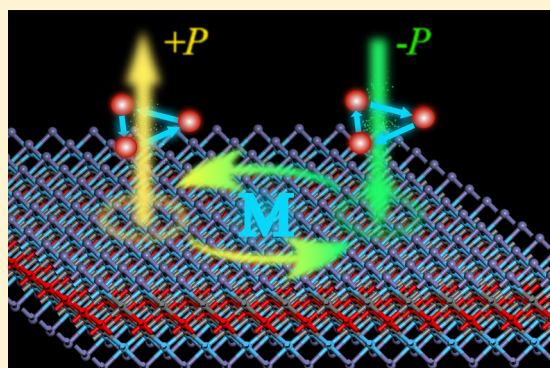


Type-II Multiferroic $\text{Hf}_2\text{VC}_2\text{F}_2$ MXene Monolayer with High Transition TemperatureJun-Jie Zhang,^{†,‡} Lingfang Lin,[†] Yang Zhang,[†] Menghao Wu,[§] Boris I. Yakobson,^{*,‡} and Shuai Dong^{*,†}[†]School of Physics, Southeast University, Nanjing 211189, China[‡]Department of Materials Science and NanoEngineering, Rice University, Houston, Texas 77005, United States[§]School of Physics and Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, Wuhan 430074, China

Supporting Information

ABSTRACT: Achieving multiferroic two-dimensional (2D) materials should enable numerous functionalities in nanoscale devices. Until now, however, predicted 2D multiferroics are very few and with coexisting yet only loosely coupled (type-I) ferroelectricity and magnetism. Here, a type-II multiferroic MXene $\text{Hf}_2\text{VC}_2\text{F}_2$ monolayer is identified, where ferroelectricity originates directly from its magnetism. The noncollinear 120° Y-type spin order generates a polarization perpendicular to the spin helical plane. Remarkably, the multiferroic transition is estimated to occur above room temperature. Our investigation should open the door to a new branch of 2D materials in the pursuit of intrinsically strong magnetoelectricity.



INTRODUCTION

Two-dimensional (2D) materials have attracted attention since the experimental discovery of graphene.¹ Diverse properties and functions have been discovered in many 2D materials, going beyond the original appeal as new semiconductors. More and more important physical properties existing in three-dimensional (3D) crystals have also been found to appear in the 2D form. For example, 2D superconductivity,^{2–6} 2D ferromagnetism,^{7–9} and 2D ferroelectricity^{10–21} have recently been confirmed in experiments or predicted via calculations.

Ferromagnetism and ferroelectricity, with switchable ferro-vectors, play crucial roles in various devices. Thus, their existence in 2D materials would be very attractive. On one hand, since the first prediction of 2D ferroelectric (FE) hydroxyl-decorated graphene in 2013,¹⁰ more 2D materials, e.g., 1T-MoS₂, In₂Se₃, and 2D materials functionalized with polar groups, have been predicted to be FE.^{11–19} Experimentally, in-plane FE polarization (*P*) was observed and manipulated in atom-thick SnTe,²⁰ while out-of-plane FE *P* was found in few-layer CuInP₂S₆.²¹ The involved mechanisms are either polar phonon modes or polar functional groups. On the other hand, many 2D ferromagnets have been predicted,^{8,9} and recently a CrI₃ monolayer was experimentally confirmed.⁷

The coexisting magnetism and polarization lead to the multiferroicity.^{22,23} The coupling between these two ferro-vectors allows the control of charge via magnetic field or the control of spin via electric field. In fact, a few 2D multiferroics were also recently predicted,^{16,19,24,25} in which the origins of

polarization and magnetism are independent of each other (i.e., they are all type-I multiferroics²⁶). Thus, their magnetoelectric coupling is indirect and weak.

