>83.98</td>
<td>9.24</td>
</tr>
<tr>
<td>7</td>
<td>NiF₂</td>
<td>3</td>
<td>4.63</td>
<td>96.69</td>
<td>7.72</td>
</tr>
<tr>
<td>8</td>
<td>PbF₂</td>
<td>6</td>
<td>8.24</td>
<td>245.20</td>
<td>9.14</td>
</tr>
<tr>
<td>9</td>
<td>CaF₂</td>
<td>3</td>
<td>8.23</td>
<td>101.54</td>
<td>7.20</td>
</tr>
</tbody>
</table>

Table 1 — Energy-separation of K'LI'—surface plasmon satellites

Further confirmation of the origin of K'LI' satellites can be made by calculating intensity relative to the Kα₂ line. The relative intensity of plasmon satellites depends on as to how the excitation of plasmon takes place.
Langreth\textsuperscript{23} and Chang & Langreth\textsuperscript{25} 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 Langreth\textsuperscript{23} and Bradshaw \textit{et al.}\textsuperscript{16} the
transition probability \( P(\alpha) \) per unit time per unit
energy range at an energy \( h\omega_r \) for the emission of a
plasmon satellite in non-conserved case is given by:

\[
P(\alpha) = \left| f \right|^2 \sum_{n} e^{-\alpha n} \frac{\alpha^n}{n!} \delta(\omega - \varepsilon_p - \alpha \omega_p + n \omega_p) \ldots (3)
\]

where, \( f \) = matrix element for the process, \( \alpha = \)
dimensionless coupling constant between plasmon
and electron and is given by\textsuperscript{23,25}

\[
\alpha = \left( \frac{e^2 d_{\text{max}}}{\pi \hbar \omega_p} \right) \approx 0.12 r_s
\]

(\( 4 \))

where \( d_{\text{max}} \) is the plasmon cut-off wave vector and \( r_s \)
is dimensionless parameter given by:

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

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

(\( 5 \))

The weight factor \( e^{-\alpha n} / n! \) in Eq. (3)
represents\textsuperscript{2} 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:

\[
i = \frac{i_1}{i_0} = \alpha = 0.12 r_s
\]

(\( 6 \))

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 \textit{et al.}\textsuperscript{8}
This comparison shows that our calculated values
are in fair agreement with the experimental values
of Endo \textit{et al.}\textsuperscript{12} for tabled fluorine compounds.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>( \omega )</th>
<th>Relative Intensity</th>
<th>Calc. value of authors ( [0.12r_s] )</th>
<th>Experimental Value of Endo \textit{et al.} (Ref.16)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaF</td>
<td>3.53</td>
<td>0.423</td>
<td>0.493</td>
<td></td>
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<tr>
<td>2</td>
<td>LiF</td>
<td>2.98</td>
<td>0.357</td>
<td>0.424</td>
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</tr>
<tr>
<td>3</td>
<td>CaF\textsubscript{2}</td>
<td>3.20</td>
<td>0.384</td>
<td>0.392</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Na\textsubscript{2}AlF\textsubscript{6}</td>
<td>3.18</td>
<td>0.382</td>
<td>0.414</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>MgF\textsubscript{2}</td>
<td>2.98</td>
<td>0.358</td>
<td>0.375</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>AlF\textsubscript{3}</td>
<td>2.96</td>
<td>0.355</td>
<td>0.332</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>NiF\textsubscript{3}</td>
<td>3.34</td>
<td>0.401</td>
<td>0.326</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>PbF\textsubscript{2}</td>
<td>2.98</td>
<td>0.358</td>
<td>0.294</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>CuF\textsubscript{2}</td>
<td>3.50</td>
<td>0.420</td>
<td>0.293</td>
<td></td>
</tr>
</tbody>
</table>

Therefore, one can conclude that the K'\textsubscript{L}'
satellites of F K\alpha emission line in these fluorides
may be due to plasmon gain process.

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\textbf{References}

Accel Prog Rep.}, 24 (1990) 50.
256.