Identifying the Nuclei of Nanoscale Lithium Colloids in LiF Crystals

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Abstract—Various spatial and charge configurations of precolloidal centers in lithium fluoride crystals are explored. Theoretical investigations are based on density functional theory and pseudopotential and supercell geometry. Band gap structure is analyzed from the energy distribution of the electronic density of states.
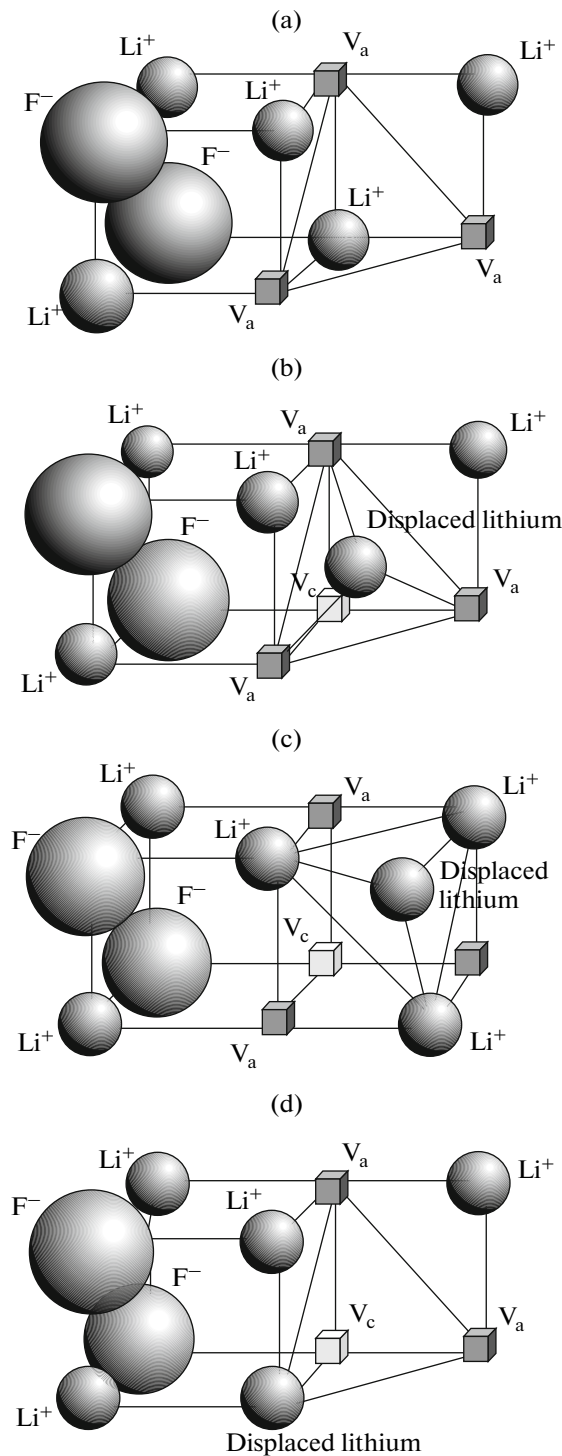
INTRODUCTION

Investigating the configurations of precolloidal centers is of great importance to the physics of nanoparticles, since they are the initial stage of the formation of nanoscale lithium colloids. The electronic structure of F, H and V_k centers in LiF crystals was calculated in [1] using the semi-empirical INDO approach. Of greater interest is [2], where Monte Carlo computer modeling was performed for the formation of metallic colloids in heavy ion tracks. The authors of [2] considered the diffusion of excited F-centers, whose lifetimes are $\sim 10^{-8}$ s. It is obvious that the rate of diffusion for excited F-centers cannot exceed that of anionic vacancies, whose lifetimes are ~60 s at room temperature. The ratio of the above time ranges is low and reflects the upper boundary of the probability of excited F-center diffusion [4]. The authors of [5] considered the formation of nanoscale lithium colloids with 10 MeV (10^{14} ion/cm^2 and $I = 120$ kA) Au ion irradiation of an LiF crystal. Such irradiation generates secondary electrons with energies of ~100 eV, which in turn produce localized cationic excitons (~62 eV). The decay of the latter results in the formation of three or four spatially correlated F-centers and highly mobile interstitial fluorine atoms. In our opinion, two or more spatially separated F_3-centers could act as nuclei in the formation of nanoscale lithium colloids. In [5–8], we considered the role of F_3 and F_3^+-centers in the formation of precolloidal defects in gamma-irradiated LiF crystals. As a result of the classical configuration, in which there are three F-centers in plane (111), favorable conditions are created for excited electron localization on the nearest regular cations with the simultaneous displacement of the forming alkaline metal atom onto (111) plane upon exposure to optical, thermal, and radiation impacts. The mechanism proposed for the formation of precolloidal center nuclei is nevertheless hypothetical, as are the earlier precolloidal center models in which the lithium atoms are located inside anionic vacancies [9] or on the cation plane [10]. The aim of this work was thus to clarify which configuration of defects can be identified with the initial stage of colloid formation.

