

Ferroelectric phase transition in LiNbO_3 : insights from molecular dynamics

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Abstract—Molecular dynamics simulations in the framework of the density functional theory are used for the first time in order to model the ferroelectric-paraelectric phase transition in LiNbO_3 . Our calculations show that the structural phase transition is not an abrupt event, but rather a continuous process occurring over about 100 K and involving different ionic species at different temperatures. Because of the different behavior of the Li and Nb sublattice, the ferroelectric transition displays both displacive and order-disorder character.

Keywords: LiNbO_3 , Ferroelectrics, Density Functional Theory, Molecular Dynamics, Phase Transition, Curie Temperature.

I. INTRODUCTION

Lithium niobate (LiNbO_3 , LN) is one of the most important optical materials as it plays in the field of optics, nonlinear optics and optoelectronics the role played by silicon in standard electronics. LN crystals have unique and favorable ferroelectric, piezoelectric, photoelastic, optical (linear and nonlinear) and electro-optical properties, furthermore they are strongly birefringent. Due to its properties LN is used extensively for applications such as optical waveguides, optical switchers, acousto-optical devices, lasers as well as in widespread devices such as motion controllers and mobile telephones.

Despite this wide range of applications, many aspects of the physics underlying the LN properties are not fully understood up to date. In particular the phase transition between the paraelectric and the ferroelectric phase is still argument of debate. A major point concerning the nature of the transition is whether it is of displacive or order-disorder type. Displacive transitions are characterized by the presence of a polar optical phonon mode, which becomes soft close to the Curie temperature θ_C . On the contrary no soft mode exists in order-disorder transitions, due to the presence of a double-well potential with a barrier much larger than the thermal energy $k_B\theta_C$. Many different studies have been therefore dedicated to the investigation of the phonon modes of LN. Unfortunately only some of the investigation, including Rayleigh scattering, Raman spectroscopy and infrared reflectivity show a soft mode behavior for a $A_1(\text{TO})$ optical phonon suggesting a displacive nature of the transition [2-4], while in other studies, including neutron and Raman scattering experiments, no mode softening could be observed, suggesting the order-disorder nature of the ferroelectric phase transition [5-7]. Wood *et al.* measured the

birefringence of lithium niobate tantalate crystals for various compositions and temperatures, finding that it changes continuously across the Curie temperature [8]. Theoretical investigations based on the modeling of the phonon modes within the frozen phonon approach support an order-disorder model for the oxygen atoms as the driving mechanism for the ferroelectric instability [9, 10]. Recently Phillpot and Gopalan used molecular dynamics within the shell-model approach to characterize the ferroelectric phase transition, showing coupled displacive and order-disorder dynamics [11].

The high temperature phase of LiNbO_3 (above 1483 K) is paraelectric and belongs to the space group $R\bar{3}c$. According to the general understanding of this structure, the Li ions lie (at least in average) in the oxygen plane, while the Nb atoms are located at the center of octahedral oxygen cages, as shown in Fig. 1 (central picture). When the temperature drops under the Curie temperature θ_C , the cations are displaced along the c -axis from their (high symmetry) sites. Nb ions are no longer at the center of the oxygen cages and the Li atoms sit either above or under the oxygen layers. Because of the Coulomb repulsion, both cations are displaced in the same direction with respect to the oxygen sublattice, as shown in Fig. 1 (left and right hand side). This atomic rearrangement has two important consequences. Firstly, the crystal loses the inversion symmetry and becomes non centrosymmetric (space group $R3c$).

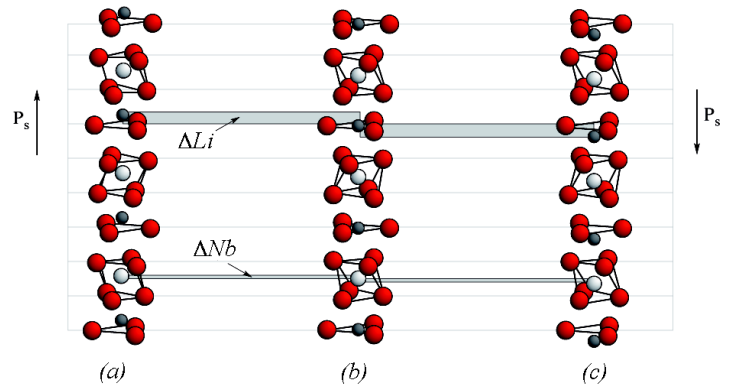


Figure 1. (color online) Atomic structure of the ferroelectric (a) and paraelectric phase of LiNbO_3 . The displacement of the Nb atoms (in white) from their positions in the paraelectric phase is labeled by ΔNb , while the displacement of the Li ions (in gray) from the oxygen planes is labeled by ΔLi . Both displacements occur along the crystal c -axis.

