Casals, Blai; Schiaffino, Andrea; Casiraghi, Arianna; Hämäläinen, Sampo J.; López González, Diego; Van Dijken, Sebastiaan; Stengel, Massimiliano; Herranz, Gervasi

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Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.120.217601

Published: 25/05/2018

Please cite the original version:
Low-Temperature Dielectric Anisotropy Driven by an Antiferroelectric Mode in SrTiO₃

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(Received 21 September 2017; revised manuscript received 9 January 2018; published 25 May 2018)

Strontium titanate (SrTiO₃) is the quintessential material for oxide electronics. One of its hallmark features is the transition, driven by antiferrodistortive (AFD) lattice modes, from a cubic to a ferroelastic low-temperature phase. Here we investigate the evolution of the ferroelastic twin walls upon application of an electric field. Remarkably, we find that the dielectric anisotropy of tetragonal SrTiO₃, rather than the intrinsic domain wall polarity, is the main driving force for the motion of the twins. Based on a combined first-principles and Landau-theory analysis, we show that such anisotropy is dominated by a trilinear coupling between the polarization, the AFD lattice tilts, and a previously overlooked antiferroelectric (AFE) mode. We identify the latter AFE phonon with the so-called “R mode” at ~440 cm⁻¹, which was previously detected in IR experiments, but whose microscopic nature was unknown.

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Because of its attractive physical properties, strontium titanate (SrTiO₃) has long captured the attention of condensed matter physicists, becoming an iconic material among oxide perovskites. At room temperature SrTiO₃ crystallizes in the cubic perovskite structure with space group Pm3m [1]. Yet, at T ~ 105 K, SrTiO₃ crystals undergo a ferroelastic transition, to a tetragonal phase (I₄/mcm space group, c/a ≈ 1.0005) [2,3]. Such transition is driven by an antiferrodistortive (AFD) lattice mode, with neighboring TiO₆ octahedra rotating in antiphase along the [001] axis. [4,5] The most obvious manifestation of tetragonality is the anisotropy of the dielectric constant [6,7], which is responsible for the observed birefringence [8]. Recently, ferroelastic domain formation was shown [9–11] to strongly influence other electronic phenomena in SrTiO₃, e.g., superconductivity [12] or two-dimensional electron gases [13–15]. The ability of controlling the electronic degrees of freedom by altering the ferroelastic domain structure provides, in principle, a tantalizing opportunity for new device concepts. To explore this route, however, one first needs to understand whether (and how) the ferroelastic degrees of freedom can be harnessed via a suitable external field. As the ferroelastic domain walls have recently been shown to be polar [16–22], it is reasonable to expect that they will respond to an electrical bias. A detailed study on the evolution of the domain wall topology upon application of a voltage is currently missing, leaving the above question largely unanswered.

Here we use optical microscopy to image ferroelastic twins under an applied electric field, as done previously (at zero field) in SrTiO₃ single crystals [23] and heterointerfaces [10,24]. We find that the domain structure undergoes dramatic changes with the applied external bias. Remarkably, however, such changes cannot be explained by invoking the intrinsic polarity of the walls; instead, we interpret our observations as a consequence of the higher polarizability of ferroelastic domains in the plane normal to the tetragonal axis. Based on our first-principles calculations, we find that such a dielectric anisotropy is largely determined by a trilinear coupling between the polarization, the AFD lattice tilts, and a previously unreported antiferroelectric (AFE) mode. Interestingly, by means of the same mechanism, the AFE mode, whose predicted frequency is ~440 cm⁻¹, becomes IR active below the transition temperature. This allows us to identify it with the “R mode,” which was reported at precisely the same frequency in earlier spectroscopic studies [25–27], but whose lattice representation was formerly unknown.

Figure 1(a) shows schematically the two types of twin structures that are visible at the surface of a (001)-oriented SrTiO₃ crystal. First, we have \{a\} and \{c\} domains, in which the elongated axes are in plane and out of plane, respectively. Second, \{a₁\} and \{a₂\} domains denote \{a\} domains having the elongated axis along orthogonal directions within the plane. Since \{a,c\} domains corrugate the surface, their emergence is revealed by optical reflection microscopy as a striped contrast along in-plane [100] and [010] directions [Fig. 1(c)]. Conversely, \{a₁,a₂\} domains do not corrugate the surface, and they cannot be detected in this way. Interestingly, our experiments reveal that \{a,c\} regions recede with the application of an electric field [Fig. 1(d)]. The recession of \{a,c\} regions is substantiated by constructing an image as the difference of the data recorded at V = +200 V and V = 0 V, which highlights the area where \{a,c\} domains recede [Fig. 1(e)].
pressed by the electric field. The striped area indicates the region were domains recede. The image in (e) is obtained by the subtraction of the images taken at $V = 0$ V and $V = +200$ V. At zero field, stripes along [010] indicate the presence of $\{a, c\}$ domains. After applying a voltage $V = +200$ V, the $\{a, c\}$ domains recede. The image in (e) is obtained by the subtraction of the images at $V = 0$ V and $V = +200$ V. The large striped area indicates the region were $\{a, c\}$ domains are suppressed by the electric field.

