Singularities in Landau-Devonshire potentials for Ferroelectrics Phase-Transitions

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SUMMARY. Ferroelectrics phase transitions are studied in terms of fourth-ordewr Landau potentials: A judicios choice of the reference configuration allows for a complete description of all the possible transitions. The study of the stability conditions at the phase interface helps to explain the fairly complex nature of the observed twins.

1 INTRODUCTION

Most ferroelectric solid/solid solutions exhibits a fairly complicated phase-diagram with phase boundaries between different crystallographic variants which depends on both temperature and relative concentrations. Amongst these there is one of the ferroelectrics which is most widely-used in practical applications, namely the PZT $Pb(Zr_{1-x}Ti_x)O_3$; the practical interest in this material lies in its exceptional dielectric and piezoelectric properties.

Both Lead Titanate and Lead Zirconate are Perovskyte-type oxides whose general formula is ABO_3: in the high-temperature paraelectric phase the symmetry is cubic with point group $m3m(O_h)$, whereas upon cooling under the Curie temperature, the material undergoes the transition to the ferro-electric phase, the resulting phase-diagram exhibits for $x \approx 0.5$ a nearly vertical morphotropic phase boundary between titanium-rich compositions (which favor a cubic-to-tetragonal phase transition $m3m(O_h) \rightarrow 4mm(C_{4v})$) and zirconium-rich compositions (which favors a cubic-to-rhombohedral phase transition $m3m(O_h) \rightarrow 3m(C_{3v})$).

At the macroscopic level compositions close to the morphotropic phase boundary are characterized by excellent physical properties, namely a very large piezoelectric coupling between electric and mechanical variables related to the presence of a maximum in the dielectric constant, an ease of poling and a maximum mechanical compliance. The recent discovery reported by Noheda and co-workers (*vid.* [3]) that the morphotropic boundary is a new phase in itself with monoclinic $m(C_s)$ symmetry whose extent is between $x = 0.47$ and $x = 0.51$ below $500K$, has shed new light on the understanding of the physical origin of PZT striking ferroelectric properties around the MPB.

Starting from the experimental data collected by Noheda, we studied in a recent paper [2] the twinning between PZT variants obtaining a complete description of domain-wall structure both in-terms of domain-wall orientations and spontaneous polarization rotations across domain-walls. The most interesting results we obtained were those for compositions close to phase boundaries where ferroelectric wells belong to different crystallographic phases:

- tetragonal and monoclinic variants are compatible and the resulting twin is of the non-generic, non-conventional type;

- rhombohedral and monoclinic variants are compatible and the resulting twin is of the non-generic, non-conventional type;

- rhombohedral and tetragonal variants are not compatible: however a tetragonal finely-twinned laminate and a rhombohedral variant admit an almost compatible interface in the sense of [1].

The aim of the present work, which deals with energies in ferroelectric solids is two-fold: first to show how with a fourth-order Landau-Devonshire potential we can describe all the phase transition which are possible in solid-solid solutions of the perovskite type provided we choose different reference configurations (this is a step ahead with respect the standard request that a, for instance, a monoclinic phase can found with at least an eigth-order Landau-Devonshire potential [4] and that al the possibile phase transitions can be arrived at with a twelve-order potential [16]); second to show that the twinning relations at morphotropic boundaries depends on the singularities of Landau-Devonshire potentials

2   VARIATIONAL FORMULATION

The most important feature of ferroelectricity is the onset, below the critical Curie temperature, of a polar phase associated with a reversible spontaneous polarization which is accompained by an electric self-field and by a spontaneous strain: the associated electrostatic and elastic energies are reduced by means of formation of many domains, *i.e.* regions of uniform spontaneous polarization in which all the electric dipoles are aligned in the same direction. This process, which render the material more stable, does not proceed indefinitely, since a certain amount of energy is stored in the domain walls, interfaces within which the spontaneous polarization undergoes large variations; ferroelectrics domain walls are thin (of the order of few lattice constants) and within a domain wall the spontaneous polarization will decrease in magnitude, passing through zero, and increase on the other side with opposite sign (*vid. e.g.* [10], II-7). At the equilibrium the material displays a twinned domain structure which is determined, as pointed out in [9], by the elements of symmetry which are lost in the paraelectric to ferroelectric transition.

