1. Introduction

Graphene with honeycomb structure has been synthesized as extremely thin layers by mechanical exfoliation because of the weak van der Waals out-of-plane interaction, also opens a new field for the two-dimensional (2D) crystal with the new physics [1–5]. 2D materials attracted intensive attention partially for their exotic properties. For example, 2D hexagonal boron nitride with a large bandgap of 4.64 eV is reported and possesses enormous potential in electronic and composite applications [6–11]. And Transition metal dichalcogenides (TMDs) with common structural formula MX2 (M = Mo, W, Ti, etc. And X = S, Se, Te) are found to show electronic properties varying from metals to wide-gap semiconductors with interesting physical characteristics [12–16]. For example, MoS2 possesses a transformation from indirect bandgap of bulk to direct bandgap of monolayer, leading to a promising luminescence quantum efficiency [12]. Besides, many other compositionally diverse 2D materials have been predicted and in some cases synthesized [17–22].

The intrinsic ferromagnetic (FM) semiconductors possess FM and semiconducting properties simultaneously with the fully spin polarization. Compared with diluted magnetic semiconductors, FM semiconductors exhibit tremendous advantages indeed in carrier injection, detection, sensors, magnetic storage and emergent heterostructure devices [23]. However, a few FM semiconductors have been reported up to now, resulting from the limitation of difficult synthesis in experiment. Furthermore, Mermin–Wagner theory illustrates the absence of intrinsic magnetization with 2D isotropic Heisenberg model at a finite temperature [24]. Yet recent studies have shown 2D magnetic crystals can also exhibit...
magnetism with an Ising model. For example, layer-dependent FM van der Waals crystal like Fe₃GeTe₂ with an out-of-plane magnetocrystalline anisotropy process a controllable Curie temperature \( T_C \) by an ionic gate, [29] and monolayer tridode chromium (CrI₃) is Ising FM material with out-of-plane spin orientation and the \( T_C \) of 45 K [30]. Also, nanosheets CrSiTe₃ showing indirect bandgap of 0.57 eV have been exfoliated successfully by Lin et al [25]. In addition, intrinsic long-range FM order in pristine Cr₂Ge₂Te₆ atomic layers has been reported that the \( T_C \) can be controlled by the very small magnetic fields (smaller than 0.3 T) [26]. Furthermore, the feasibility of exfoliation in experiment is confirmed by evaluating the cleavage energy to be very close to graphite [27]. \( T_C \) of monolayer CrSnTe₃ is determined as 170 K, higher than monolayer CrSiTe₃ and CrGeTe₃. This is attribute to the increased super-exchange coupling between the magnetic Cr atoms by enhanced ionicity of the Sn–Te bond [28].

Due to the 2D magnetism in above ABX₃-class materials, we use elemental substitution, one of the commonest experimental methods, to improve the physical properties. In this work, we investigate electronic and magnetic structures of monolayer CrGeS₃ based on first-principles calculations. The in-plane atoms of CrGeS₃ combine with each other by intense covalent bond while the weak van der Waals bonding exists between layers. Additionally, the cleavage energy is similar to graphene, therefore, we harbor the idea that CrGeS₃ can be exfoliated into monolayer successfully. Our results also demonstrate that monolayer CrGeS₃ is dynamically and mechanically stable. Moreover, the electronic calculations show that monolayer CrGeS₃ is FM semiconductor with the exchange splitting of 0.67 eV in spin-polarization band structure (2.21 eV by HSE06 calculations) and possesses bandgaps of 1.01 eV and 1.07 eV in spin-up and spin-down states, respectively. After that, the system shows FM ground state, originated from competition between direct and superexchange interactions. Finally, electronic exchange interaction and orbital hybridizations in monolayer CrGeS₃ crystal lead to the \( T_C \) of 161 K based on mean-field theory (MFT). The present results appear promising platform for studying fundamental spin behaviours and promote applications in ultra-compact spintronics.