To pursue the intrinsically strong magnetoelectricity, a possible route is to design 2D type-II multiferroics (i.e., magnetic ferroelectrics²⁶), in which the FE *P* is directly generated and thus fully controlled by magnetic order.^{22,23} Although the type-II multiferroics have been extensively studied, these materials have not gone into the zone of 2D materials. Even some type-II multiferroics have layered structures, e.g., CuFeO₂,²⁷ Sr₃NiTa₂O₉,²⁸ and Ba₃MnNb₂O₉,²⁹ and the interlayer couplings are via ionic bonds, difficult to exfoliate.

In this work, monolayer carbides and carbonitrides, i.e., MXenes ($M_{n+1}X_nT_x$; *M*: early transition metal; *X*: carbon or nitrogen), are predicted as 2D type-II multiferroics. As a new branch of 2D materials, MXenes have been experimentally produced by selectively etching the A-layer from their 3D parent compounds MAX.^{30–32} The surface can be easily covered by functional groups (e.g., T = F, O, and/or OH), resulting in diversiform chemical and physical properties.^{5,33} Recently, an ordered double transition metal MAX with Cr–Al/Mo–Al bonding was synthesized, e.g., Cr₂TiAlC₂³⁴ and Mo₂TiAlC₂,³⁵ in which a Ti-layer is sandwiched between two outer Cr/Mo carbide layers in the *M*₃AX₂ structure. Then

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ordered double transition metal carbides M_2MX_2 and $M_2M_2X_3$, e.g., $\text{Mo}_2\text{TiC}_2\text{T}_x$, $\text{Mo}_2\text{Ti}_2\text{C}_2\text{T}_x$ and $\text{Cr}_2\text{TiC}_2\text{T}_x$ were successfully realized by etching the Al layers.³⁶ In addition, considering the transition metals involved, many MXenes should be intrinsically magnetic (at least from the theoretical viewpoint), and their magnetism depends on M (M') and T .^{8,9} For instance, $\text{Cr}_2\text{TiC}_2\text{F}_2$ and $\text{Cr}_2\text{TiC}_2(\text{OH})_2$ are predicted to be antiferromagnetic (AFM), whereas $\text{Cr}_2\text{VC}_2(\text{OH})_2$, $\text{Cr}_2\text{VC}_2\text{F}_2$, and $\text{Cr}_2\text{VC}_2\text{O}_2$ are ferromagnetic (FM).⁹ Herein, derived from an experimental $\text{Hf}_3\text{C}_2\text{T}_x$ monolayer,³⁷ the ordered double transition metal carbides $\text{Hf}_2\text{MC}_2\text{T}_2$ monolayers (possibly realized via the 3D parent Hf_2MAlC_2)³⁸ are considered to be a 2D type-II multiferroics. Although both M and M' can be magnetic ions, here only the middle M layer is considered to be magnetic.

CANDIDATE 2D MXENE

According to the knowledge of type-II multiferroicity, some special frustrated magnetic orders, such as noncollinear spiral magnetism or $\uparrow\uparrow\downarrow\downarrow$ -type AFM order, may break the space inversion symmetry and thus lead to FE P .^{22,23} The in-plane geometry of M ions is triangular, which is inherently frustrated if the nearest-neighbor (NN) exchange is AFM.^{27,28,39,40} Thus, to find MXenes with NN AFM interaction is the first step. According to the Goodenough–Kanamori rule,^{41,42} the ions with a half-filled d shell usually lead to strong AFM exchanges. Besides, the half-filled Hubbard bands can lead to insulation, as required for ferroelectricity.

