Structure Optimization and Frozen Phonons in LiNbO$_3$

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Abstract

The equilibrium ground-state structure of LiNbO$_3$ in the paraelectric and ferroelectric phases is fully optimized in a first-principles calculation using the full-potential linearized augmented plane wave method. The equilibrium volume, $c/a$ ratio and all (four, in the ferroelectric phase) internal parameters are found to be in good agreement with the experimental data. Frozen phonon calculations are performed for TO-Γ phonons corresponding to the $A_1$ and $A_2$ irreducible representations of the $R3c$ space group in the ferroelectric phase. The comparison with available experimental frequencies for the $A_1$ modes is satisfactory (including the $^6$Li isotope effect), and the displacement patterns are unambiguously attributed. For the (Raman inactive) $A_2$ modes, phonon frequencies and eigenvectors are predicted.

Key words: Total energy; first-principle calculations; ferroelectric phase transitions

Introduction

Due to its various applications in non-linear optics and electro-optics, the ferroelectric material LiNbO$_3$ is being extensively studied over decades. Its ferroelectric transition temperature of 1480 K is among the highest known to date. The mechanism of the structural phase transition from paraelectric to ferroelectric phase is still an open question. Temperature dependence measurements of Raman scattering [1] and far infrared reflectivity in LiNbO$_3$ [2] suggest the displacive type phase transition. In contradiction with this picture, the absence of the $A_1$ mode softening reported in certain papers [3] is an indication towards an order-disorder type phase transition.

The study of the electronic structure and lattice dynamics from first principles was so far hindered by the relative complexity of the structure. In the ferroelectric phase, LiNbO$_3$ has 10 atoms in the unit cell; the space group is $R3c$. The atomic arrangement is given by oxygen octahedra stapled along
Fig. 1. Hexagonal unit cell of ferroelectric LiNbO$_3$ (thin lines) which includes three rhombohedral cells (thick lines). The atoms which belong to a selected rhombohedral cell are painted dark. Four internal crystal-structure parameters are shown.

Inbar and Cohen [5] calculated from first principles the total energy profile associated with the ferroelectric instability. They have shown that a broadly spread assumption about the instability being primarily related to the Li displacement out of oxygen layers was not justified. In addition to the Li displacement, the shift (with respect to Nb) and distortion of the oxygen octahedra play quite a crucial role and lower the total energy much more efficiently. These results have been essentially reproduced by Yu and Park [6]. In these previous studies, the ferroelectric distortion has been simulated by an uniform scaling of the crystal structure along the linear path between experimentally determined paraelectric and ferroelectric structures. In the present work, we fully optimize the structure of paraelectric and ferroelectric phases from first principles, adjusting the values of all internal parameters constrained only by the crystal symmetry. In the course of that, the energetics of individual atomic displacements can be analyzed and applied for the zone-center lattice dynamics simulation within the frozen-phonon scheme. With such simulation so far missing, the attribution of different experimentally measured zone-center
Table 1

| phase  | Nb  | Li  | O   |
|--------|-----|-----|-----|
| para   | 0   | 0   | 0   | 0   |
|        | ½   | 0.49| ½   | ¼   |
| ferro  | 0   | 0   | 0   | 0   |
|        | 0.283 | 0.049 | 0.346 | 0.067 |
|        | 0.279 | 0.041 | 0.344 | 0.066 |

*exp.: Ref. [4]; *calculation.

phonon modes (with respect to atomic displacement patterns) was problematic. The extraction of normal vibration coordinates in LiNbO$_3$, done in the present work, may be useful for the development of reliable lattice dynamics models in this system, including, e.g., the effects of doping.

