Large Magnetic Anisotropy Energy and Robust Half-Metallic Ferromagnetism in 2D MnXSe₄ (X = As, Sb)

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In recent years, intrinsic 2D magnetism has aroused great interest because of its potential application in spintronic devices. However, low Curie temperature (Tᵥ) and magnetic anisotropy energy (MAE) limit its application prospects. Here, using first-principles calculations based on density-functional theory, a series of stable MnXSe₄ (X = As, Sb) single-layer is predicted. The MAE of single-layer MnAsSe₄ and MnSbSe₄ is 648.76 and 808.95 μeV per Mn atom, respectively. Monte Carlo simulations suggest the Tᵥ of single-layer MnAsSe₄ and MnSbSe₄ is 174 and 250 K, respectively. The energy band calculation with hybrid Heyd–Scuseria–Ernzerhof (HSE06) function indicates the MnXSe₄ (X = As, Sb) is ferromagnetic half-metallic. Also, it has 100% spin-polarization ratio at the Fermi level. For MnAsSe₄ and MnSbSe₄, the spin-gaps are 1.59 and 1.48 eV, respectively. These excellent magnetic properties render MnXSe₄ (X = As, Sb) as promising candidate materials for 2D spintronic applications.

1. Introduction

Spintronics, which uses the spin degree freedom of electrons, is significant for future information technologies owing to its great promise in enhancing data processing speed and integration densities. Half-metals can generate 100% spin-polarized currents without any external operation and play significant roles in the spintronic applications. Half-metallic materials with high Tᵥ and large MAE are fundamental to build practical spintronic devices that can work at room temperature. In order to realize this concept at the nanoscale, the development of low-dimensional half-metallic materials with the characteristics above is a key problem. Therefore, there has been a flurry of research into magnetic half-metals, such as RbSe, CsTe, TiCl₃, VCl₃, MnX (X=P, As), and so on. However, these demonstrated half-metals have serious shortcomings, such as low Tᵥ or MAE. Until now, intrinsic half-metallic materials with both high Tᵥ and large MAE are still absent in experiments.

Unlike in bulk magnetic materials, the long-range magnetic ordering in 2D structures is impossible without magnetic anisotropy, which is required for counteracting thermal fluctuations. MAE is defined as the difference between the energy corresponding to the magnetization in the in-plane and off-plane directions (MAE = Eᵥ∥−Eᵥ⟂). Therefore, a positive (negative) value of MAE indicates that the off-plane (in-plane) is easy axis. However, MAE mainly comes from the influence of spin-orbit coupling (SOC). It is better for the magnetic ordering to resist the heat fluctuation with larger values of MAE. Noncollinear calculation showed that single-layer CrPS₄ exhibited the MAE of 40.0 μeV per Cr atom, with the spins favorably aligned along the off-plane direction. Generally, long-range ferromagnetic order mainly exists in 3d transition metals and their compounds. However, 3d elements have relatively weak SOC and strong SOC can only be found in heavy elements. So, we replaced P with As/Sb atoms, S with Se atoms, respectively. By stability calculations, we replaced Cr with Mn atoms.

In this paper, we predicted two emerging class of 2D intrinsic FM half-metallic materials (single-layer MnAsSe₄ and MnSbSe₄). Our calculations indicated that single-layer MnXSe₄ (X = As, Sb) crystals were mechanically and dynamically stable, so they may be synthesized experimentally. We also demonstrated that single-layer MnXSe₄ (X = As, Sb) had giant MAE. The single-layer MnAsSe₄ (MnSbSe₄) have abundant states at the Fermi level in one spin direction and a band gap of 1.59 eV (1.48 eV) in the opposite spin direction, and its half-metallic band gap is 0.61 eV (0.59 eV). Furthermore, we demonstrated that the MnAsSe₄ and MnSbSe₄ exhibited high Tᵥ about 174 and 250 K, respectively.

2. Experimental Section

Kohn–Sham DFT calculations were performed using the projector augmented wave method, as implemented in the plane-wave code VASP. The plane-wave cutoff energy was set to 500 eV. A Monkhorst-Pack special k-point mesh of 7 × 7 × 1 for the Brillouin zone integration was found to be sufficient to obtain the convergence. A Perdew–Burke–Ernzerhof (PBE)-type generalized gradient approximation (GGA) was used in the exchange-correlation functional. For the MAE calculation, the SOC was...
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$^{-1}$ for Hellmann–Feynman force components. The results with Hubbard U term 5 eV for Mn$^{21}$ were displayed as suggested by Dudarev et al.$^{22}$ However, for a more accurate estimation of the band structure, the hybrid functional of HSE06$^{23}$ was used. Phonon dispersions were calculated by density functional perturbation theory$^{24}$ by the Phonopy package interfaced to VASP code with a $2 \times 2 \times 1$ supercell. Moreover, a 15 Å vacuum was applied along the z axis to avoid any artificial interactions between images.

