Tuning of electronic structure, magnetic phase, and transition temperature in two-dimensional Cr-based Janus MXenes

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Two-dimensional (2D) transition metal carbides and nitrides, called as MXenes, displaying astonishing properties are emerged as a new class of 2D layered materials. In this study, we have studied the structural, electronic, and magnetic properties of 2D bare $M_2X$ and Janus Cr-based $MM'C$ metal carbides ($M \neq M' = \text{Cr, Ti, Sc, V}$) based on density functional theory. We found that 2D Janus $MM'C$ MXenes are dynamically and thermally stable and show unique electronic and magnetic properties which are not seen in their individual bare cases. Our calculated electronic band structures indicate that the Janus $MM'C$ MXenes have Dirac-type band dispersion as seen in stanene with tiny band gaps. In addition, all considered bare $M_2C$ MXenes show metallic property. However, Janus CrScC has dilute magnetic semiconducting property, CrVC shows half-metallicity, and CrTiC shows metallic property which can easily turn to half-metallicity by external effects. Our extensive density functional theory and Monte Carlo calculations indicate that Janus $MM'C$ MXenes also show different magnetic properties than their bare cases. While Cr$_2$C and Sc$_2$C have ferromagnetic spin orientations with $T_C = 2000$ and 226 K Curie temperatures, respectively, CrScC shows ferrimagnetic character with antiferromagnetic Néel spin orientation and has $T_C = 1120$ K magnetic phase transition temperature between ferrimagnetic and paramagnetic phases. Finally, external magnetic field effects on each crystal have also been elucidated in detail. The numerical outcomes reveal that Janus Cr-based $MM'C$ metal carbides have some unusual and interesting hysteresis characters. Our investigations presented here are not only interesting from a theoretical perspective, but also they show that Janus $MM'C$ MXenes are promising candidates for future spintronic applications, which should encourage their synthesis.

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I. INTRODUCTION

In the decant decade, increasing attention has been paid to the exploration of two-dimensional (2D) magnetic materials for their potential applications in quantum computation [1–3], logic and memory operations [4], and spintronics devices [5] such as spin diode, spin filter, and spin valve. A vast majority of 2D materials are nonmagnetic and magnetization generally can be generated in the nonmagnetic materials by applying external electric field and tensile strain [6,7], depositing magnetic foreign atoms on the material [8], introducing specific defects or edges in the material [9,10]. Although these effects produce high spin polarization, it is still challenging to prepare and control materials for experiments with ordered spin structure at room temperature [11,12]. For instance, the clustering of the adatoms is always inescapable, and the defect type and the edge morphology are not controllable [13]. The development of spintronics depends on exploring new materials which have unique magnetic properties. The early transition metal nitrides and/or carbides, which are known as MXenes, just recently entered the research area as a new member of 2D materials following the synthesis of Ti$_3$C$_2$ [14,15]. Because of their available structural and chemical diversity, MXenes are giving hope for obtaining intrinsic 2D magnetism. Depending on their constituent elements, MXenes have unique properties such as unique electronic [16], magnetic [17], mechanical [18], and optical properties [19] were dedicated as being topological insulator [20], metal-to-insulator transition, and superconductivity [21,22]. With the general formula $M_{n+1}X_nT$ ($M$ is for early transition metal, $X$ is for C and/or N, $T$ is for O, OF, F, $n = 1–3$) MXenes were produced by selectively etching A layers out of MAX bulk. Nowadays, experimentally more than 70 MAX phases have been synthesized [23], and there are millions of possible solid solutions with various MX systems [24,25]. Desirable magnetic properties of 2D materials may show these MXenes have intrinsic magnetism and high spin polarization depending on the number of $d$ electrons. Khazaei et al. predicted ferromagnetic (FM) ground state in pristine Cr$_2$C and Cr$_2$N MXenes for the first time [26]. Cr$_2$C MXene exhibits intrinsic half-metallic FM (8.0$\mu_\text{B}$ per unit cell) behavior with the half-metallic gap as large as 2.85 eV due to itinerant Cr $d$ electrons. FM-antiferromagnetic (AFM) transitions accompanied by a metal to insulator by terminal groups have been demonstrated [27]. Freestanding Ti$_3$C and Ti$_3$N monolayers
have reported nearly half-metallic, and also show that interesting phase transition from a nearly half-metallicity to truly half-metal spin gapless semiconductor [28]. At the same time, while 1T-Ti_{2}C is found as AFM (indirect band-gap semiconductor), 2H-Ti_{2}C exhibits ferromagnetism (half-metal with 100% spin polarization) [29,30] with strong onsite Coulomb interaction [31,32]. Therefore, the bare Ti 3d dangling bonds lead to the magnetism in the Ti_{2}C (1.92μB per unit cell) [33]. For pristine V_{2}C, while the AFM state has lower total energy than FM [28,34], it is also considered nonmagnetic by Champagne et al. due to very small magnetic moment 0.14μB [35]. As a semiconductor nonmagnetic (NM) MXene, Sc_{2}C monolayer has been predicted and has shown tunable band gap with OH, F, or O chemical groups. After these surface terminations, electronic properties of Sc_{2}C MXene transforms from metallic to semiconductor [26] with largest band gap. The ordered double transition metal (DTM) MXenes (the diversity of choices in M, X, and T atoms) with general formula M_{n}X_{n+1}T (n = 1–2) and variable number of layers (n = 1–3) in single transition metal systems. Ordered DTM Cr_{2}M_{2}C_{2}T_{3} can be found as FM, AFM, or NM and either a metal or semiconductor depending on the choice of second metal atom (M′) and termination atom (T) with high predicted magnetic phase transition temperatures and strong spin polarization with high magnetic moments [36]. Frey et al. have investigated ground-state magnetic ordering in Janus M_{2}XO_{T−1} with asymmetric surface functionalization and controlling magnetism in MXenes via electric field and doping [17]. DTM MXenes with a Ti central layer and various surface early 3d metal and cationic layers (TiM_{2}X_{2}T, M = V, Cr, Mn; X = C, N; T = H, F, O, OH) have been investigated by means of first-principle calculations and these different cationic configurations lead to diverse magnetic orders [37]. He et al. have found that Cr_{2}TiC_{2}FCl asymmetrical functionalized ternary MXenes show a novel bipolar AFM semiconductor stemming from vanishing magnetism. The mixed functionalization with F/Cl shows bipolar AFM semiconductor [38]. Hu et al. have explored four ordered DTM MXenes [39], TiMC (M = Zr, Hf, Cr and Mo), which contain one more element than Ti_{2}C and they demonstrated that the intrinsic ferromagnetism of metallic TiZrC and TiHfC whose Curie temperatures are higher than pristine Ti_{2}C. TiCrC and TiMoC are the AFM and nonmagnetic ground state, respectively.

