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Originally published:

April 2021

**ACS Applied Materials and Interfaces 13(2021), 21593-21601**

DOI: <https://doi.org/10.1021/acsami.1c01701>

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# **Enhancing ferromagnetism and tuning electronic properties of CrI<sub>3</sub> monolayers by adsorption of transition metal atoms**

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## Abstract

Among first experimentally discovered two-dimensional (2D) ferromagnetic materials, chromium triiodide ( $\text{CrI}_3$ ) monolayers have attracted particular attention due to their potential applications in electronics and spintronics. However, the Curie temperature  $T_c$  of  $\text{CrI}_3$  monolayer is below room temperature, which greatly limits practical development of the devices. Herein, using density functional theory calculation, we explore how the electronic and magnetic properties of  $\text{CrI}_3$  monolayers change upon adsorption of 3d transition metal (TM) atoms (from Sc to Zn). Our results indicate that the electronic properties of the TM- $\text{CrI}_3$  system can be tuned from semiconductor to metal/half-metal/spin gapless semiconductor depending on the choice of the adsorbed TM atoms. Moreover, the adsorption can improve the ferromagnetic stability of  $\text{CrI}_3$  monolayers by increasing both magnetic moments and  $T_c$ . Notably,  $T_c$  of  $\text{CrI}_3$  with Sc and V adatoms can be increased by nearly a factor of three. We suggest post-synthesis doping of 2D  $\text{CrI}_3$  by deposition of TM atoms as a new route towards potential applications of TM- $\text{CrI}_3$  systems in nanoelectronic and spintronic devices.

## Introduction

Two-dimensional (2D) materials have been shown to possess unique and fascinating physico-chemical properties pointing to their potential applications in electronics.<sup>1-8</sup> Unfortunately, most of these 2D materials such as graphene, boron-nitride, and transition-metal dichalcogenides are nonmagnetic, which represents a significant obstacle for applications of 2D materials in spintronic devices. Hence, substantial

research effort has been made to introduce magnetism in these nonmagnetic systems, such as doping,<sup>9-11</sup> defect<sup>12-14</sup> and strain engineering,<sup>15,16</sup> as well as the proximity effect.<sup>17</sup> However, although local magnetic moments have been successfully introduced by these methods, the formation of a macroscopic state remains as a big challenge. The other way to achieve 2D spintronic materials is to develop 2D materials with intrinsic ferromagnetic ordering. In 2017, the existence of the long-ranged ferromagnetic order was demonstrated in 2D CrI<sub>3</sub><sup>18</sup> and Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub><sup>19</sup> with spins being oriented perpendicular to the material plane in the former and with arbitrary directions of spins in the latter system. After that, some other 2D ferromagnetic materials have been successfully prepared and studied, such as Fe<sub>3</sub>GeTe<sub>2</sub>, and CrBr<sub>3</sub>.<sup>20-23</sup> Besides, several 2D ferromagnetic materials have been theoretically predicted, such as CrX (X = P, As),<sup>24</sup> GdI<sub>2</sub>,<sup>25</sup> and FeB<sub>3</sub>,<sup>26</sup> but not synthesized yet. These findings not only opened new avenues for the fundamental research on magnetism in systems with a reduced dimensionality, but also provided exciting new opportunities for 2D spintronics.

As one of the first experimentally discovered 2D ferromagnetic materials, CrI<sub>3</sub> monolayer has attracted especially much attention. Due to its intrinsic ferromagnetism, strong perpendicular magnetic anisotropy, giant magneto band-structure effect, distinct spin-lattice and spin-phonon coupling, and robust topological properties,<sup>27-31</sup> CrI<sub>3</sub> monolayer can be a potential candidate for spintronic devices. However, its Curie temperature  $T_c$  (only 45K)<sup>18</sup> is much lower than room temperature, which greatly limits its practical applications. Therefore, a crucial issue is how to adjust the magnetic

properties of CrI<sub>3</sub> and improve its ferromagnetic stability. Several approaches have been suggested to enhance the ferromagnetism of CrI<sub>3</sub>, including electrostatic doping, electric field, defect engineering, strain, etc.<sup>32-38</sup> For example, the characteristics such as saturation magnetization, coercive force and Curie temperature of CrI<sub>3</sub> monolayer can be improved by electrostatic doping.<sup>32</sup> By applying an external electric field, magnetism in CrI<sub>3</sub> bilayer can be further controlled.<sup>34</sup> It was predicted that surface iodine vacancies not only enhance the intrinsic ferromagnetism of CrI<sub>3</sub> monolayer, but also induce switchable electric polarization.<sup>35</sup> First-principles calculations also indicated that the magnetic anisotropy energy of CrI<sub>3</sub> monolayer can be increased by 47% under a 5% compressive strain.<sup>39</sup>

Doping is one of the most commonly used methods to tailor the electronic and magnetic properties of 2D materials.<sup>40-42</sup> The robust ferromagnetism was observed in Mn-doped MoS<sub>2</sub> synthesized by a hydrothermal method.<sup>43</sup> Kochat et al. found magnetism in Re-doped MoSe<sub>2</sub> monolayer.<sup>44</sup> The transition from nonmagnetic to tunable magnetic state can also be induced in ReS<sub>2</sub> due to the N doping.<sup>45</sup> Recent experimental results suggest that the V-doped MoTe<sub>2</sub> is a room-temperature ferromagnetic semiconductor.<sup>9</sup> Alkali-metal adsorption dramatically increased the magnetic anisotropy energy of monolayer Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>, leading to a significant increase in the Curie temperature.<sup>46</sup> The adsorption of Li atoms can enhance the ferromagnetism of CrI<sub>3</sub> by increasing both the magnetic moment and the Curie temperature.<sup>47</sup>

In this work, by means of systematic density functional theory (DFT) calculation, we

investigate another way to improve the magnetic characteristics of CrI<sub>3</sub>. Specifically, we study the influence of 3d transition metal (TM) atoms (from Sc to Zn) adsorption on the electronic and magnetic properties of CrI<sub>3</sub> monolayer. We demonstrate that electronic properties can be varied in a wide range depending on the TM atoms adsorbed on CrI<sub>3</sub> monolayer. In addition, ferromagnetism in CrI<sub>3</sub> monolayer can be remarkably enhanced by adsorption of TM atoms, which can be ascribed to the interplay between direct exchange and superexchange interactions. Our findings provide a promising pathway to tune the electronic properties and improve ferromagnetism in CrI<sub>3</sub> monolayers, which would make this material one step closer to the potential applications in nanoelectronics and spintronic devices.

