

## Evidence for resonance electron transfer in photon excited X-ray satellite spectra of fluorine compounds

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**Abstract.** The  $K\alpha L^1/K\alpha L^0$  intensity ratio of fluorine is measured in five fluorine compounds with a crystal spectrometer. An anomalous reduction of this intensity ratio was observed in KF and SrF<sub>2</sub>, which is attributed to resonance electron transfer from the metal ion to the spectator vacancy in the fluorine ion.  $K\alpha L^2/K\alpha L^0$  intensity ratio of fluorine is also measured. The measured relative intensities are compared with the theoretical estimates of Aberg.

**Keywords.** X-ray satellites; resonance electron transfer; crystal spectrometer.

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### 1. Introduction

When an atom ionized simultaneously in different shells de-excites, X-ray satellites are produced [1]. If some holes are present in the L-shell along with a hole in the K-shell, the transitions to the K-shell from the L-shell give rise to the  $K\alpha$  X-ray satellite lines, with the holes in the L-shell acting as spectators. These spectator holes reduce the screening of the nuclear potential felt by the other electrons in the L-shell and thus result in a higher binding energy of the L-shell and hence the  $K\alpha$  satellite lines have energies higher than that of the diagram line. These satellites are denoted as  $K\alpha L^n$ , where  $n$  stands for the number of holes in the L-shell. In the absence of any such L holes the diagram line  $K\alpha L^0$  is emitted.

The intensity of these X-ray satellite lines relative to that of the diagram line is known to be influenced by the chemical environment of the radiating atom in the case of compounds [2,3]. The motivation for the present work is (1) to look for

chemical effects on the  $K\alpha$  X-ray satellite relative intensity of fluorine atoms, (2) to test the validity of theoretical estimates of these relative intensities by comparison with the experimental values and (3) to compare the experimental values obtained by photon excitation with those measured by electron excitation in the available cases.

## 2. Experimental details

In the present investigations, a Philips 1410 wavelength dispersive plane crystal spectrometer was used. The principle involved and the general experimental details have already been reported [4]. This system, in brief, consists of an X-ray tube, a plane crystal, a microprocessor-controlled goniometer, and a continuous flow type P-10 gas (90% argon–10% methane) proportional counter with a thin (1  $\mu\text{m}$ ) polypropylene window. The wavelength of fluorine  $K\alpha$  peak is 18.32 Å and hence the plane crystal with appropriate  $2d$  spacing TlAP ( $2d = 25.75$  Å) is used as the analyzing crystal. Rhodium anode was used in the X-ray tube and the tube was operated at a suitable potential and current (30 kV and 40 mA) to get good intensities. The fluorine compounds KF, NaF, LiF, SrF<sub>2</sub> and MgF<sub>2</sub> in the form of pure powders (99.9% purity) were pressed into pellets of 50 mm diameter and 5 mm thickness and used as targets. The characteristic X-rays emitted from the target were collimated by two fine collimators, one at the target and the other at the detector.

