PHYSICAL REVIEW B **101**, 121407(R) (2020)

Rapid Communications

Strain-tunable out-of-plane polarization in two-dimensional materials

J. Z. Zhao,[1,2,3,*] L. C. Chen,[1,*] B. Xu,[4] B. B. Zheng,[1] J. Fan,[3] and H. Xu[1,†]
[1]*Department of Physics and Institute for Quantum Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China*
[2]*College of Physics and Telecommunications Engineering, South China Normal University, Guangzhou 510006, Guangdong, China*
[3]*Center for Computational Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China*
[4]*School of Physical Science and Technology, Soochow University, Suzhou 215006, China*

(Received 17 December 2019; revised manuscript received 17 February 2020; accepted 18 February 2020; published 31 March 2020)

Two-dimensional (2D) ferroelectrics are a special class of materials that fit the need of miniaturization of devices, which can lead to a plethora of applications. Up to now, albeit the breakthrough in the discovery of a handful of 2D ferroelectrics, the mechanism of which still requires better understanding. In this work, we clarify that the ferroelectric ground state in monolayer (ML) In_2Se_3 is strongly affected by in-plane strain, and the strain-induced phase transition is of a first-order transition. We further propose that strain is an effective approach to tune the ferroelectric ground state in 2D materials, which can even intrinsically introduce out-of-plane polarizations. By performing first-principles calculations, we show that the epitaxial strain is able to tune the structural transition between polar and nonpolar layer groups. According to this, the epitaxial strain can not only fully suppress the polarization in ML-In_2Se_3, but also cause out-of-plane polarizations in a group of 2D nonpolar materials, i.e., ML-Bi_2Se_3, ML-Bi_2Te_3, ML-Sb_2Te_3, and ML-Sb_2Se_3. The coupling mechanism between strain and polarization in these compounds is further illustrated.

DOI: 10.1103/PhysRevB.101.121407

The strong coupling to electric field in ferroelectric materials hinders their miniaturization of devices. The internal depolarization field originated from the accumulation of electric charge on its surfaces, if not screened by external electrodes, can fully suppress the polarization in its bulk region [1,2]. Consequently, conventional ferroelectric materials hardly work in ultrathin film samples when their thickness is below a critical value [3–5]. Driven by this, exploring a two-dimensional (2D) or quasi-2D system with robust out-of-plane polarization is of particular interest [6–8]. Although several remarkable works on oxides have been reported [9,10], only a few of them have achieved a down to the limit of one unit cell thickness [11].

Recently, a rapidly increasing number of 2D materials that can be exfoliated from their bulk counterparts to monolayer (ML) ones offer alternative opportunities for ferroelectricity in thin-film samples. However, most of the well-known 2D materials, including graphene, transition-metal dichalcogenides, and black phosphorus [12–15], present either spatial inversion symmetry (such as graphene [12]), or only break the in-plane inversion symmetry (e.g., phosphorene analogs [16,17]). After years of intensive studies, although plenty of 2D ferroelectric materials have been proposed theoretically [18–26], only a few sporadic candidate materials with out-of-plane polarization (P_z), have been confirmed by experiments, i.e., $CuInP_2S_6$ [27,28], $d1T$ phase of $MoTe_2$ [29], WTe_2 [30], and In_2Se_3 [31–33]. To explore more ferroelectric 2D materials, deeper understandings on the mechanism of 2D ferroelectricity are required.

On the one hand, as one of the most promising candidates, the mechanism of the stable out-of-plane polarization in ML-In_2Se_3 is unfortunately absent. It was suggested to be of a hyperferroelectricity [34,35]. In addition, the improper ferroelectricity [36], proposed in bulk materials, is expected to realize stable out-of-plane polarization in thin-film samples. However, according to our following studies, it is of a first-order type, which is an unusual phenomenon comparing with previous expectations. On the other hand, another important question naturally arises—whether we can find a recipe to intrinsically induce P_z in an existing nonferroelectric 2D material. In other words, can the inversion symmetry be broken along the z direction in nonpolar 2D materials under certain conditions? For instance, ML-In_2Se_3 vs ML-Bi_2Se_3 are isostructural chalcogenides with five atomic layers. Among them, ML-Bi_2Se_3 belongs to the nonpolar $P\bar{3}m1$ layer group, while ML-In_2Se_3 belongs to the $P3m1$ layer group, which is a polar subgroup of $P\bar{3}m1$. The above question now becomes whether the ground state of ML-Bi_2Se_3 can be transferred from layer group $P\bar{3}m1$ to $P3m1$ [see Fig. 1(a)] via external stimulations, such as biaxial strain.

