# Evidence for New Excess Electron Localization Sites in $Na_nF_{n-1}$ Alkali-Halide Clusters

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This Letter examines new types of localization sites for an excess electron in finite alkali-halide clusters resulting from defects on cuboidal structures, namely "edge states," $R$ center, and other surface defects. We present theoretical calculations on $Na_nF_{n-1}$ clusters with one excess electron. Comparisons with experimental results are presented for different cluster sizes ($n = 17$, 23, 28, and 29). Structures with edge or surface defects are relevant for $n = 23$, 28, and 29. [S0031-9007(97)03591-6]

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Akali halides are representative of an important type of clusters characterized by the ionic bonding, the other significant classes being metal, covalent, and Van der Waals. They were among the very first ones for which magic numbers were discovered; the pioneering work of Campana *et al.* [1] explicitly established a link between structure and magic numbers in the cluster mass spectra. They are also prototypes of other ionic salts like hydrides or noble metal salts, where bond ionicity is less pronounced. The first studied species were $M_nX_n$ and $M_nX_{n-1}^+$ [1–3], i.e., with no excess electron. In such species, the stability is governed by the balance between electrostatics and repulsion of the ion cores $M^+$ and $X^-$, a binding mechanism easy to represent through simple potential models [3,4]. However, the physics of alkali halides was further enriched with the study of halogen-deficient clusters since it was realized that they might unravel some interesting properties of electron localization [5–7] and, moreover, of the insulator-metal transitions [8]. Theoretically, when there are not too many excess electrons, their modeling still remains feasible [9,10]. One can then calculate properties such as ionization potentials or absorption spectra which can be directly compared with experimental results. Beyond the information obtained from magic numbers, this provides further insight in structural and electronic properties of clusters (see Refs. [4,6,11,12], for example).

Alkali-halide clusters with one excess electron, such as $Na_nF_{n-1}$, are essentially built around the rock-salt bulk lattice [6,8,10,13,14]; at least for small $n$, Honea *et al.* [6] have identified two categories. (i) When $2n - 1$ is the product of three integers ($2n - 1 = i \times j \times k$), the structure is an $i \times j \times k$ cuboid portion of the rock-salt bulk lattice, and the excess electron is weakly bound to the surface of the cluster, resulting in a very low ionization potential (IP); for instance, we calculate an adiabatic ionization potential ($IP_a$) of 1.99 eV for $Na_{14}F_{13}$ [10], in fair agreement with the 2.07 eV of Rajagopal *et al.* (RBL) [8]. These clusters are called surface states, and we label them $i \times j \times k$. (ii) When $2n = i \times j \times k$, the structure is a cuboid lattice with one vacancy occupied by the excess electron, as in a bulk $F$ center. Typical cases are found for $n = 4, 6, 8, 9$ whose $IP_a$'s are between 3.3 and 3.5 eV [10] (for $Na_4F_3$ we found 3.48 eV as in RBL). These clusters are called $F$ centers, and we label them $i \times j \times k$-F. Honea *et al.* place all other cases in a third class. In particular, if $2n - 2 = i \times j \times k$, it was found that the cluster consists of a sodium atom attached to the cubic lattice [10,11]. This is the strongest case of electron localization, since it belongs to the sodium atom. Our calculations give $IP_a$ between 3.1 and 4.0 eV for $n = 3, 5, 7, 10, 11$ (3.78 eV for $Na_3F_2$ to be compared to 3.55 eV according to RBL). These "sodium-tail" clusters are hereafter denoted $i \times j \times k + Na$.

