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Structure and energetics of LiF chains as a model for low dimensional alkali halide nanocrystals

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Abstract

Nanocrystals of inorganic salts constrained in geometry by encapsulation in single walled carbon nanotubes have been shown by recent high-resolution transmission electron microscopy experiments to exhibit specific distortions of their structure in comparison with the ideal bulk. These structural distortions of low dimensional crystallites are analyzed within the Hartree–Fock approximation and density functional theory based on the simplest alkali halide chains, LiF. The observed patterns of distortions in the structure of nanocrystals are the results of low dimensionality and the axial strain (end effects). The structural trends calculated ab initio for LiF are compared with analytical predictions based on the traditional Born theory of bulk crystals and experiments. The energetics of the LiF crystallites is discussed.

1. Introduction

In the past few years, carbon nanotubes filled with various inorganic materials have gained increasing interest in material science and technology. Experiments on filling single walled carbon nanotubes (SWNTs) prompt significant progress in discovery and preparation of novel materials with potential control over their intrinsic mechanical and electronic properties [1–6]. The confined environments of nanotubes permit the formation of unique encapsulated low dimensional structures with unusual properties compared with the bulk [7]. These structures can be used in several possible applications, such as nano-catalysts or one-dimensional nano-junctions and superconductors [2].

In addition to these novel materials, simple alkali halides have also been inserted within a SWNT. Particular progress has been made in synthesis of encapsulated iodides such as KI@SWNT [2,8], RbI@SWNT and CsI@SWNT [9,10]. These iodides have a highly ordered crystalline structure within nanotubes which is believed to be enforced by the low dimensional confinement provided by the SWNT inner cavity [3,11]. The crystalline structure within nanotubes is found to follow predominantly that of the rocksalt bulk with the $\langle 100\rangle$ direction parallel to the principal axis of a SWNT (only CsI forms significant quantities of bcc-type halide in SWNT). The encapsulated crystals make up crystallite chains, which are only two or three atoms across, depending on the diameter of surrounding nanotube. They exhibit a (2×2) or (3×3) arrangement of ions in cross-section. In this Letter, these cross-sections are conveniently called $(m\times m)$ planes of a low dimensional chain with m^2 ions in each plane.

Beside the synthesis itself, only few structural properties were reported in the literature on the alkali halides@SWNTs and the complete characterization of these systems is still to be made. Recent high-resolution transmission electron microscopy (HRTEM) experiments provide accurate measurements of cation–anion distances in alkali halides both parallel and perpendicular to the tube axis. Although identical in the ideal bulk structure, these cation–anion separations are found to be different in the tube. For KI (2×2), KI (3×3), RbI (3×3) and CsI (2×2) inside a SWNT, the structure observed by the HRTEM [9] shows clearly some contraction (compared

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to the bulk structure) of the cation–anion separations in the direction parallel to the tube axis and a significant dilation in the perpendicular direction.

An understanding of the structure of encapsulated nanocrystals requires one to disentangle the effects arising from the reduced dimensionality of the crystals from the effects induced by the interaction with the surrounding nanotube. The purpose of this Letter is to identify intrinsic structural properties of low dimensional crystallite chains, i.e., the properties unaffected by the presence of the tube. We study ab initio the evolution of structural trends of the simplest alkali halide chain, LiF $(2 \times 2 \times n)$, n is a number of the (2×2) planes, in relation to the system size, i.e with increasing of the number of planes. We predict the structure of the crystal infinite along the nanotube axis $(n \to \infty)$ based on extrapolation of the results obtained for the finite LiF nanocrystals.