Second, the center of mass of the positive and negative charges are displaced, giving rise to a spontaneous polarization along the c -axis as big as 0.7 C/m^2 .

In this work we perform molecular dynamics (MD) simulations in order to model the transition between the two phases and understand the mechanisms of the transition itself. To our knowledge, MD simulations in the framework of the density functional theory (DFT) are used here for the first time in order to gain insights in the transition dynamics.

II. METHODS

Our first-principles calculations within the density functional theory (DFT) use the all-electron projector augmented wave method [12] (PAW) as implemented in VASP [13]. The PW91 formulation of the generalized gradient approximation (GGA) exchange-correlation functional [14], plane wave expansions up to 400 eV and projectors up to $l=3$ for Nb and $l=2$ for Li and O have been used for the calculations. A Monkhorst-Pack (MP) $6 \times 6 \times 6$ k -point mesh [15] was used to carry out the integration in the Brillouin zone for the simulation of the crystal structure. This approach yields reliable structures and energies for bulk LN in the ferroelectric and paraelectric phase and LN surfaces [16-18]. Minimizing the interatomic forces under a threshold value of $0.01 \text{ eV/\AA}$ and the total energy, we find lattice parameters $a = 5.161 \text{ \AA}$, $c = 13.902 \text{ \AA}$ for the ferroelectric and $a = 5.342 \text{ \AA}$, $c = 13.589 \text{ \AA}$ for the paraelectric structures, which are in both cases about 1% larger than the experimental values [1, 19]. The internal parameters are not reported here for simplicity. The calculated displacement of the Nb ions from the oxygen cage center (previously called ΔNb) and of the Li ions from the oxygen planes (ΔLi) in the ferroelectric phase is $0.28 \text{ \AA}$ and $0.72 \text{ \AA}$, respectively.

Molecular dynamics calculations are performed within a supercell consisting of a $2 \times 2 \times 2$ repetition of the unit cell (i.e. 80 atoms) and $2 \times 2 \times 2$ MP k -point mesh. MD runs of about 5 ps starting with the structure in the ferroelectric phase and for temperatures of 500, 750, 1000, 1250 and 1500 K are performed coupling the system to the Nosé thermostat [20].

III. RESULTS AND DISCUSSION

To investigate the dynamics of the phase transition, we perform several the MD runs at different temperatures and study the evolution of the parameters ΔLi and ΔNb , which measure the structural differences between the two LN phases. Above the Curie temperature ΔLi and ΔNb are expected to be, at least in average, exactly zero, while at 0 K they assume the calculated values of $0.28 \text{ \AA}$ and $0.72 \text{ \AA}$, respectively. In Fig. 2 we show a Gaussian fit of the probability distribution of ΔLi at different temperatures. The curve representing the distribution at 500 K is unimodal, suggesting that all the Li ions are placed above the oxygen planes, as expected for the system in the ferroelectric phase. The fact that the calculated curves are

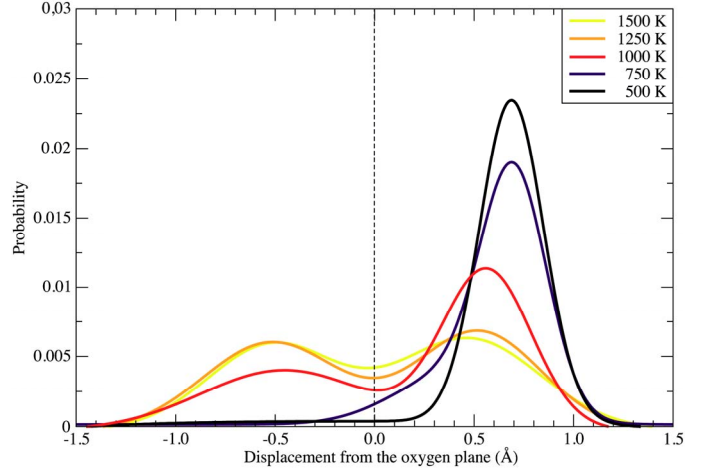


Figure 2. (color online) Probability distribution of the parameter ΔLi (representing the displacement of the Li ions from the oxygen planes) at different temperatures. The unimodal distribution at 500 K (well below the Curie temperature) means that all the Li ions are located above the oxygen planes, while the symmetric bimodal curve at 1500 K (above the Curie temperature) indicates that the Li ions are randomly distributed above or under the oxygen planes, as expected for an order-disorder phase transition.