Hereby, breaking of structural symmetry is crucial for tunable electronic and magnetic properties. We have motivated strong intrinsic magnetism of Cr_{2}C, and we have created Janus monolayers of MXenes as Cr based. The other transition metal atoms have selected from the same column in the periodic table (Ti, Sc, and V). According to our knowledge, there are few theoretical reports and no experimental evidence on the electronic and magnetic properties of Janus MXenes up to date. Very recently, the Janus monolayers of transition metal dichalcogenides, modified as the MoS_{2} structure as S-Mo-Se sandwiched layers, were successfully synthesized [40,41]. Janus structures have unique properties that they do not have in their individual bare cases [42–45]. The phenomena foreshadow that Janus structure of MXene would be synthesized in the near future. With this motivation, we have investigated the electronic and magnetic properties of Janus monolayers of MXenes and they are promising candidates for future spintronic applications, which should encourage their synthesis.

II. COMPUTATIONAL DETAILS

A. Density functional theory calculations

Our calculations are performed based on density functional theory (DFT) as implemented in the Vienna *ab-initio* simulation package (VASP) [46,47] within the generalized gradient approximation (GGA) [48] employing Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [49]. The projector augmented-wave (PAW) potential is used with the plane-wave cutoff energy set as 550 eV. The van der Waals (vdW) correction DFT-D2 proposed by Grimme describes the long-range vdW interactions [50]. We consider a vacuum layer of about ∼20 Å to avoid interaction between neighboring slabs. The Brillouin zone is a sampled 20 × 10 × 1 Monkhorst-Pack k-point mesh that corresponds to the rectangular cell. The convergence of energy criteria were set to 10−5 eV between two ionic steps, and maximum force on atoms was smaller than 3 eV Å−1. A Gaussian smearing factor was used and the pressures on the unit cell were decreased to a value of less than 0.5 kbar in all three directions. Considering the strong correlation effects between d orbitals of transition metal atoms, electronic structure calculations and structural relaxation are performed by using Dudarev’s GGA+U approach [51]. It is important to note that the structural relaxation of the transition metal atoms is strongly dependent on whether the +U parameter is included or not. In our calculations, Hubbard onsite Coulomb parameters (U) were selected from previous studies and are set to be 4 eV [35,52,53]. Phonon band structures of Janus MXenes are obtained using the finite-displacement method (for 5 × 5 × 1 supercells) as implemented in the PHONOPY code [54]. Additionally, the thermal stability analysis of the Janus MXenes was tested using finite-temperature *ab initio* molecular dynamics (MD) calculations. A Nosé thermostat was used, and Newton’s equation of motion was integrated through the Verlet algorithm with time steps of 2 fs. To visualize atomic structures we used the VESTA program [55].

B. Monte Carlo simulation details and observables

In order to clarify the magnetic properties of the Cr-based MXenes mentioned above, we proposed an atomistic J_{1}-J_{2}-J_{3} Heisenberg spin Hamiltonian as follows:

\[ H = H_{\text{int}} + H_{\text{anis}} + H_{\text{Zeeman}}, \]

where \( H_{\text{int}}, H_{\text{anis}}, \) and \( H_{\text{Zeeman}} \) terms correspond to the spin-spin interactions between first-, second-, and third-nearest neighbors, magnetic anisotropy, and the Zeeman energy, respectively. \( H_{\text{int}} \) term can be described as follows:

\[ H_{\text{int}} = -J_{1} \sum_{(ij)} \bar{\mu}_{i} \cdot \bar{\mu}_{j} - J_{2} \sum_{(kl)} \bar{\mu}_{k} \cdot \bar{\mu}_{l} - J_{3} \sum_{(il)} \bar{\mu}_{i} \cdot \bar{\mu}_{l}. \]
Magnetic anisotropy and the Zeeman parts can be given as follows, respectively:

$$H_{\text{anis}} = -k_1 \sum_i (\mu_i^x)^2 - k_2 \sum_i (\mu_i^y)^2 - k_3 \sum_i (\mu_i^z)^2$$

(3)

and

$$H_{\text{Zeeman}} = -\mu_0 \mathbf{H} \cdot \sum_i \bar{\mu}_i.$$  (4)

Here, $\bar{\mu}_i$ is the magnetic dipole moment vector located at the $i$th lattice site of the system ($\bar{\mu} = \mu_i^x \hat{x} + \mu_i^y \hat{y} + \mu_i^z \hat{z}$). Magnitudes of the magnetic dipole moment vectors ($|\bar{\mu}| = \sqrt{\mu_i^x^2 + \mu_i^y^2 + \mu_i^z^2}$) vary depending on the considered material.

In order to investigate the magnetic properties of the $\text{M}_2\text{C}$ and $\text{MM}_2\text{C}$ MXenes materials mentioned above, we implemented Monte Carlo simulation with single-site update Metropolis algorithm [56] on a two-dimensional lattice $L \times L$. Here $L$ is the linear size of the lattice, and it is fixed as $L = 120$ throughout this work. Periodic boundary conditions are applied in both $x$ and $y$ directions. At this point, it is beneficial to briefly summarize the Metropolis algorithm used in this study:

(i) A magnetic atom is chosen randomly (say $i$th site) among the $L \times L$ options for a specific material.

(ii) By using the Marsaglia algorithm, the components of the chosen magnetic dipole moment are flipped such that it will be ($\bar{\mu}_i \rightarrow \bar{\mu}_i'$). As in the conventional local update algorithms, the other magnetic dipole moment vectors are kept fixed during this operation.

(iii) Next, the energy difference is calculated as $\Delta H = H'_i - H_i$. Here, $H_i$ is the energy corresponding to the current configuration while $H'_i$ refers the energy after the trial switch. The probability to accept the proposed magnetic dipole moment components is given by

$$W_M(\bar{\mu}_i \rightarrow \bar{\mu}_i') = \begin{cases} \exp(-\Delta H/k_B T) & \text{if } H'_i \geq H_i, \\ 1 & \text{if } H'_i < H_i, \end{cases}$$

(5)

where $k_B$ and $T$ are the Boltzmann constant and the temperature, respectively.

(iii) Based on Eq. (5) it is possible to say that (1) if the energy of the system is lowered, the proposed configuration is always accepted as a new configuration. (2) If not, a random number $\Gamma$ is generated between 0 and 1 using a suitable random number generator, and if $\Gamma$ is less than or equal to $W_M(\bar{\mu}_i \rightarrow \bar{\mu}_i')$, the selected magnetic dipole moment components are flipped. (iii) Otherwise, the old configuration stays unchanged.

