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Structural and magnetic properties of 2D layered BiFeO₃
from First Principles

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ABSTRACT

Using first-principle calculations, we predict a novel BiFeO₃ (BFO) phase which is coined *I*-BFO with layered characteristics based on the ilmenite structure. The interactions between interlayer bismuth atoms cause its easiness to exfoliate monolayer BFO with a configuration in which Bi ions are above and below two-dimensional (2D) iron-oxygen octahedra sharing common edges. The calculated phonon spectra reveal the dynamic stability of both bulk and monolayer forms of *I*-BFO. Combining total energy computation and crystal structure search, we corroborate that the *I*-BFO monolayer maintains the lowest energy ground state, as compared to other 2D BFO exfoliations. We also discover that monolayer *I*-BFO is a robust antiferromagnetic material with a Néel temperature (T_N) of 4 K in its fully relaxed case. Such T_N can be prominently improved by strain, for example $T_N = 25$ K at 6% tension. Furthermore, our electronic structure calculations with PBE and hybrid HSE functionals show the *I*-BFO monolayer to be an indirect-gap semiconductor. Finally, we indicate that other ternary ABO₃ compounds have also the potential to produce layered materials from the ilmenite structure. This work thus provides a guidance to explore unconventional layered materials, and further broadens the application of BFO and other promising ilmenite oxides in two dimensions.

I. INTRODUCTION

Two-dimensional (2D) materials possess unique and fascinating physical properties which are different from their bulk counterparts [1]. Since the initial discovery of graphene in 2004, 2D materials have attracted flourishing attention from both academia and industry [2,3]. Nowadays, the family of 2D materials has grown considerably with the addition of numerous new members that have many interesting characteristics not available in graphene, for instance hexagonal boron nitride [4], transition-metal dichalcogenides MoS₂ and WSe₂ [5,6], and 2D elemental materials like silicene, borophene, and selenene [7-10]. The introduction of 2D magnetic systems provides extensive potential for new applications and fundamental research. Particularly, the magnetic anisotropy used to violate the Mermin-Wagner theorem allows the 2D magnetic semiconductor crystals with long-range correlation [11].

Layered transition metal compounds are excellent candidates to study magnetic property in the 2D landscape. In fact, an increasing amount of computational and experimental studies are currently devoted to magnetism of 2D materials, such as VSe_2 , $\text{Cr}_2\text{Ge}_2\text{Te}_6$, and CrI_3 [12-14]. The integration of 2D magnetism to future electronics opens a vast field of possibilities for unexplored physical phenomena and device concepts [15].

BiFeO_3 (BFO) is a widely investigated multiferroic material with an antiferromagnetic (AFM) transition temperature towards paramagnetism being higher than room temperature [16]. Preparations of BFO ultrathin film and superlattice have exploited its applications in spintronics and nanoelectronics devices [17,18]. However, the difficulty in realizing atomically-thick BFO has always been an important factor to impede its further development [19]. Remarkably, freestanding BFO monolayer has been synthesized in experiment by using sacrificing layer methods, which provides hope for the application of perovskite materials in two dimensions [20]. Compared with layered materials studied before, the transition-metal oxide BFO has strong interatomic ionic interaction, which causes instability in the (one-unit-cell thick) monolayer. Thus, it is of significant importance to investigate structural and other physical properties of BFO crystals in the 2D limit.

In this work, using first-principles calculations, we uncover a novel BFO phase with striking layered characteristics. We name it *I*-BFO since it is derived from the ilmenite structure. Our phonon calculation shows its stability for both bulk and monolayer conditions. The ground state energy of *I*-BFO monolayer is much less than other exfoliation from the known bulk phase, even one of them having been prepared experimentally. Then we find an antiferromagnetic Néel configuration and extract the magnetic exchange coupling constants up to the third-nearest neighbors by mapping the total energies of monolayer for different magnetic orders. The magnetic transition temperatures are further calculated by performing a Monte Carlo simulation with the *ab initio* exchange coupling constants. The results of electronic structure computation further show that monolayer *I*-BFO is an indirect-band-gap semiconductor with a gap of 2.26 eV. Finally, we inspect the strain effect for different magnetic configurations, and predict a series of 2D materials that can all be derived from the ilmenite structure.

