Engineering the electronic and magnetic properties of monolayer TiS_2 through systematic transition-metal doping

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Layered materials that exhibit magnetic ordering in their pristine form are very rare. Several standard approaches, such as adsorption of atoms, introduction of point defects, and edge engineering, have been developed to induce magnetism in two-dimensional materials. In this way, we investigate the electronic and magnetic properties of monolayer TiS_2 doped with 3d transition metals (TMs) atoms in both octahedral 1T and trigonal prismatic 1H structures using first-principles calculations. In its pristine form, TiS_2 is a non-magnetic semiconductor. The bands near the Fermi energy primarily exhibit d orbital characters, and due to the presence of ideal octahedral and trigonal arrangements, they are well separated from other bands with p character. Upon substituting 3d-TM atoms in both structures, a variety of electronic and magnetic phases emerge, including magnetic semiconductor, magnetic half-metal, non-magnetic metal, and magnetic metal. Chromium exhibits the largest magnetic moment in both the 1T and 1H structures. The 1T structure shows a slightly higher magnetic moment of 3.419 μ_B compared to the 1H structure 3.138 μ_B , attributed to the distorted octahedral structure of the 1T structure. Unlike pristine TiS₂, the deficiency in saturation of neighboring S atoms in the presence of impurities leads to the proximity of energy levels of d and p states, resulting in unexpectedly sizable magnetic moments. Another interesting case is Cobalt, which leads to a magnetic moment of approximately 0.805 μ_B in the 1H structure, while the Co exhibits a non-magnetic state in the 1H structure. These materials demonstrate a high degree of tunability and can be optimized for various magnetic applications.

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I. INTRODUCTION

The synthesis of graphene has been highly successful, sparking significant interest in other two-dimensional materials because of their unique properties and wide range of potential applications [1–3]. This interest has led to the discovery of numerous two-dimensional materials with exceptional properties and diverse applications. Among these structures, transition metal dichalcogenides (TMDs) are particularly intriguing. TMDs have the chemical formula MX₂, where M represents a transition metal (TM) and X denotes a chalcogen (S, Se, Te, or combinations) [4–7]. The bonds between layers in TMDs are van der Waals, allowing for the production of single or multiple layers through various methods. For example, techniques like chemical vapor deposition (CVD) [8, 9] and mechanical exfoliation [10, 11] are commonly employed. One notably fascinating TMD is titanium disulfide TiS_2 . In its bulk form, TiS_2 behaves as a semimetal with pronounced anisotropy. However, when exfoliated to a few layers, TiS_2 displays a range of intriguing phenomena. TiS₂ has attracted significant attention due to its potential applications in hydrogen storage [12], Lithium-Ion batteries [13–15], favorable thermal properties in thermoelectric materials [16–18], and its useful optical characteristics [19–21]. Additionally, the examination of magnetic properties in TMDs is often

conducted alongside investigations into these compelling physical properties.

Layered materials that naturally display magnetic ordering in their pristine form are rare. Among the vast number of 2D materials, only CrX₃(X=Br,I) [22-25], $Cr_2Ge_2Te_6$ [26], M_2C (M=Cr, Fe) [27], and VX_2 (X=Se,Te) [28–30] have been experimentally observed to exhibit magnetic orderings. Therefore, various innovative techniques have been employed to enhance or induce magnetic properties in 2D systems such as adsorption of atoms [34], introduction of point defects [35–37], and edge engineering[38]. In the case of TMDs, Yan Zhu et al. [31] recently published a study on the influence of vacancy defects on the magnetic characteristics of VSe₂. Through a systematic investigation, the magnetic properties of PtSe₂ were analyzed by removing platinum and selenium atoms. The findings revealed that removing the platinum atom resulted in magnetization of the system, while the elimination of the selenium atom had no impact on the system's magnetism [32]. Moreover, researchers explored the effects of vacancies in Mo atoms on the magnetization of $MoSe_2$, $MoTe_2$, and WS_2 . The research revealed that removing Mo atoms solely in MoSe₂ led to the generation of magnetic moments [33].