2. Computational details

Electronic structure and magnetic properties were carried out using density functional theory (DFT) by the projector augmented wave (PAW) method as implemented in the Vienna \textit{ab initio} simulation package (VASP) [31, 32]. Perdew–Burke–Ernzerhof (PBE) was applied to handle with Exchange-correlation function [33]. The accurate exchange splitting was calculated using the Heyd–Scuseria–Ernzerhof (HSE06) functional including 25% non-local Hartree–Fock exchange [34]. Cut-off energy for plane wave basis was set up to 450 eV. The number of \( k \) points were set as \( 11 \times 11 \times 1 \) for the mono-layer structure. The partial occupancies were set for each orbital with Gaussian smearing and the width of smearing was set up to 0.05 eV. Note that the cutoff energy and the number of \( k \) points as well as the width of smearing were all tested to ensure that the parameters reached convergence (figure S1)\(^1\). The same test was applied in the choice thickness of vacuum slab as 15 Å to separate correlation between adjacent layers. A convergence criterion of \( 10^{-6} \) eV for total energy of electronic consistence loop was employed, and 0.01 eV Å\(^{-1}\) for Hellmann–Feynman force components in the ions relaxation loop. A supercell size of \( 3 \times 3 \times 1 \) unit cells is built and a convergence criterion of \( 10^{-3} \) eV and 0.001 eV Å\(^{-1}\) for ions sites and lattice relaxation to calculate the phonon spectrum by using the density functional perturbation theory (DFPT) [35]. There might be small negligible negative frequency near \( \Gamma \) points when calculate 2D materials, and the negligible negative can be removed by refining accuracy, building large supercell and employing small external strains [36].

3. Result and discussion

CrGeS₃ is a layered material crystallized in space group \( \text{R} \bar{3} \) (No. 148) and formed by stacks of S-(Ge,Cr)-S sandwich layers with lattice parameters of \( a = b = 6.05 \) Å [25]. Due to the smaller radius of S atoms than Te atoms, the lattice parameters of \( ab \) plane exhibit a shrinkage compared with \( a = 6.86 \) Å of CrGeTe₃ [37]. As shown in figure 1, the

\(^1\) See supplemental material for the width of smearing, band structures with HSE06 functional, the pDOS of Ge and charge density (stacks.iop.org/ JPhysCM/32/015701/mmedia).
monolayer hexagonal honeycomb structure is composed of a Ge$_2$S$_6$ with two Cr ions inserted between two-layers S planes. The monolayer unit cell is composed of two Cr$^{2+}$ ions and one [Ge$_2$S$_6$]$^{4-}$. Each Ge atom possesses three neighbouring S atoms forming a tetrahedron and two of Ge-centered tetrahedrons form a dumbbell-like Ge dimer in [Ge$_2$S$_6$]$^{4-}$ bipyramid. The innerlayer atoms are combined by strong covalent bond, while the weak van der Waals interaction exist between layers. Bonds length of Ge–Ge, Cr–S and Ge–S are 2.34 Å, 2.45 Å and 2.23 Å, respectively.

Cleavage energy is the energy required to cut bulk materials into two halves and is estimated by gradually increasing distance of the two parts (figure 2). The calculated $\Delta E$ gives $\Delta E = E_F - E_S$, where $E_F$ denotes the total energy of two fractured parts and $E_S$ denotes the energy of equilibrium system [27, 37–39]. The energy difference exhibits an abrupt growing below $d=4$ Å, while there is a sharp decrease of interaction between two parts. Then the energy difference achieves convergence at an ideal value of 0.35 J m$^{-2}$ (figure 2(c)). This cleavage energy of monolayer CrGeS$_3$ closes to 0.36 J m$^{-2}$ in graphene [40] and ensures the monolayer CrGeS$_3$ is feasible for experimental synthesis.

In order to check the dynamic and mechanical stability of the monolayer structure, the phonon spectrum and projected density of states of phonon are calculated as shown in figure 3, confirming the absence of imaginary phonon modes. Therefore, the results suggest that monolayer CrGeS$_3$ is dynamically stable.

The energetic stability of monolayer CrGeS$_3$ can be evaluated by formation energy $E_f$ as

$$E_f = \frac{E(\text{CrGeS}_3) - E(\text{Cr}) - E(\text{Ge}) - 3 \cdot E(\text{S})}{5} \quad (1)$$

where $E$ is the corresponding normalized energy for different structures. The negative $E_f$ of $-0.61$ eV indicates monolayer CrGeS$_3$ is energetically stable. For a further detecting mechanical stability, we also calculate the elastic constants $C_{11}$ and $C_{12}$ of monolayer CrGeS$_3$. The two independent parameters are given as,
Figure 4. Electronic band structures of monolayer CrGeS$_3$ obtained from PBE functional. (a) and (b) the electronic band structures of spin-up and spin-down. S, Cr and Ge are denoted as blue, cyan and red respectively. (c) and (d) the projected electronic band structures for spin-up and spin-down states of Cr atoms are denoted by blue, cyan and red for $s$, $p$, $d$ orbits respectively. (e) and (f) the corresponding projected electronic band structures of S atoms.
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\[ C_{11} = \frac{1}{A_0} \cdot \frac{\partial^2 E_{\text{tot}}}{\partial \varepsilon_{11}^2} \quad \text{and} \quad C_{12} = \frac{1}{A_0} \cdot \frac{\partial^2 E_{\text{tot}}}{\partial \varepsilon_{11} \partial \varepsilon_{12}} \]  