To visualize simultaneously both types of twins, we perform Magneto-optical Kerr effect (MOKE) imaging of a 50-nm-thick CoFeB film grown on SrTiO$_3$. In this structure, similarly to the previously reported imprinting of ferroelastic domains into a magnetostrictive film on BaTiO$_3$ [28,29], the strain transfer from ferroelastic twins causes a modulation of the magnetic anisotropy via inverse magnetostriction. Here we use such magnetoelastic coupling to reveal the presence of $\{a, c\}$ and $\{a_1, a_2\}$ twins running along the [010] and [110] directions, respectively [Fig. 2(a)]. For that purpose, MOKE imaging is performed in the remanent state, after applying a magnetic field to set the initial magnetic saturated states of the CoFeB layer perpendicular to the ferroelastic domain walls ($M_{\perp} \perp$DW). In this magnetic configuration, we performed micromagnetic simulations that predict the formation of head-to-tail domains that perfectly match the underlying structure of $\{a_1, a_2\}$ twins [Fig. 2(b)] [30]. This observation is confirmed by MOKE images taken in transverselike and longitudinal configurations which, for $M_{\perp} \perp$DW, are sensitive, respectively, to the $x$ and $y$ projections of the magnetization [Figs. 2(c) and 2(d)].

In view of these results, we use transverselike MOKE imaging with $M_{\perp} \perp$DW to reveal the ferroelastic domain structure under electric fields. For instance, images recorded over a large area ($\sim 0.15$ mm$^2$) at $V = -200$, 0, and $+200$ V show the collapse of $\{a, c\}$ domains after the application of out-of-plane electric fields, while $\{a_1, a_2\}$ twins expand [Fig. 3(a)]. This conclusion is consistent with the recession of $\{a, c\}$ twins observed by the optical images shown in Fig. 1, and is further corroborated by optical reflectance images taken simultaneously with the MOKE images shown in Fig. 3(a). Note that, as discussed above, reflectance imaging only reveals the surface topography and therefore is insensitive to the redistribution of $\{a_1, a_2\}$ twins. Thus, by subtracting the optical images recorded at different electric fields (i.e., $I_V = 0 - I_V = +200$ V and $I_V = 0 - I_V = -200$ V), we disclose the areas in which $\{a, c\}$ twins are suppressed and replaced by $\{a_1, a_2\}$ domains, as shown in the slanted striped contrast in Fig. 3(b).

We will now discuss the effect of temperature on the distribution of ferroelastic twins. For that purpose, we select a region $[\text{length} \approx 400 \mu\text{m} \times \text{width} \approx 20 \mu\text{m}]$ perpendicular to the $\{a_1, a_2\}$ domain walls. At each position along the length, the MOKE intensity is averaged over the width of the selected area. This operation is repeated as a function of the magnetic field strength, thus obtaining a visualization of the magnetization direction at every point along the normal to the $\{a_1, a_2\}$ walls and at each magnetic field of the increasing hysteresis branch (from $-8$ to $+8$ mT); see Fig. S4 (Supplemental Material) [35]. Using this procedure we could visualize the effect of the emergence of ferroelastic twins on the magnetization reversal of the CoFeB film. For instance, at $T = 8$ K the presence of $\{a_1, a_2\}$ twins is already visible at $V = 0$ V [Fig. S4(a) in Ref. [35]]. After the application of a voltage $V = +200$ V, the number of $\{a_1, a_2\}$ twins increases,
while the application of higher voltages ($V = +300 \, \text{V}$) has no further effect [Fig. S4(a) [35]]. By contrast, when the temperature rises, higher electric fields are needed to increase the number of $\{a_1, a_2\}$ twins. This is shown in Fig. S4(b) [35], which shows images recorded at $T = 50 \, \text{K}$. At $V = +200 \, \text{V}$, the $\{a_1, a_2\}$ twins grow, but the effect is not saturated, since higher voltages ($V = +300 \, \text{V}$) are needed to expand further $\{a_1, a_2\}$ domains. Therefore, as temperature increases towards the transition, the electric-field-induced motion of twins becomes stiffer.

