B₄CN₃ and B₃CN₄ monolayers as the promising candidates for metal-free spintronic materials

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Abstract

The search for candidates of spintronic materials, especially among the two-dimensional (2D) materials, has attracted tremendous attentions over the past decades. By using a particle swarm optimization structure searching method combined with density functional calculations, two kinds of boron carbonitride monolayer structures (B₄CN₃ and B₃CN₄) are proposed and confirmed to be dynamically and kinetically stable. Intriguingly, we demonstrate that the magnetic ground states of the two BₓCᵧNₓ systems are ferromagnetic ordering with a high Curie temperature of respectively 337 K for B₄CN₃ and 309 K for B₃CN₄. Furthermore, based on their respective band structures, the B₄CN₃ is found to be a bipolar magnetic semiconductor (BMS), while the B₃CN₄ is identified to be a type of spin gapless semiconductor (SGS), both of which are potential spintronic materials. In particular, carrier doping in the B₄CN₃ can induce a transition from BMS to half-metal, and its spin polarization direction is switchable depending on the doped carrier type. The BMS property of B₄CN₃ is very robust under an external strain or even a strong electric field. By contrast, as a SGS, the electronic structure of B₃CN₄ is relatively sensitive to external influences. Our findings successfully disclose two promising materials toward 2D metal-free spintronic applications.

1. Introduction

Spintronic materials, using electron spin combined electron charge to carry information, form the basis of spintronics and have attracted tremendous attentions due to their unique electronic properties and practical applications [1, 2]. As shown in figure S1, half-metal (HM) [3], spin gapless semiconductor (SGS) [4, 5], and bipolar magnetic semiconductor (BMS) [6–8] are three important classes of spintronic materials. HM, in which one spin channel is metallic while the other keeps a semiconducting or insulating band gap (figure S1(a)), can thus provide completely spin-polarized currents. Followed by HM, a novel concept of SGS has been proposed and discussed in Co-doped PbPdO₂ by Wang [4]. There are four typical band structure configurations of SGS defined, one of which is shown in figure S1(b). In this subclass of SGS, both spin channels (spin-up channel and spin-down channel) have their respective band gap but are relatively energy shifted, which lead to the opposite spin channels touching with each other at the Fermi level. Another new class of spintronic materials, that is, BMS, has been proposed and realized in semi-hydrogenated carbon nanotube theoretically [6]. In BMS, both spin channels are semiconducting and possess opposite spin polarization when approaching the Fermi level. Therefore, BMSs can provide completely spin polarized currents with tunable spin polarization simply by carrier doping [6–10] or external field [7]. For the applications in nanoscale integrated circuits, low-dimensional spintronic materials with high Curie temperature (T_C) are much more desirable [11–15]. To achieve this purpose, 2D metal-free materials, due to their long diffusion lengths and spin-relaxation time arising from the weak spin–orbit and hyperfine interaction, are gaining increasing interest recently [7, 16–21].
It is know that the two most stable 2D metal-free materials are graphene [22] and hexagonal boron nitride (h-BN) [23], and which have similar lattice structures and radically different electronic properties, e.g., the graphene is a semi-metal with a zero band gap while the h-BN is a wide band gap semiconductor. However, both materials are NM, which limits the application in spintronics. It is considered that adjusting the electronic structures in the intermediates of these two materials by chemical variations is an effective way [24–28]. These intermediates are known as B,C,N monolayer compounds, which are a series of 2D metal-free materials consisting of three elements (boron, carbon and nitrogen) in varying proportions with honeycomb structure and sp² covalent bonding. Experimentally, various layered B,C,N compounds have been synthesized by using pyrolysis [29], chemical vapor deposition [30], doping [24, 31–34], etc. These 2D ternary compounds exhibit rich electronic properties ranging from metals to insulators depending on their chemical compositions and atomic arrangements. More interestingly, spin polarization has been predicated to exist in some specific C/BN heterostructures, e.g., BN islands embedded in graphene sheets and vice versa [35, 36]. This exotic property suggests a promising approach to search for 2D metal-free spintronic materials in B,C,N materials. We note that most earlier theoretical works [28, 37] only focused on the BCN structures (e.g. BCN, BC2N, BCN2, etc) with B/N = 1 ratio on account of the phase separation between graphite and h-BN observed in experiments [24, 30]. However, there are indications that it is possible to solve the problem of phase separation. For instance, both theoretical and experimental results proved that the carbon atoms tend to substitute boron sites of the BN lattice in nitrogen-rich (N-rich) B,C,N materials [38, 39]. Otherwise, Jin et al prepared B,C,N sheets with homogenously dispersed B and N atoms by carefully selecting the synthesis conditions [40]. In these B,C,N materials, the B/N ratio is not equal to 1, suggesting the existence of more B,C,N structures with x ≠ z. In addition, the electronic properties of B,C,N sheets are strongly dependent on the B/N ratio [38]. This motivates us to pursue a study of such materials.