In the continuum theory for deformable ferroelectric bodies proposed into [5, 6, 14] and which is based on that presented in [7] for deformable ferromagnetic bodies, the physical configuration of a ferroelectric body is described by means of the *deformation* and *spontaneous polarization* fields y and $\mathbf{p}$.

More precisely, for B a ferroelectric body whose *spontaneous polarization* in terms of electric dipole moments for unit volume we denote with the vector $\mathbf{p}$, we define

$$\mathbf{p} = \rho^{-1} \mathbf{p} \,, \quad \|\mathbf{p}\| \le p_0 \,,$$

the spontaneous polarization for unit mass where ρ is the mass density and the saturation value p_0 a material parameter; further, we pointwise identify B with a reference configuration $\mathcal{B}_r$, a region of the three-dimensional Euclidean space $\mathcal{E}$ (whose associated vector space we denote $\mathcal{V}$) and on $\mathcal{B}_r$ we define the *deformation* and *polarization* fields:

$$y : \mathcal{B}_r \to \mathcal{E} \,, \quad \mathbf{p} : \mathcal{B}_r \to \mathcal{S} \,, \quad \mathcal{S} \equiv \{\mathbf{p} \in \mathcal{V} \mid \quad \|\mathbf{p}\| \le p_0\} \,;$$

we assume that the deformation has a gradient $\mathbf{F}$ with positive determinant $J = \det \mathbf{F} > 0$, and we denote $\mathcal{B} \equiv y(\mathcal{B}_r)$ the current configuration of B.

Let a system of electromechanical loads on $\mathcal{B}$ be given, namely the surface densities of mechanical forces $\mathbf{t}$ and electric dipoles $\mathbf{t}$ prescribed on the boundary $\partial \mathcal{B}$ and let $\mathbf{e}_{ext}$ an applied external electric, which we assume to be unaffected by the deformation and spontaneous polarization of $\mathcal{B}$: the pair $(y \,, \mathbf{p})$ at the equilibrium under the action of these external electromechanical loads can be

found as the minimizer, in a suitable Sobolev space, of the functional

$$\mathcal{F}(y\,,\mathbf{p}) = \mathcal{F}_{int}(\operatorname{grad}\mathbf{p}\,,\mathbf{F}\,,\mathbf{p}) + \mathcal{F}_{self}(\mathbf{p}) + \mathcal{F}_{ext}(y\,,\mathbf{p})\,.^1 \tag{1}$$

The three terms which (1) is composed of denotes respectively the *Internal energy* $\mathcal{F}_{int}$, a term which is the object of a constitutive prescription, the *External energy* $\mathcal{F}_{ext}$, a term which can be disposed of during an experiment and the *Self energy* $\mathcal{F}_{self}$, a term of electric nature which can't be neither disposed of at will, nor constitutively prescribed.

In ferroelectrics it is customary to split the internal energy term into the sum of a domain-wall energy, which penalizes spatial oscillation of $\mathbf{p}$ and prevents the formation of domains, with a "coarse-grain" stored energy, which is minimized by mechanical twinning along some preferred crystallographic directions and therefore accounts for the refinement of domain structure; hence we get

$$\mathcal{F}_{int} = \mathcal{F}_w + \mathcal{F}_s\,, \quad \mathcal{F}_w(\operatorname{grad}\mathbf{p}) = \int_{\mathcal{B}} \varphi_w(\operatorname{grad}\mathbf{p})\,, \quad \mathcal{F}_s(\mathbf{F}\,,\mathbf{p}) = \int_{\mathcal{B}} \varphi(\mathbf{F}\,,\mathbf{p})\,,$$

where φ_w is the domain wall energy density and φ the stored energy density. The external energy contribution takes into account both the electrostatical interaction energy, which models the tendency of the spontaneous polarization to align with the external macroscopic electric field and the applied surface electric dipole density, and the mechanical interaction energy, which models the effects of the external electrostatic volume force and the mechanical surface force on the ferroelectric body:

$$\mathcal{F}_{ext}(y\,,\mathbf{p}) = -\int_{\mathcal{B}} (\operatorname{grad}\mathbf{e}_{ext})\mathbf{p}\cdot y + \rho\mathbf{e}_{ext}\cdot\mathbf{p} - \int_{\partial\mathcal{B}} \mathbf{t}\cdot y + \mathbf{t}\cdot\mathbf{p}\,.$$

