Robust intrinsic ferromagnetism in 2D half-metallic material MnAs$_4$

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Two-dimensional (2D) intrinsic half-metallic materials are of great interest to explore the exciting physics and applications of nanoscale spintronic devices, but no such materials have been experimentally realized. Using first-principles calculations based on density-functional theory (DFT), we predicted that single-layer MnAs$_4$ was a 2D intrinsic ferromagnetic (FM) half-metal. The half-metallic spin gap for single-layer MnAs$_4$ is about 1.46 eV, and it has a large spin splitting of about 0.49 eV in the conduction band. Monte Carlo simulations predicted the Curie temperature ($T_c$) was about 740 K. Moreover, Within the biaxial strain ranging from -5% to 5%, the FM half-metallic properties remain unchanged. Its ground-state with 100% spin-polarization ratio at Fermi level may be a promising candidate material for 2D spintronic applications.

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I. INTRODUCTION

Spintronics, which uses the spin of electrons for the information storage, transport and processing, have attracted intensive interests from the viewpoint of fundamental science and technology applications in the past decades\(^1\). It is important in the field of quantum computing and the next-generation information technology\(^2,3\). Half-metallic materials, which is conducting in one spin orientation but insulating in the opposite spin direction meet the demand of a 100% spin polarization ratio, are highly desirable for advanced spintronic applications\(^4\). The band gap for the insulating channel is termed as spin gap. To prevent spin leakage, the spin gap needs to be as wide as possible\(^5\). Since the first half-metallic material NiMnSb was predicted in 1983\(^6\), there has been a flurry of research into magnetic half-metals, such as transition metal compounds MnX (X = P, As), NbF\(_3\), CoH\(_2\), ScH\(_2\), TiCl\(_3\), VCl\(_3\)\(^7\)–\(^10\); sp half-metallic ferromagnets RbSe and CsTe\(^11\)–\(^14\).

Although half-metallic material has been studied for a long time, the demonstrated half-metals was very limited and have serious shortcomings, such as high cost or low \(T_c\). Until now, intrinsic half-metallic material with wide spin gap and high \(T_c\) is still absent in experiments. However, the single-layer CrPS\(_4\)\(^15\) was predicted to be a ferromagnetic semiconductor and the valance bands are splited for different spin orientation. As hole doping can lower Fermi level into the valence bands of one spin and lead to half-metallic ferromagnets. An obvious option is to replace Cr by Mn atoms, and by stability calculation we replace P with As atoms.

In this paper, the first-principles calculations are used to investigate the mechanical, dynamical, electronic and magnetic properties of single-layer MnAsS\(_4\). Our calculations indicate that the MnAsS\(_4\) crystal is mechanically and dynamically stable, so it is possibly prepared. It is metallic at the Fermi level in one spin direction and has a band gap of 1.46 eV in the opposite spin direction. Its half-metallic properties do not change under the biaxial strain range from -5% to 5%. It has stable ferromagnetism phase with integer magnetic moment of 8 \(\mu_B\) per primitive cell. Furthermore, we demonstrated that the MnAsS\(_4\) exhibits high \(T_c\) about 740 K.
II. METHODS

Kohn-Sham DFT calculations are performed using the projector augmented wave method, as implemented in the plane-wave code VASP\textsuperscript{16–18}. A cutoff energy of 500 eV and a Monkhorst-Pack special k-point mesh\textsuperscript{19} of $17 \times 19 \times 1$ for the Brillouin zone integration was found to be sufficient to obtain the convergence. We used a Perdew-Burke-Ernzerhof (PBE) type generalized gradient approximation (GGA) in the exchange-correlation functional\textsuperscript{20}. A conjugate-gradient algorithm was employed for geometry optimization using convergence criteria of $10^{-7}$ eV for the total energy and 0.005 eV/Å for Hellmann-Feynman force components. We used GGA+U to treat the strong on-site Coulomb interaction\textsuperscript{21}. A series of U values were selected, that is, 1.0-6.0 eV for Mn. Whatever U was, it didn’t affected the ground-state of MnAsS$_4$. Thus, the main conclusions were consistent for the different values of U. So we displayed that results with Hubbard U term 5 eV for Mn\textsuperscript{22} as suggested by Dudarev et al\textsuperscript{23}. The band structures for different U values can be found in Figure S1. Phonon dispersions were calculated by density functional perturbation theory\textsuperscript{24} by the Phonopy package interfaced to VASP code with $2 \times 2 \times 1$ supercell. We inserted a 15 Å vacuum slab to avoid the interactions between periodic images.

III. RESULTS AND DISCUSSION

FIG. 1: (Color online) The crystal structure of single-layer MnAsS$_4$ as seen from the (a) z-direction, (b) y-direction and (c) x-direction. The primitive cell is indicated by dotted line and the unit cell is indicated by solid line in (a).

