

Defect-driven switchable polarization in SrTiO₃Wahib Aggoune^{1,2,*} and Matthias Scheffler¹¹The NOMAD Laboratory at Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany²Institut für Physik and CSMB, Humboldt-Universität zu Berlin, Berlin, Germany

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Perovskites with tunable and switchable polarization hold immense promise for unlocking novel functionalities. Using density-functional theory, we reveal that intrinsic defects can induce, enhance, and control polarization in nonferroelectric perovskites, with SrTiO₃ as our model system. At high defect concentrations, these systems exhibit strong spontaneous polarization—comparable to that of conventional ferroelectrics. Crucially, this polarization is switchable, enabled by the inherent symmetry-equivalence of defect sites in SrTiO₃. Strikingly, polarization switching not only reverses the polarization direction and modulates its magnitude but also modifies the spatial distribution of localized defect states. This dynamic behavior points to unprecedented responses to external stimuli, opening new avenues for defect-engineered materials design.

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I. INTRODUCTION

Ferroelectrics have garnered significant attention over the past hundred years due to their fundamental materials properties and potential technological applications [1]. These materials possess a net spontaneous polarization arising from the collective alignment of electric dipoles. Interestingly, the polarization direction can be reversibly switched by applying an external electric field, resulting in a characteristic polarization (P) hysteresis loop. This property is critical for memory technologies such as ferroelectric field-effect transistors used in nonvolatile memory devices [2,3]. Conventional ferroelectrics are predominantly perovskite-type oxides with the general formula $A_xB_yO_3$ (A and B represent cations; O is the oxygen anion; $x, y = 1$) [4]. The formation of intrinsic defects has been proposed not only to enhance existing polarization [5] but also to induce polarization in otherwise paraelectric perovskites [6–8]. Recent progress in growth techniques, enabling precise control over sample stoichiometry, has opened new avenues for defect engineering. This, in turn, has expanded opportunities for discovering novel ferroelectric materials with unprecedented properties.

As such, recent experimental works [7,9–11] have explored the properties of off-stoichiometric (x, y = close to 1) SrTiO₃ thin films grown under Ti-rich and Sr-poor conditions. This material is one of the most studied oxide perovskites to develop original ideas/concepts due to its various, fascinating physical properties [12]. For the above purpose, its stable

cubic phase at room temperature eases to study and disentangle the role of defects and interfacial strain in ultrathin films. Emergence of room-temperature ferroelectricity at reduced dimensions in strain-free off-stoichiometric SrTiO₃ (STO hereafter), with a clear P -hysteresis, is observed [7]. The polarization switching (PS) is demonstrated and attributed to defects [7,9]. However, the details of the mechanism are hitherto unclear. Under similar off-stoichiometry (intrinsic defects), fascinating experiments also observed a resistive switching (RS) from a high- to a low-resistive state upon applied voltages, which is associated with the latter PS [10,11]. Interestingly, RS varies with the defect concentration as well as from low- to room-temperature [11]. In the latter, STO is about 20% deficient in Sr and 10% richer in Ti atoms. This suggests a defect complex, which consists of Ti-interstitial (Ti_i) and $2 \times$ Sr-vacancy (V_{Sr}). Note that in the literature the $Ti_i + V_{Sr}$ pair is called as Ti_{Sr} antisite [6–8,11] although the Ti atom shifts from the Sr site. Here, from now on, we will also adopt this nomenclature of Ti_{Sr} antisite for the $(Ti_i + V_{Sr})$ pair to ease the discussion of the $Ti_i + 2 \times V_{Sr}$ case, which will then be Ti_{Sr} antisite plus V_{Sr} defect complex ($Ti_{Sr} + V_{Sr}$).

Previous theoretical works based on density functional theory (DFT) predicted the Ti_{Sr} antisite alone to induce a switchable spontaneous polarization in STO [6–8]. Based on these reports, the Ti_{Sr} antisite is suggested as the origin of the experimentally observed PS and RS [7,9,11], although its exact role remains unclear. Specifically, this defect acts as an electron donor [6], whereas the experimental grown samples [11] exhibit an insulating character. This suggests that the Ti_{Sr} antisite is compensated by V_{Sr} . Therefore, detailed knowledge of the defect characteristics in such a prototype material, including the unexplored defect complex ($Ti_{Sr} + V_{Sr}$, see below), is crucial toward tailoring their role and developing promising applications based on the PS and RS behaviors.

So far, from the computational side, mostly semilocal and/or Hubbard functionals were used to explore the Ti_{Sr} antisite [6–8,13]. A few studies have employed the hybrid

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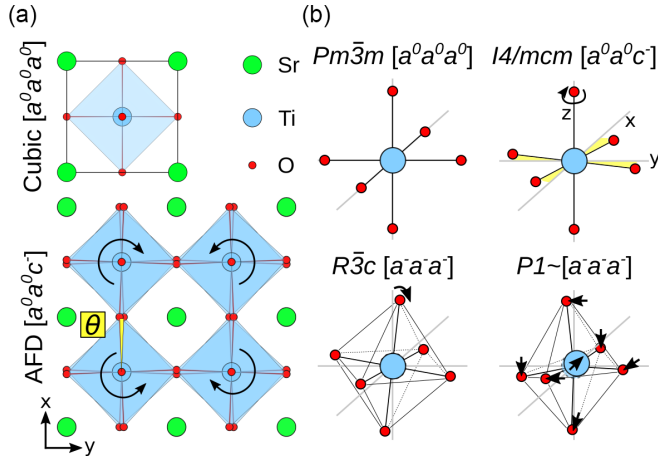


FIG. 1. (a) Top view of the cubic and the antiferrodistortive (AFD) structures reported experimentally at room and low temperature, respectively. The yellow color highlights the tilt angle θ of the AFD structure in the top view. (b) Sketch of the TiO_6 octahedral in the cubic ($Pm\bar{3}m$) and the AFD ($I4/mcm$, $R\bar{3}c$, and $P1$) geometries shown in Table I. In the $P1$ configuration, the shift of the Ti atoms ($[111]$) and distortion of the oxygen atoms are highlighted by black arrows.

exchange-correlation (XC) functional HSE06 for both energy and geometry relaxation of the defects, but either with small supercells (160 atoms) [14] or with supercells that exclude/constrain the octahedral tilt of the perovskite lattice (see Fig. 1 below) [15]. A previous report demonstrated the complexity and the importance of considering a large supercell also accommodating the octahedral tilt, spin-polarization, and a careful consideration of the XC effects to properly describe the characteristics of intrinsic defects [16]. Defect complexes,

which we intend to explore here, could uncover more challenges, and therefore necessitate thorough analysis.

In this paper, motivated by the experimentally observed PS and RS behaviors [7,9–11] as well as the challenges from the theoretical predictions, we aim to carefully explore the characteristics of defects in STO, including the unexplored defect complex “ Ti_{Sr} antisite + V_{Sr} ”. With the recent remarkable progress in the performance of the FHI-aims [17] package achieved with hybrid functionals [18], we employ DFT with the Heyd-Scuseria-Ernzerhof (HSE06) [19] XC-functional for all calculations, including the structural relaxation, unless otherwise stated. At first we will discuss the different STO phases/symmetries and report the stability diagram as function of the chemical potential of the components. Then the thermodynamic stabilities of different intrinsic point defects such as vacancies, interstitials, and their complexes, are analyzed. We demonstrate the critical role of the XC treatment in predicting the defect characteristics. We find that the Ti_{Sr} antisite is energetically favorable and acts as an electron donor. Remarkably, an additional V_{Sr} , which acts as an electron acceptor, enhances the Ti_{Sr} stability and compensates its charge. This defect complex is found to exhibit a spontaneous P comparable to typical ferroelectrics such as BaTiO_3 . By switching the defect position between equivalent sites, we explore possibilities and energy barriers for switching the polarization along different pathways. We also discuss how the switching affects the electronic properties of the material.