Following the simulation protocol mentioned above, the numerical data were collected over 100 independent samples for each material in order to have the data with high accuracy. Error bars have been estimated by using the jackknife method [56]. In each sample, the simulation starts at the configuration such that it will be the paramagnetic (PM) (or disordered) phase, i.e., randomly orientated configuration. Then, the temperature is gradually cooled down until it reaches to $T = 10^{-3}$ K for each material studied here. Typically, the first $2 \times 10^4$ Monte Carlo step per site (MCSS) were discarded for thermalization process and the numerical data were averaged over the next $8 \times 10^4$ MCSS for each temperature step. It should be noted that these amounts of discarded steps are sufficient for thermalization process based on our detailed test simulations. During the simulations, the following thermodynamic quantities of interest have been monitored:

(1) Time series of the total $(m_{\tau,a}(t))$, staggered $(m_{s,a}(t))$, and stripy $(m_{\text{Str},a}(t))$ magnetization components

$$m_{\tau,a}(t) = \frac{1}{N} \sum_{i,j} \mu_{a,i,j}^x,$$

$$m_{s,a}(t) = \frac{1}{N} \sum_{i,j} (-1)^{i+j} \mu_{a,i,j}^x, \quad \alpha = x, y, z$$

(6)

$$m_{\text{Str},a}(t) = \frac{1}{N} \sum_{i,j} (-1)^{i+j} \mu_{a,i,j}^x,$$

where $N(=L \times L)$ denotes the total number of magnetic dipole moments in the system.

FIG. 1. Top and side views of the optimized atomic configuration of the supercell of $\text{Cr}_2\text{C}$ monolayer. The rectangular $2 \times 1 \times 1$ supercell with lattice constants $a$ and $b$ is shaded and delineated with straight lines. Bond lengths ($d_1$ and $d_2$) and the thickness ($h$) of the structure are illustrated on the figure. Janus $\text{CrMC}$ ($M = \text{Ti}$, $\text{Sc}$, $\text{V}$) structures are obtained by replacing top layer Cr atoms in the same layer by $M$ atoms. $J_1$, $J_2$, and $J_3$ denote the first-, second-, and third-nearest neighbors, respectively.
(2) With the help of Eq. (6), one can define the thermal average of the total \( (M_T) \), staggered \( (M_s) \), and stripy \( (M_{s, t}) \) magnetizations and their components as follows:

\[
M_{T,a} = \langle m_{T,a}(t) \rangle, \quad \langle M_T \rangle = \left\langle \sum_a m^2_{T,a}(t) \right\rangle, \\
M_{s,a} = \langle m_{s,a}(t) \rangle, \quad \langle M_s \rangle = \left\langle \sum_a m^2_{s,a}(t) \right\rangle, \\
M_{s, t,a} = \langle m_{s, t,a}(t) \rangle, \quad \langle M_{s, t} \rangle = \left\langle \sum_a m^2_{s, t,a}(t) \right\rangle.
\]

(3) In order to determine the phase transition point separating two phases and characterize its nature (i.e., first-order phase transition or second-order phase transition), we use the susceptibility and the specific-heat curves as a function of the temperature, which are defined below:

\[
\chi_\delta = N\left(\langle M^2_\delta \rangle - \langle M_\delta \rangle^2\right)/k_B T, \quad \delta = T, S, Str \\
C = N\left(H^2 - \langle H \rangle^2\right)/k_B T^2.
\]

### III. RESULTS AND DISCUSSION

#### A. Structural and electronic properties

Figure 1 shows the crystal structure of the \( M_2C \) type MXene monolayer. Stable \( M_2C \) structures belong to space group \( P\bar{3}m1 \) with C atoms in octahedral coordination and each C atom bonds with six \( M \) atoms. This atomic geometry is also named as “1T phase” for transition metal dichalcogenides. In this study, we considered four bare \( M_2C \) (\( M = Cr, Ti, V, Sc \)) MXene monolayers and three Janus MXene monolayers. To obtain Janus \( MM'C \) (\( M \neq M' = Cr, Ti, V, Sc \)), metal atoms on the same side of \( M_2C \) are substituted with a different metal atom as illustrated in the bottom part of Fig. 1.

The optimized structure parameters such as lattice constants, bond lengths, and cohesive energies are given in Table I. The calculated lattice constants and thickness of the structures show that the lattice constants of the Janus \( MM'C \) are closer to the bare \( M_2C \) structure which has smaller lattice constants. The thickness of the Janus \( MM'C \) structures is closer to the bare \( M_2C \) structure which is thicker. The bond lengths in the Janus \( MM'C \) structures vary slightly compared with those for bare \( M_2C \) structure due to the atomic radius differences between the \( M \) atoms, which causes strain effect in the structure.

We calculate the cohesive energy (per atom) of bare \( M_2C \) and Janus \( MM'C \) structures to determine the strength of cohesion between the atoms using the following equation:

\[
E_{coh} = \frac{[2E_M + E_C - E_{M'C/MM'C}]}{3},
\]

where \( E_M \) and \( E_C \) are the total energy of single isolated (spin-polarized) \( Cr, Ti, V, Sc, \) and C atoms, \( E_{M'C/MM'C} \) is the total energy of bare or Janus MXene monolayers. The coefficient \( 3 \) is for the number of atoms in hexagonal cell of MXenes. The calculated cohesive energies of the Janus \( MM'C \) structures are almost the average of those of corresponding bare \( M_2C \) MXenes. The computed cohesive energies confirm the strong connection between the atoms in the Janus \( MM'C \) structures.

In addition to strong cohesion between the atoms in Janus \( MM'C \) MXenes, we also investigated whether Janus \( MM'C \) MXenes correspond to local minima in the Born-Oppenheimer surface and whether these minima are deep enough to provide stability against thermal excitations. For this purpose, we performed dynamical stability (at \( T = 0 \) K) and high-temperature thermal stability test calculations.

First, we calculated the vibration frequencies \( f(k) = \Omega(k)/2\pi \) of the Janus \( MM'C \) MXene structures in the \( k \) space. If all vibration frequencies in the Brillouin zone are positive, the considered structures can be dynamically stable at \( T = 0 \) K. Figure 2 illustrates the phonon band structures of the Janus \( MM'C \) MXenes along high-symmetry directions. In this calculation we used hexagonal 5 \( \times \) 5 \( \times \) 1 supercells of the Janus MXenes. The calculated vibration frequencies of all Janus \( MM'C \) MXene structures are found as \( f(k) > 0 \) and hence confirm the dynamical stability at \( T = 0 \) K except for \( CrVC \). There is imaginary frequency for out-of-plane acoustical mode (ZA) at the \( M \) high-symmetry point for Janus \( CrVC \). However, as we will mention below our molecular dynamic calculations suggest that also this Janus MXene is stable at certain temperature values. So, we attribute this imaginary frequency to the computational errors. In fact, with respect to the fundamental knowledge of coupled oscillators \( (w = \sqrt{E/m}) \) the expected thing is to obtain higher vibration frequencies for \( CrScC \) structure due to Sc atom is the lightest element among \( Cr, Ti, V \). However, \( CrTiC \) and \( CrVC \) and \( CrScC \) structures have relatively higher vibration frequencies (>700 cm\(^{-1}\)). In addition, the atomic radius of Sc atom is the largest among the other considered atoms. According to Slater’s study [57], empirically measured (in unit of picometers) covalent radii of the atoms which are considered in this study are as follows: \( Sc(160) > Ti(140) = Cr(140) > V(135) \). As can be seen in Table I, relatively longer bond lengths occurred in \( CrScC \) structure, which can imply force constants for \( CrScC \) are relatively weaker than other Janus \( MM'C \) structures and this leads to lower vibration frequencies.