The atomic structure of single-layer MnAsS$_4$ is shown in Fig. 1. The unit cell has parameters $a = 11.34$ Å, $b = 7.89$ Å. As shown in Fig. 1 (b), the As atoms bridge the twisted
MnS$_6$ octahedral chain. A Mn atom connects six S atoms, three types of bond lengths of Mn-S1, Mn-S2, Mn-S3 are 2.635Å, 2.451Å and 2.646Å, respectively. An As atom connects four S atoms and the bond lengths of As-S3, As-S4, As-S5 are 2.198Å, 2.182Å and 2.214Å, respectively, and the As-S6 bond length is the same as As-S4. In the diamond box in Fig. 1 (a) is a primitive cell. A primitive cell contains two Mn atoms. We calculated that each primitive cell is an integer magnetic moment of 8 $\mu_B$, and the local magnetic moment per Mn atom is about 4 $\mu_B$.

To determine the ground-state magnetic order, we compared the total energies of FM and different antiferromagnetic (AFM) structures$^{25}$. The energy differences $\Delta E$ relative to single-layer FM configurations are 170.69, 278.81, and 220.64 meV for the single-layer AFM1, AFM2, and AFM3 configurations, respectively. So the ground-state of single-layer MnAsS$_4$ is FM. Additionally, the non-magnetic (NM) state can be neglected owing to the great energy disparity between the NM state and magnetic states.

TABLE I: Elastic constants $C_{11}$, $C_{12}$ and $C_{22}$ (N/m) for single-layer MnAsS$_4$.

|   | $C_{11}$ | $C_{12}$ | $C_{22}$ |
|---|---------|---------|---------|
|   | 76.69   | 10.39   | 71.35   |

Next, we determined its mechanical stability by calculating the three independent elastic constants. As shown in Table I, we find that $C_{11} = 76.69$ N/m, $C_{12} = 10.39$ N/m and $C_{22} = 71.35$ N/m, respectively. The elastic constants clearly satisfy Borns stability criterion$^{26}$, i.e., $C_{11}>0$, $C_{22}>0$ and $C_{11}-C_{12}>0$, indicating that they are mechanically stable. Meanwhile, we evaluate the stability of single-layer MnAsS$_4$ by comparing their binding energies, which is defined as

$$E_b = \frac{2E(Mn) + 2E(As) + 8E(S) - E(MnAsS_4)}{12},$$

where $E(Mn)$, $E(As)$, $E(S)$ and $E(MnAsS_4)$ are the energy of Mn atom, As atom, S atom and single-layer MnAsS$_4$, respectively. According to this theory, the bigger $E_b$ is, the more stable the system will be. We find the binding energy is 4.03 eV per atom, which is bigger than the synthetic VI$_3$$^{27}$ and others$^{28,29}$.

In order to ensure the single-layer MnAsS$_4$ is dynamically stable, we calculated its phonon dispersion. As shown in Figure S2, the imaginary frequency is found to be absent in the whole Brillouin zone, it suggests that single-layer MnAsS$_4$ is dynamically stable and can
exist as free-standing 2D crystal.

FIG. 2: (Color online) Electronic band structures for single-layer MnAsS$_4$.

Next, the electronic properties of single-layer MnAsS$_4$ were investigated. The band structures of single-layer MnAsS$_4$ are shown in Fig. 2. Notably, the spin-up bands cross the Fermi level, while the spin-down channel acts as a semiconductor, indicating that it is intrinsic half-metallic material with 100% spin-polarization ratio. Comparing with previous studies where half-metallic materials occurred under certain external constraints, the half-metallic material found here is totally intrinsic, meaning that single-layer MnAsS$_4$ is more suitable for actual spintronic applications. As mentioned before, a wide half-metallic band gap and a wide spin gap are very important for half-metal in spintronic applications$^{30,31}$. Herein, the half-metallic band gap for single-layer MnAsS$_4$ is 0.44 eV, which is larger and smaller than the previous research on TiCl$_3$ (0.42 eV) and on VCl$_3$ (0.64 eV)$^{10}$. The spin gap for the semiconducting channel is 1.46 eV, which is larger than the previous report of Fe$_2$Si$^{32}$. The wide spin gap and half-metallic gap make 2D MnAsS$_4$ an ideal candidate for miniaturized spintronic materials. Considering that, approximately 25%-45% of the spin gap is underestimated by DFT method$^{33}$, the spin gap of single-layer MnAsS$_4$ obtained by experiment may be larger than the above value. However, the trends of band dispersions and density of states are qualitatively reasonable, since we are mainly interested in their relative values, and the underestimate should not change the general trends of the results$^{34,35}$.

