## Polar instability under electrostatic doping in tetragonal SnTiO<sub>3</sub>

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How to make the metallicity compatible with a polar structure for forming a "polar metal" has been an interesting and important topic since the polar structure was discovered in metallic LiOsO<sub>3</sub>. Here, we present robust polar instability under electrostatic doping in tetragonal SnTiO<sub>3</sub> based on our first-principles calculations. The mechanism for polar distortion surviving free carriers is investigated from the "weak-coupling" perspective. The contributions of different interactions between two polar modes in a "ferroelectric" phase transition are also studied. We found that the short-range interaction contributes the most for lowering the total energy during the ferroelectricphase transition. Moreover, the dipole-dipole interaction between two polar modes of oxygen atoms provides the largest energy gain among local interactions, which cannot be screened out by doping. We propose that the promising candidates for noncentrosymmetric metals obtained by doping are ferroelectrics with bonding states responsible for polar distortions away from the Fermi level. We believe that this mechanism sheds light on a method to obtain noncentrosymmetric metals from a large amount of ferroelectric perovskite oxides by doping.

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## I. INTRODUCTION

Noncentrosymmetric metals (NCSMs), or so-called "polar metals," simultaneously exhibit long-range ordered polar distortions and metallicity. Since the report of the perovskite "ferroelectric metal" LiOsO<sub>3</sub> [1], many efforts have been exerted on elucidating the physical mechanisms and designing new polar metals [2–11]. Recently, based on Anderson and Blount's proposal in 1965 [12], Puggioni and Rondinelli put forward a design strategy for NCSMs [13] that fulfills the weak coupling between electrons at the Fermi level and the soft mode phonons which are responsible for generating a noncentrosymmetric structure.

Aside from the intrinsic NCSMs such as LiOsO<sub>3</sub>, which is a metal possessing polar instability (i.e., soft mode phonons leading to a ferroelectric phase transition at low temperatures), doping a ferroelectric material can be the other way to obtain NCSMs. Although doping in BaTiO<sub>3</sub> has been tentatively studied theoretically [14,15] and explored experimentally [16–19], the screening of long-range Coulomb interactions has been proven to suppress polar distortions with doping [14,15]. To achieve "polar metals," doping in lone-pair ferroelectrics [20-22] should be a promising approach, which has been scarcely studied so far. Very recently, we reported a theoretical research on the electron doping effect in lone-pair ferroelectrics PbTiO<sub>3</sub> [22], predicting that electron doping even enhances polar distortion. However, the understanding behind the coexistence of metallicity and polar distortion in doped ferroelectrics was very limited. The following fundamental problems remain unsolved: Is the weak-coupling mechanism a suitable explanation for lone-pair ferroelectrics with the persistence of polar distortions under doping? How much do the dipole-dipole interaction and short-range interaction contribute to the energy gain via polar distortions? Is the dipole-dipole interaction really screened out completely by heavy doping, and if not, what is the intrinsic mechanism for that? The answers to above questions will not only assist in designing new NCSMs, but may also be helpful for numerous applications of ferroelectric materials. In interfacial engineering applications such as ferroelectric tunneling junctions and the epitaxial growth of ferroelectric thin films, electrostatic doping may occur and inject free charge carriers into the ferroelectric layer due to an interfacial charge transfer and electronic redistribution (Fermi level misfit, interfacial band alignment, polar discontinuity, and so on). So, the ferroelectric structure may be quenched by conductive carriers, leading to performance degradation of the corresponding devices. Considering the importance of a polar structure coexisting with metallicity, we carried out the present work.

In this paper, using density functional theory (DFT) calculations, we studied the electrostatic doping effects in another lone-pair ferroelectric perovskite oxide, SnTiO<sub>3</sub> (P4mm symmetry), with the doping of both electrons and holes taken into consideration. Although the perovskite SnTiO<sub>3</sub> is difficult to synthesize, pulsed laser deposition (PLD) epitaxial growth has given a small trace of a perovskite phase [23]. More importantly, Sn is isoelectronic to Pb and environmentally benign. Thus, SnTiO<sub>3</sub> has attracted lots of theoretical attention for its possible physical properties without doping [21,24-27]. We will present here that P4mm SnTiO<sub>3</sub> shows a great compatibility with polar distortions and mobile carriers as PbTiO<sub>3</sub> with electrostatic doping. Moreover, the weak coupling between conductive electrons at the Fermi level and soft mode phonons still holds. With an effective Hamiltonian, we studied the energy contributions from different interactions. The short-range interaction plays a major role for lowering the total energy via polar distortions in SnTiO<sub>3</sub>. Moreover, the largest energy gain among the local interactions is from the dipole-dipole interaction between the polar modes on two oxygen atoms. More interestingly, this dipole-dipole interaction is not screened out by heavy doping [the doping concentration is much larger than the critical concentration

