Structural, electronic, and magnetic properties of Vanadium-based Janus dichalcogenide monolayers: A first-principles study

Dibyendu Dey1,∗ and Antia S. Botana1,†

1Department of Physics, Arizona State University, Tempe, AZ - 85287, USA

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The structural, electronic, and magnetic properties of VSSe, VSeTe, VSTe monolayers in both 2H and 1T phases are investigated via first-principles calculations. The 2H phase is energetically favorable in VSSe and VSeTe, whereas the 1T phase is lower in energy in VSTe. For V-based Janus monolayers in the 2H phase, calculations of the magnetic anisotropy show an easy-plane for the magnetic moment. As such, they should not exhibit a ferromagnetic phase transition, but instead, a Berezinskii-Kosterlitz-Thouless (BKT) transition. A classical XY model with nearest-neighbor coupling estimates critical temperatures (T_BKT) ranging from 106 K for VSSe to 46 K for VSTe.

I. INTRODUCTION

The discovery of long-range magnetic order in twodimensional (2D) van der Waals (vdW) crystals has led to an upsurge in research activities on 2D magnets1–5. In the past two years, single atomic layers of Fe3GeTe2, CrI3, MnSe2, VSe2, etc., have been reported to exhibit long-range magnetic order. Magnetic order in 2D can only happen if there is no continuous spin symmetry, otherwise, the proliferation of low-energy spin waves, that lies behind the Mermin-Wagner theorem,6 destroys magnetic order at any finite temperature. Magnetic anisotropy is hence an important requirement for realizing 2D magnetism.1,4,5 van der Waals magnets are a perfect resort since they have an intrinsic magnetocrystalline anisotropy due to the reduced symmetry of their layered structures. 2D materials with an easy magnetization plane should not exhibit a ferromagnetic phase transition, but instead, a Berezinskii-Kosterlitz-Thouless (BKT) transition7 to a quasi-long-range ordered low-temperature phase. In contrast, 2D magnetic materials with an easy magnetization axis can exhibit a ferromagnetic (FM) low-temperature phase. 2D vdW materials offer the additional advantage to manipulate magnetic properties via strain,8 gating,9,10 or heterostructuring11,12.

Among the above examples, the magnetic ground state of single-layer VSe2 is still a matter of intense investigation and continuous debate.5,13,14 Recent experiments reveal the presence of a charge density wave (CDW) instability with no sign of FM ordering13,14, whereas earlier experimental findings claim the observation of ferromagnetism at room temperature5. 2D TMDs commonly occur in two polymorphs, namely 1T-polytype and 2H-polytype, in which the transition metal atoms are coordinated with the neighboring chalcogens either in an octahedral (1T) or trigonal prismatic (2H) environment.15–18 Experimentally, it has been reported that both bulk and monolayer of VSe2 crystallize into the 1T phase,10, with CDW getting stabilized and further enhanced in the monolayer with respect to the bulk.13,14,19 CDW could be suppressed in the 2H phase, resulting in the stabilization of ferromagnetism in this polymorph. However, VSe2 monolayer in the 2H phase is not stable.

An open question is whether one can stabilize the 2H phase along with FM by designing Vanadium-based Janus monolayers (VXY, X/Y=S, Se, Te, and X≠Y). In Janus compounds inversion symmetry is broken as different anions occupy the top and bottom layers of V atoms (see Fig.1). Prospects to grow magnetic Janus monolayers are bright as non-magnetic MoSSe has already been successfully synthesized.20 Some attention has been paid to V-based Janus dichalcogenide monolayers, but studies have focused mostly on the 1T-phase,21 Zhang et al. 22 have analyzed the piezoelectric response and valley polarization in 2H-VSSe monolayers but have not analyzed magnetic anisotropies. In addition, VSeTe and VSTe monolayers in the 2H phase have never been discussed in the literature. The latter are particularly interesting as the presence of the heavy chalcogen Te should provide strong spin-orbit coupling (SOC), and enhance the magnetic anisotropy.

In this work, we perform first-principles calculations to study the structural, vibrational, electronic, and magnetic properties of VSSe, VSeTe, VSTe monolayers. First, the dynamic stability of the 1T versus the 2H polytype has been compared. Our results show that the 2H phase is dynamically stable in all cases. 2H-VXY monolayers manifest strong in-plane magnetic anisotropy and belong to the family of XY-magnets. As a consequence, they will not exhibit ferromagnetism but rather a BKT transition to a quasi-long-range ordered low-temperature phase.