II. METHODS

In the density functional theory (DFT) simulations, we used the Vienna *ab initio* Simulation Package (VASP) [21,22] to carry out first-principles calculations. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional [23] was employed to treat the exchange correlation interaction. We considered the electron correlation of Fe atoms by using the GGA+U method, with $U=4.0$ eV [18,24]. The projector-augmented-wave (PAW) potentials [25,26] were used to describe the electron-ion interaction. The energy cutoff was selected to be 550 eV for the plane wave basis set. The Brillouin zones were set to $10 \times 10 \times 1$ k-grid mesh and sampled in the Gamma-centered Monkhorst-Pack scheme. We set the vacuum distance to be 20 Å in order to avoid periodic interactions. The forces convergence standard on each atom was chosen as 0.005 eV/Å and the self-consistent calculations

were stopped until the energy difference was smaller than 10^{-7} eV per atom. To match the band-gap value close to experiments, the screened hybrid functional (HSE06) method [27,28] was applied. In geometric optimization calculations, we used the PBE function with D2 van der Waals functionals [29]. To ensure our structures are dynamically stable, we conducted phonon spectra calculations of all predicted low-energy phases. The phonon spectra were computed based on a DFT perturbation method with the PHONOPY package [30]. We built a supercell of $4 \times 4 \times 1$ to make the lattice larger than 10 Å, and forces criterion for ionic step was set to 10^{-8} eV on each atom.

III. RESULTS AND DISCUSSION

A. Geometric Structure and Stability

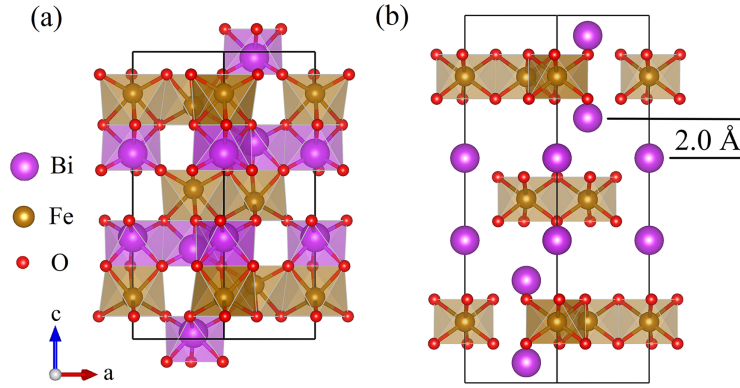


Figure 1. Ilmenite-type crystal structure side view of (a) the initial *I*-BFO bulk, and (b) the structure after the global optimization. The crystal structure is drawn by using VESTA [31].

The layered BFO phase is inspired by the ilmenite structure with R-3 space group [32], as shown in Fig. 1 and named *I*-BFO. The ilmenite is one of the representative structures of ABO_3 compounds, and is distinct from the orthorhombic perovskite and lithium-niobate types [33]. Layers of A-site and B-site cations successively alternate with a cation ordering along the *c* axis in ilmenite structure. This is different from the structure of $LiNbO_3$ -type in which every layer has mixed A and B cations, as shown in Fig. S1 [34]. In the literature, previous works have reported that ilmenite and $LiNbO_3$ types might be converted to each other under certain (e.g., pressure) conditions [35-37]. Thus, it is relevant to study properties of $BiFeO_3$ with an ilmenite structure. Importantly, *I*-BFO shows a very interesting layered configuration after structural relaxation, as illustrated in Fig. 1(b). In particular, the Bi atoms in the initial layer separate into two layers with a closest perpendicular distance of 2.0 Å and direct distance of 3.65 Å. We can relate such feature to other systems which have Bi and O atoms (Bi-O) truncation layers. For example, a recent experimental work on $Bi_2Sr_2CaCu_2O_{8+\delta}$ with Bi-O intercalation reveals a monolayer superconductor [38], and the plentiful aurivillius oxides like $Bi_2SrTa_2O_9$ also have a Bi-O truncation surface [39]. These systems suggest that Bi-O layer is a contributing factor to stabilize a layered structure. It is noted that the Fe atoms that belong to two different layers with opposite polarization in the initial

