Intrinsic ferromagnetism and restrictive thermodynamic stability in MA\textsubscript{2}N\textsubscript{4} and Janus VSiGeN\textsubscript{4} monolayers

Dibyendu Dey,\textsuperscript{1,*} Avijeet Ray,\textsuperscript{2,†} and Liping Yu\textsuperscript{1,‡}

\textsuperscript{1}Department of Physics and Astronomy, University of Maine, Orono, Maine 04469, USA
\textsuperscript{2}Department of Physics, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand 247667, India

The seminal experimental discovery of the remarkably stable MoSi\textsubscript{2}N\textsubscript{4} monolayer has led to a handful of predicted magnetic two-dimensional (2D) materials in the MA\textsubscript{2}Z\textsubscript{4} family (M = transition metals, A = Si, Ge, and Z = N, P, As). These magnetic monolayers were predicted to be dynamically stable, but none of them has been synthesized to date. In this Research Letter, from first-principles thermodynamic stability analysis, we demonstrate that only the nitrides are thermodynamically stable and this occurs under N-rich conditions. Based on this finding, we propose two ferromagnetic, semiconducting Janus monolayers in the family: VSiGeN\textsubscript{4} and VSiSnN\textsubscript{4}. They are both dynamically and thermally stable, but only the former is thermodynamically stable. Intriguingly, Janus VSiGeN\textsubscript{4} and VSiSnN\textsubscript{4} monolayers show weak in-plane anisotropy compared with the VSi\textsubscript{2}N\textsubscript{4} monolayer. These two emerging Janus magnetic semiconductors offer opportunities for studying 2D magnetism and spin control for spintronics applications.

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 the magnetic field, electric field, defects, strain, 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{9,10} 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 analogs.\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 this field.

An emerging group of 2D materials are septuple atomic layers of ternary transition metal pnictides in the form of MA\textsubscript{2}Z\textsubscript{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 the semiconductor MoSi\textsubscript{2}N\textsubscript{4} centimeter-scale monolayer, which was successfully synthesized in 2020.\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\textsubscript{2}Z\textsubscript{4} compounds\textsuperscript{18,20} with properties of interest for various applications such as spintronics,\textsuperscript{21,22} superconductors,\textsuperscript{23} and catalysts.\textsuperscript{24,25} Of these, nine were predicted to be magnetic, including five nitrides (VSi\textsubscript{2}N\textsubscript{4}, NbSi\textsubscript{2}N\textsubscript{4}, NbGe\textsubscript{2}N\textsubscript{4}, TaGe\textsubscript{2}N\textsubscript{4}, and YSi\textsubscript{2}N\textsubscript{4}), two phosphides (VSi\textsubscript{2}P\textsubscript{4} and VGe\textsubscript{2}P\textsubscript{4}), and two arsenides (VSi\textsubscript{2}As\textsubscript{4} and VGe\textsubscript{2}As\textsubscript{4})\textsuperscript{18,20}. Remarkably, they have all been determined to be ferromagnetic and semiconducting except YSi\textsubscript{2}N\textsubscript{4}, which is also ferromagnetic but is metallic.\textsuperscript{20}

However, these 2D ferromagnetic MA\textsubscript{2}Z\textsubscript{4} materials have yet to be synthesized. They were mainly predicted based on their dynamical stability, ab initio molecular dynamics, and negative heat formation energies (meaning energetically more favorable than their constituent elemental phases). The 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 spintronics functionality in 2D materials. Unfortunately, none of these proposed 2D ferromagnetic MA\textsubscript{2}Z\textsubscript{4} compounds has been identified to possess an intrinsic long-range magnetic order with a \(T_C\) above the room temperature. For example, density functional theory (DFT) and Monte Carlo calculations suggested that monolayers VSi\textsubscript{2}N\textsubscript{4} and VSi\textsubscript{2}P\textsubscript{4} in the same structure as MoSi\textsubscript{2}N\textsubscript{4} have magnetic phase transition temperatures above room temperature, but they are XY magnets.\textsuperscript{22,26} Nevertheless, the VSi\textsubscript{2}P\textsubscript{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 90 K.\textsuperscript{18}

