High-temperature ferromagnetic semiconductors: Janus monolayer vanadium trihalides

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Two-dimensional materials provide a crucial platform to investigate novel physics and show tremendous application prospects in spintronic and flexible devices due to their greater conductivity and tunability compared with the traditional bulk materials [1–5]. However, two aspects are considered to limit the progress in spintronics. One is the scarcity materials possessing ferromagnetic (FM) order and semiconducting properties. The other one is the fragile nature of two-dimensional (2D) magnetic materials [6–10]. To solve the problems, one can make the 2D materials precisely tunable by inducing magnetism and phase transition to enlarge the candidates for FM semiconductors. Meanwhile, designing and finding novel and stable magnetic semiconductors are also effective ways.

As an important member of 2D ferromagnetic semiconductors, monolayer CrI3 with \( T_C = 45 \) K has been reported for its brilliant tunability [11,12], such as the layer- and gate-voltage-dependent FM-antiferromagnetism (AFM) transition [13–16]. In addition, bilayer Cr2Ge2Te6 has a \( T_C \) of 28 K, which can be modestly elevated to 44 K by a magnetic field of 0.3 T [17]. Similarly, in monolayer Fe2GeTe2, an ionic gate voltage of 1.75 V can drastically raise \( T_C \) from 130 K to room temperature [18,19]. For application interests, it is highly expected that strong ferromagnetism will give rise to a stable FM spin array which can survive at room temperature [20–24]. However, \( T_C \) in Cr-based honeycomb transition-metal trihalides are limited under \( \sim 70 \) K due to their dilute-magnetism nature, unlike the strong ferromagnetism driven by double-exchange interaction in monolayer Fe2Si \( (T_C \approx 780 \) K) [25,26]. As a consequence, great efforts have been put into finding the approaches to boost \( T_C \) in Cr-based 2D materials, such as doping, alloying, and straining [27–30].

Recently, a new layered van der Waals FM semiconductor VI3 was synthesized via the chemical vapor transport method with \( T_C = 50 \) K. It supports a new platform to investigate 2D magnetism and van der Waals heterostructures in the \( S = 1 \) system [31–34], but the low \( T_C \) is still a considerable disadvantage. In order to find a feasible measure to elevate \( T_C \) of monolayer VI3, we take into consideration the structural symmetry breaking, which has initiated a vast amount of interest in modulating the magnetic and electronic properties [35–38]. For example, it has been found that \( T_C \) of Janus monolayer VSSe reaches as high as 400 K and the stability is comparable to pristine VSe2 [39,40]. Also utilizing the strategy of constructing Janus structure, some new stable FM semiconductors have been predicted such as the Janus monolayer X3-Cr2-Y3 [41].

In this work, a systematical study is made of Janus monolayer of VI3: V2Cl3I3 (VCII), V2Br3I3 (VBri), and V2Cl3Br3 (VCBr), which are collectively called VXY \( (X,Y = Cl, Br \text{ and } I, X \neq Y) \), based on first-principles calculations. We demonstrate that monolayer VXY freestanding films will remain stable experimentally by using the stability analysis. Based on Monte Carlo simulations with the Heisenberg model, \( T_C \) is estimated to drastically surpass monolayer VI3 due to the lower virtual exchange gap \( g_{ex} \). Furthermore, a biaxial tensile strain (6%) can elevate \( T_C \) to 280 K in monolayer VCII because when it is stretched, the direct exchange interplay is quenched, compared with the slower weakened superexchange one, leading to FM domination and the elevated \( T_C \).

II. METHODS

The first-principles calculations were performed using the projected augmented-wave method as implemented in the Vienna Ab initio Simulation Package (VASP) [42,43]. The structural optimizations and convergence tests were adopted with the Perdew-Burke-Ernzerhof (PBE) functional [44], and the band structures were given by the Heyd-Scuseria-Ernzerhof (HSE06) functional including 25% nonlocal Hartree-Fock exchange. First, the \( 3 \times 3 \times 1 \) supercell model was applied...
to perform molecular dynamic simulations and phonon-frequency calculations. Also, a $2 \times 2 \times 1$ supercell was used during simulations of different spin arrays and unit cells during the other analysis. Second, for some tunable parameters, we kept the following parameters the same from beginning to end in each analysis: plane-wave cutoff energy, width of smearing, number of $k$ points in reciprocal space, and the thickness of the vacuum slab, which were set to 450 eV, 0.05 eV, $9 \times 9 \times 1$, and 20 Å, respectively. Note that the parameters were all taken as convergence tests against total energy. Third, force and total energy convergence criteria were set to 0.1 meV/Å and $10^{-9}$ eV during relaxations and phonon-frequency calculations, 20 meV/Å and $10^{-6}$ eV in HSE06 band structures, and 1 meV/Å and $10^{-8}$ eV for the other calculations. Fourth, the energy difference and magnetic anisotropy energy (MAE) were obtained by noncollinear calculation and taking into consideration the spin-orbital coupling effect [45] with the PBE functional. By adjusting the value of the magnetic moment projected onto the $a$, $b$, and $c$ axes we can simulate the directions of spin. Last, the vibrational property analyses were obtained with the PHONOPY [46] code using the density functional perturbation theory [47], and the molecular dynamics (MD) simulations in the canonical (NVT) ensemble were performed at 300 K with a Nosé thermostat.