To check the thermal stability of Janus \( MM'C \) MXene structures we performed \textit{ab initio} molecular dynamic calculations. In these calculations, we used 4 \( \times \) 4 \( \times \) 1 supercell structures of Janus \( MM'C \) MXenes. Starting from 300 K, the temperature is stepwise increased to 500 K within 10 ps total
simulation time for each structure. In Fig. 3 we present the snapshots of atomic configurations of Janus $MM'C$ MXene structures (at the end of 10 ps) taken from MD simulations at 500 K. As can be seen, whole Janus $MM'C$ MXene structures preserve its overall shape, almost keeping their optimized atomic configuration as $T = 0$ K. In Fig. 4, we also show how the total energy and magnetic moment ($\mu_B$ in formula unit) of the considered supercells change against a time step at 500 K. Green straight lines illustrate the average of the fluctuated curves. This shows that the evolution of energy and magnetic moment in time are fluctuating in the vicinity of average values. These calculations and analysis show that Janus $MM'C$ MXene structures can be stable at room temperature and slightly above.

After providing the evidence of stability of the structures, we determine the magnetic structure of bare and Janus enes. The spin-spin interactions can be calculated by mapping the total energies (which are obtained from DFT calculations) corresponding to different magnetic configurations depicted in Fig. 1 to the $J_1$-$J_2$-$J_3$ Heisenberg Hamiltonian [Eq. (2)]. The magnetic energies to be used to extract the spin-spin interactions for four types of magnetic configurations (see Fig. 3) for the materials in bare forms can be written as follows:

$$
E_{FM} = E_0 - (3J_1 + 2J_2 + J_3)|\vec{\mu}|^2,
$$

$$
E_{AFM-Neel} = E_0 - (-3J_1 + 2J_2 - J_3)|\vec{\mu}|^2,
$$

$$
E_{AFM-stripy} = E_0 - (-J_1 - 2J_2 + J_3)|\vec{\mu}|^2,
$$

$$
E_{AFM-zigzag} = E_0 - (J_1 - 2J_2 + J_3)|\vec{\mu}|^2,
$$

(11)

where $E_0$ is the ground-state energy independent of the spin configurations. The above equations allow us to find the numerical values of exchange interactions $J_1$, $J_2$, and $J_3$ as well as $E_0$. It is worthwhile to note that the magnetic dipole moments appearing in Eq. (11) should be replaced with their own magnetic dipole moment for each bare structure. For the Janus Cr-based MXenes, i.e., CrVC, CrScC, and CrTiC considered here, the similar equations mentioned above can be easily obtained, which are not shown here for the sake of brevity. Numerical values of the spin-spin interactions and magnetic anisotropy constants (by adding SOC to the calculations), which have been calculated from the difference between total energies for two orientations of the magnetizations with respect to the crystal lattice, are given in Table II. It is obvious that both the exchange parameters and the magnetic anisotropy parameters change from compound to compound with the unique crystal character of each material.

We should note that favorable magnetic orientations (ground states) for the considered MXene monolayers which are written in Table II are determined by DFT calculations. More negative total energy of the considered supercell indicates energetically favorable magnetic orientation. As can be seen, V$_2$C and CrScC have only $J_1$ and $J_2$ exchange interaction parameters, while other all MXenes additionally have also $J_3$. Our extensive DFT calculations showed that initially FM oriented case of V$_2$C monolayer turn to AFM-Neel configuration after the geometrical optimization with exactly the same magnetic moment value and total energy. To solve this problem, we enlarged the considered supercell more. However, we obtained the same results. So, for V$_2$C monolayer...
TABLE II. The considered materials and their ground states for the magnetic orientation are given in parentheses. Calculated exchange interaction parameters \( (J_1, J_2, J_3) \) and magnetic anisotropy constants \( (k_1, k_2, k_3) \) for all of the materials studied in this paper. Here, all exchange interaction parameters and magnetic anisotropy constants are in the units of meV and \( \mu eV \), respectively. Magnetic phase transition temperature \( (T_{C,N}) \) is given in the units of K.

<table>
<thead>
<tr>
<th>Material</th>
<th>( J_1 )</th>
<th>( J_2 )</th>
<th>( J_3 )</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
<th>( T_{C,N} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(_2)C (FM)</td>
<td>9.63</td>
<td>11.1</td>
<td>-9.26</td>
<td>0</td>
<td>2.1</td>
<td>169</td>
<td>2000</td>
</tr>
<tr>
<td>Ti(_2)C (Néel)</td>
<td>-26</td>
<td>20.8</td>
<td>-5.3</td>
<td>0</td>
<td>0</td>
<td>109</td>
<td>848</td>
</tr>
<tr>
<td>V(_2)C (Néel)</td>
<td>-1.53</td>
<td>1.54</td>
<td>310</td>
<td>160</td>
<td>0</td>
<td>256</td>
<td></td>
</tr>
<tr>
<td>Sc(_2)C (FM)</td>
<td>-7.14</td>
<td>37.1</td>
<td>51.9</td>
<td>0</td>
<td>1.1</td>
<td>545</td>
<td>226</td>
</tr>
<tr>
<td>CrVC (Néel-FiM)</td>
<td>4.49</td>
<td>2.81</td>
<td>-11.2</td>
<td>258</td>
<td>253</td>
<td>0</td>
<td>918</td>
</tr>
<tr>
<td>CrScC (Néel-FiM)</td>
<td>-67.3</td>
<td>4.4</td>
<td>0</td>
<td>1.2</td>
<td>63.5</td>
<td>1120</td>
<td></td>
</tr>
<tr>
<td>CrTiC (stripy-FiM)</td>
<td>-76.2</td>
<td>-26.8</td>
<td>68.6</td>
<td>0</td>
<td>83</td>
<td>0</td>
<td>1110</td>
</tr>
</tbody>
</table>