In this work, by performing first-principles calculations (see the Supplemental Material (SM) [37]), we propose that strain engineering can effectively tune the occurrence of polarization in ML-Bi_2Se_3 and several other isostructural chalcogenides. As the prototypes, the strain-induced ferroelectric phase transitions in ML-Bi_2Se_3 and ML-In_2Se_3 are studied.

---

[*] These authors contributed equally to this work.

[†] Author to whom correspondence and requests for materials should be addressed: xuh@sustech.edu.cn.

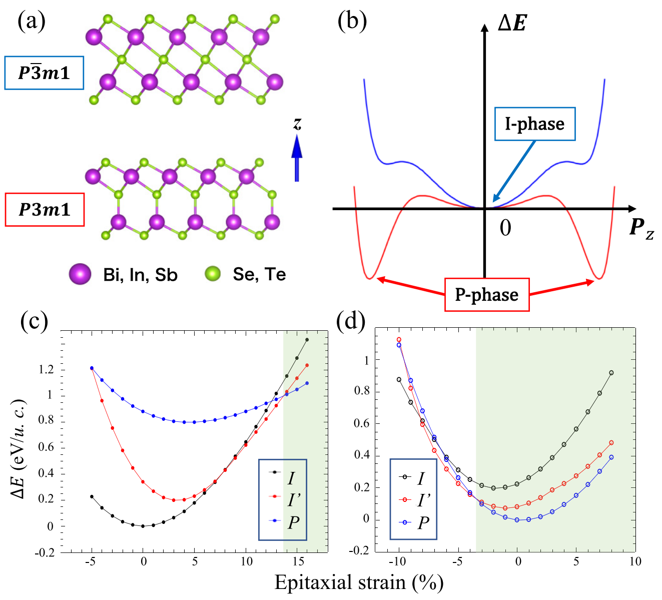

FIG. 1. (a) The scheme of studied materials in layer group $P\bar{3}m1$ and $P3m1$, respectively. (b) The PEC for the case with I phase as the minima (in blue) and the one with P phase as the minima (in red), respectively. The energy evolution of the I phase, the I′ phase, and the P phase in terms of epitaxial strain for (c) ML-Bi_2Se_3 and (d) ML-In_2Se_3, respectively. The region where the compounds present out-of-plane polarization is highlighted in light-green.

As shown in Fig. 1(b), in the potential energy curve (PEC) of ML-Bi_2Se_3 (the blue curve), there are two types of local minima. The one at the origin is the global minimum, referred to as the I phase, which belongs to the $P\bar{3}m1$ layer group. The other one has two points which are equivalent with opposite values of P_z. This type of local minima is referred to as the P phase, which belongs to the $P3m1$ layer group. In contrast, the minimum point in the PEC of ML-In_2Se_3 presents a nonzero value of P_z, corresponding to the P phase (the red curve), while the origin point is a local minima. It has been confirmed that the out-of-plane polarization of ML-In_2Se_3 is switchable both from theory and experiments [8,31–33].

We begin with the effect of strain by examining the evolution of total energy for ML-Bi_2Se_3 and ML-In_2Se_3. We note that there is an additional phase, referred to as the I′ phase, which is involved in the transition process. The structure of the I′ phase (see Supplemental Material Fig. S1) is very similar to the high symmetric I phase with small distortions by suppressing P_z as well. The relative stability of these three phases can vary under the influence of biaxial strain.