III. RESULTS AND DISCUSSION

A. Stability and feasibility of VXY

The compounds VXY have layered BiI$_3$-type structures [48–50] and are formed by stacks of halogen X–vanadium–halogen Y sandwich layers with lattice parameters $a = b = 6.62$ Å in monolayer VClI. Figures 1(a) and 1(b) show that each V atom in a VXY unit cell has three up-layer $X$ and three down-layer $Y$ atoms as nearest neighbors, forming a V-centered octahedron. We begin by establishing the formation energy $E_f$ to evaluate the stability of VXY. $E_f$ of $-0.826$ eV in VClI is very close to pristine VI$_3$ ($-0.891$ eV) and more stable than monolayer CrGeTe$_3$ ($-0.588$ eV). Then the MD simulation and phonon spectra are employed. Figure 1(c) shows VClI can remain freestanding monolayers with a honeycomb lattice at room temperature. Apart from the thermal stability from the MD simulation, the phonon dispersion relation in Fig. 1(d) shows the dynamic stability with the absence of imaginary frequency. Next, elastic stiffness tensors $C_{11}$ ($C_{11} = C_{22}$), $C_{12}$, and $C_{66}$ are established as 32.56, 12.65, and 9.97 N/m, respectively, indicating the mechanical stability according to the Born criterion for hexagonal structure ($C_{11} > 0$ and $C_{11} - C_{12} > 0$). Young’s modulus and Poisson’s rate of monolayer VClI are evaluated with values of 28.2 N/m and 0.39, respectively. The values are smaller than those of some 2D materials, such as graphene (1000 N/m) and MoS$_2$ (340 N/m) [51,52]. Thus, the softer monolayer VClI can sustain more strains.

B. Electronic properties of VXY

In a V-based octahedral environment, $d$ orbitals are split into higher degenerate $e_g$ states ($d_{x^2-y^2}$, $d_z$) and lower threefold-degenerate $t_{2g}$ states ($d_{xy}$, $d_{xz}$, $d_{yz}$). Different from Cr-based trihalides, two electrons are expected to occupy the $t_{2g}$ states, and two of three degenerate $e_g$ are half filled, leading to $S = 1$ and a valence electronic configuration of $3d^2$ with a magnetic moment of $2\mu_B$ per V atom [53,54]. The band structure of VClI in Fig. 2(a) shows the intrinsic semiconducting property with a 2.30-eV band gap, which is a little less than 2.72 and 2.65 eV for VBrl and VClBr, respectively. Figures 2(b) and 2(e) show that the indirect gap is formed between the valance band maximum (VBM) at the $\Gamma$ point and the conduction band minimum (CBM) at the $M$ point near the Fermi level. $e_g$ states of V make a major contribution to the CBM, while the VBM is dominated by $p_x$ and $p_y$ orbits of I.

C. Competitive mechanism between FM and AFM

Magnetic mechanisms that lead to the FM ground state in hexagonal trihalides are complicated. But one can confirm that FM dominates the competition between AFM and FM when the weak second-nearest-neighbor interplay is ignored. On the one hand, two electrons occupying the $t_{2g}$ level have direct interaction with $d$ $t_{2g}$ states between V atoms, leading to the spin of valence electrons having an antiparallel configuration, and the AFM is systematically favored. On the other hand, two nearest-neighbor V atoms have indirect interplay mediated by 90° angled halogen atoms: one electron located in V $d$ $t_{2g}$ is theoretically excited to the $p_x$ or $p_y$ orbits of ligands X (Y) [Figs. 3(a) and 3(b)]. This superexchange interplay between nearest-neighbor V atoms gives rise to the FM spin array in the system [55–58]. Nevertheless, various superexchange paths exist in monolayer crystals containing the nearest neighbors, second-nearest neighbors, third-nearest neighbors, etc. So it is complicated to take into consideration all the actual coupling effects.
Actually, no matter how many virtual superexchange paths exist between V atoms, electrons eventually hop from the occupied $t_{2g}$ of one to empty $e_g$ states of another. That is, the superexchange tends to be enhanced when the virtual exchange gap $G_{\text{ex}}$ between the two energy levels tends to decrease [28] [Fig. 3(c)]. To estimate $G_{\text{ex}}$, we use maximally localized Wannier functions [59] to obtain on-site energies for $d$ and $V$ $d$. The $G_{\text{ex}}$ of 1.732 eV in monolayer VClI is less than that in monolayer CrI$_3$ (2.156 eV). More importantly, from the $G_{\text{ex}}$ values of 0.395, 0.397, and 0.445 eV for VClI, VBrI, and VClI, respectively, the electrons occupying V$_1$ $d$ $t_{2g}$ in VXY have more change to hybridize with that in empty V$_2$ $d$ $e_g$ states when compared with CrI$_3$ and VClI. This consequence results in more intensive FM order and higher Curie temperature transforming to paramagnetism: $T_C(VXY) > T_C(VI\text{I}_3) > T_C(CrI\text{I}_3)$.