## **Computational Method**

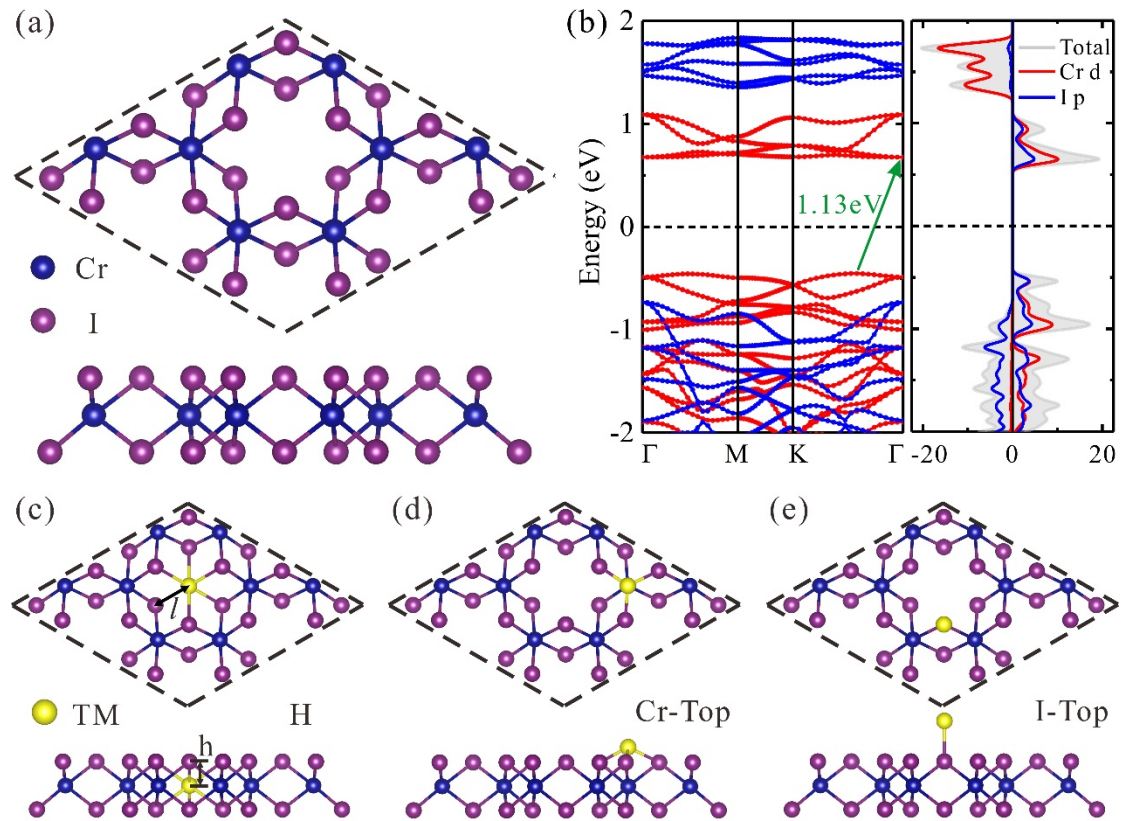
Our DFT calculations were carried out using the projector-augmented-wave (PAW) method<sup>48,49</sup> implemented in Vienna ab initio simulation package (VASP).<sup>50,51</sup> The exchange interaction and correlations were described by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)<sup>52</sup> parametrization. The PBE + U calculations was also performed to confirm our results. The Hubbard U values were chosen 3 and 2.5 eV for Cr, and 3d TM atoms,<sup>53-55</sup> respectively. Further, the hybrid functional HSE06<sup>56</sup> was adopted to investigate the geometry and electronic structures of Sc-CrI<sub>3</sub> and Mn-CrI<sub>3</sub>. We also included the SOC to examine the electronic structures of pristine CrI<sub>3</sub> monolayer and magnetic moments of TM-CrI<sub>3</sub>. An energy cutoff of 500 eV was set for the plane wave basis. The Brillouin zone k-point sampling of  $7 \times 7 \times 1$  grid mesh was used for geometry optimizations. The lattice constants and atomic

positions were fully relaxed until the total energy and force were less than  $10^{-6}$  eV and  $0.01$  eV/Å, respectively. A vacuum region of at least  $18$  Å along the out-of-plane direction was introduced to avoid interaction between periodic images of the system. The Monte Carlo (MC) simulation based on the Ising model<sup>33,54</sup> was used to estimate the Curie temperature of CrI<sub>3</sub> and TM-CrI<sub>3</sub>.

## Results and discussion

CrI<sub>3</sub> monolayer is an I-Cr-I sandwiched layer structure, where the magnetic Cr<sup>3+</sup> ions form a honeycomb network in octahedral coordination, edge-sharing with six I<sup>-</sup> ions (Figure 1a). The optimized lattice constant of CrI<sub>3</sub> monolayer is  $7.01$  Å, the bond lengths of between Cr and I atoms is  $2.74$  Å, which is in good agreement with previous reports.<sup>47,57</sup> It can be seen from Figure 1b that CrI<sub>3</sub> monolayer is an indirect semiconductor with a band gap of  $1.13$ eV,<sup>47</sup> the valence band maximum (VBM) and the conduction band minimum (CBM) are mainly contributed by the Cr  $3d$  and I  $5p$  states. To evaluate the magnetic ground states of CrI<sub>3</sub> monolayer, four different magnetic configurations were considered: the ferromagnetic (FM), Néel antiferromagnetic (Néel-AFM), Zigzag antiferromagnetic (Zigzag-AFM) and Stripy antiferromagnetic (Stripy-AFM) state, as shown in Figure S1. The calculated total energies show that the FM state is energetically most favorable, indicating that ferromagnetic coupling dominates in CrI<sub>3</sub> monolayer. The spin-density distribution of CrI<sub>3</sub> monolayer (Figure S2) indicates that the magnetism mainly originates from magnetic moments localized on Cr atoms ( $3.09 \mu_B$  per Cr atom), which is consistent

with the experimental result ( $3.1 \mu_B$  per Cr atom).<sup>58</sup> We also calculated the lattice constant, band structure and magnetic moment of CrI<sub>3</sub> monolayer using the PBE + U method, as shown in Table S1 and Figure S3. It is found that the lattice constant and magnetic moment of CrI<sub>3</sub> monolayer are consistent with the results calculated by PBE. The band gap of CrI<sub>3</sub> monolayer is 1.23 eV calculated with PBE + U, slightly larger than that of PBE (1.13 eV). When the SOC is considered, the band gap of CrI<sub>3</sub> monolayer is reduced to 0.89 eV, which is smaller than that calculated from PBE and PBE + U. The good agreement suggests that our DFT calculations correctly describe the properties of CrI<sub>3</sub> monolayers.



