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Surface polar states and pyroelectricity in ferroelastics induced by flexo-roto field

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Theoretical analysis based on the Landau-Ginzburg-Devonshire theory is used to show that the joint action of flexoelectric effect and rotostriction leads to a large spontaneous in-plane polarization (~1-5 μC/cm²) and pyroelectric coefficient (~10⁻³ C/m²K) in the vicinity of surfaces of otherwise non-ferroelectric ferroelastics, such as SrTiO₃, with static octahedral rotations. The origin of the improper polarization and pyroelectricity is an electric field we name flexo-roto field whose strength is proportional to the convolution of the flexoelectric and rotostriction tensors with octahedral tilts and their gradients. Flexo-roto field should exist at surfaces and interfaces in all structures with static octahedral rotations, and thus, it can induce surface polar states and pyroelectricity in a large class of otherwise nonpolar materials. © 2012 American Institute of Physics [http://dx.doi.org/10.1063/1.3701152]

Oxide surfaces and interfaces exhibit intriguing properties such as two-dimensional electron gas, superconductivity, charged domain walls, magnetism, and multiferroicity. Many oxide surfaces possess strong gradients of strain and octahedral rotations. Octahedral rotations (also called the antiferrodistortions) are the most common type of phase transitions involving lattice distortions in perovskite oxide systems. Improper ferroelectricity induced by octahedral rotations is inherent in a number of oxides such as YMnO₃, Ca₃Mn₂O₇, CaTiO₃, and their interfaces. Hereafter, we call the phenomena related to octahedral rotations as “roto” effects. Our primary interest is a rotostriction effect that induces the strain or stress proportional to the second powers of the octahedral rotations. It has been shown that strain and stress gradients can induce polarization near the surfaces and interfaces via the flexoelectric effect. Note that all materials are flexoelectrics, and all materials with static octahedral rotations possess rotostriction. The joint action of the flexoelectric effect and rotostriction can thus lead to a ferroelectric polarization at an interface across which the octahedral rotation varies. Therefore, every antiferrodistortive boundary, twin wall, interface, and surface can, in principle, possesses the roto-flexo effect. Since most functional oxide systems involve natural or artificial interfaces and surfaces, roto-flexo effects are quite general.

Experimental results show that surface influence systematically changes oxygen octahedral rotation behaviour (structural transitions in surface layers). Coexistence of antiferrodistortive and ferroelectric distortions was demonstrated with the help of ab initio calculations at perovskite surfaces, such as PbTiO₃ (001) surface, while it is absent in PbTiO₃ bulk. In particular, the reconstruction of the PbTiO₃ (001) surface revealed a single layer of antiferrodistortive structure with oxygen cages counter-rotated by 10° about the titanium ions. Antiferrodistortive reconstruction of the out-of-plane component of octahedral rotation was reached at the PbO-terminated (001) surface and then observed with x-ray scattering. Ab initio calculations showed that tensile strain enhances the ferroelectric distortion and suppresses the antiferrodistortive rotation in the vicinity of PbTiO₃ (001) surface, while the opposite effect is caused by compressive strain.

Recently, we have theoretically predicted that a combination of flexoelectric effect and rotostriction at oxide interfaces can generate large improper ferroelectricity and pyroelectricity at antiferrodistortive boundaries and elastic twins in SrTiO₃ below 105 K. In this letter, we report that a polar state and pyroelectricity are induced by flexo-roto fields in the vicinity of ferroelastic SrTiO₃ surface even without any elastic domains.

Using Landau-Ginzburg-Devonshire (LGD) approach, we analyze the behaviour on the polar (P_i) and structural (Φ_j) order parameter (OP) components in the presence of ferroelastic surface. Equations of state are

\[ 2h_iΦ_i + 4u^u_{ij}Φ_jΦ_i - v_{ijkl}∂^2Φ_k/∂x_j∂x_l - 2r_{mijk}μ_{mj}Φ_k - 2η_{ijkl}P_kP_lΦ_i = 0, \]