D. Both weakened direct and indirect exchange interaction as stretching

Figure 4(a) shows the V-V and V-X (Y) bonds are almost proportional to the increasing lattice constants. During the process of enlarging the crystal, the distance between nearest-neighbor V atoms shows faster growth than that between V and X (Y) atoms. The increasing bond lengths indicate the rising exchange barrier between nearest-neighbor V $d$ $t_{2g}$ as well as between $t_{2g}$ and $e_g$ states. For verification, we apply Bader charge analyses for both the strained and fully relaxed VXY. Figure 4(b) plots the tendency for the average oxidation state [60] of each element in monolayer VClI. From $-6\%$ to 6%, the oxidation state for the V ion shows a total decreasing trend from 1.45 to 1.08, while I (Cl) keeps rising from $-0.72\%$ ($-0.48\%$) to $-0.44\%$ ($-0.22\%$). This implies that the valence electrons of V hopping to I (Cl) $p$ orbits are reduced by stretching.

In order to quantify the interplay intensity between atoms, we employ crystal orbital Hamilton population analysis (COHP), and the negative integrated COHP (ICOHP) reflect the intensity of the exchange effect [61–64]. Figure 4(c) shows that V-I and V-Cl exchange intensities are decreased by 9.8% and 11.9%, respectively. This consequence is consistent with the declining number of transition electrons mentioned above. Additionally, the ICOHP between V atoms is much...
FIG. 4. (a) Bond lengths between nearest-neighbor V-V, V-I, and V-Cl and bond angles of V-Cl-V and V-I-V as a function of strain in monolayer VClI. The inset shows biaxial strain is applied. (b) The average oxidation states of I, Cl, and V ions in a unit cell of monolayer VClI. (c) Variation of the average negative ICOHP; the values are taken between V-Cl, V-I, and V-V atoms of monolayer VClI under different strains. The inset shows the absolute average of charge spilling values over occupied bands and the band gaps for monolayer VClI as a function of biaxial strain. $\Delta_1$ means the corresponding change rate of $-\text{ICHOP}$. (d) Spin density for AFM and FM of monolayer VClI. Red and blue denote majority- and minority-spin channels, respectively. The spin density panels are generated by the VESTA package [65], and the isosurface values of all panels are set to 0.0028 e/bohr$^3$.

smaller than V-Cl and V-I and drastically reduces by 69.1\% from 0.424 to 0.131. The result shows the weakened magnetic coupling effect between nearest-neighbor V atoms.

**E. Enhanced ferromagnetism in VXY**

A simultaneous decrease of direct and indirect interplay is observed. Here a question arises spontaneously: Which kind of interplay is reduced more rapidly by tensile strain? From the point of view of electrons hopping, the virtual exchange gap $G_{ex}$ of VXY is found to be sensitive to strain and is diminished by stretching. In monolayer VClI, $G_{ex}$ diminishes from 0.527 to 0.224 eV under strain from $-6\%$ to $6\%$ [Figs. 3(d)]. Thus, from the greatly reduced $G_{ex}$, it can be confirmed that the system FM is enhanced by tensile strain. To give further evidence, total energies with different spin arrays are explored. Here six cases of spin configurations are established under biaxial strain, and the zigzag array is the most energetically favorable among the AFM configurations. The energy difference between FM and AFM shows the stable FM ground state without a phase transition in the present strain range [66]. Importantly, an overall increasing tendency in the energy-difference curves of VXY implies the system is increasingly FM favorable from $-6\%$ to $6\%$. In addition, from the shapes of spin density isosurfaces [Fig. 4(d)], the magnetism of VXY is intuitively displayed. $p\sigma$ and $p\pi$ electrons locate initially around I anions in AFM and are absent in the stretching case. Inversely, the unpaired $p\pi$-bonding electrons always appear around I anions in the FM configuration. The increased system FM and the decreased AFM in monolayer VClI are clearly seen.