Summing up, the application of an out-of-plane electric field expands $\{a_1, a_2\}$ twins—i.e., domains with both elongated axes in the plane—at the expense of $\{a, c\}$ twins. This conclusion is also confirmed by birefringence images taken in transmission (Fig. S3 in the Supplemental Material [35]). To explain this result, various hypotheses are possible. As we said in the introduction, it is natural to expect an electrical bias to couple with the intrinsic polarity of the walls, and hence determine their motion. In our case, however, we can safely rule out such a mechanism as the main driving force. Indeed, the domain wall polarity ($P$) is oriented, by symmetry, towards the apex of the twin [37]; this implies [Fig. 1(a)] that only $\{a, c\}$ twin walls have a nonzero out-of-plane component of $P$ and, hence, couple to a (001) field. Thus, domain wall polarity alone would promote an expansion of the $\{a, c\}$ regions at the expense of the $\{a_1, a_2\}$ ones, which is the exact opposite of what we observe. Additionally, as shown in Fig. S4 (Supplemental Material) [35], electric fields still promote the emergence of $\{a_1, a_2\}$ domains even at temperatures where evidence of the domain wall polarity is weak [16].

Since the properties of the walls cannot explain our observations, the answer must lie within the domains. The most likely candidate in this context is the dielectric anisotropy of tetragonal SrTiO$_3$. To see the relationship between the domain structure and the dielectric anisotropy, consider the electrostatic enthalpy of a parallel-plate capacitor $F(E_j) = -\Omega(e_0/e/2)E_j^2$, where $\Omega$ is the volume of the dielectric, $e_0$ and $e$ are its vacuum and relative permittivity, and $E_j$ is the electric field. A larger value of $e$ implies an energy gain and, thus, domains with higher polarizability along the applied electric field are favored. As we show in the following, the polarizability is significantly larger along the normal to the AFD tilt axis. This implies that $a$-type domains are energetically favored under an applied electric field, which nicely fits with the experimentally observed expansion of the $\{a_1, a_2\}$ regions.

We consider the following Landau-type energy expansion around the parent cubic phase:

$$E = \frac{C_{a2}}{2} e_a e_\beta + \frac{A}{2} |\phi|^2 + B |\phi|^4 - R_{iia} \phi_i^2 e_a + \frac{a_1}{2} P^2$$

$$- Q_{iijj} \phi_i^2 \phi_j^2 - e_iia P_i^2 e_a + \frac{\beta}{2} |u_j|^2 + N e_i i_a P_j u_j^T i_j \phi_k.$$  \hspace{1cm} (1)

Equation (1) includes the standard couplings that are typically considered in the literature: the elastic energy ($C_{a2}$ is the elastic tensor), the double-well potential ($A$ and $B$) associated to octahedral tilts ($\phi_i$), the “rotostriction” ($R_{iia}$) between oxygen tilts and the tetragonal strain, the harmonic energy associated with the “soft” polar mode ($\chi_0^1$ is the inverse of its contribution to the dielectric susceptibility), the biquadratic coupling between the polar mode and oxygen tilts ($Q_{iijj}$), and electrostriction ($e_iia$). The last two terms describe a previously overlooked trilinear coupling mechanism that involves, in addition to the polarization and the tilts, an antiferroelectric mode of the Ti atoms, ($u_j^T$) [see the schematic lattice representation in Fig. 4(a)]. Such a coupling ($N$ is a scalar and $e_i j k$ is the antisymmetric Levi-Civita tensor) implies that $P$ and $u_j^T$ can mix in the ferroelastic tetragonal phase, leading to a “softening” of the polar mode [38] and to the IR activity of the AFE $u_j^T$ mode. As we shall see shortly, both effects have important implications.

To quantify the impact of Eq. (1) on the energetics of the crystal, we study the inverse dielectric constant $e^{-1}$, which in SrTiO$_3$ can be very well approximated [$e^{-1} \sim (e - 1)^{-1}$] by taking the second derivative of the energy with respect to the polarization:

$$4\pi e^{-1} \sim \frac{d^2 E}{dP^2} = \chi_0^1 (T) - 2 \sum_1 \tilde{Q}_{kii} \phi_i^2 (T).$$  \hspace{1cm} (2)

Here, $\tilde{Q}_{kii}$ is an effective biquadratic coupling tensor that includes the contribution of strain and the antiferroelectric mode [see the Supplemental Material for the derivation of Eq. (3) [39]]:

![Image](PHYSICAL REVIEW LETTERS 120, 217601 (2018))
Curie-Weiss behavior of the inverse dielectric susceptibility indicates the direction of the polar mode. Inverse dielectric constant is nearly isotropic. Although such values do indicate a relative softening of the dielectric response normal to the AFD tilt axis, the inferred anisotropy seems too weak to account for the observed field-induced ferroelastic twin redistributions. Without considering $u_{j}^{Ti}$, the calculated values of $\varepsilon^{-1}_{xx}$ and $\varepsilon^{-1}_{zz}$ are virtually the same at any temperature [see the red dashed and green dash-dotted lines in Fig. 4(b)].

