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Two-dimensional Janus transition-metal dichalcogenides with intrinsic ferromagnetism and half-metallicity

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ABSTRACT

Searching experimental feasible two-dimensional (2D) ferromagnetic crystals with room-temperature magnetic order and high spin-polarization is one key for the development of next-generation spintronic devices. Inspired by the recent experimental achievement for the synthesis of Janus MoSSe monolayer with out-of-plane symmetry, here, by *ab initio* calculation, we demonstrate this feasibility with the discovery of intrinsic 2D ferromagnetic Janus TMDs monolayer (TMXX′, TM = V, Cr and Mn; X, X′ = S, Se and Te, X ≠ X′) with large spin-polarization and high Curie temperature. Particularly, the MnSSe monolayer show half-metal with 100% spin polarization and wide half-metallic gap. A Curie temperature as high as 400 K has been found for VSSe materials. The formation energy calculation for Janus TMDs can be comparable with the TMDs monolayer. The dynamical stability for these 2D crystals also have been confirmed by phonon spectrum calculation. Our study presents a new class of 2D magnetic materials for future spintronics and valleytronics.

1. Introduction

Spintronics, which uses intrinsic spins freedom of electrons as information storage, transportation and processing, is one of the most promising next generation information technologies because of low-power operation, high-speed, and spin transistors [1–3]. Two-dimensional (2D) materials bring wide interest after exfoliated graphene from graphite by using the mechanical cleavage method [4]. Upon the novel physical, optical, and electronic properties of graphene [5], exploring other free-standing 2D materials and their potential applications [6–9] have attracted great attention. However spintronic applications of 2D materials are limited due to their intrinsically non-magnetism [10]. In practice, defects and transition-metal dopants can induce a high spin-polarization and magnetic effects in various 2D materials, but the distributions of dopants or defects cannot be easily controlled experimentally [11,12]. Thus, finding new intrinsic 2D magnetic materials with high spin-polarization will be crucial for spintronics [13,14]. Recently, some 2D magnetic materials with intrinsic magnetic order and high spin-polarization have been widely studied, such as transition-metal halide [11,14–18], MXenes [12,19–22], 2D $CrATe_3$ (A = Si, Ge and Sn) [23,24] and chromium oxyhalid monolayer [25], which shows potential application in spintronic devices. Among them, 2D half-metal (HM) materials with 100% spin-polarization have been predicted, which can be used as potential spin filter materials. Particularly, the 2D ferromagnetism have been discovered experimentally for the first time in atomically-thin 2D CrI_3 and $Cr_2Ge_2Te_6$ [13,14], opening the door for 2D spintronic application. Nevertheless, despite tremendous efforts, finding and designing new intrinsic 2D magnetic materials are still a great challenge.

2D transition metal dichalcogenides (TMDs) are mostly semiconductors of the type MX_2 [26]. M is a transition metal atom (such as Mo or W) and X is a chalcogen atom (such as S, Se or Te). MoS_2 is the most studied material in this family because of its stability as well as unusual electronic and optical properties [27–29]. TMDs exhibit a unique combination of atomic-scale thickness, strong spin-orbit coupling and favorable electronic and mechanical properties, which are attracting wide attention for fundamental studies and applications in electronics, spintronics, optoelectronics, and valleytronics [30,31]. Most TMDs is intrinsic non-magnetism except for VX_2 and CrX_2 and MnX_2 [32,33]. The tensile strain, hydrogenation, adsorption and vacancy have been performed for inducing the magnetism and spin-polarization in TMDs [34–38]. However, such approaches are still great challenge to realize experimentally ordered spin structure and high magnetic order temperature because the cluster effects of absorbed atoms and uncontrolled distribution of defect and dopant as well as the large strain requirement. For this reason, the search for 2D magnetic TMDs is of great importance for both fundamental interest and device applications but it is still challenge.

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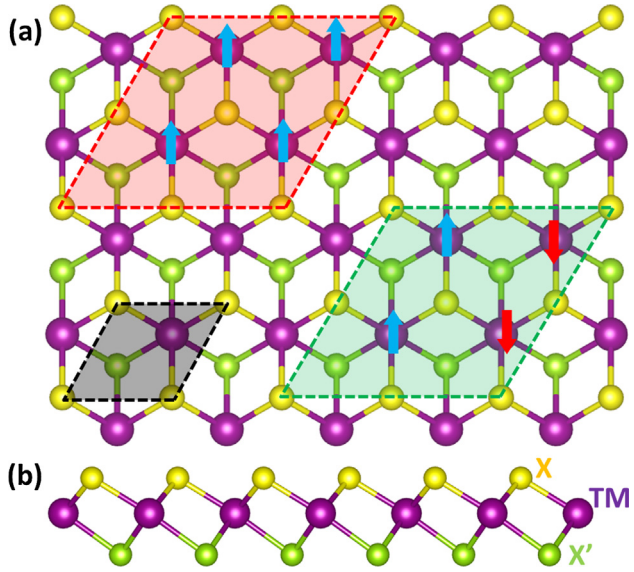

Fig. 1. A top (a) and a side (b) view of Janus TMXX′ (X, X′ = S, Se and Te) the color scheme for TM, X and X′ atoms is described in the figure. The rhombic unit cell is marked by a black dotted line, while FM and AFM states are marked by red and green dotted lines, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