However, in \( MM'C \) MXene structures C atoms are coordinated with two different metal atoms which have different atomic radii. This results in forming of distorted octahedral crystal field instead of perfect octahedral crystal field. This mentioned crystal field has \( C_{3v} \) symmetry and splits the \( t_2g \) and \( e_g \) orbitals into a single \( a(d_{3z}) \) orbital and two twofold degenerate \( e_d(d_{yz} + d_{xz}) \) and \( e_d(d_{yz} + d_{xz}) \) orbitals. This extra splitting can be seen in monolayer RuCl\(_3\) [58]. Electronic density of states (DOS) for the energetically favorable magnetic configurations of the bare and Janus MXenes are illustrated in Figs. 5 and 6, respectively. These figures illustrate only \( d \) orbital contribution of the metal atoms. Total atom projected density of states of the considered MXenes are given in the Supplemental Material (SM) [59]. We should note that in this study, electronic calculations are performed by adding \( +U \) \((U = 4 \text{ eV})\) Coulomb parameter because of partially filled \( d \) orbitals of the metal atoms in MXenes. For example, adding \( +U \) into the calculations shows itself in the Cr\(_2\)C electronic structure. Si et al. [27] found that Cr\(_2\)C shows half-metallic character using hybrid functionals (HSE) without adding Hubbard \( U \) parameter. Similar to the study of Si et al., we also performed HSE calculation for the Cr\(_2\)C monolayer and we obtained half-metallic band structure (please see Fig. S1 [59]). However, adding \( +U \) parameter changes the electronic structure. The occurred band gap in spin-down channel for HSE slips to the lower-energy levels (between \(-3 \) to \(-2 \text{ eV}\)) with added \( +U \) parameter and Cr\(_2\)C shows metallic property for both spin-down and spin-up channels (please see Fig. 5 and Fig. S1 [59]). Dominant orbital contribution at the Fermi level for Cr\(_2\)C monolayer comes from \( e_1 \) and \( e_2 \) orbitals of Cr atoms. Ti\(_2\)C and V\(_2\)C monolayers show AFM-Néel magnetic configuration and both of them show metallic property with \( d \) orbital contributions of the metal atoms. However, \( a(d_{3z}) \) orbital contribution is dominant for Ti\(_2\)C, while all \( a, e_1 \), and \( e_2 \) orbitals give contributions for V\(_2\)C in the vicinity of Fermi level. Ferromagnetic Sc\(_2\)C monolayer has metallic character for both spin-down and -up channels. In this bare MXene structure, the \( e_1 \) orbital of Sc atoms gives dominant contribution at the Fermi level for the spin-up state, while it gives ignorable contribution for the spin-down state. However, this

we could examine and obtain three different (AFM-Néel, AFM-stripy, AFM-zigzag) magnetic configurations and two exchange interaction parameters, respectively. Similar to V\(_2\)C, also CrScC has two exchange interaction parameters. In this Janus MXene, initially oriented AFM-stripy configuration turns to AFM-zigzag configuration after the geometrical optimization calculations, even for larger supercells.

In monolayer \( MM'C \) MXene structures, each carbon atom is coordinated by six metal atoms similar to the \( MnC \) MXene.

FIG. 4. Total energy versus time step in unit of fs for Janus \( MM'C \) monolayer structures given by blue. Total magnetic moment in formula unit of Janus \( MM'C \) monolayer structures versus time step in unit of fs are given in red. Green straight line indicates the average of the fluctuations. Top and side views of the snapshots of the atomic configurations of Janus \( MM'C \) monolayer structures taken from MD simulations carried out at 500 K temperature for a total duration of 10 ps.
very small $d$ orbital contribution of Sc atoms in the spin-down state makes Sc$_2$C MXene metal for both spin channels.

After creating Janus MXenes, $MM'C$ MXene structures display different and unique electronic features than their individual bare cases. Atomic radius differences between the metal atoms in the Janus $MM'C$ monolayers result in elongated or shortened bonds between carbon and metal atoms and break the inversion symmetry in out of plane. This newly occurred distortion causes changes in bond lengths of the octahedral geometry of $MM'C$ monolayers and results in band splitting in the electronic structure of Janus $MM'C$ structures. We should also note that as we mentioned above with respect to the covalent radii of the metal atoms, Cr and Ti atoms have similar radii. This means that the distortion of the bond lengths of the CrTiC is negligible if we compare them with the remaining Janus $MM'C$ monolayers. In addition, while Sc and V atoms are in the group 3 and group 5, Ti and Cr atoms are in the group 4 and group 6, which means Sc and V atoms have odd number of total electrons, while Ti and Cr have even number of total electrons. So, combining of odd and even number of electrons in the unit cell such as CrVC and CrScC gives almost similar electronic properties, while combining of the even and even number of electrons in CrTiC gives different band dispersion. As shown in Fig. 6(a), CrTiC shows metallic character for both spin-up and -down channels. However, valence band maximum of spin-up channel is only 60 meV above the Fermi level which can be attributed to the semimetallic property. There is a band gap of 120 meV between this mentioned band level and one upper band level which is in the conduction band and, as is well known, these kinds of bands can easily slip to the lower-energy levels and can obtain semiconducting property by external effects such as strain or electric field. Another interesting band dispersion appears for spin-down channel around $-0.25$ eV between the $\Gamma$ and X high-symmetry points in the band structure of CrTiC which is reminiscent of Dirac-type band dispersion as can be seen in stanene [60]. To obtain additional insight into the electronic structure of the CrTiC we calculated total, atom, and orbital projected electronic density of states displayed in Figs. 6 and S2 [59]. Interestingly, this mentioned Dirac-type band dispersion in the band structure of CrTiC occurs from two different atoms’ orbital contributions. While the dominant contribution to the lower part of the Dirac-type band dispersion comes from Cr-$e_1$ orbital, Ti-$e_1$ orbital contributes to the higher part of the band. In addition, almost whole bands under the Fermi level are occupied by $d$ orbitals of Cr atoms in the spin-down channel. For the spin-up channel $d$ orbitals of Ti atoms are dominant under and above the Fermi level and $e_1$ and $e_2$ orbitals of Ti atoms are localized in the vicinity of the Fermi level.

Figure 6(b) illustrates the band structure and corresponding orbital projected density of states for Janus CrScC MXene.
FIG. 6. Electronic band structure and corresponding orbital projected density of states of (a) Janus CrTiC, (b) Janus CrScC, and (c) Janus CrVC MXenes. Here, $a$ is for $d_{z^2}$ orbital, $e_1$ is for $d_{x^2} + d_{y^2}$, and $e_2$ is for $d_{xy} + d_{x^2-y^2}$ orbitals.

