

Phenomenological theory with nonlocal electrostatics for non-Ising polarization switching and domain walls in LiNbO_3 and LiTaO_3

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We develop the Ginzburg-Landau-Devonshire phenomenological model for trigonal ferroelectrics, which matches experimental values of the poling electric field for both near-stoichiometric and congruent compounds. The model favors a non-Ising type of polarization switching. Therefore, domain walls have nontrivial Néel and/or Bloch polarization components supported by numerical computations. Néel and/or Bloch polarization components are of the order from 1 to 10% of spontaneous polarization in the model. Numerically calculated optimal domain wall profile has bichiral Bloch behavior for near-stoichiometric LiTaO_3 and LiNbO_3 and congruent lithium niobate. The domain wall has a mixed Bloch-Néel type without including electrostatic interactions and has a Bloch character when nonlocal electrostatic interactions are accounted for in congruent lithium tantalate.

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I. INTRODUCTION

Lithium tantalate [LiTaO_3 (LT)] and lithium niobate [LiNbO_3 (LN)] crystals are widely used for electro-optical, piezoelectric, and nonlinear optics applications. Various optical devices require ferroelectric domain shape and width engineering to satisfy quasi-phase-matching conditions (e.g., periodic poling technique). The transition region between domains with opposite polarization P_z is called an uncharged 180° domain wall (DW) with upper bound for characteristic width to be a few nanometers [1–3]. DWs usually occupy a vanishingly small volume compared to domain size. Despite their small size, DW properties define the shape of domains (e.g., triangular domain shape for congruent lithium tantalate (CLT) and hexagonal shape for near-stoichiometric lithium tantalate (NSLT), near-stoichiometric lithium niobate (NSLN) and CLN at room temperature [4,5]). Unraveling the internal structure of DWs could bring light to new domain manipulation methods.

A phenomenological description of DWs in NSLT and NSLN compounds was given in Ref. [4]. The model treats the Ising polarization component as a primary order parameter, while non-Ising polarization components and strain as secondary order parameters. One downside of the model is that the theoretical coercive field values for single-domain crystals differ by two orders of magnitude from experimental values for the near-stoichiometric materials. Another

downside is that DWs have vanishingly small non-Ising polarization components in the approach (on the order of 0.01% of spontaneous polarization). Therefore, all DWs are effectively of Ising type. However, there is experimental evidence for the non-Ising DW type for LN [1,6] and LT [7]. Alternative theoretical approaches also predict non-Ising DW type in LN [8,9].

In the paper, we improve the Ginzburg-Landau-Devonshire approach developed in Ref. [4] to solve the inconsistencies mentioned above and extend it to different stoichiometry of compounds. The primary step is to make a zero polarization ($\mathbf{P} = 0$) point on a free-energy landscape a local maximum instead of a saddle point so that the Ising type DW will not be favorable. The ideas for the approach were discussed in Ref. [1]. Moreover, we include quartic terms for non-Ising polarization components (P_x , P_y) and their coupling to the component P_z . The coupling term breaks $O(2)$ symmetry in xy plane down to Z_3 of the underlying crystal structure. The coupling favors a non-Ising path for domain polarization switching. Therefore, the system has a coercive field different from Ref. [4], and the model's parameters can be adjusted to match the experimental data [10]. Furthermore, we investigate a parameter space for our phenomenological model that describes experimental evidence of Y walls (when DW plane is perpendicular to x crystal axis) in CLN, NSLN, NSLT, and X walls (DW is perpendicular to y crystal axis) in CLT. The Y walls have bichiral Bloch character for CLN, NSLN, and NSLT and mixed Néel-Bloch type for CLT without electrostatic interactions. When nonlocal electrostatics is included in the calculation, the preferred DW type remains the same for CLN, NSLN, and NSLT and changes to Bloch type for CLT.

The paper is organized as follows. A detailed description of the mathematical model and derivation of the model coefficients from material parameters are presented in Sec. II. Next, in Sec. III, we consider a single-domain model and describe the poling process using two approaches to define

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the coercive field. In Sec. IV, we study the DW structure by calculating the minimal energy DW polarization profile with and without nonlocal electrostatic interactions. There, we also compare the energies of DWs in the model to other theoretical works and estimations based on experimental data. Section V contains reasoning on nonlocal electrostatic interactions we implemented and speculations on results for more advanced models of electrostatic interaction.

II. DESCRIPTION OF THE MODEL

A. General mathematical model

Phenomenological models for ferroelectric materials have two order parameters: polarization $\mathbf{P} = (P_x, P_y, P_z)$ and strain (3×3 tensor u_{ij} or 6-vector ε_α in Voigt notation [11]). The free-energy density of a ferroelectric can be written in a general tensor form:

$$F = \frac{1}{2} G_{abcd}^o \partial_a P_b \partial_c P_d + V^o(\mathbf{P}) + \frac{1}{2} C_{\alpha\beta}^o \varepsilon_\alpha \varepsilon_\beta - q_{\alpha bc}^o \varepsilon_\alpha P_b P_c, \quad (1)$$

where the first term is the gradient energy (Ginzburg term), the second is the potential (Landau-Devonshire) energy, the third is the elastic energy, and the last is the electrostrictive coupling. Latin and Greek letters are used when summing over repeated indices, so that $a = 1, 2, 3$ but $\alpha = 1, \dots, 6$. The superscript “ o ” denotes original xy coordinates. It was shown in Ref. [11] that the last two terms can be absorbed by the potential term assuming that the energy minimizing strain ($\varepsilon_\alpha^{\text{vac}} = Q_{\alpha bc}^o P_b^{\text{vac}} P_c^{\text{vac}}$) always satisfies the elastic compatibility condition. The free energy then simplifies to

$$F = \frac{1}{2} G_{abcd}^o \partial_a P_b \partial_c P_d + \tilde{V}^o(\mathbf{P}), \quad (2)$$

where the potential energy is modified only in quartic order:

$$\tilde{V}^o(\mathbf{P}) = V^o(\mathbf{P}) - \frac{1}{2} C_{\alpha\beta}^o Q_{\alpha ef}^o Q_{\beta gh}^o P_e P_f P_g P_h. \quad (3)$$

Here we introduced the auxiliary tensor Q^o ,

$$Q_{\alpha bc}^o = (C^o)^{-1}_{\alpha\beta} q_{\beta bc}^o. \quad (4)$$

The global minimum of the free energy (vacuum polarization $\mathbf{P}^{\text{vac}}$) in the absence of an external field assuming a crystal with a single-domain can be found from

$$\left. \frac{\partial \tilde{V}^o}{\partial P_a} \right|_{\mathbf{P}=\mathbf{P}^{\text{vac}}} = 0 \quad (5)$$

and making sure that the determinant of the Hessian matrix is positive.

B. Mathematical model for a single-domain LiNbO₃ and LiTaO₃

Single crystal LiNbO₃ and LiTaO₃ have a spontaneous polarization $\mathbf{P}^{\text{vac}} = (0, 0, \pm P_z^{\text{vac}})$ in the ground state. Polarization components P_x and P_y are usually nonzero next to DW. Component P_x corresponds to polarization in the DW direction (Néel component, see Fig. 1). Component P_y corresponds to polarization perpendicular to both DW direction and z axis (Bloch component). When one describes a system without DW or Y wall, polarization components coincide with crystal axes. The polarization component P_z gives a major energy contribution in the ground state [4,12]. Néel and Bloch

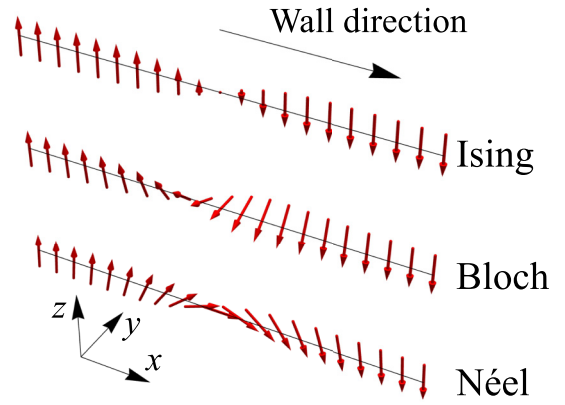


FIG. 1. Three prototypical domain walls. Coordinate system is chosen such that x axis matches wall direction, z axis coincides with spontaneous polarization $\mathbf{P}^{\text{vac}} = (0, 0, \pm P_z^{\text{vac}})$.

polarization components and strain components contribute much less to the total energy.

Experimental evidence of a sharp polarization switching on the $P_z(E)$ diagram [13–15] and a rapid switching time (on the order of tens of milliseconds) [14] motivates the approximation of a single-domain model. Therefore, we can neglect gradient energy at this stage. The free-energy density (up to a quartic term in the presence of an external field $\mathbf{E}$) for a crystal belonging to the C_{3v} point group has the form

$$F = -\frac{\alpha_{21}}{2} P_z^2 + \frac{\tilde{\alpha}_{41}}{4} P_z^4 + \frac{\alpha_{22}}{2} (P_x^2 + P_y^2) + \frac{\tilde{\alpha}_{42}}{2} (P_x^2 + P_y^2) P_z^2 + \frac{\alpha_{44}}{4} (P_x^2 + P_y^2)^2 + \alpha_{43} P_y P_z (P_y^2 - 3P_x^2) - \mathbf{P} \cdot \mathbf{E}. \quad (6)$$

Note that we used the modified potential of Eq. (3) where only the α_{41} and α_{42} terms are changed due to the form of the Q^o tensor (see Appendix A 2). Previous theoretical works on trigonal ferroelectrics used the first two [10] or three [4] terms of the expression (6) arguing that terms containing only polarization component P_z give the major energy contribution. A downside of such an approach is the theoretical coercive field values ($E_c = \frac{2\alpha_{21}^{3/2}}{3\sqrt{3}\tilde{\alpha}_{41}}$ that we call *trivial poling electric field*) which differ by one and two orders of magnitude from experimental values for congruent and near-stoichiometric materials, respectively [10].

