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Ferroelectricity in [111]-oriented epitaxially-strained $SrTiO_3$ from first principles

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We use first principles density functional theory calculations to investigate the effect of biaxial strain in the low-temperature structural and ferroelectric properties of [111]-oriented SrTiO₃. We find that [111] biaxial strain, achievable by coherent epitaxial growth along the [111] direction, induces novel structural distortions in SrTiO₃ that are not present in either bulk or [001]-oriented SrTiO₃. Under [111] biaxial strain, SrTiO₃ displays ferroelectricity at tensile strain, and paraelectricity at compressive strain. We compute the phonon spectrum and macroscopic polarization of SrTiO₃ as a function of [111] biaxial strain, and relate our results to the predictions of the free energy phenomenological model of Pertsev *et al.* [Phys. Rev. B 61, 825 (2000); Phys. Rev. B 65, 219901 (2002)].

Advances in molecular beam epitaxy have prompted tremendous interest in the effect of coherent epitaxial strain on transition metal oxides^{1,2}. Biaxial strain of [001]-oriented SrTiO₃ ultrathin films, associated with epitaxial growth on cubic perovskite substrates, has been extensively studied and predicted to provide routes to significantly tune its structural³, electronic⁴, and dielectric⁵ properties. However, the effects of biaxial strain associated with perovskite films grown along the [111] direction, on substrates with hexagonal symmetry, has received less attention. The symmetry constraints imposed by biaxial strain perpendicular to [111] for perovskite oxides can lead to new structural phases, new ways to manipulate electronic and magnetic degrees of freedom, and potentially new physical phenomena.

The structural effect of [111] biaxial strain on ABO₃ perovskites has been previously investigated by focusing on a dominant polar or antiferrodistortive instability. First principles calculations predict ferroelectricity for [111]-oriented $PbTiO_3^6$ and $BaTiO_3^{6,7}$, and the existence of Goldstone-like modes in the structural energy landscape of [111]-oriented LaAlO₃⁸ and SrMnO₃⁹. Recently, employing an automated computational workflow based on first principles methods, Angsten et al. studied the effect of [001], [011] and [111] biaxial strain on the polar instability of a large set of perovskite $oxides^{10}$. In addition, (001) and (111) surfaces of SrTiO₃ and other perovskites were recently studied from first principles calculations^{11–13}. Here, motivated by recent experimental and theoretical studies on ferroelectric^{14,15}, electronic¹⁶, magnetic¹⁷⁻²⁰, transport²¹ and topological^{9,22-24} phenomena on [111]-oriented perovskites and superlattice interfaces, we examine the case of perovskites with simultaneous polar and antiferrodistortive structural instabilities, such as $SrTiO_3$.

 $m SrTiO_3$ is a prototypical ABO₃ perovskite that, under certain conditions, display important technological properties such as photocatalysis²⁵ and superconductivity^{26,27}. In bulk form, $m SrTiO_3$ has a cubic $Pm\bar{3}m$

structure at temperatures above 105 K and a tetragonal *I4/mcm* structure at low temperatures below 105 K²⁸ characterized by oxygen octahedron rotations (a⁰a⁰c⁻ in Glazer notation). The frequency of the lowest frequency polar mode is seen to decrease with temperature with an extrapolated Curie temperature of about ~30K²⁹, but this incipient ferroelectricity³⁰ is suppressed by a combination of the oxygen octahedron rotations in the tetragonal phase ^{31–33} and quantum fluctuations at low temperature ^{29,34}.

First-principles calculations of the phonon dispersion of cubic SrTiO₃ show multiple lattice instabilities³⁵. An unstable antiferrodistortive zone-boundary R_5^- mode, corresponding to concerted rotation of the oxygen octahedra, gives rise to the low-temperature tetragonal structure, here denoted as $I4/mcm(R_5^-[001])$. An unstable zone-center polar Γ_4^- mode can be associated with the incipient ferroelectricity. Additional phonon instabilities, including finite-wavevector octahedral rotations along the R-M direction of the Brillouin zone, can lower the energy of the cubic structure in principle but are not observed in bulk phases.