\[ 2a_iP_i + 4a^u_{ijkl}P_jP_kP_l - g_{ijkl}∂^2P_k/∂x_j∂x_l - 2μ_{mijk}μ_{mj}P_k - f_{mnij}∂μ_{mn}/∂x_l - 2η_{ijkl}P_jΦ_i = E_i, \]

where (i, j, k, l) = (x, y, z).
Detailed derivation of Eqs. (1)–(3) is presented in the supplementary material.\textsuperscript{29}\ Sec. S.1 (see also Ref. 28). \( \Phi_i \) is the components \( i = 1 - 3 \) of the structural OP, which is the vector corresponding to the spontaneous octahedral rotation angle around one of their fourfold symmetry axes in a structural phase.\textsuperscript{30,33} Note, that the rotation angle is proportional to the displacement (in pm) of an appropriate oxygen atom from its cubic position, as defined by Uwe and Sakudo.\textsuperscript{31}\ For instance, the most likely case could essentially influence near surface behaviour of the structural OP. For instance, the most likely case \( b_{z}^{S} \ll b_{z}^{F} \) favors the octahedral rotations around the axis normal to the surface (as it was predicted by ab initio calculations for PbTiO\textsubscript{3} (Refs. 24, 25, and 27)).

Allowing for the flexoelectric effect boundary condition for elastic stress at mechanically free flat surface acquires the form\textsuperscript{18}

\[
\sigma_{ij} - f_{ijkl}P_{i,j} + f_{ijkl}P_{i} + q_{ijkl}P_{i}P_{i} = 0 \quad (3)
\]

FIG. 1. (a) Sketch of the problem geometry in the vicinity of SrTiO\textsubscript{3} \[100\] cut. 4-fold axis is parallel to the surface. (b) and (c) Depth z-profile of the structural OP components \( \Phi_{z} \), \( \Phi_{x} \), \( \Phi_{y} \) and \( \Phi_{z} \) (labels near the curves) calculated numerically from \textit{coupled} equation (3) (solid curves) and analytically from \textit{decoupled} equations (8a) (dashed curves) at temperatures \( T = 50 \text{K} \) (b) and \( 90 \text{K} \) (c). SrTiO\textsubscript{3} parameters are listed in Table S.I, supplementary material.\textsuperscript{29}\ and the extrapolation length \( \lambda = 0 \) is defined after Eq. (8b).

\[
\begin{align*}
\left( 2b_{z}^{S} \Phi_{z} - v_{ijkl} \frac{\partial \Phi_{z}}{\partial x_{i}} \right)_{z=0} = 0, \\
\left( 2a_{z}^{S} P_{i} - g_{ijkl} \frac{\partial P_{i}}{\partial x_{l}} + f_{ijkl} \frac{\partial \Phi_{z}}{\partial x_{k}} \right)_{z=0} = 0.
\end{align*}
\]

Third kind boundary conditions (4) and (5) reflect the surface energy contribution into the OP and polarization vector components slope near the surface that can be characterized by so-called extrapolation lengths \( \sim v_{ijkl}/2b_{z}^{S} \) and \( g_{ijkl}/2a_{z}^{S} \). The additional source of polarization in Eq. (5), \( f_{ijkl} \mu_{ik} / 2 \), is originated from the flexoelectric effect.\textsuperscript{19}\ Surface energy coefficients \( a_{z}^{S} \) and \( b_{z}^{S} \) \( i = 1 - 3 \) are regarded positive and weakly temperature dependent. Note that the values of \( b_{z}^{S} \) could be fitted with the “background” isotropic lattice permittivity.\textsuperscript{37}\ The system is considered without top electrode. External electric field is regarded absent.

General mathematical derivation of the boundary condition (6) can be found in Ref. 38. Since inhomogeneous polarization could induce the surface bending via the flexoelectric coupling, Eq. (6) differs from the conventional condition \( \sigma_{i} \mid_{z=0} = 0 \). Compatibility relations should be valid everywhere.

Hereafter, we chose tetragonal SrTiO\textsubscript{3} \( T < 105 \text{K} \), space group I4/mcm) for numerical simulations, since all necessary parameters including gradient coefficients and flexoelectric tensor are known for the material (see Table S.I, supplementary material\textsuperscript{29}). Unfortunately, exact values of gradient coefficients and flexoelectric tensor are unknown for other ferroelastics like CaTiO\textsubscript{3} or EuTiO\textsubscript{3}, but the extension of the obtained results will be valid qualitatively for them, making the flexo-roto field induced polar states at surfaces and interfaces a general phenomenon in nature.