**Figure 1.** (a) The top and side views of the crystalline structure of CrI<sub>3</sub> monolayer. (b) Spin-polarized band structure and partial density of states (PDOS) of CrI<sub>3</sub> monolayer. The red and blue dotted lines denote spin-up and spin-down channels, respectively. The

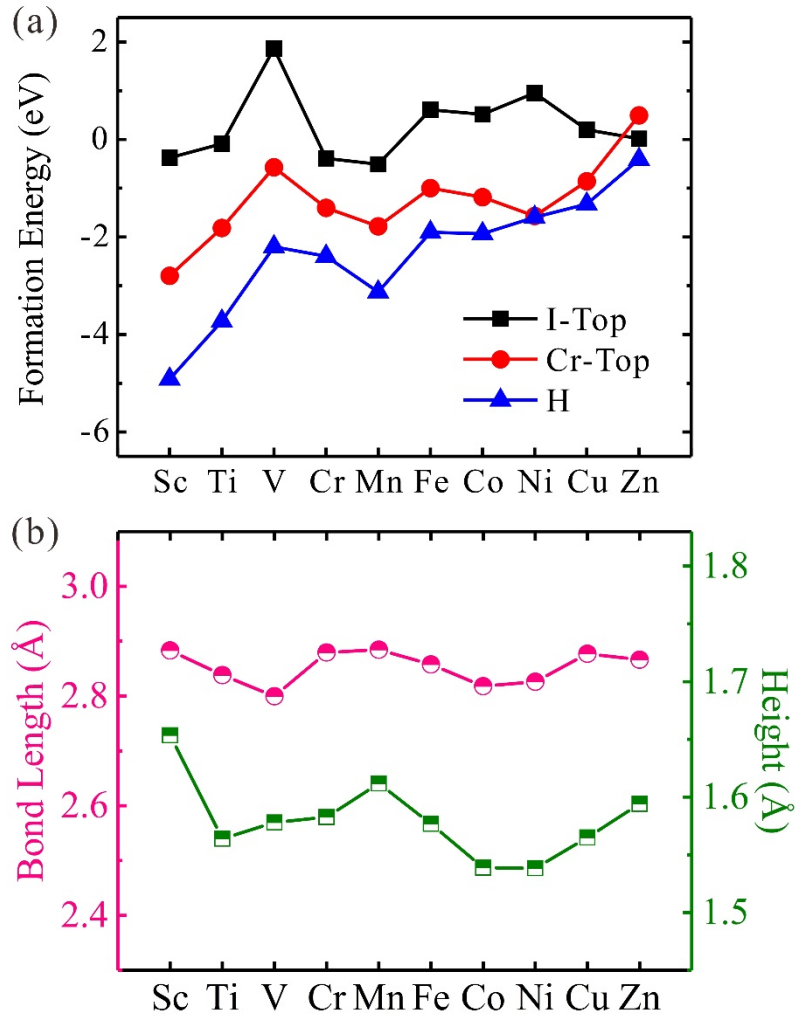


Fermi level is indicated by the black dashed lines. The top and side views of the crystalline structure of the system with TM atoms adsorbed in three different positions denoted as (c) H, (d) Cr-Top and (e) I-Top. The blue, purple and yellow balls represent Cr, I and TM atoms, respectively.

Having analyzed the properties of the pristine CrI<sub>3</sub>, we moved on to the investigations of the adsorbed configurations and formation energies of CrI<sub>3</sub> monolayer upon 3d TM atoms (from Sc to Zn) adsorption. A 2×2×1 CrI<sub>3</sub> supercell was chosen to represent the system (TM-CrI<sub>3</sub>). Three possible adsorption sites of TM atoms on CrI<sub>3</sub> monolayer were considered: the middle of a hexagon (H), on top of a Cr atom (Cr-Top) and on top of an I atom (I-Top), as shown in Figure 1c-e. The formation energy  $E_f$  of TM-CrI<sub>3</sub> defined as  $E_f = E_{\text{CrI}_3+\text{TM}} - E_{\text{CrI}_3} - \mu_{\text{TM}}$ , where  $E_{\text{CrI}_3+\text{TM}}$  is the total energy of the CrI<sub>3</sub>+TM system after structural relaxation;  $E_{\text{CrI}_3}$  are the total energy of pristine CrI<sub>3</sub>; and  $\mu_{\text{TM}}$  is the chemical potential of the TM atom in the isolated TM dimer ( $\mu_{\text{TM}} = \frac{1}{2}E_{\text{TM}_2}$ ). According to our definition of formation energy, the more negative value of  $E_f$  indicates the higher stability of the adsorption configuration. Our computations showed that the  $E_f$  of TM-CrI<sub>3</sub> for the H site are more negative than that for the Cr-Top and I-Top sites (Figure 2a), suggesting that all 3d TM atoms prefer to be adsorbed on the H site. Note that  $E_f$  of TM-CrI<sub>3</sub> for the H site are negative and sizable, which indicates that TM atoms prefer to occupy positions in the atomic network of CrI<sub>3</sub> sheet rather than form dimers and likely bigger clusters. Thus, the formation of TM clusters can be

avoided. In addition, the energy of TM atoms from bulk phase was also chosen as a reference to calculate the formation energy. It can be also seen that TM atoms adsorption on the H site is still negative, as shown in Figure S4 of the Supporting Information.

To further address the (meta)stability of CrI<sub>3</sub> after TM atoms adsorption, we carried out DFT-based molecular dynamics (MD) simulation<sup>41</sup> at 300 K. We found that the TM-CrI<sub>3</sub> structures retain their original framework after 5 ps. Although this certainly cannot be considered as a solid proof of the stability of the system, it also indicates that the system is at least metastable (see Figure S5 in the Supporting Information). Thus, we will focus on the H configuration in the following discussion. For the H configuration, the TM adatom forms covalent bonds with the nearest six I atoms, with the TM-I bond lengths being generally larger than 2.80 Å (see Figure 2b), varying with different TM atoms. The height of TM atoms with regard to the CrI<sub>3</sub> surface is in the range of 1.54-1.65 Å, see Figure 2b. Zn-CrI<sub>3</sub> has the least negative formation energy of -0.41 eV, indicating that Zn atom bonds weakly with CrI<sub>3</sub> monolayer. Except Zn atom, the  $E_f$  values for the other TM atoms are quite large (-1.33 ~ -4.92 eV), indicating that they bind strongly to the CrI<sub>3</sub> monolayer. Among them, Sc-CrI<sub>3</sub> has the most negative formation energy of -4.92 eV, which can be understood by the fact that the energy of the 3d orbital of Sc is higher than that of other 3d TM atoms.



