Polar phase transition in 180°-domain wall of lead titanate

I. Rychetsky

Institute of Physics of the Czech Academy of Sciences,
Na Slovance 2, 18221 Prague 8, Czech Republic.

W. Schranz and A. Tröster

University of Vienna, Faculty of Physics, Boltzmannasse 5, 1090 Wien, Austria.

(Dated: October 4, 2022)

A new mechanism leading to a switchable polarization in a ferroelectric domain wall (DW) is proposed. A biquadratic coupling of the primary order parameter and its gradient triggers the phase transition in the DW with softening of the local polar mode and anomalous increase of the susceptibility at the phase transition temperature $T_{DW}$. This mechanism describes the origin and properties of the polar Bloch and antipolar Néel components in the 180°-DW of PbTiO$_3$, which were recently reported from first-principles calculations.

Introduction.—The tensor properties of domain walls (DWs) in ferroic materials become recently of increasing interest driven by achievements in technological and measurement methods allowing to fabricate and observe submicron and nanoscale structures. Various methods for modeling of DWs are widely used [1], i.e. first-principle calculations [2], machine-learned force fields [3], phase-field modeling [4], and phenomenological Landau-Ginzburg theory [5], which are closely interconnected with the DW symmetry analysis described by layer groups [6–10]. Polarization inside DWs was predicted in some perovskite structures [11,12], where the crucial role was assigned to flexoelectricity [13], rotopol coupling [8,14] or biquadratic coupling of the primary and secondary order parameters [15].

The possible existence of polar 180°-DW in PbTiO$_3$ (PTO) was reported by several authors. However, the situation is not so clear yet. Based on ab initio calculations an Ising structure of the DW profile was reported in Ref. [10]. Such a DW would not carry any polarization within the wall. Other authors concluded that the DW contains also a Néel-like polarization (asymmetric polarization profile) originating from flexoelectricity [17,18] and a switchable Bloch component indicating a ferroelectric phase transition inside the DW [2,19]. The latter behavior was not found to be stable within the Landau-Ginzburg approach [17,18], where only the Néel polarization was obtained. In this contribution we show that the symmetry of the DW (layer group) together with an extended Landau-Ginzburg potential allow to properly describe the polar properties of 180°-DW in PTO.

Symmetry of 180° DW — PTO exhibits a uniaxial ferroelectric phase transition from cubic to tetragonal structure without multiplication of the unit cell. The symmetry decrease from $Pm3m$ to $P4mm$ implies 6 tetragonal domain states (DSs) $1_1 \equiv (-P_x,0,0)$, $2_1 \equiv (0,-P_y,0)$, $3_1 \equiv (0,0,-P_z)$ and $1_2$, $2_2$, $3_2$ with opposite sign of polarization.

Here we consider the 180°-DW $(3_1|\mathbf{n}, \mathbf{p}|3_2)$ between the DSs $3_1 \equiv (0,0,-P_z)$ and $3_2 \equiv (0,0,P_z)$, with the normal $\mathbf{n} \parallel x$ and the microscopic position within the unit cell $\mathbf{p} \equiv (0,2y,1)$. The macroscopic tensor properties of DWs described by Landau theory are independent of the microscopic position $\mathbf{p}$ and they are determined by the layer group symmetry of the DW twin $(3_1|\mathbf{n}|3_2)$, which contains 4 elements $T_{ij} = T\{1,m_y,2y,1\}$, $T$ are translations parallel with the DW plane. This symmetry implies that the Néel component is antisymmetric, $P_1(x) = -P_1(-x)$, and it can be nonzero in the whole temperature range below $T_c$. The Bloch component is forbidden by symmetry, since application of $m_y$ yields $P_2(x) = -P_2(-x) = 0$. Therefore it could only occur as a result of the phase transition lowering the symmetry to $T'_{ij} = T\{1,2y\}$. Then the Bloch component is nonzero and symmetric: $P_2(x) = P_2(-x) \neq 0$. The polarization profiles and the phase transition in the DW are further analyzed using the Landau-Ginzburg free energy description.

