Thermodynamic study of reconstructed crystal surfaces.: The octopolar (111) face of LiF crystals

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Thermodynamic Study of Reconstructed Crystal Surfaces.

The Octopolar (111) Face of LiF Crystals

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Abstract: Dipolar crystal faces, although reconstructed, have a high surface energy and are forbidden in a Wulff plot at 0 K, in a vacuum. However, they do grow far from equilibrium and due to the relatively open surface structure, are eligible for adsorption, epitaxy and incorporation of foreign substances. In this paper, we study the surface structure of the (111) dipolar face of LiF and calculate the thermal contribution to the surface energy, in the harmonic limit at the Hartree-Fock level.

The surface energy calculated at 0 K , of the Li and F terminated (111) faces are 0.767 and 0.698 J/m^2, respectively. When the vibrational energy and entropy is considered the surface energies at 298.15 K decrease to 0.720 (Li terminated) and 0.670 (F terminated) J/m^2. Finally, when the configurational entropy is also taken into account, the surface energies are 0.663 (Li terminated) and 0.612 (F terminated) J/m^2.

Keywords: LiF, surface relaxation, vibration frequencies, surface entropy and free energy

1. Introduction

In this paper, we report a study on the surface structure and free energy of the (111) face of the LiF crystal, performed with the same computational method of our previous work [1] on the surface structure and energy of the (100) LiF face. The interest of determining the properties of a crystal face allows for: (i) the prediction of the equilibrium shape and of the possible change of the character of a face from kinked (or stepped) to stable, [2-6] (ii) the assessment of the anisotropy of thermal and configuration entropy, (iii) the rationalization of the formation of twins and epitactic layers on crystallographic and energetic grounds, (iv) the identification of surface site candidates for foreign adsorption, and (v) the knowledge of energies needed to model interface reactivity and kinetics. For these reasons, also the less stable crystal faces, such as the (111) of LiF are clearly worth of characterization. In particular, the {111} form of crystals of NaCl type, becomes stable in several growth media, the corresponding surfaces have an open structure, high reactivity and are

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places of adsorption, absorption and epitaxy; e.g. the {111} growth sector of halite exhibits peculiar incorporations leading to anomalous solid mixtures [7] whose formation is not well explained.

The LiF crystal is cubic with space group *Fm*3*m* and $Z = 4$ formula units in the conventional cell; the lattice parameter is $a = 3.99$ Å at room temperature [8].

Its structure, in the [111] direction, shows alternating layers of cations and anions.. Therefore, the (111) surface is a dipolar one and, as a consequence, has a divergent electrostatic energy. As in case of the more studied (111) face of NaCl, the macroscopic dipole moment becomes zero if vacancies are introduced in the outermost 111 layers; this can be accomplished in several ways. As far as we know, the first paper dealing with the dipolar faces of structure of NaCl type is by Lacmann [9]; a list of reference on experimental works and on the equilibrium morphology of NaCl can be found in Bruno et al.[10]. From these works one concludes that the surface reconstruction of lowest energy, at 0 K, is the octopolar one, as originally suggested by Lacmann [9]. The octopolar reconstruction exhibits 25% of the ions in the outer layer of the slab and 75% of the ions in the subsequent one; two surface terminations, Li or F ions , are possible (Lacmann [9]). In the language of the Periodic Bond Chains [2-4] these surfaces are kinked and may not be in equilibrium with the flat (100) faces [1].

The octopolar reconstruction conserves the point symmetry of the (111) face and there are evidences [10,11] that the reconstructed surfaces preserving the maximal symmetry have the lowest energy in vacuum. For this reason, in this study, we consider only the surface configurations which exhibits octopoles.

The aim of the work is to evaluate the relative stability of the (111) faces of LiF at several temperature values, in the harmonic limit, by quantum-mechanical calculations. We are also interested to estimate the relative weight of the vibration and configuration entropy with varying temperature and to compare our results with the existing approximate estimations of the vibration entropy given by Bruno et al. [12], in the case of the (111) faces of halite.