Another approach to induce the magnetic properties of materials involves incorporating other TMs, particularly 3d elements, as dopants in the structure of TMDs. Replacing the Mo/W atom with Mn, Fe, Co, Ni, Cu, or Zn atoms stabilizes the Mo(W)S₂ monolayer and introduces magnetic properties to the compound. However, elements like Sc, Ti, V, and Cr, which have fewer

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FIG. 1. Orbital projected band structure and density of state (PDOS) for (a) 1H structure of single layer of TiS_2 and (b) 1T structure of single layer of TiS_2 . Top and side view crystal structure of (c) 1H structure and (d) 1T structure. The Fermi level is set to zero energy.

valence electrons than Mo, do not induce any magnetic moment [40, 41]. Introducing certain 3d atoms into the ZrS_2 monolayer instead of the Zr atom disrupts the symmetry of the upper and lower spins, resulting in a blend of magnetic properties [37, 42]. In another theoretical study by Yang et al., replacing W atoms with 3d elements like Zn, Cu, Ni, Co, Fe, and Mn in the single-layer of WS_2 triggers the emergence of magnetism in the system. Notably, the Ni atom generates the most significant amount of magnetism [43]. Studies on the substitution of 3d TMs and the investigation of magnetism and its origins in various TMDs, including CrS₂, HfS₂, and WSe₂, have been documented [44–46]. Yue et al. explored magnetic anisotropies in Mn, Fe, and Co-doped monolayer MoS_2 [47]. Furthermore, Chowdhury et al. [48] conducted a comprehensive investigation into the electronic structure of 3d, 4d, and 5d TM-doped WSe₂ monolayers. Several studies have analyzed the magnetism of materials in relation to their respective structural phases. For example, Ataca et al. conducted a systematic examination of the magnetism of VX₂ (X=O, S, Se, Te) in two structures, octahedral 1T and trigonal prismatic 1H, revealing that this material maintains its magnetic properties across both structures [49].

While research on the magnetic properties of TMDs has been conducted, studies on the magnetization of TiS_2 monolayers are limited. Titanium disulfide is the lightest compound among the Group-IV TMDs. In a singlelayer, TiS₂ has a band gap of 0.05 eV (0.9 eV) in 1T (1H) structure [see Figs. 1(a) and 1(b)]. The spatial and structural arrangement of these two structures is illustrated in Figs. 1(c) and 1(d). In both structures, a layer of titanium atoms is sandwiched between two layers of sulfur atoms. In 1T-TiS₂, each titanium atom is surrounded by six sulfur atoms in an octahedral arrangement, while in 1H-TiS₂, the coordination is trigonal prismatic.

Studying the substitution of 3d TM in non-magnetic

semiconductor TiS_2 provides a fundamental insight into the origin of magnetic properties in two-dimensional systems. The variation in crystal field splitting of d levels induced by neighboring chalcogen S atoms in the 1H and 1T lattices results in distinct correlated subspaces. This, in turn, elucidates the impact of orbital orientation on diverse magnetic ordering phenomena. This research delves into the electronic and magnetic characteristics of TiS₂ with the inclusion of V, Cr, Mn, Fe, Co, Ni, Cu, and Zn atoms as impurities in both the 1H and 1T phases using first-principles density functional theory (DFT). Our calculations suggest that Cr impurity is the most suitable candidates for magnetizing the system, exhibiting magnetic moments of around 3.1-3.5 μ_B . The local magnetization of early TM impurities such as V, Cr, Mn are higher in the 1T structure than in the 1H one. In the case of Cr/Mn-doped TiS_2 in the both structures, there are d_{z^2} and $d_{x^2-y^2}/d_{xy}$ impurity levels with a narrow bandwidth of approximately 0.4 eV. Due to the large DOS of Mn and Cr atoms at the Fermi energy (E_F) in both 1T and 1H structures, they can be unstable to the magnetic ordering, which is reasonably consistent with our results of spin-polarized total energy calculations and the sizable magnetic moments. The average magnetization of the six S atoms positioned as nearest neighbors to the impurity. as well as the magnetization of the closest Ti atom to the impurity, ranges between -1.3 to 0.7 μ_B . This suggests a delocalized magnetization that spreads across multiple atoms. In the 1H structure, the neighboring atoms exhibit significantly higher magnetization compared to the 1T structure, indicating a smaller charge transfer from the impurities to their neighbors in the 1H phase.



