Intrinsic ferromagnetism and highly restrictive thermodynamic stability in 2D MA$_2$N$_4$ and Janus VSiGeN$_4$ monolayers

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Searching for long-range ferromagnetic 2D materials for next-generation spintronics has been the spotlight in the last few years. The seminal experimental discovery of remarkably stable 2D MoSi$_2$N$_4$ monolayers has led to a handful of predicted magnetic 2D materials in the MA$_2$Z$_4$ family ($M =$ transition metals, $A =$ Si or Ge, and $Z =$ N, P, or As). These MA$_2$Z$_4$ monolayers were predicted dynamically stable, but none of them has been synthesized to date. In this work, from first-principles thermodynamic stability analysis, we demonstrate that only those nitrides within the family are thermodynamically stable and their stability is constrained under extremely nitrogen-rich conditions, whereby possible experimental synthesis routes are suggested. Based on this finding, we propose two new ferromagnetic, semiconducting Janus monolayers in the family: VSiGeN$_4$ and VSiSnN$_4$. They are both dynamically and thermally stable but only the former is further thermodynamically stable (albeit under extremely N-rich conditions). Intriguingly, unlike those easy-plane ferromagnetic MA$_2$Z$_4$ monolayers, the Janus VSiSnN$_4$ monolayer exhibits a long-range ferromagnetic order with Curie temperature $\sim$173K. These two emerging 2D Janus magnetic semiconductors offer new opportunities for studying 2D magnetism and spin control for spintronics applications, by harnessing their unusual features of both inversion and out-of-plane mirror asymmetry.

Atomically thin magnetic monolayers provide the ideal platform to study magnetism and spintronics device concepts in the two-dimensional (2D) limit, where magnetic properties can be effectively controlled or switched by proximity effects and external perturbations such as magnetic field, electric field, defects, strain, and optical doping, etc.\textsuperscript{1-8} In the last few years, a large number of 2D intrinsic magnetic materials have been experimentally discovered and theoretically proposed.\textsuperscript{5,10} The majority can be classified into three broad groups, namely, transition metal halides,\textsuperscript{11,12} transition metal chalcogenides,\textsuperscript{1,13} and MXenes and MXene analogues.\textsuperscript{14,15} These materials have exhibited a wide spectrum of magnetic and electronic properties. However, they also carry various disadvantages for practical manufacturing applications. For example, halides and MXenes mostly are vulnerable and reactive in the presence of ambient air and water.\textsuperscript{16,17} Besides, experimentally reported Curie temperatures ($T_c$) are usually much lower than the room temperature.\textsuperscript{1,11,12} Hence, the search for new stable magnetic 2D materials continues to be a major research direction in field.

An emerging group of 2D materials are septuple-atomic-layers of ternary transition metal pnictides in the form of MA$_2$Z$_4$, where M is the transition metal, $A =$ Si or Ge, and $Z =$ N, P, or As.\textsuperscript{18} The first member of this group discovered is semiconductor MoSi$_2$N$_4$, centimeter-scale monolayers of which were successfully synthesized in 2020 by the chemical vapor deposition method.\textsuperscript{19} This material exhibited exceptional stability to air, water, acid, and heat. Following this discovery, first-principles calculations found tens of dynamically stable MA$_2$Z$_4$ compounds\textsuperscript{18,20} with properties of interest for various applications such as spintronics,\textsuperscript{21,22} superconductors,\textsuperscript{21} and catalysts.\textsuperscript{24,25} Of these, nine were predicted magnetic, including five nitrides (VSi$_2$N$_4$, NbSi$_2$N$_4$, NbGe$_2$N$_4$, TaGe$_2$N$_4$, and YSi$_2$N$_4$), two phosphides (VSi$_2$P$_4$ and VGe$_2$P$_4$), and two arsenides (VSi$_2$As$_4$ and VGe$_2$As$_4$).\textsuperscript{18,20} Remarkably, they are all determined to be ferromagnetic and semiconducting except YSi$_2$N$_4$ which is also ferromagnetic but metallic, from HSE hybrid functional (HSE06) calculations.\textsuperscript{20}