Ab initio studies of small non-encapsulated alkali halide clusters [12,13] reveal that their basic structural features depend on both the size and chemical composition. Clusters containing, say, K and Rb show clear preferences for geometries, which are fragments of the rocksalt crystal lattice. The LiF clusters exhibit a different behaviour: hexagonal structures (stacked six-rings) are preferred to cubic lattice fragment up to $(\mathrm{LiF})_{18}$ as shown by the self-consistent field (SCF) computations of [13]. The overall structural picture is different for encapsulated nanocrystals. The radius of the inner cavity of the smallest nanotube which permits the incorporation of a 2×2 nanocrystal is too small to accommodate structures based on hexagons. However, calculations [14] using semi-empirical potentials suggest that such hexagonal structures could be accommodated by some larger nanotubes. For the non-encapsulated small neutral alkali halide clusters, the $(2 \times 2 \times n)$ crystal chains are energetically low-lying isomers [12,13] of the lowest energy structures of $(\mathrm{LiF})_{2n}$ $(n < 9)$ based on hexagons.

A major advantage of studying LiF is that its electronic and structural properties are described accurately using the Hartree–Fock (HF) approximation with relatively inexpensive basis sets [12,15–18]. The compact sizes of these ions cause the dispersion energy, which lies outside the SCF approach, to be the smallest of that for any alkali halide. The consequent reduced importance of the correlation energy, together with the high point symmetry of the LiF nanocrystals (D_2 Abelian subgroup), makes the structural optimization affordable in computational terms without sacrificing accuracy. This system appears therefore to be ideal for studying the effects of low dimensionality distortions of the encapsulated nanocrystals with the aim of gaining insight into the behaviour of other alkali halides.

Several standard techniques are available in solid state chemistry for the study of finite systems and periodic crystals. We use the Q-Chem ab initio electronic structure program [19] to study the evolution of structure and bonding in neutral $(\mathrm{LiF})_{2n}$ nanocrystalline chains, which can be also conveniently denoted as LiF $(2 \times 2 \times n)$. The Q-Chem program employs the cluster approach to perform first principles calculations on the ground state of molecules. The cluster method suffers from the obvious shortcomings when applied to the periodic ionic crystals: the crystal field is not correctly reproduced and the periodic nature of the lattice is not included. However, both HF and DFT geometry optimization methods are parallelized in Q-Chem allowing large-scale molecular computations to be performed routinely. We perform HF and DFT geometry optimization of seven LiF $(2 \times 2 \times n)$ crystal chains $(n = 2–7,\ 9)$ with the standard extended 6-311G* Pople basis set [20] for both Li and F. The DFT calculations use the B3LYP hybrid exchange-correlation functional [21]. We find that by increasing the length of the chains one can minimize the end effects on the middle part of the chain and obtain accurate information on structure and bonding of the entire periodic system.

2. Evolution of property dependence on system size

2.1. Structural trends

The simplest classical theory of cohesion in bulk ionic crystals includes only the largest dominant interactions, namely all the purely coulombic terms and the short range repulsive interactions between the closest pairs of ions, and makes no mathematical distinction between the cations and anions. Inevitably, for any low dimensional alkali halide nanocrystal, it predicts that each plane of such a crystal chain is square in cross-section with adjacent planes being rotated relative to each other by 90°. Each of the ab initio structural optimizations was started from such a configuration. Fig. 1 presents a three dimensional view of the initial structure of the $(2 \times 2 \times 9)$ LiF crystal chain which is the longest chain considered in this Letter. On the lower left of Fig. 1, a single square $(\mathrm{LiF})_2$ plane of the initial structure is shown.

