# SURFACE IONIZATION STUDY OF THE NON- STOICHIOMETRIC LinFn-1 (N = 4 – 6) CLUSTERS

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## Abstract

In this study we are presenting the results of the surface ionization of $Li_nF_{n-1}$ (n=4-6) clusters on rhenium surface impregnated with fullerenes using the magnetic mass spectrometer. The $Li_5F_4$ nanocubic cluster was detected for the first time. We determined values of ionization energies for $Li_4F_3$ and $Li_6F_5$, they are 4,3±0,2 eV, 4,0±0,2eV, respectively. The ionization energies agreed with theoretical ionization energies obtained by *ab initio* method, which indicates the excess electron localized in a specific site for non-stoichiometric clusters. The first ionization energy value for the $Li_4F_3$ was in accordance with earlier results obtained experimentally using photoionization time-of-flight mass spectrometer. There are currently no reliable experimental data for the ionization energy of $Li_6F_5$ cluster.

## Introduction

Electronic structure of metal-rich nonstoichiometric binary clusters has been widely studied to obtain better understanding of the metal-insulator transition mechanisms depending on the variations of cluster size and their chemical composition[1]. Based on observed abundances and ionization threshold Honea et al. classified of LinFn-1 clusters as follows: cubic clusters of a filled cubic lattice of ion with the extra electron occupying a weakly bound surface state; F-center clusters consist of a nearly filled cubic lattice with an electron localized in an anion vacancy; and nonocubic clusters have the excess electron bound to single cation [2].

For the $Li_nF_{n-1}$ (n = 4-6) cluster system, the electronic structure was often found to be segregated into a metallic part an ionic part. The most stable isomer of $Li_4F_3$ has a $C_{3v}$ symmetry with a cuboidal structure with a vacancy of one missing fluorine. The odd electron localizes around this vacancy, so that this cluster has a typical F-center structure. Cluster $Li_4F_3$ segregated into the metallic $Li_3^{2+}$ moiety and the ionic $LiF_3^{2-}$. The most stable isomer of $Li_5F_4$ has a $C_{3v}$ symmetry with a cuboidal $(LiF)_4$ structure with a terminal lithium attached to one of the fluorine atoms. The odd electron localized around the therminal lithium implicates the low abundances of $Li_5F_4$ nanocubic cluster. Cluster $Li_6F_5$ have F-center structure[3].

Here we are reporting the results of a mass spectrometric study of the surface ionization clusters $Li_nF_{n-1}$ (n = 4-6).

## Results and Discussion

The ionization energies of the non-stoichiometric LinFn-1 clusters were studied experimentally using a triple thermal ionization source and magnetic mass spectrometer. The mass spectrometer used in this investigation was a 12-inch radius, $90^0$ sector magnetic instrument of local design. Pressures in the analyzer region were maintained below $10^{-8}$ Torr and operating pressures in the source region below $5x10^{-7}$Torr. In these experiments for ionization of samples we used Re filament impregnated with fullerenes. The $LiF/LiI/BiF_3/C_2H_5OH$ solution was first deposited on the evaporation filaments (Re) and then dried under a heat lamp. The beam of clusters to be investigated was produced by heating the $LiF+LiI+BiF_3$ sample in the Re canoe, where a certain fractions of the neutrals are ionized. The filaments are heated with an electric current and the temperature was determined with an optical pyrometer. Identification of the gaseous species formed in the ion source was achieved from their mass-to-charge ratio, isotopic abundance and ionization energy. Figure 1 present obtained mass spectrum of ions $Li_4F_3^+$, $Li_5F_4^+$ and $Li_6F_5^+$. The mechanism of the formation of $Li_nF_{n-1}$ clusters from the alkali halide is not fully elucidated.

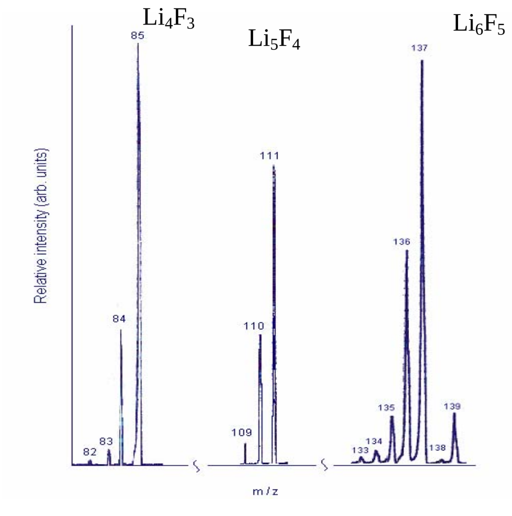

**Fig. 1**. Mass spectrum of non-stoichiometric clusters $Li_4F_3$, $Li_5F_4$ and $Li_6F_5$ produced by surface ionization technique

Surface ionization or thermal ionization is a method for generating ions at a hot metal surface. The values of the ionization energy of $Li_4F_3$ and $Li_6F_5$ were obtained from the Saha-Langmuir equation:

$$\alpha^+ = \frac{g^+}{g} e^{\frac{\Phi - IE}{kT}} \quad (1)$$

where α are the ionization coefficients; $g^+$ and g are the statistical weights of the ions and neutrals; IE is the ionization energy of clusters; k is Boltzman′s constant; T is the temperature of the surface; Φ is the work function of the surface. The value of work function of the surface shows dependence on the adsorption of the sample, fullerenes and residual gas in the working temperature range. Therefore, the work function was determined for each surface and experimental conditions rather then using literature data. The ion intensities of $Li_4F_3$ and $Li_6F_5$ clusters increased exponentially with increasing temperature of filament and the canoe. Figure 2 shows the logarithm of ion intensity of $Li_4F_3^+$ and $Li_6F_5^+$ ions as a function of temperature.

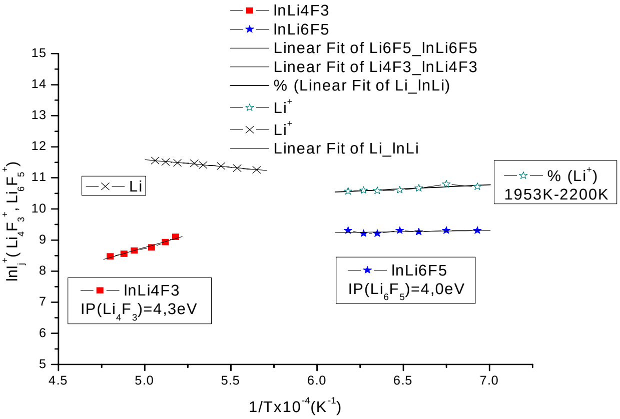

**Fig. 2.** Ionization of $Li_4F_3$ and $Li_6F_5$ on Re impregnated with fullerenes.

The values of the ionization energies obtained from the Saha-Langmuir equation where 4,3 ± 0,2eV for $Li_4F_3$ and 4, 0 ± 0,2eV for $Li_6F_5$.

## Conclusions

The surface ionization method offers the possibility of measuring ionization energies of clusters type F-center $Li_4F_3$ and $Li_6F_5$. Comparing these ionization energies values with those obtained by the *ab initio* MO calculations it has been concluded that the $Li_4F_3$ and $Li_6F_5$ clusters have ″superalkaly″ configuration in which the odd electron localization is in a specific site, characteristic for F-center clusters. The $Li_5F_4$ nanocubic cluster was detected for the first time by surface ionization method, but his low abundance prevents the measuring of its ionization energy.

## Acknowledgments

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## References

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