In this section, we consider the full model of Eq. (6) to reproduce experimental poling electric field values [13–16]. Such a model needs to consider a minimal energy barrier for the poling process of *non-Ising path*. This can be achieved by varying the terms $\tilde{\alpha}_{42}$ and α_{44} . The idea of introducing a Mexican-hat-like potential for the Néel and Bloch components of polarization for LN was mentioned in Ref. [1]. The last potential term with parameter α_{43} is introduced to lift the circular degeneracy of the P_x and P_y polarization components. When $\alpha_{43} = 0$, potential energy is the same for $(P_x, P_y) \propto (\cos \varphi, \sin \varphi)$, $\forall \varphi$. This is a good approximation for the macroscopic scale, but for the scale from a few to dozens of unit cells (DW thickness), free energy has to respect crystal symmetry. Hence, α_{43} term originates from

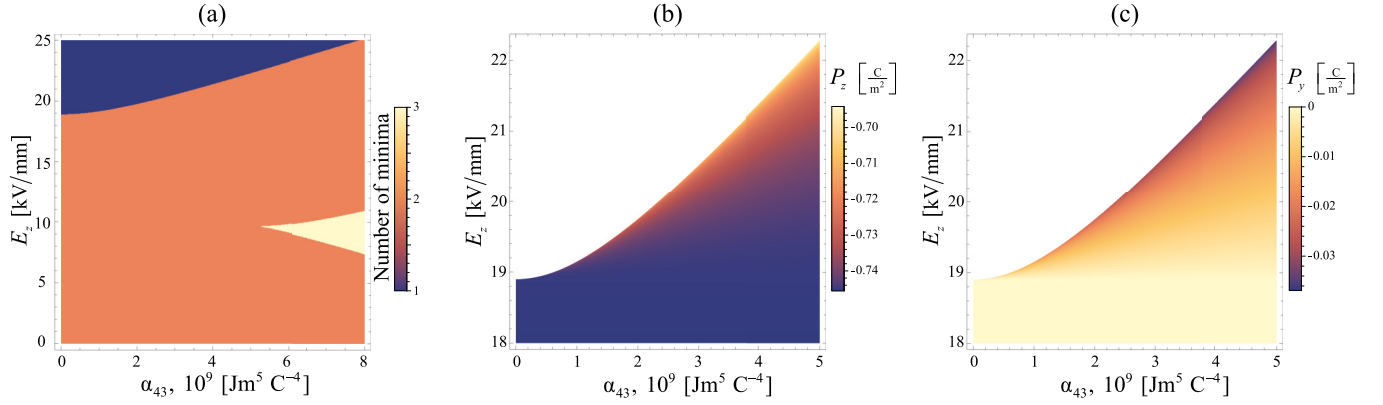


FIG. 2. (a) The number of local minima for the free energy Eq. (6) for a single-domain congruent LiNbO₃ assuming $P_x = 0$. (b) The polarization component P_z in a local minimum in the vicinity of $\mathbf{P} = (0, 0, -P_z^{\text{vac}})$ during the poling process ($E_z < E_{\text{cr}}$) for different values of the parameter α_{43} . (c) The P_y polarization component in a local minimum in the vicinity of $\mathbf{P} = (0, 0, -P_z^{\text{vac}})$ during the poling process for different values of the parameter α_{43} .

atom arrangement in the xy plane. When $\alpha_{43} \neq 0$, the energy Eq. (6) becomes threefold degenerate. The degenerate states are $(P_x, P_y) = (0, P)$, $(\pm \frac{\sqrt{3}}{2}P, -\frac{1}{2}P)$. We use $\alpha_{43} \geq 0$. Negative values of α_{43} change the sign of the P_x and P_y polarization components. At the stage of DW calculation, the α_{43} term could make Bloch to Néel (or vice versa) DW types more energetically preferable. We omit the effect of such a term in analytical derivations of the section but take it into account in our numerical investigations.

We introduce the following constraints for the model of Eq. (6) (with $\alpha_{43} = 0$): (i) the model has only two local minima $\mathbf{P}^{\text{vac}} = (0, 0, \pm P_z^{\text{vac}})$ in the absence of external field [they are also global minima; for example, see Fig. 2(a)], (ii) the point $\mathbf{P} = 0$ is a local maximum or a saddle point, (iii) there is a saddle point (region) $P_x^2 + P_y^2 = \frac{-\alpha_{22}}{\alpha_{44}} > 0$, $P_z = 0$ (iv) energy at the saddle point is higher than the energy in global minimum $\mathbf{P}^{\text{vac}}$, and (v) energy at the critical point ($\partial F / \partial P_i = 0$ together with zero determinant of Hessian at the poling field $E_c \neq 0$) should be larger than the energy at the saddle point. The first condition comes from experimental observations of only the two polarization configurations $\mathbf{P}^{\text{vac}} = (0, 0, \pm P_z^{\text{vac}})$ when $\mathbf{E} = 0$. The second one makes Ising-type DWs energetically *unfavorable* and automatically satisfies if (iii) is true. The third point is needed for the nontrivial coercive electric field. The fourth is automatically satisfied when (i) and (iii) are true. The last one ensures that when the potential at the local minimum [in the vicinity of $\mathbf{P} = (0, 0, -P_z^{\text{vac}})$ for $E_c > 0$] becomes flat, the system immediately switches to the global minimum in the vicinity $\mathbf{P} = (0, 0, P_z^{\text{vac}})$ (there is no potential barrier on an optimal path connecting the points).

The detailed parameter determination algorithm for the model is presented in Appendix A. The parameters given in Table I are derived from the material constants given in Table V. The constraints make a quite narrow window for the α_{44} parameter choice (see Table I). Varying α_{44} in this range does not qualitatively change the physics of the results presented below. Therefore, we choose $\alpha_{44} \approx (\alpha_{44}^{\text{min}} + \alpha_{44}^{\text{max}})/2$ for the numerical calculations. The congruent compound is different from the near-stoichiometric one because of defects. Our model effectively includes the average influence

of defects using different material parameters for congruent compounds (Table V). The most significant difference in material parameters is for the coercive field and spontaneous polarization.

C. Electrostriction, gradient, and nonlocal electrostatic terms

In this subsection, we present explicit forms of parts of the free energy Eq. (1) that will be used in Sec. IV for DW calculations.

The explicit form of the electrostriction coupling term is

$$-q_{abc}^o \epsilon_a P_b P_c = \gamma_1 (\epsilon_1 + \epsilon_2) P_z^2 + \gamma_2 \epsilon_3 P_z^2 + \gamma_3 [(\epsilon_1 - \epsilon_2) P_y + \epsilon_6 P_x] P_z + \gamma_4 (\epsilon_5 P_x + \epsilon_4 P_y) P_z, \quad (7)$$

where γ_p values are presented in Table I and explicit expressions are given in Eqs. (A17) and (A18). The paper [4]

TABLE I. Derived Ginzburg-Landau-Devonshire free-energy parameters for Eqs. (6), (7), and (8) of congruent and near-stoichiometric LiTaO₃ and LiNbO₃.

	CLT	NSLT	CLN	NSLN	Units
α_{21}	1.3313	1.4195	2.0583	2.2049	$\times 10^9 \text{ Jm C}^{-2}$
α_{22}	-0.9991	-10.282	-1.0992	-5.6863	$\times 10^{11} \text{ Jm C}^{-2}$
$\tilde{\alpha}_{41}$	3.6981	4.6925	3.6593	3.4451	$\times 10^9 \text{ Jm}^5 \text{ C}^{-4}$
α_{41}	3.8502	4.8543	3.8945	3.6484	$\times 10^9 \text{ Jm}^5 \text{ C}^{-4}$
$\tilde{\alpha}_{42}$	2.8358	34.0599	1.9784	8.9046	$\times 10^{11} \text{ Jm}^5 \text{ C}^{-4}$
α_{42}	2.8487	34.0765	1.9898	8.9147	$\times 10^{11} \text{ Jm}^5 \text{ C}^{-4}$
α_{44}	0.22	24.76	0.107	2.305	$\times 10^{14} \text{ Jm}^5 \text{ C}^{-4}$
α_{44}^{min}	0.2128	24.824	0.1056	2.2965	$\times 10^{14} \text{ Jm}^5 \text{ C}^{-4}$
α_{44}^{max}	0.2274	24.6713	0.1097	2.3118	$\times 10^{14} \text{ Jm}^5 \text{ C}^{-4}$
γ_1	0.2573	-0.0289	-0.9006	-0.7298	$\times 10^9 \text{ Jm C}^{-2}$
γ_2	-3.976	-4.3333	-5.1719	-4.819	$\times 10^9 \text{ Jm C}^{-2}$
γ_3	6.6457	7.4822	4.3942	4.0025	$\times 10^9 \text{ Jm C}^{-2}$
γ_4	-9.5579	-10.8191	-6.6739	-6.1871	$\times 10^9 \text{ Jm C}^{-2}$
G	56.5214	1.6487	1.4386	1.0211	$\times 10^{-11} \text{ Jm}^3 \text{ C}^{-2}$

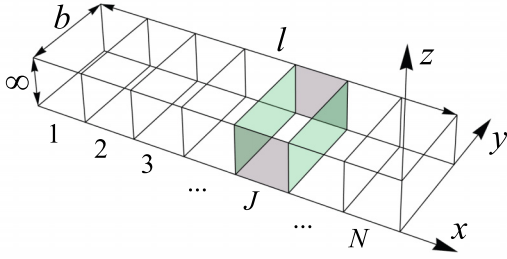


FIG. 3. System geometry and discrete partition for nonlocal electrostatic interactions. Green and gray faces of cell J represent surface charges due to P_x (Néel) and P_y (Bloch) polarization components, respectively. Polarization within the cell is assumed to be uniform.

provides more electrostriction terms; however, the additional terms cannot be accessed experimentally.

Symmetry-allowed gradient terms (with gradients only in the xy plane) are

$$\begin{aligned} F_{\text{grad}} = & G_1^o[(\partial_x P_z)^2 + (\partial_y P_z)^2] + G_2^o(\partial_x P_x + \partial_y P_y)^2 \\ & + G_3^o(\partial_y P_x - \partial_x P_y)^2 + G_4^o[\partial_y P_z(\partial_x P_x - \partial_y P_y) \\ & + \partial_x P_z(\partial_x P_y + \partial_y P_x)]. \end{aligned} \quad (8)$$

The gradient coefficients G_p^o can be accessed in experiments by measuring soft phonon dispersion relations (if a paraelectric-ferroelectric phase transition is of a displacive type) [17] and/or DW width [4]. However, the first method is not applicable for LN and LT because the phase transition is mostly likely of an order-disorder type [18–21] (for a discussion, see Ref. [22]). Hence, we are left with the DW width data-fitting approach [2,4]. The way gives one nonlinear equation that contains simultaneously all gradient parameters G_p^o . Therefore, we resort to the model case where all the gradient terms are equally important, and we use the approximation that $G_p^o = G$, $\forall p$. The value of G for different compositions of LN and LT is presented in Table I. The procedure to calculate gradient coefficients is described in Appendix A 5.

In addition, we will perform some calculations including the effect of electrostatic interactions (depolarizing energy contribution). Electrostatic interactions in the form of a capacitor model with infinite plates (like in Ref. [4]) give a local contribution to the free-energy density, which is proportional to $P_{\text{Néel}}^2$. The contribution is already included in the α_{22} term because we use experimental data to determine the α_{22} coefficient, which includes the electrostatic response of the crystal when measuring the dielectric permittivity. We consider nonlocal electrostatic interactions by analogy with ferromagnetic nonlocal interactions [23]. The model divides a sample of size $l \times b \times \infty$ into N prisms in the x direction (perpendicular to the DW plane). Each prism has a uniform polarization and a charge on the faces xz and yz (Fig. 3). The surface charges interact according to the laws of electrostatics. The contribution to the total free energy per unit length of DW (in the z direction) in SI units is

$$\mathcal{F}_{\text{el}} = \frac{1}{2} \sum_{I,J} \frac{b^2}{4\pi\epsilon_0} [A_{IJ}P_x(I)P_x(J) + B_{IJ}P_y(I)P_y(J)], \quad (9)$$

where the indices I, J are used for prism numeration, b is the sample length in the y direction, and explicit forms of

coefficients A_{IJ} and B_{IJ} are provided in Ref. [23]. Here only non-Ising polarization components contribute. The approach considers charges produced only by polarization components that vanish in the bulk of a domain. Reasoning on the applicability of the nonlocal interactions we put off to the Sec. V. Changing P_x or P_y to P_z leads to instabilities like the absence of uniform ground state. The numerical implementation of the double sum is done using the fast Fourier transform algorithm [24]. The method allows to reduce the computational complexity of the operation from $\mathcal{O}(N^2)$ to $\mathcal{O}(N \log N)$.