The coupling of lattice instabilities to epitaxial strain can alter the energy landscape and stabilize novel phases, including a rich variety of ferroelectric phases with or without nonpolar antiferrodistortive distortions 36,37 . Phenomenological models^{36–38} and first principles calculations $^{39-41}\,$ predict the emergence of ferroelectricity in [001]-oriented perovskite films under epitaxial strain. The emergence of ferroelectricity is readily explained by strain-polarization coupling, in which ferroic off centering of the Ti atoms in each unit cell arises along elongated lattice vector directions. In the free energy expansion of Pertsev $et \ al.^{36}$, this is manifested in the term $-(S_1P_1^2+S_2P_2^2+S_3P_3^2)$; $\{P_i\}_{i=1,2,3}$ and $\{S_i\}_{i=1-6}$ denote the polarization and strain (Voigt notation) components. At compressive (tensile) [001] biaxial strain: $S_1 = S_2 < 0$ and $S_3 > 0$ ($S_1 = S_2 > 0$ and $S_3 < 0$), and the system lowers its energy by adopting the $P_1 = P_2 = 0$

and $P_3 \neq 0$ ($P_1 = P_2 \neq 0$ and $P_3 = 0$) configuration.

First-principles calculations show increased instability of the polar mode with elongation along a particular direction, and predict the stabilization of the ferroelectric phases $P4mm(\Gamma_4^-[001])$ and $Amm2(\Gamma_4^-[110])$ at compressive and tensile [001] biaxial strain, respectively⁴². Indeed, thin film SrTiO₃ is observed to be ferroelectric above critical compressive and tensile [001] biaxial strains, and to posses a strain-tunable Curie temperature⁴³.

Allowing oxygen octahedral rotations increases the energy gain of polar phases and lower their symmetry. Under [001] biaxial strain, the free energy term $+(S_1Q_1^2 + S_2Q_2^2 + S_3Q_3^2)$, where $\{Q_i\}_{i=1,2,3}$, denote out-of-phase octahedral rotations along cubic lattice directions, favors out-of-plane (in-plane) octahedral rotations at compressive (tensile) strain and the system lowers its energy by adopting the $Q_1 = Q_2 = 0$ and $Q_3 \neq 0$ ($Q_1 = Q_2 \neq 0$ and $Q_3 = 0$) configuration. Consequently, first principles calculations predict the stabilization of the polar phases $I4cm(\Gamma_4^-[001]+R_5^-[001])$ and $Ima2(\Gamma_4^-[110]+R_5^-[110])$ at compressive and tensile strain, respectively.

The phenomenological approach can also be applied to the case of biaxial strain along the [111] direction induced by epitaxy. In this case, the strain-polarization coupling term takes the form $-S(P_1^2 + P_2^2 + P_3^2)$ due to the symmetry constraint $S = S_1 = S_2 = S_3$ in the reference structure. In contrast to the [001] biaxial strain case where ferroelectricity is favored at both tensile and compressive strain, the later coupling predicts ferroelectric $(|\vec{P}| \neq 0)$ and antiferrodistortive $(|\vec{P}| = 0)$ distortions at tensile (S > 0) and compressive (S < 0) [111] biaxial strain, respectively. In addition, the off-diagonal shear strain components S_4 , S_5 and S_6 , which typically cancel in the case of [001] growth direction, assume non zero values and can modify the relative energy stability of polar and antiferrodistortive distortions, as shown below.



FIG. 1. (a) Cubic unit cell displaying a (111) plane and cubic lattice vectors ([100], [010], [001]). (b) Relationship between hexagonal $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ and cartesian (x, y, z) lattice vectors. Sr, Ti and O atoms are denoted by red, green and blue spheres, respectively.

In this work, we use symmetry arguments and first principles calculations to investigate the effect of [111] biaxial strain on the structural and ferroelectric properties of $SrTiO_3$. We find that, similar to the case of [001] biaxial strain, [111]-oriented $SrTiO_3$ displays several lowsymmetry phases with polar ferroelectric and nonpolar antiferrodistortive distortions that are not present in bulk form. However, unlike the [001] case, where $SrTiO_3$ becomes ferroelectric at both tensile and compressive strain, [111] biaxially strained $SrTiO_3$ becomes ferroelectric and paraelectric at tensile and compressive strain, respectively. We list all symmetry allowed ferroelectric phases under [111] biaxial strain and investigate their behavior under strain. Our first principles results are supported by the predictions of a free energy phenomenological model and can be generalized to other perovskite oxides.