The free energy — The Gibbs free energy can be written as:

$$G(\mathbf{P}, \mathbf{\sigma}) = G_0 + G_{ex} + G_{el} + G_{flex} + G_{biq} + G_g$$

where the individual parts, pure polarization $G_0$, electrostriction $G_{ex}$, elastic energy $G_{el}$, gradient term $G_g$, flexoelectric $G_{flex}$, biquadratic OP and its gradient $G_{biq}$ read.
\[ G_0 = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{111} (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{111} (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} ((P_1^4 + P_2^4) P_1^2 + (P_1^4 + P_2^4) P_2^2 + P_1^2 (P_2^4 + P_3^4)) \]

\[ G_{ex} = -\sigma_1 (P_1^2 Q_{11} + P_2^2 Q_{12} + P_3^2 Q_{12}) - \sigma_2 (P_1^2 Q_{11} + P_2^2 Q_{12} + P_3^2 Q_{12}) - \sigma_3 (P_3^2 Q_{11} + P_2^2 Q_{12} + P_2^2 Q_{12}) - \sigma_1 (P_1^2 Q_{11} + P_2^2 Q_{12} + P_2^2 Q_{12}) \]

\[ G_{el} = -\frac{1}{2} \left( (\sigma_1^2 + \sigma_2^2 + \sigma_3^2) s_{11} + 2(\sigma_1 \sigma_2 + \sigma_3 \sigma_2 + \sigma_1 \sigma_3) s_{12} + (\sigma_2^2 + \sigma_3^2 + \sigma_3^2) s_{44} \right) \]

\[ G_g = \frac{1}{2} \left( g_{11} \left( \frac{\partial P_1}{\partial x} \right)^2 + g_{22} \left( \frac{\partial P_2}{\partial x} \right)^2 + g_{44} \left( \frac{\partial P_4}{\partial x} \right)^2 \right) \]

\[ G_{fle} = -\frac{\partial P_1}{\partial x} \left( f_{14} (P_2^2 + P_3^2) + f_{11} \sigma_1 + f_{14} (\sigma_2 + \sigma_3) \right) - f_{111} \left( \frac{\partial P_2}{\partial x} \sigma_6 + \frac{\partial P_3}{\partial x} \sigma_5 \right) \]

\[ G_{big} = f_{22} \left[ P_2^2 \left( \frac{\partial P_2}{\partial x} \right)^2 + P_3^2 \left( \frac{\partial P_3}{\partial x} \right)^2 \right] + f_{22} \left[ \sigma_2 \left( \frac{\partial P_2}{\partial x} \right)^2 + \sigma_3 \left( \frac{\partial P_3}{\partial x} \right)^2 \right] \]

\[ G_{fle} \text{ and } G_{big} \text{ are terms not considered in } \text{[18]. Since the DW properties are x-dependent the gradient terms contain only } \partial \Box / \partial x \text{ derivatives. The quasi-1D DW along x-axis requires mechanical equilibrium } \sigma_1 = \sigma_5 = \sigma_6 = 0 \text{ and compatibility of strains } e_3(x) = e_2 e_3(x) = e_3 s_1(x) = e_4 s_2, \text{ where } e_i \text{ are spontaneous strains of homogeneous domains. Therefore it is convenient to use the thermodynamic potential } F(P, \sigma_{12}, \sigma_2, \sigma_6, e_2, e_3, e_4) \text{ obtained by the Legendre transformation: } F = G + \sigma_2 e_2 + \sigma_3 e_3 + \sigma_4 e_4. \text{ For the sake of simplicity it is also convenient to assume } f_{14} = f_{22} = 0, \text{ since it only renormalizes some coefficients but does not change the overall polarization behavior. Taking into account all above the potential } F \text{ is expressed as: } \]

\[ F = F_0 + F_{fle} + F_{big}, \]

where

\[ F_0 = b_1 P_1^2 + b_2 P_2^2 + b_3 P_3^2 + b_1 P_1^4 + b_2 (P_2^4 + P_3^4) + b_12 (P_1^2 P_2^2 + P_1^2 P_3^2) + b_{22} (P_2^2 P_3^2) + \frac{1}{2} \left( g_{11} \left( \frac{\partial P_1}{\partial x} \right)^2 + g_{22} \left( \frac{\partial P_2}{\partial x} \right)^2 + g_{44} \left( \frac{\partial P_4}{\partial x} \right)^2 \right) \]

\[ F_{fle} = -f_{14} \frac{\partial P_1}{\partial x} (P_2^2 + P_3^2) \]

\[ F_{big} = f_{22} \left[ P_2^2 \left( \frac{\partial P_2}{\partial x} \right)^2 + P_3^2 \left( \frac{\partial P_3}{\partial x} \right)^2 \right] \]