As shown in Fig. 1(c), when the strain is zero, the I phase has the lowest energy. The P phase of ML-Bi_2Se_3 is 0.85 eV/unit cell (u.c.) higher than the I phase. When a tensile strain is applied, the energy of the I phase increases and eventually becomes higher than that of the P phase when the strain is more than 13%. Here, the strain is labeled by taking the fully relaxed lattice constant as the reference. The same behavior happens in the I′ phase while the energy of which will be higher than that of the P phase when the tensile strain is enhanced beyond 14%. Therefore, the polar P phase will be the one with the lowest energy when the epitaxial strain is larger than 14%. Thus, the in-plane strain can drive a phase transition between the P phase and the I phase.

Qualitatively the same behavior is found in ML-In_2Se_3; that is, the energy of the I phase decreases with increasing compressive strain. In the zero-strain state, the P phase of In_2Se_3 is the most stable one among the three phases, while the I phase has the highest energy. When we reverse the P_z, the system takes the I′ phase as the transition state, while the barrier is about 0.09 eV/u.c. as the red line shows in Fig. S2. This value is also in good agreement with previously reported value of 0.07 eV/u.c [8]. The stability sequence of the three phases is changed when the compressive strain is beyond 3.5%. Thus, when the compressive strain is larger than a critical value, ML-In_2Se_3 has a nonpolar ground state, the I′ phase. When the in-plane strain is further compressed, beyond −8%, the I phase becomes the most stable.

Thus, the competition between the I phase and the P phase strongly depends on the strain. At the critical point, the relative thermal stability of polar and nonpolar phases can be reversed and the spontaneous polarization is induced.

Since the behavior of this ferroelectric phase transition relies on the competition between metastable phases, it is interesting to study the behavior of polarization close to the transition point. When tracing the evolution of P_z, along with the in-plane strain in these two materials, one can see the amplitude of P_z discontinuously jumps at some critical points (see Fig. 2). In the case of ML-In_2Se_3, the transition occurs at −3.5% strain. As Fig. 2(a) shows, starting from the nonstrain case, the value of P_z slightly increases when the compressive strain is applied. It is fully suppressed once the compressive strain is increased beyond the transition point. In ML-Bi_2Se_3, no polarization exists in the absence of strain. When the tensile strain is applied, the value of P_z keeps its zero value. Until the strain is up to the transition point, around 13% tensile strain, the value of P_z jumps to 0.55 $\mu C/cm^2$ and is slightly changed by a larger strain [see Fig. 2(b)].

The strain-tuned phase transition between the P phase and the I phase occurs not only in ML-In_2Se_3 and ML-Bi_2Se_3 but also in ML-Bi_2Te_3, ML-Sb_2Te_3, and ML-Sb_2Se_3. Very similar with ML-Bi_2Se_3, these three materials are in the nonpolar I phase (belong to the $P\bar{3}m1$ layer group) in the absence of strain. As presented in Figs. 2(c)–2(e), the out-of-plane polarization jumps from zero to a finite value when the in-plane biaxial strains are up to 13.5%, 17.5%, and 14% for ML-Bi_2Te_3, ML-Sb_2Te_3, and ML-Sb_2Se_3, respectively. However, unlike ML-Bi_2Se_3, these three materials are metallic around the phase transition point. The electronic band gaps of ML-Bi_2Te_3, ML-Sb_2Te_3, and ML-Sb_2Se_3 remain closed by the tensile strain and reopened when it is switched to P phase. The band-gap values of studied materials are reported in Sec. 4 of the SM. It is worth pointing out that the Perdew-Burke-Ernzerhof (PBE) functional often underestimates the band-gap value. We reinvestigate the corresponding data via the Heyd-Scuseria-Ernzerhof (HSE) functional as well (see Figs. S3-1 and S3-2 in the SM). Indeed, for all the studied cases, the HSE functional provides a larger band-gap value than that of the PBE functional. According to the PBE functional, ML-Sb_2Se_3 and ML-Bi_2Te_3 are metals in a certain range of strain, while with the HSE functional they are still insulators. The HSE band-gap data is in agreement with