Density functional theory (DFT) calculations are performed, within the local density approximation (LDA)⁴⁵, using the Vienna Ab-initio Simulation Package (VASP)^{46,47}. As shown in Fig. 1, epitaxial growth on the (111) surfaces of perovskite substrates is simulated through strained bulk calculations^{3,39} in hexagonal cells. Misfit strain is measured with respect to the computed cubic lattice parameter $a_0 = 3.863$ Å. Structural relaxations are performed keeping the matching plane lattice vectors \vec{a}_1 and \vec{a}_2 fixed ($\langle \vec{a}_{\vec{a}_1,\vec{a}_2} = 120^\circ$), while the out of plane lattice vector \vec{a}_3 and the internal atomic positions are optimized until forces are smaller than 0.1 meV/Å.

Table I shows the \vec{k} -point grid and lattice vector lengths for the hexagonal cells considered in this work. Our VASP calculations use Γ centered \vec{k} -point grids and a plane wave energy cut-off of 500 eV. Projector augmented wave pseudopotentials⁴⁸ explicitly include 10 valence electrons for $Sr(4s^24p^65s^2)$, 12 for Ti $(3s^23p^63d^24s^2)$ and 6 for O $(2s^22p^4)$. Phonon dispersions are computed in the primitive cell using finite differences, $4 \times 4 \times 4$ supercell structures with $2 \times 2 \times 2 \Gamma$ centered \vec{k} -point grids, and are interpolated with PHONOPY⁴⁹. Berry phase polarization calculations are performed within the modern theory of polarization, as implemented in VASP⁵⁰. Our DFT convergence parameters provide good agreement with previous results^{51,52}.

Table II shows the energy and lattice parameters for bulk phases of SrTiO₃. Computed lattice parameters underestimate experimental lattice constants by $\sim 1\%$, as is typical for the LDA. The tetragonal *I4/mcm* structure corresponds to the ground state, in agreement with ex-

TABLE I. DFT calculations are performed in hexagonal supercells. For each supercell we report the number of formula units (# f.u.), lattice vector lengths and \vec{k} -point grid used in total-energy (polarization) calculations.

# f.u.	$ \vec{a}_1 = \vec{a}_2 $	$ \vec{a}_3 $	\vec{k} -point grid
3	$\sqrt{2}a_0$	$\sqrt{3}a_0$	$5 \times 5 \times 5 (9 \times 9 \times 9)$
6	$\sqrt{2}a_0$	$2\sqrt{3}a_0$	$5 \times 5 \times 3 \ (9 \times 9 \times 7)$
24	$2\sqrt{2}a_0$	$2\sqrt{3}a_0$	$3 \times 3 \times 3 (7 \times 7 \times 7)$



FIG. 2. Phonon dispersion for SrTiO_3 under (a) 0%, (b) -4% and (c) +4% [111] biaxial strain computed with DFT-LDA. Colors denote the atomic displacement magnitude for Sr (red), Ti (green), O (blue) at a given phonon frequency. We label longitudinal optical (LO) modes and phonon degeneracies. For easier comparison, we use the symmetry point labels $\Gamma = (0, 0, 0), X = (1/2, 0, 0), M = (1/2, 1/2, 0), M' = (1/2, -1/2, 0), R = (1/2, 1/2, 1/2)$ and R' = (1/2, -1/2, 1/2). (d) Brillouin zone for the reference structure at -4% (left) and +4% (right) strain⁴⁴. Nonzero [111] biaxial strain lowers the symmetry of the Brillouin zone, and leads to an additional symmetry line around the cubic R point.