Method

The calculations were performed using the full potential Linear Augmented Plane Wave method (see, e.g., [7]) with the addition of local orbital basis functions [8] as implemented in WIEN97 FLAPW code [9]. The exchange-correlation was treated within the local density approximation (LDA), using the parametrization by Perdew and Wang [10]. The core states were treated fully relativistically, and the semicore and valence states were computed in a scalar relativistic approximation. The structure optimization in the para- and ferroelectric phase and the frozen phonon calculations were performed using a $4 \times 4 \times 4$ special $k$-points mesh which generated 20 $k$ points in the irreducible Brillouin zone. We tested the convergence in the $k$-space integration using a $6 \times 6 \times 6$ $k$-mesh (28 irreducible $k$-points) and found the difference in the total energy trends, as compared with the results on a sparser $k$-mesh, negligible for the analysis of lattice dynamics and structure optimization. The muffin tin radii chosen were 1.9 a.u. for Nb and 1.6 a.u. for Li and O, close to the values used by Inbar and Cohen [5] in their FLAPW calculation. The convergency of the results with respect to the number of augmented plane waves used was also controlled; we used, on the average, 980 basis functions for each $k$-point.

Ground-state structure

The simultaneous optimization of the volume and the $c/a$ ratio for the paraelectric phase of LiNbO$_3$ resulted in the values of lattice parameters (in the hexagonal setting) $a_H=5.1378$ Å and $c=13.4987$ Å. As compared to the ex-
perimental data ($a_H=5.1483$ Å and $c=13.8631$ Å, see Ref. [4]), that corresponds to a volume underestimated by $\sim 3\%$ and a $c/a$ ratio deviating by $\sim 2\%$ from experiment, i.e. quite good agreement by the standards of first-principles calculations based on the density functional theory. In the subsequent optimization of atomic positions, we kept the lattice parameters fixed. The fully optimized paraelectric structure was found energetically instable with respect to the symmetry-lowering atom displacements. The paraelectric phase has one internal coordinate whereas the ferroelectric phase has four. These four parameters are actually related to the four symmetry coordinates which can be introduced to describe the $A_1$-TO phonons. Therefore, in the course of accumulating total energy data for our frozen phonon calculations (see next section), we were able simultaneously to optimize the ferroelectric ground-state structure to quite good accuracy. Moreover, the calculated forces have been used in the process of structure optimization. The experimental and calculated atomic positions (in the hexagonal coordinates, following [4]) for both paraelectric and ferroelectric phases are given in Table 1. The agreement between theory and experiment in all internal parameters is quite good, indicating a presumably nonproblematic applicability of LDA for the study of lattice dynamics in LiNbO$_3$. The energy difference we found between paraelectric and ferroelectric phases is essentially the same as determined by Inbar and Cohen [5].

**Frozen phonons**

The $\Gamma$-TO frequencies in the ferroelectric structure are split by symmetry into four $A_1$, five $A_2$ and nine $E$ modes. The frequencies of $A_1$ modes have been determined in a number of Raman spectroscopy measurements, with a satisfactory agreement of results [11–13]. The displacement patterns corresponding to different modes have not yet been unambiguously attributed, to our best knowledge. Some information to that point has been attained, however, based on a study of the isotope effect in Ref. [11], that is addressed below. The $A_2$ modes are both Raman and infrared silent. Our calculation data are therefore predictive with respect to these vibrations. The nine $E$ modes are the source of the largest controversy in the experimental study of vibrations in LiNbO$_3$. They are attributed differently in a number of publications. The discussion on this controversy can be found, e.g., in Ref. [12]. The first-principles description of $E$ modes remains beyond the scope of the present study.

The calculation of the force constants to be used in the soft-phonon calculation typically involves a second-order fit over a number of data points, corresponding to different displacements within a given symmetry constraint. For $A_1$ modes, we had to consider more than ninety different geometries in order to obtain a satisfactory total-energy fit in a sense that the results remain rela-
Table 2
Calculated and measured frequencies (cm$^{-1}$) of four $A_1$-TO modes in LiNbO$_3$

|       | calc. $^7$LiNbO$_3$ | exp. $^7$LiNbO$_3$ | calc. $^6$LiNbO$_3$ | exp. $^6$LiNbO$_3$ |
|-------|---------------------|---------------------|---------------------|---------------------|
| TO$_1$| 208                 | 256$^a$; 252$^b$; 251$^c$ | 208                 | 256$^a$             |
| TO$_2$| 280                 | 275$^a$; 275$^b$; 273$^c$ | 299                 | 289$^a$             |
| TO$_3$| 344                 | 332$^a$; 332$^b$; 331$^c$ | 344                 |                     |
| TO$_4$| 583                 | 637$^a$; 632$^b$, 631$^c$ | 583                 | 637$^a$             |