In $M_2\text{MC}_2\text{T}_2$ MXene monolayer, each MC_6 forms an octahedron [Figure 1(a)]. The crystalline field of the

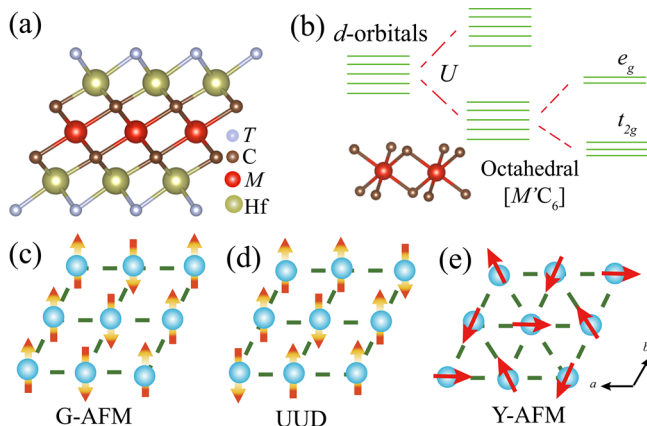


Figure 1. (a) Side views of the AA CG for $\text{Hf}_2\text{MC}_2\text{T}_2$. (b) Sketch of the energy splitting of 3d orbitals for M . (c–e) Sketch of possible AFM and ferrimagnetic spin orders in the 2D triangular lattice.

octahedron splits M 's d orbitals into low-lying t_{2g} triplets and higher-energy e_g doublets [Figure 1(b)]. To pursue the half-filled Hubbard bands, high-spin V^{2+} ($3d^3$), Nb^{2+} ($4d^3$), Mn^{4+} ($3d^3$), Mn^{2+} ($3d^5$), and Fe^{3+} ($3d^5$) are possible candidates to act as M .

To satisfy the aforementioned conditions, in the following, $\text{Hf}_2\text{VC}_2\text{F}_2$, $\text{Hf}_2\text{NbC}_2\text{F}_2$, $\text{Hf}_2\text{MnC}_2\text{F}_2$, and $\text{Hf}_2\text{MnC}_2\text{O}_2$ will be calculated using density functional theory (DFT). Since Fe^{3+} ($3d^5$) cannot be obtained if symmetric T layers are used, it is not considered here. In addition, $T = \text{OH}$ will be not calculated, considering its equal valence (and thus similar physical effects) to F.

RESULTS AND DISCUSSION

DFT calculations are performed to verify the multiferroicity of these MXene monolayers. Our calculations find that $\text{Hf}_2\text{VC}_2\text{F}_2$ is the most possible 2D type-II multiferroic material, while others are unlikely due to various reasons (see Supporting Information for more details of DFT methods and results³⁸). The possibility of synthesis for $\text{Hf}_2\text{VC}_2\text{F}_2$ is also explored, which may be realized via the 3D parent Hf_2VAlC_2 . Based on experimentally produced V_3AlC_2 ³² and Hf_3AlC_2 ,⁴³ the hybrid energy for Hf_2VAlC_2 is about -90 meV/cell, implying such a mix is more favorable. In addition, the possibility of a MAX phase to MXenes for Hf_2VAlC_2 is also verified by the crystal orbital Hamilton population (COHP) and exfoliation energy calculations.³⁸ Based on the results of COHP, the obtained bond strength between Hf and Al is much weaker than other bonds between Hf/V and C in Hf_2VAlC_2 , which is similar to that in Hf_3AlC_2 and V_3AlC_2 , indicating the iconicity/metallicity characteristic between them. To further examine the progress of exfoliation, exfoliation energies are calculated as $E_{\text{exfoliation}} = -[E_{\text{tot}}(\text{MAX phase}) - 2E_{\text{tot}}(\text{MXene}) - E_{\text{tot}}(\text{Al})]/(4S)$,⁴⁴ where $E_{\text{tot}}(\text{MAX phase})$, $E_{\text{tot}}(\text{MXene})$, and $E_{\text{tot}}(\text{Al})$ stand for the total energies of bulk MAX phase, 2D MXene, and the most stable bulk Al structure ($Fm\bar{3}m$), respectively. $S = \sqrt{3}a^2/2$ is the surface area and a is the lattice parameter of the MAX phase. Because V_3AlC_2 was experimentally exfoliated into 2D MXenes,³² Hf_2VAlC_2 , which has a lower exfoliation energy, has a better chance of being exfoliated into MXenes. In summary, we conclude Hf_2VAlC_2 is a good candidate for a 3D parent phase for the successful exfoliation into 2D Hf_2VC_2 MXenes. More details can be found in the Supporting Information.³⁸