TABLE II. For each experimental bulk phases of $SrTiO_3$ we report the space group, energy (meV/f.u.) with respect to cubic $Pm\bar{3}m$, and lattice parameters (Å). Experimental lattice parameters (in parenthesis) are taken from Ref.^{53,54}

Space group	Energy (meV/f.u.)	Latt. parameters (Å)
$Pm\bar{3}m$	0	$a_0 = 3.863(3.905)$
I4/mcm	-11	a = b = 5.442(5.507)
		c = 7.753(7.796)

periments. The [111] biaxial strain constraint lowers the symmetry of the cubic perovskite $Pm\bar{3}m$ reference structure to $R\bar{3}m$. We start by considering the effects of this symmetry lowering on the phonon dispersion of the reference $R\bar{3}m$ structure, shown for 0%, -4% and +4% [111] biaxial strain in Fig. 2. Our calculations for 0% strain are in line with previous results for cubic SrTiO₃ using the LDA^{51,52}. The polar transverse optical (TO) mode Γ_4^- is stable but soft (62 cm^{-1}), and the antiferrodistortive M_2^+ and R_5^- modes are unstable (28i cm^{-1} and 91i cm^{-1} , respectively) (see Fig. 2(a)).

At -4% (compressive) strain, the phonon dispersion is quite similar to that at 0%: the lowest frequency polar Γ_4^- mode is slightly stiffened (142 cm^{-1}) and the antiferrodistortive instabilities at M and R are slightly enhanced (65*i* cm^{-1} and 135*i* cm^{-1} , respectively) (see Fig. 2(b)). The symmetry lowering produces a visible splitting of the unstable modes at R and of the lowest frequency polar Γ_4^- mode, as well as the slight dependence of the LO mode frequencies and splittings at Γ on the direction of \vec{q} in the limit $q \to 0$.

In contrast, +4% (tensile) strain has a dramatic effect on the phonon dispersion. In addition to a suppression of the antiferrodistortive instabilities at M and R (24*i* cm^{-1} and 86*i* cm^{-1} , respectively) (see Fig. 2(c)), we find a strong polar instability at Γ (170*i* cm^{-1}), comparable to the instability in [001] biaxial strain that generates the ferroelectric phases. This lowest phonon branch is unstable all the way from Γ to X, a characteristic feature also of the phonon dispersion of cubic BaTiO₃⁵⁵.

In the following, we investigate the low-symmetry structures compatible with the reference $R\bar{3}m$ structure, obtained by freezing in the unstable cubic modes $(\Gamma_4^-, R_5^- \text{ and } M_2^+)$. Table III shows bulk, strained and polar phases of SrTiO₃. For each cubic rotational pattern, we report the nature of the oxygen octahedral tilting (in Glazer notation), symmetry mode decomposition, space group symmetry under [111] biaxial strain, number of formula units, and polar phases obtained by freezing in the polar Γ_4^- mode along different cubic directions (see Fig. 1). For each polar structure, we include the free parameters of the polarization vector in the cubic setting. We list polar phases that are invariant under at least one symmetry equivalent structures (variants).

Under [111] biaxial strain, $Pm\bar{3}m$ is reduced to $R\bar{3}m$, and the commonly known polar phases of BaTiO₃ and

TABLE III. For each bulk phase, we report the oxygen octahedral tilting (in Glazer notation), symmetry mode decomposition, space group symmetry under [111] biaxial strain, number of formula units (f.u.) and space group symmetry obtained upon freezing in the polar Γ_4^- mode along different cubic directions. Symmetry modes are given with respect to cubic $Pm\bar{3}m$ with atomic positions given by Sr (1a), Ti (1b), and O (3c). The polar structure P1 ($\pm p_1 \pm p_2 \pm p_3$) is allowed in every entry.