In this Research Letter, from first-principles thermodynamic stability analysis (cf. computational methods in Supplemental Material Sec. S1) of all the nine 2D magnetic MA\textsubscript{2}Z\textsubscript{4} monolayers, we explain why they have not been synthesized so far and suggest possible routes to grow them. Two-dimensional Janus crystals and their superlattices are a new class of 2D materials that offer extraordinary physical, chemical, and quantum properties.\textsuperscript{27,28} Although the electronic structures and piezo-electric properties of two non magnetic Janus MSiGeN\textsubscript{4}...
(M = Mo and W) monolayers were studied in a recent work\textsuperscript{29}, no magnetic Janus monolayers within the same family have been predicted to date. Here, we propose two ferromagnetic Janus monolayers, namely, VSiGe\textsubscript{4} and VSiSn\textsubscript{4}, which can be viewed as replacing one of the Si layers in a VSi\textsubscript{2}N\textsubscript{4} monolayer with Ge or Sn (Fig. 1). We demonstrate that thermodynamically stable VSiGe\textsubscript{4} and dynamically stable VSiSn\textsubscript{4} monolayers are weak XY-type 2D ferromagnets with transition temperatures above 300 K, and both of them are small-gap semiconductors.

Thermodynamic stability is a key property that must be addressed to predict new materials and understand their experimental synthesizability. It refers to the relative stability with respect to all the 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 MoSi\textsubscript{2}N\textsubscript{4} as an example, one condition is that

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

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 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

\[ \Delta \mu_{\text{Mo}} \leq 0, \quad \Delta \mu_{\text{Si}} \leq 0, \quad \Delta \mu_{\text{N}} \leq 0, \]  

and (ii) by the values that will lead to the precipitation of competing binary phases MoN and Si\textsubscript{3}N\textsubscript{4}, so that

\[ \Delta \mu_{\text{Mo}} + \Delta \mu_{\text{N}} < \Delta H_f(\text{MoN}), \]  

\[ 3\Delta \mu_{\text{Si}} + 4\Delta \mu_{\text{N}} < \Delta H_f(\text{Si}_3\text{N}_4). \]

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 monolayers MoSi\textsubscript{2}N\textsubscript{4} and WSi\textsubscript{2}N\textsubscript{4}, which have been experimentally synthesized\textsuperscript{19}. Consistent with experiment, our calculated results shown in Fig. 2(a) and Supplemental Material Fig. S2(a) demonstrate that these two compounds are indeed thermodynamically stable. Their stability regions are highlighted in yellow in the plots. It is worth mentioning that this is defined relative to the chemical potential of hexagonal layered polymeric nitrogen (hlp-N), based on which \( \Delta H_f \) are calculated. This hlp-N phase represents the extreme N-rich growth condition and was experimentally synthesized near 250 GPa\textsuperscript{30}. The N\textsubscript{2} gas under normal conditions is about 3.05 eV lower in chemical potential (poorer) than hlp-N; in between,
there are another two metastable phases, cubic gauche polymeric nitrogen (cg-N)\textsuperscript{31} and a polymeric nitrogen allotrope with black phosphorus structure (bp-N)\textsuperscript{32}, which were also experimentally synthesized. As displayed in Fig. 2(a) and Supplemental Material Fig. S2(a), the thermodynamic stability regions of MoSi\textsubscript{2}N\textsubscript{4} and WSi\textsubscript{2}N\textsubscript{4} both cover from extreme N-rich conditions to conditions that are much poorer than the N\textsubscript{2} gas.

We now perform the same thermodynamic stability analysis for all nine magnetic MA\textsubscript{2}Z\textsubscript{4} monolayers. Computational details are given in Supplemental Material Sec. S1. Our calculated results are shown in Fig. 2(b) and Supplemental Material Figs. S2(b)-S2(d). Although these monolayers were all predicted to be dynamically stable and have a negative formation enthalpy, our calculations reveal that only nitrdes, except VSi\textsubscript{2}N\textsubscript{4} are thermodynamically stable and this occurs only under some conditions for N that are richer than N\textsubscript{2} gas. Their stability regions are all much narrower than those for MoSi\textsubscript{2}N\textsubscript{4} and WSi\textsubscript{2}N\textsubscript{4}. Furthermore, to understand the relative stability of magnetic MA\textsubscript{2}N\textsubscript{4}, the distance between the vertex of each chemical potential region (marked as X and shown with a red circle) and N\textsubscript{2} gas has been calculated, $\Delta \mu_\text{N}(X) - \Delta \mu_\text{N}(\text{N}_2)$ increases in the following order: VSi\textsubscript{2}N\textsubscript{4} → TaGe\textsubscript{2}N\textsubscript{4} → NbGe\textsubscript{2}N\textsubscript{4} → NbSi\textsubscript{2}N\textsubscript{4}, along which the respective regions are far from the chemical potential of N\textsubscript{2} gas [Fig. 2(d)]. This means that VSi\textsubscript{2}N\textsubscript{4} is the most stable among these magnetic nitrdes. These results suggest that the experimental growth of these nitrdes under thermodynamic equilibrium conditions will be difficult as extreme N-rich conditions are necessary. VSi\textsubscript{2}N\textsubscript{4} may be grown via the reaction