FIG. 2. (Color online) (a) Octahedrons of the single 1T-TiS_2 layer. The tilted octahedral axis is in z' direction and one of its faces lie on xy plane. (b) Spatial arrangement of ligands S in a conventional octahedral structure. (c) Crystal field splitting of the 3d orbitals of Ti atoms in conventional octahedral structure. The d-orbital splits into two different levels. The bottom three energy levels are named d_{xy} , d_{xz} , and d_{yz} (referred to as t_{2g} states). The two upper energy levels are named $d_{x^2-y^2}$, and d_{z^2} (referred to as e_g states). (d) The non-magnetic projected DOS for d orbital of Ti atom in the 1T structure. The Fermi level is set to zero energy. (e) Crystal field splitting of the 3d orbitals of Ti atoms in tilted octahedral structure of 1T-TiS_2 .

II. COMPUTATIONAL METHOD

For DFT calculation we have used pseudopotential Quantum Espresso code [50] based on plane wave basis set within the generalized gradient approximation in the Perdew-Burke-Ernzerhof (PBE) parameterization [51]. Simulation of both pristine and impurity doped TiS_2 unit cells is based on the slab model having a 25 Å vacuum separating slabs. First, the structural properties after the ionic relaxations such as lattice parameters, x, y, and z component of the Ti, TM, and S atoms in crystal coordinates are extracted. The uniform k-point grids of $36 \times 36 \times 1$ $(12 \times 12 \times 1)$ are used for the selfconsistent field calculations of pristine TiS₂ (TM-doped TiS_2). The Kinetic energy cut-offs for the wavefunctions and the charge density are 850 and 8500 eV, respectively. For each systems, the Broyden-Fletcher-Goldfarb-Shanno quasi-Newton algorithm is used to relax the internal coordinates of atoms and possible distortions with convergence threshold on forces for ionic minimization as small as $10^{-4} \text{ eV} \text{\AA}^{-1}$. We construct a $4 \times 4 \times 1$ supercell based on the primitive cell of Figs. 1(c) and 1(d) to investigate the 3d-TM substitution in TiS₂.

III. RESULTS AND DISCUSSION

A. pristine TiS_2

First, we analyze and compare the electronic properties of a single layer of TiS_2 in both 1H and 1T structures. Fig. 1(a) presents the projected band structure, as well as the density of 3*d*-Ti and 3*p*-S states for 1H structure. The band structure of $1H-TiS_2$ reveals a semiconductor nature with an estimated gap of 0.76 eV. Fig. 1(b) displays the corresponding projected electronic structure for the $1T-TiS_2$ configuration, where the energy bands intersect the Fermi energy level partially at the Γ point. Our spin-polarized calculations show no variation in the density of high and low spin states for these structures, indicating the absence of magnetic properties. Analysis of the band structure and density of states graphs highlights the significant contribution of the 3p orbital of S atoms to the valence band region near the E_F in both structures, while the 3d orbital of Ti dominates in the conduction band region. A simple model provides insight into the electron filling mechanism, serving as a foundational framework for reviewing all samples in this study. Initially, we examine the electronic configuration of isolated Ti and S atoms. The outer electronic shell of a Ti atom is represented by $4s^2 \ 3d^2$, while an S atom is denoted by $3s^2 3p^4$. Each sulfur atom requires two electrons to complete its final shell, following the rule of eight. These electrons can be acquired from three neighboring titanium atoms, with each sulfur atom gaining approximately two-thirds electrons from each titanium atom due to its higher electronegativity. Conversely, there are six S atoms surrounding each Ti atom, necessitating each Ti to lose three or four electrons to the six S atoms. According to this model, after bond formation, the 4s and 3d orbitals of Ti atoms are expected to be nearly empty due to the completion of the $4s^2$ $3d^2$ outer shell. The DOS depicted in Figs. 1(a) and 1(b) corroborate these findings, illustrating a covalent bond between S and Ti atoms through hybridization of the 3p orbital of S and the 3d orbital of Ti.

A comprehensive understanding of TMD structures necessitates the consideration of the crystal field effect on the *d*-orbitals of TMs. The significance of the crystal field in the splitting of the 3*d* orbitals within these structures is crucial, particularly when impurities are introduced into the system. When *d* orbitals are situated in a crystal environment, the degeneracy of the *d*-orbitals is disrupted. In a 1H crystal environment, the five *d*orbitals are categorized into three groups: two degenerate d_{xz}/d_{yz} orbitals, two orbitals $d_{xy}/d_{x^2-y^2}$, and single d_{z^2} orbital.