III. SINGLE-DOMAIN POLING PROCESS

The poling is a process of switching the sign of the polarization component P_z under the influence of an external electric field $\mathbf{E} = (0, 0, E_z)$. In this section, we use two independent numerical methods to compute the poling electric field for different values of parameter α_{43} that lifts circular degeneracy of P_x and P_y . The first method is based on the *assumption* that when the electric field exceeds the poling value, the number of local free-energy minima reduces from 2 to 1. Therefore, it gives an upper bound for poling electric field estimate. The second, more advanced, approach is based on a modification of the simplified string method [11,25,26]. The simplified string method allows one to find the energy value of a saddle point (energy barrier) between two minima. It is based on the pseudotime evolution of a string connecting two minima. We modify it to find a polarization string configuration that connects the local minimum [in the vicinity of $(0, 0, -P_z^{\text{vac}})$] to a global one [in the vicinity of $(0, 0, P_z^{\text{vac}})$] without an energy barrier to describe the poling process (for details, see Appendix B). This method provides the closest possible estimate of the poling electric field and gives a polarization configuration path for the poling process. We still utilize the first method to find a free-energy landscape that sets limits on α_{43} values and check that it does not contradict the simplified string method results.

A. Congruent LiNbO₃

We numerically search for all local minima of the expression (6) assuming $P_x = 0$ (to stick to the same degenerate state when $\alpha_{43} \neq 0$). Consider a crystal with single domain initially in the ground state $\mathbf{P} = (0, 0, -P_z^{\text{vac}})$. When the poling field is less than the critical value, free energy should have one local and one global minimum in the vicinity of $\mathbf{P} = (0, 0, -P_z^{\text{vac}})$ and $\mathbf{P} = (0, 0, P_z^{\text{vac}})$, respectively. When the poling field exceeds the critical field, free energy should have only one minimum near $\mathbf{P} = (0, 0, P_z^{\text{vac}})$. After switching off the electric field, the system is in the ground state $\mathbf{P} = (0, 0, P_z^{\text{vac}})$. The calculation results for CLN are illustrated in Fig. 2(a) where α_{43} is a variable parameter. One can note the region $\alpha_{43} > 5 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ where there are three minima at the intermediate electric field. The additional minimum has a nontrivial Bloch component ($P_y > 0$). On the $P(E)$ hysteresis loop, the third minimum corresponds to an additional step not observed in an experiment. Hence, we restrict our model to the simplest switching case described above. Therefore, the parameter α_{43} has an upper boundary $5 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for further investigations. Note that the calculated upper bound

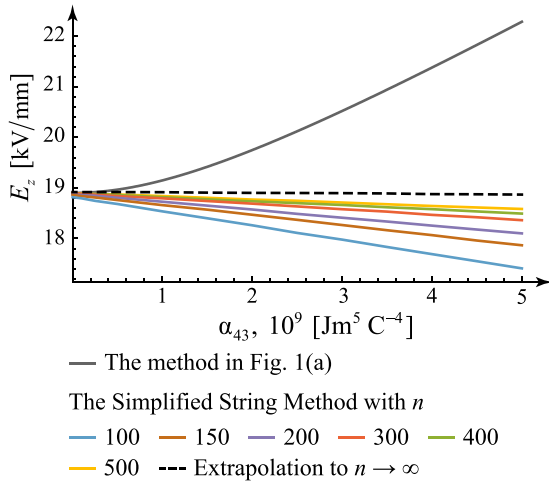


FIG. 4. The critical electric field as a function of the parameter α_{43} for single-domain congruent LiNbO_3 . For the simplified string method, n is the number of points on a string.

for poling electric field (the line between the orange and blue regions) for $\alpha_{43} = 0$ coincides with the value we used for model construction [Eq. (A2)].

Figures 2(b) and 2(c) correspond to the polarization components P_z and P_y in the local minimum in the vicinity of $\mathbf{P} = (0, 0, -P_z^{\text{vac}})$ (P_x is fixed to be zero). The amplitude of the polarization component $|P_z|$ continuously decreases as the electric field increases. In contrast, the polarization component P_y becomes nonzero in the region $E_z > 18.9$ kV/mm (verified numerically). The electric field value is the critical value for $\alpha_{43} = 0$ and corresponds to the *nontrivial poling electric field* [Eq. (A2)]. Recall that the polarization configuration is threefold degenerate in the parameter space.

Figure 4 shows the comparison of the critical electric field computed by the modification of the simplified string method and the previous method. Here we use $P_x \propto \sin(\pi s)$, $P_y \propto \sin(2\pi s)$ as an initial guess, where s parameterizes the position along the string. The simplified string method gives a lower boundary for the critical field. One can assume the simplest approximation for the critical field value obtained by the method in a form

$$E_{\text{cr}}(n \rightarrow \infty) - E_{\text{cr}}(n) \propto n^{-1}, \quad (10)$$

where n is the number of points on a string. Justification of Eq. (10) is done in Appendix B. We apply the extrapolation Eq. (10) to the numerical data, presented in Fig. 4, to get a critical field for a continuous string ($n \rightarrow \infty$, for details see Appendix C). The extrapolated critical field is approximately 18.9 kV/mm for all the α_{43} values. This means that the *nontrivial poling electric field* [Eq. (A2)] defines poling electric field not only for $\alpha_{43} = 0$ but for all α_{43} values.

The simplified string method allows us to track the path in the configuration space that describes the polarization switching process (Fig. 5). Figure 5 shows the paths for $\alpha_{43} = 0$, $4 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$. The model is rotationally symmetric in the P_x, P_y plane for $\alpha_{43} = 0$, and therefore Fig. 5 defines only the value of $\sqrt{P_x^2 + P_y^2}$ for $\alpha_{43} = 0$. The paths are qualitatively similar for all $\alpha_{43} \neq 0$. The xy plane polarization

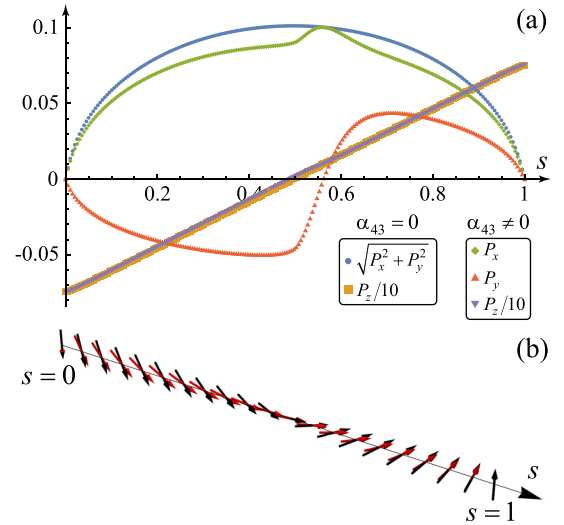


FIG. 5. Polarization configuration path during the switching process for $E_z = E_{\text{cr}}$ as a function of the distance along the string s for a single-domain congruent LiNbO_3 . The paths are computed for $\alpha_{43} = 0$ [$E_{\text{cr}} = 18.9$ kV/mm, red arrows in (b)] and $\alpha_{43} = 4 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ [$E_{\text{cr}} = 18.25$ kV/mm, black arrows in (b)]. We used the simplified string method with 200 points. (b) Every 10th point is taken.

$\sqrt{P_x^2 + P_y^2}$ perfectly obeys $\sqrt{-(\alpha_{22} + \alpha_{42}P_z^2)/\alpha_{44}}$ law which follows from minimization of the free energy Eq. (6) for all α_{43} . For $\alpha_{43} \neq 0$ and $s < 0.45$, xy polarization components satisfy $(P_x, P_y) = (\frac{\sqrt{3}}{2}P, -\frac{1}{2}P)$ ($P > 0$) and for $s > 0.75$ $(P_x, P_y) = (\frac{\sqrt{3}}{2}P, \frac{1}{2}P)$ which correspond to the minima of the term $\alpha_{43}P_yP_z(P_y^2 - 3P_x^2)$ for the negative and positive polarization component P_z . Here $s \in [0; 1]$ parameterizes the position on a string. The system must pass through a point where the $\alpha_{43}P_yP_z(P_y^2 - 3P_x^2)$ vanishes to go from one minimum to another. Therefore, it must pass through the same saddle point as $\alpha_{43} = 0$. Hence, we obtain identical (up to numerical accuracy) poling electric fields for $\forall \alpha_{43}$.

B. Congruent LiTaO_3 , near-stoichiometric LiNbO_3 and LiTaO_3

Figure 9 in Appendix C shows the number of local minima for NSLN, CLT, and NSLT. The plots are qualitatively similar to the Fig. 2(a) for CLN. However, there is a region for a small α_{43} and electric field close to the critical one, where three local minima are observed for NSLN and NSLT. This fact also sets the lowest boundary for α_{43} for near-stoichiometric compounds. From the plots, we find the range of the parameter α_{43} where the model Eq. (6) has two ground states. The upper bounds for near-stoichiometric and congruent LN and LT are the following: $\alpha_{43\text{max}} = 7 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for NSLN, $13.6 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for CLT, and $37 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for NSLT. The lowest bounds are $\alpha_{43\text{min}} = 0.65 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for NSLN and $8.5 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for NSLT.

There is a nontrivial polarization projection on xy plane (P_x and/or P_y component) in the regions with three local minima in Figs. 2(a) and 9. Consider a switching process ($E_z > 0$) in polydomain crystal. If there is a nontrivial value of P_x and/or P_y polarization component, then it leads to the appearance of charges on the faces of the domain (imagine a hexagonal

domain). There are opposite charges on the opposite faces that lead to the shrinking of the domain (in the absence of pinning effects). Only domains with $P_z > 0$ would “survive,” because there $P_x = P_y = 0$. Hence, a single-domain configuration (with $P_z > 0$ for $E_z > 0$) is formed. Therefore, the lower boundaries of the three local minima regions also define the critical electric field. The type of regions on the left side of plots for NSLN and NSLT (Fig. 9) are close to the critical electric field defined by Eq. (A2). Consequently, we assume that expression (A2) still describes the poling electric field, and we will not consider a lower boundary for α_{43} in DW calculations for near-stoichiometric compounds.