II. METHOD

All calculations are performed using FHI-aims [17], an all-electron full-potential package employing numerical atom-centered orbitals. For XC effects, the hybrid functional HSE06 [19] is considered for all calculations (structural relaxations and electronic properties). For all atomic species,

TABLE I. Structural parameters and electronic properties of the cubic and the AFD phases of STO. Space group (s.g.), lattice parameter ($a[\text{\AA}]$), c/a ratio, tilt angle (θ), the difference with the cubic phase energy (ΔE), polarization P , and electronic band gap are shown for all symmetries using different XC functionals. The experimental values are shown for the corresponding tilt modes only.

Phase	Tilt	s.g.	XC	a	c/a	θ°	ΔE meV/f.u.	P $\mu\text{C}/\text{cm}^2$	Band gap
Cubic	$a^0a^0a^0$	$Pm\bar{3}m$	PBEsol	3.889	1	0	0	0	1.83
			HSE06(20%)	3.904	1	0	0	0	2.95
			HSE06(25%)	3.896	1	0	0	0	3.28
			Exp.(~ 110 K)	3.900 ^a	1	0	—	0	3.22–3.26 ^b
			Exp.(300 K)	3.905 ^a	1	0	—	0	3.10–3.25 ^b
AFD	$a^0a^0c^-$	$I4/mcm$	PBEsol	3.879	1.0062	5.6	−7.7	0	1.94
			HSE06(20%)	3.901	1.0018	2.9	−1.1	0	2.98
			HSE06(25%)	3.895	1.0010	2.2	−0.8	0	3.29
			Exp.(< 66 K)	3.898 ^a	1.0006 ^a	2.1 ^c	—	—	3.2–3.27 ^b
	$a^-a^-a^-$	$R\bar{3}c$	PBEsol	3.887	1	4.3	−7.7	0	1.96
			HSE06(20%)	3.904	1	2.1	−2.3	0	2.99
			HSE06(25%)	3.896	1	1.5	−2.1	0	3.29
	$\sim a^-a^-a^-$	$P1$	PBEsol	~ 3.891	1	~ 4.5	−9.6	22.7	2.11
			HSE06(20%)	3.911	1	3.8	−6.2	21.3	3.26
			HSE06(25%)	3.902	1	3.2	−4.3	22.1	3.52

^aReference [20] at 66, 115, and 300 K.

^bExperimental optical gaps [21–24] at 0, 110, and 300 K.

^cReference [25] at 4.2 K.

we use an *intermediate* setting. The generalized gradient approximation (GGA) in the PBEsol parametrization [26] is considered, in selected cases, to demonstrate the important role of the XC functional. In the latter, a *tight* setting is used, but *intermediate* already converges both band gap and lattice parameter up to 20 meV and 0.003 Å, respectively.

For pristine STO, cubic with a five-atom unitcell and tetragonal with a ten-atom unitcell are considered. Tetragonal with a 20-atom $\sqrt{2} \times \sqrt{2} \times 2$ structure is also considered for exploring other symmetries. The sampling of the Brillouin zone (BZ) is performed with a $\sim 0.2 \text{ Å}^{-1}$ grid density for these pristine unit cells (i.e., an $8 \times 8 \times 8$ k grid for the five-atom cubic structure). Lattice constants and internal coordinates are optimized until the residual forces on each atom are less than 0.001 eV/Å. For these bulk phases, HSE06 incorporates $\alpha = 25\%$ of Hartree-Fock exact-exchange [HSE(25) hereafter].

For point defects simulation, we use a 320-atom $4 \times 4 \times 4$ supercell, which can accommodate the octahedral tilts. At this size, the interactions between the periodic images of different cells are negligible, as reported in Ref. [16]. The HSE06 functional is also used for atomic relaxation of all supercells, but with $\alpha = 20\%$ (HSE(20) hereafter), which is tuned to set the band gap within the range of the experimental values (see below). The reason for using $\alpha = 25\%$ in pristine STO unitcell is also discussed. BZ integration is performed on a Γ -centered $1 \times 1 \times 1$ k grid. This choice converges the defects' transition-energy level up to 50 meV compared with a Γ -centered $2 \times 2 \times 2$ k grid, as tested at the PBEsol level (with 320-atom cell) for the defect complex. Lattice parameters are fixed to those of a defect-free supercell, while all atomic positions in the supercell are optimized ($< 0.005 \text{ eV Å}^{-1}$). The impact of relaxing the lattice parameters on the point defect calculations ($4 \times 4 \times 4$ supercell) is tested at the PBEsol level and shows a negligible effect on the formation energy of the point defect. Details can be found in the Supplemental Material (SM) [27]. Spin polarization is considered in both relaxation and electronic properties for all defects calculations.

For simulating the characteristics of the defects with high concentration (12.5%), a 40-atom $2 \times 2 \times 2$ supercell is considered along with a $4 \times 4 \times 4$ k-grid sampling. The latter is employed to reproduce the experimental concentration [11], considering a homogeneous distribution. In this case, both internal coordinates and lattice parameters are optimized ($< 0.001 \text{ eV Å}^{-1}$). Their band structures are computed with an $8 \times 8 \times 8$ k grid. To evaluate the energy barriers for switching the defect positions, the *climbing* Nudged Elastic Band (*c* – NEB) method [28] can be used.

Testing the latter approach at the PBEsol level revealed the need to perform hundreds of DFT calculations [27]. For some defects the HSE06 functional is required due to the presence of localized defect states, making *c* – NEB challenging. Thus, we instead create intermediate *images* with linear interpolation of the atomic coordinates. Then, for each image, we fix the Ti_{Sr} position and the Sr atom at the origin (i.e., fix one Sr $\leftrightarrow$ Ti_{Sr} distance) and allow all other atomic positions and lattice parameters to relax. Specifically, in our peculiar high defect concentration (12.5%), all atoms within the supercell are affected by the defect. As shown in the SM, this alternative gives a similar energy barrier as the full *c* – NEB. It captures essential features of the *c* – NEB search space by approaching

the lowest energy path, and allows us to use HSE06 at low costs (compared to full *c* – NEB). For a smooth relaxation, we use the relaxed lattice parameter of an *image* as a starting lattice for optimizing the next *image*. It should be noted that some switching paths, such as AD [shown in later Fig. 4(a)], require the displacement of the eight neighboring Ti atoms to enable the antisite to move into the adjacent *pseudocube*. The relaxation of the lattice parameter is considered here as a way to approximately capture or mimic this dynamic process. The changes in the lattice parameters upon switching is discussed below. The *x* axis in the energy-barrier plots is the distance (*d*) between the *initial* and *final* Ti_{Sr} position.

The magnitude of the polarization induced in a given structure is evaluated within the Berry phase approach [29] and referenced to its perfect structure, as shown in the SM. This requires the calculation of the polarization branch going from the centrosymmetric cubic to the tetragonal to the fully relaxed defect structure. The intermediate *images* are generated with linear interpolation of the atomic coordinates. The *x* axis in the polarization plots shown in the SM represents the mass-weighted configurational coordinate (*Q*) of each *image*, referenced to the perfect structure (*Q* = 0). This is evaluated using the NONRAD package [30].

