Ab initio calculations of phonons in LiNbO₃

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Using the ab initio method within the local-density approximation with ultrasoft pseudopotentials and plane-wave basis, calculating the Hellmann-Feynman forces and applying the direct method, the phonon-dispersion relations for ferroelectric and paraelectric rhombohedral phases of LiNbO₃ crystal have been derived. The calculated phonon frequencies for the ferroelectric phase at the Γ point are compared with Raman, infrared, and neutron-scattering measurements, and they agree very well. The phonon frequencies at the Z, L, and F high-symmetry points are also calculated. It is disclosed that the force constants involving lithium ions are an order of magnitude smaller than the force constants between niobium and oxygen ions. As a consequence, the lithium ions do not contribute to high-frequency optical vibrations. In the paraelectric phase the phonon-dispersion curves show a soft branch with the soft mode of symmetry A₂u at the Γ point. This soft mode leads to the observed paraelectric-ferroelectric phase transition. The LO/TO splitting is considered by assuming formal values of ionic charges, and by fitting the longitudinal infrared active modes to the experimental data.

I. INTRODUCTION

Lithium niobate, LiNbO₃, is a well-known material for application in nonlinear optics, optoelectronics, and acoustics. The LiNbO₃ is an uniaxial crystal belonging to the trigonal system. At ambient temperature it is ferroelectric, and belongs to the rhombohedral space group R3̅c with 10 atoms (Z = 2) in the unit cell. The transition-metal atom Nb is displaced from the center of the oxygen octahedra along the trigonal axis. The next oxygen octahedron along this axis is empty, and the adjacent octahedron has a Li atom displaced from the oxygen face in the spontaneous polarization direction, i.e., along the threefold axis.

Above 1480 K LiNbO₃ undergoes a structural phase transition to paraelectric rhombohedral phase (R̅3̅c), also with 10 atoms in the unit cell. The generalized soft mode of the phase transition belongs to the A₂u irreducible representation of the D₃d point group. The early dielectric and thermal measurements have determined that the phase transition is continuous. The type of the phase transition, whether it is displacive or order-disorder type has been a matter of debate. A displacive type of phase transition should lead to a softening of A₁ (TO) mode. Recent Raman-scattering measurements in the X(ZZ)Y configuration, which selects out peaks belonging to A₁ (TO) only, confirmed that the ferroelectric-paraelectric phase transition in LiNbO₃ has mainly the order-disorder character. The same conclusion stems from the ab initio calculations of Inbar and Cohen. Calculating the local potential wells, they showed that the driving mechanism for the ferroelectric instability is a strongly coupled motion of oxygen and lithium atoms.

Part of the phonon-dispersion relations has been measured by an inelastic neutron-scattering technique. Altogether eight branches along [0,0,1] and two acoustic branches along [0,1,0] directions have been determined, and compared with the optical measurements. Postnikov et al., using the full-potential augmented plane-wave and the frozen phonon methods, have calculated for the ferroelectric phase the transverse one-dimensional frequencies of A₁ and A₂ modes. Thus far there are no calculations of frequencies of other modes and no calculations of the phonon-dispersion relations in LiNbO₃, mainly because of the low symmetry of this structure and the necessity to involve many parameters in any approach.

In this work we derive the phonon-dispersion relations and density of states for paraelectric and ferroelectric phases of LiNbO₃, using the Hellmann-Feynman forces and the direct method. The Hellmann-Feynman forces are calculated for a supercell within an ab initio approach as implemented in VASP software. The direct method in conjunction with the ab initio method has already been used to calculate phonon-dispersion curves in many crystals. Here, we recall...
alkali metals Li, Na, and K, diamond and graphite, chalcopyrites AgGaSe₂, CuInSe₂, Si, SiO₂, Ge,S, triclinic CaF₂, cubic TiC, GaAs, MgO, ZrO₂, and SrTiO₃. In ZrO₂ and SrTiO₃, soft modes have been found.