IV. DW CALCULATIONS

A. Algorithm and calculation details

In this section, we study the structure $\mathbf{P}(x)$ of one-dimensional DWs that form the xz and yz planes and compare their energies to find an optimal configuration. The algorithm we use for DW calculation is analogous to Ref. [11]. We briefly highlight the main steps: (i) rotate vectors and tensors in the xy plane by $\pi/6$ if we study X walls; (ii) calculate minimal energy strain configuration using Eqs. (21)–(23) from Ref. [11] and compute modified potential energy using Eq. (25) from Ref. [11] [note that it is different from our Eq. (3)]; (iii) choose an initial guess that connects global minima $\mathbf{P}(-\infty) = (0, 0, -P_z^{\text{vac}})$ and $\mathbf{P}(\infty) = (0, 0, P_z^{\text{vac}})$; and (iv) evolve the state using accelerated gradient descent method (namely the arrested Newton flow [11,27]) with fixed polarization boundary conditions,

$$\ddot{P}_a = -\frac{\delta F}{\delta P_a}, \quad (11)$$

where the free energy is given by Eq. (2). This method follows the same trajectory in the phase space as gradient flow [with $\dot{P}_a$ in left-hand side of Eq. (11)]. It does not provide correct time evolution but allows for much faster convergence towards the energy minimum and has better minimal energy accuracy. We are interested in static configurations of DWs. Therefore, the mathematical approach is more efficient for the problem. The procedure is repeated for various initial DW configurations, and the state with the minimal DW energy is saved. We choose the sample length l to be 100 unit cells (51.5 nm) for CLN, NSLN, NSLT, and 200 unit cells (103 nm) for CLT for numerical calculations. The doubled sample length chosen for CLT follows from the compound’s large DW width (10.7 nm) [3]. We use the finite-difference method because it is the only way to include nonlocal electrostatic interactions [Eq. (9)]. DW energy is defined as the energy of a system with stabilized DW minus the energy of the system in a uniform ground state. We investigate the influence of α_{43} term and lattice spacing on the DW energies and DW polarization profiles. By lattice spacing, we mean the distance between nearest points in a one-dimensional finite-difference method. We choose a discrete set of lattice spacing values a . The most important among the chosen a values are as follows: (i) the lattice constant $a_0 = 0.515$ nm; (ii) half of the lattice constant (≈ 0.25 nm that corresponds to the distance between closest Ta (Nb) atoms projected on the X crystal axis); (iii) a quarter of the lattice constant (≈ 0.13 nm, approximately equal

to the distance between Ta (Nb) and oxygen atoms); and (iv) one-eighth of the lattice constant (≈ 0.06 nm, approximately equal to the minimal interatomic distance projected on the X crystal axis in LiTaO₃ and LiNbO₃ compounds).

B. Domain wall polarization profiles and energies

1. No electrostatic interactions

First, we present results without electrostatic interactions. Therefore, the model is *local*. It can be viewed as a perfectly screened system. Figure 6 shows the energy ratio between Y and X wall configurations and corresponding polarization configuration profiles for congruent and near-stoichiometric compositions of lithium tantalate and lithium niobate. The green rectangle highlights the region where the ratio corresponds to experimentally observed domain configurations (Y walls for CLN, NSLN, NSLT, and X walls for CLT). The gray dashed line corresponds to lattice spacing in the calculation to be equal to half of the lattice constant. Effectively, that means considering only Ta (Nb) atom displacements. Oxygen atom contributions are also effectively included to the left of the line. To the right of the line, the model describes the mean polarization field produced by many atoms. A common feature for all the energy ratio plots Fig. 6(a) is a convergence to a constant value when lattice spacing a decreases. It is a generic feature for local Ginzburg-Landau-type models. DW thickness is much larger than unit cell and lattice spacing for congruent LiTaO₃ calculations. Therefore, one always works in the converged energy region (like in ferromagnet calculations). However, it is not always the case for CLN, NSLN, and NSLT [see Fig. 6(a)] where DW thickness is of the order of a few unit cells.

Typical polarization profiles [Fig. 6(b)] are quite easy to categorize for trigonal ferroelectrics without electrostatic interactions. When lattice spacing a is large (compared to DW thickness) and X walls are preferred (part of the plots with $E_{Y \text{ DW}}/E_{X \text{ DW}} - 1 > 0$), the first in Fig. 6(b) polarization configuration is observed. It is an unusual type of Néel domain wall. When lattice spacing a is small, and X walls are preferred, the second $\mathbf{P}$ profile in Fig. 6(b) is obtained. It is a mixed Néel-Bloch DW type. When Y walls are preferred, the polarization profile is always of the third type in Fig. 6(b). It corresponds to a Bloch-like wall. It can be viewed as two merged Bloch walls with opposite chirality called bichiral DW [28].

From Fig. 6, one can conclude that X walls are preferred for all considered compounds in the model without nonlocal electrostatics and small lattice spacing (close to the continuous limit). The parameter α_{43} significantly affects possible DW configurations. Increasing α_{43} leads to an increase of DW energy and thickness by order of a few percentages for $\alpha_{43} = 0$ and $\alpha_{43 \text{ max}}$. Moreover, it affects Bloch polarization configuration: Increasing α_{43} leads to an increase in width where $P_{\text{Bloch}} \neq 0$. The increase is of the order of 16% for CLN and CLT and of the order of 50% for NSLN and NSLT. In contrast, the width where $P_{\text{Néel}} \neq 0$ does not depend on parameter α_{43} . For $\alpha_{43 \text{ max}}$ the widths are approximately equal. The maximal value of the Néel polarization component decreases as α_{43} increases. It drops to 0.7–0.76 for $\alpha_{43 \text{ max}}$ from its value for $\alpha_{43} = 0$. However, the maximal value of

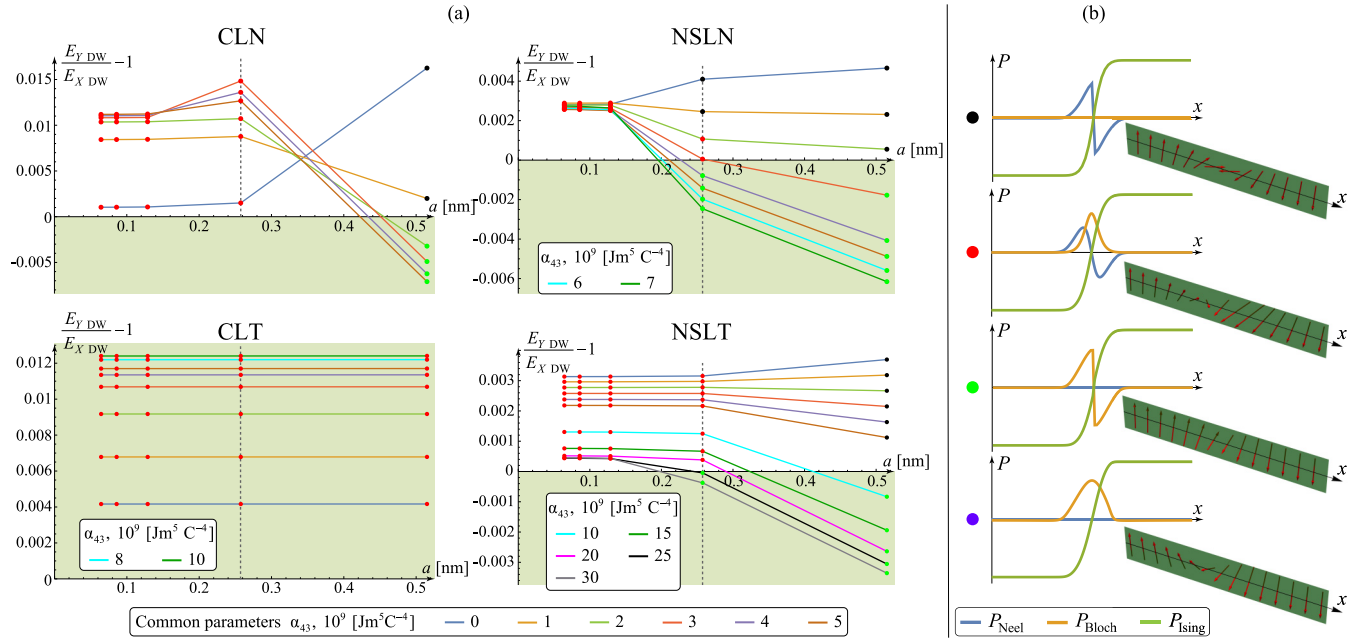


FIG. 6. (a) The energy ratio between Y and X domain wall configurations without electrostatic interactions as a function of distance between nearest points a in a finite-difference method for different values of parameter α_{43} in the allowed range (see Sec. III) for congruent and near-stoichiometric compositions of LiTaO_3 and LiNbO_3 . The green rectangle highlights the region where the ratio corresponds to experimentally observed domain configurations (Y walls for CLN, NSLN, and NSLT and X walls for CLT). The gray dashed line corresponds to lattice spacing in the calculation to be equal to half of the lattice constant [only Ta (Nb) atom displacements are considered]. The dot color corresponds to the energetically preferred polarization profile illustrated in part (b). (b) Typical domain wall polarization profiles. Ising polarization component is P_z , Néel component is a polarization projection to domain wall normal, and Bloch component is perpendicular to both of them (and perpendicular to the green plane). Néel and Bloch components are not to scale.

the Bloch polarization component remains approximately the same.

The values of amplitudes of Bloch and Néel polarization components at DW for considered compounds are presented in Table II. Typical amplitude is from a few to 10% of the ground-state polarization value. These values are achieved in the vicinity of $P_z = 0$. From minimization of Landau-Devonshire potential Eq. (6) follows that $\sqrt{P_x^2 + P_y^2} = \sqrt{-(\alpha_{22} + \alpha_{42}P_z^2)/\alpha_{44}}$. This equality holds remarkably well close to the center of any type of DW. It also works for the first and third configurations in Fig. 6(b) because there are no sites with $\mathbf{P} = 0$. The polarization line in Fig. 6(b) passes through the origin, but it is just a line to guide

the eye. In reality, it connects the points $P_{\text{Neel}} > 0$, $P_{\text{Ising}} < 0$ with $P_{\text{Neel}} < 0$, $P_{\text{Ising}} > 0$ (or $P_{\text{Bloch}} > 0$, $P_{\text{Ising}} < 0$ with $P_{\text{Bloch}} < 0$, $P_{\text{Ising}} > 0$). That is why we see a sharp change in the secondary order parameter (P_{Neel} and/or P_{Bloch}) value. The system avoids $\mathbf{P} = 0$ because it is a local maximum of potential Eq. (6). From the expression $\max(\sqrt{P_x^2 + P_y^2}) = \sqrt{-\alpha_{22}/\alpha_{44}}$ for vanishing P_z component. Comparing this analytical result to the values in Table II, one obtains that numerical values are smaller than analytical value by 0.1%. The difference originates from the discretization of the polarization configuration on a DW. This fact tells us that the potential energy $\tilde{V}(\mathbf{P})$ significantly contributes to the DW profile.

TABLE II. Maximal values of polarization components P_{Neel} , P_{Bloch} for optimal domain wall configurations with $\alpha_{43} = 0$ and lattice spacing in finite-difference method $a \approx 0.06$ nm. The results are presented for cases without and with nonlocal electrostatic interactions Eq. (9).