Vacancies (interstitials) are created by removing (adding) the corresponding atomic species. Charged defects states are obtained by adjusting the number of electrons. In these cases, a homogeneous background charge density is introduced for compensation. The formation energy (*E_f*) of a defect is given by

$$E_f^{D^q} = E_{\text{tot}}^{D^q} - E_{\text{tot}}^{\text{bulk}} - \sum_i n_i \mu_i + q(E_F + E_{\text{VBM}}^{\text{bulk}}) + E_{\text{corr}}^q, \quad (1)$$

where $E_{\text{tot}}^{D^q}$ is the total energy of the supercell containing a defect *D* in charge state *q*; $E_{\text{tot}}^{\text{bulk}}$ that of the defect-free counterpart; n_i is the number of atoms being removed (< 0) or added (> 0) to create the defect *D*, and μ_i is the corresponding chemical potential. The latter is defined as $\mu_i = \Delta\mu_i + \mu_i^{\text{ref}}$. Thus, it is referenced to the total energy per atom of a physical reservoir such as a gas or a bulk phase. The electron chemical potential (Fermi-level, *E_F*) can be in the range between the valence band maximum (VBM) and the conduction band minimum (CBM) of the perfect STO supercell. The term E_{corr}^q accounts for the finite-size effects as well as for the correct alignment of the electrostatic potential between the defected and the pristine system. Negligible values are found from the latter correction, while the former is ignored because of the high dielectric constant ($\sim 10^4$ [31]) and the large supercell considered. Thus, E_{corr} is neglected.

The formation energy of bulk SrTiO₃ is defined in terms of the atomic chemical potentials as $\Delta H_f^{\text{SrTiO}_3} = \Delta\mu_{\text{Sr}} + \Delta\mu_{\text{Ti}} + 3\Delta\mu_{\text{O}}$. The chemical potentials of the different elements are defined as

$$\begin{aligned} \mu_{\text{Sr}} &= \Delta\mu_{\text{Sr}} + E_{\text{Sr}}^{\text{bulk}}, & \mu_{\text{Ti}} &= \Delta\mu_{\text{Ti}} + E_{\text{Ti}}^{\text{bulk}}, \\ \mu_{\text{O}} &= \Delta\mu_{\text{O}} + \frac{E_{\text{O}_2}}{2}, \end{aligned}$$

where $E_{\text{Sr}}^{\text{bulk}}$, $E_{\text{Ti}}^{\text{bulk}}$, and E_{O_2} are the total energies of the Sr, Ti, and O atoms in their bulk reference stable states (FCC,

hexagonal- $P6_3/mmc$, and molecular phase, respectively). To plot the STO energy diagram as a function of $\Delta\mu_{\text{Ti}}$ and $\Delta\mu_{\text{O}}$, we consider the boundary conditions related to the formation of SrO and TiO_2 precipitations, as follows: $\Delta\mu_{\text{Sr}} + \Delta\mu_{\text{O}} < \Delta H_{\text{f}}^{\text{SrO}}$ and $\Delta\mu_{\text{Ti}} + 2\Delta\mu_{\text{O}} < \Delta H_{\text{f}}^{\text{TiO}_2}$, where ΔH_{f} is the formation enthalpy of each precipitation. The calculated ΔH_{f} of SrTiO_3 , SrO (rocksalt), and TiO_2 (anatase, rutile also have a similar value) are about -16.66 , -5.69 , and -9.60 eV/formula-unit (f.u.), respectively. The boundaries given above are expressed as a function of $\Delta\mu_{\text{Ti}}$ and $\Delta\mu_{\text{O}}$, as follows:

$$\begin{cases} \Delta\mu_{\text{Ti}} + 2\Delta\mu_{\text{O}} > \Delta H_{\text{f}}^{\text{SrTiO}_3} - \Delta H_{\text{f}}^{\text{SrO}}, \\ \Delta\mu_{\text{Ti}} + 2\Delta\mu_{\text{O}} < \Delta H_{\text{f}}^{\text{TiO}_2} \end{cases} \quad (2)$$

Atomic structures are visualized using the VESTA software [32].

III. RESULTS AND DISCUSSION

A. Characteristics of pristine SrTiO_3

As our goal is to simulate defects in large supercells, it is important to explore the pristine STO phases, the role of the XC treatment, the supercells size, and select the optimal ones to achieve our goal.

Let us first summarize the reported characteristics of the bulk STO, which have been intensively studied by both theory and experiment. At room temperature, STO crystallizes in the centrosymmetric cubic phase ($Pm\bar{3}m$ space group), making it a nonferroelectric material [Fig. 1(a)]. The experimentally measured lattice parameter is about $3.905 \text{ \AA}$ [20]. At low temperature ($<110 \text{ K}$) STO exhibits a tetragonal phase [25,33], which is described as an antiferrodistortive (AFD) structure with a space group $I4/mcm$ and a tilt mode $a^0a^0c^-$ in the Glazer notation [25,34]. As shown in Fig. 1(a), the neighboring TiO_6 octahedra tilt in an opposite and collective way around the z axis, compensating the induced polarization of each others, making STO paraelectric. Experimentally, ferroelectricity in the AFD structure only emerges upon applied strain [35]. The measured structural parameters [20,25] are shown in Table I. Notably, a differs from the c parameter and a tilt angle of 2.1° is observed [25]. Soft phonon modes, which describe the collective movement of atoms, are found as the trigger of such symmetry-lowering distortions [33,36,37]. Their frequencies vary with temperature [33,36,37] and, consequently, above $\sim 110 \text{ K}$ STO undergoes a phase transition to cubic [38].

Looking now into the electronic properties, the reported experimental optical gap of bulk cubic STO is between $3.10\text{--}3.25 \text{ eV}$ [21–24] at room temperature, $3.22\text{--}3.26 \text{ eV}$ at $\sim 110 \text{ K}$ (just above the transition), and $3.2\text{--}3.27 \text{ eV}$ [21,22,24] for the low temperature phase ($I4/mcm$). These experimental uncertainties can be attributed to both samples' quality and characterization techniques [21–24]. As the magnitude of the excitonic effect in STO ($20\text{--}120 \text{ meV}$ [24,39]) is within the optical gap uncertainties, in the following we directly comment/compare our electronic band gap to the experimental optical gap. We ignore corrections from the zero-point vibration as we aim to reproduce the experimental gaps, which will be used later for the defects' energy diagram.

From previous theoretical reports, AFD phase ($I4/mcm$) with collective $a^0a^0c^-$ tilt mode is predicted to exhibit lower energy (few meV/f.u.) than the cubic structure [40,41]. Such an energy gain is mainly from the octahedra tilt. Other tilt modes such as $a^-a^-a^-$ ($R\bar{3}c$) and $a^0b^-b^-$ ($Imma$) were also predicted theoretically to lower the STO energy compared to the cubic phase [42].

Competing instabilities are displayed in STO, including zone-boundary AFD modes that involve octahedral tilts and zone-center ferroelectric modes. This kept bulk STO from being ferroelectric at its ground state [43–45]. Here, we note that the XC-treatment plays a crucial role in capturing the phase and the tilt angle. While PBEsol largely overestimates the tilt angle, Hubbard correction on $\text{Ti-}3d$ and $\text{Sr-}4d$ states improves its prediction [46]. However, the amount of the Hubbard correction also alters the AFD and the ferroelectric instabilities [46]. In contrast, the hybrid functional HSE06 favors the ferroelectric phase, when considering a large cell (20-atom supercell), displaying off-Wyckoff displacement of the Ti-lattice as well as oxygen distortions [47]. The absence of quantum fluctuations, which prevent the polar mode from condensing into a long-range ordered ferroelectric state, is suggested as the cause of the ferroelectricity [47]. Recently, it has been found that the polar mode obtained by HSE06 rapidly decreases with the lattice constant. This stabilizes the ferroelectric structure over the AFD at the optimal lattice constant [48]. For this reason, an HSE06-based simulation favors the ferroelectric STO structure, which appears to be at odds with experimental observations [47,48]. However, energy differences below $5\text{--}10 \text{ meV/f.u.}$ should be regarded as practically degenerate, given inherent numerical and systematic uncertainties and the omission of vibrational free-energy contributions. As we will see in the following, the energy difference between the AFD and FE phases obtained here with HSE06 falls within this range, suggesting that both geometries may locally occur in real samples. Overall, these reports [46–48] reflect the high sensitivity of the results on the XC effects.