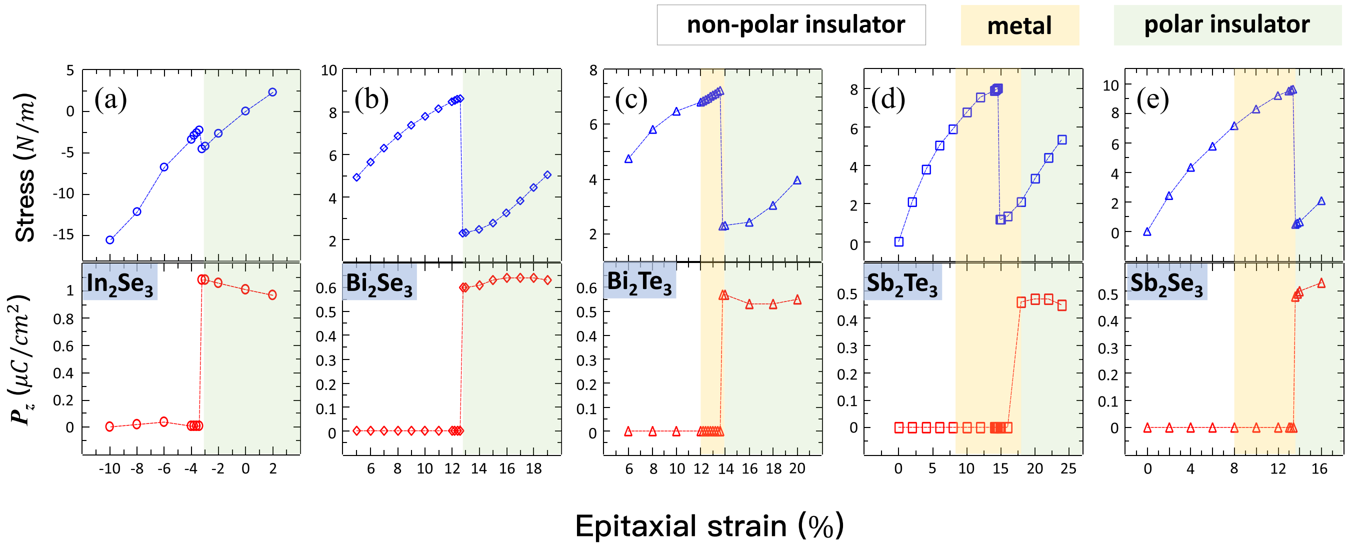

FIG. 2. The evolution of stress and P_z under biaxial epitaxial strain in ML (a) In$_2$Se$_3$, (b) Bi$_2$Se$_3$, (c) Bi$_2$Te$_3$, (d) Sb$_2$Te$_3$ and (e) Sb$_2$Se$_3$, respectively. The biaxial epitaxial strains are labeled by taking the fully relaxed lattice constant as the reference zero value. The regions of nonpolar insulator, metal, and polar insulator are highlighted by white, orange, and light-green, respectively.

experimental results. For instance, in our HSE calculations, the band gap of ML-In$_2$Se$_3$ is 1.55 eV, while the experimental measurements are in the range of 1.2–1.3 eV [50].

So far, we have shown that these three states with different layer groups can be controlled by in-plane biaxial strain. When tensile strain is applied to materials in the $P\bar{3}m1$ layer group, its symmetry is broken and the structure can transform to the $P3m1$ layer group. Such transition process can be reversed. In other words, the in-plane biaxial strain is able to tune the stabilities between the polar and the nonpolar phase, while the one with lower energy is the ground state under a certain value of strain. This strongly suggests the strain approach of introducing out-of-plane polarization in nonpolar ML materials.

One can notice that both the P phase and the I phase of these studied compounds are locally stable in the energy landscape. In addition, P_z is obviously discontinued at the transition point (see Fig. 2). The phase transition originates from the competition of the stability between local stable phases, while the evolution of polarization does not follow a continuous way but with a finite jump at the transition point. All these phenomena imply the transition is a first-order type in terms of strain.