I-BFO structure then locate at same plane in the relaxed structure. Then, we calculate its cleavage energy for the optimized structure by considering a van der Waals (vdW) correction. In Fig. 2(c), the calculated cleavage energy is 0.55 J/m² which is quite close to Cr₂Ge₂Te₆ [13], confirming the possibility of creating *I*-BFO monolayer via mechanical exfoliation. We believe that this behavior is caused by the vertical repulsion between Bi atoms that were in the same layer of the initial *I*-BFO structure (such repulsion makes the Bi ions move away from each other in the relaxed 2D monolayer material).

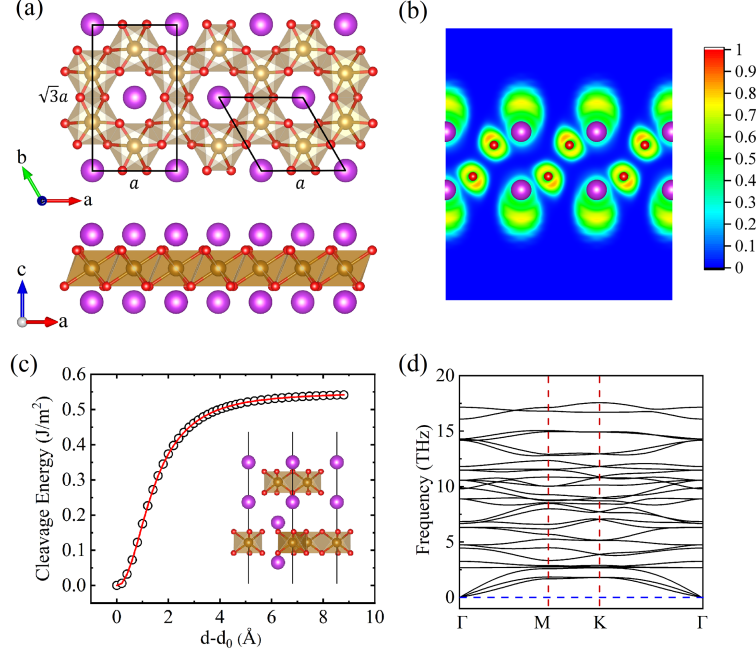


Figure 2. (a) The top and side views of monolayer *I*-BFO. (b) The electron localization function of *I*-BFO of the (010) plane. (c) The calculated cleavage energy as a function of the separation between the two monolayers experiencing vdW interactions. (d) Phonon dispersion curves.

The *I*-BFO monolayer from layered phase has 10 atoms in unit cell with a centrosymmetric hexagon. In Fig. 2(a), each Fe atom has six nearest O atoms (separated by a 2.01 Å distance) and each unit cell contains two oxygen octahedra. Notably, two neighboring oxygen octahedra in the layer are connected through the way of edge-sharing as in ilmenite-type oxide (note that this edge-sharing behavior also occurs in post-perovskite materials [40,41]), which is different from the well-known corner-sharing link type in lithium-niobate-type perovskite. The Bi atoms above and below envelop the oxygen octahedra in the middle, and form a perfect triangular lattice with the Bi-Bi separation $a = b = 5.21$ Å according to our calculations. Then, we obtain the electron localization function of (010) plane of *I*-BFO monolayer in Fig. 2(b). The localized electron around oxygen atoms forms ionic bond between Fe³⁺ and O²⁻ (see Fig. S2) [34]. It is known that the Bi³⁺ ions have 6s² lone pair electrons in BiFeO₃ materials, leading to the strong polarization of R3c phase. In *I*-BFO monolayer, the 6s² electrons are located outside the monolayer along the *c* direction.