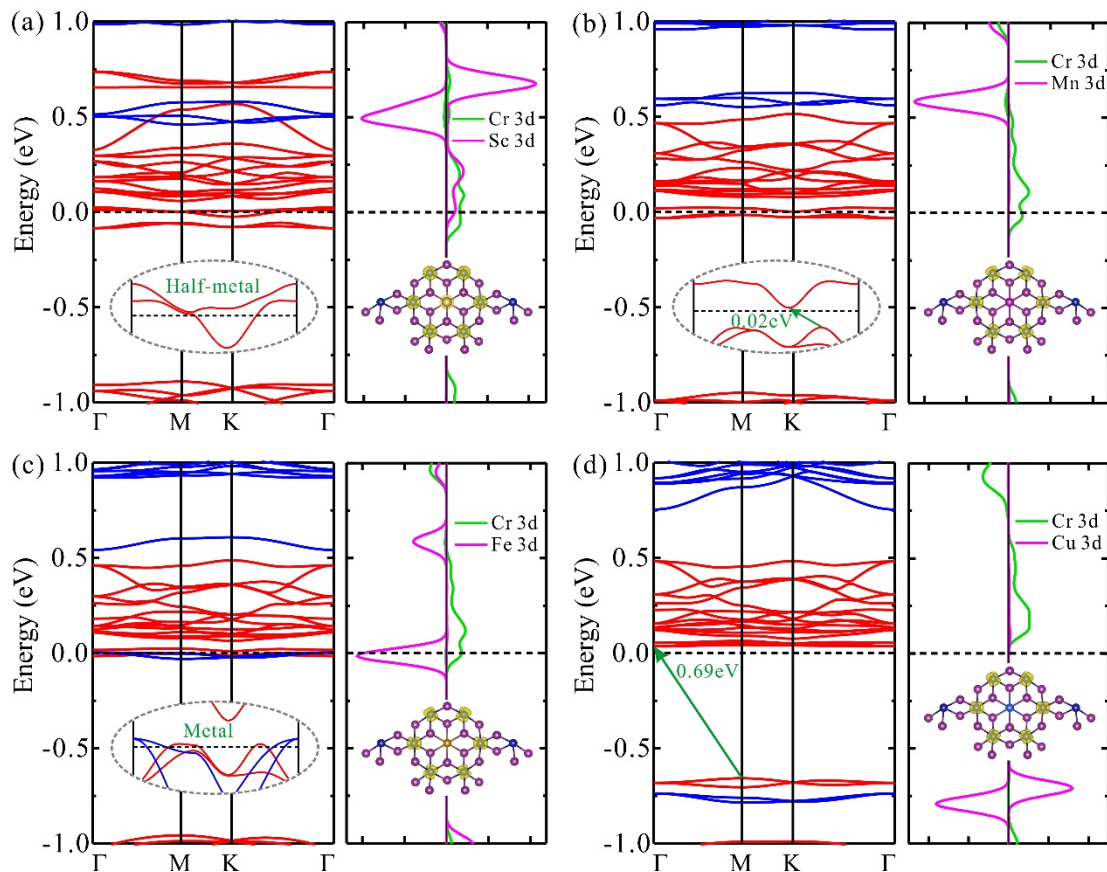
**Figure 2.** (a) The formation energy of TM atoms adsorbed on H, Cr-Top, I-top in CrI<sub>3</sub> monolayer. (b) The height of TM atoms and length of the bond to nearest I atoms for adsorption on the H site.

The spin-polarized band structures of TM atoms adsorbed on CrI<sub>3</sub> monolayer are presented in Figure 3 and Figure S3. It is evident that the adsorption of TM atoms can strongly influence the electronic properties of CrI<sub>3</sub> monolayer. After Sc adsorption, the metallic behavior is observed in the spin-up channel, while there is a band gap of 1.76 eV in the spin-down channel, as illustrated in Figure 3a. Thus, the Sc-CrI<sub>3</sub> system shows

half-metallicity and can provide 100% spin-polarized current. Examining the PDOS revealed that the bands near the Fermi level mainly come from the  $3d$  orbitals of Sc and the neighboring Cr atoms in Sc-CrI<sub>3</sub>. Similarly, the half-metal behaviors are also found for Ti, V, Cr and Zn-CrI<sub>3</sub> (see Figure S3a-c,f in the Supporting Information). Interestingly, the spin gapless semiconductor (SGS) is expected for the adsorption of Mn atom on CrI<sub>3</sub> monolayer, *i.e.*, the spin up channel has a tiny gap of 0.02 eV, while the spin down channel displays the semiconducting character with a band gap of 1.86 eV, as shown in Figure 3b. According to the definition of Wang and Hu,<sup>41,59</sup> the band gap less than 0.1 eV can be termed as “gapless”. Different from the case of Sc-CrI<sub>3</sub>, the bands near the Fermi level are dominated by the  $3d$  orbitals of Cr atoms adjacent to the Mn atom in Mn-CrI<sub>3</sub>. The SGS is also found in Co-CrI<sub>3</sub> (see Figure S3d in the Supporting Information). For SGS materials, electrons with particular spin can easily be excited from the valence band to the conduction band, giving rise to 100% spin-polarized current, which is desirable for the spintronic devices. As for Fe and Ni adsorption, the metallic behavior can be found in the spin-up and spin-down channels (see Figure 3c and Figure S3e), which leads to a semiconductor-to-metal transition in CrI<sub>3</sub> monolayer. The PDOS analysis suggests that the Fe (Ni) and Cr  $3d$  orbitals are responsible for the metallicity. For the adsorption of Cu, the system preserves the semiconducting character with the band gap of 0.69 eV, significantly decreased as compared to that of the pristine CrI<sub>3</sub> monolayer (1.13 eV). The VBM and CBM are mainly contributed by the  $3d$  orbitals of Cu atom and Cr atoms, respectively, as shown

in Figure 3d. The above PDOS analysis can be further substantiated by the partial charge densities of the bands near the Fermi level in Figure 3.

Taking Sc-CrI<sub>3</sub>, Mn-CrI<sub>3</sub>, Fe-CrI<sub>3</sub> and Cu-CrI<sub>3</sub> as examples, we examined their electronic structures using PBE + U functional, which are presented in Figure S7. It can be seen that Sc-CrI<sub>3</sub> system still exhibits the half-metal behavior, where the spin-down gap increases from 1.76 to 2.00 eV. Mn-CrI<sub>3</sub> and Cu-CrI<sub>3</sub> remain SGSs. As for Fe-CrI<sub>3</sub>, there is a transition from metal to SGS. Taking into account that the electronic structures at the Fermi level of half metals and SGSs are sensitive to the choice of the calculation method, the hybrid HSE06 functional was used to check the electronic structures of Sc-CrI<sub>3</sub> and Mn-CrI<sub>3</sub>, as shown in Figure S8 of Supporting Information. We found that Sc-CrI<sub>3</sub> and Mn-CrI<sub>3</sub> preserve the half-metal and SGS behaviors, respectively.