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FIG. 1. (a) Atomic structure of P4mm SnTiO<sub>3</sub>. The unit cell is outlined by the black solid line. Ti-O bond lengths in Å are denoted. (b) Diagram of polar distortions.  $d_{Sn}$  and  $d_{Ti}$  represent Sn displacement relative to the O1 plane (the light green plane) and Ti displacement relative to the O2 plane (the light blue plane), respectively. (c) Evolutions of  $d_{Sn}$  and  $d_{Ti}$  with electrostatic doping. Negative doping represents the hole doping.

0.1 e/u.c. (unit cell) for sustaining a polar structure in BaTiO<sub>3</sub> as reported in Refs. [14,15]]. This indicates that the Coulomb interaction is not screened out by doping in SnTiO<sub>3</sub>.

#### **II. COMPUTATIONAL METHODS**

DFT calculations are performed within the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof revised for solids (PBEsol) exchange and correlation functional [28] as implemented in the Vienna *ab initio* simulation package (VASP) [29]. The projector augmented wave method (PAW) [30] is used with the following electronic configurations:  $4d^{10}5s^25p^2$  (Sn),  $3s^23p^63d^24s^2$  (Ti), and  $2s^22p^4$  (O). A 520 eV energy cutoff of the plane-wave basis set is taken for all calculations. For structure optimizations, atomic positions are relaxed until the energy differences are within  $5 \times 10^{-7}$  eV and all forces are smaller than  $0.5 \text{ meV} \text{ Å}^{-1}$ . During structure relaxations for unit cells,  $9 \times 9 \times 9$  gamma centered k-point meshes are used. Denser k-point meshes are used for density of states (DOS) calculations. Crystal orbital overlap population (COOP) analyses are carried out with the LOBSTER [31] code. The isosurfaces of the charge density and atomic structures are visualized using the VESTA package [32].

#### **III. RESULTS AND DISCUSSIONS**

## A. Lattice structure

The *P4mm* structure of SnTiO<sub>3</sub> is illustrated in Fig. 1(a). Ti and O form three different bonds: (1) Ti and O1 form a 2.744 Å longer bond and a 1.732 Å shorter bond; (2) Ti and O2 form four equivalent 1.976 Å bonds. The shorter Ti-O1 bond is smaller than the sum of the Shannon radius

of the  $Ti^{4+}$  cation and  $O^{2-}$  anion [33], indicating that they are strongly bonded. The P4mm phase remains the most stable structure under doping among the four structures we have calculated (see Fig. S1 in the Supplemental Material [34]). Here, for simplicity, no phase transition is considered, although investigations of more complicated distortion behaviors need to be done. The ferroelectric polarization is an ill-defined quantity in metallic materials. Therefore, we focus on the polar distortions. The displacements of Sn relative to the O1 plane and Ti relative to the O2 plane ( $d_{Sn}$  and  $d_{Ti}$ ) are shown schematically in Fig. 1(b). Figure 1(c) shows that  $d_{Sn}$  and  $d_{Ti}$ increase with electron doping and decrease with hole doping, agreeing with those in  $PbTiO_3$  [22] and  $BiFeO_3$  [35], which is in sharp contrast to the case in  $BaTiO_3$  [14,15], where polar instability is suppressed monotonously with doping. Although the displacements decrease with hole doping in SnTiO<sub>3</sub>, as large as 0.54 Å for  $d_{Sn}$  and 0.47 Å for  $d_{Ti}$  still remain, respectively, with a hole doping concentration of 0.25 e/u.c. (corresponding to a hole concentration of  $p \approx$  $4.3 \times 10^{21}$  cm<sup>-3</sup>). The results in Fig. 1(c) show a remarkable compatibility of polar distortions with mobile charge carriers in SnTiO<sub>3</sub>. In addition, we considered the underestimation of the band gap of GGA calculations. We conducted the GGA + U investigations with an on-site Coulomb interaction for a Ti 3d orbital using the approach introduced by Dudarev et al. [36]. The results (in Fig. S2 in the Supplemental Material [34]) also support the above conclusion. Therefore, this remarkable compatibility is independent of the U values.