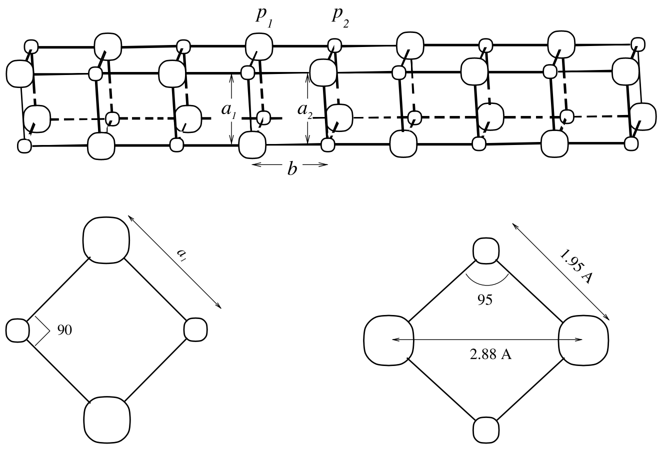

Fig. 1. The LiF $(2 \times 2 \times 9)$ chain; small circles are Li^+. Top: initial structure with two adjacent $(\mathrm{LiF})_2$ planes in the middle denoted as p_1 and p_2, the Li–F distances within the planes are designated a_1 and a_2 and the inter-plane p_1 to p_2 separation is designated b. Bottom: initial square structure (left) and optimized diamond (right) shape of the $(\mathrm{LiF})_2$ plane.

It is expected that taking into consideration the short range interactions between like pairs of ions will lead to a distortion of each square to a rhomboidal (diamond) shape. The anion–anion distance in the diamond will be dilated (compared to the cation–cation distance) both because the short range anion–anion interactions are stronger than those between the cations and because the dipoles induced on the anions on account of their larger polarizability will partially screen the cation–cation electrostatic repulsions, as described elsewhere [22]. Both effects are automatically included in the present HF computations although further work, beyond the scope of this Letter, would be needed to elucidate the relative importance of these two effects. Ab initio HF predictions for the evolution of the structures of the two adjacent middle $(LiF)_2$ planes as the length of the LiF chain grows from $n = 3$ to $n = 9$ are presented in Table 1. These two planes in the middle of the chain are denoted as p_1 and p_2 as shown in Fig. 1. The Li–F distances within the planes are designated a_1 and a_2, respectively. These distances, the F–F separations and (F–Li–F) angles in the p_1 and p_2 planes, as well as the inter-plane p_1 to p_2 separations b are presented in Table 1.

For very small pieces of a chain ($n = 3$–5), the end effects dominate the structural characteristics of the middle planes of a chain, and as a result the adjacent diamonds p_1 and p_2 can be in principle non-identical. However, two different patterns in the structural evolution of the chains can be distinguished. If the number of planes n is odd, the chain has the D_{2h} molecular point group with the reflection plane σ_h passing through the middle plane (p_2 in Fig. 1). In general, this allows the relaxed structure to have different p_1 and p_2 planes. However, the results in Table 1 show that p_1 and p_2 become identical for longer chains. If n is even, besides the axes defining the D_2 point group, the chain additionally acquires two diagonal planes σ_d. Consequently, the two halves of the chain are now identical, but at right angles to one another. This ensures the p_1 and p_2 planes remain the same. Due to the higher symmetry, the structure of the p_1 and p_2 planes in such chains converge more rapidly to a final configuration. This is seen from Table 1 to be the same as the limiting structure of the middle planes in chains with odd n (bold numbers in Table 1). The single Li–F distance in the converged middle planes, conveniently designated a, is equal to 1.95 Å with the inter-plane separation $b = 1.83$ Å. Thus, by increasing the length of the LiF $(2 \times 2 \times n)$ nanocrystal chains we find the optimized structure of the middle $(LiF)_2$ plane which can be considered as the converged limit of the infinite chain. The converged results of HF predictions do indeed confirm the diamond shape of a plane in the LiF $(2 \times 2 \times \infty)$ nanocrystal chain (see the bottom right of Fig. 1). These distortions from square to diamond are not very large in the alkali halides chains. The effect is expected to be most pronounced for the LiI chain, as it contains the smallest metal ion and the largest halide ion. It is less significant for the experimentally studied encapsulated K, Rb and Cs iodides, because the ratio of the anion to cation radii is greatest in the Li iodide. In the KI, RbI and CsI chains, the distortions are too small to be systematically found within the accuracy of experimental measurements.

