Localised Phonon Modes at LiNbO$_3$ (0001) Surfaces

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The vibrational properties of the LiNbO$_3$ (0001) surfaces have been investigated both from first principles and with Raman spectroscopy measurements. Firstly, the phonon modes of bulk and of the (0001) surface are calculated by means of the density functional theory. Our calculations reveal the existence of localised vibrational modes both at the positive and at the negative surface. The surface vibrations are found at energies above and within the bulk bands. Phonon modes localised at the positive and at the negative surface differ substantially. In a second step, the Raman spectra of LiNbO$_3$ bulk and of the two surfaces have been measured. Raman spectroscopy is shown to be sensitive to differences between bulk and surface and between positive and negative surface. The calculated and measured frequencies are in agreement within the error of the method.

Introduction

The LiNbO$_3$ (0001) surface, commonly known as Z-cut, is of particular technological relevance. Indeed, it plays a key role in many emerging applications such as substrate-assisted self-assembly of nanostructure [1] and periodically poled structures [2]. Furthermore, LiNbO$_3$ (0001) (or simply LN(0001)) is attracting attention as a substrate for the GaN growth, either for the realization of monolithic optoelectronic amplifiers [3, 4] or as an alternative substrate (to α-Al$_2$O$_3$) for the quasi lattice-matched growth of GaN [5–8]. The key advantage of this polar surface (the (0001) plane is perpendicular to the spontaneous polarization of the material) is the possibility to reverse the polarization by applying an electric field. Thus, with appropriate ferroelectric domain engineering, it is possible to switch the surface properties. However, to have control over the ferroelectric domains, a deep knowledge of the surface and of the occurring stabilization mechanisms is necessary. The LN(0001) atomic structure has been investigated with the density functional theory (DFT) [9, 10] and by co-axial impact collision ion scattering spectroscopy (CAICISS) [11]. Low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED) have revealed the absence of any other surface periodicity than the 1 × 1 [12]. The LN(0001) ionization energy has been determined by UV-photoelectron emission microscopy (PEEM) [13] and its thermal behaviour by Auger electron spectroscopy and mass spectrometry [14]. In this work we investigate the LN(0001) vibrational properties. The study of surface phonons provides valuable insight into the surface structure and other
properties specific to the surface region, which often differ from bulk. Furthermore, the knowledge of the surface modes frequency and dispersion can be used to gain information about surface relaxation, presence of surface defects and, most of all, surface adsorbates. Driven by the increasing interest about quantum dot systems, where the electron-phonon coupling may affect the electrical and optical properties of devices [15], the investigation of the surface phonons has gained a lot of attention. Investigation methods like electron energy loss spectroscopy [16], helium atom scattering [17] Raman and surface-enhanced Raman spectroscopy (SERS) [18] have been developed or improved. Besides several experimental techniques, there are different \textit{ab initio} theoretical approaches to the investigation of surface dynamics. Among the most successful approaches, we mention the (repeated) slab method in the framework of the DFT [19, 20]. In this approach, particularly suited for the investigation of broad surface phonon phenomena, a supercell (or slab) is created containing relatively thin films of 5–50 atomic layers embedded in a vacuum region. The periodic arrangement of the slabs recovers an artificial 3D periodicity, allowing for the simulation of a semi infinite solid with parallel surfaces. In our investigation of the vibrational modes of the LN(0001) we combine a theoretical study via supercell approach with Raman measurements. This allows to predict, measure, and classify the surface modes of the investigated system. In a first step eigenvectors and eigenvalues of the surface phonon modes are calculated from first principles. Surface localised vibrational modes have been found both at the positive and at the negative LN(0001) face, however, they are qualitatively different. In a second step we demonstrate that Raman spectroscopy can distinguish between LN bulk and surface and univocally identify the positive and negative LN(0001) surface. Thereby we concentrate on the detection of the different \(A\) modes revealed by the calculations. The calculated and measured frequencies are in agreement within the error of the method. The manuscript is organized as follows: in Sec. II we briefly describe the experimental setup for the measurement of the Raman spectra, illustrate the slab approach for the calculation of the surface dynamics and give the computational details of our simulation. In Sec. III we show the calculated frequencies for bulk LN and LN(0001) and classify the modes on the basis of their eigenvectors. A few \(A\) modes are selected and shown in detail. Raman spectra for LN bulk and for differently polarised LN(0001) surfaces are shown and discussed. Finally, in Sec. IV we summarize the main results of our investigation.