In this study, we propose two kinds of B,C,N monolayers (B,C,N3 and B,C,N4) with B/N x 1 by using a specifically developed particle swarm optimization (PSO) algorithm technique for crystal structures prediction [41]. The stability of the two structures is confirmed from phonon spectra and molecular dynamics (MD) calculations. Based on first-principle calculations, the B,C,N3 is predicted to be a BMS while the B,C,N4 is identified to be a type of SGS. Specifically, both Tc of the two materials are found to be above room temperature (RT). Further study shows that the system of B,C,N3 can possess half-metallicity with completely spin polarization via carrier doping. Furthermore, its BMS feature is very robust under external electric fields or strains. In contrast, the electronic structure of B,C,N4 is relatively sensitive to external influences, e.g., it changes into SGS from BMS under an external tensile strain of 3%. Our results indicate that the two types of 2D B,C,N materials could be two promising candidates for spintronic devices.

2. Computational details

A global-minimum optimization method based on the 2D PSO techniques [42], as implemented in the ’crystal structure analysis by particle swarm optimization’ (CALYPSO) code [41], was performed to predict 2D structures of B,C,N compounds. This method has been used to successfully predict stable structures for various 2D systems, including 2D boron–carbon compounds [42], boron monolayers [43], 2D boron–silicon compounds [44], 2D B,C,N compound (0 < x < 1) compounds [28], etc. The calculations of structural relaxations, electronic density of states (DOS), band structures, and spin density distributions were carried out within the generalized gradient approximation with the Perdew–Burke–Ernzerhof (GGA–PBE) functional [45] as implemented in the Vienna ab initio Simulation Package (VASP) [46–48]. Spin polarization was included through all the calculations. The cutoff energy for plane waves was chosen to 500 eV and the vacuum space along the z direction was set to 15 Å, which is enough to avoid the interaction between the two neighboring images. The 2D Brillouin zone (BZ) integration was sampled on a Monkhorst–Pack [49] grid of 9 × 9 × 1 k-points for geometry optimization of the unit cell and a 5 × 5 × 1 grid for the large 2 × 2 supercell. Further increasing the number of k-points only gave rise to an energy change of less than 0.1 meV. All the atoms in the models were allowed to relax to the minimum in the enthalpy without any constraints and the convergence of force was set to 0.001 eV Å−1. Since standard density functional theory usually significantly underestimates the size of the band gap, hybrid functional calculations based on the Heyd–Scuseria–Ernzerhof (HSE06) functional [50] have been also carried out to examine the spin-polarized band structures of primitive B,C,N3 and B,C,N4 unit cells.

The phonon spectra were calculated using the supercell method, as implemented in the phonopy code [51] and the force constant matrix was determined by the VASP. Convergence tests gave the use of a 3 × 3 supercell and a 5 × 5 × 1 k-mesh for all structures. In addition, MD simulations, as also performed in the VASP, were employed to study the thermal stability of these structures. A kinetic energy cutoff of 450 eV and the PBE functional were chosen in all MD simulations, in which the temperature controlled by Nose–Hoover thermostat [52] was fixed at RT (T = 300 K) with a time step of 1 fs. The convergence of energy was set to 1 × 10−4 eV.
3. Results and discussions

