On the microscopic mechanisms behind hyperferroelectricity

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Hyperferroelectrics are observing a growing interest thanks to their unique property to retain a spontaneous polarization even in presence of a depolarizing field, corresponding to zero macroscopic displacement field ($\mathcal{D} = 0$) conditions. Hyperferroelectricity is ascribed to the softening of a polar $\text{LO}$ mode, but the microscopic mechanisms behind this softening are not totally resolved. Here, by means of phonon calculations and force constants analysis, performed in two class of hyperferroelectrics, the ABO$_3$-LiNbO$_3$-type systems and the hexagonal-ABC systems, we unveiled the common features in the dynamical properties of a hyperferroelectric that are leading the $\text{LO}$ instability: negative or vanishing on-site force constant associated to the cation driving the $\text{LO}$ polar mode and a destabilizing cation-anion interactions; both induced by short-range forces. We also predicted a possible enhancement of the hyperferroelectric properties under increasing external positive pressures: the pressure strengthens the destabilizing short-range interactions, inducing a stronger $\text{LO}$ mode instability and the increase of the longitudinal mode effective charges associated to the unstable $\text{LO}$ mode, suggesting an eventual enhancement of the $\mathcal{D} = 0$ polarization, under compressive strain.

I. INTRODUCTION

The concept of hyperferroelectricity (hyperFE) was first introduced in semi-conducting hexagonal ABC ferroelectrics (FE) by Garrity and coauthors in Ref. [1]. The prefix $\text{hyper}$- is related to the intrinsic property of such a new class of proper ferroelectrics to display a persistent polarization even in the presence of a depolarization field; something unachievable by standard ferroelectrics (FE) [1, 2]. In fact, by analyzing the electric equation of state, Garrity et al. showed that, in contrast to standard ferroelectrics which spontaneously polarize only under zero macroscopic electric field ($\mathcal{E} = 0$), hyperferroelectrics can spontaneously polarize under both zero macroscopic electric field ($\mathcal{E} = 0$) and zero macroscopic displacement field ($\mathcal{D} = 0$), i.e. unscreened depolarization field under open circuit boundary conditions. Such features thus make hyperFE systems suitable for applications as low dimensional functional materials [3–7]; moreover, the existence of a switchable electric polarization in hyperFEs can be allowed in metals and not restricted to only insulators and semiconductors as for standard FEs [4, 8, 9].

The difference in behavior between FE and hyperFE systems stems from the different type of lattice instabilities displayed in the paraelectric phase, as it was first pointed out by Garrity et al.: the well-known FE instability is related to an unstable zone-center transverse optic (TO) mode [10, 11]; the hyperFE instability is related to an unstable zone-center longitudinal optic (LO) mode beside the unstable TO one. Moreover, they ascribed the appearance of such unstable $\text{LO}$ mode in the narrow-gap ABC hyperFEs, to a small $\text{LO-TO}$ splitting resulting from the small Born effective charges (BEC) and relatively large electronic contribution to the dielectric constant $\epsilon^\infty$ [12]. Nevertheless, in a later work, Li et al. [9] reported unstable $\text{LO}$ modes also in some LiNbO$_3$-type ferroelectrics showing, on the contrary, anomalous BEC and small $\epsilon^\infty$. This apparent contradiction motivated these authors to provide a further insight into the microscopic mechanisms behind the $\text{LO}$ mode instability. By modeling the LiNbO$_3$-type systems via an effective Hamiltonian, they identified the structural instabilities related to Li atoms, driven by short-range interactions, as the origin of the hyperferroelectricity. Even So, the identification of the common microscopic origin behind the softening of this $\text{LO}$ mode is still under debate.