To further understand the role of strain in this type of phase transition, we build a phenomenological Landau model for ML-Bi$_2$Se$_3$ and ML-In$_2$Se$_3$, in which all the coefficient parameters are fitted according to our density functional theory (DFT) data. Since the in-plane and out-of-plane polarizations in these materials are locked, here we combine them in one order parameter as the total polarization $\boldsymbol{P}$. As Eq. (1) shows, in our model, the free energy $\boldsymbol{F}$ is expanded in terms of $\boldsymbol{P}$ and the strain η. To better fit our DFT data, the free energy is expanded up to the eighth order of $\boldsymbol{P}$.

$$F(\eta,\boldsymbol{P}) = \tfrac{1}{2}\lambda(\eta-\eta_0)^2 + \tfrac{1}{2}a(\eta)\boldsymbol{P}^2 + \tfrac{1}{4}b(\eta)\boldsymbol{P}^4 + \tfrac{1}{6}c(\eta)\boldsymbol{P}^6 + \tfrac{1}{8}d(\eta)\boldsymbol{P}^8. \tag{1}$$

The value of strain η is defined by taking the fully optimized lattice constants as the reference in the absence of strain. Note, η_0 is the strain when the material presents the minimum total energy in the absence of polarization. For ML-Bi$_2$Se$_3$, $\eta_0 = 0$ since its ground state is nonpolar. For ML-In$_2$Se$_3$, $\eta_0 = -0.013$, which means if we artificially fix the symmetry in the I phase, the relaxed lattice constant is 1.3% smaller than that of the original P phase. In principle, the coefficients a, b, c, and d are strain dependent. However, according to our fitting procedure, only the biquadratic term of polarization is strongly dependent on the amplitude of strain, while the remaining three, b, c, and d, can be estimated as constants for both ML-Bi$_2$Se$_3$ and ML-In$_2$Se$_3$ systems. Therefore, we renormalize the free energy by absorbing the biquadratic term of η as follows.

$$\begin{aligned} F'(\eta,\boldsymbol{P}) &= F(\eta,\boldsymbol{P}) - \tfrac{1}{2}\lambda(\eta-\eta_0)^2 \\ &= \tfrac{1}{2}a(\eta)\boldsymbol{P}^2 + \tfrac{1}{4}b\boldsymbol{P}^4 + \tfrac{1}{6}c\boldsymbol{P}^6 + \tfrac{1}{8}d\boldsymbol{P}^8. \end{aligned} \tag{2}$$

Thus, this renormalized free energy only includes the contributions of the polarization and its coupling with strain. The zero value of $\boldsymbol{F'}$ is defined as a configuration without any polarization under a certain value of strain. The evolution of $\boldsymbol{F'}$ under different strains is shown in Fig. 3, in which we mainly focus on the strain close to the transition point. There are two types of local minimum points in the PEC, which satisfy the conditions $\frac{\partial F'}{\partial \boldsymbol{P}}|_{\boldsymbol{P}=0,\,\pm 1} = 0$ and $\frac{\partial^2 F'}{\partial \boldsymbol{P}^2}|_{\boldsymbol{P}=0,\,\pm 1} > 0$, corresponding to the I phase and the P phase.

Our results suggest that the effect of in-plane strain mainly tunes the curvature of the PEC at the origin point, which affects the stability competition between the polar and the nonpolar phases. It is interesting to see that the coupling between the in-plane strain and the $\boldsymbol{P}^2$ term nicely follows a linear function for both ML-Bi$_2$Se$_3$ and ML-In$_2$Se$_3$ systems. The detailed value and expression of each coefficient parameter are summarized in Table I. Although it is a rough