However, these 2D ferromagnetic MA$_2$Z$_4$ materials have yet to be synthesized. They were mainly predicted based on their phonon spectra (no imaginary frequencies), \textit{ab-initio} molecular dynamics, and negative heat formation energies (meaning energetically more favorable than their constituent elemental phases). Their thermodynamic stability with respect to their stable competing phases has yet to be determined. It is well known that those dynamically stable compounds can often be thermodynamically unstable and be easily decomposed into their competing phases. Such thermodynamic instability can make their experimental synthesis very challenging especially under thermodynamic (quasi-)equilibrium conditions.

Above or near room-temperature long-range magnetic ordering is necessary to realize spintronic functionality in 2D materials. Unfortunately, of these proposed 2D ferromagnetic MA$_2$Z$_4$ compounds, none has been identified to possess a long-range intrinsic magnetic order with a transition temperature above room temperature. For example, density functional theory (DFT) and Monte Carlo calculations suggested that monolayers VSi$_2$N$_4$ and VSi$_2$P$_4$ in the same structure as MoSi$_2$N$_4$ have magnetic phase transitions at temperatures above room temperature, but they are easy-plane magnets.\textsuperscript{22,26} Nevertheless, VSi$_2$P$_4$ monolayer in a different crystal structure is the only reported 2D magnet with an out-of-plane easy axis, but its predicted $T_c$ is merely about 90K.\textsuperscript{18}

In this work, we first perform first-principles thermodynamic stability analysis for all nine 2D magnetic MA$_2$Z$_4$ monolayers that were predicted dynamically sta-
FIG. 1. (a) Top and (b) side views of the crystal structures of ternary layered VSiXN₄ (X = Ge and Sn) Janus monolayers. V atoms are depicted in pink, X atoms are in blue, Si atoms are in green, and N atoms are in grey. For VSi₂N₄ monolayer, X is replaced by Si. N-V-N bond angles (~ 90°) and V-N bond lengths for top (bottom) layer are indicated as θ₁ (θ₂) and d₁ (d₂), respectively. The crystal field environments: (c) tetrahedral for Si/X and (d) trigonal prismatic for V atoms are shown.

FIG. 2. 2D/3D chemical potential regions (shaded in yellow) where (a) MoSi₂N₄, (b) VSi₂N₄, and (c) VSiGeN₄ monolayers are thermodynamically stable against the formation of constituent elements and competing binary compounds. The shaded area behind the solid (dotted) blue line in the phase diagram of MoSi₂N₄ is the chemical potential region, where the monolayer can be synthesized using chemically rich (poor) N. X (marked in red circle) represents the vertex of the chemical potential region, up to which the respective compounds can be synthesized using chemically poor N. (d) The difference in chemical potential of N at X and N₂ (gas) (hlp-N) is shown in the right (left) side. All the energies are in eV.

Consistent with experiment, our calculated results shown in Fig. 2a and supporting information S1(a) demonstrate that these two compounds are thermodynamically stable so far and to suggest possible routes to grow them. Based on this analysis, we then propose two new ferromagnetic 2D Janus compounds, namely VSiGeN₄ and VSiSnN₄, in the same crystal structure (Fig. 1) as VSi₂N₄ and MoSi₂N₄. We demonstrate that (i) VSiGeN₄ monolayer is a thermodynamically stable intrinsic XY-type 2D ferromagnet with transition temperature above 300 K and magnetocrystalline anisotropy energy (MAE) being one order of magnitude lower than VSi₂N₄; (ii) VSiSnN₄ monolayer is a dynamically stable intrinsic long-range 2D ferromagnet with an out-of-plane magnetization and Curie temperature (173K) being one fold higher than VSi₂P₄, and both Janus monolayers are small-gap semiconductors.