Therefore, to properly simulate the defect-induced properties, it is important to carefully check the effect of the XC-treatment and the characteristics of larger STO supercells without constraining their symmetry. Now we proceed with exploring the characteristics of both STO phases and selected tilt modes, based on the above reports. We also consider a large pristine-AFD supercell. In Table I, we report the structural parameters, the energy again of the AFD phase, the polarization, and the band gap for the cubic ($Pm\bar{3}m$) as well as the AFD ($I4/mcm$, $R\bar{3}c$, and $P1$) phases [see Fig. 1(b)]. The experimental counterparts are shown for comparison. We consider both PBEsol and HSE06 functionals. As we do not know how the symmetry-lowering in the AFD phase affects the band gap, we consider HSE(20) in addition to the standard HSE(25).

Looking first into the cubic phase, the calculated lattice constant of $3.896 \text{ \AA}$, obtained with the HSE(25) functional, is in good agreement with the experiment [20]. The PBEsol counterpart is slightly lower, being $3.889 \text{ \AA}$ (see Table I). Similar behavior is found for the AFD ($I4/mcm$) structure with the $a^0a^0c^-$ tilt. The HSE(25) functional produces the lattice parameter, the c/a ratio and, importantly, the tilt angle

(2.2°) very well. The latter is largely overestimated by PBEsol (5.6°). This AFD configuration is lower in energy compared to the cubic phase by about 7.7 meV/f.u. as obtained with PBEsol. As the lattice parameter of the AFD and the cubic are close, the energy gain is due to the octahedra tilt. The latter value decreases to about 1 meV/f.u. with HSE(25), reflecting the well-predicted tilt angle.

Our calculations tell that the $a^-a^-a^-$ ($R\bar{3}c$) and the $a^0a^0c^-$ tilt modes exhibit similar energy at the PBEsol level and HSE(25) slightly favors $a^-a^-a^-$ (see Table I). However, it is reported that decreasing the tilt angle (PBEsol) makes the $a^-a^-a^-$ ($R\bar{3}c$) tilt mode lower in energy [42]. For this reason, HSE(25), which gives a lower tilt angle (closer to the experiment), favors $a^-a^-a^-$ ($R\bar{3}c$).

Considering 20-atom $\sqrt{2} \times \sqrt{2} \times 2$ supercell lowers the symmetry of $a^-a^-a^-$ tilt modes ($P1$) as it allows more atomic distortions, including off-center shifts of the whole Ti-lattice along the [111] direction and the oxygen distortions [see Fig. 1(b)]. Both PBEsol and HSE(25) functionals predict that this configuration is the lowest in energy, with larger ΔE from the PBEsol which is related to its overestimated oxygen displacements. Focusing on the HSE(20) structure, the TiO_6 octahedral exhibits three shorter (1.90 Å) and three elongated (2.01 Å) Ti-O bonds, unlike the cubic, $I4/mcm$ and $R\bar{3}c$ where all Ti-O bond lengths are about 1.95 Å [Fig. 1(b)]. The off-center shift of the Ti-lattice, with respect to the center of the octahedral, is about 0.09 Å. Such a Ti-octahedral seems similar to that of the $R3m$ phase of BaTiO_3 [49]. However, here the neighboring octahedra are tilted in the opposite way, while the Ti shift is preserved in the [111] direction [50]. This makes the $P1$ structure belong to $a^-a^-a^-$ tilt mode, and thus we named it $P1$ ($\sim a^-a^-a^-$) in Table I and Fig. 1(b). It exhibits a spontaneous polarization of 22 $\mu\text{C}/\text{cm}^2$ in the [111] direction due to its distortions [see Fig. 1(b)]. Such a low-energy (and symmetrical) structure found here with a ferroelectric character is in agreement with previous findings at the PBEsol level, in which the $P1$ structure exhibited the lowest energy among the STO phases [51].

It should be noted that the $I4/mcm$ structure is obtained through PBEsol relaxation, but as a local minimum. This is also valid for larger supercells. However, HSE06 relaxes the $I4/mcm$ geometry toward the $P1$ structure. The reason why both PBEsol and HSE06 slightly favor the $P1$ instead of the experimental $I4/mcm$ structure can be attributed to the description of the Ti- d states, which affect the Ti-O hybridization. As mentioned above, it has been demonstrated that the amount of the Hubbard correction to Ti- d and Sr- d states can alter the AFD and the ferroelectric instabilities in STO [46]. This behavior was recently demonstrated for BaTiO_3 [49], where the Hubbard correction to Ti- d states localizes them and suppresses the Ti-O hybridizations, favoring the stabilization of the cubic phase instead of the experimental phase (ferroelectric, $R3m$). However, the inclusion of intersite Hubbard interactions between the Ti- d and O- p states makes the experimental phase lower again as it preserves the covalency of the Ti-O bonds [49]. Our goal to investigate defect complexes makes the adoption and tuning of the Hubbard correction challenging. Our findings indicate that HSE(20) is better at describing the structural parameters of STO (lattice

parameter, tilt angle), but slightly destabilizes the $I4/mcm$ structure (Table I).

The polarization in the PBEsol and the HSE(25) structures is about 22.7 and 22.1 $\mu\text{C}/\text{cm}^2$, respectively, along the [111] direction [see Fig. 1(b)]. We note that for a given structure, the use of PBEsol or HSE06 functional to compute the polarization gives comparable results, as the VB states are almost similar with both functionals in the pristine STO case. However, the small differences in the polarization shown in Table I come from the fact that the HSE(25) and PBEsol geometries structurally differ. Up to now, we see that considering larger supercell, which is needed later to simulate point defects, affects the crystal symmetry and induces spontaneous polarization.

Let us briefly discuss the effect of including the van der Waals (vdW) correction on the AFD($P1$) geometry. To this end, we considered the Tkatchenko-Scheffler [52] (TS) and the many-body dispersion [53] corrections. We found that both reduce the atomic distortions (and thus the polarization) of the $P1$ structure, making it close to $R\bar{3}c$ symmetry. However, the lattice parameter is largely underestimated, being 3.84 and 3.86 Å, respectively, indicating that both give too strong vdW correction. Underestimated lattice parameters largely affect the energy and electronic properties of STO. Therefore, finding an optimal functional that correctly captures all STO characteristics [46,47] needs dedicated work, specifically to understand the local distortion and the ferroelectricity observed when considering larger supercells [47]. However, for our purpose, we consider the HSE06 functional alone an optimal choice as it accurately predicts both lattice parameters and tilt angle (and later the electronic properties). In the following, we will also discuss the tests done to ensure that the obtained $P1$ structure does not affect our properties of interest.

Comparing the electronic band gaps, we clearly see that HSE(25) is more accurate at predicting the experimental gaps of bulk STO phases ($Pm\bar{3}m$, $I4/mcm$, and $R\bar{3}c$) compared to PBEsol. We found that HSE(20) gives comparable structural parameters, but largely underestimates the band gap, being 2.95 (cubic) and 2.98/2.99 eV ($I4/mcm/R\bar{3}c$). However, for the AFD $P1$ structure, the HSE(25) band gap is, instead, largely overestimated (3.52 eV). This increase compared to $Pm\bar{3}m$, $I4/mcm$, and $R\bar{3}c$ structures is mainly due to the symmetry-lowering distortions discussed above which emerge in the $P1$ geometry [46,54]. In this peculiar case, the HSE(20) is more accurate at predicting the experimental gap, being 3.26 eV. The structural parameters obtained from the HSE(20) are in close agreement with both the HSE(25) and the experiment (see Table I). This is an example where tuning the α parameter gives minor changes in the geometry but largely affects the band gap.