Finally, the self energy represent, within the ferroelectricity contest, the depolarization energy, which accounts for dipole-dipole interactions and favors the formation of domains:

$$\mathcal{F}_{self}(\mathbf{p}) = \frac{1}{2}\int_{\mathcal{E}} \|\mathbf{e}_{\mathcal{B}}(\mathbf{p})\|^2\,;$$

here the *electric depolarization* field $\mathbf{e}_{\mathcal{B}}$, generated by the charges induced on the boundary by $\mathbf{p}$, is defined as the solution of the Maxwell equations for the electrostatic in absence of volume and surface charges

$$\operatorname{div}\mathbf{e}_{\mathcal{B}} = -\operatorname{div}\mathbf{p}_{\chi_{\mathcal{B}}}\,, \quad \operatorname{curl}\mathbf{e}_{\mathcal{B}} = \mathbf{0}\,, \quad \text{in } \mathcal{E}\,, \quad [\![\mathbf{e}_{\mathcal{B}}]\!] = (\mathbf{p}_{\chi_{\mathcal{B}}}\cdot\mathbf{n})\mathbf{n}\,, \quad \text{on } \partial\mathcal{B}\,, \tag{2}$$

where $\mathbf{n}$ is the outward unit normal to $\partial\mathcal{B}$, $[\![\cdot]\!]$ denotes the jump across the boundary (outer trace minus the inner trace) and $\mathbf{p}_{\chi_{\mathcal{B}}}$ has to be interpreted as the extension of the polarization field to $\mathcal{E}$ which vanishes outside $\mathcal{B}$.

2.1 *Constitutive restrictions for the bulk stored energy*

We assume that the "bulk" stored energy density function is a mapping $\varphi : \operatorname{Lin}^+\times\mathcal{S} \to \mathbb{R}^+\cup\{0\}$, where Lin^+ denotes the space of the second order tensors with positive determinant; moreover we require that φ obeys the following restrictions:

- (i) *Frame-indifference*

$$\varphi(\mathbf{QF}\,,\cdot) = \varphi(\mathbf{F}\,,\cdot)\,, \quad \forall\mathbf{Q}\in\operatorname{Orth}\,, \quad \forall\mathbf{F}\in\operatorname{Lin}^+\,, \tag{3}$$

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[1] *cf.* [14]: for the study of (1) within the context of ferromagnetic materials see *e.g.* [12] and the references quoted therein.

where Orth denotes the proper orthogonal group. We notice that in this formulation we do not require rotational invariance for the spontaneous polarization, as for instance in [14]: indeed by a result obtained in [6] this is equivalent to the symmetry of Toupin stress tensor. Consequence of frame indifference is

$$\varphi(\mathbf{F}, \cdot) = \varphi(\mathbf{U}, \cdot) = \bar{\varphi}(\mathbf{C}, \cdot), \tag{4}$$

where $\mathbf{C} = \mathbf{F}^T \mathbf{F} \in \mathrm{Sym}^+$ and $\mathbf{U} = \mathbf{C}^{\frac{1}{2}} \in \mathrm{Sym}^+$ are respectively the right Cauchy-Green strain and right stretch tensors with Sym^+ the space of second order symmetric and positive definite tensors.

- (ii) *Material symmetry*

$$\varphi(\mathbf{FH}, \mathbf{H}^T\mathbf{p}) = \varphi(\mathbf{F}, \mathbf{p}), \quad \forall \mathbf{H} \in \mathcal{G}_p, \quad \forall(\mathbf{F}, \mathbf{p}) \in \mathrm{Lin}^+ \times \mathcal{S}; \tag{5}$$

here $\mathcal{G}_p$ denotes the point group of the paraelectric phase, *i.e.* the subgroup of $\mathrm{Orth} \cup \{-\mathbf{I}\}$ whose elements maps the reference paraelectric lattice into itself. Consequence of material symmetry is that

$$\varphi(\mathbf{FH}, \mathbf{H}^T\mathbf{p}) = \bar{\varphi}(\mathbf{H}^T\mathbf{CH}, \mathbf{H}^T\mathbf{p}); \tag{6}$$