The further prediction derived from our structural calculations is that for the infinite chain of LiF the inter-plane separation b is less than the bulk lattice spacing ($R_e^{3D} = 2.0$ Å for LiF bulk [23]). The ratio $\frac{b}{R_e^{3D}}$ describes the longitudinal change in the geometry of the low dimensional crystal compared to the bulk. The value for the ratio $\frac{b}{R_e^{3D}}$ is found to be 0.915 after introducing the experimental value for R_e^{3D}; this ratio remains essentially unchanged at 0.910 on using instead the 3.798 Bohr prediction [16] yielded by a crystal HF computation for the bulk material. Therefore, we can conclude that an axial contraction of the inter-plane distance b is present in the infinite LiF chain. The same trend is found in experiments on encapsulation of bilayer alkali iodides crystals in a SWNT. For the $(2 \times 2 \times \infty)$ chains of KI and CsI, the average ratio $\frac{b}{R_e^{3D}}$, measured from the HRTEM images, was found to be 0.994 (± 0.057, if the estimated precision of measurements is taken into account) and 0.971 (±0.052), respectively [9]. The HF value for the LiF chains falls well into the experimental range.

An overview of experimental results requires development of a general analytical theory for the structures of nanocrystalline ionic solids which contains only the dominant interactions. Such a theory [24] considers all the coulombic interactions of the ions, treated as point charges, and the short range repulsive forces between the closest pairs of ions within the Born model. It introduces the chemical dependence solely by the A and N parameters in the original Born expression $\frac{A}{R^N}$ for the short range repul-

Table 1
Evolution with chain length of the intra-plane Li–F and F–F distances (in Å), (F–Li–F) angles (in °) in adjacent middle $(LiF)_2$ planes p_1 and p_2 and of the inter-plane separations b (in Å) calculated within the HF/6-311G* approximation

Number of $(LiF)_2$ planes, n	Li–F		F–F		∠(F–Li–F)		b
	a_1	a_2	p_1	p_2	p_1	p_2	
4	1.98	1.98	2.91	2.91	94.5	94.5	1.82
6	1.95	**1.95**	2.88	**2.88**	95.0	**95.0**	**1.83**
3		2.01		2.94		94.1	1.82
5	1.98	1.95	2.90	2.88	94.1	95.0	1.83
7	1.95	1.95	2.86	2.88	94.2	95.0	1.83
9	1.95	**1.95**	2.88	**2.88**	95.0	**95.0**	**1.83**

sion between two ions separated by the distance R. The structural dependence also enters the theory through various Madelung terms. Details of this model for the structures of nanocrystalline ionic solids are presented elsewhere [24] and provide an explanation for the ratio $\frac{b}{R_e^{3D}}$ for LiF chain being less than the average experimental values for KI and CsI chains. The analytical results of [24] yield $\frac{b}{R_e^{3D}} = 0.910$ for the LiF $(2 \times 2 \times \infty)$ chain which is in excellent quantitative agreement with the HF value of 0.915.

Our calculations further predict that the b spacing between the ions along the infinite chain is less than the a spacing in the perpendicular direction, i.e., $\frac{a}{b} > 1$. In general, the ratio $\frac{a}{b}$ indicates two dimensional distortions (transverse and longitudinal) of the structure of alkali halides chains compared to their 6:6 rocksalt bulk structure for which $\frac{a}{b} = 1$. For the LiF $(2 \times 2 \times \infty)$ chain, the ab initio HF ratio $\frac{a}{b} = 1.066$ agrees well with the analytic result for $\frac{a}{b} = 1.074$ of [24]. The ratio $\frac{a}{b}$ obtained experimentally from direct lattice measurements reported in [9] is greater than unity for all $(2 \times 2 \times \infty)$ chains of alkali iodide crystals encapsulated within a SWNT. For the $(2 \times 2 \times \infty)$ chains of KI and CsI, the $\frac{a}{b}$ ratios are 1.057 (±0.057) and 1.108 (±0.054), respectively. Atomistic computer simulation models used in [11] predict the same qualitative trend and yield $\frac{a}{b} = 1.03$.