The direct method delivers correct phonon frequencies at special wave vectors of the Brillouin zone, which are compatible with the supercell size. If the interaction range would cease out within the selected supercell size, the phonon frequencies will be reproduced correctly at all wave vectors.

The above rules do not concern infrared active optic modes, since in ionic crystals such as LiNbO₃, these modes split to longitudinal (LO) and transverse (TO) components as a result of interaction with the macroscopic electric field. This LO/TO splitting breaks the crystal symmetry and cannot be entirely derived using the direct method. We solve this problem by supplementing the dynamical matrix with a nonanalytical term, which depends on the Born effective charge tensors and electronic dielectric constant. At the moment, the values of the Born effective charges and electronic dielectric constant have to be taken from fitting the phonon frequencies to the experimental data.

The aim of this paper is to derive the phonon-dispersion relations from ab initio calculations for relatively complex crystals LiNbO₃, and to provide a realistic pattern of mode behavior for analysis of Raman scattering, infrared absorption, and inelastic neutron-scattering measurements. All these experimental methods are able to trace only part of the phonon-dispersion relations; therefore, even approximate knowledge of whole dispersion curves allows better classification of the experimental setup, easier selection of the observed modes, and correct building of the pattern of phonon-dispersion relations.

II. METHOD

The calculations of the total energy and Hellmann-Feynman forces are carried on using the Vienna ab initio Simulation Package (VASP). It applies the standard method in which the Kohn-Sham equation is solved self-consistently using the Vanderbilt ultrasoft pseudopotentials and plane-wave basis. The approach is based on the local-density approximation (LDA). We have used the standard ultrasoft pseudopotential provided with VASP. The pseudopotentials for Li, Nb, and O atoms represent the electron configurations \(s^1p^6, s^1p^6d^1f^0\), and \(s^2p^6\), respectively. The cutoff energy of 400 eV is used throughout the calculations. The summation over the Brillouin zone is limited to the \(2\times2\times2\) \(k\)-point mesh, which results in four \(k\) points in the irreducible part of the Brillouin zone.

The LiNbO₃ crystallite is represented by a rhombohedral supercell \(2\times2\times2\), with 80 atoms, having edges of doublet lengths of the primitive rhombohedral unit cell. According to the direct method this size of the supercell provides correct phonon frequencies for the \(\Gamma\) (except for LO infrared active modes), \(L\), \(F\), and \(Z\) special points of the rhombohedral Brillouin zone.

The calculations start from building a \(2\times2\times2\) supercell. All atom positions are generated from nonequivalent positions of three atoms: Li, Nb, and O. Relaxing in VASP the supercell lattice parameters and atomic positions within constraints imposed by the space-group symmetry elements one obtains the optimized structure with the ground-state energy. For this configuration, the maximal magnitude of the Hellmann-Feynman forces does not exceed 0.000 400 eV/Å. Now, the Hellmann-Feynman forces are calculated for displaced atoms, one at a time. We have displaced Li, Nb, and O atoms along \(x\) and \(y\) directions in the plane perpendicular to the threefold axis, and along the threefold axis \(z\), by amplitude of 0.03 Å. To diminish systematic errors the same atoms were displaced to negative directions and the Hellmann-Feynman forces were averaged. Each displaced configuration generates \(3\times80=240\) components of Hellmann-Feynman forces. All nine displacements have been collected into a single file with 2160 data and used, with the help of the tools described in Ref. 24, to derive the force constants. In this way one establishes the symmetry of the force constants, makes the list of the independent parameters of so called cumulant force constants finds them from fitting to the collected Hellmann-Feynman forces by singular value decomposition method, constructs the dynamical matrix and finds phonon frequencies.