We limit our analysis to materials with centrosymmetric, non-piezoelectric paraelectric phase whose point group contains the central reflection $\mathbf{H} = -\mathbf{I}$. In this case then (6) implies that φ must be an even function of the spontaneous polarization:

$$\varphi(\mathbf{U}, \mathbf{p}) = \varphi(\mathbf{U}, -\mathbf{p}). \tag{7}$$

The phase transition from the primitive paraelectric phase to the ferroelectric phase is accompained by a spontaneous strain (the *transformation strain*) which reflects, at the macroscopic scale, the crystal lattice distortion which is at the origin of the ferroelectric phenomena. Accordingly, we may assume that the strain $\mathbf{U}$ can be decomposed into a purely mechanical and a spontaneous parts $\mathbf{U} = \mathbf{U}_m \mathbf{U}(\mathbf{p})$, where $\mathbf{U}(\mathbf{p})$ represents the spontaneous strain associated with the phase transition from the paraelectric to the ferroelectric phase with spontaneous polarization $\mathbf{p}$.

Whenever the material is the unpoled paraelectric phase both spontaneous polarization and strain vanishes and the stored energy coincides with the elastic energy density of the paraelectric phase:

$$\varphi(\mathbf{U}_m, \mathbf{0}) = \sigma(\mathbf{U}_m),$$

which vanishes for rigid motions, *i.e.* $\varphi(\mathbf{I}, \mathbf{0}) = \sigma(\mathbf{I}) = 0$.

2.2 *Crystallographic potentials*

In the poled ferroelectric phase let $\mathbf{U}_m = \mathbf{I}$, then the stored energy depends only on the spontaneous polarization and represents the anisotropy energy $\mathcal{W}(\mathbf{p})$, a multi-well crystallographic potential which is minimized along some preferred crystallographic directions, *i.e.* the polarization easy-axis:[2]

$$\varphi(\mathbf{U}(\mathbf{p}), \mathbf{p}) = \mathcal{W}(\mathbf{p}); \tag{8}$$

clearly, by (7) and (8)

$$\mathcal{W}(\mathbf{p}) = \mathcal{W}(-\mathbf{p});$$

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[2]In the first-principle approach followed *e.g.* in [15], the coarse-grain energy plays the role of the Hamiltonian "local mode self-energy".

and accordingly for $\bar{\mathbf{p}}$ a minimizer for $\mathcal{W}(\mathbf{p})$, $-\bar{\mathbf{p}}$ is also a minimizer

$$\mathcal{W}(\pm\bar{\mathbf{p}}) \leq \mathcal{W}(\mathbf{p}), \quad \forall \mathbf{p} \in \mathcal{S}. \tag{9}$$

By a classical result of crystallography the anisotropy energy admits $2N$ minimizers $\pm\mathbf{p}_k$, $k = 1, 2, \ldots N$ where

$$N = \frac{\text{order of } \mathcal{G}_p}{\text{order of } \mathcal{G}_f},$$

the order of a finite point group being the number of the elements in the group and with $\mathcal{G}_f$ the point group of the ferroelectric phase. By (7) and (8) the $2N$ minimizers for $\mathcal{W}(\mathbf{p})$ are associated with N *ferroelectric variants*

$$\mathbf{U}_k = \mathbf{U}(\pm\mathbf{p}_k), \quad k = 1, 2, \ldots N \tag{10}$$

and thus, for $\mathbf{p}_k$ a minimizer for the crystallographic potential (8), the pair $(\mathbf{U}(\mathbf{p}_k), \mathbf{p}_k)$ is a minimizer for the stored energy, *i.e.*

$$\varphi(\mathbf{U}(\mathbf{p}_k), \mathbf{p}_k) \leq \varphi(\mathbf{U}, \mathbf{p}), \quad \forall (\mathbf{U}, \mathbf{p}) \in \text{Sym}^+ \times \mathcal{S}. \tag{11}$$

The N *ferroelectric wells* are defined as the set of minimizers for the crystallographic potential:

$$\mathcal{K}_N \equiv \{\pm\mathbf{p}_1, \pm\mathbf{p}_2, \ldots, \pm\mathbf{p}_N\}; \tag{12}$$

let $\mathbf{p}_1$ be a minimizer and $\mathcal{G}_{f,1}$ the ferroelectric group generated by $\mathbf{p}_1$: then by a result of [13] for $\mathcal{H}_j$, $j = 2, \ldots N$ the $N-1$ cosets of $\mathcal{G}_{f,1}$ in $\mathcal{G}_p$ the other $N-1$ minimizers are given by

$$\mathbf{p}_j = \mathbf{H}^T \mathbf{p}_1, \quad \text{for any } \mathbf{H} \in \mathcal{H}_j, \quad j = 2, \ldots, N, \tag{13}$$

and the associated ferroelectric variants by

$$\mathbf{U}_j = \mathbf{H}^T \mathbf{U}_1 \mathbf{H}, \quad \text{for any } \mathbf{H} \in \mathcal{H}_j, \quad j = 2, \ldots, N. \tag{14}$$