Before studying physical properties of the BFO monolayers, we firstly examined

their stabilities. The phonon dispersion was calculated to investigate the dynamic stability in Fig. 2(d). It reveals the absence of imaginary-frequency phonon modes in the Brillouin zone, therefore indicating that this structure is stable in the freestanding form. We also calculated the phonon dispersion of *I*-BFO bulk and confirmed its stability, as displayed in Fig. S3 [34].

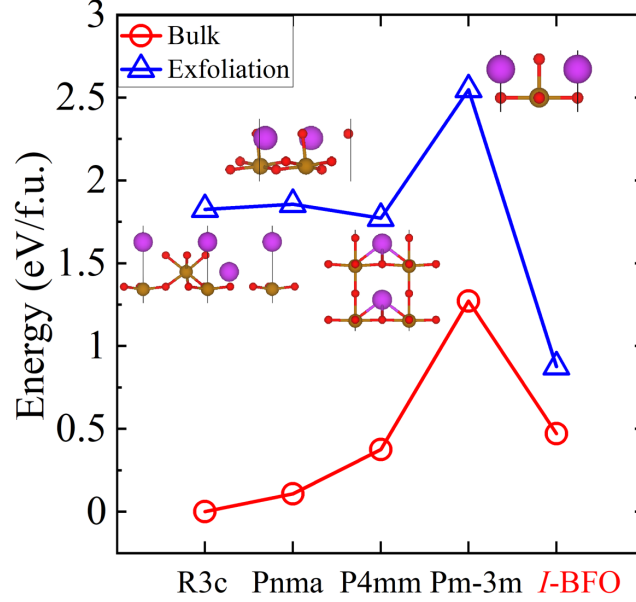


Figure 3. The energy comparison for various BiFeO_3 phases and the corresponding exfoliated 2D monolayers. The side views of four exfoliations from 3D bulk are displayed near the corresponding exfoliations. The R3c bulk phase energy is set to zero as a reference.

To further study the energy stability of *I*-BFO monolayer and bulk counterpart, we compared energy with other BFO phases. Conventionally, all known BFO bulk phases are non-layered structures, yet freestanding monolayer perovskite BFO was just synthesized experimentally by using sacrificial layer technology [20], and some related perovskite SrTiO_3 , LaAlO_3 , KTaO_3 , and BaFeO_3 monolayers have been investigated from first principles [42]. In addition, we select several phases of BFO and construct corresponding 2D structures by considering their (001) exfoliated planes. All the 2D exfoliations from the three-dimensional bulk share the same composition chemical formula of BiFeO_3 , as shown in Fig. S4 [34]. These phases are represented by the space group of bulk structures, which include the widely investigated R3c phase, the common perovskite Pnma phase, the largely polarized P4mm phase, and the cubic Pm-3m phase [43-45]. It is worth mentioning that 2D structure of P4mm phase is similar to the monolayer structure indicated in Ref. [20]. To consider the possible changes between bulk and exfoliated structures, we perform the geometry optimization for all exfoliations to compare the variation due to the dimensional reduction. The results of relaxation show that the four exfoliated phases have large structural change from bulk materials, as shown in Fig. S5 [34]. By comparing the energy of *I*-BFO bulk with other representative phases, we can see expectedly that the bulk R3c phase is the most stable,