The range of interaction represented by the derived cumulant force constants is limited to the distance from the central atom of the supercell to any atom within the supercell including supercell surfaces. The force constants of the ferroelectric and paraelectric phases depend on 735 and 431 independent parameters, respectively. The magnitude of the derived force constant elements generally diminishes with the distance between related atoms. Of course, the largest ones are the on-site force constants (zero distance). At about 5.88 Å, which is the lateral distance from the central atom to the supercell surface, the largest force constants are 20, 50, and 20 times smaller than the corresponding on-site ones, respectively for Li, Nb, and O ions. Unfortunately, this decrease is perhaps still not sufficient to derive precisely phonon frequencies at all wave vectors. At the longest available distance of 13.7 Å, along the \(z\) axis of the supercell, the force constants drop down by factor of 100, 200, and 200 times, respectively.

In many other crystals, the on-site force constants of different atoms are of the same order of magnitude. In LiNbO₃ we find an unusual behavior that the on-site force constants of niobium and oxygen ions are almost ten times larger than the same force constants of lithium. Moreover, all force constants involving lithium are three to five times smaller than those between niobium and oxygen. This observation confirms that lithium is weakly bounded in this crystal lattice.

From the force constants the dynamical matrix is built and the phonon-dispersion relations and phonon density of spectra are derived. It proves that our calculated acoustic dispersion curves diverge from the \(\omega = 0\) value at \(\Gamma\) point by about 0.5 THz. Therefore, we have imposed on the force constants the translation-rotation invariances to cause the acoustic modes to begin at \(\omega = 0\).

III. RESULTS

A. Ferroelectric phase

The ferroelectric phase of LiNbO₃ belongs to the rhombohedral space group \(R\bar{3}c\) \((C\bar{6}3m)\). We have found the lattice constants of the optimized structure (in hexagonal setting) to
be $a_H = 5.0862 \text{ Å}$ and $c_H = 13.7238 \text{ Å}$. The basic lattice vectors in the hexagonal setting are $a = (4.4047, -2.5431, 0.0) \text{ Å}$, $b = (0.0, 0.5086, 0.0) \text{ Å}$, and $c = (0.0, 0.0, 13.7238) \text{ Å}$. The experimental data of $a_H = 5.1483 \text{ Å}$ and $c_H = 13.8631 \text{ Å}$ deviate by 1.2 and 1.0%, respectively. The optimized atomic positions, given in fractional coordinates, are Li (0.0, 0.0, 0.5350), Nb (0.0, 0.0, 0.2500), and O (0.0150, 0.3731, 0.4818). These values are very close to the experimental position of Ref. 1, which in our setting are Li (0.0, 0.0, 0.533), Nb (0.0, 0.0, 0.250), and O (0.014, 0.382, 0.484). The Li and O atoms are displaced with respect to the configuration of the paraelectric phase (see below). The lithium atoms are shifted along the threefold axis by 0.480 Å, while oxygen atoms move approximately in the opposite direction by 0.259 Å. These quantities agree with the minima of potential energy surface of LiNbO$_3$ calculated in Ref. 7 by the linearized augmented plane-wave method, and with the structure optimization made by the full-potential linearized augmented plane-wave method in Ref. 8.

The phonons at the $\Gamma$ point can be classified by the irreducible representation of the point group $C_{3v}$. The group theory predicts the following symmetries of the modes: $4A_1 + 5A_2 + 9E$. The $A_1$ and $E$ modes are Raman and infrared active, while $A_2$ are silent. Using our polarization vectors we have identified the symmetry of all modes at the $\Gamma$ point. The phonon-dispersion curves related with the $E$ modes remain doubly degenerate along the $\Gamma$-Z direction. A number of Raman, infrared absorption and inelastic neutron-scattering measurement provide the mode frequencies. The phonon frequencies calculated and measured at the $\Gamma$ point are given in Table I, and they correspond to the transverse-optic modes of $A_1^T$ and $E^T$ symmetry and $A_2$ symmetry. The $A_1^T$ denotes a mode on the phonon branch pointing to $\Gamma$ from the $xy$ basal hexagonal plane. The same phonon branch pointing to $\Gamma$ from the $z$-axis direction gives another frequency of the longitudinal $A_1^L$ mode. This is in contrary to $E$ modes for which the phonon branch of $E^T$ component points to $\Gamma$ from the $z$ direction, and the $E^L$ component, with usually different frequency, is described in the $xy$ basal hexagonal plane. The symmetries of the $A_1^T$ modes are identified experimentally and that simplifies the comparison of the measured and calculated frequencies. The $A_2$ modes are not seen in Raman and infrared absorption, but are partly detected by inelastic neutron scattering.