ANALYTICAL APPROACH

To model the precolloidal centers in lithium fluoride, we considered a variety of spatial and charge defects containing F_3-, F_3^+-, and F_3^-—centers, or three anionic vacancies, one cationic vacancy, and the associated interstitial lithium. The free Quantum Espresso software [11] was used to solve the problems posed in this work. We decided to use the Vanderbilt pseudopotential, which allowed us to consider seven out of nine fluorine electrons as valent (i.e., to allow for changes in the wave functions of more electrons at the same computational load). This required a basis containing plane waves with $E_{\text{cutoff}} = 30$ Rydb. A cubic supercell of 64 atoms was used for modeling. The preudopotentials were formed with the Vanderbilt Code software (version 7.3.5). We considered $1S^2$ electrons to be spanning for both lithium and fluorine; others were correspondingly valent. We obtained a superlattice with a classical F_3-center by removing three fluorine pseudoatoms from a perfect lattice (Fig. 1a). In this configuration, the superlattice contained 32 lithium preudopotentials, 29 fluorine preudopotentials, 235 electrons (29 Li−F pairs and 3 electrons localized by anionic vacancies). We also considered alternative configurations corresponding to spatial displacement of the anionic lithium vacancies nearest the plane into anionic vacancies (Fig. 1d) and the geometric center of the cation plane (Fig. 1c), along with the results from displacing the lithium nearest the (111) plane to the latter's geometric center (Fig. 1b). The defect charge was varied in accordance with the series $3V_a^+$, $2V_a^+F$, V_a^+2F, F_3, F_3^-, F_3^{2-}, and F_3^{3-}. The total energy of

Fig. 1. Schematic of the studied spatial configurations of precolloidal centers in a superlattice: (a) base configuration; (b) the lithium nearest the plane of anionic vacancies is displaced to the geometrical center of the (111) plane; (c) the lithium nearest the plane of anionic vacancies is displaced to the geometric center of cations; (d) the lithium nearest the plane of anionic vacancies is displaced to anionic vacancies.

the system and the energy distributions of the electron state density DOS(E) with a step of 0.0001 eV were obtained for each charge state. These were analyzed to determine the levels of stratification relative to the bottom of the conduction band:

$$D(E) = \frac{\partial n}{\partial E} \cong \frac{\delta n}{\delta E} = \sum_{E(k)=E} \frac{\delta n}{\delta k} |\nabla_k E)(k)|^{-1}$$
$$\times \underset{spin}{2} = \frac{2}{(2\pi)^3} \int_{E(k)=E} d^2k |\nabla_k E(k)|^{-1}, \quad (1)$$

where n is the electron density. The results were confirmed for F_3 charged state convergence (in the superlattice with 235 electrons) relative to the size of the superlattice, the kinetic energy of wave function tearing, the number of k points, and the type of pseudopotential.

When the lithium was in the (111) anion plane (Fig. 1b), the distance to its nearest regular lithium frameworks was 2.077 Å. The strongest perturbation was observed when the superlattice charge was +3. We then detected levels 1.66 eV and 1.17 eV below the bottom of the conduction band; the densities of their electron states were 8650 and 1900, respectively. The densities of states fell to 1220 and 500 when the superlattice charge was increased by 1 electron, and the levels moved closer to the bottom of the conduction band (at 0.64 and 0.43 eV below it). No levels below the bottom of the conduction zone were observed after a further increase in charge, and the DOS(E) dependences for superlattices with charges of −2 and −3 were almost identical to those for a superlattice with a charge of −1.

When the lithium was in the cation plane (Fig. 1c), the distance to its nearest regular lithium frames was 1.64 Å. In this spatial configuration, the energy levels below the bottom of the conduction band were observed at superlattice charges of +3 to −2, inclusive. As with the previous spatial configuration, they moved closer to the bottom of the conduction band as the negative charge grew.