$^a$Ref. [11]; $^b$Ref. [12]; $^c$Ref. [13];

Table 3
Calculated eigenvectors of four $A_1$ modes

| Mode | Nb(2×) | Li(2×) | O     | O     | O     | O     | O     | O     |
|------|--------|--------|-------|-------|-------|-------|-------|-------|
|      | x      | 0      | 0     | 0.07  | -0.04 | -0.03 | 0.07  | -0.03 | -0.04 |
| TO$_1$| y      | 0      | 0     | 0.01  | 0.06  | -0.07 | -0.01 | 0.07  | -0.06 |
|      | z      | 0.39   | 0.09  | -0.33 | -0.33 | -0.33 | -0.33 | -0.33 | -0.33 |
|      | x      | 0      | 0     | -0.01 | 0.01  | 0.00  | -0.01 | 0.00  | 0.01  |
| TO$_2$| y      | 0      | 0     | -0.01 | -0.01 | 0.01  | 0.01  | -0.01 | 0.01  |
|      | z      | 0.18   | -0.68 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
|      | x      | 0      | 0     | -0.14 | -0.27 | 0.40  | -0.14 | 0.40  | -0.27 |
| TO$_3$| y      | 0      | 0     | 0.38  | -0.31 | -0.08 | -0.38 | 0.08  | 0.31  |
|      | z      | 0.02   | 0.00  | -0.01 | -0.01 | -0.01 | -0.01 | -0.01 | -0.01 |
|      | x      | 0      | 0     | -0.38 | 0.31  | 0.07  | -0.38 | 0.07  | 0.31  |
| TO$_4$| y      | 0      | 0     | -0.14 | -0.26 | 0.39  | 0.14  | -0.39 | 0.26  |
|      | z      | 0.06   | 0.04  | -0.06 | -0.06 | -0.06 | -0.06 | -0.06 | -0.06 |

The calculated frequencies of the $A_1$ modes are shown in Table 2 in comparison with the experimental data. The agreement is very good for TO$_2$ and TO$_3$ modes. Taken together with the above mentioned stability of calculated frequencies with respect to improving the total-energy fit, this indicates that these two vibration modes are with high accuracy harmonic. The corresponding eigenvectors are shown in Table 3. (Note that the displacement of both Nb atoms and both Li atoms in the unit cell is identical within the $A_1$ modes.) One can see that TO$_2$ is essentially the $z$-vibration of Li ions with respect to a (relatively rigid) rest of a crystal. Actually this is the only $A_1$ mode with a substantial amount of Li movement. It is clearly seen in the experimentally measured frequencies of $^6$Li-doped LiNbO$_3$ [11] that only the TO$_2$ mode exhibits an isotope effect, increasing its frequency by 14 cm$^{-1}$ (see Table 2). Our calculation of vibration frequencies with the decreased mass of Li ion as well indicates that only the TO$_2$ mode is affected, its frequency being increased by 19 cm$^{-1}$. 

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The displacement pattern in the TO$_1$ mode has some resemblance to that in the soft mode of cubic perovskites, like e.g. KNbO$_3$; essentially, Nb vibrates in antiphase with the oxygen sublattice along the trigonal axis, leaving Li relatively static. As follows from the frozen-phonon treatment in cubic KNbO$_3$ (see, e.g., Ref. [14,15]), this mode is instable against off-center displacements and hence exhibits in the harmonic approximation an imaginary frequency. But even when stabilized by an appropriate symmetry lowering, as was calculated for example for tetragonal [15] or orthorhombic [16] KNbO$_3$, the mode in question roughly maintains its original displacement pattern. In LiNbO$_3$, the TO$_1$ is the ultimately stabilized soft mode of the paraelectric phase. We analyzed the total energy as function of atomic displacements consistent with the TO$_1$ eigenvector and found noticeable deviations from the parabolic behaviour. Because of this, the calculated harmonic frequency strongly differs from the experimental numbers.