In this work, by means of Density Functional Theory (DFT) calculations and the analysis of the dynamical properties obtained from Density Functional Perturbation Theory (DFPT), we confirm and discuss in detail the direct relationship between unstable $\text{LO}$ mode and destabilizing short-range (SR) interactions in ABO$_3$-LiNbO$_3$-type oxides (with A=Li,Na and B=Ta,Nb,V), extending our findings to the hexagonal ABC systems, LiBeSb, LiZnP, LiZnAs and NaMgP compounds, as representative examples. In particular, the exploration of the real-space on-site and interatomic force constants (IFCs) allowed us to distinguish between specific contributions of the long-range (LR) and sort-range (SR) forces to the interatomic interactions that are, in turn, related to the structural properties of the investigated systems. Our study reveals common microscopic mechanisms driving hyperferroelectricity: a structural frustration, arising from the under-coordination of the small sized A atom in LiNbO$_3$-type systems and small sized B atom in the hexagonal ABC, induces the off-centering of the frustrated cations towards the neighboring out-of-plane anions. Such polar distortion is not only driven by LR dipole-dipole interactions but also by SR interactions; the first one contributing to the ferroelectric (TO mode) instability and the second to the hyperferroelectric
In order to provide a clear understanding of mechanisms at play in HyperFEs, we proceeded step-by-step: first, we presented the structural properties of LiTaO$_3$, LiNbO$_3$, LiVO$_3$ and NaVO$_3$ in the centrosymmetric paraelectric $R\overline{3}c$ phase and their relationship with the associated low-symmetry polar $R\overline{3}c$ phase. Then, we discussed the dynamical properties of the paraelectric phase. In particular, we reported phonons modes at the $\Gamma$-point, with a special focus on phonons associated to polar displacements along the cartesian $z$-direction - corresponding to the $R\overline{3}c$ trigonal axis- that are driving the observed ferroelectric phase transition in LiTaO$_3$ and LiNbO$_3$. Phonons frequencies, eigendisplacements and mode effective charges are reported, together with the real space on-site and interatomic force constants, That are of particular importance here to reveal the interatomic interactions behind the softening of the LO mode.

A. Structural properties

In ABO$_3$-LiNbO$_3$-type oxides, the paraelectric structure of $R\overline{3}c$ symmetry (Fig. 1) counts 10 atoms in its rhombohedral primitive cell (or 30 atoms in the hexagonal conventional cell) (See [22]). The atomic arrangement consists of chains of equidistant A-site (Li, Na) and B-sites (Ta, Nb, V) atoms along the trigonal axis (cartesian $z$-direction). As illustrated in Fig. 1, the transition-metal B atoms occupy the center of oxygen octahedra and the A atoms sit at the center of the in-plane nearest neighbors O-triangle and have six further next near neighbors out-of-plane oxygens (out-of-plane O$_1$,2,3, equivalent to O$_{2,5,6}$) (see also Fig. 2(a)). The ferroelectric structure of $R\overline{3}c$ symmetry originates from the off-centering of B and A atoms along the trigonal axis (see Fig. 2(b)). In particular, the Li-O polar displacement tends to improve the Li coordination environment by coming closer to three of the six out-of-plane oxygens (Li-O$_1$) and moving away from the three in-plane oxygens (Li-O'$_3$), as reported in Table I.

| Bond          | LiTaO$_3$ | LiNbO$_3$ | LiVO$_3$ | NaVO$_3$ |
|---------------|-----------|-----------|----------|----------|
| $A_0$-O'$_3$  | 1.97      | 2.04      | 1.96     | 2.04     |
| $A_0$-O$_1$   | 2.79      | 2.28      | 2.79     | 2.28     |
|                | 2.79      | 2.28      | 2.79     | 2.28     |
|                | 2.79      | 2.28      | 2.79     | 2.28     |
|                | 2.62      | 2.46      | 2.62     | 2.46     |

II. METHODS

Calculations were performed within DFT [13, 14] using a plane waves method as implemented in the ABINIT package [15, 16]. The exchange correlation energy functional was evaluated within the generalized gradient approximation (GGA) employing the revised Perdew-Burke-Ernzerhof functional PBEsol [17, 18]. The wave functions were expanded up to a kinetic energy cutoff of 45 Hartrees. Integrals over the Brillouin zone were approximated by sums on a 6×6×6 Monkhorst-Pack $k$-points mesh [19]. We relaxed the structure until the remaining forces on the atoms were less than 10$^{-5}$ Hartree/Bohr and the stresses on the unit cell smaller than 10$^{-7}$. Phonons frequencies, IFCs, Born effective charges and dielectric tensors were computed on the primitive rhombohedral unit cell inset). A atoms are in Green color, B atoms in Blue and Oxygen atoms in red.

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B. Phonon properties at $\Gamma$ and interatomic forces constants

Within the harmonic approximation, structural instabilities are associated to negative curvature of the internal energy with respect to specific atomic displacements, yielding imaginary phonon frequencies [26–28]. In line with the “soft-mode theory” first introduced by Cochran [29], the ferroelectric transition is ascribed to an unstable zone-center transverse optic (TO) phonon in the parent paraelectric phase associated to a polar atomic pattern of distortion; such a “ferroelectric” instability results from the delicate competition between stabilizing short-range (SR) forces and destabilizing long-range (LR) Coulomb interaction taking the form of a dipole-dipole (DD) interaction. In the following, we show that the “hyperferroelectricity” is rather resulting from an unstable zone-center longitudinal optic (LO) phonon driven by destabilizing SR forces.

