Full Length Article

High Curie temperature ferromagnetism in penta-MnN₂ monolayer

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A B S T R A C T

Two-dimensional (2D) intrinsic ferromagnetic materials with high Curie temperature have attracted increasing research interest because of their potential applications in spintronics. Here, on the basis of first principles calculations combined with Monte Carlo simulation, we report a new 2D pentagon-based monolayer, penta-MnN₂, which is not only dynamically, mechanically and thermally stable, but also exhibits half-metallicity with a band-gap of 1.12 eV in spin-down channel. More interestingly, penta-MnN₂ displays a high Curie temperature \( T_C \) of 913 K that can be further improved to 956 K when the biaxial tensile strain of 3% is applied. Compared to the reported hexagonal MnN monolayer, the exchange interaction between the Mn atoms is significantly enhanced in the penta-MnN₂ sheet due to its unique geometric configuration composed solely of the pentagons containing N₂ dimers.

1. Introduction

Spintronics has received extensive attention in science and technology in the past decades because it provides a new approach for data storage and information transmission by exploiting the spin degree of freedom of electrons [1,2]. Mn atom, because of its special electronic configuration of 3d⁷⁵s², has been widely used for the design of magnetic materials, especially for 2D ferromagnetic monolayers. For instance, it has been found that MnO₂ monolayer is an intrinsic ferromagnetic semiconductor with \( T_C \) of 140 K [3]. Mn phthalocyanine (MnPc) sheet is ferromagnetic with \( T_C \) of 150 K [4], and the ferromagnetic Curie temperature can be further tuned by chlorination [5] or by strain [6]. Mn₃C₁₂S₁₂ monolayer [7] is ferromagnetic with \( T_C \) of 212 K that can be modulated by replacing the sulfur atoms with the imino group (–NH–), the resulting Mn₃C₁₂N₁₂H₁₂ sheet exhibits strong ferromagnetism with \( T_C \) of 450 K [8]. MnS₂ and MnSe₂ monolayers are ferromagnetic with \( T_C \) of 225 and 250 K, respectively, which can be further enhanced to 330 K and 375 K by applying 5% biaxial tensile strains [9]. Very recently, a graphene-like hexagonal MnN monolayer, named Hex-MnN, was also found to be ferromagnetic with \( T_C \) about room temperature (368 K) [10].

The origin of ferromagnetism exhibiting in transition metal (TM)-based 2D materials has been explored [11–15]. It is believed that the ferromagnetic orders are generated by direct TM-TM exchange or super-exchange among TM and its ligands [16–19]. For the 2D ferromagnetic materials containing Mn atoms, the magnetic coupling between Mn atoms has been found to be sensitive to the Mn–Mn distance and geometric configurations. For example, in orthorhombic and monoclinic-layered LiMnO₂, the coupling between the two Mn atoms changes from ferromagnetic (FM) phase to antiferromagnetic (AFM) phase when the Mn–Mn distance is reduced from 2.82 to 2.79 Å [20], and AFM coupling on or near the surface of Ga₁₋ₓMnxN can be driven by Mn–Mn bond length contraction [21], and the magnetic coupling can switch for AFM to FM in bulk Mn [22]. It is such sensitivity of magnetic coupling between Mn atoms to the atomic distance and local bonding environment that make Mn-based materials display diverse magnetic properties with flexible controllability.

Here, we propose a new 2D monolayer composed exclusively of the pentagonal rings containing N₂ dimer, labeled penta-MnN₂, and systematically study its magnetic properties by using density functional theory (DFT) and Monte Carlo (MC) simulation. It is one counterpart of manganese nitride including Mn₄N₃, Mn₄N, Mn₃N₂, Mn₂N, most of which have robust ferromagnetism [23–27]. We also show that, different from previously reported 2D Mn-containing monolayers, when going from hexagonal structural units to pentagonal ones, and from atomic N to dimer N₂, the Curie temperature \( T_C \) increases significantly from 368 K in Hex-MnN sheet [10] to 913 K in the penta-MnN₂ sheet.

2. Computational method

Structural and electronic properties are performed by using Vienna Ab initio Simulation Package (VASP) [28] based on DFT. The ion-
electron interactions are treated with projector augmented wave potential (PAW) [29], and the exchange and correlation potential is described with the Perdew–Burke–Ernzerhof (PBE) functional. Considering the strong correlated interaction of d electrons, the GGA + U method with $U_{dd} = 4$ eV is applied for the d orbitals of Mn atoms [31,32]. The convergence criteria for total energy and forces are set to be $10^{-4}$ eV and $10^{-2}$ eV/Å, respectively. Plane waves with a kinetic energy cutoff of 600 eV are used to expand the valence electron wave functions. The first Brillouin zone is sampled by using a $9 \times 9 \times 1$ k-point grid within the Monkhorst-Pack scheme [33]. To confirm the dynamic stability, phonon spectra are calculated with PHONOPY package [34], Ab initio molecular dynamics (AIMD) simulations are performed to confirm the thermal stability [35].