### 3. Results and Discussion

Structural models of single-layer MnXSe$_4$ ($X = \text{As, Sb}$) are shown in Figure 1a,b. The primitive cell is indicated by dotted line in (Figure 1a), and it contains two Mn atoms. The optimized lattice parameters for MnAsSe$_4$ (MnSbSe$_4$) are $a = b = 7.20$ Å ($7.43$ Å). In order to identify their preferred magnetic ground-state, a FM and two antiferromagnetic (AFM) magnetic configurations were constructed. FM, X-AFM, and Y-AFM are shown in Figures 1c, 1d, and 1e, respectively. The energy difference ($\Delta E$) relative to FM configurations of MnAsSe$_4$ (MnSbSe$_4$) is 369.13 (263.90) and 518.83 (384.06) meV for X-AFM and Y-AFM orders, respectively.

Table 1. Bond lengths (Å) of single-layer MnXSe$_4$ ($X = \text{As, Sb}$).

|         | $d_{\text{Mn-S1}}$ | $d_{\text{Mn-S2}}$ | $d_{\text{Mn-S3}}$ | $d_{\text{X-S2}}$ | $d_{\text{X-S3}}$ | $d_{\text{X-S4}}$ |
|---------|-------------------|-------------------|-------------------|-------------------|-------------------|------------------|
| MnAsSe$_4$ | 2.76              | 2.61              | 2.77              | 2.34              | 2.39              | 2.36             |
| MnSbSe$_4$ | 2.77              | 2.62              | 2.79              | 2.51              | 2.56              | 2.53             |

Therefore, FM is the ground-state. We calculated that each primitive cell was an integer magnetic moment of 8 $\mu_B$, and the local magnetic moment per Mn atom was about 4 $\mu_B$. The magnetic moment is consistent with the +3 oxidation state of Mn, so it is 4s$^0$3d$^4$ electronic configuration. The unpaired d electrons contribute the magnetism. According to the Hund’s rule and the Pauli exclusion principle, the four unpaired d electrons left result in the magnetic moment of 4 $\mu_B$ per Mn atom.

The structural parameters of MnXSe$_4$ ($X = \text{As, Sb}$) are summarized in Table 1. The bond lengths increase from MnAsSe$_4$ to MnSbSe$_4$; it makes sense because the atomic radius of Sb is larger than the As.

The MAE is listed in Table 2; it is important to determine the thermal stability of magnetic ordering. The MAE of MnAsSe$_4$ and MnSbSe$_4$ are 648.76 and 808.95 μeV per Mn, which is larger than the previous research on CrPS$_4$ (40 μeV per Cr)$^{15}$. Clearly, the easy axis of these crystals are along the z direction. Next, we determined their mechanical stability by calculating the three independent elastic constants. As shown in Table 2, the $C_{11}$ is 64.41 (62.63) N m$^{-1}$, $C_{12}$ is 11.81 (12.18) N m$^{-1}$, and $C_{12}$ is 57.09 (59.41) N m$^{-1}$ for MnAsSe$_4$ (MnSbSe$_4$), respectively. Compared to CrPS$_4$, MnXSe$_4$ ($X = \text{As, Sb}$) exhibits a similar $C_{11}$, a smaller $C_{12}$, and a larger $C_{22}$.$^{25}$ The elastic constants fulfill the Born criteria of stability$^{26}$ that is, $C_{11} > 0$, $C_{22} > 0$ and $C_{11} \cdot C_{22} > 0$, indicating that they are mechanically stable. In-plane stiffness can be calculated by using the relation, $Y_{2D} = \frac{(C_{11} - C_{12})^2}{C_{11}}$; $Y_{2D}$ decreases from

Figure 2. Theoretical phonon spectrum of single-layer MnAsSe$_4$ (a) and MnSbSe$_4$ (b) obtained from DFT calculations.
MnAsSe$_4$ to MnSbSe$_4$. As in-plane stiffness is a measure of rigidity, the decrease of $Y_{2D}$ indicates softening of the crystal.$^{[27]}$

To further confirm the stability of free-standing single-layer MnXSe$_4$ (X = As, Sb), we calculated their phonon dispersion. As shown in Figure 2, two materials have the same overall shape with no imaginary modes; it suggests that single-layer MnXSe$_4$ (X = As, Sb) is dynamically stable and can exist as free-standing 2D crystals.

Then, the electronic properties of single-layer MnXSe$_4$ (X = As, Sb) were investigated. Since the PBE functional usually underestimates the energy band gap, a hybrid functional in the form of the HSE06 functional was used to obtain accurate electronic structures. Figure 3a,c employs the PBE+U functional; Figure 3b,d employs the HSE06 functional. Notably, all the band structures show the spin-up channel crosses the Fermi level, while the spin-down channel acts as a semiconductor, indicating that they are intrinsic FM half-metallic materials with 100% spin-polarization ratio. Most of the previously discovered FM half-metals are realized by external conditions such as pressure and doping; the number of intrinsic 2D FM half-metallic materials is small.$^{[28–30]}$ Here, we found that single-layer MnXSe$_4$ (X = As, Sb) were intrinsic FM half-metals, which offer more suitable candidate materials for actual nanoscaled spintronic applications. To achieve the great prospect for half-metallic in spintronic devices, wide half-metallic gap is extremely important.$^{[31,32]}$ Herein, the PBE+U values of the half-metallic gap are 0.30 and 0.31 eV for MnAsSe$_4$ and MnSbSe$_4$, respectively. For HSE06 functional, the half-metallic band gap are 0.61 and 0.59 eV for MnAsSe$_4$ and MnSbSe$_4$, respectively, which is large enough to efficiently prevent the thermally agitated spin-flip transition. The HSE06 value of the spin-gap is 1.59 (1.48) eV for the MnAsSe$_4$ (MnSbSe$_4$), which is wide enough to prevent spin leakage.