Now let us calculate the depth of the induced polarization penetration from the free surface \( x_{3} = 0 \). For the case when 4-fold axis is parallel to the mono-domain SrTiO\textsubscript{3} surface, the most thermodynamically preferable situation is two \( z \)-dependent components of OP vector, in-plane \( \Phi_{z} \) and out-of-plane \( \Phi_{z} \), and \( z \)-dependent in-plane polarization \( P_{i} \) that does not cause any depolarization field (\( E_{d}^{0} = 0 \), see the sketch of the problem geometry in Fig. 1(a)). Also one may consider out-of-plane polarization \( P_{z} \), but without enough concentration of free carriers its value is strongly affected by the depolarization field.
We calculated numerically that $P_{\parallel}(z)$ values are at least 10$^3$ times higher than $P_{\perp}(z)$ values without screening by free carriers. For the considered geometry, Eq. (6) reduced to the conventional form $\sigma_{33}|_{z=0} = 0$ (see supplementary material, Sec. S.3).

For the case when 4-fold axis is perpendicular to the mono-domain SrTiO$_3$ surface, the OP becomes normal to the surface (i.e., out-of-plane) in the bulk of the sample. The appearance of in-plane OP components is not likely in this case (see comments after Eq. (2)). As a result, only out-of-plane components of polarization $P_{\perp}(z)$ can be induced. The latter is strongly diminished by the depolarization field. Thus, we do not consider the case here, especially because the length scale of $P_{\perp}(z)$ distribution is of order of lattice constant.

We numerically solve coupled systems (1)–(3) when 4-fold axis is parallel to the mono-domain SrTiO$_3$ surface. Results are shown in Figs. 1–3. Our numerical simulations performed for coupled equations (1)–(3) with boundary conditions (4)–(6) demonstrate that polarization weakly affects structural OP. The fact makes it possible to decouple the polarization vector in systems (1)–(3) that reduces to the form (S.12), supplementary material. The solution for strain and stresses has the form (S.13). Decoupling gives us the possibility to look for approximate analytical expression for OP and polarization. For the considered geometry, decoupled equations for OP components have the form

$E^d_\perp = -P_{\perp}(z)/\varepsilon_0\varepsilon_b$.

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surface energy coefficient \( b_1^2 \geq 0 \). Hereinafter, we regard the extrapolation length to be not negative, otherwise higher positively defined terms should be included in the surface energy \( \int b_1^2 \phi_1^2 d^2 r \). Note, that the case \( \lambda_1 = 0 \) (i.e., \( z_0 = 0 \)) corresponds to maximal possible amplitude \( \Phi_1(0) = \text{max} \) and minimal \( \Phi_1(0) = 0 \) as shown in Fig. 1(b). At arbitrary \( \lambda_1 \) constant \( z_0 \) found from the boundary condition (4a) is

\[
z_0 = L_{\phi} \times \tan h\left( \left( \lambda_1 / L_{\phi} \right) (0.5 + \sqrt{0.25 + (\lambda_1 / L_{\phi})^2})^{-1} \right).
\]

The gradient region under the surface has the maximal depth for the case of \( z_0 = 0 \). In the general case, the characteristic depth of the gradient region is about several \( L_{\phi} \).

Numerical simulations proved that the approximate analytical expressions (8a) relatively accurately reproduce the OP distribution calculated numerically from Eq. (3) and their gradients in the near-surface region (see Figs. 1(b) and 1(c)).