Since the LiNbO$_3$ is an ionic crystal, the macroscopic electric field splits the infrared active modes $A_1$ and $E$ to transverse $A_1^T$, $E^T$ and longitudinal $A_1^L$, $E^L$ components. Generally, the $ab\initio$ methods provide means to calculate the LO/TO splitting, but in practice the size of the unit cell should be small. The ten-atom unit cell of LiNbO$_3$ is too large for this treatment. Therefore, we have decided to foresee these splitting in the following semiempirical way. We add the nonanalytical term to the dynamical matrix.

### Table I. Comparison of the mode frequencies at the $\Gamma$ point for the ferroelectric and paraelectric phases, together with the corresponding irreducible representations (IR). The infrared-active modes $A_1$ and $E$ correspond to the transverse $A_1^T$ and $E^T$ frequencies. Frequencies are in THz. Imaginary frequencies appear as negative values.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ferro Raman $^a$</th>
<th>Raman $^b$</th>
<th>Neutrons $^d$</th>
<th>linear augmented-plane-wave method (LAPW) $^e$</th>
<th>Para Raman $^b$</th>
<th>IR Neutrons $^d$</th>
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</thead>
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<tr>
<td>1.</td>
<td>4.71</td>
<td>4.56</td>
<td>4.55</td>
<td>$E_u$</td>
<td>4.32</td>
<td>2.32</td>
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<td>7.30</td>
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<td>4.57</td>
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</tr>
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<td>$A_{1g}$</td>
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<td>$E_g$</td>
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<td>$E_u$</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td>$E_u$</td>
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<td>13.65</td>
<td>13.19</td>
<td>$A_{1u}$</td>
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<tr>
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<td>17.32</td>
<td></td>
<td>$E_g$</td>
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<td></td>
</tr>
<tr>
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<tr>
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<td>$E_g$</td>
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<td></td>
</tr>
<tr>
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<td>26.47</td>
<td>27.34</td>
<td>$A_{2g}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 6.

$^b$Reference 32.

$^c$Reference 30.

$^d$Reference 5.

$^e$Reference 8.
\[ D_{\alpha,\beta}(k;\mu \nu) = D_{\alpha,\beta}^{(o)}(k;\mu \nu) + \frac{4 \pi e^2}{V \epsilon_0 M_{\alpha} M_{\nu}} \times \left| k \right|^2 \exp\left[-2 \pi i g \cdot (r(\mu) - r(\nu))\right] \times \exp\left[ -\pi i \left( \frac{k_x^2}{\rho_x} + \frac{k_y^2}{\rho_y} + \frac{k_z^2}{\rho_z} \right) \right], \]

where \( \mathbf{k} \) is the wave vector within a Brillouin zone with a center at the reciprocal-lattice vector \( \mathbf{g} \). \( V \) stays for the volume of the primitive unit cell, \( M_{\alpha} \), \( \rho_{\alpha} \) are atomic masses and positions, \( D_{\alpha,\beta}^{(o)}(k;\mu \nu) \) is the approximate dynamical matrix derived with the direct method from the Hellmann-Feynman forces. The \( \mathbf{Z}^*(\mu) \) are the tensors of the Born effective charges and \( \epsilon_0 \) is the electronic part of the dielectric constant. Here, \( \rho_{\alpha} = \rho \mathcal{K}_{\alpha} \), and \( \mathcal{K}_{\alpha} \) is the wave-vector distance from the Brillouin-zone center to the Brillouin-zone surface along the x, y, and z directions of the Cartesian coordinate system. The \( \rho \) is a free parameter which suppresses the influence of the second term of Eq. (1), once \( \mathbf{k} \) moves away from \( k=0 \). We have chosen \( \rho = 1.0 \), and then the nonanalytical term vanishes close to zone boundary.