The value of spontaneous polarization is \( P_s = \sqrt{-\frac{\alpha_{11} + \sqrt{\alpha_{11}^2 - 4\alpha_{11} \alpha_{111}}}{3\alpha_{111}}} \). The \( b \)-coefficients are explicitly written in Appendix A, and the numerical values of coefficients for PTO are shown in TABLE I. Since for further considerations \( f_{22} \leq 0, \) the stability condition requires \( f_{22} P_s^2 + g_{44}/2 > 0 \). \( F_0 \) was already discussed in \text{[18]. It is shown below that } F_0 \text{ alone does not lead to the DW polarization, while the flexoelectric coupling induces the } Néel \text{ component } P_1, \text{ and the biquadratic coupling of the OP and its gradient can cause the appearance of the Bloch component } P_3. \]

\[ 180^\circ \text{ DW — The polarization profile can be obtained by minimizing the free energy functional } \]

\[ \mathcal{L} = \int_{-\infty}^{\infty} F(P(x), \partial_x P(x)) dx \text{ with proper boundary conditions. In practice, this can be achieved by direct minimization of the discretized (finite difference) free energy. An example of the DW profile at low temperatures is shown in Fig. I. Alternatively, if possible, it can be obtained by solving Lagrange-Euler (LE) equations. Let us first assume } F = F_0, \text{ i.e. } f_{14} = f_{22} = 0. \text{ Then the LE equations can be solved explicitly and the Ising DW profile is obtained: } \]

\[ P_1 = P_2 = 0, \quad P_3 = \frac{P_s \tanh(x/2L)}{\sqrt{\eta/ \cosh^2(x/2L) + 1}} \]
and E is an electric field, see Appendix B. The analytic solution of the differential equation (13) is unknown and we solved it numerically for several values of the biquadratic (of the OP and its gradient) coefficient $f_{22}$, Fig. 2. The phase transition in the DW occurs at $T_{DW} > 0$ if $f_{22} < -0.4815$. The effect of negative $f_{22}$ can be seen from the quadratic $P_{22}$ term at the DW center $(b_{2} + f_{22}P_{3}^{2})P_{2}^{2}$, which decreases if $f_{22} < 0$. Near above $T_{DW} \omega_{2}^{2} \propto (T-T_{DW})$ (see Fig. 2). Below $T_{DW}$, the symmetric Bloch component $P_{2}(x)$ appears, its shape is similar with $P_{2}(x)$ shown in Fig. 1. Below $T_{DW}$, $\omega_{2}^{2}$ of the polar mode was calculated by solving coupled equations of motion of $\delta_{2}$ and $\delta_{3}$ obtained from (B.4). It exhibits a typical hardening $\omega_{2}^{2} \propto (T_{DW} - T)$ shown in Fig. 2. The corresponding susceptibility $\Delta \chi$ around the phase transition at $T_{DW} = 305K$ exhibits a $1/(T - T_{DW})$ divergence, Fig. 3. The temperature dependence of the amplitude of the $P_{2}(x)$ profile is $P_{2,A} \approx (T_{DW} - T)^{1/2}$, see the solid line in Fig. 4. A similar softening of the $P_{2}$ polar mode, its freeze-out below $T_{DW}$ and divergent susceptibility was obtained by the first-principles calculations in Ref. [19].

The interrelation between Néel and Bloch components comes into play when concurrently $f_{14} \neq 0$ and $f_{22} \neq 0$. The component $P_{2}$ exists in the whole temperature range and $T_{DW}$ is shifted to lower temperatures, see the dashed lines in Fig. 4 Below $T_{DW}$ the $P_{1}$ and $P_{2}$ components coexist. The inset in Fig. 4 shows that $P_{1}$ exhibits a tiny anomalous at $T_{DW}$. The polar mode softening and the anomalous susceptibility are similar as shown in Fig. 3 for the previous case.

Summary — The symmetry of $180^{\circ}$-DW indicates the existence of unswitchable antisymmetric Néel $P_{1}$ polarization at the DW center in the whole temperature range below $T_{c}$ and within the Landau-Ginzburg description it is indeed induced by the flexoelectric term. The depolarizing charges should diminish $P_{1}$, but for simplicity
The susceptibility divergence $\propto 1/[T - T_{DW}]$ at $T_{DW} = 305\,K$ ($f_{22} = -0.736$). The softening of $\omega_0^2$, the same as in Fig. 2 is also shown for reference.