		CLT	NSLT	CLN	NSLN	Units
No electrostatics	$\max P_{\text{Neel}} $	7.6	3.0	8.6	4.6	$10^{-2}P_z^{\text{vac}}$
	$\max P_{\text{Bloch}} $	11.2	3.7	13.5	6.2	$10^{-2}P_z^{\text{vac}}$
	$\max\sqrt{P_{\text{Neel}}^2 + P_{\text{Bloch}}^2}$	11.2	3.7	13.5	6.2	$10^{-2}P_z^{\text{vac}}$
Electrostatics	$\max P_{\text{Neel}} $	2.3	0.9	2.4	1.9	$10^{-4}P_z^{\text{vac}}$
	$\max P_{\text{Bloch}} $	11.2	3.7	13.5	6.2	$10^{-2}P_z^{\text{vac}}$
	$\max\sqrt{P_{\text{Neel}}^2 + P_{\text{Bloch}}^2}$	11.2	3.7	13.5	6.2	$10^{-2}P_z^{\text{vac}}$

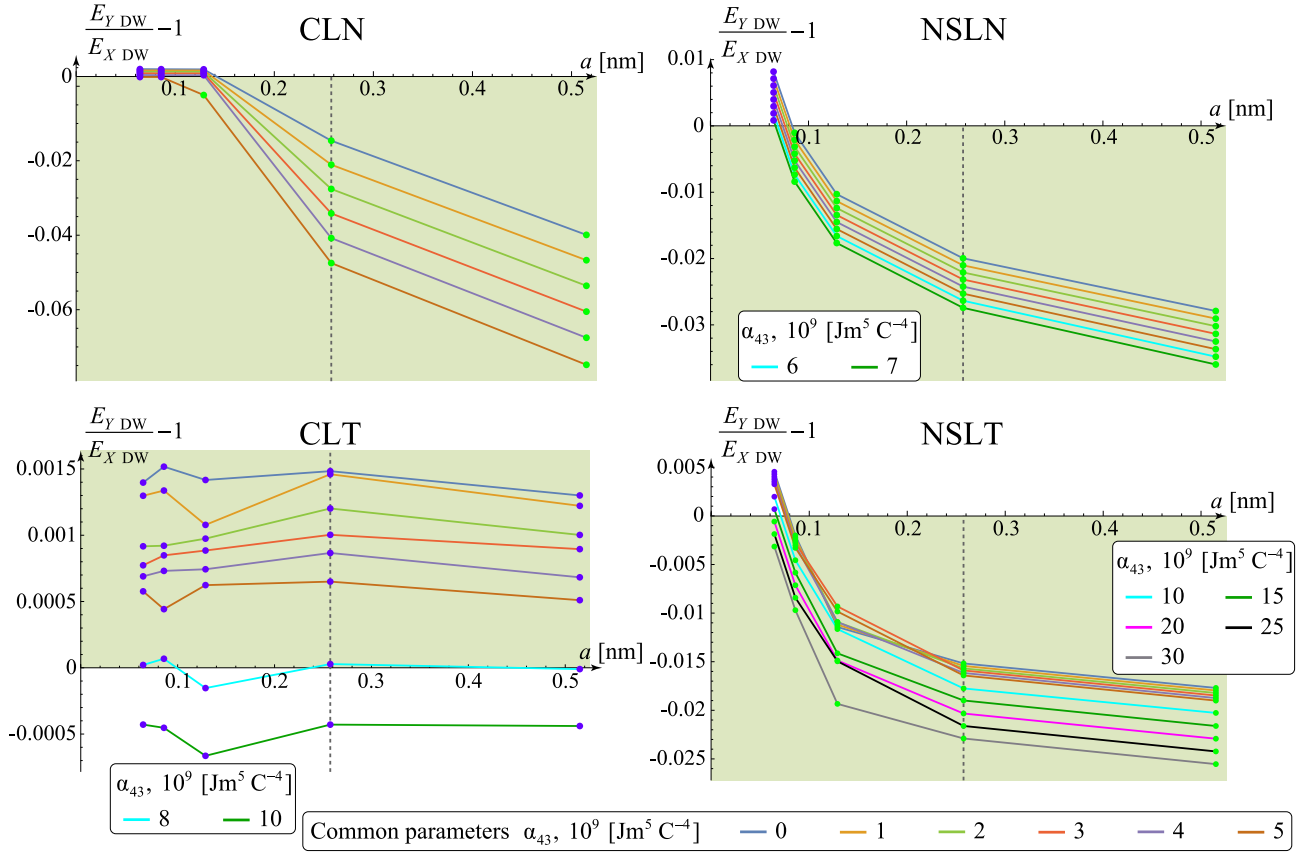


FIG. 7. The energy ratio between Y and X domain wall configurations with nonlocal electrostatic interactions as a function of distance between nearest points a in a finite-difference method for different values of parameter α_{43} in the allowed range (see Sec. III) for congruent and near-stoichiometric compositions of LiTaO_3 and LiNbO_3 . The green rectangle highlights the region where the ratio corresponds to experimentally observed domain configurations (Y walls for CLN, NSLN, and NSLT and X walls for CLT). The gray dashed line corresponds to lattice spacing in the calculation to be equal to half of the lattice constant [only Ta (Nb) atom displacements are considered]. The color of the dot corresponds to the energetically preferred polarization profile illustrated in Fig. 6(b).

2. Nonlocal electrostatic interactions

In this subsection, we add electrostatic interactions Eq. (9) to the total free energy. The results of the DW calculation are presented in Fig. 7. We choose sample width b (along the DW plane) to be 200 of sample length l . It is $10.3 \mu\text{m}$ for CLN, NSLN, and NSLT and $20.6 \mu\text{m}$ for CLT. The main difference when electrostatic interactions are included is the absence of energy convergence. By this, we mean that a nonuniform polarization configuration $\mathbf{P}(x)$ (with nontrivial Néel and Bloch components) has different energy depending on lattice spacing. The smaller the lattice spacing, the higher the electrostatic energy is due to its nonlocal nature. Therefore, we restrict the smallest lattice spacing to be $\approx 0.06 \text{ nm}$, which equals the minimal interatomic distance for the compounds considered.

The generic feature is a vanishingly small Néel polarization component for all DWs in the approach (see Table II). The origin comes from the high energy penalty from the first term in Eq. (9). Therefore, all DWs have a Bloch-like character [the third configuration in Fig. 6(b), so-called bichiral DW] or a pure Bloch character (the fourth configuration). Another important aspect is a nonvanishing Bloch polarization component far from DW for the fourth configuration in Fig. 6(b). The sign of the nonvanishing long-range Bloch component is

opposite to the sign of the Bloch component in the vicinity of DW. The origin again comes from the nonlocal electrostatic interactions: The system prefers to create extra charges on xz faces far from a DW, which cost potential energy but have negative electrostatic energy due to interaction with opposite charges on xz faces in the DW vicinity.

Note the change of the optimal DW polarization profile from the third one [illustrated in Fig. 6(b)] to the fourth one when decreasing lattice spacing a for CLN, NSLN, and NSLT and fixed α_{43} . Both polarization configurations have a nontrivial Bloch polarization component and zero Néel one. The difference is a rapid sign change of the Bloch polarization component near $P_z = 0$ for one of them and smooth kinklike Bloch polarization behavior for another. It comes from the competition between gradient energy (which tries to keep a smooth $\mathbf{P}$ profile) and electrostatic energy (which benefits from sign-changing polarization because it creates closely spaced opposite charges) together with potential energy term $\alpha_{43} P_y P_z (P_y^2 - 3P_x^2)$ (which tries to keep opposite signs for P_y and P_z). The cost of sign change of Bloch polarization component is inversely proportional to a , and the gain is approximately linear in a [29]. Therefore, the gradient term dominates and keeps polarization smooth for small lattice

TABLE III. Average value of the energy of an optimal domain wall for LiTaO₃ and LiNbO₃ compounds.

	CLT	NSLT	CLN	NSLN	Units
No electrostatics	191	17.7	55.6	45.5	mJ/m ²
Electrostatics	204	17.8	57.5	46.0	mJ/m ²

spacing. It also dominates for CLT for all lattice spacing values because the gradient coefficient is very large (see Table I), which originates from large DW width [3]. However, for the large values of α_{43} (as can be seen for NSLT in Fig. 7), sign change is favorable, as described above.

3. Analysis of domain wall energies

In this subsection, we analyze the optimal DW energies obtained by all described above methods (Table III) and compare them to values obtained from other theoretical and experimental approaches (Table IV).

Table III contains average optimal DW energy. It is defined as the mean of the optimal DW energy for all the lattice spacing values written in Sec. IV A and all α_{43} parameter values presented in Figs. 6 and 7. The average DW energy standard deviation is of the order of 1% for CLN, NSLN, and CLT and 0.16% for NSLT. The trend is that near-stoichiometric material has lower DW energy than congruent one for LN and LT. However, the authors of Ref. [30] give the opposite prediction for both compounds based on the interactions of the cation antisite defects with the DW.

DW energy estimates from the literature are summarized in Table IV. Theoretical approaches include the DFT [9,30], atomistic calculations with empirical potentials [9], and Ginzburg-Landau-Devonshire [4] models. We placed results of Ref. [4] to congruent materials because they used material parameters for congruent ones; however, their model did not take into account defects explicitly. Experimental estimates are based on DW velocity [4,32] and activation value of the electric field for movement of 180° DWs. We do not include estimates based on DW curvature in external field [33] and optical birefringence deviation [34] because they use an assumption that DW affects the region of microns scale away, which is not the case in our theory. However, DW energy estimates in Refs. [33,34] are quite close to our results for CLT.

Another important energy-related aspect is the relative energy difference between X- and Y-oriented DWs. In our case it is of the order 10^{-3} – 10^{-2} [see Figs. 6(a) and 7]. Previous phenomenological theory for trigonal ferroelectrics [4] gives 10^{-7} relative difference. The difference is 10^{-2} – 10^{-1} for the

TABLE IV. Domain wall energy for LiTaO₃ and LiNbO₃ compounds calculated in other works.

	CLT	NSLT	CLN	NSLN	Units
Theory	60 [4]	60 [30]	170 [4]	160 [9] 255 [9]	mJ/m ²
Experiment	35 [31]	>9 [4,32]			mJ/m ²

DFT approach [30]. The quantity cannot be accessed experimentally. However, the almost circular domain shape, which is observed quite regularly [3,6,35,36] allows us to assume that the difference should be small.

4. Comparison between domain walls with and without electrostatic interactions

A general trend that holds for both simulation types for CLN, NSLN, and NSLT is that for large lattice spacing system prefers to have a rapid sign-changing jump in non-Ising polarization component in the vicinity $P_z = 0$. For small lattice spacing, the polarization profile is smooth. The reason is the competition between gradient energy and potential energy terms (together with electrostatic) described above in detail.