### B. Weak-coupling mechanism

To check if the weak-coupling mechanism is suitable here, we calculated the orbital-resolved electronic DOS and crystal orbital overlap population (COOP). COOP provides bonding information, in which the positive values represent the bonding states, and the negative values represent the antibonding interactions, respectively. Figure 2 presents the DOS and COOP with 0.2 e/u.c. hole doping (corresponding to a hole concentration of  $p \approx 3.4 \times 10^{21} \text{ cm}^{-3}$ ). We divided the whole DOS and COOP into four regions (regions I-IV) according to the COOP results. Comparing DOS with COOP, we can identify that regions I and II represent the bonding interactions, while regions III and IV mainly show an antibonding feature. Region I includes the pronounced Sn 5s states and O 2p states, with some Ti 3d states. Region II comprises mostly O 2p states and Ti 3d states, with distinct Sn 5p states and a few Sn 5s states. Region III is formed prominently by Sn 5s states and O 2p states, with some admixture of Sn 5pstates and Ti 3d states. Region IV is primarily composed of Ti 3d states, with significant O 2p states and Sn 5p states, and a small amount of Sn 5s states. We also calculated the partial charge densities of the bonding regions (regions I and II) to see the evolutions of the bonding environments with various doping levels, as presented in Fig. 3. The dominant part of region I is of a Sn-O2 bonding character, with some T-O1 bonding contributions. Region II is mostly composed of Ti-O1 and Ti-O2 bonding states. In the undoped case, region II [the lower panel in Fig. 3(b)] also has a Sn-O1 bonding character, whereas in the doping cases, the decrease of electron states around Sn in region II indicates that the Sn-O1 bonding



FIG. 2. (a) Orbital projected DOS and (b) crystal orbital overlap population (COOP) of SnTiO<sub>3</sub> with 0.2 e/u.c. hole doping, respectively. The energy is shifted so that 0 eV corresponds to the Fermi level (the dashed line). The whole area is divided into four regions as denoted I–IV with different colored backgrounds, including two isolated parts (regions I and IV) and a connected area (regions II and III). The boundary of region II and region III lies roughly 2 eV below the Fermi level. The O 2p DOS is the sum of the three O 2p DOS in one unit cell.

interactions are slightly weakened by doping. Nonetheless, the bonding environments are not significantly altered by doping, and only Sn-O1 bonding interactions are affected.

Previous studies have pointed out that the polar distortions in lone-pair PbTiO<sub>3</sub> and SnTiO<sub>3</sub> result from the cooperative pseudo-Jahn-Teller effect (coop-PJTE) [21,37]. The TiO<sub>6</sub> distortion comes from the PJTE " $d^0$ -ness." The Ti bonds to an O atom at the corner would remove the near degeneracy of Ti 3d and O 2p states, and lower the total energy. The distortion of the perovskite A-site (Pb<sup>2+</sup>, Sn<sup>2+</sup>) cation comes from the double PJTE, where the O 2p states hybridize with A-site cation s and p states simultaneously. In SnTiO<sub>3</sub>, the



FIG. 3. Partial charge density maps in energy region I (upper panels) and region II (lower panels) with various doping conditions. The colored contour maps are in blue-green-red scale, where blue represents 0 in all the pictures, and red represents  $0.05 e \text{ Å}^{-3}$  in all the upper panels and  $0.25 e \text{ Å}^{-3}$  in all the lower panels, respectively. For a clear view of the bonding environments corresponding to the energy regions, two lattice planes were taken with the plane indices shown in (a).

overlap of Sn-O and Ti-O DOS along with the COOP results show a strong covalence nature. Therefore, the Sn-O and Ti-O bonding interactions are essential to polar distortions. However, as shown in Fig. 2(a), the conduction band minimum (CBM) and the valence band maximum (VBM) are a series of antibonding states. In the electron doping case [see Fig. S3(b) in the Supplemental Material [34]], the doped electrons distribute only in the Ti 3d orbital, leaving the bonding and antibonding interactions almost unchanged. This is consistent with the electron doping situations in  $PbTiO_3$  [22]. In the hole doping case, the doped holes distribute in the Sn-O antibonding states, but they do not participate in the bonding interactions. Thus, the Sn-O and Ti-O bonding environments would not be altered considerably by doping. In other words, the doped charge carriers around the Fermi level do not couple strongly to the deeply buried Sn-O or Ti-O bonding interactions that are responsible for the polar distortions, and therefore the weak-coupling mechanism still holds here.