Magnetic and Electronic Structure of $\text{Hf}_2\text{VC}_2\text{F}_2$. First, various configurations (CGs) for $\text{Hf}_2\text{VC}_2\text{F}_2$ are verified. Based on energy comparison and dynamic stability, the AA CG is confirmed to be the most favorable one,³⁸ where F ions are located just above/below the V's positions [Figure 1(a)]. Thus, our following investigation will focus on the AA CG only.

The nominal valences for Hf, V, C, and F are +4, +2, −4, and −1, respectively. Then for both C and F, the 2p orbitals are fully occupied, while for Hf the 5d orbitals are fully empty. In this sense, the magnetism can only come from V, whose 3d orbitals have three electrons, as confirmed by DFT calculations.

The magnetic ground state of $\text{Hf}_2\text{VC}_2\text{F}_2$ is searched by comparing the energies of various possible magnetic orders, including the nonmagnetic (NM), collinear FM, UUD-type ferrimagnetic (stands for the up–up–down ferrimagnetic spin order), stripe AFM (G-AFM), and the 120° noncollinear AFM order (coined as Y-AFM here), as sketched in Figure 1(c–e).

Considering the Hubbard-type correlations and spin–orbit coupling (SOC) for 3d and 5d orbitals, here a wide parameter space of $U_{\text{eff}}(\text{V})$ and $U_{\text{eff}}(\text{Hf})$ is scanned, as shown in Figure 2(a) and the Supporting Information.³⁸ As expected, the $U_{\text{eff}}(\text{Hf})$ and SOC have only tiny effects on the magnetism due to Hf's empty 5d orbitals.³⁸ In contrast, with increasing $U_{\text{eff}}(\text{V})$, the magnetic ground state undergoes two transitions, from NM to G-AFM first, then finally to Y-AFM. The local magnetic moment of V also depends on $U_{\text{eff}}(\text{V})$, increasing from 0 to more than $2 \mu_B/\text{V}$ [Figure 2(b)]. Accompanying the second magnetic transition, the metal–insulator transition also occurs when $U_{\text{eff}}(\text{V}) > 2$ eV.

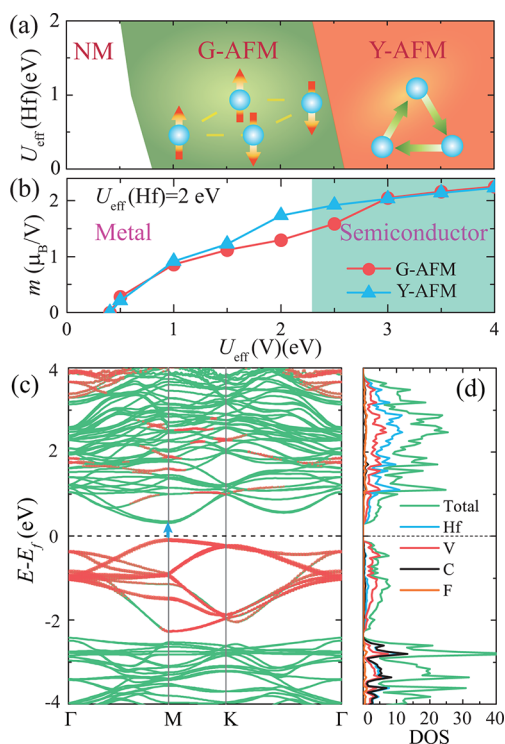


Figure 2. DFT results of $\text{Hf}_2\text{VC}_2\text{F}_2$ as a function of $U_{\text{eff}}(\text{Hf})$ and $U_{\text{eff}}(\text{V})$. (a) Ground state phase diagrams. (b) Local magnetic moment of V for G- and Y-AFM calculated within the default Wigner–Seitz sphere. Metallic and insulating regions are distinguished by colors. (c) Electronic band structure for Y-AFM with spin–orbit coupling calculated at $U_{\text{eff}}(\text{V}) = 3 \text{ eV}$ and $U_{\text{eff}}(\text{Hf}) = 2 \text{ eV}$. The fat bands (red circles) are contributed (more than 50%) by 3d orbitals of V ions. (d) Corresponding density of states (DOS) and atom-projected DOS.

