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Low-Temperature Dielectric Anisotropy Driven by an Antiferroelectric Mode in SrTiO$_3$

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Strontium titanate (SrTiO$_3$) 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 SrTiO$_3$, 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 an anisotropy is dominated by a trilinear coupling between the polarization, the AFD lattice tilts, and a previously unreported antiferroelectric (AFE) mode. We identify the latter AFE phonon with the so-called “R mode” at $\sim$440 cm$^{-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 (SrTiO$_3$) has long captured the attention of condensed matter physicists, becoming an iconic material among oxide perovskites. At room temperature SrTiO$_3$ crystallizes in the cubic perovskite structure with space group $Pm\overline{3}m$ [1]. Yet, at $T \sim 105$ K, SrTiO$_3$ crystals undergo a ferroelastic transition, to a tetragonal phase ($I4/mcm$ space group, $c/a \approx 1.0005$) [2,3]. Such transition is driven by an antiferrodistortive (AFD) lattice mode, with neighboring TiO$_6$ 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 SrTiO$_3$, 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 SrTiO$_3$ 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 tilts, and a previously unreported antiferroelectric (AFE) mode. Interestingly, by means of the same mechanism, the AFE mode, whose predicted frequency is $\sim$440 cm$^{-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 SrTiO$_3$ crystal. First, we have $\{a\}$ and $\{c\}$ domains, in which the elongated axes are in plane and out of plane, respectively. Second, $\{a_1\}$ and $\{a_2\}$ 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, $\{a_1, a_2\}$ 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. In-plane crystal directions are indicated in (c).

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 taken 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 remnant state, after applying a magnetic field to set the initial magnetic saturated states of the CoFeB layer perpendicular to the ferroelastic domain walls ($M_l$,$\perp$DW). This image reveals the presence of both \{a, c\} and \{a$_1$, a$_2$\} domains. Microscopic simulations of the remanent state for DW [30]. Using this procedure we could visualize the effect of temperature on the distribution of ferroelastic twins. For that purpose, we select a region \{length $\approx 400$ $\mu$m $\times$ (width $\approx 20$ $\mu$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 ($V = +300$ 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 $T = 50$ K. At $V = +200$ V, the $\{a_1, a_2\}$ twins grow, but the effect is not saturated, since higher voltages ($V = +300$ 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 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 $\mathcal{F}(E_j) = -\Omega (e_0 e/2) E_j^2$, 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:

$$E = \frac{C_{\alpha\beta}}{2} e_\alpha e_\beta + \frac{A}{2} |\phi|^2 + B |\phi|^4 - R_{iaa} \phi_i^2 e_a + \frac{\tilde{\chi}_0^{-1}}{2} |P|^2 - Q_{iiij} \phi_i^2 \phi_j^2 - e_{iia} \phi_i^2 e_a + \frac{\beta}{2} |u_i^T|^2 + N e_{ijkl} P_i u_j^{T_i} \phi_k. \tag{1}$$

Equation (1) includes the standard couplings that are typically considered in the literature: the elastic energy ($C_{\alpha\beta}$ is the elastic tensor), the double-well potential ($A$ and $B$) associated to octahedral tilts ($\phi_i$), the “rotostriction” ($R_{iaa}$) 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 ($Q_{iiij}$), 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, ($u_i^T$) [see the schematic lattice representation in Fig. 4(a)]. Such a coupling ($N$ is a scalar and $e_{ijk}$ is the antisymmetric Levi-Civita tensor) implies that $P$ and $u_i^T$ can mix in the ferroelastic tetragonal phase, leading to a “softening” of the polar mode [38] and to the IR activity of the AFE $u_i^T$ 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:

$$4\pi e^{-1} \sim \frac{d^2 E}{dP_i^2} = \tilde{\chi}_0^{-1}(T) - 2 \sum_k \tilde{Q}_{kkii} \phi_k^2(T). \tag{2}$$

Here, $\tilde{Q}_{kkii}$ 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]].

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**FIG. 3.** (a) Transverse MOKE images of the remanent magnetic state ($M_{r,LDW}$) at $V = -200$, 0, $+200$ V. The horizontal stripes indicate $\{a_1, a_2\}$ twins. (b) Images obtained after subtraction of the optical images taken simultaneously with MOKE images shown in (a). The left-hand image in (b) was obtained by subtracting the data at $V = 0$ V from that at $V = -200$ V ($I_{V=0} - I_{V=-200}$) and the right-hand image by subtracting data at $V = 0$ V from that at $V = +200$ V ($I_{V=0} - I_{V=+200}$). Thus, images in (b) indicate the areas where $\{a, c\}$ twins were suppressed by the electric field.
and Curie-Weiss behavior of the inverse dielectric susceptibility \( \epsilon \) indicates the direction of the polar mode. (d) Inverse dielectric constant \( \tilde{Q}_{kkii} \) octahedral tilts. Given the cubic symmetry and the nature of the crystal remained in the cubic high-symmetry structure. The red arrow in (b), the blue (no Ti), and the green dashed lines reproduce the experimental on the dielectric anisotropy are in good agreement with anomalies across the ferroelastic transition associated with the interplay of AFD, polar, and AFE lattice instabilities.