# C. Energy contributions from different interactions during phase transition

Investigations on LiOsO3 suggest that the short-range interactions between Li-displacement pairs are of great importance for the existence of polar distortions [4,6]. The computational method used by Xiang [4] has a precondition that the dipole-dipole interactions between Li pairs are completely screened out. However, in subsequent research conducted by Liu et al. [6], charge density analysis suggests that the longrange Coulomb interactions are anisotropically unscreened in LiOsO<sub>3</sub>. Therefore, to obtain short-range interactions more precisely and strictly, dipole-dipole interactions should be considered. By using the method of evaluating contributions from different interactions in Refs. [4,38], we conducted the following calculations. The effective Hamiltonian  $E^{\text{total}}$  represents the change of the total energy when the unit cell transforms from the paraelectric phase into the ferroelectric phase, including the energy contributions from the local mode self-energy, the short-range interactions, and the dipole-dipole interactions,

$$E^{\text{total}} = E^{\text{self}}(\{\mathbf{u}\}) + E^{\text{short}}(\{\mathbf{u}\}) + E^{\text{dipole}}(\{\mathbf{u}\})$$
$$= E^{\text{self}}(\{\mathbf{u}\}) + E^{\text{local}}(\{\mathbf{u}\}) + E^{\text{long}}(\{\mathbf{u}\}), \qquad (1)$$

$$E^{\text{self}}(\{u\}) = \sum_{i} \sum_{m} E^{\text{self}}(u_{i,m})$$
$$= \sum_{i} \sum_{m} \left(k_{2,m} u_{i,m}^{2} + \alpha_{m} u_{i,m}^{4}\right), \qquad (2)$$

$$E^{\text{local}}(\{\mathbf{u}\}) = \sum_{i \neq j} \left[ E_{ij}^{\text{short}}(\{\mathbf{u}\}) + E_{ij}^{\text{dipole}}(\{\mathbf{u}\}) \right]$$
$$= \frac{1}{2} \sum_{(i,m) \neq (j,n)} J_{im,jn} u_{i,m} u_{j,n}, \tag{3}$$

$$E^{\text{dipole}}(\{\mathbf{u}\}) = \sum_{i,j} E^{\text{dipole}}_{ij}$$
$$= \frac{1}{2} \sum_{\mathbf{R}} \sum_{i,j=1}^{5} {}_{'} \frac{\mathbf{p}_{i} \cdot \mathbf{p}_{j} - 3(\mathbf{\hat{R}}_{ij} \cdot \mathbf{p}_{i})(\mathbf{\hat{R}}_{ij} \cdot \mathbf{p}_{j})}{4\pi \varepsilon_{\infty} \varepsilon_{0} R^{3}_{ij}}, \quad (4)$$

TABLE I. The Born effective charges (BECs) in undoped SnTiO<sub>3</sub>.

	Atom				
BEC	Sn	Ti	01	O2	
$e_{zz}^{*}\left( e ight)$	3.61785	5.13552	-4.11943	-2.31784	

where  $E^{\text{self}}, E^{\text{short}}, E^{\text{dipole}}, u_{i,m}$ , and  $J_{im,jn}$  represents the local mode self-energy which contains harmonic  $(k_{2,m}u_{i,m}^2)$  and fourth-order anharmonic  $(\alpha_m u_{i,m}^4)$  contributions, second-order approximation short-range interactions, the dipole-dipole interaction, the amplitude of the mth isolated local mode at cell  $R_i$  (the polar modes refer to the polar displacements of corresponding atoms), and the coupling constant between the local mode  $u_{i,m}$  and  $u_{j,n}$ , respectively. In  $E^{\text{dipole}}$ ,  $\varepsilon_{\infty}$ is the optical dielectric constant of the material computed from DFT calculations,  $\varepsilon_0$  is the permittivity of vacuum,  $R_{ij} = |\mathbf{R}_{ij}| = |\mathbf{R}_i - \mathbf{R}_j|, \ \hat{\mathbf{R}}_{ij} = \mathbf{R}_{ij}/R_{ij}, \ \mathbf{p}_i = Z_i^* \cdot \mathbf{u}_i$  is the electric dipole moment, and  $Z_i^*$  is the Born effective charge (BEC) for the *i*th atom. The prime sign on the summation in Eq. (4) indicates that for the  $\mathbf{R} = 0$  terms, i = j should be excluded to avoid self-interactions. Because we can only compute the interactions within a finite range, the total energy can be also expressed as the latter part in Eq. (1).  $E^{\text{local}}$  is the interaction between two isolated modes within a radius of about 5 Å, including  $E^{\text{short}}$  and  $E^{\text{dipole}}$ .  $E^{\text{long}}$  is the interaction between two isolated modes that are very far from each other (>5 Å), which is not included in  $E^{\text{local}}$ . The elastic energy and the elastic-mode interactions are not included because cell deformation is not considered when the paraelectric P4/mmm unit cell is the same as the ferroelectric unit cell. The local modes are considered as isolated modes on isolated atoms, instead of collective modes on five atoms in one unit cell. This treatment can effectively reduce the size of the supercell for calculations, but it also increases the number of parameters. To obtain the parameters of the effective Hamiltonian from DFT calculations, the  $3 \times 3 \times 3$  supercell of the paraelectric P4/mmm phase is constructed as a background to eliminate a periodic image effect. To obtain  $k_2$  and  $\alpha$  of the self-energy term, the magnitude of one local mode is set to a series of different values, whereas the magnitudes of all the other local modes in the supercell are 0. For the coupling constants J of the local interactions between the local modes, two states need to be considered: (i) a ferroelectriclike (FE) state in which both atoms are moved along the [001] orientation by a small and reasonable distance d (0.3 Å being used in our calculations), while other atoms are kept stationary, and (ii) an antiferroelectriclike (AFE) state in which the displacements of the same atoms are opposite those in the FE state. The coupling constant Jcan be calculated from the formula  $J = [E_{\text{FE}} - E_{\text{AFE}}]/2/d^2$ . All the parameters of the effective Hamiltonian calculated from DFT are listed in Table SI in the Supplemental Material [34].