Due to the lack of experimental results on the $\text{Hf}_2\text{VC}_2\text{F}_2$ monolayer, the HSE06 functional with SOC is adopted as the benchmark to provide an alternative description.⁴⁵ As shown in Table 1, the HSE06 plus SOC calculation predicts that the Y-

Table 1. Calculated Energies (E) of Different Magnetic Structures Using the HSE06 Functional with SOC (Energy of FM Is Set as the Reference) and the Corresponding Local Magnetic Moments (m)

	NM	FM	G-AFM	UUD	Y-AFM
$E \text{ (eV/V)}$	0.09	0	−0.12	−0.14	−0.19
$m \text{ (}\mu_{\text{B}}/\text{V)}$		1.18	2.05	1.99	2.04

AFM is the ground state for the $\text{Hf}_2\text{VC}_2\text{F}_2$ monolayer, and the corresponding magnetic moment is in good agreement with the result of $U_{\text{eff}}(\text{V}) = 3 \text{ eV}$ and $U_{\text{eff}}(\text{Hf}) = 2 \text{ eV}$, implying this set of parameters is proper. In fact, the same U_{eff} parameters were also adopted in previous studies,⁸ where only FM and G-AFM were considered. Here, the four most possible ones have been considered in DFT calculations. Furthermore, the following Monte Carlo simulation, with no bias of preset magnetic configurations, will be employed to verify the results of DFT. If there is more a stable one, the Monte Carlo simulation should capture it.

The calculated electronic structure of Y-AFM with SOC is shown in Figure 2(c,d). It is clear that the $\text{Hf}_2\text{VC}_2\text{F}_2$ monolayer is a direct-gap semiconductor and the correspond-

ing band gap is about 0.4 eV with default U_{eff} 's. The HSE06 functional calculation leads to a very similar electronic structure with a larger band gap (0.9 eV).³⁸ The projection of Bloch states to V's d orbital is also displayed in Figure 2(c,d). As expected, there are nine occupied bands near the Fermi level mostly contributed by V's 3d orbitals. As expected, the d^3 configuration of V^{2+} just occupies the t_{2g} orbitals in a half-filling manner, while the e_g orbitals are above the Fermi level. According to partial density of states (PDOS), there is also moderate p–d hybridization, which is a bridge for superexchange interaction.

Ferroelectric and Multiferroic Properties of $\text{Hf}_2\text{VC}_2\text{F}_2$.

Since the Y-AFM is a type of helical spin order that breaks inversion symmetry, i.e., clockwise vs counterclockwise [Figure 3(a,b)], previous studies of triangular-lattice antiferromagnets

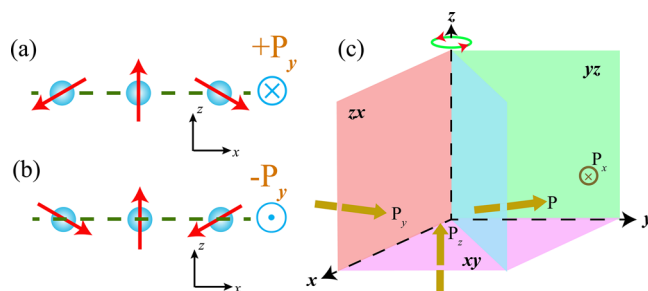


Figure 3. Schematic of helical Y-AFM-induced FE P . (a, b) Clockwise vs counterclockwise helicity. The corresponding P is perpendicular to the Y-AFM spin plane. (c) Free rotation of the spin plane along the c axis (z axis). The higher energy ab (xy) plane is also shown. Here x – y – z forms a rectangular coordinate system.

with a helical spin order have found the magnetism induced FE P .^{27,46–48} Thus, it is reasonable to expect a similar multiferroicity in the $\text{Hf}_2\text{VC}_2\text{F}_2$ monolayer.