Overall, based on the above results, a $4 \times 4 \times 4$ supercell with AFD $P1$ ($\sim a^-a^-a^-$) phase, which accommodates the octahedral tilt and other distortions, will be considered for exploring the point defects. Simulating defects with this 0 K phase will not affect our goal to understand the defect characteristics in STO. Specifically, the PS and RS phenomena are also observed at low temperatures (e.g., 10 K [11]). Also, the use of the lowest-energy $P1$ structure instead of $I4/mcm$

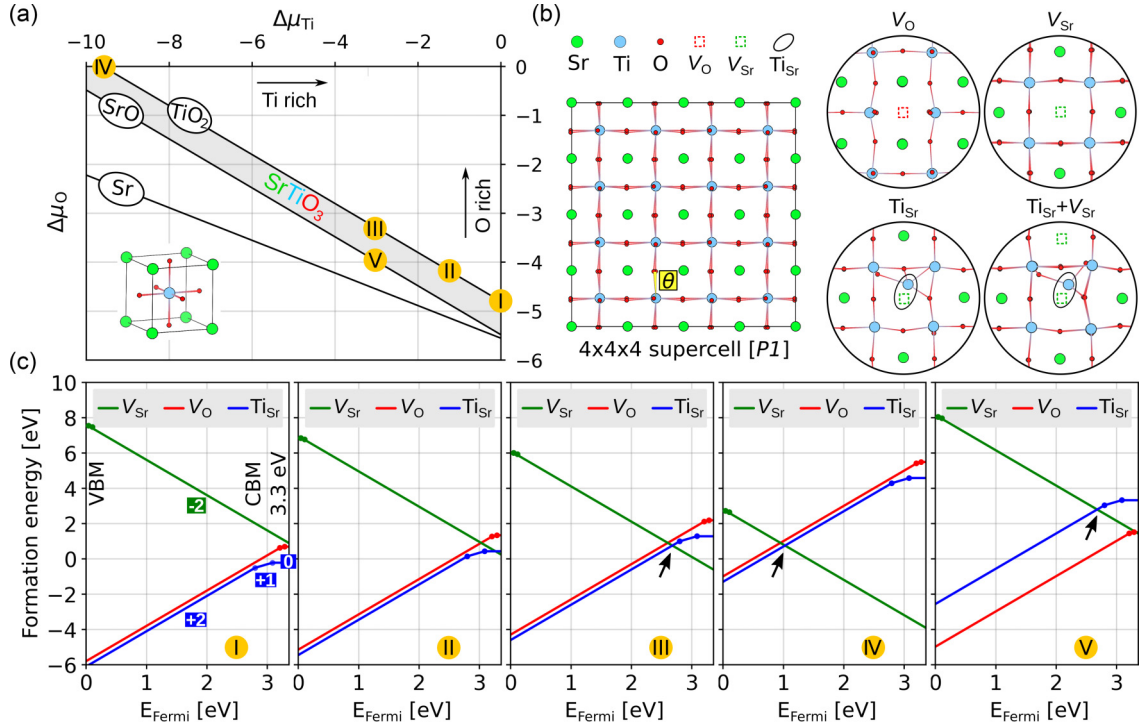


FIG. 2. (a) Stability energy diagram of bulk STO in the cubic phase as a function of the chemical potential of titanium and oxygen, in eV. The STO phase can be formed within the shaded gray area, comprised between the boundaries (solid lines) of TiO_2 and SrO precipitations. (b) Sketch of the AFD supercell and the defects considered in this work. (c) Defects' formation energy as a function of the Fermi level. The slopes of the lines reflect the charge state q . The dots represent the thermodynamic transition level between them (for explicit numbers see panel (c) left). Each panel refers to a corresponding chemical potential condition highlighted in (a) by numbered orange circles.

and $R\bar{3}c$ is because one cannot constrain the symmetry upon introducing defects. Evaluating the polarization induced by defects is also unaffected as we will subtract (refer to) the polarization of the pristine $P1$ [27]. Similar to the $P1$ ($\sim a^-a^-a^-$) structure shown in Table I, HSE(20) will be considered for all calculations of defects. This gives a band gap of ~ 3.3 eV for the $4 \times 4 \times 4$ defect-free AFD supercell, which will be considered as a reference for the defect formation energy diagram. For the latter, we note that we tested at the PBEsol level how the diagram changes, considering both the $P1$ and $a^0a^0c^-$ supercells. We found similar results in terms of relative stability and charge transition levels (see Fig. S2 in the SM).

B. Point defects characteristics

In Fig. 2, we depict a comprehensive compilation of the stability of selected intrinsic point defects in STO. The selection is based on previous theoretical and experimental reports of PS and RS [6–11]. We consider V_O , V_{Sr} , Ti_{Sr} antisite as well as defect complex $Ti_{Sr} + V_{Sr}$. These defects are introduced within a $4 \times 4 \times 4$ supercell with AFD $a^-a^-a^-$ tilt mode as mentioned above [see Fig. 2(b)].

Looking first at the stability energy diagram, the STO cubic phase can be formed within the area limited by the SrO and TiO_2 boundaries [see Fig. 2(a)]. A similar diagram is found when using PBEsol instead of HSE06 and/or AFD instead of the cubic phase. The experimental reports of the RS in STO

tuned the stoichiometry of the samples going toward *Ti-rich* and *Sr-poor* [11]. Considering this condition, we selected four points (I, II, III, IV) to compute the corresponding defect stability, which reflect the *rich-to-poor* limit of Ti, but, within the TiO_2 -rich conditions [see Fig. 2(a)]. An additional point, with SrO -rich (V), is also considered for comparison/prediction.

Focusing now on the defect stability, at point (I) the Ti_{Sr} antisite exhibits the lowest formation energy [Fig. 2(c)]. This is expected to be abundant, in line with experimental observations [11,55]. The Ti_{Sr} antisite is stable in a +2 charge state (Ti_{Sr}^{+2}) [Fig. 2(c)]. Increasing the Fermi level, a +2/+1 charge transition appears at about 2.8 eV, which is 0.50 eV below the electronic band gap of the pristine supercell (~ 3.3 eV). Here, the defect captures one electron. The Ti_{Sr}^{+1} configuration exhibits a magnetic moment of $1 \mu_B$. This defect state is suggested as the origin of the broad luminescence peak reported experimentally at 1.8–1.9 eV [14,56], considering the reported strong Stokes shift of ~ 0.9 eV [14]. Our results indicate that the Ti_{Sr} defect is a deep center, but closer to CBM than reported previously (transitions at 2.1 eV [6] and 2.6 eV [14]). These differences are attributed to the use of Hubbard correction functional along with *odd-size* supercell in the former, which excludes the octahedra tilts [6], and the use of a smaller supercell (160 atoms) in the latter [14]. Although hybrid functional is used in the latter, the supercell size is reported to affect the transition point [16]. However, our conclusions agree in terms of the transition type and behavior [6,14], compared with reports done at the semilocal functional

level where this transition point is predicted, instead, close to VBM [13]. This is mainly due to the fact that the captured electron is hosted by Ti $-d$ orbital. In the SM, we also show that the donor character of the Ti_{Sr} defect is not obtained despite using HSE(20) to compute the energies for the PBEsol relaxed structure. At 3.08 eV where a $+1/0$ transition occurs, the Ti_{Sr} antisite captures two electrons, becoming neutral. This transition (0.22 eV below the CBM) is higher than the room thermal energy $k_B T$, indicating that Ti_{Sr} is still a deep donor. The neutral Ti_{Sr} configuration exhibits a magnetic moment of $2 \mu_B$, where both electrons are mainly captured by Ti $-d$ orbital, with negligible contribution from oxygen.