As mentioned above, in order to calculate the dipole-dipole interactions, the BECs need to be known. The polarization is along the z direction, so only the zz components of the BEC tensor matter. The BECs of the atoms in the P4/mmm unit cell (as listed in Table I) deviate very much from the formal values, indicating the charge transfer as well as the hybridization

TABLE II. Polar displacements at various doping levels.

Sn         Ti         O1         O2         Au           3.61785         5.13552         -4.11943         -2.31784         Sr			Atom					
3.61785 5.13552 -4.11943 -2.31784 Sr	toms	O2	01	Ti	Sn			
Ti	1	2.31784	-4.11943	5.13552	3.61785			

Polar displacements (Å) -0.2 e/u.c.0 e/u.c.0.2 *e*/u.c. 0.202862 0.250950 0.351650 -0.044946-0.032111-0.11168901 -0.375106-0.551079-0.819791**O**2 -0.516969-0.588174-0.727547

among these atoms is significant. It also should be noted that the polar distortions refer to the polar displacements of all the atoms in the unit cell. The polar displacements should be obtained by comparing the displacements of atoms with respect to the mass center of the paraelectric and ferroelectric unit cells, respectively. The results at various doping levels are listed in Table II. Although the preceding  $d_{Sn}$  and  $d_{Ti}$  are not very appropriate to represent the polar distortions, the polar displacements have the same tendency versus the doping concentration. The polarization estimated from the BECs and polar displacements is about  $106 \,\mu C/cm^2$ .

When the unit cell transforms from the P4/mmm phase to the P4mm phase, the local interactions between two isolated polar modes contribute to the energy gain. With the expansion coefficients of all the parameters (see Table SI in the Supplemental Material [34]), the BECs, and the polar displacements, we calculated the energy gain at various doping levels, as well as the contributions from the dipole-dipole interactions and the short-range interactions without doping (the BECs' calculation requires an insulator). The results are listed in Table III. The largest contribution for lowering the total energy is from the local interaction between the polar modes on the nearest O1 and O2 atoms [E2(O1,O2) in Table III], and it does not depend on the doping conditions. This energy gain comes from the dipole-dipole interaction, and electronic doping even enhances the energy gain. This indicates that the dipole-dipole interactions between some particular atom pairs are not efficiently screened by doping. In addition, the polar modes on the secondary nearest O1-O1 atom pairs [E4(01,01)] and the ones on the nearest Sn-O2 pairs [E4(Sn,O2)] also contribute a lot to the negative energy gain, which mainly originate from the dipole-dipole interactions. The polar modes on the nearest O2-O2 pairs [E1(O2,O2)] and the ones on the nearest Sn-O1 pairs [E3(Sn,O1)] contribute to raising the total energy. This positive energy gain comes from the dipole-dipole interaction, which can be understood as the electrostatic repulsion when two electric dipole moments are aligned side by side. Interestingly, *E2*(Ti,O1) (the energy gain from the polar modes on the nearest Ti-O1 pairs) is significantly enlarged by electron doping. This is because the doped electrons distribute mainly on the Ti atom, so the electrostatic repulsion between the nearest Ti and O1 ions is increased. The positive energy gain induced by the polar modes on the nearest O1-O1 pairs [E3(O1,O1)] and that on the secondary nearest O2-O2 pairs [E3(O2,O2)] is weakened by doping. The positive energy gain of E3(O1,O1)and E3(O2,O2) comes from the dipole-dipole interactions, so the weakening may result from the screening of the doped charge carriers.