As can be seen, CrScC shows dilute magnetic semiconductor property which is very important to design advanced devices such as spin-polarized light-emitting diodes, lasers, and spin-transistor logic devices. In contrast to CrTiC, Dirac-type band dispersion in the spin-down channel of CrScC appears at the Fermi level with a band gap of 80 meV between $\Gamma$ and $X$ high-symmetry points, while there is a 580-meV band gap that occurs for the spin-up channel. Similar to the CrTiC, this Dirac-type band occurs by two different atoms and by their corresponding $d$ orbitals. The lower part of the Dirac-type band dispersion comes from Cr-$e_1$ orbital, while Sc-$e_1$ orbital dominant for the higher part of the band. For the spin-up channel of CrScC band structure, the valence band maximum (VBM) is occupied by $e_1$ and $e_2$ orbitals of Sc atoms, while there is a localized $e_1$ orbital of Sc atoms at the conduction band minimum (CBM). We expect that the Dirac-type band in the spin-down channel of CrScC monolayer can easily modulate by applying strain and can turn to exact linear Dirac band dispersion as it is done by Tang et al. for Janus transition metal dichalcogenides [61].

Another interesting and unique electronic property in this study is the half-metallicity property of Janus CrVC monolayer. Dirac-type band dispersions which are located between $\Gamma$ and $X$ high-symmetry points in the spin-down channels for CrTiC and CrScC disappear in CrVC due to opening of gap between VBM and CBM. For spin-down channel, CrVC has semiconducting property with a band gap of 0.27 eV, while it shows metallic character for spin-up channel. There is a
strong localized peak of $a(d_{z^2})$ orbital of V atoms at the Fermi level which causes metallic property for CrVC in the spin-up channel. Similar to other Janus MXenes which are studied in this study, VBM level is occupied by $e_1$ orbitals of Cr atoms, while CBM is equally occupied by $e_1$ orbitals of Cr and V atoms. We should note that these electronic band dispersions have been obtained using DFT+$U$ calculation which is used to correct the self-interaction errors and which is similar to Hartree-Fock exchange with HSE calculations.

B. Monte Carlo simulation results

1. Thermodynamic properties of the bare and Cr-based Janus MXenes

In this section, having determined the exchange parameters and magnetic anisotropy parameters, we will discuss the magnetic properties of the bare and Janus form Cr-based MXenes under the absence of the external magnetic field. As noted before, using the spin-spin interactions and magnetic anisotropy constants predicted from DFT in Monte Carlo simulation, we measure the thermal variations of the total and staggered magnetizations and their corresponding susceptibilities and also specific-heat curves. By benefiting from peak positions of these thermodynamic response functions, we estimate the transition temperature of the Cr-based Janus MXenes. Based on the DFT calculations, the ground-state configurations of the Cr$_2$C and Sc$_2$C have been found as FM. On the other hand, it is well known that AFM ordering is the most common type of ground state observed in MXenes. Our numerical results support also this fact: V$_2$C and Ti$_2$C monolayers have AFM-Néel ground states. Thermal variations of the magnetizations are illustrated in Fig. 7(a) for Cr$_2$C, Sc$_2$C, V$_2$C, and Ti$_2$C monolayers. Here, all magnetization values are normalized with their own magnetic dipole moment at zero temperature estimated by DFT calculations: They are $|\vec{\mu}| = 3.92\mu_B$, $0.49\mu_B$, $2.67\mu_B$, and $1.29\mu_B$ for Cr$_2$C, Sc$_2$C, V$_2$C, and Ti$_2$C monolayers, respectively. It also shows both the total and staggered magnetizations as a function of the temperature which are marked by dashed lines. We note that our observations reported here indicate a clear evidence which supports the results of DFT calculations in view of the ground-state configurations. It is clear from the figure that when the temperature increases starting from the relatively lower-temperature regions, the magnetization values begin to decrease from their saturation values due to the increasing thermal fluctuations. When the temperature is increased further, the considered Cr-based Janus MXenes display a phase transition between ordered and disordered phases. More specifically, these transitions are between FM and PM phases for Cr$_2$C and Sc$_2$C monolayers while they are between AFM and PM phases for V$_2$C and Ti$_2$C structures. By comparing these materials with each other, it is possible to underline that Cr$_2$C has a robust FM character than others. As shown in Figs. 7(b) and 7(c), when the temperature approaches the transition temperature, the magnetic and staggered susceptibilities as well as the specific-heat curves tend to show a divergent behavior indicating a second-order phase transition. Their peak positions in the temperature axis are in accordance with the behavior of

FIG. 7. Thermal variations of (a) magnetizations, (b) corresponding susceptibilities, and (c) specific-heat curves for Cr$_2$C, Sc$_2$C, V$_2$C, and Ti$_2$C structures. Here, varying symbols correspond to different structures as labeled in the figures. Total magnetizations are displayed for the Cr$_2$C and Sc$_2$C structures while staggered magnetizations are plotted for the V$_2$C and Ti$_2$C monolayers. Each magnetization curve normalized with its own ground-state magnetic dipole moment value. The dashed lines are added to guide the eye.
another study, magnetic properties of Cr$_2$C crystals have been originated from the Sc atoms to the total system. Temperature variations of the specific-heat and stripy susceptibilities are displayed as insets. The shaded area shown in (d) is enlarged as an inset for the CrScC material to clearly reveal the contribution of the susceptibility as follows: 2000, 226, 256, and 848 K for Cr$_2$C, Sc$_2$C, V$_2$C, and Ti$_2$C monolayers, respectively, which are extracted from the peak positions of the susceptibilities and the specific-heat curves. In a recent study, it has been shown that a high Néel temperature of more than 2000 K was achieved by adding F and OH functional groups to the Cr$_2$C structure [62]. In another study, magnetic properties of Cr$_2$C crystals have been studied by mapping DFT energies into the $J_{12}$-$J_{23}$ Heisenberg model [27]. The exchange-coupling parameters have been calculated to be $J_1 = 7.4$ meV and $J_2 = 14.7$ meV, leading to a prominent FM character in the Cr$_2$C system. The authors also showed that Cr$_2$C preserves its FM magnetic state even at room temperature. Additionally, it should be underlined that $J_1$ and $J_3$ are significantly larger than $J_1$ for Sc$_2$C crystal. If one ignores the exchange parameters $J_2$ and $J_3$, the ground state to be obtained would be changed from FM to AFM-Néel one. There will also be a considerable decrement in the critical temperature if $J_2$ and $J_3$ are ignored.

