

Temperature dependent $\text{LiNbO}_3(0001)$: Surface reconstruction and surface charge



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ABSTRACT

The polar (0001) surface of stoichiometric LiNbO_3 undergoes a series of structural transformations with temperature. This complex behavior mirrors the action of different charge compensation mechanisms at specific temperatures. In this work the surface charge associated to various surface terminations is estimated from first-principles calculations. All the thermodynamically stable terminations are found to lower the polarization charge, showing that the surface charge compensation is a major driving force for the observed morphologic transformations.

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1. Introduction

The polar surfaces of ferroelectric oxides have attracted the attention of scientists and engineers for a long time. Indeed, a variety of applications exploiting the strong electric fields at the surfaces have been realized. Among the mostly employed ferroelectric surfaces, the lithium niobate $\text{LiNbO}_3(0001)$ plays a prominent role [1]. It is in fact widely exploited, e.g. for the realization of surface acoustic wave devices [2] or to grow group III nitrides with spatially varied polarity control [3]. Novel applications exploit the possibility (exclusive to ferroelectrics) to switch the polarization, and thus the chemistry [4], of the (0001) surface. Artificial photosynthesis [5], photocatalytic dye decolorization [6] as well as activation of charged biomolecules [7] on LN surfaces have been demonstrated recently. Furthermore the high surface electric fields were found to efficiently pole electro-optic polymers [8] and to lead to the reversible fragmentation and self-assembling of nematic liquid crystals [9].

Despite many exciting applications, little detailed information on the LN surface atomic structure is available. Yun et al. [10] investigated (0001) surfaces at ambient conditions by electron diffraction, and found no indication for reconstructions. Ion scattering spectroscopy suggested that both (0001) surfaces are oxygen terminated [10], while coaxial impact-collision ion

scattering suggested a Nb surface termination [11,12]. Atomic scale investigations are hindered by the extremely challenging preparation and analysis conditions of strongly polar surfaces of insulating materials, though. While reconstructions at the weakly polar $\text{SrTiO}_3(001)$ and $\text{BaTiO}_3(001)$ surfaces have been recently demonstrated by scanning tunneling [13,14] and transmission electron [15] microscopy, charging effects prohibit the application of electron tunneling or diffraction techniques and unscreened surface charges hinder atomic force microscopy in LN. Thus, the atomic structure of the LiNbO_3 surface remained for a long time experimentally inaccessible. A breakthrough was achieved by Rode et al. [16] performing the AFM measurement in liquid environment, in order to screen the AFM tip from the surface charges. This allowed for the first time true atomic resolution imaging of the (0001) surfaces. No surface reconstruction was revealed in stoichiometric samples annealed at 1270 K. Successively, measurements on samples annealed at different temperatures showed a series of structural transformations, including a $\sqrt{7} \times \sqrt{7}$ R19° surface reconstruction [17], stable only in a limited temperature range. The evolution of the surface structure with increasing temperature was interpreted as the result of the interplay between different charge compensation mechanisms. At temperatures below 870 K the polarization charge is compensated by foreign adsorbates. However, if the temperature is sufficiently high to drive off the adsorbates, surface reconstructions are formed to compensate the surface charge. Finally, after annealing above 1270 K any reconstruction disappears. This temperature is rather close to the Curie temperature of LN ($\vartheta_C \approx 1480$ K [1]), so that the

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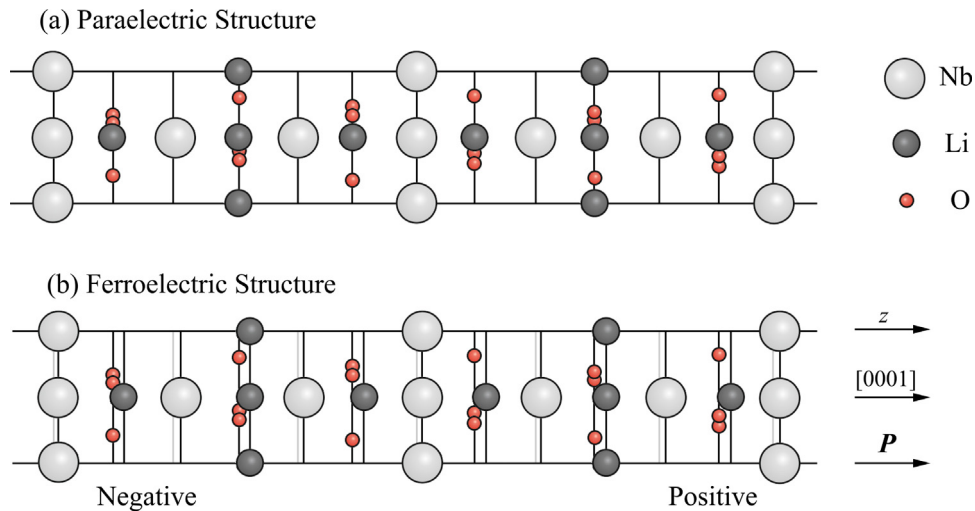


Fig. 1. Schematic representation of the paraelectric (a) and ferroelectric (b) phases of LiNbO_3 along the $[0001]$ crystallographic direction. In the ferroelectric phase Li and Nb atomic layers are shifted with respect to the oxygen sublattice along the crystal z -axis. The gray lines in the ferroelectric phase represent the position of the corresponding atomic layer in the paraelectric phase.

spontaneous polarization, and thus the surface charge, are strongly reduced (pyroelectricity). *Ab initio* thermodynamics based on density functional theory (DFT) calculations pointed out that various reconstructions might be formed at specific conditions [17].