TABLE III. The energy gain induced by the interactions between two isolated polar modes at various doping levels when the unit cell transforms from the P4/mmm phase into the P4mm phase. "Ei(A, B)" represents the energy gain from the interaction between the polar modes of *A* and *B* atoms. It is worth mentioning that this is not the interaction between *A* and *B* atoms. The counting of *i* is in line with that in Table SI in the Supplemental Material [34]. In the 0 doping conditions,  $E_{ij}^{local}$ ,  $E_{ij}^{short}$ , and  $E_{ij}^{dipole}$  represent the energy gain from the interactions (between two selected polar modes), the short-range interactions, and the dipole-dipole interactions, respectively.

				Energy gain (eV)		
			0 <i>e</i> /u.c.			
Local interactions		-0.2 <i>e</i> /u.c.	$E_{ij}^{\text{local}}$	$E_{ij}^{\rm short}$	$E_{ij}^{ ext{dipole}}$	0.2 <i>e</i> /u.c.
Polar modes on cation-cation	E1(Sn,Ti)	0.014632	0.006736	-0.023535	0.030271	0.051455
	E2(Sn,Sn)	0.041795	0.057598	-0.050627	0.108225	0.04699
	E2(Ti,Ti)	-0.000007	0.001528	-0.005467	0.006995	0.005613
	E3(Sn,Sn)	-0.047244	-0.047251	0.018945	-0.0662	-0.045246
	E3(Ti,Ti)	-0.003547	-0.005873	-0.001594	-0.00428	-0.017645
Polar modes on anion-anion	E1(O2,O2)	0.295586	0.535183	-0.672672	1.207856	0.809806
	E2(O1,O2)	-1.502673	-1.948998	0.343384	-2.29238	-3.024409
	E3(O1,O1)	0.126071	0.261172	-0.41546	0.676632	-0.00414
	E3(O2,O2)	0.079568	0.209382	-0.278662	0.488044	0.105378
	E4(O1,O1)	-0.368646	-0.550496	-0.136631	-0.41386	-0.527564
	E4(O2,O2)	-0.034565	-0.114666	0.183849	-0.29851	-0.127038
Polar modes on cation-anion	<i>E</i> 1(Ti,O2)	-0.033765	-0.087766	0.408022	-0.49579	-0.318981
	E2(Ti,O1)	0.025948	0.121161	-0.38401	0.505171	0.456355
	<i>E</i> 3(Sn,O1)	0.234585	0.399806	-0.939639	1.339445	0.393501
	<i>E</i> 4(Sn,O2)	-0.288874	-0.340962	0.575836	-0.9168	-0.73745
	E5(Ti,O2)	-0.010396	-0.03914	0.071606	-0.11075	-0.029111
	<i>E</i> 6(Ti,O1)	0.001331	0.011354	0.051358	-0.04	-0.028567

In summary, both short-range interactions and dipoledipole interactions among the local interactions contribute to a negative energy gain, but the largest one comes from the dipole-dipole interaction between the polar modes of the nearest O1-O2 atom pairs. It is worth mentioning that this interaction is not the interaction between two oxygen atoms. It is actually the interaction of the two polar modes. As shown in Table III, E2(01,02) remains the largest one with doping. It is even enlarged by electron doping. To obtain the underlying reason as to why this dipole-dipole interaction is not screened by doping, we plotted the real-space distribution of doped charge carriers in Fig. 4. The doped holes distribute on Sn and O atoms, but the distribution is anisotropic. For example, the doped holes are on the  $p_x$  or  $p_y$  orbitals of the O2 atoms [Fig. 4(a)]. As shown more clearly in Fig. 4(b), there are very few charge densities locating in between the nearest O1-O2 atom pairs. The doped electrons distribute on Ti atoms only, thus there are hardly any charge densities in between the nearest O1-O2 pairs as well. We can identify the Ti  $3d_{xy}$ orbital according to the shape of the charge density. Therefore, the dipole-dipole interaction between the polar modes on the nearest O1-O2 pairs is almost not affected by doping. It is very similar to the LiOsO3 case where the Coulomb interaction between Li-Li pairs is anisotropically unscreened [6].