Calculation shows that X walls are preferred for CLN without electrostatic interaction, which contradicts experimental observations. However, including electrostatic interactions makes Y walls energetically preferred for lattice spacing a equal to half of the lattice constant (≈ 0.25 nm) for all allowed values of parameter α_{43} . For lattice spacing equal to a quarter of the lattice constant, only $\alpha_{43} \approx 5 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ gives optimal Y DW. The optimal DWs with Y orientation have bichiral character illustrated in the third profile in Fig. 6(b).

For NSLN without electrostatic interactions Y walls (experimentally observed) can be obtained for a equal to half of the lattice constant and $\alpha_{43} > 3 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$. When nonlocal electrostatic interactions are considered, the Y walls are favorable for lattice spacing greater than one-eighth of the lattice constant for all allowed values of parameter α_{43} . The Y walls always have bichiral character.

For CLT without electrostatics, X walls are always preferred, and with nonlocal electrostatics, they are preferred when $\alpha_{43} < 8 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$. DWs are of mixed Bloch-Néel type in the former case and pure Bloch type in the latter case. Interestingly, increasing parameter α_{43} leads to increasing relative energy difference between X and Y DWs for the case without electrostatic interactions but has the opposite trend with electrostatic interactions.

For NSLT picture is qualitatively similar to the NSLN results. Without electrostatic interactions, only high values of parameter α_{43} give energetically optimal Y walls for large lattice spacing a . While including electrostatic interactions prefers Y walls for most values of α_{43} parameter and lattice spacing. The polarization profile has bichiral nature.

V. DISCUSSION

Here we discuss the limitations of the nonlocal electrostatic interaction used and speculate about potential changes in results in more advanced electrostatic calculations.

The nonlocal electrostatic interaction model we use is based on the assumption of infinite thickness in the z direction (along ground-state polarization). This approximation holds for X-cut and Y-cut LiNbO₃ and LiTaO₃. It means the crystal is cut perpendicular to the X (Y) crystal axis, and the thickness in this dimension is on the order of micrometers. A comparison of a more advanced model for nonlocal interactions [37] with the ferromagnetic analog of interaction we use Ref. [23] shows qualitative agreement in the

DW type in the central cross section. This more advanced model allows magnetization to vary through the film thickness by cutting the sample into square prisms that have infinite length in the z direction. Authors of Ref. [37] found that DW thickness increases and DW energy decreases when going from one-dimensional to two-dimensional implementation of nonlocal interactions. The DW energy decrease mostly comes from nonlocal interaction energy reduction (from 35% to 1%) due to nonuniform magnetization profile in ferromagnet.

Results for two-dimensional calculations for ferroelectric material cannot be directly predicted from ferromagnetic calculations in Ref. [37]. The main reason is that the magnetization vector length is fixed, but polarization vector lacks this constraint. One-dimensional DW calculations with nonlocal interactions for ferromagnet show that these interactions give 35% contribution to the DW energy. However, similar calculations for ferroelectric in this paper show that nonlocal interactions highly penalize the Néel component and have less than 1% contribution to the DW energy. Therefore, the Bloch DW configuration is preferred in one-dimensional calculations. Two-dimensional calculations of Bloch DW for ferroelectric would unfavor the Bloch component next to the edges. Hence, a nonuniform polarization configuration next to the edges should form. We expect that nonlocal electrostatic interactions should have a significant contribution to the DW energy in this case. This would lead to an increase in DW energy compared to current calculations.

VI. CONCLUSION

Domain wall structure in trigonal ferroelectrics is difficult to access from the experimental side. There are observed evidences of chiral properties of domain walls in lithium tantalate [7] and lithium niobate [1,6]. Some theoretical approaches also support the non-Ising character of domain walls in LiTaO₃ [8,9].

In this work, we develop a phenomenological model that supports non-Ising optimal path for the poling process with Néel and/or Bloch polarization components of the order from 1 to 10% of spontaneous polarization. It is implemented by adding higher-order terms and adjusting coefficients that $\mathbf{P} = 0$ is a local maximum instead of a saddle point. The nontrivial optimal path for the poling process gives coercive field values consistent with the experiment. The coercive field is independent on coefficient α_{43} in front of P_x, P_y asymmetric term $P_y P_z (P_y^2 - 3P_x^2)$ and defined by Eq. (A2). This coefficient α_{43} gives additional degree of freedom to the model and allows to favor X or Y type of domain wall orientation. The other model coefficients are presented in Table I. They are derived from material constants for near-stoichiometric and congruent LiNbO₃ and LiTaO₃. The effect of nonstoichiometry is captured by using material constants, coercive field, and spontaneous polarization for congruent materials. It can be seen as a mean-field treatment of the influence of internal defects.

We studied optimal domain-wall polarization profile and energetics in two cases: no electrostatic interactions and nonlocal electrostatic interactions. We found parameter ranges in our model that lead to energetically favorable domain

wall orientations consistent with experimental observations. For near-stoichiometric LiTaO₃ and LiNbO₃ and congruent lithium niobate, the optimal domain wall profile has bichiral Bloch behavior. The picture for congruent lithium tantalate is more sophisticated: The domain wall has a mixed Bloch-Néel type without including electrostatic interactions and a Bloch character when nonlocal electrostatic interactions are accounted for. Domain wall energy relative difference for X and Y orientations is of the order 10^{-3} – 10^{-2} .

Further steps for the model development include investigating the domain wall structure in the domain wall plane, which requires two-dimensional (three-dimensional) calculations. Moreover, the calculation of domain wall properties with nonlocal electrostatics in higher than one dimension could lead to a qualitative difference in the polarization profiles found in ferromagnets [37]. In particular, they found that the spatial extent of the two-dimensional domain wall is considerably greater than its one-dimensional counterpart. Another direction is to look at the influence of electro-optic coefficients [38] due to additional quartic terms in the free energy and study the influence of the domain wall on them, which was measured in experiment [34].

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: RELATIONS BETWEEN MATERIAL CONSTANTS AND GINZBURG-LANDAU-DEVONSHIRE FREE ENERGY

The model in Eq. (6) has a ground state $\mathbf{P}^{\text{vac}} = (0, 0, \pm P_z^{\text{vac}})$ with z component of polarization value,

$$P_z^{\text{vac}} = \sqrt{\frac{\alpha_{21}}{\tilde{\alpha}_{41}}}. \quad (\text{A1})$$

There are two possible critical points (assuming $\alpha_{43} = 0$) when electric field $\mathbf{E}_c = (0, 0, E_c)$ is applied: (i) *trivial poling electric field* $\mathbf{P} = (0, 0, \pm \sqrt{\frac{\alpha_{21}}{3\tilde{\alpha}_{41}}})$, $E_c = \mp \frac{2\alpha_{21}^{3/2}}{3\sqrt{3}\tilde{\alpha}_{41}}$ [10] which corresponds to Ising-type of polarization switching; (ii) *non-trivial poling electric field*:

$$\mathbf{P} = \left(0, 0, \pm \sqrt{\frac{-\alpha_{22}}{\tilde{\alpha}_{42}}}\right), \quad E_c = \mp \frac{\sqrt{-\alpha_{22}}(\alpha_{22}\tilde{\alpha}_{41} + \alpha_{21}\tilde{\alpha}_{42})}{\tilde{\alpha}_{42}^{3/2}}. \quad (\text{A2})$$

At this point, quadratic terms proportional to $P_x^2 + P_y^2$ vanish. Therefore, the potential $\tilde{V}^o$ in P_x, P_y plane becomes flat. In the absence of an electric field, it is a minimum. However, it is a saddle point for the electric value field given in Eq. (A2), which is confirmed by numerical calculations in Sec. III.

The following two subsections describe relations between experimental observables and Ginzburg-Landau-Devonshire free-energy coefficients. Then, explicit forms of the main tensors and the material parameters used will be provided. Later, we give explicit forms for the inequalities that arise from the model constraints introduced in Sec. II B. Last, we present an algorithm for parameter determination of Ginzburg-Landau-Devonshire free energy for LN and LT.

1. Relations between dielectric permittivity and free-energy parameters

Dielectric displacement in SI units has form

$$\mathbf{D}(\mathbf{E}) = \epsilon_0 \mathbf{E} + \mathbf{P}(\mathbf{E}). \quad (\text{A3})$$

Spontaneous polarization is the distinctive feature of ferroelectrics (namely, $|\mathbf{P}(0)| = |\mathbf{P}^{\text{vac}}| \neq 0$), which leads to hysteresis loop on $P(E)$ diagram. The materials are treated as piezoelectrics [where $\mathbf{P}(0) = 0$] in the many experimental papers [39–42], and consequently the dielectric permittivity tensor can be introduced in the following form [43]: $D_i = \epsilon_{ij}^T E_j + d_{ijk} \sigma_{jk}$, where the superscript T means at constant stress, σ_{jk} is a stress tensor. However, one needs to modify the expression to describe a ferroelectric with uniform spontaneous polarization (assuming stress-free boundary conditions):

$$D_i = \epsilon_{ij}^T E_j + P_i^{\text{vac}}, \quad (\text{A4})$$

which is valid for a weak external field [44]. Here we neglect the effect of background permittivity [2,6,45,46].

For a weak external electric field, one can Taylor expand polarization, which minimizes free energy Eq. (6) with the term $-\mathbf{P}\mathbf{E}$ describing interaction with external field:

$$P_i(\mathbf{E}) = P_i^{\text{vac}} + \left. \frac{\partial P_i}{\partial E_j} \right|_{\mathbf{P}=\mathbf{P}^{\text{vac}}} E_j. \quad (\text{A5})$$

Equating the expression to the polarization, which is derived from Eqs. (A3) and (A4), one comes to the result

$$\epsilon_{ij}^T E_j = \epsilon_0 E_i + \left. \frac{\partial P_i}{\partial E_j} \right|_{\mathbf{P}=\mathbf{P}^{\text{vac}}} E_j, \quad (\text{A6})$$

where the second term is

$$\left. \frac{\partial P_i}{\partial E_j} \right|_{\mathbf{P}^{\text{vac}}} = \begin{pmatrix} \frac{\tilde{\alpha}_{41}}{\alpha_{22}\tilde{\alpha}_{41} + \alpha_{21}\tilde{\alpha}_{42}} & 0 & 0 \\ 0 & \frac{\tilde{\alpha}_{41}}{\alpha_{22}\tilde{\alpha}_{41} + \alpha_{21}\tilde{\alpha}_{42}} & 0 \\ 0 & 0 & \frac{1}{2\alpha_{21}} \end{pmatrix}. \quad (\text{A7})$$

Therefore, the dielectric permittivity tensor is diagonal and corresponds to a uniaxial crystal structure:

$$\epsilon_{ij}^T = \begin{pmatrix} \epsilon_{11}^T & 0 & 0 \\ 0 & \epsilon_{11}^T & 0 \\ 0 & 0 & \epsilon_{33}^T \end{pmatrix}, \quad (\text{A8})$$

with

$$\epsilon_{11}^T = \epsilon_{r11}^T \epsilon_0 = \epsilon_0 + \frac{\tilde{\alpha}_{41}}{\alpha_{22}\tilde{\alpha}_{41} + \alpha_{21}\tilde{\alpha}_{42}}, \quad (\text{A9})$$

$$\epsilon_{33}^T = \epsilon_{r33}^T \epsilon_0 = \epsilon_0 + \frac{1}{2\alpha_{21}}. \quad (\text{A10})$$

Here the subscript r means relative permittivity.