Another example of a strongly anharmonic mode is the TO$_4$ mode. Along with TO$_3$, it is visualized in Fig. 2 in a top view (along the z-axis). The z-displacements are negligible in these two modes, and practically only oxygen ions are participating in them. The difference between these modes is the following: in TO$_3$, the whole oxygen octahedra are tilted as essentially rigid...
For the $A_2$ modes, no experimental information is available by means of Raman nor infrared spectroscopy, so our results are actually a theory prediction. We used 127 different geometries to obtain an accurate second-order total energy fit in the 5-dimensional space of symmetry coordinates. Calculated frequencies and eigenvectors are shown in Table 4. Note that in contrast to $A_1$ modes, both Nb and both Li atoms are now moving in antiphase. Apart from the softest mode which includes essentially the Nb vs. Li antiphase $z$-movement, and the hardest one, which is again a distortion of oxygen octahedra (but now including the $z$-stretching as well), three intermediate modes are have contributions from $z$- as well as $xy$-displacements of all three atomic constituents.

Summarizing, we performed from first principles in a LDA-based calculation the optimization of the ground structure of ferroelectric LiNbO$_3$ and calculated the frequencies and eigenvectors of $A_1$ and $A_2$ $\Gamma$-TO modes. Large anharmonic contributions were found for two of four $A_1$ modes. These results may present a basis for a subsequent treatment of lattice dynamics models in related systems and/or of anharmonic effects. The study of $E$ modes is now in progress.

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**Table 4**

Calculated frequencies and eigenvectors of five $A_2$ modes

| $\omega$ (cm$^{-1}$) | Nb(+/−) | Li(+/−) | O | O | O | O | O | O |
|----------------------|---------|---------|---|---|---|---|---|---|
| x                    | 0       | 0       | −0.03 | 0.02 | 0.01 | 0.03 | −0.01 | −0.02 |
| y                    | 0       | 0       | 0.00  | −0.03 | 0.03 | 0.00 | 0.03 | −0.03 |
| z                    | 0.24    | −0.66   | 0.05  | 0.05 | 0.05 | −0.05 | −0.05 | −0.05 |
| x                    | 0       | 0       | −0.08 | 0.24 | −0.16 | 0.08 | 0.16 | −0.24 |
| y                    | 0       | 0       | −0.23 | 0.05 | 0.18 | −0.23 | 0.18 | 0.05 |
| z                    | −0.51   | −0.14   | 0.12  | 0.12 | 0.12 | −0.12 | −0.12 | −0.12 |
| x                    | 0       | 0       | −0.23 | −0.04 | 0.26 | 0.23 | −0.26 | 0.04 |
| y                    | 0       | 0       | 0.17  | −0.28 | 0.11 | 0.17 | 0.11 | −0.28 |
| z                    | 0.03    | 0.11    | 0.28  | 0.28 | 0.28 | −0.28 | −0.28 | −0.28 |
| x                    | 0       | 0       | 0.01  | −0.25 | 0.24 | −0.01 | −0.24 | 0.25 |
| y                    | 0       | 0       | 0.28  | −0.13 | −0.15 | 0.28 | −0.15 | −0.13 |
| z                    | −0.42   | −0.19   | −0.12 | −0.12 | −0.12 | 0.12 | 0.12 | 0.12 |
| x                    | 0       | 0       | −0.33 | 0.21 | 0.12 | 0.33 | −0.12 | −0.21 |
| y                    | 0       | 0       | −0.06 | −0.26 | 0.31 | −0.06 | 0.31 | −0.26 |
| z                    | 0.06    | 0.02    | −0.23 | −0.23 | −0.23 | 0.23 | 0.23 | 0.23 |
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