II. COMPUTATIONAL DETAILS

Our first-principles calculations based on density functional theory (DFT)23,24 have been performed by using a plane-wave basis, as implemented in the Vienna ab-initio simulation package (VASP)25,26. For the exchange-correlation functional, we use generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)27 and the van der Waals corrected GGA functionals vdW-optPBE28,29. For monolayers, van der Waals forces are negligible, and hence the results coincide well
FIG. 1. (Color online) Crystal structure of the (a) 1T and (b) 2H polymorphs of V-based Janus (VXY) monolayers. V atoms are in golden yellow, X atoms are in dark green, and Y atoms are in red. The bond angles X-V-X, Y-V-Y, X-V-Y are indicated as $\theta_{XX}$, $\theta_{YY}$, and $\theta_{XY}$ respectively. The distance between V and X (Y) atoms are shown as $d_X$ ($d_Y$). The polyhedra for the two phases are displayed on the right side of the bottom panel of (a) and (b).

with the PBE functional without dispersion corrections. The wave functions were expanded in the plane-wave basis with a kinetic energy cutoff of 500 eV. We have used projector-augmented wave (PAW) potentials in our calculations. The reciprocal space integration was carried out with a $\Gamma$-centered $k$-mesh of $24 \times 24 \times 1$ for the conventional cell and $12 \times 12 \times 1$ $k$-mesh for the $2 \times 2 \times 1$ supercell used in phonon calculations. Electron correlation effects beyond GGA were incorporated for the 3$d$-electrons of the V ion within the GGA+U approximation, where $U= 2.7$ eV is the on-site Coulomb repulsion, and $J= 0.7$ eV is the Hund’s coupling strength. During structural relaxation, positions of the ions were relaxed until the Hellman-Feynman forces became less than $10^{-3}$ eV/Å. Phonons were calculated from DFPT (Density functional perturbation theory) as implemented in the PHONOPY code.

III. RESULTS AND DISCUSSION

A. Structural Properties

Since isolated monolayers of Vanadium-based Janus dichalcogenides have not been synthesized yet, we first benchmark the calculated lattice constant of VSe$_2$ monolayer to the experimentally reported lattice constant of single-layer VSe$_2$\textsuperscript{19}. Within GGA-PBE, we obtained a value of the lattice constant $a = 3.33$ Å, which agrees well with the experimentally reported lattice constant of VSe$_2$ monolayer\textsuperscript{19}. Thus, we adopted the same procedure in calculating the in-plane lattice constants of VXY monolayers.

Crystal structures of VXY monolayers in both the 1T and 2H phases are depicted in Fig. 1, which shows that the atomic stacking differs in the respective polymorphs.

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Lattice constants ($a$), bond lengths ($d_X$, $d_Y$), bond angles ($\theta_{XX}$, $\theta_{YY}$, $\theta_{XY}$) of each element are listed in Table I. The trend observed in lattice constants and bond lengths agrees with the size of the anions: $r_S < r_{Se} < r_{Te}$. Among the three Janus systems, VSSe has the smallest lattice constant, whereas VSTe and VSeTe have larger values. The bond lengths follow the sequence $d_{V-S} < d_{V-Se} < d_{V-Te}$. The values of anion-V-anion bond angles are close to 90° but slightly different for top and bottom layers giving rise to a distorted environment for the transition metal.

In order to address the dynamic stability of VXY monolayers in both the 1T and 2H phases, we have performed phonon calculations. The 2H phase is dynamically stable as no imaginary frequency has been observed in the phonon dispersions (see Fig. 2 (b), (d), (f)). For 1T-VSeTe and 1T-VSTe, the calculations reveal imaginary frequencies of one of the acoustic phonon branches along the $\Gamma$-M and $\Gamma$-K directions although real frequencies are found for all the optical modes (see Fig. 2 (c), (e)). The instability appears very close to the $\Gamma$ point, indicating that there might be spontaneous relaxation into a CDW phase\textsuperscript{35}. Recent studies also confirm CDW phase in 1T-VSe$_2$\textsuperscript{14,19,36} and 1T-TiSe$_2$\textsuperscript{37} monolayers. On the other hand, the 1T-VSSe monolayer does not show any imaginary modes in the phonon dispersion (Fig. 2(a)). This may be due to VSSe exhibiting a smaller structural distortion, which favors the 1T phase to be dynamically
On the contrary, single-layer VSTe is metallic (Fig. 4(e)).