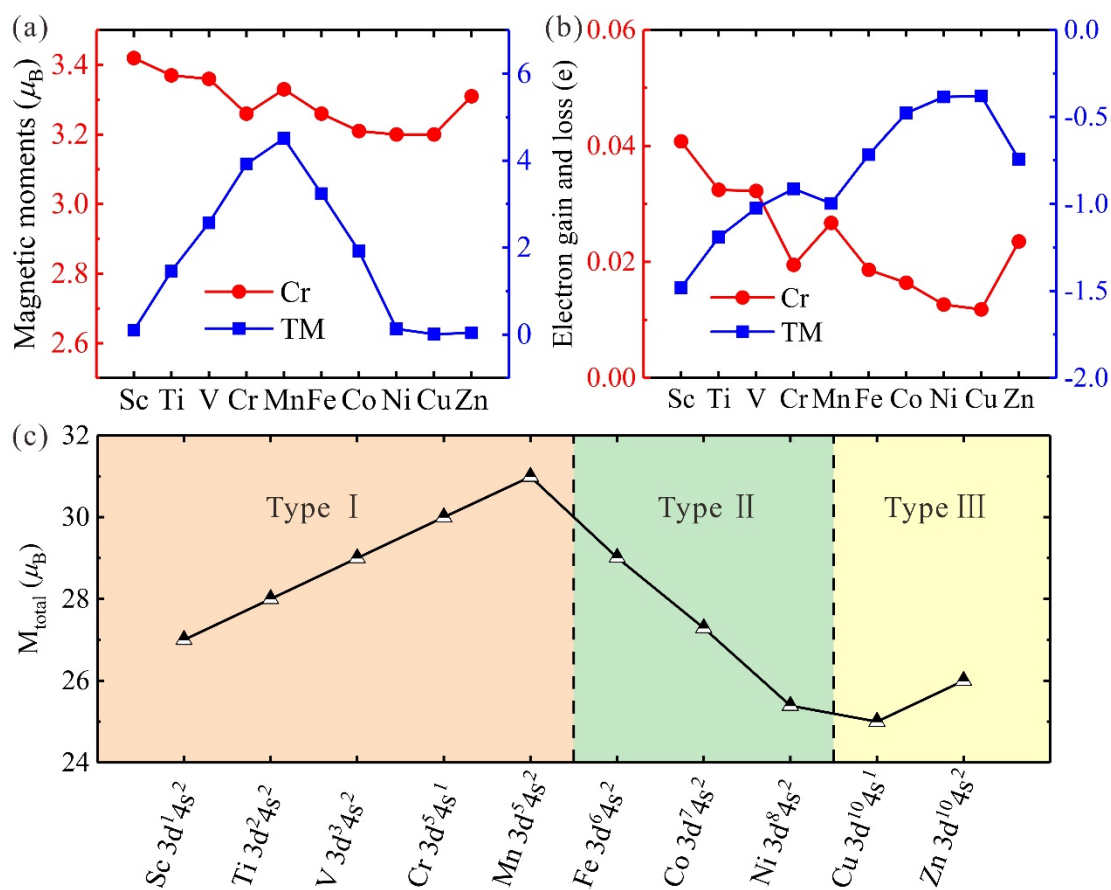
**Figure 3.** Spin-polarized band structures, partial charge densities and PDOS of (a) Sc-CrI<sub>3</sub>, (b) Mn-CrI<sub>3</sub>, (c) Fe-CrI<sub>3</sub> and (d) Cu-CrI<sub>3</sub>. The red and blue solid lines indicate spin-up and spin-down channels in the band structures, respectively. The Fermi level is indicated by the black dashed lines. The isosurface is set to be 0.002 e/Å<sup>3</sup>.

Next, we explore the effect of TM atoms on the magnetic properties of CrI<sub>3</sub> monolayer. For simplification, the local magnetic moments of Cr, TM atoms, and the total magnetic moments of TM-CrI<sub>3</sub> supercells are named as  $M_{Cr}$ ,  $M_{TM}$  and  $M_{total}$ , respectively. It can be seen from Figure 4a that the  $M_{Cr}$  is ranged from 3.20 to 3.42  $\mu_B$ , larger than that of the pristine CrI<sub>3</sub> monolayer (3.09  $\mu_B$ ). Among them, Sc adsorption has the maximum  $M_{Cr}$  of 3.42  $\mu_B$ , while the adsorption of Ni and Cu have the minimum  $M_{Cr}$  of 3.20  $\mu_B$ . The  $M_{Cr}$  variation with TM atoms can be understand from the charge transfer in TM-CrI<sub>3</sub>, presented in Figure 4b. Specifically, for Sc adsorption, each Cr atom gains a maximum electron charge of about 0.04 e, while for the adsorption of Ni and Cu the minimum electron charge about 0.01e is obtained by each Cr atom. On the other hand, the local magnetic moments of TM atoms (from Sc to Cu) are 0.10, 1.46, 2.57, 3.92, 4.51, 3.24, 1.92, 0.13 and 0.01  $\mu_B$ , respectively, smaller than those of the free TM atoms (Table S1). The reduction of the  $M_{TM}$  well correlate with the charge transfer from the TM atom to the CrI<sub>3</sub> monolayer (Figure 4b).

To gain further insights into the total magnetic moments of TM-CrI<sub>3</sub>, we examined the spin density distributions (Figure S2). The spin density distributions show that  $M_{total}$

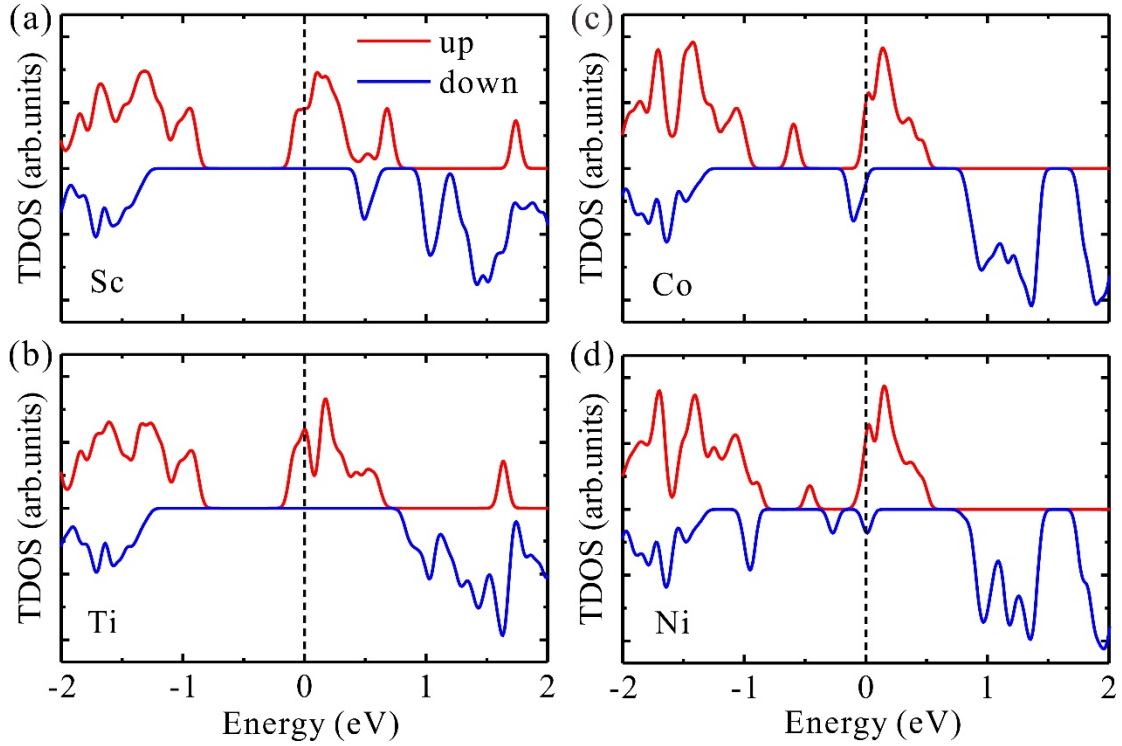
mainly stem from the Cr atoms and partly from the TM atoms in TM-CrI<sub>3</sub>. The  $M_{\text{total}}$  first increases and then decreases with increasing the TM atomic number, which exhibits a “volcano” curve, as shown in Figure 4c. The overall similar trends have also been reported in TM atoms adsorbed graphene, MoSe<sub>2</sub> and phosphorene.<sup>10,40,60</sup> The  $M_{\text{total}}$  of TM-CrI<sub>3</sub> can be divided three types: type I (TM = Sc, Ti, V, Cr, Mn), type II (TM = Fe, Co, Ni), and type III (TM = Cu, Zn). For type I, the  $M_{\text{total}}$  of TM-CrI<sub>3</sub> is integer and increases linearly from 27  $\mu_B$  to 31  $\mu_B$  (from Sc to Mn) in the 2×2 supercell. We note that the  $M_{\text{total}}$  of TM-CrI<sub>3</sub> (TM = Sc, Ti, V, Cr, Mn) is related to the number of (s + d) electrons in the outermost electron shell. For example, Sc atom has 3 outermost electrons, accordingly  $M_{\text{total}}$  increases by 3  $\mu_B$  with regard to that of pristine CrI<sub>3</sub> monolayer (24  $\mu_B$ ). As the number of (s + d) electrons increases from 4 to 7 (Ti to Mn),  $M_{\text{total}}$  increases stepwise from 28 to 31  $\mu_B$  (Ti to Mn). Different from the case of type I,  $M_{\text{total}}$  of Fe-, Co- and Ni-CrI<sub>3</sub> is approximately linearly reduced by 2  $\mu_B$  as compared to that for earlier TMs. For Cu-CrI<sub>3</sub>, the Cu atom possess 11 outermost electrons, wherein 10 electrons fill all the 3d orbitals, and the left one gives rise to  $M_{\text{total}}$  increase by 1  $\mu_B$  with regard to that of pristine CrI<sub>3</sub> monolayer. As for Zn-CrI<sub>3</sub>, the 12 outermost electrons of Zn atom fill all the 3d and 4s orbitals, leading to the zero magnetic moment of Zn, thus  $M_{\text{total}}$  mainly stems from Cr atoms. Furthermore, the change in the  $M_{\text{total}}$  trend can also be understood from the spin polarization of TM-CrI<sub>3</sub> in the total density of states (TDOS), as shown in Figure 5. For example, the spin-polarization asymmetry of Sc-CrI<sub>3</sub> is weaker than that of Ti-CrI<sub>3</sub> (Figure 5a and b), thus  $M_{\text{total}}$  of Ti-CrI<sub>3</sub> is larger.