**Methods**

The detailed description of the experimental procedure will be discussed in future publications, in this work we limit ourselves to a brief description of the experimental setup for the observation of surface phonon modes in the \(\mu\)-Raman regime. Stoichiometric Z-cut lithium niobate (Roditi Int. Corp. Ltd.) fabricated as single-domain crystal was utilized. \(\mu\)-Raman measurements were performed by the special confocal setup illustrated in Fig. 1. Thereby excitation was carried out under grazing incidence (532 nm, DPSSL). In two excitation paths different objectives were implemented, leading to sample irradiation under a short and a long focus, whereby one path enables the adjustment of different angles of incidence. The scattered light was solely collimated by the short focus objective (Mitutoyo OBJ Plan Apo SL 100, NA 0.55). For detection a spectrometer (KOSI, Holospec f/1.8i) with adapted CCD-detector (Andor Newton, BI) was applied. Concerning polarization dependent measurements, half-wave plates were utilized for defined incident laser polarization, while an appropriate analyzer implemented in front of the detection unit specifies the polarization of detection light. Excitation was accomplished in X- and Y-direction whereby these are
related to the crystallographic axes (Z parallel to the optical c-axis). For grazing incidence, calculations yield a penetration depth of about 40–45 nm for the adjusted angles.

We have performed DFT calculations within the generalized gradient approximation (GGA) [21] for exchange and correlation in its PW91 formulation [22] as implemented in the Vienna Ab-initio Simulation Package (VASP) [23]. Projector- augmented wave (PAW) potentials [24] with projectors up to $l = 3$ for Nb and $l = 2$ for Li and O as well as a plane wave cut off of 400 eV have been used. The k-space integrations in the electronic structure calculations are performed using shifted Monkhorst-Pack $4 \times 4 \times 1$ meshes [25] equivalent to 24 irreducible points in the two-dimensional Brillouin zone. The dipole corrections described in Ref. [26] and [27] have been used to correct the spurious interactions due to the slab periodic images.

In our work we accepted the LN(0001) surface structure model proposed in Ref. [9] and [10] which we used as basis for the investigation of the vibrational properties. Following this model, which is able to explain the thermal behaviour of LN surfaces and other experimental observations [9, 10], the positive surface is -Nb-O$_3$-Li$_2$ terminated and the negative surface is O-Li- terminated, as shown in Fig. 2. The LN(0001) surfaces are simulated by

![Figure 2. Top view of the positive (a) and negative (b) LN(0001) surfaces. Nb atoms are white, Li atoms are gray, O atoms are red. The surface unit cell is outlined.](image-url)
repeated hexagonal slabs with eight trilayers of stoichiometric LN, termination atoms, and a vacuum region of $\sim 15\AA$. The layers are relaxed to minimize the equilibrium forces to less than 0.02 eV/Å. Frozen-phonon calculations [28] without symmetry constraints have been performed up to a depth of 15 atomic layers within the hexagonal unit cell. Our approach does not include the long-range electric fields that accompany longitudinal phonons. For this reason, we restrict ourselves to the transverse modes.

Surface phonon modes can have very different dispersion. Surface phonon branches can be completely bound within the bulk phonon dispersion or be localised outside these bands. In the first case they are called phonon resonances while in the second case they are referred to as pure surface phonon modes. On the same way surface phonons can be divided into two groups depending on their origin. Indeed, there are surface modes which can only exist in the surface termination, and surface modes which are the counterpart of bulk vibrations in presence of a surface. The latter take place at energies above or below the corresponding bulk values due to contraction or expansion of the surface layer. In the LN(0001) surface occur both types of phonons, however we will concentrate in this work only on strongly surface-localised vibrations.

**Results and Discussion**

Firstly the phonon frequencies of bulk LiNbO$_3$ are measured and calculated. In this way we have both a check of our approach and a reference spectrum. In Fig. 3(a) we show the Raman spectrum detected for bulk LN with the $X(Y,Z)X$ configuration (the Porto notation is used throughout this work). The Raman active $T_O \ A_1$ (at 254, 275, 333 and 633 cm$^{-1}$) and $E$ (at 152, 196, 363, 432, 581 and 693 cm$^{-1}$) phonon modes are visible and in good agreement with previous measurements [29] (and references therein). An LO mode at 881 cm$^{-1}$ is also visible. Within the DFT calculations, the $A_1$ modes are found at 240, 286, 353, and 611 cm$^{-1}$, and the $E$ modes at 147, 216, 382, 420, 577 and 667 cm$^{-1}$. Within deviations of at most 26, but typically about 10 cm$^{-1}$, the calculated frequencies match the experimental findings. The accuracy of our calculations is thus comparable to earlier frozen-phonon calculations [29]. Having found a qualitative agreement concerning the bulk modes, we start to investigate the vibrational properties of the (0001) surface.