Using the same simulation parameters and the protocol used in bare $M_2$C MXene monolayers discussed above, we performed MC simulations for CrVC, CrScC, and CrTiC Janus MXene monolayers. Thermal variations of the magnetizations and corresponding susceptibilities are displayed in Figs. 8(a) and Fig. 8(b) for CrVC structure. In Fig. 8(a), the magnetizations corresponding to the Cr and V atoms as well as the overall magnetization are shown by different symbols. As noted before, CrVC structure has a ferrimagnetic (FiM) character because the magnetic dipole moments of the Cr and V atoms are different from each other. They are also aligned opposite with respect to each other but they have the same orientation within themselves. At the very low-temperature regimes, the Cr and V atoms saturate to the values obtained by DFT calculations: Their magnitudes are 3.83$\mu_B$ and 2.71$\mu_B$ for Cr and V atoms, respectively. Our numerical simulations suggest that most of the contribution to the total magnetization comes from the Cr atoms in accordance with the DFT predictions. It is clear that the magnetizations belonging to the Cr and V atoms and also the total magnetization of the system decrease with increasing temperature and they all vanish at the same transition temperature. Figure 8(b), where the susceptibilities as functions of the temperature exist, support the treatments observed in Fig. 8(a). This is also confirmed by the specific-heat curve which is given as an inset of Fig. 8(b). All these thermodynamic functions show that there is a continuous phase transition between FiM and PM phases with a transition temperature of $T_N = 918$ K. It also means that the CrVC monolayer has a strong FiM character due to having a transition temperature larger than the room temperature. Moreover, we present the MC simulation results regarding the thermal and magnetic properties of CrScC monolayer system. One of the most intriguing results is that the Janus MXene CrScC has a FiM ground state while both Cr$_2$C and Sc$_2$C crystals in bare forms have FM ground-state configurations. In a recent study, optically driven ultrafast magnetic transitions between FiM and FM configurations have been reported for some 2D ferrimagnetic MXenes [63]. Cr and Sc sublattices.
and also overall magnetization of the system versus temperature are represented in Fig. 8(c). Here, the magnetization curves corresponding to the Cr and Sc atoms are shown by different symbols. It is clear that Cr and Sc curves are saturated to the values of 3.74µ_B and 0.48µ_B, respectively. Based on these results, it can be said that the magnetization contribution originating from the Cr atoms to the total magnetization is stronger than the ones emerging in Sc atoms. When the temperature increases starting from the zero, Cr, Sc, and the total magnetizations begin to decrease. With further increment in temperature, they all vanish at the same transition temperature due to the spin-spin couplings between these Cr and Sc atoms.

As in the case of CrVC, there is a continuous phase transition between FiM and PM phases. Figure 8(d) displays the magnetic susceptibilities as functions of temperature for Cr, Sc sublattices, and the overall system. By benefiting from the susceptibility curves, the transition temperature is estimated as \( T_N = 1120 \) K (which is also confirmed by the specific-heat curves but which is not shown here). The inset given in Fig. 8(d) shows the main contribution coming from Sc atoms to the total susceptibility. Although its magnetization contribution to the total CrScC Janus system is weak when comparing the Cr atoms, the susceptibility curve of Sc atoms shows a clear peak behavior in the vicinity of phase transition point in accordance with the expectations.

As a final investigation in this section, we represent the thermal variations of the magnetization and corresponding susceptibility curves of the CrTiC structure in Figs. 8(e) and 8(f), respectively. In Fig. 8(e), the magnetizations belonging to the Cr and Ti atoms as well as the overall magnetization are plotted by using different symbols. The Janus CrTiC structure has an AFM-stripy character, which is predicted by DFT calculations: Ground-state magnetic dipole moment values of Cr and Ti atoms are 4.10µ_B and 0.41µ_B, respectively. Our MC simulations support the ground-state configurations mentioned above. This robust stripy phase vanishes above the transition temperature. By benefiting from the susceptibility and specific-heat curves [which are shown as an inset in Fig. 8(f)], the transition temperature has been estimated as \( T_N = 1110 \) K, which is beyond the room temperature. The second inset of the same figure also shows the susceptibility contribution of Ti atoms to the total system’s susceptibility. It can be concluded from both the susceptibility and specific-heat curves against the temperature that there is a second-order phase transition between AFM-stripy and paramagnetic phases. Based on the outcomes reported in this section, it is possible to say that the materials having a critical temperature above the room temperature can be good candidates for nanoscale spintronic device applications.

2. Magnetic field effects on the bare and Cr-based Janus MXenes: Hysteresis properties

In this section, we will focus our attention on the magnetic properties of the both bare and Janus form Cr-based MXenes structures under the influence of a magnetic field. Let us briefly summarize the simulation details used for obtaining the hysteresis curves. System sizes are exactly the same as those used in Sec. III B 1. Magnetic hysteresis curves are collected over 30 independent samples. In each sample, the simulation starts at the high-temperature region corresponding to a disordered spin configuration under the absence of a magnetic field. Then, the system is gradually cooled down to a specific temperature where a conventional hysteresis curve starts. When the desired temperature is reached, the magnetic field switch is opened and the last magnetic dipole moment configurations are used as an initial configuration for the decreasing branch of the hysteresis curve. At this stage, the magnetic field is traced beginning from \( H \) to \(-H\) with a suitable \( \Delta H \) step. When the magnetic field is reached to \(-H\) value, it means that the decreasing branch of the hysteresis curve is completed. Then, using a similar procedure, the increasing branch of the hysteresis curve is completed by going from \(-H\) to \( H \) value. When the applied field value is reached to \( H \) value, one can get a complete hysteresis curve. Typically, first \( 5 \times 10^3 \) MCSS is discarded during the thermalization and the magnetizations were collected over the next \( 5 \times 10^3 \) MCSS at each magnetic field step. Using these rules, the hysteresis properties of the bare and Cr-based Janus MXene structures studied in this study are obtained for some particular temperature values which vary from sample to sample. As it is well known, there are two parameters affecting the shape of the hysteresis: These are coercivity and the remanence magnetization of the magnetic material. Among them the coercivity can be accepted as an essential physical property of magnetic materials, having a significant importance in technological applications.

Thermal variation of the remanence magnetization of the bare Cr2C monolayer is displayed in Fig. 9(a). Here, external magnetic field has been applied along the \( z \) direction. At first sight, one can see that the remanence magnetization behavior is sensitively dependent on the studied temperature value. It shows a behavior in such a way that it will decrease when the temperature is increased starting from the room temperature. That is because of the competition between the thermal fluctuations and the spin-spin interactions as well as the magnetic anisotropy. With further increment in the temperature, the remanence magnetization vanishes just above the 2000 K. In addition to the remanence magnetization, temperature dependence of the coercivity curve is given in the inset of Fig. 9(a) for the Cr2C structure. Our numerical findings indicate that much more Zeeman energy is needed to reverse the sign of the magnetic dipole moment at the low-temperature regions since the Cr2C system has a robust FM character. As a matter of fact, it is possible to say that this behavior is a typical behavior emerged in the FM materials [64,65]. As in the case of remanence magnetization curve, the coercive field values tend to decrease and then disappear with increasing temperature value. The aforementioned behavior can be accepted as an expected result because an increment in the temperature leads to the existence of more fluctuating treatment in the system. Thereby, the coercive field gets narrower with increasing temperature. In the following analysis, we give the hysteresis curves of the Cr2C monolayer as a function of the temperature in Fig. 9(b). Here, different symbols denote the different temperature values. The Cr2C structure has a rectangular-shaped hysteresis curve for the low-temperature values while it tends to evolve into an S-type hysteresis curve with increasing temperature. As noted before, the Sc2C monolayer has a FM character at ground state. The same analysis followed for Cr2C structure is applied for Sc2C...
monolayer in a magnetic field applied along the z direction. The obtained results are given in Figs. 9(e) and 9(d). Although temperature dependencies of the coercivity and remanence curves of the ScC system are qualitatively similar to those obtained for the CrC system, their temperature regions where they show a clear FM character differ from each other. In particular, the CrC monolayer shows a prominent hysteresis behavior whereas the ScC one does not reveal such kind of behavior around the room temperature. Figures 9(e) and Fig. 9(f) represent the hysteresis curves of the V2C and Ti2C monolayers, respectively. Here, external magnetic fields are applied along the x and z directions for V2C and Ti2C monolayers, respectively. It is obvious that all curves corresponding to varying temperature values are almost S type because the V2C and Ti2C monolayers have antiferromagnetic characters as discussed above. As a result of the orientations of the magnetic dipole moments in the materials, the total magnetization is almost zero around the origin. However, when the strength of the magnetic field gets bigger, they tend to change their directions along the applied field direction, leading to a nonzero total magnetization value.