Similarly, Co-CrI<sub>3</sub> has a larger spin polarization relative to Ni-CrI<sub>3</sub> (Figure 5c and d), leading to a larger value of  $M_{\text{total}}$ . The  $M_{\text{total}}$  values of Sc-, Mn-, Fe- and Cu-CrI<sub>3</sub> using PBE + U calculations without and with SOC are shown in Table S3. We can see that the magnetic moments are not obviously influenced by PBE + U and SOC.



**Figure 4.** (a) The local magnetic moments of Cr (near the H site) and TM atoms in CrI<sub>3</sub> monolayer with TM atoms adsorbed on the H site. (b) Charge transfer of Cr and TM atoms in TM-CrI<sub>3</sub>. (c) The total magnetic moments of TM-CrI<sub>3</sub> in a 2×2×1 supercell. The two vertical dashed lines divide the total magnetic moments of TM-CrI<sub>3</sub> into three types.

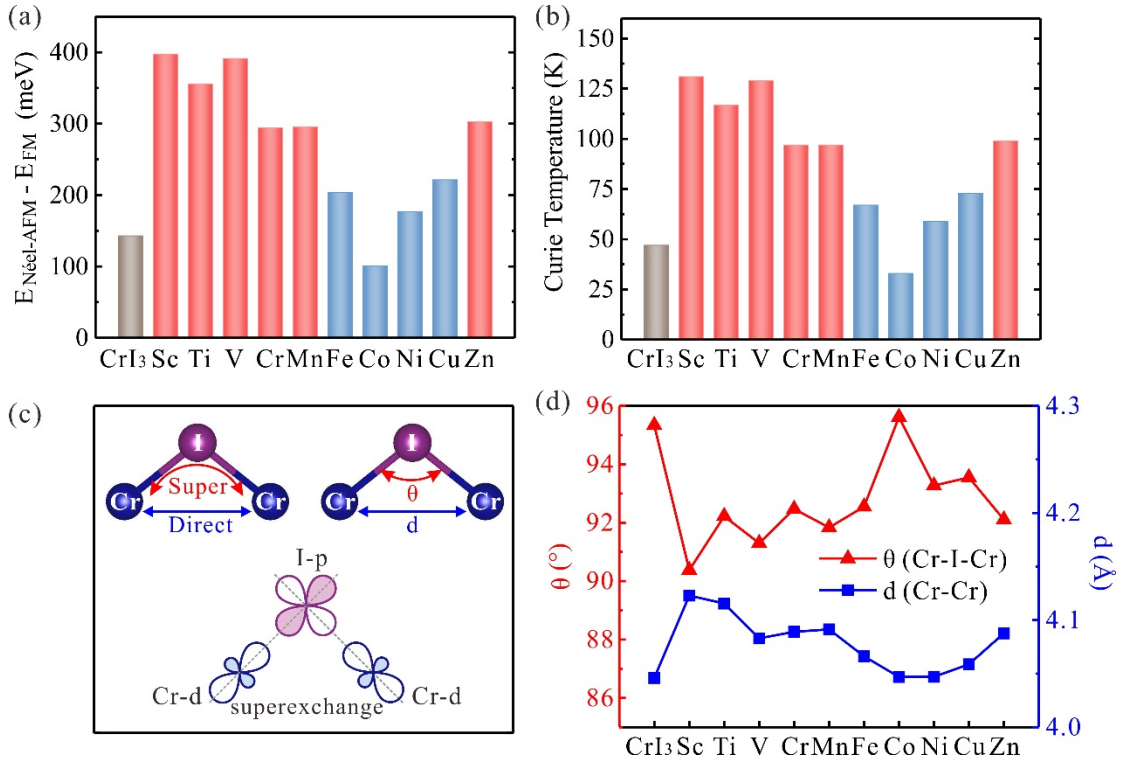




**Figure 5.** TDOS of (a) Sc-CrI<sub>3</sub>, (b) Ti-CrI<sub>3</sub>, (c) Co-CrI<sub>3</sub> and (d) Ni-CrI<sub>3</sub>. The Fermi level is set at zero, denoted by the black dashed lines. The red and blue solid lines represent spin-up and spin-down channels, respectively.

We further explore the impact of TM atoms on the FM stability of CrI<sub>3</sub> monolayer. The energy difference between the Néel-AFM and FM states ( $E_{\text{ex}} = E(\text{Néel-AFM}) - E(\text{FM})$ ) in TM-CrI<sub>3</sub> is presented in Figure 6a. Clearly, upon the TM atoms adsorption on the CrI<sub>3</sub> monolayer, the energy difference can be significantly increased. Specifically, the energy difference (except Co) is between 177 and 398 meV depending on the different TM atoms. In particular, the energy difference of Sc-CrI<sub>3</sub> can be as high as 398 meV, which is nearly 3-fold higher than that of the pristine CrI<sub>3</sub> monolayer (143 meV). These results indicate that the adsorption of TM atoms (except Co) can improve

the FM stability of CrI<sub>3</sub> monolayers.