The Raman measurements\(^{27,28,30–32,34,35}\) show that four \( A_1 \) frequencies increase by 7.4, 21, 30, and 38 \%, respectively, when going from transverse \( A_1^T \) to the longitudinal \( A_1^L \) modes. We can reproduce these shifts, when replacing the effective charge tensors by formal point charges \( Z_{\alpha,\beta}^*(\text{Li}) = 1.0 \delta_{\alpha,\beta} \). \( Z_{\alpha,\beta}^*(\text{Nb}) = 5.0 \delta_{\alpha,\beta} \), \( Z_{\alpha,\beta}^*(\text{O}) = -2.0 \delta_{\alpha,\beta} \), and assuming the dielectric constant to be equal to \( \epsilon_0 = 2.0 \). Note that the splitted frequencies depend generally on the ratio \( Z^*/\epsilon_0 \).

The phonon-dispersion relations have been calculated along several directions of the reciprocal space, and are displayed in Fig. 1. In terms of the wave numbers of the rhombohedral reciprocal lattice the coordinates of the special points are \( x(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) (a point in \( xy \) basal plane), \( \Gamma(0,0,0), Z(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), F(1, \frac{1}{2}, \frac{1}{2}), L(\frac{1}{2}, 0,0), \) and \( \Gamma(0,0,0) \). The line from \( F \) to \( L \) is parallel to the threefold axis of the crystal. According to the direct method the \( \Gamma, Z, F, \) and \( L \) phonon frequencies are correct, while the frequencies of modes between them are a result of an interpolation performed with the theory of lattice dynamics, which involves the symmetry of the crystal. The phonon-dispersion curves of Fig. 1 have been calculated under the assumption of point effective charges. Table I shows that the calculated and measured mode frequencies agree very well. The longitudinal-mode frequencies have been collected in Table II and compared with Raman measurements. The general agreement is quite good.

Part of the phonon-dispersion relations, together with labels indicating the symmetry of the modes, are shown in Fig. 2. The left part represents the \( x-\Gamma \) direction in the basal plane, while the right part corresponds to the \( \Gamma-Z \) direction. As is seen from Fig. 2, the phonons of symmetry \( A_1 \) split to the \( A_1^T \) and \( A_1^L \) modes. Phonons of \( E \) symmetry remain doubly degenerate along the \( \Gamma-Z \) axis, but split to \( E^T \) and \( E^L \) in

![FIG. 1. Phonon-dispersion relations of the ferroelectric phase of LiNbO\(_3\) calculated in local-density approximation with the ultrasoft pseudopotential, plane-wave basis, and formal point effective charges. The wave-vector directions are given in the Cartesian coordinate system \( k=(k_x, k_y, k_z) = \xi z, +\xi z, +\xi z, \) related to the longitudinal mode frequencies agree very well. The longitudinal-mode frequencies have been calculated under the assumption that the effective charges are replaced by formal charges, \( Z(\text{Li}) = 1.0, Z(\text{Nb}) = 5.0, \) and \( Z(\text{O}) = -2.0, \) and that the dielectric constant is equal to \( \epsilon_0 = 2.0 \). Frequencies are in THz.