Within the DPFT approach, the calculation of the interatomic force constants (IFCs), $C_{\alpha,\beta}(l k, l' k')$, and the analysis of the distinct SR and LR contributions, as defined in Refs [30], allow to identify which driving forces lead the system to exhibit eventual instabilities [31, 32]. In particular, within the used convention, the IFCs relates the $\alpha$-component of the force $F_{\alpha}(l k)$ on atom $k$ in cell $l$, to the induced displacement $\tau_{\beta}(l' k')$ of atom $k'$ in cell $l'$, through the expression $F_{\alpha}(l k) = -C_{\alpha,\beta}(l k, l' k')\tau_{\beta}(l' k')$ [31]: if the induced force on atom $k$ is opposite to the direction of the displacement of atom $k'$, a discordant cooperative atomic motion takes place, eventually producing break of the spatial inversion symmetry and so the creation of a dipole moment; accordingly, the IFC is positive and corresponds to a destabilizing interaction. Differently, the force on a single atom resulted from its isolated displacement from its initial crystalline position is specified by the “on-site” force constant; this can be written as a sum over IFCs: $C_{\alpha,\beta}(l k, l k) = -\sum_{l' k'} C_{\alpha,\beta}(l k, l' k') \tau_{\beta}(l' k')$ [31]. In this case, a negative on-site force constant means an instability against isolated atomic displacement: the induced force and the atomic displacement are concordant, favoring thus the off-centering from the initial position; at opposite, a positive value means stability against isolated atomic displacements, as the induced force will bring the atom back to its initial position. Accordingly, we reported in what follow the phonon properties at $\Gamma$-point and the interatomic forces constants calculated in the primitive cell of the paraelectric $R3c$ phase of LiTaO$_3$, LiNbO$_3$, LiVO$_3$ and NaVO$_3$.

Several unstable transverse optic (TO) phonon modes are revealed at $\Gamma$ (Table II), in agreement with previous DFT calculations [9, 23–25]. For LiTaO$_3$, there is one

| mode irreps | LiTaO$_3$ | LiNbO$_3$ | LiVO$_3$ | NaVO$_3$ |
|-------------|-----------|-----------|-----------|-----------|
| $\Gamma_2$ (A$\bar{2}g$) | 164i | 200i | 448i | 137i |
| $\Gamma_1^+$ (A$\bar{2}g$) | 96i | 102i | 101i | - |
| $\Gamma_1^-$ (E$_a$) | - | 95i | 386i | 442i |
| $\Gamma_3^+$ (E$_g$) | - | - | - | 279i, 7i |

**FIG. 2.** (a) In the paraelectric $R3c$ phase, Li is under-coordinated (surrounded with three in-plane oxygens). (b) In the ferroelectric $R3c$, the Li displaces toward the out-of-plane oxygens cage along the $z$-direction: its coordination is then optimized from III to VI.

TABLE II. Unstable modes at $\Gamma$ in the paraelectric $R3\bar{2}$ phase. $\Gamma_2^+$ is polar along the $z$-direction (trigonal axis), $\Gamma_2^-$ is antipolar along $z$-direction, $\Gamma_3^+$ is polar and doubly degenerated along $xy$-direction and $\Gamma_3^-$ is antipolar and doubly degenerated along the $xy$-direction. Our results are in agreements with previous works [9, 23–25].

| Atom | $Z_{xx}^*$ | $Z_{yy}^*$ | $Z_{zz}^*$ |
|------|---------|---------|---------|
| A    | 1.14    | 1.14    | 1.11    |
| B    | 7.67    | 7.67    | 8.33    |
| O$_1$ | -2.34   | -3.85   | -3.15   |
| O$_2$ | -4.12   | -1.75   | -3.15   |
| O$_3$ | -2.34   | -3.53   | -3.15   |

| Atom | $Z_{xx}^*$ | $Z_{yy}^*$ | $Z_{zz}^*$ |
|------|---------|---------|---------|
| LiVO$_3$ | 5.20 | 5.20 | 5.63 |
| NaVO$_3$ | 6.12 | 6.12 | 6.80 |

| Atom | $\varepsilon_{xx}$ | $\varepsilon_{yy}$ | $\varepsilon_{zz}$ |
|------|---------------------|---------------------|---------------------|
| A    | 1.14                | 1.14                | 1.12                |
| B    | 11.20               | 11.20               | 12.36               |
| O$_1$ | -3.11              | -5.10               | -4.50               |
| O$_2$ | -6.10              | -2.11               | -4.50               |
| O$_3$ | -3.11              | -5.10               | -4.50               |

| Atom | $\varepsilon_{xx}$ | $\varepsilon_{yy}$ | $\varepsilon_{zz}$ |
|------|---------------------|---------------------|---------------------|
| LiTaO$_3$ | 13.10 | 13.10 | 14.40 |
| LiNbO$_3$ | 15.61 | 15.61 | 14.53 |