As shown in Figure 3, the densities of states (DOS) of MnXSe$_4$ (X = As, Sb) compounds are generally similar in shape. The contribution of MnXSe$_4$ (X = As, Sb) spin-down DOS mainly comes from Se atoms, while the contribution of other atoms is little. Larger spin exchange splitting is crucial for the application in spin-polarized carrier injection and detection. For the single-layer MnAsSe$_4$ and MnSbSe$_4$, a large spin exchange splitting of 0.30 and 0.31 eV in the conduction band are observed (labeled as $\Delta 1$)
in Figure 3a). The HSE06 values of the spin exchange splitting are 0.36 and 0.33 eV for the single-layer MnAsSe₄ and MnSbSe₄, respectively, which are larger than the CrGeTe₃ (0.24 eV). Further experiments should be conducted to clarify these interesting electronic character of MnXSe₄ (X = As, Sb).

Figure 4a,b shows the differential charge density of single-layer MnAsSe₄ and MnSbSe₄. It is defined as the difference between the charge density at the bonding point and the atomic charge density at the corresponding point. The brown (green) region represents the charge accumulation (depletion). Significant charge redistributions were observed for Mn, As/Sb, and Se atoms, where the Mn and As/Sb atoms lost electrons, while the Se atoms gained electrons, meaning that there allows Mn-Se bonding to be more ionic. This redistribution makes sense because Se atoms are more electronegative. The spin densities for MnAsSe₄ and MnSbSe₄ are shown in Figure 4c,d; one can observe that the spin-polarization mainly comes from Mn atoms while the As/Sb and Se atoms are very small, which is consistent with the magnetic moment analysis.

The $T_c$ is a key parameter to the practical application of spintronic devices. Therefore, it is necessary to understand the behavior of the magnetism with temperature. Based on the Heisenberg model, the $T_c$ of MnXSe₄ (X = As, Sb) single-layer can be estimated by using MC simulations: $H = - \sum_{<ij>} J_{ij} S_i S_j - \sum_i A(S_i^z)^2$, where $J_{ij}$ is the exchange coupling parameter of nearest-neighbor Mn-Mn pairs, $S_i$ represent the spin of atom $i$, $A$ is anisotropy energy parameter, and $S_i^z$ is the spin component along the z direction. In order to compute the $J$, the energies of different magnetic configurations can be regarded as

$$E_{X-\text{AFM}} = E_0 + 4J_x S_x^2 - 4J_y S_y^2 - AS^2$$
$$E_{\text{FM}} = E_0 - 4J_x S_x^2 - 4J_y S_y^2 - AS^2$$
$$E_{Y-\text{AFM}} = E_0 - 4J_x S_x^2 + 4J_y S_y^2 - AS^2$$

The quantity $E_0$ is the ground-state energy of single-layer MnXSe₄ (X = As, Sb) without spin polarizations$^{[34]}$ and $S=2$. Our results show that the total $J_{ij}$ of MnAsSe₄ (MnSbSe₄) along the $x$ and $y$ directions are 11.54 (8.25) and 16.21 (12.00) meV, respectively. The functional relationship between magnetic moment and temperature is shown in Figure 5. At absolute zero temperature, all the spin of Mn atoms points in the same direction, forming a strict FM order, while the magnetic moment decreases rapidly when heated. The critical point from FM to paramagnetic transition was around 174 and 250 K for MnAsSe₄ and MnSbSe₄, respectively. It is significantly higher than those reported before, for example, CrI₃ monolayer (45 K)$^{[35]}$ and MnSTe monolayer (85 K)$^{[36]}$.

4. Conclusion

In summary, we report two experimentally viable 2D intrinsic ferromagnetic half-metallic materials (MnAsSe₄ and MnSbSe₄ single-layer), which expose appreciable MAE about 648.76 and 808.95 μeV per Mn. The MnXSe₄ (X = As, Sb) are mechanically and dynamically stable. We further reveal that MnXSe₄ (X = As, Sb) show a high $T_c$ about 174 and 250 K, respectively. The band structures show that single-layer MnXSe₄ (X = As, Sb) have a 100% spin-polarization ratio at the Fermi level. Also, for the semiconducting channel, the spin-gaps are 1.59 and 1.48 eV for MnAsSe₄ and MnSbSe₄, respectively. The intrinsic half-metallic with high $T_c$ and large MAE confer single-layer MnXSe₄ (X = As, Sb) as a promising functional material for spintronic applications. We hope our study will stimulate further experimental effort in this subject.

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Conflict of Interest

The authors declare no conflict of interest.
Keywords

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