At best of our knowledge, for the first time by means of quanto-mechanical calculation, we assess the thermal properties of reconstructed dipolar slices, a task showing some difficulties described in the paper and demanding intensive computations. The peculiarity of the vibration modes of the slabs can be observed by the readers using the material in the supporting information and a software referenced in the work.

2. Computational details

Bulk and slab geometry optimizations were performed by the ab initio Hartree-Fock LCAO SCF CRYSTAL09 computer program, for the study of periodic systems [13-16]. Considering that

previous calculations using HF and DFT approximations of the exact Hamiltonians [17] gave close values of the surface energy and that, due to the relatively small number of electrons in LiF, the correlation effects are negligible [18], we decided to perform calculations at the Hartree-Fock level (HF). In fact, the possible use of one of the common DFT formulations would introduce errors due to the approximate nature of the exchange functional (in comparison with the *exact non local* HF exchange) which are likely larger than the error due to lack of Coulomb correlation they pretend to correct. As a matter of fact, unit cell volume, cohesive energy, compressibility and elastic constants of LiF, calculated at the HF level, are very close the correspondent experimental data [18]; this is not the case for heavier alkali halides where correlation effects play a more significant role [18]. The multielectronic wave function is constructed as an antisymmetrized product (Slater determinant) of monoelectronic crystalline orbitals (CO) which are linear combinations of local functions (to be indicated as AO's) centered on each atom of the crystal. In turn, AO's (basis set) are linear combinations of Gaussian-type functions (GTF, the product of a Gaussian times a real solid spherical harmonic to give s-, p-, and d-type AO's). In the present case, Li is described with a 6-11G* basis [19]. It consists of six contracted GTF's for the description of the cores shell, and two uncontracted sp and one d functions for the valence shell. For F, the basis sets used is 7-311G* [20] consisting of seven contracted GTF's for the description of the core s shell, and a contraction of three and two uncontracted sp's, and one d function for the valence shell. All of the exponents of the valence sp and d GTF's have been variationally optimized. The five parameters (ITOL1, ITOL2, ITOL3, ITOL4, and ITOL5) controlling the accuracy of the calculation of Coulomb and exchange integrals[18] were set to 10^{-8} (ITOL1 to ITOL4) and 10^{-16} (ITOL5). The diagonalization of the Fock matrix was performed at 10 **k** points in the reciprocal space (Monkhorst net [21]) by setting the shrinking factor IS [22] to 8.

For both geometry and frequency calculations, the SCF convergence threshold on total energy (TOLDEE in CRYSTAL09) has been set to 10^{-10} bohr. Geometry optimization is achieved when each of the components of the gradient and of the displacement (TOLDEG, TOLDEX parameters in CRYSTAL09) are smaller than 4×10^{-5} hartree bohr^{-1} and 10^{-5} bohr, respectively.

3. Surface structure

The structures of slabs, considering two kinds of terminations (F or Li) and different thicknesses (from 3 to 25 layers), have been optimized; atoms having the same z-coordinate (in this case according to the perpendicular to the plane of interest), are considered to form a *layer*. Only slabs comprising an odd number of layers are allowed, in order to have a center symmetrical slab and to cancel the macroscopic dipole moment. 2D periodic boundary conditions have been imposed. We

could not manage slabs thicker than 25 layers while conserving 12 symmetry operations, probably for numerical round off errors; the calculations becomes unaffordable if the symmetry is relaxed.

We describe the 25 layers slab, Li terminated; the point group of the repeated unit is $\bar{3}m$, the origin being at the position of one Li atom in the central layer. The two dimensional primitive cell is a lozenge: a=b=5.688 Å, γ=120°, at whose vertices there are four atoms.