In this work we propose an approximate method to estimate the surface charge within the density functional theory (DFT), and apply it to the thermodynamically stable surface reconstructions, in order to determine the associated surface charge. Thereby we rely on the structural models proposed in Ref. [17]. Our calculations indicate that all the thermodynamically stable surface reconstructions formed at different temperatures reduce the surface charge, suggesting that the compensation of polarization charge is a driving force for the observed structural modifications.

2. Methodology

The determination of the surface polarization charge within the DFT is a delicate task, both due to the vague definition of surface layer and due to the limitations introduced by the supercell approach. This approach is very convenient for the simulation of periodic 3D systems such as bulk structures. However, it suffers from some long-ranging interactions between artificial images in 2D system such as surfaces. A vacuum layer has to be included in the supercell in order to break the periodicity in one direction and form the surface, which is then simulated in periodically repeated slabs. This is an issue in particular for ferroelectric materials with strong electric fields [18,19]. These problems and possible solutions are discussed in some detail in this section.

2.1. Computational details

As in our previous studies on LiNbO_3 surfaces [17,20–22], we perform self consistent first-principles calculations in the framework of the density functional theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package (VASP [23]). All-electron projector-augmented wave potentials [24] within the PW91 formulation of the generalized gradient approximation (GGA) [25] are used. A plane-wave basis set including waves up to an energy of 400 eV is used to expand the electronic wave functions. The atomic positions have been determined minimizing the Hellmann-Feynman forces acting on the single atoms under 0.02 eV/Å. A $4 \times 4 \times 1$ Γ -centered Monkhorst-Pack [26] k -point mesh was used to carry out the integration in the Brillouin zone for the simulation

of truncated bulk, unreconstructed and $(\sqrt{3} \times \sqrt{3})$ reconstructed surfaces. A $2 \times 2 \times 1$ k -point mesh was chosen to sample the much smaller Brillouin zone of the slabs modeling $(\sqrt{7} \times \sqrt{7})$ reconstructed surfaces. The detailed constitution of the slabs used to model surfaces of different periodicity is discussed in the following section. As shown in our previous works, this approach is accurate enough to provide reliable structures and energies for both bulk LiNbO_3 in the ferroelectric and paraelectric phase and for LiNbO_3 surfaces [17].

2.2. Surface and slab geometries

In most of the works available in the literature, the $\text{LN}(0001)$ is defined as the positive surface and the $\text{LN}(000\bar{1})$ as the negative. However, some authors use the opposite notation. To avoid any confusion, we illustrate here the definition used throughout this work. The $[0001]$ crystallographic direction is usually called z -direction or c -axis. According to the accepted model, the cations in the highly symmetric paraelectric phase are either within (Li^{+1}), or exactly between oxygen layers (Nb^{+5}), as depicted in Fig. 1(a). In the ferroelectric phase, the cations are shifted along the $[0001]$ crystallographic direction with respect to the oxygen planes, causing a permanent spontaneous polarization parallel to the cationic displacement. The positive c -direction is defined as parallel to the polarization, the negative as antiparallel (see Fig. 1)¹. Ferroelectric LiNbO_3 is thus a stacking of $-\text{Nb}-\text{O}_3-\text{Li}-$ planes along the $[0001]$ direction, and is not centrosymmetric. This is an issue within the supercell approach, as the two slab surface terminations cannot be made equivalent and only relative energetic comparisons are possible. In this work we model the $\text{LN}(0001)$ surface and all its reconstructions with 12 LN trilayers (36 atomic layers) plus surface terminations, resulting in large supercells containing from 60

¹ This defines on turn the positive and the negative z -surfaces, created by cutting the crystal perpendicularly to the $[0001]$. Indeed, the standard method of determining the orientation of the c -axis is to heat or to compress the crystal in the c -direction: by definition the $+c$ face becomes negative upon heating or compression. Upon heating or compressing the material, the cations are shifted closer to their paraelectric positions, thereby reducing the net polarization and leaving an excess amount of negative compensating (or depolarization) charge on the $+c$ face, which becomes negative [1]. Summarizing, the positive (0001) surface is characterized by an electronic charge accumulation, while the negative is characterized by an electronic charge depletion.

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