This Letter deals with the interplay between structure and localization and investigates new localization sites for a single electron in $Na_nF_{n-1}$ clusters, analogous to step defects on bulk surfaces or to an $R$ center in halogen-deficient salts. Some of these defects have recently been suggested in Refs. [4,12] in the case of clusters without excess electron. Considering their theoretical stabilities and relating the calculated results with our experimental ones [14], we show here that such structures also occur in excess electron clusters. For instance, in order to interpret the two-step photoionization curve of $Na_{23}F_{22}$ and the low ionization potentials (around 2.4 eV) of $Na_{29}F_{28}$ and $Na_{35}F_{34}$ we have proposed another kind of vacancy that we called "edge state" [14], which occurs when $2n + 2 = i \times j \times k$ (a cuboid with one $NaF_2$ missing edge). We focus here on this kind of defect and similar ones, such as a missing $NaF_2$ unit in a longer edge, a $Na_2F_3$ missing edge, and more generally the partial depopulation of a cuboid face. The first nontrivial candidate for an $NaF_2$ edge removal is $Na_{17}F_{16}$ ($3^* \times 3 \times 4 - NaF_2$, the star labels the affected edge). The next ones are obtained by adding $3 \times 4$ sides to this cluster, giving $Na_{23}F_{22}$, $Na_{29}F_{28}$, and so on. The first possibility for an $Na_2F_3$ edge removal is $3 \times 4 \times 5^* - Na_2F_3$, that is, $Na_{28}F_{27}$. This cluster is fairly large and is the only one we studied in this series. A question arises whether the edge state we found experimentally in $Na_{29}F_{28}$ is the analog of a bulk step defect or of a bulk $R$ center (a 3-atom vacancy). Besides the removal of a full edge, which is a test of the first possibility, we also studied structures with an $NaF_2$ unit removed from a longer edge ($3 \times 4^* \times 4 - NaF_2$ for $Na_{23}F_{22}$, $3 \times 4^* \times 5$-$NaF_2$ and $3 \times 4 \times 5^*$-$NaF_2$ for $Na_{29}F_{28}$). We have also considered the type of defect suggested by Dugourd *et al.* [12] where the atoms are removed from a single face ($4 \times 4 \times 4 - [Na_4F_5]$ for $Na_{28}F_{27}$ and $4 \times 4 \times 4 - [Na_3F_4]$ for $Na_{29}F_{28}$).

A detailed account of the theoretical computations is given in Ref. [10,13]. Briefly, the ionic skeleton of the cluster is treated through a simple electrostatic model which incorporates the Coulomb interactions between the $n$ $Na^+$ cations and the $(n - 1)$ $F^-$ anions (Coulomb energy), and a Born-Mayer term to account for core-ion repulsion. The excess electron is described through a monoelectronic Hamiltonian with $Na^+$ core pseudopotentials, the $F^-$ anions being taken as simple negative charges. Linear combination of Gaussian type atomic orbitals are used. Core polarization and electron-core correlation contributions are added perturbatively [15]. Geometries were optimized by simulated annealing.

For $Na_{17}F_{16}$ (see Table I), the $3^* \times 3 \times 4$-$NaF_2$ edge state lies 0.26 eV above the $2 \times 4 \times 4 + Na$ sodium-tail ground state (GS). For $Na_{23}F_{22}$, the edge state is the structural GS ($3^* \times 4 \times 4$-$NaF_2$) with a $3 \times 3 \times 5$ distorted cuboidal surface-state isomer at 0.13 eV; the electron is localized at the missing $NaF_2$ edge for the former, and at a vertex for the latter (Figs. 1 and 2). For $Na_{28}F_{27}$, the lowest isomer is a $3 \times 3 \times 6 + Na$ structure. An edge-state isomer ($3 \times 4 \times 5^* - Na_2F_3$) does exist, although energetically high (0.63 eV above the structural GS). The $4 \times 4 \times 4 - [Na_4F_5]$ isomer appears to be very stable (0.11 eV above GS), more stable than the $F$-center isomer ($2 \times 4 \times 7$-F). In $Na_{29}F_{28}$, the $4 \times 4 \times 4 - [Na_3F_4]$ isomer (Fig. 3) is actually the structural GS. The second isomer (0.11 eV) is a genuine edge state (removal of a whole 3-atom edge, analogous to a "step" defect in the bulk). Then come the isomers with partial removal of an edge, analogous to a bulk $R$ center; the energy ordering (0.21, 0.42, and 0.89 eV, respectively) indicates that the longer the edge, the less stable the removal of a $NaF_2$ unit. Moreover, concerning the 5-atom edge, it is more favorable to remove a terminal $NaF_2$ rather than one in the middle. In $Na_{23}F_{22}$, the isomer with $NaF_2$ removed from a 4-atom edge lies 0.15 eV above the genuine edge state, showing again the lower stability of the $R$-center type of defect.