eV (Fig. 4(a)) and $E_{\text{g}}$ of VSSe and VSeTe show a small energy gap $E_{\text{g}}$. GGA band structures (left panel) and GGA+U (right panel) for the FM ground state of 2H- VXY Janus are shown in Fig 4. GGA band structures within GGA (left panel) and GGA+U (right panel) for the FM ground state of 2H- VXY monolayers. A schematic representation of the magnetic ground state in this phase for all monolayers within spin polarized GGA-PBE. In our calculations, we considered FM configuration of V spins. The magnetic moments $m_{\text{V}}$, $m_{\text{X}}$, $m_{\text{Y}}$ are associated with V, X and Y (where X/Y = S, Se, Te and $r_{X} < r_{Y}$) ions. $\Delta E$ denotes the energy difference between the 1T and 2H polytypes (negative when 1T is more stable).

Further, we have calculated the energy difference $\Delta E = E_{1T} - E_{2H}$ between the 1T and 2H phases to find the energetically stable polymorph of VXY monolayers in a FM state. The energy differences are listed in Table I. For VSSe and VSeTe monolayers, the 2H phase is lower in energy than the 1T phase with a $\Delta E$ of 42.6 meV/f.u. and 6.1 meV/f.u., respectively. In a recent study, Zhang et. al also found the 2H polytype of VSSe is energetically more favorable. On the contrary, for VSTe monolayers, the 1T phase is found to be more stable with a $\Delta E$ of -30.0 meV/f.u.

### B. Electronic and Magnetic Properties

For VSSe, VSeTe, and VSTe monolayers, we calculated the total energy of three spin configurations: (i) FM, (ii) collinear AFM (AFM$_1$), and (iii) non-collinear 120° AFM (AFM$_2$) in the 2H phase of all monolayers and in the 1T phase of VSTe monolayer. A schematic representation of these three spin states is depicted in Fig. 3 (a)-(c). Magnetic moments and energy differences ($\Delta E_{m}$) with respect to the corresponding magnetic ground state are listed in Table II. The values of the magnetic moment at the V site are consistent with the ionic description that gives a V$^{4+}$: 3$d^3$ electronic configuration. As described above, VSSe and VSeTe monolayers are energetically and dynamically stable in the 2H phase, and this is also a dynamically stable polymorph for VSTe. Hence, we discuss the electronic structures of VXY monolayers in the 2H phase to draw a consistent picture. A FM spin configuration is the magnetic ground state in this phase for all VXY monolayers.

The band structures within GGA (left panel) and GGA+U (right panel) for the FM ground state of 2H- VXY Janus are shown in Fig 4. GGA band structures of VSSe and VSeTe show a small energy gap $E_{\text{g}} = 0.04$ eV (Fig. 4(a)) and $E_{\text{g}} = 0.13$ eV (Fig. 4(c)), respectively. On the contrary, single-layer VSTe is metallic (Fig. 4(e)).

In the 2H-phase, the trigonal prismatic environment of the V atom allows splitting of the d orbitals into a lower-lying $a'_1$ singlet followed by a doubly degenerate e' orbital ($d_{xy} + d_{x^2−y^2}$), and a high-energy doublet $e''$ ($d_{xz} + d_{yz}$). GGA spin-polarized band structures (Fig 4 (a), (c), (e)) are consistent with this picture as they show an isolated low-energy d-band around the Fermi level in the majority spin channel. Five d-bands in the minority spin channel lie above $E_F$ in VSSe and VSeTe, whereas the low-energy d-band in the minority spin channel of VSTe crosses $E_F$. Within GGA+U, the band gap increases in VSSe (Fig. 4(b)) and VSeTe (Fig. 4(d)) monolayers to values of $E_g = 0.51$ eV and 0.19 eV, respectively. VSTe remains metallic (Fig. 4(f)) even within GGA+U, with electron and hole pockets centered at the K (H) and $\Gamma$ (A) points, respectively.