Approximating certain aspects of a ferroelectric as a piezoelectric in experiments may be justified in the case of a large polydomain piezoelectric crystal, such that $\langle \mathbf{P}(0) \rangle = 0$ with the assumption that domain walls occupy volume much smaller than the volume of a sample (which matches experimental observations).

2. Relations between piezoelectric constants and free-energy parameters

Consider a case of a uniform spontaneous polarization of ferroelectric crystal. Using results of Appendix A 1 one can write polarization in the form

$$P_i(\mathbf{E}) = P_i^{\text{vac}} + (\epsilon_{ij}^T - \epsilon_0) E_j. \quad (\text{A11})$$

Equilibrium strain in the presence of a weak external electric field can be written as (see Ref. [11])

$$\epsilon_\alpha = Q_{\alpha ij}^o P_i(\mathbf{E}) P_j(\mathbf{E}) \approx \epsilon_\alpha^{\text{vac}} + 2Q_{\alpha ij}^o P_i^{\text{vac}} (\epsilon_{jk}^T - \epsilon_0) E_k. \quad (\text{A12})$$

One can directly [43] or indirectly [41,42] measure piezoelectric constant d_{ijk} ($d_{i\alpha}$ in Voigt notation), which describes change of the strain under external electric field (for converse piezoelectric effect in the absence of external stress):

$$\epsilon_\alpha - \epsilon_\alpha^{\text{vac}} = d_{i\alpha} E_i. \quad (\text{A13})$$

Both expressions Eq. (A12) and Eq. (A13) should give identical results. Consequently, we have the following equality:

$$2Q_{\alpha ij}^o P_i^{\text{vac}} (\epsilon_{jk}^T - \epsilon_0) E_k = d_{i\alpha} E_i, \quad (\text{A14})$$

which should be satisfied for each α . From the six equations, one can obtain the following nonzero values of Q^o tensor:

$$\begin{aligned} Q_{232}^o &= Q_{223}^o = -Q_{132}^o = -Q_{123}^o = -\frac{1}{2}Q_{631}^o = -\frac{1}{2}Q_{613}^o \\ &= \frac{d_{22}}{2P_z^{\text{vac}}(\epsilon_{11}^T - \epsilon_0)}, \\ Q_{133}^o &= Q_{233}^o = \frac{d_{31}}{2P_z^{\text{vac}}(\epsilon_{33}^T - \epsilon_0)}, \quad Q_{333}^o = \frac{d_{33}}{2P_z^{\text{vac}}(\epsilon_{33}^T - \epsilon_0)}, \\ Q_{432}^o &= Q_{423}^o = Q_{531}^o = Q_{513}^o = \frac{d_{15}}{2P_z^{\text{vac}}(\epsilon_{11}^T - \epsilon_0)}. \end{aligned} \quad (\text{A15})$$

One can find tensor q^o which couples strain to polarization knowing the Q^o tensor and using relation $q_{\alpha ij}^o = C_{\alpha\beta}^o Q_{\beta ij}^o$. Then electrostriction coupling coefficients γ_p in Eq. (7) have form

$$\begin{aligned} \gamma_1 &= -[(C_{11} + C_{12})Q_{133}^o + C_{13}Q_{333}^o], \\ \gamma_2 &= -(2C_{13}Q_{133}^o + C_{33}Q_{333}^o), \\ \gamma_3 &= 2[(C_{11} - C_{12})Q_{232}^o - C_{14}Q_{432}^o], \\ \gamma_4 &= 2(2C_{14}Q_{232}^o - C_{44}Q_{432}^o). \end{aligned} \quad (\text{A16})$$

TABLE V. Relevant physical constants of LiTaO₃ and LiNbO₃.

	CLT	NSLT	CLN	NSLN	Units
ε_{r11}^S	41.7	41.7	45.0791	44.5470	
ε_{r33}^S	41.6721	39.4100	26.6702	25.0996	
C_{11}	2.3298	2.3610	1.9872	2.0250	$\times 10^{11}$ N/m ²
C_{12}	0.4638	0.4787	0.5455	0.5749	$\times 10^{11}$ N/m ²
C_{13}	0.8352	0.8362	0.6805	0.69413	$\times 10^{11}$ N/m ²
C_{14}	-0.1064	-0.0961	0.0774	0.0989	$\times 10^{11}$ N/m ²
C_{33}	2.7572	2.7951	2.3415	2.3818	$\times 10^{11}$ N/m ²
C_{44}	0.9516	0.9552	0.5987	0.5866	$\times 10^{11}$ N/m ²
e_{15}	2.6306	2.8152	3.6510	3.9188	C/m ²
e_{22}	1.8290	1.9470	2.4039	2.5351	C/m ²
e_{31}	-0.1160	0.01121	0.3282	0.2648	C/m ²
e_{33}	1.7919	1.6790	1.8845	1.7485	C/m ²
E_f	21.15	1.7	21	4.5	$\times 10^6$ V/m
E_r	12.6	1.5	16.8	3.31	$\times 10^6$ V/m
P_z^{vac}	0.6	0.55	0.75	0.8	C/m ²

Effective potential $\tilde{V}^o$ has two terms ($\tilde{\alpha}_{41}$, $\tilde{\alpha}_{42}$) different from V^o terms related by Eq. (3):

$$\alpha_{41} = \tilde{\alpha}_{41} + 4 \left(C_{11} Q_{133}^o + C_{12} Q_{133}^o + 2C_{13} Q_{133}^o Q_{333}^o + \frac{1}{2} C_{33} Q_{333}^o \right), \quad (\text{A17})$$

$$\alpha_{42} = \tilde{\alpha}_{42} + 4 [2Q_{232}^o (C_{11} - C_{12}) + Q_{432}^o (C_{44} Q_{432}^o - 4C_{14} Q_{232}^o)]. \quad (\text{A18})$$

3. Explicit form of tensors and material constants

In this subsection, we first provide an explicit form of tensors we use to describe the ferroelectric crystal of point group $3m$ (C_{3v}). Then, we describe how material constants in Table V were extracted and calculated from experimental data.

Elastic tensor C_{ijkl} ($C_{\alpha\beta}$) has form [39,43,47,48]

$$C_{\alpha\beta} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & \frac{C_{11}-C_{12}}{2} \end{pmatrix}. \quad (\text{A19})$$

Piezoelectric tensor d_{ijk} ($d_{i\alpha}$ in Voigt notation, [d_{ijk}] = m/V) has the following form:

$$d_{i\alpha} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (\text{A20})$$

and often written through another piezoelectric tensor e_{imn} ($[e_{imn}] = \text{C/m}^2$) as

$$d_{i\alpha} = e_{i\beta} (C^{-1})_{\beta\alpha}. \quad (\text{A21})$$

It can be found from measurements of the propagation characteristics of leaky surface acoustic waves [41,42] and has the

following form [39,43,47,48]:

$$e_{i\alpha} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & -e_{22} \\ -e_{22} & e_{22} & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix}. \quad (\text{A22})$$

The relation between dielectric permittivity tensor at constant stress and constant strain [43]:

$$\varepsilon_{ij}^T = \varepsilon_{ij}^S + e_{i\alpha} d_{j\alpha}. \quad (\text{A23})$$

Elastic $C_{\alpha\beta}$, piezoelectric $e_{i\alpha}$, and dielectric ε_{rii}^S constants are calculated from ultrasonic microspectroscopy data for different compositions of LN and LT at room temperature [49]. We use linear interpolation to find material constants for CLN, NSLN, CLT, and NSLT which correspond to 48.38 [50], 49.8 [13], 48.5 [51], and 49.9 [13] mol % LiO₂ content in the compounds [52].

Ground-state polarization, forward and rear poling electric fields are taken from Refs. [14,16] for CLN, [16] for NSLN, Ref. [15] for CLT, and Ref. [13] for NSLT.

DW thickness is usually extracted using the fit of the Ising component of polarization with $P_z = P_z^{\text{vac}} \tanh(x/\omega_0)$. We use DW thickness $2\omega_0 = 1.464$ nm for CLN and NSLN, which was extracted from experimental paper [1] (measured CLN by aberration-corrected scanning transmission electron microscopy) by authors of Ref. [2]. We use averaged results of paper [3] for DW thickness of CLT (10.7 nm) and NSLT (2.9 nm) where scanning nonlinear dielectric microscopy technique was used.

4. Constraints

In order to ensure condition (iii) in Sec. II B about the existence of a saddle point $P_x^2 + P_y^2 = \frac{-\alpha_{22}}{\alpha_{44}}$, $P_z = 0$ determinant of the Hessian matrix at the saddle point (region) should be negative:

$$\alpha_{21}\alpha_{22} + \frac{\alpha_{22}^2 \tilde{\alpha}_{42}}{\alpha_{44}} < 0, \quad (\text{A24})$$

which leads to lower bound for parameter α_{44}

$$\alpha_{44} > \alpha_{44}^{\min} = -\frac{\alpha_{22}\tilde{\alpha}_{42}}{\alpha_{21}}. \quad (\text{A25})$$

For the condition (v) (energy at the critical point Eq. (A2) should be larger than the energy at the saddle point $P_x^2 + P_y^2 = \frac{-\alpha_{22}}{\alpha_{44}}$, $P_z = 0$ we have

$$\frac{-\alpha_{22}(3\alpha_{22}\tilde{\alpha}_{41} + 2\alpha_{21}\tilde{\alpha}_{42})}{4\tilde{\alpha}_{42}^2} > \frac{-\alpha_{22}^2}{4\alpha_{44}}, \quad (\text{A26})$$

which gives upper bound for α_{44} :

$$\alpha_{44} < \alpha_{44}^{\max} = \frac{\alpha_{22}\tilde{\alpha}_{42}^2}{3\alpha_{22}\tilde{\alpha}_{41} + 2\alpha_{21}\tilde{\alpha}_{42}}. \quad (\text{A27})$$

Condition (iv) (energy at the saddle point is higher than the energy in global minimum $\mathbf{P}^{\text{vac}}$) gives inequality

$$\alpha_{44} > \frac{\alpha_{22}^2 \tilde{\alpha}_{41}}{\alpha_{21}^2}. \quad (\text{A28})$$

However, for LN and LT, the inequality is less restrictive than Eq. (A25) (which is checked numerically).

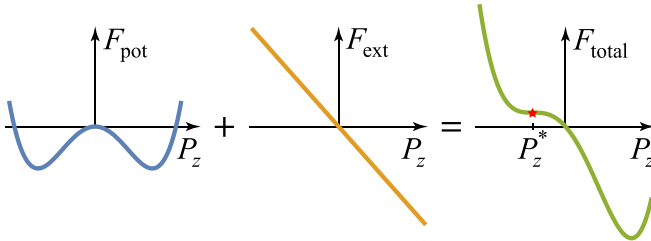


FIG. 8. Free-energy density (component-wise and total) as a function of polarization component P_z at the critical value of the electric field.