Confrontation with experiment can first be done looking at IP's. In addition to the vertical ($IP_v$) and adiabatic ($IP_a$) ionization potential, we define a local adiabatic IP ($IP_{la}$) as the difference between the energy of the locally relaxed ionic structure and that of the neutral isomer; this means that in the ionization process, only partial relaxation towards the nearest local minimum is assumed, conserving the general structure. This IP value is the most likely to be observed in experiments and can correspond either to a relaxation of the cluster structure during the ionization process or to an ionization process at a point which is not the local minimum (the vibrational temperature in the beam is around 400 K [16]). However, none of these processes can lead to a radical change of structure, since that would involve too much energy. Actually, agreement between experimental and local

TABLE I. Structural excitation energies and ionization potentials (in eV).

| Cluster | Structure | Symmetry | Theoretical | | | | Experimental |
|---|---|---|---|---|---|---|---|
| | | | $\Delta E$ | $IP_{la}$ | $IP_v$ | $IP_a$ | IP |
| $Na_{17}F_{16}$ | $2 \times 4 \times 4 + Na$ | $(C_s)$ | 0.00 | 3.76 | 3.96 | 2.53 | 2.95 ± 0.17 |
| | $3^* \times 3 \times 4 - NaF_2$ | $(C_s)$ | 0.26 | 2.26 | 2.52 | 2.26 | |
| $Na_{23}F_{22}$ | $3^* \times 4 \times 4 - NaF_2$ | $(C_{2v})$ | 0.00 | 2.41 | 2.59 | 1.72 | 2.51 ± 0.07 |
| | $3 \times 3 \times 5$ vertex loc. | $(C_s)$ | 0.13 | 1.59 | 2.15 | 1.59 | 1.75 ± 0.05 |
| | $3 \times 4^* \times 4 - NaF_2$ | $(C_1)$ | 0.15 | 2.72 | 3.51 | 1.57 | |
| | $3 \times 3 \times 5$ deloc. | $(D_{4h})$ | 0.25 | 1.47 | 1.58 | 1.47 | |
| $Na_{28}F_{27}$ | $3 \times 3 \times 6 + Na$ | $(C_s)$ | 0.00 | 3.26 | 3.70 | 2.38 | 2.90 ± 0.30 |
| | $4 \times 4 \times 4 - [Na_4F_5]$ | $(C_1)$ | 0.11 | 3.06 | 3.90 | 2.26 | |
| | $2 \times 4 \times 7 - F$ | $(C_1)$ | 0.18 | 3.40 | 4.05 | 2.20 | |
| | $3 \times 4 \times 5^* - Na_2F_3$ | $(C_s)$ | 0.63 | 1.75 | 2.07 | 1.75 | |
| | $2 \times 3 \times 9 + Na$ | $(C_1)$ | 0.81 | 3.81 | 4.12 | 1.57 | |
| $Na_{29}F_{28}$ | $4 \times 4 \times 4 - [Na_3F_4]$ | $(C_1)$ | 0.00 | 3.09 | 3.73 | 2.30 | 2.40 ± 0.10 |
| | $3^* \times 4 \times 5 - NaF_2$ | $(C_s)$ | 0.11 | 2.19 | 2.54 | 2.19 | |
| | $3 \times 4^* \times 5 - NaF_2$ | $(C_1)$ | 0.21 | 2.79 | 3.48 | 2.08 | |
| | $3 \times 4 \times 5^* - NaF_2$ | $(C_1)$ | 0.42 | 2.24 | 3.16 | 1.87 | |
| | $3 \times 4 \times 5^* - NaF_2$ | $(C_s)$ | 0.89 | 2.48 | 2.85 | 1.41 | |