The zone centre phonon modes have been calculated within slab of different thickness to test the substrate dependency of the calculated modes. We observe a slight oscillatory behaviour of the mode frequency, which, however, can be considered converged for the slabs with 24 atomic layers plus termination atoms. To quantify the localization of the

![Figure 3. Raman spectra of bulk LiNbO$_3$. Phonon frequencies in cm$^{-1}$ are indicated.](Figure 3)
Table 1
Calculated frequencies (in cm$^{-1}$) of the surface phonons at the centre of the surface Brillouin zone.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Freq.</th>
<th>Mode</th>
<th>Freq.</th>
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<tbody>
<tr>
<td>$A_1$</td>
<td>869</td>
<td>$A_1$</td>
<td>945</td>
</tr>
<tr>
<td>$A_1$</td>
<td>850</td>
<td>$A_1$</td>
<td>786</td>
</tr>
<tr>
<td>$A_2$</td>
<td>506</td>
<td>$A_1$</td>
<td>467</td>
</tr>
<tr>
<td>$A_1$</td>
<td>399</td>
<td>$A_2$</td>
<td>445</td>
</tr>
<tr>
<td>$A_1$</td>
<td>382</td>
<td>$A_1$</td>
<td>364</td>
</tr>
<tr>
<td>$A_1$</td>
<td>312</td>
<td>$A_1$</td>
<td>304</td>
</tr>
<tr>
<td>$A_2$</td>
<td>235</td>
<td>$A_1$</td>
<td>285</td>
</tr>
<tr>
<td>$A_1$</td>
<td>160</td>
<td>$A_2$</td>
<td>125</td>
</tr>
</tbody>
</table>

We consider for each mode the total atomic displacement in the slab. If the contribution to the total displacement of the first four atomic layers is larger than 50%, the mode is considered strongly localised at the surface. At the $\Gamma$ point, the optical phonons can be classified according to the irreducible representations of the space group $R\bar{3}c$ into $A_1$, $A_2$ and $E$ modes. In Tab. 1 we report the calculated frequencies of the surface localised modes. An analysis of the phonon eigenvectors allows to classify them as $A_1$ (if the mode preserves the full crystal symmetry), as $A_2$ (if the inversion symmetry with respect to a mirror plane is preserved) and E modes (on the basis of the degeneracy). As an example we show in Fig. 4 the eigenvectors of an $A_2$ mode of the positive surface (at 506 cm$^{-1}$) and of an $A_2$ mode of the negative surface (at 445 cm$^{-1}$). They are both related to displacements in the Li-sublattice along the z-directions. These modes are Raman active as they change the material polarization.

![Figure 4](image_url)

**Figure 4.** Schematic representation of the atomic displacements of the $A_2$ phonon mode at 506 cm$^{-1}$ of the positive surface (a) and of the $A_1$ phonon mode at 445 cm$^{-1}$ of the negative surface (b).
In order to demonstrate that Raman spectroscopy can be used to univocally identify differently polarised LN surfaces, different spectra have been measured and compared with the calculated frequencies. Thereby we used the $A_1$ modes as a benchmark, as they can be selectively excited in the experiment and because the calculated frequencies of $A_1$ modes of bulk and surface differ substantially. In Fig. 5 we show the Raman spectrum measured at the two surfaces in order to reveal the $A_1$ modes. In the spectra appear several features which cannot be traced back to bulk phonon modes, thus showing at a first sight that a distinction between bulk and surface is possible. An analysis of the spectrum of the negative surface reveals peaks at 117, 347, 375, 468, 774 and 939 cm$^{-1}$ which are predicted by our theoretical model. Further peaks 403, 505, 561, 669, 691, 736 and 903 cm$^{-1}$ in the spectra, but are not predicted by our model. These can be explained by different effects. First of all, even if we carry out the measurement within the $X(Y,Z)X$ orientation, it cannot be excluded that the sample is irradiated with fractions of not purely Y-polarised light, giving rise to mixed states and peaks not corresponding to $A_1$ modes. Furthermore, in our theoretical model we have only considered strongly surface localised vibrations, while our experiment is sensitive to all the vibrations close to the surface.

Concerning the spectrum of the positive surface, we observe that most of the peaks characterizing the spectrum of the negative surface are no more present. This shows that Raman spectroscopy is able to identify univocally differently polarised LN surfaces. As the main goal of our investigation is not the classification of each single peak, but rather the demonstration our approach, we do not discuss each mode of the positive surface. The peaks present in the spectra of both surfaces but not in the bulk have been labelled with $m$. The exhaustive classification of the $A_1$ and $E$ modes of the two surfaces will be the subject of future investigations.

**Conclusion**

The vibrational properties of the LN(0001) surfaces have been investigated by Raman spectroscopy and DFT calculations. Surface localised phonon modes have been revealed with both approaches. The Raman spectroscopy has been shown to be sensitive to the differences between surface and bulk and between positive and negative LN(0001) surface. Calculated and measured surface phonon frequencies are in agreement within the error of the two methods.
Acknowledgment

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