From a geometric point of view the slab is limited by two planes, but actually, we must consider the surface region, that is a volume comprising about eight layers from the outermost one towards the inside. The population of these layers is not constant due to the reconstruction: as anticipated, the outermost layer has only one atom and the adjacent one three atoms over four, the other layers are 100% occupied. As a consequence of the field discontinuity and of the reconstruction, the planes of Li and F are deformed.
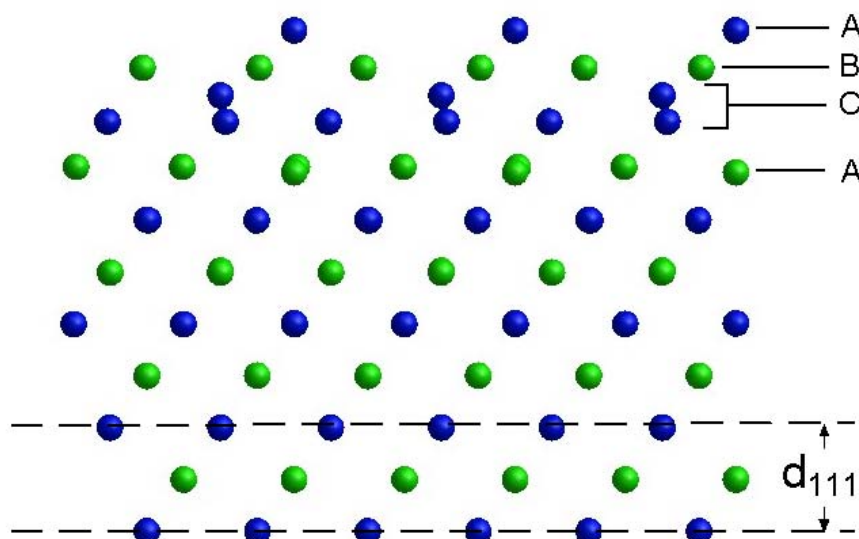
Figure 1. Projection in direction perpendicular to [111] direction of the (111) Li (blue atoms) terminated slab.

If we look to the mean displacement of the atoms, the two outer planes move towards the bulk and the six subsequent experience oscillations about the "ideal" position they have in bulky crystals (Figure 1); the displacements are negligible in the inner portion of the slab. Variable deformations (as a function of depth in the slab) of the 2D cells on (111) cannot occur for the periodicity imposed.

It is interesting to describe the atomic level deformation by the quantity $\frac{\Delta z}{z}$, being z the ideal (i.e., bulk) atomic position and Δz the displacement in direction [111]; this deformation propagates

within the slabs for about $3.5 \times d_{111}$, where $d_{111} = 2.77$ Å (Figure 1). This is shown in Figure 2 where Li is represented in blue and F in green color. In the abscissa the numbers label the layers.

In the layers from ±12 to ±5 the four atoms at the vertices of the cell are split in two groups, the first one comprises three atoms experiencing the same [111] displacements, whereas in the second group the fourth atom moves in [111] direction opposite to the previous three ones; in Figure 2 the groups of three atoms are indicated by triangles and the atoms alone by circles. Labeling ABCA… the layers from the surface towards the interior, three atoms in layer B are coplanar and equidistant from the lonely one in layer A. In layer C, the first fully occupied, the lonely atom underneath the vacancy in layer B moves outwards, and the other three inwards.