Analyzing the antisite geometry, we clearly see that the Ti atom shifts from the V_{Sr} position (off-center) along the $[\sim 110]$ direction [Fig. 2(b)]. The shift is accompanied by structural distortions, reflecting its deep donor character. This includes a shift of the neighboring Ti atoms, distortions of the O atoms (thus the octahedral tilts), and formation of bonds with neighboring O atoms.

In the case of V_{Sr} , we see that it exhibits a high formation energy compared to Ti_{Sr} . The transition points $0/-1$ and $-1/-2$ occur at about 0.03 and 0.12 eV above the VBM, respectively. Its formation energy decreases with the Fermi level (V_{Sr}^{-2}). This makes it a double acceptor with shallow character (transition point near the VBM). This character is reflected in its structure, which shows minor distortions [Fig. 2(b)]. Such a defect can act as a compensation center in n-type doped STO or with other intrinsic donor defects. Considering the V_{O} , the $+2/+1$ and $+1/0$ transition points are found at 3.21 and 3.28 eV, respectively. Despite the diversity in the previous theoretical and experimental reports, our values are in excellent agreement with the recent careful study of the V_{O} characteristics [16]. In the latter report, the role of the computational parameters and functional is found to be the origin of the broad results. Here, considering all key parameters such as spin, supercell size, and accommodating octahedral tilt along with relaxation with HSE(20), we found that the V_{O} is still a shallow donor in line with this report [16]. The V_{O}^{+1} configuration exhibits a magnetic moment of $1 \mu_B$, while the neutral V_{O} counterpart is nonmagnetic. Here, as we refer to the band gap of 3.3 instead of 3.25 eV as explained above, the $+1/0$ transition point is also a shallow donor, being 0.02 eV below the CBM. Overall, under condition (I) Ti_{Sr} is slightly lower in energy than V_{O} [Fig. 2(b)].

Given the opposite character of Ti_{Sr} antisite and V_{Sr} (deep donor and shallow acceptor, respectively), as well as the possibility to form under similar conditions (Ti-rich, Sr-poor), a charge compensation can be achieved. Moving away from the Ti-rich limit (I to IV), but within the TiO_2 -rich line, compensation between the $\text{Ti}_{\text{Sr}}^{+2}$ and V_{Sr}^{-2} is evident starting from point (III) (Fig. 2). From now on, we refer to this $\text{Ti}_{\text{Sr}}^{+2} + V_{\text{Sr}}^{-2}$ defect complex as compensated $\text{Ti}_{\text{Sr}} + V_{\text{Sr}}$. Intriguingly, such a complex can be used to pin the Fermi level within the band gap, leading to a semi-insulating material. This conclusion is in line with the insulating character observed in STO films grown under Sr-poor (i.e., V_{Sr}) and Ti-rich (i.e., Ti_{Sr}) conditions [11]. Our result indicates that one can also tune the Fermi level by tuning the chemical potential within the TiO_2 -rich boundary.

To validate this analysis and conclusion, we also computed the binding energy of this compensated ($\text{Ti}_{\text{Sr}} + V_{\text{Sr}}$) defect depicted in Fig. 2(b). The binding energy, obtained as the difference between the formation energy of the defect complex minus the formation energy of the individual components ($\text{Ti}_{\text{Sr}}^{+2}$ and V_{Sr}^{-2}), is *exothermic*, being about -0.15 eV. We also set the V_{Sr}^{-2} away from the $\text{Ti}_{\text{Sr}}^{+2}$, as a second neighbor, and found an increase of 0.12 eV in the total energy, being less favorable compared to the first-neighbor configuration [Fig. 2(b)]. Therefore, this compensated defect complex is expected to be abundant in samples grown under Ti-rich and Sr-poor conditions [11].

At point (II), this defect complex can, instead, be formed between the neutral Ti_{Sr} and V_{Sr}^{-2} , giving $(\text{Ti}_{\text{Sr}} + V_{\text{Sr}})^{-2}$ defect. This charged defect complex can also be achieved at points III and IV by increasing the Fermi level with an external stimulus, e.g., under electric voltage. Overall, the compensated defect complex ($\text{Ti}_{\text{Sr}}^{+2} + V_{\text{Sr}}^{-2}$) has a semi-insulating character, while in the charged counterpart ($\text{Ti}_{\text{Sr}} + V_{\text{Sr}})^{-2}$ the Ti_{Sr} component captures two electrons to the Ti $-d$ orbital, becoming neutral.

Under SrO-rich conditions (point V), the oxygen chemical potential (μ_{O}) is more negative (i.e., oxygen-poor) than in the TiO_2 -rich case [point III in Fig. 2(a)]. Consequently, V_{O} becomes energetically more favorable than both Ti_{Sr} and V_{Sr} , whose formation energy are shifted to higher values. This suggests that the compensated defect complex ($\text{Ti}_{\text{Sr}} + V_{\text{Sr}}$) is unlikely to form under SrO-rich conditions. Instead, V_{O} , which is the most favorable defect at point V, dominates and can influence the charge neutrality of the defect complex by acting as an electron donor. Therefore, the TiO_2 -rich regime [between points III and IV in Fig. 2(a)] represents the optimal condition to achieve the $(\text{Ti}_{\text{Sr}} + V_{\text{Sr}})$ defect complex and benefit/tune its characteristics. Experimentally, RS is observed in STO films grown under Sr deficiency and Ti excess. The deficiency is estimated at about 20%, with $\sim 10\%$ of Sr sites occupied by Ti atoms (forming Ti_{Sr} defects) and the remaining $\sim 10\%$ as V_{Sr} , thereby preserving charge neutrality [11]. Based on these considerations, we now focus on the defect characteristics at higher concentrations. It is worth noting that although oxygen vacancies are also favorable within points III – IV, where the defect complex forms, the previous study [11] reported similar characteristics of the STO films even after annealing the samples in a pure oxygen atmosphere. Thus, in the following, we restrict our analysis to Ti_{Sr} and its defect complex with V_{Sr} . Ti_{Sr} itself is reported to induce a switchable spontaneous polarization [6–8]. This compensating defect complex, formed by the oppositely charged constituents, is expected to show its potential, specifically in inducing a spontaneous polarization.