Thermodynamic stability is a key property that must be addressed for new materials prediction and understanding their experimental synthesizability. It refers to the relative stability with respect to all possible competing phases in thermodynamic equilibrium. For a material to be thermodynamically stable during growth, the chemical potentials of its constituent elements must satisfy a set of conditions. Taking MoSi₂N₄ as an example, one condition is that

$$\Delta \mu_{\text{Mo}} + 2\Delta \mu_{\text{Si}} + 4\Delta \mu_{\text{N}} = \Delta H_f(\text{MoSi}_2\text{N}_4), \quad (1)$$

where $\Delta H_f(\text{MoSi}_2\text{N}_4)$ is the enthalpy of formation, which can be calculated from first-principles. $\Delta \mu_{\text{Mo}}$, $\Delta \mu_{\text{Si}}$, and $\Delta \mu_{\text{N}}$ are the relative chemical potentials of elemental Mo, Si, and N with respect to that of their solid bulk components (extreme rich limits), respectively. These chemical potentials depend on the experimental growth conditions and are regarded as variable in the formalism. They are further bound by (i) the values that will cause precipitation of solid elemental Mo, Si, and N, so that

$$\Delta \mu_{\text{Mo}} \leq 0, \quad \Delta \mu_{\text{Si}} \leq 0, \quad \Delta \mu_{\text{N}} \leq 0; \quad (2)$$

and (ii) by the values that will lead to the precipitation of competing binary phases MoN and Si₃N₄, so that

$$3\Delta \mu_{\text{Mo}} + 4\Delta \mu_{\text{N}} < \Delta H_f(\text{MoN}), \quad \Delta \mu_{\text{Si}} + 4\Delta \mu_{\text{N}} < \Delta H_f(\text{Si}_3\text{N}_4). \quad (4)$$

The ranges of $\Delta \mu_{\text{Mo}}$, $\Delta \mu_{\text{Si}}$, and $\Delta \mu_{\text{N}}$ that satisfy Eqs. 1-4 define the thermodynamic stability region, where possible equilibrium experimental growth conditions are suggested. No solution to these equations means that the material investigated is thermodynamically unstable and its equilibrium experimental synthesis would be quite challenging or impossible as kinetic barriers between different phases at high temperatures are often ignorable or small.

As a test, we first perform the above thermodynamic stability analysis for two nonmagnetic monolayer compounds MoSi₂N₄ and WSi₂N₄, which have been experimentally synthesized. Consistent with experiment, our calculated results shown in Fig. 2a and supporting information S1(a) demonstrate that these two compounds are
indeed thermodynamically stable. Their stability regions are highlighted in color yellow in the plots. Mentionably, this is defined relative to the chemical potential of hexagonal layered polymeric nitrogen (hp-N), based on which $\Delta H_f$ are calculated. This hp-N phase represents the extreme N-rich growth condition and was experimentally synthesized near 250 GPa. The $N_2$ gas under normal condition is about 3.05 eV lower in chemical potential (poorer) than hp-N; In between, there are another two metastable phases, cubic gauche polymeric nitrogen (cg-N) and polymeric nitrogen allotrope with the black phosphorus structure (bp-N), which were also experimentally synthesized. As displayed in Fig.2a and supporting information S1(a), the thermodynamic stability regions of MoSi$_2$N$_4$ and WSi$_2$N$_4$ both cover from extreme N-rich conditions to the conditions that are much poorer than the $N_2$ gas.