For the Y-AFM spin order, the noncollinear spin texture forms a helical plane. It is necessary to know the easy plane/axis first. Our calculation with SOC finds that the out-of-plane c direction is the easy axis. Thus, in the ground state, the helical plane should be perpendicular to the monolayer. The energy of ac (or bc) plane Y-AFM is lower than that of ab plane Y-AFM by 0.14 meV/V. Our calculation also finds the rotation symmetry within the monolayer plane. Thus, the helical plane can be rotated freely along the c axis, as sketched in Figure 3(c).

The standard Berry phase calculation with SOC gives $1.98 \times 10^{-6} \mu\text{C}/\text{m}$ for the Y-AFM state, corresponding to $2700 \mu\text{C}/\text{m}^2$ in the 3D unit considering the thickness of the monolayer to be $7.0 \text{ \AA}$. To partition these two contributions, using the high-symmetric crystalline structure, the obtained pure electronic contribution (P_e) is about $1.95 \times 10^{-6} \mu\text{C}/\text{m}$, very close to the total P with ionic displacements. Therefore, here FE P is almost fully ($\sim 98.5\%$) originated from the bias of the electronic cloud, while the atomic structure is almost in the high-symmetric one. Our calculation also indicates that the direction of P is always perpendicular to the spin helical plane, as sketched in Figure 3(c). And this P can be switched to $-P$, once the chirality of Y-AFM is reversed. For comparison, the higher energy ab plane Y-AFM gives $2.9 \times 10^{-7} \mu\text{C}/\text{m}$, pointing along the c axis.

Although this P is much smaller than those of other 2D FEs, e.g. for some functionalized 2D materials (3×10^{-5} – $1.1 \times 10^{-4} \mu\text{C}/\text{m}^{15}$), 2D honeycomb binary buckled compounds (9

$\times 10^{-7}$ – $1.11 \times 10^{-5} \mu\text{C}/\text{m}^{13}$), and multiferroic $\text{C}_6\text{N}_8\text{H}$ organic network ($\sim 4500 \mu\text{C}/\text{m}^{24}$), it should be noted that the origin of FE P in the $\text{Hf}_2\text{VC}_2\text{F}_2$ monolayer is conceptually different from other 2D FEs. In fact, it is common sense that the improper FE P 's in the type-II multiferroics are weaker than typical values of proper FEs,^{22,23} even though the origin of ferroelectricity in the type-II multiferroics guarantees an intrinsically strong magnetoelectric coupling, which is rare in other multiferroics.

In fact, $2700 \mu\text{C}/\text{m}^2$ is already a very significant value in type-II multiferroics, especially considering the fact that its origin is from the SOC, not exchange striction.^{22,23} For reference, the P in polycrystal $\text{Ba}_3\text{MnNb}_2\text{O}_9$ only reaches $3.45 \mu\text{C}/\text{m}^2$,²⁹ and $\sim 600 \mu\text{C}/\text{m}^2$ in TbMnO_3 .⁴⁹ The relatively large P is probably due to 5d Hf ions, which have a larger SOC than 3d elements. Although Hf orbitals do not contribute to magnetism directly, the hybridization between orbitals always exists around the Fermi level, which may enhance the effective SOC. Thus, in principle, the macroscopic polarization should be detectable, at least in its corresponding bulk form. In addition, the second-harmonic generation (SHG) based on nonlinear optical processes can also be employed to detect the polarization and its domain without electrodes, as done for TbMnO_3 .⁵⁰ More details on experimental detection of the FE state in type-II multiferroic thin films have been summarized in a recent review paper.⁵¹ Among type-II multiferroics, some polarizations are generated by noncollinear spin order via SOC, as in our $\text{Hf}_2\text{VC}_2\text{F}_2$. Since SOC is usually weak especially for 3d electrons, the polarizations in this category are usually much smaller than those in conventional ferroelectrics.²³ Furthermore, here the high ratio of P_e/P is also an advantage for ultrafast switching. Although it is common sense that type-II multiferroics have high P_e/P (e.g., $\sim 25\%$ in TbMnO_3 ⁵² and $\sim 58\%$ in HoMnO_3 ,⁵³ which were estimated using the same method used here) than proper FE materials, the $P_e/P = 98.5\%$ is indeed very high and rather rare.