Spontanoeus strain and polarization are closely-related and a quadratic dependence of the former on the latter is assumed in most solid-state physics texts; in [6] such a dependence was arrived at by means of crystallographic symmetry requirements and the following explicit representation was given:

$$\mathbf{U}_k(\mathbf{p}_k) = \alpha \mathbf{w}^\perp \otimes \mathbf{w}^\perp + \beta \mathbf{w}_\perp \otimes \mathbf{w}_\perp + \gamma \mathbf{p}_k \otimes \mathbf{p}_k, \quad \text{k not summed}; \tag{15}$$

here $\{\mathbf{w}^\perp, \mathbf{w}_\perp, \mathbf{p}_k\}$ is an orthogonal basis, and the parameters (α, β, γ) are characteristic of the specific ferroelectric transition associated with the onset of $\mathbf{p}_k$.

Let

$$\mathbf{P} = \mathbf{p} \otimes \mathbf{p} = \|\mathbf{p}\|^2 \mathbf{w} \otimes \mathbf{w}, \quad \mathbf{w} = \|\mathbf{p}\|^{-1} \mathbf{p}:$$

then, by (15), (7) and (8) we may write:

$$\mathcal{W}(\mathbf{p}) = \hat{\mathcal{W}}(\mathbf{P}). \tag{16}$$

We focus our attention at the minimization problem for the crystallographic potential (8): in order $\mathbf{p}_k$ to be a minimizer, by (16) it must obey:

$$\mathbf{A}(\mathbf{p}_k)\mathbf{p}_k = \mathbf{0}, \quad \mathbf{B}(\mathbf{p}_k)\mathbf{u} \cdot \mathbf{u} > 0, \quad \forall \mathbf{u}/\{\mathbf{0}\}, \tag{17}$$

where:

$$\mathbf{A}(\mathbf{p}_k) = \left.\frac{\partial \hat{\mathcal{W}}}{\partial \mathbf{P}}\right|_{\mathbf{p}_k}, \quad \mathbf{B}(\mathbf{p}_k) = \left.\frac{\partial \hat{\mathcal{W}}}{\partial \mathbf{P}}\right|_{\mathbf{p}_k} + 2 \left.\frac{\partial^2 \hat{\mathcal{W}}}{\partial \mathbf{P}^2}\right|_{\mathbf{p}_k} [\mathbf{p}_k \otimes \mathbf{p}_k].$$

Condition $(17)_1$ leads to the following alternatives:

- either

$$\det \mathbf{A}(\mathbf{0}) \neq 0 \,, \quad \mathbf{p} = \mathbf{0} \,, \tag{18}$$

- or

$$\det \mathbf{A}(\mathbf{p}_k) = 0 \,, \quad \mathbf{p}_k \in \ker \mathbf{A}(\mathbf{p}_k) \,. \tag{19}$$

Condition (18) holds in the paraelectric unpoled state, which at a temperature lower than the Curie one is unstable: accordingly, since $\mathbf{A}(\mathbf{0}) = \mathbf{B}(\mathbf{0})$, conditions $(17)_2$ and (18) must be replaced by

$$\mathbf{A}(\mathbf{0})\mathbf{u} \cdot \mathbf{u} < 0 \,, \quad \forall \mathbf{u}/\{\mathbf{0}\} \,. \tag{20}$$

3   LANDAU-DEVONSHIRE POTENTIALS

The classical phenomenological model for the crystallographic potential is that proposed by Devonshire [8] which accounts for the ferroelectric phase-transition sequence by means of a Landau-type expansion in terms of even powers of the spontaneous polarization $\mathbf{p}$. In the original Devonshire paper, which is tailored on the Barium Titanate Cubic→Tetragonal→Orthorombic→Rombohedral phase-transition sequence was described by means of a sixth-order potential. Recently, it was shown in [16] that a twelve-order potential is necessary in order to describe all the possible phase transitions from a cubic parent state in the highly piezoelectric mixture compounds PZT, PMN-PT and PZN-PT. In the following we shall show how, by changing the reference configuration, we can describe the same phase transitions by means of a fourth-order potential.