In 1T structure, the octahedron is not like the conventional perovskite octahedral structure. The octahedron is tilted with respect to the standard Cartesian coordinate xyz, in such a way that the 4-fold rotation axes is in the z' direction. As shown in Fig. 2(a), in fact, one of the eight triangles of octahedron is lying on the floor and the z axis is perpendicular to this triangle.

A conventional octahedral structure is depicted in Fig. 2(b) and its energy levels are presented in Fig. 2(c). When examining the untilted octahedral crystal 1T structure, it is crucial to consider that the z-axis of the conventional octahedron is perpendicular to the monolayer. So, in a rotated primed coordinates x'y'z', the octahedral crystal environment is conventional, and d orbitals segregate into two groups: $e_g (d_{z'^2}, d_{x'^2-y'^2})$ and $t_{2g} (d_{x'y'}, d_{x'z'}, d_{y'z'})$. In the real 1T structure of TiS₂, chalcogen atoms [marked 2 to 5 in Fig. 2(a)] form a plane where the z-axis is not perpendicular to this plane. It is important to note that calculations in this structure were carried out using the xyz coordinate system; thus, the results may not align with those of the primed coordinate system. In the xyz coordinate system, the dual separation of energy states, namely e_q and t_{2q} is not well defined. In this context, our findings are akin to those in reference [52–54], where states are divided into a_1 , e_1 , and e_2 , as illustrated in Fig. 2(d). This distribution resembles the trigonal prismatic state rather than the octahedral structure as shown in Fig. 2(e). It means, these outcomes stem from the misalignment of the cartesian coordinate system when dealing with the tilted octahedral structure. Further examination will be conducted when analyzing impurities to provide a more comprehensive analysis.

B. Electronic and magnetic properties in the presence of 3d transition metals

Now we investigate the impact of substituting 3d TMs on the electronic and magnetic properties of both nonmagnetic $1H-TiS_2$ and $1T-TiS_2$ monolayer structures. Initially, the total energy difference between the magnetic (E_{sp}) and non-magnetic ground state (E_{nsp}) of the monolayers substitution with 3d TMs is calculated. This energy variance is determined using $\Delta E_{spin} = E_{sp} - E_{nsp}$. Table I presents the total energy difference between the magnetic and non-magnetic ground states of the monolayers following substitution with various TMs. A negative difference signifies a magnetic ground state. The numerical outcomes reveal that ΔE_{spin} for V, Cr, Mn, Fe, and Cu-doped monolayers is negative in both structures, indicating a magnetic ground state for systems doped with these impurities in both crystal phases. ΔE_{spin} for Sc and Ni-doped monolayers is zero, suggesting that substituting Sc and Ni does not induce magnetism in either structure. However, the ground state of Co and Zn-doped monolayers is non-magnetic in 1T structure and magnetic in 1H structure. Following the substitution of TM atoms in both structures, a variety of electronic and magnetic phases emerge, including magnetic semiconductor, magnetic semi-metal, non-magnetic semiconductor, nonmagnetic metal, and magnetic metal. This structural diversity underscores the significance of this research. Further investigation delves into the magnetic moments of

the impurity atom and its first six neighboring atoms. To explore the causes of magnetization in monolayers substituted with TMs, we will initially conduct a comprehensive examination of alloying with Cr atom due to its highest magnetic moment. Subsequently, we will closely analyze the presence of Co atom impurity, which is nonmagnetic in the 1T structure and magnetic in the 1H structure, to elucidate the reasons behind this magnetic behavior. Finally, we discuss the rest of the magnetic systems.