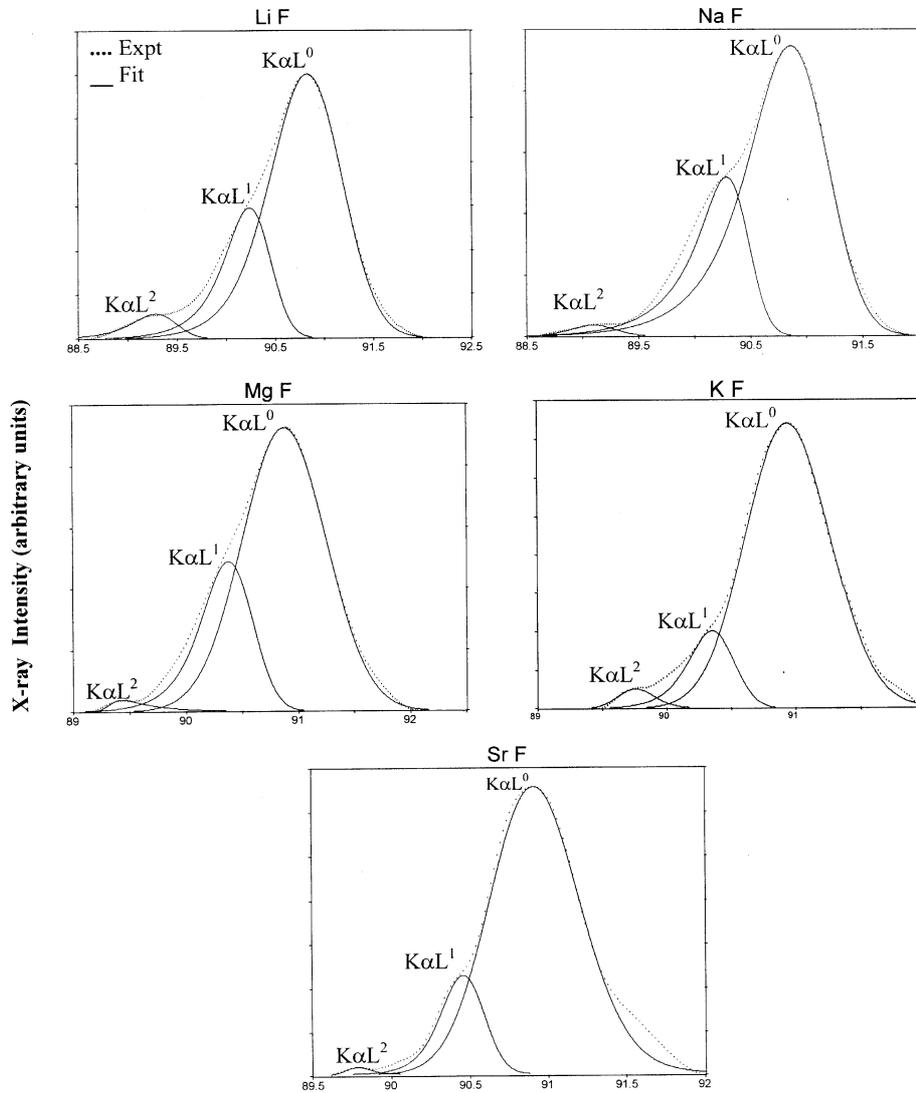
First-order spectra were recorded for all the targets in  $2\theta$  steps of  $0.02^\circ$ . In general, good statistics were maintained. But in the case of  $K\alpha L^2$  satellite line, statistics are satisfactory only in the case of LiF and hence the relative intensity of  $K\alpha L^2$  satellite is reported only for that compound. The de-convolution and estimation of intensities of different peaks are done using ‘peak-fit’ software version-4.11. In this peak-fit programme, smoothing of the raw experimental data is done by Gaussian convolution by taking FWHM value in  $2\theta$  as one degree. Next, peak fitting is done by choosing an appropriate peak-fit function which in the present case is EMG (exponentially modified Gaussian). The EMG is the mathematical convolution of a Gaussian with a first-order decay or exponential response function. There are only two components in this model, a primary Gaussian and a one-sided exponential response function which convolves or smears the Gaussian. As the exponential element increases, peaks become more right asymmetric or tailed as

$$y = \frac{a_0}{2a_3} \exp \left[ \frac{a_2^2}{2a_3^2} + \frac{(a_1 - x)}{a_3} \right] \left[ \operatorname{erf} \left( \frac{x - a_1}{\sqrt{2}a_2} - \frac{a_2}{\sqrt{2}a_3} \right) + \frac{a_3}{|a_3|} \right],$$

where  $a_0$  = area,  $a_1$  = centre,  $a_2$  = width ( $>0$ ),  $a_3$  = distortion ( $\neq 0$ ), erf: exponential response function component.

The experimental and fitted spectra are presented in figure 1. The estimated intensities are corrected for self-absorption in the sample, absorption in the window of the detector, efficiency of the detector and crystal reflectivity. All these corrections taken together do not account for more than 3%. Taking into consideration the counting statistics and the uncertainty involved in the de-convolution of the peaks, the relative intensities of the satellite lines are reported with a total error of 10%.

$K\alpha L^1/K\alpha L^0$  intensity ratio of fluorine



2θ (corresponding energies of the peaks are given in table 3)

Figure 1.  $K\alpha$  satellite spectra of F in different compounds.

The present  $K\alpha L^1$  satellite relative intensities (in %) for the five fluorine compounds LiF, NaF,  $MgF_2$ , KF,  $SrF_2$  are presented in table 1, along with the values of this ratio determined for LiF and NaF by electron excitation [5]. The theoretical value of this ratio for fluorine estimated by Aberg [6] based on sudden approximation principle is also furnished.

**Table 1.**  $K\alpha L^1$  satellite relative intensity (in %) in fluorine compounds.

| Name of the compound | $K\alpha L^1/K\alpha L^0$  |                               |                                |
|----------------------|----------------------------|-------------------------------|--------------------------------|
|                      | Present experimental value | Electron excitation value [5] | Theoretical value of Aberg [6] |
| LiF                  | 32.9±3.3                   | 35.0                          |                                |
| NaF                  | 37.5±3.7                   | 40.0                          |                                |
| MgF <sub>2</sub>     | 34.3±3.4                   | –                             | 42.5                           |
| KF                   | 15.4±1.5                   | –                             |                                |
| SrF <sub>2</sub>     | 17.2±1.7                   | –                             |                                |

The present experimental values of the  $K\alpha L^1$  relative intensity ratio for LiF and NaF are in good agreement within experimental errors with those measured by electron excitation [5].