These deformations are coupled to small variations of the fractional coordinates so that the triad of atoms in the outer B and C layers are slightly rotated with respect to the bulk configurations, always fulfilling the symmetry constraints.
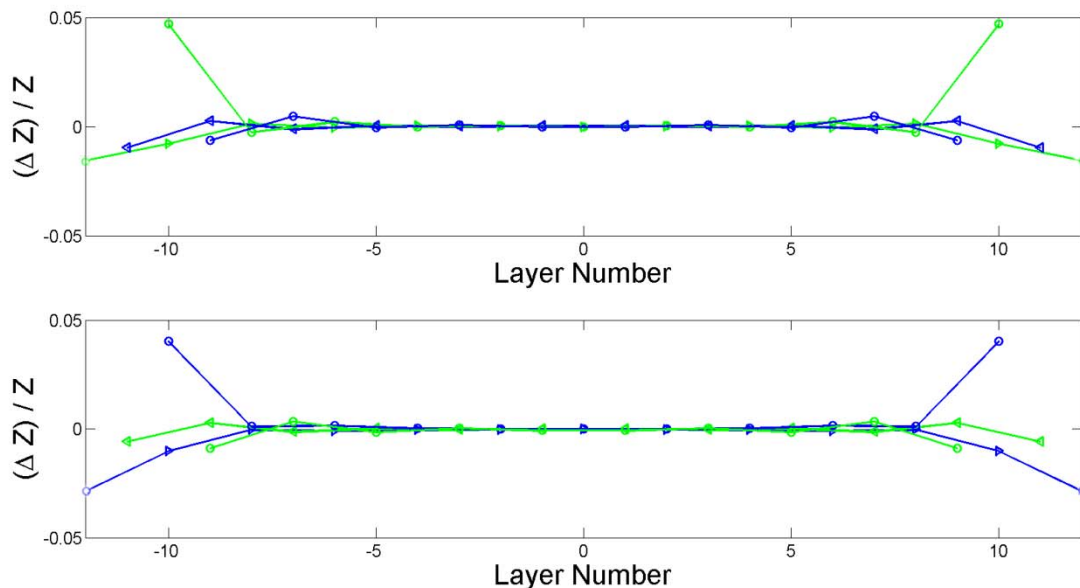
Figure 2. Atomic level deformation of the surface. Upper panel: F terminated slab; Lower panel: Li terminated slab.

It follows that in the surface region the octopoles are quite distorted, e.g. in terms of interatomic distances (in the Li terminated slab) the distance between the external Li (layer A) and the neighbor F (layer B) is 1.757 Å, the shortest distance between the latter and the Li (layer C) is 1.843 Å, then Li (layer C) – F (layer A) 2.333 Å; progressively the values tends to Li-F = 2.007 Å, in the bulk. From the layers -5 to +5 the slab has the structure of the bulk.

4. Frequency calculations

Harmonic frequency at the Γ point are calculated by CRYSTAL09 [22]: it computes numerically the second derivatives of the energy using analytical first derivatives. The calculation is done by displacing the irreducible atoms only. The full mass-weighted Hessian matrix, in Cartesian coordinates, is then generated and diagonalized to obtain eigenvalues and normal modes. The frequencies must be computed when the crystalline structure is at a minimum on the potential energy surface. Therefore, harmonic frequency calculations have been performed on the optimized (111) slabs described previously.

From the analysis of the eigenvectors of the mass weighted Hessian matrix (normal modes), we see that bulk like normal modes as well as modes peculiar of the slabs appear. A bulk like mode is for instance the LO (longitudinal optical) mode at 146.03 cm^{-1}, symmetry A_{1g} Raman active, provided as animated gif image [23] (f20_146.gif, projection in direction perpendicular to [010]). The E_u IR-active mode at 181.37 cm^{-1} (image labeled f27_181.gif) is a surface mode that can be described as a rocking of the F atoms in the 75% occupied layer around the external Li atoms in the layer which is 25% occupied. The [111] components of the movements, allowed by the vacancies, decays progressively towards the center of the slab where we observe residual small oscillations parallel to 111 planes. A peculiar mode at 275 cm^{-1} shows atoms, in the inner volume of the 25 layer slab (symmetry E_u- IR active, mode, animated image f99_275.gif), oscillating in 111 planes; approaching the surface the amplitude of the stationary wave reduces to zero. Further animations can be generated using MOLDRAW [24] and the data from the CRYSTAL09 output files which are freely available [23].

As a conclusion of this section we observe that: (i) in a given mode the amplitudes of the atomic displacements are perturbed by the surface, (ii) we observe modes, usually indicated as surface modes, characterized by a rapid decrease of the amplitude from the surface to the interior, (iii) modes exist whose amplitude decreases from the bulk to the surface.