Up to now, we have discussed the local interactions between certain polar modes. In the following, we will present the energy contributions of different interactions from an overall perspective. The energy curves of different interactions estimated from the effective Hamiltonian are plotted in Fig. 5, when the unit cell transforms from the P4/mmm phase to the P4mm phase. First, we computed the precise long-range dipole-dipole interaction by considering the interaction within

the range of the five nearest unit cells, which is precise enough. The estimated local dipole-dipole interaction [the sum of the dipole-dipole interactions within the calculated range, the green line in Fig. 5(a)] does not deviate very much from the precise one (the dashed green line), indicating  $E^{\text{long}}$  which is not computed should be most of the short-range interactions. The magnitude of the long-range dipole-dipole interaction is approximately 1/8 that of the short-range interaction. So, the largest contribution for lowering the total energy is from the short-range interaction. It is very similar to the NCSM LiOsO<sub>3</sub> where the short-range interaction plays an important role in stabilizing the polar structure [4,8]. The short-range interaction



FIG. 4. Real-space distribution of doped charge carriers. (a) Isosurface demonstration of the charge density of the doped holes at a doping level of -0.2 e/u.c. (b) The two-dimensional contour map corresponding to the three-dimensional map in (a) in the (2,0,0) plane. The nearest O1 and O2 atoms are connected by dashed lines. (c) Isosurface demonstration of the charge density of the doped electrons at a doping level of 0.2 e/u.c. The isosurface value for charge density in both (a) and (b) is  $0.02 e \text{ Å}^{-3}$ . The colored arrows represent the dipole moments. The moments of Sn and Ti atoms are not drawn.



FIG. 5. Energy contributions of different interactions when the unit cell transforms from the P4/mmm phase (0% distortion) to the P4mm phase (100% distortion). All curves are drawn in the same energy scale. In (a), the dashed green line represents the precise long-range dipole-dipole interaction.

stems from the differences in the short-range repulsion and electronic hybridization between two local modes [38]. This is in agreement with the preceding analysis on the weak-coupling mechanism. Comparing Figs. 5(b) and 5(c) with Fig. 5(a),  $E^{\text{long}}$  is much smaller in doping conditions. This may be related to the screening effect of the doped charge carriers. We are unable to determine the role of the long-range dipole-dipole interaction and short-range interaction under doping. It is possible that the role of the dipole-dipole interaction may be enhanced at certain doping levels because of the anisotropic screening effect of the doped carriers under doping. It should be noted that the results in Table III and Fig. 5 merely represent the energy difference during the "ferroelectric" phase transition. The reason why the polar instability exists in the high symmetric structure is from the Sn-O and Ti-O bonding interactions, as shown in the section on the weak-coupling mechanism.

## **IV. SUMMARY**

In conclusion, using DFT calculations, we theoretically investigated the coexistence of the metallicity introduced by electrostatic doping and polar distortions in lone-pair oxide SnTiO<sub>3</sub>, as well as the intrinsic mechanism behind it. Polar distortions remain large within a wide doping window. COOP results show that electron doping does not participate in the bonding interaction, and the doped holes only distribute on the antibonding states. The electronic densities corresponding to the bonding interactions at various doping levels do not vary significantly, indicating the weak-coupling mechanism still stands. With the effective Hamiltonian, we found that the short-range interaction contributes the most for lowering the total energy during the "ferroelectric" phase transition. Moreover, the largest energy gain among the local interactions is found from the dipole-dipole interaction between the polar modes on the nearest O1 and O2 atom pairs. Interestingly, this dipole-dipole interaction does not appear to be screened out by doping.

Our results indicate that lone-pair driven ferroelectrics holds great potential for compatibility with free charge carriers. Based on the above analysis, we propose that the promising candidates for NCSMs obtained by doping are ferroelectrics with the bonding states away from the Fermi level, so that the doped electrons (or holes) do not significantly alter the bonding interactions. We believe that this proposal should pave a way for obtaining NCSMs from many ferroelectric perovskite oxides by doping.