C. Cr-doped TiS₂

The numerical values of the magnetic moment of Cr in Table I suggest that the magnetic properties arise from the introduction of Cr impurities. The presence of Cr atoms as impurities results in the largest magnetic moment among 3d TM impurities in both structural phases. From a magnetic perspective, the 1T structure exhibits a higher magnetic moment compared to the 1H struc-



FIG. 3. (Color online) (a) The non-spin polarized projected DOS for *d* orbital of Cr atom in the 1T structure of Cr-doped TiS₂. The spin polarized projected DOS in the 1T structure of Cr-doped TiS₂ for (b) d_{z^2} (a_1), (c) $d_{xy}/d_{x^2-y^2}$ (e_1), and (d) d_{xz}/d_{yz} (e_2) orbital characters. The Fermi level is set to zero energy. (e) Crystal field splitting of the 3*d* orbitals of Cr atoms in Cr-doped tilted octahedral structure of 1T-TiS₂ in presence of exchange splitting. (f) Spin polarization around impurity Cr in 1T structure of TiS₂. Size of the arrows in the figure indicate the values of spin density distribution in presence of Cr.

ture. To further elucidate the electron configuration in the presence of Cr atoms, we apply a simplified model similar to the one used for the pristine form. Prior to bond formation, the valence shell of the Cr atom consists of $4s^1 \ 3d^5$ electrons. Suppose Cr donates the same number of electrons as the Ti atom when it replaces the Ti atom in the structure. With this assumption, and taking into account the full saturation of the sulfur atoms, the expected magnetic moment is approximately 2 μ_B which is 1-2 μ_B smaller than the calculated magnetic moments of 3.138 μ_B for the 1H state and 3.419 μ_B for the 1T state.

To provide a clear and accurate explanation of this magnetic moment difference, we delve into two fundamental physical phenomena: the splitting of the d orbitals of the Cr atom due to a crystal field and the spin exchange interaction. The spin exchange interaction involves the alignment of spins of electrons in the *d* orbitals. contributing to the overall magnetic moment of the Cr atom. We start by using a non-spin calculation with the generalized gradient approximation (GGA) method to examine the splitting of the 3d orbitals of the Cr atom in the crystal field created by sulfur ligands in the 1T and 1H structures. Contrary to our initial assumption of four electrons loss and complete saturation of neighboring sulfur atoms, Figs. 3(a) and 4(a) show that at least three electrons remain in the 3d orbital for chromium atoms in the both 1H and 1T structures. Comparing the occupied states in the 1H and 1T structures reveals that the Cr atom has lost fewer electrons in the 1T state, a trend also observed in the study of Co impurity. This observation could explain the slight increase in magnetic moment in the 1T structure compared to the 1H structure, as discussed further in our analysis.

Our non-spin electronic structures show that the correlated states, including d_{z^2} (a_1) , $d_{xy}/d_{x^2-y^2}$ (e_1) in 1H (1T), are partially filled with nearly 3-4 electrons, while the d_{xz}/d_{yz} (e₂) states are unoccupied. The energy splitting between filled and empty bands, or crystal field splitting, is approximately $E_{CF} = 2.2 \text{ eV}$. Cr-doped TiS₂ exhibits a large $D(E_F)$ due to its partially filled electronic states with a very small bandwidth. The total bandwidth of correlated subspace in the case of Cr is around $W_b = 0.65 \text{ eV}$, significantly smaller than the bandwidth of corresponding states in Ti. The flat bands formed in the presence of these impurities can create the necessary conditions for correlated phase such as magnetism. Electrons exhibit correlated behavior in this state, and considering the Hubbard U interaction can enhance the accuracy of the calculation. However, the calculation of such complex magnetic ground states using the GGA+Umethod is beyond the scope of this paper.

To deepen our comprehension of state fillings, calculations incorporating the spin effect should be conducted using the spin-polarized generalized gradient approximation (SGGA) method. The spin exchange interaction plays a critical role in further splitting the levels, laying the groundwork for estimating the high magnetic moment of the Cr atom and similar systems. The outcomes of these calculations are illustrated for the 1T and 1H structures in Figs. 3(b)-3(d) and Figs. 4(b)-4(d), respectively. Notably, a significant energy gap between the spin-up and spin-down states is evident in both structures when accounting for the spin effects.