By controlling the stoichiometric ratio of chemical vapor deposition (CVD) grown MoS_xSe_{2-x} [39], WS_xSe_{2-x} [40], and $Mo_xW_{1-x}S_2$ alloys [41], their optical and electrical properties of monolayers can be tuned. Based on those materials with tuning physical and chemical properties, in particular the stable MoS_2 monolayer, a synthetic strategy of growing Janus monolayers of TMDs breaking the out-of-plane structural symmetry is performed by top-layer S atoms fully replaced with Se atoms [42,43]. And they are proved the existence of vertical dipoles. Upon semiconducting characters and vertical dipoles, heterostructures of Janus MoSSe and WSSe [44], and MoXY (X/Y = O, S, Se and Te, X ≠ Y) [45] with an intrinsic dipole have been proposed as efficient photocatalysts for water splitting. Cheng et al. [46] also proposed that the Rashba splitting can be caused by the broken mirror symmetry in Janus MXY (M = Mo, W and X, Y = S, Se, Te), indicating the potential application for Janus TMDs in valleytronics. However, Mo/W-based Janus TMDs are intrinsic non-magnetism. Naturally a question arises: can the Janus TMDs with intrinsic ferromagnetism and high spin-polarization be achieved when Janus TMDs contained magnetic atoms of V, Cr and Mn? In this paper, we systematically investigated the geometry, stability, electronic and magnetic properties of VXX′, CrXX′ and MnXX′ (X, X′ = S, Se and Te, X ≠ X′). Results indicates that TMXX′ (TMXX′, TM = V, Cr and Mn) show robust ferromagnetic ordering large spin-polarization and high Curie temperature. The MnSSe represent half-metal with 100% spin polarization. The dynamical stability for all Janus TMDs are confirmed by phonon spectrum calculation. Various magnetic and electronic properties of Janus TMXX' are desirable for future spintronic applications.

2. Method and computational details

All calculations are performed using the Vienna *ab initio* simulation package (VASP) [47,48] within the generalized gradient approximation employing the Perdew-Burke–Ernzerhof (PBE) exchange-correlation functional. Interactions between electrons and nuclei are described by the projector-augmented wave (PAW) method [49]. The criteria of energy and atom force convergence are set to 10^{-5} eV/unit cell and 0.01 eV/Å, respectively. The Brillouin zone (BZ) is sampled using 15 × 15 × 1 and 21 × 21 × 1 Gamma-centered Monkhorst-Pack grids for the calculations of relaxation and electronic structures, respectively. For the magnetic structure calculation, the Hubbard "U" correction is employed within the rotationally invariant DFT + U approach proposed by Dudarev et al. [50] A correction of U = 3 eV is employed based on the relevant previous reports [51]. The phonon frequencies were calculated by using a supercell approach as implemented in the PHONOPY code [52,53].

3. Result and discussion

3.1. Geometric properties and stability of Janus TMXX′

TMXX′ (TM = V, Cr and Mn; X, X′ = S, Se and Te, X ≠ X′) possess the structures composing of one TM atom layer sandwiched by two different chalcogen atoms (S, Se, and Te) on two sides (Fig. 1), *i.e.* on the basis of a TMX_2 monolayer, the Janus TMXX′ monolayer is obtained by fully replacing the toplayer X with X′ atoms. After replacing one X layer by a X′ layer, nine types of Janus TMXX′ structures are formed, and the optimized lattice parameters are shown in Table 1. Our calculated lattice parameters for TMSSe, TMSTe, and TMSeTe increase with the increasing atomic radius of chalcogen atoms. It is found that the optimized lattice parameters of Janus TMXX′ structures are very close to half of the lattice parameters of TMX_2 plus TMX'_2. Meanwhile, the bond lengths of TM-X and TM-X′ in Janus TMXX′ are almost the same as those in pristine TMX_2 and TMX'_2 structures. The corresponding TM-X and TM-X′ bond lengths are shown in Table 1. The difference in atomic size and electronegativity of X and X′ breaks the pristine TMDCs structural symmetry and gives rise to inequivalent TM–X and TM–X′ bond lengths. To determine the preferred magnetic ground state structures of TMXX′ systems, the collinear FM and AFM states are considered as shown in Fig. 1a. Their magnetic properties will be discussed later.

To make sure the stability of TMXX′, the formation energy (E_f) is defined by $E_f = E(TMXX') - E(TM) - E(X) - E(X')$, where E(TMXX′) is total energy of TMXX′ at DFT level, E(TM), E(X) and E(X′) is energy of TM, X and X′ single atoms in the 15 × 15 × 15 $Å^3$ box. E_f of TMXX′ can be sorted by metal atoms: MnXX′ > VXX′ > CrXX′. We also calculated the formation

Table 1
The calculated geometry structure parameter and electronic and magnetic properties. L is the lattice constant (in Å). d_{TM} is the bond length (in Å). E.S. represent the electronic structure. J is the magnetic exchange energy. Tc is Curie temperature (in K). M_{tot} is the total magnetic moment (in μ_B).

Structure	L (Å)	d_{TM-S} (Å)	d_{TM-Se} (Å)	d_{TM-Te} (Å)	E.S.	J (meV)	Tc (K)	M_{tot} (μ_B)
VSSe	3.413	2.389	2.538	–	HM	5.16	420	1.05
VSTe	3.528	2.368	–	2.907	M	2.04	165	1.76
VSeTe	3.597	–	2.519	2.793	M	3.83	310	1.45
CrSSe	3.384	2.352	2.608	–	M	2.63	215	2.55
CrSTe	3.478	2.356	–	2.873	M	3.04	250	2.91
CrSeTe	3.565	–	2.497	2.849	M	2.35	190	2.81
MnSSe	3.533	2.394	2.520	–	HM	2.27	185	3.00
MnSTe	3.623	2.399	–	2.782	M	1.07	85	3.29
MnSeTe	3.704	–	2.537	2.772	M	1.43	115	3.23