**TABLE III.** Born effective charges (BEC) and $\varepsilon_{\infty}$. The nominal valence charges of A, B and O are +1, +5 and −2, respectively. Only the diagonal elements are reported, the complete Table is given in Supplemental Material (See [22]).
polar mode $\Gamma_2^-$ ($A_{2u}$) and one antipolar mode $\Gamma_2^+$ ($A_{2g}$) at higher frequency. For LiNbO$_3$, in addition to $\Gamma_2^-$ and $\Gamma_2^+$ modes, there is $\Gamma_3^-$ ($E_u$) polar mode at higher frequency, doubly degenerated in the $xy$-direction. For LiVO$_3$, there are two $\Gamma_2^-$ modes, one $\Gamma_2^+$ and one doubly degenerate $\Gamma_3^-$ mode. For NaVO$_3$ there is one $\Gamma_2^-$ mode, one $\Gamma_3^-$ mode and two antipolar $\Gamma_3^+$ ($E_g$) doubly degenerated in the $xy$-direction. It is worth noting that in LiVO$_3$ and NaVO$_3$, the modes are highly unstable compared to LiTaO$_3$ and LiNbO$_3$. Beside these unstable TO modes, we also found one unstable polar LO1 mode of $\Gamma_5^-$ symmetry for LiTaO$_3$, LiNbO$_3$ and LiVO$_3$ ($\omega_{LO1} = 28i$ cm$^{-1}$, 77i and 138i, respectively). Such LO1 mode is highly stable in NaVO$_3$ ($\omega_{LO1} = 154$ cm$^{-1}$).

In Table IV, we reported the eigendisplacements along the $z$-direction of the $\Gamma_2^-$-TO modes (labeled TO1, TO2 and TO3) and LO1 mode, together with their associated frequencies. Mode effective charges $Z_m$ are also reported: the $\alpha$-component of the mode effective charge vector is defined as $Z_{m,\alpha}^* = \sum_{k,\beta} Z_{m,\alpha}^{*\beta} \eta_{mq = 0} (k\beta) [33]$, where $\eta_{mq = 0}$ is the eigendisplacement associated to the mode $m$ at the $\Gamma$-point and $Z_{k,\alpha\beta}^*$ are the Born effective charges -or transverse charges $Z_{s}^{(T)}$- for the TO-modes, and the Callen effective charges -or longitudinal charges $Z_{s}^{(L)}$- for the LO-modes; $Z_{s}^{(L)}$ is directly related to the $Z_{s}^{(T)}$ via the electronic dielectric tensor $\epsilon_{\infty}$, i.e. $Z_{k}^{(L)} = \epsilon_{\infty}^{-1} Z_{k}^{(T)} [34, 35]$. Complete $Z_{s}^{(T)}$ tensor and $\eta_{mq = 0}$ components are reported in Supplemental Material (See [22]).

The eigendisplacements associated to the unstable TO1 modes showed that A- and B-sites cations displace in phase along the trigonal axis, but in antiphase with respect to the oxygens. These modes exhibit a large mode effective charge, mostly resulting from the anomalous Born effective charges on the B atoms and oxygens (A atoms show values close to their nominal ionic charge), as reported in Table IV. In particular, a very large displacement of Li atoms characterizes TO1 in LiTaO$_3$ and LiNbO$_3$, in contrast to LiVO$_3$ and NaVO$_3$, where it is the V atoms at the B-site that move the most. In these latter, the dominant B-site motion in TO1, combined with the very anomalous BEC on V and O atoms, produce the extremely large $Z_{TO1}^*$ observed in LiVO$_3$ and NaVO$_3$ compared to LiTaO$_3$ and LiNbO$_3$. The eigendisplacements associated to the TO2 mode, that is unstable only in LiVO$_3$, showed a large motion of A atoms in the four systems. However, the A-cations displace in-phase with oxygens in LiTaO$_3$ and LiNbO$_3$ and in anti-phase in LiVO$_3$ and NaVO$_3$; at the opposite, the B-cations displace in-phase with oxygens in LiTaO$_3$ and LiNbO$_3$, producing a still large $Z_{TO2}^*$; while, they displace in-phase with oxygens in LiVO$_3$ and NaVO$_3$, causing the vanishing $Z_{TO2}^*$. TO3 modes are highly stable in all the four systems.