**Figure 6.** (a) Energy difference between the Néel-AFM and FM coupling and (b) Curie temperature of CrI<sub>3</sub> monolayer with different TM atoms. (c) Schematic mechanism of direct exchange and superexchange interactions. (d) The Cr-Cr distance and the Cr-I-Cr bond angle in CrI<sub>3</sub> monolayer with different TM atoms.

To directly evaluate the stability of FM coupling, we further investigate the Curie temperature  $T_c$  of TM-CrI<sub>3</sub>. The Heisenberg spin Hamiltonian can be written as  $H = -\sum_{i,j} J S_i \cdot S_j$ , where  $J$  is the nearest exchange coupling parameter and  $S_{i/j}$  represent the spin parallel or antiparallel to the  $z$  direction. Here,  $J$  value can be obtained from the following formula  $J = E_{\text{ex}}/24S^2$ , where  $E_{\text{ex}} = E(\text{Néel-AFM}) - E(\text{FM})$  is the exchange energy between Néel-AFM and FM states of the system.  $S=3/2$  was chosen

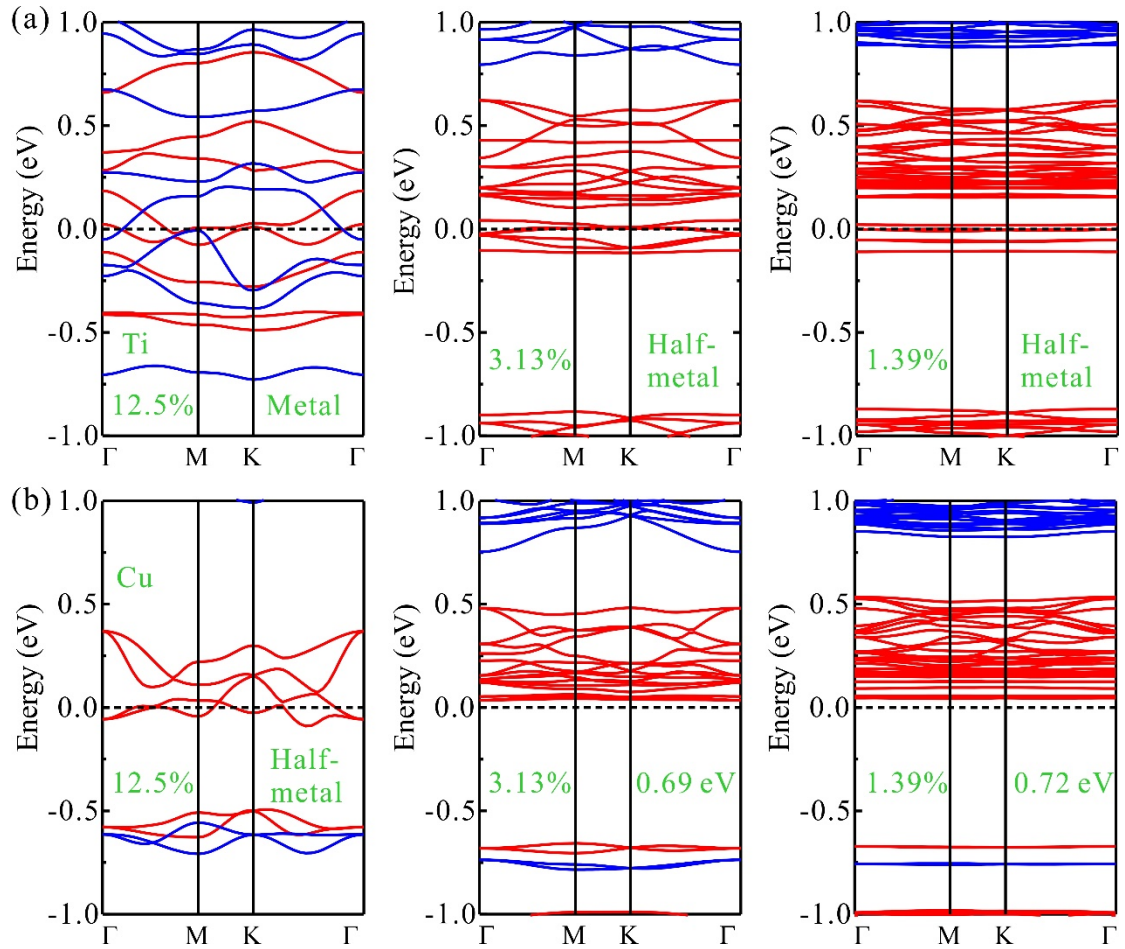
as the spin of each Cr atom. The calculated  $J$  value of pristine  $\text{CrI}_3$  is 2.65 meV, which is in a good agreement with the previous reports.<sup>39</sup> We also summarized the theoretical and experimental  $J$  values for pristine  $\text{CrI}_3$  in Table S4 in Supporting Information. From the specific heat ( $C_V$ ) of the pristine  $\text{CrI}_3$  monolayer presented in Figure S4,  $T_c$  is estimated to be 46 K, which is consistent with the experimental value (45 K),<sup>18</sup> indicating the reliability of our approach. The calculated  $J$  value of TM- $\text{CrI}_3$  are listed in Table S5 in Supporting Information. For TM- $\text{CrI}_3$  monolayers, the  $T_c$  values (except Co) are ranged from 59 to 131 K (Figure 6b), larger than that of the pristine  $\text{CrI}_3$  monolayer (46 K). Among them, the adsorption of Sc, Ti, V, Cr, Mn and Zn can enhance the  $T_c$  by more than 100% as to the pristine  $\text{CrI}_3$  monolayer. Notably, the enhanced  $T_c$  of the  $\text{CrI}_3$  monolayer upon Sc adsorption can be increased by 185%.

It is known that the FM coupling in  $\text{CrI}_3$  monolayer can be understood within the Goodenough-Kanamori-Anderson (GKA) model,<sup>61-64</sup> which is governed by the competition between two exchange interactions: the direct exchange and the superexchange interaction, as shown in Figure 6c. The direct exchange interaction originates from the direct electron hopping between two Cr atoms, and it is robust AFM coupling, sensitive to the distance ( $d$ ) between the adjacent Cr atoms. The superexchange interaction is mediated by I atom and prefers FM coupling, which is governed by the Cr-I-Cr bond angle ( $\theta$ ). To understand the enhanced FM stability of  $\text{CrI}_3$  monolayer upon TM atoms adsorption, we give the distance ( $d$ ) between the adjacent Cr atoms and Cr-I-Cr bond angle ( $\theta$ ) in TM- $\text{CrI}_3$ , as illustrated in Figure 6d.