$$2\text{Si}_3\text{N}_4 + 3\text{VN} + \text{N} \text{ (solid)} \rightarrow 3\text{VSi}_2\text{N}_4,$$

(5)

where the solid N reactant can be hlp-N, cg-N, or bp-N. For phosphides (VSi\textsubscript{2}P\textsubscript{4} and VGe\textsubscript{2}P\textsubscript{4}) and arsenides (VSi\textsubscript{2}As\textsubscript{4} and VGe\textsubscript{2}As\textsubscript{4}), we cannot find any thermodynamically stable region. Thus, under equilibrium growth conditions, the competing binary phases (e.g., V\textsubscript{3}P, VP, SiP\textsubscript{2}, GeP\textsubscript{3}, etc., for phosphides and V\textsubscript{3}As, VAs, SiAs\textsubscript{2}, GeAs\textsubscript{2}, etc., for arsenides) of these materials would form rather than the materials themselves.

To identify more stable intrinsic ferromagnetic 2D MA\textsubscript{2}Z\textsubscript{4} compounds, we extend our first-principles thermodynamic stability analysis to two Janus compounds, VSiGeN\textsubscript{4} and VSiSnN\textsubscript{4}. They are derived from the VSi\textsubscript{2}N\textsubscript{4} monolayer, which has been demonstrated to be thermodynamically stable. Janus monolayers VSiXN\textsubscript{4} (X = Ge, Sn) can be viewed as a VN\textsubscript{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\textsubscript{2}N\textsubscript{4} monolayer.

Our thermodynamic stability study reveals that both VSiGeN\textsubscript{4} and VSiSnN\textsubscript{4} monolayers have negative formation enthalpies (using hlp-N) of $-4.329$ eV and $-2.132$ eV, respectively. However, only monolayer VSiGeN\textsubscript{4} is found to be thermodynamically stable. Figure 2(c) shows our calculated stability region for VSiGeN\textsubscript{4} and its competing phases Si\textsubscript{3}N\textsubscript{4}, Ge\textsubscript{3}N\textsubscript{4}, and VN. As expected, this thermodynamic stability region is smaller than that of VSi\textsubscript{2}N\textsubscript{4} and stays $1$ eV farther from the chemical potential of N\textsubscript{2} gas [Fig. 2(d)]. However, advantageously, this stability region also covers the chemical potentials of both cg-N and bp-N phases. The VSiGeN\textsubscript{4} monolayer may thus be synthesized via

$$\text{Si}_3\text{N}_4 + \text{Ge}_3\text{N}_4 + 3\text{VN} + \text{cg-N} \rightarrow 3\text{VSiGeN}_4.$$  

(6)

For the VSiSnN\textsubscript{4} monolayer, no thermodynamic stability region is found in this paper.

Both Janus monolayers VSiGeN\textsubscript{4} and VSiSnN\textsubscript{4} are also found to be dynamically and thermally stable. Figures 3(a) and 3(b) show our calculated phonon spectra along the high-symmetry directions of the hexagonal Brillouin zone (BZ). No negative frequencies are found in either case. Figures 3(c) and 3(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 nonequilibrium techniques\textsuperscript{33,34}.