We now perform the same thermodynamic stability analysis for all nine magnetic MA$_2$Z$_4$ monolayers. Our calculated results are shown in Fig.2b and supporting information S1(b-d). Although these monolayers were all predicted to be dynamically stable and have a negative formation enthalpy, our calculations find that only nitrides, except YSi$_2$N$_4$ are thermodynamically stable only under some conditions for N that are richer than $N_2$ gas. Their stability regions are all much narrower than MoSi$_2$N$_4$ and WSi$_2$N$_4$. Further, to understand the relative stability of magnetic MA$_2$N$_4$, the distance between the vertex of each chemical potential region (marked as X) and $N_2$ gas has been calculated. $\Delta \mu_{N}(X)-\Delta \mu_{N}(N_2)$ increases in the order: VSi$_2$N$_4$ → TaGe$_2$N$_4$ → NbGe$_2$N$_4$ → NbSi$_2$N$_4$, along which the respective regions are far from the chemical potential of $N_2$ gas (Fig. 2d). It means that VSi$_2$N$_4$ is most stable among these magnetic nitrides. These results suggest that the experimental growth of these nitrides under thermodynamic equilibrium conditions be difficult as extreme N-rich conditions are necessary. For VSi$_2$N$_4$, it may be grown via reaction

$$2\text{Si}_3\text{N}_4 + 3\text{VN} + 6\text{N} \rightarrow 3\text{VSi}_2\text{N}_4.$$  \hspace{1cm} (5)

where solid N reactant can be hp-N, cg-N, or bp-N. For phosphides (VSi$_2$P$_4$ and VGe$_2$P$_4$) and arsenides (VSi$_2$As$_4$ and VGe$_2$As$_4$), we cannot find any thermodynamically stable region. Thus, under equilibrium growth conditions, the competing binary phases (e.g., V$_3$P, VP, SiP$_2$, GeP$_3$, etc., for phosphides and V$_3$As, VAs, SiAs$_2$, GeAs$_2$, etc., for arsenides) of these materials would form rather than these materials themselves.

To identify more stable intrinsic ferromagnetic 2D MA$_2$Z$_4$ compounds, we extend our first-principles thermodynamic stability analysis to two novel Janus compounds, VSiGeN$_4$ and VSiSnN$_4$. They are derived from the VSi$_2$N$_4$ monolayer, which has been demonstrated thermodynamically stable. Janus monolayers VSiXN$_4$ (X = Ge, Sn) can be viewed as a VN$_2$ layer sandwiched between Si-N and X-N layers (Fig. 1). Due to the presence of different group-IV elements in the top and bottom layers, such Janus monolayers lack both inversion and out-of-plane mirror symmetries in contrast to the VSi$_2$N$_4$ monolayer.

Our thermodynamic stability study reveals that both VSiGeN$_4$ and VSiSnN$_4$ monolayers have negative formation enthalpies (using hlp-N), -4.329 eV and -2.132 eV, respectively. However, only monolayer VSiGeN$_4$ is found to be thermodynamically stable. Fig. 2c shows our calculated stability region for VSiGeN$_4$ and its competing phases Si$_3$N$_4$, Ge$_3$N$_4$, and VN. As expected, this thermodynamic stability region is smaller than that of VSi$_2$N$_4$ and stays 1 eV farther from the chemical potential of $N_2$ gas (Fig 2d). However, goodly, this stability region also covers the chemical potentials of both cg-N and bp-N phases. The VSiGeN$_4$ monolayer may thus be synthesized via

$$\text{Si}_3\text{N}_4 + 3\text{GeN}_2 + 3\text{VN} + 6\text{N} \rightarrow 3\text{VSiGeN}_4.$$  \hspace{1cm} (6)

For the VSiSnN$_4$ monolayer, no thermodynamic stability region is found in this study.

Both Janus monolayers VSiGeN$_4$ and VSiSnN$_4$ are also found to be dynamically and thermally stable. Fig. 3(a-b) show our calculated phonon spectra along the high-symmetry directions of the hexagonal Brillouin zone (BZ). No negative frequencies are found in both cases. Fig. 3(c-d) show our ab-initio molecular dynamics simulation results for both Janus monolayers at 500 K. No indication of bond breaking or significant structural distortions is seen after 5 ps of simulation time (1 fs time step). Such stability features render these Janus materials also synthesizable using non-equilibrium techniques.