We can anticipate a significant exchange splitting in the magnetic calculations due to the sharp peaks of the DOS at E_F in the non-magnetic calculation for the Crdoped TiS_2 compound. As illustrated in Figs. 3 and 4 for the spin-polarized calculation, the spin splitting of the partially occupied states ranges between 5-6 eV. For example, the energy difference between the occupied spinup peak and the spin-down peak a_1 in 1T structure is 6 eV. In this scenario, the exchange energy E_{ex} and the crystal field splitting $E_{C}F$ are two competing effects. The Cr-doped TiS_2 exhibits a higher exchange energy compared to its crystal field splitting energy, resulting in states with a high spin configuration. The spin-polarized DOS indicates that the number of electrons in the d level is three to four, consistent with the magnetization of 3.1 μ_B and 3.5 μ_B as reported in Table I for 1H and 1T respectively. Additionally, Table I reveals a large magnetic moment of -1.33 μ_B on the S atoms in close proximity to the impurity in 1H structure, suggesting that the nearest neighbor atoms of the Cr atom are not fully saturated. The magnetization on Ti atoms $m_{Ti}=0.35 \ \mu_B$ suggests that this spin-polarization does not only originate from the Cr in the 1H structure, indicating significant hybridization between impurity Cr and host Zr/S electrons.

D. Co-doped TiS_2

In this section, we will delve into the electronic and spin properties resulting from Co substitution. It's important to note that the motivation behind this study stems from the dual behavior exhibited by Co impurities. With the introduction of this impurity atom, the 1T structure preserves its non-magnetic state, while the 1H structure displays a moderate magnetic moment of around 0.805 μ_B . Initially, the Co atom possesses a $4s^2$ $3d^7$ configuration before bonding. To accurately ascertain the electron loss from the 3d shell of the Co atom and the orbital arrangement in the presence of the crystal field, the PDOS in both the 1H and 1T structures are depicted in Fig. 5. It becomes evident from non-spin polarized calculations that there is no distinct separation between a_1 and e_1 levels in the 1T structure. Conversely, in the crystal field of the 1H structure, there is significant splitting between the d_{z^2} and $d_{xy}/d_{x^2-y^2}$ degenerate levels. Furthermore, the presence of half-filled d_{xy} and $d_{x^2-y^2}$ orbitals on the Fermi surface in the 1H structure imparts metallic properties to this state. To comprehend the moderate magnetic ordering in the 1H structure and accurately estimate the electron loss, calculations are conducted while considering the spin effect.

TABLE I. Magnetization of impurity m_d , the average magnetization of six S atoms as nearest neighbors of impurity m_S , the average magnetization of the closest Ti to impurity m_{Ti} , and spin and non-spin total energy difference $\Delta E = E_{sp} - E_{nsp}$ for different compounds in 1H and 1T structures.

	m_d		m_S		m_{Ti}		ΔE	
	1H	1T	1H	1T	1H	$1\mathrm{T}$	1H	1T
Sc	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V	0.666	0.885	-0.186	-0.181	0.489	0.0468	-76.27	-43.71
Cr	3.138	3.419	-1.332	-0.586	0.354	0.099	-1735.54	-3044.98
Mn	2.694	2.999	-0.324	-0.150	0.663	-0.030	-603.98	-1175.21
Fe	1.838	1.798	-0.048	-0.018	0.234	-0.354	-393.29	-301.60
Co	0.805	0.00	0.09	0.00	0.084	0.00	-74.81	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.117	0.345	0.868	1.002	-0.154	0.156	-26.37	-34.02
Zn	-0.023	0.00	1.228	0.00	-0.24	0.00	-88.09	0.00

The results of these calculations for the 1H structure are illustrated in Figs. 5(c)-5(e). The two levels depicted in Fig. 5(e) are completely devoid of electrons in both spin states. Conversely, the d_{z^2} level is fully occupied in both spin states [see Fig. 5(c)]. The degenerate d_{xy} and $d_{x^2-y^2}$ levels constitute half-filled states. Notably, spin-up state is located at the E_F , resulting in a majority of one spin state metal. Based on these diagrams, we can infer that there are five electrons in different levels of the cobalt atom, leading to an approximate magnetic moment of 1 μ_B , aligning closely with the reported value of 0.805 μ_B . This arrangement and the new state separations induced by spin-induced exchange interaction are roughly depicted in Fig. 5(b).