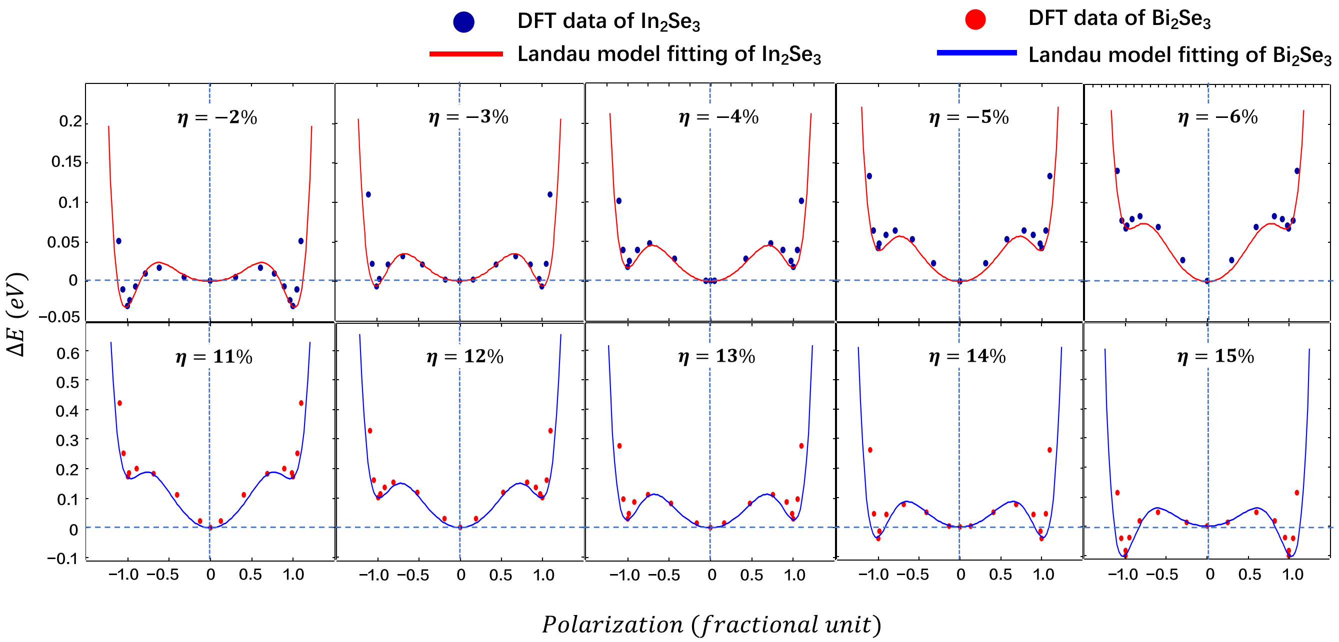

FIG. 3. The evolution of F' with respect to polarizations under the strain close to the phase transition point for ML-In_2Se_3 and ML-Bi_2Se_3, respectively. The data obtained from DFT calculations are plotted dots, while the corresponding Landau model fitting curves are shown in lines. All these DFT calculated structures are obtained from the climbing image nudged elastic band calculations. Some points are added by interpolation with small step when it is close to the polar P phase.

phenomenological model, it can qualitatively present the strain-dependent first-order phase transition in our investigated 2D materials in a very nice way. Especially, it shows us the simple linear coupling behavior of the strain.

We have presented that the in-plane strain is able to tune the transition between polar and nonpolar phases of the studied 2D materials. Still, there are several detailed issues that need to be addressed. (i) The change of electronic structures in such phase transitions. We report the electronic band structures of selected cases obtained by the HSE functional in Sec. 5 of the SM. The band-gap size changes due to the transition. In addition, the spin-orbit coupling (SOC) reduces the band gap and splits the bands in the P phase due to the lack of inversion symmetry. (ii) According to our results, the ground state of the P phase in ML-Bi_2Se_3 is not purely in the $P3m1$ layer group, but with additional distortions. The ground state beyond the transition point of tensile strain is a $p(2\times2)$ cell comparing with its original one. In this distorted phase, the finite value of P_z remains. The detailed results and discussions are listed in the SM since they will not change the global picture presented in our main text.

