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/m², respectively. When the vibrational energy and entropy are considered the surface energies at 298.15 K decrease to 0.720 (Li terminated) and 0.670 (F terminated) J/m². Finally, when the configurational entropy is also taken into account, the surface energies are 0.663 (Li terminated) and 0.612 (F terminated) J/m².

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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 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 $Fm3m$ 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 the 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 exhibit 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 the 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

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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 to 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 core shell, and two uncontracted sp and one d functions for the valence shell. For F, the basis set 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} Ha 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 become 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.

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 (Fig. 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 $\frac{\Delta z}{z}$, z being 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 (Fig. 1). This is shown in Fig. 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 the previous three ones; in Fig. 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 is slightly rotated with respect to the bulk configurations, always fulfilling the symmetry constraints.

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 is 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
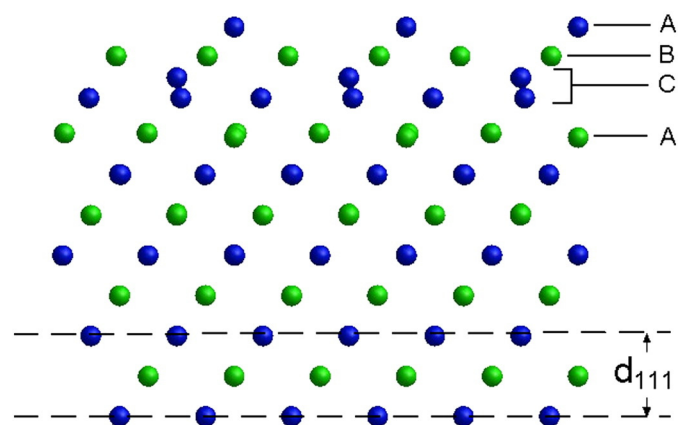

Fig. 1. Projection in direction perpendicular to [111] direction of the (111) Li (blue atoms) terminated slab. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)