Now, we turn to study the magnetic properties of VSiGeN\textsubscript{4} and VSiSnN\textsubscript{4} monolayers. To identify the magnetic ground state, we calculate the total energy difference between the ferromagnetic (FM) and stripe antiferromagnetic (AFM) spin configurations as depicted in Figs. 4(a)–4(d) using the generalized gradient approximation (GGA) + $U$ method\textsuperscript{35}. To include correlation effects in V 3$d$ orbitals, we choose $U = 3.2$ eV, at which the GGA + $U$ calculated energy difference between the AFM and FM states matches with the revised Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE06)\textsuperscript{36} calculated one. (cf. Supplemental Material Fig. S3). The $U$
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) and (b) FM and (c) and (d) AFM states. V ions are shown as pink spheres. Up and down spins are indicated by blue and gold arrows, respectively. (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. The single valence electron of the V$^{4+}$ ion predominantly occupies the $d_{z^2}$ orbital, and the corresponding spin density distribution is shown in (f).

value determined in this way has successfully predicted correct magnetic, structural properties in numerous systems $^{37,38}$.

Our GGA+$U$ calculations find that both Janus monolayers stabilize into a FM ground state, like the VSi$_2$N$_4$ monolayer. As one can see from Table I, the FM states in VSiGeN$_4$ and VSiSnN$_4$ are 65.5 and 44.8 meV lower in energy than their AFM states, respectively. Magnetic moments $m_V$ obtained from our GGA+$U$ calculations agree qualitatively with the ionic description that gives a V$^{4+}$: 3$d^1$ electronic configuration. In a trigonal prismatic crystal field environment, V $d$ orbitals split into the low-lying $d_{z^2}$ orbital followed by the $(d_{xy} + d_{x^2-y^2})$ and $(d_{xz} + d_{yz})$ orbitals [Fig. 4(e)], respectively. Our calculated spin density distribution of the occupied V $d$ orbital [Fig. 4(f)] shows that the top valence band in the majority-spin channel is predominantly of $d_{z^2}$ 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 $^{39,40}$ As a result, VSi$_2$N$_4$ and VSiXN$_4$ monolayers adopt a FM ordered ground state.

According to the Mermin-Wagner theorem $^{41}$, long-range magnetic order should be absent in the 2D isotropic spin systems at any finite temperature. However, magnetic anisotropy removes this restriction and stabilizes magnetic order in 2D materials $^{11,42-44}$. To determine the nature of magnetic anisotropy, we first calculate magnetocrystalline anisotropy (MCA) using the GGA+$U$ method including spin-orbit coupling (SOC). MCA is defined as the energy difference between two FM spin configurations, where magnetic moments are directed along the $x$ and $z$ directions, respectively. For the VSiGeN$_4$ monolayer, we obtain a negative MCA ($-4 \mu$eV) and a positive MCA ($4 \mu$eV) for the VSiSnN$_4$ monolayer. Since MCA is significantly small here, magnetic shape anisotropy (MSA), which originated from dipole-dipole interactions may become relevant and contribute to the magnetic anisotropy energy (MAE). The calculated MSA values for VSiGeN$_4$ ($-16 \mu$eV) and VSiSnN$_4$ ($-14 \mu$eV) monolayers are found to be greater than the magnitude of MCA values, whereas for VSi$_2$N$_4$, MCA ($-42 \mu$eV) remains higher than MSA ($-17 \mu$eV) (cf. Supplemental Material Sec. S5 for details). As a result, after the inclusion of MSA, the total MAE for Janus monolayers becomes negative (easy-plane anisotropy), and owing to its small magnitude (Table I), VSiXN$_4$ monolayers can be regarded as weak 2D-XY magnets like the CrCl$_3$ monolayer $^{42,45}$ A quasi-long-range order with a divergent correlation length could be observed below the Berezinskii-Kosterlitz-Thouless (BKT) transition temperature for these planar magnets. However, due to the weak anisotropy, in-plane magnetization in both Janus monolayers could easily be tuned to out-of-plane long-range order by perturbations such as strains and defects.

The magnetic transition temperature $T_{BKT} = 1.335 J/k_B$ is obtained from the results of the Monte Carlo simulation for 2D-XY magnets on a triangular lattice $^{47}$ (cf. Supplemental Material Sec. S4). We find that the transition temperatures of VSiGeN$_4$ (507 K) and VSiSnN$_4$ (347 K) are lower than that of VSi$_2$N$_4$ (687 K), but they are still higher than the room temperature.