Although greater than the inter-plane ionic separation b, the transverse spacing a remains contracted relative to the bulk: the HF ratio $\frac{a}{R_e^{3D}} = 0.975$. However, the experimental studies of [9] reveal a significant dilation of a separation relative to the bulk which leads to $\frac{a}{R_e^{3D}} > 1$. This suggests the importance of the interaction of the crystal with nanotube which may yield further dilation of the a separation. This conclusion is consistent with that of [11] which predicts that the ratio $\frac{a}{b}$ approaches the experimental values only by introducing dispersive attractions between the ions and the wall of a nanotube.

The reliability of the present computations is shown by the results for chains with smaller values of n. These have been previously studied using the SCF approach and second-order Møller–Plesset perturbation theory (MP2) in [12,13] in the context of determining the structures of small clusters not constrained by encapsulation. The Li–F bond length and (F–Li–F) angle of the T_d structure of $(LiF)_4$ ($(2 \times 2 \times 2)$ chain), D_{2h} structure of $(LiF)_6$ ($(2 \times 2 \times 3)$ chain) and D_{2d} structure of $(LiF)_8$ ($(2 \times 2 \times 4)$ chain), computed here using the HF and DFT/B3LYP approaches with 6-311G* basis set ((11s,5p,1d)/[4s,3p,1d]), are compared in Table 2 with the SCF and MP2 results of [12,13].

In all these calculations, the initial structure was optimized resulting in a distortion of each plane to a diamond. In the LiF $(2 \times 2 \times 2)$ chain, the intra- and inter-plane Li–F separations remain the same during the structural relaxation due to the symmetry and, in the HF approach, acquire the value of 1.82 Å. The single calculation of [12] for the LiF $(2 \times 2 \times 2)$ chain, in which the individual planes were constrained to be square (∠(F–Li–F) = 90°), predicted the Li–F bond length as 1.92 Å. Relaxation of the constrained cubic geometry causes a contraction of the Li–F bond length of about 0.1 Å.

It should be noted that, for all three short chains, the HF and DFT results are in close agreement, as shown in Table 2. This shows that including the electron correlation effects has minimal effect on structural properties of such nanocrystalline chains. This conclusion is additionally confirmed by the closeness of the SCF and MP2 results for the LiF $(2 \times 2 \times 2)$ chain [13], the only low dimensional chain for which reliable MP2 results are available, thus, validating the use of the HF approach to calculating structures of longer chains. Furthermore, the very close agreement

Table 2
Intra-plane Li–F distances (in Å), (F–Li–F) angles (in °) and inter-plane separations b (in Å) calculated for the LiF $(2 \times 2 \times 2)$ [T_d structure], LiF $(2 \times 2 \times 3)$ [D_{2h} structure] and $(2 \times 2 \times 4)$ [D_{2d} structure] chains within the HF/6-311G* and DFT/B3LYP/6-311G* approximations

Number of $(LiF)_2$ planes, n	Method/basis	Li–F		∠(F–Li–F)	References
2	HF/6-311G*	1.82		95.7	This work
	DFT/B3LYP/6-311G*	1.83		96.5	This work
	SCF[a]	1.81		96.7	[13]
	MP2[b]	1.82		96.7	[13]
	MP2[c]	1.92		90.0 (fixed)	[12]
		a_2	b	p_2	
3	HF/6-311G*	2.01	1.82	94.1	This work
	DFT/B3LYP/6-311G*	2.03	1.83	94.3	This work
	SCF[d]	2.00	1.84	94.8	[13]
4	HF/6-311G*	1.98	1.82	94.5	This work
	DFT/B3LYP/6-311G*	2.00	1.83	94.9	This work
	SCF[d]	1.97	1.82	95.2	[13]

For the latter two chains, these correspond to the middle p_2 plane. Comparison with literature SCF and MP2 results.

[a] Li: (11s2p1d)/[7s2p1d], F: (7s5p1d)/[3s3p1d].

[b] Li: (10s3p2d)/[6s3p2d], F: (10s7p3d2f)/[6s5p3d2f].

[c] Li: (10s)/[3s]+polarization p function, F: (10s7p)/[3s2p] + polarization d function.