<table>
<thead>
<tr>
<th>No.</th>
<th>IR</th>
<th>Ours</th>
<th>Raman (^a)</th>
<th>Raman (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( E^L )</td>
<td>6.11</td>
<td>5.82</td>
<td>5.94</td>
</tr>
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<td>2.</td>
<td>( E^L )</td>
<td>6.49</td>
<td>7.20</td>
<td>7.28</td>
</tr>
<tr>
<td>4.</td>
<td>( A_1^T )</td>
<td>9.27</td>
<td>8.18</td>
<td>8.24</td>
</tr>
<tr>
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<td>( E^L )</td>
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<td>( A_1^T )</td>
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<td>( A_1^T )</td>
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<td>( A_1^L )</td>
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<td>( E^L )</td>
<td>25.65</td>
<td>26.32</td>
<td>26.38</td>
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</table>

\(^a\)Reference 32. 
\(^b\)Reference 30.
in the high-frequency interval. This effect results from small values of the force constants which involve lithium atoms. The high-frequency region is occupied by the oxygen vibrations. The niobium atoms vibrate at low frequencies as is normal for its large atomic mass.

B. Paraelectric phase

The high-temperature paraelectric phase of LiNbO$_3$ has a rhombohedral symmetry of $Rar{3}c$ ($D_{3d}^5$) space group with $Z = 2$, and it is stable above 1480 K. We have found the optimized lattice constants in hexagonal setting to be $a_H = 5.0970$ and $c_H = 13.7081$ Å. The optimized atomic positions reads Li (0.0, 0.0, 0.5), Nb (0.0, 0.0, 0.25), and O (0.0, 0.3698, 0.5). In this phase the positions of Li and Nb atoms are fixed by symmetry. Note that the lithium and oxygen atoms reside in the same $xy$ plane.

The phonon-dispersion curves of the paraelectric phase are shown in Fig. 4. They have been calculated along several symmetry directions, the same as those used in Fig. 1. The curves of Fig. 4 are calculated with the nonanalytical term in the dynamical matrix included [Eq. (1)] and with the same effective charges as the ferroelectric phase. This approach takes into account the macroscopic electric field. At the $\Gamma$ point the modes are classified as: $A_{1g} + 3A_{2g} + 4E_g + 2A_{1u} + 3A_{2u} + 5E_u$, where $A_{1g}$, $E_g$ and $A_{2u}$, $E_u$ are Raman and infrared active, respectively. The mode frequencies and their symmetries are listed in Table I, but unfortunately there are no experimental data to compare with. The symmetry of the modes is labeled in Fig. 5. The immediate result of the macroscopic electric field is that the $A_{2u}$ and $E_u$ modes split into transverse $A_{1u}^T$, $E_u^T$ and longitudinal $A_{2u}^L$, $E_u^L$ components, respectively, similarly to the ferroelectric phase.

Figures 4 and 5 show that modes $A_{2u}$ and $A_{2g}$ are soft (imaginary). The minimum value of the $A_{1u}^T$ mode is reached at the $\Gamma$ point. This is the mode responsible for the paraelectric $\Rightarrow$ ferroelectric phase transition. It also bears the correct symmetry reduction $Rar{3}c \rightarrow (\Gamma', A_{2u}) \rightarrow R\bar{3}c$. The modes $A_{2u}$ and $A_{2g}$ are soft everywhere in the reciprocal space. Therefore, close to the phase-transition temperature a remarkable diffuse scattering could be expected in the whole Brillouin zone. The eigenvector of the soft-mode $A_{2u}$ is

$$
\begin{align*}
\text{Li}(0.0,0.0,0.537), & \quad \text{Li}(0.0,0.0,0.537), \\
\text{Nb}(0.0,0.0,0.153), & \quad \text{Nb}(0.0,0.0,0.153), \\
\text{O}(0.070,0.0,-0.241), & \quad \text{O}(-0.030,0.061,-0.241), \\
\text{O}(-0.035,-0.061,-0.241), & \quad \text{O}(0.070,0.0,-0.241), \\
\text{O}(-0.030,0.061,-0.241), & \quad \text{O}(-0.035,-0.061,-0.241).
\end{align*}
$$

The atomic displacement is proportional to the polarization vector component, and reversibly proportional to the square of the atomic mass. Taking into account a large mass of niobium, this eigenvector leads to preferential displacement of lithium and oxygen atoms along the threefold axis.