Now we turn to study the magnetic properties of VSiGeN$_4$ and VSiSnN$_4$ monolayers. To identify the magnetic ground state, we calculate the total energy difference between the ferromagnetic (FM) and stripe anti-
FIG. 4. Side and top views of the effective triangular lattice formed by V ions in VSi$_2$N$_4$ and VSiXN$_4$ Janus monolayers showing (a,b) FM and (c,d) stripe AFM states. V ions are shown as pink spheres. Up and down spins are indicated by blue and golden arrows. (e) A schematic of the energy levels of d orbitals in a trigonal prismatic crystal field environment. Here, only the middle layer containing V ions is displayed since the non-magnetic top and bottom layers of these monolayers do not contribute to the spin density distribution. Single valence electron of V$^{4+}$ ion predominantly occupies $d_{z^2}$ orbital and corresponding (f) spin density distribution is shown.

Our DFT+$U$ calculations find that both Janus monolayers stabilize into a FM ground state, like VSi$_2$N$_4$ monolayer. As one can see from Table I, the FM states in VSiGeN$_4$ and VSiSnN$_4$ are 65.5 meV and 44.8 meV lower in energy than their FM states, respectively. Magnetic moments ($m_V$) obtained from our GGA+$U$ calculations agree qualitatively with the ionic description that gives a V$^{4+}: 3d^1$ electronic configuration. In a trigonal prismatic crystal field environment, V d orbitals split into low-lying $d_{z^2}$ orbital followed by ($d_{xy}$+$d_{xz}$), ($d_{yz}$+$d_{yx}$), and ($d_{x^2-y^2}$) orbitals (Fig 4e), respectively. Our calculated spin-density distribution of occupied V d orbital (Fig 4f) show that the top valence band in the majority-spin channel is predominantly $d_{z^2}$ orbital character. Here, the V-N-V angle is close to 90°, and within this orthogonal setup, superexchange interaction between the V atoms mediated by the neighboring N atoms is the dominating exchange mechanism for ferromagnetism. This is in agreement with the Goodenough-Kanamori rules. As a result, VSi$_2$N$_4$ and VSiXN$_4$ monolayers adopt a FM ordered ground state.

Interestingly, Janus VSiGeN$_4$ and VSiSnN$_4$ monolayers exhibit distinct magnetocrystalline anisotropy. In 2D materials, out-of-plane easy-axis magnetic anisotropy is a necessary condition for stabilizing the long-range FM order. To determine the nature of magnetic anisotropy, we calculate MAE using GGA+$U$ method including spin-orbit coupling (SOC), MAE is defined as the energy difference between two FM spin configurations where magnetic moments are directed along the x and z directions, respectively. For Janus VSiGeN$_4$ monolayer, we obtain a negative MAE ($\sim 4 \mu eV/f.u.$), indicating that easy in-plane magnetization is favored. Hence like VSi$_2$N$_4$, Janus monolayer VSiGeN$_4$ belongs to the class of XY-magnets, which undergo Berezinskii-Kosterlitz-Thouless (BKT) phase transition and stabilize into a quasi long-range order. However, remarkably, note that the MAE value of VSiGeN$_4$ is one order of magnitude smaller than the MAE ($\sim 42 \mu eV/f.u.$) of VSi$_2$N$_4$, suggesting that the in-plane magnetization can be much more easily tuned to out-of-plane long-range order in Janus monolayer VSiGeN$_4$ by perturbations such as strains and defects. For Janus monolayer VSiSnN$_4$, we obtain a positive MAE ($4.0 \mu eV/f.u.$). It means that monolayer VSiSnN$_4$ shows an out-of-plane easy-axis anisotropy that favors spins to form a long-range FM order, and it can be regarded as an Ising magnet.