In Fig. 5(f) the DOS of the 3*d* orbitals of cobalt impurity atoms in 1T structure is graphed. Accounting for the spin effect, there is zero energy separation E_{spin} , indicating a non-magnetic state of the system. As shown in Fig. 5(f), the e_1 and a_1 states are fully occupied, while the e_2 state remains empty with a significant separation. Initially estimated to have six electrons, cobalt in this structure exhibits two potential arrangements as depicted in Fig. 5. When there is a small gap between the energies of the e_1 and a_1 states, as illustrated in the Fig. 5(f), arranging six electrons leads to lack of magnetic ordering. However, if there is a large energy gap between these states, as evident in Fig. 5(a), low-spin configuration emerges.

E. V-doped, Mn-doped, and Fe-doped TiS_2

In this section, we explore the substitution of V, Mn, and Fe atoms in TiS₂. The V atom carries one fewer electron than Cr, but its magnetic moment is over 2 μ_B smaller than that of Cr. Within both V-doped structures, the magnetization of neighboring S atoms is small, around -0.18 μ_B . This suggests that the *p* states of the S atoms are nearly occupied and the V atoms have lost more electrons compared to those in the Cr-doped system. Notably, even the neighboring Zr magnetic moment in the 1T structure drops to zero. The decrease in electron density within the V-doped system diminishes the exchange splitting, as illustrated in Fig. 6(a) and 6(b). Consequently, this leads to a more pronounced crystal field splitting relative to its exchange energy, resulting in states exhibiting a low spin configuration. The presence of electrons with opposite spins serves to weaken the magnetic moment of the impurity and reduce the magnetic moments in the neighboring impurity atoms. In this case, there is no significant difference observed in the magnetization between the 1H and 1T structures, so that they are the magnetic half-metal in both crystal structures.

In general, the magnetization decreases when moving from Cr to heavier atoms. Now, let's discuss the substitution of the Mn atom. As illustrated in the 3d-Mn DOS plots of Fig. 6(c) and 6(d), the Mn-doped TiS₂ compound in the 1H structure manifests as a magnetic semiconductor with a band-gap of approximately 0.30 eV, while it transforms into a magnetic half-metal in the 1T structure. The Mn atom carries one additional electron compared to Cr, and assuming similar charge transfer as in the case of Cr, along with aligned spins, it is expected to exhibit a higher magnetic moment. Contrary to this expectation, the magnetic moment value of Mn-doped TiS_2 is smaller in both structures compared to that of Cr-doped TiS₂, measuring at 2.69 μ_B and 2.99 μ_B for the 1H and 1T structures, respectively. In contrast to the Cr structure, the magnetization of neighboring S atoms is relatively low, ranging from -0.1 μ_B to -0.3 μ_B within the Mn-doped structure. Within the 1H structure, the exchange splitting value at Mn atoms is smaller than that of the crystal field, resulting in d orbitals adopting a low spin state. In this structure, with three electrons occupying the d_{z^2}, d_{xy} , and $d_{x^2-y^2}$ levels, the fourth electron with an opposite spin remains at a similar energy level. This spin arrangement maintains the magnetization within the range of 2-3 μ_B . On the other hand, in the case of the 1T structure, the d_{xz} and d_{yz} orbitals shift to lower energies, diminishing the low-spin state and boosting the magnetic moment of Mn atoms within the 1T structure.



FIG. 4. (Color online) (a) The non-spin polarized projected DOS for *d* orbital of Cr atom in the 1H structure of Cr-doped TiS₂. The spin polarized projected DOS in the 1H structure of Cr-doped TiS₂ for (b) d_{z^2} , (c) $d_{xy}/d_{x^2-y^2}$, and (d) d_{xz}/d_{yz} orbital characters. The Fermi level is set to zero energy. (e) Crystal field splitting of the 3*d* orbitals of Cr atoms in Cr-doped tilted octahedral structure of 1H-TiS₂ in presence of exchange splitting. (f) Spin polarization around impurity Cr in 1H structure of TiS₂. Size of the arrows in the figure indicate the values of spin density distribution in presence of Cr.

Moreover, by substituting Fe for Ti in TiS₂, more than five electrons occupy the Fe-3*d* levels. These additional electrons result in a magnetization of Fe atoms less than 2 μ_B . Similar to the Mn-doped TiS₂ compound, the Fedoped system in the 1H structure behaves as a magnetic semiconductor, whereas it transitions into a magnetic half-metal in the 1T structure.