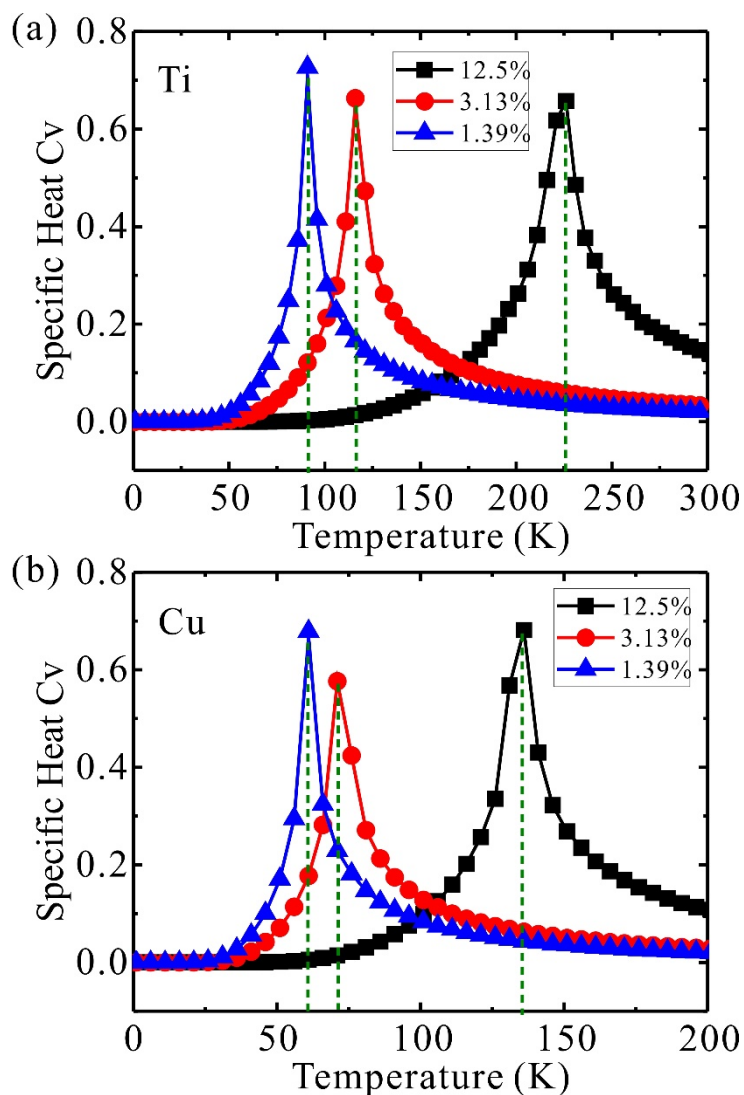
For the adsorption of Sc, Ti, V, Cr, Mn and Zn atoms, the angles ( $\theta$ ) are closer to  $90^\circ$  than that of Fe, Co, Ni, and Cu adsorption. Thus, the superexchange interaction of the former is stronger than that for the latter, resulting in the stronger FM coupling. On the other hand, due to larger distances ( $d$ ) in Sc, Ti, V, Cr, Mn and Zn-CrI<sub>3</sub>, the AFM coupling originating from the direct exchange is weaker than that of Fe, Co, Ni, and Cu-CrI<sub>3</sub>. Consequently, the FM stability in Sc, Ti, V, Cr, Mn and Zn-CrI<sub>3</sub> is significantly enhanced. Especially for Co adsorption, the distance ( $d$ ) remains almost unchanged, while the angle ( $\theta$ ) is slightly increased than that of pristine CrI<sub>3</sub> monolayer, which leads to the weaker superexchange. As a result, the FM stability of the system with Co adatoms is lower as compared to the pristine CrI<sub>3</sub> monolayer.

Furthermore, we investigated the effects of adatom concentration on the electronic and magnetic properties of the system by choosing different supercell sizes. Here, we consider that the TM atom is adsorbed in  $1\times 1\times 1$ ,  $2\times 2\times 1$  and  $3\times 3\times 1$  CrI<sub>3</sub> supercells, which correspond to the concentrations of 12.5%, 3.13% and 1.39%, respectively. Taking Ti-CrI<sub>3</sub> and Cu-CrI<sub>3</sub> as examples, we calculated their band structures, which are shown in Figure 7. It is evident that Ti-CrI<sub>3</sub> shows transition from metal to half-metal with the decrease of adatom concentration. Cu-CrI<sub>3</sub> exhibit half-metal character at a higher than 12.5% concentration, while it is of the semiconductor character at 3.13% and 1.39% concentration. In addition, the  $T_c$  values of Ti-CrI<sub>3</sub> and Cu-CrI<sub>3</sub> increase with the increase of adsorption concentration, as shown in Figure 8. In particular, the  $T_c$  values of Ti-CrI<sub>3</sub> and Cu-CrI<sub>3</sub> can be as high as 226 K and 136 K at a higher 12.5%

concentration. These results indicate that the electronic structure and FM stability are sensitive to the adatom concentration and that it should be possible to obtain desired electrical properties and FM stability by choose an appropriate adatom concentration.



**Figure 7.** Spin-polarized band structures with different adatom concentration of (a) Ti-CrI<sub>3</sub>, (b) Cu-CrI<sub>3</sub>. The red and blue solid lines indicate spin-up and spin-down channels, respectively.



**Figure 8.** Specific heat  $C_v$  with respect to temperature with different adatom concentration of (a) Ti-CrI<sub>3</sub>, (b) Cu-CrI<sub>3</sub>.

## Conclusions

In conclusion, we carried out systematic DFT calculations to study the electronic and magnetic properties of CrI<sub>3</sub> with various TM atoms adsorbed on its surface. Our results show that TM-CrI<sub>3</sub> system can possess various electronic properties. In particular, CrI<sub>3</sub> monolayer with Cu adsorption remains a semiconductor with a reduced band gap of 0.69 eV, while adsorption of other 3d TM atoms leads to a semiconductor to metal/half-

metal/spin gapless semiconductor transition. In addition, it is found that TM atom adsorption can significantly enhance the FM stability of CrI<sub>3</sub> monolayers, which is related to the interplay between direct exchange and superexchange interactions. Especially,  $T_c$  for Sc-CrI<sub>3</sub> and V-CrI<sub>3</sub> can be increased by nearly a factor of three as compared to the pristine CrI<sub>3</sub> monolayer. The deposition of TM atoms can be done after the synthesis of the material at moderate temperatures to ensure formation of adatoms in equivalent positions, but avoiding their coalescence, similar to the deposition of TMs on transition metal dichalcogenides.<sup>9,65</sup> This work suggests a practical route not only to tailor the electronic properties of CrI<sub>3</sub> monolayers, but also to improve their FM stability. We strongly believe that this strategy can be experimentally realized in the very near future, which can greatly promote the applications of CrI<sub>3</sub> in nanoelectronic and spintronic devices.

## **Acknowledgements**

This work is supported in China by the National Natural Science Foundation of China (No.11604047), the Natural Science Foundation of Jiangsu Province (No. BK20160694), Jiangsu Planned Projects for Postdoctoral Research Funds (No. 2019K010A), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX20\_1065), the Fundamental Research Funds for the Central Universities, and the open research fund of Key Laboratory of MEMS of Ministry of Education, Southeast University, and in USA by NASA (Grant Number

80NSSC19M0236) and NSF Center for the Advancement of Wearable Technologies (Grant 1849243). AVK acknowledges funding from the German Research Foundation (DFG), project KR 48661/2. We are thankful for the computational resources from the High Performance Computing Center of Nanjing Tech University, National Supercomputer Center in Tianjin.

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