The existence of the soft mode means that the configuration of the $Rar{3}c$ space group corresponds to the saddle point of the energy surface. The stability of the paraelectric phase
is retained by the anharmonic terms. The $R3\bar{c}$ symmetry is preserved due to the dynamical averaging effect of disorder of combined motion of lithium and oxygen between the two equivalent local minima.

The active soft mode $A_{2u}$ is infrared active, hence, it splits to transverse and longitudinal components. The transverse component, located at a lower frequency, drives the phase transition. According to the kinetic theory of phase transitions, modes of small wave vectors, $k \to 0$, create critical fluctuations and/or initiate the nucleation process. In LiNbO$_3$ these critical modes are limited to phonon waves propagating in the $xy$ plane. Consequently, the arising domain pattern of the ferroelectric phase should consist of domain walls being parallel to the threefold crystal axis. The electrostatic force microscope observation of the microstructure$^{36}$ confirms that the LiNbO$_3$ crystal consists of 180° domains of submicron size with the domain walls parallel to the threefold crystal axis.

In the paraelectric configuration we find that for lithium the $zz$ component of the on-site force constant is negative, $F_{zz}(\text{Li, Li}) = -4.62 \text{ N/m}$. The remaining on-site force constants of Li and nonzero elements of Nb and O ions are positive. This means that all local potentials have single-well form, except the $z$ displacement for lithium for which the local potential becomes a double-minimum curve. The curvature of the barrier of the double-minimum potential is given by $\Phi_{zz}(\text{Li, Li})$, but the position of minima would require finding the higher-order anharmonic contributions. This finding of the double-minimum potential confirms that the paraelectric $\Rightarrow$ ferroelectric phase transition is of the order-disorder type.

IV. CONCLUSIONS

Using the first-principles approach within the LDA, applying the ultrasoft pseudopotential and plane-wave basis,
we have performed the optimization of the ground-state configurations of ferroelectric and paraelectric phases of LiNbO$_3$. Constructing the 2×2×2 rhombohedral supercell with nine different displacements, one displacement at a time, we have calculated the Hellmann-Feynman forces, and hence the phonon frequencies at special points and the extrapolated phonon-dispersion curves. For the ferroelectric phase the phonon frequencies were directly compared with the measured Raman and infrared modes, and the agreement was found quite good. Unfortunately, the ab initio calculations are based on the supercell which by definition is subject to periodic boundary conditions; therefore, a direct derivation of LO/TO splitting caused by the macroscopic electric field, which breaks the crystal symmetry, is not possible. Instead, we have applied the formal ionic point charges, adjusted the dielectric constant $\varepsilon_\infty$ to the experimental longitudinal-mode frequencies, and calculated the phonon-dispersion relations which include the LO/TO splitting.

The ab initio calculations give the correct changes of the structures from paraelectric to ferroelectric phases. The soft mode $A_{2u}$, found in the paraelectric phase, correctly describes the paraelectric ⇔ ferroelectric phase transition. Moreover, since our soft mode has a symmetry of infrared active representation, the LO/TO splitting also applies to it. As a result the transverse TO component decides about the symmetry changes of the phase transition. The value of the frequency of the $A_{2u}^T$ soft mode does not depend on the effective charges. The $A_{2u}$ mode causes the domain structure in the ferroelectric phase to prefer to grow domain walls oriented parallel to the threefold symmetry axis. We would like to point out that the soft mode and double-minimum potential for lithium are consistent with the order-disorder character of the phase transition. We have found that lithium ions are weakly bound in the crystal lattice. Therefore, they do not vibrate at the optical high-frequency modes.

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