3.1. Geometric structures and stability
Considering that the 2D $B_xC_yN_z$ compounds have unnumbered possible compositions and atomic configurations, theoretically, identifying the stability and physical property of every possible structure is impossible. Hence, CALYPSO was performed for simulation $B_xC_yN_z$ cells with different chemical compositions based on the same space group ($P6m2$) with $h$-BN. To further check the feasibility of this method, we also consider the case of $B/N = 1$. Besides the earlier well-studied structures, e.g., plenty of $BC_2N$ structures [37, 53, 54], our structural searches also identify some unreported ones. Two of these new structures, which are named as $B_4CN_3$ and $B_3CN_4$ by their chemical formulas, as shown in figures 1(a) and (c), have attracted our attentions due to their extraordinary electronic structures. For comparison, one type of $BC_2N$ monolayer, which was considered to be the most stable structure among 2D $BC_2N$ compounds in the previous studies [53, 54], is also calculated and plotted in figure S2 with its phonon dispersion curve. All these systems are analogous compounds and adopt the same space group of $P6m2$ with a planar honeycomb structure. Since there are no experimental data for the size of the unit cells of these materials, their equilibrium lattice constants (shown in table 1) are obtained based on polynomial curve fitting according to the static self-consistently total energies with different constant lattices ($> 6$), as shown in figure S3.

To evaluate the feasibility of experimental synthesis and the relative stability of these $B_xC_yN_z$ structures under different stoichiometric conditions, the formation energy per atom is calculated, which is defined as

$$E_t = (E_{\text{tot}} - n_B\mu_B - n_C\mu_C - n_N\mu_N)/(n_B + n_C + n_N),$$

where $E_{\text{tot}}$ is the calculated total energy per unit cell of the $B_xC_yN_z$ monolayer, $n_B$, $n_C$, and $n_N$ are the number of boron, carbon, and nitrogen atoms in one unit cell, and $\mu_B$, $\mu_C$, and $\mu_N$ are the chemical potential of boron,

![Figure 1. Schematic representations of (a) $B_4CN_3$ and (c) $B_3CN_4$ monolayer with unit cell containing eight atoms; the corresponding calculated phonon dispersion curves are respectively plotted in (b) and (d).](image-url)
carbon, and nitrogen, respectively. Here, \( \mu_C \), which is obtained from a calculation for graphene, is chosen as a constant in the above formula. Moreover, \( \mu_N \) and \( \mu_B \) may not exceed the chemical potential of the bulk phases despite of synthesis condition \[37\]. Therefore, in this work, under N-rich condition, \( \mu_N \) is obtained from the \( \alpha \)-N\(_2\) phase of solid nitrogen, while a metallic \( \alpha \)-B phase is used as the reservoir for the boron-rich (B-rich) environment. In both cases, \( \mu_N \) and \( \mu_B \) are linked by the equilibrium thermodynamic condition, 

\[ \mu_N + \mu_B = \mu_{hBN} \]

where \( \mu_{hBN} \) is the energy per unit cell of h-BN. The formation energies of various B\(_x\)C\(_y\)N\(_z\) structures are plotted in table 1 for both N-rich and B-rich cases. It can be seen that the calculated formation energy of BC\(_2\)N is 0.22 eV/atom, in good agreement with the result reported earlier \[37\]. Notably, the formation energies of both B\(_4\)CN\(_3\) (under B-rich condition) and B\(_3\)CN\(_4\) (under N-rich condition) are smaller than that of BC\(_2\)N, indicating that they are energetically more favorable than BC\(_2\)N. Furthermore, one can see that B\(_4\)CN\(_3\) is synthesized much more easily in B-rich condition, while B\(_3\)CN\(_4\) prefer to be prepared in N-rich environment. This conclusion is qualitatively in agreement with previous theoretical result \[38\] that carbon atoms favor to get dispersed into the boron sublattice in N-rich systems of h-BN doped with carbon atoms.