The eigendisplacements associated to the unstable

### Table IV. Calculated phonon frequencies $\omega$ (cm$^{-1}$) of $\Gamma_2^-$ TO- and LO1- modes with their corresponding normalized eigendisplacements (in a.u.) and mode effective charges $Z_{m}^*$. The Callen longitudinal mode effective charge ($Z_{s}^{(L)}$) for LO1 is given between parenthesis. Decomposition of the phonon frequency into the long-range (LR) and short-range (SR) contributions is also reported ($\omega = \omega_{LR}^* + \omega_{SR}^*$).

| modes | $\omega$ | A | B | $O_{1/2/3}$ | $Z_{m}^*$ | $\omega^*$ | $\omega_{LR}^*$ | $\omega_{SR}^*$ |
|-------|---------|---|---|-----------|-----------|--------|-------------|-------------|
| LiTaO$_3$ TO1 | 164i | +0.2081 | +0.0080 | -0.0605 | 4.64 | -27056 | +29634 | -56960 |
| TO2 | 149i | +0.1611 | -0.0239 | +0.0669 | -4.42 | +22203 | -171327 | +193531 |
| TO3 | 512 | +0.0254 | +0.0022 | -0.0120 | 6.47 | +262540 | -581901 | +844442 |
| LO1 | 28i | +0.2594 | -0.0105 | +0.0021 | 0.077 | - | - | - |
| LiNbO$_3$ TO1 | 201i | +0.1544 | +0.0268 | -0.0742 | 7.79 | -40285 | -187424 | +147138 |
| TO2 | 69i | +0.2093 | -0.0357 | +0.0389 | -3.60 | +48033 | -177323 | +182127 |
| TO3 | 466 | +0.0318 | -0.0011 | -0.0024 | 6.38 | +217662 | -473571 | +691233 |
| LO1 | 77i | +0.2570 | -0.0162 | -0.0057 | 0.052 | - | - | - |
| LiVO$_3$ TO1 | 448i | +0.0216 | +0.0651 | -0.0722 | 19.70 | -290861 | -980925 | +780064 |
| TO2 | 137i | +0.2573 | -0.0218 | -0.0140 | 0.43 | -18810 | +56318 | -75128 |
| TO3 | 498 | +0.0262 | -0.0194 | +0.0168 | 4.71 | +248701 | -158808 | +407510 |
| LO1 | 138i | +0.2536 | -0.0118 | -0.0240 | -0.008 | - | - | - |
| NaVO$_3$ TO1 | 145i | +0.0021 | +0.0665 | -0.0716 | 20.18 | -210723 | -1161238 | +950515 |
| TO2 | 169i | +0.1328 | -0.0315 | -0.0301 | 1.20 | +235365 | +149090 | +11274 |
| TO3 | 538 | +0.0333 | -0.0173 | +0.0167 | 4.67 | +290176 | -190507 | +480683 |
| LO1 | 154 | +0.1318 | -0.0390 | -0.0216 | -0.034 | - | - | - |

### Table V. Overlap matrix elements ($\eta_{LO}^{*} M \eta_{TO}^{*}$) ($M = M_{s} \delta_{\omega}$) between TO modes eigenvectors and LO1 mode in the $R3c$ paraelectric phase.

| LiTaO$_3$ | LiNbO$_3$ | LiVO$_3$ | NaVO$_3$ |
|----------|-----------|----------|----------|
| TO1 | 0.73 | 0.52 | 0.96 | 0.11 |
| TO2 | 0.68 | 0.85 | 0.99 | 0.99 |
| TO3 | 0.98 | 0.06 | 0.01 | 0.03 |
TABLE VI. On-site force constants in (Hartree/bohr²) related to different atoms calculated in the R¯3c paraelectric phase.

| Atoms   | LiTaO₃ | LiNbO₃ | LiVO₃ | NaVO₃ |
|---------|--------|--------|-------|-------|
|         | Tot    | LR     | SR    | Tot    | LR     | SR    | Tot    | LR     | SR    |
| A (zz)  | +0.0008| +0.0340| −0.0331| +0.0003| +0.0319| −0.0316| +0.0020| +0.0219| −0.0239|
|         |        |        |       |        |        |       |        |        |       |
| B (zz)  | +0.3161| −0.4094| +0.7165| +0.2794| −0.1450| +0.6945| +0.1916| −0.4367| +0.6283|
|         |        |        |       |        |        |       |        |        |       |
| O (zz)  | +0.1273| −0.1954| +0.2328| +0.1111| −0.1935| +0.2207| +0.9885| −0.1170| +0.2156|
|         |        |        |       |        |        |       |        |        |       |

TABLE VII. Interatomic force constants (Hartree/bohr²) between different pairs of atoms in their local (||) and Cartesian (zz) coordinates. The two different long-range (LR) and short-range (SR) contributions to the IFCs are also reported.