In Fig. 4(a), (b) show schematically the three modes that are coupled by the trilinear term in Eq. (1). (a) AFD mode along the \( x \) axis, (b) AFE mode of the Ti atoms along the \( z \) axis, and (c) polar mode along the \( y \) direction. The yellow arrow in (c) indicates the direction of the polar mode. (d) Inverse dielectric constant \( \epsilon^{-1} \) as function of temperature. The pink dashed line is the experimental (labeled C-W law fitted by experimental data at high temperature, and represents the expected behavior if the crystal remained in the cubic high-symmetry structure. The red (labeled as \( xz \)) and the blue (\( zz \)) lines are the calculated values for \( \epsilon^{-1}_{xz} \) (out of plane) and \( \epsilon^{-1}_{zz} \) (in plane), respectively. For comparison, we also show ["zz (no Ti)," green dashed line] the hypothetical behavior of \( \epsilon^{-1}_{zz} \) if we suppressed the trilinear contributions of strain, tilts, and the antiferroelectric mode that are coupled by the trilinear term in Eq. (1). (a) AFD mode with 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 \( u_j^{(1)} \) 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.

Octahedral tilt axis, the inferred anisotropy seems too weak to account for the observed field-induced ferroelastic twin redistributions. Without considering \( u_j^{(1)} \), the calculated values of \( \epsilon^{-1}_{xz} \) and \( \epsilon^{-1}_{zz} \) 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 \( u_j^{(1)} \) mode provides a crucial contribution to the dielectric anisotropy. To understand why, note that \( Q_{kkii}^{(1)} = (N^2/2\beta)(1 - \delta_{kk}) \) in Eq. (3) is defined positive, and only affects the transverse \( \tilde{Q}_{1122} \) component. Thus, \( Q_{kkii}^{(1)} \) 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 \( Q_{kkii}^{(1)} = 0.033 \), so that \( \tilde{Q}_{1112} = Q_{1122} + Q_{1112}^{(e)} + Q_{1122}^{(1)} = -0.070; \) this is significantly smaller than \( \tilde{Q}_{1111} = -0.113 \) (see Table I). As a result, the final values of the out-of-plane \( \epsilon^{-1}_{xz} \) and in-plane \( \epsilon^{-1}_{zz} \) 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 \( u_j^{(1)} \) vibration occurs at a frequency \( \omega \sim 440 \) cm\(^{-1}\). Remarkably, an \( R \) mode with \( E_u \) symmetry, the same as \( u_j^{(1)} \), 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 \( u_j^{(1)} \) 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].

In Eq. (2), the term \( \chi_1^{-1}(T) \) reproduces the experimental Curie-Weiss behavior of the inverse dielectric susceptibility and \( \phi_2^2(T) \) accounts for the temperature dependence of the octahedral tilts. Given the cubic symmetry and the nature of the spontaneous distortion, only two components of \( \tilde{Q}_{kkii} \) are relevant to our study, namely, the longitudinal \( \tilde{Q}_{1111} \) and transverse \( \tilde{Q}_{1122} \) components.

We are now in position to determine the specific contributions of strain, tilts, and the antiferroelectric mode to the dielectric behavior of SrTiO\(_3\). For that purpose, we calculate all coefficients in Eq. (1) by following the strategy outlined in Ref. [42], i.e., employing density functional perturbation theory, and using the local-density approximation and norm-conserving pseudopotentials [48]. As a first step, we consider only the first two terms in Eq. (3), i.e., excluding the antiferroelectric mode. In these conditions, we find that the values for the longitudinal and transverse components of \( Q_{kkii}^{(e)} \) and \( Q_{kkii}^{(1)} = e_{kkii}C_{\alpha\beta}^{-1}R_{\alpha\beta} \) are similar (\( \tilde{Q}_{1111} = Q_{1111}^{(e)} + Q_{1111}^{(1)} = -0.113, \tilde{Q}_{1122} = Q_{1122}^{(e)} + Q_{1122}^{(1)} = -0.103 \), see Table I) and, thus, the calculated dielectric constant is nearly isotropic. Although such values do indicate a relative softening of the dielectric response normal to the plane.

\[
\tilde{Q}_{kkii} = Q_{kkii}^{(e)} + e_{kkii}C_{\alpha\beta}^{-1}R_{\alpha\beta} + \frac{N^2}{2\beta}(1 - \delta_{kk}). \tag{3}
\]

<table>
<thead>
<tr>
<th>( Q_{kkii} )</th>
<th>( Q_{kkii}^{(e)} )</th>
<th>( Q_{kkii}^{(1)} )</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.

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[34] S. Zhang et al., Giant electrical modulation of magnetization in Co$_{40}$Fe$_{40}$B$_{20}$/Pb(Mg$_{1/3}$Nb$_{2/3}$)$_{0.7}$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.