However, since the structure might be subject to dynamic instability, the stability of a structure cannot be determined exclusively by comparing formation energies. Thus, the phonon dispersion curves of the two structures are calculated and plotted respectively in figures 1(b) and (d). The unit cell of each structure contains eight atoms, giving twenty-four phonon branches. As found, there is no imaginary phonon mode in the phonon spectra along the highly symmetric points in the whole BZ of B\(_4\)CN\(_3\) and B\(_3\)CN\(_4\) structures, confirming their dynamical stability. To further evaluate the thermal stability of the two structures, a large 4 \times 4 supercell containing 128 atoms is built, and then, spin-polarized MD simulations based on density functional theory are performed at 300 K with a time step of 1 fs. For B\(_4\)CN\(_3\) structure, the fluctuations of temperature with time steps are shown in figure 2(a). After 3000 steps, we find no structure destruction except for some thermal fluctuations. This result shows that the B\(_4\)CN\(_3\) monolayer is thermally stable up to at least 300 K. Likewise, the thermal stability of B\(_3\)CN\(_4\) is confirmed by the same method, as illustrated in figure 2(c). Overall, although both B\(_4\)CN\(_3\) and B\(_3\)CN\(_4\) systems have positive formation energies, their structures show no imaginary frequency modes in phonon spectra and remarkable dynamic stability in MD calculations at RT, and thus can be regarded at least as stable materials on some suitable substrates under the condition of ultrahigh vacuum.

### Table 1. Lattice constants (\( L \)), formation energies per atom (\( E_f \)) of B\(_4\)CN\(_3\), B\(_3\)CN\(_4\), and BC\(_2\)N monolayer under N-rich and B-rich environment.

| Structure | \( L (\text{Å}) \) | N-rich | B-rich |
|-----------|-------------------|--------|--------|
| B\(_4\)CN\(_3\) | 5.13 | 0.53 | 0.15 |
| B\(_3\)CN\(_4\) | 4.97 | 0.18 | 0.56 |
| BC\(_2\)N | 5.00 | 0.22 | 0.22 |

### Figure 2. The fluctuations of (a) temperature and (b) magnetic moment with respect to MD steps at 300 K for B\(_4\)CN\(_3\). (c) and (d) are similar respectively to (a) and (b), but for B\(_3\)CN\(_4\).

#### 3.2. Electronic structures and magnetic properties

Obviously, in the hexagonal framework of B\(_4\)CN\(_3\) or B\(_3\)CN\(_4\), the carbon atom can provide three electrons to form sp\(^2\) hybrid bonds with either boron or nitrogen atoms around, thus leaving one electron unpaired, which...
may lead to spin polarization in such system. To verify this conjecture and study the electronic structures of B$_4$CN$_3$ and B$_3$CN$_4$ in details, their spin density distributions and spin-resolved band structures are calculated and plotted in figure 3. Remarkably, electronic bands, especially the ones near the Fermi level, are non-degeneracy and split into two branches distinctly, indicating a spontaneous spin polarization in B$_4$CN$_3$ and B$_3$CN$_4$. Additionally, it is worth noticing that the band structures of B$_4$CN$_3$ and B$_3$CN$_4$ are different with each other. Specifically, there is a small overlap between conduction and valence bands near the Fermi level of B$_3$CN$_4$, as shown in the insets of figure 3(b), while an indirect band gap of 0.31 eV is found in the band structure of B$_4$CN$_3$. It is clear that for B$_4$CN$_3$, the spin-down channel has an indirect band gap of 0.88 eV from the $\Gamma$ to the M point in the BZ, whereas the spin-up state has a direct band gap of 4.2 eV at the K point. For B$_3$CN$_4$, there is a different characteristic that the spin-down channel has an indirect band gap of 4.2 eV from the $\Gamma$ to the K point, while the spin-up channel also has an indirect band gap of 0.7 eV from the $\Gamma$ to the M point. Based on these features of the two band structures, we can take the conclusion that the B$_4$CN$_3$ is a BMS [6] while the B$_3$CN$_4$ is a type of SGS [4].