The softening of the polar mode, divergent susceptibility and the temperature dependence of $P_2$ below $T_{DW}$ are in excellent agreement with the results from first-principles calculations [2, 19]. This work was supported by Operational Program Research, Development and Education (financed by European Structural and Investment Funds and by the Czech Ministry of Education, Youth, and Sports), Project No. SOLID21-CZ.02.1.01/0.0/0.0/16_019/0000760).

**Appendix A:**

The 'b' coefficients in $F_0$:

$$b_1 = a_1 - \frac{P_s^2 Q_{12} (Q_{11} + Q_{12})}{s_{11} + s_{12}},$$
$$b_2 = a_1 + \frac{P_s^2 (s_{12} (Q_{11}^2 + Q_{12}^2) - 2Q_{11} Q_{12} s_{11})}{s_{11}^2 - s_{12}^2},$$
$$b_3 = a_1 - \frac{P_s^2 (s_{11} (Q_{11}^2 + Q_{12}^2) - 2Q_{11} Q_{12} s_{12})}{s_{11}^2 - s_{12}^2},$$
$$b_{11} = a_{11} + \frac{Q_{12}^2}{s_{11} + s_{12}},$$
$$b_{12} = a_{12} + \frac{Q_{12}(Q_{11} + Q_{12})}{s_{11} + s_{12}},$$
$$b_{22} = a_{11} + \frac{s_{11} (Q_{11}^2 + Q_{12}^2) - 2Q_{11} Q_{12} s_{12}}{2s_{11}^2 - 2s_{12}^2},$$
$$b_{23} = a_{12} - \frac{s_{12} (Q_{11}^2 + Q_{12}^2) - 2Q_{11} Q_{12} s_{11}}{s_{11}^2 - s_{12}^2} + \frac{Q_{14}^2}{2s_{44}}.$$

**Appendix B:**

The free energy functional and its variation,

$$\mathcal{L} = \int_{-\infty}^{\infty} F(P(x), \partial_x P(x)) dx$$

$$\delta \mathcal{L} = \int_{-\infty}^{\infty} \delta F \delta P dx = \int_{-\infty}^{\infty} \left( \frac{\partial L}{\partial P} - \frac{d}{dx} \frac{\partial L}{\partial \partial_x P} \right) \delta P dx$$

The DW profiles $\mathcal{P}$ are solutions of 3 equilibrium equations:

$$\frac{\delta \mathcal{L}}{\delta P_i} = \left( \frac{\partial L}{\partial P_i} - \frac{d}{dx} \frac{\partial L}{\partial \partial_x P_i} \right) = 0, \quad i = 1, 2, 3$$

A small perturbation $\mathbf{P} = \mathcal{P} + \delta$ leads to 3 equations of
motion:
\[
\Gamma^{-1} \delta_i = -\Gamma^{-1} \omega_0^2 \delta_i = -\frac{\delta \mathcal{L}}{\delta P_i} \bigg|_{P \rightarrow \varphi + \delta}
\]  
(B.4)

where in the right-hand side only the linear terms in \( \delta \) are kept. The perturbation is assumed as
\[
\delta \propto \frac{1}{\Delta \chi} \delta P_L
\]
and density of ions, respectively, \([\Gamma]\) = \(\frac{\omega_0^2}{E^0}\), where \(\omega_0^2 > 0\). The static susceptibility of the polar eigenmode \(\Delta \chi \equiv \delta_{2,A}/E = \frac{1}{\varepsilon_0} \omega_0^2\), where \(\delta_{2,A}\) is an amplitude of the polar mode. In case of the Ising profile 3 equations (B.4) are decoupled.