It can be seen that  $K\alpha L^1$  line relative intensity with respect to that of  $K\alpha$  diagram line is very much lower in the case of KF and SrF<sub>2</sub> compared to other compounds. This anomalously low value of the relative intensity was observed in these compounds in the study of Watson *et al* [7] by ion excitation and in the case of KF in the work of Fischer *et al* [5] by electron excitation. The anomalous decrease in intensity of this satellite line in these compounds is explained as being due to the ‘resonance electron transfer phenomenon’ proposed by Watson *et al* [7]. In this phenomenon electrons will be transferred from the outer  $np$  levels of neighbouring metal ions to the 2p levels of fluorine ions which have been excited to  $1s^{-1}2p^{-1}$  states by the impact of photons. In the ground state, 2p level of the fluorine atom is confined to a narrow valence band. Impact of photons causes simultaneous ionization of 1s and 2p orbitals and this results in an increase in the 2p binding energy. Thus the 2p level of the fluorine atom is brought from the valence band to a level in close proximity with the outer  $np$  levels of the metal ions. When the energy difference ( $\Delta E$ ) between the outer  $np$  levels of the metal ions and the excited level of 2p vacancy of the fluorine ion in a fluorine compound becomes small enough, electron transfer from the metal ion to the ligand fluorine atom can take place thus filling up the 2p vacancy in the fluorine atom. This condition is met in the case of KF and SrF<sub>2</sub> as demonstrated by Watson *et al* with a computation based on point charge model of Citrin and Thomas [8]. In such a situation the spectator vacancy, necessary for the emission of a satellite line, disappears and consequently a diagram line is emitted in its place. This results in reduction in the intensity of the satellite line and enhancement of the intensity of the diagram line, thus giving a lower  $K\alpha L^1$  relative intensity ratio.

The present experimental  $K\alpha L^1$  relative intensity is lower than theoretical value [6], and the experimental  $K\alpha L^2$  relative intensity value (table 2) is slightly higher than the theoretical value [9]. The main assumptions in the theoretical model of Aberg are: (i) it is based on sudden approximation, (ii) it assumes a neon core, (iii) it neglects the exchange effects between the electrons and (iv) treatment is in the L-S coupling scheme. Also, the theoretical values are estimated for the element fluorine while the experimental values are determined for the compounds of fluorine

*K $\alpha$ L<sup>1</sup>/K $\alpha$ L<sup>0</sup> intensity ratio of fluorine*

**Table 2.** Comparison of K $\alpha$ L<sup>2</sup> satellite relative intensity (in %) value with theoretical value.

| Name of the compound | Present experimental value | Theoretical value of Aberg [9] |
|----------------------|----------------------------|--------------------------------|
| LiF                  | 8.8±0.9                    | 8.0                            |

**Table 3.** K $\alpha$  X-ray satellite energies (eV) in fluorine compounds.

| Name of the compound | K $\alpha$ L <sup>0</sup> | K $\alpha$ L <sup>1</sup> | K $\alpha$ L <sup>2</sup> |
|----------------------|---------------------------|---------------------------|---------------------------|
| LiF                  | 675.8 ± 0.2               | 679.0 ± 0.4               | 685.0 ± 0.4               |
| NaF                  | 675.6 ± 0.2               | 679.0 ± 0.4               | 686.1 ± 0.4               |
| MgF <sub>2</sub>     | 675.5 ± 0.2               | 678.4 ± 0.4               | 684.1 ± 0.4               |
| KF                   | 675.2 ± 0.2               | 678.7 ± 0.4               | 682.2 ± 0.4               |
| SrF <sub>2</sub>     | 675.5 ± 0.2               | 678.1 ± 0.4               | 682.0 ± 0.4               |

as targets, where the intensities are affected by chemical bonding. The discrepancy between the theoretical and experimental values may be ascribed to these factors.

### 3. Conclusions

- (1) The anomalously low KL<sup>1</sup> satellite relative intensity ratio observed in KF and SrF is found to be independent of the mode of ionization and as in the case of ion excitation, in the present work also, it may be attributed to resonance electron transfer.
- (2) Present K $\alpha$ L<sup>1</sup> relative intensity values for fluorine are in agreement with those obtained by electron excitation.
- (3) The theoretical estimates of the relative intensities of K $\alpha$ L<sup>1</sup> and K $\alpha$ L<sup>2</sup> satellites of fluorine are in slight disagreement with the present experimental values.

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