In summary, we have proposed that biaxial epitaxial strain is able to tune the ferroelectric phase transition in 2D materials. Specifically, we present the case of ML-In_2Se_3 and ML-Bi_2Se_3 corresponding to the transition between the polar layer group $P3m1$ and the nonpolar layer group $P\bar{3}m1$. By tuning the in-plane strain we can not only suppress the polarization in ML-In_2Se_3, but also can produce the out-of-plane polarization in ML-Bi_2Se_3. We have demonstrated that this general recipe works well for the case of ML-Bi_2Te_3, ML-Sb_2Te_3, and ML-Sb_2Se_3, suggesting a promising pathway in exploring 2D ferroelectric materials with robust out-of-plane polarization. The ferroelectric phase transition, corresponding to the competition between local stable phases, is a first-order type under the epitaxial strain. The coupling between the strain and the polarization is able to be simplified to the linear coupling of the biquadratic term. These results are important presteps not only of exploring groups of 2D ferroelectric materials but also of further studying the atomistic mechanism of robust out-of-plane polarization in 2D ferroelectric materials. In addition, some interesting applications such as triple state memory can be expected due to the first-order nature of the transition.

TABLE I. The coefficient parameters (units in eV/u.c.) of the Landau model [Eq. (2)] for ML-In_2Se_3 and ML-Bi_2Se_3 at 0 K. The in-plane biaxial strain is referred to as η.

	$a(\eta)$	b	c	d	λ	η_0
In_2Se_3	$0.056-4.600\eta$	0.668	−3.886	2.888	99.561	−0.013
Bi_2Se_3	$2.466-13.420\eta$	0.900	−8.310	6.656	66.230	0

This work is supported by the National Natural Science Foundation of China (NSFC) (Grants No. 11404159, No. 11974160, No. 11674148, and No. 11704177), the Guangdong Natural Science Funds for Distinguished Young Scholars (Grant No. 2017B030306008), and the Center for Computational Science and Engineering of Southern University of Science and Technology. B.X. acknowledges the startup fund from Soochow University, and the support from Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.

J.Z.Z. and L.C.C. contributed equally to this work.

[1] C. H. Ahn, K. M. Rabe, and J.-M. Triscone, Science **303**, 488 (2004).

[2] M. Dawber, K. M. Rabe, and J. F. Scott, Rev. Mod. Phys. **77**, 1083 (2005).

[3] J. Junquera and P. Ghosez, Nature (London) **422**, 506 (2003).

[4] D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, Science **304**, 1650 (2004).

[5] N. A. Spaldin, Science **304**, 1606 (2004).

[6] A. V. Bune, V. M. Fridkin, S. Ducharme, L. M. Blinov, S. P. Palto, A. V. Sorokin, S. G. Yudin, and A. Zlatkin, Nature (London) **391**, 874 (1998).

[7] N. Sai, A. M. Kolpak, and A. M. Rappe, Phys. Rev. B **72**, 020101(R) (2005).

[8] W. Ding, J. Zhu, Z. Wang, Y. Gao, D. Xiao, Y. Gu, Z. Zhang, and W. Zhu, Nat. Commun. **8**, 14956 (2017).

[9] R. Gaynutdinov, M. Minnekaev, S. Mitko, C. A. Tolstikhina, A. Zenkevich, S. Ducharme, and V. Fridkin, Phys. B (Amsterdam, Neth.) **424**, 8 (2013).

[10] M. J. Highland, T. T. Fister, M. I. Richard, D. D. Fong, P. H. Fuoss, C. Thompson, J. A. Eastman, S. K. Streiffer, and G. B. Stephenson, Phys. Rev. Lett. **105**, 167601 (2010).

[11] D. Ji, S. Cai, T. R. Paudel, H. Sun, C. Zhang, L. Han, Y. Wei, Y. Zang, M. Gu, Y. Zhang, W. Gao, H. Huyan, W. Guo, D. Wu, Z. Gu, E. Y. Tsymbal, P. Wang, Y. Nie, and X. Pan, Nature (London) **570**, 87 (2019).

[12] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature (London) **438**, 197 (2005).

[13] Q. Tang and Z. Zhou, Prog. Mater. Sci. **58**, 1244 (2013).

[14] J. W. Jiang, B. S. Wang, J. S. Wang, and H. S. Park, J. Phys.: Condens. Matter **27**, 083001 (2015).

[15] A. Gupta, T. Sakthivel, and S. Seal, Prog. Mater. Sci. **73**, 44 (2015).

[16] M. Wu and X. C. Zeng, Nano Lett. **16**, 3236 (2016).