5. Evaluation of thermodynamic properties.

5.1 Surface energy at 0K

The calculation of the surface energy at 0 K is based on the formula:

$$\gamma(N) = \frac{E(N) - NE_{bulk}}{2A(N)} \quad (1)$$

where N is the number of formula units in the repeated column generating the slab. The same cell shape is chosen for the slab and the bulk. The calculation is reiterated increasing N, the succession

converging to $\gamma(\infty)$. Actually, in this case, the convergence is quickly achieved: the energies of the five slabs made by 17, 19, 21, 23 and 25 layers are dispersed about a mean value in both Li and F terminated surfaces. We obtain: $\gamma_F = 0.6946 \pm 2.5 \times 10^{-4}$ J/m^2 and $\gamma_{Li} = 0.7668 \pm 2.1 \times 10^{-3}$ J/m^2. The lower energy value is that of the surface exposing the more polarizable atoms. Both values are higher than that of the (100) face of LiF, 0.351 J/m^2, at 0 K [1].

5.2 Vibrational and configurational entropy

The frequency spectrum of a bulk crystal and that of a slab limited by the faces of interest determine different vibration partition functions and, by consequence, different thermodynamic properties. The difference between the values of the slabs and bulk crystal, of a given thermodynamic property, become constant when the slab reaches a macroscopic size: it corresponds to the desired value of the excess surface property.

The decreased number of symmetry operators (and the consequent partial degeneracy removal), together with the (111) truncation and reconstruction effects (surface), modifies the frequency spectra at each point of the Brillouin zones of the 2D slabs with respect to 3D crystal. Then, the comparison of the frequency distributions is meaningful provided that both slabs and bulk crystal have the same non isotropic supercell and number of vibration modes. For such a reason we calculated the bulk frequencies by considering supercells with metric $a = b = 5.706\ \text{Å}, \ c = n \times 3d_{111}, \gamma = 120°$. Furthermore, to correctly generate a 3D crystal made by a sequences of layers of alternating charges, the supercells must have a number of layers multiple of 6.

As the slabs are reconstructed and consist of an odd number of layers, we cannot calculate the excess properties comparing directly slabs and bulk; in practice we calculate the values of entropy, vibration energy, free energy of the bulk supercells having the same number of ions of the slabs by interpolation; successively, we calculate the excess property per unit area of each slab and represent the sequence of values by a truncated series of power of N^{-1}, where N is the number of formula units; the limits of the succession as $N \to \infty$ is the values of the surface property.

The thermal contribution to the specific thermodynamic properties (foot index *th*) is obtained according to the relationships:

$$S_{slab/bulk} = -k_B \sum_{k,v} ln\left[1 - exp\left(-\frac{\hbar\omega(k,v)}{k_B T}\right)\right] + \frac{1}{T}\sum_{k,v}\hbar\omega(k,v)n(\omega,T) \ (2)$$

$$E_{th\_slab/bulk} = \sum_{k,v}\hbar\omega(\mathbf{k},v)\left\{\frac{1}{2} + n[\omega(\mathbf{k},v),T]\right\} \ (3)$$

where the number of phonons of angular frequency ω in the v branch with wave vector **k** follows the Bose-Einstein distribution:

$$n(\omega,T) = [\exp(\frac{\hbar\omega(\mathbf{k},v)}{k_B T}) - 1]^{-1} \qquad (4)$$

$h\left(\hbar = \frac{h}{2\pi}\right)$ and k_B are the Planck and Boltzmann constant respectively. $S_{slab/bulk}$ is the vibration entropy of the slab/bulk, $E_{th\_slab/bulk}$ is the vibration (thermal) energy of the slab/bulk, including the contribution of the zero point energy.

$$E_{th} = \lim_{N\to\infty} E_e(N) = \lim_{N\to\infty} \frac{E(N)_{th\_slab} - E(N)_{th\_bulk}}{2A(N)} \quad (5)$$

$$S_{th} = \lim_{N\to\infty} S_e(N) = \lim_{N\to\infty} \frac{S(N)_{slab} - S(N)_{bulk}}{2A(N)} \quad (6)$$