C. Electronic properties of high defect concentration

For analysis, comparison, and predictions, in Fig. 3 we present the electronic band structure of the pristine AFD, neutral Ti_{Sr} , compensated $(\text{Ti}_{\text{Sr}} + V_{\text{Sr}})$ as well as charged $(\text{Ti}_{\text{Sr}} + V_{\text{Sr}})^{-2}$ defect, each within a $2 \times 2 \times 2$ supercell. This corresponds to 12.5% defect concentration, mimicking the high off-stoichiometry where PS and RS are experimentally

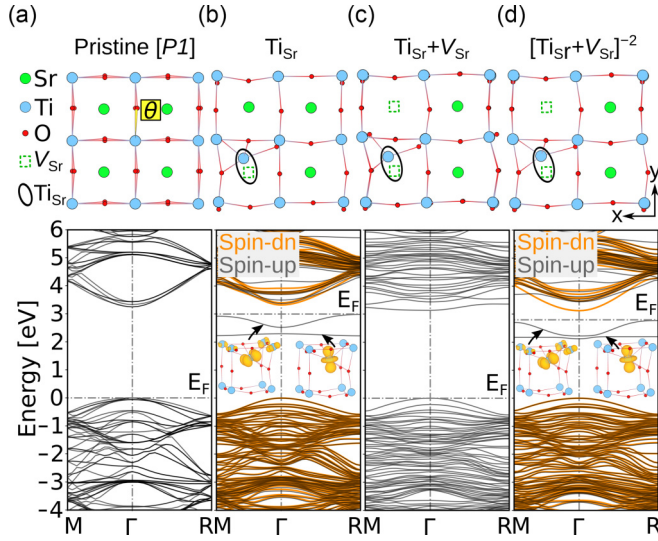


FIG. 3. Electronic band structure of (a) pristine STO in $P1$ symmetry ($\sim a^-a^-a^-$ tilt mode), (b) neutral Ti_{Sr} , (c) compensated $\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}}$, and (d) charged $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})^{-2}$. The bulklike valence band maximum is set to zero, while the Fermi level is highlighted by a dashed gray line. The spin up and down are shown with gray and orange colors, respectively. The real space distribution of the defect states is shown within each panel.

observed [7,9,11]. Homogeneous defects distribution is considered (Fig. 3). All structures are fully relaxed using HSE(20) including the lattice parameters. The structural characteristics of the defects (see Fig. 3) are almost similar to those discussed above for point defects [Fig. 2(a)]. The Ti_{Sr} in all cases is shifted within the (110) plane along the $[\sim 110]$ direction. In the neutral Ti_{Sr} (Fig. 3), the (110) plane is also the mirror symmetry plane of the structure. In the defect complexes (Fig. 3), the latter symmetry is broken by the distortions of the neighboring Ti atoms. Analyzing the band structures, we see that the neutral Ti_{Sr} antisite exhibits two midgap states, compared to the pristine material (see Fig. 3). This is due to the fact that the Ti (Sr) atom has four (two) valence electrons, thus the Ti_{Sr} defect brings in two more electrons. Both states exhibit a Ti- d character with spin up , and each is occupied by one electron. This gives a total magnetic moment of $2\mu_B$. The lowest- (highest-)energy band exhibits e_g -like (t_{2g} -like) symmetry [Fig. 3(b)]. While both are very localized in real space, the latter band is slightly dispersed compared to the former, exhibiting contribution from the four neighboring Ti atoms. In pristine STO, the octahedral crystal field splits the Ti- d states in which the t_{2g} is lower in energy. Here, the defect states show the opposite, which can indicate tetrahedral crystal field splitting, making e_g lower in energy.

The importance of the XC treatment and the inclusion of spin polarization to properly simulate the neutral Ti_{Sr} is shown in Fig. S1(a) in SM. We found that ignoring the spin polarization does not only affect the band structure of Ti_{Sr} by giving one doubly occupied midgap band, but also reduces the geometrical symmetry as the Ti_{Sr} slightly deviates from the $[110]$ direction (breaking the mirror symmetry plane mentioned above). This geometry is $+0.25$ eV higher in

energy compared to the spin-polarized ($2\mu_B$) counterpart (see Fig. S1(a) in SM). Remarkably, optimization of the neutral Ti_{Sr} using PBEsol functional gives a metallic character with two Ti- d electrons at the CBM instead of localized midgap states, despite its band structure is computed with HSE(20) [see Fig. S1(a)]. This example indicates that HSE(20), or at least Hubbard correction, is crucial also for the structural relaxation of defects as it can drastically change the electronic properties. Tuning the Hubbard parameter is challenging for the defect complex considered here (e.g., $\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}}$) where different states and hybridization are involved. For this reason also, HSE(20) is used for the structural relaxation of all defects.

For the $\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}}$ defect complex, the compensation between the donor Ti_{Sr} and the acceptor V_{Sr} preserves the insulating character of the material [Fig. 3(c)]. The structural relaxations are reflected in the band dispersion compared to its pristine counterpart. We expect this defect complex to be the dominant and the representative type in the reported off-stoichiometric samples where PS and RS are observed [7,9,11]. This is not only because of its stability, as discussed above in Fig. 2, but also because the off-stoichiometric films, with $\sim 10\%$ defect concentration, exhibit an insulating character without applied voltage [11]. Moving into the charged defect complex $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})^{-2}$ [Fig. 3(d)], this type mimics the situation with increased Fermi level, e.g., upon applied voltage, or the case with point II condition, as discussed above (see Fig. 2). We see that the two electrons are hosted by the Ti_{Sr} components, showing a similar electronic structure to the individual neutral Ti_{Sr} . Therefore, the V_{Sr} mainly enhances the stability of the Ti_{Sr} defects through the charge compensation, and preserves its electronic fingerprint (localized midgap states), under *rich* electron chemical potential. We also relaxed these defect complexes (both compensated and charged) using PBEsol. We conclude that PBEsol fails only in predicting the geometries of defects that exhibit localized midgap states. In the case of a compensated complex ($\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}}$), which has a semiconducting character without midgap states (Fig. 3), the PBEsol functional successfully predicts its geometry, being similar to that obtained with HSE(20) [27]. However, the band structures require HSE(20) in all cases.

D. Polarization and switching barriers

As discussed above, the AFD phase ($P1$), which is our pristine reference, exhibits a spontaneous polarization. Thus, to properly determine the polarization induced by the compensated $\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}}$ defect within the Berry phase approach, we deduced that of the AFD phase. The polarization branches going from the defected centrosymmetric (nonferroelectric) to the AFD into the fully relaxed defect structure are shown in Fig. S3 in SM. These calculated branches are crucial to properly determine the polarization magnitude and direction. We found that the compensated $\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}}$ defect induces a polarization of about $32 \mu\text{C}/\text{cm}^2$ oriented along the Ti-off-center direction $[110]$. Such a high value is comparable to those of common ferroelectric such as BaTiO_3 (about $29 \mu\text{C}/\text{cm}^2$ [57]). It reflects the Ti_{Sr} displacement and the structural distortions around it (displacement of neighboring Ti and O atoms)