(2)

where \( E_{\text{tot}} \) is total energy per unit cell and \( A_0 \) is the equilibrium area of monolayer CrGeS3. The calculated \( C_{11} \) and \( C_{12} \) are 64 N m^{-1} and 17 N m^{-1}, respectively. It is evident that our results satisfy the Born criterion of stability \( (C_{11} - C_{12} \geq 0) \) [41].

For exploring into the electronic properties of monolayer CrGeS3, we plot the spin-polarized band structure as shown in figure 4. The conduction band minimum (CBM) locates at \( K \) points and the valence band maximum (VBM) locates at \( \Delta \) points (between \( K \) and \( \Gamma \) ), leading to the exchange splitting of 0.67 eV figure 4(a). A more accurate value is investigated as 2.21 eV based on HSE06 functional (see figure S2) [42]. The spin-up components exhibit similar mechanism of electronic interaction of conduction bands and valence bands with spin-up state, so the spin-up components are discussed here mainly (figures 4(a), (c) and (e)). The spin-up band structure possesses the bandgap of 1.01 eV. The conduction band originates from significant hybridization between empty \( d_p \) antibonding bands of Cr \( d \)-S \( p \) orbits at \( \sim 1 \) eV above the Fermi level when valence band is the fully occupied \( d_p \)-hybridized bonding states of Cr \( d \)-S \( p \) at about \(-0.5 \) eV under the Fermi level. The highly localized antibonding bands of Cr atoms are mainly composed of unoccupied, polarized \( d \) orbits. In comparison, an effective exchange interaction of the bonding-states Cr atoms is generated by the \( s-d \) hybridization. Additionally, the occupied Ge \( sp^3 \)-S \( p \) hybridization in spin-down channel (figures 4(b), (d) and (f)) results from the tetrahedral-coordinated Ge atom surrounded by three S atoms in \([Ge_2S_6]^{2-}\), so the Ge \( sp^3 \) hybrid orbits lead to bonding states of Ge \( sp^3 \)-S \( p \).

Figure 5. (a) Total density of states (DOS) of monolayer CrGeS3. (b) Project density of states (pDOS) of Cr and (c) S. In the pDOS plot, the upper panel represents for the spin-up components and the lower panel for the spin-down components. The Fermi level is set to zero.

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\[2\] See footnote 1.

3 See footnote 2.
interaction between two neighboring Cr atoms. This interaction leads to AFM as electrons partially fill d shells of Cr atoms (figure 6(a)). The other is superexchange interaction of Cr–S–Cr mediated by halogen S atoms (figure 6(b)). In such case, the bond angles of metal-halogen-metal (Cr–S–Cr) are nearly 90°. According to Goodenough–Kanamori–Anderson (GKA) rules, the superexchange interaction in the system exhibiting 90° metal-halogen-metal bond angels is always FM [49–52]. The competition between AFM and FM components can lead to different magnetic ground states, depending on the transition metal in 2D TMDs. In the superexchange interaction of Cr-based TMDs systems, two electrons must be excited from d shell of Cr atom to different p orbits of halogen S atoms (figure 6(c)). Since the d orbits of Cr atoms are partially filled, the electron excitation energy is small. As consequence, the neighboring Cr atoms prefer superexchange to direct interaction [53]. The calculation of monolayer CrGeS3 with the FM states shows that magnetic moment of S atoms with opposite spin-polarization to Cr atoms are 0.67 μB and the total magnetic moment of the unit cell remains 6 μB.