The origin of ferroelectricity driven by helical spin order is also nontrivial. Although the spin-current model (or the Dzyaloshinskii–Moriya interaction) can explain the origin of ferroelectricity in cycloid spiral magnets,^{54,55} its equation, $\mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$, gives zero net P for Y-AFM in each triangular unit. Instead, the generalized spin-current model proposed by Xiang et al.⁵⁶ can phenomenologically explain the origin of P :

$$\mathbf{P} = \mathbf{M} \cdot \sum_{\langle ij \rangle} (\mathbf{S}_i \times \mathbf{S}_j) \quad (1)$$

where the summation is over all NN bonds; $\mathbf{S}$ denotes a (normalized) spin vector; $\mathbf{M}$ is a 3×3 matrix, which can be determined via DFT:

$$\mathbf{M} = - \begin{bmatrix} 9.571 & 0 & 0 \\ 0 & 9.571 & 0 \\ 0 & 0 & 1.401 \end{bmatrix} \times 10^{-3} e \quad (2)$$

In the above DFT calculations, only five magnetic candidates were considered, which could not exclude other possible exotic orders. Thus, the unbiased Monte Carlo (MC) simulation is performed to verify the ground state and estimate the transition temperature.³⁸ The Heisenberg spin model is adopted:

$$H = -J_1 \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_2 \sum_{[kl]} \mathbf{S}_k \cdot \mathbf{S}_l - A \sum_i (S_i^z)^2 \quad (3)$$

where J_1 (J_2) is the exchange interaction between NN (NNN) spin pairs, A is the coefficient for magnetocrystalline anisotropy, and S^z is the component of spin along the magnetic easy axis. Using the normalized $|S| = 1$, these coefficients can be extracted from DFT calculations by comparing the energies of magnetic candidates:³⁸ $J_1 = -48.1$ meV, $J_2 = 6.7$ meV, and $A = 0.14$ meV, respectively.

As expected, the NN exchange is strongly AFM, while the NNN is much weaker. The dominant J_1 leads to the Y-AFM, as confirmed using MC simulation [Figure 4(a)]. Interestingly,