Using the mean-field approximations (c.f. supporting information S3), the magnetic transition temperatures are calculated for both Janus monolayers. We find that the transition temperature of VSiGeN$_4$ (338 K) is lower than that of VSi$_2$N$_4$ (458 K) but it is still much higher than room temperature. For Janus monolayer VSiSnN$_4$, the Curie temperature ($T_c$) is determined to be 173 K, almost twice the $T_c$ of VSi$_2$P$_4$ (the only 2D intrinsic long-range ferromagnets reported in the MA$_2$Z$_4$ family).

To understand the nature of MAE variations in Janus monolayers, we also calculated the MAE for strained

| Monolayer | $a$ (Å) | $E_g$ (HSE) (eV) | $m_V$ ($\mu_B$) | $\Delta E_m$ (meV) | MAE ($\mu eV$) | $T_c$ (K) |
|-----------|--------|-----------------|----------------|------------------|--------------|--------|
| VSi$_2$N$_4$ | 2.90 | 0.50 (D) | 1.10 | 88.7 | -42 | 458 |
| VSiGeN$_4$ | 2.97 | 0.48 (D) | 1.11 | 65.5 | -4 | 338 |
| VSiSnN$_4$ | 3.07 | 0.85 (ID) | 1.14 | 44.8 | 4 | 173 |

TABLE I. Lattice constants (a), band gap ($E_g$), V magnetic moments ($m_V$), energy differences between the AFM and FM spin configurations ($\Delta E_m = (E_{AFM} - E_{FM})/\mu B$), magnetocrystalline anisotropy energy (MAE), and transition temperatures ($T_c$) of VSi$_2$N$_4$ and VSiXN$_4$ monolayers are listed here. The band gap ($E_g$) values mentioned in the third column are obtained using HSE06, which agree qualitatively with the band gap values obtained within GGA+$U$ method - VSi$_2$N$_4$: 0.3 eV (D), VSiGeN$_4$: 0.15 eV (D), VSiSnN$_4$: 0.28 eV (ID). Note, ID = Indirect and D = Direct semiconductor.
FIG. 5. (a) Comparison of Magnetocrystalline anisotropy (MAE) values between strained monolayers VSi$_2$N$_4$ and Janus monolayers VSIXN$_4$ (X=Si, Ge). $\epsilon$ is the uniform bi-axial strain with respect to the VSi$_2$N$_4$ optimized lattice constant. A positive value of MAE indicates an out-of-plane easy-axis anisotropy for spins that stabilizes a long-range order (LRO), and a negative value of MAE indicates an easy in-plane magnetization for spins that favors into a quasi-long-range order (Q-LRO). Band structures of (b) VSi$_2$N$_4$, (c) VSiGeN$_4$, and (d) VSiSnN$_4$ monolayers within HSE method in the FM ground state. Red and blue lines in the band structures represent the majority and minority spin channels, respectively.

VSi$_2$N$_4$ monolayers. Due to the presence of larger-size atoms, VSiGeN$_4$ and VSiSnN$_4$ Janus structures have their lattice constants being 2.4% and 5.8% larger than monolayer VSi$_2$N$_4$ (Table I), respectively. Fig 5a shows the comparison of MAE values between strained monolayers VSi$_2$N$_4$ and Janus monolayers. Clearly, one can observe that the MAE values of Janus monolayers (marked as red squares) are almost identical to the MAE values of VSi$_2$N$_4$ monolayers at the same lattice constants of corresponding Janus monolayers. It means that the key factor that drives the transition from the in-plane anisotropy in VSi$_2$N$_4$ and VSiGeN$_4$ to the out-of-plane anisotropy in VSiSnN$_4$ monolayer is the biaxial in-plane tensile strain. The strain effects of MAE in VSi$_2$N$_4$ has already been theoretically studied in past. These reported results, agreeing well with ours in this work, indicate that switching the spin anisotropy from in-plane to out-of-plane in VSi$_2$N$_4$ needs more than 4% of biaxial strains, which would be very challenging for experimental realization and disadvantageous for device applications. Here our results demonstrate that Janus engineering is a new useful (and probably more viable) method to tune MAE and other properties of interest.