then followed by the bulk Pnma phase. Moreover, the *I*-BFO bulk has quite a close energy to the P4mm phase, which is much lower than that of Pm-3m phase. Importantly, we find the monolayer *I*-BFO has the most favorable energy among all 2D exfoliations, i.e. the calculated energy is 0.90 eV/f.u. lower than the next lowest P4mm exfoliation, and 0.95, 0.98 and 1.67 eV/f.u. lower than the R3c, Pnma and Pm-3m exfoliations, respectively. **We also consider the influence of U parameter and a different exchange-correlation functional (PBEsol), as shown in Fig. S6 [34].** Moreover, considering the different cross sections and layer numbers, we calculate the energy of two-unit-cell-thickness exfoliations with same pseudo-cubic (001) section and further prove the low energy of *I*-BFO monolayer, as show in Fig. S7 [34]. Such facts strongly hint towards the feasibility of *I*-BFO monolayer to be prepared experimentally, and *I*-BFO has excellent stability in the case of two dimensions. The higher energy of other BFO phases is likely caused by incomplete Fe-O octahedron on the side surface, which costs increasing energy in ultrathin films. Furthermore, to consider various possible meta-stable states, the global crystal structure search is performed to find the possible 2D-BFO phase using CALYPSO code [46]. It is found that, indeed, the layered *I*-BFO phase has the lowest energy among all found structures during that search. The layered *I*-BFO phase thus appears to be an excellent candidate to produce freestanding monolayer BFO materials.

B. Magnetism and Electronic Structure

Let us also recall that R3c-like BFO perovskite shows G-type antiferromagnetic ordering in strained films and in bulks under magnetic field, and experiments also report a magnetic G-type-derived cycloidal configuration in the R3c bulk below its Néel temperature (643K), above which it becomes paramagnetic in nature [16,47-49]. In monolayer *I*-BFO crystal structure, the magnetic structure could technically show 2D ferromagnetic (FM) or AFM coupled characteristics. To describe the 2D magnetic configurations, we convert the conventional unit cell to a rectangular lattice with four Fe atoms as shown in Fig. 2(a). Here we consider four possible collinear magnetic orderings, namely FM, Néel, Zigzag, and Stripy configurations [50], as schematically shown in Fig. S8(a)–(d) [34]. Their relative energies obtained from calculations are supplied in parentheses below the magnetic configuration labels. We find that the most stable one is the Néel ordering, whereas FM has the highest energy compared to the other three configurations, and the Zigzag and Stripy configurations are slightly higher in energy than the Néel configuration. Moreover, we calculate the magnetic anisotropy by changing the parallel orientations of the local magnetic moment in Fig. S9 [34] and find that the monolayer prefers to possess an out-of-plane easy axis, like MnPS₃ [51]. The calculated magnetic anisotropic energy is found to be 117 $\mu\text{eV/f.u.}$ for our monolayer *I*-BFO. Then, we extract the exchange coupling constants up to the third-nearest neighbor by mapping the total energies of monolayer of these four different magnetic orders to the Heisenberg model on 2D hexagonal lattices. The following spin Hamiltonian is used:

$$H = -2J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j - 2J_2 \sum_{\langle\langle ij \rangle\rangle} \vec{S}_i \cdot \vec{S}_j - 2J_3 \sum_{\langle\langle\langle ij \rangle\rangle\rangle} \vec{S}_i \cdot \vec{S}_j - D \sum_i |\vec{S}_i^z|^2. \quad (1)$$

In equation (1) J_1 , J_2 , and J_3 denote the nearest, second, and third neighbor exchange coupling constants, respectively. D is the anisotropy energy parameter, and $\vec{S}_i^z$ is the z component of the spin vector. These three parameters can be calculated using the equations:

$$-E_{\text{FM/Néel}} = E_0 + (\pm 3J_1 + 6J_2 \pm 3J_3)|\vec{S}|^2, \quad (2)$$

$$-E_{\text{Zigzag/Stripy}} = E_0 + (\pm J_1 - 2J_2 \mp 3J_3)|\vec{S}|^2. \quad (3)$$

Here E_0 is the ground state energy, and we employ the $S = 5/2$ for Fe^{3+} . The J_1 , J_2 and J_3 values are found to be -0.365, -0.157, and -0.131 meV, respectively. These parameters suggest that the first, second, and third nearest neighbor exchange interactions are all AFM, and the competitive relation exists between J_2 and the other two, resulting an energy difference of 0.13 meV between Zigzag and Stripy configurations. Then, **using these J and D values**, we calculated the Néel temperature (T_N) by performing a Monte Carlo (MC) simulation of a Heisenberg model on the 2D honeycomb lattice, as well as an Ising model [52]. The 20×20 supercell lattice with periodic conditions is set up, and the MC simulation runs for 10^6 steps of equilibrium and 10^6 steps for statistics at each temperature point.