Finally, the (111) specific surface properties, E_{th}, S_{th}, (Eqs. 5 and 6), were calculated as, e.g., in case of the excess surface entropy, S_{th} [J/ (m^2 K)], by subtracting from the entropy of slabs of different thickness, $S(N)_{slab}$, that of an equal number of formula unit N, in the bulk, $S(N)_{bulk.}$, then dividing the difference by twice the surface of the 2D cell. The latter converges to the surface of the 2D mesh on 111 in the bulk, with increasing number of atoms.

$$A_{th}(\infty) = E_{th} - TS_{th} \qquad (7)$$

$$\gamma = \gamma(\infty) + A_{th}(\infty) - TS_c \qquad (8)$$

The surface free energy, γ in Eq. (8), is the sum of the surface energy at 0 K, $\gamma(\infty)$, of the Helmholtz thermal energy, $A_{th}(\infty)$, Eq. (7), and the surface configuration contribution (S_c is the surface configurational entropy), $-TS_c$ estimated in the following.

In Figure 3 we represent the (excess) surface entropy $S_e(N)$, and Helmholtz thermal function $A_e(N)$ at two temperature values (50 and 298 K) as a function of $\frac{1}{N}$. Letting P represents $S_e(N)$ thermal entropy or $A_e(N)$ Helmholtz free energy, the expansion has the following structure :

$$P = \frac{a}{N^3} + \frac{b}{N^2} + \frac{c}{N} + P_{th}(\infty) \qquad (9)$$

The coefficients are reported in Table 1 for the two temperature values and the two slabs terminations, Li or F. We observe a decrease of -46.53×10^{-3} and -25.25×10^{-3} J/m^2 in the temperature range of 0-298.15 K for the surface energy of the Li and F terminated (111) faces, respectively. This means that the vibrational contribution at 298.15 K reduces by ~6.1% and ~3.6% the surface energy at 0 K of the Li and F terminated (111) faces, respectively.

Furthermore, we observe that the excess entropy and vibration energy per unit surface are systematically higher in the case of the slabs Li terminated while the thermal Helmholtz free energy is lower than that of the F terminated surfaces. The values show that the frequency spectrum in the slabs is, on average, shifted toward the low frequency with respect to the bulk, as well as in case of the Li terminated in respect to the F terminated slabs. The thermal Helmholtz function becomes negative with increasing temperature.