In addition to remarkable stability and magnetic properties, these two Janus monolayers exhibit excellent electronic properties. Fig 5(b-d) depict the electronic band structures of VSi$_2$N$_4$ and VSIXN$_4$ monolayers as obtained from HSE06. VSi$_2$N$_4$ and VSiGeN$_4$ monolayers are direct-gap semiconductors with band gap ($E_g$) $\sim$ 0.5 eV. Interestingly, the nature of the band gap changes from direct to indirect with $E_g$ increases to 0.85 eV for VSiSnN$_4$. This band gap switching and different $E_g$ values make VSiXN$_4$ monolayers suitable candidates to operate at variable voltages, frequencies, and temperature range for device applications. Note that, these band structures are consistent with GGA+U method (supporting information S5).

Finally, we shed light on the valley polarization, which is the measure of spin-valley coupling. This quantity can be estimated from the energy difference ($\Delta E_{sv}$) between valance band maxima at -K and +K points. For this purpose, we calculate the band structures within GGA+U+SOC (see supporting information S6) with the magnetization direction along $+x$ and $+z$ directions, respectively. A relatively large valley polarization of 64 meV can be induced in for VSi$_2$N$_4$ monolayer by changing the spin directions from $+x$ to $+z$, consistent with the previous report. However, VSiXN$_4$ monolayers have less significant contribution to the spin-valley coupling because of their very small MAE values, and thus, the valley degeneracy remains preserved.

In conclusion, through the first-principles analysis, we have shown that among all dynamically stable magnetic MA$_2$Z$_4$ monolayers, only four magnetic nitrides are thermodynamically stable under some experimentally challenging growth conditions. In the group of 2D magnetic nitrides, VSi$_2$N$_4$ has been found to be the most stable monolayer, and from which, two novel Janus ferromagnetic monolayers namely VSiGeN$_4$ and VSiSnN$_4$ have been designed. Dynamical and thermal stability of these Janus monolayers ensure their non-equilibrium growth. Alternatively, thermodynamically stable VSiGeN$_4$ monolayer, can be synthesized in an equilibrium conditions. There electronic structures reveal that they are narrow band gap semiconductors. However, the most exciting features of VSiGeN$_4$ and VSiSnN$_4$ monolayers are their opposite magnetic anistropy (XY vs Ising) and the contrasting semiconducting nature (direct vs indirect). The novel magnetic properties of these 2D ternary layered vanadium-based Janus semiconductors make them emerging candidates for spintronics and optoelectronics applications. These results will provide a guidance for new experimental as well as theoretical explorations on the magnetic monolayers of the MA$_2$Z$_4$ family and two novel Janus VSiXN$_4$ monolayers.

Computational Methods. Density functional theory (DFT) calculations have been performed using a plane-wave basis with a kinetic energy cutoff of 500 eV and the projector augmented-wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA)
has been used as exchange-correlation functional. Both in-plane lattice constants and atomic positions are relaxed using spin-polarized GGA+U until the total energy is converged to \(10^{-8}\) eV, and the forces on each atom are converged to 0.001 eV/Å. The reciprocal space integration has been carried out using a \(15\times 15 \times 1\) Monkhorst-Pack k-mesh grid. The phonon dispersions are calculated using density functional perturbation theory (DFPT)\(^{44}\) as implemented in the PHONOPY code\(^{55}\) with a \(4 \times 4 \times 1\) supercell and \(3 \times 3 \times 1\) k-mesh. Ab initio molecular dynamics simulations are conducted on a \(4 \times 4 \times 1\) supercell by employing a canonical ensemble, and the Nosé Hoover method.\(^{46}\)

Acknowledgements: This work has been supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, EPSCoR-Experimental Program to Stimulate Competitive Research, under Award Number DE-SC0021127. D.D. and L.Y. gratefully acknowledge the assistance of the Advanced Computing Group of the University of Maine System for providing computational resources for this work.