In the following analysis, let us focus on the physical properties of the Janus structures considered in this study under the presence of an external magnetic field. In Fig. 10(a), we give the thermal variations of remanence magnetization and also coercivity treatment (which is depicted as an inset of the corresponding figure) of both CrVC Janus structure as functions of the temperature. As stated before, CrVC Janus structure has a ferrimagnetic character. Total magnetization has a nonzero value below the transition temperature because the magnitudes of the magnetic dipole moments of Cr and V atoms in CrVC structure are different from each other, and they do not cancel each other. Thereby, the total magnetization against the magnetic field curve shows a prominent hysteresis behavior. It should be noted that magnetic field is applied along the x direction. When the temperature increases, both the coercivity and remanence values decrease, as shown in Fig. 10(a). Further increment in the temperature leads to the destruction of the magnetic order in the material, and thereby the remanence magnetization and coercivity values become zero. Figures 10(b)–10(d) represent the hysteresis curves at various temperature values, which are denoted with different symbols. One of the most remarkable results is that the magnetization values belonging to Cr and V atoms have opposite signs despite there is an applied magnetic field. We note that the spin-spin interactions causing the existence of a ferrimagnetic behavior are responsible for the behavior observed here. Our numerical findings show that there is a strong competition between the Zeeman term and spin-spin interactions in the system. This can be seen by comparing Figs. 10(c) and 10(d) with each other. Figures 10(e)–10(h) display the hysteretic behaviors of CrScC Janus structure, which are typical behaviors for dilute magnetic semiconductors. External magnetic field is applied along the z direction. Although the similar discussions done above for CrVC case are also valid for the CrScC system, they are not given here for the sake of brevity. As a final investigation, we depict the hysteresis curves for the CrTiC system for some varying values of temperature in
FIG. 10. Variations of remanence magnetizations and coercive fields (which are given as insets) as functions of the temperature of the (a) CrVC and (e) CrScC structures. Hysteresis curves are displayed in (b), (c), and (d) for the CrVC structure while they are displayed in (f), (g), and (h) for the CrScC material, respectively. Different symbols shown in the hysteresis curves are corresponding to varying temperature values. We note that all curves depicted here are measured under the presence of an external magnetic field applied along the x and z axes for the CrVC and CrScC structures, respectively. The dashed lines are added to guide the eye.

Fig. 11. The magnetic field is in the y direction. Hence, only the y component of the total magnetization is plotted here. All hysteresis curves behave like an S-type since the CrTiC Janus structure has an AFM-stripy character discussed in Sec. III B.

IV. CONCLUSIONS

In summary, we used DFT and MC calculations to investigate the structural, electronic, and magnetic properties of 2D bare $M_2C$ and Janus $MM'C$ ($M ≠ M' = Cr, Ti, Sc, V$) MXenes. We found that 2D Janus $MM'C$ MXenes are dynamically and thermally stable. Investigated four bare $M_2C$ MXenes show metallic property by using DFT+$U$ calculations. However, created Janus $MM'C$ MXenes show unique electronic and magnetic properties. The CrScC MXene monolayer shows dilute magnetic semiconducting property which is a very important property for a wide variety of semiconductor and spintronic devices. CrScC has tiny band gap of 80 meV for its spin-down channel which are reminiscent of Dirac-type band dispersion, while there is a 0.58–eV band gap for the spin-up channel. In addition, CrVC has half-metallic band structure with a 0.27-eV band gap in the spin-down channel and metallic character for the spin-up channel. Although CrTiC shows metallic property for both spin channel in its band structure, it can easily turn to half-metallicity by external effects.

Our comprehensive DFT calculations show that Cr$_2$C and Sc$_2$C crystals have FM ground-state configurations while V$_2$C and Ti$_2$C ones display AFM-Néel states. The Cr-based Janus MXenes CrVC and CrScC represent ferrimagnetic orderings at zero temperature while the CrTiC one reveals an AFM-stripy magnetic configuration at ground state. It is worth noting that Cr$_2$C and Sc$_2$C crystals show FM characters when they are in the bare Janus MXene form. Interestingly, the CrScC Janus MXene derived from these two structures exhibits a FiM character, indicating a magnetic transition between FM and FiM phases. In order to elucidate the magnetic properties of the bare and Cr-based Janus MXenes, we undertake extensive Monte Carlo simulations with local update Metropolis algorithm. It should be underlined that the numerical results obtained from MC simulations very strongly confirm the findings obtained by DFT calculations. Most of the crystals studied in this study have transition temperatures above the room temperature, indicating a robust magnetic character. Remarkably, one of main conclusions is that while Cr$_2$C and Sc$_2$C have ferromagnetic spin orientations with $T_C = 2000$ and 226 K Curie temperatures, CrScC...
shows ferrimagnetic character with AFM-Néel spin orientation and undergoes a phase transition at $T_N = 1120$ K. As a final investigation, external magnetic field effects on the bare and Cr-based Janus MXenes have been probed in detail. It has been found that CrVC and CrScC systems have unusual and interesting hysteresis behaviors. The numerical outcomes composed of DFT and MC calculations are not only interesting from a theoretical point of view, they also show that Janus $M'M'C$ MXenes are promising candidates for future spintronic applications, which should encourage their synthesis.

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[53] Z. Tan, Z. Fang, B. Li, and Y. Yang, First-principles study of the ferromagnetic properties of Cr2CO2 and Cr2NO2 MXenes, ACS Omega 5, 25848 (2020).


[59] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevMaterials.5.083403 for Fig. S1: Total and atom projected electronic density of states for bare MXenes. Total electronic density of states of Cr2C which obtained with-out +U parameter is given in inset for comparison. Fig. S2: Total and atom projected electronic density of states for Janus MXenes.