Fig. 5 depicts spin-polarized GGA+U band structures

| Polytype | a (Å) | $d_X$ (Å) | $d_Y$ (Å) | $\theta_{XX}$ (deg) | $\theta_{XY}$ (deg) | $\theta_{YY}$ (deg) | $m_{\text{V}}$ (µB) | $m_{\text{X}}$ (µB) | $m_{\text{Y}}$ (µB) | $\Delta E$ (meV) |
|----------|-------|-----------|-----------|---------------------|---------------------|---------------------|--------------------|--------------------|--------------------|------------------|
| VSSe 1T  | 3.26  | 2.34      | 2.50      | 88.2               | 81.5               | 95.0               | -0.70              | -0.02              | -0.05              | 42.6             |
|          | 2H    | 3.25      | 2.35      | 2.50               | 87.5               | 78.6               | 1.00               | -0.02              | -0.07              |                  |
| VSeTe 1T | 3.49  | 2.48      | 2.72      | 89.5               | 79.8               | 95.1               | 1.09               | -0.04              | -0.09              | 6.1              |
|          | 2H    | 3.46      | 2.50      | 2.72               | 87.8               | 79.1               | 1.04               | -0.03              | -0.08              |                  |
| VSTe 1T  | 3.46  | 2.33      | 2.74      | 95.7               | 78.1               | 92.4               | 1.20               | -0.03              | -0.10              | -30.0            |
|          | 2H    | 3.39      | 2.35      | 2.72               | 92.2               | 77.7               | 0.79               | -0.01              | -0.05              |                  |

TABLE I. Comparison of the lattice constants (a), bond angles ($\theta$), bond lengths (d), and magnetic moments of V-based Janus monolayers within spin-polarized GGA-PBE. [et al.]

| Polytype | m$_{\text{V}}$ (µB) | m$_{\text{X}}$ (µB) | m$_{\text{Y}}$ (µB) | $\Delta E_m$ (meV) |
|----------|---------------------|---------------------|---------------------|--------------------|
| VSSe 2H  | AFM$_1$ 0.48        | -0.01              | -0.01              | 82.5               |
|          | AFM$_2$ 0.64        | -0.00              | -0.00              | 190.6              |
| VSeTe 2H | AFM$_1$ 0.88        | -0.03              | -0.03              | 63.5               |
|          | AFM$_2$ 1.42        | -0.00              | -0.00              | 151.5              |
| VSTe 2H  | AFM$_1$ 0.75        | -0.02              | -0.03              | 36.4               |
|          | AFM$_2$ 1.26        | -0.00              | -0.00              | 117.1              |
| VSTe 1T  | AFM$_1$ 1.59        | -0.02              | -0.04              | 4.2                |
|          | AFM$_2$ 1.58        | -0.00              | -0.00              | 0.0                |

TABLE II. Comparison of magnetic moments and $\Delta E_m$ values in three spin configurations of V ions: FM, AFM$_1$ (stripe phase), and AFM$_2$ (canted 120° spin ordering) within GGA+U. Energy differences ($\Delta E_m$) are in units of meV per formula unit. A zero value of $\Delta E_m$ represents the magnetic ground state.
FIG. 3. (Color online) A schematic representation of (a) FM, (b) stripe AFM (AFM$_1$), and (c) a canted 120° AFM (AFM$_2$) phase. V ions are shown in golden spheres.

FIG. 4. (Color online) Electronic band structures in the FM state of 2H-VSSe (a,b), 2H-VSeTe (c,d), and 2H-VSTe (e,f) monolayers within GGA (left panel) and GGA+U (right panel). Brick-red solid lines represent the majority, and blue dotted lines represent the minority spin channel.

as well as the V-d and anion-p orbital projected density of states (DOS) for the majority spin channel. The V-d DOS (Fig. 5 (b), (e), (h)) reveals that the isolated low-energy band is not only $d_{z^2}$ character, but it contains significant weight from the $d_{xy}$ and $d_{x^2-y^2}$ orbitals due to hybridization. Mattheiss first reported this fact in the context of band structure calculations of TMDs. It is also evident that the $e'$ and $e''$ orbitals hybridize strongly with the $p_x$ and $p_y$ orbitals to form bonding and antibonding states, while the $a'_{1}$ orbital hybridizes with the $p_z$ orbitals.

We now turn to the nature of the ferromagnetic ground state in 2H-VXY monolayers which is in agreement with the Goodenough-Kanamori (GK) rules. The anion-V-anion bond angles are close to 90° (see Table I). In this situation, superexchange is always FM. However, depending on the filling of d-orbitals, direct-exchange (with opposite sign) may become important and compete with FM superexchange. The singly occupied d-band in the 2H phase has contributions mainly from the $e_g$-like orbitals, as described above. The direct overlap between these states is negligible so the FM superexchange interaction between V atoms through neighboring chalcogens is the leading driving exchange mechanism in this phase.