In comparison to GGA-PBE, hybrid functional such as HSE06 [50] is expected to perform very well in predicting the accurate gap. Thus, we check the spin-polarized band structures of B$_4$CN$_3$ and B$_3$CN$_4$ monolayers by carrying out hybrid HSE06 functional calculations. Figures S4(a) and (b) present the calculated spin-resolved band structures of B$_4$CN$_3$ and B$_3$CN$_4$ monolayers, respectively. Clearly, the band structures (see figure S4) are similar to those based on the GGA-PBE (see figure 3), which indicates that the predicted intrinsic BMS character of B$_4$CN$_3$ and SGS nature of B$_3$CN$_4$ still survive to the hybrid HSE06 functional. Remarkably, the band gaps of both spin-up and spin-down channels obtained by hybrid HSE06 functional increase significantly compared to that obtained by GGA-PBE for both B$_4$CN$_3$ and B$_3$CN$_4$ monolayers, which can be explained by the fact that the hybrid functional usually correct the underestimation of the energy gap from GGA-PBE.

To gain more insights about the magnetism of B$_4$CN$_3$ and B$_3$CN$_4$, the spin-polarized electron densities of the two systems calculated from the spin charge density difference between the spin-up and spin-down states ($\Delta \rho = \rho_{\uparrow} - \rho_{\downarrow}$) are also plotted in figure 3. The magnetic moments per unit cell are found to be approximately 1 $\mu_B$ for both B$_4$CN$_3$ and B$_3$CN$_4$. For B$_4$CN$_3$, the $\Delta \rho$ isosurface shows that the magnetic moments are mainly localized around carbon atoms, while nitrogen atoms have a small contribution. The contributions from boron atoms are almost negligible. For B$_3$CN$_4$, spin polarization also occurs mainly at carbon atoms. However, it

![Figure 3. Spin density distributions ($\Delta \rho = \rho_{\uparrow} - \rho_{\downarrow}$) (top) and spin-resolved band structures (bottom) of (a) B$_4$CN$_3$ and (b) B$_3$CN$_4$. Enlarged drawings of the energy bands of B$_3$CN$_4$ near the Fermi level are also plotted in the insets to display the details. The Fermi energy is set to zero, and the isosurface value of spin-polarized electron density is 0.05 e Å$^{-3}$. Red color indicates the positive (spin-up) values.](image-url)
displays a slightly different image that it is boron atoms rather than nitrogen atoms give the small contribution. Furthermore, $\Delta \rho$ isosurfaces of $B_4CN_3$ and $B_3CN_4$ have similar shape, indicating that their local magnetic moments arise from the same origin, that is, primarily the $p_z$ atomic orbitals of carbon atoms. These results verify our conjecture about the origin of the spin polarization mentioned above.

To identify the preferred magnetic ground state of $B_4CN_3$ and $B_3CN_4$, we adopt a $2 \times 2$ supercell containing four unit cells to perform calculations for three different initial spin arrangements: ferromagnetic (FM), antiferromagnetic (AFM), and non-magnetic (NM) state. Shown in figure 4 are the FM and AFM configurations of $B_4CN_3$ and $B_3CN_4$. The calculated results show that the FM state is the most energetically stable, with energy 29.1 (26.7) and 564.7 (321.9) meV per $B_4CN_3$ ($B_3CN_4$) unit cell lower than that of the AFM and NM state, respectively, indicating that both $B_4CN_3$ and $B_3CN_4$ monolayer are FM coupling. The corresponding magnetic moment in a $2 \times 2$ supercell is calculated to be $4.0 \mu_B$ for the FM state of $B_4CN_3$ ($B_3CN_4$). The small magnetic moment ($< 4.0 \mu_B$) of $B_3CN_4$ is related to the feature of its band structure. More specifically, as this type of SGS, completely spin polarization cannot occur around the Fermi level due to the overlap of the majority spin (spin-up) and the minority spin (spin-down) band of $B_4CN_4$, which let a few electrons transfer from the majority spin state to the minority spin state, thus reducing its magnetic moment.