For magnetic materials, Curie temperature $T_C$ is a crucial parameter determining a temperature at which intrinsic magnetic intensity decrease to 0 and FM phase transforms into non-magnetic phase [46–48]. We main focus on predicting $T_C$ in accordance with MFT [54] as

$$T_C = \frac{2zJS(S+1)}{3k_B} \quad (3)$$

where $z = 3$ is the number of nearest-neighboring Cr atoms of a Cr atom in monolayer CrGeS3. J is the exchange coupling constant containing the nearest neighbour Cr atoms, $S = 3/2$ is the spin of each Cr atom, and $k_B$ is the Boltzmann constant. The value of $S$ is consistent with the magnetic moment of 3 μB for each Cr atom. We induce another term $E_{ex}$ as exchange energy between the two Cr atoms in a unit cell, defined as

$$E_{ex} = -2zJS^2. \quad (4)$$

The total energies of monolayer CrGeS3 primitive cell with the FM and AFM configurations $E_{FM}$ and $E_{AFM}$ can be calculated as well, and $E_{FM}/E_{AFM} = E_0 + E_{ex}$ [28, 55]. Where $E_0$ is the ground state energy without spin polarizations. Accordingly, the difference between $E_{FM}$ and $E_{AFM}$ gives $2E_{ex}$. As a result, we can obtain the exchange integral $J$ with the PBE functional as 1.85 meV. We further obtain $T_C$ of 161 K in monolayer CrGeS3. For comparison, the $T_C$ of CrGeTe3 with a similar structure via Monte Carlo (MC) simulation is 61 K [56]. Note that the MFT generally overestimates the $T_C$ [57] compared with MC simulations and we just provide a prediction of monolayer CrGeS3. The properties suggest that monolayer CrGeS3 have potential applications in spin-polarized carrier injection, detection, ultracompact spintronics, and also support a platform for studying electronic mechanism in 2D materials [27].

4. Conclusion

In summary, we have investigated the stability, electronic and magnetic properties of monolayer CrGeS3 based on

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3 See footnote 1.
4 See footnote 1.

Figure 6. (a) Spin density isosurface for AFM spin configuration and schematic diagram of direct excitations between neighboring Cr ions, the isosurface value is set to 0.011 Å$^{-3}$. (b) Corresponding spin density isosurface for FM and schematic diagram of superexchange interactions. (c) Mechanism of Cr–S–Cr superexchange interactions for a 90° bond angle.

To help a further understanding of the electronic structure of monolayer CrGeS3, we present the project density of states based on PBE functional (figure 5). The CrGeS3 crystal field splits the 3$d$ orbitals of Cr atoms into upper $e_g$ ($d_{z^2}, d_{xy}$) and lower $t_{2g}$ ($d_{xz}, d_{yz}, d_{xy}$) states, [42–44] as shown in figure 5(b). The prominent feature of the electronic structure is the fully occupied Cr $e_g$ bands at about -0.5 eV under the Fermi level and the empty spin-down $e_g$ orbitals of Cr atoms localizing at about 2.1 eV above the Fermi level, indicating a spin split between the localized Cr $e_g$ states. The bonding $dp\sigma$ hybridized states of Cr $e_g$-S $p$ and the unoccupied Cr $t_{2g}$-Ge $p$ hybridization results in VBM and CBM (figure S3)$^3$. Apart from this, each $e_g$ orbit of Cr atom hybridizes significantly with $S$ $p$ states, forming a bonding and antibonding pair bonds of Cr $e_g$-S $p$ (figure S4)$^4$. But the weaker $dp\sigma$ bonding gives rise to the localized Cr $t_{2g}$ states, which is agreed with former research on ABX3 type transition metal tri-chalcogenides [45].

Now we estimate the magnetic property of monolayer CrGeS3. The results show the AFM state possesses a higher energy about 50 meV than FM state. The hexagonal crystal structure renders the magnetic state governed by significant competition between two mechanisms. One is the direct

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first-principles calculations. Firstly, it is found that monolayer CrGeS\textsubscript{3} exhibits dynamical and mechanical stability and could be successfully synthesized due to the similar cleavage energy to graphene. Then our results show the exchange splitting of 0.67 eV (2.21 eV based on HSE06 functional). Also, bandgaps of spin-up and spin-down states are 1.01 eV and 1.07 eV, respectively, which result from the interaction between bonding $dp\sigma$ hybridized states of Cr $eg\text{-}S\ p$ and unoccupied bonds of Cr $t_{2g}\text{-}Ge\ p$. After that, honeycomb structural monolayer CrGeS\textsubscript{3} exhibits FM ground state with magnetic moment of 6 $\mu_B$ per unit cell. The reason for the magnetism is the competition mechanism between superexchange FM interactions and direct exchange AFM interactions. Further, the FM originated from superexchange interactions between neighboring Cr atoms plays a major role compared with direct exchange. In addition, we roughly estimate the $T_C$ of magnetic transition as 161 $K$ by MFT. Our results illustrate that the magnetism could be successfully synthesized due to the similar cleavage energy to graphene. Then our results show the exchange splitting of 0.67 eV (2.21 eV based on HSE06 functional).

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