It turns out that the antiferroelectric $u_{j}^{Ti}$ mode provides a crucial contribution to the dielectric anisotropy. To understand why, note that $Q_{ik}^{(Ti)} = (N^{2}/2\beta)(1 - \delta_{ik})$ in Eq. (3) is defined positive, and only affects the transverse $\tilde{Q}_{1122}$ component. Thus, $Q_{ik}^{(Ti)}$ leads to a further, pronounced softening of the components of the dielectric tensor that are normal to the AFD tilt axis. Indeed, the calculated value is $Q_{ik}^{(Ti)} = 0.033$, so that $\tilde{Q}_{1122} = Q_{1112} + Q_{1122}^{(c)} + Q_{1122}^{(Ti)} = -0.070$; this is significantly smaller than $\tilde{Q}_{1111} = -0.113$ (see Table I). As a result, the final values of the out-of-plane $\varepsilon^{-1}_{xx}$ and in-plane $\varepsilon^{-1}_{zz}$ components [red dashed and blue dotted lines in Fig. 4(b)] clearly differ. Our conclusions on the dielectric anisotropy are in good agreement with the available experimental literature [7,47,49] and earlier theoretical studies [38]. Also, the fast decrease of the dielectric susceptibility of SrTiO$_3$ with temperature and the ensuing reduction of polarizability is likely responsible for the increasingly hindered ferroelastic twin motion as the transition temperature is approached (see Fig. S4 in Supplemental Material) [35].

Now we turn to the question of the origin of the IR-active $R$ phonon. Our theory predicts that the antiferroelectric $u_{j}^{Ti}$ vibration occurs at a frequency $\omega \sim 440$ cm$^{-1}$. Remarkably, an $R$ mode with $E_u$ symmetry, the same as $u_{j}^{Ti}$, see Fig. 4(a), was observed [25] at a frequency $\omega \sim 435$ cm$^{-1}$, essentially matching our prediction. Such an $R$ mode was tentatively assigned to the doubling of the unit cell and subsequent backfolding of phonon modes from the boundary to the center of the Brillouin zone [26,27]. Clearly, our combined experimental and theoretical analysis allows us to unambiguously identify such an $R$ mode with the antiferroelectric $u_{j}^{Ti}$ phonon described in our work. Note that this mode plays a significant role in the physics of SrTiO$_3$ at low temperatures, as it also mediates an important contribution to the polarity of the twin walls [37].

Before closing, it is worth noting that our model [Eqs. (1)–(3)] also predicts the appearance of dielectric anomalies across the ferroelastic transition associated with the interplay of AFD, polar, and AFE lattice instabilities.

TABLE I. Values calculated for the coefficients $Q_{kkii}$, $Q_{kkii}^{(c)}$, $Q_{kkii}^{(Ti)}$ defined in the text. Ha/bohr units are used.

<table>
<thead>
<tr>
<th>$Q_{kkii}$</th>
<th>$Q_{kkii}^{(c)}$</th>
<th>$Q_{kkii}^{(Ti)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1111</td>
<td>-0.208</td>
<td>+0.095</td>
</tr>
<tr>
<td>1122</td>
<td>-0.031</td>
<td>-0.072</td>
</tr>
</tbody>
</table>
Such couplings should lead to measurable deviations from the Curie-Weiss behavior of SrTiO$_3$ (in addition to the well-known deviations that are due to the “quantum paraelectric” regime) below the ferroelastic transition. We regard this as an interesting topic for future studies.

We acknowledge the support of Ministerio de Economía, Industria y Competitividad (MINECO-Spain) through Grants No. MAT2017-85232-R, No. MAT2014-56063-C2-1-R, No. MAT2016-77100-C2-2-P, No. FIS2013-48668-C2-2-P, and Severo Ochoa SEV-2015-0496, the Generalitat de Catalunya through Grants No. 2017 SGR1377 and No. 2017 SGR1506, the Väisälä foundation and the STSM Grant from the COST Action MP1308. This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant Agreements No. 724529 and No. 307502). Calculations were performed at Supercomputing Center of Galicia (CESGA).


[34] S. Zhang et al., Giant electrical modulation of magnetization in Co$_{80}$Fe$_{20}$B$_{20}$/Pb$_3$(Mg$_{1/3}$ Nb$_{2/3}$)$_3$O$_7$Ti$_{0.3}$O$_3$ (011) heterostructure, Sci. Rep. 4, 3727 (2014).

[35] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.120.217601 for the temperature dependence of the electric-field-induced distribution of ferroelastic domains, which includes Ref. [36].


[39] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.120.217601 for computational methods, which includes Refs. [38,40–47].


[48] All the simulations have been performed within the local-density approximation and using norm-conserving pseudopotentials, treating explicitly 10 electrons for Sr, 12 for Ti, and 6 for O, Monkhorst-Pack $6 \times 6 \times 6$ and cutoff 70 Ha.