When the lithium was located in anionic vacancies (Fig. 1d), the distance to the nearest regular lithium frames was 2.014 Å. The perturbations caused by moving the lithium frames into anionic vacancies were not great, and the maximum DOS for this configuration was 440. At 0.61 and 0.37 eV, the levels did not lie deep. Since the depths at which the levels lay were 4 and 2.5% of the resulting band gap width and the error in the determining band gap width is 8%, we could not reliably confirm the levels in the band gap for this spatial configuration.

Since precolloidal centers can form colloids with metallic bonds [12], a model in which the energy levels are closer to the bottom of the conduction band would be appropriate. As we can see from Table 1, this model would have the lithium in the plane of anionic vacancies (where the depths at which the levels lie are com-

Positions of levels relative to the conduction band bottom in eV, percents of the band gap width, and the density of electronic states (DOS) for these levels.

Charge configuration	Resulting lithium position								
	in cation plane			in anion plane			in plane of anionic vacancies		
	DOS, rel. units	E, eV	E, %	DOS, rel. units	E, eV	E, %	DOS, rel. units	E, eV	E, %
$3V_a^+$	3380 1760	3.65 2.39	24.3 15.9	440 329	0.61 0.37	4 2.5	8650 1900	1.66 1.17	10.9 7.7
$2V_a^+F$	4700 1260	2.90 1.65	18.9 10.7				1220 500	0.64 0.43	4.1 2.7
F_3^+	3430 740	2.22 1.01	14.6 6.7						
F_3	2036 270	1.68 0.65	11.1 3.7						
F_3^-	1350 180	1.08 0.17	7.2 1.1						
F_3^{2-}	400	0.45	3.1						

parable to the error of calculation). When the lithium is in the cationic plane, a distance to the nearest cations is naturally minimal, creating the greatest perturbations. Such spatial proximities favor the deepest levels relative to the bottom of the conduction band (down to 3.65 eV, Table 1.), the greatest difference between the total energies in the initial configuration (up to 13.02 eV), and the presence of these levels even at a negative superlattice charge.

The shortest distance from the mixed lithium to its nearest cations changed in the rising series 1 : 1.23 : 1.27 for the above modified spatial configurations. As was expected, the difference between the total energies of the system in the modified and initial states changed in the descending series 1 : 0.34 : 0.28 (charge configuration $3V_a^+$), while the position of the deepest levels (configuration $3V_a^+$ charge) changes in the series 1 : 0.17 : 0.45. The last case violates the logic of the configuration with the lithium in the plane of anionic vacancies. In addition, it was only in this configuration that convergence was attained in self-consistent calculations for the +4 charge state; i.e., electrons were ejected from defects. This configuration of defects is distinguished by the shortest bonds between the atomic frames and valent electrons. Semi-metallic bonds are thus strongest in this configuration. This was confirmed by the maximum DOS values (relative to other configurations) for levels below the bottom of the conduction band: 8650 and 1900 for the +3 charge state (Table 1) and 7108 and 1220 for the +4 state. The levels' positions relative to the bottom of the conduction band were 1.55 and 1.1 eV. These high values are abnormal from the classical point of view and do not arise from the geometry of defects or Coulomb inter-

action; in all likelihood, it is a quantum–size effect that is observed. The configuration with lithium in the plane of anion vacancies is the one closest in energy to the initial configuration, where the lithium is at regular lattice points (the difference between the total energies is minimal and varies from 0.762 to 3.66 eV). In addition, the change in system's total energy when the lithium is displaced depends weakly on the charge state of the system in all finite configurations, except when the lithium atom frames are moved to the anionic plane. The change in energy as the number of valent electrons rose from 232 to 237 was reduced by a factor of almost 3; for other configurations, it did not exceed 19%. This reduction indicates that as the charge of negative defects grew, the probability of lithium being displaced to anion vacancies plane also increased by a factor of 3.

CONCLUSIONS

We studied the possible configurations of alkaline metal nuclei using ab initio quantum-chemical calculations. DOS(E) dependences describing band gap structure were obtained for each spatial charge configuration. In the band gap, levels below the bottom of the conduction band were found for two configurations: with the lithium displaced to the plane of cations and to the (111) plane of anionic vacancies. The highest DOS value was obtained for the spatial configuration with the lithium in the (111) plane at a system charge of +3. This lithium position was found to be the one closest in energy to the initial configuration. We thus conclude that lithium is most likely in the (111) plane of anionic vacancies at the initial stages of irradiation. If such formations are in the immediate prox-

imity of one another inside a crystal, they can aggregate as minute colloidal alkaline metal particles form upon optical, thermal, or radiation stimulation.

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