[d] Li: (7s2p)/[4s2p], F: (7s5p1d)/[3s3p1d].

between the HF results obtained in this Letter and the SCF results, reported in [13] and computed with larger basis sets (these basis sets are described in Table 2), confirms that the conventional 6-311G* basis set is trustworthy for calculations of structures of free low dimensional ionic nanocrystals.

2.2. Energetics of LiF $(2 \times 2 \times n)$ crystal chains

The HF computations yielding the structures of LiF crystal chains and described in Section 2.1, enable one to obtain the energy evolved on forming 1 mol of new plane contacts of the chain. Table 3 presents various reactions in which one $(LiF)_2$ plane contact can be made. For example, one can generate an additional plane contact by forming five planes of the $(LiF)_{10}$ chain from two planes of the $(LiF)_4$ and three planes of the $(LiF)_6$ chains. Another way of making a plane contact is to form nine planes of the $(LiF)_{18}$ chain by bringing together four planes of the $(LiF)_8$ and five planes of the $(LiF)_{10}$ chains.

The results presented in Table 3 show that the energy needed to form 1 mol of new plane contacts remains almost independent of the reaction. The reaction energy varies only within 4 kJ/mol reaching the value of −223.6 kJ/mol for the LiF $(2 \times 2 \times 2)$ + LiF $(2 \times 2 \times 2) \rightarrow$ LiF $(2 \times 2 \times 4)$ reaction. With only minor changes in the reaction energy, the following trend can be noticed: the shorter the composed LiF $(2 \times 2 \times n)$ crystal chain the lower the formation energy of one $(LiF)_2$ plane contact. In the limit of $n = 1$, this result is consistent with the SCF calculations of [13] using the largest basis set which produce the dimerization energy $E[\text{LiF } (2 \times 2 \times 2)] - 2 \times E[\text{LiF } (2 \times 2 \times 1)] = -224.9$ kJ/mol, thus defining the stability of the LiF $(2 \times 2 \times 2)$ structure versus the LiF $(2 \times 2 \times 1)$ dimer plane.

The lattice energy with respect to the isolated ions of an infinite $(2 \times 2 \times \infty)$ crystal can be deduced by combining the results for the energy evolved on forming one plane contact with the energy required to make a $(2 \times 2 \times 1)$ plane structure from its four constituent gas phase ions. Thus, 1 mol of LiF stoichiometric formula unit of $(2 \times 2 \times \infty)$ nanocrystal can be constructed from its constituent ions by first forming $\frac{N_A}{2}$ single $(LiF)_2$ planes (N_A is Avogadro's number) and then assembling these planes. The latter process releases about $-\frac{224}{2} = -112$ kJ/mole of formula unit. The heat of formation of these $\frac{N_A}{2}$ isolated planes was computed elsewhere [12] to be −887.2 kJ/mol. Therefore, the lattice energy of the infinite LiF nanocrystal can be predicted as follows: $U[\text{LiF } (2 \times 2 \times \infty)] = -887 - 112$ kJ/mol = −999 kJ/mol.

The Born model [24] yields directly the ratio $f = \frac{U[\text{LiF}(2\times2\times\infty)]}{U_{\text{bulk}}}$, where U_{bulk} is the negative of the usual (positive) lattice energy of the rocksalt structured bulk material. Combination of the 0.9707 result [24] for f with the experimental bulk lattice energy of −1036 kJ/mol [23] predicts $U[\text{LiF } (2 \times 2 \times \infty)]$ to be −1006 kJ/mol in good agreement with the present ab initio result. Furthermore, the resulting Born model prediction of 30 kJ/mol for the difference $U[\text{LiF}(2 \times 2 \times \infty)] - U_{\text{bulk}}$ agrees closely with that of 27 kJ/mol derived by subtracting our −999 kJ/mol value for $U[\text{LiF } (2 \times 2 \times \infty)]$ from the lattice energy of −1026 kJ/mol predicted [16] from the crystal HF computation for the bulk.