Before discussing the T_N , let us investigate their electronic structures based on the magnetic ground states. The band dispersions and density of states (DOS) from PBE+U and HSE06 hybrid functionals are displayed in Fig. 4. The monolayer *I*-BFO is an indirect-band-gap semiconductor with the gap value of 2.26 eV for PBE+U and 3.35 eV for HSE functionals. The conduction band minimum (CBM) and valence band maximum (VBM) are located at high symmetry points M and K in Brillouin zone, respectively. For DOS, we use the purple, yellow, and red lines to show the p orbital projection of Bi, the d orbital projection of Fe, and the p orbital projection of O elements, respectively. The main contribution for valence band is O element, and the d orbital of Fe mainly contributes to the conduction band. The projection of Bi element distributes in all energy band range and occupies less DOS (especially for the VBM and CBM levels) with respect to Fe and O ions.

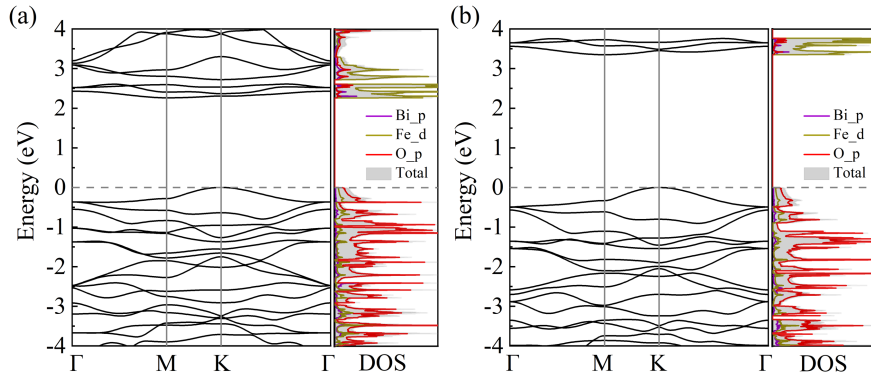


Figure 4. The calculated band structures and DOS of the monolayer *I*-BFO using (a) PBE+U and (b) hybrid HSE06 functionals.

C. Biaxial Strain and Transition Temperature

We have thus confirmed that the monolayer *I*-BFO is semiconducting with antiferromagnetic properties. Moreover, the effects of biaxial in-plane strains on magnetic configurations and electronic structures can also be investigated for applications in flexible devices. To do that, we use the lattice ratio $\varepsilon = (a - a_0)/a_0$ to represent the value of biaxial strain, for example, $\varepsilon = 1\%$ means the lattice constant is 1% larger than strain-free condition. The energy changes of *I*-BFO monolayer as a function of strain is displayed in Fig. 5(a). The black line is the energy difference between FM and Néel magnetic configurations ($\Delta E_{\text{FM-Néel}}$), the green and blue are energy difference values of Zigzag and Stripy configurations ($\Delta E_{\text{Zigzag-Néel}}$, and $\Delta E_{\text{Stripy-Néel}}$) with respect to the Néel magnetic configuration, respectively. The red line is the energy of the Néel configuration set to zero. We noted that all three AFM configurations have lower energy than FM for any strain. Our calculation also illustrates that the Néel AFM is the magnetic ground state under all tensile strain. However, the negative values $\Delta E_{\text{Zigzag-Néel}}$ and $\Delta E_{\text{Stripy-Néel}}$ reveal that Zigzag and Stripy configurations have even lower energy than the Néel configuration under compressive strain. Especially the Zigzag configuration becomes the magnetic ground state from $\varepsilon = -1\%$, with a robust AFM property for compressive strain. Overall, these results suggest that the *I*-BFO is an excellent candidate for 2D antiferromagnetic spintronics with tunable AFM configuration types [53-55]. Furthermore, as illustrated by the blue data in Fig. 5(b), the simulated T_N of monolayer BFO is enhanced significantly from 4 K to 25 K in the case of $\varepsilon = 6\%$. We provide the results of calculated J and D values under different strain as shown in Fig. S10 [34]. This further indicates that the biaxial strain has remarkable control effect on magnetic transition temperatures.