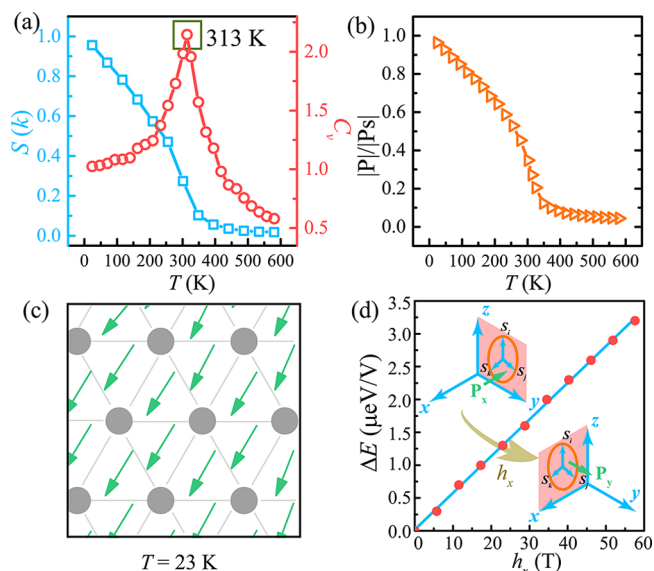


Figure 4. MC results. (a) Spin structure factor ($S(\mathbf{k}) = \sum_{ij} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)}$) for Y-AFM and specific heat (C_v) as a function of temperature (T). (b) FE $|P|$ as a function of T , calculated using eq 1 and normalized to its saturated value $|P_{\text{sl}}|$. (c) Typical MC snapshot of P_i (arrows) in a small region. Dots: V ions. (d) Energy difference between the yz plane and xz plane Y-AFM, under a magnetic field h_x along the x axis.

the estimated Néel temperature T_N reaches 313 K, a remarkable high T_N above room temperature. The FE $|P|$ just appears below T_N [Figure 4(b)], a character of type-II multiferroicity. A typical MC snapshot of local P_i 's (of V triangular units) at low temperature is shown in Figure 4(c).

For most 3D type-II multiferroics, the magnetism and ferroelectricity only appear far below room temperature.²³ High-temperature type-II multiferroicity is a highly desired property for applications, which is a bottleneck for this category of materials. Until now, in various type-II multiferroics, only a few hexagonal ferrites with very complex crystalline/magnetic structures show magnetoelectricity above room temperature.⁵⁷ $\text{Hf}_2\text{VC}_2\text{F}_2$ is another room-temperature type-II multiferroic system, with a much simpler crystalline/magnetic structure.

Physically, its high T_N is due to the ideal half-filled t_{2g} orbitals ($3d^3$), which prefer a strong superexchange according to the Goodenough–Kanamori rule.^{41,42} A similar case is for various ferrites with Fe^{3+} ($3d^5$) ions, which usually have magnetic orders above room temperature.

As a type-II multiferroic, the induced P can be fully controlled by magnetic fields via the helical plane rotation.³⁸ As shown in Figure 4(d), under an in-plane magnetic field, the energies of yz plane and xz plane Y-AFM (after slight

distortions driven by the magnetic field) are no longer degenerated. Thus, the helical plane of Y-AFM and its associated **P** should rotate accompanying the magnetic field. Since there is no intrinsic energy barrier for such a helical plane rotation, this magnetoelectric response should work under small fields.

Last, the MoSe₂ substrate is considered to test the possible substrate effect.³⁸ With proximate in-plane lattice constants, the optimized distance between Hf₂VC₂F₂ monolayer and MoSe₂ substrate is ~ 3.5 Å, indicating a van der Waals interaction. No charge transfer occurs between Hf₂VC₂F₂ and the substrate. The Y-AFM remains the ground state, and the whole system remains insulating. Therefore, the substrate will not change the conclusion of multiferroicity for the Hf₂VC₂F₂ monolayer.

CONCLUSION

The noncollinear 120° Y-type antiferromagnetic order is predicted to be the ground state in the Hf₂VC₂F₂ MXene monolayer, and the estimated Néel point can be above room temperature. More importantly, the inversion symmetry is broken by this particular Y-type antiferromagnetic order, resulting in the improper magnetism-driven ferroelectric polarization. Thus, the Hf₂VC₂F₂ monolayer is a room-temperature type-II multiferroics, which has intrinsically strong magnetoelectric coupling. The cross-over between 2D materials and magnetic ferroelectrics will be a very interesting topic, both fundamentally and to benefit nanoscale devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b06475.

More detailed method of DFT; synthetic possibility of 2D Hf₂VC₂ MXenes; DFT results of Hf₂VC₂F₂; effects of substrate; details of MC simulations; how the magnetic field controls polarization (PDF)

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Notes

The authors declare no competing financial interest.

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