IV. CONCLUSION AND OUTLOOK

We investigate the electronic and magnetic properties of TiS_2 by incorporating V, Cr, Mn, Fe, Co, Ni, Cu, and Zn atoms as impurities in both the 1H and 1T structures using first-principles density functional theory (DFT). Upon these substituting, a variety of electronic and magnetic phases emerge, including magnetic semiconductor, magnetic half-metal, non-magnetic metal, and magnetic



FIG. 5. (Color online) (a) The non-spin polarized projected DOS for *d* orbital of Co atom in the 1H structure of Co-doped TiS₂. (b) Crystal field splitting of the 3*d* orbitals of Co atoms in Co-doped tilted octahedral structure of 1H-TiS₂ in presence of exchange splitting. The spin polarized projected DOS in the 1H structure of Co-doped TiS₂ for (c) d_{z^2} , (d) $d_{xy}/d_{x^2-y^2}$, and (e) d_{xz}/d_{yz} orbital characters. The Fermi level is set to zero energy. (f) The non-spin polarized projected DOS for *d* orbital of Co atom in the 1T structure of Co-doped TiS₂. (g) Crystal field splitting of the 3*d* orbitals of Co atoms in Co-doped tilted octahedral structure of 1T-TiS₂

metal. We focus on two particularly intriguing cases. Introducing Cr atoms as impurities in monolayer TiS₂ results in the highest magnetic moment in both the 1T and 1H structures, with the 1T structure exhibiting a slightly larger magnetic moment of 3.419 μ_B compared to the 1H structure's 3.138 μ_B attributed to the distorted octahedral structure of the 1T structure. This magnetic half-metal behavior arises from the interplay of two key physical phenomena: the splitting of the TM impurity atom's d orbitals in the crystal field and the spin exchange interaction. In the 1T structure, the Cr atom retains fewer electrons than in the 1H structure due to the distorted octahedral structure. Consequently, Cr substitution can effectively induce magnetism in monolayer TiS_2 , with the magnetic moment being influenced by the structural phase. In its pristine form, TiS_2 is a non-magnetic semiconductor. The bands near the Fermi energy primarily exhibit d orbital characters, and due to the presence of ideal octahedral and trigonal arrangements, they are well separated from other bands with pcharacter. Unlike pristine TiS_2 , the deficiency in saturation of neighboring S atoms in the presence of impurities leads to the proximity of energy levels of d and p states, resulting in unexpectedly sizable magnetic moments even



FIG. 6. The spin polarized projected DOS of 3d orbital of TM impurity atoms in the 1H and 1T structures for (a), (b) V-doped TiS₂; (c), (d) Mn-doped TiS₂; (e), (f) Fe-doped TiS₂. The Fermi level is set to zero energy.

at nearest neighbors to the impurity.

The magnetic behavior of the Co atom demonstrates a significant difference between the two structures. In the 1T structure, the Co atom maintains a magnetic moment of approximately 0.805 μ_B due to the partial occupation of the degenerate d_{xy} and $d_{x^2-y^2}$ orbitals on the Fermi surface. In contrast, the Co atom in the 1H structure exhibits a non-magnetic state because of the small density of states (DOS) at E_F , preventing the formation of a magnetic moment. Our results emphasize the ability to tailor the magnetic properties of Co-doped monolayer TiS₂ through structural modifications, with the 1T structure remains non-magnetic.

Studying the substitution of 3d transition metals in the

non-magnetic semiconductor TiS_2 offers a fundamental understanding of the origin of magnetic properties in twodimensional systems. In the case of Cr/Mn-doped TiS₂ in both structures, there exist d_{z^2} and $d_{x^2-y^2}/d_{xy}$ impurity levels with a narrow bandwidth of approximately 0.4 eV. The significant DOS of Mn and Cr atoms at the E_F in both the 1T and 1H structures can lead to instability in magnetic ordering, which aligns well with our findings from spin-polarized total energy calculations and the substantial magnetic moments observed. In nonmagnetic calculations, for most of the metallic 3d TMdoped TiS₂, we observe substantial $D(E_F)$ values, exceeding those found in elementary transition metals or carbon-based materials. Consequently, the electron correlation strength increases, placing these compounds in the moderately or strongly correlated regime.

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