Bulk	Glazer	Symm.	Strained	f.u.	Polar phases
phase	notation	modes	phase		
$Pm\overline{3}m$	$a^0a^0a^0$		$R\bar{3}m$	3	$R3m \pm (ppp); C2 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Cm \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1p_2)$
I4/mcm	$\mathrm{a}^{0}\mathrm{a}^{0}\mathrm{c}^{-}$	R_5^-	C2/c	6	$C2 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Cc \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1)$
Imma	$a^0b^-b^-$	R_5^-	C2/c	6	$C2 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Cc \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1)$
$R\bar{3}c$	$a^{-}a^{-}a^{-}$	R_5^-	$R\bar{3}c$	6	$R3c \pm (ppp); C2 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Cc \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1)$
P4/mbm	$\mathrm{a}^{0}\mathrm{a}^{0}\mathrm{c}^{+}$	\tilde{M}_2^+	$P2_1/c$	6	$P2_1 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Pc \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1)$
I4/mmm	$a^0b^+b^+$	M_2^+	C2/m	6	$C2 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Cm \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1)$
$Im\bar{3}$	$\mathbf{a}^+\mathbf{a}^+\mathbf{a}^+$	M_2^+	$R\bar{3}$	6	$R3 \pm (ppp)$
C2/m	$a^0b^-c^-$	R_5^-	$P\overline{1}$	6	
Pnma	$a^+b^-b^-$	R_5^-, M_2^+	$P2_1/c$	6	$P2_1 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Pc \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1)$
C2/c	$a^{-}b^{-}b^{-}$	R_5^-	C2/c	6	$C2 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Cc \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1)$
Cmcm	$a^0b^+c^-$	R_5^-, M_2^+	$P\overline{1}$	6	
$P4_2/nmc$	$a^+a^+c^-$	R_5^-, M_2^+	C2/c	6	$C2 \pm (p\bar{p}0), \pm (p0\bar{p}), \pm (0p\bar{p}); Cc \pm (p_1p_1 \pm p_2), \pm (p_1 \pm p_2p_1), \pm (\pm p_2p_1p_1)$
Immm	$a^+b^+c^+$	M_2^+	$P\overline{1}$	6	
$P2_1/m$	$a^+b^-c^-$	R_{5}^{-}, M_{2}^{+}	$P\overline{1}$	6	
$P\bar{1}$	$a^-b^-c^-$	\mathbf{R}_{5}^{-}	$P\bar{1}$	6	

PbTiO₃ -R3m, Amm2 and P4mm– evolve smoothly to R3m, C2 or Cm^6 . The [001]-oriented ferroelectric phases with 8 (R3m), 12 (Amm2), and 6 (P4mm) variants rearrange into [111]-oriented ferroelectric phases with 2 (R3m), 6 (C2) and 3 sets of 6 (Cm) variants⁵⁶. Similarly, the I4/mcm structure lowers its symmetry to monoclinic C2/c ($a^-b^-b^-$ in Glazer notation) and leads to the ferroelectric phases C2 and Cc, combining polar and antiferrodistortive distortions.

Table III includes hypothetical bulk phases. Similar to I4/mcm, the Imma and $P4_2/nmc$ structures lower their symmetry to monoclinic C2/c. The C2/c structure, characterized by having the same rotational pattern along two different cubic directions, leads to the ferroelectric phases C2 and Cc. Freezing in the polar Γ_4^- mode in the $R\bar{3}c$ phase leads to the ferroelectric phases R3c, C2 (denoted as $C2^*$ in the following to distinguish it from the C2 structure without octahedral tilting) and Cc. The Pnma structure, the ground state of several oxide perovskites⁵⁷, lowers its symmetry to $P2_1/c$ and leads to the polar structures $P2_1$ and Pc. The P4/mbm, I4/mmm and $Im\bar{3}$ structures lower their symmetry to $P2_1/c$, C2/m and $R\bar{3}$, respectively. Finally, several phases, C2/m, Cmcm, Immm, $P2_1/m$ and $P\overline{1}$, lead to the low-symmetry $P\overline{1}$ structure.

Next, we explore the relative energy stability of the structures in Table III under [111] biaxial strain. Fig. 3 shows the energy gain with respect to $R\bar{3}m$. The strain diagram displays several low-symmetry low-energy structures. At zero-temperature, nonpolar $P2_1/c$ is favored under compressive strain. Under tensile strain, two phases –nonpolar $R\bar{3}c$ at small strain, and then polar Cc at higher strain– are predicted. At tensile strain, several polar phases are nearby in energy and display a small energy difference with $R\bar{3}m$, suggesting that is quite

likely to observe a ferroelectric phase at higher temperatures and large enough strain. We organize our following analysis by looking at the free energy coupling terms involving polar, antiferrodistortive and strain degrees of freedom. We refer to Pertsev *et al.*³⁶ for the sign and relative magnitude of the coefficients in front of the free



FIG. 3. Energy (meV/f.u.) versus [111] biaxial strain (%) diagram for SrTiO₃. For each strain value, relative energy stability is computed with respect to the reference $R\bar{3}m$ structure. Negative (positive) values represent compressive (tensile) [111] biaxial strain. The legend shows the symmetry modes for the low-symmetry structures. $C2^*$ denotes the structure obtained from C2 by freezing in the R_5^- [111] mode.

energy terms.