To understand the nature of MCA variations in Janus monolayers, we also calculated the MCA for strained VSi$_2$N$_4$ monolayers. Due to the presence of larger-size atoms, VSiGeN$_4$ and VSiSnN$_4$ Janus structures have lattice constants that are 2.4 and 5.8% larger than that of

| Monolayer | $a$ (Å) | $E_g$ (eV) | $m_V$ ($\mu_B$) | $\Delta E_m$ (meV) | MAE ($\mu$eV) | $T_{BKT}$ (K) |
|----------|--------|----------|----------------|-----------------|-------------|------------|
| VSi$_2$N$_4$ | 2.90 | 0.50 (D) | 1.10 | 88.7 | -59 | 687 |
| VSiGeN$_4$ | 2.97 | 0.48 (D) | 1.11 | 65.5 | -20 | 507 |
| VSiSnN$_4$ | 3.07 | 0.85 (ID) | 1.14 | 44.8 | -10 | 347 |
monolayer VSi$_2$N$_4$ (Table I), respectively. Figure 5(a) shows a comparison of MCA values between strained monolayer VSi$_2$N$_4$ and Janus monolayers VSiXN$_4$ (X = Ge, Sn). $\epsilon$ is the uniform biaxial strain with respect to the VSi$_2$N$_4$ optimized lattice constant. Band structures of (b) VSi$_2$N$_4$, (c) VSiGeN$_4$, and (d) VSiSnN$_4$ monolayers within HSE06 method in the FM ground state. Red and blue lines in the band structures represent the majority and minority spin channels, respectively.

In conclusion, through first-principles analysis, we have shown that among all dynamically stable magnetic MA$_2$Z$_4$ monolayers, only four magnetic nitrides are thermodynamically stable and this occurs 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, from which two Janus ferromagnetic monolayers, namely, VSiGeN$_4$ and VSiSnN$_4$, have been designed. The dynamical stability and thermal stability of these Janus monolayers ensure their non equilibrium growth. Alternatively, a thermodynamically stable VSiGeN$_4$ monolayer can be synthesized in equilibrium conditions. The electronic structures reveal that they are narrow-band-gap semiconductors. However, the most exciting feature of VSiGeN$_4$ and VSiSnN$_4$ monolayers is their weak easy-plane magnetic anisotropy, which is primarily associated with the MSA and the contrasting semiconducting nature (direct vs indirect). The magnetic properties of these 2D ternary layered vanadium-based Janus semiconductors make them emerging candidates for spintronics and optoelectronics applications. Besides, the possibility of realization of skyrmions in VSiGeN$_4$ and VSiSnN$_4$ monolayers can also be investigated, as it was for other Janus monolayers as reported in the contemporary literature$^{48,49}$. These results will provide guidance for experimental as well as theoretical explorations of the magnetic monolayers of the MA$_2$Z$_4$ family and these two Janus VSiXN$_4$ monolayers.

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* Both authors contributed equally; 
dibyendu.dey@maine.edu
† Both authors contributed equally.
‡ liping.yu@maine.edu
Both authors contributed equally.

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Supplemental Materials for

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

Dibyendu Dey,*† Avijeet Ray,‡ and Liping Yu*,¶

†Department of Physics and Astronomy, University of Maine, Orono, Maine 04469, USA
‡Department of Physics, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand 247667, India
¶Department of Physics and Astronomy, University of Maine, Orono, ME 04469, USA

E-mail: dibyendu.dey@maine.edu; liping.yu@maine.edu

S1. 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 15×15×1 Monkhorst-Pack k-mesh grid. The phonon dispersions are calculated using density functional perturbation theory (DFPT) as implemented in the
PHONOPY code\textsuperscript{6} 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.\textsuperscript{7}

S2. Thermodynamic stability of MA\textsubscript{2}N\textsubscript{4} monolayers

![Figure 1: 2D chemical potential regions (shaded in yellow) where (a) WSi\textsubscript{2}N\textsubscript{4}, (b) TaGe\textsubscript{2}N\textsubscript{4}, (c) NbGe\textsubscript{2}N\textsubscript{4}, and (d) NbSi\textsubscript{2}N\textsubscript{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.]

\[ \Delta \mu_{W} \]
\[ \Delta \mu_{Ta} \]
\[ \Delta \mu_{Nb} \]

\[ \Delta \mu_{N} (hlp-N) = 0 \]
\[ \Delta \mu_{N} (bp-N) = -0.76 \]
\[ \Delta \mu_{N} (cg-N) = -1.01 \]
\[ \Delta \mu_{N} (N_{2}) = -3.05 \]
S3. Estimation of $U$ for Janus monolayers

Figure 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.