| Atoms   | LiTaO₃ | LiNbO₃ | LiVO₃ | NaVO₃ |
|---------|--------|--------|-------|-------|
|         | Tot    | LR     | SR    | Tot    | LR     | SR    | Tot    | LR     | SR    |
|         |        |        |       |        |        |       |        |        |       |
| A₀ − O₁ (||) | +0.0150| +0.0144| −0.0295| +0.0150| +0.0124| −0.0274| −0.0161| +0.0068| −0.0229|
| (zz)    | (1.97) | (1.96) |       | (1.96) |       |       | (1.96) |       |       |
|         |        |        |       |        |        |       |        |        |       |
| A₀ − O₂ (||) | +0.0057| +0.0044| +0.0113| +0.0055| +0.0037| +0.0117| −0.0047| +0.0027| +0.0020|
| (zz)    | (1.97) | (2.79) |       | (2.79) |       |       | (2.79) |       |       |
|         |        |        |       |        |        |       |        |        |       |
| B₀ − O₁ (||) | +0.0573| −0.2994| −0.3568| +0.0182| +0.0182| +0.0000| −0.0129| −0.3136| −0.3017|
| (zz)    | (3.75) | (1.97) |       | (1.97) |       |       | (2.79) |       |       |
|         |        |        |       |        |        |       |        |        |       |
|         | +0.0121| +0.0116| +0.0066| +0.0047| −0.0103| +0.0056| +0.0013| −0.0003| +0.0116|
|         | (1.97) | (2.79) |       | (1.97) |       |       | (2.79) |       |       |
|         |        |        |       |        |        |       |        |        |       |
|         | −0.1111| −0.1095| +0.2207| +0.1111| −0.1095| +0.2207| −0.9885| −0.1170| +0.2156|
|         | (1.97) | (2.79) |       | (1.97) |       |       | (2.79) |       |       |

LO₁ mode showed a dominant A atoms motion in anti-phase with both B atoms and oxygens (A-O motion seems in-phase in LiTaO₃, but O contribution is quasi negligible). Such A-site driven character, already suggest the active role of the Li-cation in driving the LO instability.

In order to estimate the correlation between LO₁ and the TO modes, we calculated the overlap matrix elements between the corresponding eigendisplacements as \( \langle \eta^{LO₁}|M|\eta^{TO} \rangle \) (projection of LO₁ mode on the basis of the TO modes, as in [36]) where \( M = M_k \delta_{kk} \) with \( M_k \) the mass of atom \( k \). The results, reported in Table V, show that LO₁ modes displaying dominant A atoms motions. In particular, in LiTaO₃ and LiNbO₃, LO₁ results from a mixing between TO₁ and TO₂, while it is mainly associated to TO₂ in LiVO₃ and NaVO₃. It is thus important to emphasize that there is no one-to-one correspondence between LO₁ and TO₁ as considered by Li et al in Ref. [9].

Moreover, in the aim of quantifying the balance between the dipole-dipole long range interactions and the short-range interactions behind the above discussed unstable modes, we decomposed the phonons frequencies into two contributions, i.e. \( \omega^2 = \omega^2_{LR} + \omega^2_{SR} \), as discussed in Ref. [30]. From this decomposition reported in Table IV, it is interesting to note that only TO₁ instability in LiTaO₃ and TO₂ one in LiVO₃ originate from a global destabilizing SR interactions (\( \omega^2_{SR} < 0 \)), while all the other instabilities originate from destabilizing LR interactions (\( \omega^2_{LR} < 0 \)). Nevertheless, the fact that LiNbO₃ also hosts the LO instability without showing global unstable SR interactions, suggests that this is not the neces-
sary condition for hyperFE, but rather, the specific destabilizing SR interatomic interactions associated to the Li motion (dominant Li motion in LO1 mode is a common feature in LiTaO$_3$, LiNbO$_3$ and LiVO$_3$, see above).

Accordingly, to shed light on the necessary conditions that make the A-site motion active in the destabilization of the LO mode, we examined distinct atomic interactions, through the analysis of the on-site and interatomic force constants, calculated in the R3c paraelectric phase. Interestingly, we found that the \((zz)\) component (out-of-plane direction) of the on-site force constant for Li is vanishingly small in LiTaO$_3$ and LiNbO$_3$ and turns out to be negative for LiVO$_3$ (see Table VI). In particular, we noticed a negative contribution, i.e., destabilizing, of the SR part for the three systems displaying the unstable LO mode. The other components of the Li on-site force constants and all those of Na, B and O are large and positive.