Similar to the [001] biaxial strain case, antiferrodistortive oxygen octahedral rotations are stabilized in the entire strain range due to the strong R_5^- instability. At compressive strain, the paraelectric phases C2/c and $P2_1/c$ dominate at low-energy. At -4% strain, the rotational angles along the cubic directions are given by 11°, 6° and 6° for C2/c (a⁻b⁻b⁻ in Glazer notation) and 0°, 11° and 11° for $P2_1/c$ (a⁺b⁻b⁻ in Glazer notation). The unstable M_2^+ cubic mode, not included in the phenomenological model, breaks additional symmetries and favors $P2_1/c$ over C2/c by a small energy difference. At tensile strain, the paraelectric phase $R\bar{3}c$ (a⁻a⁻a⁻) corresponds to the ground state energy structure between 0% and +1.2% strain and is later suppressed above $\sim +1.5\%$ strain.

The splitting of the R_5^- mode supresses the antiferrodistortive R3c phase (a⁻a⁻a⁻) at compressive strain (see Fig. 3). For rotational patters away from the [111] axis, the coefficient in front of the free energy term $+S(Q_1^2 + Q_2^2 + Q_3^2)$ ($S = S_1 = S_2 = S_3$) is positive and predicts enhancement and suppression of octahedral tiltings at compressive (S < 0) and tensile (S > 0) strain, respectively. Accordingly, the rotational angles decrease with strain to 8 (0%) and 5 (4%) for $P2_1/c$, and to 10°, 4° and 4° (0%) for C2/c. For R3c, the rotational angles increase with strain, and are given by 2°, 6° and 7° at -4, 0 and 4% strain, respectively.

Interestingly, the splitting of the three-fold R_5^- cubic mode induces a first order transition between $P2_1/c$ and $R\bar{3}c$, as well as a discontinuity in the energy profile of C2/c. The splitting of the R_5^- mode and the discontinuity of the rotational patterns originates from the free energy term $-(S_4Q_2Q_3 + S_5Q_1Q_3 + S_6Q_1Q_2)$. Under strain, this term takes the form $+S_v(Q_2Q_3 + Q_1Q_3 + Q_1Q_2)$ $(S_v = S_4 = S_5 = S_6)$ and approaches $-S_vQ^2$ and $+S_v3Q^2$ for $C2/c(R_5^-[1\bar{1}0])$ and $R\bar{3}c(R_5^-[111])$, respectively, favoring C2/c and $R\bar{3}c$ at compressive $(S_v > 0)$ and tensile $(S_v < 0)$ strain, respectively. Above 0% strain, C2/c converges to the higher-symmetry structure $R\bar{3}c$ and display a discontinuity.

In sharp contrast to the [001] biaxial strain case, all ferroelectric phases are stabilized at tensile [111] biaxial strain, in agreement with the results of Fig. 2. The free energy term $-S(P_1^2 + P_2^2 + P_3^2)$ ($S = S_1 = S_2 = S_3$) has a negative sign and predicts suppression and enhancement of ferroelectricity at compressive (S < 0) and tensile (S > 0) strain, respectively. The ferroelectric phases Cm, C2 and R3m are stabilized at +0.5%, +0.5% and +1.3% strain, respectively, due to the stabilization of the Γ_4^- phonon mode.

The relative strain stabilization of Cm, C2 and R3m at tensile strain and the splitting of the unstable TO mode at Γ (see Fig. 2(c)) originates by the free energy term $-(S_4P_2P_3 + S_5P_1P_3 + S_6P_1P_2)$. Upon stabilization of the polar Γ_4^- mode at tensile strain, the coupling term takes the form $-S_v(P_2P_3 + P_1P_3 + P_1P_2)$ ($S_v = S_4 =$ $S_5 = S_6$), and approaches $+S_vP^2$ for $Cm(\Gamma_4^-[111])$ and $C2(\Gamma_4^-[1\bar{1}0])$, and $-S_v 3P^2$ for $R3m(\Gamma_4^-[111])$. The later effectively favors Cm and C2 over R3m by a small energy difference. As shown in Fig. 3, in the absence of oxygen octahedral rotations, the lowest energy structure corresponds to Cm^{10} .