According to the mean-field theory [10], the $T_C$ can be estimated by $\gamma k_B T_C / 2 = E_{AFM} - E_{FM}$, where $\gamma$ is the dimension of the system, $k_B$ is the Boltzmann constant, $E_{AFM}$ and $E_{FM}$ are respectively the energies of AFM and FM configurations. Naturally, $\gamma$ is set to be 2 due to the 2D structure of $B_4CN_3$ or $B_3CN_4$, and then $T_C$ of 337 K for $B_4CN_3$ and 309 K for $B_3CN_4$ are obtained, both of which are above RT. To further confirm the stability of the FM state at RT, as shown in figures 2(b) and (d), we calculate the fluctuations in the magnetic moments as a function of the simulation times during the MD simulations for $4 \times 4$ supercells of $B_4CN_3$ and $B_3CN_4$ at 300 K, respectively. Remarkably, the ground states of $B_4CN_3$ and $B_3CN_4$ remain magnetic with an average magnetic moment of respectively about 15.6 and 14.0 $\mu_B$ at RT. We note that the influence of temperature on the magnetic moments of $B_4CN_3$ is larger than that of $B_3CN_4$, which can be understood by the fact that the electronic structure of SGS is more sensitive to external influences than that of BMS due to that no threshold energy is required to move electrons or holes from majority spin state to minority spin state.

As we know, for SGS and BMS, if the Fermi levels in their band structures can be shifted up or down by external influences, the directions of spin in either the conduction or valence bands are tunable. Namely, they can become HM and provide completely spin-polarized currents with reversible spin polarization direction [4,6]. Moreover, carrier doping, external electric field and mechanical strain are three convenient methods for regulating the band structures of materials. Thus, we turn to explore these external influences on the electronic properties of both $B_4CN_3$ and $B_3CN_4$ in the following sections.

First, we examine the carrier doping effect on these two systems by introducing additional electrons or holes. For $B_4CN_3$, under the doping concentration of 0.025 electrons per atom, its Fermi level moves up to cross the conduction band, that is, the spin-down channel becomes gapless while the spin-up channel is still insulating with a band gap about 4 $eV$, which indicates that the system of $B_4CN_3$ turns into a HM with spin-down polarization, as illustrated in figure 5(a). Similarly, a spin-up polarized HM can be obtained under the holes doping (figure 5(b)). We also examine the effects of doping level of $n (0.01 \leq n \leq 0.03)$ electrons or holes per atom on $B_4CN_3$, the calculated results show the same conclusion that $B_4CN_3$ changes to HM with different spin polarization directions depending on the doping type. As shown in figure S5, the situation is different for $B_3CN_4$, that is, the $B_3CN_4$ can retain its SGS character under the low electrons doping level ($n < 0.025$ electrons per atom). Furthermore, due to the resulting decrease of spin polarization, its SGS character gradually weakens with the increase of electrons doping concentration. When the electrons doping concentration reaches 0.025 electrons per atom (see figures 5(c) and S5(c)), the band gap of spin-up channel decreases towards zero.
demonstrating that the system of B$_3$CN$_4$ converts to ordinary spin-split metal from SGS. In the case of holes doping, e.g., with the doping concentration of 0.025 holes per atom as shown in figure 5(d), B$_3$CN$_4$ turns into a HM with spin-up polarization, which is as similar as the result of holes doping in B$_4$CN$_3$. Additionally, the FM coupling is still energetically favorable in these carrier doping cases. It is worth pointing out that the maximal doping concentration of 0.03 carriers per atom used in this work, corresponding to about $1.06 \times 10^{14}$ carriers per cm$^2$, can be achieved experimentally by employing an electrolytic gate.

Considering that these materials may operate under an electric field as electronic devices, the effects of an external electric field on B$_4$CN$_3$ and B$_3$CN$_4$ are studied. The electric field with the strength ranging from 0.0 to 0.8 V Å$^{-1}$ along the z-axis is applied perpendicular to the B$_x$C$_y$N$_z$ monolayer. As shown in figure S6(a), under an electric field as strong as 0.8 V Å$^{-1}$, the energy bands near the Fermi level are very similar to that at 0.0 V Å$^{-1}$ (figure 3(a)), indicating that the B$_4$CN$_3$ is a very robust BMS material even under a strong electric field. In contrast, B$_3$CN$_4$ can retain its SGS characteristic in the case of external electric field less than 0.6 V Å$^{-1}$, meanwhile, its SGS characteristic gradually weakens with the increase of electric field (figure S6(b)). When the electric field reaches 0.6 V Å$^{-1}$, the system of B$_3$CN$_4$ shows magnetic metallic characteristic instead of SGS nature. It can be seen that the influence of electric field on B$_3$CN$_4$ is similar to the situation of electrons doping, which can be attributable to the fact that the electronic structure of B$_3$CN$_4$ is relatively sensitive to the electrostatic potentials induced by either electric field or electrons doping.