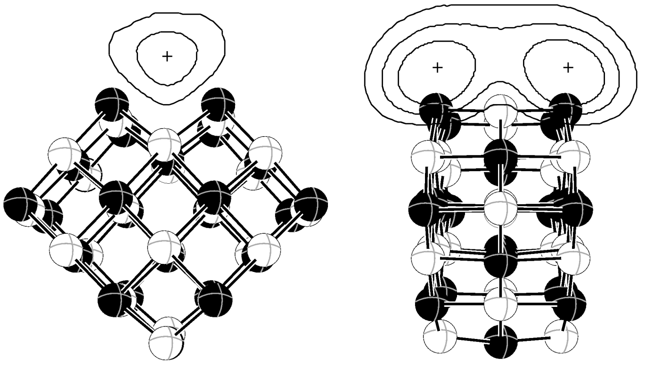

FIG. 1. Contour plots of the electronic wave function for the $3^* \times 4 \times 4$-$NaF_2$ structure of $Na_{23}F_{22}$ (two views).

adiabatic IP, rather than $IP_a$ or $IP_v$, has been found to be fairly frequent [10].

The measured $Na_{17}F_{16}$ IP (Table I) lies between the $IP_{la}$ values of the Na tail and edge-state isomers and no indication about the structure of the observed cluster can be inferred. However, the $R2PI$ + depletion spectrum (Fig. 4) compares well with the Na-tail theoretical one, while that of the edge-state geometry is quite different and has intense transitions only above 1000 nm. To be completely conclusive, the experimental spectra should be extended to the infrared, in order to check whether edge-state clusters are present in the beam. For $Na_{23}F_{22}$ the situation is quite different. The measured IP (1.75 eV) corresponds to that of the $3 \times 3 \times 5$ structure ($IP_{la} = 1.59$ eV). However, the photoionization curve shows a two-step feature [14] with the second step at 2.51 eV, close to the $IP_{la}$ values of the two edge-state isomers. Thus the beam may contain a mixture of the three isomers. This can hardly be explained by thermal considerations only, since the structural excitation (0.13 eV) is fairly high compared to the temperature ($k_B T \sim 0.03$ eV). However, 0.1 eV is the range of confidence of the calculation. The beam might also be nonthermal [16]. $Na_{28}F_{27}$ provides another interesting example for which the GS is a Na tail whose $IP_{la}$ (3.26 eV) is at the upper compatible limit with the measured IP ($2.90 \pm 0.30$ eV). However, $IP_{la}$ for the close lying surface-defect isomer is even closer (3.06 eV). In the case of $Na_{29}F_{28}$ all the lowest isomers have surface-defect or edge states. The experimental IP seems in better agreement with the $IP_{la}$ value of the second isomer, which is an edge state. It is difficult to be definitely conclusive from this unique quantity (IP), but this is an indication for the presence of the edge-state isomer in the beam. Furthermore, the photoionization yield [14] increases slowly with energy. There might be several steps in the curve which cannot be individually resolved, so that again, the beam may contain several isomers.

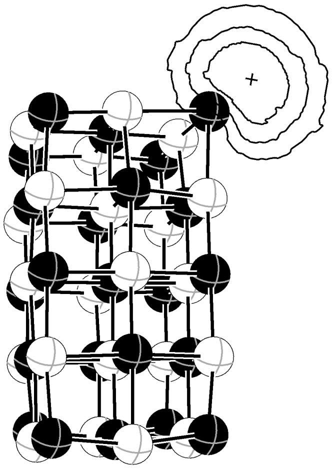

FIG. 2. Contour plots of the electronic wave function for the $3 \times 3 \times 5$ localized surface state of $Na_{23}F_{22}$.

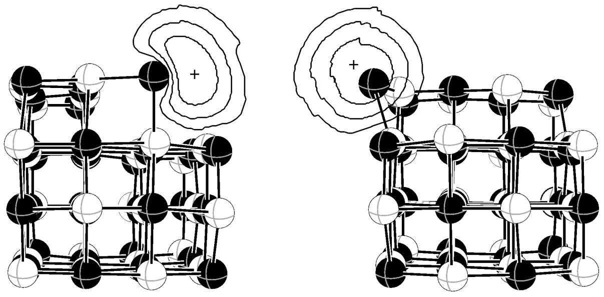

FIG. 3. Contour plots of the electronic wave function for the $4 \times 4 \times 4 - [Na_3F_4]$ structure of $Na_{29}F_{28}$ (two views).