At T > 0 K, the configurational entropy per unit surface of the (111) face, is given by Shi and Wortis:[22] $S_c = k_B \times 0.323 \times \frac{\sqrt{3}}{d^2}$. where d is the interionic distance. Then, for the (111) face, by considering $d = 2.005$ Å and $k_B = 1.3807 \times 10^{-23} \frac{J}{K}$, we obtain $S_c = 192.14 \times 10^{-6} \frac{J}{K\,m^2}$.
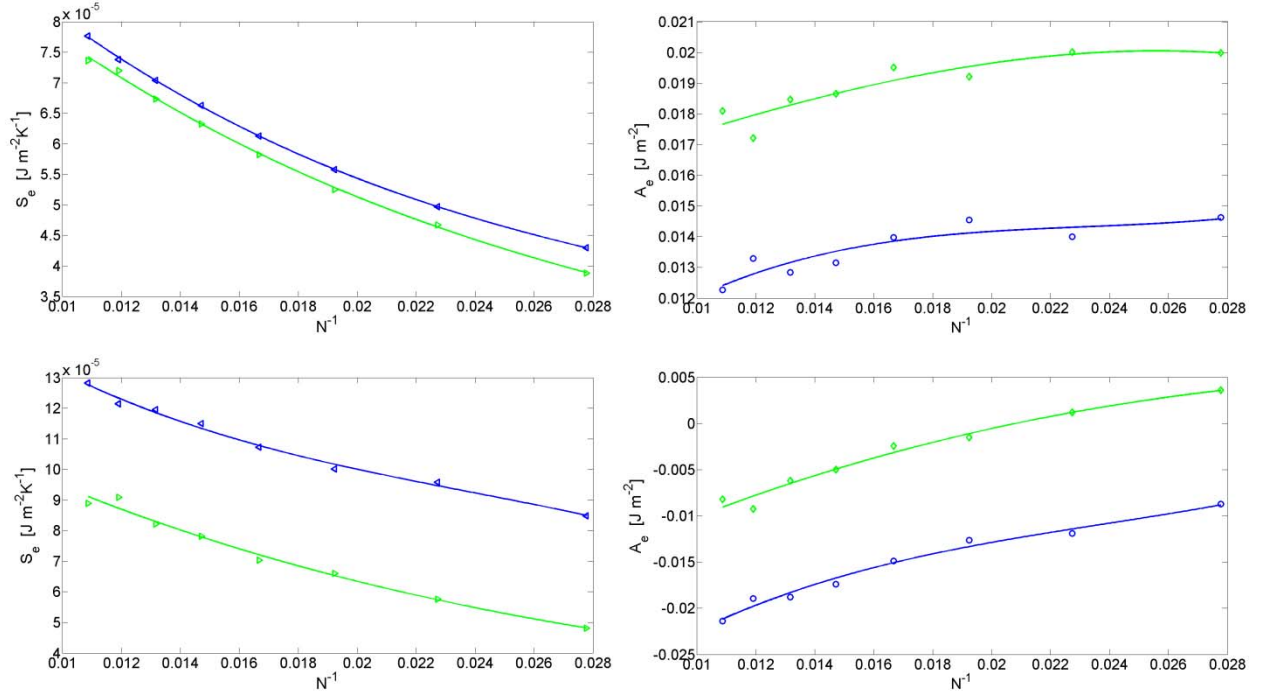
Figure 3. Thermal properties as a function of the reciprocal number of formula units of the slabs. Upper left panel: surface entropy $S_e(N)$ at 50 K; upper right panel: surface free energy $A_e(N)$ at 50 K. Lower left panel: surface entropy at 298.15 K; lower right panel: surface free energy at 298.15 K. The colors blue and green identify the Li and F terminated slabs, respectively.

Finally, including configurational and thermal contributions, the surface energy of the F terminated (111) face is reduced to 0.6121 $\frac{J}{m^2}$ (-11.9%), at 298.15 K, while, in the case of the Li terminated face, we obtain 0.6630 $\frac{J}{m^2}$ (-13.6%).

T (K)	Termination	$S_e(N) \times 10^6 \left[\frac{J}{m^2 K}\right]$				$A_e(N) \times 10^3 \left[\frac{J}{m^2}\right]$			
		a	b	c	$S_{th}(\infty)$	a	b	c	$A_{th}(\infty)$
50	Li	-1281462.92	138410.32	-5862.09	*126.47*	758933.17	-52825.04	1265.44	*3.92*
50	F	-931136.54	108752.73	-5183.65	*118.93*	-184574.25	445.71	340.19	*14.15*
298	Li	-5072929.76	361620.88	-10453.17	*205.04*	1748011.98	-125305.77	3489.95	*-46.53*
298	F	-996470.26	122018.46	-6065.29	*143.89*	154902.82	32742.20	1827.68	*-25.25*

Table 1. Coefficients of the Eq. 9 for fitting the (excess) surface entropy $S_e(N)$, and Helmholtz thermal function $A_e(N)$ at two values of temperature (50 and 298.15 K).

6. Conclusions

From ab initio quantum-mechanical calculations, we have obtained a value of the surface free energy of the (111) face of LiF after reconstructing the surface according to the octopolar Lacmann[8] model and considering two terminations, F or Li. As far as we know, this is the first time that a quite rigorous calculation is made on such rough faces. We used the CRYSTAL09 computer program which proved to produce results in agreement with experimental measurements of the surface energy of (100) LiF face [1].