Polar and antiferrodistortive coupling terms further increase the energy gain of the ferroelectric phases. The R3c, $C2^*$ and Cc structures, combining polar and antiferrodistortive distortions (Γ_4^- and R_5^- instabilities), are stabilized almost simultaneously at $\pm 1.2\%$, $\pm 1.1\%$ and $\pm 1.2\%$ strain, respectively. The strain-independent free energy term $-(P_1P_2Q_1Q_2+P_1P_3Q_1Q_3+P_2P_3Q_2Q_3)$ shifts the critical strain stabilization of the ferroelectric phases, and above $\pm 1.2\%$ strain, favors the ferroelectric cc phase as the ground state of the system. Notably, the low-symmetry polar phases $P2_1$, Pc, R3, and P1 are not stabilized in SrTiO₃ and converge to the higher-symmetry Cc phase.



FIG. 4. Polarization (P) versus [111] biaxial strain along the cartesian coordinates (x, y, z). The relation between cartesian and cubic directions is given in Fig. 1. Polar structures are separated among those without: (a) R3m, (b) C2, (c) Cm, and those with: (d) R3c, (e) $C2^*$, (f) Cc, oxygen octahedral rotations.

Finally, Fig. 4 shows the polarization as a function of [111] biaxial strain for the ferroelectric phases shown in Fig. 3. Polarization components are shown along cartesian and cubic directions in Fig. 4 and Table III, respectively, and their relation is described in Fig. 1. Similar to the [001] case, polarization becomes nonzero above a critical strain, and its magnitude increases with ten-

sile strain. The maximum polarization value at +4% [111] biaxial strain correspond to 42 $\mu C/cm^2$ for Cm (7 and 42 $\mu C/cm^2$ in-plane and out-of-plane, respectively), smaller than the maximum polarization value computed for an equivalent amount of [001] biaxial strain (53 and 50 $\mu C/cm^2$ for P4mm and Amm2 at compressive and tensile [001] biaxial strain, respectively).

Ferroelectric phases display in-plane and/or out-ofplane polarization components at tensile [111] biaxial strain. Notably, the out-of-plane polarization component of Cm can be induced by an in-plane electric field due to a symmetry allowed third-order term in the free energy expansion⁵⁶, suggesting a coupling mechanism between in-plane and out-of-plane polarization components. Our results are expected to be in qualitative agreement with experiments, and in particular, to be independent of the choice of DFT functional. In this regard, we find that the generalized gradient approximation⁵⁸ leads to qualitatively similar results than the LDA, and predicts Ccas the ground state structure at tensile strain.

More generally, the symmetry conditions imposed on the material by [111] biaxial strain are summarized by the strain conditions $S = S_1 = S_2 = S_3$ and $S_v = S_4 =$ $S_5 = S_6$ in the reference coordinates, with $S_v \ll S$. The latter shows that biaxial strain applied perpendicular to the [111] growth direction resembles the application of hydrostatic pressure. Unlike [001] biaxial strain, which favors Ti off centering along out- and in-plane lattice vectors, tensile [111] biaxial induces a uniform elongation of the unit cell and favors Ti off centering simultaeously along the out- and in-plane directions. Therefore, tensile [111] biaxial strain softens the TO mode and favors the emergence of ferroelectricity.

Our first principles results can be easily generalized to other ABO_3 perovskite oxides with polar and antiferrodistortive instabilities. In particular, the symmetry analysis of Table III is valid for any bulk or layered perovskite heterostructure. However, the relative stability of the symmetry allowed nonpolar and polar phases will depend on the stoichiometric details of the material, or equivalently, the coefficients in front of the free energy terms in the phenomenological model.

In summary, DFT calculations show that $SrTiO_3$ display ferroelectricity at tensile [111] biaxial strain and paraelectricity at compressive [111] biaxial strain. At tensile strain, ferroelectricity emerge with the softening of the lowest TO polar mode and polarization increases with tensile strain. At compressive strain, the absence of ferroelectricity can be explained by a homogeneous suppression of the polar mode.

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