* rychet@fzu.cz

[1] D. Meier, J. Seidel, M. Gregg, and R. Ramesh, Domain Walls: From Fundamental Properties to Nanotechnology Concepts (Oxford University Press, 2020).
[2] J. Íniguez, First-Principles Studies of Structural Domain Walls, in Domain Walls: From Fundamental Properties to Nanotechnology Concepts (Oxford University Press, 2020).
[3] A. Tröster, C. Verdi, C. Dellago, I. Rychetsky, G. Kresse, and W. Schranz, Hard antiphase domain boundaries in strontium titanate unravelled using machine-learned force fields, Phys. Rev. Materials 6, 094408 (2022)
[4] B. Völker, P. Marton, C. Elsässer, and M. Kamlah, Multiscale modeling for ferroelectric materials: a transition from the atomic level to phase-field modeling, Continuum Mechanics and Thermodynamics 23, 435 (2011).
[5] P. Marton, I. Rychetsky, and J. Hlinka, Domain walls of ferroelectric batio\(_3\) within the ginzburg-landau-devonshire phenomenological model, Phys. Rev. B 81, 144125 (2010).
[6] W. Schranz, I. Rychetsky, and J. Hlinka, Polarity of domain boundaries in nonpolar materials derived from order parameter and layer group symmetry, Phys. Rev. B 100, 184105 (2019).
[7] W. Schranz, A. Tröster, and I. Rychetsky, Contributions to polarization and polarization switching in antiphase boundaries of SrTiO\(_3\) and PbZrO\(_3\), Journal of Applied Physics 128, 194101 (2020)
[8] W. Schranz, C. Schuster, A. Tröster, and I. Rychetsky, Polarization of domain boundaries in SrTiO\(_3\) studied by layer group and order-parameter symmetry, Phys. Rev. B 102, 184101 (2020).
[9] I. Rychetsky, W. Schranz, and A. Tröster, Symmetry and polarity of antiphase boundaries in PbZrO\(_3\), Phys. Rev. B 104, 224107 (2021).
[10] W. Schranz, A. Tröster, and I. Rychetsky, Signatures of polarity in ferroelastic domain walls and antiphase boundaries of SrTiO\(_3\) and other perovskites, Journal of Alloys and Compounds 890, 161775 (2022).
[11] V. Stepkova, P. Marton, and J. Hlinka, Stress-induced phase transition in ferroelectric domain walls of BaTiO\(_3\), Journal of Physics: Condensed Matter 24, 212201 (2012).
[12] P. Marton, V. Stepkova, and J. Hlinka, Divergence of dielectric permittivity near phase transition within ferroelectric domain boundaries, Phase Transitions 86, 103 (2013) https://doi.org/10.1080/01411594.2012.727211.
[13] E. A. Eliseev, S. V. Kalinin, Y. Gu, M. D. Glinchuk, V. Khist, A. Borisevich, V. Gopalan, L.-Q. Chen, and A. N. Morozovska, Universal emergence of spatially modulated structures induced by flexoantiferrodistortive coupling in multiferroics, Phys. Rev. B 88, 224105 (2013).
[14] A. Schiaffino and M. Stengel, Macroscopic polarization from antiferrodistortive cycloids in ferroelastic SrTiO\(_3\), Phys. Rev. Lett. 119, 137601 (2017).
[15] A. K. Tagantsev, E. Courtens, and L. Arzel, Prediction of a low-temperature ferroelectric instability in antiphase domain boundaries of strontium titanate, Phys. Rev. B 64, 224107 (2001).
[16] B. Meyer and D. Vanderbilt, Ab initio study of ferroelectric domain walls in PbTiO\(_3\), Phys. Rev. B 65, 104111 (2002).
[17] Y.-J. Wang, J. Li, Y.-L. Zhu, and X.-L. Ma, Phase-field modeling and electronic structural analysis of flexoelectric effect at 180° domain walls in ferroelectric PbTiO\(_3\), Journal of Applied Physics 122, 224101 (2017). https://doi.org/10.1063/1.5017219.
[18] R. K. Behera, C.-W. Lee, D. Lee, A. N. Morozovska, S. B. Sinnott, A. Astthagiri, V. Gopalan, and S. R. Phillpot, Structure and energetics of 180° domain walls in PbTiO\(_3\) by density functional theory, Journal of Physics: Condensed Matter 23, 175902 (2011).
[19] J. C. Wojde l and J. Íniguez, Ferroelectric transitions at ferroelectric domain walls found from first principles, Phys. Rev. Lett. 112, 247603 (2014).
[20] M. J. Haun, E. Furman, S. J. Jang, H. A. McK instry, and L. E. Cross, Thermodynamic theory of PbTiO\(_3\), Journal of Applied Physics 62, 3331 (1987). https://doi.org/10.1063/1.339293.
[21] Y. Li, S. Hu, Z. Liu, and L. Chen, Effect of substrate constraint on the stability and evolution of ferroelectric domain structures in thin films, Acta Materialia 50, 395 (2002).