We have known the system FM is driven by direct versus indirect exchange interaction between V-V atoms. Along with the consequence that the two coupling effects are
FIG. 5. (a) Energy difference $\Delta E$ between $E_{ab}$ and $E_\theta$ per unit cell as a function of angle $\theta$. (b) MAE with respect to biaxial strain. The easy axis for VClBr is perpendicular to the $ab$ plane, while VClI and VBrI are parallel to the $ab$ plane. Purple areas in (a) and (b) denote the magnetic moment direction vertical to the $ab$ plane. Additionally, during estimation of $\Delta E$ and MAE in (a) and (b), the spin-orbit coupling effect is taken into consideration. (c) $T_C$ of VXV as a function of strain; $T_C$ is established based on Monte Carlo simulations with the Heisenberg model. Magnetic moment per V ion and specific heat $C_V$ per unit cell as a function of temperature for monolayer (d) VClI, (e) VBrI, and (f) VClBr. Orange denotes the areas above room temperature.

simultaneously weakened with tensile strain as discussed above, it can be confirmed that the direct interaction is quenched, but the superexchange one has a slower reduction, which leads to the enhanced FM and the increased $T_C$ in VXV. This result also yields agreement with the rapidly lengthened V-V bonds and the swiftly decreasing $-\text{ICOHP}$ of V-V atoms under strain from $-6\%$ to $6\%$ [Figs. 4(a) and 4(c)].

F. Magnetic anisotropy and Curie temperature

We now return to estimating the Curie temperature via Monte Carlo simulations of the Heisenberg model. We start by confirming the easy axis of VXV that is crucial for studying the magnetic coupling effect between V d orbits. Figure 5(a) plots $\Delta E = E_{ab} - E_\theta$ as a function of $\theta$, where $E_{ab}$ and $E_\theta$ denote the energies for the equilibrium FM state whose spin directions are parallel and $\theta$ angled to the $ab$ plane, respectively. Also, 0° and 90° represent in-plane and out-of-plane spin arrays, respectively. It is found that only VClBr possesses an out-of-plane spin array with an energetically increasing tendency, while VClI and VBrI favor an in-plane array and tend to decrease. Then, VBrI has the largest magnetic anisotropy energy, $\text{MAE} = -2.3$ meV [$\text{MAE} = E_{ab} - E_c$, where $E_c$ denotes the energy of the equilibrium state with an out-of-plane spin array; Fig. 5(b)]. The MAE diagram also shows the stability of the easy axis for VXV: VClI possesses a weak-coupling effect with strain, and the MAE is enhanced by 33% (from $-1.35$ eV to $-0.9$ eV) under compressive strain but decreases by 10% under tensile strain. In VClBr, MAE is asymptotically close to zero with increasing tensile strain but reaches convergence at 2.18%.

In Figs. 5(d) and 5(f), we plot the results for $T_C$ of equilibrium VXV. $T_C$ can be extracted as the point where the magnetism vanishes or as the point where $C_V$ diverges. The two methods show accordant results for temperature in this case. It is found that in comparison with the pristine monolayer VI$_3$, $T_C$ is significantly boosted, with values of 240, 224, and 232 K for VClI, VBrI, and VClBr [66]. Although the semiconducting property varies slightly with strain [inset of Fig. 4(c)], $T_C$ possesses a strain-dependent character: $T_C$ of VXV under 6% strain is more than two times the values under $-6\%$ strain. Resulting from the significant coupling effect with strain, the maximum point (280 K) occurs at VClI under 6% strain and is near room temperature [Fig. 5(c)].

IV. CONCLUSION

In summary, we revealed a general strategy that can elevate $T_C$ for the newly synthesized monolayer VI$_3$ to 240 K by replacing the crystal with an asymmetric out-of-plane Janus configuration. It is notable that $T_C$ of VXV is sensitive to strain and can be further elevated to 280 K by a tensile strain of 6%. Therefore, in combination with the stability analysis, VXV is considered to be a high-temperature and stable intrinsic FM semiconductor. The reasons for the high $T_C$ in VXV and the increasing effect of tensile strain were systematically investigated. The former is due to the lower virtual exchange gap $G_{ex}$ than in monolayer VI$_3$, and the latter originates from the rapidly quenched direct interaction. The present work gives one more step forward to enlarge the family of room-temperature FM semiconductors.
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