Even though we described above the dynamically stable 2H phase for VSTe, the 1T phase is energetically more favorable in this system (Table I). As shown in Table II, the 120°-canted AFM configuration is the magnetic ground state in 1T-VSTe. In this polytype, V atoms have an octahedral environment, and these octahedra are connected via sharing an edge. In this situation, the transition metal atoms are close, and as the low-lying $t_{2g}$ orbitals on neighboring sites point toward each other, they have a strong overlap. Consequently, direct d-d hopping becomes significant and gives rise to an antiferromagnetic exchange which is able to overcome the FM superexchange. Moreover, V atoms in 1T-VSTe form a frustrated (triangular) lattice, and the system prefers to stabilize a 120°-canted AFM spin state to minimize its energy.

In 2D materials, magnetocrystalline anisotropy energy decides whether a system exhibits a magnetically ordered phase. Hence to determine the spin easy-axis or easy-plane anisotropy in the 2H phase of VXY monolayers,
FIG. 5. (Color online) Electronic band structures, orbital projected DOS for V d-states and anions (S, Se, Te) p-states in the majority spin channel as obtained within GGA+U (FM configuration) are shown in the left, middle and the right panel respectively. (a)-(c) for 2H-VSSe, (d)-(f) for 2H-VSeTe, and (g)-(i) for 2H-VSTe. Here, we consider the hexagonal splitting of the d-orbitals.

IV. CONCLUSIONS

We determined the structural, vibrational, electronic, and magnetic properties of Vanadium-based Janus dichalcogenides at the monolayer level by using density-functional theory. After investigating two possible polymorphs (octahedral 1T and trigonal prismatic 2H) at the monolayer level, we showed that the 2H phase is energetically more favorable in VSSe and VSeTe, whereas the 1T phase is lower in energy in the single-layer VSTe. Although the 2H phase is dynamically stable in all three monolayers, instability appears very close to the Γ point in 1T-VSTe might indicate spontaneous relaxation into the CDW phase. GGA+U calculations reveal a semiconducting FM ground state in 2H-VSSe and VSeTe monolayers, whereas 2H-VSTe shows a ferromagnetic metallic state. In contrast, the 1T-VSTe monolayer exhibits canted 120° AFM ground state. Calculations including SOC show an easy magnetization plane for spins in 2H-VXY monolayers, putting them in the class of XY-magnets. Our findings suggest that a BKT transition can occur in the 2H phase, and a classical XY model with nearest-neighbor coupling estimates critical temperatures, $T_{BKT}$, of 106 K, 82 K, and 46 K for 2H-VSSe, 2H-VSeTe, and 2H-VSTe monolayers, respectively. Our findings thus motivate future experiments and theory on Vanadium-based Janus dichalcogenides monolayers.

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This class of systems shows quasi long-range order at low temperatures, in which the correlation function decays algebraically. The transition from the high-temperature disordered phase to this low-temperature quasi-ordered state is known as the BKT transition. The corresponding transition temperatures ($T_{BKT}$) can be calculated by using the formula $T_{BKT} = 0.89J/k_B^{42}$, where J is the magnetic exchange term between neighboring spins and $k_B$ is the Boltzmann constant. In a FM configuration, each V has six neighbors having the same spin (Fig 3 (a)), and the magnetic energy for this configuration is $E_{FM} = -6J$. On the other hand, AFM configuration gives $E_{AFM} = 2J$ as four neighbors have opposite spins, and two are having the same spin (Fig 3 (b)). Hence, the exchange term can be estimated from the energy difference $\Delta E_m = 8J^{17}$ between AFM and FM spin configurations listed in Table II. We obtain the nearest-neighbor FM exchange interaction $J = 10.3$ meV, 7.9 meV, 4.5 meV for 2H-VSSe, 2H-VSeTe, and 2H-VSTe monolayers, and $T_{BKT}$ computes to 106 K, 82 K, 46 K, respectively.

we consider spin-orbit coupling (SOC) in our calculations. For this purpose, we compare the energy difference $\Delta E_a (E_x-E_z)$ between two spin configurations in which moments are directed along x and z directions. Within GGA+U+SO, the estimated $\Delta E_a$ is -0.6 meV/f.u. for 2H-VSSe, -1.89 meV/f.u. for 2H-VSTe, and -2.34 meV/f.u. for 2H-VSeTe monolayers. Thus, Vanadium-based Janus dichalcogenides monolayers in the 2H phase manifest an easy magnetization plane for spins, and they belong to the class of XY-magnets. The in-plane anisotropy is higher in 2H-VSTe and 2H-VSeTe, which indicates the SOC strength is originated from the heavy chalcogen Te.

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