perfectly fitted by one (or more) Gaussian functions suggests that the form of the distribution is due to a thermal broadening around a mean value. This mean value, centered around $0.74 \text{ \AA}$ is slightly larger than the calculated value (at 0 K) and in qualitative agreement with the measured value at room temperature. The curve at 1500 K, i.e. above the transition phase, changes drastically. The distribution is now bimodal and symmetric with respect to $\Delta Li = 0$, indicating that also in the paraelectric phase most of the Li atoms lie either above or under the oxygen planes and only a small fraction exactly in the plane. The spontaneous polarization of the material will be therefore exactly zero only in average, as each unit cell is characterized by a finite, randomly distributed, polarization value. This feature is in agreement with an order-disorder character of the transition. The small fraction of Li sitting in the oxygen planes suggests that it represents a higher energy lattice site than the site occupied in the ferroelectric phase, i.e. an energetic barrier. All other curves (temperature between 750 K and 1250 K) are between the two described distributions, meaning that with increasing temperature a growing fraction of Li atoms will possess enough thermal energy to pass this barrier. At 1500 K all Li atoms have sufficient energy to move across the plane, so that they can be found with the same probability over or under an oxygen plane, and the total Li contribution to the polarization vanishes. We observe that already at temperatures substantially lower than θ_c an important fraction of the Li atoms is no more in the lattice site occupied in the ferroelectric phase. This suggests that the phase transition does not occur abruptly at a given temperature, but is rather a continuous process, occurring dynamically over a certain range of temperatures.

In Fig. 3 we show the Gaussian fit of the probability distribution of ΔNb at different temperatures. In contrast to the ΔLi probability, the distribution is unimodal at each investiga-

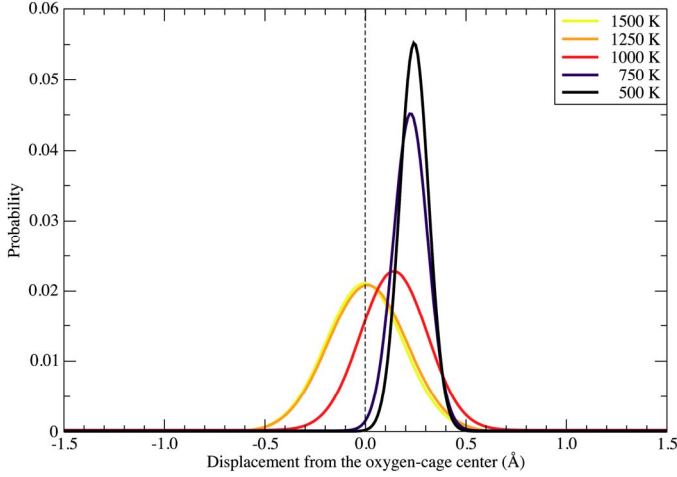


Figure 3. (color online) Probability distribution of the parameter ΔNb (representing the displacement of the Nb ions from the center of the oxygen cages) at different temperatures. The distribution becomes broader at higher temperatures but remains unimodal, as expected for a displacive phase transition. Note that already at 1000 K, i.e. well below the curie temperature, the Nb ions are already quite close to the center of the oxygen cages, indicating that the phase transition starts for the Nb sublattice at temperatures lower than θ_C .

ted temperature, as expected for a displacive transition. This also suggests that, in contrast to the Li sublattice, the Nb sublattice does not need to overcome an energy barrier to move from the ferroelectric to the paraelectric configuration. At 500 K the distribution is centered about 0.29 Å, again slightly larger than the calculated value (at 0 K) and in qualitative agreement with the measured value. At higher temperatures the mean value of the distribution moves towards $\Delta Nb = 0$, i.e. the Nb atoms move towards the center of the oxygen cages. Already for temperatures around 1000 K the Nb ions are close to the cage centers and at 1250 K they are exactly in their paraelectric lattice site. At higher temperatures the distribution becomes broader, as the atoms vibrate with larger amplitude around their equilibrium positions.

Our calculations confirm the suggestion firstly made in [10] that the phase transition is a two-step process involving a displacive transition of the Nb ions in the oxygen octahedral cages at a temperature below θ_C and an order-disorder transition in the Li-O planes completed at θ_C . The atomic structure and the spontaneous polarization change gradually between the two phases, so that the transition does not occur at a well defined temperature but rather over a temperature range of more than 100 K.

IV. CONCLUSIONS

We have performed *ab initio* MD simulations to investigate the nature of the ferroelectric-paraelectric transition in stoichiometric LiNbO_3 . As for other ferroelectrics the structural

transition in LiNbO_3 can be thought of as being of displacive nature far from the transition temperature and to show order-disorder characteristic close to the temperature θ_C . Furthermore, our calculations reveal that the paraelectric phase has to be thought of as a random distribution of Li ions above and under the oxygen planes (with a non zero value of ΔLi for most Li ions) and with an average zero net polarization, rather than in the commonly accepted configuration shown in Fig. 1(b).

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