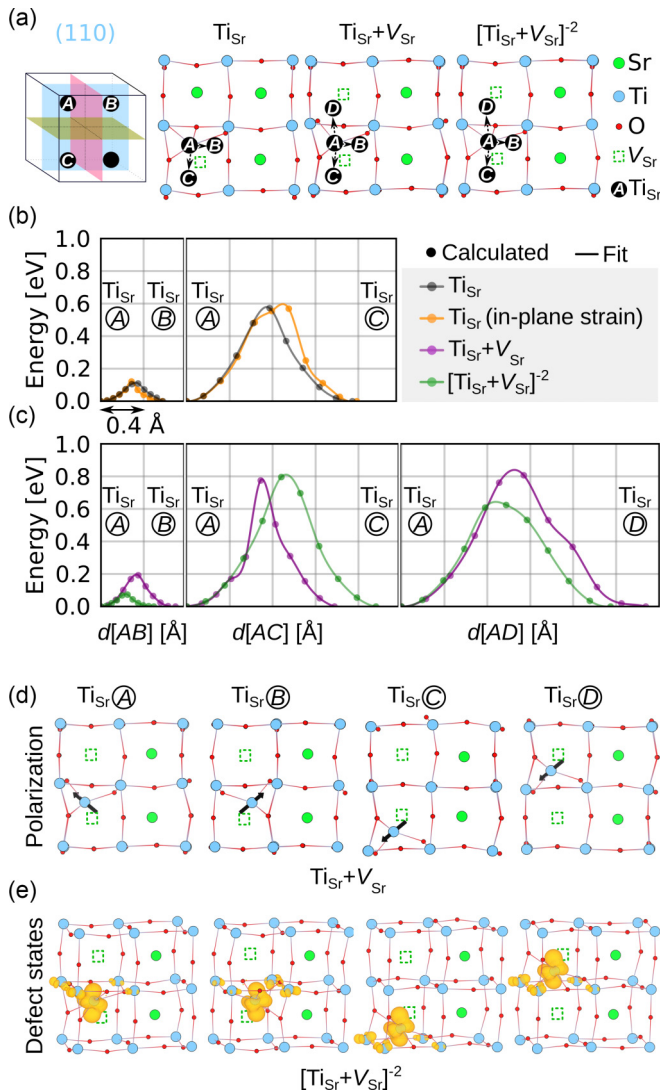


FIG. 4. (a) Sketch of the neutral Ti_{Sr} geometry within a $2 \times 2 \times 2$ supercell, corresponding to 12.5% defect concentration. The (110) plane and the equivalent defect sites considered here are highlighted in the geometry. (b) The energy barriers for switching the position of the neutral Ti_{Sr} defect along the $A-B$ and $A-C$ pathways. The x axis in the energy-barrier plots is the distance d between the *initial* and *final* Ti_{Sr} positions along each path. The orange line corresponds to the case where the in-plane lattices are fixed to those of pristine STO. (c) Similar analysis for compensated $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})$ and charged $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})^{-2}$ defect complexes. Here, an additional path ($A-D$) is considered in which the Ti atom moves into the equivalent site in the neighboring *pseudocube*. The latter is defined as the cube formed by the eight neighboring Ti atoms of Ti_{Sr} . The $A-D$ path can be seen as a local migration of the Ti_{Sr} . (d) Polarization vector of the compensated defect complex $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})$ is highlighted on the Ti atom, upon switching between A, B, C, D sites shown in (a) and (c). (e) For the charged defect complex $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})^{-2}$, the sum of the distribution of the occupied midgap states induced by the defect (see Fig. 3) is shown for the different sites.

as well as the strong dipole induced by its components $(\text{Ti}_{\text{Sr}}^{+2}$ and $\text{V}_{\text{Sr}}^{-2})$.

As depicted in Fig. 4(a), from the symmetry point of view we clearly see that the Ti_{Sr} defect can occupy other equivalent

sites, e.g., B and C . The compensated defect $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})$ can also have equivalent sites (e.g., D) in the neighboring *pseudocube* (formed by the eight Ti atoms). The energy barriers for a collective switching between the equivalent sites are shown in Figs. 4(b) and 4(c). Looking first at neutral Ti_{Sr} , we found that the switching from A to B faces an energy barrier of about 0.1 eV. While this barrier is larger than the room thermal energy $k_B T$, it can be achieved by applying low electric voltage. Following the $A-C$ pathway, the barrier increases to about 0.6 eV. From first inspection of the cubicle geometry, it seems that the $A-B$ and $A-C$ paths are equivalent. However, considering the oxygen atoms involved in the bonding with the Ti_{Sr} , one can see that the $A-C$ pathway requires breaking more bonds compared to the $A-B$ path, which can be seen as a sway/oscillation. Also, from the electronic structure view (Fig. 3), the t_{2g} -like state is shared with the neighboring four Ti atoms, which are the same along the $A-B$ path. However, along the $A-C$ path, the t_{2g} distribution moves from the four upper Ti atoms to the four bottom Ti atoms. For this reason, the $A-C$ switching pathway requires higher energy (thus higher electric voltage for switching), compared to the $A-B$ path. For both paths, we found that all the intermediate *images* exhibit localized midgap states with $2\mu_B$, preserving the semiconductinglike character. In the experiment, the films are grown on pristine STO [11]. This can lead to strain on the films due to its off-stoichiometry. Thus, we also fixed the in-plane lattice parameters of the defected structure to those of pristine STO and found similar behavior in terms of energy barriers, polarization and electronic structure [Fig. 4(b)].

Analyzing the compensated $\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}}$ complex, we also see similar characteristics along the $A-B$ and $A-C$ pathways. The latter has higher barrier (~ 0.8 eV) compared to the neutral Ti_{Sr} (~ 0.6), which is attributed to the fact that in the compensated $\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}}$ complex the components $(\text{Ti}_{\text{Sr}}^{+2}$ and $\text{V}_{\text{Sr}}^{-2})$ are oppositely charged and thus moving away from A toward C needs more energy to encounter this attraction. In the middle, the energy is maximal being ~ 0.8 eV. It decreases again because the attractive term increases again until the defect reaches site C , which is equivalent to site A (considering the periodic boundary conditions). Remarkably, going from site A to D shows similar energy barrier to the $A-C$ path. This indicates that the Ti atom can also leave its *pseudocube* and move into the neighboring one where the acceptor V_{Sr} is located [Fig. 4(a)]. In this $A-D$ switching, the four neighboring Ti atoms move away to allow the Ti_{Sr} to migrate into the neighboring *pseudocube*. This can be seen as a local defect diffusion.

In the experiment, switching the polarization is achieved by applying an electric voltage. This implies that the electron chemical potential (Fermi level) increases and according to our results this allows the compensated defect complex to capture two electrons, leading to a charged $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})^{-2}$. This gives rise to two midgap states with $2\mu_B$ as shown in Fig. 3. Overall, compared to the compensated complex, this charged counterpart shows similar barriers for switching (Fig. 4). Noticeable decrease of the barrier along the $A-D$ path (~ 0.2 eV less) can be attributed to the fact that in the charged defect the Ti atom has more bounds with the neighboring oxygen atoms and shares the t_{2g} state with the four neighboring Ti

atoms (Fig. 3). This is preserved upon moving to position D and thus it eases the switching between A and D sites, compared to compensated $(\text{Ti}_{\text{Sr}} + \text{V}_{\text{Sr}})$ complex. It can also be the reason why the barrier along the $A - B$ decreases to about 70 meV. We note that along all paths, the intermediate *images* of this charged defect complex preserve the localized midgap states and the magnetic moment of $2 \mu_B$. This preserves the semiconductinglike character.

For both compensated and charged defect complexes, the energy as well as the polarization magnitude in A , B , C , D sites is equivalent. In real samples, switching between them, in a collective way or along different pathways, allows switching not only the polarization orientation, but also the defects-state distribution in real space (Fig. 4). On the one hand, controlling the polarization direction is known to tune the potential barrier at interfaces, and thus the charge depletion/accumulation [58]. On the other hand, the conductivity in defected semi-insulating systems, that is governed by charge hopping through defect states, can be strongly tuned upon switching because of the charge redistribution. Therefore, new behaviors such as RS can be induced.

IV. CONCLUSIONS

In summary, we presented the potential of defects in intrinsically nonferroelectric perovskites with SrTiO_3 as a prototype. Our calculations show that deep electron-donor, shallow electron-acceptor defects as well as compensating defect complex can be formed. The latter allows for pinning the Fermi level far from the gap edges. Increasing the Fermi level, the compensated defect complex can capture two electrons into the deep center component, giving rise to localized midgap states with a well-defined magnetic moment. The defect complex induces a spontaneous polarization of about $32 \mu\text{C}/\text{cm}^2$. Allowed by STO symmetry, the defect can switch

between the equivalent sites. Interestingly, switching the defect position switches both the polarization direction and the spatial distribution of the localized defect states. Depending on the switching pathway, energy barriers ranging between 0.1 and 0.8 eV are found. This is expected to enrich the switching possibilities, e.g., upon applied voltages, and thus the material's response. Overall, with the advances in growth techniques with precise control of bulk/film stoichiometry, our results demonstrate the potential for achieving new behaviors by introducing and controlling defects.

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DATA AVAILABILITY

The data that support the findings of this article are openly available on the NOMAD repository [61].

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