Using the elastic solutions (S.3)–(S.4) and decoupling approximation, we simplify equation for polarization \( \partial P_1 / \partial t \) as

\[
\lambda_1(z)P_1 + \left( 4a_{11}^a - 2 \frac{q_1^2}{c_11} \right) P_1^3 - \left( g_{44} - \frac{f_{44}^2}{c_{44}} \right) \frac{\partial^2 P_1}{\partial z^2} = E_{FR}(z),
\]

(9a)

\[
P_1 + \lambda_p \frac{\partial P_1}{\partial z} + P_{FR}(z) \bigg|_{z=0} = 0.
\]

(9b)

Polarization extrapolation length is introduced as \( \lambda_p = g_{44} / 2a_{11}^a \), which geometrical sense is described in Ref. 40. The length is determined by the surface energy coefficient \( a_{11}^a \) that depends on the surface state and is poorly known for ferroelectrics.\(^{31}\) Since \( \lambda_p \) is unknown for SrTiO3, we vary it in the physically realistic range of 1–100 nm.

It follows from Eqs. (9a) that there are several sources of the polarization appearance in the vicinity of surface. The first source is the inhomogeneity in the right-hand-side of Eq. (9a): electric field \( E_{FR}(z) = \left( r_{44}a_{44} / c_{44} \right) \partial(\Phi_1 \Phi_1) / \partial z \), which strength is proportional to the convolution of the flexoelectric and rotostriction tensors with OP gradient, further regarded as gradient flexo-roto field. The depth profile of \( E_{FR}(z) \) is shown in Fig. 1(d). The second source is the inhomogeneity in the boundary condition (9b), \( P_{FR} = \left( r_{44}a_{44} / (4c_{44}a_{11}^a) \right) \Phi_1(0) \Phi_1(0), \) whose strength is also proportional to the convolution of the flexoelectric and rotostriction tensors with OP, further regarded as built-in surface flexo-roto polarization. Both these sources induce improper spontaneous polarization. Note, that \( P_{FR} = 0 \) for the case \( \lambda_1 = 0 \), since \( \Phi_1(0) = 0 \).

The condition \( x_1(z) < 0 \), which is valid near the surface at low temperatures, can lead to the roto-induced ferroelectric polarization appearance under negligibly small depolarization field. Estimations made for SrTiO3 parameters prove that coefficient

\[
x_1(z) = 2 \left( a_1 - \left( \eta_{11} - \frac{q_1^2}{c_11} \right) \Phi_1^2(z) \right) \left( \eta_{11} - \frac{q_1^2}{c_11} \right) \Phi_1^2(z)
\]

(10)
is positive in the single-domain bulk material at temperature \( T < T_S \), where \( \Phi_1(z) \approx \Phi_B \) (otherwise, a bulk material should be ferroelectric). Here, we re-introduced the biquadratic coupling coefficient \( \eta_{11}^a = \eta_{11}^a + \eta_{11}^a \), and \( \eta_{11}^a \) and \( \eta_{11}^a \) for SrTiO3, EuTiO3, and in antiferroelectrics like PbZrO3. In SrTiO3, flexo-roto effect leads to a large spontaneous polarization (\( \approx 1–5 \mu \text{C/cm}^2 \)) and pyroelectric coefficient (\( \approx 10^{-3} \text{C/m}^2 \)). The strength of the gradient flexo-roto field is proportional to the convolution of the flexoelectric and
rotostriction tensors with the gradients of octahedral rotations, which are structural order parameters. The strength of the surface flexo-roto polarization is proportional to the convolution of the flexoelectric and rotostriction tensors with octahedral rotations on the surface. Flexo-roto effects should exist at surfaces in all structures with static rotations, which are abundant in nature, it allows for contribution into polar interfaces in a large class of nonpolar materials.

Note, that there are other possible reasons for polar surface states in nonpolar materials such as SrTiO$_3$: space charge due to defect chemistry and band gap differences between surfaces and bulk, surface reconstruction and atom clustering, surface piezoelectricity, and strained polar regions that extends into the bulk at a distance much larger than a few nanometers. In accordance with these and other studies, combined rotostriction and flexoelectricity cannot be the sole contribution to the polar surface states in ferroelastics. However, the conclusion in this letter is that the surfaces of all ferroelastics and V. Gopalan, D. B. Litvin, “Rotation-reversal symmetries in crystals and V. Rabe, and X. X. Xi, Science 313, 1614 (2006).


15. See supplementary material at http://dx.doi.org/10.1063/1.3701152 for details about the form and structure of free energy, equations of state, and boundary conditions.