S4. Exchange constant and transition temperature calculations details

The magnetic transition temperature $T_{BKT} = 1.335 \, J/K_B$ is obtained from the results of the Monte Carlo simulation for 2D-XY magnets on a triangular lattice. 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 the manuscript). But in AFM configuration, V four neighbors have opposite spins, and two have the same spin (Fig. 4(d) of the manuscript). 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 (Table. 1 of the manuscript). We estimate $T_{BKT} = 687$ K for VSi$_2$N$_4$, 507 K for VSiGeN$_4$, and 347 K for VSiSnN$_4$ monolayers, respectively.
S5. Magnetic shape anisotropy (MSA) calculations

Magnetic anisotropy energy (MAE) measures the dependence of the energy on the orientation of magnetization. Magnetic anisotropy originates mainly from two sources. (i) Magnetocrystalline anisotropy (MCA), which is an intrinsic property of the material caused by the spin-orbit coupling (SOC). (ii) Magnetic shape anisotropy (MSA), which is basically the anisotropic dipolar interaction (Eq. 1) of free magnetic poles that tend to magnetize magnetic elements with magnetic moments directed parallel to the surfaces (to minimize magnetostatic energy). Usually, the MAE can be characterized by the MCA. However, for materials with weak SOC, MSA becomes relevant and contributes to MAE. We have calculated MSA energies\(^9\) (\(E_{\text{MSA}} = E_{d-d} - E_{d-d}^{d-d}\)) for VSi\(_2\)N\(_4\), VSiGeN\(_4\), and VSiSnN\(_4\) monolayers using Eq. 1. The values are listed in Table 1 along with MCA and MAE values.

\[
E_{d-d}^{d-d} = \frac{1}{2} \frac{\mu_0}{4\pi} \sum_{i\neq j} \frac{1}{r_{ij}^3} \left[ (\bf{m}_i \cdot \bf{m}_j) - 3 \frac{(\bf{m}_i \cdot \bf{r}_{ij}) (\bf{m}_j \cdot \bf{r}_{ij})}{r_{ij}^2} \right],
\]

(1)

Here \(\bf{m}_i\) represents the local magnetic moments and \(\bf{r}_{ij}\) are vectors that connect the sites i and j. MSA has been calculated as a function of the size of the lattice until the convergence is achieved (Fig. 3).

Table 1: Magnetic anisotropy energies per V-site as obtained from DFT calculations. Negative values indicate easy-plane anisotropy for spins.

| Monolayer      | MCA (µeV) | MSA (µeV) | MAE (µeV) |
|----------------|-----------|-----------|-----------|
| VSi\(_2\)N\(_4\) | −42       | −17       | −59       |
| VSiGeN\(_4\)   | −4        | −16       | −20       |
| VSiSnN\(_4\)   | +4        | −14       | −10       |
Figure 3: Convergence of the MSA energy with respect to the size of the lattice.

S6. Electronic band structures of $\text{VSi}_2\text{N}_4$ and $\text{VSiXN}_4$ monolayers within GGA

Figure 4: GGA band structures of (a) $\text{VSi}_2\text{N}_4$, (b) $\text{VSiGeN}_4$, and (c) $\text{VSiSnN}_4$. Red and blue lines in the band structures represent the majority and minority spin channels, respectively.
S7. Electronic band structures of $\text{VSi}_2\text{N}_4$ and $\text{VSiXN}_4$ monolayers within GGA+$U$

Figure 5: GGA+$U$ band structures of (a) $\text{VSi}_2\text{N}_4$, (b) $\text{VSiGeN}_4$, and (c) $\text{VSiSnN}_4$ monolayers. Red and blue lines in the band structures represent the majority and minority spin channels, respectively.
S8. Electronic band structures of VSi$_2$N$_4$ and VSiXN$_4$ monolayers within GGA+$U$+SOC

Figure 6: 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.

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