Once again, the reliability of the computations for the energetics of LiF $(2 \times 2 \times n)$ crystal chains can be tested on small systems. For the T_d structure of $(LiF)_4$, LiF $(2 \times 2 \times 2)$ chain, the total HF energy computed here with 6-311G* basis set is $E_{\text{tot}}^{\text{HF}} = -428.19$ Hartree. This value is in a good quantitative agreement with the reference SCF calculation of [13] which gives $E_{\text{tot}} = -428.25$ Hartree. The latter computations used Li and F basis sets sufficiently flexible that the energy is close to the HF limit. Although the difference in the basis sets used in this work and in [13] is insignificant for lithium, fluorine is better defined with the modified basis of [13] which leads to the discrepancy of 0.06 Hartree in the total energy of the LiF $(2 \times 2 \times 2)$ crystal.

Table 3
Reactions and energies required to form 1 mol of new plane contacts of LiF chain, as obtained within the HF/6-311G* approximation

Reaction	Energy (kJ/mol)
$(2 \times 2 \times 2) + (2 \times 2 \times 2) \rightarrow (2 \times 2 \times 4)$	−223.6
$(2 \times 2 \times 2) + (2 \times 2 \times 3) \rightarrow (2 \times 2 \times 5)$	−221.9
$(2 \times 2 \times 2) + (2 \times 2 \times 4) \rightarrow (2 \times 2 \times 6)$	−221.7
$(2 \times 2 \times 2) + (2 \times 2 \times 5) \rightarrow (2 \times 2 \times 7)$	−221.6
$(2 \times 2 \times 2) + (2 \times 2 \times 7) \rightarrow (2 \times 2 \times 9)$	−221.3
$(2 \times 2 \times 3) + (2 \times 2 \times 4) \rightarrow (2 \times 2 \times 7)$	−219.9
$(2 \times 2 \times 3) + (2 \times 2 \times 6) \rightarrow (2 \times 2 \times 9)$	−219.5
$(2 \times 2 \times 4) + (2 \times 2 \times 5) \rightarrow (2 \times 2 \times 9)$	−219.3

3. Summary

The systematic ab initio structural and energetic investigation of LiF crystallite chains with length gradually increasing from two $(LiF)_2$ planes ($n = 2$) to nine $(LiF)_2$ planes ($n = 9$) has been performed.

The structural properties of the infinite LiF chains can be summarized based on the optimized structure of the $(LiF)_{18}$ nine-plane chain which can be considered as the converged limit (i.e., structural characteristics of the middle plane of the chain do not change with increasing length). The conclusions are the following:

1. Due to the short range interactions between like pairs of ions, the initial square shape of the $(LiF)_2$ planes of the chain becomes a diamond with dilated F^-–F^- distance.
2. The diamonds in adjacent planes are identical in the limit of infinite chain, but rotated relative to each other by 90°.
3. For infinite chain of LiF, the inter-plane ionic separation b is contracted compared to the bulk lattice spacing, $\frac{b}{R_e^{3D}} < 1$.
4. The intra-plane ionic spacing a is greater than the b spacing between the ions along the infinite chain, $\frac{a}{b} > 1$.

All these structural distortional trends are purely due to the reduced dimensionality of the crystal encapsulated in a SWNT and are not affected by the presence of the surrounding tube. However, a further radial ion dilation (increase of the intra-plane ionic spacing a) can be expected as a result of the crystal–tube interaction. This will increase the value of the ratio $\frac{a}{b}$ describing crystal distortions in longitudinal and transverse dimensions.

The energy evolved on forming one plane of new contacts in the LiF $(2 \times 2 \times n)$ chain is essentially constant and independent of the lengths of the two fragments being joined. The computed value of this energy, combined with the value of [12] for the heat of formation of one isolated $(\mathrm{LiF})_2$ plane from its constituent ions, yields the value for the lattice energy of the LiF $(2 \times 2 \times \infty)$ chain. The lattice energy derived from the analytic model [24] agrees well with the present result, thus providing evidence for the reliability of the former.

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