The SR nature of the LO1 instability and the active role played by Li are also highlighted from the examination of the interatomic force constants reported in Table VII. The \(A_0\)-O$_1$ IFC (equivalent to the \(A_0\)-O$_{2\,3}\), related to the interaction between the under-coordinated A atom and the out-of-plane oxygens toward which it tends to displace, is destabilizing with respect to both the LR and the SR forces (positive values) in LiTaO$_3$, LiNbO$_3$ and LiVO$_3$ systems. On one hand, the destabilizing LR dipole-dipole interaction contributes to the instability of the TO1 mode; on the other hand the destabilizing SR interaction is responsible for the LO1 instability and its associated eigendisplacement dominated by Li motion. The destabilizing \(A_0\)-O$_1$ interaction confirms also the correlated Li-O motion reported in Ref [37]. Noteworthy, the SR part of the \(A_0\)-O$_{3\,3}$ IFC, related to the interaction between A atom and in-plane oxygens, is also destabilizing along the z-direction, but not strong enough to overcome the stable LR part. In NaVO$_3$, in which the LO1 is stable, the scenario is indeed different: it is only the LR dipole dipole interaction that is destabilizing and thus driving the cooperative Na-O polar motion (SR part of \(A_0\)-O$_1$ and \(A_0\)-O$_{3\,3}$ IFCs is negative).

The interatomic force constants between the B atoms and the oxygens exhibit a destabilizing LR dipole-dipole interaction as standard ferroelectric perovskites [31, 32]; the LR forces are destabilizing along the direction parallel to the B-O bonds. In particular, LiVO$_3$ and NaVO$_3$ exhibit much more unstable TO1 mode than LiTaO$_3$, LiNbO$_3$ that is characterized by dominant anti-phase displacement of V and O atoms and giant mode effective charges (due to anomalous BEC on V and O atoms as discussed in previous paragraph).

We finally noted negative interatomic force constants between near and next-near neighboring A and B atoms, meaning that the motion of A and/or B atoms along the \(A-B\) chain would be in-phase, propagating thus the polar distortions along this chain (i.e. along the trigonal axis) [34].

C. The effect of isotropic pressure

Ferroelectricity is known to be highly sensitive to external pressure; in particular, it was highlighted that, in the high-pressure ferroelectricity, a crucial role is played by SR range interactions, which become destabilizing [38–40]. Based on that, it appeared necessary to explore the effect of isotropic pressure (compressive strain) on hyperferroelectricity, which is, as showed in previous section, mainly driven by destabilizing SR forces on A atoms.

Interestingly, the LO1 instability increases as a function of pressure in LiTaO$_3$, LiNbO$_3$ and LiVO$_3$ [Fig. 3(a,c,e)]; opposite trend is observed in NaVO$_3$ [Fig. 3(g)]. The destabilizing SR range forces acting on Li atoms are in fact strengthened by the compressive strain, as shown in Fig. 3(b,d,f); in particular, we observe that the on-site force constants of Li atoms become more and more negative with increasing pressure, following the evolution of its SR part. At opposite, pressure increases the stiffness of Na atoms in NaVO$_3$: the on-site force constant associated to Na becomes more and more positive, as shown in Fig. 3(h).

Noteworthy, the contribution of the TO1 mode to the LO1 mode in LiTaO$_3$, LiNbO$_3$ and LiVO$_3$ also increases with pressure, as clearly shown from the evolution of the overlap matrix illustrated in Fig. 4(d,e,f). This is correlated to the increasing Li-displacement in the TO1 eigendisplacement (see Fig. 4(a,b,c)) and is consistent with the fact that LO1 is associated to the TO mode exhibiting a large motion of the frustrated atom, as discussed in the previous section.

More interestingly, we observed that the LO1 mode effective charges also increase with pressure for the three Li-based compounds (see Table VIII); this is due to the increasing, anti-phase oxygens motion in the LO1 eigendisplacement. Since the mode effective charges are giving, by construction, an idea about the polarity of the mode, this result suggests that an external pressure could enhance the hyperferroelectric polarization. The polarization under open circuit conditions (\(\mathcal{P} = 0\), not calculated in this work, is in fact found to be very small at 0GPa (see ref. [1, 7, 9]).