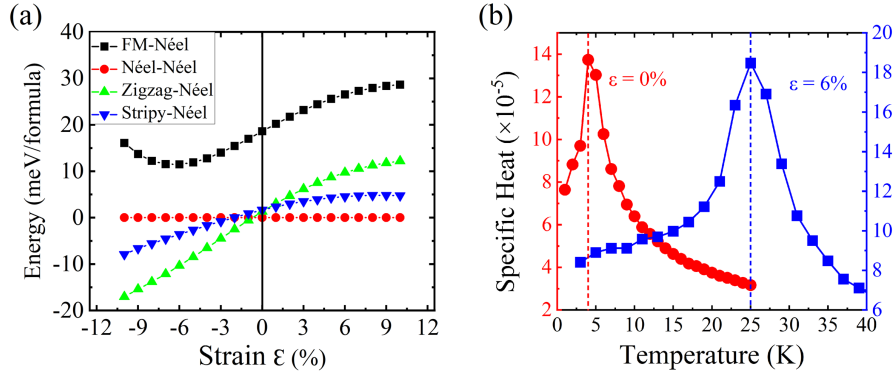


Figure 5. (a) The calculated energy difference for different magnetic configurations under biaxial strain, the Néel configuration is set to zero as reference. (b) The specific heat as a function of temperature for *I*-BFO monolayer under zero and 6% tensile strain from Monte Carlo simulations.

Finally, we consider if other ternary ABO_3 compounds can also have great potential to form the layered ilmenite structure. For example, we found that BiAlO_3 and BiYO_3 with different B^{3+} -site element have stable phonon modes and the structures are similar to that of monolayer *I*-BFO. Besides, it is interesting that in monolayer ilmenite LiNbO_3 , B-site elements show anti-polar distortion in the out-of-plane direction. The relevant

structural visualizations and phonon spectra of these materials are shown in Fig. S11 [34]. The proposed monolayer ilmenite may provide the possibility for more discovery of 2D ferroelectric and multiferroic systems.

IV. CONCLUSIONS

In summary, using DFT we have investigated a previously unknown phase of layered BiFeO_3 inspired by ilmenite structure, and named it *I*-BFO. It is found to be dynamically stable and its feasible realization and notable properties can bring a series of layered materials to expand the 2D family. Through the calculated cleavage energy and energy comparison of various phases, we confirm that *I*-BFO is a substance that has close energy with the tetragonal $P4mm$ phase, and its monolayer should possess exceptional stability with much lower energy than other 2D exfoliations from known BFO phases. We further study its magnetic properties based on the hexagonal arrangement of Fe atoms, and uncover that the Néel configuration is the magnetic ground state. In addition, we extract the magnetic exchange coupling constants up to the third-nearest neighbors in the monolayer. Performing MC simulations based on Heisenberg model, we obtain a Néel temperature of 4 K in the fully relaxed case and an enhancement up to 25 K under a 6% tensile strain. The band structure calculations show that monolayer *I*-BFO has an indirect band gap of 2.26 eV and 3.35 eV using PBE+U and HSE functionals, respectively. Additionally, we find that the lattice strain may tune the AFM configurations effectively. In particular, a strain as small as 2% can transform the magnetic ground state from AFM-Néel to AFM-Zigzag. Finally, other ternary ABO_3 compounds are proposed to also have the potential to crystallize in the same ilmenite-based structure in their layered forms. We hope that these findings provide a guide to explore novel 2D structures, which may lead to applications or unusual phenomenon, such as the anomalous quantum Hall effect [56].

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