5. Parameter determination algorithm for Ginzburg-Landau-Devonshire free energy

We assume the Ginzburg-Landau-Devonshire model in Eq. (6) without electrostatic interactions and $\alpha_{43} = 0$. The algorithm is as follows:

1. Compute d , Q^o , ε tensor components and electrostriction coupling coefficients γ_p using Eqs. (A21), (A15), (A23) and (A16), respectively.
2. Compute α_{21} from Eq. (A10).
3. Compute $\tilde{\alpha}_{41}$ from Eq. (A1) and then α_{41} from Eq. (A17).
4. Substitute α_{22} from Eq. (A9) into the critical electric field Eq. (A2) (we use the electric field value, which is the mean of the forward and rear values in Table V). Numerically solve the cubic equation for $\tilde{\alpha}_{42}$. Choose the largest real root [53]. Compute α_{42} from Eq. (A18) and α_{22} from Eq. (A9).
5. Compute bounds for α_{44} using Eqs. (A25) and (A27) and choose an intermediate value for the parameter.
6. Gradient terms are obtained by adjusting DW width $2\omega_0$ [computed by fitting DW calculation results with $P_z = P_z^{\text{vac}} \tanh(x/\omega_0)$] to a value, presented in Appendix A 3. We choose $\alpha_{43} = 0$ without electrostatic interactions for the DW calculation. DW orientation corresponds to the Y wall for CLN, NSLN, NSLT ($N = 800$, sample length 51.5 nm) and X wall for CLT ($N = 1600$, sample length 103 nm).

APPENDIX B: THE SIMPLIFIED STRING METHOD

The fundamental idea of the string method is to evolve a curve that connects two minima separated by a saddle point. Each point of the curve corresponds to a certain polarization configuration $\mathbf{P}(s, t)$, where $s \in [0; 1]$ parameterizes the position on a curve, t is a pseudotime. The string is discretized to n evenly spaced points $s_i = \frac{i-1}{n-1}$. At each time step, we minimize free energy [Eq. (6)] at all points s_i using the gradient descent method

$$\frac{d}{dt} P_i(s_j, t) = - \left. \frac{\partial F}{\partial P_i} \right|_{\mathbf{P}=\mathbf{P}(s_j, t)} \quad (\text{B1})$$

which connects the local minimum (or a saddle point) in the vicinity of $\mathbf{P} = (0, 0, -P_z^{\text{vac}})$ (position $s = 0$) and global minimum in the vicinity of $\mathbf{P} = (0, 0, P_z^{\text{vac}})$ ($s = 1$). The end points are fixed.

The initial guess for a string configuration is

$$P_z(s_i, 0) = s_i P_z(s = 0) + (1 - s_i) P_z(s = 1), \quad (\text{B2})$$

P_x and P_y at the point i are taken in the form $a \sin(\pi s_i p)$ plus random fluctuations, where a is some constant ($|a| \ll 1$), $p = 1, 2$.

After the minimization process, points s_i become unevenly spaced. The next step is to reparameterize the string. The measure of distance d_i between two points $\mathbf{P}(s_i)$ and $\mathbf{P}(s_{i+1})$ is

$$d_i = \sqrt{[\mathbf{P}(s_{i+1}) - \mathbf{P}(s_i)]^2}. \quad (\text{B3})$$

Then, the position on a string is determined by

$$s_k = \frac{\sum_{i=1}^k d_i}{\sum_{i=1}^{n-1} d_i}. \quad (\text{B4})$$

To reparameterize the string, we linearly resample the configurations to new positions $s_i^{\text{new}} = \frac{i-1}{n-1}$. If $s_{k-1} < s_i^{\text{new}} < s_k$, then the resampled configuration at that point is given by

$$\frac{s_k - s_i^{\text{new}}}{s_k - s_{k-1}} \mathbf{P}(s_{k-1}, t) + \frac{s_i^{\text{new}} - s_{k-1}}{s_k - s_{k-1}} \mathbf{P}(s_k, t), \quad (\text{B5})$$

which becomes the input to the minimization step at the next time step. The procedure is repeated until convergence.

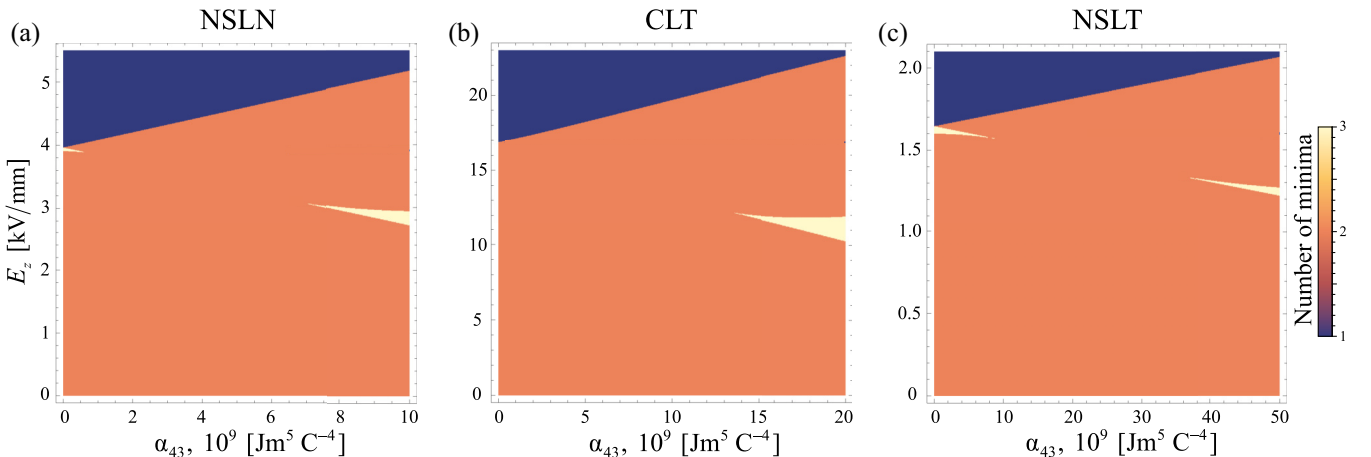


FIG. 9. The number of local minima for the free energy Eq. (6) for a single-domain crystal assuming $P_x = 0$. (a) Near-stoichiometric LiNbO₃, (b) congruent LiTaO₃, and (c) near-stoichiometric LiTaO₃.

The process generates a low-energy path in the configuration space that joins two minima and gives the energy barrier value between two configurations. We adopt it to find critical electric field for single-domain case. We increase the external field $\mathbf{E}$ until the simplified string method gives the result of no local maxima on the low-energy path. This means that the system can switch from the state with $P_z < 0$ to $P_z > 0$ due to the absence of an energy barrier. The electric field value is what we call the critical field value.

Justification of Eq. (10)

In the main text, we use an approximation that the critical electric field, given by the simplified string method, converges from below to a continuous approach result, and their difference is inversely proportional to the number of points on a string. Let us consider a simplified one-dimensional model with only polarization component P_z in the external field E_z :

$$F(P_z) = F_{\text{pot}}(P_z) - E_z P_z. \quad (\text{B6})$$

Critical electric field is determined by

$$\left. \frac{\partial F}{\partial P_z} \right|_{P_z^*} = F'_{\text{pot}}(P_z^*) - E_{z\infty} = 0, \quad \left. \frac{\partial^2 F}{\partial P_z^2} \right|_{P_z^*} = 0, \quad (\text{B7})$$

where P_z^* is the polarization value at the saddle point of F . The potential part of the free energy can be Taylor expanded in the vicinity of the point P_z^* :

$$F_{\text{pot}}(P_z) \approx F'_{\text{pot}}(P_z^*)(P_z - P_z^*) - \frac{F''_{\text{pot}}(P_z^*)}{2}(P_z - P_z^*)^2 \text{sgn}(P_z - P_z^*), \quad (\text{B8})$$

where the quadratic term has a sign function due to the free-energy shape (see Fig. 8). Substituting it to Eq. (B7), one gets

$$\left. \frac{\partial F}{\partial P_z} \right|_{P_z^*} \approx F'_{\text{pot}}(P_z^*) - F''_{\text{pot}}(P_z^*)|P_z - P_z^*| - E_z = (E_{z\infty} - F''_{\text{pot}}(P_z^*)|P_z - P_z^*|) - E_z = 0. \quad (\text{B9})$$

The expression in brackets determines the critical electric field. The polarization component P_z is discretized and quite evenly distributed along the string (even for converged strings, namely see Fig. 5) in the simplified string method. The discretization causes E_{cr} [Eq. (B9)] to be computed not exactly

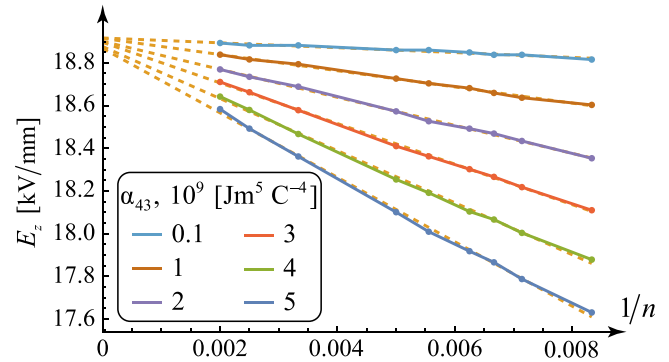


FIG. 10. The critical electric field as a function of the inverse number of sites on a string ($1/n$) for different values of parameter α_{43} for a single-domain congruent LiNbO_3 . Dashed orange lines correspond to fits with Eq. (10).

at P_z^* , but in the vicinity. The displacement is inversely proportional to the number of points on a string. Therefore, it is easy to see the relation between Eq. (10) and Eq. (B9). The model has three component order parameter in the main text, but the idea remains the same.

APPENDIX C: ADDITIONAL PLOTS FOR CONGRUENT LiNbO_3 AND ALL THE PLOTS FOR CONGRUENT LiTaO_3 , NEAR-STOICHIOMETRIC LiNbO_3 , AND LiTaO_3

Figure 9 shows the number of local minima for NSLN, CLT, and NSLT. The diagram allows us to find the range of parameter α_{43} where the model Eq. (6) has two ground states. The upper bounds for compounds are the following: $\alpha_{43 \text{ max}} = 7 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for NSLN, $13.6 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for CLT, and $37 \times 10^9 \text{ Jm}^5 \text{ C}^{-4}$ for NSLT.

Figure 10 shows fits of the model Eq. (10) applied to the critical electric field calculated from the simplified string method for congruent lithium niobate (Fig. 4). The extrapolation is done to an infinite string ($n \rightarrow \infty$). The critical electric field in the simplified string method is calculated with the error bar of $\pm 5 \text{ V/mm}$. If one considers the error bars, then all extrapolated lines could cross at the point (0, 18.9 kV/mm) in Fig. 10. This proves that the critical electric field does not depend on the parameter α_{43} .

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