The approach to the study of surfaces of CRYSTAL09 is peculiar in that the relevant properties of 3D and 2D systems are treated on an equal footing which however demands a great amount of computing time. To cope with this constraint, we have extrapolated the relevant thermodynamic properties of the face from the calculated values for the slabs, as described in section 5.2. The evaluation of the balance of thermal energy and entropy disregards, as usual, the variation of cell parameters with temperature, causing a variation of the frequency spectrum, and the possible anharmonicity of the modes. Notwithstanding this approximation, we can safely assert that both thermal and configurational entropy do not decrease the surface energy of the (111) to such extent that it may compose the equilibrium form, in vacuum. We can state that the static surface energy of the F terminated faces is significantly lower than that of the Li terminated which conversely, have higher vibration entropy and lower thermal free energy. The configurational entropy is of the order of the thermal entropy at 298 K. It results that the (111) F terminated slab is more stable than the Li terminated (estimated energy difference between the two terminations: $0.051 \frac{J}{K m^2}$, at 298.15 K).

At 298.15 K, the value, mediated over the two terminations, of the (111) surface free energy amounts to $0.6375 \frac{J}{m^2}$, by far higher than that of the (100) face, $0.3038 \frac{J}{m^2}$. For the latter the configurational entropy is negligible due to the high energy cost to form a surface vacancy (Shi and

Wortis [25], Kern [26]). So, in agreement with observations at high temperature, we expect that the face (111) eventually formed during vapor growth, breaks into a hill and valley structure limited by {100} facets, in agreement with the observations [27]. In contact with a solution, at low temperature, the surface vacances on (111), are potential sites of adsorption, two dimensional epitaxy and absorption. Adsorption on such reconstructed (111) surface occurs at several levels, which introduces additional degree of freedom to accommodate complex molecules and to reduce the interface stress in epitaxy. When such phenomena occur the (111) faces become stable and tend to be flat.

Similar conclusions about the equilibrium morphology were drawn by Bruno et al.[11] in their study on halite (NaCl); in that work the entropy of the octopolar (111) NaCl face was obtained by a calculation proposed by Kern [26], based on the Einstein model for solids: this calculation gives a mean value of $\frac{\partial \gamma}{\partial T} = -140.10^{-6} \frac{J}{K \, m^2}$ in case of halite, while in case of LiF (111), $\frac{\partial \gamma}{\partial T} = -128.10^{-6} \frac{J}{K \, m^2}$. The latter mean value is of the order of the thermal entropy calculated in this work.

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Graphical abstract
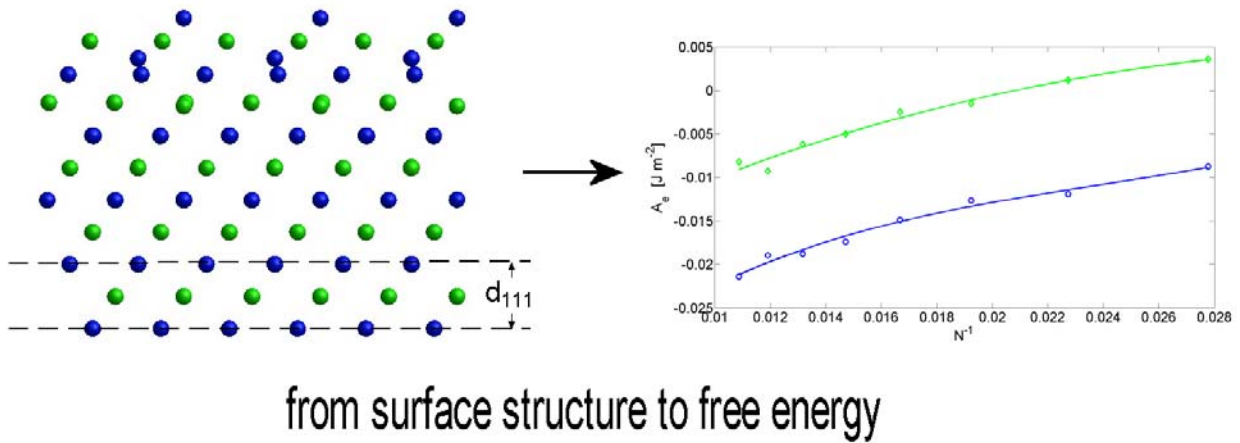
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