Considering now absorption spectra, they can be understood as follows. The electronic GS orbital of $Na_nF_{n-1}$ is always nodeless, close to an $s$-type wave function. For $i \times j \times k$ + Na, the electron is localized on the Na atom and for $i \times j \times k$-F it fills the $F$ vacancy. The excitation spectra are ruled by transitions towards $p$-type orbitals in the range 700–1000 nm [17]. In the case of a surface state, associated with an $i \times j \times k$ cluster, the excess electron is weakly localized near a sodium vertex and its excited states lie at very low transition energies (less than 1 eV). For edge-state clusters, the excess electron extends in the $NaF_2$ vacancy and the most intense transitions

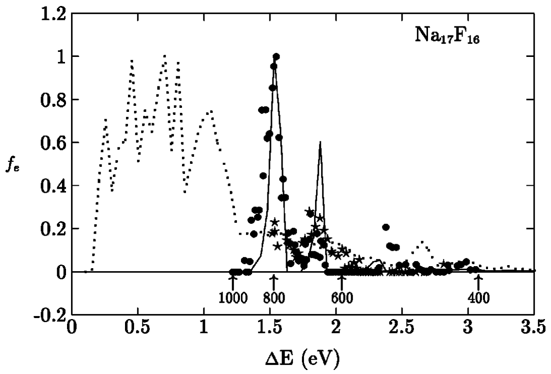

FIG. 4. Optical spectra for $Na_{17}F_{16}$. Theoretical (Na tail: solid line, edge state: dotted line) and experimental ($R2PI$: black circles, depletion: stars).

are above 1000 nm; geometries and electronic localization for surface and edge-state structures are shown in Figs. 1 and 2 for $Na_{23}F_{22}$. Finally the surface-depleted $Na_{29}F_{28}$ isomer has two complete rows and a single sodium atom on the depleted side: the electron density (Fig. 3) is localized near this sodium atom, as in the sodium-tail case, but with a more diffuse orbital. Surface-depleted $Na_{28}F_{27}$ now has an $F$-center type orbital (one fluorine atom missing in a row).

Up to now, we have recorded $R2$PI spectra up to 1000 nm and depletion spectra up to 735 nm. Further experimental work is needed to record the infrared spectra. Moreover, the depletion spectrum is lacking for $Na_{28}F_{27}$ and $Na_{29}F_{28}$. At this time, we are unable to tell whether surface-depleted clusters are present in the beam. The calculated GS of $Na_{29}F_{28}$ should exhibit lines at 660, 860, and 900 nm, which are not present in the observed $R2$PI spectra. For $Na_{29}F_{28}$ the only isomer we are sure of is the edge state, which is consistent with the measured IP. Because of the small energy difference with the GS, the actual ordering cannot be absolutely ascertained.

In conclusion, we have analyzed both theoretically and experimentally the structural stability and the electronic properties of $Na_nF_{n-1}$ clusters presenting edge and/or surface defects. Actually, step defects are known to play a significant role in the growth of alkali-halide crystals [18]. Above a few ten atoms, they are certainly involved in cluster stability and growth [12]. We predict that similar defects occur also in finite excess electron clusters. Indeed, we show theoretically that structures with edge states or with depopulated surface states are energetically low lying and sometimes even the most stable isomers for clusters with more than 40 atoms. Moreover, these structural defects appear as new sites for electron localization. Together with the sodium-tail type, these sites complement the earlier classification [6]. We have found a fair agreement between theoretical local adiabatic ionization potentials and experimental IP's, which, together with their theoretically proved stability, confirms the proposed existence of edge-states $Na_{23}F_{22}$ and $Na_{29}F_{28}$ clusters in the experiment. Other structures are possibly present as well, but no clear indication has been found yet. As concerns the surface-depleted structure of $Na_{29}F_{28}$, the nonobservation of $R2$PI spectra cannot be considered as a negative proof since the cluster may be unstable in the excited state. Further experimental work is needed to record depletion spectra in the near infrared.

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