Fig. 3 (a) shows the charge density difference of single-layer MnAsS$_4$. It is the difference between the charge density at the bonding point and the atomic charge density at the
FIG. 3: (Color online) (a) Charge density difference of single-layer MnAsS$_4$. The brown (green) region represents the net charge gain (loss). The isosurface value is 0.006 eÅ$^{-3}$. (b) Isosurface of spin density with an isovalue of 0.05 eÅ$^{-3}$. The corresponding point. The brown and green region represent the charge accumulation and depletion. It is obvious that Mn and As atoms lose electrons and S atoms gain electrons, due to that S atom has larger electronegative. This allows Mn-S bonding to be more ionic. Fig. 3 (b) shows the spin density of single-layer MnAsS$_4$, we find that the induced spin polarization is mainly contributed by Mn atoms while the contribution from As and S atoms can be neglected, which is consistent with the magnetic moment analysis.

FIG. 4: (Color online) Under biaxial strain for single-layer MnAsS$_4$. (a) Energy difference between the FM and AFM phases (black line) and total magnetic moments (red line). (b) Variation of the spin gap (black line) and half-metallic band gap (red line).

Fig. 4 (a) (red line) shows the change of total magnetic moment when a biaxial strain
is applied. We find that the total magnetic moment is not affected when the biaxial strain range from -5% to 5%. Fig. 4 (a) (black line) shows the energy difference between the FM and AFM orderings under the biaxial strain are negative, which indicates that no phase transition occurs during the process of biaxial strain and FM is always ground-state. As shown in Fig. 4 (b) (black line), when the biaxial stretch occurs, the spin gap increases, but decreases when the biaxial compression. When the strain is 5%, the spin gap increases from 1.46 eV to 1.64 eV, and when the strain is -5%, the spin gap decreases to 1.36 eV, this trend is consistent with the previous report of CrSiTe$_3$\textsuperscript{36}. When applying a biaxial strain of -3%, the half-metallic band gap becomes a maximum of 0.47 eV, but a biaxial stretch decreases the half-metallic band gap. When the biaxial strain is 5%, the half-metallic band gap is 0.30 eV.

FIG. 5: (Color online) density of states for single-layer MnAsS$_4$ under different biaxial strain. The percentage in the figure indicates the magnitude of the strain.

For the single-layer MnAsS$_4$, a large spin exchange splitting of 0.49 eV (labeled as $\Delta 1$ in Fig. 5) in the conduction band is observed, which is crucial for the application in spin-polarized carrier injection and detection\textsuperscript{37}. When applying a biaxial strain of -5% and 5%, spin exchange splitting changes from 0.49 eV to 0.47 eV and 0.35 eV, respectively, which is larger than the CrGeTe$_3$ (0.24 eV). Whether the strain is compressive or stretching, the density of states all clearly indicates that the contributions near the Fermi energy level come mainly from the electronic state of Mn and S atoms.

To realize spintronic applications for single-layer MnAsS$_4$, it is necessary to obtain the
variation trend of local magnetic moment with $T_c$ at which MnAsS$_4$ change from FM state to paramagnetic state. We thus employed Monte Carlo simulations with the Hamiltonian $H = - \sum_{<ij>} J_{ij} S_i S_j$ to predicted the FM transition temperature, where $J_{ij}$ represents the exchange interactions of over all neighbor Mn-Mn pairs, $S_i$ represents the spin of atom $i$. Herein we only consider nearest neighbors located along x and y directions. The exchange interaction parameters $J_{ij}$ are determined by the relation between the total energy and spin configurations. Our result of total $J_{ij}$ is 5.33 meV and 8.71 meV along the x and y directions, respectively, $S=2$. As shown in Fig. 6, the $T_c$ extracted from the figure is around 740 K. It is significantly higher than those reported before, e.g., CrI$_3$ monolayer (45 K)$^{38}$, CrSiTe$_3$ (35.7 K) and CrGeTe$_3$ (57.2 K)$^{37}$

IV. CONCLUSIONS

In summary, we presented a intrinsic ferromagnetic half-metallic material by using first-principles calculations. The calculations of mechanical properties, phonon dispersion and binding energy ensure the stability and the possibility of preparation of single-layer MnAsS$_4$. The band structures show that the single-layer MnAsS$_4$ has a 100% spin-polarization ratio at Fermi level. Also, for the semiconducting channel, the spin gap and half-metallic band gap are 1.46 eV and 0.44 eV, respectively. It also has a large spin exchange splitting of
0.49 eV in the conduction band. Within the biaxial strain range from -5% to 5%, the ferromagnetic half-metallic properties remain unchanged. Monte Carlo simulations estimate that $T_c$ for single-layer MnAsS$_4$ can up to 740 K. The intrinsic half-metallic with high $T_c$ and excellent stability endows single-layer MnAsS$_4$ a promising functional material for spintronic applications.

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