[17] K. Chang, J. Liu, H. Lin, N. Wang, K. Zhao, A. Zhang, F. Jin, Y. Zhong, X. Hu, W. Duan, Q. Zhang, L. Fu, Q. K. Xue, X. Chen, and S. H. Ji, Science **353**, 274 (2016).

[18] R. Fei, W. Kang, and L. Yang, Phys. Rev. Lett. **117**, 097601 (2016).

[19] J. Lu, W. Luo, J. Feng, and H. Xiang, Nano Lett. **18**, 595 (2018).

[20] W. Luo, K. Xu, and H. Xiang, Phys. Rev. B **96**, 235415 (2017).

[21] M. Wu and P. Jena, Wiley Interdiscip. Rev. Comput. Mol. Sci. **8**, e1365 (2018).

[22] X. Ma, H. Ai, H. Gao, X. Zhang, W. Li, and M. Zhao, Phys. Chem. Chem. Phys. **21**, 3954 (2019).

[23] C. Huang, Y. Du, H. Wu, H. Xiang, K. Deng, and E. Kan, Phys. Rev. Lett. **120**, 147601 (2018).

[24] P. Sharma, F.-X. Xiang, D.-F. Shao, D. Zhang, E. Y. Tsymbal, A. R. Hamilton, and J. Seidel, Sci. Adv. **5**, eaax5080 (2019).

[25] Q. Yang, M. Wu, and J. Li, J. Phys. Chem. Lett. **9**, 7160 (2018).

[26] S. N. Shirodkar and U. V. Waghmare, Phys. Rev. Lett. **112**, 157601 (2014).

[27] F. Liu, L. You, K. L. Seyler, X. Li, P. Yu, J. Lin, X. Wang, J. Zhou, H. Wang, H. He, S. T. Pantelides, W. Zhou, P. Sharma, X. Xu, P. M. Ajayan, J. Wang, and Z. Liu, Nat. Commun. **7**, 12357 (2016).

[28] W. Song, R. Fei, and L. Yang, Phys. Rev. B **96**, 235420 (2017).

[29] S. Yuan, X. Luo, H. L. Chan, C. Xiao, Y. Dai, M. Xie, and J. Hao, Nat. Commun. **10**, 1775 (2019).

[30] Z. Fei, W. Zhao, T. A. Palomaki, B. Sun, M. K. Miller, Z. Zhao, J. Yan, X. Xu, and D. H. Cobden, Nature (London) **560**, 336 (2018).

[31] J. Xiao, H. Zhu, Y. Wang, W. Feng, Y. Hu, A. Dasgupta, Y. Han, Y. Wang, D. A. Muller, L. W. Martin, P. A. Hu, and X. Zhang, Phys. Rev. Lett. **120**, 227601 (2018).

[32] C. Cui, W. J. Hu, X. Yan, C. Addiego, W. Gao, Y. Wang, Z. Wang, L. Li, Y. Cheng, P. Li, X. Zhang, H. N. Alshareef, T. Wu, W. Zhu, X. Pan, and L. J. Li, Nano Lett. **18**, 1253 (2018).

[33] Y. Zhou, D. Wu, Y. Zhu, Y. Cho, Q. He, X. Yang, K. Herrera, Z. Chu, Y. Han, M. C. Downer, H. Peng, and K. Lai, Nano Lett. **17**, 5508 (2017).

[34] T. Birol, Nature (London) **560**, 174 (2018).

[35] K. F. Garrity, K. M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. **112**, 127601 (2014).

[36] A. P. Levanyuk and D. G. Sannikov, Usp. Fiz. Nauk **112**, 561 (1974).

[37] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.101.121407 for (1) details of computational methods, (2) structures of related phases, and (3) results on electronic properties, which includes Refs. [38–49].

[38] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[39] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[40] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[41] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[42] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[43] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).

[44] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).

[45] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006).

[46] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. **125**, 224106 (2006).

[47] G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. **113**, 9901 (2000).

[48] R. Resta, Rev. Mod. Phys. **66**, 899 (1994).

[49] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).

[50] M. Emziane, S. Marsillac, and J. C. Bernéde, Mater. Chem. Phys. **62**, 84 (2000).