IV. DISCUSSION

LiTaO$_3$, LiNbO$_3$, LiVO$_3$ and NaVO$_3$ compounds all exhibit polar instabilities; in particular, the unstable TO1 modes in LiTaO$_3$, LiNbO$_3$ and the TO2 one in LiVO$_3$ are characterized by dominant anti-phase Li-O displacements (Table IV). The A-cation in these ABO$_3$-LiNbO$_3$-type systems, experiences in fact an electrostatic frustration due to its under-coordination in the R3c paraelectric phase [8]: the off-centering of Li from its central position in the O-triangle toward the three out-of-plane oxygens (Fig. 2) optimizes Li-coordination from III, in the paraelectric R3c phase, to VI in the ferroelectric R3c phase.
The instability of the polar $LO_1$ mode is ascribed, in one hand, to this frustration, as the $LO_1$ mode is mainly driven by the A-site motion and, on the other hand, to the small size of the frustrated cation. The $LO_1$ mode is in fact unstable only in the Li-based compounds, where Li has much smaller size than Na (0.76 vs 1.02 Å respectively, for six-coordinated cations [41]). Moreover, by analysing the on-site (Table VI) and the interatomic (Table VII) force constants, we found out that the $LO_1$ instability is driven by short-range interactions: LiTaO$_3$, LiNbO$_3$, LiVO$_3$ exhibit destabilizing Li-O interactions with dominant contribution coming from SR forces; in
TABLE VIII. Effect of Increasing pressure on LO1 mode frequency, on LO1 eigenvectors along z-direction and on longitudinal mode effective charges ($Z_{LO1}^z$).

| P(GPa) | $\omega_{LO1}$ | A     | B     | $O_{1/2/3}$ | $Z_{LO1}^z$ |
|--------|----------------|-------|-------|-------------|-------------|
| LiTaO$_3$ |                |       |       |             |             |
| 0      | 28             | -0.2594 | -0.0105 | +0.0021     | 0.077       |
| 5      | 64             | +0.2597 | -0.0101 | +0.0006     | 0.093       |
| 10     | 91             | +0.2598 | -0.0096 | -0.0010     | 0.110       |
| 25     | 158            | +0.2591 | -0.0083 | -0.0061     | 0.156       |
| 50     | 243            | +0.2549 | -0.0059 | -0.0145     | 0.224       |
| 70     | 299            | +0.2491 | -0.0040 | -0.0207     | 0.270       |
| 90     | 347            | +0.2415 | -0.0022 | -0.0265     | 0.310       |
| 105    | 381            | +0.2347 | -0.0008 | -0.0306     | 0.336       |
| LiNbO$_3$ |                |       |       |             |             |
| 0      | 77            | +0.2570 | -0.0162 | -0.0057     | 0.053       |
| 5      | 99            | +0.2571 | -0.0155 | -0.0072     | 0.068       |
| 10     | 121           | +0.2570 | -0.0147 | -0.0087     | 0.084       |
| 25     | 181           | +0.2556 | -0.0123 | -0.0132     | 0.127       |
| 50     | 263           | +0.2501 | -0.0081 | -0.0205     | 0.192       |
| 70     | 318           | +0.2429 | -0.0046 | -0.0262     | 0.236       |
| 90     | 368           | +0.2334 | -0.0011 | -0.0315     | 0.274       |
| 105    | 402           | +0.2248 | +0.0014 | -0.0353     | 0.299       |
| LiVO$_3$ |                |       |       |             |             |
| 0      | 138            | +0.2559 | -0.0258 | -0.0096     | -0.008      |
| 5      | 158            | +0.2562 | -0.0250 | -0.0105     | 0.001       |
| 10     | 162           | +0.2565 | -0.0243 | -0.0113     | 0.010       |
| 25     | 202           | +0.2570 | -0.0221 | -0.0136     | 0.033       |
| 50     | 263           | +0.2569 | -0.0188 | -0.0172     | 0.064       |
| 70     | 305           | +0.2561 | -0.0162 | -0.0198     | 0.085       |
| 90     | 344           | +0.2549 | -0.0137 | -0.0223     | 0.104       |
| 105    | 371           | +0.2536 | -0.0119 | -0.0241     | 0.116       |

FIG. 5. ABC-hexagonal cell in the paraelectric $P6_3/mmc$ and polar $P6_3/mmc$(186) phases.

In this paper we have investigated the dynamical properties of LiTaO$_3$, LiNbO$_3$, LiVO$_3$ and NaVO$_3$ compounds by means of first-principles calculations revealing microscopic mechanisms of general validity behind hyperferroelectricity; we have provided in fact a confirmation also for the ABC-hexagonal systems. In particular, we have shown that, beyond the small $LO - TO$ splitting claimed in literature, the $LO$ mode instability is driven by destabilizing short-range forces acting on the small sized cations at the A-site of the ABO$_3$-LiNbO$_3$-type systems and at the B-site of the ABC-hexagonal ones, which experience an electrostatic frustration caused by their under-coordination in their respective centrosymmetric...
The signature of such SR-driven LO instability is a vanishingly small or negative on-site force constant associated to the frustrated cation, which reflect its tendency to displace, combined to destabilizing SR forces. Moreover, we have also predicted a possible enhancement of hyperferroelectricity upon external isotropic pressure, which can be suitable for technological applications.

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