We consider the following Landau-Devonshire potential found *e.g.* in [11]:

$$\hat{\mathcal{W}}(\mathbf{p}) = \mathcal{W}_0 - \frac{1}{2}\mathbf{S} \cdot \mathbf{P} + \frac{1}{4}\mathbb{S}[\mathbf{P}] \cdot \mathbf{P} \,, \tag{21}$$

here $\mathbb{S}$, represent a crystallographic tensor and the second order symmetric and positive-definite tensor $\mathbf{S}$ represents the inverse susceptibility of the material in the paraelectric phase.

3.1   *Transitions from a cubic phase*

We begin to assume that the tensors $\mathbf{S}$ and $\mathbb{S}$ have cubic symmetry $m3m(O_h)$; accordingly we have the following fourth-order Landau potential (*vid.* [9, 11]):

$$\mathcal{W}(\mathbf{p}) = \mathcal{W}_0 - \frac{1}{2}\alpha\|\mathbf{p}\|^2 + \frac{1}{4}\gamma_1(p_1^4 + p_2^4 + p_3^4) + \frac{1}{2}\gamma_2(p_1^2 p_2^2 + p_1^2 p_3^2 + p_2^2 p_3^2) \,, \quad \alpha > 0 \,, \tag{22}$$

where $p_i = \mathbf{p} \cdot \mathbf{w}_i \,, i = 1, 2, 3$ are the components of the spontaneous polarization in an orthonormal frame $\{\mathbf{w}_1 , \mathbf{w}_2 , \mathbf{w}_3\}$. The double-well potential (22), by (19) admits the following minimizers:

- cubic-to-tetragonal phase transition, six minimizers, easy axis $[0, 0, 1]$:

$$\pm\mathbf{p}_k = \pm p_s \mathbf{w}_k \,, \quad k = 1, 2, 3 \,, \quad p_s^2 = \frac{\alpha}{\gamma_1} \,; \tag{23}$$

- cubic-to-rhomboedral phase transition, eight minimizers, easy axis $[1, 1, 1]$:

$$\pm\mathbf{p}_k = \pm\frac{1}{\sqrt{3}}p_s(\mathbf{w}_1 \pm \mathbf{w}_2 \pm \mathbf{w}_3) \,, \quad k = 1, 2, 3, 4 \,, \quad p_s^2 = \frac{\alpha}{\gamma_1 + 2\gamma_2} \,, \tag{24}$$

- cubic-to-orthorombic phase transition, four minimizers, easy axis $[1,1,0]$:

$$\pm\mathbf{p}_k = \pm\frac{1}{\sqrt{2}}p_s(\mathbf{w}_1 \pm \mathbf{w}_2)\,, \quad k=1,2\,, \quad p_s^2 = \frac{\alpha}{\gamma_1 + \gamma_2}\,, \tag{25}$$

where the material parameter $p_s < p_0$ represents the value of spontaneous polarization.

By the stability condition (18) we have that the Orthorhombic minimizers are unstable for all the values of the constitutive parameters γ_1 and γ_2. The Tetragonal minimizers are stable provided $\gamma_2 > \gamma_1 > 0$ whereas the Rhomboedral minimizers are stable provided $\gamma_1 > \gamma_2$ and $\gamma_1 + 2\gamma_2 > 0$. When $\gamma_1 = \gamma_2$, $\mathbf{B}(\mathbf{p}_k)$ is a rank-one tensor: we have therefore a saddle-point and the so-called *tetragonal-rhomboedral ambiguity*.

This is the situation we have for two specific perovskites, namely the (PZT) PbZr$_x$Ti$_{1-x}$O$_3$ (*vid.* [10, 11]) and the (PZN-PT) Pb(Zn$_{1/3}$Nb$_{2/3}$)$_{1-x}$Ti$_x$O$_3$ (*vid.* [17]); Titanium-rich compositions favor a cubic-to-tetragonal phase transition $m3m(O_h) \to 4mm(C_{4v})$, with sizable elongation along the crystallografic direction $[001]$, large spontaneous polarization in the same direction and six possible domain states. A transition to a rhombohedral ferroelectric state $m3m(O_h) \to 3m(C_{3v})$ is favored for zirconium-rich compositions: the distortion and polarization are along the $[111]$ (body diagonal) directions, giving rise to eight possible domain states.