3. Results and discussion

The optimized structure of penta-MnN$_2$ monolayer is shown in Fig. 1(a), which is purely composed of the pentagons, belonging to the 2D pentagon-based structure family initiated by penta-graphene [36]. The side view shows that penta-MnN$_2$ has planar geometric configuration with $P4/mmb$ symmetry (space group No. 127), similar to penta-PtN$_2$ and penta-PdN$_2$ [37]. The lattice parameters are found to be $a = b = 4.80$ Å with Mn−N bond length of 2.00 Å, N−N bond length of 1.30 Å, bond angles $\theta_{N-Mn-N} = 90^\circ$, $\theta_{N-N-Mn} = 118^\circ$ and $\theta_{N-N-N} = 121^\circ$.

To verify the dynamic stability of penta-MnN$_2$ sheet, we calculate the phonon dispersion as shown in Fig. 1(b). The absence of imaginary modes in the entire Brillouin zone indicates that the penta-MnN$_2$ monolayer is dynamically stable. Then, the AIMD simulations are performed to further confirm the thermal stability. The $4 \times 4 \times 1$ supercell is used in simulation for 8 picoseconds (ps) with a time step of 1 fs ($\mu$s) at 800, 1000 and 1200 K, respectively. The structure remains almost intact at 800 K, while it does not suffer from significant distortion at 1000 K, but the geometry breaks when the temperature is increased to 1200 K. The total potential energy only fluctuates slightly around constants at 800 and 1000 K. The simulation results at 1000 K are plotted in Fig. 1(c), showing that penta-MnN$_2$ has good thermal stability.

We then check the mechanical stability by calculating the linear elastic constant using the finite distortion method [38]. The calculated elastic constants are found to be $C_{11} = C_{22} = 116.10$ N/m, $C_{12} = 21.13$ N/m, $C_{44} = 31.48$ N/m, which meet Born-Huang criteria [39], namely, $C_{11}C_{12} - C_{12}^2 > 0$, $C_{44} > 0$, indicating that the penta-MnN$_2$ monolayer is mechanically stable. Moreover, using the formula $E = (C_{11}^2 - 2C_{12}^2)/C_{11}$, the in-plane Young modulus is found to be 112.25 N/m, which is comparable to that of MoS$_2$ monolayer (120 N/m), and significantly larger than that of Germanene (42 N/m) and silicon (61 N/m) [40], suggesting that the penta-MnN$_2$ sheet is stable enough for avoiding the curling.

Next, we carry out calculations for the FM, AFM, ferrimagnetic (FIM) and non spin-polarized (NSP) states, in a total of 8 configurations, as shown in Fig. 2. We set the total energy of the FM configuration as 0 eV, and the energy difference are also given in Fig. 2. One can see that the FM state has the lowest energy and is the most energetically stable among all the configurations. The large energy difference between the FM and AFM or the FM and FIM states indicates that penta-MnN$_2$ would have robust ferromagnetism. Our calculations show that the local magnetic moments are 3.6 $\mu_B$ on each Mn site and −0.3 $\mu_B$ on each N site, leading to a net magnetic moment of 6.0 $\mu_B$ per unit. The isosurface of the spin density ($\rho_{\uparrow} - \rho_{\downarrow}$) is plotted in Fig. 3(a), the yellow
and blue regions represent the positive and negative values, respectively. It is obvious that the Mn atoms are highly spin-up polarized, while the N atoms are slightly spin-down polarized and antiferromagnetically coupled with Mn, exhibiting the FM ordering between Mn atoms and weak AFM ordering between Mn and N atoms.

To study the charge distribution, we calculate the deformation charge density defined as the difference of charge density between the sheet and the corresponding isolated Mn and N atoms. The slice on the (0 0 1) plane is shown in Fig. 3(b), where the blue and red regions represent the depletion and accumulation of charge, respectively. One can see that the electrons transfer from Mn to N atom. Bader charge analysis [41–43] shows that each Mn atom transfers 1.36 $e$ to each N$_2$ dimer. From the electron localization functions (ELF) slice on the (0 0 1) (Fig. 3(c)), it is obvious that the valence electrons are accumulated at N sites and partly localized on N–N bonds, showing covalent bond between N–N and ionic bond between Mn and N$_2$.

The spin-polarized electronic structures of the FM phase of penta-MnN$_2$ at GGA + U level are plotted in Fig. 4(a). One can see that penta-MnN$_2$ is an intrinsic ferromagnetic half-metal in which the spin-up bands cross the Fermi Level showing metal properties and the spin-down channel acts as a semiconductor with a gap of 1.12 eV, which is large enough to prevent the thermally excited spin-flip transition. Due to 100% spin polarization ratio near the Fermi level of half-metal, penta-MnN$_2$ shows good promise for spintronic devices.