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Supporting Information for
Intrinsic ferromagnetism and highly restrictive thermodynamic stability in 2D MA$_2$N$_4$
and Janus VSiGeN$_4$ monolayers

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(Dated: March 23, 2022)

I. THERMODYNAMIC STABILITY OF MA$_2$N$_4$ MONOLAYERS

FIG. 1. 2D chemical potential regions (shaded in yellow) where (a) WSi$_2$N$_4$, (b) TaGe$_2$N$_4$, (c) NbGe$_2$N$_4$, and (d) NbSi$_2$N$_4$ monolayers are thermodynamically stable against the formation of constituent elements and their respective competing binary compounds. The shaded area behind the solid (dotted) blue line in the phase diagram is the chemical potential region, where these monolayers can be synthesized using chemically rich (poor) N. All the energies are in eV

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II. ESTIMATION OF U FOR JANUS MONOLAYERS

FIG. 2. Energy difference $\Delta E = E_{AFM} - E_{FM}$ between AFM and FM spin configurations, as a function of U calculated using the GGA+U methods ($\Delta E_{+U}$). The red and green horizontal dotted lines label the $\Delta E_{HSE}$ calculated using the HSE06 functional for VSiGeN$_4$ and VSiSnN$_4$ monolayers, respectively. The points, where $\Delta E_{+U}$ and $\Delta E_{HSE}$ become equal are marked as X.

III. CALCULATIONS DETAILS OF EXCHANGE CONSTANT AND TRANSITION TEMPERATURE

Using the mean-field approximations (MFA), we estimated transition temperatures $T_{BKT} = 0.89 \, J/k_B$ [1] and $T_c = \frac{2}{\pi} \, J/k_B$ [2] associated with XY and Ising spin systems, respectively. Here, $k_B$ is the Boltzmann constant, and $J$ is the exchange coupling parameter calculated by mapping the DFT total energy to the Heisenberg spin model. In a FM configuration, each V has six neighbors with the same spin (Fig. 4(b) of main text). But in AFM configuration, V four neighbors have opposite spins, and two have the same spin (Fig. 4(d) of main text). Hence, $J$ has been calculated directly from the energy difference $\Delta E_m = 8JS^2$ (where $S=\frac{1}{2}$) between AFM and FM spin configurations of each monolayer and listed in Table. 1 of the main text. Finally, we estimate $T_{BKT} = 458$ for VSi$_2$N$_4$, 338 K for VSiGeN$_4$, and $T_c = 173$ K for VSiSnN$_4$ monolayers, respectively.
IV. ELECTRONIC BAND STRUCTURES OF VSi$_2$N$_4$ AND VSIXN$_4$ MONOLAYERS WITHIN GGA

![GGA band structures](image)

**FIG. 3.** GGA band structures of (a) VSi$_2$N$_4$, (b) VSiGeN$_4$, and (c) VSiSnN$_4$. Red and blue lines in the band structures represent the majority and minority spin channels, respectively.

V. ELECTRONIC BAND STRUCTURES OF VSi$_2$N$_4$ AND VSIXN$_4$ MONOLAYERS WITHIN GGA+U

![GGA+U band structures](image)

**FIG. 4.** GGA+U band structures of (a) VSi$_2$N$_4$, (b) VSiGeN$_4$, and (c) VSiSnN$_4$ monolayers. Red and blue lines in the band structures represent the majority and minority spin channels, respectively.
VI. ELECTRONIC BAND STRUCTURES OF VSI$_2$N$_4$ AND VSIXN$_4$ MONOLAYERS WITHIN GGA+U+SOC

FIG. 5. GGA+U+SOC band structures of (a, d) VSi$_2$N$_4$, (b, e) VSiGeN$_4$, and (c, f) VSiSnN$_4$ monolayers along the M-(-K)-Γ- (+K)-M path for the magnetization direction along +x (top panel) and +z (bottom panel) directions. Only VSi$_2$N$_4$ monolayer shows significant valley polarization.

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