At the morphotropic phase boundary between the tetragonal and the rhombohedral states, which corresponds to $x \approx 0.5$, the two solid phases that remain in a near-equilibrium state over a very wide temperature range with a nearly ambiguous polarization easy axis (either $[001]$ or $[111]$).

3.2 *Transitions from a tetragonal phase*

To describe a transition from a parent tetragonal phase we assume the tensors $\mathbf{S}$ and $\mathbb{S}$ with tetragonal symmetry $4mm(C_{4v})$; accordingly we have:

$$\mathcal{W}(\mathbf{p}) = \mathcal{W}_0 - \frac{1}{2}(\alpha_1(p_1^2 + p_2^2) + \alpha_2 p_3^2) + \frac{1}{4}(\gamma_1(p_1^4 + p_2^4) + \gamma_2 p_3^4)) + \frac{1}{2}(\gamma_3 p_1^2 p_2^2 + \gamma_4(p_1^2 + p_2^2)p_3^2)\,, \tag{26}$$

which, provided $\alpha_1 > 0$ and $\alpha_2 > 0$, admits the following, non-trivial, minimizers:

- tetragonal-to-rhomboedral phase transition, eight minimizers, easy axis $[1,1,1]$, as in (23) with

$$p_s^2 = \frac{3\alpha_1}{\gamma_1 + \gamma_3 + \gamma_4}\,, \tag{27}$$

provided the following compatibility condition is satisfied:

$$\frac{\alpha_1}{\alpha_2} = \frac{\gamma_1 + \gamma_3 + \gamma_4}{\gamma_2 + \gamma_4}\,; \tag{28}$$

- tetragonal-to-monocline phase transition, twentyfour minimizers, easy axis $[u,u,v]$, $u < v$:

$$\begin{aligned}
\pm\mathbf{p}_k &= \pm(u\mathbf{w}_1 \pm u\mathbf{w}_2 \pm v\mathbf{w}_3)\,, \quad k=1,\ldots,8\,, \\
\pm\mathbf{p}_k &= \pm(u\mathbf{w}_1 \pm v\mathbf{w}_2 \pm u\mathbf{w}_3)\,, \quad k=9,\ldots,16\,, \\
\pm\mathbf{p}_k &= \pm(\pm v\mathbf{w}_1 + u\mathbf{w}_2 \pm u\mathbf{w}_3)\,, \quad k=17,\ldots,24\,,
\end{aligned} \tag{29}$$

where

$$\begin{aligned}
u^2 &= \frac{\gamma_2\alpha_1 - 2\alpha_2\gamma_4}{(\gamma_1 + \gamma3)\gamma_2 - 2\gamma_4} > 0\,, \\
v^2 &= \frac{(\gamma_1 + \gamma_3)\alpha_1 - \alpha_2\gamma_4}{(\gamma_1 + \gamma3)\gamma_2 - 2\gamma_4} > 0\,,
\end{aligned} \tag{30}$$

provided of course that $\gamma_2\alpha_1 - 2\alpha_2\gamma_4 < (\gamma_1 + \gamma_3)\alpha_1 - \alpha_2\gamma_4$.

By the stability condition (18), the Rhomboedral solution is stable provided:

$$\gamma_1 > \gamma_3 > 0 \,, \quad \gamma_1\gamma_2 - \gamma_4^2 > 0 \,; \tag{31}$$

the stability conditions for the Monoclinic solution are quite complicated: for our purpose it is enough to observe that there exists a *monoclinic-rhomboedral ambiguity* for $\gamma_4 = 0$ which gives stable a solution.

We have a similar situation for the transitions from a rhomboedral phase, with a stable *monoclinic-tetragonal ambiguity*.

Interestingly enough, the results obtained in [2] show how that the ferroelectric variants are compatible with non-generic, non-conventional twins arise whenever the ambiguity gives a stable solution whereas the non compatibility of rhombohedral and tetragonal variants corresponds to a saddle-point type ambiguity.

4 CONCLUSIONS

We show that with a fourth-order Landau-Devonshire potential we can describe all the possible phase transition from a paraelectric cubic phase: by studying the stability conditions and the behaviour at the phase boundary, we can also have an insight at the twinning relations, a matter which deserves further investigations.

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