To further understand the electronic structures and ferromagnetism behavior, the density of states (DOS) projected on atomic orbitals is calculated using GGA + U method, as plotted in Fig. 4(b), which indicates that penta-MnN$_2$ is half-metallic, the spin-up channel shows metallic characteristics whereas the spin-down channel is semiconducting. Furthermore, magnetism mainly comes from the contribution of d orbitals of Mn atoms and p orbitals of N atoms.

The electronic structure can further be tuned by applying strain $\epsilon$ defined as $\frac{(a - a_\text{0})}{a_\text{0}} \times 100\%$, where $a_\text{0}$ and $a$ are the lattice constants of the penta-MnN$_2$ in its equilibrium and strained states, respectively. To simulate the real situation, we apply biaxial tensile strain $\epsilon$ from 0 to 5%. The band structures are recalculated to check if the half-metallicity can be preserved. As shown in Fig. 5, when the $\epsilon$ is changed from 0 to 5%, the conduction band minimum (CBM) of spin-down channel goes up and the valence band maximum (VBM) keeps nearly unchanged. However, the VBM of spin-down channel shifts up crossing the Fermi level, thus leading to metallicity when the biaxial strain is more than 3%. Namely, penta-MnN$_2$ remains ferromagnetic half-metallic when biaxial tensile strain is below 3%, and becomes ferromagnetic metal otherwise.

To evaluate the stability of ferromagnetic state, the Curie temperature ($T_C$) of penta-MnN$_2$ is calculated using Monte Carlo (MC) simulation based on Ising model, which has been extensively and successfully employed to evaluate the $T_C$ of 2D FM materials [4,44–46]. The Hamiltonian of Ising model is defined as

$$\text{Fig. 3. (a) Spin-charge density (isosurfaces = 0.064 e/Å$^{-3}$), (b) deformation charge density and (c) ELF of penta-MnN$_2$.}

\text{Fig. 4. (a) Spin-polarized band structures, and (b) the total and projected DOS of penta-MnN$_2$ using GGA + U (U_{eff} = 4 eV) method.}

\text{Fig. 5. Band structure of penta-MnN$_2$ under biaxial tensile strain of (a) 1%, (b) 3%, and (c) 5%.}$$

where \( J_{ij} \) represents the magnetic exchange coupling parameter between the two nearest-neighbor spins, \( M_i \) and \( M_j \) are the spin magnetic moments on \( i \) and \( j \) sites. In penta-MnN\(_2\), \( J \) is 3.0 \( \mu_B \) for Mn atoms. The exchange parameter \( J \) can be estimated from the exchange energy with the formula \( J = E_{ex}/8 M^2 = 5.97 \) meV, where the exchange energy is defined as \( E_{ex} = E_{AFM} - E_{FM} \) and \( E_{AFM} = +4JM^2 \), \( E_{FM} = -4JM^2 \). The MC simulation is implemented using an 80 \( \times \) 80 \( \times \) 1 supercell to reduce the periodic constraints, and 5 \( \times \) 10\(^5\) steps are taken for each temperature. In our simulations, the spins on all magnetic sites flip randomly. Fig. 6(a) shows the variation of the magnetic moment with respect to temperature. The \( T_C \) of the penta-MnN\(_2\) sheet is found to be 913 K, which is higher than most reported 2D materials [3,45–49] but comparable to that of MnP and MnAs monolayers [18]. When applying 3% biaxial tensile strain which can keep the half-metallicity of penta-MnN\(_2\), the \( T_C \) increases to 956 K. The results are shown in Table 1.

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H = -\sum_{ij} J_{ij} M_i M_j
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4. Conclusion

In summary, we have reported a robust intrinsic ferromagnetism in the penta-MnN\(_2\) sheet composed of only pentagonal structural units, which is stable dynamically, thermally and mechanically. The ferromagnetism is mainly contributed by the Mn\(_d\) and N\(_p\) orbitals. The ferromagnetic ordering state is energetically more favorable than the antiferromagnetic one. The unique geometric configuration of the pentagon with N\(_2\) dimer in penta-MnN\(_2\) makes the system highly intriguing: exhibiting stable half-metallicity and robust ferromagnetism with a Curie temperature of 913 K, which is much higher than other reported Mn-containing 2D structures. Moreover, the \( T_C \) can be further increased to 956 K under 3% tensile strain. From the ferromagnetic transition in Mn\(_2\) dimer mediated by N, to the room temperature ferromagnetism in the hexagonal MnN sheet, and to the high Curie temperature ferromagnetism in the pentagonal MnN\(_2\), the displayed diversity of magnetism in Mn-based structures suggests that it is highly flexible to design new magnetic Mn-containing materials. The penta-MnN\(_2\) sheet with the high \( T_C \) and half-metallicity has the potential for future spintronic applications with high performance.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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