Since a substrate can apply a stress onto the material in practical applications, it is essential to confirm whether the electronic properties of B$_4$CN$_3$ and B$_3$CN$_4$ are robust under an external strain. By changing the lattice of system, homogeneous biaxial strains are applied to B$_4$CN$_3$ and B$_3$CN$_4$. This external tensile or compression strain can be defined as $\varepsilon = (a - a_0)/a_0$, where $a$ and $a_0$ are the lattice parameters with and without deformation, respectively. As shown in figure 6, it can be seen that the BMS property of B$_4$CN$_3$ is well preserved under the strains of $\pm 3\%$. The system of B$_3$CN$_4$ retains the SGS characteristic under the strain of $-3\%$, however, turns into BMS with an indirect band gap of 0.193 eV under $+3\%$. This transition is reasonable since

Figure 5. Band structures and total DOS of (a) B$_4$CN$_3$ with doping concentration of 0.025 electrons per atom, (b) B$_4$CN$_3$ with doping concentration of 0.025 holes per atom, (c) B$_3$CN$_4$ with doping concentration of 0.025 electrons per atom and (d) B$_3$CN$_4$ with doping concentration of 0.025 holes per atom. The Fermi energy is set to zero.
the distances between atoms are increased under a tensile stress and the exchange couplings are thus efficiently weakened, which leads to the separation of valence and conduction band. Furthermore, the FM coupling in every case is still found to be the energetically favorable magnetic configuration. More detailed results about the influences of carrier doping, electric field and external strain on B$_4$CN$_3$ and B$_3$CN$_4$ are summarized together in table S1, from which we can take the conclusion that B$_4$CN$_3$ is a very robust BMS under an external strain or even a strong electric field, while B$_3$CN$_4$ is relatively sensitive to external influences.

4. Conclusions

In summary, based on first-principle calculations, we have proposed two B$_x$C$_y$N$_z$ monolayers (B$_4$CN$_3$ and B$_3$CN$_4$) with dynamical and thermal stability. Both of the two frameworks have spin-polarized ground states with magnetic moments preferring to form stable FM ordering even at RT. Their band structures clearly reveal that the B$_4$CN$_3$ is a typical BMS material, while the B$_3$CN$_4$ is a kind of SGS. For B$_4$CN$_3$, carrier doping can induce a transition from BMS to HM with switchable spin polarization direction depending on the doped carrier type. Furthermore, its BMS feature is very robust under external electric fields or strains. In contrast, though B$_3$CN$_4$ turns into HM under holes doping, it can retain its SGS character under low electrons doping level ($n < 0.025$ electrons per atom) and change to magnetic metal under high electrons doping level. In addition, the system of B$_3$CN$_4$ is also sensitive to external electric fields and strains. For instance, it changes to magnetic metal under the electric field of 0.6 V Å$^{-1}$ or turns into BMS under the external tensile strain of +3%. Our findings show a rich variety of magnetic and electronic properties of B$_4$CN$_3$ and B$_3$CN$_4$ monolayer, implying their great potentials for spintronic applications. We hope that our study will stimulate further experimental effort in B$_x$C$_y$N$_z$ monolayer compounds.

Figure 6. Band structures of (a) B$_4$CN$_3$ ($\varepsilon = -3\%$), (b) B$_4$CN$_3$ ($\varepsilon = +3\%$), (c) B$_3$CN$_4$ ($\varepsilon = -3\%$), and (d) B$_3$CN$_4$ ($\varepsilon = +3\%$). The Fermi energy is set to zero.
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