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- [1] Y. Shi et al., Nat. Mater. 12, 1024 (2013).
- [2] G. Giovannetti and M. Capone, Phys. Rev. B 90, 195113 (2014).
- [3] H. Sim and B. G. Kim, Phys. Rev. B 89, 201107(R) (2014).
- [4] H. J. Xiang, Phys. Rev. B 90, 094108 (2014).
- [5] C. He, Z. Ma, B.-Z. Sun, Q. Li, and K. Wu, Comput. Mater. Sci. 105, 11 (2015).
- [6] H. M. Liu, Y. P. Du, Y. L. Xie, J. M. Liu, C.-G. Duan, and X. Wan, Phys. Rev. B 91, 064104 (2015).
- [7] D. Puggioni, G. Giovannetti, M. Capone, and J. M. Rondinelli, Phys. Rev. Lett. 115, 087202 (2015).
- [8] N. A. Benedek and T. Birol, J. Mater. Chem. C 4, 4000 (2016).
- [9] F. Jin, A. Zhang, J. Ji, K. Liu, L. Wang, Y. Shi, Y. Tian, X. Ma, and Q. Zhang, Phys. Rev. B 93, 064303 (2016).
- [10] I. Lo Vecchio, G. Giovannetti, M. Autore, P. Di Pietro, A. Perucchi, Jianfeng He, K. Yamaura, M. Capone, and S. Lupi, Phys. Rev. B 93, 161113(R) (2016).
- [11] A. Filippetti, V. Fiorentini, F. Ricci, P. Delugas, and J. Iniguez, Nat. Commun. 7, 11211 (2016).

- [12] P. W. Anderson and E. I. Blount, Phys. Rev. Lett. 14, 217 (1965).
- [13] D. Puggioni and J. M. Rondinelli, Nat. Commun. 5, 3432 (2014).
- [14] Y. Iwazaki, T. Suzuki, Y. Mizuno, and S. Tsuneyuki, Phys. Rev. B 86, 214103 (2012).
- [15] Y. Wang, X. Liu, J. D. Burton, S. S. Jaswal, and E. Y. Tsymbal, Phys. Rev. Lett. **109**, 247601 (2012).
- [16] L. Liu, H. Guo, H. Lü, S. Dai, B. Cheng, and Z. Chen, J. Appl. Phys. 97, 054102 (2005).
- [17] K. Page, T. Kolodiazhnyi, T. Proffen, A. K. Cheetham, and R. Seshadri, Phys. Rev. Lett. 101, 205502 (2008).
- [18] S. Raghavan, J. Y. Zhang, O. F. Shoron, and S. Stemmer, Phys. Rev. Lett. **117**, 037602 (2016).
- [19] T. Kolodiazhnyi, M. Tachibana, H. Kawaji, J. Hwang, and E. Takayama-Muromachi, Phys. Rev. Lett. 104, 147602 (2010).
- [20] R. E. Cohen, Nature (London) 358, 136 (1992).
- [21] K. C. Pitike, W. D. Parker, L. Louis, and S. M. Nakhmanson, Phys. Rev. B 91, 035112 (2015).
- [22] X. He and K.-j. Jin, Phys. Rev. B 94, 224107 (2016).

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- [23] T. Fix, S. L. Sahonta, V. Garcia, J. L. MacManus-Driscoll, and M. G. Blamire, Cryst. Growth Des. 11, 1422 (2011).
- [24] W. D. Parker, J. M. Rondinelli, and S. M. Nakhmanson, Phys. Rev. B 84, 245126 (2011).
- [25] Y. Uratani, T. Shishidou, and T. Oguchi, Jpn. J. Appl. Phys. 47, 7735 (2008).
- [26] S. F. Matar, I. Baraille, and M. A. Subramanian, Chem. Phys. 355, 43 (2009).
- [27] M. F. M. Taib, M. K. Yaakob, O. H. Hassan, A. Chandra, A. K. Arof, and M. Z. A. Yahya, Ceram. Int. **39**, S297 (2013).
- [28] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008).
- [29] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- [30] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).

- [31] S. Maintz, V. L. Deringer, A. L. Tchougréeff, and R. Dronskowski, J. Comput. Chem. 34, 2557 (2013).
- [32] K. Momma and F. Izumi, J. Appl. Crystallogr. 41, 653 (2008).
- [33] R. D. Shannon, Acta Crystallogr. A 32, 751 (1976).
- [34] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.96.035140 for details of the doping influences on the crystal structure, the electronic structure, and the bonding interactions in SnTiO<sub>3</sub>, and the table for computed coefficients of the effective Hamiltonian.
- [35] X. He, K.-j. Jin, H.-z. Guo, and C. Ge, Phys. Rev. B 93, 174110 (2016).
- [36] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
- [37] I. B. Bersuker, Ferroelectrics 164, 75 (1995).
- [38] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. B 52, 6301 (1995).